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NAME OF AUTHOR/*NOM DE L'AUTEUR* JACKIE DEAN JAMERSON

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NAME OF SUPERVISOR/*NOM DU DIRECTEUR DE THÈSE* DR. JOSEF TAKATS

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DATED/*DATÉ* SEPTEMBER 26, 1974 SIGNED/*SIGNÉ* Jackie D. Jamerson

PERMANENT ADDRESS/*RÉSIDENCE FIXÉ* 226 FAIRBANKS AVE.
JOLIET, ILLINOIS 60432
U.S.A.

NL-91 (11-73)

THE UNIVERSITY OF ALBERTA

AMIDO DERIVATIVES OF THE ACTINIDES: PREPARATION AND SYNTHETIC UTILITY

by

(C) JACKIE DEAN JAMERSON

A THESIS

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled Amido Derivatives of the Acitinides: Preparation and Synthetic Utility

submitted by Jackie Dean Jamerson

in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

Supervisor

External Examiner

Date Oct. 4, 1977

To my loving wife Joyce,

your patience has

finally been rewarded.

Abstract

Various chemical studies have been carried out on the reported Cp_2UCl_2 which led to the conclusion that the reaction reported to give Cp_2UCl_2 does not actually do so. Attempts to determine the nature of the components of this system were made. Instead of Cp_2UCl_2 the reaction gives a mixture of Cp_3UCl and either $CpUCl_3$ or $(Cp_3U)_2UCl_6$, though a distinction between the two could not be made.

In an attempt to expand the very limited work done to date on the tetrakisamides of thorium and uranium, the synthesis of various derivatives of $M(NR_2)_4$ was attempted and found to be successful when R = Me, Et, i-Pr, and C_6H_5 but was unsuccessful when R = $SiMe_3$. The compounds, in addition to their extreme air- and moisture-sensitivity, were also found to be heat- and light-sensitive. The isopropyl and phenyl derivatives were found to be four-coordinate, presumably tetrahedral molecules, while the others are somewhat associated. The tetrakisamides, with the exception of the isopropyl derivative, were found to be reactive toward cyclopentadiene yielding complexes of the type $Cp_2U(NR_2)_2$ and $Cp_3U(NR_2)$, the reactivity pattern being interpreted in terms of the bulkiness of the amide group. The mass, infrared, and the NMR spectra are reported and the spectral properties are discussed.

In the absence of Cp_2UCl_2 as a starting material for the preparation of Cp_2U-derivatives, the reactivity of $Cp_2U(NEt_2)_2$ toward protic reagents was investigated. It was found that the reaction of the bisamide with monodentate thiols gave complexes

of the type, Cp_3USR, as the major product except for the reaction of the bulky t-butanethiol which gave the desired $Cp_2U(SR)_2$. The results of the reaction have been interpreted in terms of disproportionation of the formed $Cp_2U(SR)_2$ complexes. The reactions of $Cp_2U(NEt_2)_2$ with diprotic chelating ligands were found to yield chelated complexes of the type $Cp_2U(Chel)$, with o-mercaptophenol and catechol. However, reactions with toluene-3,4-dithiol and 4-methylcatechol proved to be more complicated. In addition it was found that CS_2 could be inserted into the uranium-nitrogen bond of $Cp_2U(NEt_2)_2$ to form the corresponding dithiocarbamate complex.

The ^1H- and ^{13}C-NMR spectra of the paramagnetic complexes have been tabulated and their general features discussed. The tetrahedral tetrakisamides are well-suited for qualitative discussions concerning the origin of the observed isotropic chemical shifts. Finally the ^1H-NMR spectra of various Cp_3UR (R = alkyl, halide, OR, SR, NR_2, etc.) complexes are compared and contrasted.

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TABLE OF CONTENTS

Table of Contents

Table of Contents

LIST OF TABLES

List of Tables

List of Tables

List of Tables

List of Figures

List of Figures

ABBREVIATIONS USED IN THIS THESIS

THF	tetrahydrofuran
DME	1,2-dimethoxyethane
Cp	cyclopentadienyl
NMe_2	dimethylamido
NEt_2	diethylamido
$N(i\text{-}Pr)_2$	diisopropylamido
$N(SiMe_3)_2$	bis(trimethylsilyl)amido
dtc	N,N-diethyldithiocarbamato
tdt	toluene-3,4-dithiolato
omp	o-mercaptophenolato
cat	catecholato
Me-cat	4-methylcatecholato
edt	1,2-ethanedithiolato
SMe	methanethiolato
SEt	ethanethiolato
tbt	t-butanethiolato
bdt	benzenedithiolato

CHAPTER I - GENERAL BACKGROUND OF BISCYCLOPENTADIENYLURANIUM CHEMISTRY

INTRODUCTION

Organoactinide chemistry had its beginning around 1940 partially as a result of World War II. The United States' Manhattan project was established to develop nuclear power. Several researchers,[1,2] as part of the Manhattan project, were attempting to synthesize uranium compounds of "high volatility, high stability, and low molecular weight"[1] for isotope separation. It had been hoped that the tetraalkyls of uranium would have the desired characteristics. These hopes, however, were soon dissipated as the tetraalkyls were found to be extremely unstable, decomposing rapidly at ambient temperature.[1]

One of the most interesting compounds seemed to be tetrakis-(diethylamido)uranium(IV), $U(NEt_2)_4$, which was reported in 1956 by Gilman, et al.[3] $U(NEt_2)_4$ presumably was prepared prior to 1956 but was not reported until then as seems to have been the case with other uranium compounds which were prepared earlier but reported in the early 1950's[1,2] In light of the kind of compound which was sought during the Manhattan project, $U(NEt_2)_4$ was the most interesting in that it could be distilled under high vacuum. However yields of the reaction were low (<30%). The low yields were due to a combination of factors: thermal decomposition during distillation,

sensitivity to air and moisture, and photodecomposition (as will be described later)

Reynolds and Wilkinson reported the preparation of triscyclopentadienyluranium chloride, Cp_3UCl, in the same year.[4] In dramatic contrast to the thermal instability of the tetraalkyls, Cp_3UCl could be sublimed at 200°C under high vacuum. Another very surprising property of Cp_3UCl was its stability toward degassed water. In fact the chloride ligand could be removed in aqueous solution generating the cation, Cp_3U^+, which was also stable towards water!

The successful preparations of $U(NEt_2)_4$, Cp_3UCl, and Cp_3U^+, along with the remarkable stability of Cp_3UCl demonstrated that, in contrast to the tetraalkyls, stable well-behaved organoactinides could be prepared. However at a period in history when the chemical literature was mushrooming with reports of new organometallic compounds of the transition metals, virtually nothing was being reported on organoactinides. From 1956 up to, and including, 1968 there had been approximately twenty organoactinide compounds reported in the literature. All of the reported compounds contained the cyclopentadienyl ligand (Cp) with the exception of tetraallylthorium(IV)[5] and bis(cyclooctatetraenyl)uranium(IV), $(COT)_2U$, commonly referred to as uranocene.[6] It was uranocene, the actinide "analog" of ferrocene, which seemed to revitalize interest in organoactinide chemistry. This renewed interest has been seen in both the synthesis of new compounds and in the physical study of organoactinides.

Since 1968 there have been reports on a variety of compounds, such as Cp_3UX (X=alkyl,[7-9] aryl,[7-9] BH_4,[10] halide,[11-13] and Cp[14,15]), Cp_3M (M=Th,[16] U,[12,17] Np,[12] Pu,[18,19] Am,[20] Cm,[21,22] Bk,[23*] and Cf[23*]), $(Cp_2BkCl)_2$,[24*] $(indenyl)_{4-x}MCl_x$ (M=Th,U),[25,26] $CpUCl_3$,[27] Cp_2UCl_2,[28,29] $(Cp_3UCl)_2UCl_4$,[29] $(COT)_2M$ (M=Th,[30-33] Pa,[34] U,[31,33,35-42] Np,[35,38,41,43] and Pu,[33,38,41,43]), $U(alkyl)_4$,[44] and $U[Mn(CO)_5]_4$.[45] Most of these reports have been on the synthesis and characterization of the compounds. Physical studies (NMR, UV, Mössbäuer, and X-ray crystallography) have been done mainly on the two systems, Cp_3MX and $(COT)_2M$.

Three review articles have also been published on the organo-actinide literature.[46-48] The reviews by Hayes and Thomas,[47] and Kanellakopulos and Bagnall[48] together serve as an excellent introduction into this area of chemistry in that considerable discussion is given not only to synthetic routes but also to the results of the then published physical studies.

It has already been mentioned that the Cp_3UX system has received much attention. At the start of this research nothing had been reported on the Cp_2UX_2 system except the preparation of Cp_2UCl_2.[28] Hence this work was started in an attempt to expand our basic knowledge of Cp_2U-chemistry in particular, and our knowledge of organo-actinide chemistry in general.

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* Microchemical preparation

SYNTHESIS AND CHEMICAL BEHAVIOR OF THE REPORTED Cp_2UCl_2

Since metathesis has proven to be one of the most generally applicable reactions in all of organometallic chemistry,[49] the most obvious starting material for the synthesis of Cp_2U-derivatives (equation I-1) is one of the dihalides, Cp_2UX_2 (X=Cl, Br, I).

$$Cp_2UX_2 + 2MR \longrightarrow Cp_2UR_2 + 2MX \qquad \text{I-1}$$

M = Li, Na, K, Tl, MgCl, etc.

R = alkyl, aryl, OR, SR, etc.

Hence the report of Zanella, et al.[28] on the preparation of Cp_2UCl_2 was a most exciting and welcome contribution to organoactinide chemistry.

The objective of this research was to utilize Cp_2UCl_2 for the synthesis of a wide variety of representative Cp_2U-derivatives and to compare their properties and chemistry to those of their transition metal counterparts.[50-52]

Zanella, et al. reported that Cp_2UCl_2 could be prepared by the reaction of a mixture of UCl_4 and two equivalents of cyclopentadienylthallium (I), TlCp, in 1,2-dimethoxyethane,[28] DME, as shown in equation I-2. The product was isolated by filtering off the

$$UCl_4 + 2TlCp \xrightarrow{DME} Cp_2UCl_2 + 2TlCl \qquad \text{I-2}$$

insoluble TlCl, followed by removal of the solvent from the filtrate in vacuo. Elemental analyses (not extremely good but explicable by the above isolation procedure), infrared (showed the presence of a η-Cp ligand), and UV spectra were said to characterize the solid as Cp_2UCl_2. It was also reported the Cp_3UCl (which starts to sublime at 180°C at 10^{-3}mm Hg) was not present since nothing could be sublimed from the green-brown solid even at 200°C and 10^{-4}mm Hg.

The formulation of the green-brown solid as Cp_2UCl_2 seemed reasonable. First of all the route used in the synthesis of Cp_2UCl_2 has been used to prepare various cyclopentadienyl derivatives of transition metals[49] and even Cp_3UCl.[10] Secondly the apparent absence of Cp_3UCl and $UCl_4 \cdot 2DME$ (reported to be absent on the basis of the UV spectrum) along with the production of the required amount of TlCl seemed to be indirect evidences for the formation of Cp_2UCl_2.

The reaction reported by Zanella, et al. was repeated in both DME and THF with the two reactions producing similar results. In addition the reaction of UCl_4 and two equivalents of NaCp seemed to produce the same material as the TlCp reaction. Crystallization from THF, however, produced a bright green solid in contrast to the green-brown color of the original material. The bright green crystals were slightly soluble in benzene. Nonetheless the ^{1}H-NMR spectrum showed a single resonance at approximately 6.8 p.p.m. relative to internal benzene. This, together with the infrared spectrum, which showed bands at 3093, 2960, 2890, 1015, 1008(sh), 799(sh), and 791 cm^{-1}, indicated the presence of the cyclopentadienyl ligand. However

the mass spectrum showed only the presence of Cp_3UCl (m/e 468, $Cp_3U^{35}Cl$) with nothing seen at m/e 438 as would be expected for $Cp_2U^{35}Cl_2$. The observation of Cp_3UCl, and not Cp_2UCl_2, was thought to be due to a lower volatility of Cp_2UCl_2 compared to Cp_3UCl and to slight thermal decomposition which generated Cp_3UCl. The latter argument was enforced by our observation, contrary to Zanella's claim, of small amounts of Cp_3UCl every time an attempt was made to sublime Cp_2UCl_2. At this point the green crystalline material was formulated as pure Cp_2UCl_2 and the discrepancy in color between it and the original solid was attributed to the presence of a small amount of Cp_3UCl in the latter. Several reactions were run (Table I) utilizing the green compound as pure Cp_2UCl_2.

The known stability of transition metal aryls and the reported synthesis of $Cp_3UC_6X_5$ (X=H,F) by Brandi, et al.[53] provided sufficient reasons to believe that the corresponding $Cp_2U(C_6X_5)_2$ (X=H,F) should also be stable complexes. Hence Cp_2UCl_2 and LiC_6F_5 were reacted at -78°C with an immediate change in the color of the reaction mixture being observed. After the solvent was removed from the reaction solution in vacuo, the resulting solid was found to be much less soluble than before the solvent was removed. ^1H- and ^{19}F-NMR, infrared, and mass spectra failed to characterize the reaction product. The reaction was repeated two more times, but each time the same results were obtained.

The same apparent change in solubility properties and inability to isolate a characterizable product were also observed when Cp_2UCl_2

TABLE I

SUMMARY OF THE REACTIONS PERFORMED WITH "Cp_2UCl_2"

ACCORDING TO EQUATION I-1

2MR	SOLVENT(S)	REACTION TEMP (^oC)	COLOR CHANGES OBSERVED
$2C_6F_5Li$	THF-Et_2O[a]	-78^o	yellow-green to dark brown
$2C_6H_5Li$	THF-Et_2O	a.t.[b]	yellow-green to dark red-brown
$(C_6H_5CH_2)_2Mg$	THF-DIOXANE	0^o	yellow-green to dark red-brown
$2(C_6F_5)MgCl$	THF	-15^o	yellow-green to dark brown
$2,2'-C_{12}H_8Li_2$	THF	a.t.	yellow-green to dark brown
$2,2'-C_{12}F_8Li_2$	THF	-78^o	yellow-green to dark green
K_2COT	THF	a.t.	yellow-green to dark green
$2LiNMe_2$	THF	a.t.	yellow-green to dark yellow-brown
$2NaSC_6H_5$	THF	a.t.	yellow-green to dark red-brown

[a] Et_2O is diethyl ether

[b] a.t. is ambient temperature

was reacted with LiC_6H_5, $(C_6H_5CH_2)_2Mg$, $(C_6F_5)MgCl$ and 2,2'-$C_{12}X_8Li_2$ (X=H,F). In light of the fact that at the time a wide variety of Cp_3UR (R=alkyl, aryl) compounds were being isolated and studied,[7,53] it seemed unlikely that the uranium-carbon σ-bond in Cp_2UR_2 should be so unstable as to produce the difficulties we had encountered. Even in the case of the 2,2'-$C_{12}X_8Li_2$ (X=H,F) reactions where the resulting metallofluorene complexes[54] would be anticipated to be even more stable than the corresponding aryl complex (i.e. $Cp_2U(C_6X_5)_2$) as a result of the formation of a delocalized metallocyclic system,[54,55] the same change in solutility properties was seen. As a result of the above observations and the logic which caused us to think that the uranium-carbon bond should not be so unstable in the anticipated compounds, it seemed very possible that the green crystalline solid was not Cp_2UCl_2.

In an attempt to verify the nature of the green crystalline material chemically, further reactions were attempted. If the green starting material is actually Cp_2UCl_2 then reactions with K_2COT, $2NaSC_6H_5$ and $2LiNMe_2$ should lead to $Cp_2U(COT)$ or $CpU(COT)$, $Cp_2U(SC_6H_5)_2$, and $Cp_2U(NMe_2)_2$, respectively. It was thought that the $NaSC_6H_5$ and $LiNMe_2$ reactions would be more informative than the K_2COT reaction since all of the corresponding transition metal derivatives (i.e. $Cp_2M(NMe_2)_2$, M=Ti, Zr, Hf [56] and $Cp_2U(SR)_2$, M=Ti, Zr, Hf [56,57]; M=Mo, W [58,59]) are stable well-behaved compounds.

The reaction of Cp_2UCl_2 with K_2COT produced uranocene as the only isolable product. More importantly, the $NaSC_6H_5$ and $LiNMe_2$

reactions gave no characterizable complexes. Furthermore, at about this same time it was also noticed that after successive crystallizations of Cp_2UCl_2 from the mother liquor, Cp_3UCl started to crystalize as well. Though it was earlier thought that Cp_3UCl could be an impurity in the crude Cp_2UCl_2, the amounts crystallized were much more than would be expected from a simple impurity. As a whole all these observations cast very serious doubts on the formulation of the green crystalline solid as Cp_2UCl_2. It was therefore decided to investigate the nature of this solid in somewhat more detail.

ATTEMPTS TO DETERMINE THE NATURE OF "Cp_2UCl_2"

An initial set of ^{1}H-NMR experiments was performed in order to decide the nature of "Cp_2UCl_2". The same group that reported the preparation of Cp_2UCl_2 had later reported the preparation of $CpUCl_3$ by the same basic route.[27] The compounds reported to be $CpUCl_3$ and "Cp_2UCl_2" were both prepared using the same reaction conditions (i.e. amounts of reactants, length of reaction time, etc.) as reported in the literature and their ^{1}H-NMR spectra (Table II) were recorded. The ^{1}H-NMR spectra of samples of "Cp_2UCl_2" prepared by various routes were also recorded. The results in Table II indicate that Cp_2UCl_2 has not been formed, but the synthesis rather, produced a mixture of Cp_3UCl and possibly $CpUCl_3$. The alternative explanation that the low field resonance is due to Cp_2UCl_2 can be ruled out based on our mass spectral work which did not show any peaks corresponding to Cp_2UCl_2 whereas some very recent work has shown that Cp_2UCl_2, when present, can be seen in the mass spectrum.[60] The possibility that Cp_2UCl_2 was formed, but then disproportionated (equation II-3), seemed an attractive mechanism for the formation

$$2Cp_2UCl_2 \longrightarrow Cp_3UCl + CpUCl_3 \qquad \text{I-3}$$

of the components found by NMR and is in line with the results of the crystallization process which would give the more insoluble $CpUCl_3$.

TABLE II

INITIAL ^{1}H-NMR RESULTS OF "Cp_2UCl_2" IN C_6D_6.

SIGNALS[a]	SAMPLE NO.	MATERIAL USED FOR ^{1}H-NMR
6.89 10.33	1	$UCl_4 + 2TlCp \xrightarrow[3\ HR.]{DME}$ [b]
6.94	2	$UCl_4 + TlCp \xrightarrow[7\ HR.]{DME}$ [c]
6.83 10.30	3	$UCl_4 + 2TlCp \xrightarrow[-72^oC]{DME}$
6.78 10.38	4	$UCl_4 + 2NaCp \xrightarrow[0^oC]{THF}$
6.88	5	Recrystallized "Cp_2UCl_2"
6.98 4.80[d]	6	Sample #2 + DME
10.40	7	Cp_3UCl

[a] given in p.p.m. relative to C_6H_6; recorded on Varian A-60 spectrometer

[b] prepared under the same conditions reported by Zanella, et al.[28]

[c] prepared under the same conditions reported by Doretti, et al.[27]

[d] DME

However a recent report by Kanellakopulos, et al.[29] gave an apparently different explanation for the reaction scheme. The compound obtained after quantitative extraction with DME followed by crystallization was formulated as $(Cp_3U)_2UCl_6 \cdot 2DME$ on the basis of elemental analyses, a molecular weight determination (>1200 as compared to 439 for Cp_2UCl_2), and UV spectra. In addition they report the preparation of the same compound by two different methods (equations I-4 and I-5), the solvent-free complex (equation I-6), and the closely related compound $(Cp_3U)UCl_5$ (equation I-7).

$$3Cp_4U + 3UCl_4 \xrightarrow{DME} 2(Cp_3U)_2UCl_6 \cdot 2DME \qquad \text{I-4}$$

$$2Cp_3UCl + UCl_4 \xrightarrow{DME} (Cp_3U)_2UCl_6 \cdot 2DME \qquad \text{I-5}$$

$$2Cp_3UCl + UCl_4 \xrightarrow[C_6H_6]{\Delta} (Cp_3U)_2UCl_6 \qquad \text{I-6}$$

$$Cp_3UCl + UCl_4 \xrightarrow[C_6H_6]{\Delta} (Cp_3U)UCl_5 \qquad \text{I-7}$$

At first the product reported by Kanellakopulos, et al. does not seem to agree with the disproportionation of Cp_2UCl_2 into Cp_3UCl and $CpUCl_3$ as earlier postulated. However the formation of $(Cp_3U)_2UCl_6$ by the reaction of Cp_4U and UCl_4 (equation I-4) seems to provide the first clue linking his results with equation I-3. Given that Cp_4U and UCl_4 react to form $(Cp_3U)_2UCl_6$, there must be some association between the two since there is a rather large covalent contribution to the uranium-ring bonding in Cp_4U.[14] The crystal structure of Cp_4U[14] indicates that there is no room around the uranium in Cp_4U for

the association to occur via a chloride bridge, so most likely a cyclopentadienyl ligand bridges both metals. The bridging cyclopentadienyl ligand, though not common, is well documented (e.g. $TlCp$[61] and crystalline Cp_3Sm[62]). Hence if one Cp is transferred from one uranium to the other the two products formed are Cp_3UCl and $CpUCl_3$, but these are exactly the products postulated for the disproportionation of Cp_2UCl_2. If indeed $CpUCl_3$ and Cp_3UCl are common products of both the reactions mentioned (i.e., equations I-3 and I-4), then the question arises as to how they in turn react to form $(Cp_3U)_2UCl_6$.

The reactions reported by Kanellakopulos, et al. show that Cp_3UCl and UCl_4 react to give $(Cp_3U)_2UCl_6$. Hence it is not unreasonable to assume that both Cp_3UCl and UCl_4 must somehow be generated in the reaction forming "Cp_2UCl_2" in order to form $(Cp_3U)_2UCl_6$. Since there is no evidence to suggest that Cp_3UCl can disproportionate, it is not unreasonable to assume that $CpUCl_3$ is the one that disproportionates to give Cp_3UCl and UCl_4 (equation I-8). The overall reac-

$$3CpUCl_3 \longrightarrow Cp_3UCl + 2UCl_4 \qquad \text{I-8}$$

tion for the formation of $(Cp_3U)_2UCl_6$ from $CpUCl_3$ and Cp_3UCl can be seen in equation I-9. However at this point it was still conceivable

$$3CpUCl_3 + 3Cp_3UCl \longrightarrow 2(Cp_3U)_2UCl_6 \qquad \text{I-9}$$

that $CpUCl_3$ and Cp_2UCl_2 were both nothing more than transient species and that the disproportionation of Cp_2UCl_2 was essentially that of equation I-10, or for that matter it is conceivable that Cp_2UCl_2 is

$$3Cp_2UCl_2 \longrightarrow 2Cp_3UCl + UCl_4 \longrightarrow (Cp_3U)_2UCl_6 \qquad \text{I-10}$$

not even formed and the yields essentially are a mixture of Cp_3UCl, UCl_4, and $(Cp_3U)_2UCl_6$.

In an effort to determine the nature of the "Cp_2UCl_2" system a second set of NMR experiments was designed. The ^{1}H-NMR spectra of $(Cp_3U)_2UCl_6$ (prepared by the reaction of Cp_3UCl and UCl_4 in hot DME), $CpUCl_3$ (prepared by the slow addition of TlCp to UCl_4 in DME), crude "Cp_2UCl_2" (the product isolated after following the conditions reported by Zanella, et al.[28] as closely as possible), and Cp_3UCl, were recorded. (See Table III.) Much to our surprise the spectra of $CpUCl_3$ and $(Cp_3U)_2UCl_6$ showed singlets in approximately the same place.

It was not certain whether the small differences in chemical shifts seen in Table III were due to different complexes, as originally hoped for, or were only reflections of slightly different experimental conditions (e.g. different concentrations). In order to decide between the two possibilities it was decided to record the ^{1}H-NMR spectrum of crude "Cp_2UCl_2" and to add successively to that sample, solutions of $(Cp_3U)_2UCl_6$ and $CpUCl_3$ and record the spectrum after each addition. The results of this study are shown in Table IV. It can be seen that there are only two peaks observed and that the relative areas of the two changed after each addition. (i.e. the peak at about 6.8 p.p.m. grew in intensity).

TABLE III

^{1}H-NMR STUDIES ON THE "Cp_2UCl_2" SYSTEM

SIGNAL[a]	SAMPLE
6.94	$CpUCl_3$[b]
10.35	Cp_3UCl
6.82	crude "Cp_2UCl_2"[c]
10.45	
6.86	$(Cp_3U)_2UCl_6$[d]

[a] given in p.p.m. relative to C_6H_6; recorded on Varian A-60

[b] prepared under the same conditions reported by Doretti, et al.[27]

[c] prepared under the same conditions reported by Zanella, et al.[28]

[d] prepared according to equation I-5

TABLE IV

^{1}H-NMR SPECTRA OF MIXTURES OF THE

PROPOSED COMPONENTS OF THE "Cp_2UCl_2" SYSTEM

SIGNAL[a]	RELATIVE AREA	SAMPLE
6.83	1.0	crude "Cp_2UCl_2"
10.52	5.2	
6.83	1.0	crude "Cp_2UCl_2" + $(Cp_3U)_2UCl_6$
10.48	2.3	
6.86	1.0	crude "Cp_2UCl_2" + $(Cp_3U)_2UCl_6$ +
10.34	0.90	$CpUCl_3$

[a] given in p.p.m. relative to internal benzene; recorded on a Varian HA-100 spectrometer

At this point a simple conclusion seems to be emerging if one accepts the assumption that it would be unlikely that accidental chemical shift equivalence could produce a single, very sharp line (a 3.5 Hz line width at half-height). It seems that in the course of making Cp_2UCl_2 indeed one forms a mixture of $(Cp_3U)_2UCl_6$, Cp_3UCl, and UCl_4, and with time the generated Cp_3UCl and UCl_4 react to form more $(Cp_3U)_2UCl_6$. More importantly it would also appear that "$CpUCl_3$" is a mixture of $(Cp_3U)_2UCl_6$ and UCl_4, and has no real existence.

It was of interest to confirm the NMR conclusions on this system by some chemical reactions which were monitored by NMR (Table V). For instance heating crude "Cp_2UCl_2" in DME, or heating "$CpUCl_3$" and Cp_3UCl together in DME, should produce only $(Cp_2U)_2UCl_6$. Indeed this was found though the reaction was slow. Interestingly it was found that if the DME was removed <u>in vacuo</u> and replaced with THF the reaction proceeded much faster. However when an attempt was made to dissolve "$CpUCl_3$" in THF so that it could be added to a solution of Cp_3UCl in THF to observe the accelerated reaction, the "$CpUCl_3$" very quickly precipitated after dissolution. Since $(Cp_3U)_2UCl_6$ and UCl_4 are soluble in THF, this unexpected observation seemed to indicate that $(Cp_3U)_2UCl_6$ and "$CpUCl_3$" are different. Another observation which tends to support this is the fact that a sample of crude "Cp_2UCl_2" (earlier postulated to be a mixture of $(Cp_3U)_2UCl_6$, Cp_3UCl, and UCl_4) dissolved completely in toluene, for if "Cp_2UCl_2" was actually this mixture then the UCl_4 should not have dissolved.

TABLE V

FURTHER ^{1}H-NMR STUDIES ON THE "Cp_2UCl_2" SYSTEM

SIGNAL[a]	RELATIVE AREA	NMR SAMPLES IN BENZENE
6.94	--	$CpUCl_3$
10.35	--	Cp_3UCl
6.86	--	$(Cp_3U)_2UCl_6$ = K
6.72		crude "Cp_2UCl_2" = A
10.45		
6.87	1.0	A heated in DME = B
10.32	4.0	
6.88	--	K heated in DME
6.93	--	$CpUCl_3$ heated in DME
6.83	1.0	$CpUCl_3$ + Cp_3UCl heated in DME = C
10.30	1.2	
6.79	1.0	B stirred in THF for six hours
10.47	1.2	
6.75	1.0	C stirred in THF for ten hours
10.30	0.1	
6.72	1.0	A extracted at ambient temperature into toluene = D
10.39	3.3	
6.85	1.0	D stirred in THF for three hours
10.38	2.0	
6.82	1.0	D stirred in THF for 19 hours
10.45	0.6	
6.93		K in THF and benzene

[a] given in p.p.m. relative to internal benzene; recorded on Varian A-56/60 spectrometer

Therefore at this point the composition of "Cp_2UCl_2" is not known with certainty (i.e. the conflicting NMR and chemical observation), but it is clear that "Cp_2UCl_2" does not contain any real Cp_2UCl_2. In all probability the green crystalline solid which was earlier used for reactions and assumed to be Cp_2UCl_2 was $(Cp_3U)_2UCl_6$. It is also clear that this reaction system (equation I-2) does not give pure $(Cp_3U)_2UCl_6$ as reported by Kanellakopulos, et al.,[29] but is much more complicated.

The formulation of the green, crystalline solid as $(Cp_3U)_2UCl_6$ rather than Cp_2UCl_2 provides a rationale for the difficulties encountered in the synthesis of Cp_2UR_2 (Table I) since one of the expected products of $(Cp_3U)_2UCl_6$ and LiR would be UR_4. The corresponding alkyl derivatives are known to be extremely unstable.[1,44] The reason why the other reaction product, Cp_3UCl,[7] could not be isolated is unclear.

SEARCH FOR A POTENTIAL STARTING MATERIAL FOR THE SYNTHESIS OF Cp_2U-DERIVATIVES

The elusiveness of Cp_2UCl_2 raised several questions: 1) was the disproportionation seen in the attempted preparation of Cp_2UCl_2 a result of an inherent instability of Cp_2U-derivatives relative to the corresponding Cp_3U-derivatives?; 2) was the inability to isolate the dichloride a result of the synthetic route rather than an inherent instability?; 3) in the absence of Cp_2UCl_2 what else could be used as a starting material for the synthesis of other Cp_2U-derivatives?; 4) what factors govern the disproportionation?; etc.

Taking the optimistic outlook we hoped that it was the synthetic route which was the cause of our inability to isolate Cp_2UCl_2. As a result another starting material was sought which would allow us entry into the study of Cp_2U-derivatives. In this regard, two known reactions of transition metal complexes seemed relevant. First it was shown by Bradley[63] and Lappert[56,64] that amido derivatives of the transition metals react with a variety of protic reagants (i.e. HX) forming new complexes in a simple acid-base reaction by the elimination of an amine with the concurrent formation of the corresponding transition metal-X bond. Secondly it was also known that the tetrakisamido derivatives of Ti, Zr, and Hf react with cyclopentadiene to form $Cp_2M(NR_2)_2$ complexes (equation I-11) where the metal-nitrogen

$$M(NR_2)_4 + 2CpH \longrightarrow Cp_2M(NR_2)_2 + 2HNR_2 \qquad I\text{-}11$$

M = Ti; R = Me

M = Zr, Hf; R = Me, Et

bond is susceptible to further acidic displacement reactions (equation I-12).[56] It seemed that such a synthetic route, in the absence of Cp_2UCl_2, could be ideally suitable for uranium chemistry.

$$Cp_2M(NR_2)_2 + 2HX \longrightarrow Cp_2M(X)_2 + 2HNR_2 \qquad I\text{-}12$$

X = OR, SR, etc.

The research therefore took on a new direction. The objectives now became the synthesis of various tetrakisamido derivatives of U (i.e. $U(NR_2)_4$), their utility toward the preparation of $Cp_2U(NR_2)_2$ complexes, and the reactivity of these derivatives toward acidic ligands with the hope of preparing other Cp_2U-derivatives.

CHAPTER II - TETRAKISAMIDO DERIVATIVES OF THORIUM AND URANIUM

INTRODUCTION

Amido derivatives of the transition metals and, lately, those of the lanthanides, $M(NR_2)_x$, have occupied a very important place in the chemistry of these metals.[65] Indeed Bradley and his school have demonstrated that by the choice of suitable amido groups unusually low coordination numbers can be achieved for both groups of metals.[66,67] The synthetic utility of the amides for the preparation of other transition metal complexes by acid displacement (equation II-1)[56,63,64] and by insertion of a dipolar molecule AB (equation II-2)[68-70]

$$M(NR_2)_x + zHY \longrightarrow M(NR_2)_{x-z}(Y)_z + zHNR_2 \qquad \text{II-1}$$

$$M(NR_2)_x + xA = B \longrightarrow M(A\text{-}B\text{-}NR_2)_x \qquad \text{II-2}$$

have been investigated by both Bradley and Lappert. It is then ironic that even though the synthesis of the first actinide amido complex, $U(NEt_2)_4$, by Gilman, et al.[3] has preceeded these studies and seems to have provided the impetus needed for their initiation[71] studies on the synthesis and chemistry of actinide amides has been largely neglected. Indeed at the start of this research the only other report of an actinide amide was that of Bradley and Gitlitz in which $Th(NEt_2)_4$ was synthesized,[72] although the yield of the reaction was very small. This, in hind-sight, can be attributed to the distillation of the product which is now known to be heat-sensitive. In contrast to their transition metal counterparts, only the reactivity

of $U(NEt_2)_4$ toward ROH and RSH (yielding $U(OR)_4$ and $U(SR)_4$, respectively) has been investigated.[3] Presumably since better ways were known to make either U(OR) or $U(SR)_4$ Gilman, et al. did not pursue the reactivity of the amide.[3]

Our main interest in the amido complexes of the actinides was the study of their synthetic utility. However due to the fact that $U(NEt_2)_4$ is a very sticky solid at ambient temperature, transfer of appropriate amounts for further reactions is not easily accomplished. Therefore we were led to investigate the synthesis of other $U(NR_2)_4$ derivatives, the principal prerequisite being the isolation of a solid for easy handling. It goes without saying that the uranium-nitrogen bond must still be rather reactive for the compound to be useful as a starting material in subsequent reactions. It also occurred to us that some of these complexes might be monomeric making them four-coordinate complexes.

Isolation of four-coordinate complexes would in themselves be of interest for several reasons. It is well known that the chemistry of the actinides is characterized by higher coordination numbers (i.e. ≥ 6) in their compounds.[73] In fact coordination numbers of 12[73] and 14[74] are known, but there are only a small number of known four-coordinate complexes.[75] In addition it would be expected that such complexes would have a tetrahedral geometry.[14,76] A tetrahedral geometry would be most helpful in analyzing NMR spectra of the uranium amides since contributions due to the pseudo-contact mechanism in such complexes will be negligible.[77] As a result one would not

have to worry about the standard problem of the separation of contact and pseudo-contact contributions to the total isotropic shift.[77]

An extension of this work to the thorium amides should also be quite useful as there are only two known four coordinate complexes of thorium[75] and the corresponding thorium amide would be best to use as a diamagnetic reference in determining the isotropic shifts in the uranium amides.[77] In addition nothing has been reported in the literature on the reactivity of the only thorium amide, $Th(NEt_2)_4$.

SYNTHESIS AND PROPERTIES OF Th- AND $U(NR_2)_4$ COMPLEXES

R=Et

The preparation and isolation of $U(NEt_2)_4$ by the method of Gilman, et al. is at best inconvenient. $U(NEt_2)_4$ is prepared by the reaction of UCl_4 and $LiNEt_2$ in ether (equation II-3) for about two hours. The

$$MCl_4 + 4LiNR_2 \longrightarrow M(NR_2)_4 + 4LiCl \qquad \text{II-3}$$

removal of ether under vacuum yielded the crude product which was heated at 60-80°C and 20 mm Hg followed by distillation under higher vacuum (0.06 mm Hg) at 80-120°C. A yield of less than 30% was obtained after distillation.

There are several bad points about this preparation. First of all diethylether is not the best choice as reaction solvent. This is no reflection against the synthetic abilities of Gilman, et al. since the solvent used here, THF, was seldom employed in 1956. Besides not being very soluble in ether, UCl_4 has a tendency to form clumps of solid in ether which must be broken up. This in turn means that the flask must be opened thereby increasing the chances of the decomposition of $U(NEt_2)_4$ by air or moisture. On the other hand the use of THF allows the reaction of solutions of UCl_4 and $LiNEt_2$ rather than a solid UCl_4 and a solution ($LiNEt_2$).

Secondly, it is questionable whether or not the reaction is complete in one or two hours as postulated by Gilman. In our

experience with several other amide reactions, such a short time invariably produces a mixture of compounds containing, besides the desired tetrakisamides, haloamido derivatives.

Thirdly, a general characteristic of the tetrakisamides of thorium and uranium is that they are heat sensitive. Hence the distillation naturally resulted in some thermal decomposition. The amount of decomposition, of course, depends on how high the amide is heated.

Several attempts were made to distill $U(NEt_2)_4$ in the earlier stages of this work. It was found that if the distillation was carried-out with a normal distillation set-up the yields were indeed very low. Trap to trap distillation, attempted in an effort to reduce the path length of the distillation apparatus, was plagued by problems arising from bumping.

It was then decided to prepare $U(NEt_2)_4$, remove the solvent under vacuum, then redissolve the product in pentane. Filtration would then get rid of the other product, LiCl. This procedure was followed in the preparation of $Cp_2U(NEt_2)_2$ (Chapter III.) The observation of both $Cp_2U(NEt_2)_2$ and $Cp_3U(NEt_2)$ in the reaction product (24% $Cp_3U(NEt_2)$ - Chapter III) indicated that the intermediate formation of $U(NEt_2)_4$ was still not quantitative since the amount of cyclopentadiene added should have only produced the biscyclopentadienyl derivative. It was discovered that when light was excluded during the preparation of $U(NEt_2)_4$ the presence of $Cp_3U(NEt_2)$ could be eliminated and excellent yields of pure $Cp_2U(NEt_2)_2$ were

obtained even after crystallization (i.e. approximately 88%) indicating a near quantitative conversion to $U(NEt_2)_4$. (A separate attempt to isolate $U(NEt_2)_4$ in this way resulted in at least a 97% yield.) The discovery of the light-sensitivity of $U(NEt_2)_4$, though it was determined indirectly and qualitatively, shows that, contrary to Gilman's[3] and later Watt's[78] procedure, $U(NEt_2)_4$ can be isolated essentially pure and in high yields without distillation. Recently Bagnall and Yanir also reported that $U(NR_2)_4$, prepared *in situ*, could be used to make various tetrakiscarbamate derivatives.[79] However their method of preparation, which will be discussed in connection with the preparation of $U(NMe_2)_4$, does require experimental details not published in their paper.

$Th(NEt_2)_4$ was prepared exactly as $U(NEt_2)_4$ and is also presumed to be light-sensitive, though the point was not pursued. Like its uranium analog, $Th(NEt_2)_4$ was found to be a very sticky solid when properly dried *in vacuo*. Typically a sample of the tetrakisamide was left under vacuum at ambient temperature overnight to remove last traces of solvents before spectral studies were undertaken.

The very sticky nature of these amides makes their transfers very difficult and in fact was the very reason the study of other tetrakisamides was undertaken. Nevertheless, should the use of these particular amides become necessary, there are two ways in which they may be efficiently transferred: 1) the amide may be cooled down to liquid nitrogen temperature. With a high positive pressure of nitrogen, the flask containing the amide may be opened and the amide

pulverized with either a spatula or a glass rod. Then the solid may be transferred as any other extremely air-sensitive solid would be provided that all glassware is kept cold. Extra care must be taken in using this procedure since moisture is more easily condensed on cold glassware. However with care and patience, the procedure is quite satisfactory. 2) The amide may be dissolved in a volatile solvent (e.g. pentane) and the solution can be carefully transferred to a preweighed flask. Removal of the solvent under vacuum at ambient temperature followed by a reweighing of the flask will give the weight of the amount transferred. Care must be employed when transferring solutions due to the extreme air-sensitivity. Even so one may transfer the solution with a syringe if the precautions outlined in Chapter VI are followed.

R=$SiMe_3$

In light of Bradley's successful preparation of three-coordinate complexes of Sc, Ti, V, Cr, and Fe[66] and the lanthanides[67] using the bis(trimethylsilyl)amido ligand, attempts were made to prepare the corresponding uranium(IV) derivative, $U[N(SiMe_3)_2]_4$. $Li[N(SiMe_3)_2]$ was reacted with UCl_4 according to equation II-3 for 20 hours at ambient temperature in THF. Removal of the solvent under vacuum yielded a brown solid, part of which was soluble in pentane and part of which was soluble in toluene. The ^{1}H-NMR spectrum of the brown pentane-soluble solid was quite complex showing singlets at 6.46, 6.80, 6.88 and 7.09 p.p.m. (relative to internal benzene) with the

addition of broader singlets at 9.44 and 10.34 p.p.m. in the toluene soluble fragment. Even after a second sample was refluxed for 60 hours a complex ^{1}H-NMR spectrum was obtained for the pentane and toluene soluble fragments. However the peak at 9.44 p.p.m. was larger than that in the ^{1}H-NMR spectrum of the previously obtained reaction product. The mass spectra of both the pentane- and toluene-soluble solids showed that $U[N(SiMe_3)_2]_3{}^{35}Cl^+$ (m/e 753) was by far the most abundant uranium containing ion. A small peak at m/e 878 can be attributed to $U[N(SiMe_3)_2]_4^+$, but this was seen only after the reaction solution was refluxed for 60 hours.

Hence it must be concluded that the bis(trimethylsilyl)amido ligand is simply too bulky to replace all four of the chloride ligands in UCl_4 even under the more forcing conditions of reflux. Bradley, et al. have also attempted the preparation of the tetrakisamido derivative of thorium, but have failed. The only isolable product was $Th[N(SiMe_3)_2]_3Cl$.[75] If the larger thorium(IV) is unable to accomodate four bis(trimethylsily)amido ligands then it is not at all surprising that the small uranium(IV) (Table VI) will not be able to do so either.

Undoubtedly $U[N(SiMe_3)_2]_3Cl$ is a four-coordinate complex. But since our attention was focused mainly on synthetically useful reagents and since structural work on $Th[N(SiMe_3)_2]_3Cl$ is in progress by Bradley[80], attention was focused on less bulky amido groups.

TABLE VI

EFFECTIVE IONIC RADII OF VARIOUS METALS[a,b]

METAL	RADIUS (A°)
Ti(IV)	0.61
Zr(IV)	0.72
Hf(IV)	0.71
Mo(IV)	0.65
W(IV)	0.65
Th(IV)	1.06
U(IV)	1.00

[a] reference 81

[b] based on the more common coordination numbers of the transition metals (i.e. six) and actinides (i.e. eight)

R=i-Pr

The reaction of UCl_4 with $Li[N(i\text{-}Pr)_2]$ (equation II-3) for 24 hours at ambient temperature produced a mixture of $U[N(i\text{-}Pr)_2]_3Cl$ and $U[N(i\text{-}Pr)_2]_4$ as determined by a combination of ^1H-NMR and mass spectra. On refluxing UCl_4 and $Li[N(i\text{-}Pr)_2]$ for 60 hours in THF, pure $U[N(i\text{-}Pr)_2]_4$ was obtained but in low yields (approximately 50%). The very dark brown solid obtained was very soluble in all solvents including pentane. In fact $U[N(i\text{-}Pr)_2]_4$ is so soluble that crystallization from butane at -78°C could not be effected. Hence the crude reaction product was freed of LiCl by dissolution in pentane followed by filtration and removal of the pentane under vacuum. The resulting solid showed only a broad resonance at 1.25 p.p.m. (relative to internal benzene; one ^1H) and a doublet at 7.15 p.p.m. (six ^1H). (Figure 1.) A mass spectrum confirmed that the compound was indeed $U[N(i\text{-}Pr)_2]_4$ by observation of the expected molecular ion at m/e 638. A trace of $U[N(i\text{-}Pr)_2]_3{}^{35}Cl$ was revealed by a peak at m/e 573. Amine analyses were consistently low but always gave an amine/uranium ratio of at least 3.5/1. In addition samples sent away for C,H analyses were always low by about 5%. The low C,H analyses combined with the low yields obtained caused us concern. The difficulties encountered in the analysis were ascribed to the presence of small amounts of impurities. It was thought that the extended interaction of $Li[N(i\text{-}Pr)_2]$, a very strong base, with refluxing THF might be a potential problem since it has been shown that $Li[N(i\text{-}Pr)_2]$ will remove a hydrogen from a carbon atom α to a carbonyl group.[82-83]

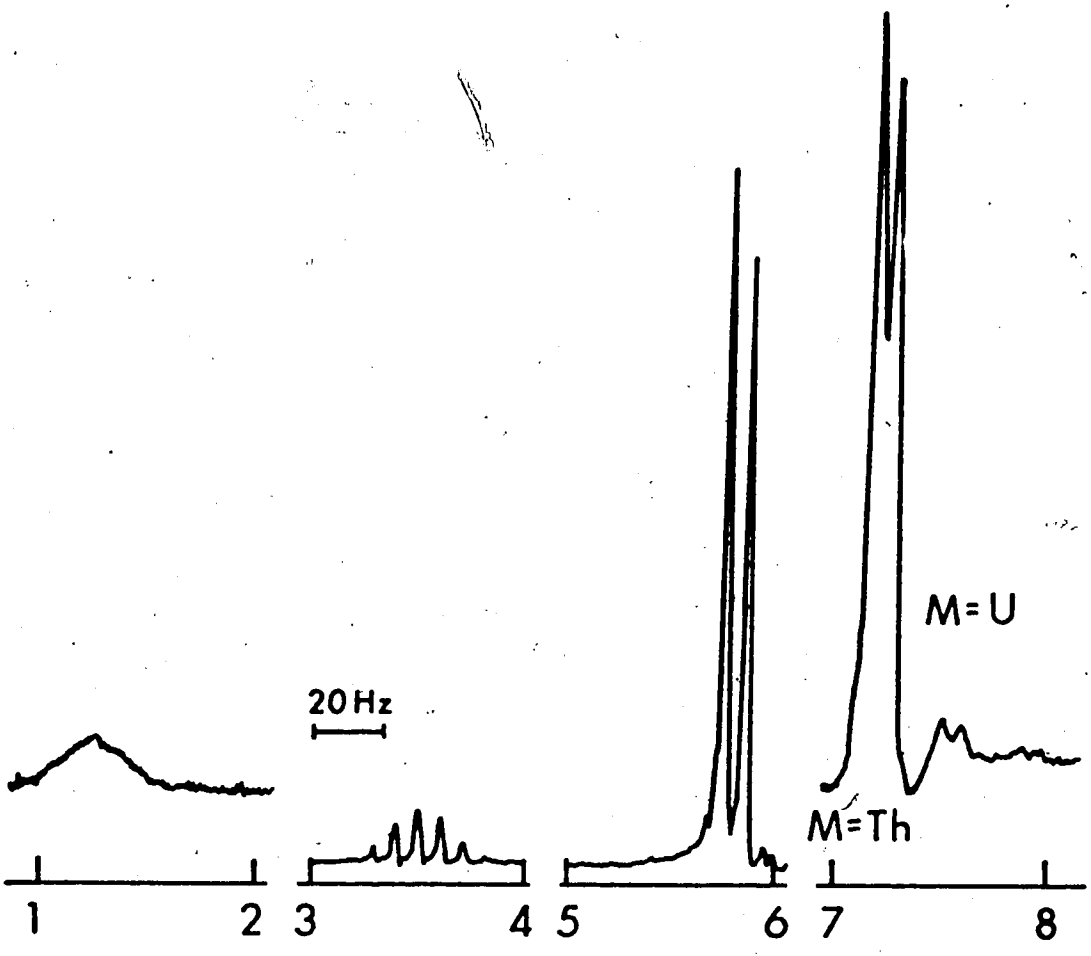


Figure 1. ^{1}H-NMR Spectra of $M[N(i\text{-}Pr)_2]_4$ Complexes. Chemical shifts given in p.p.m. relative to internal benzene.

In order to eliminate this and hopefully improve the yield and the purity of the product, the following two variations of the synthesis were carried out. In the first UCl_4 and $Li[N(i\text{-}Pr)_2]$ were allowed to react at 0^oC for a few hours. The THF was removed under vacuum and was replaced with pentane. Refluxing for about 48 hours gave a 57% yield of $U[N(i\text{-}Pr)_2]_4$. In the second $[(i\text{-}Pr)_2N]MgBr$ was prepared (equation II-4) and then reacted with UCl_4 (equation II-5).

$$(i\text{-}Pr)MgBr + HN(i\text{-}Pr)_2 \longrightarrow [(i\text{-}Pr)_2N]MgBr + C_3H_8 \quad \text{II-4}$$

$$4[(i\text{-}Pr)_2N]MgBr + UCl_4 \longrightarrow U[N(i\text{-}Pr)_2]_4 + 4MgClBr \quad \text{II-5}$$

After 24 hours at room temperature the reaction solution consisted mainly of $U[N(i\text{-}Pr)_2]_4$ but other weak peaks were seen in the ^1H-NMR spectrum. After changing the reaction solvent from THF to pentane the solution was refluxed for 12 hours during which time all of the extra peaks disappeared leaving only those due to $U[N(i\text{-}Pr)_2]_4$. The product was isolated in 63% yield. Although the yields of the isolated complexes were improved somewhat, the improvement was not spectacular and unfortunately analyses were still unsatisfactory as the carbon was 3% and the hydrogen 0.7% lower than the calculated values. (See Chapter VI.)

However confidence could be placed in the fact that the product was indeed $U[N(i\text{-}Pr)_2]_4$: there was no AgCl formed after the sample was decomposed in HNO_3 and H_2O_2, and $AgNO_3$ was added; the mass spectrum showed only $U[N(i\text{-}Pr)_2]_4$; and the ^1H- and ^{13}C-NMR spectra showed no other H or C containing species. We therefore attributed

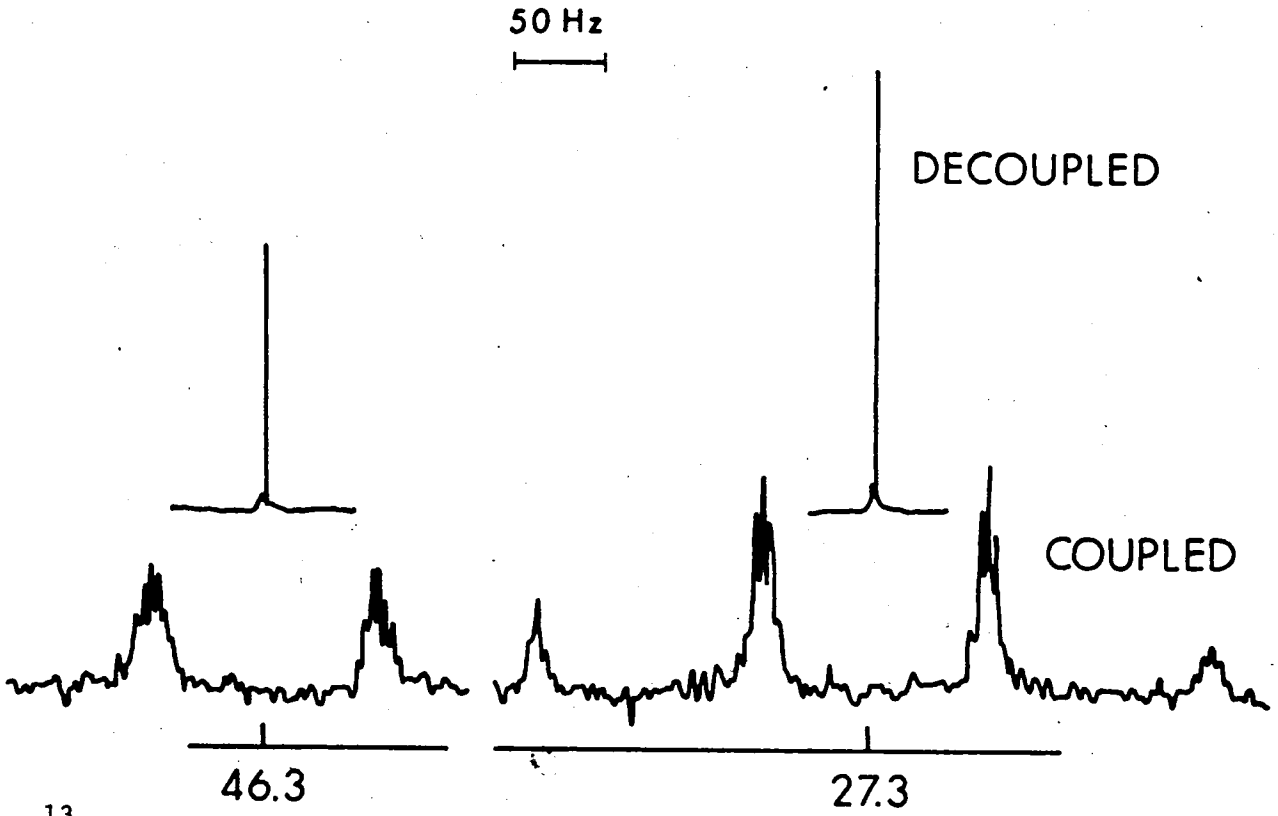


Figure 2. ^{13}C-NMR Spectra of Th$[N(i\text{-}Pr)_2]_4$. Chemical shifts given in p.p.m. relative to TMS

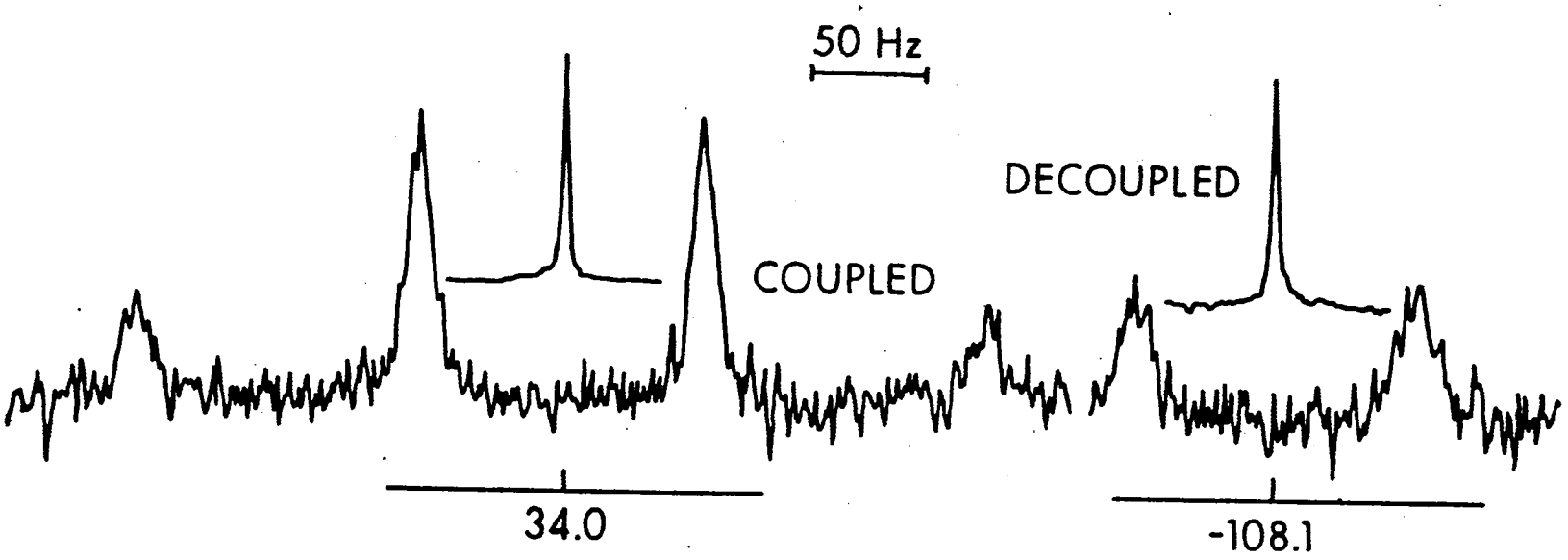


Figure 3. ^{13}C-NMR Spectra of U[N(i-Pr)$_2$]$_4$. Chemical shifts given in p.p.m. relative to TMS

the difficulties encountered in analyses to thermal instability of the amides (samples were also sent away to Bernhardt but they gave even poorer results), air-sensitivity, and of course, our inability to crystallize the samples does not allow us to exclude the presence of small amounts of impurities in the isolated amides.

Similar behavior was seen in the preparation of $Th[N(i\text{-}Pr)_2]_4$ except that the yields of the reaction were higher than for $U[N(i\text{-}Pr)_2]_4$. A 78% yield was obtained in the preparation of $Th[N(i\text{-}Pr)_2]_4$ while, at best, only a 63% yield was obtained for $U[N(i\text{-}Pr)_2]_4$. The difference in yields reflects the difference in sizes of the two metals (Table VI). As will be elaborated later on the mass spectra of both Th- and $U[N(i\text{-}Pr)_2]_4$ show a large number of intramolecular H_2 eliminations brought about by the sterically crowded molecules. (The construction of a molecular model quickly eliminated all skepticism that might have existed about the steric crowding in the molecule.)

The NMR and mass spectra, combined with the observance of steric crowding in molecular models, clearly indicate that both t[illegible] Th- and $U[N(i\text{-}Pr)_2]_4$ are monomeric, four-coordinate molecules. However due to their extreme solubility in even butane, no crystalline products could be obtained. Therefore their utility as far as x-ray structural work was concerned was nil, and the search went on for a more suitable complex for crystallization.

$\underline{R=C_6H_5}$

Even though both Th- and $U[N(i\text{-}Pr)_2]_4$ are undoubtedly four coordinate complexes, their low reactivity (which will be discussed later) and solubility properties caused us to turn to a different amido ligand. What was needed was a less bulky amide which would also be less soluble than the diisopropyl complexes. It was decided to investigate the preparation of the diphenylamido complexes.

An initial reaction was tried using $LiN(C_6H_5)_2$ as in equation II-3 in THF, but extraction of the presumed $U[N(C_6H_5)_2]_4$ with benzene produced a sticky material which could not be freed from benzene except under heat and vacuum. However in so doing the sample was decomposed by the amount of heat necessary to liberate the benzene. The presumed $U[N(C_6H_5)]_4$ was insoluble in pentane or hexanes and behaved in toluene the same way as it did in benzene. Attempted cyrstallization from toluene also failed. Since LiCl has moderate solubility in THF the separation of LiCl and $U[N(C_6H_5)_2]_4$ posed a problem once the reaction had gone to completion. In addition the reaction of $LiN(C_6H_5)_2$ with $ThCl_4$ in THF produced a purple solid which is very unusual in that Th(IV) has no d or f electrons and it's complexes, in all probability are all either white or light yellow. So it seemed that the $LiN(C_6H_5)_2$ route was not the best.

Dermer and Fernelius reported the preparation of $Ti[N(C_6H_5)_2]_4$ in 1934 using $KN(C_6H_5)_2$ and $TiCl_4$.[84] Since KCl is insoluble in THF it should precipitate out as soon as it is formed thus solving the problem of separation outlined above. The reaction of $KN(C_6H_5)_2$ and

UCl_4 at 0°C in THF produced a deep red solution. Indeed it was seen that KCl precipitated out and that it could be removed by filtration. A reaction time of 24 hours produced 96% $U[N(C_6H_5)_2]_4$ and 4% $U[N(C_6H_5)_3]Cl$ as determined by ^{1}H-NMR. Stirring the reaction solution for an additional 12 hours at ambient temperature saw complete conversion to $U[N(C_6H_5)_2]_4$ (Figure 4).

Attempts were made to crystallize this compound from a THF-pentane solution. Due to the extremely air-sensitive nature of the solution and the long times generally required for the growth of well-formed single crystals, no crystals suitable for structural work could be obtained.

Due to the extreme air-sensitivity of Th- and $U[N(C_6H_5)_2]_4$, satisfactory elemental analyses could not be obtained. The ^{1}H-NMR spectrum of $U[N(C_6H_5)_2]_4$ showed no other signals, while no such conclusion could be drawn about the Th analog since all of the phenyl resonances occur very near to benzene and only a broad single peak was observed. However both samples were found to be chlorine free. Hence confidence could be placed in the purity of the compound as was confirmed by chemical reactivity, but this will later be described in more detail.

R=Me

The preparation of one final amide, $U(NMe_2)_4$, was attempted. It was hoped that this complex would be less soluble than $U[N(i\text{-}Pr)_2]_4$ and more stable than $U[N(C_6H_5)_2]_4$ complex so that purification of the

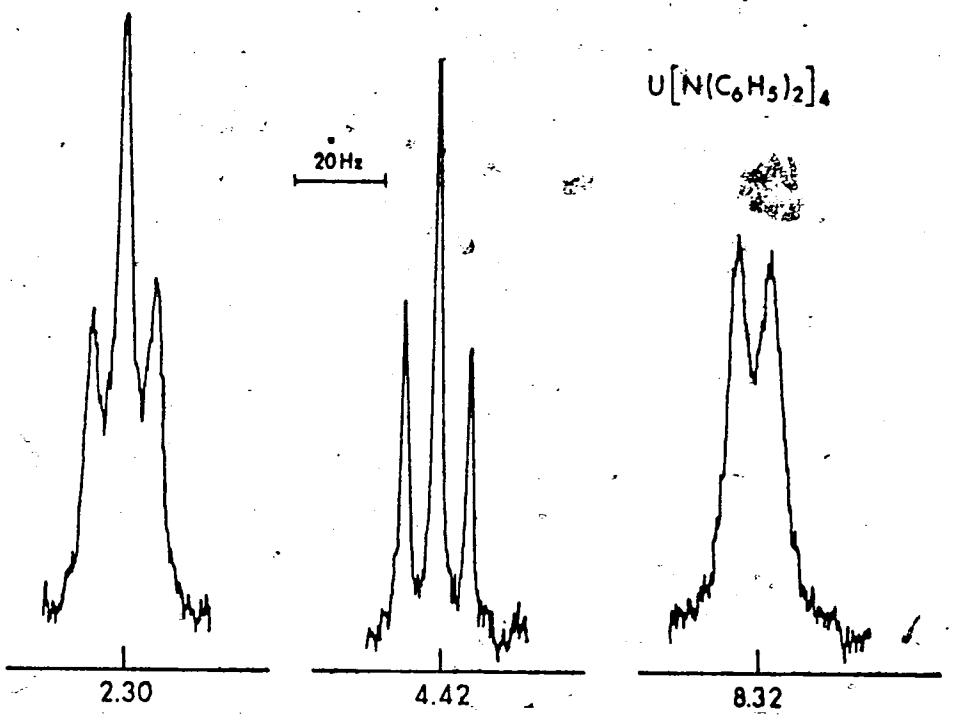


Figure 4. ^{1}H-NMR Spectrum of U[N$(C_6H_5)_2]_4$. Chemical shifts given in p.p.m. relative to internal benzene.

complex would be more convenient. Of course, the possibility that the complex would not be monomeric (and therefore not four-coordinate) was real, but at this point in the research this seemed hardly a factor to be considered.

The reaction of UCl_4 and $LiNMe_2$ (equation II-3) in THF yields $U(NMe_2)_4$. In contrast to the high solubilities of $U(NEt_2)_4$ and $U[N(i\text{-}Pr)_2]_4$, $U(NMe_2)_4$ was found to be less soluble in common solvents. It is nearly insoluble in pentane, slightly soluble in benzene, but rather soluble in THF. The solubility properties of $U(NMe_2)_4$ render the separation of LiCl from $U(NMe_2)_4$ difficult. Utilization of a mixed solvent system, THF-hexanes (1:3 v/v), helps in this regard although not all of the LiCl was removed as shown by positive lithium and chloride tests. The low amine analysis obtained on this sample, 93% of the theoretical value, can at least partly, be explained by the known presence of LiCl as an impurity.

Since the "ideal" starting material was not realized in this amide either, and especially since its reactivity toward cyclopentadiene was less than desirable (Chapter IV), further experimentation with the synthesis was not undertaken.

However a recent report by Bagnall and Yanir[79] on various tetrakiscarbamate complexes of Th and U (synthesized by the insertion of either CO_2, COS, CS_2 or CSe_2 into the corresponding tetrakisamido

derivative) contains a brief mention of the preparation of the amides, $M(NR_2)_4$ where R = Me, Et, i-Bu. It is said that the reactions were carried out in hexanes and the complexes were isolated by filtration and evaporation of the solvent from the filtrate. That the dimethylamido derivative could be obtained in this way was rather surprising to us since we have observed it to be insoluble in hexanes. To remove any ambiguity about the two synthetic methods and contrasting properties of $U(NMe_2)_4$, the method of Bagnall was repeated. Since no experimental details are given by Bagnall, the first reaction of $LiNMe_2$ and UCl_4 (equation II-3) in hexanes was performed using $LiNMe_2$ which had been isolated and weighed out, as is our usual practice. A dark precipitate appeared which would not redissolve even after 48 hours (Bagnall isolated his amides after 17 hours). However the addition of THF caused rapid dissolution of the solid and complete conversion to $U(NMe_2)_4$. It should also be noted that similar observations were also made in an attempted preparation of $Th(NEt_2)_4$ (which is soluble in hexanes) using this procedure. The intermediate precipi[illegible] is postulated to be amido-chloro-species which are insoluble in the hexanes and results in the very slow conversion to the tetrakisamides.

A second reaction was then performed. This time, however, the $LiNMe_2$ was not isolated but was prepared in the presence of excess amine and the UCl_4 was added to the resultant slurry. The reaction seemed to proceed as before in the early stages (i.e. a dark precipitate formed), but after 24 hours a dark solution was obtained.

Filtration of the solution followed by removal of the solvent from the filtrate resulted in a dark brown solid. A mass spectrum of the solid showed only $U(NMe_2)_4$ (m/e 414). A ^1H-NMR spectrum in C_6D_6 (it was qualitatively observed that this solid was more soluble in either hexanes or benzene than that obtained from either the THF reaction or THF-hexanes mixture) was most puzzling as several strong emission peaks were observed. The peaks remained even after one hour with their positions changing slightly. The nature of the species in solution which caused this phenomenon is not known. (The NMR spectra of the other products were very poor due to limited solubility, however the emission peaks observed above were not seen.)

Bagnall's method (i.e.) the use of excess amine when preparing $LiNR_2$ *in situ*) could presumably be applied to other amide complexes. However it must be remembered that the actual isolation and weighing out of $LiNR_2$ permits a more stringent control of the stoichiometry, a very important consideration when the amide is prepared *in situ* for further reactions.

SPECTRAL STUDIES

NMR SPECTRA

The ^{1}H-NMR spectra of Th- and $U[N(i\text{-}Pr)_2]_4$, and $U[N(C_6H_5)_2]_4$ are shown in Figures 1 and 4, respectively. The ^{1}H-NMR spectrum of $Th[N(C_6H_5)_2]_4$ was uninformative since, in the absence of paramagnetic shifts, only a complicated multiplet was observed at the same position as that of the residual protons in C_6D_6. The ^{1}H-NMR spectrum of $U(NMe_2)_4$ cannot be given with any certainty due to the low solubility of $U(NMe_2)_4$ in benzene, (a spectrum run in THF did nothing to clarify the situation). In addition the ^{13}C-NMR spectra of Th- and $U[N(i\text{-}Pr)_2]_4$ were recorded and are shown in Figures 2 and 3, respectively. Besides noting the sharp resonances, including spin-spin coupling (inspite of the presence of a paramagnetic uranium atom) and drawing attention to the small isotropic shifts, we defer the discussion of these spectra to Chapter V.

INFRARED SPECTRA

A priori one would predict from simple group theoretical consideration that a MN_4 framework (as in the tetrakisamides) which is tetrahedrally disposed about M would exhibit one metal-nitrogen stretching mode, $\nu(M\text{-}N)(F_2)$ in the infrared spectra. Hence the observance of a single strong band at 590 cm^{-1} in the infrared spectrum and a single polarized Raman band at 532 cm^{-1} in $Ti(NMe_2)_4$ led Burger, et al. to assign the bands to $\nu(Ti\text{-}N)(F_2)$ and $\nu(Ti\text{-}N)(A_1)$,

respectively, on the basis of a tetrahedral geometry about titanium.[85] Later Bradley and Gitlitz similarly assigned the single band in the 700-500 cm^{-1} region of the IR spectra of $M(NR_2)_4$ complexes (R = Me, Et, n-Pr, n-Bu, i-Bu; M = Ti, Zr, Hf) to $\nu(M-N)(F_2)$ based on a tetrahedral geometry.[72]

In contrast to the IR spectra of the transition metal derivatives, the spectra of Th- and $U(NEt_2)_4$ (Figure 5; Table VII) exhibit three bands below 600 cm^{-1}. The observance of more than one band in the $\nu(M-N)$ region, indicates that the geometry of $U(NEt_2)_4$ is lower than tetrahedral. On the basis of the infrared spectrum and the following observations it is proposed that the lower symmetry of $U(NEt_2)_4$ is a result of molecular association: 1) Bradley has found Zr- and $Hf(NMe_2)_4$ to be slightly associated (degree of association is 1.22, where 1.0 indicates a monomer); 2) the mass spectrum of $U(NMe_2)_4$ which will be discussed later on shows dimeric ions in the gas phase; and 3) the much larger size of Th(IV) and U(IV) compared to Hf(IV) (Table VI) allows for more association. This would result in more than one $\nu(M-N)$ mode to be infrared active.

As can be seen from the data in Table VII the highest frequency band of the trio is in good agreement with the previously reported $\nu(M-N)$ bands of Th- and $U(NEt_2)_4$. Bradley and Gitlitz report that the infrared spectrum of EtN = $Ta(NEt_2)_3$ (local C_{3v} symmetry) showed only one metal-nitrogen stretch (E) at 585 cm^{-1} while two bands (A_1, E) are expected.[72] They did, however, note that a weak band was present at 495 cm^{-1} which could be due to the A_1 mode. In addition the

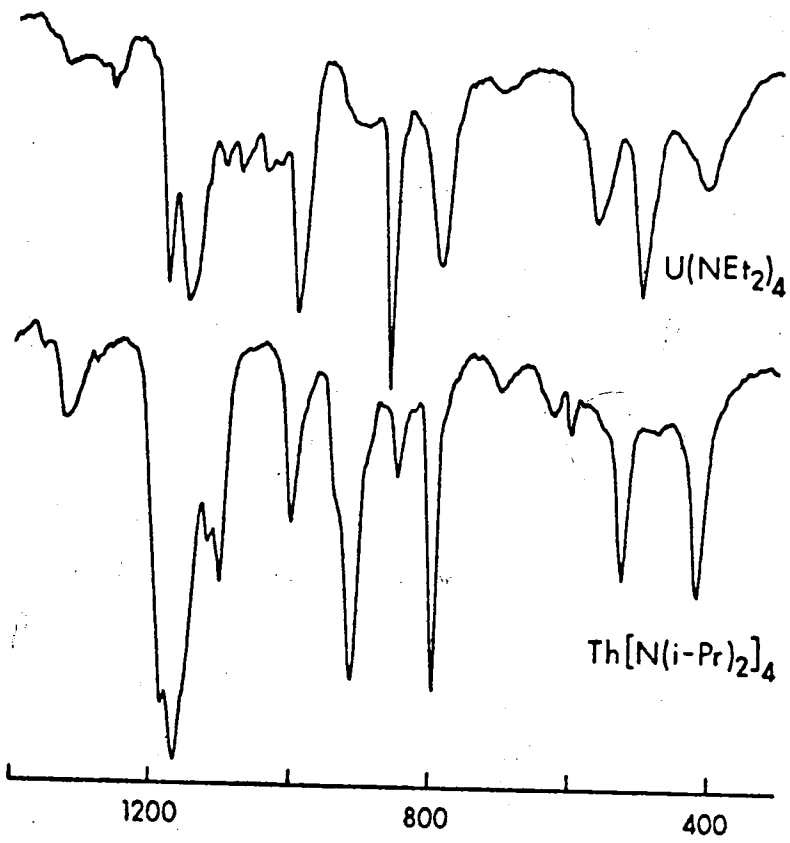


Figure 5. Infrared Spectra of $U(NEt_2)_4$ and $Th[N(i\text{-}Pr)_2]_4$. Recorded in hexanes solutions.

TABLE VII

SUMMARY OF SOME BANDS IN THE INFRARED SPECTRA[a]
$M(NR_2)_4$ COMPLEXES

R	M	symν(NC_2)	ν(M-N)	REFERENCE
Me	Th	990s[b]	530s	d
	U	980s	520m	d
		-	500s 482sh[f]	e
		--	498s 438s[g]	e
Et	Th	998s	540s	c
		995s	540s	c
		993s	549s 499s	e
	U	990s	560s 496s	e
		990s	555s	d
i-Pr	Th	998s	521s	e
	U	996s	520s	e
i-Bu	Th	--	645s	d
	U	--	638s	d
C_6H_5	U	--	497m	e

[a] given in cm^{-1}

[b] s = strong; m = medium; w = weak; sh = shoulder

[c] from reference 72

[d] from reference 97

[e] this work

[f] mull

[g] benzene solution

infrared spectrum of $Cp_2U(NEt_2)_2$ (Chapter III) shows bands at 561 and 494 cm^{-1} which are consistent with the two ν(M-N) modes expected for local C_{2v} symmetry. Hence it seems reasonable to assign the two high frequency bands to metal-nitrogen stretching modes, while the assignment of the lowest frequency band is uncertain. (It should be noted that Bagnall and Yanir make no mention of the 495 cm^{-1} band.)

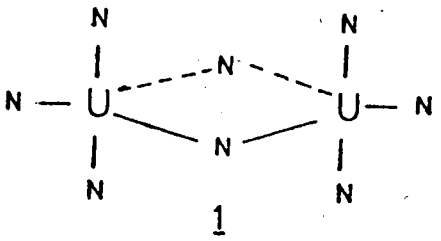
Since the only clear-cut example of an associated actinide amide, albeit in the gas phase, was the tetrakisdimethylamidouranium(IV) for which only one ν(M-N) band was reported,[79] it was decided to reinvestigate the infrared spectrum of this complex both in the solid state and in a non-coordinating solvent. The low frequency portion (i.e. below 600 cm^{-1}) of the infrared spectra (spectra were recorded in a mineral oil mull and a benzene solution) was somewhat similar to that of Th- and $U(NEt_2)_4$. Bands were seen at 500 and 482 cm^{-1} (mull, both were broad) and, at 498, 438 and 392 cm^{-1} (benzene solution) with the 438 and 392 bands also being broad. This broadness may indicate the presence of several bands but this is uncertain.

Nonetheless it is apparent by the appearance of more than one band in the ν(M-N) region that $U(NMe_2)_4$, like Th- and $U(NEt_2)_4$, is neither a monomer in benzene solution nor in the solid state. Also in the Th- and $U(NEt_2)_4$ complexes, the two higher frequency bands are assigned to ν(M-N) while the assignment of the lowest frequency band is uncertain. What is important is that one indeed sees strong bands in the region which is associated with metal-nitrogen stretching modes for a molecule which is most probably associated. This we

believe provides further support for our conclusion about the diethylamides.

The ν(M-N) frequencies of Bagnall and Yanir (Table VII) are 20–30 cm^{-1} higher than those reported in this work, whereas the frequencies of the other assigned bands are close. The reason for the discrepancy of the low frequency bands is not known. It should also be noted that we obtained identical infrared spectra from $U(NMe_2)_4$ samples prepared by our method and by the presumed method of Bagnall.

The simplest association of these molecules would be a dimeric unit. One possible structure would be



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possessing an overall D_{2h} symmetry and three terminal, IR active, metal-nitrogen stretching modes would be expected. More associated species (i.e. trimers, tetramers, etc.) would also cause one to predict more than one band.

In line with the predicted tetrahedral geometry for Th- and $U[N(i\text{-}Pr)_2]_4$ (Figure 5) and for $U[N(C_6H_5)_2]_4$, their infrared spectra show only one band in the metal-nitrogen stretching region at 521, 420, and 497 cm^{-1}, respectively (Table VII). Each of these three bands is assigned to the ν(M-N) (F_2) mode based on a local tetrahedral geometry.

There are three possible ways in which the metal-nitrogen stretching frequency, ν(M-N) can be affected: an increase in the mass of the NR_2 ligand should cause a decrease in ν(M-N); an increase in steric interactions should cause a decrease in ν(M-N) because they produce a weaker metal-nitrogen bond; and an electronic effect would increase or decrease in ν(M-N) depending on the relative contributions of resonance forms 2 and 3. Electron donating groups will

$$\underset{\sim}{2}\quad M-\ddot{N}R_2 \longleftrightarrow \bar{M}=\overset{+}{N}R_2 \quad \underset{\sim}{3}$$

cause an increase of contribution 3 thereby increasing ν(M-N) while electron withdrawing groups will have the opposite effect. Hence the observation by Bradley and Gitlitz that the ν(M-N) decreased in the order,

$$N(i\text{-}Bu)_2 > N(n\text{-}Bu)_2 \sim N(n\text{-}Pr)_2 > NEt_2 > NMe_2$$

for complexes of Ti, Zr, Hf, and Ta caused them to explain the trend in terms of nitrogen $\rightarrow$ metal $p\pi$-$d\pi$ bonding (i.e. a larger relative contribution of 2).[72] Similarly Bagnall and Yanir interpretted the decrease of ν(M-N)

$$(i\text{-}Bu)_2N > NEt_2 > NMe_2$$

in terms of the same type of electronic effect.

Table VII summarizes the available data on tetrakisamido derivatives of Th and U. It can be seen from Table VII that ν(M-N) decreases in the following order

$$N(i\text{-}Bu)_2 > NEt_2 > NMe_2 \sim N(i\text{-}Pr)_2 > N(C_6H_5)_2.$$

The explanation given by Bradley and Gitlitz would predict the decrease in ν(M-N) as seen above except for the $N(i\text{-}Pr)_2$ complex. If the electronic effect predominates in all of these derivatives the $N(i\text{-}Pr)_2$ complex's metal-nitrogen stretching frequency should be greater than that of the NEt_2 complex. The decrease in ν(M-N) of the $N(i\text{-}Pr)_2$ complex is best interpretted in terms of a predominance of the steric effect over the electronic effect and a weakening of the metal-nitrogen bond as compared to the other complexes with similar electron donating properties.

MASS SPECTRA

Mass spectrometry in organometallic chemistry has become one of the most powerful tools for identification of compounds, for the determination of fragmentation patterns which can help in the elucidation of molecular geometries, and for estimates of bond dissociation energies and heats of formation of ions.[86-88] Here, and elsewhere in this thesis, it will mainly be used for identification purposes though several decomposition schemes will be mentioned.

The mass spectra of several $M(NR_2)$ complexes (R = Me, M = U; R = Et, M = Th, U; R = i-Pr, M = Th, U; R = C_6H_5, M = U) have been recorded. This is in contrast to Watt and Gadd's failure to obtain the mass spectra of either the Th- or $U(NEt_2)_4$.[78] They report that the mass spectra of the two compounds were identical showing m/e 446 as the highest peak which was attributed to polymeric decomposition. Based on our experience in running the mass spectra of extremely

air-sensitive samples, it would seem that their failure is a result of an inadequate procedure for the direct insertion of air-sensitive compounds into the mass spectrometer. The results shown in Table VIII through XI establish that the tetrakisamido derivatives of Th and U do indeed give reasonable mass spectra.

The mass spectral data of $U(NMe_2)_4$ is given in Table VIII. Unfortunately there was some thermal decomposition as the sample was volatized (140°C) as seen by the fact that peaks at m/e 45 and 44 ($HNMe_2^+$ and NMe_2^+, respectively) go off-scale. As a result the peak at m/e 414 is not the base peak of the spectrum but rather is the largest metal-containing ion.

One of the most interesting aspects of the spectrum is the occurrance of a peak at m/e 838 which corresponds to $[U(NMe_2)_4]_2$, the dimeric tetrakisamide. This is in keeping with the earlier postulation that the compound was much less soluble in non-coordinating solvents than the other dialkylamido derivatives presumably as a result of a greater amount of association than in the other derivatives. In addition small peaks corresponding to $U_2(NMe_2)_7^+$ (m/e 784), $U_2(NMe_2)_6(MeN{=}CH_2)^+$ (m/e 783), $U_2(NMe_2)_5(MeN{=}CH_2)^+$ (m/e 501), $U(NMe_2)_5^+$ (m/e 458), and $U(NMe_2)_4(MeN{=}CH_2)^+$ (m/e 457) were also observed.

The fragmentation of $U(NMe_2)_4$ is relatively simple and straightforward. The monomeric molecular ion, $U(NMe_2)_4^+$, loses a molecule of dimethylamine to give an ion formulated as $U(NMe_2)_2(MeN{=}CH_2)^+$ which in turn loses the $MeN{=}CH_2$ radical to give the $U(NMe_2)_2^+$ ion. These reactions are verified by the observance of metastable peaks

TABLE VIII

SUMMARY OF THE MASS SPECTRAL DATA ON $U(NMe_2)_4$ [a]

MAJOR PEAKS

MASS (m/e)	RELATIVE ABUNDANCE (%)	PROPOSED ASSIGNMENT
828	9	$U_2(NMe_2)_8^+$
414	100[b]	$U(NMe_2)_4^+$
369	11	$U(NMe_2)_2[(Me)N + CH_2]^+$
326	27	$U(NMe_2)_2^+$

PROCESSES OBSERVED

PROCESS	METASTABLE PEAKS Calculated	Observed
$U(NMe_2)_4^+ \longrightarrow U(NMe_2)_2[(Me)N{=}CH_2]^+ + HNMe_2$	328.9	329.0
$U(NMe_2)_2[(Me)N{=}CH_2]^+ \longrightarrow U(NMe_2)_2^+ + MeN{=}CH_2$	288.0	288.0

[a] 140°C

[b] is the largest metal-containing ion

at m/e 329 and 288 (Table VIII). There were only insignificant amounts of other ions seen. On the whole the spectrum is quite simple since only a few decomposition processes were occurring.

The mass spectra of Th- and $U(NEt_2)_4$ are given in Table IX. The 70 ev (i.e. normal operating conditions) spectra of both the Th- and $U(NEt_2)_4$ complexes show only the monomeric molecular ion (i.e. m/e 520 and 526, respectively), in contrast to $U(NMe_2)_4$. Any associations between monomeric units would be a result of Lewis acid-base type interactions between the formal lone pair of electrons on the amido group (2) and another uranium atom. It has previously been seen that weak Lewis acid-base adducts of the type, CpLn(COT)·B (Ln = a lanthanide metal; B = a Lewis base), do not show the expected molecular ion at 70 ev but do so at much lower electron beam energies.[89] Hence an attempt was made to search for dimeric (or trimeric) ions at lower electron beam energies. It was found that an electron beam energy of 12 ev gave the simplest spectrum and the peaks with the highest intensities but still no peaks at higher mass were seen.

It can be seen from Table IX that the spectrum of $U(NEt_2)_4$ at 12 ev is simple and straightforward with the molecular ion being of comparable abundance to that of the base peak. Fragmentation appears to occur by losses of $HNEt_2$ (e.g. m/e 526 → m/e 453) and H_2 molecules at 12 ev, while at 70 ev loss of the NEt_2 radical from the molecular ion (i.e. m/e 526 → m/e 454) followed by loss of a molecule of hydrogen is comparable to the loss of diethylamine followed by loss of a H_2 molecule. This is seen by the small peak at m/e 454 at 12 ev

TABLE IX

SUMMARY OF MASS SPECTRA OF Th- AND $U(NEt_2)_4$

Th[a]		U			
MASS (m/e)	RELATIVE ABUNDANCE (%)	MASS (m/e)	RELATIVE ABUNDANCE[b] (%)	RELATIVE ABUNDANCE[c]	PROPOSED ASSIGNMENT
520	10	526	97	25	$M(NEt_2)_4^+$
448	d	454	d	5	$M(NEt_2)_3^+$
447	10	453	22	7	$M(NEt_2)_2[(Et)N{=}C(H)Me]^+$
445	8	451	13	7	$M(NEt_2)[(Et)N{=}C(H)Me]^+[(Et)N{-}C(H){=}CH_2]^+$
376	d	382	17	d	$M(NEt_2)_2^+$
374	d	380	21	14	$M(NEt_2)[(Et)N{-}C(H){=}CH_2]^+$
73	100	73	100	65	$HNEt_2^+$
72	71	72	55	100	NEt_2^+

[a] 75°C; 70 ev

[b] 140°C; 12 ev

d = very small amount

[c] 140°C; 70 ev

(its intensity is explained just by ^{13}C contributions to m/e 453) while at 70 ev m/e 454 is nearly comparable to m/e 543.

The mass spectra of the diisopropylamido derivatives (Table X) are much more complicated than the other spectra observed to date on amido compounds. A complete assignment of the spectra, or even a complete assignment of the peaks which are present in significant abundance (i.e. >10%), would be quite involved and tentative at best due to the many possible sources of ions. The more complicated nature of the spectra than those reported here or any of the other published mass spectra of transition metal amides[65] is due to the very sterically crowded nature of the molecule. The steric interactions increase as the branching from the carbon α to the nitrogen increases. Hence the order of steric interactions, $N(i\text{-}Pr)_2 > NEt_2 > NMo_2$, is exactly the same as the order of complication of the spectra.

One important feature of the spectra is the much larger amount of the $M(NR_2)_3^+$ ion in the diisopropyl derivatives than in either the dimethyl or diethyl derivatives. It appears that the diisopropylamido group is lost quite readily from the molecular ion while losses of amine are more predominant in the other derivatives. The earlier explanation of the low ν(M-N) in $M[N(i\text{-}Pr)_2]_4$ being due to steric effects is in fact supported by the present mass spectral data. The low ν(M-N) indicated that the metal-nitrogen bond had been weakened as a result of steric interactions, so if this explanation is indeed correct, one would expect this bond to be more easily cleaved than in the other amides. By losing one $N(i\text{-}Pr)_2$ group the molecule greatly

TABLE X

SUMMARY OF THE MASS SPECTRA OF Th- AND U[N(i-Pr)$_2$]$_4$

Th[a,b]		U[b,c]		
MASS (m/e)	RELATIVE ABUNDANCE (%)	MASS (m/e)	RELATIVE ABUNDANCE (%)	PROPOSED ASSIGNMENTS
632	8.0	638	52.2	M[N(i-Pr)$_2$]$_4^+$
532	30.0	538	11.3	M[N(i-Pr)$_2$]$_3^+$
530	100[b]	536	100	[(i-Pr)$_2$N]M(N$_2$C$_{12}$H$_{26}$)$^+$
528	36.9	534	33.5	[(i-Pr)$_2$N]M(N$_2$C$_{12}$H$_{26}$)$^+$
526	9.4	532	10.0	M(N$_3$C$_{18}$H$_{36}$)$^+$
488	5.1	494	5.6	M(N$_3$C$_{15}$H$_{34}$)$^+$
487	1.0	483	10.4	M(N$_3$C$_{15}$H$_{33}$)$^+$
486	7.5	492	9.6	M(N$_3$C$_{15}$H$_{32}$)$^+$
447	4.5	453	10.4	M(N$_2$C$_{13}$H$_{31}$)$^+$
445	40.8	451	23.9	M(N$_2$C$_{13}$H$_{29}$)$^+$
431	9.4	437	7.0	MN$_2$C$_{12}$H$_{27}^+$
430	3.5	436	15.7	MN$_2$C$_{12}$H$_{26}^+$
429	16.7	435	6.1	MN$_2$C$_{12}$H$_{25}^+$
389	2.2	3.95	13.0	M(NC$_{10}$H$_{23}$)$^+$
387	11.6	393	22.6	M(NC$_{10}$H$_{21}$)$^+$
373	5.3	379	10.0	MNC$_9$H$_{19}^+$

[a] 140°C

[b] the main representative metal-containing peaks are given

[c] 125°C

reduces the number of steric interactions as the NUN angle would most probably be 109° in the tetrakisamide and 120° in $U[N(i\text{-}Pr)_2]_3^+$.

Another interesting aspect of the spectra is the successive losses of three H_2 molecules once the $M[N(i\text{-}Pr)_2]_3^+$ ion is generated. These ions appear at m/e 530, 528 and 526 for the thorium amide and at m/e 536, 534, and 532 for the uranium amide. The losses of H_2 are verified by the observance of the expected metastable peak four mass units below the ion that loses the hydrogen. It is interesting to note that the mass spectrum of $U[S_2CN(i\text{-}Pr)_2]_4$ (i.e. the CS_2-inserted product) does not show such losses of H_2. The clear implication of this is that steric interaction is a necessary requirement for the H_2 losses. Whether the loss of H_2 happens between two adjacent amido groups or within one is not certain. However the rather different behavior of the amide and the dithiocarbamate and significant changes of the fragmentation pattern after the observation of the fragment $(MN_3C_{18}H_{36})^+$ could be taken as an indication of interligand H_2 abstraction.

The mass spectrum of $U[N(C_6H_5)_2]_4$ (Table XI) is relatively simple and straightforward. The large abundance of the $U[N(C_6H_5)_2]_3^+$ ion (m/e 742) is interpreted in terms of a weaker metal-nitrogen bond in the tetrakisamide than in the other dialkylamido derivatives (cf. the low ν(M-N) of $U[N(C_6H_5)_2]_4$ in Table VI). The constitution of the peaks at m/e 573, 569, and 403 is indeed puzzling since one would have to violate normal rules of chemical bonding to explain them.

TABLE XI

SUMMARY OF THE MASS SPECTRUM OF $U[N(C_6H_5)_2]_4$ [a]

MASS (m/e)	RELATIVE ABUNDANCE (%)	PROPOSED ASSIGNMENT
910	23.7	$U[N(C_6H_5)_2]_4^+$
742	100[b]	$U[N(C_6H_5)_2]_3^+$
740	8.9	$U[N(C_6H_5)_2]_2[N(C_6H_8)]^+$
573	21.0	$U[N(C_6H_5)_2][N(C_{12}H_9)]^+$
569	13.2	$UN_2C_{24}H_{15}^+$
403	10.5	$UNC_{12}H_7^+$
336	28.4	$(C_6H_5)_2N\text{-}N(C_6H_5)_2^+$

[a] 230°C

[b] not actually the base peak but the largest metal-containing ion

REACTIVITY OF Th- AND $U(NR_2)_4$ COMPLEXES

REACTIVITY TOWARD TWO EQUIVALENTS OF CYCLOPENTADIENE

One of the main reasons for preparing the various $M(NR_2)_4$ complexes was their expected (or more honestly, their hoped for) reactivity toward two equivalents of cyclopentadiene to form the corresponding $Cp_2M(NR_2)_2$ complexes. It was found that $U(NEt_2)_4$ and $U[N(C_6H_5)_2]_4$ would indeed react in this way to give pure $Cp_2U(NEt_2)_2$ and $Cp_2U[N(C_6H_5)_2]_4$, while the same reaction with $U(NMe_2)_4$ and $Th(NEt_2)_4$ did not give the pure bisamides. On the other hand neither of the diisopropylamido complexes would react with cyclopentadiene, presumably as a result of the very sterically crowded environment of the metals. The reactivity of the $M(NR_2)_4$ complexes towards two equivalents of cyclopentadiene will be discussed in more detail in the following chapter. A summary of these reactions and their conditions is given in Table XII.

REACTIVITY TOWARD ALCOHOL

Gilman, et al. reported that $U(NEt_2)_4$ would react with four equivalents of either an alcohol or a thiol to give the corresponding tetraalkoxide or tetrakisthiolate (equation II-6).[3] Since the

$$U(NEt_2)_4 + 4HX \longrightarrow UX_4 + 4HNEt_2 \qquad \text{II-6}$$

$$X = OR, SR$$

TABLE XII

REACTIONS OF $M(NR_2)_4$ WITH

TWO EQUIVALENTS OF CYCLOPENTADIENE

$M(NR_2)_4$	REACTION TEMPERATURE	SOLVENT	PRODUCTS
$U(NMe_2)_4$	a.t.[a]	THF	$Cp_2U(NMe_2)_2 + Cp_3U(NMe_2)$
$Th(NEt_2)_4$	a.t.	pentane	$CpTh(NEt_2)_3 + Cp_2Th(NEt_2)_2 + Cp_3Th(NEt_2)$
$U(NEt_2)_4$	0^oC	pentane	$Cp_2U(NEt_2)_2$
$Th[N(i\text{-}Pr)_2]_4$	a.t.	pentane	no reaction
	reflux	pentane	no reaction
	a.t.	THF	no reaction
$U[N(i\text{-}Pr)_2]_4$	a.t.	pentane	no reaction
	reflux	pentane	no reaction
	a.t.	THF	no reaction

[a] ambient temperature

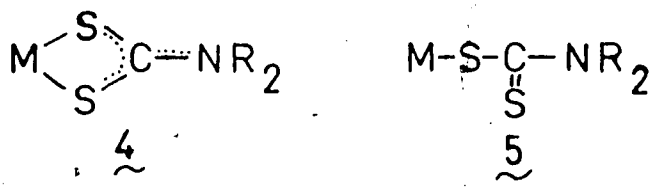
diisopropylamido derivatives would not react with cyclopentadiene it was decided to see if they would react with the stronger acid, t-BuOH. Indeed it was seen that there was an immediate reaction when a t-BuOH solution was added to $U[N(i\text{-}Pr)_2]_4$ in THF. Removal of the solvent under vacuum gave a green solid which was identified as $U(t\text{-}BuO)_4$ by mass spectrometry (i.e. m/e 530). This green solid is also easily oxidized by small amounts of air to give $U(t\text{-}BuO)_5$ just as reported by Gilman.[3] The pentakisbutoxide was also identified by mass spectrometry (m/e 603).

REACTIVITY TOWARD CARBON DISULFIDE

Bagnall and Yanir have recently reported that the tetrakisamides of thorium and uranium will react with CO_2, COS, CS_2 and CSe_2 to yield the corresponding carbamate complexes.[79] The reaction of $U[N(i\text{-}Pr)_2]_4$ with excess CS_2 was found to also produce the corresponding thiocarbamate, $U[S_2CN(i\text{-}Pr)_2]_4$, identified by mass spectrometry (m/e 942). The tetrakisdithiocarbamates of the actinides are well-known, and all appear to be eight-coordinate.[99,100] Hence the preparation of $U[S_2CN(i\text{-}Pr)_2]_4$ was of interest to see if the very bulky $U[N(i\text{-}Pr)_2]_4$ would react with CS_2.

The mass spectrum of $U[S_2CN(i\text{-}Pr)_2]_4$, however, did not show the successive loss of three hydrogen molecules as seen in the parent amide. Instead loss of a dithiocarbamate ligand from the molecular ion, producing $U[S_2CN(i\text{-}Pr)_2]_3^+$ (m/e 766), followed by the losses of a CS_2 molecule are the two major decomposition reactions.

The infrared spectrum of $U[S_2CN(i\text{-}Pr)_2]_4$ shows peaks at 1480 and 1041 cm^{-1} which are assignable to the $\nu(C \doteq N)$ and $\nu(C \doteq S)$, respectively, of the dithiocarbamate ligand. In addition unassigned yet characteristic peaks of dithiocarbamates were observed at 1262, 1197, and 1147 cm^{-1}.[99-101] One of the points of interest in the study of dithiocarbamate complexes is relating their infrared spectra to the type of bonding in the complex. There are two ways in which a dithiocarbamate ligand may be attached to a metal: as a bidentate ligand, 4, or as a S-bond monodentate ligand, 5. It seems that the appearance



4 5

of only one ν(C-N) band (circa 1490 cm^{-1} for dithiocarbamate complexes of the actinides)[99,100] and one (C-S) band (1000 cm^{-1} region)[99,100] is indicative of only bidentate ligands, 4.[102] Those complexes in which it has been established by x-ray crystallography that there are both types of bonding (e.g. $Ru(NO)(S_2CNR_2)_3$[103,104] $Rh(PPh_3)(S_2CNMe_2)_3$[105], and $Sn(S_2CNEt_2)_4$[106]) seem to exhibit additional infrared bands not found for complexes having only bidentate ligands. Of the extra bands there is one around 1470 cm^{-1} assigned to ν(C-N)[103,105] and one around 1000 cm^{-1} which is assigned to $\nu(C{=}S)$.[107] The absence of these extra bands in all the reported tetrakisdithiocarbamate complexes of actinides indicates that they are eight-coordinate complexes.[77,99,100]

CONCLUSION

It has been shown that tetrakisamido derivatives of the actinides can be prepared and indeed some are true four-coordinate complexes. The tetrakisamides are much more delicate than their transition metal counterparts being sensitive to heat and light in addition to air and moisture. The isolation of analytically pure samples is consequently extremely difficult. Nevertheless the complexes do appear to be versatile starting materials for the synthesis of otherwise inaccessible actinide derivatives both by acid displacement and by insertion reactions. Indeed both of these routes have only been touched upon and it is expected that the demonstration of their utility will only mark the beginning of intense research on the chemistry of the amido derivatives of the actinides.

CHAPTER III - SYNTHESIS, CHARACTERIZATION, AND PROPERTIES OF CYCLOPENTADIENYL-AMIDO COMPLEXES OF THORIUM AND URANIUM

INTRODUCTION

As indicated in Chapter I of this thesis, the elusiveness of Cp_2UCl_2 forced us to look for other suitable starting materials for the preparation of Cp_2U-derivatives. Bradley[63] and Lappert[56,64] have shown the dialkylamido derivatives of the transition metals to be synthetically useful reagents. The amido complexes react with a variety of protic ligands to form new transition metal complexes by simple acid-base reactions. Of particular interest was the report of Chandra and Lappert in which it was shown that the tetrakisamido derivatives of titanium, zirconium, and hafnium react with excess cyclopentadiene to form the corresponding $Cp_2M(NR_2)_2$ complexes (equation III-1).[56] Since the complexes still contain two

$$M(NR_2)_4 + \text{excess } CpH \longrightarrow Cp_2M(NR_2)_2 + 2HNR_2 \qquad \text{III-1}$$

reactive metal-nitrogen bonds they will in turn react with other ligands which have acidic hydrogens (equation III-2). It was hoped

$$Cp_2M(NR_2)_2 + 2HX \longrightarrow Cp_2MX_2 + 2HNR_2 \qquad \text{III-2}$$

that similar amides of thorium and uranium could be made and that they would react like their transition metal analogs, thereby providing in the absence of Cp_2UCl_2 the next best starting material for the

preparation of other Cp_2U-derivatives. In Chapter II it was shown that a variety of tetrakis amido derivatives of thorium and uranium can be prepared and that, except for the very sterically crowded Th- and $U[N(i\text{-}Pr)_2]_4$, they will react with cyclopentadiene (equation III-1) to give the desired $Cp_2M(NR_2)_2$ complexes. This chapter describes the full details of the synthesis and reports on the properties of the formed complexes.

SYNTHESIS AND CHARACTERIZATION OF $Cp_2M(NR_2)_2$ COMPLEXES

BIS(η-CYCLOPENTADIENYL)BIS(DIETHYLAMIDO)URANIUM(IV)

It was hoped that essentially the same synthetic procedure as used to prepare the corresponding $Cp_2M(NR_2)_2$ derivatives of the transition metals could be utilized for uranium. However, as mentioned in Chapter II, Gilman *et al.* could only isolate $U(NEt_2)_4$ in less than 30% yield.[3] Since it seemed that the low yield of $U(NEt_2)_4$ was mainly a result of thermal decomposition, we decided to try to prepare $Cp_2U(NEt_2)_2$ by the *in situ* preparation of $U(NEt_2)_4$ followed by its reaction with two equivalents of cyclopentadiene (equations III-3 and III-4). Work up of the reaction resulted in the isolation of the

$$UCl_4 + 4LiNEt_2 \longrightarrow U(NEt_2)_4 + \qquad \text{III-3}$$

$$U(NEt_2)_4 + 2CpH \longrightarrow Cp_2U(NEt_2)_2 + 2HNEt_2 \qquad \text{III-4}$$

product as golden leaves as described in Chapter VI. A ^{1}H-NMR spectrum of the product (Figure 6) showed a singlet at 20.94 p.p.m. upfield from internal benzene, a singlet at 18.86 p.p.m., a weak triplet at 8.40 p.p.m., a much stronger triplet at 5.70 p.p.m., and a quartet at -1.5 p.p.m. (downfield). The relative areas of the singlet at higher field, the stronger triplet and the quartet were found to be 5:6:4 (or 10:12:8) which is what would be expected for $Cp_2U(NEt_2)_2$! The relative area of the two other peaks was found to be 5:2 (or 15:6) indicating that these were probably due to $Cp_3U(NEt_2)_2$.

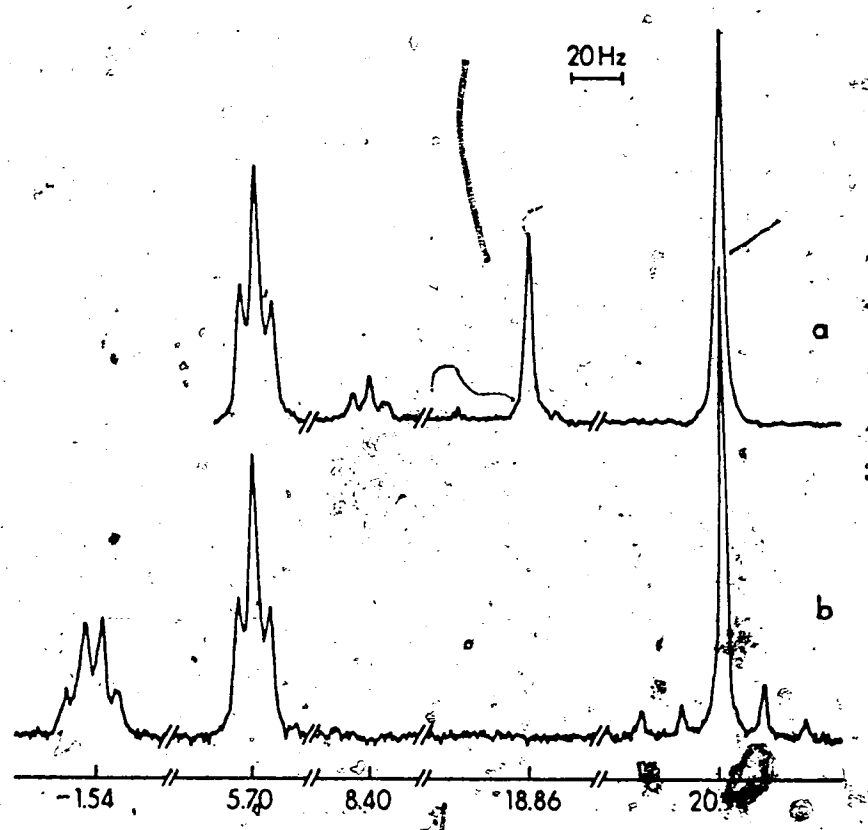


Figure 6. ^{1}H-NMR Spectra of $Cp_2U(NEt_2)_2$ before and after removal of $Cp_3U(NEt_2)$. Chemical shifts given in p.p.m. relative to internal benzenes.

However the expected quartet of the ethyl group was not observed in this spectrum. If this assignment was correct then the solid contained 76% $Cp_2U(NEt_2)_2$ and 24% $Cp_3U(NEt_2)$. A mass spectrum of the product showed the presence of $Cp_2U(NEt_2)_2$ (m/e 512) and $Cp_3U(NEt_2)$. The ^{1}H-NMR spectrum of a genuine sample of $Cp_3U(NEt_2)$ (prepared by the reaction of Cp_3UCl and $LiNEt_2$) confirmed that the two extra peaks seen in the spectrum of $Cp_2U(NEt_2)_2$ were indeed due to $Cp_3U(NEt_2)$. The preparation and spectral properties of $Cp_3U(NEt_2)$ will be discussed later.

After several fractional crystallizations pure $Cp_2U(NEt_2)_2$ could be isolated, but significant amounts of $Cp_2U(NEt_2)_2$ were lost. Nevertheless the important point was established, $Cp_2U(NEt_2)_2$ could be prepared and isolated as a pure solid. The formation of a mixture of $Cp_3U(NEt_2)$ and $Cp_2U(NEt_2)_2$ in the original product seemed to indicate that the <u>in situ</u> generation of $U(NEt_2)_4$ did not proceed quantitatively and, as a result, the added amount of cyclopentadiene was more than the amount needed for the intended 2:1 stoichiometry. The excess cyclopentadiene in turn reacted with $Cp_2U(NEt_2)_2$ to give $Cp_3U(NEt_2)$ (equation III-5). The verification of this hypothesis is simple

$$Cp_2U(NEt_2)_2 + CpH \longrightarrow Cp_3U(NEt_2) + HNEt_2 \qquad \text{III-5}$$

since the original ^{1}H-NMR spectrum can serve as a guide for the determination of the actual amount of $U(NEt_2)_4$ generated. Having done this it was concluded that the yield of $U(NEt_2)_4$ was no more than 76%. The reaction was repeated, but this time the added amount of cyclopentadiene was based on the above "observed" yield of $U(NEt_2)_4$.

$Cp_2U(NEt_2)_2$ was obtained after the first crystallization. The procedure, however, was somewhat unsatisfactory since the yield of the intermediate tetrakisamide was low (Table XIII).

A very brief note by Watt and Gadd on both Th- and $U(NEt_2)_4$ appeared about this time in which they observed that the uranium amide was light sensitive at 25°C.[78] Their report at least offered an explanation for the low yield of $U(NEt_2)_4$ and, in the absence of anything better, their claim was easily verified. Essentially the same reaction which gave 24% of $Cp_3U(NEt_2)$ was repeated with steps taken to exclude light from the reaction solution. Much to our surprise and joy the yield of $Cp_2U(NEt_2)_2$ was excellent (88%) and no $Cp_3U(NEt_2)$ was seen in the ^{1}H-NMR spectrum! It therefore became obvious that $U(NEt_2)_4$ was indeed light-sensitive and that its rate of photodecomposition was significant at ambient temperature.

Our primary objective had thus been achieved and at least for one Cp_2U-derivative, no indications of disproportionation was observed. The isolation of the pure product also provided the impetus for a attempting the synthesis of other Cp_2U-derivatives. The reactivity of $Cp_2U(NEt_2)_2$ and its utility as a starting material for the preparation of other Cp_2U-derivatives will be discussed in the next chapter.

In subsequent preparation of $Cp_2U(NEt_2)_2$ the purity of the sample was monitored by ^{1}H-NMR spectra. Since the cyclopentadienyl resonances in $Cp_2U(NEt_2)_2$ and $Cp_3U(NEt_2)$ are reasonably well separated (20.9 versus 18.9 p.p.m.) and since both compounds are soluble in

TABLE XIII

SYNTHESIS OF $Cp_2U(NEt_2)_2$

NO. MMOLES UCl_4 (No. equiv.)	NO. MMOLES $LiNEt_2$ (No. equiv.)	NO. MMOLES CpH (No. equiv.)	REACTION TIME (HRS.) UN_4[a]	REACTION TIME (HRS.) Cp-UN_4[b]	%Cp_3[c] (^{1}H-NMR)	%Cp_2[d]	LIGHT?[e]	TOTAL YIELD (%)[f]
67.9 (1.00)	272 (4.01)	135 (1.99)	21	1.5	24	76	yes	n.d.[g]
20.6 (1.00)	82.5 (4.00)	38.0 (1.84)	19	17.5	16	84	yes	n.d.
16.7 (1.00)	67.7 (4.05)	23.6 (1.41)	17	2.5	7	93	yes	n.d.
62.9 (1.00)	255 (4.05)	124 (1.97)	18	2.0	0	100	no	88.8
35.2 (1.00)	143 (4.06)	66.4 (1.89)	24	2	0	100	no	85.3

[a] refers to the length of time for reaction shown in equation III-3

[b] refers to the length of time for reaction shown in equation III-4

[c] %$Cp_3U(NEt_2)$ as determined by ^{1}H-NMR

TABLE XIII CONTINUED

c $\%Cp_3U(NEt_2)$ as determined by ^1H-NMR

d $\%\ Cp_2U(NEt_2)_2$ as determined by ^1H-NMR

e yes means light was not excluded in the preparation of $U(NEt_2)_4$; no means light was excluded

f based on cyclopentadiene

g not determined

benzene, an integrated ^{1}H-NMR spectrum gave a good estimate of the purity of the sample.

PROPERTIES OF $Cp_2U(NEt_2)$

$Cp_2U(NEt_2)_2$ instantly decomposed upon contact with air. In addition it very slowly decomposes over a period of several months as a solid even though it is stored under nitrogen in a refrigerator. The small amount of decomposition material may be removed by dissolution in pentane followed by either filtration and solvent removal *in vacuo* or crystallization from the pentane solution (Chapter VI). It may not be as intuitively satisfying to remove the solvent from the filtrate as it would be to crystallize from this solution but ^{1}H-NMR spectra revealed virtually no impurities present after this extraction was performed.

$Cp_2U(NEt_2)_2$ is very soluble in benzene, toluene, and THF, is soluble in pentane and hexanes, and is decomposed by acetone, in addition it reacts with CS_2 (Chapter IV).

OTHER $Cp_2M(NR_2)_2$ DERIVATIVES

In order to test the general applicability of our method for the preparation of $Cp_2U(NEt_2)_2$, the following amides were also reacted with two equivalents of cyclopentadiene as per equation III-4: $Th(NEt_2)_4$, $U[N(C_6H_5)_2]_4$, $U(NMe_2)_4$, $Th[N(i\text{-}Pr)_2]_4$, and $U[N(i\text{-}Pr)_2]_4$.

Tetrakis(diethylamido)thorium(IV)

The reaction of $Th(NEt_2)_4$ with two equivalents of cyclopentadiene did not produce pure $Cp_2Th(NEt_2)_2$. A ^1H-NMR spectrum of the product showed mainly $Cp_2Th(NEt_2)_2$ (i.e. singlet at 1.02 p.p.m., relative to internal C_6H_6), a triplet at 6.17 p.p.m. and a quartet at 4.12 p.p.m.) and small singlets at 0.88 p.p.m. and 0.95 p.p.m. assigned to $Cp_3Th(NEt_2)$ and $CpTh(NEt_2)_3$, respectively. Attempted extraction with pentane or fractional crystallization from THF did not produce pure $Cp_2Th(NEt_2)_2$. Indeed it was observed that in the above processes the relative amount of $Cp_3Th(NEt_2)$ and $CpTh(NEt_2)_3$, as determined by ^1H-NMR, was increasing with time. Since the above behavior indicates disproportionation of the formal $Cp_2Th(NEt_2)_2$, further work with this system was not carried out.

Tetrakis(diphenylamido)uranium(IV)

$Cp_2U[N(C_6H_5)_2]_2$ was prepared in near quantitative yields according to equation III-4. The dark red compound, like its precursor $U[N(C_6H_5)_2]_4$, is extremely air-sensitive, decomposing instantly upon contact with air. Attempts were made to grow single crystals of this compound, but even though every possible safeguard was employed the crystallizing solution decomposed after the first batch of micro-crystalline material was collected. Hence even minute traces of air cause decomposition. This behavior is the same as that of $U[N(C_6H_5)_2]_4$ whose preparation and properties were described in Chapter II. While air- and moisture-sensitivity are characteristic features of metal-amide chemistry, the diphenylamido derivatives of

uranium and thorium are by far the most sensitive reported to date. The greater susceptibility of the uranium-nitrogen bond to attack is without doubt due to the greater polarity of that bond in the diphenylamide than in the dialkylamide derivatives.

The high reactivity of $Cp_2U[N(C_6H_5)_2]_2$ coupled with the fact that diphenylamine is a solid made either elemental or amine analysis very difficult. Hence ^{1}H-NMR and mass spectra were used to verify purity. In contrast to the easy removal of diethylamine from reaction solutions, it is much more difficult to free a reaction product of diphenylamine. It was necessary to wash the sticky, crude $Cp_2U[N(C_6H_5)_2]_2$ with several portions of pentane before complete removal of diphenylamine was accomplished.

$Cp_2U[N(C_6H_5)_2]_2$ is soluble in benzene, toluene and THF but is insoluble in pentane or hexanes and, in general is much less soluble in a given solvent than $U[N(C_6H_5)_2]_4$. The compound is instantly decomposed by acetone.

Tetrakis(dimethylamido)uranium(IV)

In contrast to the previously two $Cp_2U(NR_2)_2$ derivatives, the reaction of $U(NMe_2)_4$ with two equivalents of cyclopentadiene (equation III-4) always gave a mixture of $Cp_2U(NMe_2)_2$ and $Cp_3U(NMe_2)$. An ^{1}H-NMR spectrum of the reaction product showed singlets at about -7.5 p.p.m., -3.8 p.p.m., 18.3 p.p.m., and 18.9 p.p.m relative to internal benzene. The singlets at -7.5 and 18.9 p.p.m integrated in a 6:10 ratio (i.e. $Cp_2U(NMe_2)_2$) while the singlets at -3.8 and 18.3 p.p.m. gave a 6:15 ratio (i.e. $Cp_3U(NEt_2)$). A mass spectrum

of the reaction product verified the presence of $Cp_2U(NMe_2)_2$ (m/e 456) and $Cp_3U(NMe_2)$ (m/e) 477).

The formation of $Cp_3U(NMe_2)$ can be envisioned in either of two ways: 1) $Cp_2U(NMe_2)_2$ is formed but because of the presence of the smaller dimethylamido ligand undergoes disproportionation after some type of molecular association (equations III-6 and III-7); or

$$2Cp_2U(NMe_2)_2 \longrightarrow CpU(NMe_2)_3 + Cp_3U(NMe_2) \qquad \text{III-6}$$

$$3Cp_2U(NMe_2)_2 \longrightarrow 2Cp_3U(NMe_2) + U(NMe_2)_4 \qquad \text{III-7}$$

2) $U(NMe_2)_4$ is somewhat associated even in THF so that the reaction with cyclopentadiene is slow; the various $Cp_xU(NMe_2)_{4-x}$ species formed in the reaction in turn react faster with cyclopentadiene than any unreacted $U(NMe_2)_4$. Both of these routes would explain a mixture $Cp_2U(NMe_2)_2$ and $Cp_3U(NMe_2)$ but do not account for the apparent absence of either $U(NMe_2)_4$ or $CpU(NMe_2)_3$. In order to better understand what was happening a sample of the mixture was dissolved in THF and warmed overnight at about 40-50°C. An aliquot of the solution was removed, taken to dryness under vacuum, then benzene was added to the solid. The ^{1}H-NMR spectrum of this solution showed only singlets at -3.8 and 18.3 p.p.m. assigned to $Cp_3U(NMe_2)$.

Hence it seems that the smaller dimethylamido ligand will allow molecular associations with resulting disproportionation. The absence of other peaks in the ^{1}H-NMR spectrum speaks for the disproportionation path depicted by equation III-7 since it is known that $U(NMe_2)_4$,

the other disproportionation product, is quite insoluble in benzene and gives a rather featureless ^{1}H-NMR spec[illegible] this solvent.

Tetrakis(diisopropylamido)thorium(IV) and [illegible]um(IV)

The preparations of $Cp_2U[N(i\text{-}Pr)_2]_2$ and $Cp_2Th[N(i\text{-}Pr)_2]_2$ were attempted but the mixing of cyclopentadiene (equation III-4) with the corresponding amide produced no reaction in pentane. Neither did the reaction proceed in refluxing pentane or in THF at ambient temperature. This lack of reactivity is attributed to the low acidity of cyclopentadiene and to the sterically crowded nature of $M[N(i\text{-}Pr)_2]_4$. (Chapter II.)

SYNTHESIS AND CHARACTERIZATION OF $Cp_3U(NR_2)$ COMPLEXES

R=C_2H_5

In the earliest stages of the development of the synthesis of $Cp_2U(NEt_2)_2$ it became apparent by ^{1}H-NMR that the previously unreported $Cp_3U(NEt_2)$ was also being produced. To be completely sure that the extra peaks seen in the ^{1}H-NMR spectra of $Cp_2U(NEt_2)_2$ (i.e. a singlet at about 18.9 p.p.m. and a weak triplet at about 6.4 p.p.m.; the expected quartet was not seen) were indeed due to $Cp_3U(NEt_2)$, the compound was prepared by a different route (equation III-8).

$$Cp_3UCl + LiNEt_2 \longrightarrow Cp_3U(NEt_2) + LiCl \qquad \text{III-8}$$

The ^{1}H-NMR spectrum of the product showed a singlet at 18.80 p.p.m., a triplet at 8.40 p.p.m., and a quartet at 6.40 p.p.m. in a 15:6:4 ratio thus confirming the earlier assignments.

In addition to the reaction given above, $Cp_3U(NEt_2)$ may be prepared by either of the reactions given in equations III-5 and III-9.

$$U(NEt_2)_4 + 3CpH \longrightarrow Cp_3U(NEt_2) + 3HNEt_2 \qquad \text{III-9}$$

Of the three routes the one given in equation III-8 is the most convenient since Cp_3UCl is easily made and the stiochiometry of the reaction is also more conveniently controlled since both reactants are solids.

R=CH_3

$Cp_3U(NMe_2)$ was not prepared independently as was $Cp_3U(NMe_2)$. The ^{1}H-NMR spectrum of the reaction product of $U(NMe_2)_4$ and cyclopentdiene showed unambiguously that $Cp_3U(NMe_2)$ was present and that it could be prepared pure simply by warming the reaction mixture in THF.

SPECTROSCOPIC STUDIES

MASS SPECTRA

The mass spectra of $Cp_2U(NR_2)$ (R = [redacted], C_6H_5), $Cp_2Th(NEt_2)_2$, $Cp_2Hf(NEt_2)_2$, and $Cp_3U(NEt_2)$ have been recorded. Tables XIV through XXI summarize the mass spectral data obtained for $Cp_2M(NEt_2)_2$ (M = Hf, Th, U) and $Cp_3U(NEt_2)$ while Figure 7 gives the general decomposition scheme for the $Cp_2M(NEt_2)_2$ complexes.

The expected molecular ion for $Cp_2U(NEt_2)_2$ (m/e 512) was seen in relatively high abundance (40%) (Table XIV). The calculated and observed abundances for the presummed $Cp_2U(NEt_2)_2^+$ ion ($C_{18}H_{30}N_2U_1$) seen in Table XI agree quite well indicating that the peak at m/e 512 was indeed due to the bis-amide. To remove all doubts about the composition of this ion, a high resolution mass spectral study was undertaken (Table XVI). The calculated mass for $C_{18}H_{30}N_2U_1$, 512.2918, and the observed mass, 512.2891, are in excellent agreement.

The base peak of the low resolution mass spectrum of Cp_2[redacted] was found to be at m/e 438. This peak was at first puzzling since it corresponded to the loss of a fragment corresponding to H_2NEt_2 (an unlikely molecule) from the molecular ion. No metastable peak corresponding to such a loss could be found, even though the high resolution data (Table XVI) did show that the formulation (M-"H_2NEt_2"), or more simply $C_{14}H_{18}N_1U_1$, was indeed correct. However the calculated and observed abundances for the m/e 438 peak did not match (Table XV). The larger abundances of the (M+1) and (M+2) peaks for m/e 438

TABLE XIV

SUMMARY OF THE LOW RESOLUTION MASS SPECTRUM OF $Cp_2U(NEt_2)_2$

MASS (m/e)	RELATIVE ABUNDANCE (%)	PROPOSED ASSIGNMENT
512	40.4	$Cp_2U(NEt_2)_2^+$
440	11.4[a]	$Cp_2U(NEt_2)^+$
439	20.7[b]	$Cp_2U[(Et)N{=}C(H)Me]^+$
438	100	$Cp_2U[(Et)N{-}C(H){=}CH_2]^+$
436	10.1	$Cp_2U[CH_2{=}C(H){-}N{-}C(H){=}CH_2]^+$
383	9.9	Cp_2UMe^+
368	76.6	Cp_2U^+
318	7.2	$CpUMe^+$
303	18.6	CpU^+
72	7.2[c]	NEt_2^+
71	4.6	$(Et)N{=}C(H)Me^+$
65	9.3	Cp^+
57	18.2	$CH_2{=}NEt^+$

a ^{13}C contribution from m/e 439 included

b ^{13}C contribution from m/e 438 included

c ^{13}C contribution from m/e 71 included

TABLE XV

CALCULATED[a] VERSUS OBSERVED RELATIVE ABUNDANCES OF SOME PEAKS IN THE LOW RESOLUTION MASS SPECTRUM OF $Cp_2U(NEt_2)_2$

NOMINAL MASS (m/e)	CALCULATED ABUNDANCE (%)	OBSERVED ABUNDANCE (%)	PEAK	ASSUMED FORMULATION
514	1.8	3.5	512	$C_{18}H_{30}N_2U_1$
513	21.4	21.0		
512	100	100		
440	0.9	12.5	438	$C_{14}H_{18}N_1U_1$
439	16.4	20.8		
438	100	100		

[a] Computer program WAGG:ISOC, which was written by Drs. R.S. Gray and E.G. Brooks and was kindly supplied by Professor W.A.G. Graham.

TABLE XVI

HIGH RESOLUTION MASS SPECTRUM

OF $Cp_2U(NEt_2)_2$

NOMINAL MASS (m/e)	ASSUMED FORMULA	MASS (m/e)		ERROR (p.p.m.)
		Calculated	Observed	
512	$C_{18}H_{30}N_2U_1$	512.2918	512.2891	5.2
438	$C_{14}H_{18}N_1U_1$	438.1947	438.1924	5.2

indicated that there must be other contributors to m/e 439 and 440 besides $(M-H_2NEt_2)^+$.

A priori it would be expected that losses of NEt_2 and $HNEt_2$ would be observed since such losses have been observed in the mass spectra of the tetrakisamides of Nb,[90] Cr,[91] and Mo.[70] The apparent loss of H_2NEt_2 can be visualized either by successive losses of NEt_2 and H_2 or by successive losses of $HNEt_2$ and 1/2 H_2. Losses of each of these four species have been previously observed in amide complexes.[65,70,90,91] That the base peak (i.e. m/e 438) is actually generated by each of these two processes (Figure 6) can be seen from the data in Table XVII.

The metastable peak observed at m/e 436 is indicative of the loss of a H_2 molecule from the m/e 440 ion, $(M-NEt_2)^+$, since characteristically the loss of a H_2 molecule from an ion whose mass is at least m/e 50 should result in a metastable peak four mass units lower than the mass of that ion. A relatively strong metastable peak at m/e 376.5 corresponds to the loss of $HNEt_2$ from the molecular ion. Unfortunately the identification of metastable peaks corresponding to the loss of NEt_2 from the molecular ion and 1/2 H_2 from the $(M-HNEt_2)^+$ is less certain. The appearance of a shoulder on the high mass side of the m/e 376.5 metastable peak at about m/e 378 could correspond to the former loss since the metastable ion is calculated to appear at m/e 378.1. A weak broadening of the base of the peak at m/e 437 can be taken as evidence for the loss of 1/2 H_2 (as the metastable is calculated to appear at m/e 437.0).

TABLE XVII

SOME DECOMPOSITION PROCESSES OBSERVED IN THE LOW RESOLUTION MASS SPECTRUM OF $Cp_2U(NEt_2)_2$

PROCESS	METASTABLE PEAK	
	Calculated	Observed
1) $Cp_2U(NEt_2)_2^+ \longrightarrow Cp_2U(NEt_2)^+ + NEt_2$	378.1	378.0(?)
2) $Cp_2U(NEt_2)^+ \longrightarrow Cp_2U[(Et)N\text{-}C(H)=CH_2]^+ + H_2$	436.0	436.0
3) $Cp_2U(NEt_2)_2^+ \longrightarrow Cp_2U[(Et)N=C(H)Me]^+ + HNEt_2$	376.4	376.5
4) $Cp_2U[(Et)N=C(H)Me]^+ \longrightarrow Cp_2U[(Et)N\text{-}C(H)=CH_2]^+ + \frac{1}{2}H_2$	437.0	437.0(?)
5) $Cp_2U(NEt_2)^+ \longrightarrow Cp_2U^+ + NEt_2$	307.8	307.5(?)
6) $Cp_2U[(Et)N=C(H)Me]^+ \longrightarrow Cp_2U^+ + [(Et)N=C(H)Me]$	308.5	308.5
7) $Cp_2U^+ \longrightarrow CpU^+$	249.5	249.5

Even though all the metastable peaks are not clearly observed, the total picture is taken as good evidence for the proposed routes of generation of the base peak.

After the formation of the base peak the only other significant peaks are at m/e 368 and m/e 303. These peaks correspond to Cp_2U^+ and CpU^+, respectively.

After noting the interesting decomposition scheme of $Cp_2U(NEt_2)_2$, we wondered whether the decomposition scheme would be a general one for other $Cp_2M(NEt_2)_2$ complexes. The inability to isolate pure $Cp_2Th(NEt_2)_2$ at first seemed to exclude its use to investigate the generality of the decomposition scheme, but a mass spectrum of the $Cp_xTh(NEt_2)_{4-x}$ (x = 1,2,3) mixture obtained (which was mainly $Cp_2Th(NEt_2)_2$) put those fears to rest. The data given in Tables XVIII and XIX show the same qualitative results as those of the uranium complex. The only reported transition metal analogs of $Cp_2U(NEt_2)_2$ are Cp_2Zr- and $Cp_2Hf(NEt_2)_2$ on which no spectroscopic data has yet been reported. Hence a mass spectrum of $Cp_2Hf(NEt_2)_2$ was recorded to see if the decomposition scheme which held for both Cp_2Th- and $Cp_2U(NEt_2)_2$ would also hold for a transition metal analog. Even though hafnium has several naturally occurring isotopes and the decomposition schemes given in Figure 6 cannot be verified due to the very broad nature of the anticipated metastable peaks, the mass spectrum of $Cp_2Hf(NEt_2)_2$ (Tables XIX and XX) seems to indicate that the decomposition scheme given in Figure 6 is indeed a general one for $Cp_2M(NEt_2)_2$ complexes.

TABLE XVIII

COMPARISON OF SOME METASTABLE PEAKS IN THE LOW RESOLUTION MASS SPECTRA OF $Cp_2U(NEt_2)_2$ AND $Cp_2Th(NEt_2)_2$

PROCESS NUMBER [a]	METASTABLE PEAKS (U)		METASTABLE PEAKS (Th)	
	Calculated	Observed	Calculated	Observed
1	378.1	378 (?)	372.2	372 (?)
2	436.0	436	430.0	430
3	376.4	376.5	370.5	370.5
4	437.0	437 (?)	431.0	431 (?)

[a] process numbers given in Table XVII

TABLE XIX

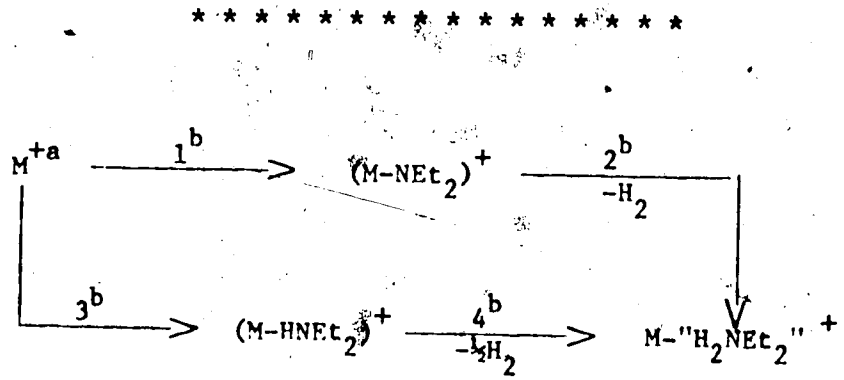
COMPARISON OF PARTS OF THE MASS SPECTRA OF $Cp_2Met(NEt_2)_2$ COMPLEXES

Met	$Cp_2Met(NEt_2)^+ = M^+$	$(M-NEt_2)^+$	$(M-HNEt_2)^+$	$(M-"H_2NEt_2")^+$
Hf[a]	12.9[b]	19.0	51.6	100
Th[c]	14.9	11.2	43.3	100
U	40.4	11.4	20.7	100

[a] data based on ^{180}Hf

[b] relative abundance (%)

[c] from the mass spectrum of $Cp_xTh(NEt_2)_{4-x}$ mixture (x=1,2,3); $(M-"H_2NEt_2")^+$ was the most abundant metal-containing ion in that spectrum



[a] $Cp_2Met(NEt_2)_2^+ = M^+$

[b] refers to process numbers given in Table XVII

Figure 7. General decomposition scheme for $Cp_2Met(NEt_2)_2$

The mass spectrum of $Cp_2U[N(C_6H_5)_2]_2$ consists of basically three peaks: m/e 704 ($Cp_2U[N(C_6H_5)_2]_2^+$), 536 ($Cp_2U[N(C_6H_5)_2]^+$), and 368 (Cp_2U^+). The peak at m/e 536 is by far the largest metal-containing ion. Since the peak at m/e 168 ($N(C_6H_5)_2^+$) goes off-scale the relative abundances cannot be given. However if the main metal-containing ion at m/e 536 is taken as 100%, then the peaks at m/e 704 and 368 have abundances of 8.0% and 24.8%, respectively.

The difference in fragmentation patterns seen between the $Cp_2U(NEt_2)_2$ and $Cp_2U[N(C_6H_5)_2]_2$ complexes can be taken as indirect evidence that the decomposition of $Cp_2U(NEt_2)_2$ (Table XIV) occurs mainly within the NEt_2 framework. However it must be noted that the abstraction of protons from the cyclopentadienyl ligand has previously been observed by Marks, et al. in their thermolysis studies on $Cp_3U(alkyl)$.[7]

The mass spectrum of $Cp_3U(NEt_2)$ is summarized in Table XXI. This spectrum is indeed quite simple. In contrast to the mass spectra of Cp_3UX (X = halide) where ions of the type Cp_yUX^+ (y = 3,2,1,0) are seen, no such ions were seen for $Cp_3U(NEt_2)$. This is most likely the result of steric interactions between the NEt_2 and the Cp ligands, of the Cp_3U moiety. Similar steric interactions have been found to be of importance in $Cp_3U(alkyl)$ complexes. Indeed in their thermolysis studies of $Cp_3U(alkyl)$ complexes, Marks, et al. have shown that the lifetimes of these complexes are drastically reduced with increased

TABLE XX

SUMMARY OF THE MASS SPECTRUM

OF $Cp_2Hf(NEt_2)_2$

MASS[a] (m/e)	RELATIVE ABUNDANCE (%)	PROPOSED ASSIGNMENT
454	12.9	$Cp_2Hf(NEt_2)_2^+ = M^+$
382	19.0	$Cp_2Hf(NEt_2)^+$
381	51.6	$Cp_2Hf[(Et)N{=}C(H)Me]^+$
380	100	$Cp_2Hf[(Et)N{-}C(H){=}CH_2]^+$
325	13.9	Cp_2HfMe^+
310	32.2	Cp_2Hf^+
245	3.5	$CpHf^+$
72	5.2	NEt_2^+
66	8.1	CpH^+
65	5.2	Cp^+
58	11.3	$CH_2{=}N(H)Et^+$

[a] based on ^{180}Hf

TABLE XXI

SUMMARY OF THE MASS SPECTRUM OF $Cp_3U(NEt_2)_2$

MASS (m/e)	RELATIVE ABUNDANCE (%)	ASSIGNMENT
505	25.3	$Cp_3U(NEt_2)^+$
433	100	Cp_3U^+
368	72.1	Cp_2U^+
303	9.1	CpU^+
66	3.2	CpH^+
65	1.8	Cp^+

branching on the atom directly bonded to uranium (i.e. the order of the half-lives of Cp_3U(alkyl) were found to be Me>>n-Bu>>i-Pr>>t-Bu).[7]

INFRARED SPECTRA

The infrared spectra of Cp_2Hf- and $Cp_2U(NEt_2)_2$ were recorded with fluorolube mulls in the 3200-1350 cm^{-1} region and with a hexanes solution in the 1600-400 cm^{-1} region. The spectra are reproduced in Figure 8 while Table XXII summarizes the spectra.

The spectra of both compounds exhibit medium intensity bands in the 570-560 and the 494 cm^{-1} region. This pair of bands in each complex is assigned to metal-nitrogen stretches, ν(M-N). Each $Cp_2M(NEt_2)_2$ molecule would be expected to have a local C_{2v} symmetry. As a result two metal-nitrogen stretches (A_1 and B_1) are predicted from simple group theoretical considerations. The high frequency band of each pair is assigned to the A_1 mode (i.e. a symmetric stretch) while the low frequency band is assigned to the B_1 (asymmetric stretch) mode. The high frequency band is in good agreement with previously reported bands for ν(M-N) in tetrakisdiethylamido complexes of Th (540-549 cm^{-1}) and U (555-560 cm^{-1}) as discussed in Chapter II. The assignment of the lower frequency band to an asymmetric ν(M-N) is more tentative although Bradley and Gitlitz report a weak band at 495 cm^{-1} in the infrared spectrum of $EtN=Ta(NEt_2)_3$ which they assign to an asymmetric ν(M-N).[67] Furthermore

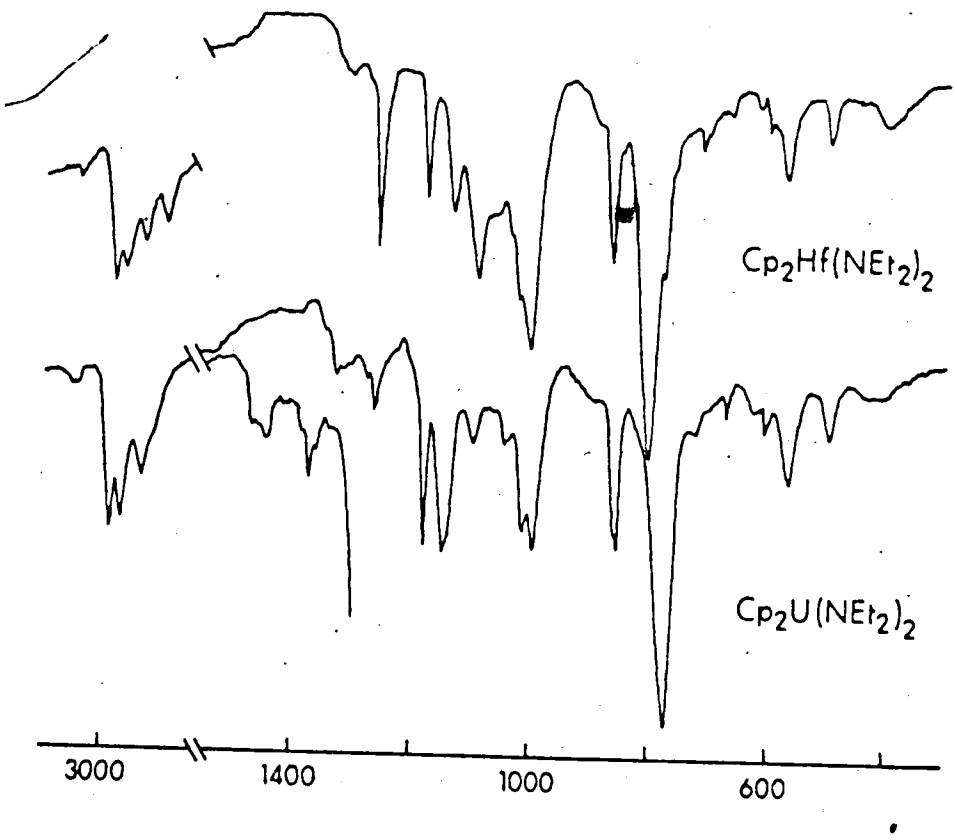


Figure 8. Infrared Spectra of Cp_2Hf- and $Cp_2U(NEt_2)_2$.

TABLE XXII

INFRARED SPECTRA [a] OF $Cp_2Hf(NEt_2)_2$, $Cp_2U(NEt_2)_2$, and $Cp_3U(NEt_2)$

$Cp_2Hf(NEt_2)_2$ [b]	$Cp_2U(NEt_2)_2$ [b]	$Cp_3U(NEt_2)$ [c]	ASSIGNMENTS
3090w	3090w	3085w	ν(C-H)
2960s	2970s	2970s	ν(C-H)
2930s	2935s	2935s	ν(C-H)
2860m	2865m	2865m	ν(C-H)
1450sh	1465sh		
1441m	1439m	1445m	ω(C-C) of Cp
1375sh	1370m	1385w	
	1357sh	1356w	
1315m	1324w		
1306w	1313sh		
	1274w		
1258s	1269m	1264w	
1178m	1177s	1169sh	
1135m	1145s	1149sh	asym$\nu(NC_2)$
	1136sh	1115br [d]	
1091s	1095m		
1072w			
	1043m		
1023s	1012s	1014s	δ(C-H) of Cp
1002s	994s		sym$\nu(NC_2)$
892sh		892w	
853s	852s		

(Table continued)

Table XXII continued

$Cp_2Hf(NEt_2)_2$[b]	$Cp_2U(NEt_2)_2$[b]	$Cp_3U(NEt_2)_2$[c]	ASSIGNMENTS
848w			
801s		808s	γ(C-H) of Cp
777m	768vs	777vs	
759sh			
714w	718w	725s	
704 h	696sh		
666w	667w		
617w	620w	627s	
603w	600w	602m	
570m	561m		ν(U-N), A_1
497m	494m		ν(U-N), B_1
398m	420br[d]		

[a] given in cm^{-1}

[b] fluorolube mull from 4000 to 1350 cm^{-1}; hexanes solution

[c] mulls

[d] broad

our observations of a second band at 499 and 496 cm^{-1} in Th- and $U(NEt_2)_4$, respectively, (Chapter II) tend to support the above conclusion.

The assignment of other prominent bands in the infrared spectrum is not as straightforward as that of the ν(M-N)'s since bands which are characteristic of both the Cp and NEt_2 ligands are expected around the 1000 and 800 cm^{-1} regions. A pair of strong bands is seen at 1023 and 1002 cm^{-1} for $Cp_2Hf(NEt_2)_2$ and at 1012 and 994 cm^{-1} for $Cp_2U(NEt_2)_2$. There are two possible assignments for each pair of bands: the symmetric stretch of the nitrogen-carbon framework of the amide, sym$\nu(NC_2)$,[72] can be assigned to the higher frequency peak and lower frequency peak can be assigned to the in-plane carbon-hydrogen deformation of the Cp ligand, δ(C-H);[92] or vice-versa.

To date the infrared spectra of all reported organouranium complexes which contain the Cp ligand show an absorption at 1012±2 cm^{-1} assignable to δ(C-H).[4,8,92-95] The available infrared data on cyclopentadienyl derivatives of Hf is limited mainly to that of Cp_2HfX_2 (X = F, Cl, Br, I).[96] Druce, et al. have found that peaks which are assignable to δ(C-H) fall in the 1021±2 cm^{-1} range.[96] Hence it would appear that the 1012 cm^{-1} peak in $Cp_2U(NEt_2)_2$ and the 1023 cm^{-1} peak in $Cp_2Hf(NEt_2)_2$ are best assigned to the δ(C-H) ligand which would in turn assign the lower frequency peak of the pair in question to sym$\nu(NC_2)$ of the NEt_2 ligand. This assignment is further supported by the reported assignment of sym$\nu(NC_2)$ to peaks at 1002 cm^{-1} in the infrared of $Hf(NEt_2)_4$,[72] 995 cm^{-1} [79] and

993 cm^{-1} (Chapter II) for $Th(NEt_2)_4$, and 990 cm^{-1} [79] and 990 cm^{-1} (Chapter II) for $U(NEt_2)_4$.

Cyclopentadienyl containing complexes characteristically exhibit a band around 800 cm^{-1} which has been assigned to an out-of-plane carbon-hydrogen deformation mode, γ(C-H).[92] This band also gives an indication of the amount of covalency or ionicity in the metal-Cp bond.[92] Shifts of the band to lower frequency (about 750 cm^{-1} is reported to be the lower limit) indicate more ionic character. A first glance at the infrared spectrum of $Cp_2U(NEt_2)_2$ would cause one to conclude that the metal-Cp bond is essentially ionic since the 768 cm^{-1} band is in the region where ionic cyclopentadienyls absorb (cf. the γ(C-H) of the essentially ionic cyclopentadienyl-lanthanides in the 770-780 cm^{-1} region[97]). However Bradley and Gitlitz report that there is a strong, but unassigned, band in this region for the $M(NEt_2)_4$ complexes of Ti, Zr, Hf, V, Nb, and Th.[72] Indeed the infrared spectra of Th- and $U(NEt_2)_4$ reported in Chapter IV bear this out. This band is found at 768 cm^{-1} in $Cp_2U(NEt_2)_2$ and at 777 cm^{-1} in $Cp_2Hf(NEt_2)_2$ and $Cp_3U(NEt_2)$ (Table XXII). Both $Cp_2Hf(NEt_2)_2$ and $Cp_3U(NEt_2)$ have peaks assignable to γ(C-H) at 801 and 808 cm^{-1}, respectively. The absence of this peak in $Cp_2U(NEt_2)_2$ indicates that the unassigned NEt_2 peak and the δ(C-H) peak of the Cp must be close enough to form an asymmetric peak. The asymmetry of the 768 cm^{-1} peak around 790-780 cm^{-1} could be taken as an estimate of the position of the band assignable to γ(C-H). The same band is found at 784 cm^{-1} in Cp_3UCl[4], 788 cm^{-1} in $Cp_3U(C_6H_5)$[8],

792 cm^{-1} in $Cp_3U(C_2C_6H_5)$[8], 790 cm^{-1} in $Cp_3U(alkyl)$[9], and at 789 cm^{-1} in Cp_4U.[95]

Fritz reports that the indication of an ionic Cp by a low δ(C-H) frequency is accompanied by a higher shift in the symmetric carbon-carbon stretch, ω(C-C), to about 1445 cm^{-1} while the peak around 1100 cm^{-1}, which is due to an in-plane carbon-hydrogen deformation of the Cp ligand, δ(C-H), vanishes.[92] The spectrum of $Cp_2U(NEt_2)_2$ has peaks at 1439 and 1095 cm^{-1} which are probably due to the Cp ligand. The ω(C-C) band is reported to be at 1435 cm^{-1} in $Cp_3U(alkyl)$[9], 1440 cm^{-1} in $Cp_3U(C_6H_5)$[8], 1443 cm^{-1} in $Cp_3U(C_2C_6H_5)$[8], and 1449 cm^{-1} in Cp_4U.[95] Hence it would appear that the U-Cp bonding is about the same in $Cp_2U(NEt_2)_2$ as in other organoactinide complexes and has some amount of ionic nature.

The asymmetric stretch of the nitrogen-carbon framework, asym-ν(NC_2), has been assigned to peaks at 1158 cm^{-1} for $Hf(NEt_2)_4$,[72] 1160,[72] 1150,[79] and 1148 cm^{-1} (Chapter II) for $Th(NEt_2)_4$, and at 1145[79] and 1146 cm^{-1} (Chapter II) for $U(NEt_2)_4$. By analogy this mode is assigned to bands at 1135 and 1145 cm^{-1} for Cp_2Hf- and $Cp_2U(NEt_2)_2$, respectively.

The infrared spectrum of $Cp_3U(NEt_2)$ is summarized in Table XXII. The appearance of only one peak in the 1000 cm^{-1} region (i.e. 1014 cm^{-1}) is necessarily explained by coincidental overlap of the sym ν(NC_2) band of the NEt_2 ligand and the δ(C-H) band of the Cp ligand. As already mentioned the γ(C-H) band of the Cp ligand (808 cm^{-1}) is well-separated from the unassigned NEt_2 band at

777 cm^{-1}. The higher frequency of the γ(C-H) band in $Cp_3U(NEt_2)$ as compared to the estimated 790-780 cm^{-1} in $Cp_2U(NEt_2)_2$ would tend to indicate a more covalent U-Cp bond in $Cp_3U(NEt_2)$ than in $Cp_2U(NEt_2)_2$. This can be explained in terms of the stronger basicity of the NEt_2 group compared to that of the Cp ligand. [illegible] here are more amido groups in the bisamide the uranium does not require as much of the electron density from the cyclopentadienyls as in $Cp_3U(NEt_2)$. Hence there is more electron density remaining on the cyclopentadienyl groups in $Cp_2U(NEt_2)_2$.

From the data in Table XXIII it would appear that the U-Cp bond in $Cp_3U(NEt_2)$ is more covalent than those in other reported Cp_3UR complexes since its γ(C-H) band is at higher frequency and its ω(C-C) band at lower frequency than in the other complexes.

The metal-nitrogen stretch in $Cp_3U(NEt_2)$ was not observed since the spectrum was recorded with a mull. (The sample was not soluble enough in hexanes so that a solution spectrum could be recorded.) The spectrum began to tail-off below 520 cm^{-1} and hence could not be recorded. The lower ν(U-N) in $Cp_3U(NEt_2)$ than in $Cp_2U(NEt_2)_2$ indicates a weaker uranium-nitrogen bond. This observation is enforced by the fact that only a loss of the NEt_2 group is seen in the mass spectrum as compared to decomposition reactions within the NEt_2 group in $Cp_2U(NEt_2)_2$.

The infrared spectrum of $Cp_2U[N(C_6H_5)_2]_2$ (Table XXIV) leads one to say that the amount of ionicity in the U-Cp bond in $Cp_2U[N(C_6H_5)_2]_2$ is about the same as that in $Cp_3U(NEt_2)$ since γ(C-H) is found at 802 cm^{-1}. The apparently more covalent nature of the

TABLE XXIII

COMPARISON OF SELECTED BANDS IN THE INFRARED SPECTRA[a] OF Cp_3UR COMPLEXES

R	ω(C-C)	γ(C-H)	REFERENCE NUMBER
NEt_2	1435	808	t.w.[b]
Cl	--	789	4
alkyl	1435	790-780	9
C_6H_5	1440	788	8
$C_2C_6H_5$	1443	792	8
Cp	1449	789	95

[a] given in cm^{-1}

[b] this work

TABLE XXIV

SUMMARY OF THE INFRARED SPECTRUM[a] OF $Cp_2U[N(C_6H_5)_2]_2$

PEAK	ASSIGNMENT
1309m	
1261s	
1171m	
1146m	asym$\nu(NC_2)$
1096s,br[b]	
1016s	sym$\nu(NC_2)$ of $[N(C_6H_5)_2]_2$ and δ(C-H) of Cp
876w,br	
826sh	
820sh	
802vs	γ(C-H) of Cp
778sh	
747m	
725s	
691m	
666m	
622m	

[a] given in cm^{-1}

[b] broad

U-Cp bond in $Cp_2U[N(C_6H_5)_2]_2$ as compared to $Cp_2U(NEt_2)_2$ can be explained in terms of the basicity of the amido ligands. The $[N(C_6H_5)_2]$ ligand is a weaker base than the NEt_2 ligand due to the electron-with-drawing nature of the phenyl groups. Hence less electron density is donated to the uranium by the $[N(C_6H_5)_2]$ ligand than by the NEt_2 ligand which thereby causes more electron density to be donated to the uranium by the Cp ligands in $Cp_2U[N(C_6H_5)_2]_2$ than in $Cp_2U(NEt_2)_2$.

The metal-nitrogen stretch probably was not observed since again the spectrum was recorded as a mull and could not be recorded below about 520 cm^{-1}. Since the metal-nitrogen stretch in $Cp_2Zr[N(C_6H_5)_2]_2$ was reported to be at 507 cm^{-1},[98] simple mass effects would cause one to expect the uranium complex to show a metal-nitrogen stretch at an even lower frequency. As was argued in the case of $Cp_3U(NEt_2)$ the lower ν(U-N) as compared to that of $Cp_2U(NEt_2)_2$ is indicative of a weaker uranium-nitrogen bond. Here, too, the argument is enforced by the mass spectrum of $Cp_2U[N(C_6H_5)_2]_2$ which shows only the loss of $[N(C_6H_5)_2]$ groups.

NMR SPECTRA

The ^{1}H-NMR spectra of $Cp_2U(NR_2)_2$, where = Me, Et, C_6H_5, are given in Figure 9, the ^{13}C-NMR spectra of $Cp_2U(NEt_2)_2$ and $Cp_2Hf(NEt_2)_2$ are given in Figures 10 and 11, respectively, while the ^{1}H-NMR spectra of $Cp_3U(NMe_2)$ and $Cp_3U(NEt_2)$ are given in Figure 12. It can be seen from the reproduced spectra that the paramagnetic uranium samples

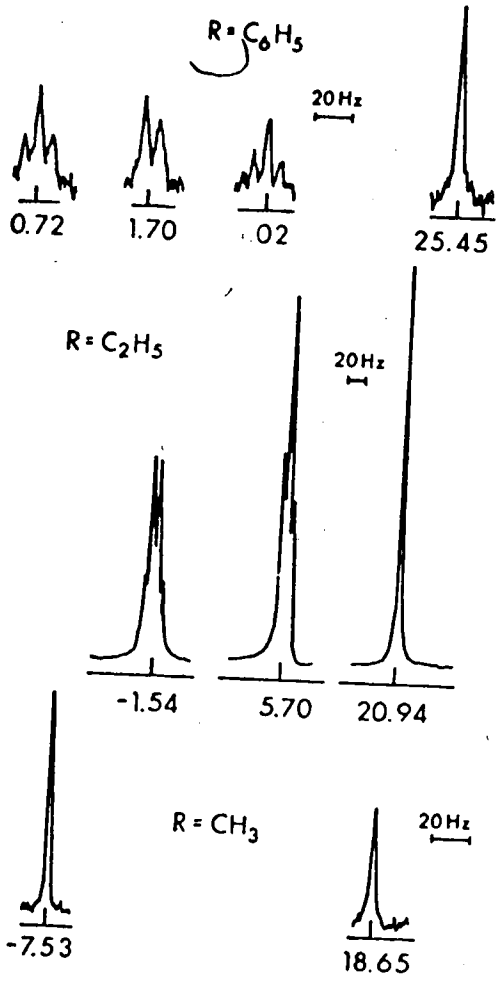


Figure 9. ^{1}H-NMR spectra of various $Cp_2U(NR_2)_2$ Complexes. Chemical shifts given in p.p.m. relative to internal benzene.

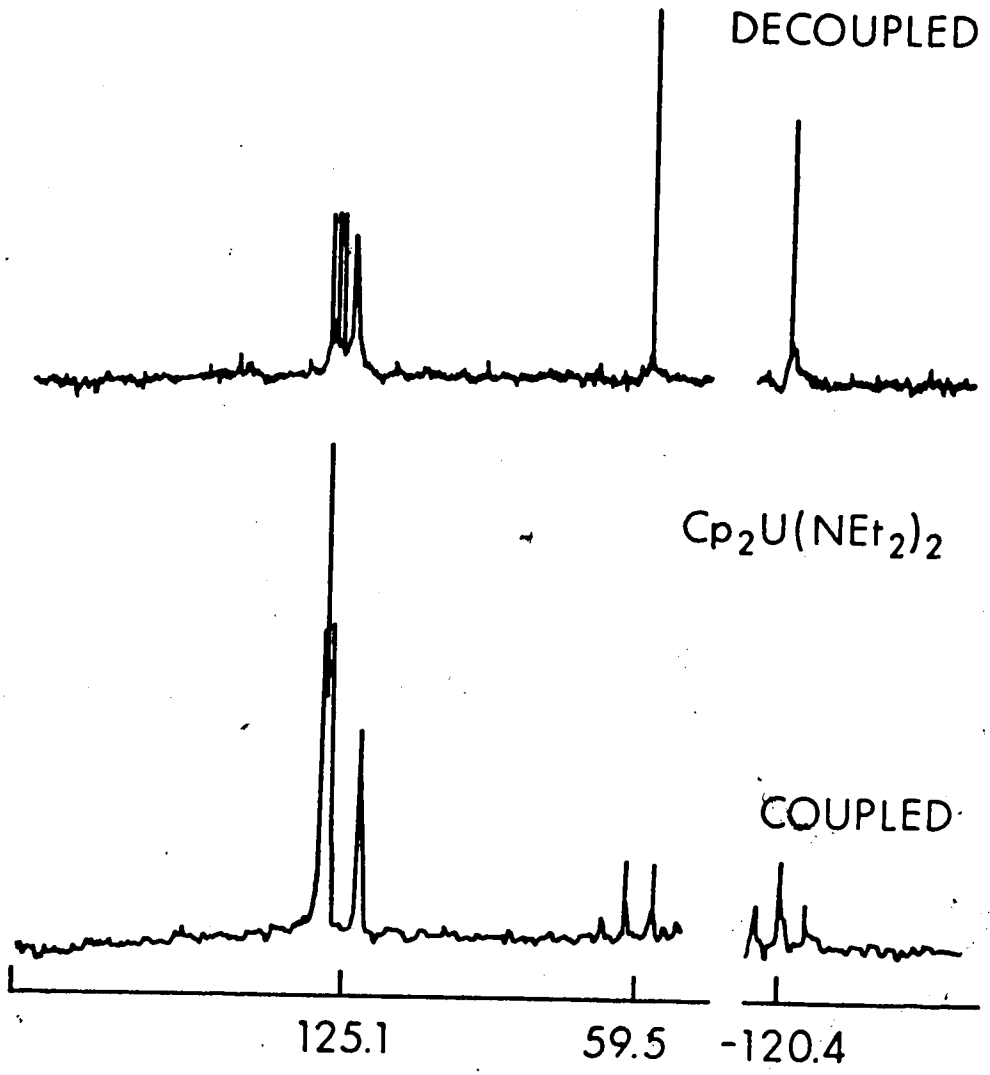


Figure 10. ^{13}C-NMR spectra of $Cp_2U(NEt_2)_2$. Chemical shifts given in p.p.m. relative to TMS.

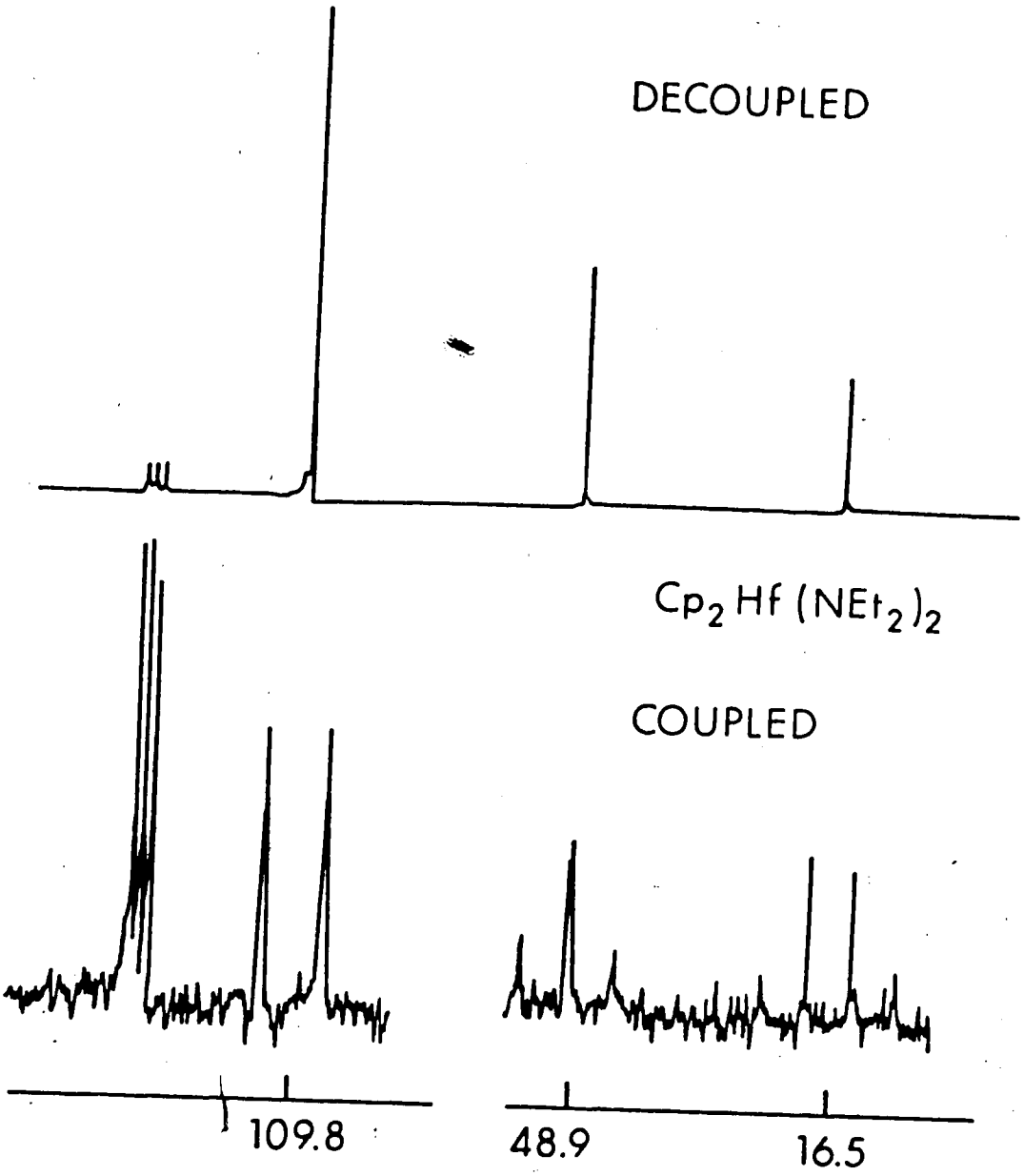


Figure 11. ^{13}C-NMR spectra of $Cp_2Hf(NEt_2)_2$. Chemical shifts given in p.p.m. relative to TMS.

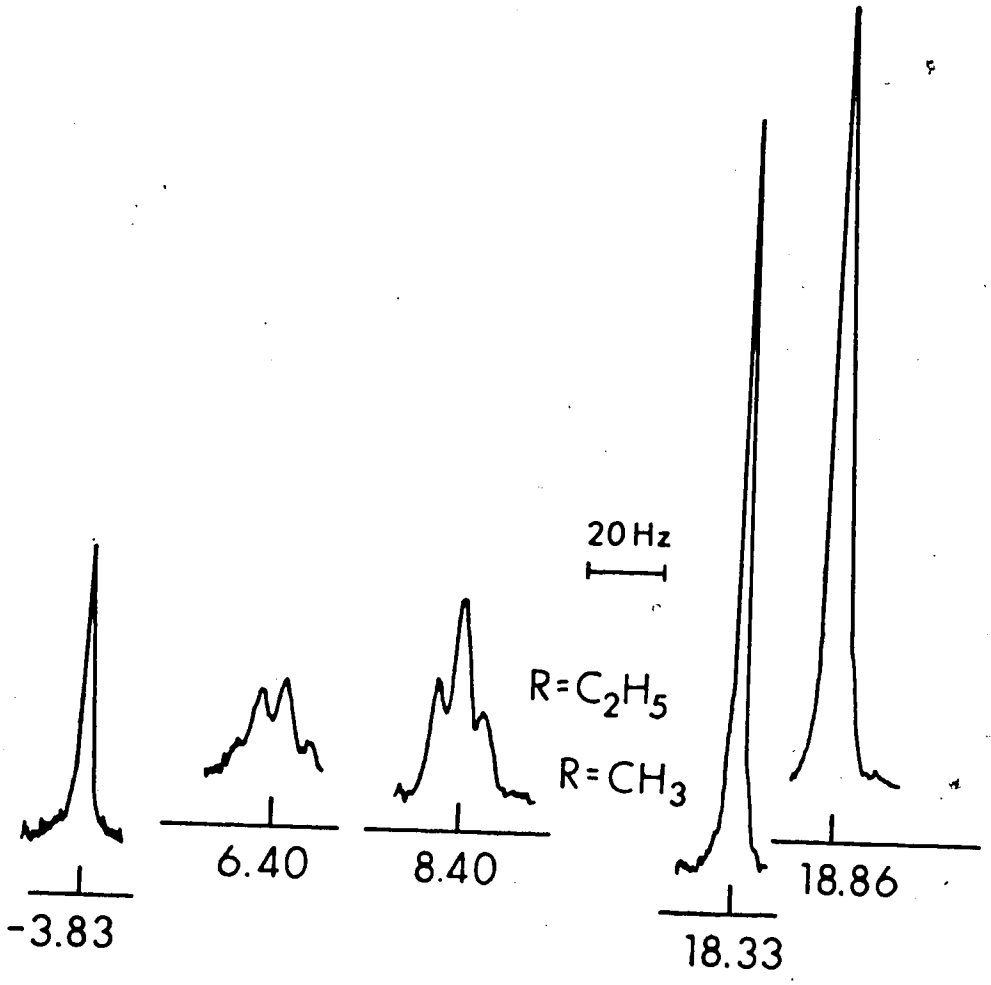


Figure 12. ^{1}H-NMR spectra of $Cp_3U(NMe_2)$ and $Cp_3U(NEt_2)$. Chemical shifts given in p.p.m. relative to internal benzene.

give spectra having very sharp resonances in which even spin-spin couplings are seen.

These spectra will be compared with those of other organoactinide complexes in Chapter V.

CHAPTER IV - REACTIVITY OF CYCLOPENTADIENYL-AMIDO DERIVATIVES OF URANIUM

INTRODUCTION

Once it had been established that the $Cp_2U(NR_2)_2$ complexes could be isolated as pure solids (Chapter III), our attention naturally turned to the synthetic utility of these complexes. Lappert, et al. have shown the amido derivatives of the transition metals to be synthetically useful reagents reacting with either of two types of compounds: 1) those containing a hydrogen which is more acidic than the parent amine, HNR_2 (i.e. a simple acid-base, or acid displacement, reaction); or 2) those which contain an unsaturated group (e.g. CS_2) which inserts itself into the metal-nitrogen bond.[69] It was anticipated that the $Cp_2U(NR_2)_2$ complexes would react in the same way to give other Cp_2U-derivatives as in equations IV-1 and IV-2. Hence in

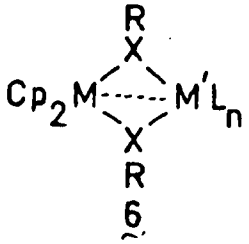
$$Cp_2U(NR_2)_2 + 2HL \longrightarrow Cp_2U(L)_2 + 2HNR_2 \qquad \text{IV-1}$$

$$Cp_2U(NR_2)_2 + 2A{=}B \longrightarrow Cp_2U(ABNR_2)_2 \qquad \text{IV-2}$$

the absence of Cp_2UCl_2, the $Cp_2U(NR_2)_2$ complexes offered potential routes for the preparation of other Cp_2U-derivatives.

In this connection it is particularly interesting to note that transition metal complexes of the type $Cp_2M(XR)_2$ (where X=O,S; M=Ti, Zr, Hf,[56,57] Mo, or W[58,59]) are well-known. In addition these complexes can serve as a metal containing bidentate ligand system reacting with $Mo(CO)_6$,[108] metal carbonyl complexes which contain

labile ligands (e.g. $(CH_3CN)_2Mo(CO)_4$),[108-110] $(R_3P)_2MCl_2$ (M=Ni, Pt),[110] or metal halides[110-112] to yield complexes of the type



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Similarly $Cp_2Nb(SMe)_2^+$ reacts with $NiCl_2$ to yield $[Cp_2Nb(SMe)_2Ni(SMe)_2Cp_2Nb]^{21}$ [112] while $(R_3P)_2M(SR)_2$ complexes (M=Pd, Pt) react with (norbornadiene)$Mo(CO)_4$ to yield $(R_3P_2)M(SR)_2Mo(CO)_4$.[113] On the basis of structural and spectral studies performed on a series of complexes, $Cp_2M(SR)_2M'(CO)_4$, it has been argued that a metal-metal bond is present when M=Ti and M'=Mo but that no metal-metal bond exists when M=W and M'=Cr, Mo, or W.[108-110,114,115] Furthermore structural work on the cationic $[Cp_2Nb(SMe)_2Ni(SMe)_2NbCp_2]^{21}$ is said to indicate the presence of a metal-metal bond.[112] Hence it was hoped that a series of new complexes, $Cp_2U(XR)_2$ (X=O, S), could be prepared and that they would also act as a bidentate ligand to form new complexes as in 6 where the influence of an actinide could be studied. In addition the possibility of isolating complexes where a uranium-transition metal metal-metal bond would be formed seemed real. To date there has been only one report of a complex in which an actinide-transition metal metal-metal bond has been formed $U[Mn(CO)_5]_4$[45]

RESULTS AND DISCUSSION

Most of the reactivity studies reported here have been done using $Cp_2U(NEt_2)_2$. There are several reasons for doing this: 1) $Cp_2U(NMe_2)_2$ could not be isolated as a pure solid; 2) the preparation of $Cp_2U[N(C_6H_5)_2]_2$ is much less convenient than that of $Cp_2U(NEt_2)_2$; 3) $Cp_2U[N(C_6H_5)_2]_2$ is much more sensitive to moisture, heat, and air than $Cp_2U(NEt_2)_2$; and 4) it is much easier to eliminate the by-product diethylamine (b.p. 56°C) than diphenylamine which is a solid.

ACID DISPLACEMENT REACTIONS

Reactivity Toward Cyclopentadiene

It was mentioned in the previous chapter that $Cp_3U(NEt_2)$ was produced along with $Cp_2U(NEt_2)_2$ before it was discovered that $U(NEt_2)_4$ was light-sensitive. At that time it seemed apparent that $Cp_3U(NEt_2)$ was formed as a result of the reaction of the formed $Cp_2U(NEt_2)$ with one equivalent of cyclopentadiene (equation IV-3). Later it was found

$$Cp_2U(NR_2)_2 + CpH \longrightarrow Cp_3U(NR_2) + HNR_2 \qquad \text{IV-3}$$

that $U(NEt_2)_4$ reacts with an excess of cyclopentadiene to give, after 24 hours, $Cp_3U(NEt_2)$ and a small amount of $Cp_2U(NEt_2)_2$ as determined by ^{1}H-NMR. The absence of Cp_4U in the ^{1}H-NMR spectrum indicates that $Cp_3U(NEt_2)$ will not react with cyclopentadiene to yield Cp_4U[95] as in equation IV-4. Even when the reaction of $Cp_3U(NEt_2)$ and excess

$$Cp_3U(NR_2) + CpH \longrightarrow Cp_4U + HNR_2 \qquad \text{IV-4}$$

cyclopentadiene was attempted at 80°C no Cp_4U was produced. Also, the fact that some $Cp_2U(NEt_2)_2$ remained after 24 hours indicates that the rate of formation of $Cp_3U(NEt_2)$ is a much slower process than that of $Cp_2U(NEt_2)_2$ (cf. Table I where the reaction of $U(NEt_2)_4$ and two equivalents of cyclopentadiene yielded a high yield of $Cp_2U(NEt_2)_2$ in only two hours).

The above reactivity is in contrast to that of the transition metal counterparts, Cp_2Zr- and $Cp_2Hf(NEt_2)_2$, which will not react with excess cyclopentadiene even in refluxing benzene. However just as the difference in reactivity of the tetrakisamides of titanium and zirconium and hafnium with excess cyclopentadiene is explained in terms of steric effects,[56] similar arguments can be utilized to account for the differences observed here between the transition metals and uranium amides. As can be seen from Table VI uranium is much larger than either zirconium or hafnium which are in turn larger than titanium. The parallel between the size of the metal and the reactivity of that metal's tetrakisamide with excess cyclopentadiene is seen in the products of the reaction, $Cp_3U(NEt_2)$, Cp_2Hf- and $Cp_2Zr(NEt_2)_2$, and $CpTi(NEt_2)_3$, respectively. Hence there is not enough room around either zirconium or hafnium for a third cyclopentadiene molecule to enter, while the larger size of the uranium allows this to occur though the reaction is slow. The failure of $Cp_3U(NEt_2)$ to react with cyclopentadiene to form Cp_4U is also explained by steric effects. It is apparent that there is just not enough room around the uranium for the fourth cyclopentadiene to

interact favorably with the last uranium-amide bond. In support of this one may note that in the Cp_3UR complexes (R=Me, i-Pr, t-Bu, etc.) the very facile ß-hydrogen elimination process which is prevalent in transition metal alkyls is not observed but thermolysis instead yields radical type decomposition products.[7] Here also the protective cavity provided by the three cyclopentadienyl groups is taken as being responsible for the great thermal stability of these uranium-alkyl complexes.

The $Cp_3U(NMe_2)$-$Cp_2U(NMe_2)_2$ mixture was found to react with excess cyclopentadiene to yield only Cp_4U (m/e 498) as determined by mass spectrometry. (Peaks due to $Cp_2U(NMe_2)_2^+$ (e.g. m/e 456) had vanished but there was just a trace of $Cp_3U(NMe_2)$ still present at m/e 477.) The smaller size of the dimethylamido ligand as compared to the diethylamido ligand apparently cuts down the steric interactions sufficiently for the fourth cyclopentadiene to interact favorably with the uranium-amide bond resulting in the formation of Cp_4U.

Similarly the $Cp_{4-x}Th(NEt_2)_x$ mixture (which contained mainly $Cp_2Th(NEt_2)_2$) was found to very slowly react with excess cyclopentadiene to yield Cp_4Th.[116] (The reaction was monitored by mass spectrometry.) The mass spectrum originally showed no Cp_4Th (m/e 492) but after the reaction mixture had stirred for 24 hours with excess cyclopentadiene, a mass spectrum of the product showed both the Cp_4Th^+ and $Cp_3Th(NEt_2)^+$ (m/e 499) ions. Previously the difference in reactivity between $Cp_3U(NMe_2)$ and $Cp_3U(NEt_2)$ was explained in

terms of the different steric requirements of the amides. Here, though, it is seen that by slightly increasing the size of the central metal atom from uranium to thorium (Table VI) the lengthening of the thorium-nitrogen bond is apparently sufficient to allow a fourth cyclopentadiene molecule to react producing Cp_4Th.

The $Cp_2U[N(C_6H_5)_2]_4$ complex was also allowed to react with excess cyclopentadiene for two days. A mass spectrum of the product showed Cp_4U (m/e 498) to be by far the major product of the reaction though a trace of $Cp_3U[N(C_6H_5)_2]$ was found at m/e 601. Even though a diphenylamido ligand group occupies more total space than a diethylamido ligand, the steric requirements of the diphenylamido group are smaller than the diethylamide's. As a result the reaction of $Cp_2U[N(C_6H_5)_2]_2$ with excess cyclopentadiene will go completely to Cp_4U while the corresponding reaction with the diethylamide stops at $Cp_3U(NEt_2)$.

The above reactivities of the $Cp_2U(NR_2)_2$ and $Cp_3U(NR_2)$ complexes and the reactivity differences seen between the reactivity of the actinide and the transition metal amides can be explained in terms of steric effects and the following general conclusions seem to be apparent: 1) for a given R group of the NR_2 ligand, as the size of the metal increases so will the number of cyclopentadiene molecules that can react with amido groups on the metal; and 2) for a given metal, as the bulkiness of the amido group increases the lower the number of cyclopentadienyl groups that can be accommodated (an

extreme case of this is the inability of $U[N(i\text{-}Pr)_2]_4$ to react with cyclopentadiene).

Reactivity Toward Monodentate Thiols

A priori it would be expected that $Cp_2U(NEt_2)_2$ would react with two equivalents of a monodentate thiol (RSH) according to equation IV-5. Of course, to us, this proposal is very attractive since, as

$$Cp_2U(NEt_2)_2 + 2RSH \longrightarrow Cp_2U(SR)_2 + 2HNEt_2 \qquad \text{IV-5}$$

mentioned previously, it exactly describes our anticipated synthetic route for the preparation of $Cp_2U(SR)_2$. Hence it was not surprising to note that the dropwise addition of thiophenol to a solution of $Cp_2U(NEt_2)_2$ in toluene produced an immediate color change in the solution indicating that a reaction had indeed occurred. Removal of the solvent from the reaction solution yielded a solid which gave a mass spectrum indicative of $Cp_3U(SC_6H_5)$ (m/e 542) rather than the expected $Cp_2U(SC_6H_5)_2$ which should have appeared at m/e 586. In addition a ^{1}H-NMR spectrum of the product consisted basically of a singlet at about 6.9 p.p.m. above internal benzene and another singlet at about 11.9 p.p.m. Based on the mass spectrum and on the relative consistant position of the proton resonances of the Cp_3U moiety[7,47,48] the high field singlet was tentatively assigned to the cyclopentadienyl protons of $Cp_3U(SC_6H_5)$. The phenyl protons in $Cp_3U(SC_6H_5)$ would probably be rather difficult to see due to the low solubility of the complex, to the anticipated spin-spin couplings which would decrease the height of each of the three expected aromatic

resonances, and to the low relative intensities of these aromatic resonances as compare to the cyclopentadienyl resonance (i.e. 15:2:2:1).

The possibility that one of the singlets was due to the aromatic protons of the thiophenolate and not a cyclopentadienyl ligand was excluded by the observation that the high field resonance had grown with respect to the low field singlet after crystallization from THF. The reaction of $Cp_2U(NEt_2)_2$ and thiophenol was repeated in the coordinating solvent THF but the same qualitative results were obtained, as when the reaction was performed in toluene. Hence it was decided to repeat the reaction with ethanethiol rather than thiophenol. It would be expected that the ethanethiolate derivatives would be more soluble than the thiophenolate derivative and that its ^{1}H-NMR spectrum should be easier to interpret.

As ethanethiol was added to a solution of $Cp_2U(NEt_2)_2$ in THF the same type of reaction was observed as with thiophenol (i.e. the reaction solution immediately turned from a yellow-brown to a deep red color). Removal of the solvent <u>in vacuo</u> yielded a red solid. The ^{1}H-NMR spectrum of this solid showed only singlets at about 6.9 and 12.1 p.p.m. relative to internal benzene. If the assignments made in the thiophenol case were correct then the low field resonance is due to the cyclopentadienyl protons of $Cp_2U(SEt)_2$ while the high field resonance is due to cyclopentadienyl protons of $Cp_3U(SEt)$. However it was rather disturbing not to see the expected triplet and quartets of the ethyl groups. As with the thiophenolate

product the high field singlet was more intense after crystallization from THF than before crystallization. It was seen in the diethylamido derivatives that $Cp_3U(NEt_2)$ was less soluble than $Cp_2U(NEt_2)_2$. Hence the assignment of the high field singlet to the Cp_3U-derivative seemed to be in keeping with the solubility behavior previously seen.

In order to verify the assignment of the high field singlet to the $Cp_3U(SR)$ complex, $Cp_3U(SEt)$ was prepared by the reaction of Cp_3UCl and KSEt (equation IV-6). A ^{1}H-NMR spectrum (at 100 MHz)

$$Cp_3UCl + KSEt \longrightarrow Cp_3U(SEt) + KCl \qquad \text{IV-6}$$

of the product obtained indeed showed a singlet at 12.08 p.p.m. as anticipated. In addition the methyl group was found as a triplet at 26.12 p.p.m. and the methylene group was found as a quartet at 41.05 p.p.m. above internal benzene. Therefore our inability to see these high field signals previously in the mixture of compounds was only a feature of instrumental limitation. The observation of the cyclopentadienyl reasonance at 12.08 p.p.m. clearly indicates that the major component of the mixture was indeed the $Cp_3U(SR)$ complex.

The clear implicatinn of the above results is that the $Cp_2U(SR)_2$ complexes are indeed formed but disproportionate into $Cp_3U(SR)$ and either $U(SR)_4$[3] (equation IV-7) or $CpU(SR)_3$ (equation IV-8). Of the

$$3Cp_2U(SR)_2 \longrightarrow 2Cp_3U(SR) + U(SR)_4 \qquad \text{IV-7}$$

$$2Cp_2U(SR)_2 \longrightarrow CpU(SR)_3 + Cp_3U(SR) \qquad \text{IV-8}$$

two possible disproportionation routes it would seem that the one represented by equation IV-7 is favored over equation IV-8 for the following reasons: 1) the $U(SR)_4$ complexes are known to be rather insoluble;[3] 2) when any of the thiol reaction products were treated with benzene a small amount of undissolved material always remained, $U(SR)_4$; 3) in addition to the observance of $Cp_3U(SEt)^+$ (m/e 494) in the mass spectrum of the product obtained with ethanethiol, a small peak at m/e 482 was also seen which can be attributed to $U(SEt)_4^+$, while no peak was seen at m/e 486 (i.e. $CpU(SEt)_3^+$).

The absence of peaks due to $Cp_2U(SR)_2^+$ in the mass spectrum, even though the singlet at about 6.8 p.p.m. in the ^{1}H-NMR seems to indicate its presence, was bothering. However due to the high temperatures necessary to record the mass spectra (i.e. about 140°C) it is possible that the disproportionation has gone to completion or nearly so as evidenced by the observance of $U(SEt)_4^+$.

The results of previous studies on cyclopentadienyl actinide complexes indicated that there is a certain amount of covalent nature to the cyclopentadienyl-metal bond[4,12] in contrast to the lanthanide cyclopentadienyls which are almost exclusively ionic.[47,48] Hence it would be expected that disproportionation in the $Cp_2U(SR)_2$ complexes is a result of molecular associations rather than a random redistribution of ligands. If indeed this is the case then a very bulky thiol would minimize the possibility of disproportionation and increase the possibility of isolating the desired $Cp_2U(SR)_2$ complex.

To test this postulation t-butanethiol (Htbt) was reacted with $Cp_2U(NEt_2)_2$ as per equation IV-5. Analogous to the other thiol reactions, the addition of t-butanethiol to a solution of $Cp_2U(NEt_2)_2$ in THF produced an immediate color change from yellow-brown to deep red. Removal of the solvent in vacuo yielded a red solid whose ^{1}H-NMR spectrum consisted of a sharp singlet at about 17.1 p.p.m., a broader singlet at 8.9 p.p.m. and a very small peak at 12.2 p.p.m. The peaks at 17.1 p.p.m. and 8.9 p.p.m. integrated in a 9:5 (or 18:10) ratio as would be expected for $Cp_2U(tbt)_2$. Hence it seemed apparent that the peak at 12.2 p.p.m. was due to $Cp_3U(tbt)$. If this assignment is correct then the $Cp_2U(tbt)_2$ was contaminated with 1-2% $Cp_3U(tbt)$. As further evidence that disproportionation through associations was occurring it was found that if the reaction was repeated in pentane then about 5-6% $Cp_3U(tbt)$ was formed. When $Cp_2U(SR)_2$ is dissolved in a coordinating solvent such as THF, the THF can compete with (SR) ligands from another uranium complex for vacant coordination sites on a uranium while such competition is non-existent in non-coordinating solvents as in pentane. Hence one would expect more $Cp_3U(SR)$ to be produced in a non-coordinating solvent than in a coordinating solvent if molecular associations are important. As mentioned above this indeed is found.

The mass spectrum of $Cp_2U(tbt)_2$ is summarized in Table XXV. The molecular ion, $Cp_2U(tbt)_2^+$, is observed together with a small amount of $Cp_3U(tbt)^+$. In contrast to the mass spectra of the $Cp_2U(SR)_2$-$Cp_3U(SR)$ mixtures (where R=Et, C_6H_5) which showed only

TABLE XXV

SUMMARY OF THE MASS SPECTRUM OF $Cp_2U(tbt)_2$

MASS (m/e)	RELATIVE ABUNDANCE (%)	ASSIGNMENT
546	29	$Cp_2U(tbt)_2^+$
522	2	$Cp_3U(tbt)^+$
490	7	$Cp_2U(tbt)(SH)^+$
434	21[a]	$Cp_2U(SH)_2^+$
433	14	Cp_3U^+
401	37[b]	Cp_2USH
400	100	Cp_2US
368	11[c]	Cp_2U^+
367	22	$CpUS_2^+$
335	57[d]	$CpUS^+$
334	40	$C_5H_4US^+$-or-US_3^+
270	9	US^+

a ^{13}C contribution from m/e 433 included

b ^{13}C contribution from m/e 400 included

c ^{13}C contribution from m/e 367 included

d ^{13}C contribution from m/e 334 included

the $Cp_3U(SR)$ to be present, $Cp_2U(tbt)_2$ predominates in the above spectrum, and $Cp_3U(tbt)$ is only a minor impurity. In addition there were no significant changes in the relative abundances of the $Cp_2U(tbt)_2^+$ and $Cp_3U(tbt)^+$ peaks even after 12 minutes at 170°C, the temperature at which the spectrum was recorded (i.e. after 15 minutes the relative abundance of $Cp_2U(tbt)_2^+$ to $Cp_3U(tbt)^+$ had changed from 14.5:1 to about 5:1). Hence it can be concluded that the t-butanethiolate ligand is so bulky that the amount of molecular associations is indeed minimized and that disproportionation has been quite effectively limited though not entirely eliminated.

It can also be seen from Table XXV that decomposition occurs almost exclusively within the t-butanethiolate ligand. In addition there are high abundances of ions in which a bare sulfur atom is attached to an organouranium moiety. In fact the base peak of the spectrum, m/e 400 corresponds to such an ion (i.e. Cp_2US^+).

Table XXVI lists the four main decomposition processes observed in the mass spectrum of $Cp_2U(tbt)_2$. The molecular ion loses two molecules of $CH_2 = CMe_2$ successively, then a molecule of H_2S in generating the base peak, Cp_2US^+. The main decomposition process then is the expulsion of a cyclopentadienyl ligand from the Cp_2US^+ ion.

Tables XXVII and XXVIII summarize the mass spectra of $Cp_3U(SEt)$ and $Cp_3U(SC_6H_5)$, respectively. It should be noted that the mass spectra of the $Cp_2U(SEt)_2$-$Cp_3U(SEt)$ mixture and the $Cp_3U(SEt)$ sample prepared by the route shown in equation IV-6 were virtually

TABLE XXVI

SOME DECOMPOSITION PROCESSES OBSERVED IN THE MASS SPECTRUM OF $Cp_2U(tbt)_2$

PROCESS	METASTABLE PEAKS	
	Calculated	Observed
$Cp_2U(tbt)_2^+ \longrightarrow Cp_2U(tbt)(SH)^+ + CH_2{=}CMe_2$	439.7	440.0
$Cp_2U(tbt)(SH)^+ \longrightarrow Cp_2U(SH)_2^+ + CH_2{=}CMe_2$	384.4	384.5
$Cp_2U(SH)_2^+ \longrightarrow Cp_2US^+ + H_2S$	368.7	368.5
$Cp_2US^+ \longrightarrow CpUS^+ + Cp$	217.6	218.0

TABLE XXVII

SUMMARY OF THE MASS SPECTRUM OF $Cp_3U(SEt)$

MASS (m/e)	RELATIVE ABUNDANCE (%)	ASSIGNMENT
494	39	$Cp_3U(SEt)^+$
433	100	Cp_3U^+
429	23	$Cp_2U(SEt)^+$
401	10[a]	Cp_2USH^+
400	23	Cp_2US^+
368	43	Cp_2U^+
335	41[b]	$CpUS^+$
334	35	$(C_5H_4)US^+$ -or- US_3^+
303	10	CpU^+
270	14	US^+

a ^{13}C contribution from m/e 400 included

b ^{13}C contribution from m/e 334 included

TABLE XXVIII

SUMMARY OF THE MASS SPECTRUM OF $Cp_3U(SC_6H_5)$

MASS (m/e)	RELATIVE ABUNDANCE (%)	ASSIGNMENT
542	27	$Cp_3U(SC_6H_5)^+$
447	34	$Cp_2U(SC_6H_5)^+$
433	88	Cp_3U^+
411	15	$CpU(SC_6H_5)^+$
368	34	Cp_2U^+
335	8	$CpUS^+$
218	100	$C_6H_5SSC_6H_5^+$

identical. It is interesting to note that the base peak in the $Cp_3U(SEt)$ mass spectrum is Cp_3U^+ (m/e 433) while a peak corresponding to the disulfide, $(C_6H_5)S\text{-}S(C_6H_5)^+$, m/e 218, is the base peak in the mass spectrum of $Cp_3U(SC_6H_5)^+$. Whether the formation of $C_6H_5S\text{-}SC_6H_5^+$ results from a very rapid decomposition of $Cp_2U(SC_6H_5)_2^+$, from an ion-molecule reaction in the spectrometer, or from both is hard to say. However it should be pointed out that whenever it was checked in this research, the mass spectrum of a genuine Cp_3UR sample agreed almost exactly with that of a mixture which showed Cp_3UR^+ in its mass spectrum. The decomposition of $Cp_3U(SEt)$ occurs both through loss of the ethanethiolato ligand and through losses within the ethanethiolato ligand. However the peaks which correspond to the loss of the thiol followed by losses of cyclopentadienyl from the resulting Cp_3U^+ are, on the whole, more abundant than those peaks which appear to be due to losses within the thiol (e.g. Cp_2USH, m/e 401).

In contrast to the mass spectrum of $Cp_3U(SEt)$, the mass spectrum of $Cp_3U(SC_6H_5)$ shows that ions of the type, $Cp_xU(SC_6H_5)^+$ (where x=3,2,1) are more abundant. It is also seen that there is only one ion of significance which shows that any decomposition has occurred within the thiophenolato ligand (i.e. m/e 335).

The $Cp_2U(tbt)_2$ complex is soluble even in non-coordinating solvents such as pentane. As a result of its high solubility, both its ^1H- and ^{13}C-NMR spectra could be recorded and are shown in Figures 13 and 14, respectively. However the comparison of these

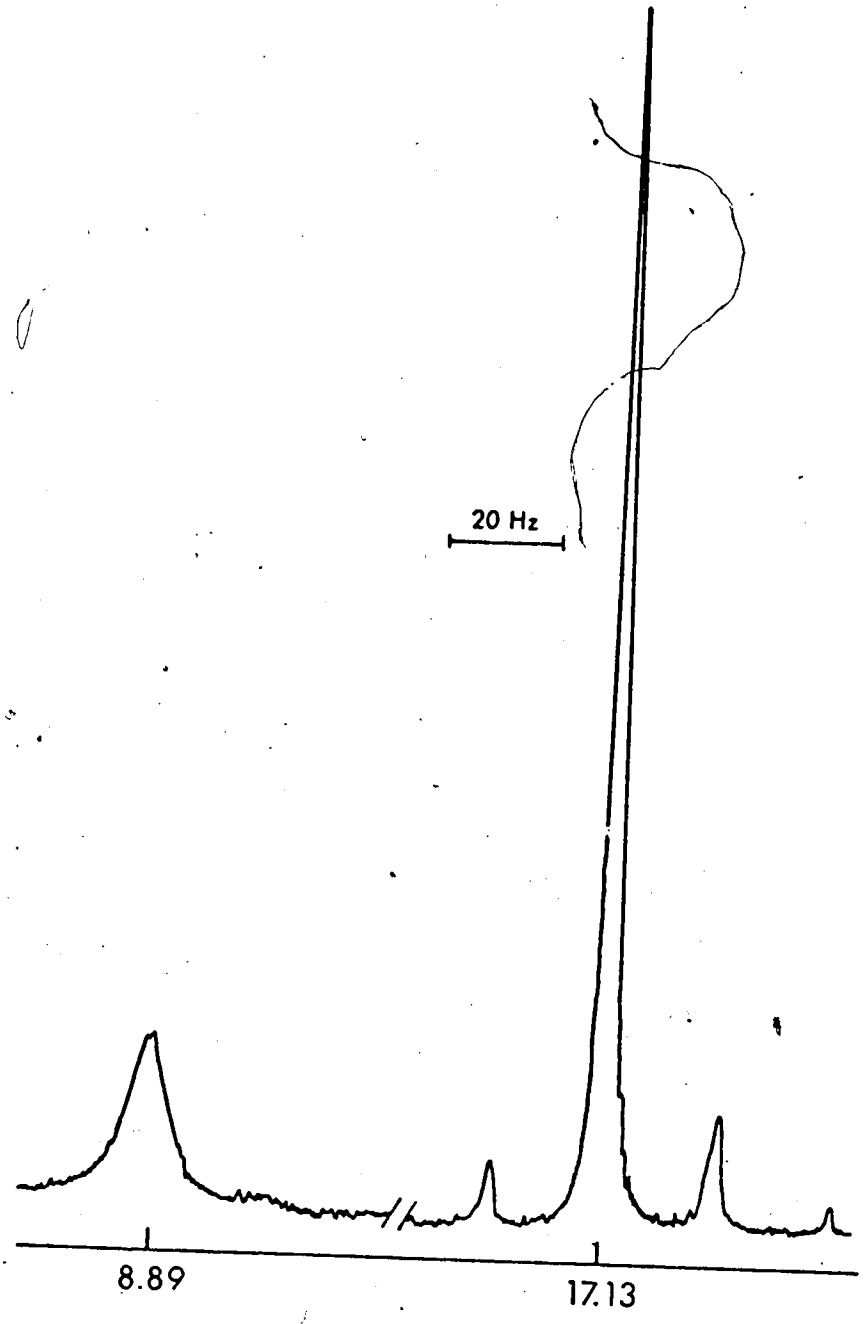


Figure 13. ^{1}H-NMR spectrum of $Cp_2U(tbt)_2$. Chemical shifts given in p.p.m. relative to internal benzene.

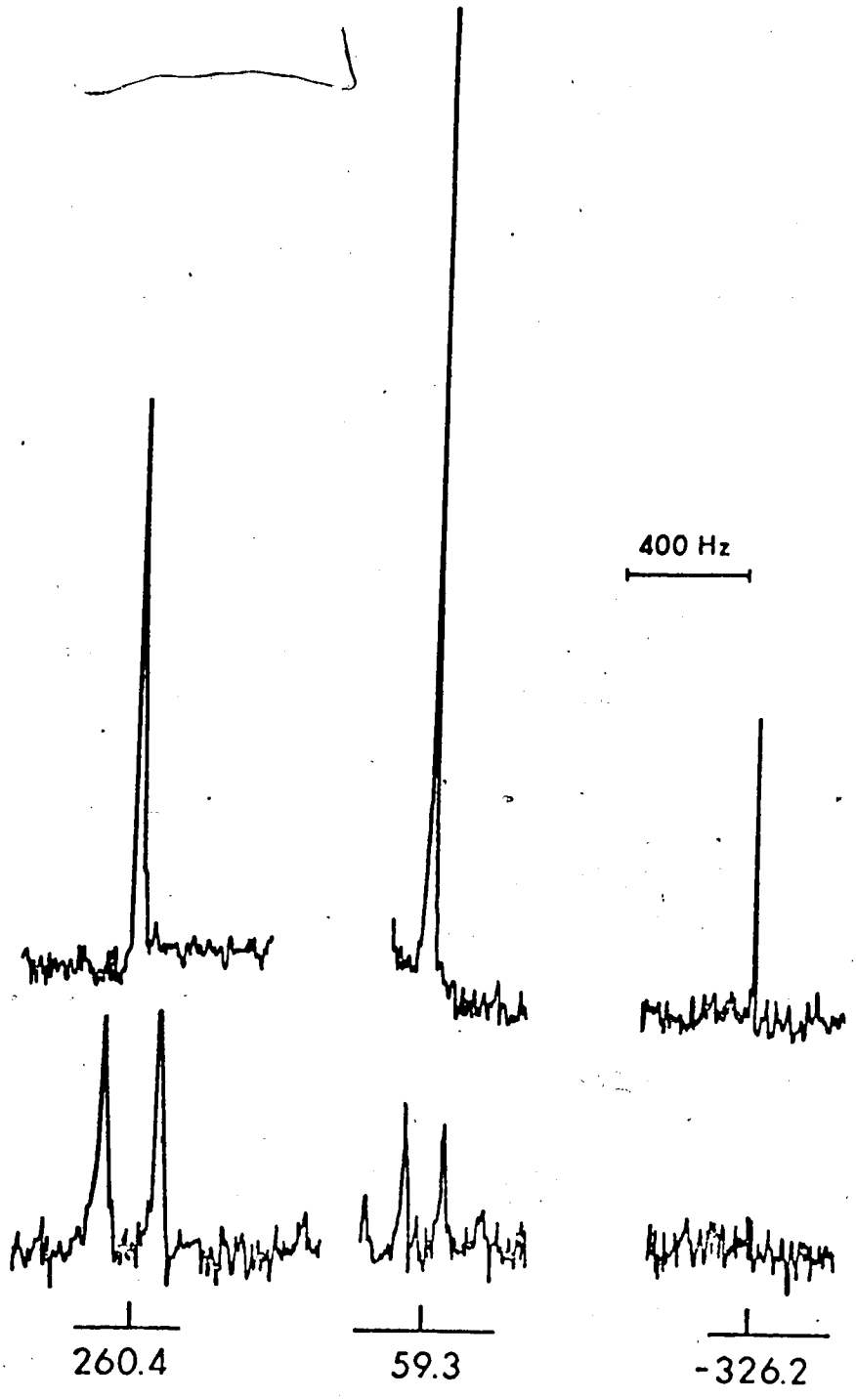
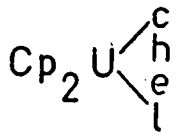


Figure 14. ^{13}C-NMR spectrum of $Cp_2U(tbt)_2$. Chemical shifts given in p.p.m. relative to TMS.

spectra with those of other organoactinides will be deferred until Chapter V.

Reactivity Toward Diprotic Chelating Ligands

Since the reactivity toward monoprotic ligands was complicated by disproportionation reactions, it was decided to study the reactivity of $Cp_2U(NEt_2)_2$ toward potentially chelating diprotic ligands, H_2chel. It was hoped that the formation of a chelating ring by uranium would confer added stability to the Cp_2U-moiety and eliminate disproportionation. The enhanced stabilities of chelated complexes with respect to their monodentate counterparts is well-known in inorganic chemistry.[117] In order to increase the probability that chelation would indeed occur, as in 7, rather than bridge formation, as in 8, rigid diprotic ligands capable of forming five-membered rings were chosen: o-metcaptophenol (H_2 omp), catechol (H_2 cat), etc.



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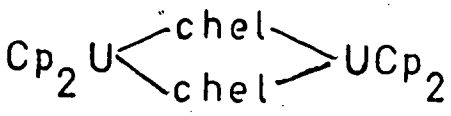

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As o-mercaptophenyl was added dropwise to a solution of $Cp_2U(NEt_2)_2$ (equation IV-9) an immediate color change from yellow-brown to deep

$$Cp_2U(NEt_2)_2 + H_2(chel) \rightarrow Cp_2U(chel) + 2HNEt_2 \qquad \text{IV-9}$$

red was observed. Removal of the solvent under vacuum gave a near

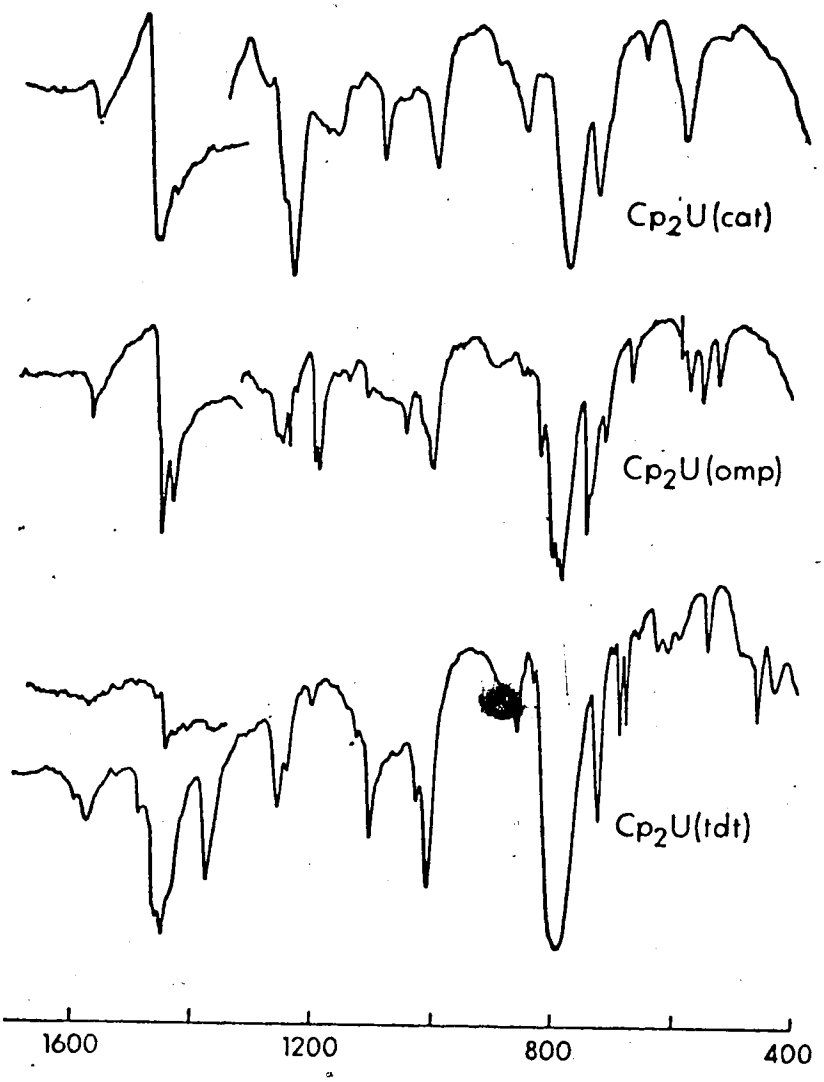


Figure 15. Infrared spectra of Cp_2U(chel) Complexes.

quantitative yield of $Cp_2U(omp)$. The crude reaction product was recrystallized and the nature of the complex was ascertained by the following routine measurements. The infrared spectrum (Figure 15) showed bands at 1573, 1436, 1270, and 753 cm^{-1} indicative of an o-disubstituted benzene [118] which, together with the absence of a band around 3300 cm^{-1} (i.e. ν(OH)) and one around 2540 cm^{-1} (i.e. ν(SH)), are taken as evidence that indeed a chelated complex has been formed. In addition bands at 1012, 808, 801 and 794 cm^{-1} are indicative of the cyclopentadienyl ligand. [92]

The mass spectrum of $Cp_2U(omp)$ showed the expected molecular ion at m/e 492 (60%) but surprisingly also showed a peak at m/e 984 (36%) which corresponds to $[Cp_2U(omp)]_2^+$. Dimer formation was not expected since the analogous transition metal $Cp_2M(chel)$ complexes are known to be monomeric, [58, 119-123] although complexes where these and related bidentate bridging positions are known. [124,125] The base peak in the spectrum was that corresponding to $Cp_3U_2(omp)_2^+$ (i.e. the dimeric molecular ion minus one Cp) at m/e 919. The metastable peak corresponding to the formation of the base peak was observed at m/e 858.5 (calculated 858.3) while the metastable peak corresponding to the loss of a cyclopentadienyl ligand from the monomer

$$Cp_2U(omp)^+ \rightarrow CpU(omp)^+ + Cp \qquad \text{IV-10}$$

was observed at m/e 370.5 (calculated 370.6). It was quite surprising to see that the mass spectrum of the complex showed no signs of thermal decomposition even though the spectrum was recorded at 180°C.

The ^{1}H-NMR spectrum was run but only one resonance was observed

at 6.87 p.p.m. above internal benzene which was assigned to the cyclopentadienyl ligand. Our inability to observe the aromatic protons can be explained as follows. At best the four aromatic protons will form an A_2X_2 pattern, each triplet representing two protons. The intensity ratio between the cyclopentadienyl protons and the highest member of the triplet then would be 10 : 1. Due to the low solubility of the complex in suitable deuterated solvents assignments of such small peaks could not be made with certainty.

The same reaction (equation IV-9) was repeated using freshly sublimed catechol. Here, too, the recrystallized product gave a good analysis, and the infrared spectrum (Figure 15; bands were at 1576, 1476, 1440, 1265, and 744 cm^{-1} together with no ν(OH) bands around 330 cm^{-1}) indicated a chelated complex.

Just as the mass spectrum of $Cp_2U(omp)$ showed a dimer so the $Cp_2U(cat)$ complex also showed a dimer at m/e 952. The main decomposition process was loss of a cyclopentadienyl ligand from the dimer as observed by a relatively strong metastable peak at m/e 826.5 (calculated 826.4). In contrast to the mass spectrum of the $Cp_2U(omp)$ complex that of $Cp_2U(cat)$ showed only a small amount of the monomer at m/e 476 which was the monomer plus a small amount of $[Cp_2U(cat)]_2^{2+}$ as indicated by a peak at m/e 476.5. Another striking difference between the mass spectra of $Cp_2U(omp)$ and $Cp_2U(cat)$ was the observance of a small peak at m/e 974 (3%) which corresponds to $(Cp_3U)_2(cat)^+$. In keeping with this and the large amount of steric interactions expected between two Cp_3U moieties ortho to one another, a relatively strong peak corresponding to Cp_3U^+ is observed at m/e 433 (88%). The

analysis of the sample clearly showed that if $(Cp_3U)_2(cat)$ was present in the product it had to be present in very small amounts (the % C required for $Cp_2U(cat)$ is 40.35%, for $(Cp_3U)_2(cat)$ 44.95%; found 40.06, 40.12 %C). Due to the very low solubility of the $Cp_2U(cat)$ complex a complete ^1H-NMR spectrum could not be obtained. A sharp singlet was observed at 6.88 p.p.m. relative to internal benzene which was assigned to the cyclopentadienyl ligand.

In an effort to improve the solubility of the complexes and to extend the known $Cp_2U(chel)$ derivatives it was decided to react $Cp_2U(NEt_2)_2$ with toluene-3,4-dithiol with the hope of getting $Cp_2U(tdt)$ (equation IV-9). The addition of one equivalent of toluene-3,4-dithiol (H_2tdt) to a solution of $Cp_2U(NEt_2)_2$ resulted in an immediate color change from yellow-brown to deep red. A mass spectrum of the reaction product exhibited only weak metal-containing peaks. This was probably due to a combination of low volatility and thermal decomposition as evidenced by the fact that peaks at m/e 154 (tdt^+), 66 (CpH^+), 65 (Cp^+), and other low mass peaks were off-scale. The mass spectrum was rather simple consisting of peaks attributable to the molecular ion, $Cp_2U(tdt)^+$, at m/e 522 (82%), to $CpU(tdt)^+$ at m/e 457 (100%; the base peak of the metal-containing fragments, but not the base peak of the spectrum), to Cp_2U^+ at m/e 368 (78%), and to $U(tdt)^+$ at m/e 392 (16%). It must also be mentioned that a trace of what might be the dimer (i.e. $[Cp_2U(tdt)]_2^+$) was seen around m/e 1045 though the mass could not be determined for certain. There were some other peaks which could not be attributed to reasonable decomposition products of either $Cp_2U(tdt)^+$ or $[Cp_2U(tdt)]_2^+$. Most disturbing was

a strong peak at m/e 433 attributable to Cp_3U^+ (68%). The presence of this peak was taken as indirect evidence for $(Cp_3U)_2(tdt)$ though this molecular ion was not seen at the expected m/e 1020. (More will be said about this later).

In marked contrast to the mass spectra of the other $Cp_2U(chel)$ complexes, the mass spectrum of $Cp_2U(tdt)$ exhibited at best a trace of the dimeric molecular ion. From Pearson's hard-soft acid-base concepts uranium (IV), a hard acid, would be expected to form a more stable complex with an oxygen-donor ligand, a hard base, than with a sulfur-donor ligand, a soft base. Thus the interaction of two uranium (IV) ions with four oxygen-donors would be more favorable than that with two oxygen-donors and two sulfur-donors while the interaction with four sulfur-donors would be the least favored. The strength of uranium-donor interactions predicted by hard-soft acid-base considerations is the same as the apparent order of mass spectral stability of the dimeric units, $[Cp_2U(chel)]_2^+$, as can be seen from Table XXIX. (It should be noted that the data in Table XXIX is presented in a manner different from that of the other mass spectra. For sake of comparison of each of the complexes the $Cp_2U(chel)^+$ ion was assigned a value of 100%. Though one cannot make quantitative comparisons of the various spectra one can, nonetheless, see the trend).

The infrared spectrum of the product (Figure 15; Table XXX) was quite comparable to that of the analogous transition metal compounds $Cp_2Zr(tdt)$ [119] and $Cp_2Mo(tdt)$. [58] The absence of a band at about 2540 cm^{-1} (i.e. ν(S-H)) together with the presence of bands at 1600, 1579, 1492, and 865 cm^{-1} which are characteristic of a 1,2,4-trisub-

stituted benzene ring [118] were also taken as evidence that a chelated complex had been formed. In addition bands assigned to the cyclopentadienyl resonance were seen at 1451, 1012, 798 and 789 cm^{-1}.

A ^{1}H-NMR spectrum (Figure 16) consisted of a singlet at 0.12 p.p.m. (Cp) relative to internal benzene, a singlet at 4.93 p.p.m. (aromatics) and a singlet at 6.88 p.p.m. (Me) which were in an approximate 10 : 3 : 3 ratio, respectively. The ratio fits the $Cp_2U(tdt)$ formulation if all three of the aromatic protons resonate at the same position. The singlet for the cyclopentadienyl ligand is consistent with the spectra of $Cp_2Ti(chel)$ complexes where chel = tdt, benzenedithiol (bdt), and 1,2-ethylenedithiol. [120] However, Köpf, in a variable temperature study of the $Cp_2Ti(chel)$ complexes, found that the room temperature singlet was split into two singlets of equal intensity at -50°C. This is in keeping with the crystal structure of $Cp_2Ti(bdt)$ [121] which shows that the Ti metallocycle (i.e. TiS_2C_2) is bent along the S-S vector so that an angle of 46°C is formed thereby generating two different cyclopentadienyl rings.

In order to see if the $Cp_2U(tdt)$ complex would behave like its titanium analog, ^{1}H-NMR spectra were recorded from -60°C to +60°C (Figure 17). Indeed it was seen that at low temperatures the room temperature singlet had split into two resonances, but the peaks were not in a 1 : 1 ratio as found for the titanium complexes. Instead an approximate 1 : 2 ratio was observed. Hence the flipping of the metallocycle ring postulated by Köpf [120] cannot account for the results of the $Cp_2U(tdt)$ complex. The splitting of the two resonances into two peaks of unequal intensity was explained in terms of a monomer-dimer

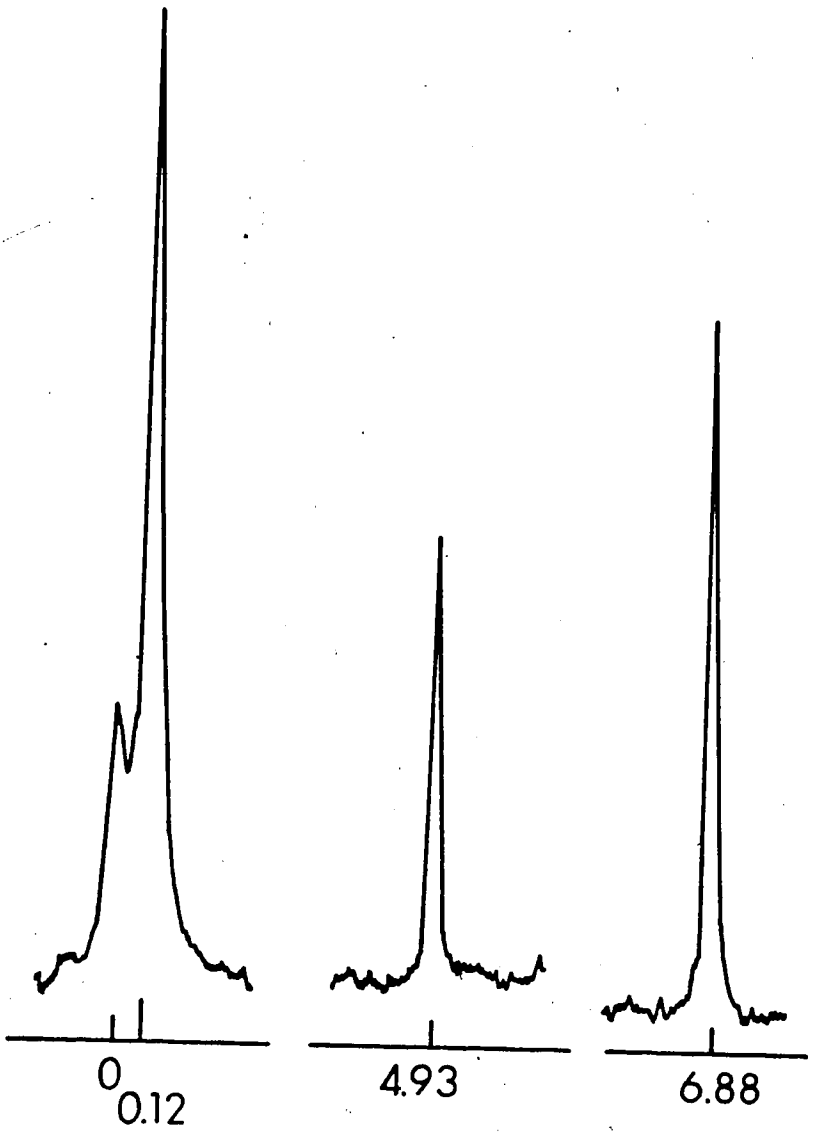


Figure 16. ^{1}H-NMR spectrum of the presumed $Cp_2U(tdt)$. Chemical shifts given in p.p.m. relative to internal benzene.

TABLE XXIX

COMPARISON OF THE MASS SPECTRA OF $Cp_2U(chel)$ COMPLEXES

chel	Temperature	$Cp_4U_2(chel)_2^+$	$Cp_3U_2(chel)_2^+$	$Cp_2U(chel)^+$	$CpU(chel)^+$	Cp_2U^+
tdt	210	trace [a]	-	100	122	95
omp	180	79	215	100	186	16
cat	210	736	3010	100	395	1180
Me-cat	200	298	1050	100	216	382

[a] relative abundance (%) assuming $Cp_2U(chel)$ to be 100

TABLE XXX

SUMMARY OF THE INFRARED SPECTRA [a] OF $Cp_2M(tdt)$ COMPLEXES

Zr[b]	Mo[c]	U[d]	ASSIGNMENT
3080w	3111m	3075w	ν(C-H)
	3013w	3020w	
2920m	2910w		
	2853w		
	1858w		
		1600mw	
1580w		1579m	
	1533w		
		1492m	
1450s	1451m	1451s	
	1436sh		
	1414sh		
1380w	1370m		
1260w	1278w	1260m	
1250w	1247w	1246m	
	1206w	1206w	
	1140vw	1142sh	
	1126vw		
1110w	1105m	1107m	
		1080w	
	1061w	1062w	
	1038w	1032ms	
1015s	1013w	1012s	δ(C-H) of Cp
	1000w		
	937m		
	914m		
		890sh	
	862sh	865m	
	832s	840mw	
		810sh	
		805sh	
805s	799s	798vs	γ(C-H) of Cp
		789vs	γ(C-H) of Cp
		729s	
	794vw	695m	
680m	685w	684m	
		699w	
		665w	
		634mw	
		615mw	
		600mw	
550w		550m	

(Table continued)

Table XXX continued

Zr[b]	Mo[c]	U[d]	ASSIGNMENT
		497sh	
		468m	
		440m	

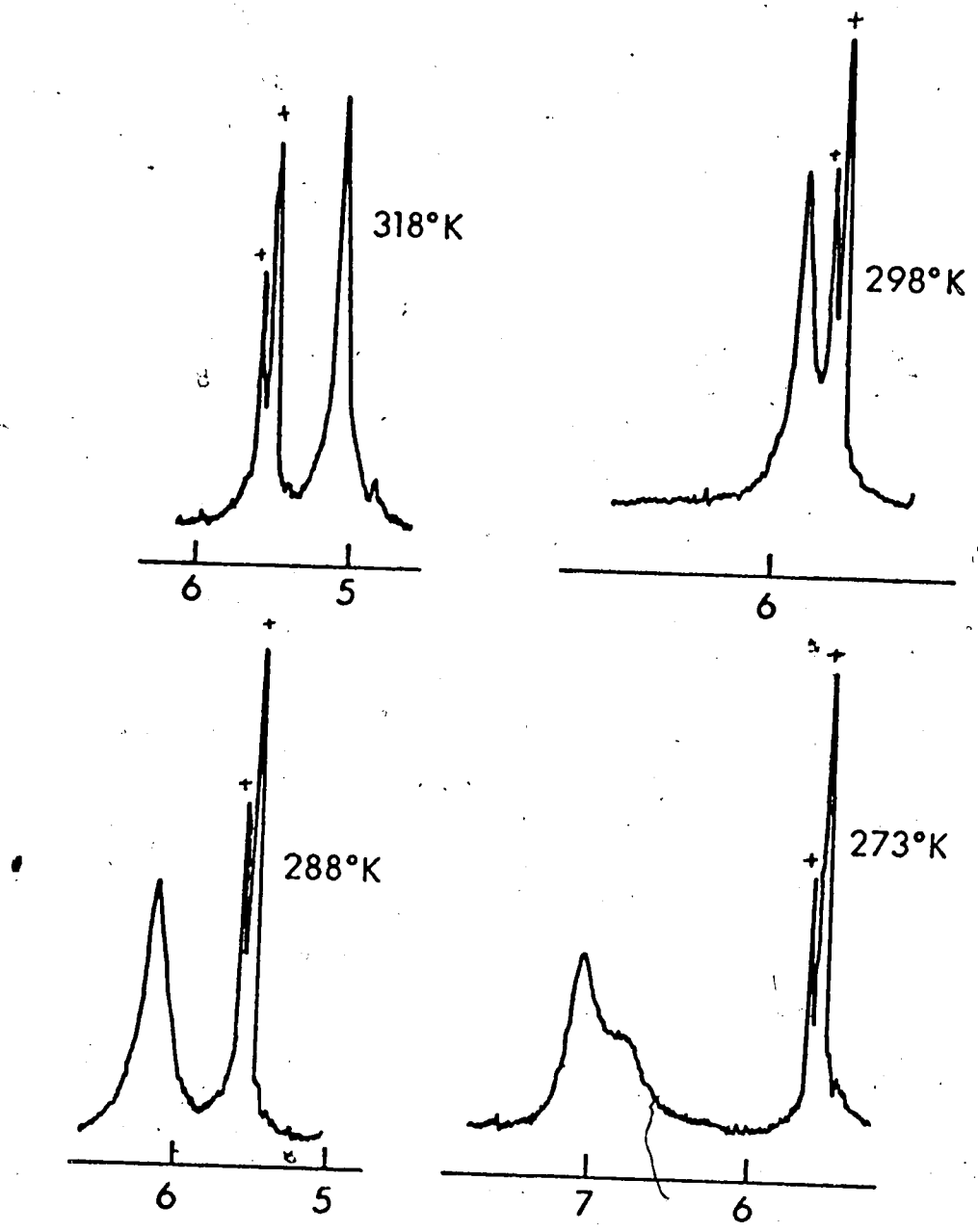
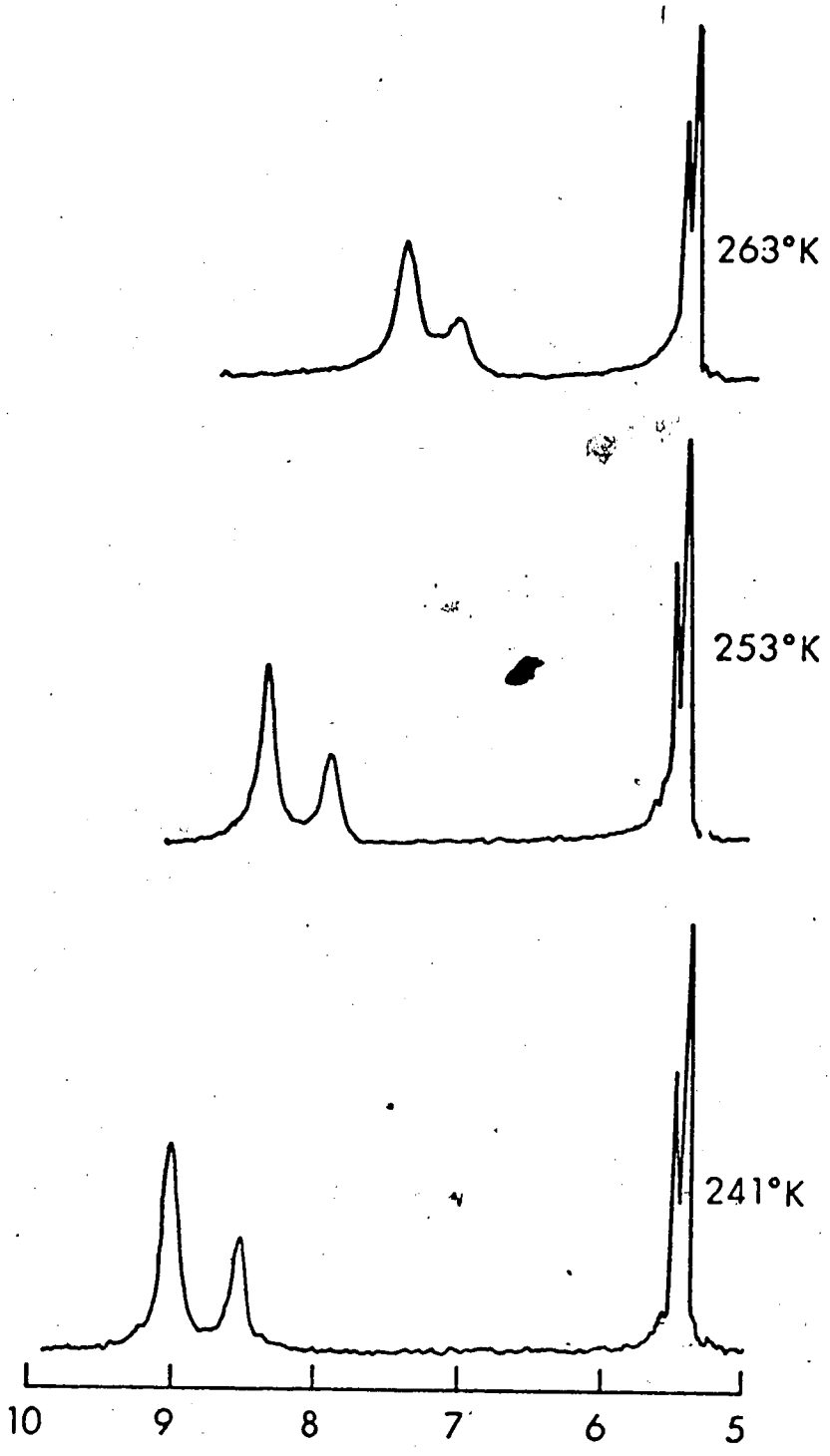


Figure 17. Variable temperature ^{1}H-NMR spectra of the Cp protons of the presumed $Cp_2U(tdt)$. The chemical shifts are given in p.p.m. (downfield) from internal cyclohexane and maybe converted to chemical shifts relative to benzene by the equation, $\delta_{Ben} = 5.80 - \delta_{C_6H_6}$. Residual protons of toluene-d_8 are marked by +.

Figure 17 continued



equilibrium such that at higher temperatures the rate of interconversion of the two forms is faster than the NMR time scale while at lower temperatures the rate of interconversion is slowed down sufficiently to allow observance of both the monomer and dimer.

To verify that the observation of two peaks at low temperature was indeed due to a monomer-dimer equilibrium, a concentration dependent study was initiated. To do so we had to prepare a new sample; however the product obtained when the preparation of $Cp_2U(tdt)$ was repeated did not give a good analysis and its ^{1}H-NMR spectrum was different from the previously described spectrum. This ^{1}H-NMR spectrum showed a singlet around benzene and a singlet at 6.84 p.p.m. as before but two features of the spectrum had changed: (1) the peak previously seen at 4.98 p.p.m. was absent; and (2) a broad peak now appeared at 11.04 p.p.m.

The mass spectrum of this solid also exhibited a peak at m/e 433, Cp_3U^+. In fact if the largest metal-containing ion of the first mass spectrum (i.e. m/e 457) was still taken as 100% then the m/e 433 peak was 114% and the m/e 522 peak was 89%. The appearance of the Cp_3U^+ ion at m/e 433 was again taken as indirect evidence for the formation of some $(Cp_3U)_2(tdt)$ though this was not directly seen in the mass spectrum.

At this point a ^{1}H-NMR spectrum of the toluene-3,4-dithiol used for this second preparation was recorded since a sample from another company was used for the first preparation. The spectrum showed that water was also present in about 20%! Hence the sample of toluene-3,4-dithiol was discarded, a fresh commercial sample was

opened, added to anhydrous $MgSO_4$ and vacuum distilled. A ^{1}H-NMR spectrum showed no water.

The reaction was then repeated using thefreshly distilled ligand and a freshly prepared $Cp_2U(NEt_2)_2$, the reaction time being slightly longer than in the original preparation. Nevertheless the ^{1}H-NMR spectrum was still different from our original sample, the main difference being the absence of the peak at 4.98 p.p.m. The absence of this resonance did not cause too much concern since we had a difficult time explaining the appearance of a singlet for the three chemically different protons in the first place. However, the observation that the two peaks were not in the expected 10 : 3 ratio was very puzzling (in fact we could not account for it). A mass spectrum was run and again it showed peaks at m/e 368 (Cp_2U^+; 73%), 433 (Cp_3U^+; 82%), 457 ($CpU(tdt)^+$; 100%), 522 ($Cp_2U(tdt)^+$; 76%), and a few unassignable weak peaks at higher mass indicating the probable formation of some $(Cp_3U)_2(tdt)$. It was thought that the formation of the latter complex was due to a disproportionation reaction (equation IV-11) similar to the ones observed with monodentate thiols. Such

$$3Cp_2U(tdt) \longrightarrow (Cp_3U)_2(tdt) + U(tdt)_2 \qquad \text{IV-11}$$

a disproportionation reaction hopefully was not fast and it was thought that possibly the long reaction time utilized in the previous syntheses contributed to the formation of the Cp_3U-derivatives. Furthermore the acid-base type of reaction utilized for the preparation of the complexes should be nearly instantaneous. It was then decided to attempt a quick reaction in the hope that this

would cut down the amount of $(Cp_3U)_2(tdt)$ that would be formed.

A new reaction was carried out with a total reaction time of one hour. The ^{1}H-NMR spectrum (Table XXXI) of this product showed only a singlet around benzene and a broad unresolvable multiplet at about 11 p.p.m., the peak previously observed at 6.86 $\pm$ 0.02 p.p.m. being absent. The spectrum, though puzzling, indicated that a complete reaction indeed had occurred since peaks due to $Cp_2U(NEt_2)_2$ were absent. A mass spectrum again showed peaks at m/e 368 (Cp_2U^+; 23%), 433 (Cp_3U^+; 53%) 457 ($CpU(tdt)^+$; 100%), 522 ($Cp_2U(tdt)^+$; 78%), and a few very weak unassignable peaks at higher mass possibly indicating the presence of $(Cp_3U)_2(tdt)$ even though the ^{1}H-NMR spectrum showed only one major peak.

Similarly complicated results were obtained when 4-methylcatechol (H_2Me-cat) was reacted with the amide (Table XXXI). The only consistent picture comes from mass spectral work. After a short reaction time only traces of $(Cp_3U)_2(Me\text{-}cat)^+$ (m/e 988) are observed along with smaller amounts of m/e 433, Cp_3U^+, whereas longer stirring of the reaction mixture apparently produces more of the $(Cp_3U)_2(Me\text{-}cat)$. The ^{1}H-NMR spectra were puzzling. It was expected that the cyclopentadienyl resonance for this compound would be at about the same position as observed for the catechol derivative. However, the three main resonances observed in both of the above complexes were at 7.02 p.p.m. (2.7 ^{1}H), 17.16 p.p.m. (5.0 ^{1}H), and 17.44 (5.0 ^{1}H). Additional small peaks occurred at 4.44 p.p.m. and 7.62 p.p.m. whose intensities changed somewhat from the two syntheses. This seems to imply that the two high field resonances (i.e. at 17.16 and 17.44 p.p.m.) cor-

TABLE XXXI

SUMMARY OF THE ^{1}H-NMR SPECTRA OF THE VARIOUS $Cp_2U(tdt)$ AND $Cp_2U(Me\text{-}cat)$ PREPARATIONS

COMPLEX	REACTION TIME (HOURS)	PURIFICATION OF H_2chel	^{1}H-NMR [a]
$Cp_2U(tdt)$	12	degass [b]	0.12 (10 ^{1}H); 4.93 (3 ^{1}H); 6.88 (3 ^{1}H)
	18	degass	0.10 (?)[c]; 6.84 (?); 11.04(?)
	20	distill [d]	-0.10 (12 ^{1}H); 6.87 (3 ^{1}H)
	1	distill	-0.10 (?) [c]; 11.04 (?)
$Cp_2U(Me\text{-}cat)$	18	sublimed [f]	4.44 (0.5 ^{1}H); 7.02 (2.8 ^{1}H); 7.62 (1.1 ^{1}H); 17.16 (5.0 ^{1}H); 17.44 (5.0 ^{1}H)
	1	sublimed	4.45 (1.3 ^{1}H); 7.02 (2.7 ^{1}H); 7.63 (1.0 ^{1}H); 17.16 (5.0 ^{1}H); 17.44 (5.0 ^{1}H)

[a] given in p.p.m. relative to internal benzene

[b] $H_2(tdt)$ was stored over molecular sieves and degassed

[c] reliable integrations could not be obtained

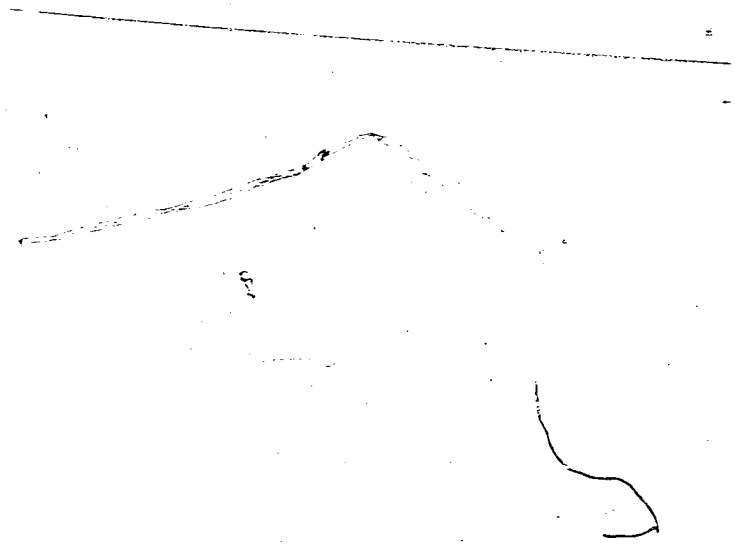
[d] $H_2(tdt)$ was distilled under vacuum from $MgSO_4$ and stored under nitrogen

(Table continued)

Table XXXI continued

[e] the relative areas are only approximate

[f] H_2(Me-cat) was sublimed then stored under nitrogen



respond to the cyclopentadienyl rings (since Me-cat is an asymmetric ligand and the complex presumably exists in solution as a dimer, it is conceivable that isomers exist which produce the two cyclopentadienyl resonances) and the low field resonance to the methyl group. This is indeed a drastic change from the unsubstituted complex. It could also be that the two high field resonances are due to the two different types of Cp_3U moiety and that one of the smaller peaks is due to the methyl group to produce the 30 : 3 ratio demanded by the structure. The constancy of the ratio observed in the ^{1}H-NMR spectra for these three peaks (Table XXXI), even though the mass spectra showed drastically different amounts of $[Cp_2U(Me\text{-}cat)]_2^+$ and $(Cp_3U)_2(Me\text{-}cat)^+$, seems to eliminate the latter possibility.

To gain a clearer idea of the situation it was decided to make the $(Cp_3U)_2(chel)$ complexes by the most rational way

$$2Cp_3UCl + Na_2(chel) \longrightarrow (Cp_3U)_2(chel) + 2NaCl \qquad IV\text{-}12$$

An obvious reaction occurred in both cases as evidenced by color changes. However, the isolated products showed very disappointing mass spectra, with the only identifiable fragments being Cp_3U^+ (m/e 433), Cp_3UCl^+ (m/e 468) and its fragments [127], and $(Cp_3U)_2O^+$. Hence the object of this synthesis, the recording of the ^{1}H-NMR spectra of the pure $(Cp_3U)_2(chel)$ complexes could not be achieved. It is then impossible at the present time to tell which, if any, of the resonances in the previous ^{1}H-NMR spectra (Table XXXI) belong to $(Cp_3U)_2(chel)$, and to tell if the production of the $(Cp_3U)_2(chel)$

complexes occurs in solution or in the mass spectrometer.

At this point it is believed that the good analyses, the ^{1}H-NMR and mass spectral work on $Cp_2U(omp)$ and $Cp_2U(cat)$ show that the complexes can be obtained, though the ^{1}H-NMR spectra of the tdt and Me-cat derivatives remain unexplained. It is clear however, that the inability to reproduce the very simple ^{1}H-NMR spectrum for the "purest" $Cp_2U(tdt)$ sample (i.e. from the quick preparation) casts doubt on the monomer $\rightleftarrows$ dimer equilibrium proposed to explain the variable temperature studies (Figure 17). Further work is yet required to understand these systems.

INSERTION REACTIONS

Lappert, et al. have shown that the amido derivatives of the transition metals will insert a wide variety of unsaturated ligands into the metal-nitrogen bond as in equation IV-2.[64,69] More recently Bagnall and Yanir have reported that the tetrakisamides of thorium and uranium will insert either CO_2, COS, CS_2 or CSe_2 into the metal-nitrogen bond[78] thereby establishing the generality of the previously observed insertion of CS_2 into the uranium-nitrogen bond $U[N(i\text{-}Pr)_2]_4$ (Chapter II).

Hence the exothermic dissolution of $Cp_2U(NEt_2)_2$ in carbon disulfide was anticipated to yield the CS_2-inserted product, bis(cyclopentadienyl)bis(N,N-diethyldithiocarbamato)uranium (IV), $Cp_2U[S_2CNEt_2]_2$ ($Cp_2U(dtc)_2$). Removal of the excess CS_2 under vacuum gave a solid whose weight corresponded to a quantitative yield of $Cp_2U(dtc)_2$. A mass spectrum of the solid showed the expected molecular ion to be present at m/e 664 while a ^{1}H-NMR spectrum of

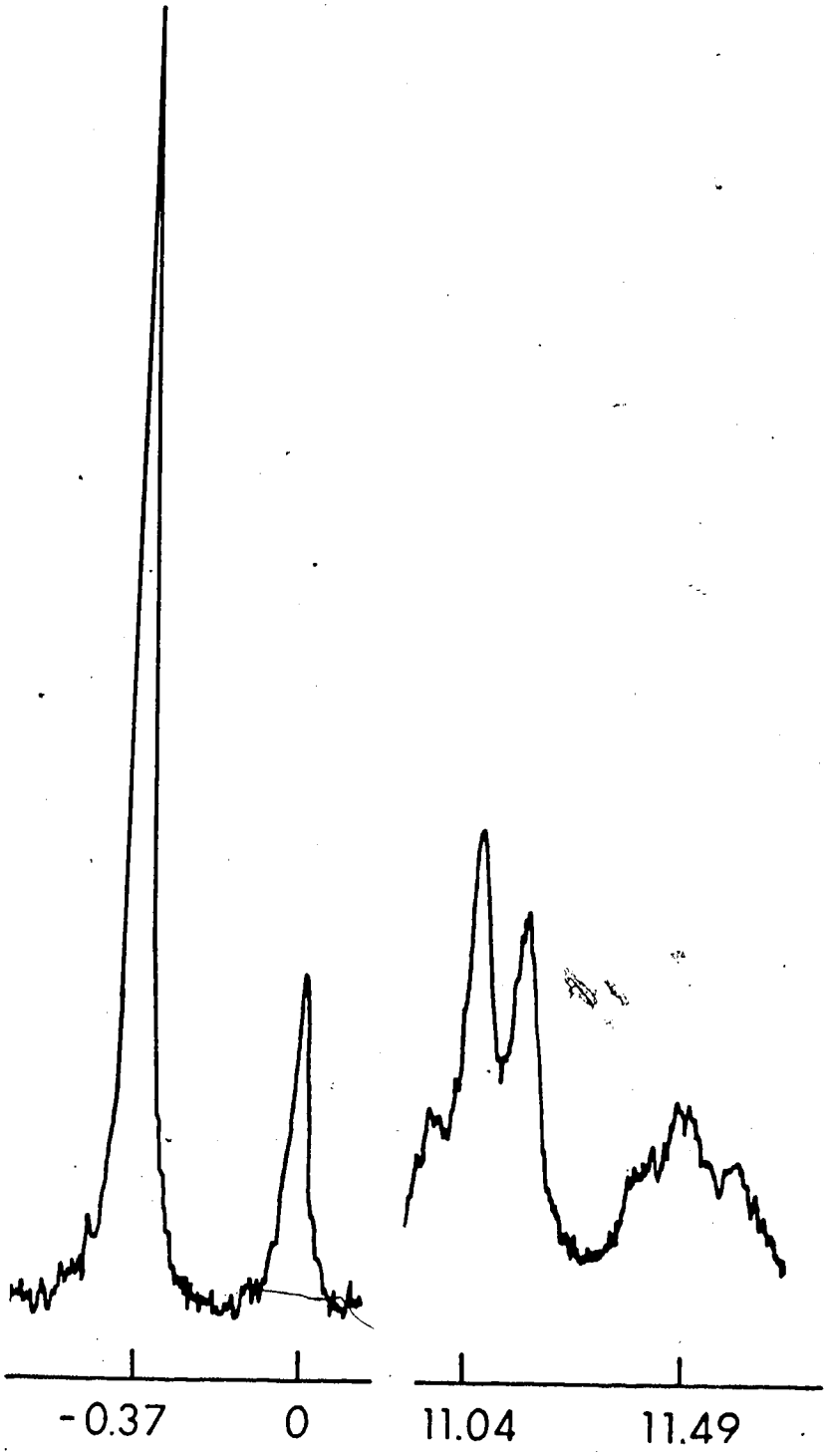


Figure 18. ^{1}H-NMR spectrum of $Cp_2U(dtc)_2$. Chemical shifts given in p.p.m. relative to internal benzene.

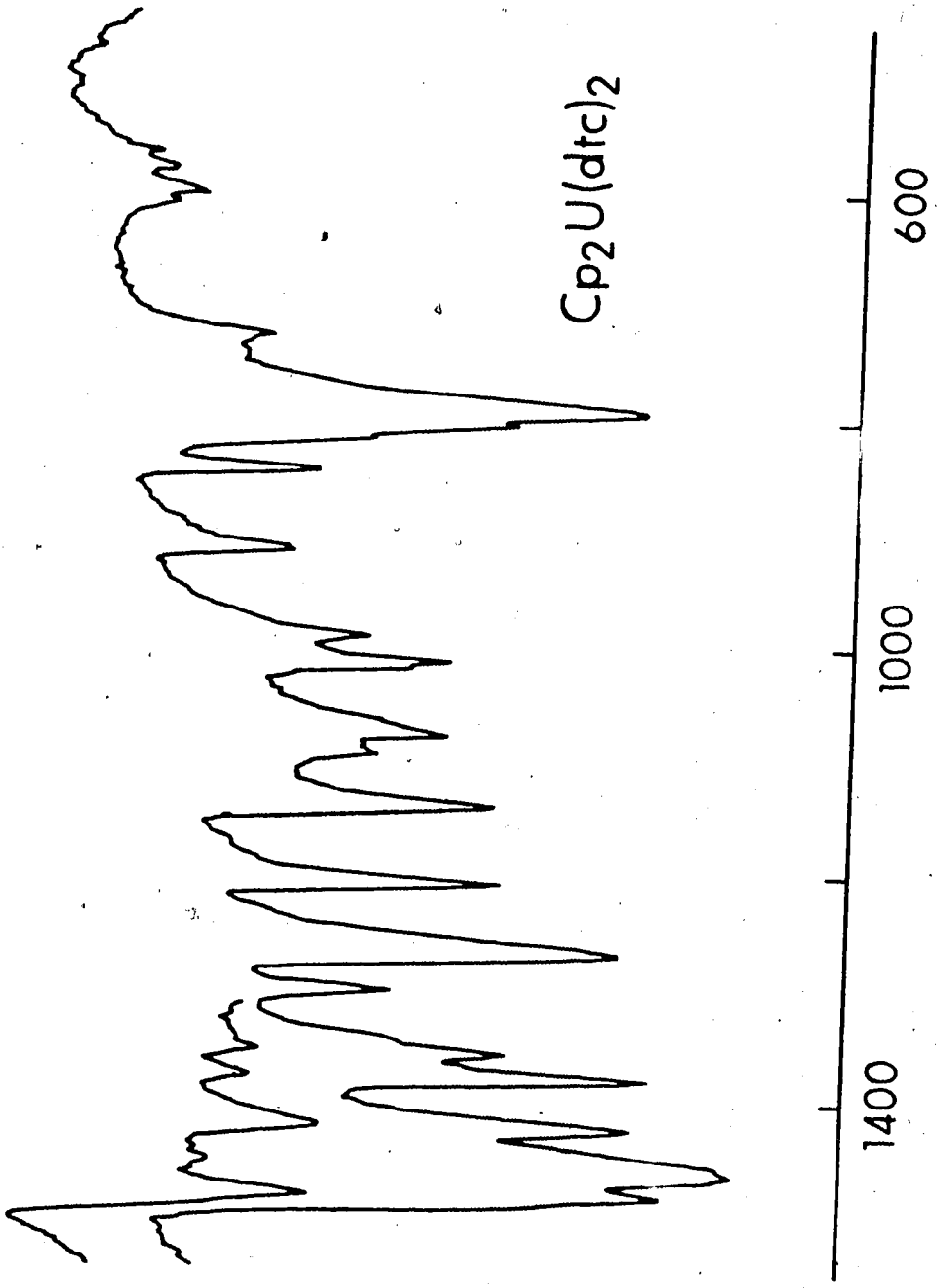
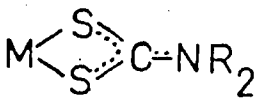


Figure 19. Infrared Spectrum of $Cp_2U(dtc)_2$

the solid (Figure 18) showed a singlet at -0.37 p.p.m. relative to internal benzene, and a pair of broad peaks at 11.04 and 11.49 p.p.m. which tend to resemble a triplet and a quartet, respectively. A reliable integration of each peak was not possible due to the closeness of the two high field peaks. However, the intensity ratio of the combined high field peaks to the low field resonance was 2 : 1 as would be expected for $Cp_2U(dtc)_2$. In contrast to the dimeric nature of the $Cp_2U(chel)$ complexes, a molecular weight determination (osmometry) in benzene; Bernhardt) indicated that the complex was monomeric.

The infrared spectra of numerous N,N-diethyldithiocarbamate complexes have been reported [79,99,100,104] as have characteristic infrared bands of dithiocarbamate ligands.[79,99-103] However, only a few of these characteristic bands have been assigned.[99-103] The results presented in Table XXXII (see also Figure 19) reflect this lack of knowledge and our assignments are restricted to those bands where comparison with previous studies gives confidence to such a task.

Most of the structural determinations on dithiocarbamate complexes have found the dithiocarbamate moiety to be present as a bidentate ligand as shown in 9 rather than as a monodentate ligand, 10. The number of reported structures in which dithiocarbamate ligands



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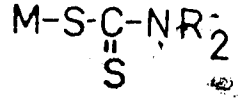


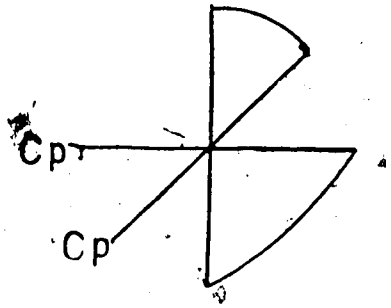
10

are known to be present both as a monodentate and a bidentate ligand is indeed small [102] being confined to the following complexes: $Ru(NO)(dtc)_3$ [103,104], $Rh(PPh_3)(dtc)_3$ [105], and $Sn(dtc)_4$ [106]. Nevertheless both bonding possibilities have been observed. Thus the bonding possibilities of the two dithiocarbamate ligands in $Cp_2U(dtc)_2$ are indeed numerous and the arrival at a conclusive decision here is difficult. In principle the complex can have both dithiocarbamate ligands chelated to the metal, both acting as monodentate ligands, or one bidentate and one monodentate ligand. This last possibility can be eliminated with some degree of confidence since only one $\nu(CN)$ bond at 1483 cm^{-1} was observed in the infrared spectrum whereas in previous studies containing both types of ligands two such bands were always seen.[103-106,129] A choice between the other two possibilities is more ambiguous. Bonati and Ugo found the 1000 cm^{-1} region to be a more reliable criterion for the presence of monodentate dithiocarbamate ligands. [107] Since the monodentate ligand possesses two quite different carbon sulfur bonds (i.e. one C=S and one C-S), two carbon-sulfur stretching modes should be seen around the 100 cm^{-1} region with the $\nu(C=S)$ being found above 1000 cm^{-1} and the $\nu(C-S)$ somewhat below 1000 cm^{-1}. Unfortunately the region above 1000 cm^{-1} in the spectrum of $Cp_2U(dtc)_2$ is obscured by absorptions of the cyclopentadienyl ring and hence cannot be used as an indicator for the type of dithiocarbamate bonding.

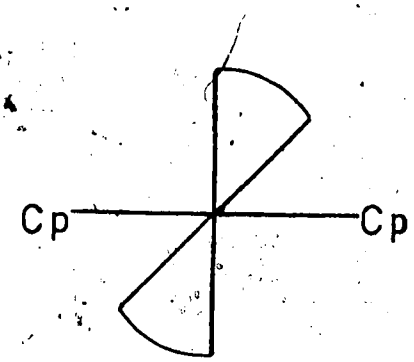
Nevertheless noting the preference of uranium for high coordination numbers we are inclined to think that in $Cp_2U(dtc)_2$ both dithiocarbamate ligands are in fact bidentate. To support this con-

clusion we note that the $Cp_2U(chel)$ complexes tend toward dimer formation whereas the $Cp_2U(dtc)_2$ complex is monomeric in solution. Also the dithiocarbamates, by virtue of their low charge and small "bites" (i.e. 2.8 - 2.9 Å) are indeed one of the chelating ligands that stabilize high coordination numbers already in the transition metals (cf. $Ti(dtc)_4$ is eight coordinate.[128])

Accepting the hypothesis of bidentate dithiocarbamates we still have to consider the possibility of cis and trans geometric isomers, 11 and 12, for the above complex.



11



12

(In 11 and 12 the Cp ligand is assumed to occupy one coordination position.) In the absence of dipole moment measurements, or better yet a structural determination, a choice between the two cannot be made with certainty *.

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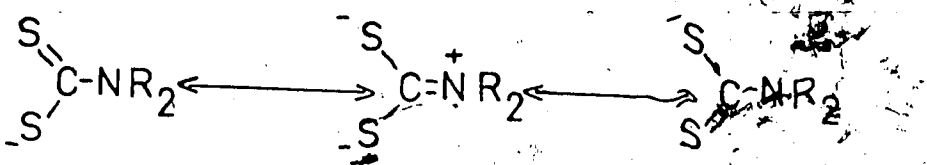
* Since everything we have said so far is speculative we cannot resist but offer a preference between 11 and 12. The cis can easily be related to the structures of other angular bis-cyclopentadienyl type compounds and hence it is favored.

The assignable ν(C-N) stretching frequency at 1483 cm^{-1} can nevertheless be utilized to say something about the electronic structure of the coordinated dithiocarbamate ligand. The anionic dithiocarbamate ligand can be written in terms of resonance structures 13, 14 and 15. Hence the band position of ν(C-N) gives an



13 14 15

indication of the relative importance of the different forms. As can be seen from Table XXXII the ν(C-N) band of $Cp_2U(dtc)_2$ at 1483 cm^{-1} is about half-way between that of $U(dtc)_4$, 1490 or 1494 cm^{-1}, and Na(dtc), 1478 cm^{-1}. The values indicate that on going from $U(dtc)_4$ to $Cp_2U(dtc)_2$ the electron demanding power of the uranium has decreased and thus has caused a decrease in the relative importance of resonance structure 14 which can be taken to mean that the cyclopentadienyl ligand is a better electron donor in this complex than the dithiocarbamate. In support of this the infrared spectrum indicates that this uranium-cyclopentadienyl bond is more covalent than that in other Cp_2U-derivatives (see later on). However, in light of the uncertainty of the structure this explanation is tentative at best.

TABLE XXXII

SUMMARY OF THE INFRARED SPECTRA [a] OF SOME DITHIOCARBAMATE COMPLEXES

$Cp_2U(dtc)_2$ [b]	$U(dtc)_4$ [c]	$U(dtc)_4$ [d]	$Na(dtc)$ [d]	Assignment
3095w				
2970m				
2940m				
1483s	1490s	1494s	1478s	ν(C-N)
1451m				
1424s	1428s	1430s	1412s	
	1422s			
1377m	1376s			
1357m	1355s	1357s	1360m	
1302m		1305m	1302m	
1268s	1264s	1267s	1267s	
1207s	1200s	1205s	1210s	
1148s	1140s	1144s	1135s	
1095m	1085m	1087s	1090m	
1077m	1072s	1074s		
1065sh	1060m	1062m	1068m	
1017m				
1012m				δ(C-H) of Cp
990m	983m	996s	996sh	
		984sh	990s	
915m	913m	913s	913s	

(Table continued)

Table XXXII continued

$Cp_2U(dtc)_2$[b]	$U(dtc)_4$[c]	$U(dtc)_4$[d]	$Na(dtc)$[d]	Assignment
915m	913m	913s	913s	
845m	840m	842s	838s	
815sh				
805s				γ(C-H) of Cp
792s				γ(C-H) of Cp

[a] given in cm^{-1}

[b] mulls

[c] from reference 99

[d] from reference 100

The additional bands in the infrared spectrum at 3095, 2970, 2940, 1017 and/or 1012, 805, and 792 cm^{-1} can be assigned to the cyclopentadienyl ligand. The splitting of the bands around 1000 and around 800 cm^{-1} is an indication of lower than C_{5v} symmetry for these groups which is consistent with the structures previously proposed. The trans "octahedral" structures. 12, is the least reconcilable with the above splitting of the bands but since This would be the first such structure, its infrared spectrum is not readily established. The band positions of the γ(C-H) mode at 805 and 798 cm^{-1} are somewhat higher than those of the other Cp_2U-derivatives (e.g. about 780-790 cm^{-1} in $Cp_2U(NEt_2)_2$ and 799 cm^{-1} in $Cp_2U(tdt)$) implying a somewhat more covalent uranium-cyclopentadienyl bond.[92]

The mass spectrum of $Cp_2U(dtc)_2$ is summarized in Table XXXIII. The expected molecular ion was observed at m/e 664 while the base peak of the spectrum was observed at m/e 599, $CpU(dtc)_2^+$. There were always two weak peaks seen at m/e 747 and 682 belonging to $CpU(dtc)_3^+$ (2.1%) and $U(dtc)_3^+$ (5.1%) respectively. These two peaks are probably a result of slight thermal decomposition as borne out by the relatively high abundance of the peaks at m/e 116 ($SC_2NEt_2^+$), 66 (CpH^+), and 65 (Cp^+). In support of this the two peaks at higher mass, as well as the low mass peaks, increased in abundance after a sealed mass spectral sample was heated to 120°C then admitted to the mass spectrometer.

As mentioned previously the ^{1}H-NMR spectrum of the complex exhibited two broad peaks at high field which very closely resembled a quartet and triplet. The observance of a quartet and triplet for

Table XXXIII

SUMMARY OF THE MASS SPECTRUM OF $Cp_2U(dtc)_2$

MASS (m/e)	RELATIVE ABUNDANCE (%)	PROPOSED ASSIGNMENTS
664	27.1	$Cp_2U(dtc)_2^+ = M^+$
599	100	$CpU(dtc)_2^+$
521	16.1	$[CpU(dtc)_2-H_2-CS_2]^+$
516	5.7	$Cp_2U(dtc)^+$
451	5.7	$CpU(dtc)^+$
368	6.0	Cp_2U^+
213	22.5	$CpS(S)CNEt_2^+$
116	54.7	$SCNEt_2^+$
88	39.1	$SCN(H)Et^+$
84	34.9	$CNEt_2^+$
76	11.5	CS_2^+
66	47.8	CpH^+
65	23.0	Cp^+

the ethyl group would be consistent with either the trans-octahedral structure or the one having two monodentate dithiocarbamate ligands. However, for the cis-octahedral structure, with a maximum C_2 symmetry, the methylene hydrogens are diastereotopic and should give rise to a more complex resonance pattern, that of an ABX_3. In the hope of resolving the question of molecular geometry, a variable temperature ^{1}H-NMR study was performed and the results are shown in Figure 20. Unfortunately as the temperature was lowered below about 20 - 25°C, the ethyl resonances broadened out and remained so down to -60°C (though the cyclopentadienyl resonance remained sharp) so that no useful information could be obtained from them. The 100°C spectrum appeared to be even simpler. However it must be said that such a simple pattern does not exclude the cis-octahedral structure since in related transition metal dithiocarbamates so-called metal-centered rearrangements [102,131,132] are fast and could cause a deceptively simple spectrum. In fact in $Cl_2Ti(dtc)_2$, which is known to be cis-octahedral, the limiting spectrum could not be obtained even at low temperatures implying very rapid rearrangement.

The variable temperature work nevertheless brings out something interesting. As mentioned before a characteristic feature of the NMR spectra of paramagnetic molecules is the temperature dependence of the chemical shifts. A plot of the two chemical shifts of the ethyl group versus 1/T is shown in Figure 21. As can be seen in the figure the two lines cross at about 357°K. Notice, too in Figure 20, that at 363°K a singlet was observed. Though this was an unexpected result, it is not unreasonable since such behavior is

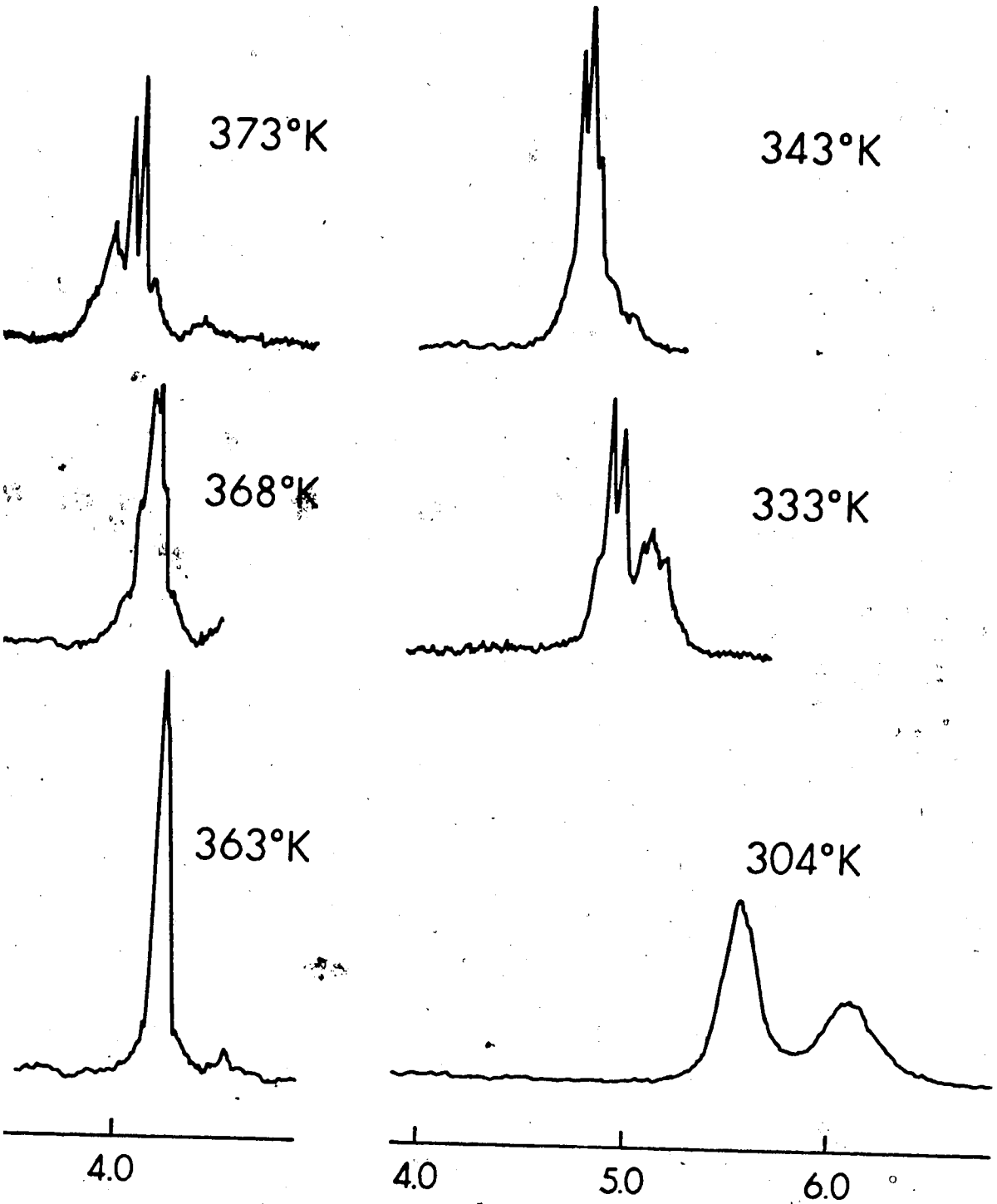


Figure 20. Variable temperature ^{1}H-NMR spectra of $Cp_2U(dtc)_2$. Chemical shifts given in p.p.m. relative to internal cyclohexane.

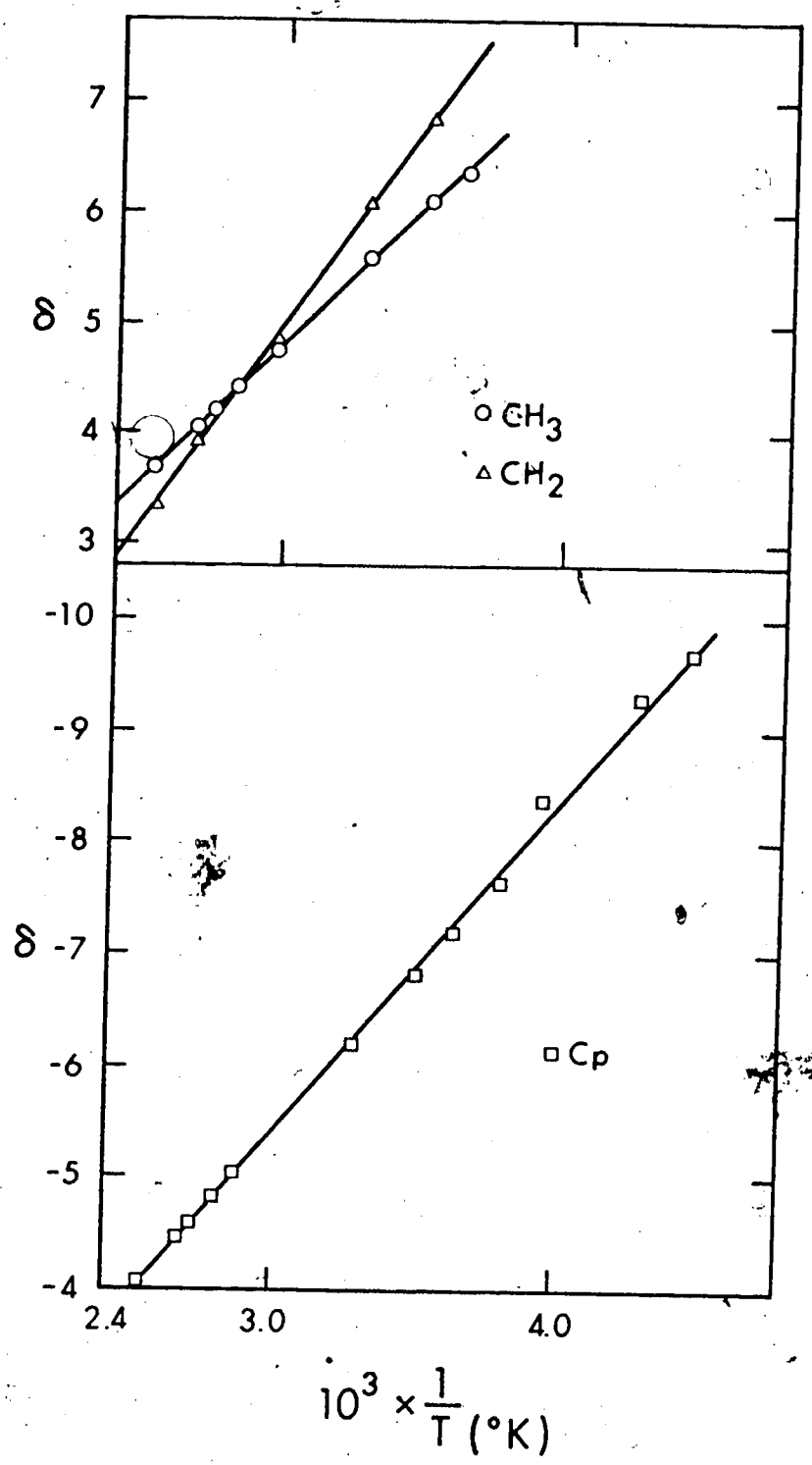


Figure 21. A plot of the chemical shifts of $Cp_2U(dtc)_2$ versus 1/T(°K).

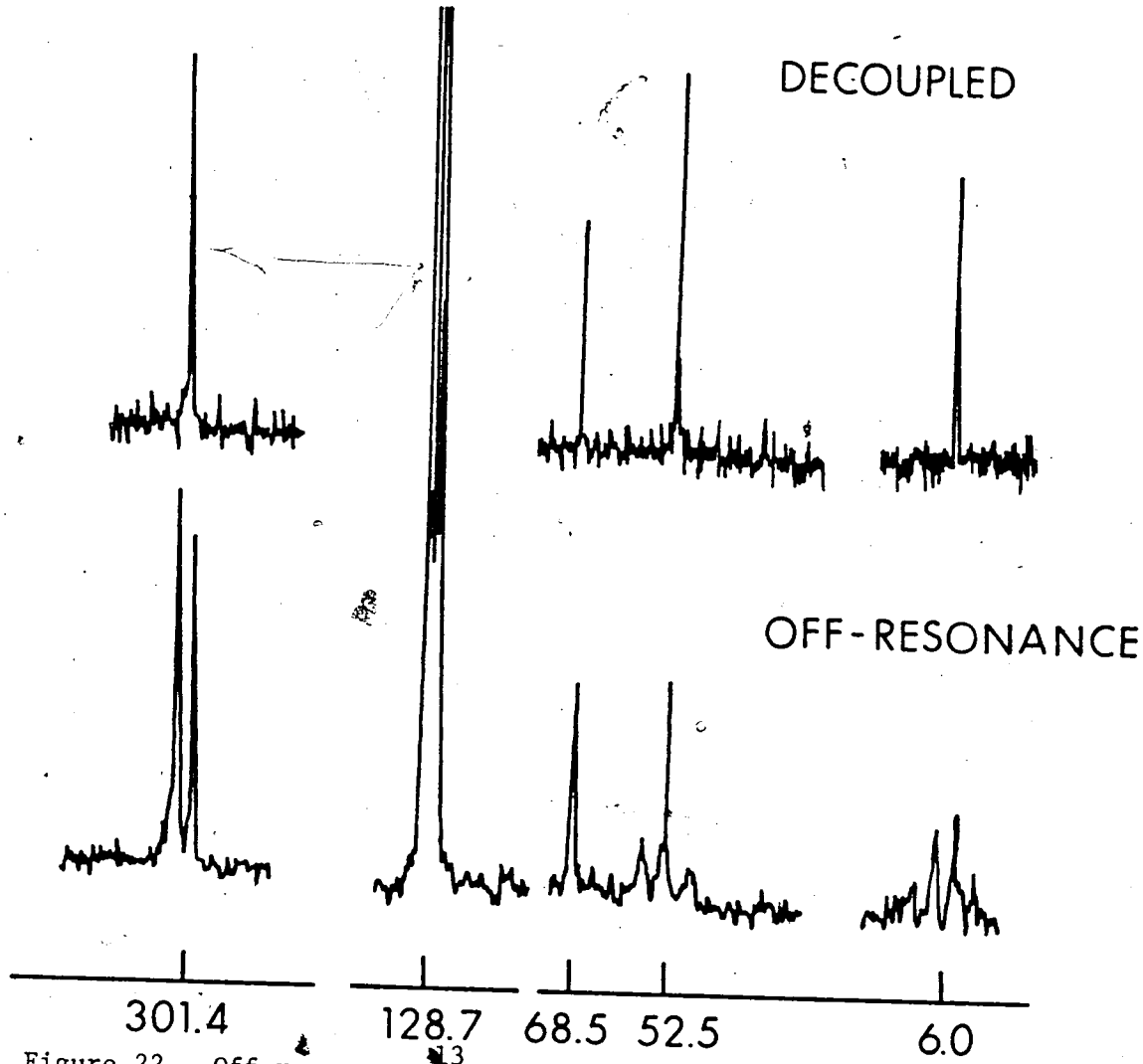


Figure 22. Off-resonance ^{13}C-NMR spectrum of $Cp_2U(dtc)_2$. Chemical shifts in p.p.m. relative to TMS.

predicted for an A_2B_3 spin system as $\nu_A - \nu_B$ approaches zero.[133] That is, at this particular temperature the chemical shift difference between the methylene and methyl protons of the dithiocarbamate ligand is zero. Not unexpectedly, the signal for these protons is indeed a singlet at this temperature. At higher temperatures as the chemical shift difference is becoming larger the singlet separates and, by 373°K the triplet and quartet pattern is again emerging. However, the order of the chemical shifts of the two multiplets is now reversed. The danger of reaching hasty conclusions from the NMR spectrum of a paramagnetic molecule recorded at one temperature is clearly demonstrated by this example.

CONCLUSIONS

It has been shown that $Cp_2U(NEt_2)_2$ can be used as a starting material for the preparation of Cp_2U-derivatives. However, it has also been shown that, unlike their titanium (IV) and molybdenum (IV) counterparts, the Cp_2U-derivatives show a marked tendency toward disproportionation to the corresponding Cp_3U-derivative. Though this research has not yielded the wide variety of Cp_2U-derivatives as initially hoped, it has nonetheless allowed us to see that in order to minimize disproportionation certain factors are important: 1. the R group in Cp_2UR_2 compounds should be bulky; 2. chelate complexes (i.e. when R_2 is a chelate ligand) disproportionate very little compared to the non-chelated complexes; and 3. the stronger the tendency of a chelated complex to dimerize the lower the tendency of that complex to disproportionate.

Finally, if the disproportionation of the complexes is a result

of molecular associations (as postulated in this thesis), then it would be predicted that an R group in Cp_2UR_2 which is directly bonded to the uranium through an atom which has no Lewis basic character (e.g. the carbon atom of an alkyl or a transition metal) would be stable toward disproportionation.

CHAPTER V - NMR OF ORGANOURANIUM (IV) COMPOUNDS

INTRODUCTION

In the first four chapters of this thesis a variety of organouranium (IV) compounds, together with a few examples of organothorium (IV) compounds were reported. As expected for diamagnetic complexes, the NMR spectra of the thorium derivatives display sharp resonances with well-resolved spin-spin couplings. Such features are rare in the NMR spectra of paramagnetic molecules which often exhibit very broad resonances (e.g. the width at half-height of the signal in the ^{1}H-NMR spectrum of Cp_2V is 2250 Hz [134,135]) where all coupling are lost. Consequently the utility of such NMR spectra for structural elucidations is virtually non-existent. However for complexes containing uranium (IV) the above limitations do not apply. Due to a very short electronic relaxation time (see later on) the resonances are sharp and indeed spin-spin couplings are usually observed. Hence in the characterization of new uranium complexes, NMR spectroscopy proved to be a very valuable tool. For example in the case of $U[N(i\text{-}Pr)_2]_4$, where satisfactory analyses could not be obtained, a combination of the ^{1}H- and ^{13}C-NMR spectra showed other carbon- or hydrogen-containing species to be present.

Besides its more limited use for structural elucidations, the NMR spectra of paramagnetic molecules, by virtue of the varying sizes and direction of the observed chemical shifts can yield very useful information about the electronic structure of the molecule, the amount of delocalization of unpaired electron spin-density on the attached

ligands, etc. For instance there is an ongoing discussion about f orbital participation in the bonding of uranium complexes [42,47,48], and the amount of covalent character of the bond to uranium. Such information can, in principle, be extracted from the NMR spectra. The process, however, is tedious, difficult, and requires among other things magnetic susceptibility measurements and structural data.

Since this thesis is primarily synthetic in nature, a quantitative treatment of the NMR data was not attempted. The purpose of this chapter, therefore, is mainly to summarize the NMR data on the systems reported in this thesis as a convenience to the reader and to, whereever possible, give a qualitative discussion concerning the origin of the observed chemical shifts.

GENERAL PRINCIPLES OF NMR SPECTRA OF PARAMAGNETIC SAMPLES

Since only a qualitative description of a few principles governing the NMR of paramagnetic compounds is given below, the reader is referred to several articles and reviews for more detail. [77,136-141] (It should be noted for those who desire to puruse this topic further that the articles are listed in what seems to be the order of increasing sophistication except for reference 77 which would fit in between references 138 and 139).

LINE WIDTHS AND RELAXATION

In the early 1950's it was thought that the NMR spectra of paramagnetic compounds would be too extensively broadened to be of any value. [138] However, in 1957, McConnell and Holm reported that

the paramagnetic nickelocene, Cp_2Ni, gave a well-resolved (relatively speaking) ^{1}H-NMR spectrum.[142] Since that time there has been a large amount of interest generated in the study of paramagnetic compounds by NMR. The line widths (at half-height) of the resonances observed in the NMR spectra of paramagnetic transition metal complexes vary greatly, from lines so wide that they are mere bumps in the base line to resolvable peaks (e.g. Cp_2V has a line width of 2250 Hz[134,135]) to very sharp resonances (e.g. 3-5 Hz[143]). On the other hand the ^{1}H-NMR spectra of organolanthanide complexes (e.g. Cp_3La) have, on the whole, sharper resonances (from 3 to 300 Hz[48]) than those of transition metal complexes while organouranium compounds have even sharper resonances (Table XXXIV).

It is well-known that for the appearance of sharp lines in an NMR spectrum of a paramagnetic molecule the molecule must have a very short electronic relaxation time, T_{1e}.[77,136-141] To understand this consider the following argument which, for the sake of simplicity, are based on the presence of only one unpaired electron in an f orbital. In the presence of a strong external magnetic field a pair of energy levels is generated: the lower energy level corresponds to the alignment of the magnetic moment of the electron with the field while the higher energy level corresponds to the moment being aligned against the field. Once the system has attained thermal equilibrium there is a certain probability that each level will be populated.[144] In the NMR experiment transitions occur between certain nuclear levels. The process of the return of the nuclear spin (after excitation) to its ground state is the relaxation

TABLE XXXIV

LINE WIDTHS OF CYCLOPENTADIENYL-URANIUM (IV) COMPOUNDS

Compound	Width[a] (Hz)	Reference
$Cp_3U(BH_4)$	2.9	b
Cp_3U^+	1.0	b
Cp_3U(halide)	1.1-3.2	b
$Cp_3U(NR_2)$	3	c
Cp_3U(SR	2-3	c
Cp_2U(N	3	c
$Cp_2U(SR)_2$	2-3	c
$Cp_2U(dtc)_2$	3	c
$Cp_2U(dtc)_2$	3-6[d]	c

[a] line width at half-height

[b] from reference 48

[c] this work

[d] from variable temperature studies

process. The factor which is most important in paramagnetic complexes for the return of the nuclear spin to its ground state is the spin-lattice relaxation mechanism. Now if the electronic relaxation time is very short, there is a very rapid rate of transfer of spin between electronic energy levels which produces a very rapidly fluctuating magnetic field. However, the excited nuclear spin cannot couple with such a rapidly fluctuating magnetic field and thus it is deprived of an additional path for relaxation.[77,136-141] Hence in the absence of this extra potential relaxation process, the nucleus should have a nearly normal spin-relaxation time (i.e. a relatively long-lived excited state). If the excited nuclear state is relatively long-lived (i.e. if Δt is large), then on the basis of the Heisenberg uncertainty principle, $\Delta t \Delta E \simeq h/2\pi$: the uncertainty in the energy differences between the nuclear states is small; only a narrow range of frequencies will induce nuclear transitions; and sharp lines are observed.

ISOTROPIC SHIFTS

As mentioned above when a paramagnetic sample containing one unpaired electron is placed in a magnetic field, two energy levels are produced and there is a certain probability that each level will be populated.[14] If one would have a static system (i.e. a slow rate of exchange of spin between electronic states), then a nucleus of spin 1/2 could couple with each electron producing two resonances whose separation would correspond to the value of the hyperfine coupling constant A.[77,138,144] However, the peaks would be too broad to be observed (cf. the uncertainty principle above). Instead

a single peak is seen which is shifted, either upfield or downfield, from its normal position. This results from the fact that the nucleus experiences some kind of weighted average field produced by the rapidly fluctuating magnetic field of electron spin exchange and the signal is shifted in one direction.

This shift from the normal position is most commonly referred to as the isotropic shoft, δ_{iso}, since it is an average of all possible orientations of the molecule with respect to the applied field. There are two contributions to this shift, the contact and pseudo-contact contributions (equation V-1).

$$\delta_{iso} = \delta_C \pm \delta_D \qquad \text{V-1}$$

The contact shift is a measure of the amount of unpaired electron spin density that has been transferred to a given nucleus (i.e. the amount that comes in contact with the nucleus). This unpaired electron spin density is transferred in various ways through bonds from the paramagnetic ion to the nucleus. There is in turn a certain probability of finding the unpaired electron at a given nucleus (i.e. the square of the wave functions at the nucleus) which can be derived from the contact shift (equation V-2) [146,*]

$$\delta_C = \frac{2\bar{g}\beta A_s}{3kT(\gamma_N/2\pi)}\left[1 - \frac{(g_\parallel - g_\perp)}{9\bar{g}}\frac{D}{kT}\right], \qquad \text{V-2}$$

Hence that fraction of the electron spin density found at a given nucleus (i.e. the probability) can be envisioned as also generating

---

* Definitions for the symbols utilized in equations V-2 and V-3 are to be found in reference 146.

an additional magnetic field in the immediate vicinity of the nucleus which causes the contact shift to occur.

On the other hand the pseudo-contact (or dipolar) mechanism is dependent upon the geometry of the complex and can be in operation only if there is magnetic anisotropy.[77] A common general equation to express the pseudo-contact shift is (equation V-3)[146]

$$\delta_D = -\frac{2\beta^2(g_\parallel^2 - g_\perp^2)(3\cos^2\theta - 1)}{kT} \frac{}{R^3} \left[1 - \frac{(g_\parallel^2 + 4g_\perp^2)\, D}{3(g_\parallel^2 - g_\perp^2)kT}\right] \qquad \text{V-3}$$

The origin of this shift is seen if one considers (for sake of simplicity) the unpaired electron(s) of the molecule to be centered mainly on the paramagnetic metal. The presence of an external field causes the unpaired electron(s) to generate a magnetic field centered around the metal atom. The amount of through space interaction, then between the lines of flux of this additional magnetic field and another magnetic nucleus in the molecule will depend upon 1) the distance of the magnetic nucleus from the metal, r; and 2) the angle, θ, between R and the principal axis of the molecule, (assuming at least axial symmetry).

SEPARATION OF CONTACT AND PSEUDO-CONTACT SHIFTS

The total isotropic shift, δ_{iso}, is the sum of the contact shift, δ_c, and the pseudo-contact shift, δ_D,[77,136-141] as in equation V-1. Hence in order to gain any insight into the electronic structure of the molecule one must know δ_c. If the molecule in question has strict spherical symmetry (i.e. T_d or O_h symmetry), at the limit of D = 0 (no zero field splitting), the pseudo-contact shift vanishes since $g_\parallel = g_\perp$ in such cases (equation

V-3) and the isotropic and contact shifts are the same.

However in compounds where this is not the case, the separation is much more complicated. The results of variable temperature magnetic susceptibility studies and structural determination (sometimes reasonable estimates of molecular paramaters will suffice) must be available. The pseudo-contact shift is calculated and then subtracted from the isotropic shift to give the contact shift. After the electron density at each nucleus has been found molecular orbital calculations are usually performed until one can match the calculated and experimental electron densities.

R E S U L T S A N D D I S C U S S I O N

^{13}C-NMR SPECTRA

Only recently has ^{13}C-NMR spectroscopy been applied to paramagnetic systems.[145] To date the published interpretations of the ^{13}C-NMR spectra of paramagnetic compounds are more suspect than those of ^{1}H-NMR spectra due to the more complicated origins of ^{13}C-NMR shifts (e.g. unpaired spin density in ligand p orbitals can contribute to the dipolar shift) and the assumptions that have been employed in their interpretations.[145]

As a result the purpose of this section mainly is to summarize the ^{13}C-NMR data given in this thesis (Table XXXV.) The spectra were all recorded in C_6D_6 with the solvent being used as an internal reference (δ_{BEN}). For the sake of comparison these chemical shifts were converted to the TMS scale (δ_{TMS}) by the equation

$$\delta_{TMS} = 128.7 - \delta_{BEN}$$

where 128.7 is taken to be the chemical shift of benzene relative to TMS. Therefore a negative value of δ_{TMS} refers to a shift upfield from TMS.

There was one main difference observed between the coupled ^{13}C-NMR spectra of diamagnetic and paramagnetic systems: long-range coupling constants, $^{2}J_{^{13}C-H}$, were observed in the spectra of the diamagnetic compounds but not in the spectra of the corresponding uranium compounds. The coupled ^{13}C-NMR spectrum of $Cp_2Hf(NEt_2)_2$ (Figure 11, Chapter III) exhibited a doublet for the cyclopentadienyl ligand which was split into a quintet. Since no long-range coupling was seen for the amido ligand, the pentet structure arises from long-range ^{1}H and ^{13}C coupling within the cyclopentadienyl ring with accidental equality of the two, $^{2}J_{^{13}C-^{1}H}$, and three bond, $^{3}J_{^{13}C-^{1}H}$, coupling constants. The ^{13}C-NMR spectrum of $Cp_2U(NEt_2)_2$ (Figure 10, Chapter III) exhibited only the expected doublet for the cyclopentadienyl ligand. Similarly the coupled ^{13}C-NMR spectrum of $Th[N(i\text{-}Pr)_2]_4$ (Figure 2, Chapter II) showed a doublet of septets for the methyne carbon and a quartet of approximate quintets for the methyl carbon while the ^{13}C-NMR spectrum of $U[N(i\text{-}Pr)_2]_4$ (Figure 3, Chapter II) showed the expected quartet and doublet. The doublet of septets arises, of course, as a result of the methyne carbon coupling with the six methyl protons. To explain the observance of a quartet of approximate pentets it is necessary that a one methyl carbon couple with the methyne proton

TABLE XXXV

SUMMARY OF THE ^{13}C-NMR SPECTRA[a] REPORTED IN THIS THESIS

COMPOUND	CHEMICAL SHIFT				
	Cp	CH_3	CH_2	CH	OTHER
$Th[N(i\text{-}Pr)_2]_4$	–	27.3,q[b]	–	46.3,d	
	–	J = 124[c]	–	J = 124	–
		$^2J \simeq {}^3J \simeq 4$	–	$^2J \simeq 4$	–
$U[N(i\text{-}Pr)_2]_4$	–	34.0, q	–	-108.1	–
		J = 124	–	J = 124	–
$Cp_2U(NEt_2)_2$	125.1,d	59.5,q	-120.4,s	–	–
	J = 161	J = 125	J = 129	–	–
$Cp_2Hf(NEt_2)_2$	109.8,d	16.5,q	48.9,t	–	–
	J = 170	J = 124	J = 130	–	–
	$^2J \simeq {}^3J \simeq 8$				
$Cp_2U(dtc)_2$	301.4,d[d]	6.0,q	52.5,t	–	68.5,s
$Cp_2U(tbt)_2$	260.4,d	59.3,q	–	–	-326.2,s
	J = 171	J = 126	–	–	–

[a] coupled spectra given in p.p.m. relative to TMS; a negative shift is a shift upfield from TMS

[b] See Table XXXIII

[c] $J_{^{13}C-H}$ given in Hz

[d] off-resonance spectrum

(i.e. $^{2}J_{^{13}C-H}$), that it also couple with the protons of the other methyl group (i.e. $^{3}J_{^{13}C-H}$), and that the two coupling constants are equal (i.e. $^{2}J_{^{13}C-H} = {}^{3}J_{^{13}C-H}$).

Discussions relating to the qualitative contributions of contact and pseudo-contact shifts will be incorporated in the following section on the ^{1}H-NMR spectra.

^{1}H-NMR SPECTRA

Table XXXX summarizes the ^{1}H-NMR spectra of the compounds reported in this thesis while Table XXXVI lists several isotropic shifts. In the discussions to follow the isotropic shift, δ_{iso}, is taken to be the chemical shift of the uranium compound, δ_{U}, less that of its diamagnetic reference, δ_{Th} or δ_{Hf} [141]. When calculating isotropic shifts it is best to have a diamagnetic reference which is as similar as possible to the paramagnetic sample (e.g. a thorium (IV) compound would be the best reference for its uranium (IV) analog.) However, the chemical shift differences between possible diamagnetic references are usually much smaller than the isotropic shift so that the absence of the best diamagnetic reference is not a critical point.

1. Tetrakisamides

The $Th[N(i\text{-}Pr)_2]_4$, $U[N(i\text{-}Pr)_2]_4$, $Th[N(C_6H_5)_2]_4$, and $U[N(C_6H_5)_2]_4$ complexes are well-suited for qualitative discussions concerning the origin of their shifts since the compounds are all four-coordinated with a local T_d symmetry for the MN_4 framework. With such a high molecular symmetry it would be anticipated that the pseudocontact

TABLE XXXVI

SUMMARY OF THE ^{1}H-NMR SPECTRA REPORTED IN THIS THESIS

COMPOUND	CHEMICAL SHIFT				
	Cp	CH_3	CH_2	CH	AROMATIC
$Th[N(i\text{-}Pr)_2]_4$	-	5.78,d[b]	-	3.52,sp	-
$U[N(i\text{-}Pr)_2]_4$	-	7.15,d	-	1.25,br	-
$U[N(C_6H_5)_2]_4$	-	-	-	-	8.32,d(o)[c]; 2.30,(m); 4.42,(p)
$Cp_2U(NMe_2)_2$	18.65,s	-7.53,s	-	-	-
$Cp_2U(NEt_2)_2$	20.94,s	5.70,t	-1.54,q	-	-
$Cp_2U[N(C_6H_5)_2]_2$	25.45,s	-	-	-	1.70,d(o); 0.72,t(m); 4.02,t(p)
$Cp_3U(NMe_2)$	18.28,s	-3.81,s	-	-	-
$Cp_3U(NEt_2)$	18.86,s	8.40	6.40	-	-
$Cp_3U(SMe)$	11.50,s	-[d]	-	-	-
$Cp_3U(SEt)$	11.80,s	26.12,t	41.05,q	-	-
$Cp_3U(SC_6H_5)$	-	-	-	-	-[d]
$Cp_2U(tbt)_2$	8.85,br	17.13,s	-	-	-
$Cp_2U(dtc)_2$	-0.37,s	11.04br	11.49br	-	-

(Table continued)

Table XXXVI continued

[a] relative to internal benzene; negative shift is a downfield shift

[b] s = singlet; d = doublet; t = triplet; q = quartet; sp = septet; br = broad

[c] o = ortho; m = meta; p = para

[d] positions not determined (see Chapter IV)

contribution to the isotropic shift would vanish [77,136-141] at the limit $D = 0$, since $g_{\perp} = g_{||}$ for Td symmetry. Whether this is the case for the above complexes or not can be tested by the following considerations.

Since amides are good σ- and π-donor ligands and have no low lying empty orbitals, the delocalization of unpaired spin density from the metal onto the amide must occur through the ligand σ-framework. In such cases the mechanism for the delocalization of spin density involves the transfer of electron density from the ligand (i.e. $-NR_2$) to partially filled metal orbitals [8], probably to the f orbitals for uranium. Hund's rule requires that this be done parallel to the spin on uranium thereby leaving unpaired spin density of opposite sign on the ligand. As a result if only the contact

$$U - NR_2 \longrightarrow U \leftarrow NR_2$$

mechanism is in operation, the unpaired spin density is expected to fall off rather rapidly with an increasing number of bonds separating the magnetic nucleus in question from the paramagnetic metal atom. It would also be expected that the isotropic shifts would all be in the same direction. Hence the observance of isotropic shifts for $U[N(i\text{-}Pr)_2]_4$ (Table XXXVII) of -1.27 p.p.m. (downfield) for the methyne protons and 1.37 p.p.m. (upfield) for the methyl protons together with an isotropic shift of 6.7 p.p.m. (downfield) for the methyl carbon and -154.4 p.p.m. for the methyne carbon, rules out the possibility of only the contact mechanism being in operation.

It can also be seen from Table XXXVII that the isotropic shifts (which are presumably the same as the contact shifts) of ortho, meta, and para protons of $U[N(C_6H_5)_2]_4$ are 8.32, 2.30, and

TABLE XXXVII

ISOTROPIC SHIFTS OF ORGANOURANIUM COMPOUNDS

FORMULA	NUCLEUS	R	TH	U	Δ_{iso}
$M(NR_2)_4$	^1H	i-Pr	5.78[b]	7.15	1.37
			3.52	1.25	-1.27
		C_6H_5	0.0	8.32[c]	8.32
			0.0	2.30	2.30
			0.0	4.42	4.42
	^{13}C	i-Pr	27.3	34.0	6.7
			46.3	-108.1	-154.4
$Cp_2M(NR_2)_2$	^1H	Et	1.02[e]	20.94[e]	19.92
			6.17	5.70	-0.47
			4.12	-1.54	-5.66
	^{13}C	Et	109.8[e,f]	125.1[e]	15.3
			16.5	59.5	43.0
			48.9	-120.4	-169.3

[a] $\delta_{iso} = \delta_U - \delta_{Th}$ (reference 141)

[b] methyl position given first then methyne position

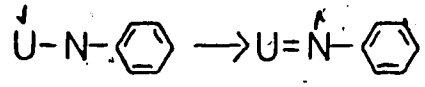
[c] ortho position given first, then meta position, then para position

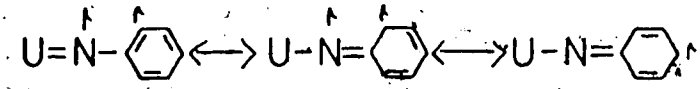
[d] due to closeness of $Th[N(C_6H_5)_2]_4$ protons to the residual protons of C_6H_6 positions are taken a 0.0 (Chapter II)

[e] Cp protons given first, then methyl position, then methylene position

[f] $Cp_2Hf(NEt_2)_2$ used instead of $Cp_2Th(NEt_2)_2$

4.42 p.p.m., respectively. It can be seen from the following resonance structures that the positive spin density can be transferred from the metal to the nitrogen, and to both the ortho and





para positions. However, there is no simple structure which can be written which places positive spin density onto the meta position. This is taken to mean that this position should only experience negative spin density as a result of the contact mechanism. Hence the observation of a positive isotropic shift for all the aromatic protons indicates that, like the $U[N(i\text{-}Pr)_2]_4$ complex, the $U[N(C_6H_5)_2]_4$ complex must also be experiencing some amount of pseudo-contact contribution to the total isotropic shift.

Deviations from what would be expected for the contact mechanism clearly indicates that the pseudo-contact contributions in the above tetrakisamides are most likely due to either a symmetry which is less than T_d ($D \neq 0$), a mixing of low-lying excited states through spin-orbit coupling, or a combination of both. The usual treatment of such systems is to assume that the free ion $^3H_4$ ground state of uranium (IV), an f^2 system, is split by a tetrahedral crystal field giving rise to a low-lying triply degenerate T_2 state and a higher A_2 state, and that the separation between the crystal field levels is much smaller than the separation between free ion states.[7,35,36,146] Even if this type of treatment would be applicable to the tetrakis-

amides, it would not be surprising that pseudo-contact contribution could also be present since Horrocks has shown that magnetic anisotropy (which must be present for pseudo-contact shifts to arise) is expected to be largest for complexes derived from $\tilde{T}$ ground states as a result of spin-orbit coupling which reduces the degeneracy of the ground state.[147]

2. Biscyclopentadienylbis(diethylamide)uranium (IV)

In calculating the isotropic shifts for $Cp_2U(NEt_2)_2$ (Table XXXVII), the resonances previously assigned to $Cp_2Th(NEt_2)_2$ (Chapter III) were used for the proton shifts while the resonances of $Cp_2Hf(NEt_2)_2$ were used to calculate the carbon shifts since $Cp_2Th(NEt_2)_2$ could not be isolated pure.

The isotropic shifts of $Cp_2U(NEt_2)_2$ at first glance would tend to cause one to think that contact contributions were dominant since the isotropic shifts of the methyl group are much smaller than those of the methylene group. However the carbon isotropic shifts are in opposite directions which tends to negate this idea. As a result of low molecular symmetry of $Cp_2U(NEt_2)_2$ (i.e. C_{2v}) undoubtedly pseudo-contact contributions to the isotropic shift are important.

3. Triscyclopentadienyl Derivatives

A summary of the ^{1}H-NMR spectra of representative Cp_3UR derivatives is given in Table XXXVIII. It should be noted that there is an apparent discrepancy between the reported value of the chemical shift of Cp_3UCl and that observed in this work. Presumably the difference is a result of the spectra being recorded at different temperatures. It can be seen from Table XXXVIII that the cyclo-

pentadienyl position is relatively constant for the halide and alkyl derivatives. However, a varied cyclopentadienyl resonance is seen for the alkoxide thiolate and amide derivatives.

There have been three reported attempts of separating the contact and pseudo-contact contributions to the isotropic shift which seem to be relevant to the present discussion.[7,150,151] The geometric factors for the Cp_3U-moiety have been calculated by von Ammon, et al. and a contact shift of 17.6 p.p.m. has been calculated for the cyclopentadienyl ring in the Cp_3UOR system,[18] while Marks, et al. have calculated a contact shift of approximately 28 p.p.m. in the Cp_3U(alkyl) system.[7] From Table XXXVII it can be seen that the alkoxy shifts are to low fields while those of the ethanethiolate are to high field and that the cyclopentadienyl resonances are quite different. It is interesting to note that both the protons of the cyclopentadienyl and of the thiolate ligands are comparable to those observed in the related Cp_3UR complexes. The changes observed in the cyclopentadienyl resonance on going from Cp_3UOR to Cp_3USR were rather surprising since the overall geometry and structure of an alkoxide and its corresponding thiolate derivative would be expected to be quite similar. As a result it would be expected that the geometric factors for the Cp_3UOR and Cp_3USR (and hence the magnitude of their pseudo-contact shifts) should be quite similar. The most reasonable explanation for these changes is that the sign of the magnetic anisotropy (equation V-3) has changed which would cause shifts of opposite directions. It should be noted that similar arguments have been presented in the discussion of Cp_3UR derivatives.[7]

TABLE XXXVIII

SUMMARY OF THE ^{1}H-NMR SPECTRA OF Cp_3UR DERIVATIVES

R	Chemical Shift [a]		Reference Number
	Cp	R	
F	12.6	-	15
Cl	9.57	-	15
	10.36	-	b
Br	9.79	-	15
I	10.4	-	15
Me	10.0	202.0	7
t-Bu	11.4	23.2	7
$C_2C_6H_5$	9.98	4.65 (m), 14.7(p)	8
BH_4	13.77	67.2	16
OMe	24.3	-45.4	17
OEt	25.6	-9.6 (CH_3), -51.8 (CH_2)	17
SMe	11.80	d	b
SEt	11.80	26.12 (CH_3), 46.05 (CH_2)	b
NMe_2	18.28	-3.81	b
NEt_2	18.86	8.40 (CH_3), 6.40 (CH_2)	b

[a] given in p.p.m. relative to internal benzene; a negative shift is a downfield shift

[b] this work

[c] methyl signal was not recorded (See Chapter IV)

However further study, such as structural determinations, magnetic susceptibilities, and calculations, will have to be done before a clear picture is obtained.

The $Cp_3U(NR_2)$ derivatives are indeed most interesting. It can be seen from Table XXXVIII that the replacement of a hydrogen by a methyl group has resulted in an inversion of the observed chemical shift (i.e. from -3.81 p.p.m. in $Cp_3U(NMe_2)$ to 8.40 p.p.m. in $Cp_3U(NEt_2)$). Such a behavior is usual taken as an indication of large contact contributions to the observed chemical shifts.[35,141] This possibility can immediately be dismissed by the observation that the methylene protons in $Cp_3U(NEt_2)$ have also undergone a change in the direction of their chemical shift as compared to $Cp_3U(NMe_2)$. Without a doubt the contact contribution at this position is nearly the same in $Cp_3U(NMe_2)$ and in $Cp_3U(NEt_2)$. The difference in the direction of the shift must therefore be traced to the pseudo-contact shift. In $Cp_3U(NMe_2)$ the methyl protons are most probably free to rotate about the nitrogen-carbon bond so that the geometric factor will be an average of all the possible conformers. However in $Cp_3U(NEt_2)$ the presence of a methyl group in place of a hydrogen will cause some conformational preference. As a result the geometric factors of the methyl and the remaining methylene groups could be rather different from that of the methyl protons in $Cp_3U(NMe_2)$ and produce the unexpected results mentioned above.

4. Temperature Dependence

It was shown in the previous chapter that the ^{1}H-NMR spectrum of $Cp_2U(dtc)_2$ (Figure 20) varied considerably with temperature both in

appearance and in chemical shifts. Plots of 1/T versus the chemical shift yielded straight lines (Figure 21) showing that near Curie behavior was seen over the temperature range studied.

C O N C L U S I O N S

The ^{1}H- and ^{13}C-NMR spectra of organoactinide complexes on the whole show very sharp resonances with spin-spin couplings even though a paramagnetic metal is present. However, the analysis of these spectra is only in its infancy and before much information can be extracted from these very interesting, yet very complicated, systems more physical and theoretical studies will have to be performed. It is hoped that more theoretically oriented chemists than myself will become sufficiently interested in these and related systems to attempt their solutions.

CHAPTER VI - EXPERIMENTAL

TECHNIQUES, PROCEDURES, ETC.

GENERAL

In general the organoactinides studied here were extremely air- and moisture-sensitive, decomposing instantly upon contact with air. As a result oxygen and moisture were rigorously excluded from all operations by working under either vacuum or an atmosphere of purified nitrogen.

All reactions were carried out in Schlenk-type apparatus [152-154] attached to a double manifold where one manifold was for vacuum and one for nitrogen. The two manifolds were connected with a three-way stopcock thus allowing a given piece of apparatus to either be evacuated or filled with nitrogen from the same stopcock. This allows complete elimination of air from the apparatus, including the amount contained in the vacuum tubing connecting the apparatus to the double manifold, by successively evacuating and refilling with nitrogen. The vacuum manifold was routinely operated at a pressure below 0.025 mm Hg. The nitrogen (approximately 99.7%), which was purified before admission to the manifold, was first deoxygenated by passing it through a column containing hot (approximately 90-100°C), activated BASF Cu-based catalyst (R3-11), and then dried by passing it through a column containing Aquasorb (Mallinkrodt).

Solvents were dried by both refluxing and distilling from the appropriate drying agent under an atmosphere of nitrogen (Table XXXIX)

TABLE XXXIX

DRYING AGENTS USED FOR SOLVENTS

Solvent	Drying Agent
Diethyl ether	Sodium-potassium alloy (1:5 weight ratio)
Tetrahydrofuran	Sodium-potassium alloy
1,2-Dimethoxyethane	Calcium hydride
Benzene	Potassium metal
Toluene	Sodium metal
Pentane	Calcium hydride
Hexanes	Sodium-potassium alloy
Carbon disulphide	Phosphorus pentoxide

In the earlier stages of this work each freshly distilled solvent was transferred to a three-neck flask and subjected to three freeze-thaw degassing cycles. However in the later stages all solvents (except diethyl ether) were used directly from the stills via syringe technique. This could be done after the nitrogen on the stills was purified as previously described.

With the exceptions of 2,2'-$C_{12}H_8Br_2$, 2;2'-$C_{12}F_8Br_2$, K_2COT, o-$(OH)C_6H_4(SH)$, $Hf(NEt_2)_4$, and those compounds whose preparations are described here, all reagants were commercially available. 2,2'-dibromobiphenyl (2,2'-$C_{12}H_8Br_2$) was prepared by the method of Gilman and Gaj[4] while 2,2'-dibromooctafluorobiphenyl (2,2'-$C_{12}F_8Br_2$) was prepared by the method of Massey, et al.[156] o-Mercaptophenol (omp) was prepared according to U.S. Patent No. 3,468,961 with the permission of Hooker Chemical Corp. by Mr. Joel Martin who kindly provided a sample and who also kindly provided a sample of $Hf(NEt_2)_4$ which was prepared by the method of Chandra and Lappert.[56] A solution of K_2COT in THF was prepared by the method of Katz, et al.[157] by Mr. Albert Masino who graciously supplied a sample.

Each thiol used was stirred at 0°C with a small amount of $LiAlH_4$ until the violent reaction subsided. The thiol was then fractionally distilled and stored under nitrogen. Diethylamine was distilled from potassium and stored over molecular sieves, dimethylamine was passed through a column containing KOH pellets before use, diphenylamine was freshly sublimed before use, and diisopropylamine

was distilled before use. Catechol and 4-methylcatechol were sublimed before use and stored under nitrogen.

All glassware used was dried before use either by sitting in an oven (110°C) for at least fifteen minutes or by flaming-out with a heat gun. The hot glassware was immediately evacuated then filled with nitrogen before any operations were done.

Syringes were used quite often in the transfer of solvents and air-sensitive solutions. Whenever possible syringes with a Luer lock (American Hospital Supply) were used. Two precautions were always taken to minimize the contact of solvents and/or solutions with air: the syringe was "wetted" with the solvent to be used then "flushed" with nitrogen. The "wetting" was done by drawing the appropriate solvent into the syringe then slowly discharging the solvent. A solvent seal is formed between the barrel and the syringe thereby cutting down the amount of air that can come in contact with the solvent (or solution). By exercising care, the solvent seal can always be maintained. One may "flush" a syringe with nitrogen by drawing nitrogen into the "wetted" syringe and discharging the gas into the air. This "flushing" process was routinely repeated four more times. Having taken these two precautions, solutions which were instantly decomposed upon contact with air could be transferred in a syringe with no apparent decomposition.

It should be noted that most of the time this technique was unsatisfactory when dissolving organoactinides in diethylether.

Solutions of organoactinides in ether decomposed much faster than in other solvents.

The volatility and non-wetting nature of ether makes a solvent seal in the syringe much more difficult to maintain. As a result air is more readily accessible to the solution and a much faster rate of decomposition is seen. So instead of using a syringe with ether, the freshly distilled solvent was transferred to a three-neck flask, repeatedly freeze-thaw degassed, then trap-to-trap distilled onto the solid to be dissolved. In some cases this added precaution produced good results.

NMR

^{1}H-NMR spectra were recorded on either a Varian HA-100 or A-60 spectrometer. ^{13}C-NMR spectra were recorded on a Bruker HFX-90 spectrometer operating under the Fourier transform mode. All deuterated solvents were repeatedly freeze-thaw degassed in a Schlenk tube and stored over molecular sieves. For ^{1}H-NMR samples, serum stoppered NMR tubes (Wilmad) were used while standard 10 mm NMR tubes (Wilmad) fitted with a #36 serum stopper (Fischer Scientific) were used for ^{13}C-NMR samples. The #36 serum stopper fits snuggly over the top of the 10 mm tube. Once stoppered, each hot NMR tube was attached to the double manifold by the syringe adapter shown in Figure 23, evacuated and refilled with nitrogen. Each solution used to record a NMR spectrum was prepared in a three-necked flask (usually 50 ml) then syringed into the NMR tube. The filtration of a small volume (≤2 ml)

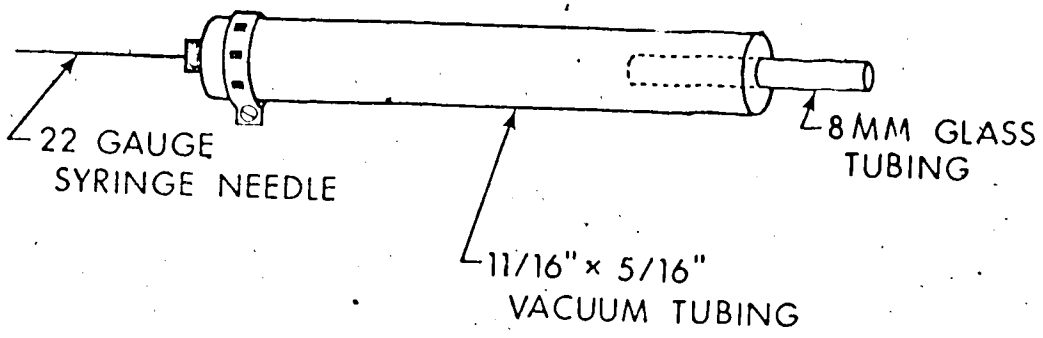


Figure 23. Syringe Adapter.

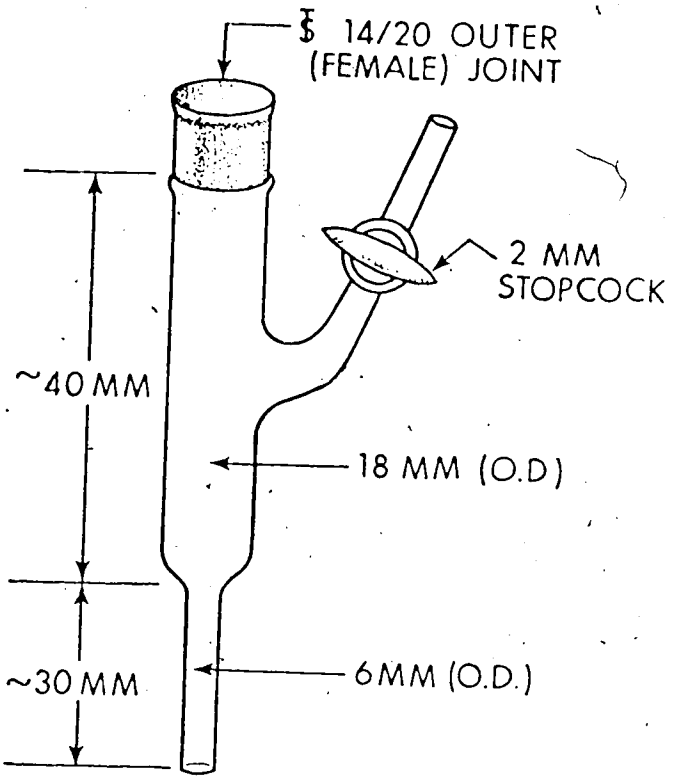


Figure 24. Filling Adapter.

of an extremely air-sensitive solution, which was usually saturated, was not practical. However, particles could be effectively eliminated from most samples by centrifuging the inverted NMR tube for one minute then slowly turning the NMR tube upright, leaving the solid firmly compressed against the serum stopper.

For most variable temperature ^{1}H-NMR studies, the serum stoppered tubes proved to be useable if almost all of the serum stopper was cut away from the tube once the stopper was placed on the NMR tube. This was done so that the NMR tube would fit under the pressure cap of the spectrometer. The serum stoppered NMR tube was used in the $-60^{\circ}C$ to $+60^{\circ}C$ range. Outside this range a sealed NMR tube was used. To a standard 5 mm NMR tube was sealed another piece of Pyrex 5 mm tubing. The elongated tube was attached to the filling adapter (see Figure 24 by means of a piece of Tygon tubing. The assembled apparatus was evacuated as the elongated NMR tube was heated with the heat gun then refilled with nitrogen. The NMR solution was syringed into the NMR tube. The solution was then subjected to three freeze-thaw degassing cycles. After freezing the sample a fourth time the NMR tube was carefully sealed under vacuum just below the point at which the NMR tube and the 5 mm Pyrex tubing were attached.

INFRARED

All infrared spectra were recorded on a Perkin Elmer 467 spectrometer and calibrated with polystyrene. Mulls were prepared in a glove-bay which had been evacuated and filled with purified nitrogen

five times. The light mineral oil and fluorolube used as mulling agents were stored over molecular sieves. The solution spectra were recorded in matched 0.5 mm KBr cells which could be evacuated and filled with nitrogen. Serum stoppers were used on the entries to the sample cell so that solutions could be syringed into a cell under nitrogen and diluted if necessary in the cell. Each spectrum was recorded as soon as possible. Another spectrum was recorded five minutes after the initial spectrum had been recorded or after a diluted sample had been run. With mulls the plates were then opened to the air for 10 seconds and another spectrum was recorded. This procedure helped monitor any decomposition that might be occurring. Only rarely could decomposition be seen except after mulls had been exposed to air.

MASS SPECTROMETRY

An A.E.I. MS 12 mass spectrometer was used for all mass spectral studies except those of high resolution for which an A.E.I. MS 9 mass spectrometer was utilized. Each spectrometer was adapted so that either the conventional electron impact or the newer chemical ionization technique[158] could be used. Each sample for mass spectral study was sealed in a capillary under nitrogen (see "Filling a capillary under nitrogen" which appears later) and admitted into the spectrometer using a direct probe technique. Exact details of this technique, which allowed the introduction of extremely air-sensitive samples into

the spectrometer with no apparent decomposition, may be obtained from Dr. A. Hogg of this department.

FILLING A CAPILLARY RIGOROUSLY UNDER NITROGEN

Quite often it was necessary to seal a small quantity of an air-sensitive solid in a small container (e.g., a capillary). The use of a glove-bag was unsatisfactory due to the extreme air-sensitivity of most compounds, the build up of static charge which resulted from numerous evacuation - refilling cycles, etc. A solution to this problem was the design of the filling adapter shown in Figure 24 Another piece of glass (e.g., glass tubing, sealable vial, disposable pipette, etc.) can be attached to the bottom neck of the adapter by a piece of rubber tubing allowing the sealing of samples to be done under rigorously anaerobic conditions. When the glass attached to the neck of the adapter is a disposable pipette, one has a sealable "capillary". After the bottom end of a disposable pipette (9 inch, Fischer Scientific) was closed in a flame, the pipette was attached to the bottom neck of the filling adapter with a piece of Tygon tubing (1/4 inch x 3/8 inch). The Tygon tubing was secured to the neck of the adapter with a piece of copper wire. A $\mathfrak{T}$ 14/20 stopper was placed in the ground glass joint of the adapter, the apparatus was CAREFULLY flamed out while being evacuated and refilled with nitrogen. This process was then repeated. (Besides bringing the apparatus under a nitrogen atmosphere, this procedure also served as a check to see if the end of the pipette had been properly sealed.)

As nitrogen was blowing through the Schlenk tube (male joint) used to store the sample and the filling adapter (female joint), they were connected and a small amount of solid was transferred to the pipette through the adapter. Then after separating the two, the filling adapter was evacuated and refilled with nitrogen.

The capillary was carefully sealed under nitrogen. Care must be taken when sealing the pipette for if it is heated either too quickly or too hot, the glass will pop allowing air into the sample.

Capillaries filled in this way were used for melting point determinations and for mass spectral studies. The mass spectral sample was smeared along the sides of the capillary whenever possible to insure that at least part of the sample was sitting in the source once the sample was introduced into the spectrometer. Otherwise, higher temperatures were needed to record the spectrum.

ANALYSIS OF COMPOUNDS

Except where otherwise noted all elemental analyses and molecular weight determinations were performed by Bernhardt Microanalytical Laboratories, West Germany. Carbon-hydrogen analyses performed in this department were done on a Coleman carbon-hydrogen analyzer. Amine analyses were performed using the standard technique of decomposing a sample in aqueous KOH, distilling the liberated amine into excess acid followed by back-titration[159] using methyl red as an indicator.

Since satisfactory elemental analyses could not be obtained on some samples which were shown to be pure by spectral studies (e.g., $Cp_2U(NEt_2)_2$, $U[N(i\text{-}Prop)_2]_4$, etc.; see text), attempts were made to have the analyses performed in this department even though the departmental microanalytical laboratory is not equipped to handle air-sensitive compounds. Our success in the use of the filling adapter (Figure 24) led us to try and submit the samples in pre-weighed disposable pipettes.

A pre-weighed disposable pipette was charged with an estimated 5-10 mg of sample and sealed under nitrogen as previously described. Both pieces of glass were re-weighed to give the sample weight. The sealed capillary was then broken and placed into the analyzer within an elapsed time of five seconds. However, the sample was incompletely ignited resulting in low carbon-hydrogen values as would be expected. (See Table XXXX.) The same procedure was repeated using 5 mm Pyrex tubing. Since reproducible numbers could not be obtained, the procedure was checked using sucrose. Sucrose was added to a pre-weighed tube, weighed before sealing (real sample weight), sealed under nitrogen, then re-weighed after sealing (apparent weight.) Weight losses were seen as a result of sealing (i.e., 0.155 mg, 1.55% weight loss; and .036 mg, 1.18% loss). The weight losses combined with small losses of sample when the sealed tube was broken caused us to abandon this technique.

The same basic procedure was repeated using 5 mm Pyrex tubing and an NMR cap. The weighed, capped glass was charged using the

TABLE XXXX

ANALYTICAL TECHNIQUES ATTEMPTED AT THE U. OF ALBERTA

TECHNIQUE	COMPOUND	%C (calculated)	%H (calculated)	%C (found)	%H (found)
Filled capillary	$U[N(i\text{-}Prop)_2]_4$	45.13	8.84	24.26	5.04
				29.71	3.42
				23.57	5.31
Sealed Pyrex	" "	"	"	40.59	7.75
				39.55	8.01
				33.57	7.31
Normal[a]	Sucrose	42.11	6.48	42.19	6.53
Sealed Pyrex	"	"	"	42.86[b]	6.62[b]
				42.69[b]	6.60[b]
Capped Pyrex	"	"	"	42.18	6.52
" "	"	"	"	42.20	6.53
" "	15% $Cp_2U(SEt)_2$ - 85% $Cp_3U(SEt)$ mixture	40.24	4.08	40.24	4.06
				40.26	4.07
Bernhardt	" "	"	"	[illegible].89	3.90
				[illegible]2	3.93

[a] Normal procedure used in the microanalytical laboratory

[b] Based on the apparent weight after sealing

filling adapter. The cap was placed on the tube once it had been taken into a dry box (Vacuum Atmospheres). The capped Pyrex tube technique worked only for larger crystals due to high amounts of static charge in the dry box.

SYNTHESES

PREPARATION OF UCl_4

The same basic procedure of Hermann and Suttle[160] was followed. UO_3[161,162] (48.7 g) was placed in a 500 ml one-neck flask. To this were added 260 ml of hexachloropropene. A reflux condensor fitted with a drying tube which contained $CaCl_2$ was placed on the flask and the reaction mixture was cautiously warmed to 60-70°C. (Hermann and Suttle[160] claim that a very exothermic reaction takes place when the solution temperature reaches 60°C. Though this preparation has been repeated numerous times, only once was a vigorous reaction observed. If after 15 minutes at 60-70°C no such reaction occurred, the heating was continued.) The temperature of the heating bath was raised to approximately 160-170°C during which time all of the yellow UO_3 dissolved to give a deep red solution and UCl_4 separated out of solution as a microcrystalline, green solid. The temperature of 160-170°C was maintained for at least six hours. After the reaction mixture cooled to ambient temperature, it was poured into a Schlenk filter. (From this point on, all work was done under a nitrogen atmosphere.) The green UCl_4 was washed with several portions of CCl_4 (dried over molecular sieves), then with several portions of pentane before drying under high vacuum. The dried solid was transferred to a Schlenk tube collecting 61.9 g (96.2% yield) of UCl_4. Calculated: U, 62.7; found: U, 62.6.

Notes on preparation:

1.) No mention is made in the reported synthesis of UCl_4 about the grade of hexachloropropene used. The commercially available hexachloropropene (Aldrich) is technical grade and may be used as received. Fresh fractionally distilled hexachloropropene improved neither the yield of the reaction nor the purity of the product.

2.) Hermann and Suttle[160] distilled off the by-product, trichloroacryloylchloride before collecting the UCl_4. However we find this step is not necessary since its inclusion has no apparent effect on either the yield or purity of UCl_4.

DEHYDRATION OF $ThCl_4 \cdot 8H_2O$

$ThCl_4 \cdot 8H_2O$ was recrystallized before dehydration by the method of Brauer.[163] To a 500 ml three-necked flask fitted with a gas inlet, a stopper, and a reflux condensor which was fitted with a drying tube containing $CaCl_2$ were added 58.5 g of recrystallized $ThCl_4 \cdot 8H_2O$. $SOCl_2$ (170 ml) was added and the mixture was warmed until the $SOCl_2$ was gently refluxing. The mixture was left refluxing overnight. Excess $SOCl_2$ was then decanted off and another 150 ml of $SOCl_2$ were added. After refluxing for two hours, the excess $SOCl_2$ was removed by filtration. (From this point on all work was done under nitrogen.) The white solid was washed with several portions of CCl_4 before drying in vacuo. A yield of 41.7 g (98.8%) $ThCl_4$ was obtained.

PREPARATION OF TlCp[164]

Tl_2SO_4 (49.13 g; 97.33 mmole) were added to 20g of KOH in 250 ml of water. While stirring the suspension 16.0 ml (12.8 g; 194 mmole) of freshly distilled cyclopentadiene were added dropwise with a syringe. A yellow precipitate resulted. The reaction mixture was stirred for another 15 minutes after the addition of C_5H_6 was complete. The mixture was filtered and air was pulled through the yellow solid for five minutes. The solid was transferred to a sublimer. A yellow microcrystalline solid was sublimed at 107°C, 0.03 mm Hg and 37.95 g TlCp were collected in a Schlenk tube (72.6% yield). The TlCp was stored under nitrogen.

PREPARATION OF NaCp

Metallic sodium (24.3 g; 1.06 mole) was placed in a three-necked, 1000 ml flask fitted with a high speed stirrer, a condensor and a gas inlet. Enough toluene was added so that the toluene level was about half an inch above the sodium. The toluene was heated until it was gently refluxing, then the mixture was stirred at a high speed for approximately 20 minutes. The stirring was stopped and the heat immediately removed. When all of the sodium sand finally settled down (about one and one half hours later) the toluene was removed with a syringe and the condensor was replaced with a dropping funnel. Then 200 ml THF were added to the sand before a solution of 100 ml (79.8 g; 1.21 mole) of freshly distilled cyclopentadiene in 100 ml THF was added dropwise. After the reaction solution was stirred overnight,

the solvent was removed from the light pink solution to give white, solid NaCp in near quantitative yield. The solid was stored in a Schlenk tube under nitrogen.

PREPARATION OF "Cp_2UCl_2" USING NaCp AND UCL_4 IN THF

UCl_4 (7.22 g; 19.0 mmole) was dissolved in 150 ml of THF. To this were added 32.8 ml of a NaCp solution in THF (1.16 M; 38.0 mmole). The resulting dark green solution was stirred overnight. After removing the NaCl by filtration, the reaction solution was concentrated to an estimated volume of 50-60 ml. Cooling the solution to $-78^{o}C$ produced a crystalline green solid which was collected on a filter, washed with ether and dried under vacuum. The yield was 5.89 g (70.7%).

PREPARATION OF "Cp_2UCl_2" USED FOR REACTIONS

To a mixture of 36.91 g (97.2 mmole) of UCl_4 and 52.35 g (194 mmole) of TlCp at $0^{o}C$ were added 300 ml of THF. The reaction mixture was stirred for about five minutes at $0^{o}C$ and then it was allowed to stir overnight at ambient temperature. The dark green-brown solution was filtered and cooled to $-78^{o}C$. The resulting crystalline material was collected on a filter, washed with ether and dried. The yield was 14.5 g (34.2%).

Concentration of the filtrate and cooling to $-78^{o}C$ produced some Cp_3UCl.

REACTION OF "Cp_2UCl_2" WITH LiC_6F_5

To a solution of 1.20 ml (2.34 g; 9.45 mmole) of C_6F_5Br in 20 ml of freshly distilled ether was added dropwise a solution of 5.0 ml (9.0 mmole) of 1.8M n-BuLi in hexanes at -78°C. The solution was stirred for 30 minutes at -78°C and then a solution of 1.99 g (4.54 mmole) of "Cp_2UCl_2" in 40 ml of THF was added dropwise to the LiC_6F_5 solution at -78°C. The reaction solution was stirred at -78°C for four hours and then for one hour at ambient temperature before filtering. The solvent was removed from the dark brown solution under vacuum and the resulting dark brown solid was dried in vacuo. Mass, ^1H- and ^{19}F-NMR spectra failed to characterize the product.

The other reactions with "Cp_2UCl_2" (Table I) gave products which could not be identified by ^1H-NMR and mass spectra. The one reaction that gave an identifiable product was with K_2COT. The mass spectrum showed only uranocene (m/e 446).

PREPARATION OF Cp_3UCl [10]

UCl_4 (3.75 g; 9.87 mmole) and (7.98 g; 29.6 mmole) of TlCp were added to a 100 ml three-necked flask. To the mixture of solids were added 50 ml of THF. After stirring at ambient temperature for four hours, the TlCl produced was removed by filtration. The solvent was removed from the filtrate under vacuum to give 4.30 g (92.2% yield) Cp_3UCl.

REPEAT OF ZANELLA'S PREPARATION OF Cp_2UCL_2 [28]

To a mixture of 1.20 g (3.16 mmole) of UCl_4 and 1.69 g (6.27 mmole) of TlCp were added 50 ml of DME. The reaction was stirred at room temperature for three hours then filtered. The dark green reaction solution was taken to dryness under vacuum, yielding 1.16 g (84.7%) of a green-brown solid.

REPEAT OF DORETTI'S PREPARATION OF $CpUCl_2$ [28]

To a mixture of 1.50 g (3.95 mmole) of UCl_4 and 1.06 g (3.93 mmole) of TlCp were added 50 ml of DME. After stirring the reaction mixture for seven hours at ambient temperature, the mixture was filtered. The solvent was removed from the filtrate under vacuum, yielding 1.00 g (62.3%) of the light green solid.

REPITITION OF $(Cp_3UCl)_2UCl_4\{2DME$ AS REPORTED BY KANELLAKOPULOS, ET AL.[29]

A solution of 0.607 g (1.29 mmole) of Cp_3UCl in 50 ml of DME was added to a slurry of 0.250 g (0.658 mmole) of UCl_4 in 10 ml of DME. After heating the reaction mixture for eight hours at 73°C the hot solution was filtered and the filtrate was taken to dryness in vacuo. The yield of the green solid was 0.645 g (64.2%).

THE REACTION OF $CpUCl_3$ AND Cp_3UCl IN DME

To a mixture of 0.627 g (1.34 mmole) of Cp_3UCl and 0.557 g (1.36 mmole) of "$CpUCl_3$" were added 40 ml of DME. The solution was stirred overnight at 76°C. Filtration of the reaction solution followed by

solvent removal from the filtrate yielded 0.693 g (69.1%) of a dark green-brown solid.

PREPARATION OF TETRAKIS(DIETHYLAMIDO)URANIUM(IV), $U(NEt_2)_4$

This reaction must be done in the dark to avoid significant photodecomposition.

A solution of 2.69 g (7.07 mmole) of UCl_4 in 35 ml of THF was added dropwise to a solution of 2.23 g (28.2 mmole) of $LiNEt_2$ in 5 ml of THF at 0°C. After stirring the reaction solution for 21 hours at ambient temperature, the solvent was removed under vacuum. Pentane (30 ml) was added and the resulting dark green-brown solution was filtered. The flask and filter were washed with two 10 ml portions of pentane. After removal of the pentane under vacuum, 3.60 g (97.0% yield) of $U(NEt_2)_4$ were obtained. Calculated: C, 36.50; H, 7.66. Found (Alberta): C, 35.45; H, 7.43. $Th(NEt_2)_4$ was prepared analogously.

PREPARATION OF $Cp_2U(NEt_2)_2$

$U(NEt_2)_4$ was prepared as described above using 20.15 g (255 mmole) $LiNEt_2$, 23.89 g (62.9 mmole) UCl_4 and a total volume of 200 ml THF. The solid $U(NEt_2)_4$ was extracted into 200 ml of pentane and a solution of 10.3 ml (8.30 g; 124 mmole; 98.8% of the amount required) of freshly distilled cyclopentadiene in 30 ml pentane was added dropwise to it. The resulting yellow-brown solution was stirred for an

additional two to three hours at ambient temperature. (After the addition of cyclopentadiene is complete the reaction solution may be exposed to light.) The reaction solution was poured into a jacketed Schlenk filter and cooled to -78°C causing $Cp_2U(NEt_2)_2$ to crystallize as thin golden leaves (see crystallization procedure which follows). A total yield of 20.0 g (88.7% -based on cyclopentadiene) was obtained. Calculated: NEt_2, 28.3. Found: 28.4, 28.2, 28.5.

CRYSTALLIZATION OF $Cp_2U(NEt_2)_2$

The apparatus used for the low temperature crystallization of $Cp_2U(NEt_2)_2$ is shown in Figure 25. After the assembled equipment was flamed-out under vacuum and refilled with nitrogen; the jacket was filled with crushed dry ice. The filtration apparatus was tilted and the flask containing the $Cp_2U(NEt_2)_2$ solution was attached to the filter after the cap was removed. As much acetone as possible was added to the jacket. At this point stopcock A is closed to nitrogen as well as the stopcock on the flask containing the $Cp_2U(NEt_2)_2$ solution (stopcock C), but stopcock B is left open to nitrogen. The stopcock on the manifold which was attached to stopcock C was changed to vacuum. Then as the solution was poured onto the filter, stopcock C is rapidly turned enough times so that the solution does not go through the filter. The solution was left at -78°C for 30 minutes during which time a golden crystalline (leaves) solid separated. Stopcocks A and C were reopened to nitrogen while a partial vacuum was created below the filter in the receiving flask

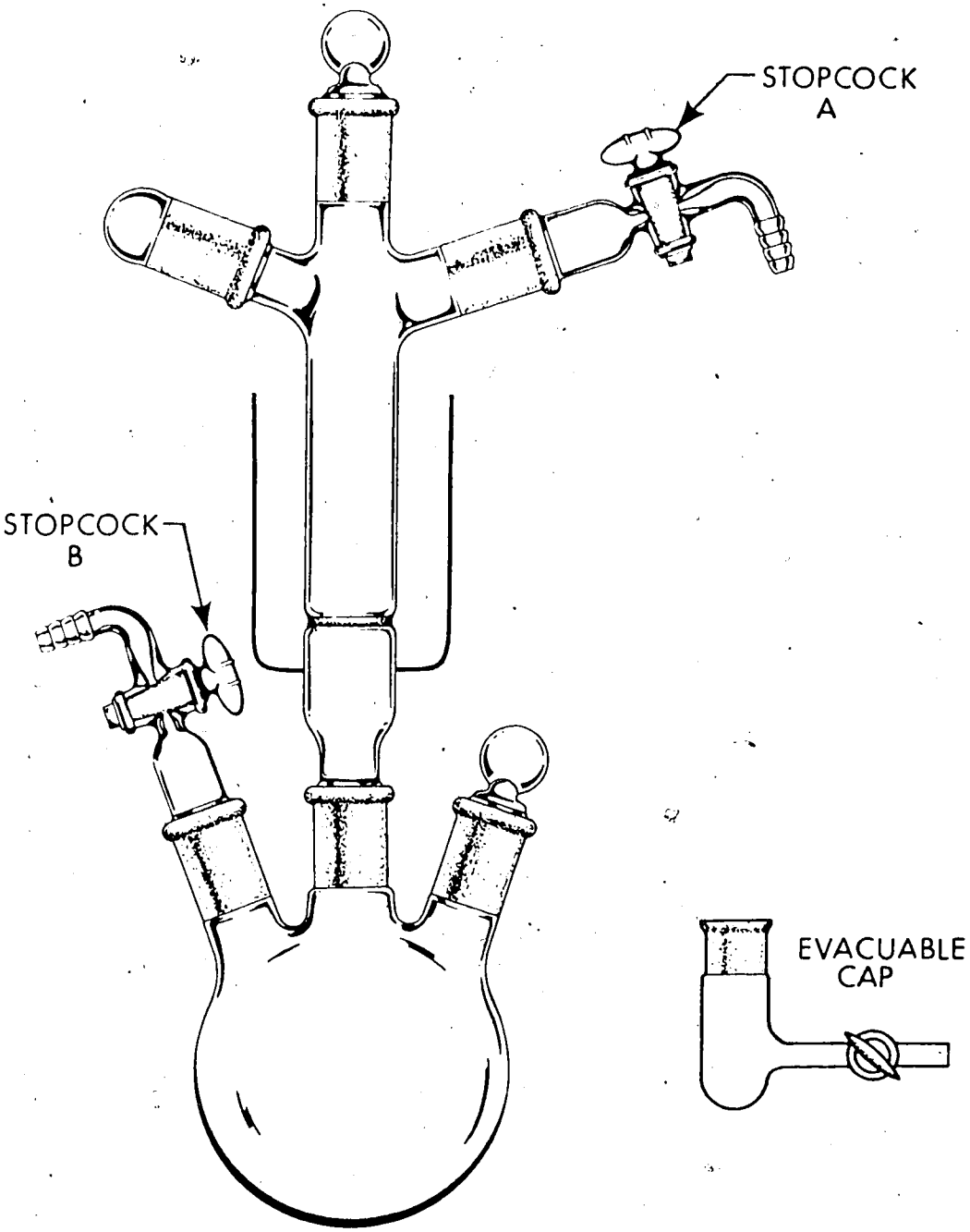


Figure 25. Apparatus for the low temperature crystallization of $Cp_2U(NEt_2)_2$.

pulling through the solution. It was necessary to keep a partial vacuum in the receiving flask for about an hour to get rid of solution trapped in the leaves. The leaves were washed by adding 15 ml of pentane to the filter and letting it sit at -78°C for another five minutes before pulling the solvent through the filter. Removal of solution from the leaves was sped up if the leaves were occasionally stirred with a spatula.

Once the majority of the solvent had been pulled through the filter, the receiving flask was placed under nitrogen, the filter was removed, and an evacuable cap was placed on the bottom of the filter. The contents of the filter were first evacuated from below and then simultaneously from above and below the filter.

In the preparation described, 16.4 g (72.7% yield) of $Cp_2U(NEt_2)_2$ were collected in the first crystallization. Concentration of the filtrate followed by crystallization as above yielded another 3.6 g (88.7% total yield) of $Cp_2U(NEt_2)_2$.

PREPARATION OF $Cp_3U(NEt_2)$

To a solution of 2.63 g (6.92 mmole) of Cp_3UCl in 20 ml of THF was added a solution of 0.54 g (6.9 mmole) of $LiNEt_2$ in 10 ml of THF. The color of the solution turned from dark brown to red-brown. The solution was removed under vacuum. The resulting solid was stirred with 60 ml of benzene and the resulting solution was filtered. The filtrate was slowly concentrated under vacuum to an estimated volume of 10 ml and a red crystalline material formed. The crystalline

material was collected on a filter, washed with 5 ml of pentane and then dried under vacuum. A yield of 2.12 g (74.8%) of $Cp_3U(NEt_2)$ was collected. Calculated: NEt_2, 14.3. Found: NEt_2, 13.9.

PREPARATION OF $Cp_2Hf(NEt_2)_2$

The basic procedure of Chandra and Lappert [56] was followed. Into a 100 ml flask were syringed 1.5 ml (2.2 g; 4.6 mmole) of $Hf(NEt_2)_4$, 10 ml of benzene and 1.5 ml (1.2 g; 18 mmole) of freshly distilled cyclopentadiene. The reaction solvent was refluxed at 90°C for ten hours. The solvent was removed under vacuum. The resulting light yellow solid was dried under vacuum for two hours at 50°C. After sublimation (130°C/0.025 mm Hg) of the solid, 1.26 g (60.6% yield) of $Cp_2Hf(NEt_2)_2$ were collected in a Schlenk tube. The compound was identified by its mass spectrum and shown to be pure by ^1H- and ^{13}C-NMR.

ATTEMPTED PREPARATION OF TETRAKIS{BIS(TRIMETHYLSILYL)AMIDO}URANIUM(IV), $U[N(SiMe_3)_2]_4$

A solution of 3.4 g (20 mmole) of $Li[N(SiMe_3)_2]$ in 25 ml of THF was added dropwise to a solution of 1.75 g (4.61 mmole) of UCl_4 in 25 ml of THF. The reaction solution was stirred for 16 hours at ambient temperature, and then refluxed for 48 hours giving a dark brown solution. Removal of the solvent under vacuum gave a solid which was successively extracted with 70 ml of pentane then with 50 ml of toluene. Removal of the solvent from the pentane solution

yielded a dark brown solid, while removal of the solvent from the toluene solution yielded a sticky dark brown solid which could only be dried after washing with pentane.

Both the pentane and toluene soluble solids showed complex ^{1}H-NMR spectra. In addition the mass spectrum of each showed $U[N(SiMe_3)_2]_3Cl$ to be the main uranium containing material.

PREPARATION OF TETRAKIS(DIISOPROPYLAMIDO)THORIUM(IV), $Th[N(i\text{-}Prop)_2]_4$

To 5.87 g (15.7 mmole) of $ThCl_4$ in 100 ml of THF, was added dropwise a solution of 6.77 g (63.2 mmole) of $LiN(i\text{-}Prop)_2$ in 50 ml of THF. (The reaction flask was covered with foil as a precaution against photodecomposition.) The solution was stirred at room temperature for seven hours before removing the solvent under vacuum. Then 120 ml of hexanes were added and the solution was warmed to 60-70°C for six hours. The solution was filtered and the filtrate was taken to dryness under vacuum. A yield of 7.78 g (78.3%) $Th[N(i\text{-}Prop)_2]_4$ were obtained. Calculated: C, 45.56; H, 8.92. Found (Alberta): C, 44.53, 44.83; H, 8.46, 8.61.

$U[N(i\text{-}Prop)_2]_4$ was prepared similarly.

PREPARATION OF $U[N(i\text{-}Prop)_2]_4$ USING $[(i\text{-}Prop)_2N]MgBr$

$[(i\text{-}Prop)_2N]MgBr$ was prepared by a very slow addition of a solution of 10 ml (7.2 g; 71 mmole) of diisopropylamine in 10 ml of ether to 40 ml of 1.78 M isopropylmagnesiumbromide (71 mmole). During the addition of diisopropylamine to isopropylmagnesiumbromide vigorous

gas evolution was seen along with the formation of a white precipitate. The reaction mixture was left stirring for two hours at ambient temperature after the gas evolution had ceased. Removal of the solvent under vacuum gave a white solid. The white solid was dissolved in 50 ml of THF and 30 ml of pentane. Then a solution of 6.59 g (17.4 mmole) of UCl_4 in 30 ml of THF was added to the solution of $[(i\text{-Prop})_2N]MgBr$. (As a precaution the reaction flask was wrapped in foil.) After 18 hours the ^{1}H-NMR showed mainly $U[N(i\text{-Prop})_2]_4$ but other signals presumably due to $U[N(i\text{-Prop})_2]_{4-x}Cl_x$ (x=1,2) were also seen. The reaction mixture was then evaporated to dryness *in vacuo* and 100 ml of hexanes were added. Heating this mixture for 12 hours at 60°C caused complete conversion of UCl_4 to $U[N(i\text{-Prop})_2]_4$ as determined by the ^{1}H-NMR. Filtration of the dark yellow-brown solution followed by removal of solvent from the filtrate, gave 6.98 g (63.0%) of $U[N(i\text{-Prop})_2]_4$. Calculated: C, 45.13; H, 8.84. Found (Alberta): C, 42.05, 42.03; H, 8.20, 8.20.

ATTEMPTED PREPARATION OF $Cp_2U[N(i\text{-Prop})_2]_2$

$U[N(i\text{-Prop})_2]_4$ (1.3 g; 2.0 mmole) was dissolved in 15 ml of pentane. Then 0.33 ml (0.26 g; 3.9 mmole) of freshly distilled cyclopentadiene was added with a syringe. The reaction solution was stirred at ambient temperature for 15 hours. The solvent was removed under vacuum and the resulting solid was dried *in vacuo*. A ^{1}H-NMR spectrum showed only the starting material.

The reaction was then attempted in THF but still no reaction occurred.

PREPARATION OF POTASSIUM DIPHENYLAMIDE, $KN(C_6H_5)_2$

Approximately 7 g (40 mmole) of freshly sublimed diphenylamine were dissolved in 125 ml of benzene. To this was added 1.95 g mg - atom) of clean potassium. The solution was refluxed for 24 hours. The solvent was removed under vacuum. Once the solid was dry, 80 ml of THF were added, and the solution was filtered to remove excess potassium. This solution was taken to dryness under vacuum and the solid was weighed (7.83 g; 91.0% yield).

PREPARATION OF TETRAKIS(DIPENYLAMIDO)URANIUM(IV), $U[N(C_6H_5)_2]_4$

A solution of 3.46 g (9.11 mmole) of UCl_4 in 60 ml of THF was added dropwise to a solution of 7.83 g (37.8 mmole) of $KN(C_6H_5)_2$ in 75 ml of THF at 0°C. After stirring for five hours at 0°C, the dark red-brown solution was allowed to stir at ambient temperature for another 30 hours. The solution was filtered and the solvent was removed under vacuum. After drying the solid under vacuum, 7.13 g (85.9% yield) of $U[N(C_6H_5)_2]_4$ were collected. Calculated: C, 63.29; H, 4.43. Found (Alberta): C, 56.04; H, 4.89.

PREPARATION OF $Cp_2U[N(C_6H_5)_2]_2$

Freshly distilled cyclopentadiene (0.30 ml; 0.24 g; 3.6 mmole) was added dropwise with a syringe to a solution of 1.69 g (1.85 mmole)

of $U[N(C_6H_5)_2]_4$ in 20 ml of THF. After stirring the deep red reaction solution for three hours at room temperature, the solvent was removed under vacuum. The dried solid was transferred to a Schlenk filter and washed with four 10 ml portions of pentane to yield 1.21 g (92.4%) of $Cp_2U[N(C_6H_5)_2]_2$. The sample was shown to be pure by a combination of ^{1}H-NMR and mass spectra.

PREPARATION OF $U(NMe_2)_4$

To a solution of 5.19 g (13.7 mmole) of UCl_4 in 60 ml of THF and 15 ml of hexanes at -30°C was added all but 1-2 ml of a solution of 2.830 g (55.5 mmole) of $LiNMe_2$ in 100 ml of THF. The reaction solution was allowed to come to ambient temperature after the addition of $LiNMe_2$ was complete. After 17 hours the solvent was removed under vacuum. To the resulting red-brown solid was added 50 ml of THF and 50 ml of pentane. Filtration followed by removal of the solvent under vacuum gave 5.04 g (89.5% yield) of $U(NMe_2)_4$. Calculated: NMe_2, 42.2. Found: NMe_2, 40.1.

ATTEMPTED PREPARATION OF $Cp_2U(NMe_2)_2$

The tetrakisamide prepared above was dissolved in 50 ml of THF. To this solution was added very slowly a solution of 1.35 g (20.4 mmole) of freshly distilled cyclopentadiene in 75 ml of THF. The reaction solution was stirred for another 18 hours at ambient temperature after the addition was complete. Removal of the solvent

in vacuo yielded a dark brown solid which was found by ^{1}H-NMR to be a mixture of $Cp_2U(NMe_2)_2$ (56.2%) and $Cp_3U(NEt_2)$ (43.8%).

PREPARATION OF $Cp_2U(dtc)_2$

$Cp_2U(NEt_2)_2$, 1.61 g (3.15 mmole), was dissolved in 15 ml of CS_2 with the evolution of heat. After the red-brown solution was stirred for one hour at ambient temperature, the solvent was removed under vacuum and 2.07 g (99.0% yield) were collected. Calculated: C, 36.14; H, 4.55; N, 4.21; S, 19.29; MW, 665. Found: C, 36.01, 35.96; H, 4.53, 4.54; N, 4.10, 4.12; S, 19.11, 19.06; MW, 713 (Osmometric determination in benzene).

PREPARATION OF $Cp_2U(chelate)$

Since all of the chelate complexes* were prepared in the same way, the preparation of $Cp_2U(omp)$ is given as an example.

o-Mercaptophenol (omp), 0.36 ml (0.45 g; 3.6 mmole), was added dropwise with a syringe into a solution of 1.80 g (3.51 mmole) of $Cp_2U(NEt_2)_2$ in 20 ml of THF. The color of the reaction solution immediately changed form a yellow-brown to a deep red. The reaction solution was stirred at ambient temperature for another six hours before removing the solvent under vacuum. A dark brown solid

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* The chelating ligands used were toluene-3, 4-dithiol (tdt), o-mercaptophenol (omp), catechol (cat), 4-methylcatechol (Me-cat)

(1.72 g; 99.4% yield) was collected. Calculated: C, 39.03; H, 2.87. Found: C, 39.19, 39.04; H, 3.05, 3.05.

PREPARATION OF $Cp_2U(SR)_2$

All of the reactions involving mondentate thiols were performed in the same way. Hence the attempted preparation of $Cp_2U(SEt)_2$ is given as an example.

Ethanethiol, 0.40 ml (0.33 g; 5.3 mmole), was syringed dropwise into a solution of 1.39 g (2.71 mmole) of $Cp_2U(NEt_2)_2$ with the immediate appearance of a deep red color. After the reaction solution was stirred for four hours at ambient temperature, the solvent was removed under vacuum. A yield of 0.704 g (89.4%) assuming the product is $(Cp_2U(SEt)_2$ was obtained.

Recrystallization from THF gave large prismatic crystals which by elemental analyses were seen to contain 85% $Cp_3U(SEt)$ and 15% $Cp_2U(SEt)_2$. Calculated (for the mixture of $Cp_3U(SEt)$ and $Cp_2U(SEt)_2$): C, 40.24; H. 4.08. Found (Alberta): C, 40.24, 40.26; H, 4.11, 4.08.

PREPARATION OF $Cp_3U(SEt)$

A mixture of 1.61 g (3.43 mmole) of Cp_3UCl, and 0.416 g (4.15 mmole) of KSEt was stirred in 20 ml of THF and the reaction solution turned red. After stirring the reaction solution overnight, it was taken to dryness <u>in vacuo</u>. Then 60 ml of benzene were added to the solid and the mixture was warmed to 50 ^{o}C while stirring. Filtration of the hot solution followed by cooling of the filtrate produced

elongated prisms with a yield of 1.09 (64.5%). Calculated: C, 41.30; H, 4.08. Found: C, 40.14; H, 3.88.

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