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Crystal Structure, Optical and Magnetic Properties of Tetrakis(diethylamido)uranium(IV), a Five-coordinate Dimeric Complex in the Solid State[1]

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ABSTRACT

The volatile U(IV) compound $U[N(C_2H_5)_2]_4$ is dimeric in the solid state and exhibits an unusual and possibly unique five coordination about the U ion for an f series ion. The crystals are monoclinic, space group $P2_1/n$. At 23°C $\underline{a} = 9.326(4)$ Å, $\underline{b} = 17.283(8)$ Å, $\underline{c} = 13.867(6)$ Å, $\beta = 108.43(5)°$, $\underline{d}_{\underline{c}} = 1.65$ g/cm^3 for Z = 4. X-ray diffraction intensity data were collected by an automated diffractometer using graphite monochromated Mo Kα radiation. For 1809 reflections with $F^2 > 2\sigma(F^2)$; $R_1 = 0.035$ and $R_2 = 0.031$. The five-coordinate uranium atom is at the center of a distorted trigonal bipyramid of nitrogen atoms; two of these bipyramids share an edge to make a dimeric complex located on a center of symmetry. The nearest approach of the uranium atoms is 4.004(1) Å. The three non-bridging U-N distances average 2.22(2) Å whereas the bridging U-N distances are 2.46 and 2.57 Å. The N-U-N and U-N-U angles in the central cluster are 74.4(3)° and 105.6(3)° respectively. The optical and proton magnetic resonance spectra of $U[NEt_2]_4$ at room temperature in various solvents are reported. Temperature-dependent magnetic susceptibility measurements on the solid show Curie-Weiss behavior from 10°K to 100°K. Below 10°K the susceptibility becomes temperature independent and there is no indication of magnetic ordering. A greater tendency in U amide chemistry towards oligomerization than in the d transition series is suggested.

INTRODUCTION

The compound tetrakis(diethylamido)uranium(IV), $U[N(C_2H_5)_2]_4$, was first synthesized by Jones, et al.,[2] by the reaction of lithium diethylamide with UCl_4 in diethyl ether. After filtration of the LiCl and removal of the solvent the uranium amide was purified by distillation under vacuum. An emerald-green liquid which crystallized at approximately 35°C was obtained. This material was extremely reactive to oxygen and water and proved useful as an intermediate for preparing uranium(IV) mercaptides and alkoxides. Bagnall and Yanir[3] allowed other dialkylamides to react with UCl_4, but the products could not be purified by distillation. After filtration of the LiCl, the crude residue, dissolved in hexane, was allowed to react with CS_2, CO_2, and COS to achieve insertion of these compounds into the uranium-nitrogen bond to form the corresponding carbamates. Jamerson and Takats[4] allowed uranium(IV) diethylamide to react in situ with two moles of cyclopentadiene to form $(\eta\text{-}C_5H_5)_2U[N(C_2H_5)_2]_2$ which appears to be an intermediate useful for the formation of compounds of the type $(\eta\text{-}C_5H_5)_2UX_2$. Because of the apparent synthetic utility of uranium(IV) diethylamide and its known volatility we have investigated its structural and spectroscopic properties.

EXPERIMENTAL SECTION

Solvents

All solvents were dried and deoxygenated by refluxing with sodium and benzophenone under purified argon.

Reagents and Syntheses

All reactions and manipulations were done in a purified argon atmosphere. The amines were purchased from the Aldrich Chemical Co. N-butyl lithium and Li(NEt_2) were purchased from Alfa-Ventron Corp. and used as delivered. Li(NEt_2) was also synthesized by the slow addition of diethyl amine mixed with pentane (dried with KOH, then Drierite) to n-butyl lithium in hexane at ice-bath temperatures. The resulting precipitate was filtered and vacuum dried. Other $LiNR_2$ compounds were synthesized by the same procedure as $LiNEt_2$.

UCl_4. This compound was prepared by the method of Hermann and Suttle[5] with special attention given to the modified procedure by Sherill, et al.[6] UCl_4 purchased from ROC/RIC Corp. was sometimes used.

$U(NEt_2)_4$. The method of Jones, et al.[2] proved the most satisfactory with minor refinements. 10 grams (.0263 moles) UCl_4 and 8.3 grams (.105 moles) $LiNEt_2$ were placed in a 250 ml flask. Approximately 100 ml of diethylether was transferred into the flask under vacuum at liquid N_2 temperature. The heterogeneous mixture was warmed to room temperature and was continuously stirred during the reaction. The reaction was complete after 24 hours at which time the LiCl ppt was distinctly visible. The solution was then filtered and the filtrate reduced to a high viscosity liquid by vacuum evaporation. This residue was placed in a distillation apparatus and distilled between 40° and 50°C at $< 10^{-4}$ mm Hg, yielding a crystalline product. Anal. (by A. Bernhardt, Mikroanalytisches Laboratorium, Elbach über Engelskirchen, West Germany). Calcd for $U[N(C_2H_5)_2]_4$: U, 45.21; N, 10.64; C, 36.50; H, 7.66. Found: U, 44.90; N, 10.34; C, 36.44; H, 7.48.

The above reaction was tried with hexane as solvent but appeared to procede very slowly due to low solubility of UCl_4 in hexane. With THF as solvent the reaction appeared to go to completion but the purification of the product was hindered by the solubility of LiCl in THF.

The lithium salts of diisopropylamine, piperidine, pyrrolidine, ethylenediamine, and dibenzylamine were allowed to react with UCl_4 in diethylether following the above procedure. Reaction appeared to be complete in 24 hours for all amides but no sublimable products were obtained.

Physical Measurements

Proton magnetic resonance spectra were obtained by dissolving $U(NEt_2)_4$ in pentane, benzene, THF, and diethylether to form concentrated solutions ($\geqslant$ 1M). A Varian T-60 spectrometer was used for all measurements.

For optical measurements weighed amounts of $U(NEt_2)_4$ were dissolved in pentane, benzene, THF, and diethylether to form $\sim$.02M solutions. The solutions were put in .5 cm cells in an inert atmosphere box and sealed with wax. All measurements were obtained on a Cary 17 spectrophotometer containing only the solvent in a .5 cm cell in the reference compartment.

Magnetic susceptibility measurements were obtained with a PAR model 155 vibrating sample magnetometer used with a homogeneous magnetic field produced by a Varian Associates 12 inch eletromagnet capable of a maximum field strength of 12.5 kg. The magnetometer was calibrated with $HgCo(CNS)_4$.[7] A variable temperature liquid helium dewar produced sample temperatures in the range 1.5 - 100°K which were measured by a calibrated GaAs diode placed approximately one-half inch above the sample.

X-ray Diffraction

Because of the great reactivity of $U(NEt_2)_4$ the quartz capillaries for the x-ray work were heated under vacuum at ∿100° for four hours, then placed in the inert atomosphere box for two days before a crystal was placed in each one with a tungsten needle. The capillaries were sealed under vacuum. A sealed capillary was mounted on a Picker FACS-I automated diffractometer equipped with a graphite monochromator and molybdenum tube. The cell dimensions were obtained by a least-squares-refinement procedure from the angular positions of 12 manually centered reflections for which $K\alpha_1$ peaks were resolved. The space group and cell dimensions are given in Table I with some other details of the experiment. Omega scans of several low angle reflections showed widths at half-peak height of 0.1 to 0.2°. A total of 9411 scans were measured and later averaged to give a set of 2780 unique reflections. Three standard reflections were measured after each 100th scan to monitor for crystal decay, instrumental stability and crystal alignment. After some 180 hours of irradiation, the standards exhibited about 5% decay in intensity.

Absorption corrections were calculated using an analytical algorithm.[8] The measurement of the physical dimensions of the crystal was somewhat hampered by its containment inside a capillary. The crystal shape was described by nine surface planes. Azimuthal scans of integrated intensity were performed for eight different reflections in as diverse a region of reciprocal space as the instrument would allow, and the dimension of the crystal were adjusted to fit these scans. The data were processed, averaged, and given estimated standard deviations using formalae presented in the Supplementary Material.[9] The factor p = 0.03 was used in the calculation of $\sigma(F^2)$.

The Patterson function revealed the position of the uranium atom, and the subsequent electron density Fourier using the uranium phases gave the positions of all of the nitrogen and carbon atoms. The structure was refined by full-matrix least squares where the function $\Sigma\, w\left|(|F_o|-|F_c|)\right|^2$ was minimized. The 34 reflections below sin Θ/λ of 0.16 were given zero weights because a few of them had excessively large discrepancies; these discrepancies were mainly in the region where the background peaked due to the scattering from the quartz capillary. No correction for extinction was indicated, and none was made.

A ΔF Fourier map showed 110 peaks that were greater then 0.6e/Å^3; the largest was 1.4e/Å^3. Although many of these could be interpreted as hydrogen atoms, the majority could not. No attempt was made to refine the hydrogen atoms.

The final R factors are as follows: $R_1 = \Sigma\left||F_o|-|F_c|\right|/\Sigma\,|F_o|$=0.035 for the 1809 data where $F^2 > 2\sigma(F^2)$, and 0.074 for all 2780 data; $R_2 = [\Sigma\, w\left||F_o|-|F_c|\right|^2/\Sigma\, w|F_o|^2]^{1/2}$ = 0.031. The goodness of fit was 1.09.

Final positional and thermal parameters are given in Table II, and distances and angles are listed in Tables III and IV.[9]

DISCUSSION

The structure analysis shows that in the crystalline state uranium(IV) diethylamide exists as a dimer, di-μ-diethylamido-bis[tris(diethylamido)-uranium(IV)], with two nitrogen bridges between two uranium atoms as shown in Figures 1 and 2. The uranium atoms are 4.004(1) Å apart. A novel feature of this complex is the five-coordination of the uranium. Five nitrogen atoms are at the corners of a distorted trigonal bipyramid with N(1) and N(4') in axial positions and N(2), N(3), and N(4) in equatorial ones. Two of these bypyramids share an edge to complete the centrosymmetric dimer.

As is expected on steric ground, the U-N distances are greater for bridging nitrogen than for terminal nitrogen, and for each type of nitrogen axial bonds are longer than equatorial bonds. The largest angular distortions of the bipyramid from trigonal symmetry are associated with the bridging nitrogens. The U-N(4)-U' and N(4)-U-N(4') angles of necessity add to 180°, but this sum is incompatible with 90° at uranium and an ideal tetrahedral angle (109.47°) at nitrogen. The compromise existing in the structure puts most of the distortion at uranium with the two angles being 74.4° and 105.6° respectively.

While the bonds for the bridging nitrogen atom are approximately tetrahedral, those of the terminal ones are very nearly coplanar. Each terminal nitrogen atom is within 0.07 Å of the plane defined by uranium and the two alpha carbon atoms. For bridging nitrogen the C-N-C angle is 109°. For the others these angles (112°, 116°, 114°) are intermediate between those for sp^3 and sp^2 bonding. The N-C bond lengths are all within the range reported for dimethylamides of various metals,[10-15] and differences among them are not experimentally significant.

The proton magnetic resonance spectra of $U(NEt_2)_4$ in various solvents at ambient temperature are shown in Figure 3 and tabulated in Table V. There are two peaks in each spectrum of approximate relative intensity 3:2.

The smaller peak is assigned to the methylene protons and in all four solvents is shifted to a greater extent than the larger peak which is assigned to the methyl protons. According to freezing point depression $U(NEt_2)_4$ is monomeric in benzene;[2] thus one expects that in this solvent (and pentane) the structure is tetrahedral. If we assume this hypothesis is correct then the large methylene proton shifts would be due to a Fermi contact hyperfine interaction because the pseudo-contact term would vanish with this symmetry.[16] The large upfield shifts observed in the ether solvents are probably due to pseudo-contact shifts since these solvents would be expected to coordinate to the metal ion and lower the symmetry. However, we can not rule out a possible dimer-monomer equilibrium. Further studies are underway on the temperature dependence of the pmr spectra.

The optical and near ir spectra of $U(NEt_2)_4$ at room temperature in various solvents are shown in Figure 4. The peak positions and extinction coefficients (Table VI) are in the same spectral regions and of the same magnitude as found for UCl_4 in a number of solvents.[17] As in the pmr data the spectra in benzene and hexane are very similar while the spectra in the ether solvents are markedly different. Again we attribute these spectral differences to the complexing ability of the solvents.

The inverse of the molar magnetic susceptibility of $[U(NEt_2)_4]_2$ in the temperature range 4.2°K - 100°K is shown in Figure 5. At low temperatures ($T < 10$°K) the susceptibility becomes temperature independent. Above 20°K the susceptibility follows the Curie-Weiss law

$$\chi_M = \frac{C}{T + \Theta}$$

with C = 1.052, (μ_{eff} = 2.81 BM) and Θ = 2.4°K.

If we assume $[U(NEt_2)_4]_2$ to be a U^{4+} compound (Rn core, $5f^2$) with approximately C_{3v} crystal symmetry about the U^{4+} ion, then the ground L-S state will be $^3H_4$ which will be split into three singlets and three doublets.[18] The magnetic susceptibility appears to be due to a ground state singlet with a doublet state approximately $20 cm^{-1}$ higher in energy. The third crystal field state must be greater than $70 cm^{-1}$ from the ground state. It is interesting to note that there is no indication of magnetic ordering in this dimeric compound down to 4.2°K.

The bonding of nitrogen in terminal amide groups of metal dialkylamides invariably is nearly planar,[10-15,19,20] and this planarity has been attributed to $p\pi$-$d\pi$ interactions between the nitrogen lone pair and the d metal orbitals.[21] Infrared data suggest that steric effects are of secondary importance.[3,21] Since the lowest orbitals for the U ion are 5f orbitals we expect the $p\pi$ to metal-orbital interaction to be weaker in the uranium complex. If this is true then the amide nitrogen should act as a better bridging ligand in the f transition series than in the d transition series. We speculate that this effect may be related to the apparent thermal instability and, or oligomerization of other uranium amides which have not been isolated by vacuum distillation. But the structures of other tetraamides in the solid state are yet unknown, and much work remains to be done.

The five-coordination found in this compound is unusual and perhaps unique for uranium; it has been stated that no five-coordinate complex of a lanthanide or actinide is known,[22] and it appears that this compound must be considered the first example. The existence of bridged dimer structures is also uncommon for actinides; but oxygen-bridged dimers have been reported for $Th_2(OH)_2(NO_3)_6(H_2O)_8$ and $U_2(OH)_2(ClO_4)_6(H_2O)_x (x \sim 13)$ with Th-Th and U-U distances 3.99 and 4.03 Å respectively.[23,24] It may be that the diethylamide group is just the proper size to stabilize the dimer, but is too large for further coordination and polymerization.

Supplementary Material Available: A listing of structure factor amplitudes and formulae used in data reduction (12 pages). Ordering information is given on any current masthead page.

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Table I. Summary of Crystal Data and Intensity Collection

Compound	$U[(C_2H_5)_2N]_4$
Formula Weight	526.552
a	9.326(4) Å
b	17.283(8) Å
c	13.867(6) Å
β	108.43(5)°
V	2120 $Å^3$
Z	4
Density (calc)	1.649 g/cm^3
Space Group [a]	C_{2h}^5 - $P2_1/n$
Crystal Shape and Size	Irregular elongated shape with 9 faces; $01\bar{3}$, $\bar{1}\bar{1}0$, $\bar{1}10$, $0\bar{1}\bar{1}$, $0\bar{1}0$, 001, 120, 110, $\bar{1}31$. Long dimension ∿.3mm with width ∿.13mm.
Crystal Volume	0.00254 mm^3
Temperature	23°
Radiation	Mo $K\alpha_1$ (λ 0.70926 Å), monochromatized from (002) face of mosaic graphite
Transmission Factors	.30 to .54
μ	73 cm^{-1}
Receiving Aperture	6mm wide x 6mm high, 22cm from crystal
Data Collection Method	Θ-2Θ scan (2°/min along 2Θ)
Scan Range	0.75° below $K\alpha_1$ to 0.75° above $K\alpha_2$
Background Counts	4 sec. Backgrounds offset from scan limits by 0.8°
2Θ Limits	3.0 - 45.0°

Table I. Summary of Crystal Data and Intensity Collection (continued)

Final No. of Variables	190
Unique Data Used $F_o^2 > 2\sigma(F_o^2)$	1809

a) Space group is uniquely determined by extinctions h0l, h + l ≠ 2n and 0k0, k ≠ 2n. The general positions are ±(x,y,z; 1/2 + x, 1/2 - y, 1/2 + z).

Table II. Atomic Parameters and Standard Deviations [a]

ATOM	X	Y	Z
U	.06983(5)	.06494(2)	.12579(3)
N(1)	-.011(1)	.1798(5)	.1629(7)
N(2)	.022(1)	.0021(5)	.2506(7)
N(3)	.303(1)	.1105(5)	.1594(7)
N(4)	-.1214(9)	.0607(6)	-.0431(6)
C(1)	-.136(1)	.1858(8)	.205(1)
C(2)	-.081(2)	.205(1)	.322(1)
C(3)	.065(2)	.2555(7)	.163(1)
C(4)	-.037(2)	.3147(9)	.086(1)
C(5)	-.122(2)	-.0032(7)	.275(1)
C(6)	-.153(2)	-.0886(9)	.306(2)
C(7)	.156(2)	-.0294(9)	.326(1)
C(8)	.192(2)	.009(1)	.433(1)
C(9)	.360(1)	.1333(8)	.267(1)
C(10)	.511(2)	.092(1)	.328(1)
C(11)	.402(2)	.1304(7)	.100(1)
C(12)	.438(2)	.2209(8)	.099(1)
C(13)	-.263(1)	.0551(8)	-.0158(9)
C(14)	-.413(1)	.0652(9)	-.1064(9)
C(15)	-.125(1)	.1350(7)	-.101(1)
C(16)	.041(2)	.1584(7)	-.091(1)

ATOM	B11	B22	B33	B12	B13	B23
U	2.44(2)	2.45(2)	2.35(2)	.01(2)	.87(1)	-.28(2)
N(1)	3.7(5)	3.1(5)	4.7(5)	-.5(4)	2.2(4)	-.8(4)
N(2)	3.8(5)	4.6(5)	2.7(4)	.2(4)	1.9(4)	.3(4)
N(3)	2.7(4)	4.0(5)	3.5(5)	-.5(4)	1.2(4)	-.2(4)
N(4)	3.5(4)	2.8(4)	3.0(4)	1.5(4)	.8(3)	.5(4)
C(1)	4.8(7)	5.6(7)	6.3(8)	-1.3(6)	3.9(6)	-2.3(6)
C(2)	11.2(12)	9.0(11)	6.9(10)	-1.9(10)	6.1(9)	-3.8(9)
C(3)	4.7(7)	2.7(5)	8.6(10)	.1(5)	3.7(7)	.0(6)
C(4)	9.2(11)	3.4(7)	11.0(12)	1.0(7)	4.1(9)	2.8(8)
C(5)	7.2(9)	4.1(7)	8.4(9)	.2(6)	5.6(8)	1.8(6)
C(6)	11.0(13)	5.3(9)	11.8(13)	-2.4(8)	6.9(11)	-.0(8)
C(7)	7.3(9)	7.5(9)	2.7(6)	2.3(7)	1.3(6)	2.0(6)
C(8)	7.6(10)	13.1(13)	3.1(7)	1.2(10)	.5(7)	1.1(8)
C(9)	3.1(6)	6.3(7)	3.6(7)	1.1(6)	-.8(5)	-1.7(6)
C(10)	5.3(8)	10.7(13)	4.4(8)	2.5(8)	-1.2(6)	-.5(7)
C(11)	5.5(7)	3.5(6)	6.2(8)	-.5(5)	3.3(6)	.5(5)
C(12)	7.2(10)	4.1(8)	10.8(12)	-1.3(7)	4.3(9)	.0(7)
C(13)	2.2(5)	6.7(8)	4.3(6)	-.1(6)	.4(4)	-2.3(6)
C(14)	2.1(5)	5.7(7)	5.6(7)	1.4(7)	.0(5)	-.7(7)
C(15)	2.9(6)	3.8(6)	5.2(7)	.4(5)	.2(5)	.8(5)
C(16)	5.5(8)	3.2(6)	5.1(7)	-.2(5)	2.1(6)	.5(5)

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[a] The temperature factor has the form $\exp[-0.25(h^2a^{*2}B_{11} + \ldots + 2hka^*b^*B_{12} + \ldots)]$.

Table III. Interatomic Distances [a]

U-U	4.004(1)
U-N(1)	2.24(1)
U-N(2)	2.21(1)
U-N(3)	2.22(1)
U-N(4)	2.46(1)
U-N(4')	2.57(1)
N(1)-C(1)	1.47(2)
N(1)-C(3)	1.49(2)
N(2)-C(5)	1.49(2)
N(2)-C(7)	1.46(2)
N(3)-C(9)	1.48(2)
N(3)-C(11)	1.46(2)
N(4)-C(13)	1.48(2)
N(4)-C(15)	1.51(2)
C(1)-C(2)	1.57(2)
C(3)-C(4)	1.57(2)
C(5)-C(6)	1.59(2)
C(7)-C(8)	1.57(2)
C(9)-C(10)	1.57(2)
C(11)-C(12)	1.60(2)
C(13)-C(14)	1.57(2)
C(15)-C(16)	1.57(2)

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a) Uncorrected for thermal motion.

Table IV. Selected Angles

N(1)-U-N(2)	95.2(3)
N(1)-U-N(3)	90.8(3)
N(1)-U-N(4)	92.9(3)
N(1)-U-N(4')	167.1(3)
N(2)-U-N(3)	115.9(3)
N(2)-U-N(4)	117.9(3)
N(2)-U-N(4')	92.7(3)
N(3)-U-N(4)	125.4(3)
N(3)-U-N(4')	94.9(3)
N(4)-U-N(4')	74.4(3)
U-N(1)-C(1)	121.4(8)
U-N(1)-C(3)	125.8(7)
U-N(2)-C(5)	129.0(8)
U-N(2)-C(7)	114.1(7)
U-N(3)-C(9)	109.2(7)
U-N(3)-C(11)	136.1(8)
U-N(4)-C(13)	101.2(6)
U-N(4)-C(15)	111.8(7)
U'-N(4)-C(13)	111.4(7)
U'-N(4)-C(15)	117.2(6)
U'-N(4)-U	105.6(3)
C(1)-N(1)-C(3)	112(1)
C(5)-N(2)-C(7)	116(1)
C(9)-N(3)-C(11)	114(1)
C(13)-N(4)-C(15)	109(1)
N(1)-C(1)-C(2)	112(1)
N(1)-C(3)-C(4)	113(1)
N(2)-C(5)-C(6)	112(1)
N(2)-C(7)-C(8)	114(1)

Table IV. Selected Angles (continued)

N(3)-C(9)-C(10)	114(1)
N(3)-C(11)-C(12)	114(1)
N(4)-C(13)-C(14)	115(1)
N(4)-C(15)-C(16)	108(1)

Table V. Proton Magnetic Resonance of $U(NEt_2)_4$ in Various Solvents (Referenced to TMS, T ∿ 24°C).

Solvent	$H(CH_3)$ ppm	$H(CH_2)$ ppm
Pentane	5.3	-10.8
Benzene	5.4	-13.0
Diethylether	11.5	12.2
THF	13.8	18.2

Table VI. Peak Positions and Extinction Coefficients of $U(NEt_2)_4$ in Various Solvents.

Peak	1		2		3		4		5		6	
	λ (microns)	ε	λ (microns)	ε	λ (microns)	ε	λ (microns)	ε	λ (microns)	ε	λ (microns)	ε
Solvent												
Hexane	.704	50	*a*		*b*		1.104	25	1.188	25	*b*	
Benzene	.692	47	*a*		*b*		1.090	27	1.172	26	*b*	
Diethylether	.638	28	.660	24	.718	15	.990	20	1.070	32	1.302	19
THF	.630	30	.653	25	.715	15	.985	25	1.061	36	1.287	25

a) Peaks were not split into two components

b) Peaks masked by solvent bands

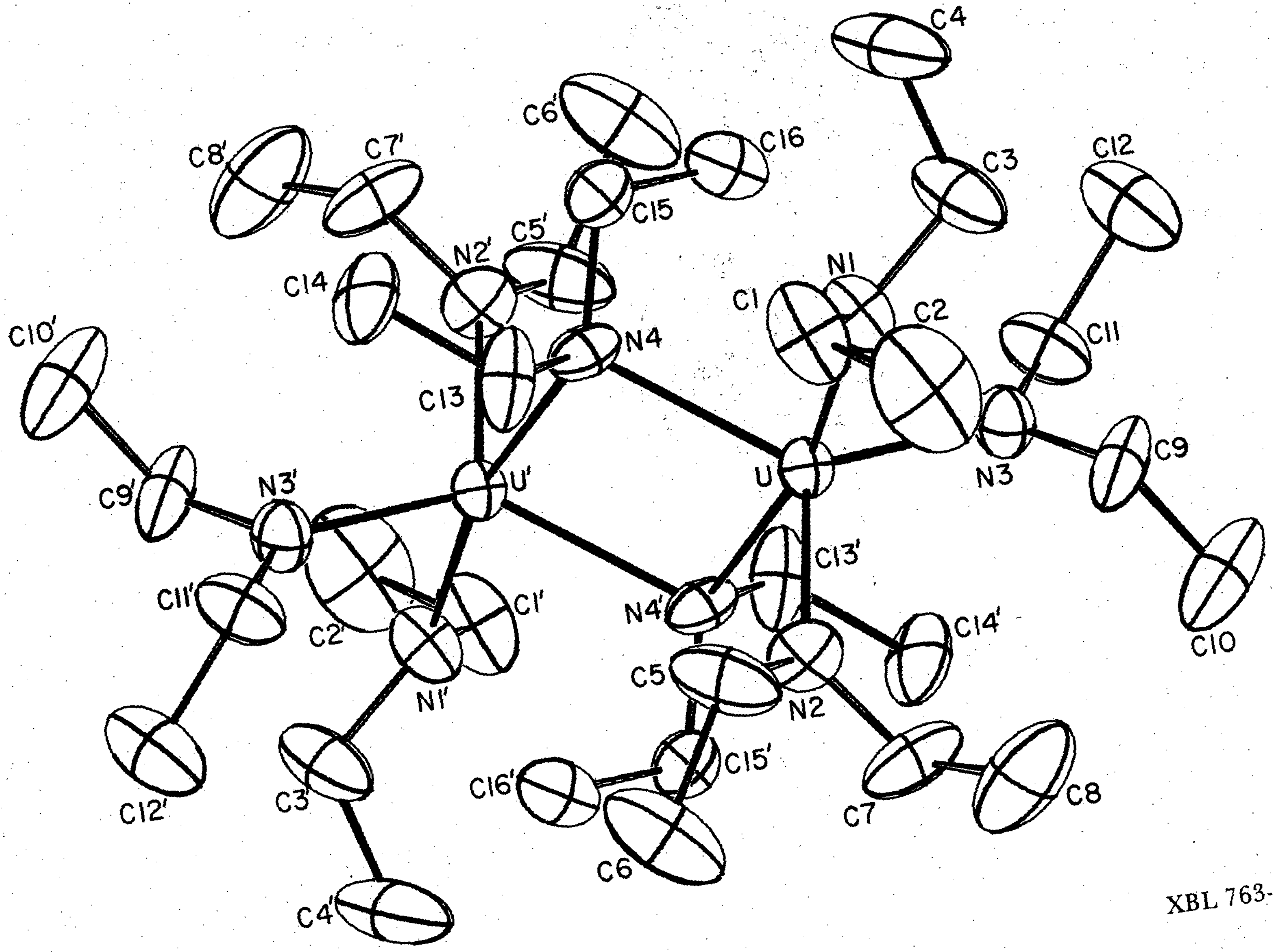
Figure 1 Molecular structure of the uranium diethylamide dimer.(XBL763-683)

Figure 2 Stereo view of the complex.(XBL 7512-9893)

Figure 3 Proton magnetic resonance of $U(NEt_2)_4$ in various solvents at room temperature.(XBL 7512-9946)

Figure 4 Optical spectra of $U(NEt_2)_4$ in various solvents at room temperature.(XBL 7512-9945)

Figure 5 Inverse susceptiblity of $[U(NEt_2)_4]_2$ vs temperature. The straight line is the calculated inverse susceptibility in that temperature range with the parameters obtained from a least-squares fit as given in the text.(XBL7512-9944)



XBL 763-683

Fig. 1

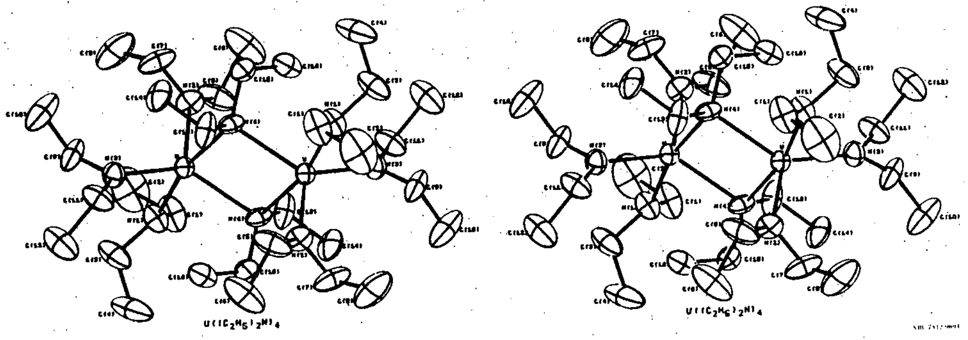
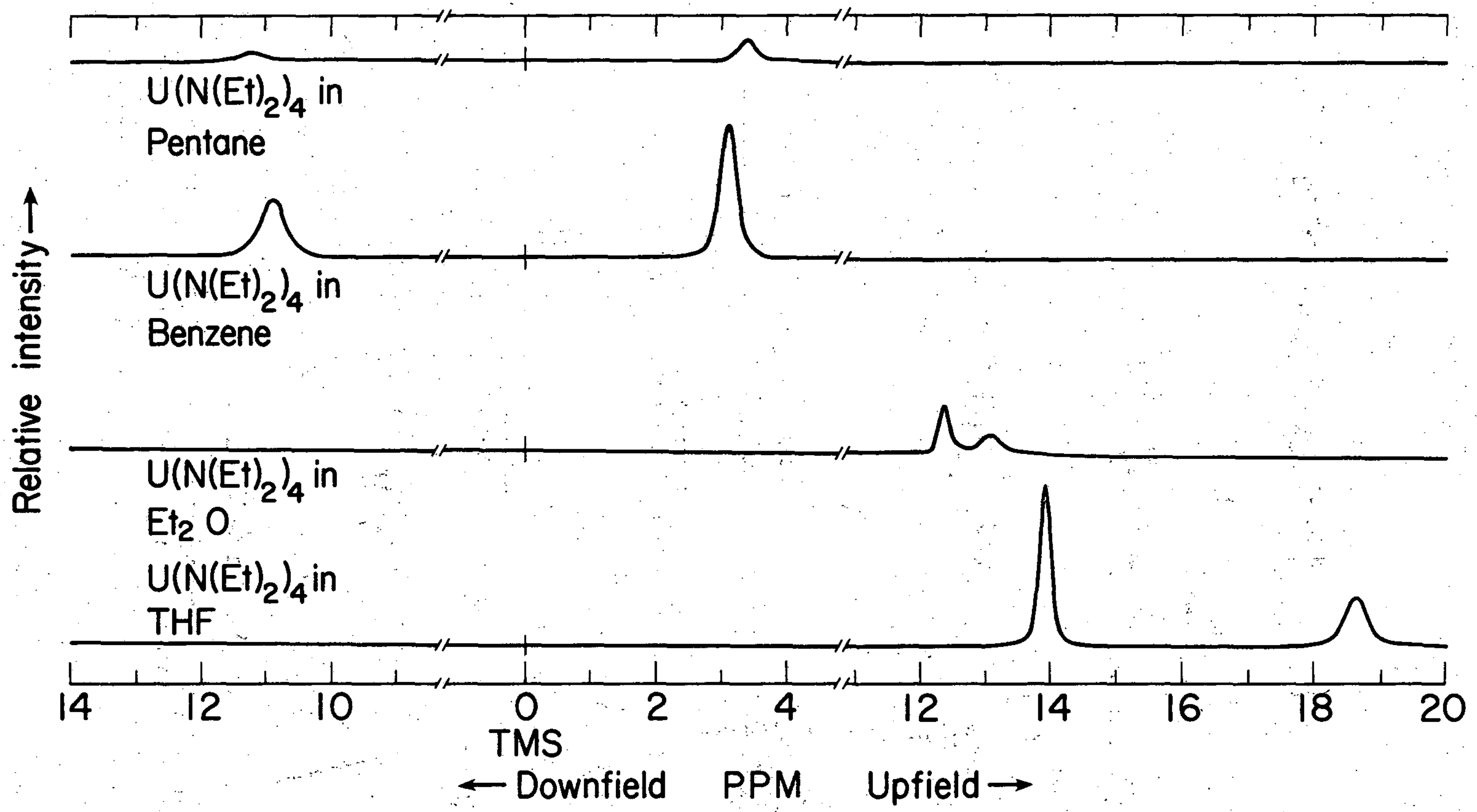
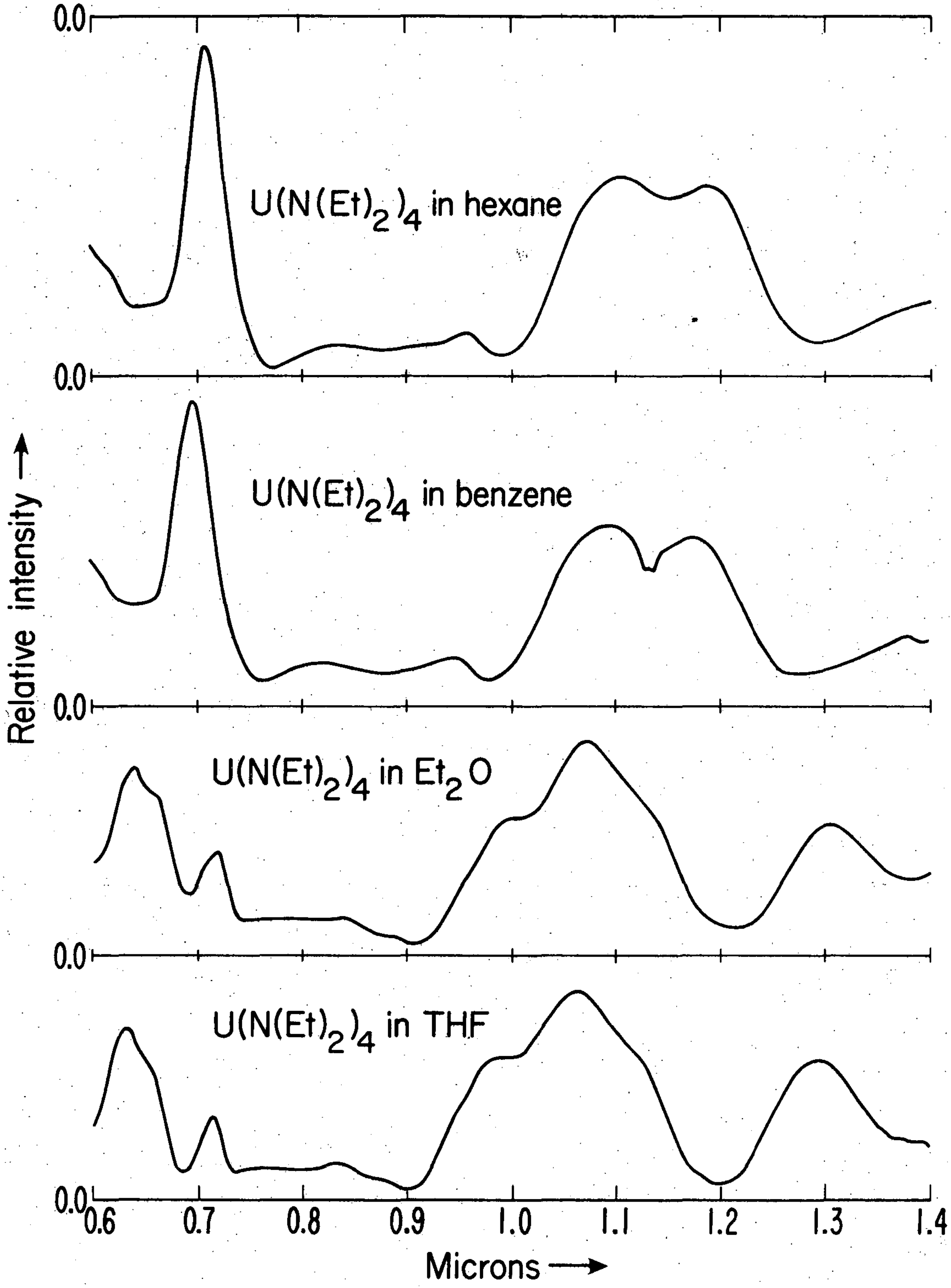


Fig. 2



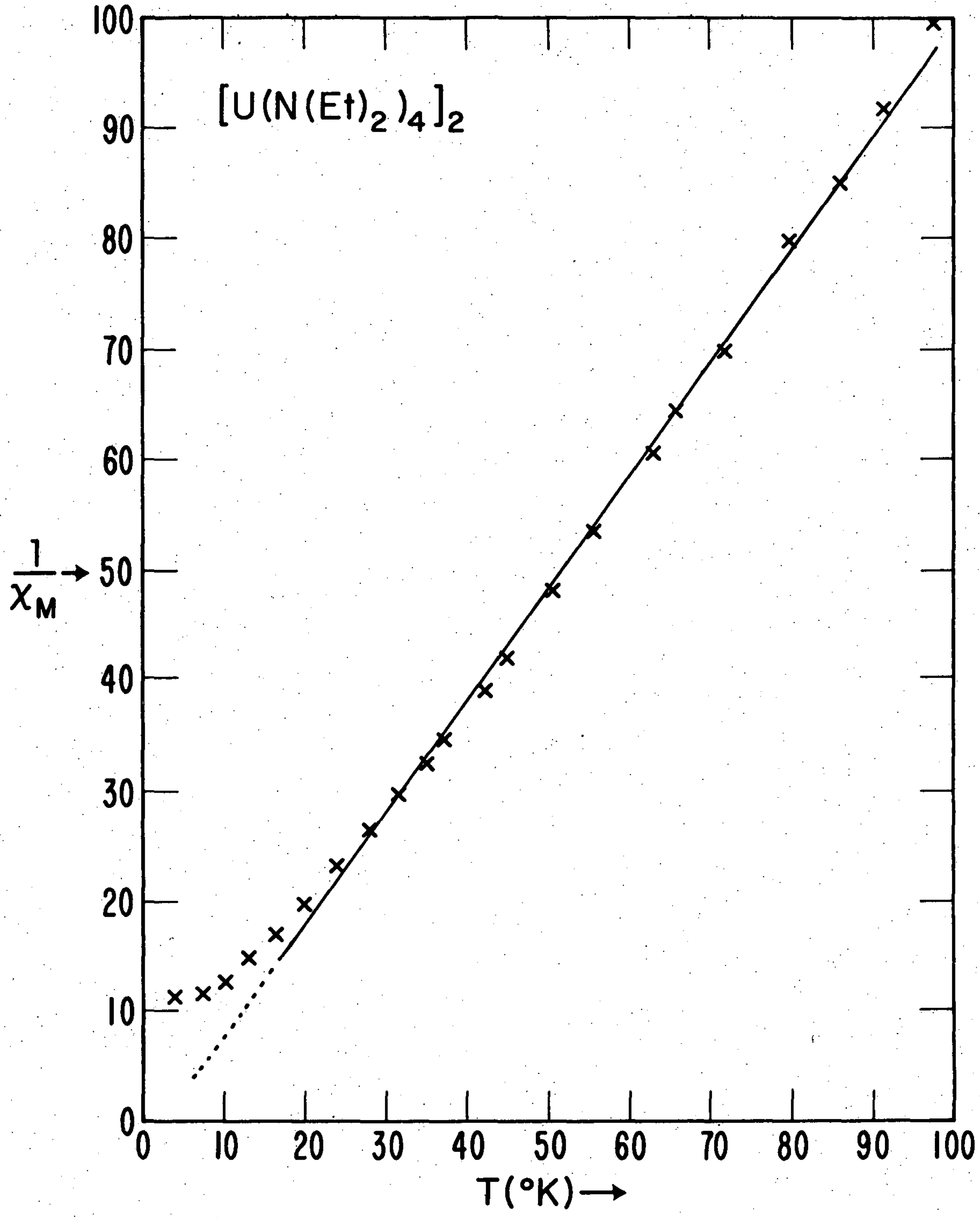
XBL 7512-9946

Fig. 3



XBL 7512-9945

Fig. 4



XBL7512-9944

Fig. 5

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