Inorganica Chimica Acta, *204* (1993) 251–256

Tetrahydrofuran adducts of uranium tetrachloride

William G. Van Der Sluys*
Department of Chemistry, University of Montana, Missoula, MT 59812 (USA)

John M. Berg, David Barnhardt and Nancy N. Sauer*
Isotope and Nuclear Chemistry Division, Los Alamos National Laboratory, Los Alamos, NM 87545 (USA)

(Received March 13, 1992; revised October 12, 1992)

Abstract

Pale green crystals of $UCl_4(THF)_3$ (**1**) were isolated from saturated THF solutions after standing undisturbed for 12 h. The molecular structure of the compound was determined by single crystal X-ray diffraction. The molecule adopts a unique structure based on a distorted pentagonal bipyramid with two chlorides occupying the axial positions and the other two chlorides occupying adjacent positions in the pentagonal plane. Crystal data for **1** ($UCl_4O_4C_{12}H_{24}$) at 203 K: monoclinic space group $P2_1$, $a=7.835(1)$, $b=14.428(1)$, $c=8.456(1)$ Å, $\beta=100.97(1)°$, $Z=2$, $D_{calc}=2.110$ g cm^{-3}.

Introduction

The development of the non-aqueous chemistry of uranium has been assisted by the use of a few readily prepared, key starting materials. The most widely used starting material for the 4+ oxidation state is uranium tetrachloride UCl_4, which can be prepared by the liquid phase chlorination of UO_3 at 210 °C using hexachloropropene [1]. Alternate high temperature methods (>500 °C), such as the chlorination of UO_2 with vigorous chlorinating agents such as phosgene or thionyl chloride produce UCl_4 of low solubility and thus limited synthetic utility [2, 3]. In contrast, the UCl_4 formed by liquid phase chlorination readily coordinates Lewis bases to form soluble adduct complexes. Structural studies have shown that the coordination geometry around the uranium in these adducts is dictated by the basicity and steric demand of the Lewis base. Sterically demanding phosphine and arsine oxides form $UCl_4(L)_2$ ($L=OP\{N(CH_3)_2\}_3$, $OP(C_6H_5)(N\{CH_3\}_2)_2$, $OP\{C_6H_5\}_3$, $OAs(CH_2CH_3)_3$) compounds in which the uranium coordination environment is roughly octahedral with the neutral ligands in both *cis* or *trans* configurations [4]. For Me_3PO, a more basic and less sterically demanding phosphine oxide ligand, a very different compound is isolated in which displacement of chlorides results in the formation of an ionic complex, $[UCl\{OP(CH_3)_3\}_6{}^{3+}][Cl^-]_3$ [5]. UCl_4 forms adducts in a number of coordinating solvents, including nitriles [6], isonitriles [7], ethers [1, 8], and phosphines [9]. These solutions are a convenient source of soluble UCl_4. In particular, tetrahydrofuran solutions have been extensively used for the synthesis of a wide variety of inorganic and organometallic compounds [1, 10]. As a result of recent interest in the fate of uranium species in the environment, we are using absorption and NMR spectroscopy to elucidate simple alcoholysis and hydrolysis reactions of uranium adducts such as $UCl_4(thf)_x$. The spectra can give structural information for uncharacterized species if they can be compared with spectra of similar complexes for which crystal structures can be obtained. As an initial study of this type, the structural characterization of the crystalline THF adduct of UCl_4 is reported here along with a comparison of its Vis–near-IR absorption spectrum with the spectra of related species in solution.

Experimental

NMR spectra were recorded at 22 °C on a Bruker AM 250 spectrometer in toluene-d_8. All ^1H NMR chemical shifts are reported in ppm relative to the ^1H impurity in toluene-d_8 set at δ 2.09. NMR spectra of these paramagnetic uranium adducts are very temperature dependent, thus it is important to note that the temperatures quoted represent average room temperatures and so are approximate values. IR spectra were recorded on a Digilab FTS-40 spectrophotometer as Nujol mulls between KBr salt plates. Elemental analyses

---

*Authors to whom correspondence should be addressed.

0020-1693/93/$6.00

were performed on a Perkin-Elmer 2400 CHN analyzer. Elemental analysis samples were prepared and sealed in tin capsules in the glove box prior to combustion. UV–Vis spectra were recorded using matched 1.0 cm quartz cells or Nujol mulls with polished KBr salt plates on a Perkin-Elmer Lambda-9 spectrophotometer.

All manipulations were carried out under an oxygen-free (<5 ppm O_2) He atmosphere in a Vacuum-Atmospheres glove box. Solvents were dried over NaK, distilled and stored in the glove box. Deuterated solvents were degassed via three freeze–pump–thaw cycles and stored in the glove box over 3 Å molecular sieves. UCl_4 was prepared according to published methods [1].

Preparation of $UCl_4(THF)_3$ (1)

In a tarred 200-ml filter flask, 3.02 g (7.95 mmol) of UCl_4 was dissolved in *c.* 40 ml of THF. After all of the UCl_4 was dissolved, the solvent was removed *in vacuo* to produce a green powder. The green powder was dried *in vacuo* for 2 h, after which the flask and contents were weighed. Drying was continued until a constant mass was achieved, providing 4.74 g (100.2% yield) of product. Crystals of **1** were obtained by dissolving approximately 100 mg of UCl_4 in 1 ml of THF-d_8 in a 5-mm NMR tube. After standing undisturbed for 12 h, large light green rhombohedral crystals had formed.

Anal. Calc. for **1**, $UCl_4O_3C_{12}H_{24}$: C, 24.18; H, 4.06; N, 0.00. Found: C, 23.91; H, 4.47; N, <0.05%. ^1H NMR (25 °C, toluene-d_8 (2.09 ppm), 250 MHz): -4.2 (br s, β); -10.5 (br s, α). IR data (cm^{-1}): 577(w), 669(m), 721(w), 734(w), 837(vs), 924(m), 954(mw), 1005(s), 1035(m), 1071(w), 1135(w), 1173(m), 1248(mw), 1298(mw), 1316(w), 1342(m), 1367(mw).

Crystal data and structure determination

Pale green, X-ray quality crystals of **1** were obtained after a UCl_4-saturated THF-d_8 solution was allowed to stand undisturbed for 12 h. Data were collected at -70 °C by variable speed 2θ–θ scans (3.0 to 14.5 °/min in ω) on a Siemens R3m/V diffractometer equipped with a graphite monochromator and using Mo Kα radiation. Data were reduced using SHELEX and corrected for absorption empirically using high chi psi-scans. The structure was solved using direct methods and refined via full-matrix least-squares methods. After the structure was fully refined, an attempt was made to locate residual (hydrogen) peaks off the THF ligands, but none appeared. All structure solution, refinement and graphics were performed using the SHELXTL PLUS software package licensed by Siemans Analytical X-ray Corporation. Least-squares minimized $R_F = \Sigma w[F_o - F_c]^2$ with $w = [\sigma 2(F) + 0.0007F^2]$. Final $R = 2.66\%$. A summary of crystal data, positional parameters, selected bond distances and angles can be found in Tables 1–4.

TABLE 1. Crystal data for $UCl_4(THF)_3$

Empirical formula	$C_{12}H_{24}Cl_4O_3U$
Color of crystal	green
Crystal dimensions	0.20 × 0.20 × 0.20 mm
Space group	$P2_1$
Cell dimensions	
(at 203 K; 25 reflections)	
a (Å)	7.835(1)
b (Å)	14.428(1)
c (Å)	8.456(1)
β (°)	100.97(1)
Z (molecules/cell)	2
Volume (Å^3)	938.4(2)
Calculated density (g/cm^3)	2.110
Wavelength	0.71069
Absorption correction	empirical
Scan speed (°/min in ω)	variable, 3.0 to 14.5
Scan width (ω) (°)	1.20 + Kα-separation
Min. 2θ (°)	2.0
Max. 2θ (°)	50.0
Total no. reflections	1866
Independent reflections	1733 ($R_{int} = 3.04\%$)
No. with $F > 4.0\sigma(F)$	1631
$R(F)$	0.0266
$R_w(F)$	0.0333

TABLE 2. Fractional coordinates and isotropic thermal parameters for $UCl_4(THF)_3$ (Fractional coordinates are $\times 10^4$ for non-hydrogen atoms; B_{iso} values are $\times 10$)

Atom	*x*	*y*	*z*	$U_{eq}{}^a$
U(1)	1182(1)	8824(1)	8336(1)	19(1)
Cl(1)	2585(3)	9609(2)	6111(3)	38(1)
Cl(2)	4303(4)	8483(2)	9929(4)	39(1)
Cl(3)	1406(5)	7127(2)	7395(4)	45(1)
Cl(4)	− 660(4)	8297(2)	10394(3)	35(1)
O(1)	− 782(9)	10239(5)	7832(9)	28(2)
C(1)	−1069(17)	10802(10)	6379(16)	41(4)
C(2)	−2247(22)	11576(12)	6723(20)	62(6)
C(3)	−3184(17)	11209(10)	7985(20)	48(5)
C(4)	−1789(20)	10620(11)	8987(17)	56(5)
O(2)	1938(10)	10096(5)	10329(9)	31(2)
C(5)	2242(18)	9987(9)	12085(13)	40(4)
C(6)	3543(38)	10729(16)	12666(19)	115(11)
C(7)	3996(32)	11164(21)	11384(22)	121(12)
C(8)	2866(19)	10900(9)	9897(17)	46(5)
O(3)	−1303(9)	8631(5)	6110(10)	27(3)
C(9)	−1218(15)	8348(10)	4481(14)	39(4)
C(10)	−2796(19)	7737(12)	3967(19)	59(6)
C(11)	−4105(16)	8169(15)	4855(22)	70(6)
C(12)	−3112(13)	8612(9)	6287(17)	42(5)

Isotropic values for those atoms refined anisotropically are calculated using the formula given in ref. 11. [a]Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

TABLE 3. Bond distances (Å) for $UCl_4(THF)_3$

U(1)–Cl(1)	2.612(3)
U(1)–Cl(2)	2.605(3)
U(1)–Cl(3)	2.591(3)
U(1)–Cl(4)	2.578(3)
U(1)–O(1)	2.543(7)
U(1)–O(2)	2.486(7)
U(1)–O(3)	2.453(7)
O(1)–C(1)	1.455(16)
O(1)–C(4)	1.474(18)
C(1)–C(2)	1.512(23)
C(2)–C(3)	1.502(25)
C(3)–C(4)	1.511(20)
O(2)–C(5)	1.467(13)
O(2)–C(8)	1.453(16)
C(5)–C(6)	1.496(28)
C(6)–C(7)	1.357(32)
C(7)–C(8)	1.445(24)
O(3)–C(9)	1.450(15)
O(3)–C(12)	1.454(13)
C(9)–C(10)	1.514(20)
C(10)–C(11)	1.516(24)
C(11)–C(12)	1.457(21)

TABLE 4. Bond angles (°) for $UCl_4(THF)_3$

Cl(1)–U(1)–Cl(2)	88.4(1)	C(1)–O(1)–C(4)	109.6(9)
Cl(1)–U(1)–Cl(3)	97.2(3)	O(1)–C(1)–C(2)	104.6(11)
Cl(2)–U(1)–Cl(3)	82.4(1)	C(1)–C(2)–C(3)	106.0(13)
Cl(1)–U(1)–Cl(4)	168.8(4)	C(2)–C(3)–C(4)	101.4(12)
Cl(2)–U(1)–Cl(4)	100.7(1)	O(1)–C(4)–C(3)	105.0(11)
Cl(3)–U(1)–Cl(4)	90.5(4)	U(1)–O(2)–C(5)	125.3(6)
Cl(1)–U(1)–O(1)	81.7(2)	U(1)–O(2)–C(8)	119.0(6)
Cl(2)–U(1)–O(1)	135.8(2)	C(5)–O(2)–C(8)	110.4(9)
Cl(3)–U(1)–O(1)	141.4(2)	O(2)–C(5)–C(6)	103.0(11)
Cl(4)–U(1)–O(1)	87.2(2)	C(5)–C(6)–C(7)	109.5(16)
Cl(1)–U(1)–O(2)	95.1(2)	C(6)–C(7)–C(8)	111.3(22)
Cl(2)–U(1)–O(2)	73.1(2)	O(2)–C(8)–C(7)	104.2(14)
Cl(3)–U(1)–O(2)	152.2(2)	U(1)–O(3)–C(9)	126.0(6)
Cl(4)–U(1)–O(2)	81.5(2)	U(1)–O(3)–C(12)	124.8(7)
O(1)–U(1)–O(2)	65.1(2)	C(9)–O(3)–C(12)	108.3(8)
Cl(1)–U(1)–O(3)	83.0(2)	O(3)–C(9)–C(10)	104.7(11)
Cl(2)–U(1)–O(3)	154.9(2)	C(9)–C(10)–C(11)	102.2(13)
Cl(3)–U(1)–O(3)	75.4(2)	C(10)–C(11)–C(12)	106.7(11)
Cl(4)–U(1)–O(3)	91.2(2)	O(3)–C(12)–C(11)	107.4(11)
O(1)–U(1)–O(3)	66.2(2)		
O(2)–U(1)–O(3)	131.0(2)		
U(1)–O(1)–C(1)	125.5(7)		
U(1)–O(1)–C(4)	124.9(7)		

Results and discussion

Synthesis

Anaerobic dissolution of UCl_4 in THF followed by solvent removal *in vacuo* produces the pale green THF adduct, **1**, which is very soluble in THF, sparingly soluble in toluene and insoluble in other hydrocarbon solvents such as hexane or benzene [8c–e]. Elemental analysis supports the formulation of this product as $UCl_4(THF)_3$. This is in contrast to Ortega and Perry [8d] who suggest $UCl_4(THF)$ as the product, but is consistent with the formula proposed by Herzog *et al.* [8e] ($UCl_4(THF)_3$). The coordination of three THF ligands in **1** is quite unusual, as other characterized neutral actinide-halide Lewis base complexes typically coordinate four neutral ligands, e.g. AnX_4L_4 (An = Th, X = Br, L = THF, X = Cl, L = $(C_6H_5)_2SO$; An = U, X = Cl, L = $NCCH_3$) [6, 12, 13]. Tris adducts of UCl_4 are uncommon, and few have been described in the literature. Gans and Marriage have reported the formation of UCl_4(t-BuCN)$_3$ by reaction of UCl_4 with the nitrile [14]. They attribute the formation of the tris adduct to the steric bulk of the t-butyl group. Reaction of UCl_4 and UBr_4 with smaller nitriles such as MeCN gave UX_4L_4 adducts (X = Cl or Br; L = MeCN, EtCN, i-PrCN or n-BuCN).

Solid-state molecular structure

The solid-state structure of **1** is shown in Fig. 1. The coordination environment about uranium is best described as a distorted pentagonal bipyramid, with the axial positions occupied by two chloride ligands. For actinide complexes, the bonding is dominated by ionic interactions, and the steric requirements of the ligands generally account for the observed structures. Of the numerous possible configurational isomers for a MX_4Y_3 species adopting a pentagonal bipyramidal structure, an arrangement with chlorides in axial positions maximizes the angles between the most sterically demanding ligands*. It is interesting to note that **1** adopts a configuration where the two chloride ligands in the basal plane of the molecule are adjacent, **I**, rather than

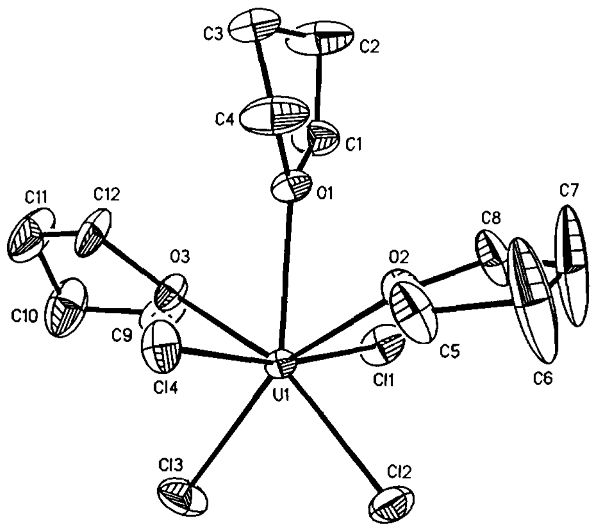
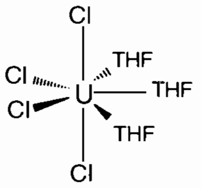


Fig. 1. An ORTEP drawing of $UCl_4(THF)_3$.

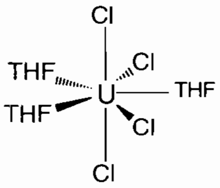
---

*This is based on the assumption that chloride, due to lp–lp interactions, is more sterically demanding than THF which is bladed.

separated by THF ligands, **II**. This is contrary to what would be anticipated based on steric arguments for the idealized structure. Examination of the crystal packing arrangement, shown in Fig. 2, suggests that configuration **I** is favored because it minimizes Cl–Cl and THF–THF interactions between neighbouring complexes by allowing the molecular units to arrange themselve in such a way that the face with the THF ligands always points in the same general direction. As a result of this configuration, the Cl(3)–U(1)–Cl(2) angle is increased from the idealized 72° to the observed 82.4(1)°, and the O(1)–U(1)–O(2) and O(1)–U(1)–O(3) angles are compressed to 65.1(2) and 66.2(2)°, respectively. The O(2)–U(1)–Cl(2) and the O(3)–U(1)–Cl(3) angles are intermediate, 73.1(2) and 75.4(2)°, respectively. The average U–Cl distance, 2.595(2) Å, is in the range observed for other U(IV) chloride complexes [1, 4–7]. For example, in the reported structure of crystalline UCl_4 each uranium is coordinated by eight chlorines in two sets of four equivalent positions with U–Cl distances of 2.60(4) and 2.95(5) Å [15]. The U–Cl distance in **1** is quite close to that of the nearer set. However, $UCl_4(depa)_4{}^+$, the only other pentagonal bipyramidal complex of UCl_4 reported in the literature, has U–Cl bonds that are longer than those in **1**, at 2.62 and 2.72 Å [16]. The average U–O distance in **1** 2.51 Å is significantly longer than the average U–O distances in $UCl_4(depa)_4{}^+$ at 2.29 Å. The shorter U–Cl bonds and the longer U–O bonds are probably a result of the relatively weak donating ability of the etheral THF ligands. The IR spectrum of **1**, like that reported by other investigators [8c–e] indicates coordinated THF but suggests only one type of THF ligand.



I



II

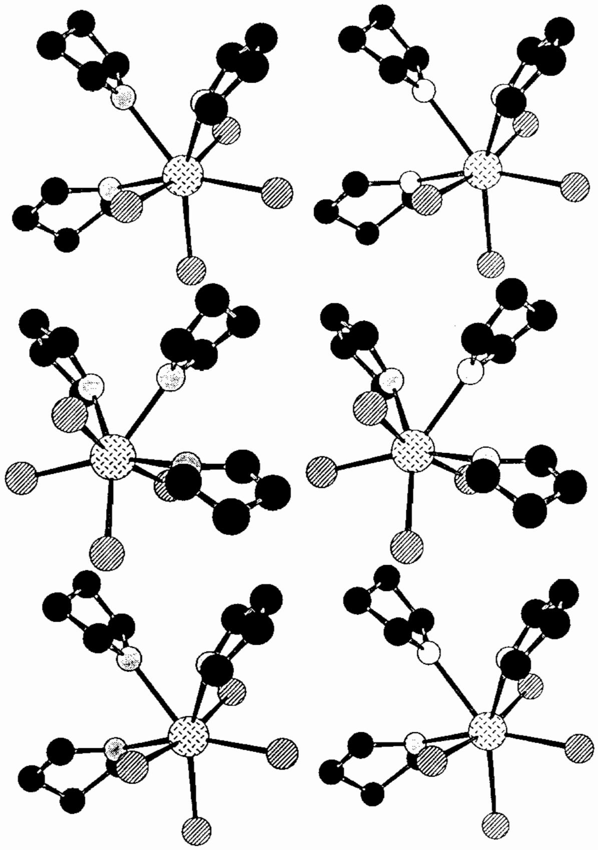


Fig. 2. Packing diagram of **1** showing the relative orientations of the molecular units. The view is normal to the *ab* plane. The two molecules in the center are closer to the view than are the other four. Note the interlocking of the ligands and the general alignment of the THF-dominated faces along the *b* axis (vertical direction).

Solution spectra and structure

Visible to near-IR absorption spectra of **1** as a Nujol mull and in toluene solution, as well as of UCl_4 in 2-methyl-THF and THF solutions are shown in Fig. 3. Each of these spectra consists of a complex series of relatively weak ($\epsilon_{max} = 60$ mol^{-1} cm^{-1}) and narrow (~200 cm^{-1}) peaks, which are characteristic of f→f

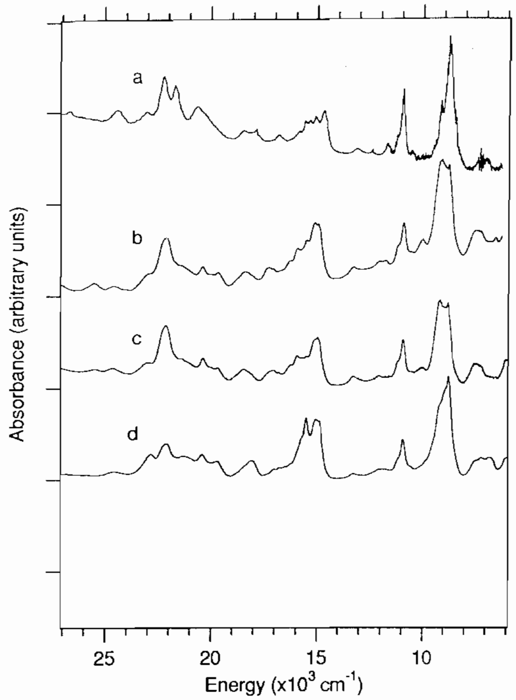


Fig. 3. Electronic absorption spectra of: (a) $UCl_4(THF)_3$ solid in Nujol mull; (b) $UCl_4(THF)_3$ in saturated toluene solution; (c) $UCl_4(THF)_3$ in 2-methyltetrahyrofuran solution; (d) UCl_4 dissolved in THF.

transitions between individual states of the $5f^2$ electron configuration centered on the U^{4+} ion. This configuration can give rise to approximately 75 electronic states in the energy range which is shown. While the properties of these states are dominated by the uranium, the energies and intensities of transitions between them are strongly influenced by the identities and arrangement of the ligands [17]. By coupling knowledge of the structure of some THF adducts with general properties of the spectra, provisional conclusions may be drawn about the identities of solution complexes for which direct structural information does not exist.

Figure 3(a) shows **1** in a Nujol mull, and is thus the spectrum of the molecular unit described by the crystal structure reported above. Substantial changes occur in the spectrum when **1** is dissolved in toluene (Fig. 3(b)). Since toluene is not expected to displace THF in the inner coordination sphere of uranium, the differences between Fig. 3(a) and (b) may result solely from ligand rearrangement upon removal of the intermolecular packing forces present in the solid. Such a rearrangement is reasonable because the energetic advantage of configuration **I** due to interaction with neighboring molecular units in the crystal does not exist in solution. Thus, another configuration such as **II** might dominate in solution. The ^1H NMR spectrum of $UCl_4(THF)_3$ in toluene-d_8 solution shows one type each of paramagnetically shifted α and β resonances associated with coordinated THF, which is consistent with a single configuration, however, this is not conclusive because we cannot rule out the possibility of rapid exchange with any free THF which could have been liberated upon dissolution.

An alternate possibility is that addition of toluene to the solution results in the formation of uranium dimers or oligomers in solution. The structure of a chloride-bridged dimer, $\{[UCl_4(THF)_2]_2\}$, which was crystallized from 10% THF in n-pentane, has been recently reported [18]. In crystalline $\{[UCl_4(THF)_2]_2\}$, each uranium ion is seven-coordinate, but there is one fewer THF per uranium than there is in **1**. It is possible that the dissolution of **1** in toluene results in the partial loss of coordinated THF and the formation of similar chloride-bridged species in solution.

The spectrum produced by a solution of UCl_4 in 2-methyl-THF (Fig. 3(c)) is nearly identical to that of **1** in toluene (Fig. 3(b)), indicating that the dominant solution species have the same ligands in very similar geometrical arrangements. If no condensation of the metal units has occurred, then the resulting solution species in 2-methyl-THF is $UCl_4(2\text{-methyl-THF})_3$. Alternatively, if Fig. 3(c) represents similar chloride-bridged species, the steric bulk of the 2-methyl-THF ligand must make formation of the tris adduct unfavored. We favor the former possibility. The similarity of the two spectra (3(a) and (b)) indicates that the two dominant solution species are the same. It seems unlikely that the same chloride-bridged species would result in neat 2-methyl-THF and in toluene.

Dissolution of UCl_4 in neat THF produces a solution whose spectrum (Fig. 3(d)) differs significantly from those in Fig. 3(b) and (c) which suggests a different inner sphere coordination when excess THF is available. It is possible that in solution the sterically less-demanding THF is sufficiently compact so that an additional solvent molecule can fit into the inner coordination sphere to give $UCl_4(THF)_4$. This complex could adopt an eight-coordinate, pseudo-D_{2d}, dodecahedral structure. Not surprisingly, addition of THF to **1** in toluene solution produces a spectrum similar to that obtained in THF solution (Fig. 3(d)), supporting the conclusion that THF is added to the coordination sphere.

Conclusions

We have shown, in agreement with Herzog *et al.* [8e], that the principal isolable species formed when UCl_4 is dissolved in THF is $UCl_4(THF)_3$. The solid-state structure represents a unique interplay between the steric requirements of the THF and the chloride ligands. Electronic absorption spectra demonstrate that the uranium inner coordination spheres in toluene, 2-methyl-THF and THF solutions are different from that of this solid, either through ligand rearrangement or ligand substitution. At this point, further interpretation of the spectroscopic data requires assumptions about the importance of oligomerization in solution. We plan to test these assumptions in future work.

Supplementary material

Isotropic thermal parameters for $UCl_4(THF)_3$ have been submitted for review purposes and can be ordered using any current masthead address.

Acknowledgements

This work has been supported in part by The University of Montana, University Grants Program, the State of Montana, NSF-EPSCOR Program, and W.G.V.D.S. acknowledges a 1991 Associated Western Universities-DOE Summer Fellowship. J.M.B. acknowledges the Director's office of Los Alamos National Laboratory for a postdoctoral fellowship. We also thank R. R. Ryan for helpful discussions and the Los Alamos Structure Center for use of equipment.

References

1 J. A. Hermann and J. F. Suttle, *Inorg. Synth., 5* (1957) 143.

2 J. J. Katz, G. T. Seaborg and L. R. Morss, *The Chemistry of the Actinide Elements,* Chapman and Hall, New York, 1986.

3 J. M. Carter, *US Patent No. 2 677 592* (1954).

4 (a) J. G. H. du Preez, B. J. Gellatly, G. Jackson, L. R. Nassimbeni and A. L. Rodgers, *Inorg. Chim. Acta, 27* (1978) 181; (b) M. R. Caira and L. R. Nassimbeni, *J. Inorg. Nucl. Chem., 39* (1977) 455; (c) P. Sommerville and M. Laing, *Acta Crystallogr., Sect. B, 32* (1976) 1551; (d) G. Bombieri, D. Brown and R. Graziani, *J. Chem. Soc., Dalton, Trans.,* (1975) 1873.

5 G. Bombieri, E. Forsellini, D. Brown and B. J. Whittaker, *J. Chem. Soc., Dalton, Trans.,* (1976) 735.

6 F. A. Cotton, D. O. Marler and W. Schwotzer, *Acta Crystallogr., Sect. C, 40* (1984) 1186.

7 F. Lux and U. B. Bufe, *Angew. Chem. Int. Ed. Engl., 10* (1971) 274.

8 (a) D. C. Moody, R. A. Penneman and K. V. Salazar, *Inorg. Chem., 18* (1979) 208; (b) D. C. Moody and J. D. Odom, *J. Inorg. Nucl. Chem., 41* (1979) 533; (c) G. B. Deacon and T. D. Tuong, *Polyhedron, 7* (1988) 249; (d) J. D. Ortega and D. L. Perry, *J. Inorg. Nucl. Chem., 36* (1974) 1179; (e) S. Herzog, K. Gustav, E. Kruger, H. Oberender and R. Schuster, *Z. Chem., 3* (1963) 428.

9 P. G. Edwards, R. A. Andersen and A. Zalkin, *J. Am. Chem. Soc., 103* (1981) 7792.

10 (a) S. J. Simpson, H. W. Turner and R. A. Andersen, *Inorg. Chem., 20* (1981) 2991; (b) W. G. Van Der Sluys, A. P. Sattelberger and M. W. McElfresh, *Polyhedron 9* (1990) 1843; (c) E. R. Sigurdson and G. Wilkinson, *J. Chem. Soc., Dalton Trans.,* (1977) 812; (d) E. A. Mintz, K. G. Moloy, T. J. Marks and V. W. Day, *J. Am. Chem. Soc., 104* (1982) 4692; (e) J. H. Burns and P. G. Laubereau, *Inorg. Chem., 10* (1971) 2789; (f) K. W. Bagnall and J. Edwards, *J. Organomet. Chem., 80* (1974) C14; (g) L. T. Reynolds and G. Wilkinson, *J. Inorg. Nucl. Chem., 2* (1956) 246; (h) R. G. Jones, G. Karmas, G. A. Martin, Jr. and H. Gilman, *J. Am. Chem. Soc., 78* (1956) 4285.

11 W. C. Hamilton, *Acta Crystallogr., 12* (1959) 609.

12 C. E. F. Rickard and D. C. Woollard, *Acta Crystallogr., Sect. B, 36* (1980) 292.

13 D. L. Clark, T. M. Frankcom, J. C. Huffman and J. G. Watkin, *Inorg. Chem., 31* (1992) 1628.

14 P. Gans and J. Marriage, *J. Chem. Soc., Dalton Trans.,* (1972) 46.

15 D. Brown, T. L. Hall and P. T. Moseley, *J. Chem. Soc., Dalton Trans.,* (1973) 686.

16 K. W. Bagnall, R. L. Beddoes, O. S. Mill and L. Xing-fu, *J. Chem. Soc., Dalton Trans.,* (1982) 1361.

17 N. Edelstein, *J. Less-Common Met., 133* (1987) 39.

18 J. Rebizant, M. R. Spirlet, C. Apostolidis, G. Van den Bossche and B. Kanellakopulos, *Acta Crystallogr., Sect. C, 47* (1991) 864.