

Uranium(IV)-Crown-ether Complexes and Cryptates. ^1H Nuclear Magnetic Resonance Study, and X-Ray Crystal and Molecular Structure of Tetrachloro-(2,5,8,15,18,21-hexaoxatricyclo[20.4.0. $^9,^{14}$]hexacosane)uranium(IV)

By GEORGE C. de VILLARDI,* PIERRETTE CHARPIN, ROSE-MARIE COSTES, GERARD FOLCHER,
PIERRE PLURIEN, and PAUL RIGNY

(Centre d'Etudes Nucléaires de Saclay, 91190 Gif sur Yvette, France)

and COLETTE DE RANGO

(Centre Universitaire Pharmaceutique, Chatenay Malabry, France)

Summary ^1H N.m.r. evidence for direct co-ordination of uranium to the oxygen atoms in a new UCl_4 -dicyclohexyl-18-crown-6 complex is confirmed by an X-ray structural determination; several uranium(IV) salt-crown-ether complexes and cryptates also exhibiting very large n.m.r. shifts are reported.

In some examples of crown-ether or cryptate derivatives of uranium(IV)¹ or UO_2^{2+} the metal ion has been shown not to be directly bonded to the donor atom of the macrocyclic

ligand, in contrast to the recently published lanthanum nitrate crown complex.³ The ^1H n.m.r. spectra for such compounds show very small shifts induced by the paramagnetic U^{IV} or UO_2 cation. However, in a solvent with a high dielectric constant, the interactions between the ionic species would be reduced, thus enabling complete co-ordination of the cation by the ligand. This has now been observed in the spectra of complexes of U^{IV} salts with crown-ethers or cryptands in nitromethane or acetonitrile (Figure 1).

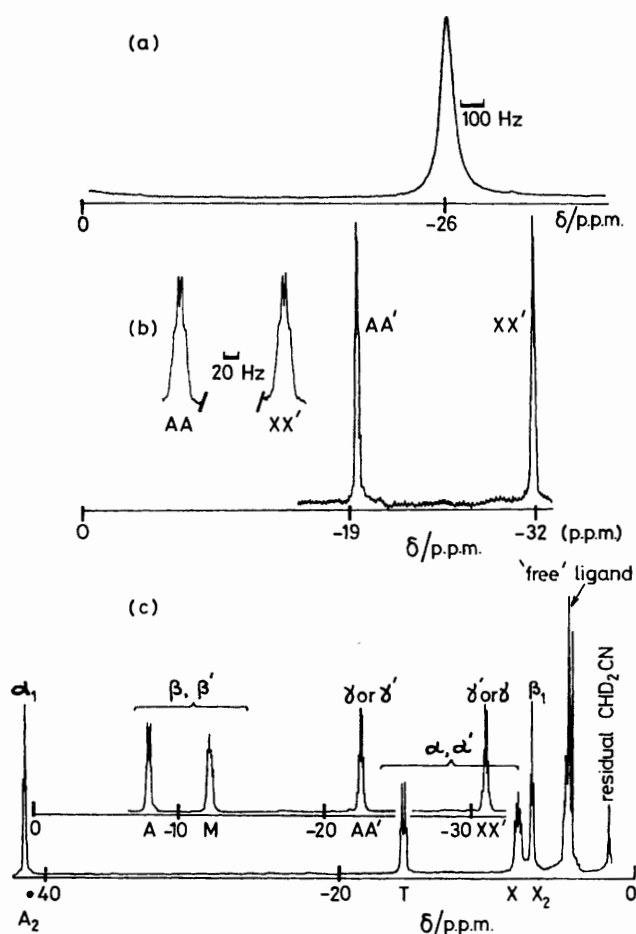


FIGURE 1. ^1H N.m.r. spectra at 60 MHz of: (a) $\text{U}(\text{tfa})_4$ -18-crown-6, in CD_3CN at 37°C ; (b) UCl_4 -18-crown-6 in MeNO_2 at 10°C ; (c) $\text{U}(\text{tfa})_4$ - $\langle 221 \rangle$ in CD_3CN at 37°C : the assignments are based on the observed spin-spin splittings.

Figure 1a shows the spectrum in CD_3CN of $\text{U}(\text{tfa})_4$ -18-crown-6 ($\text{tfa} = \text{CF}_3\text{CO}_2^-$; 18-crown-6 = 1,4,7,10,13,16-hexaoxacyclo-octadecane) (I). The value of the ligand-induced shift ($\Delta\delta$ ca. 29.5 p.p.m. \dagger) is as large as those found for 1:1 amine or alcohol adducts of uranium(IV) β -diketonates (Table).

TABLE. Induced shifts (p.p.m.) for butanol and butylamine ligand protons in uranium(IV) β -diketonate adducts^a.

Adduct	α -CH ₂	β -CH ₂	γ -CH ₂	Me
$\text{U}(\text{tfba})_4$ -n-butanol ^b	16	7.4	4	2.4
$\text{U}(\text{fod})_4$ -n-butylamine ^c	30.9	16	9	5.4

^a Shifts upfield from corresponding free ligand resonances; substrate to ligand ratio = 1:1. ^b T 32°C ; CCl_4 solution; $\text{tfba} = 4,4,4$ -trifluoro-1-phenylbutane-1,3-dione (G. Folcher, J. Paris, P. Plurien, P. Rigny, and E. Soulie, *J.C.S. Chem. Comm.*, 1974, 3). ^c T 37°C ; n-pentane solution; $\text{fod} = 1,1,1,2,2,3,3$ -heptafluoro-7,7-dimethyloctane-4,6-dione (G. de Villardi, unpublished work).

This shows that all the crown protons are located on carbon atoms α to oxygen atoms directly bonded to uranium.

\dagger High-field chemical shifts are measured negatively from Me_4Si ; upfield induced shifts are measured positively.

\ddagger Standard deviations are 0.02 Å for U-Cl distances and 0.06 Å for U-O distances.

Moreover, intermolecular exchange is slow on an n.m.r. time-scale even in the presence of an excess of ligand, which suggests a high activation energy for the complexation process.

Very large induced shifts are also observed in the spectrum of UCl_4 -18-crown-6 (II) in MeNO_2 (Figure 1b). The two AA'XX'-type multiplets coalesce at 140°C (nitrobenzene solution, $\tau = 0.44$ ms at 140°C and ca. 1 s at 37°C). This is likely to correspond to an intramolecular exchange between two D_{3d} conformations as in the KSCN -18-crown-6 complex.⁴ $\text{U}(\text{tfa})_4$ -(dcc) (III) and UCl_4 -(dcc) (IV) (dcc = dicyclohexyl-18-crown-6 = 2,5,8,15,18,21-hexaoxatricyclo-[20.4.0.0^{9,14}]hexacosane, mixed *cis,syn,cis* and *cis,anti,cis*-isomers) present similar but more complex spectra in acetonitrile or nitromethane. The broad resonances are in the range 0 to -30 p.p.m. as in compounds (I) and (II). Here too ligand exchange is slow at room temperature.

Compound (IV) (*cis,syn,cis*-isomer) has been isolated. Preliminary results from a single-crystal X-ray study are as follows:⁵ space group $P2_1/c$, $a = 12.17 \pm 0.01$, $b = 22.97 \pm 0.02$, $c = 24.38 \pm 0.02$ Å, $\beta = 98.99 \pm 0.01^\circ$, $U = 6734$ Å³. 3831 reflexions above background were recorded

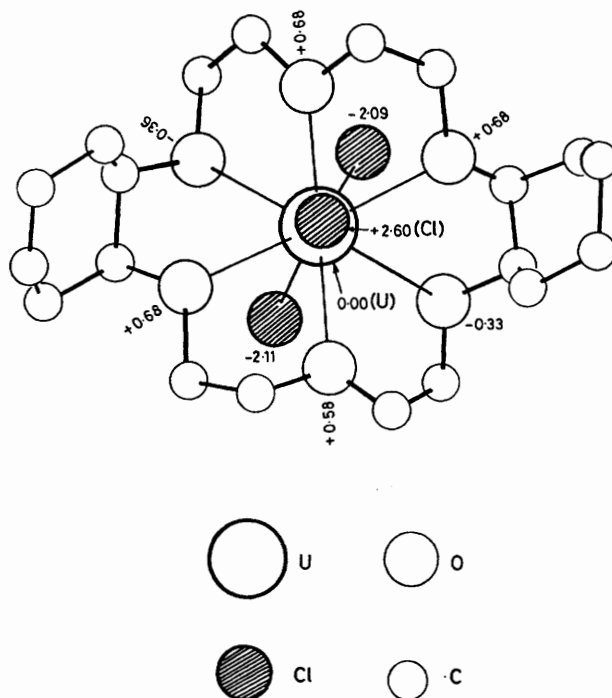
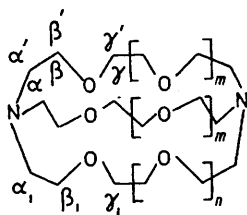


FIGURE 2. The UCl_3 -dcc unit viewed in the direction normal to its mean plane and showing distances from the plane (Å).

on a Nonius CAD-4 automatic diffractometer using $\text{Mo-K}\alpha$ radiation. The structure was refined (U and Cl anisotropically, C and O isotropically) to R 0.088. The asymmetric unit is composed of $\text{UCl}_6[\text{UCl}_3(\text{dcc})]_2$ units, with $Z = 4$. One uranium atom is surrounded by six Cl atoms forming an octahedron (U-Cl distances ranging from 2.55 to 2.67 Å \ddagger). The other two uranium atoms are directly bonded to the crown oxygen atoms (all six U-O distances in

the range 2.40—2.68 Å[†]), with three Cl atoms as neighbours (U—Cl between 2.62 and 2.66 Å[†]).§

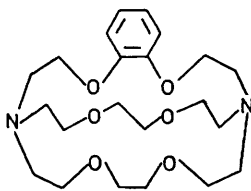
The ¹H n.m.r. spectrum in CD₃CN of the U(tfa)₄-<221> [<221> = cryptand (a)] complex (V) displays signals over a range of 75 p.p.m. (Figure 1c). All peaks are of first



a: $m = 1, n = 0; <221>$

b: $m = 1, n = 1; <222>$

c: $m = 0, n = 1; <211>$



d: <222B>

order and can be assigned by using the double irradiation technique.

The assignment in Figure 1c necessarily leads to C_{2v} symmetry. The large induced shifts and the symmetry are what would be expected in an insertion complex. The large low-field induced shifts could be due (a) to an important contact shift contribution, or (b) to 'unusual' values of the angular parameter in the dipolar interaction.

The U(tfa)₄-<222> [<222> = cryptand (b)] complex (VI) displays a very similar spectrum with one chain of the ligand different from the other two. Here again the symmetry is C_{2v} . The U(tfa)₄-<211> and U(tfa)₄-<222B> [<211> = cryptand (c); <222B> = cryptand (d)] cryptates (VII) and (VIII) have also been obtained. A lower symmetry was found. In all these cases, induced shifts were large suggesting that insertion of the uranium into the polycyclic ligand cavity was highly probable.

(Received, 21st June 1977; Com. 611.)

§ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

¹ P. Charpin, R. Costes, G. Folcher, P. Plurien, A. Navaza, and C. de Rango, *Inorg. Nuclear Chem. Letters*, 1977, **13**, 341; R. M. Costes, G. Folcher, P. Plurien, and P. Rigny, *ibid.*, 1976, **11**, 13; 1976, **12**, 491.

² G. Bombieri, G. de Paoli, A. Cassol, and A. Immirzy, *Inorg. Chim. Acta*, 1976, **18**, L23.

³ M. E. Harman, F. A. Hart, M. B. Hursthouse, G. P. Moss, and P. R. Raithby, *J.C.S. Chem. Comm.*, 1976, 396.

⁴ J. D. Dunitz, M. Dobler, P. Seiler, and R. P. Phizacker, *Acta Cryst.*, 1974, **B30**, 2733.

⁵ Complete details of the structure determination and n.m.r. results will be published elsewhere.