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Reactivity of dicyclopentadienyluranium(IV) derivatives: formation and structural characterization of an oxygen bridged cluster containing both inorganic and organometallic uranium atoms

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Abstract

Reactions of $[U(Cp)_2(NEt_2)_2]$ (Cp = η^5-cyclopentadienyl) and $[U(Cp)_2(BH_4)_2]$ with $LiAlH_4$ in diethyl ether give $[U(Cp)_2(AlH_4)_2NEt_2]Li$ (**1**) and $[U(Cp)_2(AlH_4)_2] \cdot nEt_2O$ (**2**), respectively. Reaction of **2** with CH_3COOH gives a low yield of the cluster $[Cp(CH_3COO)_5U_2O]_2$ (**3**), whose crystal structure is reported. Complex **3** is a centrosymmetric tetranuclear dimer in which two $Cp(CH_3COO)_5U_2O$ moieties are connected by chelating carboxylato and oxide bridges. A peculiarity of **3** is the presence of two oxygens each of them bridging three uranium atoms.

Introduction

Organometallic uranium(IV) compounds of the type $[U(Cp)_2X_2]$ have been neglected compared with the homologous derivatives $[U(Cp^{Me})_2X_2]$($Cp^{Me} = \eta^5 - C_5(CH_3)_5$) [1]. This is probably due to the enhanced stability of $[U(Cp^{Me})_2X_2]$ complexes towards the ligand redistribution which occurs readily with $[U(Cp)_2X_2]$ derivatives:

$$2Cp_2UX_2 \xrightarrow{S} Cp_3UX + CpUX_3 \cdot 2S$$

(S = O or N monodentate coordinating solvents)

The matter has been extensively discussed by Li Xing-fu in respect of coordination and organometallic compounds of lanthanide and actinide elements on the basis of the steric packing of the ligands [2], and he concluded that the dispro-

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portionation process can be avoided only for a suitable combination of steric features of both the Cp group (which can be varied by replacing the ring hydrogen atoms by organic groups) and the X ligands. Thus compounds with substituted cyclopentadienyl groups ($C_5H_{5-n}R_n$; R = CH_3, $(CH_3)_3Si$) [3] or bulky X ligands [4] have mainly been described so far.

The poor stability of $[U(Cp)_2Cl_2]$ means that it cannot be used as a precursor for other $[U(Cp)_2X_2]$ compounds through simple metathetical displacement of Cl^- by X^-, but such $[U(Cp)_2X_2]$ compounds can be expected to show interesting structural and electronic properties and reactions if the analogy with their group 4 congeners $[M(Cp)_2X_2]$ (M = Ti, Zr, Hf) [5] and the peculiarities of uranium are taken into consideration. Here we report on a convenient synthesis of $[U(Cp)_2(BH_4)_2]$ starting from $[U(Cp)_2(NEt_2)_2]$ and $BH_3 \cdot S(CH_3)_2$, and on the reactivity of $[U(Cp)_2X_2]$ (X = NEt_2, BH_4) involving replacement of X by the tetrahydroaluminate anion. This process leads to the formation of other new $[U(Cp)_2X_2]$ derivatives with no or negligible tendency towards disproportionation. The synthesis and the structural characterization of the cluster $[Cp(CH_3COO)_5U_2O]_2$, formed unexpectedly in the reaction of $[U(Cp)_2(AlH_4)_2]$ with CH_3COOH, are described.

Experimental

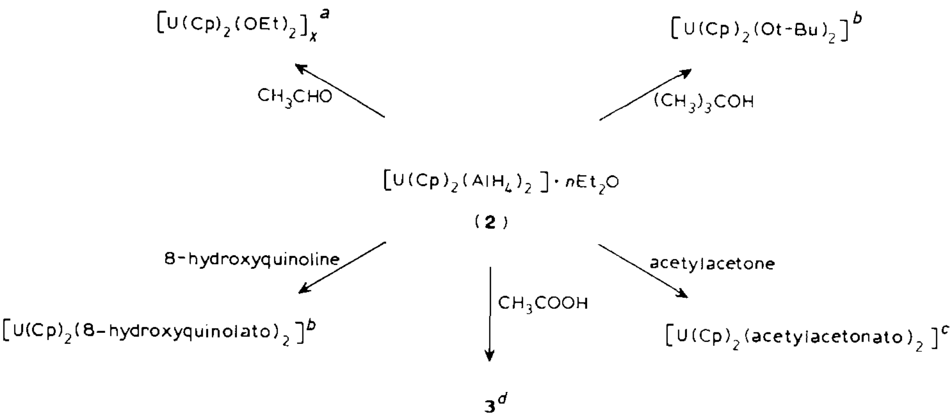
All the reactions were carried out in glove boxes filled with dry nitrogen.

Solvents were purified by distillation from potassium under nitrogen in presence of benzophenone as an indicator. $[U(Cp)_2(NEt_2)_2]$ was prepared as described in ref. 4b. Borane-methyl sulphide (Janssen) in toluene solution was titrated against t-butylamine and used without further purification. Elemental analyses were performed by Dornis und Kolbe Mikroanalytisches Laboratorium Mulheim, F.G.R. Infrared spectra were recorded with a Perkin–Elmer 580 B apparatus (Nujol mulls sandwiched between KBr plates in a sealed air-tight holder). The ^1H NMR spectra were recorded with a Varian FT-80A spectrometer. (C_6D_5H as internal standard, chemical shifts calculated respect to TMS).

$[U(Cp)_2(BH_4)_2]$. 2 mmol of $[U(Cp)_2(NEt_2)_2]$ were dissolved in 50 ml of toluene and 4 ml of $BH_3 \cdot$ DMS 2*M* in toluene were added. The mixture was stirred for one day and the solvent then evaporated to leave a red-brown solid, which was dissolved in Et_2O. The solution was filtered and then evaporated to give $[U(Cp)_2(BH_4)_2]$ in almost quantitative yield. This new method of making $[U(Cp)_2(BH_4)_2]$ proved to be more convenient than that described in ref. 6.

$[U(Cp)_2(NEt_2)(AlH_4)_2]Li$ (1). A saturated solution of $LiAlH_4$ in Et_2O was added dropwise to a brown solution of $[U(Cp)_2(NEt_2)_2]$ (2 mmol) in 50 ml of Et_2O at room temperature, a green precipitate immediately separated out. After addition of a moderate excess of $LiAlH_4$ the precipitate was filtered off, washed several times with Et_2O and dried under vacuum. Complex **1** was oxygen and moisture sensitive, and ignited spontaneously on exposure to the atmosphere. (Found: C, 32.23; H, 5.26; N, 2.49; U, 46.18; Al, 10.59. $C_{14}H_{28}Al_2NULi$ calcd.: C, 33.02; H, 5.54; N, 2.75; U, 46.74 Li, 1.36; Al, 10.59%). IR(Nujol, KBr disks) ν_{max}: 1750–1600 broad, 1080 sh, 1050 m, 1010 m, 860 broad, 775 s, 740sh, 720 sh cm^{-1}.

$[U(Cp)_2(AlH_4)_2] \cdot nEt_2O$ (2). A saturated solution of $LiAlH_4$ in Et_2O was added dropwise to a red-brown solution of $[U(Cp)_2(BH_4)_2]$(2 mmol) in 50 ml of Et_2O at room temperature. The green precipitate that immediately separated out



Scheme 1. Reactions of **2**. (*a*) see text ref. 4c. (*b*) P. Zanella, G. Rossetto and G. Paolucci, Inorg. Chim. Acta, 82 (1984) 227. (*c*) A. Dormond, A. Dahchour and C. Duval-Huet, J. Organomet. Chem., 224 (1982) 251. (*d*) this work.

was filtered off, washed with Et_2O, and dried. The elemental analysis was consistent with the formulation $[U(Cp)_2(AlH_4)_2]\cdot 0.75Et_2O$. Complex **2** was oxygen and moisture sensitive and ignited spontaneously on exposure to the atmosphere. (Found: C, 32.01; H, 4.80; U, 48.71; Al, 10.54. $C_{13}H_{25.5}UAl_2O_{0.75}$ calcd.: C, 32.13; H, 5.08; U, 49.02; Al, 11.12%). IR(Nujol,KBr disks): ν_{max}: 1750 (broad)s, 1010 s, 780 s, 705 (broad)m cm^{-1}.

The IR spectrum was also recorded for the compound obtained by treatment of $[U(Cp)_2(BH_4)_2]$ with $LiAlD_4$. The spectrum was the same as before except that the absorptions at 1750 and 705 cm^{-1} were absent, and broad bands were observed at ca. 1280 and 505 cm^{-1}.

Reaction of 2 with t-butyl alcohol, acetylacetone, 8-hydroxyquinoline and acetaldehyde

These reactions were performed by adding a stoichiometric quantity of the reagent to a suspension of **2** in diethyl ether (n-hexane with acetylacetone). In each case, after some minutes' stirring the solutions were filtered and the solvent removed under vacuum. The residues were redissolved in C_6D_6 and examined by ^1H NMR spectroscopy. The spectra revealed the presence of organouranium products only (see Scheme 1), which were identified by use of ^1H NMR data in the literature.

Reaction of 2 with CH_3COOH:

A suspension of ca. 80 mg of **2** in 15 ml of Et_2O was treated dropwise with an excess of CH_3COOH. Gas evolution was observed for about 30 min, the solution became pale green, and an unidentified greenish residue separated out. The solution was filtered, and after 48 h at room temperature gave a small amount of green crystals, which were characterized by X-ray diffraction as $[Cp(CH_3COO)_5U_2O]_2$ (**3**). The exact stoichiometry of the reaction was not assessed, but the preparation was repeated several times. Yields were always very low, but in each case the identity of the product **3** was confirmed by determining the unit cell and main structural parameters for the crystals isolated.

Crystal structure determination of $[Cp(CH_3COO)_5U_2O]_2$. A crystal of maximum dimension 0.2 mm was selected for the measurement of intensities. Data were collected on a Philips diffractometer with a graphite monochromator and Mo-K_α radiation. Cell dimensions were determined by least-squares refinement of 25 medium-angle settings.

Crystal data. $C_{30}H_{40}O_{22}U_4$, M = 1704, monoclinic, space group $P2_1/n$, a 14.127(5), b 12.366(5), c 12.793(5) Å, β 109.43(3)°, U 2108 Å^3, $Z = 2$ *, $D_c = 2.68$ g cm^{-3}, $\lambda(\text{Mo}-K_\alpha)$ 0.7107 Å, $\mu(\text{Mo}-K\alpha)$ 230.3 cm^{-1}. Intensities were measured by the ϑ–2ϑ method with a scan speed of 2° min^{-1} between 2 and 25°, yielding 4093 independent reflexions, 2666 of which were significantly above background ($I > 3\sigma(I)$). Data were corrected for Lp and for absorption [7]. Two standard reflexions measured periodically were constant within experimental uncertainty. The structure was solved by the heavy-atom method through Patterson and Fourier maps. Refinement, converged to give a final agreement index R of 0.036, when the largest parameter shift in the last cycle was ca. 0.1σ. The structure was refined by full-matrix least-squares, minimizing the function $\Sigma w \Delta F^2$ with $w = 1$. Scattering

Table 1

Atomic coordinates for **3**

Atom	x	y	z
U(1)	0.80675(4)	0.49244(5)	0.61029(4)
U(2)	0.92306(4)	0.43583(4)	0.36872(4)
O(1)	0.6907(7)	0.5233(10)	0.4307(8)
O(2)	0.7590(6)	0.5004(10)	0.2982(8)
O(3)	0.9190(8)	0.3554(9)	0.7182(9)
O(4)	1.0688(7)	0.3937(8)	0.7092(9)
O(5)	0.8133(7)	0.6811(8)	0.5693(8)
O(6)	1.0320(7)	0.2876(8)	0.4326(9)
O(7)	0.8953(8)	0.3633(10)	0.1853(8)
O(8)	0.9525(7)	0.5784(8)	0.7500(8)
O(9)	0.7573(8)	0.3173(9)	0.5271(10)
O(10)	0.8270(8)	0.2939(8)	0.3980(8)
O(11)	0.9189(5)	0.4897(7)	0.5288(7)
C(1)	0.6882(11)	0.5287(12)	0.3320(14)
C(2)	0.5930(10)	0.5718(14)	0.2407(13)
C(3)	1.0064(11)	0.3278(13)	0.7262(13)
C(4)	1.0359(15)	0.2139(15)	0.7556(22)
C(5)	0.8761(10)	0.7387(11)	0.5466(11)
C(6)	0.8447(12)	0.8454(14)	0.4917(16)
C(7)	0.9783(11)	0.3772(13)	0.1729(13)
C(8)	0.9955(16)	0.3384(18)	0.0697(16)
C(9)	0.7807(10)	0.2604(11)	0.4614(12)
C(10)	0.7576(15)	0.1416(13)	0.4533(16)
C(11)	0.7484(13)	0.4846(17)	0.7949(14)
C(12)	0.7150(13)	0.5877(15)	0.7505(15)
C(13)	0.6399(14)	0.5707(16)	0.6474(17)
C(14)	0.6227(11)	0.4581(17)	0.6330(16)
C(15)	0.6918(13)	0.4045(15)	0.7245(16)

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* The molecules are dimeric, each dimer being formed by two asymmetric units. Thus there are four asymmetric units, but only two molecules in the unit cell.

Table 2

Selected bond and contact distances (Å) for **3**. (a) Average U–C distance for the five carbons of the η^5-C_5H_5 ring. The C–C bonds in the ring are all 1.41(2) Å. U...Cp indicates the distance from the centroid of the ring.

U(1)–O(1)	2.37(1)	U(2)–O(2)	2.33(1)
U(1)–O(3)	2.42(1)	U(2)–O(44)	2.35(1)
U(1)–O(5)	2.40(1)	U(2)–O(66)	2.36(1)
U(1)–O(88)	2.47(1)	U(2)–O(7)	2.42(1)
U(1)–O(9)	2.41(1)	U(2)–O(8)	2.69(1)
U(1)–O(11)	2.17(1)	U(2)–O(10)	2.32(1)
U(1)–Cp^a	2.75(2)	U(2)–O(11)	2.17(1)
U...Cp	2.49(1)	U(22)–O(11)	2.37(1)
C(1)–O(1)	1.25(2)	C(3)–O(3)	1.25(2)
C(1)–O(2)	1.26(2)	C(3)–O(4)	1.27(2)
C(1)–C(2)	1.55(2)	C(3)–C(4)	1.48(2)
C(5)–O(5)	1.24(2)	C(7)–O(7)	1.25(2)
C(5)–O(6)	1.28(2)	C(7)–O(8)	1.26(2)
C(5)–C(6)	1.49(2)	C(7)–C(8)	1.50(2)
C(9)–O(9)	1.22(2)	U(1)...U(2)	4.015(1)
C(9)–O(10)	1.27(2)	U(1)...U(22)	3.840(1)
C(9)–C(10)	1.50(2)	U(2)...U(22)	3.697(1)
		O(11)...O(111)	2.64(1)

factors for *U* were from ref. 8 and those for C and O were suplied internally by SHELX [9]. The uranium scattering factor was corrected for anomalous dispersion by use of constant average values of $\Delta f' = -10.67$ and $\Delta f'' = 9.65$ for the real and imaginary components. Calculations were carried out with the SHELX program system [9]. Final atomic coordinates are listed in Tab. 1 and bond lengths and angles in Tables 2 and 3.

Results and discussion

Both $[U(Cp)_2(BH_4)_2]$ and $[U(Cp)_2(NEt_2)_2]$ react quantitatively and immediately with $LiAlH_4$ in diethyl ether to give **2** and **1**, respectively. The products were characterized by elemental analysis and infrared spectroscopy. The reactions may be represented as follows:

$$[Cp_2U(BH_4)_2] + 2LiAlH_4 \xrightarrow{Et_2O} [Cp_2U(AlH_4)_2] \cdot nEt_2O + 2LiBH_4$$

$$[Cp_2U(NEt_2)_2] + 2LiAlH_4 \xrightarrow{Et_2O} [Cp_2U(AlH_4)_2(NEt_2)]Li + LiNEt_2$$

Both **1** and **2** are green microcrystalline powders and easily separable from the other reaction products because they are completely insoluble in Et_2O, in which $LiBH_4$ or $LiNEt_2$ are very soluble. Et_2O appears to be the most suitable solvent for the synthesis, aromatic solvents (toluene or benzene), THF and DME, causing more or less rapid decomposition of **1** and **2**. The IR bands at 1010 and at 770 cm^{-1} for both **1** and **2** can be ascribed to η^5-coordinated Cp groups [10]. Complex **2** shows broad bands in its infrared spectrum at about 1750 and 705 cm^{-1}, characteristic of

Table 3

Selected bond angles (°) for **3**

Angles at U(1)			
Cp...U(1)–O(11)	177.6(3)	O(5)–U(1)–O(11)	79.7(3)
Cp...U(1)–O(1)	96.2(3)	O(88)–U(1)–O(11)	77.9(3)
Cp...U(1)–O(3)	100.4(3)	O(9)–U(1)–O(11)	85.7(4)
Cp...U(1)–O(5)	98.8(3)	O(1)–U(1)–O(5)	72.3(4)
Cp...U(1)–O(88)	99.9(3)	O(5)–U(1)–O(88)	69.8(4)
Cp...U(1)–O(9)	96.6(3)	O(88)–U(1)–O(3)	70.0(4)
O(1)–U(1)–O(11)	85.3(3)	O(3)–U(1)–O(9)	70.2(4)
O(3)–U(1)–O(11)	79.5(3)	O(9)–U(1)–O(1)	73.2(4)
Angles at U(2)			
O(7)–U(2)–O(11)	169.0(3)	O(11)–U(2)–O(66)	73.9(3)
O(7)–U(2)–O(8)	49.7(3)	O(11)–U(2)–O(111)	71.0(3)
O(7)–U(2)–O(2)	86.1(4)	O(11)–U(2)–O(10)	83.1(3)
O(7)–U(2)–O(44)	86.3(4)	O(2)–U(2)–O(44)	73.2(3)
O(7)–U(2)–O(66)	85.7(4)	O(44)–U(2)–O(66)	136.6(4)
O(7)–U(2)–O(111)	120.0(4)	O(66)–U(2)–O(111)	73.9(4)
O(7)–U(2)–O(10)	87.8(4)	O(66)–U(2)–O(11)	97.5(4)
O(11)–U(2)–O(2)	85.6(3)	O(10)–U(2)–O(2)	76.3(4)
O(11)–U(2)–O(44)	98.3(3)	O(11)–U(2)–O(44)	73.5(3)
Angles at bridging oxygens			
U(1)–O(11)–U(2)	135.3(4)	U(2)–O(11)–U(22)	108.9(4)
U(1)–O(11)–U(22)	115.7(4)	U(11)–O(8)–U(2)	96.1(4)
Angles at acetate oxygens			
U(1)–O(1)–C(1)	140(1)	U(2)–O(2)–C(1)	140(1)
U(1)–O(3)–C(3)	133(1)	U(22)–O(4)–C(3)	141(1)
U(1)–O(5)–C(5)	134(1)	U(22)–O(6)–C(5)	140(1)
U(11)–O(8)–C(7)	175(1)	U(2)–O(7)–C(7)	102(1)
U(1)–O(9)–C(9)	136(1)	U(2)–O(10)–C(9)	143(1)
		U(2)–O(8)–C(7)	89(1)
Acetates			
C(2)–C(1)–O(1)	120(1)	C(4)–C(3)–O(3)	118(2)
C(2)–C(1)–O(2)	115(2)	C(4)–C(3)–O(4)	120(1)
O(1)–C(1)–O(2)	125(1)	O(3)–C(3)–O(4)	122(2)
C(6)–C(5)–O(5)	120(1)	C(8)–C(7)–O(7)	120(2)
C(6)–C(5)–O(6)	117(1)	C(8)–C(7)–O(8)	121(2)
O(5)–C(5)–O(6)	124(1)	O(7)–C(7)–O(8)	119(1)
C(10)–C(9)–O(9)	121(1)		
C(10)–C(9)–O(10)	115(1)		
O(9)–C(9)–O(10)	124(1)		

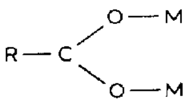
bridging and terminal aluminohydrides [11], which are shifted to 1280 and 505 cm^{-1} in the corresponding deuterated compounds (shift factor 1.37 and 1.40, respectively). Complex **1** shows a similar absorption spectrum; unfortunately features attributable to the NEt_2 group cannot be distinguished from those due to the AlH_4 group. The insolubility and involatility of both **1** and **2**, together with the tendency of the aluminohydrides to dimerize or polymerize [11,12] suggest a polymeric structure for the two compounds; their properties contrast with those of the corresponding borohydrides $[U(Cp)_{4-n}(BH_4)_n]$ ($n = 1,2,3$), which are volatile, well soluble, and monomeric [3c].

Complex **2** is very reactive, and some of its reactions are ilustrated in Scheme 1. (The products were identified by ^1H NMR spectroscopy by use of data in the literature). Complex **2**, like $[U(Cp)_3AlH_4]$ [12,13], was found to react with solvents such as benzene, toluene, and tetrahydrofuran, but we could not identify the products. However, well defined products of the type $[U(Cp)_2X_2]$ (X = t-butoxide, acetylacetonato, 8-hydroxyquinolato) are formed by reaction with XH. With CH_3CHO, **2** gives a mixture which in benzene-d_6 shows a set of ^1H NMR signals corresponding to those ascribed to the compound $[U(Cp)_2(OC_2H_5)_2]$ and some weaker signals corresponding to those of $[(Cp_3U)_2U(OC_2H_5)_6]$ [4c].

In all the above reactions the Cp_2U moiety does not undergo any significant disproportionation. Noteworthy is also the reduction of acetaldehyde to an ethoxide group. Moreover **2** reacts with acetic acid to give a very low yield of green crystals of **3**. Preliminary tests on the reactions of **1** have shown that it is inert towards alcohols and $BH_3 \cdot L$. This considerable difference in reactivity between **1** and **2** could be attributed to the difference in the degree of coordinative unsaturation, since in **1** there is an additional NEt_2 ligand. In contrast with $[U(Cp)_2(BH_4)_2]$, which is solvent-free [6], there is an additional NEt_2 ligand bonded to uranium in **1** and an Et_2O ligand in **2**. This is probably due to the fact that whereas BH_4 is tri-hapto bonded to uranium [13,14], AlH_4 usually behaves as mono- or bi-hapto ligand [11], and so could leave the metal coordinatively unsaturated. Whereas the IR spectra of tetrahydroborate complexes have been fully interpretated and shown to indicate whether the BH_4 ligands are mono-, bi- or tri-hapto bonded [15], those of tetrahydroaluminate compounds do not provide this kind of information.

Crystal structure of $[Cp(CH_3COO)_5U_2O]_2$. The structure of **3** is shown in Fig. 1. The bonding parameters are reported in Table 2. Complex **3** may be regarded as a tetranuclear dimer in which two binuclear $[Cp(CH_3COO)_5U_2O]$ fragments are connected by chelating carboxylato and oxide bridges. The two binuclear units in turn are formed by the junction, also through oxygen bridges, of the moieties $[U(Cp)(ac)_2O_{1/2}]$ and $[U(ac)_3O_{1/2}]$ (where ac = CH_3COO), i.e. an organometallic uranium moiety and an inorganic one. The entire molecule is centrosymmetric and each asymmetric unit (one half of the molecule) comprises the two independent uranium atoms U(1) and U(2) (Fig. 1). Its geometry closely resembles that of the $[U_4O_2(O_2CNEt_2)_{12}]$ (**4**) [16]; both molecules have an almost planar U_4O_2 core in which each oxygen is bonded to three uranium atoms. Moreover the ligands (acetate or diethylcarbamate) behave either as bridging or as terminal and bridging ligands (see below).

Several interesting geometrical and structural features of **3** are noteworthy. Eight of the ten acetato groups show the usual bidentate *syn–syn* bridging coordination with the two carboxylate oxygen atoms bound to two different uranium atoms. The U–O–C angles for U = U(1), U(11) (i.e. organometallic uranium atoms) range from 133° to 140°, while for U = U(2), U(22) the angle is in the range 140–143°; both values are larger than those found for analogous polynuclear complexes of the type:



(M = Cu, Zn)

in which they are ca. 123° (Cu) [17a] and 132° (Zn) [17b]. It is noteworthy that in **4**, where M = U and R = NEt_2, the M–O–C angles of the bridging carbamates are in

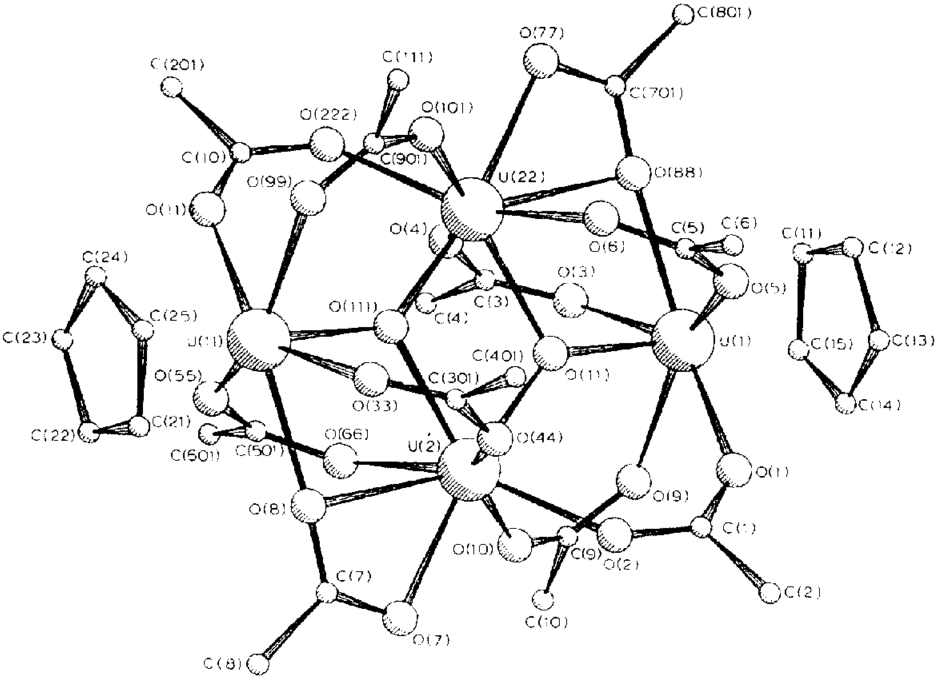
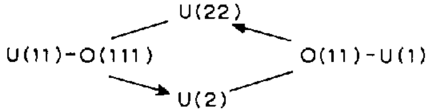


Fig. 1. Crystal structure of 3.

the range 131.6–140.5°. The range of values for M–O–C angles can be related to the different ionic radius of M, and so to the metal–metal distance, which is 2.645 Å for M = Cu [17a], 3.162 Å for M = Zn [17b] and 3.697 Å in the present case. However, the M–M distance does not significantly affect the O–C–O angle, which in all cases is between 119° and 125°. On the other hand the C–C and C–O bond lengths and the O–C–O bond angles are in the normal range. The two carboxylato groups of the remaining acetates act also as bridging ligands but one of the O atoms (O(8) and O(88)) is bonded to a pair of adjacent U atoms (U(1), U(22) and U(11), U(2) respectively). This coordination mode is rather unusual, but not unprecedented; a similar oxygen bonding has been observed in **4** and in the polymeric $[U(CH_3COO)_4]_n$ structure [18], even though in the latter the two U–O bond distances are longer (2.52 and 2.80 Å) than in **3**, where the U(1)–O(88) distance is 2.47 Å, while U(2)–O(8) is 2.69 Å. However, although the related C–O distances are not affected by the bonding situation (in fact C(7)–O(8), 1.26 Å, is quite similar to C(7)–O(7) which is 1.25 Å), the angles in this carboxylate group are very different from those in the others (see Table 3). Thus C(7)–O(8)–U(11) is almost linear (175°), C(7)–O(8)–U(2) and U(11)–O(8)–U(2) are almost right angles (89° and 96°, respectively), and U(2)–O(7)–C(7) is unusually small (102°) compared with the other U–O–C angles in the molecule. The extra-coordination of O(8) moves it nearer to U(2), rotating jointly the C(8)–C(7)–O(8) system around O(7), reducing the U(2)–O(7)–C(7) angle and opening the C(7)–O(8)–U(11) angle; U(2)–O(7) and U(11)–O(8) are slightly, and U(2)–O(8) significantly, longer than the other U–O bonds. Thus O(8) represents one of the few known examples of very distorted carboxylate trigonal planar oxygen geometry [19]. This is also the geometry of the oxide O(11) and O(111) ligands, each bonding to three uranium atoms, viz. U(1), U(2), U(22) and U(11), U(2), U(22), respectively. Both of the U(1)–O(11) and U(2)–O(11) bond distances are 2.17 Å, while U(22)–O(11) is 2.37 Å. As in **4**, in the U_4O_2 core the U–O distances range from 2.147 to 2.294 Å, and the U_3O system can be considered planar. This feature suggests a formulation such as:



in which the O(11)–U(22) (O(111)–U(2)) bond could be considered to be coordinative **. The geometry of the whole system can be explained in term of a distorted sp^2-hybridization at O(11)(O(111)), which would make the remaining *p*-lone pair on the oxygen atom available for π-donation to uranium atoms; this possibility is supported by the similarity of the O(11)–U(1) (O(111)–U(11)) and O(11)–U(2) (O(111)–U(22)) bond distances to those in other systems for which partial U–O double bonding has been suggested [21].

The four uranium atoms form a parallelogram of sides 3.840 Å and 4.015 Å, respectively, (the shorter diagonal U(2)–U(22) is 3.697 Å) as represented in the above diagram. These figures indicate that no U–U bonds are present, since the distances are all longer than the value of 3.5° Å suggested by Cotton [22] to represent the upper limit for U–U bonding interactions. Similarly, O(11)–O(111) interactions can be ruled out, since the distance (2.64 Å) is of the same order as that found in 8-coordinated [U(dibenzoylmethanato)$_4$] [23] for independent adjacent oxygen atoms.

In respect of the U–Cp coordination, we note that the mean U–C bond lengths (Table 2) agree well with those for other [$UCpX_3$] complexes [24]. In particular the geometry around the U(1) and U(11) atoms is strongly reminiscent of that around the uranium atoms in compounds such as [U(Cp)Cl(ac-ac)$_2$(OPPh$_3$)] (**5**) [25], [UCp(phosphoylide)$_3$] (**6**) [26] and [$\{UIndBr(CH_3CN)_4\}_2O]^{2+}[(UBr_6)]^{2-}$ (**7**) [27], which are examples of unusual pentagonal bipyramidal coordination around the uranium atom. In our compound the apical positions are occupied by the Cp centroids and by O(11) and O(111) atoms respectively (the angles Cp–U(1)–O(11) and Cp–U(11)–O(111) are both 177°, i.e. almost linear) while five acetate oxygens are approximately in the basal plane of the bipyramid (they actually deviate within ±0.25 Å from the base plane) and the U(1) atom is slightly displaced towards the Cp ring by 0.35 Å. Consequently the Cp–U(1)–O_{eq} and O(11)–U(1)–O_{eq} angles are respectively a little above (96–100°) and below (77–86°), a right angle. This situation probably arises from intramolecular Cp ligand–O_{eq} repulsion, which is also responsible for the staggered disposition of the Cp and the O_{eq} pentagon. The nearest C_{cp}–O_{eq} distance (3.30 Å) is fairly similar to the distances found for the atoms in the corresponding positions of the above mentioned compounds **5**, **6** and **7**.

Complex **3** therefore represents one of the few structurally characterized examples of an organometallic uranium species having five bonded atoms in the equatorial plane. Moreover U(2) (U(22)) is eight coordinated in a rather irregular geometry, which cannot be easily compared with any of the usual models for U with

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** Typical examples of U–O dative bonds are found in [UBr_3]·THF·TPPO in which U–O_{THF} and U–O_{TPPO} are 2.47 Å and 2.32 Å, respectively [20].

8 coordination. However, this coordination number does represent a stable situation for U(1) being reached via an unusual bonding of O(88), which results in significant distortion in the carboxylato group (vide infra).

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