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A dinuclear uranium(IV) complex of the chelating ligand 1,2,3,4-tetramethyl-5-(2-pyridyl)cyclopentadiene

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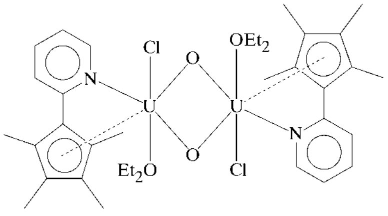
The ligand 1,2,3,4-tetramethyl-5-(2-pyridyl)cyclopentadiene (cp*py) forms a dinuclear complex with U^{IV}, *i.e.* di-μ-oxo-bis{chloro(diethyl ether-κO)[(η^5,κN)-1,2,3,4-tetramethyl-5-(2-pyridyl)cyclopentadienyl]uranium(IV)}, $[U_2Cl_2O_2(C_{14}H_{16}N)_2(C_4H_{10}O)_2]$, in which cp*py acts as a chelating ligand, being bound to the metal atom by the cyclopentadienyl unit and also by the N atom of the pyridyl ring.

Comment

In the course of our studies on the uranium-complexing properties of the ligand 1,2,3,4-tetramethyl-5-(2-pyridyl)-cyclopentadiene, denoted cp*py, with a view to obtaining uranium-containing heterobimetallic species, we obtained the title compound, (I), which is a dinuclear U^{IV} complex presenting some interesting features.



(I)

The asymmetric unit in (I) comprises one neutral complex molecule, which possesses approximate inversion symmetry. cp*py acts as a chelating ligand, as in another previously described U^{IV}–cp*py complex (Moisan *et al.*, 2002*a*). Whereas several examples have been reported in which the two ligating sites of cp*py are bound to different metal atoms (Neumann *et al.*, 1997), these uranium complexes are the first examples in which cp*py (or its equivalent without methyl groups, cppy) is bound by the η^5-cp* ring and the N atom to the same metal centre. The mean U—C bond length is 2.78 (8) Å, the U···centroid distances are 2.509 and 2.519 Å for U1 and U2, respectively, and the mean U—N bond length is 2.57 (3) Å; the U—C distance, in particular, may be slightly longer than in the previous complex [mean U—C 2.72 (9) Å and mean U—N 2.553 (9) Å]. Such a coordination mode in cp*py, where the N atom is brought closer to the U atom, results in a distortion which is seen in the displacement of atoms C2/C5 and C16/C19 out of the corresponding tetramethylcyclopentadienyl mean planes. These displacements are 1.76 (6), 0.52 (4), 1.69 (5) and 0.47 (4) Å, respectively, slightly larger than in the previous complex [1.62 (3) and 0.42 (2) Å] because of the larger U—C bond lengths. The dihedral angles between the five- and six-membered rings are 74 (1) and 73 (1)° for the two ligands, slightly greater than in the previous compound [71.7 (4)°], probably for the same reason. The two cyclopentadienyl rings in (I) are nearly parallel, with a dihedral angle of 3 (1)°, as are the pyridyl units, with a dihedral angle of 4.0 (9)°, in accord with the presence of a pseudosymmetry centre.

Atoms U1 and U2 are each also bound to a chloride ion, with a mean bond length of 2.62 (2) Å, and to a diethyl ether molecule, with a mean U—O bond length of 2.15 (4) Å, much shorter than the mean U—O(diethyl ether) bond length found from the Cambridge Structural Database (CSD; Allen & Kennard, 1993) of *ca* 2.50 Å. Furthermore, the range of published U—O(ether) distances is fairly narrow and does not extend much below 2.40 Å, and the short distances observed here are more compatible with U—O(anion) distances. However, the assignment of these ligands as anions is not chemically rational and would upset the charge balance in the structure; moreover, both diethyl ether molecules are clearly visible in difference Fourier syntheses. Accordingly, this aspect of the structure must be treated with some caution. Two μ-oxo ions bridge the two metal atoms, with a mean U—O bond length of 2.10 (3) Å and a mean U—O—U angle of 108.6 (4)°, in good agreement with the mean values for structures of di-μ-oxo-bridged uranium(IV) dimers found in the CSD [2.14 (4) Å and 106.7 (5)°].

If the cyclopentadienyl ring is represented by its centroid and the difference in nature between the donor atoms is

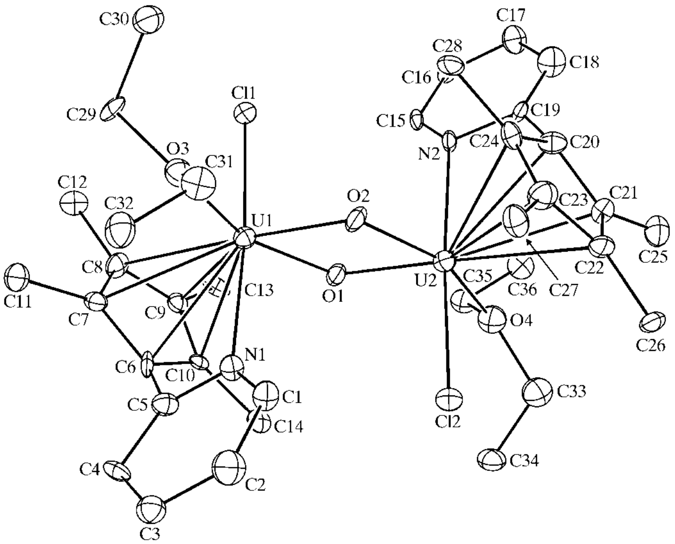


Figure 1
View of the title molecule with the atom-numbering scheme. H atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 10% probability level.

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neglected, the U ions are in very distorted octahedral environments, with the common edge O1···O2. Atoms U1, U2, O1 and O2 define a plane with a maximum deviation of 0.03 (2) Å. This plane is nearly orthogonal to that defined by atoms U1, U2, Cl1 and Cl2 [maximum deviation 0.054 (9) Å], with a dihedral angle of 80.4 (5)°. Atoms N1 and N2 are close to the second plane, with respective deviations of 0.15 (2) and −0.02 (2) Å, but atoms O3 and O4 and the centroids of the cyclopentadienyl rings are more distant from the first plane, with deviations in the range 0.22 (3)–1.00 (2) Å. The U···U distance [3.401 (2) Å] matches the mean distance in the three dinuclear di-μ-oxo-bridged U^{IV} complexes reported in the CSD [3.43 (7) Å]. This U···U distance is much larger than that corresponding to a U—U single bond (2.85 Å; Cayton *et al.*, 1991), indicating that no bonding interaction is present between the metal atoms in (I).

Experimental

The lithium salt of the cp*py ligand was synthesized by a procedure described in the literature (Siemeling *et al.*, 1995). The reaction of two equivalents of Li(cp*py) with UCl_4 in tetrahydrofuran (THF) at ambient temperature gives the complex $UCl_2(cp*py)_2$ (Moisan *et al.*, 2002*b*). Single crystals of (I) were obtained from a solution of $UCl_2(cp*py)_2$ in THF/Et_2O, in the presence of adventitious traces of oxygen.

Crystal data

$[U_2Cl_2O_2(C_4H_{10}O)_2(C_{14}H_{16}N)_2]$
M_r = 1123.76
Monoclinic, $P2_1/c$
a = 11.6695 (8) Å
b = 18.2129 (12) Å
c = 19.1940 (13) Å
β = 106.420 (4)°
V = 3913.0 (5) Å^3
Z = 4
D_x = 1.908 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 20 390 reflections
θ = 3.2–25.7°
μ = 8.44 mm^{-1}
T = 100 (2) K
Parallelepiped, black
0.35 × 0.15 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer
φ scans
Absorption correction: empirical *PLATON* (Spek, 2000)
T_{min} = 0.108, T_{max} = 0.430
20 386 measured reflections
7087 independent reflections
2097 reflections with $I > 2\sigma(I)$
R_{int} = 0.093
θ_{max} = 25.7°
$h = -14 \rightarrow 14$
$k = -22 \rightarrow 22$
$l = -23 \rightarrow 23$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.087
$wR(F^2)$ = 0.184
S = 0.92
7087 reflections
427 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0166P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.81 e Å^{-3}
$\Delta\rho_{min}$ = −1.13 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

U1—U2	3.401 (2)	U2—O1	2.116 (15)
U1—O1	2.081 (17)	U2—O2	2.054 (17)
U1—O2	2.129 (16)	U2—O4	2.18 (2)
U1—O3	2.12 (2)	U2—N2	2.55 (2)
U1—N1	2.59 (2)	U2—Cl2	2.604 (8)
U1—Cl1	2.637 (7)	U2—C20	2.70 (3)
U1—C6	2.71 (3)	U2—C21	2.79 (3)
U1—C7	2.78 (3)	U2—C22	2.92 (3)
U1—C8	2.85 (3)	U2—C23	2.87 (3)
U1—C9	2.84 (2)	U2—C24	2.69 (3)
U1—C10	2.69 (2)		
U1—O1—U2	108.3 (7)	U1—O2—U2	108.8 (7)

The atoms of the diethyl ether units were refined with anisotropic displacement ellipsoids restrained to an approximate isotropic behaviour. All H atoms were introduced at calculated positions as riding atoms, with C—H bond lengths of 0.93 (CH), 0.97 (CH_2) and 0.96 Å (CH_3), and a displacement parameter equal to 1.2 (CH and CH_2) or 1.5 (CH_3) times that of the parent atom. The methyl groups were refined as rigid rotating units.

Data collection: *KappaCCD Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXTL* and *PARST*97 (Nardelli, 1995).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1473). Services for accessing these data are described at the back of the journal.

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