

tacts. The $Cu(NCS)_2^-$ moiety deviates from linearity, e.g. $N'-Cu-N = 173(1)$ and $Cu-N-C = 166(3)^\circ$, with a $3.055(9)$ Å separation between S' of one molecule and $Cu(-x, -1-y, 1-z)$ of another. In the BEDT-TTF superconducting salts the $Cu(NCS)_2^-$ ions form tricoordinated two-dimensional sheets which lie at the ends of the BEDT-TTF stacks and allow short $S \cdots S$ interstack contacts. The DBTTF ion is slightly bowed with the two planar phenyl rings (0.03 and 0.04 Å r.m.s. deviation) making an angle of $5(1)^\circ$. The EPR spectrum of a single crystal gave a single intense line (width 3.5×10^{-3} T). Attempts to measure the conductivity of the single crystal used for X-ray diffraction studies were unsuccessful, and compressed powders did not maintain their integrity.

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Structure of Dibenzoatodioxouranium(VI)

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Abstract. $[U(C_7H_5O_2)_2O_2]$, $M_r = 512.26$, monoclinic, $C2/m$, $a = 7.604(2)$, $b = 17.408(3)$, $c = 5.296(2)$ Å, $\beta = 95.81(2)^\circ$, $V = 697(2)$ Å³, $Z = 2$, $D_x = 2.44$ Mg m⁻³, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu = 11.0$ mm⁻¹, $F(000) = 468$, room temperature, $R = 0.058$ for 946 observations with $I > 3\sigma(I)$. The uranyl ion has a fourfold coordination. The coordination polyhedron around the uranium center approximates to an octahedron with the carboxylate groups acting as bridging donors.

Introduction. In the frame of a general study of the complexation of actinides by polycarboxylic ligands, we have undertaken the study of the complexation of

U^{VI} , Np^{VI} and Np^V by benzoic, 2-pyridinecarboxylic and 2,6-pyridinedicarboxylic acids. The aim of this work is to determine the influence of the N atom, which is present in the 2-pyridinecarboxylate and the 2,6-pyridinedicarboxylate, on the complexation, i.e. the nature of the metal–nitrogen bond. In this paper we present the structural study of a uranyl benzoate, benzoic acid being representative of aromatic polycarboxylic acids.

Experimental. Yellow single crystal of dimensions $0.060 \times 0.036 \times 0.330$ mm, grown during the reaction of uranyl hydroxide and benzoic acid in a sealed Pyrex tube at 400 K. Enraf–Nonius CAD-4 diffrac-

tometer with graphite monochromator, lattice parameters by a least-squares procedure from setting angles of 25 reflections, θ between 16 and 16.5° , collection of data up to $2\theta = 70^\circ$, measured for $-12 \leq h \leq 12$, $0 \leq k \leq 28$, $0 \leq l \leq 8$ using an $\omega/2\theta$ scan technique, corrections for background and Lorentz-polarization effects, negligible decay of intensity for the two standard reflections (4,10,0 and $1, \bar{1}, \bar{1}$) measured every hour (decomposition less than 2%), empirical absorption correction ($\mu = 11.0 \text{ mm}^{-1}$) using *DIFABS* (Walker & Stuart, 1983): ($T_{\text{max}} = 0.95$, $T_{\text{min}} = 0.72$), 1709 reflections measured, 1578 unique (merging factor 0.039). Structure solved by Patterson method and successive Fourier maps, H atoms found from difference series, complex atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99–101). All non-H atoms were given anisotropic thermal parameters, isotropic thermal parameter for H atoms. Full-matrix least-squares refinement on *F*. Final *R* values: $R_F 0.058$, $R_{F_2(w)} 0.066$ (unit weights) for 946 reflections ($I > 3\sigma$). $S = 1.1$ and $(\Delta/\sigma)_{\text{max}} = 0.2$. Max. height in final difference Fourier synthesis $3.6 \text{ e } \text{\AA}^{-3}$ localized on U atom. All calculations performed using *CRYSTALS* (Watkin, Carruthers & Betteridge, 1985) with a MicroVAX II computer.

Discussion. Atomic positional and thermal parameters are reported in Table 1* and intramolecular distances and angles are listed in Table 2. The numbering is shown in Fig. 1. Fig. 2 is a stereoscopic view of the packing [figures drawn using *ORTEP*; Johnson (1965)].

The primary coordination sphere of U^{VI} is octahedral with the $\text{O}(1)\text{—U—O}(1)$ axis (180°) perpendicular to the plane of the carboxylate groups, with the U atom located slightly above the plane of the carboxylate O atoms. The structure, in general, can be viewed as being built up from layers of infinite chains of the octahedral units bridged by the bidentate carboxylate groups. The forces between the sheets must be rather weak since no short distances have been observed in the *x* direction indicating the presence of hydrogen bonds.

The U—O distances vary between 1.75 (1) Å [for the $(\text{UO}_2)^{2+}$ group] to 2.282 (8) Å [for the U—O(2)]. The difference in bond length gives rise to a flattened polyhedron, commonly observed in uranyl compounds. A comparison of the bond length of U—O(2) to that determined for the U—O (carboxylate) of the uranyl benzene 1,2,4,5-tetracarboxylate

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53074 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Positional and thermal parameters (\AA^2)

$$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}	B_{iso}
U(1)	0.0000	0.0000	0.0000	0.0245	
O(1)	0.227 (2)	0.0000	0.096 (3)	0.0370	
O(2)	−0.041 (1)	0.0920 (5)	0.295 (2)	0.0418	
C(1)	0.0000	0.1275 (8)	0.5000	0.0294	
C(2)	0.0000	0.2127 (8)	0.5000	0.0231	
C(3)	0.078 (2)	0.2512 (7)	0.710 (3)	0.0404	
C(4)	0.079 (2)	0.3300 (8)	0.705 (4)	0.0476	
C(5)	0.0000	0.3700 (9)	0.5000	0.0458	
H(3)	0.12 (3)	0.23 (1)	0.86 (4)		0.08 (5)
H(4)	0.08 (3)	0.35 (1)	0.80 (5)		0.08 (5)
H(5)	0.0000	0.42 (2)	0.5000		0.08 (5)

Table 2. Selected interatomic distances (Å) and angles ($^\circ$)

U(1)—O(1)	1.75 (1)	C(2)—C(3)	1.38 (1)
U(1)—O(2)	2.282 (8)	C(3)—C(4)	1.37 (2)
C(1)—O(2)	1.26 (1)	C(4)—C(5)	1.38 (2)
C(1)—C(2)	1.48 (2)		
O(1)—U(1)—O(1)	180	O(2)—C(1)—O(2)	121.2 (13)
O(2)—U(1)—O(1)	89.9 (4)	C(3)—C(2)—C(1)	119.1 (7)
O(2)—U(1)—O(1)	90.1 (4)	C(3)—C(2)—C(3)	121.8 (14)
O(2)—U(1)—O(2)	180	C(4)—C(5)—C(4)	119.3 (15)
O(2)—U(1)—O(2)	90.8 (4)	C(1)—O(2)—U(1)	153.7 (8)
O(2)—U(1)—O(2)	89.2 (4)	C(4)—C(3)—C(2)	118.6 (14)
O(2)—C(2)—C(2)	119.4 (7)	C(3)—C(4)—C(5)	120.9 (15)

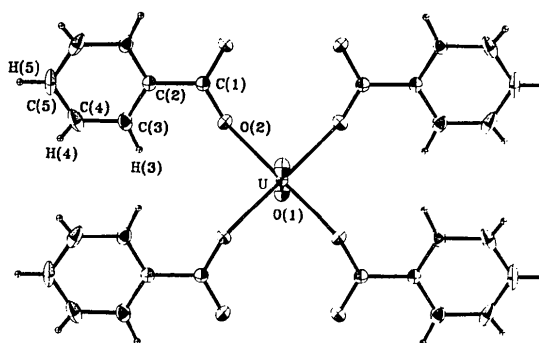


Fig. 1. ORTEP drawing of the molecule.

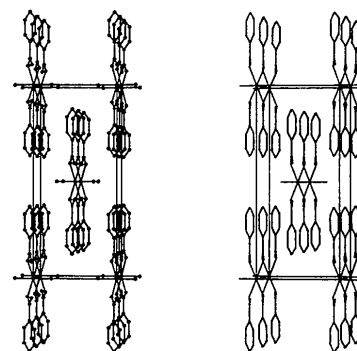


Fig. 2. ORTEP stereoview of the structure.

dihydrate (Cousson, Stout, Nectoux, Pagès & Gasperin, 1986) indicate a significant shortening in the benzoate complex. The same conclusions can be extended to comparisons with the structure of the diaqua(benzoato)chlorodioxouranium(VI) (Charpin, Keller, Lance & Vigner, 1989). Such shortening is associated with the expansion in the coordination sphere of the U atom (hexagonal bipyramid in the latter cases). According to Evans (1963), the uranyl group tends to coordinate four, five or six donor atoms in the equatorial plane with a strong tendency to arrange these atoms in a planar way. Fourfold and fivefold coordination provide the most stable arrangement. Stable planar sixfold coordination is observed when the coordination sphere contains

highly polarized bidentate anionic groups, otherwise a puckered, less stable structure is formed with a possible expansion in the bond length.

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Structure of Tris(η^5 -cyclopentadienyl)phenolatouranium(IV)

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Abstract. $[\text{U}(\text{C}_6\text{H}_5\text{O})(\text{C}_5\text{H}_5)_3]$, $M_r = 526.42$, orthorhombic, $P2_12_12_1$, $a = 8.331(3)$, $b = 8.899(3)$, $c = 23.337(5)$ Å, $V = 1730(2)$ Å³, $Z = 4$, $D_x = 2.021$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 88.973$ cm⁻¹, $F(000) = 984$, $T = 295(1)$ K, $R = 0.025$ for 2190 observed reflections. The three cyclopentadienyl rings are η^5 -covalently bonded to uranium to form a distorted tetrahedron with the oxygen of the phenoxide. The most important feature is the presence of the oxo functional group with a U—O distance of 2.119(7) Å and a U—O—C(16) angle of 159.4(5)°.

Introduction. The geometry of the large class of compounds of the type Cp_3MY , where M is a lanthanide or an actinide, Y a monodentate Lewis base,

anion or η^1 -bridging Cp ring, is best described as a flattened tetrahedron (Lippard, 1979) in which the Cp rings are shifted towards the sterically less bulky Y ligand, decreasing the $Y-M-Cp$ (centroid) angles and increasing the $Cp-M-Cp$ angles. Among this class, organometallic uranium(IV) compounds have been widely investigated in recent years but little information has been reported on the mixed-ligand complexes $\text{Cp}_3\text{U}(XR)$ where $R = \text{alkyl}$ or aryl, $X = \text{Group VI donor atom}$ (e.g. O or S). The title compound was prepared and its structure determined in order to verify that its geometry was consistent with that of the Cp_3MY species.

Experimental. The title compound was prepared by reaction of tricyclopentadienyluranium chloride with potassium phenoxide in tetrahydrofuran (von Ammon, Fischer & Kanellakopoulos, 1972). Extraction with n -pentane followed by crystallization pro-

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