Orthorhombic
Pbca
$a = 11.8271\ (4)$ Å
$b = 11.9869\ (4)$ Å
$c = 13.0821\ (5)$ Å
$V = 1854.7\ (2)$ Å^3
$Z = 8$
$D_x = 2.045$ Mg m^{-3}

Cell parameters from 25 reflections
$\theta = 11\text{-}14°$
$\mu = 2.49$ mm^{-1}
$T = 295$ K
Flattened octahedron
0.33 × 0.32 × 0.18 mm
Amber

Data collection

Enraf-Nonius CAD-4 diffractometer
ω-2θ scans
Absorption correction: empirical
$T_{\min} = 0.933$, $T_{\max} = 0.998$
4544 measured reflections
4065 independent reflections

3105 observed reflections $[I > 3\sigma(I)]$
$\theta_{\max} = 35°$
$h = 0 \rightarrow 19$
$k = 0 \rightarrow 19$
$l = 0 \rightarrow 21$
3 standard reflections
frequency: 166.7 min
intensity variation: <1%

Refinement

Refinement on F
Final $R = 0.022$
$wR = 0.029$
$S = 1.455$
3105 reflections
149 parameters
All H-atom parameters refined
$w = 4F_o^2[\sigma^2(I) + (0.02F_o^2)^2]^{-1}$
$(\Delta/\sigma)_{\max} = 0.04$

$\Delta\rho_{\max} = 0.44$ e Å^{-3}
$\Delta\rho_{\min} = -0.17$ e Å^{-3}
Extinction correction: $(1 + gI_c)^{-1}$ applied to F_c
Extinction coefficient: $g = 2.86\ (8) \times 10^{-7}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Pd	0.35479 (1)	0.60963 (1)	0.69883 (1)	2.029 (2)
Cl1	0.34127 (5)	0.54235 (5)	0.86362 (4)	3.76 (1)
Cl2	0.48296 (4)	0.47290 (4)	0.65451 (5)	3.58 (1)
C1	0.4148 (2)	0.7088 (2)	0.5692 (1)	2.54 (3)
C2	0.3195 (2)	0.6521 (2)	0.5371 (1)	2.58 (3)
C3	0.2024 (2)	0.7012 (2)	0.5266 (2)	3.06 (4)
C4	0.1298 (2)	0.6852 (2)	0.6222 (2)	3.13 (4)
C5	0.1932 (2)	0.6972 (2)	0.7201 (2)	2.80 (3)
C6	0.2789 (2)	0.7728 (2)	0.7406 (1)	2.71 (3)
C7	0.3192 (2)	0.8626 (2)	0.6690 (2)	2.85 (3)
C8	0.4216 (2)	0.8262 (2)	0.6071 (2)	2.84 (3)

Table 2. *Geometric parameters* (Å, °)

Pd—Cl1	2.3072 (6)	C1—C8	1.494 (3)
Pd—Cl2	2.3065 (6)	C2—C3	1.511 (3)
Pd—C1	2.189 (2)	C3—C4	1.528 (3)
Pd—C2	2.216 (2)	C4—C5	1.492 (3)
Pd—C5	2.198 (2)	C5—C6	1.385 (3)
Pd—C6	2.221 (2)	C6—C7	1.504 (3)
C1—C2	1.382 (3)	C7—C8	1.520 (3)
Cl1—Pd—Cl2	91.84 (2)	C4—C5—C6	126.6 (2)
C2—C1—C8	127.4 (2)	C5—C6—C7	125.5 (2)
C1—C2—C3	125.7 (2)	C6—C7—C8	112.3 (2)
C2—C3—C4	113.0 (2)	C1—C8—C7	113.8 (2)
C3—C4—C5	114.1 (2)		
C8—C1—C2—C3	4.8 (3)	C3—C4—C5—C6	37.9 (3)
C2—C1—C8—C7	35.3 (3)	C4—C5—C6—C7	4.0 (3)
C1—C2—C3—C4	−93.3 (3)	C5—C6—C7—C8	−95.4 (3)
C2—C3—C4—C5	38.0 (3)	C6—C7—C8—C1	41.1 (3)

Programs used include *MolEN* (Fair, 1990) and *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and bond distances and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71258 (30 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH1058]

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Bis(μ-benzoato-κO:$\kappa O'$)-bis[(benzoato-$\kappa^2 O,O'$)(*N*,*N*-dimethylformamide-κO)dioxouranium(VI)]

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Abstract

The action of dimethylformamide on diaqua(benzoato)chlorodioxouranium(VI), in the presence of β-cyclodextrin, yields the title compound. The crystal structure of this new complex reveals that the linear uranyl is equatorially surrounded by five O

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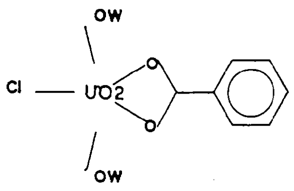
atoms, one from a dmf molecule, two from a bidentate benzoate anion and one each from two separate bridging benzoate ligands, shared by the U atoms forming a neutral dimeric entity. The average U—O distance involving the bridging benzoates [2.31 (1) Å] is significantly shorter than that involving the other benzoates [2.44 (2) Å].

Comment

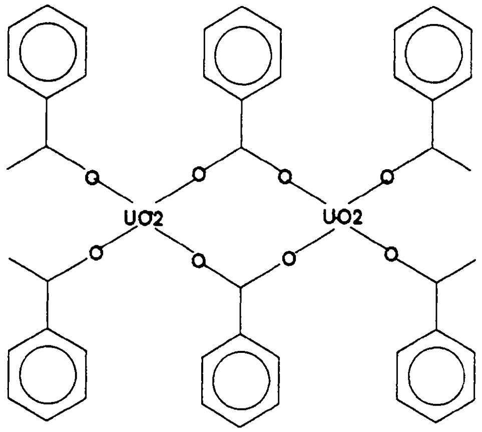
Previous crystallographic studies of [UO_2]–benzoato compounds showed that the anion acts either as a bidentate ligand on the same uranyl or as a bridge between two neighbouring ones.

In diaqua(benzoato)chlorodioxouranium(VI) (I) (Charpin, Keller, Lance & Vigner, 1989), a monomeric entity is observed, the equatorial uranyl plane containing one Cl, two water O and the two carboxyl O atoms.



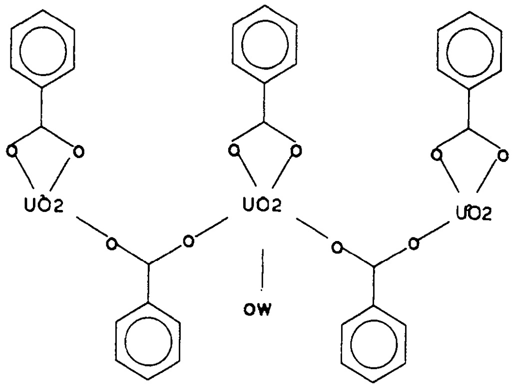
(I)

In dibenzoatodioxouranium(VI) (II) (Cousson, Proust & Pages, 1990), the uranyl coordinates four different bridging benzoate ligands, leading to octahedra around the U atoms, arranged in polymeric chains.



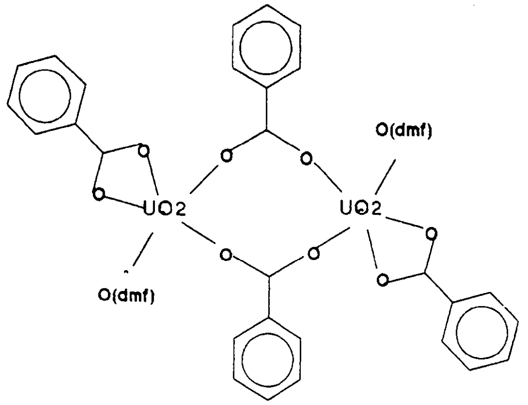
(II)

In the reported structure of *catena*-poly[{aqua(benzoato)dioxouranium(VI)}-μ-(benzoato)] ethanol solvate (III) (Nierlich, Iroulart, Vigner, Keller & Lance, 1990), both types of benzoato–UO_2 coordination are found and polymeric chains of pentagonal bipyramids are observed. The uranyl coordinates two bridging benzoate ligands, a bidentate benzoate ligand and one water molecule.



(III)

The title compound $[U(C_7H_5O_2)_2(O)_2(C_3H_7NO)]_2$ (IV) also contains both types of benzoate coordination. It was obtained while studying the influence of different solvents on the reactivity of β-cyclodextrin with (I). The presence of dimethylformamide (dmf) leads to (IV).



(IV)

A view of the molecule with atom labelling is shown in Fig. 1 and a stereoview of the packing, which is stabilized by van der Waals forces, is shown in Fig. 2.

The uranyl in (IV) is pentacoordinated and the equatorial pentagon is planar with a maximum deviation for the equatorial atoms of ± 0.06 Å. The essential difference from (III) is, besides the substitution of the water molecule by a dmf, that in the pentagonal oxygen sequence the bridging benzoates are adjacent in (IV), whereas they are separated by the neutral H_2O ligand in (III). This leads, respectively, to a neutral dimeric unit and a uranyl polymer, where the corresponding neighbouring U atoms are separated by 5.63 and 5.88 Å, respectively. The atoms of the two linked equatorial pentagons of the dimeric unit lie on the same plane (angle between the two equatorial planes less than 1°). A significant shortening of the equatorial U—O distances corresponding to the bridging anions is observed, the same occuring in (II) and (III). This is probably related to the bridging character of the benzoate anions and is not exclusively due to the coordination number of the uranyl cation, as previously suggested (Cousson, Proust & Pages, 1990). Distances and angles involving the dmf molecule agree with those found in pentakis(*N*,*N*-dimethylformamide)dioxouranium(VI) tetrafluoroborate (Deshayes, Keller, Lance, Nierlich & Vigner, 1992).

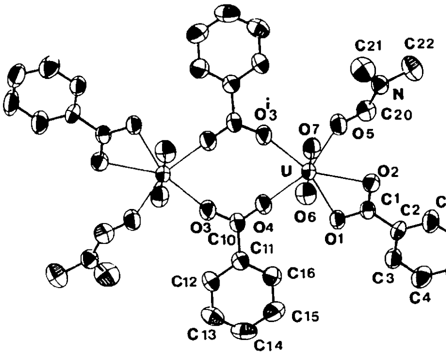


Fig. 1. The dimeric unit $[UO_2(\text{benzoato})_2(\text{dmf})]_2$.

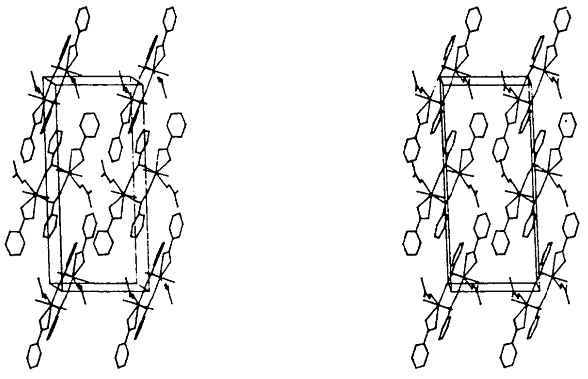


Fig. 2. Stereoscopic view of the structure in the unit cell.

Experimental

Crystal data

$[U_2O_4(C_7H_5O_2)_4(C_3H_7NO)_2]$
M_r = 1170.70
Monoclinic
$P2_1/c$
a = 9.387 (5) Å
b = 9.507 (5) Å
c = 21.279 (8) Å
β = 92.63 (4)°

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 8–12°
μ = 8.15 mm^{-1}
T = 295 K
Prismatic

V = 1897 (3) Å^3
Z = 2
D_x = 2.05 Mg m^{-3}

0.40 × 0.30 × 0.20 mm
Yellow

Data collection

Enraf-Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: analytical
$T_{\min}$ = 0.824, $T_{\max}$ = 1.215
3778 measured reflections
3318 independent reflections

2191 observed reflections $[I_{\text{net}} > 3\sigma(I_{\text{net}})]$
R_{int} = 0.016
$\theta_{\max}$ = 25°
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 11$
$l = -25 \rightarrow 25$
3 standard reflections
frequency: 60 min
intensity variation: 0.8%

Refinement

Refinement on F
Final R = 0.025
wR = 0.028
S = 2.4
2191 reflections
235 parameters
H-atom parameters not refined
Unit weights applied

$(\Delta/\sigma)_{\max}$ = 0.01
$\Delta\rho_{\max}$ = 0.9 e Å^{-3}
$\Delta\rho_{\min}$ = −1.1 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2B and 2.3.1)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$B_{\text{eq}} = \tfrac{4}{3}\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
U	0.15816 (3)	0.21775 (3)	0.05994 (1)	3.178 (5)
O(1)	0.2040 (6)	0.1920 (6)	0.1721 (2)	3.9 (1)
O(2)	0.3095 (6)	0.3705 (6)	0.1289 (3)	4.1 (1)
O(3)	−0.0560 (7)	−0.1724 (7)	0.0381 (3)	5.8 (2)
O(4)	0.0401 (7)	0.0122 (7)	0.0846 (3)	5.3 (2)
O(5)	0.2469 (7)	0.4094 (6)	−0.0010 (3)	4.8 (1)
O(6)	0.3113 (6)	0.1191 (7)	0.0422 (3)	5.1 (1)
O(7)	0.0061 (6)	0.3184 (6)	0.0773 (3)	4.5 (1)
N	0.3127 (7)	0.6306 (7)	−0.0227 (3)	4.0 (2)
C(1)	0.2823 (8)	0.3005 (8)	0.1778 (4)	3.5 (2)
C(2)	0.3421 (8)	0.3424 (9)	0.2407 (4)	3.5 (2)
C(3)	0.3010 (9)	0.270 (1)	0.2925 (4)	4.4 (2)
C(4)	0.350 (1)	0.312 (1)	0.3527 (4)	5.9 (3)
C(5)	0.443 (1)	0.424 (1)	0.3588 (5)	6.3 (3)
C(6)	0.487 (1)	0.495 (1)	0.3067 (5)	7.0 (3)
C(7)	0.433 (1)	0.454 (1)	0.2468 (5)	5.5 (2)
C(10)	0.0095 (8)	−0.1147 (9)	0.0844 (4)	3.6 (2)
C(11)	0.0488 (8)	−0.2026 (9)	0.1393 (3)	3.6 (2)
C(12)	0.0142 (9)	−0.3435 (9)	0.1392 (4)	3.9 (2)
C(13)	0.047 (1)	−0.427 (1)	0.1909 (4)	5.2 (2)
C(14)	0.112 (1)	−0.370 (1)	0.2434 (5)	5.9 (2)
C(15)	0.154 (1)	−0.230 (1)	0.2427 (5)	6.4 (3)
C(16)	0.121 (1)	−0.146 (1)	0.1912 (4)	4.9 (2)
C(20)	0.2646 (9)	0.534 (1)	0.0142 (4)	4.4 (2)
C(21)	0.345 (1)	0.599 (1)	−0.0862 (5)	6.7 (3)
C(22)	0.325 (1)	0.778 (1)	−0.0029 (5)	6.2 (2)

Table 2. *Geometric parameters* (Å, °)

U—O(1)	2.418 (3)	C(3)—C(4)	1.400 (8)
U—O(2)	2.467 (4)	C(4)—C(5)	1.376 (9)
U—O(3^i)	2.296 (4)	C(5)—C(6)	1.38 (1)
U—O(4)	2.319 (4)	C(6)—C(7)	1.400 (8)
U—O(5)	2.407 (4)	C(10)—C(11)	1.469 (8)
U—O(6)	1.771 (4)	C(11)—C(12)	1.379 (8)
U—O(7)	1.772 (4)	C(11)—C(16)	1.377 (8)

O(1)—C(1)	1.269 (6)	C(12)—C(13)	1.378 (9)
O(2)—C(1)	1.270 (6)	C(13)—C(14)	1.365 (9)
O(3)—C(10)	1.263 (6)	C(14)—C(15)	1.39 (1)
O(4)—C(10)	1.239 (6)	C(15)—C(16)	1.376 (9)
O(5)—C(20)	1.234 (7)	N—C(20)	1.303 (7)
C(1)—C(2)	1.482 (6)	N—C(21)	1.432 (7)
C(2)—C(3)	1.371 (7)	N—C(22)	1.469 (8)
C(2)—C(7)	1.365 (8)		
O(6)—U—O(1)	92.7 (2)	O(7)—U—O(1)	87.5 (2)
O(6)—U—O(2)	89.3 (2)	O(7)—U—O(2)	90.3 (2)
O(6)—U—O(3^i)	90.9 (2)	O(7)—U—O(3^i)	89.1 (2)
O(6)—U—O(4)	90.2 (2)	O(7)—U—O(4)	90.6 (2)
O(6)—U—O(5)	89.0 (2)	O(7)—U—O(5)	90.3 (2)
O(6)—U—O(7)	179.3 (2)	O(1)—U—O(2)	53.2 (1)
O(2)—U—O(5)	70.8 (1)	O(5)—U—O(3^i)	78.1 (1)
O(3)—U—O(4^i)	82.1 (1)	O(4)—U—O(1)	75.9 (1)
O(5)—C(20)—N	124.5 (6)	C(20)—N—C(21)	120.9 (6)
C(20)—N—C(22)	121.9 (6)	C(21)—N—C(22)	117.1 (6)
O(1)—C(1)—O(2)	119.0 (5)	O(1)—C(1)—C(2)	119.8 (5)
O(2)—C(1)—C(2)	121.1 (5)	C(1)—C(2)—C(3)	118.9 (5)
C(1)—C(2)—C(7)	120.3 (5)	C(3)—C(2)—C(7)	120.7 (5)
C(2)—C(3)—C(4)	119.9 (6)	C(3)—C(4)—C(5)	119.3 (6)
C(4)—C(5)—C(6)	120.7 (6)	C(5)—C(6)—C(7)	119.5 (6)
C(2)—C(7)—C(6)	119.9 (6)	O(3)—C(10)—O(4)	122.0 (5)
O(3)—C(10)—C(11)	117.9 (5)	O(4)—C(10)—C(11)	120.1 (5)
C(10)—C(11)—C(12)	120.1 (5)	C(10)—C(11)—C(16)	120.9 (6)
C(12)—C(11)—C(16)	119.0 (6)	C(11)—C(12)—C(13)	121.0 (6)
C(12)—C(13)—C(14)	119.9 (7)	C(13)—C(14)—C(15)	119.4 (7)
C(14)—C(15)—C(16)	120.5 (7)	C(11)—C(16)—C(15)	120.1 (7)

Symmetry code: (i) $-x, -y, -z$.

The compound was prepared by dissolving stoichiometric amounts of solid diaqua(benzoato)chlorodioxouranium(VI) in a dmf solution of β-cyclodextrin. The mixture was stirred at 313 K until a solid non-homogeneous residue was obtained. The residue was dissolved by heating in dmf and the turbid solution was left at room temperature to crystallize.

The structure was solved by the heavy-atom method. The H atoms were located in geometrically calculated positions and allowed to ride on the parent C atoms during the refinements, with a fixed isotropic temperature factor $B = 6$ Å^2. The few residual peaks on the final difference synthesis were close to the U atom. Cell refinement and data collection: Enraf-Nonius CAD-4 software. Data reduction, structure resolution and refinement: *SDP* software (Frenz, 1985). Absorption correction: *DIFABS* (Walker & Stuart, 1983). Molecular graphics: *ORTEP* (Johnson, 1976). All calculations were performed using a MicroVAX II.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, least-squares-planes data and r.m.s. amplitudes of thermal vibration have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71236 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA1039]

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Structure and Bonding in [$TaCl_4(C_5H_5N)_2$]

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(*Received* 6 *October* 1992; *accepted* 16 *April* 1993)

Abstract

The title structure, tetrachlorobis(pyridine)tantalum, is characterized by monomeric octahedral complexes, $TaCl_4(py)_2$ (py is pyridine), with the pyridine ligands coordinated in a *trans* configuration. In addition to packing (steric) arguments, an electronic driving force for the observed structure is incorporated, which is evaluated using extended Hückel calculations.

Comment

Thirty years ago, McCarley and coworkers first reported the synthesis and magnetic susceptibility measurements of $TaCl_4(py)_2$ (McCarley & Boatman, 1963). Their investigations of $TaCl_4(py)_2$ and $TaBr_4(py)_2$ concluded that there is a strong π-bonding component in the Ta–halide interaction, while the weak paramagnetism precluded the existence of Ta_2 dimers, as recognized, for example, in $TaCl_4$ (Schäfer & Kahlenberg, 1960).

During the course of new synthetic approaches towards transition-metal chalcogenide halides in supercritical amines (Miller & Lin, 1992), we have isolated red–brown needles suitable for single-crystal X-ray diffraction, and determined them to be $TaCl_4(py)_2$. We report its crystal structure and discuss the chemical bonding in this communication.

Although the strict crystallographic symmetry of each $TaCl_4(py)_2$ complex is $2/m$ (C_{2h}), the observed geometry is quite close to mmm (D_{2h}). Whereas many Ta and Nb tetrahalide complexes, MX_4L_2, in which L is a two-electron neutral ligand like phosphine and amine, show *cis* conformations (Cotton & Wilkinson, 1988), our determination confirms an earlier

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