$N1^{ii}—H1^{ii}\cdots O8$	0.95	2.17	3.073 (6)	158
$N3^{iii}—H16^{iii}\cdots O9$	0.95	2.12	3.049 (4)	165

Symmetry codes: (i) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (ii) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $x, \frac{1}{2}-y, z-\frac{1}{2}$.

The positions of the H atoms were idealized (C—H or N—H 0.95 Å), assigned isotropic displacement parameters $B(\text{H}) = 1.2B_{\text{eq}}$(C or N), and allowed to ride on their parent C or N atoms. The H atoms in the water molecule were refined isotropically. An orientational disorder of the perchlorate anion was observed in compound (2).

For both compounds, data collection: *MSC/AFC Diffractometer Control* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1989); program(s) used to solve structures: *TEXSAN*; program(s) used to refine structures: *TEXSAN*; molecular graphics: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1068). Services for accessing these data are described at the back of the journal.

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Bis(1,3-dibutylimidazolidin-2-one-*O*)bis(nitrato-*O*,*O*′)dioxouranium(VI)

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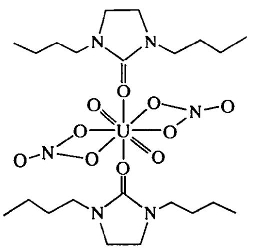
Abstract

In the title complex, $[UO_2(NO_3)_2(C_{11}H_{22}N_2O)_2]$, the central UO_2^{2+} cation is centrosymmetrically coordinated by six further O atoms, of which two are from the carbonyl groups of the 1,3-dibutylimidazolidin-2-one ligands and four from the two nitrate anions, forming a distorted hexagonal bipyramid. The average carbonyl U—O bond length is 2.345 (3) Å, which is the shortest value among similar dinitratodioxouranium complexes.

Comment

It has been reported that *N*,*N*-dialkylamides and *N*-alkylcaprolactam are effective agents for the extraction of actinides. We have found recently that 1,3-dibutylimidazolidin-2-one is even more effective for this purpose. Its stronger coordinating ability means that the carbonyl group conjugates with the two N atoms and the two alkyl groups supply electrons to the two N atoms. We have used 1,3-dibutylimidazolidin-2-one to extract UO_2 to give the title complex, (I), and this paper describes its X-ray crystallographic structure.



(I)

In (I), the UO_2^{2+} cation is centrosymmetrically coordinated by six further O atoms, two from the carbonyl groups of the 1,3-dibutylimidazolidin-2-one ligands and four from the two nitrate anions, thus forming a distorted hexagonal bipyramid similar to another UO_2^{2+} complex reported by Wang *et al.* (1995). Selected bond lengths and angles for (I) are given in Table 1 and the molecular

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structure is shown in Fig. 1. From the average carbonyl U—O bond lengths for similar complexes in the literature [2.363 (7) (*N,N,N′,N′*-tetrabutylmalonamide; Wang *et al.*, 1995), 2.360 (5) (caprolactam; Cao, Wang, Gu *et al.*, 1993), 2.353 (8) (octylcaprolactam; Cao, Wang, Zhu *et al.*, 1993), 2.350 (5) (triethyl phosphate; Fleming & Lynton, 1960) and 2.345 (3) Å (this work)], one can see a very clear trend, *i.e.* the more charged the O atom from the organic ligand, the stronger its coordination ability and the shorter the U—O bond length.

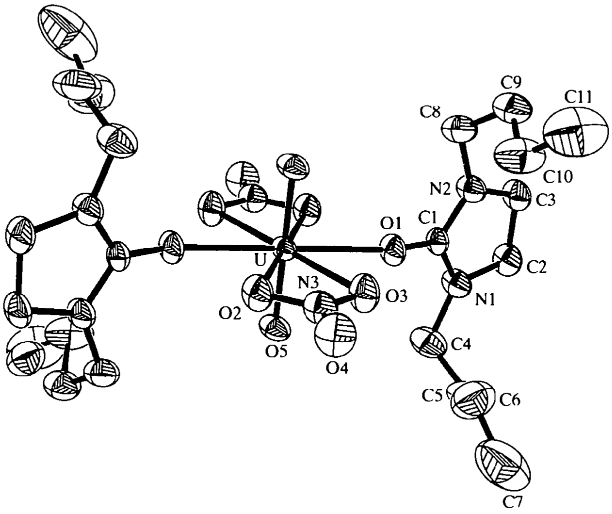

Fig. 1. The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity.

Experimental

A solution of $UO_2(NO_3)_2$ in 3 *M* HNO_3 was extracted with 1,3-dibutylimidazolidin-2-one dissolved in petroleum ether (333–336 K) at room temperature until the organic phase was saturated. The yellow precipitate which formed was washed successively with deionized water and petroleum ether. Crystals of (I) suitable for X-ray diffraction analysis were obtained by recrystallization from a toluene solution.

Crystal data

$[UO_2(NO_3)_2(C_{11}H_{22}N_2O)_2]$
$M_r = 790.66$
Triclinic
$P\overline{1}$
$a = 8.647 (1)$ Å
$b = 8.701 (2)$ Å
$c = 11.683 (2)$ Å
$\alpha = 84.68 (1)°$
$\beta = 70.24 (2)°$
$\gamma = 74.96 (1)°$
$V = 798.9 (2)$ Å^3
$Z = 1$
$D_x = 1.643$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 34 reflections
$\theta = 3.17–18.20°$
$\mu = 5.14$ mm^{-1}
$T = 290 (2)$ K
Prism
0.58 × 0.44 × 0.36 mm
Yellow

Data collection

Siemens *P*4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (*SHELXS*86; Sheldrick, 1985)
$T_{min} = 0.10$, $T_{max} = 0.16$
3845 measured reflections
3473 independent reflections
3408 reflections with $I > 2\sigma(I)$

$R_{int} = 0.013$
$\theta_{max} = 26.99°$
$h = 0 \rightarrow 10$
$k = -10 \rightarrow 11$
$l = -14 \rightarrow 14$
3 standard reflections every 97 reflections frequency: 60 min intensity decay: 3.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.061$
$S = 1.003$
3472 reflections
179 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0417P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.005$

$\Delta\rho_{max} = 1.16$ e Å^{-3}
$\Delta\rho_{min} = -1.20$ e Å^{-3}
Extinction correction: *SHELXS*86 (Sheldrick, 1985)
Extinction coefficient: 0.0130 (9)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

U—O5	1.773 (3)	O1—C1	1.244 (4)
U—O1	2.345 (3)	O2—N3	1.268 (5)
U—O2	2.504 (3)	O3—N3	1.263 (5)
U—O3	2.518 (3)	O4—N3	1.204 (5)
O5—U—O1	89.49 (12)	O5—U—O3	90.19 (14)
O5—U—O2	90.39 (13)	O1—U—O3	64.85 (10)
O1—U—O2	114.93 (10)	O2—U—O3	50.08 (10)
O5^i—U—O2^i	90.39 (13)		

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

The rather large displacement parameters of the terminal alkyl groups indicate their partial disorder. However, refinement using a disordered model showed even worse results and so an ordered model was used. The rather large maximum (1.004 Å from U) and minimum peaks in the final difference map were caused by the termination effect of the Fourier summation and the not very accurate absorption correction.

Data collection: *P*4 software. Cell refinement: *P*4 software. Data reduction: *P*4 software. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXL*93. Software used to prepare material for publication: *SHELXL*93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1467). Services for accessing these data are described at the back of the journal.

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Three Pt^{II} catecholate and 1,2-dithiocatecholate complexes

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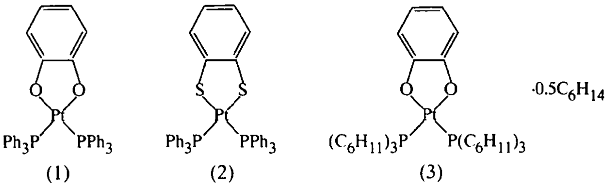
Abstract

In the crystal structures of the three title complexes, (benzene-1,2-diolato-*O,O′*)bis(triphenylphosphine)platinum(II), $[Pt(C_6H_4O_2)(C_{18}H_{15}P)_2]$, (1), (benzene-1,2-dithiolato-*S,S′*)bis(triphenylphosphine)platinum(II), $[Pt(C_6H_4S_2)(C_{18}H_{15}P)_2]$, (2), and the *n*-hexane hemisolvate of (benzene-1,2-diolato-*O,O′*)bis(tricyclohexylphosphine)platinum(II), $[Pt(C_6H_4O_2)(C_{18}H_{33}P)_2]\cdot 0.5C_6H_{14}$, (3), the Pt atoms are tetracoordinate with distorted square-planar geometry. Compounds (1) and (2) are isostructural.

Comment

Metal catecholates have been extensively studied due to their unique electronic (Bhattacharya & Pierpont, 1992), magnetic (Coucouvanis *et al.*, 1993) and catalytic activity (Persson & Andersson, 1993). Metal thiolates are important as biological electron-transfer mediators (Blower & Dilworth, 1987). While many catecholate and thiocatecholate complexes have been characterized, for platinum, there are only two closely related cases where the crystal structures are known, namely $[Pt\{1,2\text{-}O_2\text{-}3,5\text{-}(NO_2)_2C_6H_2\}(PMe_2Ph)_2]$ (Clemente *et al.*, 1994) and $[Pt\{1,2\text{-}O_2\text{-}4,5\text{-}(3\text{-ethynylthiophene})_2C_6H_2\}(PPh_3)_2]$ (Kinder & Youngs, 1996). Other related compounds containing group ten elements and catecholate or thiocatecholate derivatives have also been structurally characterized (Abakumov *et al.*, 1996; Pierpont & Downs, 1975; Darkwa, 1997; Cao *et al.*, 1996).

Selected bond lengths and angles are given for complexes (1), (2) and (3) in Tables 1, 2 and 3, respectively. The Pt—P bond lengths for (2) [mean Pt—P bond length of 2.283 (7) Å] compared with (1) [mean Pt—P 2.247 (6) Å] are consistent with the thiocatecholate group having a stronger *trans* influence than the catecholate group. The increased steric bulk of the $P(C_6H_{11})_3$ ligand compared with PPh_3 [cone angles of 170 and 145°, respectively (Tolman, 1977)] leads to a larger P—Pt—P angle (by approximately 11°) for (3) than for (1) and (2). This results in smaller O—Pt—P angles for (3) [mean 85.0 (5)°] compared with the mean O—Pt—P angle for (1) [91 (5)°] and the mean S—Pt—P angle for (2) [89 (3)°]. The bite angles of the chelating ligands are consistent with the larger radius of sulfur compared with oxygen.



Significantly more distortion of the atoms that define the square plane around platinum is observed for (2) than for (1) or (3). The average displacement of the atoms from the square plane defined by Pt, P and S in (2) is 0.20 (4) Å [maximum of 0.250 (1) Å for S1] compared with mean values of 0.10 (2) Å for (1) and 0.058 (12) Å

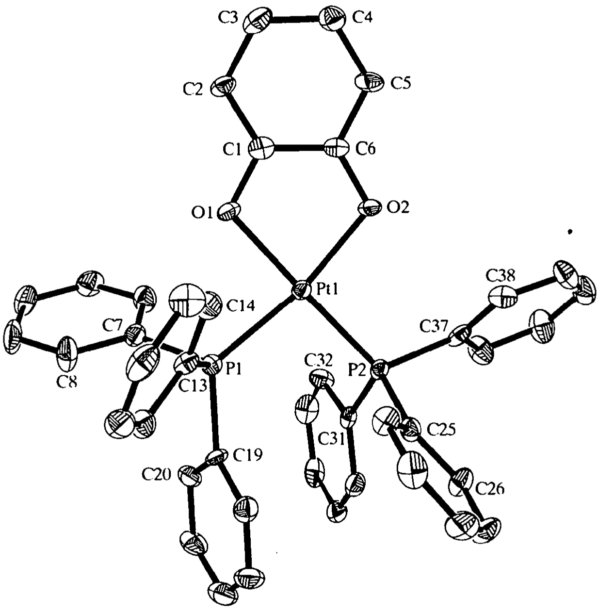


Fig. 1. The structure of (1) with displacement ellipsoids drawn at the 50% probability level. H atoms have been omitted for clarity.

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