Bis(tetraphenylphosphonium) Tetrachlorodioxouranate(VI) Dichloromethane Solvate

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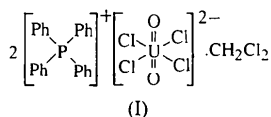
Abstract

Crystals of the title compound, $(C_{24}H_{20}P)_2[UO_2Cl_4]$.$CH_2Cl_2$, contain pseudo-octahedral tetrachlorouranyl anions having approximate D_{4h} and exact C_i point symmetry. The asymmetric unit contains two such anions, each distinct and isolated, and each unperturbed by close anion–anion packing, hydrogen bonding or the presence of small polarizing cations. The U=O bond lengths are 1.75 (1) and 1.77 (1) Å, and provide points of reference for the recently reported oxouranium (phosphorane iminato) complex containing the O=U=N— group.

Comment

The linearity of the UO_2^{2+} group and its remarkable chemical stability have excited considerable theoretical and experimental study (Denning, 1992). We prepared recently the first example of a stable nitrogen-containing structural analogue of the uranyl ion, namely, $(Ph_4P)[UOCl_4\{NP(m\text{-tol})_3\}]$ (where *m*-tol is 3-methylphenyl), which contains the linear and isoelectronic O=U=N— group (Brown, Denning & Jones, 1994). In order to analyse the bonding in this species, it is useful to compare the U=O bond length with that found in a related uranyl complex which is unperturbed either by small cationic neighbours or by hydrogen bonding. The title compound, (I), meets these requirements and indeed contains the same cation as the O=U=N— compound.

$$2\left[\begin{array}{c} Ph \quad Ph \\ P \\ Ph \quad Ph \end{array}\right]^+ \left[\begin{array}{c} O \\ Cl \quad \| \quad Cl \\ Cl \quad \| \quad Cl \\ O \end{array}\right]^{2-} .CH_2Cl_2$$

(I)

A structural survey of uranyl compounds shows that U=O bond distances can vary between 1.52 and 2.00 Å (Denning, 1983). In most examples of the $[UO_2Cl_4]^{2-}$ ion, this distance appears to be close to 1.75 Å, but reported values range from 1.58 to 1.94 Å. In $(Bu_4N)_2[UO_2Cl_4]$, for example, the U=O bond lengths

are 1.68 (1) and 1.69 (1) Å (Di Sipio, Tondello, Pelizzi, Ingletto & Montenero, 1974*a*) and in $(Pr_4N)_2[UO_2Cl_4]$ they are 1.65 (1) and 1.58 (2) Å (Di Sipio, Tondello, Pelizzi, Ingletto & Montenero, 1974*b*). Several other structures contain organic cations which can hydrogen bond to the uranyl O atoms and this generally leads to longer U=O distances and deviations from Badger's
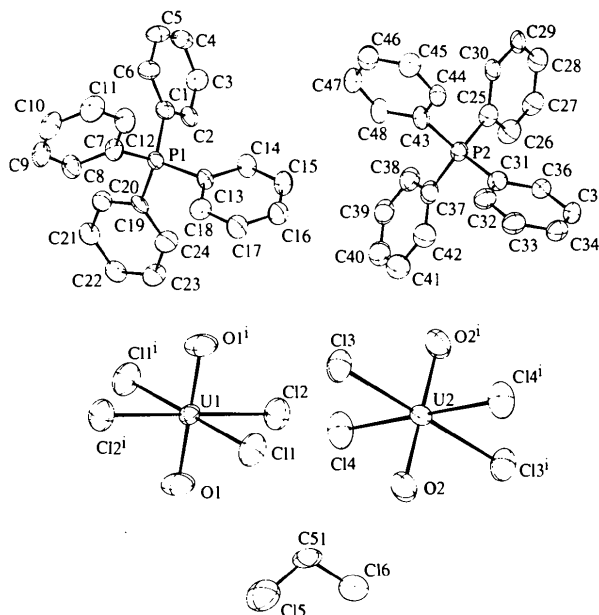

Fig. 1. A view of the title compound showing the atomic labelling scheme and displacement ellipsoids plotted at the 50% probability level (*CAMERON*; Pearce, Watkin & Prout, 1992).
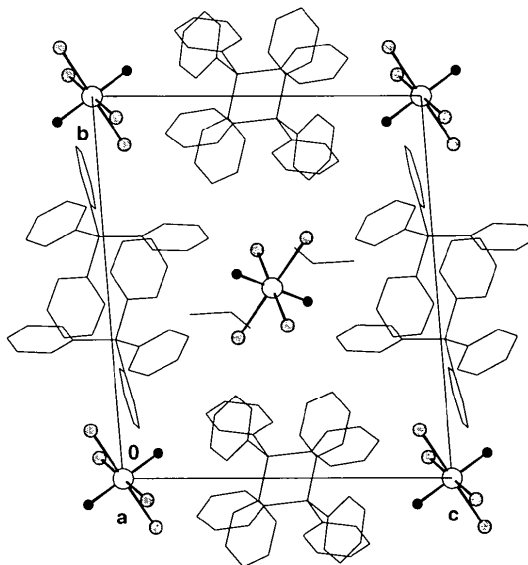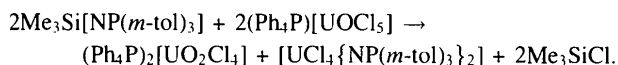

Fig. 2. View (*CAMERON*; Pearce, Watkin & Prout, 1992) of the unit cell along the *a* axis. The dichloromethane Cl atoms are directed towards the U atom. H atoms have been omitted for clarity.

rule relating the U=O bond length to the vibrational frequency (Bartlett & Cooney, 1989). Variations in the structures of compounds of the same type, for example, [$M_2UO_2Cl_4$] (M = Li, Na, Rb, Cs), have been attributed to steric factors (Vorobei, Skiba, Bevz & Kapshukov, 1971), as well as to the cation polarizability and the interanionic spacing (Vorobei, Skiba, Desyatnik & Kapshukov, 1969; Vorobei, Skiba & Bevz, 1970).

There are two structurally similar, although crystallographically distinct, [UO_2Cl_4]$^{2-}$ and Ph_4P^+ ions in the unit cell of the title compound (Figs. 1 and 2). The geometries of the Ph_4P^+ cations are similar to those reported elsewhere (de Wet & du Preez, 1978). The dichloromethane molecule is far removed from the anions and its H atoms are directed away from the nearest O atoms, precluding any hydrogen-bonding interactions. The U=O bond lengths [1.75(1) and 1.77(1) Å] are close to those observed in (Et$_4$N)$_2$[UO$_2$Cl$_4$] [1.76(2) and 1.77(3) Å; Bois, Nguyen & Rodier, 1976] and are in good agreement with the U=O distance of 1.76(1) Å found in (Ph$_4$P)[UOCl$_4${NP(m-tol)$_3$}] (Brown, Denning & Jones, 1994), in which the local U=O environment is similar to that observed here.

Experimental

Single crystals of (Ph$_4$P)$_2$[UO$_2$Cl$_4$].CH$_2$Cl$_2$ were obtained from the reaction mixture used to prepare (Ph$_4$P)[UOCl$_4${NP-(m-tol)$_3$}] (Brown, Denning & Jones, 1994). The uranyl compound is formed in a secondary reaction, together with the uranium bis(iminato) complex [UCl$_4${NP(m-tol)$_3$}$_2$] (Brown & Denning, 1996; Brown, 1996), according to

2Me$_3$Si[NP(m-tol)$_3$] + 2(Ph$_4$P)[UOCl$_5$] →

(Ph$_4$P)$_2$[UO$_2$Cl$_4$] + [UCl$_4${NP(m-tol)$_3$}$_2$] + 2Me$_3$SiCl.

The uranyl complex was isolated as small orange parallelepipeds which were sealed into capillaries under dry N$_2$. The IR spectrum of the solid when pressed into a KBr disk was identical to that of unsolvated (Ph$_4$P)$_2$[UO$_2$Cl$_4$] (Day & Venanzi, 1966), implying that the clathrated dichloromethane is lost by efflorescence.

Crystal data

(C$_{24}$H$_{20}$P)$_2$[UO$_2$Cl$_4$].CH$_2$Cl$_2$
M_r = 1175.57
Triclinic
$P\bar{1}$
a = 11.755(8) Å
b = 14.521(3) Å
c = 15.884(5) Å
α = 89.333(1)°
β = 77.715(1)°
γ = 67.027(1)°
V = 2431.36 Å^3
Z = 2
D_x = 1.61 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 4.33–11.51°
μ = 0.36 mm^{-1}
T = 298 K
Parallelepiped
0.50 × 0.15 × 0.15 mm
Orange

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
T_{min} = 0.87, T_{max} = 1.00
5467 measured reflections
4794 independent reflections

2589 observed reflections [$I > 2\sigma(I)$]
R_{int} = 0.04
θ_{max} = 23.0°
h = −12 → 11
k = −14 → 13
l = −1 → 15
3 standard reflections frequency: 60 min intensity decay: 25.5%

Refinement

Refinement on F
R = 0.0461
wR = 0.0491
S = 1.0864
2589 reflections
545 parameters
H atoms placed geometrically after each cycle; U(H) = U_{eq}(C)
Weighting scheme: 3-term Chebychev polynomial (Carruthers & Watkin, 1979)

$(\Delta/\sigma)_{max}$ = 0.05
$\Delta\rho_{max}$ = 0.78 e Å^{-3}
$\Delta\rho_{min}$ = −0.71 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

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

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
U1	0	0	0	0.0428
U2	0	1/2	1/2	0.0414
Cl1	−0.1021 (4)	−0.0869 (4)	0.1263 (3)	0.0764
Cl2	0.2158 (5)	−0.0678 (4)	0.0550 (3)	0.0758
Cl3	0.1827 (4)	0.3841 (3)	0.3693 (3)	0.0655
Cl4	−0.1692 (5)	0.5368 (4)	0.4008 (3)	0.0763
Cl5	0.5353 (6)	0.2414 (6)	0.4299 (5)	0.1260
Cl6	0.5759 (6)	0.4243 (5)	0.3944 (5)	0.1093
P1	−0.2365 (4)	0.4456 (3)	0.0578 (3)	0.0439
P2	0.2461 (4)	0.0132 (3)	0.3651 (3)	0.0495
O1	−0.058 (1)	0.1112 (8)	0.0663 (8)	0.0777
O2	0.030 (1)	0.6055 (9)	0.4629 (7)	0.0734
C1	−0.357 (1)	0.405 (1)	0.1144 (6)	0.0483
C2	−0.314 (1)	0.304 (1)	0.1252 (6)	0.0476
C3	−0.401 (1)	0.266 (1)	0.1703 (7)	0.0682
C4	−0.524 (1)	0.328 (1)	0.2030 (7)	0.0647
C5	−0.564 (1)	0.428 (1)	0.1927 (7)	0.0629
C6	−0.480 (1)	0.468 (1)	0.1477 (7)	0.0593
C7	−0.296 (1)	0.579 (1)	0.0705 (7)	0.0547
C8	−0.255 (1)	0.630 (1)	0.1222 (8)	0.0627
C9	−0.313 (1)	0.733 (1)	0.1336 (8)	0.0675
C10	−0.410 (1)	0.787 (1)	0.0977 (9)	0.0784
C11	−0.453 (1)	0.737 (1)	0.0460 (9)	0.0754
C12	−0.395 (1)	0.632 (1)	0.0322 (8)	0.0639
C13	−0.1935 (9)	0.408 (1)	−0.0565 (8)	0.0428
C14	−0.214 (1)	0.3265 (9)	−0.089 (1)	0.0379
C15	−0.172 (1)	0.295 (1)	−0.175 (1)	0.0639
C16	−0.108 (1)	0.343 (1)	−0.228 (1)	0.0618
C17	−0.086 (1)	0.423 (1)	−0.198 (1)	0.0657
C18	−0.130 (1)	0.455 (1)	−0.112 (1)	0.0595
C19	−0.099 (1)	0.3879 (8)	0.0997 (9)	0.0383
C20	−0.101 (2)	0.4069 (9)	0.184 (1)	0.0565
C21	0.003 (1)	0.3619 (9)	0.218 (1)	0.0556
C22	0.116 (1)	0.293 (1)	0.166 (1)	0.0487
C23	0.119 (1)	0.2733 (9)	0.081 (1)	0.0606
C24	0.012 (1)	0.3193 (9)	0.047 (1)	0.0595
C25	0.094 (1)	0.082 (1)	0.3470 (9)	0.0584
C26	0.048 (2)	0.046 (1)	0.2874 (8)	0.0710

C27	−0.067 (1)	0.102 (1)	0.2719 (9)	0.0651
C28	−0.141 (2)	0.195 (1)	0.3130 (9)	0.0660
C29	−0.099 (1)	0.235 (1)	0.3731 (9)	0.0538
C30	0.020 (1)	0.179 (1)	0.3909 (8)	0.0525
C31	0.364 (1)	0.0314 (6)	0.2809 (9)	0.0577
C32	0.481 (1)	0.0168 (7)	0.292 (1)	0.0709
C33	0.573 (1)	0.0236 (7)	0.226 (1)	0.0702
C34	0.545 (1)	0.0455 (6)	0.146 (1)	0.0597
C35	0.427 (2)	0.0615 (7)	0.130 (1)	0.0608
C36	0.337 (1)	0.0527 (6)	0.1991 (9)	0.0619
C37	0.276 (2)	−0.116 (1)	0.3644 (7)	0.0661
C38	0.177 (2)	−0.146 (1)	0.4004 (7)	0.0707
C39	0.204 (2)	−0.251 (1)	0.4024 (7)	0.0728
C40	0.322 (2)	−0.318 (2)	0.3708 (8)	0.0902
C41	0.420 (2)	−0.291 (2)	0.3360 (8)	0.0988
C42	0.397 (2)	−0.187 (1)	0.3317 (7)	0.0921
C43	0.2532 (9)	0.058 (1)	0.470 (1)	0.0491
C44	0.2747 (8)	0.146 (1)	0.475 (1)	0.0577
C45	0.2603 (9)	0.188 (1)	0.557 (1)	0.0649
C46	0.2261 (9)	0.144 (1)	0.630 (1)	0.0810
C47	0.2062 (9)	0.058 (1)	0.622 (1)	0.0692
C48	0.2188 (8)	0.013 (1)	0.542 (1)	0.0658
C51	0.468 (2)	0.370 (2)	0.438 (1)	0.0882

Table 2. *Selected geometric parameters (Å, °)*

U1—Cl1	2.676 (4)	U2—Cl3	2.667 (4)
U1—Cl2	2.672 (4)	U2—Cl4	2.684 (5)
U1—O1	1.75 (1)	U2—O2	1.77 (1)
Cl1—U1—Cl2	90.1 (2)	Cl3—U2—Cl4	89.8 (1)
Cl1—U1—O1	90.8 (4)	Cl3—U2—O2	89.9 (4)

In the full-matrix least-squares refinement, a total of 632 restraints were applied to the parameters of the Ph_4P^+ groups; each phenyl ring was restrained to planarity, P—C and C—C bond lengths were restrained to their common mean, and the U_{ij} parameters were restrained so that $\Delta U \simeq 0$ along bond vectors. Anisotropic displacement parameters were refined for all non-H atoms.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *CRYSTALS* (Watkin, Carruthers & Betteridge, 1985). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *CRYSTALS*. Molecular graphics: *CAMERON* (Pearce, Watkin & Prout, 1992). Software used to prepare material for publication: *CRYSTALS*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1235). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Bartlett, J. R. & Cooney, R. P. (1989). *J. Mol. Struct.* **193**, 295–300.
Bois, C., Nguyen, Q. D. & Rodier, N. (1976). *Acta Cryst.* **B32**, 1541–1549.
Brown, D. R. (1996). DPhil thesis, University of Oxford, England.
Brown, D. R. & Denning, R. G. (1996). In preparation.
Brown, D. R., Denning, R. G. & Jones, R. H. (1994). *J. Chem. Soc. Chem. Commun.* pp. 2601–2602.
Carruthers, J. R. & Watkin, D. J. (1979). *Acta Cryst.* **A35**, 698–699.

Day, J. P. & Venanzi, L. M. (1966). *J. Chem. Soc. A*, **1**, 1363–1367.
Denning, R. G. (1983). *Gmelin Handbook of Inorganic Chemistry*, Vol. A6, edited by R. G. Denning, pp. 31–79. Heidelberg: Springer Verlag.
Denning, R. G. (1992). *Struct. Bond.* **79**, 215–276.
Di Sipio, L., Tondello, E., Pelizzi, G., Ingletto, G. & Montenero, A. (1974a). *Cryst. Struct. Commun.* **3**, 527–530.
Di Sipio, L., Tondello, E., Pelizzi, G., Ingletto, G. & Montenero, A. (1974b). *Cryst. Struct. Commun.* **3**, 731–734.
Enraf–Nonius (1989). *CAD-4 Software*. Enraf–Nonius, Delft, The Netherlands.
Pearce, L., Watkin, D. J. & Prout, C. K. (1992). *CAMERON. Program for Plotting Molecular Structures*. Chemical Crystallography Laboratory, University of Oxford, England.
Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
Vorobei, M. P., Skiba, O. V. & Bevz, A. S. (1970). *At. Energ.* **28**, 139–145.
Vorobei, M. P., Skiba, O. V., Bevz, A. S. & Kapshukov, I. I. (1971). *Russ. J. Phys. Chem.* **45**, 12–14.
Vorobei, M. P., Skiba, O. V., Desyatnik, V. N. & Kapshukov, I. I. (1969). *At. Energ.* **27**, 121–129.
Walker, N. & Stuart, D. (1983). *Acta Cryst.* **A39**, 158–166
Watkin, D. J., Carruthers, J. R. & Betteridge, P. W. (1985). *CRYSTALS User Guide*. Chemical Crystallography Laboratory, University of Oxford, England.
Wet, J. F. de & du Preez, J. G. H. (1978). *J. Chem. Soc. Dalton Trans.* pp. 592–597.

Bis(*N,N*-dimethylformamide)(pyrocatecholato-*O,O'*)lithium

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Abstract

Reaction of catechol with *n*-butyllithium in absolute *n*-hexane yields the corresponding monoanion, which crystallizes from *N,N*-dimethylformamide/*n*-hexane solution as the title compound, $[Li(C_6H_5O_2)(C_3H_7NO)_2]$. The structure contains Li cations each coordinated by one catechol monoanion and two *N,N*-dimethylformamide molecules with nearly tetrahedral coordination geometry. The anions are connected *via* very short O···H···O hydrogen bridges to form an infinite polymeric one-dimensional structure.

Comment

o-Benzoquinone and its reduction products *o*-benzo-semiquinone and catechol (1,2-dihydroxybenzene) are