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Structure of Bis(2-pyridylthio-2-pyridinium) Tetrachlorodioxouranate(VI)

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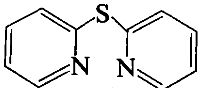
Abstract. $C_{20}H_{18}N_4Cl_4O_2S_2U$, triclinic $F\bar{1}$, a = 13·96 (2), b = 16·59 (2), c = 10·92 (2) Å, α = 91·85 (3), β = 90·15 (3), γ = 91·38 (3)°, M_r = 790·4, U = 2526 Å^3, Z = 4, D_m = 2·02, D_c = 2·08 g cm^{-3}. (Standard primitive cell parameters are: a = 8·85, b = 10·08, c = 10·92 Å, α = 124·63, β = 52·07, γ = 111·4°. The transformation used to convert the F cell to the P cell is as follows: $\mathbf{a}_P = \frac{1}{2}\mathbf{a}_F + \frac{1}{2}\mathbf{c}_F$; $\mathbf{b}_P = \frac{1}{2}\mathbf{b}_F - \frac{1}{2}\mathbf{c}_F$; $\mathbf{c}_P = \mathbf{c}_F$.) The linear uranyl group (U—O, 1·77 Å) is equatorially bonded to four Cl atoms, with U—Cl distances of 2·66 Å, thus forming the anion of a salt-like complex. The two pyridine planes of the cation are twisted by about 5 and 2° with respect to the C—S—C plane.

Introduction. The chelating ability of di-2-pyridyl sulphide (L) toward d transition-metal atoms has been already discussed, but there is no definite evidence for the existence of stable complexes in which this ligand is coordinated to larger cations, such as lanthanide or uranyl ions. In order to ascertain the possibility of coordination of this potentially bidentate ligand, a single-crystal X-ray analysis has been carried out on the complex obtained by reacting solutions of the ligand in acetonitrile with uranyl chloride in anhydrous ethanol (Pappalardo & Seminara, 1976).



(L)

Crystals suitable for X-ray analysis were kindly supplied by Dr G. C. Pappalardo. A crystal of approximate dimensions 0·2 × 0·1 × 0·5 mm was mounted on an automated Siemens AED diffractometer with the c axis along the φ axis of the diffractometer. The unit-cell dimensions were obtained by a least-squares refinement of the angular measurements of 25 selected reflexions.

The intensities of 1747 reflexions with 2θ less than 50° were collected by the θ–2θ scan technique with a four-circle diffractometer using Mo $K\alpha$ radiation (λ = 0·7107 Å).

The intensity of a monitor reflexion measured after 20 reflexions showed that the crystal did not suffer any deterioration during data collection. The data were corrected for Lorentz and polarization factors, but not for absorption, because the irregular shape of the crystal did not allow accurate measurement of its dimensions [μ(Mo $K\alpha$) = 86·7 cm^{-1}]. The structure was solved by use of the heavy-atom method and refined isotropically to R = 11·4%. Further refinement cycles following introduction of anisotropic temperature factors for all non-hydrogen atoms and the inclusion of the H atoms bonded to C, in calculated positions (assuming C—H 0·95 Å, and C—C—H 120°) with assigned temperature factors of 5 Å^2, reduced R to

Table 1. *Fractional coordinates* (×10^4; ×10^3 *for the hydrogens attached to carbon atoms*)

The H atoms bonded to C are in calculated positions.

	x	y	z
U	0	0	0
Cl(1)	1686 (4)	557 (3)	849 (4)
Cl(2)	−784 (4)	475 (3)	212 (4)
O	228 (9)	−952 (6)	608 (9)
S	1740 (4)	1640 (3)	−2317 (4)
N(1)	1086 (11)	3174 (8)	−2254 (12)
N(2)	1275 (10)	2423 (7)	−4390 (12)
C(1)	1350 (12)	2539 (9)	−1588 (15)
C(2)	1331 (13)	2554 (10)	−331 (16)
C(3)	1062 (14)	3260 (11)	279 (16)
C(4)	809 (14)	3927 (10)	−396 (16)
C(5)	812 (15)	3867 (10)	−1633 (17)
C(6)	1600 (13)	1714 (10)	−3893 (16)
C(7)	1854 (14)	1070 (10)	−4658 (17)
C(8)	1744 (14)	1121 (11)	−5883 (18)
C(9)	1378 (14)	1821 (11)	−6405 (16)
C(10)	1174 (14)	2468 (10)	−5595 (16)
H(N1)	980	3140	−3154
H(C2)	150	209	11
H(C3)	105	329	115
H(C4)	64	442	1
H(C5)	62	432	−209
H(C7)	210	60	−432
H(C8)	192	68	−640
H(C9)	128	185	−726
H(C10)	96	296	−592

Table 2. *Bond distances* (Å) *and angles* (°), *with e.s.d.'s in parentheses*

		U–O	1·77 (1)
		U–Cl(1)	2·662 (5)
		U–Cl(2)	2·665 (5)
S–C(1)	1·76 (2)	S–C(6)	1·75 (2)
C(1)–C(2)	1·37 (2)	C(6)–C(7)	1·42 (2)
C(2)–C(3)	1·39 (2)	C(7)–C(8)	1·35 (3)
C(3)–C(4)	1·40 (2)	C(8)–C(9)	1·42 (3)
C(4)–C(5)	1·35 (2)	C(9)–C(10)	1·40 (2)
C(5)–N(1)	1·38 (2)	C(10)–N(2)	1·33 (2)
N(1)–C(1)	1·36 (2)	N(2)–C(6)	1·36 (2)
O–U–Cl(1)	89·9 (4)	Cl(1)–U–Cl(2)	88·6 (2)
O–U–Cl(2)	90·0 (3)	C(1)–S–C(6)	108 (1)
S–C(1)–N(1)	121 (1)	S–C(6)–N(2)	123 (1)
S–C(1)–C(2)	116 (1)	S–C(6)–C(7)	117 (1)
N(1)–C(1)–C(2)	123 (1)	N(2)–C(6)–C(7)	120 (2)
C(1)–C(2)–C(3)	118 (2)	C(6)–C(7)–C(8)	118 (2)
C(2)–C(3)–C(4)	120 (2)	C(7)–C(8)–C(9)	121 (2)
C(3)–C(4)–C(5)	119 (2)	C(8)–C(9)–C(10)	117 (2)
C(4)–C(5)–N(1)	122 (2)	C(9)–C(10)–N(2)	122 (2)
C(5)–N(1)–C(1)	118 (1)	C(10)–N(2)–C(6)	120 (1)

the final value of 6·1% for the 1730 observed reflexions $[I < 2\sigma(I)]$. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = 1$.

All ring atoms of the ligand were initially treated as C atoms. Isotropic refinement showed that the temperature factors of these atoms were between 3·6 and 4·5 Å^2, except two which were 2·02 and 1·92 Å^2. After substitution of the form factors of these two atoms with those of the N atoms, the temperature factors assumed normal values, thus confirming the choice. A final difference electron-density map including all atoms, except the H bonded to the N atom, showed no significant residual, apart from a peak of about 0·8 e Å^{-3} which, because of its position, could be attributed to the proton of the ligand [N(1)–H bond distance 1·0 Å].

The scattering factors for U were from Cromer & Waber (1965), for H from *International Tables for X-ray Crystallography* (1962) and for the other atoms from Cromer & Mann (1968). Anomalous dispersion corrections were introduced for U, the values used ($f' = -9·19$, $f'' = 9·09$) being taken from Cromer (1965). All calculations were performed with the XRAY system (Stewart, Kundell & Baldwin, 1970). The final atomic coordinates are given in Table 1 and interatomic distances and angles in Table 2.*

Discussion. The compound has a salt-like structure, being composed of complex $[LH]^+$ cations and $[UO_2Cl_4]^{2-}$ anions as shown in Fig. 1, in which the molecular structure is projected down **b**. Four Cl atoms occupy the corners of a square around the linear uranyl group, the symmetry of the anion being D_{4h} within the limit of the experimental errors. The U–O distance (1·77 Å) is normal and the values of the two crystallographically independent U–Cl distances (2·662 and 2·665 Å) are consistent with the sum of the covalent radii (2·68 Å) (Shannon & Prewitt, 1970).

As shown in Fig. 1 the protonated ligand has the N,N-inside conformation. Least-squares-plane calculations indicate that the pyridine planes make angles of 5 and 2° with the C–S–C plane so that the entire molecule can be considered approximately planar. A similar all-planar structure agrees with that predicted

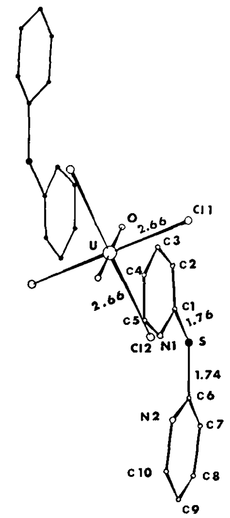


Fig. 1. The molecular structure with the atom numbering used.

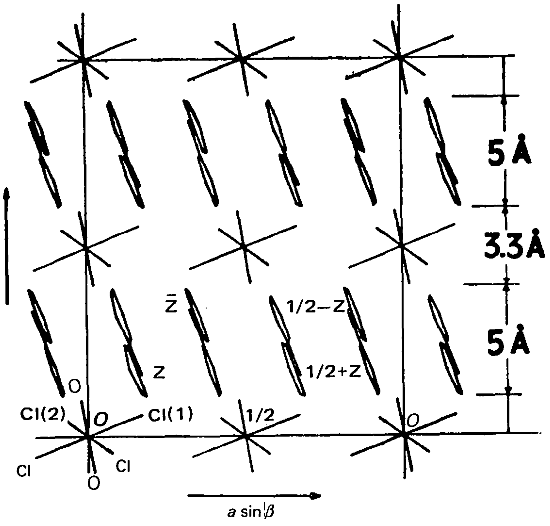


Fig. 2. Projection of the structure along [001]. The relative positions with respect to the z coordinate are indicated for some units.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33396 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

on the basis of energy calculations for the non-protonated molecule (Chachaty, Pappalardo & Scarlata, 1976). On the other hand, theoretical calculations (Galasso, De Alti & Bigotto, 1971) and molar Kerr constant studies (Aroney, Le Fevre & Saxby, 1963; Le Fevre & Saxby, 1966) predict for the diphenyl sulphide molecule a non-planar structure with angles of *ca* 42–48° between the phenyl ring planes because of the steric contact between *ortho* H atoms. It is therefore reasonable that in this case the presence of a single H atom in the *ortho* position has too little steric influence to alter significantly the planar structure of the molecule. In addition, the contact distance of 2·63 Å between the two N atoms strongly suggests the existence of an intramolecular N–H···N hydrogen bond. The C–S–C angle of 108 (1)° shows that the S atoms are sp^3-hybridized. The mean value of the two C–S bond lengths is 1·755 Å, which is appreciably shorter than the paraffinic distance of 1·81 Å, but is in agreement with the C(sp^2)–S bond with two atoms bonded to the S atoms, *e.g.* 1·77 Å in phenothiazine (Bell, Blount, Briscoe & Freeman, 1968), and 1·765 Å in methixene (Chu, 1972). The relative shortness of the S–C bonds could indicate involvement of the sulphur *d* orbitals with the pyridine π systems and *via* hyperconjugation they also contribute to the cation's planarity. Bond distances and angles in the pyridine rings have normal values. As shown in the [001] projection of the unit cell (Fig. 2) the entire structure comprises alternate cationic and anionic units developing along [100]. The thickness of the $[UO_2Cl_4]^{2-}$ groups and of the protonated ligands is roughly 3·3 and 5 Å, respectively, in the **b** direction.

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(2-Oxopropyl)mercury Bromide

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Abstract. C_3H_5OHgBr, triclinic, $P\bar{1}$, $a = 6{\cdot}752$ (1), $b = 5{\cdot}733$ (1), $c = 7{\cdot}979$ (1) Å, $\alpha = 83{\cdot}14$ (1), $\beta = 95{\cdot}53$ (1), $\gamma = 101{\cdot}47$ (1)°, $Z = 2$, $D_o = 3{\cdot}70$ (5), $D_c = 3{\cdot}741$ g cm^{-3}. The structure contains two short intermolecular Hg···O(CO) contacts [2·81 (2), 2·82 (2) Å] which are consistent with the relatively low carbonyl stretching frequency observed (1645 cm^{-1}), assuming that formation of weak intermolecular Hg···O bonds also weakens the carbonyl bond. The Hg–Br and Hg–C distances are 2·441 (5) and 2·08 (4) Å, respectively, while the C–Hg–Br angle is 176 (1)°.

Introduction. Milky-white, irregularly shaped crystals of (2-oxopropyl)mercury bromide, obtained from acetone–petroleum ether, were provided by Mr John Feeney (1976). A large crystal was air blown around a