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Uranyl Complexes with Bidentate Derivatives of Pyridine N-Oxide. The Crystal Structure of Dimethylsulphoxidebis(1-oxo-2-thiopyridinato)-dioxouranium(VI) and Aquabis(1,2-dioxo-pyridinato)dioxouranium(VI) Monohydrate

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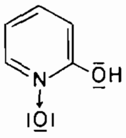
Some uranyl complexes with bidentate derivatives of pyridine-N-oxide have been prepared and their crystal structures determined by X-ray crystallography. Dimethylsulphoxidebis(1-oxo-2-thio-pyridinato)dioxouranium(VI) is monoclinic, space group $P2_1/n$ *with* a = *18.70(2),* b = *13.57(1),* c = *6.87(1)* Å, and β = *99.80(3)°. Two bidentate ligands and one dmso molecule are equatorially bonded to the uranyl group in a distorted pentagonal bipyramidal coordination geometry. The U–O (equatorial) bond distances (mean 2.33* Å*) are of the same order and the U–S bond distances are 2.85 and 2.88* Å*. The N–O and the N–C bonds are partial double and C–S is double, suggesting the presence of a mesomeric distribution of electronic density over the ligand system. Aquabis(1,2-dioxopyridinato)dioxouranium(VI) monohydrate is orthorhombic, space group Pnam, with* a = *12.26(1),* b = *6.89(1) and* c = *15.81(1)* Å*. Two bidentate ligands and one water molecule are equatorially bonded to the uranyl group in the pentagonal bipyramidal coordination geometry. The U–O(equatorial) bond distances (mean 2.37* Å*) are of the same order and the N–O, N–C and C–O bonds are partial double. One additional water molecule is clathrate. The molecule has the Cs symmetry, with the uranyl group and the water oxygen atoms on the mirror plane.*

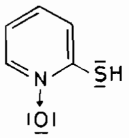
Introduction

The ability of the actinide ions to coordinate pyridine N-oxide [1a] and other oxygen donor ligands [1b] to form stable compounds is well known. Bonding of these neutral monodentate ligands is achieved through the oxygen atom and some correlations have been put forward between the basicity of the ligand and the shift of the νNO stretching band upon coordination [2].

We have extended the study of complexes of U(VI), Th(IV), and La(III) with a series of bidentate ligands: (I), (II), and (III), derived from pyridine N-oxide.



(I)



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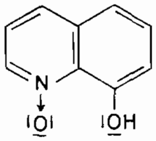

(III)

We report here the preparation of the corresponding uranyl complexes and the crystal structure of $[UO_2(pyOS)_2dmso]$ and $[UO_2(pyOO)_2H_2O]\cdot H_2O$.

Experimental

Preparation of Compounds

Dimethylsulphoxidebis(1-oxo-2-thiopyridinato)-dioxouranium(VI)

A solution of $UO_2(NO_3)_2\cdot 6H_2O$ (1 mmol) in MeOH was added to a methanolic solution of pyOSH

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TABLE I(a). Positional and Thermal* ($\times10^4$) Parameters for [$UO_2(pyOS)_2(dmso)$].

Atom	x	y	z
U	0.2257(1)	0.3569(0)	0.3904(1)
S(1)	0.0863(2)	0.4112(3)	0.4705(8)
S(2)	0.3691(2)	0.4221(3)	0.3496(8)
S(3)	0.2676(2)	0.1057(3)	0.8865(8)
O(1)	0.1920(6)	0.3850(8)	0.1420(16)
O(2)	0.2592(6)	0.3298(8)	0.6373(16)
O(3)	0.1467(6)	0.2234(8)	0.3885(18)
O(4)	0.2982(6)	0.2325(7)	0.3037(18)
O(5)	0.2272(6)	0.5239(7)	0.4609(17)
N(1)	0.0745(6)	0.2206(9)	0.3898(18)
N(2)	0.3718(6)	0.2263(9)	0.3401(18)
C(1)	0.0405(9)	0.1310(11)	0.3610(25)
C(2)	−0.0296(10)	0.1256(15)	0.3625(28)
C(3)	−0.0696(9)	0.2086(15)	0.3845(26)
C(4)	−0.0353(8)	0.2971(14)	0.4140(25)
C(5)	0.0391(8)	0.3042(12)	0.4229(24)
C(6)	0.4014(8)	0.1342(12)	0.3473(23)
C(7)	0.4744(9)	0.1232(13)	0.3821(26)
C(8)	0.5174(9)	0.2062(15)	0.4080(26)
C(9)	0.4867(9)	0.2976(13)	0.4008(25)
C(10)	0.4128(8)	0.3099(11)	0.3655(24)
C(11)	0.1794(10)	0.1578(14)	0.8841(30)
C(12)	0.2549(16)	0.0455(16)	0.6548(31)
H(1)	0.069	0.070	0.340
H(2)	−0.055	0.059	0.345
H(3)	−0.124	0.204	0.381
H(4)	−0.065	0.359	0.428
H(6)	0.369	0.074	0.325
H(7)	0.497	0.055	0.388
H(8)	0.572	0.199	0.435
H(9)	0.519	0.358	0.421

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
U	290(3)	251(3)	267(3)	6(2)	22(2)	16(3)
S(1)	398(23)	294(22)	737(34)	16(18)	189(23)	−76(22)
S(2)	380(22)	299(21)	664(32)	−56(18)	158(22)	7(22)
S(3)	422(24)	341(22)	617(31)	26(19)	130(22)	97(22)
O(1)	515(69)	432(67)	266(59)	54(54)	−60(52)	−1(53)
O(2)	468(66)	399(64)	257(59)	58(51)	−12(50)	80(50)
O(3)	354(58)	314(58)	488(70)	8(48)	90(53)	58(56)
O(4)	346(58)	228(53)	567(77)	−4(45)	3(55)	−24(54)
O(5)	538(69)	204(52)	420(67)	8(49)	5(57)	−64(50)
N(1)	337(66)	285(66)	248(65)	18(54)	60(54)	79(56)
N(2)	335(67)	288(66)	256(66)	−2(54)	58(55)	−24(56)
C(1)	445(92)	217(77)	423(94)	−71(68)	−12(76)	20(72)
C(2)	490(105)	554(121)	457(108)	−123(91)	19(88)	48(96)
C(3)	342(88)	669(127)	333(94)	−82(87)	−26(74)	6(92)
C(4)	308(81)	565(110)	328(89)	13(77)	86(71)	−20(84)
C(5)	333(82)	382(91)	301(85)	46(70)	30(68)	24(73)
C(6)	421(88)	365(89)	279(81)	35(74)	4(69)	−15(75)
C(7)	414(92)	411(99)	397(96)	89(75)	62(77)	39(80)
C(8)	319(87)	686(128)	374(98)	68(86)	81(76)	30(93)
C(9)	399(90)	427(98)	320(88)	−103(75)	96(74)	−118(76)
C(10)	321(79)	312(81)	340(87)	−10(65)	92(68)	3(71)
C(11)	510(105)	504(114)	548(118)	206(92)	27(93)	−21(99)
C(12)	1482(235)	558(133)	369(114)	450(145)	266(134)	38(101)

*Temperature factors are in the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + U_{12}hka^*b^* + U_{13}hla^*c^* + U_{23}klb^*c^*)]$.

TABLE I(b). Positional and Thermal* ($\times 10^4$) Parameters for $[UO_2(pyOO)_2H_2O]\cdot H_2O$.

Atom	x	y	z
U	0.3730(1)	0.3717(2)	0.7500
O(1)	0.4013(10)	0.1235(8)	0.7500
O(2)	0.3558(10)	0.6208(5)	0.7500
O(3)	0.2130(10)	0.3372(3)	0.6699(7)
O(4)	0.4025(10)	0.3777(34)	0.6009(8)
O(5)	0.5634(20)	0.4396(38)	0.7500
O(6)	0.5779(30)	0.8230(52)	0.7500
N	0.2188(16)	0.3555(42)	0.5829(11)
C(1)	0.3178(16)	0.3714(49)	0.5505(12)
C(2)	0.3302(20)	0.3789(50)	0.4602(13)
C(3)	0.2383(20)	0.3734(50)	0.4128(14)
C(4)	0.1353(22)	0.3590(49)	0.4476(14)
C(5)	0.1231(22)	0.3454(39)	0.5367(14)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
U	291	465	226	31	–27	–37
O(1)	623	1297	–152	–189	23	5
O(2)	646	1080	122	632	–9	35
O(3)	233	823	244	–92	–17	–79
O(4)	261	962	137	82	3	–46
O(5)	365	607	459	315	–22	27
O(6)	725	730	1370	181	–105	–69
N	419	600	276	138	–27	–14
C(1)	300	616	121	106	–33	–69
C(2)	595	633	209	–183	–28	–27
C(3)	639	422	309	103	–114	–111
C(4)	565	654	296	60	–137	48
C(5)	526	410	404	–97	–236	–22

(2 mmol) and LiOH (2 mmol). On evaporating *in vacuo* at room temperature $UO_2(pyOS)_2\cdot 2H_2O$ was obtained as a red precipitate which was filtered, washed with MeOH and dried (Found: C 21.56; H 1.72; N 5.15%; Calcd. for $C_{10}H_{12}N_2O_6S_2U$: C21.50; H 2.15; N 5.02%). By reacting the compound with dmso in MeOH well shaped crystals of $[UO_2(pyOS)_2\text{-}dmso]$ were obtained.

Aquabis(1,2-dioxo-pyridinato)dioxouranium-(VI)monohydrate

By reacting a solution of $UO_2(NO_3)_2\cdot 6H_2O$ (1 mmol) in MeOH with a methanolic solution of pyOOH (2 mmol) and LiOH (2 mmol) $UO_2(pyOO)_2\text{-}H_2O$ was obtained as an orange precipitate (Found: C 23.92; H 2.18; N 5.28%; Calcd. for $C_{10}H_{10}N_2O_7U$: C 23.62; H 1.96; N 5.51%). Well shaped crystals of $[UO_2(pyOO)_2H_2O]\cdot H_2O$ formed from the mother liquor.

Bis(quinolinolato)dioxouranium(VI)dihydrate

A solution of $UO_2(NO_3)_2\cdot 6H_2O$ (1 mmol) in MeOH was added to a yellow methanol solution of quinOH (2 mmol). On evaporating *in vacuo* at room temperature $UO_2(quinO)_2\cdot 2H_2O$ was obtained as a red precipitate, which was filtered, washed with methanol and dried (Found: C 34.19; H, 2.20; N 4.42%; Calcd. for $C_{18}H_{16}O_8N_2U$: C 34.40; H 2.55; N 4.67%).

X-Ray Data

Dimethylsulphoxidebis(1-oxo-2-thio-pyridinato)-dioxouranium(VI)

A small fragment was used for the X-ray work. Cell dimensions were calculated from the accurate settings of 25 medium angle reflections on a PW-1100 Philips diffractometer with monochromated MoKα radiation. Crystal data are: $C_{12}H_{14}N_2O_5S_3U$, FW = 600, F(000) = 1120, monoclinic, space group $P2_1/n$ from systematic absences h0l for h + l odd, and 0k0 for k odd; general positions ±(x, y, z; ½ + x, ½ – y, ½ + z); cell parameters $a = 18.70(2)$, $b = 13.57(1)$, $c = 6.87(1)$ Å; $\beta = 99.80(3)^\circ$, $V = 1718$ Å^3; $D_c = 2.32$ g cm^{-3} for $Z = 4$, and μ(MoKα) = 145.5 cm^{-1}.

Intensities for reflections having θ in the range 2–25° were measured on the same instrument with a scan speed of 2° min^{-1} and the ω–2θ scan. Of the

TABLE II(a). Distances and Angles for $[UO_2(pyOS)_2(dmso)]$.

Bond Distances (Å) Coordination			
U–O(1)	1.75(1)	U–O(3)	2.34(1)
U–O(2)	1.74(1)	U–O(4)	2.31(1)
U–S(1)	2.85(1)	U–O(5)	2.32(1)
U–S(2)	2.88(1)		
Ligands			
S(1)–C(5)	1.70(2)	S(2)–C(10)	1.72(2)
O(3)–N(1)	1.35(2)	O(4)–N(2)	1.36(2)
N(1)–C(1)	1.37(2)	N(2)–C(6)	1.36(2)
N(1)–C(5)	1.35(2)	N(2)–C(10)	1.36(2)
C(1)–C(2)	1.31(2)	C(6)–C(7)	1.36(2)
C(2)–C(3)	1.38(3)	C(7)–C(8)	1.38(2)
C(3)–C(4)	1.36(3)	C(8)–C(9)	1.36(3)
C(4)–C(5)	1.39(2)	C(9)–C(10)	1.37(2)
dmso			
S(3)–O(5)	1.52(1)	S(3)–C(11)	1.79(2)
		S(3)–C(12)	1.77(2)
Bond Angles (°) Coordination			
O(1)–U–O(2)	179.6(0.5)	O(3)–U–O(4)	80.2(0.4)
S(1)–U–O(3)	66.6(0.3)	S(1)–U–O(5)	71.7(0.3)
S(2)–U–O(4)	66.6(0.3)	S(2)–U–O(5)	75.0(0.3)
Ligands			
U–S(1)–C(5)	102(1)	U–S(2)–C(10)	99(1)
U–O(3)–N(1)	131(1)	U–O(4)–N(2)	128(1)
S(1)–C(5)–N(1)	120(1)	S(2)–C(10)–N(2)	118(1)
O(3)–N(1)–C(5)	120(1)	O(4)–N(2)–C(10)	120(1)
C(1)–N(1)–C(5)	123(1)	C(6)–N(2)–C(10)	123(1)
N(1)–C(1)–C(2)	119(1)	N(2)–C(6)–C(7)	120(1)
C(1)–C(2)–C(3)	121(2)	C(6)–C(7)–C(8)	119(2)
C(2)–C(3)–C(4)	119(2)	C(7)–C(8)–C(9)	120(2)
C(3)–C(4)–C(5)	121(2)	C(8)–C(9)–C(10)	121(2)
C(4)–C(5)–N(1)	117(1)	C(9)–C(10)–N(2)	117(1)
dmso			
U–O(5)–S(3)	149(1)	O(5)–S(3)–C(11)	104(1)
C(11)–S(3)–C(12)	101(1)	O(5)–S(3)–C(12)	105(1)
Contact distances (Å)			
S(1)···O(3)	2.88(1)	S(2)···O(4)	2.89(1)
S(1)···O(5)	3.06(1)	S(2)···O(5)	3.20(1)
O(3)···O(4)	2.99(2)		

TABLE II(b). Distances and Angles for $[UO_2(pyOO)_2H_2O]\cdot H_2O$.

Bond Distances (Å) Coordination			
U–O(1)	1.71(4)	U–O(3)	2.35(1)
U–O(2)	1.73(4)	U–O(4)	2.38(1)
		U–O(5)	2.38(2)

(continued on facing page)

TABLE II(b). *(continued)*

Ligands			
O(3)–N	1.38(2)	C(1)–C(2)	1.44(3)
O(4)–C(1)	1.31(2)	C(2)–C(3)	1.35(3)
N(1)–C(1)	1.32(2)	C(3)–C(4)	1.38(4)
N(1)–C(5)	1.38(3)	C(4)–C(5)	1.42(3)
Bond angles (°) Coordination			
O(1)–U–O(2)	175(1)		
O(3)–U–O(4)	66.1(0.4)		
O(3)–U–O(3^{i})	65.3(0.4)		
O(4)–U–O(5)	81.6(0.3)		
Ligands			
U–O(3)–N	119(1)	C(1)–N–C(5)	125(2)
U–O(4)–C(1)	119(1)	N–C(1)–C(2)	119(2)
O(3)–N–C(5)	118(2)	C(1)–C(2)–C(3)	117(2)
O(4)–C(1)–C(2)	121(2)	C(2)–C(3)–C(4)	123(2)
O(3)–N–C(1)	116(2)	C(3)–C(4)–C(5)	120(2)
O(4)–C(1)–N	120(2)	C(4)–C(5)–N	115(2)
Contact Distances (Å)			
O(3)···O(3^{i})	2.53(2)	O(5)···O(6)	2.65(4)
O(3)···O(4)	2.58(2)	O(5)···O(3^{ii})	2.93(3)
O(4)···O(5)	3.10(2)		

Symmetry code: (i) x, y, ¾ – z; (ii) ¼ + x, ¼ – y, ¾ – z.

3292 reflections measured, 2882 had I > 3σ(I) and were considered to be observed. Corrections were made for Lorentz polarization and for absorption [3]. The intensities of two central reflections were monitored and showed negligible deterioration. The structure was solved by the use of the heavy-atom method. Refinement of positional and isotropic parameters for all non-hydrogen atoms converged to a conventional R of 8.3%. Further refinement including anisotropic temperature factors and the ring hydrogen atoms in calculated positions gave the final R of 4.4%. To the hydrogen atoms was assigned a fixed isotropic temperature factor B of 8 Å^2. Scattering factors for U, S, O, N and C were those of Cromer and Mann [4], and for H those tabulated in the International Tables for X-ray Crystallography [5]. The uranium scattering factor was corrected for anomalous dispersion with constant average values [6] for the real and imaginary components. All calculations were done using the X-ray program system [7]. Final atomic coordinates are listed in Table I(a). Intramolecular distances and angles are tabulated in Table II(a). Information concerning selected molecular planes and dihedral angles are in Table III(a).

Aquabis(1,2-dioxopyridinato)dioxouranium(VI)-monohydrate

Cell dimensions were calculated from the accurate settings of 25 medium angle reflections with the MoKα radiation. Crystal data are: $C_{10}H_{12}N_2O_8U$, FW = 526, F(000) = 968, orthorhombic, systematic absences 0kl for k + l odd, and h0l for h odd, possible space groups Pnam and Pna2$_1$. The centrosymmetric space group was chosen and confirmed by the structure determination; general positions ±(x, y, z; ½ + x, ½ – y, ½ – z; $\bar{x}$, $\bar{y}$, ½ + z; ½ – x, ½ + y, $\bar{z}$); cell parameters a = 12.26(1), b = 6.89(1), c = 15.81(1) Å, V = 1336 Å^3, D_c = 2.61 g cm^{-3} for Z = 4, and μ(MoKα) = 182.2 cm^{-1}. Intensities for reflections having θ in the range 2–25° were measured on a Philips diffractometer with a scan speed of 2° min^{-1} and the ω–2θ scan. Of the 1224 intensities, 866 had I > 3σ(I) and were considered to be observed. Corrections were made for Lp and also for absorption effects [3]. The intensities of two central reflections were monitored at intervals and showed no observable deterioration of the crystal. The structure is governed by the heavy atom. The presence of four molecules in a space group with eight general positions implies that the uranium atoms lie on special positions. It was found

TABLE III(a). Equations of Mean Planes through Sets of Atoms of $[UO_2(pyOS)_2(dmso)]$ and Distances (Å) of Atoms from the Plane (in square brackets). Fractional coordinates X, Y, and Z are referred to the crystallographic axes.

Plane I:	S(1), S(2), O(3), O(4), O(5). $3.04X - 2.42Y + 6.38Z = 2.33$ Å [S(1) −0.06, S(2) 0.00, O(3) 0.06, O(4) −0.04, O(5) 0.04m U* −0.02]
Plane II:	N(1), C(1) to C(5). $-0.09X - 2.19Y + 6.69Z = 2.13$ Å [N(1) −0.01, C(1) −0.01, C(2) 0.02, C(3) −0.01, C(4) −0.01, C(5) 0.02, U* −0.32]
Plane III:	N(2), C(6) to C(10) $-3.32X - 0.51Y + 6.86Z = 0.98$ Å [N(2) 0.00, C(6) 0.00, C(7) 0.00, C(8) 0.00, C(9) 0.00, C(10) 0.00, U* 0.77]

*Atom not introduced in plane calculation

Angle (°) between the planes

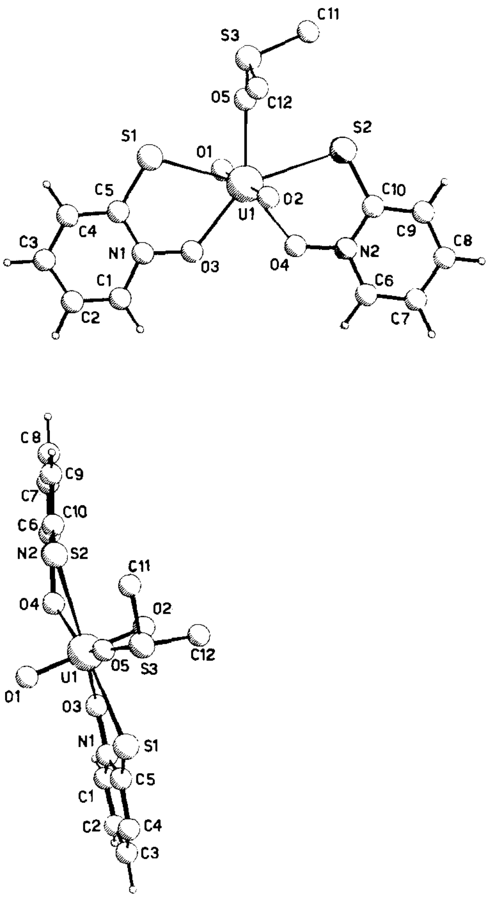
I–II	9.7
I–III	21.2
II–III	12.2

TABLE III(b). Equations of Mean Planes through Sets of Atoms of $[UO_2(pyOO)_2H_2O]\cdot H_2O$ and Distances (Å) of Atoms from the Plane (in square brackets). Fractional coordinates X, Y, and Z are referred to the crystallographic axes.

Plane I:	O(3), O(4), O(5), O(3^{i}), O(4^{i}) $-1.89X + 6.81Y = 1.87$ Å [O(3) 0.03, O(4) −0.06, O(5) 0.06, O(3^{i}) −0.03, O(4^{i}) 0.06, U* −0.04]
Plane II:	O(3), O(4), N, C(1). $-0.97X + 6.85Y + 1.16Z = 2.89$ Å [O(3) −0.01, O(4) 0.01, N 0.01, C(1) −0.01]

*Atom not introduced in plane calculation.

The angle between I and II is 6.0°.

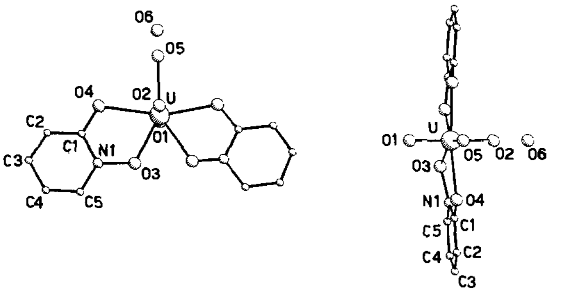


Figs. 1 and 2. Perspective views of the $[UO_2(pyOS)_2dmso]$ molecule.

that the uranium atom, the uranyl oxygens and the oxygen atoms of both water molecules lie on the mirror plane so that the Cs molecular symmetry corresponds to the crystallographic one. Refinement of the positional and individual anisotropic temperature factors converged at the final R of 5.8% when the last shift was about 20% of the e.s.d. An alternative refinement in space group $Pna2_1$, in which all atoms are in general positions, converged to about the same final R, was complicated by the presence of strong correlations between the two halves of the molecule, which resulted in very bad values for several bond distances, although the overall molecular structure remained unchanged. Scattering factors for U, O, N were those of ref. 4, and for H those of ref. 5. The uranium scattering factor was corrected for the anomalous dispersion [6]. All calculations were done using the X-ray program system [7]. Final atomic coordinates are listed in Table I(b). Intramolecular distances and angles are tabulated in Table II(b). Information concerning selected molecular planes and dihedral angles are given in Table III(b).

Discussion

Figures 1 and 2 show two projections of the $[UO_2(pyOS)_2dmso]$ molecule with the numbering scheme used. Two bidentate monoanionic ligands and one dmso molecule bind equatorially to the uranyl group leading to seven coordinated uranium(VI) in a distorted bipyramidal coordination geometry. The UO_2^{2+}



Figs. 3 and 4. Perspective views of the $[UO_2(pyOO)_2H_2O] \cdot H_2O$ molecule.

group is linear with usual values (means 1.75 Å) for the U=O distances; the equatorial U–O(ligands) (mean 2.33 Å) and the U–O(dmso) bond distances (2.33 Å) are of the same order. The U–S bond length (2.85 and 2.88 Å) compare well with 2.84 Å (mean) in $[UO_2(Et_2NCS_2)_2Ph_3AsO]$ [8], with 2.85 Å (mean) in $[UO_2(Et_2NCS_2)_2Ph_3PO]$ [8], with 2.85 Å (mean) in $[UO_2(MeCS_2)_2Ph_3PO]$ [9] and with 2.87 Å (mean) in $[UO_2(Et_2NCS_2)_2Me_3NO]$ [10] although in the above complexes the sulphur atoms take part of a four membered ring with the uranium atom. The C–S (ligands) distance (mean 1.71 Å) has the value usually quoted for a double bond. This, and the fact that N–O and N–C are partial double bonds, indicates that the formal negative charge of the sulphur atom is actually distributed over the mesomeric ligand system. Least squares calculations show that atoms equatorially bonded to uranium are only approximately coplanar, being alternatively displaced by *ca.* ±0.05 Å from the mean plane. On the contrary the two ligand rings can be considered planar within the experimental error: they are slightly inclined to the equatorial plane in the characteristic chair-like configuration. Figures 3 and 4 show two different projections of $[UO_2(pyOO)_2H_2O] \cdot H_2O$, whose structure, apart from the obvious chemical differences, strictly resembles that of $[UO_2(pyOS)_2\text{-}dmso]$.

The equatorial U–O distances (mean 2.37 Å) are normal for uranyl complexes with five oxygen atoms bonded in the equatorial plane. The fact that the U–O bonds in $[UO_2(pyOS)_2dmso]$ are significantly shorter is probably due to the fact that in this compound two oxygen atoms are replaced by the less electronegative sulphur atoms. Bond lengths in the ligand are indicative of a statistical presence of the electronic density over the entire chelating moiety. The five equatorial oxygens are approximately coplanar with deviations of *ca.* ±0.04 Å from the mean plane. The two ligands are slightly inclined with respect to the equatorial plane in the characteristic 'boat' configuration.

The O(5)···O(6) contact distance suggests the presence of relatively strong hydrogen bonding between the coordinated and the non-coordinated water molecules.

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References

1 a) P. V. Balakrishnan, S. K. Patil and H. V. Venkatasetty, *J. Inorg. Nucl. Chem.*, *28*, 537 (1966);
B. Zarli, L. Volponi, L. Sindellari and G. De Paoli, *ibid.*, *35*, 231 (1973);
b) K. W. Bagnall, D. Brown and P. J. Jones, *J. Chem. Soc. (A)*, 1763 (1966);
B. C Smith and M. A. Wassef, *ibid.*, 181 (1968);
P. R. Murthy and C. C. Patel, *Can. J. Chem.*, *42*, 856 (1964).
2 P. A. Vigato, U. Casellato and M. Vidali, *Gazz. Chim. Ital.*, *107*, 61 (1977) and references therein.
3 A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Cryst.*, *A24*, 351 (1968).
4 D. T. Cromer and J. B. Mann, *Acta Cryst.*, *A24*, 321 (1968).
5 International Tables for X-Ray Crystallography, Vol. IV, pp. 99–101, Birmingham, Kynoch Press (1974).
6 D. T. Cromer and D. Libermann, *J. Chem. Phys.*, *53*, 1891 (1970).
7 J. M. Stewart, F. A. Kundell and J. C. Baldwin, 'X-Ray System of Crystallographic Programs', Univ. of Maryland, U.S.A. (1973).
8 R. Graziani, B. Zarli, A. Cassol, G. Bombieri, E. Forsellini and E. Tondello, *Inorg. Chem.*, *9*, 2116 (1970).
9 G. Bombieri, U. Croatto, E. Forsellini, B. Zarli and R. Graziani, *J. Chem. Soc.*, 560 (1972).
10 E. Forsellini, G. Bombieri, R. Graziani and B. Zarli, *Inorg. Nucl. Chem. Lett.*, *8*, 461 (1972).