Inorganica Chimica Acta, 51 (1981) 195–199

The Preparation and Crystal Structure of N,N′-bis(salicylidene)-1,5-diamino-3-thiapentane-dioxouranium(VI)

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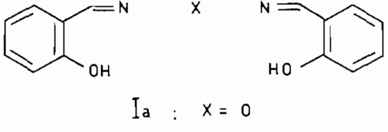
Received February 17, 1981

The title compound has been prepared and crystallized from acetonitrile. The crystals are orthorhombic, space group Pcab, with a = *18.91(2),* b = *16.13(2),* c = *12.10(1) Å, z = 8. The structure was determined from MoKα diffractometer data by standard methods and refined to* R = *0.066. The coordination geometry of the uranium atom is a pentagonal bipyramid with the pentadentate ligand coordinated in the plane normal to the uranyl group. The U–O (ligand) bonds (mean 2.25 Å) are shorter than the U–N bonds (2.60 Å). The sulphur atom is significantly displaced from the equatorial plane and makes with uranium a bond of 2.96 Å.*

Introduction

The crystal structures of the dioxouranium(VI) complexes of two pentadentate α, ω-aminoethers (Ia, Ib) have recently been reported [1–3]. It was shown that the dianionic ligand was bound equatorially to the dioxouranium(VI) moiety, and that all of the donor atoms were coordinating. We report here the synthesis and structure of the dioxouranium(VI) complex, UO$_2$ (Ic). This complex affords opportunity for structural comparison of a series of ligands with -NH-, -O-, and -S- as donor atoms, and introduces the unusual UO$_2$-S interaction.



Ia : X = O
Ib : X = NH
Ic : X = S

Experimental

N,N′-bis(salicylidene)-1,5-diamino-3-thiapentane, (Ic), was prepared by the reaction of salicylaldehyde and 1,5-diamino-3-thiapentane in 2:1 ratio in ethanol. UO$_2$ (Ic) was prepared by the reaction of stoichiometric amounts of dioxouranium(VI) acetate and (Ic) in ethanolic solution. The reaction mixture was warmed gently and on cooling the orange–red product precipitated out. It was filtered off, washed with cold ethanol and dried *in vacuo*. [UO$_2$ (Ic). *Anal.* Found: C, 36.1; H, 3.1; N, 4.3; S, 5.2%. Calcd: C, 36.2; H, 3.0; N, 4.7; S, 5.4%; IR 1618 cm^{-1} (C = N), 885 cm^{-1} (O = U = O)]. Recrystallization from acetonitrile gave crystals suitable for structure determination.

Intensity Data

A crystal of approximate dimensions 0.1 × 0.1 × 0.2 mm was used for the X-ray work. Cell dimensions were calculated from the centred settings of 25 medium angle reflections, on a PW-1100 Philips diffractometer with monochromated MoKα radiation. 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 3231 reflections measured, 923 had $I > 3\sigma(I)$ and were considered to be observed. Corrections were made for Lorentz and polarization effects. The intensities of two central reflections were monitored and showed negligible deterioration. Crystal data are given in Table I.

The structure was solved by the use of the heavy-atom method. Refinement of positional and isotropic parameters for all nonhydrogen atoms converged to a conventional R of 8.2%. Further refinement including anisotropic temperature factors for the non carbon atoms gave a final R factor of 6.6%. The positions of

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TABLE I. Crystal Data for UO_2 (Ic).

Formula	$C_{18}H_{18}N_2O_4SU$
FW	596
a	18.91(2) Å
b	16.13(2) Å
c	12.10(1) Å
V	3691 Å^3
Z	8
System	orthorhombic
Systematic absences	hk0 k = 2n + 1
	h01 h = 2n + 1
	0kl 1 = 2n + 1
Space group	Pcab
General positions	$\pm(x, y, z; \frac{1}{2} - x, \frac{1}{2} + y, \bar{z}; \bar{x}, \frac{1}{2} - y, \frac{1}{2} + z; \frac{1}{2} + x, \bar{y}, \frac{1}{2} - z)$
*D*x	2.14 g cm^{-3}
μ(MoKα)	111.3 cm^{-1}
θ_{max}	25°
Reflections measured	3231
Significant reflections	923

TABLE II. Positional (x10^4) and Thermal (x10^2) Parameters.

Atom	x	y	z	U
U	1149(0)	−853(0)	7053(1)	*
S	1458(9)	633(7)	5696(12)	*
O(1)	392(16)	−1156(18)	6485(30)	*
O(2)	1884(17)	−490(17)	7605(32)	*
O(3)	614(16)	−1162(16)	8628(22)	*
O(4)	1758(18)	−2087(17)	7040(32)	*
N(1)	404(20)	424(21)	7657(25)	*
N(2)	1790(23)	−1034(22)	5172(37)	*
C(1)	645(36)	1289(38)	5963(56)	7.5
C(2)	613(28)	1268(32)	7221(50)	5.4
C(3)	−163(26)	413(28)	8202(39)	3.9
C(4)	−457(26)	−340(30)	8833(43)	4.3
C(5)	−1068(26)	−285(24)	9258(33)	2.7
C(6)	−1381(24)	−912(36)	9854(38)	4.2
C(7)	−1020(27)	−1607(29)	10092(41)	4.4
C(8)	−329(27)	−1731(32)	9605(44)	4.5
C(9)	−25(22)	−1060(24)	8965(35)	2.5
C(10)	2401(21)	−1412(21)	5064(31)	1.2
C(11)	2774(24)	−1918(26)	5917(36)	3.0
C(12)	2394(21)	−2210(22)	6833(34)	2.1
C(13)	2716(22)	−2769(28)	7600(38)	3.8
C(14)	3444(26)	−2936(29)	7393(42)	4.8
C(15)	3826(31)	−2618(29)	6479(37)	4.9
C(16)	3453(22)	−2077(24)	5753(35)	2.5
C(17)	1211(48)	194(46)	4335(60)	10.9
C(18)	1451(35)	−652(42)	4177(56)	8.6

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
U	3.8	2.8	3.1	0.3	−0.3	0.4
S	8.1	2.2	5.7	−0.3	0.7	1.1
O(1)	7.8	5.2	12.4	6.1	6.4	3.5
O(2)	5.7	2.2	9.6	1.7	4.1	3.1
O(3)	3.9	2.6	1.4	0.9	1.2	1.8
O(4)	8.7	3.0	3.8	−0.6	−2.6	3.2
N(1)	5.3	2.1	0.9	−0.9	0.7	0.0
N(2)	6.6	2.3	7.6	−2.3	−3.9	4.2

*Anisotropic thermal parameters in the form

$T = \exp[-2\pi^2(U_{11}a^{*2} + \ldots + 2U_{23}b^*C^*kl)]$

the hydrogen atoms were not determined. Scattering factors for uranium were those of Cromer and Waber [4a], and for the other atoms those of Cromer and Mann [4b]. The uranium scattering factor was corrected for anomalous dispersion with constant average values [5] for the real and imaginary components. All calculations were done using the X-ray '72 program system [6]. Final atomic coordinates are listed in Table II*. Intramolecular distances and angles are tabulated in Table III. Information concerning selected molecular planes and dihedral angles are in Table IV.

Results and Discussion

The dioxouranium(VI) complex of N,N′-bis-(salicylidene)-1,5-diamino-3-thiapentane, UO_2 (Ic) was prepared by warming together ethanolic solutions of Ic and dioxouranium(VI) acetate in stoichieometric amounts. On cooling non-solvated crystals of UO_2 (Ic) were recovered, and these were recrystallized from acetonitrile to give a sample for X-ray structure determination. UO_2 (Ic), was not soluble in

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*Tables of |Fo| and |Fc| values may be obtained from the Editor on request.

TABLE III. Distances and Angles.

Bond distances (Å)			
Coordination			
U–O(1)	1.66(3)	U–O(2)	1.65(3)
U–O(3)	2.21(3)	U–O(4)	2.29(3)
U–N(1)	2.60(4)	U–N(2)	2.60(4)
U–S	2.96(1)		
Ligand			
O(3)–C(9)	1.28(5)	O(4)–C(12)	1.25(5)
N(1)–C(3)	1.26(6)	N(2)–C(10)	1.31(6)
N(1)–C(2)	1.51(6)	N(2)–C(18)	1.50(8)
S–C(1)	1.89(7)	S–C(17)	1.85(8)
C(3)–C(4)	1.54(7)	C(10)–C(11)	1.49(6)
C(1)–C(2)	1.52(9)	C(17)–C(18)	1.45(10)
Bond angles (°)			
Coordination			
O(1)–U–O(2)	176(1)	O(1)–U–S	100(1)
O(3)–U–O(4)	92(1)	O(2)–U–S	77(1)
O(3)–U–N(1)	72(1)	N(1)–U–S	68(1)
O(4)–U–N(2)	70(1)	N(2)–U–S	61(1)
Ligand			
U–O(3)–C(9)	132(3)	U–O(4)–C(12)	129(2)
U–N(1)–C(3)	127(3)	U–N(2)–C(10)	123(3)
U–N(1)–C(2)	118(3)	U–N(2)–C(18)	117(3)
U–S–C(1)	101(2)	U–S–C(17)	98(2)
O(3)–C(9)–C(4)	127(4)	O(4)–C(12)–C(11)	127(4)
N(1)–C(3)–C(4)	125(4)	N(2)–C(10)–C(11)	127(4)
C(3)–C(4)–C(9)	119(4)	C(10)–C(11)–C(12)	119(4)
C(3)–N(1)–C(2)	115(4)	C(10)–N(2)–C(18)	119(4)
N(1)–C(2)–C(1)	112(4)	N(2)–C(18)–C(17)	115(5)
S–C(1)–C(2)	101(4)	S–C(17)–C(18)	113(5)
C(1)–S–C(17)	99(3)		
Contact distances (Å)			
S···O(1)	3.12	O(3)···O(4)	3.25
S···O(2)	2.83	O(3)···N(1)	2.84
S···N(1)	3.12	O(4)···N(2)	2.82
S···N(2)	3.04		

non-polar solvents, and only sparingly so in most donor solvents. This contrasts with the dioxouranium(VI) complexes of Ia and Ib where ready solution was obtained, and, for Ib, where solvates were accessible [7]. Only one crystalline modification of UO (Ic) was found, unlike UO_2 (Ia) where two modifications were observed [2].

The IR spectrum for UO (Ic) shows a single band attributable to the ν_3, antisymmetric stretch [8], at 885 cm^{-1}. This is in accord with the presence of a linear, symmetric dioxouranium(VI) grouping.

The crystal structure analysis shows that the pentadentate dianionic ligand binds equatorially to the dioxouranium(VI) group leading to seven coordinated uranium(VI) in a distorted bipyramidal coordination geometry. Figure 1 gives a projection of the molecule together with the atom numbering scheme used. The uranyl U–O distances (1.65 and 1.66 Å) are surprisingly shorter (by about 0.1 Å) than the values normally found in most uranyl complexes, and are probably unrealistic, even if similar or even smaller values have been sometimes observed [9, 10].

TABLE IV. Least-squares Planes with the Deviations (Å) of Relevant Atoms in Square Brackets Given by PX + QY + RZ = S, where X, Y, and Z are Fractional Unit-Cell Coordinates.

Plane I: O(3), O(4), N(1), N(2)
15.11X + 6.70Y + 5.25Z = 4.82 Å
[O(3) −0.14, O(4) 0.14, N(1) 0.10, N(2) −0.10, U[a] 0.05, S[a] 0.80].

Plane II: O(3), C(3) to C(9)
7.22X + 6.29Y + 10.14Z = 8.44 Å
[O(3) 0.02, C(3) 0.02, C(4) −0.02, C(5) 0.00, C(6) −0.01, C(7) 0.05, C(8) −0.02, C(9) −0.03].

Plane III: O(4), C(10) to C(16).
5.00X + 12.98Y + 6.43Z = 2.68 Å
[O(4) 0.02, C(10) −0.06, C(11) 0.02, C(12) 0.03, C(13) −0.04, C(14) −0.02, C(15) 0.00, C(16) 0.05].

Angles between the planes

Planes	Angle (°)
I–II	34
I–III	39
II–III	31

[a] Atoms not defining the plane.

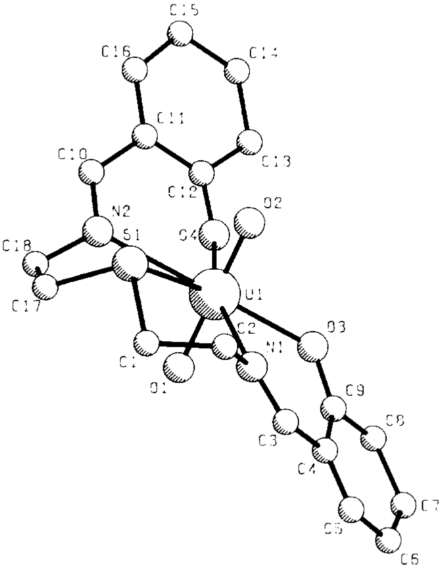

Fig. 1. Projection along the *b* axis.

The uranyl group slightly deviates from linearity with an O–U–O angle of 176(1)°, and is bent in the direction of the sulphur atom, that is in the direction which allows a diminishment of the steric repulsions between uranyl- and ligand-oxygens, as it was already found in UO_2(Ia). The U–O (ligand) and U–N distances compare well with corresponding values in UO_2(Ia) and UO_2(Ib). The two rings of the ligand are inclined with each other by 31° and also from large dihedral angles of 34° and 39° with the equatorial plane. Comparison with the α and β forms of UO_2(Ia), with the solvated UO_2(Ia), and with UO_2(Ib), shows that a large variety of values has been found for these angles, confirming that these differences in ligand conformation do not influence the comparable bond distances and angles. The U–S distance of 2.96 Å is in good agreement with 2.94(1) Å which represented the first determination of a U^{VI}–S (thioether) bond distance [11]. It has been already observed that the difference of *ca.* 0.4 Å between the U–S (thioether) and the U–O (ether) bond distance (2.55(1) Å) [12] compares well with the difference in covalent radii of oxygen and sulphur. It is noticeable that the sulphur atom, probably because of steric requirements due to the ligand geometry, is significantly out of the ideal equatorial plane, so that it is unreliable to include it in the calculation of this plane. An equatorial plane was then calculated as the best plane passing through the ligand oxygen and nitrogen atoms, from which the sulphur atom is displaced by 0.80 Å toward O(2), a circumstance that seems to have no detectable influence on the U–S bond distance. Angles at the sulphur atom (in the range 98–101°) show that it can be considered sp^3 hybridized. A projection of the molecule along the normal to the equatorial plane is given in Fig. 2. The significant displacement of the sulphur atom from the equatorial plane seems to permit a better arrangement of the other coordinated atoms in this plane. In fact the O···O intramolecular contact distance of 3.25 Å is about 0.15 Å longer than in the oxa and aza compounds. In addition the corresponding O–U–O angle (92°) is mainly 2° larger and the N–U–N angle (126°) shorter than in the above mentioned compounds.

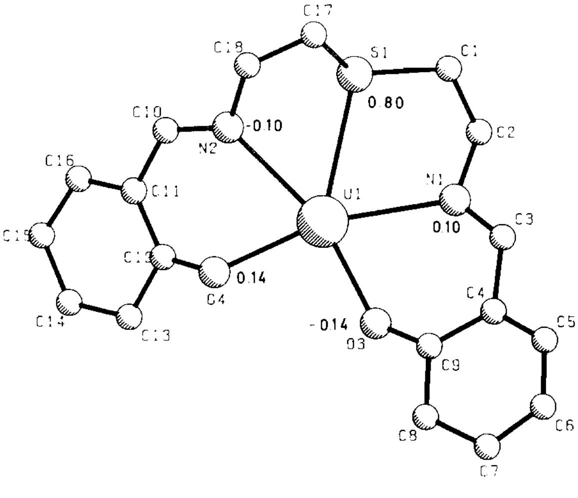

Fig. 2. Projection on the equatorial plane with deviations from the plane. Atoms O1 and O2 are omitted.

Acknowledgements

We thank Mrs. M. Magnabosco for useful technical assistance.

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