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Preparation, Properties, Crystal and Molecular Structure of Uranyl(VI) Complexes with a New Cyclic Schiff Base Compartmental Ligand

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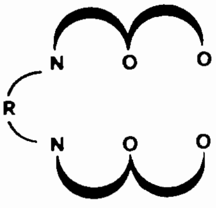
Abstract

Some uranyl(VI) complexes with new acyclic and cyclic Schiff base compartmental ligands have been prepared and characterized. The ligands have been obtained by reaction of 4-chloro-2,6-diformylphenol and polyamines of the type NH_2–$(CH_2)_2$–X–$(CH_2)_2$–NH_2 (X = NH, S). The structure of the uranyl(VI) complex with the ligand 1,7,15,21-tetraaza-4,18-dithia-11,25-dichloro 8,22-bis-*meta*diphenyl cyclophane-δ-7,14,21,28 has been determined by X-ray crystallography. The compound crystallizes in the orthorhombic space group *Pbca* with eight formula units in a cell of dimensions $a = 26.654(3)$, $b = 22.871(3)$, $c = 8.875(5)$ Å. The structure was solved by standard methods and refined by full-matrix least squares to the conventional *R* index of 4.6% for 2678 independent observed reflexions. Five donor atoms (including sulphur) of the ligand are equatorially bonded to the uranyl group to form discrete monomeric molecules with the seven-coordinated metal in the usual distorted pentagonal bipyramidal coordination geometry. Selected bond distances are: U–O (equatorial), 2.22(1) and 2.25(1) Å; U–N, 2.60(1) and 2.59(1) Å; U–S, 3.018(4) Å.

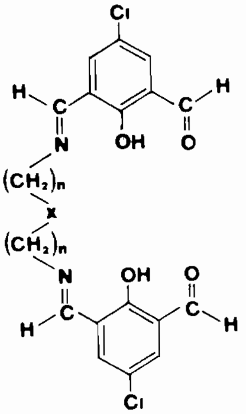
Introduction

The interaction of the uranyl(VI) ion with hexadentate compartmental ligands has been the subject of several studies [1–3]. Generally these compartmental ligands contain two different coordination sites of the type **I** and can be obtained by the reaction of an α,ω-diamine with one terminal keto function of a β,δ-triketone, ketophenol or keto carboxylic acid.



I

By using these compartmental ligands it has been possible to prepare heterodinuclear complexes because the site occupancy of the metal, e.g., Ni(N_2O_2) and $UO_2(O_2O_2)$, can be guaranteed. The positions of the metals have been confirmed by separate X-ray studies [19–21]. The uranyl(VI) ion is always coordinated to the outer O_2O_2 site, and a solvent molecule generally fills the fifth equatorial position to give rise to the very common pentagonal bypyramidal coordination geometry.



II

However, no dinuclear uranyl complexes of Schiff base ligands have been synthesized, probably because of the steric inhibition in the inner compartment. A facultative amine with a potential further donor atom was therefore employed, not only to form dinuclear uranyl complexes but to enforce heptacoordination on the uranyl in the inner compartment using each type of donor atoms. Accordingly, we have synthesized ligands of the type **II** and we were able to verify that binuclear uranyl(VI) complexes can be obtained.

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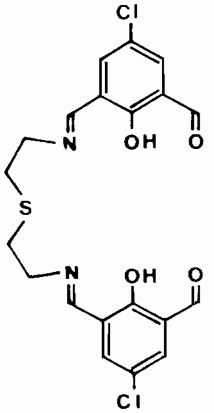
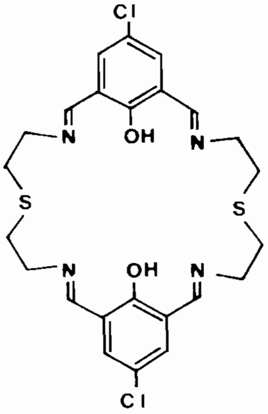
It has already been established that Schiff bases derived from salicylaldehyde or *o*-hydroxyacetophenon and amines of the type NH_2–$(CH_2)_2$–X–$(CH_2)_2$–NH_2 (X = NH, S, O, Pϕ) form, with UO_2^{2+}, stable complexes in which the organic group acts as a pentadentate dianionic ligand [4–10]. With the potentially heptadentate ligands reported above (**II**), the uranyl ion can also be coordinated in the inner N_2XO_2 chamber. We have thus prepared the Schiff bases by condensation of 2,6-diformyl-4-chlorophenol and 1,5-diamino-3-thiapentane [16, 17].



H_2A



H_2B

The acyclic and cyclic ligands reported above contain the same Schiff base; they can coordinate UO_2^{2+} in one chamber leaving the second chamber free as a further coordination site. We have prepared and characterized some uranyl complexes with these ligands. Moreover, the structure of the uranyl(VI) complex with the cyclic Schiff base 1,7,15,21-tetraaza-4,18-dithia-11,25-dichloro 8,22-bis-*meta*diphenylcyclophane-δ-7,14,21,28 has been determined by X-ray crystallography.

Experimental

2,6-diformyl-4-chlorophenol was prepared according to the literature [11]; 1,5-diamino-3-thiapentane is a K and K product and was used without further purification. The ligands H_2A and H_2B were prepared by condensation of 2,6-diformyl-4-chlorophenol and 1,5-diamino-3-thiapentane in a 2:1 or 1:1 molar ratio, respectively, and in chloroform solution, following the methods previously reported [16]. Their purity was checked by elemental analysis and mass spectra [17].

Preparation of Complexes

Preparation of $UO_2(A)$

(a) A methanolic solution of $UO_2(CH_3COO)_2 \cdot 2H_2O$ (424 mg 1 mmol) was added to a methanolic solution of 2,6-diformyl-4-chlorophenol (368 mg, 2 mmol). To the suspension obtained, LiOH (48 mg, 2 mmol) and 1,5-diamino-3-thiapentane (120 mg, 1 mmol) were added. The precipitate obtained was stirred for 2 h, filtered, washed with methanol and dried *in vacuo.*

(b) Alternatively, to a methanolic suspension of the acyclic ligand H_2A (452 mg, 1 mmol), 1 mmol of $UO_2(CH_3COO)_2 \cdot 2H_2O$ (424 mg) and LiOH (48 mg, 2 mmol) in methanol were added. The resulting precipitate was washed with methanol and dried *in vacuo.*

Anal. Calc. for $C_{20}H_{16}N_2O_6SCl_2U$: C, 33.28; H, 2.21; N, 3.88. Found: C, 33.93; H, 2.44; N, 4.35%.

Preparation of $UO_2(B)$

(a) 1,5-diamino-3-thiapentane (120 mg, 1 mmol) was added to a chloroformic solution of the acyclic complex $UO_2(A)$ (721 mg, 1 mmol). The resulting solution was stirred for 2 h and then treated with methanol. The precipitate obtained was filtered, washed with methanol and dried *in vacuo.*

(b) To a $CHCl_3$ solution of H_2B (536 mg, 1 mmol) a methanolic solution of $UO_2(CH_3COO)_2 \cdot 2H_2O$ (424 mg, 1 mmol) was added. The precipitate obtained by removal of $CHCl_3$ was filtered, washed with methanol and then refluxed for 3 h with $CHCl_3$. The precipitate was filtered and dried *in vacuo.*

The same cyclic complex can be obtained by addition of 2 mmol of LiOH to 1 mmol of H_2B, followed by the addition of 1 mmol of $UO_2(CH_3COO)_2 \cdot 2H_2O$. By this procedure it is not necessary to reflux the precipitate with $CHCl_3$. Yellow–orange crystals of $UO_2(B)$ were grown from a $CHCl_3$/MeOH solution.

Anal. Calc. for $C_{24}H_{26}N_4O_5S_2Cl_2U$: C, 35.77; H, 2.92; N, 6.95. Found: C, 35.35; H, 3.02; N, 6.65%.

X-ray Data for $UO_2(B)$

A small crystal with a maximum dimension of 0.2 mm was used for data collection. Cell parameters were calculated from accurate settings of 25 medium angle reflexions on a PW-1100 Philips diffractometer with the Mo Kα radiation. Crystal data are: $C_{24}H_{24}Cl_2N_4O_4S_2U$, $M = 795$, orthorhombic, with $a = 26.654(3)$, $b = 22.871(3)$, $c = 8.875(5)$ Å, $V = 5410(3)$ Å^3, space group *Pbca* from systematic absences $0kl$ for k odd, $h0l$ for l odd and $hk0$ for h odd, general positions $\pm(x,y,z;\ \frac{1}{2}+x,\ \frac{1}{2}-y,\ \bar{z};\ \bar{x},\ \frac{1}{2}+y,\ \frac{1}{2}-z;\ \frac{1}{2}-x,\ \bar{y},\ \frac{1}{2}+z)$, $D_c = 1.95$ g cm^{-3} for $Z \doteq 8$, μ(Mo Kα) = 60.7 cm^{-1}, $\lambda = 0.7107$ Å.

Intensities for reflexions up to $\theta = 25°$ were recorded with a scan speed of 2° min^{-1} and the $\theta/2\theta$ scan. Of the 5844 unique reflexions, 2678 with $I > 3\sigma(I)$ were considered to be significantly above background and were used in subsequent calculations. Corrections were made for Lorentz polarization and for absorption [12]. No deterioration of the crystal was observed during irradiation. The structure was solved by Patterson and Fourier methods and refined to the final conventional R of 4.6%, when the largest parameter shift in the last cycle was 0.1σ for atom coordinates and 0.3σ for temperature factors. The structure was refined with full matrix least-squares, minimizing the function $\Sigma\omega(\Delta F)^2$, with $\omega = 1$.

During the refinement the ring carbon atoms were treated as rigid bodies (C–C = 1.395 Å) and the hydrogen atoms were introduced in calculated positions with a fixed temperature factor (C–H = 1.08 Å, $U_{iso} = 0.05$ Å^2). A final Fourier difference map showed no significant residuals. Scattering factors for *U* were from ref. 13, those for Cl, S, O, N, C and H being supplied internally by SHELX [14]. The uranium scattering factor was corrected for the anomalous dispersion. Final atomic positional and thermal parameters are listed in Tables Ia,b,c. Bond distances and angles and selected mean planes are reported in Tables II–IV.

TABLE Ia. Atomic Coordinates

Atom	*x/a*	*y/b*	*z/c*
U1	0.34922(2)	−0.02734(2)	0.05354(6)
O1	0.3465(4)	−0.0009(4)	−0.1365(11)
O2	0.3511(4)	−0.0494(4)	0.2454(11)
O3	0.4271(3)	−0.0604(4)	0.0261(11)
O4	0.3130(3)	−0.1133(4)	−0.0060(11)
C7	0.4561(5)	0.0504(6)	0.1620(16)
N1	0.4114(4)	0.0581(5)	0.1046(14)
C8	0.3963(5)	0.1199(6)	0.0787(19)
C9	0.3403(5)	0.1256(6)	0.0615(19)
S1	0.3104(1)	0.0821(2)	0.2036(4)
C10	0.2449(6)	0.0853(7)	0.1444(19)
C11	0.2349(6)	0.0446(7)	0.0138(18)
N2	0.2544(4)	−0.0146(4)	0.0480(13)
C12	0.2219(5)	−0.0518(6)	0.0822(17)
Cl1	0.5882(2)	−0.0546(2)	0.4758(5)
C3	0.5302(3)	−0.1087(4)	0.2666(12)
N4	0.5102(6)	−0.2088(7)	0.0964(17)
C4	0.5432(3)	−0.0561(4)	0.3356(12)
C5	0.5173(3)	−0.0049(4)	0.2997(12)
C6	0.4784(3)	−0.0064(4)	0.1947(12)
C1	0.4653(3)	−0.0591(4)	0.1257(12)
C2	0.4912(3)	−0.1102(4)	0.1617(12)
C24	0.4796(6)	−0.1655(7)	0.0759(20)
C23	0.4990(8)	−0.2603(8)	0.0013(23)
C22	0.4919(7)	−0.3141(8)	0.1021(22)
S2	0.4318(2)	−0.3220(2)	0.1852(6)
C21	0.3964(7)	−0.3586(8)	0.0405(24)
C20	0.3665(7)	−0.3198(8)	−0.0671(23)
N3	0.3248(6)	−0.2912(6)	0.0121(19)
C19	0.3235(6)	−0.2350(7)	0.0180(20)
Cl2	0.1525(2)	−0.2440(2)	0.2957(7)
C14	0.1947(3)	−0.1461(4)	0.1771(12)
C15	0.2000(3)	−0.2060(4)	0.2010(12)
C16	0.2434(3)	−0.2347(4)	0.1539(12)
C17	0.2816(3)	−0.2033(4)	0.0829(12)
C18	0.2763(3)	−0.1434(4)	0.0590(12)
C13	0.2328(3)	−0.1147(4)	0.1061(12)

TABLE Ib. Calculated Positional Parameters for the Hydrogen Atoms. The Numbers in Parentheses refer to the Carbon Atoms to Which they are Attached

Atom	*x*	*y*	*z*
H(3)	5502	−1483	2944
H(5)	5274	358	3531
H(7)	4781	889	1870
H1(8)	4070	1460	1749
H2(8)	4151	1362	−207
H1(9)	3284	1706	705
H2(9)	3300	1086	−477
H1(10)	2358	1297	1140
H2(10)	2216	717	2376
H1(11)	2542	611	−844
H2(11)	1951	427	−84
H(12)	1836	−372	951
H(14)	1610	−1239	2135
H(16)	2475	−2811	1724
H(19)	3547	−2105	−270
H1(20)	3511	−3459	−1574
H2(20)	3908	−2866	−1136
H1(21)	3706	−3884	943
H2(21)	4230	−3830	−264
H1(22)	4998	−3532	380
H2(22)	5188	−3100	1925
H1(23)	4648	−2531	−612
H2(23)	5297	−2673	−763
H(24)	4476	−1688	16

Results and Discussion

By reaction of 2,6-diformyl-4-chlorophenol and polyamines of the type NH_2–$(CH_2)_2$–X–$(CH_2)_2$–NH_2 (X = NH,S) in the presence of uranyl(VI) acetate, the complexes reported in Scheme 1 have been obtained.

The acyclic complex UO_2(A) can be obtained by reaction of the preformed ligand with $UO_2(CH_3COO)_2 \cdot 2H_2O$ or by template synthesis. The uranyl(VI) occupies the internal chamber N_2SO_2. It could bind in the outer O_2O_2 compartment using a solvent molecule to make up heptacoordination; the physicochemical data rule out this coordination.

The infrared spectrum of UO_2(A) shows an intense $\nu_{C=O}$ band at 1671 cm^{-1}, the $\nu_{C=N}$ at 1625 cm^{-1} while the presence of the O–U–O group is easily detected by the strong ν_{3O-U-O} at 905 cm^{-1}. In this complex the two formyl groups are close enough to be cyclized, and by condensation with polyamines, cyclic complexes have been obtained. In particular, the symmetric cyclization was easily carried out in $CHCl_3/CH_3OH$ to give the mononuclear cyclic complex UO_2(B) of Scheme 1.

The complex UO_2(B) has also been prepared by reaction of the preformed cyclic ligand with uranyl(VI) diacetate and LiOH in a 1:1:2 molar ratio; UO_2(B) can also be obtained in the absence of LiOH. For this complex the infrared spectrum

TABLE Ic. Thermal Parameters ($\times 10^2$). Anisotropic Thermal Parameters are in the Form $T = \exp[-2\pi^2(\Sigma U_{ij} h_i h_j a_i{}^* a_j{}^*)]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U	3.30(2)	3.07(2)	3.52(3)	0.20(3)	−0.09(3)	0.00(3)
O(1)	4.1(5)	5.2(6)	4.1(6)	−0.7(5)	−0.4(6)	−0.9(5)
O(2)	5.3(6)	4.9(5)	3.8(5)	0.4(5)	−0.2(6)	−0.5(6)
O(3)	4.3(5)	4.3(5)	3.7(6)	−0.2(5)	0.0(5)	−0.6(4)
O(4)	2.0(4)	3.9(5)	6.3(7)	−0.5(5)	0.5(4)	0.7(4)
N(1)	4.3(6)	2.6(6)	4.7(8)	1.1(5)	0.7(6)	−1.2(5)
N(2)	4.0(6)	3.6(6)	3.7(6)	0.4(6)	0.7(7)	0.2(5)
N(3)	5.8(9)	3.2(7)	9.8(1)	0.4(7)	−0.4(9)	0.1(6)
N(4)	6.8(9)	4.1(8)	6.1(1)	−0.7(7)	−0.3(8)	0.0(7)
S(1)	4.9(2)	4.0(2)	4.4(2)	−0.3(2)	0.3(2)	0.2(2)
S(2)	8.4(4)	6.9(3)	5.9(3)	−0.1(3)	0.0(3)	−0.4(3)
Cl(1)	4.0(2)	10.6(4)	5.2(3)	−1.0(3)	−0.7(2)	0.6(2)
Cl(2)	10.6(4)	6.9(3)	11.0(4)	−2.7(3)	5.5(4)	−4.7(3)

Atom	U	Atom	U	Atom	U
C(1)	3.5(4)	C(9)	4.8(4)	C(17)	5.1(4)
C(2)	3.2(3)	C(10)	5.4(4)	C(18)	4.1(3)
C(3)	3.8(4)	C(11)	5.3(4)	C(19)	4.8(5)
C(4)	5.4(4)	C(12)	4.2(4)	C(20)	6.4(5)
C(5)	4.6(4)	C(13)	4.7(4)	C(21)	6.7(5)
C(6)	3.8(4)	C(14)	5.0(4)	C(22)	6.2(5)
C(7)	3.9(3)	C(15)	5.8(4)	C(23)	6.1(5)
C(8)	4.7(4)	C(16)	5.9(5)	C(24)	4.6(4)

TABLE II. Bond and Contact Distances (Å)

Coordination			
U–O(1)	1.79(1)	U–N(1)	2.60(1)
U–O(2)	1.78(1)	U–N(2)	2.54(1)
U–O(3)	2.22(1)	U–S(1)	3.018(4)
U–O(4)	2.25(1)		
Ligand (non-quoted e.s.d.s are less than 0.02 Å)			
S(1)–C(9)	1.79	S(1)–C(10)	1.82
C(9)–C(8)	1.51	C(10)–C(11)	1.51
C(8)–N(1)	1.49	C(11)–N(2)	1.48
N(1)–C(7)	1.31	N(2)–C(12)	1.25
C(7)–C(6)	1.46	C(12)–C(13)	1.48
C(1)–O(3)	1.35	C(18)–O(4)	1.33
C(4)–Cl(1)	1.73(1)	C(15)–Cl(2)	1.75(1)
C(2)–C(24)	1.51	C(17)–C(19)	1.48
C(24)–N(4)	1.30	C(19)–N(3)	1.28
N(4)–C(23)	1.48	N(3)–C(20)	1.47
C(23)–C(22)	1.53	C(20)–C(21)	1.53
C(22)–S(2)	1.77	C(21)–S(2)	1.80
Contact distances			
N(1)···O(3)	2.83	N(2)···O(4)	2.79
N(1)···S(1)	2.88	N(2)···S(1)	3.00
O(3)···O(4)	3.29		

TABLE III. Bond Angles (deg)

Coordination			
O(1)–U–O(2)	176.8(4)	O(3)–U–O(4)	94.4(3)
O(3)–U–N(1)	71.3(3)	O(4)–U–N(2)	70.7(3)
N(1)–U–S(1)	61.2(3)	N(2)–U–S(1)	74.7(2)
Ligand (non quoted e.s.d.s. are less than 1.5°)			
U–S(1)–C(9)	89.8(5)	U–S(1)–C(10)	103.5(5)
U–N(1)–C(8)	121.0(8)	U–N(2)–C(11)	117.2(8)
U–N(1)–C(7)	123.2(8)	U–N(2)–C(12)	127.3(9)
U–O(3)–C(1)	128.8(7)	U–O(4)–C(18)	131.7(7)
S(1)–C(9)–C(8)	109	S(1)–C(10)–C(11)	111
C(9)–C(8)–N(1)	111	C(10)–C(11)–N(2)	110
N(1)–C(7)–C(6)	125	N(2)–C(12)–C(17)	124
C(7)–C(6)–C(5)	114	C(12)–C(13)–C(14)	115
O(3)–C(1)–C(6)	120	O(4)–C(18)–C(13)	120
Cl(1)–C(4)–C(3)	120	Cl(2)–C(15)–C(14)	119
Cl(1)–C(4)–C(5)	119	Cl(2)–C(15)–C(16)	121
C(24)–C(2)–C(1)	119	C(19)–C(17)–C(18)	120
N(4)–C(24)–C(2)	116	N(3)–C(19)–C(17)	120
C(23)–N(4)–C(24)	114	C(20)–N(3)–C(19)	117
C(22)–C(23)–N(4)	109	C(21)–C(20)–N(3)	111
S(2)–C(22)–C(23)	116	S(2)–C(21)–C(20)	117
C(9)–S(1)–C(10)	102	C(21)–S(2)–C(22)	103

shows the $\nu_{C=N}$ at 1632 cm^{-1}; while the $\nu_{C=O}$ disappears. The $\nu_{3\,O-U-O}$ lies at 896 cm^{-1}. There is a simultaneous shift of the $\nu_{C=N}$ (= 7 cm^{-1}) and $\nu_{3\,O-U-O}$ (= 9 cm^{-1}) at higher and lower frequency, respectively. However, this trend is not always followed. Similar complexes, having an inner N donor atom instead of S, have the $\nu_{C=N}$ and the $\nu_{3\,O-U-O}$ at 1630 and 892 cm^{-1} for the acyclic complex and

TABLE IV. Selected Mean Planes

Plane 1: O(3), N(1), S(1), N(2), O(4)
$-0.091x + 0.412y - 0.907z = -1.57$ Å
[O(3) −0.24, N(1) 0.28, S(1) −0.04, N(2) 0.43, O(4) −0.20]

Plane 2: C(1) to C(6)
$0.653x + 0.185y - 0.734z = 7.03$ Å

Plane 3: C(13) to C(18)
$-0.423x - 0.181y - 0.888z = -2.98$ Å

Dihedral angles (deg)

Planes	Angle
1–2	46.9
1–3	39.7
2–3	70.0

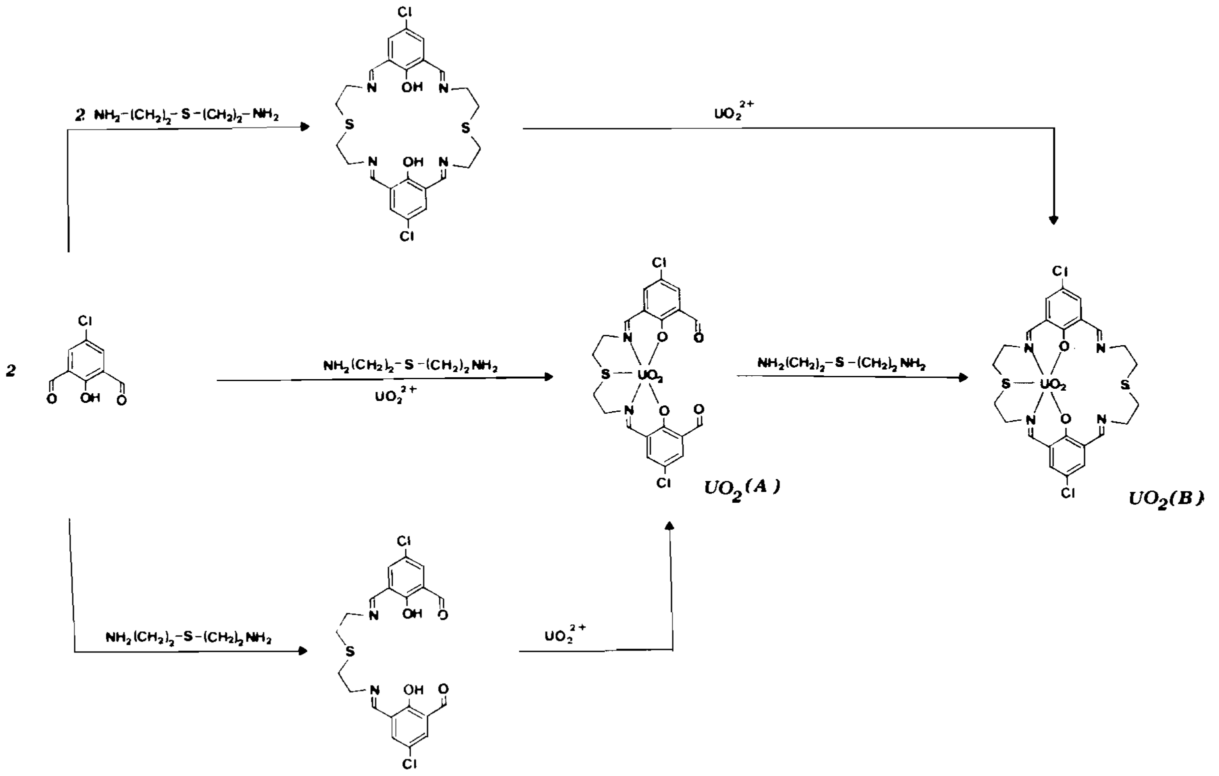
at 1632 and 897 cm^{-1} for the cyclic complex [18].

In the compounds UO_2(A) and UO_2(B) the uranyl ion is also bonded to the thioetheric sulphur. This is not a very surprising result; as reported above we have already synthesized similar Schiff base uranyl complexes [9].

Figure 1 shows a perspective view of the molecular structure of UO_2(B) with the numbering scheme used. The ligand is pentadentate, but structural constraints allow coordination only with severe deviations of atoms from the equatorial plane (see Table IV) so that the five-coordinated atoms form a strongly puckered pentagon. Although the molecule has no imposed symmetry, the two wings of the ligand are approximately symmetrical, forming dihedral angles of 40° and 47° with the coordination plane. They are also strongly inclined to each other (Fig. 2) so that the ligand as a whole has the shape of an umbrella.

The U–O(ligand) and U–N distances compare well with corresponding values in a series of analogous compounds [4–10], and the U–S distance of 3.018(4) Å is in good agreement with 2.96(1) Å and 2.94(1) Å which are, to our knowledge, the only U–S(thioether) bond distances previously determined [9–15]. It is noteworthy that although valency angles at the sulphur atoms indicate these atoms to be sp^3 hybridized, structural models clearly show that the U–S direction does not precisely coincide with any of the available sp^3 orbitals; this probably accounts for the relative weakness of the resulting bond.

Corresponding bond lengths and angles in the two independent halves of the molecule are fully comparable and support the accuracy of the results obtained. The C=N double bonds are well localized, with a mean value of 1.28 Å. The C–O bonds (mean 1.34 Å) are partial double. Other structural details



Scheme 1.

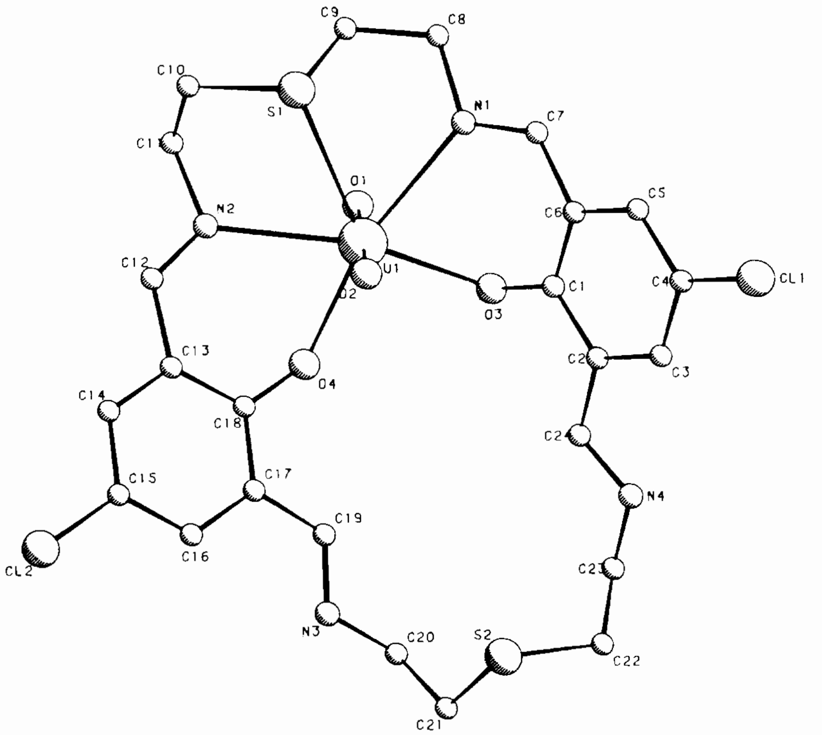


Fig. 1. Crystal structure of $UO_2(B)$ with atom numbering. H atoms have been omitted for the sake of clarity.

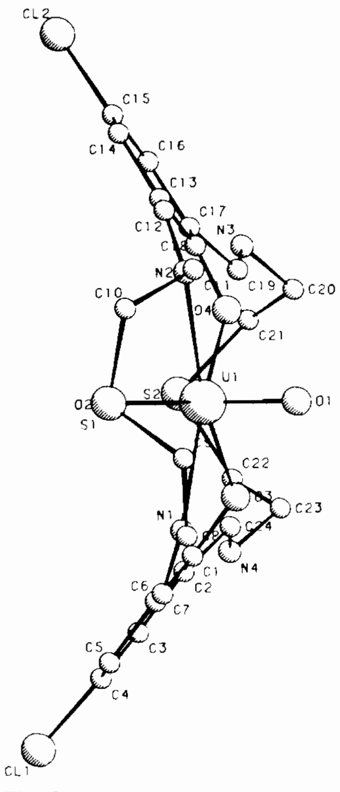


Fig. 2. Crystal structure of $UO_2(B)$. The two wings of the ligand are inclined with respect to the coordination plane.

are normal and need no comment. The mass spectrum supports the cyclic structure of the complex, showing the parent peak P^+ at 805 m/z.

The cyclic organic ligand of the above compound includes a second compartment which, at least in principle, could act as a second coordination set. Nevertheless, the peculiar conformation of the ligand and the reciprocal positions of the available donor atoms seem to indicate that it would be difficult for a second metal ion to be coordinated.

Attempts to prepare the homobinuclear uranyl(VI) complex, also by template effect, were not successful. Complexes roughly formulable as $[UO_2(B)]_2UO_2(CH_3COO)_2 \cdot nS$ have been obtained. A second uranyl(VI) ion seems to be too large to enter into the second chamber when the first is occupied by one UO_2^{2+} group. On the contrary, this chamber can serve as coordinating site for a second smaller metal ion, such as nickel(II) and copper(II). The reaction of the $UO_2(B)$ with nickel(II) or copper(II) salts produces the heterodinuclear complexes.

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