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# Uranyl Complexes with Pentadentate Ligands. Crystal Structures of $UO_2[o\text{-}OC_6H_4\text{–}CH{=}N(CH_2)_3]_2C_6H_5PO$ and $UO_2[o\text{-}OC_6H_4\text{–}C(CH_3){=}N(CH_2)_2]_2NH$

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*The crystal structures of the title complexes were determined by X-ray crystallography from single-crystal diffractometer data. Crystal data:* $UO_2[o\text{-}OC_6H_4\text{–}CH{=}N(CH_2)_3]_2C_6H_5PO$, *orthorhombic, Pnma,* $Z = 4$, $a = 10.85(1)$ Å, $b = 14.23(1)$ Å, $c = 16.17(1)$ Å, $V = 2497$ Å$^3$, $R = 5.7\%$, *1593 observed reflections;* $UO_2[o\text{-}OC_6H_4\text{–}C(CH_3){=}N(CH_2)_2]_2NH$, *monoclinic,* $P2_1/c$, $Z = 4$, $a = 6.31(1)$ Å, $b = 13.22(1)$ Å, $c = 24.14(1)$ Å, $\beta = 92.61(2)°$, $V = 2014$ Å$^3$, $R = 7.4\%$, *1819 observed reflections.*

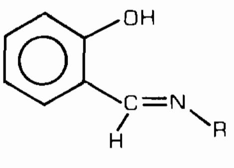
*The complexes are monomeric. The* $PhPOUO_2$ *fragment of the first molecule lies on the crystallographic mirror plane. The coordination geometry of the uranium atom is bipyramidal pentagonal with the ligand pentadentate in the equatorial plane of the uranyl ion. Bond distances are: U–O (charged) = 2.21–2.24 Å, U–O (neutral) = 2.33(1) Å, U–N = 2.56–2.71 Å, other distances and angles were similar to analogous complexes.*

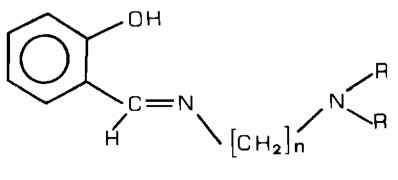
## Introduction

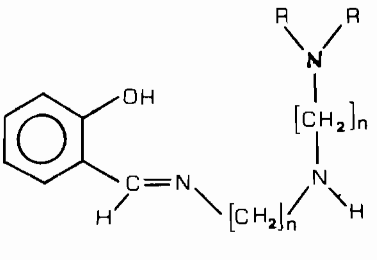
Uranyl(VI) complexes with Schiff bases have been extensively studied (1). Using potentially bi-, ter-, tetra- and penta-dentate ligands of the type shown below: pentagonal bipyramidal coordination geometries are always obtained, where a solvent molecule or an anion eventually fills the equatorial pentagon, as in $UO_2$(salen)MeOH, $UO_2$(salophen)EtOH or $UO_2$ [salenN–$(CH_2)_2$–NH–$(CH_2)_2$–$N(CH_3)_2$] $(NO_3)$ [1–6]. Recently we focused our interest on the preparation of a series of uranyl(VI) complexes with the pentadentate ligands mentioned above,

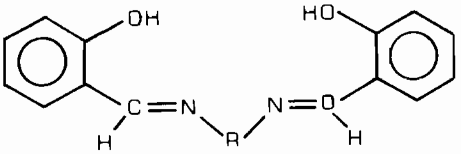
with X = $>$NH, $>$O, $>$S, $>$PR, testing the ability of

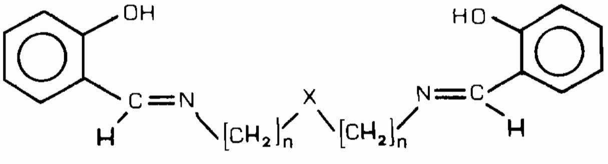
'soft' donor atoms as sulphur or phosphorus to bind the 'hard' uranyl(VI) ion, as found in $UO_2$(salsen) [7]. The difficulty to direct coordination of the











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$>$PR group is due to the easy oxidation of $P^{III}$ to $P^{V}$. The oxidation of phosphines, if aryl-substituted, in the uranium compounds is well known, and several complexes in which a U–$PR_3$ bond had been originally postulated contain a U–$OPR_3$ bond.

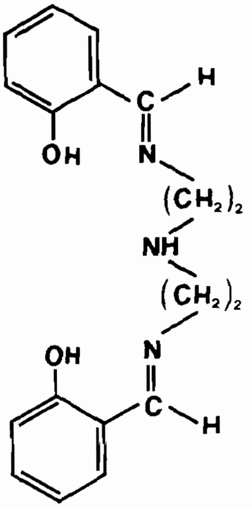
This paper reports the preparation of uranyl complexes with the anions of the Schiff bases $H_2L^1$, $H_2L^2$, $H_4L^3$ and the crystal structures of $UO_2(L^1)$ and $UO_2(OL^2)$ determined by X-ray crystallography.

## Crystal Structures

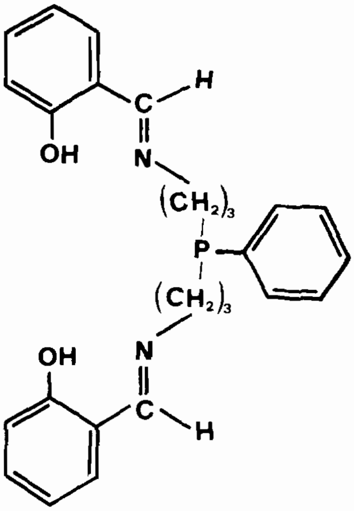
### *$UO_2(OL^2)$*

Figure 1 shows a perspective view of the molecular structure with the numbering scheme used. Final positional parameters, bond lengths and angles, and the equations of selected mean planes are given in Tables I–IV.

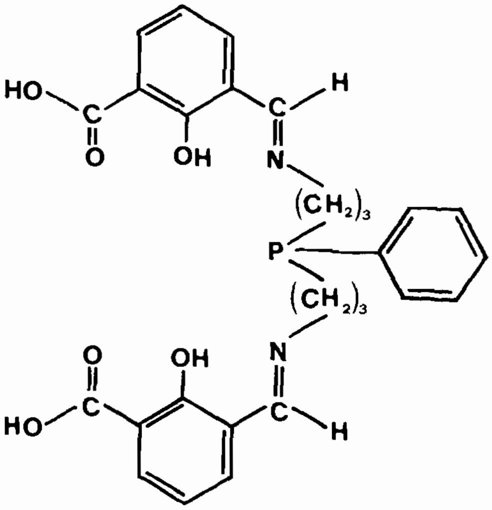
The five donor atoms of the ligands are equatorially bonded to the uranyl group to form discrete, monomeric molecules of $UO_2(OL^2)$ with the seven-



$H_2L^1$



$H_2L^2$



$H_4L^3$

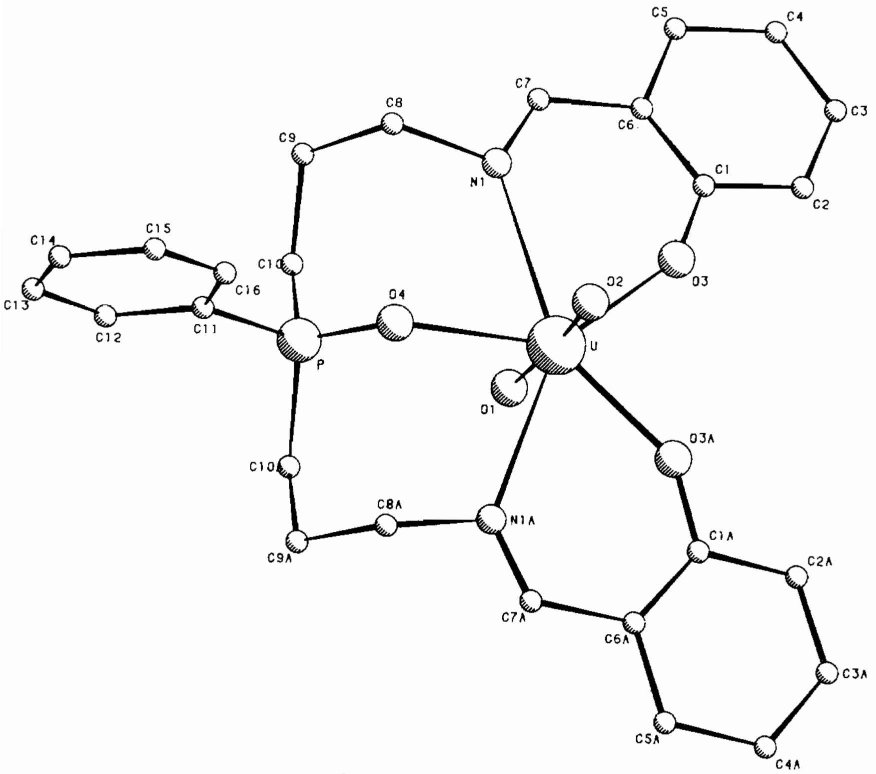


Fig. 1. Crystal structure of $UO_2(OL^2)$.

TABLE I. Atomic Parameters for $UO_2(OL^2)$.

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| U | 0.45796(8) | 0.2500 | 0.40857(6) |
| P | 0.1356(6) | 0.2500 | 0.4109(4) |
| O(1) | 0.3994(20) | 0.2500 | 0.3032(10) |
| O(2) | 0.5005(19) | 0.2500 | 0.5158(10) |
| O(3) | 0.6067(11) | 0.3512(10) | 0.3801(8) |
| O(4) | 0.2567(13) | 0.2500 | 0.4583(8) |
| N | 0.3814(12) | 0.4311(11) | 0.4159(8) |
| C(1) | 0.6388(15) | 0.4359(14) | 0.3582(9) |
| C(2) | 0.7621(17) | 0.4477(15) | 0.3279(9) |
| C(3) | 0.8019(22) | 0.5373(17) | 0.3056(11) |
| C(4) | 0.7193(29) | 0.6144(17) | 0.3100(14) |
| C(5) | 0.5992(22) | 0.6020(17) | 0.3416(12) |
| C(6) | 0.5606(16) | 0.5106(13) | 0.3640(9) |
| C(7) | 0.4322(16) | 0.5052(13) | 0.3970(9) |
| C(8) | 0.2504(15) | 0.4538(14) | 0.4533(10) |
| C(9) | 0.1378(18) | 0.4471(16) | 0.3913(11) |
| C(10) | 0.1263(15) | 0.3536(15) | 0.3474(10) |
| C(11) | 0.0145(25) | 0.2500 | 0.4863(14) |
| C(12) | 0.1105(22) | 0.2500 | 0.4634(17) |
| C(13) | −0.2023(25) | 0.2500 | 0.5254(18) |
| C(14) | −0.1685(28) | 0.2500 | 0.6065(17) |
| C(15) | −0.0496(29) | 0.2500 | 0.6290(16) |
| C(16) | 0.0436(31) | 0.2500 | 0.5710(15) |

*(continued overleaf)*

TABLE I *(continued)*

Anisotropic thermal parameters ($\times 10^2$) in the form: $T = \exp[-2\pi^2 \Sigma_{ij} U_{ij} h_i h_j a^*_i a^*_j]$

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| U | 3.56(4) | 7.43(6) | 3.83(4) | 0.0 | 0.45(4) | 0.0 |
| P | 3.63(29) | 9.78(51) | 2.97(28) | 0.0 | 0.17(29) | 0.0 |
| O1 | 9.67(1.56) | 13.89(1.86) | 2.69(87) | 0.0 | −1.69(95) | 0.0 |
| O2 | 8.30(1.41) | 12.17(1.73) | 4.74(1.06) | 0.0 | −3.50(97) | 0.0 |
| O3 | 4.28(69) | 7.62(91) | 8.88(98) | −0.77(66) | 0.41(64) | 0.49(75) |
| O4 | 3.12(84) | 10.60(1.37) | 2.44(76) | 0.0 | 1.22(63) | 0.0 |
| N | 5.01(78) | 8.03(1.01) | 2.75(67) | −0.89(78) | 0.07(62) | 0.28(76) |
| C(1) | 4.40(91) | 7.60(1.31) | 2.94(80) | −1.63(97) | −0.79(71) | −0.25(83) |
| C(2) | 6.39(1.20) | 10.13(1.55) | 2.66(83) | −1.80(1.13) | 0.73(77) | −0.76(92) |
| C(3) | 9.49(1.59) | 9.41(1.61) | 3.77(96) | −4.04(1.46) | 0.72(1.03) | 0.15(1.07) |
| C(4) | 14.87(2.43) | 7.80(1.61) | 6.36(1.31) | −1.99(1.79) | −2.77(1.54) | 0.95(1.26) |
| C(5) | 8.60(1.55) | 10.11(1.75) | 4.77(1.06) | −2.05(1.37) | −1.61(1.06) | 0.26(1.14) |
| C(6) | 5.16(1.03) | 6.96(1.16) | 3.64(82) | 0.36(1.01) | −1.64(78) | −0.59(82) |
| C(7) | 6.74(1.20) | 7.61(1.19) | 2.18(76) | 0.30(1.01) | −0.67(73) | −0.54(80) |
| C(8) | 4.45(95) | 9.35(1.40) | 3.91(89) | 0.79(94) | 1.10(76) | 0.09(95) |
| C(9) | 6.54(1.18) | 10.20(1.63) | 5.01(1.18) | 1.67(1.21) | −1.08(93) | 0.65(1.09) |
| C(10) | 4.52(95) | 9.66(1.52) | 4.14(90) | 0.76(1.04) | −0.23(77) | 2.22(99) |
| C(11) | 6.34(1.82) | 9.81(2.17) | 3.44(1.29) | 0.0 | −0.08(1.18) | 0.0 |
| C(12) | 3.06(1.43) | 9.65(2.19) | 6.74(1.74) | 0.0 | −0.06(1.20) | 0.0 |
| C(13) | 3.20(1.37) | 15.60(3.2) | 6.78(1.87) | 0.0 | 0.22(1.35) | 0.0 |
| C(14) | 5.87(1.84) | 17.56(3.64) | 4.89(1.83) | 0.0 | 2.25(1.42) | 0.0 |
| C(15) | 4.21(1.61) | 35.26(3.66) | 3.19(1.33) | 0.0 | 0.08(1.41) | 0.0 |
| C(16) | 6.19(1.74) | 24.75(4.63) | 3.12(1.40) | 0.0 | 0.36(1.45) | 0.0 |

TABLE II. Bond and Contact Distances (Å) for $UO_2(OL^2)$.

| | | | |
|---|---|---|---|
| *Bond Distances* | | | |
| Coordination | | | |
| U–O(1) | 1.82(2) | U–O(3) | 2.21(1) |
| U–O(2) | 1.79(2) | U–O(4) | 2.33(1) |
| | | U–N | 2.71(1) |
| Ligand | | | |
| O(3)–C(11) | 1.30(2) | C(9)–C(10) | 1.51(3) |
| C(6)–C(7) | 1.49(2) | P–O(4) | 1.52(2) |
| N–C(7) | 1.23(2) | O–C(10) | 1.80(2) |
| N–C(8) | 1.58(2) | P–C(11) | 1.79(2) |
| C(8)–C(9) | 1.58(2) | | |
| *Contact Distances* | | | |
| O(3)···O(3A) | 2.88(2) | | |
| O(3)···N | 2.76(2) | | |
| O(4)···N | 2.99(2) | | |

Bond distances and angles in the C(1)–C(6) and C(11)–C(16) rings are normal

coordinated metal in the usual distorted pentagonal bipyramidal coordination geometry. The molecule lies across a crystallographic mirror plane which contains the uranyl group and the PhPO fragment.

The five coordinated atoms form a puckered pentagon where the oxygen atoms are slightly displaced above and the nitrogen atoms below the equatorial mean plane. The two wings of the ligand

TABLE III. Bond Angles (deg) for $UO_2(OL^2)$. (Errors not reported are less than 1°).

| | | | |
|---|---|---|---|
| Coordination | | | |
| O(1)–U–O(2) | 175 | N–U–O(3) | 67 |
| O(3)–U–O(3A) | 81 | N–U–O(4) | 72 |
| Ligand | | | |
| U–O(3)–C(1) | 149(1) | C(8)–C(9)–C(10) | 114(2) |
| U–O(4)–P | 129 | C(9)–C(10)–P | 116(1) |
| U–N–C(7) | 132(1) | O(4)–P–C(10) | 110 |
| U–N–C(8) | 119(1) | O(4)–P–C(11) | 107(1) |
| C(6)–C(7)–N | 123(2) | C(10)–P–C(10A) | 110 |
| C(7)–N–C(8) | 109(1) | C(10)–P–C(16) | 110 |
| N–C(8)–C(9) | 116(1) | | |

TABLE IV. Least-Squares Planes for $UO_2(OL^2)$. Deviations (Å) of atoms from the planes are given in square brackets; $X$, $Y$, and $Z$ are fractional coordinates in the direct cell. Atoms not used in the plane calculation are marked with an asterisk.

Plane 1: O(3), O(3$^{i}$), N(1), N(1$^{i}$), O(4)
$3.168X - 0.0Y + 15.466Z = 7.750$
[O(3) and O(3$^{i}$) 0.04, N(1) and N(1$^{i}$) −0.11, O(4) 0.14, U* 0.02, P* −0.96, C(7)* −0.24, C(8)* 0.04, C(9)* −1.26, C(10)* −1.97]

Plane 2: O(3), C(1) to C(7)
$3.460X + 2.445Y + 15.073Z = 8.683$
The atoms are coplanar within 0.02 Å

Angle (°) between planes 1–2 is 10.1

are symmetrical and form a dihedral angle of 10° with the coordination plane. The U–O (charged) distances of 2.21 (Å) are in agreement with the values found in this type of compound. The U–N bond distance of 2.71(1) Å is significantly longer than generally found for U(VI)–N($sp^2$) bonds. It is well known that U–N equatorial distances are always longer than U–O equatorial distances and much greater than suggested by the difference in covalent radii. This fact was tentatively explained by Pearson on the basis of the 'hard' and 'soft' acid–base concept [12]. It was claimed [6, 13] that the U(VI)–N($sp^2$) bond distances average 2.55 Å and that the lengthening to 2.70 Å for U(VI)–N($sp^3$) accounts for the difference between the covalent radii of nitrogen in the two different hybridization states. This determination shows that this is not always true and that other factors can play a role in determining the length of the U–N bonds, as for example the competition of the other coordinated atoms, the reciprocal positions of these and of the nitrogen atoms, or the number of atoms which make up the chelated ring.

The U–O (4) distance of 2.33(1) Å agrees with 2.37(3) Å and 2.34(2) Å found in $[UO_2(OAc)_2\text{-}Ph_3PO]_2$ [18] and $[UO_2(DTC)_2Ph_3PO]$ [19] irrespective of the nature of the remaining ligands. The P–O distance of 1.52(2) Å confirms the strong $\pi$ contribution to this bond [21]; the U–O–P angle of 129° is significantly smaller than 143° or 162° found in the above complexes and is probably determined by geometrical constraints because P is part of the multidentate ligand. Bond distances in the ligand are normal: C–O [1.30(2) Å] is partial double, through the influence of the aromatic ring, and C(7)–N is double.

### *$UO_2(L^1)$*

Figure 2 shows a perspective view of the molecular structure with the numbering scheme used. Final positional parameters, bond lengths and angles and the equations of selected mean planes are given in Tables V–VIII. The ligand is pentadentate in the equatorial plane of the uranyl ion and the five coordinated atoms form a rather puckered pentagon. Although the molecule has no imposed symmetry, the two wings of the ligands are approximately symmetrical forming dihedral angles of 37° and 40° with the coordination plane. They are also strongly inclined with each other with a dihedral angle of 71°, so that the ligand as a whole has approximately the shape of an umbrella.

Perhaps because of the limited degree of crystallinity of the compound, suggested by the high number of reflexions with low intensity (about 50% of the recorded reflexions had $I < 3\sigma(I)$) and by the fact that the temperature factors, especially those of the light atoms, are generally high, the estimated standard deviations on atomic coordinates are relatively large and prevent a detailed discussion of the molecular parameters. Despite this, bond distances and angles in the two halves of the molecule are comparable and agree with the values found in a number of parent compounds [14–17].

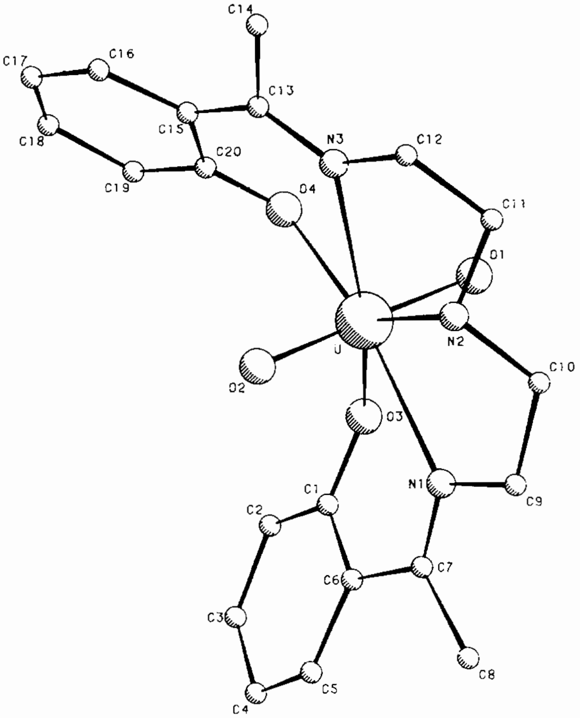


Fig. 2. Crystal structure of $UO_2(L^1)$.

## Complexes

All complexes can be obtained as orange-red powders by reacting the preformed Schiff bases with uranyl nitrate. $UO_2(L^2)$ is sparingly soluble in the common organic solvents, and more soluble in coordinating solvents as py or dmso, even if no coordination takes place in these solvents. The IR spectrum shows the antisymmetric $\nu_3$O–U–O at 905 cm$^{-1}$ and the characteristic $\nu$C=N in the region 1657–1610 cm$^{-1}$.

The mass spectrum shows a very intense peak (due to the parent $P^+$ ion) at m/z 699.

The elemental analysis fits well with the formula $UO_2(L^2)\cdot H_2O$ but the presence of water, or of other solvents (essentially MeOH) used in the preparation or purification of the compound, is not confirmed by the thermogravimetric analysis.

Taking into account the low tendency of P to coordinate $UO_2^{2+}$, the alternative structures (I) or (II) could be expected.

TABLE V. Atomic Parameters for $UO_2(L^1)$.

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| U | 0.3637(2) | 0.4590(1) | 0.3365(1) |
| O(1) | 0.2809(36) | 0.5743(17) | 0.3611(9) |
| O(2) | 0.4658(33) | 0.3640(16) | 0.3113(8) |
| O(3) | 0.0842(25) | 0.4582(20) | 0.2776(7) |
| O(4) | 0.1776(29) | 0.3744(18) | 0.3985(8) |
| N(1) | 0.4650(34) | 0.5390(24) | 0.2435(10) |
| N(2) | 0.7168(35) | 0.5531(26) | 0.3429(11) |
| N(3) | 0.5970(31) | 0.4271(22) | 0.4302(9) |
| C(1) | 0.0572(49) | 0.4199(25) | 0.2266(14) |
| C(2) | −0.1186(47) | 0.3590(24) | 0.2125(13) |
| C(3) | −0.1440(57) | 0.3222(29) | 0.1589(16) |
| C(4) | 0.0008(65) | 0.3432(33) | 0.1170(18) |
| C(5) | 0.1719(56) | 0.4018(29) | 0.1309(16) |
| C(6) | 0.2049(43) | 0.4452(25) | 0.1848(12) |
| C(7) | 0.3876(54) | 0.5188(28) | 0.1942(15) |
| C(8) | 0.4749(63) | 0.5673(33) | 0.1426(17) |
| C(9) | 0.6496(43) | 0.6174(29) | 0.2448(17) |
| C(10) | 0.6925(55) | 0.6426(30) | 0.3041(17) |
| C(11) | 0.7481(54) | 0.5934(28) | 0.3989(17) |
| C(12) | 0.7668(46) | 0.5033(33) | 0.4368(15) |
| C(13) | 0.5666(45) | 0.3472(24) | 0.4629(12) |
| C(14) | 0.7336(61) | 0.3461(31) | 0.5115(16) |
| C(15) | 0.4097(52) | 0.2725(27) | 0.4575(14) |
| C(16) | 0.4418(62) | 0.1786(32) | 0.4826(17) |
| C(17) | 0.2901(68) | 0.1076(35) | 0.4767(18) |
| C(18) | 0.0977(65) | 0.1250(35) | 0.4468(18) |
| C(19) | 0.0630(56) | 0.2147(30) | 0.4194(16) |
| C(20) | 0.2214(50) | 0.2911(27) | 0.4236(14) |

Anisotropic thermal parameters (×10²) in the form: $T = \exp[-2\pi^2\Sigma_{ij}U_{ij}h_ih_ja^*_ia^*_j]$

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| U | 3.44(0.04) | 6.06(0.06) | 5.02(0.06) | 0.14(0.08) | 0.20(0.04) | −1.32(0.08) |
| O(1) | 8.6(1.6) | 7.5(1.7) | 6.5(1.5) | −1.9(1.3) | −0.4(1.3) | −0.4(1.2) |
| O(2) | 8.6(1.5) | 6.0(1.4) | 3.3(1.1) | −3.2(1.2) | −0.2(1.0) | −0.2(1.0) |
| O(3) | 3.2(0.9) | 9.3(1.5) | 5.1(1.1) | 1.9(1.3) | −0.6(0.8) | 0.6(1.4) |
| O(4) | 4.6(1.2) | 8.3(1.7) | 5.4(1.4) | 0.9(1.2) | −0.4(1.0) | −0.2(1.2) |
| N(1) | 4.4(1.3) | 8.1(1.8) | 6.0(1.6) | 1.0(1.6) | 0.6(1.1) | 0.5(1.8) |
| N(2) | 4.0(1.3) | 10.8(2.5) | 6.7(1.7) | −1.2(1.7) | 0.4(1.2) | −2.8(2.1) |
| N(3) | 2.5(1.1) | 10.1(2.4) | 4.7(1.4) | −0.2(1.2) | −0.4(1.0) | −2.3(1.4) |
| C(9) | 2.9(1.5) | 9.3(2.8) | 11.1(3.1) | −3.3(1.7) | 0.7(1.7) | 2.9(2.5) |
| C(10) | 6.8(2.3) | 7.4(2.8) | 8.7(2.9) | −2.9(2.1) | 1.0(2.1) | −1.1(2.4) |
| C(11) | 6.8(2.3) | 5.6(2.3) | 10.2(3.0) | −1.6(1.9) | −0.3(2.1) | −3.7(2.3) |
| C(12) | 3.7(1.7) | 12.7(3.7) | 7.6(2.5) | −0.6(1.8) | −0.2(1.7) | −2.8(2.4) |

Isotropic thermal parameters (×10²)

| Atom | *U* | Atom | *U* |
|---|---|---|---|
| C(1) | 5.9(9) | C(13) | 5.0(8) |
| C(2) | 5.6(8) | C(14) | 8.7(1.2) |
| C(3) | 7.9(1.1) | C(15) | 6.8(9) |
| C(4) | 9.2(1.2) | C(16) | 8.4(12) |
| C(5) | 7.7(1.0) | C(17) | 9.7(1.3) |
| C(6) | 5.4(8) | C(18) | 9.3(1.3) |
| C(7) | 7.4(1.0) | C(19) | 7.7(1.1) |
| C(8) | 9.5(1.3) | C(20) | 6.1(9) |

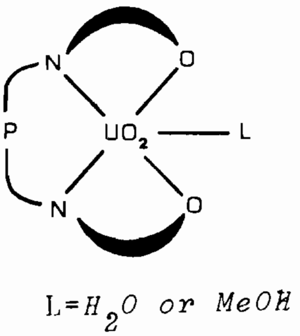
TABLE VI. Bond and Contact Distances (Å) for $UO_2(L^1)$.

| | | | |
|---|---|---|---|
| *Bond Distances* | | | |
| Coordination | | | |
| U–O(1) | 1.73(2) | U–N(1) | 2.59(3) |
| U–O(2) | 1.75(2) | U–N(2) | 2.55(3) |
| U–O(3) | 2.21(2) | U–N(3) | 2.68(2) |
| U–O(4) | 2.24(2) | | |
| Ligand | | | |
| O(3)–C(1) | 1.34(4) | O(4)–C(20) | 1.28(4) |
| N(1)–C(7) | 1.29(4) | N(3)–C(13) | 1.34(4) |
| N(1)–C(9) | 1.56(4) | N(3)–C(12) | 1.48(4) |
| N(2)–C(10) | 1.51(5) | N(2)–C(11) | 1.46(5) |
| C(7)–C(8) | 1.53(6) | C(13)–C(14) | 1.54(5) |
| C(9)–C(10) | 1.48(6) | C(11)–C(12) | 1.50(6) |
| *Contact Distances* | | | |
| O(3)···O(4) | 3.15(3) | N(1)···N(2) | 2.82(3) |
| O(3)···N(1) | 2.79(3) | N(2)···N(3) | 2.81(4) |
| O(4)···N(3) | 2.81(3) | | |

Bond distances and angles in the two phenylene rings are normal

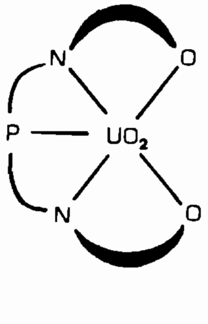
TABLE VII. Bond Angles (deg) for $UO_2(L^1)$.

| | | | |
|---|---|---|---|
| Coordination | | | |
| O(1)–U–O(2) | 176(1) | O(4)–U–N(3) | 69(1) |
| O(3)–U–O(4) | 90(1) | N(1)–U–N(2) | 66(1) |
| O(3)–U–N(1) | 70(1) | N(3)–U–N(2) | 65(1) |
| Ligand | | | |
| U–O(3)–C(1) | 131(2) | N(1)–C(7)–C(8) | 122(3) |
| U–O(4)–C(20) | 130(2) | N(1)–C(9)–C(10) | 106(3) |
| U–N(1)–C(7) | 128(2) | C(9)–C(10)–N(2) | 116(3) |
| U–N(1)–C(9) | 118(2) | C(10)–N(2)–C(11) | 107(3) |
| U–N(2)–C(10) | 106(2) | N(2)–C(11)–C(12) | 106(3) |
| U–N(2)–C(11) | 108(2) | C(11)–C(12)–N(3) | 116(3) |
| U–N(3)–C(12) | 111(2) | C(12)–N(3)–C(13) | 127(2) |
| U–N(3)–C(13) | 122(2) | N(3)–C(13)–C(14) | 110(3) |
| C(6)–C(7)–C(8) | 117(3) | N(3)–C(13)–C(15) | 128(3) |
| C(6)–C(7)–N(1) | 121(3) | C(14)–C(13)–C(15) | 121(3) |



L=$H_2O$ or MeOH

I



II

TABLE VIII. Least Squares Planes for $UO_2(L^1)$.

Derivations (Å) of atoms from the planes are given in square brackets; $X$, $Y$, and $Z$ are fractional coordinates in the direct cell. Atoms not used in the plane calculation are marked with an asterisk.

| | |
|---|---|
| Plane 1: | O(3), O(4), N(1), N(2), N3<br>$-2.434X + 11.290Y + 8.859Z = 7.316$<br>O(3) −0.01, O(4) 0.01, N(1) −0.20, N(2) 0.22, N(3) −0.14, U −0.04, C(9) 0.24, C(10) 0.95, C(11) 1.09, C(12) 0.37 |
| Plane 2: | O(3), C(1) to C(7)<br>$-3.444X + 10.501Y - 5.866Z = 2.911$<br>These atoms are coplanar within 0.06 Å |
| Plane 3: | O(4), C(13), C(15) to C(20)<br>$-2.943X + 4.688Y + 20.064Z = 9.234$<br>These atoms are coplanar within 0.03 Å |

Angles (°) between planes: 1–2 37.4; 1–3 40.0; 2–3 71.4

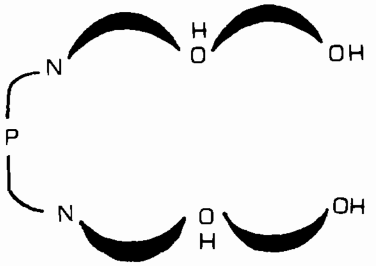
If (I) were the correct structure, then it should be possible to replace the solvent molecule by more basic ligands, such as dmso. On the contrary, the starting compound remained unchanged upon dissolving in dmso and precipitating with $Et_2O$, and this seems to indicate that structure (II) is more probable. By slowly recrystallizing the product, crystals suitable for the X-ray analysis were obtained.

However, the physico-chemical properties of the crystals are completely different from those of the original compound, and, as it was clearly revealed by the X-ray work, the crystalline compound must be formulated as $UO_2$ with the P atom being bonded to $UO_2^{2+}$ through the O atom.

Apparently the $R_3P$ group was oxidized to $R_3PO$ during the long period required for growing good crystals and these results suggest that in solution the starting uranyl–phosphine complex converts with time into the more stable uranyl–phosphineoxide complex.

Tentatively we can suppose a reduction of $U^{VI}$ to lower oxidation states with the oxidation of $R_3P$ to $R_3PO$ followed by the fast reoxidation of the uranium atom due to the presence of the atmospheric oxygen.

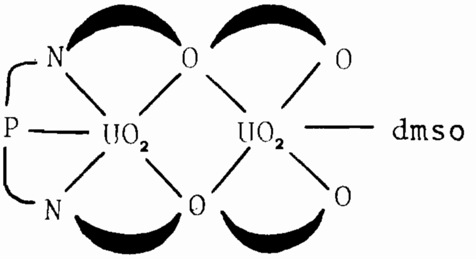
In the binuclear $(UO_2)_2(L^3)MeOH$ complex, one $UO_2^{2+}$ group must occupy the internal $O_2N_2P$ site of the ligand, with $R_3P$ probably bonded to the



$H_4L^3$

uranium atom, whereas the 'outside' $UO_2^{2+}$ group must occupy the external $O_2O_2$ chamber, with a solvent molecule in the fifth equatorial coordination site. The thermal behaviour in air of the binuclear complex $(UO_2)_2(L_3)$MeOH shows that the release of the molecule of methanol begins at about 70 °C, followed by the decomposition of the organic moiety at about 120 °C.

The solvent molecule is easily replaced by dmso and $(UO_2)_2(L^3)$ (dmso) can be obtained by dissolving $(UO_2)_2(L^3)$MeOH in dmso and precipitating with $Et_2O$. The appearance of a new intense band at 1020 cm$^{-1}$ is ascribed to the $\nu$S–O of dmso, with a small shift toward the lower frequency upon coordination. On these bases the molecular structure(III) should be proposed for $(UO_2)_2(L^3)$(dmso).



(III)

## Experimental

### X-Ray Crystallography

*$UO_2(OL^2)$, $C_{26}H_{27}N_2O_5PU$*

A parallelepiped crystal of approximate dimensions 0.18 × 0.10 × 0.12 mm was mounted on a glass fibre and examined on a Philips four-circle diffractometer. The crystal was found to belong to the orthorhombic system with $a = 10.85(1)$ Å, $b = 14.23(1)$ Å, $c = 16.17(1)$ Å. By use of MoK$\alpha$ radiation ($\lambda = 0.7107$ Å), the cell dimensions were determined by least-squares refinement of the setting angles for 25 reflections in the range $8° < \vartheta < 10°$. The systematic absences Okl for k + l = 2n + 1 and hkO for h = 2n + 1 indicated the possible space groups *Pnma* and *Pn2$_1$a*.

The structure determination was carried out in the centrosymmetric space group *Pnma*, which has the general positions $\pm(x, y, z;\ 1/2 + x,\ 1/2 - y,\ 1/2 - z;\ \bar{x},\ 1/2 + y,\ \bar{z};\ 1/2 - x,\ \bar{y},\ 1/2 + z)$, and was verified by the successful refinement. From the unit cell volume of 2497 Å$^3$ and a molecular weight of 716, a density of 1.90 g cm$^{-3}$ was calculated for $Z = 4$.

Intensity data up to $\vartheta = 25°$ were collected using MoK$\alpha$ radiation monochromatized with a graphite crystal. The $\vartheta$–$2\vartheta$ scan method was used with a scan rate of 2°/min. Of the 2290 reflections recorded, 1593 were found to have $I > 3\sigma(I)$ and were employed in solving and refining the structure. Since the linear absorption coefficient was high, $\mu$(MoK$\alpha$) = 98.2 cm$^{-1}$, an absorption correction was made [8].

The structure was solved by the heavy atom method from Patterson and Fourier syntheses. Least-squares refinement of the atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms converged with the conventional $R$ of 0.057. Neutral scattering factors were used throughout, that for uranium being corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$) [9, 10]. All calculations were carried out using the X-RAY program system [11].

*$UO_2(L^1)$, $C_{20}H_{23}N_3O_4U$*

A parallelepiped crystal of approximate dimensions 0.20 × 0.15 × 0.15 mm was mounted in a glass fibre and examined on a Philips four-circle diffractometer. The crystal was found to belong to the monoclinic system with $a = 6.31(1)$ Å, $b = 13.22(1)$ Å, $c = 24.14(1)$ Å, $\beta = 92.61(2)°$. By use of MoK$\alpha$ radiation ($\lambda = 0.7107$ Å), the cell dimensions were determined by least-squares refinement of the setting angles for 25 reflections in the range $8° < \vartheta < 16°$. Systematic absences indicated the space group *P2$_1$/c*. From the unit cell volume of 2014 Å$^3$ and a molecular weight of 607, a density of 2.00 g cm$^{-3}$ was calculated for $Z = 4$.

Intensity data up to $\vartheta = 25°$ were collected using MoK$\alpha$ radiation monochromatized with a graphite crystal. The $\vartheta$–$2\vartheta$ scan method was used with a scan rate of 2°/min. Of the 3655 reflections recorded, 1819 were found to have $I > 3\sigma(I)$ and were employed in solving and refining the structure. Since the linear absorption coefficient was high, $\mu$(MoK$\alpha$) = 121.2 cm$^{-1}$, an absorption correction was made [8].

The structure was solved by the heavy atom method from Patterson and Fourier syntheses. Least squares refinement of the atomic coordinates and thermal parameters, including anisotropy for U, O, N and for some chain carbon atoms, converged with the conventional $R$ of 0.074. Neutral atom scattering factors were used throughout, that for uranium being corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$) [9, 10]. All calculations were carried out using the X-RAY program system [11].

### Preparation

*o*-Hydroxyacetophenone, salicylaldehyde and 1,7-diamino-4 phenyl phosphine-heptane are commercial products and were used without further purification. *o*-Hydroxyacetophenone and salicylaldehyde were distilled before use. All manipulations regarding the preparation of the phosphine ligand and related $UO_2^{2+}$ complexes were carried out in a dry-box.

3-Formylsalicylic acid was prepared according to the literature [20]; bis(3-aminopropyl)phenylphosphine is a Stream Chemicals product and was used without further purification.

### *N,N'-bis(salicylidene)-1,7-diamino-4-heptane* $(H_2L^1)$

*o*-Hydroxyacetophenone (2 mmol) and 1,5-diamino-3-aza-penthane (1 mmol) were stirred in methanol at room temperature for 3 h. By evaporation of the solution, previously clarified by treatment with activated carbon; a yellow compound was obtained which was purified by crystallization from methanol.

### *N,N'-bis(salicylidene)-1,7-diamino-4-phenylphosphine heptane,* $(H_2L^2)$

To a methanolic solution (25 ml) of bis(3-aminopropyl)phenylphosphine (896 mg, 4 mmol) a methanolic solution (25 ml) of salicylaldehyde (976 mg, 8 mmol) were added dropwise. The resulting yellow solution was stirred at room temperature for 2 h. The yellow oil obtained by evaporation of the solvent was washed two times with methanol, dissolved in diethyl-ether and dried over $Na_2SO_4$. The solution was kept overnight at room temperature and was filtered. By removing the solvent, $H_2L^2$ was obtained as pure yellow oil.

### *Preparation of 2-hydroxy-3-[bis-aldiminopropylphenylphosphine]benzoic acid,* $(H_4L^3)$

To bis(3-aminopropyl)phenylphosphine (224 mg, 1 mmol), in anhydrous methanol, a methanol solution of 3-formylsalicylic acid (330 mg, 2 mmol) was added. The resulting solution was stirred for 3 h; by evaporation of the solvent a yellow oil of $H_4L^3$ was obtained which was washed two times with anhydrous methanol, dissolved in diethylether, and dried overnight over $Na_2SO_4$. By removing the solvent, pure $H_4L^3$ was obtained as a yellow oil.

### *Preparation of* $UO_2(L^1)$

To a methanolic solution of $H_2L^1$ (339 mg, 1 mmol), $UO_2(OAc)_2\cdot 2H_2O$ (424 mg, 1 mmol) dissolved in methanol was added. The yellow-orange precipitate was stirred for 3 h, filtered, washed with methanol and dried *in vacuo*.

### *Preparation of* $UO_2(L^2)\cdot H_2O$

To a methanolic solution (25 ml) of $UO_2(CH_3COO)_2\cdot 2H_2O$ (449 mg, 1.06 mmol), a methanolic solution of $H_2L^2$ (432 mg, 1 mmol) was added. The orange precipitate obtained was stirred at room temperature in a dry box for 2 h, then filtered, washed with anhydrous methanol and dried *in vacuo*.

### *Preparation of* $(UO_2)_2(L^3)MeOH$

To a methanolic solution (20 ml) of $H_4L^3$ (533 mg, 1.06 mmol) $UO_2(CH_3COO)_2\cdot 2H_2O$ (899 mg, 2.12 mmol) in 25 ml of methanol was added dropwise. The yellow precipitate obtained was stirred for 2 h, washed several times with methanol and dried *in vacuo*.

### *Preparation of* $(UO_2)_2(L^3)(dmso)$

$(UO_2)_2(L^3)\cdot CH_3OH$ was dissolved in the minimum quantity of dmso (dimethylsulphoxide) and stirred at room temperature for 6 h. The orange precipitate obtained by addition of diethylether to this solution was filtered, washed with diethylether and dried *in vacuo*.

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