Preparation and Crystal Structure of Diaquabis(1,2-naphthoquinone-2-oximato-*ON*)dioxouranium(VI)–Trichloromethane (1/2) and Aquabis(1,2-naphthoquinone-1-oximato-*ON*)(triphenylphosphine oxide)dioxouranium(VI)[†]

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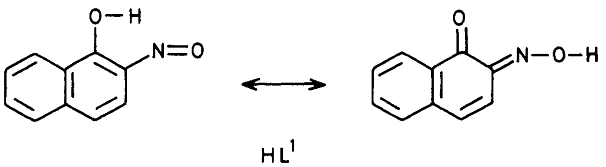
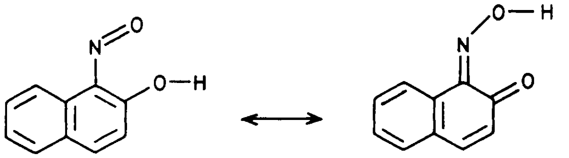
Two complexes of a uranyl group with the anions of nitrosonaphthols have been prepared and their crystal structures have been determined by *X*-ray crystallography. The first compound $[UO_2(L^1)_2(H_2O)_2]\cdot2CHCl_3$ (L^1 = 1,2-napthoquinone-2-oximate) is triclinic, space group $P\bar{1}$, with a = 11.975(5), b = 10.536(5), c = 6.372(5) Å, α = 86.51(3), β = 99.68(3), γ = 113.75(3)°, and Z = 1. The second compound $[UO_2(L^2)_2(OPPh_3)(H_2O)]$ (L^2 = 1,2-naphthoquinone-1-oximate) is triclinic, space group $P\bar{1}$, with a = 14.527(5), b = 12.115(5), c = 10.932(5) Å, α = 104.35(3), β = 108.15(3), γ = 97.21(3)°, and Z = 2. In both cases co-ordination of L^1 and L^2 to uranium is achieved through bidentate bonding from the oxygen and nitrogen atoms of the nitroso-groups. Both complexes are stabilized by intramolecular hydrogen bonds.

It is known that 2-nitrosonaphth-1-ol (HL^1) and 1-nitrosonaphth-2-ol (HL^2) have been widely used as analytical reagents for the determination of several metal ions as well as for the selective extraction of actinides ions from aqueous solutions.[1]

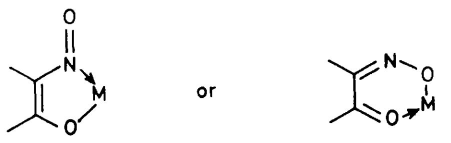


HL^1



HL^2

These ligands, which can also tautomerize to the corresponding quinone monoximes, can act as monoanionic bidentate donors: five- and six-membered chelate rings of the type shown below have been proposed on the basis of i.r. spectra,[2,3]



and the presence of five-membered rings in the copper(II) complexes have been confirmed by *X*-ray data.[4] To a better comprehension of their behaviour toward lanthanides and actinides ions we report here the crystal structures of two uranyl compounds.

Experimental

Diaquabis(1,2-*naphthoquinone-2-oximato*-ON)*dioxouranium*(VI)–*Trichloromethane* (1/2) $[UO_2(L^1)_2(H_2O)_2]\cdot2CHCl_3$.—On adding a solution of $[UO_2(NO_3)_2(H_2O)_2]\cdot4H_2O$ (504 mg, 1 mmol) in H_2O (10 cm^3) to a green H_2O–MeOH solution (100 cm^3) of 2-nitrosonaphth-1-ol (346 mg, 2 mmol) and LiOH (48 mg, 2 mmol) at room temperature, a red precipitate of $[UO_2(L^1)_2(H_2O)_2]$ formed, which was washed with MeOH. Removal of the solvent and recrystallization from $CHCl_3$ gave well formed crystals of $[UO_2(L^1)_2(H_2O)_2]\cdot2CHCl_3$.

Crystal data. $C_{20}H_{16}N_2O_6U\cdot2CHCl_3$, $M = 618 + 247$, Triclinic, space group $P\bar{1}$, $a = 11.975(5)$, $b = 10.536(5)$, $c = 6.372(5)$ Å, $\alpha = 86.51(3)$, $\beta = 99.68(3)$, $\gamma = 113.75(3)°$, $U = 725$ Å^3, $D_c = 1.98$ g cm^{-3}, $Z = 1$,[‡] $F(000) = 406$, Mo-K_α radiation, $\lambda = 0.7107$ Å, μ(Mo-K_α) = 89.9 cm^{-1}; neutral-atom scattering factors from ref. 5, those for U being corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$).[6]

A small regular crystal of approximate dimensions 0.10 × 0.15 × 0.15 cm was used for the crystallographic work. Unit-cell parameters were determined by a least-squares fit of the angular parameters of 25 reflections centred in the counter aperture of a Philips four-circle diffractometer. A unique data set up to $2\theta = 50°$ was obtained by a conventional θ—2θ scan, yielding 2 714 reflections, of which 2 711 with $I > 3\sigma(I)$ were used in the structure solution and refinement. The intensities were corrected for Lorentz polarization and absorption effects following the method of ref. 7. A slow deterioration of the crystal was observed during irradiation, but, owing to its small magnitude, no correction to the intensities was applied.

Structure determination. The absence of relevant peaks on the Patterson map clearly showed that only one molecule of the compound was present in the unit cell, with the heavy atom on the origin, and the centrosymmetric space group was

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[†] *Supplementary data available* (No. SUP 23500, 37 pp.): structure factors, thermal parameters, H-atom co-ordinates. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

[‡] The unit cell contains one molecule of the comolex and two molecules of $CHCl_3$.

Table 1. Atomic parameters for $[UO_2(L^1)_2(H_2O)_2]\cdot2CHCl_3$ with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
U	0.0	0.0	0.0
O(1)	0.096 5(5)	0.170 2(6)	−0.046 8(10)
O(2)	−0.068 6(5)	0.087 1(7)	0.263 7(9)
O(3)	−0.322 1(6)	0.053 1(7)	0.262 6(10)
O(4)	0.136 2(5)	0.008 3(7)	0.338 1(10)
N	−0.151 3(6)	0.080 1(7)	0.089 8(12)
C(1)	−0.325 5(8)	0.111 3(9)	−0.103 4(15)
C(2)	−0.232 3(7)	0.132 4(9)	0.093 9(14)
C(3)	−0.236 6(8)	0.202 8(10)	0.277 9(15)
C(4)	−0.326 9(8)	0.251 6(10)	0.271 8(16)
C(5)	−0.510 3(9)	0.287 0(10)	0.085 4(19)
C(6)	−0.599 0(9)	0.270 5(11)	−0.092 5(21)
C(7)	−0.600 0(8)	0.201 8(10)	−0.273 2(19)
C(8)	−0.512 3(8)	0.146 9(10)	−0.277 7(17)
C(9)	−0.421 2(7)	0.164 8(8)	−0.099 2(16)
C(10)	−0.420 8(8)	0.233 2(9)	0.086 1(16)
C(11)	0.171 8(12)	0.408 4(12)	0.316 7(21)
Cl(1)	0.142 2(3)	0.363 7(4)	0.573 0(6)
Cl(2)	0.331 7(4)	0.477 8(4)	0.317 9(8)
Cl(3)	0.114 3(4)	0.532 3(5)	0.222 2(8)

Table 2. Distances (Å) and angles (°) for $[UO_2(L^1)_2(H_2O)_2]\cdot2CHCl_3$ [a]

(*i*) Bond distances			
U−O(1)	1.74(1)	C(4)−C(10)	1.45(1)
U−O(2)	2.37(1)	C(5)−C(10)	1.40(2)
U−O(4)	2.46(1)	C(5)−C(6)	1.38(2)
U−N	2.44(1)	C(6)−C(7)	1.39(2)
N−O(2)	1.34(1)	C(7)−C(8)	1.39(2)
N−C(2)	1.30(1)	C(8)−C(9)	1.40(1)
O(3)−C(1)	1.23(1)	C(9)−C(1)	1.47(2)
C(1)−C(2)	1.50(1)	C(9)−C(10)	1.42(2)
C(1)−C(9)	1.47(1)	C(11)−Cl(1)	1.73(1)
C(2)−C(3)	1.44(1)	C(11)−Cl(2)	1.75(1)
C(3)−C(4)	1.37(2)	C(11)−Cl(3)	1.74(2)
(*ii*) Bond angles [b]			
N−U−O(2)	32.3(2)	O(2)−N−C(2)	120(1)
N−U−O(4^{I})	75.2(2)	N−C(2)−C(1)	116(1)
O(2)−U−O(4)	72.5(2)	N−C(2)−C(3)	123(1)
U−O(2)−N	76.9(5)	C(1)−C(2)−C(3)	121(1)
U−N−O(2)	70.7(5)	C(2)−C(1)−O(3)	122(1)
U−N−C(2)	167.1(6)	C(2)−C(1)−C(9)	117(1)
		C(9)−C(1)−O(3)	121(1)
(*iii*) Contact distances			
O(4) ··· O(2)	2.85(1)		
O(4) ··· O(3^{I})	2.67(1)		
O(4) ··· N^{I}	2.99(1)		

[a] The Roman numeral superscript corresponds to the symmetry code $\bar{x}, \bar{y}, \bar{z}$. [b] Other angles in the rings are comprised between 119 and 122°. The three Cl−C−Cl angles in $CHCl_3$ are all 109(1)°.

chosen (and then confirmed) according to the possible molecular symmetry. The Patterson map itself revealed the positions of all non-hydrogen atoms, including those of one molecule of chloroform.

Refinement of the atomic parameters using anisotropic thermal parameters converged with the conventional R = 0.043, when the maximum shift/e.s.d. was 0.02 for the positional and 0.03 for the thermal parameters. Atomic parameters are given in Table 1, bond distances and angles in Table 2, and selected mean planes in Table 3.

Aquabis(1,2-*naphthoquinone*-1-*oximato*-ON)(*triphenylphosphine oxide*)*uranium*(VI), $[UO_2(L^2)_2(OPPh_3)(H_2O)]$.—A solution of $[UO_2(NO_3)_2(H_2O)_2]\cdot4H_2O$ (504 mg, 1 mmol) in H_2O (10 cm^3) was added to a dark green H_2O–MeOH solution (100 cm^3) of 1-nitrosonaphth-2-ol (346 mg, 2 mmol) and LiOH (48 mg, 2 mmol) at room temperature, and $[UO_2(L^2)_2(H_2O)_2]$ immediately formed as a dark brown precipitate. The product was stirred for 2 h, washed with MeOH, and dried *in vacuo*. To a suspension of $[UO_2(L^2)_2(H_2O)_2]$ in CH_2Cl_2 a large excess of $P(O)Ph_3$ in the same solvent was added and the resulting solution was stirred for 2 h and reduced in volume. On adding Et_2O a green product was collected, which was washed with Et_2O. Removal of the solvent and recrystallization from acetone gave well formed crystals of $[UO_2(L^2)_2(OPPh_3)(H_2O)]$.

Table 3. Least-squares planes for $[UO_2(L^1)_2(H_2O)_2]\cdot2CHCl_3$. The equation of a plane is in the form $Ax + By + Cz = D$ where x, y, and z are the fractional co-ordinates of the atoms in the direct cell. Deviations (Å) from the plane are given in square brackets

Plane 1: O(2), O(4), N^{I}, O(2^{I}), O(4^{I}), N

$$3.347x + 7.871y - 1.600z = 0.000$$

[O(2) 0.03, O(4) −0.02, N^{I} 0.03, O(2^{I}) −0.03, O(4^{I}) 0.02, N −0.03]

Plane 2: C(1)—C(10)

$$3.948x + 7.051y - 2.603z = -0.247$$

These atoms are coplanar within 0.02 Å

Plane 2 is inclined by 10° to Plane 1.

Crystal data. $C_{38}H_{33}N_2O_8PU$, M = 914, Triclinic, space group $P\bar{1}$, a = 14.527(5), b = 12.115(5), c = 10.932(5) Å, α = 104.35(3), β = 108.15(3), γ = 97.21(3)°, U = 1 727 Å^3, D_c = 1.76 g cm^{-3}, Z = 2, $F(000)$ = 892, Mo-K_α radiation, λ = 0.7107 Å, μ(Mo-K_α) = 71.5 cm^{-1}; neutral-atom scattering factors from ref. 5, those for U being corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$).[6]

A small regular crystal of approximate dimensions 0.12 × 0.20 × 0.18 cm was used for the crystallographic work. Unit-cell parameters were determined by a least-squares fit of the angular parameters of 25 reflections centred in the counter aperture of a Philips four-circle diffractometer. A unique data set up to 2θ = 50° was obtained by a conventional θ—2θ scan, yielding 6 170 reflections, of which 5 456 with $I > 3\sigma(I)$ were used in the structure solution and refinement. The intensities were corrected for Lorentz polarization and for the absorption effects following the method of ref 7. No deterioration of the crystal was observed during irradiation.

Structure determination. The position of the uranium atom was determined from the Patterson map and the positions of the non-hydrogen light atoms were found in the successive Fourier difference calculations based on the $|F_o|$'s with the signs determined by the heavy-atom position. The ring hydrogen atoms were introduced in calculated positions. Refinement of the atomic parameters using anisotropic thermal parameters converged with the conventional R = 0.085, when the maximum shift/e.s.d. was 0.03 for the positional and 0.06 for the thermal parameters.

Atomic parameters are given in Table 4, bond distances and angles in Table 5, and selected mean planes in Table 6. The calculations were performed with the *X*-RAY system.[8]

Discussion

The structure of $[UO_2(L^1)_2(H_2O)_2]\cdot2CHCl_3$ is shown in Figure 1 together with the numbering scheme. The organic ligands are chelated through the O and N atoms of the nitroso-groups

Table 4. Atomic parameters for $[UO_2(L^2)_2(OPPh_3)(H_2O)]$ with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
U	0.245 0(1)	0.059 7(1)	0.216 0(1)	C(14)	0.129(2)	−0.168(2)	0.643(2)
P	0.187 6(4)	0.357 5(5)	0.249 2(7)	C(15)	0.076(2)	−0.000(2)	0.762(2)
O(1)	0.360(1)	0.149(2)	0.328(2)	C(16)	0.065(2)	0.116(2)	0.791(3)
O(2)	0.131(12)	−0.030(2)	0.101(2)	C(17)	0.081(2)	0.182(2)	0.701(2)
O(3)	0.291(1)	0.108(2)	0.040(2)	C(18)	0.116(2)	0.131(2)	0.601(2)
O(4)	0.361(1)	−0.203(2)	0.033(2)	C(19)	0.132(2)	0.014(2)	0.581(3)
O(5)	0.175(1)	0.109(1)	0.386(2)	C(20)	0.112(2)	−0.050(2)	0.663(3)
O(6)	0.224(2)	−0.213(2)	0.382(2)	C(21)	0.276(2)	0.444(2)	0.203(3)
O(7)	0.182(1)	0.230(1)	0.197(2)	C(22)	0.318(2)	0.562(2)	0.273(3)
O(8)	0.310(2)	−0.109(2)	0.244(2)	C(23)	0.387(2)	0.623(3)	0.232(4)
N(1)	0.317(1)	0.004(2)	0.036(2)	C(24)	0.407(2)	0.566(3)	0.122(3)
N(2)	0.191(1)	0.004(2)	0.390(2)	C(25)	0.370(2)	0.447(3)	0.052(3)
C(1)	0.354(2)	−0.040(2)	−0.056(2)	C(26)	0.303(2)	0.383(3)	0.093(3)
C(2)	0.378(2)	−0.154(2)	−0.047(2)	C(27)	0.220(2)	0.409(2)	0.430(2)
C(3)	0.425(2)	−0.209(2)	−0.136(2)	C(28)	0.325(3)	0.421(3)	0.513(3)
C(4)	0.443(2)	−0.163(2)	−0.226(2)	C(29)	0.341(3)	0.467(3)	0.650(3)
C(5)	0.443(2)	−0.011(2)	−0.340(2)	C(30)	0.269(4)	0.499(4)	0.702(4)
C(6)	0.419(2)	0.096(2)	−0.355(2)	C(31)	0.168(3)	0.471(3)	0.624(3)
C(7)	0.377(2)	0.162(2)	−0.269(2)	C(32)	0.147(2)	0.431(3)	0.484(3)
C(8)	0.355(2)	0.118(2)	−0.170(2)	C(33)	0.066(2)	0.390(2)	0.169(2)
C(9)	0.379(2)	0.012(2)	−0.156(2)	C(34)	0.056(2)	0.502(2)	0.190(2)
C(10)	0.421(2)	−0.053(2)	−0.240(2)	C(35)	−0.041(2)	0.518(3)	0.134(3)
C(11)	0.170(2)	−0.040(2)	0.478(2)	C(36)	−0.122(2)	0.422(3)	0.062(3)
C(12)	0.190(2)	−0.161(2)	0.465(2)	C(37)	−0.108(2)	0.309(3)	0.048(2)
C(13)	0.165(2)	−0.224(2)	0.552(3)	C(38)	−0.014(2)	0.294(2)	0.098(3)

Table 5. Selected distances (Å) and angles (°) for $[UO_2(L^2)_2(OPPh_3)(H_2O)]$

Bond distances

(*i*) Co-ordination

U–O(1)	1.75(1)	U–O(7)	2.38(2)
U–O(2)	1.75(1)	U–O(8)	2.41(2)
U–O(3)	2.40(2)	U–N(1)	2.48(2)
U–O(5)	2.37(2)	U–N(2)	2.47(2)

(*ii*) Ligands

N(1)–O(3)	1.35(3)	N(2)–O(5)	1.32(3)
N(1)–C(1)	1.33(2)	N(2)–C(11)	1.33(2)
C(1)–C(2)	1.46(3)	C(11)–C(12)	1.49(2)
C(1)–C(9)	1.52(2)	C(11)–C(19)	1.46(3)
C(2)–C(3)	1.42(3)	C(12)–C(13)	1.47(3)
C(2)–O(4)	1.25(3)	C(12)–O(6)	1.21(3)
C(3)–C(4)	1.32(3)	C(13)–C(14)	1.35(3)
C(4)–C(10)	1.42(3)	C(14)–C(20)	1.45(3)
C(9)–C(10)	1.41(2)	C(19)–C(20)	1.42(3)

(*iii*) $OPPh_3$

P–O(7)	1.49(2)	P–C(27)	1.84(1)
P–C(21)	1.86(1)	P–C(33)	1.86(1)

Contact distances

O(7) ··· O(3)	2.94(2)	O(8) ··· O(4)	2.67(2)
O(7) ··· O(5)	2.83(2)	O(8) ··· O(6)	2.68(2)
O(8) ··· N(1)	2.95(2)		
O(8) ··· N(2)	2.94(2)		

Bond angles

(*i*) Co-ordination (e.s.d.s are 1° or less)

O(1)–U–O(2)	179	N(1)–U–O(8)	74
O(3)–U–N(1)	32	N(2)–U–O(8)	74
O(5)–U–N(2)	32	O(3)–U–N(2)	178
O(3)–U–O(7)	76	O(5)–U–N(1)	179
O(5)–U–O(7)	73	O(7)–U–O(8)	178

(*ii*) Ligands (e.s.d.s are 2° or less)

U–N(1)–O(3)	70	U–N(2)–O(5)	70
U–O(3)–N(1)	77	U–O(5)–N(2)	78
U–N(1)–C(1)	171	U–N(2)–C(11)	169
O(3)–N(1)–C(1)	118	O(5)–N(2)–C(11)	121
N(1)–C(1)–C(2)	112	N(2)–C(11)–C(12)	112
N(1)–C(1)–C(10)	128	N(2)–C(11)–C(19)	123
C(2)–C(1)–C(9)	119	C(12)–C(11)–C(19)	123
C(1)–C(2)–O(4)	123	C(11)–C(12)–O(6)	126
C(3)–C(2)–O(4)	119	C(13)–C(12)–O(6)	117
C(1)–C(2)–C(3)	118	C(11)–C(12)–C(13)	117
C(2)–C(3)–C(4)	124	C(12)–C(13)–C(4)	118
C(3)–C(4)–C(10)	121	C(13)–C(14)–C(20)	126
C(4)–C(10)–C(19)	122	C(14)–C(20)–C(19)	116
C(1)–C(9)–C(10)	116	C(11)–C(19)–C(20)	117

(*iii*) $OPPh_3$ (e.s.d.s are 1° or less)

U–O(7)–P	151	O(7)–P–C(27)	113
O(7)–P–C(21)	112	O(7)–P–C(33)	109

and two water molecules are also co-ordinated. These six atoms are in a staggered configuration being alternatively displaced by 0.2—0.3 Å from the mean plane.

The fact that the O(2)–N–C(2) angle is 120° shows that N is sp^2 hybridized, as expected, and therefore the direction of the nitrogen sp^2 donor orbital strongly deviates from that of the U–N bond. Moreover, the U–O(nitroso) bond of 2.37 Å is significantly shorter than the usual value of *ca.* 2.45 Å generally found for the U–O(charged) bond in uranyl compounds with six atoms equatorially bonded to uranium, while it compares well with U–O(charged) distances in compounds where five atoms are equatorially bonded. These features appear to indicate the relative weakness of the U–N bond if compared with U–O. The asymmetry of the N–O fragment with respect to the uranium atom is confirmed by the circumstance that the U–O–N angle in both compounds is systematically larger by 6—8° than the U–N–O angle. Bond lengths in the ligand show that the N–O and N–C bonds are partial

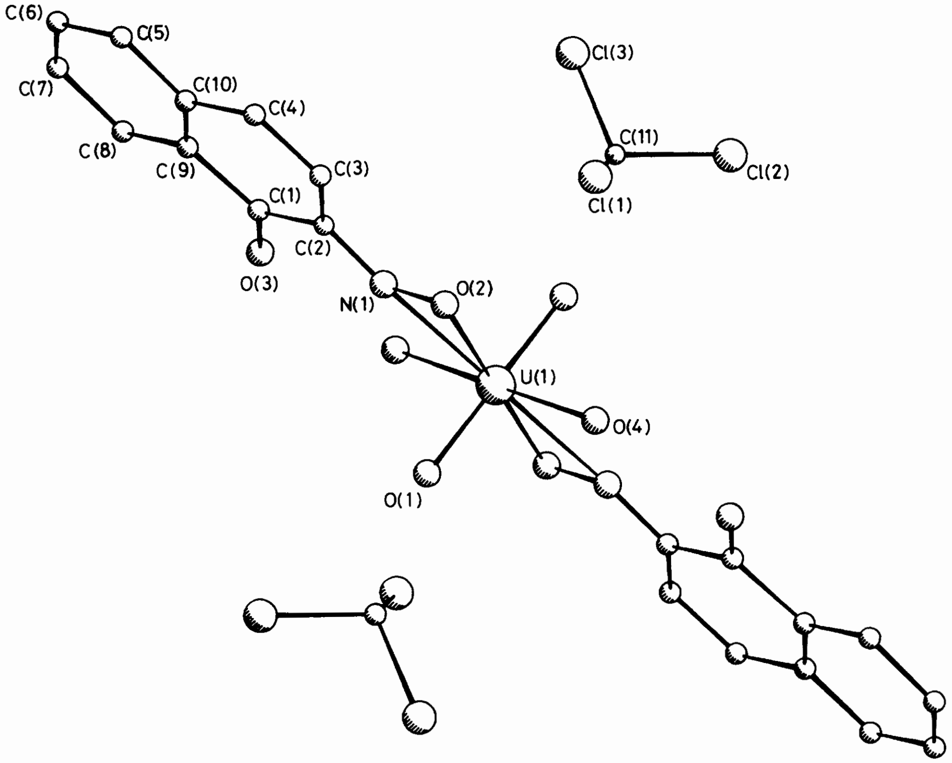

Figure 1. The molecular structure of $[UO_2(L^1)_2(H_2O)_2]\cdot 2CHCl_3$. Projection down the *c* axis

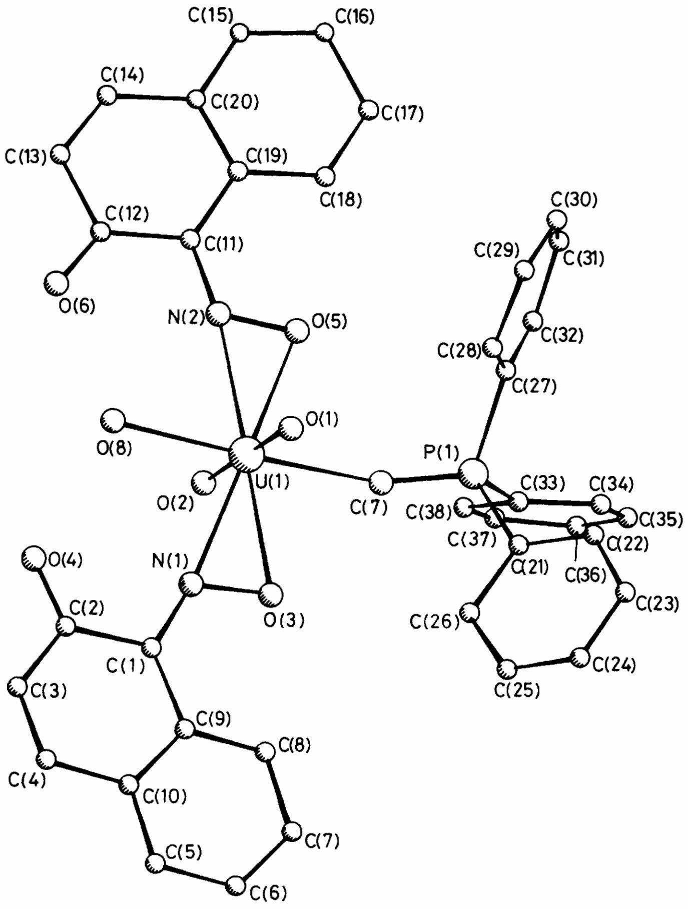

Figure 2. The molecular structure of $[UO_2(L^2)_2(OPPh_3)(H_2O)]$. Projection down the *a* axis

Table 6. Least-squares plane for $[UO_2(L^2)_2(OPPh_3)(H_2O)]$. The equation is of the same form as in Table 3

Plane: N(1), N(2), O(3), O(5), O(7), O(8)

$$9.292x + 3.653y + 3.190z = 3.167$$

[N(1) −0.10, N(2) −0.13, O(3) 0.05, O(5) 0.09, O(7) −0.01, O(8) 0.09, U * 0.02, O(4) * −0.46, O(6) * −0.65]

* Atom not used for plane calculation.

double bonds and that C(1)–O(3) is ketonic. Accordingly no appreciable electronic mesomerism is present in the first ring and the C=C double bond is mainly localized at the C(3)–C(4) level. The contact distance of 2.67 Å strongly suggests the presence of intramolecular hydrogen bonds between the co-ordinated water oxygen atoms and the ketonic oxygens.

The molecular structure of $[UO_2(L^2)_2(OPPh_3)(H_2O)]$, shown in Figure 2, is, apart from obvious differences in the chemical stoicheiometry, basically similar to that of $[UO_2(L^1)_2(H_2O)_2]\cdot 2CHCl_3$. In this case the symmetrical reciprocal positions of the anionic ligands whose ketonic groups converge toward the bonded water molecule appear to be determined both by the presence of the sterically bulky triphenylphosphine and by the possibility of hydrogen bonding.

The co-ordination mode of the ligands as well as the more significant bond lengths and angles confirm all features observed in the analogous compound, and in particular a diffuse delocalization of electronic density over the C–N–O fragments. This, and the contemporary presence of the ketonic C=O bonds, cause the localization of the carbon-carbon double bonds at C(3)–C(4) and C(13)–C(14). In addition the presence of strong hydrogen bonds between the oxygen atom of the co-ordinated water and the ketonic oxygens of both anionic ligands makes the molecule more stable and favours the coplanarity of the ligands. A very similar bidentate bonding with the formation of a three-membered UNO ring has already been observed in a series of uranyl hydroxylamido-complexes.[9] It is noteworthy that corresponding bond distances and angles compare favourably despite the fact that the nitrogen atom is sp^3 hybridized in these compounds.

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