Synthesis, Properties, and Crystal Structures of New Mono- and Homo-binuclear Uranyl(VI) Complexes with Compartmental Schiff Bases†

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Mono-and homo-binuclear uranyl(VI) complexes of the type $[UO_2(H_2L^1)]$·solv, $[(UO_2)_2(L^1)(solv)]$, $[UO_2(H_2L^2)]$·solv, and $[(UO_2)_2(L^2)(solv)]$, where solv is a co-ordinating solvent $[H_2O$, dimethylformamide (dmf), or dimethyl sulphoxide (dmso)] and H_4L^1 and H_4L^2 are the potentially heptadentate dinucleating ligands derived by the condensation of 2,3-dihydroxybenzaldehyde with 1,5-diamino-3-azapentane or 1,5-diamino-3-thiapentane, have been prepared by a template procedure or by reaction of the preformed ligands with $[UO_2(CH_3CO_2)_2]$·2H$_2$O and characterized by i.r., ^{1}H and ^{13}C n.m.r. spectroscopic and X-ray diffraction techniques. The crystal structures of $[UO_2(H_2L^1)]$·dmf, $[(UO_2)_2(L^1)(dmso)]$, and $[(UO_2)_2(L^1)(dmf)]$ have been determined by X-ray crystallography and refined to conventional R values of 0.044, 0.054, and 0.039 respectively: $[UO_2(H_2L^1)]$·dmf is monoclinic, space group $P2_1/n$, with $a = 21.155(5)$, $b = 11.833(8)$, $c = 9.679(8)$ Å, $\beta = 102.34(3)°$, $Z = 4$; $[(UO_2)_2(L^1)(dmso)]$ is monoclinic, space group $P2_1/c$, with $a = 14.985(5)$, $b = 16.536(5)$, $c = 19.956(5)$ Å, $\beta = 90.13(3)°$, $Z = 8$; $[(UO_2)_2(L^1)(dmf)]$ is monoclinic, space group $P2_1/c$, with $a = 9.285(6)$, $b = 16.187(5)$, $c = 17.544(5)$ Å, $\beta = 104.56(3)°$, and $Z = 4$. In $[UO_2(H_2L^1)]$·dmf the ligand behaves as a quinquedentate dianionic and, using the inner co-ordination chamber, binds equatorially to UO_2^{2+} leading to seven-co-ordinated uranium in a distorted bipyramidal co-ordination geometry. A dmf molecule is hydrogen bonded to the phenolic oxygens of the ligand. Selected bond distances for this compound are U–O(uranyl) 1.79 (mean), U–O(ligand) 2.235 (mean), and U–N (mean) 2.59 Å. In $[(UO_2)_2(L^1)(dmso)]$ and $[(UO_2)_2(L^1)(dmf)]$ the tetra-anionic chelating ligand co-ordinates the inner UO_2^{2+} as in $[UO_2(H_2L^1)]$·dmf, while the outer UO_2^{2+} is co-ordinated by four oxygen atoms of the dinucleating ligand and by the oxygen atom of the solvent molecule. Structural details of the binuclear complexes are comparable. Comparison of the structures in the solid and in solution revealed some conformational differences.

Several homo- and/or hetero-binuclear co-ordination complexes have previously been prepared in order to study the mutual influence of metal ions held in close proximity on the physico-chemical properties of the molecules as a whole.[1–5] It was found that reactivity and catalysis (*i.e.* multielectron redox reactions) are strongly influenced by the presence of a binuclear entity.[6–11] In addition, peculiar optical and magnetic properties have been observed in these systems, which make them good candidates for possible use in materials science.[12–16]

In order to facilitate the synthesis of these compounds, appropriate binucleating ligands have been designed and prepared, often with the aim of template procedures.[4,17,18] Recent reviews have summarized these ligands and the related complexes.[4,5] Several ligands are Schiff bases derived from suitable keto- and amino-precursors. The synthesis of these precursors is sometimes not trivial and very often time consuming. Basically, dinucleating ligands for *d*-transition-metal ions have been synthesized, and many complexes have been prepared and studied by different techniques.[19,20] Of course, the same or very similar ligands have successfully been applied to the preparation of *f*-transition-metal complexes.[17,18,21]

We have extended the series of dinucleating ligands to compounds especially designed for *f*-transition-metal ions, starting from commercially available, possibly not very expensive, precursors. This paper reports the preparation of the potentially heptadentate dinucleating Schiff bases H_4L^1 and H_4L^2, by condensation of 2,3-dihydroxybenzaldehyde with 1,5-

	X
H_4L^1	NH
H_4L^2	S
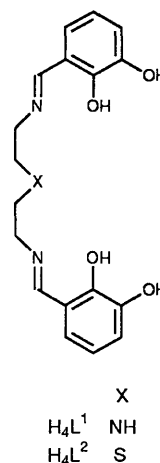
diamino-3-azapentane and 1,5-diamino-3-thiapentane, and the preparation and properties of the corresponding mono-and bi-nuclear uranyl(VI) complexes. The X-ray structures of $[UO_2(H_2L^1)]$·dmf, $[(UO_2)_2(L^1)(dmso)]$, and $[(UO_2)_2(L^1)$-$(dmf)]$ (dmf = dimethylformamide, dmso = dimethyl sulphox-

ide) are also reported; the last two structures represent, to our knowledge, the first crystal structure determinations for binuclear uranyl(VI) species within a compartmental Schiff-base ligand.

Experimental

The keto-precursor 2,3-dihydroxybenzaldehyde and the polyamines 1,5-diamino-3-azapentane and 1,5-diamino-3-thiapentane were commercial products used without further purification.

Synthesis of the Ligands.—2,3-Dihydroxybenzaldehyde (2 mmol, 276 mg) and 1,5-diamino-3-thiapentane (1 mmol, 120 mg) were allowed to react at room temperature for 2 h in methanol. The solution was evaporated to dryness under reduced pressure and the oil obtained after complete removal of water gave, as final product, a yellow-brown precipitate by addition of diethyl ether. It was filtered off, washed with diethyl ether, and dried *in vacuo* (Found: C, 59.55; H, 6.15; N, 7.50. Calc. for $C_{18}H_{20}N_2O_4S$: C, 60.00; H, 5.60; N, 7.75%).

The condensation of 2,3-dihydroxybenzaldehyde (2 mmol, 276 mg) and 1,5-diamino-3-azapentane (1 mmol, 103 mg) produced only a pale yellow oil which was not purified.

Preparation of $[UO_2(H_2L^1)]\cdot H_2O$ *and* $[UO_2(H_2L^2)]\cdot$ $3H_2O$.—2,3-Dihydroxybenzaldehyde (2 mmol, 276 mg) and the appropriate amine precursor [(1,5-diamino-3-azapentane (1 mmol, 103 mg) or 1,5-diamino-3-thiapentane (1 mmol, 120 mg)] were allowed to react at room temperature in methanol (50 cm³). To the yellow-orange solution obtained, [UO₂(CH₃-CO₂)₂]·2H₂O (1 mmol, 424 mg) in methanol (100 cm³) was added. The resulting suspension was refluxed for 3 h. The red-brown precipitate obtained was filtered off, washed with methanol, and dried *in vacuo* (Found: C, 34.45; H, 3.50; N, 6.40. Calc. for $C_{18}H_{19}N_3O_6U\cdot H_2O$: C, 34.35; H, 3.35; N, 6.65. Found: C, 31.50; H, 3.45; N, 4.20. Calc. for $C_{18}H_{18}N_2O_6SU\cdot$ $3H_2O$: C, 31.70; H, 3.55; N, 4.10%).

Crystals of $[UO_2(H_2L^1)]\cdot dmf$, suitable for X-ray investigation, were obtained by dissolving the crude product $[UO_2(H_2L^1)]\cdot H_2O$ in dimethylformamide and maintaining the solution under an atmosphere of diethyl ether for 2 d. The crystals were collected by filtration, washed with methanol and diethyl ether, and dried *in vacuo*. A similar procedure was employed for the preparation of $[UO_2(H_2L^1)]\cdot dmso$ [Found: C, 36.55; H, 3.80; N, 8.45. Calc. for $C_{18}H_{19}N_3O_6U\cdot$

$HCON(CH_3)_2$: C, 36.85; H, 3.80; N, 8.20. Found: C, 35.00; H, 3.60; N, 6.20. Calc. for $C_{18}H_{19}N_3O_6U\cdot(CH_3)_2SO$: C, 34.85; H, 3.65; N, 6.10%].

Preparation of $[(UO_2)_2(L^1)]\cdot CH_3OH$ *and* $[(UO_2)_2(L^2)]\cdot$ $2H_2O$.—2,3-Dihydroxybenzaldehyde (2 mmol, 276 mg) and the appropriate amine precursor [1,5-diamino-3-azapentane (1 mmol, 103 mg) or 1,5-diamino-3-thiapentane (1 mmol, 120 mg)] were allowed to react at room temperature in methanol (50 cm³). The colour of the resulting yellow-orange solution turned to amber on addition of LiOH (4 mmol, 96 mg) under reflux. Subsequent addition of $[UO_2(CH_3CO_2)_2]\cdot 2H_2O$ (2 mmol, 848 mg) in methanol (100 cm³) gave a red-brown precipitate. The suspension was refluxed for 3 h. The solid was collected by filtration, washed with methanol, and dried *in vacuo* (Found: C, 24.95; H, 2.30; N, 4.65. Calc. for $C_{18}H_{17}N_3O_8U_2\cdot$ CH_3OH: C, 25.05; H, 2.30; N, 4.60. Found: C, 23.50; H, 2.25; N, 3.10. Calc. for $C_{18}H_{16}N_2O_8SU_2\cdot 2H_2O$: C, 23.15; H, 2.15; N, 3.00%).

By dissolving $[(UO_2)_2(L^1)]CH_3OH$ in dimethyl sulphoxide and maintaining the solution under an atmosphere of diethyl ether, crystals of $[(UO_2)_2(L^1)(dmso)]$, suitable for X-ray investigation were obtained. They were collected by filtration, washed with methanol and diethyl ether, and dried *in vacuo*. The complex $[(UO_2)_2(L^1)(dmf)]$ was prepared in a similar way [Found: C, 25.70; H, 2.45; N, 4.45. Calc. for $C_{18}H_{17}$-$N_3O_8U_2\cdot(CH_3)_2SO$: C, 25.50; H, 2.45; N, 4.45. Found: C, 26.70; H, 2.35; N, 5.65. Calc. for $C_{18}H_{17}N_3O_8U_2\cdot HCON(CH_3)_2$: C, 26.50; H, 2.55; N, 5.90%].

X-Ray Crystallography.—Crystals of maximum dimensions 0.2 mm were selected. Data collection was on a Philips diffractometer with monochromatized Mo-K_α radiation. Cell dimensions were determined by least-squares refinement of 25 medium-angle settings. Crystal and intensity data for the compounds are reported in Table 1. The crystals are stable under irradiation. Solution of the structures was achieved by Patterson and Fourier methods alternated with cycles of least-squares refinement of the atomic parameters. Hydrogen atoms for the polydentate ligands were introduced in calculated positions and the regular hexagons of carbon atoms were refined as rigid bodies.

Anisotropy was introduced for all non-hydrogen atoms in $[UO_2(H_2L^1)]\cdot dmf$ but only for the non-carbon and non-hydrogen atoms in $[(UO_2)_2(L^1)(dmso)]$ and $[(UO_2)_2(L^1)$-

Table 1. Crystal and intensity data *

Compound	$[UO_2(H_2L^1)]\cdot dmf$	$[(UO_2)_2(L^1)(dmso)]$	$[(UO_2)_2(L^1)(dmf)]$
Formula	$C_{21}H_{25}N_4O_7U$	$C_{20}H_{22}N_3O_9SU_2$	$C_{21}H_{24}N_4O_9U_2$
M	683	956	952
$a/\text{Å}$	21.155(5)	14.985(5)	9.285(6)
$b/\text{Å}$	11.833(8)	16.536(5)	16.187(5)
$c/\text{Å}$	9.679(8)	19.956(5)	17.544(5)
$\beta/°$	102.34(3)	90.13(3)	104.56(3)
$U/\text{Å}^3$	2 367	4 945	2 552
$D_c/\text{g cm}^{-3}$	1.92	2.57	2.48
Z	4	8	4
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$
$\mu(\text{Mo-}K_\alpha)/\text{cm}^{-1}$	6.58	126.3	121.7
Reflections measured	4 659	7 941	4 424
Observed reflections			
$[I > 3\sigma(I)]$	2 994	3 304	2 970
Final conventional			
R factor	0.044	0.054	0.039

* Details in common: system, monoclinic; $\lambda(\text{Mo-}K_\alpha)$ 0.7107 Å; scan method θ—2θ; scan speed 2° min⁻¹; $2 < 2\theta < 50°$; Lorentz polarization correction applied (A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351).

(dmf)] in order to reduce the number of parameters. A fixed thermal parameter of 0.07 Å^2 was assigned to the hydrogen atoms. Refinement of scale factors, positional and thermal parameters proceeded by minimizing the function $\Sigma w(\Delta F)^2$ with $w = 1$. At convergence, the largest parameter shift of the refined parameters of the non-hydrogen atoms was 0.2 times the standard deviation.

No significant residuals of electronic density were observed in the final Fourier difference maps. Form factors for U, corrected for anomalous dispersion,[22] were taken from ref. 23, those for the other atoms being supplied internally by the SHELX program system.[24] Final atomic parameters are listed in Tables 2—4, bond distances and angles in Table 5 for [UO$_2$(H$_2$L^1)]·dmf and in Table 6 for [(UO$_2$)$_2$(L^1)(dmso)]. Selected bond lengths and angles for [(UO$_2$)$_2$(L^1)(dmf)] are reported in Figure 5 to facilitate comparison with the corresponding values found in the dmso analogue (Figure 3).

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

Physico-chemical Measurements.—The i.r. spectra were measured as KBr pellets on a Perkin-Elmer 580B spectrometer. Proton n.m.r. spectra were recorded at 200 MHz on a Bruker AC200 spectrometer at room temperature. Some of the signals were assigned by spin decoupling and two-dimensional techniques. Two dimensional phase sensitive correlation spectroscopy (COSYPH) was performed using standard pulse sequences and microprogrammes from the Bruker manual. Carbon-13 n.m.r. spectra were recorded on a Bruker AM400 instrument at the probe temperature (300 K) with and without ^{1}H (broad band) decoupling. All the samples examined were in the crystalline form and were dissolved in hot (CD$_3$)$_2$SO which was also used as internal reference.

Results and Discussion

Attempts to prepare the free H$_4$L^1 ligand by reaction in methanolic solution of the precursors produced only oils difficult to characterize. On the contrary, as already found with other similar Schiff bases, the substitution of the NH group with a thioether S allows the formation of solid, well characterizable products. Thus, using 1,5-diamino-3-thiapentane as amine precursor, the orange-brown ligand H$_4$L^2 is obtained as a powder which is stable in the solid state over long periods. It is soluble in the common organic solvents.

Mono- and homo-binuclear uranyl(vi) complexes can be conveniently prepared, also by a template procedure, according to the reactions reported in the Scheme. When X = S the rection of the preformed ligand with UO$_2$$^{2+}$ in the appropriate ratio produces the same complexes as those obtained by template techniques. As already found with Schiff-base complexes containing UO$_2$$^{2+}$,[25] the solvent molecule, directly bonded to the outer uranyl(vi) ion in the binuclear complexes, can be substituted by other unidentate oxygen-donor ligands (*i.e.* dimethyl sulphoxide or dimethylformamide).

The crystal structure of [UO$_2$(H$_2$L^1)]·dmf is shown in Figure 1. The uranium atom is seven-co-ordinate in the usual pentagonal bipyramidal co-ordination geometry. The five equatorial donor atoms are approximately coplanar being displaced by a maximum of 0.01 Å from the calculated mean plane. These atoms form a rather irregular pentagon, the O(4)···O(5) bite (3.09 Å) being significanly longer than all O···N and N···N bites (between 2.80 and 2.82 Å). Deviations from the ideal pentagon are even more evident in that the N–U–N angles of the penta-atomic metallacycles are about 66°, the N–U–O angles of the hexa-atomic metallacycles are about 71°, and the O–U–O angle (no cycle) is 87.5°.

Table 2. Atomic co-ordinates for [UO$_2$(H$_2$L^1)]·dmf

Atom	X/a	Y/b	Z/c
U	0.701 32(2)	0.325 58(4)	0.657 42(5)
O(1)	0.669 5(5)	0.461 2(7)	0.596 4(9)
O(2)	0.738 2(5)	0.196 0(7)	0.729 0(10)
O(3)	0.500 3(4)	0.135 3(8)	0.484 9(8)
O(4)	0.600 5(3)	0.259 5(7)	0.631 3(8)
O(5)	0.698 1(3)	0.269 9(7)	0.434 9(8)
O(6)	0.647 6(4)	0.114 1(7)	0.234 4(9)
N(1)	0.664 0(5)	0.345 3(8)	0.895 7(10)
N(2)	0.780 0(4)	0.437 3((8)	0.850 3(9)
N(3)	0.810 0(4)	0.371 5(8)	0.592 4(10)
C(2)	0.471 7(3)	0.081 3(6)	0.700 1(7)
C(3)	0.481 4(3)	0.089 0(6)	0.846 9(7)
C(4)	0.531 7(3)	0.155 3(6)	0.922 4(7)
C(5)	0.572 2(3)	0.213 9(6)	0.851 0(7)
C(6)	0.562 4(3)	0.206 2(6)	0.704 1(7)
C(1)	0.512 2(3)	0.139 9(6)	0.628 7(7)
C(7)	0.620 8(6)	0.287 1(10)	0.936 4(12)
C(8)	0.704 4(6)	0.415 7(13)	1.002 9(13)
C(9)	0.774 0(6)	0.406 2(11)	0.995 7(12)
C(10)	0.849 7(5)	0.431 1(11)	0.832 9(14)
C(11)	0.850 8(6)	0.455 9(11)	0.682 0(13)
C(12)	0.834 4(5)	0.326 7(11)	0.495 0(13)
C(14)	0.842 3(3)	0.196 1(7)	0.303 5(9)
C(15)	0.815 4(3)	0.119 8(7)	0.197 4(9)
C(16)	0.749 6(3)	0.093 6(7)	0.173 8(9)
C(17)	0.710 8(3)	0.143 8(7)	0.256 4(9)
C(18)	0.737 7(3)	0.220 2(7)	0.362 5(9)
C(13)	0.803 5(3)	0.246 3(7)	0.386 1(9)
C(19)	0.435 8(9)	0.371 4(23)	0.222 7(34)
C(20)	0.505 6(11)	0.540 7(17)	0.308 8(35)
N(4)	0.501 3(6)	0.419 2(11)	0.280 4(17)
C(21)	0.553 3(7)	0.354 5(14)	0.304 6(16)
O(7)	0.551 0(4)	0.252 4(9)	0.277 2(10)
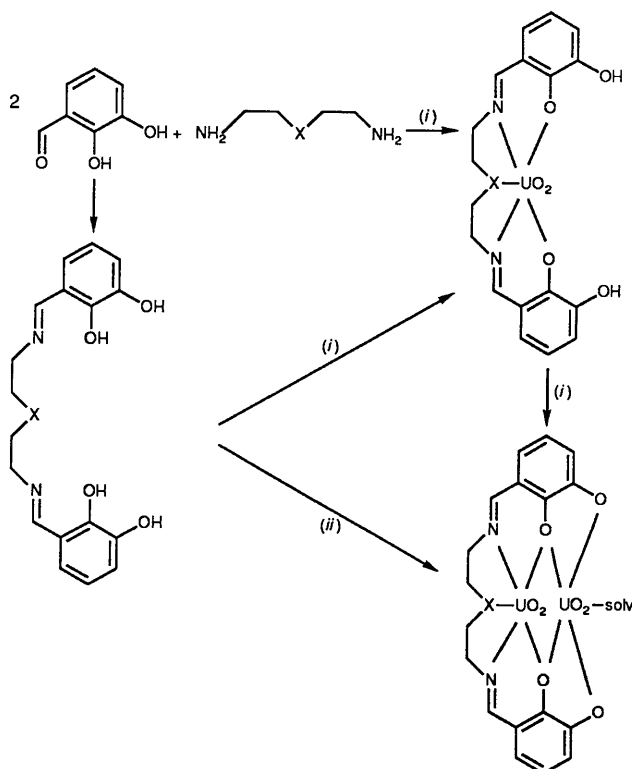
Scheme. solv = Solvent, X = NH or S. (*i*) [UO$_2$(CH$_3$CO$_2$)$_2$]·2H$_2$O; (*ii*) 2[UO$_2$(CH$_3$CO$_2$)$_2$]·2H$_2$O and 4LiOH.

Table 3. Atomic co-ordinates for $[(UO_2)_2(L^1)(dmso)]$

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
U(1)	0.917 04(8)	0.755 62(8)	−0.167 77(6)	U(3)	0.458 45(8)	0.738 23(7)	0.091 96(6)
U(2)	0.991 62(8)	0.785 16(8)	0.018 80(6)	U(4)	0.379 13(11)	0.810 06(8)	0.271 18(7)
S(1)	0.765 7(6)	0.750 2(6)	−0.311 0(4)	S(2)	0.601 1(6)	0.697 0(5)	−0.055 5(4)
O(1)	0.980 5(17)	0.635 9(14)	−0.193 3(10)	O(6)	0.539 7(16)	0.846 8(13)	0.062 8(11)
O(2)	1.002 7(12)	0.694 9(11)	−0.070 0(9)	O(7)	0.462 0(15)	0.849 9(11)	0.180 7(10)
O(3)	0.919 6(13)	0.849 8(12)	−0.068 4(9)	O(8)	0.369 4(13)	0.703 7(11)	0.196 3(10)
O(4)	0.834 6(17)	0.868 5(16)	−0.184 3(13)	O(9)	0.394 5(16)	0.616 5(13)	0.087 9(12)
O(5)	0.855 0(15)	0.731 8(13)	−0.277 0(10)	O(10)	0.512 6(12)	0.696 1(12)	−0.015 8(10)
O(11)	0.820 0(13)	0.710 5(14)	−0.129 9(11)	O(31)	0.361 0(14)	0.779 6(13)	0.052 0(13)
O(12)	1.015 7(15)	0.800 9(14)	−0.199 6(11)	O(32)	0.554 6(14)	0.694 5(13)	0.129 9(10)
O(21)	1.092 1(15)	0.826 6(12)	−0.004 3(11)	O(41)	0.471 2(14)	0.766 3(14)	0.310 2(12)
O(22)	0.894 1(15)	0.746 0(14)	0.051 2(11)	O(42)	0.282 6(18)	0.855 2(16)	0.241 4(13)
N(1)	1.073 2(21)	0.664 7(20)	0.064 2(14)	N(4)	0.437 5(29)	0.947 8(19)	0.301 8(16)
N(2)	1.040 5(20)	0.805 3(17)	0.140 3(14)	N(5)	0.334 1(30)	0.851 1(20)	0.390 1(17)
N(3)	0.945 6(15)	0.922 1(15)	0.066 1(12)	N(6)	0.277 1(20)	0.705 6(17)	0.326 6(13)
C(2)	1.055 7(15)	0.516 6(13)	−0.164 1(8)	C(22)	0.569 7(15)	0.987 0(14)	0.064 5(8)
C(3)	1.100 3(15)	0.468 9(13)	−0.117 1(8)	C(23)	0.569 2(15)	1.059 5(14)	0.100 2(8)
C(4)	1.111 9(15)	0.496 8(13)	−0.051 7(8)	C(24)	0.534 1(15)	1.061 9(14)	0.164 9(8)
C(5)	1.078 7(15)	0.572 5(13)	−0.033 3(8)	C(25)	0.499 6(15)	0.991 8(14)	0.193 8(8)
C(6)	1.034 1(15)	0.620 1(13)	−0.080 3(8)	C(26)	0.500 0(15)	0.919 3(14)	0.158 1(8)
C(1)	1.022 6(15)	0.592 2(13)	−0.145 7(8)	C(21)	0.535 1(15)	0.916 9(14)	0.093 4(8)
C(7)	1.093 8(24)	0.596 3(22)	0.036 1(18)	C(27)	0.472 4(21)	0.999 4(21)	0.263 1(18)
C(8)	1.086 3(20)	0.669 9(25)	0.134 1(22)	C(28)	0.411 6(35)	0.977 8(35)	0.366 0(26)
C(9)	1.111 6(28)	0.751 0(26)	0.159 3(23)	C(29)	0.347 5(29)	0.930 3(27)	0.404 0(24)
C(10)	1.053 1(26)	0.890 0(23)	0.151 5(21)	C(30)	0.260 6(32)	0.811 7(30)	0.408 3(25)
C(11)	0.981 2(25)	0.940 7(23)	0.136 1(19)	C(31)	0.248 8(29)	0.730 2(27)	0.393 3(22)
C(12)	0.886 2(21)	0.970 2(19)	0.045 8(16)	C(32)	0.245 5(24)	0.641 4(22)	0.303 0(18)
C(14)	0.773 1(13)	1.023 1(10)	−0.027 9(8)	C(34)	0.225 3(14)	0.526 7(14)	0.230 9(10)
C(15)	0.725 4(13)	1.027 6(10)	−0.087 9(8)	C(35)	0.239 9(14)	0.482 6(14)	0.172 3(10)
C(16)	0.745 3(13)	0.974 7(10)	−0.140 3(8)	C(36)	0.297 3(14)	0.512 4(14)	0.123 3(10)
C(17)	0.812 8(13)	0.917 3(10)	−0.132 6(8)	C(37)	0.340 3(14)	0.586 4(14)	0.132 8(10)
C(18)	0.860 4(13)	0.912 8(10)	−0.072 6(8)	C(38)	0.325 8(14)	0.630 5(14)	0.191 3(10)
C(13)	0.840 6(13)	0.965 7(10)	−0.020 3(8)	C(33)	0.268 3(14)	0.600 7(14)	0.240 4(10)
C(19)	0.682 2(28)	0.739 2(27)	−0.247 2(22)	C(39)	0.629 7(26)	0.796 8(24)	−0.074 1(20)
C(20)	0.739 2(28)	0.661 9(25)	−0.352 4(21)	C(40)	0.685 7(26)	0.675 9(23)	0.004 5(20)
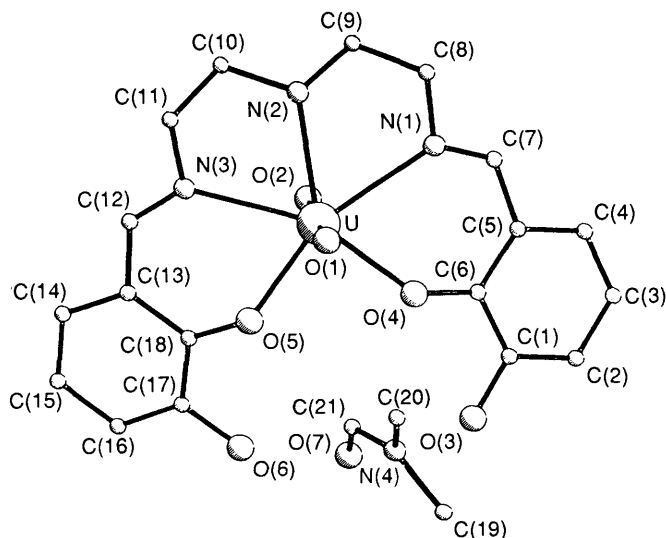
Figure 1. The molecular structure of $[UO_2(H_2L^1)]\cdot dmf$

The U–O (equatorial) bond distances (mean 2.235 Å) with the negatively charged oxygen atoms are very short if compared with the U–N distances (mean 2.59 Å), as expected. Structural details are normal and compare well in the two halves of the ligand. The N=C double bonds are well localized (1.275 Å). As shown in the figures, the dmf molecule makes, through its oxygen atom, two relatively strong hydrogen bonds with the

free terminal OH groups of the ligand, being in some way part of the molecular complex.

The monoclinic cell of the red-brown crystals of $[(UO_2)_2(L^1)(dmso)]$, grown from dimethyl sulphoxide, contains eight molecules of this compound so that two independent formula units (Figure 2) are present in the asymmetric portion of the cell. This is not a rare event and we experienced several examples of this type with other compounds. As the structural details of the molecules are fully comparable, which is a confirmation of their reliability, we will eventually refer to the complex molecules as a single entity (Figure 3).

In this compound two uranyl ions occupy the compartmental sites of the polydentate ligand, the fifth co-ordination position in the equatorial pentagon being supplied, for the 'outer' uranyl ion, by a dmso molecule. It is noteworthy that the presence of two heavy atoms in each molecule severely increases the absorption effects, which, notwithstanding the correction applied, unavoidably influence the accuracy of the diffraction data and, therefore, of the results obtained. For example, even if the discrepancy factor R is low and comparable with that of the above structure, standard deviations estimated for the atomic co-ordinates and, as a consequence, those for bond lengths and angles in the binuclear complex $[(UO_2)_2(L^1)(dmso)]$ are about twice the values found in the mononuclear $[UO_2(H_2L^1)]\cdot dmf$. Despite this, the information obtained, apart from some distances involving light atoms, is realistic and, owing to the favourable circumstance that of two different molecules and that the two halves of each molecule are chemically equivalent, we can consider the structural characteristics of this complex with a high degree of confidence.
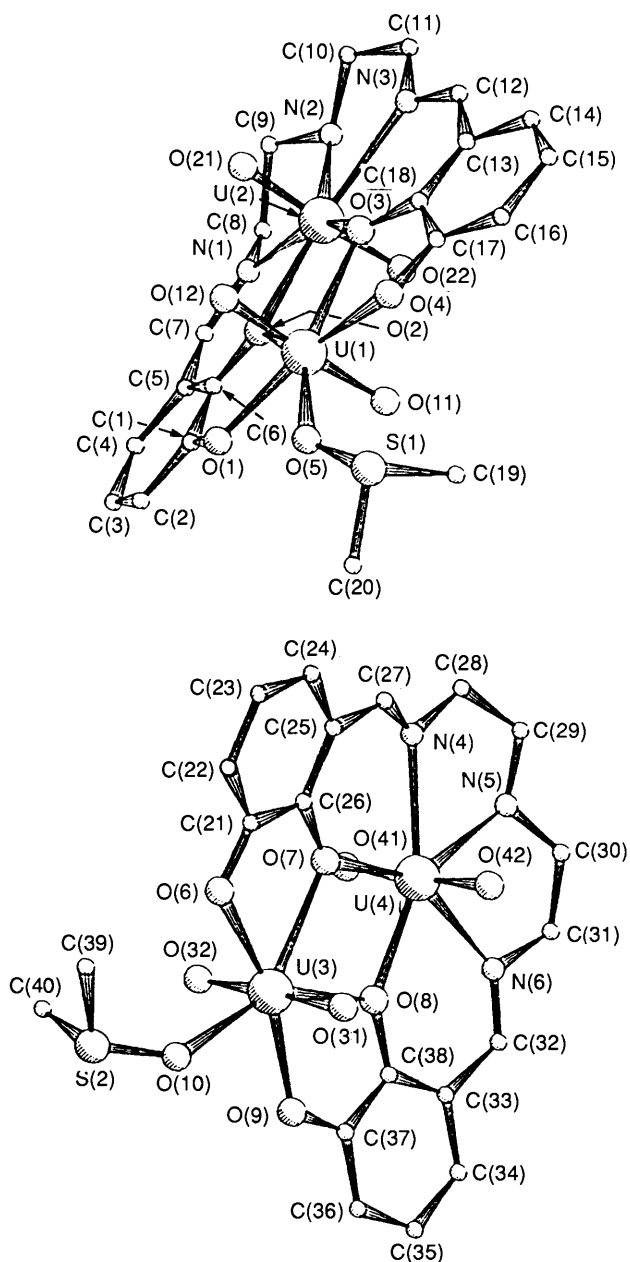
Figure 2. The molecular structure of the two independent units of $[(UO_2)_2(L^1)(dmso)]$

Figure 3. Schematic drawing of the $[(UO_2)_2(L^1)(dmso)]$ molecule. Bond lengths (Å) and angles (°) are the means of the values observed in the two independent molecules which are present in the asymmetric unit of the monoclinic cell

From a general point of view the co-ordination mode of the uranyl ion in the 'inner' $N_3O_2^-$ co-ordination site of the ligand strictly resembles that in the mononuclear complex. However, a first difference lies in the fact that, since the oxygen atoms bridge a second uranyl ion, the O $\cdots$ O bite is significantly shorter (mean 2.82 vs. 3.09 Å) and the O–U–O angle (mean 75.5 vs. 87.5°) is of the same order as the O–U–N angles, which makes the pentagonal girdle more regular. In addition, since the oxygens are shared between two metals, the U–O bond distances are longer, and therefore the U–N ones a little shorter, than found in $[UO_2(H_2L^1)]\cdot dmf$.

The uranyl ion in the 'outer' co-ordination site is directly bonded to five oxygen atoms. Bonding with the terminal negatively charged oxygens is very strong (mean 2.25 Å) and compares well with the values found in $[UO_2(H_2L^1)]\cdot dmf$. A longer distance (2.40 Å) is associated with the bond to the
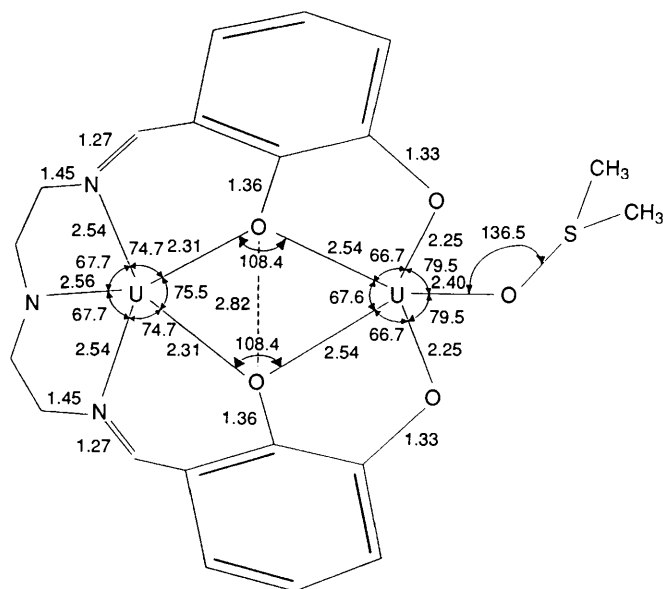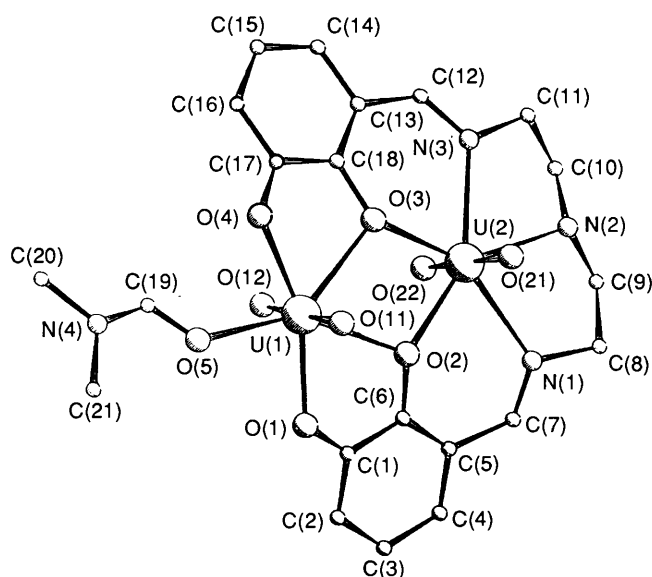
Table 4. Atomic co-ordinates for $[(UO_2)_2(L^1)(dmf)]$

Atom	X/a	Y/b	Z/c
U(1)	0.241 01(7)	0.359 18(3)	0.196 29(3)
U(2)	0.210 75(6)	0.132 67(3)	0.267 56(3)
O(11)	0.067 2(12)	0.356 0(7)	0.122 6(6)
O(12)	0.412 0(11)	0.362 0(8)	0.270 7(7)
O(21)	0.027 9(11)	0.120 2(6)	0.209 4(6)
O(22)	0.394 8(12)	0.136 9(7)	0.327 5(6)
O(1)	0.367 6(13)	0.338 5(6)	0.103 1(6)
O(2)	0.287 2(11)	0.208 0(6)	0.174 0(6)
O(3)	0.155 9(12)	0.266 7(6)	0.292 3(6)
O(4)	0.127 9(13)	0.431 3(6)	0.275 8(6)
O(5)	0.265 7(14)	0.501 3(6)	0.162 9(7)
N(1)	0.308 8(14)	0.028 0(7)	0.186 6(7)
N(2)	0.194 4(16)	−0.013 9(7)	0.317 2(8)
N(3)	0.130 8(13)	0.126 4(7)	0.395 7(7)
C(1)	0.434 9(14)	0.265 9(6)	0.097 1(7)
C(2)	0.540 4(14)	0.260 4(6)	0.053 1(7)
C(3)	0.602 5(14)	0.184 0(6)	0.042 7(7)
C(4)	0.559 0(14)	0.113 2(6)	0.076 5(7)
C(5)	0.453 5(14)	0.118 8(6)	0.120 5(7)
C(6)	0.391 5(14)	0.195 2(6)	0.130 9(7)
C(7)	0.401 3(18)	0.038 7(10)	0.144 2(10)
C(8)	0.269 4(22)	−0.057 4(10)	0.196 4(12)
C(9)	0.291 5(21)	−0.071 7(10)	0.287 3(10)
C(10)	0.223 5(20)	−0.016 4(9)	0.402 9(10)
C(11)	0.119 0(23)	0.042 6(10)	0.427 9(10)
C(12)	0.119 6(16)	0.188 7(10)	0.441 5(8)
C(13)	0.121 8(12)	0.275 7(6)	0.425 7(4)
C(14)	0.104 3(12)	0.325 1(6)	0.488 0(4)
C(15)	0.099 2(12)	0.410 9(6)	0.480 0(4)
C(16)	0.111 6(12)	0.447 3(6)	0.409 9(4)
C(17)	0.129 2(12)	0.397 9(6)	0.347 7(4)
C(18)	0.134 3(13)	0.312 1(6)	0.355 6(4)
N(4)	0.259 5(14)	0.640 2(7)	0.171 3(8)
C(19)	0.260 0(19)	0.566 0(9)	0.200 3(9)
C(20)	0.256 1(20)	0.711 6(9)	0.221 9(12)
C(21)	0.271 0(21)	0.655 0(11)	0.090 3(10)

Table 5. Bond and contact distances (Å) and angles (°)* for [UO$_2$(H$_2$L^1)]·dmf

U–O(1)	1.79(1)		N(1)–C(8)	1.46(2)
U–O(2)	1.79(1)		C(8)–C(9)	1.49(2)
U–O(4)	2.23(1)		C(9)–N(2)	1.49(2)
U–O(5)	2.24(1)		N(2)–C(10)	1.52(2)
U–N(1)	2.60(1)		C(10)–C(11)	1.49(2)
U–N(2)	2.59(1)		C(11)–N(3)	1.47(2)
U–N(3)	2.57(1)		N(3)–C(12)	1.28(2)
O(4)–C(6)	1.34(1)		C(12)–C(13)	1.47(2)
O(5)–C(18)	1.34(1)		O(7)–C(21)	1.24(2)
O(3)–C(1)	1.36(1)		C(21)–N(4)	1.32(2)
O(6)–C(17)	1.35(1)		N(4)–C(19)	1.49(3)
C(5)–C(7)	1.46(1)		N(4)–C(20)	1.46(3)
C(7)–N(1)	1.27(2)			
O(6)···O(7)	2.72(1)		O(5)···N(3)	2.80(1)
O(3)···O(7)	2.83(1)		N(2)···N(1)	2.81(1)
O(4)···O(5)	3.09(1)		N(2)···N(3)	2.81(1)
O(4)···N(1)	2.81(1)			
O(1)–U–O(2)	175.1(4)		C(5)–C(7)–N(1)	128(1)
O(4)–U–O(5)	87.5(3)		C(13)–C(12)–N(3)	128(1)
O(4)–U–N(1)	70.6(3)		C(7)–N(1)–C(8)	116(1)
O(5)–U–N(3)	70.8(3)		C(12)–N(3)–C(11)	116(1)
N(1)–U–N(2)	65.5(3)		N(1)–C(8)–C(9)	111(1)
N(3)–U–N(2)	66.2(3)		N(3)–C(11)–C(10)	108(1)
U–O(4)–C(6)	140.7(6)		C(8)–C(9)–N(2)	108(1)
U–O(5)–C(18)	137.6(6)		C(11)–C(10)–N(2)	108(1)
U–N(1)–C(7)	126.8(8)		C(9)–N(2)–C(10)	112(1)
U–N(3)–C(12)	127.9(9)		N(4)–C(21)–O(7)	122(2)
U–N(1)–C(8)	116.0(8)		C(21)–N(4)–C(19)	121(2)
U–N(3)–C(11)	116.2(7)		C(21)–N(4)–C(20)	121(2)
U–N(2)–C(9)	112.6(7)		C(19)–N(4)–C(20)	117(2)
U–N(2)–C(10)	112.7(7)			

* Estimated standard deviations in parentheses in this and subsequent tables refer to the last significant digit.

Figure 5. Schematic drawing of the [(UO$_2$)$_2$(L^1)(dmf)] molecule. Selected bond lengths (Å) and angles (°) for this compound are reported in order to make easier comparison with the means of the corresponding values found in [(UO$_2$)$_2$(L^1)(dmso)] (see Figure 4). E.s.d.s are 0.01 Å for U–O and U–N bonds and 0.02 Å for the other bonds. Bond angles have been rounded to unity

Figure 4. The molecular structure of [(UO$_2$)$_2$(L^1)(dmf)]

Figure 6. The ^{1}H n.m.r. spectrum in (CD$_3$)$_2$SO of the aliphatic chain contained in [UO$_2$(H$_2$L^1)] (a) and the corresponding simulation spectrum (b)

neutral dmso molecule, and still longer distances (2.54 Å) for the U–O (bridging) bonds, showing that these oxygen atoms are asymmetrically shared between the uranyl ions. The three O–U–O angles with the ligand oxygens of the equatorial pentagon are very similar (mean 67°) and somewhat smaller
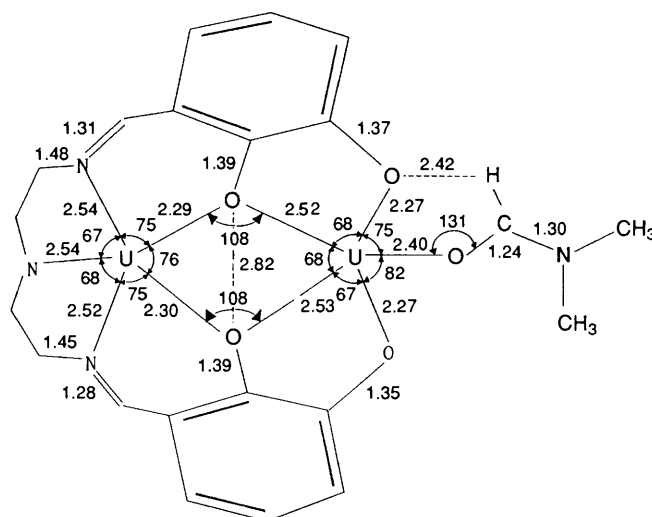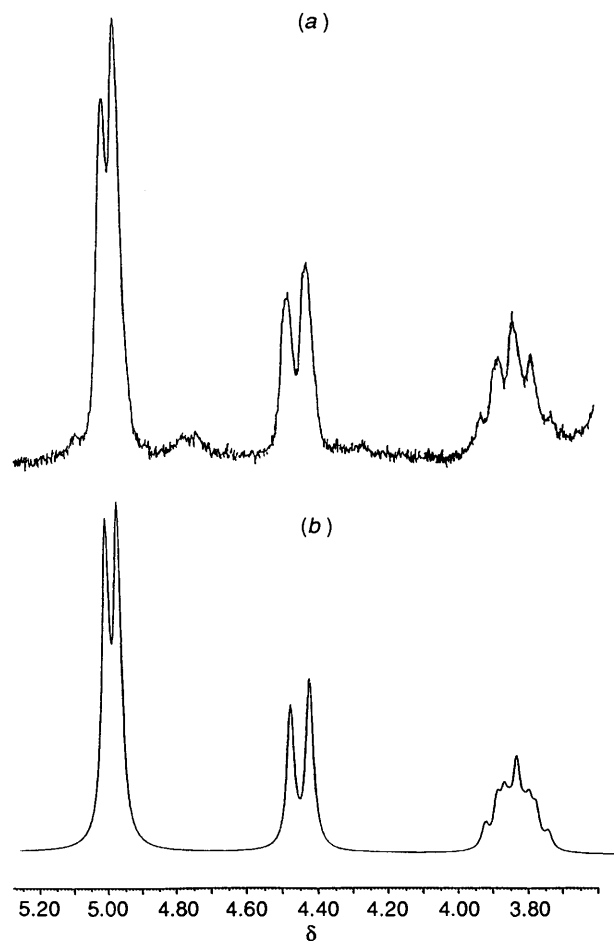
Table 6. Bond and contact distances (Å) and angles (°) for [(UO₂)₂(L¹)(dmso)]

Molecule A		Molecule B		Molecule A		Molecule B	
U(1)–O(11)	1.80(2)	U(3)–O(31)	1.80(2)	C(5)–C(7)	1.46(4)	C(25)–C(27)	1.45(4)
U(1)–O(12)	1.78(2)	U(3)–O(32)	1.78(2)	C(7)–N(1)	1.30(4)	C(27)–N(4)	1.26(4)
U(1)–O(1)	2.25(2)	U(3)–O(6)	2.25(2)	N(1)–C(8)	1.41(5)	N(4)–C(28)	1.43(5)
U(1)–O(2)	2.54(2)	U(3)–O(7)	2.56(2)	C(8)–C(9)	1.48(5)	C(28)–C(29)	1.45(6)
U(1)–O(3)	2.52(2)	U(3)–O(8)	2.54(2)	C(9)–N(2)	1.44(5)	C(29)–N(5)	1.36(5)
U(1)–O(4)	2.26(2)	U(3)–O(9)	2.23(2)	N(2)–C(10)	1.43(4)	N(5)–C(30)	1.33(5)
U(1)–O(5)	2.40(2)	U(3)–O(10)	2.40(2)	C(10)–C(11)	1.48(5)	C(30)–C(31)	1.39(5)
U(2)–O(21)	1.72(2)	U(4)–O(41)	1.74(2)	C(11)–N(3)	1.53(4)	C(31)–N(6)	1.45(5)
U(2)–O(22)	1.73(2)	U(4)–O(42)	1.73(2)	N(3)–C(12)	1.26(4)	N(6)–C(32)	1.25(4)
U(2)–O(3)	2.32(2)	U(4)–O(7)	2.29(2)	C(12)–C(13)	1.49(4)	C(32)–C(33)	1.46(4)
U(2)–O(3)	2.31(2)	U(4)–O(8)	2.31(2)	O(3)–C(18)	1.37(3)	O(8)–C(38)	1.38(3)
U(2)–N(1)	2.51(3)	U(4)–N(4)	2.52(3)	O(4)–C(17)	1.35(3)	O(9)–C(37)	1.31(3)
U(2)–N(2)	2.56(3)	U(4)–N(5)	2.56(3)	S(1)–O(5)	1.53(2)	S(2)–O(10)	1.55(2)
U(2)–N(3)	2.55(3)	U(4)–N(6)	2.56(3)	S(1)–C(19)	1.80(4)	S(2)–C(39)	1.75(4)
O(1)–C(1)	1.35(3)	O(6)–C(21)	1.31(3)	S(1)–C(20)	1.72(4)	S(2)–C(40)	1.78(4)
O(2)–C(6)	1.34(3)	O(7)–C(26)	1.36(3)	U(1)···U(2)	3.915(2)	U(3)···U(4)	3.954(2)

Uranyl groups

O(11)–U(1)–O(12)	176(1)	O(21)–U(2)–O(22)	174(1)	O(31)–U(3)–O(32)	178(1)	O(41)–U(4)–O(42)	173(1)

Equatorial co-ordination

O(1)–U(1)–O(2)	67.3(7)	O(6)–U(3)–O(7)	65.9(7)	O(2)–U(2)–O(3)	75.9(7)	O(7)–U(4)–O(8)	75.1(7)
O(2)–U(1)–O(3)	68.5(6)	O(7)–U(3)–O(8)	66.7(6)	O(2)–U(2)–N(1)	74.3(8)	O(7)–U(4)–N(4)	75.0(9)
O(3)–U(1)–O(4)	67.2(8)	O(8)–U(3)–O(9)	66.5(8)	N(1)–U(2)–N(1)	67.8(9)	N(4)–U(4)–N(5)	68(1)
O(1)–U(1)–O(5)	79.2(8)	O(6)–U(3)–O(10)	79.4(7)	N(2)–U(2)–N(3)	67.0(9)	N(5)–U(4)–N(6)	68(1)
O(4)–U(1)–O(5)	78.0(8)	O(9)–U(3)–O(10)	81.5(8)	N(3)–U(2)–O(3)	75.1(8)	N(6)–U(4)–O(8)	74.3(8)

Ligands

U(1)–O(1)–C	120(1)	U(3)–O(6)–C	124(2)	U(1)–O(3)–U(2)	108.3(8)	U(3)–O(8)–U(4)	109.1(8)
U(1)–O(2)–C	115(1)	U(3)–O(7)–C	113(1)	C(5)–C(7)–N(1)	128(3)	C(25)–C(27)–N(4)	130(3)
U(1)–O(3)–C	114(1)	U(3)–O(8)–C	113(1)	C(7)–N(1)–C(8)	117(4)	C(27)–N(4)–C(28)	116(4)
U(1)–O(4)–C	121(2)	U(3)–O(9)–C	126(2)	N(1)–C(8)–C(9)	115(4)	N(4)–C(28)–C(29)	118(5)
U(1)–O(5)–S	135(1)	U(3)–O(10)–S	138(1)	C(8)–C(9)–N(2)	107(4)	C(28)–C(29)–N(5)	121(4)
U(2)–O(2)–C	137(1)	U(4)–O(7)–C	137(1)	C(9)–N(2)–C(10)	118(3)	C(29)–N(5)–C(30)	123(4)
U(2)–N(1)–C(7)	131(2)	U(4)–N(4)–C(27)	127(3)	N(2)–C(10)–C(11)	117(4)	N(5)–C(30)–C(31)	122(4)
U(2)–N(1)–C(8)	112(2)	U(4)–N(4)–C(28)	116(3)	C(10)–C(11)–N(3)	110(3)	C(30)–C(31)–N(6)	116(4)
U(2)–N(2)–C(9)	112(2)	U(4)–N(5)–C(29)	114(3)	C(11)–N(3)–C(12)	114(3)	C(31)–N(6)–C(32)	118(3)
U(2)–N(2)–C(10)	108(2)	U(4)–N(5)–C(30)	110(3)	N(3)–C(12)–C(13)	125(3)	N(6)–C(32)–C(33)	128(3)
U(2)–N(3)–C(11)	115(2)	U(4)–N(6)–C(31)	113(3)	O(5)–S(1)–C(19)	106(2)	O(10)–S(2)–C(39)	109(2)
U(2)–N(3)–C(12)	129(2)	U(4)–N(6)–C(32)	129(2)	O(5)–S(1)–C(20)	104(2)	O(10)–S(2)–C(40)	105(2)
U(2)–O(3)–C	134(1)	U(4)–O(8)–C	138(2)	C(19)–S(1)–C(20)	95(2)	C(39)–S(2)–C(40)	99(2)
U(1)–O(2)–U(2)	107.2(7)	U(3)–O(7)–U(4)	109.1(7)				

than the corresponding ones involving the dmso oxygen atom (mean 79.5°).

As shown in Figure 4, the crystal and molecular structure of [(UO₂)₂(L¹)(dmf)] strictly resembles that of the dmso adduct. Structural details of this compound (Figure 5) compare well with the corresponding values in [(UO₂)₂(L¹)(dmso)] (Figure 3) confirming that the role of the solvent molecule is essentially that of occupying the fifth equatorial co-ordination site of the outer uranyl group. The only appreciable structural difference between these similar compounds is the presence of a relatively strong intramolecular hydrogen bond between the co-ordinated dmf molecule and one adjacent oxygen atom. This fact causes the formation of a five-membered ring and, as a consequence, an evident asymmetry in the O–U–dmf angles, that internal to the ring being about 5° smaller than the external one.

The homobinuclear complexes are more soluble than the analogous mononuclear complexes in co-ordinating solvents such as dimethyl sulphoxide or dimethylformamide this being probably due to the co-ordination of a solvent molecule to the outer UO_2^{2+}. The i.r. spectra of the mono- and bi-nuclear complexes show several analogies but also remarkable differences. In particular, for the complexes derived from H_4L^1, v_3(O–U–O) shifts toward higher frequencies on going from the mononuclear (879—887 cm⁻¹) to the binuclear complexes (915—917 cm⁻¹) while v(C=N) (1 623—1 627 cm⁻¹) and v(NH) (3 209—3 235 cm⁻¹) are slightly affected by co-ordination of the second metal ion. A broadening is observed in the latter band for some binuclear complexes. The v(C–OH) band is present only for the mononuclear complexes (1 296 cm⁻¹) while v(CO), present at 1 559—1 561 cm⁻¹ as a single strong band for the mononuclear species, shows two strong absorptions at 1 554 and 1 586—1 581 cm⁻¹ for the binuclear complexes. The co-ordination of solvent molecules (*i.e.* dimethyl sulphoxide or dimethylformamide) is shown by the strong bands at 1 645 [v(C=O)] and 995 cm⁻¹ [v(S=O)]; when these molecules are hydrogen bonded to the oxygens of the free compartment of the monuclear complexes the characteristic absorptions due to v(C=O) and v(S=O) shift to 1 668 and 1 015 cm⁻¹ respectively.

The i.r. spectrum of the ligand H_4L^2 shows a strong band due to v(C=N) at 1 655 cm⁻¹. The spectra of the mono- and bi-nuclear uranyl(VI) complexes derived from H_4L^2, are almost comparable: v(C=N) lies at 1 650 and 1 652 cm⁻¹ while

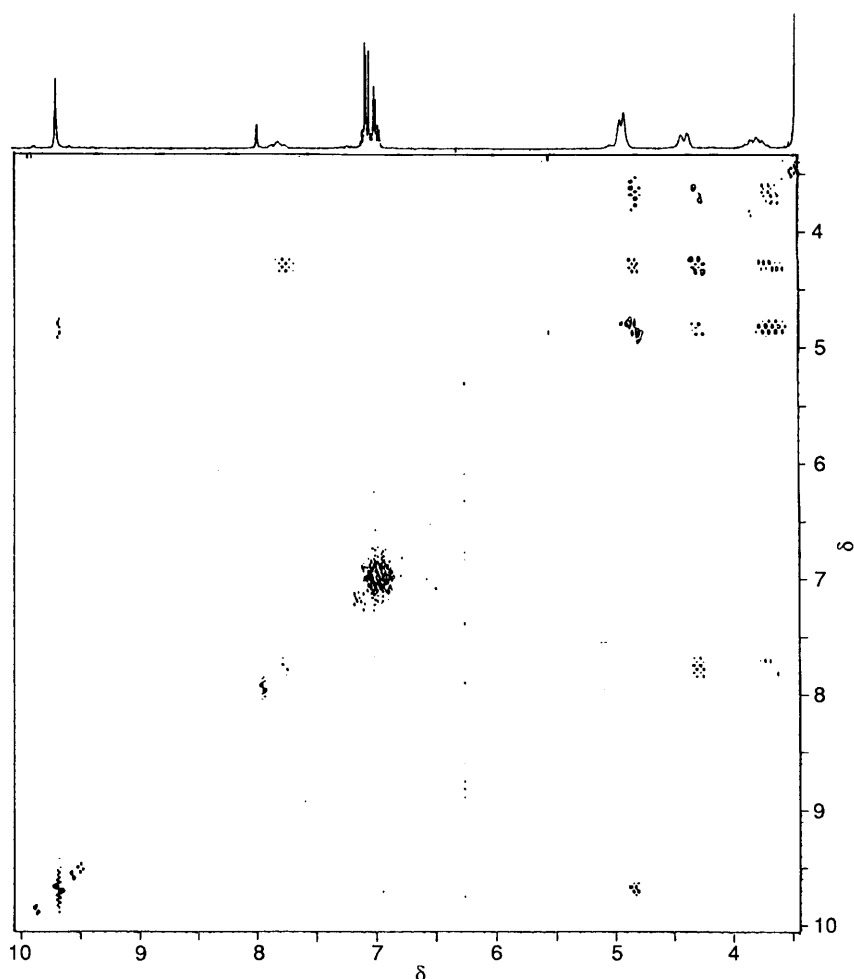Figure 7. The ^{1}H–^{1}H COSYPH spectrum of $[(UO_2)_2(L^1)]$ in $(CD_3)_2SO$

$v_3(O–U–O)$ occurs at 910 and 905 cm^{-1} respectively. In the spectra of both samples a new band at about 1 590 cm^{-1} is attributable to $v(C–O)$.
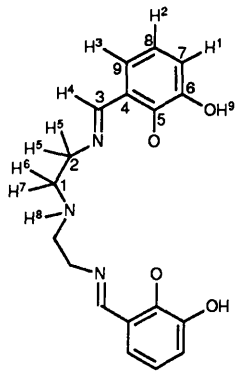
Also the ^{1}H and ^{13}C n.m.r. spectra show differences between mono- and bi-nuclear species. As shown in Table 7 the ^{1}H aromatic peaks are clearly affected by the co-ordination of the second uranyl(vi) group. The peak at δ 8.92, attributed to the free OH proton in the mononuclear complex, disappears for the binuclear one. In addition, the co-ordination of these phenolic oxygens to the second UO_2^{2+} ion produces a deshielding of the protons H^2 with a consequent shift of these peaks from δ 6.54 (mononuclear complex) to 6.95 (binuclear complex). The chemical shifts and the coupling constants of the aliphatic chain of both mono- and bi-nuclear complexes are indicative of the co-ordination behaviour of the ligand, substantially different from that found in the solid. There are two doublets at δ 4.61 and 4.15 with integrals respectively 4 and 2 and one multiplet at 3.42 with integral 2. The methylenic protons H^7 and H^6 at 3.42 and 4.15 are geminal and show a different coupling behaviour with the vicinal H^5 and H^8. As the coupling constant between the vicinal protons depends on the dihedral angle between them ('Karplus–Conroy curve') the small coupling constant (J) between H^6–H^5 and H^6–H^8 suggests the two ethylenic chains are arranged in the same way with respect to the uranyl atom whereas in the solid state they adopt the different conformations reported in the Figures. Simulation spectra fit very

well the experimental data (Figure 6) confirming the structure proposed in solution.

The ^{1}H–^{1}H COSYPH[26] of $[(UO_2)_2(L^1)(dmf)]$ (Figure 7) confirmed the previous assignments and evidenced some long-range correlation between protons H^4 and H^5 not previously found with the normal decoupling experiments.

Co-ordination of the second uranyl causes considerable variations also in the ^{13}C n.m.r. spectra (Table 8): bonding of the outer oxygens substantially deshields the C^6 atoms with the consequent shift of their peaks from 148.3 (mononuclear complex) to 159.7 p.p.m. (binuclear complex). In agreement with the ^{1}H n.m.r. spectra, the peaks due to the C^8 atoms, meta to C^6, shift from 117.8 to 123.09 p.p.m. on going from the mono- to the bi-nuclear complex. A mesomeric effect, induced by co-ordination of the second cation, is evidenced by the shift of about 6 p.p.m. towards higher δ values for the C^5 atom.

It was found that, with similar compartmental ligands, the uranyl(vi) ion co-ordinates in the outer O_2O_2 site.[27,28] It must be noted, however, that in these ligands, the inner co-ordination sphere is too small to accommodate the large UO_2^{2+} ion. Sometimes a change in the co-ordination chamber was found, depending on the solvent used. In the mononuclear complexes with H_2L^1 and H_2L^2, UO_2^{2+} prefers the inner N_2XO_2 co-ordination chamber and this does not change when the complexes are dissolved in hot co-ordinating solvents (i.e. dimethylformamide or dimethyl sulphoxide).

Table 7. Proton n.m.r. data for the compounds examined

	[(UO$_2$)(H$_2$L^1)]					[(UO$_2$)$_2$(L^1)]				
	δ	Multiplicity	Intensity	J(Hz)		δ	Multiplicity	Intensity	J(Hz)	
H^1	7.07	q	2	8.5	H^1–H^2	7.05	q	2	6.9	H^1–H^2
				1.7	H^1–H^3				2.9	H^1–H^3
H^2	6.54	t	2	7.7	H^2–H^3	6.95	t	2	7.7	H^2–H^3
H^3	7.03	q	2			6.93	q	2		
H^4	9.52	s	2			9.69	s	2		
H^5	4.61	d	4	8	H^5–H^7	4.84	d	4	8	H^5–H^7
				<1	H^5–H^4				<1	H^5–H^4
H^6	4.15	d	2	11.2	H^6–H^7	4.29	d	2	11.2	H^6–H^7
				<2	H^6–H^5				<2	H^6–H^5
H^7	3.42	m	2	11	H^7–H^8	3.68	m	2	11	H^7–H^8
H^8	6.86	t	1			7.77	t	1		
H^9	8.92	s	1							
H^{10}						2.53	s	6		

Table 8. ^{13}C N.m.r. data for the compounds examined

	[(UO$_2$)(H$_2$L^1)]			[(UO$_2$)$_2$(L^1)]		
	δ/ p.p.m.	Multi- plicity	J(^{1}H–^{13}C) (Hz)	δ/ p.p.m.	Multi- plicity	J(^{1}H–^{13}C) (Hz)
C^1	52.66	t	130	52.22	t	132
C^2	63.15	t	130	63.28	t	132
C^3	169.05	d	165	172.71	d	165
C^4	122.23	s		122.4	s	
C^5	156.96	s		162.98	s	
C^6	148.35	s		159.74	s	
C^7	123.99	d	162	123.76	d	160
C^8	117.82	d	162	123.09	d	160
C^9	116.69	d	162	119.28	d	160
C^{10}				30.64	q	123

Acknowledgements

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