Mononuclear and polynuclear complexes containing f ions

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Abstract

Dinuclear and tetranuclear uranyl(VI) complexes ($(UO_2)_2(L_A)\cdot 2H_2O$ and $(UO_2)_4(L_B)\cdot nS$, $n=2$; $S = H_2O$, dmf, dmso), where H_4L_A and H_8L_B are the Schiff bases obtained by condensation of 1,4-bis-[bis(2-aminoethyl)aminomethyl]benzene with salicylaldehyde or 2,3-dihydroxybenzaldehyde, respectively, have been prepared by template procedure or by reaction of the preformed ligands with uranyl(VI) salts. The ligands and the complexes have been characterized by physicochemical data, particularly by IR and NMR spectroscopy. Their properties have been compared with those of the similar mono-, homo- and heterodinuclear complexes containing uranyl(VI) and/or lanthanide(III) ions with the potentially heptadentate compartmental Schiff bases H_4L_C and H_4L_D, derived by condensation of 2,3-dihydroxybenzaldehyde with 1,5-diamino-3-azapentane and 1,5-diamino-3-thiapentane, respectively. The X-ray structure of the dinuclear uranyl complex $(UO_2)_2(L_A)\cdot dmso\cdot C_6H_6$ has been determined by X-ray diffractometry and compared with that of $UO_2(H_2L_C)\cdot dmf$, $(UO_2)_2(L_C)(dmf)$ and $(UO_2)_2(L_C)(dmso)$. The crystals of $(UO_2)_2(L_A)\cdot dmso\cdot C_6H_6$ grown from a dmso/C_6H_6 solution are triclinic, space group $P\bar{1}$ with $a = 13.459(4)$, $b = 13.179(3)$, $c = 11.418(4)$ Å, $\alpha = 75.80(4)$, $\beta = 108.30(4)$m $\gamma = 116.77(5)°$, $U = 1704(1)$ Å^3, $D_c = 1.38$ g cm^{-3} for $Z = 1$. The asymmetric unit is half of the molecule, this being centrosymmetric. The structure was refined to the final R of 4.9%. The compound forms a centro-symmetric binuclear complex as the benzene ring, bridging the two macroacyclic coordination moieties, is centered on inversion point $\frac{1}{2}, 0, \frac{1}{2}$. The uranium atom is in the usual, slightly distorted, bipyramidal pentagonal configuration; the quasi linear (175°) uranyl UO_2^{2+} ion is equatorially coordinated by the O_2N_3 donor set of the Schiff base ligand forming an irregular puckered pentagon. Selected bond distances for this compound are: U–O (uranyl) 1.77 (mean), U–O (ligand) 2.22 (mean) and U–N 2.61 Å (mean). The two uranium atoms displace 1.20 Å above and below the central benzene ring plane and are 12.686(1) Å apart (the shortest intermolecular U···U distance is 6.954(1) Å. One dmso and one benzene molecule are present, as clathrate solvents, in disordered positions and do not present any type of interaction with the remaining cell content.

Introduction

In recent years, binucleating macrocyclic and/or macroacyclic compounds have been extensively studied since these structural units are thought to be involved in a variety of biochemical and industrial processes [1–4].

The organization provided by an appropriately designed binucleating ligand may confer unusual structural features and/or magnetic, optical catalytic, etc. properties [4–11].

It was verified that the presence of bridging groups within the macrocyclic or macroacyclic coordination moiety promotes the binding of several metal ions, as well as mediating magnetic and electronic interaction between them [12–16]. Thus macrocyclic and macroacyclic ligands have also been used for the generation of compounds with specific spectroscopic and magnetic properties. It was found that complexes containing magnetic metal centres, at a suitable distance (3–6 Å), exhibit magnetic properties which are not simply the sum of those of the individual ions surrounded by their nearest neighbour ligands. These properties result from both the nature and the magnitude of the interactions between the metal ions within the molecular unit. Using compartmental ligands, binuclear complexes can be synthesized where the two metal centres, if paramagnetic, can interact with each other through the endogenous and/or the exogenous bridges in a ferromagnetic or antiferromagnetic way. By changing the type of the ligand, i.e. the distance between the two cages and/or the paramagnetic centres, it is possible to vary considerably the magnetic interaction and with particular

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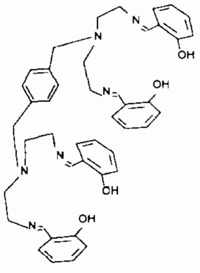
complexes, ferromagnetic interactions have been observed [8, 9].

Complexes in which a single ligand organizes more than two metal centres into some predetermined arrangement may similarly show unique behaviour.

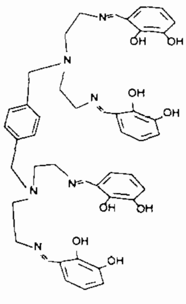
The interaction of O_2 with mono and dinuclear complexes has been extensively studied [2, 5, 17]. Most recently the attention has been devoted also to tri- or tetranuclear clusters owing to the possible multielectron reduction or oxidation of substrates [12–16, 18–25].

The relatively accessible arrangement of four metal centres provided by an appropriate ligand may enable substrates to be brought under the influence (not necessarily entirely by direct coordinate bonds) of two or three or even all four metals simultaneously; only a modest $2e^-$ change per metals is required for the transfer of up to $8e^-$ either to or from the substrate. Thus for example, the interaction of appropriate complexes with substrates such as O_2 and N_2, which are of considerable chemical, biological and industrial importance, could prove interesting and possibly useful.

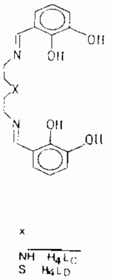
As a part of a long term programme devoted to the synthesis and characterization of polynuclear coordination complexes we have prepared the ligands H_4L_A and H_8L_B, the related f-containing complexes and compared the results with those obtained with the related binucleating ligand H_4L_C and H_4L_D.



H_4L_A



H_8L_B



In addition the X-ray structure of the dinuclear uranyl(VI) complex $(UO_2)_2(L_A)\cdot dmso\cdot C_6H_6$ has been determined.

Experimental

Materials

2,3-Dihydroxybenzaldehyde, 1,5-diamino-3-azapentane and 1,5-diamino-3-thiapentane are commercial products (Aldrich) and were used without further purification. The ligands H_4L_C, H_4L_D and the related mono- and dinuclear uranyl(VI) complexes $UO_2(H_2L_C)\cdot(S)$; $UO_2(H_2L_D)\cdot(S)$; $(UO_2)_2(L_C)\cdot(S)$ and $(UO_2)_2(L_D)\cdot(S)$ (S = coordination solvent molecule H_2O, dmf, dmso) were prepared according to a literature procedure [26]. 1,4-Bis[bis(2-aminoethyl)aminomethyl]benzene was prepared following, with minor modifications, a method already reported in the literature for very similar polyamines [27, 28].

Synthesis to the ligand H_4L_A

To an ethanolic solution of 1,4-bis[bis(2-aminoethyl)aminomethyl]benzene·6HCl (1 mmol, 550 mg) salicylaldehyde (4 mmol, 488 mg) and NaOH (6 mmol, 239 mg) were added. The resulting yellow solution was refluxed for $\frac{1}{2}$ h, reduced in volume and then resolubilized in CH_2Cl_2. The white powder precipitated was filtered off and the yellow dichloromethane solution used without other treatments.

Synthesis of the ligand H_8L_B

To a hot ethanolic solution of 1,4-bis[bis(2-aminoethyl)aminomethyl]benzene·6HCl (1 mmol, 550 mg), NaOH (6 mmol, 239 mg) and 2,3-dihydroxybenzaldehyde (4 mmol, 560 mg) were added. The resulting yellow solution was refluxed for 1 h. The solution was evaporated to dryness under reduced pressure and, by addition of CH_2Cl_2 a light brown powder precipitated. It was filtered, washed with CH_2Cl_2 and dried *in vacuum*.

Anal. Found: C, 63.98; H, 5.98; N, 10.30. Calc. for $C_{44}H_{46}O_8N_6Na_2$: C, 63.46; H, 5.57; N, 10.09%.

By gentle acidification the free ligand H_8L_B was obtained.

Found: C, 66.78; H, 6.03; N, 10.90. Calc. for $C_{44}H_{48}O_8N_6$: C, 66.996; H, 6.13; N, 10.65%.

Preparation of $(UO_2)_2(L_A)\cdot 2H_2O$

H_4L_A (1 mmol, 700 mg), $UO_2(NO_3)_2\cdot 6H_2O$ (2 mmol, 1004 mg) and NaOH (4 mmol, 159 mg) were reacted at room temperature in 100 ml of CH_2Cl_2. The resulting suspension was refluxed for 1 h. The orange precipitate obtained was filtered, washed with methanol and dried *in vacuum*,

Anal. Found: C, 39.95; H, 3.23; N, 6.87. Calc. for $C_{44}H_{48}O_{10}N_6U_2$: C, 40.75; H, 3.73; N, 6.48%.

Preparation of $(UO_2)_2(L_A)\cdot dmso\cdot C_6H_6$

By dissolving $(UO_2)_2(L_A)\cdot 2H_2O$ in dmso and benzene (5:1), crystals of $(UO_2)_2(L_A)\cdot dmso\cdot C_6H_6$ suitable for X-ray investigation were obtained. They were collected by filtration, washed with diethyl ether and dried *in vacuum*.

Anal. Found: C, 44.15; H, 3.66; N, 6.06. Calc. for $C_{52}H_{56}O_9N_6SU_2$: C, 44.07; H, 3.98; N, 5.93%.

	Calc			Found		
	C	H	N	C	H	N
$UO_2La(L_C)OH{\cdot}1H_2O$	27.60	2.57	5.36	27.52	2.79	5.73
$UO_2Tb(L_C)OH{\cdot}1H_2O$	28.03	2.61	5.45	27.96	2.76	5.69
$UO_2Eu(L_C)OH{\cdot}1H_2O$	26.55	2.72	5.16	26.28	2.59	5.40
$UO_2Gd(L_C)OH{\cdot}2H_2O$	26.97	2.51	5.24	26.99	2.73	5.62
$UO_2La(L_D)OH{\cdot}1H_2O$	27.01	2.39	5.30	26.84	2.58	5.32

Preparation of $(UO_2)_4(L_B){\cdot}2H_2O{\cdot}2dmf$

To a hot MeOH/dmf (1/1) (100 ml) solution of H_8L_B (1 mmol, 788 mg), NaOH (8 mmol, 318 mg) and $UO_2(CH_3COO)_2{\cdot}2H_2O$ (4 mmol, 1696 mg) were added in order. The resulting suspension was refluxed for 1 h. The orange precipitate obtained was fitered, washed with methanol and dried *in vacuum.*

Anal. Found: C, 29.03; H, 2.77; N, 5.20. Calc. for $C_{44}H_{40}O_{16}N_6U_4{\cdot}2H_2O{\cdot}2dmf$; C, 29.03; H, 2.93; N, 5.44%.

Preparation of $UO_2Ln(L_C)OH{\cdot}nH_2O$ *(Ln = La, Eu, Tb, Gd)*

To a methanolic solution (100 ml) containing the appropriate mononuclear lanthanide complex $Ln(H_4L_C)(NO_3)_3$ (0.5 mmol), freshly prepared as reported elsewhere [29], LiOH (48 mg, 2 mmol) and $UO_2(CH_3COO)_2{\cdot}2H_2O$ (0.5 mmol, 212 mg) were added in order.

The orange solution turned to red–brown and after few minutes a brown precipitate was formed; the suspension was refluxed for 3 h, then the precipitate was filtered, washed with methanol and dried *in vacuum.*

Preparation of $UO_2La(L_D)OH{\cdot}H_2O$

The same procedure used in the synthesis of the complex of the type $UO_2Ln(L_C)OH{\cdot}nH_2O$ was carried out. 1,5-Diamino-3-thiapentane was used instead of 1,5-diamino-3-azapentane.

X-ray crystallography

Well formed crystals, stable in air, of max. dimension 0.2 mm, were chosen for the X-ray work. Lattice parameters were refined by least-squares from 25 reflections with $7 < \theta < 13°$.

Crystal data. $[(UO_2)_2(L_A)]{\cdot}dmso{\cdot}C_6H_6$, $C_{52}H_{56}N_6O_9SU_2$, $M = 1417.2$, triclinic, space group $P\bar{1}$, $a = 13.459(4)$, $b = 13.179(3)$, $c = 11.418(4)$ Å, $\alpha = 75.80(4)$, $\beta = 108.30(4)$, $\gamma = 116.77(5)°$, $U = 1704(1)$ Å^3, $D_c = 1.38$ g cm^{-3} for $Z = 1$ (the asymmetric unit is half of the molecule, this being centrosymmetric), μ (Mo Kα) $= 45.7$ cm^{-1}, $F(000) = 682$.

Intensities were measured by a $\theta/2\theta$ scan on a four-circle Philips PW1100 diffractometer with a scan rate of 2° min^{-1} up to $\theta_{max} = 25°$, using graphite-monochromatized Mo Kα radiation ($\lambda = 0.7107$ Å). The crystal is stable under irradiation. A total of 5812 reflections was recorded of which 3722 were 'observed' ($I > 3\sigma(I)$). The intensities were corrected for Lorentz polarization and for absorption [30] with max. and min. transmission coefficients of 0.96 and 0.85.

The structure was solved by the heavy-atom method and refined by full-matrix least-squares to the final conventional R factor of 0.049, when the maximum shift in the refined parameters was 0.2σ. The two phenyl groups (C1–C6 and C13–C18) were refined as rigid bodies (C–C 1.395, C–H 1.08 Å), with fixed isotropic thermal parameters for H atoms ($U_{iso} = 0.07$ Å^2). All non-hydrogen atoms apart from those in the solvent molecules were refined anisotropically. Hydrogen atoms were introduced in calculated positions.

The function minimized during the least-squares refinement was $\Sigma w(\Delta F)^2$. Unit weights were applied since these gave acceptable agreement analyses.

Scattering factors for U were from [31] and corrected for anomalous dispersion ($\Delta f' = -10.67$ and $\Delta f'' = 9.65$); those for the other atoms were supplied internally by SHELX [32].

A different Fourier synthesis showed the presence of a disordered benzene molecule statistically distributed in two different positions twisted of about 30° round the ring centroid; it was refined as a rigid body with an occupancy factor of 0.5. A disordered molecule of dmso is also present as clathrate solvent and was introduced in two statistical positions with a population parameter of 0.5.

Final atomic parameters are listed in Table 1, selected bond distances and angles in Tables 2 and 3, respectively.

Physicochemical measurements

IR spectra were measured as KBr pellets with a Perkin-Elmer 580B model spectrophotometer.

^{1}H NMR spectra were recorded at 200.132 MHz on a Bruker AC200 spectrometer equipped with an Aspect 3000 computer at room

Table 1. Fractional coordinates with isotropic or equivalent isotropic thermal parameters[a]

Atom	x	y	z	$U_{\mathrm{iso/eq}}$[c] (Å^2)
U(1)	0.19989(5)	0.25288(5)	0.12066(5)	0.0403(2)
O(1)	0.3314(8)	0.3112(8)	0.0763(8)	0.054(5)
O(2)	0.0734(9)	0.1864(9)	0.1742(9)	0.062(5)
O(3)	0.2015(10)	0.4251(9)	0.0918(8)	0.072(6)
O(4)	0.0989(9)	0.2400(8)	0.0764(8)	0.065(5)
N(1)	0.2905(9)	0.3398(10)	0.3313(9)	0.046(6)
N(2)	0.2805(9)	0.1205(8)	0.3021(9)	0.040(5)
N(3)	0.1641(9)	0.0611(9)	0.0560(9)	0.045(5)
C(2)	0.1537(9)	0.5788(8)	0.0733(6)	0.063(8)
C(3)	0.1546(9)	0.6639(8)	0.1267(6)	0.08(1)
C(4)	0.2031(9)	0.6727(8)	0.2532(6)	0.07(1)
C(5)	0.2505(9)	0.5965(8)	0.3262(6)	0.064(9)
C(6)	0.2496(9)	0.5114(8)	0.2728(6)	0.048(6)
C(1)	0.2011(9)	0.5026(8)	0.1464(6)	0.053(7)
C(7)	0.2924(12)	0.4287(12)	0.3547(12)	0.050(7)
C(8)	0.3391(13)	0.2720(12)	0.4340(12)	0.056(8)
C(9)	0.2745(12)	0.1474(13)	0.4200(11)	0.053(8)
C(10)	0.1957(11)	0.0005(10)	0.2800(12)	0.049(6)
C(11)	0.1855(11)	−0.0279(10)	0.1552(11)	0.046(6)
C(12)	0.1429(11)	0.0400(11)	−0.0552(12)	0.045(7)
C(14)	0.1104(8)	0.0750(8)	−0.2799(9)	0.064(9)
C(15)	0.0808(8)	0.1344(8)	−0.3949(9)	0.07(1)
C(16)	0.0590(8)	0.2297(8)	−0.4008(9)	0.08(1)
C(17)	0.0668(8)	0.2656(8)	−0.2918(9)	0.066(8)
C(18)	0.0965(8)	0.2061(8)	−0.1768(9)	0.054(7)
C(13)	0.1183(8)	0.1108(8)	−0.1708(9)	0.047(7)
C(19)	0.3993(10)	0.1409(11)	0.3021(11)	0.042(6)
C(20)	0.4517(10)	0.0652(11)	0.4054(10)	0.041(6)
C(21)	0.5151(11)	0.1042(11)	0.5220(12)	0.046(6)
C(22)	0.4389(11)	−0.0383(11)	0.3870(11)	0.047(7)
# S(1)*[b]	0.6549(5)	0.5048(5)	0.2862(5)	0.043(3)
# O(5)*	0.5930(12)	0.4115(12)	0.3757(12)	0.029(3)
# C(23)*	0.6366(23)	0.4388(23)	0.1583(25)	0.051(7)
# C(24)*	0.5594(26)	0.5717(26)	0.2095(28)	0.060(8)
# S(1)A*	0.4476(7)	0.1525(6)	−0.0417(7)	0.052(4)
# O(5)A*	0.3927(17)	0.0366(17)	0.0236(18)	0.066(5)
# C(23)A*	0.4502(32)	0.1265(32)	−0.1875(35)	0.09(1)
# C(24)A*	0.5939(35)	0.2004(34)	0.0234(37)	0.09(1)
# C(25)*	0.0570(20)	0.6172(31)	0.7020(35)	0.066(9)
# C(26)*	0.0930(20)	0.7219(31)	0.7441(35)	0.065(9)
# C(27)*	0.1846(20)	0.8173(31)	0.7073(35)	0.11(2)
# C(28)*	0.2401(20)	0.8080(31)	0.6284(35)	0.08(1)
# C(29)*	0.2042(20)	0.7033(31)	0.5863(35)	0.07(1)
# C(30)*	0.1126(20)	0.6079(31)	0.6231(35)	0.09(1)
# C(25)A	0.1410(39)	0.7831(32)	0.7231(31)	0.07(1)
# C(26)A*	0.199(39)	0.8175(32)	0.6509(31)	0.11(2)
# C(27)A*	0.2188(39)	0.7386(32)	0.5879(31)	0.08(2)
# C(28)A*	0.1389(39)	0.6253(32)	0.5972(31)	0.08(1)
# C(29)A*	0.0601(39)	0.5908(32)	0.6695(31)	0.07(1)
# C(30)A*	0.0611(39)	0.6697(32)	0.7324(31)	0.054(8)

[a] e.s.d.s. in parentheses in this and subsequent tables refer to the last significant digit. [b] Isotropic thermal parameters are denoted by*. Atoms introduced with occupancy factor 0.5 are denoted by #. [c] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

temperature. Some of the signals were assigned by the spin decoupling technique. All the samples examined were in the crystalline form and were dissolved in hot dmso-d_6 that was used also as internal reference.

The homogeneity of the heterodinuclear samples was checked with a Philips SEM 505 model scanning electron microscope equipped with an EDAX model data station. Metal ratios were determined by an integral counting of back scattered X-ray fluorescence radiation [33].

All mass spectrometric measurements were performed on a VG ZAB 2F instrument (VG analytical Ltd.) operating in electron impact (EI) (70 eV, 200 mA, ion source temperature 200 °C) and fast atom bombardment (FAB) (8 KeV Xe atom bombarding a thioglycerol/acetic solution of the sample) conditions [34].

TABLE 2. Selected bond distances (Å)

Coordination			
U(1)-O(1)	1.77(1)	U(1)-O(2)	1.76(1)
U(1)-O(3)	2.20(1)	U(1)-O(4)	2.235(8)
U(1)-N(1)	2.61(1)	U(1)-N(2)	2.65(1)
U(1)-N(2)	2.60(1)		
Ligand			
O(3)-C(1)	1.32(2)	O(4)-C(18)	1.31(2)
N(1)-C(7)	1.25(2)	N(3)-C(12)	1.28(2)
N(1)-C(8)	1.46(2)	N(3)-C(11)	1.48(2)
N(2)-C(9)	1.50(2)	N(2)-C(10)	1.50(1)
N(2)-C(19)	1.50(2)	C(19)-C(20)	1.55(2)
C(20)-C(21)	1.41(2)	C(20)-C(22)	1.36(2)
C(21)-C(22^1)	1.36(2)	C(6)-C(7)	1.46(2)
C(12)-C(13)	1.46(2)	C(8)-C(9)	1.50(2)
C(10)-C(11)	1.51(2)		
Clathrate dmso			
S(1)-O(5)	1.50(1)	S(1)A-O(5)A	1.49(2)
S(1)-C(23)	1.78(3)	S(1)A-C(23)A	1.79(5)
S(1)-C(24)	1.77(4)	S(1)A-C(24)A	1.74(4)
Contact distances			
U(1)···U(1^1)	12.686(1)	U(1)···U(1^2)	6.954(1)
O(3)···O(4)	3.04(1)	N(1)···N(2)	2.93(2)
O(3)···N(1)	2.80(1)	N(2)···N(3)	2.86(1)
O(4)···N(3)	2.81(2)		

Symmetry codes: $^1 1-x, -y, 1-z$; $^2 -x, -y, -z$.

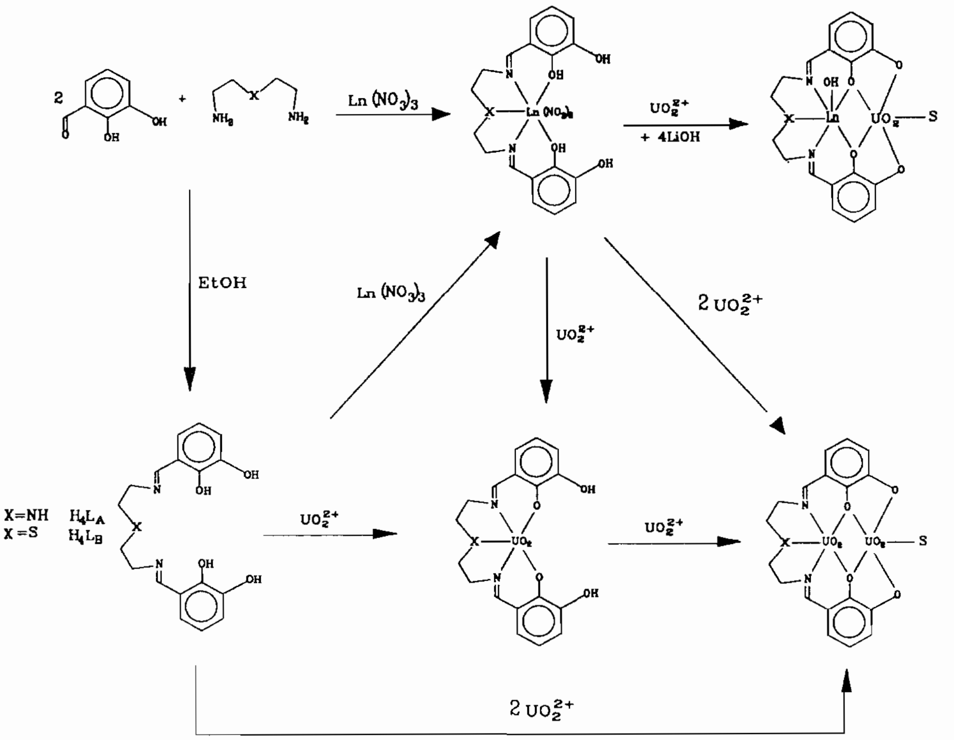
TABLE 3. Selected bond angles (°)

Coordination			
O(1)-U(1)-O(2)	175.0(5)	O(4)-U(1)-N(3)	70.6(4)
O(3)-U(1)-O(4)	85.9(4)	N(1)-U(1)-N(2)	67.6(3)
O(3)-U(1)-N(1)	70.4(3)	N(2)-U(1)-N(3)	65.9(3)
Ligand			
U(1)-O(3)-C(1)	144.4(7)	C(7)-N(1)-C(8)	117(1)
U(1)-O(4)-C(18)	138.6(9)	C(11)-N(3)-C(12)	113(1)
U(1)-N(1)-C(7)	127.7(9)	C(10)-N(2)-C(19)	113(1)
U(1)-N(1)-C(8)	114.9(8)	C(9)-N(2)-C(19)	113(1)
U(1)-N(2)-C(9)	105.1(8)	C(9)-N(2)-C(10)	109(1)
U(1)-N(2)-C(10)	104.6(7)	N(1)-C(7)-C(6)	130(1)
U(1)-N(2)-C(19)	112.0(7)	N(3)-C(12)-C(13)	126(1)
U(1)-N(3)-C(12)	126.2(9)	N(2)-C(19)-C(20)	115(1)
U(1)-N(3)-C(11)	118.1(7)	N(2)-C(9)-C(8)	112(1)
C(19)-C(20)-C(21)	120(1)	N(2)-C(10)-C(11)	113(1)
C(19)-C(20)-C(22)	122(1)	C(21)-C(20)-C(22)	118(1)
N(1)-C(8)-C(9)	110(1)	N(3)-C(11)-C(10)	109(1)
Clathrate dmso			
C(23)-S(1)-C(24)	97(1)	C(23)A-S(1)A-C(24)A	97(2)
O(5)-S(1)-C(24)	104(1)	O(5)A-S(1)A-C(24)A	107(1)
O(5)-S(1)-C(23)	107(1)	O(5)A-S(1)A-C(23)A	105(1)

Results and discussion

The dinucleating compartmental ligands H_4L_C or H_4L_D, obtained by condensation of 2,3-dihydroxybenzaldehyde and the faculative polyamines 1,5-diamino-3-azapentane or 1,5-diamino-3thiapentane, respectively, are particularly suitable for the formation of f-containing complexes. Mono-, homo- and heterodinuclear lanthanide(III)-uranyl(VI) complexes have been prepared according to reaction Scheme 1.

The inner occupancy of UO_2^{2+} in the mononuclear complexes and the formation of binuclear complexes have been recently confirmed by single crystal X-ray diffraction determinations [26]. In $UO_2(H_2L_C)$·dmf the potentially, heptadentate



Scheme 1.

compartmental ligand behaves as a pentadentate dianionic chelate coordinating the linear uranyl(VI) group, almost in its equatorial plane, with the N_3O_2 inner donor set. In the homodinuclear uranyl(VI) complexes $(UO_2)_2(L_C)$(dmf) and $(UO_2)_2(L_C)$(dmso) the inner UO_2^{2+} groups show the same coordination shape as in the mononuclear analogue while the second UO_2^{2+} ion coordinates in the outer O_2O_2 coordination chamber, the equatorial pentacoordination about the central metal ion being reached by the coordination of a solvent molecule [26].

By using mild conditions, it is possible to obtain the mononuclear lanthanide(III) complexes $Ln(H_4L_C)(NO_3)_3$, where the Schiff base behaves as a neutral pentadentate ligand. The inner occupancy of the metal ion cannot be clearly identified in these complexes, because attempts to obtain crystals, suitable for X-ray diffraction, were unsuccessful. Nevertheless, the N_3O_2 inner occupancy in the mononuclear lanthanide(III) complexes may be suggested by analogy with the uranyl(VI) mononuclear complex [26].

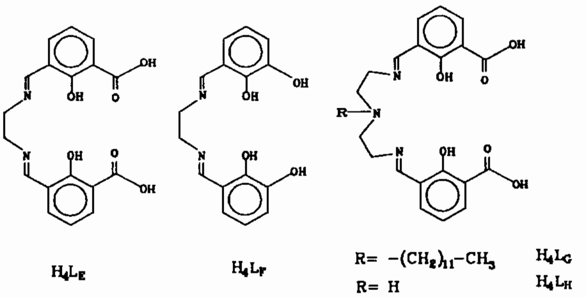
It was also observed that the mononuclear lanthanide(III) and uranyl(VI) complexes can be used as a ligand for a second uranyl(VI) ion. Hetero-dinuclear Ln–UO_2 complexes have been prepared by reaction in alcoholic solution of the preformed mononuclear lanthanide(III) complexes with uranyl(VI) ions in a 1:1 molar ratio.

The use of LiOH in the synthesis of Ln–UO_2 heterodinuclear complexes is necessary in order to obtain negatively charged phenolate groups that bind the lanthanide ion in a stronger manner than phenolic oxygen, thus avoiding the transmetallation process as already observed when LiOH is not used.

Therefore the reaction of $Ln(H_4L_C)(NO_3)_3$ with UO_2^{2+} in alcoholic solution leads to the formation of $UO_2(H_2L_C)$ and $(UO_2)_2(L_C)(S)$, while the same reaction, carried out in the presence of the appropriate amount of LiOH produces $UO_2Ln(L)OH \cdot (S)$.

The homogeneity and the metal ratio in these heterobinuclear lanthanide(III)–uranyl(VI) complexes have been established by electron microscopy together with X-ray fluorescence analysis [33]: they show the correct 1:1 molar ratio.

The shape of the external O_2O_2 coordination chamber is again suitable for the coordination of a uranyl(VI) metal ion as recently observed for analogous heterodinuclear, complexes containing d–f metal ions [35–37] with the ligands H_4L_E and H_4L_F. The d-transition metal ion occupies the internal cage, which is too small to accommodate the larger lanthanide(III) ion. Thus the inner coordination site must be considerably enlarged to coordinate the f-metal ion. By lengthening the aliphatic chain and adding an additional donor



atom inside this chain as in H_4L_C, H_4L_D, H_4L_G and H_4L_H, it is possible to prepare heterodinuclear f–f complexes [29].

In these complexes, the presence of the uranyl group is clearly detectable by a strong IR band in the 888–910 cm^{-1} range due to ν_3(O–U–O). ν(C–N) lies as a single strong band at 1626–1632 cm^{-1} while, two bands attritbutable to ν(C–O) are present at 1585–1582 and 1555–1552 cm^{-1}. Finally ν(NH) lies as a broad or sharp band in the range 3240–3213 cm^{-1}.

$UO_2(H_2L_C)$, $(UO_2)_2(L_C)$ and $UO_2La(L_c)OH$ show almost similar electronic spectra when dissolved in coordinating solvents (i.e. dimethyl sulfoxide or dimethylformamide). Three bands at about 300, 400 and 500 nm are detectable, the last one being attributed to ligand-to-metal charge transfer.

It was quite easy to extend the knowledge, acquired with these 'planar ligands', to similar 'tridimensional' dinucleating or tetranucleating Schiff base systems, obtained according to Scheme 2.

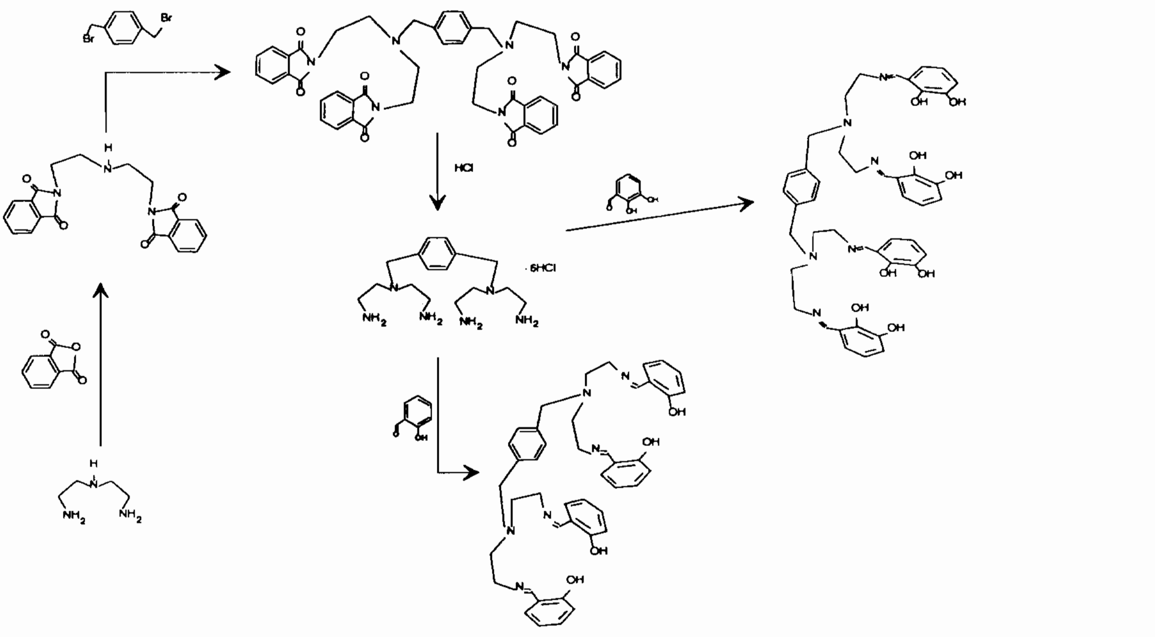
In particular the ligands H_4L_A and H_8L_B have been obtained by condensation of the polyamine 1,4-bis[bis(2-aminoethyl)aminomethyl]-benzene, respectively, with salicylaldehyde or 2,3-dihydroxybenzaldehyde in a molar ratio 1:4 and in methanolic solution. H_8L_B is a yellow solid, soluble in $CHCl_3$, MeOH and DMF while H_4L_A has been used in solution, without prior isolation of the product.

An El mass spectrometry investigation of the ligands does not give useful information about the structure while a FAB study has revealed the presence of the parent peak at the appropriate m/z value for both ligands, confirming the structures proposed in Scheme 2.

In particular, FAB mass spectra for H_8L_B show well detectable peaks attributable to $[M+H]^+$ and $[M+Na]^+$. Other peaks may not immediately be correlated with the proposed structure of the ligand and are quite probably due to rearrangements, actually under investigation.

The reaction of H_4L_A and H_8L_B with $UO_2(CH_3COO)_2{\cdot}2H_2O$ in the appropriate molar ratio in boiling methanol produces the dinuclear $(UO_2)_2(L_A){\cdot}2H_2O$ and the tetranuclear $(UO_2)_4(L_B){\cdot}2H_2O{\cdot}2dmf$ complexes; a dinuclear complex $(UO_2)_2(H_2L_B){\cdot}2H_2O{\cdot}2dmf$ has been also prepared.

An X-ray investigation on $(UO_2)_2(L_A){\cdot}dmso{\cdot}C_6H_6$ has been carried out and the structure is reported in Fig. 1, together with the atom numbering scheme. The crystal packing is reported in Fig. 2. The compound forms a centrosymmetric



Scheme 2.

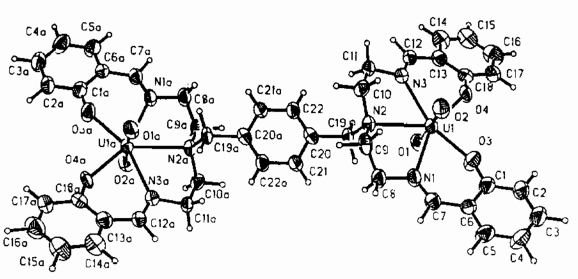


Fig. 1. Molecular structure of $(UO_2)_2(L_A)$ with thermal ellipsoids at the 50% level. H atoms are represented by spheres of arbitrary size.

binuclear complex as the benzene ring, bridging the two macroacyclic coordination moieties, is centered on inversion point $\frac{1}{2}, 0, \frac{1}{2}$; thus the discussion of one half of the molecule is the same for the other.

Several analogies can be found between this structure and other similar uranyl Schiff base complexes already published [38–40]. The uranium atom is in the usual, slightly distorted, bipyramidal pentagonal configuration; the quasi linear (175°) uranyl ion UO_2^{2+} is equatorially coordinated by the O_2N_3 donor set of the Schiff base ligand forming an irregular puckered pentagon. The O3···O4 bite (3.04 Å) is quite large compared to the O···N and N···N bites that lie between 2.91 and 2.80 Å. The angles subtended at uranium are 85.9(3)° (O3–U–O4), 70.5° (mean O–U–N exa-metallocycles) and 66.8° (mean N–U–N penta-metallocycles).

The two ligand wings (O3, C1–C6, C7, N1 and O4, C13–C18, C19, N3) are inclined (12.5 and 22.1°, respectively) with respect to the coordination plane, thereby forming the known (or already found) umbrella shape and the corresponding bonds and angles are completely comparable. The C=N bond lengths (1.25(2) and 1.28(2) Å) indicate a well localized double bond; the U–O and U–N equatorial bonds are similar to those found in the cited works [26, 38] including also the U–N(2) (aminic) bond of 2.65(1) Å which is longer than the other U–N(iminic) bonds (mean 2.61 Å).

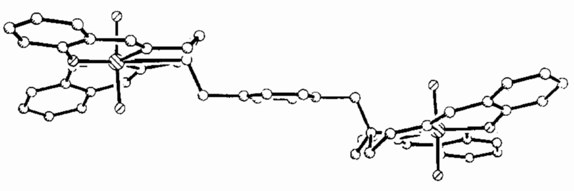


Fig. 3. Three step conformation of the complex $(UO_2)_2(L_A)$.

The entire molecule can be depicted as a three step conformation (Fig. 3). The two least-squares planes containing the central benzene ring and the equatorial O_2N_3 coordination pentagon are approximately parallel, forming a dihedral angle of 4.0(5)°; the two uranium atoms displace 1.20 Å above and below the central benzene ring plane and are 12.686(1) Å apart.

As reported in the crystal data, one molecule of dmso and one of benzene are present, as clathrate solvents, in disordered positions and do not present any type of interaction with the remaining cell content. It must be noted that the intermolecular U...U distances are considerably shorter than the intramolecular one. The shortest intermolecular distance is 6.954(1) Å (Table 2).

A comparison of the properties of the complexes $(UO_2)_2(L_A)\cdot nS$, $(UO_2)_2(H_2L_B)\cdot nS$ and

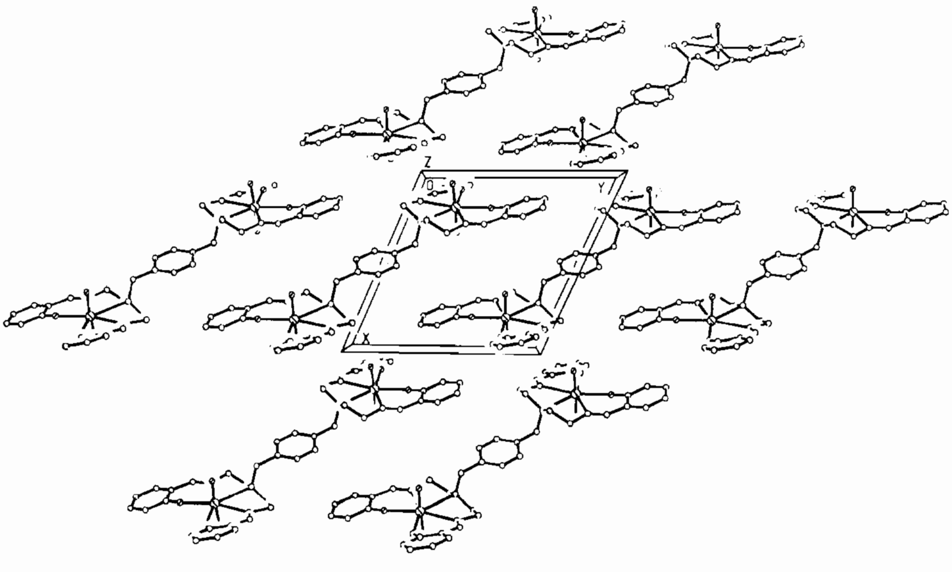
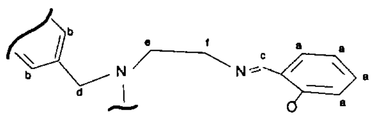


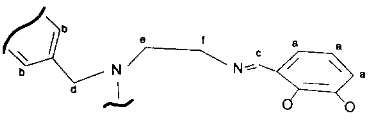
Fig. 2. Crystal packing of the complex $(UO_2)_2(L_A)$ along *c*.

TABLE 4. ^{1}H NMR data for the dinuclear and tetranuclear uranyl(VI) complexes prepared

	$(UO_2)_2(L_A)\cdot 2H_2O$			$(UO_2)_4(L_B)\cdot 2H_2O\cdot 2dmf$		
	Multiplicity	Intensity	δ	Multiplicity	Intensity	δ
H_a	t	8	7.63	t	12	7.06
H_a	d	4	6.94			
H_a	t	4	6.76			
H_b	s	4	7.78	s	4	7.90
H_c	s	4	9.72	s	4	9.88
H_d	s	4	4.91	s	4	5.02
H_e	m	4	5.56	m	4	5.86
H_e	d	4	4.64	d	4	4.90
H_f	m	8	3.66	m	8	3.90
dmf				s	2	7.95
dmf				s	6	2.72
dmf				s	6	2.88



H_4L_A



H_8L_B

$(UO_2)_4(L_B)\cdot nS$ with the mononuclear $UO_2(H_2L_C)\cdot nS$ and $(UO_2)_2(L_C)\cdot nS$ can offer useful information on a series of very similar compounds.

It was already observed that for the complexes derived from H_4L_C ν_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}) [26]. The same trend has been observed on going from $(UO_2)_2(L_A)$ or $(UO_2)_2(H_2L_B)$ to $(UO_2)_4(L_B)\cdot 2H_2O\cdot$dmf or $(UO_2)_4(L_B)\cdot 2H_2O$ complexes; ν_3(O–U–O) lies at 898 cm^{-1} in the binuclear compounds and at 922 or 909 cm^{-1} for the tetranuclear complexes. ν(C=N) is present as a strong band at 1630 for $(UO_2)_2(L_A)$, while two bands at 1628 and 1648 cm^{-1} and at 1655 and 1629 cm^{-1} are present for $(UO_2)_4(L_B)\cdot 2H_2O\cdot 2$dmf and $(UO_2)_2(H_2L_B)$, respectively.

The ^{1}HNMR spectra of the whole series of complexes are very similar to each other (Table 4).

The presence of two additional uranyl(VI) groups in the tetranuclear complexes $(UO_2)_4(L_B)\cdot nS$ causes only a shift toward lower field (0.15 ppm) of the whole pattern of the spectra with respect to the spectrum of the binuclear complex $(UO_2)_2(L_A)$. The shape of the spectra of the $-(CH_2)_2-N-(CH_2)_2-$groups remain substantially identical on going from dinuclear to tetranuclear species, clearly indicating that the coordination geometry of the uranyl(VI) ion in the inner N_2O_2 site occurs in an identical way.

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