Synthesis, structure and magnetic behaviour of dinuclear uranium(IV) complexes with a 'calixsalophen' type macrocycle

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Treatment of UCl_4 with the octadentate tricompartmental 'calixsalophen' type macrocycle H_4L^1 [*N*,*N*:*N*′,*N*′-bis(2,2′-dihydroxy-3,3′-dimethylidene-5,5′-di-*tert*-butylbiphenyl)benzene-1,2-diamine] in THF or pyridine gave the complexes $[U_2L^1Cl_4]$ (**1**) and $[U_2L^1Cl_4(py)_2]$ (**2**), respectively. The crystal structures of **1**·4THF and **2**·3py are centrosymmetric, the metal atoms occupying the N_2O_2 cavities with either a pentagonal bipyramidal environment in **1**, two Cl atoms being in apical positions, or a dodecahedral environment in **2**. Reaction of $U(acac)_4$ (acac = MeCOCHCOMe) with H_4L^1 in THF did not afford the corresponding acetylacetonate product but gave instead the isomeric complex $[U_2L^1(acac)_4]$ (**3**), in which one of the two N_2O_2 cavities is empty, one of the uranium atoms occupying the central O_4 site. The dinuclear complex $[U_2(HL^3)(acac)_5]$ (**4**) was obtained by treating $U(acac)_4$ with H_4L^1 in pyridine; in this case, the macrocyclic ligand L^1 was transformed into its mono(benzimidazole) derivative L^3. The eight-coordinate uranium atoms in **3**·5THF and **4**·2py adopt a distorted square antiprismatic configuration. The magnetic properties of compounds **1** and **3** were investigated.

Introduction

In contrast to the considerable amount of work devoted to the synthesis, structure and magnetic properties of polynuclear lanthanide complexes of Schiff bases,[1] little attention has been paid to polynuclear complexes of 5f elements, except uranyl.[2] We recently demonstrated that bicompartmental salen type Schiff base ligands, used for the synthesis of heterodinuclear[3] MU and heterotrinuclear[4] M_2U complexes (M = Cu, Zn), can also be useful for the synthesis of homopolynuclear uranium(IV) compounds.[5] However, small structural modifications of the parent Schiff base ligand leads to drastic differences in the polynuclear uranium assemblies formed (mono- to octanuclear complexes), and the reaction outcome is thus difficult to predict and even to rationalize. In order to avoid the serendipitous character of the syntheses and get an access to strictly homodinuclear species, we used the more rigid cyclic tricompartmental ligand [*N*,*N*:*N*′,*N*′-bis(2,2′-dihydroxy-3,3′-dimethylidene-5,5′-di-*tert*-butylbiphenyl)benzene-1,2-diamine] (H_4L^1), represented in Scheme 1. This macrocycle, which can be viewed as a dimeric form of *N*,*N*′-bis(salicylidene)benzene-1,2-diamine (salophen), contains two lateral N_2O_2 coordination sites identical to those found in the acyclic Schiff bases used previously, and a central tetraphenolic cavity similar to those which are present in calixarenes (albeit with direct links and not methylene bridges between adjacent phenolic rings); it can thus be considered as a 'calixsalophen' type ligand. This type of macrocyclic ligand[6] was recently utilized in the synthesis of 3d transition metal complexes.[7] Here we present the syntheses and X-ray crystal structures of the dinuclear uranium(IV) complexes which were isolated from reactions of UCl_4 and $U(acac)_4$ (acac = MeCOCHCOMe) with H_4L^1 in THF or pyridine. The $[U_2L^1Cl_4]$ and $[U_2L^1(acac)_4]$ complexes, in which the uranium atoms occupy, respectively, the two N_2O_2 sites and the O_4 and N_2O_2 sites of L^1, have also been characterized by magnetic measurements.

Results and discussion

Syntheses

The 'calixsalophen' type ligand H_4L^1 was synthesized by following a procedure similar to that used for the preparation of its unsubstituted congener,[8] *i.e.* Schiff base condensation of 2,2′-dihydroxy-3,3′-diformyl-5,5′-di-*tert*-butylbiphenyl and *o*-phenylenediamine (Scheme 1); in the presence of $B(OH)_3$ as a template reagent,[6a,b] the reaction was carried out at room temperature and afforded, after crystallization from a mixture of CH_2Cl_2 and MeOH, yellow prisms of H_4L^1 in 66% yield. Replacing *o*-phenylenediamine with the 4,5-dimethylated homologue gave H_4L^2 in 70% yield. Compound H_4L^2 was readily converted in refluxing pyridine into the mono(benzimidazole) derivative H_4L^4 which was isolated as pale orange microcrystals in almost quantitative yield (Scheme 2). A recent example of such a transformation of a salophen type Schiff base was provided by the synthesis of a benzimidazole with

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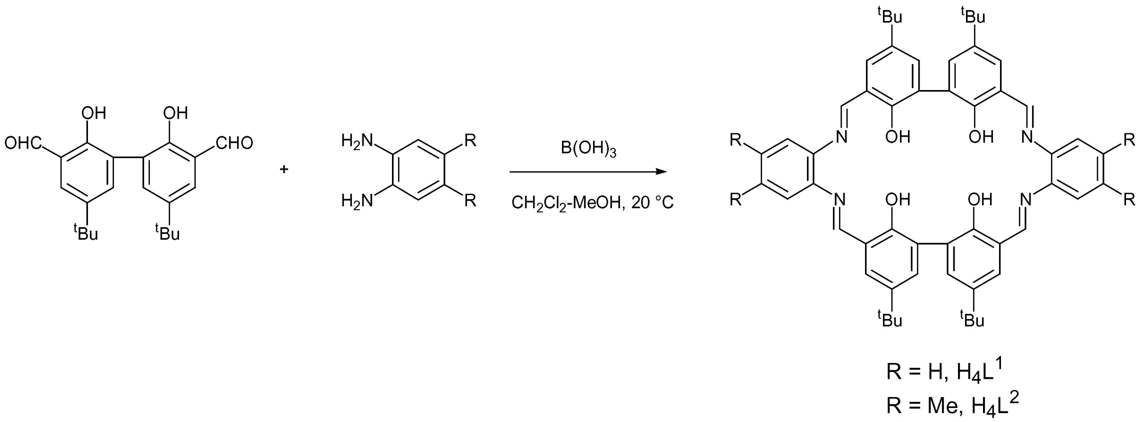


Scheme 1 Synthesis of H_4L^1 and H_4L^2.

two 3-methoxy-5-bromo phenolic substituents from reaction of *o*-phenylenediamine with 3-methoxy-5-bromo salicylaldehyde in refluxing ethanol.[9] The ring closure likely proceeds by the intramolecular addition reaction of the nitrogen atom across the neighboring C═N double bond and implies hydride migration.[10] Other types of inner ring rearrangement of cyclic Schiff bases have been reported.[11] However, H_4L^1 was found to be inert in refluxing pyridine, failing to give the corresponding benzimidazole H_4L^3; the distinct reactivities of H_4L^1 and H_4L^2 are difficult to explain.

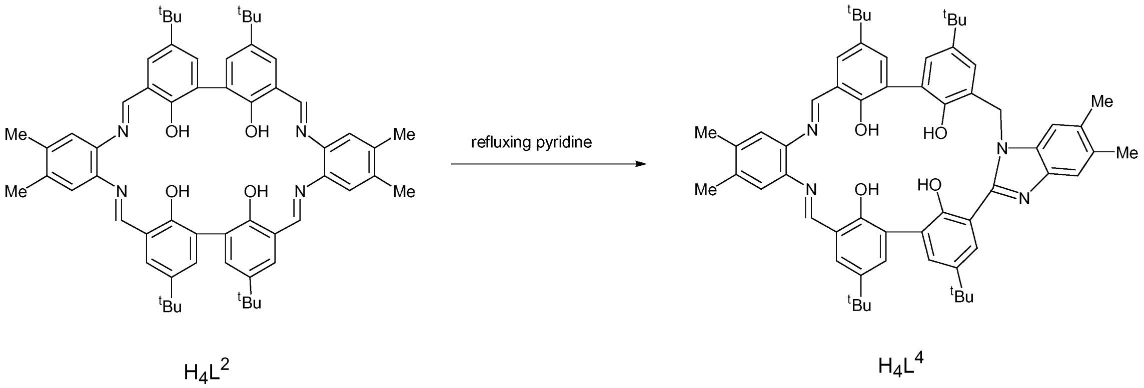
The synthesis of $[U_2L^1Cl_4]$ (**1**) was achieved by mixing the protonated ligand H_4L^1 and two equivalents of UCl_4 in THF; light orange crystals of **1** · 4THF were deposited in 35% yield (Scheme 3). The similar experiment in pyridine led to the formation of a mixture of light orange crystals of $[U_2L^1Cl_4(py)_2]$ · 3py (**2** · 3py) and colourless crystals of [HpyCl]. Complex **1** was characterized by its elemental analyses; the ^1H NMR spectrum indicates that **1** adopts a symmetrical structure in solution, as shown in particular by the single signal corresponding to the ^{t}Bu groups, implying that the two uranium atoms occupy both N_2O_2 cavities. The crystal structures of the solvates **1** · 4THF and **2** · 3py were determined.

Changing UCl_4 for $U(acac)_4$ in its reaction with H_4L^1 in THF gave light orange crystals of $[U_2L^1(acac)_4]$ · 5THF (**3** · 5THF) in 70% yield; the analytically pure powder of **3** was obtained after drying the crystals under vacuum but the poor solubility in organic solvents prevented recording the ^1H NMR spectrum. The crystal structure revealed that, in contrast to **1** and **2**, the uranium atoms are linked to the N_2O_2 and the central O_4 cavities, and the second N_2O_2 site remains free. This difference would possibly reflect the harder character of the $U(acac)_2$ fragment, by comparison with the UCl_2 moiety, leading to its preferential bonding to the harder oxygen atoms. Treatment of $U(acac)_4$ with H_4L^1 in pyridine afforded, after 5 days at 80 °C, a few light orange crystals of $[U_2(HL^3)(acac)_5]$ · 2py (**4** · 2py) which were characterized by X-ray diffraction analysis. The ligand L^1 was thus converted into the mono(benzimidazole) derivative L^3, a transformation which is obviously mediated by the uranium(IV) centre, since H_4L^1 is inert in refluxing pyridine.

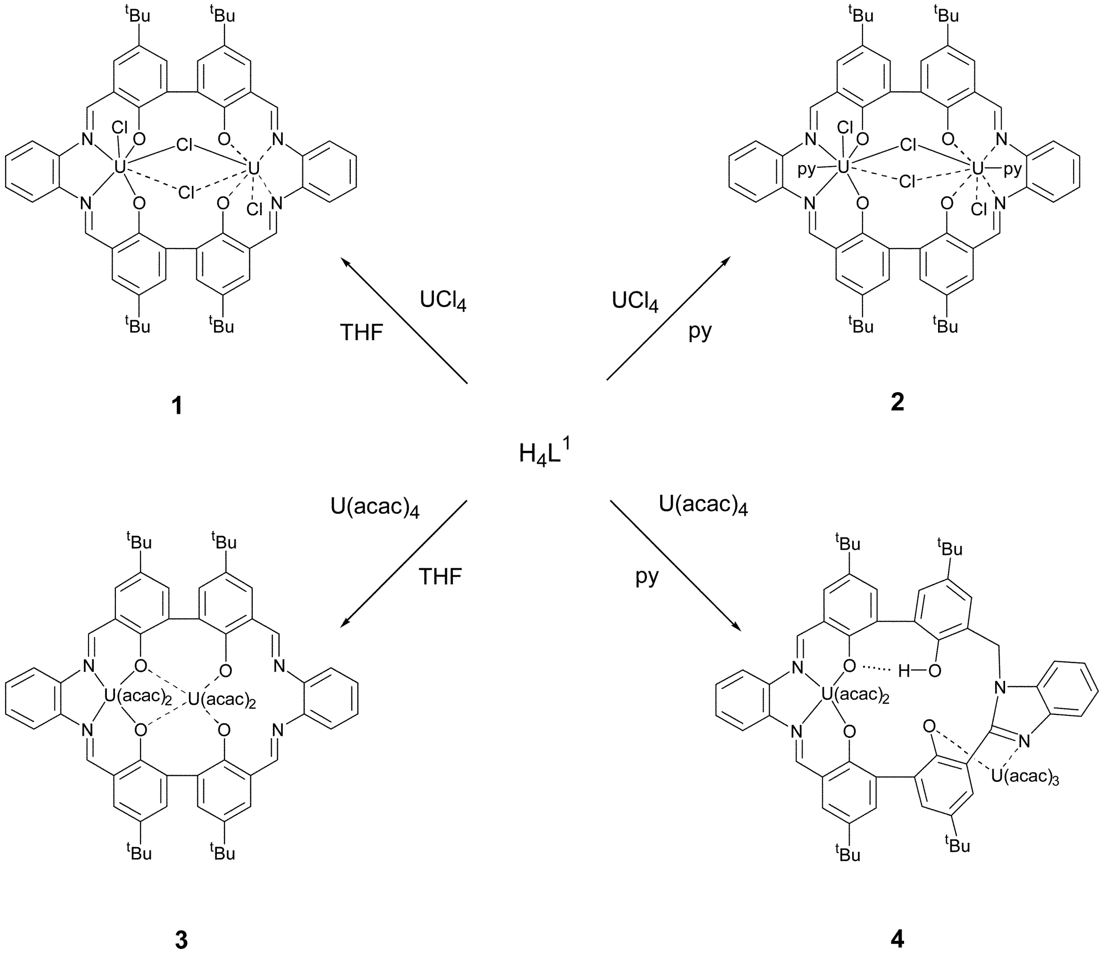
Reactions of H_4L^1 with one equivalent of UX_4 (X = Cl or acac) invariably led to the formation of complexes **1–4**.

Crystal structures

A view of the centrosymmetric complex **1** is shown in Fig. 1, and selected bond lengths and angles are listed in Table 1. The seven-coordinate uranium atom adopts a distorted pentagonal bipyramidal configuration with Cl1 and Cl2 in apical positions and N1, N2, O1, O2 and Cl1′ in the basal plane, with a maximum deviation of 0.243(2) Å. The metal atom is located at 0.313(2) Å from the N_2O_2 mean plane and 0.1393(14) Å



Scheme 2 Synthesis of H_4L^4.



Scheme 3 Synthesis of the complexes.

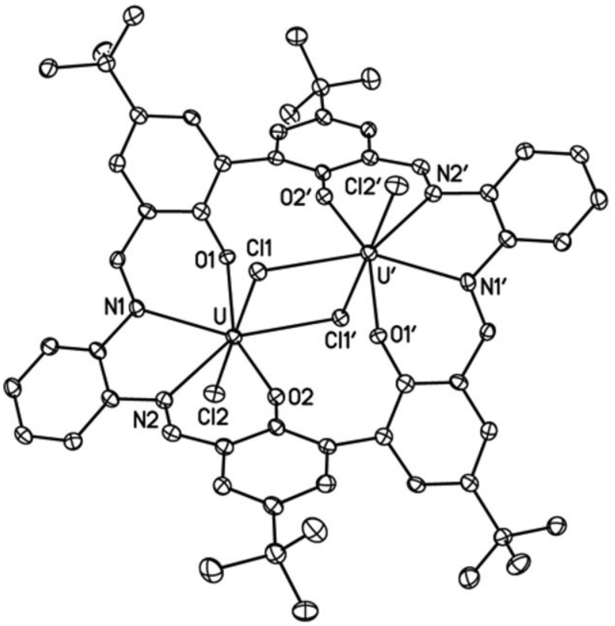


Fig. 1 View of the complex molecule in **1**·4THF. The hydrogen atoms are omitted for clarity. Displacement ellipsoids are drawn at the 30% probability level. Symmetry code: ′ = 2 − x, 2 − y, 1 − z.

from the mean basal plane defined by the five donor atoms. The two uranium atoms are on either side of the macrocycle, being bridged by two chlorine atoms and distant from one another by 4.1010(4) Å. The mean values of the U–O and U–N bond lengths, 2.166(12) and 2.55(4) Å, respectively, are shorter than the mean values of 2.23(2) and 2.63(6) Å measured in the uranium complex of the corresponding acyclic Schiff base ligand.[5] The U–O bond length is comparable to those encountered in acyclic polyphenoxide complexes [2.15(2) Å][12] and the recently reported U^{IV} complexes with calixarenes [mean value 2.13(2) Å].[13] The U–Cl(terminal) bond length of 2.6180(12) Å is in agreement with those reported in the Cambridge Structural Database (CSD, Version 5.27).[14]

The centrosymmetric crystal structure of **2**, represented in Fig. 2, differs from that of **1** by the presence of one pyridine molecule linked to each of the uranium atoms. It is noteworthy that pyridine, and not THF, coordinates to the metal centres of **1** without breaking the Cl bridges. The U atom in **2** is located at 0.472(3) Å from the N_2O_2 site and the eight coordinate environment geometry is dodecahedral, with the two trapezia, N1–O1–Cl1′–O2 and Cl1–N2–Cl2–N3 (rms deviations 0.06 and 0.05 Å, respectively) forming an angle of 87.90(10)°. The modification of the distance between the uranium atom and the N_2O_2 plane, larger than in **1**, leads to an increase in the U···U′ separation, 4.4335(5) Å. The

Table 1 Environment of the uranium atoms in complexes **1–4**: selected bond lengths (Å) and angles (°). Primed atoms are related to unprimed ones by inversion centres

1·4THF			
U–N1	2.514(4)	O1–U–N1	70.18(12)
U–N2	2.590(4)	N1–U–N2	62.97(12)
U–O1	2.177(3)	N2–U–O2	69.16(12)
U–O2	2.154(3)	O2–U–Cl1′	79.84(9)
U–Cl1	2.7741(12)	Cl1′–U–O1	79.27(9)
U–Cl1′	2.8602(12)	Cl1–U–Cl2	179.27(4)
U–Cl2	2.6180(12)	Cl1–U–Cl1′	86.60(3)
U···U′	4.1010(4)	U–Cl1–U′	93.40(3)
2·3py			
U–N1	2.602(6)	O1–U–N1	67.19(17)
U–N2	2.625(6)	N1–U–O2	127.33(17)
U–N3	2.789(6)	O2–U–Cl1′	76.47(12)
U–O1	2.183(5)	Cl1′–U–O1	81.39(12)
U–O2	2.173(5)	N2–U–Cl1	84.25(13)
U–Cl1	2.7351(17)	Cl1–U–N3	133.07(14)
U–Cl1′	2.9683(18)	N3–U–Cl2	71.23(14)
U–Cl2	2.7011(19)	Cl2–U–N2	71.50(13)
U···U′	4.4335(5)		
3·5THF			
U1–N1	2.572(6)	N1–U1–O1	71.04(16)
U1–N2	2.587(5)	O1–U1–O2	73.08(15)
U1–O1	2.295(4)	O2–U1–N2	70.37(16)
U1–O2	2.296(4)	N2–U1–N1	61.45(16)
U1–O5	2.340(4)	O5–U1–O6	72.62(17)
U1–O6	2.312(5)	O6–U1–O7	77.54(16)
U1–O7	2.344(4)	O7–U1–O8	71.51(16)
U1–O8	2.303(4)	O8–U1–O5	79.10(16)
U1···U2	4.0252(4)		
U2–O1	2.628(5)	O1–U2–O2	64.01(13)
U2–O2	2.527(4)	O2–U2–O3	71.38(15)
U2–O3	2.213(3)	O3–U2–O4	86.95(17)
U2–O4	2.182(5)	O4–U2–O1	68.48(15)
U2–O9	2.346(5)	O9–U2–O10	71.32(16)
U2–O10	2.355(4)	O10–U2–O11	80.22(16)
U2–O11	2.332(4)	O11–U2–O12	69.43(16)
U2–O12	2.423(5)	O12–U2–O9	68.84(16)
4·2py			
U1–N1	2.618(3)	N1–U1–O1	69.75(10)
U1–N2	2.611(3)	O1–U1–O2	87.09(10)
U1–O1	2.265(2)	O2–U1–N2	69.50(10)
U1–O2	2.196(3)	N2–U1–N1	61.24(10)
U1–O5	2.377(3)	O5–U1–O6	69.48(10)
U1–O6	2.386(3)	O6–U1–O7	72.75(10)
U1–O7	2.335(3)	O7–U1–O8	72.02(10)
U1–O8	2.331(3)	O8–U1–O5	76.43(10)
U1···U2	6.8795(3)		
U2–O3	2.205(3)	O3–U2–N3	71.43(10)
U2–O9	2.317(3)	N3–U2–O9	71.22(10)
U2–O10	2.363(3)	O9–U2–O10	70.92(10)
U2–O11	2.351(3)	O10–U2–O3	72.76(10)
U2–O12	2.403(3)	O11–U2–O12	70.18(10)
U2–O13	2.383(3)	O12–U2–O13	75.11(10)
U2–O14	2.373(3)	O13–U2–O14	69.74(10)
U2–N3	2.576(3)	O14–U2–O11	73.62(10)

macrocyclic ligand in complexes **1** and **2** adopts the same chair-shaped conformation (Fig. 2) than the free, unsubstituted, congener,[8] with dihedral angles of 44.1(2) and 34.3(2)° in **1** and 48.7(2) and 39.7(3)° in **2** between the phenyl rings of the diimino chain and the phenoxide rings; besides, the two adjacent phenoxide rings are twisted relative to one another by an angle of 51.2(2) and 62.3(2)° in **1** and **2**, respectively [76.8(4)° in the free molecule].

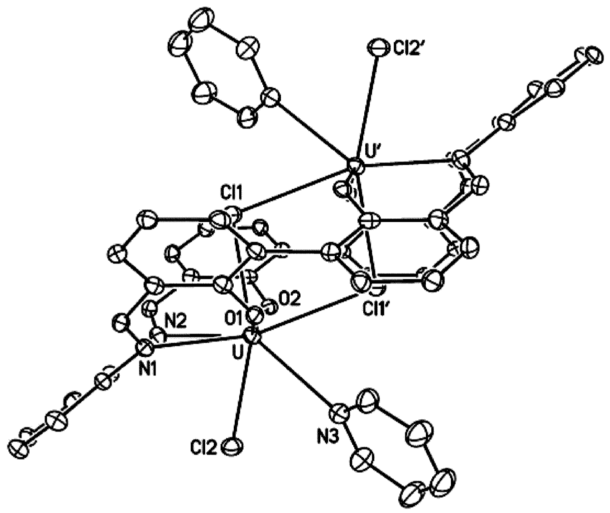


Fig. 2 View of the complex molecule in **2**·3py. The hydrogen atoms and *tert*-butyl groups are omitted for clarity. Displacement ellipsoids are drawn at the 30% probability level. Symmetry code: ′ = 2 − *x*, 2 − *y*, 2 − *z*.

The crystal structure of **3** is represented in Fig. 3 and selected bond lengths and angles are listed in Table 1. The dinuclear complex is devoid of any symmetry element, even approximate. By comparison with **1** and **2**, the uranium atoms move away on both sides of the ligand with distances to the N_2O_2 and O_4 mean planes of 1.444(2) and 1.266(2) Å for U1 and U2, respectively. However, the U1···U2 distance, 4.0252(4) Å, is shorter than in **1** and **2** due to the occupation of proximal coordination sites. The phenoxide rings bearing O1 and O2 and the phenyl ring of the diimino chain bound to them are nearly parallel to one another [dihedral angles in the range 8.5(2)–12.7(2)°] and the first two are close to coplanarity [maximum deviation 0.124(6) Å]; the conformation is thus different from the chair one since half the ligand is nearly planar. The mean values of the U–N and U–O(terminal) bond lengths [2.580(7) and 2.198(16) Å, respectively] for both

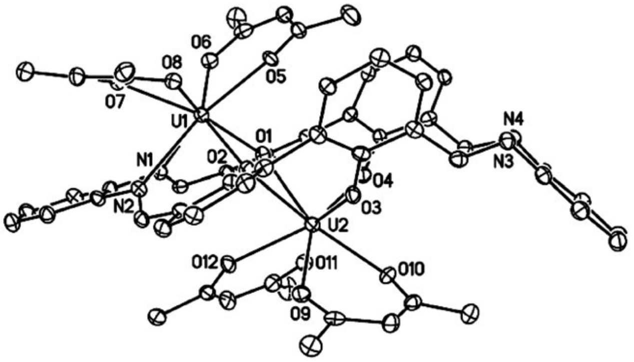


Fig. 3 View of the complex molecule in **3**·5THF. The hydrogen atoms and *tert*-butyl groups are omitted for clarity. Displacement ellipsoids are drawn at the 30% probability level.

uranium atoms compare well with those in the previous dinuclear uranium(IV) complexes. The phenoxide bridges are not symmetric, with in each case a short U1–O [2.295(4) and 2.296(4) Å] and a long U2–O [2.628(5) and 2.527(4) Å] bond lengths. These values are in agreement with those measured in the trinuclear uranium(IV) Schiff base compound $[Hpy]_3[U_3LCl_9O]$ (H_4L = *N*,*N*′-bis(3-hydroxysalicylidene)-2-methyl-1,2-propanediamine).[15] The coordination sphere of each uranium atom in **3** is completed by the four oxygen atoms of two acetylacetonate ligands, with a mean U–O bond length of 2.34(3) Å, comparable with the values of 2.36(2) Å in the mononuclear $[UL(acac)_2]$ complex[16] and 2.32(5) Å, the mean value for acac complexes of U^{IV} present in the CSD. The coordination geometry of the uranium atoms is distorted square antiprismatic with the N_2O_2 (O_4) site and the oxygen acac atoms O5 to O8 (O9 to O12) defining the two square faces for U1 (U2).

The dinuclear compound **4** is represented in Fig. 4. The U1 atom is linked to the N_2O_2 cavity of the ligand and to the oxygen atoms of two acac groups, the values of the bond lengths and angles and the geometry being similar to those reported for atom U1 in compound **3**. Only the U1–O1 bond length [2.265(2) Å] is slightly larger than the mean value for the other $U–O_{phenoxide}$ bond lengths [2.201(5) Å for both U atoms] because O1 is involved in a hydrogen bond with the O4H hydroxy group [O4···O1 2.615(4) Å, O4–H···O1 157°]. The eight-coordinate U2 atom adopts a distorted square antiprismatic configuration, one face being defined by the N3 atom of the benzimidazole group, the phenoxide atom O3 and the acac oxygen atoms O9 and O10 [rms deviation 0.133 Å] and the other by the oxygen atoms of the two other acac groups [rms deviation 0.057 Å]; atom U2 is located at 1.3321(14) and 1.3165(14) Å from these two faces, respectively. The novel, dissymmetric macrocycle L^3 adopts a very irregular conformation, with the adjacent phenolic rings twisted with respect to one another [dihedral angles 42.30(15) and 60.80(15)°] and dihedral angles between the aromatic ring of the diimino chain and the adjacent phenoxide rings of 17.57(19) and 15.53(15)°. Concerning the benzimidazole group, the N3–C39 distance of 1.326(5) Å clearly indicates the presence of a double bond in the five-membered ring, in contrast to the N4–C39 simple bond length [1.374(5) Å] and in agreement with the values for the imine double bond lengths [N1–C11 1.292(5), N2–C18 1.304(5) Å]. The part of the macrocycle containing the benzimidazole ring is buckled away so as to permit the coordination of atom N3 to the uranium centre U2, located out of the cavity. As a consequence, the dihedral angles between the benzimidazole mean plane [rms deviation 0.005 Å] and the two adjacent phenolic rings are 39.86(14) and 78.34(11)° and that between these two phenolic rings is 69.25(14)°.

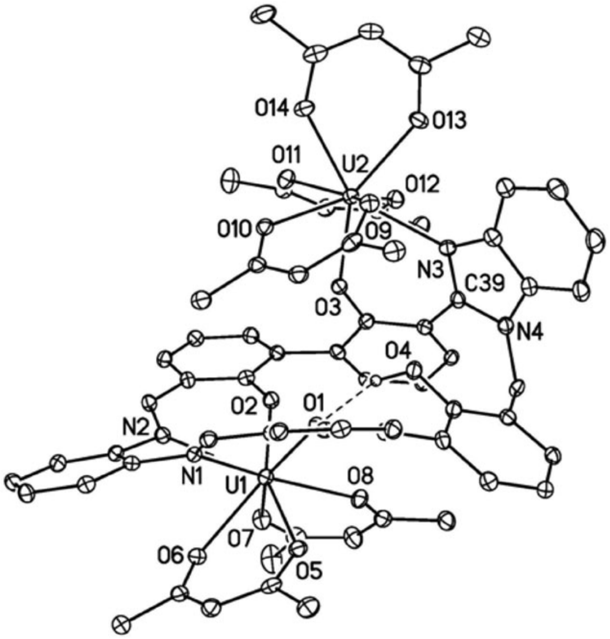


Fig. 4 View of the complex molecule in **4**·2py. The hydrogen atoms (except when involved in a hydrogen bond) and the *tert*-butyl groups are omitted for clarity. The hydrogen bond is shown as a dashed line. Displacement ellipsoids are drawn at the 30% probability level.

Magnetism

The magnetic behaviour of the dinuclear complexes **1** and **3** is shown in Fig. 5 in the form of $\chi_M T$ *vs.* *T*. The magnetic susceptibility of **1** varies from 0 at 2 K to 3.00 cm^3 mol^{-1} K (μ = 4.9 μ_B) at 300 K. The $\chi_M T$ value at room temperature is close to that theoretically expected for two free $5f^2$ ions (3.2 cm^3 mol^{-1} K). For compound **3**, the $\chi_M T$ value at 300 K, *ca.* 1.80 cm^3 mol^{-1} K (μ = 3.79 μ_B), represents the contribution of the two U^{IV} ions in their different crystal fields. This value is lower than the theoretical value and the difference can be explained by the reduction in symmetry and the covalency in the bonding which removes the orbital degeneracies.[17] The $\chi_M T$ values of **1** and **3** decrease with *T* and this could be due to both the depopulation of the Stark sublevels and an antiferromagnetic interaction between the uranium atoms. Finally, $\chi_M T$ tends towards 0 cm^3 mol^{-1} K at 2 K, as the ground state for $5f^2$ uranium(IV) is an orbital singlet.[17] Very few examples of magnetic investigations on polynuclear bridging

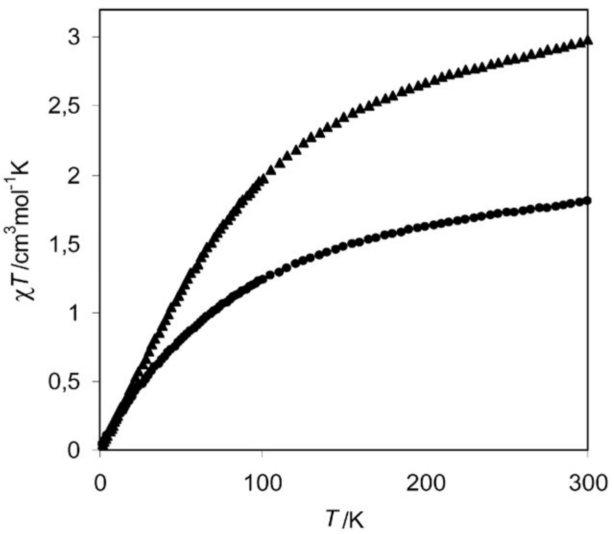


Fig. 5 Thermal dependence of $\chi_M T$ for the complexes **1** (▲) and **3** (●).

uranium(IV) compounds have been reported.[18–20] The magnetic moment at room temperature of the tetranuclear compound $[U_4(O_2CNEt_2)_{12}(\mu_3\text{-}O)_2]$[18] is equal to 2.76 μ_B per uranium atom, which corresponds to a χT value of 0.95 cm^3 mol^{-1} K. A weaker magnetic moment of 2.17 μ_B per uranium atom was measured in the dinuclear complex $[\{U(C_5H_5)_3\}_2(\mu\text{-}O)]$,[19] suggesting the presence of a slight intramolecular interaction. More recently, the dinuclear complex $[\{U((ArO)_3tacn)\}_2(\mu\text{-}O)]$[20] [$(ArO)_3$tacn = 1,4,7-tris(3,5-*tert*-butyl-2-hydroxybenzylate)-1,4,7-triazacyclononane] was found to have an effective moment varying from 4.55 at room temperature to approximately 1 μ_B at 5 K.

Conclusion

Compounds **1–4** demonstrate the potential of the 'calixsalophen' type macrocycle H_4L^1 as an associating ligand for the design of dinuclear uranium(IV) complexes. Depending on the nature of the auxiliary ligands, the uranium atoms can occupy the N_2O_2 or O_4 sites of the compartmental ligand, a property which would be interesting for the controlled synthesis of heterodinuclear 3d–5f complexes.

Experimental

All reactions with uranium complexes were carried out under argon (<5 ppm oxygen or water) using standard Schlenk-vessel and vacuum-line techniques or in a glove box. Solvents were dried by standard methods and distilled immediately before use; $[^2H_8]$THF and $[^2H_5]$pyridine (Eurisotop) were dried over Na/K alloy or NaH, respectively, and stored over 3 Å molecular sieves. The ^{1}H NMR spectra of the organic compounds were recorded on a Nippon Denshi JEOL FT-300 spectrometer in $CDCl_3$ with Me_4Si as an internal reference; the ^{1}H NMR spectra of the uranium complexes were recorded on a Bruker DPX 200 instrument and referenced internally using the residual protio solvent resonances relative to tetramethylsilane (δ 0). The IR spectra were measured as KBr pellets on a Nippon Denshi JIR-AQ2OM spectrometer. The mass spectra were obtained on a Nippon Denshi JMS-01SA-2 spectrometer at 75 eV using a direct-inlet system. Magnetic susceptibility data were collected on powdered samples with a SQUID-based sample magnetometer Quantum Design MPMS5. Elemental analyses of the uranium complexes were performed by Analytische Laboratorien at Lindlar (Germany), and those of the organic compounds were performed at the Center of Advanced Instrumental Analysis, Kyushu University, Fukuoka (Japan). 2,2′-Dihydroxy-5,5′-di-*tert*-butylbiphenyl,[21] UCl_4[22] and $U(acac)_4$[23] were prepared as previously reported.

Syntheses

2,2′-Dihydroxy-3,3′-diformyl-5,5′-di-*tert*-butylbiphenyl. To a solution of 2,2′-dihydroxy-5,5′-di-*tert*-butyl-biphenyl (200 mg, 0.67 mmol) in CF_3COOH (2 mL) was added hexamethylenetetramine (282 mg, 2.01 mmol). After stirring for 24 h at 90 °C, the reaction mixture was cooled and poured into a 10% HCl aqueous solution. After 1 h, the mixture was extracted with CH_2Cl_2. The extracts were washed with 10% HCl aq. and distilled water, dried with Na_2SO_4, and concentrated under vacuum to give a yellow solid. Recrystallization from methanol afforded the product (141 mg, 0.41 mmol, 61%) as yellow prisms (mp 201–202 °C) (Found: C 74.21, H 7.34. $C_{22}H_{26}O_4$ requires C 74.55, H 7.39%); ν(KBr) cm^{-1} 2858, 1699, 1652, 1634, 1456, 1436, 955, 891, 826, 680, 629, 564 and 497; δ_H ($CDCl_3$, 20 °C) 1.37 (18 H, s, ^{t}Bu), 7.56 and 7.71 (2 × 2 H, d, J = 2.37 Hz, aromatic H), 9.95 (2 H, s, OH) and 11.23 (2H, s, CH=O); m/z (ESI) = 354 (M).

H_4L^1. To a solution of 2,2′-dihydroxy-3,3′-diformyl-5,5′-di-*tert*-butylbiphenyl (1,00 g, 5.64 mmol) in CH_2Cl_2 (30 mL) and CH_3OH (30 mL) was added boric acid (87 mg, 2.82 mmol). After stirring for 1 h at room temperature, *o*-phenylenediamine (305 mg, 5.64 mmol) was added and a yellow precipitate was formed. After 24 h, the precipitate was collected by filtration, washed with methanol and dried under vacuum. Recrystallization from CH_2Cl_2–methanol (1 : 5) afforded H_4L^1 (797 mg, 1.86 mmol, 66%) as yellow prisms (mp >200 °C, decomp.) (Found: C 78.52, H 7.21, N 6.61. $C_{56}H_{60}N_4O_4$ requires C 78.84, H 7.09, N 6.57%); ν(KBr) cm^{-1} 3625, 3325, 2975, 2470, 1625, 1570, 1437, 1375, 1250, 1212, 1150, 1100, 956, 875, 743 and 662; δ_H ($CDCl_3$, 20 °C) 1.32 (36 H, s, ^{t}Bu), 7.21 (16 H, m, aromatic H), 8.57 (4 H, s, CH=N) and 12.73 (4 H, br s, OH); m/z (ESI) = 852.5 (M).

H_4L^2. To a solution of 2,2′-dihydroxy-3,3′-diformyl-5,5′-di-*tert*-butylbiphenyl (3.00 g, 8.46 mmol) in CH_2Cl_2 (100 mL) and CH_3OH (100 mL) was added boric acid (523 mg, 8.46 mmol). After stirring for 1 h at room temperature, 4,5-dimethyl-1,2-diaminobenzene (1.15 g, 8.46 mmol) was added and a yellow precipitate was formed. After 24 h, the precipitate was collected by filtration, washed with methanol and dried under vacuum. Recrystallization from CH_2Cl_2–tetrahydrofuran (1 : 10) afforded H_4L^2 (3.32 g, 3.65 mmol, 86%) as yellow prisms (mp >200 °C, decomp.) (Found: C 79.21, H 7.43, N 6.19. $C_{60}H_{68}N_4O_4$ requires C 79.26, H 7.54, N 6.16%); ν(KBr) cm^{-1} 3702, 3525, 2939, 2414, 1615, 1500, 1455, 1362, 1246, 1182, 1162, 963, 882, 671, 646, 595 and 494; δ_H ($CDCl_3$, 20 °C) 1.31 (36 H, s, ^{t}Bu), 2.30 (12 H, s, Me), 6.81 (4 H, s, aromatic H of the diimino chain), 7.25 and 7.36 (2 × 4 H, d, J = 3.12 Hz, aromatic H), 8.56 (4 H, s, CH=N) and 12.83 (4H, br s, OH); m/z (ESI) = 908.5 (M).

H_4L^4. A solution of H_4L^2 (100 mg, 0.11 mmol) in pyridine (3 mL) was heated under reflux for 24 h. After the reaction mixture was cooled to room temperature, the solvent was evaporated under vacuum to afford a pale orange solid. Recrystallisation from MeOH–$CHCl_3$ (5 : 1) afforded H_4L^4 (98 mg, 96%) as pale orange prisms (mp 285–287 °C) (Found: C 78.94, H 7.48, N 6.05. $C_{60}H_{68}N_4O_4$ requires C 79.26, H 7.54, N 6.16%); δ_H ($CDCl_3$, 20 °C) 1.30, 1.36, 1.37 and 1.39 (4 × 9 H, s, ^{t}Bu), 2.29, 2.30, 2.31 and 2.34 (4 × 3 H, s, Me), 3.49 (2 H, s, CH_2), 6.87, 7.01, 7.20, and 7.45 (4 × 1 H, s, aromatic H of the diimino chain), 7.11, 7.29, 7.32, 7.33, 7.39, 7.42, 7.46 and 7.61 (8 × 1 H, d, J = 2.4 Hz, aromatic H), 7.31 and 7.36 (2 × 1 H, s, OH), 8.48 and 8.68 (2 × 1 H, s, CH=N), 13.24 and 13.64 (2 × 1 H, br s, OH); m/z (ESI) = 909 (M).

$[U_2L^1Cl_4]$ (1). A flask was charged with H_4L^1 (30 mg, 0.035 mmol) and UCl_4 (27 mg, 0.070 mmol) in THF (10 mL). The

Table 2 Crystal data and structure refinement details

	1 · 4THF	**2** · 3py	**3** · 5THF	**4** · 2py
Empirical formula	$C_{72}H_{88}Cl_4N_4O_8U_2$	$C_{81}H_{81}Cl_4N_9O_4U_2$	$C_{96}H_{124}N_4O_{17}U_2$	$C_{91}H_{102}N_6O_{14}U_2$
M/g mol^{-1}	1755.32	1862.41	2082.05	1979.85
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a/Å	11.8168(5)	14.2822(9)	16.2734(4)	15.5199(4)
b/Å	12.6942(7)	12.0928(3)	29.7951(10)	16.7753(6)
c/Å	12.9752(7)	21.8206(12)	20.3134(5)	18.1932(8)
α/°	86.737(2)	90	90	77.591(2)
β/°	65.501(3)	91.604(3)	111.161(2)	81.494(3)
γ/°	79.661(4)	90	90	68.004(2)
V/Å^3	1742.02(16)	3767.2(3)	9185.2(5)	4277.3(3)
Z	1	2	4	2
D_c/g cm^{-3}	1.673	1.642	1.506	1.537
μ(Mo-Kα)/mm^{-1}	4.853	4.491	3.589	3.847
F(000)	864	1828	4192	1972
Reflections collected	53 669	115 077	171 065	158 460
Independent reflections	6616	7153	16 467	16 208
Observed reflections [$I > 2\sigma(I)$]	5735	5783	12 106	13 016
R_{int}	0.080	0.030	0.082	0.053
Parameters refined	412	488	1092	1040
R_1	0.033	0.041	0.049	0.031
wR_2	0.072	0.116	0.109	0.074
S	1.041	1.102	1.016	1.022
$\Delta\rho_{min}$/e Å^{-3}	−1.36	−1.56	−1.70	−1.86
$\Delta\rho_{max}$/e Å^{-3}	0.74	2.37	1.30	0.90

reaction mixture was heated for 5 days at 80 °C. The light orange crystals of **1** · 4THF were filtered off, washed with a small quantity of THF and dried under vacuum, thus giving an orange powder of the unsolvated compound **1** (18.0 mg, 35%) (Found: C, 45.4; H, 4.0; N, 4.0. $C_{56}H_{56}N_4O_4Cl_4U_2$ requires C, 45.8; H, 3.8; N, 3.8%). δ_H ([$^2H_8$]THF, 23 °C) –9.87 and –8.83 (2 × 4 H, s, aromatic H of the diimino chain), 17.26 (36 H, s, ^{t}Bu), 22.46 and 29.64 (2 × 4 H, s, aromatic H), 69.27 (4 H, s, CH=N).

[$U_2L^1Cl_4(py)_2$] (2). An NMR tube was charged with H_4L^1 (10.0 mg, 0.012 mmol) and UCl_4 (9.0 mg, 0.024 mmol) in [$^2H_5$]pyridine (0.4 mL). After heating for 5 days at 80 °C, light orange crystals of **2** · 3py were deposited from the orange solution, together with colourless crystals of [HpyCl].

[$U_2L^1(acac)_4$] (3). A flask was charged with H_4L^1 (30 mg, 0.035 mmol) and U(acac)$_4$ (44.6 mg, 0.070 mmol) in THF (10 mL). The reaction mixture was heated for 5 days at 80 °C. The light orange crystals of **3** · 5THF were filtered off, washed with a small quantity of THF and dried under vacuum, thus giving an orange powder of the unsolvated compound **3** (42 mg, 70%) (Found: C, 52.2; H, 5.1; N, 3.3. $C_{76}H_{84}N_4O_{12}U_2$ requires C, 53.0; H, 4.9; N, 3.3%). The ^{1}H NMR spectrum of **3** could not be recorded because of the poor solubility of this compound in organic solvents.

[$U_2(HL^3)(acac)_5$] (4). An NMR tube was charged with H_4L^1 (10.0 mg, 0.012 mmol) and U(acac)$_4$ (14.8 mg, 0.024 mmol) in [$^2H_5$]pyridine (0.4 mL). After heating for 5 days at 80 °C, few light orange crystals of **4** · 2py were deposited from the orange solution.

Crystallography

The data were collected at 100(2) K on a Nonius Kappa-CCD area detector diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). The crystals were introduced in glass capillaries with a protecting "Paratone-N" oil (Hampton Research) coating. The unit cell parameters were determined from ten frames, then refined on all data. The data (ϕ- and ω-scans)[24] were processed with HKL2000.[25] The structures were solved by Patterson map interpretation or by direct methods with SHELXS-97 and subsequent Fourier-difference synthesis and refined by full-matrix least squares on F^2 with SHELXL-97.[26] Absorption effects were corrected empirically with the program DELABS in PLATON[27] or with SCALEPACK.[25] All non-hydrogen atoms were refined with anisotropic displacement parameters. One ^{t}Bu group in **2** · 3py was found to be rotationally disordered over two positions which were refined with occupancy parameters constrained to sum to unity; one pyridine solvent molecule is also disordered around a symmetry centre. Some restraints on bond lengths and/or displacement parameters were applied for the disordered atoms in **2** · 3py and for some badly behaving atoms (particularly in the solvent molecules) in the other compounds. The hydrogen atom bound to O4 in **4** · 2py was found on a Fourier-difference map and all the other hydrogen atoms were introduced at calculated positions (except those of the disordered pyridine molecule in **2** · 3py). All were treated as riding atoms with a displacement parameter equal to 1.2 (OH, CH, CH_2) or 1.5 (CH_3) times that of the parent atom. Crystal data and structure refinement details are given in Table 2. The molecular plots were drawn with SHELXTL.[28]

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For crystallographic data in CIF or other electronic format see DOI: 10.1039/b606035h

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