

# Synthesis and crystal structure of uranium(IV) complexes with compartmental Schiff bases: from mononuclear species to tri- and tetranuclear clusters

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Treatment of  $\text{U}(\text{acac})_4$  with the hexadentate Schiff base  $\text{H}_2\text{L}^i$  gave the  $[\text{UL}^i_2]$  complexes **1–4** [ $\text{H}_2\text{L}^1 = N,N'$ -bis(3-methoxysalicylidene)-2-methyl-1,2-propanediamine,  $\text{H}_2\text{L}^2 = N,N'$ -bis(3-methoxysalicylidene)-1,2-phenylenediamine,  $\text{H}_2\text{L}^3 = N,N'$ -bis(3-methoxysalicylidene)-2-aminobenzylamine and  $\text{H}_2\text{L}^4 = N,N'$ -bis(3-methoxysalicylidene)-2,2-dimethyl-1,3-propanediamine for **1–4**, respectively]. The  $[\text{U}(\text{L})_2(\text{acac})_2]$  compounds could not be isolated because of their ready disproportionation into  $[\text{UL}^i_2]$  and  $\text{U}(\text{acac})_4$ . Compounds **2** and **4** adopt a meridional configuration in the solid state and in solution, while **3** exists in solution as the two equilibrating meridional and sandwich isomers and crystallizes in the meridional isomeric form. Reaction of  $\text{U}(\text{acac})_4$  with  $\text{H}_4\text{L}^5$  afforded the expected compound  $[\text{U}(\text{H}_2\text{L}^5)(\text{acac})_2]$  (**5**) [ $\text{H}_4\text{L}^5 = N,N'$ -bis(3-hydroxysalicylidene)-2-methyl-1,2-propanediamine] but, in the presence of  $\text{H}_4\text{L}^6$  and  $\text{H}_4\text{L}^7$ ,  $\text{U}(\text{acac})_4$  was transformed in a serendipitous and reproducible manner into the tri- and tetranuclear  $\text{U}(\text{IV})$  complexes  $[\text{U}_3(\text{L}^6)(\text{HL}^6)_2(\text{acac})_2]$  (**6**) and  $[\text{U}_4(\text{HL}^7)_4(\text{H}_2\text{L}^7)_2]$  (**7**) [ $\text{H}_4\text{L}^6 = N,N'$ -bis(3-hydroxysalicylidene)-1,2-phenylenediamine and  $\text{H}_4\text{L}^7 = N,N'$ -bis(3-hydroxysalicylidene)-2-aminobenzylamine]. The crystal structures of **6**·3thf and **7**·5thf show the assembling role of the Schiff-base ligands.

## Introduction

Metal complexes derived from Schiff bases occupy an important position in the development of coordination chemistry, as witness the huge number of accounts devoted to their synthesis, structure, reactivity and physicochemical properties. Such mononuclear complexes proved to be valuable catalysts in a range of organic reactions, especially in enantioselective transformations with the use of chiral Schiff-base ligands.<sup>1</sup> As compartmental polydentate ligands, Schiff bases have been much considered in the study of homo- and hetero-polymetallic compounds. Many Schiff-base complexes have potential biological interest in an attempt to mimic the structural and functional features of multimetal active sites.<sup>2</sup> Schiff bases have also found useful applications in the synthesis of molecular and supramolecular polymetallic functional systems exhibiting specific optical or magnetic properties.<sup>3</sup> The design of such edifices has received in recent years a new impulse with the emergence of modern synthetic tools based on lock-and-key and induced fit principles, self-assembly and self-organization concepts.<sup>4</sup>

By comparison with the wealth of information available on transition metal and lanthanide complexes of Schiff bases,<sup>5</sup> reports on such compounds of the 5f elements are much less numerous. These are dealing essentially with the  $\text{UO}_2^{2+}$  ion, in mononuclear and homo- or hetero-polynuclear species.<sup>6</sup> A few mononuclear actinide(IV) complexes with tetra- or hexadentate Schiff bases have been crystallographically characterized: two thorium compounds  $[\text{ThL}_2]$  [ $\text{H}_2\text{L} = N,N'$ -bis(salicylidene)-1,2-phenylenediamine (salophen)<sup>7</sup> and  $\text{H}_2\text{L} = N,N'$ -bis(3-methoxysalicylidene)ethylenediamine (3-MeOsalen)<sup>8</sup>] and three uranium complexes with a single Schiff-base coordinated, i.e.  $[\text{U}(\text{salen})\text{Cl}_2(\text{thf})_2]$ ,<sup>9</sup>  $[\text{U}(3\text{-MeOsalen})\text{Cl}_2(\text{py})_2]$ <sup>10</sup> and  $[\text{U}(\text{H}_2\text{L}^5)(\text{acac})_2]$ <sup>11</sup> [ $\text{H}_4\text{L}^5 = N,N'$ -bis(3-hydroxysalicylidene)-2-methyl-1,2-propanediamine]. We found that such uranium complexes are useful building blocks for the synthesis of a series of  $\text{UCu}^{12}$  and  $\text{UCu}_2^{13}$  compounds in which the magnetic  $\text{U}(\text{IV})$  and  $\text{Cu}(\text{II})$  ions are associated with hexadentate Schiff bases. In order to prepare other complexes of general formula  $[\text{UL}^i(\text{acac})_2]$  or  $[\text{U}(\text{H}_2\text{L}^i)(\text{acac})_2]$  which would serve for the synthesis of new heteropolymetallic derivatives, we carried out

reactions of  $\text{U}(\text{acac})_4$  with a variety of Schiff bases,  $\text{H}_2\text{L}^i$  or  $\text{H}_4\text{L}^i$ , represented in Fig. 1. The reactions with  $\text{H}_2\text{L}^i$  ( $i = 1–4$ ) did not afford the expected products but gave instead the  $[\text{UL}^i_2]$  complexes while reactions with  $\text{H}_4\text{L}^6$  and  $\text{H}_4\text{L}^7$  afforded tri- and tetranuclear clusters which are, with the octanuclear compound  $[\text{U}_8\text{L}_4\text{Cl}_{10}\text{O}_4]^{2-}$ ,<sup>14</sup> unique examples of homo-polynuclear complexes containing  $\text{U}(\text{IV})$  ions and Schiff-base ligands. Here we present the synthesis and crystal structures of these complexes or their thf solvates, emphasizing the versatility, flexible nature and associating capacity of the Schiff-base ligands.

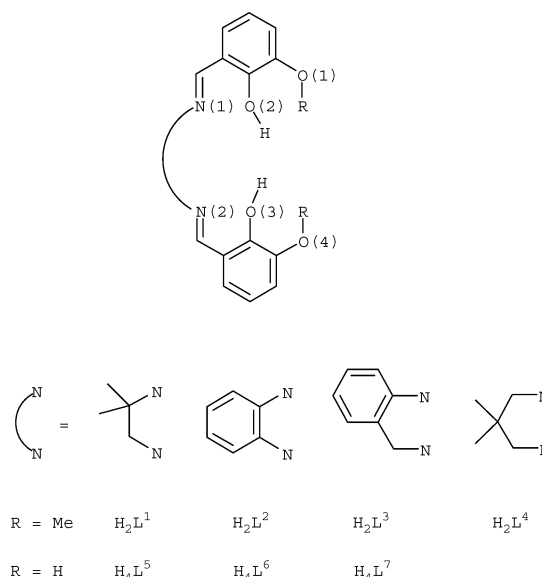


Fig. 1 The Schiff bases under study, with numbering scheme.

## Results and discussion

### Synthesis of the complexes

Treatment of  $\text{U}(\text{acac})_4$  with one mol equivalent of the Schiff bases  $\text{H}_2\text{L}^1$  or  $\text{H}_2\text{L}^2$  [ $\text{H}_2\text{L}^1 = N,N'$ -bis(3-methoxysalicylidene)-2-methyl-1,2-propanediamine,  $\text{H}_2\text{L}^2 = N,N'$ -bis(3-methoxy-

salicylidene)-1,2-phenylenediamine] in refluxing thf led to the formation of the  $[\text{UL}^i_2]$  complexes (**1** and **2** for  $i = 1$  or  $2$ , respectively). Only one of the two possible isomers of **1** and **2**, with the Schiff-base ligands adopting either a meridional or sandwich orientation (Fig. 2), was detected in solution by  $^1\text{H}$  NMR spectroscopy. The non equivalence of the methyl group of the diimino chain of  $\text{L}^1$  in **1** indicates that the complex exists as the sandwich isomer in solution. Complete conversion of  $\text{U}(\text{acac})_4$  into **1** and **2** was achieved after further addition of one mol equivalent of  $\text{H}_2\text{L}^i$ . At the early stages of these transformations, the  $^1\text{H}$  NMR spectra of the reaction mixtures showed, in addition to the signals corresponding to  $\text{U}(\text{acac})_4$  and **1** or **2**, other resonances which revealed the presence of the mono-(Schiff-base) compounds  $[\text{UL}^i(\text{acac})_3]$ . Thus, the expected products of reaction (1) were transiently observed but they could not be isolated because equilibrium (2) was totally shifted towards the formation of **1** and **2**. The rapid disproportionation of  $[\text{UL}^i(\text{acac})_2]$  is in contrast to the stability of  $[\text{U}(\text{salen})(\text{acac})_2]$ , which was synthesized from  $[\text{U}(\text{salen})\text{Cl}_2(\text{thf})_2]$ ; it is also noteworthy that the latter was isolated in quantitative yield from the comproportionation reaction of  $[\text{U}(\text{salen})_2]$  and  $\text{UCl}_4$ .<sup>15</sup>

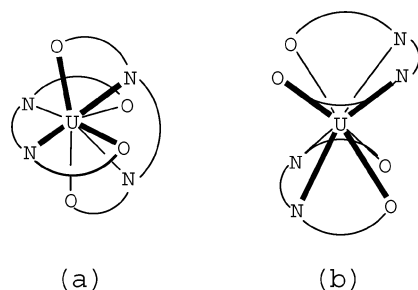
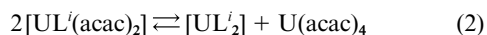
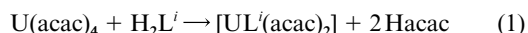


Fig. 2 Schematic representation of the meridional (a) and sandwich (b) isomers of the  $[\text{ML}^i_2]$  complexes.



Compounds **1** and **2** were alternatively obtained by treating  $\text{U}(\text{acac})_4$  with the sodium salts  $\text{Na}_2\text{L}^1$  and  $\text{Na}_2\text{L}^2$  of the Schiff bases. These reactions, being slower than those with  $\text{H}_2\text{L}^i$  and giving  $\text{Na}(\text{acac})$  as a by-product, are less practical for preparative syntheses of the  $[\text{UL}^i_2]$  complexes. The dark brown powder of **1** and dark brown crystals of **2** were deposited from their thf solution, with yields of 76 and 88%, respectively. X-Ray diffraction analysis (*vide infra*) revealed that **2** presents in the solid state a meridional orientation of the two Schiff-base ligands (Fig. 2) and it is likely that it adopts the same isomeric form in solution. The other isomer of **2**, with the  $\text{L}^2$  ligands in a sandwich arrangement, was neither observed in solution nor in the solid state.

Distinct facts emerged from the reactions of  $\text{U}(\text{acac})_4$  and  $\text{H}_2\text{L}^3$  [ $\text{H}_2\text{L}^3 = N,N'$ -bis(3-methoxysalicylidene)-2-aminobenzylamine]. An equimolar mixture of the two reactants led to equilibrium (2) in which  $[\text{UL}^3(\text{acac})_2]$  and  $[\text{UL}^3_2]$  (**3**) were in the relative proportions of 60 : 40. Moreover, the  $^1\text{H}$  NMR spectra showed the presence of the two possible isomers of **3**, in a molar ratio of 65 : 35. These two isomers, in the same molar ratio of 65 : 35, were the sole uranium compounds obtained by treatment of  $\text{U}(\text{acac})_4$  with two mol equivalents of  $\text{H}_2\text{L}^3$  or  $\text{Na}_2\text{L}^3$ . Dark orange crystals of the meridional isomer of **3** (*vide infra*) were isolated in 73% yield by crystallization from thf solutions. These crystals were homogeneous in their colour and their parallelepiped shape, and all the crystals selected for X-ray diffraction analysis presented the same cell parameters. However, their  $^1\text{H}$  NMR spectra in thf solution showed, here again, the presence of the two isomers in the same 65 : 35 molar ratio; this ratio was equal to 85 : 15 at  $-80^\circ\text{C}$ . These results can

be explained by the occurrence of a rapid equilibrium between the two isomers of **3** in solution; it is likely that the most abundant and stable isomer is the meridional, which is the only one to have been isolated in crystalline form. To the best of our knowledge, these observations provide the first indications of the existence of such an equilibrium between the isomeric forms of a bis(Schiff base) metal compound. In contrast to **3**, the meridional and sandwich isomers of the zirconium compound  $[\text{Zr}(\text{salophen})_2]$ , which were respectively synthesized by reactions of  $\text{ZrCl}_4$  with  $\text{H}_2\text{salophen}$  and  $\text{Na}_2\text{salophen}$ , and crystallographically characterized, were found to be thermally non-interconvertible.<sup>16,17</sup> It is possible that reactions of  $\text{U}(\text{acac})_4$  with  $\text{H}_2\text{L}^3$  or  $\text{Na}_2\text{L}^3$  gave initially the two isomers of **3** with distinct molar ratios, before their rapid equilibration. The distinct behaviour of **3** in solution, with respect to that of  $\text{Zr}(\text{salophen})_2$ , can be accounted for by the greater size of the 5f ion and the more ionic character of the U–O and U–N bonds which facilitate the intramolecular exchange of the Schiff-base ligands.

Reaction of  $\text{U}(\text{acac})_4$  with  $\text{H}_2\text{L}^4$  [ $\text{H}_2\text{L}^4 = N,N'$ -bis(3-methoxysalicylidene)-2,2-dimethyl-1,3-propanediamine] was similar to those with  $\text{H}_2\text{L}^1$  and  $\text{H}_2\text{L}^2$ ;  $[\text{UL}^4_2]$  (**4**) was the only final uranium compound which was isolated as dark orange crystals in 65% yield. X-Ray crystallography showed that **4**, like **2** and **3**, exists as the meridional isomer in the solid state (*vide infra*). However, reactions with  $\text{H}_2\text{L}^4$  and  $\text{Na}_2\text{L}^4$  followed a distinct course since the latter gave in its first steps a mixture of  $[\text{UL}^4(\text{acac})_2]$  and the two isomeric forms of **4**. The sandwich isomer of **4** distinguishable by the two magnetically non equivalent methyl groups of the diimino chain, appeared as a kinetic product which was rapidly transformed into the more stable meridional isomer. This difference between the reactions of  $\text{U}(\text{acac})_4$  with  $\text{H}_2\text{L}^4$  and  $\text{Na}_2\text{L}^4$  is reminiscent of that between the reactions of  $\text{ZrCl}_4$  with  $\text{H}_2\text{salophen}$  and  $\text{Na}_2\text{salophen}$ .<sup>16,17</sup>

The syntheses of complexes **1–4** show that the relative stabilities of the mono- and bis(Schiff base) complexes of general formula  $[\text{ML}^i\text{X}_2]$  and  $[\text{ML}^i_2]$ , and of the meridional and sandwich isomers of  $[\text{ML}^i_2]$ , are much influenced by the nature of X and the structure of the diimino chain of the  $\text{L}^i$  ligand. In particular, the distinct substitution of the three-carbon diimino bridge in  $\text{H}_2\text{L}^3$  and  $\text{H}_2\text{L}^4$  led to very different products distribution in their reactions with  $\text{U}(\text{acac})_4$ . First studies on the crystal structures of  $[\text{M}(\text{salophen})_2]$  compounds ( $\text{M} = \text{Zr}$ ,<sup>16</sup>  $\text{Ce}$ ,<sup>18</sup>  $\text{Th}$ <sup>7</sup>) suggested that the smaller Zr ion could accommodate the two Schiff-base ligands in a meridional configuration, while this geometry was not possible in the case of the larger Ce and Th ions because of severe torsional strains on the ligands. In line with these arguments, it was also asserted that, in contrast to  $[\text{Th}(\text{salophen})_2]$ <sup>7</sup> which would be constrained to adopt a sandwich structure, formation of the meridional isomer of  $[\text{Th}(\text{MeOsalen})_2]$ <sup>8</sup> was permitted owing to the greater flexibility of the salen ligand. This hypothesis was invalidated after the later isolation of the sandwich isomer of  $[\text{Zr}(\text{salophen})_2]$  which demonstrated that the structure of this compound was dependent on its mode of preparation.<sup>17</sup> The results reported here also indicate, contrary to previous assumptions, that  $[\text{Th}(\text{salophen})_2]$  and **2** adopt distinct configurations, although the size of the 5f ions and the flexibility of the Schiff-base ligands in these compounds are quite similar. On the other hand, the equilibrium between the two isomeric forms of **3** clearly shows that such isomers of a  $[\text{ML}^i_2]$  complex would have comparable stabilities, even if a single isomer is obtained by crystallization.

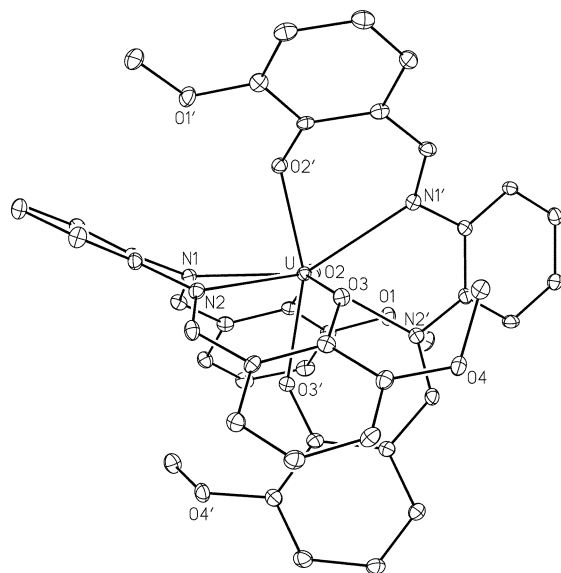
The  $[\text{UL}^i(\text{acac})_2]$  complexes ( $i = 1–4$ ) were characterized by their  $^1\text{H}$  NMR spectra. Compounds **1–4** were characterized by their elemental analyses (C, H, N) and their  $^1\text{H}$  NMR spectra; the crystal structures of **2**·thf, **3** and **4**·thf have been determined.

Reaction of  $\text{U}(\text{acac})_4$  with one mol equivalent of  $\text{H}_4\text{L}^5$  in thf afforded the expected product  $[\text{U}(\text{H}_2\text{L}^5)(\text{acac})_2]$  (**5**) in 65%

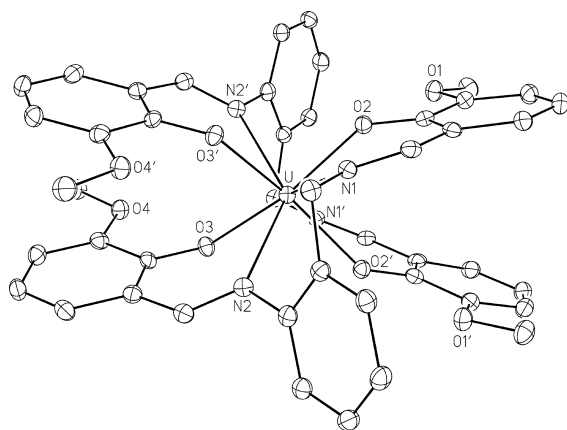
yield.<sup>11</sup> The crystal structure of **5**·thf consists of dimers ensured by intermolecular hydrogen bonds that link the terminal uncoordinated OH groups of  $\text{H}_2\text{L}^5$  to one another and to oxygen atoms of the acac ligands. In contrast, similar reactions of  $\text{U}(\text{acac})_4$  with  $\text{H}_4\text{L}^6$  and  $\text{H}_4\text{L}^7$  [ $\text{H}_4\text{L}^6 = N,N'$ -bis(3-hydroxysalicylidene)-1,2-phenylenediamine and  $\text{H}_4\text{L}^7 = N,N'$ -bis(3-hydroxysalicylidene)-2-aminobenzylamine] led to the unpredicted formation of the tri- and tetranuclear  $\text{U}(\text{IV})$  complexes  $[\text{U}_3(\text{L}^6)(\text{HL}^6)_2(\text{acac})_2]$  (**6**) and  $[\text{U}_4(\text{HL}^7)_4(\text{H}_2\text{L}^7)_2]$  (**7**) in which the uranium atoms are associated by Schiff-base ligands. While the  $[\text{U}_8\text{L}_6\text{Cl}_{10}\text{O}_4]^{2-}$  ion, one of the highest nuclearity assemblages in the chemistry of uranium compounds, was obtained accidentally and could not be synthesized in a controlled way,<sup>14</sup> compounds **6** and **7** were formed in a serendipitous but reproducible manner and were isolated as analytically pure dark brown and light brown crystals, in 45 and 63% yield, respectively. The  $^1\text{H}$  NMR spectra of **6** and **7** are very complicated, exhibiting a number of overlapping signals which were not attributed. The crystal structures of thf solvates of **6** and **7** were determined by X-ray diffraction analysis.

### Crystal structures of the complexes

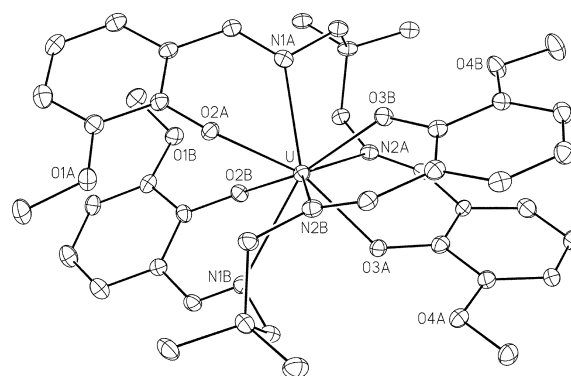
The crystal structures of **2**·thf, **3** and **4**·thf, shown in Figs. 3–5, present many common features and will be discussed together. These compounds are the first mononuclear Schiff-base



**Fig. 3** View of the complex  $[\text{U}(\text{L}^2)]\cdot\text{thf}$  (**2**·thf). The hydrogen atoms and the tetrahydrofuran molecule are omitted for clarity. Displacement ellipsoids are drawn at the 20% probability level. Symmetry code: '  $-x, y, 1.5 - z$ .



**Fig. 4** View of the complex  $[\text{U}(\text{L}^3)]$  (**3**). The hydrogen atoms are omitted for clarity. Displacement ellipsoids are drawn at the 20% probability level. Symmetry code: '  $-x, y, 0.5 - z$ .



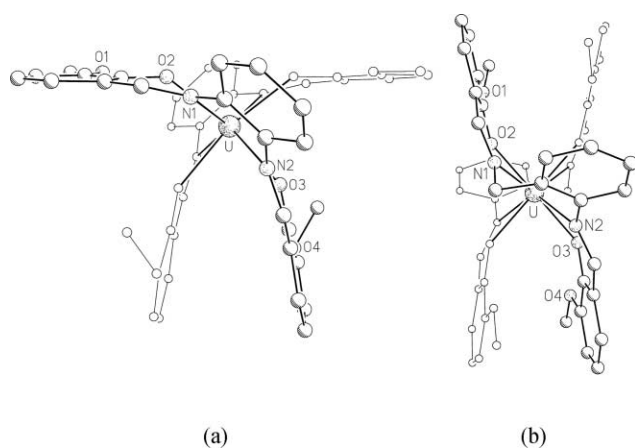
**Fig. 5** View of the complex  $[\text{U}(\text{L}^4)]\cdot\text{thf}$  (**4**·thf). The hydrogen atoms and the tetrahydrofuran molecule are omitted for clarity. Displacement ellipsoids are drawn at the 20% probability level.

complexes of uranium(IV) with a 1 : 2 stoichiometry to be structurally characterized, since the three other examples reported previously are 1 : 1 species, the uranium coordination sphere being completed either by two chlorine and two thf,<sup>9</sup> two chlorine and two pyridine<sup>10</sup> or two acetylacetonate ligands.<sup>11</sup> Among the present ligands,  $\text{L}^2$  is the only one with a two-carbon diimino chain comparable in size to those found in the 1 : 1 complexes, albeit more rigid, whereas  $\text{L}^3$  and  $\text{L}^4$  contain larger and more flexible three-carbon diimino bridges.

The asymmetric unit corresponds to half a molecule in compounds **2**·thf and **3**, the other half being generated by the binary axis containing the uranium atom, and to a complete molecule in **4**·thf. In all cases the metal ion is bound to the two oxygen and two nitrogen atoms defining the inner site of each Schiff base, which is also the case in the previous 1 : 1 complexes. The mean U–O and U–N bond lengths are 2.23(2) and 2.596(12) Å in **2**, 2.214(13) and 2.63(6) Å in **3** and 2.228(7) and 2.610(6) Å in **4** (Table 1). These values can be compared to those in the 1 : 1 compounds, 2.15(4) and 2.62(4),<sup>9</sup> 2.17(2) and 2.62(3)<sup>10</sup> and 2.22(3) and 2.64(4) Å.<sup>11</sup> The two mean planes defined by the atoms N(1), N(2), O(2) and O(3) are nearly perpendicular in each complex, with dihedral angles of 87.70(9), 89.94(6) and 89.04(13)° in **2**, **3** and **4**, respectively; the two Schiff bases are thus in the meridional orientation. However, the maximum deviations of these atoms from their mean planes are 0.009(3), 0.196(2) and 0.257(3)/0.296(3) Å and the uranium atoms are displaced from the planes by 0.196(3), 0.007(2) and 0.034(3)/0.019(3) Å in **2**, **3** and **4**, respectively (two independent Schiff bases in the last case). These values evidence a difference between complex **2** and complexes **3** and **4**, which is related to the higher rigidity of ligand  $\text{L}^2$  with respect to  $\text{L}^3$  and  $\text{L}^4$ . The Schiff base in **2** adopts the usual “umbrella” or “boat” shape,<sup>19</sup> with the four atoms of the inner site nearly coplanar, a dihedral angle of 78.8(2)° between the two terminal aromatic rings and roughly equivalent dihedral angles of 43.09(15) and 37.3(2)° between each terminal aromatic ring and the mean  $\text{N}_2\text{O}_2$  plane. This conformation allows the uranium atom to be close to, but not exactly inside the  $\text{N}_2\text{O}_2$  plane, its displacement being towards the convex side of the ligand. In contrast, the Schiff bases in **3** and **4** are in the so-called “stepped” conformation,<sup>19</sup> with the terminal aromatic rings on either side of the mean  $\text{N}_2\text{O}_2$  plane. The dihedral angle between these two rings is 14.6(2)° in **3** and 18.8(3)° for the two ligands in **4**, whereas the dihedral angles between the aromatic rings and the  $\text{N}_2\text{O}_2$  plane are 33.00(17) and 39.84(14)° in **3** and 40.7(2), 40.6(2), 32.9(2) and 34.21(19)° in **4**. As a result of these different conformations, the overall shape of **2** is markedly different from that of **3** and **4**, as shown in Fig. 6: two terminal aromatic rings are nearly parallel one to the other and the other two are nearly coplanar in **2**, while two pairs of nearly parallel rings are encountered in **3** and **4**. The uranium atom in **2** is in a distorted dodecahedral environment<sup>20,21</sup> defined by the two trapezia

**Table 1** Selected bond lengths (Å) and angles (°) in the complexes

|        |            |           |                  |            |            |           |                  |            |
|--------|------------|-----------|------------------|------------|------------|-----------|------------------|------------|
| 2·thf  | U–O(2)     | 2.246(4)  | O(2)–U–N(1)      | 70.04(15)  |            |           |                  |            |
|        | U–O(3)     | 2.218(4)  | N(1)–U–N(2)      | 62.65(15)  |            |           |                  |            |
|        | U–N(1)     | 2.587(5)  | N(2)–U–O(3)      | 69.97(15)  |            |           |                  |            |
|        | U–N(2)     | 2.604(5)  | O(3)–U–O(2)      | 154.56(15) |            |           |                  |            |
| 3      | U–O(2)     | 2.205(3)  | O(2)–U–N(1)      | 69.90(11)  |            |           |                  |            |
|        | U–O(3)     | 2.223(3)  | N(1)–U–N(2)      | 73.13(11)  |            |           |                  |            |
|        | U–N(1)     | 2.583(4)  | N(2)–U–O(3)      | 69.61(11)  |            |           |                  |            |
|        | U–N(2)     | 2.667(4)  | O(3)–U–O(2)      | 148.63(11) |            |           |                  |            |
| 4·thf  | U–O(2A)    | 2.236(4)  | O(2A)–U–N(1A)    | 70.36(17)  | U–O(2B)    | 2.222(4)  | O(2B)–U–N(1B)    | 70.44(16)  |
|        | U–O(3A)    | 2.232(4)  | N(1A)–U–N(2A)    | 70.18(17)  | U–O(3B)    | 2.222(4)  | N(1B)–U–N(2B)    | 70.26(17)  |
|        | U–N(1A)    | 2.603(6)  | N(2A)–U–O(3A)    | 70.07(16)  | U–N(1B)    | 2.616(6)  | N(2B)–U–O(3B)    | 70.06(16)  |
|        | U–N(2A)    | 2.615(6)  | O(3A)–U–O(2A)    | 151.50(16) | U–N(2B)    | 2.606(5)  | O(3B)–U–O(2B)    | 152.10(16) |
| 6·3thf | U(1)–O(2A) | 2.365(6)  | O(2A)–U(1)–N(1A) | 65.8(2)    | U(3)–O(2B) | 2.379(6)  | O(2B)–U(3)–N(1B) | 72.3(2)    |
|        | U(1)–O(3A) | 2.323(6)  | N(1A)–U(1)–N(2A) | 61.0(2)    | U(3)–O(3B) | 2.175(6)  | N(1B)–U(3)–N(2B) | 61.1(3)    |
|        | U(1)–N(1A) | 2.589(7)  | N(2A)–U(1)–O(3A) | 68.1(2)    | U(3)–N(1B) | 2.546(8)  | N(2B)–U(3)–O(3B) | 69.3(2)    |
|        | U(1)–N(2A) | 2.607(8)  | O(3A)–U(1)–O(2A) | 61.9(2)    | U(3)–N(2B) | 2.602(8)  | O(3B)–U(3)–O(2B) | 83.6(2)    |
|        | U(1)–O(1B) | 2.622(6)  | O(1B)–U(1)–O(2A) | 65.7(2)    | U(3)–O(2C) | 2.327(6)  | O(2C)–U(3)–N(1C) | 72.0(2)    |
|        | U(1)–O(1)  | 2.326(6)  | O(1B)–U(1)–O(3A) | 67.0(2)    | U(3)–O(3C) | 2.167(6)  | N(1C)–U(3)–N(2C) | 60.2(2)    |
|        | U(1)–O(2)  | 2.316(7)  | O(1B)–U(1)–O(2)  | 83.7(2)    | U(3)–N(1C) | 2.577(8)  | N(2C)–U(3)–O(3C) | 69.4(2)    |
|        | U(1)–O(3)  | 2.423(6)  | O(1)–U(1)–O(2)   | 72.2(2)    | U(3)–N(2C) | 2.622(8)  | O(3C)–U(3)–O(2C) | 84.5(2)    |
|        | U(1)–O(4)  | 2.321(6)  | O(3)–U(1)–O(4)   | 68.5(2)    |            |           |                  |            |
|        | U(2)–O(1A) | 2.326(6)  | O(1A)–U(2)–O(2A) | 66.3(2)    |            |           |                  |            |
|        | U(2)–O(2A) | 2.398(6)  | O(2A)–U(2)–O(3A) | 60.5(2)    |            |           |                  |            |
|        | U(2)–O(3A) | 2.392(6)  | O(3A)–U(2)–O(4A) | 65.8(2)    |            |           |                  |            |
|        | U(2)–O(4A) | 2.370(6)  | O(4A)–U(2)–O(1A) | 167.2(2)   |            |           |                  |            |
|        | U(2)–O(1B) | 2.342(6)  | O(1B)–U(2)–O(2B) | 69.1(2)    |            |           |                  |            |
|        | U(2)–O(2B) | 2.468(6)  | O(2B)–U(2)–O(2C) | 70.8(2)    |            |           |                  |            |
|        | U(2)–O(1C) | 2.222(6)  | O(2C)–U(2)–O(1C) | 66.8(2)    |            |           |                  |            |
|        | U(2)–O(2C) | 2.520(6)  | O(1C)–U(2)–O(1B) | 154.0(2)   |            |           |                  |            |
| 7·5thf | U(1)–O(2A) | 2.226(13) | O(2A)–U(1)–N(1A) | 71.5(5)    | U(3)–O(2C) | 2.230(15) | O(2C)–U(3)–N(1C) | 71.1(5)    |
|        | U(1)–O(3A) | 2.388(13) | N(1A)–U(1)–N(2A) | 73.1(6)    | U(3)–O(3C) | 2.352(14) | N(1C)–U(3)–N(2C) | 72.2(6)    |
|        | U(1)–N(1A) | 2.580(17) | N(2A)–U(1)–O(3A) | 70.1(5)    | U(3)–N(1C) | 2.608(18) | N(2C)–U(3)–O(3C) | 69.8(6)    |
|        | U(1)–N(2A) | 2.586(16) | O(3A)–U(1)–O(2A) | 146.2(5)   | U(3)–N(2C) | 2.601(18) | O(3C)–U(3)–O(2C) | 147.6(5)   |
|        | U(1)–O(3B) | 2.473(12) | O(3B)–U(1)–O(4B) | 68.0(5)    | U(3)–O(3D) | 2.523(12) | O(3D)–U(3)–O(4D) | 66.8(5)    |
|        | U(1)–O(4B) | 2.191(13) | O(1F)–U(1)–O(2F) | 68.4(5)    | U(3)–O(4D) | 2.183(14) | O(1E)–U(3)–O(2E) | 66.9(5)    |
|        | U(1)–O(1F) | 2.442(13) | O(3B)–U(1)–O(1F) | 68.1(3)    | U(3)–O(1E) | 2.445(14) | O(3D)–U(3)–O(1E) | 66.1(5)    |
|        | U(1)–O(2F) | 2.266(12) |                  |            | U(3)–O(2E) | 2.310(13) |                  |            |
|        | U(2)–O(2B) | 2.237(13) | O(2B)–U(2)–N(1B) | 71.1(5)    | U(4)–O(2D) | 2.246(14) | O(2D)–U(4)–N(1D) | 70.5(6)    |
|        | U(2)–O(3B) | 2.408(12) | N(1B)–U(2)–N(2B) | 73.7(5)    | U(4)–O(3D) | 2.427(14) | N(1D)–U(4)–N(2D) | 77.3(6)    |
|        | U(2)–N(1B) | 2.589(17) | N(2B)–U(2)–O(3B) | 70.6(5)    | U(4)–N(1D) | 2.581(18) | N(2D)–U(4)–O(3D) | 71.1(5)    |
|        | U(2)–N(2B) | 2.628(16) | O(3B)–U(2)–O(2B) | 145.7(5)   | U(4)–N(2D) | 2.601(17) | O(3D)–U(4)–O(2D) | 143.2(5)   |
|        | U(2)–O(3A) | 2.539(14) | O(3A)–U(2)–O(4A) | 66.3(5)    | U(4)–O(3C) | 2.522(15) | O(3C)–U(4)–O(4C) | 67.1(5)    |
|        | U(2)–O(4A) | 2.214(15) | O(4E)–U(2)–O(1F) | 76.2(5)    | U(4)–O(4C) | 2.181(16) | O(1E)–U(4)–O(4F) | 76.4(5)    |
|        | U(2)–O(4E) | 2.163(15) | O(3A)–U(2)–O(1F) | 64.3(3)    | U(4)–O(1E) | 2.496(12) | O(3C)–U(4)–O(1E) | 65.4(3)    |
|        | U(2)–O(1F) | 2.496(13) |                  |            | U(4)–O(4F) | 2.168(17) |                  |            |

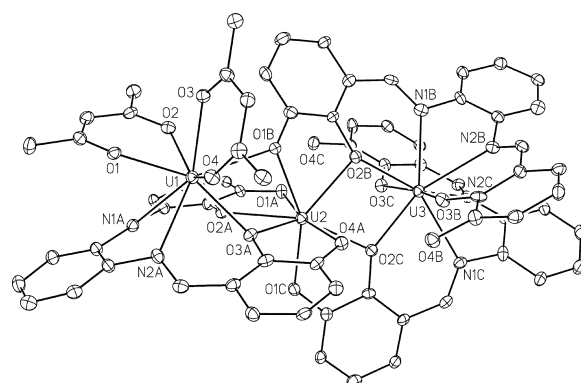


**Fig. 6** Views of (a)  $[U(L^2)_2] \cdot \text{thf}$  (**2**·thf) and (b)  $[U(L^3)_2]$  (**3**) showing the different conformations of the Schiff bases. Hydrogen atoms and solvent molecules are omitted for clarity. The atoms of one of the Schiff bases have been reduced for clarity.

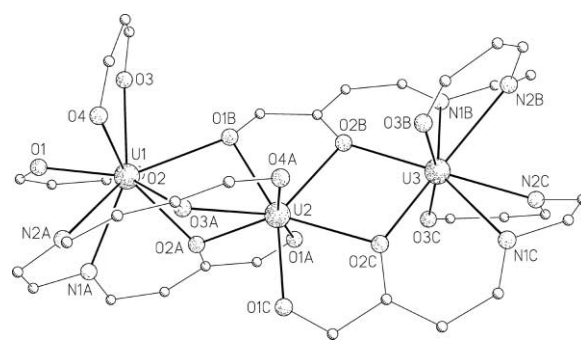
formed with the nitrogen and oxygen atoms of each  $N_2O_2$  cavity; the *A* and *B* sites of the dodecahedron are occupied by the N and O atoms, respectively. A dodecahedral configuration was also observed in the other uranium(IV) complexes with Schiff bases, either 1 : 1 mononuclear with the metal in the inner site,<sup>10,11</sup> 1 : 1 heterobinuclear with the uranium in the outer site,<sup>12</sup> or 1 : 2 heterotrinuclear with the uranium atom in the outer sites of two perpendicular Schiff bases.<sup>13</sup> The structure of **2** is very similar to that of  $[\text{Th}(3\text{-MeOsalen})_2]$ <sup>8</sup> and the meridional isomer of  $[\text{Zr}(\text{salophen})_2]$ .<sup>16</sup> In relation with the lengthening of the diimino chain of  $L^3$  and  $L^4$ , the coordination geometry of **3** and **4** is distorted away from the dodecahedron (DOD) towards the square antiprism (SAP) which is defined by the distorted square faces N(1), O(2), N(2'), O(3') and N(2), O(3), N(1'), O(2') in **3** or N(1A), O(2A), N(2B), O(3B) and N(2A), O(3A), N(1B), O(2B) in **4**; these faces are planar within  $\pm 0.09$  Å and almost parallel with dihedral angles of  $0.39(13)$  and  $1.8(2)^\circ$  in **3** and **4**, respectively. As previously outlined,<sup>21</sup> the  $\delta$  dihedral angle is the most powerful criterion to clearly distinguish the DOD and SAP polyhedra. In **2**, the  $\delta$  angles are equal to  $23.51(10)$ ,  $27.9(2)$ ,  $27.9(2)$  and  $31.13(12)^\circ$ ; these values are close to that of  $29.5^\circ$  characterizing the DOD. The corresponding  $\delta$  angles are equal to  $8.42(19)$ ,  $8.42(19)$ ,  $28.14(8)$  and  $31.32(8)^\circ$  in **3**, and to  $8.0(3)$ ,  $6.2(3)$ ,  $36.9(3)$  and  $36.5(3)^\circ$  in **4**, showing the approach to the SAP geometry where  $\delta_1 = \delta_2 = 0^\circ$  and  $\delta_3 = \delta_4 = 52.4^\circ$ . It is interesting to note that in the crystal structures of the cerium and thorium complexes  $[\text{M}(\text{salophen})_2]$  ( $\text{M} = \text{Ce}, ^{18} \text{Th}^7$ ) and of the second isomer of  $[\text{Zr}(\text{salophen})_2]$ ,<sup>17</sup> the two Schiff-base ligands adopt the “sandwich” orientation and the metal is found in a SAP configuration, the square faces being defined by two nitrogen and two oxygen atoms from the same ligand. Such isomers of **3** and **4** have been obtained from reaction of  $\text{U}(\text{acac})_4$  and  $\text{H}_2\text{L}^i$  ( $i = 3, 4$ ), as shown by the NMR spectra, but crystals of these species were not isolated.

The arrangement of the two Schiff bases around the metal atom in **2** brings the aromatic ring bearing O(3) and its symmetry-related equivalent in such proximity that an intramolecular  $\pi$ – $\pi$  interaction between them is likely [distance between centroids  $3.802(4)$  Å, dihedral angle between the two rings  $19.7^\circ$ ]. Due to the different Schiff-base conformations, two such interactions (thus involving all the terminal aromatic rings) are found in compounds **3** [distances between centroids  $4.034(3)$  and  $3.609(3)$  Å, dihedral angles  $24.4$  and  $12.3^\circ$ , respectively] and **4** [distances between centroids  $4.006(4)$  and  $3.756(4)$  Å, dihedral angles  $17.9$  and  $15.9^\circ$ , respectively].

The crystal structure of a thf solvate of **6**,  $[\text{U}_3(\text{L}^6)(\text{HL}^6)_2(\text{acac})_2] \cdot 3\text{thf}$ , is represented in Fig. 7, and a simplified view is shown in Fig. 8. No symmetry element, even approximate, is present. The three uranium atoms are in different environments



**Fig. 7** View of  $[\text{U}_3(\text{L}^6)(\text{HL}^6)_2(\text{acac})_2] \cdot 3\text{thf}$  (**6**·3thf). Hydrogen atoms and solvent molecules are omitted for clarity. Displacement ellipsoids are drawn at the 20% probability level.



**Fig. 8** Simplified view of **6**·3thf. The complex core and the carbon skeleton only are represented. Atoms are shown as spheres, the carbon ones being arbitrarily reduced.

and the Schiff bases A, B and C are involved differently in complexation. This is at variance with the much more symmetrical octanuclear cluster with the same ligand  $L^6$ ,  $[\text{U}_8(\text{L}^6)_4\text{Cl}_{10}\text{O}_4]^{2-}$ , which we have described previously.<sup>14</sup> The uranium atom U(1) in **6** is bound to the inner  $N_2O_2$  site of Schiff base A, to the terminal oxygen atom O(1B) of Schiff base B and to two acac ligands; U(3) is bound to the inner sites of the two Schiff bases B and C and U(2), which bridges these two subunits, is bound to the outer O<sub>4</sub> site of Schiff base A and to the oxygen atoms O(1) and O(2) of Schiff bases B and C. The first of these subunits is very different from the complex  $[\text{U}(\text{H}_2\text{L}^5)(\text{acac})_2]$  (**5**) since U(1) is as far as  $1.621(4)$  Å from the mean  $N_2O_2$  plane of the inner cavity [maximum deviation  $0.030(4)$  Å] whereas the uranium atom in **5** is located in the mean  $N_2O_2$  plane and the two acac ligands are on either side of this plane. The Schiff base A adopts an “umbrella” conformation, with U(1) on the convex side, but the dihedral angle between the two terminal aromatic rings,  $17.6(5)^\circ$ , is much smaller than in compound **2**, and the two acac ligands are on the same side of the mean  $N_2O_2$  plane. The mean U(1)–O(phenoxide) and U(1)–N bond lengths are  $2.34(3)$  and  $2.598(13)$  Å; the latter is close to the values in compounds **2**, **3** and **4**, but the former is larger by about  $0.1$  Å, in line with the bridging nature of O(2A) and O(3A) and the different location of the metal atom. The mean U(1)–O(acac) bond length is  $2.35(5)$  Å, equal to the value in **5** and in agreement with the mean value of  $2.32(5)$  Å for the uranium(IV) acac complexes present in the Cambridge Structural Database.<sup>22</sup> Finally, the U(1)–O(1B) bond length,  $2.622(6)$  Å, is a very long one, in keeping with the bridging role of O(1B). The coordination geometry of U(1) is distorted capped square antiprismatic,<sup>20</sup> with atoms O(2A), N(1A), N(2A), O(3A) and O(1B), O(1), O(2), O(4) defining the two square faces and the acac atom O(3) in capping position.

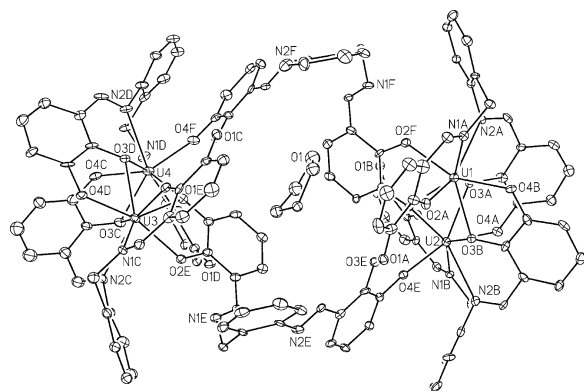
The mean U(3)–N bond length of  $2.59(3)$  Å and the average U(3)–O distances of  $2.35(4)$  and  $2.171(6)$  Å for bridging [O(2B)

and O(2C)] and non-bridging [O(3B) and O(3C)] oxygen atoms are unexceptional. The two Schiff bases B and C adopt “umbrella” conformations, with dihedral angles of 66.2(3) and 72.4(3)° between the two terminal aromatic rings, slightly smaller than in **2**. The displacements of U(3) with respect to the mean N<sub>2</sub>O<sub>2</sub> planes [maximum deviations 0.002(4) and 0.135(4) Å] are 1.336(4) and 1.334(4) Å, smaller than in the case of U(1). The two N<sub>2</sub>O<sub>2</sub> planes are nearly parallel, with a dihedral angle of 11.4(3)°, and the eight-coordination geometry of U(3) is distorted square antiprismatic, each N<sub>2</sub>O<sub>2</sub> site corresponding to one square face.

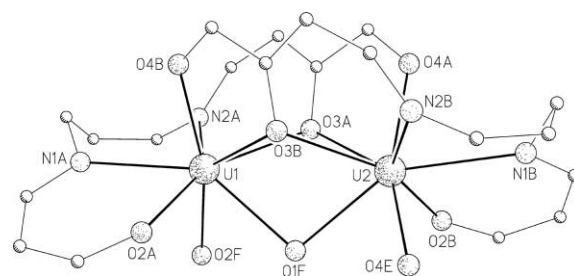
The mean U(2)–O distance is 2.42(7) Å for bridging atoms [O(2A), O(3A), O(1B), O(2B), O(2C)], whereas O(1C) only is associated to a bond length [2.222(6) Å] characteristic of non-bridging oxygen atoms. The U(2)–O(1A) and U(2)–O(4A) distances are longer than usual due to the involvement of O(1A) and O(4A) in hydrogen bonds, as will be seen hereafter. Charge equilibrium requires two oxygen atoms to be protonated in **6**. In the absence of crystallographic evidence as to the location of these protons, the most likely hypothesis is that they are located on the non-coordinating atoms O(4B) and O(4C). These two atoms are at hydrogen bonding distances from O(1A) and O(4A) [O(4B) ⋯ O(4A) 2.746(9), O(4C) ⋯ O(1A) 2.845(9) Å]. It has been shown that, in such Schiff-base complexes, involvement of a uranium-coordinated phenoxide group in a hydrogen bond results in a lengthening of the U–O bond by about 0.09 Å.<sup>19,23</sup> If such a value is taken into account, the U(2)–O(1A) and U(2)–O(4A) bond lengths of 2.326(6) and 2.370(6) Å are only slightly longer than expected for non-bridging oxygen atoms. The coordination geometry of the eight-coordinate U(2) atom is distorted dodecahedral, with a dihedral angle of 85.26(18)° between the mean planes defined by O(1A)–O(4A) [maximum deviation 0.058(4) Å] and O(1B), O(2B), O(1C) and O(2C) [maximum deviation 0.167(4) Å], which both contain U(2) within 0.054(4) Å.

No intramolecular  $\pi$ – $\pi$  stacking interaction is present in **6**, but intermolecular ones, between the aromatic ring bearing O(1A) and the central phenyl group of a neighbouring molecule (and reciprocal) result in dimerisation by weak interactions. A significant intramolecular CH– $\pi$  interaction is also noticeable, between a proton of the acac methyl group in  $\beta$  of O(4) and the aromatic ring bearing O(3A) [H ⋯ centroid distance 2.615 Å, C–H ⋯ centroid angle 155.6°].

The thf solvate of compound **7**, [U<sub>4</sub>(HL<sup>7</sup>)<sub>4</sub>(H<sub>2</sub>L<sup>7</sup>)<sub>2</sub>]·5thf, is a large species which can be viewed as two [U<sub>2</sub>(HL<sup>7</sup>)<sub>2</sub>] moieties bridged by two much distorted and elongated H<sub>2</sub>L<sup>7</sup> ligands (Fig. 9). No symmetry is crystallographically imposed, but the complex admits a pseudo-binary axis which links U(1) to U(3) and U(2) to U(4). Two nearly identical subunits corresponding to the pairs U(1), U(2) and U(3), U(4) can thus be considered (Fig. 10). In contrast to complex **6**, the four uranium atoms in **7** are in rather similar environments, each of them being bound



**Fig. 9** View of [U<sub>4</sub>(HL<sup>7</sup>)<sub>4</sub>(H<sub>2</sub>L<sup>7</sup>)<sub>2</sub>]·5thf (**7**·5thf). Hydrogen atoms and solvent molecules (except the central tetrahydrofuran) are omitted for clarity. Displacement ellipsoids are drawn at the 10% probability level.



**Fig. 10** View showing the coordination sphere of one dinuclear subunit in **7**·5thf. The complex core and the carbon skeleton only are represented. Atoms are shown as spheres, the carbon ones being arbitrarily reduced.

to the four atoms of the inner N<sub>2</sub>O<sub>2</sub> site of a Schiff base (the ligands labelled A, B, C and D correspond to U(1), U(2), U(3) and U(4), respectively), to the two oxygen atoms O(3) and O(4) of the other Schiff base in the subunit, and to two oxygen atoms from the bridging ligands, denoted E and F. The difference between the two uranium atoms in each dinuclear subunit results from the dissymmetric ligation mode of E and F. Thus, the Schiff base F [or E] is linked to U(1) [or U(3)] *via* its two oxygen atoms O(1) and O(2), and to U(4) [or U(2)] *via* O(4) only. However, the two uranium atoms in each subunit are bound to two oxygen atoms from E and F because U(1) and U(2), and U(3) and U(4), are bridged by O(1F) and O(1E), respectively. Each of the six Schiff-base ligands has one non-coordinated oxygen atom, two coordinated to one metal atom and one bridging. Eight oxygen atoms must be protonated for charge equilibrium, which, in the most likely hypothesis, correspond to the six non-coordinated ones and the two atoms O(2E) and O(2F), the latter being associated to U–O bond lengths of 2.310(13) and 2.266(12) Å, larger than usual for mono-coordinated phenoxide groups. Overall, the mean U–O bond lengths are 2.20(3) Å for mono-coordinating oxygen atoms [O(2E) and O(2F) excluded] and 2.46(6) Å for bridging ones.

The conformation of ligands A–D does not match the usual descriptions as “umbrella” or “stepped”, since the four atoms of the inner N<sub>2</sub>O<sub>2</sub> site are nearly coplanar with the aromatic ring bearing O(1) and O(2), whereas the second terminal aromatic ring and the phenyl group of the diimino chain are located on either side of this plane. The mean N<sub>2</sub>O<sub>2</sub> planes are associated to rather large maximum deviations in the range 0.158(10)–0.269(11) Å and the displacements of the metal atoms out of these planes are in the range 0.021(7)–0.061(8) Å. The dihedral angles between the mean N<sub>2</sub>O<sub>2</sub> planes and the nearly coplanar terminal aromatic rings are 5.7(11)–16.5(10)° and those with the other terminal rings are 48.7(7)–52.5(7)°. The Schiff bases E and F display a much elongated shape for which inner and outer sites cannot be defined any more. With respect to usual conformations, the two terminal aromatic rings are rotated so that their respective oxygen atom pairs are pointing towards divergent directions, thus converting a compartmental ligand into a bridging one with coordinating sites located wide apart from each other.

The four uranium atoms are in dodecahedral environments. As indicated above, each metal atom is located in the mean N<sub>2</sub>O<sub>2</sub> plane of ligands A–D, albeit this plane is more distorted than in the previous complexes. The four other oxygen atoms around each metal, originating from two or three Schiff-base ligands, define mean O<sub>4</sub> planes with maximum deviations of 0.021(9)–0.105(7) Å which make dihedral angles of 88.9(3)–89.4(3)° with the mean N<sub>2</sub>O<sub>2</sub> planes; the displacement of uranium atoms out of these planes does not exceed 0.181(6) Å.

Few  $\pi$ – $\pi$  stacking interactions are present in **7** and these are intermolecular ones only. Concerning the weak interactions, more noticeable is the inclusion of a tetrahydrofuran molecule in the cavity defined by the two extended, bridging ligands E and F and the two dinuclear subunits. Apart from van der

Waals forces, CH– $\pi$  interactions involving in particular one terminal ring of ligands A and F [shortest CH...centroid distance 2.785 Å, C–H...centroid angle 154.5°] may contribute in maintaining this solvent molecule in the cavity.

## Conclusion

The synthesis of the  $[\text{UL}^i(\text{acac})_2]$  or  $[\text{U}(\text{H}_2\text{L}^i)(\text{acac})_2]$  compounds, by treatment of  $\text{U}(\text{acac})_4$  with  $\text{H}_2\text{L}^i$  or  $\text{H}_4\text{L}^i$ , can be impeded either by the disproportionation reaction of  $[\text{UL}^i(\text{acac})_2]$ , giving the more stable  $[\text{UL}^i_2]$  complexes, or by further assembling reaction of  $[\text{U}(\text{H}_2\text{L}^i)(\text{acac})_2]$ , leading to polynuclear species. The distribution and the structure of the products clearly depend on small structural variations of the diimino chain of the Schiff base, and are difficult to predict and rationalize. The formation of clusters evidences the potential of Schiff bases as associating ligands for the design of polynuclear assemblies.

## Experimental

All reactions 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 thoroughly dried and deoxygenated by standard methods and distilled immediately before use;  $[\text{H}_8]\text{thf}$  and  $[\text{H}_5]\text{pyridine}$  were distilled over Na/K alloy or NaH, respectively, and stored over 3 Å molecular sieves. The Schiff bases  $\text{H}_2\text{L}^i$  ( $i = 1-4$ ) and  $\text{H}_4\text{L}^i$  ( $i = 6, 7$ )<sup>24</sup> and  $\text{U}(\text{acac})_4$ <sup>25</sup> were synthesized by published methods. The  $^1\text{H}$  NMR spectra were recorded on a Bruker DPX 200 instrument and referenced internally using the residual protio solvent resonances relative to tetramethylsilane. Elemental analyses were performed by Analytische Laboratorien at Lindlar (Germany).

### Synthesis of the complexes

**$[\text{UL}^1_2]$  (1).** A flask was charged with  $\text{U}(\text{acac})_4$  (17.8 mg, 0.0281 mmol) and  $\text{H}_2\text{L}^1$  (20.0 mg, 0.0562 mmol) in thf (2 mL). The reaction mixture was refluxed for 4 d and the dark brown powder of **1** was deposited from the orange solution. The product was filtered off and dried under vacuum (20.2 mg, 76%) (Found: C, 50.61; H, 4.67; N, 6.06.  $\text{C}_{40}\text{H}_{44}\text{N}_4\text{O}_8\text{U}$  requires C, 50.74; H, 4.65; N, 5.92%). The  $^1\text{H}$  NMR spectrum showed the presence of the sandwich isomer of **1** in solution.  $\delta_{\text{H}}$  ( $[\text{H}_8]\text{thf}$ , 23 °C) –34.90 and –30.16 (2  $\times$  2H,  $\text{NCH}_2$ ), –27.99 and –19.89 (2  $\times$  6H, Me), 3.96 and 5.47 (2  $\times$  6H, OMe), 10.67, 10.72, 10.76, 10.94, 11.51, 13.37, 15.48 and 15.98 (8  $\times$  2H, aromatic H and  $\text{CH}=\text{N}$ ).

**$[\text{UL}^2_2]$  (2).** A flask was charged with  $\text{U}(\text{acac})_4$  (16.8 mg, 0.0266 mmol) and  $\text{H}_2\text{L}^2$  (20.0 mg, 0.0532 mmol) in thf (2 mL). The reaction mixture was refluxed for 1 d and single crystals of **2** were deposited as dark brown needles from the dark red solution. The product was filtered off and dried under vacuum (23.1 mg, 88%). (Found: C, 53.60; H, 3.85; N, 5.81.  $\text{C}_{44}\text{H}_{36}\text{N}_4\text{O}_8\text{U}$  requires C, 53.55; H, 3.65; N, 5.68%). The  $^1\text{H}$  NMR spectrum showed the presence of a single isomer of **2** in solution, which is likely the meridional isomer in view of the crystal structure.  $\delta_{\text{H}}$  ( $[\text{H}_5]\text{pyridine}$ , 23 °C) –8.18 and –1.23 (2  $\times$  4H,  $\text{N}-\text{C}_6\text{H}_4-\text{N}$ ), 4.24 (12H, OMe), 4.96, 10.71, 10.78 and 15.89 (4  $\times$  4H, aromatic H and  $\text{CH}=\text{N}$ ).

**$[\text{UL}^3_2]$  (3).** A flask was charged with  $\text{U}(\text{acac})_4$  (16.3 mg, 0.0256 mmol) and  $\text{H}_2\text{L}^3$  (20.0 mg, 0.0512 mmol) in thf (2 mL). The reaction mixture was refluxed for 1 d and single crystals of **3** were deposited as dark orange parallelepipeds from the yellow-orange solution. The product was filtered off and dried under vacuum (18.9 mg, 73%) (Found: C, 54.46; H, 4.07; N, 5.66.  $\text{C}_{46}\text{H}_{40}\text{N}_4\text{O}_8\text{U}$  requires C, 54.44; H, 3.94; N, 5.52%). The

$^1\text{H}$  NMR spectra of **3** showed the presence of two equilibrating isomers in relative proportions of 65 : 35 at 23 °C; this ratio was equal to 85 : 15 at –80 °C. More stable isomer  $\delta_{\text{H}}$  ( $[\text{H}_8]\text{thf}$ , 23 °C) –53.20 and –28.65 (2  $\times$  2H,  $\text{NCH}_2$ ), –10.03, –1.36, –0.73 and 1.28 (4  $\times$  2H, Ph of diimino chain), 1.82 and 3.10 (2  $\times$  6H, OMe), 10.96, 11.01, 11.92, 12.77, 14.98, 15.03, 15.64 and 17.70 (8  $\times$  2H, aromatic H and  $\text{CH}=\text{N}$ ). Less stable isomer  $\delta_{\text{H}}$  ( $[\text{H}_8]\text{thf}$ , 23 °C) –58.81 and –27.28 (2  $\times$  2H,  $\text{NCH}_2$ ), –8.88, –1.46, –0.92 and 1.38 (4  $\times$  2H, Ph of diimino chain), 2.56 and 3.05 (2  $\times$  6H, OMe), 10.57, 10.83, 11.21, 11.84, 13.34, 15.10, 15.30 and 20.10 (8  $\times$  2H, aromatic H and  $\text{CH}=\text{N}$ ). It is likely that the more stable isomer is the meridional one, in view of the crystal structure of **3**.

**$[\text{UL}^4_2]$  (4).** A flask was charged with  $\text{U}(\text{acac})_4$  (17.1 mg, 0.0270 mmol) and  $\text{H}_2\text{L}^4$  (20.0 mg, 0.0540 mmol) in thf (2 mL). The reaction mixture was refluxed for 1 d and single crystals of **4** were deposited as dark orange platelets from the yellow-orange solution. The product was filtered off and dried under vacuum (17.1 mg, 65%) (Found: C, 52.01; H, 5.08; N, 5.90.  $\text{C}_{42}\text{H}_{48}\text{N}_4\text{O}_8\text{U}$  requires C, 51.75; H, 4.93; N, 5.75%). The  $^1\text{H}$  NMR spectrum showed the presence of the meridional isomer of **4** in solution.  $\delta_{\text{H}}$  ( $[\text{H}_8]\text{thf}$ , 23 °C) –53.55 and –25.85 (2  $\times$  4H,  $\text{NCH}_2$ ), –17.75 (12H, Me), 4.73 (12H, OMe), 11.12, 11.73, 15.86 and 16.56 (4  $\times$  4H, aromatic H and  $\text{CH}=\text{N}$ ).

**$[\text{U}_3\text{L}^6(\text{HL}^6)_2(\text{acac})_2]$  (6).** A flask was charged with  $\text{U}(\text{acac})_4$  (36.4 mg, 0.0575 mmol) and  $\text{H}_4\text{L}^6$  (20.0 mg, 0.0575 mmol) in thf (2 mL). The reaction mixture was refluxed for 1 d and single crystals of **6** were deposited as dark brown parallelepipeds from the dark red solution. The product was filtered off and dried under vacuum (16.8 mg, 45%) (Found: C, 42.15; H, 2.52; N, 4.73.  $\text{C}_{70}\text{H}_{52}\text{N}_6\text{O}_{16}\text{U}$  requires C, 43.17; H, 2.67; N, 4.32%).

**$[\text{U}_4(\text{HL}^7)_4(\text{H}_2\text{L}^7)_2]$  (7).** A flask was charged with  $\text{U}(\text{acac})_4$  (23.4 mg, 0.0368 mmol) and  $\text{H}_4\text{L}^7$  (20.0 mg, 0.0552 mmol) in thf (2 mL). The reaction mixture was refluxed for 1 d and light brown crystals of **7**·5thf were deposited from the orange-brown solution. The product was filtered off and dried under vacuum (18.0 mg, 63%) (Found: C, 48.38; H, 3.05; N, 5.56.  $\text{C}_{126}\text{H}_{92}\text{N}_{12}\text{O}_{24}\text{U}$  requires C, 48.65; H, 2.96; N, 5.41%).

### Reactions of $\text{U}(\text{acac})_4$ with one mol equivalent of $\text{H}_2\text{L}^i$ or $\text{Na}_2\text{L}^i$ ( $i = 1-4$ )

**Reaction with  $\text{H}_2\text{L}^1$ .** An NMR tube was charged with  $\text{U}(\text{acac})_4$  (8.9 mg, 0.0140 mmol) and  $\text{H}_2\text{L}^1$  (5.0 mg, 0.0140 mmol) in  $[\text{H}_8]\text{thf}$  (0.4 mL). After 12 h at 20 °C, the spectrum of the dark red solution showed the presence of  $\text{U}(\text{acac})_4$  (two signals at  $\delta$  –3.95 and 12.45 in relative intensities 6 : 1), **1** (the same isomer as the one obtained in the preparative synthesis) and  $[\text{UL}^1(\text{acac})_2]$  in relative proportions of 20 : 20 : 60.  $\delta_{\text{H}}$  ( $[\text{H}_8]\text{thf}$ , 23 °C) –47.07 and –38.98 (2  $\times$  1H,  $\text{NCH}_2$ ), –29.02 (6H, Me), –23.75 (12H, acac), –23.05 and –21.78 (2  $\times$  1H, acac), 14.32 and 17.59 (2  $\times$  3H, OMe), 20.59, 21.82, 27.35, 28.05, 28.58, 30.38, 32.11 and 37.86 (8  $\times$  1H, aromatic H and  $\text{CH}=\text{N}$ ). The tube was heated at 80 °C for 24 h and the spectrum showed the presence of an equimolar mixture of  $\text{U}(\text{acac})_4$  and **1**.

**Reaction with  $\text{H}_2\text{L}^2$ .** An NMR tube was charged with  $\text{U}(\text{acac})_4$  (8.4 mg, 0.0133 mmol) and  $\text{H}_2\text{L}^2$  (5.0 mg, 0.0133 mmol) in  $[\text{H}_8]\text{thf}$  (0.4 mL). After 1 h at 20 °C, dark brown crystals were deposited from the dark red solution and the spectrum showed the signals of  $\text{U}(\text{acac})_4$  and other very weak resonances which have not been attributed. The crystalline product was identified as **2** (the same isomer as the one obtained in the preparative synthesis) by recording the NMR spectra in  $[\text{H}_5]\text{pyridine}$ .

**Table 2** Crystal data and structure refinement details

|   | 2·thf   | 3   | 4·thf   | 6·3thf  | 7·5thf   |
|---|---|---|---|---|--|
| Empirical formula                                 | C <sub>48</sub> H <sub>44</sub> N <sub>4</sub> O <sub>9</sub> U | C <sub>46</sub> H <sub>40</sub> N <sub>4</sub> O <sub>8</sub> U | C <sub>46</sub> H <sub>56</sub> N <sub>4</sub> O <sub>9</sub> U | C <sub>82</sub> H <sub>76</sub> N <sub>6</sub> O <sub>19</sub> U <sub>3</sub> | C <sub>146</sub> H <sub>132</sub> N <sub>12</sub> O <sub>29</sub> U <sub>4</sub> |
| <i>M</i> /g mol <sup>−1</sup>                     | 1058.90   | 1014.85   | 1046.98   | 2163.58   | 3470.76  |
| Crystal system                                    | Monoclinic  | Monoclinic  | Monoclinic  | Triclinic   | Triclinic  |
| Space group                                       | <i>C</i> 2/ <i>c</i>  | <i>C</i> 2/ <i>c</i>  | <i>P</i> 2 <sub>1</sub> / <i>c</i>                              | <i>P</i> 1  | <i>P</i> 1   |
| <i>a</i> /Å                                       | 21.8781(12)   | 16.2340(9)  | 13.5520(8)  | 12.7267(7)  | 16.1915(19)  |
| <i>b</i> /Å                                       | 13.3968(8)  | 15.5787(10)   | 30.4244(18)   | 15.4321(10)   | 16.7590(16)  |
| <i>c</i> /Å                                       | 14.9141(6)  | 17.2083(10)   | 11.2771(5)  | 19.6494(11)   | 27.666(3)  |
| <i>α</i> /°                                       | 90  | 90  | 90  | 75.846(5)   | 86.586(7)  |
| <i>β</i> /°                                       | 110.327(3)  | 111.144(4)  | 111.138(3)  | 87.788(5)   | 89.518(6)  |
| <i>γ</i> /°                                       | 90  | 90  | 90  | 78.112(5)   | 63.252(7)  |
| <i>V</i> /Å <sup>3</sup>                          | 4099.0(4)   | 4059.1(4)   | 4336.8(4)   | 3661.4(4)   | 6690.6(12)   |
| <i>Z</i>  | 4   | 4   | 4   | 2   | 2  |
| <i>D</i> <sub>c</sub> /g cm <sup>−3</sup>         | 1.716   | 1.661   | 1.604   | 1.962   | 1.723  |
| <i>μ</i> (MoKα)/mm <sup>−1</sup>                  | 4.025   | 4.059   | 3.803   | 6.698   | 4.907  |
| <i>F</i> (000)                                    | 2096  | 2000  | 2096  | 2076  | 3384   |
| Reflections collected                             | 13990   | 13741   | 29627   | 24724   | 39048  |
| Independent reflections                           | 3766  | 3833  | 8193  | 12772   | 21991  |
| Observed reflections [ <i>I</i> > 2σ( <i>I</i> )] | 3376  | 3235  | 5507  | 8498  | 9842   |
| <i>R</i> <sub>int</sub>                           | 0.065   | 0.073   | 0.109   | 0.072   | 0.073  |
| Parameters refined                                | 296   | 269   | 549   | 994   | 1726   |
| <i>R</i> <sub>1</sub>                             | 0.039   | 0.035   | 0.046   | 0.049   | 0.082  |
| <i>wR</i> <sub>2</sub>                            | 0.098   | 0.063   | 0.080   | 0.089   | 0.156  |
| <i>S</i>  | 1.143   | 1.049   | 1.001   | 1.026   | 1.012  |
| Δρ <sub>min</sub> /e Å <sup>−3</sup>              | −1.01   | −1.05   | −0.64   | −1.50   | −1.47  |
| Δρ <sub>max</sub> /e Å <sup>−3</sup>              | 1.26  | 0.65  | 0.50  | 1.18  | 1.24   |

**Reaction with H<sub>2</sub>L<sup>3</sup>.** An NMR tube was charged with U(acac)<sub>4</sub> (8.1 mg, 0.0128 mmol) and H<sub>2</sub>L<sup>3</sup> (5.0 mg, 0.0128 mmol) in [2H<sub>8</sub>]thf (0.4 mL). After 24 h at 20 °C, the spectrum of the dark red solution showed the presence of U(acac)<sub>4</sub>, the two isomers of **3** and [UL<sup>3</sup>(acac)<sub>2</sub>] in relative proportions of 18 : 12 : 6 : 64. δ<sub>H</sub> ([2H<sub>8</sub>]thf, −40 °C) −93.80 (1H, NCH<sub>2</sub>), −32.34 (3H, acac), −31.86 (1H, NCH<sub>2</sub>), −30.22, −24.21 and −19.31 (3 × 3H, acac), −18.80 and −14.41 (2 × 1H, acac), −13.22, −5.84, −2.75 and 0.78 (4 × 1H, Ph of diimino chain), 11.47 and 9.26 (2 × 3H, OMe), 20.03, 23.64, 28.03, 28.38, 32.37, 33.11, 41.58 and 45.97 (8 × 1H, aromatic H and CH=N). The relative proportions of the products did not change after prolonged heating of the solution. Further addition of one equivalent of H<sub>2</sub>L<sup>3</sup> led to the quantitative formation of the two isomers of **3**, in the same molar ratio of 65 : 35.

**Reaction with Na<sub>2</sub>L<sup>4</sup>.** An NMR tube was charged with U(acac)<sub>4</sub> (7.7 mg, 0.0121 mmol) and H<sub>2</sub>L<sup>4</sup> (5.0 mg, 0.0121 mmol) in [2H<sub>8</sub>]thf (0.4 mL). After 1 h at 20 °C, the spectrum of the yellow–orange solution showed the presence of U(acac)<sub>4</sub>, two isomers of **4** and [UL<sup>4</sup>(acac)<sub>2</sub>] in relative proportions of 28 : 14 : 14 : 44. The tube was heated at 65 °C for 24 h and the spectrum showed the presence of an equimolar mixture of U(acac)<sub>4</sub> and a single isomer of **4**, the same than the one obtained in the preparative synthesis. δ<sub>H</sub> for [UL<sup>4</sup>(acac)<sub>2</sub>] ([2H<sub>8</sub>]thf, 23 °C) −48.01 and −24.99 (2 × 2H, NCH<sub>2</sub>), −20.01 (1H, acac), −18.55 (12H, acac), −15.02 (3H, Me), −11.71 (1H, acac), −10.67 (3H, Me), 13.28 (2 × 3H, OMe), 19.97, 27.10, 28.85 and 37.67 (4 × 2H, aromatic H and CH=N). The other isomer of **4** which was transiently observed is the sandwich isomer. δ<sub>H</sub> ([2H<sub>8</sub>]thf, 23 °C) −41.03 and −24.52 (2 × 4H, NCH<sub>2</sub>), −20.06 and −14.62 (2 × 6H, Me), 8.68 (12H, OMe), 10.61, 11.52, 15.28 and 15.31 (4 × 4H, aromatic H and CH=N).

### Crystallography

The data were collected at 100(2) K on a Nonius Kappa-CCD area detector diffractometer<sup>26</sup> using graphite-monochromated Mo-Kα radiation (λ = 0.71073 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. A 180° φ-range was scanned with 2° steps during data collection, with a crystal-to-detector distance fixed to 28 mm, giving complete

data sets up to an angle θ<sub>max</sub> of 25.7°. The data were processed with DENZO-SMN.<sup>27</sup> The structures were solved by Patterson map interpretation (compound **1**) or by direct methods (all other compounds) with SHELXS-97 and subsequent Fourier-difference synthesis and refined by full-matrix least-squares on *F*<sup>2</sup> with SHELXL-97.<sup>28</sup> Absorption effects were corrected empirically with the program DELABS from PLATON.<sup>29</sup> The tetrahydrofuran solvent molecule in 2·thf is disordered around a symmetry centre and the oxygen atom was not located. All non-hydrogen atoms were refined with anisotropic displacement parameters, with some restraints on bond lengths, angles and/or displacement parameters for some disordered or badly behaving atoms, particularly those of the tetrahydrofuran molecules in compounds 2·thf and 7·5thf. The hydroxy protons were not found, nor introduced, in compounds 6·3thf and 7·5thf. All other hydrogen atoms in all compounds were introduced at calculated positions (except in the disordered tetrahydrofuran in 2·thf) and were treated as riding atoms with a displacement parameter equal to 1.2 (CH, CH<sub>2</sub>) or 1.5 (CH<sub>3</sub>) times that of the parent atom. Some short C ⋯ C or H ⋯ H contacts in 2·thf and 7·5thf involve atoms of the disordered or badly behaving solvent molecules and are likely due to their imperfect location. Some voids in 6·3thf and 7·5thf indicate the presence of other, unresolved solvent molecules. Crystal data and structure refinement details are given in Table 2. The molecular plots were drawn with SHELXTL.<sup>30</sup> All calculations were performed on a Silicon Graphics R5000 workstation.

CCDC reference numbers 233078–233082.

See <http://www.rsc.org/suppdata/dt/b4/b403459g/> for crystallographic data in CIF or other electronic format.

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