

# The template synthesis and X-ray crystal structure of the first dinuclear lanthanide(III) iminophenolate cryptate

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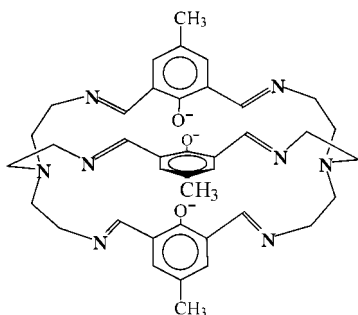
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Lanthanide ions act as templates in the formation of dinuclear Ln(III) complexes with a cryptand ligand bearing three phenolate groups; the presence of both lanthanide ions into the cavity of the cryptand was confirmed by X-ray structure analysis and spectroscopic data.

Encapsulating ligands can enhance some interesting properties that make complexes of the lanthanide(III) ions valuable for the development of different technological applications such as the selective extraction of metals, NMR shift and relaxation reagents, contrast-enhancing agents in magnetic resonance imaging and fluoroimmunoassay agents.<sup>1</sup> In particular, current interest in binuclear lanthanide complexes arises from their potential value in studying the nature and application of lanthanide metal–metal compounds in lasers<sup>2</sup> and phosphors,<sup>3</sup> the molecular recognition processes which govern lanthanide(III) cation pairing events<sup>4</sup> and their application in novel tunable photonic devices.<sup>5</sup>

Although a dinuclear europium(III) cryptate, synthesised by reaction of a europium salt with a preformed macrotricyclic tetralactam containing 1,10-phenanthroline units, has been reported without structural details<sup>6</sup> no examples, to date, of dinuclear lanthanide cryptates derived from iminophenolato-cryptands have appeared. This is surprising as several examples of homo- and hetero-polynuclear complexes of lanthanides with macrocycles have been described in the literature.<sup>7–9</sup> Here we report the first examples of dinuclear lanthanide complexes of an iminophenolate cryptand together with the crystal structure of a dilutetium(III) complex.

Metal-templated reactions between triethylammonium 2,6-diformyl-4-methylphenolate and tris(2-aminoethyl)amine in the presence of hydrated lanthanide nitrates (Ln = Gd–Lu) in a 3:2:2 mole ratio in absolute ethanol for ca. 12 h yield orange solids of formula  $[Ln_2L(NO_3)_2][NO_3] \cdot xH_2O \cdot yEtOH$  where L is the anionic cryptand shown in Scheme 1. Their FAB mass spectra display intense peaks corresponding to fragments  $[Ln_2L(NO_3)_2]^+$  and  $[Ln(L+H)]^+$ , confirming the presence of the macrobicycle in the complex. It is found that in all cases the former peak is clearly more intense than the latter, particularly



Scheme 1 Anionic cryptand L.

in case of Tb, Ho, Tm and Lu for which the peak due to  $[Ln_2L(NO_3)_2]^+$  appears with 100% base peak intensity.

Slow evaporation of ethanolic solutions of the lutetium cryptate gave orange crystals of X-ray quality. The structural analysis of this complex<sup>‡</sup> confirmed the presence of two metal ions in the cavity of the anionic Schiff-base macrobicycle receptor. The crystals contain the cation  $[Lu_2L(NO_3)_2]^+$ , an independent nitrate anion and highly disordered molecules of ethanol and water. Fig. 1 illustrates the structure of the cation. Both lutetium(III) ions have crystallographically identical coordination environments; each is bound to one bridgehead nitrogen atom, three imino-nitrogen atoms, and to the three  $\mu$ -phenolate oxygen atoms. Eight coordination is completed by one oxygen of a monodentate nitrate ion and the coordination polyhedron can be best described as distorted dodecahedron. The Lu–azomethine nitrogen distances are in the range 2.359–2.445 Å, similar and even shorter than those found in literature.<sup>11</sup> A strong interaction between Lu and the phenolate oxygens is shown by the short distance between them that falls in the range 2.286–2.363 Å. Only two X-ray crystal structures

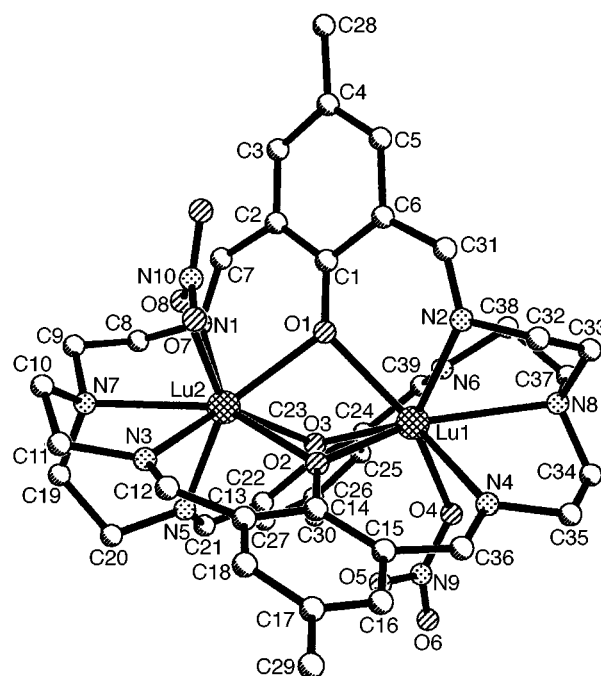


Fig. 1 Crystal structure of  $[Lu_2L(NO_3)_2]^+$ ; hydrogen atoms are omitted for simplicity. Selected bond lengths (Å): Lu(1)–O(3) 2.288(8), Lu(1)–O(2) 2.347(8), Lu(1)–O(1) 2.316(9), Lu(1)–N(6) 2.359(11), Lu(1)–O(4) 2.372(9), Lu(1)–N(4) 2.421(12), Lu(1)–N(2) 2.445(10), Lu(1)–N(8) 2.675(9), Lu(2)–O(1) 2.286(8), Lu(2)–O(7) 2.329(10), Lu(2)–O(3) 2.329(8), Lu(2)–O(2) 2.363(8), Lu(2)–N(1) 2.363(11), Lu(2)–N(5) 2.420(12), Lu(2)–N(3) 2.414(13), Lu(2)–N(7) 2.609(10).

of binuclear lutetium complexes with macrocycles have been reported.<sup>9</sup> In both cases the macrocycle receptors are calixarenes. The distance between the lutetium ions encapsulated into the cryptate we present here is 3.447(1) Å. This is considerably shorter than those reported in the literature (3.56 and 3.68 Å).<sup>9</sup>

The cryptand adopts a conformation resembling a triple helix twisting around a pseudo  $C_3$ -axis which runs through the two bridgehead nitrogen atoms. Both metal ions are deviated from this axis; nevertheless, the deviation is so slight that the symmetry of the cryptate can also be described as threefold. The angles between the phenolate ring planes are 69.9, 76.2 and 79.9°, while the distances between each two phenolate oxygens are O(1)···O(2) 2.73 Å, O(1)···O(3) 2.53 Å and O(2)···O(3) 2.80 Å. The distance between the bridgehead nitrogens is 8.65 Å, longer than that found for mononuclear lanthanide cryptates (8.36 Å)<sup>12</sup> with the protonated macrobicycle L, but shorter than that of [Cd<sub>2</sub>L]<sup>3+</sup> (9.01 Å).<sup>13</sup> This shows that the cryptand can expand or contract to fit the metal size or to accommodate two metal ions inside the cavity.

That the dinuclear structure is retained in solution is evidenced by the proton NMR spectrum run in (CD<sub>3</sub>)<sub>2</sub>SO. The spectrum of the related mononuclear lutetium complex<sup>12</sup> shows two signals for the azomethine hydrogens [ $\delta$  8.87 (d), 8.43 (s)], the latter is ascribed to the coordinated azomethines and the former arises as a consequence of proton transfer from the phenolic groups to the non-coordinated azomethines.<sup>12,14–16</sup> There is also a very broad signal centered on  $\delta$  12.50 which may be assigned to the O···HN<sup>+</sup> protons and signals due to the aromatic hydrogens [ $\delta$  7.73 (d,  $J = 1$ ), 7.59 (d,  $J = 1$  Hz)], ethylene bridges [ $\delta$  3.82 (3H), 3.68 (3H), 3.59 (3H), 3.27 (3H), 3.08 (3H), 2.94 (3H), 2.81 (6H)] and the methyl groups [ $\delta$  2.27 (s)]. The proton NMR spectrum of the dilutetium cryptate is simpler in the low field region and agrees with an effective  $C_3$  symmetry in solution. As expected, the very broad signal due to the phenolic protons presented in the mononuclear complex spectrum does not appear in that of the binuclear complex. Likewise, the two signals due to the azomethine hydrogens and the signals due to the aromatic protons became now in one signal for each type [ $\delta$  8.45 (s), 7.57 (s), respectively]. A complicated group of very broad signals [ $\delta$  2–4 (m)] due to the ethylene bridges are present indicating that the protons bonded to the same carbon atom are non-equivalent. The signal of the methyl groups [ $\delta$  2.29 (s)] is also observed.

Mononuclear lanthanide(III) cryptates derived from ligands closely related to L (the *para*-substituent on the phenol being *t*-Bu, CH<sub>3</sub>O or Cl) have been prepared by transmetallation of the appropriate sodium cryptates.<sup>14–17</sup> Attempts to introduce a second lanthanide ion cation have been unsuccessful, and it has been stated that this is probably due to the high coordination numbers and large radii of the lanthanides.<sup>15</sup>

In order to design cryptand receptors for more than one lanthanide(III) ion certain key features must be kept in mind: the high coordination numbers preferred by these cations, their large ionic radii and their high charge. In this respect the influence of the lanthanide contraction would suggest that accommodation of two cations from the second half of the series would be preferred. To be useful for dinuclear reception the ligands must have a large receptor cavity comprised of an adequate number of suitably disposed donor atoms. The anionic cryptand L possesses these features together with three phenolic groups which can serve as endogenous anionic groups capable of providing bridges between the lanthanide(III) ions so helping to overcome the electrical repulsions that would otherwise occur between two tripositive ions placed in close proximity. Previously we have described the lanthanide-assisted synthesis of Schiff-base macrobicycles as mononuclear lanthanide cryptates.<sup>12</sup> In the present work we have extended the application of this metal template method to assemble homodinuclear lanthanide(III) cryptates so providing the first opportunity to study the properties of two lanthanide ions held in close proximity and isolated from interaction with the solvent.

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## Notes and references

† [Gd<sub>2</sub>L][NO<sub>3</sub>]<sub>3</sub>·H<sub>2</sub>O·EtOH: yield: 30%. Found: C, 39.8; H, 4.3; N, 12.4. C<sub>41</sub>H<sub>53</sub>N<sub>11</sub>O<sub>14</sub>Gd<sub>2</sub> requires C, 39.6; H, 4.1; 12.8%. [Tb<sub>2</sub>L][NO<sub>3</sub>]<sub>3</sub>·H<sub>2</sub>O·EtOH: yield: 35%. Found: C, 39.7; H, 4.3; N, 12.4. C<sub>41</sub>H<sub>53</sub>N<sub>11</sub>O<sub>14</sub>Tb<sub>2</sub> requires C, 39.7; H, 4.3; N, 12.5%. [Dy<sub>2</sub>L][NO<sub>3</sub>]<sub>3</sub>·H<sub>2</sub>O·EtOH: yield: 15%. Found: C, 39.9; H, 4.3; N, 12.3. C<sub>41</sub>H<sub>53</sub>N<sub>11</sub>O<sub>14</sub>Dy<sub>2</sub> requires C, 39.6; H, 4.4; N, 12.4%. [Ho<sub>2</sub>L][NO<sub>3</sub>]<sub>3</sub>·H<sub>2</sub>O·EtOH: yield: 20%. Found: C, 39.3; H, 4.3; N, 12.3. C<sub>41</sub>H<sub>53</sub>N<sub>11</sub>O<sub>14</sub>Ho<sub>2</sub> requires C, 39.8; H, 4.4; N, 12.8%. [Tm<sub>2</sub>L][NO<sub>3</sub>]<sub>3</sub>·4H<sub>2</sub>O: yield: 30%. Found: C, 36.9; H, 4.2; N, 12.1. C<sub>39</sub>H<sub>53</sub>N<sub>11</sub>O<sub>16</sub>Tm<sub>2</sub> requires C, 36.3; H, 4.0; N, 12.3%. [Yb<sub>2</sub>L][NO<sub>3</sub>]<sub>3</sub>·2H<sub>2</sub>O·EtOH: yield: 15%. Found: C, 38.2; H, 4.3; N, 12.0. C<sub>41</sub>H<sub>53</sub>N<sub>11</sub>O<sub>15</sub>Yb<sub>2</sub> requires C, 38.3; H, 4.3; N, 12.0%. [Lu<sub>2</sub>L][NO<sub>3</sub>]<sub>3</sub>·2H<sub>2</sub>O·EtOH: yield: 15%. Found: C, 38.1; H, 4.3; N, 11.9. C<sub>41</sub>H<sub>53</sub>N<sub>11</sub>O<sub>15</sub>Lu<sub>2</sub> requires C, 38.5; H, 4.3; N, 12.1%.

‡ *Crystal data:* [Lu<sub>2</sub>C<sub>39</sub>H<sub>45</sub>N<sub>8</sub>O<sub>3</sub>(NO<sub>3</sub>)<sub>3</sub>]·CH<sub>3</sub>CH<sub>2</sub>OH·2.5H<sub>2</sub>O, Lu<sub>2</sub>C<sub>41</sub>H<sub>56</sub>N<sub>11</sub>O<sub>15.5</sub>,  $M = 1300.92$ ; orange block, 0.35 × 0.20 × 0.10 mm, tetragonal, space group  $P4_12_12$ ,  $a = 17.7057$  (2),  $b = 17.7057$  (2),  $c = 29.0649$  (5) Å,  $V = 9111.6$  (2) Å<sup>3</sup>,  $Z = 8$ ;  $D_c = 1.881$  Mg m<sup>-3</sup>,  $\mu = 4.392$  mm<sup>-1</sup>. Using Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 173 K, a total of 42911 reflections was collected, of which 5957 were independent. Owing to crystal nature and diffraction capabilities, only data to  $2\theta = 45^\circ$  were used for crystal refinement. Refinement converged with  $R_1 = 0.0429$ ,  $wR_2 = 0.0974$  for  $I > 2\sigma(I)$  and  $R_1 = 0.0595$ ,  $wR_2 = 0.1090$  for all data. CCDC 182/1101.

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