New Ligands for Complexation of Lanthanoids: The Synthesis and Structures of a Nonadentate Schiff-base Ligand (L^1) and of the Complexes $[ML^1(OH_2)](ClO_4)_3{\cdot}3MeNO_2$ (M = La, Pr) and $[YL^1](ClO_4)_3{\cdot}3MeCN$

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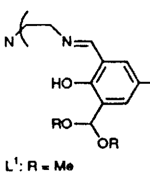
The synthesis and structures of a nonadentate Schiff-base ligand L^1, prepared from tris(2-aminoethyl)amine and 2,6-diformyl-4-methylphenol, and of its complexes with M^{III} ions (M = La, Pr and Y) are reported; $[ML^1(OH_2)](ClO_4)_3{\cdot}3MeNO_2$ (M = La, Pr) are ten-coordinate species while $[YL^1](ClO_4)_3{\cdot}3MeCN$ is nine-coordinate.

There is growing interest in polydentate and macrocyclic complexes of lanthanoids due to their uses as contrast agents in magnetic resonance imaging,[1] for rapid cleavage of RNA,[2] and because of their photochemical propeties.[3] As part of a study of complexation of compartmental ligands containing 2,6-diimino-4-methylphenol moieties,[4] we report herein a new polydentate ligand which forms stable complexes with lanthanoids, and which can be readily functionalised to give a series of related polydentate ligands. Our strategy is based on the use of open-chain polychelates for the rapid complexation of metal ions.

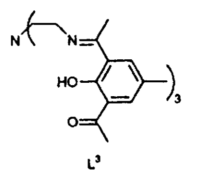
Reaction of 3 equivalents of 2,6-diformyl-4-methylphenol with 1 or 2 equivalents of tris(2-aminoethyl)amine (tren) in refluxing MeOH leads to the formation of a yellow solution. Concentration of the solution afforded a yellow product in high yield. This species has been fully characterised† and an X-ray diffraction study‡ of crystals grown by slow evaporation of a solution of the product in DMSO–MeOH reveals a tripodal Schiff-base ligand, L^1 (Fig. 1). Each arm contains four potential binding sites, an imine nitrogen, a phenolic oxygen and two acetal oxygens, the latter being formed by reaction of a formyl group with methanol used as solvent during synthesis. This appears to be more favourable than reaction of the formyl groups with a second equivalent of tren which would give a macrobicyclic ligand similar to those reported by Gagné and coworkers.[5] Related cyclised cryptand ligands based upon 2,6-diiminopyridyl moities have been reported recently.[6]

L^1 crystallises with a non-crystallographic threefold axis passing through N(1), the bridgehead nitrogen, the lone pair of which points into a cavity formed by the three arms of the ligand lying in the same direction. The strands are oriented such that the planes between the aromatic rings in neighbouring arms lie approximately 60° to one another, but with each ring perpendicular to the plane passing through the three imine nitrogens. Importantly, the O-atoms of the acetal groups point away from the central cavity of the metal-free ligand. The structure also shows evidence of hydrogen-bonding between phenol oxygens and imine nitrogens within the same arm.

Reaction of L^1 with hydrated $M(ClO_4)_3$§ (M = La, Pr, Y) in MeOH leads to the formation of a bright yellow solid which can be crystallised from $MeNO_2$–Et_2O (M = La, Pr) or MeCN–Et_2O (M = Y). Single-crystal X-ray structural determinations‡ reveal that the La and Pr complexes are isostructural and each crystallises as $[ML^1(H_2O)](ClO_4)_3{\cdot}3MeNO_2$. The cation shows ten-coordination with six acetal and three phenolic oxygens [O(1), O(4) and O(7)] of L^1 and an additional water molecule, O(10), bound to the metal centre [Fig. 2(*a*)]. The ligand is completely reorganised from the conformation observed in the metal-free structure, although there is still a non-crystallographic three-fold axis in the complex which passes through N(1), the metal centre and O(10) of the coordinated H_2O molecule. The M–O bond



L^1: R = Me
L^2: R = Et



L^3

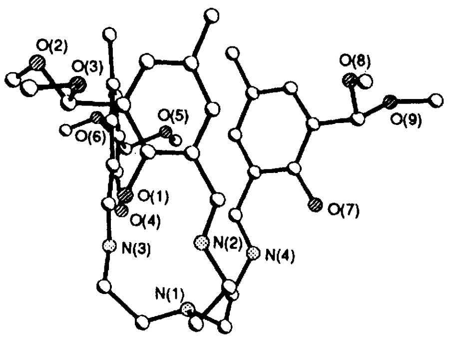


Fig. 1 View of structure of L^1 with numbering scheme adopted

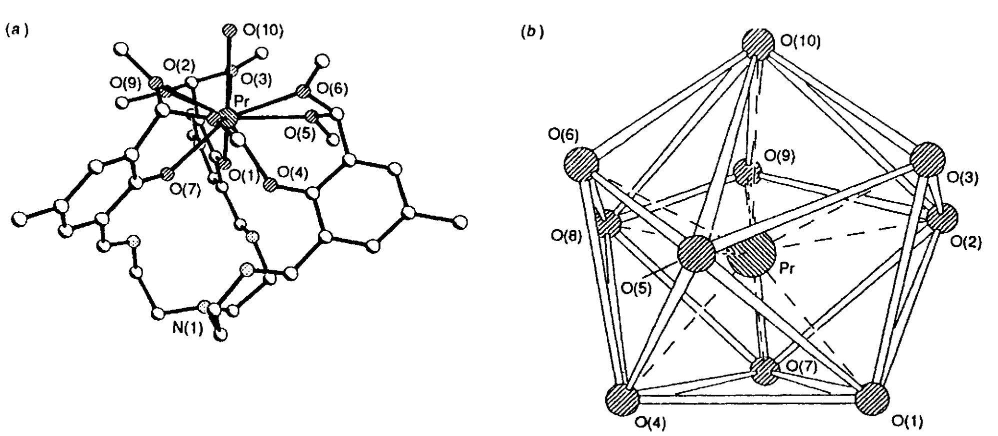


Fig. 2 View of structure (*a*) and metal core (*b*) of $[PrL^1(H_2O)]^{3+}$ with numbering scheme adopted Pr–O(1) 2.396(3), Pr–O(4) 2.409(3), Pr–O(7) 2.438(3), Pr–O(2) 2.567(3), Pr–O(3) 2.613(3), Pr–O(5) 2.658(3), Pr–O(6) 2.560(3), Pr–O(8(2.531(3), Pr–O(9) 2.654(3), Pr–O(10) 2.588(3) Å. Bond lengths for $[LaL^1(H_2O)]^{3+}$: La–O(1) 2.453(5), La–O(4) 2.462(5), La–O(7) 2.490(5), La–O(2) 2.650(5), La–O(3) 2.663(5), La–O(5) 2.697(5), La–O(6) 2.631(5), La–O(8) 2.587(5), La–O(9) 2.674(5), La–O(10) 2.626(5) Å.

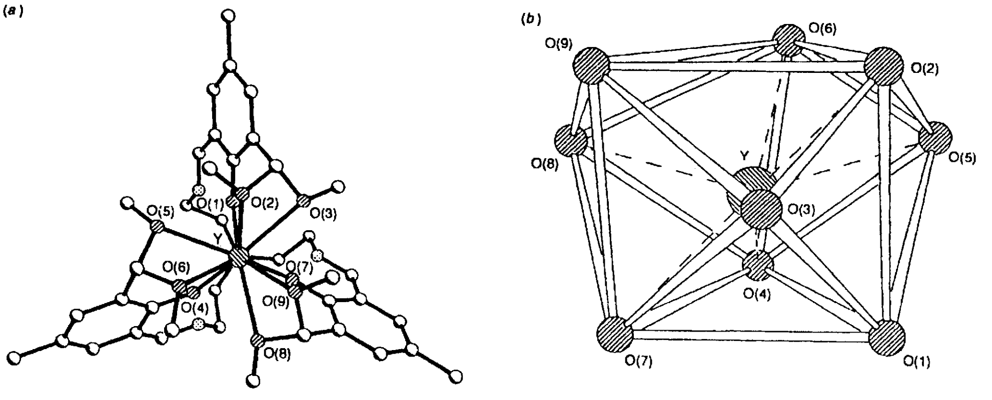


Fig. 3 View of structure (*a*) and metal core (*b*) of $[YL^1]^{3+}$ with numbering scheme adopted Y O(1) 2.240(5), Y–O(4) 2.230(5), Y–O(7) 2.243(5), Y–O(2) 2.432(5), Y–O(3) 2.526(5), Y–O(5) 2.542(5), Y–O(6) 2.400(5), Y–O(8) 2.526(5), Y–O(9) 2.412(5) Å

lengths depend on the nature of the O-donor. The shorter bonds involve the phenolic oxygen atoms {for $[LaL^1(H_2O)]^{3+}$ La–O 2.453(5)–2.490(5) Å; for $[PrL^1(H_2O)]^{3+}$ Pr–O 2.396(3) –2.438(3) Å[4]}, while those to acetal oxygens are longer {for $[LaL^1(H_2O)]^{3+}$ La–O 2.587(5)–2.697(5) Å; for $[PrL^1(H_2O)]^{3+}$ Pr–O 2.531(3)–2.658(3) Å}. The coordination polyhedra at M can be related to an icosahedron, with the three phenolic oxygens forming one triangular face, the six acetal oxygens forming a puckered six-membered ring above this triangular face, and the water molecule at the centre of what would be a final triangular face in an ideal icosahedron [Fig. 2(*b*)].

The complex $[YL^1](ClO_4)_3\cdot 3MeCN$ contains a nine-coordinate metal centre [Fig. 3(*a*)]. The lower coordination number compared to the La^{III} and Pr^{III} complexes is consistent with the smaller ionic radius of Y compared with La or Pr. As above, the bond lengths vary depending upon the type of O-donor: Y–O (phenol) 2.230(5)–2.243(5) Å, Y–O (acetal) 2.400(5)–2.542(5) Å. The coordination geometry is derived from a tricapped trigonal prism, with one triangular face formed by the three phenolic oxygens O(1), O(4) and O(7), and each pair of acetal oxygens, O(2), O(3), O(5), O(6), O(8) and O(9) occupying one face capping position and one vertex of the second triangle of the prism [Fig. 3(*b*)].

L^1 is the first ligand characterised of a series of related compounds, all of which are accessible from related reactions. Use of ethanol as a solvent leads to L^2 in which ethoxides rather than methoxides are present in the acetal. Condensation of 2,6-diacetyl-4-methylphenol with tren leads to L^3 in which the ketone is retained. Okawa and co-workers have reported related open chain mixed aldehyde-imino ligands using diamine substrates.[7] Metal complexation reactions of these polychelate ligands will be the subject of a future report.

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Footnotes

† Satisfactory elemental analyses were obtained for all compounds.

‡ *Crystal Data.* $C_{39}H_{54}N_4O_9$ **1**: M = 722.8, monoclinic, space group $P2_1/n$, a = 16.088(9), b = 13.353(10), c = 18.798(12) Å, β = 93.92(5)°, V = 4029 Å^3 [from 12 setting reflections ($17 \leqslant 2\theta \leqslant 25°$), λ = 0.71073 Å], Z = 4, D_c = 1.192 g cm^{-3}, T = 293 K, yellow tablet, μ = 0.085 mm^{-1}.

$C_{39}H_{56}Cl_3LaN_4O_{22}\cdot 3CH_3NO_2$ **2**: M = 1361.3, monoclinic, space group $P2_1/n$, a = 13.013(3), b = 25.73(2), c = 17.869(8) Å, β = 92.27(5)°, V = 5977 Å^3 [from 2θ values of 29 reflections measured at $\pm\omega$ ($24 \leqslant 2\theta \leqslant 28°$), λ = 0.71073 Å], Z = 4, D_c = 1.553 g cm^{-3}, T = 150 K, yellow lath, μ = 0.937 mm^{-1}.

$C_{39}H_{56}Cl_3N_4O_{22}Pr\cdot 3CH_3NO_2$ **3**: M = 1363.3, monoclinic, space group $P2_1/n$, a = 12.998(2), b = 25.265(8), c = 17.771(3) Å, β = 92.282(12)°, V = 5831 Å^3 [from 2θ values of 30 reflections measured at $\pm\omega$ ($30 \leqslant 2\theta \leqslant 32°$), λ = 0.71073 Å], Z = 4, D_c = 1.553 g cm^{-3}, T = 150 K, yellow lath, μ = 1.064 mm^{-1}.

$C_{39}H_{54}Cl_3N_4O_{21}Y\cdot 3CH_3CN$ **4**: M = 1233.3, monoclinic, space group $P2_1/c$, a = 17.381(13), b = 17.070(12), c = 19.835(14) Å, β = 94.74(6)°, V = 5865 Å^3 [from 9 setting reflections ($24 \leqslant 2\theta \leqslant 28°$), λ = 0.71073 Å], Z = 4, D_c = 1.397 g cm^{-3}, T = 220 K, yellow block, μ = 1.208 mm^{-1}.

Data collection and processing: Crystals of **2**–**4** were transferred in a film of mineral oil from the mother-liquor to a Stoë STADI-4 four-circle diffractometer, graphite-monochromated Mo-Kα X-radiation, ω-2θ scans, with learnt-profile method (W. Clegg, *Acta Crystallogr., Sect. A*, 1981, **37**, 22) and low-temperature (J. Cosier and A. M. Glazer, *J. Appl. Crystallogr*, 1986, **19**, 105). The structure of **1** was solved by direct methods, all other structures were solved by heavy-atom methods. Absorption corrections were applied to the data for the metal complexes. All structures displayed some disorder. L^1 was refined with all non-H atoms anisotropic, and with a similarity constraint linking the refinement of the three side-arms of the ligand, to give: $wR2$ = 0.386 for 6113 unique data ($2\theta \leqslant 50°$) [$R1$ = 0.0938 for 1810 observed reflections, $F > 4\sigma(F)$]. For the metal complexes the oxygen atoms of two of the three perchlorate anions were disordered over several sites, and were refined with partial site occupancies. The solvent molecules were also disordered over two orientations for each such molecule. All non-H atoms within the cations were refined anisotropically as were the Cl atoms of the anions to give: for **2** $wR2$ = 0.1439 for all 7604 unique data ($2\theta \leqslant 45°$) [$R1$ = 0.0500 for 5589 reflections with $F > 4\sigma(F)$]; for **3** $wR2$ = 0.1602 for all 10080 unique data ($2\theta \leqslant 45°$) [$R1$ = 0.0372 for 8917 reflections with $F > 4\sigma(F)$]; for **4** $wR2$ = 0.1830 for all 7628 unique data ($2\theta \leqslant 45°$) [$R1$ = 0.0553 for 4411 reflections with $F > 4\sigma(F)$]. All calculations used SHELXL-93 (G. M. Sheldrick, *J. Appl. Crystallogr.*, 1994, in the press).

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallograpic Data Centre. See Information for Authors, Issue No. 1.

§ Complexes of perchlorate salts are potentially explosive and should be handled in small quantities and with great care.

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