DALTON
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Formation of oligomeric lanthanide complexes with new tripodal poly(imino carboxylate) ligands

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Reaction of hydrated lanthanide(III) chloride ($LnCl_3 \cdot 6H_2O$) with tris-(2-aminoethyl)amine and the sodium salt of an α-ketocarboxylic acid afforded the trinuclear species $[(LnL)_2Na]^+$ which, on removal of Na^+, aggregate further in MeOH to yield the neutral eight-co-ordinate cyclic tetranuclear species $[Ln_4(L^1)_4]$ (Ln = Yb^{III} or Y^{III}), and the linear polymer $[Y_2(L^2)_2(MeOH)]_\infty$ with alternating eight- and nine-co-ordinate Y^{III} centres: recrystallisation of adducts of $[L^1]^{3-}$ from H_2O affords the nine-co-ordinate mononuclear species $[Ln(L^1)(OH_2)_2]$ (Ln = Sm^{III} or Gd^{III}).

There is currently considerable interest in the design of polydentate chelating ligands capable of forming stable complexes of lanthanides for the development of radiopharmaceuticals,[1] and as contrast agents for magnetic resonance imaging (MRI).[2] Much of the work on MRI agents has focused on poly(amino carboxylate) ligands,[3] especially 1,4,7,10-tetrakis(carboxymethyl)-1,4,7,10-tetraazacyclododecane (DOTA) and its derivatives.[4,5] As part of a study of the synthesis of new water-soluble, water-stable neutral lanthanide complexes, we report on a new series of tripodal complexes formed by the Schiff-base condensation of tris(2-aminoethyl)-amine and the sodium salt of an α-ketocarboxylic acid in the presence of the lanthanide ion (Ln) as templating agent. Related tripodal ligands formed by Schiff-base condensation of tris-(2-aminoethyl)amine with 2,6-diformyl-4-methylphenol,[6] 2,6-diformylpyridyl,[7] salicycaldehyde[8] and acetylacetone[8] have been reported previously, as have related dimeric bismuth[9] and trimeric gadolinium[4] complexes.

Addition of $LnCl_3 \cdot 6H_2O$ (Ln = Y^{III}, Sm^{III}, Gd^{III} or Yb^{III}) to 3 mol equivalents of the sodium salts of either pyruvic acid or α-ketobutyric acid in MeOH, followed by addition of 1 mol equivalent of tris-(2-aminoethyl)amine under reflux, affords a clear, pale yellow solution after 2 h. Addition of excess Et_2O affords a white precipitate of **1** (see Scheme 1) and NaCl in high yield. The fast atom bombardment mass spectrum of **1** shows a peak for $[(LnL)_2Na]^+$ although the assignment of **1** remains tentative, with co-ordination of additional solvent to Ln^{III} being likely. Sodium chloride can be removed by elution of a MeOH solution of **1** through a Sephadex LH-20 column, yielding crystals of the Na^+-free neutral complex **2**.† Crystals suit-

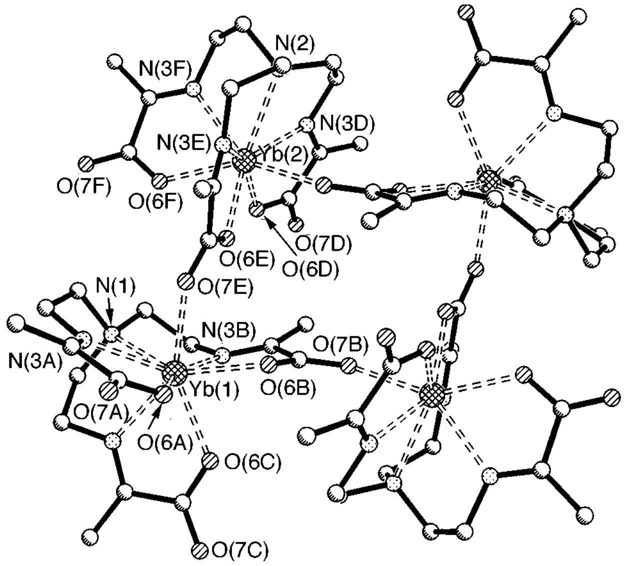
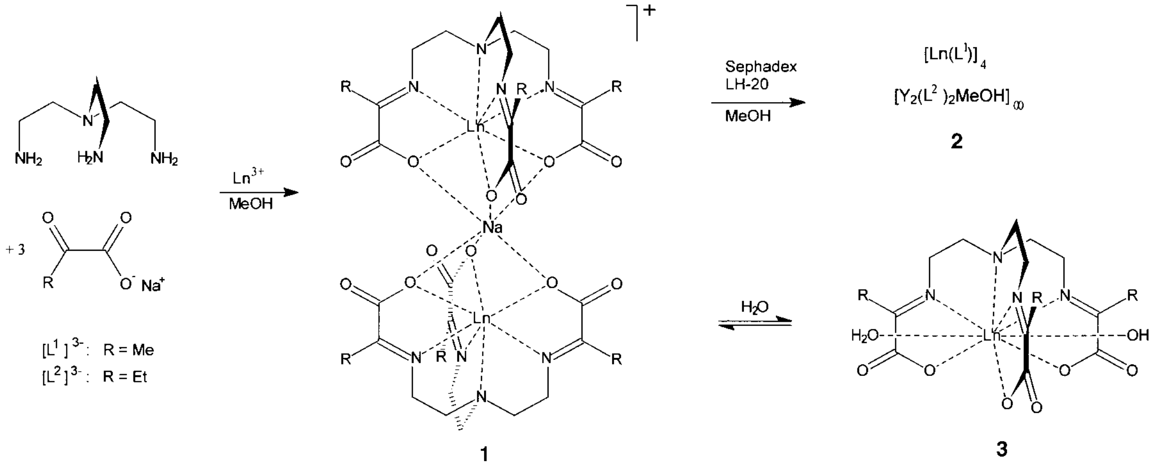


Fig. 1 View of the structure of $[Yb_4(L^1)_4]$ with the numbering scheme adopted. Selected bond lengths (Å) and angles (°): Yb(1)–N(1) 2.609(8), Yb(1)–N(3A) 2.475(9), Yb(1)–N(3B) 2.448(9), Yb(1)–N(3C) 2.434(9), Yb(1)–O(6A) 2.250(8), Yb(1)–O(6B) 2.304(7), Yb(1)–O(6C) 2.288(7), Yb(1)–O(7E) 2.290(8), Yb(2)–N(2) 2.588(9), Yb(2)–N(3D) 2.447(9), Yb(2)–N(3E) 2.447(9), Yb(2)–N(3F) 2.439(8), Yb(2)–O(6D) 2.226(8), Yb(2)–O(6E) 2.283(7), Yb(2)–O(6F) 2.287(7), Yb(2A)–O(7B) 2.278(7), Yb(1)···Yb(2) 6.01(1), Yb(1)···Yb(2A) 6.28(1); Yb(1)–Yb(2)–Yb(1A) 102(1). Atoms Yb(1) and Yb(1A) are related by inversion through (0, 0, ½) as are Yb(2) and Yb(2A)



Scheme 1

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† Satisfactory elemental analyses, IR and mass spectral data were obtained for all compounds.

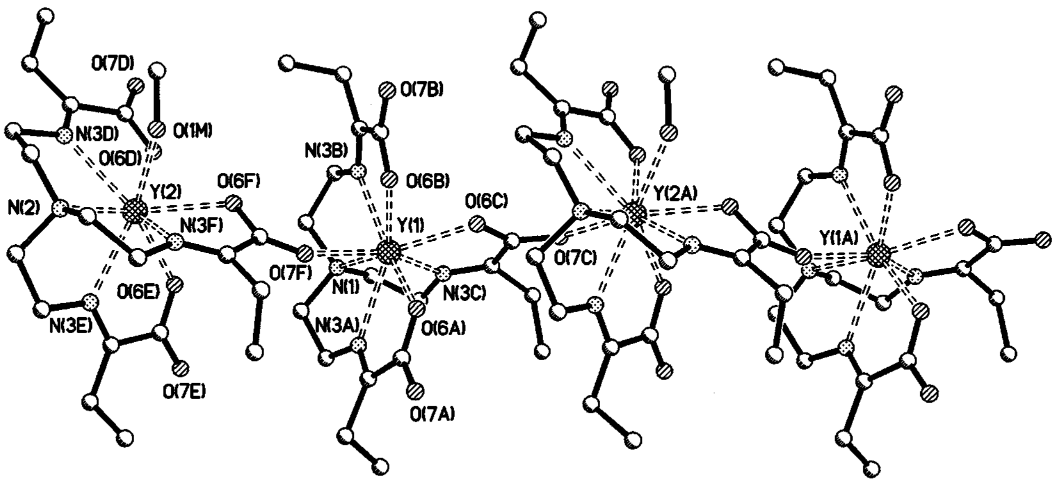

Fig. 2 View of the structure of $[Y_2(L^2)_2MeOH]_\infty$ with the numbering scheme adopted. Selected bond lengths (A): Y(1)–O(6A) 2.267(14), Y(1)–O(6B) 2.309(14), Y(1)–O(6C) 2.323(11), Y(1)–N(3A) 2.50(2), Y(1)–N(3B) 2.43(2), Y(1)–N(3C) 2.47(2), Y(1)–N(1) 2.61(2), Y(1)–O(7F) 2.225(11), Y(2)–O(6D) 2.313(14), Y(2)–O(6E) 2.313(14), Y(2)–O(6F) 2.413(12), Y(2)–N(3D) 2.57(2), Y(2)–N(3E) 2.54(2), Y(2)–N(3F) 2.452(14), Y(2)–N(2) 2.65(2), Y(2A)–O(7F) 2.366(13), Y(2)–O(1M) 2.53(2). Atoms Y(1A) and Y(2A) are related to Y(1) and Y(2), respectively, by a unit cell translation along *a*

able for X-ray diffraction were obtained for the Y^{III} and Yb^{III} complexes with $[L^1]^{3-}$ and the Y^{III} complex with $[L^2]^{3-}$.

The Yb^{III} (Fig. 1) and Y^{III} complexes of $[L^1]^{3-}$ were found to be isostructural tetrameric structures $[Ln(L^1)]_4$ with one carboxylate group from each ligand bridging to the next metal centre.‡ Since the two halves of the tetramer are related by an inversion centre, the four Yb atoms are exactly planar, forming a parallelogram. The Yb^{III} and Y^{III} centres are eight-co-ordinate, bound by the heptadentate tripodal ligand and an additional carboxylate oxygen of an adjacent complexed ligand. There is a high degree of planarity in the fragments C(2)–C(8) due to conjugation between the imine and carboxylate groups with mean deviations from the plane of only 0.024–0.132 Å. The tetrameric structure is surrounded by independent MeOH and H_2O solvent molecules, which are involved in intermolecular hydrogen bonding. These Yb^{III} and Y^{III} complexes are, to our knowledge, the first structurally characterised cyclic tetramers of the lanthanides.[10] Interestingly, electrospray mass spectrometry suggests that the Y^{III} tetramer does exist, at least in part in aqueous solution.

In contrast, the Y^{III} complex of $[L^2]^{3-}$ is a linear polymer $[Y_2(L^2)_2MeOH]_\infty$ (Fig. 2) rather than a cyclic tetramer as observed for $[L^1]^{3-}$. The complex aggregates *via* a bridging carboxylate group linking metal centres. The Y^{III} centres alternate between eight-co-ordinate Y(1) and nine-co-ordinate Y(2), respectively, with the ninth co-ordination site filled by a MeOH molecule. The Y^{III}–donor atom bond lengths are generally longer for the nine-co-ordinate centres. These linear polymeric chains are hydrogen bonded to each other and to MeOH molecules. The remarkable differences in structure between $[Y_2(L^2)_2MeOH]_\infty$ and $[Y(L^1)]_4$ show how an apparently minor change of an organic substituent remote from the metal centres can have a dramatic effect on the observed structure.

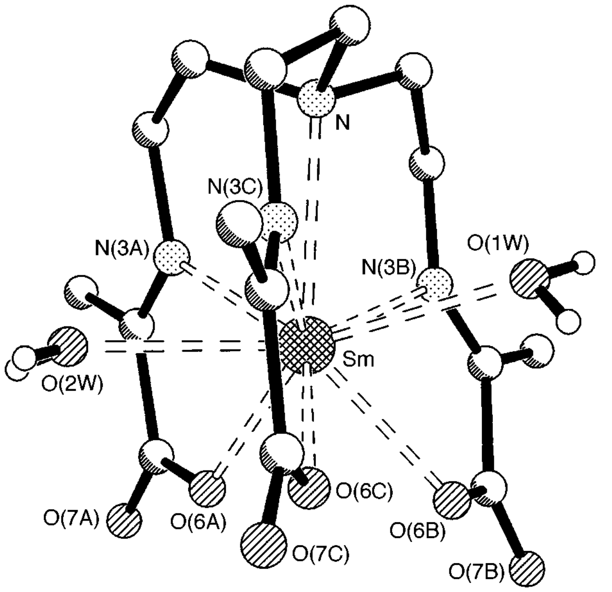

Fig. 3 View of the structure of $[Sm(L^1)(OH_2)_2]$ with the numbering scheme adopted. Selected bond lengths (Å): Sm–N 2.625(3), Sm–N(3A) 2.595(3), Sm–N(3B) 2.518(3), Sm–N(3C) 2.533(3), Sm–O(6A) 2.444(3), Sm–O(6B) 2.424(3), Sm–O(6C) 2.360(3), Sm–O(1W) 2.507(3), Sm–O(2W) 2.522(3)

Dissolution of the Sm^{III} and Gd^{III} complexes of **1** in H_2O results in the slow growth of X-ray quality crystals of the mononuclear species $[Ln(L^1)(OH_2)_2]$ **3**.† Both **2** and **3** are of much lower solubility in H_2O and MeOH than **1**. It is thought that **1** and **3** are in equilibrium in H_2O, thereby explaining the slow crystallisation of **3** from a solution of **1**. The structure of $[Sm(L^1)(OH_2)_2]$ shows (Fig. 3) a tripodal, heptadentate Schiff-base ligand co-ordinated to a nine-co-ordinate Sm^{III} centre. The two remaining co-ordination sites on Sm are occupied by two H_2O molecules, each positioned between two tripod arms. Each arm of $[L^1]^{3-}$ shows a high degree of planarity allowing effect-

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‡ All crystals were mounted on a two-stage fibre with RS3000 perfluoropolyether oil before being transferred to the diffractometer. Crystal data for $C_{64}H_{104}N_{16}O_{32}Yb$ $[Yb_4(L^1)_4]$, $M = 2301.8$, triclinic, space group $P\bar{1}$ (no. 2), $a = 11.16(2)$, $b = 14.75(3)$, $c = 14.94(2)$ Å, $\alpha = 87.91(13)$, $\beta = 69.06(13)$, $\gamma = 87.94(15)°$, $U = 2295(7)$ Å^3, $T = 150$ K, Mo-Kα X-radiation ($\lambda = 0.710\ 73$ Å), $Z = 1$, $D_c = 1.668$ g cm^{-3}, μ(Mo-Kα) = 4.106 mm^{-1}. 9231 Data from two crystals, 6053 unique [$R_{int} = 0.104$] and 5174 with $F_o \geqslant 4\sigma(F_o)$. Final $R1$ [$F_o \geqslant 4\sigma(F_o)$] = 0.0390, $wR2$ [all data] = 0.1013 for 527 parameters, $S = 1.15$, $(\Delta/\sigma)_{max} = 0.02$, $\Delta\rho_{max} = 1.25$ e Å^{-3} near Yb. Crystal data for $C_{40}H_{70}N_8O_{16}Y_2$ $[Y_2(L^2)_2MeOH]_\infty$, $M = 1096.86$, monoclinic, space group $P2_1/n$ (no. 14), $a = 12.348(3)$, $b = 31.304(14)$, $c = 12.762(4)$ Å, $\beta = 96.35(3)°$, $U = 4903(2)$ Å^3, $T = 150$ K, Mo-Kα radiation, $Z = 4$, $D_c = 1.486$ g cm^{-3}, μ(Mo-Kα) = 2.430 mm^{-1}. 7155 Data, 6964 unique [$R_{int} = 0.213$] and 2935 with $F_o \geqslant 4\sigma(F_o)$, were used in all calculations. Final $R1$ [$F_o \geqslant 4\sigma(F_o)$] = 0.1364, $wR2$ [all data] = 0.3212 for 374 parameters, $S = 1.03$, $(\Delta/\sigma)_{max} = 0.04$, $\Delta\rho_{max} = 1.48$ e Å^{-3} near Y. Crystal data for $C_{15}H_{39}N_4O_{15}Sm$ $[Sm(L^1)(OH_2)_2]$, $M = 665.85$, monoclinic, space group $P2_1/c$ (no. 14), $a = 10.708(3)$, $b = 12.487(3)$, $c = 19.358(6)$ Å, $\beta = 98.38(6)°$, $U = 2560.7(12)$ Å^3, $T = 150$ K, Mo-Kα radiation, $Z = 4$, $D_c = 1.727$ g cm^{-3}, μ(Mo-Kα) = 2.368 mm^{-1}. 5365 Data from two crystals, 4509 unique [$R_{int} = 0.044$] and 3883 with $F_o \geqslant 4\sigma(F_o)$. Final $R1$ [$F_o \geqslant 4\sigma(F_o)$] = 0.0296, $wR2$ [all data] = 0.0670 for 374 parameters, $S = 1.19$, $(\Delta/\sigma)_{max} = 0.06$, $\Delta\rho_{max} = 1.19$ e Å^{-3} near Sm. CCDC reference number 186/711.

ive conjugation of the imine with the carboxylate groups and stabilising the imine moiety. In $[Sm(L^1)(OH_2)_2]$, the angle between the mean planes of chains A and B is 56.3°, whereas A–C = 104.0° and B–C = 160.1° where there is a H_2O molecule separating the arms. The complex $[Sm(L)(OH_2)_2]$ crystallises as a heptahydrate with extensive intermolecular hydrogen bonding. The Gd^{III} complex $[Gd(L^1)(OH_2)_2]$ is isostructural.

The novel tripodal ligands reported here are heptadentate, whereas the lanthanide metal ions are usually of eight- or nine-co-ordination. It is therefore necessary for the Ln^{III} centres to include additional donors in their co-ordination spheres. Complex **2** is crystallised from MeOH, in which the best donors available are the carboxylate oxygens of neighbouring complexes, resulting in the observed oligomeric structures. However, **3** is crystallised from H_2O which is itself a good donor, resulting in a monomeric complex.

In conclusion, aggregation in the above systems appears to be controlled by Na^+ cations, by solvent, and by variation in the tripodal polychelate as illustrated by the formation of mononuclear, cyclic tetranuclear and polymeric complexes.

Acknowledgements

We thank Amersham International for a CASE award (to D. M. J. D.), the EPSRC National Mass Spectrometry Service at Swansea University, and the EPSRC for support.

References

1 S. E. Order, J. L. Klein, P. K. Leicher, J. Frinke, C. Lollo and D. J. Carlo, *Int. J. Radiat. Oncol. Biol. Phys.*, 1986, **12**, 277; J. P. L. Cox, K. J. Jakowski, R. Kataky, R. A. Beely, B. A. Boyce, M. A. W. Eaton, K. Miller, A. T. Millican, S. Harrison, C. Walker and D. Parker, *J. Chem. Soc., Chem. Commun.*, 1989, 797; T. J. Norman, D. Parker, L. Royle, A. Harrison, P. Antoniw and D. J. King, *J. Chem. Soc., Chem. Commun.*, 1995, 1877; D. Parker, *Chem. Br.*, 1994, **30**, 818.

2 R. B. Laufer, *Chem. Rev.*, 1987, **87**, 901.

3 P. J. Wong and G. R. Choppin, *ACS Symp. Ser.*, **565**, 346; V. Alexander, *Chem. Rev.*, 1995, **95**, 273; S. L. Wu, S. J. Franklin, K. N. Raymond and W. DeW. Horrocks, jun., *Inorg. Chem.*, 1996, **35**, 162.

4 C. A. Chang, L. C. Francesconi, M. F. Malley, K. Kumar, J. Z. Gougoustras, M. F. Tweedle, D. W. Lee and L. J. Wilson, *Inorg. Chem.*, 1993, **32**, 3501.

5 S. Aime, M. Botta, D. Parker and J. A. G. Williams, *J. Chem. Soc., Dalton Trans.*, 1995, 2259; S. Aime, M. Botta, G. Ermondi, E. Terreno, P. L. Anelli, F. Fedeli and F. Uggeri, *Inorg. Chem.*, 1996, **35**, 2726 and refs. therein.

6 S. J. Archibald, A. J. Blake, M. Schröder and R. E. P. Winpenny, *J. Chem. Soc., Chem. Commun.*, 1994, 1669; S. J. Archibald, A. J. Blake, M. Schröder and R. E. P. Winpenny, *J. Chem. Soc., Dalton Trans.*, 1997, 173; see also, A. J. Amoroso, A. M. Cargill Thompson, J. C. Jeffrey, P. L. Jones, J. A. McCleverty and M. D. Ward, *J. Chem. Soc., Chem. Commun.*, 1994, 2751.

7 V. McKee, M. R. J. Dorrity, J. F. Malone, D. Marrs and J. Nelson, *J. Chem. Soc., Chem. Commun.*, 1992, 383.

8 D. J. Berg, S. J. Rettig and C. Orvig, *J. Am. Chem. Soc.*, 1991, **113**, 2528; P. Caravan, T. Hedlund, S. Liu, S. Sjoberg and C. Orvig, *J. Am. Chem. Soc.*, 1995, **117**, 11 230.

9 H. Wulens, M. Devillers, J. P. Declercq and D. Tinant, *J. Chem. Soc., Dalton Trans.*, 1996, 2023.

10 See also G. B. Deacon, T. Feng, D. C. R. Hockless, P. C. Junk, B. W. Skelton and A. H. White, *Chem. Commun.*, 1997, 341.

Received 15*th August* 1997; *Communication* 7/06000I