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Unprecedented self-assembly of M_3L_2 trinuclear lanthanide complexes assisted by a flexible tripodal ligand containing terpyridine binding units†

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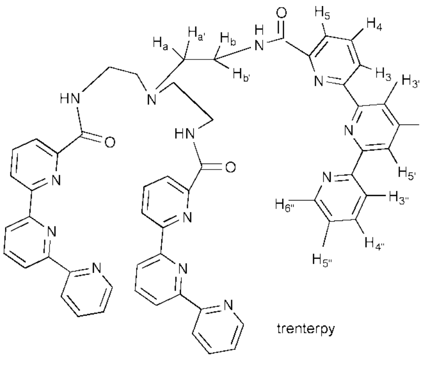
The new dodecadentate tripodal ligand trenterpy in the presence of lanthanide triflates leads to the self assembly of homotrinuclear lanthanide complexes.

In recent years there has been a proliferation in the coordination chemistry of lanthanide(III) ions with polydentate ligands owing to their potential applications in biology, medicine and materials science.[1] However, while the assembly of oligonuclear coordination compounds is a burgeoning field,[2] only limited research has focused on the preparation of polymetallic molecular or supramolecular lanthanide-containing complexes, in spite of the interesting magnetic and luminescence properties of Ln(III) ions.[3] Moreover the creation of highly organised polymetallic architectures is crucial for the design of lanthanide-based functional devices such as light converters[2b] or MRI contrast agents,[4] with, for example, the aggregation of Gd(III) ions in trimeric centres by non-covalent pseudo-octahedral tripods leading to an increase of the relaxivity.[5] We and others have recently shown that the assembly of three neutral bidentate binding units such as phenanthroline[6] or pyridine–carboxamide[7] to [tris(2-aminoethyl)amine] (tren) through an amide linkage yields covalent tripods which form mononuclear nine-coordinate lanthanide complexes with a rigid solution structure.

Here, we report the complexation properties of the new potentially dodecadentate tripodal ligand trenterpy‡ containing three tridentate terpyridine binding units connected to a common anchor (tren) through amide linkages. 2,2′:6′,2″-Terpyridine has been widely used as a building block in metallosupramolecular chemistry[8] and the incorporation of terpyridine or tridentate terpyridine analogues in non-covalent podating ligands has led, in the presence of lanthanide ions, to the formation of mononuclear monohelical complexes[9] or to the self-assembly of dinuclear triple-helical homo- or hetero-dinuclear[10] complexes. Nevertheless the ligand trenterpy is, to our knowledge, the first example of the incorporation of terpy in a covalent tripod.



trenterpy

Here, we show that the high number of coordination sites and the likely presence of interstrand interactions in trenterpy prevent the formation of mononuclear 1 : 1 complexes and lead to the self-assembly of discrete homotrinuclear lanthanide complexes. Very recently Orvig and coworkers have reported another example of how the mismatch of ligand denticity and Ln(III) coordination number can be used to create polynuclear arrays.[11] While rigid C_3-symmetric ligands have often been used for the 'designed assembly' of oligonuclear compounds,[12] the work we present here is, to our knowledge, the first example of self-assembly directed by a flexible tripod.

The reaction of trenterpy with lanthanum triflate leads to the isolation, after addition of diethyl ether, of the crystalline M_3L_2 complex $[La_3(\mu_3\text{-trenterpy})_2(OTf)_4(H_2O)_2](OTf)_5$ **1**§ independently of the starting M : L stoichiometric ratio (1 : 1 or 3 : 2). Yellow crystals of **1** suitable for X-ray diffraction analyses were obtained by slow diffusion of diethyl ether in a solution of **1** in acetonitrile. The structure of the La complex is shown in Fig. 1 and an atomic numbering scheme of the asymmetric unit which contains 1.5 La ions is shown in Fig. 2. The $[La_3(\mu_3\text{-trenterpy})_2(OTf)_4(H_2O)_2]^{5+}$¶ cation lies on a twofold crystallographic axis passing through La(1) and between the capping nitrogens N(1) and N(1)A of the two ligands. Each trenterpy ligand is spread out such that each of its tetradentate carboxyterpyridine arms is coordinated to a different metal ion. Each La ion is coordinated by six terpyridine nitrogens and two amide oxygens provided by two different ligands. All La ions are ten-coordinate with two triflate oxygens binding La(1) and one water oxygen and one triflate oxygen binding the two symmetry related ions La(2) and La(2)A; the La–O distances are standard.[13] The average value of the La–N distance (2.748 Å) is longer than the average La–N bond distance found for a ten-coordinate mononuclear cationic complex of terpyridine $[La(NO_3)_2(terpy)_2]^+$ [13] (2.68 Å) but is similar to the La–N distances previously found in $[La(tbpa)(H_2O)(\eta^2\text{-}ClO_4)]^{2+}$ (2.728 Å)[14] and in $[La(edta)(H_2O)_3]^-$ (2.755 Å).[15] The geometry of the coordinated terpyridine arms is strongly distorted from planarity with the dihedral angles between two neighbouring pyridine rings ranging from 9.7 to 23.3°. Significant distortion from planarity had also been observed in the bisterpyridine La(III) complex[13] and for the complex $[Eu(terpy)_3](ClO_4)_3$[16] [dihedral angle between the two pyridine planes is: 4.8–28.6° for the La(III) complex and 12–26° for the Eu(III) complex].

The ^1H NMR spectrum of the trinuclear lanthanum complex in CD_3CN shows the presence of sharp signals with four resonances for the ethylene protons, one resonance for the amide proton and 10 overlapping signals for the terpyridine protons, in accord with an averaged D_3-symmetric structure on the NMR time-scale of the solution species. The ^1H NMR spectrum of a 1 : 1 solution of $La(OTf)_3$ and trenterpy in

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† Electronic supplementary information (ESI) available: experimental details. See http://www.rsc.org/suppdata/cc/b0/b004152l/

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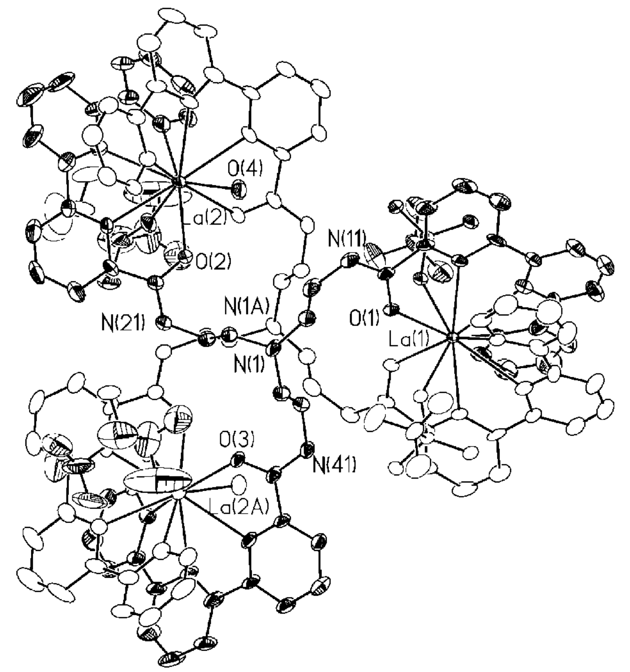

Fig. 1 Crystal structure of the $[La_3(\mu_3\text{-trenterpy})_2(OTf)_4(H_2O)_2]^{5+}$ cation in **1** with thermal ellipsoids at 30% probability. Selected bond lengths (Å): La(1)–O(1) 2.487(4), La(1)–O(11) 2.565(4), La(1)–N(14) 2.750(6), La(1)–N(12) 2.748(5), La(1)–N(13) 2.781(6), La(2)–O(2) 2.514(5), La(2)–O(3)A 2.523(5), La(2)–O(21) 2.542(5), La(2)–O(4) 2.565(5), La(2)–N(42)A 2.747(5), La(2)–N(43)A 2.717(5), La(2)–N(44)A 2.740(6), La(2)–N(22) 2.753(6), La(2)–N(23) 2.750(6), La(2)–N(24) 2.752(7) (symmetry transformations used to generate equivalent atoms A: $-x + 1$, y, $-z + 1/2$).

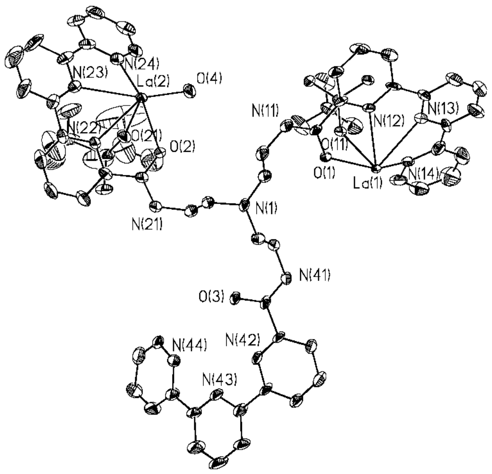

Fig. 2 Atomic numbering scheme of the $[La_3(\mu_3\text{-trenterpy})_2(OTf)_4(H_2O)_2]^{5+}$ cation in **1**. Ellipsoids are shown at the 30% probability level.

acetonitrile shows the presence of broad signals resulting from intermolecular ligand exchange. The ESMS spectra of 1:1 and 3:2 solutions of $La(OTf)_3$ and trenterpy in acetonitrile show a set of peaks which are in accord with the presence in solution of the trinuclear M_3L_2 complex. The ESMS spectrum of the 1:1 solution also shows another set of prominent peaks which were assigned to a mononuclear ML complex {$[La(\text{trenterpy})(CF_3SO_3)_2]^+$ *m/z* 1360} and a set of minor peaks which were assigned to a dinuclear M_2L complex {$[La_2(\text{trenterpy})(CF_3SO_3)_5]^+$ *m/z* 1945.6}. The preferential formation of the trinuclear species at different stoichiometric ratios, and its rigid solution structure indicate that **1** is the thermodynamic product of a self-assembly process. The ESMS spectra of 3:2 solutions of $Ln(OTf)_3$ (Ln = Pr, Eu, Lu) and trenterpy in acetonitrile also show the presence of peaks assigned to the M_3L_2 species. The ^1H NMR spectra of these solutions indicate a higher fluxionality of the solution species with respect to the La(III) complex.

In conclusion, the predisposition of three terpyridine units in a covalent tripod directs the process of self-assembly toward the formation of homotrinuclear lanthanide complexes of potential interest for the study of intramolecular metal-to-metal energy transfer. This work shows that tripodal ligands can be used to predetermine the geometric arrangement of flexible polydentate binding units containing neutral N-donors around lanthanide ions, allowing an improved control over the structure of the final polymetallic array with respect to single-stranded ligands.

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Notes and references

‡ The ligand trenterpy was prepared from 2,2′:6′,2″-terpyridine-6-carboxylic acid chloride and tris(2-aminoethyl)amine (tren).

§ $\delta_H(CD_3CN$, 298 K): 3.32 (br t, 6H, $H_{a/a'}$), 4.14 (br s, 3H, $H_{b/b'}$), 4.38 (br s, 3H, $H_{b/b'}$), 7.01 (q, 3H, $H_{5''}$), 7.80–7.84 (m, 12H), 8.02 (d, 3H), 8.05 (d, 3H), 8.13–8.17 (m, 6H), 8.23 (t, 3H), 9.55 (br s, 3H, NH). ES-MS (*m/z*): $[La_3(\text{trenterpy})_2(CF_3SO_3)_8]^+$ (3451), $[La_3(\text{trenterpy})_2(CF_3SO_3)_7]^{2+}$ (1653.6), $[La_3(\text{trenterpy})_2(CF_3SO_3)_6]^{3+}$ (1052.6), $[La_3(\text{trenterpy})_2(CF_3SO_3)_5]^{4+}$ (752.1).

¶ *Crystal data*: $[La_3(\mu_3\text{-trenterpy})_2(OTf)_4(H_2O)_2](OTf)_5\cdot 2H_2O\cdot 2MeCN$, $C_{121}H_{104}N_{28}O_{37}F_{27}S_9La_3$, M = 3760.59, monoclinic, space group $C2/c$, a = 19.2737(9), b = 26.4590(12), c = 30.2609(14) Å, β = 93.8740(10)°, V = 15396.7(12) Å^3, Z = 4, D_c = 1.622 g cm^{-3}, μ = 1.054 mm^{-1}. 18848 independent reflections (θ_{max} = 29.12°) were collected at 143 K. Refinement using the SHELXTL 5.05 package on all data converged at $R_1[F > 4\sigma(F)]$ = 0.0947, $wR2$ = 0.2492.

CCDC 182/1717. See http://www.rsc.org/suppdata/cc/b0/b004152l/ for crystallograpic files in .cif format.

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