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ChemComm www.rsc.org/chemcomm

The first self-assembled trimetallic lanthanide helicate: different coordination sites in symmetrical molecular architectures†

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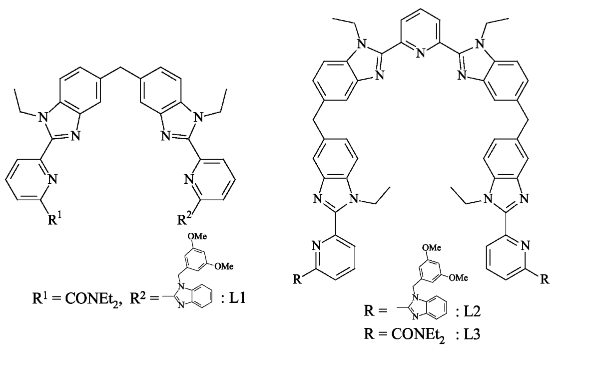
Received (in Cambridge, UK) 22nd February 2002, Accepted 21st March 2002
First published as an Advance Article on the web 8th April 2002

A tris-tridentate segmental ligand has been designed for the self-assembly of homotrimetallic triple-stranded lanthanide helicates possessing different coordination sites along the threefold axis.

During the last two decades, an exceptional research activity has been focused on the use of labile coordination bonds involving d-block ions and multidentate receptors for the selective preparation of sophisticated polymetallic edifices such as helicates, racks, grids, polyhedrons, polygons and clusters.[1] 4f-Block ions, Ln^{III}, have been less studied in this context because of their weak stereochemical preferences which prevent reliable molecular programming in solution.[2] Although considerable efforts have been made to prepare and to characterize homopolymetallic lanthanide complexes in solution,[3,4] reliable structural and electronic control often relies on the serendipitous isolation of solid-state aggregates involving multidentate ligands with negatively charged oxygen donors.[5] However, the recent developments of (i) luminescent sensors exhibiting directional intramolecular energy transfer processes[6] and (ii) sensitive paramagnetic NMR structural probes[6] require the rational design of pure heterometallic lanthanide-containing edifices in which isolated Ln^{III} occupy different coordination sites.[7] The connection of two different tridentate binding units within the segmental receptor L1 indeed produced non-statistical mixtures of homodimetallic ($[(Ln^1)_2(L1)_3]^{6+}$ and $[(Ln^2)_2(L1)_3]^{6+}$) and heterodimetallic ($[(Ln^1)(Ln^2)(L1)_3]^{6+}$) triple-stranded helicates upon reaction with two different lanthanides.[7] However, the formation of mixtures of head-to-head-to-head (HHH)-$[(Ln^1)(Ln^2)(L1)_3]^{6+}$ and head-to-head-to-tail (HHT)-$[(Ln^1)(Ln^2)(L1)_3]^{6+}$ isomers severely limits the programming of specific and predictable electronic properties within the final helicates.[8] D_3-Symmetrical trimetallic helicates may overcome these limitations because (i) the two terminal coordination sites are intrinsically different from the central one for symmetry reasons and (ii) no (HHH)↔(HHT) isomerism occurs. A preliminary attempt used the lipophilic tris-tridentate ligand L2, but the elusive detection of highly unstable $[Ln_3(L2)_3]^{9+}$ complexes in the gas-phase (ESI-MS) with no counterpart in solution suggested that the formation of trimetallic triple-stranded helicates with neutral ligands was precluded by strong intermetallic electrostatic repulsions.[9] The recent development of mixed tridentate NNO segments (benzimidazole–pyridine–carboxamide as in L1) displaying significant affinity for Ln^{III} leads us to reconsider the preparation of C_2-symmetrical tris-tridentate ligands for the self-assembly of trimetallic triple-stranded helicates possessing different coordination sites.

L3·H_2O is obtained in seven steps from dipicolinic acid and *o*-nitrochlorobenzene in 14% yield by using a modified Phillips reaction as the key step for the simultaneous cyclization of four benzimidazole rings (ESI,† Scheme S1).‡ ESI-MS titrations of L3 (10^{-4} M) with $Ln(CF_3SO_3)_3\cdot xH_2O$ (Ln = La, Eu, Gd, Tb, Lu; x = 1–3) in acetonitrile show the successive formation of $[Ln_2(L3)_3]^{6+}$ and $[Ln_3(L3)_3]^{9+}$ together with their gas-phase adduct with triflate counter-anions $[Ln_2(L3)_3(CF_3SO_3)_i]^{(6-i)+}$ (i = 0–2) and $[Ln_3(L3)_3(CF_3SO_3)_i]^{(9-i)+}$ (i = 2–7, Table S1, ESI†). Although the high positive charge in the trimetallic complexes prevents the detection of trimetallic cations with i = 0, 1, $[Ln_3(L3)_3]^{9+}$ is the only significant species observed in the gas-phase for Ln : L3 $\geqslant$ 1.0 and only traces of $[Ln_2(L3)_3]^{6+}$ can be detected. Parallel ^1H NMR titrations of L3 (10^{-2} M in CD_3CN) with $Ln(CF_3SO_3)_3\cdot xH_2O$ (Ln = La, Lu; x = 1–3) for Ln : L3 ratios in the range 0.1–0.9 show complicated spectra dominated by the co-existence of L3, $[Ln_3(L3)_3]^{9+}$ together with minor quantities ($\approx$15–20%) of other complexes tentatively assigned to $[Ln_2(L3)_3]^{6+}$ according to ESI-MS. For Ln : L3 = 1.0, well-resolved ^1H NMR spectra corresponding to the almost quantitative formation of $[Ln_3(L3)_3]^{9+}$ ($\geqslant$ 95%) are observed along the complete lanthanide series (Ln = La–Lu except Pm, Gd). The detection of 25 signals including the systematic diastereotopicity of all methylene protons (H^{12-16}) is compatible with a racemic mixture of the helicates *PPP*-$[Ln_3(L3)_3]^{9+}$ and *MMM*-$[Ln_3(L3)_3]^{9+}$ or of the side-by-side complexes *PMP*-$[Ln_3(L3)_3]^{9+}$ and *MPM*-$[Ln_3(L3)_3]^{9+}$, because both compounds belong to the same D_3 point group (Fig. 1). The large upfield complexation shifts of the protons bound to the 4-position of the benzimidazole rings ($H^{5,6}$) in diamagnetic complexes $[La_3(L3)_3]^{9+}$ ($\Delta\delta$ = 1.83–1.94 ppm) and $[Lu_3(L3)_3]^{9+}$ ($\Delta\delta$ = 2.31–2.51 ppm) are diagnostic for a regular helication which puts these protons in the shielding region of the connected benzimidazole ring[10] and rules out the existence of the amphiverse *PMP* conformer. The observation of weak but significant interstrand nuclear Overhauser enhancement effects involving protons of the terminal and of the central binding units (for instance H^4–H^{18}) points to three strands tightly wrapped about the helical axis,[10] which excludes complexes possessing a central lanthanide with no helicity (*P–P-*



† Electronic supplementary information (ESI) available: least-square planes, selected bond distances and bite angles and a figure showing the atomic numbering scheme for $[Eu_3(C_{63}H_{65}N_{13}O_2)_3](CF_3SO_3)_9(CH_3CN)_9(H_2O)_2$. A scheme summarizing the multistep synthesis of L3 and tables collecting ESI-MS and ^1H NMR data, and elemental analyses. See http://www.rsc.org/suppdata/cc/b2/b201859d/

DOI: 10.1039/b201859d

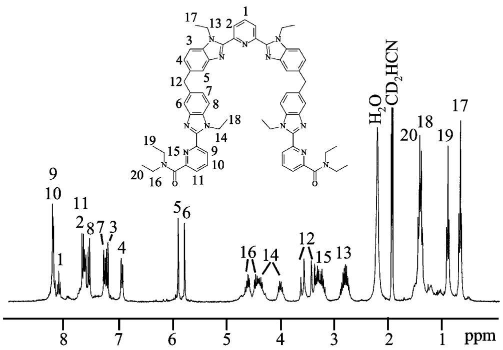


Fig. 1 ^{1}H NMR spectrum of $[La_3(L3)_3]^{9+}$ (CD_3CN, 298 K) with the numbering scheme for the protons.

$[Ln_3(L3)_3]^{9+}$ (D_3-symmetry) or *P–M*-$[Ln_3(L3)_3]^{9+}$ (C_{3h}-symmetry). The NMR data unambigously establish that the expected triple-stranded helicates *PPP*-$[Ln_3(L3)_3]^{9+}$ and *MMM*-$[Ln_3(L3)_3]^{9+}$ are quantitatively formed in solution along the complete lanthanide series (Table S2, ESI†).

Diffusion of diethyl ether into concentrated acetonitrile solutions of $[Ln_3(L3)_3]^{9+}$ produces crystals suitable for X-ray structure determinations. Upon filtration and drying, these crystals are transformed into microcrystalline powders of $[Ln_3(L3)_3](CF_3SO_3)_9.mH_2O$ (Ln = La, Eu, Gd, Tb, Lu, m = 2–12, yield: 77–89%, Table S3, ESI†). The crystal structure of $[Eu_3(L3)_3](CF_3SO_3)_9(CH_3CN)_9(H_2O)_2$§ confirms the formation of the trimetallic triple-helical cation $[Eu_3(L3)_3]^{9+}$ in which the three strands are wrapped around a helical axis defined by the three approximately aligned Eu^{III} atoms (angle Eu2–Eu1–Eu3 173.7°, Fig. 2, Table S4, ESI†). As previously reported for dimetallic lanthanide helicates,[3] the helical twist of the ligands results from a combination of successive torsions around the interannular C–C bonds of each coordinated tridentate segments (12–41°, Table S5, ESI†) and approximate orthogonal arrangements (60–87°, average 76°) of the benzimidazole rings connected to the same methylene spacer. The total length of an helical strand in $[Eu_3(L3)_3]^{9+}$ amounts to 21.5 Å [distance between the facial planes defined by the terminal oxygen atoms O1(a,b,c) and O2(a,b,c)] for 1.58 turn, thus leading to an average pitch of 13.6 Å.

No significant interstrand stacking interactions is evidenced and the stability of the final helicate relies on the formation of 27 dative bonds (21 Eu–N and 6 Eu–O bonds) which overcome the electrostatic repulsions associated with Eu^{III} atoms separated by 9.3165(7) Å (Eu1···Eu2) and 9.0762(7) Å (Eu1···Eu3, Fig. 3). The three metals are nine-coordinated by three wrapped tridentate segments leading to slightly distorted tricapped trigonal prisms in which the three nitrogen atoms of the pyridine rings occupy the capping positions. The replacement of the terminal O atoms of the carboxamide groups (Eu2, Eu3) by heterocyclic nitrogen atoms for Eu1 is responsible for the reinforced non-equivalence of the coordination sites along the helix. The Eu–N(benzimidazole), Eu–N(pyridine) and Eu-O(amide) bond distances are standard (Table S4, ESI†),[3,7]

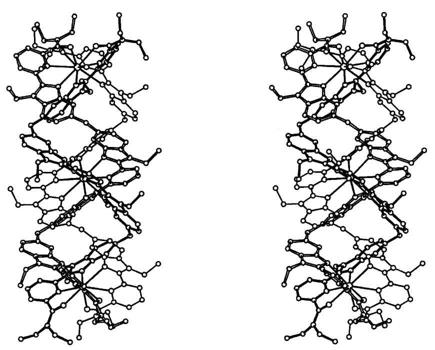


Fig. 2 Stereoview of the cation $[Eu_3(L3)_3]^{9+}$ perpendicular to the helical axis. H-atoms have been omitted for clarity.

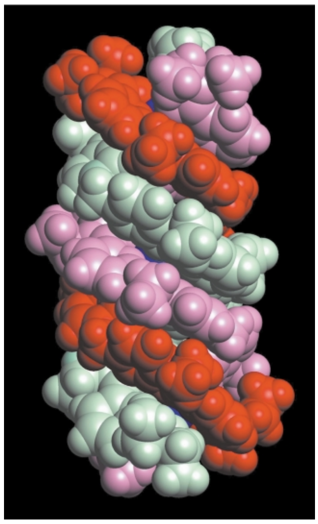


Fig. 3 View of the cation $[Eu_3(L3)_3]^{9+}$ represented with van des Waals radii and showing the tight helical wrapping of the strands.

although considerable bendings of the pyridine and benzimidazole rings preclude ideal alignments of the nitrogen lone pairs with the coordinated Eu^{III} (Fig. 2).

In conclusion, the detection of the triple-stranded helicates $[Ln_3(L3)_3]^{9+}$ in the gas-phase and their subsequent characterization in solution, and isolation in the solid state unambigously demonstrate that three highly charged Ln^{III} cations can be held at approximately 9 Å if sufficient bond strength compensates electrostatic repulsions. In this contect, the use of Ln–O bonds is crucial and provides coordination sites which differ by the nature of the donor atoms along the helix. The detailed thermodynamics of the self-assembly process is currently under investigation, but trimetallic lanthanide-containing helicates offer fascinating potentials for the preparation of pure heterometallic complexes working as directional light-converting devices and paramagnetic NMR probes containing several sites with different crystal-field parameters.[6]

This work is supported through grants from the Swiss National Science Foundation.

Notes and references

‡ L3·H_2O: Found: C, 71.72; H, 6.42; N, 17.14. $C_{63}H_{65}N_{13}O_2·H_2O$ requires C, 71.77; H, 6.41; N, 17.27%.

§ *Crystal data*: $[Eu_3(C_{63}H_{65}N_{13}O_2)_3](CF_3SO_3)_9(CH_3CN)_9(H_2O)_2$, M = 5312.3, triclinic, $P\bar{1}$, a = 14.9286(7), b = 21.7201(11), c = 39.2254(17) Å, α = 96.885(5)°, β = 99.428(5)°, γ = 104.033(6)°, U = 12002(1) Å^3, T = 200 K, Z = 2, μ = 0.95 mm^{-1}. 131723 measured reflections, 42677 unique reflections (R_{int} = 0.071), R = 0.055, wR = 0.055 for 3024 variables and 24081 contributing reflections ($|F_o| > 4\ \sigma(F_o)$).

CCDC reference number 180632. See http://www.rsc.org/suppdata/cc/b2/b201859d/ for crystallgraphic data in CIF or other electronic format.

1 For recent reviews, see: (*a*) M. Fujita, K. Umemoto, M. Yoshizawa, N. Fujita, T. Kusukawa and K. Biradha, *Chem. Commun.*, 2001, 509; (*b*) G. F. Swiegers and T. J. Malefetse, *Chem. Rev.*, 2000, **100**, 3483.
2 C. Piguet and J.-C. G. Bünzli, *Chem. Soc. Rev.*, 1999, **28**, 347.
3 M. Elhabiri, R. Scopelliti, J.-C. G. Bünzli and C. Piguet, *J. Am. Chem. Soc.*, 1999, **121**, 10747.
4 Z. Zheng, *Chem. Commun.*, 2001, 2251 and references therein.
5 (*a*) B. D. Alleyne, A. R. Williams, L. A. Hall, A. J. P. White and D. J. Williams, *Inorg. Chem.*, 2001, **40**, 1045; (*b*) D.-L. Long, A. J. Blake, N. R. Champness, C. Wilson and M. Schröder, *J. Am. Chem. Soc.*, 2001, **123**, 3401 and references therein.
6 C. Piguet, C. Edder, S. Rigault, G. Bernardinelli, J.-C. G. Bünzli and G. Hopfgartner, *J. Chem. Soc., Dalton Trans.*, 2000, 3999 and references therein.
7 N. André, R. Scopelliti, G. Hopfgartner, C. Piguet and J.-C. G. Bünzli, *Chem. Commun.*, 2002, 214.
8 (*a*) C. Piguet, G. Bernardinelli and G. Hopfgartner, *Chem. Rev.*, 1997, **97**, 2005; (*b*) M. Albrecht, *Chem. Rev.*, 2001, **101**, 3457.
9 C. Piguet, J.-C. G. Bünzli, G. Bernardinelli, G. Hopfgartner and A. F. Williams, *J. Alloys Compds.*, 1995, **225**, 324.
10 C. Piguet, J.-C. G. Bünzli, G. Bernardinelli, G. Hopfgartner, S. Petoud and O. Schaad, *J. Am. Chem. Soc.*, 1996, **118**, 6681.