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Tetrahedral Assembly with Lanthanides: Toward Discrete Polynuclear Complexes

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We report on the preparation of discrete 3D tetrametallic edifices containing trivalent lanthanides (Eu–Lu). Their formation is thermodynamically controlled through self-assembly with a new tripodal ligand **L** possessing short binding strands. X-ray crystallography shows that four nine-coordinate cations adopt a regular tetrahedral arrangement in the solid state. These remarkable, highly charged structures are maintained in solution, as demonstrated by NMR spectroscopy, ESI-MS and spectrophotometry.

Introduction

The peculiar optical and magnetic properties of lanthanide ions motivated coordination chemists to prepare discrete supramolecular assemblies and new functional materials. The incorporation of lanthanides as functional centres in molecular edifices has found various applications such as light-conversion devices, luminescent probes and switches, near-IR-emitting probes, contrast agents for medical imaging, etc.[1] Recent interest in modern supramolecular chemistry is focused on the use of predictive tools to increase the stability and kinetic inertness, especially of lanthanide-containing compounds. Thermodynamic modelling has been applied to linear polynuclear helicates with lanthanides in order to extract key energetic parameters for programming the first linear tetrametallic helicate.[2] In order to achieve structural control and improved stability in monometallic lanthanide complexes, preorganised podand-like ligands with different degrees of denticity have been investigated.[3] However, the thermodynamic analysis of tripodal complexes has recently shown that the preorganisation of the tripodal receptor, modelled by the effective-concentration c^{eff}, strongly disfavours the intramolecular binding.[4] If the rational thermodynamic assemblies of monodimensional helicates are extensively investigated,[2,5] only few reports describe discrete polynuclear 2D lanthanide complexes.[6] To the best of our knowledge, 3D lanthanide complexes were reported with (i) a monotopic ligand,[7] where the tetrametallic assembly is templated by the μ_3-OH group (the typical motif for polynuclear clusters[8]) and with (ii) a tritopic ligand providing octahedral cages either with transition metals or with f-block elements, where the coordination sphere is completed by nitrate anions.[9] It is worth noting here that the supramolecular chemistry providing discrete 3D assemblies with d-block elements is well-established[10] and that such polymetallic assemblies, especially Raymonds tetrahedra with Ga^{III}, have been recently used for studying host–guest chemistry.[11] However, the rational concepts of related 3D, and in particular tetrahedral complexes, with labile lanthanide ions are still rare because of the specific requirements for their efficient coordination.

In this context, we report here on the synthesis, isolation, and structural and thermodynamic characterisation of a 3D tetrametallic lanthanide complex with saturated coordination spheres. Its regular tetrahedral arrangement is controlled by the rational ligand design inducing the same helicity about the four nine-coordinate trivalent cations (Figure 1). These remarkable, highly symmetrical compounds (point symmetry *T*) are of particular interest (i) for the fundamental understanding of thermodynamics within multimetallic assemblies, particularly with polytopic multivalent receptors, and (ii) for exploring intramolecular optical and paramagnetic communication in homo- and heterometallic edifices.

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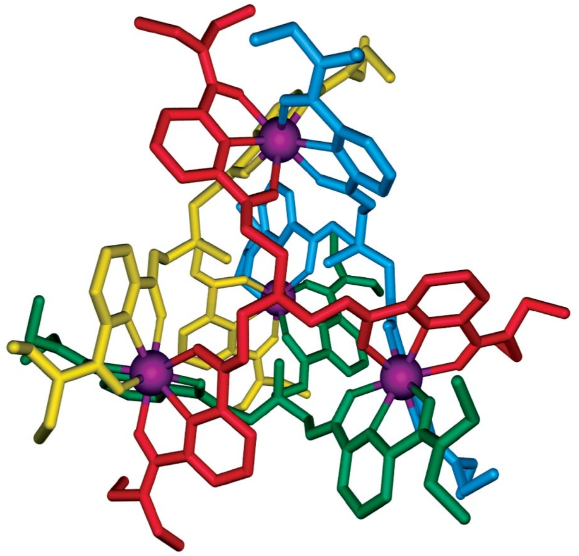
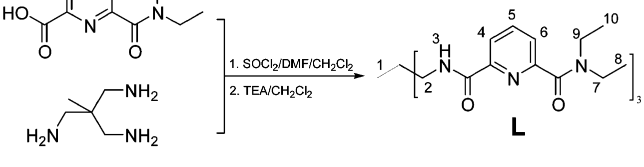


Figure 1. Molecular structure of the tetrahedral cation $[Tb_4\mathbf{L}_4]^{12+}$. Hydrogen atoms, anions and solvent molecules were removed for clarity.

Results and Discussion

Lanthanide coordination in these supramolecular complexes is achieved by a new tripodal ligand **L** synthesised by coupling 1,1,1-tris(aminomethyl)ethane with activated 6-(*N*,*N*-diethylcarbamoyl)pyridine-2-carboxylic acid (Scheme 1). Receptor **L** possesses three tridentate binding strands for lanthanide coordination connected with a short spacer to an apical carbon atom. The room-temperature ^1H NMR spectrum of L in acetonitrile (Figure 2) shows ten well-resolved signals pointing to a dynamically average C_{3v} symmetry with equivalent arms possessing enantiotopic methyl (H1, H8, H10) and methylene groups (H2-H2′, H7-H7′, H9-H9′). All proton signals were completely assigned by using 2D NMR spectroscopy techniques (COSY, NOESY). The rotation about OC–NH amide bonds is blocked on the NMR time scale as demonstrated by non-equivalent ethylene groups (H8, H10).



Scheme 1. Synthesis of **L**.

^1H NMR titrations of **L** ($[\mathbf{L}] = 5\times10^{-3}$ M, $[Ln]_{tot}/[\mathbf{L}]_{tot}$ = 0–2) with Eu^{III} and Lu^{III} perchlorates show the stepwise conversion of free **L** to complexes with complicated spectra, which are significantly simplified for the ratio $[Ln]_{tot}/[\mathbf{L}]_{tot}$ = 1. The ^1H NMR spectrum exhibits 13 signals, which correspond to the three equivalent bound strands and are compatible with the C_3 symmetrical environment in the tetrametallic tetrahedral complexes $[Ln_4\mathbf{L}_4]^{12+}$. The related chemical shifts are given in Table S2 as Supporting Information. The observation of two quadruplets for the methylene groups H2-H2′, H7-H7′ and H9-H9′ (6 diastereotopic protons) is diagnostic for the Ln^{III} complexation of **L** in a helical pattern. The large paramagnetic shift observed for the methyl protons H1 in $[Eu_4\mathbf{L}_4]^{12+}$ (δ_{H1} = 12.93 ppm) compared with that observed for the diamagnetic complex $[Lu_4\mathbf{L}_4]^{12+}$ (δ_{H1} = 0.41 ppm), confirms its location close to the three paramagnetic Eu^{III} centres (Figure 2), as evidenced by the crystal structure (the average distance of methyl protons to three lanthanide cations bound to the same ligand is 5.7 Å). When the metal is in excess ($[Ln]_{tot}/[\mathbf{L}]_{tot} > 1$), the spectra become more complicated. This behaviour points to the existence of low-symmetrical intermediates, probably unsaturated complexes. It is worth noting that the ^1H NMR spectrum with La^{III} at $[La]_{tot}/[\mathbf{L}]_{tot}$ = 1 provides only large unresolved peaks, which excludes the formation of tetrahedral complexes with the larger lanthanides.

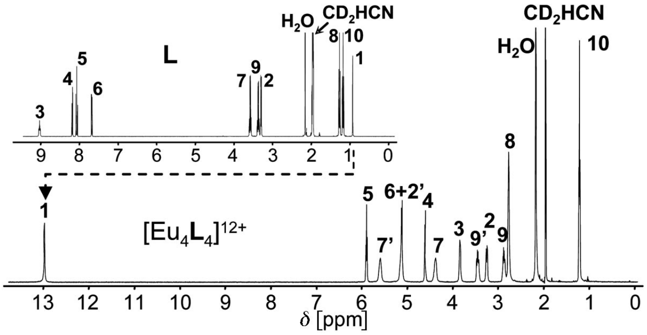


Figure 2. ^1H NMR spectrum of L and of the tetrahedral complex $[Eu_4\mathbf{L}_4]^{12+}$ in CD_3CN (298 K, numbering given in Scheme 1).

Parallel ESI-MS spectra ($[\mathbf{L}] = 1\times10^{-4}$ M) almost exclusively show the formation of the tetrametallic complexes $[Ln_4\mathbf{L}_4]^{12+}$ (Ln = Eu, Tb, Lu) for $[Ln]_{tot}/[\mathbf{L}]_{tot} \approx 1$ (Figure 3 and Figure S2). Intense signals for the series of perchlorate adducts $[Ln_4\mathbf{L}_4(ClO_4)_n]^{(12-n)+}$, together with specific isotopic distribution profiles, clearly demonstrate the formation of the tetrametallic complexes. Series of signals for species with different stoichiometries are observed when the ligand ($Ln\mathbf{L}_3$, $Ln\mathbf{L}_2$, $Ln_2\mathbf{L}_3$ $Ln_3\mathbf{L}_4$) and the metal ($Ln_4\mathbf{L}_3$, $Ln_3\mathbf{L}_2$) are in excess, which is in agreement with the ^1H NMR titrations. The traces of $[Ln_2\mathbf{L}_3]^{6+}$ in the ESI-MS spectrum of $[Ln_4(\mathbf{L})_4]^{12+}$ result from partial fragmentation of the tetrametallic complex in the gas phase, despite the optimised ionisation temperature.

Quantitative information about the thermodynamic stabilities of complex species in acetonitrile has been obtained from spectrophotometric batch titration of **L** (3×10^{-4} M) with $Tb(ClO_4)_3\cdot xH_2O$ ($[Ln]_{tot}/[\mathbf{L}]_{tot}$ = 0–5). The solutions were allowed to equilibrate for 48 hours and measured at 25.0 ± 0.1 °C. Complicated variations of the absorption spectra can be fitted with four absorbing complex species, $[Tb\mathbf{L}_3]^{3+}$, $[Tb_3\mathbf{L}_4]^{9+}$, $[Tb_4\mathbf{L}_4]^{12+}$ and $[Tb_3\mathbf{L}_2]^{9+}$, previously observed during ESI-MS titrations. The associated macro-

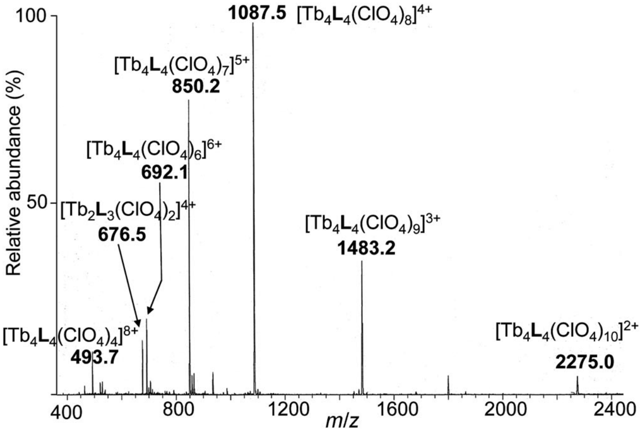


Figure 3. ESI-MS spectrum of $[Tb_4\mathbf{L}_4]^{12+}$ ($[Tb]_{tot}/[\mathbf{L}]_{tot}$ = 1, CH_3CN).

scopic formation constants, $\log\beta_{1,3}^{\mathrm{Tb},\mathbf{L}} = 15.1(5)$, $\log\beta_{3,4}^{\mathrm{Tb},\mathbf{L}} = 34.4(9)$, $\log\beta_{4,4}^{\mathrm{Tb},\mathbf{L}} = 39.7(9)$, $\log\beta_{3,2}^{\mathrm{Tb},\mathbf{L}} = 21.7(6)$, confirm that the tetrametallic complex exists as the major species for $[Tb]_{tot}/[\mathbf{L}]_{tot} = 1$ (Figure 4, Figure S3).

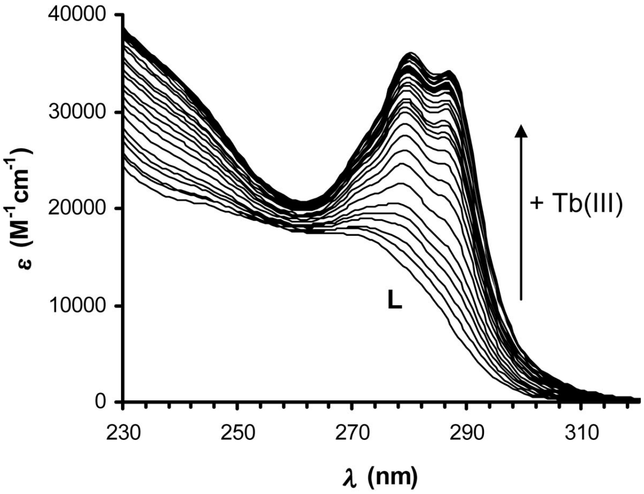


Figure 4. Variation of the absorption spectra observed for the spectrophotometric batch titration of **L** with $Tb(ClO_4)_3$ (298 K, CH_3CN).

The lanthanide complexes, $[Ln_4\mathbf{L}_4]^{12+}$ (Ln = Eu, Gd, Tb, Lu), were then prepared by mixing equivalent amounts of **L** and lanthanide perchlorates in propanonitrile. The resulting white microcrystals of the tetrametallic compounds were obtained in 92–95% yield and give satisfactory elemental analyses (see Supporting Information). ESI-MS and NMR spectra of solutions of these crystals in acetonitrile are identical to those obtained upon direct titrations.

X-ray quality crystals were obtained by slow diffusion of *tert*-butyl methyl ether into a solution of $[Tb_4\mathbf{L}_4](ClO_4)_{12}$ in methanol/acetonitrile with addition of 1 equiv. of $(Bu)_4$-$N[B(Ph)_4]$. The crystal structure[12] is composed of the expected tetrametallic $[Tb_4\mathbf{L}_4]^{12+}$ cations together with eleven disordered noncoordinated perchlorates, one tetraphenylborate anion and solvent molecules. The tetrahedral cation $[Tb_4\mathbf{L}_4]^{12+}$ nearly possesses the rotation symmetry of the tetrahedron *T* (23), and each pseudo-threefold axis passes through an anchoring carbon atom of one **L** and the Tb cation to which this **L** is not coordinated. The average Tb–Tb distance is 9.83 Å. Each Tb atom is coordinated by three different ligands to give a coordination number of 9. The methyl groups attached to the anchoring carbon atoms point towards the centre of the tetrahedron. The average distance between the centre of the tetrahedron and the planes defined by three Tb atoms is 2.00(3) Å. The $[Tb_4\mathbf{L}_4]^{12+}$ cation is chiral, and the crystal is a racemate. Each arm of the four ligands adopts the same chiral conformation. The Tb–O and Tb–N bond lengths are close to those found in triple-helical complexes with analogous dicarboxamidepyridine ligands.[13]

In order to confirm the presence of tetrahedral complexes in solution, we have resorted to ^1H diffusion ordered spectroscopy of $[Eu_4\mathbf{L}_4]^{12+}$ in CD_3CN to estimate its molecular weight from the autodiffusion coefficient, D_m, which is proportional to $(\bar{v}_m MM_m)^{-1/3}$, where $\bar{v}_m$ stands for the specific volume and MM_m for the molecular mass of the molecule. With $[Ru(bipy)_3]^{2+}$ as the reference, the measurements at 296 K give $D_m([Ru(bipy)_3]^{2+}) = 13.5(1)\times10^{-10}\,m^2s^{-1}$, $D_m(\mathbf{L}) = 12.2(1)\times10^{-10}\,m^2s^{-1}$ and $D_m([Eu_4\mathbf{L}_4]^{12+}) = 6.35(7)\times10^{-10}\,m^2s^{-1}$. If a spherical shape can be reasonably considered in solution for the reference compound $[Ru(bipy)_3]^{2+}$, **L** and the tetrametallic complex $[Eu_4(\mathbf{L})_4]^{12+}$, the application of Stokes-Einstein equations with the approximation $\bar{v}_{Ru(bipy)_3} \sim \bar{v}_{\mathrm{L}} \sim \bar{v}_{Eu_4L_4}$ leads to $MM(\mathbf{L}) = 827(3)\,g\,mol^{-1}$ and $MM([Eu_4\mathbf{L}_4]^{12+}) = 5500(100)\,g\,mol^{-1}$. It reasonably compares with the values of 729 and 3525 g mol^{-1} calculated for **L** and the complex, respectively, taking into account the difference in specific volumes of **L**, $[Eu_4\mathbf{L}_4]^{12+}$ and $[Ru(bipy)_3]^{2+}$ (see Supporting Information).

Conclusions

This work unambiguously demonstrates that the self-assembly of the tripodal multidentate ligand **L** with small lanthanides is thermodynamically driven to the quantitative formation of discrete 3D tetrahedral complexes. The thermodynamic modelling of the stability constant of $[Ln_4\mathbf{L}_4]^{12+}$ shows [Equation (S4), Supporting Information], that the number of intramolecular processes is significantly reduced relative to monometallic podates,[4] which favours multicomponent self-assembly. However, a deeper thermodynamic analysis is required for unravelling all energetic parameters. The exploitation of four lanthanides in a small volume for producing novel luminescence and magnetic properties is currently in progress in our laboratory (Figure S7).

Experimental Section

Electronic spectra in the UV/Vis region were recorded from solutions in CH_3CN with a Perkin–Elmer Lambda 900 spectrometer by using quartz cells of 0.1 cm path length. Mathematical treatment of the spectrophotometric titration was performed with the

SPECFIT program.[14] ^{1}H NMR spectra were recorded with a high-field NMR spectrometer (400 MHz, Bruker). Pneumatically assisted electrospray (ESI-MS) mass spectra were recorded from 10^{-4} M acetonitrile solutions with a Finnigan SSQ7000 instrument at the optimised ionisation temperature (150 °C). Emission spectra were recorded with a Perkin–Elmer LS-50 spectrometer.

The detailed procedure for the synthesis of **L** is given as Supporting Information.

L: ^{1}H NMR (CD_3CN): δ = 0.94 (s, 3 H, CH_3), 1.18 (t, J^3 = 7 Hz, 9 H, CH_3), 1.27 (t, J^3 = 7 Hz, 9 H, CH_3), 3.30 (d, J^3 = 7 Hz, 6 H, CH_2), 3.37 (q, J^3 = 7 Hz, 6 H, CH_2), 3.58 (q, J^3 = 7 Hz, 6 H, CH_2), 7.67 (d, J^3 = 8 Hz, 3 H, CH), 8.06 (t, J^3 = 8 Hz, 3 H, CH), 8.17 (d, J^3 = 8 Hz, 3 H, CH), 9.01 (t, J^3 = 7 Hz, 3 H, NH) ppm. ^{13}C NMR (CD_3CN): δ = 12.2 (3 C, CH_3), 13.71 (3 C, CH_3), 18.4 (1 C, CH_3), 39.5 (3 C, CH_2) 42.3 (1 C, CH_3), 42.7 (3 C, CH_2), 42.9 (3 C, CH_2), 122.8 (3 C, CH), 125.1 (3 C, CH), 138.8 (3 C, CH), 148.8 (3 C, CN), 154.5 (3 C, CN) 164.9 (3 C, CO), 167.7 (3 C, CO) ppm. ESI-MS ($CHCl_3$/MeOH/HCOOH: 9:1:0.01): *m/z* = 730.3 $[M + H]^+$. Thermogravimetry (30–140 °C): weight loss 2.76%, calcd. for 1.15 H_2O in $C_{38}H_{51}N_9O_6\cdot 1.15H_2O$ 2.8%.

Supporting Information (see footnote on the first page of this article): Full experimental procedures, ^{1}H NMR spectroscopic data, spectrophotometric titration, ESI-MS, crystallographic data, thermodynamic model, phosphorescence spectra.

Acknowledgments

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[12] X-ray data for $[Tb_4(C_{38}H_{51}N_9O_6)_4]\cdot 11(ClO_4)\cdot [B(C_6H_5)_4]\cdot 3(CH_3CN)\cdot 5(CH_3OH)\cdot 2(H_2O)$: M = 5288.3, monoclinic, space group $P2_1/c$, a = 27.0222(12) Å, b = 22.489(2) Å, c = 42.333(2) Å, β = 102.388(5)°, V = 25127(2) Å^3, D_c = 1.259 g cm^{-3}, μ = 1.31 mm^{-1}, Z = 4, λ = 0.7107 Å, T = 150 K, 135545 reflections collected, 26613 independent (R_{int} = 0.078) and 13740 observed reflections [$F_o > 4\sigma(F_o)$], 2182 refined parameters, R = 0.102, ωR = 0.100. It should be noted that this complex shows at least two other polymorphic forms with Z' = 2 and 4 (see Supporting Information). CCDC-679893 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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