Supramolecular Chemistry

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Switchable Chiral Architectures Containing Pr^{III} Ions: An Example of Solvent-Induced Adaptive Behavior**

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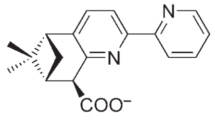
Discrete metallosupramolecular architectures are attractive synthetic targets and have found applications recently in catalysis, cavity-directed synthesis, and chemical sensing.[1] Some of these entities are the result of self-assembly processes that respond to environmental changes (solvent,[2] concentration,[3] template effect,[4] etc.) and represent interesting examples of dynamic combinatorial libraries[5] of interconverting self-assembled structures. As the lability of the metal–ligand coordination bonds is a prerequisite for such behavior, superstructures that contain arrays of lanthanide (Ln^{III}) ions are expected to be relevant toward this end.[6] On the other hand, the complexation of f metal ions with chiral ligands opens new, little-explored, perspectives in the lanthanide series for a) the synthesis of configurationally stable, polynuclear, enantiopure species by using enantiopure ligands[7] and b) the study of chiral recognition phenomena when enantiomeric mixtures of ligands are employed.[8]

Recently, we demonstrated that a chiral bipyridine-carboxylate ligand (+)-L$^-$ self-assembles in the presence of Eu^{III} cations to form a trinuclear helix, which displays an interesting version of supramolecular helical chirality.[9] Herein, we describe a solvent-dependent process in which a mixture of Pr^{III} ions and the (+)-L$^-$ ligand with the same metal-to-ligand ratio (1:2.25) can follow two distinct self-assembly pathways that lead dia-



(+)-L$^-$

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stereoselectively to two enantiopure architectures: a two-dimensional trinuclear array (in methanol) and a three-dimensional tetranuclear pyramidal polyhedron (in acetonitrile). Furthermore, the two polynuclear structures can be reversibly interconverted in acetonitrile simply by varying the amount of water that is present in the solvent.

In acetonitrile, the reaction between $Pr(ClO_4)_3$ and the ligand (+)-HL·HCl (2.25 equiv) in the presence of triethylamine (5.2 equiv) did not give a precipitate, as was the case when the reaction was performed in methanol (see below), but gave a clear solution. This solution was homogeneous according to analysis by electrospray ionization mass spectrometry (ESI-MS), and the sole peak detected corresponded to the formula $[Pr_4L_9(OH)]^{2+}$ (see Supporting Information). Slow evaporation of the acetonitrile under anhydrous conditions (dessicator) led to the formation of crystals that were suitable for X-ray diffraction studies.[10] The crystal structure revealed a tetranuclear self-assembled compound, $[Pr_4\{(+)\text{-}L\}_9(\mu_3\text{-}OH)](ClO_4)_2$ (**1**), in which nine bridging ligands form three distinct helical domains with predetermined configuration (Figure 1).

The four metal ions, each displaying a coordination number of nine, form a pseudo-trigonal-pyramidal polyhedron. The basis of this metallic framework is a pseudo-equilateral triangle (metal–metal distances: 4.045(1), 4.076(1), and 4.070(1) Å), which is held together by a) six bridging ligands that are divided into two sets of three and b) a μ_3-hydroxy group, whose oxygen atom is situated on the pyramidal pseudo-C_3 axis and lies slightly above (0.96 Å) the triangular base. The fourth metal cation, which is situated 5.5 Å above the triangular base on the pseudo-C_3 axis on the same side as the μ_3-OH group, represents the top vertex of the pyramidal metallic framework (averaged edge 6.0 Å). Three tridentate ligands (in gray), coordinated through the two nitrogen atoms from the bipyridine and one oxygen atom from the carboxylate, are wrapped helically around this stereogenic metal center and induce a Λ configuration. Every second carboxylate oxygen atom from these three ligands is coordinated to one metal center from the triangular base to create a small cavity (see Figure 1b). The other six ligands included in this suprastructure are arranged in two distinct sets (yellow and violet) and are coordinated solely to the three basal Pr^{III} cations. In one set (yellow), the three ligands bridge symmetrically (μ^2-η^1:η^1) two adjacent metal ions through the two oxygen atoms from the carboxylate groups. Their uncoordinated bipyridine moities adopt a *trans* conformation (dihedral angles vary from 2.05 to 16.43°) and form a supramolecular *M* helix. The term *supramolecular* as used here refers to the chirality and indicates the propeller-like arrangement of the ligands around a metallic core and not just one metal center as seen in classical mononuclear helical complexes. The three ligands of the other set (violet) are coordinated not only through the carboxylate oxygen atoms (one oxygen atom bridges asymmetrically two metal centers: μ^2-η^2:η^1; the second is monocoordinated) but also through the aromatic nitrogen centers. This set adopts a supramolecular *P*-helical arrangement.

The ^{1}H NMR spectra of the crystals and the powder recovered from the reaction mixture displayed identical patterns, that is, 39 distinct signals spread over a large field (about 40 ppm in CH_3CN or CH_2Cl_2) owing to the paramagnetism of the Pr^{III} ions (see Supporting Information). Different 2D NMR techniques (COSY, ROESY) allowed the grouping of these signals into three sets of 13 peaks (1:1:1). This result is not only an indication that the polyhedral structure is maintained in solution but also that the reaction occurs with high diastereoselectivity (>95%). To further demonstrate this, we synthesized the complex by using an isotopically marked ligand, with a ^{13}C label at the carboxylate carbon center. Indeed, the ^{13}C NMR spectrum showed three distinct signals that confirmed the presence of three distinct magnetic sites (Figure 2).

When the reaction between $Pr(ClO_4)_3$ and the ligand (+)-HL·HCl (2.25 equiv) in the presence of triethylamine (5.2 equiv) was conducted in methanol, a precipitate was obtained quantitatively. All the data collected in solution (NMR, ESI-MS) and in the solid state (X-ray,[10] elemental analysis, IR) are in agreement with the formation of a helical trinuclear array with the formula $[Pr_3\{(+)\text{-}L\}_6(\mu_3\text{-}OH)(H_2O)_3](ClO_4)_2$ (**2**; see Figure 3a and Supporting Information)). This C_3-symmetrical compound is isostructural with the Eu^{III} analogue[9] obtained under the same experimental

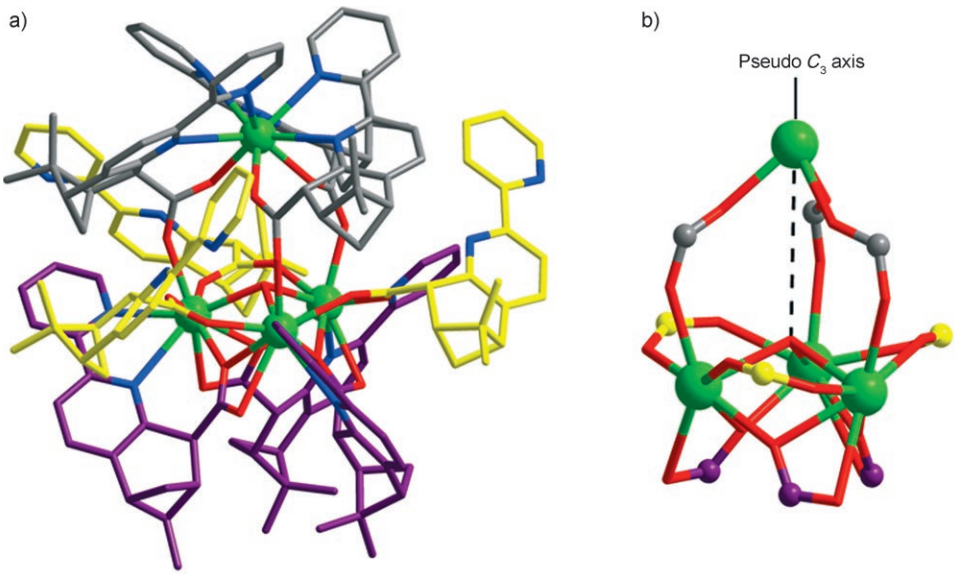

Figure 1. a) Crystal structure of $[Pr_4\{(+)\text{-}L\}_9(\mu_3\text{-}OH)](ClO_4)_2$ (**1**). Hydrogen atoms, perchlorate counterions, and acetonitrile molecules of crystallization have been omitted for clarity. b) Pyramidal metallic framework with the nine bridging carboxylic groups. Pr green, O red, N blue; the three sets of L ligands are colored gray, yellow, and violet.

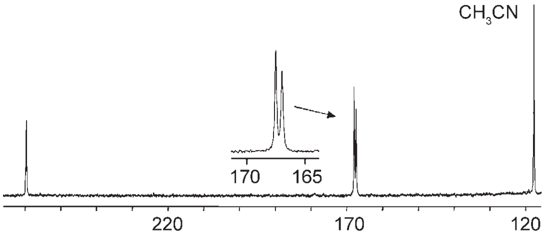

Figure 2. ^{13}C NMR spectrum (CD_3CN, $c = 1\cdot10^{-2}$ M) of a labeled sample ($^{13}COOH$) of **1**.

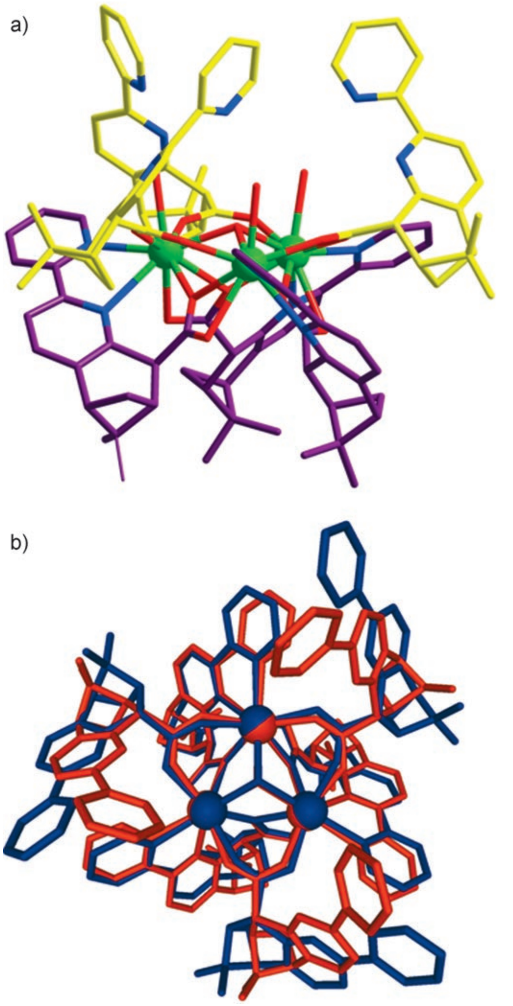

Figure 3. a) Crystal structure of $[Pr_3\{(+)\text{-}L\}_6(\mu_3\text{-}OH)(H_2O)_3](ClO_4)_2$ (**2**) viewed perpendicular to the C_3 crystallographic axis. Hydrogen atoms, perchlorate counterions, water, and acetonitrile molecules of crystallization have been omitted for clarity. Pr green, O red, N blue; L ligands are shown in yellow and violet. b) Superposition of the trinuclear bases of **1** (blue) and **2** (red) viewed down the C_3 axis.

conditions. Moreover the discrete trinuclear structure of **2** is structurally very similar to the triangular base of the pyramidal array **1**. The main differences lie with the uncoordinated bipyridine moieties: a) To accommodate the new mononuclear unit PrL_3, they adopt a more "flattened" orientation in **1** as compared with **2** (Figure 3b). b) The pseudo-*cis* conformation of the bipyridine, which is stabilized in **2** by a hydrogen-bonded network that involves six water molecules (three coordinated and three uncoordinated), is replaced by the energetically more favored *trans* conformation in the anhydrous compound **1**.

Compound **2** is stable in low-polar solvents, namely CH_2Cl_2. ^1H NMR spectroscopy of a solution of **2** in CD_2Cl_2 revealed 26 signals, which were attributed to the two magnetically distinct sets of ligands and remained unchanged with time. However, the spectrum recorded on a solution of **2** in dry CD_3CN was time-dependent. After about three hours, the initial 26 signals were completely replaced by 39 major peaks accompanied by some minor signals. The similarities in terms of chemical shifts and integration ratios between these dominant signals and those recorded for the pure tetranuclear species **1** (see Supporting Information) indicate the conversion **2**(trinuclear)→**1**(tetranuclear) + minor species.

This conversion was also confirmed by ESI-MS (see Supporting Information) and ^{13}C NMR spectroscopy on a sample obtained from an isotopically marked ligand (see above). In the ^{13}C NMR spectrum of the ^{13}C-labeled sample (Figure 4), the two signals that correspond to the trinuclear structure are replaced by three other signals that originate from the three sets of ligands in compound **1.** Four small peaks are also visible therein and confirm that a part of the ligands make up the composition of the minor species. Detailed investigations by NMR and circular dichroism (CD) spectroscopy aimed to gain insights into the nature of the minor species as well as the reaction stoichiometry and mechanism are in progress.

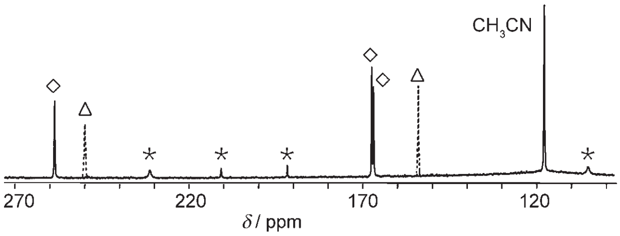

Figure 4. Superposed ^{13}C NMR spectra (in CD_3CN) of the labeled ($^{13}COOH$) sample of **2** before the conversion (dashed peaks, △) and after the conversion **2**→**1** + minor species (◇ signals from **1**; * signals from minor species.

Interestingly, the mixture containing **1** and the minor species in CD_3CN could be reconverted into **2** in the presence of water. After the addition of 40 equivalents of H_2O per equivalent of metal ion, the initial peaks in the ^1H NMR spectrum were replaced by those of the trinuclear species **2** together with a few minor sharp signals that are associated to the decarboxylated ligand (see Supporting Information). In fact, during the regeneration of **2**, a small proportion of the anionic ligand (less than 10%) is neutralized by the water molecules and then decarboxylated according to a well-known mechanism.[11] Thus, the trinuclear array is stabilized in hydrated acetonitrile. A possible explanation is that the removal of water from the first coordination sphere in **2**, which is a necessary step in building up the water-free compound **1**, is unlikely due to the presence of solvated water molecules. This hypothesis is supported by another experiment in which the water was removed from the acetonitrile solution by using molecular sieves, again leading to the conversion $\mathbf{2}\rightarrow\mathbf{1}$ + minor species. The trinuclear cluster without water molecules in the first coordination sphere is unstable and generates a mixture that contains mainly the tetranuclear compound **1**. Consequently, such successive reversible cycles can be carried out simply by addition/removal of the water from the medium (acetonitrile). The number of interconversion cycles is limited only by the decarboxylation of the ligand which leads to its "consumption".

Another interesting feature of the self-assembly processes presented here is their aptitude for chiral self-recognition. The reaction between the racemic ligand (±)-HL and Pr^{III} ions in methanol led to a racemate of **2** (*rac*-**2**). Its ^{1}H NMR spectrum, which is identical in every respect with that for the enantiopure complex **2**, as well as its CD spectrum, which is devoid of any signal, denotes a high degree of chiral self-recognition (homorecognition) between the ligands. The same phenomenon takes place when *rac*-**2** is converted into *rac*-**1** upon dissolution in acetonitrile. As expected and furthermore demonstrated by X-ray analysis,[10] in *rac*-**1** each of the two enantiomeric structures is made up from one single enantiomer of the ligand to show opposite helical orientations (Figure 5). In contrast to the observations made above, the self-assembly of the racemic ligand (±)-HL and Pr^{III} ions in acetonitrile is highly perturbed. The tetranuclear species, which is obtained quantitatively when the enantiopure ligand is used, are in this case a minor part of a complicated mixture. This result shows the limits in terms of chiral recognition capabilities of the system; these limits are reached when a higher number of fundamental components (metal ions and ligands; 13 in the case of tetranuclear complexes and 9 in the case of trinuclear complexes) have to recognize and self-assemble.

In summary, we have described the first example in the lanthanide series of a solvent-adaptive system that can follow two distinct reaction pathways that lead diastereoselectively to discrete enantiopure polynuclear architectures **1** and **2**, respectively. In the pyramidal polyhedron **1**, an original combination of two types of helical arrangement of the ligands was revealed: one classical—around one metal center—and the other supramolecular—around a metallic triangular core. Their helical sense is predetermined by the ligand chirality. Facile reversible interconversion between the two structures **1** and **2** can be carried out in acetonitrile by the removal or addition of water, although no obvious templating effects or intra-/intermolecular interactions are involved in this process. If the racemic ligand is used instead of the enantiopure ligand, either chiral recognition processes are observed or the self-assembly is drastically affected.

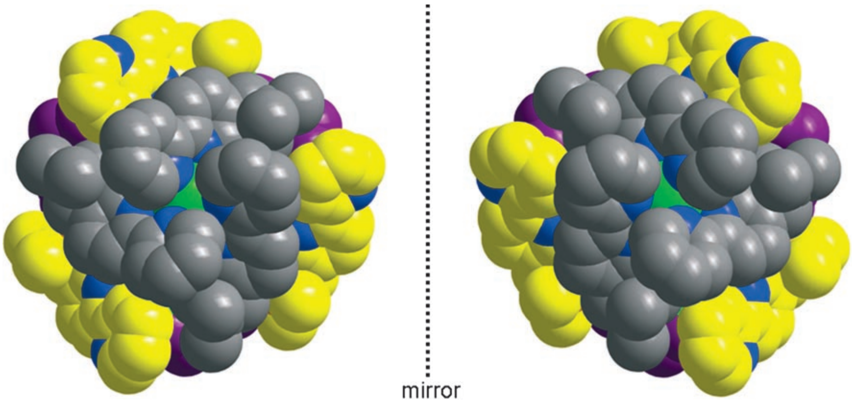

Figure 5. Space-filling representation of the two enantiomers present in *rac*-**1** viewed along the pseudo-C_3 axis. Ligands L^- coordinated around the metal center situated at the top of the pyramidal metallic framework are shown in gray; the other two sets of ligands are shown in yellow (coordination solely through carboxylate groups) and violet (coordination through carboxylate and nitrogen groups). Pr green, N blue.

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[10] Details regarding the X-ray crystal structure determinations for $[Pr_4\{(+)\text{-}L\}_9(\mu_3\text{-}OH)](ClO_4)_2\cdot 10\,CH_3CN$ (**1**), $[Pr_3\{(+)\text{-}L\}_6(\mu_3\text{-}OH)(H_2O)_3](ClO_4)_2\cdot 4\,CH_3CN\cdot 3H_2O$ (**2**), and $[Pr_4\{(\pm)\text{-}L\}_9(\mu_3\text{-}OH)](ClO_4)_2\cdot 4\,CH_3CN$ (*rac*-**1**) are given in the Supporting Information. CCDC 607510 (**1**), 607511 (**2**), and 607512 (*rac*-**1**) contain 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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