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Title

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Controlled heterometallic composition in linear trinuclear [LnCeLn] lanthanide molecular assemblies

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Abstract: The combination of two different β-diketone ligands facilitates the size-controlled assembly of pure heterometallic [LnLn'Ln] linear compounds thanks to two different coordination sites present in the molecular scaffold. [HoCeHo], [ErCeEr] and [YbCeYb] analogues are presented here and are characterized both in the solid state and solution, demonstrating the selectivity of this unique method to produce heterometallic 4f molecular entities.

Molecular-based systems featuring lanthanide ions constitute a very active research area within materials science due to their exceptional physical properties.[1-4] The characteristics of these molecules allow their exploitation in numerous disciplines, such as in optical and magnetic resonance imaging,[5] magnetic refrigeration,[6-8] light-emitting diodes[9] or information storage[10-13] and processing.[14-17] In view of this potential, strong efforts focus on lying out strategies to develop molecules with more than one type of lanthanide ion in order to tune or enhance their properties and performance. Combinations of different lanthanides can, for example, improve up-conversion efficiency in luminescent systems,[18] modify the colour or brightness of their emission,[19] or produce contrast agents covering both visible and near-IR regions.[20] The controlled production of such materials is, however, highly challenging due to the similar chemical behaviour of the lanthanide ions. In order to prepare selectively heterometallic lanthanide complexes, chemists have developed synthetic methods based mainly in two strategies. On the one hand, by performing two chemical reactions sequentially, engaging a different Ln metal each time.[21-30] On the other, by using organic ligands with different encapsulating pockets, designed to bind two types of Ln ions, as discriminated by their different ionic radii.[31-33] This latter strategy often leads to metal distributions only partially removed from statistical mixtures. Overcoming this challenge, our group reported a very selective asymmetric ligand featuring β-diketone (O,O) and dipicolinate-like (O,N,O) pockets able to promote pure heterometallic dinuclear [LnLn'] complexes for a large number of combinations (H_3L, Fig. 1).[34-36] The selective distribution of each lanthanide ion, based exclusively on their different ionic radii, was found to be extremely efficient, both in the solid state and solution. This synthetic resource was used to study specific [LnLn'] combinations as two quantum bit (qubit) molecular logical quantum gates (qugate), each lanthanide ion embodying a qubit.[37] Based on low-temperature magnetic and EPR measurements, the [CeEr] analogue was found to perform successfully as a CNOT (controlled-NOT) qugate.[34] In view of these exciting results, the possibility to increase the complexity and incorporate an additional Ln ion into the system was explored. The aim was to produce molecules with three qubits capable to realize more complex qugates, such as quantum error correction protocols.[38-39] We thus turned our attention to the ligand H_2LA (Fig 1), which had been synthesized by us as the precursor of another multidentate ligand.[40] H_2LA exhibits an additional β-diketone (O,O) unit as compared with H_3L, thus having the ability to chelate a third Ln, while featuring still only two different environments and thus two-metal selectivity.

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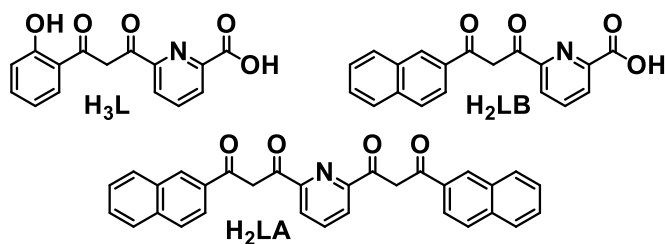   Supporting information for this article is given via a link at the end of the document

Figure 1. Representation of ligands H₃L, H₂LA and H₃LB.

By analogy with the dinuclear [LnLn'] complexes,[36, 41-42] the central position of H₂LA is expected to host the largest lanthanide, while the smaller ions would be allocated at the external sites. We explored this eventuality through reactions in pyridine of H₂LA with $Ce(NO_3)_3$/$Ln(NO_3)$ mixtures in the 1:2 molar ratio, Ln being Ho[III], Er[III] or Yb[III], thus with a marked smaller ionic radius than Ce[III]. The choice of metals is justified by our future interest in studying these compounds as qugates to perform quantum error correction protocols[38] or other three qubit qugates. The Ce and Er metals are interesting for their low content of nuclear spin ($I = 0$ for Ce and only 23% of $I = 7/2$ for Er), reducing the sources of decoherence. Being Kramers ions, Ce[III] and Er[III] are potential good realizations of qubits, as they likely present isolated $S_{eff} = \frac{1}{2}$ doublets in the ground state.[34] Yb[III] offers the possibility of studying a qubit with a lower magnetic moment at the ground state, thus leading to a weaker coupling with Ce[III], of potential interest for some applications. Non-Kramers ion Ho[III] was investigated for completeness. Slow diffusion of hexane within the resulting orange solutions afforded orange oils, which after several weeks turned into orange crystals. Single-crystal X-ray diffraction (SCXRD) enabled the analysis of the structure for the resulting compounds (Fig 2 and S1-S4). The three systems were found to be isostructural, crystallizing in the *P*-1 triclinic space group (Table S1). As expected, three Ln ions are chelated at the predicted positions of two LA^{2-} donors (following the double deprotonation of H₂LA). Interestingly, the coordination is also brought about by two deprotonated fragments of the original ligand (H₂LB, Fig 1 and Figure S4), following a process of hydrolysation *in situ*. As a result, one β-diketone group of H₂LA converts to a carboxylic acid, yielding H₂LB. The latter hydrolysis has been documented as a metal catalyzed retro-Claysen process, occurring through the nucleophilic attack of one of the β-diketone carbonyl groups by a molecule of water.[43-44] Since the nature of each Ln ion was clearly identified during the refinement of the crystal structures (see Experimental Section, SI), the following formulae could be anticipated: $[CeLn_2(LA)_2(LB)_2(py)(H_2O)_2](NO_3) \cdot n(py)$ (hereafter [LnCeLn], where Ln = Ho (**1**), Er (**2**) or Yb (**3**), py = pyridine and $n = 11$ for Ho and Er, and 10 for Yb). Most lattice pyridine molecules are exchanged by varying amounts of water molecules upon exposure to the atmosphere (see microanalysis at the SI). The analysis evidenced thus a central Ce[III] ion encapsulated by two dipicolinate-like units (O,N,O) from LA^{2-} ligands, and two (O,O) β-diketonate groups from LB^{2-}. Its coordination is completed with a pyridine molecule, producing a distorted undecacoordinated capped pentagonal antiprism as calculated by continuous-shape measures (CShMs, Table S2, Fig. S5).[45] In turn, the peripheral ions are Ho[III], Er[III] or Yb[III] for **1**, **2** and **3** respectively. Their eight-vertices coordination polyhedron is produced with two (O,O) β-diketonate groups from LA^{2-} ligands, only one (O,N,O) dipicolinate-like unit from LB^{2-} and one molecule of H₂O. Such environment was found to be best described as a distorted bi-augmented trigonal prism by CShMs (Table S2, Fig. S5).
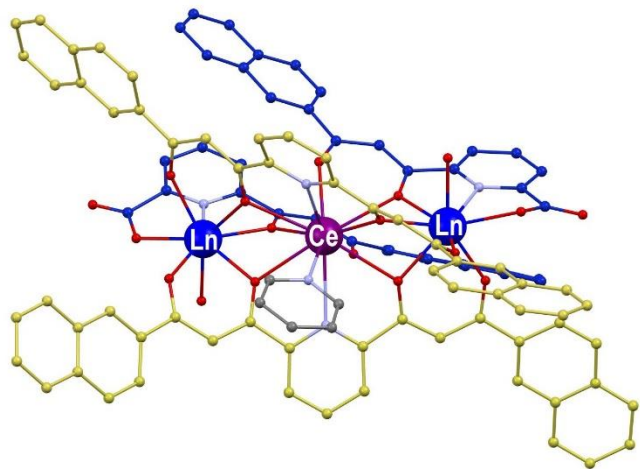

Figure 2. Representation of the cation $[CeLn_2(LA)_2(LB)_2(py)(H_2O)_2]^+$ present in **1-3**. Color code: O, red; N, purple; C of py, grey; C of LA^{2-}, yellow; C of LB^{2-}, blue. H atoms not shown.

Table 1. Average bond distances to the metal ions in **1-3**, and differences betwee these averages, in Å (Ln1 and Ln2 refer to two crystallographically independent ions of the same metal in each molecule).

	[HoCeHo] (1)	[ErCeEr] (2)	[YbCeYb] (3)
av. d(Ce–O)	2.622(11)	2.622(11)	2.614(15)
av. d(Ce–N)	2.790(7)	2.785(7)	2.786(14)
av. d(Ln1–O)	2.344(11)	2.323(11)	2.301(15)
d(Ln1–N)	2.417(5)	2.409(5)	2.387(7)
av. d(Ln2–O)	2.335(11)	2.325(11)	2.303(14)
d(Ln2–N)	2.411(5)	2.400(4)	2.381(7)
$\Delta O_{Ce–Ln1}$	0.29	0.30	0.31
$\Delta O_{Ce–Ln2}$	0.29	0.30	0.31
$\Delta N_{Ce–Ln1}$	0.37	0.38	0.40
$\Delta N_{Ce–Ln2}$	0.38	0.38	0.41

The selective allocation of the metals occurs on grounds of relative ionic radii. The analysis of bond distances helps to corroborate this distribution (Tables 1 and S3). For consistency, only the M–O distances involving LA^{2-} and LB^{2-} are compared here. Thus, the central Ce^{III} ion exhibits systematically larger Ce–O values compared with the Ln–O distances (Ln=Ho, Er, Yb). This is consistent with the central cavity of the molecule favouring the metal with larger ionic radius (1.220 Å for Ce^{III} when surrounded by a nine-coordinate) in comparison with the external locations, which stabilize the smaller ions (1.055, 1.040 and 1.010 Å for Ho^{III}, Er^{III} and Yb^{III}, respectively, if all nine-coordinate).[46] This feature is in perfect analogy to that discovered for the [LnLn'] family, where a majority of (O,N,O) pockets with respect to (O,O) sites favour larger metal ions. The selectivity can be quantified by the metric parameters ΔO (or ΔN), here the difference between the average of Ce-O (or Ce-N) and Ln-O (or Ln-N) bond distances (Table 1). These values (in the range of 0.29-0.31 Å for ΔO, and 0.37-0.41 for ΔN) suggest a strong site selectivity, found to be even larger than observed for the [LnLn'] system.[34-36] The crystal lattice is completed with pyridine molecules, together with one nitrate anion per cluster, which ensures the electroneutrality of the system. Within the lattice, the cationic complexes are interacting through a network of H-bonding and π-π stacking interactions, imposing short distances between Ln ions of neighbouring molecules (6.07, 6.07 and 6.05 Å for **1**, **2** and **3**, respectively, Fig S6). In view of the molecular structures of these clusters, their synthesis was attempted in a rational manner, through the reaction in pyridine of $Ce(NO_3)_3$ and $Ln(NO_3)_3$ (1:2 molar ratio) with two equivalents of H_2LA and H_2LB, respectively. The latter was synthesized with a procedure analogous to that for H_3L.[41] In addition, we noticed that the addition of $CuCl_2$ helped significantly the crystallization. During this process, crystals of $[Cu(py)_4(NO_3)_2]$ develop first, before large single crystals of compounds **1-3**, easy to separate, originate from the original oil (Experimental Section, SI). Small deviations from ideal microanalysis results are attributed to unperfect burning due to a large amount of aromatic rings, rather than to impurities, especially in view of the homogeneity of the samples and the good behavior of bulk magnetic data (see below).

The bulk magnetic properties of complexes **1-3** were determined by magnetometry. In Fig 3 are represented $\chi_M T$ *vs T* plots of polycrystalline samples (χ_M being the molar magnetic susceptibility per [LnCeLn] unit). The $\chi_M T$ product for **1** at room temperature (26.4 cm^3 K mol^{-1}) is only slightly lower than expected for a Ce^{III} ($^2F_{5/2}$, $g_J = 6/7$) and two Ho^{III} ($^5I_8$, $g_J = 5/4$) non-coupled ions (28.1 cm^3 K mol^{-1}). For compounds **2** and **3**, the values observed (24.7 and 5.56 cm^3 K mol^{-1}, respectively) are very close to the expected values for the uncoupled systems (23.8 and 5.84 cm^3 K mol^{-1}, respectively) as derived by adding the contribution from the Ce^{III} ion to that of the Er^{III} ($^4I_{15/2}$, $g_J = 6/5$) or Yb^{III} ($^2F_{7/2}$, $g_J = 8/7$) ions. This is consistent with the predicted composition of **1-3** and shows that, as expected, all the Stark sublevels of the ground state for each Ln^{III} ion are almost equally populated at room temperature. In the three cases, $\chi_M T$ decreases upon cooling, first smoothly and then increasingly faster as temperatures get lower. As for other lanthanide compounds, this is most likely due to the depopulation of the sublevels, with the additional contribution of weak magnetic interactions. From inspection of the lattice (see above), the latter may derive both, from intra- or intermolecular interactions.
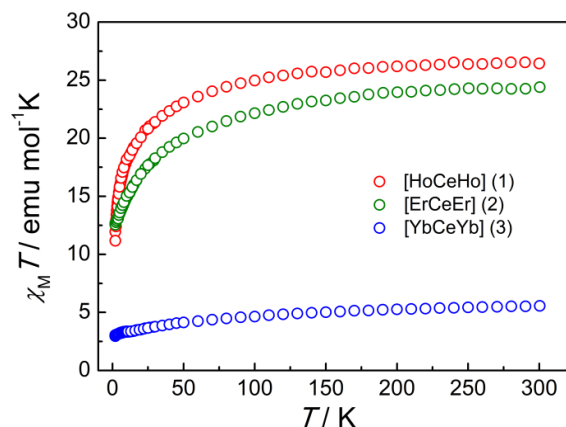
Figure 3. Plots of $\chi_M T$ *vs* T for **1-3** (χ_M is the molar paramagnetic susceptibility per [LnCeLn] unit).

The selectivity in the formation of **1-3** was corroborated by by mass spectrometry (MS). Crystalline samples dissolved in a mixture of DMSO and MeOH were analysed by the electrospray ionization (ESI) MS technique. The ionization caused the removal of the pyridine and water ligands from the complexes, producing moieties exclusively for the [LnCeLn] metal composition for the three compounds. Of upmost relevance is the fact that for each of the complexes, no signals for other metal distributions was detected (Figs 4, S7 to S14).
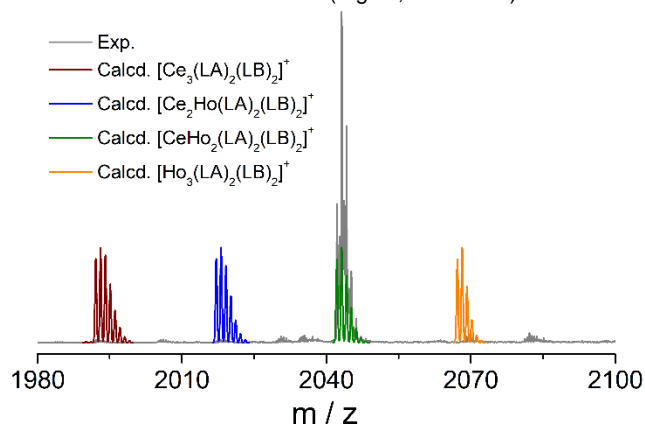

Figure 4. Selected region of the ESI-MS spectrum of **1** ([HoCeHo], gray line), the calculated signals for [Ce$_3$] (red line), [CeHo$_2$] (green line), [Ce$_2$Ho] (blue line) and [Ho$_3$] (orange line) fragments superimposed.

This constitutes very strong evidence of the selective distribution of lanthanide ions in the molecular scaffolds of **1-3** and establishes the robustness of their molecular architecture in solution. The absence of metal ion scrambling further confirms the enhanced stability of the [LnCeLn] assemblies compared to the related [LnLn'] systems[36] and shows the powerful ability of this reaction to produce, for the first time, purely heterometallic trinuclear lanthanide molecules through simple one-pot reactions.

In conclusion, we have demonstrated that a combination of two new chelating ligands gives access to a potentially large collection of pure heterometallic [LnLn'Ln] trinuclear complexes with a precise distribution of both types of metals present. The selectivity is solely based on the ionic radii disparity of these two different Ln ions. This unique new family of complexes will constitute a valuable platform to investigate the benefits of combining selectively different lanthanides within molecules. In the context of quantum computing, some combinations of metals, such as in the case of [ErCeEr] provide the ideal molecular hardware to implement quantum error correction protocols, using the ions as qubit realizations. Pulsed EPR and very low temperature magnetic measurements together with the state evolution predictions to implement this quantum gate will be published in due time.

Acknowledgements

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