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Synthesis and Properties of a Family of Unsymmetric Dinuclear Complexes of Ln^{III} (Ln = Eu, Gd, Tb)

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A new ligand has been synthesized with the aim of favoring distinct coordination environments within lanthanide polynuclear complexes. It has led to the formation of three unsymmetrical $[Ln^{III}{}_2]$ (Ln=Gd, Tb, Eu) complexes, exhibiting weak antiferromagnetic coupling and, for Eu and Tb, high single-ion magnetic anisotropy. All of these attributes are necessary for these clusters to behave as possible 2qubit quantum gates.

Because of their unique spectroscopic and electronic properties, lanthanides have for a long time been at the forefront of many frontier research fields. The presence of this group of metals in the area of molecular magnetism dates back to pioneering reports describing the nature of the magnetic exchange between Cu^{II} and Gd^{III} ions.[1] This interest has experienced a renewed impetus since slow relaxation of magnetization in single molecules was observed for mononuclear Tb^{III} and Dy^{III} complexes, resulting from splitting of their J multiplets into various $|J_z|$ sublevels.[2,3] Following this discovery, many other lanthanide complexes of varying nuclearity and exhibiting single-molecule-magnet[4,5] or single-chain-magnet[6] behavior have been made. This raised new expectations with respect to the goal of using single molecules as bits for magnetic memories. In addition, magnetic clusters with a ground-state doublet (effective spin $^1/_2$) fulfill some of the basic requirements needed to implement quantum logical operations, in particular, relatively long decoherence times and a good definition of qubit states.[7,8] In this context, it can be envisaged that individual lanthanide ions with strong anisotropy are potential candidates for embodying the qubits of scalable quantum gates (QGs).[9] A universal quantum computer (QC) can be built through a combination of single qubits and 2qubit C-NOT QGs. The operation of such a QG requires *dissimilar* qubits exhibiting weak interaction.[10] These conditions are necessary for the selective preparation of the quantum states required for the gate operations. The most advanced current attempts to prepare spin-based molecular QGs involve the synthesis of single molecules containing two connected coordination clusters, each in the form of a heterometallic wheel of the type $[Cr_7M]$ (M = various divalent metals).[11] We have also been attempting to prepare candidates of 2qubit QGs through the synthesis of poly(β-diketone) ligands, designed to cause the assembly of transition metals as pairs of magnetic clusters within molecules.[12−15] We have now turned our attention to lanthanides as possible spin carriers within such molecular models. In order to introduce the necessary inequivalence between both halves of the targeted assemblies, the synthesis of a suitable ligand [6-3-oxo-3-(2-hydroxyphenyl)propionyl)-2-pyridinecarboxylic acid, H_3L; Chart 1, left] has been devised and carried out successfully.

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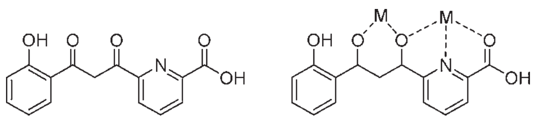
Chart 1. Ligand H_3L and the Coordination Mode of H_2L^- in **1**−**3** (the Mode for HL^{2-} Would Be Analogous)



It features a rich variety of donor atoms distributed asymmetrically, which has allowed the production of an analogous series of dinuclear Ln^{III} complexes with formulas $[Gd_2(HL)_2(H_2L)Cl(py)(H_2O)]$ (**1**), $[Tb_2(HL)_2(H_2L)Cl(py)_2]$ (**2**), and $[Eu_2(HL)_2(H_2L)(NO_3)(py)(H_2O)]$ (**3**). Each complex displays two metals with distinct coordination environments.

While dinuclear Ln_2 coordination compounds are very numerous in the literature (104, 113, and 99 hits for Gd, Tb, and Eu, respectively, on the CCDC, version 5.31, Feb 2010), examples involving two dissimilar metal sites are comparatively extremely scarce. More precisely, only four, two, and six examples (see the Supporting Information for references) respectively have been found for the cases of Gd, Tb, and Eu. Especially interesting is a gadolinium(III) semiquinonato complex,[16] which is the only asymmetric system that has seen its magnetic properties investigated. These were interpreted using a giant spin approach, and, therefore, no attempt was made to put into evidence the difference between both ions from a magnetic point of view. This would be easier if, contrary to Gd^{III}, the metal centers exhibit significant anisotropy, as would be likely for Eu^{III} and Tb^{III}.

The ligand H_3L was prepared as was previously done for a similar asymmetric β-diketone,[17] from the Claisen condensation between 2-hydroxyacetophenone and the appropriate ester (see the Supporting Information). Complexes **1**−**3** were obtained as crystals from layers with either of the reaction systems formed by H_3L and the corresponding LnX_3 salt ($X^- = Cl^-$ or NO_3^-; see the Supporting Information). They exhibit virtually the same IR spectrum (the only difference is caused by the anion), and their identity could be established by single-crystal X-ray diffraction.

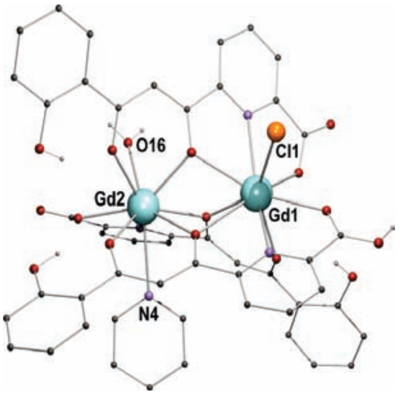


Figure 1. PovRay representation of **1**. The smallest gray atoms are hydrogen; the other gray atoms are carbon. Only hydrogen atoms riding on oxygen atoms are represented. The structures of **2** and **3** are analogous, with one py ligand instead of H_2O in the former and one monodentate NO_3^- ligand instead of Cl^- in the latter. Selected bond distances (Å) and angles (deg) in a **1**/**2**/**3** format: Ln−Cl, 2.7758(9)/2.727(3)/-; $Ln{-}O_{nitrate}$, -/-/2.458(9); $Ln{-}O_{water}$, 2.460(3)/-/2.462(9); $Ln{-}N_{py}$, 2.700(3)/2.644(9)−2.652(10)/2.703(12); Ln−N (range), 2.486(3)−2.622(3)/2.505(10)−2.547(9)/2.511(11)−2.652(10); Ln−O (range), 2.353(2)−2.597(2)/2.320(6)−2.537(6)/2.368(8)−2.647(8); Ln···Ln, 3.8127(4)/3.7853(13)/3.8192(10); Ln−O−Ln (range), 98.86(8)−103.36(9)/99.9(3)−103.7(2)/97.4(3)−103.6(3).

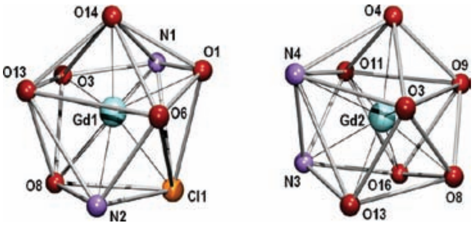


Figure 2. Labeled representation of the coordination environment around the metals of complex **1**, emphasizing their disparity and the reference polyhedra lying closest to their geometry. According to CShMs,[18] Gd1 (left) is not close enough to any reference shape, with the closest one being the so-called "irregular muffin shape". Gd2 (right) lies close to a "capped square antiprism". For complexes **2** and **3**, the geometries are analogous.

The three compounds exhibit very similar molecular structures (Figure 1 and Figures S1−S3 and Tables S1−S4 in the Supporting Information) with one dinuclear molecule per asymmetric unit and pyridine (**2** and **3**) or pyridine/water (**1**) lattice solvent molecules. The Ln^{III} metals are bridged and chelated by two HL^{2-} ligands disposed along the molecular axis in a head-to-tail manner and by one H_2L^- donor. This renders both metallic sites nonequivalent. The ligands H_3L, therefore, lose upon coordination either the carboxylic and β-diketonic protons or just the latter. The carboxylic proton of H_2L^- was found crystallographically for **1** and **3** (see Figure 1) and forms a strong hydrogen bond with a solvate py molecule (see Figure S4 in the Supporting Information). In complex **2**, the proton is likely to be distributed over two carboxylate oxygen atoms, forming a triangular hydrogen bond with a py molecule oriented accordingly (see Figure S5 in the Supporting Information). In all complexes, these ligands coordinate two metals through their β-diketonate- and dipicolinate-like coordination pockets, respectively, thus linking both centers via the common oxygen atom of these two pockets. Nonacoordination around Ln1 (Figure 2) is completed with one terminal Cl^- (**1** and **2**) or NO_3^- (**3**) ligand, whereas the same coordination number in Ln2 is reached through binding of either one H_2O and one py ligand (**1** and **3**) or two py groups (**2**). The stereochemical disparity between both metals within each complex has been quantified by means of continuous-shape measures (CShMs).[18] These have established that the coordination geometry of the sites Ln1 is very irregular and does not sufficiently approach any of the known reference polyhedra proposed for coordination number 9.[18] By contrast, these calculations show that the shape of metals Ln2 is best described as a distorted capped square antiprism (see Table S5 in the Supporting Information for CShMs on all of the metals with respect to eight reference polyhedra for **1**−**3**). In general, the bond distances to the metals (see the caption of Figure 1 or the Supporting Information for a complete list) follow the trend expected from an increase of the atomic number within the period.

For their relevance in QC, the presence of weak antiferromagnetic (AF) coupling within complexes **1**−**3** and of magnetic anisotropy in the metals was evaluated by means of bulk magnetic measurements on polycrystalline samples. Figure 3

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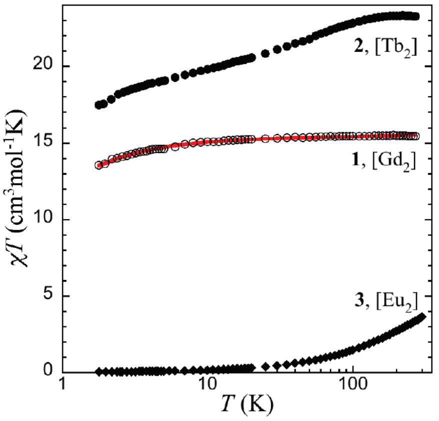

Figure 3. χT vs T curves for compounds **1**−**3**. χ is the molar paramagnetic susceptibility per [Ln$_2$] unit. The full line is the best fit of the experimental data for **1** (see the text).

shows the temperature dependence of χT (with χ being the molar paramagnetic susceptibility per Ln$_2$ unit) for the three compounds. Complex **1** presents a stable χT value of ca. 15.5 cm^3 K mol^{-1} from 280 K down to near 30 K, where a small decrease is observed down to 13.58 cm^3 K mol^{-1} at 1.8 K. In the absence of anisotropic effects (as is confirmed by isothermal magnetization data; see Figure S6 in the Supporting Information), this decline can only be ascribed to weak AF interactions. On the other hand, at 2 K the reduced magnetization of **1** saturates rapidly, reaching $M_S = 13.84\,\mu_B$ at 5 T (Figure S6 in the Supporting Information). The experimental values of M_S and χT agree with those expected for two weakly antiferromagnetically coupled Gd^{III} ions with $g = 2$ ($\chi T = 15.75$ cm^3 K mol^{-1} at high temperature and $M_S = 14$). Indeed, the χT vs T curve was reproduced satisfactorily (Figure 3) with a model based on the isotropic spin Hamiltonian $H = -J(S_{Gd1} \cdot S_{Gd2})$ including a fixed temperature-independent paramagnetism (TIP) term,[19] which yielded the following best parameters; $J/k_B = -0.041(1)$ K, $g = 1.98(1)$, and TIP $= 6 \times 10^{-4}$ cm^3 K mol^{-1}. These values are in correct agreement with the literature data.[20] For **2**, χT remains stable at ca. 23.3 cm^3 K mol^{-1} at 280 K down to 150 K, when a gradual decrease begins. The shape of the χT vs T curve below 25 K is very similar to that of **1**, reaching a value of 17.46 cm^3 K mol^{-1} at 1.8 K. The high-temperature values agree well with those expected for two uncoupled Tb^{III} ions ($^7F_6$, $S = 3$, $L = 3$, $g = {}^3/_2$, $\chi T = 23.62$ cm^3 K mol^{-1}). By analogy with **1**, the decline at low temperature is probably due to the weak AF coupling between Tb^{III} ions, while the higher temperature behavior can be ascribed to the effects of the strong spin−orbit coupling of Tb^{III}, thus unveiling the strong magnetic anisotropy in **2**. For compound **3**, χT decreases continuously from 3.45 cm^3 K mol^{-1} at 280 K, slightly above the calculated value for two uncoupled Eu^{III} ions, which suggests that excited states with higher J values are populated. At near 20 K, χT is already close to zero, indicating a $J = 0$ ground state of the Eu^{III} ions ($^6F_0$). The observed χT vs T curve should thus be attributed to depopulation of the Stark levels of the Eu^{III} ions, masking the possible weak AF interaction that could be inferred by analogy with **1** and **2**.

The above results demonstrate a successful synthetic strategy for locating two Ln^{III} ions within a molecule, exhibiting two distinct environments and weak AF coupling. In addition, for compounds **2** and **3**, the metals present strong spin−orbit coupling, resulting in strong magnetic anisotropy and thus gathering many of the requirements needed for these species to operate as QGs. Single-crystal, ultralow-temperature magnetic studies are in progress in order to put into evidence the magnetic dissymmetry of both metals within complex **2** and therefore evaluate its potential as hardware in QC.

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Supporting Information Available: Synthetic and crystallographic details, CShMs, and various structural figures and tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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