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Linear Trinuclear Mixed-Metal Co^{II}–Gd^{III}–Co^{II} Single-Molecule Magnet: $[L_2Co_2Gd][NO_3]\cdot 2CHCl_3$ ($LH_3 = (S)P[N(Me)N{=}CH{-}C_6H_3\text{-}2\text{-}OH\text{-}3\text{-}OMe]_3$)

Vadapalli Chandrasekhar,*,† Balasubramanian Murugesa Pandian,† Ramachandran Azhakar,†
Jagadese J. Vittal,‡ and Rodolphe Clérac*,§

Department of Chemistry, Indian Institute of Technology-Kanpur, Kanpur-208016, India,
Department of Chemistry, National University of Singapore, Singapore, Université Bordeaux 1;
CNRS, Centre de Recherche Paul Pascal - UPR8641, 115 avenue du Dr. Albert Schweitzer,
33600 Pessac, France

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A linear trinuclear mixed-metal Co_2Gd complex supported by two phosphorus-based multisite coordination ligands has been shown to be a single-molecule magnet.

The synthesis of the dodecanuclear manganese cluster $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]$[1a] followed by the discovery that it functions as a single-molecule magnet (SMM)[1b,c] has spurred a wide interest in the phenomenon of single-molecule magnetism and the design of molecules that can function as SMMs.[2–3] This interest emanates from the fact that SMMs display magnetic properties which are normally associated with mesoscale magnetic particles and super paramagnetism. Thus, SMMs can be magnetized, below certain temperatures, with retention of their magnetization after the magnetic field is switched off. Many potential applications have been envisaged for SMMs including information processing and data storage.[4] Furthermore, the discovery of magnetization quantum tunneling effects in SMMs has led to the view that these nano-objects could be exploited as qubits in quantum computing.[5] In general, the design of SMM molecules is guided by the thinking that their unique properties are derived from a combination of intrinsic factors including a large spin ground state (S) and a large uniaxial magnetic anisotropy (large negative D and small E considering the following Hamiltonian anisotropy term: $H = DS_{Tz}^2 + E(S_{Tx}^2 - S_{Ty}^2)$).[6] Accordingly, polynuclear complexes containing high-spin metal ions have been investigated as SMMs.[7] More recently mononuclear lanthanide complexes[8] and mixed-metal assemblies[9–11] containing transition metal and lanthanide ions have also been studied as potential SMMs. However, there have been no reports of SMM behavior from mixed 3d–4f complexes involving Gd(III) ions. Indeed, this is not surprising considering that in these mixed-metal SMMs the anisotropy is mainly brought by the lanthanide ions and that usually Gd(III) ion is considered as an isotropic magnetic center as it possesses a half-filled 4f shell with a quenched

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* To whom correspondence should be addressed. Fax: (+91)-512-2597436 (V.C.); (+33)-5-5684-5600 (R.C.). E-mail: vc@iitk.ac.in (V.C.); clerac@crpp-brodeaux.cnrs.fr (R.C.).

† Indian Institute of Technology-Kanpur.

‡ National University of Singapore.

§ Centre de Recherche Paul Pascal.

(1) (a) Lis, T. *Acta Crystallogr.* **1980**, *B36*, 2042. (b) Sessoli, R.; Tsai, H.-L.; Schake, A. R.; Wang, S.; Vincent, J. B.; Folting, K.; Gatteschi, D.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1993**, *115*, 1804. (c) Sessoli, R.; Gatteschi, D.; Caneschi, A.; Novak, M. A. *Nature* **1993**, *365*, 141.

(2) (a) Dendrinou-Samara, C.; Alexiou, M.; Zaleski, C. M.; Kampf, J. W.; Kirk, M. L.; Kessissoglou, D. P.; Pecoraro, V. L. *Angew. Chem., Int. Ed.* **2003**, *42*, 3763. (b) Andres, H.; Basler, R.; Blake, A. J.; Cadiou, C.; Chaboussant, G.; Grant, C. M.; Güdel, H.-U.; Murrie, M.; Parsons, S.; Paulsen, C.; Semadini, F.; Villar, V.; Wernsdorfer, W.; Winpenny, R. E. P. *Chem. Eur. J.* **2002**, *8*, 4867. (c) Murrie, M.; Stöeckli-Evans, H.; Güdel, H. U. *Angew. Chem., Int. Ed.* **2001**, *40*, 1957. (d) Oshio, H.; Hoshino, N.; Ito, T. *J. Am. Chem. Soc.* **2000**, *122*, 12602. (e) Sun, Z.; Grant, C. M.; Castro, S. L.; Hendrickson, D. N.; Christou, G. *Chem. Commun.* **1998**, 721. (f) Langley, S. J.; Helliwell, M.; Sessoli, R.; Rosa, P.; Wernsdorfer, W.; Winpenny, R. E. P. *Chem. Commun.* **2005**, 5029. (g) Ishikawa, N.; Otsuka, S.; Kaizu, Y. *Angew. Chem., Int. Ed.* **2005**, *44*, 731. (h) Schelter, E. J.; Prosvirin, A. V.; Dunbar, K. R. *J. Am. Chem. Soc.* **2004**, *126*, 15004.

(3) (a) Li, D.; Parkin, S.; Wang, G.; Yee, G. T.; Clérac, R.; Wernsdorfer, W.; Holmes, S. M. *J. Am. Chem. Soc.* **2006**, *128*, 4214. (b) Oshio, H.; Nihei, M.; Koizumi, S.; Shiga, T.; Nojiri, H.; Nakano, M.; Shirakawa, N.; Akatsu, M. *J. Am. Chem. Soc.* **2005**, *127*, 4568. (c) Kachi-Terajima, C.; Miyasaka, H.; Sugiura, K.-i.; Clérac, R.; Nojiri, H. *Inorg. Chem.* **2006**, *45*, 4381.

(4) Ritter, S. K. *Chem. Eng. News* **2004**, *82* (50), 29.

(5) Leuenberger, M. N.; Loss, D. *Nature* **2001**, *401*, 789.

(6) (a) Gatteschi, D.; Sessoli, R. *Angew. Chem., Int. Ed.* **2003**, *42*, 268. (b) Wernsdorfer, W. *Adv. Chem. Phys.* **2001**, *118*, 99.

(7) (a) Boudalis, A. K.; Raptopoulou, C. P.; Abarca, B.; Ballesteros, R.; Chadlaoui, M.; Tuchagues, J.-P.; Terzis, A. *Angew. Chem., Int. Ed.* **2006**, *45*, 432. (b) Boudalis, A. K.; Donnadieu, B.; Nastopoulos, V.; Clemente-Juan, J. M.; Mari, A.; Sanakis, Y.; Tuchagues, J.-P.; Perlepes, S. P. *Angew. Chem., Int. Ed.* **2004**, *43*, 2266. (c) Winpenny, R. E. P. *J. Chem. Soc., Dalton Trans.* **2002**, 1.

(8) (a) Ishikawa, N.; Sugita, M.; Ishikawa, T.; Koshihara, S.; Kaizu, Y. *J. Am. Chem. Soc.* **2003**, *125*, 8694. (b) Ishikawa, N.; Sugita, M.; Ishikawa, T.; Koshihara, S.; Kaizu, Y. *J. Phys. Chem. B* **2004**, *108*, 11265. (c) Sugita, M.; Ishikawa, N.; Ishikawa, T.; Koshihara, S.; Kaizu, Y. *Inorg. Chem.* **2006**, *45*, 1299.

(9) (a) Osa, S.; Kido, T.; Matsumoto, N.; Re, N.; Pochaba, A.; Mrozinski, J. *J. Am. Chem. Soc.* **2004**, *126*, 420. (b) Costes, J. P.; Dahan, F.; Wernsdorfer, W. *Inorg. Chem.* **2006**, *45*, 5. (c) Costes, J. P.; Auchel, M.; Dahan, F.; Peyrou, V.; Shova, M.; Wernsdorfer, W. *Inorg. Chem.* **2006**, *45*, 1924. (d) He, F.; Tong, M.-L.; Chen, X.-M. *Inorg. Chem.* **2005**, *44*, 8285.

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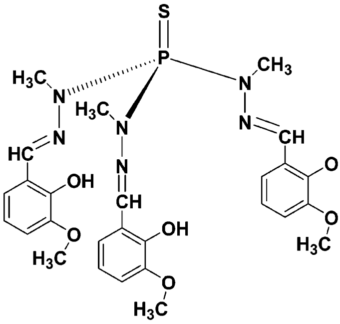
Chart 1. Ligand LH$_3$



orbital contribution. Nevertheless the high-spin ground state of Gd(III) ($S = 7/2$) can still be viewed as an advantage in order to get high-spin complexes. Associating trivalent gadolinium with highly anisotropic metal ions such as Co(II) is a new and interesting strategy to obtain SMMs that, as far as we know, has not been explored. In this paper we report the design of a new phosphorus-based multisite coordination ligand LH$_3$ (**1**) (Chart 1) that allows a one-step facile synthesis of the heterobimetallic trinuclear [L$_2$Co$_2$Gd][NO$_3$]·2CHCl$_3$ (**2**) complex. Synthesis, structural characterization, and magnetic studies of this complex are discussed herein. It may be noted that this compound is the first example of a cobalt−lanthanide system that has been shown to function as a SMM.

Our experience with phosphorus-based tris hydrazone ligands[12] allowed us to design LH$_3$, which was prepared by the condensation of (S)P[N(Me)NH$_2$]$_3$ and *o*-vanillin (Scheme S1). This ligand has nine potential coordination sites in the form of three imino nitrogen atoms, three phenolic oxygen atoms, and three oxygen atoms of the −OCH$_3$ groups. Reaction of LH$_3$ with Co(O$_2$CCH$_3$)$_2$·4H$_2$O followed by Gd(NO$_3$)$_3$·6H$_2$O afforded [L$_2$Co$_2$Gd][NO$_3$]·2CHCl$_3$ (**2**)[13] (Scheme S2). Two trianionic ligands, L^{3-}, are involved in holding the three metal ions together[14] (Figure 1 and Figure S1). Each ligand utilizes all nine coordination sites in the formation of **2**. The coordination environment around cobalt is made up of three nitrogen and three oxygen (phenolic) atoms. The coordination geometry around cobalt is distorted octahedral (Figure S2). The central Gd(III) is encapsulated by 12 oxygen atoms in a distorted icosahedral geometry (Figure S3). Two types of Gd−O bond distances are observed: six short distances ranging from 2.395(4) to 2.424(4) Å involving the phenolic oxygen atoms and six long distances ranging from 2.877(5) to 2.917(5) Å involving the methoxy oxygen atoms. The phenolate oxygen atoms are involved in bridging cobalt and gadolinium ions. Interestingly, the Co−Gd−Co array in **2** is perfectly linear, which arises as a result of the gadolinium ion occupying the inversion center of the $P\bar{1}$ space group.[14] Because of this linear arrangement of the three metal ions, a perfect paddlewheel geometry is seen for **2** when viewed from one end (Figure S4). While the Co−Gd distance in **2** is 3.307(1) Å, the intercobalt distance is 6.614(2) Å. The end−end distance of the trinuclear array, as measured by the separation between the two terminal sulfur atoms, is 17.120(5) Å.

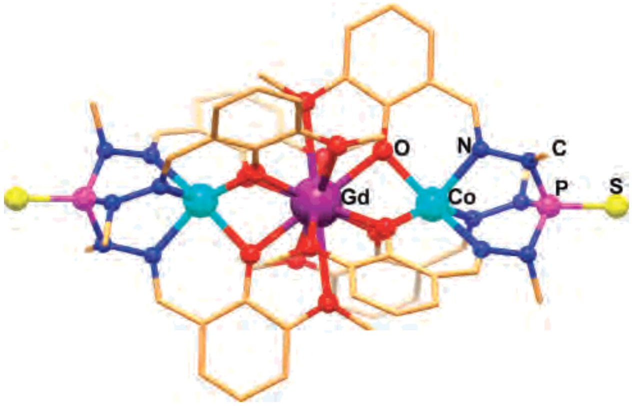


Figure 1. Structure of the cationic portion of **2** [L$_2$Co$_2$Gd]$^+$.

Magnetic susceptibility measurements were carried out on a polycrystalline sample of **2** in the temperature range 1.8−300 K. The room temperature χT product estimated at 14.3 cm^3·K/mol (Figure 2a) is in good agreement with the presence of one Gd^{III} ($S = 7/2$; $C = 7.875$ cm^3·K/mol expected for $g = 2$)[15] and two Co^{II} ions (with an effective $S = 3/2$ spin and a Curie constant around 3 cm^3·K/mol). Decreasing the temperature, the χT product at 1000 Oe continuously increases to reach 28.5 cm^3·K/mol at 3.6 K, indicating dominant ferromagnetic interactions in the trinuclear complex (Figure 2a). The final decrease of the χT product (at 1000 Oe) below 3.5 K is probably induced by the presence of magnetic anisotropy and/or weak antiferromagnetic interaction between trinuclear complexes. It is worth noting the difficulty to further analyze the temperature dependence of the susceptibility due to the presence of Co(II) metal ions and their intrinsic complicated magnetic properties

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(10) (a) Zaleski, C. M.; Depperman, E. C.; Kampf, J. W.; Kirk, M. L.; Pecoraro, V. L. *Angew. Chem., Int. Ed.* **2004**, *43*, 3912. (b) Mishra, A.; Wernsdorfer, W.; Abboud, K. A.; Christou, G. *J. Am. Chem. Soc.* **2004**, *126*, 15648. (c) Mori, F.; Nyui, T.; Ishida, T.; Nogami, T.; Choi, K.-Y.; Nojiri, H. *J. Am. Chem. Soc.* **2006**, *128*, 1440. (d) Aronica, C.; Pilet, G.; Chastanet, G.; Wernsdorfer, W.; Jacquot, J.-F.; Luneau, D. *Angew. Chem., Int. Ed.* **2006**, *45*, 4659. (e) Mishra, A.; Wernsdorfer, W.; Parsons, S.; Christou, G.; Brechin, E. K. *Chem. Commun*. **2005**, 2086. (f) Ferbinteanu, M.; Kajiwara, T.; Choi, K.-Y.; Nojiri, H.; Nakamoto, A.; Kojima, N.; Cimpoesu, F.; Fujimura, Y.; Takaishi, S.; Yamashita, M. *J. Am. Chem. Soc.* **2006**, *128*, 9008.

(11) Murugesu, M.; Mishra, A.; Wernsdorfer, W.; Abboud, K. A.; Christou, G. *Polyhedron* **2006**, *25*, 613.

(12) Chandrasekhar, V.; Azhakar, R.; Andavan, G. T. S.; Krishnan, V.; Zacchini, S.; Bickley, J. F.; Steiner, A.; Butcher, R. J.; Kögerler, P. *Inorg. Chem.* **2003**, *42*, 5989.

(13) The LH$_3$ ligand (0.10 g 0.17 mmol) was dissolved in a mixture of 30 mL of chloroform and 30 mL of methanol. Cobalt acetate tetrahydrate (0.04g, 0.17 mmol) was added to this solution and stirred at room temperature (5 min). At this stage, gadolinium nitrate hexahydrate (0.04 g, 0.08 mmol) was added and the reaction mixture was further stirred for 6 h to afford a red-colored solution. It was filtered, and the filtrate evaporated to dryness. The residue obtained was washed with *n*-hexane and dried. This powder was identified as **2**. Yield: 85 mg (68 %) Mp: >300 °C. Anal. Calcd (%) for [L$_2$Co$_2$Gd][NO$_3$]·2CHCl$_3$: C 38.01, H 3.51, N 10.29, S 3.62. Found: C 37.88, H 3.47, N 10.12, S 3.58. FT-IR $\upsilon_{C=N}$/cm^{-1}: 1600. MS(FAB): 1469.4 [(L$_2$Co$_2$Gd) − 1]$^+$.

(14) Crystal data for compound **2**: C$_{56}$H$_{62}$Cl$_6$Co$_2$GdN$_{13}$O$_{15}$P$_2$S$_2$, M_r = 1771.06, triclinic, space group $P\bar{1}$, $a = 11.493(3)$ Å, $b = 12.151(4)$ Å, $c = 15.795(4)$ Å, $\alpha = 83.390(6)°$, $\beta = 72.027(5)°$, $\gamma = 61.945(4)°$, $V = 1850.4(8)$ Å^3, $T = 223(2)$ K, $Z = 1$, $\rho = 1.589$ g cm^{-3}, $\mu = 1.713$ mm^{-1}, $F(000) = 891$, cryst dimens 0.38 × 0.25 × 0.13 mm^3, 10 604 reflns collected, 6522 unique ($R_{int} = 0.0271$), R1 = 0.0641, wR2 = 0.1825, using 903 reflections with $I > 2\sigma(I)$.

(15) Benelli, C.; Gatteschi, D. *Chem. Rev.* **2002**, *102*, 2369.

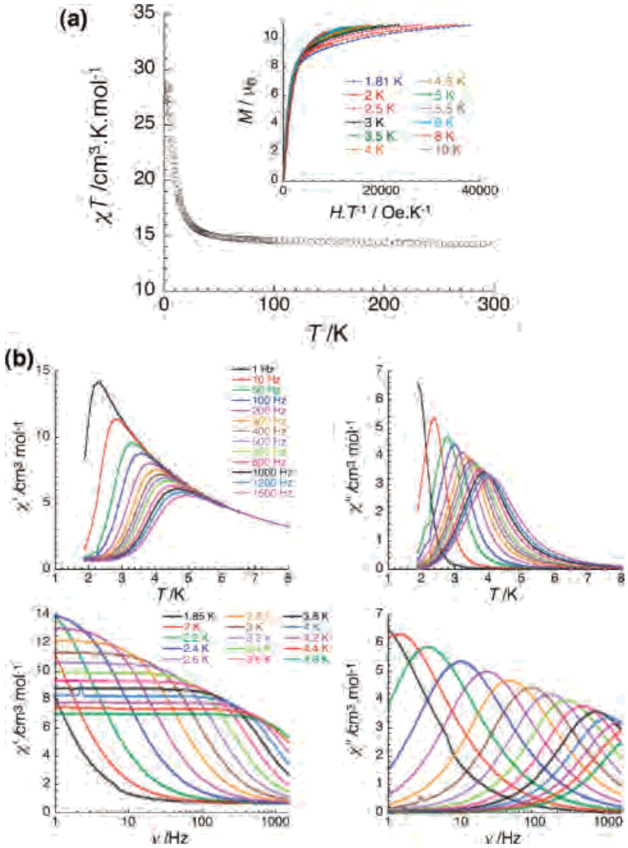

Figure 2. (a) Temperature dependence of χT (where $\chi = M/H$) at 1000 Oe for complex **2**. Inset: Plot of magnetization vs *H*/*T* between 1.8 and 10 K. (b) Temperature (top) and frequency (bottom) dependence of the in-phase and out-of-phase ac susceptibility at different frequencies and different temperatures under zero dc field.

(including the presence of spin−orbit coupling and magnetic anisotropy).

The field dependences of the magnetization measured between 1.85 and 10 K (Figure S5 and inset of Figure 2a) reveal a lack of a true saturation even at 7 T and 1.81 K. At this lowest available temperature, no significant hysteresis effect is observed on the *M* vs *H* plot (Figure S6). Indeed, *M* increases first rapidly below 6000 Oe up to 8.3 μ_B and then reaches slowly to 10.9 μ_B at 7 T, which suggests at least a spin ground state of 9/2 for the complex (note that an effective $S = 1/2$ ground state is expected for the Co^{II} ions at low temperature with a large and anisotropic *g* value). This high-field behavior confirms also the presence of a significant anisotropy that prevents the rapid saturation of the magnetization. This point is further confirmed by the *M* vs *H*/*T* plot shown in the inset of Figure 2a as the data do not superimpose on a single master curve as expected for isotropic systems.

In order to check for the presence of SMM behavior in **2**, ac susceptibility measurements have been performed as a function of the temperature at different frequencies and as a function of the frequency at different temperatures (Figure 2b). This complete set of data demonstrates that **2** exhibits slow relaxation of the magnetization and strongly suggests a SMM behavior. Indeed, the deduced relaxation time (τ) confirms this hypothesis (Figure 3). Fit of the τ vs T^{-1} data by an Arrhenius law allows an estimation of the characteristic SMM energy gap, Δ, at 27.2 K and the pre-exponential factor, τ_0, at 1.7×10^{-7}s.

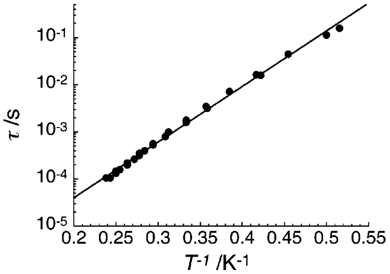

Figure 3. τ vs T^{-1} plot at $H_{dc} = 0$. The solid lines represent an Arrhenius fit of the data.

As observed in many SMMs, it is likely that the observed Δ takes an effective value, resulting from a "short-cut" of the thermal barrier by quantum tunneling of the magnetization (QTM). Therefore, additional ac measurements have been performed applying small magnetic fields in order to remove the degeneracy of the m_S states and thus possible zero-field QTM between the $\pm m_S$ states.[6]

The frequency dependence of the ac susceptibility was measured at 3.8 K under a small dc field. At this temperature, the characteristic frequency (maximum of the χ'' vs ν plot) decreases only slightly from 690 Hz at 0 Oe, to reach a minimum of 600 Hz around 1000 Oe (Figures S7−S9). As shown by this result, the QTM relaxation pathway remains only slightly efficient at 3.8 K in zero-field explaining the observed slowing down of the system for fields under 1000 Oe. For **2**, the relaxation time estimated using ac measurements under 1000 Oe follows an Arrhenius behavior with $\tau_0 = 1.5 \times 10^{-7}$ s and $\Delta/k_B = 27.4$ K (Figure S10) almost superposed with the data at zero dc field. The thermally activated relaxation is thus almost unchanged, illustrating the weak influence of the zero-field QTM above 1.8 K.

In conclusion, we report a facile synthesis of a new linear trinuclear Co_2Gd complex that behaves as a SMM. This compound illustrates the success of our synthetic strategy to design new SMMs: using Gd(III) ions in order to increasing the spin ground state of the resulting complex and associating ferromagnetically this trivalent lanthanide with anisotropic Co(II) metal ions.

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Supporting Information Available: Experimental details, additional schemes and figures, crystal data, and a CIF file for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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