Molecular Magnetism

[GdNi₆] and [LaNi₆]: High-Field EPR Spectroscopy and Magnetic Studies of Exchange-Coupled Octahedral Clusters**

Yasuhiko Yukawa,* Guillem Aromí,* Satoshi Igarashi, Joan Ribas, S. A. Zvyagin, and J. Krzystek

The preparation of transition-metal clusters with relevance in molecular magnetism has been a very prolific area of coordination chemistry,[1–3] and has become of primary importance since the discovery of single-molecule magnets (SMMs).[4,5] As a result, a high level of understanding has been achieved of the nature and mechanism of the magnetic super exchange between 3d metals.[6–8] Indeed, the vast majority of SMMs known to date are made of manganese,[9] iron,[10] nickel,[11] cobalt,[12] and vanadium.[13] In contrast, the magnetic coupling between 3d and 4f metals is still not understood very well and has therefore not been exploited as a potential entry to a new category of SMMs.[14,15]

Of all open-shell 4f ions, Gd^{III} has been studied the most since it does not show the complicating effect of spin-orbit coupling. The quasi-systematic ferromagnetic nature of the coupling between Cu^{II} and Gd^{III} has been corroborated by a considerable amount of experimental data,[16] and a recent report has established the theoretical grounds of this observation.[17] In contrast, the magnetic exchange between Ni^{II} and Gd^{III}—always found to be ferromagnetic so far[18–23]—has not been explored as extensively. The few systems where this coupling has been analyzed are almost all dinuclear compounds.

As a continuation of our studies on heterometallic 3d–4f clusters,[24–26] we have prepared a series of isostructural and highly symmetric exchange-coupled clusters of the formula

[*] Prof. Dr. Y. Yukawa, Dr. S. Igarashi
    Department of Environmental Science
    Faculty of Science
    Niigata University
    8050 Ikarashi Nino-cho, Niigata 950-2181 (Japan)
    Fax: (+81) 25-262-6361
    E-mail: yukawa@env.sc.niigata-u.ac.jp

    Dr. G. Aromí, Prof. Dr. J. Ribas
    Departament de Química Inorgànica
    Universitat de Barcelona
    Diagonal 647, 08028 Barcelona (Spain)
    Fax: (+34) 93-490-7725
    E-mail: guillem.aromi@qi.ub.es

    Dr. S. A. Zvyagin, Dr. J. Krzystek
    National High Magnetic Field Laboratory
    Florida State University
    Tallahassee, FL 32310 (USA)

$(NMe_4)[LnNi_6(pro)_{12}](ClO_4)_4$ (Ln = Gd, La; Hpro = proline). Similar compounds with other amino acids (Gly, Ala, Thr) have been recently reported.[27] This family of clusters provides a good opportunity to systematically study the magnetic exchange between 3d and 4f metals. We started by investigating coupling between Ni^{II} and Gd^{III}, the only case in which first-order spin-orbit coupling is absent, in the cluster $(NMe_4)[GdNi_6(pro)_{12}](ClO_4)_4$ (**1**). We were able to single out the contribution of Ni^{II} by comparing **1** with the lanthanum analogue **2** (La^{III} is diamagnetic). We report here the preparation and structures of **1** and **2** along with the first quantitative study of the magnetic properties of this category of compounds through the use of bulk magnetometry and high-frequency and high-field EPR (HF-EPR) spectroscopy.

The heterometallic complexes **1** and **2** were obtained as pure[28] purple precipitates after addition of NMe_4ClO_4 (694 mg, 4 mmol) to mixtures of $Gd(ClO_4)_3$ (911 mg, 2 mmol) or $La(ClO_4)_3$ (875 mg, 2 mmol) and $[Ni(pro)_2]$ (3.47 g, 12 mmol) in acetonitrile (80 mL). The two clusters are isostructural[29] and display the same structure as the Sm^{III} and Eu^{III} analogues.[24–26] The two molecules consist of a Ln^{III}-centered cage of six symmetry-equivalent Ni^{II} ions, which form a perfect octahedron (Figure 1). The nickel centers are
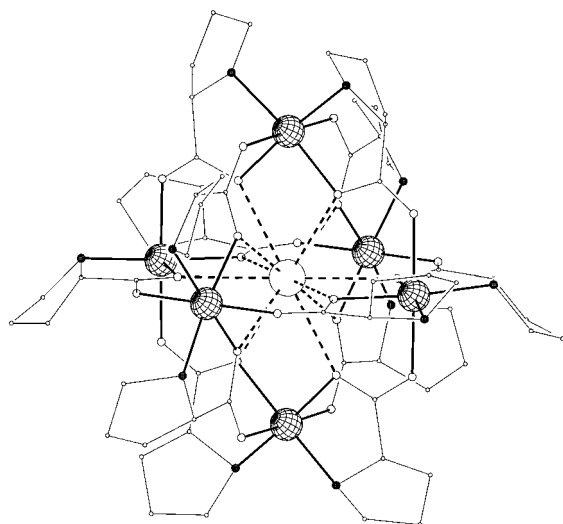

Figure 1. Molecular drawing of the cluster cation of $(NMe_4)[LnNi_6(pro)_{12}](ClO_4)_4$ (Ln = Gd^{III} (**1**), La^{III} (**2**)). Hydrogen atoms are not shown. Code for atoms: Ln: large empty sphere, Ni: large globes, N: medium-sized black spheres, O: medium-sized empty spheres, C: small spheres. Selected average distances [Å] for **1**/**2**: Ln–O 2.681(2)/2.713(2), O···O (within icosahedron) 2.83(3)/2.86(4), Ni–O 2.04(1)/2.05(2), Ni–N 2.059(4)/2.069(4), Ln···Ni 3.6970(6)/3.7114(7), Ni···Ni (*cis*) 5.2283(6)/5.2486(7), Ni···Ni (*trans*) 7.3939(9)/7.4227(9).

equatorially *cis*-chelated by two prolinate ligands. The oxygen donor of the chelate rings is also connected to the central lanthanide, providing dodeca coordination around this ion. The other oxygen donor of each prolinate group occupies one axial position of an adjacent $[Ni(pro)_2]$ unit, forming Ni···Ni carboxylate bridges in a *syn,anti* fashion. Replacement of Gd^{III} by La^{III} has very little influence on the metric parameters of the cluster.
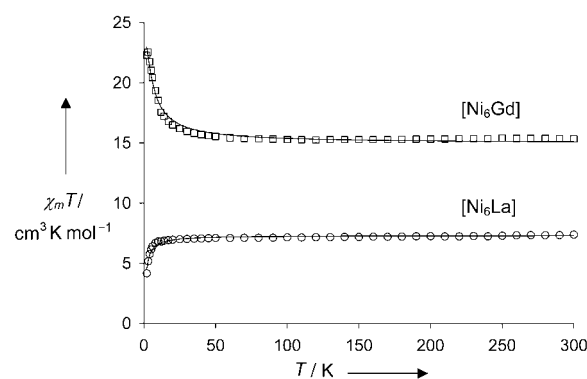

Figure 2. Plots of $\chi_m T$ versus T for compounds **1** and **2**. The solid lines represent fits to the experimental data (see text for details).

In contrast, there is a dramatic influence on the magnetic behavior of the cluster upon replacement of La^{III} in **2** (f^0, diamagnetic) with Gd^{III} in **1** (f^7, paramagnetic). Figure 2 shows the plots of the molar paramagnetic susceptibility $\chi_m T$ (corrected for the diamagnetic contribution) as a function of temperature T. The measurements were made under a constant magnetic field of 0.3 T between 2 and 300 K. The product $\chi_m T$ for **1** is 15.34 $cm^3 K mol^{-1}$ at room temperature, consistent with six independent Ni^{II} centers and one Gd^{III} ion in the molecule, following a Curie law with an average of $g \approx 2.2$. This value remains unchanged with decreasing temperature until about 50 K, where it increases to 22.29 $cm^3 K mol^{-1}$ at 2 K. This shows that the coupling within the cluster is predominantly ferromagnetic in character.

To describe this behavior, the spin Hamiltonian in Equation (1) was used (S_1 to $S_6 = 1$ and $S_7 = 7/2$, see

$$\hat{H} = -2J(\hat{S}_1\hat{S}_2 + \hat{S}_1\hat{S}_3 + \hat{S}_1\hat{S}_4 + \hat{S}_1\hat{S}_5 + \hat{S}_2\hat{S}_3 + \hat{S}_2\hat{S}_5 + \hat{S}_2\hat{S}_6$$
$$+ \hat{S}_3\hat{S}_4 + \hat{S}_3\hat{S}_6 + \hat{S}_4\hat{S}_5 + \hat{S}_4\hat{S}_6 + \hat{S}_5\hat{S}_6) - 2J'\hat{S}_7\sum_{i=1}^{6}\hat{S}_i \quad (1)$$

Figure 3). This Hamiltonian, which can be solved analytically by using the Kambe vector-coupling approach,[30] incorporates the Ni···Ni coupling (J) and the Ni···Gd exchange (J'), whereas the coupling between nonadjacent Ni^{II} atoms as well as zero-field splitting effects (ZFS) are not included.
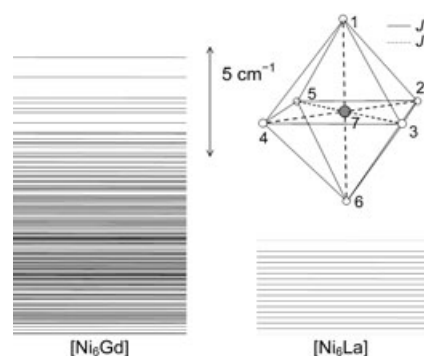

Figure 3. Schematic representations of the spin-level ladders for compounds **1** (left) and **2** (right). The number of spin states are 694 and 141, and the energy ranges spanned by the ladders are 12.70 and 5.67 cm^{-1} for **1** and **2**, respectively. Also shown is the numbering scheme employed for the magnetic models.

This model affords a total of 694 $|S_T, S_{ABC}, S_A, S_B, S_C\rangle$ spin states ranging from $S_T = 1/2$ to $19/2$, with a total degeneracy of 5832. Their energies were inserted into a $\chi_m = f(T)$ expression derived from the Van Vleck equation to fit the experimental data. The calculation yielded the fit parameters $J = -0.12$ cm^{-1}, $J' = 0.13$ cm^{-1}, and $g = 2.02$. The difference between this g value and that estimated at 300 K with a Curie law underscores the sensitivity to the model used in fitting the data. The calculated coupling constants give rise to a fivefold degenerate spin ground state with $S_T = 13/2$ corresponding to $|13/2, 3, 2, 2, 2\rangle$, in an example of spin frustration in the strictest sense of the word.[31] This ground state is close in energy to a threefold degenerate excited state, with $S_T = 15/2$ lying only 0.01 cm^{-1} higher in energy. The energies of the spin states span an energy range of 12.70 cm^{-1} (see spin-level ladder in Figure 3).

The possible influence of a D parameter on the $\chi_m T$ versus T curve was evaluated by means of simulations from full-matrix diagonalization using the program MAGPACK.[32] It was found that reasonable values for this parameter have almost no influence on the curve for this system (see Figure S1 in the Supporting Information). This, and the results from HF-EPR spectroscopy (see below), justify the omission of D from the model used to fit this curve. Variable-temperature isofield-reduced magnetization measurements on **1** (not shown) indicate that at high enough fields, the $|M_s| = 19/2$ level becomes the ground state, since $M/N\mu_B$ reaches a value of 18.41 reduced units, higher than expected for the $S_T = 13/2$ ground state. The AC susceptibility measurements showed that complex **1** does not display slow relaxation of the magnetization (as ascertained by the absence of an out-of-phase component of χ_m). This might be due to the lack of ZFS or by the accumulation of spin states within a very narrow energy range near the ground state. The above results confirm the observations made on the very few cases of Gd···Ni exchange previously studied; all were found to be very weakly ferromagnetic. Furthermore, these findings supplement the limited data on Ni···Ni coupling through only one *syn,anti* carboxylate ligand. The reported J values are also very small, two of them antiferromagnetic[33, 34] and the third ferromagnetic.[35]

Complex **2** was studied to establish the properties of the Ni$_6$ moiety without the influence of a paramagnetic ion at the central position. The value of $\chi_m T$ at room temperature is 7.38 cm^3 K mol^{-1}, which corresponds to the expected value for a cluster of six isolated Ni^{II} centers ($S = 1$) with $g \approx 2.2$. This value remains essentially constant until approximately 10 K, where it drops suddenly to 4.15 cm^3 K mol^{-1} at 2 K. These results can be explained in terms of very weak antiferromagnetic coupling between Ni^{II} centers within the molecule. This is in contrast with preliminary results for a cluster with the same spin topology.[27] The magnitude of the coupling under this hypothesis was calculated by using a numerical method based on the Heisenberg spin Hamiltonian in Equation (2) ($S_i = 1$, see Figure 3).

$$\hat{H} = -2J(\hat{S}_1\hat{S}_2 + \hat{S}_1\hat{S}_3 + \hat{S}_1\hat{S}_4 + \hat{S}_1\hat{S}_5 + \hat{S}_2\hat{S}_3 + \hat{S}_2\hat{S}_5 + \hat{S}_2\hat{S}_6 \\ + \hat{S}_3\hat{S}_4 + \hat{S}_3\hat{S}_6 + \hat{S}_4\hat{S}_5 + \hat{S}_4\hat{S}_6 + \hat{S}_5\hat{S}_6)$$

(2)

This equation gives rise to 141 spin states, with a total degeneracy of 729. The energies of these states can be found by applying the Kambe vector-coupling method, as previously reported for a Mn$_6$ cluster with the same spin topology.[36] These energies allowed least-squares fitting of the experimental data to the Van Vleck expression of the susceptibility (Figure 2, bottom, solid line), yielding $J = -0.14$ cm^{-1} and $g = 2.20$ as best-fit parameters. This value is remarkably close to that obtained with **1** for the Ni···Ni coupling. The spin ground state originated is $S_T = 0$, with three degenerate $S_T = 1$ states lying 0.27 cm^{-1} higher in energy. Accordingly, all 141 spin states would be contained within an energy range 5.67 cm^{-1} wide (see the spin-level ladder in Figure 3). In addition to small antiferromagnetic coupling as assumed by the above analysis, the drop of $\chi_m T$ at low temperatures observed in **2** could also be caused by small magnetic anisotropy, or a combination of both factors. To explore this possibility, the susceptibility data were fit to the corresponding expression for six independent octahedral Ni^{II} ions that included a ZFS parameter D.[37] The best fit (not shown) was obtained for $g = 2.18$ and $D = 4.98$ cm^{-1}. Since the two factors considered are expected to have the same effect on $\chi_m T$, it is not possible to determine which one is dominating. Comparison with complex **1** suggests that exchange coupling predominates in **2**, since the values obtained for J are almost the same for both complexes. Additional insight into this problem was obtained following HF-EPR measurements.

Complexes **1** and **2** were further characterized by EPR spectroscopy in both the conventional X-band as well as the high-frequency and high-field versions ($\tilde{\nu} \sim 150$–600 GHz; B_0 up to 25 T). Complex **1** produces spectra at any frequency employed, as expected from a Kramers (half-integer) spin state. The best spectra were obtained at low temperatures (5–40 K) and consist of one broad resonance at $g \approx 2$ (not shown). A careful look at this signal reveals that it is asymmetric, and cannot be fitted with a single absorption of any shape. Also, the actual g value is higher than 2.00, and weakly frequency dependent, varying from $g = 2.20(2)$ at 186 GHz to 2.11(2) at 368 GHz. These two features point to the presence of a small ZFS, for which an upper limit of $D \geq 0.02$ cm^{-1} could be established by simulation.

In contrast to **1**, complex **2** does not produce EPR spectra at X-band, as expected for a non-Kramers (integer-spin) system of large ZFS. The HF-EPR spectra are totally different from those of **1**, consisting at low temperatures of two broad lines characterized by g_{eff} that strongly vary with frequency. The spectrum at 189.9 GHz contains a transition at or near zero-field (infinite g_{eff}, inset of Figure 4) identified as a typical $\Delta M_s = \pm 2$ transition and a resonance at higher field corresponding to a "double-quantum" transition.[38] No $\Delta M_s = \pm 1$ resonances were observed, presumably due to their low intensity and/or large line width. The dependence of the EPR resonances for **2** on the full field (Figure 4) can be best explained by assuming single-ion anisotropy of Ni^{II} with the spin Hamiltonian parameters $S = 1$, $D = 5.5(1)$ cm^{-1}, $E = 0.8(3)$ cm^{-1}, $g_x = 2.06(3)$, $g_y = 2.21(4)$, and $g_z = 2.30(3)$. Thus, the magnetic properties of the six Ni^{II} ions determine the properties of **2**, and the coupling between these ions is clearly of much less magnitude than the single-ion ZFS anisotropy.
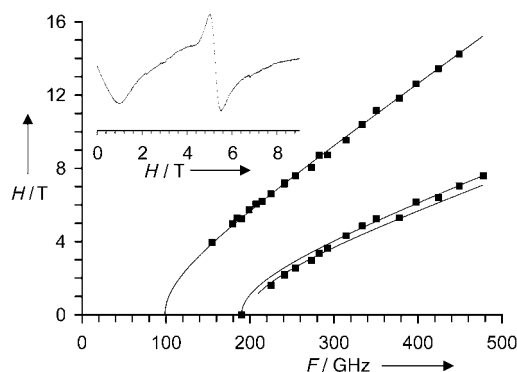
Figure 4. Plot of the magnetic field *H* versus the operating frequency *F* for the HFEPR resonances of complex **2**. The squares represent experimental data, while the lines were drawn using best-fitted spin Hamiltonian parameters as described in the text. Inset: The HFEPR spectrum of **2** at 189 GHz and 10 K. See text for details.

This conclusion can only be reconciled with the results from the susceptibility studies in the hypothesis that both, ZFS and weak Ni···Ni antiferromagnetic super-exchange have an influence in the low temperature behavior of complex **2**. The fact that complex **1** is a spin-frustrated system, caused by the presence of such Ni···Ni coupling, suggests that this coupling should not be ruled out in **2**.

In conclusion, two rare heterometallic clusters containing Ni and a lanthanide ion have been prepared and their magnetic properties analyzed with the methods used typically to study SMMs. Synthetic efforts aimed at expanding the small family of heterometallic 3d–4f clusters and understanding their magnetic properties should lead to the development of a new generation of molecular nanomagnets, with potentially new and improved properties.[39]

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[28] Elemental analysis calcd (%) for **1**: C 32.96, H 4.67, N 7.81; found: C 32.53, H 4.75, N 7.81. Calcd (%) for **2**: C 32.70, H 4.63, N 7.75; found: C 32.39, H 4.52, N 7.87.
[29] Crystal data for **1** ($C_{64}H_{108}Cl_4GdN_{13}O_{40}Ni_6$): Data were collected on a purple block-shaped crystal ($0.30 \times 0.30 \times 0.32$ mm), cubic, space group *F*23 (no. 196) with $a = 21.275(1)$, $b = 21.2750$, $c = 21.2750$ Å, $V = 9629.6(6)$ Å³, $Z = 4$, $\alpha = 89$, $\beta = 90$, $\gamma = 89°$; of 4779 reflections measured, 1564 were independent; $R_{int} = 0.028$. Crystal data for **2** ($C_{64}H_{108}Cl_4LaN_{13}O_{40}Ni_6$): Data were collected on a purple block-shaped crystal ($0.30 \times 0.30 \times 0.24$ mm), cubic, space group *F*23 (no. 196) with $a = 21.305(2)$, $b = 21.3052$, $c = 21.3052$ Å, $V = 9670.7(10)$ Å³, $Z = 4$, $\alpha = 89$, $\beta = 90$, $\gamma = 89°$; of 4736 reflections measured, 1575 were independent; $R_{int} = 0.028/0.029$. Measurements were carried out on a Rigaku AFC7R diffractometer ($2\theta_{max} = 65°$, $T = 296.2$ K, Mo$_{K\alpha}$ radiation, $\lambda = 0.7107$ Å) with intensity data corrected for Lorentz and polarization effects. The structures were solved by heavy-atom Patterson methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation. Refinement of 98 parameters converged at a final w*R*2 value of 0.1373, *R*1 = 0.0415 (for 1053 reflections with $I > 2\sigma(I)$), $S = 1.042$, $-0.70 < \Delta\rho < 1.20$ e Å⁻³. CCDC-253529 (**1**) and CCDC-253530 (**2**) 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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[39] **Note added in proof** (14.2.2005): After submission of this paper, an important article on the preparation of a new example of a mixed 3d–4f single-molecule magnet appeared: A. Mishra, W. Wernsdorfer, K. A. Abboud, G. Christou, *J. Am. Chem. Soc.* **2004**, *126*, 15648.

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