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Ferromagnetic Ni^{II}–Gd^{III} interactions in complexes with NiGd, NiGdNi, and NiGdGdNi cores supported by tripodal ligands†

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Dinuclear $[(NiL)Gd(hfac)_2(EtOH)]$ (H_3L = 1,1,1-tris(*N*-salicylideneaminomethyl)ethane, Hhfac = hexafluoroacetylacetone), trinuclear $[(NiL)_2Gd(NO_3)]$, and tetranuclear $[(NiL)Gd(CH_3CO_2)_2(MeOH)]_2$ complexes, were prepared by treating $[Ni(HL)]$ with $[Gd(hfac)_3(H_2O)_2]$, $Gd(NO_3)_3{\cdot}6H_2O$, and $Gd(CH_3CO_2)_3{\cdot}4H_2O$, respectively, in the presence of Et_3N. All the complexes show that ferromagnetic interactions occur between the Ni^{II} and Gd^{III} ions.

Heteronuclear complexes containing 3d transition metal and lanthanide (Ln) metal ions have attracted increasing attention in the field of molecular-based magnetic materials.[1] Magnetic studies of mixed Ni^{II}, especially octahedral Ni^{II}, and Ln^{III} complexes are scarce[2] compared with those of Cu^{II} and Ln^{III} complexes. Magnetic interactions between high-spin Ni^{II} (S = 1) and Gd^{III} (S = 7/2) ions have been reported to be ferromagnetic and the Ni^{II} ion possesses magnetic anisotropy. Thus, synthetic development is necessary to investigate their magnetostructural properties and to create new 3d/4f mixed-metal single-molecule magnets.[3] We have focused on the structure of $[M(NiL)_2]$ (M = Ni, Co, Mn), where L^{3-} denotes a tripodal hexadentate Schiff base–phenolate ligand (H_3L = 1,1,1-tris(*N*-salicylideneaminomethyl)ethane, Fig. 1(a)).[4] In this Ni^{II}–M^{II}–Ni^{II} complex, each terminal high-spin Ni^{II} unit is coordinated by the L^{3-} ligand in an octahedral fashion and functions as a tridentate ligand, and the central M^{II} ion is bridged by six phenolate oxygen atoms to the terminal Ni^{II} ions. By using $[NiL]^-$ as the *ligand-complex* and by replacing the central M^{II} ion with a Gd^{III} ion, we could prepare di-, tri-, and tetranuclear mixed Ni^{II} and Gd^{III} complexes. Here we report the preparation, structures, and ferromagnetic properties of these complexes.

The dichroic (pale green and pink) dinuclear complex, $[(NiL)Gd(hfac)_2(EtOH)]{\cdot}EtOH{\cdot}H_2O$ (**1**, Hhfac = hexafluoroacetylacetone), was prepared by the reaction of $[Ni(HL)]$ and $[Gd(hfac)_3(H_2O)_2]$ in ethanol in a 1:1 mole ratio with the addition of a base to deprotonate the HL^{2-} ligand. The pale green trinuclear complex, $[(NiL)_2Gd(NO_3)]{\cdot}2MeOH{\cdot}2H_2O$ (**2**) was prepared by the reaction of $[Ni(HL)]$, $Gd(NO_3)_3{\cdot}6H_2O$, and Et_3N in a 2:1:2 mole ratio in methanol. When $Gd(CH_3CO_2)_3{\cdot}4H_2O$ was allowed to react with $[Ni(HL)]$ in the presence of Et_3N in methanol, we obtained the Ni^{II}–Gd^{III}–Gd^{III}–Ni^{II}-type heterotetranuclear complex, $[(NiL)Gd(CH_3CO_2)_2(MeOH)]_2{\cdot}4MeOH$ (**3**). Appropriate selection of the ligand on the initial Gd^{III} compound plays an important role in controlling the nuclearity of the complex. Since $hfac^-$ ligands on Gd^{III} are bulky and not very labile, they will prevent a second $[NiL]^-$ unit from coordinating and the Ni^{II}–Gd^{III}-type dinuclear complex (**1**) is formed. The NO_3^- ligands of $Gd(NO_3)_3{\cdot}6H_2O$ are small and have low coordination ability, and thus, the reaction with $[Ni(L)]^-$ yields the Ni^{II}–Gd^{III}–Ni^{II}-type heterotrinuclear complex (**2**). The Ni^{II}–Gd^{III}–Gd^{III}–Ni^{II}-type tetranuclear complex (**3**) is formed using the acetate ligands functioning as bridging ligands connecting two Ni^{II}–Gd^{III} units.

The structures of **1–3** were determined using single-crystal X-ray diffraction analysis.‡ Fig. 1(b) shows the molecular structure of **1**. The complex is a face-sharing dinuclear molecule, and the Ni···Gd distance is 3.1697(4) Å. The Ni^{II} ion is in an approximately octahedral environment composed of three facially coordinated imine nitrogen atoms and three phenolate oxygen atoms. In **1**, the three phenolate oxygen atoms coordinate to a Gd^{III} ion as bridging atoms, with an average Gd–O bond distance of 2.36 Å. The Gd^{III} ion is eight coordinate, with four oxygen atoms of two $hfac^-$, three phenolate oxygen atoms of L^{3-}, and one ethanol oxygen atom. Fig. 1(c) shows the molecular structure of **2**. Complex **2** contains two octahedral Ni^{II} ions, each ion is coordinated by the L^{3-} ligand in an N_3O_3 coordination sphere, and each $[NiL]^-$ unit caps the Gd^{III} ion *via* three bridging phenolate oxygen donor atoms. The Gd^{III} ion is eight coordinate, being coordinated by two $[NiL]^-$ complex ligands and one didentate NO_3^- ion. The complex is not linear (Ni–Gd–Ni 139.94(2)°) and the Ni···Gd distances are 3.1669(7) and 3.1702(6) Å. Fig. 1(d) shows the molecular structure of **3**. Complex **3** is regarded as being a dimer of a heterodinuclear Ni^{II}–Gd^{III} complex. Two central acetate ligands bridge the two dinuclear units, which are connected by a crystallographic inversion center. These acetate ligands serve as bridging ligands as well as chelating ligands. The other two acetate ions coordinate to the Gd^{III} ions as didentate

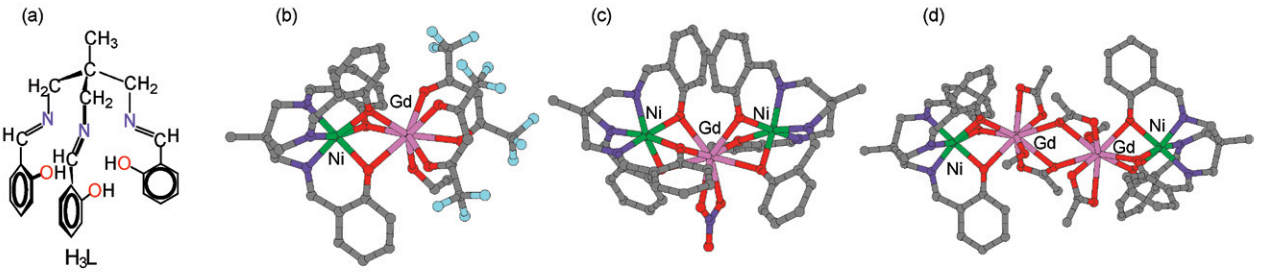

Fig. 1 The structure of the H_3L ligand (a), and molecular structures of **1** (b), **2** (c), and **3** (d). Pink, Gd^{III}; dark green, Ni^{II}; red, O; blue, N; gray, C; light blue, F. H atoms are omitted.

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† Electronic supplementary information (ESI) available: synthesis and characterization of **1**, **2**, and **3**. See http://www.rsc.org/suppdata/cc/b4/b401033g/

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ligands. The structure of the central Gd–Gd moiety is similar to that of the starting material, $Gd(CH_3CO_2)_3 \cdot 4H_2O$, which has a dimeric structure.[5] The two terminal Ni cores are surrounded octahedrally by the L^{3-} ligands, as in **1** and **2**. Each Gd^{III} ion is nine coordinate, being coordinated by three phenolate oxygen atoms, five acetate oxygen atoms, and one methanol oxygen atom. The Ni···Gd distance is 3.211(1) Å, which is a little longer than those of **1** (3.1697(4) Å) and **2** (3.1669(7) and 3.1702(6) Å). The two Gd^{III} ions are separated by a greater distance (4.3357(6) Å).

Temperature-dependent molar susceptibility measurements of powdered samples of **1–3** were carried out at an applied field of 0.1 T in the temperature range 2–300 K. The data are presented as plots of $\chi_M T$ *vs*. T in Fig. 2, where χ_M is the molar magnetic susceptibility and T is the absolute temperature. The profiles of the curves indicate that the overall magnetic interactions between the metal ions are ferromagnetic in all the complexes. Fits to the experimental data were performed using average g-value for the Ni^{II} and Gd^{III} ions, and included a zero field splitting (ZFS) term for Ni^{II}. The inclusion of such a term is consistent with the analysis of the magnetization data (*vide infra*), and allows for an improved fit at low temperatures.[6] The best fit parameters to the data were $g = 2.15$, J (Ni–Gd) $= +0.34$ cm^{-1}, and $D = +1.5$ cm^{-1} for **1**; $g = 2.24$, J (Ni–Gd) $= +0.19$ cm^{-1}, and $D = +2.1$ cm^{-1} for **2**; and $g = 2.20$, J (Ni–Gd) $= +0.32$ cm^{-1}, J (Gd–Gd) $= +0.0$ cm^{-1}, and $D = +2.0$ cm^{-1} for **3**.[7] The calculated J (Ni–Gd) values are lower than that calculated by Costes *et al*. for a Gd^{III}–Ni^{II} dimer with two phenoxo bridges of $J = +3.6$ cm^{-1},[2a] but are similar to the value observed by Chen *et al*. for a Gd^{III}–Ni^{II} compound with three phenoxo bridges, which had $J = +0.56$ cm^{-1}.[2c]

The field dependence of the magnetization at 2 K was also measured, and the M *vs*. H curves are shown in Fig. 3. These data are only qualitatively reproduced by Brillouin curves for $S = 9/2$, $S = 11/2$, and two independent $S = 9/2$ spin systems, respectively, for **1**, **2**, and **3**, demonstrating that the spin ground states are derived from the ferromagnetic coupling between Ni^{II} ($S = 1$) and Gd^{III} ($S = 7/2$) ions. The data are well simulated (see the solid lines in Fig. 3) including ZFS for the same spin systems, and the best fit to the experimental data yields the following values: $g = 2.21$ and $D = +0.22$ cm^{-1} for **1**, $g = 2.06$ and $D = +0.15$ cm^{-1} for **2**, and $g = 2.02$ and $D = +0.06$ cm^{-1} for **3**. It is worth noting that the D values obtained from the fit of the magnetization data refer to the $S = 9/2$ or 11/2 state, and can be compared to the single ion values for Ni^{II} obtained from a fit of the magnetic susceptibility using the Wigner–Eckart theorem.[8] For instance for **1**, using equations 6.4.3 and 6.4.4 of ref. 8 and taking into account that the zero-field splitting of the Gd(III) ion is negligible, it can be shown that $D_{9/2} = (1/36)D_{Ni(II)}$. This justifies, at least qualitatively, the smaller values of D, by one order of magnitude, obtained from the fit of the magnetization data.

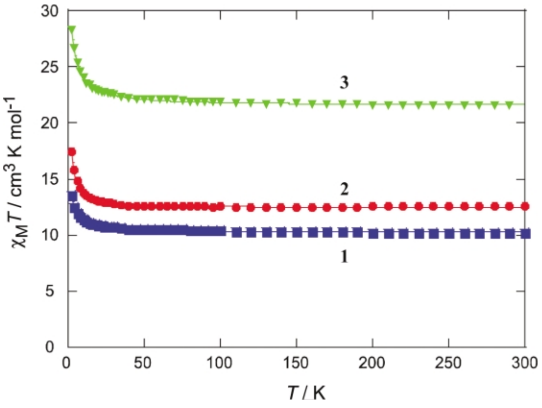

Fig. 2 Magnetic behaviors of **1**, **2**, and **3** in the form of the $\chi_M T$ *vs*. T plots; the solid lines correspond to the best data fits (*cf*. text).

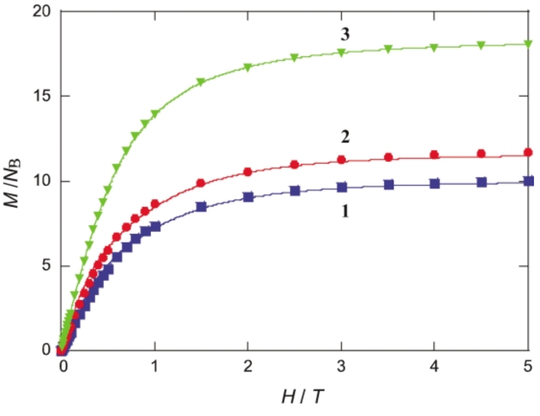

Fig. 3 Field dependence of magnetization at 2 K for **1**, **2**, and **3**; the solid lines correspond to the best data fits (*cf*. text).

This study has shown that by using $[NiL]^-$ as a complex ligand, di-, tri-, and tetranuclear mixed Ni^{II} and Gd^{III} complexes with ferromagnetic interactions can be prepared easily, where the selection of the additional ligand on the Gd^{III} ion plays an important role in controlling the nuclearity of the complex.

Notes and references

‡ Crystal data for **1**: $C_{40}H_{40}F_{12}GdN_3NiO_{10}$, $M = 1166.70$, triclinic, space group $= P\bar{1}$ (no.2), $a = 13.027(1)$, $b = 13.346(1)$, $c = 15.242(1)$ Å, $\alpha = 95.100(5)$, $\beta = 115.364(2)$, $\gamma = 91.537(6)$°, $V = 2378.8(3)$ Å^3, $Z = 2$, F(000) $= 1162.00$, $D_c = 1.629$ g cm^{-3}, $\lambda = 0.71069$ Å, $T = -50 \pm 1$ °C, μ(Mo–Kα) $= 18.83$ cm^{-1}, 18741 reflections measured, 10009 unique ($R_{int} = 0.020$), $R = 0.047$ ($I > 2\sigma(I)$), $R_w = 0.119$ (all data). CCDC 229921.

Crystal data for **2**: $C_{54}H_{60}GdN_7Ni_2O_{13}$ $M = 1289.76$, triclinic, space group $= P\bar{1}$ (no.2), $a = 13.2245(5)$, $b = 13.8535(4)$, $c = 16.4979(5)$ Å, $\alpha = 90.290(2)$, $\beta = 104.022(2)$, $\gamma = 111.761(1)$°, $V = 2708.3(2)$ Å^3, $Z = 2$, $F(000) = 1314.00$, $D_c = 1.581$ g cm^{-3}, $\lambda = 0.71069$ Å, $T = -180 \pm 1$ °C, μ(Mo–Kα) $= 19.72$ cm^{-1}, 40228 reflections measured, 10631 unique ($R_{int} = 0.033$), $R = 0.050$ ($I > 2\sigma(I)$), $R_w = 0.128$ (all data). CCDC 229922.

Crystal data for **3**: $C_{66}H_{84}N_6O_{20}Ni_2Gd_2$, $M = 1713.32$, triclinic, space group $= P\bar{1}$ (no.2), $a = 10.971(3)$, $b = 12.584(2)$, $c = 14.195(3)$ Å, $\alpha = 63.82(2)$ (5), $\beta = 70.819(4)$, $\gamma = 81.437(7)$°, $V = 1661.1(6)$ Å^3, $Z = 1$, $F(000) = 866.00$, $D_c = 1.713$ g cm^{-3}, $\lambda = 0.71069$ Å, $T = -180 \pm 1$ °C, μ(Mo–Kα) $= 26.13$ cm^{-1}, 10051 reflections measured, 6137 unique ($R_{int} = 0.059$), $R = 0.063$ ($I > 2\sigma(I)$), $R_w = 0.155$ (all data). CCDC 229923.

See http://www.rsc.org/suppdata/cc/b4/b401033g/ for crystallographic data in .cif or other electronic format

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6 We also performed the fittings taking interactions between the adjacent molecules into account. The results revealed the intermolecular interactions are very small.

7 Since the J (Gd–Gd) value is negligibly small and the J (Gd–Gd) and D parameters are strongly coupled, we fixed J (Gd–Gd) $= 0.0$ cm^{-1} and fit only the g, J (Ni–Gd) and D parameters.

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