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Structure and magnetism of the first cyano-bridged hetero-one-dimensional Gd^{III}–Cr^{III} complexes

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A reaction between $Gd(NO_3)_3·6H_2O$, $K_3[Cr(CN)_6]$ and dmf or bpy has allowed the synthesis of two new ferrimagnetic Gd^{III}–Cr^{III} chains which are the first low-dimensional 4f–Cr^{III} systems; magnetic susceptibilty data indicate antiferromagnetic coupling between Gd^{III} and Cr^{III}.

The association of 3d–4f ions in cyanide-bridged low dimensional arrays is original and may open new perspectives for the use of the optical properties of rare earth ions included in magnetic molecular media.[1,2] In general, little is known about the nature of the exchange interactions of rare earth ions either with one another or with other magnetic groups. Until recently few simple compounds containing magnetically coupled f-block ions were available. Most of them are Gd^{III}–Cu^{II} or Gd^{III}–radical organic systems.[3,4] Among those with cyanide bridges, several tri-dimensional polycyano metallates(III) (Fe, Co, Cr) with 4f ions[5] and two heteropolynuclear Ln^{III}–Fe^{III} compounds have been reported.[6] Some heterometallic one-dimensional arrays containing cyanide-bridged lanthanide(III) and diamagnetic $[M(CN)_4]^{2-}$ (M = Ni, Pd, Pt) have also been described.[7] In contrast, to the best of our knowledge, discrete or low-dimensional derivatives of $[Cr(CN)_6]^{3-}$ with 4f ions have not been reported. This communication is devoted to the preparation,† characterization including structural determination, and magnetic properties of the two first one-dimensional derivatives from $[Cr(CN)_6]^{3-}$ and Gd^{III}: *cis*-$[Cr(CN)_4(\mu\text{-}CN)_2Gd(H_2O)_2(dmf)_4]_n·nH_2O$ **1** and *trans*-$[Cr(CN)_4(\mu\text{-}CN)_2Gd(H_2O)_4(bpy)]_n·4nH_2O·1.5n$bpy **2**. Fig. 1 shows the X-ray crystal structure of **1**.‡ The crystallographic analysis of **1** revealed that its crystal structure is a one-dimensional (1D) chain polymer. The chain shows an alternation of Gd^{III} and Cr^{III} units linked by cyanide bridges in *cis* geometry with respect to Cr^{III}. The coordination sphere around gadolinium comprises four oxygen atoms of dimethylformamide (dmf) ligands, two oxygen atoms of two water molecules and two nitrogen atoms of the cyanide bridges. The eight-coordinate gadolinium atom lies in a distorted dodecahedral environment. The Gd–Cr intramolecular distance is 5.65 Å and the Gd–Cr–Gd angle is 98.432° indicating the *cis*-geometry. As shown in Fig. 1, the chains are aligned in the *x*-direction where two neighboring chains are linked by water molecules, giving a slipped packing.

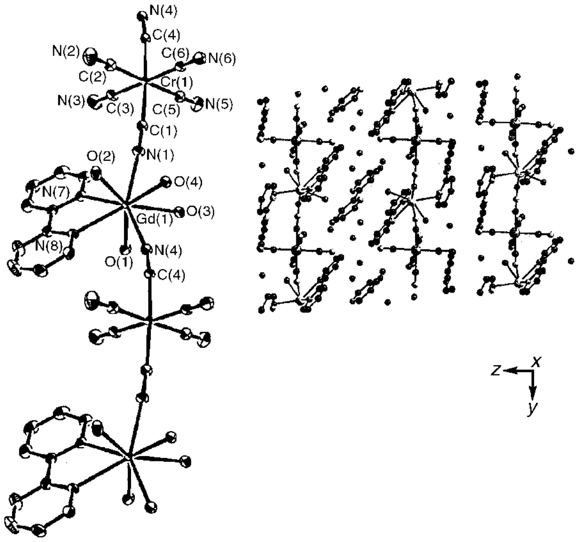

Fig. 2 Left: Crystal structure of *trans*-$[Cr(CN)_4(\mu\text{-}CN)_2Gd(H_2O)_4(bpy)]_n·4nH_2O·1.5n$bpy. Selected bond lengths [Å] and angles [°], hydrogen atoms are omitted for clarity: Gd(1)–O(1) 2.392(2), Gd(1)–O(2) 2.348(2), Gd(1)–O(3) 2.417(2), Gd(1)–O(4) 2.393(2), Gd(1)–N(1) 2.479(3), Gd(1)–N(7) 2.537(3), Gd(1)–N(8) 2.569(2), Cr(1)–C(1) 2.074(3), Cr(1)–C(2) 2.068(3), Cr(1)–C(3) 2.062(3), Cr(1)–C(4) 2.072(3), Cr(1)–C(5) 2.076(3), Cr(1)–C(6) 2.080(3), C(1)–N(1) 1.151(4), C(1)–N(1)–Gd(1) 176.0(3), Cr(1)–C(1)–N(1) 174.8(3), O(2)–Gd(1)–O(4) 73.76(8), O(1)–Gd(1)–O(3) 70.21(8), O(1)–Gd(1)–N(4) 77.75(8), O(4)–Gd(1)–N(4) 72.66(8), O(3)–Gd(1)–N(4) 81.42(8), O(2)–Gd(1)–N(1) 80.20(9), O(4)–Gd(1)–N(1) 74.64(8), N(1)–Gd(1)–N(4) 145.06(9). Right: Arrangement in the crystal.

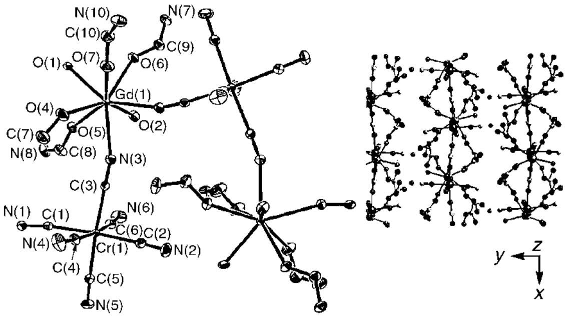

Fig. 1 Left: Crystal structure of *cis*-$[Cr(CN)_4(\mu\text{-}CN)_2Gd(H_2O)_2(dmf)_4]_n·nH_2O$. Selected bond lengths [Å] and angles [°], hydrogen atoms and the methyl groups of the dmf ligands are omitted for clarity: Gd(1)–O(1) 2.3552(17), Gd(1)–O(2) 2.4026(17), Gd(1)–O(4) 2.3768(18), Gd(1)–O(5) 2.3617(17), Gd(1)–O(6) 2.3805(16), Gd(1)–O(7) 2.3946(18), Gd(1)–N(1′) 2.521(2), Gd(1)–N(3) 2.517(2), Cr(1)–C(1) 2.092(2), Cr(1)–C(2) 2.065(2), Cr(1)–C(3) 2.084(2), Cr(1)–C(4) 2.074(2), Cr(1)–C(5) 2.069(2), Cr(1)–C(6) 2.069(2), C(1)–N(1) 1.152(3), Cr(1)–C(1)–N(1) 170.6(2), C(1)–N(1)–Gd(1) 163.58(18), O(1)–Gd(1)–O(5) 71.84(6), O(1)–Gd(1)–O(4) 79.69(7), O(5)–Gd(1)–O(4) 79.89(7), O(1)–Gd(1)–O(6) 73.35(6), O(1)–Gd(1)–O(7) 81.93(7), O(4)–Gd(1)–O(7) 70.77(7), N(1′)–Gd(1)–N(3) 74.80(6). Right: Arrangement in the crystal.

Fig. 2 shows the X-ray crystal structure of **2**.‡ The crystallographic analysis of **2** revealed that its crystal structure is a one-dimensional (1D) chain polymer. The chain shows an alternation of Gd^{III} and Cr^{III} units linked by cyanide bridges in *trans* geometry with respect to Cr^{III}. The coordination sphere around gadolinium comprises two nitrogen atoms of the 2,2′-bipyridine (bpy) ligand, four oxygen atoms of four water molecules and two nitrogen atoms of the cyanide bridges. The eight-coordinate gadolinium atom lies in a distorted dodecahe-

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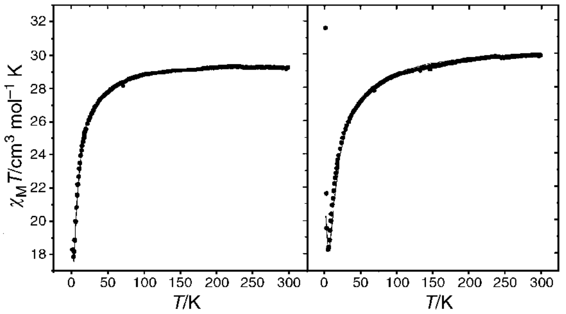

Fig. 3 Left: Temperature dependence of $\chi_M T$ for **1**. The solid line represents the best-fit curve (see text for parameters). Right: Temperature dependence of $\chi_M T$ for **2**. The solid line represents the best-fit curve (see text for parameters).

dral environment. The Gd–Cr intramolecular distance is 5.59 Å and the Gd–Cr–Gd angle is 159.28° indicating the *trans*-geometry. As shown in Fig. 2 the chains are aligned in the *y*-direction. Between two neighboring chains are water molecules and two different bpy crystallization molecules. One of them is not planar showing a dihedral angle between the two pyridine planes of 20° and the other is planar but the same dihedral angle is 180°.

The susceptibility measurements for complexes **1** and **2** are shown in Fig. 3 as $\chi_M T$ *vs.* T respectively. There is no mathematical expression for fitting a one-dimensional system with alternated $S = 7/2$ and 3/2. To fit the experimental data we have assumed a ring of six atoms (three Gd^{III} and three Cr^{III}) (Fig. 4), which should describe the behavior of the infinite chain when J is small. The fit of experimental data was performed according to the following Hamiltonian:

$$H = -J(S_1S_2 + S_2S_3 + S_3S_4 + S_4S_5 + S_5S_6 + S_6S_1)$$

where J corresponds to the coupling through the cyanide bridges. The free parameters were J and g (average). The fit made by the irreducible tensor operator formalism (ITO) using the CLUMAG program[8] gave the following results: $J = -0.52$ cm^{-1}, $g = 2.01$ and $R = 2.07 \times 10^{-5}$ for complex **1** (Fig. 3) and $J = -1.06$ cm^{-1}, $g = 2.05$ and $R = 2.137 \times 10^{-4}$ for complex **2** (Fig. 3). Both complexes show a weak antiferromagnetic interaction between Cr^{III} and Gd^{III} ions to give a ferrimagnetic chain. For complex **2**, the two values of $\chi_M T$ at low temperatures are not fitted because in our model the limit of $\chi_M T$ is that corresponding to three Gd^{III} + three Cr^{III} ($\chi_M T = 21$ cm^3 mol^{-1} K; $S_T = 6$). In the actual structure (one-dimensional complex) $\chi_M T$ tends to infinity, as shown in Fig. 4.

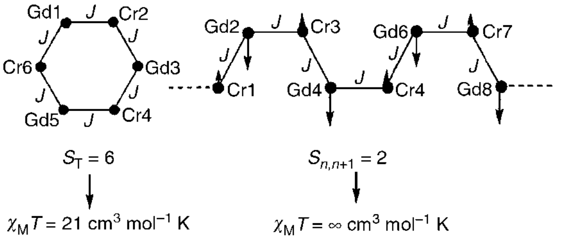

Fig. 4 Left: Scheme of a ring of six atoms used in the fit made by the ITO formalism. Right: Scheme of the spin topology assuming antiferromagnetic coupling.

A simulation of $\chi_M T$ *vs.* T for the ring of six atoms was calculated using the same method as that described above. The g value was fixed as 2.00. The value of J was simulated between 0 cm^{-1} and -2 cm^{-1}. As expected, with these small J values, the variation of $\chi_M T$ *vs.* T is observed only at low temperatures. The theoretical $\chi_M T$ *vs.* T curves are shown in Fig. 5. When the J coupling is more negative the minimum of $\chi_M T$ is shifted to a higher temperature.

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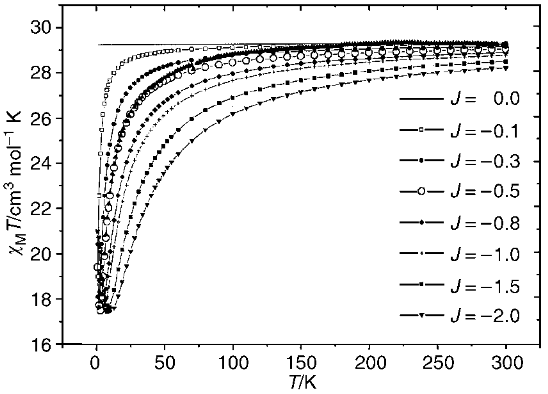

Fig. 5 Theoretical curves obtained by the CLUMAG program for different J values; g was maintained constant and equal to 2.00.

Notes and references

† *Experimental*: Compound **1** was obtained by adding a solution of K$_3$[Cr(CN)$_6$] (0.43 g, 1.33 mmol) in water (15 mL) to a solution of Gd(NO$_3$)$_3$·6H$_2$O (0.60 g, 1.33 mmol) in dimethylformamide (10 mL). The solution was left undisturbed and well-formed yellow crystals were obtained after several days (yield 63%). Anal. Calc. for C$_{18}$H$_{34}$CrGdN$_{10}$O$_7$: C, 30.37; H, 4.81; N, 19.68. Found: C, 30.14; H, 4.99; N, 19.50%. Compound **2** was obtained by adding a solution of K$_3$[Cr(CN)$_6$] (0.713 g, 2.2 mmol) in water (50 mL) to a solution of Gd(NO$_3$)$_3$·6H$_2$O (1.00 g, 2.2 mmol) in water (50 mL). To this mixture, an ethanolic solution (10 mL) of 2,2′-bipyridine (1.03 g, 6.6 mmol) was added. The solution was left undisturbed and well-formed yellow crystals were obtained after several days (yield 60%). Anal. Calc. for C$_{31}$H$_{36}$CrGdN$_{11}$O$_8$: C, 41.37; H, 4.03; N, 17.12. Found: C, 41.15; H, 3.97; N, 17.30%.

‡ *Crystal data* for **1**: C$_{18}$H$_{34}$CrGdN$_{10}$O$_7$, M = 711.80, monoclinic, space group $P2_1/n$, a = 13.159(1), b = 12.878(1), c = 18.978(1) Å, β = 109.835(1)°, V = 3025.3(1) Å^3, Z = 4, D_c = 1.563 g cm^{-3}, μ = 2.582 mm^{-1}, T = 173.2 K, Bruker SMART CCD, Mo-Kα radiation (λ = 0.71073 Å), 20152 reflections measured, 7471 unique (R_{int} = 0.0321) which were used in all calculations. The final $wR(F^2)$ = 0.0678 (all data). 342 variables. For **2**: C$_{31}$H$_{36}$CrGdN$_{11}$O$_8$, M = 899.96, triclinic, space group $P\bar{1}$, a = 9.815(1), b = 10.773(1), c = 19.704(1) Å, α = 83.549(1), β = 83.775(1), γ = 65.092(1)°, V = 1873.3(1) Å^3, Z = 2, D_c = 1.595 g cm^{-3}, μ = 2.107 mm^{-1} , T = 173.2 K, Bruker SMART CCD, Mo-Kα radiation (λ = 0.71073 Å), 12920 reflections measured, 8824 unique (R_{int} = 0.0308) which were used in all calculations. $wR(F^2)$ = 0.0810 (all data), 488 variables. The structures were solved using the Bruker SHELXTL-PC software by direct methods and refined by full-matrix least-squares methods and non-hydrogen atoms refined anisotropically.

CCDC reference numbers 150442 and 150443. See http://www.rsc.org/suppdata/cc/b1/b102739p/ for crystallographic data in CIF or other electronic format.

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