A rational synthetic route leading to 3d–3d′–4f heterospin systems: self-assembly processes involving heterobinuclear 3d–4f complexes and hexacyanometallates†

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A novel heterospin system, $[\{CuL\}Gd(H_2O)_3\{Fe(CN)_6\}]\cdot4H_2O$, is obtained by reacting the mononuclear complex, [CuL], with gadolinium(III) nitrate, followed by the substitution of the nitrato groups with $[Fe(CN)_6]^{3-}$ ions (L^{2-} = N,N'-propylenedi(3-methoxysalicylideneiminato)).

The design of new synthetic routes leading to heteropolynuclear complexes with novel topologies of the spin carriers is currently of interest in molecular magnetism. An extremely rich chemistry, stimulated by the search for molecule-based magnets and for models in studying the exchange interactions, has been developed by combining different spin carriers within the same molecular/supramolecular entity: 3d–3d′,[1] 3d–4d,[2] 3d–5d,[3] 3d–4f,[4] 3d–5f,[5] 3d-Rad·,[6] 4f-Rad·.[7] The first oligonuclear complexes containing three different paramagnetic 3d transition metal ions have been reported by Chaudhuri *et al*.[8]

Recently, we have shown that 3d–4f heteronuclear complexes can be successfully used as nodes in constructing extended structures with interesting solid-state architectures.[9] The bimetallic nodes are interconnected through *exo*-bidentate organic ligands. Moreover, following this strategy we were able to obtain the first 2p–3d–4f (TCNQ·⁻, Cu^{2+} and Gd^{3+}) heterospin system (TCNQ·⁻ = the radical anion of 7,7,8,8-tetracyano-*p*-quinodimethane).[10] This synthetic concept can be enlarged by using hexacyanometallate ions, $[M(CN)_6]^{3-}$, as versatile linkers.

In this paper we report on the synthesis, crystal structure and the magnetic properties of a novel coordination compound containing three different spin carriers, two 3d metal ions (Cu^{2+} and Fe^{3+}) and a rare earth cation (Gd^{3+}): $[\{CuL\}Gd(H_2O)_3\{Fe(CN)_6\}]\cdot4H_2O$, **1** ($L^{2-}$ = N,N'-propylenedi(3-methoxysalicylideneiminato)). Compound **1** was obtained stepwise: (i) synthesis of the mononuclear copper(II) complex, [CuL]; (ii) reaction of the copper(II) complex with gadolinium nitrate; (iii) substitution of the nitrato groups with paramagnetic $[Fe(CN)_6]^{3-}$ ions.‡ The isomorphous Co(III) derivative, $[\{CuL\}Gd(H_2O)_3\{Co(CN)_6\}]\cdot3.5H_2O$ **2**, has been also synthesized and characterized.

The crystal structure of compound **1** and the one of the Co(III) derivative, **2**, have been solved.§ Since compound **2** is isomorphous with compound **1**, only the crystal structure of the iron(III) derivative will be described here. The [CuGd] moiety preserves the structural features of the whole $[Cu^{II}Ln^{III}]$ family of complexes with compartmental Schiff-base ligands derived from 3-methoxysalicylaldimine:[11] the copper(II) ion is hosted in the inner N_2O_2 compartment, and the oxophilic gadolinium ion occupies the outer O_4 cavity (two oxygen atoms arise from the bridging phenoxo groups, two others from the methoxy ones). The Cu–Gd distance is 3.5083(6) Å. The $[Fe(CN)_6]^{3-}$ ion connects three metal ions, through three meridially disposed cyano groups. Two *cis* cyano ligands bridge the Fe^{3+} and Gd^{3+} ions, while the third one connects the Fe^{3+} and Cu^{2+} ions. It results in a unique ladder topology built up from distorted $\{Gd_2Fe_2Cu\}$ pentagons sharing the FeGd edges. The coordination number of gadolinium is eight: four oxygen atoms arising from the organic ligands, three aqua ligands and one nitrogen atom from the bridging cyano group. The Gd–O distances fall in the range 2.379(4)–2.567(4) Å. The Gd–N distances are 2.491(4) Å and 2.522(5) Å. The stereochemistry of copper(II) is square-pyramidal with the cyano nitrogen atom coordinated in the apical position [Cu–N = 2.501(5) Å]. The two Fe–Gd distances are 5.503 and 5.580 Å, and the Fe–Cu distance is 5.302 Å. A perspective view of the ladder chain is shown in Fig. 1. The structure is expanded into three dimensions through hydrogen bond interactions involving the aqua and cyano ligands, as well as the crystallization water molecules.

The most intriguing properties of a heterospin system, such as complex **1**, are the magnetic ones. Magnetic susceptibility data
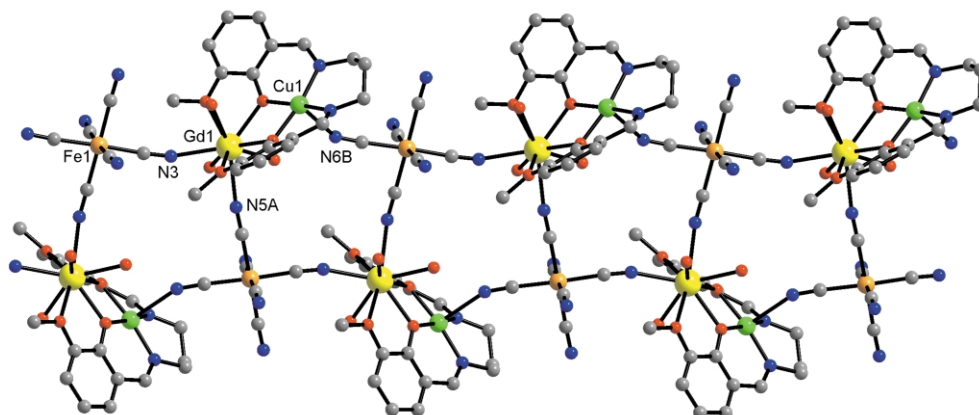

Fig. 1 Perspective view of a ladder chain running along the crystallographic *a* axis. Selected interatomic distances: Cu(1)–N(6B) = 2.501(5); Gd(1)–N(3) = 2.491(4); Gd(1)–N(5A) = 2.522(5) Å. Color code: gadolinium, yellow; copper, green; iron, orange; nitrogen, blue; oxygen, red; carbon, grey.

for **1** were collected in the temperature range 1.9–300 K (Fig. 2). The value of the $\chi_M T$ product at room temperature is 8.89 cm³ mol^{-1} K, which is higher than the calculated one (8.62 cm³ mol^{-1} K) corresponding to the sum of the contributions of the three uncoupled ions, $(\chi_M T)_{HT} = (Ng^2\beta^2/3k)[S_{Gd}(S_{Gd} + 1) + S_{Cu}(S_{Cu} + 1) + S_{Fe}(S_{Fe} + 1)]$, with $g_{Cu} = g_{Gd} = g_{Fe} = 2$. The first-order orbital momentum associated to the low-spin iron(III) ion is responsible for this difference. Upon lowering the temperature, $\chi_M T$ remains constant down to about 95 K, then increases and reaches a maximum (9.86 cm³ mol^{-1} K) at 13.8 K. Below this temperature, $\chi_M T$ decreases abruptly (7.12 cm³ mol^{-1} K at 1.9 K). The complex topology of the spin carriers in **1** makes difficult the interpretation of its magnetic properties. Additional information is obtained by analyzing the magnetic properties of the isostructural [CuGdCo] compound, **2**, where Fe(III) ions are replaced by diamagnetic Co(III) ones. The temperature dependence of the $\chi_M T$ product for **2** (Fig. 2) exhibits the well-known characteristic feature of the [CuGd] binuclear units, namely a ferromagnetic interaction of the two metal ions.[11] Moreover, this ferromagnetic interaction is further supported by the field dependence of the magnetization (Fig. S1†), which shows a $S = 4$ ground state. No decrease of $\chi_M T$ at low temperatures is observed. This indicates that no anti-ferromagnetic interaction occurs between the [CuGd] units within the chain. The best fit to the data leads to the following parameters: $J_{CuGd} = 7.24$ cm^{-1}, $g_{av} = 2.00$ ($H = - JS_{Cu}S_{Gd}$). Let us come back to compound **1**. First of all, we notice that the difference between the room temperature value of its $\chi_M T$ product and that of the cobalt(III) derivative, $\chi_M T(\mathbf{1}) - \chi_M T(\mathbf{2}) = 0.61$ cm³ mol^{-1} K, represents the contribution of Fe(III). This value is close to those found for Fe(III) in several bimetallic [Gd(III)Fe(III)] compounds.[12] The [CuGd] units are connected through paramagnetic [Fe(CN)$_6$]$^{3-}$ building-blocks, each one coordinating simultaneously to Cu(II) and Gd(III) ions. Since one CN group is coordinated to the axial position of the square pyramidal Cu(II), its magnetic orbital, $d_{x^2 - y^2}$, being localized in the basal plane, one may assume that no magnetic interaction occurs between Cu(II) and Fe(III). On the other hand, the Gd(III)–NC–Fe(III) pathway is effective, as shown with several [Gd(III)Fe(III)] cyano-bridged systems which have been recently investigated.[12] Very weak ferro- and antiferromagnetic interactions were found ($|J| < 1$ cm^{-1}). A tentative interpretation of the magnetic behavior of **1** is as follows: below 14 K, the Cu(II) and Gd(III) ions are ferromagnetically coupled, resulting in units with $S = 4$, as in the isostructural compound **2**. These units further interact antiferromagnetically with the paramagnetic [Fe(CN)$_6$]$^{3-}$ linkers. This explains the decrease of the $\chi_M T$ product bellow 14 K. According to the literature data,[12] the
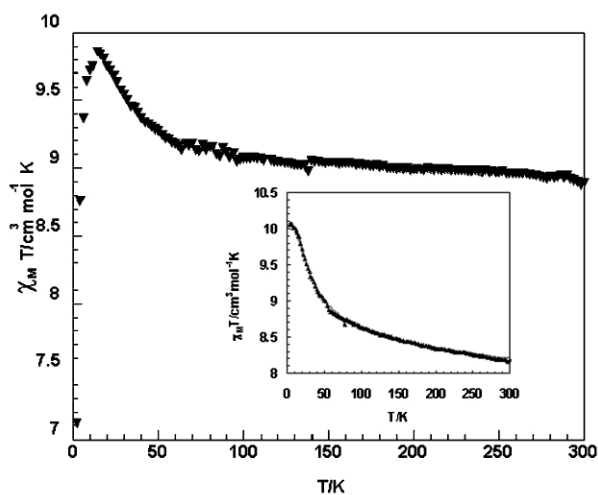
Gd(III)–NC–Fe(III) interaction is supposed to be much weaker than that of Cu(II)–Gd(III). Theoretically, a ferrimagnetic chain $[(S = 4) - (S = -1/2) - (S = 4) - (S = -1/2) - \ldots]$ may result.

During the preparation of this manuscript, Kou *et al.* reported on another 3d–3d′–4f system, which has been obtained by assembling pentanuclear [Cu$_4$Gd]$^{3+}$ cations with [Cr(CN)$_6$]$^{3-}$ anions.[13]

The unique topology of the spin carriers in the compounds reported herein stimulates the elaboration of new theoretical models in order to simulate quantitatively their magnetic properties. Moreover, this family of compounds can open interesting perspectives in the search for new magnetic nanowires. Further work on similar compounds containing Ln(III) cations with a strong anisotropy is in progress.

Notes and references

‡ Preparation of [{CuL}Gd(H$_2$O)$_3$[Fe(CN)$_6$}]·4H$_2$O, **1**. The [CuGdL(NO$_3$)$_3$] precursor has been obtained following the general procedure reported by Costes *et al.*[11] To a solution containing 0.074 g (0.1 mmol) [CuLGd(NO$_3$)$_3$] in 10 mL water was added an aqueous solution (10 mL) of 0.1 mmol K$_3$[Fe(CN)$_6$]. The resulting green micro-crystalline precipitate was filtered off and washed with water. Yield: 90%. Single crystals were obtained by slow diffusion, in an H-shaped tube, of two aqueous solutions, one of them containing [CuLGd(NO$_3$)$_3$] and the other one K$_3$[Fe(CN)$_6$]. After one week, dark green crystals resulted, which were filtered off, washed with water and finally dried *in vacuo* over P$_4$O$_{10}$. Elem. anal.: found: C, 33.69; H, 3.62; N, 12.18; calcd: C, 33.4; H, 3.78; N, 12.46%. Compound **2** has been obtained following the same procedure, by using K$_3$[Co(CN)$_6$]. Elem. anal.: found: C: 33.11; H: 3.23; N: 12.15; calcd: C: 33.28; H:3.76; N: 12.42%.
§ Crystallographic analysis: **1** C$_{25}$H$_{34}$CuFeGdN$_8$O$_{11}$, orthorhombic, space group $P\,2_12_12_1$, $a = 13.0095(6)$, $b = 14.9900(8)$, $c = 16.9710(10)$ Å, $V = 3309.6(3)$ Å³, $Z = 4$, $D_c = 1.776$ g cm^{-3}, $F(000) = 1788$; $\mu = 3.116$ mm^{-1}; $R_1 = 0.0277$ for 4542 [$I > 4\sigma(I)$], and 0.0289 for all 4719 data. The diffraction intensities were collected at 180 K on a four circles Kappa CCD Xcalibur Oxford diffractometer equipped with an Oxford Instruments cryojet. Crystal data for **2**: $a = 12.945(3)$, $b = 15.010(3)$, $c = 16.955(3)$ Å, $V = 3294.3(11)$ Å³. CCDC reference number for **1**: 216452 and for **2**: 216453. See http://www.rsc.org/suppdata/cc/b3/b310082k/ for crystallographic data in CIF or other electronic format.

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Fig. 2 Magnetic behavior of compounds **1** and **2** (insert) ($\chi_M T$ *vs. T* plot).