A Heterotrimetallic Complex

A 2D Cyano- and Oxamidato-Bridged Heterotrimetallic Cr^{III}-Cu^{II}-Gd^{III} Complex**

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Coordination Chemistry provides a powerful tool for the construction of extended or isolated compounds with a particular structure and tunable physical properties.[1] Magnetism of coordination compounds is an active field of research, involving chemistry, physics, biology, and material science.[2]

The ability of the oxamidato group to transmit efficiently magnetic coupling has been well documented.[3] The oxamidato-bridged Gd^{III}–Cu^{II} complexes have been investigated magnetically since the pioneering research by Gatteschi et al., who first found that the Gd^{III}–Cu^{II} exchange is ferromagnetic.[4] Recently, a four-coordinate macrocyclic oxamido–Cu^{II} complex has been used as "the complex ligand" to successfully construct polynuclear Cu_6Nd_2 complexes.[5] It is anticipated that the coordinated CuL group (L = 1,4,8,11-tetraazacyclotradecane-2,3-dione) could accept donor atoms

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at the axial positions giving rise to a five- or six-coordinate environment around the Cu^{2+} ion.

The nitrogen ends of the cyanide ligands of hexacyanometallates are strong donor atoms that could connect two metal ions. Cyanide-bridged transition metal (3d) complexes or 4f–3d complexes have attracted extensive interest because they might be used as magnetic, magneto-optical, porous, or catalytic materials with practical applications.[6–11]

Combining the above two approaches, we have designed a unique 2D mixed bridging-ligand complex $[Gd(CuL)_4Cr(CN)_6 \cdot 5H_2O]_\infty$ (**1**), which contains three different paramagnetic metal ions.

Complex **1** is prepared by the treatment of [CuL],[12] $GdCl_3 \cdot 6H_2O$ with $K_3[Cr(CN)_6]$ in an H_2O/EtOH mixture. Single-crystal X-ray crystallography[13] reveals that **1** consists of a 2D neutral polymer $[Gd(CuL)_4Cr(CN)_6]_\infty$ (Figure 1). The

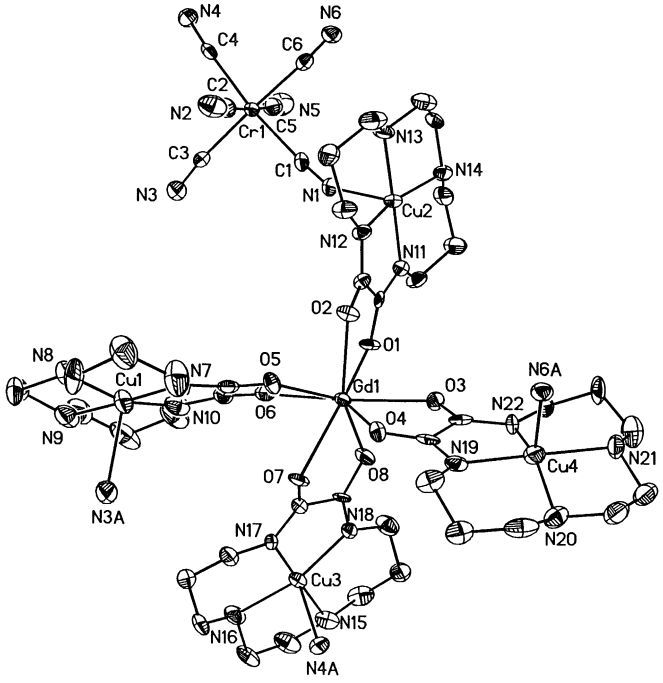

Figure 1. ORTEP plot of the polymeric complex **1** (thermal ellipsoids set at the 30% probability level.

structure comprises a bridging $[Cr(CN)_6]^{3-}$ ion, four macrocyclic Cu^{II} units and one Gd^{III} ion. The Gd^{III} ion is surrounded by eight oxygen atoms from four {CuL} groups, thus yielding a local $[Gd(CuL)_4]$ moiety. Each $[Cr(CN)_6]^{3-}$ ion connects to four different CuL units through four equatorial CN^- bridges with two *trans*-CN^- ligands intact. Therefore, each Cu^{2+} ion of {CuL} is five coordinate with four nitrogen atoms of L located at the equatorial plane and one cyano nitrogen atom of $[Cr(CN)_6]^{3-}$ at the apical position. The $Cu{-}N_{apical}$ bond lengths range from 2.317(11) to 2.548(14) Å. The adjacent metal–metal separations are from 5.145(3) to 5.296(3) Å for Cu–Cr and from 5.704(3) to 5.787(3) Å for Cu···Gd, respectively. The mixed cyanide and oxamidato bridges connect the metal ions generating a nonplanar 2D layer (Figure 2 and Supporting Information). The layer topology can be described as a distorted gridlike molecular structure with two Cr^{III} and two Gd^{III} ions at the vertices and four {CuL} groups at the four sides of each "propeller". The propellers pack in such a way that two different types of holes are formed (Figure 2b, labeled I and II, see also Supporting Information). Within the layer, three pairs (Cu1···Cu1A, Cu2···Cu2B and Cu3···Cu3C) of CuL groups arrange in a face-to-face fashion, with the Cu···Cu distances ranging from 4.629(3) to 5.534(3) Å.[14] The long Cu···Cu separations preclude the interactions between the Cu^{II} ions. The interstitial water molecules are situated between the layers.

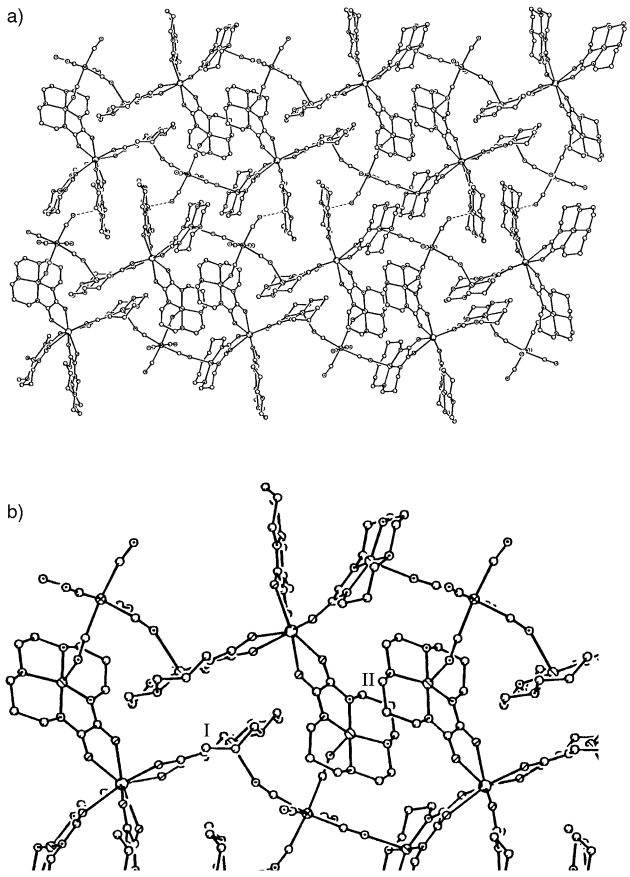

Figure 2. a) Layer structure of **1**. b) Layer structure enlarged to show both types of holes present (labeled I and II).

Figure 3 shows the $\chi_m T$ vs. T plot of **1** measured on a SQUID magnetometer in the temperature range of 5–290 K under 1000 Oe. The room temperature $\chi_m T$ value of 11.0 emu K mol^{-1} is close to the expected spin-only value of 11.25 emu K mol^{-1}. The increase of $\chi_m T$ with a decrease in temperature suggests the presence of global ferromagnetic interactions between adjacent metal ions. The Weiss constant derived from the χ_m^{-1} versus T plot is equal to $+3.8$ K with the Curie constant of 11.0 emu K mol^{-1}, which is consistent with the calculated value of 11.25 emu K mol^{-1} ($g = 2.0$) per $GdCu_4Cr$. As shown in Inset of Figure 3, $\chi_m T$ decreases below 3.2 K (10 kOe data), which can be assigned to the saturation effect. The low field data (≤ 2 kOe) do not show the decrease in $\chi_m T$ below 3 K, which supports the above supposition. The field-cooled magnetization (FCM) curve of **1** measured in a

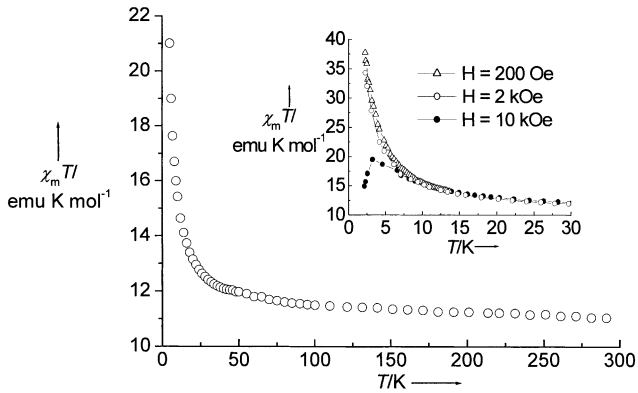

Figure 3. Temperature dependence of $\chi_m T$ for **1** in a 1000 Oe applied field. Inset: Temperature dependences of $\chi_m T$ for **1** in different applied magnetic fields (solid lines are a guide for the eye).

low field of 200 Oe and the zero-static AC magnetization measurements show the absence of spontaneous magnetization down to 1.8 K. The field dependence of the magnetization (0–70 kOe) measured at 1.8 K shows the saturation of the magnetization (Figure 4), reaching 14.6 Nβ at 70 kOe for a

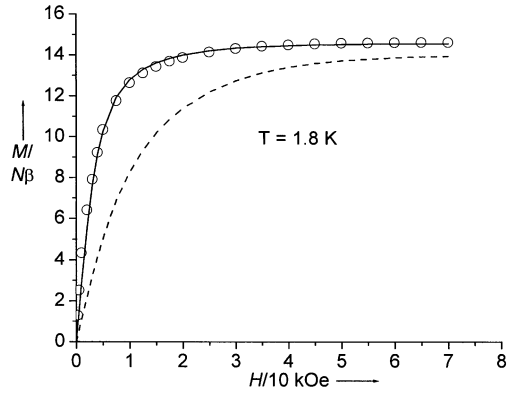

Figure 4. Field dependence of magnetization of **1** at 1.8 K. The lines represent the Brillouin function that corresponds to noninteracting $S = S_{Gd} + 4S_{Cu} + S_{Cr}$ ions (dashed, with $g = 2.0$) and $S = 7$ spin state (solid, with $g = 2.08$).

ferromagnetic Cr^{III}–Cu^{II}–Gd^{III} system with $S_T = 7$. The theoretical Brillouin curve for an $S = 7$ spin state with $g = 2.08$ fits well the experimental curve. The experimental curve lies above that corresponding to noninteracting S_{Gd}, S_{Cr} and four S_{Cu} spins, thus indicating the presence of intermetallic Cu^{II}–Cr^{III} and Cu^{II}–Gd^{III} ferromagnetic coupling.[15] This also shows the absence of Cr^{III}–CN–Gd^{III} linkages, which have been shown to be antiferromagnetic.[16] Future work will be devoted to designing extended species with such linkages that might exhibit magnetic ordering and new bifunctional behavior.

Heterobimetallic or heterotrimetallic complexes with two different spins are often seen, but those with three different spins are rare.[11,17] Complex **1** is the first structurally characterized 2D heterotrimetallic complex with three different spin carriers. This research opens new synthetic pathways for the design of novel and complicated materials with potentially new functional properties.

Experimental Section

1: Platelet violet single crystals of **1** were formed reproducibly by slow diffusion of [CuL] and $GdCl_3 \cdot 6H_2O$ (molar ratio = 4:1) in H_2O into $K_3[Cr(CN)_6]$ in an H_2O/EtOH (2:1) mixture after a few weeks. Yield: 40 %. IR: $\tilde{\nu} = 2122\ cm^{-1}$ (C≡N), $1600\ cm^{-1}$ (C=O).

Magnetic measurements were performed on a few manually selected single crystals (ca. 11.0 mg) by using a MagLab 2000 magnetometer, and the variable-temperature magnetic susceptibility measurements in an applied field of 1000 Oe were performed on a Quantum Design MPMS-7 SQUID magnetometer. Plots of field-cooled magnetization (FCM) and zero-field AC magnetic susceptibilities have been deposited in Supporting Information.

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[13] Crystal data: **1** ($C_{46}H_{82}N_{22}O_{13}Cu_4GdCr$), $M_w = 1614.75$, $T = 293$ K, triclinic, space group $P\bar{1}$, $a = 12.892(1)$, $b = 15.965(1)$, $c = 17.471(1)$ Å, $\alpha = 72.902(3)$, $\beta = 81.444(3)$, $\gamma = 77.166(3)°$, $U = 3337.8(7)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.607$ g cm^{-3}, $\mu = 2.734$ mm^{-1}, $2\theta_{max} = 50°$, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, 18880 measured reflections, 11507 unique reflections, 6049 observed reflections ($I > 2\sigma(I)$). The structure was solved by direct methods (SHELXS-97). All nonhydrogen atoms were refined anisotropically (SHELXL-97). All hydrogen atoms were added geometrically and refined by using a riding model. $R1 = 0.0968$, $wR2 = 0.1846$ (all data), GOF = 1.062 based on 802 parameters. CCDC-204380 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[14] Symmetry operations: *A*: $1-x, 1-y, 1-z$; *B*: $1-x, 1-y, z$; *C*: $-x, 2-y, z$.

[15] Previous reports have unambiguously demonstrated that the Cu^{II}–Cr^{III} magnetic coupling through the cyano bridges is ferromagnetic. See Reference [8].

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