Structure and magnetic properties of a new ferrimagnet containing a paramagnetic $[Cr(CN)_5(NO)]^{3-}$ building block

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A new Prussian-blue type molecular magnet containing a paramagnetic $[Cr(CN)_5(NO)]^{3-}$ building block has been synthesized and characterized; the observed magnetic behavior displays the nature of a ferrimagnet.

The search for molecule-based compounds with long-range magnetic order at room temperature is one of the current goals of research in the field of molecular magnetism.[1,2] A popular approach to the synthesis of these materials has been to use a paramagnetic $[M(CN)_6]^{3-}$ (M = Cr^{3+}, Mn^{3+}, Fe^{3+}, or V^{2+}) building block in conjunction with another paramagnetic 3d metal ion, and this resulted in the formation of a large number of one-, two-, and three-dimensional polymers that exhibit various magnetic behaviors.[3]

On the other hand, paramagnetic $[Cr(CN)_5(NO)]^{3-}$, which carries one unpaired electron in a d_{xy} orbital,[4] is also an ideal building block for obtaining new and high T_c molecular magnets. The effect of moving electron density away from the transition metal center is an interesting way of modulating superexchange behaviour for magnetic coupling. Molecular orbital calculations show that the nitrosyl ligand is a very strong π-acceptor;[5] and the coordinated NO^+ accepted a considerable amount of electron density from the metal ion into the antibonding π orbital of NO^+.[6b] Consequently, there should be extensive delocalization of spin density onto the nitrosyl ligand and magnetic exchange coupling with an adjacent metal center could be enhanced if M–N=O–M′ bridges can be formed. Furthermore, nitroprussides or binding in nitrosyl complexes has been the subject of much interest, research and conjecture. Such systems are important in coordination and organometallic chemistry. Nitroprusside also acts as a vasodilator because the NO is easily detachable from it, especially by photochemical means, and during its use the five cyano ligands become labile after the loss of the active substance, NO. Under this condition the body can tolerate a certain amount of cyanide because of the presence of the enzyme, rhodanase, which converts it into harmless thiocyanate.[6]

Previously, Holmes and Girolami have initiated studies on some bimetallic complexes containing $[Cr(CN)_5(NO)]^{3-}$.[7] Based on powder XRD analysis, the ferrimagnetic complex $K_{0.5}Mn[Cr(CN)_5(NO)]_{0.83}\cdot 4H_2O\cdot 1.5MeOH$ has a cubic structure, and the NO^+ group is involved in bridging based on the IR spectrum, in which the N=O stretching frequency is *ca.* 60 cm^{-1} higher than that in $K_3[Cr(CN)_5(NO)]$ (1630 cm^{-1}). However, the complexes were not structurally characterized by single-crystal X-ray diffraction. Until recently, only two molecular magnets containing $[Cr(CN)_5(NO)]^{3-}$ have been fully characterized by some of us and others.[8] Taking this fact into consideration, in this paper, we report a new three-dimensional Prussian-blue type ferrimagnet $\{Mn(III)[Cr(I)(CN)_5(NO^+)]\}\cdot H_2O$, **1**, which exhibits long-range magnetic order at about 28 K. This is the third example of a molecular magnet containing the paramagnetic $[Cr(CN)_5(NO)]^{3-}$ building block, but the T_c of this complex is much higher than those of the two molecular magnets previously reported (T_c = 4.5 K and 3.3 K, respectively).[8] This complex is a stoichiometric one rather than the non-stoichiometric formulation assigned by Holmes and Girolami.[7] The IR spectrum of complex **1** shows a sharp and intense absorption at 1698 cm^{-1} for the nitrosyl group; the increase of the ν_{NO} stretching frequency can be ascribed to the formation of Mn–NO–Cr bridges. Although there has been much debate[9,10] in the literature on the assignment of Cr oxidation states in such complexes (Cr^{I}–NO^+, Cr^{II}–$NO^{\bullet}$, or Cr^{III}–NO^-), we assigned the title complex as a Cr(I) species based on the magnetic susceptibility data for the title complex and other complexes containing nitrosyl.[8]

The single crystals of complex **1** were obtained by the diffusion method using an H-shaped tube. Aqueous solutions of $K_3[Cr(CN)_5(NO)]$ and $Mn(ClO_4)_2\cdot 6H_2O$ diffused into each other, and green crystals suitable for X-ray determination were formed after several months. X-Ray analysis reveals **1** crystallized in the cubic space group *Fm-3m*.[11] The molecules consist of the species $[Cr(CN)_5(NO)]^{3-}$ and Mn^{3+}; Mn/Cr disorder was precluded due to the difference in the bond lengths of Cr–CN (1.9–2.0 Å) and Mn–NC (2.1–2.2 Å), The CN ligands and NO ligand are disordered, and are located on a special position with an occupancy factor the same as the stoichiometric proportion; they were modeled to the same position (NO same as CN) in the refinement. Consideration of the magnetic susceptibility data supports the existence of high-spin Mn(III) and low-spin Cr(I) in the complex **1**. The Mn(II) species have been oxidised to Mn(III) species due to air.

An ORTEP diagram and projection view of the cubic network of complex **1** are shown in Fig. 1. This structure is a direct analogue of that of Prussian blue, which in turn is a variant on the sodium chloride structure as has been well shown now. Each Cr(I) ion is linked to six Mn(III) ions by five C≡N bridges and one N=O bridge, and assumes an octahedral environment. A face-centered

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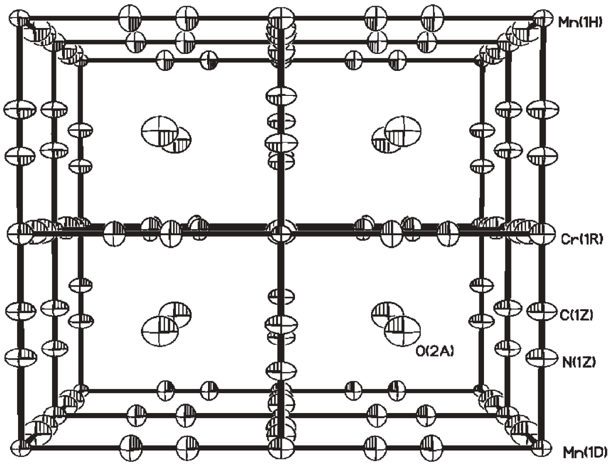

Fig. 1 An ORTEP diagram of the cubic network of complex **1**. The bond lengths are 1.93(2) Å for Cr–C/N, and 2.264(18) Å for Mn–N/O respectively.

cubic framework forms from the Cr–CN/NO–Mn linkages. All metal ions stay on the corners of the smallest Mn_4Cr_4 cube. The shortest Mn···Cr distance is 5.359 Å. Mn···Mn and Cr···Cr distances are the same at 7.579 Å. The adjacent Mn···N/O distances are 2.264(18) Å, and Cr···C/N distances are 1.93(2) Å. Water molecules are located at the center of the smallest Mn_4Cr_4 cube. The distances between adjacent water molecules are all 5.359 Å. The water occupancy was refined to fit the TGA value. We did not try to remove it *via* the SQEEZE routine in Platon.

The magnetic behavior of complex **1** was measured using a SQUID magnetometer. Data were collected in the temperature range 1.8–300 K for a powder obtained from single crystal samples. The temperature dependence of $\chi_m T$ values is displayed in Fig. 2. The $\chi_m T$ value is 3.598 cm^3 mol^{-1} K (5.36 μ_B) at 300 K, which is slightly larger than the expected spin-only value (5.20 μ_B with $g = 2$) for one high-spin Mn(III) ion ($S = 2$) and one low-spin Cr(I) ion ($S = 1/2$). The $\chi_m T$ value decreases gradually with decreasing temperature down to a minimum value of 3.531 cm^3 mol^{-1} K (5.31μ_B) at 170 K and then increases to a large maximum value of 44.37 cm^3 mol^{-1} K at 20 K. Then the $\chi_m T$ value decreases below this temperature. A plot of $1/\chi_m$ *versus* T in the range 300–170 K obeys the Curie–Weiss law with a Weiss temperature $\theta = -9.2$ K (Fig. 3). This value indicates that antiferromagnetic interactions operate between adjacent Mn(III) and Cr(I) ions through the C≡N or N=O bridges above 170 K. The abrupt increase in $\chi_m T$ around 50 K suggests the onset of three-dimensional magnetic ordering. In both the field-cooled (FC) and zero-field-cooled (ZFC) cycles, and with a low applied field (3 Oe) in the temperature range 1.8–300 K for FC and 1.8–60 K for ZFC, long-range magnetic ordering is observed below 28 K (Fig. 4). We investigated the variation of magnetization M *versus* the applied field H for a powder of single crystal samples. The curve at 2 K is shown in Fig. 5. As can be seen from Fig. 5, the magnetization increases sharply with applied field and is saturated rapidly. The saturation magnetization is $M_s = 3.09\ \mu_B$, which is slightly higher

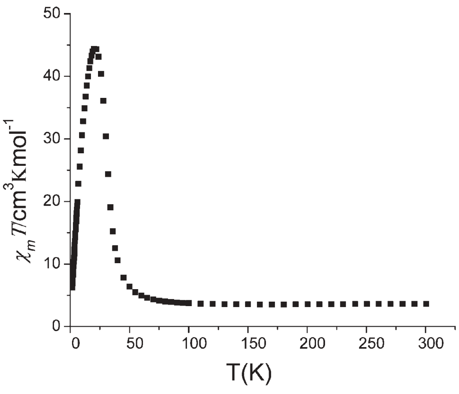

Fig. 2 Temperature dependence of $\chi_m T$ for complex **1**.

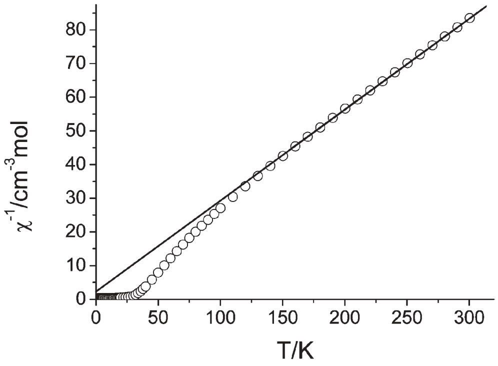

Fig. 3 A plot of $1/\chi_m$ *versus* T in the range 300–170 K obeys the Curie–Weiss law with a Weiss temperature $\theta = -9.2$ K.

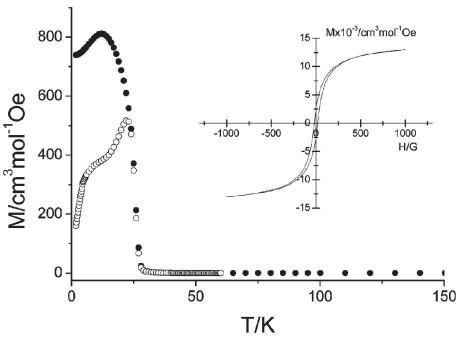

Fig. 4 Temperature dependence of the magnetization for complex **1** at 3 Oe: zero-field-cooled (ZFC, ○) and field-cooled magnetization (FC, ●). Insert: hysteresis loop $M = f(H)$ for complex **1** at 2 K.

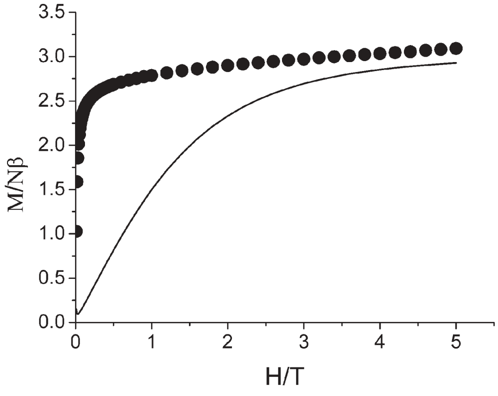

Fig. 5 Field dependence of the magnetization of complex **1** at 2 K.

than the theoretical value for antiferromagnetic coupling between high-spin Mn(III) and low-spin Cr(I) ions (4/2 – 1/2 = 3/2), perhaps due to a canting of the spins[1] or Zeeman interactions[12] between S = 3/2 and S = 5/2 at low-temperature and high-field. The Brillouin function for S = 3/2 is included in Fig. 5, where g is assumed to be 2.0. It is seen that the observed magnetization (per $Mn^{III}Cr^{I}$) reaches saturation more quickly than that expected from the Brillouin function for S = 3/2. This is a strong indication of long-range ordering in the bulk sample. A hysteresis loop (with a remnant magnetization of 2500 cm^3 mol^{-1} Oe and a coercive field of 10 Oe) was observed at 2 K, which suggests soft magnetic behavior, as shown in the insert of Fig. 4.

In conclusion, we have synthesized and characterized a new molecular magnet containing paramagnetic $[Cr(CN)_5(NO)]^{3-}$. The observed magnetic properties display the nature of a ferrimagnet. We believe that this complex is a potential candidate for constructing more high T_c magnets containing $[Cr(CN)_5(NO)]^{3-}$ building block. Also of interest should be the nature of the "green colour" of the crystals obtained. It could have potential applications as an optical material. A further study of the electronic absorption spectrum will be done in future work. Furthermore, such systems are important in coordination and organometallic chemistry. Thus, it is necessary that this kind of system is studied in more detail by us and others in the future.

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11 Crystal data for **1**: $C_5H_2CrMnN_6O_2$, M_w = 285.07, cubic, space group *Fm-3m*; $a = b = c$ = 10.718(2) Å, α = 90°; V = 1231.3(4) $Å^3$; Z = 4; D_c = 1.538 g cm^{-3}; T = 293(2) K. The goodness-of-fit on F^2 is 1.262. 1526 data collected, 77 unique (R_{int} = 0.0346). Final R indices $[I > 2\sigma(I)]$, $R_1(F_o)$ = 0.0895, $wR_2(F_o^2)$ = 0.2437. The higher R-value may be due to the disorder of H_2O molecules and the CN/NO groups. The data were collected on a Bruker Smart 1000 diffractometer. The structure was solved by direct methods and refined by a full-matrix least-squares technique based on F^2 using the SHELXL 97 program. CCDC reference number 266778 for **1**. See http://dx.doi.org/10.1039/b506465a for crystallographic data in CIF or other electronic format.

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