Crystal structure and magnetic behavior of a three-dimensional cyano-bridged assembly [CuL¹]₂[Cr(CN)₆]ClO₄ · 0.5H₂O (L¹ = 3,10-dipropyl-1,3,5,8,10,12- hexaazacyclotetradecane)

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Reaction of $K_3[Cr(CN)_6]$ with $[CuL^1](ClO_4)_2$ (L^1 = 3,10-dipropyl-1,3,5,8,10,12-hexaazacyclotetradecane) leads to a novel three-dimensional (3-D) cyano-bridged bimetallic assembly $[CuL^1]_2[Cr(CN)_6]ClO_4\cdot0.5H_2O$ (**1**), in which each hexacyanochromate(III) ion connects four copper(II) ions using four co-planar CN^- groups, which coordinate axially to the copper ion in a *trans* fashion forming *trans*-$CuL^1(N\equiv C)_2$ moieties. Magnetic studies reveal that the complex displays a ferromagnetic interaction between the Cu(II) ($S = 1/2$) and Cr(III) ($S = 3/2$) ions through cyano bridges.

Introduction

There has been continuous interest in the molecule-based magnetic materials of cyano-bridged bimetallic assemblies because of their interesting magnetic, magneto-optical and optoelectronic properties.[1,2] It is known that Prussian Blue analogues, derived from hexacyanometalate ions $[M(CN)_6]^{n-}$ and simple transition metal ions, exhibit magnetic ordering at T_C as high as 376 K and form a family of magnetic materials.[2] In order to clarify the magnetostructural correlation of cyano-bridged bimetallic systems, a wide variety of hybrid Prussian Blue complexes derived from $[M(CN)_6]^{n-}$ (M = Fe, Cr, Mn, Co) and coordinatively unsaturated transition metal complexes have been studied structurally and magnetically.[3] These complexes assume oligonuclear, 1-D, 2-D and 3-D structures and exhibit ferro-, ferri- and meta-magnetic behaviour. For instance, the reaction between $[NiL]^{2+}$ (L = polyaza macrocyclic ligand) and $[M(CN)_6]^{3-}$ (M = Fe, Cr) has already led to a series of 2-D Ni_3M_2 assemblies,[4] in which the intralayer coupling between Ni(II) and M(III) is normally ferromagnetic, while the interlayer interactions are often antiferromagnetic. Okawa and coworkers recently reported two 3-D Mn_3Cr_2 ferrimagnets, $[Mn(en)]_3[Cr(CN)_6]_2\cdot4H_2O^5$ and $[Mn(glya)]_3[Cr(CN)_6]_2\cdot2.5H_2O^6$ (glya = glycineamide), which show magnetic ordering at $T_C = 69$ K and 71 K, respectively. Since copper(II) complexes exhibit a great stereochemical plasticity, they are expected to give rise to a large variety of assembled complexes with hexacyanometalates. Nevertheless, well-characterized Cu(II)-containing hybrid Prussian Blue complexes are very limited up to now.[7] Recently, using $[CuL]^{2+}$ (L = polyaza macrocyclic ligand) instead of $[NiL]^{2+}$ as a building block, we obtained the new cyano-bridged Cu(II)–Cr(III) assembly $[CuL^1]_2[Cr(CN)_6]ClO_4\cdot0.5H_2O$ (**1**; where L^1 = 3,10-dipropyl-1,3,5,8,10,12-hexaazacyclotetradecane), which shows a novel 3-D network structure and ferromagnetic behaviour. Here we report its synthesis, crystal structure and magnetic properties.

Experimental

Measurements

Elemental analyses for C, H and N were performed on a Perkin–Elmer 240C analyzer. Cu and Cr analyses were made on a Jarrell–Ash 1100 + 2000 inductively coupled plasma quantometer. IR spectra were recorded on a Nicolet FT-170SX spectrometer with KBr pellets in the 4000–400 cm⁻¹ region. Variable-temperature magnetic susceptibilities (5–300 K) in a 10 kOe field were measured with a Quantum Design MPMS-5 SQUID susceptometer. Low-field (100 Oe) dc and zero-field ac magnetic susceptibilities, as well as the field dependence magnetization, were obtained on a Maglab System 2000 magnetometer. Diamagnetic corrections were made using Pascal's constants. Effective magnetic moments were calculated using the equation $\mu_{eff} = 2.828(\chi_M \times T)^{1/2}$, where χ_M is the magnetic susceptibility per formula unit.

Preparations

All chemicals and solvents were reagent grade and were used without further purification. The Cu(II) macrocyclic complex $[CuL^1](ClO_4)_2$ was synthesized according to the method reported previously.[8] $K_3[Cr(CN)_6]$ was prepared by the literature method.[9]

Caution! *Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled in small quantities with great care.*

$[CuL^1]_2[Cr(CN)_6]ClO_4\cdot0.5H_2O$ (**1**). Complex **1** was obtained as purplish-red single crystals by slow diffusion of a DMF solution (15 cm³) of $[CuL^1](ClO_4)_2$ (0.15 mmol) and an aqueous solution (15 cm³) of $K_3[Cr(CN)_6]$ (0.15 mmol) through a U-tube containing silica gel at room temperature. The resulting crystals were collected, washed with H_2O and

EtOH, then dried in air. They were insoluble in most inorganic and organic solvents. Anal. found: C, 40.45; H, 6.59; N, 25.04; Cr, 5.13; Cu, 12.27%. Calcd for $C_{34}H_{69}ClCrCu_2N_{18}O_{4.5}$: C, 40.17; H, 6.84; N, 24.81; Cr, 5.12; Cu, 12.50%. IR: $\nu_{max}/$ cm^{-1} 3448(w), 3254(s), 3183(m), 2960(s), 2939(m), 2875(m), 2123(m), 1468(m), 1425(m), 1274(m), 1214(m), 1091(vs), 1061(s), 1012(vs), 944(s), 843(m), 628(s), 449(s).

X-Ray crystallography

Diffraction data were collected at 294(2) K on an Siemens P4 diffractometer using graphite-monochromated Mo-K_{α} radiation ($\lambda = 0.71073$ Å) with the ω scan mode. The structures were solved by direct methods and refined by full-matrix least-squares techniques based on F^2. All non-hydrogen atoms were refined with anisotropic thermal parameters. The idealized positions of the hydrogen atoms were located by using a riding model and the hydrogen atoms bonded to the water molecule were not found. All computations were carried out using the SHELXTL-PC program package.

Crystal data. $[CuL]_2[Cr(CN)_6]ClO_4 \cdot 0.5H_2O$, $C_{34}H_{69}ClCr$-$Cu_2N_{18}O_{4.5}$, $M = 1016.60$, hexagonal, space group $P6(5)22$, $a = b = 14.304(1)$, $c = 42.791(7)$ Å, $\gamma = 120°$, $U = 7581.9(15)$ Å^3, $Z = 6$, $D_c = 1.336$ g cm^{-3}, $F(000) = 3204$, $\mu = 1.152$ mm^{-1}; 15 521 reflections measured, 4442 unique; the final wR was 0.0951 (all data).†

Results and discussion

Crystal structure

An ORTEP diagram of complex **1** with the atom numbering scheme is shown in Fig. 1. The projection along the a axis is given in Fig. 2. Selected bond distances and angles are listed in Table 1. The molecular structure consists of one $[Cr(CN)_6]^{3-}$ anion, two $[CuL^1]^{2+}$ cations, one ClO_4^{-} anion and half a water molecule. Each $[Cr(CN)_6]^{3-}$ anion coordinates with four $[CuL^1]^{2+}$ cations *via* four equatorial C≡N groups, whereas each $[CuL^1]^{2+}$ cation is linked to two $[Cr(CN)_6]^{3-}$ ions in *trans* conformation. The Cu^{II} ion assumes an elongated octahedral coordination geometry, in which the equatorial sites are occupied by four nitrogen atoms of the macrocyclic ligand L^1 with the Cu–N$_{eq}$ bond distances in the range of 1.976(5) to 2.024(5) Å, while the axial positions
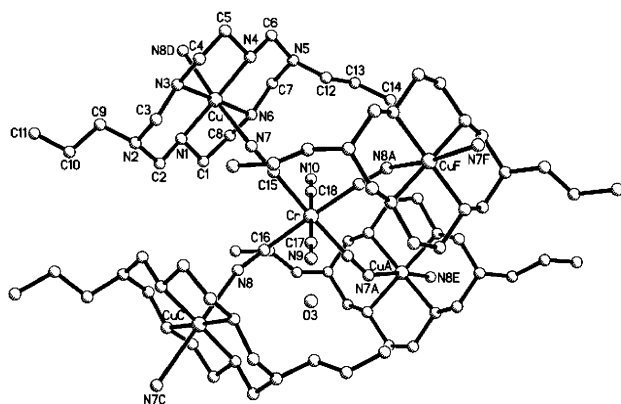

Fig. 1 An ORTEP drawing of complex **1** with the atom numbering scheme. Perchlorate anion is omitted for clarity.

† CCDC reference number 234805. See http://www.rsc.org/suppdata/nj/b4/b401557f/ for crystallographic data in .cif or other electronic format.

are occupied by two nitrogen atoms from CN^{-} groups with Cu–N$_{ax}$ distances of 2.539 and 2.577 Å. Due to the Jahn–Teller effects, the Cu–N$_{ax}$ distances are much longer than the Cu–N$_{eq}$ bond distances, but they are comparable with those observed in other cyanometalate analogs,[7d,10] for example $[Cu(en)_2]_3[W(CN)_8]_2 \cdot H_2O$,[10a] with Cu–N$_{ax}$ distances in the range 2.329(6)–2.967(7) Å. In addition, the Cu–N≡C bond angles are far from linear with the angles Cu–N(7)–C(15) = 136.7° and Cu(C)–N(8)–C(16) = 139.5°. As usual, the $[Cr(CN)_6]^{3-}$ fragment exhibits a distorted octahedral structure. The Cr–C–N angles for the terminal CN^{-} groups are linear and those for the bridging CN^{-} groups are slightly bent. The Cr–C distances for the bridging CN^{-} [2.042(6) and 2.047(6) Å] are slightly shorter than those for the terminal CN^{-} [2.081(9) and 2.087(9) Å], while the C–N distances of the bridging CN^{-} [1.153(6) and 1.154(6) Å] are almost equal to that of the terminal CN^{-} [1.141(8) Å]. According to the Cr–CN–Cu linkage, $[Cr(CN)_6]^{3-}$ ions can be divided into two types: one forms Cr–CN–Cu linkages in the bc plane, the other in the ac plane, which results in a novel 3-D honeycomb-like structure (Fig. 2). The 3-D structure is unique because the reactions of hexacyanometalate with copper(II) complexes containing only two available coordination sites usually produce low-dimensional species.[7d–h] The Cr···Cu and Cr···Cu(C) distances through the cyanide bridges are 5.299 and 5.309 Å, respectively. There is a hydrogen bond between the water molecule oxygen and the terminal CN nitrogen [O(3)···N(9) = 2.909 Å]. The bonding parameters of the macrocyclic ligand L^1 are close to those found in related complexes reported previously.[4]

Magnetic properties

The magnetic susceptibilities of complex **1** were measured with an applied field $H = 10$ kOe in the temperature range 5–300 K. The plots of $\chi_M T$ vs. T and $1/\chi_M$ vs. T are given in Fig. 3. At room temperature, the $\chi_M T$ per Cu$_2$Cr unit is 2.43 emu K mol^{-1} (4.41 μ_B), which is slightly lower than the spin-only value of 2.62 emu K mol^{-1} (4.58 μ_B) expected for an uncoupled spin system (two $S_{Cu} = 1/2$, one $S_{Cr} = 3/2$) with $g = 2.0$. On lowering the temperature, the $\chi_M T$ value monotonically increases, first gradually down to *ca.* 16 K and then sharply up to a value of 5.3 emu K mol^{-1} (6.51 μ_B) at 5 K, which is larger than the value of 4.38 emu K mol^{-1} (5.92 μ_B) for the $S_T = 5/2$ state resulting from the ferromagnetic coupling of two copper(II) ($S = 1/2$) and one chromium(III) ($S = 3/2$) ions. The plot of $1/\chi_M$ vs. T above 40 K obeys the Curie–Weiss law with a positive Weiss constant $\theta = +9.6$ K, which also indicates the presence of a ferromagnetic coupling between the copper(II) and chromium(III) ions through a cyano bridge. The FCM (field-cooled magnetization) curve under 100 Oe shows a rapid increase around 2 K (Fig. 4), implying a possible magnetic phase transition below this temperature. No ordering was observed above 2 K from the temperature dependence of the zero-field alternating current (ac) magnetic susceptibility (Fig. 5).

The field dependence of the magnetization measured at 1.82 K is shown in Fig. 6. The magnetization increases very rapidly in low field and reaches a saturation of the magnetization above *ca.* 30 kOe. The saturation magnetization $M_s = 5.49$ $N\mu_B$ is close to the expected $S = 5/2$ value of 5 $N\mu_B$ for the ferromagnetic Cu$_2$Cr system, confirming further ferromagnetic coupling between the adjacent Cu(II) and Cr(III) ions. The ferromagnetic interaction between the Cu(II) and Cr(III) can be rationalized in terms of the strict orthogonality of the magnetic orbitals of these ions. The low magnetic ordering temperature may be interpreted from the character of the structure of complex **1**. As discussed in the structural description, the axial Cu–N$_{cyanide}$ bond lengths are very long due to Jahn–Teller effects and the Cu–N≡C angles are far from linear. This will markedly
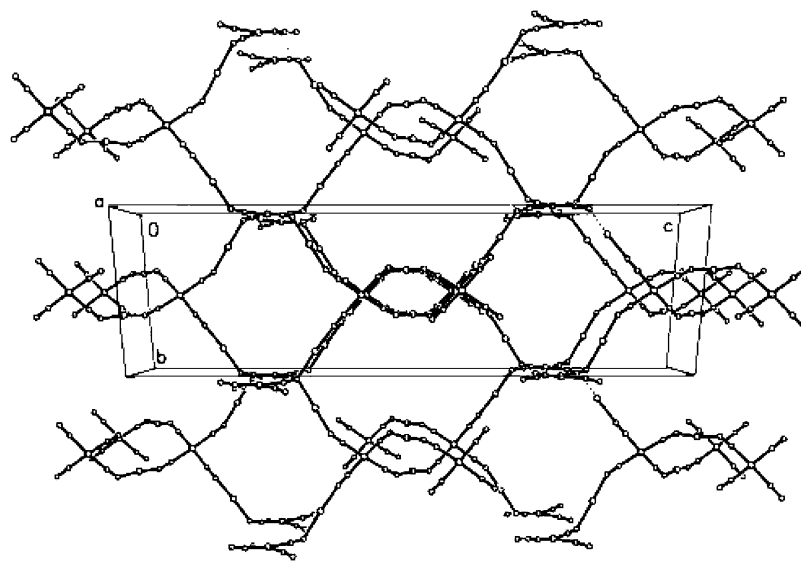
Fig. 2 Projection of the 3-D honeycomb-like structure onto the *bc* plane for complex **1**. Non-bridged cyanides, L¹ ligands, perchlorate anions and water molecules are omitted for clarity.

Table 1 Selected bond distances (Å) and bond angles (°) for complex **1**[a]

Cu–N(1)	1.976(5)	Cu–N(3)	1.985(5)
Cu–N(6)	1.995(5)	Cu–N(4)	2.024(5)
Cr–C(15)	2.042(6)	Cr–C(16)	2.047(6)
Cr–C(18)	2.081(9)	Cr–C(17)	2.087(9)
N(7)–C(15)	1.153(6)	N(8)–C(16)	1.154(6)
N(9)–C(17)	1.141(8)	N(10)–C(18)	1.141(8)
N(1)–Cu–N(3)	92.9(2)	N(1)–Cu–N(6)	86.8(2)
N(3)–Cu–N(6)	178.7(2)	N(1)–Cu–N(4)	178.0(2)
N(3)–Cu–N(4)	87.0(2)	N(6)–Cu–N(4)	93.4(2)
C(15)–Cr–C(15)#1	171.2(3)	C(15)–Cr–C(16)	88.8(2)
C(15)#1–Cr–C(16)	91.7(2)	C(16)–Cr–C(16)#1	174.1(3)
C(15)–Cr–C(18)	85.62(16)	C(16)–Cr–C(18)	92.97(17)
C(15)–Cr–C(17)	94.38(16)	C(16)–Cr–C(17)	87.03(17)
C(18)–Cr–C(17)	180.000(1)	C(1)–N(1)–Cu	108.1(3)
C(2)–N(1)–Cu	114.9(4)	C(4)–N(3)–Cu	105.7(4)
C(3)–N(3)–Cu	115.6(4)	C(6)–N(4)–Cu	116.5(4)
C(5)–N(4)–Cu	105.3(4)	C(8)–N(6)–Cu	106.8(4)
C(7)–N(6)–Cu	115.4(4)	N(7)–C(15)–Cr	174.3(6)
N(8)–C(16)–Cr	173.2(6)	N(9)–C(17)–Cr	180.0(4)
N(10)–C(18)–Cr	180.0(4)		

[a] Symmetry transformations used to generate equivalent atoms: #1 $-y+1$, $-x+1$, $-z+7/6$.

Fig. 4 FCM (field-cooled magnetization *vs. T*) curve under 100 Oe for complex **1**.
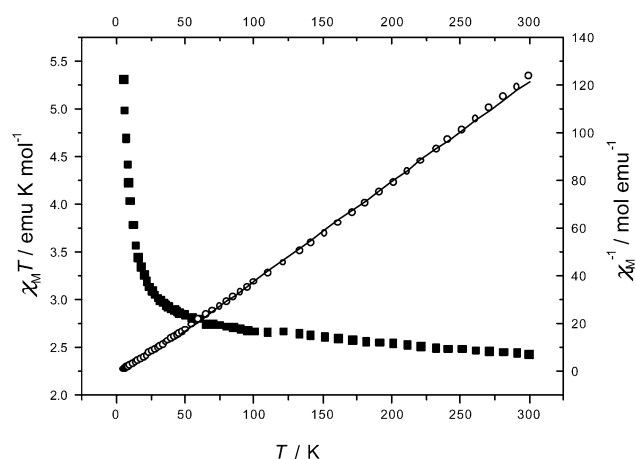

Fig. 3 Temperature dependence of $\chi_M T$ (■) and $1/\chi_M$ (○) for complex **1** measured at 10 kOe. The solid line represents the fit obtained by the Curie–Weiss law (see text).
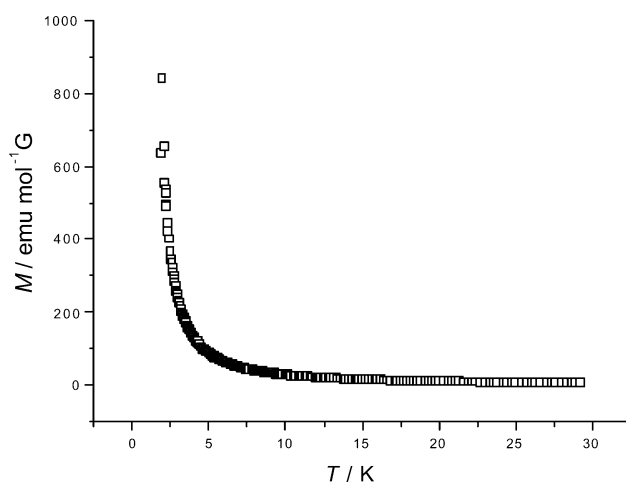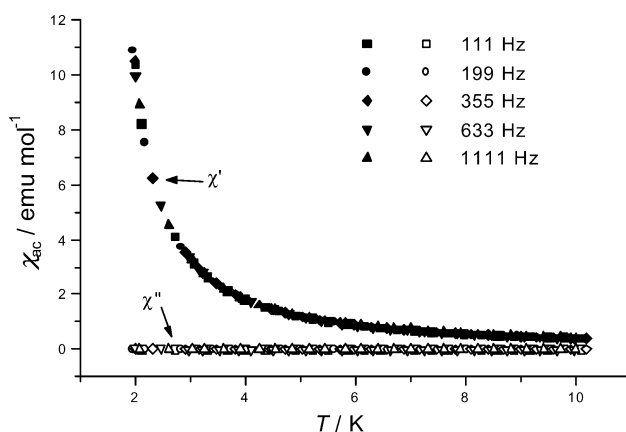

Fig. 5 Real (χ') and imaginary (χ'') ac magnetic susceptibilities as a function of temperature taken at 111, 199, 355, 633 and 1111 Hz for complex **1**.
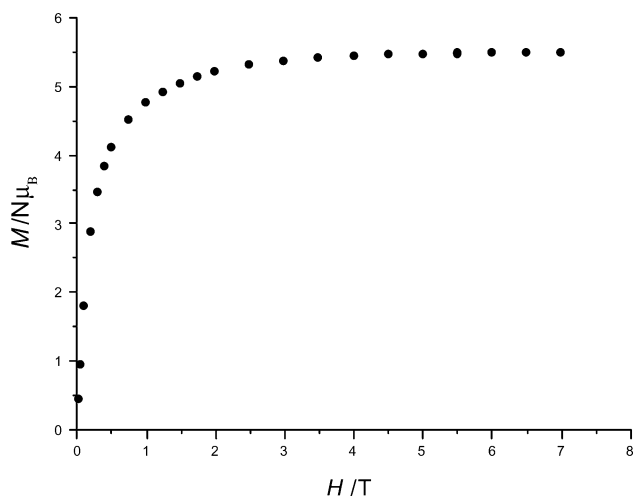
Fig. 6 Field dependence of the magnetization for complex **1** at 1.82 K.

weaken the ferromagnetic interactions through the Cr–C–N–Cu linkages.

Conclusion

A novel cyano-bridged bimetallic assembly, $[CuL^1]_2[Cr(CN)_6]$-$ClO_4 \cdot 0.5H_2O$, has been characterized structurally and magnetically. It has a unique 3-D honeycomb-like structure and shows ferromagnetic behaviour, which is completely different from the cyano-bridged Ni-based macrocyclic complexes $[NiL]_3[M(CN)_6]_2 \cdot nH_2O$ having 2-D structures and metamagnetic behavior.[4] Three-dimensional Cu(II)–Cr(III) cyano-bridged compounds have been scarcely reported and as far as we are aware, only $[Cu(EtOH)_2][Cu(en)]_2[Cr(CN)_6]_2$[7b] has been structurally characterized, which exhibits ferromagnetic ordering below 57 K. The present example further illustrates the structural diversity of bimetallic assemblies constructed from hexacyanometalates and copper(II) complexes. At present, our study on the corresponding Cu(II)–Fe(III) 3-D complex is under way.

Acknowledgements

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