Crystal structure and magnetic properties of a new two-dimensional cyano-bridged bimetallic assembly [NiL′]$_3$[Cr(CN)$_5$(NO)]$_2$·10H$_2$O (L′ = 3,10-dimethyl-1,3,5,8,10,12-hexaazacyclotetradecane)

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A new cyano-bridged Ni(II)–Cr(I) complex, [NiL′]$_3$[Cr-(CN)$_5$(NO)]$_2$·10H$_2$O (L′ = 3,10-dimethyl-1,3,5,8,10,12-hex-aazacyclotetradecane) with a honeycomb molecular structure, displays a long-range magnetic ordering at T_c = 4.5 K.

In the area of molecule-based magnets, many chemists have been interested in the topologies leading to ferromagnetic interactions between paramagnetic metal ions. The approach of the strict orthogonality of magnetic orbitals has been most frequently utilized. On this basis, cyanide-bridged bimetallic assemblies derived from low-spin [M(CN)$_6$]$^{3-}$ (M = Cr^{III}, Mn^{III}, Fe^{III}) and high-spin [ML]$^{2+}$ (M = Cu^{II}, Ni^{II}, L = neutral ligand) are anticipated to be ferromagnetic, which has been verified by many experimental results.[1] Some of them exhibit spontaneous magnetization owing to the efficient propagation of magnetic coupling through the cyanide bridges and the hydrogen bonds.

Very recently, square-planar macrocyclic Ni(II) complexes have been employed to construct cyano-bridged 2D Ni$_3$M$_2$ (M = Cr^{III}, Fe^{III}) assemblies that exhibit ferromagnetic behaviour.[1j–m] In order to construct new molecule-based magnetic materials it is desirable to explore alternative building blocks containing cyanide groups. Most recently, Holmes and Girolami have presented some Prussian blue analogues containing [Cr^I(CN)$_5$(NO)]$^{3-}$, and found that the complex K$_{0.5}$Mn[Cr(CN)$_5$(NO)]$_{0.83}$·4H$_2$O·1.5MeOH possesses a cubic structure based on powder XRD analysis, and that the NO$^+$ group in [Cr(CN)$_5$(NO)]$^{3-}$ is involved in bridging on the basis of 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}).[2] In order to gain further evidence on the binding modes of [Cr(CN)$_5$(NO)]$^{3-}$ with transition metal complexes, we have studied the reaction of [NiL′]$^{2+}$ (L′ = 3,10-dimethyl-1,3,6,8,10,12-hexaazacycloctadecane) with [Cr(CN)$_5$(NO)]$^{3-}$, and obtained a new two-dimensional honeycomb assembly, [NiL′]$_3$[Cr(CN)$_5$(NO)]$_2$·10H$_2$O **1**. The adoption of [Cr(CN)$_5$(NO)]$^{3-}$ is due to the electronic configuration [3d^5, (3d$_{xz}$)^2(3d$_{yz}$)^2(3d$_{xy}$)^1] of low-spin Cr(I) ion together with the approximate C_{4v} symmetry of [Cr(CN)$_5$(NO)]$^{3-}$ that is quite different from the O_h symmetry of [Fe(CN)$_6$]$^{3-}$.[3] The magnetic coupling between the magnetic orbitals of the neighbouring nickel(II) and chromium(I) ions is expected to be ferromagnetic. Here, we present the synthesis, single crystal structure analysis and magnetic properties of the new complex.

To an aqueous solution (15 mL) of [NiL′](ClO$_4$)$_2$[4] (0.3 mmol) was added dropwise, with stirring, a solution of K$_3$[Cr(CN)$_5$(NO)]·H$_2$O[5] (0.2 mmol) in 10 mL of water. This led to the immediate precipitation of yellow microcrystals that were collected by suction filtration, washed with water and dried in air.† The complex is insoluble in most organic and inorganic solvents and stable in air.

The IR spectrum of the complex shows two sharp bands in the range 2000–2200 cm^{-1} which are attributed to C≡N stretching modes. The shift of ν(C≡N) to higher wavenumber (2140 cm^{-1})

compared with that of K$_3$[Cr(CN)$_5$(NO)] (2120 cm^{-1})[6] suggests the formation of CN$^-$ bridges, as observed for other cyano-bridged systems.[1] Further, the blue shift of ν(N=O) with respect to that of K$_3$[Cr(CN)$_5$(NO)] (1630 cm^{-1})[6] also suggests the distortion of [Cr(CN)$_5$(NO)]$^{3-}$ from C_{4v} symmetry as a result of the formation of Cr–C≡N–Ni linkages and that the cyanide ligand *trans* to the NO ligand has been involved in bridging.

The structure of **1** was determined by single crystal X-ray crystallography (Fig. 1).‡ It consists of a neutral stair-shaped layer network with the stoichiometry [NiL′]$_3$[Cr(CN)$_5$(NO)]$_2$. Each [Cr(CN)$_5$(NO)]$^{3-}$ unit uses three *cis*-C≡N groups to connect with three [NiL′]$^{2+}$ groups, whereas the two remaining CN$^-$ and the NO$^+$ groups are monodentate. The adjacent Cr···Ni distances are 5.293(2) Å for Cr···Ni(1), 5.300(1) Å for Cr···Ni(2) and 5.270(1) Å for Cr···Ni(2a), respectively (a denotes the symmetry operation $-x + 0.5$, $y - 0.5$, $-z + 0.5$). Each NiL′ unit is linked to two [Cr(CN)$_5$(NO)]$^{3-}$ ions in *trans* positions. Four secondary amine nitrogen atoms of the macrocycle coordinate to the nickel center with an average Ni–N distance of 2.097(4) Å for Ni(1), 2.074(4) Å for Ni(2). Two nitrogen atoms of the bridging C≡N ligands axially coordinate to the Ni(II) ions with Ni–N$_{ax}$ contacts of 2.153(3) Å for Ni(1)–N(3) and 2.105(4) Å (average) for Ni(2)–N, respectively, which are slightly larger than those of the corresponding Ni–N$_{eq}$ bonds. The bridging cyanide ligands coordinate to the nickel(II) ions in a bent fashion with the Ni–N≡C bond angles ranging from 164.3(3) to 172.8(4)°. The coordination symmetry about the Cr atom is C_{4v} or distorted octahedron, and the Cr–N–O and Cr–C–N groups are nearly linear. The Cr–C distances range from 1.926(5) to
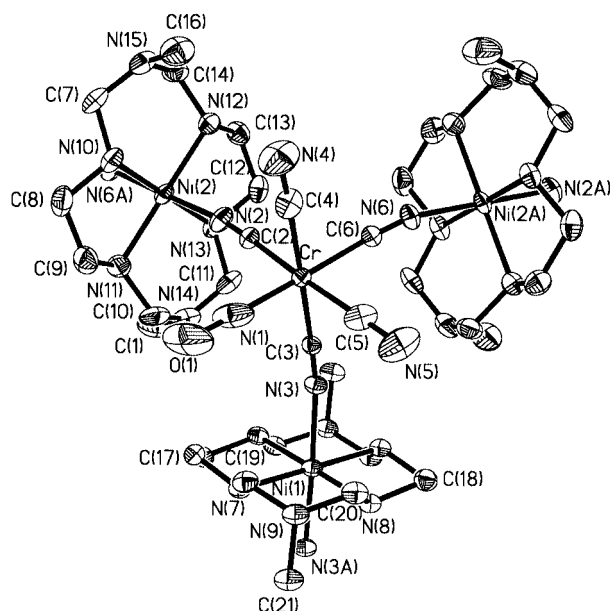

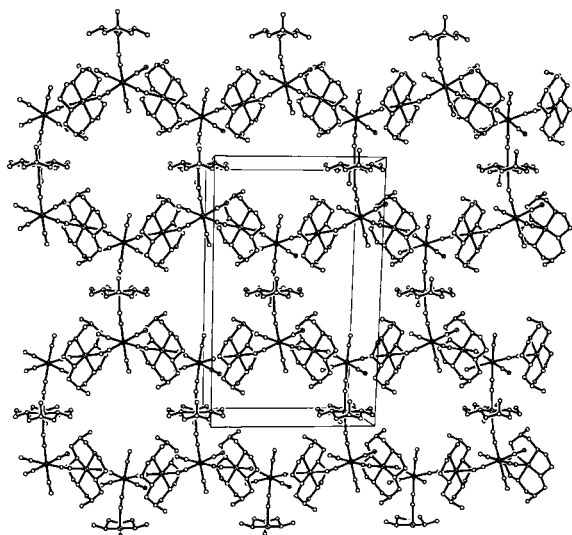**Fig. 1** ORTEP plot of **1** (hydrogen atoms are omitted for clarity).

Fig. 2 Projection showing the 2D honeycomb-like layer containing Cr_6Ni_6 hexagons.

2.083(5) Å, whereas the Cr–N distance of 1.866(5) Å is comparatively long. These compare with the structural results for the double salt $[Co(en)_3][Cr(CN)_5(NO)]\cdot 2H_2O$.[7] The particular local molecular disposition leads to a honeycomb-like layered structure (Fig. 2). The shortest interlayer metal–metal distance is 6.910 Å for Cr···Ni(2m) (m: x, $1 - y$, $-0.5 + z$).

The magnetic susceptibilities of **1** have been measured on a Model Maglab System[2000] magnetometer in the temperature range 2.0–280 K. A plot of $\chi_m T$ vs. T for **1** ($H = 1$ T) is shown in Fig. 3, where χ_m is the magnetic susceptibility per Ni_3Cr_2 unit. The $\chi_m T$ value at 280 K is ca. 4.8 emu K mol^{-1} (6.2 μ_B), higher than expected (3.75 emu K mol^{-1}) for three high spin nickel(II) ions ($S = 1$, $g = 2.0$) and two low-spin chromium(I) ions ($S = 1/2$,[5] $g = 2.0$) in a dilute system, and equal to that calculated assuming the g_{Ni} value of 2.32. With a decrease of the temperature, $\chi_m T$ increases smoothly down to ca. 50 K and then sharply reaches a maximum value of 14.2 emu K mol^{-1} (10.66 μ_B) at 6.4 K, which is much larger than the spin-only value of 10.0 emu K mol^{-1} (8.9 μ_B) for $S_T = 4$ resulting from the ferromagnetic coupling of three nickel(II) ions ($S = 1$, $g = 2.0$) and two low-spin chromium(I) ions ($S = 1/2$, $g = 2.0$), suggestive of the occurrence of magnetic ordering. Below 6.4 K, $\chi_m T$ decreases rapidly, which indicates the presence of interlayer antiferromagnetic interaction and/or the zero-field splitting effect of the nickel(II) ions. The magnetic susceptibility above 6 K obeys the Curie–Weiss law with a positive Weiss constant $\theta = +10.0$ K, which also proves the presence of ferromagnetic coupling within the Ni_3Cr_2 sheet of **1**. The abrupt increase in M at ca. 11 K suggests a phase transition in the complex (Fig. 3).
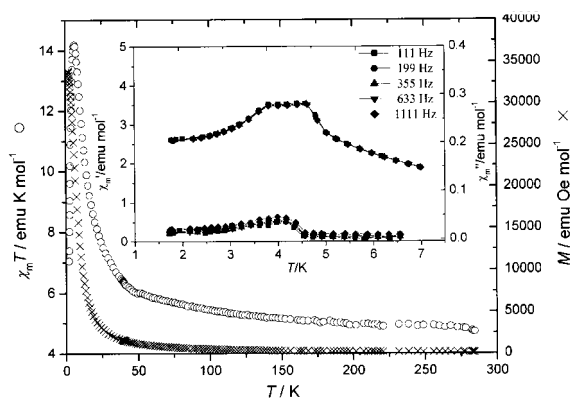

Fig. 3 Temperature dependences of $\chi_m T$ and M for **1**. Inset: real, χ' (top), and imaginary χ'' (bottom) ac magnetic susceptibilities as a function of temperature taken at 111, 199, 355, 633 and 1111 Hz for **1**.

The onset of a long-range magnetic phase transition is further confirmed by the temperature dependence of ac molar magnetic susceptibilities displayed in the inset of Fig. 3. The real part of the zero field ac magnetic susceptibility, $\chi'(T)$, has a maximum at ca. 4.5 K for frequencies of 111, 199, 355, 633 and 1111 Hz, suggesting that T_c of complex **1** is about 4.5 K. The frequency independence of χ_{ac}' and χ_{ac}'' suggests a non-glassy ground state. The field dependence of the magnetization at 1.75 K reveals a hysteresis loop with a coercive field of 170 Oe and a remnant magnetization of ca. 0.19 $N\mu_B$.

The ferromagnetic interaction between the chromium(I) and nickel(II) ions is due to the strict orthogonality of the magnetic orbitals of the low-spin Cr(I) [d^5, $(3d_{xy})^1$] and high-spin Ni(II) [d^8, $(d_{x^2-y^2})^1(d_{z^2})^1$] ions. According to ligand field theory, the high-spin nickel(II) ion in octahedral surroundings has two unpaired electrons in $d_{x^2-y^2}$ and d_{z^2} orbitals that interact with the MOs of the cyano bridge with the same symmetry producing a magnetic orbital with σ-character. The low-spin chromium(I) ion in distorted octahedral surroundings has an unpaired electron in the d_{xy} orbital[3] that interacts with the MOs of the cyano bridge with the right symmetry generating a magnetic orbital with π-character. Consequently, strict orthogonality is obeyed and the interaction between Ni(II) and Cr(I) ions through the cyano bridge should be ferromagnetic.

Notes and references

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