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A [Cr2Ni] coordination polymer

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A [Cr$_2$Ni] coordination polymer: slow relaxation of magnetization in quasi one-dimensional ferromagnetic chains

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The reaction between [Cr$_3^{III}$O(OAc)$_6$(H$_2$O)$_3$]NO$_3$·AcOH with 2-hydroxynaphthaldehyde, 2-amino-isobutyric acid and NiCl$_2$·6H$_2$O in MeOH, under basic and solvothermal conditions, led to the formation of the quasi-1D coordination polymer {[Cr^{III}$_2$Ni^{II}(L)$_4$(MeOH)$_2$]}$_n$ (where L = the dianion of the Schiff base between 2-hydroxynaphthaldehyde and 2-amino-isobutyric acid), which behaves as a ferromagnetic chain, displaying slow relaxation of magnetization.

The field of coordination polymers has recently grown to an extremely active area or research due to the potential that such species display for new technological applications. For example, 3D metal-organic frameworks (MOFs) have been proposed as candidates for applications ranging from gas absorption and hydrogen storage to catalysis, non-linear optics and sensing.[1] In the field of molecular magnetism, while polymeric species had been studied since the early days of magnetochemistry,[2] it was only in 2001 that an 1D coordination polymer, [Co(hfac)$_2$(NITPhOMe)] (hfac= hexafluoroacetylacetonate; NITPhOMe = 4'-methoxy-phenyl-4,4,5,5-tetramethyl imidazoline-1-oxyl-3-oxide), was found to display slow relaxation of magnetization below 4 K.[3] Such species were termed as Single Chain Magnets (SCMs),[4] by analogy to Single Molecule Magnets (SMMs), which are 0-D species (discrete molecules) that can retain their magnetization in the absence of an external magnetic field, once magnetized at very low temperatures.[5] In both SCMs and SMMs, the slow relaxation of

magnetization originates from easy-axis magnetic anisotropy and has, therefore, similar characteristics. However, the underlying mechanism of the spin reversal is rather different; in SMMs, the magnetic anisotropy leads to a splitting of the ground-state, S, in a 2S+1 multiplet, with the ±mS microstates lower in energy, thus, resulting in an energy barrier (double-well) for the re-orientation of the magnetization, according to which the spin has to climb over the barrier in order for the magnetization to flip. On the other hand, the relaxation for SCMs follows *Glauber* dynamics,[6] according to which the relaxation begins with one spin reversing its orientation, and then this reversal being transmitted throughout the chain with a single spin flip at each step.

Following our initial work on employment of the artificial amino acid 2-amino-isobutyric acid, aibH, on various 3d-4f and 4f chemistry,[7] we herein expand our work and report on the synthesis and magnetic characterization of the quasi-1D mixed metal Cr^{III}/Ni^{II} coordination polymer {[Cr^{III}$_2$Ni^{II}(L)$_4$(MeOH)$_2$]}$_n$ (**1**) upon the use of aibH and 2-hydroxynaphthaldehyde. Furthermore, to the best of our knowledge complex **1** is the first example of a Cr^{III}-Ni^{II} based ferromagnetic chain, displaying slow relaxation of magnetization.

Into an equimolar solution of [Cr^{III}$_3$O(OAc)$_6$(H$_2$O)$_3$]NO$_3$·AcOH[8] and NiCl$_2$·6H$_2$O in MeOH were added equivalent amounts of aibH, 2-OH-naphthaldehyde and NEt$_3$. The solution was then transferred to a Teflon-lined autoclave and kept at 120 °C for 14 hours. After slow cooling to room temperature single crystals of the {[Cr^{III}$_2$Ni(L)$_4$(MeOH)$_2$]}$_n$ (**1**) (L = the dianion of the Schiff base between 2-hydroxynaphthaldehyde and 2-amino-isobutyric acid, Figure 1, top) formula were obtained in good yield. ‡ The preparation of **1** is summarized in the following chemical eqn. (1):

2/3 [Cr$_3$O(OAc)$_6$(H$_2$O)$_3$]NO$_3$·AcOH + NiCl$_2$·4H$_2$O + 4 aibH + 4 2-OH-naph $\longrightarrow$
[Cr^{III}$_2$Ni^{II}(L)$_4$(MeOH)$_2$] + 32/3 H$_2$O + 2HCl + 2/3 HNO$_3$ + 14/3 AcOH (1)
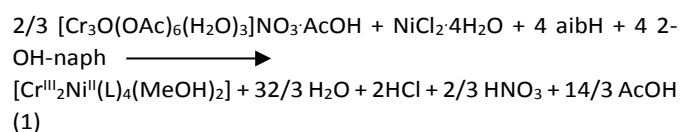
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In order to further verify the purity of the crystalline sample, we performed Energy Dispersive X-ray Spectroscopy analysis (EDS) in bulk crystalline material of **1** and the Cr^{III}/Ni^{II} ratio found was 1.93:1 (Fig. S1), *i.e.* very close to the theoretical value of 2:1 established from crystallography.

Complex **1** crystallizes in the triclinic space group *P*-1. Its repeating unit consists of linear $\{[Cr^{III}_2Ni^{II}(L)_4(MeOH)_2]\}$ species, which are further connected *via* four coordination bonds to two neighboring units (Figure 1, bottom). Within each trimetallic unit the central Ni^{II} atom is located at a distance of ~ 5.3 Å from the terminal Cr^{III} atoms, while each Cr^{III} atom is connected to the central Ni^{II} atom *via* one *syn, anti* η^1: η^1: μ carboxylate belonging to a fully deprotonated, L^{2-}, ligand. On each Cr^{III} two fully deprotonated L^{2-} ligands are bound in η^1: η^1: η^1: η^1: μ fashion, forming two six- and two five-member chelate rings around the metal ion; one of the ligands is responsible for the intra-trimetallic linkage, while the other is responsible for linking neighboring trimetallic units *via* an *anti, anti* η^1: η^1: μ carboxylate. All metallic centres are six-coordinate adopting octahedral geometry, while the central Ni atom completes its coordination geometry with two terminal MeOH molecules. The assembly of the trimetallic repeating units affords a ribbon-like quasi-1D coordination polymer propagating parallel to the *a* axis with the mean plane of the ribbon parallel to the *ac* plane, in which all metallic centers are coplanar. The ribbon-like polymer can be described as corner sharing $\{Cr_2Ni_2\}$ rhombs, with intra-ribbon Cr⋯Cr and Ni⋯Ni distances of ~7.1 and 8.8 Å, respectively and Cr⋯Ni distances of ~6.0 and ~5.3 Å, respectively. A number of O-H⋯O and C-H⋯O intra-ribbon hydrogen bonds stabilize the quasi-1D polymer (Fig. S2 and Table S1). In the crystal lattice, ribbons are connected through C-H⋯O and C-H⋯π interactions (Fig. S3 and Table S2) to create a 2D layer parallel to the *ac* plane. These layers are separated by ~11.7 Å. The mean metallic planes of closest intra-layer ribbons are separated by ~2.4 Å, while the closest inter-ribbon metallic distances are ~ 8 Å.
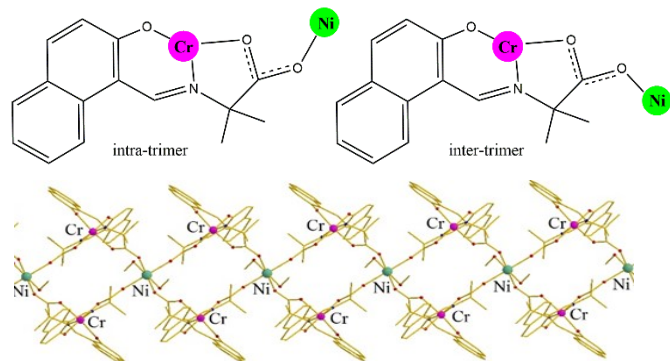

Figure 1. (Top). The coordination modes of the dianion of the Schiff base between 2-hydroxynaphthaldehyde and 2-amino-isobutyric acid. (Bottom) The molecular structure of **1**; each $\{Cr_2Ni\}$ unit is connected to two neighbours *via* four coordination bonds. Colour code: Cr^{III}= violet, Ni^{II}= green, O=red, N= blue, C= yellow.

Direct current magnetic susceptibility measurements were performed on a polycrystalline sample of **1** in the 5 − 300 K range under an applied field of 0.1 T, and the results are plotted

as the $\chi_M T$ product vs. *T* in Figure 2. For **1** the room temperature $\chi_M T$ value of 4.90 $cm^3 mol^{-1}$ K, slightly larger than the theoretical value of 4.85 $cm^3 mol^{-1}$ K corresponding to two Cr^{III} (g=2.00) and one non-interacting Ni^{II} ions (g=2.10), remains constant until ~ 50 K, below which it increases to reach the maximum value of 11.17 $cm^3 mol^{-1}$ K at 7 K, before it drops to 11.03 $cm^3 mol^{-1}$ K at 5 K. This behaviour is indicative of dominant ferromagnetic interactions, while the drop below ~7 K may be attributed to ZFS and/or intermolecular interactions. Indeed, the presence of dominant ferromagnetic interactions was further supported by the Curie-Weiss analysis yielding a positive ϑ value of 3.05 K. A quantum Monte Carlo study (QMC) using the stochastic series expansion (SSE) algorithm[9] was adopted instead of the usual ITO (Irreducible Tensor Operators) method, in order to simulate the magnetic behaviour of the compound. The reason for using the QMC method instead of the classical Monte Carlo (CMC) is the quantum nature of the Ni^{II} (*s* = 1) and Cr^{III} (*s* = 3/2) ions. The QMC calculations are based on the ALPS (Algorithms and Libraries for Physical Simulations) project.[10] For each site 5×10^6 Monte Carlo steps were performed, and 10% of them were discarded as the initial transient stage. The magnetic model used for this simulation is shown in Figure 2 (inset), according to which J_1 is the intra-trimer interaction and J_2 is the interaction between the trimers within the chain. In order to take into account the inter-chain interaction, a mean-field correction (MFC), zJ, was also adopted; furthermore, the different nature of the magnetic ions concerning the g-values was also taken under consideration, and the following fixed values were employed (in order to avoid over-parameterization), g_{Cr}=2.0, g_{Ni}=2.3. The final simulation values yielded: J_1=4.5 K (0.5), J_2=2.8 K (0.5) K, zJ = −0.4 cm^{-1}, and the simulated curves are shown in Figure 2 (top). The red solid line
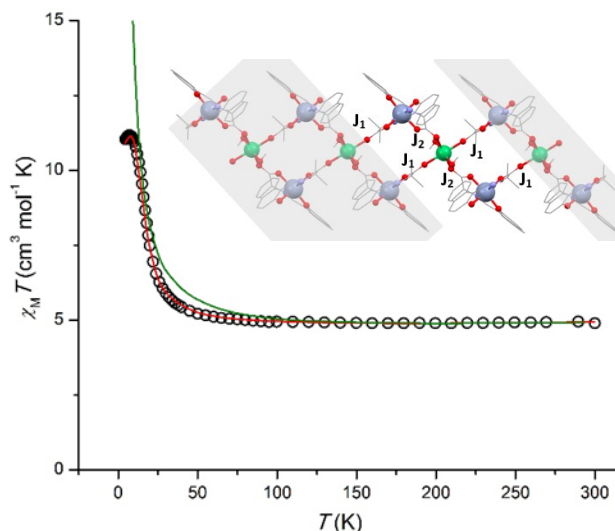

Figure 2. Plot of $\chi_M T$ vs *T* for complex **1** in the 5 − 300 K temperature range (top). The solid lines represent simulations with (red) and without (green) a mean-field correction (see text for details). Inset: The *J* intra-chain interaction scheme employed. Colour code: Ni^{II}: green, Cr^{III}: blue, O: red.

is after applying the MFC correction, while the green solid line is without the MFC term. According to the QMC results, there are two different ferromagnetic intra-chain interactions, and a negative zJ to account for the inter-chain correlations. Note

that, in the mean-field approximation, we can interpret zJ as an effective interaction constant resulting from any source of magnetic ordering, e.g., magnetic anisotropy and/or magnetic interactions, which are likely dipole-dipole interactions because there are no significant exchange pathways inter-connecting the chains. Various models were also tested in order to take into account the zero-field contribution to the low-temperature susceptibility, but due to the complexity of the system and the different nature of the magnetic ions, it was difficult to safely derive conclusions regarding the magnitude of these terms.

The presence in **1** of dominant ferromagnetic interactions is also established by magnetization measurements (Fig. S4), which display a rapid increase to the saturation value corresponding to an "$S=4$" ground-state, while fitting attempts using the giant spin model[11] gave $D = -0.01(1)$ cm and g=1.93(1).

The dynamic magnetic behavior of **1** was investigated under a 3.5 AC field oscillating at various frequencies, revealing strong temperature and frequency dependence for both the in-phase, χ_M', and out-of-phase, χ_M'', signals, in the temperature range between ca. 3 and 9 K (Figs. 3 and S5). The χ_M'' data were fitted to the Arrhenius relationship (eq. 2):

$$\tau = \tau_0 \exp(\Delta\tau/kT) \qquad (2)$$

where $\Delta\tau$ is the effective relaxation barrier, τ is the relaxation time, τ_0 is the pre-exponential factor and k is the Boltzmann constant, yielding $\Delta\tau = 143.4$ K and $\tau_0 = 0.4 \times 10^{-13}$ s (Figure S6),
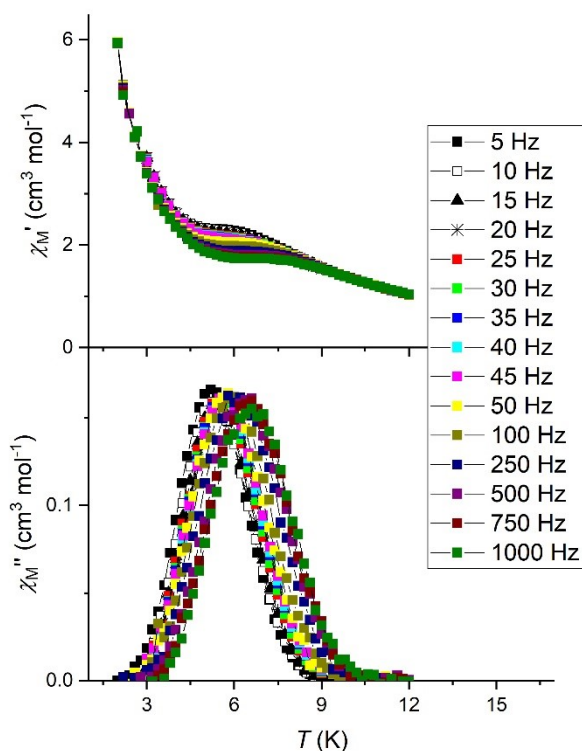

Figure 3. (Top) In-phase, $\chi_M'T$, and out-of-phase (bottom), χ_M'', signals for **1** at various frequencies in the 5 – 1000 Hz range.

thus potentially establishing **1** among SCMs with the highest energy barrier values,[3,12] with the record value of $\Delta\tau = 252$ K ($\tau_0 = 1.5 \times 10^{-13}$ s) reported for an octacyanotungstate-based SCM.[13]

Yet, the small χ_M': χ_M'' ratio along with the small τ_0 value, clearly indicates that **1** may not be treated as a conventional SCM. The inter-chain interactions along with the small anisotropy present in the system, clearly favor the slow relaxation of magnetization *via* many possible relaxation pathways. This is further corroborated by the Cole-Cole plot (χ_M'' *vs.* χ_M', Figure S7) at several temperatures. Fits to the generalized Debye model, which takes into account the width of the τ distribution by an α parameter ($0 \leq \alpha \leq 1$),[16] provide α values in the 0.27-0.43 range, suggesting multiple relaxation processes. However, we exclude spin-glass behaviour. We calculated the *Mydosh* parameter, $\phi = (\Delta T_P / T_P)/\Delta\log f$, from the shift of the peak temperature (T_P) of the out-of-phase signal as a function of the frequency, f.[14] The resulting $\phi = 0.14$ is almost two orders of magnitude larger than that of a spin-glass compound ($\phi < 0.01$).[15]

The increase of the in-phase susceptibility on lowering T below the temperatures of maximum dissipation (Fig. 3) is an unusual behavior, which apparently sets **1** apart from "conventional" SCMs. To shed further light on the magnetic properties of **1**, we measured the heat capacity down to ca. 0.3 K (Fig. 4). The zero-field c_p shows a lambda-like peak, which is centered at a critical temperature $T_c = 0.6$ K and is promptly modified into a broad Schottky-like anomaly by applying a magnetic field of 1 T. This behavior is unequivocally associated with a magnetic phase transition, which is likely driven by dipole-dipole interactions. The peak is superimposed to a long high-T tail, as expected from the low-dimensional magnetic correlations, which predominantly exist within the quasi-1D chains. Above ~6 K, c_p is dominated by lattice phonon modes of the crystal, which can be described by the Debye model (solid line) and simplify to $c_p/T^3 = 6.5 \times 10^{-3}$ K^{-3} at the lowest temperatures.

The present system falls in the same class of SCMs and ferromagnetic quantum chains studied previously, in connection with the problem of 1D soliton excitations.[17] In fact,
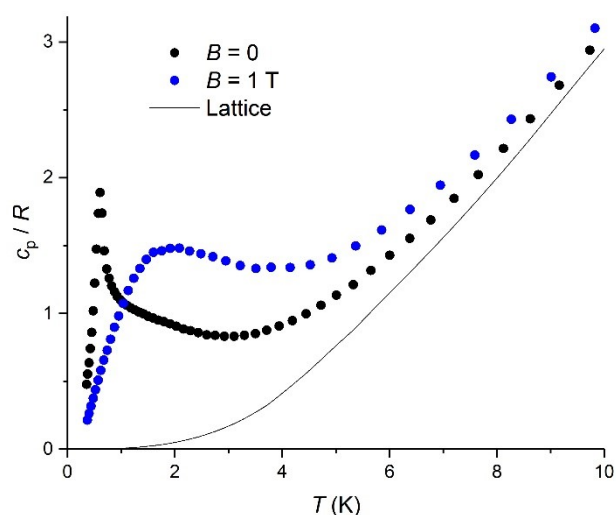

Figure 4. Molar heat capacity c_p, normalized to the gas constant R, collected for 0 and 0.1 applied magnetic field, for complex **1**. The solid line is the estimated lattice contribution.

the behaviour observed here appears to be analogous to that of $[(CH_3)_4N]NiCl_3(TMNC)$.[17b] Above T_c, magnetic correlations

develop principally within the quasi-1D chains. The dissipation in the AC susceptibility is due to domain-wall motion along individual chains, promoted by the intra-chain ferromagnetic exchanges and the anisotropy brought about by the Ni^{II} ions. This is strictly reminiscent of SCM behaviour, the main difference being on the strength of the inter-chain coupling. On lowering the temperature towards $T_c = 0.6$ K, dipole-dipole interactions become sizeable and, gradually, a crossover from SCM behaviour to a 3D magnetically ordered phase takes place. Since the projection of the ferromagnetic chains in the ac plane is a simple-hexagonal lattice, dipole-dipole interactions should align the spins perpendicular to the a axis, i.e., the direction of the chains.[18]

In conclusion, the employment of 2-hydroxynaphthaldehyde, and 2-amino-isobutyric acid in mixed-metal Cr^{III}-Ni^{II} chemistry, has led to the synthesis of the quasi-1D coordination polymer {[$Cr^{III}_2Ni^{II}(L)_4(MeOH)_2$]}$_n$, **1**, which consists of repeating linear trimetallic units forming a ribbon-like structure. Furthermore, compound **1** was found to display slow relaxation of magnetization with a high relaxation energy barrier of ~143 K above $T_c = 0.6$ K. Work is underway in order to: i) isolate other divalent metallic analogues of **1**, as a means of obtaining a series of [$Cr_2^{III}M$] analogues and investigate their magnetic properties, ii) decrease the inter-chain interactions, to make the excitations more strongly localized within the chains.

Notes and references

‡ Crystal data for **1**: $C_{62}H_{60}Cr_2N_4NiO_{14}$, M = 1247.85, triclinic space group P-1, a = 8.8310(18) Å, b = 13.443(4) Å, c = 13.675(4) Å, α = 118.00(3)°, β= 103.90(2)º, γ= 92.20(2)º, V = 1369.6(9)Å³ , Z = 1, T = 80 K, R1 (I > 2σ) = 0.046 and wR2 (all data) = 0.103 for 10133 reflections collected, 4767 observed reflections (I > 2σ(I)) of 6177 (R_{int} = 0.032) unique reflections and 385 parameters, GOF = 1.04. CCDC reference number: 1833818.

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