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Hexacyanometalate molecular chemistry: trinuclear $CrNi_2$ complexes; micro-SQUID magnetisation studies of intermolecular interactions

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Abstract

Three different $CrNi_2$ complexes were synthesised. They differ from each other by the nature of the terminal ligand and of the counter anion: $[Cr(CN)_4\{CN-Ni(tetren)\}_2]Cl$, that crystallises in two different crystallographic systems and $[Cr(CN)_4\{CN-Ni(dienpy2)\}_2](ClO_4)$. The ground state spin value is 7/2 for the three systems (ferromagnetic interaction between chromium(III) and nickel(II) ions). The magnetisation of the three $CrNi_2$ complexes was measured using an array of micro-SQUIDs in a temperature range between 0.04 and 7 K, under a magnetic field up to ± 1 T. The three samples present a three-dimensional magnetic ordering. The correlation between the structure and the intermolecular coupling is analysed in terms of steric hindrances of the terminal ligand, orientation of the molecules in the unit cell (canted structure) and crystal symmetry.

Keywords: Molecular magnetism; Hexacyanometalates; Trinuclear cyanocomplexes; Intermolecular interactions

1. Introduction

The search for new polynuclear molecules displaying high spin ground state and anisotropy raises the interest of synthetic chemists [1–6] and physicists [7–9] involved in the field of molecular magnetism [10,11]. These anisotropic high spin molecules exhibit original magnetic properties such as single molecule magnet (SMM) behaviour [12–17] (long relaxation time for the magnetisation below a so-called blocking temperature, T_B) or magnetic quantum tunnelling effect [18,19]. Our research approach is devoted to the synthesis of such complexes in order to get SMMs.

In order to understand the SMM behaviour, it is important to remind that a phenomenological Hamiltonian correlated to a spin state diagram might describe all polynuclear complexes. In presence of a uniaxial anisotropy, a zero-field splitting is observed which splits the ground state in $2S+1$ levels. The activation energy of the anisotropy barrier, E_a, between the spin states $M_S = \pm S$, is a direct function of D (uniaxial anisotropy) and S (ground state spin value), $E_a = DS^2$. To obtain a SMM i.e. to avoid a rapid relaxation process, the spin as well as the absolute value of the anisotropy have to be as high as possible and D has to be negative so that the state of highest M_S lies below in energy. The exchange coupling J between two spin carriers has to be important to well separate the ground state from the first excited states. The intermolecular interaction, J'_{inter}, plays also an essential role: it has to be negligible, necessary condition to avoid a three-dimensional magnetic ordering and to observe the properties of an isolated nanoscale object. Very few examples of clusters responding to all these criteria have been described in the literature, among them Mn_{12} [14,15,20], Fe_8 [21] and Mn_4 [9] are reference compounds.

To obtain anisotropic high spin molecules, we developed a step by step synthetic strategy based on the coupling reaction of polycyanometalate precursors

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(viewed as Lewis bases) and mononuclear complexes of transition metal ions with a polydentate ligand, leaving a unique accessible position only (as Lewis acids) [22–24]. Starting with hexacyanometalate precursors, this strategy allows to obtain: (i) isotropic high spin molecules such as $CrCu_6$ ($S = 9/2$), $CrNi_6$ ($S = 15/2$) and $CrMn_6$ ($S = 27/2$) [24]; (ii) complexes with various structural anisotropy but low ground state spin, for instance CoNi ($S = 1$), $CoNi_3$ ($S = 1$) and $CoNi_5$ ($S = 1$) or even singlets $CoNi_2$ ($S = 0$) and $CoNi_6$ ($S = 0$) [25]; (iii) anisotropic high spin molecules like CrNi ($S = 5/2$), $CrNi_2$ ($S = 7/2$), $CrNi_3$ ($S = 9/2$) and $CrNi_5$ ($S = 13/2$) [25–27].

In the present paper, different $CrNi_2$ complexes ($[Cr(CN)_4\{CN{-}Ni(L)\}_2]^+$ L, being a polydentate ligand) are investigated below 2 K in order to search a potential SMM behaviour or to evaluate the intermolecular magnetic exchange interaction. After presenting briefly the structural parameters of the various complexes, we discuss the low temperature magnetic properties on oriented single crystals and evaluate the main parameters involved in the intermolecular exchange interaction which induces the three-dimensional ordering at very low temperature (See also Refs. [28–30]).

2. $CrNi_2$ complexes, presentation and structure

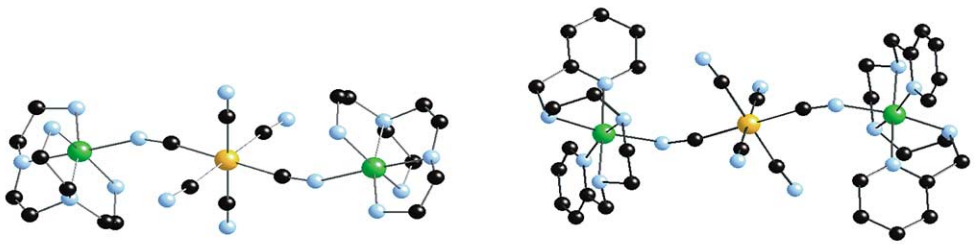
Five different $[Cr(CN)_4\{CN{-}Ni(L)\}_2]^+$ complexes, abbreviated as $CrNi_2$ in the following, have been isolated and characterised, including by single crystal X-ray diffraction. The compounds differ from each other by the nature of the polydentate ligand, L, [tetraethylenepentamine (tetren), tris(2-aminoethyl)-*N*,*N*,*N′*-ethyldiamine (trenen) and bis(2-pyridylmethyl)-*N*,*N″*-diethylenetriamine (dienpy$_2$)] or by the nature of the counter anions (tetrafluoroborate, chloride or perchlorate). The magnetic studies (4–300 K) indicate in all cases a ferromagnetic intramolecular interaction between the chromium and the nickel spin carriers, as predicted for orthogonal magnetic orbitals and a $S = 7/2$ value for the ground state. The intramolecular exchange coupling value, J_{CrNi}, varies from $+4.5$ to $+10$ cm^{-1} according to the distortion of the Cr–CN–Ni unit and especially to the change in the C–N–Ni angle. The uniaxial anisotropy, D, computed from fitting of the susceptibility data, is around -0.3 cm^{-1}. High-field EPR experiments are in progress in order to determine precisely the anisotropy factor. The synthesis, the characterisation, the magnetic properties and magneto-structural correlation studies of these species are presented elsewhere [24].

Three of the five complexes are involved in the present study: (i) $[Cr(CN)_4\{CN{-}Ni(tetren)\}_2]Cl$, noted $CrNi_2$(tetren) that crystallises in two different crystallographic systems: monoclinic, space group = $P2_1/c$ and orthorhombic, space group = $Pbc2_1$, named **1** and **1***, respectively; (ii) $[Cr(CN)_4\{CN{-}Ni(dienpy2)\}_2](ClO_4)$ that crystallises in the monoclinic system, space group = $C2/c$, noted $CrNi_2$(dienpy2) or **3**. This compound is formed with a bulky ligand which influences the intermolecular distance and the intermolecular exchange coupling. The two cationic complexes are presented in Fig. 1. Projections of the three cells are in Fig. 2.

The $CrNi_2$(tetren) monoclinic system **1**, forms pink distorted hexagonal crystals. The hexagonal face corresponds to the (1 0 0) crystallographic plane. The three others faces are the (−1 −1 1), (1 −1 −1) and (1 1 −1) planes. In the crystal, the molecules are aligned in a two-dimensional sheet, parallel to the (1 0 0) plane. The planes are separated by the counter anions, Cl^- and water molecules that form a network of hydrogen bonds as schematised in Fig. 2. In each plane, the molecules are crystallographically equivalent but present two different orientations. The shorter intermolecular Cr···Cr, Cr···Ni and Ni···Ni distances are 8.50, 6.23 and 7.50 Å, respectively. The shortest distance between two nearest molecules is less than 3.08 Å, corresponding to the distance between a free cyanide ligand on the central chromium and a nitrogen atom of the tetren ligand. Even if this distance appears slightly too long for a hydrogen bond, it can account for a possible pathway for intermolecular exchange interaction. For all the (1 0 0) planes, the direction of the molecular NiCrNi axis forms a 36° angle with the *a* axis.

The $CrNi_2$(tetren) orthorhombic system, **1***, crystallises also as hexagonal plates. The two-dimensional molecular arrangement is exactly the same than in compound **1**. The shortest intermolecular Cr···Cr, Cr···Ni and Ni···Ni distances are 8.55, 6.29 and 7.50 Å, respectively. Only differs the crystallographic plane of the hexagonal face, which is (0 0 1) and the molecular orientation from one plane to another. Instead of having the same orientation, the molecules are aligned in chevrons, with an angle of 90° between the molecular Ni–Cr–Ni axes. As in the previous case, the chloride ions and the hydrogen bond network formed by the water molecules separate the molecular layers.

Finally, the crystals obtain from the $CrNi_2$(dienpy2) system, **3**, are red–pink parallelepipeds that belong to the monoclinic system. As indicated in Fig. 2, the molecules are aligned in a two-dimensional arrangement and the planes are separated by the ClO_4^- counterions. The orientations of the molecules in the crystal are very similar to the one observed in compound **1**. Despite the facts that the dienpy2 ligand, due to the presence of pyridine rings, is more bulky than the tetren ligand and that the perchlorate is bigger than chloride, the intermolecular distances in **3** are only slightly longer than in complexes **1** and **1***. The shorter intermolecular Cr···Cr, Cr···Ni and Ni···Ni distances are 9.17, 6.84 and 8.56 Å,



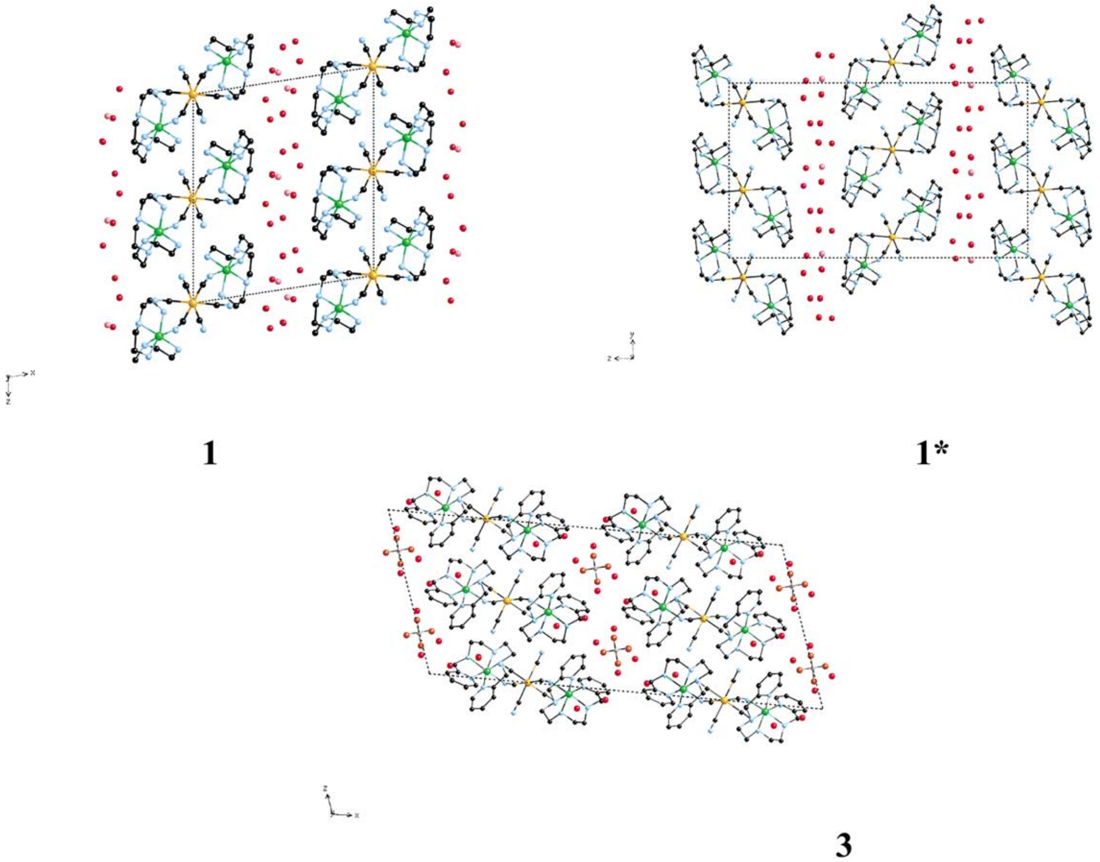
$CrNi_2$(tetren) **$CrNi_2$(dienpy2)**

Fig. 1. X-ray crystal structure of $[Cr(CN)_4\{CN{-}Ni(tetren)\}_2]^+$ and $[Cr(CN)_4\{CN{-}Ni(dienpy2)\}_2]^+$ entities in **1** and **3**.

respectively. This is due to π–π interaction and to hydrogen bonds between two free cyanides through a water molecule.

3. $CrNi_2$ complexes, magnetic behaviour

The magnetisation versus applied field was recorded on single crystals of the three $CrNi_2$ using an array of micro-SQUIDs [31]. Different from a classical SQUID magnetometer where the flux coupling between sample and SQUID is made by using a pick up coil, a micro-SQUID magnetometer allows a much better flux coupling since the sample is placed directly on the SQUID loops. The sensitivity achieved with our device is 10^{-17} emu, that is ten orders of magnitude better than a traditional SQUID magnetometer [32]. The sensitivity is smaller when the sample is much larger than the micro-SQUID. The high sensitivity of the magnetometer allows to study single crystals with dimensions from 10 to 500 μm. The magnetometer works in a temperature range between 0.035 and 10 K, in applied fields up to 1.4



1 **1*** **3**

Fig. 2. Projection of the unit cells of **1** (along the *b* axis), of **1*** (along the *a* axis) and of **3** (along the *b* axis).

T with sweeping rates as high as 1 T s^{-1} and a field stability better than a microtesla. The field can be applied in any direction of the micro-SQUID plane by separately driving three orthogonal coils. In order to ensure a good thermalisation, the crystal is fixed by using Apiezon grease.

Here we report on the observation of canted ferromagnetic structure for the three different compounds of $CrNi_2$ with the same ground state spin 7/2. First we analyse the hysteresis loops of compound **1**. Second, we correlate the structure with the magnetic behaviour. Third, we conclude with a comparison between the magnetisation data of the three crystals in order to establish if the intermolecular coupling is sensitive to small variations of the structure: terminal ligands or crystal symmetry.

We used the micro-SQUID to measure magnetisation hysteresis loops at different temperatures and different field sweep rates and also the magnetic susceptibility below 7 K. A single crystal was placed on the SQUID array with the (1 0 0) plane parallel to the SQUID plane. The hysteresis loops are independent on the field sweep rate, suggesting that either resonant quantum tunnelling is hindered by intermolecular interactions or is much faster than the time scale of the micro-SQUID technique.

The magnetisation loops measured for different directions of the applied field in the (1 0 0) plane, proved that the magnetic behaviour is not isotropic in the plane. We have chosen two symmetry directions in the (1 0 0) plane which present distinct magnetic behaviour. The first direction, is along the projection in the (1 0 0) plane of the bisecting line of two Ni–Cr–Ni molecular directions, showed to be an easy axis of magnetisation. The second direction perpendicular to the first one, showed to be a hard axis of magnetisation. The corresponding magnetisations versus applied field curves are presented in Fig. 3(a and b).

In the first orientation (Fig. 3(a)), the magnetisation is reversed from the negative saturation value to the positive saturation value in zero field. When increasing the temperature, the saturation magnetisation decreases, but the zero field slope remains constant below 0.6 K. This is confirmed by the magnetic susceptibility measured in this direction (see Fig. 4(a)). A fit to a Curie–Weiss law gives a positive Curie–Weiss constant of + 0.6 K. Both results are typical of a system with ferromagnetic intermolecular coupling leading to long range ferromagnetic ordering. However, when the field is applied perpendicular to the easy axis of magnetisation (second direction above), hysteresis loops (Fig. 3(b)) and susceptibility measurements (Fig. 4(b)) suggest an antiferromagnetic intermolecular coupling. This is established by the hysteresis loop shapes and the negative Curie–Weiss constant (−0.25 K).

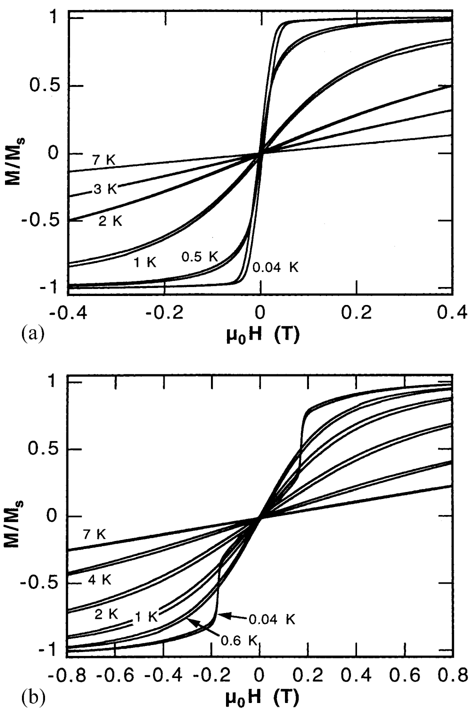


Fig. 3. Temperature dependence of the hysteresis loops, measured for two perpendicular directions in (1 0 0) plane. The temperatures are indicated. In (a) the field is applied along the easy axis and the behaviour is typical of a system with ferromagnetic intermolecular coupling. In (b) the field is applied perpendicular to the easy axis and the hysteresis loops present an antiferromagnetic plateau.

The magnetic behaviour can be explained using the crystallographic structure. The $CrNi_2$ compound, **1**, presents an uniaxal anisotropy with a small ferromagnetic exchange interaction between the molecules. The central chromium ions of the molecules define the (1 0 0) planes (Fig. 1), which are separated from each other by a water and halide layer (Fig. 5). There might be weak antiferromagnetic interactions via hydrogen bonds between the planes but that are not clearly established. There are two different orientations of the molecules centred in the same (1 0 0) plane. The angle between the two directions is 64°; the angle between each direction and (1 0 0) plane is 36°.

The magnetic moments have therefore two orientations corresponding to the two orientations of the molecules. The micro-SQUID magnetometer is sensitive only to the in plane component of the magnetisation, in this case to the projected magnetisation into the (1 0 0) plane. The projection coupling of magnetic moments can be decomposed into two independent contributions: a net ferromagnetic coupling along the bisecting line of two moments and a net antiferromagnetic one perpendicular to this direction. The magnetisation measured along the bisecting line of two moments (Fig. 6(a)) is sensitive only to the net ferromagnetic component (the antiferromagnetic one is perpendicular to the direction

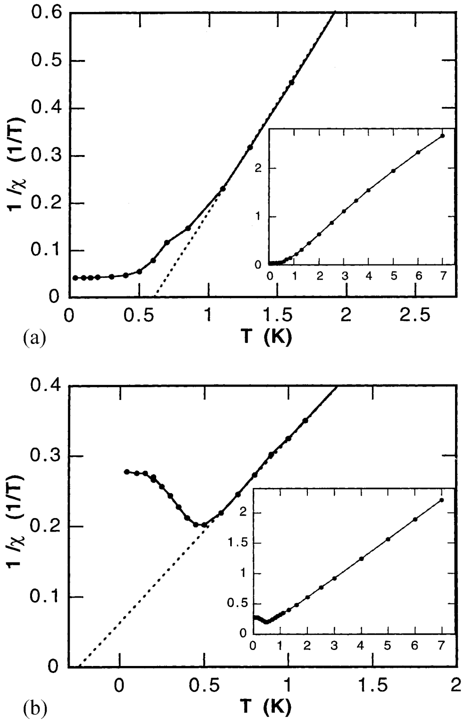


Fig. 4. Temperature dependence of the magnetic susceptibility in the two orthogonal directions of Fig. 3. The dashed lines represent the fit with a Curie–Weiss law. Parallel to the easy axis (a), a positive Curie–Weiss constant is observed, (+0.6 K, ferromagnetic coupling). Perpendicular to the easy axis (b) the Curie–Weiss constant is negative (−0.25 K, antiferromagnetic coupling).

of magnetic field, that is insensitive to field variation). The two moments are reversed at the same time near zero field.

Perpendicular to the bisecting line (Fig. 6(c)) only the net antiferromagnetic component of the couple is sensitive to the magnetic field. When the field increases (respectively decreases), one of the spins flips in order to align the couple with the maximum of the ferromagnetic component parallel to the field.

For any other orientation, the behaviour is a mixture of the two limiting cases. At zero-field we recover the projection of the ferromagnetic component of the couple on the field direction. When the field increases one of magnetic moment flips and the couple changes; the ferromagnetic projections on the field direction increase.

Measured in similar conditions, compounds **1*** and **3** shows the same behaviour (Fig. 7). The field amplitude of the antiferromagnetic plateau for compound **1*** is lower than for compound **1** and higher than for compound **3** in good agreement with the estimation of exchange interaction constant and with the fact that the molecules are closer in compound **1** than in compound **3**. This points out the necessity to use bulkier ligands to reduce the intermolecular interaction.

Other studies are in progress to better understand the correlation between the crystallographic structure and the magnetic behaviour in other directions of space.

4. Conclusions

The two different orientations of molecules in the crystals together with the intermolecular exchange interactions make $CrNi_2$ a model system for canted ferromagnetic structures. It is established that the

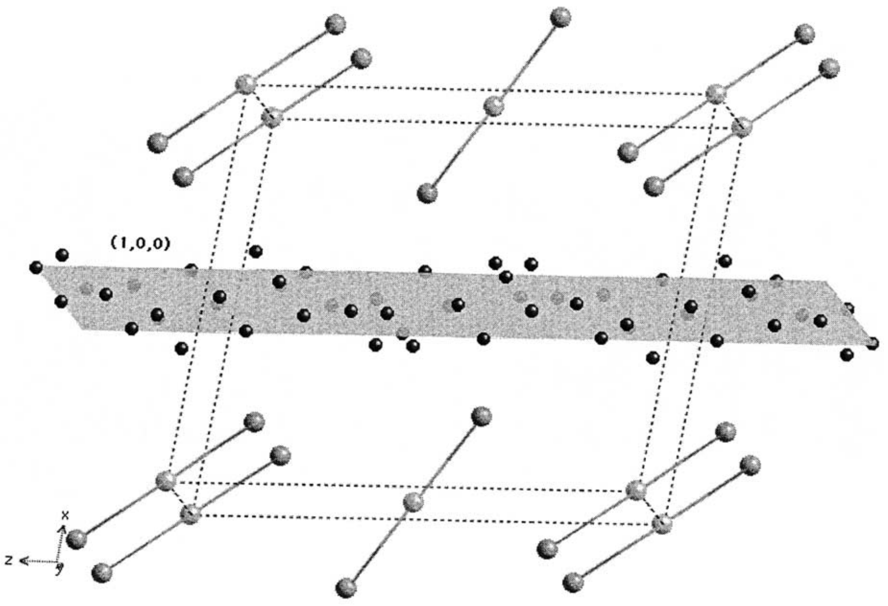


Fig. 5. Schematic perspective view of compound **1**. The molecules are represented by a straight-line nickel–chromium–nickel. Ligands are removed for clarity. There are two different orientations of the molecules. The angle between the two directions is 64°; the angle between each direction and the (1 0 0) plane is 36°.

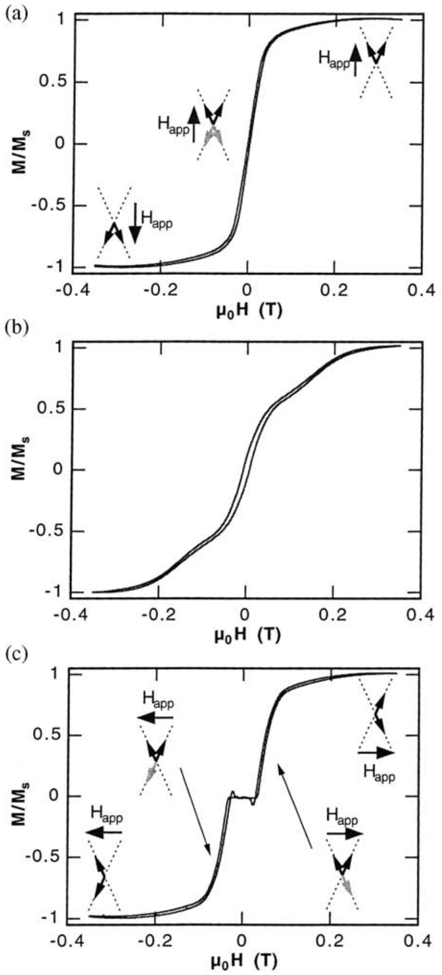


Fig. 6. Hysteresis loops for different orientations of the field in **1**: (a) parallel to the easy axis; (b) parallel to an intermediate axis; (c) parallel to the hard axis. The temperature is 0.05 K. The insert depicts the orientations of the molecular moments relative to the applied field H_{app}. The easy axis correspond to the bisecting line of two in plane moments (a). Perpendicular to this direction, only the net antiferromagnetic component of the coupling is sensitive to the field variation (c). For intermediate orientations (b), the behaviour is a mixture of the two limiting cases.

intermolecular coupling is sensitive to small variations of the structure such as the crystal symmetry or the steric hindrance of the terminal ligand. Our study allows to better understanding the synthetic parameters that have to be tuned in order to minimise intermolecular exchange interactions, necessary condition to get SMMs. The ligand, as well as the counter anions has to be as bulky as possible. To isolate the high spin molecules, it is also conceivable to dilute the molecules in a diamagnetic or a paramagnetic matrix. Preliminary results performed on the $CrNi_2$(tetren) compound co-crystallised in presence of $CoNi_2$(tetren) complex, viewed as an ordered paramagnetic medium indicate the validity of such a strategy, which is beyond the scope of the present communication.

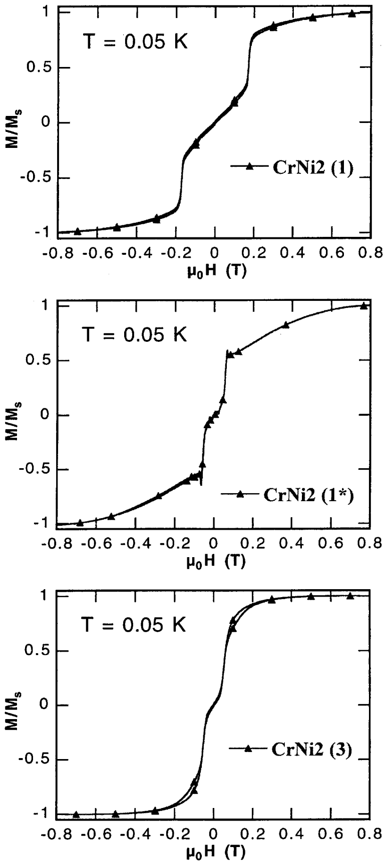


Fig. 7. Hysteresis loops for the three samples **1**, **1*** and **3**, with the magnetic field applied along the hard axis. The temperature is 0.05 K. All the samples present the same behaviour. The field amplitude of the antiferromagnetic plateau for compound **1*** is lower than for compound **1** and higher than for compound **3** in agreement with the estimation of exchange interaction coupling.

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