Magnetisation inverted hysteresis loops in the molecular magnets [M(Cp*)₂][Ni(α-tpdt)₂] (M = Fe, Mn)

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The low temperature magnetic properties of the compounds belonging to the family [M(Cp*)₂][Ni(α-tpdt)₂], where M = Fe (**1**), Mn (**2**) and Cr (**3**) (α-tpdt = 2,3-thiophenedithiolate) are studied, with emphasis on the magnetisation curves. These compounds share a common structure, composed of alternating layers, each consisting of mixed parallel D⁺A⁻D⁺A⁻D⁺A⁻ chains; the chains of adjacent layers being perpendicular. At low temperatures, a rather unusual inverted hysteresis loop with negative remanence is observed in **1**, and a similar reversed hysteresis is also detected in the magnetic field induced transition of **2**. This effect is associated with the layered structure of these compounds, together with the considerable magnetic anisotropy of the [Fe(Cp*)₂]⁺ and [Mn(Cp*)₂]⁺ donors, being to the best of our knowledge, the first time such inverted hysteresis loops are observed in a bulk molecule based material.

1. Introduction

During the past two decades molecular magnetism has experienced significant advancements, and molecular materials have been able not only to display the different type of magnetic behaviours initially identified in simpler solids including ferromagnetism, but they have also been able to provide examples of materials exhibiting novel magnetic phenomena. Examples include, magnetic hysteresis at the molecular level, quantum effects in the dynamics of the macroscopic magnetisation, photoswitchable magnetism, and multifunctionality combining electrical conduction and bulk ferromagnetism confined in different sub-lattices and in mutual interactions.[1] All these advances rely on an increasingly more detailed knowledge of structure properties, and a more precise control of the molecular and crystalline structure offered by contemporary molecular chemistry and nanosciences.

One unusual magnetic behaviour, so far essentially restricted to some sputtered bilayer[2] and multilayer thin films,[3] and a few alloy bulk materials,[4] is the appearance of inverted hysteresis loops in the magnetisation cycles with negative remanence. In this paper we describe, what to the best of our knowledge are, the first examples of molecule based materials with such type of inverted hysteresis loops and negative remanence, due to a combination of anisotropic interactions and single ion magnetic anisotropy, with a peculiar molecular layered structure (Scheme 1).

A molecular protagonist of such behaviour is [Ni(α-tpdt)₂]⁻ (α-tpdt = 2,3-thiophenedithiolate) which belongs to a family of new transition metal bis(dithiolene) complexes with extended
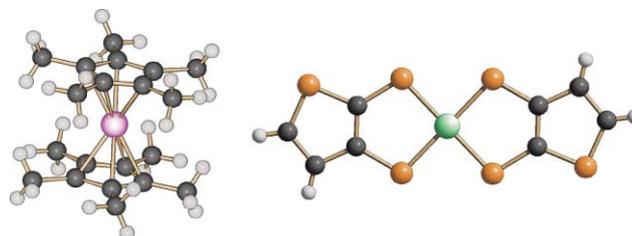
Scheme 1 [Fe(Cp*)₂][Ni(α-tpdt)₂].

conjugated ligands, based on thiophenedithiolate ligands that we have explored in the last few years.[5–8] It is an anionic paramagnetic $S = 1/2$ complex, early recognised as a suitable building block to obtain new molecular magnetic materials and that has been combined among other cations[6,7,9] with the $S = 1/2$ [Fe(Cp*)₂]⁺ donor, thus forming [Fe(Cp*)₂][Ni(α-tpdt)₂] (**1**).[6] This salt presents a peculiar structure consisting of alternating layers, each composed of parallel D⁺A⁻D⁺A⁻ chains, where the chains in adjacent layers are nearly perpendicular. It was found to display an interesting metamagnetic behaviour below 2.5 K with a critical field of *ca.* 600 G at 2 K.[6] More recently the analogous salts with other metallocenium cations with different magnetic moments and magnetic anisotropy, such as [M(Cp*)₂]⁺ with M = Mn ($S = 1$) (**2**), and Cr ($S = 3/2$) (**3**) have also been studied.[9] Compound **2**, based on a strong anisotropic cation, is a frustrated magnet while **3**, based on a isotropic cation remains paramagnetic down to 1.5 K.

In this paper we report a more detailed characterisation of the magnetic behaviour of these compounds presenting a similar crystal structure, with emphasis on the low temperature magnetic properties, showing that they are the first examples of bulk molecule based materials exhibiting inverted hysteresis behaviour in the magnetisation.

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2. Experimental

Samples of [M(Cp*)$_2$][Ni(α-tpdt)$_2$], with M = Fe (**1**), Mn (**2**), Cr (**3**), were obtained following previously described procedures.[6,9] Special care was employed to guarantee sample purity. Since **2** and **3** are unstable when exposed to air, and even as solids tend to decompose after longer periods of time, magnetic measurements were performed in freshly prepared polycrystalline samples, using a combination of different instruments; a SQUID magnetometer (Quantum Design MPS), with a 55 kG superconducting magnet in the range 1.8–300 K and a Maglab 2000 system (Oxford Instruments), for DC magnetisation and AC susceptibility under fields of up to 120 kG down to a lower temperature limit of 1.5 K. The Maglab 2000 system was used for magnetisation measurements of polycrystalline samples (in previously measured gelatin capsules) at different magnetic fields using an extraction technique and for AC susceptibility measurements using a typical AC field of 1 G. The SQUID magnetometer was used particularly to measure the magnetisation temperature dependence at low fields (1–200 G).
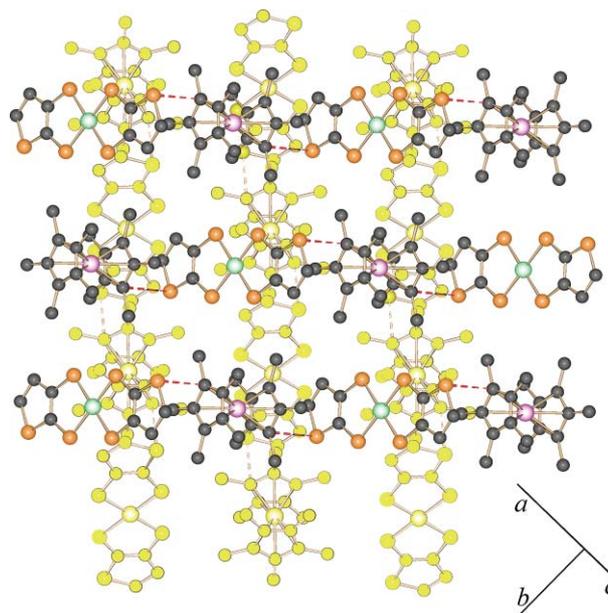
3. Crystal structure

The small crystal size of **2** and its poor quality precluded so far a structural refinement, but X-ray powder diffraction data indicate that, as expected in view of similar molecular composition, compounds **2** and **3** are isostructural.[9] The structure of **1** is also identical and almost isostructural to **3**, with just a lattice doubling that is related with a very slight alternation in the AA and DA contacts.[9] In this context it is useful to review the crystal structure of **1** that consists of alternated layers, each one composed by an out of registry arrangement of parallel mixed donor acceptor chains, $\cdots$D$^+$A$^-$D$^+$A$^-$D$^+$A$^-\cdots$. In this multilayer structure, consecutive layers are rotated by 90° so that chains in adjacent layers are perpendicular, alternatively aligned either along the [0,2,−1] direction (A layers), or along the [0,2,1] direction (B layers), as illustrated in Fig. 1, where a view of the crystal structure of **1** along the [2,0,1] direction is shown. In Fig. 1 it is possible to observe two adjacent layers, where part of an A layer (with dark atoms and bonds) is in front and part of a B layer (with lighter atoms and bonds) is in the back.

Short contacts between the Cp and the thiophenic rings were observed in the mixed DA chains. Besides those, slightly longer additional contacts were detected between chains within the layers (DA) as well as involving chains in adjacent layers (AA). As mentioned before in this compound there is a slight alternation of DA and AA contacts, not seen in **3**, associated to the doubling of the lattice parameters.[9]

4. Magnetic properties

As previously reported[6] and further explained in detail in a recent analysis[9] the magnetic properties of **1** are dominated by a competition of FM intrachain and AF interchain interactions and this compound presents an antiferromagnetic transition with a Néel temperature of 2.5 K. Below this temperature a metamagnetic behaviour with a critical field of ~700 G at 1.5 K is observed. The metamagnetism of this compound results from the coexistence of

Fig. 1 View of the crystal structure of **1** along [2,0,1]. Two adjacent layers with perpendicular chains are shown. For clarity the H atoms were omitted.

strong DA FM intrachain coupling and weaker AF interchain interactions within the layers.[9]

The temperature–magnetic field (*T*, *H*) phase diagram of compound **1** was subject to a careful re-investigation by a combination of AC susceptibility and DC magnetisation measurements as a function of temperature and magnetic field. The results are summarised in Fig. 2 revealing, in comparison with previous studies, an additional intermediate phase (I) between the low temperature–low magnetic field AF phase and the low temperature–high field aligned paramagnetic region (FAP). This field aligned paramagnetic region appears separated from the high temperature paramagnetic phase (P) by an unclear boundary, dashed line in Fig. 2, denoted by broad peaks in AC susceptibility, which however cannot be clearly ascribed to a real phase transition.
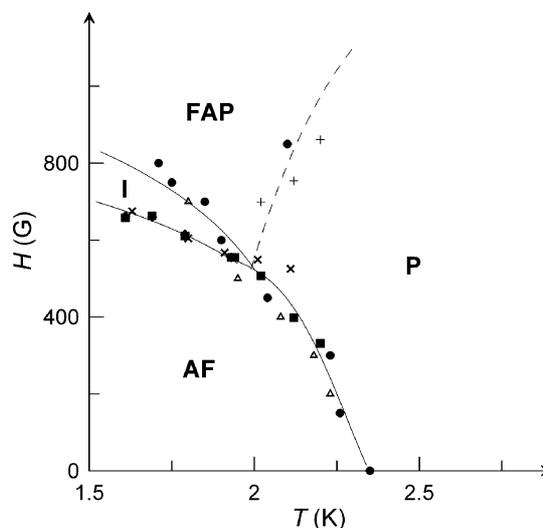

Fig. 2 Phase diagram of compound **1**. Boundaries detected by different measurements: *M*(*T*) (△); *M*(*H*) (×); χ(*T*) (●) and χ''(*H*)(■ and +).

The most striking feature of this compound at low temperatures was revealed by a close inspection of the magnetisation isothermals showing a rather unusual behaviour as shown in Fig. 3; the hysteresis loops display a partially inverted behaviour with a crossover between the increasing and decreasing field curves at ~1 kG and a negative coercivity in the field induced transition region (~0.65 kG). For this hysteresis loop (H between 0 and 3 kG) the coercivity in the field induced transition is of the order of −20 G. However the coercivity increases significantly with higher applied magnetic fields as seen in the inset of Fig. 3, where the detail of a loop between −10 and 10 kG is shown, revealing a coercivity of the order of −100 G. Furthermore the hysteresis was found to decrease slightly with increasing temperatures and it increases with the sweeping rate of the applied magnetic field. As imposed by thermodynamic considerations the inverted hysteresis loop area is compensated by a larger area of normal hysteresis at larger field amplitude (above 1 kG). This negative coercivity is unprecedented among metamagnets and to the best of our knowledge it was observed for the first time in this compound. The inverted coercivity decreases drastically with the value of the inversion of the applied magnetic field and it also decreases with increasing temperatures. The origin of this effect is not clear, although it seems reasonable to suggest that it must be related to the inversion of the spins of the donors, which exhibit a considerable magnetic anisotropy, with the applied magnetic field and to the AF coupling between neighbouring layers.
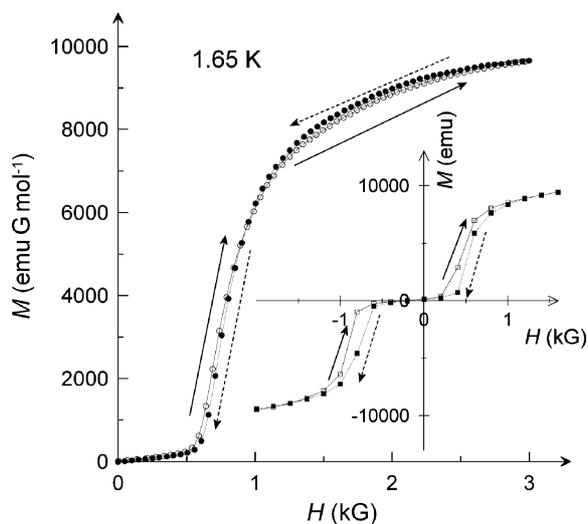
Fig. 3 Magnetisation hysteresis loop (1.65 K) of compound **1** obtained between 0 and 3 kG. The inset shows a detail from a similar loop obtained between −10 and 10 kG.

In this regard it is of obvious interest to compare the magnetic behaviour of this compound with that of **2**. Unlike **1** compound **2** does not display any signs of AF ordering down to 1.5 K. The FC and ZFC magnetisation temperature dependencies of **2**, measured with a 100 G applied field, are shown in Fig. 4. Both FC and ZFC measurements show a similar behaviour, with magnetisation increasing regularly upon cooling. However, at low temperatures ($T < 4$ K), small differences between the FC and the ZFC magnetisation measurements ($\Delta M = M^{FC} - M^{ZFC}$) were detected depending on the applied field; from 1.6 to 2 K, M^{FC} is slightly larger than M^{ZFC}; at *ca.* 2 K a crossover between the two curves
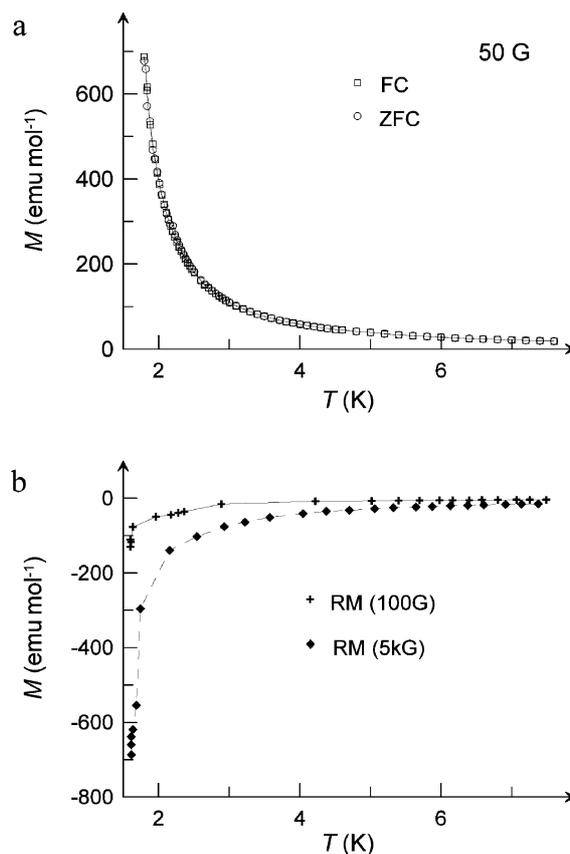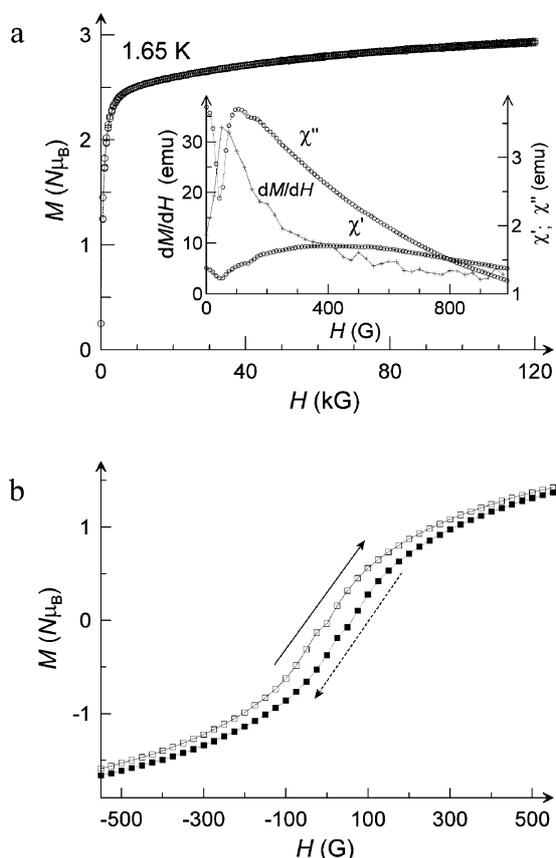

Fig. 4 (a) Temperature dependence of M^{ZFC} (◯), M^{FC} (▢) with $H = 50$ G for compound **2**. The inset shows the temperature dependence of $\Delta M = M^{FC} - M^{ZFC}$. (b) Temperature dependence of RM of **2** for $H = 100$ G (+) and 5 kG (◆).

is observed; above 2 K M^{ZFC} becomes slightly larger than M^{FC}; at *ca.* 4 K this difference seems to vanish and for higher temperatures the two curves are superposed. The difference between M^{FC} and M^{ZFC} in the range 2–4 K can be very small as in the case shown in Fig. 4(a) for measurements under a field of 50 G and becomes more significant under larger fields. In all cases this difference between M^{FC} and M^{ZFC} vanishes above 4 K, the two curves becoming superimposed. This slight difference between M^{FC} and M^{ZFC} was consistently observed in measurements with low applied magnetic fields, from 5 G to 300 G. However for higher fields it was no longer detected.

The temperature dependence of the remnant magnetisation (RM) with an applied field of 100 G is shown in Fig. 4. RM is negative and increases upon warming. This increase is quite drastic at $T < 1.85$ K, then it increases more slowly, gradually approaching zero. At *ca.* 4 K the obtained RM value is zero within the error margin of the measurement. The RM obtained after application of a 5 kG field, also shown in Fig. 4, displays a similar temperature dependence with large absolute values. In agreement with previous findings[9] the present results of the magnetisation temperature dependence in compound **2** suggests the existence of an "ordering process" occurring at *ca.* 3–4 K. AC susceptibility measurements revealed that this process corresponds to a spin-freezing, and, at low temperatures, this compound behaves as a frustrated magnet.[9]

At variance with compound **1**, no clear metamagnetic behaviour was detected in **2** which does not display any AF ordering. The isothermal magnetisation curve obtained at 1.65 K for **2**, is shown in Fig. 5. At low applied magnetic fields ($H < 1$ kG), the magnetisation increases drastically and much faster than the predicted by the Brillouin function. For high fields ($H > 10$ kG) the magnetisation increase is much more gradual and it does not saturate up to 120 kG, where it attains a value of the order of $3 N\mu_B$, still smaller than the calculated saturation magnetisation, $3.3 N\mu_B$, for $S_A = 1/2$, $S_D = 1$, $g_A = 2.06$[6] and $g_D = 2.2$.[10] At very low fields (<100 G) the magnetisation isothermal ($T = 1.65$ K) shows a weak sigmoidal-like anomaly suggesting the existence of a field induced phase transition, occurring at 85 G as indicated by the maximum in dM/dH, shown in the inset of Fig. 5(a). The AC susceptibility field dependence, at this temperature, exhibits a rather complex behaviour, where the real component, χ', shows, besides a minimum at 55 G, a shoulder at *ca.* 100 G and a broad maximum at 420 G, while the imaginary component, χ'', besides the corresponding minimum at 45 G, presents a clear maximum at 105 G. These results indicate the existence of at least two field induced transitions, which must correspond to gradual processes as suggested by the behaviour of the AC susceptibility.

In view of the magnetic anisotropy of **2** those transitions must be strongly dependent on the field direction, and the broad character of the AC susceptibility peaks may result from the random orientation of the polycrystalline sample. This absence of a clear

metamagnetic behaviour in **2**, at variance with compound **1**, can be attributed to a significant decrease of the AF interchain intralayer coupling or to a change in the nature of the interchain magnetic coupling.[9]

Most relevant is the fact that, as in the field induced transition observed in compound **1**, a similar inverted hysteresis loop was observed in **2**, as illustrated in Fig. 5(b) showing a detail of a cycle between -500 and 500 G. Although not shown in this figure the larger amplitude regions of the magnetisation cycle display the normal hysteresis behaviour with an area larger than the inverted portion of the cycle. The inverted coercivity at 1.65 K is of the order of -30 G.

These uncommon reversed hysteresis loops, contrasting with the ones of conventional ferromagnets, in which the magnetisation turns positive even though the applied field maintains negative and *vice versa*, have been observed in several sputtered bilayer[2] and multilayer films.[3] However, in these materials the thin film structure seems to play a crucial role in the origin of the inverted hysteresis loops. More recently this phenomena was also reported for some bulk magnetic materials, such as the alloys $Sm^{III}_x Gd^{III}_{1-x}[Cr^{III}(CN)_6]\cdot H_2O$ ($x \approx 0.5$),[4a] and $Fe_{1-x}Co_xSi$ ($x \approx 0.1$–0.45).[4b] While for the first alloy compound the negative coercivity was attributed to the competition effect between the spin-flip transition and the uniaxial magnetic anisotropy, no clear explanation was reported concerning the negative hysteresis observed in the case of the second compound. In spite of the differences in these materials they share as a common feature, the existence of field induced transitions, in similitude with **1** and **2**. At this point it is not possible to suggest a detailed microscopic model for the origin of the inverted hysteresis loops observed in salts **1** and **2**. However the unique layered supramolecular arrangement together with the lattice magnetic anisotropy (FM intrachain coupling and AF interlayer coupling) and the magnetic anisotropy of the donors, leading to a magnetic multilayer structure with competing uniaxial anisotropies between the adjacent layers, are expected to be crucial ingredients of that uncommon effect.

Finally it should be mentioned that compound **3** was also subject to a careful re-investigation of the low temperature magnetisation behaviour. In this compound the $Cr(Cp^*)_2$ cation presents a larger spin ($S = 3/2$) but its single ion anisotropy is negligible. In spite of the structural similarities and probably as a consequence of this lack of anisotropy and due to weaker interactions, this analogue remains paramagnetic down to the lowest temperatures measured (1.5 K).

Conclusions

In conclusion the molecule based compounds $[M(Cp^*)_2][Ni(\alpha\text{-}tpdt)_2]$ with M = Fe, Mn were found to display an unusual magnetic behaviour with reverted hysteresis loops, previously seen only in some rare cases of inorganic layered and alloy systems. These findings open the way to new possibilities yet unexplored in the crystal engineering of molecular magnetic materials. The possibility of these molecule based compounds to mimic this rare behaviour of simple inorganic layered and alloy systems, is due to a unique combination of a layered structure with single ion anisotropy and anisotropic intermolecular magnetic interactions.

Fig. 5 (a) Magnetisation field dependence, at 1.65 K, for **2**. The inset shows the temperature dependence of dM/dH, χ' and χ''. (b) Detail of the inverted hysteresis loop.

Acknowledgements

Notes and references

1 For a general overview see for instance: (a) π-*Electron Magnetism. From molecules to magnetic materials*, ed. J. Veciana, Springer Verlag, 2001; (b) *Magnetism: Molecules to Materials*, ed. J. S. Miller and M. Drillon, Wiley VCH, vol. 1–5, 2005; (c) M. Almeida and M. Andruh, *Inorg. Chim. Acta*, **360**, 3785–3786. Special issue on the First European Conference on Molecular Magnetism (ECMM).

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