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Cluster glass-like behavior in a 2D bimetallic molecule-based magnet

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Abstract

The compound of formula $Na_2[Co_2\{Cu(opba)\}_3]\cdot 2DMSO\cdot 6H_2O$ has been synthesized where opba stands for *ortho*-phenylenebis(oxamato) and DMSO is dimethylsulfoxide. Magnetic properties have been investigated in the 2–300 K temperature range. The compound presents a large coercive field, around 3.5 kOe at 4.2 K, and the A.C. susceptibility measurements has revealed a cluster glass-like behavior.

Keywords: Molecule-based magnet; Magnetic properties; Cobalt; Cluster glass

1. Introduction

With the discovery of magnetic order in molecule-based compounds [1,2] considerable efforts are being directed towards understanding the nature of magnetic interactions, the magnetic dimensionality of the spin system and/or the possible occurrence of short range order and magnetic frustration. Dynamic magnetic measurements became an effective tool for elucidating aspects of short range magnetic order. This is due to the fact that the slow time dependence of the magnetization may be attributed to a typical behavior of superparamagnets, spin glasses and spins glass-like mictomagnetic systems or cluster glasses [3]. Usually these kind of systems are investigated by the use of complex susceptibility studies under a wide frequency range.

The dianionic Cu(II) precursor, $[Cu(opba)]^{2-}$, where opba stands for the ligand *ortho*-phenylenebis(oxamato), can be thought as a two-way connector linking two metal ions (Fig. 1). By using this building block, a high diversity of structures was obtained: chains [4], honeycomb planes and interlocked 3D compounds [5–7] with paramagnetic, metamagnetic, ferrimagnetic behavior, the later behaving as either soft or even very hard magnets [8]. These compounds may be obtained by reacting the dianionic precursor with a divalent metal ion by controlling the reaction stoichiometry. Therefore, the 1:1 stoichiometry favors the synthesis of unidimensional compounds. The excess of the precursor, on the other hand, promotes the synthesis of 2D systems as the series $[cat]_2[M_2\{Cu(opba)\}_3]\cdot S$. In this case, cat^+ is a monovalent cation which could be an alkali-metal such as Na^+, K^+; tetraalkylammonium (R_4N^+; R = Me, Et, Pr, Bu); or even an organic radical $(rad)^+$; and S stands for the solvent molecules as dimethylsulfoxide (DMSO), water or dimethylformamide (DMF). The first reported example of this series was the soft molecule-based-magnet $[Bu_4N]_2[Mn_2\{Cu(opba)\}_3]\cdot 6DMSO\cdot H_2O$ with $T_c = 15$ K [4]. When M = Co(II), a hard magnet is obtained ($H_C = 4$ kOe at 4.2 K) namely $[Bu_4N]_2[Co_2\{Cu(opba)\}_3]\cdot DMF\cdot H_2O$ [9]. Recently, EPR measurements on $[Bu_4N]_2[Mn_2\{Cu(opba)\}_3]\cdot 6DMSO\cdot H_2O$ compound gave evidence for the dynamic fluctuation of magnetic order in a wide temperature range around 15 K. Short range order or spin glass

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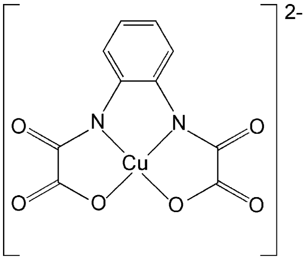


Fig. 1. Structure of the bisbidentate building block $[Cu(opba)]^{2-}$.

behavior were observed below 40 K, with the coexistence of a paramagnetic phase [10].

In this paper we report a detailed static and dynamic magnetic measurements in a compound of the same family, $Na_2[Co_2\{Cu(opba)\}_3]\cdot 2DMSO\cdot 6H_2O$ ($Na_2Co_2Cu_3$), which shows additional indications of the cluster glass state.

2. Experimental

2.1. Synthesis

All the reagents used for the sample preparation were of analytical grade. The ligand opba and the sodium salt of the copper(II) precursor $Na_2[Cu(opba)]\cdot 3H_2O$ were prepared as described elsewhere [4]. The molecule-based magnet $Na_2[Co_2\{Cu(opba)\}_3]\cdot 2DMSO\cdot 6H_2O$ was prepared by adding 80 mg of $Co(NO_3)_2\cdot 6H_2O$ (0.27 mmol) previously dissolved in 20 ml of DMSO to a solution of 200 mg (0.49 mmol) of $Na_2[Cu(opba)]\cdot H_2O$ in DMSO under stirring. The well-shaped small crystals obtained after ten days were collected by filtration, washed with DMSO and dried in a dessicator. Yield: 105 mg (29%). Elemental analyses calculated (%) for $C_{34}H_{36}N_6O_{26}S_2Cu_3Co_2$: C, 29.95; H, 2.64; N, 6.16; S, 4.71; Cu, 13.98; Co, 8.65. Found: C, 28.30; H, 2.69; N, 5.96; S, 5.12; Cu, 13.23; Co, 8.38. IR (KBr): $\bar{\nu} = 3410$ (O–H), 3026, 2921, 2910 (C–H), 1589, 1575 (C=O), 1030 (S=O) cm^{-1}.

2.2. Physical techniques

IR spectra were recorded on a Perkin Elmer 882 spectrophotometer as KBr pellets. X-ray powder diffraction patterns were obtained using a Rigaku–Geigerflex diffractometer at room temperature (r.t.). Data were collected in the Bragg–Bretano mode and monochromatic Cu Kα radiation was used. The A.C. magnetic properties have been studied in a commercial A.C. susceptometer/magnetometer Lake Shore 7020 and the D.C. measurements were performed in Quantum Design SQUID MPMS XL7 instrument. The diamagnetism of the sample and sample holder were taken into account.

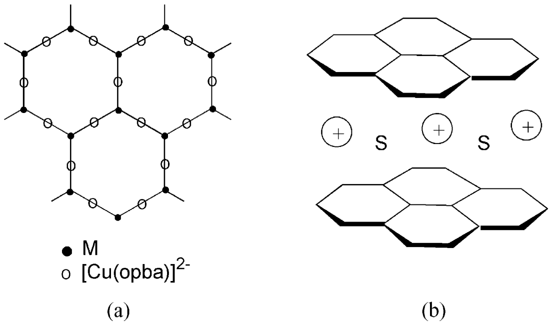
3. Results and discussion

In comparison with the chemistry and physics of the $[cat]_2[M_2\{Cu(opba)\}_3]$ series, the expected structure of $Na_2Co_2Cu_3$ is that shown in Fig. 2(a), consisting of a 2D network with edge-sharing M_6Cu_6 hexagons; the M(II) ions are in distorted octahedral positions at the corners and the Cu(II) ions are in elongated tetragonal positions at the middle of each edge.

The X-ray powder diffraction pattern is very similar to other compounds of the $[cat]_2[M_2\{Cu(opba)\}_3]$ family [11,12]. The most relevant feature is the occurrence of two very strong diffraction peaks corresponding to interplanar spacing of 8.5 Å and another of 7.7 Å. These peaks could be assigned to the separation between adjacent anionic 2D Co_2Cu_3 layers. The cations and solvent molecules act as spacers of the sheets (Fig. 2(b)). The comparison with other compounds of the same family with cat^+ as R_4N^+ (R = Me, Et, Pr, Bu) and PPh_4N^+ shows that $Na_2Co_2Cu_3$ has the smallest interlayer distances, as expected for the smaller cation used [11–13].

The magnetic properties of $Na_2Co_2Cu_3$ have been investigated in the 2–300 K temperature range using polycrystalline powder. The temperature dependence of the field cooled magnetization was measured under a magnetic field of 50 Oe (Fig. 3). The molar magnetization displays an abrupt increase around 30 K and this behavior is attributed to the occurrence of short range ferrimagnetic order within each plane [14].

The temperature dependence of the magnetic susceptibility is shown in the inset of Fig. 3 in the form of the $\chi_M T$ versus T plot. At r.t. $\chi_M T$ is 6.0 emu K mol^{-1}, which is slightly below what would be anticipated for two Co(II) and three Cu(II) uncoupled ions ($\chi_M T = 6.1$ emu K mol^{-1}) [2]. The decrease of $\chi_M T$ down to the minimum around 85 K ($\chi_M T = 3.7$ emu K mol^{-1}) is typical of strong AF coupling between Cu(II) and Co(II) ions bridged by oxamato ligands of the order of $J_{Cu-Co} \approx -18$ cm^{-1} [15]. When the sample is further cooled down $\chi_M T$ increases due to short range order



(a) (b)

Fig. 2. (a) View of the plane $[cat]_2[M_2\{Cu(opba)\}_3]$ showing the edge-sharing M_6Cu_6 hexagons; (b) packing of the planes where S stands for solvents molecules and the positives charges, cat^+.

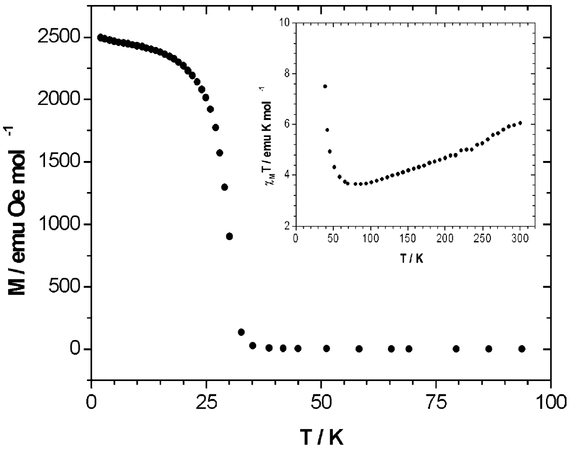


Fig. 3. Molar magnetization versus temperature curve within a field of 50 Oe. Inset: $\chi_M T$ versus T for $H = 50$ Oe.

settling within the honeycomb planes. This would lead, in principle, to a long range ferrimagnetic order at absolute zero in the absence of interlayer interaction.

The magnetization hysteresis loop was also measured at 4.2 K (Fig. 4). The coercive field of the $Na_2Co_2Cu_3$ is characteristic of a hard magnet achieving values up to 3.5 kOe at 4.2 K. Note that the initial magnetization has a rather small slope up to 950 Oe, indicating a weak AF coupling between the planes. The magnetization does not saturate even for fields as high as 65 kOe, where it reaches a value of 1.2 Bohr magnetons per mole (Nβ).

The A.C. susceptibility data presented in Fig. 5 show that this compound has a strong frequency dependence typical of glassy behavior. The value of the relative variation of the peak temperature (T_f) per decade of frequency (f), $\Delta T_f/(T_f \Delta \log f)$ is 0.015, strongly suggesting a cluster glass-like behavior [16]. A tentative trial to fit the temperature dependence of the relaxation time from the maxima of $\chi''(T)$ by an Arrhenius law leads to a totally unphysical attempt frequency ($f_0 \sim 10^{80}$ Hz) and an apparent energy barrier $\Delta E/k_B \sim 5 \times 10^3$ K. The coercive field values are also in agreement with this large energy barrier. This cluster glass behavior, also similar to a short range spin glass or even an interacting superparamagnetic system, appears often in low dimensional molecule-based magnets. In our case the clusters are most probably originated from the randomly nucleated short range ordered magnetic plaquettes in the different honeycomb layers. These plaquettes tend to grow in size as the temperature is lowered, but this growth is inhibited by the large effective anisotropy and become blocked, leading to the observed frequency dependence of the susceptibility.

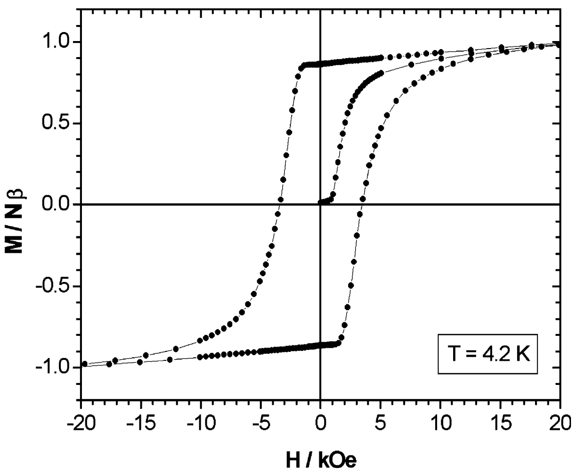
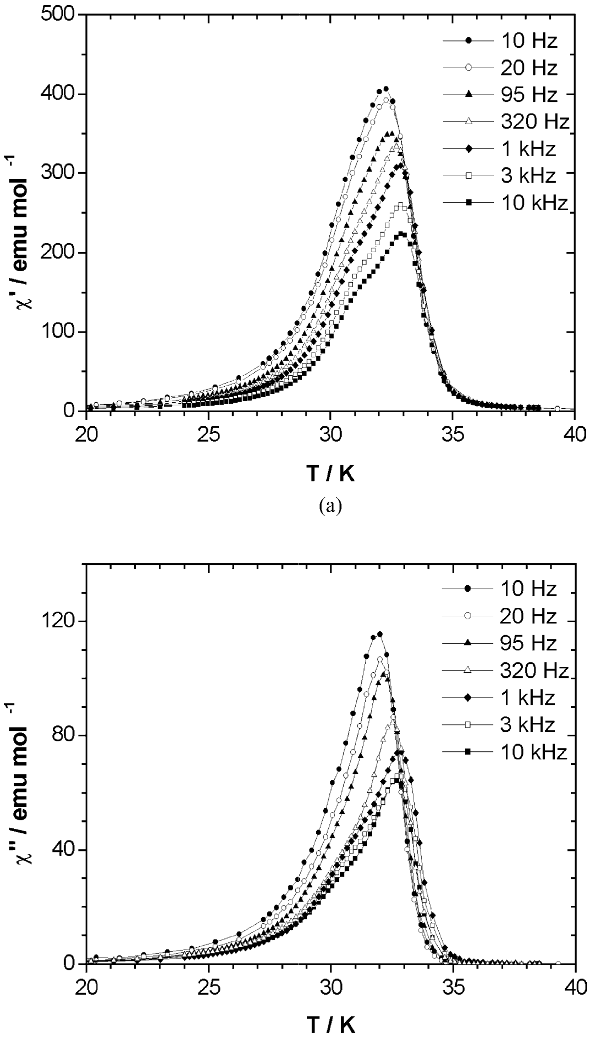


Fig. 4. Hysteresis loop at 4.2 K. The solid lines joining the experimental points are just eye guides.



(a)

(b)

Fig. 5. The real (top) and imaginary (bottom) components of the A.C. magnetic susceptibility at frequencies between 10 and 10 kHz, in A.C. field of 1 Oe. The solid lines joining the experimental points are just eye guides.

Small variations of solvent molecule content may increase the disorder and randomness of the magnetic moments of the plaquettes in the sample, acting as domains. The increase of the magnetic field imposes an order to the domains in the same direction, leading to a hysteretic behavior with a large coercive field typical of an ordered ferro- or ferri-magnet with large anisotropy.

4. Conclusions

The results presented give further support for the cluster glass behavior in the 2D bimetallic molecule-based magnet. The short range magnetic order observed is probably due to the presence of structural disorder which would lead to competing interactions with some degree of frustration. The frequency dependence of the A.C. susceptibility and the irreversible behavior of the D.C. magnetization indicate a slow relaxation processes characteristic of a cluster glass-like behavior.

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