Available online at www.sciencedirect.com
ScienceDirect
Polyhedron 26 (2007) 1838–1844
POLYHEDRON
www.elsevier.com/locate/poly

Spin crossover Fe^{II} complexes as templates for bimetallic oxalate-based 3D magnets

Eugenio Coronado [a,*], José R. Galán Mascarós [a,*], Mari Carmen Giménez-López [a], Manuel Almeida [b], João C. Waerenborgh [b]

[a] *Instituto de Ciencia Molecular, Universidad de Valencia, Polígono de la Coma, s/n, E-46980 Paterna, Spain*
[b] *Dept. Quimica, ITN/CFMC-UL, P-2686-953 Sacavém, Portugal*

Received 4 September 2006; accepted 19 September 2006
Available online 29 September 2006

Abstract

We present the synthesis and structural characterization of the salt $[Fe(bpp)_2][MnCr(ox)_3]_2 \cdot bpp \cdot CH_3OH$. It crystallizes in the monoclinic space group. This material contains an anionic $[MnCr(ox)_3]^-$ 3D 10-gon ferromagnetic network, that orders below 3.0 K. The channels created by this architecture are filled by the spin crossover cations $[Fe(bpp)_2]^{2+}$ (bpp = 2,6(bispyrazol-3-yl)pyridine), free ligand and solvent molecules. No spin transition has been observed at ambient pressure.

Keywords: Coordination chemistry; Molecular materials; Spin crossover; Magnetic properties; Mössbauer spectroscopy

1. Introduction

The families of molecule-based magnets built from polymeric bimetallic oxalate complexes represent one of the most explored series in the search for molecule-based magnets. One of the key reasons is the synthetic control reached over the lattice dimensionality. Indeed, bimetallic dimers [1], trimers [2], tetramers [3], 1D chains [4], and extended 2D [5,6] and 3D lattices [7,8] have been reported from essentially the same building blocks, where the counterion and synthetic conditions dictate the formation of a given oxalate-bridged structure. Magnetic ordering has been observed in dimensionalities 1 or higher.

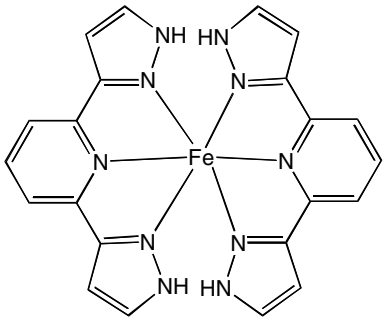
Ferromagnetic bimetallic anionic chains $[K(18\text{-crown-6})][Mn(H_2O)_2Cr(ox)_3]$ are formed in the presence of flat monocationic complexes of alkali metals with crown-ether ligands [4]. Ferromagnetic interchain interactions yield ferromagnetic ordering below 3.5 K, due to the short proximity between these chains in the solid state, where they appear related by hydrogen bonding. These same cations, in different synthetic conditions, can also yield anionic 2D networks $[K(18\text{-crown-6})]_3[Mn_3(H_2O)_4\{Cr(ox)_3\}_3]$ where the presence of water molecules as ligands induces the formation of a distorted honeycomb network [9]. The onset of ferromagnetic ordering is observed below 4 K.

The formation of anionic 2D hexagonal networks of formula $[M^{II}M^{III}(ox)_3]^-$ (M^{II} = Mn, Fe, Co, Ni, Cu; M^{III} = Cr, Fe, Ru, Rh) [5,10,11] is promoted by the use of bulky organic monocations of the tetraalkylammonium type. In these layers, where only oxalate ligands are present to achieve maximum magnetic connectivity, the metal centers show alternating chirality. Ferro- or ferrimagnetic ordering with critical temperatures up to 44 K and coercive fields over 2 T, have been reported in this series.

Chiral octahedral trischelated complexes, on the other hand, promote the formation of homochiral 3D anionic networks of the same formula, with critical temperatures much lower than those of their 2D counterparts [12]. This has been related to the weaker magnetic interactions present in this case promoted by a different relative orientation

* Corresponding author. Tel.: +34 963544420; fax: +34 963543273.
E-mail addresses: eugenio.coronado@uv.es (E. Coronado), jose.r.galan@uv.es (J.R. Galán Mascarós).

0277-5387/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2006.09.064



Scheme 1.

of the magnetic orbitals and to larger metal to metal distances. Most of these compounds show Tc's below 3 K, with few exceptions reaching up to 6 K.

The use of "electroactive" cations, instead of the electronically "innocent" ones in the formation of such anionic networks has been one of the most successful approaches to multifunctional materials, where unprecedented multifunctional magnets have been obtained, such as ferromagnetic molecular metals [13,14], chemically-built magnetic multilayers [15], photoactive magnets [16], or chiral magnets [7,8,17]. Most of these examples are built from the hexagonal 2D honeycomb $[M^{II}M^{III}(ox)_3]^-$ networks. The 3D analogs have been much less explored on this regard, probably due to the more synthetically strict conditions needed. Spin crossover complexes [18] and other cations with interesting photophysical properties [19] have been embedded into these 3D systems, but including diamagnetic alkali metals in the network, preventing the appearance of magnetic ordering.

We have been investigating for several years the possibility to use Fe^{II} complexes as templates for oxalate-based magnets. Until now, all our attempts yielded the highly insoluble salts $[A^I][Fe(L)_3][M^{III}(ox)_3]\cdot xH_2O$ (A = Li, Na, K, NH_4^+) [20]. These compounds exhibit indeed spin crossover behavior, but no magnetic ordering is observed, since the paramagnetic centers are isolated from one another in the structure. Here we report how the complex $[Fe(bpp)_2]^{2+}$ (Scheme 1); bpp = 2,6(bis(pyrazol-3-yl)pyridine) that exhibits spin crossover behavior in other simple salts [21] including the LIEST effect [22], is able to be used as cationic guest for bimetallic oxalate-based 3D magnets.

2. Experimental

2.1. Synthesis

All reagents were commercially available and used without further purification The precursor $Ag_3Cr(ox)_3\cdot 3H_2O$ was prepared by metathesis in water from $K_3Cr(ox)_3\cdot 3H_2O\cdot Ag_3Cr(ox)_3\cdot 3H_2O$ (0.098 g, 0.142 mmol) was suspended in 7.5 mL methanol, and then a solution of $MnCl_2\cdot 4H_2O$ (0.042 g, 0.213 mmol) in 7.5 mL methanol was added dropwise. The white AgCl precipitate formed was filtered, and the green solution was added to a red solution of $Fe(ClO_4)_2\cdot H_2O$ (0.090 g, 0.355 mmol) and bpp (0.149 g, 0.71 mmol) in 15 mL of hot MeOH. This solution was refluxed for 2 h. The yellowish precipitate formed was hot filtered, and washed with methanol and acetone. This powder was dissolved in DMF and crystals of $[Fe(bpp)_2][MnCr(ox)_3]_2\cdot bpp\cdot CH_3OH$ (1) were grown from layering this solution with acetone. Yield: 30%. IR (cm^{-1}): 3427, w; 3124, w; 2929, w; 1654, s; 1652, s; 1628, m; 1629, m; 1462, m; 1384, m; 1277, m; 906, w; 811, w; 669, s; 541, m; 478, m; 414, m. $Mn_2N_{15}O_{25}Cr_2FeC_{46}H_{31}$, $M_w = 1463.59$. Elemental *Anal.* Calc.: C, 37.75; H, 2.13; N 14.36. Found: C, 37.12; H, 2.45; N, 15.20%. Desolvation of the sample was carried out by heating the crystals in air at 125 °C for 6 h.

2.2. Structural characterization

A reddish prismatic single crystal of **1** was fixed on a glass fiber and mounted on a Kappa CCD diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Cell refinements and data reduction were performed at 150 K using the DENZO and SCALEPACK programs [23]. The structure was solved by direct methods using the SIR97 program [24] and refined on F^2 with the SHELXL-97 program [25]. All atoms belonging to the anionic network were located by successive Fourier transform routines, and refined anisotropically. The cations and solvent molecules, occupying the wholes left in the structure, could no be located due to the presence of severe crystallographic disorder. Two crystallographic independent positions for the Fe centers were found, with partial occupancy. Only the first coordination sphere of N atoms could be located. No good model for these complexes and solvent molecules, including the interstitial bpp moiety could be found due to heavy disorder. Crystal, data collection, and refinement parameters are summarized in Table 1.

Table 1
Crystallographic data and refinement parameters for $[Fe(bpp)_2][MnCr(ox)_3]_2\cdot bpp\cdot CH_3OH$ (**1**)

Space group	monoclinic, $P2_1/n$
a (Å)	21.0100(3)
b (Å)	15.9880(4)
c (Å)	21.9630(6)
β (°)	90.3390(7)
V (Å^3)	7377.4(3)
Z	4
ρ_{calc} ($g\cdot cm^{-3}$)	1.318
T (K)	150(2)
λ (Å)	0.71073
2θ (°) range	$5.88 < 2\theta < 36.08$
Total reflections/unique	19091/4965
parameters	415
$R[I > 2\sigma(I)]$	R_1[a] = 0.1281, wR_2[b] = 0.3350
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^3)	0.854/−0.386

[a] $R_1 = \sum(F_o - F_c)/\sum(F_o)$.

[b] $wR_2 = [\sum[w(F_o^2 - F_c^2)]/[\sum[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.2P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$.