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A cyanido-bridged two-dimensional network based on a Ru^{III} schiff base complex and Mn^{II} ions: Synthesis, crystal structure and magnetic properties

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Dedicated to Alfred Werner on the 100th anniversary of his Nobel Prize in chemistry in 1913.

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ABSTRACT

The reaction between $(Bu_4N)[Ru(salen)(CN)_2]$ and $MnCl_2$ yielded a bidimensional (2D) network $[\{Ru(salen)(CN)_2\}_2Mn(CH_3CN)]\cdot H_2O$ (**1**) incorporating square pyramidal Mn^{II} centers. The single crystal X-ray structure, heat capacity and magnetic properties of **1** are herein reported. From the magnetic measurements, antiferromagnetic interactions were detected between Ru^{III} ($s = 1/2$) and Mn^{II} ($S = 5/2$) ions through the cyanido bridges (J) in the 2D framework as well as antiferromagnetic interplane interactions (J'). These interactions were estimated using a three-dimensional model in the frame of the mean field approximation ($J/k_B = -0.86(2)$ K and $J'/k_B = -0.067(6)$ K, $g_{Ru} = 2.33(5)$). Furthermore, a three dimensional antiferromagnetic order was evidenced by dc susceptibility measurements with a Néel temperature of 2.6 ± 0.1 K that was also confirmed by heat capacity measurements.

1. Introduction

The promising potential applications of molecule-based materials in catalysis, gas separation/storage or as molecular switches [1] appeal to researchers working across the world in different fields ranging from chemistry to physics. Fine tuning of their properties is enabled by coordination chemistry, providing chemists with a quasi-infinite number of coordinating and accepting units. Molecule-based magnetic materials are nowadays routinely designed by association of appropriate building blocks following a “bottom-up” approach. This elegant synthetic approach is indeed perfectly suited to modulate the magnetic properties of the final compounds. On the other hand, this class of materials is gaining attention due to their unique physical features such as bulk magnet behaviors for 2D or 3D systems or magnet-like properties in Single Molecule Magnets (SMMs) or Single Chain Magnets (SCMs) [2]. Numerous networks 2D [3] and 3D systems built with cyanido-based building blocks (as the Prussian blue analogs family from hexa-, hepta- [4] and octacyanido-metalates) [5] have been reported. These materials are broadly studied for their high critical temperatures, ferri- and ferro-magnetic orders and photomagnetic properties [4,5]. Examples have also been described in the literature incorporating organic ligands on the cyanidometalate unit [6] or hexacyanido units connected to RCO_2^- (R = Me, tBu) or CO_3^{2-} bridged $[Ru_2^{II,III}]$ building blocks. Ferrimagnet, canted ferrimagnet and ferromagnet behaviors were reported in these materials [7]. In particular, the use of Ru^{III} precursors incorporating a limited number of cyanido groups allows a better control of the dimensionality of the resulting material. For example, *trans*-cyanido Ru^{III} precursors such as $[Ru(acac)_2(CN)_2]^-$ and $[Ru(salen)(CN)_2]^-$ were combined with Mn^{II} salts leading to different bimetallic materials showing similar properties [8]. It should be pointed out that the geometry around the Mn^{II} center is totally different in $[\{Ru(acac)_2(CN)_2\}_2Mn]$ [8a] and $[\{Ru(salen)(CN)_2\}_2Mn(H_2O)_2]\cdot H_2O$ [8b]: tetrahedral versus octahedral, respectively; as is the nature of the intermetallic magnetic interaction: antiferromagnetic versus ferromagnetic, respectively. In this context, it is interesting from a magnetic point of view to synthesize a pentacoordinated square pyramidal Mn^{II} analog for comparison purposes and to quantify the magnetic interactions. The reaction of $[Ru(salen)(CN)_2]^-$ with $MnCl_2$ yielded a new 2D $[\{Ru(salen)(CN)_2\}_2Mn(CH_3CN)]\cdot H_2O$ (**1**) network composed of pentacoordinated Mn^{II} metal ions. Herein, we report its synthesis, crystal structure and magnetic properties studied using dc magnetic susceptibilities and heat capacity measurements.

2. Experimental

2.1. General procedures

All the chemicals used in the synthesis were reagent grade and used as received. $(Bu_4N)[Ru(salen)(CN)_2]$ was synthesized according to literature procedures [8b,9].

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Caution! Although no problems were encountered during our studies, cyanides are toxic and should be handled with great care.

2.2. Synthesis

$[\{Ru(salen)(CN)_2\}_2Mn(CH_3CN)]\cdot H_2O$ (**1**): An acetonitrile solution of $(Bu_4N)[Ru(salen)(CN)_2]$ (50 mg, 0.08 mmol, 4 mL) was layered with an aqueous solution of $MnCl_2\cdot 4H_2O$ (8 mg, 0.04 mmol, 4 mL) intercalated with 2 mL of a CH_3CN/H_2O mixture. After 1 week, dark green crystals suitable for X-ray diffraction analysis formed at the interface were collected and dried in air. Yield 21 mg (55% based on Ru). *Anal.* Calc. for $C_{38}H_{33}Ru_2MnN_9O_5$ (952.81 g mol^{-1}): C 47.89; H 3.46; N 13.22. Found: C 47.85; H 3.36; N 13.37%. IR (KBr)/cm^{-1}: 2245 (b), 2109 (s), 1615 (s), 1597 (s), 1527(m), 1463 (sh), 1434 (m), 1387 (sh), 1338 (m), 1234 (w), 1291 (s), 1193 (m).

2.3. Physical characterization

Elemental analysis for C, H and N were performed using the classical Pregl-Dumas technique on a ThermoFischer Flash EA1112. FTIR spectra were recorded in the 4000–400 cm^{-1} range on a Nicolet 750 Magna-IR spectrometer using KBr pellets. All the samples were checked by X-ray diffraction prior to any magnetic measurements. Magnetic susceptibility measurements were performed using a Quantum Design MPMS-XL SQUID magnetometer. The measurements were carried out on freshly filtered polycrystalline samples introduced in a polyethylene bag ($3 \times 0.5 \times 0.02$ cm). dc measurements were conducted from 300 to 1.8 K and between −70 kOe and 70 kOe applied dc fields. An *M* versus *H* measurement was performed at 100 K to confirm the absence of ferromagnetic impurities. The field dependence of the magnetization was measured between 1.8 and 8 K with dc magnetic fields between 0 and 7 T. The ac susceptibility experiments were performed at various frequencies ranging from 1 to 1500 Hz with an ac field amplitude of 3 Oe in zero dc field. Experimental data were corrected for the sample holder and for the diamagnetic contribution of the sample. Heat capacities were measured on polycrystalline samples of **1** (0.8 mg) between 50 and 1.9 K by a thermal relaxation technique with a Quantum Design Physical Property Measurement System (PPMS-9) in zero dc field. The blank heat capacity from a small amount of Apiezon N grease (1.5 mg) used for adhesion was measured prior to sample mounting and the heat capacity of **1** was determined by subtraction of this blank data from the total measured heat capacity. Surface reflectivity measurements were performed on a home-built system at different temperatures ranging from 10 to 300 K. The polycrystalline samples were grounded and diluted in $BaSO_4$ prior to measurements. Heating and cooling rates were maintained at 4 K min^{-1} during the measurements. The setup collects the light reflected by the sample (sum of direct and diffuse reflected light), which was analyzed by a high sensitivity Hamamatsu 10083CA spectrometer between 400 and 1000 nm. The spectra were compared to a white reference obtained with a NSIT traceable standard for reflectance (SphereOptics, ref SG3054). The background, collected with the light source switched off, was subtracted from all measurements. The reflectivity can be plotted as a function of temperature or wavelength.

2.4. Structure determinations and refinements

A single crystal was coated in N paratone oil and mounted on a fiber loop. X-ray crystallographic data were collected on a Bruker APEX II CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 100(2) K. The program SAINT was used to integrate the data while the absorption correction was based on multiple and symmetry-equivalent reflections in the data set using the SADABS program [10]. The structure was solved by direct methods and refined by full-matrix least squares on F2 using SHELXL-97 [11]. All the atoms were refined anisotropically (except for hydrogen atoms). The H atoms were included in ideal positions (using the appropriate AFIX command in SHELXL-97) except those on the coordinated acetonitrile group and on the disordered water molecule. Nevertheless, the latters were taken into account in the total formula. Crystal data, selected details of structure determinations and geometrical parameters (selected bond distances and angles) are summarized in Tables 1 and 2.

Table 1
Crystallographic data and structure refinement for **1**.

Formula	$C_{38}H_{33}Ru_2MnN_9O_5$
Formula weight (g/mol)	952.81
λ (Å)	0.71073
Temperature (K)	100(2)
Crystal system	Tetragonal
Space group	P4/ncc
a (Å)	14.7300(4)
b (Å)	14.7300(4)
c (Å)	16.7816(7)
V (Å^3)	3641.2(2)
Z	4
ρ_{calcd} (mg m^{-3})	1.738
F (000)	1908
R_{int}	0.0514
R_1 ($I > 2\ \sigma(I)$)[a]	0.0291
wR_2[b]	0.0673

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ with $w = 1/\sigma^2(|F_o|)$.

Table 2
Selected bond distances (Å) and angles (°) for **1**.

Ru1–C1	2.0638(18)	Ru1–N2	2.0052(16)
Ru1–O1	2.0208(13)	Mn1–N1	2.1667(16)
Mn1–N3	2.181(3)		
Mn1–N1–C1	167.99(15)	Ru1–C1–N1	174.65(16)
Mn1–N3–C10	180.000(10)		

3. Results and discussion

3.1. Synthesis

In this work, the $[Ru(salen)(CN)_2]^-$ precursor was combined with different metallic salts (Mn^{II}, Mn^{III}, Fe^{III} and Ni^{II}). Crystals suitable for X-ray diffraction were only obtained with manganese sources while powder samples were systematically isolated in the other cases. Layering an acetonitrile solution of $(Bu_4N)[Ru(salen)(CN)_2]$ on an aqueous solution of $MnCl_2$ yielded dark green crystals of $[\{Ru(salen)(CN)_2\}_2Mn(CH_3CN)]\cdot H_2O$ (**1**) after a few days. The layering technique was used since systematic precipitation occurred when adding both reactants in H_2O/CH_3CN mixtures. Crystals of **1** were also obtained in low yield starting from $Mn(OAc)_3$ due to a partial reduction of the Mn^{III} ions by methanol, $Mn(OAc)_3$ being dissolved in a minimum amount of MeOH. The infrared spectra recorded on both powder samples and crystals are identical proving that the obtained polycrystalline samples are identical to the crystals of **1**. The infrared spectrum of **1** presents a strong and narrow stretching band at 2109 cm^{-1} characteristic of the cyanido groups. In comparison to the CN band of the Ru^{III} precursor located at 2088 cm^{-1}, the observed band shift clearly indicates a coordination of these groups to a metallic ion.

3.2. Crystallographic studies

Compound **1** crystallizes in the tetragonal *P*4/*ncc* space group (Table 1). The repeating unit consists of a $\{Ru_2Mn\}$ motif with