Synthesis and magnetic properties of one-dimensional metal oxalate networks as molecular-based magnets[†]

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Abstract. The homo- and heteropolymetallic assemblies of $MM'(OX)_2(H_2O)_4$, where MM' represents MnMn, CoMn, NiMn, CuMn, CoCo, NiCo, CuCo, NiNi, CuNi, and CuCu; and the respective complexes, numbered 1–10, have been prepared by reacting metal(II) salts—i.e. of Mn, Co, Ni, and Cu—and potassium oxalate monohydrate in hot water (90–100°C). The magnetic susceptibility data of the complexes 8 and 9 in the 300 K–20 K temperature range obeys the Curie–Weiss law and exhibits Weiss constants – 50 K and – 100 K, respectively. On lowering the temperature, the effective magnetic moment decreases gradually and is indicative of antiferromagnetic phase transition. The complexes have also been characterized by ES mass spectrometry, infrared (IR), electronic, and electron spin resonance (ESR) spectra.

Keywords. Molecular-based magnets; magnetic properties; one-dimensional metal oxalate; synthesis and structure of metal-oxalates.

1. Introduction

Synthesis and characterization of the polymetallic complexes with a goal to report molecular ferromagnets have been subject of numerous studies in recent years (Miller *et al* 1986, 1988a, b; Pei *et al* 1986; Nakaozawa *et al* 1992; Kahn 1993, 1995; Miller and Epstein 1994). Ferromagnets can be described as assemblies having magnetic vectors constituting paramagnetic centres which are aligned parallel over a three-dimensional matrix. They should exhibit bulk properties, such as long-range magnetic ordering, with spontaneous magnetization below the critical temperature (T_c), preferably around room temperature. Molecular ferromagnets reported so far are based on one-dimensional chains as the constituents in which the magnetic vectors are assembled by ferromagnetic interaction. In these one-dimensional chain-based magnets, magnetic phase transition temperature (T_c or T_N) is governed by both intra- and interchain magnetic interactions, and remains low because these interactions are weak.

The occurrence of long-range magnetic ordering in lattices, composed of molecular transition metal complexes, has been attracting attention of the workers in the field of materials science. These compounds are of interest because they are insulating and, hence, frequently transparent, and offer the opportunity of creating novel

lattice architectures. They also offer the chemists the opportunity to investigate how magnetic exchange interactions are propagated through extended polyatomic ligands.

In the search for molecular-based magnets, the oxalate ion is an attractive building block because its ambidentate coordinating ability enables it to form an exchange pathway between two metal ions. Discrete dimeric complexes have been synthesized to study the detail of the exchange process (Julve *et al* 1984; Pei *et al* 1989). But recently oxalate ions are used to create bi-metallic arrays that are infinite in two- or three-dimensions (Tanaki *et al* 1992; Descurtins *et al* 1994a). Magnetic exchange between moments localized on the two different metal ions may be ferro- or antiferromagnetic according to their respective electron configurations in conformity with the Kanamori–Goodenough rules (Goodenough 1963). The lattice topologies may also be highly unusual, for example the hexagonal honeycomb type of structure in the case of two-dimensional arrays are changed to helical structure in three-dimensional ones (Atovmyan *et al* 1993; Descurtins *et al* 1994b). Such materials may also be interesting by reason of their optical transparency, since this carries the possibilities of unusual optical phenomena (Bellitto and Day 1992) resulting from the onset of magnetic order. Finally, the synthetic opportunity to combine organic molecular species with inorganic complexes within the same lattice brings with it the chance of affecting very subtle influences on the ligand field symmetry through small changes in molecular packing.

In view of simplicity and potential magnetic interest, the oxalate ion has been used widely to construct transition metal containing clusters and arrays in the search

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for new molecular magnets. The synthesis of bimetallic assemblies and their magnetic and spectroscopic characterization are described in the present paper.

2. Experimental

Metal(II) chlorides (BDH) and potassium oxalate (E Merck) of AR grade were used as obtained.

2.1 Synthesis of $K_2[M(OX)_2(H_2O)_2] \cdot 4H_2O$: ($M^{II} = Mn, Co, Ni$ and Cu)

To an aqueous solution (10 cm^3) of $MCl_2 \cdot nH_2O$ (0.05 mmol) at $\sim 90^\circ\text{C}$ was added a solution (20 cm^3) of $K_2C_2O_4 \cdot H_2O$ (0.2 mmol) in hot water. The compounds crystallized on cooling the reaction solution to room temperature. The complexes were filtered, washed with cold water and dried under reduced pressure.

2.2 Synthesis of $[M_2M(OX)_2(H_2O)_4]$: ($M = M' = Mn^{II}, Co^{II}, Ni^{II}$ and Cu^{II})

To an aqueous solution (10 cm^3) of $MCl_2 \cdot nH_2O$ (0.05 mmol) at $\sim 90^\circ\text{C}$ was added a hot (90°C) solution of potassium

oxalate monohydrate (0.2 mmol) with stirring. In this hot solution a hot aqueous solution (10 cm^3) of $M'Cl_2 \cdot nH_2O$ (0.05 mmol) was added. After a few min, the complexes precipitated out, which were filtered, washed with hot water and dried under reduced pressure.

3. Analysis and physical measurements

The metal content in the complexes was determined volumetrically by EDTA titration after removing organic moiety by treating with aquaregia followed by sulphuric acid. The compounds gave satisfactory C and H values (table 1).

The water content was determined by heating a known amount of the complexes to a constant weight at 110°C , 120°C , and 150°C ; and evaluating the loss in weight. The IR spectra of complexes were recorded in KBr disc and in Nujol on a Jasco-5300 spectrophotometer. Electronic spectra of complexes were recorded on a Shimadzu 160A spectrophotometer. The ESR spectra of the powder complexes were recorded at liquid nitrogen temperature on a Varian X band E_4 spectrometer using TCNE as the g marker. The variable-temperature magnetic susceptibility measurements were carried out with a Faraday-balance magnetometer equipped with helium continuous flow cryostat in the

Table 1. Analytical data and general properties of the complexes.

Complex		Molecular weight (M.W.)	Yield (%)	Decomposition temperature ($^\circ\text{C}$)	Magnetic moment (B.M.)	Found (calcd.) (%)			
						M	M'	C	H
$[MnMn(OX)_2(H_2O)_4]$	(1)	357.92	86	340	7.83	15.80 (15.35)	15.80 (15.35)	13.10 (13.42)	2.46 (2.55)
$C_4H_8O_{12}Mn_2$									
$[CoMn(OX)_2(H_2O)_4]$	(2)	361.90	82	270	7.73	15.94 (16.28)	15.03 (15.18)	13.60 (13.28)	2.63 (2.23)
$C_4H_8O_{12}CoMn$									
$[NiMn(OX)_2(H_2O)_4]$	(3)	361.66	90	280	5.61	16.79 (16.23)	15.06 (15.19)	13.57 (13.28)	2.01 (2.23)
$C_4H_8O_{12}NiCo$									
$[CuMn(OX)_2(H_2O)_4]$	(4)	366.52	76	290	4.88	17.60 (17.34)	14.45 (14.98)	12.98 (13.11)	2.48 (2.19)
$C_4H_8O_{12}CuCo$									
$[CoCo(OX)_2(H_2O)_4]$	(5)	365.89	79	290	6.69	16.42 (16.16)	16.53 (16.10)	13.52 (13.13)	2.38 (2.20)
$C_4H_8O_{12}Co_2$									
$[NiCo(OX)_2(H_2O)_4]$	(6)	365.65	74	340	4.67	16.35 (16.12)	16.38 (16.05)	13.52 (13.14)	2.42 (2.12)
$C_4H_8O_{12}NiCo$									
$[CuCo(OX)_2(H_2O)_4]$	(7)	370.51	73	340	4.52	17.67 (17.15)	15.75 (15.90)	12.78 (12.96)	2.06 (2.18)
$C_4H_8O_{12}CuCo$									
$[NiNi(OX)_2(H_2O)_4]$	(8)	365.41	68	330	3.37	16.58 (16.06)	16.27 (16.06)	13.41 (13.15)	2.06 (2.20)
$C_4H_8O_{12}Ni_2$									
$[CuNi(OX)_2(H_2O)_4]$	(9)	370.27	81	320	3.47	17.49 (17.16)	15.67 (15.85)	12.72 (12.98)	2.37 (2.18)
$C_4H_8O_{12}CuNi$									
$[CuCu(OX)_2(H_2O)_4]$	(10)	375.18	77	320	2.33	17.15 (16.94)	17.23 (16.94)	12.62 (12.81)	2.03 (2.15)
$C_4H_8O_{12}Cu_2$									

N.B: In column one, the numbers 1–10, enclosed within brackets, are the numbers assigned to the respective complexes. In the text, for the discussion of a particular complex, its corresponding number has been used.

20–300 K temperature range at 6 and 8 kG magnetic fields. The diamagnetic corrections were made by using Pascal constants.

4. Results and discussion

The oxalate-bridged bi-metallic assemblies were readily obtained by a one-pot reaction of a M(II) chloride, pota-

Figure 1a. ES mass spectrum of $[\text{CuNi}(\text{OX})_2(\text{H}_2\text{O})_4]$.

Figure 1b. Fragmentation pattern of $[\text{CuNi}(\text{OX})_2(\text{H}_2\text{O})_4]$.

ssium oxalate and $\text{M}'(\text{II})$ salt in water at 90°C . The complexes are insoluble in common organic solvents. Loss of water molecules at 150°C indicates their coordinate nature. The ES mass spectrum (figure 1a) of $[\text{CuNi}(\text{OX})_2(\text{H}_2\text{O})_4]$ shows a base peak at $m/z = 205$ due to $\text{Cu}(\text{OX})(\text{H}_2\text{O})_3$. The molecular ion peak appears at $m/z = 371$. The fragmentation pattern of complex is shown in figure 1b. The chelated oxalate groups generally show an asymmetric $\nu(\text{C}=\text{O})$ vibration at 1700 and $\delta(\text{CO})$ at ca 800 cm^{-1} . In the infrared spectra (figures 2 and 3) of the complexes 1–10 (see table 1), the vibrations due to oxalate group appear at $1650\text{--}1610\text{ cm}^{-1}$ and $810\text{--}780\text{ cm}^{-1}$, respectively, indicating that the oxalate ions function as bridging moieties. The bonding of oxalate to metal ions is shown by the presence of bands at $520\text{--}490\text{ cm}^{-1}$ and $460\text{--}405\text{ cm}^{-1}$ due to $\nu(\text{MO}) + \nu(\text{CC})$ and $\nu(\text{MO}) + \text{ring deformation modes}$, respectively. A band at $3400\text{--}3350\text{ cm}^{-1}$ in the IR spectra of the complexes, indicates presence of water molecule(s). The coordinated nature of water is inferred from the presence of IR bands at $725\text{--}710\text{ cm}^{-1}$ and $670\text{--}660\text{ cm}^{-1}$, which is assigned to the $\nu_t(\text{H}_2\text{O})$ and $\nu_w(\text{H}_2\text{O})$, respectively.

The bands appearing at 15385 cm^{-1} and 20000 cm^{-1} in the electronic spectrum of the complex **2** are attributed to

Figure 2. Infrared spectrum of oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$).

Figure 3. Infrared spectra of a. $[\text{K}_2\text{Ni}(\text{OX})_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$; and b. $[\text{CuNi}(\text{OX})_2(\text{H}_2\text{O})_4]$.

${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions, respectively, assuming an octahedral geometry. The spectrum of the complex **3** exhibits bands at 9216 cm^{-1} , and 13793 cm^{-1} , which are assigned to the ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ transitions, respectively, on the basis of an octahedral geometry. Only one absorption band observed at 14815 cm^{-1} in the spectrum of complex **4** is assigned to the ${}^2E_g \rightarrow {}^2T_{2g}(D)$ transition, which suggests octahedral arrangement of the ligand atoms around the metal ion. Three bands appear in the complex **6** at 9049 cm^{-1} , 15384 cm^{-1} , and 19230 cm^{-1} , which are

Figure 4. Electronic spectrum of $[\text{NiNi}(\text{OX})_2(\text{H}_2\text{O})_4]$.

Figure 5. Electronic spectrum of $[\text{CuNi}(\text{OX})_2(\text{H}_2\text{O})_4]$.

assigned to the ${}^3A_{2g} \rightarrow {}^3T_{2g}$ transition of Ni(II) and ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions of Co(II), respectively, assuming octahedral geometry. The spectrum of complex **7** exhibits bands at 9302 cm^{-1} and 20000 cm^{-1} , which are assigned to the ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions of Co(II), respectively. A band at 13885 cm^{-1} is attributed to ${}^2E_g \rightarrow {}^2T_{2g}(D)$ transition. These spectral features indicate an octahedral geometry around the metal ions. Two bands at 9523 cm^{-1} and 13513 cm^{-1} appearing in the spectrum (figure 4) of the complex **8** are attributed to ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$ and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ transitions, respectively, showing an octahedral geometry. The complex **9** exhibited bands (figure 5) at 10101 cm^{-1} and 25974 cm^{-1} , which are assigned to ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transitions of Ni(II), respectively. A band at 13605 cm^{-1} is assigned to ${}^2E_g \rightarrow {}^2T_{2g}(D)$ transition of Cu(II). These spectral features are characteristic of an octahedral stereochemistry around the metal ions. Only one absorption band at 14925 cm^{-1} in the spectrum of complex **10** is assigned to ${}^2E_g \rightarrow {}^2T_{2g}(D)$ transition which suggests octahedral stereochemistry around the metal ion. These features of electronic spectra are the characteristic of octahedral bonding of oxalate with metal ions. The ESR spectrum (figure 6) of the powder $[\text{CuNi}(\text{OX})_2(\text{H}_2\text{O})_4]$ recorded at liquid nitrogen temperature shows a signal at 3090 G yielding a g value of 2.093 for copper(II), and a signal at 2830 G yielding a g value of 2.283 for nickel(II). This suggests magnetic interaction between the metal ions in the bi-metallic assembly.

5. Magnetic properties

The room temperature magnetic moments of complexes **1–10** are given in table 1. The cryomagnetic properties of the bimetallic assemblies $[\text{CuNi}(\text{OX})_2(\text{H}_2\text{O})_4]$ and $[\text{NiNi}(\text{OX})_2(\text{H}_2\text{O})_4]$ were studied and the respective cryomagnetic behaviour is shown in figures 7 and 8 in the form of C_M vs T , C_M^{-1} vs T , $C_M T$ vs T and μ_{eff} vs T plots, where C_M is magnetic susceptibility per M_2 and T is

Figure 6. ESR spectrum of $[\text{CuNi}(\text{OX})_2(\text{H}_2\text{O})_4]$.

temperature in Kelvin. The magnetic moment, μ_{eff} (BM) is calculated by using the equation,

$$\mu_{\text{eff}} = [8 C_M T]^{1/2}.$$

The magnetic susceptibility 1.54 cm^3 of $[\text{CuNi}(\text{OX})_2(\text{H}_2\text{O})_4]$ at 6 kG and 300 K results in the magnetic moment value of $3.51 \mu_B$, which is lower than spin-only value of $3.87 \mu_B$ for the magnetically dilute $\text{Cu}(\text{II})$ – $\text{Ni}(\text{II})$ [$S_{\text{Cu}} = 1/2$, $S_{\text{Ni}} = 1$] assembly. When the temperature is lowered, $C_M T$ and μ_{eff} decrease and reach a plateau

around 20 K with $C_M T = 0.3496 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ and $\mu_{\text{eff}} = 1.67 \mu_B$. The magnetic susceptibility obeys the Curie–Weiss law with Weiss constant of -100 K . The observed magnetic behaviour suggests the antiferromagnetic interaction within the assembly. The similar cryomagnetic magnetic behaviour is observed at 8 kG magnetic field, indicating that it is field independent.

The complex $[\text{NiNi}(\text{OX})_2(\text{H}_2\text{O})_4]$ exhibits magnetic susceptibility value of $1.585 \text{ cm}^3 \text{ mol}^{-1}$ and magnetic moment $3.56 \mu_B$ at 6 kG and 300 K. The magnetic moment value is lower than the spin-only value of $4.90 \mu_B$

Figure 7a. Thermal variation of C_M (·) and inverse susceptibility, $1/C_M$ (+) of complex $[\text{CuNi}(\text{OX})_2(\text{H}_2\text{O})_4]$.

Figure 7b. Thermal dependence of $C_M T$ (·) and inverse susceptibility, $1/C_M$ (+) of complex $[\text{CuNi}(\text{OX})_2(\text{H}_2\text{O})_4]$.

Figure 7c. Plot of the temperature dependence of the reciprocal magnetic susceptibility (+) and magnetic moment (·) per $\text{Cu}(\text{II})$ – $\text{Ni}(\text{II})$ for $[\text{CuNi}(\text{OX})_2(\text{H}_2\text{O})_4]$.

Figure 8a. Thermal variation of C_M (·) and inverse susceptibility, $1/C_M$ (+) of complex $[\text{NiNi}(\text{OX})_2(\text{H}_2\text{O})_4]$.

Figure 8b. Thermal dependence of $C_M T$ (·) and inverse susceptibility, $1/C_M$ (+) of complex $[\text{NiNi}(\text{OX})_2(\text{H}_2\text{O})_4]$.

Figure 8c. Plot of the temperature dependence of the reciprocal magnetic susceptibility (+) and magnetic moment (·) per $\text{Ni}(\text{II})$ – $\text{Ni}(\text{II})$ for $[\text{NiNi}(\text{OX})_2(\text{H}_2\text{O})_4]$.

Figure 9. Schematic representation of the ox-bridged network: structure of $M-OX-M'$ [$M = M' = Mn^{II}$, Co^{II} , Ni^{II} and Cu^{II}].

for the magnetically dilute $Ni(II)-Ni(II)$ ($S_{Ni} = 1$, $S_{Ni} = 1$) assembly. On lowering the temperature $C_M T$ decreases and it shows a value $0.932 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ yielding the $\mu_{\text{eff}} = 2.78 \mu_B$ at 50 K. The magnetic susceptibility obeys the Curie-Weiss law in the 50–300 K temperature range with a Weiss constant of -50 K . The same cryomagnetic behaviour is observed at 8 kG magnetic field also which implies presence of the antiferromagnetic interaction between $Ni(II)-Ni(II)$ ions.

On the basis of the above studies the structure proposed for the oxalate-bridged molecular assembly is shown in figure 9.

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