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Synthesis and Characterization of a Bimetallic Oxalate-Based Magnet: $[(C_4H_9)_4P][M(II)Cr(ox)_3]$ M(II) = Mn, Fe, Co, Ni, Cu*

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Abstract: The mixed-metal $[(C_4H_9)_4P][M(II)Cr(ox)_3]$ M(II) = Mn(1), Fe(2), Co(3), Ni(4), Cu(5) and ox is oxalate, has been prepared. X-ray powder diffraction patterns and their Rietveld refinement show that all the compounds along the series are isostructural and single-phased. X-ray powder diffraction profiles are indexed in hexagonal and $P6_3$ space group. The magnetic susceptibility data obey Curie-Weiss law in temperature 300-5 K with a positive constants of 15.1 (1), 13.5 (2), 12.7 (3), 12.0 (4) and 11.0 K (5). The temperature dependence of the molar magnetization exhibits a magnetic phase transition at T_c = 12 K (1), 11 (2), 10 (3), 8(4), 7 K (5). At low temperature, the compounds complex exhibit long-range ordered magnetic behavior.

Key words: Oxalate networks, dinuclear complexes, chromium complexes, magnetic properties, X-ray powder diffraction, ferromagnetic interaction

INTRODUCTION

Binuclear complexes have been the subject of numerous studies in recent years (Tamaki *et al*., 1992; Coronado *et al*., 2006), due to their magnetic properties are superior compared to the mononuclear complex. The binuclear complexes could be resulted from the combination of metal ions with oxalate ligands. Oxalate is capable of binding metal centre in versatile coordination modes, leading to a wide variety extended structure. Moreover, oxalate is frequently used as magnetic superexchange pathways between the metal ions, due to their versatile oxalate-bridging coordination modes, which can transmit magnetic coupling interaction to different degrees. Recently, a few novel metal-organic networks based oxalate has been reported which exhibit different magnetic behaviors (Pointilart *et al*., 2004). The magnetic properties of oxalate-bridged binuclear complex have been reported (Pellaux *et al*., 1997). Difference magnetic properties were obtained by changing complex building block. Complex building block Cr(III)-oxalate in $\{[(C_4H_9)_4N][M(II)Cr(III)(oxalate)_3]\}_n$ compound (M(II) = Mn, Fe, Co, Ni, Cu) was reported by Tamaki *et al*. (1992). These compounds were reported to exhibit ferromagnetic properties. Carling *et al*. (2002) showed antiferromagnetic interaction was obtained in $\{[(C_4H_9)_4N][M(II)Fe(III)(oxalate)_3]\}$ binuclear complex with Fe(III)-oxalate building block.

In this report we describe conceptually the different synthetic route and counter ion was used in this study, with the aim to obtain a possible new magnetic material.

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MATERIALS AND METHODS

Materials

All chemicals were of reagent grade and were used as commercially obtained. $K_3[Cr(ox)_3].3H_2O$ was prepared according to literature methods (Nelson and Kemp, 2003).

Synthesis of $\{[(C_4H_9)_4P][M(II)Cr(III)(oxalate)_3]\}_n$

One millimole of $K_3[Cr(ox)_3]$ dissolved in 10 mL of water, then 3 mmol silver nitrate dissolved in 10 mL of water was added drop wise and stirred for 1 h. The precipitated silver chrome oxalate were filtered of, washed with water and dried at room temperature. The solid silver chrome oxalate was dissolved in 10 mL methanol, then M(II) salt (chloride) dissolved in 10 mL methanol was added. The precipitated silver chloride were filtered of and solution $[M(II)Cr(ox)_3]^-$ were found. To 1 mmol solution of $[M(II)Cr(ox)_3]^-$ was added 1 mmol solution $[(C_4H_9)_4P]Br$.

Physical Techniques

The IR spectra were recorded on Perkin Elmer GX IRFT spectrophotometer as KBr pellets in the 4000-400 cm^{-1} region. Elemental analyses were completed at Fison EA 1108, Malaysia. The metal concentrations were determined by atomic absorption spectrophotometry measurements using a Shimadzu AA8801S apparatus.

Powder X-Ray Measurements

Powder X-ray diffraction measurements were performed on a Siemens D5000 diffractometer using CuKα radiation and high-resolution data were collected at room temperature using synchrotron radiation of wavelength 1.00 Å in 0.01 steps at the Australian National Beamline Facility, Beamline 20 B, at the Photon Factory, Japan. For these measurements the diffractometer was operated in θ- 2θ mode and the flat plate sample was rotated through-out the measurements.

Magnetic Measurements

The variable temperature magnetic susceptibility measurements were carried out on samples constituted of small crystals (20-30 mg) using a Quantum Design MPMS7 squid magnetometer equipped with a 5.5 T magnet and operating at 1 T and 5-300 K . The susceptometer was calibrated with $(NH_4)_2Mn(SO_4)_2.12H_2O$. Experimental susceptibilities were corrected for diamagnetism of the constituent atoms by the use of Pascal's constants.

RESULTS AND DISCUSSION

The coordination binuclear complexes $[(C_4H_9)_4P][M(II)Cr(ox)_3]$ M(II) = Mn(1), Fe(2), Co(3), Ni(4), Cu(5) were synthesized. Characteristic IR bands as KBr pellets of the complexes are given in Table 1. Anal. Calcd. for $[(C_4H_9)_4P][MnCr(ox)_3]$: Mn 8.72, Cr 8.25, C 41.25, H 5.70; found: Mn 8.41, Cr 8.69, C 42.76, H 5.34; for $[(C_4H_9)_4P][FeCr(ox)_3]$: Fe 8.87, Cr 8.24 C 40.49, H 5.86; found: Fe 8.91,

Table 1: Characteristic IR bands of the complexes $\{[P(n\text{-}C_4H_9)_4][M(II)Cr(III)(ox)_3]\}$ M(II) = Mn(1), Fe(2), Co(3), Ni(4), Cu(5)

	1	2	3	4	5
IR bands	(cm^{-1})				
ν(C-H)	2970.2	2936.6	2969.2	2963.2	2963.8
ν_{asym}(C-O)	1611.9	1633.0	1620.3	1627.8	1620.3
ν_{sym} (C-O)	1362.8	1339.9	1337.1	1384.8	1344.9
δ(O-C-O)	822.2	808.4	811.5	810.0	807.7
ν(M-O)	410.9	416.8	417.9	420.5	425.8
ν(Cr-O)	469.7	472.7	475.9	478.3	480.8

Cr 8.50, C 40.86, H 5.46; for $[(C_4H_9)_4P][CoCr(ox)_3]$: Co 9.30, Cr 8.20, C 41.25, H 5.70; found: Co 9.50, Cr 8.59, C 42.76, H 5.34; for $[(C_4H_9)_4P][NiCr(ox)_3]$: Ni 9.26, Cr 8.21, C 41.25, H 5.70; found: Ni 9.44, Cr 8.38, C 42.76, H 5.34; for $[(C_4H_9)_4P][CuCr(ox)_3]$: Cu 9.95 Cr 8.14, C 41.25, H 5.70; found: Cu 10.22, Cr 8.43, C 42.76, H 5.34. These compounds is stable in air and is soluble in some organic solvent are dimethyl sulfoxide and dimethyl formamide, but attempts to obtain single crystal suitable for X-ray structure determination has so far been unsuccessful. However, the binuclear complexes were further characterized on the basis of the following results.

Chelated oxalate groups generally an antisymmetric ν(CO) vibration at ca. 1700 cm^{-1}, ν_{sym}(CO) vibration at ca. 1356 cm^{-1} and δ(CO) vibration at ca. 800 cm^{-1}. In IR spectra of 1-5 the vibrations due to oxalate group appear at 1385-1337 cm^{-1}, 1633-1612 cm^{-1} and 822-807 cm^{-1}, indicating that all the oxalate group function as bridging ligand. A weak band around 421 cm^{-1} in the complexes is assigned to ν(M-O) vibration. The IR spectra for compounds 1-5 is shown in Fig. 1. The M-O distance of the complexes showed decrease in series Mn-Cr, Fe-Cr, Co-Cr, Ni-Cr and Cu-Cr. This is supported from X-ray data, the cell volume decrease in series of the complexes. It is indicate that the Cu-O interaction shows the strongest variations since this is the shortest bond distance.

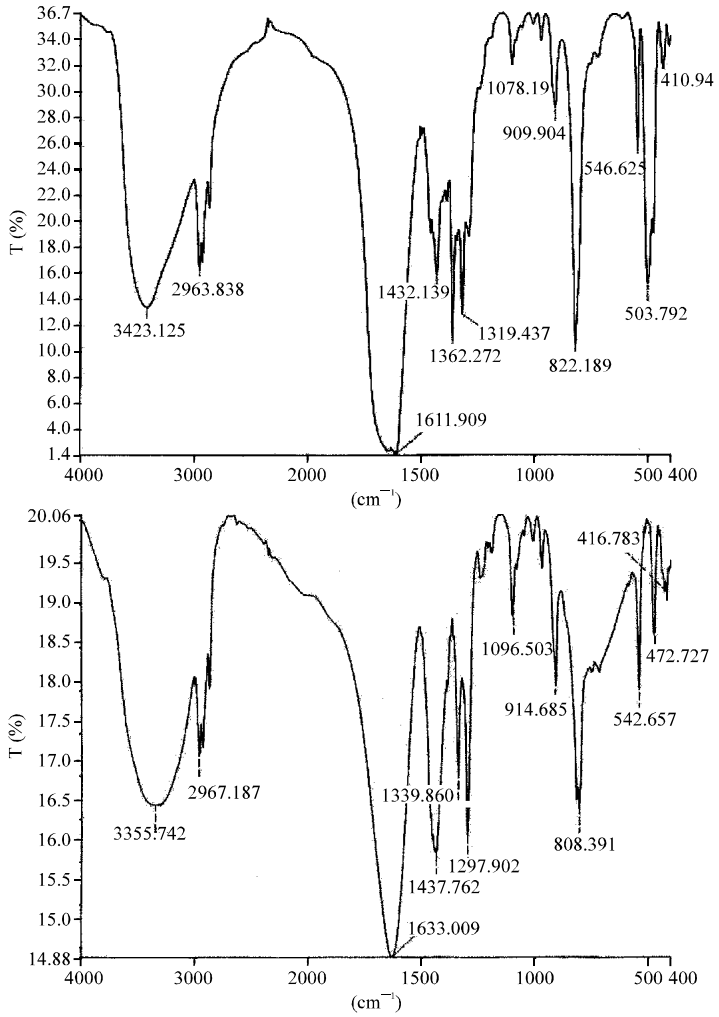

Fig. 1: Continued

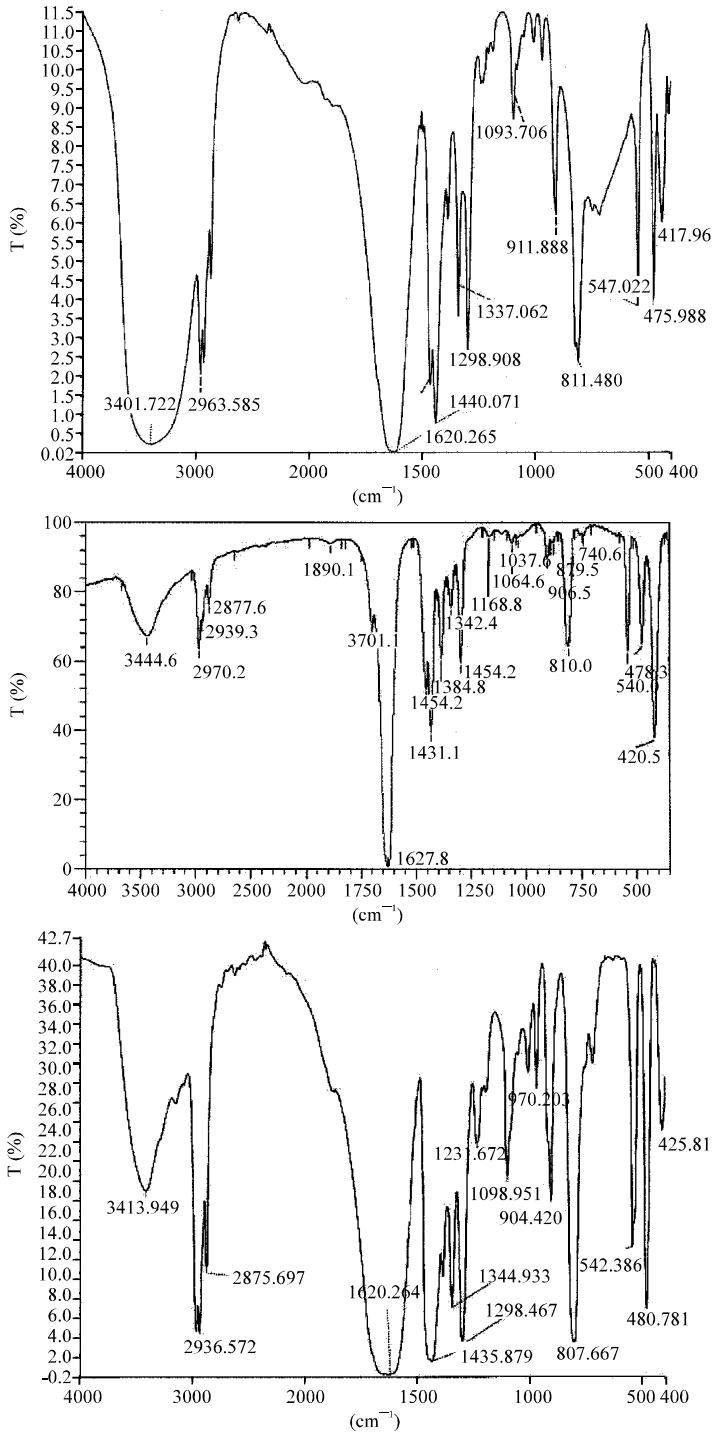

Fig. 1: IR spectra for $[(C_4H_9)_4P][M(II)Cr(ox)_3]$ M(II) = Mn(1), Fe(2), Co(3), Ni(4), Cu (5)

Attempts to obtain crystals of 1-5 suitable for single crystal x-ray diffraction analysis so far has been unsuccessful. Compounds 1-5 were obtained as polycrystalline materials. It was characterised The X-ray powder diffraction showed an isostructural pattern to each other is similar, indicating that by X-ray powder diffraction (XRPD) data and indexed in $P6_3$ hexagonal space group to derive unit cell parameters by Le Bail refinement in the RIETICA program. The series of compounds all have similar crystal structure. The cell parameters obtained from this refinement are listed in Table 2 (Mathoniére *et al*., 1996). These data are similar to those found from X-ray single-crystal diffraction for $[N(n\text{-}C_4H_9)_4][M(II)Cr(III)(ox)_3]$. The experimental and calculated XRPD patterns are shown in Fig. 2. Taking into account the different size and shape of the cationic counterions and the chemical constitutions of compounds this similarity by fortuitous. The magnetic behaviour also gives support to the existence of two dimensional bimetallic $[M(II)Cr(ox)_3]^-$ anionic networks. This network is formed bis-bidentate oxalate ligand connecting M^{2+} and Cr^{3+} ions in such a way that each M^{2+} ion is surrounded by three Cr^{3+} ions and vice versa, leading to polymeric nets with all metal ions maintaining the different chirality.

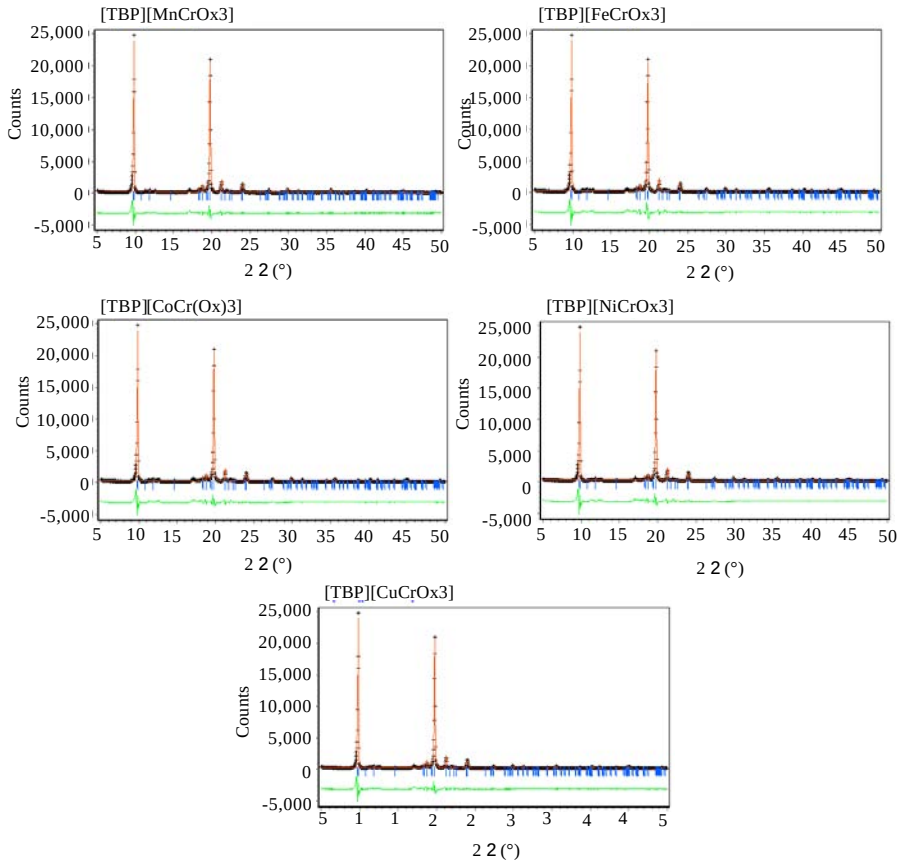

Fig. 2 : Le Bail of the X-ray powder diffraction for;

(a) : $[P(n\text{-}C_4H_9)_4][Mn(II)Cr(III)(ox)_3]$

(b) : $[P(n\text{-}C_4H_9)_4][Fe(II)Cr(III)(ox)_3]$ (c) $[P(n\text{-}C_4H_9)_4][Co(II)Cr(III)(ox)_3]$,

(d) : $[P(n\text{-}C_4H_9)_4][Ni(II)Cr(III)(ox)_3]$ (e) $[P(n\text{-}C_4H_9)_4][Cu(II)Cr(III)(ox)_3]$. Experimental data (++), calculated data (solid red line) and difference (solid green line) for X-ray powder pattern diffraction profile of the complexes

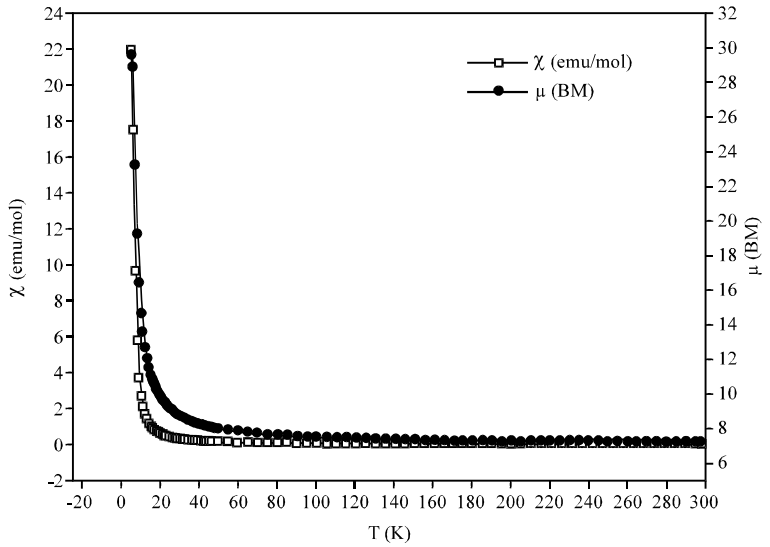

Fig. 3: Plots χ vs T and μ vs T for $[P(n\text{-}C_4H_9)_4][Mn(II)Cr(ox)_3]$

Table 2: Refined unit cell constants of the complexes $\{[P(n\text{-}C_4H_9)_4][M(II)Cr(III)(ox)_3]\}$ M(II) = Mn, Fe, Co, Ni, Cu

Cell parameters	1	2	3	4	5
Space group	$P6_3$	$P6_3$	$P6_3$	$P6_3$	$P6_3$
a (Å)	9.4363 (0)	9.4254 (0)	9.4153 (0)	9.4037 (0)	9.4011 (0)
b (Å)	9.4363 (0)	9.4254 (0)	9.4153 (0)	9.4037 (0)	9.4011 (0)
c (Å)	17.946 (0)	17.9361 (0)	17.9370 (0)	17.9261 (0)	17.9239 (0)
V (Å^3)	1383.89	1379.93	1377.05	1373.86	1371.89
Rp (%)	17.27	17.97	16.40	17.41	17.50
Rwp (%)	13.46	13.58	13.30	13.43	13.31
χ^2	285.76	290.34	279.36	285.25	280.62
Z	2	2	2	2	2

Table 3: Summary of Magnetic of the complexes $[P(n\text{-}C_4H_9)_4][M(II)Cr(ox)_3]$ M(II) = Mn, Fe, Co, Ni and Cu

Compounds	T_c/K	θ/K	S_{Tot}	μ
1	12	15.1	4	8.5
2	11	13.5	7/2	7.5
3	10	12.7	3	6.9
4	8	12.0	5/2	5.6
5	7	11.0	2	4.8

The magnetic susceptibility behaviors of all these compounds are essentially similar. All members obey the Curie-Weiss law from 7 to 12 K. In all compounds the Weiss constants, θ, are positive, indicating ferromagnetic interactions between neighboring Cr(III) and M(II) ions. This is also supported by the gradual increase observed in μ product upon cooling from room temperature. At low temperature (below 25 K) both χ and μ show sharp increase. The magnetic behaviour of the compound $[P(n\text{-}C_4H_9)_4][Mn(II)Cr(ox)_3]$ in the susceptibility and magnetic moment against temperature is shown in Fig. 3, χ is the magnetic susceptibility per MCr unit and μ is the effective magnetic moment calculated by the equation $\mu = 2.828(\chi T)^{1/2}$. These features suggest the onset of long-range ferromagnetic ordering. The mixed-metal system whose magnetic orbitals are strictly orthogonal to each other can give the ferromagnetic interaction between the mixed-metal ions. The maximum magnetic moment is very large compared with the corresponding spin-only value expected for the highest total spin of binuclear Cr(III)-M(II) system ($S_T = S_{Cr} + S_M$). For example, the maximum magnetic moment of 1 is 22.0 μ_B at 5.0 K, which very large compared with 8.5 μ_B, the spin only value of $S_T = 4$ expected for the largest total spin of Cr(III)-M(II) system. The magnetic parameters of the compounds (phase-transition temperature, Weiss constant total spin and magnetic moment) are shown in Table 3.

In all cases the critical temperature of the $[P(n\text{-}C_4H_9)_4][M(II)Cr(ox)_3]$ series are higher than the compound $[P(C_6D_5)_4][Mn(II)Cr(III)(ox)_3]$ (Tc =6 K) because of the higher electrostatic interactions as well as C-H(butyl)···O(oxalate) hydrogen bonds in the $[P(n\text{-}C_4H_9)_4][M(II)Cr(ox)_3]$.

CONCLUSION

With this report, binuclear complexes of 3d-metal ion bridged by chelating oxalate ligands have been presented, the counter ions, $[P(C_4H_9)_4]^+$ may play a dominating role in the crystal packing. There is correlation between these cell volume and distance M-O of the complexes. The magnetic measurement exhibits the ferromagnetic interactions in all complexes.

In addition, more data on analogous, chemically modified compounds are needed in order to tackle successfully the interpretation of the magnetic interactions which are occurring.

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