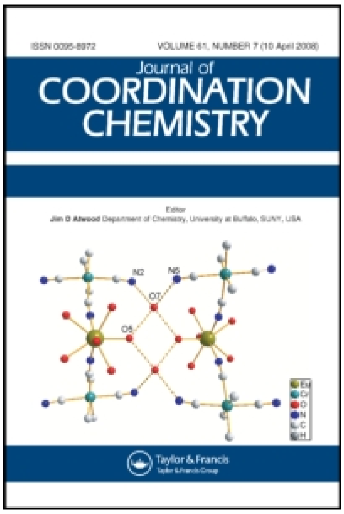

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Malonato-bridged hexamethylenetetramine coordination polymers containing Mn(II) and Cu(II)

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Malonato-bridged hexamethylenetetramine coordination polymers containing Mn(II) and Cu(II)

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Two malonato-bridged hexamethylenetetramine coordination polymers, $M_2(hmt)(H_2O)_2(mal)_2$ [hmt = hexamethylenetetramine, mal = malonate(2-), M = Mn (**1**), Cu (**2**)] were prepared and structurally characterized. The isostructural complexes are orthorhombic, space group *Imm*2, with $a = 7.104(1)$, $b = 15.982(3)$, $c = 7.702(1)$ Å, $Z = 2$, $D_{calc} = 1.862\,g\,cm^{-3}$ (**1**) and $a = 6.962(3)$, $b = 15.500(7)$, $c = 7.627(3)$ Å, $Z = 2$, $D_{calc} = 2.047\,g\,cm^{-3}$ for **2**. The transition metals are octahedrally coordinated by one nitrogen atom of an hmt ligand and five oxygen atoms of a water molecule and three malonate anions. The latter coordinate in chelating/*bis*-monodentate mode to give 2D layers with a (4, 4) topology, and which are pillared by bridging bidentate hmt ligands to generate an open 3D framework with channels extending in the [001] direction. Over the temperature range 5–300 K, **2** behaves paramagnetically, following the Curie–Weiss law $\chi_m(T - \theta) = 4.521(6)\,cm^3\,mol^{-1}\,K$ with a Weiss constant $\theta = -4.8(2)$ K.

Keywords: Coordination polymer; Copper; Manganese; Malonate; Hexamethylenetetramine; X-ray structure; Magnetic properties

1. Introduction

The design and synthesis of metal-organic coordination polymers has attracted considerable recent attention, since such supramolecular assemblies have interesting structures as well as potential applications in the fields of molecular magnetism, electrical conductivity, inclusion chemistry, molecular recognition and catalysis [1]. One extensively used strategy for designing such materials relies on the utilization of multidentate *N*- or *O*-donor ligands which have the capacity to bridge between metal centres to form polymeric structures [2]. Aliphatic α,ω-dicarboxylates are useful for construction of coordination polymers with specific topologies. However, the α,ω-dicarboxylato coordination polymers normally exhibit little porosity [3–6]. To circumvent this problem, studies have extended to simultaneous use of *N*-donor bridging ligands and aliphatic α,ω-dicarboxylates [7,8]. In this contribution, we report two malonato-bridged hexamethylenetetramine coordination polymers,

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$M_2(hmt)(H_2O)_2(mal)_2$ [hmt = hexamethylenetetramine, mal = malonate(2-), M = Mn (**1**), Cu (**2**)], in which 2D layers with a (4, 4) topology result from metal atoms bridged by malonate anions being pillared by bidentate hmt ligands.

2. Experimental

2.1. *Physical measurements*

All chemicals were of reagent grade and used without further purification. Elemental analyses were performed using a Perkin-Elmer 2400II CHNS/O instrument. IR spectra (KBr pellets) were recorded over the range 4000–400 cm^{-1} using a Shimadzu FTIR-8900 spectrophotometer. Magnetic measurements were performed on polycrystalline samples with a Quantum Design MPMS-7 SQUID magnetometer with an applied field of 10 000 G in the temperature range $5 \leq T(K) \leq 300$. Diamagnetic corrections were estimated from Pascal's constants [9].

2.2. *Syntheses*

2.2.1. $Mn_2(hmt)(H_2O)_2(mal)_2$, 1. Dropwise addition of 1.0 cm^3 of 1 M aqueous Na_2CO_3 to a stirred solution of $MnSO_4 \cdot H_2O$ (0.085 g, 0.50 mmol) in 5.0 cm^3 of H_2O produced a yellowish precipitate, $Mn(OH)_{2-2x}(CO_3)_x \cdot yH_2O$, which was centrifuged and washed with doubly distilled water until no SO_4^{2-} anions were detectable in the supernatant. The precipitate was subsequently added to a stirred solution of malonic acid (0.052 g, 0.50 mmol) in 20.0 cm^3 of H_2O. The resulting solution was mixed with a solution of hexamethylenetetramine (0.070 g, 0.50 mmol) in 5.0 cm^3 of CH_3OH. The mixture was vigorously stirred for 20 min to produce a nearly colourless solution (pH = 5.92), which was allowed to stand at room temperature. Slow evaporation over several days afforded nearly colourless crystals of the product (yield: 42% based on initial $MnSO_4 \cdot H_2O$). Anal. Calc. for $C_{12}H_{20}Mn_2N_4O_{10}$ (%): C, 29.40; N, 11.43; H, 4.11. Found: C, 29.29; N, 11.41; H, 3.50. IR (cm^{-1}): 3389w, 3233m, 2980w, 1622s, 1574s, 1447m, 1358s, 1244m, 1225m, 1164w, 1055w, 1026m, 991s, 972w, 943w, 931w, 924w, 822w, 802w, 777w, 696s, 662m, 594m, 575m, 517w, 482w.

2.2.2. $Cu_2(hmt)(H_2O)_2(mal)_2$, 2. A synthetic procedure analogous to that used for **1** was applied except $CuCl_2 \cdot 2H_2O$ (0.085 g, 0.50 mmol) was used instead of $MnSO_4 \cdot H_2O$. A blue filtrate (pH = 6.02) was allowed to stand at room temperature and blue crystals were formed by slow evaporation over several days (yield: less than 5% based on initial $CuCl_2 \cdot 2H_2O$). IR (cm^{-1}): 3427w, 3136m, 2999w, 1607s, 1578s, 1462w, 1433m, 1394w, 1369w, 1340m, 1248w, 1225w, 1161w, 1065w, 1030w, 991m, 947w, 924w, 840w, 812w, 710m, 687m, 658w, 638w, 579w, 502w, 453w.

2.3. *X-ray crystallography*

Suitable single crystals of **1** and **2** were selected under a polarizing microscope and fixed with epoxy cement on fine glass fibres which were mounted on a Bruker P4 diffractomerter with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) for cell determination and data collection. Lattice parameters were refined from 2θ

Table 1. Summary of crystal data, data collection, structure solution and refinement details for **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{12}H_{20}Mn_2N_4O_{10}$	$C_{12}H_{20}Cu_2N_4O_{10}$
Formula weight	490.20	507.40
Description	colourless prisms	blue plates
Crystal size (mm)	0.222 × 0.200 × 0.133	0.356 × 0.267 × 0.222
Temperature (K)	293(2)	293(2)
Crystal system	orthorhombic	orthorhombic
Space group	*Imm*2	*Imm*2
Unit cell dimensions		
a (Å)	7.104(1)	6.962(3)
b (Å)	15.982(3)	15.500(7)
c (Å)	7.702(1)	7.627(3)
V (Å^3)	874.5(2)	823.0(6)
Z	2	2
D_{calc} (g cm^{-3})	1.862	2.047
F(000)	500	516
μ (mm^{-1})	1.508	2.652
Absorption correction	empirical	empirical
Refinement method	Full-matrix least-squares on F^2	
θ Range (°)	2.55–30.02	2.63–29.79
Reflections collected	834	790
Independent reflections (R_{int})	689 (0.0313)	652 (0.0640)
Data, restraints, parameters	674, 1, 88	645, 1, 88
Goodness of fit on F^2	1.107	1.182
R_1, wR_2 [$I \geq 2\sigma(I)$][a]	0.0246, 0.0653	0.0569, 0.1577
R_1, wR_2 (all data)[a]	0.0255, 0.0659	0.0572, 0.1577
Extinction coefficients	0.000(1)	0.002(2)
A, B values in weighting scheme[b]	0.0404, 0.3234	0.0765, 12.4326
$\delta\rho_{max}$, $\delta\rho_{min}$ (e Å^{-3})	0.497, −0.422	1.335, −1.398

[a] $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$. [b] $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$ with $P = (F_o^2 + 2F_c^2)/3$.

values (10–25°) of 25 carefully centred reflections and reflection intensities were collected at 293 K using the θ–2θ scan technique. Corrections for Lorentz polarization and absorption effects were performed on the basis of ψ-scans. The structures were solved by direct methods using SHELXS-97 [10]. Subsequent difference Fourier syntheses enabled all non-hydrogen atoms to be located. After several cycles of refinement, hydrogen atoms associated with C atoms were added in the calculated positions and hydrogen atoms of H_2O molecules were derived from difference Fourier syntheses. Final full-matrix least-squares refinement using SHELXL-97 [11] converged smoothly with anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms. Crystal data, intensity collection and structure refinement details are summarized in table 1, and the final non-hydrogen atomic positional parameters for **1** and **2** are listed in table 2. Selected interatomic distances and bond angles are given in table 3.

3. Results and discussion

3.1. *Syntheses*

$Mn_2(hmt)(H_2O)_2(mal)_2$ (**1**) and $Cu_2(hmt)(H_2O)_2(mal)_2$ (**2**) result from reaction of hexamethylenetetramine (hmt) and malonic acid with precipitated

Table 2. Final atomic coordinates and equivalent isotropic thermal parameters (Å^2) for non-hydrogen atoms. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	Site	x	y	z	U_{eq}
1					
Mn	4*d*	1/2	0.69596(3)	0.5051(1)	0.0179(2)
O(1)	8*e*	0.7217(3)	0.6380(1)	0.6390(4)	0.0275(5)
O(2)	8*e*	0.8144(3)	0.7349(1)	0.8385(4)	0.0296(5)
C(1)	8*e*	0.8335(3)	0.6675(2)	0.7464(4)	0.0193(5)
C(2)	4*d*	0	0.6180(2)	0.7714(7)	0.0239(9)
O(3)	4*d*	1/2	0.7946(2)	0.7284(5)	0.0286(8)
N(1)	4*d*	1/2	0.5771(2)	0.3130(5)	0.0180(6)
C(3)	2*a*	1/2	1/2	0.4302(8)	0.018(1)
C(4)	8*e*	0.6567(4)	0.5744(2)	0.1893(5)	0.0240(6)
N(2)	4*c*	0.6583(5)	1/2	0.0688(5)	0.0248(7)
C(5)	2*a*	1/2	1/2	−0.0461(8)	0.029(1)
2					
Cu	4*d*	1/2	0.69148(8)	0.5021(3)	0.0185(5)
O(1)	8*e*	0.720(1)	0.6351(4)	0.646(1)	0.039(2)
O(2)	8*e*	0.810(1)	0.7410(5)	0.838(1)	0.045(2)
C(1)	8*e*	0.835(2)	0.6699(7)	0.753(2)	0.035(3)
C(2)	4*d*	0	0.620(1)	0.782(3)	0.038(4)
O(3)	4*d*	1/2	0.7884(7)	0.698(2)	0.034(2)
N(1)	4*d*	1/2	0.5795(7)	0.330(2)	0.017(2)
C(3)	2*a*	1/2	1/2	0.451(2)	0.016(4)
C(4)	8*e*	0.659(1)	0.5760(6)	0.204(1)	0.025(2)
N(2)	4*c*	0.657(2)	1/2	0.083(2)	0.025(2)
C(5)	2*a*	1/2	1/2	−0.035(3)	0.026(5)

Table 3. Selected interatomic distances (Å) and bond angles (°) for **1** and **2**.

	1	**2**		**1**	**2**
M–O(1)	2.098(2)	2.077(9)	O(1)–M–O(1)$^{\#2}$	97.3(1)	94.9(5)
M–O(1)$^{\#2}$	2.098(2)	2.077(9)	O(1)–M–O(2)$^{\#3}$	93.43(9)	93.5(4)
M–O(2)$^{\#3}$	2.147(3)	2.099(9)	O(1)–M–O(2)$^{\#4}$	169.2(1)	171.5(4)
M–O(2)$^{\#4}$	2.147(3)	2.099(9)	O(1)–M–O(3)	86.3(1)	85.7(4)
M–O(3)	2.333(4)	2.12(1)	O(1)–M–N(1)	87.36(8)	89.1(3)
M–N(1)	2.408(4)	2.18(1)	O(2)$^{\#3}$–M–O(2)$^{\#4}$	75.8(1)	78.1(5)
C(1)–O(1)	1.240(4)	1.26(1)	O(2)$^{\#3}$–M–O(3)	95.3(1)	93.8(4)
C(1)–O(2)	1.296(4)	1.29(1)	O(2)$^{\#3}$–M–N(1)	92.3(1)	92.2(4)
			O(3)–M–N(1)	170.4(1)	172.4(5)
			O(1)–C(1)–O(2)	127.9(2)	126.8(8)

Symmetry codes: #1 = $-x+3/2$, $-y+3/2$, $z+1/2$; #2 = $-x+1$, y, z; #3 = $-x+3/2$, $-y+3/2$, $z-1/2$; #4 = $x-1/2$, $-y+3/2$, $z-1/2$; #5 = $-x+2$, y, z; #6 = $-x+1$, $-y+1$, z; #7 = x, $-y+1$, z.

$M(OH)_{2-2x}(CO_3)_x \cdot yH_2O$ (M = Mn, Cu) in aqueous methanol. The low synthetic yield of **2** reflects the poor solubility of $Cu(OH)_{2-2x}(CO_3)_x \cdot yH_2O$. In the synthesis of the copper complex, no $[Cu_4(hmt)(C_3H_2O_4)_4] \cdot 7H_2O$ was isolated, which was reportedly prepared by reaction of hmt, copper(II) perchlorate hexahydrate and disodium malonate in a 1 : 1 : 1 mol ratio in water [12].

3.2. *Structure description*

Both title compounds are isostructural with $Co_2(hmt)(H_2O)_2(C_3H_2O_4)_2$ [12] and $Cd_2(hmt)(H_2O)_2(C_3H_2O_4)_2$ [13]. As shown in figure 1, the metal atoms in **1** and **2** lie

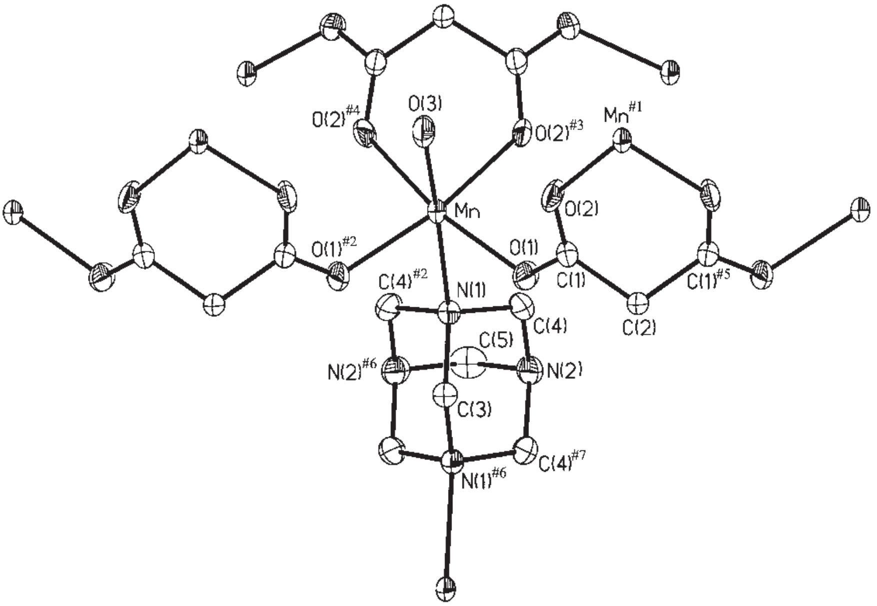

Figure 1. Coordination environment of Mn(II) in **1** together with atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

in a distorted octahedral environment with an NO_5 donor set, coordinated by one aqua ligand, one hexamethylenetetramine ligand and three malonate anions. Four equatorial M–O bond distances to the carboxylate oxygen atoms range from 2.098 to 2.147 Å for **1** (2.077 to 2.099 Å for **2**). Axial bond distances to aqua oxygen and hmt nitrogen atoms are, respectively, 2.333 and 2.408 Å for **1** (2.12 and 2.18 Å for **2**). *Cisoid* bond angles fall in the ranges 75.8–97.3° and 78.1–94.9° for **1** and **2**, respectively, and *transoid* angles are 169.2° and 170.4° for **1**, and 171.5° and 172.4° for **2** (table 3), showing significant deviation from the ideal values. In comparison with cadmium and cobalt analogues [12,13], and with the present copper malonate complex, distortion of the coordination geometry around Mn in **1** is significant.

Bond distances and angles of the malonate anions and hmt ligands in **1** and **2** fall in the usual range [14–17]. Malonate anions function as tetradentate ligands, chelating one metal atom to form a six-membered ring adopting a boat conformation and bridging two metal atoms through non-chelating carboxylate oxygen atoms. The C–O bond length to the chelating oxygen atom is substantially longer than that to the bridging one (table 3). Hmt acts as a bidentate, bridging metal ions along the b axis.

In **1** and **2**, the divalent metal ions are linked by malonate anions to form open 2D layers with a (4, 4) topology (figure 2). The resulting 2D layers are arranged parallel to (010) and pillared by hmt ligands to form a 3D framework with channels extending in the [001] direction. The channels are too small to accommodate any guest molecules.

3.3. *Magnetic properties of 1*

The magnetic behaviour of **1** is depicted in figure 3 in the form of χ_m^{-1} and μ_{eff} *versus* T with χ_m^{-1} being the inverse molar magnetic susceptibility per Mn^{2+} ion and T the

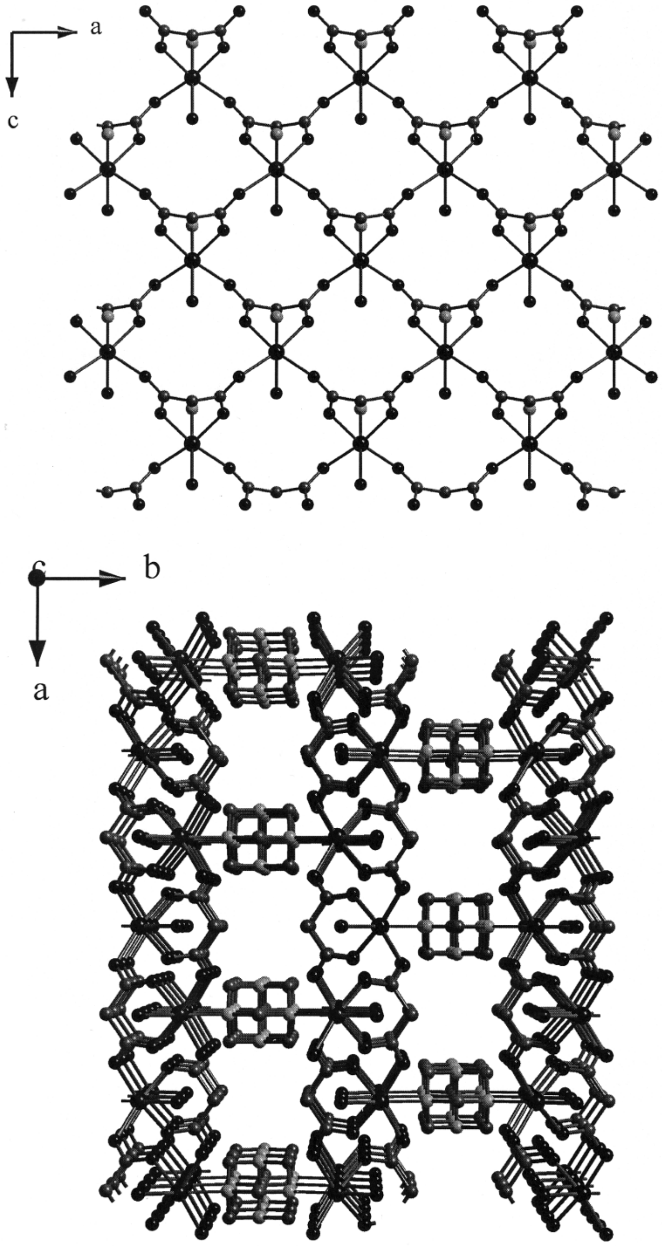

Figure 2. 2D layer of Mn ions interconnected by malonate anions in **1** (upper) and a view of the crystal structure of **1** along [001] (below).

temperature. Effective magnetic moments were calculated using the equation $\mu_{\mathrm{eff}} = 2.828(\chi_{\mathrm{m}}T)^{1/2}$. The effective magnetic moment at room temperature is $5.94\,\mu_{\mathrm{B}}$, equal to the spin-only value of ($5.92\,\mu_{\mathrm{B}}$) expected for an isolated Mn ion ($S = 5/2$) [9]. As the temperature is lowered to 115 K, μ_{eff} remains essentially constant and then decreases gradually, indicative of antiferromagnetic coupling between Mn^{2+} ions.

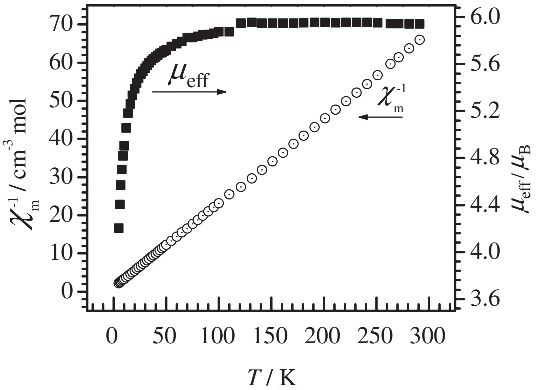

Figure 3. Temperature dependence of inverse susceptibility (χ_m^{-1}) and effective magnetic moment (μ_{eff}) of **1** (χ_m is the magnetic susceptibility per mol of Mn^{2+} ion and the magnetic moments were calculated using the equation $\mu_{eff} = 2.828(\chi_m T)^{1/2}$).

Over the temperature range 5–300 K, the compound **1** obeys the Curie–Weiss law $\chi_m(T-\theta) = 4.521(6)\,cm^3\,mol^{-1}\,K$ with the Weiss constant θ equal to $-4.8(2)$ K.

Supplementary data

Crystallographic data (excluding structure factors) for the structures in this article have been deposited with Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 256349 (**1**) and CCDC 256350 (**2**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

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