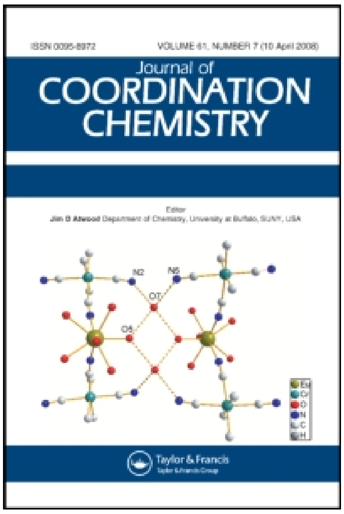

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, Crystal Structure and Magnetic Property of $[Mn_2(mal)_2(H_2O)_2(\mu_2\text{-}hmt)]$_n: A Novel Three-Dimensional Network Self-Assembled by hmt (hmt = Hexamethylenetetramine and mal = Malonate)

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To cite this Article Liu, Qi , Li, Baolong , Xu, Zheng , Sun, Xiaoqiang , Yu, Kai-Bei and Li, Yi-Zhi(2003) 'Synthesis, Crystal Structure and Magnetic Property of $[Mn_2(mal)_2(H_2O)_2(\mu_2\text{-}hmt)]$*_n*: A Novel Three-Dimensional Network Self-Assembled by hmt (hmt = Hexamethylenetetramine and mal = Malonate)', Journal of Coordination Chemistry, 56: 9, 771 — 777

To link to this Article: DOI: 10.1080/0095897031000100043
URL: http://dx.doi.org/10.1080/0095897031000100043

J. Coord. Chem., Vol. 56, No. 9, 15 June 2003, pp. 771–777

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SYNTHESIS, CRYSTAL STRUCTURE AND MAGNETIC PROPERTY OF $[Mn_2(mal)_2(H_2O)_2(\mu_2\text{-hmt})]_n$: A NOVEL THREE-DIMENSIONAL NETWORK SELF-ASSEMBLED BY hmt (hmt = HEXAMETHYLENETETRAMINE AND mal = MALONATE)

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(Received 24 January 2002; Revised 18 July 2002; In final form 30 January 2003)

A novel three-dimensional coordination polymer $[Mn_2(mal)_2(H_2O)_2(\mu_2\text{-hmt})]_n$ (hmt = hexamethylenetetramine, and mal = malonate) was synthesized and characterized by elemental analysis, crystal structure, IR, TG-DTA and magnetic susceptibility. The compound $[Mn_2(mal)_2(H_2O)_2(\mu_2\text{-hmt})]_n$ crystallizes in the orthorhombic system, space group 12 mm, with $a = 7.1059(11)$, $b = 7.6986(6)$, $c = 15.9824(13)$ Å, and $Z = 2$. Mn(II) ion has octahedral geometry coordinated by four oxygen atoms from three malonate, one oxygen atom of water and one nitrogen atom of hmt ligand. The two oxygen atoms of each malonate coordinate to the same Mn(II) ion and the other two oxygen atoms connect to two adjacent Mn(II) ions to form an infinite layer. These layers are bridged by the μ_2-hmt ligands to form a three-dimensional structure. The magnetic susceptibility data show that there is an antiferromagnetic exchange interaction in the title compound.

Keywords: Crystal structure; Three-dimensional manganese(II) compound; Malonate; Hexamethylenetetramine; Magnetic property

INTRODUCTION

Recently, there has been growing interest in "nanoporous" molecular crystals, which, in principle, can provide molecular scale voids with controlled sizes, shapes, and chemical environments that may be exploited for separations, shape selective catalysis

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ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/0095897031000100043

and optoelectronics [1]. It is a great challenge for crystal engineers to synthesize three-dimensional compounds (3D) with nanoporous and non-interpenetrating structures. In order to obtain 3D functional materials, a synthetic method has been adopted recently by combining octahedral metal centers with suitable polydenate ligands. For instance, the complex $[Ag(pyrazine)_3]SbF_6$ is sustained by octahedral Ag(I) cations and pyrazine ligands [2], $[Zn_4O(bdc)_3]$(bdc = benzene-1,4-dicarboxylate) [3] and $[Cu(4,4'\text{-bipy})_2][SiF_6]_2$ (bipy = bipyridine) [4] contain octahedral coordinated Zn(II) and Cu(II), respectively, all are coordination polymers. As a potential tetradenate ligand, hmt has been used to connect Ag(I), Cd(II), Hg(II), Zn(II) and Ni(II) ions to form multidimensional coordination polymers [5–8]: $[Ag(hmt)]PF_4 \cdot H_2O$ and $[Ag_4(hmt)_3(H_2O)](PF_6)_4 \cdot 3EtOH$ with 3D networks, $[Ag_2(\mu_4\text{-hmt})(SO_4)(H_2O)] \cdot 4H_2O$ with a non-interpenetrating 2D network, $[Ag_2(\mu_3\text{-hmt})(CF_3SO_3)(H_2O)](CF_3SO_3) \cdot H_2O$ with a 2D structure, $[Cd(tcm)(hmt)(H_2O)](tcm)$ (tcm = tricyanomethanide, $C(CN)_3{}^-$) with a rutilelike structure, $[Hg(hmt)_{1/2}Br]$ with a 3D network, and $[Ni(hmt)(NCS)_2(H_2O)_2]_n$ with a 2D network linked by hydrogen bonds [5–8]. On the other hand, malonate, a flexible ligand with four potential coordinating oxygen atoms, has been used to assemble coordination polymers such as $[Cu_2(C_3H_2O_4)_2(H_2O)_2(4,4'\text{-bpy})] \cdot H_2O$ [9] and $[MnCu(mal)_2(H_2O)_4] \cdot 2H_2O$ [10]. Considering that the formation of multidimensional framework depends not only on the coordination geometry at the metal centers and the bridging ligands but also the nature of the anion [5], a new supramolecular architecture *via* self-assembly of malonate, hmt and octahedral Mn(II) ion is of interest. We report herein the synthesis, crystal structure and magnetic property of a 3D coordination polymer $(Mn_2(mal)_2(H_2O)_2(\mu_2\text{-hmt})]_n$ (**1**) with channels.

EXPERIMENTAL

Materials and Physical Measurements

Hexamethylenetetramine (hmt) and $MnCl_2 \cdot 4H_2O$ were used as purchased. Elemental analyses (C, H, N) were determined on a Perkin-Elmer 2400 microanalysis instrument. An IR absorption spectrum (KBr pellet) was recorded on a Nicolet FTIR 170X spectrophotometer. Variable-temperature magnetic susceptibilities were determined on a SQUID Quantum Design MPMS-2 magnetometer. Diamagnetic corrections were made using Pascal's constants.

Preparation of $[Mn_2(mal)_2(H_2O)_2(\mu_2\text{-hmt})]_n$

$MnCl_2 \cdot 4H_2O$ (1 mmol) was added to an aqueous solution (4 mL) containing malonic acid (1 mmol) and NaOH (2 mmol) with stirring until all $MnCl_2 \cdot 4H_2O$ was dissolved. Then, 6 mL aqueous solution of hmt (1 mmol) was added to the solution. The resulting colorless solution was allowed to stand at ambient temperature for several days, yielding colorless crystals in 45% yield. Anal. calcd. for $C_{12}H_{20}Mn_2N_4O_{10}$(%) C, 29.38; H, 4.08; N, 11.42. Found: C, 29.29; H 4.11; N, 11.44. IR spectrum: 3237 cm^{-1} (s, br), 2978 (m), 1572 (s), 1470 (w), 1460 (m), 1445 (s), 1393 (w), 1371 (m), 1358 (s), 1260 (w), 1243 (m), 1226 (m), 1160 (w), 1054 (w), 1026 (m), 992 (s), 970 (w), 802 (w), 710 (m), 675 (m), 659 (m), 576 (m), 515 (w).

TABLE I Summary of crystal data, data collection and structure refinement for the complex $[Mn_2(mal)_2(H_2O)_2(\mu_2\text{-hmt})]_n$

Formula	$C_{12}H_{20}Mn_2N_4O_{10}$
M_r	490.20
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	12 mm
Unit cell dimensions	$a = 7.1059(11)$ Å, $\alpha = 90°$ $b = 7.6986(6)$ Å, $\beta = 90°$ $c = 15.9824(13)$ Å, $\gamma = 90°$
Volume	874.32(17) $Å^3$
Z	2
Density (calculated)	1.862 Mg/m^3
Absorption coefficient	1.508 mm^{-1}
$F(000)$	500
Crystal size	0.52 × 0.48 × 0.16 mm
θ range	2.55–27.98°
Index ranges (h, k, l)	$-1/9$, $-10/10$, $-21/21$
Reflections collected	2477
Independent reflections	721 (R_{int})
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	721/4/80
Goodness-of-fit on F^2	1.132
Final R, wR indices ($I > 2\sigma(I)$)	0.0188, 0.0479
R, wR indices (all data)	0.0189, 0.0480
Extinction coefficient	0.0110(13)
Largest diff. peak and hole	0.275 and -0.508 $eÅ^{-3}$

X-ray Structure Determination of $[Mn_2(mal)_2(H_2O)_2(\mu_2\text{-hmt})]_n$*

A colorless crystal with dimensions of 0.52 × 0.48 × 0.16 mm was mounted on a Siemens P4 diffractometer for data collection by graphite-monochromatic Mo-Kα radiation ($\lambda = 0.71073$ Å) at 298(2)K; 2477 reflections were collected of which 721 were independent and 716 were observed with $F_0 > 4\sigma(F_0)$. Data were corrected for empirical absorption. The structure was solved by direct methods followed by difference Fourier synthesis. The structure was refined by full-matrix least-squares techniques with anisotropic thermal parameters for all the non-hydrogen atoms.

All calculations were performed on an IBM PC computer with Siemens SHELXL-97 program package. The final R value is 0.0188 and refinement with complete data set yielded $wR = 0.0479$. The scattering factors were taken from [11]. The crystallographic data are summarized in Table I.

RESULTS AND DISCUSSION

Crystal Structure

The extended symmetrical Complex **1** has a 3D network, which is constructed from the building block unit shown in Fig. 1. The Mn and Mn1F atoms are located in an octahedral environment, formed by four oxygen atoms from three malonate, one oxygen

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*CCDC code 167163.

atom of water and one nitrogen atom of hmt ligand, with bond angles N1–Mn–O1 95.42(6)°, O1–Mn–O3 91.82(6)°, O1A^{i}–Mn–O1 82.92(8)° (i, symmetry code: x, $-y$, z), O1–Mn–O2B^{ii} 86.46(6)° (ii, symmetry code: $x-1/2$, $-y+1/2$, $-z-1/2$), O2C^{iii}–Mn–O3 89.28(5)° (iii, symmetry code: $x-1/2$, $y-1/2$, $-z-1/2$). The bond length of Mn–N1 (2.336(2) Å) is shorter than that of Mn–N (hmt) (2.4213(13)Å) in $[Mn(NCS)_2(hmt)_2(H_2O)_2][Mn(NCS)_2(H_2O)_4] \cdot 2H_2O$ [12]. The values of the Mn–O (malonate) bond distance are 2.1583(14) and 2.1611(13) Å, which is slightly shorter than that of a previously reported compound (2.164(4) and 2.212(3) Å) [10].

As we can see in Fig. 2, two oxygen atoms of each malonate coordinate to the same Mn(II) ion and the other two oxygen atoms connect to two adjacent Mn(II) ions to form an infinite layer. These layers are further bridged by the μ_2-hmt ligands, resulting in a three-dimensional polymer with 2.62 × 5.35 Å effective channels. The distance of Mn···Mn1F is 6.265 Å, adjacent the nearest Mn···Mn distance is 5.515 Å. No solvent molecules are clathrated in the channels as shown in Fig. 3. The coordinated water molecules are all linked with oxygen atoms of malonates by hydrogen bonds (O_3–$H_4 \cdots O_1$ 2.7124 (4) Å). One of the most noticeable structural features of Complex **1** is that each hmt has two uncoordinated N atoms which might serve as Lewis base sites in catalytic reactions [13].

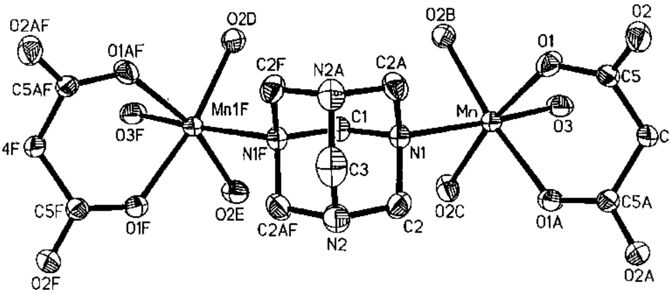

FIGURE 1 Metal ion coordination geometry and atom-numbering scheme for **1**: atoms are shown as 30% thermal ellipsoids. Selected bond distances (Å) and angles (°): Mn–O1 2.1583(14), Mn–O3 2.234(2), Mn–O1A 2.1583(14), Mn–O2B 2.1611(13), Mn–N1 2.336(2), O1A–Mn–O1 82.92(8), O1A–Mn–O2B 169.36(6), O1–Mn–O2B 86.46(6), O1–Mn–O3 91.82(6), O2C–Mn–O3 89.28(5), O1–Mn–N1 95.42(6), O3–Mn–N1 170.33(8).

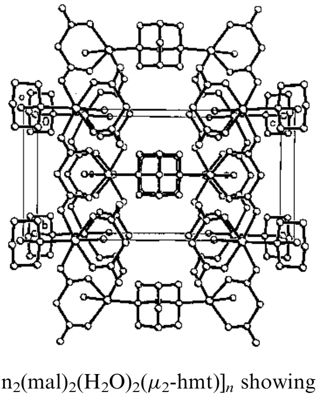

FIGURE 2 Structure of $[Mn_2(mal)_2(H_2O)_2(\mu_2\text{-hmt})]_n$ showing the channels along the a-axis.

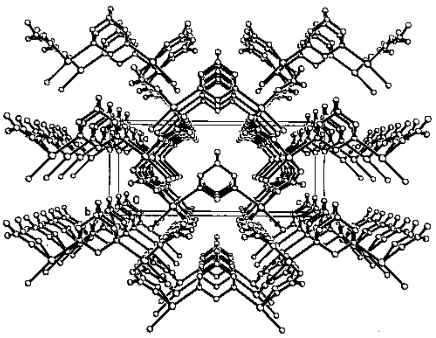

FIGURE 3 Packing diagram for $[Mn_2(mal)_2(H_2O)_2(\mu_2\text{-hmt})]_n$ along the *b*-axis.

To the best of our knowledge, there are only two examples of complexes containing hmt the multidimensional Mn(II) compounds, $[Mn(CO)_3(\mu\text{-OH})_4]\cdot$hmt [14], and $[Mn(NCS)_2\ (hmt)_2(H_2O)_2][Mn(NCS)_2(H_2O)_4]\cdot 2H_2O$ [12]. A 3D coordination polymer containing both μ_2-hmt and flexible malonate like Complex **1** is unprecedented.

IR Spectrum

The strong broad absorption band in the region 3500–3000 cm^{-1} corresponds to ν (OH) of the coordinated water molecules (3237 cm^{-1}) [15]. The 2979 cm^{-1} band is attributed to the ν (CH_2) of methylene groups is hmt [8]. The strong peaks at 1572 cm^{-1}, and 1445, 1358 cm^{-1} are the ν_a (OCO), and ν_s (OCO) stretching modes of malonate, respectively, while medium intensity absorption at 710 and 695 cm^{-1} are the δ (OCO) bent vibration of malonate. The difference values of 214 and 127 cm^{-1} defined as the difference between ν_a (OCO) and ν_s (OCO) indicate that both bridging and chelating modes of the malonate are present [15] as proved by the X-ray crystal structure analysis of $[Mn_2(mal)_2(H_2O)_2(\mu_2\text{-hmt})]_n$.

Thermogravimetric Study

The TG-DTA curve for Complex **1** shows that coordinated water molecules are lost in the temperature range 225–250°C with weight loss of 8.0%, which corresponds to two water molecules per formula unit (7.3%). Then hmt was lost in the range of 290–310°C with 28% weight loss, which is close to the theoretical value (28.6). The sample decomposes completely at about 390°C and the pyrolysis product is MnO with 30% remaining.

Magnetic Property

Variable temperature magnetic susceptibility measurements of a powder sample were performed in the range of 300 K to 5 K with a SQUID QUANTUM Design MPMS-2 magnetometer. The $1/\chi_m$ and μ_{eff} *vs* T plots for Complex **1** are shown in Fig. 4. The Weiss constant determined from the plot based on the equation $1/\chi_m = C(T-\theta)$ is -6 K, which shows that overall antiferromagnetic coupling exists between magnetic centers *via* the bridging malonate and hmt. The effective magnetic moment (μ_{eff}) per $[Mn(II)_2]$ unit is 8.21 μ_B at room temperature, which is less than the spin-only value of Mn(II) ions. As the temperature decreases, the magnetic moment first decreases gradually and finally sharply decreases to 5.84 μ_B at 5 K.

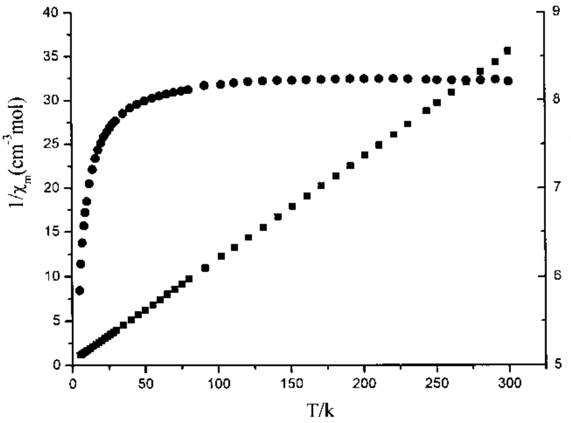

FIGURE 4 The $1/\chi_m$ and μ_{eff} *vs* T plots for Complex **1** (■ and ● stand for $1/\chi_m$ and μ_{eff} respectively).

Acknowledgement

We thank the National Natural Science Foundation of China and the Science and Technology Foundation of Jiangsu Institute of Petrochemical Technology for financial support.

Supplementary Material

Crystallographic data for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. 167163.

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