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The rational syntheses of manganese-chloranilate compounds: crystal structures and magnetic properties

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Abstract

 $[Mn(CA)(terpy)]_n$ (1) and $\{[Mn(CA)(bipym)_{0.5}(H_2O)](H_2O)(C_2H_5OH)\}_n$ (2) $(H_2CA = chloranilic acid, terpy = 2,2':6',2''-ter$ pyridine and bipym = 2,2'-bipyrimidine) have been synthesized and their crystal structures determined by a single-crystal X-raydiffraction. Compound 1 is made up of infinite chains of chloranilate-bridged manganese(II), affording a zig-zag pattern, withterpyridine ligands stacking between the chains. Compound 2 has a novel honeycomb layered structure, where each hexagonconsists of six Mn(II) ions, four CA²⁻ and two bipym ligands. Mn(II) ions in both compounds are unusually hepta-coordinated.Magnetic susceptibility measurements of both compounds show weak antiferromagnetic coupling between the nearest Mn(II) ions.© 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Metal-organic hybrid compounds with higher dimensional network structures are currently under intense investigation in the field of molecule-based magnets [1-3]. The proper choice of bridging ligands is important since they affect the magnetic exchange pathways between paramagnetic metal centers and influence the magnetic strength and behavior of the materials, as well as the dimensionality of the assembled compounds. Usage of mixed organic ligands with the suitable metal ions helps to obtain predictable molecular architecture. In this context manganese assembled structures of chloranilic acid (H₂CA) are rationally designed by using 2,2':6',2"-terpyridine (terpy) and 2,2'-bipyrimidine (bipym). The dianion of chloranilic acid (CA^{2-}) consists of two allyl systems connected by C-C single bonds, with four oxygen atoms partially negatively charged. This potentiality allows for the coordination of transition-metal ions through CA²⁻ bridges and permits the probable propagation of magnetic super-exchange interactions between the paramagnetic centers [4]. Moreover, CA^{2-} is able to form a monomeric building block, chain, and layer structures of various metal ions [5-7]. Extensive magneto-structural work has also been carried out with metal complexes containing bipym, which is known to transmit strong antiferromagnetic coupling when coordinating in the bis-bidentate mode to the metal ions lying in the same plane of nitrogen atoms [8-11]. On the other hand, nitrogen atoms containing planar organic molecule terpy can act as a non-bridging neutral ligand. However, terpy and bipym with the common ligand, H₂CA, control the dimensionality of the crystal structures and help to design predictable molecular architectures. In this regard, two compounds of manganesechloranilate system, $[Mn(CA)(terpy)]_n$ (1) and $\{[Mn(CA)(bipym)_{0.5}(H_2O)](H_2O)(C_2H_5OH)\}_n$ (2) have been synthesized. Compound 1 consists of CA2--

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bridged chain of Mn(II) and compound **2** is made up of honeycomb layer with $[Mn(CA)(bipym)_{0.5}(H_2O)]$ units. In this paper we present the crystal structures and the magnetic properties of the two compounds.

2. Experimental

2.1. Materials

2,2'-Bipyrimidine, 2,2':6',2"-terpyridine, chloranilic acid, manganese chloride and manganese perchlorate were purchased from commercial sources and used as received.

Table 1 Crystallographic data for 1 and 2

	1	2
Formula	MnO ₄ Cl ₂ N ₃ C ₂₁ H ₁₁	MnO ₇ Cl ₂ N ₂ C ₁₂ H ₁₃
Formula weight	495.18	423.09
Crystal system	triclinic	triclinic
Space group	$P\overline{1} (\#2)$	$P\overline{1}$ (#2)
Diffractometer	Rigaku AFC7R	Rigaku AFC7R
a (Å)	10.259(2)	9.903(3)
b (Å)	10.250(2)	11.165(2)
c (Å)	9.997(2)	8.778(2)
α (°)	98.00(2)	111.97(1)
β (°)	113.76(1)	97.77(2)
γ (°)	85.17(2)	69.86(2)
V (Å ³)	952.2(3)	845.1(4)
Ζ	2	2
$D_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.727	1.663
μ (Mo K α) (cm ⁻¹)	10.10	11.33
F(000)	498.00	428.00
R, wR_2^{a}	0.052; 0.158	0.040; 0.126
$2\theta_{\max}$ (°)	55.0	55.0
Goodness-of-fit	1.03	1.07

^a $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|;$ $R_w = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w (F_o^2)^2]^{1/2}$ where $w = [\sigma^2 (F_o^2) + (0.0643P)^2 + 0.0000P]^{-1}$ (1); $[\sigma^2 (F_o^2) + (0.0672P)^2 + 0.6178P]^{-1}$ (2) and $P = (F_o^2 + 2F_c^2)/3$.

Table 2 Selected bond distances (Å) and angles (°) for ${\bf 1}$

Bond distances				
Mn-O(1)	2.188(3)	Mn-O(2)	2.293(4)	
Mn-O(3)	2.260(4)	Mn-O(4)	2.324(3)	
Mn-N(1)	2.361(3)	Mn-N(2)	2.256(3)	
Mn-N(3)	2.312(4)			
Bond angles				
O(1)-Mn-O(2)	71.9(1)	O(3)-Mn-O(4)	69.3(1)	
O(1)-Mn-O(3)	106.4(1)	O(2)-Mn-O(3)	158.5(1)	
O(1)-Mn-O(4)	82.2(1)	N(1)-Mn-N(2)	70.3(1)	
O(1)-Mn-N(1)	87.3(1)	O(2)-Mn-O(4)	130.1(1)	
N(2)-Mn-N(3)	70.9(1)	O(1)-Mn-N(3)	123.7(1)	
O(2)-Mn-N(1)	84.4(1)	O(3)-Mn-N(3)	114.3(1)	
O(2)-Mn-N(3)	82.2(1)	O(1)-Mn-N(2)	150.7(1)	
O(2)-Mn-N(2)	86.8(1)	O(3)-Mn-N(2)	86.0(1)	

2.2. Syntheses

2.2.1. $[Mn(CA)(terpy)]_n$ (1)

To the solution of terpyridine (0.116 g) in 1:1 (v/v) EtOH/H₂O (100 ml), manganese chloride hexahydrate (0.063 g) was mixed. After stirring for a few minutes a yellow powder of Mn(terpy)Cl₂ was precipitated out from the mixture (yield 85%). Then a solution of sodium salt of chloranilic acid (0.1 mM) in 1:1 (v/v) EtOH/H₂O was added to an aqueous solution of [Mn-(terpy)Cl₂] (0.1 mM) in the tubes without mixing the two solutions. Red plate-like crystals began to form in a week. One of these crystals was used for X-ray crystallography.

2.2.2. $\{[Mn(CA)(bipym)_{0.5}(H_2O)](H_2O)(C_2H_5OH)\}_n$ (2)

An aqueous solution of manganese perchlorate hexahydrate (0.26 g, 1 mmol) was transferred to a glass tube. Then a mixture of 2,2'-bipyrimidine and chloranilic acid (0.20 g, 1 mmol) in 1:1 (v/v) EtOH/H₂O was poured into the tube without mixing the two solutions. Red-purple plate crystals began to form at ambient temperature in a week. One of these crystals was used for X-ray crystallography.

2.3. Crystallographic data collection and refinement of the structures

Crystallographic data for the complexes 1 and 2 were collected on a Rigaku AFC7R diffractometer with Mo K α radiation at room temperature. Crystallographic data for the complexes are given in Table 1. The structures were solved by direct methods (Rigaku texsan crystallographic software package of Molecular Structure Corporation) and refined with full-matrix least-squares technique (SHELXL-93) [12] to R = 0.052, $wR_2 = 0.158$ (1); R = 0.040, $wR_2 = 0.126$ (2). All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were located in the Fourier maps. However, they were not refined.

2.4. Physical measurements

Temperature dependence of magnetic susceptibility of the polycrystalline samples were measured from 2 to 300 K using a Quantum Design Model MPMS computer-controlled SQUID magnetometer. Corrections for the diamagnetism of the complex were estimated from Pascal's table.

3. Results and discussion

3.1. Crystal structures

The structure of compound 1 is made up of neutral [Mn(CA)(terpy)] units. Each Mn(II) ion in 1 is unusu-



Fig. 1. (a) ORTEP drawing of 1 with the atom numbering scheme and thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. (b) View of a one-dimensional chain formed by 1.

ally hepta-coordinated [13,14]; four oxygen atoms from the two CA^{2-} and three nitrogen atoms from one terpyridine. Selected bond distances and angles of the compound are listed in Table 2 and an ORTEP [15] drawing with the atom numbering scheme is shown in Fig. 1(a). The geometry around the Mn(II) ion is not ideal, pentagonal bipyramidal as found for the seven coordinated Mn(II) ions [14], but rather distorted octahedral. The CA^{2-} bridges Mn(II) ions, which leads to infinite chains exhibiting a zig-zag pattern along the (0,1, -1) direction with terpyridine ligands stacking between the chains (Fig. 1(b)). The nearest C-C distance of the stacked terpyridine ligands is 3.57 Å. This stacking interaction makes three-dimensional packing structure. The electroneutrality of the chain is supported by the three nitrogen atoms of the terminal terpyridene. There are two types of CA^{2-} in the chain, but Mn–Mn distances through the CA^{2-} are almost the same; average distance is 8.39 Å. However, this Mn–Mn separation is a little larger than the Mn–Mn (8.201 Å) separation in the chain of $\{[Mn(CA)-(H_2O)_2](H_2O)\}_n$ [16]. Two CA^{2-} rings around a manganese ion in 1 are not parallel, dihedral angle being 78.53°. Thus, the chain becomes zig–zag.

Compound **2** is formally made up of neutral $[Mn(CA)(bipym)_{0.5}(H_2O)]$ units and interstitial water

and ethanol molecules. The Mn(II) ion in **2** is also unusually hepta-coordinated; two nitrogen atoms of bipym, four oxygen atoms of two CA^{2-} anions and one oxygen from a water molecule. An ORTEP drawing of **2** with the atom numbering scheme is shown in Fig. 2(a) and the selected bond distances and angles are listed in Table 3. Two coordinated CA^{2-} are not in the same plane of bipym. The dihedral angles between bipym and CA^{2-} planes are 0.00 and 88.15°. Two CA^{2-} rings make the zig-zag chain, which is very similar to that of 1. The seven-coordinated manganese atom adopts the distorted pentagonal bipyramidal geometry. Manganese atoms make parallel sheets linked by two CA^{2-} anions and one bipym ligand. Each sheet is made up of CA^{2-} bridged corrugated chains of manganese ions that are connected by bipym ligands, leading to the formation of a honeycomb network. Thus the two-dimensional polymer, as shown in Fig.



Fig. 2. (a) ORTEP drawing of the 2 with the atom numbering scheme and thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. (b) View of a layer of 2 (hydrogen atoms and solvent molecules have been omitted for clarity).

Table 3								
Selected	bond	distances	(Å)	and	angles	(°)	for	2

Bond distances				
Mn-O(1)	2.222(2)	MnO(2)	2.304(3)	
Mn–O(3)	2.201(2)	Mn–O(4)	2.282(2)	
Mn-O(5)	2.175(3)	Mn-N(1)	2.390(3)	
Mn-N(2)	2.381(3)			
Bond angles				
O(1)-Mn-O(2)	70.69(8)	O(3)-Mn-O(4)	72.02(8)	
O(1)-Mn-O(4)	135.0(1)	O(1)– Mn – $O(3)$	85.59(8)	
O(1)-Mn-O(5)	87.11(9)	O(2)-Mn-O(4)	76.19(8)	
O(2)–Mn–O(3)	101.6(1)	O(2)-Mn-O(5)	84.4(1)	
O(3)–Mn–O(5)	168.48(9)	O(4)-Mn-O(5)	119.27(8)	
N(1)-Mn-N(2)	68.84(9)	O(1)-Mn-N(2)	79.54(9)	
O(3)–Mn–N(1)	99.44(9)	O(3)-Mn-N(2)	83.27(9)	
O(4)-Mn-N(1)	76.56(9)	O(4)-Mn-N(2)	133.10(8)	
O(5)-Mn-N(1)	82.00(10)	O(5)-Mn-N(2)	86.64(10)	



Fig. 3. Temperature dependence of $\chi_{\mathbf{M}}(\Delta)$ and $\chi_{\mathbf{M}}T(\bigcirc)$ of 1. Solid line represents fit of 1 to Fisher one-dimensional chain model.

2(b), extending in the *ab* plane is formed by the repetition of CA^{2-} and bipym-bridged hexagons. The average distance between the nearest Mn(II) ions in the CA^{2-} -bridged chain of **2** is 8.34 Å, which is very similar to that of **1**. One ethanol and one water molecule are located in the hole of each hexagon of the sheets. However, the thermal parameters of the carbon and oxygen atoms of ethanol molecules are too high, which suggests the presence of disorder. The interstitial water molecules are hydrogen-bonded with the coordinated oxygen atoms of CA^{2-} . From the structural view of the two compounds it can be concluded that the Mn–CA²⁻ chain is able to extend its dimensionality with the bridging ligand bipym.

3.2. Magnetic properties

The temperature dependence of the molar magnetic susceptibility $\chi_{\rm M}$ for **1** and **2** are measured over the temperature range 2–300 K in a field of 0.5 T. The $\chi_{\rm M}$ vs. T and $\chi_{\rm M}T$ vs. T plots for **1** are shown in Fig. 3. $\chi_{\rm M}T$ of **1** exhibits a continuous decrease upon cooling, with $\chi_{\rm M}T = 4.4$ at the room temperature. This behavior is the characteristic of antiferromagnetic interaction between high-spin Mn(II) ions through CA²⁻. CA²⁻ mediated antiferromagnetic interaction is well supported by the calculation assuming Heisenberg-type chain using Fisher's formula, scaled to a spin value of 5/2 for Mn(II):

$$\chi_{\rm M} = Ng^2\beta^2 S(S+1)/3kT(1+u)/(1-u)$$

$$u = \operatorname{coth}(2JS(S+1)/kT) - kT/2JS(S+1)$$

where the parameters have their usual meaning. The best fit leads to the following parameters: g = 2.022, J = -0.50 cm⁻¹. The J values of -0.74 and -0.65 cm⁻¹ are reported for the similar CA²⁻ bridged chain of hexacoordinated Mn(II) ions [16]. The absolute value of J in 1 is a little smaller than that reported for these compounds, which maybe due to the larger Mn–Mn separation in 1.

The χ_M vs. *T* and $\chi_M T$ vs. *T* plots for **2** are shown in Fig. 4. The product of the molar susceptibility and temperature, $\chi_M T$ exhibits a continuous decrease upon cooling, with $\chi_M T = 4.4$ at the room temperature. χ_M per Mn(II) ion of the complex **2** shows the antiferromagnetic interaction similar to **1**. The honeycomb layer of **2** consists of CA²⁻ bridged chain connected by bipym, where antiferromagnetic exchange pathways through bipym and CA²⁻ are possible. Both the CA²⁻ and bipym are able to mediate exchange coupling be-



Fig. 4. Temperature dependence of χ_{M} (Δ) and $\chi_{M}T$ (\bigcirc) of **2**. Solid line represents fit of **2** to Fisher one-dimensional chain model.

tween the Mn(II) ions. In this regard, the J values of -0.93 and -0.74 cm⁻¹ have been reported for CA²⁻ and bipym bridged chain structures of Mn(II) ions in $\{[Mn(CA)(H_2O)_2](H_2O)\}_n$ and $[Mn(bipym)(NO_3)_2]$, respectively [16,17]. For compound 2, two simple models can be considered to evaluate the magnitude of the exchange coupling. The first model is based on a Heisenberg-type chain of CA²⁻, in which interchain interactions are treated with the molecular field approximation [18]. The second model is a honeycomb Heisenberg two-dimensional lattice [19]. Attempts to fit the magnetic data of 2 to the second model lead to a bad fit. On the basis of the first model, magnetic data are analyzed using Fischer's formula scaled to a spin value of 5/2 for Mn(II). The best fit for $\chi_M T$ leads to the parameters g = 2.033, J = -0.49 cm⁻¹, J = -0.06cm⁻¹ and z = 2 (solid line in Fig. 4), where the interchain coupling constant J' is associated with bipym. The degree of interaction between the Mn(II) centers through CA²⁻ and bipym is different, which is attributed from the large difference between J and J'values. Moreover, the value of J is almost the same for both compounds 1 and 2. Although the interaction is possible through both CA²⁻ and bipym, the lower value of J' suggests that the effective pathway for the magnetic interaction in 2 is CA^{2-} , not bipym.

4. Conclusions

One of the striking features of the reported two compounds is that 2,2'-bipyrimidine as a bis-bidentate ligand bridges the chloranilate chains of manganese ions making honeycomb layer structure, whereas the tridentate terpyridine with the help of the unusual hepta coordination capability of Mn(II) ions retains the chloranilate chain structure. To our knowledge, **2** is the first compound consisting of the honeycomb layer structure of Mn(II) with CA^{2-} and bipym. To conclude, we can emphasize, based on the structural view of the compounds, that the dimensionality of the crystal structures of the metal-assembled compounds can be designed by the proper choice of the organic ligands. In this strategy, usage of mixed organic ligands help to get predictable molecular architecture to a large extent.

5. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 149139 and 149140. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc. ac.uk).

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