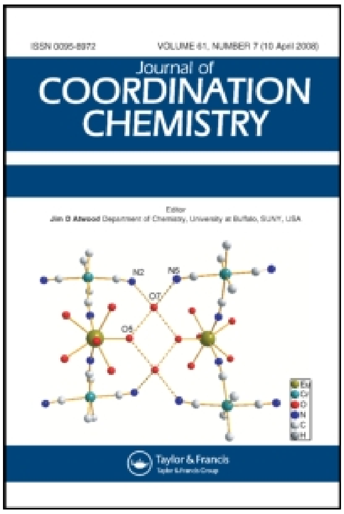

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Synthesis, crystal structure and anti-ferromagnetic behavior of a two-dimensional manganese(II) complex with 3,6-dinitro-1,2,4,5,-benzenetetracarboxylate anion as bridging ligand

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A two-dimensional complex $\{[Mn_2(DBT)(DMF)_4]\cdot 2H_2O\}_n$ ($DBT = 3,6$-dinitro-1,2,4,5- benzenetetracarboxylate anion; $DMF = N,N$-dimethylformamide) has been synthesized and its crystal structure determined by X-ray crystallography. The complex crystallizes in a triclinic system and the space group is $P\bar{1}$ with $a = 9.012(5)$, $b = 9.196(6)$, $c = 9.910(6)$ Å. In the complex there exist two kinds of coordination environments for Mn(II) ions; each DBT coordinates four Mn(II) ions by its four carboxylate groups and in this way a two-dimensional sheet was constructed. The variable-temperature magnetic susceptibility of the complex was measured in the 5–300 K range and the magnetic data indicate that the magnetic interaction between the bridged manganese(II) ions displays an anti-ferromagnetic coupling.

Keywords: Synthesis; Crystal structure; Manganese(II) complex; Magnetism

1. Introduction

The field of molecular magnetism has attracted considerable attention, and major advances have been made in both theoretical description and application as new molecular-based materials. In order to understand magnetic interactions between bridging metal ions many complexes with different bridging ligands have been prepared and their magnetic properties have been studied; special attention has been paid to complexes with polycarboxylatobenzenic anions as bridging ligands [1–9]. However, complexes with DBT as bridging ligand have not been published. Here we report the synthesis, crystal structure and the magnetic properties of the title complex.

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2. Experimental

2.1. *Preparation*

The ligand H_4DBT was synthesized by nitration of 1,2,4,5-tetramethylbenzene and then the product of 3,6-dinitro-1,2,4,5-tetramethylbenzene was oxidized into H_4DBT with potassium permanganate in H_2O solution.

The two-dimensional complex $\{[Mn_2(DBT)(DMF)_4]\cdot 2H_2O\}_n$ was prepared as follows: a dilute NaOH solution was added in drops in a mixture of H_4DBT (0.0441 g, 0.13 mmole) and 5 cm^3 H_2O until the pH reached a value of 5, then $Mn(ClO_4)_2\cdot 6H_2O$ (0.0925 g, 0.26 mmole) and 5 cm^3 DMF were added to the mixture and a clear pale-yellow solution appeared. Pale-yellow single crystals were obtained after the solution rested at room temperature for a few days (yield: 0.0696 g, 69.8%). Anal, Calcd. for $C_{22}H_{32}Mn_2N_6O_{18}$: C, 33.94; H, 4.14; N, 10.80; Mn, 14.12%. Found: C, 34.23; H, 4.46; N, 10.43; Mn, 14.55%. Infrared spectra were recorded with a Bruker I.R. spectrophotometer using KBr discs, and the variable-temperature magnetic susceptibility measurements were performed using microcrystalline powder sample in the 5–300 K range with a SQUID magnetometer and applied magnetic field of 10 K Oe.

2.2. *Crystal structure determination*

A single crystal with dimensions 0.35 × 0.10 × 0.08 mm was selected and the determination of the single crystal was carried out with graphite-monochromatic MoK_α radiation ($\lambda = 0.71073$ Å) on a Bruker Smart-1000 diffractometer using ω scan mode. A total of 4671 reflections were collected in the range of $2.13 \le \theta \le 26.37^\circ$ at 298(2) K, of which 3170 reflections were independent (R(int) = 0.0677) and 1222 reflections with $I > 2\sigma(I)$ were considered to be observed and used in the succeeding refinement. Corrections for *Lp* factors were applied and all non-hydrogen atoms were refined with anisotropic thermal parameters. The final refinement including hydrogen atoms converged to $R = 0.0666$ and $wR = 0.1344$. $w = 1/[\sigma^2(F_O)^2 + (0.0636P)^2 + 0.0000P]$ where $P = (Fo + 2Fo^2)/3$, $S = 0.796$, $(\Delta\rho)_{max} = 0.483\ e/Å^3$, $(\Delta\rho)_{min} = -0.669\ e/Å^3$, $(\Delta/\sigma)_{max} = 0.000$. The programs of structure solution and refinement are SHELXS-97 (Sheldrick, 1990) and SHELXL-97 (Sheldrick, 1997), respectively.

3. Results and discussion

3.1. *Crystal structure*

3.1.1. Crystal data. $C_{22}H_{32}Mn_2N_6O_{18}$, $M = 778.42$, triclinic, space group $P\bar{1}$, $a = 9.012(5)$, $b = 9.196(6)$, $c = 9.910(6)$ Å, $V = 789.6(8)$ Å^3, $Z = 1$, $Dc = 1.637\ g\,cm^{-3}$, $F(000) = 400$, μ (Mo K_α) = 0.889 mm^{-1}. Selected bond distances and angles are listed in table 1.

Figure 1 shows the coordination diagram of the complex with the atom numbering scheme. The coordination environments of Mn(1) and Mn(2) are different with Mn(1) atom coordinated by O(1), O(1A), O(3), O(3A), O(7) and O(7A) atoms with O(7) and O(7A) atoms from two DMF molecules, O(1) and O(3) atoms from two carboxylate groups of a DBT ligand, and O(1A) and O(3A) from two carboxylate groups of another DBT ligand, whereas Mn(2) atom is coordinated by O(2), O(2D),

Table 1. Selected bond lengths (Å) and bond angles (°).

Mn(I)–O(3)	2.078(5)	Mn(I)–O(1)	2.167(4)	Mn(I)–O(7)	2.215(4)
Mn(II)–O(8)	2.138(5)	Mn(II)–O(2)	2.154(4)	Mn(II)–O(9)	2.209(5)

O(3)–Mn(I)–O(1)	87.18(17)	O(3A)–Mn(I)–O(1)	92.82(17)
O(3)–Mn(I)–O(7)	88.80(17)	O(3A)–Mn(I)–O(7)	91.20(17)
O(1)–Mn(I)–O(7)	88.57(16)	O(1A)–Mn(I)–O(7)	91.43(16)
O(8)–Mn(II)–O(2)	92.55(17)	O(8)–Mn(II)–O(2D)	87.45(17)
O(8B)–Mn(II)–O(9)	92.3(2)	O(8)–Mn(II)–O(9)	87.7(2)
O(2D)–Mn(II)–O(9)	93.17(17)	O(2)–Mn(II)–O(9)	86.83(17)

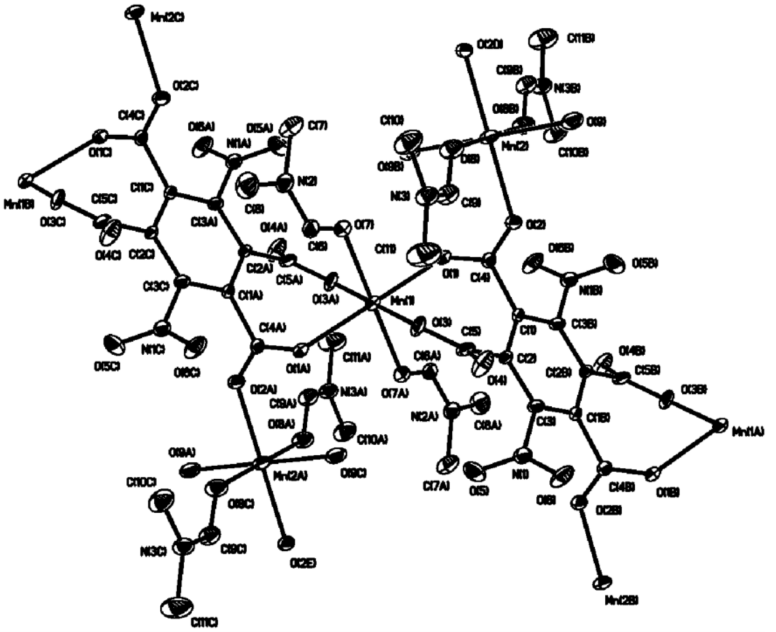

Figure 1. A diagram of the title complex coordination with atom numbering scheme.

O(8), O(8B), O(9) and O(9B) atoms and in which O(9) and O(9B) atoms come from two H_2O molecules, O(8) and O(8B) from two DMF molecules and O(2) and O(2D) from carboxylate groups of two DBT ligands. The bond lengths and associated bond angles dealing with Mn(1) and Mn(2) atoms indicate that both Mn(1) and Mn(2) atoms are located in a distorted octahedral environment. Each plane of the four carboxylate groups deviates seriously from the plane of the benzene, and it obviously arises from the larger volume of carboxylate group. Figure 2 displays the two-dimensional sheet structure, and it indicates that each DBT bridging ligand provides six carboxylate oxygen atoms to coordinate four manganese(II) ions and in this way the two-dimensional sheet structure was formed. Figure 3 shows the unit cell and the arrangement of the sheets in the crystal. Obviously, the two-dimensional sheets extend along the *ac* plane and the sheets pile up along the *b* axis to form a three-dimensional crystal structure. In addition, the inversion center is located in manganese(II) ions and the centre of benzene ring. The deposition number of the crystal at CCDC is 201852.

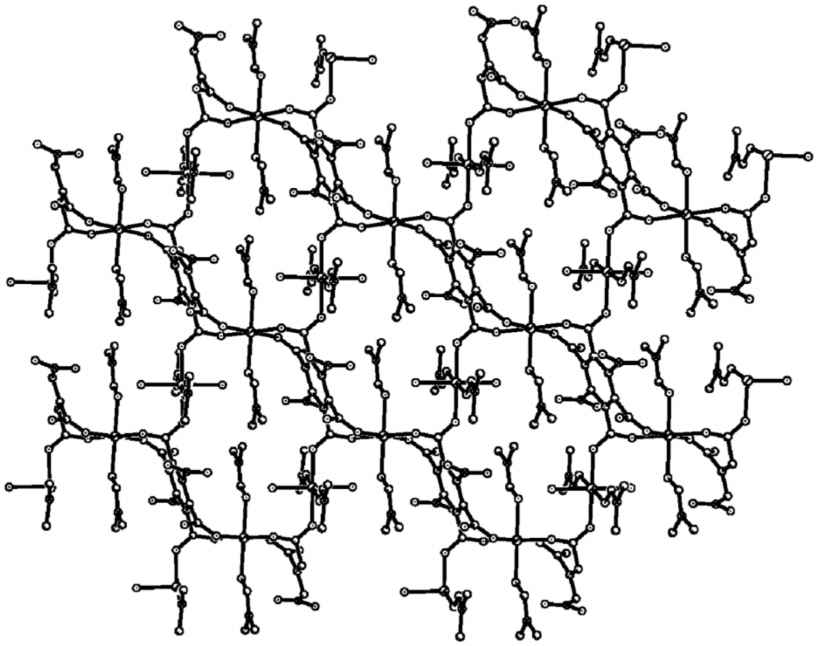

Figure 2. Structure of the two-dimensional sheet.

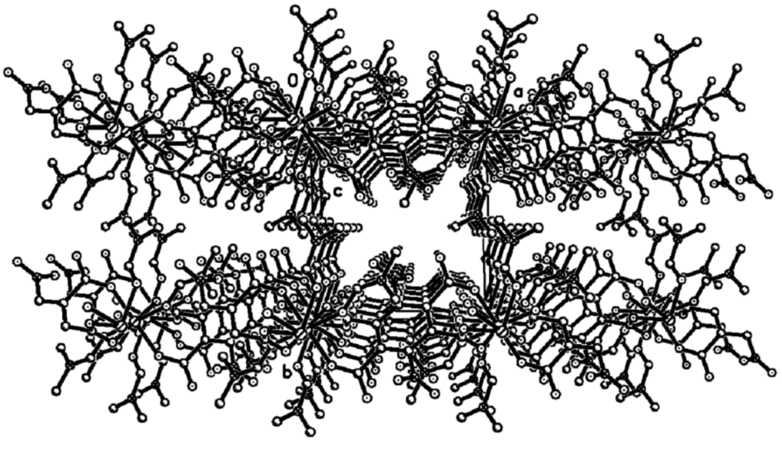

Figure 3. Packing plot of the complex viewed along *c* axis of the unit cell.

3.1.2. Infrared spectrum. The characteristic absorption of the carboxylic group for 3,6-dinitro-1,2,4,5-benzentetracarboxylic acid at $1725\,\mathrm{cm}^{-1}$ has shifted to $1645\,\mathrm{cm}^{-1}$ in the complex, which indicate that the carboxylates take part in coordination. In addition, a strong and broad band for H_2O appears at *ca.* $3410\,\mathrm{cm}^{-1}$.

3.1.3. Magnetic properties. Figure 4 shows the relationship of χ_M *versus* T, and $\chi_M T$ *versus* T, where (χ_M is the molar magnetic susceptibility for a two-Mn(II) unit. At 300 K

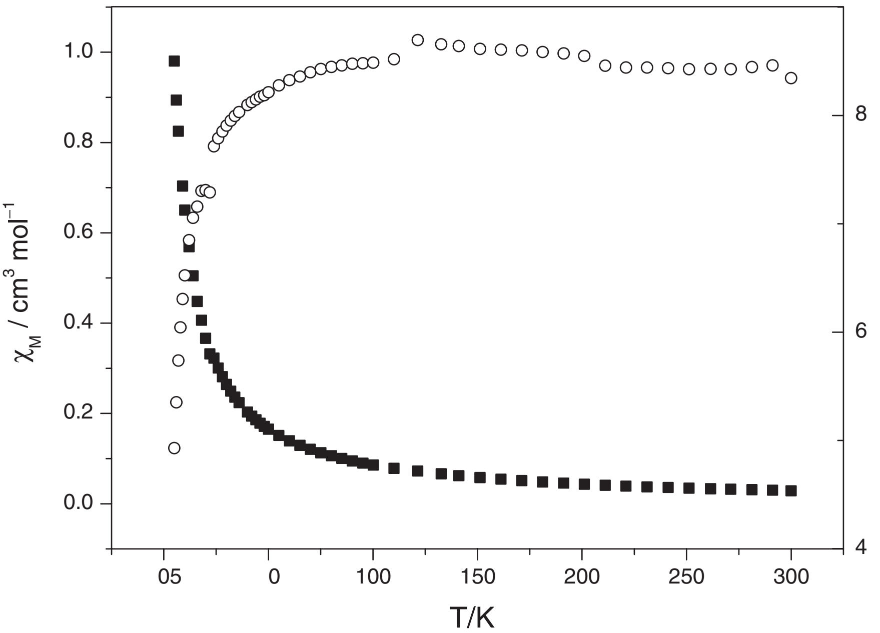

Figure 4. The relationships of χ_M (■) *versus T*, and $\chi_M T$ (○) *versus T*.

to 55.1 K, the values of $\chi_M T$ change around 8.4 cm$^3 \cdot$ K mol^{-1}, which is close to expected for two S = 5/2 spins (8.753 for $g_{Mn} = 2$). Below 50 K the $\chi_M T$ values decrease gradually with the decreasing temperature, from 8.209 cm^3 K mol^{-1} at 50.05 K to 4.926 cm^3 K mol^{-1} at 5 K, as shown in figure 4. Viewed from the crystal structure, the major magnetic interactions of the present complex are with Mn(1) and Mn(2) ions, and Mn(1) and Mn(1A) ions, and Mn(2) and Mn(2B) ions. Up to now there is no appropriate theoretic model to be used in two-dimensional structures. We use the Curie–Weiss law to analyze the magnetic data tentatively, and the values of magnetic susceptibility obey the Curie–Weiss law with a negative Weiss constant $\theta = -1.37$ K. The θ value suggests that there exists a very weak antiferromagnetic coupling between the Mn(II) ions. In the present complex there exist no bridging planes between Mn(1) and Mn(1A) atoms and between Mn(2) and Mn(2B) atoms, and because the planes of carboxylate groups are not coplanar with the benzene ring as mentioned above, there exist no delocalized π orbitals between Mn(1) ion and Mn(IA) ion, or between Mn(2) and Mn(2B) atoms, leading to the very weak magnetic interaction between these manganese(II) ions [10–11]. Although Mn(1) and Mn(2) atoms are bridged by a carboxylate group, obviously it does not make effective coupling between Mn(1) and Mn(2) atoms.

Supplementary material

The X-ray crystallographic file, in CIF format, is available from the Cambridge Crystallographic Data Centre on quoting the deposition number CCDC 201852.

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