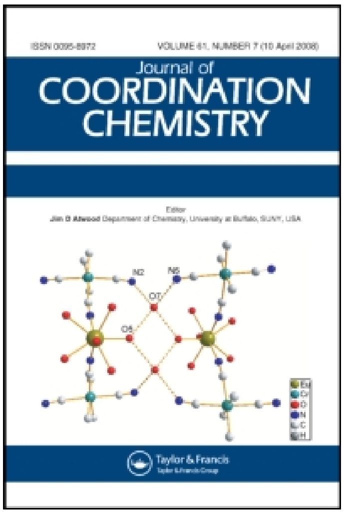

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SYNTHESIS AND STRUCTURE OF A POLYMERIC 1,3-BENZENEDICARBOXYLATO COMPLEX OF Mn(II) WITH PHENANTHROLINE

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SYNTHESIS AND STRUCTURE OF A POLYMERIC 1,3-BENZENEDICARBOXYLATO COMPLEX OF Mn(II) WITH PHENANTHROLINE

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A novel Mn(II) complex bridged by 1,3-benzenedicarboxylate (BDC) has been synthesized by the diffusion method. The complex crystallizes in space group $P2_1/c$ with $a = 8.345(2)$, $b = 10.427(1)$, $c = 18.756(2)$ Å, $\beta = 100.19(1)°$. Each BDC bridges three Mn(II) atoms through two carboxyl groups with different coordination modes to form a complex polymeric chain. The coordination geometry around the Mn(II) atom is seriously distorted from the normal octahedron. Large deviations of the donor atoms out of the coordination planes and unexpected bond angles around Mn(II) and donor O atoms suggest the existence of an electrostatic interaction between Mn(II) and donor atoms in the complex. Close stacking of aromatic rings is observed in the complex, the distance between the neighboring phen planes being 3.2085 Å.

Keywords: Mn(II) complex; Benzenedicarboxylate; Crystal structure; Electrostatic interaction; Aromatic ring stacking

INTRODUCTION

Structural investigations of transition metal complexes bridged by aromatic molecules have continued in our laboratory for several years, with the aim of studying the magnetic behaviour of these multinuclear complexes in

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*Corresponding author.

relation to their structure [1]. Owing to the possible coordination capability of carboxyl groups, the benzenedicarboxylate anion has recently been used as a bridging ligand to synthesize multinuclear complexes. A series of interesting benzenedicarboxylato complexes was obtained and crystal structure analysis showed a variety of coordination modes for the carboxylic anions in these complexes [2–7]. As a part of this research, we have synthesized a novel 1,3-benzenedicarboxylatomanganese(II) complex and X-ray structure analysis has revealed an unexpected coordination mode in the complex.

EXPERIMENTAL

Synthesis

Excess $MnCO_3$ was added to a hot aqueous solution containing 0.203 g (1.2 mmol) of 1,3-benzenedicarboxylic acid (BDC) with stirring, and the solution was boiled for 15 min. to remove CO_2. The resulting solution was slowly cooled to room temperature and filtered to give a transparent solution of the Mn(II) salt. Another 10 cm^3 of a saturated ethanol solution of 1,10-Phenanthroline (phen) was also prepared for use. The title complex was synthesized by diffusion of the solutions. Aqueous solutions of the Mn(II) salt (6 cm^3), distilled water (4 cm^3) and an ethanol solution of phen (6 cm^3) were carefully removed to a standing test tube in turn, preserving the distinct boundary surface between neighboring solution phases. The test tube was covered with a piece of saran wrap and stood aside to yield light yellow complex crystals suitable for X-ray diffraction.

Infrared Spectra

IR spectra of the title complex were recorded with a Shimadzu IR-470 spectrophotometer (4000–400 cm^{-1}) using a powdered sample spread on a KBr plate.

Crystal Structure Determination

X-ray diffraction data for a single crystal of the title complex were collected on a Rigaku AF7R diffractometer to a 2θ value of 50° with graphite-monochromatized MoKα radiation ($\lambda = 0.71073$ Å) by the $\omega - 2\theta$ scan technique. A total of 2903 independent reflections was collected, of which 1947 reflections were considered as observed [$I > 2\sigma(I)$] and there were used for the structure refinement. Usual Lp and empirical absorption [$T_{max} = 0.999$, $T_{min} = 0.887$] corrections were applied.

The structure was solved by the Patterson method followed by Fourier syntheses. Refinement was carried out by full-matrix least-squares procedures using the TEXSAN program package [8]. H atoms were located in a difference Fourier map and fixed in the refinement. The final anisotropic refinement including all non-H atoms converged to agreement factors $R = 0.038$ and $wR = 0.043$, where $w = 1/\sigma^2(F)$. Atomic scattering factors used were taken from International Tables for X-ray Crystallography [9].

RESULTS AND DISCUSSION

Crystal Structure

Crystal data: $C_{20}H_{12}MnN_2O_4$, $M = 399.27$, monoclinic, $P2_1/c$, $a = 8.345(2)$, $b = 10.427(1)$, $c = 18.756(2)$ Å, $\beta = 100.19(1)°$, $V = 1606.4(7)$ Å^3, $Z = 4$, $F(000) = 812$, $D_c = 1.651$ g cm^{-3}, $\mu(\text{MoK}\alpha) = 0.818$ mm^{-1}, $(\Delta/\sigma)_{max} = 0.03$, $(\Delta\rho)_{max} = 0.306$, $(\Delta\rho)_{min} = -0.325$ e.Å^{-3}, $S = 1.274$.

Final fractional atomic coordinates and equivalent isotropic thermal parameters for all non-H atoms are listed in Table I. Selected bond distances and angles are listed in Table II. While a phen chelates to a Mn(II) atom through two N atoms, three BDC anions coordinate to the Mn(II) atom with different coordination modes one chelating and two u-bridging, as illustrated in Figure 1. The coordination geometry around the Mn(II) atom is seriously distorted from the normal octahedron. The donor atom O(4B) deviates by some 1.5 Å out of the coordination plane composed of Mn, O(1), N(1) and N(2) atoms, and the O(4B) – Mn – N(2) bond angle of 139.3° is much smaller than the expected value of 180°. It is surprising that the Mn – O(4B) distance of 2.177(2) Å is quite normal. Moreover, although the O(2A) – Mn – N(2) bond angle of 119.2° is significantly larger than the normal value of 90°, the Mn – O(2A) distance of 2.104(2) Å is much shorter than the Mn – O(3B) distance of 2.360(2) Å. A similar relationship has been found in a Mn(II) complex of benzenetetracarboxylate [10]. It is difficult to interpret the phenomenon using the covalent theory and the observation may implies the existence of electrostatic interactions between Mn(II) and donor atoms in these complexes.

Each BDC anion bridges three Mn(II) atoms through two carboxyl groups to form a polymeric chain. One of carboxyl groups chelates to the

TABLE I Fractional atomic coordinates and equivalent isotropic thermal parameters (Å^2) of non-H atoms for the complex

Atom	*X/a*	*Y/b*	*Z/c*	B_{eq}(Å^2)
Mn	0.13657(6)	0.17529(5)	0.67264(3)	2.084(9)
O(1)	0.2615(3)	0.0466(3)	0.7509(1)	3.02(5)
O(2)	0.1051(3)	0.1103(3)	0.8258(1)	3.38(6)
O(3)	0.3438(3)	−0.2225(3)	1.1058(1)	3.55(6)
O(4)	0.1510(3)	−0.0831(3)	1.0698(1)	3.36(6)
N(1)	−0.0022(3)	0.3463(3)	0.6152(2)	2.60(6)
N(2)	0.2279(4)	0.3547(3)	0.7365(1)	2.56(6)
C(1)	−0.1196(4)	0.3379(4)	0.5573(2)	3.43(9)
C(2)	−0.1951(5)	0.4460(5)	0.5229(2)	4.3(1)
C(3)	−0.1470(5)	0.5649(5)	0.5484(2)	4.5(1)
C(4)	−0.0216(5)	0.5770(4)	0.6094(2)	3.70(9)
C(5)	0.0386(6)	0.6974(4)	0.6389(3)	5.0(1)
C(6)	0.1582(6)	0.7026(4)	0.6994(3)	4.9(1)
C(7)	0.2236(5)	0.5880(4)	0.7344(2)	3.66(9)
C(8)	0.3446(5)	0.5866(4)	0.7974(2)	4.5(1)
C(9)	0.4035(5)	0.4735(5)	0.8269(2)	4.2(1)
C(10)	0.3440(5)	0.3578(4)	0.7945(2)	3.35(9)
C(11)	0.1700(4)	0.4674(4)	0.7056(2)	2.59(7)
C(12)	0.0448(4)	0.4632(4)	0.6414(2)	2.65(8)
C(13)	0.2181(4)	0.0458(3)	0.8119(2)	2.22(7)
C(14)	0.3137(4)	−0.0326(3)	0.8716(2)	1.98(7)
C(15)	0.4638(4)	−0.0843(3)	0.8644(2)	2.32(7)
C(16)	0.5499(4)	−0.1560(4)	0.9206(2)	2.52(8)
C(17)	0.4885(4)	−0.1779(4)	0.9833(2)	2.48(7)
C(18)	0.3402(4)	−0.1241(3)	0.9913(2)	2.02(7)
C(19)	0.2533(4)	−0.0508(3)	0.9354(2)	2.07(7)
C(20)	0.2752(4)	−0.1436(3)	1.0602(2)	2.43(8)

TABLE II Selected bond distances (Å) and angles (°) for the complex

Mn − O(1)	2.121(2)	Mn-O(2)^a	2.104(2)
Mn − O(3)^b	2.360(2)	Mn − O(4)^b	2.177(2)
Mn − N(1)	2.290(3)	Mn − N(2)	2.271(3)
O(1) − C(13)	1.261(4)	O(2) − C(13)	1.247(4)
O(3) − C(20)	1.251(4)	O(4) − C(20)	1.253(4)
C(13) − C(14)	1.497(4)	C(18) − C(20)	1.500(4)
O(1) − Mn − O(2)^a	97.8(1)	O(1) − Mn − O(3)^b	100.52(9)
O(1) − Mn − O(4)^b	103.66(9)	O(1) − Mn − N(1)	164.62(9)
O(1) − Mn − N(2)	94.7(1)	O(2)^a − Mn − O(3)^b	149.00(8)
O(2)^a − Mn − O(4)^b	94.08(9)	O(2)^a − Mn − N(1)	81.8(1)
O(2)^a − Mn − N(2)	119.2(1)	O(3)^b − Mn − O(4)^b	57.40(8)
O(3)^b − Mn − N(1)	86.82(9)	O(3)^b − Mn − N(2)	83.92(9)
O(4)^b − Mn − N(1)	91.7(1)	O(4)^b − Mn − N(2)	139.3(1)
N(1) − Mn − N(2)	72.4(1)	Mn − O(1) − C(13)	116.6(2)
Mn − O(2)^a − C(13)^a	161.8(2)	O(1) − C(13) − O(2)	123.0(3)
O(3) − C(20) − O(4)	121.5(3)		

Symmetry code: ^{a} $-x, y, 1.5-z$; ^{b} $x, -y, -0.5+z$.

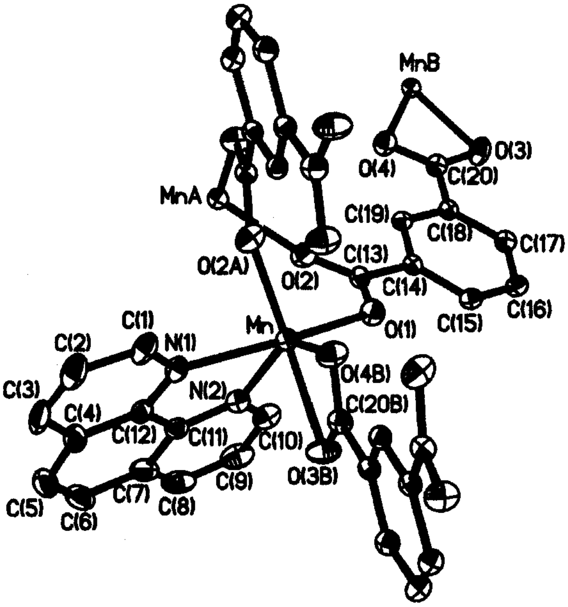

FIGURE 1 Coordination environment around the Mn(II) atom showing 30% probability displacement ellipsoids. H atoms are omitted for clarity.

MnB atom and the other u-bridges Mn and MnA atoms as shown in Figure 1. The Mn atom is coplanar with the carboxyl plane as expected, but the MnA atom deviates by some 1.5 Å out of the carboxyl plane formed by the C(13), O(1) and O(2) atoms. It is also notable that the MnA–O(2)–C(13) bond angle of 161.7° greatly deviates from the expected value of 120°. These facts suggest electrostatic interaction between Mn(II) and O atoms in the complex.

Figure 2 shows the packing of polymeric chains viewed along the phen plane. Two phen ligands chelating to Mn(II) atoms, u-bridged by one carboxyl group, are approximately parallel to each other, the dihedral angle being 0.7°, with an average distance of 3.5 Å. A close stack of aromatic rings is observed between neighboring polymeric chains. The phen plane parallels those chelating to MnF and MnG atoms of neighboring chain. The overlap projection of phen ligands, the distance of 3.2 Å between phen planes and the short contact of 3.328 Å between C(2A) and C(4F) atoms from neighboring complex chains clearly show the close stacking of phen rings in the complex.

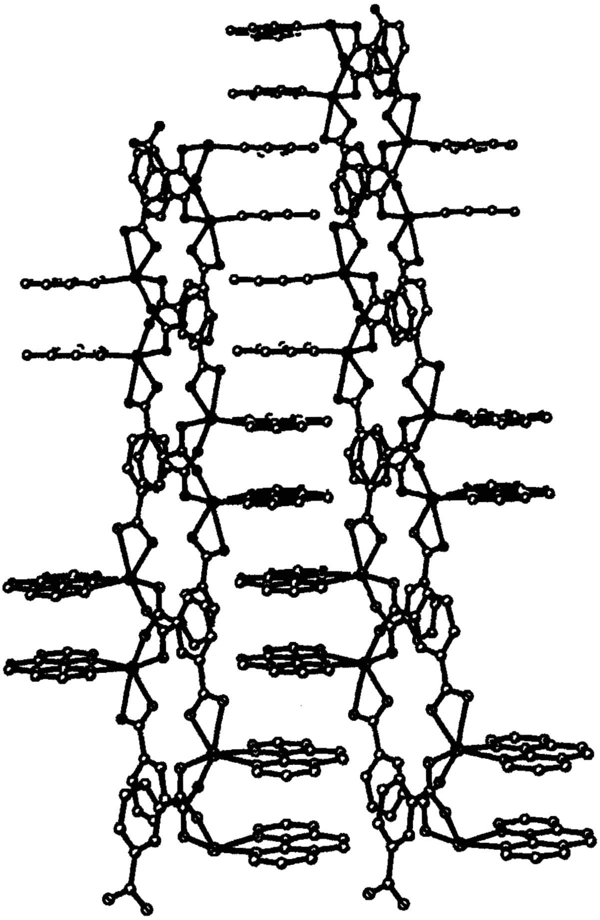

FIGURE 2 Packing diagram of polymeric chains viewed along the phen planes.

Infrared Spectrum

Based on two kinds of coordination modes of carboxyl groups in the complex, the most important absorptions are assigned to the peaks at 1370 and 1575 cm^{-1} (asymmetrical and symmetrical stretching vibration of the carboxyl group acting as a u-bridge ligand). These compare with 1385 and 1570 cm^{-1} found in $[Mn_2(bipy)_4(ta)]$ $[ClO_4]_2$ [2]; peaks at 1450 and 1520 cm^{-1} are assigned to asymmetrical and symmetrical stretching vibrations of the carboxyl group chelated to the Mn(II) atom. The difference of 70 cm^{-1} between the symmetrical and asymmetrical stretching vibration agrees well with results reported previously [12].

Acknowledgement

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Supplementary Material

Full lists of H atom positions, anisotropic thermal parameters for non-H atoms, and observed and calculated structure factors are available from the authors upon request.

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