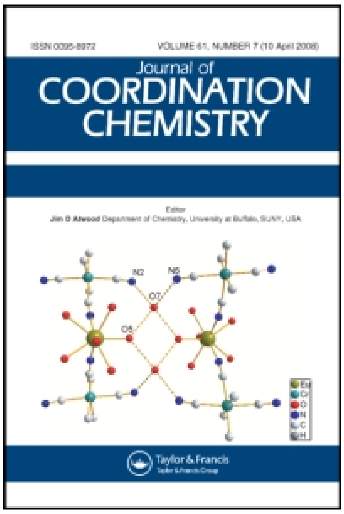

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SYNTHESIS AND CRYSTAL STRUCTURE OF A 1,3-BENZENEDICARBOXYLATO-MANGANESE(II) COMPLEX WITH 2,2-BIPYRIDINE

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The title complex has been prepared by the reaction of Mn(2,2′-bipy)Cl_2 with 1,3-benzenedicarboxylate (BDC) in ethanol solution. The complex crystallizes in space group $C2/c$ with $a = 13.847(6)$, $b = 15.629(7)$, $c = 17.106(6)$ Å, $\beta = 107.90(3)°$ and $z = 8$. Three BDC and one bipy ligands coordinate to Mn(II) to form a distorted octahedron. Each BDC bridges three Mn(II) atoms to form a polymeric chain. It is notable that although the Mn(II) atom deviates 1.084 Å from the bridging carboxyl plane it still has a normal coordination distance of 2.141(2) Å. This might suggest an electrostatic interaction between Mn(II) and carboxyl O atoms in the title complex. The IR spectrum is discussed, based on the molecular structure.

Keywords: Manganese(II); Crystal structure; Benzenedicarboxylate; Bridging ligand; Electrostatic interaction

INTRODUCTION

Structural investigation of transition metal complexes bridged by aromatic molecules has been continuing in our laboratory for several years with the aim of studying the magnetic behaviour of these multinuclear complexes in relation to their spatial structure [1]. Owing to the possible coordination capability of the carboxyl group, benzendicarboxylate and benzenetetracarboxylate anions have recently been used as the bridging ligand to synthesize a series of multinuclear complexes. Crystal structure analysis

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showed several different coordination modes for the carboxylic anions in these complexes [2–5]. It is especially interesting that an electrostatic interaction between Mn(II) and donor atoms was found in a 1,3-benzendicarboxylato complex [6]. We have recently synthesized another novel Mn(II) complex with 1,3-benzenedicarboxylate and present here its X-ray structure.

EXPERIMENTAL

Synthesis

A 15 cm^3 ethanol solution containing 0.78 g (5 mmol) of 2,2-bipyridine was mixed with an aqueous solution containing 0.99 g (5 mmol) of $MnCl_2 \cdot 4H_2O$ to give a light yellow solution. Some 0.83 g (5 mmol) of 1,3-benzenedicarboxylic acid was dissolved in water containing 0.40 g (10 mmol) of NaOH. The benzencarboxylate solution was added to the light yellow solution obtained above with stirring at room temperature. The mixture changed colour to yellow. It was filtered and stood for several days until well formed, yellow, single crystals were obtained.

C, H and N were analyzed using a Carlo-Erba 1160 instrument. Found mol: C 56.41, H 4.02, N 6.83; Calc. for $C_{18}H_{12}MnN_2O_4 \cdot 1/2C_2H_5OH$: C 57.24, H 3.80, N 7.03.

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

Crystal Structure Determination

Diffraction data were collected on a Rigaku AFC7R diffractometer with graphite-monochromated MoKα radiation up to $2\theta_{\max}$ of 55°. Among 3921 collected reflections 3746 were unique ($R_{int} = 0.028$). Usual Lp and empirical absorption corrections were applied. The structure was solved by the Patterson method and expanded using Fourier techniques. The non-H atoms were refined anisotropically using 2932 observed reflections [$I > 2\sigma(I)$] with the SHELX93 program package [7], and H atoms were included in structure factor calculation but not refined. The site occupancy factors of the crystalline ethanol molecule were taken as 0.5. Scattering factors used were taken from International Tables for X-ray Crystallography [8].

Crystal Data

$C_{18}H_{12}MnN_2O_4 \cdot 1/2C_2H_5OH$, FW = 398.27, monoclinic, $C2/c$, $a = 13.847(6)$, $b = 15.629(7)$, $c = 17.106(6)$ Å, $\beta = 107.90(3)^\circ$, $V = 3522(2)$ Å^3, $Z = 8$, $D_x = 1.50\ \mathrm{Mg \cdot m^{-3}}$, $\mu(\mathrm{Mo-K\alpha}) = 0.78\ \mathrm{mm^{-1}}$, $R_1 = 0.0476$, $wR_2 = 0.1394$, GOF = 1.098, No. of variable = 256, $(\Delta\rho)_{\max} = 0.631\ \mathrm{e \cdot Å^{-3}}$.

RESULTS AND DISCUSSION

Crystal Structure

Final atomic fractional coordinates and equivalent isotropic thermal parameters of non-H atoms are listed in Table I. Selected bond distances and angles are presented in Table II. The molecular structure is illustrated in Figure 1 with the atom numbering scheme. Besides bipy chelated to Mn(II), three BDC anions coordinate to the Mn(II) atom with different coordination modes to complete a distorted octahedral. Donor atoms

TABLE I Atomic coordinates and equivalent isotropic thermal parameters of non-H atoms

Atom	*x/a*	*y/b*	*z/c*	U_{eq}(Å^2)
Mn	0.1486(1)	0.8950(1)	0.3100(1)	0.031(1)
O(1)	0.4787(2)	0.6481(2)	0.6546(1)	0.042(1)
O(2)	0.6303(2)	0.7015(2)	0.7203(1)	0.043(1)
O(3)	0.3200(2)	0.9013(2)	0.3531(2)	0.067(1)
O(4)	0.2464(2)	0.8420(2)	0.4333(2)	0.054(1)
O(5)	0.4794(9)	1.0451(9)	0.2799(6)	0.145(5)
N(1)	0.1687(2)	0.9973(2)	0.2192(2)	0.037(1)
N(2)	0.1136(2)	1.0235(2)	0.3525(2)	0.037(1)
C(1)	0.2033(3)	0.9799(3)	0.1563(2)	0.049(1)
C(2)	0.2300(3)	1.0432(3)	0.1102(2)	0.059(1)
C(3)	0.2231(3)	1.1273(3)	0.1309(3)	0.059(1)
C(4)	0.1880(3)	1.1458(2)	0.1962(2)	0.050(1)
C(5)	0.1620(2)	1.0794(2)	0.2396(2)	0.036(1)
C(6)	0.1255(2)	1.0938(2)	0.3118(2)	0.036(1)
C(7)	0.1053(3)	1.1744(2)	0.3367(3)	0.051(1)
C(8)	0.0734(3)	1.1818(3)	0.4059(3)	0.062(1)
C(9)	0.0619(4)	1.1097(3)	0.4474(3)	0.060(1)
C(10)	0.0819(3)	1.0319(3)	0.4187(2)	0.049(1)
C(11)	0.5477(2)	0.7022(2)	0.6624(2)	0.034(1)
C(12)	0.4274(2)	0.8482(2)	0.4809(2)	0.031(1)
C(13)	0.5113(3)	0.8952(2)	0.4779(2)	0.041(1)
C(14)	0.6051(3)	0.8812(2)	0.5353(2)	0.048(1)
C(15)	0.6169(3)	0.8186(2)	0.5949(2)	0.044(1)
C(16)	0.5331(2)	0.7703(2)	0.5979(2)	0.032(1)
C(17)	0.4390(2)	0.7856(2)	0.5414(2)	0.031(1)
C(18)	0.3259(2)	0.8648(2)	0.4194(2)	0.034(1)
C(19)	0.4452(10)	0.9438(9)	0.2557(8)	0.102(4)
C(20)	0.4246(12)	0.8490(8)	0.2519(8)	0.109(5)

TABLE II Selected bond distances [Å] and angles [°]

Mn—O(1)A	2.141(2)	Mn—O(2)C	2.111(2)
Mn—O(3)	2.262(3)	Mn—O(4)	2.284(3)
Mn—N(1)	2.305(3)	Mn—N(2)	2.240(3)
O(1)—C(11)	1.251(4)	O(2)—C(11)	1.261(4)
O(3)—C(18)	1.250(4)	O(4)—C(18)	1.246(4)
MnA—MnB	3.993(2)		
O(1)A—Mn—O(2)C	93.2(1)	O(1)A—Mn—O(3)	142.6(1)
O(1)A—Mn—O(4)	86.0(1)	O(1)A—Mn—N(1)	133.6(1)
O(1)A—Mn—N(2)	84.9(1)	O(2)C—Mn—O(3)	98.5(1)
O(2)C—Mn—O(4)	108.5(1)	O(2)—Mn—N(1)	91.1(1)
O(2)C—Mn—N(2)	152.6(1)	O(3)—Mn—O(4)	56.6(1)
O(3)—Mn—N(1)	81.8(1)	O(3)—Mn—N(2)	99.5(1)
O(4)—Mn—N(1)	135.5(1)	O(4)—Mn—N(2)	98.7(1)
N(1)—Mn—N(2)	71.3(1)	O(1)—C(11)—O(2)	123.8(3)
O(4)—C(18)—O(3)	119.2(3)		

Symmetry codes are A: $-x+0.5$, $-y+1.5$, $-z+1$; B: $x+0.5, -y+1.5, z+0.5$; C: $x-0.5, -y+1.5, z-0.5$.

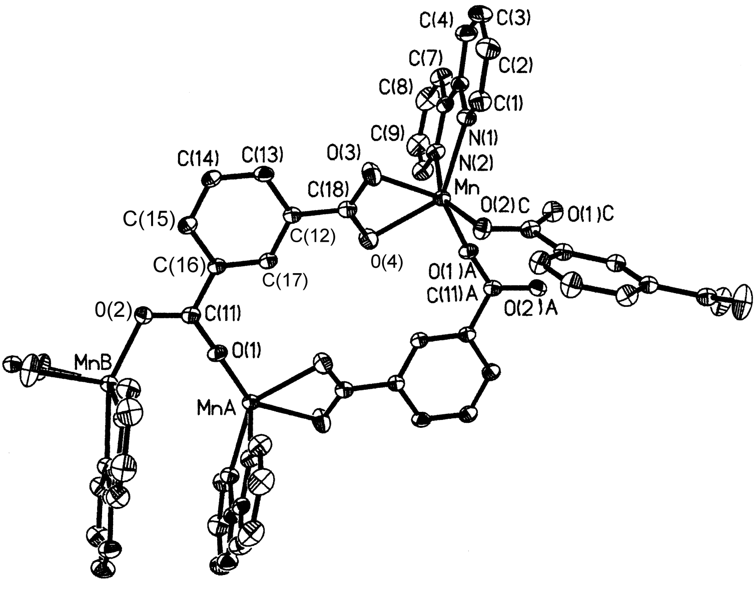

FIGURE 1 Coordination environment around the Mn(II) atom showing 30% probability ellipsoids. H atoms are omitted for clarity.

O(1)A, O(3), O(4) and N(1) are located on the equatorial plane around the Mn(II) atom while O(2)C and N(2) occupy apical positions. The O(2)C—Mn—N(2) bond angle of 152.63° and N(1) atomic deviation of 0.645 Å out of the coordination plane defined by Mn, O(1)A, O(3) and O(4) atoms show the extent of distortion of the coordination octahedron. Each

BDC anion bridges three Mn(II) atoms *via* two carboxyl groups. One carboxyl group chelates to the Mn atom and another *u*-bridges MnA and MnB atoms as shown in Figure 1. As found in most transition metal complexes, the metal atom is usually coplanar with the coordinated carboxyl group because of electron delocalization in the coordinated carboxyl group. As expected, the Mn atom is coplanar with the O(3) carboxyl group [the carboxyl group including O(3) atom] and the O(2)C carboxyl group in the present structure, but the Mn atom deviates 1.084 Å from the O(1)A carboxyl plane. Moreover the C(11)A—O(1) A—Mn bond angle of 148.3° deviates greatly from the expected value of 120°. However, the O(1)A—Mn distance of 2.141(2) Å is quite normal. These facts might imply that the O(1)A atom coordinates to the Mn atom with an electrostatic interaction, just as is found in a similar Mn(II) complex [6]. Electrostatic interactions between Mn(II) and donor atoms was found in a seven coordinate Mn(II) complex [9]. The present work provides new evidence of the electrostatic interaction in six coordination Mn(II).

The packing of polymeric chains viewed along the crystallographic *b* axis is presented in Figure 2. The distance of 3.397 Å between C(13) and C(13)′

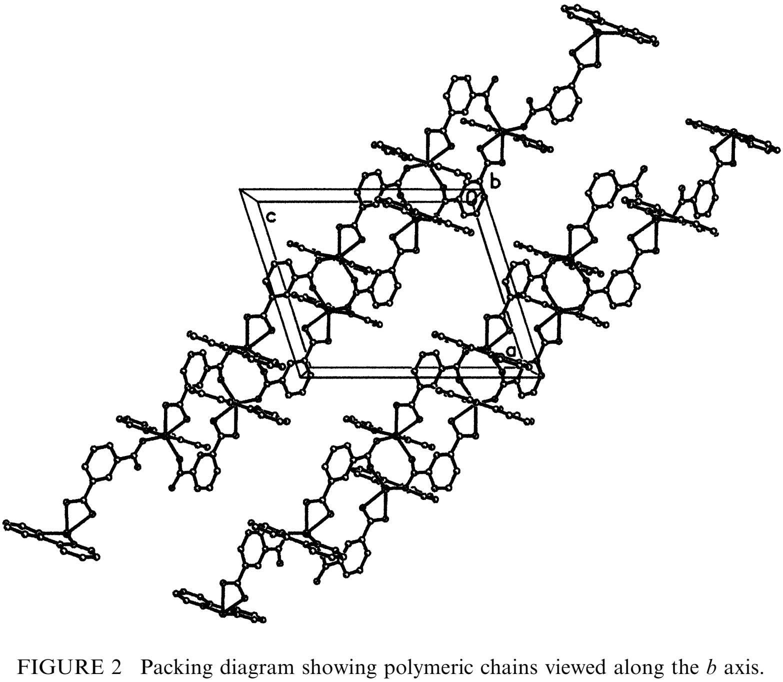

FIGURE 2 Packing diagram showing polymeric chains viewed along the *b* axis.

[$1-x$, $2-x$, $1-z$] atoms shows the normal van der Waals contact between chains. Bipy ligands chelating to neighboring Mn(II) atoms, *u*-bridged by a carboxyl group, are approximately parallel to each other (dihedral angle 2.3°). Distances from non-H atoms of a bipy ligand to the neighboring bipy plane are in the range 3.377 to 3.615 Å. The shortest atomic separation between bipy ligands is 3.466 Å [C(7)A—C(7)B]. This suggest a close stack of bipy rings in the crystal.

Infrared Spectra

Peaks at 1540 cm^{-1} and 1475 cm^{-1} are assigned to asymmetrical stretching vibrations of carboxyl groups while the peak at 1390 cm^{-1} is assigned to symmetrical stretching vibrations of carboxyl groups. Differences of 150 cm^{-1} and 85 cm^{-1} in the values correspond to monodentate and chelate coordination modes of the carboxyl group, respectively [10]. They agree well with the molecular structure as mentioned above.

Supplementary Material

Full lists of crystallographic data are available from the authors upon request.

Acknowledgements

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