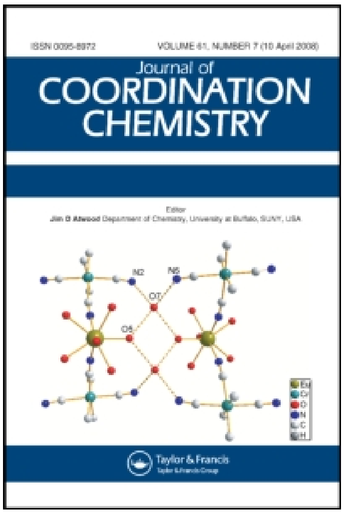

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STRUCTURE OF A POLYMERIC BENZENETETRACARBOXYLATO COMPLEX OF Mn(II) WITH IMIDAZOLE

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A novel polymeric μ-BTC complex of Mn(II) with imidazole has been synthesized, where BTC is the 1,2,4,5-benzenetetracarboxylato tetravalent anion, and its crystal structure has been determined by X-ray diffraction methods. The complex crystallizes in the monoclinic space-group $P2_1/n$ with $a = 11.184(5)$, $b = 9.177(2)$, $c = 18.243(1)$ Å and $\beta = 107.84(1)°$. Each BTC ligand, located around the crystallographic inversion centre, bridges four Mn(II) atoms through four carboxyl groups to form a three dimensional polymeric structure. The carboxyl groups in the *ortho*-position of BTC bridges Mn(II) atoms related by the crystallographic screw axis to form helical complex chains along the *b* axis. Coordination around the Mn(II) atom is distorted octahedral; two BTC anions coordinate to Mn(II), one in unidentate fashion and the other as a chelate. The coordination distance of the unidentate ligand is much shorter than in the chelated ligand.

Keywords: Manganese(II); X-ray structure; Benzenetetracarboxylato; Polymer

INTRODUCTION

Structural investigations of transition metal complexes bridged by aromatic molecules have been continuing in our laboratory for several years, with the aim of studying magnetic behaviour of multinuclear complexes in relation to structure [1]. Owing to the possible coordination capability of four carboxyl groups, the benzenetetracarboxylate anion (BTC) has been used as a bridging ligand to synthesize a series of multinuclear manganese complexes.

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[*] Corresponding author.

Some polymeric complexes with linear or three dimensional network structures have been reported [2–3]. As a part of this research, we present here the novel helical polymeric structure and coordination mode of the title complex.

EXPERIMENTAL

Preparation

The complex has been synthesized in a manner similar to that for the linear BTC complex of Mn(II) reported previously [4]. Some 20 cm^3 of an aqueous solution containing 5 mmol of sodium 1,2,4,5-benzene-tetracarboxylate was mixed with 20 cm^3 of an aqueous solution containing 10 mmol of manganese acetate. Then, imidazole was added to the above mixture with stirring at 50°C. After filtering, 5 cm^3 of methanol was added to the filtrate in order to obtain well-shaped crystals. Crystals suitable for X-ray analysis were obtained by slow evaporation of solvent from solution kept at 5°C.

Physical Measurements

C, H and N were analyzed using a Carlo–Erba 1160 instrument. *Anal.* Cald. for $C_{28}H_{28}O_9N_{12}Mn_2$%:C, 41.77; H, 3.73; N, 20.89. Found: C, 41.65; H, 3.52; N, 20.68. IR spectra of the complex were recorded with a Shimazu IR–470 spectrophotometer (4000–400 cm^{-1}) using a powdered sample spread on a KBr plate.

Crystal Structure Determination

X-ray diffraction data of a single crystal of the title complex were collected on a Rigaku AF7R diffractometer up to a 2θ value of 55° with graphite-monochoromatized MoKα radiation ($\lambda = 0.71073$ Å) by the ω-2θ scan technique. A total of 4362 independent reflections was collected, of which 3491 reflections were considered as observed [$I > 3\sigma(I)$] and used for structure refinement. Usual Lp and empirical absorption [$T_{max} = 1.00$, $T_{min} = 0.82$] corrections were applied.

The structure was solved by the Patterson method followed by Fourier syntheses. Structure refinement was carried out by full-matrix least-squares procedures using the SHELX-93 program package [5]. H atoms were located in a difference Fourier map and fixed in the refinement. The final anisotropic refinement including all the non-H atoms converged to agreement factors $R_1 = 0.0341$ and $wR_2 = 0.0951$, where $w = 1/[\sigma^2 (Fo^2) + (0.0505P)^2 + 0.2541P]$ and $P = (Fo^2 + 2Fc^2)/3$. Atomic scattering factors were taken from International Tables for X-ray Crystallography [6].

RESULTS AND DISCUSSION

Crystal Structure

Crystal data: $C_{28}H_{26}Mn_2N_{12}O_8 \cdot H_2O$, $M = 394.24$, monoclinic, $P2_1/n$, $a = 11.184(5)$, $b = 9.177(2)$, $c = 18.243(1)$ Å, $\beta = 107.84(1)°$, $V = 1782.5(7)$ Å^3, $Z = 2$, $F(000) = 800$, $D_c = 1.46\,\mathrm{g \cdot cm^{-3}}$, $\mu(\mathrm{MoK}\alpha) = 0.775\,\mathrm{mm^{-1}}$, $(\Delta/\sigma)_{max} = 0.002$, $(\Delta\rho)_{max} = 0.774$, $(\Delta\rho)_{min} = -0.451$ e.Å^{-3}, $S = 1.064$, No. of variables = 235.

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. The coordination environment around

TABLE I Fractional atomic coordinates ($\times 10^4$) of non-H atoms and equivalent isotropic thermal parameters ($\times 10^3$)

Atom	*x/a*	*y/b*	*z/c*	U_{eq}(Å^2)
Mn	9398(1)	2037(1)	2263(1)	24(1)
O(1)	7649(1)	1110(1)	1583(1)	33(1)
O(2)	8384(1)	−665(2)	1012(1)	39(1)
O(3)	4458(1)	−1592(2)	1715(1)	34(1)
O(4)	6463(1)	−1879(2)	1845(1)	33(1)
O(5)	9665(8)	1012(9)	−130(4)	144(3)
N(1)	8915(2)	4033(2)	1516(1)	37(1)
N(2)	8460(2)	6257(2)	1082(1)	56(1)
N(3)	11006(2)	1603(2)	1861(1)	36(1)
N(4)	12620(2)	447(2)	1710(1)	53(1)
N(5)	9804(2)	154(2)	3090(1)	32(1)
N(6)	9232(2)	−1739(2)	3636(1)	42(1)
C(1)	7528(2)	107(2)	1088(1)	25(1)
C(2)	6213(2)	−26(2)	530(1)	23(1)
C(3)	5990(2)	612(2)	−193(1)	25(1)
C(4)	5212(2)	−651(2)	722(1)	23(1)
C(5)	5401(2)	−1410(2)	1478(1)	25(1)
C(6)	8632(2)	5356(2)	1682(1)	48(1)
C(7)	8613(3)	5470(3)	487(2)	65(1)
C(8)	8901(3)	4105(3)	760(1)	55(1)
C(9)	11521(2)	327(3)	1842(2)	48(1)
C(10)	12828(3)	1879(3)	1632(2)	69(1)
C(11)	11833(2)	2594(3)	1725(2)	55(1)
C(12)	9046(2)	−974(2)	2991(1)	38(1)
C(13)	10161(3)	−1069(3)	4194(1)	50(1)
C(14)	10512(2)	93(2)	3852(1)	44(1)

TABLE II Selected bondlengths [Å] and angles [°]

Mn—O(1)	2.1456(14)	Mn—O(3)[a]	2.2884(13)
Mn—O(4)[a]	2.3520(14)	Mn—N(1)	2.249(2)
Mn—N(3)	2.177(2)	Mn—N(5)	2.247(2)
O(1)—C(1)	1.267(2)	O(2)—C(1)	1.232(2)
O(3)—C(5)	1.268(2)	O(4)—C(5)	1.248(2)
N(2)—H(3)	0.859	O(2)—H(3)	1.995
N(2)—O(2)	2.828	N(4)—H(7)	0.860
N(4)—O(3)	1.928	N(4)—O(3)	2.777
N(6)—H(11)	0.980	O(1)—H(11)	1.913
N(6)—O(1)	2.822		
O(1)—Mn—N(3)	115.73(7)	O(1)—Mn—N(5)	92.55(6)
N(3)—Mn—N(5)	93.89(6)	O(1)—Mn—N(1)	88.02(6)
N(3)—MnN(1)	90.83(7)	N(5)—Mn—N(1)	174.44(6)
O(1)—Mn—O(3)[a]	150.72(5)	N(3)—Mn—O(3)[a]	93.54(6)
N(5)—MnO(3)[a]	85.88(6)	N(1)—Mn—O(3)[a]	90.91(6)
O(1)—Mn—O(4)[a]	94.22(5)	N(3)—Mn—O(4)[a]	150.05(6)
N(5)—MnO(4)[a]	84.35(6)	N(1)—Mn—O(4)[a]	90.09(6)
O(3)[a]—Mn—O(4)[a]	56.51(5)	C(1)—O(1)—Mn	125.36(12)
C(5)—O(3)—Mn[b]	92.02(11)	O(4)—C(5)—O(3)	121.7(2)
N(2)—H(3)—O(2)	182.82	N(4)—H(7)—O(3)	169.14
N(6)—H(11)—O(11)	153.27		

Symmetry code, a: $-x+3/2, y+1/2, -z+1/2$; b: $-x+3/2, y-1/2, -z+1/2$.

the Mn(II) atom is illustrated in Figure 1 together with the atom numbering scheme. The coordination around the Mn(II) atom is a distorted octahedron. Three imidazole molecules coordinate to a Mn(II) atom with normal bond distances and angles and two BTC anions coordinate to the Mn(II) atom, one as a unidentate and the other in bidentate chelation fashion.

As expected, the chelate coordination of the carboxyl group is restrained; the bond angle O(3A)—Mn—O(4A) of 56.50° shows the atomic orbitals of the oxygen atoms do not overlap maximally with the *d* orbital of the manganese atom. Contrary to the carboxyl group chelated to Mn(II) atom, the coordination of three imidazole molecules is quite free, the bond angles of *N*(1)—Mn—N(3)[90.84], N(3)—Mn—O(5)[93.89] and N(1)—Mn—O(5) [174.44] clearly showing maximal overlap between manganese and nitrogen atoms.

It is somewhat surprising that the Mn−O(1) bond distance of 2.146(1) Å is much shorter than the Mn(II)—O(3A)[2.288(1) Å], Mn(II)—O(4A) [2.352(1) Å] distances in the present complex and the distance 2.241(1) Å in a reported TCB complex of Mn(II) [8]. The reason for the difference in coordination distances between O(1), O(3A) and O(4A) atoms may be attributed to the chelation tension of the carboxyl group involving O(3A) and O(4A) atoms, but we do not know why the difference of 0.1 Å occurs between the present complex and the complex cited above; in both

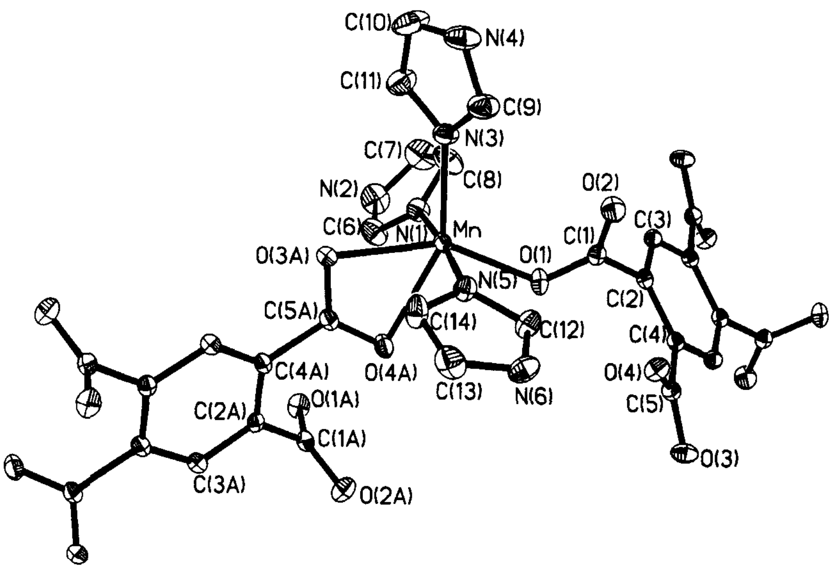

FIGURE 1 Molecular structure of the title complex showing 30% probability displacement ellipsoids. H atoms are omitted for clarity.

structures the carboxyl group coordinates to the Mn(II) atom as a unidentate ligand.

In BTC complexes reported previously, BTC has exhibited a variety of coordination modes [3]. In the present complex the BTC ligand exhibits a novel coordination fashion, *i.e.*, all four carboxyl groups in BTC ligand take part in coordination but with different unidentate or bidentate behaviour. The BTC ligand located around a crystallographic inversion centre bridges four Mn(II) atoms through four carboxyl groups to form a three dimensional polymeric structure. The carboxyl groups in the *ortho*-position of the BTC ligand bridge Mn(II) atoms related by the crystallographic screw axis to form helical complex chains along the *b* axis. Neighboring helical chains are linked each other through the benzene rings as shown in Figure 2. They also contact through H-bonding between carboxyl groups and imidazole molecules as verified by atomic separations and angles listed in Table II. The crystal water molecule [O(5)] is distributed across the unit cell with a site occupancy factor of 0.5.

Infrared Spectrum

Important strong absorptions are assigned according to two kinds of carboxyl groups in the complex. Peaks at 1362 and 1578 cm^{-1} are assigned

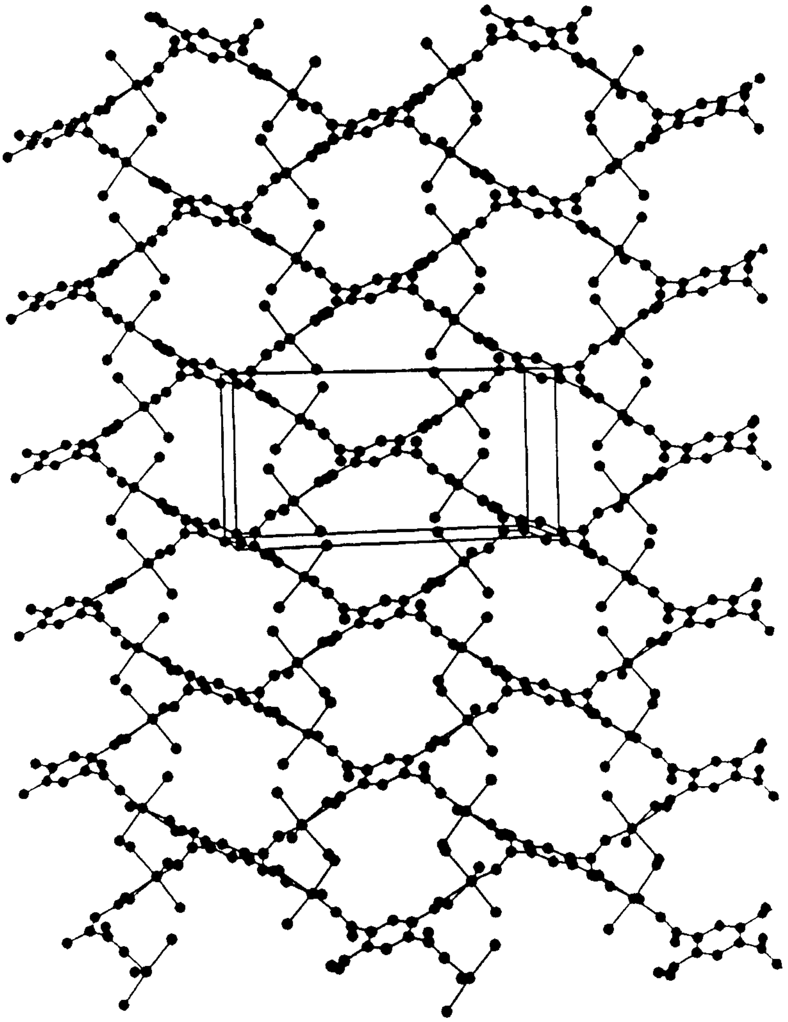

FIGURE 2 Packing diagram of polymeric helical chains in the unit cell, imidazole rings and crystalline water molecules are omitted for clarity.

to the asymmetrical and symmetrical stretching vibration of the carboxyl group coordinated to the Mn(II) atom as a unidentate ligand, respectively. This agrees with values of 1360 and 1580 cm^{-1} reported previously for the linear BTC complex [4]. Peaks at 1440 and 1490 cm^{-1} are assigned to the asymmetrical and symmetrical stretching vibration of the carboxyl group chelated to the Mn(II) atom; the difference of 50 cm^{-1} is also in agreement with values found for carboxyl groups chelated to other metal atoms [9].

Synthesis

Although the title helical BTC complex of Mn(II) was synthesized in a manner similar to the linear BTC complex of Mn(II) [4], a different complex has been obtained. In the case of the linear structural complex, two carboxyl groups of a BTC ligand are freed from coordination while the Mn(II) atom is surrounded by coordinated water molecules and unidentate carboxyl groups. It seems that the higher reaction temperature and slow crystallization procedure in the case of the present complex results in ligand exchange between free carboxyl groups and coordinated water molecules to construct the three dimensional network structure of the title complex.

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.

Acknowledgements

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