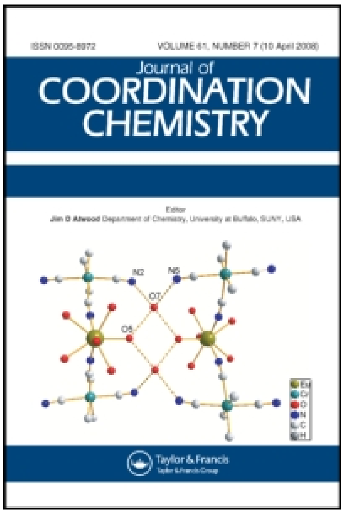

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Hydrothermal synthesis and structural characterization of a three-dimensional coordination polymer, $[MnNa_2(Hbtc)_2(H_2O)_3]$ (btc = 1,2,4-benzenetricarboxylate)

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HYDROTHERMAL SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF A THREE-DIMENSIONAL COORDINATION POLYMER, $[MnNa_2(Hbtc)_2(H_2O)_3]$ (btc = 1,2,4-BENZENETRICARBOXYLATE)

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A new three-dimensional metal-organic polymer, $[MnNa_2(Hbtc)_2(H_2O)_3]$ (where btc = 1,2,4-benzenetricarboxylate), has been prepared under hydrothermal conditions and characterized by single crystal X-ray diffraction. The compound crystallized in the monoclinic space group $C2/c$, with cell parameters: $a = 8.2349(10)$, $b = 11.191(2)$, $c = 22.837(3)$ Å, $\beta = 100.193(10)°$, $V = 2071.3(6)$ Å^3 and $Z = 4$. In the three-dimensional structure of the compound, each Na and Mn atom is six-coordinate with distorted octahedral geometry.

Keywords: Hydrothermal synthesis; Metal-organic polymer; 1,2,4-Benzenetricarboxylate; Crystal structures

INTRODUCTION

Interest in crystal engineering of polymeric coordination networks stems from their potential applications as zeolite-like materials for molecular selection, ion exchange, and catalysis, as well as for the variety of architectures and topologies [1–6]. One of the basic strategies for crystal engineering utilizes metal–ligand bonding between transition metals and organic ligands to create coordination polymers. In terms of molecular building blocks, coordination compounds have advantages over organic compounds, because metals have a variety of coordination geometries and a wide range of physical properties.

Many of the most interesting metal–organic polymers with one-, two- and three-dimensional (3-D) networks have been engineered using anionic, aromatic polycarboxylate ligands, such as 1,3,5-benzenetricarboxylate (btc), 1,2,4,5-benzenetetracarboxylate (btec) and 1,4-benzenedicarboxylate (bdc) [7–12]. Compared with the rich coordination

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chemistry exhibited by 1,3,5-btc, 1,2,4,5-btec and 1,4-bdc, metal–organic polymeric or supramolecular structures based on 1,2,4-btc are less reported, for steric reasons [13]. As far as we are aware, there are only a few examples of 3-D metal–organic coordination polymers with 1,2,4-btc as bridging ligand found in the literature [13–18]. Here, we report the hydrothermal synthesis and crystal structure of a three-dimensional coordination polymer $[MnNa_2(Hbtc)_2(H_2O)_3]$ (**1**) (btc = 1,2,4-benzenetricarboxylate).

EXPERIMENTAL

Synthesis

All chemicals and solvents used in the synthesis were of reagent grade and used as purchased without further purification. Single crystals were prepared from a mixture of $MnCl_2 \cdot 4H_2O$ (79.2 mg, 0.4 mmol), 1,2,4-H_3btc (168 mg, 0.8 mmol), NaOH (48 mg, 1.2 mmol) and distilled water (8 cm^3) with a molar composition of 1 : 2 : 3 : 1111. The crystallization took place under hydrothermal conditions in a Teflon container under autogenous pressure at 140°C for 24 h. After cooling pale yellow prismatic crystals of the title complex suitable for X-ray analysis were obtained, collected by suction filtration and air-dried.

Yield: 47%. Calcd. for $C_{18}H_{14}O_{15}MnNa_2$: C, 37.85; H, 2.45. Found: C, 37.54; H, 2.70%.

Physical Measurements

The IR spectrum of the complex in the range of 400–4000 cm^{-1} was recorded in KBr by using an Nicolet AVATAR 360 FT-IR E.SP. The IR spectrum of the compound shows the characteristic bands of the organic at 1619–1594 cm^{-1} for the asymmetric vibration and at 1367 cm^{-1} for the symmetric vibration. The broad band centred at 3348 cm^{-1} is assigned to the absorption of coordinated water.

Structure Determination

Room temperature (294 ± 1°K) single-crystal X-ray experiments were performed on a Brüker P4 diffractometer equipped with graphite monochromatized Mo K_α radiation ($\lambda = 0.71073$ Å). The unit cell was obtained and refined by 52 well-centered reflections with $3.5 < \theta < 18.4°$. Data collection was monitored by three standards every 100 reflection collected. No decay was observed except for a statistical fluctuation in the range of ±5.6%. Raw intensities were corrected for Lorentz and polarization effects, and for absorption by empirical methods based on ψ-scan data (Kopfmann and Huber, 1968). Direct phase determination yielded the positions of Mn, Na, O and most C atoms; the other C atoms were located in successive difference Fourier syntheses. Hydrogen atoms of phenyl were generated theoretically and the other hydrogen atoms were found on a difference Fourier map. They rode on their parent atoms in the final refinement. All non-hydrogen atoms were subjected to anisotropic refinement. The final full-matrix least-squares refinement on F^2 converged with $R1 = 0.0492$ and $wR2 = 0.1049$ for 1364 observed reflections [$I \geq 2\sigma(I)$]. The final difference electron density map shows no features.

TABLE I Crystallographic data and structure refinement for $[MnNa_2(H_2O)_3(C_9H_4O_6)_2]$

Molecular formula	$C_{18}H_{14}O_{15}MnNa_2$
Molecular weight	571.21
Color and habit	Pale yellow prism
Crystal size, mm	0.2 × 0.2 × 0.3
Crystal system	Monoclinic
Space group	*C*2/*c* (No. 15)
a, Å	8.2349(10)
b, Å	11.191(2)
c, Å	22.837(3)
α,°	90.00
β,°	100.193(10)
γ,°	90.00
V (Å^3), Z	2071.3(6), 4
Density (calcd.), g/cm^3	1.832
Reflections measured/ unique	2512/1834
Absorption coefficient, mm^{-1}	0.764
λ, Å	0.71073
R^a	0.0694
$R_w{}^b$	0.1139
GOF	1.029
$^aR = (\Sigma\|\|F_o\| - \|F_c\|\|)/(\Sigma\|F_o\|)$	$^bR_w = \sqrt{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2}$

Data collection was controlled by the XSCANS program (Bruker, 1997). Computations were performed using the SHELXTL NT ver. 5.10 program package (Sheldrick, 1985) on an IBM PC 586 computer. Analytical expressions of atomic scattering factors were employed, and anomalous dispersion corrections were incorporated (International Tables for X-ray Crystallography, 1989). Crystal drawings were produced with XP (Bruker, 1998).

RESULTS AND DISCUSSION

A packing view along the *a* direction is shown in Fig. 2. The crystal data and structure refinement parameters are listed in Table I, and selected bond lengths and angles in Table II. A single-crystal X-ray diffraction study revealed an extended 3-D porous framework formulated as $[MnNa_2(Hbtc)_2(H_2O)_3]$, which is consistent with the elemental analyses. The fundamental building unit of the crystal structure is shown in Fig. 1, where one sodium atom, one manganese atom, two coordinated waters and one 1,2,4-Hbtc anion are crystallographically unique. Each Mn ion is six-coordinate and is coordinated by two identical bidentate carboxylate groups and two identical monocarboxylate groups from Hbtc anions. The co-ordination geometry around Mn(II) ions can be described as a distorted octahedron with a MnO_6 core: six oxygen atoms [two O(1), two O(3), two O(4)] from four different carboxylate groups of four separate 1,2,4-Hbtc ligands. O(1), O(1A), O(4B) and O(4A) comprise the corresponding basal plane; the apical positions of the octahedra are occupied by O(3A) and O(3B), [2.084(3), 2.112(3) and 2.468(3) Å for Mn(1)–O(1), Mn(1)–O(3A) and Mn(1)–O(4A), respectively], the equatorial donor atoms around each manganese are nearly coplanar [maximum deviations 0.0106 Å for O(1) and O(1A)]. The sodium ion is tightly bonded by four oxygen atoms from four different carboxylate groups of four separate

TABLE II Selected bond lengths (Å) and angles (°) for $[MnNa_2(Hbtc)_2(H_2O)_3]$

Mn(1)–O(1)	2.084(3)	Na(1)–O(3C)	2.414(4)
Mn(1)–O(3A)	2.112(3)	Na(1)–O(2)	2.429(4)
Mn(1)–O(4A)	2.468(3)	Na(1)–O(7)	2.473(4)
Na(1)–O(6Δ)	2.336(3)	Na(1)–O(2A)	2.477(3)
Na(1)–O(8)	2.388(5)		
O(1)–Mn(1)–O(1A)	91.65(17)	O(3A)–Mn(1)–O(4B)	87.13(11)
O(1)–Mn(1)–O(3B)	123.88(11)	O(3A)–Mn(1)–O(4A)	56.75(11)
O(1)–Mn(1)–O(3A)	96.63(11)	O(3B)–Mn(1)–O(3A)	122.25(17)
O(1)–Mn(1)–O(4B)	174.09(12)	O(4B)–Mn(1)–O(4A)	103.43(17)
O(1A)–Mn(1)–O(4B)	82.46(12)	O(2)–Na(1)–O(7)	112.53(13)
O(2)–Na(1)–O(8)	82.43(12)	O(7)–Na(1)–O(3C)	84.86(12)
O(2)–Na(1)–O(2A)	82.59(13)	O(8)–Na(1)–O(6A)	101.84(13)
O(2)–Na(1)–O(3C)	161.26(13)	O(8)–Na(1)–O(2A)	81.42(12)
O(2)–Na(1)–O(6A)	95.68(13)	O(8)–Na(1)–O(3C)	79.57(11)
O(7)–Na(1)–O(2A)	93.76(12)	O(6A)–Na(1)–O(2A)	176.12(15)
O(7)–Na(1)–O(6A)	83.67(12)	O(6A)–Na(1)–O(3C)	93.09(13)
O(7)–Na(1)–O(8)	163.70(12)	O(3C)–Na(1)–O(2A)	89.57(12)

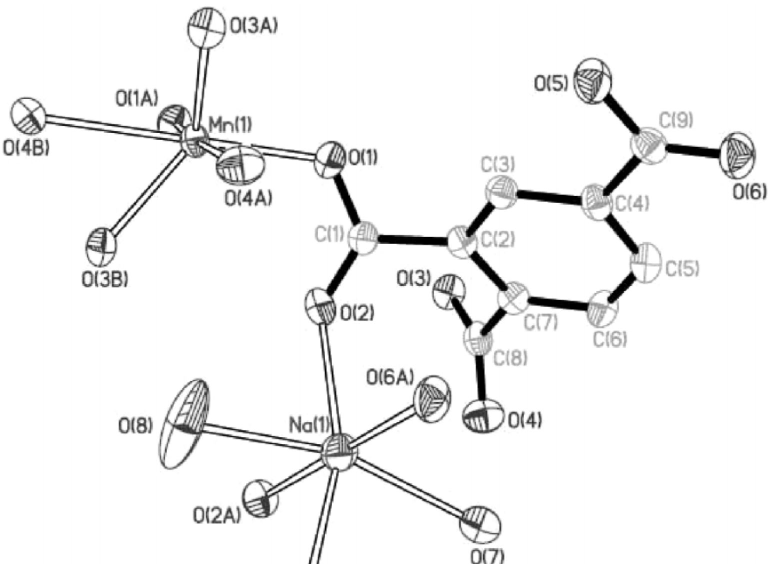

FIGURE 1 Perspective view of $[MnNa_2(Hbtc)_2(H_2O)_3]$. Thermal ellipsoids are drawn at the 35% probability level. Hydrogen atoms have been omitted for clarity.

1,2,4-Hbtc ligands and two oxygen atoms from coordinated water. The coordination sphere of Na can be described as a distorted octahedron; O(2), O(7), O(8) and O(3C) form an equatorial plane. The four oxygen atoms are nearly coplanar [maximum deviations 0.041 Å for O(8) and -0.0039 Å for O(3C)]. Two carboxylate oxygen atoms from two neighboring btc ligands occupy the axial sites. Na(1) lies out of its mean least-squares basal plane by 0.1245 Å. Each multifunctional Hbtc unit acts as a bridging ligand connecting four sodium ions and two manganese ions through its three carboxylate groups. Based on these connection modes, all Mn and Na centers

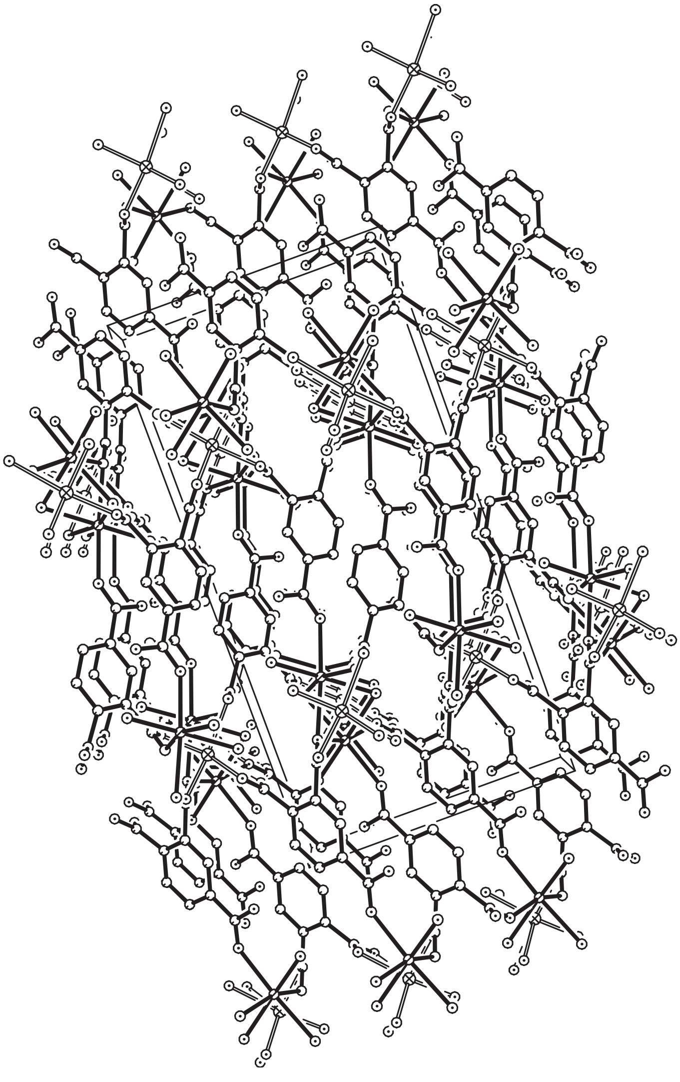

FIGURE 2 A packing view along the *a* direction in [$MnNa_2(Hbtc)_2(H_2O)_3$].

are linked by four 1,2,4-Hbtc ligands to form a 3-D coordination network (see Fig. 2). There are two kinds of benzene ring with different spatial directions parallel and nearly vertical (see Fig. 3) crystallized in the compound. The average distance between adjacent aromatic units is 3.3659 Å. For the non-parallel benzene rings, the dihedral angle between different benzene rings is about 86.8°.

Herein we have reported a 3-D metal–organic polymer synthesized under hydrothermal conditions, which cannot be obtained by traditional methods, such as slow evaporation or H-tube diffusion at room temperature. The coordination ability of organic ligands is greatly strengthened under hydrothermal or solvothermal conditions and multidimensional structures are more readily formed under these conditions. Our results further confirm this, as 1,2,4-H_3btc can only form zero-dimensional mononuclear complexes with rare-earth ions by slow evaporation.

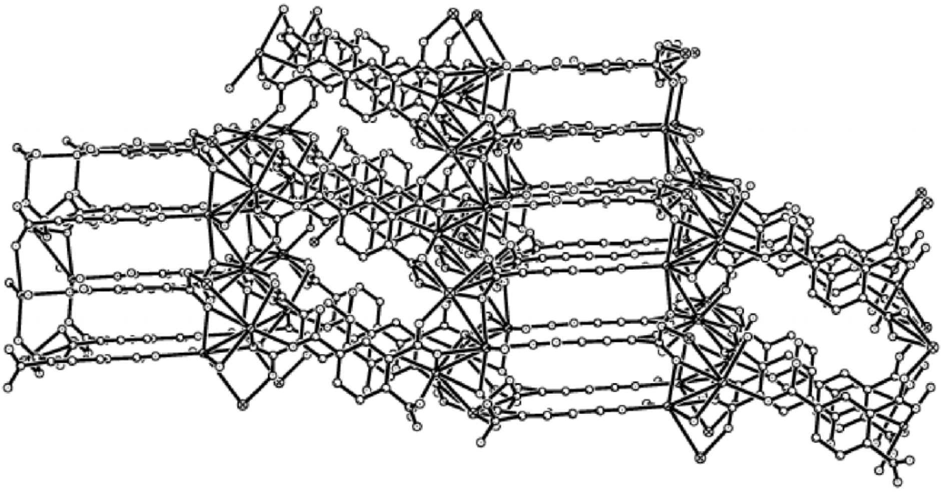

FIGURE 3 The 3-D channels of [$MnNa_2(Hbtc)_2(H_2O)_3$]. H atoms are omitted for clarity.

CONCLUSION

In this work, a three-dimensional metal–organic polymer, [$MnNa_2(H_2O)_3(C_9H_4O_6)_2$], has been prepared by hydrothermal synthesis and characterized by single crystal X-ray diffraction. The compound contains a novel coordination mode of 1,2,4-btc where the three asymmetric carboxylate groups adopt three different bonding modes. In the 3-D structure of the compound, each Mn atom and Na atom is coordinated by six oxygen atoms in a distorted octahedral geometry.

Acknowledgment

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Supplementary data

Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 235750. 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 http://www.ccdc.cam.ac.uk) or also from the author.

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