Asian Journal of Chemistry Vol. 21, No. 9 (2009), 7411-7415

Hydrothermal Synthesis and Crystal Structure of *Bis*(pyrazinium-2,3-dicarboxylato)manganate dihydrate

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The coordination compound $Mn(C_6H_3N_2O_4)_2{\cdot}2H_2O$ has been synthesized and its crystal structure was determined by X-ray diffraction. Crystal data: orthorhombic, space group C2/c, a = 14.4451(16) Å, b = 8.4711(11) Å, c = 13.0204(14) Å, β =11.689(2)º, V = 1447.6(3) $Å^3$, M_r = 425.18, F(000) = 860, Z = 4, D_c = 1.951 Mg/m^3, μ = 0.986 mm^{-1}. The final R_1 = 0.0585 and wR_2 = 0.1449 for 1270 observed reflections ($I > 2\sigma(I)$). In the title compound, *bis*(pyrazinium-2,3-dicarboxylato)-manganate dihydrate $[Mn(C_6H_3N_2O_4)_2{\cdot}2H_2O]$, the Mn^{2+} ions are bridged by the pyrazine-2,3-dicarboxylate (PZDA) ligands to build two-dimensional polymeric layers. Each Mn^{2+} ion is six-coordinated by two N and two O atoms with chelating mode, respectively from the two PZDA ligands and two O atoms with mono-mode, respectively from other different PZDA ligands. The lattice water molecules lie between the polymeric layers, which form strong hydrogen bonds to form three-dimensional crystal structure.

Key Words: Heteronuclear coordination compound, Cerium, Silver, Crystal structure.

INTRODUCTION

Takusagawa and Shimada[1] first determined the structure of pyrazine-2,3-dicarboxlic acid by single-crystal X-ray analysis. Almost at the same time, the first metal-organic compound of pyrazine-2,3-dicarboxylic acid was reported[2]. Among many reported compounds containing pyrazine-2,3-dicarboxylic acid, most are complexes of transition metal ions, including manganese[3], copper[4], zinc[5], iron[6] and cadmium[7]. There are many reported compounds of pyrazine-2,3-dicarboxylic acid with main group metals such as calcium[8,9], magnesium[10] and sodium[11] complexes. For further investigation of pyrazine-2,3-dicarboxylic acid, the compound, *bis*-(pyrazinium-2,3-dicarboxylato)manganate dihydrate $[Mn(C_6H_3N_2O_4)_2{\cdot}2H_2O]$ has been synthesized.

EXPERIMENTAL

All reagents were of AR grade and used without further purification.

Synthesis: Yellow block-shaped crystals of the title compound were obtained by hydrothermal reaction of $MnCl_2{\cdot}4H_2O$ (0.20 mmol, 0.0395 g), pyrazine-2,3-

dicarboxylic acid (0.20 mmol, 0.0342 g) and deionized water (15 mL) in a 23 mL Teflon-lined reaction vesset at 433 K for 120 h, followed by slow cooling to room temperature.

Crystal structure determination: A yellow single crystal (0.20 mm × 0.17 mm × 0.03 mm) was carefully selected under microscope and was mounted on a glass fiber capillary for intensity data collection on a Bruker CCD area detector diffactometer with a graphite-monochromatized MoK_α radiation (λ = 0.71073 Å) from a generator operating at 50 kV and 30 mA. The intensity data were collected in the range of $0.998° \leq \theta \leq 25.01°$ using φ-ω mode at 298(2) K. A total reflections of 3510 were collected, of which 1270 reflections with R_{int} = 0.073 were unique and 961 were observed ($I > 2\sigma(I)$). Empirical absorption corrections were performed with the SADABS program. The structure has been solved by direct methods (SHELXS-97)[12] and refined by full-matrix-least squares techniques on F^2 with anisotropic thermal parameters for all of the non-hydrogen atoms (SHELXL-97)[12]. All hydrogen atoms were located by Fourier difference synthesis and geometrical analysis. These hydrogen atoms were allowed to ride on their respective parent atoms. The final full-matric least-squares refinements including 961 parameters for 1270 reflections with $I>2\sigma(I)$ gave $R_1 = 0.0585$, $wR_2 = 0.1449$ $\{w = 1/[\sigma^2(F_0^2) + (0.0816(F_o^2 + 2F_c^2)/3)^2 + 0.09 (F_0^2 + 2F_c^2)/3]\}$, $(\Delta\rho)_{max}$ = 0.80 eÅ^{-3}, $(\Delta\rho)_{min}$ = -0.45 eÅ^{-3}. All structural calculations were carried out using the SHELX-97 program package[12].

RESULTS AND DISCUSSION

The atomic coordinates and thermal parameters, the selected bond lengths and bond angles, anisotropic displacement parameters, hydrogen coordinates and the hydrogen bonds for the title compound are listed in Tables 1-5, respectively. Structure of the layer and Ortep view of the title compound are illustrated in Figs. 1 and 2, respectively.

In compound, $Mn(C_6H_3N_2O_4)_2{\cdot}2H_2O$, the Mn^{2+} ions are bridged by the pyrazine-2,3-dicarboxylate (PZDA) ligands to build two-dimensional polymeric layers. As illustrated Fig. 1, each Mn^{2+} ion is six-coordinated by two N and two O atoms with chelating mode respectively from the two PZDA ligands and two O atoms with mono-mode respectively from other different PZDA ligands.

TABLE-1
ATOMIC COORDINATES (×10^4) AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS (×10^3 Å^2)

Atom	x	y	z	U(eq)	Atom	x	y	z	U(eq)
Mn(1)	5000	5113(1)	7500	28(1)	O(5)	8551(3)	5454(4	6310(3)	38(1)
N(1)	5606(3)	3493(4)	6508(3)	26(1)	C(1)	3837(4)	3717(6)	5233(4)	26(1)
N(2)	6106(3)	1782(5)	5017(3)	28(1)	C(2)	4902(3)	3125(5)	5482(4)	23(1)
O(1)	3735(2)	4612(4)	5921(3)	31(1)	C(3)	5144(3)	2288(5)	4720(4)	24(1)
O(2)	3140(3)	3256(4)	4323(3)	36(1)	C(4)	5588(4)	8082(6)	6490(4)	27(1)
O(3)	5820(3)	7005(4)	7185(3)	32(1)	C(5)	6557(4)	3031(6)	6771(4)	31(1)
O(4)	5837(3)	9496(4)	6687(3)	41(1)	C(6)	6804(4)	2154(6)	6031(4)	33(1)

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE-2
SELECTED BOND LENGTH (Å) AND ANGLES (º)

MN(1)-O(3)	2.132(3)	O(3)-MN(1)-O(3)#1	82.54(19)	O(1)-MN(1)-N(1)	73.44(13)
MN(1)-O(3)#1	2.132(3)	O(3)-MN(1)-O(1)	106.46(13)	O(1)#1-MN(1)-N(1)	92.78(13)
MN(1)-O(1)	2.147(3)	O(3)#1-MN(1)-O(1)	90.79(12)	O(3)-MN(1)-N(1)#1	158.66(13)
MN(1)-O(1)#1	2.147(3)	O(3)-MN(1)-O(1)#1	90.79(12)	O(3)#1-MN(1)-N(1)#1	88.16(13)
MN(1)-N(1)	2.294(4)	O(3)#1-MN(1)-O(1)#1	106.46(13)	O(1)-MN(1)-N(1)#1	92.78(13)
MN(1)-N(1)#1	2.294(4)	O(1)-MN(1)-O(1)#1	157.20(19)	O(1)#1-MN(1)-N(1)#1	73.44(13)
		O(3)-MN(1)-N(1)	88.16(13)	N(1)-MN(1)-N(1)#1	106.5(2)
		O(3)#1-MN(1)-N(1)	158.66(13)		

Symmetry transformations used to generate equivalent atoms: #1 -x+1,y,-z+3/2; #2 -x+1,-y+1,-z+1

TABLE-3
ANISOTROPIC DISPLACEMENT PARAMETERS ($\times 10^3$ Å^2)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mn(1)	24(1)	31(1)	27(1)	0	8(1)	0
N(1)	18(2)	27(2)	26(2)	1(2)	3(2)	2(2)
N(2)	20(2)	37(2)	28(2)	2(2)	11(2)	6(2)
O(1)	21(2)	38(2)	32(2)	-7(2)	8(2)	5(1)
O(2)	19(2)	50(2)	32(2)	-10(2)	4(2)	2(2)
O(3)	26(2)	34(2)	31(2)	8(2)	6(2)	-4(2)
O(4)	47(3)	30(2)	35(2)	-3(2)	8(2)	-8(2)
O(5)	26(2)	46(2)	37(2)	4(2)	9(2)	11(2)
C(1)	17(3)	32(3)	26(2)	3(2)	6(2)	0(2)
C(2)	19(3)	21(2)	27(2)	3(2)	8(2)	0(2)
C(3)	20(3)	23(2)	31(2)	4(2)	11(2)	-1(2)
C(4)	17(2)	35(3)	29(2)	-2(2)	10(2)	-1(2)
C(5)	18(3)	35(3)	30(3)	4(2)	-1(2)	1(2)
C(6)	19(3)	38(3)	37(3)	4(2)	9(2)	2(2)

TABLE-4
HYDROGEN COORDINATES ($\times 10^4$) AND ISOTROPIC DISPLACEMENT PARAMETERS ($\times 10^3$ Å^2)

	x	y	z	U(eq)		x	y	z	U(eq)
H(2)	6262	1229	4558	34	H(5)	7067	3307	7469	38
H(5A)	7982	5928	6095	45	H(6)	7472	1818	6249	39
H(5B)	8645	4924	6899	45					

TABLE-5
HYDROGEN BONDS (Å AND º) FOR *BIS*(PYRAZINIUM-2,3-DICARBOXYLATO)MANGANATE DIHYDRATE

D-H	d(D-H)	d(H···A)	∠DHA	d(D···A)	A	(Symmetry transformation)
N2-H2	0.860	1.908	164.07	2.745	O5	[-X+3/2, -Y+1/2, -Z+1]
O5-H5A	0.850	1.632	176.89	2.481	O2	[-X+1, -Y+1, -Z+1]
O5-H5B	0.850	1.711	156.49	2.513	O4	[-X+3/2, Y-1/2, -Z+3/2]

Each PZDA acts as three-denates ligand to link two Mn^{2+} ions, in which one N and O atom from a PZDA ligand are coordinated to one Mn^{2+} with chelating mode and one O atom from the same PZDA ligand is coordinated to another Mn^{2+} to form two-dimensional polymeric layers.

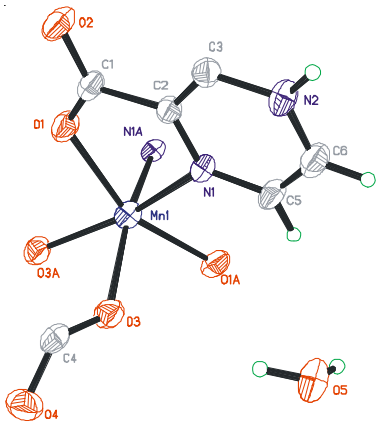

Fig. 1. Ortep III drawing of the partial structure of the title compound. Displacement ellipsoids are drawn at the 50 % probability level

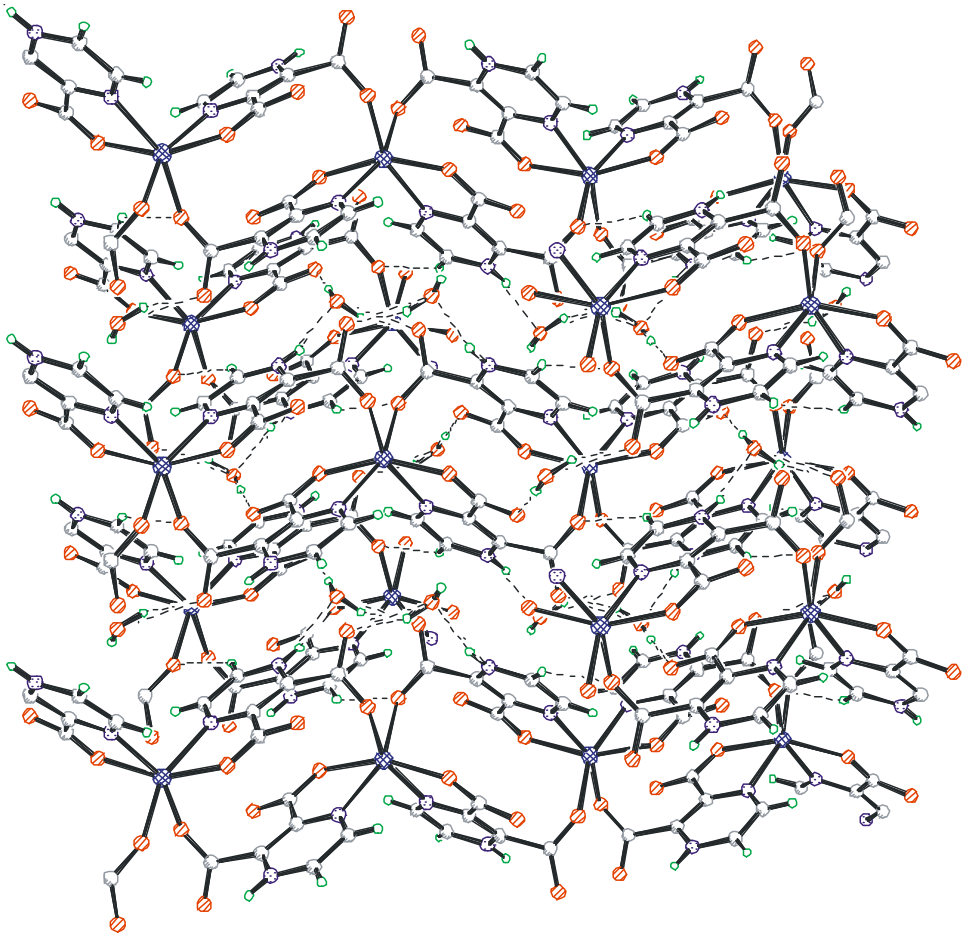

Fig. 2. Tha packing view of the title compound

The lattice water molecules lie between the polymeric layers to form strong hydrogen bonds with N and O atoms from PZDA lgands, which link the two-dimensional polymeric layers into three-dimensional crystal structure.

ACKNOWLEDGEMENTS

This work is financially supported by Funding Project for Academic Human Resources Development in Institutions of Higher Learning Under the Jurisdiction of Beijing Municipality(Grant no. BJE10016200611) and the Research Fund of Beijing University of Civil Engineering and Architecture (grant no. 100700502).

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(*Received*: 19 May 2009; *Accepted*: 25 August 2009) AJC-7782