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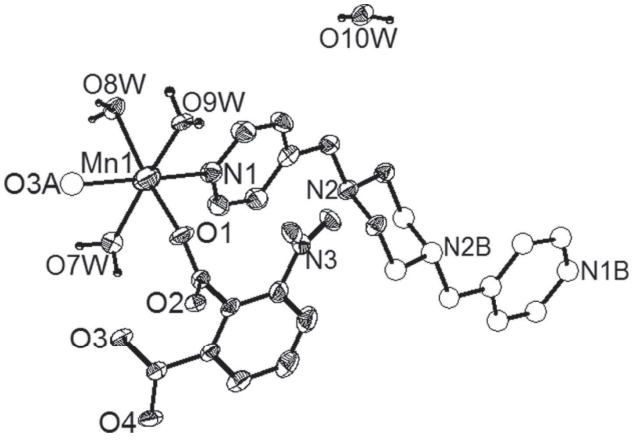
Crystal structure of catena-poly[hexaaquabis(μ$_2$-3-nitrophthalate-κ^2*O*:*O*′)-(μ$_2$-1,4-bis(4-pyridylmethyl)piperazine-κ^2*N*:*N*′)dimanganese(II)] dihydrate, $C_{32}H_{42}Mn_2N_6O_{20}$



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Abstract

$C_{32}H_{42}Mn_2N_6O_{20}$, monoclinic, $P2_1/c$ (no. 14), $a = 10.200(2)$ Å, $b = 19.893(4)$ Å, $c = 11.3785(17)$ Å, $b = 123.118(12)°$, $V = 1933.7(7)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0602$, $wR_{ref}(F^2) = 0.1673$, $T = 293$ K.

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The crystal structure is shown in the figure. Tables 1–3 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

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Table 1: Data collection and handling.

Crystal:	Colorless, Block, size 0.21×0.29×0.33 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	7.45 cm^{-1}
Diffractometer, scan mode:	CCD area detector, φ and ω scans
$2\theta_{max}$:	50.52°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	12161, 3474
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2715
$N(param)_{refined}$:	271
Programs:	SHELX [17]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(4)	4*e*	0.9659	0.1767	0.5804	0.043
H(5A)	4*e*	0.9614	0.2816	0.6659	0.053
H(6A)	4*e*	0.8266	0.2984	0.7718	0.051
H(10)	4*e*	0.4215	0.2078	0.4081	0.041
H(11)	4*e*	0.4056	0.3227	0.3892	0.041
H(13)	4*e*	0.1858	0.3219	0.5913	0.044
H(14)	4*e*	0.2075	0.2075	0.6044	0.045
H(15A)	4*e*	0.1667	0.4216	0.3970	0.038
H(15B)	4*e*	0.2803	0.4278	0.5600	0.038
H(16A)	4*e*	0.5746	0.3949	0.6031	0.037
H(16B)	4*e*	0.5453	0.4594	0.6652	0.037
H(17A)	4*e*	0.3446	0.5373	0.5150	0.033
H(17B)	4*e*	0.2377	0.5250	0.3525	0.033
H(1W)	4*e*	0.3662	0.0507	0.3040	0.049
H(2W)	4*e*	0.4972	0.0692	0.4131	0.049
H(3W)	4*e*	0.0491	0.0541	0.3950	0.060
H(4W)	4*e*	0.0377	0.0872	0.2834	0.060
H(5W)	4*e*	0.3030	0.0749	0.7589	0.045
H(6W)	4*e*	0.1625	0.0714	0.6496	0.045
H(7W)	4*e*	0.0427	0.4615	0.6206	0.080
H(8W)	4*e*	−0.0253	0.4210	0.5203	0.080

Source of material

A mixture of $Mn(OAc)_2{\cdot}4H_2O$ (0.025 g, 0.10 mmol), 3-nitro-1,2-benzenedicarboxylic acid (0.2 mmol, 42.2 mg), 1,4-bis(4-pyridylmethyl)piperazine (0.027 g, 0.10 mmol), EtOH (4 mL)

Table 3: Atomic displacement parameters (Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn(1)	4*e*	0.31485(6)	0.08228(3)	0.51672(6)	0.0170(3)	0.0247(3)	0.0285(3)	−0.0014(2)	0.0104(3)	−0.0006(2)
N(1)	4*e*	0.3154(3)	0.1956(2)	0.5064(3)	0.032(2)	0.027(2)	0.039(2)	−0.002(1)	0.021(2)	0.001(1)
N(2)	4*e*	0.3838(3)	0.4475(1)	0.4572(3)	0.017(1)	0.021(2)	0.029(2)	−0.001(1)	0.011(1)	−0.001(1)
N(3)	4*e*	0.6815(4)	0.2133(2)	0.8333(4)	0.034(2)	0.050(2)	0.045(2)	−0.004(2)	0.018(2)	−0.019(2)
O(1)	4*e*	0.5488(3)	0.0711(1)	0.6812(3)	0.016(1)	0.050(2)	0.035(2)	−0.006(1)	0.010(1)	−0.004(1)
O(2)	4*e*	0.7892(3)	0.0334(1)	0.8228(3)	0.029(2)	0.041(2)	0.036(2)	0.008(1)	0.013(1)	0.012(1)
O(3)	4*e*	0.7147(3)	0.0273(1)	0.5238(3)	0.016(1)	0.031(1)	0.038(2)	−0.005(1)	0.013(1)	−0.006(1)
O(4)	4*e*	0.9644(3)	0.0419(1)	0.5986(3)	0.027(2)	0.038(2)	0.076(2)	−0.007(1)	0.034(2)	−0.012(1)
O(5)	4*e*	0.6825(4)	0.1679(2)	0.9067(4)	0.080(3)	0.063(2)	0.068(2)	−0.013(2)	0.056(2)	−0.018(2)
O(6)	4*e*	0.6225(4)	0.2688(2)	0.8205(4)	0.060(2)	0.063(2)	0.077(3)	0.017(2)	0.035(2)	−0.018(2)
C(1)	4*e*	0.6932(4)	0.0761(2)	0.7410(4)	0.021(2)	0.031(2)	0.023(2)	−0.003(2)	0.010(2)	−0.004(1)
C(2)	4*e*	0.7617(4)	0.1369(2)	0.7127(4)	0.013(2)	0.030(2)	0.021(2)	−0.001(1)	0.001(1)	−0.001(1)
C(3)	4*e*	0.8376(4)	0.1284(2)	0.6420(4)	0.016(2)	0.027(2)	0.026(2)	−0.002(1)	0.007(2)	−0.000(1)
C(4)	4*e*	0.9133(4)	0.1828(2)	0.6254(4)	0.027(2)	0.036(2)	0.042(2)	−0.006(2)	0.018(2)	0.001(2)
C(5)	4*e*	0.9097(5)	0.2458(2)	0.6761(5)	0.039(2)	0.031(2)	0.050(3)	−0.011(2)	0.017(2)	0.001(2)
C(6)	4*e*	0.8316(5)	0.2559(2)	0.7405(5)	0.037(2)	0.026(2)	0.052(3)	−0.005(2)	0.016(2)	−0.007(2)
C(7)	4*e*	0.7601(4)	0.2016(2)	0.7584(4)	0.026(2)	0.033(2)	0.032(2)	−0.001(2)	0.010(2)	−0.005(2)
C(9)	4*e*	0.8405(4)	0.0610(2)	0.5837(4)	0.021(2)	0.031(2)	0.028(2)	−0.004(2)	0.012(2)	−0.001(2)
C(10)	4*e*	0.3727(5)	0.2310(2)	0.4451(4)	0.039(2)	0.027(2)	0.047(2)	−0.003(2)	0.030(2)	−0.003(2)
C(11)	4*e*	0.3635(5)	0.3003(2)	0.4331(4)	0.040(2)	0.030(2)	0.041(2)	−0.005(2)	0.028(2)	0.000(2)
C(12)	4*e*	0.2914(4)	0.3363(2)	0.4869(4)	0.020(2)	0.028(2)	0.028(2)	−0.005(1)	0.011(2)	−0.001(2)
C(13)	4*e*	0.2338(5)	0.2999(2)	0.5523(5)	0.044(2)	0.030(2)	0.051(3)	−0.000(2)	0.037(2)	−0.000(2)
C(14)	4*e*	0.2475(5)	0.2309(2)	0.5599(5)	0.043(2)	0.033(2)	0.050(3)	−0.002(2)	0.034(2)	0.003(2)
C(15)	4*e*	0.2715(5)	0.4113(2)	0.4757(5)	0.029(2)	0.027(2)	0.042(2)	−0.004(2)	0.022(2)	−0.005(2)
C(16)	4*e*	0.5438(4)	0.4418(2)	0.5850(4)	0.022(2)	0.026(2)	0.031(2)	0.000(2)	0.007(2)	0.003(2)
C(17)	4*e*	0.3429(4)	0.5196(2)	0.4348(4)	0.022(2)	0.024(2)	0.033(2)	0.002(1)	0.011(2)	0.001(2)
O(7W)	4*e*	0.4003(3)	0.0782(1)	0.3719(3)	0.032(2)	0.033(2)	0.035(2)	−0.000(1)	0.018(1)	−0.002(1)
O(8W)	4*e*	0.0547(3)	0.0924(1)	0.3648(3)	0.028(2)	0.038(2)	0.038(2)	−0.000(1)	0.009(1)	0.002(1)
O(9W)	4*e*	0.2536(3)	0.0824(1)	0.6712(3)	0.019(1)	0.042(2)	0.027(1)	−0.003(1)	0.012(1)	0.002(1)
O(10W)	4*e*	0.0144(4)	0.4205(2)	0.6082(3)	0.037(2)	0.068(2)	0.039(2)	−0.004(1)	0.012(2)	−0.000(1)

and H_2O (3 mL) was placed in a 23 mL Teflon-lined autoclave at 393 K for 4 days, then cooled to room temperature and obtained colourless block crystals in ca. 79% yield. Elemental analysis calcd. (%) for $C_{16}H_{21}N_3O_{10}Mn$: C, 40.92; H, 4.61; N, 8.92. Found: C, 40.86; H, 4.50; N, 8.93. Selected IR (KBr, cm^{-1}): 2800–3600(m), 1639(w), 1597(m), 1563(s), 1523(m), 1452(w), 1433(m), 1340(m), 1304(m), 1232(w), 1158(w), 1145(w), 1068(s), 1000(m), 920(m), 847(m), 825(s), 802(w), 779(w), 755(w), 713(m), 695(s), 665(w).

Discussion

Interest in coordination polymers is rapidly increasing in recent years not only owing to their versatile intriguing architectures and topologies [1, 2] but also for their potential applications in a variety of areas, including catalysis, gas storage/separations, fluorescent sensing, nonlinear optics, electronic, and magnetic devices etc. [3–5]. The mixed-ligands strategy by the judicious choice of various organic linkers, for example, the combination of rigid aromatic benzenedicarboxylic acid and its derivatives and N-donor ligands, has been proven to be high-efficient for the construction of novel coordination polymers because of having strong coordination ability and diverse coordination modes. Recently, the subtle control over the structures and functional properties of coordination polymers can be implemented by using various functionalized benzene-carboxylates, for example, 3-nitrophthalate acid ($NbdcH_2$) [6–9]. Our group chose the 3-nitrophthalate acid as organic bridging ligands to self-assemble and produced versatile 1D, 2D and 3D metal-organic framework with the diverse properties [10–14]. Though the nitro group does not participate in coordination, $NbdcH_2$ may provide the potential to construct unpredictable and interesting network structures due to the existence of an electron-withdrawing nitro-group on the aromatic backbone. In the title compound we use 3-nitrophthalate as a main ligand, and 1,4-bis(4-pyridylmethyl)piperazine (bpmp) as coligand to construct a new coordination polymer not only because bpmp has twisted conformation, also its four nitrogen atoms may improve the structures and properties of coordination polymers [15, 16].

The title structure is a 1D coordination polymer with dinuclear units. The asymmetry unit contains one crystallographic Mn(II) ion, one completely deprotonated 3-Nbdc dianion, a half bpmp molecule, three coordinated water and one free water, as shown in the figure (A: $1-x$, $-y$, $1-z$; B: $1-x$, $1-y$, $1-z$). The Mn(II) ion is six-coordinated with a distorted

octahedral [$MnNO_5$] geometry, which is coordinated by four oxygen atoms in the equatorial plane, three oxygen atoms from three coordination water molecules and one carboxylate oxygen atom from one 3-Nbdc anion, and one nitrogen atom from one bpmp coligand and another oxygen atom from one 3-Nbdc anion at the axial positions. The Mn—O bond distances fall in the range of 2.090(3)–2.249(3) Å, the Mn—N bond length is 2.257(3) Å, respectively. The adjacent Mn(II) centers are bridged by the 3-Nbdc ligands with two carboxyl groups adopting a monodentate coordination mode to form binuclear units with the Mn···Mn separation of 5.1670(12) Å. The binuclear units are interlinked together with bpmp coligands to form a one-dimensional chain coordination polymer with the Mn···Mn distance of 17.093(4) Å across bpmp ligands. As the existence of the coordinated water and free water molecules, there exist multitudinous H-bond interactions: (a) between coordinated water molecules and carboxylate O atoms (O(7W)—H(1W)···O(2): d = 2.981(4) Å; O(7W)—H(1W)···O(1): d = 3.130(4) Å; O(7W)—H(2W)···O(3): d = 2.871(4) Å; O(8W)—H(3W)···O(4): d = 2.728(4) Å; O(8W)—H(3W)···O(3): d = 3.090(4) Å; O(9W)—H(6W)···O(4): d = 2.715(4) Å); (b) between the coordinated and uncoordinated water molecules (O(8W)—H(4W)···O(10W): d = 2.729(4) Å); (c) between the coordinated water ligands and the bpmp N atom (O(9W)—H(5W)···N(2): d = 2.826(4) Å); (d) between the uncoordinated water molecule and one carboxylate O atom (O(10W)—H(7W)···O(2): d = 2.819(4) Å; O(10W)—H(8W)···O(2): d = 2.917(4) Å). Individual chains are interlinked forming a three-dimensional supramolecular structure via H-bond interactions.

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