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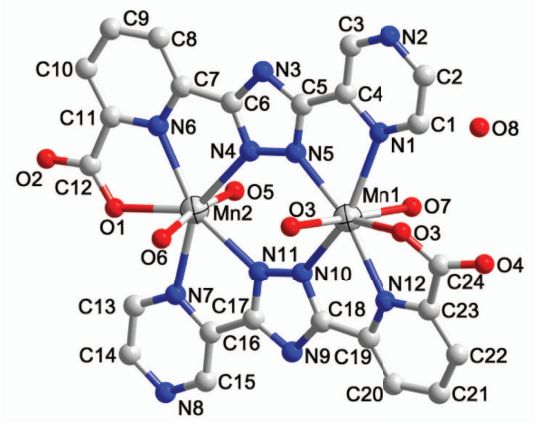
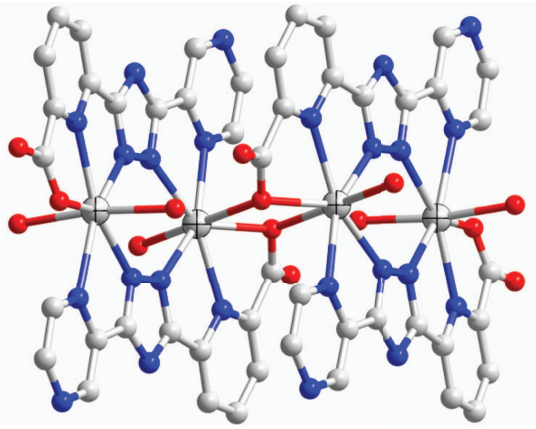
Crystal structure of hexaaquabis(μ$_2$-3-(6-carboxylatopyridin-2-yl)-5-(pyrazin-2-yl)-1,2,4-triazol-1-ido)bis(μ$_3$-3-(6-carboxylatopyridin-2-yl)-5-(pyrazin-2-yl)-1,2,4-triazol-1-ido)tetra-manganese(II) dihydrate, $C_{48}H_{40}Mn_4N_{24}O_{16}$





DOI 10.1515/ncrs-2014-9097
Received May 8, 2015; accepted January 18, 2016; available online February 26, 2016

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Abstract

$C_{48}H_{40}Mn_4N_{24}O_{16}$, monoclinic, $P2_1/c$ (no. 14), $a = 13.458(7)$ Å, $b = 14.095(8)$ Å, $c = 14.679(8)$ Å, $b = 96.535(7)°$, 2766(3) Å^3, $Z = 2$, $R_{gt}(F) = 0.0570$, $wR_{ref}(F^2) = 0.1273$, $T = 296$ K.

CCDC no.: 1446342

Table 1: Data collection and handling.

Crystal:	Yellow, block size 0.26×0.28×0.32 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	9.87 cm^{-1}
Diffractometer, scan mode:	CCD area detector, φ and ω scans
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	18530, 4673
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2170
$N(param)_{refined}$:	416
Programs:	SHELX [10]

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

Atom	Site	x	y	z	U_{iso}
H(1W)	4e	0.2688	0.4456	0.0727	0.094
H(2W)	4e	0.1692	0.4853	0.0255	0.094
H(3W)	4e	0.0625	0.5289	0.3381	0.083
H(4W)	4e	0.1584	0.5272	0.3888	0.083
H(5W)	4e	0.5972	0.4929	0.2447	0.080
H(6W)	4e	0.6101	0.3909	0.2652	0.080
H(7W)	4e	0.7658	0.5575	0.1519	0.151
H(8W)	4e	0.7097	0.5916	0.1955	0.151
H(1)	4e	0.7088	0.5967	0.4652	0.059
H(2)	4e	0.7683	0.7438	0.4909	0.058
H(3)	4e	0.5277	0.8493	0.3539	0.055
H(8)	4e	0.2228	0.8771	0.1915	0.071
H(9)	4e	0.0636	0.9187	0.1269	0.083
H(10)	4e	−0.0505	0.8009	0.0849	0.076
H(13)	4e	−0.0463	0.3784	0.1049	0.082
H(14)	4e	−0.1061	0.2283	0.0863	0.078
H(15)	4e	0.1432	0.1304	0.2096	0.074
H(20)	4e	0.4541	0.1120	0.3733	0.064
H(21)	4e	0.6077	0.0803	0.4569	0.068
H(22)	4e	0.7058	0.2051	0.5176	0.070

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*	0.48161(6)	0.48274(6)	0.37823(6)	0.0395(6)	0.0306(5)	0.0371(5)	0.0021(4)	−0.0008(4)	−0.0010(4)
Mn(2)	4*e*	0.16522(7)	0.50685(6)	0.20175(6)	0.0510(6)	0.0363(6)	0.0523(6)	0.0014(4)	−0.0008(5)	−0.0030(5)
O(1)	4*e*	0.0053(3)	0.5255(4)	0.1388(4)	0.071(3)	0.054(3)	0.126(5)	0.011(3)	−0.029(3)	−0.004(3)
O(2)	4*e*	−0.1135(4)	0.6210(4)	0.0678(4)	0.072(4)	0.105(5)	0.109(5)	0.016(3)	−0.027(3)	−0.031(3)
O(3)	4*e*	0.6045(3)	0.4726(3)	0.5098(2)	0.050(3)	0.052(3)	0.037(2)	0.013(2)	0.000(2)	0.000(2)
O(4)	4*e*	0.7477(4)	0.3910(3)	0.5412(3)	0.054(3)	0.083(4)	0.088(4)	0.011(3)	−0.011(3)	−0.022(3)
O(5)	4*e*	0.2190(3)	0.4830(3)	0.0667(3)	0.062(3)	0.068(3)	0.058(3)	−0.004(2)	0.006(2)	0.000(2)
O(6)	4*e*	0.1203(3)	0.5100(3)	0.3402(3)	0.047(3)	0.053(3)	0.064(3)	0.006(2)	0.003(2)	−0.006(2)
O(7)	4*e*	0.5847(3)	0.4444(3)	0.2759(3)	0.064(3)	0.035(2)	0.063(3)	0.005(2)	0.021(2)	−0.002(2)
O(8)	4*e*	0.7223(4)	0.5342(3)	0.1832(4)	0.107(4)	0.045(3)	0.162(5)	0.006(3)	0.066(4)	0.014(3)
N(1)	4*e*	0.5830(4)	0.6317(3)	0.3925(3)	0.051(3)	0.037(3)	0.043(3)	0.003(3)	0.006(3)	0.009(2)
N(2)	4*e*	0.6557(4)	0.8142(4)	0.4251(4)	0.059(4)	0.045(4)	0.056(4)	−0.010(3)	0.011(3)	0.008(3)
N(3)	4*e*	0.3701(4)	0.7544(3)	0.2700(3)	0.039(3)	0.029(3)	0.047(3)	−0.002(2)	0.000(3)	0.003(2)
N(4)	4*e*	0.3053(4)	0.6075(3)	0.2523(3)	0.049(3)	0.033(3)	0.038(3)	0.003(2)	0.001(3)	0.004(2)
N(5)	4*e*	0.3990(4)	0.5994(3)	0.2975(3)	0.043(3)	0.037(3)	0.040(3)	0.000(2)	0.002(3)	0.004(2)
N(6)	4*e*	0.1302(4)	0.6662(3)	0.1693(3)	0.044(3)	0.043(3)	0.047(3)	0.001(3)	0.001(3)	−0.005(3)
N(7)	4*e*	0.0839(4)	0.3483(4)	0.1724(4)	0.054(4)	0.039(3)	0.066(4)	0.005(3)	0.006(3)	0.008(3)
N(8)	4*e*	0.0139(5)	0.1632(4)	0.1423(4)	0.067(5)	0.066(4)	0.063(4)	−0.022(4)	−0.008(3)	0.001(3)
N(9)	4*e*	0.2996(4)	0.2318(3)	0.2946(3)	0.044(3)	0.039(3)	0.045(3)	−0.002(3)	0.000(3)	−0.006(2)
N(10)	4*e*	0.3584(4)	0.3807(3)	0.3151(3)	0.042(3)	0.033(3)	0.039(3)	−0.003(2)	0.002(3)	−0.009(2)
N(11)	4*e*	0.2688(4)	0.3848(3)	0.2651(4)	0.052(4)	0.031(3)	0.056(4)	−0.003(3)	0.002(3)	−0.009(3)
N(12)	4*e*	0.5229(4)	0.3262(3)	0.4219(3)	0.052(4)	0.037(3)	0.040(3)	0.006(3)	0.009(3)	−0.001(2)
C(1)	4*e*	0.6708(5)	0.6480(4)	0.4412(4)	0.044(4)	0.044(4)	0.056(4)	−0.001(3)	−0.011(4)	0.015(3)
C(2)	4*e*	0.7062(5)	0.7362(5)	0.4567(4)	0.043(4)	0.060(5)	0.041(4)	−0.009(4)	0.001(3)	0.013(3)
C(3)	4*e*	0.5666(5)	0.7981(4)	0.3763(4)	0.047(4)	0.038(4)	0.051(4)	−0.009(3)	0.003(3)	0.004(3)
C(4)	4*e*	0.5318(4)	0.7075(4)	0.3587(4)	0.040(4)	0.034(4)	0.037(4)	−0.007(3)	0.015(3)	0.001(3)
C(5)	4*e*	0.4346(4)	0.6891(4)	0.3082(4)	0.039(4)	0.032(3)	0.033(4)	−0.002(3)	0.008(3)	0.000(3)
C(6)	4*e*	0.2917(5)	0.7007(4)	0.2371(4)	0.040(4)	0.043(4)	0.034(4)	0.005(3)	0.002(3)	0.002(3)
C(7)	4*e*	0.1954(5)	0.7361(4)	0.1908(4)	0.057(5)	0.044(4)	0.028(4)	−0.001(3)	0.006(3)	0.000(3)
C(8)	4*e*	0.1745(5)	0.8309(4)	0.1757(5)	0.050(5)	0.042(4)	0.084(5)	0.011(3)	0.003(4)	0.005(4)
C(9)	4*e*	0.0808(6)	0.8553(5)	0.1368(5)	0.058(5)	0.054(5)	0.093(6)	0.007(4)	−0.003(5)	0.007(4)
C(10)	4*e*	0.0130(5)	0.7856(6)	0.1128(5)	0.045(5)	0.079(6)	0.063(5)	0.011(4)	0.001(4)	0.001(4)
C(11)	4*e*	0.0391(5)	0.6906(5)	0.1302(4)	0.051(5)	0.050(4)	0.050(4)	−0.004(4)	0.008(4)	0.001(3)
C(12)	4*e*	−0.0276(6)	0.6060(6)	0.1114(6)	0.060(6)	0.089(7)	0.082(6)	0.008(5)	−0.006(5)	−0.006(5)
C(13)	4*e*	−0.0060(5)	0.3284(6)	0.1280(5)	0.049(5)	0.074(6)	0.078(6)	−0.001(4)	−0.010(4)	0.006(4)
C(14)	4*e*	−0.0416(6)	0.2377(6)	0.1150(5)	0.060(5)	0.073(6)	0.058(5)	−0.020(4)	−0.005(4)	0.006(4)
C(15)	4*e*	0.1030(5)	0.1810(5)	0.1877(5)	0.061(5)	0.043(4)	0.081(6)	−0.010(4)	0.002(4)	−0.005(4)
C(16)	4*e*	0.1379(5)	0.2728(5)	0.2034(4)	0.046(4)	0.052(4)	0.045(4)	−0.004(4)	0.017(3)	0.002(3)
C(17)	4*e*	0.2342(5)	0.2951(4)	0.2546(4)	0.048(4)	0.032(4)	0.057(4)	0.006(3)	0.007(4)	−0.003(3)
C(18)	4*e*	0.3755(5)	0.2870(4)	0.3317(4)	0.042(4)	0.041(4)	0.037(4)	−0.001(3)	0.012(3)	−0.003(3)
C(19)	4*e*	0.4663(5)	0.2545(4)	0.3855(4)	0.050(4)	0.041(4)	0.040(4)	−0.001(3)	0.007(3)	−0.006(3)
C(20)	4*e*	0.4949(5)	0.1610(4)	0.3979(4)	0.064(5)	0.037(4)	0.058(5)	0.009(3)	0.004(4)	0.001(3)
C(21)	4*e*	0.5858(5)	0.1425(4)	0.4478(5)	0.066(5)	0.031(4)	0.076(5)	0.012(4)	0.015(4)	0.001(4)
C(22)	4*e*	0.6441(5)	0.2168(5)	0.4842(4)	0.056(5)	0.059(5)	0.061(5)	0.011(4)	0.007(4)	0.002(4)
C(23)	4*e*	0.6107(5)	0.3076(4)	0.4708(4)	0.046(4)	0.045(4)	0.048(4)	0.006(3)	0.010(3)	−0.007(3)
C(24)	4*e*	0.6600(5)	0.3962(5)	0.5105(4)	0.048(5)	0.061(5)	0.039(4)	0.002(4)	−0.006(3)	−0.004(3)

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.

Experimental details

A mixture of 6-(5-(pyrazin-2-yl)-4H-1,2,4-triazol-3-yl)picolinic acid (0.05 mmol) and $MnCl_2{\cdot}H_2O$ (0.1 mmol) in 10 mL mixed solvent (CH_3CN/H_2O, V/V, 7:3) was placed in a 25 mL Teflon-lined stainless steel vessel, and the vessel was sealed and heated to 160°C for 72 h. The mixture cooled to room temperature over 24 h. Yellow crystals of the title complex were obtained with a yield of 68% (based on Mn).

Discussion

In recent years, there has been great interest in the construction of metal-organic frameworks (MOFs) due to their

interesting properties such as magnetic, electronic, nonlinear optical properties and intriguing structural motifs varying from extended coordination polymers to discrete molecular entities such as cages, metallomacrocycles, and many others [1–6]. A successful strategy in building such networks is to employ appropriate bridging ligands that can bind metal ions in different modes and provide a possible way to achieve more robust polymeric structures [7–9].

The asymmetric unit of the title structure contains two Mn(II) ion, two 3-(6-carboxylatopyridin-2-yl)-5-(pyrazin-2-yl)-1,2,4-triazol-1-ido ligands, three coordinated water molecules and one free water molecule (see the upper part of the figure). The Mn1 ion is coordinated by three organic ligands as well as one coordinated water molecule, resulting in a seven N_4O_3 coordination. The Mn2 ion is coordinated by four N atoms and one O atom from two different organic ligands, and two water molecules, to finish a N_4O_3 coordination geometry. The Mn–O bond lengths range from 2.187(6) to 2.379(5) Å, whereas the Mn–N bond lengths vary from 2.260(6) to 2.517(7) Å. The bond angles around both Mn(II) ion vary from 69.0(2) to 172.9(2)°. The dinuclear moiety is connected by two O atoms of two carboxylic groups to an adjacent one to give a tetranuclear structure, with a Mn···Mn distance of 3.580(2) Å for Mn1-Mn1A and 4.738(2) for Mn1-Mn2 (see the lower part of the figure). These tetranuclear complexes are connected by O—H···O, and O—H···N hydrogen bonds to generate a 3D framework.

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