Crystal structure of aqua(benzene-1,2-dicarboxylato-κ^2*O,O′*)bis[2-(1*H*-pyrazol-3-yl)pyridine-κ^2*N,N′*]manganese(II), $C_{24}H_{20}MnN_6O_5$

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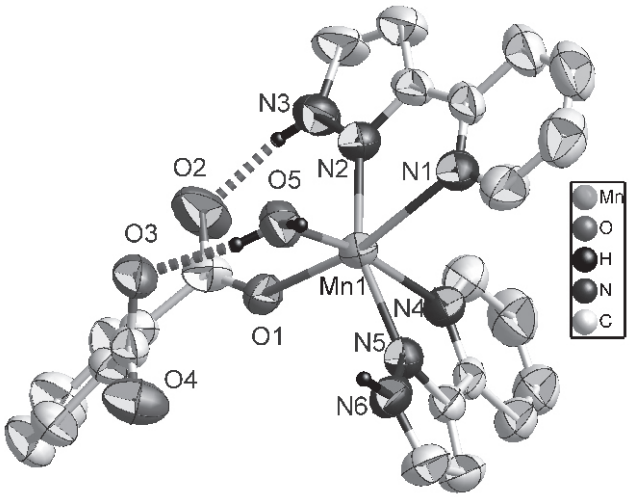

Abstract

$C_{24}H_{20}MnN_6O_5$, triclinic, $P\bar{1}$ (no. 2), a = 10.442(4) Å, b = 11.450(4) Å, c = 11.487(4) Å, α = 75.534(7)°, β = 64.803(7)°, γ = 82.086(7)°, V = 1202.5 Å^3, Z = 2, $R_{gt}(F)$ = 0.0598, $wR_{ref}(F^2)$ = 0.1756, T = 296 K.

Table 1. Data collection and handling.

Crystal:	colourless blocks, size 0.10×0.22×0.28 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	5.97 cm^{-1}
Diffractometer, scan mode:	CCD area detector, φ and ω
$2\theta_{max}$:	50.06°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6085, 4232
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1862
$N(param)_{refined}$:	325
Programs:	SHELX [8]

Source of material

A mixture containing $Mn(OAc)_2{\cdot}4H_2O$ (24.5 mg, 0.10 mmol), *HL* (14.5 mg, 0.10 mmol), benzene-1,2-dicarboxylic acid (16.6 mg, 0.10 mmol) and H_2O (10 mL) was sealed in a Teflon-lined stainless steel vessel (20 mL), which was heated at 413 K for 3 days. After cooled to room temperature at a rate of 5 K h^{-1}, colourless block-shaped crystals suitable for X-ray analysis were obtained in 45% yield. **Elemental analysis** calcd. for $C_{24}H_{20}MnN_6O_5$: C 54.66, H 3.82, N 15.94%; found: C 54.57, H 3.79, N 15.99%.

Experimental details

The R1(for all reflections) factor which refines to 0.1777 was mainly affected by the weak diffraction data (σ(I)/net(I) = 13.5).

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Discussion

Weak intramolecular interactions such as hydrogen bonding and π–π stacking interactions play important roles in the creation of a variety of molecular architectures for molecular self-assembly and recognition [1–4]. The geometries of ligands also play important roles in adjusting the topologies of their metal complexes, especially for low-dimensional coordination complexes [5–7]. In this regard, we are interested in investigating the influence of intramolecular hydrogen bonding interactions and the geometries of pendant ligands on the topologies of low-dimensional coordination complexes. In this paper, we select 3-(2-pyridyl)pyrazole (*HL*) and benzene-1,2-dicarboxylic acid (1,2-H_2bdc) to react with Mn(II) ions to obtain a new MOF. Single crystal X-ray diffraction analysis revealed that the asymmetric unit of the title structure consists of one Mn^{2+} ion that is distorted octahedrally coordinated by two chelating 3-(2-pyridyl)pyrazole ligands, one carboxylate coordinated in κ^2O,O' fashion from one bdc^{2-} ligand and one coordinated water molecule leading to an overall $[MnN_4O_2]$ coordination environment (Figure). If the chelating *L* ligand is treated as one connecting node, the Mn^{II} center in complex has a pseudo-tetrahedral geometry. The dihedral angle between the two 3-(2-pyridyl)-1*H*-pyrazole planes is 86.28(1)°. The Mn–N and Mn–O bond distances are in the range of 2.178(5)-2.360(6) and 2.097(4)-2.123(4) Å, respectively. All bond lengths Mn–O and Mn–N fall into normal ranges. It is worth noting that N3 and N6 atom of *L* present strong intramolecular / intermolecular hydrogen bonding interactions with the uncoordinated O2 and O3 atom of bdc^{2-} with N3···O2 and N6···O3 separation of 2.633(7) and 2.790(7) Å, respectively. Furthermore, the adjacent discrete $[Mn(L)_2(bdc)(H_2O]$ units are arranged into a dinuclear units by intermolecular/intramolecular O–H···O and N–H···O hydrogen bonding interactions. Intermolecular π–π stacking interactions with a face-to-face separation of 3.561(5) and 3.811(4) Å between the 3-(2-pyridyl)pyrazole ligands are observed.

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(5A)	2*i*	0.8566	0.4935	0.6810	0.104
H(5B)	2*i*	0.8249	0.5454	0.5676	0.104
H(3)	2*i*	0.4405	0.7786	0.6917	0.086
H(6)	2*i*	1.1249	0.6062	0.5944	0.080
H(1)	2*i*	0.8995	0.5905	0.9217	0.109
H(2)	2*i*	0.8289	0.5169	1.1461	0.130
H(3')	2*i*	0.5942	0.5255	1.2798	0.135
H(4)	2*i*	0.4260	0.5946	1.1941	0.110
H(7)	2*i*	0.2647	0.6750	1.0707	0.106
H(8)	2*i*	0.2165	0.7637	0.8719	0.110
H(9)	2*i*	0.5814	0.9509	0.8011	0.090
H(10)	2*i*	0.6073	1.1466	0.8098	0.110
H(11)	2*i*	0.8362	1.2108	0.7293	0.111
H(12)	2*i*	1.0245	1.0833	0.6561	0.094

Table 2. continued.

Atom	Site	x	y	z	U_{iso}
H(15)	2*i*	1.2265	0.9250	0.5767	0.085
H(16)	2*i*	1.3215	0.7227	0.5374	0.093
H(19)	2*i*	1.0004	0.7445	0.0609	0.090
H(20)	2*i*	0.9139	0.9083	–0.0497	0.110
H(21)	2*i*	0.7128	1.0120	0.0644	0.125
H(22)	2*i*	0.6057	0.9574	0.2908	0.099

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn(1)	2*i*	0.7659(1)	0.71412(8)	0.69830(8)	0.0570(7)	0.0549(6)	0.0473(6)	–0.0155(4)	–0.0179(5)	–0.0079(4)
O(1)	2*i*	0.7547(4)	0.7850(4)	0.5158(4)	0.059(3)	0.076(3)	0.057(3)	–0.016(2)	–0.031(2)	–0.005(2)
O(2)	2*i*	0.5409(5)	0.7986(6)	0.5129(5)	0.055(4)	0.228(7)	0.071(4)	–0.007(4)	–0.021(3)	–0.018(4)
O(3)	2*i*	0.8257(5)	0.5654(4)	0.3972(4)	0.092(4)	0.062(3)	0.055(3)	–0.019(3)	–0.028(2)	0.000(2)
O(4)	2*i*	1.0438(6)	0.6236(4)	0.2641(5)	0.077(4)	0.088(4)	0.091(4)	0.002(3)	–0.020(3)	0.009(3)
O(5)	2*i*	0.8059(4)	0.5425(3)	0.6479(4)	0.086(3)	0.068(3)	0.056(3)	–0.004(2)	–0.031(2)	–0.010(2)
N(1)	2*i*	0.7111(7)	0.6332(5)	0.9236(5)	0.086(5)	0.064(4)	0.056(4)	–0.026(3)	–0.024(4)	–0.006(3)
N(2)	2*i*	0.5369(6)	0.7139(4)	0.8085(5)	0.062(4)	0.062(4)	0.058(4)	–0.012(3)	–0.020(3)	–0.011(3)
N(3)	2*i*	0.4297(6)	0.7515(5)	0.7721(5)	0.058(4)	0.087(4)	0.059(4)	–0.006(3)	–0.012(3)	–0.014(3)
N(4)	2*i*	0.7795(6)	0.9025(4)	0.7271(5)	0.068(4)	0.054(3)	0.059(3)	–0.011(3)	–0.024(3)	–0.010(3)
N(5)	2*i*	0.9933(6)	0.7434(5)	0.6467(4)	0.061(4)	0.059(3)	0.052(3)	–0.005(3)	–0.023(3)	–0.014(3)
N(6)	2*i*	1.1175(6)	0.6801(5)	0.6015(5)	0.073(4)	0.062(4)	0.071(4)	–0.017(3)	–0.034(3)	–0.010(3)
C(1)	2*i*	0.8035(9)	0.5910(7)	0.9767(8)	0.102(7)	0.098(6)	0.077(6)	–0.037(5)	–0.046(5)	0.009(5)
C(2)	2*i*	0.763(1)	0.5477(7)	1.111(1)	0.16(1)	0.095(7)	0.099(8)	–0.033(7)	–0.079(7)	0.004(6)
C(3)	2*i*	0.623(1)	0.5518(8)	1.1893(9)	0.18(1)	0.101(7)	0.062(6)	–0.035(8)	–0.048(7)	–0.008(5)
C(4)	2*i*	0.522(1)	0.5937(6)	1.1397(7)	0.141(8)	0.072(5)	0.055(5)	–0.028(5)	–0.025(5)	–0.016(4)
C(5)	2*i*	0.5723(9)	0.6348(5)	1.0029(6)	0.097(6)	0.057(4)	0.043(4)	–0.026(4)	–0.016(4)	–0.014(3)
C(6)	2*i*	0.4761(8)	0.6795(5)	0.9399(7)	0.077(6)	0.055(4)	0.049(5)	–0.024(4)	–0.005(4)	–0.013(3)
C(7)	2*i*	0.3311(9)	0.6940(7)	0.9841(8)	0.071(6)	0.103(6)	0.071(6)	–0.025(5)	0.000(5)	–0.026(5)
C(8)	2*i*	0.3046(8)	0.7420(7)	0.8744(8)	0.051(5)	0.115(7)	0.083(6)	–0.012(4)	0.005(5)	–0.029(5)
C(9)	2*i*	0.6722(8)	0.9779(6)	0.7714(6)	0.081(6)	0.068(5)	0.078(5)	–0.007(4)	–0.031(4)	–0.019(4)
C(10)	2*i*	0.686(1)	1.0959(6)	0.7767(7)	0.119(8)	0.063(5)	0.091(6)	0.006(5)	–0.035(5)	–0.032(4)
C(11)	2*i*	0.821(1)	1.1323(7)	0.7302(7)	0.125(8)	0.068(5)	0.085(6)	–0.028(6)	–0.035(5)	–0.021(4)
C(12)	2*i*	0.9333(9)	1.0570(7)	0.6856(6)	0.100(6)	0.073(5)	0.068(5)	–0.032(5)	–0.035(4)	–0.009(4)
C(13)	2*i*	0.9136(8)	0.9403(6)	0.6836(5)	0.090(6)	0.054(4)	0.040(4)	–0.024(4)	–0.035(4)	0.002(3)
C(14)	2*i*	1.0259(7)	0.8521(6)	0.6421(5)	0.070(5)	0.059(4)	0.044(4)	–0.020(4)	–0.026(3)	–0.001(3)
C(15)	2*i*	1.1751(7)	0.8586(7)	0.5915(6)	0.066(5)	0.075(5)	0.073(5)	–0.028(4)	–0.031(4)	0.001(4)
C(16)	2*i*	1.2265(8)	0.7476(7)	0.5694(7)	0.062(5)	0.088(6)	0.084(5)	–0.023(4)	–0.028(4)	–0.011(4)
C(17)	2*i*	0.7389(6)	0.8188(6)	0.3097(6)	0.050(4)	0.065(4)	0.047(4)	–0.010(3)	–0.022(3)	–0.004(4)
C(18)	2*i*	0.8537(7)	0.7526(5)	0.2444(6)	0.059(4)	0.050(4)	0.048(4)	–0.009(3)	–0.021(3)	0.001(3)
C(19)	2*i*	0.9204(7)	0.7875(6)	0.1074(7)	0.081(5)	0.078(5)	0.054(4)	–0.008(4)	–0.022(4)	–0.003(4)
C(20)	2*i*	0.869(1)	0.8847(7)	0.0414(7)	0.119(7)	0.096(6)	0.051(5)	–0.015(5)	–0.038(5)	0.011(5)
C(21)	2*i*	0.750(1)	0.9473(8)	0.1094(9)	0.123(8)	0.099(7)	0.081(6)	0.007(6)	–0.055(6)	0.011(5)
C(22)	2*i*	0.6856(8)	0.9144(7)	0.2442(7)	0.095(6)	0.085(6)	0.071(5)	0.012(4)	–0.047(5)	–0.004(4)
C(23)	2*i*	0.6725(8)	0.7972(6)	0.4601(7)	0.048(5)	0.075(5)	0.068(5)	–0.010(4)	–0.014(4)	–0.009(4)
C(24)	2*i*	0.9132(9)	0.6404(6)	0.3070(6)	0.078(5)	0.060(5)	0.050(4)	–0.013(4)	–0.020(4)	–0.016(4)

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References

1. Lehn, J. M.: Supramolecular Chemistry, VCH, Weinheim, 1995.
2. Murray, L. J.; Dinca, M.; Long, J. R.: Hydrogen storage in metal-organic frameworks. Chem. Soc. Rev. **38** (2009) 1294–1314.
3. Whitesides, G. M.; Mathiasand, J. P.; Seto, C. T.: Molecular self-assembly and nanochemistry: a chemical strategy for the synthesis of nanostructures. Science. **254** (1991) 1312–1319.
4. Rebek, J. Jr.: Molecular Recognition with Model Systems. Angew. Chem., Int. Ed. **29** (1990) 245–255.
5. Bu, X. H.; Tong, M. L.; Chang, H. C.; Kitagawa, S.; Batten, S. R.: A neutral 3D copper coordination polymer showing 1D open channels and the first interpenetrating NbO-Type network. Angew. Chem., Int. Ed. **43** (2004) 192–195.
6. Zou, R. Q.; Liu, C. S.; Shi, X. S.; Bu, X. H.; Ribas, J.: Tuning the topologies of MnII complexes with 3-(2-pyridyl)pyrazole and carboxylate ligands by intramolecular hydrogen bonds and the geometries of pendant ligands: crystal structures and magnetic properties. CrystEngComm. **7** (2005) 722–727.
7. Zhu, X.; Liu, X. G.; Li, B. L.; Zhang, Y. Solvent–controlled assembly of supramolecular isomers: 2D (4,4) network, 1D ribbons of ring, and both 2D (4,4) networks and 1D ribbons of rings polycatenated in a 3D array. CrystEngComm. **11** (2009) 997–1000.
8. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.