Crystal structure of di(methanol)-bis(2,4-dihydroxypyrimidine-5-carboxylato)manganese(II) — methanol (1:2), $Mn(CH_3OH)_2(C_5H_3N_2O_4)_2 \cdot 2CH_3OH$

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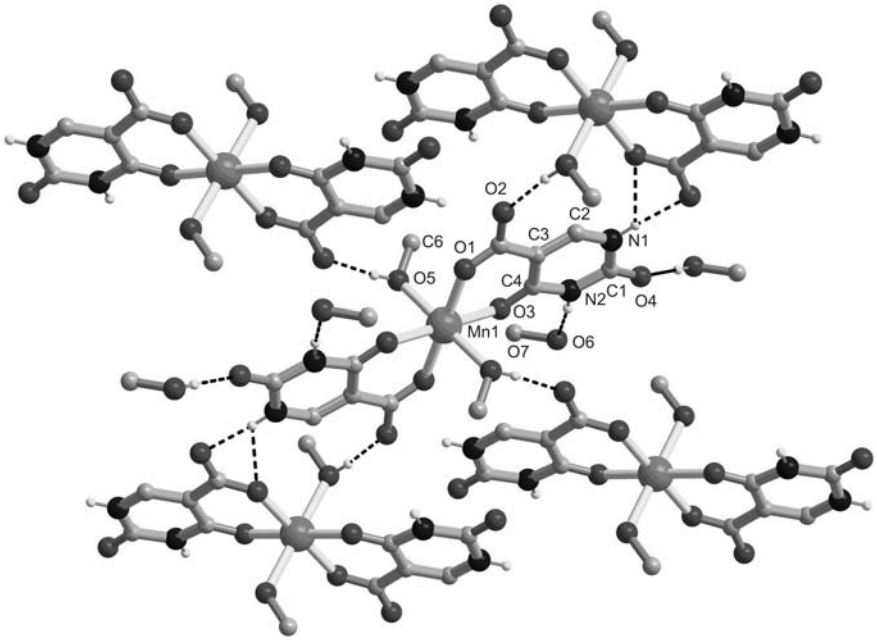

Abstract

$C_{14}H_{22}MnN_4O_{12}$, monoclinic, $P2_1/n$ (no. 14), a = 8.6675(4) Å, b = 11.1241(4) Å, c = 11.3889(5) Å, β = 108.093(4)°, V = 1043.8 Å^3, Z = 2, $R_{gt}(F)$ = 0.029, $wR_{ref}(F^2)$ = 0.050, T = 296 K.

Source of material

2,4-Dihydroxypyrimidine-5-carboxybic acid (Hdpca) was commercially available and used without further purification. To a colorless solution of Hdpca (0.1 mmol) and 2,6-lutidine (0.5 mL) dissolved in MeOH (15 mL) was added $Mn(ClO_4)_2$ (0.2 mmol) under stirring for a few minutes. The solution was then filtered and left to stand at room temperature. Yellow single crystals were obtained after 3 days with the solvent evaporation (yield 30 % based on Hdpca). Elemental analysis — found: H, 4.43 %; C, 34.13 %; N, 11.24 %; O, 38.83 %; calculated for $C_{14}H_{22}MnN_4O_{12}$: H, 4.49 %; C, 34.09 %; N, 11.36 %; O, 38.92 %.

Experimental details

The hydrogen atoms were included in calculated positions and treated as riding with d(N—H) = 0.86 Å, d(C—H) = 0.93 - 0.96 Å and U_{iso}(H) =1.2 U_{eq}(C,N) or 1.5 U_{eq}(C_{methyl}).

Discussion

Crystal engineering of novel coordination complexes has attracted great interest for both the structural and topological novelty along with potential applications in many areas [1-3]. Undoubtedly, the most effective and facile approach is the appropriate choice of the well-designed organic bridging ligands (building blocks) containing modifiable backbones and connectivity information, together with the metal centers (nodes) with different coordination preferences [4]. Among various ligands, N-containing heterocycles are extensively used as bridging ligands in coordination and metallosupramolecular chemistry [5]. In comparison to the hetero-aromatic ring systems, for example pyridine, pyrazine, quinoline, quinoxaline, pyrazole, imidazole, thiazoles, and their benzoanalogues [6,7], rigid multifunctional pyrimidylcarboxylate ligands combining hydroxyl group, remains largely unexplored.

The asymmetric unit of the title crystal structure contains one Mn(II) atom, two $dpca^-$ ligands, two coordinating methanol molecules as well as two lattice methanol molecules. The Mn(II) atom is six-coordinated by four oxygen atoms from hydroxyl and carboxylate groups of two chelating $dpca^-$ ligands, which form the equatorial plane and two oxygen atoms from two methanol molecules located at the axial sites forming a distorted octahedron with d(Mn1—O1) = 2.088(1) Å, d(Mn1—O3) =

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2.154(1) Å, *d*(Mn1—O5) = 2.203(1) Å and ∠O1–Mn–O3 = 83.62(5)°.

Hydrogen bonding interactions are usually important in the supramolecular architectures. There are intermolecular O–H···O and N–H···O hydrogen bonding between carboxyl oxygen atoms, coordinated methanol molecules and lattice methanol molecules, N2–H2···O6 [*d*(N2–H2···O6) = 2.795(2) Å, ∠N2–H2···O6] N1–H1···O1 [*d*(N1–H1···O1) = 3.096(2) Å, ∠N1–H1···O1], N1–H1···O2 [*d*(N1–H1···O2) = 2.811(2) Å, ∠N1–H1···O2], O6–H6···O4 [*d*(O6–H6···O4) = 2.846(2) Å, ∠O6–H6···O4], O5–H5···O2 [*d*(O5–H5···O2) = 2.649(2) Å, ∠O5–H5···O2], which further consolidate the two-dimensional supramolecular network running parallel to [100].

Table 1. Data collection and handling.

Crystal:	yellow block, size 0.19 × 0.23 × 0.25 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	7.02 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	51°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4287, 1942
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1356
$N(param)_{refined}$:	145
Programs:	SHELXS-97, SHELXL-97, SHELXTL [8]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(5D)	4*e*	–0.0159	0.6665	–0.1725	0.032
H(6)	4*e*	0.4240	0.8416	0.9341	0.055
H(1D)	4*e*	0.0443	1.0539	0.1863	0.022
H(2D)	4*e*	–0.2792	0.8374	0.0019	0.020
H(2)	4*e*	0.2251	0.9090	0.2388	0.021
H(6A)	4*e*	0.1576	0.4899	–0.2252	0.061
H(6B)	4*e*	0.1317	0.6161	–0.2898	0.061
H(6C)	4*e*	–0.0146	0.5268	–0.3121	0.061
H(7A)	4*e*	0.4986	0.6781	1.0589	0.081
H(7B)	4*e*	0.5201	0.6194	0.9398	0.081
H(7C)	4*e*	0.3484	0.6633	0.9401	0.081

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*c*	0	½	0	0.0150(3)	0.0100(2)	0.0162(2)	0.0001(2)	0.0012(2)	–0.0011(2)
O(1)	4*e*	0.1913(2)	0.5822(1)	0.1348(1)	0.0189(9)	0.0107(8)	0.0225(8)	0.0002(7)	–0.0025(7)	–0.0050(7)
O(2)	4*e*	0.3493(2)	0.7100(1)	0.2645(1)	0.018(1)	0.0148(8)	0.0268(8)	–0.0008(7)	–0.0048(7)	–0.0023(7)
O(3)	4*e*	–0.1350(2)	0.6547(1)	0.0265(1)	0.0155(9)	0.0108(8)	0.0256(8)	–0.0003(7)	0.0023(7)	–0.0048(7)
O(4)	4*e*	–0.2416(2)	1.0496(1)	0.0548(1)	0.0210(9)	0.0160(7)	0.0337(8)	0.0059(7)	0.0083(7)	0.0000(6)
O(5)	4*e*	0.0453(2)	0.6056(1)	–0.1497(1)	0.0212(9)	0.0198(8)	0.0241(8)	0.0077(7)	0.0079(7)	0.0057(7)
O(6)	4*e*	0.4939(2)	0.7941(1)	0.9287(2)	0.021(1)	0.032(1)	0.056(1)	0.0054(8)	0.0107(9)	–0.0006(9)
N(1)	4*e*	0.0133(2)	0.9834(2)	0.1578(1)	0.019(1)	0.009(1)	0.0252(9)	–0.0003(9)	0.0031(8)	–0.0043(8)
N(2)	4*e*	–0.1805(2)	0.8511(1)	0.0459(1)	0.011(1)	0.0131(9)	0.0230(9)	–0.0004(8)	0.0012(8)	–0.0032(8)
C(1)	4*e*	–0.1433(3)	0.9678(2)	0.0842(2)	0.018(1)	0.018(1)	0.023(1)	–0.0007(9)	0.0108(9)	–0.0002(9)
C(2)	4*e*	0.1209(3)	0.8922(2)	0.1873(2)	0.014(1)	0.018(1)	0.018(1)	0.000(1)	0.001(1)	0.001(1)
C(3)	4*e*	0.0873(3)	0.7775(2)	0.1468(2)	0.016(1)	0.012(1)	0.014(1)	0.0016(9)	0.004(1)	–0.0007(9)
C(4)	4*e*	–0.0766(3)	0.7533(2)	0.0703(2)	0.019(1)	0.015(1)	0.014(1)	0.004(1)	0.008(1)	0.002(1)
C(5)	4*e*	0.2169(3)	0.6846(2)	0.1837(2)	0.018(1)	0.016(1)	0.015(1)	–0.001(1)	0.005(1)	0.001(1)
C(6)	4*e*	0.0831(3)	0.5555(2)	–0.2526(2)	0.052(2)	0.044(2)	0.035(1)	0.016(1)	0.026(1)	0.006(1)
C(7)	4*e*	0.4627(3)	0.6795(2)	0.9702(3)	0.035(2)	0.043(2)	0.088(2)	–0.009(1)	0.024(2)	–0.003(2)

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