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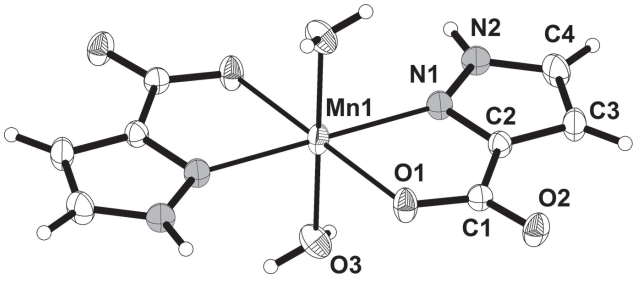
Crystal structure of *trans*-diaqua-bis(1*H*-pyrazole-3-carboxylato-κ²*N*,*O*)manganese(II), $C_8H_{10}N_4O_6Mn$



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Abstract

$C_8H_{10}N_4O_6Mn$, monoclinic, $P2_1/c$ (no. 14), $a = 5.1531(5)$ Å, $b = 11.7052(11)$ Å, $c = 9.4154(7)$ Å, $\beta = 95.1540(10)°$, $V = 565.62(9)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0227$, $wR_{ref}(F^2) = 0.0611$, $T = 298$ K.

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The crystal structure is shown in the figure. The asymmetric unit of the title structure is labelled. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

A mixture of 1*H*-pyrazole-3-carboxylic acid (0.0224 g, 0.2 mmol), $Mn(OAc)_2{\cdot}4H_2O$ (0.0245 g, 0.1 mmol), and distilled water (10 mL) was heated under reflux at 180 °C for 72 h, and then cooled to room temperature. The resulting block crystals of the title compound were obtained and washed with distilled water. The yield is ca. 55% based on Mn.

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Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.38 × 0.35 × 0.30 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	1.20 mm^{-1}
Diffractometer, scan mode:	Bruker SMART, φ and ω-scans
$2\theta_{max}$, completeness:	25°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	2751, 1001, 0.021
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 900
$N(param)_{refined}$:	89
Programs:	Bruker programs [1], SHELX [2, 3]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Mn1	0.5000	0.5000	0.5000	0.02409(19)
N1	0.3875(3)	0.68580(12)	0.50559(15)	0.0237(4)
N2	0.2305(3)	0.76013(13)	0.56490(16)	0.0259(4)
H2	0.1274	0.7417	0.6281	0.031*
O1	0.7423(2)	0.58436(11)	0.35255(14)	0.0277(3)
O2	0.8443(2)	0.75116(11)	0.25642(14)	0.0296(3)
O3	0.1991(3)	0.47570(12)	0.32306(15)	0.0322(3)
H3C	0.0513	0.5061	0.3310	0.039*
H3D	0.1757	0.4063	0.2984	0.039*
C1	0.7152(3)	0.69161(15)	0.33378(18)	0.0213(4)
C2	0.5139(3)	0.74888(15)	0.41438(17)	0.0211(4)
C3	0.4345(4)	0.86296(16)	0.4160(2)	0.0297(4)
H3	0.4916	0.9232	0.3624	0.036*
C4	0.2531(4)	0.86614(16)	0.5143(2)	0.0317(5)
H4	0.1626	0.9303	0.5408	0.038*

Experimental details

H atoms attached to C atoms were placed in geometrically idealized positions (C—H 0.93 Å) and treated as riding on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$. The water H-atoms were located in a difference Fourier map, and were included riding on the O3 atom.

Discussion

Many mononuclear complexes containing the 1*H*-pyrazole-3-carboxylate ligand have been reported, for example:

mononuclear cobalt(II), nickel(II) and zinc complexes with the 1*H*-pyrazole-3-carboxylate ligand [4, 5], but manganese complex based on 3-carboxy-pyrazole have not been reported.

There is one half of a Mn^{2+} cation, one $Hpca^-$ anion and one water molecule in the asymmetric unit of the title crystal structure. The Mn^{2+} center shows a distorted $\{MnO_4N_2\}$ octahedral coordination geometry with two nitrogen atoms from two separate $Hpca^-$ anions, two chelate oxygen atoms from two water molecules and two carboxylic oxygen atoms (O1, O3) from two separate $Hpca^-$ anions. In the title compound, the equatorial plane is formed by two *N*,*O*-bidentate 1*H*-pyrazole-3-carboxylate ligands in a *trans* configuration. The axial positions are occupied by two water molecules. The mononuclear complex molecules are arranged in layers parallel to the ab plane. The distances of the Mn—O and Mn—N are 2.185(2) Å and 2.253(3) Å, respectively, for the organic ligand, and 2.190(2) Å for the water ligand, which is larger than the homologous Zn complex [5]. The bond angles around the Mn^{2+} ion are in the range of 73.2(1)–167.5(1)°.

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