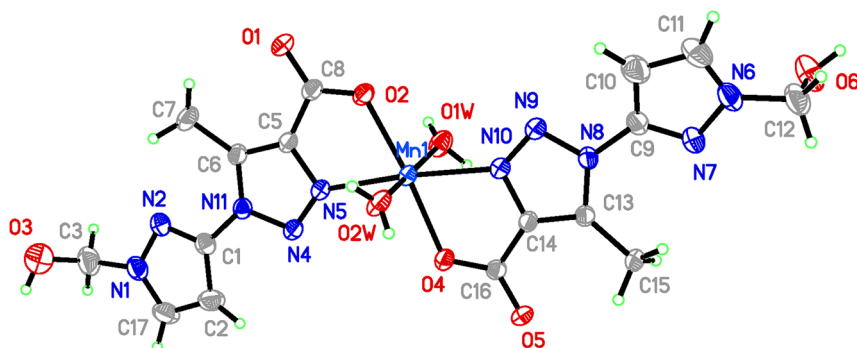


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Crystal structure of diaqua-bis[1-(1-(hydroxymethyl)-1*H*-pyrazol-3-yl)-5-methyl-1*H*-1,2,3-triazole-4-carboxylato- κ^2 N,O)]manganese(II), $C_{16}H_{20}MnN_{10}O_8$



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Abstract

$C_{16}H_{20}MnN_{10}O_8$, monoclinic, $P2_1/c$ (no. 14), $a = 11.1178(7)$ Å, $b = 12.7838(6)$ Å, $c = 15.6649(10)$ Å, $\beta = 105.692(6)^\circ$, $V = 2143.4(2)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0638$, $\omega R_{ref}(F^2) = 0.2034$, $T = 293$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

1 Source of material

All chemical reagents were purchased from commercial sources and used without further purification. The ligand 1-(1-(hydroxymethyl)-1*H*-pyrazol-3-yl)-5-methyl-1*H*-1,2,3-triazole-4-carboxylic acid was prepared according to the literature

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.17 × 0.15 × 0.11 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.69 mm ⁻¹
Diffractometer, scan mode:	SuperNova
θ_{max} , completeness:	29.2°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	10,468, 4940, 0.033
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 3488
$N(param)_{refined}$:	320
Programs:	SHELX [1, 2]

reported by Feng [3, 4]. A mixture of $MnCl_2 \cdot 4H_2O$ (0.0126 g, 0.1 mmol) and 1-(1-(hydroxymethyl)-1*H*-pyrazol-3-yl)-5-methyl-1*H*-1,2,3-triazole-4-carboxylic acid (0.0446 g, 0.2 mmol) was dissolved in 10 mL DMF, and the mixture was stirred at room temperature for 10 min. The resulting solution was transferred to a Teflon-lined autoclave (25 mL) for 3 days at 100 °C, and then naturally cooled. Finally, colorless block crystals were obtained by filtration.

2 Experimental details

The crystal structure was solved in SHELXT [1] and refined in SHELXL2014/7 [2]. The H atoms were placed in idealized positions and treated as riding on their parent atoms. Hydrogen atoms from water were located from a difference–Fourier map and their positions were refined with $U_{iso}(H) = 1.5U_{eq}(O)$.

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
Mn1	0.42053 (5)	0.42936 (4)	0.62799 (4)	0.0387 (2)
C1	0.8604 (4)	0.2576 (3)	0.5641 (2)	0.0433 (9)
C2	0.9398 (4)	0.3423 (4)	0.5677 (4)	0.0687 (14)
H2	0.9266	0.4119	0.5798	0.082*
C17	1.0421 (4)	0.2984 (4)	0.5493 (4)	0.0673 (14)
H17	1.1142	0.3338	0.5469	0.081*
C5	0.5612 (3)	0.2329 (3)	0.6045 (2)	0.0364 (8)
C6	0.6624 (3)	0.1820 (3)	0.5897 (2)	0.0403 (8)
C7	0.6888 (5)	0.0681 (3)	0.5852 (4)	0.0650 (13)
H7A	0.6796	0.0483	0.5247	0.097*
H7B	0.6311	0.0288	0.6084	0.097*
H7C	0.7726	0.0538	0.6197	0.097*
C8	0.4433 (4)	0.1974 (3)	0.6238 (2)	0.0396 (8)
C9	0.0067 (3)	0.6369 (3)	0.6985 (2)	0.0429 (9)
C10	−0.0562 (5)	0.5663 (4)	0.7355 (4)	0.0715 (15)
H10	−0.0312	0.4991	0.7552	0.086*
C11	−0.1636 (4)	0.6159 (5)	0.7372 (3)	0.0696 (14)
H11	−0.2277	0.5890	0.7584	0.083*
C12	−0.2544 (5)	0.7916 (5)	0.6844 (4)	0.0766 (16)
H12A	−0.3059	0.7850	0.7251	0.092*
H12B	−0.2147	0.8598	0.6931	0.092*
C13	0.2103 (3)	0.6958 (3)	0.6715 (2)	0.0364 (8)
C14	0.3030 (3)	0.6368 (3)	0.6528 (2)	0.0365 (8)
C15	0.1997 (4)	0.8107 (3)	0.6840 (3)	0.0483 (10)
H15A	0.1634	0.8431	0.6276	0.073*
H15B	0.2812	0.8395	0.7096	0.073*
H15C	0.1476	0.8234	0.7228	0.073*
C16	0.4222 (3)	0.6630 (3)	0.6327 (2)	0.0363 (8)
N1	1.0211 (3)	0.1968 (3)	0.5354 (2)	0.0543 (9)
N2	0.9077 (3)	0.1690 (3)	0.5444 (3)	0.0533 (9)
N11	0.7394 (3)	0.2597 (2)	0.57820 (19)	0.0377 (7)
N4	0.6885 (3)	0.3548 (2)	0.5843 (2)	0.0409 (7)
N5	0.5815 (3)	0.3374 (2)	0.6007 (2)	0.0381 (7)
N6	−0.1593 (3)	0.7102 (3)	0.7026 (3)	0.0568 (10)
N7	−0.0541 (3)	0.7250 (3)	0.6772 (3)	0.0539 (9)
N8	0.1247 (3)	0.6245 (3)	0.6803 (2)	0.0404 (7)
N9	0.1598 (3)	0.5251 (3)	0.6677 (2)	0.0475 (8)
N10	0.2684 (3)	0.5336 (2)	0.6509 (2)	0.0431 (7)
O1	0.4228 (3)	0.1024 (2)	0.6270 (2)	0.0563 (8)
O2	0.3699 (3)	0.2690 (2)	0.63449 (18)	0.0450 (6)
O4	0.4886 (2)	0.5866 (2)	0.62118 (19)	0.0437 (6)
O5	0.4496 (3)	0.7564 (2)	0.62705 (19)	0.0468 (7)
O6	−0.3293 (3)	0.7829 (4)	0.5968 (3)	0.0848 (12)
H6	−0.4030	0.7885	0.5961	0.127*
O1W	0.3167 (3)	0.4275 (2)	0.48728 (19)	0.0582 (8)
H1WA	0.3016	0.3808	0.4526	0.087*
H1WB	0.3052	0.4903	0.4546	0.087*
O2W	0.5039 (3)	0.4312 (2)	0.76961 (19)	0.0537 (8)
H2WA	0.5194	0.3794	0.8048	0.081*
H2WB	0.5314	0.4804	0.8017	0.081*
O3	1.1685 (4)	0.0535 (4)	0.5739 (4)	0.1033 (14)
H3	1.2366	0.0803	0.5965	0.155*
C3	1.1005 (5)	0.1170 (5)	0.5055 (4)	0.0781 (16)
H3A	1.0470	0.0733	0.4603	0.094*
H3B	1.1581	0.1530	0.4789	0.094*

3 Comment

Pyrazole is a unique class of compounds containing two adjacent nitrogen atoms. Due to the special electronic effect of the pyrazole ring, the nitrogen atoms on the ring are easily coordinated with transition metals [5]. When the substitution position on the pyrazole ring is at the carbon atom, the melting and boiling points of the synthesized compound will increase. When the substitution position on the pyrazole ring is at the nitrogen atom, the melting and boiling points of the synthesized compound will decrease. Because pyrazole has four different substitution positions and the substituent groups are diverse and variable, it is easy to alkylation and acylation reactions [6]. At the same time, pyrazole is also an important organic chemical and basic raw material, and as an important organic ligand [7].

1,2,3-triazole compounds are a fundamental and important nitrogen-containing heterocyclic compound, and compared to 1,2,4-triazole compounds, 1,2,3-triazole rings are more stable. The triazole ring has a high electron cloud density. From the perspective of orbital theory, it is easy to coordinate with metal ions, and multiple nitrogen atoms on the triazole ring can easily form metal clusters [8].

Based on the above description, we combine the advantages of pyrazole and triazole, and introduce the carboxyl group as a flexible group to synthesize a new azole ligand 1-(1-(hydroxymethyl)-1*H*-pyrazol-3-yl)-5-methyl-1*H*-1,2,3-triazole-4-carboxylic acid, and use this to prepare one Mn-based complex.

X-ray single crystal diffraction shows that the title complex crystallizes in the monoclinic system in the space group *P*2₁/*c*, and the asymmetric unit consists of one Mn(II) ion, two ligand ions and two coordinated water molecules. The central Mn(II) ion adopts a distorted octahedral coordination configuration, and is coordinated to two O atoms (O1W, O2W) from lattice water molecules, two carboxylate oxygen atoms (O2, O4) and two nitrogen atoms (N5, N10) of pyrazole rings. In the octahedron, the bond length of Mn1–N5 and Mn1–N10 is 2.276(3) Å and 2.257(3) Å, respectively. Meanwhile, the bond lengths of Mn1–O2, Mn1–O4, Mn1–O1W and Mn1–O2W are 2.136(3) Å, 2.160(3) Å, 2.194(3) Å and 2.161(3) Å, respectively, which are similar to that reported in Mn(II) complexes [9]. The bond angles of O–Mn1–O, N–Mn1–N and N–Mn1–O all fall within the normal range. In the crystal structure, there exists two lattice water molecules, carboxyl groups and uncoordinated hydroxymethyl groups, intermolecular hydrogen bonds O–H...O link the title complex into a supramolecular structure.

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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