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Crystal structure of [diaqua-bis(2-((1*H*-tetrazol-1-yl)methyl)-5-carboxy-1*H*-imidazole-4-carboxylato- $\kappa^2 N,O$) manganese(II)] dihydrate, $C_{14}H_{18}MnN_{12}O_{12}$

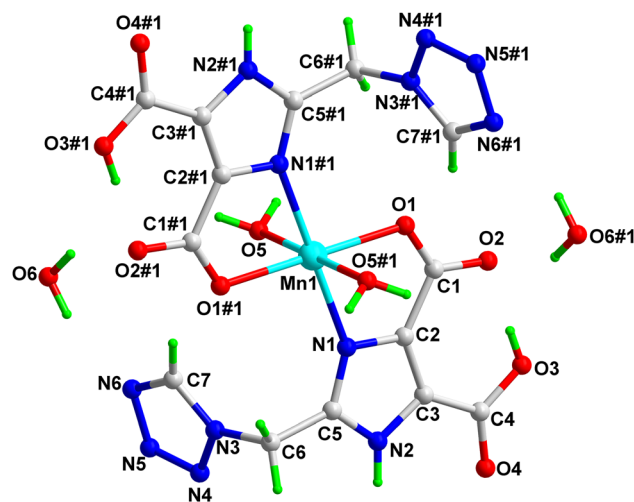


Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.21 × 0.19 × 0.15 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.66 mm ⁻¹
Diffractometer, scan mode:	Bruker D8 VENTURE PHOTON, φ and ω
$\theta_{\max}$, completeness:	26.0°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	6299, 2274, 0.029
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2044
$N(\text{param})_{\text{refined}}$:	179
Programs:	SHELX [1], Bruker [2, 3]

Source of material

All reagents used were purchased from commercial sources and used without further purification. An aqueous solution (4 mL) of $MnCl_2 \cdot 4H_2O$ (0.05 mmol) was added dropwise to a methanol solution (2 mL) of 2-((1*H*-tetrazol-1-yl)methyl)-1*H*-imidazole-4,5-dicarboxylic acid (0.05 mmol, $H_3\text{tmidc}$). The resulting solution was placed in a 25 mL Teflon-lined stainless steel reactor, which was sealed and heated to 333 K for 24 h. After the mixture was cooled to room temperature, light-yellow crystals of the title compound were obtained (yield 48%, based $H_3\text{tmidc}$).

Experimental details

Hydrogen atoms on carbon and nitrogen atoms were positioned geometrically and refined as riding atoms, with C–H = 0.97 (CH₂) or 0.93 Å (aromatic) and N–H = 0.86 Å. The hydrogen atom of the carboxy group of $H_2\text{tmidc}^-$ was refined as riding atoms, with O–H = 0.82 Å. Hydrogen atoms of the water molecule were located in a difference Fourier map and O–H distance were constrained to 0.85 Å. Hydrogen atoms were refined with $U_{\text{iso}}(H) = 1.2 U_{\text{eq}}(C, N)$ or $1.5 U_{\text{eq}}(O)$.

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Abstract

$C_{14}H_{18}MnN_{12}O_{12}$, monoclinic, $P2_1/c$ (no. 14), $a = 9.333(7)$ Å, $b = 19.038(13)$ Å, $c = 7.042(5)$ Å, $\beta = 111.989(10)^\circ$, $V = 1160.2(14)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0301$, $wR_{\text{ref}}(F^2) = 0.0809$, $T = 293(2)$ 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.

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$).

Atom	x	y	z	U_{iso}^*/U_{eq}
Mn1	0.000000	0.000000	0.500000	0.02757 (12)
N1	0.21062 (13)	0.06186 (7)	0.66507 (18)	0.0249 (3)
N2	0.42115 (14)	0.12472 (7)	0.8164 (2)	0.0262 (3)
H2	0.494239	0.154470	0.833242	0.031*
N3	0.16252 (15)	0.20702 (7)	0.4187 (2)	0.0286 (3)
N4	0.21137 (18)	0.27273 (8)	0.4839 (2)	0.0398 (3)
N5	0.0882 (2)	0.31075 (8)	0.4443 (3)	0.0458 (4)
N6	−0.04050 (18)	0.27110 (9)	0.3552 (3)	0.0452 (4)
O1	0.07674 (12)	−0.04037 (6)	0.81637 (17)	0.0335 (3)
O2	0.25555 (13)	−0.02912 (7)	1.13221 (17)	0.0388 (3)
O3	0.48860 (14)	0.04431 (7)	1.31055 (17)	0.0377 (3)
H3	0.411187	0.020700	1.251256	0.057*
O4	0.62014 (14)	0.12876 (7)	1.23134 (19)	0.0428 (3)
O5	−0.13607 (13)	0.08068 (6)	0.57979 (18)	0.0358 (3)
H5A	−0.218308	0.093900	0.483501	0.054*
H5B	−0.163958	0.071480	0.678971	0.054*
C1	0.19466 (18)	−0.01250 (8)	0.9439 (2)	0.0274 (3)
C2	0.27247 (16)	0.04369 (8)	0.8681 (2)	0.0238 (3)
C3	0.40436 (16)	0.08279 (8)	0.9648 (2)	0.0250 (3)
C4	0.51267 (17)	0.08670 (8)	1.1807 (2)	0.0300 (3)
C5	0.30271 (16)	0.11098 (8)	0.6394 (2)	0.0251 (3)
C6	0.27201 (18)	0.14902 (8)	0.4421 (2)	0.0305 (3)
H6A	0.368200	0.167492	0.439746	0.037*
H6B	0.229701	0.116561	0.328516	0.037*
C7	0.0085 (2)	0.20726 (9)	0.3406 (3)	0.0381 (4)
H7	−0.054156	0.168612	0.285044	0.046*
O6	0.62761 (17)	0.21592 (8)	0.7621 (3)	0.0739 (5)
H6C	0.723143	0.209969	0.786431	0.111*
H6D	0.623153	0.260479	0.754741	0.111*

Comment

N-heterocyclic carboxylic acids have been often used in the synthesis of coordination compounds (CPs) since they not only contain O donors but also N donors, which have abundant coordination modes [4–8]. Many CPs have been constructed from these kinds of ligands, like 2,2'-(ethane-1,2-diyl)bis(1*H*-imidazole-4,5-dicarboxylic acid)-2-phenyl-1*H*-imidazole-4,5-dicarboxylic acid, 2-(hydroxymethyl)-1*H*-imidazole-4,5-dicarboxylic acid, 2,2'-(1,2-phenylene)bis(1*H*-imidazole-4,5-dicarboxylic acid), 2-(1*H*-tetrazol-1-methyl)-1*H*-imidazole-4,5-dicarboxylic acid and 2-(pyridin-4-yl)-1*H*-imidazole-4,5-dicarboxylic acid [9–16]. Among the reported ligands, 2-((1*H*-tetrazol-1-yl)methyl)-1*H*-imidazole-4,5-dicarboxylic acid (H_3tmidc) and corresponding deprotonated anions (H_2tmidc^- , $Htmidc^{2-}$ and $tmidc^{3-}$) are excellent ligands since there are five potential N-donors and four potential O-donors that can coordinate to metal ions with various coordination modes. So

far, several CPs based on H_3tmidc have been synthesized and characterized, such as Ba(II), Co(II), Cd(II), Zn(II), and Fe(II) CPs [15, 17–19]. In order to further enrich the categories and numbers of CPs based on this ligand, here we have used H_3tmidc as a starting material to selfassemble with $MnCl_2 \cdot 4H_2O$ and successfully obtained a new CP $[Mn(H_2tmidc)_2(H_2O)_2] \cdot 2H_2O$.

The asymmetric unit of the title structure consists of one half of Mn(II) ion, one H_2tmidc^- anion, one coordinated water molecule, and one solvent water molecule. Each Mn1 is six-coordinated by N1, N1#1, O1 and O1#1 from two H_2tmidc^- anions together with two H_2O molecules (O5 and O5#1), exhibiting a slightly deformed MnN_2O_4 octahedral geometry. The bond angles of N1–Mn1–N1#1, O1–Mn1–O1#1 and O5–Mn1–O5#1 are 180°. The other bond angles around the Mn1 are more or less deviated from the normal values (76.48(5)°–103.52(5)°). The Mn–N bond length is 2.2116(16) Å, while the Mn–O bond lengths are 2.1959(15) and 2.2073(18) Å. All parameters are in the normal range of those observed in the reported Mn(II) CPs [11, 14]. The N1/N2/C2/C3/C5 imidazole ring and the Mn1/O1/C1/C2/N1 chelate ring are almost coplanar [dihedral angle = 1.36(10)°]. But the imidazole ring N1/N2/C2/C3/C5 and the tetrazole ring N3/N4/N5/N6/C7 are not coplanar [dihedral angle = 73.64(8)°]. The dihedral angles between the mean plane defined by the imidazole ring N1/N2/C2/C3/C5 and the planes of the carboxylate groups are 2.49(16)° and 2.6(3)°, respectively. There are N–H⋯O, O–H⋯O and O–H⋯N hydrogen bonds involving imidazole rings, tetrazole rings, coordinated water molecules, solvent water molecules, carboxyl and carboxylate groups. In addition, there are intermolecular π – π interactions between tetrazole rings with the centroid-centroid distance of 3.524(3) Å, which is in the range for common π – π interactions [15, 17]. $[Mn(H_2tmidc)_2(H_2O)_2]$ units are linked by the aforementioned hydrogen bonds and π – π interactions to a three-dimensional architecture in the solid state.

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