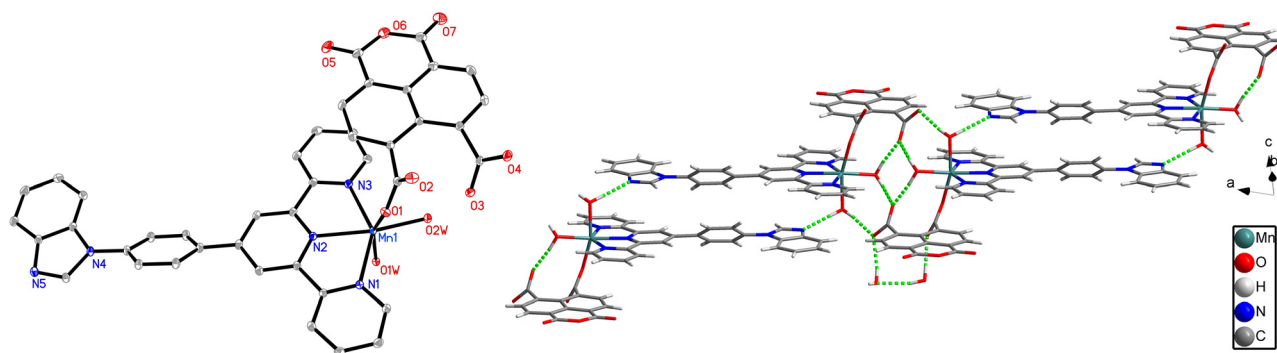


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The crystal structure of diaqua-(*naphthalene-4,5-dicarboxylate-1,8-dicarboxylic anhydride-κ¹O*)-(4'-(4-(1*H*-benzimidazolyl-1-yl)phenyl)-2,2':6',2''-terpyridine-κ³N,N',N'')-manganese(II) dihydrate, C₄₂H₂₇MnN₅O₉·2H₂O



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Abstract

C₄₂H₂₇MnN₅O₉·2H₂O, triclinic, $P\bar{1}$ (no. 2), $a = 12.4250(8)$ Å, $b = 12.7259(8)$ Å, $c = 14.2946(9)$ Å, $\alpha = 64.102(2)^\circ$, $\beta = 79.774(2)^\circ$, $\gamma = 62.453(2)^\circ$, $V = 1801.9(2)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0344$, $wR_{\text{ref}}(F^2) = 0.0951$, $T = 150$ K.

CCDC no.: 2268378

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.20 × 0.15 × 0.10 mm
Wavelength:	Ga Kα radiation (1.34138 Å)
μ :	2.45 mm ⁻¹
Diffractometer, scan mode:	Bruker SMART APEX-II, φ and ω
θ_{max} , completeness:	57.0°, >99 %
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	24,998, 7320, 0.034
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 6995
$N(\text{param})_{\text{refined}}$:	540
Programs:	Bruker [1], SHELX [2, 3], Olex2 [4]

Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

1 Source of material

The reagents were purchased from standard commercial sources and used without further purification. A mixture of MnCO₃ (0.011 g, 0.10 mmol), 1,4,5,8-naphthalenetetracarboxylic acid (contains monoanhydride) (0.030 g, 0.10 mmol), and 2262-phimptpy (0.043 g, 0.10 mmol) was dispersed in mixed solvent of H₂O (4 mL) and C₂H₅OH (4 mL) solutions in a 16 mL Teflon-lined stainless steel autoclave, which was heated for 3 d

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}^*/U_{eq}
C1	0.27754 (14)	1.06304 (15)	0.36388 (12)	0.0185 (3)
H1	0.194091	1.081205	0.366117	0.022*
C2	0.31347 (15)	1.15417 (16)	0.28889 (12)	0.0208 (3)
H2	0.256168	1.233232	0.240454	0.025*
C3	0.43511 (15)	1.12688 (16)	0.28644 (13)	0.0232 (3)
H3	0.462595	1.187341	0.235675	0.028*
C4	0.51709 (14)	1.01067 (16)	0.35851 (12)	0.0201 (3)
H4	0.600826	0.990896	0.357942	0.024*
C5	0.47404 (13)	0.92419 (14)	0.43127 (11)	0.0149 (3)
C6	0.55378 (14)	0.79673 (15)	0.51235 (11)	0.0156 (3)
C7	0.67991 (14)	0.74805 (15)	0.51795 (12)	0.0174 (3)
H7	0.720245	0.796917	0.469915	0.021*
C8	0.74594 (14)	0.62557 (15)	0.59588 (12)	0.0182 (3)
C9	0.68217 (14)	0.55818 (15)	0.66497 (12)	0.0188 (3)
H9	0.724679	0.474829	0.718189	0.023*
C10	0.55665 (14)	0.61323 (15)	0.65570 (11)	0.0167 (3)
C11	0.48122 (14)	0.54860 (15)	0.72610 (12)	0.0167 (3)
C12	0.53062 (15)	0.42921 (16)	0.81052 (12)	0.0214 (3)
H12	0.615364	0.385732	0.826379	0.026*
C13	0.45404 (16)	0.37469 (16)	0.87116 (13)	0.0244 (3)
H13	0.485864	0.293401	0.929144	0.029*
C14	0.33089 (16)	0.43998 (16)	0.84626 (12)	0.0220 (3)
H14	0.276937	0.404191	0.886238	0.026*
C15	0.28823 (15)	0.55902 (16)	0.76143 (12)	0.0191 (3)
H15	0.203692	0.604299	0.744486	0.023*
C16	0.88009 (14)	0.56570 (15)	0.60686 (12)	0.0188 (3)
C17	0.94391 (14)	0.63969 (15)	0.58409 (12)	0.0200 (3)
H17	0.901187	0.731573	0.557279	0.024*
C18	1.06926 (14)	0.58050 (15)	0.60017 (12)	0.0189 (3)
H18	1.111675	0.631341	0.586412	0.023*
C19	1.13188 (14)	0.44607 (15)	0.63662 (12)	0.0179 (3)
C20	1.07064 (14)	0.37115 (15)	0.65493 (13)	0.0200 (3)
H20	1.114317	0.279875	0.676443	0.024*
C21	0.94552 (14)	0.43086 (16)	0.64150 (13)	0.0210 (3)
H21	0.903397	0.379550	0.656011	0.025*
C22	1.32833 (14)	0.26314 (15)	0.73166 (12)	0.0173 (3)
C23	1.29628 (15)	0.17456 (16)	0.81579 (13)	0.0221 (3)
H23	1.213986	0.188906	0.828598	0.027*
C24	1.39074 (16)	0.06429 (17)	0.87995 (13)	0.0270 (4)
H24	1.372821	0.000531	0.937408	0.032*
C25	1.51253 (16)	0.04430 (18)	0.86218 (13)	0.0273 (4)
H25	1.574780	−0.032564	0.907811	0.033*
C26	1.54343 (15)	0.13401 (16)	0.77984 (13)	0.0227 (3)
H26	1.625541	0.120970	0.768693	0.027*
C27	1.44938 (14)	0.24466 (15)	0.71358 (12)	0.0175 (3)
C28	1.34159 (14)	0.42881 (15)	0.59467 (12)	0.0182 (3)
H28	1.318222	0.509705	0.536059	0.022*
C29	0.17876 (14)	0.97187 (15)	0.70556 (12)	0.0170 (3)
C30	0.18701 (14)	0.85198 (15)	0.80137 (11)	0.0154 (3)
C31	0.30275 (14)	0.76766 (16)	0.84478 (12)	0.0209 (3)
H31	0.368630	0.787308	0.812064	0.025*
C32	0.32578 (15)	0.65464 (16)	0.93515 (13)	0.0212 (3)
H32	0.405990	0.599157	0.963995	0.025*
C33	0.23167 (15)	0.62444 (15)	0.98186 (12)	0.0188 (3)
C34	0.11092 (14)	0.70866 (15)	0.94217 (11)	0.0166 (3)

Table 2: (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}^*/U_{eq}
C35	0.08566 (14)	0.82631 (14)	0.85069 (11)	0.0148 (3)
C36	0.01533 (15)	0.67568 (16)	0.99367 (12)	0.0210 (3)
C37	−0.10299 (16)	0.75960 (18)	0.95996 (13)	0.0265 (4)
H37	−0.166925	0.738129	0.995851	0.032*
C38	−0.12917 (15)	0.87635 (17)	0.87299 (13)	0.0243 (3)
H38	−0.211584	0.934920	0.851856	0.029*
C39	−0.03855 (14)	0.90941 (15)	0.81655 (12)	0.0172 (3)
C40	−0.08264 (13)	1.03079 (15)	0.71613 (12)	0.0170 (3)
C41	0.04162 (17)	0.55059 (17)	1.08325 (13)	0.0276 (4)
C42	0.25848 (16)	0.50011 (16)	1.07230 (13)	0.0246 (4)
Mn1	0.29453 (2)	0.80915 (2)	0.56406 (2)	0.01468 (8)
N1	0.35552 (11)	0.95020 (12)	0.43352 (10)	0.0158 (3)
N2	0.49429 (11)	0.73061 (12)	0.58049 (10)	0.0152 (3)
N3	0.36087 (12)	0.61288 (13)	0.70241 (10)	0.0166 (3)
N4	1.26014 (11)	0.38371 (12)	0.65354 (10)	0.0169 (3)
N5	1.45487 (12)	0.34989 (13)	0.62675 (10)	0.0191 (3)
O1W	0.31244 (10)	0.71768 (10)	0.45505 (8)	0.0180 (2)
H1WA	0.264634	0.775209	0.400678	0.027*
H1WB	0.385146	0.696325	0.430482	0.027*
O1	0.23290 (10)	0.95302 (11)	0.62611 (8)	0.0198 (2)
O2W	0.11053 (10)	0.83413 (10)	0.56663 (8)	0.0181 (2)
H2WA	0.064860	0.886830	0.596045	0.027*
H2WB	0.081048	0.873871	0.503208	0.027*
O2	0.12934 (12)	1.07665 (11)	0.71403 (9)	0.0257 (3)
O3	−0.03961 (10)	1.01641 (11)	0.63370 (8)	0.0212 (2)
O3W	0.08445 (16)	1.07305 (19)	0.91338 (12)	0.0515 (4)
H3WA	0.099073	1.068205	0.853217	0.077*
H3WB	0.005729	1.113478	0.913978	0.077*
O4	−0.16537 (10)	1.13257 (11)	0.72126 (9)	0.0236 (3)
O4W	−0.1811 (2)	1.1763 (2)	0.90384 (18)	0.0769 (7)
H4WA	−0.167306	1.171801	0.843562	0.115*
H4WB	−0.220129	1.129273	0.936976	0.115*
O5	0.35812 (13)	0.42007 (12)	1.10932 (10)	0.0351 (3)
O6	0.16235 (12)	0.47052 (12)	1.11754 (10)	0.0316 (3)
O7	−0.03107 (14)	0.51016 (14)	1.12796 (11)	0.0411 (3)

at 413 K under autogenous pressure and slowly cooled to room temperature. Yellow block crystals were obtained.

2 Experimental details

The structure was solved with the SHELXT-2018 program. All H-atoms from C atoms were positioned with idealized geometry and refined isotropically ($U_{iso}(H) = 1.2U_{eq}(C)$) using a riding model with C–H = 0.93 and 0.97 Å.

3 Comment

2,2':6',2''-Terpyridine (tpy) as a building unit with its large π conjugation, has received great interest in the realm

of metal-organic frameworks (MOFs) [5–12]. By using a grafting strategy [13], 4'-(4-(1H-benzimidazolyl-1-yl)phenyl)-2,2':6',2'' terpyridine(2262-phimphtpy) has been designed and synthesized with a combination of benzimidazole and terpyridine functional groups. A discrete neutral mononuclear Mn(II) complex was obtained successfully along with naphthalene-4,5-dicarboxylate-1,8-dicarboxylic anhydride (ntdda²⁻) [14, 15] and its structure has been determined. To the best of our knowledge, it is the first report of the first Mn(II) complex coordinated with the ntdda²⁻ anion.

The ORTEP diagram is presented in the left part of the figure. The asymmetric unit contains one Mn(II) ion, one phimphtpy ligand, and one ntdda²⁻ anion. As shown in the left part of the figure, Mn1 is coordinated by three pyridine nitrogen atoms (Mn1–N, 2.2185(13)–2.2779(13) Å) from one phimphtpy ligand, one oxygen atom from one ntdda²⁻ anion and two oxygen atoms from two coordinated water molecules showing a distorted octahedral geometry with N1, N2, N3 and O2W in the equatorial plane and O1 and O1W in axial positions. Mn(II) to O/N distances and bond angles are within the normal ranges and similar to that of previously reported complexes [16, 17].

The supramolecular association of the molecules in the title complex is essentially based on hydrogen bonds between the water molecules as donors and the diverse oxygen atoms from water molecules and ntdda²⁻ anion and nitrogen atoms from benzimidazole as acceptors. One-dimensional (1D) chains are formed through seven kinds of hydrogen bonds with the distances of H atoms and acceptors between 1.80 Å and 2.09 Å as shown in the right part of the figure. The 3D structure is obtained through these 1D chains which are linked by weak hydrogen bond O4W–H4WB...O3W with the distance of H atom and acceptor 2.55 Å and six kinds of π – π interactions between aromatic benzene, pyridine and imidazole rings with Cg–Cg (the aromatic rings center was defined as Cg) distances between 3.44 Å and 3.90 Å.

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