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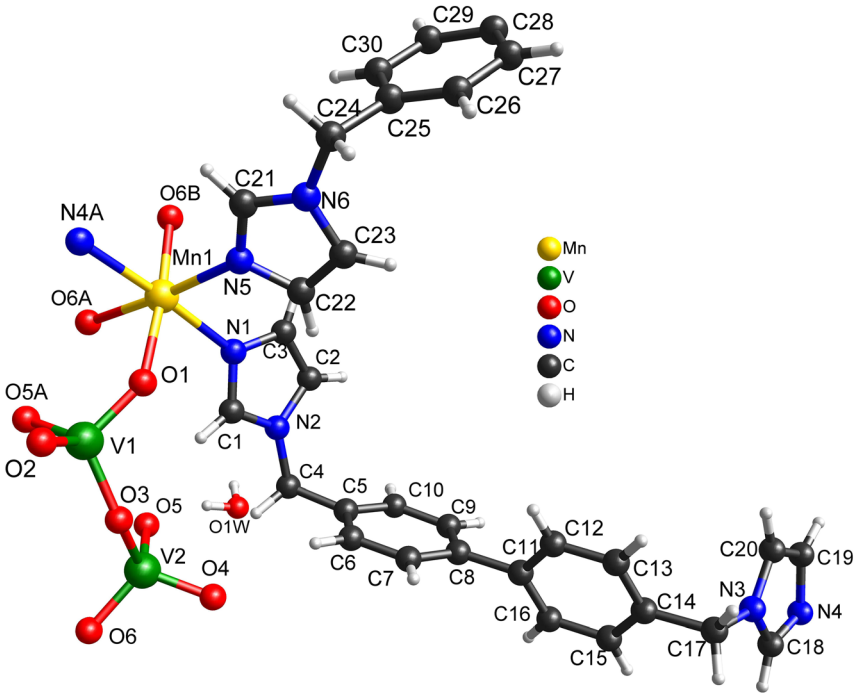
Crystal structure of poly[octakis(μ-oxido)-tris(μ-1,1′-[[1,1′-biphenyl]-4,4′-diylbis(methylene)] bis(1H-imidazole))-tetrakis(oxido)-tetra-vanadium-dimanganese(II)dihydrate], $C_{30}H_{29}MnN_6O_7V_2$



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Abstract

$C_{30}H_{29}MnN_6O_7V_2$, triclinic, $P\bar{1}$ (no. 2), a = 9.0806(3) Å, b = 11.1937(3) Å, c = 16.3585(5) Å, α = 102.2430(10)°, β = 100.090(1)°, γ = 97.7410(10)°, V = 1574.09(8) Å^3, Z = 2, $R_{gt}(F)$ = 0.0335, $wR_{ref}(F^2)$ = 0.0886, T = 100 K.

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Table 1: Data collection and handling.

Crystal:	Red block
Size:	0.22 × 0.21 × 0.20 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	1.03 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	29.6°, 99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	20461, 8754, 0.040
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 7493
$N(param)_{refined}$:	418
Programs:	Bruker,[1] Olex2,[2] SHELX[3,4]

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.

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

Atom	x	y	z	U_{iso}*/U_{eq}
Mn1	0.08351 (2)	0.43771 (2)	0.07793 (2)	0.00901 (6)
V1	0.41899 (3)	0.31707 (2)	0.04087 (2)	0.01094 (6)
V2	0.73956 (3)	0.54233 (2)	0.10127 (2)	0.00932 (6)
O1	0.29237 (13)	0.36147 (11)	0.09690 (8)	0.0154 (2)
O2	0.41738 (14)	0.16744 (11)	0.02952 (9)	0.0213 (3)
O3	0.60607 (13)	0.40293 (11)	0.08941 (9)	0.0204 (3)
O4	0.81290 (14)	0.59937 (12)	0.20145 (8)	0.0208 (3)
O5	0.64009 (13)	0.65512 (11)	0.06354 (8)	0.0177 (2)
O6	0.87633 (12)	0.51279 (10)	0.04525 (7)	0.0110 (2)
N1	0.21646 (15)	0.61824 (12)	0.15768 (8)	0.0121 (2)
N2	0.41141 (15)	0.77252 (12)	0.21469 (8)	0.0116 (2)
N3	0.92245 (15)	1.05943 (12)	0.91941 (8)	0.0129 (3)
N4	0.96379 (15)	1.25359 (12)	0.99559 (8)	0.0116 (2)
N5	0.02485 (15)	0.39073 (13)	0.19559 (9)	0.0140 (3)
N6	−0.08807 (16)	0.31673 (13)	0.28808 (9)	0.0159 (3)
C1	0.36340 (17)	0.65715 (14)	0.16324 (10)	0.0128 (3)
H1	0.426803	0.609820	0.134634	0.015*
C2	0.28751 (18)	0.80997 (15)	0.24399 (11)	0.0156 (3)
H2	0.285649	0.887051	0.281380	0.019*
C3	0.16845 (18)	0.71454 (15)	0.20868 (10)	0.0151 (3)
H3	0.067798	0.714018	0.217628	0.018*
C4	0.56659 (18)	0.84452 (15)	0.23587 (10)	0.0151 (3)
H4A	0.564222	0.926067	0.221738	0.018*
H4B	0.630226	0.799788	0.201123	0.018*
C5	0.63577 (17)	0.86426 (15)	0.32979 (10)	0.0144 (3)
C6	0.6971 (2)	0.76987 (18)	0.35942 (12)	0.0256 (4)
H6	0.700655	0.695135	0.319997	0.031*
C7	0.7531 (2)	0.78448 (19)	0.44643 (12)	0.0288 (4)
H7	0.792763	0.718825	0.465979	0.035*
C8	0.7518 (2)	0.89435 (16)	0.50530 (11)	0.0188 (3)
C9	0.6942 (2)	0.98926 (17)	0.47547 (11)	0.0227 (4)
H9	0.694665	1.065377	0.514610	0.027*
C10	0.6353 (2)	0.97389 (16)	0.38825 (11)	0.0211 (3)
H10	0.594572	1.039185	0.368801	0.025*
C11	0.8066 (2)	0.90785 (16)	0.59862 (11)	0.0191 (3)
C12	0.7295 (2)	0.83149 (18)	0.64066 (12)	0.0264 (4)
H12	0.643439	0.770985	0.609327	0.032*
C13	0.7776 (2)	0.84310 (17)	0.72790 (12)	0.0244 (4)
H13	0.723396	0.791203	0.755812	0.029*
C14	0.9040 (2)	0.92978 (15)	0.77443 (10)	0.0173 (3)
C15	0.98291 (19)	1.00514 (17)	0.73286 (11)	0.0197 (3)
H15	1.070567	1.063956	0.764207	0.024*
C16	0.9342 (2)	0.99486 (17)	0.64556 (11)	0.0202 (3)
H16	0.988128	1.047322	0.617883	0.024*
C17	0.9525 (2)	0.94305 (15)	0.86946 (11)	0.0193 (3)
H17A	0.897255	0.871849	0.885326	0.023*
H17B	1.062586	0.941062	0.883761	0.023*
C18	1.02595 (18)	1.16323 (14)	0.95613 (10)	0.0135 (3)
H18	1.130644	1.170999	0.954099	0.016*
C19	0.81080 (18)	1.20369 (15)	0.98190 (10)	0.0134 (3)
H19	0.735864	1.246565	1.002139	0.016*
C20	0.78400 (18)	1.08347 (15)	0.93489 (10)	0.0150 (3)
H20	0.689258	1.027969	0.916670	0.018*
C21	−0.08954 (18)	0.31159 (15)	0.20501 (11)	0.0144 (3)
H21	−0.163420	0.257891	0.158880	0.017*
C22	0.1027 (2)	0.44954 (17)	0.27777 (11)	0.0197 (3)
H22	0.190973	0.512198	0.291844	0.024*
C23	0.0348 (2)	0.40481 (17)	0.33563 (11)	0.0210 (3)
H23	0.065715	0.429224	0.396212	0.025*
C24	−0.1961 (2)	0.24075 (16)	0.32138 (12)	0.0208 (4)
H24A	−0.140246	0.193135	0.356930	0.025*
H24B	−0.267847	0.180564	0.272993	0.025*
C25	−0.2845 (2)	0.31965 (16)	0.37462 (12)	0.0188 (3)
C26	−0.2784 (2)	0.31846 (18)	0.45943 (12)	0.0251 (4)
H26	−0.215352	0.269417	0.485018	0.030*
C27	−0.3631 (2)	0.38800 (18)	0.50815 (12)	0.0255 (4)
H27	−0.358404	0.383916	0.565953	0.031*
C28	−0.45434 (19)	0.46311 (15)	0.47394 (12)	0.0184 (3)
C29	−0.4576 (3)	0.4645 (3)	0.38850 (16)	0.0439 (7)
H29	−0.518269	0.515261	0.363173	0.053*
C30	−0.3754 (3)	0.3942 (2)	0.33934 (15)	0.0415 (6)
H30	−0.381254	0.397052	0.281242	0.050*
O1W	0.63013 (15)	1.04705 (12)	0.11624 (8)	0.0230 (3)
H1WA	0.570121	1.090666	0.093043	0.034*
H1WB	0.617167	0.977710	0.077574	0.034*

1 Source of materials

A mixture comprising $NaVO_3$ (0.5 mmol, 61.0 mg) and $N_2H_4 \cdot H_2O$ (0.1 mmol, 6.2 µL) in H_2O (9.5 mL) was stirred for a duration of 30 min at ambient temperature. The mixture was stirred for an additional hour after being enriched with a solution containing 4,4′-bis(imidazol-1-ylmethyl)biphenyl (bibp; 0.15 mmol, 47.1 mg) in DMF (0.5 mL) and $Mn(OAc)_2 \cdot 4H_2O$ (0.1 mmol, 24.5 mg). The pH of this mixture was then adjusted by adding HCl (aq 1.0 M) to 3.42, and the resulting mixture was poured into a 23 mL Teflon-lined autoclave reactor and kept at 393 K for 3 days. The product was obtained as a green crystalline solid after the autoclave was cooled to room temperature.

2 Experimental details

The structure was solved by Direct Methods with the SHELXS-2018 program. All the non–H atoms were refined anisotropically. All H-atoms from C atoms were positioned with idealized geometry and refined isotropic (U_{iso}(H) = 1.2U_{eq}(C)) and (U_{iso}(H) = 1.5U_{eq}(C)) using a riding model with C–H = 0.950 Å (imidazole and phenyl groups) and C–H = 0.990 Å (methylene), respectively. The water H-atom positions were fixed with O–H = 0.870 Å (U_{iso}(H) = 1.5U_{eq}(O)).

3 Comment

Vanadium-based functional complexes have attracted widespread research interest due to their rich topological structural types.[5–16] The bibp is a linear bridging ligand containing rigid biphenyls and flexible alkyl groups, and if applied to the synthesis of polyvanadates-based coordination complexes, it may yield very interesting crystal structures. However, to our knowledge, only two polyvanadate based compounds containing bibp ligands have been reported up to now.[9] Here, we prepared a new polyvanadate manganese complex based on bibp ligand using a simple one pot method. Single-crystal X-ray diffraction study shows the title compound crystallizes in the space group $P\bar{1}$ and exhibits a very complicated 3D framework. The asymmetric unit consists of 2 V atoms, 1 Mn atom, 1.5 bridging ligands bibp, and one water molecule. The V1 and V2 are coordinated by four O atoms (O1, O2, O3, O5) and (O3, O4, O5A, O6), respectively. All the V–O bond lengths are in the range of 1.611–1.803 Å, which are comparable with other vanadium cluster structures.[9–17] Four VO_4 units are joined together with each sharing two of its O atoms, resulting in the ring-like $\{V_4O_{12}\}$ motif. The Mn(II) ion is hexacoordinated in a distorted octahedral coordination sphere formed by three N atoms of different bibp ligands [Mn–N: 2.217–2.231 Å] and three O atoms from two of the above-mentioned $\{V_4O_{12}\}$ units [Mn–O: 2.183–2.190 Å]. The two Mn(II) atoms are bridged into a dinuclear unit $\{Mn_2\}$ by two crystallographically equivalent μ_3-O (O6) atoms of the $\{V_4\}$ rings. The bibp ligands show two distinct conformations in the crystal structure. In one of the ligands, the two benzene rings on the biphenyl are in the same plane, while in the other biphenyl, the two benzene rings appear perpendicular to each other.

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