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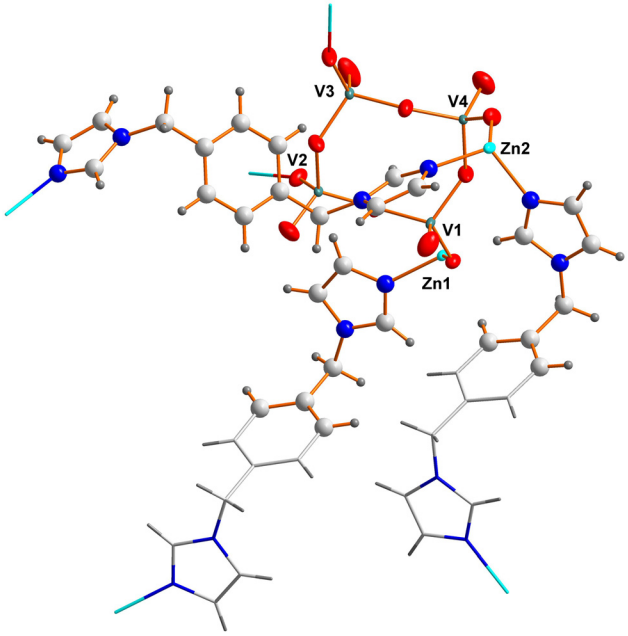
Crystal structure of poly[oktakis(μ_2-oxido-κ^2*O:O*)-tetrakis(oxido-κ^1*O*)-bis(μ_2-1,1′-[1,4-phenylenebis(methylene)]di(1*H*-imidazole-κ^2*N:N′*))-tetravanadium(V)-dizinc(II)] monohydrate, $C_{28}H_{30}Zn_2N_8O_{13}V_4$



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Abstract

$C_{28}H_{30}Zn_2N_8O_{13}V_4$, monoclinic, $P2_1/n$ (no. 14), a = 15.7458(8) Å, b = 12.3628(7) Å, c = 19.5668(10) Å, β = 102.0143(19)°, V = 3725.5(3) Å^3, Z = 4, $R_{gt}(F)$ = 0.0267, $wR_{ref}(F^2)$ = 0.0709, T = 100 K.

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Table 1: Data collection and handling.

Crystal:	Clear light colourless block
Size:	0.21 × 0.20 × 0.19 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	2.30 mm^{-1}
Diffractometer, scan mode:	Bruker APEX II, φ and ω scans
θ_{max}, completeness:	26.4°, 100 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	32975, 7617, 0.045
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 7086
$N(param)_{refined}$:	499
Programs:	Bruker,[1] Olex2,[2,3] SHELX[4]

A part of the polymeric structure is shown in the figure Table 1 contains the crystallographic data.

1 Source of materials

A homogeneous solution was prepared by dissolving sodium metavanadate (48.8 mg, 0.4 mmol), 80 % hydrazine hydrate (6.2 mL, 0.1 mmol), 1,4-bis(imidazol-1-ylmethyl)benzene (48 mg, 0.2 mmol), and zinc nitrate hexahydrate (120 mg, 0.4 mmol) in a mixed solvent system containing 9.5 mL deionized water and 0.5 mL *N,N′*-dimethylformamide. The resulting mixture was magnetically stirred for 2 h at ambient temperature, followed by pH adjustment to 4.27 using HCl (aq 1.0 M). The homogeneous solution was subsequently sealed in a 23 mL Teflon-lined stainless steel autoclave and subjected to hydrothermal treatment at 403 K for 3 days under autogenous pressure. Then the system was cooled to room temperature and the colorless block-shaped crystals were collected by vacuum filtration (yield: 62 % based on Zn).

2 Experimental details

The structure was solved by Direct Methods with the SHELXS-2019 program. All H-atoms from C atoms were

positioned with idealized geometry and refined isotropically (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 = 0.99 Å (methylene), respectively. The water H-atom positions were fixed with O–H = 0.869 and 0.870 Å (U_{iso}(H) = 1.5U_{eq}(O)).

3 Comment

The nitrogen-containing ligands have been preferentially employed for constructing multifarious structural polyoxovanadate-based complexes owing to their strong coordination capacities.[5–11] The semi-rigid N-donor ligand 1,4-bis(imidazol-1-ylmethyl)benzene (Bix), which adopts a bent conformation, possesses imidazolyl groups containing nitrogen atoms with lone electron pairs capable of coordinating transition metal ions.[12–17] Here, we designed and synthesized a novel coordination compound through the combination of Bix with zinc ions and a vanadium precursor.

Single-crystal X-ray diffraction analysis reveals that the title compound crystallizes in the monoclinic system with space group $P2_1/n$ (no. 14). The asymmetric unit contains two crystallographically independent Zn atoms, four distinct V atoms, one full Bix ligand, two half Bix ligands, and one lattice water molecule. Structural analysis demonstrates that the four independent V centers (V1–V4) adopt distorted VO_4 tetrahedral geometries (V–O bond lengths: 1.60–1.79 Å), which interconnect via μ–O bridges to form a cyclic $\{V_4O_{12}\}$ cluster, and all the bond lengths are comparable with other vanadium cluster structures.[7–17] This polyoxovanadate cluster functions as a tetradentate ligand, coordinating to four Zn atoms through terminal O atoms to generate a bimetallic octanuclear $\{Zn_4V_4O_{12}\}$ cluster. Within this hybrid cluster, two symmetry-independent Zn centers (Zn1 and Zn2) exhibit distorted tetrahedral coordination environments. Each Zn atom is ligated by two nitrogen donors from separate Bix ligands and two bridging oxygen atoms from adjacent $\{V_4O_{12}\}$ clusters (Zn–O: 1.93–1.95 Å; Zn–N: 1.98–1.99 Å), which are comparable with other Zn complexes.[17] Adjacent $\{V_4O_{12}\}$ clusters and Zn atoms assemble through corner-sharing terminal oxygen atoms into one-dimensional $\{Zn_4V_4O_{12}\}$ chains. These chains are further interconnected via Zn nodes and $\{V_4O_{12}\}$ clusters, propagating into a two-dimensional layered architecture. Each $\{Zn_4V_4O_{12}\}$ cluster serves as an octatopic node, bridging eight Bix ligands to extend the framework into a three-dimensional (3D) network. It is noteworthy that the 3D network architecture and secondary building units in this work are entirely distinct from those previously reported in the system, despite the identical ligand and metal ion composition.[17]

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