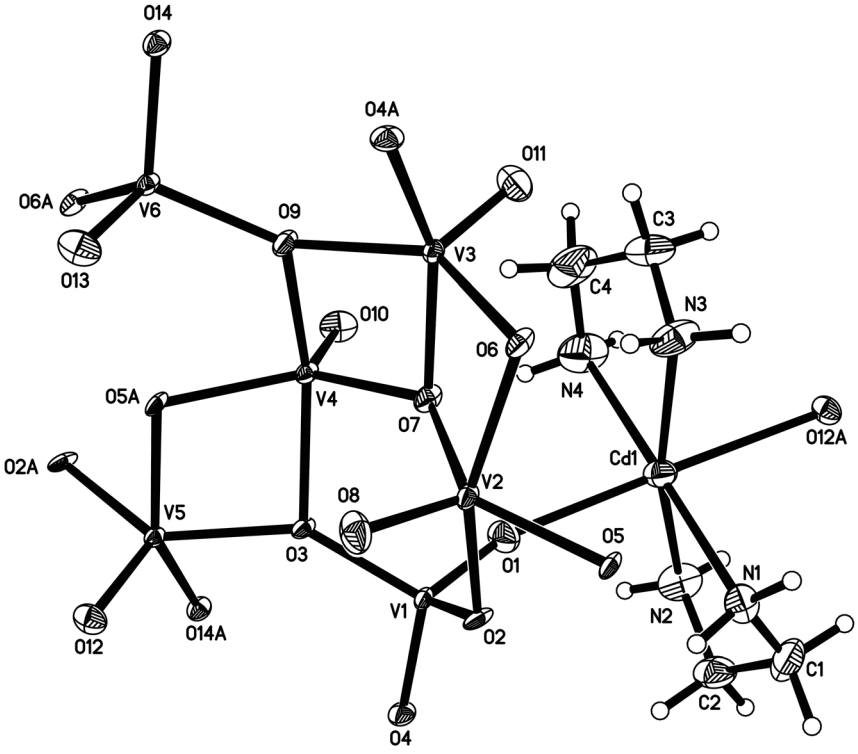
Zi-Long Yue and Yu-Quan Feng*

Crystal structure of poly[(di-ethylenediamine-κ^2N,N′)cadmium(II) tetradedocyloxidohexavanadate] (V^{4+}/V^{5+} = 2/1), $C_4H_{16}CdN_4O_{14}V_6$



https://doi.org/10.1515/ncrs-2025-0169
Received April 4, 2025; accepted May 27, 2025;
published online June 19, 2025

Abstract

$C_4H_{16}CdN_4O_{14}V_6$, orthorhombic, $Pca2_1$, a = 16.545(6) Å, b = 6.515(3) Å, c = 17.096(7) Å, V = 1842.9(13) Å^3, Z = 4, $R_{gt}(F)$ = 0.0306, w$R_{ref}(F^2)$ = 0.0796, T = 296 (2) K.

CCDC no.: 2454409

Table 1: Data collection and handling.

Crystal:	Block
Size:	0.26 × 0.24 × 0.19 mm
Wavelength:	Mo$K\alpha$ radiation (0.71073 Å)
μ:	4.12 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω scans
θ_{max}, completeness:	26.0°, 99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	10909, 3577, 0.037
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 3449
$N(param)_{refined}$:	264
Programs:	Bruker,[1] Olex2,[2,3] SHELX[4]

1 Source of materials

The title compound $[Cd(C_2H_8N_2)_2][V^{IV}_4V^{V}_2O_{14}]$ (Table 1) was prepared under the hydrothermal conditions. The mixture of $Cd(NO_3)_2{\cdot}4H_2O$ (0.32 g), NH_4VO_3 (0.38 g), ethylenediamine ($C_{10}H_8N_2$, 0.60 mL), glacial acetic acid (CH_3COOH, 0.8 mL) and

***Corresponding author: Yu-Quan Feng**, College of Chemistry and Pharmacy Engineering, Nanyang Normal University, Nanyang 473061, China, E-mail: fengyuquan@nynu.edu.cn. https://orcid.org/0000-0002-3232-1680
Zi-Long Yue, College of Chemistry and Pharmacy Engineering, Nanyang Normal University, Nanyang 473061, China

H_2O (5.0 mL) was stirred for 2 h, transferred to a 50 mL Teflon-lined stainless steel vessels and heated at 150 °C for 5 days. The black block crystals were obtained, washed with deionized water and dried at RT (yield: *ca.* 72 % based on NH_4VO_3).

2 Experimental details

H atoms from the organic ligand ethylenediamine were positioned geometrically and refined using a riding model, with C–H = 0.97 Å and N–H = 0.90 Å, with U_{iso} (H) = 1.2 times U_{eq}(C) and U_{eq}(N). The absolute structure was established by refinement of the Flack parameter (0.41(5) from 3577 selected quotients) according to the method from ref.[5]. The restrictive refinement of "twin –1 0 0 0 –1 0 0 0 –1" was applied to deal with the crystal structure (BASF 0.411).

3 Comment

In recent years, polyoxovanadates have attracted extensive attention due to their fascinating structural features, multiple valence states and flexible coordination geometry.[6–11] The use of vanadate anions as building blocks has become an effective strategy for the preparation of organic-inorganic hybrid polyoxovanadates.[12,13] Here, we have synthesized a novel Cd^{2+}-based polyoxovanadate $[Cd(C_2H_8N_2)_2][V^{IV}_4V^{V}_2O_{14}]$ (V^{4+}/V^{5+} = 2/1) by means of organic ligand ethylenediamine under hydrothermal conditions. X-ray single-crystal diffraction structural analysis reveals that its molecular structure is composed of one coordinating cation $[Cd(C_2H_8N_2)_2]^{2+}$ and one vanadate anion $[V^{IV}_4V^{V}_2O_{14}]^{2-}$. A part of the title crystal structure is shown in the Figure. In order to determine the valence states of the V and Cd sites in the crystal structure, the oxidation state of each metal site in the crystal structure is obtained by the method of bond-valence calculation. The results show that the valence states of V(1) and V(6) sites are +V, the valence states of V(2), V(3), V(4) and V(5) sites are +IV, and the valence state of Cd site is +II. Within the vanadate anion $[V^{IV}_4V^{V}_2O_{14}]^{2-}$, the V sites can be divided into two types depending to their coordination numbers: each V(1) and V(6) site adopts a 4-coordinated tetrahedral geometry with four surrounding oxygen atoms, while each V(2), V(3), V(4) and V(5) site is respectively coordinated with five surrounding oxygen atoms to lead to a 5-coordinated distorted square pyramidal geometry. The coordination geometries of V(1) and V(6) sites are similar as those of the reported vanadate compounds α-$[Cu(mIM)_4]V_2O_6$, and β-[Cu(mIM)4]V_2O_6 (mIM = 1-methylimidazole),[14] while the coordination geometries of V(2), V(3), V(4) and V(5) sites are compared with those of known $\{V_6O_{18}\}$ cluster-containing compounds $[Cu^{II}(en)_2]_4\{Na(H_2O)(\mu$–$OH)[B(OH)_2]\}_2[(V^{V}O)_2(V^{IV}O)_{10}O_6(B_{18}O_{36}$-$(OH)_6)]\cdot 7H_2O$[15] and $[Cd^{II}_3(H_2O)_6][(V^{IV}O)_6(V^{V}O)_6(O_6)(B_{18}O_{36}(OH)_6)]\cdot 10H_2O$ (en = ethylenediamine).[16] The lengths of the V–O bonds in the title compound range from 1.586(3) Å to 2.014(4) Å, and the bond angles of O–V–O range from 77.41(13)° to 152.22(16)°. These parameters of bond lengths and bond angles are within their reasonable ranges and can be compared with previously reported vanadate compounds.[12–14] The distorted $\{VO_5\}$ square pyramids are linked by bridging oxygen atoms [O(3), O(5), O(6), O(7) and O(9)], forming a tetranuclear $\{V_4O_{14}\}$ cluster. Then, the tetranuclear clusters $\{V_4O_{14}\}$ are further connected with the surrounding $\{VO_4\}$ units by the bridging oxygen atoms [O(3) and O(9)], resulting in the formation of the vanadate anion $[V^{IV}_4V^{V}_2O_{14}]^{2-}$. These adjacent vanadate anionic structural units are finally extend to a 2D layered anionic structure along the *a*, *b* and *c* axis by bridging oxygen atoms [O(1), O(5), O(4) and O(14)]. The adjacent anionic layers are linked to $[Cd(C_2H_8N_2)_2]^{2+}$ cations by bridging oxygen atoms (O1 and O12), generating a 3D framework architecture. The bond lengths of Cd–O and Cd–N fall in the ranges of 2.372(4) Å–2.555(4) Å and 2.253(5) Å–2.278(6) Å, respectively. The bond angles of O–Cd–N, N–Cd–N fall in the ranges of 81.7(2)°–91.2(2)° and 76.5(2)°–179.3(2)°, respectively. The bond angle O–Cd–O is 176.73(13)°. These bond lengths and bond angles can be compared with the known related Cd-containing compounds $[Cd(en)_3]\{[Cd(H_2O)(en)]_6[B_{20}V_{12}O_{60}$-$(OH)_2]\}\cdot 8H_2O$ (en = ethylenediamine)[17] and poly[aqua-(pyridine-3-carboxylato-κ^1N)(pyridine-3-carboxylato-κ^2O,O′) cadmium(II)] dihydrate ($C_{12}H_{14}N_2O_7Cd$).[18] In addition, the N–H···O hydrogen bonds, which contribute to the stability of the crystal structure, can be observed in the title compound.

Acknowledgments: This work was financially supported by the Natural Science Foundation of Henan (no. 252300421341) and the National Natural Science Foundation Project Cultivation Fund of Nanyang Normal University (no. 2025PY032).

References

1. Bruker Corporation, Bruker Smart Apex–II, Germany, 2008.
2. Bourhis, L. J.; Dolomanov, O. V.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. The Anatomy of a Comprehensive Constrained, Restrained Refinement Program for the Modern Computing Environment – Olex2 Dissected. *Acta Crystallogr.* **2015**, *A71*, 59–75.
3. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. Olex2: a Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Crystallogr.* **2009**, *42*, 339–341.

4. Sheldrick, G. M. Crystal Structure Refinement with *SHELXL*. *Acta Crystallogr.* **2015**, *C71*, 3–8.
5. Flack, H. D. On Enantiomorph-polarity Estimation. *Acta Crystallogr.* **1983**, *A39*, 876–881.
6. Liu, Y.; Xuan, W.; Cui, Y. Engineering Homochiral Metal–Organic Frameworks for Heterogeneous Asymmetric Catalysis and Enantioselective Separation. *Adv. Mater.* **2010**, *22*, 4112–4135.
7. Hagrman, P.-J.; Finn, R.-C.; Zubieta, J. Molecular Manipulation of Solid State Structure: Influences of Organic Components on Vanadium Oxide Architectures. *J. Solid State Sci.* **2001**, *3*, 745–774.
8. Jiang, H.-L.; Xu, Q. Porous Metal–Organic Frameworks as Platforms for Functional Applications. *Chem. Commun.* **2011**, *47*, 3351–3370.
9. Meek, S.-T.; Grathouse, J.-A.; Allenford, M. Metal–Organic Frameworks: a Rapidly Growing Class of Versatile Nanoporous Materials. *Adv. Mater.* **2011**, *23*, 249–267.
10. Dhakshinamoorthy, A.; Alvaro, M.; Corma, A.; García, H. Delineating Similarities and Dissimilarities in the Use of Metal Organic Frameworks and Zeolites as Heterogeneous Catalysts for Organic Reactions. *Dalton Trans.* **2011**, *40*, 6344–6360.
11. Rocha, J.; Carlos, L.-D.; Paz, F.-A.-A.; Ananias, D. Luminescent Multifunctional Lanthanides-based metal–organic Frameworks. *Chem. Soc. Rev.* **2011**, *40*, 926–940.
12. Chen, H.; Yu, Z.; Bacsik, Z.; Zhao, H.; Yao, Q.; Sun, J. Construction of Mesoporous Frameworks with Vanadoborate Clusters. *Angew. Chem., Int. Ed.* **2014**, *53*, 3608–3611.
13. Chen, H.; Deng, Y.; Yu, Z.; Zhao, H.; Yao, Q.; Zou, X.; Bäckvall, J.-E.; Sun, J. 3D Open–Framework Vanadoborate as a Highly Effective Heterogeneous Pre-catalyst for the Oxidation of Alkylbenzenes. *Chem. Mater.* **2013**, *25*, 5031–5036.
14. Li, J.; Huang, X.; Yang, S.; Xu, Y.; Hu, C. Controllable Synthesis, Characterization, and Catalytic Properties of Three Inorganic–Organic Hybrid Copper Vanadates in the Highly Selective Oxidation of Sulfides and Alcohols. *Cryst. Growth Des.* **2015**, *15*, 1907–1914.
15. Feng, Y.-Q.; Ding, C.-H.; Fan, H.-T.; Zhong, Z.-G.; Qiu, D.-F.; Shi, H.-Z. Employing a New 12-connected Topological open-framework Copper Borovanadate as an Effective Heterogeneous Catalyst for Oxidation of benzyl-alkanes. *Dalton Trans.* **2015**, *44*, 18731–18736.
16. Feng, Y.-Q.; Qiu, D.-F.; Fan, H.-T.; Li, M.; Huang, Q.-Z.; Shi, H.-Z. A New 3–D Open-Framework Cadmium Borovanadate with Plane-Shaped Channels and High Catalytic Activity for the Oxidation of Cyclohexanol. *Dalton Trans.* **2015**, *44*, 8792–8796.
17. Feng, Y.-Q.; Wu, J.-H.; Zhong, Z.-G.; Meng, Z.-H.; Chen, S.-Y.; Liu, K.-C. Heptanuclear Cadmium Borovanadate Containing a Sandwich–Type Anionic Partial Structure $\{B_{20}V_{12}\}$ as a Heterogeneous Photocatalyst for the Reduction of CO_2 into CH_4. *Inorg. Chem.* **2024**, *63*, 16515–16522.
18. Feng, Y.-Q.; Chen, S.-Y.; Yue, Z.-L. Crystal Structure of poly[Aqua-(pyridine-3-carboxylato-κ^1N)(pyridine-3-carboxylato-κ^2 O,O′) cadmium(II)] Dihydrate. *Z. Kristallogr. – N. Cryst. Struct.* **2024**, *239* (6), 1065–1067.