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SYNTHESIS, CRYSTAL STRUCTURE AND PROPERTIES OF A NEW BI-DENTATE DECAVANADATE $[CO(H_3SO_3)+(H_2O)_5]_2[H_2V_{10}O_{28}]\cdot 2H_2O\cdot 2SO_3$

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Abstract

A new bi-dentate decavanadate compound formulated $[Co(H_3SO_3)^+(H_2O)_5]_2[H_2V_{10}O_{28}]\cdot 2H_2O\cdot 2SO_3$ (1), has been synthesized under hydrothermal condition by using sulfuric acid as the initiator at 110 °C. And 1 crystallizes in the triclinic, space group P-1 with a = 9.8954(7) Å, b = 10.4827(9) Å, c = 12.8466(7) Å, α = 76.395(6), β = 82.024(6), γ = 68.836(7), V = 1205.7 Å^3, R1(I > 2s(I) = 3.61), and Z = 5. X-ray diffraction analysis reveals that 1 is constructed from bi-dentate decavanadate formed by decavanadate clusters coordinated to $[Co(H_3SO_3)^+(H_2O)_5]^{2+}$ complexes and free water molecules.

Keywords: *X-ray diffraction, cobalt complex, polyoxovanadate, sulfate coordination, triclinic crystal structure, supramolecular assembly*

Introduction

Polyoxometalates (POMs) are a unique class of metal-oxygen clusters that display remarkable structural diversity and a wide range of physicochemical properties. Among them, polyoxovanadates (POVs), particularly decavanadate anions $[H_nV_{10}O_{28}]^{6-}$, have attracted significant attention due to their high stability in acidic media, versatile coordination behavior, and potential applications in catalysis, materials science, and biomedicine (Liu, H., Wang, J., Jian, F., & Xiao, H., 2009; Msaadi, I., Rayes, A., Benito, M., Issaoui, N., Molins, E., & Ayed, B., 2022). The decavanadate unit, which consists of ten edge-sharing VO_6 octahedra, exhibits rich structural chemistry and can form hybrid frameworks with transition metal ions and organic ligands.

Transition metal–POM hybrids have become an important area of research due to their multifunctional characteristics, such as redox activity, magnetism, photoluminescence, and catalytic efficiency. In particular, cobalt-based polyoxovanadate complexes have been intensively studied because Co(II) ions can provide redox flexibility and variable coordination geometries, leading to extended hydrogen-bonded supramolecular architectures. Moreover, their synthesis under hydrothermal or aqueous acidic conditions often results in well-defined crystalline frameworks stabilized by

extensive O–H···O interactions (Pope, M. T., & Müller, A., 2001).

Recent investigations have demonstrated that modifying the cationic environment or introducing auxiliary ligands, such as protonated amines or sulfate groups, significantly influences the structural organization and electronic properties of decavanadate-based systems (Hill, C. L., 1998). These hybrid materials have shown potential as model systems for redox catalysis, photoactive materials, and biologically active agents due to their stability and charge-transfer capabilities.

In this study, we report the X-ray crystal structure of a new cobalt(II)–polyoxovanadate complex formulated as 0.4($H_{13}CoO_8S$)·0.2($H_2O_{28}V_{10}$)·0.4(O_3S)·0.4(H_2O). The complex was synthesized under mild aqueous conditions using cobalt(II) nitrate, sodium metavanadate, and sodium sulfate, and characterized by single-crystal X-ray diffraction. The structure reveals a triclinic crystal system (space group $P1^-$) composed of Co(II) centers octahedrally coordinated by oxygen atoms from sulfate and polyoxovanadate groups. The study focuses on the crystallographic parameters, coordination geometry, and supramolecular hydrogen-bonding framework of the newly obtained compound, contributing to a deeper understanding of cobalt–decavanadate hybrid assemblies.

Materials and Methods

Synthesis of the Complex

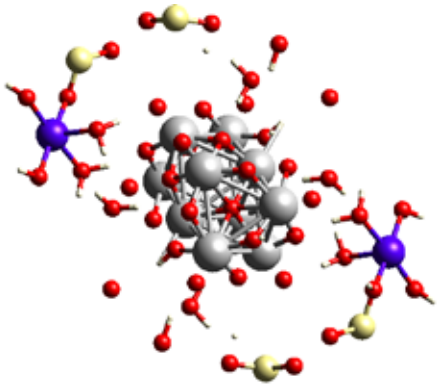
The complex was obtained by slow evaporation of an aqueous solution containing cobalt(II) nitrate, sodium metavanadate, and sodium sulfate in stoichiometric proportions. The reaction mixture was kept at room temperature for several days, during which blue crystals suitable for X-ray diffraction were formed.

X-ray Diffraction Analysis

Single-crystal X-ray diffraction data were collected on a Bruker D8 QUEST diffractometer using Mo Kα radiation (λ = 0.71073 Å) at 298 K. The structure was solved by direct methods and refined by full-matrix least squares on F^2 using SHELX-2018 software.

The compound crystallizes in the triclinic crystal system with space group $P1^-$. Crystallographic parameters:

Picture 1. *The chemical formula was refined as 0.4($H_{13}CoO_8S$)·0.2($H_2O_{28}V_{10}$)·0.4(O_3S)·0.4(H_2O), confirming the presence of both cobalt–sulfate and polyoxovanadate fragments*



Formula	0.4(H_{13} Co O_8 S),0.2(H_2 O_{28} V_{10}),0.4(O_3 S),0.4(H_2 O)
Formula weight	321.22 g/mol
Crystal system	triclinic
Space-group	P –1 (2)
Cell parameters	a=9.895(7) Å, b=10.482(9) Å, c=12.846(7) Å α=76.395(6)° β=82.024(6)° γ=68.836(7)°
Cell ratio	a/b=0.9440 b/c=0.8160 c/a=1.2982
Cell volume	1205.70(17) Å^3
Z	5
Calc. density	2.21185 g/cm^3
RAll	0.189
R(I>2σ(I))	3,61
Temperature	Room Temp.(283–303)
Packing coefficient	0.685956

3. Results and Discussion

3.1. Molecular and Crystal Structure

The cobalt(II) ion is octahedrally coordinated by oxygen atoms from sulfate and polyoxovanadate groups. The Co–O bond lengths range between 2.04–2.21 Å, typical for Co(II)–O coordination. The asymmetric

unit also includes crystallization water molecules that participate in hydrogen bonding. The polyoxovanadate cluster ($H_2O_{28}V_{10}$) acts as a polynuclear anion with bridging oxygen atoms connecting vanadium centers. Sulfate groups serve as charge-compensating and hydrogen-bond donors, leading to the formation of an extended 3D network.

Picture 2. *The appearance of the complex compound* $[Co(H_3SO_3)(H_2O)_5]_2[H_2V_{10}O_{28}]\cdot 2H_2O\cdot 2SO_3$ *in the a, b, and c projections*

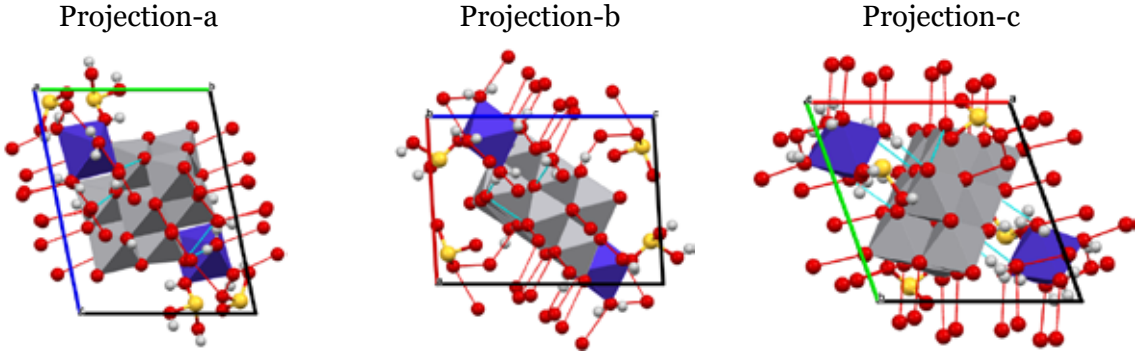


Table 1.

Atomic parameters							
Atom	**Ox.**	**Wyck.**	**Site**	**x/a**	**y/b**	**z/c**	**U [Å²]**
Co01		2i	1	–0.1063(2)	0.7681(2)	0.73379(15)	
V02		2i	1	0.3489(2)	0.4743(2)	0.55360(15)	
V03		2i	1	0.6236(2)	0.2269(2)	0.48889(15)	
V004		2i	1	0.5478(2)	0.5437(2)	0.68995(14)	
V005		2i	1	0.5297(2)	0.2462(2)	0.72770(15)	
V006		2i	1	0.8113(2)	0.2974(2)	0.62959(16)	
S00		2i	1	–0.2565(3)	0.6689(4)	0.9565(3)	
S1		2i	1	0.1806(3)	0.9260(4)	0.9435(3)	
O009		2i	1	0.4177(9)	0.3477(8)	0.4565(6)	
O00A		2i	1	0.3552(9)	0.6149(9)	0.6258(7)	
O00B		2i	1	0.5569(9)	0.1447(9)	0.6171(7)	
O00C		2i	1	0.4216(8)	0.6018(8)	0.4233(6)	
O00D		2i	1	0.8069(9)	0.1881(9)	0.5282(7)	
O00E		2i	1	0.7286(9)	0.1938(9)	0.7356(6)	
O00F		2i	1	0.7459(8)	0.4513(9)	0.6928(6)	
O00G		2i	1	0.3326(9)	0.3552(8)	0.6653(6)	
H00K		2i	1	0.2440(15)	0.377(7)	0.689(4)	0.0050
O00H		2i	1	–0.079(1)	0.6158(9)	0.6422(8)	
H00A		2i	1	–0.05864	0.64640	0.57620	0.0180
H00B		2i	1	–0.15981	0.60352	0.64161	0.0180
O00I		2i	1	0.5000(9)	0.4053(9)	0.7821(7)	
O00J		2i	1	0.1801(9)	0.5571(9)	0.5115(7)	
O00K		2i	1	–0.1478(9)	0.9178(9)	0.8258(8)	
H00C		2i	1	–0.13171	0.99311	0.78791	0.0170

Atomic parameters							
Atom	**Ox.**	**Wyck.**	**Site**	**x/a**	**y/b**	**z/c**	**U [Å²]**
H00D		2i	1	–0.08588	0.88919	0.87639	0.0170
O00L		2i	1	0.5231(9)	0.6601(9)	0.7612(7)	
O00M		2i	1	–0.0677(10)	0.8953(9)	0.5893(7)	
H00E		2i	1	0.01649	0.85425	0.55741	0.0160
H00F		2i	1	–0.05713	0.97084	0.60056	0.0160
O00N		2i	1	–0.3305(10)	0.8586(10)	0.6927(9)	
H00G		2i	1	–0.37362	0.79774	0.71493	0.0250
H00H		2i	1	–0.33602	0.87743	0.62395	0.0250
O00O		2i	1	0.6461(10)	0.1144(9)	0.4154(7)	
O00P		2i	1	0.1168(10)	0.6939(12)	0.7615(8)	
H00I		2i	1	0.13254	0.72733	0.81293	0.0260
H00J		2i	1	0.16564	0.72593	0.70615	0.0260
O00Q		2i	1	0.9802(10)	0.2366(11)	0.6510(8)	
O00R		2i	1	0.4828(10)	0.1427(10)	0.8312(7)	
O00S		2i	1	–0.1409(10)	0.6337(9)	0.8654(8)	
H00S		2i	1	–0.101(14)	0.5456(17)	0.874(7)	0.0260
O00T		2i	1	0.2580(11)	0.1756(11)	0.5412(10)	
H00L		2i	1	0.34396	0.16030	0.55664	0.0310
H00M		2i	1	0.26528	0.10814	0.51232	0.0310
O00		2i	1	0.1058(11)	0.8316(12)	0.9238(10)	
O00V		2i	1	–0.3018(17)	0.5143(16)	0.9979(13)	
H00V		2i	1	–0.35064	0.51675	1.05490	0.0680
O00W		2i	1	–0.1573(18)	0.6547(19)	1.0686(13)	
H00W		2i	1	–0.21077	0.65544	1.12342	0.0780
O1		2i	1	0.352(2)	0.817(3)	0.984(2)	
O2		2i	1	0.233(4)	1.009(4)	0.818(2)	

Table 2. *Torsion bond angle*

Atoms 1,2,3,4	**Tors. an. 1,2,3,4 [°]**	**Atoms 1,2,3,4**	**Tors. an. 1,2,3,4 [°]**
V02-V005-O00E-V006	2.1(6)	O00C–V02-O00J-V006^{i}	1.9(4)
V02-V005-O00I–V004	–52.1(4)	O00C–V02-O00J-V006^{i}	0.9(19)
V02-V006-O00E-V005	–3.2(6)	O00C–V03-O00B-V005	–8.6(4)
V02-V006-O00F-V004	55.1(4)	O00C–V03-O00D-V006	9.7(4)
V03-V004-O00F-V006	–86.2(5)	O00C–V004-O00F-V006	–11.1(4)
V03-V004-O00I–V005	82.0(5)	O00C–V004-O00I–V005	6.8(4)
V03-V005-O00E-V006	48.2(4)	O00C–V005-O00E-V006	2.2(4)
V03-V005-O00I–V004	–6.3(6)	O00C–V005-O00I–V004	–6.7(4)
V004-V03-O00B-V005	–85.8(5)	O00C–V006-O00E-V005	–2.2(4)
V004-V03-O00D-V006	86.2(5)	O00C–V006-O00F-V004	11.0(4)

Atoms 1,2,3,4	Tors. an. 1,2,3,4 [°]	Atoms 1,2,3,4	Tors. an. 1,2,3,4 [°]
V004-V005-O00E-V006	–44.8(4)	O00D-V03-O00B-V005	71.4(5)
V004-V006-O00E-V005	45.0(4)	O00D-V006-O00E-V005	–79.1(5)
V005-V02-O00J-V006^{i}	–178.73(15)	O00D-V006-O00F-V004	29.8(11)
V005-V03-O00D-V006	–38.5(4)	O00E-V005-O00I–V004	73.8(5)
V005-V004-O00F-V006	37.1(4)	O00E-V006-O00F-V004	–70.3(5)
V005-V006-O00F-V004	–37.6(4)	O00F-V004-O00I–V005	–71.7(5)
V006-V02-O00G-V005	178.44(16)	O00F-V006-O00E-V005	76.1(5)
V006-V004-O00I–V005	–41.1(4)	O00G-V02-O00J-V006^{i}	–178.1(4)
V006-V005-O00I–V004	41.5(4)	O00G-V005-O00E-V006	3.3(12)
O009-V02-O00G-V005	80.3(4)	O00G-V005-O00I–V004	–83.2(5)
O009-V02-O00J-V006^{i}	–78.7(4)	O00I–V004-O00F-V006	68.3(5)
O009-V03-O00B-V005	–84.9(5)	O00I–V005-O00E-V006	–75.4(5)
O009-V03-O00D-V006	31.7(11)	O00J-V02-O00G-V005	–179.4(4)
O009-V004-O00F-V006	–86.2(5)	O00J-V006-O00E-V005	–8.4(12)
O009-V004-O00I–V005	25.2(11)	O00J-V006-O00F-V004	86.2(5)
O00A-V02-O00G-V005	–79.8(4)	O00L–V004-O00F-V006	174.1(5)
O00A-V02-O00J-V006^{i}	82.2(4)	O00L–V004-O00I–V005	–175.6(5)
O00A-V03-O00B-V005	–33.5(12)	O00O-V03-O00B-V005	176.3(5)
O00A-V03-O00D-V006	86.1(5)	O00O-V03-O00D-V006	–174.6(5)
O00A-V004-O00F-V006	–34.8(11)	O00Q-V006-O00E-V005	179.8(5)
O00A-V004-O00I–V005	83.6(5)	O00Q-V006-O00F-V004	–176.7(5)
O00B-V03-O00D-V006	–70.9(5)	O00R-V005-O00E-V006	–178.5(5)
O00B-V005-O00E-V006	79.5(5)	O00R-V005-O00I–V004	177.8(5)
O00B-V005-O00I–V004	–20.3(12)	O00V-S00-O00S-Co01	147.0(9)
O00C–V02-O00G-V005	0.4(18)	O00W-S00-O00S-Co01	–108.6(10)
O00C–V02-O00G-V005	0.8(4)		

(i) 1-x, 1-y, 1-z.

Hydrogen Bonding and Packing Analysis

Intermolecular O–H···O hydrogen bonds link neighboring clusters, creating a layered supramolecular arrangement along the b-axis. Weak van der Waals forces stabilize the packing along c. The overall structure displays a typical polyoxometalate–transition metal framework with water-mediated hydrogen bridges.

Crystallographic Features

The triclinic symmetry ($P1^{-}$) results in non-equivalent Co–O coordination environments, indicating slight distortions from ideal octahedral geometry. The moderate cell volume (V = 1205.7 Å³) suggests dense packing with strong inter-anionic interactions.

Conclusion

The single-crystal X-ray diffraction study revealed that the synthesized cobalt–polyoxovanadate complex crystallizes in a triclinic system (space group $P1^{-}$) with mixed sulfate and vanadate anionic species. The structure consists of Co(II) centers octahedrally coordinated by oxygen donors, forming a robust hydrogen-bonded framework. These findings

contribute to the understanding of cobalt–POM hybrid materials and open perspectives for their potential applications in redox catalysis and materials chemistry.

References

Liu, H., Wang, J., Jian, F., & Xiao, H. (2009). *Synthesis and crystal structure of two decavanadates cluster metal complexes: [Co(H2O)6]2[H2V10O28]·6H2O and (NH4)2[Ca(H2O)7]2[V10O28]. Journal of Cluster Science,* – 20(4). – P. 621–627. URL: https://doi.org/10.1007/s10876-009-0265-2

Msaadi, I., Rayes, A., Benito, M., Issaoui, N., Molins, E., & Ayed, B. (2022). *A combined experimental and theoretical study of two new decavanadates: (C6N2H9)4[H2V10O28]·4H2O and (C7H9NF)4[H2V10O28]·2H2O. Journal of Molecular Structure, – 1262*. – 133085 p. URL: https://doi.org/10.1016/j.molstruc.2022.133085

Pope, M.T., & Müller, A. (2001). *Polyoxometalate Chemistry: From Topology via Self-Assembly to Applications*. Springer.

Hill, C.L. (1998). *Polyoxometalates: Reactivity and catalytic applications. Chemical Reviews, – 98*(1). – P. 1–390. URL: https://doi.org/10.1021/cr9603980

Sheldrick, G.M. (2015). *Crystal structure refinement with SHELXL. Acta Crystallographica Section C: Structural Chemistry,* – 71(1). – URL: 3–8. https://doi.org/10.1107/S2053229614024218

Sheldrick, G.M. “Crystal structure refinement with SHELXL.” Acta Crystallographica Section C 71 (2015): 3–8.

Pope, M.T., Müller, A. Polyoxometalate Chemistry: From Topology via Self-Assembly to Applications. Springer, 2001.

Hill, C.L. “Polyoxometalates: Reactivity and Catalytic Applications.” Chemical Reviews – 98. – No. 1 (1998): 1–390.

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