

Synthesis and Structural Characterization of a Novel Thiamine-Molybdovanadate Organic-Inorganic Hybrid Polyoxometalate

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Yeni Bir Tiamin-Molibdovanadat Organik-İnorganik Hibrit Polioksometalatın Sentezi ve Yapısal Karakterizasyonu

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Abstract

A novel organic-inorganic hybrid polyoxometalate compound, (Thiamine)₆[Mo₆V₂O₂₆]·4H₂O, was obtained by the reaction of K₅Na[Mo₆V₂O₂₆]·4H₂O with thiamine hydrochloride in aqueous medium. This study aimed to create a vitamin-derived supramolecular polyoxometalate system and evaluate its structural integrity and physicochemical properties. The resulting yellow compound was characterized by elemental analysis, ICP-MS, FT-IR spectroscopy, and thermogravimetric analysis (TGA). This study highlights the potential of vitamin-based organic molecules for the design of functional polyoxometalate hybrid materials with tunable structural and thermal properties.

Keywords: Molybdenum, Vanadium, Polyoxometalate, Thiamine Hydrochloride, Vitamin B1.

Öz

K₅Na[Mo₆V₂O₂₆]·4H₂O'nun tiamin hidroklorür ile sulu ortamdaki reaksiyonu sonucunda yeni bir organik-inorganik hibrit polioksometalat bileşiği (Tiamin)₆[Mo₆V₂O₂₆]·4H₂O elde edilmiştir. Bu çalışma, vitamin türevi bir supramoleküler polioksometalat sistemi oluşturmayı, yapısal bütünlüğünü ve fizikokimyasal özelliklerini değerlendirmeyi amaçlamıştır. Elde edilen sarı renkli bileşik, elementel analiz, ICP-MS, FT-IR spektroskopisi ve termogravimetrik analiz (TGA) ile karakterize edilmiştir. Bu çalışma, ayarlanabilir yapısal ve termal özelliklere sahip fonksiyonel polioksometalat hibrit malzemelerin tasarımı için vitamin bazlı organik moleküllerin potansiyelini vurgulamaktadır.

Anahtar Kelimeler: Molibden, Vanadyum, Polioksometalat, Tiamin Hidroklorür, Vitamin B1.

1. Introduction

Although polyoxometalate (POM) chemistry has been extensively investigated for several decades, the design of biologically relevant organic-inorganic hybrid systems based on mixed molybdenum/vanadium oxo-clusters remains comparatively underexplored (Anyushin et al. 2020, Gumerova et al. 2020, Long et al. 2010, Dolbecq et al. 2010). Polyoxometalates are discrete nanoscale metal-oxygen assemblies generally formed by the condensation of early transition metal oxanions in aqueous media (Pope 1983). Their structural versatility, reversible redox activity, proton-coupled electron transfer behavior, and controllable self-assembly characteristics have made them attractive candidates for applications ranging from catalysis and electrochemical energy storage to molecular electronics and medicinal chemistry (Aureliano 2020, Bijelic et al. 2019, Verissimo et al. 2022, Wang et al. 2020). In particular, molybdenum- and vanadium-containing POMs are of considerable interest because the coexistence of Mo and V centers can

substantially alter the electronic structure and physicochemical properties of the inorganic framework (Cao et al. 2021, Zheng and Yang 2012).

Recent developments in hybrid POM chemistry have shifted attention from purely inorganic clusters toward multifunctional supramolecular architectures incorporating organic species with specific electronic or biological functionalities (Cameron et al. 2022, Gao et al. 2022, Izarova et al. 2012). Such hybridization approaches enable modulation of solubility, structural stability, intermolecular interactions, and charge-transfer behavior while simultaneously introducing additional functional properties associated with the organic component (Sun et al. 2020). Consequently, hybrid POM materials have recently attracted increasing interest in photocatalysis, proton-conductive systems, sensing devices, antibacterial materials, and bioactive inorganic frameworks (Miras et al. 2012, Rhule et al. 1998).

One of the most promising strategies in this field involves the use of protonated nitrogen-containing organic

molecules as counter-cations for highly charged polyoxometalate anions (Guan et al. 2023, Zhuang et al. 2023). Beyond simple charge compensation, these organic species frequently participate in supramolecular organization through hydrogen bonding, electrostatic interactions, and aromatic stacking effects (Cameron et al. 2022). Such interactions may strongly influence crystal packing, stabilization of the inorganic cluster, and the overall physicochemical behavior of the resulting hybrid material (Stuckart et al. 2019). Therefore, the selection of an appropriate organic component plays a decisive role in the construction of functional POM-based supramolecular systems.

Among biologically active organic molecules, thiamine hydrochloride (vitamin B₁) represents a particularly interesting candidate for hybrid POM synthesis because of its heteroaromatic pyrimidine and thiazolium rings together with protonatable amino functionalities (Tonkushina et al. 2022). These structural features provide multiple possibilities for hydrogen-bond formation and electrostatic interaction with metal-oxo clusters. Furthermore, incorporation of vitamin-derived molecules into inorganic frameworks may offer opportunities for developing hybrid materials with enhanced biological compatibility and unique supramolecular properties (Anyushin et al. 2020, Cheng et al. 2020, Soria-Carrera et al. 2023, Şahin et al. 2021). Despite these advantages, studies involving vitamin-assisted polyoxometalate assemblies remain very limited, especially for mixed molybdovanadate systems.

Previous investigations have mainly focused on hybrid POMs containing imidazolium, pyridinium, ammonium, phosphonium, or ligand-based organic cations (Cameron et al. 2022, Dolbecq et al. 2010, Hong et al. 2023). In contrast, reports concerning thiaminium-stabilized molybdenum/vanadium polyoxometalates are scarce. Furthermore, the structural behavior of mixed Mo/V isopolyoxometalates in the presence of biologically active heterocyclic cations has not been systematically examined. Since vanadium substitution is known to affect the redox behavior and metal-oxygen connectivity of molybdate frameworks (Avcı Özbek 2023) the interaction of protonated thiamine species with Mo/V oxo-clusters may lead to distinct supramolecular arrangements and stabilization mechanisms compared with conventional hybrid POM systems.

Current research trends published between 2022 and 2025 demonstrate a rapidly growing interest in supramolecular and bio-inspired polyoxometalate materials designed for sustainable catalysis, molecular

recognition, and functional inorganic architectures (Avcı Özbek 2023, Avcı Özbek 2025, Liu et al. 2022, Zhang and Wang 2022). Nevertheless, the synthesis and spectroscopic characterization of vitamin-containing mixed-metal polyoxometalates remain largely unexplored. In this context, the preparation of new thiaminium-based molybdovanadate hybrids is expected to contribute to the development of biologically relevant organic-inorganic polyoxometalate systems.

In the present study, a new hybrid compound formulated as (Thiamine)₆[Mo₆V₂O₂₆]·4H₂O was synthesized through the reaction of K₅NaMo₆V₂O₂₆·4H₂O with thiamine hydrochloride under aqueous conditions. The synthesized material was investigated by FT-IR spectroscopy, TGA, ICP-MS and elemental analysis in order to evaluate the preservation of the mixed molybdovanadate framework and the incorporation of protonated thiamine species into the resulting organic-inorganic hybrid structure.

2. Materials and Methods

All reagents and solvents employed in this study were purchased from Aldrich and utilized as received without further purification. The compound K₅Na[Mo₆V₂O₂₆]·4H₂O was prepared according to the previously reported synthetic procedure (Nenner 1985). Elemental analyses for carbon, hydrogen, nitrogen, and sulfur were carried out using a LECO-932 CHNS elemental analyzer, while the molybdenum and vanadium contents were quantified by ICP-MS using an Agilent Technology 7700 instrument. Fourier-transform infrared (FT-IR) spectra were recorded on a Perkin Elmer LR 64912 C spectrometer over the 400–4000 cm⁻¹ region using KBr pellets. Thermal behavior was investigated by thermogravimetric analysis (TGA) with a Hitachi Exstar TG/DTA 7300 instrument under flowing nitrogen atmosphere at a flow rate of 50.0 mL min⁻¹ and a heating rate of 10 °C min⁻¹ within the temperature range of 25–800 °C.

2.1 Synthesis of (Thiamine)₆[Mo₆V₂O₂₆]·4H₂O

The two reactant solutions were prepared separately prior to the reaction. In the first solution, K₅Na[Mo₆V₂O₂₆]·4H₂O (138 mg, 0.10 mmol) was dissolved in 10 mL of distilled water under continuous stirring until a clear solution was obtained. In the second solution, an excess amount of thiamine hydrochloride was dissolved in 5 mL of distilled water with stirring. Subsequently, the two solutions were combined and the resulting mixture was stirred at room temperature for 2 hours. After completion of the reaction, the formed precipitate was collected by filtration. The obtained yellow solid was

washed thoroughly with a mixture of ethanol and water, and finally dried at 60 °C. Yield: 140 mg, 50%. FT-IR data (cm^{-1}): 521 (m), 569 (m), 644 (m), 678 (m), 728 (m), 805 (m), 866 (m), 912 (s), 990 (m), 1046 (m), 1108 (m), 1218 (m), 1384 (m), 1437 (m), 1434 (m), 1473 (m), 1538 (s), 1616 (m), 1659 (s), 2283 (m), 2918 (m), 3091 (m), 3215 (m), 3326 (m). Anal. Calcd. (%) for $\text{C}_{72}\text{H}_{110}\text{N}_{24}\text{S}_6\text{Mo}_6\text{V}_2\text{O}_{36}$ (2757.69 g/mol): C, 31.36; H, 4.02; N, 12.19; S, 6.98; Mo, 20.87; V, 3.69. Found (%): C, 30.67; H, 3.87; N, 12.17; S, 5.43; Mo, 20.00; V, 3.41. TGA (loss of 4 H_2O): calcd. 2.61%, found 2.61%; (loss of 6 $(\text{C}_{12}\text{H}_{17}\text{N}_4\text{OS})^+$): calcd. 57.73%, found 57.38%.

3. Results and Discussions

Thiamine hydrochloride and $\text{K}_5\text{Na}[\text{Mo}_6\text{V}_2\text{O}_{26}]\cdot 4\text{H}_2\text{O}$ were selected as the precursors for the preparation of the organic-inorganic hybrid polyoxomolybdate. The target compound, $(\text{Thiamine})_6[\text{Mo}_6\text{V}_2\text{O}_{26}]\cdot 4\text{H}_2\text{O}$, was synthesized via the reaction pathway depicted in Figure 1. The elemental analysis and ICP-MS data provide strong evidence for the successful formation of the target compound with the nominal composition $(\text{Thiamine})_6[\text{Mo}_6\text{V}_2\text{O}_{26}]\cdot 4\text{H}_2\text{O}$. A comparison between the calculated and experimentally found values reveals a generally good agreement, supporting the proposed structural formulation. For the organic framework, the calculated contents of C, H, and N are 31.36%, 4.02%, and 12.19%, respectively, whereas the experimental values were determined as 30.67%, 3.87%, and 12.17%. The close correspondence between these values indicates that thiamine-based organic moieties are effectively incorporated into the hybrid structure without significant decomposition or loss during synthesis. The minor deviations observed can reasonably be attributed to residual solvent molecules, surface-adsorbed impurities, or slight variations in hydration level.

Regarding the inorganic framework, the ICP-MS results further confirm the preservation of the polyoxometalate core. The theoretical and experimental contents for Mo are 20.87% and 20.00%, respectively, while for V they are 3.69% and 3.41%. These results suggest that the $\text{Mo}_6\text{V}_2\text{O}_{26}$ anionic cluster remains structurally intact under the employed synthetic conditions, with only marginal losses that fall within acceptable experimental uncertainty. The more pronounced deviation observed for sulfur (calculated 6.98%, found 5.43%) may be associated with partial loss of the organic cation during washing steps, differences in protonation state, or limitations inherent to sample preparation and analytical measurement.

Overall, the combined elemental analysis and ICP-MS results are consistent with the proposed formulation and

confirm the successful synthesis of the $(\text{Thiamine})_6[\text{Mo}_6\text{V}_2\text{O}_{26}]\cdot 4\text{H}_2\text{O}$ hybrid material. The small discrepancies between calculated and experimental values are within the expected range for multicomponent coordination systems and do not affect the validity of the proposed composition.

The FT-IR spectrum of the synthesized yellow solid (Figure 2) indicates the formation of an organic-inorganic hybrid material containing both thiamine-derived organic groups and a molybdenum/vanadium oxo-cluster framework. The broad absorptions observed at 3326 and 3215 cm^{-1} are assigned to overlapping $\nu(\text{O}-\text{H})$ and $\nu(\text{N}-\text{H})$ stretching vibrations, arising from lattice water molecules together with protonated amino functionalities of the thiamine species (Arıcı et al. 2017). The weak absorption at 2918 cm^{-1} corresponds to aliphatic $\nu(\text{C}-\text{H})$ stretching vibrations associated with the organic component (Avcı Özbek 2023, Avcı Özbek 2025, Ostroushko et al. 2018).

In the mid-infrared region, the band centered at 1659 cm^{-1} is attributed mainly to the bending vibration of coordinated or adsorbed water molecules, although aromatic ring contributions from the thiamine structure may also overlap in this region. The absorptions located at 1616, 1538, 1437, and 1384 cm^{-1} are characteristic of heteroaromatic ring vibrations and C-N stretching modes originating from the pyrimidine and thiazolium fragments of thiamine (Avcı Özbek 2025, Ostroushko et al. 2018). The appearance of these bands demonstrates that the organic species remains associated with the inorganic framework after the reaction process.

The low-frequency region below 1000 cm^{-1} provides important evidence for the existence of a polyoxometalate-type metal-oxygen cluster. The intense absorption near 990 cm^{-1} is characteristic of terminal $\nu(\text{M}=\text{O})$ stretching vibrations, particularly Mo=O bonds commonly observed in molybdate-based polyoxometalates. The band observed at approximately 912 cm^{-1} can be attributed to bridging oxygen vibrations involving Mo-O-Mo and/or V-O-Mo linkages within the condensed metal-oxo structure. Furthermore, the strong absorption around 805 cm^{-1} is consistent with edge-sharing or corner-sharing M-O-M bridge vibrations typical of condensed molybdenum oxide clusters (Avcı Özbek 2023, Tewari et al. 2019, Thabet et al. 2013).

Additional bands appearing at 728, 678, 569, and 521 cm^{-1} are associated with deformation and bending modes of Mo-O-Mo and V-O-Mo bridges in the inorganic skeleton (Avcı Özbek 2023, Tewari et al. 2019, Thabet et al. 2013). The preservation of these characteristic metal-oxygen vibrations suggests that the Mo/V oxo-cluster core

remains structurally intact during interaction with protonated thiamine molecules.

The FT-IR results support the formation of a thiamine-associated Mo/V polyoxometalate hybrid structure in

which the inorganic metal-oxo cluster is preserved and stabilized through electrostatic interactions and hydrogen bonding with protonated thiamine species.

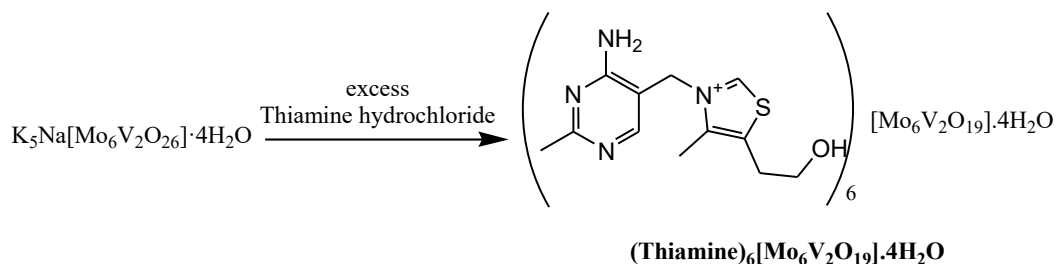


Figure 1. Synthesis of $(\text{Thiamine})_6[\text{Mo}_6\text{V}_2\text{O}_{19}] \cdot 4\text{H}_2\text{O}$

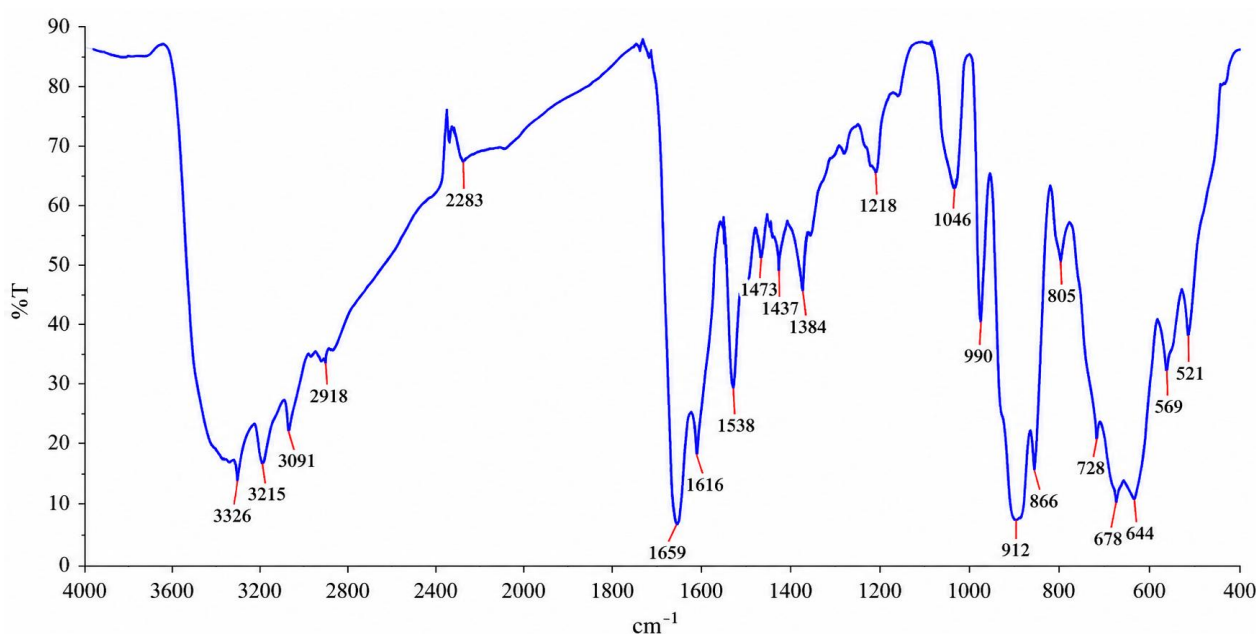


Figure 2. FT-IR spectrum of $(\text{Thiamine})_6[\text{Mo}_6\text{V}_2\text{O}_{19}] \cdot 4\text{H}_2\text{O}$

The thermal decomposition profile of $(\text{Thiamine})_6[\text{Mo}_6\text{V}_2\text{O}_{19}] \cdot 4\text{H}_2\text{O}$ (Figure 3) exhibits characteristic multistep behavior commonly observed for organic-inorganic polyoxometalate hybrids. The initial weight loss detected below approximately 300 °C is attributed to the removal of lattice and weakly bound water molecules. Similar dehydration behavior has been reported for polyoxometalate-based hybrid materials containing protonated organic ligands, where crystallization water is generally released at relatively low temperatures without significant structural collapse (Avci Özbek 2025, Thabet 2012).

The significant mass loss occurring between 300 and 400 °C corresponds to the thermal decomposition of thiamine ligands coordinated within the hybrid framework. The gradual weight losses observed between 450 and 600 °C suggest continued oxidation and carbonization of the

remaining thiamine moieties, along with partial rearrangement of the metal oxide framework. Yu et al. (2024) reported that hybrid polyoxometalates generally undergo gradual decomposition rather than a single abrupt event due to strong electrostatic interactions between the inorganic cluster and organic cations. They also observed comparable multi-step decomposition patterns in polyoxometalate supermolecular systems and noted that the removal of the organic ligand extends over a wide temperature range before the formation of stable oxide residues.

At temperatures above 600 °C, the remaining mass can be assigned to thermally stable mixed molybdenum-vanadium oxide phases. The final residue value of approximately 39.70% at 800 °C is consistent with literature reports for Mo/V-containing polyoxometalate compounds, which typically yield stable metal oxide

frameworks after complete elimination of the organic fraction (Yu et al. 2024). The relatively high residual mass further supports the presence of a robust inorganic polyoxometalate core within the synthesized hybrid material.

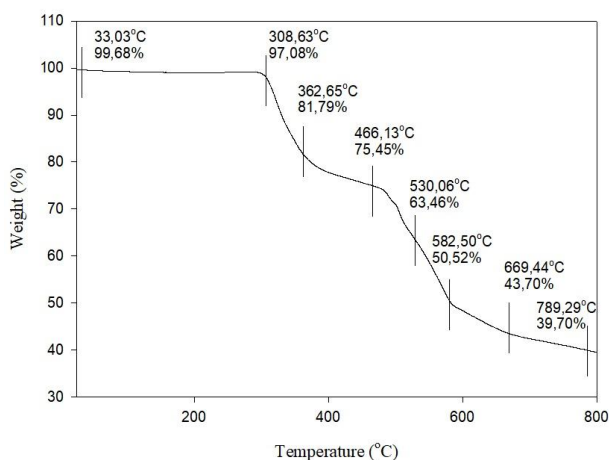


Figure 3. TGA spectrum of $(\text{Thiamine})_6[\text{Mo}_6\text{V}_2\text{O}_{26}]\cdot 4\text{H}_2\text{O}$

4. Conclusions

In this study, a novel vitamin-based organic-inorganic hybrid polyoxometalate, $(\text{Thiamine})_6[\text{Mo}_6\text{V}_2\text{O}_{26}]\cdot 4\text{H}_2\text{O}$, was successfully synthesized under mild aqueous conditions through the interaction of a mixed molybdenum-vanadium precursor with thiamine hydrochloride. The formation of the target compound was confirmed by elemental analysis and ICP-MS, which showed satisfactory agreement between theoretical and experimental values, indicating successful incorporation of protonated thiamine cations and preservation of the $\text{Mo}_6\text{V}_2\text{O}_{26}$ anionic framework. FT-IR spectroscopic results further verified the coexistence of organic and inorganic components, while clearly demonstrating that the characteristic metal-oxygen vibrational modes of the polyoxometalate core remain intact after hybrid formation.

Thermogravimetric analysis revealed a well-defined multistep decomposition pathway involving initial dehydration followed by stepwise degradation of the organic thiamine moieties, ultimately leading to stable mixed Mo-V oxide residues at elevated temperatures. The observed thermal behavior is consistent with strongly interacting hybrid architectures, in which electrostatic forces and hydrogen bonding between the inorganic cluster and organic cations play a key role in structural stabilization.

Overall, the results confirm that thiamine can effectively function as a structure-directing and stabilizing organic component in mixed-metal polyoxometalate systems. This work expands the scope of vitamin-derived organic

molecules in POM chemistry and provides a useful strategy for designing biologically relevant hybrid materials with stable inorganic frameworks and tunable physicochemical properties.

Declaration of Ethical Standards

The author declare that they comply with all ethical standards.

Credit Authorship Contribution Statement

Author-1: Conceptualization, investigation, methodology and software, visualization and writing, original draft. Supervision, review and editing.

Declaration of Competing Interest

The author declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability Statement

The authors declare that the main data supporting the findings of this work are available within the article.

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