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# **Research Article**

# Synthesis, Structure and Hirshfeld Surface Analysis of A New Decavanadate Compound: Na<sub>2</sub>[H<sub>4</sub>V<sub>10</sub>O<sub>28</sub>]·14H<sub>2</sub>O

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## Abstract

**Objective:** The synthesis and structural study of a new acid decavanadate compound with a monovalent inorganic cation. This compound makes a contribution to inorganic decavanadate family.

**Methods:** The synthesis of the compound was carried out by evaporation at room temperature. Good quality crystals were chosen for single crystal x-ray diffraction using a polarizing microscope. Hirshfeld surface analysis, in particular dnorm surface and fingerprint plots, is used to decode intermolecular interactions in the structure of the studied decavanadate compound.

**Results:** A new acid decavanadate compound, Na<sub>2</sub>[H<sub>4</sub>V<sub>10</sub>O<sub>28</sub>]·14H<sub>2</sub>O, was synthesized and characterized by single crystal X-ray diffraction. The decavanadate compound crystallizes in the triclinic system and the cell parameters are: a=11.282(5) Å, b=10.424(3) Å, c=8.502(1) Å,  $\alpha$ =112.81(2)°,  $\beta$ =87.25(2)°,  $\gamma$ =111.49(5)°, V=852.4(5) Å3 and Z=2. The formula unit of Na<sub>2</sub>[H<sub>4</sub>V<sub>10</sub>O<sub>28</sub>]·14H<sub>2</sub>O compound is formed by an acidic decavanadate group [H<sub>4</sub>V<sub>10</sub>O<sub>28</sub>]<sup>2-</sup>, a Na<sub>2</sub>(H<sub>2</sub>O)10<sup>2+</sup> dimer and four molecules of water. The decavanadate group is formed by ten distorted VO<sub>6</sub> octahedra interconnected by edge sharing. Decavanadate groups [H<sub>4</sub>V<sub>10</sub>O<sub>28</sub>]<sup>2-</sup>, the Na<sub>2</sub>(H<sub>2</sub>O)10<sup>2+</sup> dimers and the water molecules stack in layers parallel to the (010) plane. The cohesion of the structure is ensured by hydrogen bonds and van der Waals interactions. The study of the Hirshfeld surface shows that O...H/H...O and H...H interactions dominate the structure.

**Conclusion:** A novel synthesized decavanadate compound decorated by inorganic cations is reported and studied by X-ray diffraction. The cohesion is assured by: O-H...O hydrogen bonds and van der Waals interactions. The Hirshfeld surface analysis confirms the presence of O...H/H...O and H...H contacts in the structure.

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#### **1 INTRODUCTION**

Polyoxometalates (POM) are oxo clusters of transition metal ions, such as Mo, W, V, Nb, and Ta, forming a variety of structures. POMs have different sizes and shapes which may allow for the inclusion of other anions. In the structure of POMs, one or more of the metal oxoanions can be substituted<sup>[1-3]</sup>.

Polyoxometalates (POM) have potential applications in various fields of science and technology, catalytic, magnetic, and electrochemical, in light of their properties such as thermal stability, redox activity, solubility in polar and non-polar solvents<sup>[4,5]</sup>. POMs have dominated medicinal chemistry for their intriguing antiviral and anti-tumor activities. Among the POMs, polyoxovanadate compounds (POVs) are known for their extensive applications in several fields such as chemical, physical and biological sciences. Vanadium plays an important role in biological systems and biochemistry<sup>[6,7]</sup>. Although POVs generally contain vanadium in the +5 oxidation state, recent reports have described POVs with two oxidation states, V(IV) and V(V). Several decavanadate compounds are stable under physiological conditions. The stability of POV under the given experimental conditions requires due consideration in the research on the effects of  $POV^{[1,8]}$ .

Decavanadate compounds are formed in the pH range 6-8 and show a potential interest in several fields such as catalysis, nanotechnology, electrochemistry, materials science, anticancer, antibacterial and antiviral activity<sup>[1,8-10]</sup>. In the present work, we will focus on the synthesis, structure and Hirshfeld surface analysis of a new decavanadate compound:  $Na_2[H_4V_{10}O_{28}]$ ·14H<sub>2</sub>O.

#### **2 EXPERIMENTAL**

#### 2.1 Materials and Measurements

All solvents and reagents were obtained from commercial sources and used without further purification.

#### 2.2 Synthesis of Na<sub>2</sub>[H<sub>4</sub>V<sub>10</sub>O<sub>28</sub>]·14H<sub>2</sub>O Compound

The compound Na<sub>2</sub>[H<sub>4</sub>V<sub>10</sub>O<sub>28</sub>] $\cdot$ 14H<sub>2</sub>O was obtained from a mixture of 0.6 g of V<sub>2</sub>O<sub>5</sub> (99.99%, FLUKA) and 0.5 g of NaVO<sub>3</sub> (Prolabo, 98%) in 100 mL of pure water. The mixture obtained was placed under magnetic stirring and heating for approximately 2 hours. After five days of slow evaporation at room temperature, orange good quality crystals were obtained.

#### 2.3 Hirshfeld Surface Study

Hirshfeld surfaces (HS) were constructed to represent

the asymmetric unit of the compound and the analysis was performed using the Crystal-Explorer program<sup>[11]</sup>.

#### 2.4 X-ray Crystallography

An Enraf-Nonius CAD4<sup>[12]</sup> 4-circle diffractometer was used to collect the diffracted intensities ( $\lambda = 0.71067$ Å). The resolution of the structure was performed by the direct method using the SHELXS-97<sup>[13]</sup> program and the refinement was performed by the least-squares method using SHELXL-2014<sup>[14]</sup>. Hydrogen atoms were attached using the HFIX instruction. The absorption correction was performed by psi-scan<sup>[15]</sup>. All the figures of the structure have been represented by the DIAMOND software<sup>[16]</sup>.

Crystal data, data collection, and structural refinement details are summarized in Table 1.

# **3 RESULTS AND DISCUSSION**

#### 3.1 Crystal Structure

The formula unit of  $Na_2[H_4V_{10}O_{28}] \cdot 14H_2O$  compound was formed by an acidic decavanadate group  $[H_4V_{10}O_{28}]^2$ , a  $Na_2(H_2O)_{10}^{2+}$  dimer, and four molecules of water. The structure of the decavanadate group  $[V_{10}O_{28}]^6$  is formed by ten VO<sub>6</sub> octahedra interconnected by sharing of edges <sup>[17,18]</sup> (Figure 1).

The projection, according to c, of the structure of the compound  $Na_2[H_4V_{10}O_{28}] \cdot 14H_2O$  shows that the decavanadate groups  $[H_4V_{10}O_{28}]^{2^2}$ , the  $Na_2(H_2O)_{10}^{2^+}$  dimers, and the water molecules stack in layers parallel to the (010) plane (Figure 2).

The cohesion of the structure is ensured by O-H...O hydrogen bonds and van der Waals interactions (Figure 3). These bonds are weak according to Brown's criterion<sup>[19]</sup> (Table 2). The comparison of the studied structure with the two structures  $(NH_4)_4Li_2[V_{10}O_{28}] \cdot 10H_2O$  and Na<sub>5.22</sub>Li<sub>0.78</sub>[V<sub>10</sub>O<sub>28</sub>]·20H<sub>2</sub>O: studied by Ksiksi et al.<sup>[18,20]</sup>, shows that sodium and lithium form dimers in the structure studied and the compound  $(NH_4)_4Li_2[V_{10}O_{28}]\cdot 10H_2O$ . The cohesion in these two structures is ensured only by hydrogen bonds and van der Waals interactions. In the structure of Na<sub>5,22</sub>Li<sub>0.78</sub>[V<sub>10</sub>O<sub>28</sub>]·20H<sub>2</sub>O, sodium forms infinite chains. The cohesion of the decavanadate structure  $Na_{5.22}Li_{0.78}[V_{10}O_{28}] \cdot 20H_2O$  is ensured by the pooling of oxygen vertices, ridges and vertices, and by van der Waals interactions. Sodium forms chains, interconnected by the pooling of vertices, edges and faces. These strong bonds can provide better stability to decavanadates compounds, which encourages the synthesis of decavanadates compounds containing sodium.

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Crystal Data				
Chemical formula				
Formula weight (g;mol <sup>-1</sup> )	$Na_{2}[H_{4}V_{10}O_{28}]$ 14 $H_{2}O$			
Crystal system, space group	1263.67			
Т (К)	Triclinic, P-1			
a b c (Å)	298(2)			
α, β, γ (°)	11.282(5), 10.424(3), 8.502(1)			
V(Å <sup>3</sup> )	112.81(2), 87.25(2), 111.49(5)			
Ζ	852.4(5)			
Radiation λ (Å)	2			
Crystal size (mm <sup>3</sup> )	ΜοΚ <sub>α</sub> 0.71073			
μ (mm <sup>-1</sup> )	0.68x0.54x0.39			
F(000)	2.771			
Data Collection	682			
Diffractometer				
Absorption correction	Enraf-Nonius CAD4			
T <sub>min</sub> , T <sub>max</sub>	Ψ-scan			
Range for data collection (°)	0.181,0.339			
h, k, l ranges	2.3≤θ≤ 27			
Scan mode	-14≤ h ≤14, -12≤ k ≤13, -10≤ l ≤1			
No. of measured, independent, and observed	ω/2θ			
$[I > 2\sigma(I)]$ reflections	4205, 3713, 3304			
R <sub>int</sub>				
Refinement	0.0160			
R1 $[F^2 > 2 \sigma (F^2)]$				
wR2(F <sup>2</sup> )	0.033			
S	0.100			
No. of parameters	1.090			
Maximum residual electron density	301			
$\Delta \rho_{max} (e. \text{\AA}^{-3})$	0.642			
Minimum residual electron density				
$\Delta \rho_{\min} (e. \text{\AA}^{-3})$	-0.705			

# Table 1. Crystallographic Characteristics, X-ray Data Collection, and Structure-refinement Parameters of $Na_2^ [H_4V_{10}O_{28}]$ ·14H<sub>2</sub>O Compound



Figure 1. Formula unit of  $Na_2[H_4V_{10}O_{28}]$ ·14H<sub>2</sub>O compound.

D–Н…А	d(D-H)	<b>d(H</b> …A)	d(D …A)	<d-h···a></d-h···a>
O20-H5O13	0.901	1.902	2.800	173.97
O15-H15AO1	0.776	2.114	2.719	135.00
O15-H15AO6 <sup> i</sup>	0.776	2.168	2.665	122.37
O15-H15AO8 <sup> i</sup>	0.776	2.268	2.682	114.28
O15-H15AO11	0.776	2.299	2.668	110.16
O16-H16AO8 <sup>ii</sup>	0.873	2.203	3.040	160.52
O16-H16BO15 <sup>iii</sup>	0.811	2.048	2.853	172.50
O17-H17AO2	0.813	2.058	2.866	172.12
O17-H17BO11	0.848	1.987	2.829	172.09
O18-H18AO1 <sup>iii</sup>	0.769	2.252	2.954	152.11
O18-H18AO10 <sup>iv</sup>	0.769	2.539	3.110	132.27
O18-H18BO9	0.869	2.039	2.869	159.32
O19-H19AO3	0.888	1.914	2.799	174.07
O19-H19BO8 <sup>iv</sup>	0.871	2.306	2.979	134.05
O19-H19BO10 <sup>iv</sup>	0.871	2.310	3.054	143.32
O20-H20AO12 <sup>v</sup>	0.860	2.248	2.982	143.22
O21-H21AO14 <sup>vi</sup>	1.063	2.187	3.222	164.03
O21-H21BO11	0.909	2.490	3.079	122.83
O21-H21BO13 <sup>I</sup>	0.909	2.336	3.093	140.60
O21-H21BO15 <sup>i</sup>	0.909	2.341	3.161	150.04
O22-H22AO2	0.855	2.485	3.031	122.49
O22-H22AO7 <sup>vii</sup>	0.855	2.126	2.863	144.07
O22-H22BO3	0.884	2.440	3.038	125.43
O22-H22BO10 <sup>iv</sup>	0.884	2.255	2.924	132.32

Table 2. Hydrogen Bonds of  $Na_2[H_4V_{10}O_{28}]{\cdot}14H_2O$  Compound

*Symmetry codes: i*: -*x*+1, -*y*+1, -*z*+1, *ii*: *x*+1, *y*+1, *z*+1, *iii*: *x*, *y*+1, *z*+1, *iv*: -*x*+1, -*y*+2, -*z*+1, *v*: -*x*+2, -*y*+2, -*z*+2, *vi*: *x*-1, *y*-1, *z*, *vii*: -*x*+1, -*y*+1, -*z*.



Figure 2. A Projection of the structure of  $Na_2[H_4V_{10}O_{28}]$ ·14H<sub>2</sub>O compound according to the c axis; B Decavana-date group; C  $Na_2(H_2O)_{10}^{2+}$  dimer.

**A** 



Figure 3. Cohesion of the structure by O-H...Ohydrogen bonds.





## 3.2 Hirshfeld Surface Analysis of $Na_2[H_4V_{10}O_{28}]$ ·14H<sub>2</sub>O

The Hirshfeld surface of the decavanadate compound studied in normal mode  $d_{norm}$  is shown in Figure 4A. This figure shows that the main interactions are between the surfaces H...H and O...H/H...O<sup>[21,22]</sup>. The structure of the compound Na<sub>2</sub>[H<sub>4</sub>V<sub>10</sub>O<sub>28</sub>]·14H<sub>2</sub>O is dominated by the interactions O...H/H...O (59.5 %), H...H (14.9 %), and V...O/O...V contacts (11.8 %) (Figures 4 A, B and C). The O...O contacts represent 9.3 %.

#### **4 CONCLUSION**

A new compound decavanadate,  $Na_2[H_4V_{10}O_{28}] \cdot 14H_2O$ , was synthesized by slow evaporation at room temperature. The structure is formed by the decavanadate groups,  $Na_2(H_2O)_{10}^{2+}$  dimers, and water molecules. The cohesion of the structure is ensured by hydrogen bonds and van der Waals interactions. The study of the HS surface shows that the structure is dominated by O...H/H...O, H...H and V...O/O...V contacts.

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## **Conflicts of interest**

There is no conflict of interest between the authors of this article.

#### **Author Contribution**

Ksiksi R wrote the manuscript; Ksiksi R and Nasri R

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performed the data curation; Graia M reviewed the article, and Zid MF supervised the project.

## **Abbreviation List**

A, b, c,  $\alpha$ ,  $\beta$ ,  $\gamma$ , Cells

- Dnorm, Normalized contact distance
- F(000), Structure factor
- R, Reliability factors
- T, Absorption transmission factor
- T, Temperature
- V, Volume
- M, Absorption coefficient

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