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Research Article

Structure, Physic-chemical Characterizations and Hirshfeld Surface Analysis of $[C_7ON_2H_{18}]_3V_{10}O_{28}\cdot 2H_2O$ Compound

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Abstract

Objective: Structural study and physico-chemical characterization of a new decavanadate compound.

Methods: The compound was synthesized using distilled water as solvent. By stirring and magnetic heating and by evaporation at room temperature, a good quality crystal was chosen for single crystal X-ray diffraction.

Results: A new decavanadate compound, tri[2-[2-(dimethylamino) ethyl-methylaminium]ethanol] decavanadate dehydrate, was synthesized by slow evaporation, the formula unit is composed by one decavanadate cluster, three $[C_7ON_2H_{18}]^{2+}$ organic cations and two water molecules. Different characterization techniques are used such as: crystal X-ray diffraction, Scanning electron microscopy with energy dispersive X-Ray analysis and thermal analysis. The X-ray structure determination revealed that the compound crystallizes in the triclinic system, space group P-1 with the cell parameters: a=10.815 (9) Å, α=112.97 (3)°, b=11.624 (4) Å, β=111.73 (7)°, c=11.840 (5) Å, γ= 96.86 (6)° and V=1195.8 (6) Å3. The cohesion of the structure is ensured by hydrogen bonds of the type O-H...O, N-H...O and van der Waals interactions. The study of the Hirshfeld surface of the decavanadate compound shows us that it is dominated by O…H/H…O (56.7%) and H…H (30.2%) type contacts.

Conclusion: A new decavanadate compound was synthesized and characterized by different physico-chemical techniques. The detailed structural study shows that the different groupings of the structure pile up in layers parallel to the planes (010). The cohesion of the structure is ensured by hydrogen bonds and van der Waals interactions.

Keywords: decavanadate, synthesis, physico-chemical characterizations, hirshfeld surface analysis

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1 INTRODUCTION

Polyoxametallates have potential applications in various fields of science and technology, catalytic, magnetic and electrochemical, due to their properties such as thermal stability, selective inhibitors of an impressive variety of enzymes redox activity as well as solubility[1-3]. Among the various polyoxometalates, we have focused our attention on polyoxovanadates due to the relatively low toxicity of vanadium in biological media[4]. Vanadium acts as an inorganic cofactor in haloperoxidases and alternative azoteases, exhibits insulin-mimetic activities related to diabetes mellitus, and exhibits anticancer activities in several cell lines[5]. The decavanadate compounds have shown a strong affinity for certain kinases, phosphorylase and reverse transcriptase[6]. In previous works we have published several decavanadate structures such as: $Na_{5.22}Li_{0.78}[V_{10}O_{28}]20H_2O$[7], $[Zn(H_2O)_6][Zn_2V_{10}O_{28}(H_2O)_{10}]\cdot 6H_2O$[8], we have also published articles which show the important biological activity of decavanadate compounds studied by Aissa et al.[9], Ksiksi et al.[10] and Louati et al[11]. The study of the antitumor activities of these compounds encouraged us to synthesize new pure decavanadate phases and to study their structures.

In this work we will study: Structure, physico-chemical characterizations and Hirshfeld surface analysis of $[C_7ON_2H_{18}]_3V_{10}O_{28}\cdot 2H_2O$ compound.

2 MATERIALS AND METHODS

2.1 Materials and Physical Measurements

Scanning electron microscope coupled to an X-ray energy dispersive analysis spectrometer is performed using an FEI Quanta 200 environmental apparatus (LEUVEN Belgium, PHILIPS/FEI). The Thermogravimetry (TG) and Differential thermal analysis (DTA) analysis were carried out using a SETERAM Labsys™ typeapparatus (France, Setaram Instrumentation), by exploring the temperature range between ambient and 300°C.

2.2 Synthesis of $[C_7ON_2H_{18}]_3V_{10}O_{28}\cdot 2H_2O$ Compound

The phase was prepared with a vanadium oxide V_2O_5 and 2-[2(Dimethylamino) ethyl]-methylamino] ethanol in 50mL of water with the following molar proportion 1:3. The solution is placed under magnetic stirring and with slight heating for 3h. After filtration, the mixture is brought to room temperature. After a few days, there is appearance of crystals of good quality for X-ray diffraction.

2.3 Hirshfeld Surface Study

The study of the Hirshfeld surface analysis was done using the software Crystal Explorer[12,13].

2.4 X-ray Study

A good quality orange single crystal was chosen for single crystal X-ray diffraction. An Enraf-Nonius CAD4 type automatic four-circle diffractometer[14] was used for data collection using Mo-Kα radiation (λ=0.71073 Å). The resolution of the structure was carried out by Farrugia[15]. The SHELXS-97 program[16] was used for the structure resolution and the SHELXL-2014[17] for the refinement. The absorption correction was performed by psi-scan method[18]. The figures were represented using the program Diamond[19]. The HFIX statement for fixing hydrogen atoms. The X-ray crystallographic data are given in Table 1.

3 RESULTS AND DISCUSSION

3.1 Crystal Structure

The structure of the decavanadate compound, $[C_7ON_2H_{18}]_3V_{10}O_{28}\cdot 2H_2O$, is composed by the centro-symmetric decavanadate group $[V_{10}O_{28}]^{6-}$, two non-centrosymmetric 2-[2-(Dimethylamino) ethyl]-methylaminium] ethanol $[C_7ON_2H_{18}]^{2+}$ cations, one centrosymmetric cation $[C_7ON_2H_{18}]^{2+}$ and two water molecules (Figure 1). The centrosymmetric cluster $[V_{10}O_{28}]^{6-}$ is formed by ten VO_6 octahedra interconnected by edge sharing. There are different types of V-O distances: they are between 1.598 (4) and 1.612 (4) Å for the terminal oxygen atoms, between 1.795 (4) and 1.879 (4) Å for doubly coordinated oxygen atoms, between 1.942 (3) and 2.023 (4) Å for triply coordinated oxygen atoms and between 2.097 (4) and 2.353 (4) Å for oxygen atoms hexacoordinated (Figure 2). The distances V-V vary from 3.066 (1) to 3.119 (1) Å. The distances and angles of bond in this group are in agreement with other similar compounds found in the bibliography[9, 11].The representation of the organic cation 2-[2-(Dimethylamino) ethyl]-methylaminium] ethanol $[C_7ON_2H_{18}]^{2+}$ is given in Figure 3.

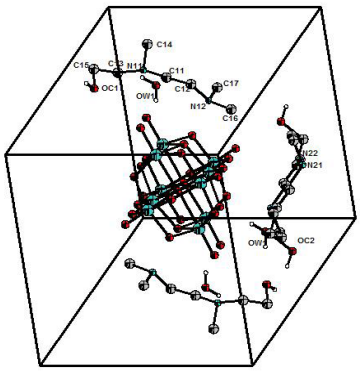

Figure 1. Formula unit of $[C_7ON_2H_{18}]_3V_{10}O_{28}\cdot 2H_2O$ compound.

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Table 1. Crystallographic Characteristics, X-ray Data Collection, and Structure-Refinement Parameters for $[C_7ON_2H_{18}]_3V_{10}O_{28}\cdot 2H_2O$ Compound

Crystal Data	
Chemical formula	$[C_7ON_2H_{18}]_3V_{10}O_{28}\cdot 2H_2O$
Formula weight Mr ($g.mol^{-1}$)	1432.13
Crystal system, space group	Triclinic, P-1
T (K)	298(2)
a b c (Å)	10.815 (9), 11.624 (4), 11.840 (5)
α, β, γ (°)	112.97 (3), 111.73 (4), 96.86 (6)
V($Å^3$) , Z	1195.8(6), 1
Radiation λ (Å)	Mo-Kα 0.71073
Crystal size (mm^3)	0.16 x 0.31 x 0.55
μ (mm^{-1})	1.989
F (000)	720
Data collection	
Diffractometer	Enraf-Nonius CAD4
Absorption correction	Ψscan
$T_{min,}T_{max}$	0.3337, 0.7232
Range for data collection (°)	2≤θ≤ 27
h, k, l ranges	-1≤ h ≤13, -14≤ k ≤14, -15≤ l ≤14
Scan mode	ω/2θ
No. of measured, independent, and observed	6018, 5181, 3298
[I >2σ(I)]] reflections	
R_{int}	0.0713
Refinement	
R1 [$F^2 > 2\ \sigma\ (F^2)$]	0.077
wR2(F^2)	0.2241
S	1.013
No. of parameters	375
Maximum residual electron density	1.218
$\Delta\rho_{max,}$($e.Å^{-3}$)	
Minimum residual electron density	-1.075
$\Delta\rho_{min}$ ($e.Å^{-3}$)	

Notes: a, b, c, α, β, γ: cells; F (000): Structure factor; V: Volume; μ: Absorption coefficient; R: Reliability factors; T: Absorption transmission factor; wR: Weighted R factor; h,k,l: Miller Indices, S: GOOF on F^2.

Decavanadate groups, organic cations and water molecules stack up in layers parallel to the (010) plane. Cohesion between layers is ensured by van der Waals interactions (Figure 4).

In one layer, the $[C_7ON_2H_{18}]^{2+}$ cations and water molecules form a two-dimensional network in which the decavanadate groups are nested. The cohesion of the structure is ensured by O-H…O, N-H...O hydrogen bonds (Table 2) which engage the $[C_7ON_2H_{18}]^{2+}$ cations, water molecules and decavanadate groups (Figure 5).

3.2 Comparison of the Structure Studied with $(NH_4)_4Li_2V_{10}O_{28}\cdot 10H_2O$ Compound

The projection according to c of the structure studied in this work and of the structure $(NH_4)_4Li_{2-}V_{10}O_{28}\cdot 10H_2O$[10] shows that the decavanadate groups, organic cations and water molecules stack up in layers parallel to the (010) plane and in the decavanadate structure of ammonium and lithium the decavanadate groups and the $Li_2(H_2O)_{10}^{2+}$ dimers stack up in layers parallel to the (010) plane. The cohesion of the two structures is ensured by hydrogen bonds and van der Waals interactions.

The Hirshfeld area of $[C_7ON_2H_{18}]_3V_{10}O_{28}\cdot 2H_2O$ compound was determined from the asymmetric unit of the compound. The Hirshfeld surfaces of $[C_7ON_2H_{18}]_3V_{10}O_{28}\cdot 2H_2O$ compound is studied in d_{norm} (normalized contact distance) and d_i(The both contact distances between nearest atoms present inside)(Figure

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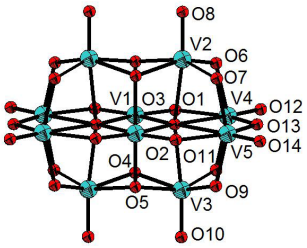

Figure 2. Decavanadate group in $[C_7ON_2H_{18}]_3V_{10}O_{28}\cdot 2H_2O$ compound.

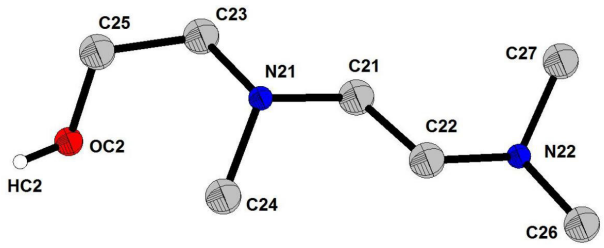

Figure 3. Representation of organic cation 2-[2-(Dimethylamino)ethyl]-methylaminium] ethanol $[C_7ON_2H_{18}]^{2+}$.

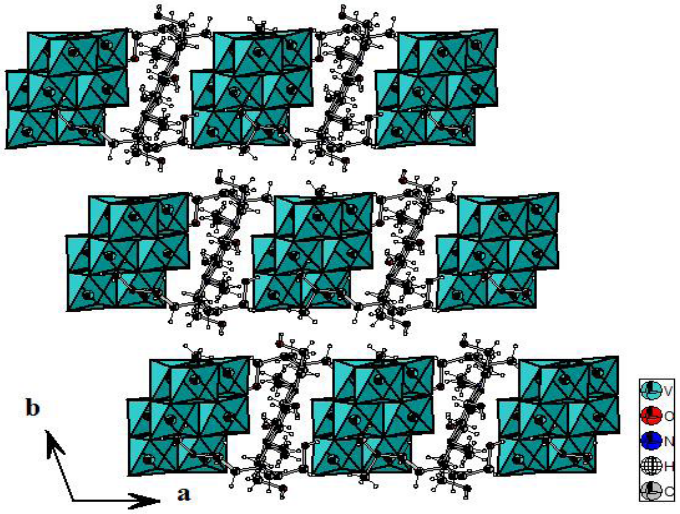

Figure 4. Projection along (a, b) plane of $[C_7ON_2H_{18}]_3V_{10}O_{28}\cdot 2H_2O$ compound.

Table 2. Hydrogen Bonds Length in $(C_4H_7N_2)_6V_{10}O_{28}\cdot 3H_2O$ $[C_7ON_2H_{18}]_3V_{10}O_{28}\cdot 2H_2O$ Compound

D-H ⋯A	D (D-H) (Å)	d (H ⋯A) (Å)	d (D ⋯A) (Å)	<D-H ⋯A> (°)
N11-H11...OW1^{i}	0.91	2.148	2.905	139.97
N11-H11...O8	0.91	2.522	3.015	114.52
N12-H12...O5	0.91	1.758	2.665	173.49
OC1-HC1...O6^{i}	0.82	1.892	2.71	175.24
N21-H21...O4^{ii}	0.91	1.705	2.606	169.74
N22-H22...O4^{iii}	0.91	1.865	2.77	172.97
OW1-HW1...O7	0.824	2.158	2.947	160.14
OW1-HW1 O8	0.824	2.574	3.025	115.81
OW1-HW2…OC1	0.815	2.025	2.836	173.19

Notes: Symmetry codes: i: -x, -y+1, -z; ii : x+1, y, z ; iii : -x+1, -y+1, -z+1

6). Figure 6 shows us the existence of O-H…O hydrogen bonds (red spots) they correspond to O⋯H/H⋯O bonds. H...H type interactions (white areas). Areas where neighboring atoms are too far apart to interact with each other (bluish areas).

The contribution of intermolecular contacts to Hirshfeld surfaces in the structure of the compound $[C_7ON_2H_{18}]_3V_{10}O_{28}\cdot 2H_2O$ reveals that the structure is dominated by O…H/H…O (56.7%), H…H (30.2%), V...O/O...V (10.9%) (Figure 7). The comparison of the interactions O...H/ H...O, H...H, V...O/O...V between the studied compound and $(NH_4)_4Li_2V_{10}O_{28}\cdot 10H_2O$ compound, shows a considerable increase in the H…H interactions in the structure of the compound studied (Table S1)[10] (30.2% relative to 18.4%). This increase can be the cause of the increase in the mesh parameters as well as the volume in our compound.

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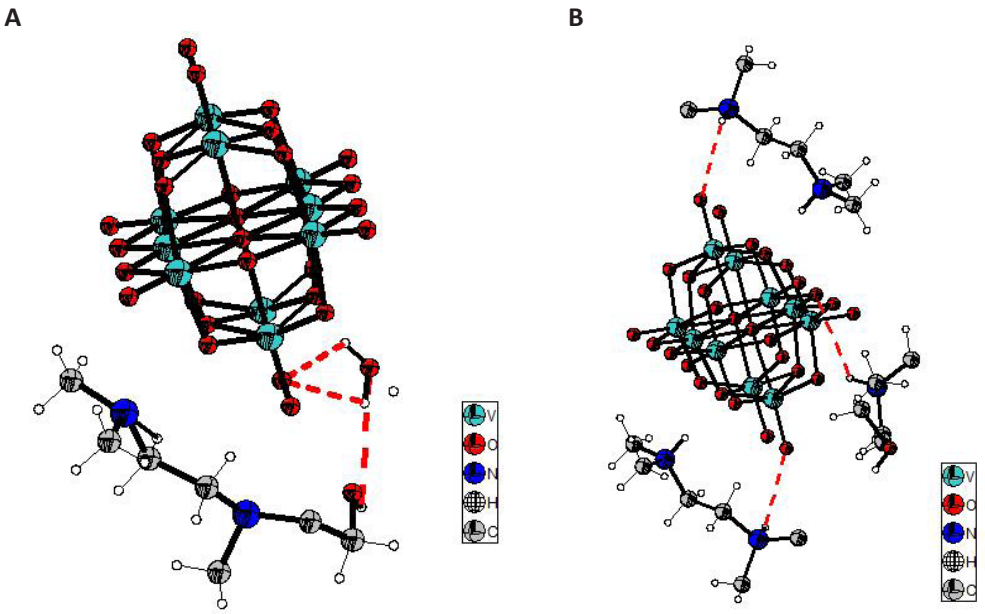

Figure 5. Cohesion of the structure by hydrogen bonds. A: O-H…O hydrogen bonds; B: N-H...O hydrogen bonds.

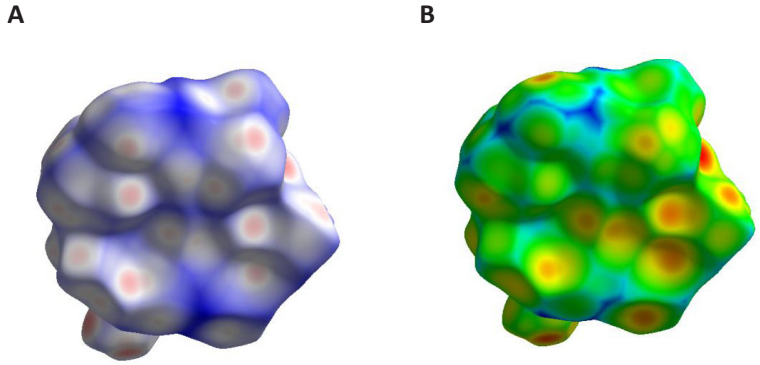

Figure 6. Hirshfeld surface mapped over d_{norm} (A) and d_i (B) of $[C_7ON_2H_{18}]_3V_{10}O_{28}\cdot 2H_2O$ compound.

3.3 EDX (Energy Dispersive X-ray) Analysis

The EDX analysis of $[C_7ON_2H_{18}]_3V_{10}O_{28}\cdot 2H_2O$ compound is given in Figure 8. This figure shows the presence of the following chemical elements: vanadium, oxygen and carbon.

3.4 DTA and TG Curve of $[C_7ON_2H_{18}]_3V_{10}O_{28}\cdot 2H_2O$ Compound

The DTA-TG analysis of this compound was carried out on a sample with a mass of 9.01mg placed in a platinum crucible.

The TG curve of $[C_7ON_2H_{18}]_3V_{10}O_{28}\cdot 2H_2O$ compound (Figure 9) reveals that the departure of water molecules begins around 60°C and ends around 80°C. The loss percentage is 2.4%. This is reflected on the DTA curve by an endothermic peak around 70°C. Theoretically, the departure of two water molecules would correspond to a loss percentage of 2.5%.

The second mass loss on the TG curve of the order of 16.7% concerns the departure of CO_2, it begins around 110°C. The theoretical percentage of CO_2 departure is 16.14%.

4 CONCLUSION

A new decavanadate compound was synthesized and characterized by different physico-chemical techniques: $[C_7ON_2H_{18}]_3V_{10}O_{28}\cdot 2H_2O\cdot[C_7ON_2H_{18}]^{2+}$ cations, water molecules and decavanadate groups stack in layers parallel to the (010) plane. The cohesion of the structure is ensured by hydrogen bonds and van der Waals interactions.

The EDX analysis of $[C_7ON_2H_{18}]_3V_{10}O_{28}\cdot 2H_2O$ confirms the presence of the following chemical elements: vanadium, nitrogen, oxygen and carbon. The thermal analysis informs us about the stability of the studied compound.

In perspective we will study the antitumor activity of $[C_7ON_2H_{18}]_3V_{10}O_{28}\cdot 2H_2O$ compound against the

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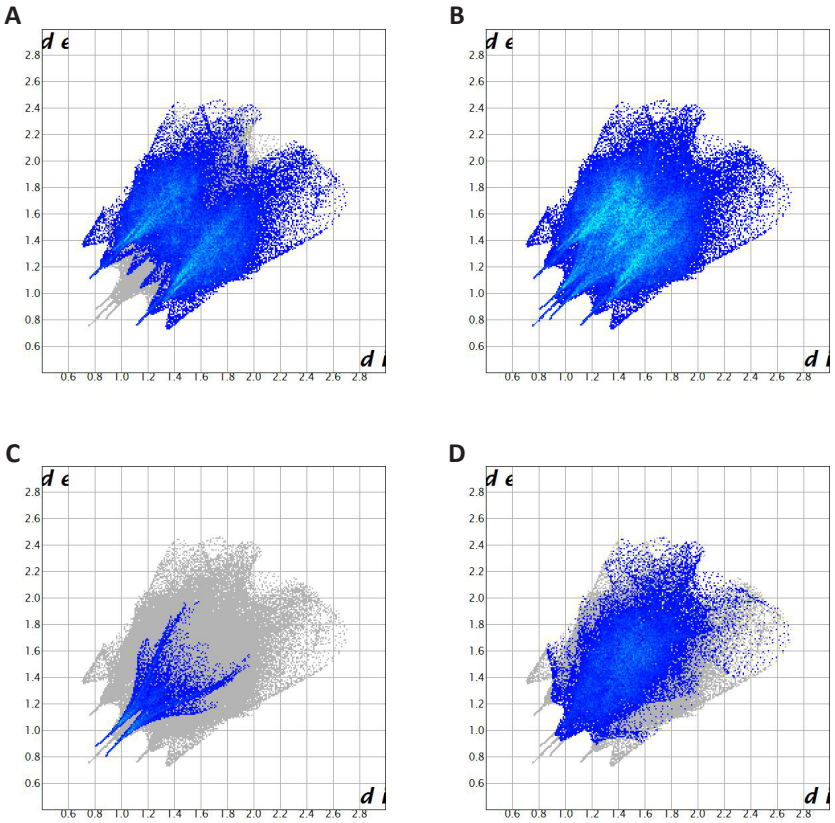

Figure 7. 2D fingerprint plots of the studied compound resolved into all contacts (A), O…H/H…O (56.7 %) (B), H…H (30.2 %) (C), and O…V/V…O (7.1 %) (D)contacts.

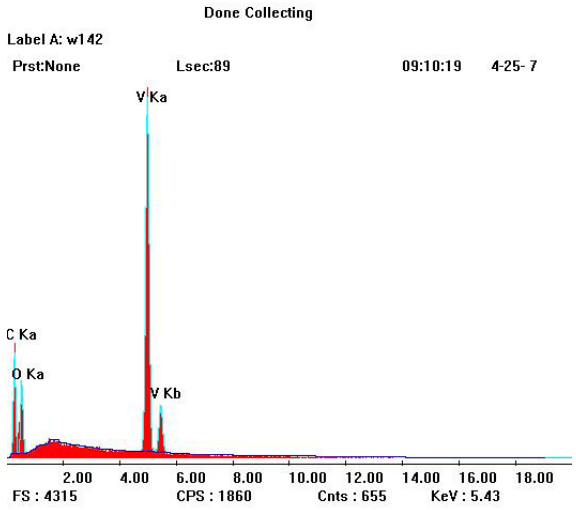

Figure 8. EDX of $[C_7ON_2H_{18}]_3V_{10}O_{28}\cdot 2H_2O$ compound.

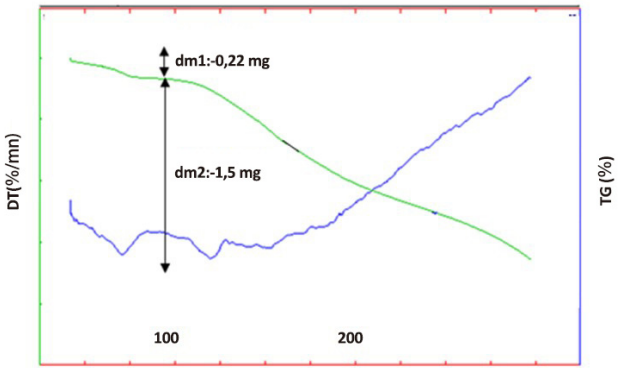

Figure 9. DTA and TG of $[C_7ON_2H_{18}]_3V_{10}O_{28}\cdot 2H_2O$ compound.

three cell lines: U87, IGR39 and MDA-MB-231 and the compared with the antitumor activity of $(NH_4)_4Li_2V_{10}O_{28}\cdot 10H_2O$compound that we have already compared the two structures.

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Conflicts of Interest

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

Author Contribution

Ksiksi R was responsible for data curtion, writing, and original-draft. Graia M was responsible for review. Zid MF was responsible for supervision.

Abbreviation List

a, b, c, α, β, γ, cells

d_i, The both contact distances between nearest atoms present inside.
d_{norm}, Normalized contact distance
DTA, Differential thermal analysis
EDX, Energy dispersive X-ray
F(000), Number of electrons per cell
TG, Thermogravimetry

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