Different Polyoxometalate Structures Obtained from the $Na_{11}H[H_{(2-x)}Bi_2W_{20}O_{70}(HWO_3)_x]\cdot 46H_2O(x=1.4)$.

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In the supramolecular chemistry world, Polyoxometalates (POMs) are considered as a new family of inorganic molecular containers, construct itself by self-assembly reaction from very small units, to form a cluster with unique structural and properties. three structures reported in this paper - differ in their unit cell parameters and also differ from the well-known - as the result of reaction of the $Na_{11}H[H_{(2-x)}Bi_2W_{20}O_{70}(HWO_3)_x]\cdot 46H_2O$ (x=1.4) with Ca ion at different pH conditions. These structures are $[Ca(H_2O)_7]_2[Na(H_2O)_2]_2[HBi_2W_{20}O_{70}(HWO_3)].14H_2O$(1), $H_2[NH_4]_{10}[HBi_2W_{20}O_{70}(HWO_3)]$ (2), and $[NH_4]_6[Na(H_2O)_4]_2[Ca(H_2O)_4]_2[W_{12}O_{42}].2H_2O$ (3). The last one is bismuth-free and it is formed through reassembly of the precursor. Full structural characterization was made by multiple testing techniques such as single-crystal X-ray diffraction, UV-visible spectroscopy, FT-IR, thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDS). The single-crystal X-ray diffraction results for the three compounds are as follows:(1), Triclinic, space group P-1, while (2) and (3) crystallize in monoclinic space groups C2/m and P21/n respectively.

Keywords: sandwich polyoxometalates, Bismuth, crystal structure, inorganic lattice, calcium.

Introduction

Polyoxometalates (POMs) present themselves as a new special class of intriguing metal−oxygen cluster compounds which are preferably formed by complex self-assembly processes of W, Mo, and V in their high oxidation states. The chemistry of POMs is a rapidly developing field, which present a wide range of properties and applications (Hutin, *et al*., 2013), (Miras, *et al*., 2012), (Long, *et al*., 2010), (Mansergh, *et al*., 2016), (Liu, *et al*., 2015), (Rasmussen, *et al*., 2016), (Breitwieser, *et al*., 2016), (Lai, *et al*., 2013), among diverse applications, POMs-catalysts for many organic reactions are receiving special attention, (Ni, *et al*., 2012), (Hasenknopf, 2005), (Chen, *et al*., 2012), (Hussain, *et al*., 2016), another applications also determined and studied such as magnetism, (Clemente, *et al*., 2012), (Kortz, *et al*., 2009), (Vonci, *et al*., 2014), water oxidation catalysts and reduction catalysts, (Yu, *et al*., 2016), (Schwarz, *et al*., 2016), (Lv, *et al*., 2013), (Von, *et al*., 2015), (Rausch, *et al*., 2014), POMs shown also promising performance in both photo catalytic and electro processes (Evangelisti, *et al*., 2013). Compared with the large numbers of sandwich polyanions containing Si (IV), P (V) and Ge (IV) as tetrahedrally coordinated heteroatoms, the POMs containing bismuth ion as the heteroatom are largely unexplored. The synthesis and structural characterization of the tungstobismutates are still difficult because of the lone pair of electrons located on the top of the pyramid of coordination. The first tungstobismutates structures synthesized are, $[HnXIIIW_{18}O_{60}]^{(9-n)-}$ (X = As(III), Sb(III) or Bi(III)) (Krebs and Klein, 1993), (Ozawa and Sasaki, 1987), (Patrut, *et al*., 2007), Later a few dimeric tungstobismutates were reported based on β- BiW_9O_{33} units such as $[Bi_2W_{22}O_{74}(OH)_2]^{12-}$ (Rodewald and Jeannin, 1998) and its derivatives $[Mn^{+}{}^{3}(H_2O)x(BiW_9O_{33})_2]^{(18-3n)-}$ (Mn^{+} = (VO)II, x = 0 and Mn^{+} = CrIII, MnII, FeIII, CoII, NiII, CuII, x = 3) (Rusu, *et al*., 2001), $Na_3H_2[Ce_3(H_2O)_{18}Bi_2W_{22}O_{76}]\cdot 23H_2O$ (Wang, *et al*., 2004). Patrut and coworker reported the synthesis and investigation of a new sodium neutral salt of a hetero polyoxometalate, $Na_{11}H[H(2\ x)Bi_2W_{20}O_{70}(HWO_3)_x]\cdot 46H_2O$ (x = 1.4) which contains two heteroatoms Bi(III) with unshared electron pair, and W(VI) as addend/metal centers. (Patrut, *et al*., 2010). Recently six new Cu-containing tungstobismutates were synthesized and their structures have been also characterized by Allmen. (Allmen, *et al*., 2017). However, no calcium tungstobismutates was synthesized or characterized, from this point of view, we are interested to synthesize and characterize a new tungstobismutates POM's with and without the existence of calcium ion, and study the coordination behavior of POMs structures in the presence of this ion.

1. Materials and Methods

All chemicals were obtained commercially and used without further purification. The lacunary precursor $Na_{11}H[H_{(2-x)}Bi_2W_{20}O_{70}(HWO_3)_x]\cdot 46H_2O$ (x=1.4) was prepared according to published procedures and characterized by FT-IR spectroscopy [30]. UV-Vis data were collected from 200 to 700nm at room temperature on a Varian Cary-100 UV/VIS spectrophotometer.

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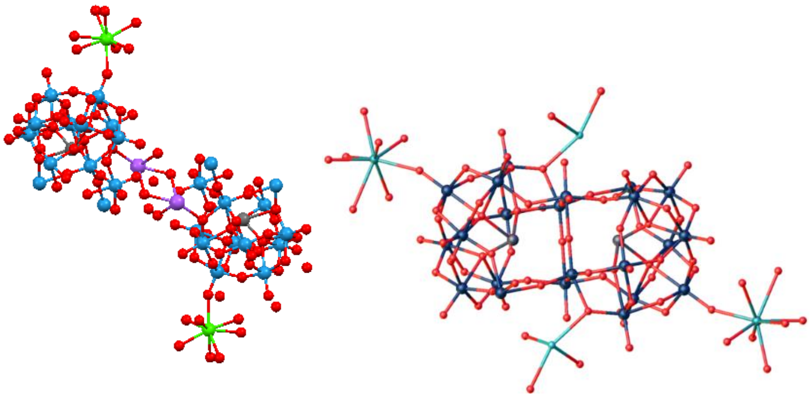
IR spectra were recorded by a Nicolet Impact 400 Fourier transform infrared Spectrophotometer (Madison, WI) in the 400–4000 cm^{-1} region. KBr discs for solid samples were made by grinding 2mg of the solid sample with about 0.2 g of KBr. Atomic absorption was recorded on a Varian Atomic Absorption spectrophotometer (Mulgrave, Victoria, Australia) model AA-250 plus. Single-crystal X-ray diffraction data were collected using an Oxford Diffraction Super Nova, Dual, equipped with mirror SuperNova (Mo) X-ray Source (λ= 0.71073 A°) at 173(2) K.

For Scanning Electron Microscopy (SEM) dehydrated crystals were molded and attached to 10 mm metal mounts using carbon tape, and then sputter-coated with platinum under vacuum in an argon atmosphere. The surface morphology of the coated samples was visualized by a Scanning Electron Microscope (FEI Company Inspect, F50/FEG, High Vacuum <6e−4 Pa, Eindhoven, the Netherlands) with combined Energy Dispersive X-ray Analyzer at a voltage of ~10 keV. SEM allowed the identification of any interesting structural features on the seaweed surface with EDS (BRUKER QUANTAX, EDS systems, Bruker AXS Microanalysis Gmbtt, X Flash Detector 410-M Silicon Drift (SDD), Berlin, Germany). $[Ca(H_2O)_7]_2[Na(H_2O)_2]_2[HBi_2W_{20}O_{70}(HWO_3)].14H_2O$ (1). Solid powder $Na_{11}H[H_{(2-x)}Bi_2W_{20}O_{70}(HWO_3)_x]$ $46H_2O$ (1.49 g, 0.225 mmol) was dissolved in 10 mL H_2O at 80 °C, then added to a solution of 0.08 g $CaCl_2$ in 10 mL H_2O, The mixture was stirred for 10 min. To this solution, 0.1 M HCl was added very slowly with vigorous stirring until pH reached 5 and remained stable for 5 min. The solution was then stirred for 2 h under reflux. After cooling to room temperature the turbidity was removed by filtration. Finally, 5 mL of 1 M of NH_4Cl was added to the stirred solution, and the solution was left to evaporate slowly at ambient temperature. Stable colorless crystals were separated after 6 days. $H_2[NH_4]_{10}[HBi_2W_{20}O_{70}(HWO_3)]$ (2) and $[NH_4]_6[Na(H_2O)_4]_2$ $[Ca(H_2O)_4]_2[W_{12}O_{42}].2H_2O$ (3) were synthesized as Similar procedure as (1) except the pH was adjusted to 5.5 and 6 respectively. Stable colorless crystals were separated after 4-5 days. All the obtained crystals were stable in solutions. However, they start to decompose slowly due to dehydration.

2 Results and Discussion

2.1 Crystal structure

Three structures were reported in this work differs in their unit cell and space group, the last one (3) differ from the others, as this structure does not contain bismuth. The structure of compound 1 $H_{66}Ca_2Na_2Bi_2W_{21}O_{105}$ has the lowest lattice symmetry among all. It crystallizes in the space group *P-1*, with one molecular per unit cell, while **2** and **3** crystallize in monoclinic space groups *C2/m* and *P*21/n respectively**. Table 1** summarizes the crystallographic data for the three crystals. The single-crystal X-ray diffraction analysis **(Figure 1)** also indicates that the molecular unit for **1** is constituted from two asymmetric units. A packing diagram is shown in **Figure 2** illustrating the 2-dimensional nature of the structure. And it consists of two identical trilacunary *β*-$[BiW_9O_{33}]$ pseudo-Keggin type units in which three W_3O_{13} groups is turned by 60° relative to each other.



(a) **(b)**

Fig. 1 (A) Molecular unit in compound (1) view down a-axis (Bi gray, W blue, Na purple, Ca green). (b) The two W9O33Bi subunits joined throw W(8) and W(1). Pending Ca and Na attached polyhedra are shown.

The single-crystal X-ray diffraction analysis (Fig. 1) also indicates that the molecular unit for (1) is constituted from two asymmetric units. A packing diagram is shown in **Figure 2** illustrating the 2-dimensional nature of the structure. And it consists of two identical trilacunary β-[BiW_9O_{33}] pseudo-Keggin type units in which three W_3O_{13} groups is turned by 60° relative to each other. In the polyoxometalate $H_6[Ca(H_2O)_7]_2[Na(H_2O)_2]_2$ $[HBi_2W_{20}O_{70}(HWO_3)].14H_2O$ (1) the molecule consists of two identical trilacunary β-[BiW_9O_{33}] *pseudo*-Keggin type units in which three W_3O_{13} groups is turned by 60° relative to each other. Each W(VI) is hexacoordinated to oxygen with nine W octahedra sharing corners encapsulating the Bi(III) heteroatom inside the W_9O_{33} unit (**Figure 3**). The Bi(III) itself is tricoordinated to O in a triangular based pyramidal units of BiO_3 with one direction occupied by a lone pair of electrons. The two units are connected by two *facial* $O_2(OH)$ and two WO_2 groups or by two hydrated Na cations. Each W(VI) is hexa-coordinated to oxygen with nine W octahedra sharing corners encapsulating the Bi(III) heteroatom inside the W_9O_{33} unit (Fig. 3). The Bi(III) itself is tricoordinated to O in a triangular based pyramidal units of BiO_3 with one direction occupied by a lone pair of electrons. The two units are connected by two *facial* $O_2(OH)$ and two WO_2 groups or by two hydrated Na cations.

Table 1 Crystal data and structure refinement for the crystals of three salts

Parameter **1**	(1)	(2)	(3)
Chemical formula	$H_{66}Ca_2Na_2Bi_2W_{21}O_{105}$	$H_{44}N_{10}Bi_2W_{21}O_{73}$	$H_{60}N_6Na_2Ca_2W_{12}O_{60}$
Formula Mass	6151.37	5631.16	3436.80
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	P-1	C2/m	$P2_1/n$
a/Å	12.8969(6)	17.5821(16)	12.1812(3)
b/Å	12.9951(7)	18.7384(13)	17.4026(4)
c/Å	12.9951(7)	14.2156(12)	14.4490(5)
α/°	71.506(5)	90	90
β/°	83.758(4)	113.349(12)	114.027(4)
γ/°	62.581(5)	90	90
Volume/Å^3	2531.8(3)	4299.9(6)	2797.57(16)
Z	1	2	2
Pcalc mg/mm^3	4.035	4.349	4.080
μ/mm-1	27.429	32.131	24.887
F(000)	2688	4836	3064
2Θ range for data collection	5.84 to50.06°	6.46 to 50.06°.	5.98 to 50.06°
Index ranges	-14 ≤ h ≤ 15, -15≤ k ≤ 15, -21≤ l ≤ 21	-11 ≤ h ≤ 20, -18 ≤ k ≤ 22, -16 ≤ l ≤ 16	-14 ≤ h ≤ 13, -20 ≤ k ≤ 11, -17 ≤ l ≤ 13
Reflections collected	16118	8722	7661
Independent reflections	8945[R(int) = 0.0967]	3810[R(int) = 0.3141]	4362[R(int) = 0.0305]
Data/restraints/parameter	8945 / 0 / 614	3810/0/264	4362/0/370
GOOF on F2	1.062	0.983	1.029
Final R indexes [I>=2σ (I)]	R1 = 0.0783, wR2 = 0.2025	R1 = 0.0576, wR2 = 0.1433	R1 = 0.0277, wR2 = 0.0635
Final R indexes [all data]	R1 = 0.0919, wR2 = 0.2168	R1 = 0.1031, wR2 = 0.1645	R1 = 0.0364, wR2 = 0.0671
Largest diff. peak/hole/eÅ-3	7.054/-6.664	5.61/-2.55	1.978/-1.624

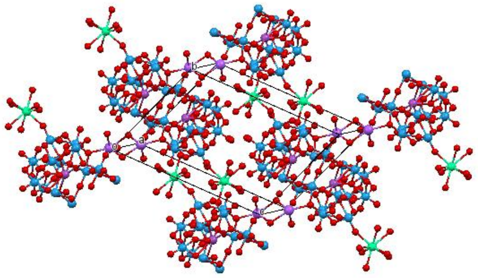
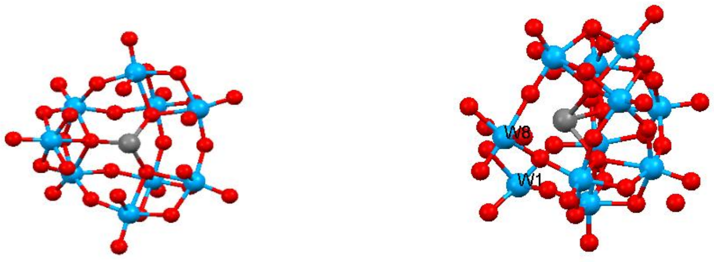


Fig. 2 Packing diagram showing 2D array of compound (1) in approximately the bc-plane (Bi gray, Na purple, Ca green).



(a) **(b)**

Fig. 3 Different views in compound (1) showing (a) the heteroatom Bi inside W_9O_{33}octahedra cluster. (b) A side view with the bridging W8 and W1 atoms added to figure A (Bi gray W blue).

The three Bi-O bonds in the BiO_3 polyhedron are of length 2.097, 2.141 and 2.166 A° with the O-Bi-O acute angles of 84.9, 87.3, 87.8° indicating a large wedge around Bi of empty space probably occupied by a lone pair. The W(8) as well as W(1), are outside the BiW9O33 cage and bridge two cages together. The terminal W(8)-O bonds are in the range 1.700 to 2.117Å indicating double as well as single bonds. Probably the O(1I) in the W(8)-O(1I)=2.117Å is protonated and of the type W-OH. An additional W(1) atom (occupancy 0.5) is outside the BiW_9O_{33} cage with terminal W(1)-O distances in the range of 1.856 to 2.190Å. The terminal W(1)-O(1J) of 2.190Å bond distances is again probably of the type W-OH. In the W_9O_{33} cage, the W atoms are hexa-coordinated octahedral with the terminal W=O bonds of length approximately 1.720Å. The W-O bond length of the bridging oxygen in the W-O-W groups are longer than the terminal W=O bonds as expected, and with some of the bridging O atoms probably protonated as OH. The group of nine octahedra in three groups of three share corners in **Figure 4**. There are at least seven H_2O molecules per asymmetric unit that were located in the Fourier maps. Some additional water molecule, if present, will be badly disordered and if positioned exhibit very high isotropic thermal parameters. The Ca^{2+} is surrounded by eight O atoms in a square antiprismatic coordination with one of the eight O atoms, O(1K) bridging with W(3) of the W_9O_{33} cage with Ca(1)-O(1K)=2.520Å. The Ca-O bond distance range from 2.430 to 2.540Å. Two $Na^+_{(aq)}$ bridge two W_9O_{33} cages together.

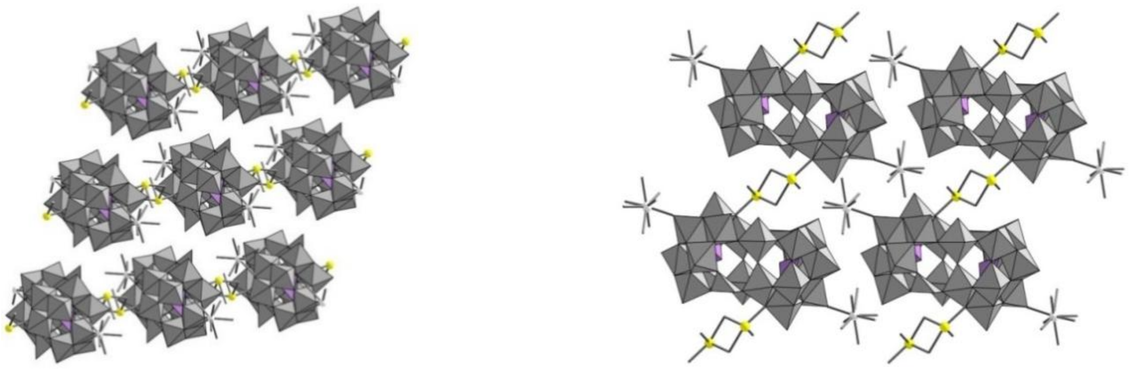


Fig. 4 W octahedra with Bi encapsulated in compound (1) Ca and Na coordination spheres are shown as lines.

In the case of case 2 **Figure 5**, the substance crystallizes in the space group C2/m, with two formula units per unit cell. The unit cell is monoclinic C2/m with each formula unit occupying four asymmetric units. The anion $[HBi_2W_{20}O_{70}(HWO_3)]^{12-}$ in 2 consists of two identical $[BiW_9O_{33}]$ Keggin type units, separated by a square of W_4O_8. Each W is hexacoordinated to O and each Bi(III) heteroatom is tricoordinated as a trigonalpyramidal BiO_3 unit inside the W_9O_{33} unit. The two $[BiW_9O_{33}]$ units are connected by four WO_2 groups and two facial WO_2 (OH).

The three Bi-O bonds in the trigonal BiO_3 pyramid are two symmetry-related Bi-O = 2.197Å and one 2.150Å. The O-Bi-O angles are two symmetry-related 89.4° and one 84.6°. For W(3) that joins the cages, two W(3)-O bridging W(3)-O(18) = 2.191Å and two W(3)-O(6) = 1.767Å on the mirror plane. The two shorter values correspond to W=O double bonds, while the longer values correspond to a protonated bridging W-OH group. W(2) also falls on the plane between the two cages. the addenda/metal centers Bi/W are linked via W-O-W and Bi-O-W oxygen bridged covalent bonds. The addenda atom is located in the center of nine distorted WO_6octahedra that are linked together. W(8) has 0.25 occupancy and will correspond to $(HWO_3)^+$ in the formula unit $H_2[NH_4]_{10}[HBi_2W_{20}O_{70}(HWO_3)]$. W(8) falls lateral to the molecule as shown in **Figure 6,** and **Figure 7**

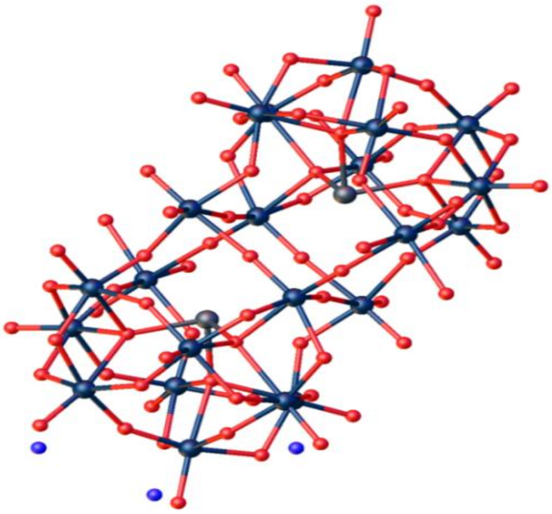


Fig. 5 The anion in compound (2) constituted from 4 asymmetric units. The 2.5 NH_4^+ that belong to one of the asymmetric units are also shown.

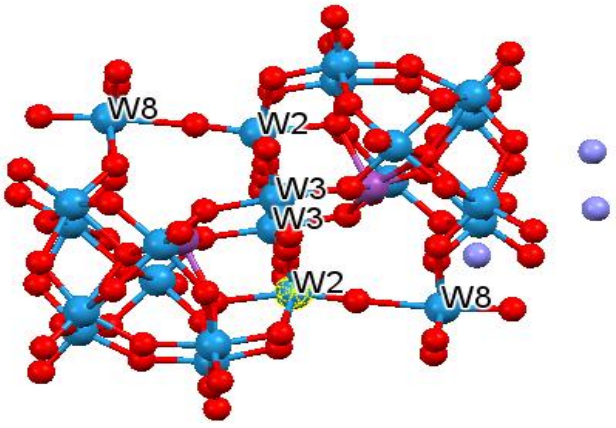


Fig. 6 Molecular unit showing the disposition of W(8) as well as (W(2) and W(3). Only 2.5 $NH4^+$ in one asymmetric unit is shown. (Bi gray, W blue. N light blue).

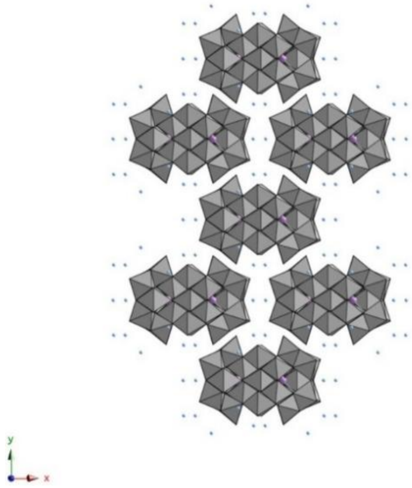


Fig. 7 Packing diagram of compound (2) in ab-plane showing W octahedra. NH_4^+ cations are discrete.

Changing the preparation procedure of compound (2) by increasing the pH from 5.5 to 6 led to the production of a different polyoxometalate that did not contain Bi, with a sodium $Na(H_2O)_4$ and calcium $[Ca(H_2O)_4]_2$ as linkers. The $[W_{12}O_{42}]^{12-}$ anion present in the structure indicates that a dynamic decomposition and reconstruction process happened during the reaction, where it was slowly reassembled from the $Na_{11}H[H_{(2-x)}Bi_2W_{20}O_{70}(HWO_3)x]\cdot 46H_2O$ precursor (**Figure 8**).

The single-crystal X-ray also indicates that each polyanion $[W_{12}O_{42}]^{12-}$ in compound (3) coordinates with two identical calcium atoms via terminal oxygen atoms and each calcium cation bridges two $[W_{12}O_{42}]^{12-}$ anions **Figure 9**. Each calcium cation is only seven coordinated with oxygen atoms, two of which are bridging, in an approximately mono-capped trigonal prismatic geometry. The Ca–O bond lengths are in the range of 2.369 to 2.525Å.

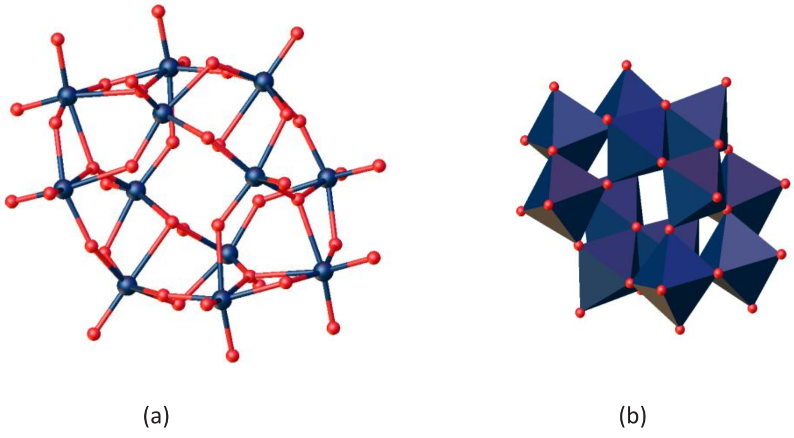

(a) (b)

Fig. 8 The anion in compound (3), $[W_{12}O_{42}]^{12-}$, as tungstate polyhedra (a), and as ball and stick (b).

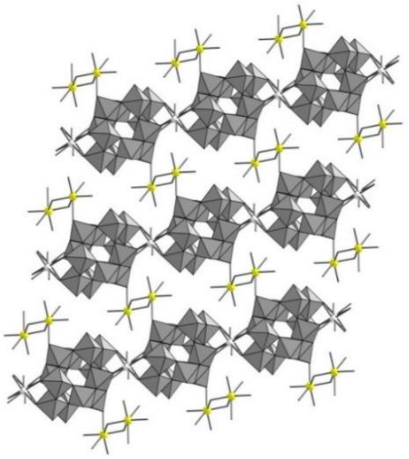


Fig. 9 Compound (3) showing the anionic W polyhedral units joint together into chains by hydrated Ca^{2+}. The chains are built into layers by connecting hydrated Na^+

2.2 Electronic spectra

In general, UV-visible spectra of polyoxometalate clusters without transition metals or lanthanides exhibit two charge transfer (CT) bands. These bands are characteristic of the polyoxoanionic framework and are ascribed to oxygen-to-metal charge transfer transitions. All compounds (1), (2), and (3) show identical UV spectra. The UV spectrum in **Figure 10** shows one CT band, due to dπ-pπ-dπ transitions from the tricentric W-O-W bonds, while a shoulder recorded at 256 nm. The spectrum point to another band that should appear below 200 nm which is attributed to dπ-pπ charge transfer transitions of the terminal W=O bonds. This charge transfer is of the type (W←O).

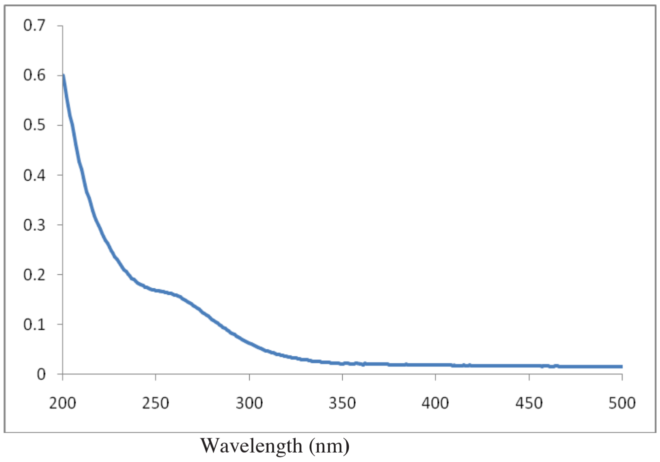


Fig. 10 UV-Visible spectra of compound (1), (2) and (3) spectra recorded at random concentrations

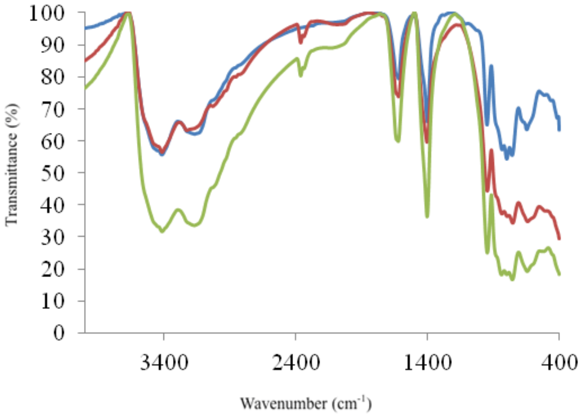


Fig. 11 FTIR spectra of compound (1) (red), (2) (blue), and (3) (green).

The vibration bands of the FTIR spectrum of three compounds are strictly like **Figure 11**. The four characteristic asymmetric vibrations present are characteristic to the W-O bonds are recorded in the 640-950 cm^{-1} range. The antisymmetric stretching vibrations (W—Ot) appear at 945 cm^{-1}, and the two (W—Obrid) appear at, 798 and 754 cm^{-1}, very strong bands at 1633 cm^{-1} is assigned to H-O-H bending and two bands ascribed to the presence of hydrogen-bonded O—H stretching modes at 3415 and 3174 cm^{-1}.

2.3 Thermogravimetric Analysis

Thermal stability of the compound (3) was determined by TGA measurements (**Figure 12**). No significant change takes place from 800-1200C^o. At 1212.12C^o the residual mass is measured to be 87.89%. The calculated % H_2O and NH_4^+ in the proposed and determined formula $[NH_4]_6[Na(H_2O)_4]_2[Ca(H_2O)_4]_2[W_{12}O_{42}].2H_2O$ **(3)** is 12.6% in close agreement with % mass loss in TGA.

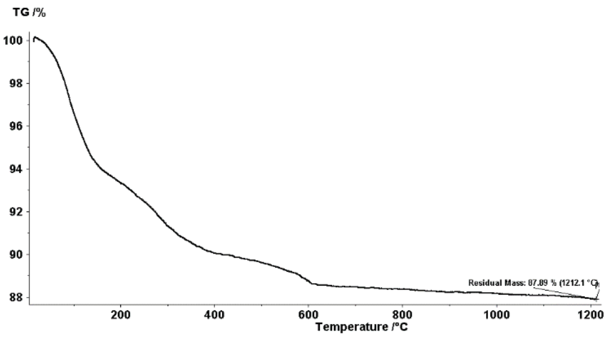


Fig. 12 Thermogravimetric analysis (TGA) of compound $[NH_4]_6[Na(H_2O)_4]_2[Ca(H_2O)_4]_2[W_{12}O_{42}]2H_2O$ (3).

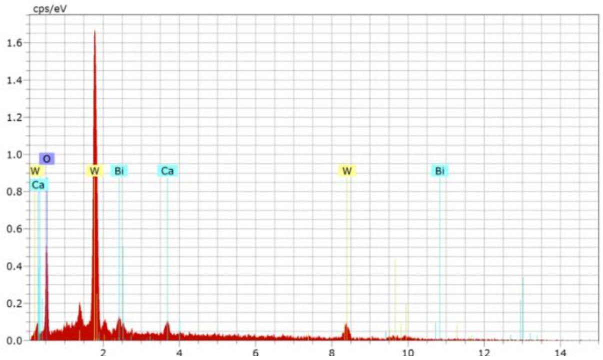


Fig. 13 EDS mapping of (1) $H_6[Ca(H_2O)_7]_2[Na(H_2O)_2]_2[HBi_2W_{20}O_{70}(HWO_3)]14H_2O$ (1).

2.4 Analysis Energy-dispersive X-ray spectroscopy (EDS) mapping

More than one spot on the surface of one crystal was used for analysis by EDS and was confirmed to give identical results. The EDS mapping of (1) Figure 13 confirms the existence of O, W, Bi, and Ca within the crystal.

Conclusions

This work reports the synthesis and structural investigation of three new polyoxometalate based in the polyanion $[HBi_2W_{20}O_{70}(HWO_3)]^{12.}$ This lead to the formation of three new crystalline products, the last of which did not contain Bi. These are $H_6[Ca(H_2O)_7]_2[Na(H_2O)_2]_2[HBi_2W_{20}O_{70}(HWO_3)].14H_2O$ (1), $H_2[NH_4]_{10}[HBi_2W_{20}O_{70}(HWO_3)]$ (2), and $[NH_4]_6[Na(H_2O)_4]_2[Ca(H_2O)_4]_2[W_{12}O_{42}].2H_2O$ (3). Three structures were reported in this work differs in their unit cell and space group the last one does not contain bismuth. The structure of compound $H_{66}Ca_2Na_2Bi_2W_{21}O_{105}$ has the lowest lattice symmetry amongst all. It crystallizes in the space group P-1, with one molecular per unit cell, while 2 and 3 crystallize in monoclinic space groups C2/m and P21/n respectively. Our work provides a new strategy to have a calcium-containing polyanion $[HBi_2W_{20}O_{70}(HWO_3)]^{12-}$ with differ lattice symmetry.

Nomenclature

EDS = Energy-dispersive spectroscopy [-]
TGA = Thermogravimetric Analysis [-]
SEM =Scanning Electron Microscopy [-]
UV = Ultraviolet [nm]

Acknowledgment

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