Different Polyoxometalate Structures Obtained from the Na$_{11}$H$[\text{H}_{(2-x)}\text{Bi}_2\text{W}_{20}\text{O}_{70}(\text{HWO}_{3})_x]\cdot46\text{H}_2\text{O}(x=1.4)$.

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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$[\text{H}_{(2-x)}\text{Bi}_2\text{W}_{20}\text{O}_{70}(\text{HWO}_{3})_x]\cdot46\text{H}_2\text{O}(x=1.4)$ with Ca ion at different pH conditions. These structures are $[\text{Ca(H}_2\text{O)}_2][\text{Na(H}_2\text{O)}_2][\text{Bi}_2\text{W}_{20}\text{O}_{70}(\text{HWO}_{3})_x]\cdot14\text{H}_2\text{O}(1)$, $\text{H}_2\text{[NH}_3\text{]}_2\text{[Bi}_2\text{W}_{20}\text{O}_{70}(\text{HWO}_{3})_x]\cdot15\text{H}_2\text{O}(2)$, and $[\text{NH}_4\text{]}_3\text{[Na(H}_2\text{O)}_3][\text{Ca(H}_2\text{O)}_3][\text{W}_5\text{O}_{23}]\cdot2\text{H}_2\text{O}(3)$. 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/h 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), (Hasenkopf, 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 polyonians 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, [HnXIII$\text{W}_{(9-n)}$O$\text{m}^{\text{(3n-3)}}$] (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-Bi$_2$W$_{18}$O$_{60}$ units such as [Bi$_2$W$_3$O$_{24}$(OH)$_2$]$^{18+}$ (Rodelwald and Jeannin, 1998) and its derivatives [M$^{n+}$$(\text{H}_2\text{O})_x$(Bi$_2$W$_{18}$O$_{60}$)$_3$$]^{(18-x)+}$ (M$^{n+}$ = VOII, x = 0 and M$^{n+}$ = CrIII, MnII, FeIII, CoII, NiII, CuII, x = 3) (Rusu, et al., 2001). Na$_{11}$H$_3$[Ce$_3$(H$_2$O)$_{18}$Bi$_2$W$_{22}$O$_{74}$]·8·H$_2$O (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$[\text{H}(2\times)\text{Bi}_2\text{W}_{20}\text{O}_{70}(\text{HWO}_{3})_x]\cdot46\text{H}_2\text{O}(x=1.4)$ 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$[\text{H}_{(2-x)}\text{Bi}_2\text{W}_{20}\text{O}_{70}(\text{HWO}_{3})_x]\cdot46\text{H}_2\text{O}(x=1.4)$ was prepared according to published procedures and characterized by FT-IR spectroscopy [30].

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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 2 mg 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 (\(\lambda = 0.71073 \text{ Å}\)) 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 \(\approx 10\) keV. SEM allowed the identification of any interesting structural features on the seaweed surface with EDS (BRUKER QUANTAX, EDS systems, Bruker AXS Microanalysis Gmbbt, X Flash Detector 410-M Silicon Drift (SDD), Berlin, Germany). \([\text{Ca(H}_2\text{O)}_7]\)_2[\text{Na(H}_2\text{O)}_2]\_2[\text{HBi}_2\text{W}_2\text{O}_{70}(\text{HWO}_3)]\_14\text{H}_2\text{O}\) (1).

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 \(\text{H}_{66}\text{Ca}_{2}\text{Na}_{2}\text{Bi}_{2}\text{W}_{21}\text{O}_{105}\) has the lowest lattice symmetry among all. It crystallizes in the space group \(\beta\)-\([\text{BiW}_{9}\text{O}_{33}]\) pseudo-Keggin type units in which three \(\text{W}_{3}\text{O}_{13}\) groups is turned by 60° relative to each other. Each \(\text{W}(\text{VI})\) is hexa-coordinated by six oxygen atoms, two of which are part of the \(\text{Bi}(\text{III})\) itself is tricoordinated to \(\text{O}\) in a triangular based pyramidal units of \(\text{BiO}_3\) with one direction occupied by a lone pair of electrons. The two units are connected by two \(\text{O}\) atoms.

2 Results and Discussion

2.1 Crystal structure

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units. A packing diagram is shown in Figure 2 illustrating the 2-dimensional nature of the structure. And it consists of two identical trilacunary \( \beta-[\text{BiW}_{12}\text{O}_{33}] \) pseudo-Keggin type units in which three \( \text{W}_3\text{O}_{13} \) groups is turned by 60° relative to each other. In the polyoxometalate \( \text{H}_2\text{[Ca(H}_2\text{O})_4]\text{[Na(H}_2\text{O})_2]\text{[HBi}_2\text{W}_8\text{O}_{28}(\text{HWO}_3)]\text{.14H}_2\text{O} \) (1) the molecule consists of two identical trilacunary \( \beta-[\text{BiW}_{12}\text{O}_{33}] \) pseudo-Keggin type units in which three \( \text{W}_3\text{O}_{13} \) 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 \( \text{W}_3\text{O}_{13} \) 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 \textit{facial} O\(_2\)OH and two WO\(_2\) groups or by two hydrated Na cations. Each W(VI) is hexacoordinated to oxygen with nine W octahedra sharing corners encapsulating the Bi(III) heteroatom inside the \( \text{W}_3\text{O}_{13} \) 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 \textit{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 | Chemical formula | (1) \( \text{H}_{66}\text{Ca}_2\text{Na}_2\text{Bi}_2\text{W}_{21}\text{O}_{105} \) | (2) \( \text{H}_{44}\text{N}_10\text{Bi}_2\text{W}_{21}\text{O}_{73} \) | (3) \( \text{H}_{60}\text{N}_6\text{Na}_2\text{Ca}_2\text{W}_{12}\text{O}_{60} \) |
|-----------|-----------------|----------------|----------------|----------------|
| Formula Mass | 6151.37 | 5631.16 | 3436.80 |
| Crystal system | Triclinic | Monoclinic | Monoclinic |
| Space group | P-1 | C2\(\text{i}\) | P2\(\text{1})\text{\textit{n}} |
| \( a/\text{Å} \) | 12.8969(6) | 17.5821(16) | 12.1812(3) |
| \( b/\text{Å} \) | 12.9951(7) | 18.7384(13) | 17.4026(4) |
| \( c/\text{Å} \) | 12.9951(7) | 14.2156(12) | 14.4900(5) |
| \( \alpha/° \) | 71.506(5) | 90 | 90 |
| \( \beta/° \) | 83.758(4) | 113.349(12) | 114.027(4) |
| \( \gamma/° \) | 62.581(5) | 90 | 90 |
| Volume/\(\text{Å}^3\) | 2531.8(3) | 4299.9(6) | 2797.57(16) |
| \( Z \) | 1 | 2 | 2 |
| \( \mu/\text{mm}^{-1} \) | 27.429 | 32.131 | 24.887 |
| \( F(000) \) | 2688 | 4836 | 3064 |
| \( 2θ \) range for data collection | 5.84 to 50.06° | 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 | 38100 / 264 | 43620 / 370 |
| GOOF on F2 | 1.062 | 0.983 | 1.029 |
| Final R indexes \([\text{l}≥2\sigma(i)]\) | 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 |
The three Bi-O bonds in the BiO$_3$ polyhedron are of length 2.097, 2.141 and 2.166 Å 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 BiW$_9$O$_{33}$ cage and bridge two cages together. The terminal W(8)-O bonds are in the range 1.700 to 2.117 Å indicating double as well as single bonds. Probably the O(1I) in the W(8)-O(1I)=2.117 Å is protonated and of the type W-OH. An additional W(1) atom added to figure A (W blue). Bi/W are linked via W-O-W and Bi-O-W oxygen bridged covalent bonding. 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 bonding. W(3) has 0.5 occupancy and will be represented with a 0.5 sphere. W(3)-O bridging W(3)-O(18) = 2.191 Å and two W(3)-O(6) = 1.767 Å 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. The O-Bi-O angles are two symmetry-related 89.4° and one 84.6°. For W(3) that joins the cages, two W-O-W bond lengths are in the range of 2.369 to 2.525 Å.

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$_2$W$_{12}$O$_{42}$]$_{12}$ in 2 consists of two identical [BiW$_9$O$_{33}$] Keggin type units, separated by a square of W$_6$O$_{18}$. Each W is hexacoordinated to O and each Bi(III) heteroatom is tricoordinated as a trigonalpyramidal BiO$_3$ unit inside the W$_6$O$_{18}$ unit. The two [BiW$_9$O$_{33}$] units are connected by four WO$_2$ groups and two facial WO$_2$(OH).

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

Fig. 3 Different views in compound (1) showing (a) the heteroatom Bi inside W$_6$O$_{18}$octahedra cluster. (b) A side view with the bridging W8 and W1 atoms added to figure A (Bi gray W blue).

Fig. 4 Different views in compound (1) showing (a) the heteroatom Bi inside W$_6$O$_{18}$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 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$_6$octahedra that are linked together. W(8) has 0.25 occupancy and will correspond to (HWO$_3$)$_2^-$ in the formula unit H$_2$[NH$_4$]$_{10}$[HBi$_2$W$_5$O$_{20}$(HWO$_3$)]. W(8) falls lateral to the molecule as shown in Figure 6, and Figure 7.

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$_2$O)$_4$ and calcium [Ca(H$_2$O)$_4$]$_2$ 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$_2$W$_2$O$_{70}$(HWO$_3$)$_x$]·46H$_2$O 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.
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 transitions from the tricentric W-O-W bonds, while a shoulder recorded at 256 nm. This spectrum points 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).

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→O) 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 800-1200°C. At 1212.12°C the residual mass is measured to be 87.89%. The calculated % H2O and NH4+ in the proposed and determined formula [NH4]6[Na(H2O)4][Ca(H2O)4][W12O42]\cdot2H2O (3) is 12.6% in close agreement with % mass loss in TGA.

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 \([\text{HBi}_2\text{W}_{20}\text{O}_{70}(\text{HWO}_3)]^{12-}\). This lead to the formation of three new crystalline products, the last of which did not contain Bi. These are H6[Ca(H2O)7][Na(H2O)2][WBi2W20O70(HWO3)].14H2O (1), H2[NH4][HBi2W30O84(HWO3)] (2), and [NH4]6[Na(H2O)4][Ca(H2O)4][W12O42]\cdot2H2O (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 H6Ca2Na2Bi2W21O105 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 \([\text{HBi}_2\text{W}_{30}\text{O}_{84}(\text{HWO}_3)]^{12-}\) with differ lattice symmetry.

Nomenclature

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

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