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**INORGANIC ARCHITECTURE BASED ON A $\{[\text{Ca}(\text{H}_2\text{O})_6[\text{P}_4\text{W}_6\text{O}_{34}]_2\}^{12-}$
BUILDING BLOCK: COUNTERCATION EFFECT ON THE LATTICE SYMMETRY****M.A. AlDamen, S.B. Atta, S.F. Haddad***Department of Chemistry, Faculty of Science, the University of Jordan, Amman, Jordan*

E-mail: maldamen@ju.edu.jo

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Three new salts of the $\{[\text{Ca}(\text{H}_2\text{O})_6[\text{P}_4\text{W}_6\text{O}_{34}]_2\}^{12-}$ polyanion, namely $(\text{NH}_4)_{12}\{[\text{Ca}(\text{H}_2\text{O})_6 \cdot [\text{P}_4\text{W}_6\text{O}_{34}]_2\} \cdot 24\text{H}_2\text{O}$ (**1**), $\text{H}_2[\text{Na}(\text{H}_2\text{O})_{1.6}]_{10}\{[\text{Ca}(\text{H}_2\text{O})_6[\text{P}_4\text{W}_6\text{O}_{34}]_2\} \cdot 10\text{H}_2\text{O}$ (**2**), and $[\text{Ca}(\text{H}_2\text{O})_5]_6\{[\text{Ca}(\text{H}_2\text{O})_6[\text{P}_4\text{W}_6\text{O}_{34}]_2\} \cdot 11\text{H}_2\text{O}$ (**3**) are prepared. The change in the lattice as a function of the countercation and its coordination, specially calcium, is investigated. Full characterization is made by single crystal X-ray diffraction and also UV-visible spectroscopy, FT-IR, thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDS).

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INTRODUCTION

Polyoxometalates (POMs) are a well-known class of metal oxygen clusters with a large variety in composition and structure [1]. These compounds have been extensively studied due to their potential applications in many fields [2—7]. Well-known metal oxide with calcium is the naturally occurring tungsten-calcium (CaWO_4) mineral — scheelite — that has many electronic [8] and engineering applications [9]. In addition, studies of calcium coordination and its bond values are important due to its frequent occurrence in biological and bio-inspired materials [10]. From this point of view, we are interested in the structural and coordination behavior of calcium with rigid structures, such as POMs. A literature survey of POMs and their derivatives shows that only few calcium-containing POMs have been synthesized and their structure determined by X-ray diffraction. These compounds are $[\{\text{Ca}(\text{DMF})_5\}_2\text{SiMo}_{12}\text{O}_{40}]^{n-}$ [11] and $\text{H}_2[\text{Ca}_2(\text{P}_2\text{W}_{18}\text{O}_{62})(\text{H}_2\text{O})_5] \cdot 7.5\text{H}_2\text{O}$ based on the Wells—Dawson polyanion [12]. Also, Wang's group isolated a novel type of the heteropolyoxoanion (HPOA) precursor $\{[\text{Ca}(\text{H}_2\text{O})_6[\text{P}_4\text{M}_6\text{O}_{34}]_2\}^{12-}$ [$\text{M} = \text{W}^{\text{VI}}, \text{Mo}^{\text{VI}}$] [13]. Prior to the present work, the latest calcium-containing POMs were: $[\text{Ca}(\text{H}_2\text{O})_2][\text{Ca}(\text{H}_2\text{O})_3]\text{H}_2[\text{P}_2\text{W}_{18}\text{O}_{62}] \cdot 9\text{H}_2\text{O}$ [14] $[\text{K}_3\text{Ca}(\text{H}_2\text{O})_4(\text{HP}_2\text{Mo}_5\text{O}_{23})] \cdot 6\text{H}_2\text{O}$ [15], $[\text{NH}_3\text{H}_2\text{O}]_6 \cdot \text{H}_6[\text{Ca}_4\text{V}_{12}\text{O}_{40}] \cdot 6\text{H}_2\text{O}$ [16], and $\text{Ca}_2\text{Na}_6[\text{H}_2\text{W}_{12}\text{O}_{42}] \cdot 30\text{H}_2\text{O}$ [17]. Recently, the control of the countercation has been reported to lead to interesting properties such as semiconduction as well as photocatalysis and light-to-electricity conversion [17, 18]. During the last years we were interested in the coordination of transition metals [19—24] and lanthanides [25]. Recently, we synthesized the first dual transition metal POM with calcium that has the formula $\text{Na}_6\text{Ca}_3[\text{Ca}_2(\text{H}_2\text{O})_6\text{Co}_9(\text{OH})_3(\text{H}_2\text{O})_6(\text{HPO}_4)_2(\text{PW}_9\text{O}_{34})_3]$ [26].

EXPERIMENTAL

All complexes were prepared and characterized using laboratories and instruments located in The University of Jordan, Faculty of Science. All chemicals used for synthesis were of reagent grade and used without further purification.

1: Sodium tungstate dihydrate $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (2.50 g, 7.5 mmol), hydrated sodium hydrogen phosphate $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ (1.34 g, 3.7 mmol), and CaCl_2 (0.415 g, 3.7 mmol) were dissolved in 20 ml of water in 50-ml RBF equipped with a magnetic stirring bar. To this solution 2 M HCl was added very slowly with vigorous stirring until pH reached 6.50 and remained stable for 5 min. The solution was then stirred on heating at 80–90 °C for 45 min. After cooling to room temperature, the turbidity was removed by filtration. Finally, NH_4Cl (0.35 g, 6.5 mmol) was added to the solution, stirred, and left to slowly evaporate at ambient temperature. Colorless hydrated crystals separated in 5 days. The product had trigonal morphology and was slightly soluble in water.

2: A similar procedure as in **1** was followed except that the pH was adjusted to 6.0 and no NH_4Cl was added. The crystals were colorless with triclinic morphology.

3: A solid powdered precursor $\text{K}_{24}[\text{P}_4\text{W}_{52}\text{O}_{178}] \cdot 47\text{H}_2\text{O}$ was synthesized according to the literature procedure [27] and confirmed by FT-IR spectroscopy. Solid $\text{K}_{24}[\text{P}_4\text{W}_{52}\text{O}_{178}] \cdot 47\text{H}_2\text{O}$ (0.352 g, 0.0246 mmol) was dissolved in 10 ml of H_2O and then mixed with a CaCl_2 solution (0.030 g, 3.1 mmol) in 5 ml of H_2O . To this mixture, 1 M NaOH was added dropwise with vigorous stirring until pH stabilized at 6.50. Finally, 2 ml of 1 M KCl was added to the solution, stirred for 30 min at 45 °C, and left to slowly evaporate at ambient temperature. After 5 min, the turbidity was removed by filtration and the solution was left to slowly evaporate. Colorless transparent crystals separated in a week.

All the obtained crystals are stable in solutions and decompose slowly in its absence due to dehydration. FT-IR spectra were recorded with a Nicolet Impact 400 Fourier transform infrared spectrophotometer (Madison, WI) in the range 400–4000 cm^{-1} using KBr pellets. UV-Vis data were recorded from 200 to 700 nm at room temperature on a Varian Cary-100 UV/VIS spectrophotometer. Thermogravimetric analyses were performed by Kanti Labs Ltd. in Missisunga, Canada. 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. Single crystal X-ray diffraction data were collected using an Xcalibur/Oxford diffractometer equipped with a Eos CCD detector. $\lambda(\text{MoK}\alpha) = 0.71073 \text{ \AA}$ at 20 °C. Data reduction was performed using the CrysAlisPro software package [28]; the crystal structure solution and refinements were carried out using Olex [29] and SHELXTL [30].

RESULTS AND DISCUSSION

Crystal structure. The three structures reported in this paper differ in their unit cell parameters and also differ from the well-known Wang et al. structure. The structure of $(\text{NH}_4)_{12}\text{L} \cdot 24\text{H}_2\text{O}$ has the highest lattice symmetry amongst all. It crystallizes in the space group $R\bar{3}$, with three molecular units **1** per unit cell, while **2** and **3** crystallize in triclinic and monoclinic space groups $P\bar{1}$ and $P2_1/n$ respectively. Table 1 summarizes the crystallographic data for the three crystals as well as for the previously published one. A schematic representation of b axis in these lattices is shown in Fig. 1.

In three out of the four lattices, the polyanions are not arranged with their planes parallel to axes. **1** is the only structure of the reported three in which the polyanions are arranged with their planes parallel to the axes. The $\{[\text{Ca}(\text{H}_2\text{O})]_6[\text{P}_4\text{W}_6\text{O}_{34}]_2\}^{12-}$ polyanion is the main building block in all reported salts in this article. This polyanion is the same anion found in ammonium-sodium salts **1** previously

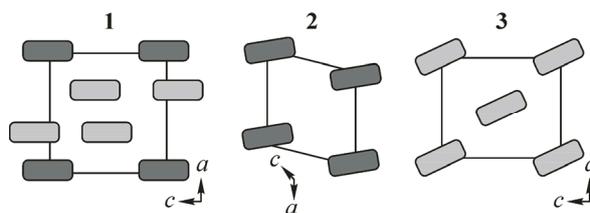


Fig. 1. Schematic representation of the lattices shows the arrangement of the $\{[\text{Ca}(\text{H}_2\text{O})]_6[\text{P}_4\text{W}_6\text{O}_{34}]_2\}^{12-}$ polyanion, **1**, **2**, and **3** structures

Table 1

Crystal data and structure refinement for the crystals of three salts and that reported by Wang et al.

Parameter	1	2	3	(NH ₄) ₁₀ Na ₂ · ·{[Ca(H ₂ O)] ₆ [P ₄ W ₆ O ₃₄] ₂ }· ·14H ₂ O
Chemical formula	H ₈₈ W ₁₂ P ₈ N ₁₂ Ca ₆ O ₉₈	H ₆₆ Na ₁₀ Ca ₆ P ₈ W ₁₂ O ₁₀₀	H ₄₇ Ca ₁₂ P ₈ W ₁₂ O ₁₁₅	H ₈₀ Ca ₆ N ₁₀ Na ₂ O ₈₈ P ₈ W ₁₂
Formula mass	2215.22	2262.11	4774.80	4369.16
Crystal system	Trigonal	Triclinic	Monoclinic	Monoclinic
Space group	<i>R</i> -3	<i>P</i> -1	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> , Å	21.9423(9)	13.3377(8)	13.9834(3)	13.773(7)
<i>b</i> , Å	21.9423(9)	13.8984(5)	21.8674(4)	21.669(12)
<i>c</i> , Å	16.5886(6)	15.0590(8)	16.7441(3)	16.636(9)
α, deg.	90	105.149(4)	90	90
β, deg.	90	110.392(5)	92.5023(19)	106.860(6)
γ, deg.	120	99.669(4)	90	90
Volume, Å ³	6916.8(6)	2420.0(2)	5115.14(17)	4752(4)
<i>Z</i>	6	2	2	2
ρ _{calc} , mg/mm ³	3.255	3.1501	3.131	
μ, mm ⁻¹	15.514	14.821	14.300	15.050
<i>F</i> (000)	6252	2104	4430	4008
2θ range for data collection, deg.	6.182 to 58.4	6.16 to 50.06	5.84 to 50.06	
	-29 ≤ <i>h</i> ≤ 27,	-11 ≤ <i>h</i> ≤ 15,	-16 ≤ <i>h</i> ≤ 13,	
Index ranges	-28 ≤ <i>k</i> ≤ 29,	-16 ≤ <i>k</i> ≤ 16,	-26 ≤ <i>k</i> ≤ 26,	
	-21 ≤ <i>l</i> ≤ 10	-17 ≤ <i>l</i> ≤ 17	-18 ≤ <i>l</i> ≤ 19	
Reflections collected / independent	5862 / 3501	16404 / 8516	28400 / 9022	33957 / 8349
	[<i>R</i> (int) = 0.0231]	[<i>R</i> (int) = 0.0592]	[<i>R</i> (int) = 0.0303]	[<i>R</i> (int) = 0.0440]
Data / restraints / parameters	3501 / 0 / 205	8516 / 0 / 622	9022 / 6 / 676	8349
GOOF on <i>F</i> ²	1.034	1.067	1.123	1.023
Final <i>R</i> indices [<i>I</i> ≥ 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0349, <i>wR</i> ₂ = 0.0832	<i>R</i> ₁ = 0.0610, <i>wR</i> ₂ = 0.1577	<i>R</i> ₁ = 0.0251, <i>wR</i> ₂ = 0.0605	<i>R</i> ₁ = 0.0330, <i>wR</i> ₂ = 0.0846
Final <i>R</i> indices (all data)	<i>R</i> ₁ = 0.0460, <i>wR</i> ₂ = 0.0891	<i>R</i> ₁ = 0.0719, <i>wR</i> ₂ = 0.1693	<i>R</i> ₁ = 0.0286, <i>wR</i> ₂ = 0.0618	
Largest diff. peak / hole, e/Å ³	2.633 / -1.721	4.544 / -4.807	1.634 / -1.096	

reported [13], with some nitrogen atoms being replaced by sodium atoms. In this structure as well as in the previously reported one, in each crystal the core polyanion consists of six asymmetric units related by threefold rotation as well as inversion. The single crystal X-ray diffraction analysis also indicates that this compound is a centrosymmetric dimer with the {[Ca(H₂O)]₆[P₄W₆O₃₄]₂}¹²⁻ anion having a center of inversion (Fig. 2) and it is formed from two [P₄W₆O₃₄]¹²⁻ subunits linked by a trigonal antiprismatic hexacalcium cluster [Ca₆]¹²⁺ via O atoms from two [P₄W₆O₃₄]¹²⁻ subunits.

Each Ca²⁺ ion has one H₂O molecule that solely belongs to it ([Ca(H₂O)]²⁺ in the formula) while the other seven O atoms of the CN = 8 coordination of Ca²⁺ are shared as bridging. Crystal data and structure refinement details for the three salts as well as for those reported by Wang et al. are summarized in Table 1. The hexacalcium [Ca₆]¹²⁺ cluster is made of inversion related pair of three Ca²⁺. Each Ca²⁺ ion adopts an eight coordinate geometry with Ca—O distances of 2.327—2.668 Å with one bond to terminal H₂O. The six Ca²⁺ ions are arranged with the neighboring Ca—Ca distances of ca. 4.00 Å (Fig. 2) to establish a perfect trigonal antiprism. Interestingly, in the case of **3** the Ca—Ca bonds are longer (3.8489(39), 4.5148(20), and 4.4722(26) Å) and the trigonal antiprismatic geometry becomes distorted. This means that the hexacalcium [Ca₆]¹²⁺ cluster is expanded due to the introduction of a large countercation such as Ca²⁺. The other components of the lattice are hydrated water and ammonium in **1** (Fig. 3). In the case of **2** (Fig. 4), [Na(H₂O)_{*x*}]⁺ (*x* = 1 to 2 with an average of 1.6H₂O mole-

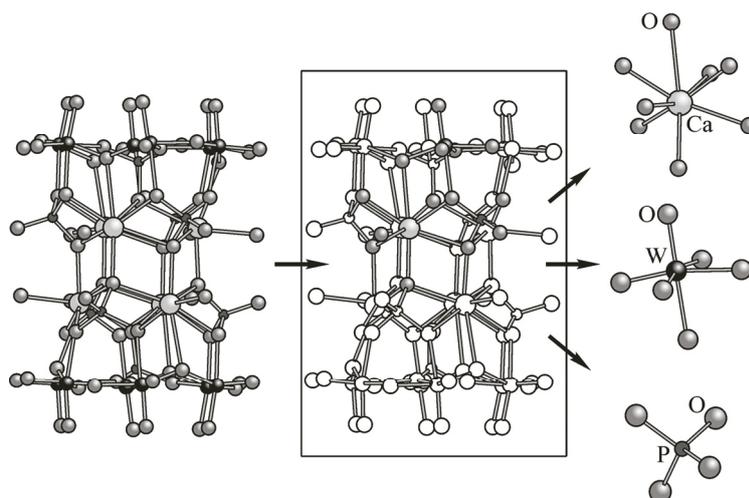


Fig. 2. General ball-and-stick structure of the $\{[\text{Ca}(\text{H}_2\text{O})_6][\text{P}_4\text{W}_6\text{O}_{34}]_2\}^{12-}$ polyanion

cules per Na^+) chains are connected together through hydrated molecules and bridge the polyanions together. The lattice system of **3** (Fig. 5) has three different calcium countercation units: $[\text{Ca}(\text{H}_2\text{O})_4]$, $[\text{Ca}(\text{H}_2\text{O})_5]$, and $[\text{Ca}(\text{H}_2\text{O})_6]$ (Fig. 6). In these fragments, the calcium coordinations are 7 (Ca4 and Ca5) and 8 (Ca6) (Fig. 5). In **Ca4**, the calcium ion is bonded to $(\text{W}_2\text{O}_{11})^{10-}$ and $(\text{PO}_4)^{3-}$ through their oxygen atoms and also to four water molecules. The Ca—O (in Ca—O—P) distance is 2.3876(51) Å while Ca—O (in Ca—O—W) is slightly longer with an average bond distances of 2.4270 Å ($\sigma = 0.01$). Second moiety **Ca5** has a bond between a calcium atom and only two units (WO_6^{6-} and $(\text{PO}_4)^{3-}$) with similar distances to Ca4; Ca—O (in Ca—O—W) is 2.4440(45) Å. The Ca—O distance (in Ca—O—P) is short and amounts to 2.2625(49) Å. In the literature, the shortest Ca—O distance has a value of 2.105 Å with CN = 8. Up to our knowledge, this value of 2.2625(49) Å is one of the shortest reported Ca—O distances with CN = 7 with good *R*-factor [31]. Third calcium unit **Ca6** is located between

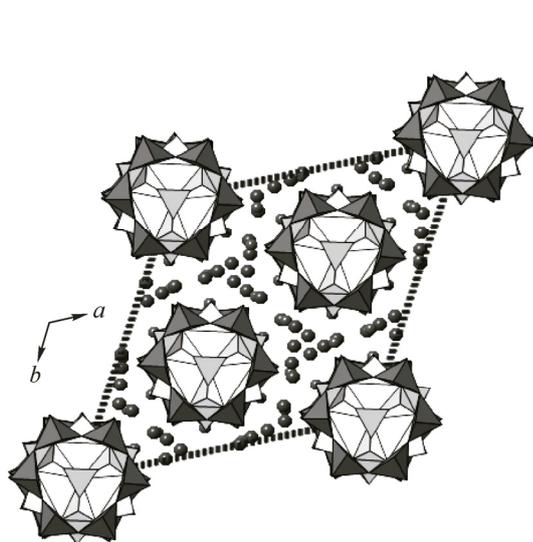


Fig. 3. Polyhedral representation of **1** along the *c* axis showing the unit cell of $\{[\text{Ca}(\text{H}_2\text{O})_6][\text{P}_4\text{W}_6\text{O}_{34}]_2\}^{12-}$

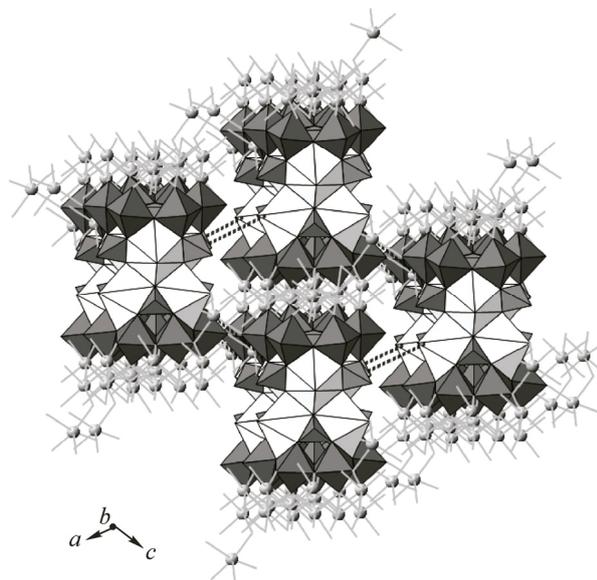


Fig. 4. Polyhedral representation of **2** along the *b* axis showing the unit cell of $\{[\text{Ca}(\text{H}_2\text{O})_6][\text{P}_4\text{W}_6\text{O}_{34}]_2\}^{12-}$. Ball-and-stick representations are coordinated sodium hydrates in the structure

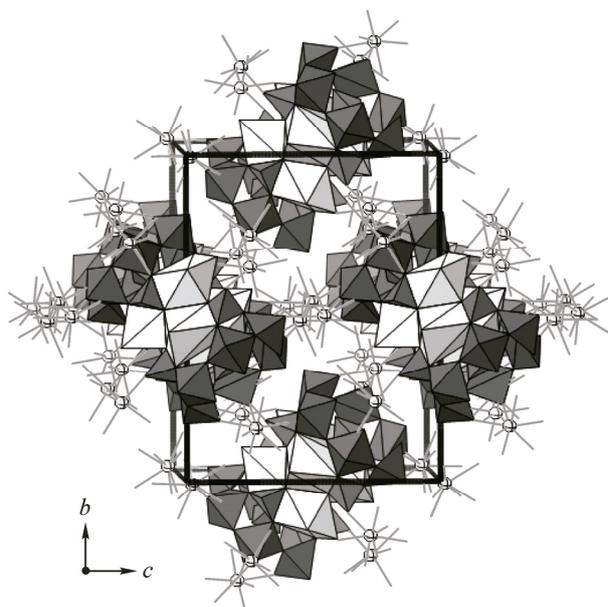


Fig. 5. Polyhedral representation of **3** along the *a* axis showing the unit cell of $\{[\text{Ca}(\text{H}_2\text{O})]_6[\text{P}_4\text{W}_6\text{O}_{34}]_2\}^{12-}$. Ball-and-stick representations are coordinated calcium hydrates in the structure

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 [33]. In the three structures there is a broad CT UV absorption band (Fig. 7) attributed to $d\pi-p\pi-d\pi$ transitions within the tricentric W—O—W bonds, which are shown as shoulders at about 250, 258, and 250 nm for the three structures respectively. The sharper CT bands at below 200 nm are attributed to $d\pi-p\pi$ CT transitions of the terminal W=O bonds. CT is of the type (O→W).

FT-IR spectrum. The solid was characterized by its IR spectrum as a KBr pellet (Fig. 8). The four antisymmetric stretching vibrations for W=O and W—O—W, characteristic of the W—O bonds, are observed in the range 700—1029 cm^{-1} . The antisymmetric stretching vibrations (W—O_i) appear at 930 cm^{-1} , and two (W—O_{brid}) appear at 878 and 692 cm^{-1} . These bridging vibrations are characteristic of the investigated polyoxotungstate cluster. The main vibration due to the heteroatom P—O stretching is recorded at 1088 cm^{-1} . This wavelength confirms the presence of P as a heteroatom in the polyoxometalate framework. The band at 1653 cm^{-1} is attributed to the H—O—H bending mode and

two (WO₆)⁶⁻ units. The average Ca—O distance (in Ca—O—W) is 2.5807 Å ($\sigma = 0.05$) and is notably longer than that in the other two moieties. The Ca—O(H₂O) distances are in agreement with those reported for similar structures in the literature within a range of 2.328—2.551 Å, which may be explained by the higher coordination number of calcium (CN = 8) in this case. Also, these Ca—O(H₂O) distances are in the range accepted for seven and eight coordinated Ca²⁺ [32]. The bond lengths and angles for the three compounds are shown in Table 2.

Electronic spectra. In general, UV-visible spectra of polyoxometalate clusters without transition

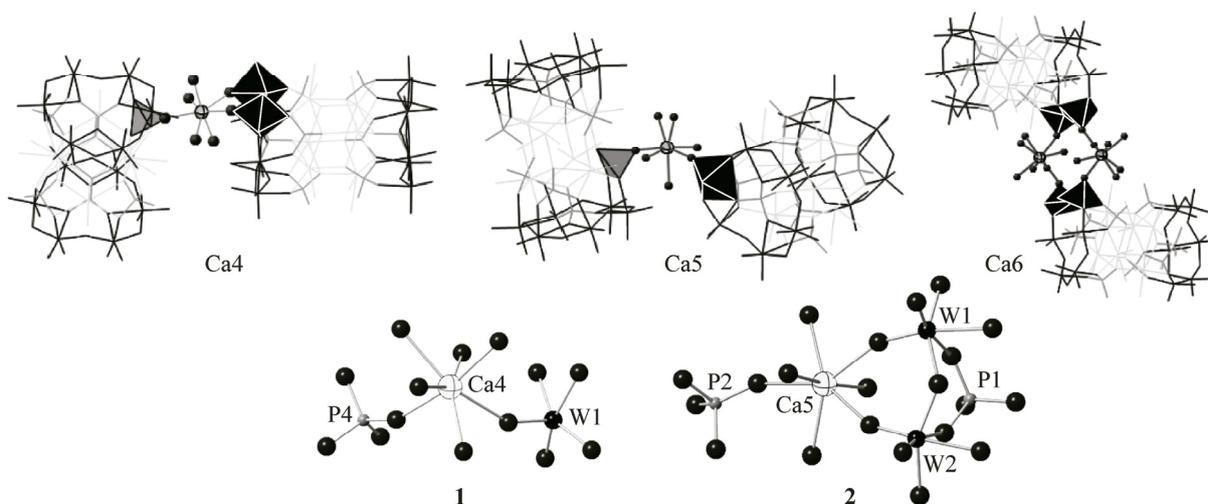


Fig. 6. above: Different calcium connections in **3**, PO₄(Ca(OH₂)₄)(W₂O₁₂) in Ca4, PO₄(Ca(OH₂)₅)(WO₆) in Ca5, and (W₂O₁₂)(Ca(OH₂)₅)₂(W₂O₁₂) in Ca6. below: clearer ball-and-stick view of the connections

Table 2

Selected bond lengths (Å) for **1**, **2**, and **3**

Bonds	1	2	3
W—O _{axial}	1.728 (1.713—1.743)	1.728 (1.713—1.743)	1.733 (1.720—1.740)
W—O _{equatorial}	1.734 (1.713—1.752)	1.734 (1.713—1.752)	1.730 (1.724—1.737)
W—O (W—O—W)	1.929 (1.926—1.934)	1.929 (1.926—1.934)	1.935 (1.922—1.943)
W—O (O—Ca & W)	1.922 (1.916—1.933)	1.922 (1.916—1.933)	1.926 (1.917—1.936)
W—O (O—P _{central} & W)	2.333 (2.294—2.375)	2.333 (2.294—2.375)	2.315 (2.303—2.328)
W—O (O—P _{basal} & Ca)	2.149 (2.126—2.157)	2.149 (2.126—2.157)	2.161 (2.144—2.179)
P _{center} —O (O—W & W)	1.545 (1.545—1.546)	1.545 (1.534—1.554)	1.550 (1.543—1.558)
P _{center} —O (O—Ca & Ca & Ca)	1.5179 (105)	1.5351 (116)	1.5268 (48)
Ca—O _{eq}	2.4194 (125)	2.417 (2.399—2.439)	2.381 (2.327—2.467)
Ca—O (O—P _{center})	2.578 (2.577—2.579)	2.561 (2.524—2.595)	2.456 (2.433—2.479)
Ca—O (O—W & P)	2.409 (2.397—2.420)	2.410 (2.383—2.428)	2.433 (2.384—2.500)
Ca—O (O—P _{basal} & Ca & Ca)	2.489 (2.480—2.497)	2.506 (2.483—2.545)	2.584 (2.461—2.668)
Ca—O from 2nd sandwich	2.3463(69)	2.363 (2.355—2.369)	2.349 (2.349—2.360)

strong bands around 3470 cm^{-1} are ascribed to the presence of hydrogen bonded O—H stretching modes of water as well as N—H stretching modes of ammonium. The Ca—O bond vibration must appear in the range $300\text{—}350\text{ cm}^{-1}$ but it cannot be observed because the IR spectrophotometer used operates only within the range $400\text{—}4000\text{ cm}^{-1}$. The vibrational bands in the FT-IR spectrum of **2** and **3** strictly resemble those in **1**. There are four characteristic asymmetric vibrations present in the range $700\text{—}1100\text{ cm}^{-1}$.

Thermogravimetric analysis. The TGA analysis of **1** shows more than one weight loss regions due to two bonding modes for water in POM. Some H₂O molecules are coordinated to W or Ca while other H₂O molecules are interstitial as water of crystallization. Most of the interstitial water of crystallization is released at about $100\text{ }^{\circ}\text{C}$. The second weight loss region is observed in a range of $250\text{—}600\text{ }^{\circ}\text{C}$,

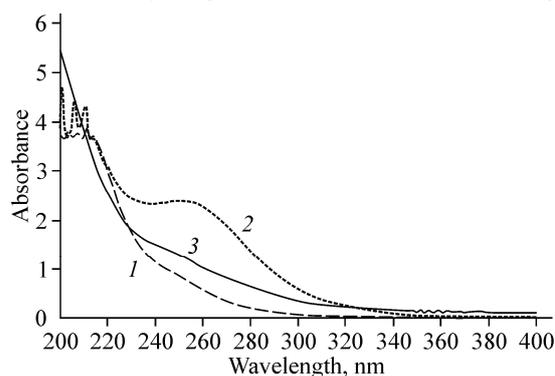


Fig. 7. UV-Visible spectra of **1**, **2**, and **3**. Spectra are recorded at random concentrations

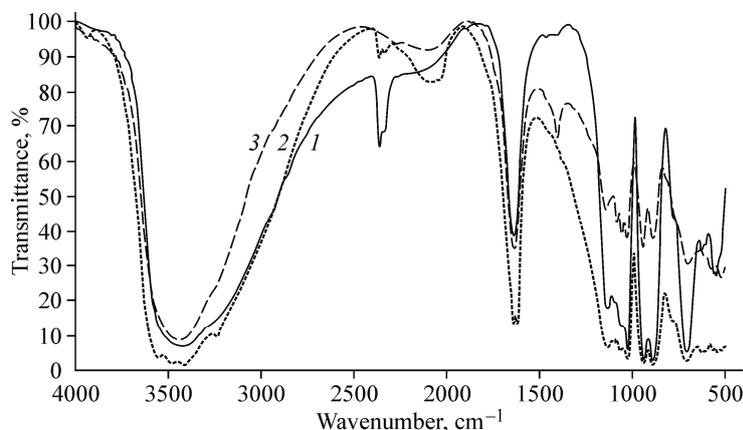


Fig. 8. FT-IR spectra of **1**, **2**, and **3**

reflecting the loss of metal-bonded water. No significant change takes place from 600 to 1200 °C. At 1224 °C the residual mass was measured to be 84.42 %. Calculated % H₂O and NH₄ in the proposed and determined formula of **1** is 15.58 %. This value is in agreement with 4.8 and 9.5 % percentages of NH₄⁺ and H₂O respectively. In the case of **2**, the system losses all the water molecules at 400 °C and starts losing part of sodium hydrated molecules. Calculated % H₂O and % H₂[Na(H₂O)_{1.6}]₁₀ in the proposed and determined formula is 3.9 and 11.3 % respectively and the residual mass was measured to be 88.75 %.

Scanning electron microscopy (SEM-EDS) analysis. SEM was used to investigate the morphology of the crystals, and cracks on the surface demonstrate that the crystals lose water with time and slowly decompose. The EDS mapping of **1** confirms the presence of P, O, W, and Ca within the crystal, with Na showing up as a weak peak. No Na was present in the structure determined by X-ray diffraction. The weak peak for Na in EDS is probably due to a picked impurity. The EDS mapping of **2** confirms the presence of P, O, W, Ca, and Na within the crystal. Minor distinctions from theoretical values can be explained based on that EDS is an averaging technique.

CONCLUSIONS

Three new crystals containing calcium in the {[Ca(H₂O)]₆[P₄W₆O₃₄]₂}¹²⁻ polyanion are reported and structurally characterized. These are **1**, **2**, and **3**. The first compound is ammonium salt, the second one is sodium salt with Na(H₂O)_x as a linker forming arrays of the 1D framework. The last structure has different types of calcium countercations with different coordination numbers (7 and 8) on different crystallographic positions forming a dimensional framework.

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