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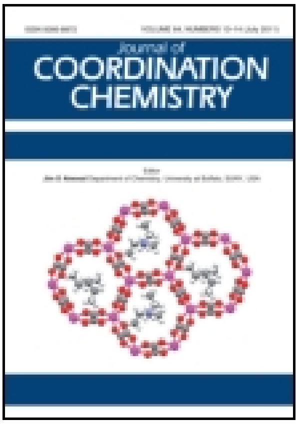

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A new mixed multi-metallic calcium-cobalt-phosphotungstate with nano wheel-like polyanion: $Na_6Ca_3[Ca_2(H_2O)_6Co_9(OH)_3(H_2O)_6(HPO_4)_2(PW$

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A new mixed multi-metallic calcium–cobalt-phosphotungstate with nano wheel-like polyanion: $Na_6Ca_3[Ca_2(H_2O)_6Co_9(OH)_3(H_2O)_6(HPO_4)_2(PW_9O_{34})_3]$

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A new 3-D wheel-like calcium–cobalt phosphotungstate, $Na_6Ca_3[Ca_2(H_2O)_6Co_9(OH)_3(H_2O)_6(HPO_4)_2(PW_9O_{34})_3]$, is reported and characterized by IR, UV, and single-crystal X-ray diffraction. The crystal structure consists of an infinite 3-D array of $[Ca_2(H_2O)_6Co_9(OH)_3(H_2O)_6(HPO_4)_2(PW_9O_{34})_3]^{12-}$ anions (**1**) connected by sodium and calcium metal cations. The novel feature is the presence of two Ca^{2+}, bonded to oxygen of HPO^{4-} and to H_2O spanning opposite sides in the complex anion. The stability of the crystalline product and its morphology were studied by SEM-EDX and DSC techniques.

Keywords: Sandwich polyoxometalates; Alkaline earth metals; Crystal structure; SEM-EDX; DSC

1. Introduction

Polyoxometalates (POMs) [1] exhibit unique structural features which lead to applications in catalysis, medicine, magnetism, electrochemistry, and photochemistry [2].

A survey of the literature reveals that few cobalt containing polyoxotungstates have been structurally characterized [3–25]; the most recent one is 36-tungsto-8-phosphate polyanion that is considered as single-molecule magnets (SMMs) [26]. Compared to other types of POMs, multiple dimensional multi-metallic complex anions containing both transition metals and alkali earth metals are rare [27–45]. In general, such complexes are difficult to prepare due to their low solubility. A literature survey of POMs with an alkali earth metal in the complex anion shows that very few POMs were synthesized and structure determined by X-ray diffraction. The most important of these are: $[CaP_5W_{30}O_{110}]^{13-}$ "Preyssler" [46], $[\{Ca(DMF)_5\}_2SiMo_{12}O_{40}]_n$ [47], $[Me_4N]_{3.5}H_{1.5}[PW_{11}O_{39}Ca(H_2O)_2]\cdot 3H_2O$ [48], $H_2[Ca_2(P_2W_{18}O_{62})(H_2O)_5]\cdot 7.5H_2O$ [27], $\{[Ca(H_2O)]_6[P_4M_6O_{34}]_2\}^{12-}$ [$M = W^{VI}$, Mo^{VI}] [49], $M/[PW_{11}O_{39}]$ ($M = Ca$, Sr) [50], $[Ca_2(GeW_{11}O_{39})(H_2O)_5]$ [51].

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We undertook investigation of POMs with bimetallic centers, a paramagnetic transition metal and a diamagnetic alkaline earth metal. We used cobalt/calcium system as our starting point due to the fact that both cobalt and calcium have +2 oxidation states and are of comparable radii. Other paramagnetic transition metal +2 cations could serve in place of Co^{2+}.

2. Experimental

2.1. *Material and synthesis*

All chemicals were of reagent grade and used without purification. A mixture of $Na_2WO_4 \cdot 2H_2O$ (10.00 g, 30.3 mmol), $Na_2HPO_4 \cdot 12H_2O$ (5.37 g, 15.0 mmol), $CaCl_2$ (1.66 g, 15.0 mmol), and $Co(NO_3)_2 \cdot 6H_2O$ (5.82 g, 20.0 mmol) was dissolved in 100 mL water with vigorous stirring. After dissolution, the pH was adjusted to 6.30 by dropwise addition of 4 mol L^{-1} HCl. The solution was then incubated at 80–90°C for 30 min and turbidity removed by filtration. Finally, NH_4Cl (1.40 g, 26.2 mmol) was added to the solution, stirred, and left to evaporate slowly at ambient temperature. Light purple transparent crystals separated after several days (see "Supplementary material" for crystal shape and color, figure S1).

2.2. *Physical measurements*

IR spectra were recorded with 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. The glass transition temperature (T_g), values were studied with a Netzsch DSC 204 F1 Differential Scanning Calorimeter (Selb Bavaria, Germany). The T_g measurements were conducted on 10 ± 2 mg samples under dry nitrogen. In 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). UV-Vis data were collected from 200 to 700 nm at room temperature on a Varian Cary-100 UV/VIS spectrophotometer. Single-crystal X-ray diffraction data were collected using an Oxford Diffraction SuperNova, Dual, equipped with mirror SuperNova (Mo) X-ray Source ($\lambda = 0.71073$ Å) at 173(2) K. Data collection, reduction, and cell refinement were performed using the software package CrysAlisPro [52]. Empirical absorption corrections were applied using spherical harmonics implemented in SCALE3 (ABSPACK) scaling algorithm. Crystal structure was solved by direct methods, using the program OLEX2 [52], followed by Fourier synthesis, and refined on F^2 with

Table 1. Crystallographic data for the polyanion **1**.

Empirical formula	$W_{27}Co_9P_5O_{132.92}Na_6Ca_{5.28}$
M (g mol^{-1})	2013.53
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal system	Hexagonal
Space group	$P6_{3/m}$
Unit cell dimensions (Å)	
a	20.7334(4)
c	19.7199(4)
Volume (Å^3), Z	7341.4(2), 8
Calculated density (Mg m^{-3})	3.644
Absorption coefficient (mm^{-1})	22.336
F(000)	7031
θ range for data collection (°)	3.1671–28.6393
Index ranges	$-24 \le h \le 15; -13 \le k \le 26; -26 \le l \le 20$
Reflections collected	16,229
Independent reflections	5752 [R(int) = 0.0312]
Completeness to $\theta = 30.13$ (%)	99.53
Max. and min. transmission	1.00000 and 0.67283
Data/restraints/parameters	5752/0/324
Goodness-of-fit on F^2	1.065
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0406$, $wR_2 = 0.1137$
R indices (all data)	$R_1 = 0.0560$, $wR_2 = 0.1182$
Largest difference peak and hole (e Å^{-3})	0.323 and 2.72

SHELXL-97 [53]. Anisotropic least-squares refinement of non-H atoms was applied. All crystallographic plots were obtained using the CrystalMaker program [54]. A summary of the crystallographic data and structure refinement parameters is given in table 1. Full Cartesian coordinates are provided in "Supplementary material" and selected bond distances and angles are given in table 2.

3. Results and discussion

3.1. *Synthesis*

Synthesis of **1** was through a routine procedure involving mixing various amounts of $Na_2WO_4 \cdot 2H_2O$, $Na_2HPO_4 \cdot 12H_2O$, $CaCl_2$ and $Co(NO_3)_2 \cdot 6H_2O$ at different pH. Two different crystalline complexes with the same empirical formula, $Na_6Ca_3[Ca_2(H_2O)_6Co_9(OH)_3(H_2O)_6(HPO_4)_2(PW_9O_{34})_3]$, were separated during the investigation; however, only one proved to be of high enough quality for X-ray structural determination. Weakley synthesized the same polyanion excluding $2Ca^{2+}[P_5Co_9W_{27}O_{119}H_{17}]^{16-}$ as a byproduct (*ca* 5%) in the preparation of $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ [55].

The Weakley synthetic method was by the reaction of HPO_4^{2-}, Co^{2+}, and WO_4^{2-} (1 : 2 : 9) in hot aqueous solution near pH = 7. Then by using KCl, a mixture of salts was precipitated. Extraction by warm water (40°C) containing several salts, potassium, rubidium, cesium, and guanidinium, gave diversified salts of the polyanion with the Rb salt most suited for diffractional studies. The Rb salt crystal structure was determined

Table 2. Selected geometric parameters (Å, °) for **1**.

W1–O13	1.718(8)	P1–O3	1.543(11)
W1–O15	1.781(8)	P1–O7	1.548(12)
W1–O20	1.936(8)	P1–O17	1.560(8)
W1–O6	1.939(8)	P2–O24	1.504(13)
W1–O14	2.022(8)	P2–O2	1.542(8)
W1–O17	2.431(8)	Ca1–O24	2.297(13)
W2–O23	1.738(8)	Ca1–O1C	2.440(16)
W2–O1	1.775(7)	O23–Ca2	2.349(16)
W2–O8	1.917(3)	Co1–O4	2.042(11)
W2–O6	1.938(8)	Co1–O1	2.061(8)
W2–O9	2.008(8)	Co1–O3	2.222(10)
W2–O17	2.415(8)	Co2–O15	2.039(8)
W3–O19	1.728(8)	Co2–O5	2.042(8)
W3–O5	1.771(8)	Co2–O10	2.157(8)
W3–O20	1.924(9)	Co2–O3	2.224(7)
W3–O12	1.952(6)	Co1–O3–Co2	90.6(3)
W3–O16	2.029(9)	O24–Ca1–O1C	80.5(4)
W3–O7	2.432(8)		
W4–O22	1.723(12)		
W4–O16	1.861(9)		
W4–O18	1.947(10)		
W4–O7	2.509(11)		
W5–O21	1.719(9)		
W5–O14	1.861(8)		
W5–O9	1.882(9)		
W5–O18	1.891(9)		
W5–O11	1.926(4)		
W5–O17	2.496(8)		

and reported as hexagonal, $P6_{3/m}$. Our synthesis was slightly different. The Ca salt of the same polyanion core was obtained in high yield by mixing sodium tungstate, disodium hydrogen phosphate, and calcium chloride, adjusting the pH to 6.5, and finally salting out crystals by NH_4^+. Ca^{2+} was included in the original mixture of salts as calcium chloride. Our crystal so obtained came out to be also hexagonal, $P6_{3/m}$, similar to that obtained by Weakley, but in our case Ca^{2+} proved to be bonded to the core polyanion, $[P_5Co_9W_{27}O_{119}H_{17}]^{16-}$, giving $[Ca_2(H_2O)_6Co_9(OH)_3(H_2O)_6(HPO_4)_2(PW_9O_{34})_3]^{12-}$. Ca^{2+} also serves in our structure, together with Na^+, as counter cations.

3.2. *UV spectrum*

The UV spectrum has two absorption bands, the lower energy band at 200 nm attributed to the charge transfer of O_d–W and O_b/O_c–W. The visible spectrum has an absorption band at 557 nm, which is attributed to d–d transitions of Co^{2+}. Longer wavelength transitions may take place with less probability at *ca* 710 nm. **1** in aqueous medium at pH = 6.5 is stable for at least one week as seen clearly in figure S2.

3.3. *DSC*

DSC analysis (figure S3) shows thermal stability of **1** to about 120°C when water is evaporated. No significant change takes place from 200°C to 500°C.

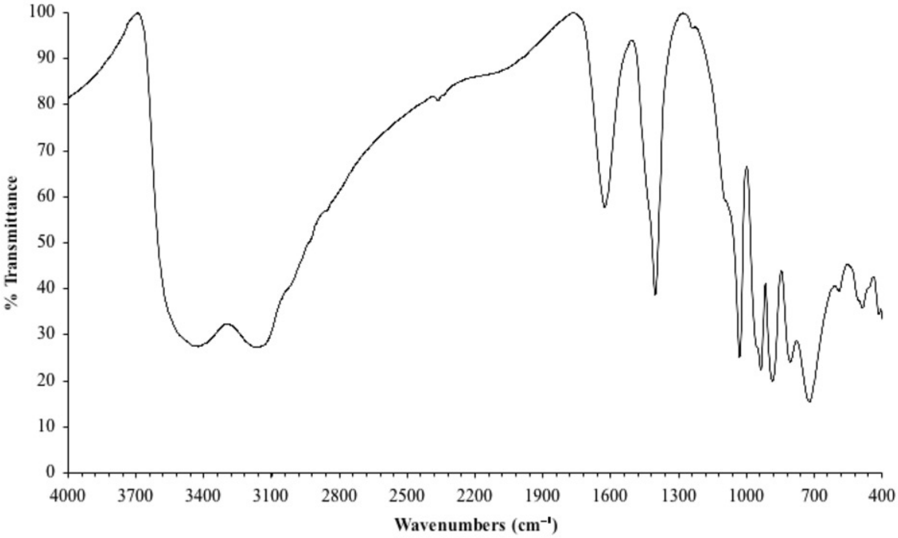

Figure 1. FT-IR spectra of **1**.

3.4. *IR spectrum*

In the IR spectrum of **1**, peaks at 3455 (b), 3170 (b), 1628 (sh), 1097 (w), 1030 (sh), 955 (w), 935 (sh), 887 (sh), 808 (sh), 725 (sh), 595 (sh), and 509 (m) cm^{-1} are attributed to $\nu(\mathrm{P{-}O_a})$, $\nu(\mathrm{W{-}O_d})$, $\nu(\mathrm{W{-}O_a})$, $\nu(\mathrm{W{-}O_b})$, and $\nu(\mathrm{W{-}O_c})$ of **1** (figure 1).

3.5. *SEM-EDX analysis*

SEM was used to investigate the morphology of **1**. Figure 2 shows the morphology of a crystal of **1** obtained from aqueous media at pH = 6.3 and 7.0 (figure 2A1 and B1), respectively, and after exposure to air for one week (figure 2A2 and B2), respectively. The SEM images show that the stability of the crystals is relative to the pH; the higher the pH the more stable the crystals. Other conclusion from these images is that crystal size is pH-dependent. The higher the pH the larger are the crystals. Finally, higher crystalline purity is favorable at pH = 6.5. The EDX mapping of **1** confirms the existence of P, W, Ca, and Na within the crystal. The existence of Na and Ca was also confirmed using atomic absorption spectroscopy technique.

3.6. *Crystal structure*

The complex anion exhibits $\mathrm{Co_9}$ core similar to that in the anion reported by Weakley [11]. This complex anion is important due to its magnetic properties studied extensively by Galán-Mascarós *et al.* [56]. The core anion of **1** has crystallographic symmetry $3/m$-C_{3h}.

Polyhedral representation of the core nanocobalt of **1** is shown in figure 3. This complex contains a central $\mathrm{Co_9O_{36}}$ cluster, formed from three aggregates of $\mathrm{Co_3O_{13}}$.

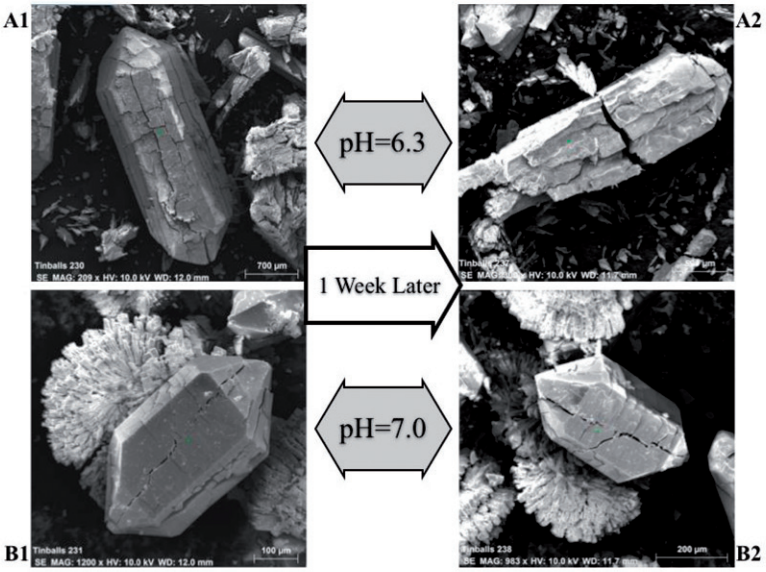

Figure 2. SEM images for **1** under different conditions (pH and time).

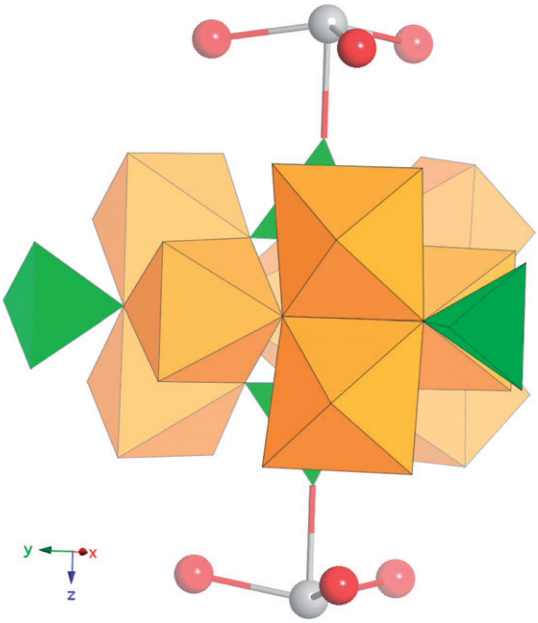

Figure 3. Structure of the Co_9 cluster showing the connections through oxygen and HPO_4^{2-} and $Ca(H_2O)_n$ groups. Orange: cobalt octahedra, green: phosphorous tetrahedra, gray: calcium, red: oxygen.

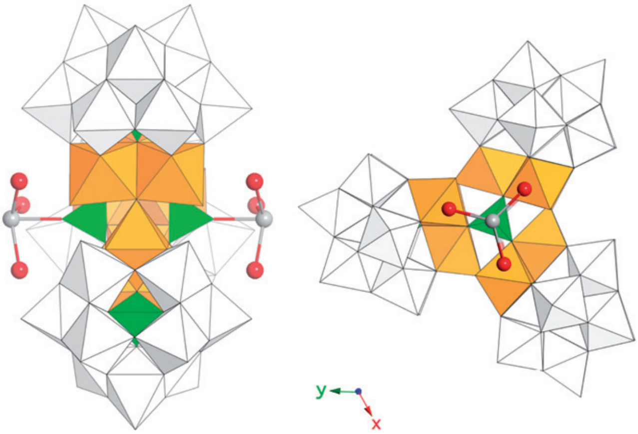

Figure 4. Different polyhedral representations of **1**. Right: along the *z*-axis, left: along the *y*-axis. Orange: cobalt octahedra, red: oxygen, green: phosphorous tetrahedra, gray: calcium, white: tungsten octahedra.

Each Co_3O_{13} aggregate is made from three octahedra sharing edges. Three OH^- bridging groups and two central HPO_4^{2-} groups connect each two Co_3O_{13} aggregates to each other forming a triangle (figure 3). Only two of the three Co centers have a coordinated water molecule, as the third has an OH^- bridging two Co_3O_{13} aggregates.

On the periphery of this central Co_9O_{36} cluster, three diamagnetic $(PW_9O_{34})^{9-}$ encapsulate the Co_9O_{36} core, coordinating to Co_3O_{13} triangles forming a reconstituted Keggin-like structure $\{PCo_3W_9O_{40}\}$. Hence, the polyoxoanion may be viewed as resulting from condensation of three of these Keggin units. The structural parameters are in the recognized range for phosphotungstates found in the literature [57–61]. The main bonds are: W–O (apical), 1.718–1.738 Å; W–O (terminal), 1.771–2.029 Å; P–O, 1.542–1.560 Å whereas the P–O (hydroxyl) P–O–H is 1.504 Å. The three cobalt centers in each triad of **1** are not equivalent because only one of them has a terminal water molecule. All cobalt centers are basically octahedrally coordinated to oxygen with cobalt–oxygen distances (2.038–2.224 Å) pending on the disposition of the bridging oxygen atoms. Selected distances are shown in table 2 and full distances and angles are in table S1.

The interesting point in **1** is in the $(H_2O)_x$Ca–O–P surface aggregates. Figure 4 shows wheel-like structure $(H_2O)_3Ca(POM)Ca(H_2O)_3$. $Ca^{2+}(1)$ falls on the C_3-axis, however, the three oxygen atoms of bonded water are disordered over several positions. Another oxygen atom of water is *trans* to the Ca–O–P bond, however, this was highly disordered and could not be located. The calcium to hydroxide oxygen of HPO_4^{2-}, Ca–O–P, has bond distance of 2.297 Å along the *z*-axis while the Ca–O(H_2O) is 2.440 Å. These bond lengths are in the range accepted for five and six coordinated Ca^{2+} according to ICSD [62]. The Ca–Ca distance across the anion is 11.601 Å (~1.6 nm).

Whereas $Ca^{2+}(1)$ is bonded to a phosphate tetrahedron *via* an oxygen, $Ca^{2+}(2)$ is bonded to a tungstate octahedron *via* an oxygen, and is hydrated by a number of water molecules, as shown in figure 5. The $Ca^{2+}(2)$ is coordinated to four water molecules and one oxygen atom of the POM. One of these water molecules bridges two O(W)Ca(H_2O) moieties. The Ca(2)–O distances are in the range 2.339–2.620 Å, average 2.509 Å.

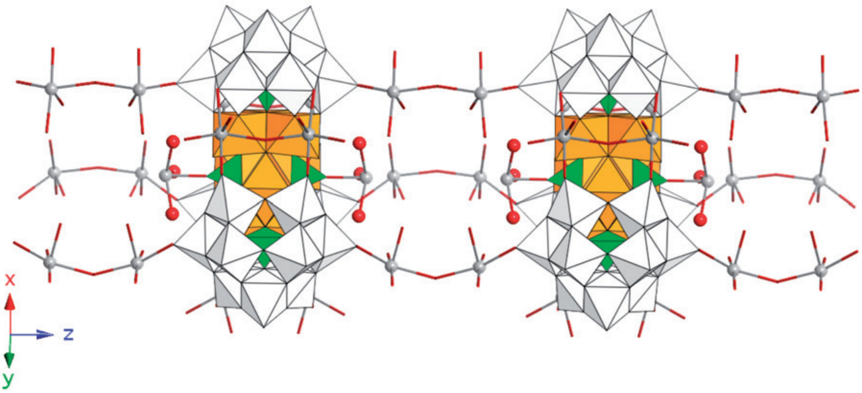

Figure 5. A view of $Ca^{2+}(2)$ connecting the polyanion **1** into chains along the *z*-axis.

The coordination sphere of $Ca^{2+}(2)$ is distorted trigonal bipyramidal. The equatorial angles are 74.884°, 89.821°, and 150.918° and the average of the six axial angles is 93.03°, which is close to the ideal 90°. These distances are in range with other calcium systems reported in the literature [27, 46–51, 63].

Sodium ions maintain electrical neutrality and function to hold the polyanion chains together making a 3-D framework (figure 5). These sodium ions are disordered over different sites; disorder in sodium is common and encountered in many reported polyoxotungstates.

We are now trying to obtain solid multi-metallic calcium POMs with interesting 2-D/3-D frameworks.

4. Conclusion

We report the synthesis and structure of an interesting new calcium–cobalt-containing POM. This species provides a new example of nanoscale tungstophosphate aggregates with calcium–cobalt metals. The morphology of the crystal under pH/time conditions was studied by EDX-SEM. The difficulty in obtaining calcium-containing POMs due to limited solubility makes the crystal structure of this complex novel. The P–O and Co–O distances in **1** are comparable with the corresponding cobalt analogs in the literature [3–45, 57–61]. Also, M–O bond lengths for μ_3-OH, μ_2-O, and OH_2 are close to those found in other phosphotungstate clusters. If calcium cations can be substituted by other metals, e.g. lanthanide or actinide, we will obtain other derivatives of this POM. The interesting point in the systems is in the Ca–O–P surface aggregates on the POM. The structure is wheel-like and could be abbreviated as $(H_2O)_xCa(POM)Ca(H_2O)_x$. Although the phosphotungstate is found in the literature, we have synthesized a complex of such with crystals of high quality. Further investigation to obtain other polyanions with calcium is currently underway.

Supplementary material

CSD-CCDC 849276 contains the supplementary crystallographic data for this article. Full bond lengths and angles are supplied.

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