Synthesis, Structure, and Properties of Alkaline-earth-substituted Tungstogermanate: $[K_{2.5}(H_2O)_{1.5}]_2H_3[Ca_2(GeW_{11}O_{39})(H_2O)_5]_2 \cdot 7H_2O$

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A novel alkaline-earth-metal-substituted tungstogermanate derivative $[K_{2.5}(H_2O)_{1.5}]_2H_3[Ca_2(GeW_{11}O_{39})(H_2O)_5]_2 \cdot 7H_2O$ (**1**) has been synthesized and characterized by IR, UV spectroscopy, ICP, TG, electrochemical behavior, and X-ray diffraction. The title compound consists of an infinite 2D arrangement built up of $[\alpha\text{-GeW}_{11}O_{39}]^{8-}$ anions connected by alkaline earth metal cation Ca^{II}.

Polyoxometalates (POM) are rich and diverse class of compounds that are of interest for both fundamental studies and practical applications.[1] Recently, POM chemistry has provoked great interest, and numerous novel compounds with fascinating topological beauty and important electronic, optical, magnetic, and catalytic properties have been developed.[2] Since Peacock and Weakley first reported that the monovacant Keggin anions $[XW_{11}O_{39}]^{n-}$ (X = Si^{IV} and P^{V}) form both 1:1 and 1:2 compounds with rare earth ions in solution,[3] a fascinating interest in rare earth/monovacant POMs system was provoked.[4] Phosphotungstates and silicotungstates are the most intensively studied systems so far, because they have a large variety of lacunary precursor species. However, the derivatives based on the monovacant tungstogermanates are rare, and s-block elements in POMs crystals had been paid less attention.[5] Furthermore, the alkaline earth metal ions possess the outer electronic configuration of ns^2np^6, showing the larger ionic radii, higher positive charge, owing the high coordination requirement, and oxophilicity. Thus, the alkaline earth metal ions may also be the excellent bridge in the process of building multiple dimensional complexes. Herein, we report on a new compound $[K_{2.5}(H_2O)_{1.5}]_2H_3[Ca_2(GeW_{11}O_{39})(H_2O)_5]_2 \cdot 7H_2O$ (**1**) which is the first example that introduced the alkaline earth metal cation Ca^{II} into the lacunary tungstogermanate system.

Compound **1** was synthesized in aqueous solution under the moderate condition.[6] Single-crystal X-ray diffraction study[7] reveals that the title compound displays an infinite 2D arrangement built up of $[\alpha\text{-GeW}_{11}O_{39}]^{8-}$ anions connected by alkaline earth metal cations Ca^{II}. The structure unit of compound **1** consists of two $[K_{2.5}(H_2O)_{1.5}]^{2.5+}$ cations, two $[Ca_2(GeW_{11}O_{39})(H_2O)_5]^{4-}$ polyanions and seven crystal water molecules.

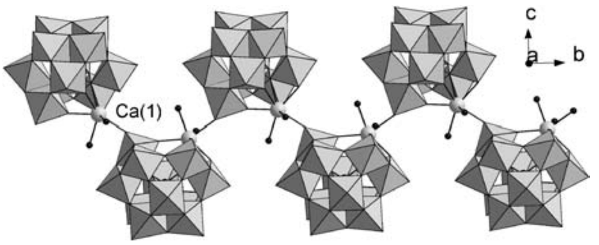

Figure 1. Polyhedral view of the zigzag chain in compound **1** along the *a* axis.

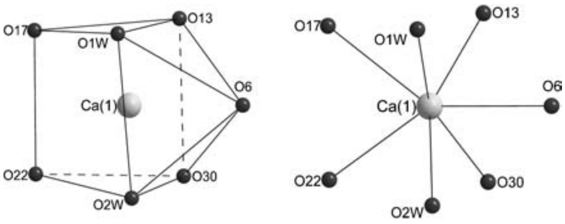

Figure 2. (a) The coordination polyhedron around Ca(1). (b) The coordination environment around Ca(1).

The $Ca^{2+}(1)$ cation occupies the vacant site of an $[\alpha\text{-GeW}_{11}O_{39}]^{8-}$ unit and is coordinated to the four available oxygen atoms of the lacunary site ($d_{\text{Ca–Ob,c}} = 2.397(18)$ Å). Connection of the neighboring $[\alpha\text{-GeW}_{11}O_{39}]^{8-}$ subunit occurs via Ca(1)–O_d bonds ($d_{\text{Ca(1)–Od}} = 2.472(18)$ Å) forming one-dimensional infinite zigzag chain (Figure 1) with the shortest interchain Ca(1)–Ca(1) distances, 7.223(10) Å. The coordination sphere of the $Ca^{2+}(1)$ center is completed by two water molecules ($d_{\text{Ca(1)–Ow}} = 2.48(2)$ Å). Thus, the $Ca^{2+}(1)$ center is seven-coordinated adopting a distorted monocapped trigonal prism geometry, which is very similar to that of the rare earth centers (Yb^{3+} and Y^{3+}) in compounds $KCs_4[Yb(\alpha\text{-SiW}_{11}O_{39})(H_2O)_2] \cdot 24H_2O$[4c] and $[(CH_3)_4N]_{2.5}H_{2.5}[Y(GeW_{11}O_{39})(H_2O)_2] \cdot 4H_2O$,[5d] and is different from the square pyramidal coordinated alkaline metal center Na^+ in $[(CH_3)_4N]_4Na_2H[\alpha\text{-GeW}_{11}O_{39}] \cdot 8H_2O$.[5e] As shown in Figure 2, the oxygen atom (O6) occupies the cap position, and the distance from the cap to the relative side plane formed by O30, O2W, O1W, and O13 is 1.9518 Å. The mean plane deviations of three side planes (formed by O22, O30, O13, O17; O2W, O22, O17, O1W; and O30, O2W, O1W, O13) are 0.0120, 0.0536, and 0.0385 Å, respectively. Two sets of O atoms (O17, O13, O1W and O22, O30, O2W) constitute the two basal planes, and the distances from them to Ca(1) are 1.5486 and 1.5431 Å, respectively.

The coordination environment of $Ca^{2+}(2)$ center is similar to that of $Ca^{2+}(1)$, but the ligands are rather different. The $Ca^{2+}(2)$ coordination cation is also heptacoordinated displaying a distorted monocapped trigonal prism geometry and an increase of the distortion probably caused by various ligands. It bonds to the $[\alpha\text{-GeW}_{11}O_{39}]^{8-}$ building block (Figure 3a) via both one terminal oxygen atom (O11) ($d_{\text{Ca(2)–O11}} = 2.80(2)$ Å) and one bridging oxygen atom (O33) ($d_{\text{Ca(2)–O33}} = 2.936(16)$ Å) and is coordinated to other two $[\alpha\text{-GeW}_{11}O_{39}]^{8-}$ anions (subunits 3 and 4) via two terminal oxygen atoms (O5#8 and O8#5) ($d_{\text{Ca(2)–O5\#8}} = 2.95(2)$ Å, $d_{\text{Ca(2)–O8\#5}} = 2.76(2)$ Å) forming the two-dimensional framework (Figure 3b). Three water molecules complete the coordination sphere of the calcium center

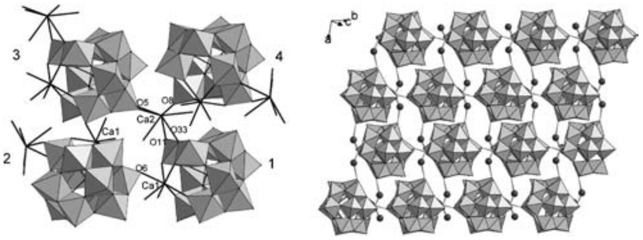

Figure 3. The molecular coordination mode (a) and arrangement (b) of the polyanion in $[K_{2.5}(H_2O)_{1.5}]_2H_3[Ca_2(GeW_{11}O_{39})(H_2O)_5]_2 \cdot 7H_2O$.

($d_{\mathrm{Ca(2)–Ow}} = 2.877(2)$ Å). In addition, the two polyanions $[\alpha\text{-}GeW_{11}O_{39}]^{8-}$ (subunits 2 and 3) are connected by another Ca(1) center, together with the two Ca^{2+} centers supported by the same subunit $[\alpha\text{-}GeW_{11}O_{39}]^{8-}$ (subunit 1) displays a ring around by four vacant Keggin-type heteropolyanions $[\alpha\text{-}GeW_{11}O_{39}]^{8-}$ with the distances of the Ca–Ca ranging from 6.258(9) to 7.223(10) Å. The incorporation of the K^+ coordinated cations results in a three-dimensional network. Thus, the 3D structure may be rationalized in terms of layers connected by K(3) atoms via K3–O_d and K3–O_b bonds ($d_{\mathrm{K(3)–Ob,d}} = 2.972(19)$ Å). The K(3) center is six-coordinated adopting a distorted hexagonal planar geometry which is rather unusual. In addition, the bond valence sum calculations of oxygen atoms are 1.512 for O1, and 1.483 for O4, which are far from 2, suggesting that O1 and O3 atoms have been monoprotoned. However, they cannot be accurately located by X-ray diffraction and BVS calculations, the remaining one proton may be delocalized in the polyanion.

The IR spectra of compound **1** show the characteristic vibrational patterns of the Keggin-type structure. In comparison with the IR spectrum of precursor $\alpha\text{-}K_8GeW_{11}O_{39} \cdot nH_2O$,[9] the ν_{as}(W–Ot) vibrational frequency (949 cm^{-1}) has a red shift of 12 cm^{-1}, the possible major reasons for which may be that the Ca^{II} cation has stronger interaction to the W–Ot bond, reducing the W–Ot bond force constant and leading to a decrease in the W–Ot vibration frequency. This indicates that the alkaline earth metal cation Ca^{II} behaves similarly to the rare earth cations in the substituted tungstogermanate.[5d] The ν_{as}(W–Ob–W) frequencies show two peaks at 878 and 791 cm^{-1}, as for ν_{as}(W–Oc–W), only one absorption peak at 706 cm^{-1}. The ν_{as}(Ge–O) frequency at 523 cm^{-1} is almost equal to that of the precursor. The UV spectra in aqueous solution for compound **1** in the range of 400–190 nm reveal an absorption band at 253 nm, which is assigned to the pπ–dπ charge-transfer transitions of $O_{b(c)} \rightarrow W$ band.

The TG curve of the title compound shows only one stage weight loss, giving a total loss of 5.88% of its initial weight in the range of 30–290 °C, which approximately corresponds to the release of 7 crystal water, three coordination water molecules, and 11.5 structural water molecules (6.28% calculated) per formula unit of the title compound.

Cyclic voltammograms of compound **1** indicate that two redox waves with midpoint potentials at −0.84 and −0.61 V are observed in the pH 4.50 medium. However, both redox waves are chemically irreversible owing to the peak potential separations of 190 mV for the first wave and 150 mV for the second.

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6 Synthesis: $\alpha\text{-}K_8GeW_{11}O_{39} \cdot nH_2O$ was prepared according to the literature[8] and confirmed by IR spectroscopy. Other reagents were purchased commercially and used without further purification. Preparation of $[K_{2.5}(H_2O)_{1.5}]_2H_3[Ca_2(GeW_{11}O_{39})(H_2O)_5]_2 \cdot 7H_2O$: A 2.32 g (0.71 mmol) portion of $\alpha\text{-}K_8[GeW_{11}O_{39}] \cdot nH_2O$ was dissolved in 20 mL of water at 80 °C, followed by a dropwise addition of 0.16 g (1.42 mmol) of $CaCl_2$ in 5 mL water. After 1 h, the solution was cooled to room temperature, and the precipitate was removed by filtration. Then 0.4 g of potassium chloride was added. The resulting clear solution was filtered and left to evaporate at room temperature. The next day, colorless crystals suitable for X-ray diffraction were collected. Yield: 1.6 g (72%). Anal. Calcd for $K_5H_{43}O_{98}Ge_2Ca_4W_{22}$: K, 3.18; Ge, 2.36; Ca, 2.60; W, 65.69. Found: K, 3.28; Ge, 2.27; Ca, 2.54; W, 66.19.

7 Crystallographic data: For **1**: $K_5H_{43}O_{98}Ge_2Ca_4W_{22}$, $M_r = 6157.04$, monoclinic, $C2/c$, $a = 41.05(5)$, $b = 13.854(17)$, $c = 19.29(2)$ Å, $\beta = 113.268(18)°$, $V = 10075(22)$ Å^3, $T = 293(2)$ K, $Z = 4$, $\mu = 26.108\ \mathrm{mm}^{-1}$, 22409 reflections measured, 8318 independent ($R_{\mathrm{int}} = 0.1126$), $R_1 = 0.0651$ ($I > 2\sigma(I)$), $wR_2 = 0.1276$ (all data). CSD number: 418550.

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