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Self-assembly of a lacunary α-Keggin undecatungstophosphate into a three-dimensional network linked by *s*-block cations†‡

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The crystal structure of $[(CH_3)_4N]_4Na_2H[\alpha\text{-}PW_{11}O_{39}]\cdot 8H_2O$ has been determined by using the Weissenberg camera at the BL04B2 beamline of SPring-8, revealing that it contains a disorder-free lacunary $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ anion with one sodium cation embedded into its lacuna that links the oxometalate building blocks into a one-dimensional chain, which is then woven into a three-dimensional latticework by another Na^+.

Recent interest in synthetic chemistry of polyoxometalates (POMs) largely focuses on rational syntheses of larger complexes, having either extended[2–9] or discrete[2,10–15] structures. Most of their syntheses utilize the strategy of self-assembly of building blocks. As the linker atoms to bridge building blocks, *f*-block elements have been widely used to connect complete[2,3,10] or lacunary[2,4,11] POMs. Other linkers hitherto reported include *d*-block[2,5–7,12–14] and, less frequently, *p*-block[15] elements. Assembly of organic derivatives of POMs *via* their organic moieties has also been reported.[8] However, *s*-block elements in POM crystals have been paid much less attention as linker atoms assisting the self-assembly of POM building blocks. Exceptions include, for example, $[Et_3NH]_3[NaMo_8O_{26}]$, where a Na^+ cation links complete β-octamolybdate anions into a zigzag chain.[9] Here we report the first extended POM structure wherein sodium, an *s*-block element, links lacunary Keggin anions into infinite linear chain, which exemplifies a new mode of self-assembly of POMs.

During an attempt to introduce Ti atoms into lacunary tungstophosphates, crystals of $[(CH_3)_4N]_4Na_2H[\alpha\text{-}PW_{11}O_{39}]\cdot 8H_2O$ (**1**) were obtained.§ It is a polymorphic modification of the compound reported by Fuchs and coworkers, in which the anion was fully disordered.[16] Since efforts to grow larger crystals had been unsuccessful, a single crystal X-ray diffraction experiment was carried out at a synchrotron facility. A colorless crystal measuring 0.070 × 0.015 × 0.010 mm was mounted on the imaging plate Weissenberg camera installed in the BL04B2 beamline of SPring-8.[1] 35 diffraction images were obtained in the oscillation mode with high-energy X-rays (λ = 0.3282 Å). The procedure for the data reduction was the same as that described in ref. 1. The structure was solved by direct methods and refined by the use of *SHELX97*.[17]¶

An asymmetric unit of **1** includes an $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ anion with the lacunary α-Keggin structure, two Na^+ cations, four tetramethylammonium cations, eight water molecules of crystallization, plus one proton that could not be located by this structure analysis. As depicted by Fig. 1, one of the two independent Na^+ cations, Na1, is embedded into the lacuna of the $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ anion with four shorter Na–O contacts (to O12–O15, 2.210–2.312 Å) plus one longer contact (to O36, 2.711 Å). Na1 is also coordinated by a terminal O atom, O10, of an adjacent $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ anion at 2.269 Å, to complete a square pyramidal (disregarding the Na1··O36 contact) or distorted octahedral (Na1··O36 contact taken into account) coordination. Through the linkage at Na1, the lacunary $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ anions form a one-dimensional chain structure running along the crystallographic *a* + *c* direction as illustrated in Fig. 2. The lacunary anions in this chain are related by a glide plane, just like those in $[NEt_3H]_5[XCo^{II}W_{11}O_{39}]\cdot 3H_2O$ (X = P or As).[5] Similar chain structures, $(Et)_{8n}[PMnW_{11}O_{39}]_n\cdot 2nH_2O$[6] and $[Co(dpa)_2(OH_2)_2]_2[Hdpa][PCoW_{11}O_{39}]$,[7] have also been reported. As this linkage aligns the $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ building blocks almost parallel with respect to their dipoles, the resultant linear chain is highly polarized. And all these polarized chains run parallel to each other, giving a highly polarized nature to the whole crystal. Fig. 1 also illustrates that another Na^+ cation, Na2, is coordinated by two terminal O atoms of two $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ anions related by a lattice translation, $(a \pm b)/2$. With three O atoms of water molecules of crystallization, Na2 completes a trigonal bipyramidal coordination with the POM moieties as equatorial ligands. A similar linkage where

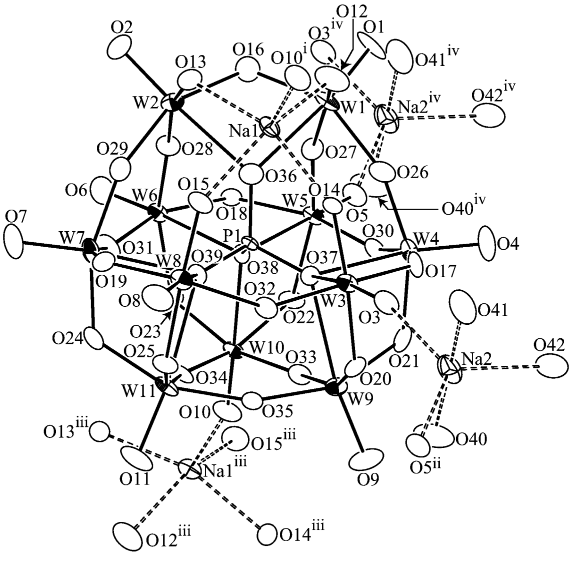

Fig. 1 An *ORTEP*[18] drawing of the $[PW_{11}O_{39}]^{7-}$ anion and its associated Na^+ cations. Displacement ellipsoids are scaled to enclose 50% probability levels. Selected distances (Å): Na1–O12–W1–O27–W5–O22–W10–O34–W11–O25–W8–O15–Na1: 2.312, 1.730, 2.081, 1.788, 1.941, 1.906, 1.885, 1.924, 1.825, 2.056, 1.738, 2.292; Na1–O13–W2–O28–W6–O23–W10–O33–W9–O20–W3–O14–Na1: 2.305, 1.761, 2.067, 1.812, 1.977, 1.889, 1.890, 1.934, 1.863, 2.052, 1.732, 2.210; W1–O16–W2–O29–W7–O24–W11–O35–W9–O21–W4–O26–W1: 1.893, 1.939, 1.904, 1.897, 1.912, 1.925, 1.889, 1.934, 1.873, 1.935, 1.829, 1.965; W3–O17–W4–O30–W5–O18–W6–O31–W7–O19–W8–O32–W3: 1.986, 1.870, 1.901, 1.915, 1.931, 1.910, 1.929, 1.885, 1.899, 1.952, 1.940, 1.873; Na1–O10^{i} 2.269, Na1-O36 2.711, Na2-O3 2.342, Na2-O5^{ii} 2.395, Na2-O41 2.413, Na2-O40 2.38, Na2-O42 2.28 Å. Standard uncertainties associated with these distances are 0.010–0.016 Å for W–O and 0.013–0.03 Å for Na–O. Symmetry codes: (i) $x+1/2, -y+1/2, z+1/2$; (ii) $x+1/2, y-1/2, z$; (iii) $x-1/2, -y+1/2, z-1/2$; (iv) $x-1/2, y+1/2, z$.

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† High-Energy X-ray Structure Determinations Using Synchrotron Radiation. Part 3. Part 2: reference 1.

‡ Electronic supplementary information (ESI) available: *ORTEP* plot of the asymmetric unit of **1** and rotatable 3-D crystal structure diagrams in CHIME format. See http://www.rsc.org/suppdata/cc/b2/b209076g/

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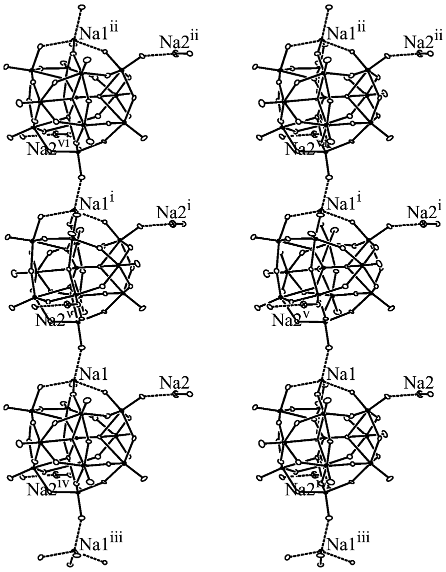

Fig. 2 A stereoscopic diagram of the infinite $(Na^+\cdots[PW_{11}O_{39}]^{7-})_\infty$ chain structure running along the $a + c$ axis, viewed along the b axis. Symmetry codes: (i) $x+1/2, -y+1/2, z+1/2$; (ii) $x+1, y, z+1$; (iii) $x-1/2, -y+1/2, z-1/2$; (iv) $x-1/2, y+2/1, z$; (v) $x, -y, z+1/2$; (vi) $x+1/2, y+1/2, z+1$.

octahedrally coordinated Na^+ links POMs has been reported.[12] Through the connection at Na2, the $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ anions are linked into secondary one-dimensional chain structure running alternately along the $a + b$ and $a - b$ directions. The chains running along $a + b$ are arranged parallel to each other into a layer parallel to the 001 plane without any interactions with each other. A layer above it accommodates chains running along $a - b$, which are perpendicular to the chains in the layer below. Thus the interaction at Na2 links the $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ anions into alternating perpendicular arrays of parallel chains like the logs in a log cabin (see Fig. S1†). The interaction at Na1 are running through the eclipsed points in this arrangement.

These cation linkages are pinning down the orientation of the $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ anion, which had been disordered in other salts with *s*-block cations,[16,19] and thus the effect of the incorporation of the *s*-block element into the lacuna of the anion is clearly observed. The W–O(–Na1) distances (1.730 to 1.761 Å) are shorter than the other W–μ_2-O distances, to compensate for the smaller Na1–O bond valences. Their *trans* influences propagate to the W atoms four bonds away from Na1 in the NaW_5O_6 closed loops[20] (Na1–O12–W1–O27–W5–O22–W10–O34–W11–O25–W8–O15–Na1 and Na1–O13–W2–O28–W6–O23–W10–O33–W9–O20–W3–O14–Na1), exhibiting the alternating long and short W–O distances. Average distances for the Na–O–W–O–W–O–W sequence are 2.28(5), 1.74(1), 2.06(1), 1.82(3), 1.94(2) and 1.89(1) Å, respectively. The average W–O distances in the other two W_6O_6 closed loops is 1.91(3) Å. Although Na^+ cations in lacunae of a lacunary POM have already been structurally characterized,[13] the present study is the first to reveal that the structural distortion caused by the incorporation of Na^+ propagates over the whole POM framework. These structural features may provide the closest approximation to isolated (if there are any) lacunary Keggin $[XM_{11}O_{39}]^{n-}$ anions, since other disorder-free structures incorporate *f*-block[4,11] or *d*-block[7] atoms that would more tightly bind to the lacunae than Na^+.

A common feature observed in **1** and $[Et_3NH]_3[NaMo_8O_{26}]$,[9] where linkages of POM building blocks by *s*-block elements are observed, is that the crystals are double salts of *s*-block cations and organic cations. As the charge of the *s*-block cations is only +1, simple salts of highly charged POMs with solely the *s*-block cations would require a considerable number of cations, which would then lead to complicated intermolecular interactions. Introduction of organic cations reduces the number of *s*-block cations and its relevant intermolecular interactions, leading to, at least in these examples, well organized and easily distinguishable extended three-dimensional structure. This double salt strategy might be applied for designing various kinds of ionic solids, especially those with highly charged ions.

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Notes and references

§ The crystal used for the X-ray diffraction experiment was obtained as follows: 5.00 g of $Na_2WO_4\cdot 2H_2O$ and 0.90 g of NaH_2PO_4 were dissolved in 20 mL of H_2O. After adjusting its pH to 6.0 with hydrochloric acid, 0.15 mL of $TiCl_4$ was added to the filtrate. The mixture was refluxed for 1 h. After cooling the solution to room temperature, the solution was filtered and 1.00 g of $(CH_3)_4NCl$ was added. After keeping the solution at room temperature, colorless thin-plate crystals were obtained. Found: C, 6.30; H, 2.25; N, 2.05%. Calcd for $C_{16}H_{65}N_4O_{47}Na_2PW_{11}$: C, 6.07; H, 2.07; N, 1.77%. ν_{max}/cm^{-1} 1078(m), 1042(m), 947(vs), 892(sh), 858(s), 803(vs), 762(vs), 515(w). This compound was confirmed to be also obtainable by a similar procedure without $TiCl_4$.

¶ Crystal data for **1**: $C_{16}H_{65}N_4O_{47}Na_2PW_{11}$, $M = 3165.0$, monoclinic, $a = 18.494(1)$, $b = 18.102(1)$, $c = 19.214(1)$ Å, $\beta = 106.206(3)$ °, $V = 6176.8(6)$ Å^3, $T = 153$ K, space group Cc (no. 9), $Z = 4$, $\mu(0.3282$ Å$) = 2.73$ mm^{-1}, $D_x = 3.403$ Mg m^{-3}, 25381 reflections measured, 14592 unique ($R_{int} = 0.0391$) which were used in all calculations. The final $wR(F^2) = 0.1385$ for all data and $R = 0.0543$ for 13509 reflections with $F^2 > 2\sigma(F^2)$. CCDC reference number 194132. See http://www.rsc.org/suppdata/cc/b2/b209076g/ for crystallographic data in CIF or other electronic format.

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