

Investigating Cation Binding in the Polyoxometalate-Super-Crown [P₈W₄₈O₁₈₄]⁴⁰⁻

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From alicyclic and aromatic rings to organic macrocycles,^[1] and giant inorganic nanowheels,^[2] the ring structure is pervasive throughout chemistry. In particular, ring-shaped polyoxometalates (POMs) are common.^[3] POMs comprise early transition-metal centers in high oxidation states linked together through oxygen bridges to give clusters of well-defined size and shape.^[4] Two main factors may explain the tendency of POMs to form crown-type species in aqueous solution: this type of assembly minimizes the potential for further self-aggregation, otherwise causing precipitation, whilst allowing the optimal interaction with the solvent.

The crown-type heteropolyanion, [P₈W₄₈O₁₈₄]⁴⁰⁻ (**1**, abbreviated as {P₈W₄₈}) was first reported as a mixed potassium/lithium salt, K₂₈Li₅H₇[P₈W₄₈O₁₈₄]·92H₂O by Contant and Tézé in 1985.^[5] In the years immediately following their publication in *Inorganic Chemistry*, {P₈W₄₈} was largely ignored by POM chemists, perhaps due to the reported “inertness” of the material. Although the suggestion that {P₈W₄₈} was unreactive towards divalent and trivalent transition-metal cations was misleading, this should not detract from its comprehensive and considerable contribution to POM chemistry. Indeed, not only did Contant and Tézé provide us with the largest polytungstate species of that time, and for some years following, their strategy in utilizing lacunary heteropolyanion building blocks in the construction of larger POM aggregates has been repeated many times over.^[6]

Potassium cations are commonly encountered as a means of balancing heteropolyanion charge in POM chemistry. However, the presence of K⁺ often limits the solubility of the material and increases the tendency towards aggregation in solution, causing precipitation. Therefore, to explore the functionality of {P₈W₄₈} as a POM macrocycle, the large number of potassium cations present in the compound must be removed. Presented herein are two novel compounds containing the {P₈W₄₈} ring, which are entirely deficient of potassium. The preparation of Li₁₇(NH₄)₂₁H₂[P₈W₄₈O₁₈₄]·85H₂O (**1a**), and the related com-

pound Li₁₂(NH₄)₂₁H_{6.6}{W_{0.1}O_{0.1}(OH₂)_{0.1}}[P₈W₄₈O₁₈₄]·69H₂O (**1b**),^[7] have enabled us to study cation binding in the cyclic heteropolyanion and investigate the effect these supra-molecular interactions have on the {P₈W₄₈} unit. The ability to characterize binding sites in the cluster would be an important step towards designing materials based on {P₈W₄₈}, crucially allowing control over internal and external functionalization.

The building block adopted in the synthesis of {P₈W₄₈} is the hexalacunary Wells–Dawson-derived tungstophosphate [α-H₂P₂W₁₂O₄₈]¹²⁻ (abbreviated as {P₂W₁₂}). Four units of this metastable precursor combine in solution to give the distinctive crown-type {P₈W₄₈} assembly with approximate *D*_{4h} symmetry. Within the (ca. 1 nm-sized) cavity reside eight potassium ions, each in one of two critical, templating sites (Figure 1). These alkali metal cations play a key role in lowering the repulsive interactions of the exposed, nucleophilic, inner-ring oxygen surface. As a result, {P₈W₄₈} is stable over a broad pH range—remarkable for such a poly-lacunary cluster, and in contrast to the complex equilibration of its {P₂W₁₂} precursor in solution (particularly with α₁-[P₂W₁₇O₆₁]¹⁰⁻).^[8,9] Under carefully selected conditions, the electrochemistry of {P₈W₄₈} proceeds through three successive, chemically reversible eight-electron waves. This considerable electron-storage capability, combined with the unique stability of the {P₈W₄₈} heteropolyanion, confers effective catalytic properties, as demonstrated in the reduction of nitrites.^[8]

Over the past decade, the initial indifference of the POM community towards {P₈W₄₈} has been redressed, with a number of papers published concerning transition-metal substitution,^[10] transition-metal-linked networks,^[11] electrochemistry,^[12] and vesicle-like “blackberry” formation.^[13] However, this relative explosion of interest has created an imbalance, with the fundamental physical properties of the heteropolyanion rarely addressed.^[14] Compounds **1a** and **1b** are potassium-free analogues to previously published {P₈W₄₈},^[5] with key K⁺ sites substituted for NH₄⁺. Their preparation allows us to not only study the host–guest chemistry of {P₈W₄₈} in regards to cation selectivity, but reveals a unique and intriguing solution behavior of the heteropolyanion conferred by the bound cations. The internal stabilization/templating role of potassium was previously considered to be crucial in the formation of {P₈W₄₈}, whilst lithium cations must be present for solubility, a common requirement for many of the lacunary POMs. Though

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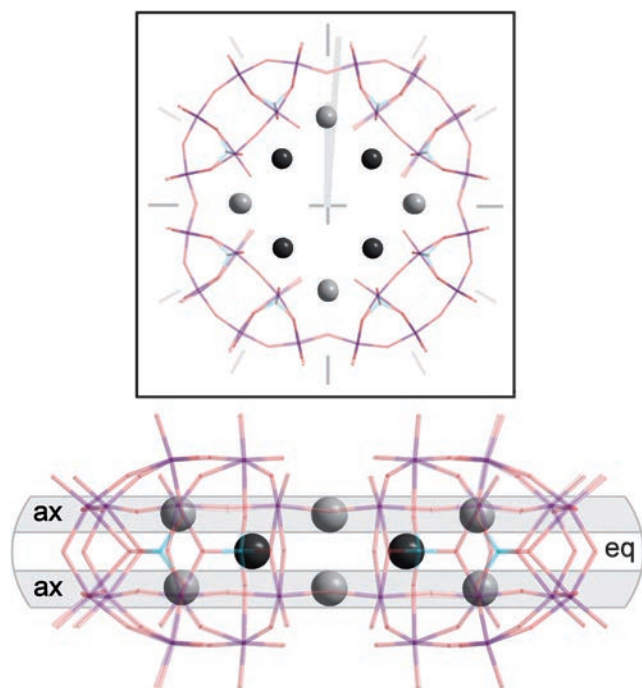


Figure 1. $\text{K}_{28}\text{Li}_5\text{H}_7[\text{P}_8\text{W}_{48}\text{O}_{184}]\cdot 92\text{H}_2\text{O}^{[5]}$ showing the positions of internal potassium ions, located at regular sites within the cavity. At 12, 3, 6, and 9 o'clock, are located eight half-occupancy sites of the hinge positions, bridging $\{\text{P}_2\text{W}_{12}\}$ subunits. Other key K^+ binding sites lie directly between these positions on the nucleophilic faces of the $\{\text{P}_2\text{W}_{12}\}$ subunits. These sites, which are fully occupied, are located around the equatorial belt, with each cation coordinated to four terminal oxygen atoms of the exposed lacunary sites. This gives a total of eight complexed K^+ ions $[(4 \times 1\text{eq}) + (8 \times 1/2\text{ax})]$ contained within the ring cavity. Representation: Wire/stick model, heteropolyanion framework; black spheres, fully occupied equatorial potassium; gray spheres, half-occupied axial potassium.

similarly sized, (ionic radii: K^+ , 1.33 Å; NH_4^+ , 1.44 Å), the binding modes of ammonium and potassium to POMs can be distinguished.^[15] In particular, NH_4^+ ions commonly bind to POMs through hydrogen bonds, preferentially in tetrahedral sites.

The preparation of $\{\text{P}_8\text{W}_{48}\}$ follows a classic three-step, assembly–partial disassembly–reassembly, POM pathway. A parallel route of formation was followed in the synthesis of **1a** and **1b**, avoiding the use of potassium salts from the outset to ensure purity of the final product (see Scheme S1 in the Supporting Information). Two distinct crystal forms of **1** may be prepared in the presence of ammonium and lithium cations; large needle-like crystals (**1a**) are evident within two weeks when crystallization conditions are between pH 4.3–6.0, whilst smaller block crystals (**1b**) form at pH 4.0 within three to five weeks. Between pH 4.0–4.3, a mixture of the crystals is formed.

Compound **1a** retains the approximate fourfold symmetry of the potassium salt, with ammonium cations directly replacing potassium in binding pockets surrounding the cluster, and internally on the nucleophilic faces of the $\{\text{P}_2\text{W}_{12}\}$ subunits. Adjoining subunits are therefore oriented at right angles to each other, and all hinge sites are equivalent. In contrast, **1b** has approximate D_{2h} symmetry, lowered in rela-

tion to its sister compound, with NH_4^+ ions forced axially away from the templating pockets at opposing hinge sites, creating strain on the heteropolyanion (see Table S1 in the Supporting Information for a full list of N–O bond lengths in **1a** and **1b**). As a result, the hinge angles of adjoining $\{\text{P}_2\text{W}_{12}\}$ subunits are inequivalent; 87.58° and 92.42°. This structural distortion allows the incorporation of an additional tungsten, identified by single-crystal X-ray diffraction, and present in a disordered fashion across roughly one in every ten clusters in the solid state. Consequently, **1b** assumes an ellipsoidal conformation from the associated lengthening and narrowing of the cluster in two dimensions, and the internal environment of the crown is therefore different to both **1a** and the potassium salt.

The ^{31}P NMR spectrum of $\{\text{P}_8\text{W}_{48}\}$ is also dependent on both pH, and the cations present. Therefore, the distinction between the potassium salt,^[5] and **1a** and **1b** can be made in solution (Figure 2). In a solution of 9:1 1 M $\text{LiCl}:\text{D}_2\text{O}$, **1a**

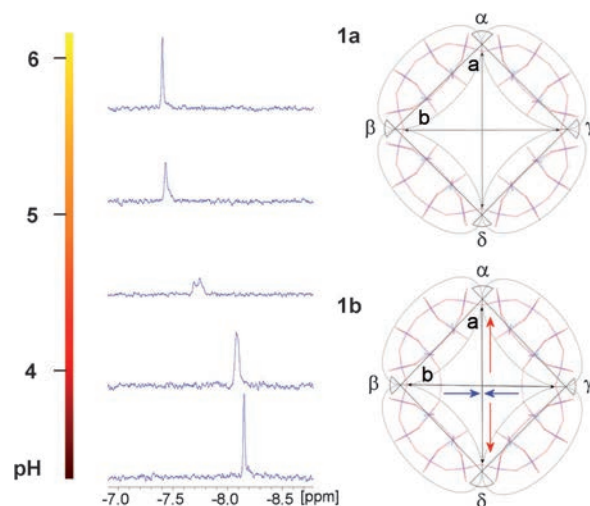


Figure 2. The solid state structures of **1a** and **1b** are controlled by pH. This dependence of the polyanion on its environment is also observed in solution by ^{31}P NMR, where splitting of the peak at approximately pH 4.3 indicates inequivalence of phosphorus centers. Reduced symmetry of the cluster arises from closing the hinge angle at opposing $\{\text{P}_2\text{W}_{12}\}$ bridging sites, causing the other two hinges to open. **1a**: $a=b=16.64$ Å; $\alpha=\beta=\delta=\lambda=90^\circ$. **1b**: $a=17.18$ Å, $b=15.97$ Å; $\alpha=\delta=87.58^\circ$, $\beta=\lambda=92.42^\circ$.

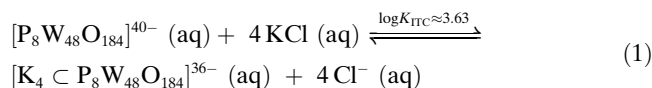
shows one sharp peak indicating equivalence of each phosphorus center in the structure. Compared to the potassium salt, this is shifted upfield, suggesting shielding of the phosphorus nuclei by closer association with the ammonium cations present in solution. Upon addition of 0.1 M H_3PO_4 , the peak initially broadens before showing as a doublet, indicating inequivalence between phosphorus centers. This may be caused by the weakening of hydrogen bonds between NH_4^+ and the nucleophilic oxygen centers of $\{\text{W}-\text{O}-\text{W}\}$ bridges, leading to the removal of ammonium from two of the four hinge sites. Crystallographically, this is observed by a lengthening of hydrogen bonds in **1b** compared with those in **1a**

(see Table S1 in the Supporting Information). Further acidification produces a broad, then sharp singlet indicating that the phosphorus centers are once again equivalent. Following on from the previous observation, this may be attributed to full replacement of the NH_4^+ centers by protons in the hinge region. The observation that $\{\text{P}_8\text{W}_{48}\}$ cannot be crystallized in the presence of ammonium cations below pH 4 further supports this theory. The potassium salt does not show the same pattern of spectra under identical experimental conditions, with little change observed in the signal when the pH of the solution is lowered. This indicates that pH influences the nature of hydrogen bonding between ammonium cations and the cluster, and subsequently the polyanion electron distribution and structure.

The flexibility of $\{\text{P}_8\text{W}_{48}\}$ has previously only been observed before with the incorporation of transition metals, with several of the reported structures having lower symmetry than the parent $\{\text{P}_8\text{W}_{48}\}$ structure.^[16] In some cases, this has allowed a 49th,^[17] and even a 50th tungsten atom to become incorporated into the ring.^[18] This adaptability suggests that the electron distribution of the $\{\text{P}_8\text{W}_{48}\}$ host is manipulated by its guest species.

Host–guest relationships of POMs is an area of great interest, though only tentatively explored by direct methods such as calorimetry.^[19] Isothermal titration calorimetry (ITC) is regularly employed in biological systems and other areas of supramolecular chemistry for studying such relationships. The binding stoichiometry, n_{ITC} , and thermody-

amic parameters, K_{ITC} , ΔH_{ITC} , and ΔS_{ITC} determined here are complicated by the presence of multiple binding sites and by competition from the native cations. However, careful experimental refinement to ensure the titrated guest cations were in large excess, over a range of complementary conditions, has enabled us to make assumptions concerning these interactions. In solution, **1** has a complex array of cations and water molecules associated with it at all times, which influence the electron distribution and overall structure of the host (see Figure 3). The native cations are likely to be bound most strongly to the highly nucleophilic sites of the inner-ring cavity, where crystallographically we see the most well-defined potassium and ammonium positions. Although $\{\text{P}_8\text{W}_{48}\}$ compounds can be prepared with either cation in combination with lithium (Li^+ ions improve the solubility of many lacunary POMs, and $\{\text{P}_8\text{W}_{48}\}$ is no different), the crown-type POM selectively binds potassium over ammonium. The logarithm of the binding constant for K^+ to **1** ($\log K_{\text{ITC}}$) in 0.1 M LiAc at pH 7 has been determined to be 3.63 [Eq. (1)]. This compares favorably to an average (over varied conditions) of about 2.04 for the potassium-selective crown ether, [18]crown-6.^[20]



In addition to obtaining the first reported binding constant for potassium to $\{\text{P}_8\text{W}_{48}\}$, ITC studies have given in-

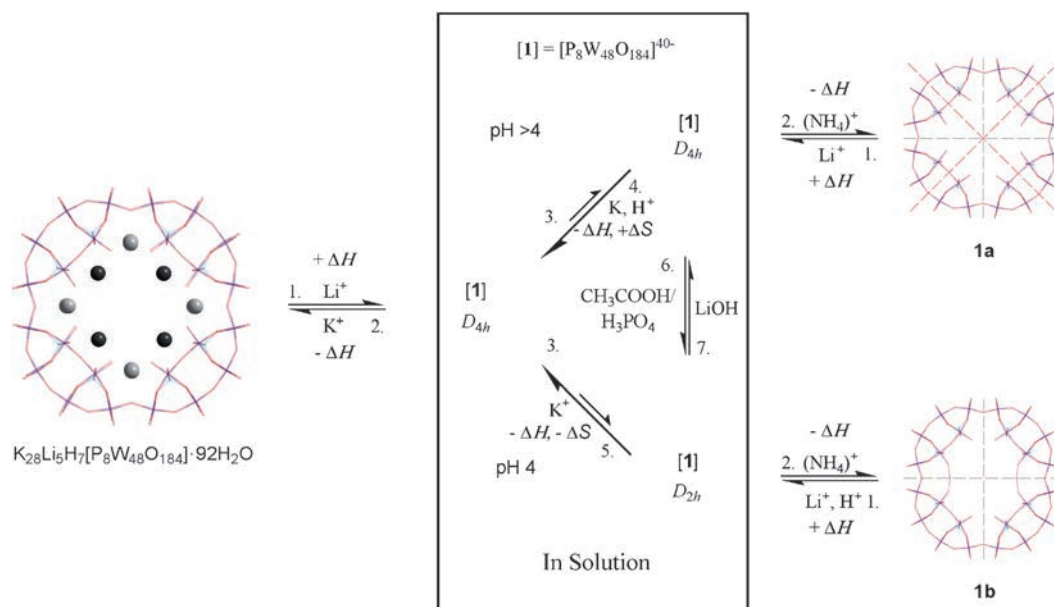


Figure 3. Thermodynamic interpretation of cation binding to $\{\text{P}_8\text{W}_{48}\}$ from ^{31}P NMR spectroscopy and ITC: 1. Binding of lithium cations to $\{\text{P}_8\text{W}_{48}\}$ is endothermic, indicating a greater solubility of the polylacunary cluster in their presence. 2. Each of the species present in solution can be crystallized in the presence of potassium or ammonium cations—the binding of both of these cations is exothermic. 3. $\{\text{P}_8\text{W}_{48}\}$ does not bind NH_4^+ in the presence of native potassium cations. 4. At pH greater than 4, $\{\text{P}_8\text{W}_{48}\}$ binds K^+ with negative enthalpy and positive entropy, mainly due to the displacement of water. 5. At pH 4, $\{\text{P}_8\text{W}_{48}\}$ binds K^+ with negative enthalpy and negative entropy, indicating that despite significant displacement of water, a conformational change is taking place. 6. Lowering the pH of the $\{\text{P}_8\text{W}_{48}\}$ solution with native ammonium cations also causes a conformational change, as seen by ^{31}P NMR spectroscopy. 7. The reverse of this is also true—raising the pH causes structural rearrangement (see Figures S1–S6 in the Supporting Information). Representation: blue spheres, nitrogen. All other elements represented as in Figure 1. Dashed lines indicate mirror planes in the polyanion structures of **1a** and **1b**: gray mirror planes are present in both compounds, whilst red mirror planes are lost in the reduced-symmetry cluster anion of **1b**.

sight into other aspects of cation binding in the cluster. The role played by lithium cations in aiding solvation of {P₈W₄₈} is shown by the positive enthalpy observed upon addition of LiCl to a solution of the cluster; solvation is endothermic. Conversely, addition of either KCl or NH₄Cl promotes interactions with negative enthalpy. As already witnessed, the presence of potassium or ammonium cations is required for crystallization, an exothermic process. However, addition of NH₄Cl to a solution of the potassium salt of {P₈W₄₈} does not appear to produce binding. This indicates that a core number of potassium cations cannot be replaced by ammonium, highlighting the importance of the bottom-up approach undertaken in the synthesis of **1a** and **1b**. Despite this, potassium binds to both ammonium-bound clusters (interchangeable by pH alteration) in solution. Addition of KCl to the fourfold symmetrical cluster at pH 7 incurs a positive entropy difference, indicative of significant water displacement associated with the binding events. In contrast, KCl addition to the cluster with D_{2h} symmetry (pH 4) gives a negative entropy change. This would appear to be a manifestation of the structural rearrangement witnessed by ³¹P NMR spectroscopy.

The preparation of **1a** and **1b**, {P₈W₄₈} compounds with mixed lithium and ammonium cations, has enabled a study of some important physical properties of the heteropolyanion. The unprecedented stability of {P₈W₄₈} may in part be due to the flexibility observed here, both crystallographically and in solution. The complementary use of ITC and ³¹P NMR spectroscopy in this study, has given an insight into the complex solution behavior of a material with unique and intriguing properties. Investigation of the cation-binding characteristics of {P₈W₄₈} is crucial for any potential applications that exploit the intrinsic porosity of the material, such as catalysis.^[21] The use of ITC in POM chemistry may be extended to become as integral for studying host-guest relationships as in other areas of supramolecular chemistry. Additionally, characterization of the sites of highest nucleophilicity in {P₈W₄₈} may allow us to explain the formation of discrete anionic cluster compounds as opposed to extended framework materials when reacted with transition metals, and allow selective functionalization of the internal cavity for guest encapsulation, or externally for network reticulation (see Figure S7 in the Supporting Information). A key goal in developing this work will therefore be the ability to characterize, and selectively functionalize the internal and external surfaces independently. This would be a major step in the continuing quest for greater control over POM self-assembly, rather than relying on serendipity alone.

Experimental Section

In general, {P₂W₁₂} will condense to form {P₈W₄₈} below pH 5.5 in the presence of lithium and ammonium salts. Therefore, compounds **1a** and **1b** will form in the same reaction mixture, with only pH altered. However, the conditions detailed in the Supporting Information are given as the

optimum for the two products, and therefore differ in more than one parameter. Acid-washed plastic reaction vessels were used throughout to ensure no leaching of potassium from glassware. Greater yields are obtained when using freshly prepared polyoxometalate material in each step.

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Keywords: host-guest chemistry • NMR spectroscopy • polyoxometalates • self-assembly • thermodynamics

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- [7] Crystal data and structural refinements for compound **1a**: H₂₅₀Li₁₇N₂₁O₂₆₀P₈W₄₈, M_r = 14051.41 g mol⁻¹; a colorless rodlike crystal (0.39 × 0.18 × 0.14 mm³) was mounted on an Oxford Diffraction Gemini Ultra S and data collected by using MoK_α radiation (λ = 0.71073 Å) at 150(2) K. Monoclinic, space group C2/m, a = 28.0128(6), b = 37.8771(5), c = 14.1421(2) Å, β = 111.500(2)°, V = 13961.3(4) Å³, ρ_{calcd} = 3.341, 2θ_{max} = 58.60, Z = 2, 17477 unique,

- 11951 observed with $I > 2\sigma(I)$. $R_1 = 0.0519$, wR_2 (all data) = 0.1058. Compound **1b**: $\text{H}_{228-8}\text{Li}_{12}\text{N}_{21}\text{O}_{253-2}\text{P}_8\text{W}_{48-1}$, $M_r = 13\,754.59\text{ g mol}^{-1}$; a colorless block crystal ($0.34 \times 0.21 \times 0.15\text{ mm}^3$) was mounted on an Oxford Diffraction Gemini Ultra S and data collected by using $\text{MoK}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$) at 150(2) K. Triclinic, $P\bar{1}$, $a = 14.1186(3)$, $b = 22.3044(4)$, $c = 22.8563(4)\text{ \AA}$, $\alpha = 111.500(2)$, $\beta = 111.500(2)$, $\gamma = 111.500(2)^\circ$, $V = 6414.0(2)\text{ \AA}^3$, $\rho_{\text{calcd}} = 3.559$, $2\theta_{\text{max}} = 52.00$, $Z = 1$, 25 190 unique, 17 400 observed with $I > 2\sigma(I)$. $R_1 = 0.0333$, wR_2 (all data) = 0.0755. Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request_for_deposited_data.html) on quoting the depository numbers CSD-423064 (**1a**) and CSD-423063 (**1b**).
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