

Controlling nucleation of the cyclic heteropolyanion $\{P_8W_{48}\}$: a cobalt-substituted phosphotungstate chain and network†

Scott G. Mitchell,^a David Gabb,^a Chris Ritchie,^a Nick Hazel,^b De-Liang Long^a and Leroy Cronin^{**}

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Two cyclic cobalt-substituted heteropolyoxometalates $K_{15}Li_5[Co_{10}(H_2O)_{34}(P_8W_{48}O_{184})] \cdot 54H_2O$ (**1**) and $K_8Li_{12}[Co_{10}(H_2O)_{44}(P_8W_{48}O_{184})] \cdot 60H_2O$ (**2**) have been synthesised from the reaction of Co(II) ions and the superlacunary $\{P_8W_{48}\}$ polyanion in mildly acidic aqueous media. The cluster's anion cavities are filled with Co(II) and K cations and careful manipulation of reaction conditions determines the formation of distinct Co-linked frameworks.

Polyoxometalates (POMs) possess many attractive electronic and molecular properties¹ that give rise to a variety of applications in diverse fields such as catalysis,² medicine³ and materials science.^{4,5} Heteropolyoxometalates (HPOMs) are of special interest for the engineering of novel framework structures since they combine high stability with extensive structural variety⁶ which ultimately leads to their application as superacidic catalysts.⁷

The most convenient method towards the synthesis of high nuclearity POMs involves the condensation of basic lacunary precursors into larger anionic motifs. This system thus allows for the possibility, at various stages, to introduce new elements and reagents which will interact with the self-assembly process.⁸ One of the most attractive and stable POMs to date is the superlacunary $[H_7P_8W_{48}O_{184}]^{33-}$ polyoxoanion, isolated by Contant and Tézé in 1985.⁹ This highly stable and versatile cluster is in fact an oligomer formed from the linking of four subunits of the hexavacant $[H_2P_2W_{12}O_{48}]^{12-}$ polyoxoanion. These vacant subunits are in turn derived from the phosphotungstate Dawson-type anion $[P_2W_{18}O_{62}]^{6-}$.¹⁰ Therefore development in the design and synthesis of new $\{P_8W_{48}\}$ -based polyoxoanions presents promising routes for assembling new high nuclearity mixed-metal aggregates. In this respect we are interested in working towards new metal-oxide assemblies, with well-defined cavities in which functionalities can be positioned for host-guest chemistry that could result in new reactivity of physical properties.

In the original $\{P_8W_{48}\}$ report the authors suggested that this polyoxoanion was unreactive towards divacant or trivacant transition metal elements such as cobalt(II), despite the available coordination sites present within this crown HPA. Some 20 years later however, Kortz *et al.* published the first Cu-containing $\{P_8W_{48}\}$

assembly, thus proving this molecule to be a large superlacunary polyanion precursor.¹¹ Since this discovery, a series of novel structures based on the tetrameric $\{P_8W_{48}\}$ unit have been reported in the literature including $\{V_{12}\}$ aggregates;¹² $\{Cu_{20}\}$ studies;¹³ $\{Fe_{16}\}$ ¹⁴ and Ln-containing cluster anions;¹⁵ as well as organoruthenium-based composites.¹⁶ Interestingly, the majority of these recent $\{P_2W_{12}\}$ -based crown HPAs encapsulate various transition metal and alkali metal ions in the central crown cavity.¹⁷ With $\{P_8W_{48}\}$ polyoxometalate chemistry becoming such a rapidly growing research area, a fuller understanding and better control of the assembly process of these TM-doped clusters as a function of the reagents used, should lead to the ability to controllably produce more interesting materials.¹⁸

The work described herein reports the first cobalt-containing $\{P_8W_{48}\}$ structures, **1**: a 1D chain and **2** a 3D network, both featuring covalent coordination between discrete clusters through cobalt atoms. The title compounds $K_{15}Li_5[Co_{10}(H_2O)_{34}(P_8W_{48}O_{184})] \cdot 54H_2O$ (**1**) and $K_8Li_{12}[Co_{10}(H_2O)_{44}(P_8W_{48}O_{184})] \cdot 60H_2O$ (**2**) were obtained from one-pot synthetic procedures involving precise control of pH and buffer.‡ Both compounds have been characterised in the solid state† by single-crystal X-ray diffraction§, IR and UV spectroscopy, TGA, flame atomic absorption (FAAS) and flame photometry (FPS) spectroscopy, showing that both frameworks **1** and **2** are based on similar discrete cluster units which have been extended into higher dimensionality arrays through distinct Co–O–W bonds.

The simple one-pot method reported here is adapted from previous experimental observations and from the original $\{P_8W_{48}\}$ paper which indicated that the $\{P_8W_{48}\}$ crown HPA was unreactive towards cobalt (II). Since we now know that POMs strongly interact with 3d and 4d transition metal elements we supposed that we could use this highly anionic cluster to effectively yield new high nuclearity supramolecular arrangements.¹¹ One key to the successful synthesis of the 48-tungstophosphate materials appears to be precisely buffered mildly acidic aqueous media. There are several studies which show the degree of sensitivity of the polyoxometalate self-assembly process, for example how pH value, ionic strength, temperature and reagent type and ratios play an important role in the synthesis of novel structures.¹⁹

Recently, an interesting lacunary Preyssler-type Co(II)- $\{P_4W_{24}\}$ -based POM was reported.²⁰ However, to our best knowledge, **1** and **2** represent the first example of Co(II)- $\{P_8W_{48}\}$ compounds. Compound **1** crystallises in the triclinic system with space group $P\bar{1}$ and **2** in the monoclinic system with space group $P2_1/c$. The extended structures of both compounds thus demonstrate space group-imposed inversion symmetry. In each crystal structure, the asymmetric unit contains a $\{P_4W_{24}\}$ unit and five Co(II) centres. Both

^aWestCHEM, Department of Chemistry, The University of Glasgow, University Avenue, Glasgow, UK G12 8QQ. E-mail: L.Cronin@chem.gla.ac.uk; Fax: +41 (0)141 330 4888; Tel: +41 (0)141 330 6650

^bBP Chemicals Ltd, Saltend, Hull, UK HU12 8DS

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frameworks **1** and **2** are therefore comprised of $\{P_8W_{48}\}$ anions, where the central crown cavity is functionalised by a total of six cobalt(II) ions. Additional Co(II) ions are grafted onto the outer rings extending the Co(II)- $\{P_8W_{48}\}$ anions into 1D chains, **1**, and 3D networks, **2** (Fig. 1 and 2).

Pink needle crystals of $K_{15}Li_5[Co_{10}(H_2O)_{34}(P_8W_{48}O_{184})] \cdot 54(H_2O)$ **1** were crystallised as a mixed potassium-lithium salt from a 2 M lithium acetate-buffered solution; adjusted to pH 5.75 with 2 M HNO_3 . Crystallisation was assisted by cooling the solution to 4 °C over the period of one week.

In this metal-substituted $\{P_8W_{48}\}$, a total of six cobalt(II) centres have been incorporated in the ring and a further four cobalt(II) atoms are ligated to oxygen atoms on the outside edge of the crown ring. The cobalt atoms on the inside of the cavity are bonded to what appear to be the most sterically accessible oxygens, nestled in the "hinges" between two $\{P_2W_{12}\}$ units. There are three different types of octahedral Co(II) inside the ring. Co1 and Co2 are essentially equal, located opposite one another at a distance of 8.97(1) Å apart at a $\{P_2W_{12}\}$ hinge. Each atom has two μ_2 -Co-O(W) bonds of average length 2.04(0) Å, while the four remaining octahedral coordination sites on each atom are occupied by H_2O , average bond length 2.11(0) Å. The two further cobalt atoms within the ring are located at the other hinge point at a distance of 4.06(5) Å from each other. Co6 has two μ_2 -Co-O(W) bonds of average length 2.09(0) Å while Co5, which has a distorted octahedral geometry, is bonded to W through four μ_3 Co-O(W) bonds averaging 2.31(4) Å. The 1D chain framework of this POM assembly is achieved *via* intramolecular Co-O(W) bonding. The discrete $\{Co_8P_8W_{48}\}$ molecules are linked into long one-dimensional step-like chains by two cobalt ions and one potassium ion. Located on the outside of the cluster, Co3 links two $\{Co_8P_8W_{48}\}$ clusters through three μ_2 -Co-O(W) bonds of average length 2.09(2) Å. The remaining coordination sites on this Co^{II} are

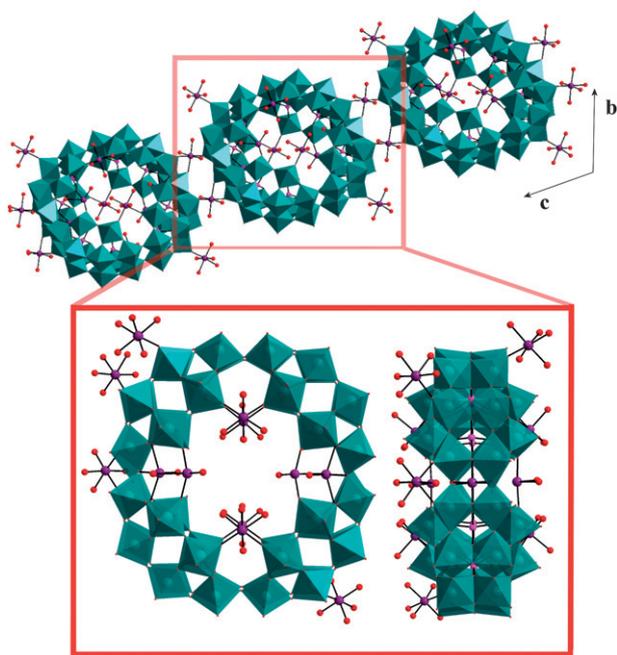


Fig. 1 Representation of the crystal lattice of **1**, Cobalt-linked chains of $[Co_{10}(H_2O)_{34}(P_8W_{48}O_{184})]^{20-}$ **1**. Teal polyhedra: WO_6 ; purple octahedra: CO_6 ; pink tetrahedra: PO_4 . Alkali metal cations omitted for clarity.

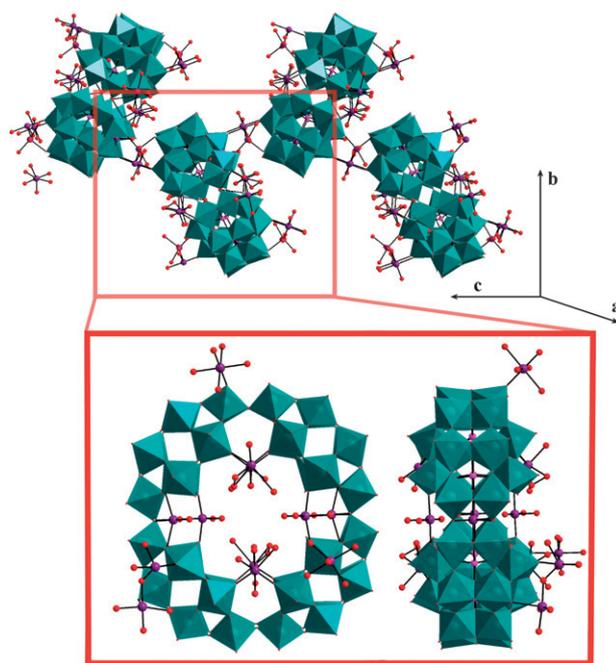


Fig. 2 Representation of the crystal lattice of **2**, Cobalt-linked chains of $[Co_{10}(H_2O)_{44}(P_8W_{48}O_{184})]^{20-}$ **2**. Teal polyhedra: WO_6 ; purple octahedra: CO_6 ; pink tetrahedra: PO_4 . Alkali metal cations omitted for clarity.

occupied by H_2O (Co-H $_2O$ 2.06(9) Å). In addition, there is one further antenna Co^{II} atom on the outside edge of the cluster although this contains only one μ_2 -Co-O(W) bond of 2.09(5) Å and five H_2O ligands.

When the experimental procedure for **1** was repeated and LiAc buffer replaced by LiCl, large well-behaved square plate crystals formed in solution after only a few days. These high quality crystals were characterised by the aforementioned methods and found to have the formula $K_8Li_{12}[Co_{10}(H_2O)_{44}(P_8W_{48}O_{184})] \cdot 60H_2O$ **2**. In this molecule the anion cavities of $\{P_8W_{48}\}$ are filled primarily by encapsulating six Co(II) ions in a similar fashion to **1**. Bond distances are almost identical: for example, the distance between Co1 and Co2 is 8.82(1) Å apart and the two μ_2 -Co-O(W) bonds associated with each cobalt atom have an average length of 2.02(8) Å. The main difference therefore between **1** and **2** lies in the location and coordination of Co^{II} atoms located on the outside of the crown ring. In compound **2**, each $\{P_8W_{48}\}$ ring is linked to another through four separate μ_2 -Co-O(W) bonds with an average length of 2.01(7) Å. The bonding between clusters leads to a distorted 3D chain (Fig. 2). The presence of K^+ and Li^+ counter cations also assists in stabilizing the structure.

In conclusion, we were able to obtain two novel heteropolyoxometalate-based framework materials based on the $\{P_8W_{48}\}$ superlacunary crown heteropolyanion *via* careful control of reaction conditions and crystallisation procedure. Closely related Co(II)-substituted $\{P_8W_{48}\}$ units were extended into network arrays by multiple covalent Co-O(W) bonding between discrete cluster units. These structures represent only the second example whereby a functionalized $\{P_8W_{48}\}$ has been extended into an assembly with long-range crystalline order. This has been possible as the transition metal has been attached to the outer parts of the $\{P_8W_{48}\}$ moiety, similar to $\{Ln_4(H_2O)_{28}[K-P_8W_{48}O_{184}(H_4W_4O_{12})_2Ln_2(H_2O)_{10}]^{13-}\}$, where

Ln = Ln, La, Ce, Pr, Nd, rather than solely the central cavity area.¹⁵ We hypothesize this to be outer- $\{P_8W_{48}\}$ functionalization to be possible with a range of transition metal elements. Linking the $\{P_8W_{48}\}$ crown-type POMs could have potentially valuable applications in molecular recognition and separation as well as rigid selective catalysts. As a result, we plan to fully investigate this possibility aiming towards the synthesis of polyoxometalate-based functional materials with a focus on molecular recognition of specific reactants. In this way we aim to expand the host-guest chemistry aspect of this molecule. Further investigation will also aim to explore the prospect of enantioselective catalysis using functionalized $\{P_8W_{48}\}$ moieties.

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Note added at proof

During the time this paper was submitted we became aware that Prof. U. Kortz and coworkers of Jacobs University (Bremen, Germany) have also obtained very similar results that will be published soon, as eluded in the conclusions of an earlier paper by that group (S. S. Mal, N. H. Nsouli, M. H. Dickman and U. Kortz, *Dalton Trans.* 2007, 2627–2630).

Notes and references

† Synthesis of **1**: the pH of a 10 mL solution of 2 M LiAc solution was adjusted to 5.75 by addition of a few drops of 4 M HNO₃ solution. To this solution was then added successively CoSO₄·7H₂O (75 mg, 0.27 mmol) followed by K₂₈Li₅[H₇P₈W₄₈O₁₈₄]·92H₂O (75 mg, 5.06 mmol). The deep-red mixture was then heated at 70 °C overnight (approx. 20 h) and transferred to a glass vial. The vial was allowed to cool to room temperature and placed in a fridge at ca. 4 °C. After two days red-pink needle crystals began to form in solution and were separated 7 days after crystallisation began. Yield: 0.018 g, 1.2 μmol (23.3%). Characteristic IR-bands: 1644(s), 1567(s), 1421(s), 1385(w), 1136(s), 1082(s), 1019(m), 932(s), 800(s), 669(s), 521(w), 460(w), 419(w). UV-bands, nm(Abs): 550(1.305), 629(1.109), 470(1.265). Elemental analysis for the dehydrated material, K₁₅Li₅[Co₁₀(H₂O)₃₄(P₈W₄₈O₁₈₄)]·54H₂O, MW = 14814.30 g mol⁻¹. Calcd (found, partial solvent water lost): Co 4.14 (4.32), W 62.17 (62.82), K 4.11 (3.14), Li 0.25 (0.25)%. TGA water loss from 0 to 250 °C, calculated (found): 10.7 (8.99)%. Synthesis of **2**: the pH of a 10 mL solution of 2 M LiCl solution was adjusted to 5.75 by addition of a few drops of 4 M HNO₃ solution. To this solution was then added successively CoSO₄·7H₂O (75 mg, 0.27 mmol) followed by K₂₈Li₅[H₇P₈W₄₈O₁₈₄]·92H₂O (75 mg, 5.06 mmol). The mixture was then heated at 70 °C overnight (approx. 20 h) and transferred to a glass vial. The liquor was allowed to cool to room temperature and after 3 days well-behaved, square planar red-pink crystals began to form in solution. These were isolated 7 days after crystallisation began. Yield: 0.032 g, 2.2 μmol (42.7%). Characteristic IR-bands: 1629(s), 1137(s), 1083(s), 1019(m), 932(s), 800(m), 671(s), 529(w), 465(w). UV-bands, nm (Abs): 547(1.340), 630 (1.041), 468(1.346). Elemental analysis for the dehydrated material, K₈Li₁₂[Co₁₀(H₂O)₄₄(P₈W₄₈O₁₈₄)]·60H₂O MW = 14878.83 g mol⁻¹. Calcd (found, partial solvent water lost) Co 4.22 (4.40), W 63.25 (61.93), K 2.23 (2.68), Li 0.60 (0.65). TGA water loss to 250 °C, calculated (found): 12.99 (12.38) %.

‡ Crystallographic data for **1**: triclinic, $P\bar{1}$, $a = 15.8572(6)$ Å, $b = 20.4459(8)$ Å, $c = 23.5480(9)$ Å, $\alpha = 106.003(2)$, $\beta = 103.677(2)$, $\gamma = 95.378(2)^\circ$, $V = 7026.7(5)$ Å³, $Z = 1$, $T = 100$ K, $\rho_{\text{calcd}} = 3.500$ g cm⁻³, $\mu(\text{Mo K}\alpha) = 20.490$ mm⁻¹, 49275 reflections measured, 17813 unique ($R_{\text{int}} = 0.0786$) which were used in all calculations; structure solution and refinement as done using WINGX.²¹ Final $R1 = 0.0573$ and $wR2 = 0.1216$ (all data).

Crystallographic data for **2**: monoclinic, $P2_1/c$, $a = 25.336(6)$ Å, $b = 24.223(9)$ Å, $c = 25.780(4)$ Å, $\alpha = 90.00$, $\beta = 111.24(7)$, $\gamma = 90.00^\circ$, $V = 14747.2(7)$ Å³, $Z = 2$, $T = 150$ K, $\rho_{\text{calcd}} = 3.151$ g cm⁻³, $\mu(\text{Mo K}\alpha) = 19.427$ mm⁻¹, 80850 reflections measured, 26145 unique ($R_{\text{int}} = 0.0715$) which were used in all calculations; structure solution and refinement as done using WINGX. Final $R1 = 0.0733$ and $wR2 = 0.1880$ (all data). Data for **1** was measured on a Bruker Nonius X8 Advance diffractometer equipped with an APEX II CCD detector [$\lambda(\text{Mo K}\alpha) = 0.71073$ Å], graphite monochromator and data for **2** was measured on an Oxford Diffraction Gemini Ultra with a CrysAlis CCD detector [$\lambda(\text{Mo K}\alpha) = 0.71073$ Å]. Structure solution and refinement were performed by using SHELXTL via APEX2 or CrysAlis software packages respectively. Atomic absorption data: Perkin-Elmer 1100B Atomic Absorption Spectrophotometer. K/Na data: Corning Flame Photometer 410. TGA data: TA Q500 instrument under a nitrogen atmosphere. The initial heating range was from RT to 150 °C at 2.00° per min followed by a second range from 150 to 1000 °C at 5.00° per min. Vibrational and electronic spectra were recorded on samples dispersed in a KBr disk on a Jasco FT/IR-4100 and a Shimadzu UV-3101PC, respectively.†

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