

Isolation of extendable transition metal incorporated polyoxometalate intermediates with structural control†

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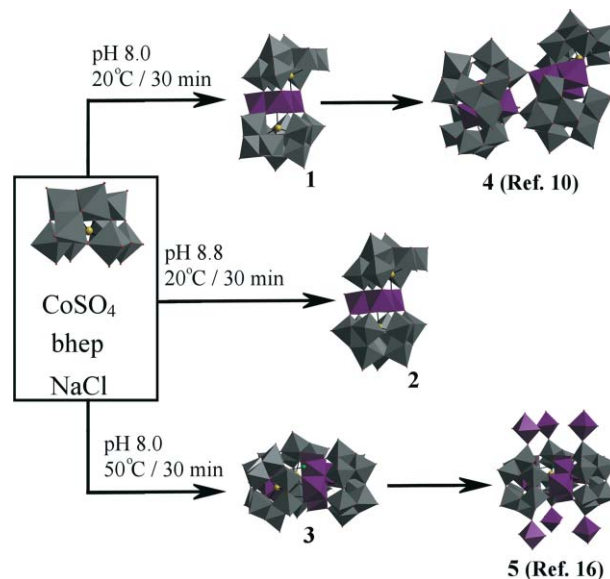
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Three discrete cobalt-substituted silicotungstates, $[\text{Co}_3(\text{H}_2\text{O})(\text{B}-\beta\text{-SiW}_9\text{O}_{34})(\text{B}-\beta\text{-SiW}_8\text{O}_{29}(\text{OH})_2)]^{12-}$ (**1**), $[\text{Co}_3(\text{H}_2\text{O})(\text{B}-\alpha\text{-SiW}_9\text{O}_{34})(\text{B}-\beta\text{-SiW}_8\text{O}_{31})]^{14-}$ (**2**), and $[\text{Co}_9\text{Cl}_2(\text{OH})_3(\text{H}_2\text{O})_9(\text{B}-\beta\text{-SiW}_8\text{O}_{31})_3]^{17-}$ (**3**), have been synthesized using a synthetic approach involving Co(II) ions, the dilacunary $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ polyanion and a bulky organic cation in basic media; all three compounds have been fully characterized and their position as structural intermediates in Co-containing silicotungstate chemistry is described.

Polyoxometalates are becoming an increasingly important class of materials¹ with applications as molecular devices,^{2,3} catalysts,^{4,5} magnetic materials,⁶ and even pharmaceuticals.⁷ The fine tuning of discrete polyoxometalate (POM) building blocks to produce versatile cluster-types that can be assembled in a controlled manner therefore represents a fundamental objective in this area of science.¹ Careful control of reaction conditions still remains the most fruitful and widespread method employed to yield novel cluster fragments or closely related architectures. One heteropolyoxometalate sub-class, the transition metal-substituted POMs (TMSPs),⁸ represents an attractive system to work towards the grand aim of real design since they exhibit many interesting properties and are often easily prepared and manipulated. A common synthetic strategy to obtain a TMSP normally involves the reaction of a preformed lacunary POM with a transition metal in a one-pot procedure.^{9–11} Given that each well defined lacunary species possesses its own reactivity and stability trend and is particularly sensitive to certain synthetic conditions, the outcome of a reaction can often be highly unpredictable. Fine changes in pH, temperature, buffer capacity, ionic strength, and cation size all have a considerable effect on the polyanion equilibria and formation of products.^{12–14} One such example is the divacant silicodecatungstate $\text{K}_8[\gamma\text{-SiW}_{10}\text{O}_{36}]$,¹⁵ which has variable stability in aqueous media, and is observed to undergo structural transformations at both low¹⁶ and high^{17,18} pH in the presence of additional transition metals.

In the course of our work we have observed many novel interesting and uncommon structures resulting from syntheses employing organic ligands which function as cations and pH buffer systems.^{19,20} The use of bulky organic amines such as hexamethylene tetramine (HMTA), triethanol amine (TEA), and *N,N'*-bis-(2-hydroxyethyl)-piperazine (bhep) has enabled us to efficiently manipulate the assembly of POM structures and 'trap'

a diverse range of compounds prior to their reorganization into more stable structures. Herein we present a study of the divacant silicodecatungstate $\text{K}_8[\gamma\text{-SiW}_{10}\text{O}_{36}]$ and its reaction with cobalt sulfate in the presence of the ligand *N,N'*-bis-(2-hydroxyethyl)-piperazine (bhep) from pH 8.0–9.0. As a result, we have successfully isolated three Co-containing silicotungstates: structural isomers $[\text{Co}_3(\text{H}_2\text{O})(\text{B}-\beta\text{-SiW}_9\text{O}_{34})(\text{B}-\beta\text{-SiW}_8\text{O}_{29}(\text{OH})_2)]^{12-}$ **1** and $[\text{Co}_3(\text{H}_2\text{O})(\text{B}-\alpha\text{-SiW}_9\text{O}_{34})(\text{B}-\beta\text{-SiW}_8\text{O}_{31})]^{14-}$ **2** as well as the trimeric $[\text{Co}_9\text{Cl}_2(\text{OH})_3(\text{H}_2\text{O})_9(\text{B}-\beta\text{-SiW}_8\text{O}_{31})_3]^{17-}$ **3**.[‡] The tungsten-oxo framework of the dilacunary $\{\text{SiW}_{10}\}$ precursor was not preserved but rapidly rearranged to give other incomplete Keggin fragments which covalently bonded with Co^{II} ions forming compounds **1** to **3** as detailed in Scheme 1.



Scheme 1 Summary of reaction between $\text{K}_8[\gamma\text{-SiW}_{10}\text{O}_{36}]$, CoSO_4 and bhep highlighting the effect of temperature and pH on the reaction products. Colour scheme: WO_6 (grey octahedra), CoO_6 (purple octahedra), Si (yellow spheres), Cl (green spheres).

Red cubic crystals of **1** were isolated from an aqueous basic NaCl solution of cobalt(II) sulfate and $\text{K}_8[\gamma\text{-SiW}_{10}\text{O}_{36}]$ in the ratio of 0.92 : 1 in the presence of bhep as a buffer (pH 8.0) after 14 days. The crystallization of **1** can be hastened by the addition of potassium ions. This monomeric sandwich compound is composed of three cobalt ions encapsulated by two nonequivalent lacunary Keggin units, $(\text{B}-\beta\text{-SiW}_9\text{O}_{34})$ and $(\text{B}-\beta\text{-SiW}_8\text{O}_{31})$, resulting in an asymmetric (C_1) cobalt sandwich compound. Formation of **1** must therefore involve rotational isomerization of $\{\gamma\text{-SiW}_{10}\}$ ($\gamma \rightarrow \beta$ -lacunary Keggin) followed by loss of tungsten ($\text{SiW}_{10} \rightarrow \text{SiW}_9 \rightarrow \text{SiW}_8$) followed by cobalt insertion.

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Compound **1** can be considered a half-unit monomer of $[\{Co_3(H_2O)(B-\beta-SiW_9O_{33}(OH))(B-\beta-SiW_8O_{29}(OH)_2)\}_2]^{22-}$ **4** reported in 2005.¹⁰ The cobalt-containing silicotungstate sandwich dimer **4** can be considered as two equivalent units of **1** bound together *via* two Co–O–W bonds, yielding a chiral cluster assembly of C_2 symmetry. The publication of this TMSF hinted at the existence of **1** as an intermediate precursor to the formation of the title polyanion and also stated that **1**, being relatively unstable, would therefore dimerize as a consequence. Bond valence sum calculations of **1** showed that oxygens 23 and 60 of the $\{SiW_8\}$ unit of **1** are protonated. The long W–O–W bonds (average bond lengths of 2.05(2) Å and 2.14(1) Å respectively) are consistent with the equivalent fragment of **4**. Crystallographic disorder and elemental analysis, however, are consistent with the bridging O44 contained within the $\{SiW_9\}$ portion of this isomer being unprotonated. This observation is in disagreement with the protonation state of the equivalent oxygen in **4**.

Increasing the pH of the reaction medium from 8.00 to 8.80 gave well-formed red planar rectangular crystals of heteropolyanion **2** after several days. These crystals are easily distinguished from **1** and at no point did we observe co-crystallization of both sandwich POMs **1** and **2** from the same reaction mixture.²¹ Common to both **1** and **2** is the (B- β - SiW_8O_{31}) unit; however, **1** contains the more commonly observed (B- β - SiW_9O_{34}), while **2** includes the (B- α - SiW_9O_{33}) fragment. Isomerisation from the $\beta \rightarrow \alpha$ isomer occurs *via* 60° rotation of a W_3O_{13} triad to give a more symmetrical fragment (Fig. 1) which reflects the transformation $\gamma \rightarrow \beta \rightarrow \alpha$ -Keggin. This (B- α - SiW_9O_{33}) unit is the basic lacunary fragment of the Weakley-type sandwich polyanion $[M_4(H_2O)_2(B-\alpha-SiW_9O_{33})_2]^{n-}$,²² where M = Ni, Zn, Cu but, interestingly, not Co. In both sandwich compounds **1** and **2**, each incomplete Keggin unit is held together by three octahedral Co^{II} ions. Each Co atom shares two oxygen atoms with each lacunary unit, meaning that there are four corner sharing Co–O–W bonds to each Co^{II} centre. Two equivalent Co atoms have three μ_2 Co–O bonds (average Co–O bond 2.05(8) Å) and three μ_3 Co–O bonds (average Co–O 2.10(5) Å). The third Co atom sandwiched between the two lacunary Keggin consists of two μ_2 Co–O bonds (average Co–O bond 2.02(3) Å), three μ_3 Co–O bonds (average Co–O bond

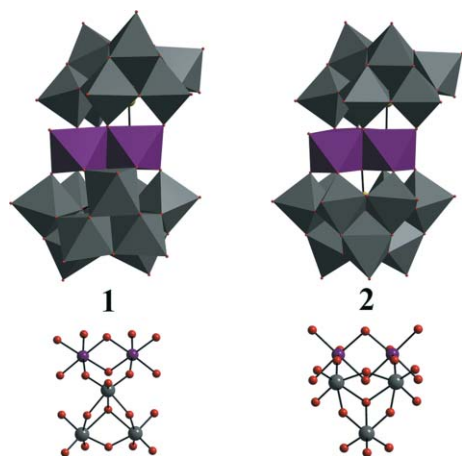


Fig. 1 Polyhedra representations of isomers $[Co_3(H_2O)(B-\beta-SiW_9O_{34})(B-\beta-SiW_8O_{29}(OH)_2)]^{12-}$ **1** and $[Co_3(H_2O)(B-\alpha-SiW_9O_{34})(B-\beta-SiW_8O_{31})]^{14-}$ **2**. WO_6 (grey), CoO_6 (purple), Si (yellow).

2.11(0) Å) and a Co–H₂O bond (2.09(1) Å). The increase in pH also resulted in both lacunary Keggin units of **2** being unprotonated. Further study and development of the reaction systems may even allow us to produce clusters with *desired* protonation states.

Increasing the temperature of the reaction medium from room temperature to 50 °C at pH 8 led to the formation of **3** (Fig. 2): a trimeric 9-Co-substituted polyoxotungstate, an outcome that could actually be predicted by examination of ref. 16. This intermediate was reported as the core unit of $Na_5[Co_6(H_2O)_{30}\{Co_9Cl_2(OH)_3(H_2O)_9(B-\beta-SiW_8O_{31})_3\}] \cdot 37H_2O$, **5**: isolated from a 50 °C reaction at pH 5.5.¹⁶ This 15-Co-substituted cluster anion contains the basic core unit **3**, $[Co_9Cl_2(OH)_3(H_2O)_9(B-\beta-SiW_8O_{31})_3]^{17-}$, plus 6 antenna $Co^{II}(H_2O)_5$ groups. Once again, the key synthetic differences between the higher nuclearity compound **5** and compound **3** are the addition of bhep and increased pH of reaction. In the publication of compound **5**, it was postulated that the core unit (**3**) could exist on its own; we have confirmed its existence, and verified that stabilization of this core fragment is provided by potassium and sodium counter cations. Unfortunately, we have been unsuccessful in isolating anything resembling a dimeric intermediate such as $[Co_3(H_2O)(B-\beta-SiW_8O_{31})_2]$, which may form between isomerization of $\{SiW_{10}\} \rightarrow \{SiW_8\}$ and the formation of **3**. The observation of such a fragment would have given even greater insight into the formation of this **3**. What we can confirm is that the six Co^{II} ions on the outside of the cluster core of **5** are most likely covalently attached *after* formation of the principal core unit **3**. The terminal oxygen ligands associated with each of the nine Co^{II} ions have an average bond length of 2.10(4) Å and therefore correspond to water molecules. We believe that at lower pH, compound **3** can be extended into **5** and possibly even more interesting, higher nuclearity mixed-metal structures with attractive magnetic properties.

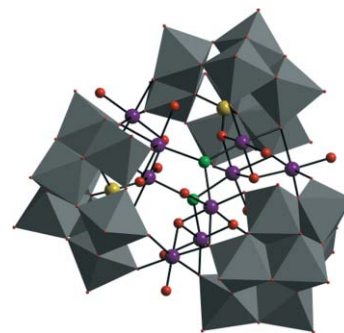


Fig. 2 $[Co_9Cl_2(OH)_3(H_2O)_9(B-\beta-SiW_8O_{31})_3]^{17-}$ **3**. WO_6 (grey), Co (purple), Si (yellow), Cl (green).

The fact that we have been able to isolate a selection of products from a simple one-pot procedure in basic media shows the facility by which transition metal-substituted polyanions can be isolated from rearrangement of the $[\gamma-SiW_{10}O_{36}]^{8-}$ precursor through slight variations in reaction conditions. Although the bhep ligand is not incorporated in the structures, these clusters do not form without its presence in the reaction, and this is a key observation. We therefore believe that this amine ligand plays a vital role in the isolation of these intermediate clusters while acting as a buffer at high pH and it is likely that the pH buffering capacity of the bhep ligand makes the isolation of these intermediates possible. The

crucial role of this organic ligand at high pH is currently under investigation.

In summary, we have synthesized three intermediate Co(II)-containing silicotungstate intermediates: fragments which have been observed before as either dimeric or higher nuclearity cluster complexes. Observation and more importantly isolation of these intermediates means that we can contribute to a fuller understanding of the formation of TMSP sandwich compounds and from here develop syntheses which incorporate these clusters as starting materials for the next generation of mixed-metal POM complexes.

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Notes and references

‡ All starting materials were used as purchased without any further purification. $K_8[\gamma\text{-SiW}_{10}\text{O}_{36}]\cdot 12\text{H}_2\text{O}$ was prepared by standard literature methods.¹⁵

Synthesis of $K_9\text{Na}_3[\text{Co}_3(\text{H}_2\text{O})(\text{B}-\beta\text{-SiW}_9\text{O}_{34})(\text{B}-\beta\text{-SiW}_8\text{O}_{29}(\text{OH})_2)]\cdot 18\text{H}_2\text{O}$ **1** FW 5163.36. In 100 mL 1M NaCl was dissolved $K_8[\gamma\text{-SiW}_{10}\text{O}_{36}]$ (2.972 g, 1.00 mmol) and CoSO_4 (0.259 g, 0.92 mmol). In a separate vessel, N,N' -9-bis(2-hydroxyethyl)piperazine (bhep) (2 g, 11 mmol) was dissolved in 20 mL H_2O and pH lowered to 8.0 using 2M H_2SO_4 . Both solutions were then mixed together and pH subsequently adjusted to exactly 8.00. This vivid red solution was stirred at room temperature for 30 min. The solution yielded small red cubic crystals of **1** after 14 days and were separated after 18 days. (530 mg, 0.1 mmol) 35.7% yield based on W.

Analytical data: $K_9\text{Na}_3[\text{Co}_3(\text{H}_2\text{O})(\text{B}-\beta\text{-SiW}_9\text{O}_{34})(\text{B}-\beta\text{-SiW}_8\text{O}_{29}(\text{OH})_2)]\cdot 18\text{H}_2\text{O}$ ($\text{H}_4\text{Co}_3\text{K}_9\text{Na}_3\text{O}_{66}\text{Si}_7\text{W}_{17}\cdot 18\text{H}_2\text{O}$) **1**: FTIR (KBr pellet) cm^{-1} : 3408 s, 1625 w, 892 m. Atomic absorption calcd (found): W 60.53 (58.73%)²³, Co 3.42 (3.20%). K/Na Analysis: K calcd (found): 6.82 (7.15%), Na calcd (found): 1.34 (1.14%). TGA water loss experimental (calcd): 8.087 (6.27%). Solvent lost in dry compound compared to crystallographic data: 33%. Crystal data: triclinic, $P\bar{1}$, $a = 12.7351(6)$ Å, $b = 18.3684(8)$ Å, $c = 19.3171(9)$ Å, $\alpha = 82.947(3)$, $\beta = 78.214(3)$, $\gamma = 79.073(3)^\circ$, $V = 4326.6(3)$ Å³, $Z = 2$, $T = 100$ K, $\rho_{\text{calcd}} = 4.088$ g cm^{-3} , $\mu(\text{Mo K}\alpha) = 23.654$ mm^{-1} , 45471 reflections measured, 15051 unique ($R_{\text{int}} = 0.0945$) which were used in all calculations. Final $R1 = 0.1023$ and $wR2 = 0.1200$ (all data).

Synthesis of $K_2\text{Na}_{12}[\text{Co}_3(\text{H}_2\text{O})(\text{B}-\alpha\text{-SiW}_9\text{O}_{34})(\text{B}-\beta\text{-SiW}_8\text{O}_{31})]\cdot 26\text{H}_2\text{O}$ **2** FW 5206.48. In 100 mL 2M NaCl was dissolved $K_8[\gamma\text{-SiW}_{10}\text{O}_{36}]$ (1.486 g, 0.50 mmol) and CoSO_4 (0.1295 g, 0.46 mmol). In a separate vessel, bhep (2.5 g, 14.4 mmol) was dissolved in 15 mL H_2O and pH lowered to 8.62 using 2M H_2SO_4 . Both solutions were then mixed together and pH subsequently adjusted to exactly 8.80. This radiant deep red solution was stirred at room temperature for 30 min. The solution yielded well-formed long red planar rectangular crystals of **2** after 2 days and were separated after 18 days. (345 mg, 0.073 mmol) 23.2% yield based on W.

Analytical data: $K_2\text{Na}_{12}[\text{Co}_3(\text{H}_2\text{O})(\text{B}-\alpha\text{-SiW}_9\text{O}_{34})(\text{B}-\beta\text{-SiW}_8\text{O}_{31})]\cdot 26\text{H}_2\text{O}$ ($\text{H}_2\text{Co}_3\text{K}_2\text{Na}_{12}\text{O}_{66}\text{Si}_7\text{W}_{17}\cdot 26\text{H}_2\text{O}$) **2**: FTIR (KBr pellet) cm^{-1} : 3399 s, 1618 w, 689 m. Atomic absorption calcd (found): W 59.66 (60.46%)²³, Co 3.37 (3.06%). K calcd (found): 1.49 (0.66%). Na analysis: Na calcd (found): 5.27 (5.66%). Water loss experimental (calcd): 9.32 (8.98%). Crystal data: triclinic, $P2(1)2(1)2(1)$, $a = 12.0890(12)$ Å, $b = 21.174(2)$ Å, $c = 33.888(4)$ Å, $V = 8674.2(17)$ Å³, $Z = 4$, $T = 100$ K, $\rho_{\text{calcd}} = 4.012$ g cm^{-3} , $\mu(\text{Mo K}\alpha) = 23.304$ mm^{-1} , 30303 reflections measured, 23465 unique ($R_{\text{int}} = 0.0864$) which were used in all calculations. Final $R1 = 0.0684$ and $wR2 = 0.1819$ (all data).

Synthesis of $K_{15}\text{Na}_2[\text{Co}_9\text{Cl}_2(\text{OH})_3(\text{H}_2\text{O})_9(\text{B}-\beta\text{-SiW}_8\text{O}_{31})_3]\cdot 29\text{H}_2\text{O}$ **3** FW 7953.72 The same procedure as for **1** but the red solution was stirred at 50 °C for 30 min to yield red cubic crystals of **3** after 14 days. (180 mg, 0.023 mmol) 12.1% yield based on W.

Analytical data: $K_{15}\text{Na}_2[\text{Co}_9\text{Cl}_2(\text{OH})_3(\text{H}_2\text{O})_9(\text{B}-\beta\text{-SiW}_8\text{O}_{31})_3]\cdot 29\text{H}_2\text{O}$ ($\text{H}_{21}\text{Cl}_2\text{Co}_9\text{K}_{15}\text{Na}_2\text{O}_{105}\text{Si}_3\text{W}_{24}\cdot 29\text{H}_2\text{O}$) **3**: FTIR (KBr pellet) cm^{-1} : 3398 s,

1625 w, 891 m, 510. Atomic absorption calcd (found): W 55.47 (58.71%)²³, Co 6.67 (6.28%). K/Na analysis: K calcd (found): 7.37 (8.72%). Na calcd (found): 0.58 (0.57%). Water loss experimental (calcd): 7.011 (6.53%). Solvent lost in dry compound compared to crystallographic data: 34%. Crystal data: triclinic, $P\bar{1}$, $a = 13.4409(4)$ Å, $b = 18.2739(5)$ Å, $c = 28.8546(7)$ Å, $\alpha = 86.139(2)$, $\beta = 85.279(2)$, $\gamma = 82.646(2)^\circ$, $V = 6993.5(3)$ Å³, $Z = 2$, $T = 150$ K, $\rho_{\text{calcd}} = 3.906$ g cm^{-3} , $\mu(\text{Mo K}\alpha) = 21.325$ mm^{-1} , 44919 reflections measured, 25394 unique ($R_{\text{int}} = 0.0418$) which were used in all calculations. Final $R1 = 0.0731$ and $wR2 = 0.0781$ (all data). Data 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. Structure solution and refinement were performed using SHELTLX via APEX2 software package. 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 °C per min followed by a second range from 150 °C to 1000 °C at 5.00 °C per min.

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