Grafting ligands to direct the self-assembly of Co/Ni^{2+} substituted polyoxometalate clusters†

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Four transition metal incorporated phosphotungstates have been synthesized through the reaction of Na_2WO_4, H_3PO_4, Co/Ni$(NO_3)_2$, and the multifunctional amine N,N′-Bis(2-hydroxyethyl) piperazine (bhep). $Na_2\{MHbhep(H_2O)_4\}[PW_{10}M_2O_{38}\{Hbhep\}_2]$ M = Co^{2+} (**1**), and Ni^{2+}(**2**) represent rare examples of complete transition metal chelate encapsulation within a Keggin polyanion. Slight modification of the reaction procedure yielding **1** also yields the two dimensional material $(H_2bhep)_3Na_4[Co_4(H_2O)_2(PW_9O_{34})_2].15H_2O$ (**3**). Finally, the isolation of a phosphotungstate cluster containing 18 Co^{2+} ions is achieved through the bridging of two $[Co_9(OH)_3(H_2O)_6(HPO_4)_2(B\text{-}\alpha\text{-}PW_9O_{34})_3]^{16-}$ clusters by the bhep ligand to form the $[\{Co_9(OH)_3(H_2O)_3(HPO_4)_2(B\text{-}\alpha\text{-}PW_9O_{34})_3\}_2\ \{C_8H_{18}N_2O_2\}_3]^{32-}$ dimer (**4**). The dimerisation process is achieved *via* the monodentate coordination of the hydroxyl groups from three bhep ligands to each polyanion by displacing the water ligands typically found coordinated to the $\{Co_9\}$ core forming a nanoscale cylinder-like capsule capped by two $\{Co_9P_5W_{27}\}$ with three BHEP-based ligand spacers.

Introduction

The massive increase in research activity in the area of polyoxometalates (POMs), and related anions, during the last two decades has been facilitated mostly by the great advances in structural and analytical techniques.[1] Further, the advances in POM research underlines the exceptionally diverse range of accessible building blocks,[1] their ease of synthesis, and range of properties of the resulting POMs from catalysis to medicine,[2] with the area of lacunary POMs probably seeing the greatest increase in synthetic interest due to the possibility of extensive derivatisation. Traditionally the study of lacunary Keggin and Wells-Dawson clusters has been to investigate their interactions with additional electrophiles which can fill the vacant positions in the metal oxide framework, commonly resulting in the reformation of the parent cluster type with varying degrees of metal substitution.[3] There is also a considerable number of materials containing Knoth[4] and Weakley[5] type POM motifs that have been synthesized using the appropriate $\{XM_9\}$ or $\{X_2M_{15}\}$ precursors. More recently it has been identified that particular clusters such as the metastable $K_8[\gamma\text{-}SiW_{10}O_{36}]$ are extremely susceptible to structural rearrangement, dependant on relatively subtle differences in reaction conditions.[6] This discovery has consequently resulted in a wealth of new Transition Metal Substituted Polyoxometalates (TMSPs), of vast structural variation and composition.[3,7] The interaction of metal complexes with POMs has also received significant attention, due to the highly anionic nature of the clusters, and it is not at all surprising that they are highly susceptible to coordination with cationic species.[8] These properties have consequently, resulted in the formation of a large number of functionalized molecules,[9] chains[10] and multidimensional materials based upon POM clusters and building blocks.[11] More fundamentally, it is well known that the polyanion self-assembly process occurs *via* acidification and is in most cases extremely sensitive to the cation effects.[12] Therefore we hypothesized that the use of bhep as a trifunctional unit which can act as a ligand, as a cation, and a buffer would exert considerable influence over the assembly of the overall polyoxometalate architecture.[13] As an extrapolation of previous work, that resulted in the isolation of two novel network materials including the layered material containing the phosphate linked $[(PMnW_{11}O_{39})_2\{PO_4\}]^{13-}$ dimer, we have continued to explore the influence of N,N′-Bis(2-hydroxyethyl)piperazine (bhep) on the assembly process.[14] Using the first row transition metals Co^{2+} and Ni^{2+}, two new phosphotungstates of general formula $Na_2\{Mbhep(H_2O)_4\}\ [PW_{10}M_2O_{38}\{Hbhep\}_2]\cdot 8H_2O$ (M = Co^{2+}, Ni^{2+}) have been crystallised each encapsulating a transition metal coordination complex, that is also observed as an isolated countercation in the crystal structure. This process highlights an important advance towards the extension of transition metal incorporated polyoxometalates that are distinctly different from the large quantity of well established structural types highlighted earlier. In 2005 Pope *et al.* reported the first example of chelated transition metal embedded into a phosphotungstate vacancy using the preformed $K[Co(en)(CO_3)_2]$ complex and the $Na_9[A\text{-}PW_9O_{34}]\cdot 7H_2O$ cluster anion, whereby the chelated metal forms a number of coordination bonds to the polyanion.[15] However, (**1**) and (**2**) can be seen as further building on this report through the complete encapsulation of a Co^{2+}/Ni^{2+} ligand-complex into the self-assembled divacant polyanion where the ethanol arm of the ligand is involved in the formation of an unusual

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W-O-C linkage. In addition to $[PW_{10}M_2O_{38}\{Hbhep\}_2]^{5-}$ (**1–2**), $[(P_2Co_4W_{18}O_{68})]^{10-}$ (**3**) represents an isostructural analogue of a 2D hybrid framework reported previously by extending our work based on the $[P_2W_{18}Co_4O_{68}]^{12-}$ polyanion, with (**4**) representing one of the largest cobalt containing phosphotungstates to date crystallizing as a secondary product in the preparation of (**3**). As in the original synthesis of the $[P_2W_{18}Co_4O_{68}]^{12-}$ polyanion reported by Weakley in 1984, (**4**) contains the same trimeric $[Co_9(OH)_3(H_2O)_6(HPO_4)_2(B\text{-}\alpha\text{-}PW_9O_{34})_3]^{16-}$ polyanion which co-crystallizes with a triply bhep linked molecule which represents a large hybrid cobalt phosphotungstate containing eighteen Co^{2+} ions. Importantly (**1–4**) are all synthesized *via* self-assembly utilizing the multifunctional properties of bhep such as the multiple accessible protonation states and the range of coordination modes (Fig. 1).

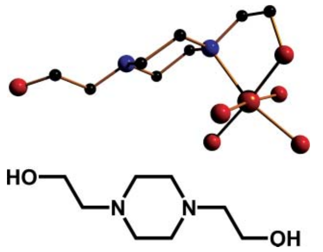

Fig. 1 Graphical representation of the $[Co^{II}(Hbhep)(H_2O)_4]^{3+}$ complex that is present as an isolated countercation and as the encapsulated chelate found in (**1**), and the N,N′-Bis(2-hydroxyethyl)piperazine (bhep) ligand that exhibits chelation tendency in (**1–2**), and end-on coordination in (**3–4**). Co = orange sphere, O = red spheres, N = blue spheres, C = black spheres.

Experimental

Materials, methods and instrumentation

All reagents were used as purchased without purification under ambient reaction conditions. Infrared spectra were measured using a Jasco FTIR-410 spectrometer. Carbon, nitrogen and hydrogen content were determined by the microanalysis services within the Department of Chemistry, University of Glasgow using an EA 1110 CHNS, CE-440 Elemental Analyser. X-Ray diffraction intensity data for (**1**,**2** and **4**) were measured at 100 K on an APEX II diffractometer with [λ(Mo-Kα) = 0.71073 Å] radiation and a graphite monochromator while (**3**) was measured on a Nonius Kappa-CCD diffractometer with Mo-Kα radiation and a graphite monochromator. Structure solution and refinement for (**1–4**) was performed using SHELXTL *via* the APEX II software package.[16] Corrections for incident and diffracted beam absorption effects were applied using empirical or numerical methods. All structures were solved by a combination of direct methods and difference Fourier syntheses and refined against $|F|^2$ by the full-matrix least-squares technique, see Table 1.

Synthesis of compounds

Preparation of $Na_2\{CoHbhep(H_2O)_4\}[PW_{10}Co_2O_{38}\{Hbhep\}_2]\cdot 8H_2O$ (1). $Na_2WO_4\cdot 2H_2O$ (8.25 g, 25 mmol) was dissolved in 100 mL of 1 M NaCl, and the solution acidified to pH 3.5 using 4 M nitric acid. To this solution is added N,N′-Bis(2-hydroxyethyl)piperazine (4.75 g, 27 mmol), followed by 85% H_3PO_4 (2.05 g, 17.7 mmol) resulting in a white precipitate that re-dissolves on stirring. $Co(NO_3)_2\cdot 6H_2O$ (1.55 g, 5.3 mmol) is then added resulting in a red solution and a large amount of purple precipitate. The solution is then stirred overnight, and filtered after 18hrs. A small amount of compound (**3**) is isolated as purple blocks, however the major product is isolated as a red crystalline material that can be recrystallised by dissolving in hot water followed by diffusion of ethyl acetate. Large red blocks begin to form within 3–4 days. Yield = (900 mg, 0.26 mmol, 10.45% based on W). Elemental analysis for $Na_2\{Co(C_8H_{19}N_2O_2)(H_2O)_4\}[PW_{10}Co_2O_{38}\{C_8H_{19}N_2O_2\}_2]\cdot 8H_2O$ $C_{24}H_{81}N_6Co_3Na_2O_{56}P_1W_{10}$, MW = 3442 g mol^{-1}, calcd (found)%: C 8.37 (8.26), H 2.37 (1.75), N 2.44 (2.27). FTIR (KBr pellet), cm^{-1}: 3386 (br), 1625 (m), 1446 (sh), 1404 (sh), 1058 (sh), 954 (sh), 885 (sh), 803 (sh), 697 (sh), 590 (sh), 501 (sh), 484 (sh), 410 (sh).

Preparation of $Na_2\{NiHbhep(H_2O)_4\}[PW_{10}Ni_2O_{38}\{Hbhep\}_2]\cdot 8H_2O$ (2). $Na_2WO_4\cdot 2H_2O$ (1.65 g, 5 mmol) is dissolved in 20 ml 1 M NaCl and the solution acidified to pH 3.5 with 4M nitric

Table 1 Summary of the structural data and refinements for compounds **1–4**

	1	**2**	**3**	**4**
Empirical formula	$C_{24}H_{81}Co_3N_6$ $Na_2O_{56}P_1W_{10}$	$C_{24}H_{81}N_6Na_2$ $Ni_3O_{56}P_1W_{10}$	$C_{12}H_{45}Co_2N_3$ $Na_2O_{44.50}P_1W_9$	$C_{144}H_{553}Co_{27}N_{36}$ $Na_{18}O_{467}P_{15}W_{81}$
F_w (g mol^{-1})	3442.19	3441.53	2792.97	27624.55
Crystal system	Monoclinic	Monoclinic	Triclinic	Hexagonal
a (Å)	19.8809(6)	19.7772(8)	12.460(2)	34.7146(5)
b (Å)	15.1911(4)	14.9644(7)	13.112(2)	34.7146(5)
c (Å)	25.0011(7)	24.4378(11)	17.209(2)	31.5499(14)
α (°)	90	90	80.46(1)	90
β (°)	106.846(2)	106.709(3)	80.38(1)	90
γ (°)	90	90	67.59(1)	120
Space group	*C*2/*c*	*C*2/*c*	*P*-1	*P*63/*m*
V ($Å^3$)	7226.6(4)	6927.1(5)	2546(1)	32927(2)
Z	4	4	2	2
ρ_{calcd} (g cm^{-1})	3.164	3.300	3.643	2.786
μ (mm^{-1})	16.657	17.474	21.028	14.887
T (K)	100(2)	100(2)	150(2)	100(2)
No. reflections (unique)	30329(7112)	28971(6635)	38101(11644)	50661(9830)
Residuals: $R_{1(obs)}$;$R_{w2(all\ data)}$	0.0357; 0.0793	0.0374;0.1080	0.0585; 0.1244	0.1181;0.3587
R_{int}	0.0591	0.0465	0.0709	0.0870

acid. To this is then added N,N′-Bis(2-hydroxyethyl)piperazine (0.84 g, 4.82 mmol) and 85% H_3PO_4 (0.44 g 3.8 mmol) and the pH adjusted to 6.3 using 4 M nitric acid. $Ni(NO_3)_2{\cdot}6H_2O$ (0.17 g, 0.58 mmol), is then added and the solution heated to 50 °C for 15 minutes. The resulting lime green solution is then centrifuged and left to crystallize by slow evaporation, at a final pH of 6.1. Large green block crystals form over the course of a week. Yield = (800 mg, 0.23 mmol, 46.89% based on W). Elemental analysis for $Na_2\{Ni(C_8H_{19}N_2O_2)(H_2O)_4\}[PW_{10}Ni_2O_{38}\{C_8H_{19}N_2O_2\}_2]{\cdot}8H_2O$, $C_{24}H_{81}N_6Na_2Ni_3O_{56}P_1W_{10}$, MW = 3441 g mol^{-1}, calcd (found)%: C 8.38 (8.14), H 2.37 (1.67), N 2.44 (2.25). FTIR (KBr pellet), cm^{-1}: 3433 (br), 1632 (m), 1458 (wk), 1040 (sh), 943 (m), 882 (m), 754 (m), 665 (s), 483 (wk).

Preparation of $(H_2bhep)_3Na_4[(P_2Co_4W_{18}O_{68})].15H_2O$ (3). $Na_2WO_4{\cdot}2H_2O$ (8.25 g, 25 mmol) was dissolved in 100 mL of 1 M NaCl, and the solution acidified to pH 3.5 using 4 M nitric acid. To this solution is added N,N′-Bis(2-hydroxyethyl)piperazine (4.75 g, 27 mmol) followed by 85% H_3PO_4 (2.05 g, 17.7 mmol) resulting in a white precipitate that re-dissolves on stirring. $Co(NO_3)_2{\cdot}6H_2H_2O$ (1.55 g, 5.3 mmol) is then added resulting in a red solution and a large amount of purple precipitate. The solution is immediately centrifuged and purple block crystals begin to form within 3 hours, and are collected after 2 days. Recrystalisation of the purple precipitate from 1 M NaCl also yields the desired compound. Yield = (1 g, 0.18 mmol, 12.88% based on W). Elemental analysis for $(H_2bhep)_3Na_4[Co_4(H_2O)_2(PW_9O_{34})_2]{\cdot}15H_2O$, $C_{24}H_{90}N_6Co_4Na_4O_{89}P_2W_{18,}$ MW = 5585 g mol^{-1}, calcd (found)%: C 5.16 (4.91), H 1.62 (1.20), N 1.50 (1.33). FTIR (KBr pellet), cm^{-1}: 3468 (br), 2695 (wk), 2607 (wk), 1632 (m), 1379 (sh), 1028 (s), 941 (s), 885 (s), 760 (br), 591 (wk), 497 (sh), 415 (wk).

Preparation of $Na_{18}(H_2bhep)_{15}[\{Co_9(OH)_3(H_2O)_3\ (HPO_4)_2(B\text{-}\alpha\text{-}PW_9O_{34})_3\}_2\{C_8H_{18}N_2O_2\}_3][Co_9(OH)_3(H_2O)_6\ (HPO_4)_2(B\text{-}\alpha\text{-}PW_9O_{34})_3]{\cdot}80H_2O$ (4). $Na_2WO_4{\cdot}2H_2O$ (8.25 g, 25 mmol) was dissolved in 100 mL 1 M NaCl, followed by the addition of N,N′-Bis(2-hydroxyethyl)piperazine (4.75 g, 27 mmol). The solution is then acidified using 85% H_3PO_4 (2.05 g, 17.7 mmol), and 4 M nitric acid until the pH falls to 6.4. $Co(NO_3)_2{\cdot}6H_2O$ (1.55 g, 5.3 mmol), is then added and stirred for 3 min. At this point the pH falls rapidly, and the solutions pH is then raised using saturated NaOH to 6.24, followed by heating at 75 °C for 100 minutes, before briefly heating to 100 °C. The now deep red solution is cooled using an ice bath, and centrifuged to remove the purple precipitate of (**3**) (Fig. 2). Pink hexagonal crystals form within 24 h. Yield = (100 mg, 3.6 μmol, 1.17% based on W). Elemental analysis for $Na_{18}(C_8H_{20}N_2O_2)_{15}[\{Co_9(OH)_3(H_2O)_3(HPO_4)_2\ (B\text{-}\alpha\text{-}PW_9O_{34})_3\}_2\text{-}\{C_8N_2O_2H_{18}\}_3][Co_9(OH)_3(H_2O)_6(HPO_4)_2(B\text{-}\alpha\text{-}PW_9O_{34})_3]{\cdot}80H_2O$, $C_{144}H_{553}N_{36}Co_{27}Na_{18}O_{467}P_{15}W_{81,}$ MW = 27624.55 g mol^{-1}, calcd (found)%: C 6.28 (6.32), H 2.02 (1.72), N 1.83 (1.78), Na 1.50 (1.33). FTIR (KBr pellet), cm^{-1}: 3422 (br), 1627 (m), 1448 (wk), 1033 (sh), 942 (m), 880 (m), 722 (m), 589 (wk), 497 (wk).

Discussion and structural analysis

The syntheses of compounds (**1–4**) all involve self-assembly from simple commercial starting materials, and significantly do not involve the use of a preformed cluster anion. Of importance in the preparation of these compounds, is the presence of a large excess of the ligand N,N′-Bis(2-hydroxyethyl)piperazine (bhep) (Fig. 3).

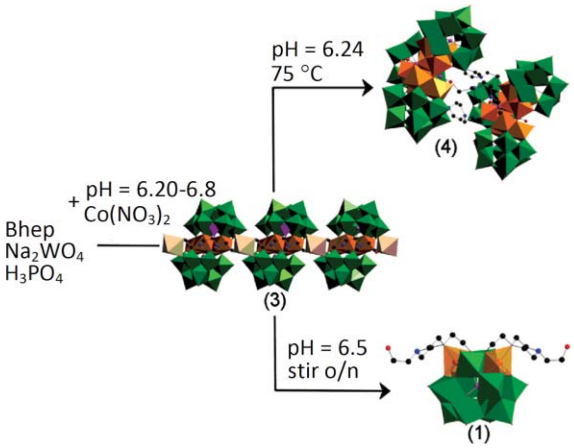

Fig. 2 Simplified reaction scheme of the cobalt containing polyanions highlighting the similar synthetic conditions used to isolate $Na_2\{CoHbhep(H_2O)_4\}[PW_{10}Co_2O_{38}\{Hbhep\}_2]{\cdot}8H_2O$ (**1**), $(H_2bhep)_3Na_4[Co_4(H_2O)_2(PW_9O_{34})_2].15H_2O$ (**3**) and $Na_{18}(H_2bhep)_{15}[\{Co_9(OH)_3(H_2O)_3(HPO_4)_2(B\text{-}\alpha\text{-}PW_9O_{34})_3\}_2\{C_8H_{18}N_2O_2\}_3][Co_9(OH)_3(H_2O)_6(HPO_4)_2(B\text{-}\alpha\text{-}PW_9O_{34})_3]{\cdot}80H_2O$.

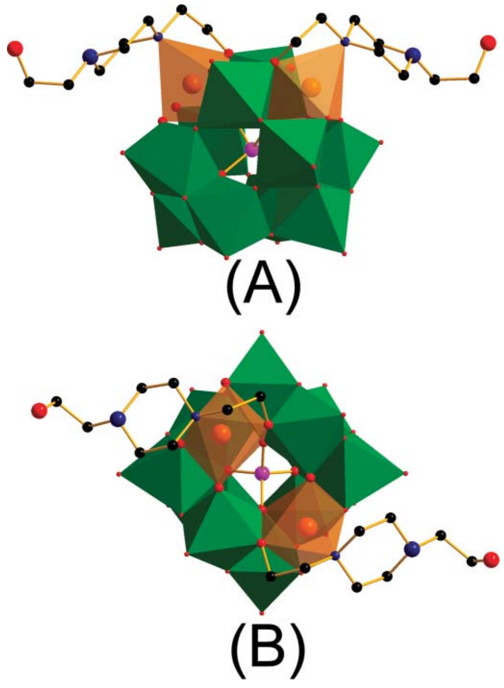

Fig. 3 (A) Encapsulation of two $[Co(Hbhep)(H_2O)_4]^{3+}$ moieties into an α-Keggin resulting in the formation of the saturated $[PW_{10}Co_2O_{38}\{Hbhep\}_2]^{5-}$ cluster anion (**1**). (B) Top down view of (**1**) highlighting the capping $\{W_2Co_2(Hbhep)_2\}$ unit that is shown in ball and stick representation. W = green polyhedra/spheres, Co = orange polyhedra/spheres, O = red spheres, N = blue spheres, C = black spheres.

N,N′-Bis(2-hydroxyethyl)piperazine was chosen as a suitable ligand to investigate the possibility of synthesizing new cluster species, as it is an effective buffer within the pH range 4–8 allowing precise pH control. This essential property has facilitated our efforts to explore its effects as a structure directing cation and as a ligand for transition metals used in the reaction system. The ethanol arms attached to the nitrogen donors of the piperazine ring add flexibility to the ligand, while also forming an ideal coordination environment for the ligation of transition metals. During the complex self-assembly process required for the formation of (**1–2**), the simple transition metal complex $[X(bhep)(H_2O)_4]^{3+}$ ($X = Co^{2+}, Ni^{2+}$) is formed, under conditions that also appear conducive to the formation of a hypothetical dilacunary $[PW_{10}O_{36}(OH)_2]^{9-}$ species, that has resulted in the crystallization of $Na_2\{Mbhep(H_2O)_4\}[PW_{10}M_2O_{38}\{Hbhep\}_2]\cdot 7H_2O$ *via* the insertion of this electrophilic species into the cluster vacancies.

The encapsulated cobalt complex found in (**1**) has a distorted octahedral environment with four equatorial Co–O coordination bonds to the polytungstate in the range (2.018(5)–2.071(5) Å), with a weaker long interaction of 2.265(5) Å between the cobalt and the μ_3 oxo of the Keggins phosphate template. Completion of the metal centres octahedral environment is achieved by a Co–N bond of 2.175(7) Å to the coordinated bhep ligand. Therefore this Co complex can be envisaged to insert into the $\{PW_{10}\}$ moiety *via* loss of the four labile water molecules bound to the coordination complex (Fig. 1), followed by coordination into the clusters nucleophilic vacancy. In order to complete the insertion however, a W–O–C linkage must be formed with this oxygen originating from the hydroxyl group of the bhep ligand that is involved in chelation of the Co^{2+} ion. It is proposed that this process may be driven by a dehydration process which occurs *via* the combination of the proton from the hydroxyl group on the ligand arm with that of a hydroxyl group from a W–OH bond at the appropriate position on the hypothetical $[PW_{10}O_{36}(OH)_2]^{9-}$ species. The resulting $[PW_{10}X_2O_{38}\{Hbhep\}_2]^{5-}$ polyanion can be described as a disubstituted α-Keggin cluster anion that is decorated by two grafted bhep ligands, which are connected to the cluster through X–N and W–O–X bonds whereby the N and O donor atoms belong to that of the organic ligand. Such direct covalent grafting of organic moieties onto polyoxometalate surfaces is an uncommon phenomenon, with the use of preformed organosilyls[17] or organophosphates[18] a common approach. However the examples presented herein closely resemble the more uncommon examples such as the trishydroxymethylamine functionalized cluster species and analogues thereof.[19] Although, to the best of our knowledge compounds (**1**) and (**2**) represent rare examples of the direct surface coordination of a fully embedded metal chelate through two different donor atoms. On viewing of (**1**) along the crystallographic *b*-axis, the clusters can be seen to be close-packed and have an alternate arrangement resulting in the formation of a layered structure. The coordination complex that acts as a counterion is located between these layers and is disordered over two distinct crystallographic positions. Each of the cobalt centres has been modelled with half occupancy and the position of the ligand has also been modeled in association with a number of water molecules that are disordered over the same positions. In addition to these counterions, the charge balance is completed by the presence of two sodium ions. As with most cobalt incorporated tungstophosphates the solution chemistry is extremely complex, and the isolation of a multiple products from any given reaction is reasonably common.[20]

Significantly, both (**1**) and (**3**) $(H_2bhep)_3Na_4[Co_4(H_2O)_2(PW_9O_{34})_2]\cdot 15H_2O$ can be isolated as pure compounds from the same reaction mixture of 8.25 g Na_2WO_4, 4.75 g bhep, 2.05 g H_3PO_4 and 1.55 g $Co(NO_3)_2$ and are separated by differences in solubility and the stirring duration of the reaction mixture. On addition of $Co(NO_3)_2$ to the reaction mixture a large amount of purple precipitate forms, and if immediately filtered the favoured product from this reaction mixture is (**3**). However, if stirred for 18 h at room temperature this purple precipitate re-dissolves with the favoured product being (**1**). These synthetic considerations are complicated further by the additional formation of $Co_3(PO_4)_2$ if the reaction mixture is stirred for longer, eventually resulting in a mixture of products (**1**) and (**3**). The synthesis of (**4**) is achieved by heating a reaction mixture, that otherwise yields (**3**) to 75 °C at pH 6.25 for 100 minutes. The solution is subsequently cooled in an ice bath, resulting in the precipitation of a small amount of (**3**) that is then removed by centrifugation. If the precipitate of (**3**) is not removed at this point, both (**3**) and (**4**) crystallize simultaneously making further purification difficult.

Compound (**3**) is isostructural to a previous compound reported by us[14] based on the $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ cluster anion. It is composed of two [B-α-PW_9O_{34}] units with four cobalt centres sandwiched between these in the well-known belt-like fashion and is formulated as $(H_2bhep)_3Na_4[Co_4(H_2O)_2(PW_9O_{34})_2]\cdot 15H_2O$. The hydroxyl groups of the ligand are involved in the formation of the 2D layered material through Na-bhep-Na linkages that run parallel to the clusters (Fig. 4 and 5), with sodium ions connecting the clusters through a *trans*-Na–O–W linkage (Na–O: 2.42(5) Å, W–O: 1.71(1) Å) with the Na ion located on an inversion centre. The remaining two equatorial coordination sites are occupied by the hydroxyl groups of the bhep ligand and have a slightly shorter contact of 2.24(6) Å (Na–O), with the remaining apical positions occupied by water ligands.

Fig. 4 Packing diagram of (**1**) viewed along the crystallographic *b*-axis. Space filling is used to illustrate the location and orientation of the disordered complex cations, with the additional Na^+ counterions omitted for clarity. W = green polyhedra, Co = orange polyhedra, P = purple spheres, O = red spheres, N = blue spheres, C = black spheres.

The interlaminar space of the crystal structure, is occupied by well defined doubly protonated bhep ligands that complete charge balance requirements, along with further water molecules. By modifying the synthesis of (**3**), $Na_{18}(H_2bhep)_{15}[\{Co_9(OH)_3(H_2O)_3(HPO_4)_2(B\text{-}\alpha\text{-}PW_9O_{34})_3\}_2\{C_8H_{18}N_2O_2\}_3][Co_9(OH)_3(H_2O)_6(HPO_4)_2(B\text{-}\alpha\text{-}PW_9O_{34})_3]$ (**4**) can also be isolated as a minor by-product. (**4**) is composed of a co-crystallised 1:1 mixture of monomeric $[Co_9(OH)_3(H_2O)_6(HPO_4)_2(B\text{-}\alpha\text{-}PW_9O_{34})_3]$ clusters as previously reported by Weakley, and the novel dimeric $[\{Co_9(OH)_3(H_2O)_3(HPO_4)_2(B\text{-}\alpha\text{-}PW_9O_{34})_3\}_2\{C_8H_{18}N_2O_2\}_3]$ polyanion (Fig. 6) which represents the largest hybrid, cobalt containing tungstophosphate to date.

The $[P_5Co_9W_{27}O_{119}H_{17}]^{16-}$ cluster is constructed from three $[B\text{-}\alpha\text{-}PW_9O_{34}]^{9-}$ ligands, with its vacancies filled by three Co^{II}

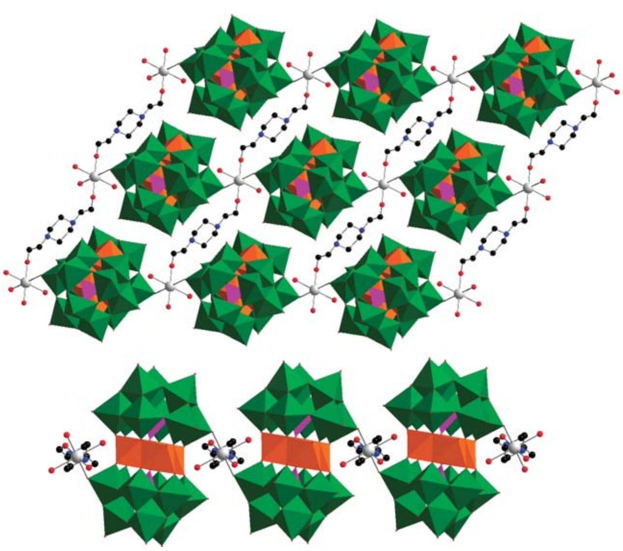

Fig. 5 Packing of (**3**) viewed along both the *c* and *a*-axes showing the layered nature of the hybrid material through Na and bhep linkages. W = green polyhedra, Co = orange polyhedra, P = purple polyhedra, O = red spheres, N = blue spheres, C = black spheres.

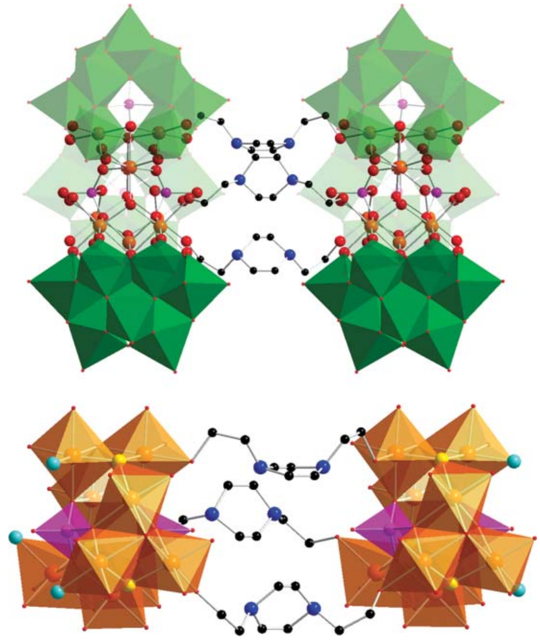

Fig. 6 Faded representation of the dimeric species $[\{Co_9(OH)_3(H_2O)_3(HPO_4)_2(B\text{-}\alpha\text{-}PW_9O_{34})_3\}_2\{C_8H_{18}N_2O_2\}_3][Co_9(OH)_3(H_2O)_6(HPO_4)_2(B\text{-}\alpha\text{-}PW_9O_{34})_3]^{48-}$ (top), with a polyhedral representation of the two bhep linked $[Co_9(OH)_3(H_2O)_6(HPO_4)_2]^{11+}$ cationic cores (bottom).

ions to yield a $[\beta\text{-}PW_9Co_3O_{40}]^{n-}$ Keggin anion which differs from the alpha isomer by rotation of the $\{Co_3\}$ triad by 60°. Each of the $[\beta\text{-}PW_9Co_3O_{40}]^{n-}$ Keggin anions are then connected through a total of three μ_3 hydroxyl ligands which bridge the cobalt centres of neighbouring Keggin units, resulting in an $\{Co_9\}$ core with average Co–OH bond lengths of 2.068 Å. The $\{Co_9\}$ core is also templated by two monoprotonated phosphate groups which bind to the cobalt unit through three μ_3 oxo ligands with average P–O bond lengths of 1.534 Å. Through the inclusion of bhep in a modified synthesis of the $[P_5Co_9W_{27}O_{119}H_{17}]^{16-}$ polyanion, the extension of this nonacobaltate containing cluster into the dimeric $[\{Co_9(OH)_3(H_2O)_3(HPO_4)_2(PW_9O_{34})_3\}_2\{C_8N_2O_2H_{18}\}_3]^{32-}$ occurs.

This new polyanion is the first example of an organic derivatised $[P_5Co_9W_{27}O_{119}H_{17}]^{16-}$ cluster, with it also becoming the highest nuclearity cobalt containing phosphotungstate to date with eighteen cobalt centres in the discreet molecule. In order to form the dimeric cluster anion, three bhep molecules act as bridging units which connect two $[P_5Co_9W_{27}O_{116}H_{11}]^{16-}$ clusters by coordination to a single cobalt centre from each of the $\{Co_3\}$ triads in the structure. Coordination of bhep to the polyanions occurs through the ethanolic hydroxyl groups of the ligands at sites normally occupied by terminal water ligands, thus connecting two $\{Co_9\}$ cores and the polyanions as a result. The Co–OL bonds are all equivalent with bonds of 2.233(5) Å in length. This type of displacement has also been reported recently by Dolbecq[21] and Wang,[22] showing that the aqua ligands commonly found coordinated to sandwich complexes can also be replaced by organic ligands such as oxalate and ethylenediamine under hydrothermal and bench reaction conditions.

Conclusions

Four new phosphotungstate compounds have been synthesized, demonstrating the significant influence of multifunctional water soluble tertiary amines on the self-assembly of polyoxometalates. Through fine control of the reaction system we have successfully isolated the first two examples of truly embedded transition metal chelates into a Keggin polyanion. The decoration of the polyanion surface with modifiable organic moieties indicates the real possibility of producing functional inorganic-organic hybrid materials using this synthetic approach. Additionally, the use of more sophisticated organic moieties will allow us to develop this methodology to tailor the molecules physical properties and we are also attempting to see if we can construct rigid composite cages with polyoxometalate ‘caps’ and organic ‘spacer’ arms similar to compound **4**.

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References

1 (*a*) M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer, Berlin, 1983; (*b*) D. L. Long, E. Burkholder and L. Cronin, *Chem. Soc. Rev.*, 2007, **36**, 105–121; (*c*) P. J. Hagrman, D. Hagrman and J. Zubieta, *Angew. Chem. Int. Ed.*, 1999, **38**, 2638–2684.

2 (*a*) C. Sanchez, G. J. D. A. A. Soler-Illia, F. Ribot, T. Lalot, C. R. Mayer and V. Cabuil, *Chem. Mater.*, 2001, **13**, 3061–3083; (*b*) T. Yamase, *Chem. Rev.*, 1998, **98**, 307–325; (*c*) M. Clemente-Leon, B. Agricole, C. Mingototaud, C. J. Gomez-Gaecia, E. Coronado and P. Delhaes, *Langmuir*, 1997, **13**, 2340–2347; (*d*) R. Neumann and M. Dahan, *Nature*, 1997, **388**, 353–355; (*e*) J. T. Rhule, C. L. Hill, D. A. Judd and R. F. Schinazi, *Chem. Rev.*, 1998, **98**, 327–357.

3 (*a*) C. M. Tourné and G. Tourné, *C R Seances Acad. Sci. Ser C*, 1968, **266**, 1363; (*b*) X.-Y. Zhang, C. J. O’Connor, G. B. Jameson and M. T. Pope, *Inorg. Chem.*, 1996, **35**, 30; (*c*) B. Botar, Y. V. Geletii, P. Kögerler, D. G. Musaev, K. Morokuma, I. A. Weinstock and C. L. Hill, *Dalton Trans.*, 2005, 2017; (*d*) C. Tourné and G. Tourné, *J. Chem. Soc. Dalton Trans.*, 1988, 2411; (*e*) C. J. Gómez-García, E. Coronado, P. Gomez-Romero and N. Casan-Pastor, *Inorg. Chem.*, 1993, **32**, 89; (*f*) P. J. Domaille and W. H. Knoth, *Inorg. Chem.*, 1983, **22**, 818; (*g*) R. G.

Finke, D. K. Lyon, K. Nomiya and T. J. R. Weakley, *Acta. Crystallogr.*, 1990, **C46**, 1592 and references therein; (*h*) R. Contant, M. Abbessi, R. Thouvenot and G. Hervé, *Inorg. Chem.*, 2004, **43**, 3597; (*i*) L. C. W. Baker, V. S. Baker, S. H. Wasfi, G. A. Candela and A. H. Kahn, *J. Am. Chem. Soc.*, 1972, **94**, 5499–5501; (*j*) C. J. Goméz-García, E. Coronado and L. Ouahab, *Angew. Chem. Int. Ed.*, 1992, **31**, 649–651.

4 (*a*) R. D. Farlee, P. J. Domaille and W. H. Knoth, *Organometallics*, 1985, **4**, 62–68; (*b*) R. L. Harlow, P. J. Domaille and W. H. Knoth, *Inorg. Chem.*, 1986, **25**, 1577–1584.

5 J. S. Showell, H. T. Evans and T. J. R. Weakley, *J. Chem. Soc. Chem. Commun.*, 1973, 139–140.

6 Z. Zhang, Y. Li, E. Wang, X. Wang, C. Qin and H. An, *Inorg. Chem.*, 2006, **45**, 4313.

7 S. B. Bassil, S. Nellutla, U. Kortz, C. A. Stowe, Jv Tol, S. N. Dalal, B. Keita and L. Nadjo, *Inorg. Chem.*, 2005, **44**, 2659.

8 (*a*) Z. Han, Y. Zhan, J. Peng, H. Ma, Q. Liu, E. Wang, N. Hu and H. Jia, *Eur. J. Inorg. Chem.*, 2005, **2**, 264–271; (*b*) C. Ritchie, E. Burkholder, P. Kögerler and L. Cronin, *Dalton. Trans.*, 2006, **14**, 1712; (*c*) P.-Q. Zheng, Y.-P. Ren, L.-S. Long, R.-B. Huang and L.-S. Zheng, *Inorg. Chem.*, 2005, **44**, 1190.

9 (*a*) R. N. Devi, E. Burkholder and J. Zubieta, *Inorg. Chem. Acta*, 2003, **348**, 150; (*b*) S.-T. Zheng, J. Zhang and G.-Y. Yang, *Eur. J. Inorg. Chem.*, 2004, **10**, 2004–2007.

10 (*a*) H. Jin, Y. Qi, E. Wang, Y. Li, C. Qin, X. Wang and S. Chang, *Eur. J. Inorg. Chem.*, 2006, 4541–4545; (*b*) D. Drewes, E. V. Limanski and B. Krebs, *Eur. J. Inorg. Chem.*, 2004, 4849–4853.

11 (*a*) Z. Zhang, D. Wang, J. Dou, S. Yan, X. Yao and J. Jiang, *Inorg. Chem.*, 2006, **45**, 10629–10635; (*b*) D. Hagrman, C. Zubieta, D. J. Rose, J. Zubieta and R. C. Haushalter, *Angew. Chem. Int. Ed. Engl.*, 1997, **36**, 873; (*c*) J. Sha, J. Peng, A. Tian, H. Liu, J. Chen, P. Zhang and Z. Su, *Cryst. Growth. Des.*, 2007, **7**, 2535; (*d*) L.-M. Duan, C.-L. Pan, J.-Q. Xu, X.-B. Cui, F.-T. Xie and T.-G. Wang, *Eur. J. Inorg. Chem.*, 2003, 2578–2581; (*e*) C. Ritchie, C. Streb, J. Thiel, S. G. Mitchell, H. N. Miras, D.-L. Long, T. Boyd, R. D. Peacock, T. McGlone and L. Cronin, *Angew. Chem. Int. Ed.*, 2008, **47**, 6881–6884.

12 N. Laronze, J. Marrot and G. Hervé, *Chem. Commun.*, 2003, 2360–2361.

13 (*a*) D. L. Long, P. Kögerler, L. J. Farrugia and L. Cronin, *Dalton Trans.*, 2005, **8**, 1372; (*b*) D. L. Long, P. Kögerler, L. J. Farrugia and L. Cronin, *Angew. Chem. Int. Ed.*, 2003, **42**, 4180; (*c*) D. L. Long, H. Abbas, P. Kögerler and L. Cronin, *J. Am. Chem. Soc.*, 2004, **126**, 13880; (*d*) D. L. Long, P. Kögerler, A. D. C. Parenty, J. Fielden and L. Cronin, *Angew. Chem. Int. Ed.*, 2006, **45**, 4798; (*e*) D. L. Long, O. Brücher, C. Streb and L. Cronin, *Dalton Trans.*, 2006, **23**, 2852.

14 C. Ritchie, E. Burkholder, D. L. Long, D. Adam, P. Kögerler and L. Cronin, *Chem. Commun.*, 2007, 468–470.

15 (*a*) N. Belai and M. T. Pope, *Chem. Commun.*, 2005, 5760–5762; (*b*) P. Mialane, A. Dolbecq, E. Rivière, J. Marrot and F. Sécheresse, *Angew. Chem. Int. Ed.*, 2004, **43**, 2274.

16 *Crystallographic software package APEX2 v2 PC version*, Bruker Analytical X-Ray systems, Madison, WI, USA, 2006.

17 G.-S. Kim, K. S. Hagen and C. L. Hill, *Inorg. Chem.*, 1992, **31**, 5316.

18 C. N. Kato, K. Kasahara, K. Hayashi, T. Yamaguchi, W. Hasegawa and K. Nomiya, *Eur. J. Inorg. Chem.*, 2006, 4834.

19 (*a*) B. Hasenknopf, R. Delmont, P. Herson and P. Gouzerh, *Eur. J. Inorg. Chem.*, 2002, 1081; (*b*) S. Favette, B. Hasenknopf, J. Vaissermann and P. Gouzerh, *Chem. Commun.*, 2003, 2664; (*c*) Y.-F. Song, D. L. Long and L. Cronin, *Angew. Chem. Int. Ed.*, 2007, **46**, 3900.

20 J. M. Clemente-Juan, E. Coronado, A. Forment-Aliaga, J. R. Galán-Mascarós, C. Giménez-Saiz and J. Gómez-Garcia, *Inorg. Chem.*, 2004, **43**, 2689.

21 A. Dolbecq, J.-D. Compain, P. Mialane, J. Marrot, E. Rivière and F. Sécheresse, *Inorg. Chem.*, 2008, **47**, 3371–3378.

22 L.-H. Bi, E.-B. Wang, J. Peng, R.-D. Huang, L. Xu and C.-W. Hu, *Inorg. Chem.*, 2000, **39**, 671.