Polyoxometalate Clusters

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Hybrid Organic–Inorganic Polyoxometalates: Functionalization of V^{IV}/V^{V} Nanosized Clusters to Produce Molecular Capsules**

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Dedicated to Professor John Corish on the occasion of his 65th birthday

The assembly of metal–ligand mediated molecular capsules comprises one of the most vibrant areas of chemistry. A key issue for the formation of such metallosupramolecular entities is the identification of pre-organized, kinetically stable building blocks that provide ligand-accessible coordination sites to direct assembly into the desired molecules. Depending on their dimension and composition, the cavities in molecular capsules can provide unique chemical environments, serving, for instance, as reaction vessels or supramolecular containers.[1] Polyoxometalates can form inorganic capsular entities. Their structures can be rationalized by a set of connection modes and emerge as a result of growth reactions from oligonuclear compounds through giant nanosized molecular aggregates,[2] into extended 3D structures. However, the interest in these materials results not only from their remarkable structural characteristics but also from their intrinsic physicochemical attributes which prompt applications in areas including catalysis, electronics, medicine, and environmental sciences.[3]

Early transition metal ions polarize terminal O^{2-} ligands efficiently, which results in "closed" clusters in which metal–oxygen bonds point radially to the outside. These short M–O bonds, with stabilizing $d\pi$–$p\pi$ contributions, protect the molecular entities but also hamper functionalization and limit the applications of the desired hybrid organic–inorganic materials. Methodologies to functionalize polyoxometalates have recently been reviewed.[4a] Synthetic approaches to incorporate organic moieties include the preparation of imido, diazenido, organosilyl, and alkoxo derivatives.[4] The synthesis of a squarato vanadate(IV) underlines the accessibility of hybrid frameworks using polyoxometalates.[4f] $[V_{12}O_{14}(OH)_4(PhAsO_3)_{10}]^{4-}$, $[V_{14}O_{22}(OH)_4(PhPO_3)_8]^{6-}$, $[ClV_7O_{12}(O_3PC_6H_5)_6]^{2-}$, $[(V_{12}O_{20})(H_2O)_{12}(Ph_2CHPO_3)_8]$, and $[V_{10}O_{24}(O_3AsC_6H_4\text{-}4\text{-}NH_2)_3]^{4-}$ are examples where organic arsonates and phosphonates bind to polyoxovanadate cages.[5] The synthesis of V^{III} and V^{IV} phosphonate-stabilized clusters has been further developed to prepare single-molecule magnets.[6]

We are interested in hybrid materials[7] and, inspired by the synthetic approaches of Zubieta, Clearfield, and Müller,[5] we studied the formation of V^{V}/V^{IV} polyoxometalates in the presence of (4-aminophenyl)arsonic acid, 1,4-benzenebisphosphonic acid, and [1,1′-biphenyl]-4,4′-diylbis-phosphonic acid. These experimental efforts resulted in four synthetically related, unprecedented polyoxometalates: $[V_5O_9(O_3AsC_6H_4NH_2)_4]^{5-}$ (**1**), $[V_{12}O_{14}(OH)_4(H_2O)_2(O_3AsC_6H_4NH_2)_{10}]^{4-}$ (**2**), $[H_2V_{10}O_{18}(O_3PC_6H_4PO_3)_4]^{8-}$ (**3**), and $[H_2V_{10}O_{18}(O_3PC_{12}H_8PO_3)_4]^{8-}$ (**4**). We identified a {V–O} building unit in **1** (see Figure 1) and utilized this pre-organized structural motif to produce a novel class of hybrid capsules, **3** and **4**, whose dimensions can be controlled by those of the organic ligands.

The compounds form reproducibly in good yields in H_2O/dimethyl formamide (DMF) mixtures upon partial reduction of sodium *meta*-vanadates using hydrazine hydrate in the presence of arsonates or phosphonates.

Cluster anion **1**, shown in Figure 1, consists of five vanadium atoms that are surrounded by O donors in a square pyramidal coordination mode. The base of the central

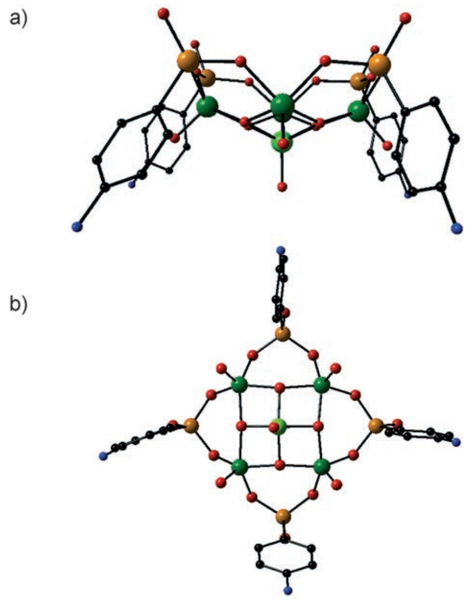

Figure 1. a,b) Different perspectives of the $[V_5O_9(O_3AsC_6H_4\text{-}4\text{-}NH_2)_4]^{5-}$ "calix" structure in $Na_5\cdot\mathbf{1}\cdot 20.5\,H_2O\cdot 3\,DMF$; H atoms neglected for clarity; V^{IV} darker green, V^{V} light green, As orange, O red, N blue, C grey.

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$\{V^VO_5\}$ pyramid shares common edges with its four surrounding $\{V^{IV}O_5\}$ polyhedra to give the typical convex mixed-valent $\{V^VO(\mu_3\text{-}O)_4V^{IV}{}_4O_{12}\}$ unit. The remaining two O donors in the base of each $\{V^{IV}O_5\}$ square pyramid are provided by four (4-aminophenyl)arsonate ligands; each bridging between two V atoms in an O,O′-*syn, syn* coordination mode. The nitrogen functionalities and aromatic ring systems point in the direction of the pyramid tips shaping the appearance of this hybrid organic–inorganic "calix" structure of **1**. Bond valence sum analysis[8] confirms the assigned oxidation states and identifies the μ_3-O donors as O^{2-} oxido ligands. The resulting polyoxovanadate cluster carries an overall charge of −5 which is compensated by solvated sodium ions that further extend the rim of the calix and mediate between the cluster anions in the solid state.

Upon decreasing the pH value of the reaction system, the characteristic green color of the solution of **1** changes into a light blue appearance and blue cubic crystals of $Na_4(H_2O)_{10}$-$[H_2O\subset\mathbf{2}]\cdot1.5\,DMF\cdot1.25\,H_2O$ form (Figure 2). A similar V–O core structure has been reported and is further related to a phosphonate-stabilized polyoxometalate.[5a,b] The polyoxometalate cage **2** contains twelve vanadium atoms and ten (4-aminophenyl)arsonate ligands. Four solvated sodium ions are incorporated in the framework of the cage and compensate the negative charge of the vanadium cluster anion. The cluster can be visualized as the linkage of two calix clusters **1** by eight arsonate functionalities and two partially hydrated $\{O_4V^{IV}(OH)_2V^{IV}O_4\}$ units in which the V ions share a common edge of their distorted octahedral coordination polyhedra. Within one $\{O_4V^{IV}(OH)_2V^{IV}O_4\}$ unit the O donors opposite to the common edge are provided by four (4-aminophenyl)arsonate ligands; two of the ligands link to the same calix rim. However, the $\{V^VO(\mu_3\text{-}O)_4V^{IV}{}_4O_{12}\}$ motif present in **1** is not exactly replicated in **2**; instead of the $\{V^VO_5\}$ unit, arsonate groups of the organic ligands extend the apex of the convex caps of the cage. Differently to the structure reported by Zubieta and Khan,[5a] the solid-state structure of the cage in **2** is completed and closed by two $\{O_2(H_2O)Na(\mu\text{-}H_2O)_3Na(H_2O)O_2\}$ units to give an overall neutral charge. The metal–oxygen core structure of **2** has dimensions of 11.8 Å × 8.6 Å × 8.2 Å.

The structures of **1** and **2** demonstrate the ability to functionalize vanadates using organic ligands. Functionalization with rigid ligands can allow polyoxometalate clusters to be used to prepare porous networks, applicable, for instance, for catalytic, gas storage, or separation purposes.[9] Functionalization may improve their selectivity and performance as antiviral/cancer drugs allowing specific binding to complementary functionalities of proteins, receptors, or infected tissues.[1c]

The transformation between the clusters **1** and **2** can be monitored by UV/Vis spectroscopy (see Supporting Information). The formation conditions for both compounds are distinguishable in the visible region of the spectrum. DMF/H_2O solutions containing **1** show absorption maxima at 721, 602 (shoulder), and 395 nm whilst comparable solutions containing **2** display signals at 700, 624, and 404 nm.

Valence-bond considerations predict almost identical $As^V{-}O$ and $V^V{-}O$ bond lengths which explains the structural equivalence of the apical moieties, $\{As^VO_4\}$ and $\{V^VO_4\}$, in **1** and **2**. In contrast, homologous organophosphonates display significantly shorter P−O distances thus limiting the mutual displacement of $\{V^V\text{–}O\}$ with {P–O} units.[5a] The accessibility of **1** and our motivation to exploit the structural motif for the preparation of hybrid cages and capsules prompted us to use diphosphonates (in place of (4-aminophenyl)arsonate ligands). The ligands 1,4-benzenebisphosphonic acid and [1,1′-biphenyl]-4,4′-diylbisphosphonic acid were synthesized by the Michaelis–Arbuzov reaction.[10] This approach resulted in two unprecedented molecular capsules,

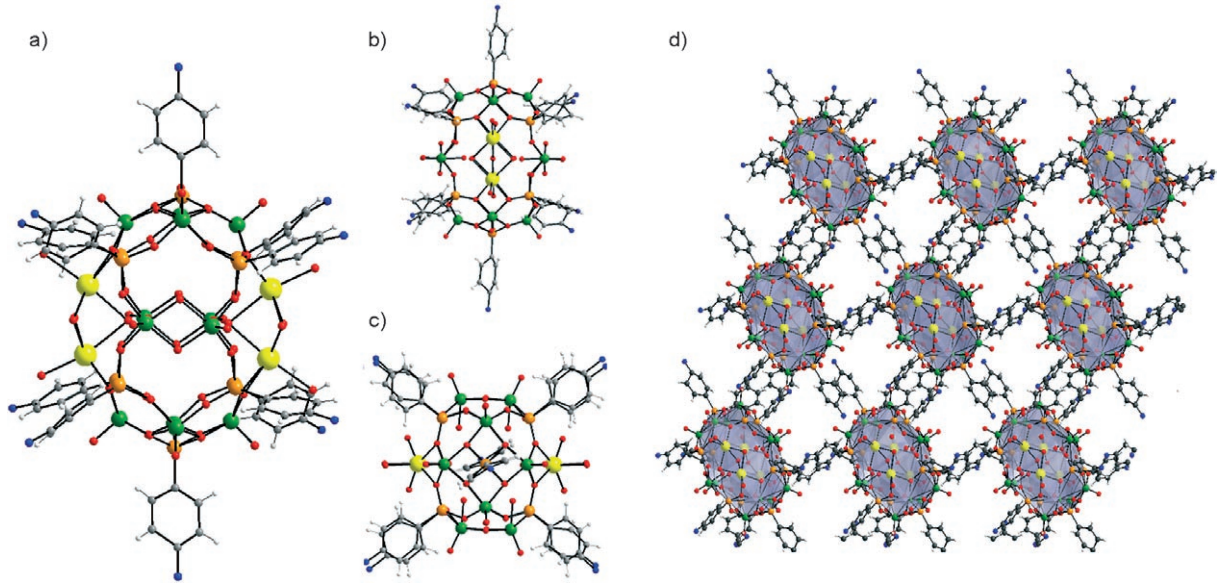

Figure 2. a–c) Different perspectives of **2**. d) Packing of the $\{Na_4(H_2O)_{10}\}[V_{12}O_{12}(OH)_4(H_2O)_2(O_3AsC_6H_4NH_2)_{10}]$ clusters in the crystal structure viewed in the direction of the crystallographic *b*-axis (crystallization solvent molecules have been omitted for clarity). Cage dimensions shaded in mauve: approximately 11.8 Å × 8.6 Å × 8.2 Å. V green, As orange, O red, N blue, C dark grey, Na yellow.

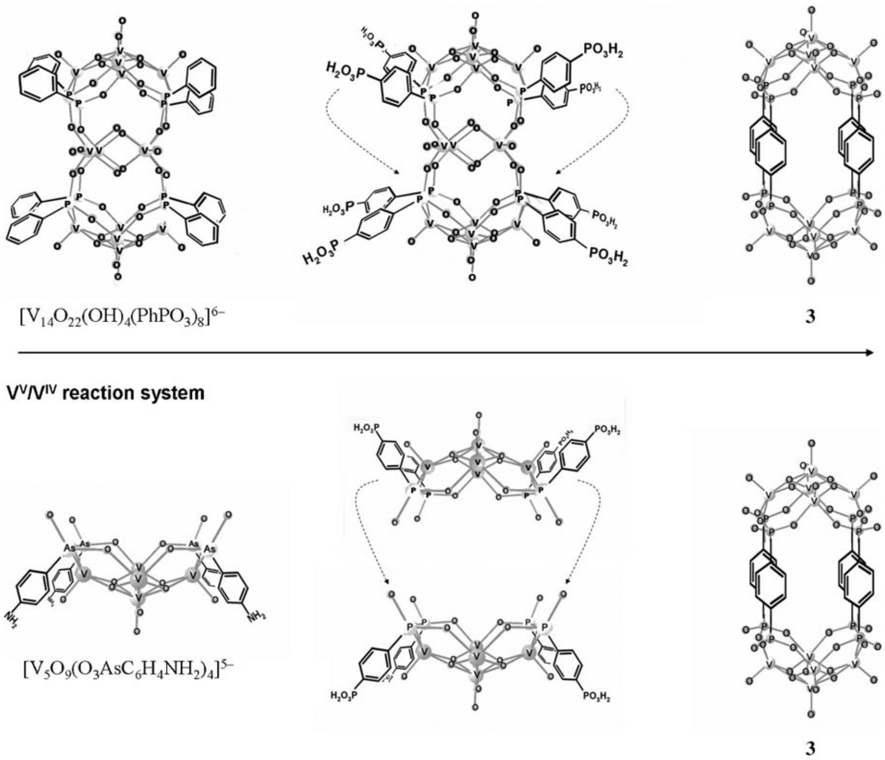

Figure 4. Rationalization of the formation of **3** by comparison of its structure with those of $[V_{14}O_{22}(OH)_4(PhPO_3)_8]^{6-}$ and $[V_5O_9(O_3AsC_6H_4NH_2)_4]^{5-}$ (**1**).[5b] Dotted arrows indicate possible connection modes of the diphosphonate ligands involved.

$[H_2V_{10}O_{18}(O_3PC_6H_4PO_3)_4]^{8-}$ (**3**) and $[H_2V_{10}O_{18}(O_3PC_{12}H_8PO_3)_4]^{8-}$ (**4**), shown in Figure 3.

In both compounds two convex $\{V^VO(\mu_3\text{-}O)_4V^{IV}_4O_{12}\}$ motifs are linked intramolecularly by four diphosphonate ligands. The 1,4-benzenediphosphonate ligands in **3** can easily be replaced by their extended homologues and we anticipate that the resulting cages can thus be elongated. Compound **3** has a length of 15.7 Å (polar diameter) and its capsular entity is characterized by intramolecular V^V–V^V distances of 12.5 Å, a square arrangement of four P atoms with closest P–P distances of 5.5 Å and an average distance of 5.6 Å between the planes of closest parallel-aligned aromatic rings. Respective distances in **4** are: 20.1 Å (polar diameter), 16.9 Å (V^V–V^V), and 5.5 Å (P–P distance). The biphenyl moieties in **4** are slightly disordered, convex curved to the outside of the cages and the distances between the planes of opposite, parallel aligned aromatic rings deviate between 8.2 and 8.4 Å, leading to a larger cavity, which contains two disordered DMF molecules.

Even though structural differences to calixarenes and other cavitands are evident, the potential of the structural motif in **1** to form molecular cages and capsules is comparable.[11] Considering the structure of **1** and the fact that the phosphonates are unlikely to substitute V^V ions, the assembly of the molecular structures of **3** and **4** can be rationalized as shown in Figure 4. The formation of the hybrid capsules can be envisaged as the substitution of the arsonate ligands through binary phosphonates and their conformational rearrangement to link two $\{V^VO(\mu_3\text{-}O)_4V^{IV}_4O_{12}\}$ core structures of **1**. In a slightly less-apparent approach, the structures can be rationalized considering the $[V_{14}O_{22}(OH)_4(PhPO_3)_8]^{6-}$ structure, where four introduced diphosphonates substitute the eight phenyl phosphonates and replace the two bridging $\{O_3V^{IV}(OH)_2V^{IV}O_3\}$ subunits.

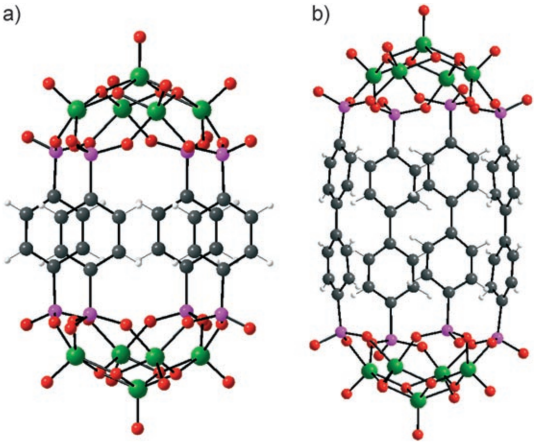

Figure 3. a) Molecular structure of $[H_2V_{10}O_{18}(O_3PC_6H_4PO_3)_4]^{8-}$ (**3**); b) structure of $[H_2V_{10}O_{18}(O_3PC_{12}H_8PO_3)_4]^{8-}$ (**4**). Encapsulated H_2O and DMF molecules have been omitted for clarity. Color code: V green, O red, N blue, C dark grey, P pink.

In summary we report an approach to functionalize polyoxovanadates through partial reduction of V^V salts in the presence of organic arsonates and phosphonates. We identified a {V–O} motif in **1** that can be utilized to construct a novel class of hybrid capsules. Simple extension of the organic ligands affects the formation of elongated capsules; the preparation of further extended analogues of **3** and **4** that incorporate a variety of guests are the subject of ongoing investigations in our laboratory. Bond valence sum analyses (see Supporting Information) and preliminary magnetic studies confirm the assigned oxidation states of **1**–**4**. Moreover, magnetic studies, which will be published elsewhere, indicate that antiferromagnetic interactions in **1** and **2** result in $S=0$ ground states whilst **3** and **4** stabilize higher spin ground states.

Experimental Section

1: A mixture of $NaVO_3$ (0.19 g, 1.53 mmol), NaN_3 (0.25 g, 3.85 mmol), *p*-arsanilic acid (0.44 g, 0.79 mmol), H_2O (20 mL) and DMF (10 mL) was stirred in a 100 mL beaker at 70 °C until a clear solution formed (pH 7.0, 70 °C). After the addition of $N_2H_4{\cdot}H_2O$ (0.045 mL), conc.

aqueous HCl (0.10 mL) was added (pH 7.3, 70 °C). The dark green solution was stirred for 15 min, filtered and allowed to cool to room temperature. The solution was filtered again after one day and crystals of $Na_5\cdot\mathbf{1}\cdot 20.5\,H_2O\cdot 3\,DMF$ were obtained within two days. Yield: 82 %. FTIR ν_{max}: 3349(w), 3222(w), 2928(w), 2194(w), 1648(s), 1621(s), 1592(s), 1503(s), 1297(m), 1184(m), 1092(s), 980(s), 805(s) cm^{-1}, CHN analysis on dried sample: expected for $As_4C_{24}H_{40}N_4Na_5O_{29}V_5$ (corresp. to the cryst. formula and a loss of 3 DMF and 12.5 H_2O): C 18.99, H 2.66, N 3.69 % found: C 18.29, H 2.83, N 4.54 %.

2: Synthetic procedure as for **1**, adding additional conc. aqueous HCl (0.50 mL) to adjust the final pH value to 4.9 (70 °C). Crystals of $Na_4(H_2O)_{10}[H_2O\subset 2]\cdot 1.5\,DMF\cdot 1.25\,H_2O$ were obtained after a five days. Yield 43 %. FTIR ν_{max}: 3365(br), 2932(w), 2035(m), 1650(s), 1594(m), 1505(m), 1438(w), 1413(w), 1388(m), 1254(w), 1095(s), 1062(w), 990(s), 823(s) cm^{-1}. CHN analysis for $As_{10}C_{64.5}H_{95}N_{11.5}Na_4O_{59.75}V_{12}$ (corresp. to the cryst. formula and a loss of 4 H_2O), expected: C 22.52, H 2.78, N 4.68 %; found: C 23.08, H 3.46, N 5.28 %.

3: A mixture of $NaVO_3$ (0.189 g, 1.525 mmol), NaN_3 (0.250 g, 3.850 mmol), 1,4-benzenebisphosphonic acid (0.20 g, 0.86 mmol), H_2O (30 mL), DMF (10 mL) and NEt_3 (0.25 mL) was stirred in a 100 mL beaker at 70 °C until a clear solution formed. Conc. aqueous HCl (0.20 mL), $N_2H_4\cdot H_2O$ (0.045 mL, 0.93 mmol) and further conc aqueous HCl (0.15 mL) were added sequentially, resulting in a green solution (pH 7.5, 70 °C). Crystals of $Na_8[2\,H_2O\subset\mathbf{3}]\cdot 34\,H_2O$ were obtained after one day. Yield: 41 %. FTIR ν_{max}: 3187(br), 2616(br), 2164(w), 2039(m), 1641(s), 1604(sh), 1384(m), 1306(w), 1098(sh), 1050(s), 992(sh), 950(br), 818(m) cm^{-1}, CHN analysis expected for $C_{24}H_{82}Na_8O_{74}P_8V_{10}$ (corresp. to the cryst. formula and a loss of 4 H_2O): C 11.55, H 3.31 %; found: C 11.37, H 2.87 %.

4: Synthetic procedure as for **3** using 0.27 g, (0.86 mmol) of [1,1′-biphenyl]-4,4′-diylbis-phosphonic acid as ligand. Crystals of $Na_8[2\,DMF\subset\mathbf{4}]\cdot 29\,H_2O$ were obtained after five days. Yield: 36 %. FTIR ν_{max}: 3343(br), 2160(w), 2037(w), 1639(s), 1537(w), 1454(w), 1389(m), 1102(s), 1045(s), 1030(s), 1022(s), 966(s), 817(s)cm^{-1}. CHN analysis for $C_{54}H_{98}N_2Na_8O_{73}P_8V_{10}$, expected: C 22.49, H 3.42, N 0.97 %; found: C 21.82, H 2.79, N 1.51 %. Quantitative V and As analyses (ICP-MS) agree with the formulae of **1**–**4**.

Crystallographic Data: Data were measured at 150 K on a Bruker SMART Apex diffractometer using graphite-monochromated $Mo_{K\alpha}$ radiation. Structure solution was carried out by direct methods and full-matrix refinement against F^2 (all data) using SHELXTL.[12] Crystallographic data, CCDC 684567, 684568, 684569, and 684570 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

$Na_5\cdot\mathbf{1}\cdot 20.5\,H_2O\cdot 3\,DMF$: $As_4C_{33}H_{86}N_7Na_5O_{44.5}V_5$, 3924.84 $g\,mol^{-1}$, green plates, 0.25 × 0.2 × 0.1 mm, triclinic, $P\bar{1}$, $a = 13.9310(16)$ Å, $b = 15.1369(17)$ Å, $c = 17.502(2)$ Å, $\alpha = 82.657(2)°$, $\beta = 78.338(2)°$, $\gamma = 88.612(2)°$, $V = 3584.9(7)$ Å^3, Z. = 2, $F(000) = 1982$, $\rho_{calc} = 1.818\,Mg\,m^{-3}$, $\mu(Mo_{K\alpha}) = 2.593\,mm^{-1}$, 50501 reflections measured ($2\theta_{max} = 56.64°$) of which 17776 unique ($R_{int} = 0.0776$), 1032 parameters, $wR_2 = 0.0818$, $S = 0.977$ (all data), R_1 (14474 data with $I > 2\sigma(I)) = 0.0329$.

$Na_4(H_2O)_{10}[H_2O\subset\mathbf{2}]\cdot 1.5\,DMF\cdot 1.25\,H_2O$: $As_{10}C_{64.5}H_{62}N_{11.5}Na_4O_{63.75}V_{12}$, 3470.70 $g\,mol^{-1}$, blue blocks, 0.25 × 0.25 × 0.1 mm, triclinic, $P\bar{1}$, $a = 16.542(3)$ Å, $b = 16.822(4)$ Å, $c = 16.822(4)$ Å, $\alpha = 115.620\ (3)°$, $\beta = 100.758(3)°$, $\gamma = 100.758(3)°$, $V = 3953.1(14)$ Å^3, $Z = 1$, $F(000) = 1690$, $\rho_{calc} = 1.458\,Mg\,m^{-3}$, $\mu(Mo_{K\alpha}) = 2.837\,mm^{-1}$, 42687 reflections measured ($2\theta_{max} = 50.0°$) of which 13928 unique ($R_{int} = 0.1114$). 758 parameters, $wR_2 = 0.2355$, $S = 1.049$ (all data), R_1 (7840 data with $I > 2\sigma(I)) = 0.0791$.

$Na_8[2\,H_2O\subset\mathbf{3}]\cdot 34\,H_2O$: $C_{12}H_{16}Na_4O_{39}P_4V_5$, 1255.25 $g\,mol^{-1}$, green plates, 0.2 × 0.2 × 0.1 mm, tetragonal, $P4/mnc$, $a = 12.1276(15)$ Å, $c = 30.574(6)$ Å, $V = 4496.8(12)$ Å^3, $Z = 4$, $F(000) = 2476$, $\rho_{calc} = 1.853\,Mg\,m^{-3}$, $\mu(Mo_{K\alpha}) = 1.292\,mm^{-1}$, 17802 reflections measured ($2\theta_{max} = 50.0°$) of which 2043 unique ($R_{int} = 0.1512$), 186 parameters, $wR_2 = 0.1921$, $S = 1.162$ (all data), R_1 (1557 data with $I > 2\sigma(I)) = 0.0856$.

$Na_8[2\,DMF\subset\mathbf{4}]\cdot 29\,H_2O$: $C_{27}H_{47}NNa_4O_{36.5}P_4V_5$, 1439.19 $g\,mol^{-1}$, green octahedra, 0.2 × 0.15 × 0.15 mm, tetragonal, $P4/mnc$, $a = 12.2764(17)$ Å, $c = 38.948(8)$ Å, $\alpha = 97.662(10)°$, $Z = 4$, $F(000) = 2904$, $\rho_{calc} = 1.629\,Mg\,m^{-3}$, $\mu(Mo_{K\alpha}) = 0.998\,mm^{-1}$, 30020 reflections measured ($2\theta_{max} = 51.0°$) of which 2792 unique ($R_{int} = 0.0327$), 292 parameters, $wR_2 = 0.1801$, $S = 1.177$ (all data), R_1 (2635 data with $I > 2\sigma(I)) = 0.0570$. Aromatic rings in **2**–**4** are disordered.

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