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A coordination network containing non-coordinating polyoxometalate clusters as counterions

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This report describes the synthesis and characterization of a 2D coordination network that directly incorporates an aniline-functionalized polyoxometalate (POM) cluster. By reacting a cobalt(II) salt of the POM cluster $[Mo_{12}O_{46}(AsC_6H_4NH_2)_4]^{4-}$ with a bifunctional ligand, 4,4′-bipyridylethylene, a 2D coordination network was synthesized through a self-assembly process. The POM behaves as a non-coordinating anion and does not interfere with the coordination network other than occupying space. Thermal analysis reveals that the structure is stable to 350 °C.

Introduction

Since the influential work of Hoskins and Robson in 1990,[1] an enormous number of coordination polymer structures have been reported.[2] The main emphasis of these studies has been the prediction of structure and architecture, and exploration of the porous nature of these systems.[3] Coordination network materials may find application in specific guest adsorption,[4–6] catalysis,[7] chiral separation,[8] ion-exchange,[9] or uses that depend on magnetic and electrical properties of the single metal centers.[10,11]

A limitation of coordination polymers has been network and framework interpenetration, which occurs commonly and can result in loss of porosity.[12,13] Because large void spaces are thermodynamically unfavorable, two or more independent networks may become interpenetrated during assembly of the coordination framework to fill the voids within each of the independent structures. In an effort to decrease the likelihood of interpenetration, large anions, such as PF_6^- or BF_4^- are often used. While these hinder interpenetration, they are chemically uninteresting in these structures. Another drawback is that with few exceptions, they lack specific chemical functionality. A few materials contain open coordination sites,[14,15] or sites occupied by labile ligands. Functionalization has also been introduced by employing ligands such as porphyrins.[16–18]

The goal of the work presented here was to synthesize a coordination network that was both chemically functional and noninterpenetrating. To this end, metal salts of polyoxometalates (POMs) were employed as molecular building blocks. These precursors allowed the formation of coordination polymers with POM clusters occluded within the metal–ligand network. The dimensionality of the coordination polymers produced was 1D with 4,4-bipyridine[19] and 2D with 4,4′-bipyridyl ethylene (4,4′-bpe) groups as tethers between metal ions, although with the use of longer linkers, 3D frameworks may be synthesized. Recently, however, incorporation of a non-coordinated, Keggin-type POM within a 3D coordination framework using a shorter 4,4′-bipyridine ligand has been reported.[20] Organically modified POMs were chosen because they are easily functionalized with a wide variety of organic groups,[21] which could be tailored for specific properties, such as coordination sites or acidity. POM–metal salts with Co^{2+}, Mn^{2+}, Ni^{2+}, Zn^{2+} and Cu^{2+} as counterions have been obtained by metathesis. We report here a structure containing Co^{2+}, as this was the first studied, but the other POM–metal salts may produce similar structures in the presence of bifunctional ligands. By decorating a coordination polymer with potentially interesting anions, properties involving these anions may be realized.

Results and discussion

By a slow diffusion reaction of 4,4′-bipyridyl ethylene in H_2O–EtOH with $Co_2[Mo_{12}O_{46}(AsC_6H_4NH_2)_4]$ in DMSO, crystals of **1** were obtained after one week. The coordination polymer obtained was two-dimensional with two octahedral Co^{2+} environments, one referred to as bridging (Co1) because it provides the linkages into the second dimension; the other (Co2) is capping (Fig. 1). Co2 is located on either end of linear chains, comprised of four Co ions and three 4,4′-bpe ligands, the planes of which run along the <−411> crystal plane and extend over four unit cells for a total Co ··· Co span of 40.56 Å (Fig. 2). Co2 is coordinated by five oxygen donors (one H_2O, four DMSO) and one nitrogen from 4,4′-bpe (average bond distance 2.10 Å). It appears that due to the relatively high donor capacity of DMSO the coordinated DMSO ligands hinder coordination of 4,4′-bpe and "cap" the Co^{2+} site at the end of the chains, preventing further growth. The Co1 sites are located in the two middle points of the linear chain and are coordinated by three oxygen ligands (one H_2O, two DMSO) and nitrogen atoms from three 4,4′-bpe molecules (average distance of 2.12 Å). These sites act as bridging points to Co1 sites of the linear chain in the neighboring cell. The overall motif is that of a descending "H" pattern with the top and bottom of each side of the "H" capped by the Co2 site and the bridging sites occupied by Co1 (see Fig. 3). This may also be viewed as zigzag chains of Co–L–Co (L = 4,4′-bpe) in which each bridging Co1

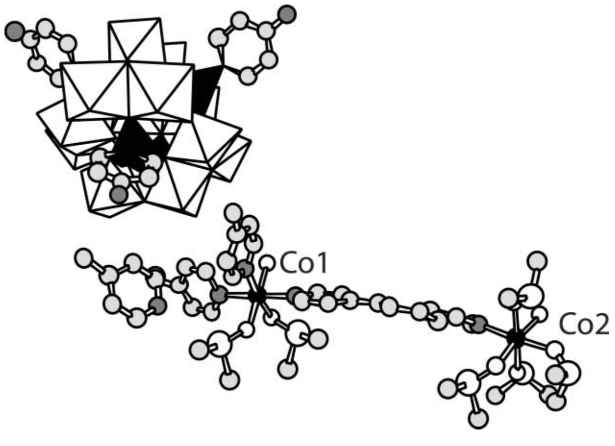

Fig. 1 View of the unit cell contents. Non-bonded solvent and hydrogen atoms were removed for clarity. The guest 4,4′-bpe can be seen in the lower left corner, it is shared with the neighboring unit cell. Mo – white octahedra; As – black tetrahedra; Co – black circles; S – large, white circles; N – grey circles; C – light grey circles; O – small, white circles.

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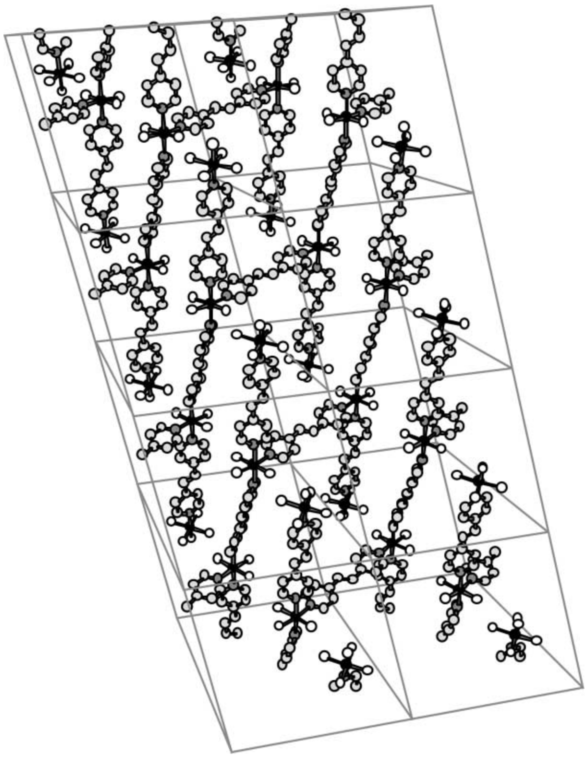

Fig. 2 Unit cell of **1** showing only the coordination network. Co – black circles; O atoms of solvent molecules (H_2O, DMSO) – white circles; C – light grey circles; N – grey circles. Non-bonded solvent molecules, hydrogen atoms and clusters are removed for clarity.

center has pendant (4,4′-bpe)Co(solvent)$_5$ groups capping the vertices. The distance between Co1 and Co2 sites is 13.55 Å, between Co1 ⋯ Co1 within the same linear chain, 13.52 Å, and between Co1 sites bridging chains, 13.69 Å. In the third dimension, the zigzag chains are separated by an average distance of 7.5 Å.

One guest 4,4′-bpe molecule is located between the POM and the coordination network. It does not participate in coordination or hydrogen bonding to occluded solvent and appears to be space filling. There were also six solvent molecules occluded within the structure (five H_2O and one DMSO) that were identified by X-ray crystallography.

The cluster anion, $[Mo_{12}O_{46}(AsC_6H_4NH_2)_4]^{4-}$, was identical in this structure to the starting cluster,[22] and no significant differences in bond lengths or angles were noted. The FTIR spectrum of **1** also indicated the presence of the POM with characteristic peaks in the region 1100–800 cm^{-1}. This cluster is often referred to as an "inverse-Keggin" cluster; it has tetrahedral symmetry, but the heteroatoms are located on the outer surface of the cluster as opposed to the interior. The cluster occupies space between networks above and below the perpendicular "H" bridges (Fig. 4). The pendant aniline moieties do not take part in coordination to either Co center, but hydrogen-bond to solvent molecules. No hydrogen bonds were located between the aniline hydrogens and terminal oxo ligands on the POM cluster, in contrast with those structures discussed in previous work.[23,24] This is probably due to the distance between POMs induced by the coordination network. The POM clusters used in this work are inert to redox chemistry as they are "*cis*-dioxo" POMs, which cannot undergo reduction without significant structural changes.[25] The advantage of this POM is that the organic groups may be modified. Clusters with other organic groups such as sulfonic or carboxylic acids would have charged sites possibly leading to acidic or ion-exchange sites.

A thermal analysis (TGA-DSC) of the crystals revealed that the material was stable up to 350 °C and up to that temperature loses only solvent (see Fig. 5). Loss of solvent water takes place at 100 °C and DMSO loss begins at 280 °C. The mass losses correspond to 15 water and three DMSO molecules, which agreed well with the number of solvent molecules determined by elemental analysis. Above 350 °C, a large mass loss with three distinct exothermic peaks was noted. This corresponded to the loss of coordinated DMSO molecules and the combustion of 4,4′-bpe and aniline moieties attached to the POM cluster. No exothermic events without mass loss appeared until the temperature was raised above 350 °C, indicating that the crystal structure does not undergo restructuring within this temperature range.

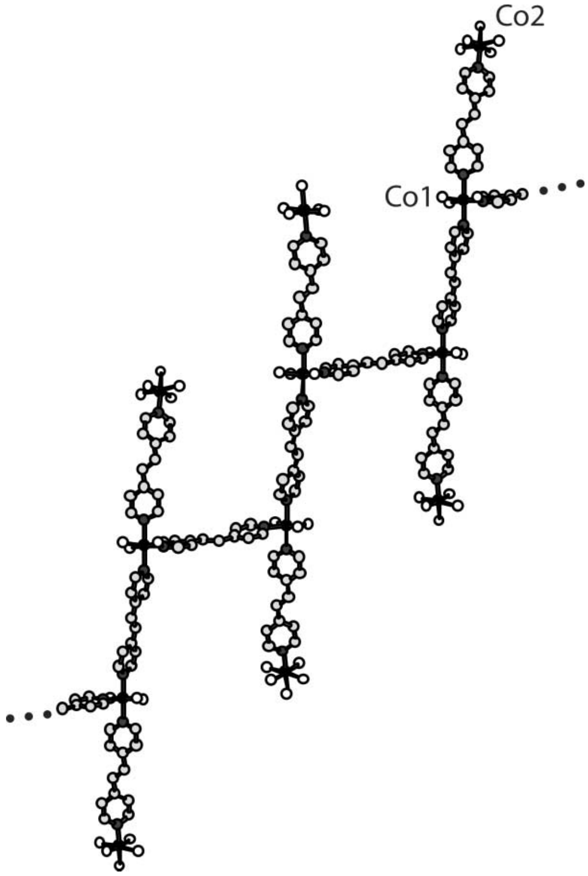

Fig. 3 Structure of one Co–L–Co (L = 4,4′-bpe) zigzag chain with pendant 4,4′-bpe-Co capping sites. The distance from Co2–Co2 is 40.56 Å. Co – black circles; O atoms of solvent molecules (H_2O, DMSO) – white circles; C – light grey circles; N – grey circles.

Conclusion

It has been shown that non-interpenetrated coordination networks may be constructed, which directly incorporate organically functionalized POM clusters into the structure. The metal–POM precursors were easily obtained by metathesis and the coordination network was grown around the POM by standard slow diffusion methods. The product consisted of an infinite Co^{2+}/4,4′-bpe zigzag chain with pendant (4,4′-bpe)-Co(solvent)$_5$ groups capping each of the vertices. The POM clusters are located near each of the capping Co sites, but no bonding between the aniline groups of the POM and the metal ions was present. Thermal analysis revealed that the crystal structure was retained upon loss of solvent molecules and that the material is thermally stable to 350 °C. The work presented here serves as an example for how chemically interesting anions may be occluded within the network of a coordination polymer.

Experimental

$[Mo_{12}O_{46}(AsC_6H_4NH_3^+)_4]$ was synthesized according to literature procedures.[22]

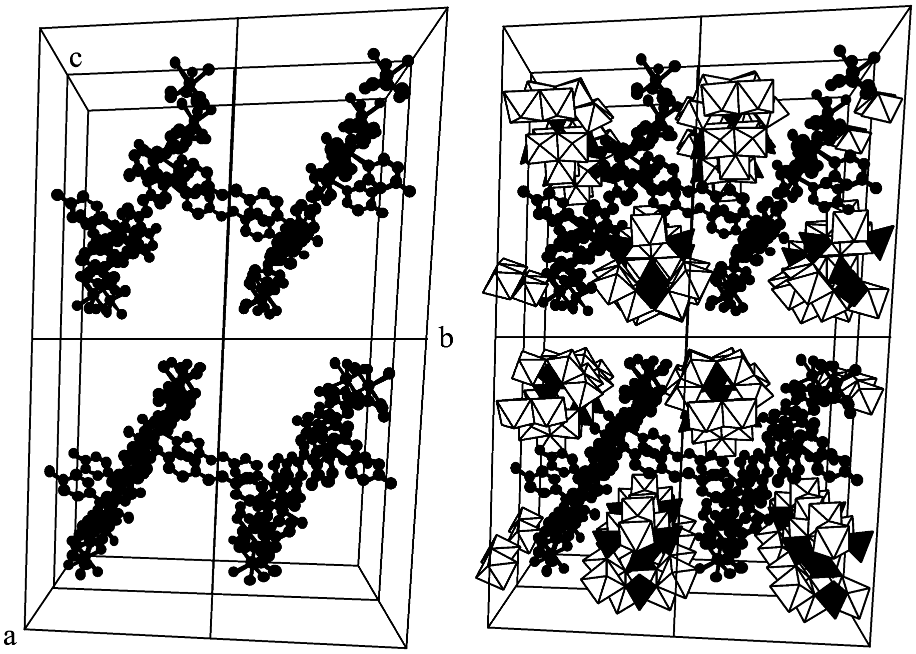

Fig. 4 Left: Unit cell viewed down the *a*-axis showing only the coordination network skeleton. Right: The same view portraying the position of the POM clusters in relation to the coordination network. Solvent molecules, guest 4,4′-bpe, and aniline groups have been removed for clarity; the metal–ligand network has been depicted in black to guide the eye.

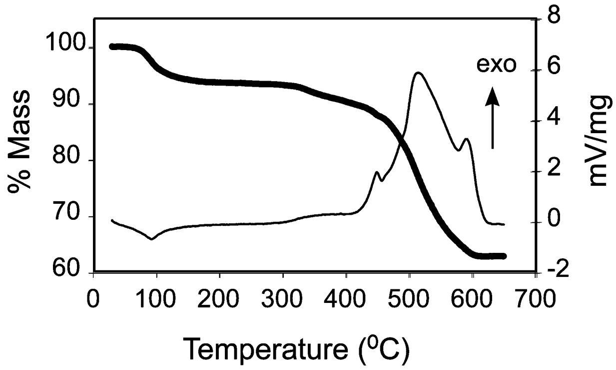

Fig. 5 TGA (thick line) and DSC (thin line) traces of **1**. Solvent water and DMSO are lost up to 300 °C. No exothermic peaks are present in the DSC until the loss of 4,4′-bpe and aniline moieties.

$Co_2[Mo_{12}O_{46}(AsC_6H_4NH_2)_4]$

0.512 g (0.2 mmol) of $[Mo_{12}O_{46}(AsC_6H_4NH_3^+)_4]$ was dispersed in 25 mL of H_2O. To this was added 0.067 g (0.8 mmol) of $NaHCO_3$. Once the evolution of gas had ceased and the solid was dissolved, 1.10 g (0.276 mol) of $Co(ClO_4)_2{\cdot}6H_2O$ was added as a solid. Almost immediately an orange microcrystalline powder precipitated from the solution and was collected by filtration. Elemental analysis (Found: Mo, 38.20; As, 9.68; Co, 3.74. Calc. for $Co_2[Mo_{12}O_{46}(AsC_6H_4NH_2)_4]{\cdot}xH_2O$, $x = 19$: Mo, 38.18; As, 9.94, Co, 3.91%). FT-IR (KBr): ν_{max}/cm^{-1} 3349, 1625, 1591, 1504, 1427, 1299, 1191, 1122, 1090 (As–C), 978, 952 (Mo–O), 932 (Mo–O), 873 (Mo–O), 843, 587, 486.

$[Co(bpe)_{1.5}(H_2O)(DMSO)_2][Co(bpe)_{0.5}(H_2O)(DMSO)_4]$-$[Mo_{12}O_{46}(AsC_6H_4NH_2)_4]{\cdot}0.5bpe{\cdot}10DMSO{\cdot}5H_2O$

0.100 g of $Co_2[Mo_{12}O_{46}(AsC_6H_4NH_2)_4]$ was dissolved in 20 mL of DMSO, filtered with a 0.2 μm filter and the solution placed into a 10 dram vial. On top of this was carefully layered 10 mL of H_2O. To the top layer a solution of 0.027 g (1.5 mmol) 4,4′-bpe in 2 mL of H_2O–EtOH (2 : 1) was slowly added. After one week, red-pink crystals suitable for X-ray diffraction had appeared. Elemental analysis (Found: Mo, 27.81; As, 7.29; Co, 2.79; S, 6.52. Calculated for $[Co(bpe)_{1.5}(H_2O)(DMSO)_2]$-$[Co(bpe)_{0.5}(H_2O)(DMSO)_4][Mo_{12}O_{46}(AsC_6H_4NH_2)_4]{\cdot}0.5bpe{\cdot}xH_2O{\cdot}y$DMSO ($x = 18$, $y = 3$): Mo, 27.84; As, 7.25; Co, 2.85; S, 6.59%). FT-IR (KBr): ν_{max}/cm^{-1} 3519, 3434, 3363, 3213, 3064, 3003, 2916, 2851, 1610, 1593, 1507, 1423, 1315, 1191, 1090 (As–C), 1007, 947 (Mo–O), 922 (Mo–O), 863 (Mo–O), 843, 715, 590, 514, 485.

Crystal data for 1

$C_{68}H_{101}N_9O_{60}Mo_{12}As_4Co_2S_7$: flat, pink block 0.20 × 0.10 × 0.05 mm, M_r = 3797.82, triclinic, space group $P\bar{1}$, a = 15.5503(8), b = 16.3975(8), c = 25.6754(4) Å, α = 86.4690(10), β = 83.7720(10), γ = 80.4230(10)°, V = 6411.2(6) Å^3, Z = 2, T = 173 K, μ = 2.608 mm^{-1}, D_c = 1.967 g cm^{-3}, Mo-Kα radiation (λ = 0.71073 Å), F(000) = 3708, $2\theta_{max}$ = 25.03°, 22584 independent reflections, 11711 observed reflections, 1364 parameters, R_1 = 0.0523, wR_2 = 0.1029. Data were collected on a Siemens SMART system. The structure was solved by direct methods. Full-matrix least squares/difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. Electron density associated with all but one DMSO solvent molecule was removed using the SQUEEZE function in the program PLATON.[26] 226 electrons in a volume of 762 Å^3 were removed, which results in incorrect values for the empirical formula, formula weight and F(000). This volume contained three identifiable DMSO molecules and additional water molecules. The bound DMSO molecules could not be properly modeled due to disorder and poor resolution. Most of the atoms associated with them were treated isotropically and were refined with restraints (SIMU, SADI) with stringent esds.

CCDC reference number 184058.

See http://www.rsc.org/suppdata/dt/b3/b309453g/ for crystallographic data in CIF or other electronic format.

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