Directed Synthesis of a 1D Double-Chain Polyoxometalate Assembly: $\{[Ag_2(bppy)_3][Ag(bppy)_2][Ag(bppy)]_2PW_{11}Co(bppy)O_{39}\}\cdot 2H_2O$

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A 1D double-chain assembly based on the monosubstituted Keggin polyoxometalate (POM) with pendant ligands and of formula $\{[Ag_2(bppy)_3][Ag(bppy)_2][Ag(bppy)]_2PW_{11}Co(bppy)O_{39}\}\cdot 2H_2O$ (**1**) [bppy = 5-(4-bromophenyl)-2-(4-pyridinyl)pyridine] has been synthesised and characterised. The crystals of **1** belong to the space group $P\bar{1}$, $Mr = 5801.06$, $a = 18.720(4)$ Å, $b = 19.474(4)$ Å, $c = 19.815(4)$ Å, $\alpha = 96.30(3)$, $\beta = 96.07(3)$, $\gamma = 90.12(3)°$, $V = 7139(2)$ Å^3, $Z = 2$, $D_{\text{calcd.}} = 2.699$ Mg·m^{-3}. The final statistics based on F^2 are $GOF = 1.007$, $R_1 = 0.0620$ and $wR_2 = 0.1346$ for $I > 2\sigma(I)$. X-ray diffraction analysis revealed that the structure of **1** contains a 1D chain constructed from a monosubstituted tungstophosphate with one pendant conjugated ligand, five silver–bppy groups and two water molecules. The periphery of the Keggin cluster consists of five Ag–bppy groups so that a bicapped trisupporting Keggin structure is obtained. It is rare that a Keggin anion cluster is simultaneously coordinated to five transition metal atoms.

Introduction

The construction of various intriguing molecular frameworks based on inorganic polyoxometalates (POMs) and organic species with delocalised π systems is of significant contemporary interest owing to their interesting electrical and optical properties such as electrochromism, photochromism, conductivity and redox activity.[1−11] In recent years, research in this field has focused on functionalisation and immobilisation of POMs.[12−20] In addition, conjugated organic molecules and polymers are electrically active organic materials.[21] Thus, these hybrids should offer the potential for broadening the application of POMs in the field of material science.

Despite the deficient charge density on the surface oxygen atoms of many Keggin- and Dawson-type POMs, these oxygen atoms may nevertheless still be involved in more distant bonding with other cations. According to a basic concept, as the charge density on the surface oxygen atoms of the POM increases there should appear a significant affinity for the polyoxoanions to coordinate to transition metal complex cations. A frequent and effective method for obtaining such highly negative polyoxoanions is to substitute the six valent metal centres of W^{VI} and Mo^{VI} with lower valent metal atoms such as V^V and Nb^V. However, we noticed that the number of transition metal complexes supported by these kinds of POMs rarely exceeds two.[22−24] We previously reported a polyoxoanion coordinated to four transition metal complex moieties, i.e. $\{PW_9V_3O_{40}[Ag(2,2'\text{-}bipy)]_2[Ag_2(2,2'\text{-}bipy)_3]_2\}$ which contains a discrete, neutral molecular unit.[25]

In our ongoing efforts to develop synthetic and functional analogues of large inorganic clusters, we have explored an approach to the synthesis of POMs with covalently bonded pendant ligands which, as mentioned in our prior study on the interactions of adenosine triphosphate (ATP) and adenosine monophosphate (AMP) with 3d transition metal complexes in the presence of the monovacant polyoxotungstate anion $\alpha\text{-}[SiW_{11}O_{39}]^{8-}$, leads to metal-substituted tungstosilicates and simultaneously increases the charge density on the surface oxygen atoms of POMs.[26−27] The strategy is to cross-link the inorganic clusters and to anchor the clusters via terminal ligand-support linkages and perhaps through H-bonding interactions thereby avoiding structural collapse.

Recently, the secondary metal coordination groups (SMGs) have been widely used to put POM clusters into high dimensional framework structures which has proved helpful in directing the formation of a given structure.[28−30] Hence, the synthetic strategy here starts firstly by generating a metal-substituted Keggin POM with a pendant-conjugated organic ligand as a building block. A suitable SMG as a connector must then be found in order to assemble the

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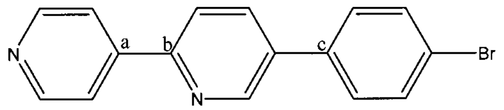
inorganic clusters into a high-dimensional network. Through this route, directed synthesis of a 1D double chain complex {[Ag_2(bppy)$_3$][Ag(bppy)$_2$][Ag(bppy)]$_2$$PW_{11}$Co(bppy)$O_{39}$}·2$H_2O$ (**1**) [bppy = 5-(4-bromophenyl)-2-(4-pyridinyl)pyridine] has been obtained. Compound **1** contains a chain structure constructed from a monosubstituted tungstophosphate with one pendant conjugated ligand, five silver-bppy groups and two water molecules. To the best of our knowledge, it is rare to observe a Keggin anion cluster simultaneously coordinated to five metal atoms, let alone extended into a 1D array.

Results and Discussion

Organic Ligand and Silver(I): Combining known transition-metal coordination environments with multifunctional multidentate ligands can generate interesting crystallographic architectures with implications for the rational design of functional solids. Linear bifunctional "spacer" or "rod" ligands have been used to propagate a number of motifs.[33−35] In this experiment, we chose bppy (see Scheme 1) as the organic ligand based on the following considerations: (i) One terminal N site in this molecule is advantageous for forming polyoxometalate complexes with pendant ligands. The middle N atom and the terminal Br atom are potential coordination sites which may help to extend the linkage into an unprecedented high-dimensional structure. (ii) The length of the linear molecule bppy (ca.13.2 Å) is sufficient to overcome the disadvantage of the repulsion of adjacent polyanions.



Scheme 1. The molecular structure of the organic ligand bppy; the angle *a*−*b*···*c* is ca. 180°, the length N_t···Br is ca.13.2 Å (N_t = terminal N)

Silver(I) exists in the following possible coordination environments: linear, T-shaped and tetrahedral. In its complexes, silver also displays an ability to coordinate readily to both hard and soft donor centers.[36−40] Considering that the coordination positions of two N atoms in a bppy ligand are similar to those in 2,4′-bipyridine, we anticipated that treatment of Ag with bppy would afford linear, T-shaped or diamond shaped structural subunits with the potential to link POMs into high-dimensional crystallographic architectures.

Synthesis: Compound **1** was synthesised by hydrothermal methods. The pH of the solution plays an important role in the isolation of phases of a given composition and structure. The starting material H_3PO_4 not only plays a central atom role but also adjusts the pH of the reaction mixture. When the pH value is beyond the range of 4.5−4.9 (values prone to the formation of mono-vacant polyoxometalates) the isolation of **1** was unsuccessful affording only amorphous powders. During the course of our reiterative experiments, a yellow crystalline phase besides compound **1** was observed when the reaction was allowed to proceed for three days but this disappeared upon prolonging the reaction time to four days. The material was identified as a salt of $[PW_{12}O_{40}]^{3-}$ by its IR spectrum (see Supporting information Figure S1(b); For Supporting Information see also the footnote on the first page of this article). This may indicate that $[PW_{12}O_{40}]^{3-}$ may initially form and then change to other species, e.g. compound **1**. The mechanism needs to be studied further.

Structure Description: Single-crystal X-ray diffraction analysis revealed that **1** consists of {[Ag(bppy)$_2$][Ag(bppy)]$_2$$PW_{11}$Co(bppy)$O_{39}$} clusters linked by Ag_2(bppy)$_3$ units into an infinite 1D arrangement along the direction of the *a* axis (see Figure 1). The periphery of the Keggin cluster consists of five Ag-bppy groups and a bicapped tri-supporting Keggin structure is thus obtained (see Figure 2). Two adjacent chains form a double-stranded structure via Ag−Br linkages which further extends into a 3D framework via hydrogen bonding and π-π stacking interactions.

The monosubstituted tungstophosphate anion contains a paramagnetic Co^{II} centre covalently linked by a rigid, π-conjugated organic ligand on a peripheral octahedral site of the Keggin core. The P−O bond lengths range from 1.525(8) to 1.534(9) Å. The W−O_d (O_d = terminal oxygen) bonds are in the usual range of 1.669(11)−1.737(8) Å. All W−W distances are nearly equal, ranging from 3.412 to 3.488 Å (mean value: 3.440 Å) in each triplet except for the triplet substituted with a Co atom [W(1)−W(9): 3.382 Å]. The octahedral coordination Co is defined by one quadruple (bridging) oxygen atom (O_q), four triply bridging oxygens and one terminal N atom from the bppy ligand with the following bond lengths: Co(1)−O(25): 2.018(9), Co(1)−O(35): 2.049(8), Co(1)−O(13): 2.056(9), Co(1)−O(38): 2.087(10), Co(1)−O(3): 2.310(8) and Co(1)−N(1): 2.081(11) Å. The distance P(1)−O(3) is the longest of all the P−O bonds, whereas the distance Co(1)−O(3) is the shortest of all M−O_q linkages (M = W or Co). The most unusual structural feature of compound **1** is that nine surface bridging oxygen atoms of the Keggin anion $[PW_{11}O_{39}Co(bppy)]^{5-}$ are coordinated to five silver-bppy complex cations. To the best of our knowledge, such types of monosubstituted Keggin anions simultaneously supporting so many transition metal complexes has not been reported.

Another remarkable aspect of **1** is that the five silver atoms have different coordination environments: four-coordinate Ag(1) and Ag(2) and three-coordinate Ag(3), Ag(4) and Ag(5). The Ag(1) and Ag(2) atoms are defined by one terminal nitrogen atom of the bppy ligand and three bridging oxygen atoms of the pseudo-Keggin anion, respectively. The distances Ag(1)−O(15), Ag(1)−O(23), Ag(1)−O(21) are 2.402(8), 2.520(9) and 2.603(8) Å, respectively, while the distance Ag(1)−N(3) is 2.152(16) Å. The Ag(2) atom lies in the opposite position to Ag(1) in the POM cluster with the bond lengths of 2.337(8), 2.526(9), 2.684(47) and 2.181(13)

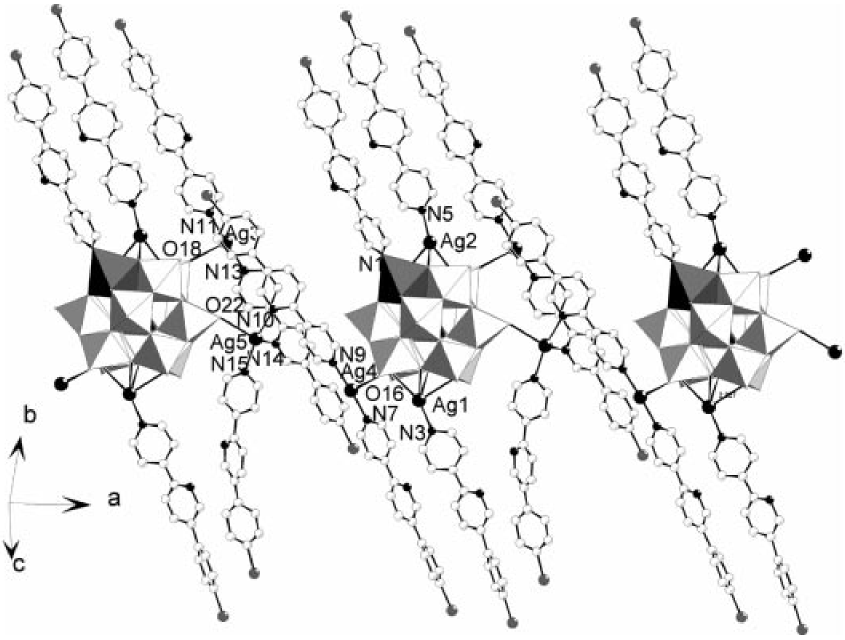


Figure 1. Polyhedral representation of the 1D chain structure of **1**; dark octahedra: $\{Co^{II}O_4N\}$; light octahedra: $\{W^{VI}O_6\}$ and $\{PO_4\}$

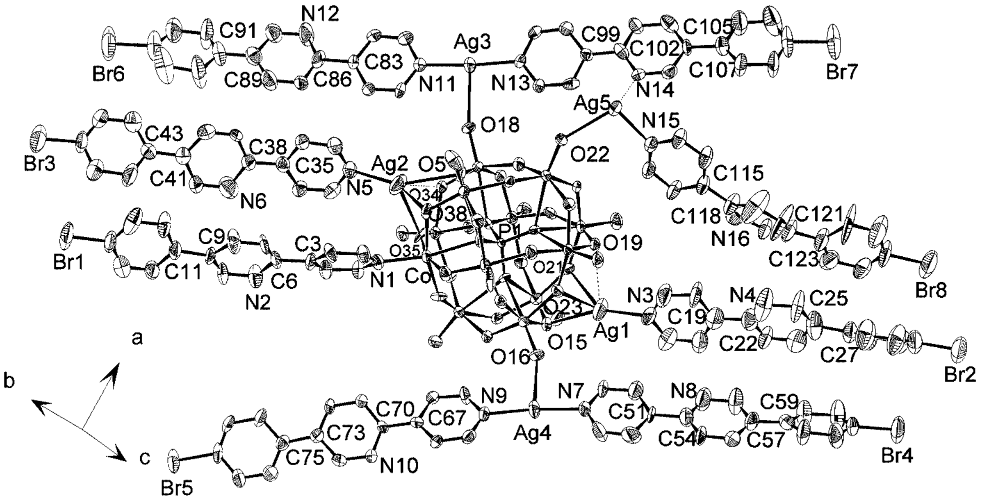


Figure 2. ORTEP view of the building block unit of the 1D chain of **1** showing the linkage mode of the polyanion and the silver-bppy fragments; ellipsoids are drawn at the 50% probability level

Å for Ag(2)−O(38), Ag(2)−O(35), Ag(2)−O(5) and Ag(2)−N(5), respectively. The proximity of the fourth oxygen atom O(19) to Ag(1), [Ag(1)−O(19): 2.823(41) Å] (the sum of the van der Waals radii of Ag and O is 3.20 Å),[41] implies a weak binding and leads to the coordination geometry around Ag(1) being a distorted square pyramid. Similarly, there is a weak interaction between Ag(2) and O(34) with a distance of 3.015(34) Å. The significant variation in the Ag(1) and Ag(2) − oxygen bond lengths may be due to the effect of the coordination environment described below. Ag(1) and Ag(2) cover two opposite faces of the polyanion to form a bicapped α-Keggin-type structure. As is known, in fully oxidised POMs (all W or Mo atoms in the VI oxidation state), terminal oxygen atoms are weakly basic and nonreactive. However, in compound **1**, three terminal oxygen atoms O(18), O(16) and O(22) further extend their linkages via Ag−bppy groups with distances of 2.627(32) Å for Ag(3)−O(18), 2.665(38) Å for Ag(4)−O(16) and 2.644(38) Å for Ag(5)−O(22). For the three-coordinate “T-shaped” Ag(3), Ag(4) and Ag(5) atoms, the other two coordination sites are occupied by N atoms from two bppy ligands with Ag−N distances in the range of 2.116(11)−2.227(12) Å. The bond angles are 175.0(4)°for N(11)−Ag(3)−N(13), 173.2(5)° for N(9)−Ag(4)−N(7) and 166.3(4)° for N(15)−Ag(5)−N(10). A longer distance of 2.839(51) Å between Ag(5) and a N donor atom of another bppy ligand is beyond the usual limits of covalent bonding and may be considered as a weak interaction. Therefore, the Ag(5) atom exhibits a coordination environment which is intermediate between “T-shaped’ and tetragonal. Ag(4)

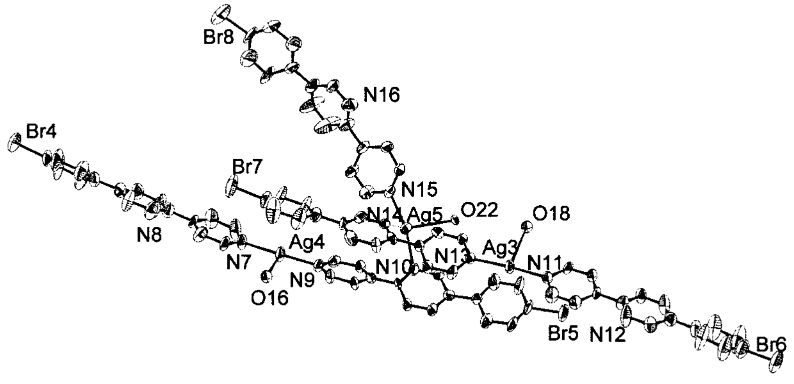


Figure 3. Coordination environments of the Ag(3), Ag(4) and Ag(5) atoms in **1**

and Ag(5) share three bppy molecules to form $[Ag_2(bppy)_3]^{2+}$ which connects adjacent polyanion clusters via Ag−O linkages into a chain structure (see Figure 3). Compound **1** shows that the charge deficient monosubstituted tungstophosphate is capable of bonding with transition metal complexes to form a high-dimensional structure. Compound **1** also shows the flexible coordination mode of silver(I) and provides a good prototype between polyoxoanions with surface-bound inorganic moieties and actually extended polyoxoanion-coordination compound assemblies.

In the crystal structure of **1**, an additional noteworthy fact is that the Br(8) atom lies significantly within the coordination sphere of Ag(1) at a distance of 3.179(51) Å in terms of the sum of the van der Waals radii (1.72 Å for Ag and 1.85 Å for Br).[42] Severe bending of the originally linear bppy containing Br(8) also reflects this interaction with a C(115)−C(118)···C(123) angle of 167.54° and a N(15)···Br(8) length of 12.95 Å (see Figure 2). Thus, taking the Ag(1)−Br(8) into account, a double-strand ladder structure is formed (see Figure 4). Additionally, the distance Ag(2)···Br(1) of 3.726(58) Å, which is beyond the sum of the van der Waals radii of Ag and Br, is too long to be considered as a significant interaction. For comparison, the ligand containing Br(1) is almost linear with the C3−C6···C11 angle being 176.73° and the N(1)···Br(1) length being 13.21 Å. These different interactions between Ag and Br may explain the above mentioned differences of the Ag(1) and Ag(2) − oxygen bond lengths. The two adjacent silver-silver distances of Ag(3)···Ag(3): 3.849(40) Å and Ag(4)···Ag(4): 3.598(34) Å are longer than the van der Waals contact distance (3.44 Å) of silver.[42] As shown in Figure 5, there are significant π-stacking interactions of ligands linked to Ag(3) or Ag(4) (the centre-to-centre and interplane distances are 3.849 and 3.598 Å, respectively.) which implies the formation of a 3D structure in compound **1**. However, ligand packing effects are not responsible for the pairing as is demonstrated by the crystal structure of $[3,5\text{-}Me_2pzH]_3$ which exhibits a planar trimeric association rather than a dimeric "packing".[43] On the contrary, ligand repulsion may actually prevent the silver atoms from fully eclipsing to give Ag−Ag contacts.[44]

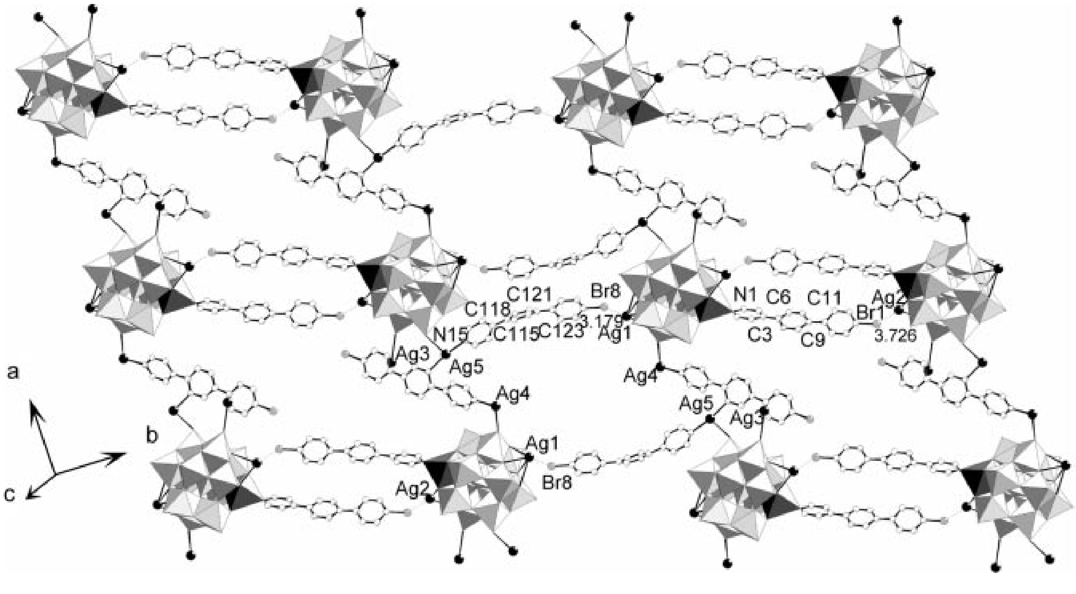


Figure 4. View of the 1D double-chain structure of **1** based on the interaction Ag(1)−Br(8); distances [Å]: Ag(1)···Br(8) 3.179(51), Ag(2)···Br(1) 3.726(58); some bppy groups are omitted for clarity; dark octahedra: $\{Co^{II}O_4N\}$; light octahedra: $\{W^{VI}O_6\}$

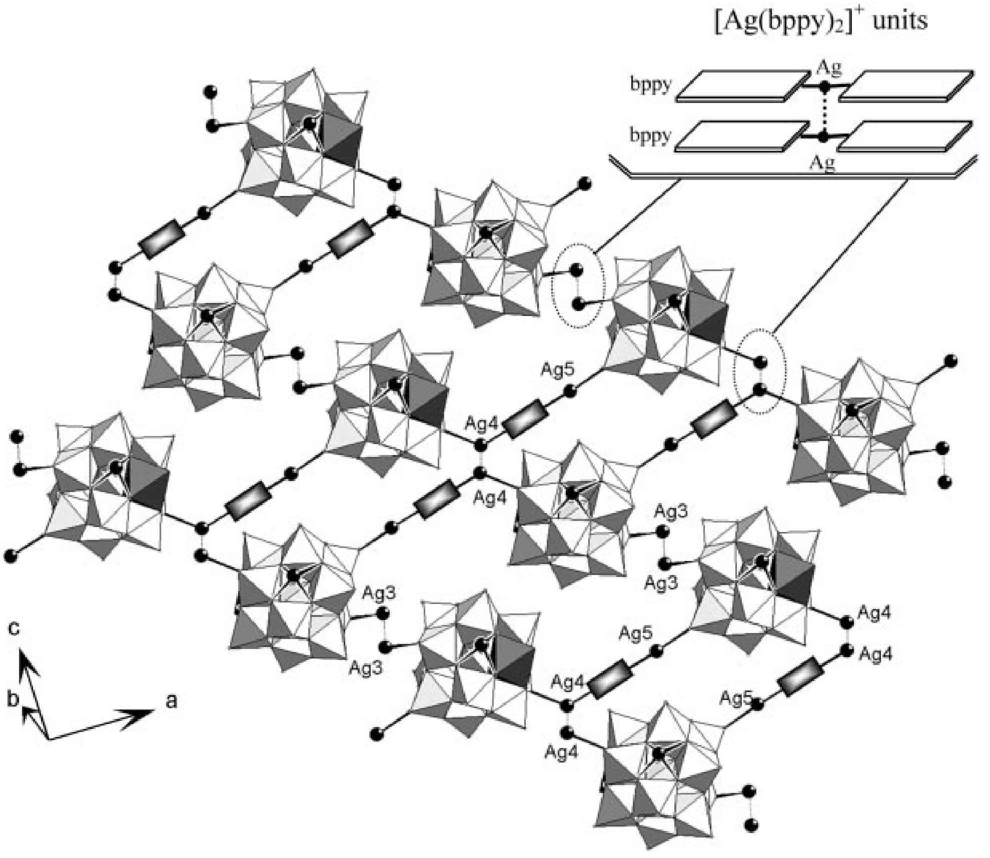


Figure 5. A schematic diagram of **1** showing the extension of 1D chains into a 3D sturctrure via π-stacking interactions of the ligands (see the inset) bonded to Ag(3) and Ag(4); Ag(3)···Ag(3) 3.849(40), Ag(4)···Ag(4) 3.598(34) Å; the dark rectangle blocks represent the covalent linkage of Ag(4) and Ag(5) via bppy groups; organic ligands are omitted for clarity; dark octahedra: $\{Co^{II}O_4N\}$; light octahedra: $\{W^{VI}O_6\}$

The interesting aspect of this structure is the multiple role of the conjugated organic bppy: its first function is to act as a pendant ligand to functionalise the polyanions. The second is to form SMG groups linking the polyanions into chains and the third function is to produce strong aromatic-aromatic interactions giving a 3D structure. 3D supramolecular architectures fabricated from layers by means of hydrogen bonds or π-stacking are common in coordination polymers.[45–46] However, such 3D supramolecular architectures constructed from 1D chains are rare.

The crystal structure of **1** is further strengthened by hydrogen bonding. Two waters of crystallisation have multipoint hydrogen bonding interactions with the organic ligands and the surface oxygen atoms of the POM. The short distances [Å] are (see Figure 6): Ow(1)···Ow(2) 3.070, Ow(1)···O(12) 2.949, Ow(1)···O(25) 3.018, Ow(2)···O(17) 2.902, Ow(2)···C(72) 3.146, Ow(2)···C(4) 3.195, Ow(3)···Ow(3) 2.779, Ow(3)···O(26) 3.057 and Ow(3)···O(7) 2.724.

In summary, the structure of **1** can be described as a monosubstituted tungstophosphate anion $[PW_{11}Co(bppy)O_{39}]^{5-}$ linked by Ag-bppy units into a 1D chain structure running along the direction of the *a* axis. The chains further extend into a double-strand structure based on the interaction of Ag(1) with Br(8) and the π-π interactions of the bppy ligands. These double-strand structures then form a 3D framework structure by hydrogen bonding and a number of π-π interactions of the bppy groups.

Bond valence sum calculations (BVS)[47] indicate that the W centres are in the highest oxidation state and that the Co atom possesses 2.223 of its formal oxidation state in compound **1**. The calculated valence sums for Ag(1) to Ag(5) are 0.902, 0.789, 0.895, 0.960 and 0.792, respectively, indicating the oxidation state of the Ag atoms is +1. The ESR spectrum at room temperature shows the paramagnetic signal of Co^{2+} with $g = 2.258$ which is consistent with the calculation result.[48]

FT-IR Spectrum, XPS Spectrum and TG-DTA Analysis: The IR spectrum [see Supporting Information Figure S1(a)] of **1** exhibits characteristic peaks of the Keggin anion at 999, 953, 885 and 814 cm^{-1}, attributable to ν $(W-O_c-W)$, ν$(W-O_b-W)$ and ν$(W-O_d)$ (O_d = terminal oxygen, O_b = bridged oxygen of two octahedral sharing a corner, O_c = bridged oxygen of two octahedral sharing an edge), respectively. The informative bands at 1080 and 1048 cm^{-1} can be assigned to the P–O stretching vibrations in **1**. Compared with a typical value of about 1067 cm^{-1} for the Keggin anion,[49–50] the P–O stretch of the mono-substituted Keggin tungstophosphate ion splits into two bands because of the lower symmetry than that in the T_d parent Keggin

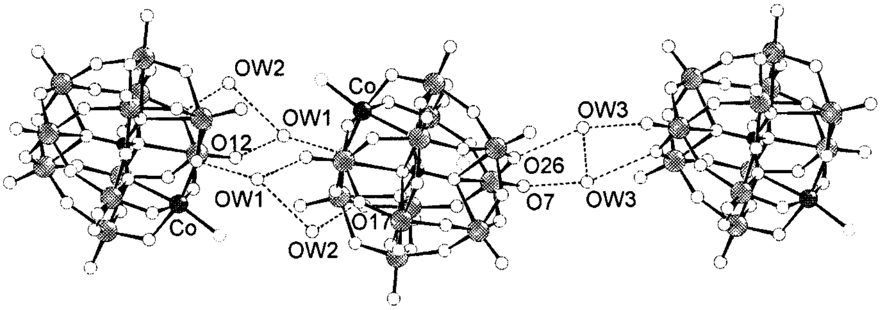


Figure 6. Hydrogen bonds between water and the POM (the silver atoms and organic ligands are omitted for clarity)

anion. The bands in the 3000−1080 cm^{-1} region can be attributed to characteristic vibrations of bppy. Comparatively, the P−O stretch of the by-product salt of $[PW_{12}O_{40}]^{3-}$ does not split into two bands but shows a peak at 1090 cm^{-1} [see Supporting Information Figure S1(b)].

The XPS spectrum (see Supporting Information Figure S2) shows a peak at 368.3 eV, attributable to Ag^+, a peak at 70.2 eV attributable to Br^- and a peak at 35.2 eV attributable to W^{6+}. These results further confirm the composition of compound **1**.

The TG curve (see Figure 7) shows that compound **1** is stable below 368 °C. A noteworthy finding is that there is still weight loss above 800 °C, indicating that organic material is still being lost even at the upper limit of measurement range. In this range, the DTA curve reveals three exothermic peaks at 396, 510 and 720 °C which correspond to the oxidation of the bppy ligands and/or a phase transformations of inorganic components, respectively. The thermal behaviour of **1** may be largely attributed to the effect of the pendant surface ligand, H-bonding and strong π-π stacking interactions.

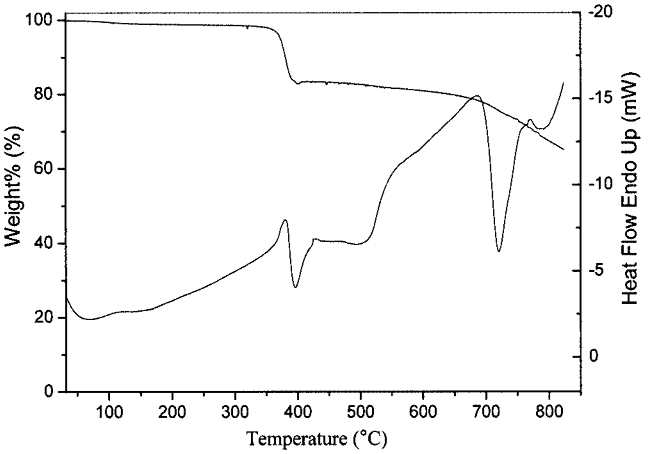


Figure 7. TG and DTA curves of compound **1**

Conclusion

A 1D double chain assembly based on the monosubstituted Keggin POM with pendant ligands has been synthesised and structurally characterised. The successful isolation of crystalline **1** suggests a promising approach for preparing extend arrays of polyoxometalate clusters. By generating metal-substituted polyoxometalates with increased negative charge density on the surface oxygen atoms of the POMs and introducing suitable structure-directing linkages via the secondary metal-ligand complex, rational design and synthesis of a target structure may be achieved, to a certain degree, under hydrothermal conditions. The conjugated organic bppy plays several roles in the structural formation. In particular, the 2′ N-donor is involved in forming a 1D chain through binding to the transition metal. Work on further extending these kind of linkages into 2 or 3D frameworks by this route is underway.

Experimental Section

Materials and Methods: All reagents were purchased and used without further purification; bppy was synthesised and identified by IR and ^{1}H NMR spectroscopy. Elemental analyses were carried out with an MOD 1106 elemental analyser. The infrared spectrum was recorded with an Alpha Centaur FT/IR spectrometer with a KBr pellet in the 4000−400 cm^{-1} region. XPS analysis was performed with a VGESCALAB MK II spectrometer with a Mg-K_α (1253.6 eV) achromatic X-ray source. The vacuum inside the analysis chamber was maintained at 6.2 × 10^{-6} Pa during analysis. The EPR spectrum was recorded with a Bruker ER 200D EPR spectrometer at 293 K. The thermal gravimetric analysis (TGA) and the differential thermal analysis (DTA) were carried out under N_2 with a Perkin−Elmer DTA 1700 differential thermal analyser at a rate of 10.00 °C /min in the range 30−800 °C.

Preparation of Compound 1: A mixture of $Na_2WO_4{\cdot}2H_2O$ (660 mg, 2 mmol), $Co(NO_3)_2{\cdot}6H_2O$ (291 mg, 1 mmol), $AgNO_3$ (213 mg, 1.3 mmol), bppy (62 mg, 0.2 mmol) and H_2O (10 mL) was adjusted to pH = 4.7 with dilute H_3PO_4 solution. The resultant mixture was sealed in a 25 mL Teflon-lined autoclave (70% full) and heated at 170 °C for 96 h. The autoclave was then cooled at 10 °C·per hour to room temperature. Pink crystals of **1** were obtained (yield: 82% based on bppy) along with an amorphous powder which was characterised as a simple compound by its IR spectrum [see Supporting Information Figure S1(c)]. The crystals were washed with water and dried in a desiccator at ambient temperature. The final pH value of the filtrate was 3.6. $C_{128}H_{92}Ag_5Br_8CoN_{16}O_{41}PW_{11}$: calcd. C 26.48, H 1.59, N 3.86; found C 26.51, H 1.63, N 3.82. IR (cm^{-1}): $\tilde{\nu}$ = 1610 (s), 1590 (m), 1540 (w), 1470 (s), 1420 (m), 1370 (w), 1080 (s), 1048 (s), 999 (m), 953 (s), 885 (s) 814 (s), 750 (m), 656 (w), 515 (w) and 417 (w).

Table 1. Selected bond lengths [Å] and angles [°] for compound **1**

W(1)−O(11)	1.686(9)	Co(1)−O(3)	2.310(8)	Ag(5)−N(10)	2.227(12)
W(1)−O(13)	1.765(9)	Ag(1)−N(3)	2.152(16)	Ag(5)−O(22)	2.644(38)
W(1)−O(10)	1.935(9)	Ag(1)−O(15)	2.402(8)	C(14)−Br(1)	1.879(18)
W(1)−O(39)	1.947(10)	Ag(1)−O(23)	2.520(9)	C(30)−Br(2)	1.91(2)
W(1)−O(8)	2.036(9)	Ag(1)−O(21)	2.603(8)	C(46)−Br(3)	1.854(17)
W(1)−O(3)	2.429(8)	Ag(2)−N(5)	2.181(13)	C(62)−Br(4)	1.907(17)
P(1)−O(4)	1.525(8)	Ag(2)−O(38)	2.337(8)	C(78)−Br(5)	1.892(14)
P(1)−O(1)	1.531(9)	Ag(2)−O(35)	2.526(9)	C(94)−Br(6)	1.92(2)
P(1)−O(3)	1.534(9)	Ag(3)−N(11)	2.132(11)	C(110)−Br(7)	1.962(17)
P(1)−O(2)	1.532(8)	Ag(3)−N(13)	2.164(11)	C(126)−Br(8)	1.905(19)
Co(1)−O(25)	2.018(9)	Ag(3)−O(18)	2.627(32)	Ag(1)···O(19)	2.823(41)
Co(1)−O(35)	2.049(8)	Ag(4)−N(9)	2.116(11)	Ag(2)···O(34)	3.015(34)
Co(1)−O(13)	2.056(9)	Ag(4)−N(7)	2.127(12)	Ag(1)···Br(8)	3.179(51)
Co(1)−N(1)	2.081(11)	Ag(4)−O(16)	2.665(38)	Ag(2)···Br(1)	3.726(58)
Co(1)−O(38)	2.087(10)	Ag(5)−N(15)	2.161(12)		
Angles					
O(11)−W(1)−O(13)	104.1(4)	N(3)−Ag(1)−O(23)	122.7(5)		
O(11)−W(1)−O(10)	100.3(5)	O(15)−Ag(1)−O(23)	63.7(3)		
O(13)−W(1)−O(10)	93.5(4)	N(3)−Ag(1)−O(21)	136.9(4)		
O(11)−W(1)−O(39)	102.3(5)	O(15)−Ag(1)−O(21)	63.5(3)		
O(13)−W(1)−O(39)	93.1(4)	O(23)−Ag(1)−O(21)	76.9(3)		
O(10)−W(1)−O(39)	154.2(3)	N(5)−Ag(2)−O(38)	141.8(4)		
O(11)−W(1)−O(8)	97.6(4)	N(5)−Ag(2)−O(35)	118.9(4)		
O(13)−W(1)−O(8)	158.1(4)	O(38)−Ag(2)−O(35)	72.3(3)		
O(10)−W(1)−O(8)	85.2(4)	N(11)−Ag(3)−N(13)	175.0(4)		
O(39)−W(1)−O(8)	79.5(4)	N(9)−Ag(4)−N(7)	173.2(5)		
O(11)−W(1)−O(3)	173.8(5)	N(15)−Ag(5)−N(10)	166.3(4)		
O(13)−W(1)−O(3)	77.8(3)	O(25)−Co(1)−O(38)	163.9(4)		
O(10)−W(1)−O(3)	73.6(3)	O(35)−Co(1)−O(38)	88.0(4)		
O(39)−W(1)−O(3)	83.4(3)	O(13)−Co(1)−O(38)	87.9(4)		
O(8)−W(1)−O(3)	80.9(3)	N(1)−Co(1)−O(38)	93.4(4)		
O(25)−Co(1)−O(35)	87.5(3)	O(25)−Co(1)−O(3)	90.0(3)		
O(25)−Co(1)−O(13)	92.4(4)	N(13)−Ag(3)−O(18)	95.56(36)		
O(35)−Co(1)−O(13)	164.6(4)	N(11)−Ag(3)−O(18)	89.39(37)		
O(25)−Co(1)−N(1)	102.0(4)	Ag(3)−O(18)−W(3)	163.93(51)		
O(35)−Co(1)−N(1)	90.7(4)	N(7)−Ag(4)−O(16)	89.18(38)		
O(13)−Co(1)−N(1)	104.3(4)	N(9)−Ag(4)−O(16)	97.58(38)		
O(35)−Co(1)−O(3)	89.0(3)	Ag(4)−O(16)−W(2)	158.51(52)		
O(13)−Co(1)−O(3)	75.6(3)	N(15)−Ag(5)−O(22)	103.09(38)		
N(1)−Co(1)−O(3)	168.0(4)	N(10)−Ag(5)−O(22)	89.46(36)		
O(38)−Co(1)−O(3)	74.5(3)	Ag(5)−O(22)−W(6)	142.72(42)		
N(3)−Ag(1)−O(15)	157.8(5)				

X-ray Crystallographic Study: A single crystal of **1** with dimensions 0.18 × 0.10 × 0.08 mm was glued on a glass fibre. Data were collected on a CCD diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71703 Å) at 293 K. Semi-empirical from equivalents were applied. The structure was refined by the full-matrix least-squares method on F^2 using the SHELXTL crystallographic software package.[31−32] Anisotropic thermal parameters were used to refine all nonhydrogen atoms. Hydrogen atoms were located in idealised positions. Selected bond lengths (Å) and angles (°) for compound **1** are listed in Table 1. Crystal data: $C_{128}H_{92}Ag_5Br_8CoN_{16}O_{41}PW_{11}$, triclinic, $P\bar{1}$, $Mr = 5801.06$, a = 18.720(4) Å, b = 19.474(4) Å, c = 19.815(4) Å, α = 96.30(3)°, β = 96.07(3)°, γ = 90.12(3)°, V = 7139(2) Å^3, Z = 2, $D_{\text{calcd.}}$ = 2.699 Mg·m^{-3}, μ = 11.935 mm^{-1}, crystal size: 0.18 × 0.10 × 0.08 mm. The final statistics based on F^2 are GOF = 1.007, R_1 = 0.0620 and wR_2 = 0.1346 for $I > 2\sigma(I)$. CCDC-238955 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Supporting Information Available (see also footnote on the first page of this article): IR and XPS spectra for **1**.

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