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Hydrothermal syntheses and structures of three one-dimensional heteropolytungstates formed by Dawson or Keggin cluster units

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Single crystals of $[Cu(en)_2(OH_2)]_2[H_2en][\{Cu(en)_2\}P_2CuW_{17}O_{61}]\cdot 5H_2O$ **1**, $[Cu(en)_2(OH_2)]_2[Cu(en)_2]_{0.5}[H_2en]_{0.5}$-$[\{Cu(en)_2\}P_2CuW_{17}O_{61}]\cdot 5H_2O$ **2** and $[Co(dpa)_2(OH_2)_2]_2[Hdpa][PCoW_{11}O_{39}]$ **3** (dpa = di-2-pyridylamine) have been hydrothermally synthesized and characterized by IR, TGA and single-crystal structural analysis. Compounds **1** and **2** contain an unprecedented chain of Dawson polyoxoanions, whereas **3** has a chain structure similar to that of $[NEt_3H]_5[XCoW_{11}O_{39}]$, (X = P or As).

There is a significant contemporary interest in inorganic solid state materials, due to their applications to fields as diverse as catalysis, ion exchange, sorption and molecular electronics,[1–6] although the synthesis of such materials by rational design remains elusive.[7,8] One of the strategies, exploiting molecular building blocks in the synthesis of solid state materials, relies on linking molecular cluster subunits from the vast family of chemically robust polyoxoanions, either through direct condensation to form oxo-bridged arrays of clusters or through transition metal coordination compounds acting as inorganic bridging ligands. Practicing this strategy results in the successful synthesis of a number of chain and layered structures.[9–15] On the other hand, hydrothermal techniques have proven well suited for the preparation and crystal growth of inorganic solid state materials including polyoxometalates. However, the hydrothermal synthesis of tungsten oxide based organic–inorganic hybrid materials remains largely unexplored, except for a few structures containing Lindquist-,[16] Keggin-[17,18] or Dawson-type anions.[19]

Transition metal substituted polyoxotungstates based on Keggin or Dawson frameworks have received considerable attention for their catalytic properties in organic oxidations.[20–24] For example, Hill and Zhang found that under mildly acidic conditions α-$[PCoW_{11}O_{39}]^{5-}$ will catalyze epoxidation of alkanes, with the ability to restore itself following this function.[24] However, the synthesis and complete characterization of the substituted polyoxometalates remain a challenge. Meanwhile, structures of extended tungsten heteropolyanions showing chain-like structure are rarely reported.[12–15] Two structures, $[ET]_8[PMnW_{11}O_{39}]\cdot 2H_2O$,[13] (ET = bis (ethylenedithio)tetrathiofulvalene) and $[NEt_3H]_5[XCoW_{11}O_{39}]\cdot 3H_2O$ (X = P or As)[15] have to be mentioned, both of which consist of Keggin-type molecules joined by W–O–M links (M = Co or Mn). However the monosubstituted metal atoms are disordered in two positions.

Here, we report the hydrothermal syntheses and single crystal structure analysis of three extended heteropolyanions showing a chain-like structure: $[Cu(en)_2(OH_2)]_2[H_2en][\{Cu(en)_2\}P_2CuW_{17}O_{61}]\cdot 5H_2O$ **1**, $[Cu(en)_2(OH_2)]_2[Cu(en)_2]_{0.5}[H_2en]_{0.5}[\{Cu(en)_2\}P_2CuW_{17}O_{61}]\cdot 5H_2O$ **2** and $[Co(dpa)_2(OH_2)_2]_2[Hdpa][PCoW_{11}O_{39}]$ **3** (dpa = di-2-pyridylamine). To our knowledge, **1** and **2** represent the first characterized compounds to contain a one-dimensional chain of oxo-bridged Dawson units.

Experimental

Synthesis

$[Cu(en)_2(OH_2)]_2[H_2en][\{Cu(en)_2\}P_2CuW_{17}O_{61}]\cdot 5H_2O$ 1. Single crystals of $[Cu(en)_2(OH_2)]_2[H_2en][\{Cu(en)_2\}P_2CuW_{17}O_{61}]\cdot 5H_2O$ **1** suitable for single-crystal structure analysis were synthesized from a mixture of ethylenediamine, sodium tungstate dihydrate, water, phosphoric acid, copper nitrate, and sodium fluoride. A typical synthesis was as follows: 0.20 g of NaF was dissolved in 20 mL water, and 0.26 g $Cu(NO_3)_2\cdot 3H_2O$, 0.15 g en, 0.60 g $Na_2WO_4\cdot 2H_2O$ and 0.71 g H_3PO_4 (85%) were successively added at room temperature with stirring until the mixture became homogeneous. The final mixture was sealed in a Teflon-lined stainless steel autoclave and heated at 140 °C for 18 days. After the autoclave had cooled to room temperature over 5–6 h, purple plate crystals were recovered by filtration, washed with distilled water, and dried at ambient temperature. Elemental analysis data for **1**: W (obs. 61.5, calc. 62.7%), P (1.18, 1.24), Cu (4.88, 5.10), N (3.75, 3.91), C (3.17, 3.35), H (1.42, 1.46).

$[Cu(en)_2(OH_2)]_2[Cu(en)_2]_{0.5}[H_2en]_{0.5}[\{Cu(en)_2\}P_2CuW_{17}O_{61}]\cdot 5H_2O$ 2. Single crystals of $[Cu(en)_2(OH_2)]_2[Cu(en)_2]_{0.5}[H_2en]_{0.5}$-$[\{Cu(en)_2\}P_2CuW_{17}O_{61}]\cdot 5H_2O$ **2** suitable for single-crystal structure analysis were synthesized from a mixture of ethylenediamine, sodium tungstate dihydrate, water, phosphoric acid, copper nitrate, and sodium fluoride. A typical synthesis was as follows: 0.20 g of NaF was dissolved in 20 mL water and 0.26 g $Cu(NO_3)_2\cdot 3H_2O$, 0.15 g en, 1.50 g $Na_2WO_4\cdot 2H_2O$ and 0.78 g H_3PO_4 (85%) were successively added at room temperature with stirring until the mixture became homogeneous. Treatment as for **1** gave purple plate crystals. Elemental analysis data for **2**: W (obs. 63.2, calc. 61.4%), P (1.29, 1.23), Cu (5.48, 5.67), N (4.08, 4.18), C (3.49, 3.58), H (1.44, 1.50).

$[Co(dpa)_2(OH_2)_2]_2[Hdpa][PCoW_{11}O_{39}]$ 3. Single crystals of $[Co(dpa)_2(OH_2)_2]_2[Hdpa][PCoW_{11}O_{39}]$ **3** suitable for single-crystal X-ray structure analysis were synthesized from a mixture of di-2-pyridylamine, sodium tungstate dihydrate, water, phosphoric acid, cobalt chloride, and sodium fluoride. A typical synthesis was as follows: 0.32 g of NaF was dissolved in 25 mL water, and 0.49 g dpa, 0.62 g $CoCl_2\cdot 6H_2O$, 1.92 g $Na_2WO_4\cdot 2H_2O$ and 0.92 g H_3PO_4 (85%) were successively

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added at room temperature with stirring until the mixture became homogeneous. The final mixture was sealed in a Teflon-lined stainless steel autoclave and heated at 140 °C for 12 days. After the autoclave had cooled to room temperature over 5–6 h, deep red prismatic crystals were recovered by filtration, washed with distilled water, and dried at ambient temperature. Elemental analysis data for **3**: W (obs. 51.3, calc. 52.1%), P (0.779, 0.798), Co (3.10, 3.04), N (5.44, 5.54), C (14.9, 15.9), H (1.40, 1.43).

Characterization

TGA measurements were performed on a Setaram thermal analyzer. The samples were contained within alumina crucibles and heated at a rate of 5 °C min^{-1} from room temperature to 900 °C.

XRD patterns were collected using a Siemens D5005 diffractometer with graphite-monochromated Cu-Kα radiation ($\lambda = 1.5406$ Å) in the range $10 < 2\theta < 60°$. FTIR spectra (KBr pellet) were collected on a Nicolet FTIR (for compounds **1** and **2**) or a Perkin-Elmer FTIR instrument (for **3**) in the range 4000 to 400 cm^{-1}.

The crystal structures of **1**-**3** were determined from single crystal X-ray diffraction data. The intensity data were collected by θ–2θ scan on a Siemens P4 diffractometer using graphite monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation at 20 °C. The crystal parameters and details of the structure solution and refinement of are summarized in Table 1. Empirical absorption corrections were made from ψ-scan data using the program SHELXTL 97[25] at the data reduction stage along with the correction for Lorentz and polarization effects. The structures were solved by direct methods[26] and refined by full-matrix least squares on F^2 using SHELXTL 97. Positions of non-hydrogen atoms were located from Fourier difference maps. Thermal vibrations were treated anisotropically for all non-hydrogen atoms except for a number of O, N and C atoms in **1** and **3**, while in **2** thermal vibrations were treated anisotropically for W, Cu and P atoms only. Positions of the hydrogen atoms attached to oxygen atoms were located from difference maps and those attached to carbon and nitrogen atoms were placed in calculated positions. All hydrogen atoms were refined isotropically using a riding model. The structure of **3** was solved and refined in the space group *Cm*. The final structure was examined with the program PLATON[27] and no additional symmetry element was detected.

CCDC reference numbers 153419–153421.

See http://www.rsc.org/suppdata/dt/b1/b103024h/ for crystallographic data in CIF or other electronic format.

Results and discussion

The hydrothermal method has been exploited recently as a routine method for the synthesis of a larger number of novel inorganic solid state materials. Under hydrothermal conditions new phases are accessed with often previously unseen compositions and topologies. Aluminosilicate zeolites are perhaps the best known group of materials thus prepared. Another group of compounds prepared in this way, and that have received much attention, are low-dimensional hybrid organic–inorganic phases, for example transition-metal oxo clusters linked by organoamine groups which have been discussed as models for the rational modification of the properties of inorganic oxides.[28] Inspired by the recent success in the self-assembly of novel organic–inorganic hybrid materials,[9–15] we set out to study the crystal engineering of W–Cu or W–Co oxides in the presence of aromatic diamines and aliphatic diamines of various sizes. Since we have observed the successful synthesis of organic–inorganic hybrid materials constructed from diphosphopentamolybdate(VI) clusters and $[Cu(en)]^{2+}$ complex groups,[9] we attempted syntheses of isostructural analogs of W. However, we were unsuccessful in doing so, instead we separated **1** and **2**. Compounds **1** and **2** were crystallized from hydrothermal reactions of ethylenediamine, sodium tungstate dihydrate, water, phosphoric acid, copper nitrate, and sodium fluoride. Compound **1** was made from a mixture with molar ratio of $NaF : Cu(NO_3)_2 : en : H_3PO_4 : Na_2WO_4 : H_2O = 4.4 : 1.0 : 2.4 : 5.7 : 1.7 : 1032$ at 140 °C for 18 days. Compound **2** can be synthesized from a mixture containing more Na_2WO_4, about 250% of the amount used in the synthesis of **1**. It is likely that the phase-determining factor in these syntheses is the concentration of sodium tungstate. Notice that the use of $CuCl_2$ instead of $Cu(NO_3)_2$ in the synthesis does not affect the formation of the phase type at 140 °C. However, at higher temperature using $CuCl_2$ instead of $Cu(NO_3)_2$ leads to the formation of a novel compound that contains two linked Dawson clusters.[29] In either case, the products contain an unknown phase that can be washed away. **3** can be prepared at 140 °C for 8–12 days. Increasing the concentration of Na_2WO_4 increases the yield. The presence of F^- ions is found to be critical for the successful syntheses of **1**–**3**. The role of F^- ions is as a mineralizer, which has been used in numerous syntheses of open-framework phosphate materials.[30] It is not clear whether F^- ion is a temporary complexing agent for WO_4^{2-}. However, as previously suggested[31] it seems to induce more homogeneous and better crystallized phases. We believe that the strong coordination effect of F^- ions plays a role in controlling the reaction between Cu^{2+} and the N donors of en molecules, and between Cu^{2+} and the O donors of Dawson or Keggin clusters or H_2O molecules.

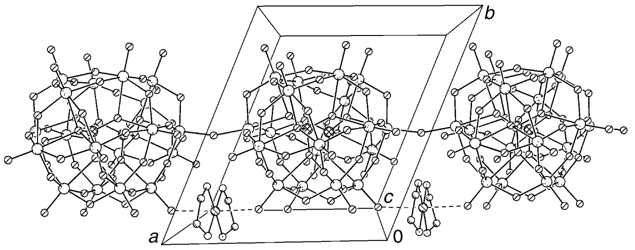

Fig. 1 A view of the one-dimensional chain in **1**.

1 consists of infinite chains of Dawson anions $[P_2CuW_{17}O_{61}]^{8-}$, with water molecules, H_2en^{2+} and $[Cu(en)_2]^{2+}$ cations as charge compensation occupying interchain regions. The parent anion $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$ of compound **1** contains two $[\alpha\text{-}APW_9O_{31}]^{3-}$ units (each derived from the well known $[\alpha\text{-}PW_{12}O_{40}]^{3-}$ anion by removal of a set of three corner-sharing WO_6 octahedra) which are linked through corner-sharing with the elimination of six oxygen atoms.[32,33] The parent anion has point group symmetry D_{3h} and contains only two structurally distinct types of W atoms: six "cap" atoms on vertical mirror planes and grouped in two sets of three, and 12 "belt" atoms that do not lie on mirror planes and that are grouped in two sets of six. In compound **1**, W–O distances were 1.67–1.73 Å for terminal oxygen (W–O_t), 1.81–2.01 Å for O bonded to two W atoms (corner-sharing W–O_c and edge-sharing W–O_e), and 2.29–2.44 Å for O bonded to two or three W atoms and one P atom (W–O_i). P–O distances varied between 1.51 and 1.59 Å, average 1.54 Å (*cf.* in $[P_2W_{18}O_{62}]^{6-}$ the P–O distances range from 1.50 to 1.59 Å, average 1.55 Å).

The Dawson anions are connected through a common oxygen atom and a $[Cu(en)_2]^{2+}$ group to give an infinite chain parallel to the *b* axis as shown in Fig. 1. The bridging oxygen atom connects two opposite positions of the Dawson unit occupied by Cu(II) and W(VI) with an occupancy of one half (this position is denoted M). This situation is analogous with that in $[ET]_8[MnW_{11}PO_{39}]\cdot 2H_2O$, whose anion is made up of chains of Keggin units.[13] There the two sites linked to the bridging oxygen atom are occupied by Mn(II) and W(VI) with an occupancy of one half. It should be pointed out that the Cu atom occupies a belt position in **1**. This is different from the

Table 1 Crystal data for **1**–**3**

	1	**2**	**3**
Molecular formula	$C_{14}H_{72}Cu_4N_{14}O_{68}P_2W_{17}$	$C_{15}H_{75}Cu_{4.5}N_{15}O_{68}P_2W_{17}$	$C_{25}H_{27}Co_{1.5}N_{7.5}O_{21.5}P_{0.5}W_{5.5}$
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	Cm
a/Å	11.710(4)	11.724(3)	16.331(3)
b/Å	13.228(4)	13.239(3)	25.873(4)
c/Å	28.161(8)	29.571(6)	10.726(2)
α/°	90.58(2)	89.30(1)	
β/°	95.76(2)	79.36(1)	118.90(1)
γ/°	112.52(2)	66.70(1)	
V/Å^3	4004(2)	4134(2)	3968(2)
Z	2	2	4
μ/mm^{-1}	25.50	24.82	16.60
Total no. of reflections	16250	14257	6732
Independent reflections	14016	12185	6469
$R1$ ($I > 2\sigma(I)$)	0.065	0.073	0.040
$wR2$ ($I > 2\sigma(I)$)	0.142	0.153	0.076

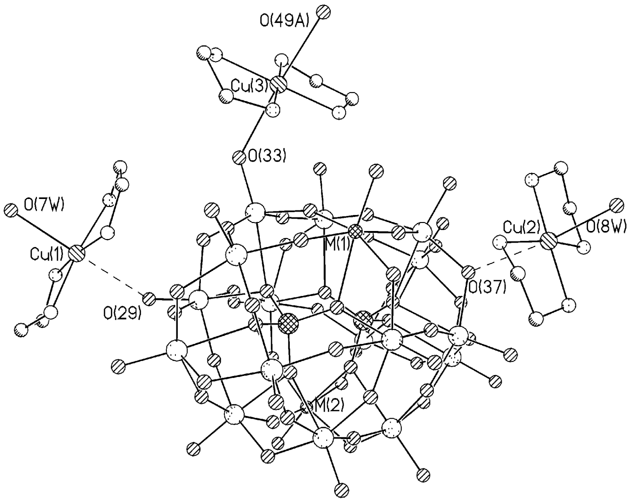

Fig. 2 Dawson anion connected to three copper(II) sites in **1**.

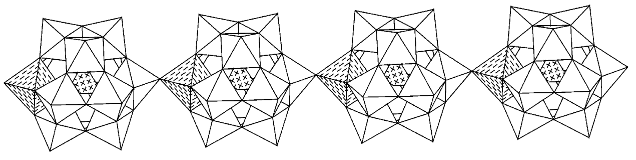

Fig. 3 A polyhedral view of the one-dimensional chain in **3**. Blank octahedra are WO_6, dashed octahedra are CoO_6 and crossed tetrahedra are PO_4.

structure of $[Me_2NH_2]_8[P_2CoW_{17}O_{61}]\cdot 11H_2O$ in which the Co atom occupies a cap position.[34] Details of the link are obscured by the disorder coupled with the orientation. The bridging copper(II) sites exhibit strong covalent attachment to the adjacent clusters with distances of 2.56 and 2.59 Å. This copper site is defined by four nitrogen donors from two en ligands, and *trans*-oxo groups (terminal oxygen atom) from adjacent Dawson anions.

In contrast to the bridging copper(II) site, the copper(II) sites of the $[Cu(en)_2(OH_2)]^{2+}$ groups exhibit only weak interactions with the Dawsons with axial Cu···O distances of 3.08 Å for Cu(1) and 3.07 Å for Cu(2) (Fig. 2). Each of these two copper sites is defined by four nitrogen donors from two en ligands, and two oxygen atoms from a water molecule and a Dawson anion. The Cu(1) and Cu(2) octahedra are distorted by elongation of the axis opposite the water oxygen atoms.

It is noteworthy that the structure of **1** exhibits hydrogen-bonding interaction between the amine nitrogen atoms and the terminal and bridging oxo groups of the Dawson anions. Each chain is linked to two other chains by hydrogen bonds to give a layer parallel to the *ab* plane. The layers are in turn connected by the isolated en through hydrogen bonds to give a three dimensional network. The layers are stacked along the *c* axis in ABAB… sequence. Selected bond lengths and angles are given in Table 2.

The structure of **2** is essentially similar to that of compound **1**. It contains chains of Dawson anions as in **1**. The chains are connected by hydrogen bonds giving a layer parallel to the *ab* plane. The layers are stacked along the *c* axis in ABAB… sequence. The striking differences between the structures **1** and **2** lie in (i) the types of copper coordination sites and (ii) the packing patterns. There are two types of copper coordination sites in **1**: one type is the copper in $[Cu(3)(en)_2]^{2+}$ in which the octahedrally coordinated copper atom bridges to two Dawson units, the other type is the copper in $[Cu(1)(en)_2(OH_2)]^{2+}$ and $[Cu(2)(en)_2(OH_2)]^{2+}$ in which the octahedrally coordinated copper atoms link to one Dawson unit. In **2** there is a third type, namely Cu(5) which is square coordinated by four N atoms from two en molecules. In **1**, the inter-layer regions are occupied solely by H_2en^{2+} cations, while those in **2** are occupied by H_2en^{2+} and $[Cu(en)_2]^{2+}$ cations alternatively. Selected bond lengths and angles are given in Table 3.

The structure of **3** contains Keggin anions $[PCoW_{11}O_{39}]^{5-}$, $[Co(dpa)_2(OH_2)_2]^{2+}$ and $Hdpa^+$ cations. The α-dodecatungstophosphate molecule from which it is derived has been described in a crystal determination of $[H_5O_2]_3[PW_{12}O_{40}]$.[35] The $[PW_{12}O_{40}]^{3-}$ anions can be described as usual α-Keggin ions, formed by four tetrahedrally corner-shared M_3O_{13} units consisting of three edge-sharing distorted MO_6 octahedra, the M atoms forming a cubio-octahedral framework. In **3** the oxygen atoms connected to W atoms can be classified into five groups: O_t bonded to one M atom [d(W–O_t) 1.67–1.71 Å], O_c bridging two M atoms in different M_3O_{13} units [d(W–O_c) 1.75–1.99 Å], O_e bridging two M atoms inside each M_3O_{13} unit [d(W–O_e) 1.82–2.00 Å], O_b bridging two M atoms in two Dawson anions [d(W–O_b) 1.74 Å] and O_i coordinated to three M atoms and a P atom [d(W–O_i) 2.41–2.47 Å]. The bond lengths of mono-substituted Co(2) are quite different from those of W atoms. Five of the Co(2)–O lengths, which are close to those of Co(1)–O(1W) and Co(1)–O(2W), are nearly equal (2.02–2.03 Å). The sixth, corresponding to W–O_i, is very long (2.35 Å) (Table 4).

Similar to compound **1**, the Keggin anion in compound **3** is connected by a common oxygen atom forming chains that run along the *a* axis (Fig. 3). This bridging oxygen atom connects two opposite positions of the Keggin unit occupied by Co(II) and W(VI). At the center of the Keggin anion the average P–O bond length is 1.53 Å. The chain structure of compound **3** is closely related to those of $[ET]_8[MnW_{11}PO_{39}]\cdot 2H_2O$ and $[NEt_3H]_5[PCoW_{11}O_{39}]\cdot 3H_2O$. However, it is noteworthy that unlike these compounds, in which the link of the chains is

Table 2 Selected bond distances (Å) and angles (°) for compound **1**

W(1)–O(1)	1.67(2)	W(7)–O(27)	1.86(2)	M(2)–O(44)	1.94(1)	P(1)–O(6)	1.59(2)
W(1)–O(2)	1.84(2)	W(7)–O(28)	1.87(1)	M(2)–O(48)	1.94(2)	P(2)–O(52)	1.51(2)
W(1)–O(3)	1.89(2)	W(7)–O(24)	1.94(2)	M(2)–O(17)#1	1.98(3)	P(2)–O(58)	1.52(2)
W(1)–O(4)	1.96(2)	W(7)–O(12)	2.01(2)	M(2)–O(46)	2.40(2)	P(2)–O(46)	1.52(2)
W(1)–O(5)	1.97(2)	W(7)–O(25)	2.31(2)	W(14)–O(49)	1.70(2)	P(2)–O(39)	1.55(2)
W(1)–O(6)	2.37(2)	W(8)–O(29)	1.71(2)	W(14)–O(48)	1.81(2)	Cu(1)–N(5)	1.99(2)
W(2)–O(7)	1.71(2)	W(8)–O(30)	1.87(2)	W(14)–O(31)	1.92(2)	Cu(1)–N(14)	2.00(3)
W(2)–O(8)	1.85(2)	W(8)–O(31)	1.87(2)	W(14)–O(50)	1.95(2)	Cu(1)–N(9)	2.03(3)
W(2)–O(9)	1.89(2)	W(8)–O(28)	1.91(1)	W(14)–O(51)	1.96(2)	Cu(1)–N(8)	2.05(2)
W(2)–O(4)	1.92(2)	W(8)–O(13)	1.94(2)	W(14)–O(52)	2.41(2)	Cu(1)–O(7W)	2.31(2)
W(2)–O(10)	1.95(2)	W(8)–O(32)	2.38(2)	W(15)–O(53)	1.73(2)	Cu(1)–O(29)	3.08(2)
W(2)–O(6)	2.38(2)	W(9)–O(33)	1.71(2)	W(15)–O(51)	1.88(2)	Cu(2)–N(10)	1.96(2)
W(3)–O(11)	1.71(2)	W(9)–O(15)	1.81(2)	W(15)–O(34)	1.89(2)	Cu(2)–N(1)	2.04(3)
W(3)–O(12)	1.87(2)	W(9)–O(34)	1.91(2)	W(15)–O(36)	1.88(2)	Cu(2)–N(6)	2.06(3)
W(3)–O(5)	1.91(2)	W(9)–O(3)	1.95(2)	W(15)–O(54)	1.93(2)	Cu(2)–N(13)	2.07(3)
W(3)–O(13)	1.91(2)	W(9)–O(30)	1.96(2)	W(15)–O(52)	2.36(2)	Cu(2)–O(8W)	2.44(3)
W(3)–O(10)	1.92(2)	W(9)–O(32)	2.36(2)	W(16)–O(55)	1.71(2)	Cu(2)–O(37)	3.07(2)
W(3)–O(6)	2.36(2)	W(10)–O(35)	1.70(2)	W(16)–O(38)	1.86(2)	Cu(3)–N(3)	1.99(3)
M(1)–O(14)	1.88(2)	W(10)–O(14)	1.89(2)	W(16)–O(56)	1.89(2)	Cu(3)–N(2)	2.00(2)
M(1)–O(15)	1.93(2)	W(10)–O(36)	1.91(2)	W(16)–O(54)	1.90(2)	Cu(3)–N(7)	2.01(2)
M(1)–O(16)	1.94(2)	W(10)–O(37)	1.92(1)	W(16)–O(57)	1.94(2)	Cu(3)–N(4)	2.02(2)
M(1)–O(2)	1.94(2)	W(10)–O(38)	1.98(2)	W(16)–O(58)	2.44(2)	Cu(3)–O(49)#2	2.56(2)
M(1)–O(17)	1.97(3)	W(10)–O(39)	2.32(2)	W(17)–O(59)	1.72(2)	Cu(3)–O(33)	2.59(2)
M(1)–O(18)	2.39(2)	W(11)–O(40)	1.69(2)	W(17)–O(45)	1.89(2)		
W(5)–O(19)	1.71(2)	W(11)–O(41)	1.89(2)	W(17)–O(60)	1.89(2)	O(32)–P(1)–O(18)	112.0(9)
W(5)–O(16)	1.88(2)	W(11)–O(42)	1.90(2)	W(17)–O(57)	1.91(2)	O(32)–P(1)–O(25)	112.2(9)
W(5)–O(20)	1.89(2)	W(11)–O(20)	1.91(2)	W(17)–O(41)	1.94(2)	O(18)–P(1)–O(25)	110.3(9)
W(5)–O(21)	1.94(2)	W(11)–O(37)	1.93(2)	W(17)–O(58)	2.40(2)	O(32)–P(1)–O(6)	106.1(9)
W(5)–O(8)	1.96(2)	W(11)–O(39)	2.34(1)	W(18)–O(61)	1.71(2)	O(18)–P(1)–O(6)	108(1)
W(5)–O(18)	2.31(1)	W(12)–O(43)	1.72(1)	W(18)–O(47)	1.82(2)	O(25)–P(1)–O(6)	108(1)
W(6)–O(22)	1.69(2)	W(12)–O(44)	1.87(1)	W(18)–O(50)	1.89(1)	O(52)–P(2)–O(58)	107(1)
W(6)–O(21)	1.87(2)	W(12)–O(23)	1.88(2)	W(18)–O(60)	1.93(2)	O(52)–P(2)–O(46)	112(1)
W(6)–O(23)	1.90(2)	W(12)–O(42)	1.93(2)	W(18)–O(56)	2.00(2)	O(58)–P(2)–O(46)	107(1)
W(6)–O(24)	1.91(2)	W(12)–O(45)	1.93(2)	W(18)–O(58)	2.40(2)	O(52)–P(2)–O(39)	112(1)
W(6)–O(9)	1.92(2)	W(12)–O(46)	2.29(1)	P(1)–O(32)	1.52(2)	O(58)–P(2)–O(39)	108(1)
W(6)–O(25)	2.35(1)	M(2)–O(27)	1.89(2)	P(1)–O(18)	1.54(2)	O(46)–P(2)–O(39)	111(1)
W(7)–O(26)	1.69(2)	M(2)–O(47)	1.93(2)	P(1)–O(25)	1.55(2)	M(1)–O(17)–M(2)#2	162(1)

Symmetry transformations used to generate equivalent atoms: #1 $x + 1, y, z$; #2 $x - 1, y, z$; #3 $-x + 2, y + 1, -z$ #4 $-x + 2, -y + 2, z + 1$; M = Cu(50%) + W(50%).

disordered, the link in compound **3** can clearly be determined, with W(6)–O(11) 1.75 Å (which is longer than the average W–O$_t$ 1.70 Å) and Co(2)–O(11) 2.03 Å. The angle at O(11) is 160.4°.

The chains of compound **3** form layers parallel to the *ab* plane. The isolated Hdpa$^+$ cations are located between the chains inside the layer. The $[Co(dpa)_2(OH_2)_2]^{2+}$ cations occupy the inter-layer regions.

It should be noted that although the 11-tungstates are well known, no discrete crystal structure analysis has been made up to now that would allow a detailed description of the bonding environment of the monosubstituted M atom, which occupies one position in the oxometalate shell of the α-Keggin molecule. In many crystalline salts of the monosubstituted Keggin anions the metal atom is randomly distributed over all twelve heavy atom positions as a consequence of the cubic crystal structure or two positions as reported in $[ET]_8[MnW_{11}PO_{39}]\cdot 2H_2O$[13] and $[NEt_3H]_5[XCoW_{11}O_{39}]\cdot 3H_2O$ (X = P or As).[15] The chain-linked monosubstituted Keggin molecules revealed here provide a well characterized system to study the monosubstituted Keggin complex and its catalytic properties.

It is notable that the cations in **1**–**3** are mixed ions. This may be due to the competition between the formation of metal complex and the protonation of the organic amines in the acid medium. It is also noteworthy that the transition metal coordination compounds in **1**–**3** play a twofold role: as ligand covalently linked to the tungsten oxide chain and as charge-compensating cation.

The IR (KBr pellet) spectra of compounds **1** and **2** (Fig. 4a and b) exhibit the four characteristic terminal W–O$_t$ 943 cm^{-1}, corner-sharing W–O$_c$–W 898 cm^{-1}, edge-sharing W–O$_e$–W 777 cm^{-1}, P–O 1078 cm^{-1} asymmetric vibrational peaks for heteropolyanions with Dawson structure. The IR spectrum of **3** (Fig. 4c) exhibits bands around 1059, 963, 900, and 816 cm^{-1}.

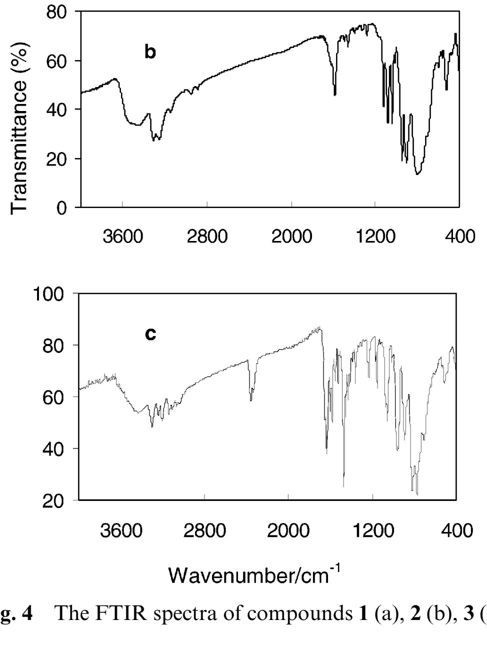

Fig. 4 The FTIR spectra of compounds **1** (a), **2** (b), **3** (c).

Table 3 Selected bond distances (Å) and angles (°) for compound **2**

W(1)–O(1)	1.70(2)	W(7)–O(28)	1.92(2)	M(2)–O(17)#1	2.00(3)	P(2)–O(39)	1.55(2)
W(1)–O(2)	1.84(2)	W(7)–O(24)	1.94(2)	M(2)–O(46)	2.39(2)	P(2)–O(58)	1.58(2)
W(1)–O(3)	1.88(2)	W(7)–O(13)	1.99(2)	W(14)–O(49)	1.67(2)	Cu(1)–N(1)	1.93(3)
W(1)–O(4)	1.97(2)	W(7)–O(25)	2.31(2)	W(14)–O(48)	1.86(2)	Cu(1)–N(10)	2.01(3)
W(1)–O(5)	1.97(2)	W(8)–O(29)	1.66(2)	W(14)–O(31)	1.93(2)	Cu(1)–N(8)	2.04(4)
W(1)–O(6)	2.38(2)	W(8)–O(30)	1.87(2)	W(14)–O(50)	1.94(2)	Cu(1)–N(6)	2.07(3)
W(2)–O(7)	1.72(2)	W(8)–O(31)	1.87(2)	W(14)–O(51)	1.97(2)	Cu(1)–O(1W)	2.33(3)
W(2)–O(8)	1.87(2)	W(8)–O(28)	1.89(2)	W(14)–O(52)	2.37(2)	Cu(1)–O(29)	3.13(2)
W(2)–O(4)	1.89(2)	W(8)–O(12)	1.96(3)	W(15)–O(53)	1.71(2)	Cu(2)–N(3)	1.98(3)
W(2)–O(9)	1.90(2)	W(8)–O(32)	2.34(2)	W(15)–O(51)	1.84(2)	Cu(2)–N(12)	2.01(3)
W(2)–O(10)	1.94(2)	W(9)–O(33)	1.72(2)	W(15)–O(37)	1.87(2)	Cu(2)–N(2)	2.02(3)
W(2)–O(6)	2.34(2)	W(9)–O(14)	1.85(2)	W(15)–O(34)	1.91(2)	Cu(2)–N(4)	2.05(3)
W(3)–O(11)	1.71(3)	W(9)–O(34)	1.89(2)	W(15)–O(54)	1.92(2)	Cu(2)–O(36)	3.05(3)
W(3)–O(12)	1.89(2)	W(9)–O(3)	1.93(2)	W(15)–O(52)	2.33(2)	Cu(2)–O(5W)	2.47(3)
W(3)–O(13)	1.88(2)	W(9)–O(30)	1.98(2)	W(16)–O(55)	1.74(3)	Cu(3)–N(13)	1.97(3)
W(3)–O(5)	1.95(2)	W(9)–O(32)	2.35(2)	W(16)–O(56)	1.88(2)	Cu(3)–N(11)	2.01(3)
W(3)–O(10)	1.96(2)	W(10)–O(35)	1.73(2)	W(16)–O(38)	1.91(2)	Cu(3)–N(5)	2.01(3)
W(3)–O(6)	2.38(2)	W(10)–O(15)	1.85(2)	W(16)–O(57)	1.91(2)	Cu(3)–N(9)	2.01(3)
M(1)–O(14)	1.90(2)	W(10)–O(36)	1.90(2)	W(16)–O(54)	1.92(2)	Cu(3)–O(33)#2	2.61(2)
M(1)–O(15)	1.91(2)	W(10)–O(37)	1.92(2)	W(16)–O(58)	2.40(2)	Cu(3)–O(49)#3	2.62(2)
M(1)–O(16)	1.92(2)	W(10)–O(38)	1.94(2)	W(17)–O(59)	1.70(2)	Cu(5)–N(15)#4	2.00(3)
M(1)–O(2)	1.96(3)	W(10)–O(39)	2.35(2)	W(17)–O(45)	1.84(2)	Cu(5)–N(15)	2.00(3)
M(1)–O(17)	1.96(3)	W(11)–O(40)	1.70(2)	W(17)–O(42)	1.91(2)	Cu(5)–N(7)	2.03(4)
M(1)–O(18)	2.37(2)	W(11)–O(41)	1.88(2)	W(17)–O(57)	1.91(2)	Cu(5)–N(7)#4	2.03(4)
W(5)–O(19)	1.69(2)	W(11)–O(20)	1.88(2)	W(17)–O(60)	1.91(2)		
W(5)–O(16)	1.86(2)	W(11)–O(42)	1.90(2)	W(17)–O(58)	2.36(2)	O(32)–P(1)–O(25)	113(1)
W(5)–O(20)	1.93(2)	W(11)–O(36)	1.94(2)	W(18)–O(61)	1.71(2)	O(32)–P(1)–O(18)	112(1)
W(5)–O(21)	1.94(2)	W(11)–O(39)	2.31(2)	W(18)–O(50)	1.88(2)	O(25)–P(1)–O(18)	110(1)
W(5)–O(8)	1.96(2)	W(12)–O(43)	1.69(2)	W(18)–O(47)	1.89(2)	O(32)–P(1)–O(6)	107(1)
W(5)–O(18)	2.28(2)	W(12)–O(44)	1.80(2)	W(18)–O(60)	1.95(2)	O(25)–P(1)–O(6)	109(1)
W(6)–O(22)	1.73(2)	W(12)–O(23)	1.87(2)	W(18)–O(56)	1.99(2)	O(18)–P(1)–O(6)	106(1)
W(6)–O(21)	1.87(2)	W(12)–O(41)	1.96(2)	W(18)–O(58)	2.37(2)	O(46)–P(2)–O(52)	112(1)
W(6)–O(23)	1.92(2)	W(12)–O(45)	1.99(2)	P(1)–O(32)	1.54(2)	O(46)–P(2)–O(39)	111(1)
W(6)–O(9)	1.93(2)	W(12)–O(46)	2.31(2)	P(1)–O(25)	1.56(2)	O(52)–P(2)–O(39)	113(1)
W(6)–O(24)	1.93(2)	M(2)–O(47)	1.88(2)	P(1)–O(18)	1.58(2)	O(46)–P(2)–O(58)	107(1)
W(6)–O(25)	2.35(2)	M(2)–O(48)	1.924(2)	P(1)–O(6)	1.59(2)	O(52)–P(2)–O(58)	106(1)
W(7)–O(26)	1.71(2)	M(2)–O(27)	1.93(2)	P(2)–O(46)	1.52(2)	O(39)–P(2)–O(58)	107(1)
W(7)–O(27)	1.82(2)	M(2)–O(44)	1.96(2)	P(2)–O(52)	1.53(2)	M(1)–O(17)–M(2)#5	162(1)

Symmetry transformations used to generate equivalent atoms: #1 $x + 1, y, z$; #2 $x + 1, y - 1, z$; #3 $x, y - 1, z$; #4 $-x - 1, -y + 3, -z + 1$; #5 $x - 1, y, z$; M = Cu(50%) + W(50%).

Table 4 Selected bond distances (Å) and angles (°) for compound **3**

W–O$_t$		W(1)–O(5)	1.929(14)	Co(2)–O(11)#2	2.03(2)
W(1)–O(3)	1.713(16)	W(2)–O(10)	1.823(12)	Co(2)–O(17)	2.353(16)
W(2)–O(9)	1.666(17)	W(2)–O(18)	1.941(9)		
W(3)–O(6)	1.714(15)	W(3)–O(20)	1.889(11)	Co(1)–O(2W)	2.077(16)
W(4)–O(4)	1.698(13)	W(3)–O(23)#1	1.932(15)	Co(1)–N(2)	2.092(19)
W(5)–O(15)	1.700(11)	W(4)–O(14)	1.953(12)	Co(1)–N(6)	2.101(18)
W–O$_b$		W(4)–O(20)#1	2.006(13)	Co(1)–N(1)	2.103(18)
W(6)–O(11)	1.75(2)	W(5)–O(14)	1.913(12)	Co(1)–O(1W)	2.118(16)
W–O$_c$		W(5)–O(23)	1.924(16)	Co(1)–N(5)	2.129(17)
W(1)–O(16)	1.836(12)	W(6)–O(5)	1.920(13)		
W(1)–O(7)	1.911(13)	W(6)–O(5)#1	1.920(13)	P(1)–O(17)	1.477(18)
W(2)–O(13)	1.904(14)	W—O$_i$		P(1)–O(19)	1.529(16)
W(2)–O(16)	1.996(11)	W(1)–O(19)	2.469(11)	P(1)–O(22)	1.557(12)
W(3)–O(12)	1.926(11)	W(2)–O(17)	2.438(11)	P(1)–O(22)#1	1.557(12)
W(3)–O(1)	1.893(5)	W(3)–O(22)	2.454(11)		
W(4)–O(2)	1.897(6)	W(4)–O(22)#1	2.464(10)	W(6)–O(11)–Co(2)#3	160.4(19)
W(4)–O(8)	1.754(15)	W(5)–O(22)#1	2.430(11)	O(17)–P(1)–O(19)	112.3(10)
W(5)–O(7)	1.897(12)	W(6)–O(19)	2.418(14)	O(17)–P(1)–O(22)	111.2(6)
W(5)–O(13)	1.894(15)			O(19)–P(1)–O(22)	107.4(6)
W(6)–O(12)	1.894(11)	Co(2)–O(8)#1	2.022(14)	O(17)–P(1)–O(22)#1	111.2(6)
W(6)–O(12)#1	1.894(11)	Co(2)–O(8)	2.022(14)	O(19)–P(1)–O(22)#1	107.4(6)
W–O$_e$		Co(2)–O(10)	2.029(12)	O(22)–P(1)–O(22)#1	107.2(10)
W(1)–O(21)	1.926(8)	Co(2)–O(10)#1	2.029(12)		

Symmetry transformations used to generate equivalent atoms: #1 $x, -y + 1, z$; #2 $x, y, z - 1$; #3 $x, y, z + 1$.

The two peaks at 1059 and 963 cm^{-1} are very typical for Keggin anions and can be attributed to P–O$_i$ bands and terminal W–O$_t$ bands respectively. The other two bands can be assigned to W–O$_c$–W and W–O$_e$–W vibrations.

The thermal analysis of **1** (Fig. 5) gives a total loss of 11.1% in the range of 50–850 °C, which agrees with the calculated weight loss of 11.17%. The weight loss of 2.7% at 50–170 °C corresponds to the loss of two molecules of water per formula (calc. 2.54%). The weight loss of 8.4% at 270–720 °C arises from the decomposition of organic amine (calc. 8.70%). **2** shows a total weight loss of 12.2% in the temperature range 50–720 °C which was attributed to the loss of waters (calc. 2.51%, 50–190 °C) followed by the decomposition of organic amine (calc. 9.52%, 190–710 °C). The X-ray powder pattern of the

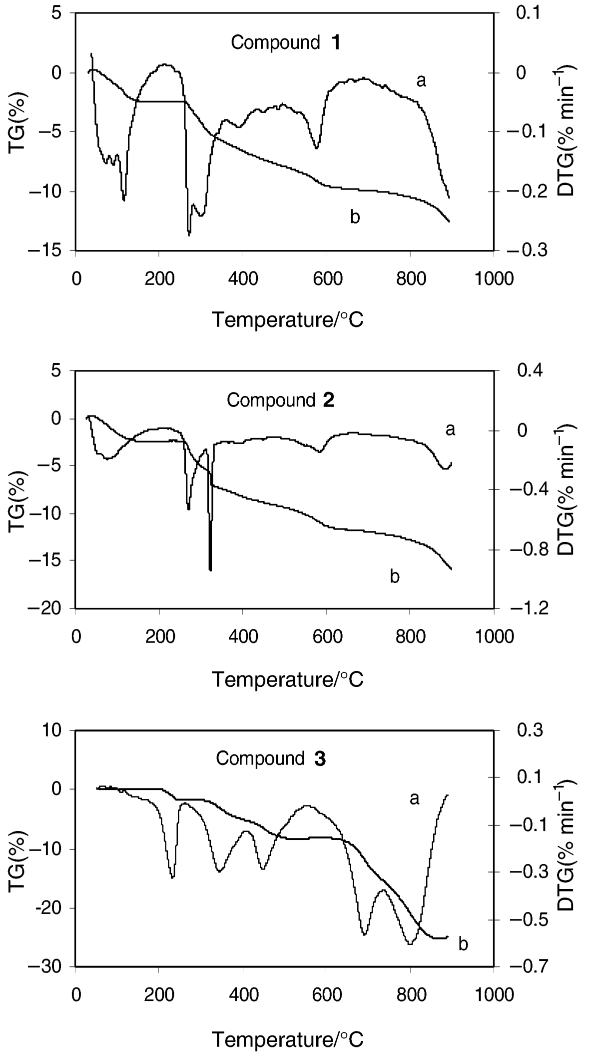

Fig. 5 TGA plots of **1**–**3** under nitrogen from room temperature to 900 °C at 5 °C min^{-1}. (a) DTG, (b) TG.

post-TGA residue of **1** and **2** is in agreement with that of $W_{18}P_2O_{59}$ (JCPDS: 41–371), indicating that the bulk residue is most likely $W_{17}CuP_2O_{57}$. For compound **3**, mass losses at 200–250 (1.7) and 300–870 °C (23.5%) are attributed to the release of water molecules (calc. 1.90%) and the decomposition of organic amines (calc. 22.63%). X-Ray powder data indicated that the post-TGA residue of **3** is possibly $W_{11}CoPO_{36.5}$ [JCPDS: 41-369($W_{12}PO_{38.5}$)], $CoWO_4$ [JCPDS: 15-867] and other unidentified phases.

Conclusion

Three novel one-dimensional heteropolytungstates compounds have hydrothermally been synthesized and their structures elucidated by single crystal X-ray diffraction. The chain structures in **1**–**3** provide novel examples of condensation of discrete clusters and/or the connection of discrete clusters through transition metal coordination complexes into extended structures.

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