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Synthesis and characterization of nanoclusters: Inorganic-organic hybrid copper and cobalt containing arsenotungstates(III) with lone pair on heteroatom incorporating bidentate N-donating ligands

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Three inorganic-organic hybrid nanoclusters of copper and cobalt containing arsenotungstates with lone pair on heteroatom have been synthesized under mild reactions conditions. All the compounds have been characterized by single crystal X-ray diffraction, Fourier transform infrared, UV/visible spectroscopy, thermogravimetric and field emission scanning electron microscopic (FE-SEM) analysis. The compound $[NaRb\{Cu(phen)(H_2O)_2Cl\}_2][\{Cu(phen)(H_2O)\}_2\{Cu(phen)(H_2O)Cl\}_2\{Cu_2As_2W_{19}O_{67}(H_2O)]$ **(1a)** is a sandwiched type arsenotungstate with two copper atoms in square planar environment in the belt region. The polyanion-**1** is decorated by four copper phenanthroline complexes through a terminal oxygen atom of the polyanion. In addition, two other cobalt containing inorganic-organic hybrid lone pair containing arsenotungstates(III) with 1,10-phenanthroline $[NaRbCo(phen)_3][\{Co(phen)(H_2O)_3\}CoAs_2W_{20}O_{67}(H_2O)_3]$ **(2a)** and 2,2'-bipyridine$[Na_3RbCo(2,2\text{-bipy})_3][CoAs_2W_{20}O_{67}(H_2O)_3]$ **(3a)** has also been synthesized under mild conditions. The polyanion (**2**) is a mono cobalt substituted sandwiched type structure that is decorated by a cobalt phenanthroline complex attached to the polyanion through a terminal oxygen atom. Meanwhile the other complex (**3**) is also a monocobalt substituted sandwiched type structure which contains a cobalt 2,2'-bipyridine complex in the cationic part. Polyanion-**1** shows intermolecular π-π stacking interaction between the phenanthroline ligand in the cationic part and one that is attached directly to the polyanion. The compounds are also characterized by FE-SEM analysis and the compound **3a** shows ultra- smooth cuboids with grain size in the range of 1 to several micrometer though some very small irregular particles with the size of a few micrometer were also observed.

Keywords: Arsenotungstates, Inorganic organic hybrid polyoxometalates, 1,10-phenanthroline, 2,2'-bipyridine

Polyoxometalates (POMs) are metal oxygen nanoclusters, which are structurally diverse and possess a wide range of tunable properties[1]. The applications of POMs are already well-known in the field of catalysis and medicine[2,3] but in the recent years, several new applications such as in hybrid energy storage devices, solar cells, along with other applications in the field of nanoscience and nanotechnology has been on the rise.[4,5] Out of the various types of POMs, the Keggin type polyanion which comprises of a central metal XO_4 unit in tetrahedral geometry surrounded by four octahedral edge sharing M_3O_{13} [M= $W^{V,\ VI}$, $Mo^{V,\ VI}$] units through corner sharing oxygen atoms is an important precursor for the synthesis of various substituted POMs.[6,7]Apart from that, the heteroatom on the polyanion can also be a lone pair containing species such as As^{III}, Sb^{III} or Bi^{III}. These are particularly important in the synthesis of inorganic-organic hybrid polyanions as the presence of a lone pair of electrons on the heteroatom inhibits the formation of closed structures. This, in turn leads to the possibility of the formation of a large number of open-ended extended structures.[8] Thus, a large number of structures have been reported for several transition metal substituted lone pair containing arsenotungstates ranging from mono substituted to hexa-substituted POMs.[9,10]

Various transition metal substituted sandwiched type arsenotungstates are reported in the literature. The very first cobalt containing arsenotungstates(III) was reported by Te´ze´ et al.[11] in 1980 with the formula $[NH_4As_4W_{40}O_{140}Co_2(H_2O)_2]^{23-}$. In 1982, Robert et al.[12] structurally characterized the crystal structure of copper containing arsenotungstates $[As_2W_{18}Cu_3O_{66}(H_2O)_2]^{7-}$. All the copper ions here were not equivalent as the coordination environment of one of the copper ion was different from the rest. In 1984, Weakley[13] reported the crystal structures of mono-cobalt and zinc substituted aresenotungstate $[As_2MW_{20}O_{68}(OH_2)_2]$ (M= Co^{2+}, Zn^{2+}). Furthermore, in 2001, Sadakane et al.[14] reported a series of transition metal substituted sandwich type structures of the type $[(XW_9O_{33})_2M_3(H_2O)_3]^{n-}$ (X = As^{III}, Sb^{III}) and (M = Cu^{2+}, Zn^{2+}) and $[(AsW_9O_{33})_2WO(H_2O)M_2(H_2O)_2]^{10-}$ (M= Co^{2+}, Zn^{2+}, Mn^{2+}). Mialane et al.[15] in the same year reported the tri-metal substituted $[As_2W_{18}(M(H_2O))_3O_{66}]$ (M = Co^{2+}, Mn^{2+}). Following which Kortz et al. reported the tetra-copper substituted heteropolyanion $[Cu_4K_2(H_2O)_8(AsW_9O_{33})_2]^{8-}$ which showed interesting magnetic properties.[16]

A number of attempts have been made to incorporate an organic moiety, mainly with an N or O donating ligands within the complex with the aim of forming inorganic-organic hybrid clusters. In 2009, Hussain et al.[17] reported a trinuclear and a tetranuclear copper (II) complex that each incorporated a AsW_9O_{33} unit along with several 2,2'-bipyridine ligands of the formula $[\{Cu(2,2'\text{-bpy})\}_3(AsW_9O_{33})].[\{Cu(2,2'\text{-bpy})_2\}\{Cu(2,2'\text{-bpy})\}_3(AsW_9O_{33})]$. Another example which include both oxalic acid and 1, 10-phenanthroline is the complex reported by Niu et al.[18] consisting of the formula $[(Cu_2(phen)_2(u\text{-}ox)][Cu(phen)(H_2O)_2][Cu_4(H_2O)_4Cu_2(phen)_2(AsW_9O_{33})_2]$. Lastly, Ma et al.[19] in 2014 reported the hydrothermal synthesis of $[Cu(dien)(H_2O)_2][Cu_2(dien)_2(OH)]_2[Cu_4(AsW_9O_{33})_2]$. It is interesting to note that the synthesis of most of the inorganic-organic POM hybrids are done under high pressure hydrothermal conditions, but a few exceptions are present when such hybrids are synthesized under open air conditions. An example of such are the polyanions reported by Liu et al. in 2015, when a 1,2,4-1H triazole ligand replaced the terminal water molecule of the sandwiched type polyanion mentioned earlier to give rise to the formula $[Na(H_2O)_3M(HTaz)_3(AsW_9O_{33})_2]$ (M = Ni^{2+}, Mn^{2+}, Co^{2+}).[20] Such compounds along with the nona-copper substituted $[H_4\{Cu^{II}_9As^{III}_6O_{15}(H_2O)_6\}(\alpha\text{-}As^{III}W_9O_{33})_2]^{8-}$ reported by Zhou et al. were useful not only due to their magnetic properties but also mainly due to their antiviral and antitumor properties.[21] Another interesting example is the two penta-manganese substituted sandwiched type polyanion with the formula $[Mn(bpy)_2Na(H_2O)_2(MnCl)(Mn(H_2O)(AsW_9O_{33})_2]$ and $[(Mn(bpy)_2Na(H_2O)_2(MnCl)\text{-}Mn(H_2O)_2(SbW_9O_{33})_2]$ (bpy= 2,2' -bipyridine).[22]

Herein, we report the crystal structures of three inorganic-organic hybrid copper and cobalt substituted arsenotungstates(III) with N donating bidentate ligands. The polyanion-**1** is a bi-copper substituted complex with several copper phenanthroline complexes attached to the polyanion through a corner sharing oxygen atoms. Polyanion-**2** and **3** are mono-cobalt substituted sandwiched type arsenotungstates incorporating a cobalt organic moiety.

Materials and Methods

The trilacunary lone pair containing $Na_9[AsW_9O_{33}]$ was synthesized according to the published literature procedure[23] and was confirmed by Fourier transform infrared (FTIR) spectroscopy. All other chemicals were commercially purchased and were used without further purifications. The FTIR spectra were recorded by using a Perkin-Elmer BX spectrometer on KBr pellets in the range of 400-4000 cm^{-1}. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA 4000 in the temperature range of 30-900 °C with a heating rate of 5 °C/min on flowing nitrogen atmosphere.

Synthesis of $[NaRb\{Cu(phen)(H_2O)_2Cl\}_2][\{Cu(phen)(H_2O)\}_2\{Cu(phen)(H_2O)Cl\}_2\{Cu_2As_2W_{19}O_{67}(H_2O)]\cdot 17H_2O$(1a)

To 25 mL of 1M NaCl solution, 0.051 g (0.3 mmol) $CuCl_2\cdot 2H_2O$ was dissolved with stirring in a beaker. To it, 0.2464 g (0.1 mmol) $Na_9[AsW_9O_{33}]$ and 0.0180 g (0.1 mmol) 1,10-phenanthroline were added under constant stirring. The turbid yellowish solution was stirred and the pH of the solution was adjusted to 2.5 by dropwise addition of 1M HCl solution upon which the color changed to green. The mixture was heated at 80 °C for 1 h and then left for cooling (Final pH = 3.4). 1 mL of 0.5 M RbCl solution was added dropwise. Solid dark green crystals were collected after a two weeks those were suitable for single crystal diffraction. The crystalline material was collected and used for further analysis. FTIR ($\bar{\nu}$): 1428(w), 1148(w), 1107(w), 951(s), 889(s), 793(s), 735(s) cm^{-1}. The number of crystalline water molecules was determined by TGA. Elemental analysis calc (found) (%): C 12.57 (12.73) As 2.18(2.21), Cl 2.06 (1.84), Cu 7.39 (7.48), N 2.44 (2.47), Na 0.33 (0.43) Rb1.24 (1.25), W 50.78(51.41).

Synthesis of $[NaRbCo(phen)_3][\{Co(phen)(H_2O)_3\}CoAs_2W_{20}O_{67}(H_2O)_3]\cdot 22H_2O$(2a)

The synthesis and method of crystallization is same for this compound as that of **1** except for the fact that, 0.0713 g (0.3 mmol) $CoCl_2\cdot 2H_2O$ was used instead of $CuCl_2\cdot 2H_2O$ and the pH of the solution was adjusted to 5 upon which the green turbid solution turned pink. The color of the reaction mixture turned green during the course of the reaction. 1 ml 0.5 M RbCl solution was added dropwise and light green crystals were collected after 2 weeks and used for further analysis. FTIR ($\bar{\nu}$): 1426 (w), 1148(w), 1107(w), 947(s), 875(s), 790(s), 734(s) cm^{-1}. The number of crystalline water molecules was determined by TGA. Elemental analysis calcd (found)(%): C 9.0 (6.95), As 2.34 (2.47), Co 2.76 (1.99), N1.75 (1.16), Na 0.36 (0.45), Rb 1.33(1.41), W 57.37 (59.18).

Synthesis of $[Na_3RbCo(2,2'\text{-bipy})_3][CoAs_2W_{20}O_{67}(H_2O)_3]\cdot 25H_2O$ (3a)

The synthesis and method of crystallization is same for this compound as that of **2** except for the fact that 0.0156 g (0.1 mmol), 2,2'-bipyridine was added instead of 1, 10-phenanthroline and the pH of the solution was adjusted to 4 upon which the green turbid solution turned pink. The color of the reaction mixture turned green during the course of the reaction. 1 mL 0.5 M RbCl solution was added dropwise and light green crystals were collected after 2 weeks and used for further analysis. FTIR ($\bar{\nu}$): 1408(w), 1172(w), 1157(w) 1101(w), 947(s), 875(s), 784(s) and 734(s) cm^{-1}. The number of crystalline water molecules was determined by TGA. Elemental analysis calc (found)(%): C 5.51 (6.04), As 2.29 (2.51), Co 1.80 (1.98), N 1.28 (1.41), Na 1.05 (1.32), Rb 1.31 (1.81), W 56.19 (59.82).

X-ray Data Collection and Structure determination

Suitable crystals of compounds **1a**, **2a** and **3a** were mounted on an Oxford Xcalibur Sapphire 3 diffractometer (single wavelength Enhance X-ray source with Mo*Kα* radiation, λ = 0.7103 Å. Pre-experiment, data collection and absorption corrections were performed with CrysAlisPro.[24] The structures were solved using direct methods using SHELXL-97 which readily revealed all the heavy atom positions (W, Cu, Co) and helped us to locate the other non-hydrogen atoms (C, N, O) positions from the difference Fourier maps.[25,26] The non-hydrogen atoms (C, N, O) were refined isotropically. All H atoms were placed in geometrically idealized positions and refined using a riding model, with C-H = 0.93 Å with U_{iso} (H) 1.2 U_{eq} (C) for aromatic H atoms. In the polyanion **2**, the tungsten atoms and the cobalt atom in the belt region are refined with partial occupancies due to disorder. The crystal data of the three structures are summarized in Table 1.

Results and Discussion

The crystal structure of complex **1a** shows that the complex crystalizes in orthorhombic crystal system with space group *Pnma*. The structure of **1** (as seen in Fig. 1) comprises of two trilacunary B-α-AsW_9O_{33}

Table 1 — Crystal data and structure refinement

	1a	**2a**	**3a**
Empirical formula	$C_{72}H_{100}As_2Cl_4Cu_8N_{12}NaO_{84}RbW_{19}$	$C_{48}H_{88}As_2Co_3N_8NaO_{95}RbW_{20}$	$C_{30}H_{80}As_2Co_2N_6Na_3O_{120}RbW_{20}$
Formula weight	6879.03	6409.11	6543.87
Crystal system	orthorhombic	monoclinic	Triclinic
Space group	Pnma	$P2_1/c$	$P\bar{1}$
a/Å	26.5699(3)	18.8681(2)	19.0408(4)
b/ Å	29.3899(4)	24.2196(3)	24.3354(5)
c/ Å	16.5416(2)	47.4378(5)	25.6029(5)
α/°	90	90	92.037(2)
β/°	90	96.3690(10)	103.049(2)
γ/°	90	90	100.971(2)
V/ Å^3	12917.1(3)	21544.2(4)	11307.6(4)
Z	4	8	4
D_c/g cm^{-3}	3.509	3.725	3.502
μ/mm^{-1}	19.195	22.225	21.274
F_{000}	12214	21245.0	10480
Crystal size/mm^3	0.09 × 0.08 × 0.01	0.09 × 0.08 × 0.01	0.09 × 0.07 × 0.01
Reflns collected	158351	383026	148203
Indepreflns	12505	42388	42821
R_{int}	0.1708	0.1631	0.1101
Goodness-of-fit on F^2	1.042	1.051	1.005
$R_1[I > 2\sigma(I)]$[a]	0.0673	0.0932	0.0676
wR_2 (all data)[b]	0.1776	0.2740	0.1823

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$

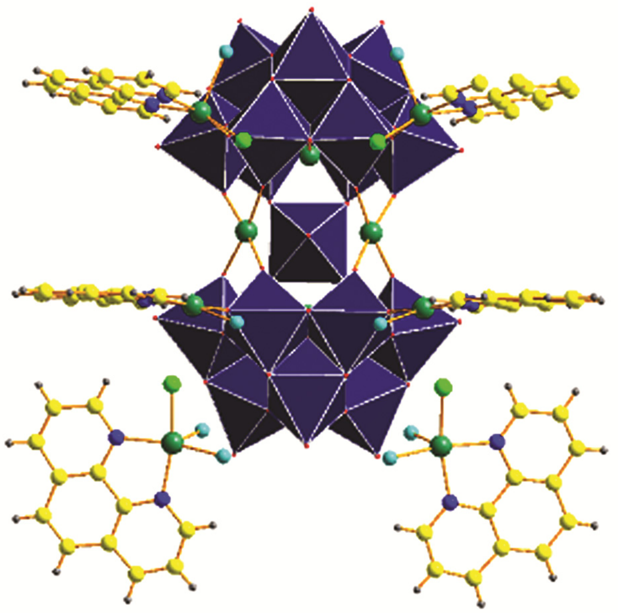

Fig. 1 — Polyhedral representation of polyanion **1a** (The blue polyhedron, green ball, red ball, blue ball, yellow ball, grey ball and aqua ball are shown as W, Cu, O, N, C, H and water molecule, respectively)

Keggin units which sandwich between them an octahedral WO(H_2O) fragment along with two copper ions which are present in square planar geometry. Alternatively **1** can also be described as a dilacunary $As_2W_{19}O_{67}(H_2O)$ fragment which has been substituted by two square planar copper centers. This polyanion bears a resemblance to the $[M_2(OH_2)_2As_2W_{19}O_{67}(H_2O)]^{10-}$ (M = Co^{2+}, Ni^{2+}, Zn^{2+}) which was reported in 2001 by Kortz et al.[14] but no such bi-metallic analogue was reported for copper until now. The primary difference between the reported polyanions and **1** is that the metal ion is present in a four coordinate (square planar) environment i.e. the absence of a terminal water molecule as opposed to the penta-coordinate (square pyramidal) geometry.

Apart from that, we can also see four copper phenanthroline complexes attached to the polyanion. These moieties can be divided into two types i.e. $\{Cu(phen)(H_2O)\}^{2+}$ and $\{Cu(phen)(H_2O)_2Cl\}^{+}$. Among them the two $\{Cu(phen)(H_2O)\}^{2+}$ units are attached to the AsW_9O_{33} fragment each through a terminal shared oxygen with the polyanion. Here the copper ions are in a square planar geometry as seen in Supplementary Data, Fig. S1. The coordination sites are satisfied by two nitrogen from the 1,10-phenanthroline ligand and one terminal water molecule as confirmed by bond valence sum calculations.[27] In addition, the other two $\{Cu(phen)(H_2O)Cl\}^{+}$ moieties are attached to the polyanion though a terminal oxygen atom of the polyanion. Here, the copper ions are in penta-coordinate state with two of its coordination sites satisfied by the nitrogen atoms of the phenanthroline ring, one water molecule, one chlorine atom and the fifth site is attached to the polyanion.

In addition, we can also observe two charge compensating $\{Cu(phen)(H_2O)_2Cl\}^{+}$ moieties present in the cationic part. The copper ions here are in square pyramidal geometry with two of its coordination sites satisfied by the nitrogen atoms of the 1,10-phenanthroline ligand and two terminal water molecules and the final by a chlorine atom. A rubidium cation acts as linker for the polyanion to form a 1-D chain. The structure is also extended by Na cations which further act as linkers. The packing diagram can be seen in Supplementary Data, Fig. S2. There is also evidence of intermolecular π-π stacking interaction between one of the phenanthroline present in the cationic part of one molecule and the phenanthroline ligand which is directly attached to another polyanion. The distance between the centroids is found to be 3.628(3) Å. Thus 1,10-phenanthroline acts as a linker between the polyanions further extending the dimensions of the structure.

The single crystal structural determination of compound **2a** shows that the complex crystallizes in monoclinic crystal system with $P2_1/c$ space group. The structure comprises of two α-AsW_9O_{33} units which exists in a sandwiched structure which resembles the structure reported by Weakley in 1984.[13] The belt region comprises of one cobalt center in square pyramidal geometry which is connected to 4 terminal oxo group of the AsW_9O_{33} fragment and a terminal water molecule. There is also the presence of a $W_2O(H_2O)_2$ unit in the belt region as shown in the Fig. 2, where both the tungsten atoms are in six coordination environment. Bond valence calculations indicate that both the oxygen attached to the outer part of the tungsten centers in the belt region are water molecules. A cobalt phenanthroline organic moiety of the formula $\{Co(phen)(H_2O)_3\}^{2+}$ is attached to the AsW_9O_{33} fragment through a shared oxygen atom to the polyanion. The cobalt ion here is in six-coordinate octahedral environment with two of its sites satisfied by the nitrogen atoms of the 1, 10 phenanthroline ligand. There are three terminal water molecules and the sixth site is attached to an oxygen atom which is shared with the polyanion as confirmed by BVS calculations.[27]

A charge compensating $\{Co(phen)_3\}^{2+}$ moiety is present alongside the anionic polyanion in which the cobalt ion is in 6-coordinate octahedral geometry with all six sites satisfied by the nitrogen atoms of the 1,10-phenanthroline ligand. The units are further linked to one another through a Rubidium cation which acts as a linker and helps in extending the structure in higher dimension. There is no evidence of π-π stacking in this case (Supplementary Data, Fig. S3).

The single crystal analysis of compound **3a** shows that the complex crystalizes in triclinic crystal system with $P\overline{1}$ space group. The structure of **3** is similar to that of **2** with two α-AsW_9O_{33} units which sandwich between them a $Co(H_2O)(W_2O)(H_2O)_2$ unit as shown in Fig. 3. There is no direct attachment of the organic complex to the polyanion, but there is a $[Co(bipy)_3]^{2+}$ (bipy = 2, 2'-bipyridine) present in the cationic part. The structure is further extended by sodium and rubidium cations which acts as linkers as seen in the packing diagram (Supplementary Data, Fig. S4). The difference in structures of **1** and **2** clearly demonstrates the role of the N donating ligand in the formation of such complexes. We also tried varying the reaction parameters but could not isolate such a structure where there is a direct attachment of the organic complex to the polyanion. Thus 1,10-phenanthroline seem to play a crucial role in the formation for such hybrids.

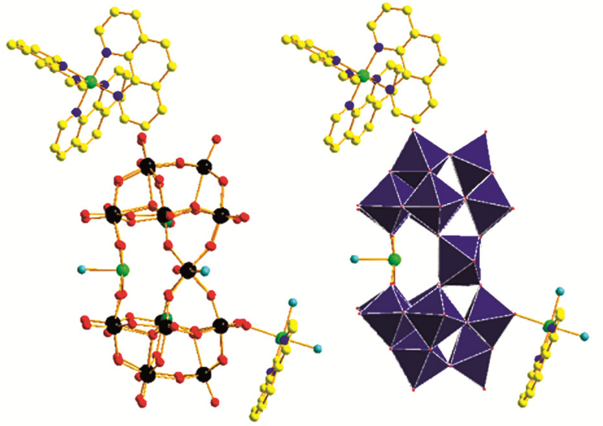

Fig. 2 — Ball-stick and polyhedral representation of compound **2a** (The blue polyhedron, green ball, red ball, blue ball, yellow ball, grey ball and aqua ball are shown as W, Co, O, N, C, H and water molecule, respectively)

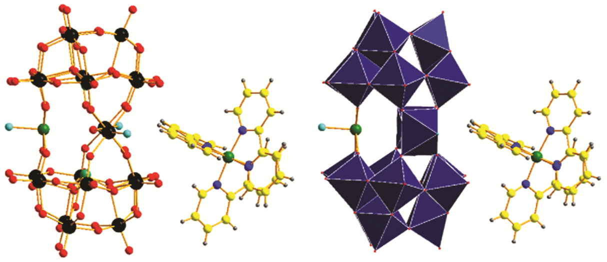

Fig. 3 — Ball-stick and polyhedral representation of polyanion **3a** (The blue polyhedron, green ball, red ball, blue ball, yellow ball, grey ball and aqua ball are shown as W, Co, O, N, C, H and water molecule, respectively)

The FTIR spectra of the compounds are shown in Supplementary Data, Fig. S5. All the compound exhibit similar peaks which are a characteristic of the sandwich type dimeric structures. The characteristics peaks in the POM fingerprint region is shown at 951, 889, 793, 735 cm^{-1} by compound **1a**, 947, 875, 790, 734 cm^{-1} for compound **2a** and at 947, 875, 784 and 734 cm^{-1} for **3a**. These can be attributed to terminal $\nu(W–O_t)$, corner sharing $\nu(W–O_b)$, $\nu(As–O_a)$, and edge sharing $\nu(W–O_c)$, respectively. The other peaks in the region of 1500-1000 cm^{-1} for **1a** and **2a** can be attributed to the numerous C=C, C-N and C-C bonds which are characteristic of the 1, 10 phenanthroline moiety attached. More prominent were the peaks observed at 1147 and 1107 cm^{-1}which can be attributed to the various δ(C=C-H) of the aromatic rings. In case of **3a** several peaks can be seen in the range of 1500-1000 cm^{-1} ones can be seen out of which more prominent peaks occur at 1172, 1157 and 1101 cm^{-1} attributed to the various δ(C=C-H) of the aromatic rings.[28]

The thermogravimetric analyses of the three compounds were done in the range of 37-800 °C in order to determine the number of crystalline water molecules. As seen in Supplementary Data, Fig. S6 the polyanion **1a** shows a two-step weight loss. The first weight loss in the region of 30 to 350 °C corresponds to approximately 7.4 % which can be accounted for 17 crystallized and 9 coordinated water molecules. The next step (~16%) which occurs in the range of 250-800 °C corresponds to 6 Phenanthroline molecules and some to the decomposition into As_2O_3 and O_2. The polyanion **2a** also shows a two-step weight loss in the region of 37-850 °C. The first weight loss in the region of 30 to 350 °C corresponds to ~7% which can be accounted for 22 crystallized and 6 coordinated water molecules. A second step weight loss ~10% in the 250-700 °C region can be accounted for four phenanthroline molecules. Polyanion **3a** also shows a two-step weight loss with the first in the range of 25 crystal water molecules and

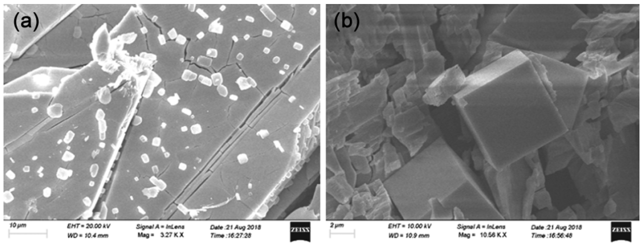

Fig. 4 — FESEM images of compounds (a) **2a** and (b) **3a**

3 coordinated water molecules. The second step weight loss in the region of 300-700 °C correspond to ~7.2% which is due to the 2,2'-bipyridine ligands.

The solution UV-visible spectra of the three compounds **1a**, **2a** and **3a** were recorded in the range of 200–600 nm by dissolving a small amount of sample in water. As seen in Supplementary Data, Fig. S7, all the three compounds show a peak in the region of 250-260 nm which corresponds to the characteristic pπ-dπ charge transfer band of $O_{b,c}$-W bond.

Field emission scanning electron microscopy (FESEM) images of compounds **2a**-**3a** are provided in Fig. 4, which clearly show the ultra-smooth cuboids of compound **3a** and have the grain size in the range of 1 to several micrometer though some very small irregular particles with the size of a few micrometer were also observed. The EDX analyses of compounds **2a** and **3a** as seen in Supplementary Data, Fig. S8 revealed the presence of O, Co, W and As elements at the surface.

Conclusions

Three sandwiched type inorganic-organic hybrids were synthesized with lone pair containing arsenotungstates using 1,10-Phenanthroline under mild conditions at room temperature. Polyanion**1** is a di-copper substituted sandwiched type polyanion which contained the copper ion in a square planar environment. The organic part of the compound contained two different copper phenanthroline complexes wherein the copper ions are in two different coordination environments (square planar and square pyramidal). The polyanions **2** and **3** are mono-cobalt substituted complex in which a square pyramidal as well as a hexa-coordinate octahedral environment was observed. Such inorganic organic hybrid complexes are usually synthesized under hydrothermal conditions, but these compounds have been synthesized under milder open air conditions. The role played by the organic ligands in the formation of such structures is clearly demonstrated by the difference in structures of polyanion **2** and **3**. All the compounds were characterized by SC-XRD, FTIR, TGA, UV-visible Spectroscopy and FESEM analysis. Compound **1a** showed intermolecular π-π stacking interaction between the phenanthroline ligand in the cationic part and one that is attached directly to the polyanion further extending the structure.

Supplementary Data

Further details on the crystal structure data may be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.on quoting the depository number CCDC-No–1941122 for compound (**1a**), 1941123 for compound (**2a**) and 1941124 for compound (**3a**). Supporting Data also includes crystal packing diagrams, FTIR spectra, solution UV/visible spectra and thermogravimetric analyses curves for all compounds. Supplementary Data associated with this article are available in the electronic form at http://nopr.niscair.res.in/jinfo/ijca/IJCA_59A(11)1602-1608_SupplData.pdf.

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