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Notes

Early lanthanoid substituted organic-inorganic hybrids of silico- and germano-tungstates: Syntheses, crystal structures and solid-state properties

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Organic-inorganic hybrid of 3*d*-4*f* heterometallic derivatives of lacunary Keggin type silico- and germano-tungstates: $[\{Cu_2(1,10\text{-}phen)_2(\mu\text{-}CH_3COO)_2\}Ln(\alpha\text{-}XW_{11}O_{39})_2]^{11-/10-}$ {Ln = La^{III}, Ce^{III} and Ce^{IV}, X = Si^{IV}; La^{III}, Ce^{III}, Ce^{IV}, X = Ge^{IV}; 1,10-phen = 1,10-Phenanthroline} have been synthesized by conventional aqueous solution method under mild reaction conditions. Solid crystalline materials isolated from the solution as an alkali salts (Na^+/K^+) are characterized by single crystal X-ray diffraction, FT-IR spectroscopy, powder-XRD, ICP-AES, liquid UV/vis and thermogravimetric analysis. FT-IR spectra and PXRD suggest that these compounds are isomorphous. Further, single crystal XRD analyses show that all are organic-inorganic hybrids comprising Peacock and Weakley type sandwich-type $[Ln(\alpha\text{-}XW_{11}O_{39})_2]^{13-/12-}$ (X = Si^{IV} and Ge^{IV}) polyanion as the fundamental building block unit. These sandwich type species form polymeric chain assistance with copper organic complexes. These polymeric chains further assemble into 2-D structures by π-π stacking.

Keywords: Polyoxometalates, 3*d*-4*f* Heterometallic complexes, Organic-inorganic hybrids, Single crystal XRD

Polyoxometalates (POMs) depict an unusual family of interesting metal-oxygen cluster compounds, which can be synthesized by self-assembly of oxo-anions of early transition metals (W^{VI}, Mo^{VI}, V^{V} and Nb^{VI}) in higher oxidation states. POMs exhibit a noticeable structural diversity and a superfluity of potential applications in catalysis, biomedicine nanotechnology and material science[1-10]. Tungsten-based POMs are durable and this has been utilized to develop Keggin and Wells-Dawson anions with vacancies. Lacunary POMs with empty sites on addendum metal positions are much more reactive to act as inorganic multidentate O-donor ligands towards electrophiles. Due to a highly negative charged surface they can coordinate with transition metal (TM) or rare-earth (RE) cations to construct interesting architectures[11-19].

In the recent year, POMs have been combined with the TM and RE cations for producing heterometallic species. These heterometallic species combine the properties of 3*d* and 4*f*, due to which have vital applications in the fields of molecular magnet, molecular absorption and catalysis[20-22]. However, the chemistry of heterometallic species still remains largely unexplored[23-25]. This is because the TMs are less reactive towards the polyoxoanions as compared to oxophilic Ln cations, and result in amorphous precipitate instead of crystalline material. Therefore, it is very difficult to synthesize heterometallic compounds as single crystalline materials. To improve the quality of the crystals, TM and RE cations have been reacted in the presence of organic N-, O- or both N, O-donating chelator. Of these, the Cu(II) ion is most widely used for the isolation of organic-inorganic heterometallic species because of its various coordination number and different linkage modes.

The investigations on TM-Ln hetero metals with 1,10-phen are rare in the literature. A few examples of organic-inorganic hybrid silico- and germano-tungstates comprising TM-Ln hetero metals and mixed organic ligands have been isolated including $[Cu(en)_2H_2O]_3[(\alpha\text{-}SiW_{11}O_{39})Ln(H_2O)\text{-}(\eta^2,\mu\text{-}1,1)CH_3COO]$ (Ln = Nd^{III} and Sm^{III}; en = ethylenediamine) and a 1D ladder-like $H_2[Cu(en)_2H_2O]_8[Cu(en)_2]_3\text{-}[\{(\alpha\text{-}SiW_{11}O_{39})\text{-}Ce(H_2O)\text{-}(\eta^2,\mu\text{-}1,1)CH_3COO\}_4]$ (Ref. 26), $[\{Ln(GeW_{11}O_{39})_2\}\text{-}\{Cu_2(bpy)_2(\mu\text{-}ox)\}]^{11-}$ (Ln = La^{III}, Nd^{III}, Sm^{III}, Eu^{III} and Gd^{III}; bpy = 2,2-bipyridine and ox = oxalate)[27], $[Cu(en)_2(H_2O)]_5[Cu(en)_2]\text{-}[Tb(\alpha\text{-}GeW_{11}O_{39})\text{-}(CH_3COO)(H_2O)]_2$ (Ref. 28); $\{[Cu(en)_2]_3\text{-}[Ce(GeW_{11}O_{39})(H_2O)_2]_2(C_2O_4)\}^{6-}$ (Ref. 29), $[Cu(en)_2(H_2O)]_6[Ln(H_2O)(CH_3COO)(\alpha\text{-}GeW_{11}O_{39})]_2$ (Ln = Nd^{III}, Sm^{III}, Eu^{III}, Gd^{III}, Dy^{III} and Ho^{III})[30] and $\{[Cu(en)_2]_3\text{-}[Cu(en)(ox)]_2[Ln_2(ox)(\alpha\text{-}SiW_{11}O_{39})_2]\}^{6-}$ (Ln = Sm^{III} and Er^{III})[31].

Wang *et al.*[32] hydrothermally prepared a dimeric 3*d*-4*f* cubane-like cluster $\{[Cu(en)_2(H_2O)][DyCu_3(en)_3\text{-}(OH)_3(H_2O)_2(GeW_{11}O_{39})]\}_2$. Mialane *et al.*[33]

have reported $\{[Cu(en)_2(H_2O)][(Cu(en)(OH))_3\text{-}Ln(SiW_{11}O_{39})(H_2O)]\}_2$ (Ln = Gd^{III} and Eu^{III}), where the lanthanide center is connected to the copper cations via hydroxo ligands. Zhang *et al*.[34] have well documented a few examples of organic-inorganic hybrids, including $\{[Cu(en)_2]_{1.5}Ln[(\alpha\text{-}SiW_{11}O_{39})_2]\}_2^{20-}$ (Ln = Gd^{III}, Tb^{III}, Dy^{III}, Er^{III} and Lu^{III}), $\{[Cu(en)_2]_{1.5}Ln[(\alpha\text{-}SiW_{11}O_{39})]\}^{2-}$ (Ln = La^{III} and Ce^{III}) and $\{[Cu(en)_2(H_2O)][Cu(en)_2]_nLn[(\alpha\text{-}SiW_{11}O_{39})_2]\}^{m-}$ [(Ln, n, m) = (Pr^{III}, 2, 7) and (Sm^{III}, 3, 5)][34], 1-D double chain like organic-inorganic hybrids, viz., $[Cu(dap)_2(H_2O)]_2\{Cu(dap)_2[\alpha\text{-}H_2SiW_{11}O_{39}\text{-}Ln(H_2O)_3]_2\}$ (Ln = Ce^{III}, Pr^{III}, Nd^{III}, Sm^{III}, Eu^{III}, Gd^{III}, Tb^{III}, Dy^{III} and Er^{III}; dap = 1,2-diaminopropane)[35], three copper-lanthanide heterometallic germanotungstates, viz., $\{[Cu(en)_2(H_2O)][Cu_3Ln(en)_3\text{-}(OH)_3(H_2O)_2](\alpha\text{-}GeW_{11}O_{39})\}_2$ (Ln = Eu^{III}, Tb^{III} and Dy^{III}) and three compounds built by lanthanide-sandwich germanotungstates and copper-ethylendiamine complexes $\{Cu(en)_2[Ln(\alpha\text{-}GeW_{11}O_{39})_2]_2\}^{24-}$ (Ln = La^{III}, Pr^{III} and Er^{III})[36]. Zhao *et al*.[37] synthesized three monolacunary Keggin silicotungstate derivatives: $NaH[Cu(dap)_2(H_2O)]\text{-}[Cu(dap)_2]_{4.5}[Ln(\alpha\text{-}SiW_{11}O_{39})_2]$ (Ln = Sm^{III}, Dy^{III} and Gd^{III}) and two germanotungstate derivatives: $\{Cu(en)_2[Ln(\alpha\text{-}GeW_{11}O_{39})_2]_2\}^{24-}$ (Ln = La^{III} and Eu^{III})[38] under hydrothermal conditions. Yao *et al*.[39] described two tetrameric species $\{K_4Na_2[Ln(SiW_{11}O_{39})_2]_2\}$ (Ln = Dy^{III} and Ho^{III}) which were further extended into one dimensional chains with $[Cu(en)_2]^{2+}$ cations. Yang *et al*.[40] reported 1-D double chain of germano-tungstate derivatives $[H_2dap][Cu(dap)_2]_{0.5}[Cu(dap)_2\text{-}(H_2O)][Ln(H_2O)_3(\alpha\text{-}GeW_{11}O_{39})]$ (Ln = La^{III}, Pr^{III}, Nd^{III}, Sm^{III}, Eu^{III}, Tb^{III} and Er^{III}). Recently, we have isolated lanthanoid substituted 3*d*-4*f* heterometallic derivatives, $[Ln\{PCo_2W_{10}O_{38}(H_2O)_2\}_2]^{11-}$ (Ln = Sm^{III}, Eu^{III}, Gd^{III}, Tb^{III}, Dy^{III}, Ho^{III}, Er^{III}, Tm^{III}, Yb^{III} and Lu^{III}), following a single step reaction procedure. The polyanion consists of two alpha-(*1,5*) isomer of dicobalt substituted Keggin type phosphotungstate $[PCo_2W_{10}O_{38}(H_2O)_2]^{7-}$ sandwiched Ln^{III} cation[41].

We have documented earlier a similar silicon analogue $[\{Cu_2(1,10\text{-}phen)_2(\mu\text{-}CH_3COO)_2\}Ln(\alpha\text{-}SiW_{11}O_{39})_2]^{11-}$ {Ln = Pr^{III}, Nd^{III}, Sm^{III}, Eu^{III}, Gd^{III} and Dy^{III}}[42] and germanium analogues $[\{Cu_2(1,10\text{-}phen)_2(\mu\text{-}CH_3COO)_2\}]Ln(\alpha\text{-}GeW_{11}O_{39})_2]^{11-}$ (Ln = Pr^{III}, Nd^{III}, Sm^{III}, Eu^{III} and Gd^{III}), isolated from potassium acetate buffer[43]. Herein, we have synthesized early lanthanoid substituted organic-inorganic hybrid 3*d*-4*f* heterometallic derivatives of lacunary Keggin type silico- and germano-tungstates: $[\{Cu_2(1,10\text{-}phen)_2(\mu\text{-}CH_3COO)_2\}Ln(\alpha\text{-}XW_{11}O_{39})_2]^{11-/10-}$ {Ln = La^{III} (**1**), Ce^{III} (**2**) and Ce^{IV} (**3**), X = Si^{IV}; La^{III} (**4**), Ce^{III} (**5**), Ce^{IV} (**6**), X = Ge^{IV}; 1,10-phen = 1,10-Phenanthroline} in potassium acetate buffer (pH 4.7) solution under mild reaction conditions.

Experimental

The trilacunary $Na_{10}[A\text{-}\alpha\text{-}SiW_9O_{34}]\cdot 16H_2O$[44] and monolacunary $K_6Na_2[\alpha\text{-}GeW_{11}O_{39}]\cdot 13H_2O$[45] precursors were synthesized according to the published literature procedure and confirmed by FT-IR spectroscopy. All other chemicals were commercially purchased and used without further purifications. The precursors, $Na_2WO_4\cdot 2H_2O$ (≥99%), $Na_2SiO_3\cdot 5H_2O$ (≥97.0%), GeO_2 (99.99%) and KOH (≥85%) were purchased from Sigma-Aldrich. CH_3COOH (≥99.7%) and 37% HCl were also purchased from Sigma-Aldrich (New Delhi, India). Anhydrous NaCl and KCl were purchased from Fisher Scientific with 99.5% assay (New Delhi, India). KBr for IR spectroscopy was purchased from Merck, India). The FT-IR spectra were recorded on the KBr pellets using a Perkin-Elmer BX instrument. Liquid UV/vis spectra were investigated with an Analytic Jena Specord 250 spectrometer. Thermogravimetric analysis (TGA) were performed on a Perkin-Elmer TGA 4000 instrument in the temperature range of 30–900 °C with heating rate of 5 °C/min on flowing nitrogen atmosphere. Powder X-ray diffraction (PXRD) patterns were recorded using a high resolution Rigaku X-ray diffractometer employing Cu-Kα radiation (λ= 1.54056 Å) with a scan rate of 58.39 s per step and step size of 0.01313° at 298 K over the range of 2θ = 5°–70°. Elemental analyses were investigated on an ARCOS ICP-AES instrument (M/s Spectro, Germany).

The $K_4Na_7[\{Cu_2(1,10\text{-}phen)_2(\mu\text{-}CH_3COO)_2\}La(\alpha\text{-}SiW_{11}O_{39})_2]\cdot 27H_2O$ (**1a**) was synthesized as follows: 0.072 g (0.3 mmol) of $Cu(NO_3)_2\cdot 5H_2O$, 0.043 g (0.1 mmol) of $La(NO_3)_3\cdot 6H_2O$ and 0.255 g (0.1 mmol) of $Na_{10}[A\text{-}\alpha\text{-}SiW_9O_{34}]\cdot 16H_2O$ were dissolved in 25 mL of 1 M potassium acetate buffer (pH 4.7) solution. Then, 1,10-phen (0.018 g, 0.1 mmol) was added to it slowly, resulting in a turbid solution which was heated to 80 °C for 1 h with continuous stirring. During the heating, the solution became clear blue color. After heating, solution was cooled down to room temperature. Further, followed by its filtration, filtrate was set aside for crystallization at room temperature. After about one week, block type blue single crystals were found in good yield. The crystalline material (compound **La-1a**) was collected and further analysed. Yield: 0.196 g (77%) (on the basis of $Na_{10}[A\text{-}\alpha\text{-}SiW_9O_{34}]\cdot 16H_2O$). FT-IR: (ν) = 1608(w), 1576(w), 1558(m), 1518(s), 1496(m), 1456(m), 1426(s), 1350(m), 1222(m), 1148(s), 1108(s), 1002(s), 948(s), 890(s), 820(s), 766(s), 720(s), 540(w), 524(m), 508(w), 476(w). The number of crystal water molecules was determined by TGA. Anal. (%): **1a**: calcd. (found): Cu 1.86 (1.57), W 58.64 (57.21), Si 0.81 (1.01), K 2.26 (2.59), Na 2.33 (2.18).

For the synthesis of $K_4Na_7[\{Cu_2(1,10\text{-phen})_2(\mu\text{-}CH_3COO)_2\}Ce(\alpha\text{-}SiW_{11}O_{39})_2]\cdot 26H_2O$ (**2a**), the above synthetic procedure was followed using 0.043 g (0.1 mmol) of $Ce(NO_3)_3\cdot 6H_2O$ instead of $La(NO_3)_3\cdot 6H_2O$. Yield: 0.186 g (73%) (on the basis of $Na_{10}[A\text{-}\alpha\text{-}SiW_9O_{34}]\cdot 16H_2O$). FT-IR: (ν) = 1608(w), 1576(w), 1558(w), 1518(m), 1496(w), 1456(w), 1426(s), 1350(w), 1222(w), 1148(w), 1108(w), 1006(m) 950(s), 892(s), 812(s), 766(s), 720(s), 540(w), 522(m), 494(w), 476(w). Anal. (%): calcd. (found): Cu 1.86 (1.74), W 58.80 (57.29), Si 0.82 (0.96), K 2.27 (2.36), Na 2.34 (2.17).

The $K_3Na_7[\{Cu_2(1,10\text{-phen})_2(\mu\text{-}CH_3COO)_2\}Ce(\alpha\text{-}SiW_{11}O_{39})_2]\cdot 25H_2O$ (**3a**), was synthesized like (**1a**) with 0.055 g (0.1 mmol) of $(NH_4)_2Ce(NO_3)_6$ instead of $La(NO_3)_3\cdot 6H_2O$. Yield: 0.143 g (56%) (on the basis of $Na_{10}[A\text{-}\alpha\text{-}SiW_9O_{34}]\cdot 16H_2O$). FT-IR: (ν) = 1618(w), 1610(w), 1590(w), 1426(s), 1420(w), 1414(w), 1226(w), 1150(w), 1110(w), 1010(m) 948(s), 894(s), 854(m), 798(s), 746(w), 736(w), 720(w), 544(w), 534(w), 528(w), 514(w). Anal. (%): calcd. (found): Cu 1.86 (1.69), W 58.95 (56.70), Si 0.82 (1.06), K 1.71 (1.43), Na 2.34 (2.12).

The $K_4Na_7[\{Cu_2(1,10\text{-phen})_2(\mu\text{-}CH_3COO)_2\}La(\alpha\text{-}GeW_{11}O_{39})_2]\cdot 28H_2O$ (**4a**) was synthesized by the same procedure as for (**1a**) using 0.323 g (0.1 mmol) of $K_6Na_2[\alpha\text{-}GeW_{11}O_{39}]\cdot 13H_2O$ instead of $Na_{10}[A\text{-}\alpha\text{-}SiW_9O_{34}]\cdot 16H_2O$. Yield: 0.247 g (76%) (on the basis of $K_6Na_2[\alpha\text{-}GeW_{11}O_{39}]\cdot 13H_2O$). FT-IR: (ν) = 1626(s), 1574(s), 1520(s), 1494(w), 1428(s), 1340(w), 1226(w), 1148(w), 1110(w), 944(s), 882(s), 814(s), 782(m), 756(s), 720(m), 520(m), 498(w), 470(m). Anal. (%): calcd. (found): Cu 1.83 (1.47), W 57.75 (56.69), Ge 2.08 (1.95), K 2.23 (2.17), Na 2.30 (2.43).

For the synthesis of compound $K_4Na_7[\{Cu_2(1,10\text{-phen})_2(\mu\text{-}CH_3COO)_2\}Ce(\alpha\text{-}GeW_{11}O_{39})_2]\cdot 28H_2O$ (**5a**), the above synthetic procedure for (**4a**) was followed using 0.043 g (0.1 mmol) of $Ce(NO_3)_3\cdot 6H_2O$ instead of $La(NO_3)_3\cdot 6H_2O$. Yield: 0.242 g (75%) (on the basis of $K_6Na_2[\alpha\text{-}GeW_{11}O_{39}]\cdot 13H_2O$). FT-IR: (ν) = 1628(s), 1574(s), 1520(s), 1494(w), 1428(s), 1342(w), 1226(w), 1150(w), 1110(w), 946(s), 878(s), 814(s), 784(m), 756(s), 718(m), 523(m), 496(w), 470(m). Anal. (%): calcd. (found): Cu 1.82 (1.72), W 57.74 (56.79), Ge 2.08 (2.11), K 2.22 (2.38), Na 2.29 (2.13).

The $K_3Na_7[\{Cu_2(1,10\text{-phen})_2(\mu\text{-}CH_3COO)_2\}Ce(\alpha\text{-}GeW_{11}O_{39})_2]\cdot 26H_2O$ (**6a**) was synthesed by the above synthetic procedure using 0.055 g (0.1 mmol) of $(NH_4)_2Ce(NO_3)_6$ instead of $La(NO_3)_3\cdot 6H_2O$. Yield: 0.208 g (64%) (on the basis of $K_6Na_2[\alpha\text{-}GeW_{11}O_{39}]\cdot 13H_2O$). FT-IR: (ν) = 1612(s), 1584(s), 1462(s), 1428(w), 1414(s), 1392(w), 1226(w), 1150(w), 1110(w), 950(s), 880(s), 816(s), 784(m), 772(s), 720(m), 528(m), 496(w), 480(m). Anal. (%): calcd. (found): Cu 1.84 (1.80), W 58.04 (57.26), Ge 2.09 (2.19), K 1.65 (1.41), Na 2.31 (2.07).

A single crystal suitable for X-ray diffraction was mounted on a capillary tube for indexing and intensity data collection at 298 K on an Oxford Xcalibur CCD single-crystal diffractometer (Mo-K_α radiation, λ = 0.71073 Å). Pre-experiment data collection and data reduction were performed with the Oxford program suite CrysAlisPro[46]. Routine Lorentz and polarization corrections were applied, and an absorption correction was performed using the ABSCALE 3 program[47]. Direct methods were used to locate the heavy metal atoms (SHELXS-97)[48,49]. The remaining atoms were located from successive Fourier maps (SHELXL-97), which readily revealed the entire heavy atom positions (Cu, Ln and W) and enabled us to locate the other non-hydrogen (C, and O) positions from the difference Fourier maps. The non-hydrogen atoms (C, and O) were refined isotropically.

Results and discussion

The phase purity of all polyanions has been characterized by the powder XRD patterns of all the bulk products (Supplementary data, Figs S1 & S2). Their peak positions show a slight difference in peak intensity, which may be due to the preferred orientation of the powder samples and different compound composition present in the samples. Single crystal X-ray diffraction analysis reveals that all **1a**-**6a** are isostructural and crystallize in triclinic crystal system with space group $P\bar{1}$ (Table 1). In the solid state, the polyanion consists of Peacock and Weakley type structure $[Ln(\alpha\text{-}XW_{11}O_{39})_2]^{13-/12-}$ as a fundamental building block unit and paddle wheel shaped $[Cu_2(1,10\text{-phen})_2(\mu\text{-}CH_3COO)_2)]^{2+}$ organic species in

Table 1 – Crystallographic data for the compounds **1a** and **4a**

Comp.	**1a**	**4a**
Emp. formula	$C_{28}H_{22}Cu_2K_2La$ $N_4Na_{4.5}O_{87}Si_2W_{22}$	$C_{28}H_{22}Cu_2Ge_2K_2$ $LaN_4Na_4O_{91}W_{22}$
FW	6355.02	6496.52
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	14.271(4)	14.257(3)
b (Å)	21.293(16)	21.566(4)
c (Å)	21.629(4)	21.616(4)
α (°)	76.69(4)	72.167(10)
β (°)	81.13(3)	84.548(10)
γ (°)	83.25(4)	81.260(9)
V (Å^3)	6297(5)	6245(2)
Z	2	2
T (K)	293(2)	296.15
ρ_{calcd} (g cm^{-3})	3.352	3.455
μ (mm^{-1})	20.851	21.478
Gof (on F^2)	0.997	1.035
F(000)	5545.0	5670.0
Ref. Collect.	77426	75456
Unique (R_{int})	0.1838	0.1304
Ind. reflections	23024	23542
Data/restraints/parameters	23024/0/753	23542/0/776
R_1[a]/wR_2[b] [I >2σ(I)]	0.0988/0.2403	0.0850/0.2148
R_1[a]/wR_2[b] [all data]	0.1821/0.3120	0.1542/0.2612

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

which two copper ions are coordinated with two acetate ligands and two 1,10-phen organic moiety in the planar manner. The sandwich type structure is built up by two monolacunary $[\alpha\text{-}XW_{11}O_{39}]^{8-}$ units and one lanthanoid cation. Each monolacunary $[\alpha\text{-}XW_{11}O_{39}]^{8-}$ unit acts as a tetradentate ligands and coordinates with the lanthanoid cation through four axial oxygen atoms, resulting in eight-coordinated lanthanoid cation possessing square antiprismatic geometry (pseudo D_{4d}). The sandwich type $[Ln(\alpha\text{-}XW_{11}O_{39})_2]^{13-/12-}$ species is decorated with the copper complex $[Cu_2(1,10\text{-phen})_2(\mu\text{-}CH_3COO)_2)]^{2+}$. In the copper complex, copper ion is five coordinated and has a square pyramidal geometry. The coordination sites of the copper ion is satisfied with two nitrogen atoms of 1,10-phen [Cu-N: 1.89(3) – 2.19(3) Å], two oxygen atoms of acetate [Cu-O: 1.86(3) – 2.06(2) Å] ligands and one terminal oxygen atom of $[Ln(\alpha\text{-}XW_{11}O_{39})_2]^{13-/12-}$ [Cu-O: 2.19(2) − 2.28(3) Å] species (Fig. 1b). The copper complex acts as a connector. It is coordinated with the terminal oxygen atom of the building block unit $[Ln(\alpha\text{-}XW_{11}O_{39})_2]^{13-/12-}$, leading to formation of a 1-D polymeric chain. The 1-D polymeric chain further assembles into a 2-D structure due to the π-π stacking

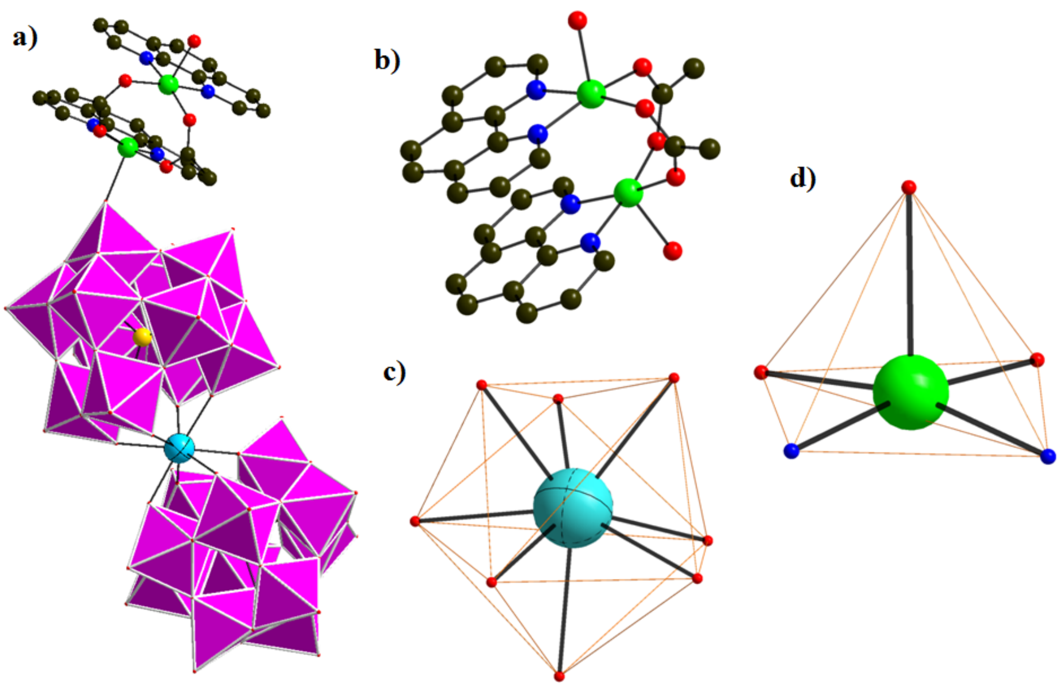

Fig. 1 – (a) Ball-stick and polyhedron representation of $[\{Cu_2(1,10\text{-phen})_2(\mu\text{-}CH_3COO)_2\}Ln(\alpha\text{-}XW_{11}O_{39})_2]^{11-/10-}$ {Ln = La^{III} (**1**), Ce^{III} (**2**) and Ce^{IV} (**3**), X = Si^{IV}; La^{III} (**4**), Ce^{III} (**5**), Ce^{IV} (**6**), X = Ge^{IV}}. (b) Copper coordinated organic species $[Cu_2(1,10\text{-phen})_2(\mu\text{-}CH_3COO)_2)]^{2+}$. (c) Square-antiprismatic geometry for the lanthanoid ion. (d) Square pyramidal geometry for copper ions. [Color code: aqua: Ln; bright green: Cu; pink: W polyhedra; gold: Ge; red: O; blue: N; olive green: C].

between the 1,10-phen moiety. The alkali cations K^+ and Na^+ located in the periphery of the polyanions act as external linkers forming a 3-D structure (Fig. 2). The bond valence sum (BVS) calculations[50,51] for all the oxygen atoms present in the polyanion show that neither the oxygen atoms in the two (α-$XW_{11}O_{39}$) units nor the bridging oxygen atoms in Ln–O–W are protonated. Besides, BVS calculation for Cu and W atoms show that these are in the +2 and +6 oxidation state respectively. The net charge of the title polyanion is −11/−10 which is compensated by the alkali sodium and potassium cations.

The FT-IR spectra for all the compounds show that **1a-3a** and **4a-6a** are isomorphous. These compounds exhibit four types of characteristic antisymmetric stretching vibrations, i.e., ν_{as}(X–O_a), terminal ν_{as}(W–O_t), corner sharing ν_{as}(W–O_b–W) and edge-sharing ν_{as}(W–O_c–W) in the finger print region (1200 to 400 cm^{-1}) of POMs. In the compounds **1a-3a**, band at 1006 or 1010 cm^{-1} is attributed to ν_{as}(Si−O_a) bonds. Band at around 948 or 950 cm^{-1} corresponds to ν_{as}(W−O_t). The band at 890 or 892 cm^{-1} represents the antisymmetric vibration of ν_{as}(W−O_b−W) and those at 766 and 720 cm^{-1} are due to ν_{as}(W−O_c−W) vibrations[42]. In the compounds **4a-6a** the band at 944 or 948 cm^{-1} corresponds to the antisymmetric stretching modes of terminal ν_{as}(W–O_t), while ν_{as}(W−O_t) is found at almost similar positions in all the polyanions, which indicates that the cation has little influence on the terminal oxygen atoms. Band at around 878–882 cm^{-1} is due to the ν_{as}(Ge–O_a) vibration. Two bands at 814 and 784, cm^{-1} are attributed to the corner sharing ν_{as}(W–O_b–W) and bands at ~756 and 720 cm^{-1} correspond to the antisymmetric vibration of edge-sharing ν_{as}(W–O_c–W)[19,43].

Besides, four vibration bands are also observed in the range of 1608–1426 cm^{-1} which correspond to the antisymmetric vibrations, ν_{as}(C=O) and ν_{as}(C–O) and weak intense bands in the range of 1340 to 1108 cm^{-1} correspond to ν_{as}(C−N), which signify the presence of acetate ligand and 1,10-phen moiety in the polyanions (Supplementary data, Figs S3 & S4).

We also recorded the liquid UV/vis for all the polyanions in aqueous medium. All the polyanions exhibit two characteristic absorption bands in the ultra violet region. In **1a-3a**, one strong band in the range of 190–195 nm and a broad, weak intense band centered at ~253 nm are observed (Supplementary data, Fig. S5), whereas **4a-6a** show a strong band in the range of 190-192 nm and a weak intense band at 254 nm (Supplementary data, Fig. S6). The high energy absorption (190–195 nm) is attributed to the *p*π-*d*π charge-transfer transition of the terminal oxygen to the tungsten (O_t→W) bonds, whereas the lower-energy absorption band (253 or 254 nm) corresponds to the *p*π-*d*π charge-transfer transition of the bridging oxygen to the tungsten ($O_{b,c}$→W) bonds[42,43].

The thermal stability of the all the polyanions **1a-6a** were investigated in the temperature range of 30–900 °C at the heating rate of 5 °C/min on flowing nitrogen atmosphere. All the compounds exhibit overall three steps weight loss. The weight loss correspond to loss of crystal water molecules, acetate ligand and 1,10-phen organic moiety present in the polyanion. The first step weight loss was found in the temperature range of ~30–280 °C. The weight loss of 7.11% for **1a**, 6.74% for **2a**, 6.27% for **3a**, 7.40% for **4a**, 7.21% for **5a** and 6.74% for **6a** corresponds to loss of 27, 26, 25, 28, 28 and 26 crystal water molecules, respectively. The second step weight loss was in the

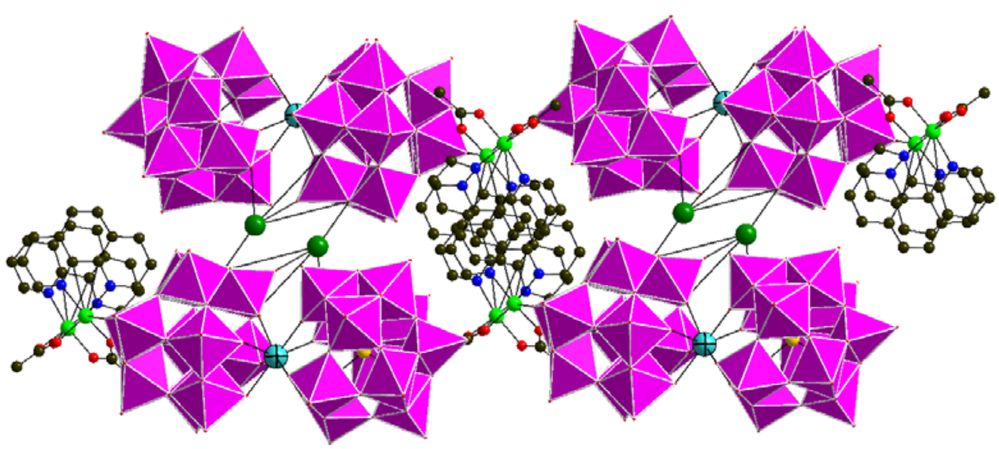

Fig. 2 – The two-dimensional polymeric chain showing π-π stacking and alkali cations as a linker.

temperature range of ~280–500 °C. The weight loss (%) is as follows: calcd.(found): 1.71 (2.35) for **1a**, 1.71 (2.29) for **2a**, 1.71 (2.89) for **3a**, 1.68 (2.32) for **4a**, 1.68 (2.82) for **5a** and 1.69 (2.25) for **6a**. This is attributed to loss of two acetate ligands coordinated with copper ions. Finally, the third step of weight loss occurred in the temperature range of ~500–900 °C. The weight loss (%) ((calcd.(found): 5.23 (8.58) for **1a**, 5.24 (7.43) for **2a**, 5.25 (7.60) for **3a**, 5.15 (9.29) for **4a**, 5.14 (9.79) for **5a** and 5.17 (7.49) for **6a)** is due to loss of 1,10-phen moiety, present in the compounds (Supplementary data, Fig. S7 & S8).

In summary, we have synthesized six organic-inorganic hybrid 3*d*-4*f* heterometallic derivatives of lacunary Keggin type silico- and germano-tungstates, viz., $[\{Cu_2(1,10\text{-phen})_2(\mu\text{-}CH_3COO)_2\}Ln(\alpha\text{-}XW_{11}O_{39})_2]^{11-/10-}$ (Ln = La^{III} (**1**), Ce^{III} (**2**) and Ce^{IV} (**3**), X = Si^{IV}; La^{III} (**4**), Ce^{III} (**5**), Ce^{IV} (**6**), X = Ge^{IV}; 1,10-phen = 1,10-phenanthroline), by conventional aqueous solution method. All the compounds were isolated as mixed alkali Na^+/K^+ salts and further characterized by various analytical techniques such as single crystal XRD, FT-IR, powder-XRD, liquid UV/vis, elemental analysis and thermogravimetric analysis. FT-IR spectra and PXRD patterns suggest that **1a**-**3a** and **4a**-**6a** are isomorphous. Further, single crystal XRD analysis shows that all the polyanions comprise the Peacock and Weakley type $[Ln(\alpha\text{-}XW_{11}O_{39})_2]^{13-/12-}$ (X = Si^{IV} and Ge^{IV}) species as the fundamental building block unit. These sandwich type species formed polymeric chains assisted by copper organic complexes and further assembled into 2-D structures by π-π stacking in between 1,10-phen moieties.

Supplementary data

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 under depository numbers CCDC No. 1534567 for compound (**1a**) and 1534566 for compound (**4a**). Other supplementary data associated with this article are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_56A(01)52-58_SupplData.pdf.

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