Polyhedron 81 (2014) 147–153

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Decavanadate-based discrete compound and coordination polymer: Synthesis, crystal structures, spectroscopy and nano-materials

Sridevi Yerra, Bharat Kumar Tripuramallu, Samar K. Das *

School of Chemistry, University of Hyderabad, Hyderabad 500 046, India

ARTICLE INFO

Article history:
Received 13 February 2014
Accepted 11 May 2014
Available online 24 May 2014

Keywords:
Decavanadate cluster anion
Two dimensional coordination polymer
Tri-sodium aqua-complex cation
Ultra-sonication
Nano-crystal

ABSTRACT

Two decavanadate based compounds, $[\{HMTAH\}_2\{Na(H_2O)_6\}_2][H_2V_{10}O_{28}]\cdot 6H_2O$ (**1**) (HMTA = hexamethylenetetramine) and $[Na_3(H_2O)_9]_{2n}[V_{10}O_{28}]_n$ (**2**), have been synthesized in aqueous medium. Compound **1** (a discrete compound) is synthesized with organic and inorganic cations, whereas compound **2** (a coordination polymer) has been isolated using only inorganic cations. An acidified aqueous solution of sodium metavanadate, on heating at 70 °C followed by addition of acetonitrile, results in the isolation of compound **2**, the crystal structure of which showing it to be a two-dimensional coordination polymer, formed from the decavanadate cluster anion and the tri-sodium aqua-complex cation. Compounds **1** and **2** have been characterized by routine elemental analyses, FT-IR spectroscopy and unambiguously by single crystal X-ray crystallography. Among these two compounds, compound **2** exhibits an emission in the visible region at room temperature in its solid state (on excitation at 380 nm). Nanocrystals of compound **2** in the size range 50–70 nm were synthesized by ultrasonication of macrocrystals of compound **2** in acetonitrile solvent (0.5 mM). The nanoparticles were characterized by FT-IR and PXRD studies. The morphology of the nanoparticles of compound **2** were studied using FE-SEM, TEM and AFM techniques. As expected, these nanoparticles also display emission spectra at room temperature. The connectivity of the decavanadate oxygens with the metal cations plays an important role in compound **2** exhibiting emission spectra, because decavanadate cluster (as such) containing compounds generally do not show emission.

1. Introduction

Polyoxometalates (POMs) are extremely versatile building blocks for the construction of inorganic functional materials with a range of physical and chemical properties that are significant for their applications in the areas of materials science [1], magnetism [2], medicinal [3] and industrial chemistry [4]. Functionalized POMs give rise to vast diversity of materials, being used as building blocks for creating highly classy hierarchical systems with various interdependent functionalities [5]. The functionalization of the POM cluster anions to explore more selective applications [6] is an interesting aspect in recent POM chemistry. The functional POM frameworks have been achieved by using either pure organic linkers [7] or metal coordination complexes (with organic ligands) as linkers [8]; however, both these approaches are limited by the reduced stability of the concerned framework, because both linkers contain organic moieties that are not thermally stable. The assembly of a purely inorganic POM building unit offers high stability to the concerned network for the formation of new type of pure inorganic materials [9]. Thus, the planned synthesis of pure inorganic based materials, for example, the synthesis of polyanion-inorganic cation based polymeric compounds, is a big challenge in modern inorganic chemistry [10].

Programmable POM-based multi-functional nano-structures are reported on silica surfaces, that yield 0-D, 2-D and 3-D architectures, including nano-dots, discs, porous networks and layer-by-layer assemblies [11]. POMs are dynamically entered into the realm of the synthesis of metal nano-particles, and serve both as catalytic agents and stabilizers for the synthesis of Ag, Au, Pd and Pt nano-particles of reasonably good dispersity [12]. Silver and gold nano-particles containing POM-based organic–inorganic nano-composites find applications in the areas of sensing materials, catalysis and composite materials [13]. The large scale synthesis of POM-based spheres-, belts-, flake-, cube-, prism-, trigonal- and snowflake-like nanocrystals/nanoparticles were performed by a solution phase route using a wide range of surfactants [14]. Among the polyoxometalates, polyoxovanadates (POVs) are an important class of materials that have various applications in the fields of materials science, industrial chemistry and biology

* Corresponding author. Tel.: +91 40 2301 1007; fax: +91 40 2301 2460.
E-mail address: skdsc@uohyd.ernet.in (S.K. Das).

http://dx.doi.org/10.1016/j.poly.2014.05.035
0277-5387/

[15]. POV clusters have also been used as linkers for constructing vanadium framework containing materials, which can be called vanadium MOFs (VMOFs) [16]. Among several polyoxovanadate (POV) anions, the decavanadate cluster anion $[V_{10}O_{28}]^{6-}$ seems to be best known in the solid state phase [17]. Several discrete decavanadate cluster containing compounds have been isolated with alkali metals and transition metals, as macro-crystals [18]. Ramanan and co-workers have made a considerable contribution to fully oxidized vanadium based polyoxoanions in the presence of cage-like hexamethylenetetramine as a structure director [19]. Cronin and his group have described silver linked polyoxometalate open frameworks for the directed fabrication of silver nano-materials [20]. The electrical properties of ammonium decavanadate single crystalline nano-rods have been reported by Mai and Han [21]. Pure inorganic polymeric complexes based on decavanadate complexes are relatively less explored. We have been exploring the self-assembly process of the decavanadate cluster, including its nano morphological studies [22]. In the present article, we have chosen the decavanadate cluster anion $[V_{10}O_{28}]^{6-}$ as the central core and we have reported two decavanadate based compounds, $[\{HMTAH\}_2\{Na(H_2O)_6\}_2][H_2V_{10}O_{28}]\cdot 6H_2O$ (**1**) (HMTA = hexamethylenetetramine) and $[Na_3(H_2O)_9]_{2n}[V_{10}O_{28}]_n$ (**2**). We have chosen a pure inorganic linker to extend the dimensionality of the decavanadate cluster in compound **2**. In the crystal structure of compound **2**, a tri-sodium-aqua cluster (supported on the decavanadate anion by a coordinate covalent bond) is observed. Overall, in this article we have described the supramolecular assembly of the decavanadate cluster anion $[V_{10}O_{28}]^{6-}$ using an organic linker, hexamethylenetetramine (compound **1**), and the coordination assembly of the decavanadate cluster anion using an inorganic linker, the tri-sodium aqua cluster cation (compound **2**). We also have reported nano-crystals of compound **2**, which are synthesized by ultra-sonication of the macro-crystals of compound **2** in acetonitrile solvent at room temperature. The compound $[Na_3(H_2O)_9]_{2n}[V_{10}O_{28}]_n$ (**2**) is unique in the sense that it is an emissive inorganic coordination polymer based on a decavanadate cluster.

2. Experimental

2.1. Materials and physical methods

All the reactions were performed under ambient conditions. The starting materials, sodium metavanadate and HMTA were obtained from SISCO, acetonitrile from Sigma Aldrich and distilled water was used in all the experiments.

2.2. Characterization

Micro analytical (C, H, N) data were obtained with a FLASH EA 1112 Series CHNS analyzer. Infrared (IR) spectra were recorded on a KBr pellet with a JASCO FT/IR-5300 spectrometer in the region 400–4000 cm^{-1}. Electronic absorption spectra were obtained on a Cary 100 Bio UV–Vis spectrophotometer. Emission spectra were recorded on a spectrofluorimeter (FluoroLog-3, Horiba Jobin Yvon). Confocal fluorescence microscopic images of compound **2** nanoparticles were recorded on a Leica Laser Scanning confocal microscope (TCS SP2 AOBS), Germany. The morphology of the nanoparticles of compound **2** was obtained using a field emission-scanning electron microscope (FE-SEM) (Carl Zeiss, Ultra55). Transmission electron microscopic studies were carried out on a FEI Tecnai G^2 S-Twin, FEI electron microscope operating at 200 kV and using a Gatan CCD camera. The vanadium content of the compound $[Na_3(H_2O)_9]_{2n}[V_{10}O_{28}]_n$ (**2**) was analyzed using a Varian 720-ES Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES).

2.2.1. Synthesis

*2.2.1.1. Synthesis of the compound $[\{HMTAH\}_2\{Na(H_2O)_6\}_2][H_2V_{10}O_{28}]\cdot 6H_2O$ (**1**).* To the 100.0 mL aqueous solution of sodium metavanadate (2.0 g, 8.26 mmol) and hexamine (0.14 g, 1 mmol), acetic acid was added to maintain the pH value at 4.0. The resulting reaction mixture was stirred for 2 h and kept for crystalization. After 10 days, yellow needle shaped crystals of compound **1** appeared and were isolated by filtration. Yield: 40% based on V. IR (KBr, cm^{-1}): 3452(br), 2947(w), 2865(w), 1649(m), 1457(m),1369(m), 1238(s), 1013(s), 986(br), 953(sh), 805(m), 778(sh), 668(w), 509(w). *Anal.* Calc. for. $C_{12}H_{64}N_8Na_2O_{46}V_{10}$ (1612.05): C, 8.94; H, 4.00; N, 6.95. Found: C, 8.91; H, 3.84; N, 6.91%.

*2.2.1.2. Synthesis of the compound $[Na_3(H_2O)_9]_{2n}[V_{10}O_{28}]_n$ (**2**).* A 100.0 mL aqueous solution of sodium metavanadate (2.0 g, 8.26 mmol) was heated for 2 h at 70 °C. To this hot solution, acetic acid was added to maintain the pH value at 5.0; subsequently 60.0 mL acetonitrile was added to crystallize yellow color block-shaped crystals of **2**. Yield: 50% based on V. IR (KBr, cm^{-1}): 3463(br), 1621(s), 953(s), 849(s), 739(s), 602(w), 526(w), 449(w). *Anal.* Calc. for. $V_{10}Na_6O_{46}H_{36}$ (1419.42): V, 35.88; H, 2.55. Found: V, 35.02 (ICP-OES); H, 2.43%.

*2.2.1.3. Synthesis of compound **2** nanoparticles.* Nanoparticles of compound **2** were synthesized by the simple ultrasonication method. Hexagonal macrocrystals of compound **2** were taken in acetonitrile solvent and ultrasonicated for an hour under an ambient atmosphere. The solution drop was casted onto a glass plate and analyzed using various spectroscopic and microscopic techniques. IR (KBr, cm^{-1}): 3567(br), 1621(s), 986(sh), 947(s), 843(m), 723(w). *Anal.* Calc. for nanoparticles: H, 2.55. Found: H, 2.48%.

2.3. Crystal structure determination

Single crystal X-ray diffraction data were collected at 298(2) K on a Bruker SMART APEX CCD area detector system with Mo Kα radiation (λ = 0.71073 Å) and with a graphite monochromator. 2400 frames were recorded with an ω scan width of 0.3°, each for 10 s with a crystal detector distance of 60 mm and collimator distance of 0.5 mm. The data were reduced using SAINTPLUS [23] and a multi-scan absorption correction was performed using SADABS [23]. Structure solution and refinement were done using the programs of SHELX-97 [24]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on the C atoms of the hexamine were introduced in calculated positions and were included in the refinement, riding on their respective parent atoms. The Na atom in compound **1** suffers from a significant disorder problem, for which resolving was tried by applying the restraints ISOR or SIMU to the displacement parameters, but this was not successful. The hydrogen atoms of the water molecules were located in the crystal structures of **1** and **2** through Fourier electron density maps. The crystallographic details and refinement parameters of compounds are listed in Table 1.

3. Results and discussion

3.1. Synthesis

The syntheses of polyoxovanadates have classically been performed in aqueous solutions (wet synthesis) or under hydrothermal conditions [25]. Compound **1** has been synthesized by the direct one pot reaction of sodium metavanadate aqueous solution together with hexamethylenetetramine (HMTA) at an ambient temperature. The pH of the concerned reaction mixture was adjusted to 4.0 by adding acetic acid. Addition of acetonitrile solvent to the hot

Table 1
Crystallographic data for compounds **1** and **2**.

	1	**2**
Molecular formula	$C_{12}H_{64}N_8Na_2O_{46}V_{10}$	$H_{36}Na_6O_{46}V_{10}$
Formula weight	1612.08	1419.63
T (K)	298	298
λ (Å)	0.71073	0.71073
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	9.6133(15)	8.5430(11)
b (Å)	11.9795(19)	10.8231(14)
c (Å)	12.611(2)	11.6268(15)
α (°)	100.204(2)	105.485(2)
β (°)	105.023(2)	99.414(2)
γ (°)	113.619(2)	101.233(2)
V (Å^3)	1218.7(3)	989.4(2)
Z	1	1
D_{calc} (Mg m^{-3})	2.194	2.383
$F(000)$	810	700
Crystal size (mm)	0.34 × 0.20 × 0.18	0.32 × 0.20 × 0.18
θ range for data collection (deg)	1.76–26.12	1.87–25.01
Reflections collected/unique	12 483/4796	8927/3468
R (int)	0.0290	0.0296
Data/restraints/parameters	4796/0/476	3468/0/353
Goodness-of-fit (GOF) on F^2	1.050	1.104
R_1/wR_2 [$I > 2\sigma(I)$]	0.0324	0.0251
R_1/wR_2 (all data)	0.08630.381/ 0.0897	0.0716/0.0265/ 0.0727
Largest difference in peak/hole (e Å^{-3})	0.724/−0.621	0.324/−0.460

acidified aqueous solution of sodium metavanadate at pH 5.0 results in the formation of compound **2**, which is a purely inorganic polymer with a trisodium-aqua complex as the cation. Notably, the decavanadate (POV) cluster anion exists in the di-protonated state in the compound $[\{HMTAH\}_2\{Na(H_2O)_6\}_2][H_2V_{10}O_{28}]\cdot 6H_2O$ (**1**). It is well known that under an aqueous conditions, a number of vanadium species, for example $[H_6V_{10}O_{28}]$, $[H_5V_{10}O_{28}]^-$, $[H_4V_{10}O_{28}]^{2-}$, $[H_3V_{10}O_{28}]^{3-}$, $[H_2V_{10}O_{28}]^{4-}$, $[HV_{10}O_{28}]^{5-}$, $[V_{10}O_{28}]^{6-}$ etc. can exist in equilibrium, depending upon the pH of the concerned reaction mixture [19].

3.2. Infrared spectroscopy

The infrared (IR) spectra exhibit characteristic features of the decavanadate cluster anion for both compounds **1** and **2**. Compound **1** additionally shows the IR bands for hexamethylenetetramine. The IR spectra of both compounds are shown in Fig. S1 (Supporting information). The V–O vibrations of the decavanadate anion are observed in the region 450–1000 cm^{-1}; the strong IR bands at around 950 cm^{-1} for both compounds (**1** and **2**) are attributed to stretching vibrations of the V–O terminal oxygen atom. The bands in the 750–600 cm^{-1} region are due to bridging V–O–V groups. The asymmetric vibrations of the V–O–V bridges are observed at 778 cm^{-1} (compound **1**) and 739 cm^{-1} (compound **2**), while the symmetric bands are observed at 668 cm^{-1} (compound **1**) and 602 cm^{-1} (compound **2**).

3.3. Description of the crystal structures

3.3.1. Compound $[\{HMTAH\}_2\{Na(H_2O)_6\}_2][H_2V_{10}O_{28}]\cdot 6H_2O$ (**1**)

The asymmetric unit of compound **1** consists of half of the decavanadate cluster anion, one hexa-hydrated sodium coordination complex cation, one protonated HMTA cation and three lattice water molecules (Fig. 1). Thus the formulation of compound **1** is given as $[\{HMTAH\}_2\{Na(H_2O)_6\}_2][H_2V_{10}O_{28}]\cdot 6H_2O$. The oxygen atoms of the decavanadate cluster are not coordinated to either the sodium cation or the HMTA cation directly, resulting in **1** being a discrete compound. In the decavanadate polyanion, all the V–O oxygen bond lengths (V–O_t, V–O_b and V–O_c) are in the expected ranges according to reported literature (Table 2). The sodium cation, coordinated to six water molecules, forms a octahedral coordination complex cation $[Na(H_2O)_6]^+$. The Na–O bond distances are in the expected range of 2.012–2.110 Å. Along with the sodium cation, the monoprotonated HMTA cation is present in the crystal structure. Two protons have been added to the decavanadate cluster anion to neutralize the overall charge (see the formula of compound **1**). The possibility of di-protonation to HMTA has been ruled out, because it is generally very difficult for the hexamethylenetetramine (HMTA) molecule to be di-protonated and is rarely known, especially at a pH value of 4.0 (it is the pH, at which compound **1** has been synthesized). Due to presence of the sodium coordinated water molecules and lattice water molecules, extensive supramolecular interactions have been observed involving surface oxygen atoms of decavanadate anion (O–H···O_{dec}) as well as lattice molecules (O–H···O_{water}). The hexamethylenetetramine (HMTA) cation, having twelve protons, is also involved in hydrogen bonding interactions (C–H···O) with the surface oxygen atoms of the decavanadate cluster anion and with the lattice water molecules. Each HMTA cation interacts with four adjacent decavanadate cluster anions. The combination of both O–H···O and C–H···O hydrogen bonding interactions results in the formation of a 3-D supramolecular network (Fig. S3, Supporting information), as observed in the crystal structure of compound **1**. The relevant hydrogen bonding parameters are presented in Table S1 (Supporting information). The bond lengths and bond angles are shown in Tables S3 and S4, respectively (see Supporting information).

3.3.2. Compound $[Na_3(H_2O)_9]_2n[V_{10}O_{28}]_n$ (**2**)

The asymmetric unit in the crystal structure of compound **2** consists of half of the decavanadate cluster anion that supports

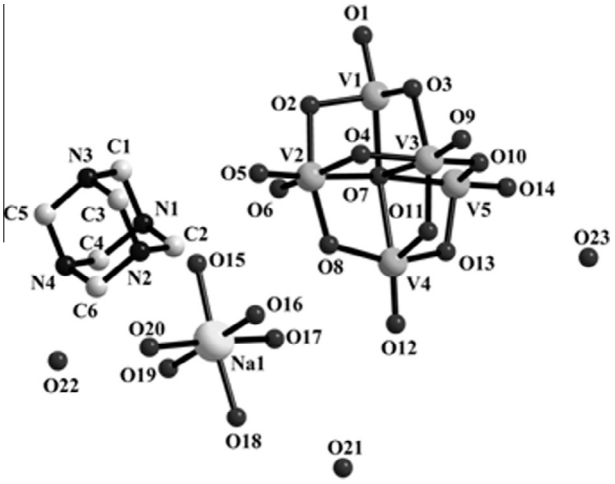

Fig. 1. Ball and stick representation of the asymmetric unit in the crystal structure of compound **1** (hydrogen atoms are omitted for clarity).

Table 2
Selected V–O distance ranges (Å) in compounds **1** and **2**.

	$\{H_2V_{10}O_{28}\}^{4-}$ **1**	$\{V_{10}O_{28}\}^{6-}$ **2**
V–O(t)[a]	1.599(3)–1.610(3)	1.597(2)–1.610(1)
V–O(μ_2)[a]	1.690(5)–2.063(4)	1.683(3)–2.047(2)
V–O(μ_3)[a]	1.910(3)–2.015(4)	1.894(1)–2.014(2)
V–O(μ_6)[a]	2.087(3)–2.343(4)	2.110(2)–2.316(2)

[a] t, μ_2, μ_3 and μ_6 are terminal, doubly, triply and hexa bridged oxygen atoms respectively.

the tri-sodium aqua-complex cation. The 6− charge of decavanadate cluster anion $[V_{10}O_{28}]^{6-}$ is counter-balanced by two $[Na_3(H_2O)_9]^{3+}$ cations, and accordingly compound **2** can be formulated as $\{[Na_3(H_2O)_9]_2[V_{10}O_{28}]\}_n$ (it is a coordination polymer). The full decavanadate cluster anion, coordinated to tri-sodium aqua-complex $[Na_3(H_2O)_9]^{3+}$ cation, is shown in Fig. 2(a). In the trisodium cluster, two sodium cations, namely Na3 and Na2, have an octahedral geometry, whereas the Na1 ion has a square pyramidal geometry. The Na3 octahedron is furnished by two bridging water molecules (O19 and O20), two monodentate coordinated water molecules (O22 and O23) and two terminal oxygen atoms (O9 and O12) from two different $\{V_{10}\}$ cluster anions. On the other hand, the coordination of the Na2 octahedron is completed by five bridging water molecules (O16, O17, O18, O19 and O20) and one monodentate coordinated water molecule (O21); notably no $\{V_{10}\}$ cluster oxygen atoms are coordinated to the Na2 cation, unlike the Na3 cation. The square pyramidal geometry around the Na1 cation can be described by three bridging water molecules (O16, O17 and O18), one monodentate coordinated water molecule (O15) and one μ_3-oxygen atom (O3) of the $\{V_{10}\}$ cluster anion. In total, two water molecules (O19 and O20) bridge between the Na3 and Na2 cations, and three water molecules (O16, O17 and O18) bridge between the Na2 and Na1 cations to form a tri-sodium-aqua-cluster $\{Na_3(H_2O)_9\}^{3+}$, as shown in Fig. 2(b). The terminal sodium cations Na1 and Na3 are connected to the oxygen atoms of the $\{V_{10}\}$ cluster anions to extend the dimensionality into the layer-like structure, as shown in Fig. 2(c). Interestingly, the mode of connectivity of the terminal sodium cations (Na1 and Na3) with surrounding different decavanadate clusters is different from each other: the Na3 cation is connected to two different V=O type terminal oxygen atoms (O9 and O12) from two different decavanadate cluster anions, whereas the Na1 cation is connected to the μ_3-O type oxygen atom (O3) of the decavanadate cluster. This interesting connectivity from the μ_3-O type oxygen atom of the $\{V_{10}\}$ cluster to a sodium cation is very rare in decavanadate chemistry; this mode of connectivity probably causes the deviation of the geometry of Na1 polyhedron from a normal octahedral geometry to an unusual square pyramidal geometry around sodium. The coordination of the terminal Na1 with the $\{V_{10}\}$ cluster through the μ_3-type oxygen atom (O3) precludes water molecules from entering into its (Na1) coordination sphere, thereby it forms relatively longer bonds with the μ_2-type bridging water oxygen atoms. Overall, in the crystal structure, each tri-sodium aqua-cluster connects to three $\{V_{10}\}$ cluster anions (Fig. 2(b) and also Fig. S4 in the Supporting information) and extends its dimensionality along a layer to form a 2D coordination polymer, as shown in Fig. 2(c). The water hydrogen atoms of the tri-sodium aqua-complex cation show extensive hydrogen bonding interactions (O–H···O) with the surrounding five decavanadate cluster anions. These O–H···O interactions between the anion and cation extends the 2D coordination polymer/sheet into a 3D-supramolecular network (Fig. S5, Supporting information). The bond lengths and bond angles are presented in Tables S5 and S6, respectively.

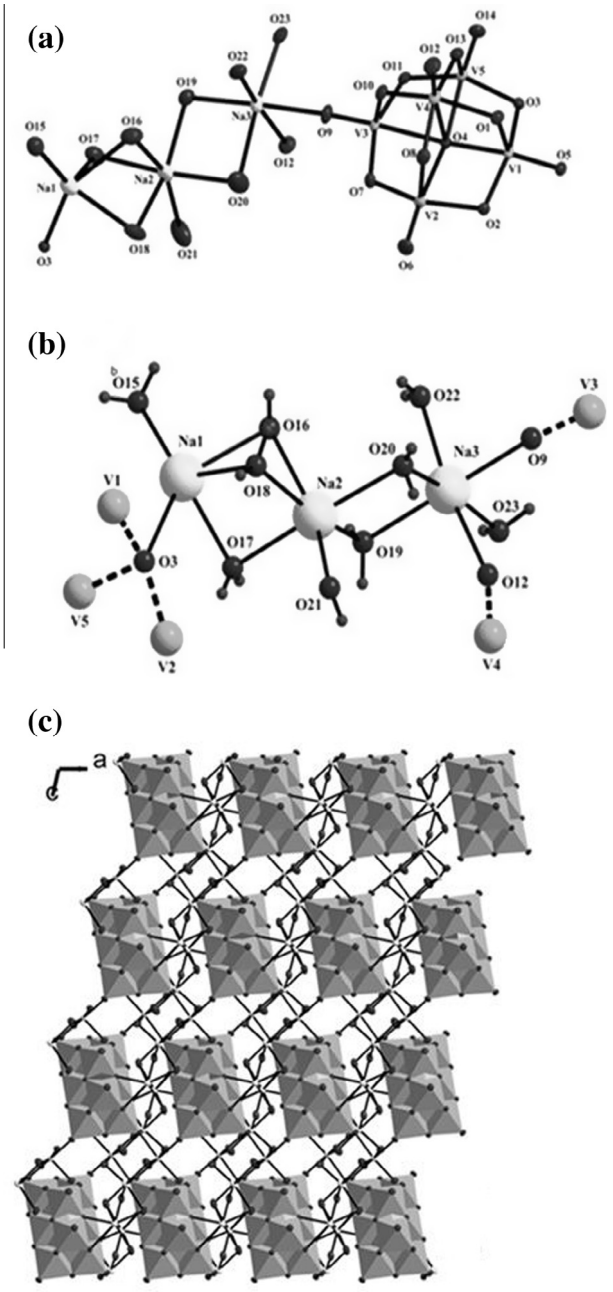

Fig. 2. (a) Ball and stick representation of compound **2** (hydrogen atoms are omitted for clarity). (b) The tri-sodium cation coordinated with the decavanadate cluster anion. (c) 2-D network, established in the crystal structure of coordination polymer containing compound **2**, along the crystallographic *ac* plane.

3.4. Comparision of the crystal structures

The compound $[\{HMTAH\}_2\{Na(H_2O)_6\}_2][H_2V_{10}O_{28}]\cdot 6H_2O$ (**1**) is a doubly protonated discrete decavanadate cluster anion with a sodium hexahydrate coordination complex and protonated HMTA as the cations. The synthesis of compound **1** is a very simple and well known method to isolate the decavanadate cluster with protonated organic cations. In the relevant crystal structure (compound **1**), the singly protonated HMTA cation neither coordinates to the sodium octahedral hexa-aqua complex nor coordinates to the decavanadate cluster anion; this is because the N atoms of the organic ligand hexamethylenetetramine (HMTA) are generally reluctant to be involved in any metal ion coordination. The compound $[Na_3(H_2O)_9]_{2n}[V_{10}O_{28}]_n$ (**2**) is a purely inorganic coordination polymer with an interesting tri-sodium aqua-complex cation, which is supported by the decavanadate cluster anion. The further coordination of these $[Na_3(H_2O)_9]^{3+}$ cations, supported on the $[V_{10}O_{28}]^{6-}$ cluster anion, to other surrounding $[V_{10}O_{28}]^{6-}$ cluster anions result in the formation of a two-dimensional (2D) extended structure (coordination polymer) in the crystals of compound **2**. Interestingly, in the crystal structure, the trisodium cluster cation connects to the decavandate cluster anion involving terminal oxygen atoms as well as μ_3-type bridging oxygen atom. The connectivity through this μ_3-type bridging oxygen atom is very rare in polyoxovanadate (POV) chemistry. Each tri-sodium aqua-complex cation connects with three surrounding decavanadate

cluster anions (Fig. S4, Supporting information) in a cation to anion ratio of 1:3, resulting in a 2D sheet. These 2D sheets are further extended into a 3D supramolecular network due to extensive hydrogen bonding interactions between the water molecules of the trisodium aqua complex cations and surface oxygen atoms of the decavanadate anion. The connectivity of the disodium aqua cations to the decavanadate cluster anions are vastly reported in the literature; however, to our knowledge, the coordination connectivity of a tri-sodium aqua cluster cation to the decavanadate cluster anion is not much explored. The obvious comparison between **1** and **2**, as far as crystal structures are concerned, is that the cage-like organic cation HMTA (protonated hexamethylenetetramine) forms a zero-dimensional (0D) structure in case of compound **1** and the tri-sodium aqua cluster forms a 2D structure in case of compound **2**.

3.5. UV–Vis and fluorescence spectroscopy

The electronic absorption spectra of solid macro-crystals of compounds **1** and **2** were measured at room temperature (Fig. 3(a)). The UV–Vis spectra of compounds **1** and **2** are very similar due to the presence of same decavanadate cluster anion in both compounds. The electronic spectra of these compounds reveal peaks at around 220 nm and a shoulder at 280 nm (compound **1**) and 380 nm (compound **2**), which have been assigned to O→V charge transfer transitions [18e].

Interestingly, compound **2** exhibits emission in the solid state as well as in its nano-particle suspension state in acetonitrile. The macro-crystals of compound **2**, upon excitation at 380 nm, show an emission peak at around 460 nm, as shown in Fig. 3(b). On the other hand, compound **1** does not exhibit any emission (on excited at a wavelength of 290 nm), even though compound **1** contains the same POV cluster anion as contained by compound **2**. The most striking difference in coordination chemistry between compound **2** and compound **1** is the coordination of the triply-bridged oxygen atom of the decavanadate cluster anion to a sodium atom of tri-sodium aqua-complex cation $[Na_3(H_2O)_9]^{3+}$ in the crystal of compound **2**, which is absent in compound **1.** This special coordination of a triply-bridged oxygen atom of the decavanadate cluster anion to a sodium cation (in compound **2**) can be correlated with a charge transfer from the 'p' orbital of the oxygen atom to the 'd' orbital of vanadium. Thus upon excitation at 380 nm, compound **2** exhibits an emission at around 460 nm which can be attributed to the O→V charge transfer transition [26].

3.6. Synthesis, characterization and photo-physical studies of nano-crystals of the compound $[Na_3(H_2O)_9]_{2n}[V_{10}O_{28}]_n$ (2)

The macro-crystals of compound **2** were subjected to ultrasonication in acetonitrile solvent. During the ultrasonication, the macro-crystals are dispersed into smaller sized nanoparticles. The nanoparticles are synthesized at two different concentrations, 1 mM (14.2 mg in 10 mL of solvent) and 0.5 mM (7.1 mg in 10 mL of solvent) by ultrasonication for 1 h. The FT-IR spectra of the nanoparticles exhibit the decavanadate-type characteristic features in the range 450–1000 cm^{-1}. V–O terminal oxygen vibrations are found at 947 cm^{-1}, the asymmetric vibrations of V–O–V bridges are observed at 723 cm^{-1}, while the symmetric bands are located at around 590 cm^{-1}. The FT-IR spectra of the nanoparticles and macro-crystals are shown in Fig. S6 (Supporting information). The observed powder X-ray diffraction pattern of the nano-crystals of compound **2** were matched with the theoretical powder pattern, simulated from single crystal data of the corresponding macro-crystal data (Fig. S7, Supporting information). The chemical composition of compound **2** nano-particles was confirmed by EDS equipped with FE-SEM, which shows that the obtained

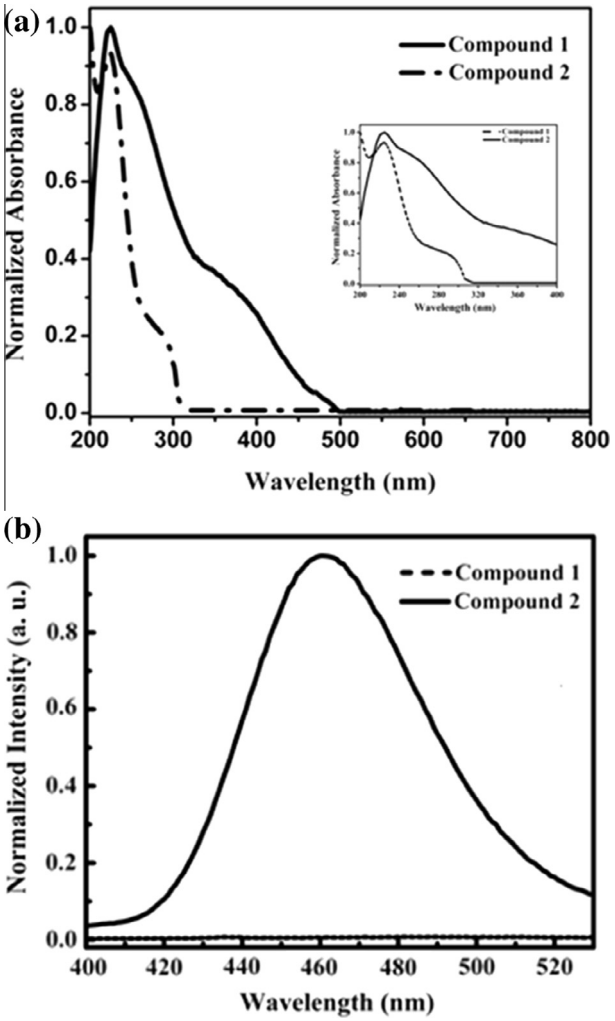

Fig. 3. (a) Diffuse reflectance (solid state electronic absorption) spectra of compounds **1** and **2**. (b) The emission spectra of the macro-crystals of compounds **1** and **2**.

nanoparticles have the same elemental composition as the bulk macro-crystals (Fig. S9(a)], Supporting information).

The morphology of these nanoparticles was studied using the TEM, FE-SEM and AFM techniques. The sizes of the nanoparticles (synthesized from 1 mM concentration) span the range 100 to 500 nm, with no particular morphology (Fig. S8, Supporting information). For the nanoparticles synthesized from 0.5 mM concentration, the TEM and FE-SEM images show a uniform size distribution (about 70–50 nm range) which are well dispersed with nearly spherical morphology. The selected area electron diffraction (SAED) pattern of the nanoparticles (Fig. 4(a) inset) shows that the nanoparticles are crystalline in nature. From the SAED pattern, the measured d-spacing values of 5.89, 3.31, 3.08, 2.96, 2.78, 2.74, 2.69 and 2.29 correspond to the *hkl* planes (101), (121), (−203), (222), (−104), (2−32), (−302) and (−1−43) respectively. These lattice planes belong to triclinic macro-crystals of compound **2**, as far as single crystal X-ray data are concerned. Examination of the AFM images (Fig. S8(c), Supporting information) reveals that the size of the nanoparticles are consistent with the TEM and FE-SEM studies. The nanoparticles, formed by drop casting the suspension on a quartz plate, on excitation at 380 nm, show an emission band at around 460 nm, as displayed in the Fig. 5, like that shown by the corresponding macro-crystals. Thus, the re-sizing of the particles from macro-size to nano-size does not have any influence on the emission features of compound **2**. The laser confocal fluorescence

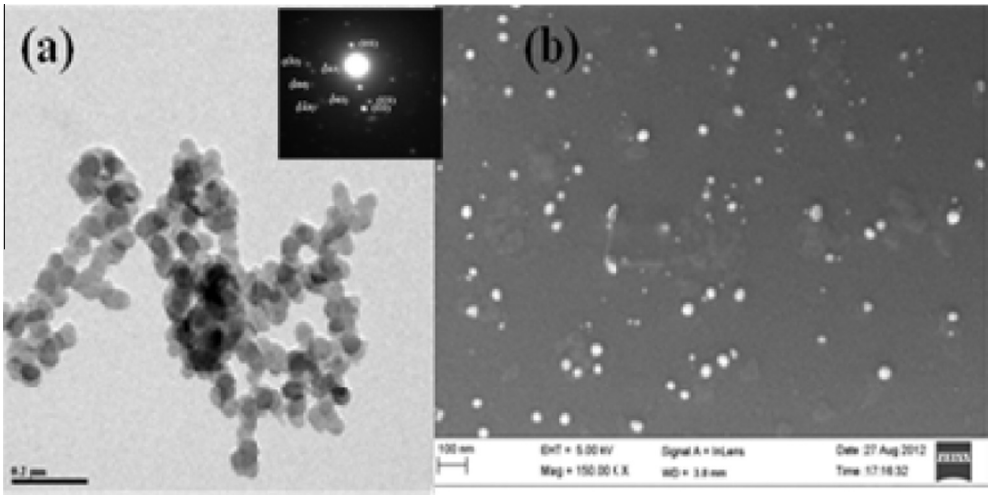

Fig. 4. (a) TEM (scale bar = 0.2 μm) image of nanoparticles of compound **2** (prepared from 0.5 mM concentration); inset: SAED pattern. (b) FE-SEM (scale bar = 100 nm) image of nanoparticles of compound **2** (prepared from 0.5 mM concentration).

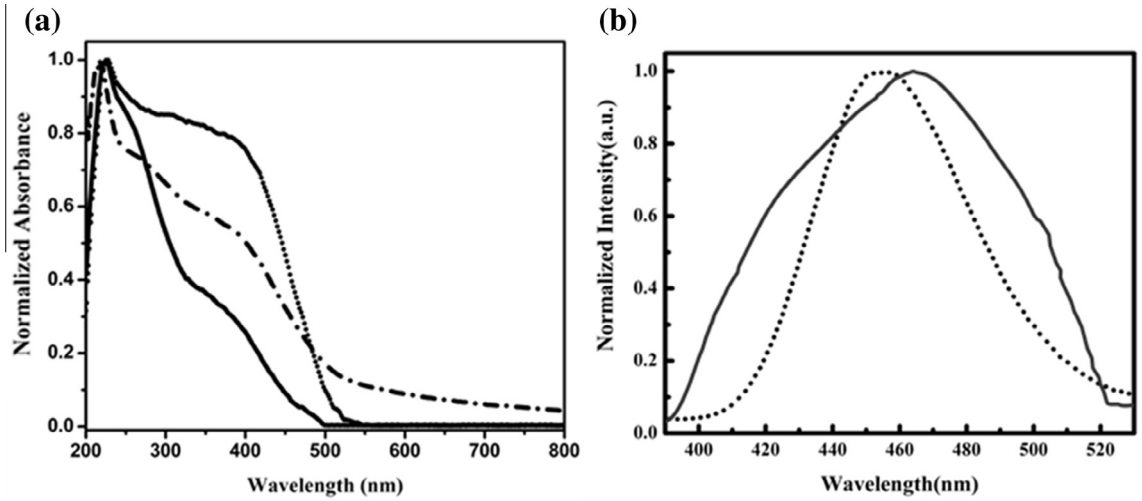

Fig. 5. (a) Electronic absorption spectra of nanoparticles of compound **2**: dotted line, diffuse reflectance spectrum of nano-crystals of compound **2**; dashed-dotted line, electronic spectrum of the nanoparticle suspension of compound **2** in acetonitrile; solid line, diffuse reflectance spectrum of macro-crystals of compound **2**. (b) Solid line: solid state emission spectrum of nanoparticles (solid on quartz plate) of compound **2** and dotted line: emission spectrum of the nanoparticle suspension of compound **2** in acetonitrile (excited at 380 nm).

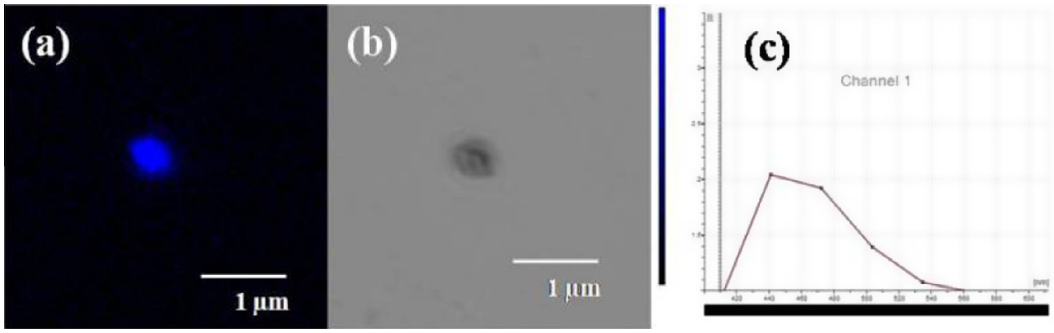

Fig. 6. Laser confocal microscopy images of nanoparticles of compound **2**: (a) after excitation at 380 nm, (b) before excitation and (c) the corresponding emission spectrum recorded by the excitation at 380 nm.

microscopy images of nanoparticles of compound **2** (Fig. 6) also display a blue emission peak at 460 nm (on excitation with a 380 nm Ar^+ laser), which is consistent with the conventional emission spectroscopic data.

3.7. Thermal properties

Thermogravimetric analyses (TGA) were performed in the temperature range 30–1000 °C on polycrystalline samples under

nitrogen atmosphere. The TG curve for the compound $[\{HMTAH\}_2\{Na(H_2O)_6\}_2][H_2V_{10}O_{28}]\cdot 6H_2O$ (**1**) shows a first weight loss of 6.85% in the temperature range 94–153 °C. This weight loss corresponds to the loss of six water molecules (calculated mass loss for six water molecules is 6.7%). This includes six non-coordinated lattice water molecules. The second weight loss of 31.7% in the temperature range 120–219 °C might be due to the loss of two hexamine moieties and twelve sodium coordinated water molecules (calculated mass loss for two hexamine moieties is 17.53% and for twelve water molecules is 13.4%). The TG curve for the compound $[Na_3(H_2O)_9]_{2n}[V_{10}O_{28}]_n$ (**2**) shows a weight loss of 22.34% in the temperature range 42–164 °C, which corresponds to the loss of 18 water molecules, coordinated to the tri-sodium cation (calculated 22.8% for 18 sodium coordinated water molecules). On further heating, the cluster disintegrates. The TG curves of the two compounds **1** and **2** are graphically presented in Fig. S2 (Supporting information). The thermal behavior of the related compound $[Na_2(H_2O)_{10}][H_3V_{10}O_{28}[Na(H_2O)_2\}]\cdot 3H_2O$ [19a], which on heating around 250 °C forms the cluster decomposition product $Na_xV_2O_5$, is quite comparable to that of compound **2** (present study). Similar thermal plots have been observed for the related decavanadate cluster containing compounds $(NH_4)_2[Ni(H_2O)_5(NH_3)]_2[V_{10}O_{28}]\cdot 4H_2O$ and $(NH_4)_2[Zn(H_2O)_6]_2V_{10}O_{28}\cdot 4H_2O$ [27,28]. Thus it is always not true that the assembly of purely inorganic polyoxometalate building units offers high stability to the concerned network.

4. Conclusion

In summary, we have synthesized and characterized two decavanadate based compounds, where compound **1** is a discrete cluster containing compound with the protonated organic ligand HMTA and sodium hexahydrate as cations and compound **2** is an organic free inorganic coordination polymer, which contains the decavanadate cluster anion supported tri-sodium-aqua-cluster cation. The connectivity of terminal and triply bridging oxygen atoms of the decavanadate cluster anion with the trisodium aqua cations (in the case of compound **2**), extends the dimensionality to a 2D sheet-like structure. We have successfully synthesized and characterized nanoparticles of compound **2** by ultrasonication of the relevant macro-crystals. It is worth mentioning that compound **2** displays emission at room temperature in both the macro crystal and nanoparticle states, which is a rare example for a decavanadate cluster system.

Acknowledgements

We thank the Science & Engineering Research Board (a statutory body under the Department of Science and Technology), Government of India, for financial support (Project No. SB/SI/IC/034/2013). The National X-ray Diffractometer facility at the University of Hyderabad by the Department of Science and Technology, Government of India, is gratefully acknowledged. We are grateful to UGC, New Delhi, for providing the infrastructure facility at the University of Hyderabad under the UPE grant. YS thanks UGC, CAS (RFSMS), New Delhi, for her fellowship.

Appendix A. Supplementary data

CCDC-984689 and CSD-427324 contain the supplementary crystallographic data for compounds **1** and **2**, respectively. For compound **1**, the crystal data can 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. For compound **2**, the details of the crystal structure investigation may be obtained from the Fachinformationszentrum, Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-427324. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2014.05.035.

References

[1] (a) D.-L. Long, H. Abbas, P. Kögerler, L. Cronin, Angew. Chem. Int. Ed. 44 (2005) 3415;
(b) C. Streb, D.-L. Long, L. Cronin, Chem. Commun. (2007) 471;
(c) H. Zeng, G.R. Newkome, C.L. Hill, Angew. Chem. 112 (2000) 1841.
[2] (a) A. Müller, P. Kögerler, A.W.M. Dress, Coord. Chem. Rev. 222 (2001) 193;
(b) T. Yamase, K. Fukaya, H. Nojiri, Y. Ohshima, Inorg. Chem. 45 (2006) 7698;
(c) T. Arumuganathan, A.S. Rao, T.V. Kumar, S.K. Das, J. Chem. Sci. 120 (2008) 95.
[3] T. Tiago, P. Martel, C. Guitiérrez-Merino, M. Aureliano, Biochim. Biophys. Acta 1774 (2007) 474.
[4] H. Zeng, G.R. Newkome, C.L. Hill, Angew. Chem., Int. Ed. 39 (2000) 1771.
[5] D.-L. Long, R. Tsunashima, L. Cronin, Angew. Chem., Int. Ed. 49 (2010) 1736.
[6] T. Arumuganathan, A.S. Rao, S.K. Das, Cryst. Growth Des. 10 (2010) 4272.
[7] (a) B.K. Tripuramallu, S.K. Das, Cryst. Growth Des. 13 (2013) 2426;
(b) Y. Ishii, Y. Takenaka, K. Konishi, Angew. Chem. 116 (2004) 2756;
(c) C. Streb, D.-L. Long, L. Cronin, Cryst. Eng. Commun. 8 (2006) 629.
[8] (a) X.-L. Wang, C. Qin, E.-B. Wang, Z.-M. Su, Y.G. Li, L. Xu, Angew. Chem. 118 (2006) 7571;
(b) A. Dolbecq, C. Mellot-Draznieks, P. Mialane, J. Marrot, G. Férey, F. Sécheresse, Eur. J. Inorg. Chem. (2005) 3009.
[9] C. Streb, C. Ritchie, D.-L. Long, P. Kögerler, L. Cronin, Angew. Chem., Int. Ed. 46 (2007) 7579.
[10] D. Venegas-Yazigi, P. Hermosilla-Ibáñez, J. Costamagna, E. Spodine, A. Vega, V. Paredes-García, E.L. Fur, Macromol. Symp. 304 (2011) 80.
[11] C. Musumeci, A. Luzio, C.P. Pradeep, H.N. Miras, M.H. Rosnes, Y.-F. Song, D.-L. Long, L. Cronin, B. Pignataro, J. Phys. Chem. C 115 (2011) 4446.
[12] A. Troupis, T. Triantis, A. Hiskia, E. Papaconstantinou, Eur. J. Inorg. Chem. (2008) 5579.
[13] P.S. Kishore, B. Viswanathan, T.K. Varadarajan, Nanoscale Res. Lett. 3 (2008) 14.
[14] (a) X.-H. Wang, Z.-H. Kang, E.-B. Wang, Chin. J. Inorg. Chem. 22 (2006) 2186;
(b) Y. Shen, J. Peng, H. Pang, P. Zhang, D. Chen, C. Chen, H. Zhang, C. Meng, Z. Su, Chem. Eur. J. 17 (2011) 3657.
[15] (a) M.T. Pope, A. Müller, Angew. Chem., Int. Ed. Eng. 30 (1991) 34;
(b) M.T. Pope, Heteropoly and Isopoly Oxometalates, Springer-Verlag, Berlin, 1983;
(c) M.T. Pope, A. Müller (Eds.), Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity, Kluwer Academic, The Netherlands, 1994.
[16] P. Kanoo, A.C. Ghosh, T.K. Maji, Inorg. Chem. 50 (2011) 5145.
[17] K. Bukietynska, K. Krot, P. Starynowicz, Transition Met. Chem. 26 (2001) 311.
[18] (a) U. Lee, Y.-H. Jung, H.-C. Joo, Acta Cystallogr., Sect. E 59 (2003) i72;
(b) U. Lee, Acta Cystallogr., Sect. E 62 (2006) i176;
(c) M.I. Khan, S. Tabussum, C. Zheng, J. Clust. Sci. 12 (2001) 583;
(d) I. Mestiri, B. Ayed, A. Haddad, J. Clust. Sci. 24 (2013) 85;
(e) Y. Lü, Y. Feng, Chin. J. Chem. 28 (2010) 2404;
(f) V.N. Krasil'nikov, A.P. Shtin, L.A. Perelyaeva, I.V. Baklanova, A.P. Tyutyunnik, V.G. Zubkov, Russ. J. Inorg. Chem. 55 (2010) 162;
(g) L.R. Guilherme, A.C. Massabni, A.C. Dametto, R.d.S. Corrêa, A.S.d. Araujo, J. Chem. Crystallogr. 40 (2010) 897;
(h) J. Nilsson, E. Nordlander, U. Behrens, D. Rehder, Acta Cryst. E66 (2010) i30;
(i) J. Pei, B. Yu, H.-b. Song, X.q. Yan, Y. Zhang, X. Geng, Y. Wang, J. Yan, B. Sun, J. Mol. Struct. 779 (2005) 43.
[19] (a) T. Duraisamy, A. Ramanan, J.J. Vittal, Cryst. Eng. 3 (2000) 237;
(b) T. Duraisamy, N. Ojha, A. Ramanan, J.J. Vittal, Chem. Mater. 11 (1999) 2339.
[20] T. McGlone, C. Streb, M. Busquets-Fité, J. Yan, D. Gabb, D.-L. Long, L. Cronin, Cryst. Growth Des. 11 (2011) 2471.
[21] L. Mai, C. Han, Mater. Lett. 62 (2008) 1458.
[22] S. Yerra, S. Supriya, S.K. Das, Inorg. Chem. Commun. 35 (2013) 54.
[23] Bruker, SADABS, SMART, SAINT and SHELXTL, Bruker AXS Inc., Madison, Wisconsin, USA, 2000.
[24] G.M. Sheldrick, SHELX-97, Program for Crystal Structure Solution and Analysis, University of Gottingen, Gottingen, Germany, 1997.
[25] D.-L. Long, E. Burkhholder, L. Cronin, Chem. Soc. Rev. 36 (2007) 105.
[26] R.Q. Sun, H.H. Zhang, X.Y. Wu, C.C. Huang, Y.P. Chen, Spectrosc. Spect. Anal. 26 (2006) 282.
[27] N.R. Putrevu, R.J. Doedens, M.I. Khan, Inorg. Chem. Commun. 38 (2013) 5.
[28] A. Udomvech, P. Kongrat, C. Pakawatchai, H. Phetmung, Inorg. Chem. Commun. 17 (2012) 132.