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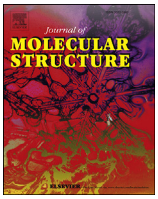

Organic free decavanadate based materials: Inorganic linkers to obtain extended structures

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ABSTRACT

Decavanadate based extended structures containing compounds $[\{Na_3(H_2O)_8(\mu_2\text{-}H_2O)_6Ag_2\}HV_{10}O_{28}]_n \cdot 6nH_2O$ (**1**), $[Co(H_2O)_6]_n[\{Na_2(H_2O)_6(\mu_2\text{-}H_2O)_4Co(H_2O)_2\}V_{10}O_{28}]_n \cdot 4nH_2O$ (**2**) and $[Zn(H_2O)_6]_n[\{Na_2(H_2O)_6(\mu_2\text{-}H_2O)_4Zn(H_2O)_2\}V_{10}O_{28}]_n \cdot 4nH_2O$ (**3**) have been synthesized from respective aqueous solutions of sodium metavanadate. Compounds **1**, **2** and **3** crystallize in a triclinic space group *P*-1. Compound **1** is a three-dimensional inorganic solid, whereas compounds **2** and **3** are isomorphous one-dimensional inorganic polymers. In the crystal structure of compound **1**, the silver (I) cation is coordinated to the terminal oxygen as well as bridging oxygen atoms of decavanadate anion and it is also connected to bridging oxygen atom of trimeric sodium aqua cluster cation. In the crystals of compound **2**, one hexa-hydrated cobalt cation is present as a counter cation and one "di-sodium cobalt aqua-complex" cation is supported on the $[V_{10}O_{28}]^{6-}$ cluster anion by coordinate covalent bond. Compound **3** is isomorphous with compound **2**, with Zn^{2+} present (in compound **3**) in the place of Co^{2+} (in compound **2**). Compounds **1**, **2** and **3** are characterized by routine elemental analyses, FT-IR spectroscopy and unambiguously by single crystal X-ray crystallography. In the crystal structure of compound **1**, an unusual silver dimer is observed.

1. Introduction

The research on coordination polymers (CPs) has rapidly progressed over the past decades because of the multipurpose utility of such materials in a wide range of potential applications, such as functional solid materials, light emitting diodes, proton conductors, heterogeneous catalysts, gas sorbants, and supercapacitors [1]. The multi-dimensional infinite structures of metal complexes are of considerable interest in perceptive of solid state chemistry of metal complexes [2]. The chemistry of metal coordination polymers with specific network topologies has become a very active field in the structural design of crystalline materials [2]. The assembly of extended structures of 1-D to 3-D heterometallic coordination polymers without organic ligands is less explored and remains a challenge for chemists. Many factors play important role in the synthesis of such materials, including nature (coordination preferences of the metal ions) and stoichiometric ratio of the reacting partners, reaction conditions/environment, and the solvents used [1]. It is also possible that the metal centers (such as, Co (II), Ni (II), Cu (II) and Ag (I) ions) can entirely dictate the topology of the resulting networks.

The modern chemical research on polyoxometalate-based inorganic materials has attracted synthetic chemists because of their prospective applications in various research areas, such as catalysis [3–5], conductive materials [6], medicinal chemistry [7,8], and materials science [9]. Polyoxometalates (POMs) [10–12] cover a wide range of metal-oxide based compounds that are versatile as far as size and topology of the relevant POM clusters are concerned. The important step in the assembly of well-designed POM clusters in obtaining metal-oxide based frameworks has so far been achieved by using transition metal coordination complex (with organic ligands) fragments as linkers or by using pure organic linkers. Both these strategies, however, are limited by the reduced framework stability intrinsic to metal–organic framework materials, because organic fragments of metal-organic frameworks are not thermally stable. Thus, designing and synthesizing new materials [13], formed from POM cluster anion and pure inorganic cationic entity (organic free) are of considerable interests in modern inorganic chemistry as far as metal-oxide based inorganic materials are concerned.

Among POMs, the polyoxovanadates (POVs) are important in many areas, for example, biological sciences [14–17], industrial

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chemistry [18], materials chemistry [19,20], electrochemistry [21] and magnetochemistry [22]. The decavanadate cluster anion, $[V_{10}O_{28}]^{6-}$ is one of the important building blocks among POVs in constructing inorganic-organic hybrid materials [23,24]. Decavanadate based pure inorganic polymeric compounds are also reported [25–28] including $[Ni(H_2O)_6]_2[Na(H_2O)_3]_2[V_{10}O_{28}]\cdot 4H_2O$ [29], $Na_4Ni(V_{10}O_{28})\cdot 23H_2O$ [30] and $CuNa_4V_{10}O_{28}\cdot 23H_2O$ [31]. We have been working on POM/POV based organic free polymeric inorganic materials [13,32–34]. Inorganic linkers are generally metal-aqua coordination complexes, that are often formed in situ during synthesis. Metal ions, that act as linkers, include Na^+, K^+, Ln^{3+} (lanthanides), transition metal cations etc. The literature on silver ion as a linker to link POV cluster anions into extended structures is hardly known [35–37]. The good affinity of silver ion makes the coordination, a dynamic range varied from two to six, even seven and eight, showing strong tendency to display versatile coordination spheres. Further, Ag(I) ion possesses flexible coordination geometries with high affinity to O and N donors, which may easily form covalent links between Ag(I) ions and POMs resulting in extended Ag-POM structures [38]. In these extended structures, the silver ion linker is mostly stabilized with organic ligands (for example, organic solvent molecules). Pure inorganic silver ion linker, that connects POM cluster anions into a material, is not yet known. In this report, we have described synthesis and crystal structure of a decavanadate based material $[\{Na_3(H_2O)_8(\mu_2\text{-}H_2O)_6Ag_2\}HV_{10}O_{28}]_n\cdot 6nH_2O$ (**1**), in which the decavanadate cluster anions (building blocks) are linked by sodium-aqua-silver-aqua cluster cation resulting in an extended three-dimensional structure. We also wish to report two more decavanadate based compounds $[Co(H_2O)_6]_n[\{Na_2(H_2O)_6(\mu_2\text{-}H_2O)_4Co(H_2O)_2\}V_{10}O_{28}]_n\cdot 4nH_2O$ (**2**) and $[Zn(H_2O)_6]_n[\{Na_2(H_2O)_6(\mu_2\text{-}H_2O)_4Zn(H_2O)_2\}V_{10}O_{28}]_n\cdot 4nH_2O$ (**3**) for comparison reason, though the nickel analogue of these two compounds (compounds **2** and **3**) has already been reported earlier [29].

2. Experimental

2.1. Materials and general consideration

The starting materials, sodium metavanadate, sodium tungstate dihydrate, cobalt chloride and zinc chloride were obtained from SISCO, acetonitrile was from Sigma Aldrich; distilled water was used throughout the experiment. Micro analytical data (only for hydrogen in the present work) were obtained with a FLASH EA 1112 Series CHNS Analyzer. Infrared (IR) spectra were recorded on a JASCO FT/IR-5300 spectrometer with KBr pellets of corresponding compounds in the region of 400–4000 cm^{-1}. Powder X-ray diffraction patterns were recorded on a Bruker D8-Advance diffractometer using graphite monochromated Cu $K\alpha 1$ (1.5406 Å) and $K\alpha 2$ (1.54439 Å) radiations. Thermogravimetric analyses were carried out on a STA 409 PC analyzer and corresponding masses were analyzed by QMS 403 C mass analyzer, under the flow of N_2 gas with a heating rate of 5 °C min^{-1}, in the temperature range of 30–1000 °C.

2.2. Synthesis

The title compounds have been synthesized by simple one-pot reactions as described below.

2.2.1. Synthesis of compound $[\{Na_3(H_2O)_8(\mu_2\text{-}H_2O)_6Ag_2\}HV_{10}O_{28}]_n\cdot 6nH_2O$ (**1**)

100.0 mL aqueous solution of sodium metavanadate (2.0 g, 8.26 mmol) was heated for 6 h at70 °C. To this hot solution, acetic acid was added to maintain the pH 5.0; subsequently 25.0 mL of aqueous suspension of silver oxide (0.5 g, 2.15 mmol) and 60.0 mL acetonitrile were added to crystallize reddish-yellow color block-shaped crystals of compound **1**. The crystals of compound **1** have been isolated by filtration. Yield: 1.2 g (45% based on vanadium). Anal. Calcd. For. $Ag_2H_{41}Na_3O_{48}V_{10}$ (1603): H, 2.58; Na, 4.30; V, 31.77; Ag, 13.45. Found: H, 2.71; Na, 4.24 (ICP); V, 31.26 (ICP); Ag, 13.32 (ICP). IR (KBr, cm^{-1}): 3473(br), 1616(s), 1145(w), 991(sh), 958(s), 849(m), 739(m), 597(m), 520(w).

2.2.2. Synthesis of compound $[Co(H_2O)_6]_n[\{Na_2(H_2O)_6(\mu_2\text{-}H_2O)_4Co(H_2O)_2\}V_{10}O_{28}]_n\cdot 4nH_2O$ (**2**)

This synthesis is same as the procedure described for compound **1** except the addition of anhydrous $CoCl_2\cdot 6H_2O$ (0.5 g, 2.10 mmol) in place of silver oxide (which was used for the synthesis of compound **1**). The crystals of compound **2** have been isolated by filtration. 1.25 g (50% based on vanadium). Anal. Calcd. For. $Co_2H_{44}Na_2O_{50}V_{10}$ (1517): H, 2.92; Na, 3.02; V, 33.56; Co, 7.76. Found: H, 2.86; Na, 2.98 (ICP); V, 32.95 (ICP); Co, 7.40 (ICP). IR (KBr, cm^{-1}): 3547 (br), 1616 (s), 991(sh), 953(s), 843(s), 805(w), 745(m), 591(w), 526(w).

2.2.3. Synthesis of compound $[Zn(H_2O)_6]_n[\{Na_2(H_2O)_6(\mu_2\text{-}H_2O)_4Zn(H_2O)_2\}V_{10}O_{28}]_n\cdot 4nH_2O$ (**3**)

This synthesis is same as the procedure described for compound **1** except the addition of anhydrous $ZnCl_2$ (0.5 g, 3.66 mmol) in place of silver oxide (which was used for the synthesis of compound **1**). The crystals of compound **3** were isolated by filtration. . Yield: 1.26 g (50% based on vanadium). Anal. Calcd. For. $Zn_2H_{44}Na_2O_{50}V_{10}$ (1530): H, 2.90; Na, 3.00; V, 33.28; Zn, 8.54. Found: H, 2.83; Na, 3.01 (ICP); V, 32.68 (ICP); Zn, 8.39 (ICP). IR (KBr, cm^{-1}): 3424 (br), 1632 (s), 991(sh), 964(s), 843(s), 810(w), 750(m), 597(w), 531(w).

2.3. X-ray crystallography

The data were collected at 298(2) K on a Bruker SMART APEX CCD area detector system [$\lambda(Mo\text{-}K_\alpha) = 0.71073$ Å] with graphite monochromator; 2400 frames were recorded with an ω scan width of 0.3°, each for 10 s exposure. Crystal-detector distance was 60 mm with collimator diameter of 0.5 mm. The data were reduced by using SAINTPLUS [39] and a multi-scan absorption correction was performed using SADABS [40]. Structure solution and refinement were done using programs of SHELXS-97 and SHELXL-97 respectively [41,42]. All non hydrogen atoms were refined anisotropically. Hydrogen atoms of the lattice water molecules as well as coordinated water molecules could not be found in the crystal structures of the title compounds. The crystallographic information of compounds **1**, **2** and **3** is described in Table 1.

3. Results and discussion

3.1. Synthesis

The synthetic method for these compounds is simple one pot wet fashion reaction. Compound $[\{Na_3(H_2O)_8(\mu_2\text{-}H_2O)_6Ag_2\}HV_{10}O_{28}]_n\cdot 6nH_2O$ (**1**) is synthesized by adding acetonitrile and aqueous silver oxide suspension to the hot acidified aqueous solution of sodium metavanadate at pH 5.0. The isolated compound **1** is a purely inorganic polymer, where the di-silver tri-sodium aqua complex $\{Na_3(H_2O)_8(\mu_2\text{-}H_2O)_6Ag_2\}^{5+}$ act as the cation. When, in the same synthesis, a first row transition metal salt, namely, cobalt chloride is added instead of silver oxide, compound $[Co(H_2O)_6]_n[\{Na_2(H_2O)_6(\mu_2\text{-}H_2O)_4Co(H_2O)_2\}V_{10}O_{28}]_n\cdot 4nH_2O$ (**2**) is formed, whereby the mono-cobalt di-sodium aqua-complex $\{Na_2(H_2O)_6(\mu_2\text{-}H_2O)_4Co(H_2O)_2\}^{4+}$ and $[Co(H_2O)_6]^{2+}$ act as the cations to counter balance the negative charge of the decavanadate anion. Zinc analogue (compound **3**) of compound **2** has been