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# Hydrothermal Synthesis and Structural Characterization of Metal Organophosphonate Oxide Materials: Role of Metal-Oxo Clusters in the Self Assembly of Metal Phosphonate Architectures

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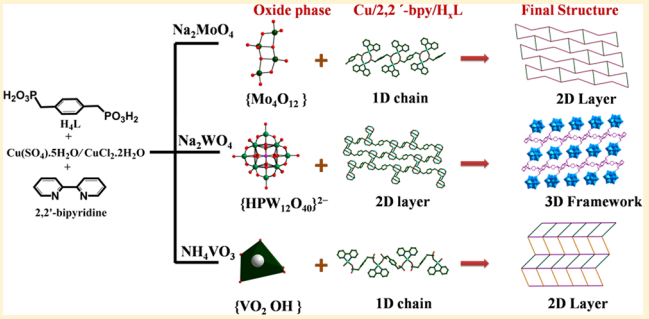
Supporting Information

**ABSTRACT:** Two new metal organophosphonate oxide materials with formulas $[Cu^{II}_4Cu^{I}_2(L)_2(2,2'\text{-bpy})_6(HPW_{12}O_{40})]_n \cdot 4nH_2O$ (**1**) and $[Cu(2,2'\text{-bpy})VO_2(OH)(H_2L)]_n$ (**2**) have been synthesized starting from the Cu(II) salts, 2,2′-bipyridine (2,2′-bpy), *p*-xylylenediphosphonic acid ($H_4L$), and sodium tungstate (for **1**)/ammonium metavanadate (for **2**). Both the compounds **1** and **2** are characterized by routine elemental analyses, IR spectroscopy, thermogravimetric (TG) analysis, and unambiguously characterized by single crystal X-ray crystallography. The crystal structure of compound **1** consists of 2D copper phosphonate layers connected by the Keggin heteropolyanion to form a three-dimensional (3D) framework. The copper phosphonate layers in compound **1** are fabricated by the rare copper hexanuclear clusters in which the four terminal Cu(II) centers form two eight-membered Cu-dimer ($Cu_2P_2O_4$) rings (top and the bottom) that are connected to each other by the two central Cu(I) atoms of four-membered $Cu_2O_2$ rings. These hexanuclear assemblies are connected to each other along the plane through the p-xylyl linkers to form a two-dimensional (2D) layer. Compound **1** is a unique example in terms of the existence of a hexanuclear copper phosphonate cluster in the 3D coordination matrix. Compound **2** has a 2D structure, in which the one-dimensional $[Cu(2,2'\text{-bpy})(H_2L)]_n$ chains are connected by the $VO_2OH$ subunits to from a 2D layer. The formation of $VO_2OH$ in compound **2** ceases the formation of eight-membered Cu-dimer rings. The self-assembly of the polyoxometalates plays an important role in the formation of the metal organophosphonate phases.




## INTRODUCTION

Metal oxide-based solids belong to an important class of materials showing their promising applications in the contemporary research areas during the past several years. Significant research in this area has been directed partly due to interest in their basic chemistry as well as their applications in the fields of separations, molecular electronics, energy storage, and catalysis.[1−6] In general, there is a correlation between the complexity of the structure and functionality of the material.[7] The constant evolution of complexity of metal oxides in terms of functionality requires more knowledge on synthetic strategies to understand the oxide structures.[8] Polyoxometalates refer to a vast family of metal oxides in the molecular level with diverse nuclearities, different sizes, and oxidation states.[9] One such strategy for the modification of oxide structures (in terms of linking the metal oxide building blocks) involves introduction of organic molecules or secondary metal complexes as structure directors. Zubieta et al. reported a vast number of compounds based on this approach and exploited the structural chemistry of metal oxide-based inorganic−organic hybrid materials in the domain of secondary metals, binucleating ligands, tether lengths, etc.[10] Among the ligand bridges, which are used to tether the metal oxides, organophosphonic acids are known to be efficient in terms of charge compensation due to a greater number of coordinating atoms.

Moreover, organophosphonic acids are considered as structure-directing components owing to their flexibility in altering the organic groups.[11a−d] Organoamines, such as pyridine derivatives, imidazoles, and tetrazoles, are also used to link the metal oxides.[11e-g]

Metal organophosphonates are among the earliest and extensively studied examples of coordination polymers/metal-organic frameworks that are important because of their potential applications in the areas of sorption, ion exchange, sensing, and catalysis, etc.[12] Additionally, metal phosphonates have offered great opportunities to understand fundamental magnetic phenomena, such as spin canting, anisotropy, relaxation dynamics, and field-induced magnetic transitions.[13] Due to availability of more ligating sites, phosphonic acids ($PO_3H_2$ groups) coordinate to a greater number of metal sites, thereby forming layered structures and the bisphosphonic acids form pillared-layered structures.[14] A control over the protonation states and introduction of secondary chelating

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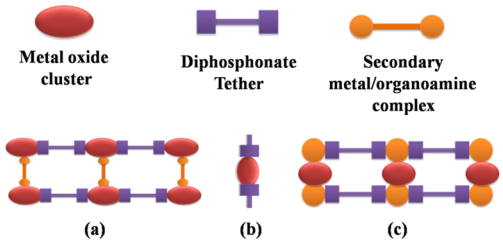
ligands results in the formation of clusters with different nuclearities.[15] This approach results in the stabilization of molecular phosphonates with interesting magnetic properties because the O−P−O bridge is known to be efficient in transmitting weak to moderately strong antiferromagnetic and ferromagnetic interactions.[16] In the recent era, the research progresses on metal phosphonates led to the evolution of two-dimensional (2D) and three-dimensional (3D) coordination networks.[17]

Metal organophosphonate (MOP) oxide materials are the combination of the metal oxides and metal organophosphonates architectures, in such a way that it can be exploited as functional materials having applications from both phases. Typically, hydrothermal methods have been commonly used to synthesize the metal organophosphonate oxide-based materials; the technique offers an excellent route to isolate metastable phases and stabilizes the reliability of the structure.[18] In the MOP oxides, both the polyoxometalate oxygen atoms and phosphonate oxygen atoms are involved in the formation of oxide microstructures, to which secondary metal/ligand components are attached to the peripherals of these oxide microstructures (Scheme 1). Zubieta et al. reported a class of

**Scheme 1. Scheme Representing the Different Types of Self Assembly Process in the MOP Oxide Materials**




compounds, $Mo_xO_y$/diphosphonate/M(II)-organo nitrogen families of bimetallic oxides, in which the $PO_3H_2$ groups are directly coordinated to the Mo(VI) atoms to form oxides of type $\{Mo_xO_y(O_3PR)\}^{n-}$, and these phases are linked with the aid of tethers attached to the phosphonic groups and metal organonitrogen cations.[19] Different classes of MOP oxides of type oxomolybdate-organodiphosphonates,[20] vanadium oxides with di- and tri- phosphonates,[21] are well-studied with metal organoimine cationic complex subunits. Another class of MOP oxide materials involves the functionalization of polyoxometalates with mono- and di- phosphonate anions.[22] Kortz et al. functionalized the heteropolymolybdates with amino acids through the phosphate, phosphonate, and phosphate groups.[23] However, polyoxometalate anionic clusters with the secondary metal cationic complexes containing both the organonitrogen and organophosphonic acids are very rare in the literature.[24]

We have chosen *p*-xylylenediphosphonic acid ($H_4L$) as a phosphonate source to study the effect on the oxide phases $Na_2WO_4$ and $NH_4VO_3$ with Cu as a secondary metal and 2,2′-bipyridine as an organoimine under hydrothermal conditions. Recently, we have studied the mechanistic aspects in the formation of the Cu-dimer with an $H_4L$ ligand and extended its dimensionality with organic and inorganic linkers in the presence of a secondary ligand component.[25] In this article, we describe the synthesis and structural characterization of two new compounds $[Cu^{II}_4Cu^{I}_2(L)_2(2,2'\text{-bpy})_6(HPW_{12}O_{40})]_n{\cdot}4nH_2O$ (**1**) and $[Cu(2,2'\text{-bpy})VO_2(OH)(H_2L)]_n$ (**2**). Compound **1** is a peculiar example, in which the Keggin-type heteropolyanion acts as a linker in connecting the metal organoimine phosphonate layers to form a 3D architecture, and in compound **2**, $VO_2OH$ connects the metal phosphonate chains to form a two-dimensional (2D) layer.

## EXPERIMENTAL SECTION

**General Comments.** All the chemicals were received as reagent grade and used without any further purification. $H_4L$ was prepared according to the reported procedure.[27] Elemental analyses were determined by FLASH EA series 1112 CHNS analyzer. Infrared spectra of solid samples obtained as KBr pellets on a JASCO − 5300 FT-IR spectrophotometer. Thermogravimetric analyses were carried out on a STA 409 PC analyzer and corresponding masses were analyzed by a QMS 403 C mass analyzer, under a flow of $N_2$ gas with a heating rate of 5 °C $min^{-1}$, in the temperature range of 30−1100 °C.

**Synthesis of the Compound $[Cu^{II}_4Cu^{I}_2(L)_2(2,2'\text{-bpy})_6(HPW_{12}O_{40})]_n{\cdot}4nH_2O$ (1).** A mixture of copper sulfate pentahydrate (0.2 mmol, 0.049 g), 2,2′-bpy (0.2 mmol, 0.031 g), sodium tungstate dihydrate (0.5 mmol, 0.165 g), $H_4L$ (0.1 mmol, 0.026 g), and water (555.5 mmol, 10.0 g) in the 2:2:5:1:5555 mole ratio was taken; to this reaction mixture, $H_3PO_4$ (0.1 mL) was added, and the pH was adjusted to 4.20 by 5 M HCl. Then, it was stirred for 30 min. The resulting solution was then transferred to 23 mL in a Teflon-lined autoclave in the stainless steel vessel and heated at 180 °C for 72 h, followed by cooling to room temperature over two days, resulting in the formation of tiny crystals of **1** in about a 10% yield (based on Cu) Anal. Calcd for $C_{76}H_{73}Cu_6N_{12}O_{56}P_5W_{12}$ (4792.69): C, 19.04; H, 1.53; N, 3.50. Found: C, 19.20; H, 1.32; N, 3.78. IR (KBr pellet) ($\upsilon$/$cm^{-1}$): 3437, 3084, 1602, 1572, 1512, 1494, 1468, 1444, 1311, 1251, 1201, 1157, 1130, 1097, 1060, 1030, 976, 958, 887, 817, 769, 729, 661, 561, 513.

**Synthesis of the Compound $[Cu(2,2'\text{-bpy})VO_2(OH)(H_2L)]_n$ (2).** A mixture of copper chloride dihydrate (0.34 mmol, 0.057 g), 2,2′-bpy (0.32 mmol, 0.050 g), ammonium metavanadate (0.43 mmol, 0.050 g), $H_4L$ (0.407, 0.109 g), and water (555.5 mmol 10.0 g) in the 1.08:1:1.36:1.27:1735 mole ratio was taken; the resulting reaction mixture with initial pH 2.70 was stirred for 30 min. The solution was then transferred to 23 mL in a Teflon-lined autoclave in the stainless steel vessel and heated at 180 °C for 72 h and cooled to room temperature over two days to give blue block crystals of **2**. Yield: 32% (based on Cu) Anal. Calcd for $C_{18}H_{19}CuN_2O_9P_2V$ (583.78): C, 37.03; H, 3.28; N, 4.79. Found: C, 37.64; H, 3.01; N, 4.99. IR (KBr pellet) ($\upsilon$/$cm^{-1}$): 3354, 3099, 2096, 1637, 1520, 1385, 1199, 1047, 956, 906, 841, 814, 754, 707, 596, 516, 480.

**X-ray Crystallography.** Single-crystals, suitable for structural determination of the compounds **1** and **2**, were mounted on a three-circle Bruker SMARTAPEX CCD area detector system under Mo K$\alpha$ ($\lambda$ = 0.71073Å) graphite monochromated X-ray beam, a crystal to detector distance of 60 mm, and a collimator of 0.5 mm. The scans were recorded with an $\omega$ scan width of 0.3°. Data reduction was performed by SAINTPLUS,[28a] empirical absorption corrections using equivalent reflections performed by program SADABS,[28b] structure solution using SHELXS-97,[28c] and full-matrix least-squares refinement using SHELXL-97[28d] for the above compounds. All the nonhydrogen atoms were refined anisotropically. Hydrogen atoms on the C atoms were introduced on calculated positions and were included in the refinement riding on their respective parent atoms. Attempts to locate the hydrogen atoms for the solvent water molecules in the crystal structure of compounds through Fourier electron density were failed. However, no attempts were made to fix these atoms on their parents. The hydrogen atoms on some of the P−OH groups in the compounds are fixed by the proper HFIX commands and some are located by the Fourier electron density map. Compound **1** suffers from a significant disorder problem due to disorder in the central $PO_4$ oxygen atoms in the keggin anion. The oxygen atoms O19 and O20 were split over two positions (O19A, O19B and O20A, O20B) after fixing their occupancies 0.5 to each atom. Due to this disorder problem, the central $PO_4$ group is changed to $PO_8$; as a result of this, the Keggin anion experiences an unresolved disorder problem. The maximum and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minimum main axis ADP ratio of the oxygen atoms O16, and carbon atoms C11, C25, C32, are more than 5.0, indicating the unresolved disorder. However, no proper model (by applying restraints ISOR or SIMU to displacement parameters) has been found to resolve this problem. $\alpha$-Disordered Keggin ions are known to show this type of unresolved disorder problem that is very common in the literature.[29] In compound **2**, the oxygen atoms, connected to vanadium atom O13 and O12, also suffer from a significant disorder problem, which has been resolved by splitting oxygen atoms into two positions using part command in the refined ratio 0.53:0.47 for O13 and 0.53:0.47 for O12. Crystal data and structure refinement parameters for both the compounds are summarized in Table 1 and selected bond lengths in Table 2.

**Table 1. Crystal Data and Structural Refinement Parameters for Compounds 1 and 2**

| | 1 | 2 |
|---|---|---|
| empirical formula | $C_{76}H_{73}Cu_6N_{12}O_{56}P_5W_{12}$ | $C_{18}H_{19}CuN_2O_9P_2V$ |
| formula weight | 4792.69 | 583.78 |
| $T$ (K) | 100 | 100 |
| $\lambda$ (Å) | 0.71073 | 0.71073 |
| crystal system | triclinic | triclinic |
| space group | $P\bar{1}$ | $P\bar{1}$ |
| $a$ (Å) | 12.784(17) | 8.006(7) |
| $b$ (Å) | 12.392(18) | 10.619(9) |
| $c$ (Å) | 17.908(2) | 12.539(11) |
| $\alpha$ (deg) | 77.94(2) | 83.59(10) |
| $\beta$ (deg) | 79.05(2) | 75.42(10) |
| $\gamma$ (deg) | 66.86(2) | 88.44(10) |
| $V$ (Å$^3$) | 2737.5(6) | 1025.3(15) |
| $Z$ | 1 | 2 |
| $D_{calc}$ (mg m$^{-3}$) | 2.907 | 1.891 |
| $\mu$ (mm$^{-1}$) | 13.856 | 1.707 |
| $F$[000] | 2197 | 590 |
| Crystal size (mm$^3$) | 0.12 × 0.08 × 0.08 | 0.40 × 0.30 × 0.18 |
| $\theta$ range for data collection (deg) | 1.67 to 25.00 | 1.69 to 26.39 |
| reflections collected/ unique | 26015/9587 | 10844/4168 |
| $R$ (int) | 0.0682 | 0.0225 |
| data/restraints/ parameters | 9587/0/767 | 4168/0/319 |
| goodness-of-fit on $F^2$ | 1.128 | 1.067 |
| $R_1/wR_2$ [$I > 2\sigma(I)$] | 0.0761/0.1582 | 0.0339/0.0884 |
| $R_1/wR_2$ (all data) | 0.1035/0.1699 | 0.0377/0.916 |
| largest difference Peak/ hole (e Å$^{-3}$) | 2.911 and −3.014 | 0.759 and −0.769 |

## RESULTS AND DISCUSSION

**Synthesis.** The reactions of Cu salts [$Cu(SO_4)_2{\cdot}5H_2O$ for **1** and $CuCl_2{\cdot}2H_2O$ for **2**], with organoamine ligand 2,2′-bipyridine, phosphonic acid ($H_4L$), and $Na_2WO_4$ for **1**/ $NH_4VO_3$ for **2** at 180 °C under hydrothermal conditions for 72 h afford crystalline compounds **1** in low yield and **2** in modest yield. Compound **1** is formed in the pH range between 4.0 to 4.5, and its formation is purely pH dependent. The initial pH of the reaction mixture before the addition of $H_3PO_4$ is 7.32; by addition of 0.1 mL $H_3PO_4$, the initial pH decreases to 6.27, finally the pH was adjusted to 4.20 with 5 M HCl to obtain compound **1** in a very low yield in pure crystalline form. The further decrease in pH results in the formation of two different products {i.e., $[Cu(2,2'\text{-bpy})(H_2L)]_n{\cdot}nH_2O$ (pH 2.5−3.5) and $[\{Cu(H_2O)(2,2'\text{-bpy})(H_3L)\}_2(H_2L)]{\cdot}2H_2O$ (pH below 2.0)}.[25] Increasing the pH above 4.5 results in the formation of amorphous blue-colored powder but does not increase the yield of the compound.

Compound **1**, a mixed-valent compound with Cu(II)/Cu(I) oxidation states, even though the starting copper precursor is in only a +2 oxidation state. The probable reducing agent is 2,2′-bipyridine at the elevated temperature (180 °C, hydrothermal synthesis condition), which itself can be oxidized to the corresponding N-oxide. The low yield of compound **1** (in

**Table 2. Selected Bond Lengths (Å) for Compounds 1 and 2[a]**

| compound 1 | | | |
|---|---|---|---|
| W(1)−O(1) | 1.672(15) | W(1)−O(7) | 1.893(17) |
| W(1)−O(8) | 1.87(2) | W(1)−O(9) | 1.927(12) |
| W(1)−O(10) | 1.858(17) | W(1)−O(19A) | 2.36(2) |
| W(1)−O(20B) | 2.53(2) | W(2)−O(2) | 1.684(13) |
| W(2)−O(10) | 1.881(18) | W(2)−O(11) | 1.90(2) |
| W(2)−O(12) | 1.85(2) | W(2)−O(19A) | 2.39(2) |
| W(2)−O(15)#1 | 1.872(19) | W(2)−O(19B)#1 | 2.50(2) |
| W(3)−O(3) | 1.677(16) | W(3)−O(8) | 1.874(18) |
| W(3)−O(12) | 1.889(17) | W(3)−O(13) | 1.886(14) |
| W(3)−O(19A) | 2.29(2) | W(3)−O(17)#1 | 1.886(15) |
| W(3)−O(20A) | 2.550(21) | W(4)−O(4) | 1.673(15) |
| W(4)−O(13) | 1.877(14) | W(4)−O(14) | 1.903(18) |
| W(4)−O(20A) | 2.424(19) | W(4)−O(19B) | 2.29(2) |
| W(4)−O(18)#1 | 1.868(15) | W(4)−O(11)#1 | 1.898(16) |
| W(5)−O(5) | 1.676(15) | W(5)−O(9) | 1.827(13) |
| W(5)−O(14) | 1.840(19) | W(5)−O(15) | 1.883(17) |
| W(5)−O(16) | 1.904(16) | W(5)−O(19B) | 2.39(2) |
| W(5)−O(20B) | 2.41(2) | W(6)−O(7) | 1.880(18) |
| W(6)−O(16) | 1.854(13) | W(6)−O(17) | 1.894(14) |
| W(6)−O(18) | 1.919(15) | W(6)−O(20B) | 2.27(2) |
| W(6)−O(20A)#1 | 2.38(2) | | |
| Cu(1)−O(26) | 1.926(13) | Cu(1)−O(23) | 1.939(11) |
| Cu(1)−N(1) | 2.008(18) | Cu(1)−N(2) | 2.020(16) |
| Cu(1)−O(2) | 2.235(13) | Cu(2)−O(25) | 1.928(12) |
| Cu(2)−O(22) | 1.964(12) | Cu(2)−N(3) | 2.005(14) |
| Cu(2)−N(4) | 2.015(14) | Cu(2)−O(22)#2 | 2.264(11) |
| Cu(3)−O(21) | 1.901(12) | Cu(3)−O(24) | 1.907(12) |
| Cu(3)−N(5) | 1.983(16) | Cu(3)−N(6) | 2.014(15) |
| P(1)−O(20A) | 1.52(2) | P(1)−O(20B) | 1.62(2) |
| P(1)−O(19B) | 1.63(2) | P(1)−O(19A) | 1.70(2) |
| P(2)O(21)− | 1.503(12) | P(2)−O(22) | 1.515(11) |
| P(2)−O(23) | 1.498(12) | P(2)−O(24) | 1.503(13) |
| P(2)−O(25) | 1.518(13) | P(2)−O(26) | 1.511(13) |
| compound 2 | | | |
| O(13)−V(1) | 1.584(5) | O(2)−P(1) | 1.4977(18) |
| O(13)−Cu(1)#1 | 2.229(5) | O(3)−P(1) | 1.5174(19) |
| O(13A)−V(1) | 1.731(9) | O(4)−P(1) | 1.5483(19) |
| O(13A)−Cu(1)#1 | 2.297(9) | O(4)−V(1) | 1.8761(18) |
| O(12)−V(1) | 1.617(11) | O(5)−P(2) | 1.5137(18) |
| O(12A)−V(1) | 1.555(7) | O(6)−P(2) | 1.537(2) |
| Cu(1)−O(2) | 1.9146(18) | O(6)−V(1)#4 | 1.872(2) |
| Cu(1)−O(5) | 1.9358(18) | O(7)−P(2) | 1.533(2) |
| Cu(1)−N(1) | 2.001(2) | V(1)−O(6)#1 | 1.872(2) |
| Cu(1)−N(2) | 2.003(2) | V(1)−O(9) | 2.332(3) |
| Cu(1)−O(13)#4 | 2.229(5) | O(9)−O(9)#5 | 1.847(7) |
| Cu(1)−O(13A)#4 | 2.297(9) | | |

[a]Symmetry transformations used to generate equivalent atoms: #1 −x + 1, −y, −z, #2 −x, −y +1, −z +1 (compound 1); #1 x − 1, y, z; #4 x + 1, y, z; and #5 −x − 1, −y, −z + 1 (compound 2).


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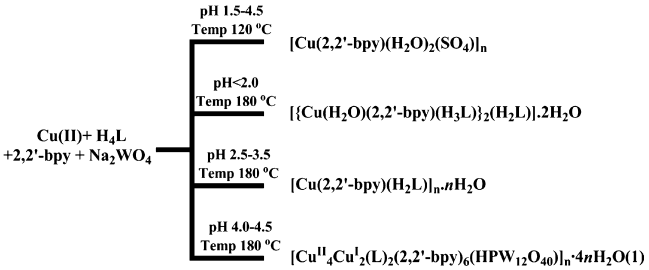
comparison to the yield of compound **2**) is consistent with this fact.

When we use $H_3PW_{12}O_{40}$ instead of $Na_2WO_4$ in stiochiometric ratio, the initial pH of the reaction mixture drastically decreases to 1.80, and in this pH range, the hydroxyl groups in the $H_4L$ do not deprotonate and the reaction mixture favors the formation of the more thermodynamically and kinetically stable phase $[\{Cu(H_2O)(2,2'\text{-bpy})(H_3L)\}_2(H_2L)]\cdot 2H_2O$.[25] The observations in the synthetic procedure imply that the thermodynamic equilibrium in the formation of compound **1** is much less and pertained to a particular pH range and the concentration of the reactants (see Scheme 2). The initial pH of the reaction mixture in the case of compound **2** is 2.70; in this pH range, $H_4L$ exists in the doubly deprotonated form $H_2L$. The formation of compound **2** is straightforward and does not require much stringent synthetic conditions to be obtained in modest yields, unlike compound **1**.

**Scheme 2. Different Products Formed in the Synthesis of Compound 1**




**Description of the Crystal Structures.** *$[Cu^{II}_4Cu^{I}_2(L)_2(2,2'\text{-bpy})_6(HPW_{12}O_{40})]_n\cdot 4nH_2O$ (1).* Compound **1**, that has a 3D structure, crystallizes in the triclinic space group $P\bar{1}$; the relevant crystal data and structural refinement parameters are presented in Table 1. The molecular structure consists of $\alpha$-disordered classical Keggin polyanion connected to a hexa-nuclear copper phosphonate complex; there are four solvent water molecules per formula unit in the crystal lattice (Figure 1a). The 3D structure is composed of 2D hexa-nuclear copper phosphonate layers connected by the disordered classical Keggin heteropolyanions $[HPW_{12}O_{40}]^{2-}$.

The well-known Keggin anion structure is constituted by the central $PO_4$ tetrahedron that shares its oxygen atoms with four $W_3O_{13}$ groups, which are made up of three edge-sharing $WO_6$ octahedra. Each $W_3O_{13}$ subunits are joined to each other by a corner-sharing mode. The central phosphorus atom is surrounded by a cube of eight oxygen atoms $\{PO_8\}$, with each oxygen site half occupied, in contrast to the regular $PO_4$ tetrahedron (Figure 1b). The W−O bond distances in the polyanion $[HPW_{12}O_{40}]^{2-}$ are in the range of 1.673−1.686 Å for terminal oxygen atoms, 1.847−1.913 Å for $\mu_2$-bridging oxygen atoms, and 2.285−2.542 Å for $\mu_3$-bridging oxygen atoms, respectively. The P−O bond distances vary in the range of 1.524−1.683 Å, with a mean value of 1.614 Å. The disorder in the oxygen atoms connected to the central atom reflects in the slight deviation of the W−O bond distances in the cases of $\mu_2$ and $\mu_3$ bridging oxygen atoms from the predicted distances.[30]

Bond valence sum calculations show that all the tungsten sites exhibit a +6 oxidation state in the $PW_{12}$ polyanion.[31] The coordination environment and W−O distances of the all the tungsten atoms are almost similar, which ruled out the +5 oxidation states of the W atoms (i.e., $\{PW^{VI}_{11}W^{V}\}^{4-}$ and $\{PW^{VI}_{10}W^{V}_{2}\}^{5-}$). Usually, the W−O distances around the $W^V$ centers (av. 1.810 for terminal oxygen atoms) are slightly longer than those around the $W^{VI}$ centers (av 1.680 for terminal oxygen atoms in compound **1**).[32] On the basis of the bond valence sum calculations and W−O distances, the polyanion was formulated as $[HPW_{12}O_{40}]^{2-}$ and a proton was added to balance the charge of the compound.[33] The $PW_{12}$ polyanions coordinate to two Cu ions (Cu1 and Cu1#) in a bidentate para coordination mode.

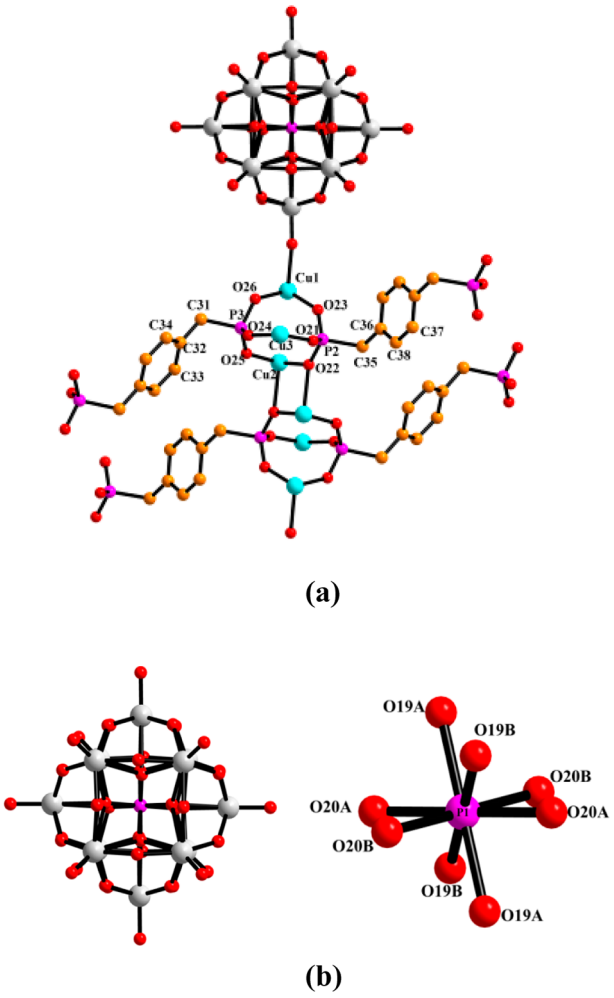



**Figure 1.** (a) Molecular diagram of compound **1** (2,2′-bpy moieties and lattice water molecules are removed for clarity). (b) Pictorial representation of classical keggin ion and disordered $PO_4$ group.

The most striking structural feature of compound **1** is the presence of 2D layers constituted by the mixed valent hexa-nuclear copper phosphonate clusters $[Cu^{II}_4Cu^{I}_2(L)_2(2,2'\text{-bpy})_6]^{2+}$. The hexa-nuclear cluster is an assembly of four Cu atoms (Cu1, Cu2, Cu1*, and Cu2*) in a dipositive state which are in $\{CuN_2O_3\}$ square pyramidal geometry and two Cu atoms (Cu3 and Cu3*) in the +1 oxidation state and exist in $\{CuN_2O_2\}$ distorted square planar geometry. The oxidation states of the Cu atoms are confirmed by the bond-valence sum calculations and particular coordination geometries around Cu. Two coordination sites of each Cu atom are blocked by the 2,2′-bpy ligands to form a $[Cu(bpy)]^{n+}$ subunits, and these units are connected by the coordination of four $L^{4-}$ (*p*-xylylenediphosphonic acid, $H_4L$) ligands to form a hexanuclear cluster (Figure 2a). Among the two pairs of terminal Cu atoms (Cu1, Cu3 and Cu1*, Cu3*), each pair is connected by the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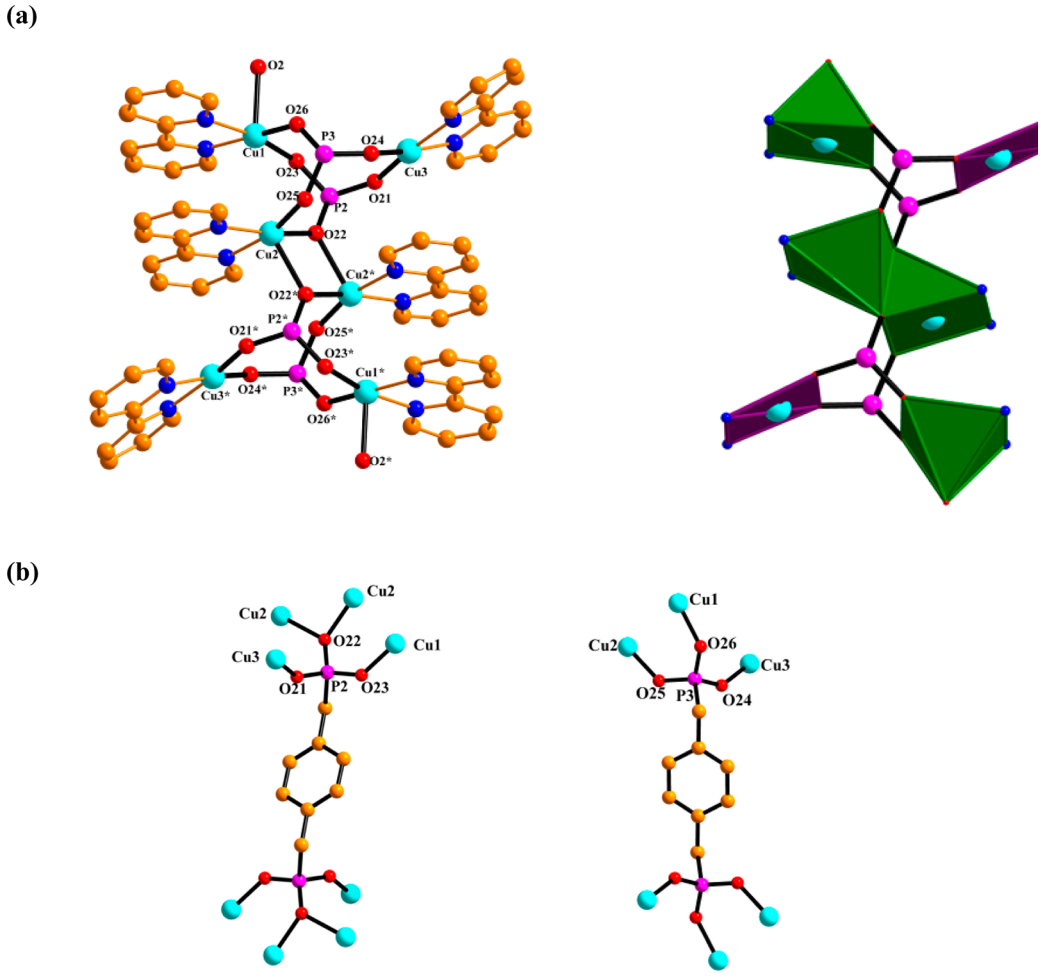


**Figure 2.** (a) Cu-hexamer, present in compound **1** with atom labeling, and its polyhedral representation, (b) different coordination modes of the $L^{4-}$ ligand (4.211 left and 3.111 right).

OPO bridges from two $L^{4-}$ ligands to form an eight- membered {Cu1(OPO)$_2$Cu3} ring. The central Cu atoms (Cu2 and Cu2*) are bridged by the two oxygen atoms (O22 and O22*) from two $L^{4-}$ ligands to form a four-membered $Cu_2O_2$ ring, which is sandwiched between the two eight-membered rings (as described above) to form a hexa nuclear assembly as shown in Figure 2a. The four phosphonate ligands $L^{4-}$, used for coordination of six Cu atoms, are classified into two types (P2, P2* and P3, P3*) which differ mainly in terms of their coordination mode. The ligands, namely, P2 and P2* coordinate to the four Cu atoms in the 4.211 coordination mode by bridging the terminal Cu atoms through the phosphonate oxygen atoms (O21, O23 and O21*,O23*), and the residual oxygen atoms O22 and O22* of the phosphonate groups bridge the two central Cu atoms as shown in Figure 2b. On the other hand, the ligands P3 and P3* coordinate to three Cu atoms in the 3.211 coordination mode by bridging the terminal Cu atoms through the phosphonate oxygen atoms (O24, O26 and O24*, O26*), but the residual oxygen atoms O25 and O25* are just connected to the central Cu atoms of the four-membered ring $Cu_2O_2$, as shown in Figure 2b. Each hexanuclear cluster connects to four other clusters through a pair of phosphonate ligands to form a 2D layer, as shown in Figure 3a. These 2D layers are connected to $PW_{12}$ polyanions through terminal oxygen atoms O2 and O2* to form a 3D framework as shown in Figure 3b. The hexanuclear cluster, reported in the compound **1**, is structurally related to the hexanuclear complexes reported in the literature.[26] But, in the reported compounds, all the Cu atoms in the cluster are present in the +2 oxidation state and in square pyramidal geometry. However, in the present work, the hexanuclear cluster in compound **1** is comprised of two different coordination geometries (square pyramidal and distorted square planar) and two different valence states (+2 and +1) of copper atoms. These exclusive features distinct the hexanuclear cluster in compound **1** from the other reported hexanuclear clusters.[26]

Compound **1** represents a unique example, in which the dimensionality of the $Cu_6$ cluster is extended in the layer through the *p*-xylyl linkers, and the layers are connected to each other by the inorganic $PW_{12}$ linkers. The distance between two layers along the length of the $PW_{12}$ is 14.69 Å. In the reported compounds, only monophosphonic acid was used, and thereby the dimensionality of $Cu_6$ has been extended by the terminal Cu atoms through the apically connected linkers like 4,4′-bpy etc., which results in the formation of only 1D chains. But in the present study, the use of a bisphosphonic acid and inorganic linker result in the formation of a novel 3D framework, based on the $Cu_6$ cluster and Keggin-type polyoxometalate (POM) anion.

*[Cu(2,2′-bpy)VO$_2$(OH)(H$_2$L)]$_n$* (**2**). Compound **2** is a 2D coordination polymer that crystallizes in the triclinic space


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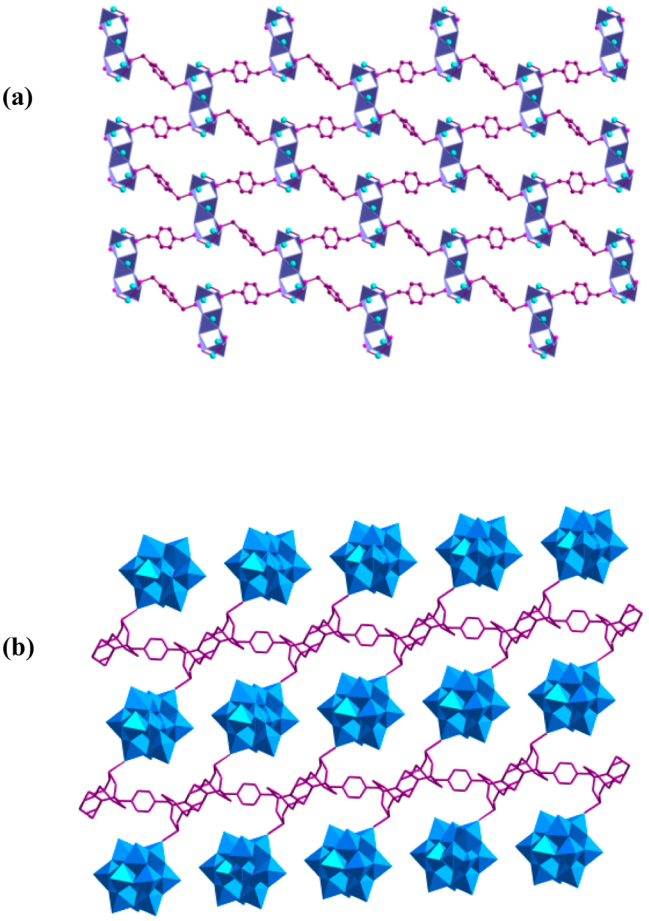


**Figure 3.** (a) 2D Metal phosphonate layers in compound **1**; blue polyhedra represent the hexameric units. (b) 3D Framework formed due to connectivity of metal phosphonate layers with keggin ions (2,2′-bpy units are removed for clarity).

group $P\bar{1}$. The relevant asymmetric unit contains the Cu atom in a dipositive state, one 2,2′-bipyridine, two $H_2L$ ligands, $VO_2$ group, and one hydroxyl group. Bond valence sum calculations show that the Cu and V atoms are present in the +2 and +5 oxidation states, respectively. As shown in the Figure 4, the square pyramidal $CuN_2O_3$ completes its coordination sphere through two nitrogen atoms from the bpy ring (Cu−N1: 2.001 Å and Cu−N2: 2.003 Å), two phosphonate oxygen atoms (O5 and O2) from two different $H_2L$ ligands in the basal plane, and the apical site is coordinated to oxygen atoms from the $VO_2OH$ group. V(V) atom is also present in the square pyramidal $VO_4OH$ geometry in which two phosphonate oxygen atoms (V1−O4: 1.876 Å and V1−O6: 1.874 Å), two terminal oxygen atoms (V1−O13: 1.584 Å and V1−O12: 1.617 Å), and one hydroxyl group (V1−O9: 2.332) complete its coordination sphere. The square pyramidal polyhedra of two metal centers, $CuN_2O_3$ and $VO_4OH$ are connected to each other by the corner sharing oxygen atom, O1, as shown in Figure 5a. These

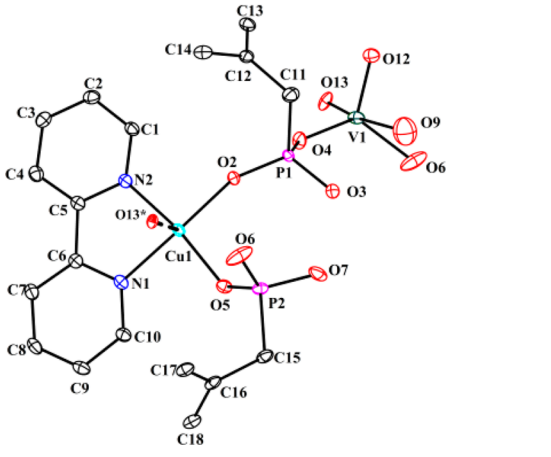


**Figure 4.** A ORTEP view of the basic unit of **2**. Hydrogen atoms are removed for clarity. Thermal ellipsoids are at the 40% probability level.

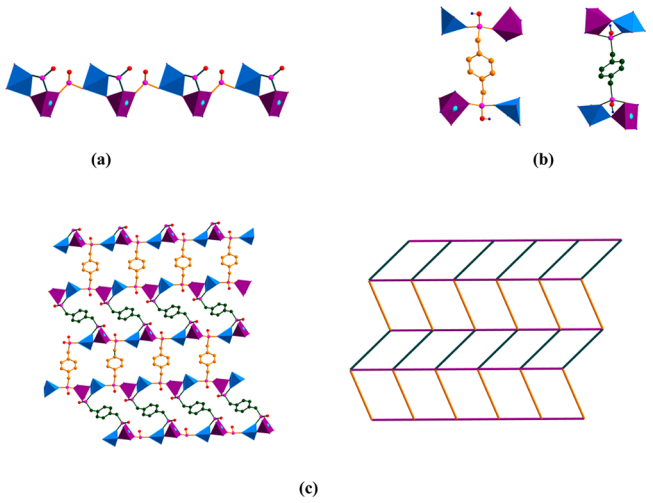


**Figure 5.** (a) 1D chain, formed due to connectivity of $CuN_2O_3$ (purple colored) and $VO_4OH$ (blue colored) polyhedra with $H_2L$ ligand in **2**, (b) connectivity of $H_2L_A$ (right) and $H_2L_B$ (left) ligands, and (c) a 2D layer in compound **2** and its topological representation (2,2′-bpy units are removed for the clarity).

double polyhedra are connected to another such set along the axis and along the layer with the aid of bisphosphonate ligand $H_2L$ in a 2.110 coordination mode. Two types of $H_2L$ ligands are present in the crystal structure, which differs in the orientation and mode of coordination. Let us consider the phosphonic acid $H_2L_A$ (shown in orange in Figure 5b) that links the adjacent of double polyhedra through the phosphonate oxygens O2 and O4 along the *a* axis, to form a 1D chain, and another phosphonic acid $H_2L_B$ (shown in green in the Figure 5b) that chelates the Cu(II) and V(V) atoms of the double polyhedra with the phosphonate oxygens O6 and O5, resulting in the formation of a six-membered ring.

The 1D chains, formed due to connectivity of $H_2L_A$ with the double polyhedra along the crystallographic *a* axis, are extended to 2D layers by the *p*-xylyl spacers in both $H_2L_A$ and $H_2L_B$ ligands to form a 2D layer with alternate grids, as shown in the Figure 5c. Due to the difference in the type of coordination mode, the length of the ligand changes; as a result, the distance between the chains in the layer vary.

**Comparison among the Structures Involving Metal Oxides and Metal Phosphonate Complexes.** In our previous report, we discussed the mechanistic aspects in the formation and stabilization of the eight-membered Cu-dimer ring in the coordination matrix and extended the dimensionality of the Cu-dimer by organic and inorganic linkers.[25] When we introduce sodium molybdate in the Cu/*p*-xylylenebisphosphonic acid/2,2′-bipyridine system, it results in the formation of a 2D network, in which the 1D Cu-dimer chains


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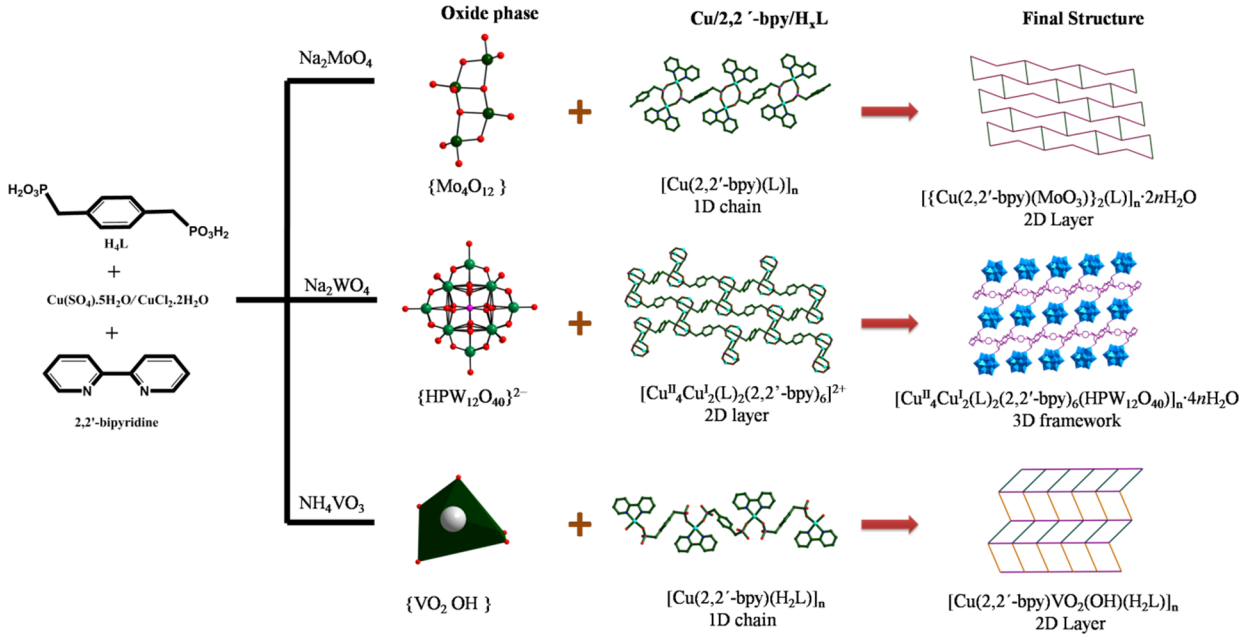
**Scheme 3. Schematic Representation of the Self Assembly of the Metal-oxides and Metal Organophosphonate Phases**




$$CuSO_4.5H_2O \xrightarrow{H_2O} [Cu(H_2O)_6]^{2+}\,SO_4^{2-}$$

$$[Cu(H_2O)_6]^{2+}\,SO_4^{2-} + 2,2'\text{-bpy} \xrightarrow{120\ ^oC} [Cu(2,2'\text{-bpy})(H_2O)_2SO_4]_n$$

$$12WO_4^{2-} + PO_4^{3-} + 25H^+ \xrightarrow{pH=4.20} \{HPW_{12}O_{40}\}^{2-} + 12H_2O$$

$$6[Cu(2,2'\text{-bpy})(H_2O)_2SO_4]_n + 2nH_4L \xrightarrow{180\ ^oC}$$

$$[Cu^{II}_4Cu^{I}_2(L)_2(2,2'\text{-bpy})_6]_n^{2n+} + 6nSO_4^{2-} + 12nH_2O + 8nH^+ - 2ne^-$$

$$[Cu^{II}_4Cu^{I}_2(L)_2(2,2'\text{-bpy})_6]_n^{2n+} + n\{HPW_{12}O_{40}\}^{2-} + 4nH_2O \xrightarrow{180\ ^oC}$$

$$[Cu^{II}_4Cu^{I}_2(L)_2(2,2'\text{-bpy})_6(PW_{12}O_{40})]_n\cdot 4nH_2O\ (1)$$

$$[Cu(2,2'\text{-bpy})(H_2O)_2SO_4]_n + nH_4L \xrightarrow{180\ ^oC} [Cu(2,2'\text{-bpy})H_2L]_n + nSO_4^{2-} + 2nH_2O + 2nH^+$$

$$VO_3^- + H^+ \xrightarrow{pH=2.70} VO_2OH$$

$$[Cu(2,2'\text{-bpy})H_2L]_n + nVO_2OH \xrightarrow{180\ ^oC} [Cu(2,2'\text{-bpy})VO_2OH(H_2L)]_n\ (2)$$

$[Cu(2,2'\text{-bpy})(L)]_n$ are linked by the inorganic linker tetramolybdate ($Mo_4O_{12}$). In this process of extending the dimensionality of the Cu dimers by inorganic linkers, we introduced (in the present study) sodium tungstate and ammonium metavanadate in the Cu/*p*-xylylenebisphosphonic acid/2,2′-bipyridine system to form compounds **1** and **2**, respectively. The plausible mechanism for the formation of compounds **1** and **2** is shown in the following equations and in Scheme 3. As shown in Scheme 3, the tungstate $WO_4^{2-}$ ions in the presence of $H_3PO_4$, undergo a self-assembly process to form a $\alpha$-disordered Keggin anion and the metal/organoamine/phosphonate favors the formation of 2D $[Cu^{II}_4Cu^{I}_2(L)_2(2,2'\text{-bpy})_6]$ layers, consisting of the mixed-valent hexanuclear assemblies. The overall assembly of the polyanion Keggin with the metal phosphonate layers result in the formation of 3D architecture, in which the 2D metal phosphonate layers are linked by the Keggin anions.

In a similar way, the employment of ammonium metavandate in the synthesis results in the formation of $VO_2OH$ and 1D $[Cu(2,2'\text{-bpy})H_2L]_n$ chains, and the connectivity of these subunits gives rise a 2D layer. In this compound, the Cu/*p*-xylylenebisphosphonic acid/2,2′-bipyridine system does not form a dimer or a hexamer, as shown in the above-described compounds. The phosphonate oxygen atoms, which are accountable for the formation of the dimer, are connected to the $VO_2OH$ group and thereby prevents the formation of the dimer. As shown in the scheme 3, different POMs favor the different metal phosphonates phases. In these compounds,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POMs increase the dimensionality of the metal phosphonates by linking them in different directions.

The $\chi_M T$ value of compound **1** at room temperature (300 K) is 1.9 $cm^3$ K $mol^{-1}$, which is slightly higher than the expected value of four uncoupled $Cu^{II}$ ions (1.5 $cm^3$ K $mol^{-1}$ for $S = 1/2$ and $g = 2$). This value also indicates the presence of four $Cu^{II}$ and two $Cu^{I}$ ions in the pertinent cluster (ideal value for six $Cu^{II}$ ions is 2.25 $cm^3$ K $mol^{-1}$). From the crystal structure, the dominant exchange interactions are observed only between the two central $Cu^{II}$ ions, bridged by the $\mu_2$ oxygen atoms (O22 and O22*) from two phosphonate ligands with a $Cu^{II}$–$Cu^{II}$ separation of 3.160 Å. The other possible exchange interactions between the $Cu^{II}$ ions through the O–P–O bridges of phosphonate ligands are supposed to be very weak due to long $Cu^{II}$–$Cu^{II}$ separation.

## CONCLUSION

Inorganic oxides represent the most important class of materials as far as stability and application aspects are concerned. In order to investigate the self-assembly process of bimetallic inorganic oxides involving metal organophosphonates, herein, we have identified a 3D covalently linked material $[Cu^{II}_4Cu^{I}_2(L)_2(2,2'\text{-bpy})_6(HPW_{12}O_{40})]_n \cdot 4nH_2O$ (**1**) and a 2D compound $[Cu(2,2'\text{-bpy})VO_2(OH)(H_2L)]_n$ (**2**). The attractive feature of this article is that in compound **1**, hexanuclear assemblies of Cu metal phosphonates layers are extended by the inorganic linker $PW_{12}$ (so-called Keggin cluster anion). Compound **1** is a distinct example that features the existence of mixed-valent Cu-hexamer in the 3D coordination matrix. The formation of $VO_2OH$ in compound **2** prevents the formation of the eight-membered Cu dimer rings, which has been discussed in mechanistic relevance. The isolation of the different metal phosphonate phases under different metal oxides reveals the mechanistic aspects in the self-assembly process of MOP oxide materials.

## ASSOCIATED CONTENT

### Supporting Information

Thermogravimetric curves and tables of complete bond distances and angles for compounds **1** and **2** and X-ray crystallographic files in CIF format for compounds **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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