Construction of 1D Chain from Diphosphopentamolybdate Cluster and Copper Complex: Synthesis and Characterization of $\{Cu(DETA)\}_2[\{Cu(DETA)(H_2O)\}Mo_5P_2O_{23}]\cdot 4.5H_2O$

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A novel organic–inorganic hybrid based on diphosphopentamolybdate cluster, $\{Cu(DETA)\}_2[\{Cu(DETA)(H_2O)\}Mo_5P_2O_{23}]\cdot 4.5H_2O$ [DETA: diethylenetriamine] (**1**), has been synthesized by hydrothermal method and characterized by X-ray crystallography, showing that the $[Mo_5P_2O_{23}]^{6-}$ cluster, which supported by the $\{Cu(DETA)(H_2O)\}^{2+}$ unit, is linked through two $\{Cu(DETA)\}^{2+}$ bridging units to construct a 1D chain-like infinitely extended structure. Each chain is further linked to two adjacent chains by hydrogen bonds to yield a 2D layer parallel to the *ac* plane.

Much contemporary research activity in polyoxometalate (POM) chemistry is driven by potential and realized applications in many different areas, including catalysis, separations, magnetism, photochemistry, and medicine.[1] Recently, the study of POMs covalently linked by transition-metal complex fragments has received considerable attention, leading to new classes of compounds exhibiting unique structures and properties.[2] Among the wide variety of POMs, the Keggin series,[3] with formula $[XM_{12}O_{40}]^{n-}$, has been most studied. In contrast, few studies have been devoted to Strandberg-type POM,[4] in particular, to diphosphopentamolybdate cluster supported or bridged transition-metal complexes. To date, only several of this kind of compound have been reported, examples including $[H_2en]_2[\{Cu(en)(OH_2)\}[Mo_5P_2O_{23}]\cdot 4H_2O]$,[4a] $(Hbpy)_2\{[(H_2O)_3\text{-}Ni(bpy)_{0.5}Ni(bpy)(H_2O)_4]_2[Mo_5P_2O_{23}][Ni((bpy)_{0.5})_2(H_2O)_2]\text{-}Mo_5P_2O_{23}]\}\cdot 8H_2O$,[4c] $(H_2bpy)_{0.5}\{[Ni(H_2O)_5][Ni(Hbpy)(H_2O)_4][Mo_5P_2O_{23}]\}$,[4d] and $[Cu(phen)(H_2O)]_3[(PO_4)_2Mo_5O_{15}]\cdot 5H_2O$.[4e] As is clear from the extensive significance of Strandberg-type polyoxometalate supported transition-metal complexes, great efforts have been made by us to study the assembly of diphosphopentamolybdate with secondary metal–organicamine complexes. By using hydrothermal technique under appropriate conditions, a novel diphosphopentamolybdate cluster-supported transition-metal complex $\{Cu(DETA)\}_2[\{Cu(DETA)(H_2O)\}\text{-}Mo_5P_2O_{23}]\cdot 4.5H_2O$ (**1**) [DETA: diethylenetriamine] with an interesting one-dimensional chain-like structure has been obtained.

Compound **1** was synthesized by a hydrothermal method.[5] The X-ray diffraction analysis[6] reveals that the structure unit of compound **1** consists of one $[Mo_5P_2O_{23}]^{6-}$ cluster anion, one supporting group $\{Cu(DETA)(H_2O)\}^{2+}$, two bridging groups $\{Cu(DETA)\}^{2+}$ and 4.5 water molecules. In the compound unit, the $[Mo_5P_2O_{23}]^{6-}$ cluster anion[8] is covalently bonded to one $\{Cu(DETA)(H_2O\}^{2+}$ and two $\{Cu(DETA)\}^{2+}$ cations as shown in Figure 1. As in other diphosphopentamolybdate clusters,[7] the geometry of the $[Mo_5P_2O_{23}]^{6-}$ cluster can be described as a puckered ring of five distorted $[MoO_6]$ octahedra with two $[PO_4]$ tetrahedra capped on each side. Each phosphate unit shares three oxo groups with the molybdate ring. In turn, one of these oxo groups adopts the μ_2-bridging mode, linking one molybdenum site and the phosphorous atom, and the other two adopt the μ_3-bridging mode, linking two molybdenum sites and the phosphorous atom (Figure S1).[4d] The Mo–O bond distances range from 1.707(3) to 1.745(2) Å for terminal oxygen, from 1.901(2) to 1.948(2) Å for O bonded to two Mo atoms, from 2.181(2) to 2.201(2) Å for O bonded to one Mo atom and one P atom, and from 2.1796(19) to 2.396(2) Å for O bonded to two Mo atoms and one P atom. The P–O bond distances range from 1.519(2) to 1.562(2) Å.

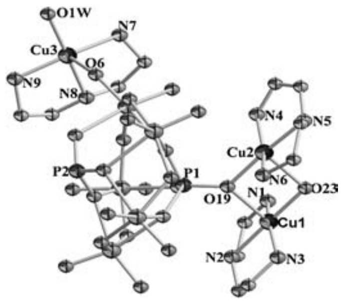

Figure 1. ORTEP drawing of the structure unit of compound **1** (50% thermal ellipsoids), H atoms are omitted for clearity.

In each structure unit of compound **1**, $[Mo_5P_2O_{23}]^{6-}$ cluster anion is linked to three copper atoms (Cu(1), Cu(2), and Cu(3)) through two $[PO_4]$ tetrahedra and one $[MoO_6]$ octahedron to form two kinds of covalent interactions of the types Cu–O–P and Cu–O–Mo. The coordination geometry for the three copper atoms are all in five-coordinate square-pyramidal structures, in which Cu(1) and Cu(2) are coordinated by two terminal P=O groups and Cu(3) is coordinated by a terminal Mo=O group of the $[Mo_5P_2O_{23}]^{6-}$ cluster. The $Cu(1)^{2+}$ center of $\{CuN_3O_2\}$ square pyramid receives contributions from three nitrogen atoms belonging to one DETA molecule and two oxygen atoms from two $[PO_4]$ tetrahedra belonging to two $[Mo_5P_2O_{23}]^{6-}$ cluster anions (the Cu(1)–N and Cu(1)–O distances are in the range of 2.006–2.024 and 2.307–1.967 Å, respectively). The coordination environment of Cu(2) is similar to that of Cu(1) (Cu(2)–N and Cu(2)–O distances are in the range of 1.999(5)–2.012(5) and 1.954(3)–2.282(3) Å, respectively). The Cu(3) site is defined by three nitrogen donors from a tridentate ligand of DETA molecule with average Cu(3)–N distance of 2.014 Å, one oxygen donor from water and one oxygen from $[MoO_6]$ octahedron with Cu(3)–O(1W) and Cu(3)–O(6) distances of 2.016(5) and 2.399 Å, respectively. Thus, the $\{CuN_3O_2\}$ square-pyramidal coordination spheres of Cu(1), Cu(2), and Cu(3) centers are Jahn–Teller distorted.[8] The copper coordination cation of $\{Cu(DETA)(H_2O)\}^{2+}$ supported on the cluster anion $[Mo_5\text{-}$

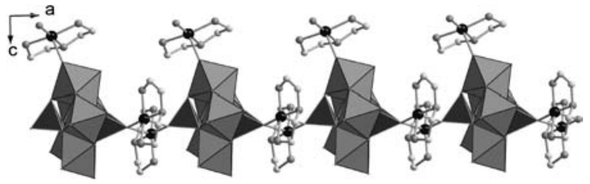

Figure 2. Polyhedral and ball-stick representation of the 1D organic–inorganic hybrid chain in compound **1**.

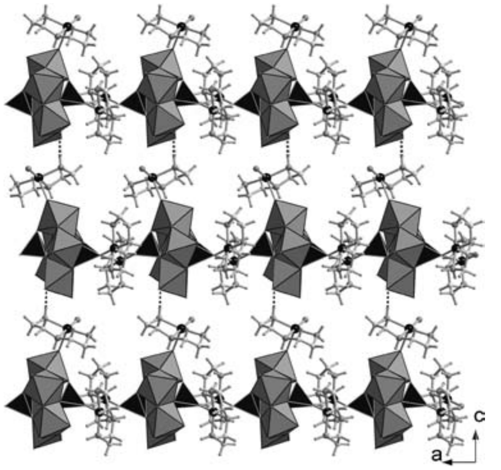

Figure 3. View of the 2D layer-like structure constructed from 1D chains linked through hydrogen-bonding interaction. (The dotted lines represent the NH···O hydrogen bonds).

$P_2O_{23}]^{6-}$ through the terminal oxo group of a common $[MoO_6]$ octahedron to form a building block of $[\{Cu(DETA)(H_2O)\}\text{-}Mo_5P_2O_{23}]^{4-}$, each of which is connected to two other neighboring cluster units via four $\{Cu(DETA)\}^{2+}$ bridging groups through the oxo groups of $[PO_4]$ tetrahedra forming a 1D infinitely extended chain composed of $[\{[Cu(DETA)(H_2O)]Mo_5\text{-}P_2O_{23}\}\{Cu(DETA)\}_2\{[Cu(DETA)(H_2O)]Mo_5P_2O_{23}\}]_n$, which align in parallel to the *a* axis (Figure 2).

An unusual structural feature of compound **1** is that the bridging groups of $\{Cu(DETA)\}^{2+}$ always occur in pairs and function as double bridges, these double bridges connect two adjacent diphosphopentamolybdate clusters via corner-sharing interactions of the type Cu–O–P. Therefore, the oxo groups of $[PO_4]$ units which coordinate to Cu(1) and Cu(2) adopt the μ_3-bridging mode. That is, Cu(1) and Cu(2) are connected to each other by sharing two terminal oxygen atoms of two $[PO_4]$ tetrahedra belonging to two $[\{Cu(DETA)(H_2O)\}Mo_5P_2O_{23}]^{4-}$ units with the Cu(1)–Cu(2) distance of 3.3039 Å.[8] To the best of our knowledge, the structural connection motif employed in the $[PO_4]$ units of $[Mo_5P_2O_{23}]^{6-}$ cluster has never been reported.

It is noteworthy that the structure of compound **1** exhibits hydrogen-bonding interaction among DETA ligands, $[Mo_5\text{-}P_2O_{23}]^{6-}$ units and water molecules with the NH···O distances of 2.840–2.985 Å. Each chain is linked to two adjacent chains by hydrogen bonds to yield a 2D layer parallel to the *ac* plane as shown in Figure 3. The space between the layers is filled with water molecules.

In summary, we have synthesized the 1D chain-like compound **1**, which constructed from cluster anion $[Mo_5P_2O_{23}]^{6-}$, supporting group $\{Cu(DETA)(H_2O\}^{2+}$ and bridging groups $\{Cu(DETA)\}^{2+}$. And a layer structure is formed via hydrogen-bonding interaction. Considering the variations in the transition-metal coordination complex linkers, the scope for the further synthesis of diphosphopentamolybdate-based hybrid organic–inorganic material appears to be very noteworthy.

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5 Synthesis of compound **1**: A mixture of $CuCl_2 \cdot 2H_2O$ (1.2 g), $Na_2MO_4 \cdot 2H_2O$ (1.6 g), H_3PO_4 (0.5 mL, 85%), diethylenetriamine ($NH(CH_2CH_2NH_2)_2$) (0.8 mL) and water (15 mL) was simply stirred (the initial pH value was adjusted to 6.20 by 2 M KOH), then sealed in a Teflon-lined strainless steel autoclave and heated at 170 °C for 7 days. After cooling to room temperature over 48 h, crystals as blue needles were obtained in 48% yield based on molybdenum. Elemental analysis Calcd for $C_{12}H_{50}N_9Cu_3Mo_5O_{28.5}P_2$ (1508.85): C, 9.55; H, 3.34; N, 8.35%. Found: C, 9.33; H, 3.43; N, 8.24%. IR (KBr) pellets, ν/cm^{-1}): 3317(w), 3238(w), 1621(m), 1454(w), 1384(w), 1262(w), 1096(m), 1068(m), 1034(s), 1017(s), 977(w), 961(w), 902(s), 882(s), 680(s), and 566(w).

6 Crystal data for **1** $C_{12}H_{50}Cu_3Mo_5N_9O_{28.50}P_2$: $M_r = 1508.85$, orthorhombic, $P2(1)2(1)2(1)$, $a = 9.2933(16)$ Å, $b = 17.967(3)$ Å, $c = 25.271(4)$ Å, $V = 4219.57(121)$ Å^3, $Z = 4$, $D_{calcd} = 2.358$ g/cm^3, $\mu = 3.093$ mm^{-1}, $F(000) = 2916$, $T = 296(2)$ K. 23690 reflections measured, 8288 independent ($R_{int} = 0.0332$), $R_1 = 0.0294$ ($I > 2\sigma(I)$), $wR_2 = 0.0828$ (all data). CCDC number: 696832.

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8 Supporting Information is available electronically on the CSJ-Journal web site, http://www.csj.jp/journals/chem-lett/index.html.

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