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Formation of a Spiral-Shaped Inorganic–Organic Hybrid Chain, $[Cu^{II}(2,2'\text{-bipy})(H_2O)_2Al(OH)_6Mo_6O_{18}]_n^{n-}$: Influence of Intra- and Interchain Supramolecular Interactions

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A novel chainlike coordination polymer $[Cu^{II}(2,2'\text{-bipy})(H_2O)_2Al(OH)_6Mo_6O_{18}]_n^{n-}$, formed from a heteropolyanion $[Al(OH)_6Mo_6O_{18}]^{3-}$ as a building unit and a copper(II) complex fragment, $[Cu^{II}(2,2'\text{-bipy})(H_2O)_2]^{2+}$, as a linker, provides the first example of an extended structure based on an Anderson type of polyanion and a transition metal complex with organic ligand. The intra- and interchain O–H···O hydrogen-bonding interactions are seemingly responsible for the spiral shape of this chain. Crystal data: triclinic space group $P\bar{1}$, $a = 11.2253(18)$ Å, $b = 14.5194(17)$ Å, $c = 15.2672(10)$ Å, $\alpha = 112.191(8)°$, $\beta = 106.693(9)°$, $\gamma = 93.916(13)°$, and $Z = 2$.

Polyoxometalate compounds have received much attention because of their potential applications in catalysis, sorption, magnetism, photochemistry,[1] etc. These metal oxo clusters are even more interesting when they support/attach transition metal (mainly d-block element) complexes, because of their applications in many interdisciplinary areas.[2] Structurally characterized examples of isopoly/heteropoly anion cluster-supported transition metal complexes include $[\{Cu(en)\}_2(Mo_8O_{26})]$,[3] $[\{Cu(4,4'\text{-bpy})\}_4(Mo_8O_{26})]$,[4] $[Ni(2,2'\text{-bpy})_3]_{1.5}[PW_{12}O_{40}Ni(2,2'\text{-bpy})_2(H_2O)]\cdot 0.5H_2O$,[5] $[H_2en]_2[\{Cu(en)(H_2O)\}Mo_5P_2O_{23}]\cdot 4H_2O$,[6] $[Cu_2(C_8H_6N_2)_2(C_7H_6N_2)]_2[Mo_8O_{26}]$, etc.[7]

We have been working on an Anderson type of heteropolyanion, $[Al(OH)_6Mo_6O_{18}]^{3-}$, and exploiting its linking propensity with metal ions to obtain extended structures of new materials. Recently, we have demonstrated that this discrete anionic cluster can be used as a building block to construct a one-dimensional chain using lanthanide ion ("f" block) as linker.[8] In addition, we[9] and also Perloff[10] have reported a three-dimensional network structure based on an Anderson type anion as a building unit using an "s" block element, sodium, as connecting ion. Now we have succeeded in connecting this versatile building unit by a transition metal ("d" block element) complex $Cu^{II}(2,2'\text{-bipy})(H_2O)_2^{2+}$ to form a new type of chain in the compound $[Cu^{II}(2,2'\text{-bipy})(H_2O)_2Cl][Cu^{II}(2,2'\text{-bipy})(H_2O)_2Al(OH)_6Mo_6O_{18}]\cdot 4H_2O$ **1**.

Compound **1** was prepared[11] as blue blocks from methanolic aqueous solution dissolving copper nitrate, 2,2′-bipyridine, sodium molybdate, aluminum chloride, acetic acid, and hydrochloric acid. The crystals of **1** were characterized by IR, elemental analysis, magnetic moment measurements,[12] visible and ESR spectroscopy, thermogravimetric analysis, and unambiguously by single-crystal X-ray diffraction technique.[13]

The crystal of **1** is made up of spiral-type chains, $[Cu^{II}(2,2'\text{-bipy})(H_2O)_2Al(OH)_6Mo_6O_{18}]_n^{n-}$ as anions, chloro−copper complexes, $[Cu^{II}(2,2'\text{-bipy})(H_2O)_2Cl]_n^{n+}$ as cations, and lattice waters. The chain is formed by Anderson anions $[Al(OH)_6Mo_6O_{18}]^{3-}$ linked to $[Cu^{II}(2,2'\text{-bipy})(H_2O)_2]^{2+}$ complexes as shown in Figures 1 and 2.

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(11) To an aqueous (50 mL) solution of $AlCl_3\cdot 6H_2O$ (1.5 g, 6.21 mmol), the 100 mL aqueous solution of $Na_2MoO_4\cdot 2H_2O$ (3.5 g, 14.46 mmol) was mixed followed by the addition of 10 mL of glacial CH_3CO_2H. 2,2′-Bipyridine (0.2 g, 1.28 mmol) dissolved in a mixture 15 mL of water and 25 mL of methanol and $Cu(NO_3)_2\cdot 2H_2O$ (0.5 g, 2.06 mmol) were added, and the pH of the resulting mixture was adjusted to 2.6 with the concentrated HCl and filtrate kept at room temperature. Blue blocks appeared within a week and were washed with water and dried at room temperature. Yield: 0.48 g (12% based on Mo).

(12) Selected data for **1**. IR (KBr pellet) (ν/cm^{-1}): 1602m, 1473m, 1444m, 1317w, 1246w, 898s, 767m, 636s, 567w, 443m. Anal. Calcd for $C_{20}H_{38}AlClCu_2Mo_6N_4O_{32}$ (1611.69): C, 14.90; H, 2.38; N, 3.48. Found: C, 14.96; H, 2.40; N, 3.44. Room temperature magnetic moment, 2.55 μ_B.

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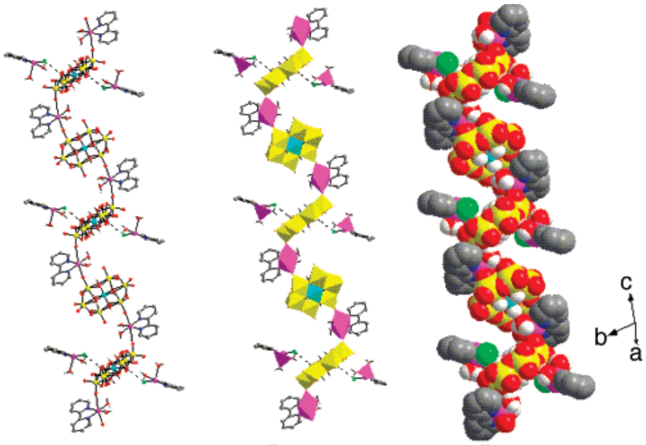

Figure 1. The structure of [Cu^{II}(2,2′-bipy)(H$_2$O)$_2$Cl][Cu^{II}(2,2′-bipy)(H$_2$O)$_2$-Al(OH)$_6$Mo$_6$O$_{18}$] showing spiral-type chainlike array of {Al(OH)$_6$Mo$_6$O$_{18}$}$^{3-}$ cluster anions interconnected through {Cu^{II}(bipy)(H$_2$O)$_2$}$^{2+}$ bridging copper complex fragments. Two chloro−copper complexes are hydrogen bonded, alternatively, to only one type of Anderson anion in the chain. Left: Ball-and-stick representation. Middle: Polyhedral representation. Right: Space-filling plot. Color code: Al, cyan; Mo, yellow; O, red; Cu, purple; Cl, green; N, blue; C, gray; H, white.

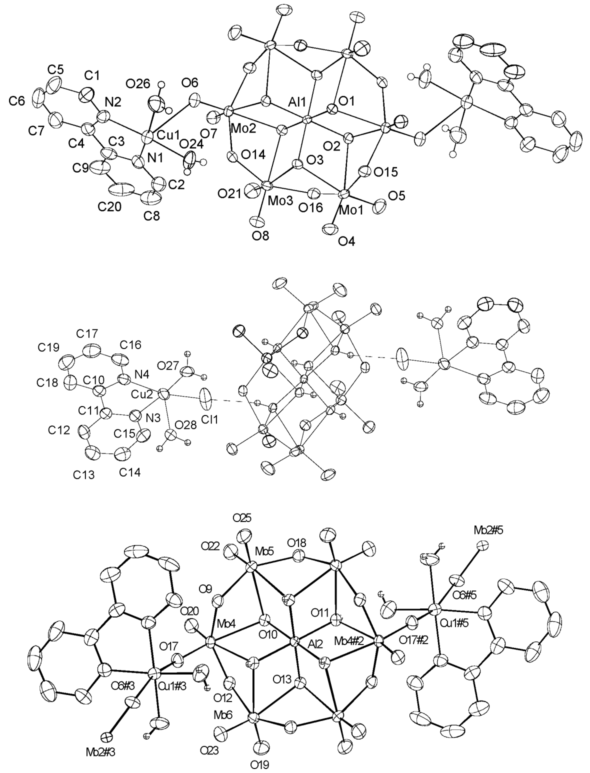

Figure 2. Top: Coordination of an Anderson anion via terminal oxygen atoms on molybdenum to Cu(bipy)(H$_2$O)$_2$$^{2+}$ complex fragments. Middle: Hydrogen-bonding interaction of the cation Cu(bipy)(H$_2$O)$_2$Cl^{1+} via O−H···Cl bonds to the same Anderson anion. Bottom: Linked Anderson heteropolyanion to Cu(bipy)(H$_2$O)$_2$$^{2+}$ complex fragments resulting in the formation of a chain. Thermal ellipsoid plots with 50% probability. Atoms with additional labels #2, #3, and #5 are related to each other by symmetry operations: #2 $-x + 1, -y + 1, -z + 1$; #3 $-x, -y + 1, -z + 1$; #5, $x + 1, y, z$.

The structure of the Anderson anion [Al(OH)$_6$Mo$_6$O$_{18}$]$^{3-}$ in the chain is similar to the structures reported earlier for other Anderson type anions.[14] This consists of seven edge-shared octahedra, six of which are molybdenum octahedra arranged hexagonally around the central octahedron, which is Al^{3+} in the present case (Figures 1 and 2).

The Anderson anion is centrosymmetric. The asymmetric unit in the crystal structure of **1** consists of two crystallographically independent "one-half" Anderson anions, in which both aluminum ions (Al(1) and Al(2) of two Anderson anions) occupy special positions. The chain (Figure 1) consists alternatively of Al(1) and Al(2) containing Anderson anions, which have two different orientations: alternatively they have identical configurations along the chain. In the polymer chain each cluster anion acts as a bidentate ligand coordinating two {Cu^{II}(2,2′-bipy)(H$_2$O)$_2$}$^{2+}$ complex fragments through the terminal oxygen atoms (Figure 1) of two nonadjacent MoO$_6$ octahedra.

There are two crystallographically independent copper sites comprising two different coordination environments around copper. The first one, the linker of the chain, is a distorted octahedron (Figure 1 and Figure 2, top and bottom), which is defined by two nitrogen coordination from the 2,2′-bipyridine ligand (Cu(1)−N(1) = 1.986(3), Cu(1)−N(2) = 1.980(3)), two water ligation (Cu(1)−O(24) = 1.945(3), Cu(1)−O(26) = 1.986(3)), and two trans terminal oxygen atoms from two different Anderson anions (Cu(1)−O(6) = 2.738(3), Cu(1)−O(17) = 2.283(3)). The second copper site (Figure 2, middle) is coordinated by two nitrogen atoms from 2,2′-bipyridine ligand (Cu(2)−N(3) = 1.989(3), Cu(2)−N(4) = 2.012(4)), two water molecules (Cu(2)−O(27) = 1.960(4), Cu(2)−O(28) = 2.206(3)), and a chloride anion (Cu(2)−Cl(1) = 2.2899(16)) to complete a roughly square pyramidal geometry of [Cu^{II}(2,2′-bipy)(H$_2$O)$_2$Cl]$^+$. Two such chloro complexes are always associated with only Al(1) containing Anderson anion via hydrogen bonding in the chain (Figure 1 and Figure 2, middle). The O−H···Cl hydrogen-bonding interactions of two chloro−copper complex cations with one Anderson anion (alternatively in the chain) instead of each Anderson anion interacting one cation [Cu^{II}(2,2′-bipy)(H$_2$O)$_2$-Cl]$^+$ are surprising and unusual. This is possibly the result of optimal crystal packing. Along the chain, the significant difference in MoO−Cu bond distances (Cu(1)−O(6) = 2.738(3), Cu(1)−O(17) = 2.283(3)) is worth noting (Figures 1 and 2). One copper−oxygen distance is considerably longer. The relevant oxygen atom (O(6)) belongs to an

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(13) A blue block-shaped crystal was mounted on an Enraf-Nonius Mach 3 diffractometer by using graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation, and data were collected at 20 °C. An empirical absorption correction based on a series of ψ scans was applied. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the bipyridine ring were introduced on calculated positions and included in the refinement riding on their respective parent atoms. The hydrogen atoms of the coordinated and solvent water molecules were located in the differential Fourier maps and were refined using isotropic thermal parameters. Crystal data of **1**: $C_{20}H_{38}AlClCu_2Mo_6N_4O_{32}$, M = 1611.69 g mol^{-1}, triclinic, space group $P\bar{1}$, a = 11.2253(18) Å, b = 14.5194(17) Å, c = 15.2672(10) Å, α = 112.191(8)°, β = 106.693(9)°, γ = 93.916(13)°, U = 2162.6 (5) Å^3, Z = 2, D_C = 2.475 g cm^{-3}, μ = 2.834 mm^{-1}, F(000) = 1564, crystal size = 0.56 × 0.38 × 0.32 mm^3. 7597 measured with 7597 unique reflections, of which 6757 ($I > 2\sigma(I)$) were used for the structure solution. Final R1 (wR2) = 0.0205 (0.0500), 678 parameters. The final Fourier difference synthesis showed minimum and maximum peaks of −0.656 and +1.181 e Å^{-3}.

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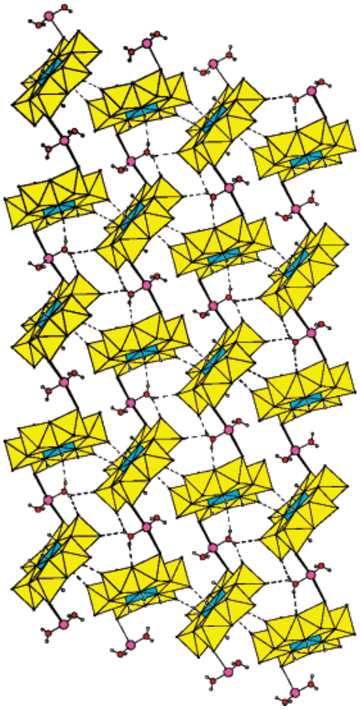

Figure 3. The extensive supramolecular network involving intra- and interchain O−H···O hydrogen bonding. The Anderson anions are shown in polyhedral representation. Color code: Al, cyan; Mo, yellow; O, red; Cu, purple; H, white circle. The bipyridine ligands, coordinated to Cu(II) linkers, are not shown here for clarity.

Anderson anion, which is associated with two $[Cu^{II}(2,2'\text{-bipy})(H_2O)_2Cl]^+$ complexes via hydrogen bonding and covalently bonded to two $\{Cu^{II}(2,2'\text{-bipy})(H_2O)_2\}^{2+}$ complexes. The bipyridine−bipyridine steric interaction between the linker copper and hydrogen-bonded chloro−copper complexes seems to play an important role in lengthening this MoO−Cu bond (Figure 1). The other oxygen atom (O(17)), related to shorter MoO−Cu bond, is the terminal oxygen atom of an Anderson anion, which does not show any interaction with chloro−copper complex, and, therefore, it does not experience such bipyridine−bipyridine steric interaction.

In order to gain more insight into the spiral-type structure of the chain, we investigated more on supramolecular interactions among the components of the crystal and found that there are both intra- and interchain O−H···O hydrogen-bonding interactions (see Supporting Information). We believe that the spiral-type structure of the present chain is governed by this intrachain hydrogen bonding, because this involves a terminal oxygen atom from one Anderson anion and a bridging oxygen atom from other Anderson anion (Figure 3). This, in turn, results in two types of orientations of the Anderson anions along the chain. The spiral nature of the chain is also influenced by the (lateral) interchain O−H···O hydrogen-bonding interactions. This includes three types of hydrogen bonds (see Supporting Information). The resulting hydrogen-bonding supramolecular network is presented in Figure 3. The geometrical parameters of the relevant hydrogen bonds are provided in a table as Supporting Information.

In conclusion, compound **1** is the first example of an inorganic−organic hybrid, in which an Anderson type of heteropolyanion is linked to a transition metal complex with an organic ligand. We have described a new type of chain based on a polyoxometalate anion and a transition metal complex fragment. Intra- and interchain supramolecular hydrogen-bonding interactions play an important role in forming such spiral-shaped chains.

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Supporting Information Available: Text depicting IR, magnetic moment, ESR, TGA and electronic spectral studies, a figure of the asymmetric unit, a figure of a chain consisting of Anderson anion and copper bipyridine complex associated with chloro−copper−bipyridine complex, a figure showing intra- and interchain hydrogen-bonding interactions, a table describing the geometrical parameters of hydrogen bonds, a figure of solvent waters, hydrogen bonded to the host, and a complete X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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