Synthesis and Crystal Structure of the First Two-dimensional Inorganic/Organic Composite Solid of Iron(III) Molybdate

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A novel two-dimensional inorganic–organic composite solid material of iron(III) molybdate $[enH_2][Fe_2(MoO_4)_4]$ (**1**) (en = ethylenediamine) has been hydrothermally synthesized and structurally characterized by elemental analysis, IR spectra, and X-ray diffraction analysis. The sheet structure is constructed by binuclear $\{FeO_6\}$ octahedra and bridging $\{MoO_4\}$ tetrahedra. The two iron octahedra are edge-shared, and all of the oxygen atoms in iron coordination spheres are provided from the $\{MoO_4\}$ tetrahedral units which interconnect the diiron core through the corner sharing, leading to a novel two-dimensional framework.

The study of metal oxide solid materials with structural and chemical diversities is flourishing.[1,2] Most of them bear intriguing topologies and potential applications in catalysis, sorption, biology, medicine, and material science,[3] which have stimulated the preparation of many new complexes. In recently reported work, organic components have been introduced as functional ligands covalently linking to inorganic backbones of solids or as charge compensation cations to form one-, two-, and even three-dimensional structures,[4–11] such as $[MoO_3(2,2'\text{–bpy})]$[5] and $[Ni(2,2'\text{–bpy})_2Mo_4O_{13}]$.[6]

Since the first structure determination of the iron molybdate $[Fe_2(MoO_4)_3]$ was reported in 1966,[12] the derivatives of $[Fe_x(MoO_4)_y]$ have developed into one of the most important subfamilies in metal oxide chemistry. However, to the best of our knowledge, only one- or three-dimensional compounds have been discovered to date,[13] and there is no report that iron molybdenum chains and organic ligands aggregate into multidimensional compounds. Herein, we report the synthesis and structure of $[enH_2][Fe_2(MoO_4)_4]$ (**1**), showing the first example in which hybrid iron molybdenum chains are self-aggregated into novel two-dimensional structures in the presence of amines under hydrothermal conditions.

Compound **1** was synthesized by a hydrothermal method.[14] It should be noted that **1** could not be formed when Sb_2O_3 was removed from the reaction system, which suggested Sb_2O_3 played an important role in the formation of **1**. However, the specific role of Sb_2O_3 is not well understood. Single-crystal X-ray structural analysis[15] indicates that **1** consists of an extended two-dimensional architecture constructed from binuclear $\{FeO_6\}$ octahedra and bridging $\{MoO_4\}$ tetrahedra (Figure 1) with diprotonated ethylenediamine cations filling the space between adjacent sheets as counter cations. The two independent $\{FeO_6\}$ octahedra which form a diiron edge-shared unit are interlinked through two independent $\{MoO_4\}$ bridging groups in an asymmetric unit. All of the coordinated oxygen atoms of the iron center are provided by $\{MoO_4\}$ units. There are two types of $\{MoO_4\}$ units. The tetrahedron of Mo1 is defined by three μ_2-O atoms, which bridge between iron and molybdenum atoms, and one terminal oxygen atom. The Mo2 tetrahedron has one μ_2-O atom, one μ_3-O atom, and two terminal oxygen atoms. The μ_2-O atom bridges an iron atom and a molybdenum atom, while the μ_3-O atom bridges two iron atoms and one molybdenum atom. The Mo–O bonds are categorized in the following three: Mo–O$_t$, Mo–μ_2-O and Mo–μ_3-O bonds. Their distances fall in the range of 1.701(3)–1.719(3), 1.759(3)–1.791(3), and 1.872(3) Å, respectively. The Fe1 unit is coordinated by four Mo1 units and two Mo2 units, which bridge through the μ_3-O atoms, whereas the Fe2 unit is coordinated by four Mo2 units and two Mo1 units. The Fe–O distances are in the range of 1.952(3)–2.048(3) Å, average 1.999 Å.

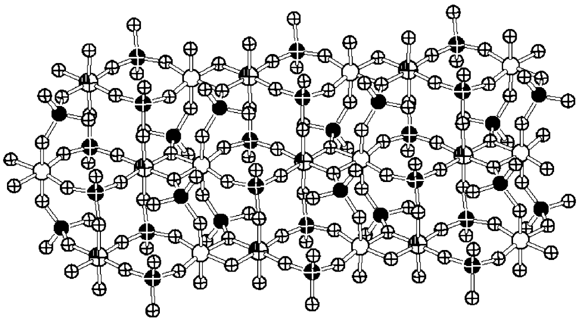

Figure 1. The ball-and-stick representation of 2D framework of $[Fe_2(MoO_4)_4]^{2-}$. Fe1 atoms are denoted by open circles, Fe2 atoms by 3/4 open circles, Mo1 atoms by black crosshatched circles, Mo2 by black circles, and oxygen atoms by crosshatched circles.

The framework of **1** can be also considered to be a layer structure (Figure 2). We can find $\{FeO_6\}$ layers sandwiched by $\{MoO_4\}$ layers. There are two types of $\{MoO_4\}$ layers. One is the Mo1 layer that is close to the iron layer, and the other is the Mo2 layer that makes a groove between $\{MoO_4\}$ units where one of the ammonium groups of enH_2 cation is hydrogen-bonded to bridging oxygen atoms of the Fe1 unit. It is interesting to point out that unlike the Fe1 sphere, the Fe2 sphere has no hydrogen bonds because the Mo2 units are blocking the surface, consistent with the position that the other ammonium group is away from the surface. From the viewpoint of supramolecular chemistry, supramolecular interactions are also observed in **1** considering hydrogen-bonding interactions between nitrogen atoms of organoamines and terminal oxygen atoms as well as μ_2-O atoms from the inorganic backbone. Specifically, nitrogen atoms on enH_2 cations act as the proton donors, terminal oxygen atoms and μ_2-O atoms from $\{MoO_4\}$ units work as the proton acceptors, and then donors and acceptors are hydrogen-bonded together generating the infinitely 3-D extended supramolecular network. The N–H···O distances range from 2.778 to 2.954 Å.

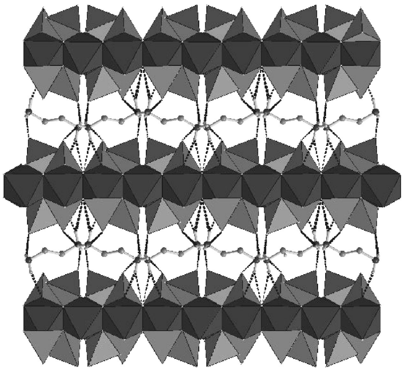

Figure 2. Packing of alternative appearance of inorganic layer $[Fe_2(MoO_4)_4]^{2-}$ cluster and organic cations $[enH_2]^{2+}$ in the *ab* plane in the title compound. Gray (80%) octahedra, FeO_6; Gray (50%), MoO_4. Gray (80%) spheres, N; Gray (50%) spheres, C; Gray (25%) spheres, H; White spheres, O.

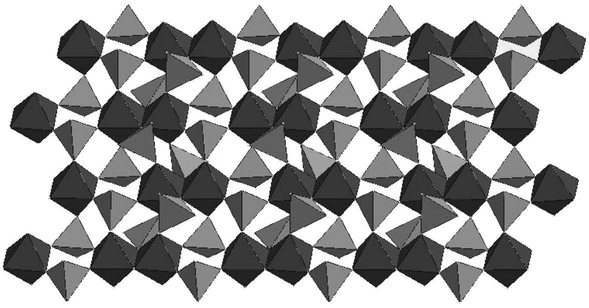

Figure 3. The polyhedra representation of 2D framework in **1**. Gray (80%) octahedra, FeO_6; Gray (50%), MoO_4.

Moreover, hydrogen-bonding interactions can be functioned as a key factor to distinguish Fe1 and Fe2 atoms. While a unique two-dimensional network is formed in **1** (Figure 3), interestingly, in which there are no {Mo–O–Mo} linkages and each peripheral metal component, in contrast, can be considered as an integral part of the two-dimensional structure.

It should be noted that the polyhedral rings observed in **1** bear a pronounced resemblance to the chains in reported $[Mo_3O_{12}\{Fe(2,2'\text{-bpy})\}_2]\cdot 0.25H_2O$ (**A**)[13a] (Figure S1).[16] They are both constructed from binuclear $\{FeO_6\}$ octahedra and bridging $\{MoO_4\}$ tetrahedra. The obvious difference between them is that in the latter structure, iron octahedra and molybdenum tetrahedra are all corner-sharing whereas a unique connectivity between iron octahedra and molybdenum tetrahedra is all edge- and corner-sharing modes in **1**. **A** is constructed from discrete $\{MoO_4\}$ clusters linked through $\{Fe(2,2'\text{-bpy})\}^{3+}$ moieties, while **1** is exclusively constructed from two kinds of $\{MoO_4\}$ units linked via Fe^{3+} clusters and organic molecules acting as counter cations.

In the IR spectrum of **1**, the characteristic peak at 966 cm^{-1} is ascribed to ν(Mo=O). Multiple bands attributed to the bridging (Mo–O–Fe) group absorptions are found in 897, 869, 827, 800, 741, 702, and 605 cm^{-1} (Figure S2).[16] In addition, those bands at 3444, 3211, 1044, and 1021 cm^{-1} are assigned to characteristic vibrations of ethylenediamine.

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14 Synthesis of compound **1**: $(NH_4)_6Mo_7O_{24}$ (1.6 g) was dissolved in water (25 mL) and heated to 50 °C. Then Sb_2O_3 solution (0.15 g dissolved in 2 mL of concentrated HCl) was added dropwise, adjusted to pH 3.0, and kept at 60 °C for 20 min; the solution was allowed to cool to room temperature and then $FeCl_3$ (0.1 g) and en (0.05 mL) were added in aforementioned solution (5 mL). The mixture was adjusted to pH 6.5 by 4 M NaOH. Then the resulting solution was transferred to a Teflon-lined steel autoclave and kept at 160 °C for 3 days. After slow cooling to room temperature, dark yellow crystals were isolated by filtration. Anal. Calcd for compound **1**: C, 2.95; H, 1.24; N, 3.44%. Found: C, 3.02; H, 1.29; N, 3.39%.

15 Crystal data for **1** $C_2H_{10}N_2Fe_2Mo_4O_{16}$: $M_r = 813.58$, monoclinic, space group $C2/c$, $a = 20.810(5)$ Å, $b = 8.614(2)$ Å, $c = 9.860(2)$ Å, $\beta = 112.878(14)^\circ$, $V = 1628.5(7)$ Å^3, $Z = 4$, $D_{calcd} = 3.318$ g cm^{-3}, $T = 296(2)$ K. 3855 reflections measured, 1444 independent ($R_{int} = 0.0342$, $R_1 = 0.0273$ ($I > 2\sigma(I)$), $wR_2 = 0.0610$ (all data). CCDC number: 704846.

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