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(Citation)
Journal of Solid State Chemistry,180(12):3588-3593

(Issue Date)
2007-12

(Resource Type)
journal article

(Version)
Accepted Manuscript

(URL)
https://hdl.handle.net/20.500.14094/90000962

Fabrications of some kinds of 2D frameworks consisting of nanosized polyoxomolybdate anion $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$ via condensation processes

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Abstract

We succeeded to prepare novel $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$ (**{Mo$_{36}$}**) compounds by using 1,3-diamino-2-propanol (**βOHC$_3$-DA**) and 1,3,5-tris(aminomethyl)benzene (**MES-TA**) + 1,3-diaminopropane (**C$_3$-DA**) as linkers, and determined their crystal structures. We have confirmed they have unique 2-D molybdenum oxide frameworks, which are formed by condensation of **{Mo$_{36}$}**s. Side-staggered arrays of **{Mo$_{36}$}**s, connected in lying position by eight bridges per a **{Mo$_{36}$}**, are formed in the compound with **βOHC$_3$-DA**, while herringbone arrays of **{Mo$_{36}$}**s, connected in standing position by four bridges per a **{Mo$_{36}$}**, are built in the compound with **MES-TA+C$_3$-DA**. The latter compound exhibited non-stoichiometric property, and its composition and cell parameters varied depending on the relative concentration of **MES-TA** in the mother solution.

Keywords

nanosized polyoxometalate, Mo$_{36}$ polymolybdate, crystal engineering, 2-dimensional framework, synthesis, crystal structure

Introduction

Various species of nano-sized polyoxometalate have been known.[1-7] Many of them exhibit interesting structural and/or physical features such as "nano-sized cavity" available for specific reaction field, “dense color” due to intense intramolecular charge transfer, “mesoscopic properties” derived from their nano-sized structure, and so on. They thus are fascinating research subjects, and have been expected as building blocks efficient for crystal engineering of novel functional materials.[8-10] The structural characteristics of the polyoxometalate species are illustrated in Fig. 1a.

In 1997 Zhang et al. [11] first reported an unique 1-dimensional (1-D) framework consisting of a kind of nanosized polyoxometalate species $[Mo_{36}(NO)_4O_{108}(H_2O)_{16}]^{12-}$ (**{Mo$_{36}$}'**) (Fig. 1b) as a quantum line based on molecular quantum dots. Since their works[11,12] the crystal engineering with species concerning Mo_{36}-polyoxometalate (**<Mo$_{36}$>**), including $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$ (**{Mo$_{36}$}**), as a building block has become an exciting research subject.

Then Izarova et al.[13] and we[14] systematically prepared the **<Mo$_{36}$>**s frameworks with various dimensionalities via coordination processes and condensation processes respectively (Figs. 1c and 1d). In addition some interesting organic-inorganic frameworks of **{Mo$_{36}$}** have been fabricated (Fig. 1e).[15,16] Of all fabrications mentioned above, only ours provided the high-dimensional frameworks consisting only of **<Mo$_{36}$>** (Fig. 1d). It, however, should be noted that this result was achieved through the linker-function of α,ω-alkanediamine **C$_n$-DA**.[14]

In general, orthoanion (monomeric oxometalate anion) exists preferentially in alkaline to neutral or slightly acidic solution, and on acidifying solution of oxometalate, polyoxometalate anions are formed from orthoanion by the condensation initiated through a nucleophilic attack of negatively charged OH groups to positively charged central metal cations as follows:

$M\text{-}OH^{\delta-} + {}^{\delta+}M\text{-}OH \rightarrow M\text{-}O\text{-}M + H_2O.$

As the pH of the solution decreases, successive condensation reaction proceeds leading to the formation of larger polyoxometalates. But release of OH_2 group due to the condensation raises mean electronegativity of the resulting polyoxometalates, giving rise to shifts of the partial charge density of the OH groups on the polyoxometalates to the positive side. So the condensation reaction terminates when the partial charge density approaches zero or becomes positive (because such situation is not favorable for the nucleophilic reaction of the OH group). **<Mo$_{36}$>** has no OH group, but it has been known that the OH_2 groups on **<Mo$_{36}$>** are formed from neutral or positively charged OH groups via a prototropic transfer.[17] Thus, **{Mo$_{36}$}** usually takes part in no further condensation, which gives even larger species, and has consequently been known as the largest of all aqueous Mo(VI) oxometalate species.[18] In the formation of **{Mo$_{36}$}** compounds with **C$_n$-DA** (n=3-6), however, we found a new condensation process which leads to the formation of high-dimensional frameworks consisting only of **{Mo$_{36}$}**.[14] Since we have been interested in this rare type of condensation, we have studied the crystal chemistry of the **{Mo$_{36}$}** compounds with **C$_n$-DA**. The details of the chemistry will be reported elsewhere in near future.

In the present work, on the basis of understanding the chemistry we tried to fabricate 2-D frameworks of {Mo_{36}} with various kinds of packing and linking sequences of {Mo_{36}}s. Fortunately we succeeded to prepare expected compounds and to determine their crystal structures. As the result we have found out three kinds of unique 2-D molybdenum oxide (Mo-O) frameworks, including the 2-D framework of the {Mo_{36}} compounds with **C_3-DA**[14]: the three types are the frameworks with herringbone arrays of {Mo_{36}}s, connected in lying position by four oxygen bridges ({Mo_{36}}-O-{Mo_{36}} bridges) per a {Mo_{36}} unit (1), side-staggered arrays of {Mo_{36}}s, connected in lying position by eight oxygen bridges (2), and herringbone arrays of {Mo_{36}}s, connected in standing position by four bridges (3), as shown below. These frameworks can be regarded as Mo-O sheets having various modifications.

The Mo-O sheets with variations in packing and connectivity of {Mo_{36}} are expected to exhibit diversity in physical properties, and are of interest for material and applied science. Therefore, we will report herein the preparations and structural details of the two kinds of 2-D frameworks newly obtained, comparing with the 2-D framework of the {Mo_{36}} compounds with **C_3-DA**, $L_4[Mo_{36}O_{112}(H_2O)_{14}] \cdot nH_2O$ (L = protonated **C_3-DA^{2+}**, n=ca. 36) (0).[14]

Linkers suitable for high-dimensional frameworks consisting of {Mo_{36}}

Our study on the {Mo_{36}} compounds with **C_n-DA** suggested a following condensation reaction lead to the formation of high-dimensional frameworks consisting of {Mo_{36}}:

$\{\text{-Mo}^{\delta+}\}\text{-OH}_2^{\delta+} + \{\text{-Mo}\}\text{-O}^{\delta-} \rightarrow \{\text{-Mo}^{\delta+}\}\text{:} + H_2O + \{\text{-Mo}\}\text{-O}^{\delta-} \rightarrow \{\text{-Mo}\}\text{-O-}\{\text{Mo-}\} + H_2O$.

The OH_2 groups on {Mo_{36}} have slightly positive partial charge density, and are easy to be released because of the repulsion with (positively charged) central metal cation. After the release of the OH_2 groups, the condensation is completed by a successive electrophilic attack of negatively charged oxo groups to the partially naked metal center. But, because {Mo_{36}} itself has a large negative charge (-8), the above attack (or the condensation) is usually difficult in solution of oxometalate. Then it is necessary to introduce an additional mechanism which enables mutual access of {Mo_{36}}s to result in the condensation. Short multitopic linkers, such as **C_3-DA**, were found to be suitable to connect {Mo_{36}}s to each other. They thus plays an important role for the fabrication of high-dimensional frameworks consisting of {Mo_{36}} via the above condensation reaction.

Atomic numbering used in the present work

For easy comparison about linkage centers of the frameworks, we use an original labeling system with an atomic symbol and two or three digits (A$lm(n)$, A=Mo or O, l =0-4, m=1-8, and n=1-6), shown in Fig. 2. The crystallographic asymmetric unit of **$\{Mo_{36}\}$** consists of two **$\{Mo_8\}$** and two **$\{Mo_1\}$** subunits. The digit l shows which subunit the atoms belong to. l=0 is for the atoms that belong to both two **$\{Mo_8\}$** subunits. The digit m tells to which MoO_n polyhedra of the subunits the atoms belong. The digit n is only for oxygen atoms. In this system n=1 is for oxygen atoms having a Mo-O bond projecting perpendicularly on the outer surface of $\{Mo_{36}\}$, n=2 for those having Mo-O bonds projecting on the inner (cavity) surface, and n=3-6 for other ones. And the atoms labeled with n=1 and 3 are all terminal in an isolated **$\{Mo_{36}\}$**. A1$m(n)$ and A2$m(n)$ as well as O413 and O411 are regarded to be equivalent to each other, because **$\{Mo_{36}\}$** possesses $2/m$ of symmetry along the axis Mo41---Mo41'. Furthermore oxygen atoms labeled with O131, O141, O151, O231, O241, O251, O072, and O082 belong to aqua groups, and the first six with n=1, which are projecting on the outer surface, might take part in the condensation to make a connection between **$\{Mo_{36}\}$**s.

Experimental

In order to fabricate 2-D frameworks having different arrangements and linkages of **$\{Mo_{36}\}$**, we tested two approaches. The one is to introduce functional groups, which give additional interactions among linkers, to the short linker (**C$_3$-DA**). The other is to use short linkers having more than two linkage centers. For the former approach 1,3-diamino-2-propanol (**βOHC$_3$-DA**) was used. And for the latter approach, 1,3,5-triaminobenzene, in which each two amino groups were separated by a carbon chain of 3 carbon atoms (comparative with the amino-amino separation of **C$_3$-DA**), was selected at first. But it exhibited strong reducing power enough to reduce **$\{Mo_{36}\}$**, and was not suitable for the present fabrications. So 1,3,5-tris(aminomethyl)benzene (=mesitylenetriamine **MES-TA**), which had the amino-group separation corresponding to that of **C$_5$-DA**, was used instead. Crystal-like precipitates were obtained by using MES-TA as a linker. But no crystals suitable for X-ray structural analysis could be obtained in spite of all our efforts for preparation and structural determination of the compound. To obtain the good crystals containing **MES-TA**, mixed linker (**MES-TA+C$_3$-DA**) system was studied.

Materials: **MES-TA** ($C_9H_{15}N_3 \cdot 0.2H_2O$) was prepared according to the procedures of

Garrett et al.[19,20] Commercial grades of other chemicals, such as **C$_3$-DA** and **βOHC$_3$-DA**, were used without further purification.

Preparations of crystals: The aqueous solution of **{Mo$_{36}$}** was prepared by passing aqueous sodium molybdate through an ion-exchange resin (Dowex 50W-X8). The solution was once spray-dried into soluble amorphous powder. Subsequently by dissolving the powder in water, {Mo$_{36}$} solution with a desired concentration was obtained. The linkers (**C$_3$-DA**, **βOHC$_3$-DA**, **MES-TA**) were protonated to be used as cations. For protonation of the amine groups of linkers, corresponding equivalents of HCl were added to solutions of linkers. To obtain the **{Mo$_{36}$}** compounds with the linkers, an appropriate amount of the protonated linker solution was added to the **{Mo$_{36}$}** solution with vigorous stirring. (For example, [Mo], [**βOHC$_3$-DA**], and [HCl] concentrations of the resulting solution, which provided good crystals of the **βOHC$_3$-DA** compound, were 100, 5.5, 11 mM (M≡mol/dm^3), respectively.) Then the resulting solution was allowed to stand for several days at 293 K in order to obtain single crystals of the products.

Measurements: A SMART 1000/CCD diffractometer (Bruker) was employed for X-ray diffraction measurements using graphite monochromated Mo K_α radiation (λ =0.71073 Å). Data collections were carried out at 193 K. The structures were solved by the direct method and refined by full-matrix least-squares calculations based on F_o^2 using SHELXL-97.[21] Nonhydrogen atoms of each compound were included in the least-squares calculations with anisotropic displacement parameters, except for some linker's atoms of the **{Mo$_{36}$}** compound with **MES-TA+C$_3$-DA**, which were refined with isotropic displacement parameters. As shown below, the compound with **MES-TA+C$_3$-DA** exhibited non-stoichiometry of linker cations, and the occupancies of the linker's atoms were estimated from the results of compositional analysis and were fixed during the structural refinements. The compositions of the samples were determined using a Yanaco MT-5 CHN CORDER. ^{1}H NMR spectra were recorded using a JEOL JNM-LA400 spectrometer (400 MHz).

Results and Discussion

βOHC$_3$-DA-{Mo$_{36}$} system: The compound, $L_4[\mathrm{Mo_{36}O_{112}(H_2O)_{12}}]\cdot n\mathrm{H_2O}$ (L = protonated **βOHC$_3$-DA^{2+}**, n=ca. 18) (1),[22,23] crystallized in the triclinic space group $P\bar{1}$ with a=13.232(3), b=13.553(3), c=20.189(4) Å, α=80.166(3), β=76.850(3), γ=69.458(3) °, V=

3285.1(11) Å^3, and Z=1.

As shown in Figs. 3a and 3b, this compound also exhibits a 2-D but different type of framework from that of **0**. In the framework {Mo$_{36}$}s are closely packed in a side-staggered pattern and are connected to each other via eight {Mo$_{36}$}-O-{Mo$_{36}$} bridges per a {Mo$_{36}$} (Fig. 4b), giving a more "compact" 2-D framework than that of **0** (Fig. 3). This compactness of the framework results in the smallest value of cell volume/the number of chemical unit V/Z in Table 1. In **1** the aqua groups Mo15-O151 and Mo23-O231 are used as linkage centers, while only the group Mo23-O231 is used in **0**. The groups Mo15-O151 and Mo23-O231 are coupled with the oxo groups Mo17-O171 and Mo41-O413 respectively in **1**. Mo15-O151 and Mo17-O171 as well as Mo23-O231 and Mo41-O413 are located close to each other on {Mo$_{36}$} (Fig.2). Consequently geminal linkages (for example Mo15$_A$-O-Mo17$_B$ and Mo17$_A$-O-Mo15$_B$, where subscripts A and B are used to distinguish atoms of two neighboring {Mo$_{36}$}s.) are formed in the case of **1**, resulting in eight linkages per a {Mo$_{36}$}.

As {Mo$_{36}$} has a charge of -8, the crystal contains four protonated (divalent) diamine linkers per a {Mo$_{36}$} for charge compensation. Half of them (βOHC$_3$-DA$_C$) are captured in the hollow of {Mo$_{36}$}, and fill the free space of the cavity to minimize the lattice volume, as C$_3$-DA (C$_3$-DA$_C$) does in **0** (Figs. 4a and 4b). The remaining half (βOHC$_3$-DA$_L$) indeed act as a linker to connect {Mo$_{36}$}s via hydrogen bonding with oxo groups of {Mo$_{36}$}. The βOHC$_3$-DA$_L$ is located so as to cover the {Mo$_{36}$}-O-{Mo$_{36}$} bridge. The corresponding C$_3$-DA (C$_3$-DA$_L$) in **0** is also located on the bridge site. These results support that the short linkers such as βOHC$_3$-DA and C$_3$-DA play an important role for the mutual access of {Mo$_{36}$}s and the consequent formation of the {Mo$_{36}$}-O-{Mo$_{36}$} bridges via the above-mentioned condensation. And it should be noted that each two βOHC$_3$-DA$_L$ molecules (cations) form dimer through hydrogen bonding of OH---HO in **1** (Fig. 4b). The double bridges seen in this compound and the consequent compact framework consisting of {Mo$_{36}$} might be related to the dimering of the linker molecules (i.e., to the additional interaction between linker molecules).

(MES-TA + C$_3$-DA)-{Mo$_{36}$} system: The MES-TA + C$_3$-DA compounds crystallized in the same monoclinic space group $P2_1/c$ with Z=2, but their composition and lattice size varied depending on the composition of mother solution. The solution with [Mo]= 125 mM, [MES-TA]=0.1 mM, [C$_3$-DA]=3.5 mM, [HCl]=7.3 mM gave the compound $L^1_{1.12}L^2_{2.32}[Mo_{36}O_{112}(H_2O)_{14}] \cdot nH_2O$ (L^1= protonated MES-TA^{3+}, L^2=protonated C$_3$-DA^{2+}, n= ca. 44) (**2**)[22,23] with the lattice parameters of a=23.343(5), b=15.811(3), c=24.378(5) Å, β=118.85(3) °, V=7881(3) Å^3. And the solution with [Mo]= 125 mM, [MES-TA]=0.1 mM, [**C$_3$-DA**]=4.0 mM, [HCl]=8.3 mM provided the compound $L^1_{0.39}L^2_{3.41}[Mo_{36}O_{112}(H_2O)_{14}]\cdot nH_2O$ (n=ca. 44) (**2'**)[22,23] with a=23.144(6), b=15.826(4), c=24.460(5) Å, β=118.989(17) °, and V=7837(3) Å^3. These results indicate that a small change in the relative concentration of **MES-TA** in the mother solution makes remarkable changes in the [**MES-TA**] and [**C$_3$-DA**] contents of the resulting crystal.

In spite of the difference in the composition these compounds exhibit a common 2-D framework (Fig. 3c) as well as the quite similar unit cell. Thus we regard the compounds as a kind of solid solution. The framework was apparently different from those of **0** and **1**, and was a new type. In this framework **{Mo$_{36}$}**s are non-closely packed in the herringbone pattern as same as in **0** (resulting in a “loose” framework). But they are packed in standing position (i.e., in the fashion that the long axis of **{Mo$_{36}$}** is roughly perpendicular to the plane of the 2-D framework) in **2** and **2'**. As **{Mo$_{36}$}**s are packed in lying position (where the long axis is roughly parallel to the framework plane) in **0** and **1**, we also call the frameworks of **0** and **1** “slim” and those of **2** and **2'** “fat” (Fig. 3). Furthermore, **{Mo$_{36}$}**s are linked by four **{Mo$_{36}$}**-O-**{Mo$_{36}$}** bridges per a **{Mo$_{36}$}**. These linkage are formed between the aqua group Mo14-O141 and the oxo group Mo18-O181. The linkage concerning Mo14-O141 (or Mo24-O241) was observed for the first time, as Mo15-O151 (or Mo25-O251) and/or Mo13-O131 (or Mo23-O231) are usually used as linkage centers in our fabrications of the high-dimensional frameworks consisting of **{Mo$_{36}$}**.

Because of disorder of the linker molecules as well as the non-stoichiometry of the compound, there still is room to improve the structural quality in spite of our various efforts for crystal preparation and structural determination. But it has been revealed that two **C$_3$-DA**s per a **{Mo$_{36}$}** are captured in the hollow of **{Mo$_{36}$}**, as same as in the other compounds under discussion (Fig. 4). Though the detailed role of **MES-TA** and **C$_3$-DA** as linkers are still not clear, it should be noted that the present “fat” and “loose” (“fat-loose”) Mo-O framework mentioned above could not be obtained without the presence of **MES-TA** in the mother solution.

As mentioned above, non-stoichiometry of this compound makes the structural determination (or basic study) difficult. However it may afford functional variations on this compound. For example, the cell volume varies with the preparation condition (Table 1). As this compound have the common 2-D Mo-O framework, the variation in the cell volume may be directly related to the variation in the separation between adjacent 2-D Mo-O frameworks. As the 2-D Mo-O framework can be regarded as a quantum sheet (or well), the separation might become an important parameter to control properties of the quantum sheet or of materials consisting of the sheet.

Conclusion

By using the short linkers with additional functional groups, which give additional interactions among linker molecules, or additional centers of linkage, we succeeded to obtain two kinds of novel {Mo_{36}} compounds that have unique 2-D frameworks consisting only of {Mo_{36}}s. As the result, including our previously work, three kinds of 2-D frameworks were fabricated by our method. These frameworks can be regarded as "slim-loose", "slim-compact" and "fat-loose" Mo-O sheets having various modifications in packing and linking sequences of {Mo_{36}}s. As the variations in packing and connectivity of {Mo_{36}} are expected to afford diversity in physical properties, our fabrication method will provide various materials, interesting to material and applied scientists.

Acknowledgements

The authors thank Dr. M. Hashimoto for helpful discussion in many points. This work was supported by the Grant-in-Aid for Scientific Research (C) No. 18550057 of the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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(22) Anal. Calcd for dried **1**, $\boldsymbol{\beta}\mathbf{OHC_3\text{-}DA}_4[Mo_{36}O_{112}(H_2O)_{12}] \cdot 16H_2O$ (Found): C, 2.4 (2.5); H, 1.8 (1.9); N, 1.8 (1.7); MoO$_3$, 85.32 (85.36), Calcd for dried **2**, $\mathbf{MES\text{-}TA}_{1.13}\mathbf{C_3\text{-}DA}_{2.32\text{-}}[Mo_{36}O_{112}(H_2O)_{14}] \cdot 26H_2O$ (Found): C, 3.2 (3.3); H, 2.0 (2.0); N, 1.8 (1.8); MoO$_3$, 81.84 (81.76), Calcd for dried **2'**, $\mathbf{MES\text{-}TA}_{0.39}\mathbf{C_3\text{-}DA}_{3.41}[Mo_{36}O_{112}(H_2O)_{14}] \cdot 14.5H_2O$ (Found): C, 2.7 (2.8); H, 1.7 (1.9); N, 1.8 (1.9); MoO$_3$, 85.16 (85.11).

(23) The number of water of crystallization was estimated from the volume of voids in the crystals.

Table 1. Cell volumes of the compounds **0**, **1**, **2**, and **2’**

	0	**1**	**2**	**2’**
V / Å^3	7455.2(14)	3285.1(11)	7881(3)	7837(3)
Z	2	1	2	2
V / Z Å^3	3727.6	3285.1	3940.5	3918.5

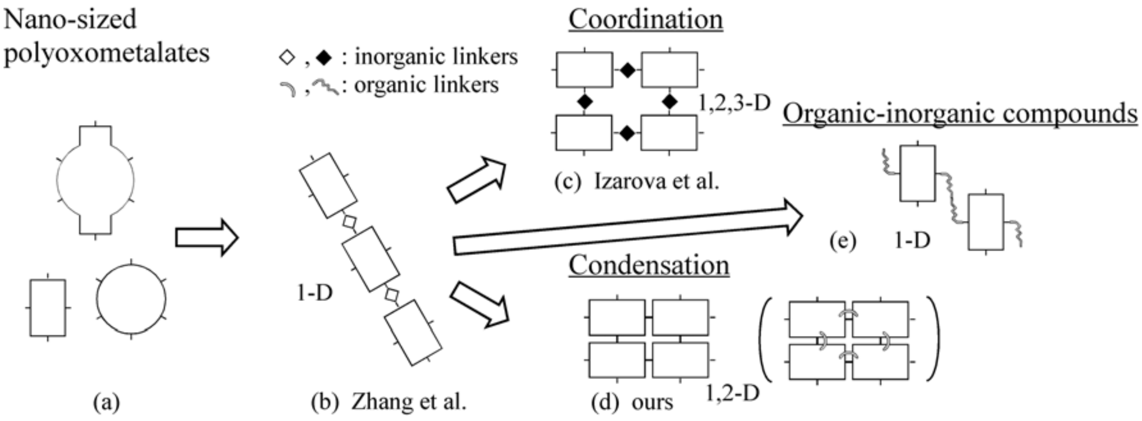


Fig. 1 by K. Eda et al.

Fig. 1 Conceptual overview of background for the present study.

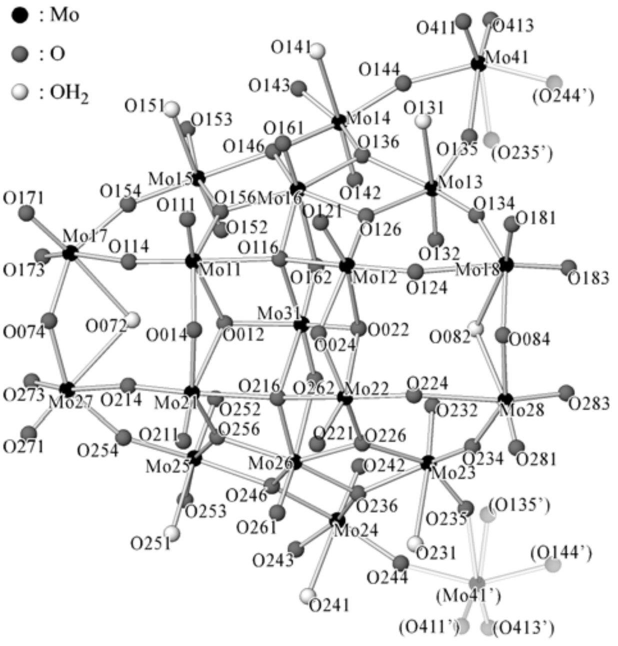
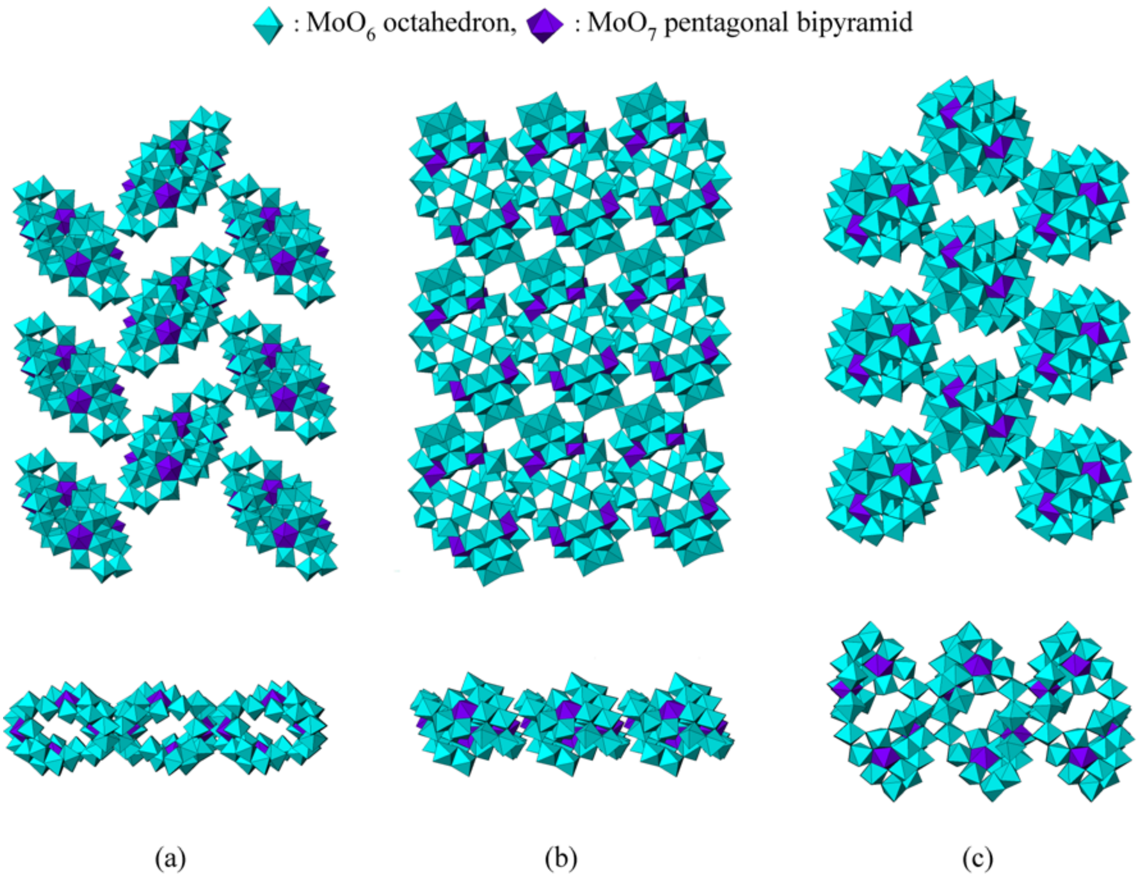


Fig. 2 by K. Eda et al.

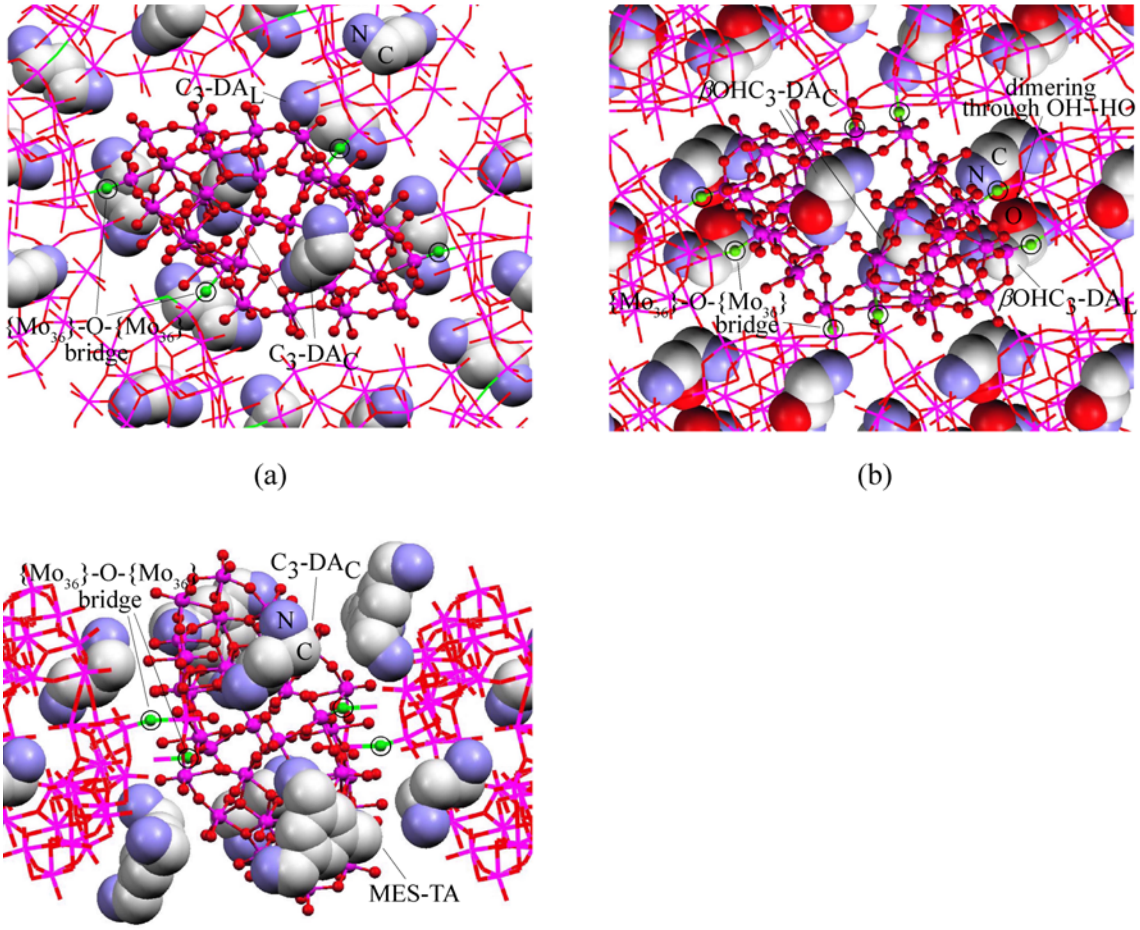
Fig. 2 Atomic numbering of the asymmetric unit for {Mo$_{36}$} in the crystals discussed.



(a) (b) (c)

Fig. 3 by K. Eda et al.

Fig. 3 The 2-D Mo-O frameworks: **0** (a), **1** (b), and **2** (c). Upper and lower drawings show top- and side-views, respectively, of the frameworks.



(a)

(b)

(c)

Fig. 4 by K. Eda et al.

Fig. 4 Amines (linkers) and {Mo_{36}}-O-{Mo_{36}} bridges in the compounds: 0 (a), 1 (b), and 2 (c). Amines are drawn in a space filling model. {Mo_{36}}s are given in a wire frame model, but the central {Mo_{36}}s are highlighted using a ball and stick model. Oxygen atoms concerning the bridge are marked with a small circle. In the drawing of 2 only {Mo_{36}}s linked in one direction are shown, but those in another direction are omitted for clarity.