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Molybdenum Cluster Halide Compound $Mo_6Cl_{12}(OH_2)_2$ with Six-Handed Linkage Hydrogen Bonding

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A hexanuclear Mo cluster compound $Mo_6Cl_{12}(OH_2)_2$ was synthesized for the first time and its crystal structure was analyzed by powder X-ray diffraction and Rietveld analysis. The initial structure model for the Rietveld analysis was developed by a cut and try method of manipulating the hexanuclear molecule(s) in the unit cell using a computer modeling program. In this paper the characteristic network structure of hydrogen bonding is discussed. In the refined structure ($I4/m$, $Z = 2$, $a = 0.89869(3)$ nm, $c = 1.14471(3)$ nm), the $Mo_6Cl_{12}(OH_2)_2$ molecules are connected to form a three-dimensional network by hydrogen-bonding of the aquo ligands. This is a newly reported compound and is isostructural to $Mo_6Br_{12}(OH_2)_2$ in an earlier report (L. J. Guggenberger et al., *Inorg. Chem.* **1969**, *8*, 2041) which focused on the skeletal structure of the molecule. The $Mo_6Cl_{12}(OH_2)_2$ molecule has four terminal Cl atoms at equatorial positions and two aquo ligands at axial positions. The four terminal Cl atoms from four different molecules and two aquo ligands from two different molecules formed a linkage to connect the six molecules via H-bonding, where the two aquo ligands engaged with each other. Infrared absorption in the OH stretching region gave sharp peaks at 3159 and 3235 cm^{-1}, of which the low wavenumbers indicate strong hydrogen bonding of the water molecules. ^{1}H MAS NMR gave a signal at 6.8 ppm as the major species accompanied by well-resolved spinning side bands, indicating that the large cluster molecules separate the water molecules to weaken the dipole–dipole interaction between the protons. The flexible hydrogen-bonding linkages adopt angles such that the cluster molecules contact each other and form the densely packed crystal structure. This compound highlights an example in which molecules at nanometer scale have multisites for bonding that form a unique network structure.

Transition-metal hexanuclear cluster halides have attracted the attention of chemists for long time.[1–9] Mo_6Cl_{12}, a typical cluster halide, has been studied extensively in terms of coordination chemistry,[1–3] photochemistry,[4–6] and electrochemistry.[7–9] Attempts of application of this compound range from oxygen sensors[8] to electronic conductors.[9] Recent studies have also focused on construction of three-dimensional molecular networks using the cluster molecules.[10–14]

Design of three-dimensional architectures at the nanometer scale is a current topic in materials chemistry. Porous coordination polymers or metal organic frameworks (MOF) constructed from a variety of molecular building blocks provide three-dimensional structures.[15–17] These materials are formed by coordination bonds between metal centers (or clusters) and organic ligands as linkers having two or more linking sites. Current areas of interest for these materials are, for example, the adsorption (or absorption) properties of hydrogen[18] and sophisticated host–guest interactions such as reversible topochemical transformations triggered by guest molecules.[19]

Transition-metal hexanuclear cluster halide molecules ca. 1 nm in diameter were also used as building blocks with some linkers to form nanostructured frameworks.[10,11] As self-assembled structures of nanometer scale building blocks, ionic crystals of hexanuclear cluster halides have been also studied. They include crystalline compounds comprised of anionic and cationic hexanuclear clusters[12] and organic salts of hexanuclear cluster compounds.[13] An organic salt of Mo hexanuclear cluster halide has been reported to show a reversible and unusual transformation between layered and isotropic structures that is driven by the absorption of alcohols.[14]

It is interesting to revisit known structures of cluster compounds focusing on networking by linkers such as water molecules. Linkers with more than three "hands" involve two water molecules and a proton to form a "four-handed" linker (i.e., $H_2O\cdots H^+\cdots OH_2$) which is found in various ionic crystals.[20–22] These compounds contain inorganic molecules at nanometer scale sizes, such as a six nuclear metal cluster halide compound[20] $[(18\text{-crown-}6)_2(H_5O_2)]_3[Nb_6Cl_{18}]$, and a polyoxometalate[21,22] $H_3PW_{12}O_{40}\cdot 6H_2O$ ($=(H_5O_2)_3PW_{12}O_{40}$). The $H_9O_4^+$ cation is another interesting linker.[23,24] For example, $[(C_2H_5)_4N]_2(H_9O_4)[Mo_3S_7Cl_6]$ is a cluster compound that contains helical chains of polymeric $H_9O_4^+$, which H-bonds with four Cl atoms. These cations can be regarded as "four-handed" and "two-handed" linkers.

Here we focus on a characteristic three-dimensional hydrogen-bonding network in a hexanuclear cluster halide, $Mo_6Cl_{12}(OH_2)_2$, a new compound. X-ray powder diffraction and Rietveld refinement have shown a characteristic structure, which is isostructural to $Mo_6Br_{12}(OH_2)_2$ (Ref. 25). The literature on

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$Mo_6Br_{12}(OH_2)_2$ do not discuss much the hydrogen-bonding network structure between the cluster molecules. The structure molecules were connected by "six-handed" unique linkages to form a three-dimensional hydrogen-bonding network of the cluster molecules. The present study highlights an example in which building blocks at the nanometer scale have multisites for bonding to form unique three-dimensional structure.

Experimental

Materials and Synthesis. $MoCl_5$ and Mo powder were obtained from Aldrich Co., Ltd. NaCl was purchased from Wako Pure Reagent (Tokyo). Mo_6Cl_{12} was synthesized as follows.[26] In an Ar-filled glove box, 0.656 g of $MoCl_5$ and 0.117 g of NaCl were mixed and ground using a mortar, and 1.036 g of Mo was added to the mixture. The mixed powder was sealed into a quartz tube under vacuum, and over 8 h the sample was gradually heated in a box furnace up to 993 K. The temperature was kept at 993 K for one night. The resulting solid was ground and dispersed into ca. 10 mL of ethanol. After stirring this mixture for 4 h, the material was filtered to obtain an orange solution. HCl (35%) was added and aged for 1 h to precipitate NaCl. The mixture was filtered again and the solution was heated to reduce the volume by half and then cooled on ice to obtain $(H_3O)_2Mo_6Cl_{14}\cdot 6H_2O$ yellow needle-like crystals. The $(H_3O)_2Mo_6Cl_{14}\cdot 6H_2O$ crystals were heated at 473 K under vacuum to obtain Mo_6Cl_{12}.

The reaction of Mo_6Cl_{12} with water was carried out by adding anhydrous Mo_6Cl_{12} solid to liquid water. Crystals of Mo_6Cl_{12} were initially dissolved in water and this was followed by the rapid formation of a pale yellow precipitate. The product was filtered and dried at ambient atmosphere. In another experiment, anhydrous Mo_6Cl_{12} solid was exposed to the ambient atmosphere for reaction with atmospheric moisture.

Characterization. Powder X-ray diffraction patterns were measured with a Bruker AXS, D8 ADVANCE, equipped with a position sensitive detector ("Vantec") using Nickel-filtered Cu Kα radiation ($\lambda = 0.15418$ nm). The measurement for structural analysis was carried out for the range of $2\theta = 5$–120° (the step width, 0.0074°, which was defined by the cell spacing of the position sensitive detector). The structural refinement was performed using a TOPAS Academic 4 Rietveld program.[27] The initial model structure was made using a Visualizer program in the Material Studio package (Accelrys). At first the diffraction peaks were indexed and the space group candidates were listed. The indexing was carried out by using the TREOR90 program[28] build in the Crysfire program package.[29] We used Checkcell[30] to select plausible candidates of the cell parameters and space groups. Then, assuming each candidate, we put a cluster molecule Mo_6Cl_{12} in the unit cell and manipulated the molecules using the Visualizer program so that the molecules are reasonably packed in the unit cell. We calculated the powder diffraction pattern for the structural models and compare it to the experimental diffraction pattern. Structural models were tested with the Rietveld program. Various positions (axial or equatorial) of the aquo-ligands were assumed and tested with the Rietveld program, and only one case gave a reasonable structure. In the analysis, 16 variables were refined by calculating 374 structure factors. Infrared absorption spectrum of the powder sample was recorded using a JASCO IR-4200 spectrometer equipped with an ATR attachment. The sample powder was pressed onto the diamond prism and the absorption spectrum was directly taken without using KBr. This method could eliminate the effect of water adsorbed on KBr. Thermogravimetry (TG) measurement of the product was carried out with a MacScience TG-DTA 2000S apparatus.

^{1}H MAS NMR of the sample was measured with a Varian spectrometer at 600 MHz. Pulse width was set to 4.2 µs. Acquisition time and recycle delay were 20 ms and 5 s, respectively. The data accumulation was 100 times. The spinning rate was 9 kHz. Chemical shifts were corrected by using an external standard (adamantane) and were expressed relative to $(CH_3)_4Si$.

Results and Discussion

Formation of $Mo_6Cl_{12}(OH_2)_2$ by the Reaction of Mo_6Cl_{12} with Liquid Water. The reaction was carried out by adding anhydrous Mo_6Cl_{12} solid to liquid water at ambient temperature. The yellow product was filtered and dried under ambient atmosphere. As will be shown in a later section, this product is $Mo_6Cl_{12}(OH_2)_2$. Figure 1 shows the powder X-ray diffraction patterns of Mo_6Cl_{12} and the product. The source material Mo_6Cl_{12} showed intense peaks only at low diffraction angles around 10 degrees (Figure 1a). The diffraction pattern of the product (Figure 1b) was completely different from that of Mo_6Cl_{12}. The product showed clear intense peaks over a wide range of 2θ from 5 to 50 degrees (Figure 1b). This may be due to the characteristic orientation of the cluster molecules in the structure, which will be discussed in a later section.

Figure 2 shows an IR absorption spectrum of the product. Intense absorption bands around 3200 and 1600 cm^{-1} are characteristic representing H-bonded aquo ligands[31] or water molecule.[32,33] The former band consists of two peaks. The wavenumbers of the H_2O stretching modes were lower than those reported for Mo organometallic complexes (e.g. 3263–3373 cm^{-1} for $[Mo(acac)(\eta^7\text{-}C_7H_7)H_2O]BF_4$) (Ref. 31), suggesting the presence of strong hydrogen bonds of aquo ligands. TG measurement of the sample showed a weight decrease

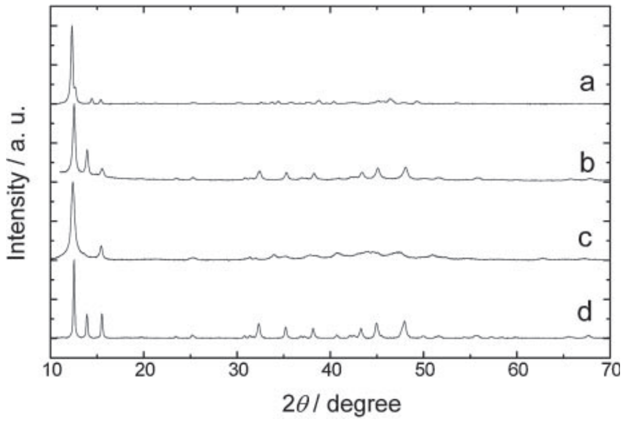

Figure 1. Powder X-ray diffraction patterns of the samples. (a) Mo_6Cl_{12}; (b) product of Mo_6Cl_{12} after reaction with liquid water ($Mo_6Cl_{12}(OH_2)_2$); (c) product after evacuation of sample (b) at 473 K; (d) the product of sample (c) after reaction with liquid water.

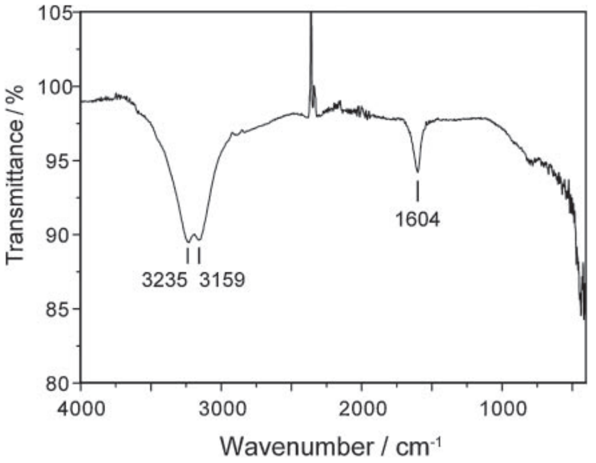

Figure 2. IR absorption spectrum of the reaction product.

Table 1. Rietveld Refinement Results of the X-ray Diffraction Data for $Mo_6Cl_{12}(OH_2)_2$

Space group	*I*4/*m* (No. 87)			
Crystal system	tetragonal			
Cell parameters	*a* (nm) = 0.89869(3)			
	c (nm) = 1.14471(3)			
Z	2			
Atom	*x*	*y*	*z*	*Beq*
Mo1	0	0	0.1583(4)	1.8(2)
Mo2	0.8185(7)	0.9082(6)	0	1.6(1)
Cl1	0.916(1)	0.7381(9)	0.1546(5)	1.5(2)
Cl2	0.788(2)	0.422(1)	0	2.8(3)
O1	0	0	0.347(3)	3.0(1)
R_p/%	7.7			
R_{wp}/%	10.1			
GOF	1.37			

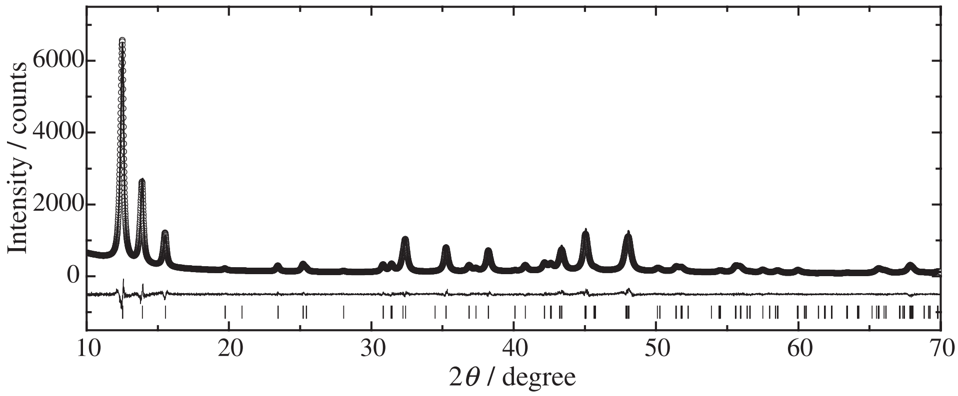

Figure 3. Fitting of the powder X-ray diffraction pattern of $Mo_6Cl_{12}(OH_2)_2$ in the Rietveld analysis.

corresponding to 2.1 molecules of water per cluster for treatment at 620 K for 1 h in an Ar flow.

To test the presence of water in the product, the material was heated at 473 K under vacuum for 1 h and its powder X-ray diffraction was measured. The pattern (Figure 1c) was different from Figure 1b. This sample was confirmed to react with liquid water again and the product gave the same X-ray diffraction pattern (Figure 1d) as Figure 1b. Consequently, this showed that the aquo ligands were reversibly removed and restored by heating in vacuum and by the reaction with water.

Construction of the Structural Model for the Rietveld Refinement. Considering the data shown above, we assumed that the product would retain the Mo_6Cl_{12} cluster structure and contain water molecules. Using this information, we developed model structures and carried out Rietveld analysis using the powder X-ray diffraction pattern.

At first we indexed the powder pattern by using auto-indexing programs build in the Crysfire program package. TREOR90 indexing program succeeded in giving plausible candidates for the cell parameters. Chekcell was used to select candidates for cell parameters and space groups. We then tried to construct a structural model. The Visualizer program in Materials Studio (Accelrys) was used for manipulation of Mo_6Cl_{14} molecules in unit cell candidates suggested by TREOR90. In this process, we used Mo_6Cl_{14} molecular structure cut out from the structure of a known compound Mo_6Cl_{12}. Considering the cell volume, *Z* values equaled 2 for all candidates. First we put one Mo_6Cl_{12} molecule at the corner of the cell, and then apply the candidate space group to the model. We checked the packing of the resulting structure by drawing the model with van der Waals radii (i.e., space filling model). We rotated the molecule at the corner of the cell step by step and calculated powder the X-ray pattern to compare to the experimentally obtained pattern each time. This trial and error processes yielded a reasonable molecular packing that gave a diffraction pattern resembling the experimental one. The obtained structure was monoclinic with a (nm) = 1.271, b (nm) = 1.139, c (nm) = 0.898, β (°) = 134.97 with $C2/m$ (No. 12) symmetry. In this cell, all the molecules had the same orientation. Finally, by using a function of the Visualizer program ("Find symmetry"), we found a cell with higher symmetry in the structure: a tetragonal cell with a (nm) = 0.898, c (nm) = 1.139, and the space group *I*4/*m* (No. 87).

Results of the Rietveld Refinement. By using the model structure described above, Rietveld analysis was carried out. The two axial Cl atoms were replaced by oxygen atoms of water. Table 1 and Figure 3 show the results of the Rietveld analysis. The simulated diffraction pattern reproduced the experimental data well (Figure 3). In Figure 3, the region of $2\theta > 70°$ was omitted for clarity, where the peaks in the region

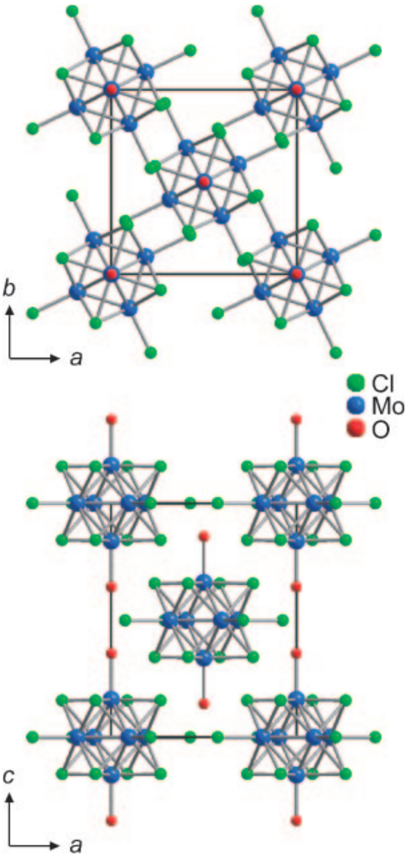

Figure 4. Crystal structure of $Mo_6Cl_{12}(OH_2)_2$ obtained by Rietveld analysis.

were very weak and the fitting was good. The Goodness of Fit factor is 1.365, showing that the refinement was done without serious problem. Since the fitting for peaks at low angles was not perfect, we tried a refinement with diffraction data of higher angles ($2\theta \geq 17°$) to eliminate the three peaks at lower angles. This analysis gave a good fitting (GOF = 1.125, $R_p = 7.88$, $R_{wp} = 10.1$), confirming that the obtained structure was reliable. When equatorial Cl atoms were replaced by oxygen, the structure did not converge to give an acceptable position of oxygen atoms.

Figure 4 shows the crystal structure of the compound obtained by this analysis. This is the first report, to our knowledge, of the compound $Mo_6Cl_{12}(OH_2)_2$, but it is isostructural to $Mo_6Br_{12}(OH_2)_2$ (Ref. 25). The final refinement procedure was done with no constraint conditions, and the structure converged to a reasonable molecular structure: The final refinement gave Mo–Mo and Mo–Cl(octahedral face bridging) distances were 0.257–0.259 and 0.247–0.250 nm, respectively (Table 2). These bond lengths are close to those in $(H_3O)_2Mo_6C_{14}\cdot 6H_2O$ structure determined by single-crystal analysis and reported in the literature[34] (Mo–Mo = 0.257–0.262 nm; Mo–Cl(octahedral face bridging) = 0.245–0.247 nm), demonstrating that the refined structure is highly reliable. In the obtained structure $Mo_6Cl_{12}(OH_2)_2$ molecules were densely packed to form hydrogen-bonded network structure. The distance between the oxygen of an aquo-ligand and the terminal Cl atom was 0.3195(20) nm, which is close to the typical value of a Cl···H–O H-bond length (0.312 nm). The bond angle of Cl–O–Cl was 113.8(9)°, which was reasonable as the angle between the hydrogen bonds of a water molecule. An aquo-ligand is thereby H-bonding with two Cl atoms pointing outwards from two neighboring cluster molecules.

Table 2. Selected Bond Lengths (nm)

Mo1–Cl1	0.2473(8)
Mo2–Cl1	0.2481(8)
	0.2497(8)
Mo1–Mo2	0.2574(5)
Mo2–Mo2	0.2585(8)
Mo1–O1	0.217(3)

Although the presence of the $Mo_6Cl_{12}(OH_2)_2$ molecule was previously reported for a compound with crystal water, $Mo_6Cl_{12}(OH_2)_2\cdot 6H_2O$,[35] the crystal of $Mo_6Cl_{12}(OH_2)_2$ containing no water molecules except the two aquo ligands is reported here for the first time. In the known $Mo_6Cl_{12}(OH_2)_2\cdot 6H_2O$ structure, the cluster molecules form double layers separated by layers of water molecules. In the present study, the $Mo_6Cl_{12}(OH_2)_2$ molecules are connected to each other by H-bonding without extra linking ligands to form a three-dimensional network.

Results of ^{1}H MAS NMR Measurements. An ^{1}H MAS NMR spectrum of the sample is shown in Figure 5. A broad signal was observed at 6.8 ppm accompanied by well-resolved intense spinning side bands (SSBs). Total intensity of the signal including the SSBs was stronger than a sharp signal observed at 5.1 ppm, which showed no SSBs. Volke et al. reported an ^{1}H MAS NMR spectrum of ice (diluted with D_2O).[36] The signal had a peak top at ca. 5 ppm and a very broad continuous shape spread from ca. −60 to 60 ppm even at a spinning rate of 4 kHz. Our present measurement gave the ^{1}H signal with clearly resolved SSBs, indicating that the dipole–dipole interactions between the ^{1}H nuclei are not strong in the present compound. This is probably because the ca. 1 nm cluster molecules separate the water molecules at long distances. The minor component at 5.1 ppm should be due to (a) highly mobile species. The tentative assignment of this component is Mo–(OH_2) at surfaces of the crystals. Another possibility is a residual water molecule in the structure of which one of the two water molecules is deficient from the six-handed linkage. The detailed analysis and dynamics of the protons are an interesting subject for future studies.

The Network Structure of the Self-Assembled Molecules Formed by the Unique H-Bonding Linkages. The crucial factor for network structures is the position of the binding sites in a molecule. Figure 6 shows schematic models of the $Mo_6Cl_{12}(OH_2)_2$ molecule and the self-assembled structure. As shown in Figure 6a, the H-bonds between terminal Cl atoms and aquo-ligands are presented as flexible joints, because the bond angles of Mo–Cl–O (or Mo–Cl···H) in Mo–Cl···H–O H-bonding bridges are flexible. The aquo-ligand is rotatable around the O–Mo bonds. Consequently, these bonds can be modeled as freely rotating around the O–Mo bond (Figure 6a). In Figure 6b, the $Mo_6Cl_{12}(OH_2)_2$ molecule was modeled to have the two joints with two "cups" of H-bonds at the position

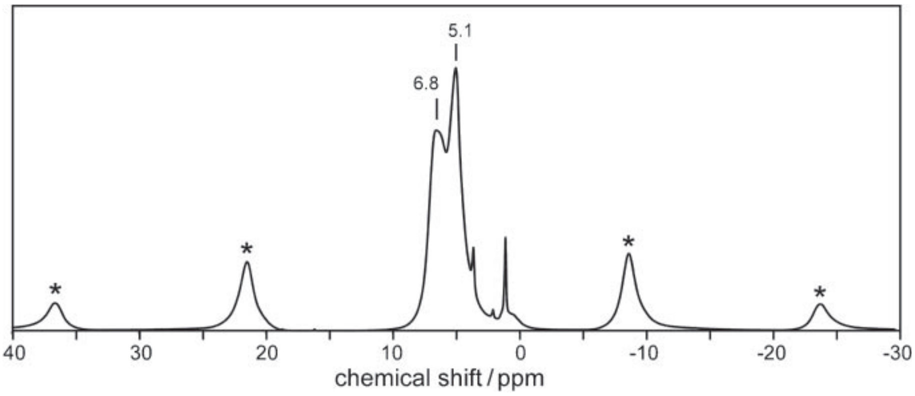

Figure 5. ^{1}H MAS NMR spectrum of the $Mo_6Cl_{12}(OH_2)_2$ sample. The asterisks indicate spinning side bands for the signal at 6.8 ppm. The structure at around 2 ppm is due to the sample rotor and the cap.

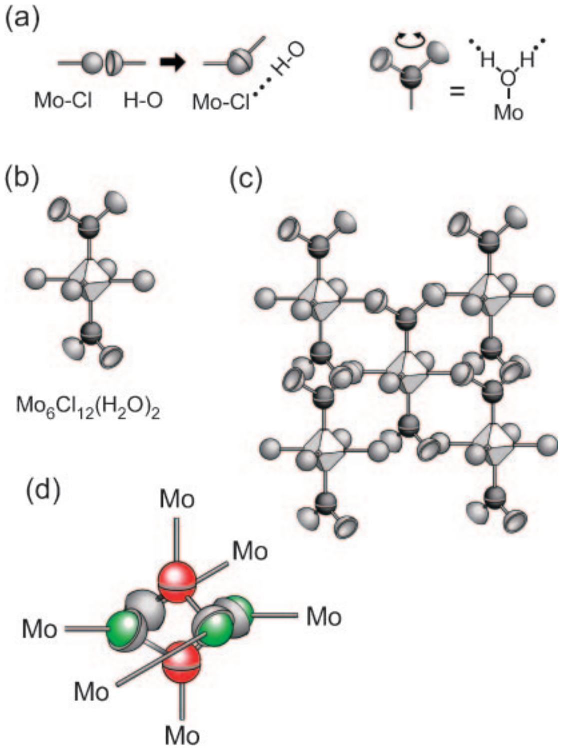

Figure 6. Schematic model presentation of the $Mo_6Cl_{12}(OH_2)_2$ molecule and the network of H-bonding.

of aquo ligands and the four spheres sticking out in equatorial positions. Figure 6c illustrates a model of five molecules joining with each other in the self-assembled structure in the crystal of $Mo_6Cl_{12}(OH_2)_2$. The notable point for this network structure is the characteristic six-handed linkage, which is formed by equatorial terminal Cl atoms and axial aquo ligands. The four terminal Cl atoms from four different molecules and two aquo ligands from two different molecules formed a linkage to connect the six molecules via H-bonding. Figure 6d illustrates a model of the six-handed linkage. Each of the two aquo ligands links three cluster molecules and these engage with each other.

The linkage is interesting in terms of two points: (1) it links as many as six hexanuclear clusters. (2) The linkage is expected to be flexible. The second point will be discussed in a later section. Here we discuss the first point. In general, a water molecule or an aquo-ligand can act as a three-handed linker. As stated earlier, linkers with more than three "hands" involve two water molecules and a proton to form a kind of "four-handed" linker (i.e., $H_2O\cdots H^+\cdots OH_2$) which is found in various ionic crystals.[14–16] In a similar manner to the compound presented in this study, these compounds contain inorganic molecules at nanometer scale, such as a six nuclear metal cluster halide compound[14] $[(18\text{-crown-}6)_2(H_5O_2)]_3[Nb_6Cl_{18}]$, and a polyoxometalate[15,16] $H_3PW_{12}O_{40}\cdot 6H_2O$ $(=(H_5O_2)_3PW_{12}O_{40})$. As stated in the introduction, the $H_9O_4{}^+$ cation is another interesting linker.[18,19] For example, $[(C_2H_5)_4N]_2(H_9O_4)[Mo_3S_7Cl_6]$ is a cluster compound that contains helical chains of polymeric $H_9O_4{}^+$, which H-bonds with four Cl atoms. In contrast, $[(C_2H_5)_4N]_2(H_9O_4)[Mo_3S_7Br_6]$ forms a different structure that contains isolated $H_9O_4{}^+$ cations. In this cation, a H_3O^+ molecule is H-bonded to three other H_2O molecules. This H-bonding network positions four oxygen atoms to form a trigonal pyramid. This cation forms H-bonding to two Br atoms of the cluster molecules. These cations can be regarded as "four-handed" and "two-handed" linkers. However, the six-handed linkage formed by water molecules (or aquo ligands) is very rare. As shown in Figure 6d, the two aquo ligands are not bonded directly, but merely engage each other. However, the two aquo ligands do not detach from each other, because the $Mo_6Cl_{12}(OH_2)_2$ molecules, to which the aquo ligands are bonded, are clamped by other molecules. In this sense, at the linkage the four Cl atoms and two aquo ligands connect six Mo atoms of different cluster molecules (Figure 6d). These characteristics of the structure are ascribed to the symmetric shape of the building blocks (i.e., $Mo_6Cl_{12}(OH_2)_2$ molecule) at the nanometer scale having multiple sites for H-bonding.

The Flexibility of the Six-Handed Linkages Reflected in the Crystal Structure. It is notable here that the angles between the four bonds in the six-handed linkage could be changeable like a hinge (Figure 6d), because the aquo ligands are rotatable and the Mo–Cl$\cdots$(HO) angles are flexible (Figure 6a). Here let us construct a virtual structure having network connectivity the same as that of the real structure, by connecting the cluster molecules with the six-handed linkages. The real crystal structure can be derived from the virtual

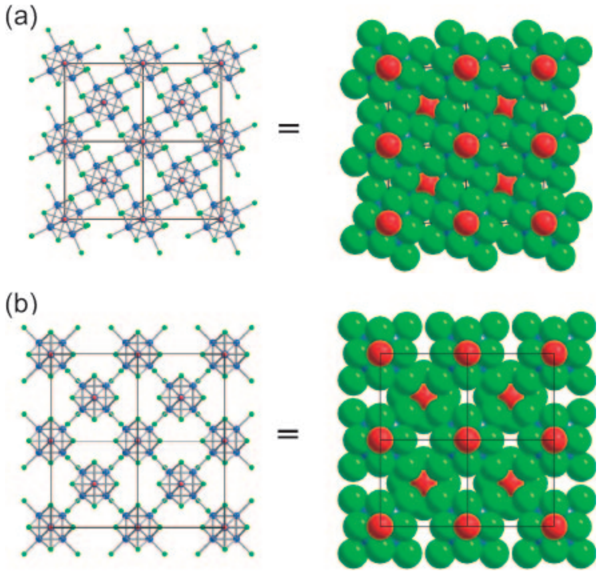

Figure 7. A comparison between the real (a) and virtual crystal structures (b). The flexible six-handed linkages adopt angles such that the cluster molecules are densely packed in the real structure.

structure only by changing the angles of the six-handed linkages. For example, atoms in a Mo–Cl···H–O–H···Cl–Mo linkage can be complanate, and the virtual crystal structure in this case is presented in Figure 7. The space group of the virtual structure is $I4/mmm$, having symmetry higher than the real crystal structure ($I4/m$). Figure 7 also shows the virtual and the real structures drawn using van der Waals radii (i.e., space-filling model). The virtual structure has a larger volume compared with the real structure. In the real structure, the cluster molecules contact each other and form a densely packed structure, whereas the cluster molecules in the virtual structure are separated by small spaces. That is, in the real structure, the flexible linkages adopt angles so that the cluster molecules contact each other. Upon changing the angles of the linkages, the cluster molecules are always parallel to each other. Therefore, in the real structure, all the cluster molecules have the same orientation as found in the virtual symmetric structure. This may reflect that the X-ray diffraction pattern of this compound shows intense peaks in the high angle region ($2\theta > 30°$).

Conclusion

We found a molecular compound $Mo_6Cl_{12}(OH_2)_2$, with a characteristic three-dimensional H-bonding network. The molecules were connected by a characteristic and rare six-handed flexible linkage in the structure. The present study highlights an interesting example in which building blocks at the nanometer scale have multisites for bonding. These molecules form a symmetric and characteristic structure by using the multisites capable of H-bonding in a molecule.

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