Crystal Engineering with $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$ Anion as Nanosized Building Block

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Successfully we prepared crystalline compounds of $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$ ($\{Mo_{36}\}$) anion with various α,ω-alkanediamines (C_n-DA, $n = 3$–11) aiming at crystal engineering with nanosized building blocks. 2-, 1-, and 0-D frameworks of $\{Mo_{36}\}$ were obtained depending on length of alkane moiety of C_n-DA. These frameworks were linked by C_n-DA molecules (or protonated cations) using hydrogen bonds. In the crystalline compounds with C_n-DA cations of $n = 3$–5 some fraction of the cations were captured in the hollows of $\{Mo_{36}\}$, indicating the ability of $\{Mo_{36}\}$ as receptor.

Various nanosized polyoxomolybdate (NS-POM) species with interesting structural features such as "nanosized cavity" have been known since the pioneer work of Müller group.[1–6] They are expected to be used as building blocks efficient for crystal engineering of novel functional materials.

On the other hand, a large polyoxomolybdate anion $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$ ($\{Mo_{36}\}$) has been known long before the Müller group's work.[7–10] This POM species also has nanosized dimensions (ca. $2 \times 1 \times 1\,nm^3$) and consists of subunits (such as $\{Mo_8\}$ composed of seven MoO_6 octahedra and one MoO_7 bipyramid) common to those of the above NS-POM species.[1–6,10] We regard it, therefore, as one of NS-POMs. The structure of $\{Mo_{36}\}$ is shown in Figure 1. It has a shape like two half-cut bivalve shells symmetrically adhered by sharing cut corners, and thus has a hole, like a bead, and hollows symmetrically at the both ends. Surface of the hollow is decorated with some –O and $–OH_2$ functional groups, and hence some specific molecules might be captured in the hollows. Therefore, $\{Mo_{36}\}$ species might become an interesting building block to build solids with receptor ability.

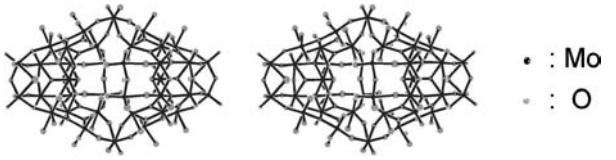

Figure 1. Structure of $\{Mo_{36}\}$ anion (stereo view).

As the first attempt on systematic use of NS-POMs as building blocks, we tried to build up $\{Mo_{36}\}$ species into crystalline solids by linking them with various α,ω-alkanediamines $NH_2(CH_2)_nNH_2$ ($n = 2$–12), aiming at crystal engineering of functional materials with nanosized building blocks.

The aqueous solution of $\{Mo_{36}\}$ was prepared by treating aqueous sodium molybdate with an ion-exchange resin. Presence of $\{Mo_{36}\}$ as a main species in the solution was confirmed by Raman bands at ca. 985, 955, and $900\,cm^{-1}$.[8] 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 prepared. Appropriate amounts of C_n-DA and HCl solutions were added to the $\{Mo_{36}\}$ solution with vigorous stirring. (For example, [Mo], [C_3-DA], and [HCl] of the resulting solution, which provided good crystals of the C_3-DA compound, were 100, 4, and 8 mmol/L, respectively.) Then the resulting solution was allowed to stand for several days at room temperature in order to obtain single crystals of the products.

Single crystals of various $\{Mo_{36}\}$ compounds with C_n-DAs ($n = 3$–11) were successfully obtained and their crystal structures were determined by single crystal X-ray analysis. Although further improvement in crystallinity is still necessary for C_4- and C_6-DA compounds (as for the latter only information about $\{Mo_{36}\}$ anions has been obtained), understanding of fundamental crystal structures of them was achieved. Information on the structural analyses is given in Table 1. Chemical compositions determined from the structural analysis of the crystals were as follows:[11] $(NH_3(CH_2)_nNH_3)_4[Mo_{36}O_{112}(H_2O)_{14}]\cdot mH_2O$ for $n = 3, 5$; and $(NH_3(CH_2)_nNH_3)_4[Mo_{36}O_{112}(H_2O)_{16}]\cdot mH_2O$ for $n = 7$–11. The number of water of crystallization that could be located (m) is shown in Table 1. The cell volume/Z (V/Z) tends to increase with increasing n of C_n-DA. The space group of the compounds obtained was $P\bar{1}$, except for the C_3-DA compound ($P2_1/n$).

The compounds in Table 1 show three types of common $\{Mo_{36}\}$ frameworks depending on C_n-DA, which are shown in Figure 2. In the crystals $\{Mo_{36}\}$ anions align in side-staggered pattern. Exceptionally they do in herringbone pattern in the C_3-DA compound. For the C_n-DA compounds with $n = 3$–6, direct linkages between neighboring $\{Mo_{36}\}$ anions occured via condensation reaction of surface groups of $\{Mo_{36}\}$ anions; $Mo=O + Mo–OH_2 \rightarrow Mo–O–Mo + H_2O$ (see the Mo–O–Mo linkages surrounded by small circles in Figures 2a and 2b). In the C_3-DA compound a $\{Mo_{36}\}$ anion is bound to the nearest four, resulting in the formation of two-dimensional (2-D) framework consisting of $\{Mo_{36}\}$ anions (Figure 2a). For the C_n-DA compounds with $n = 4$–6 each one is bound to the nearest two, and the one-dimensional (1-D) framework is formed (Figure 2b). For the C_n-DA compounds with $n > 6$ there is no direct linkage between $\{Mo_{36}\}$ anions. We refer to the resulting

Table 1. Information on structural analyses of C_n-DA compounds

n	SG	R_1(F)	$wR_2(F^2)$	$V/Z/Å^3$	m	CCDC No.
3	$P2_1/n$	0.0509	0.1358	3728(1)	26	262176
4	$P\bar{1}$	0.0912	0.2934	3401(1)	—	—
5	$P\bar{1}$	0.0644	0.1691	3540(1)	12	262177
6	$P\bar{1}$	0.1585	0.4198	4033(2)	—	—
7	$P\bar{1}$	0.0658	0.1612	4054(2)	32	262178
8	$P\bar{1}$	0.0846	0.2348	4188(2)	28	262179
9	$P\bar{1}$	0.0799	0.2479	4259(2)	28	—
10	$P\bar{1}$	0.0773	0.2184	3935(1)	14	262180
11	$P\bar{1}$	0.0913	0.2381	4210(1)	18	262181

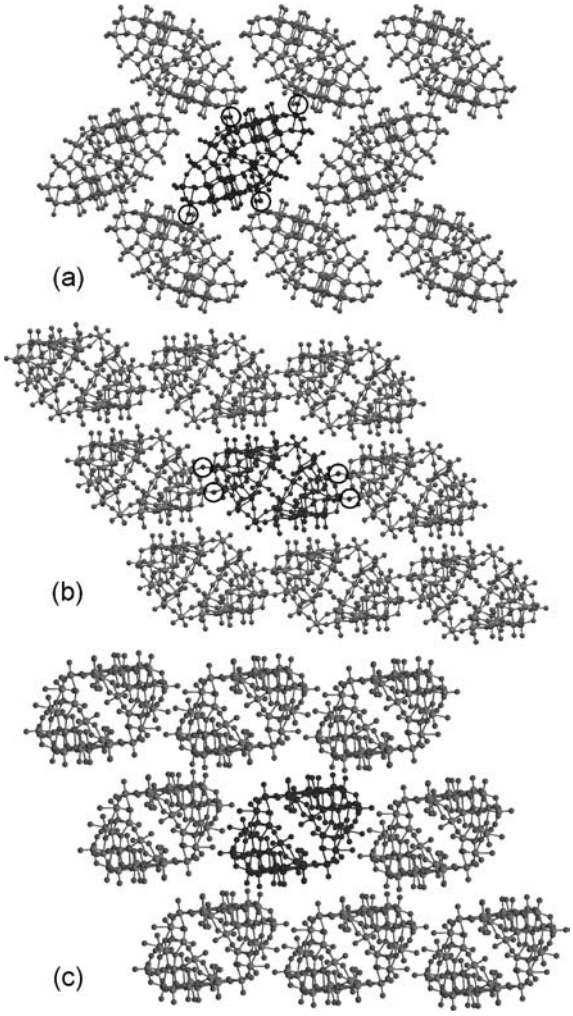

Figure 2. Extended $\{Mo_{36}\}$ frameworks observed in $\{Mo_{36}\}$ compounds with C_n-DAs: (2-D) sheet structure in the C_3-DA compound (a), (1-D) chain structure in the C_5-DA compound (b), and 0-D structure in the C_7-DA compound (c). The frameworks are depicted by a ball and stick model. For clarity C_n-DA and crystallization water molecules are omitted. For discernment of $\{Mo_{36}\}$ moiety one of $\{Mo_{36}\}$'s is highlighted (darkened) in respective frameworks. Direct linkages between highlighted $\{Mo_{36}\}$ anions and their neighbors are shown by surrounding with small circles.

framework as a zero-dimensional (0-D) one (Figure 2c). Because the pH of the solution where the compounds were formed was almost constant (ca. 1.7) independently of C_n-DA, dimensionality of the resulting $\{Mo_{36}\}$ framework was related not to variation in nature of solution caused by addition of C_n-DA, but to length of C_n-DA, which acted as a linker connecting $\{Mo_{36}\}$ frameworks (as mentioned below).

Crystallization water molecules are mainly located in free space among $\{Mo_{36}\}$ frameworks, and a part of them are captured in the hole (or hollow) of $\{Mo_{36}\}$ anions in many cases. C_n-DA molecules are protonated, and present as divalent cation, $(NH_3(CH_2)_nNH_3)^{2+}$, in the crystals. There are four C_n-DA cations per one $\{Mo_{36}\}$ anion, except for the C_4-DA compound that has possibility of five C_4-DA/$\{Mo_{36}\}$. Figure 3 shows structural information about C_n-DA cations in the compounds. These cations play a role to connect $\{Mo_{36}\}$ frameworks by hydrogen

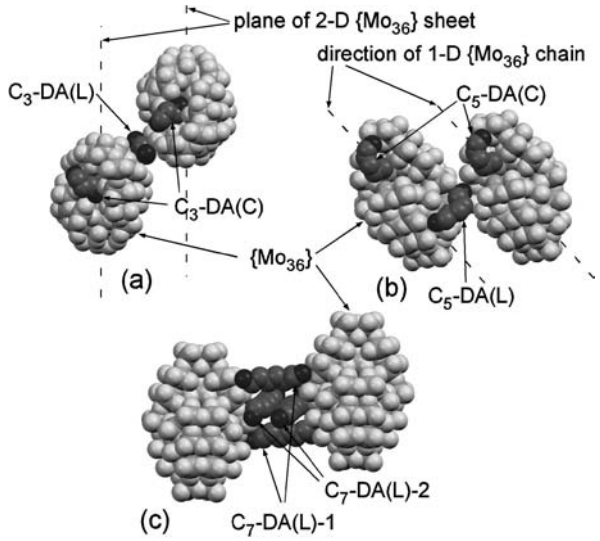

Figure 3. C_n-DA molecules (protonated cations) in the $\{Mo_{36}\}$ compounds: C_3-DA (a), C_5-DA (b), and C_7-DA compound (c). For clarity depicted are only parts of structures related mainly to connection of $\{Mo_{36}\}$ anions by C_n-DA cations. C_n-DA(L) and (C) denote C_n-DA as a linker and one completely captured in the hollow, respectively.

bonding to the surface groups of $\{Mo_{36}\}$ anions. In the C_n-DA compounds with $n < 6$ isolated C_n-DA cations act as linkers or adhesives (C_3-DA(L) and C_5-DA(L) in Figures 3a and 3b), while in the C_n-DA compounds with $n > 6$ aggregates of four C_n-DA cations act as multitopic linkers (C_7-DA(L)-1 and C_7-DA(L)-2 in Figure 3c). The linkers bind with various surface sites of the $\{Mo_{36}\}$ anion, depending on C_n-DA. Furthermore, it is noted that in the C_n-DA compounds with $n = 3$–5 there are some fractions of C_n-DA cations that are not related to connections of $\{Mo_{36}\}$ anions (C_3-DA(C) and C_5-DA(C) in Figures 3a and 3b). These C_n-DA cations are completely captured in the hollows of $\{Mo_{36}\}$ species. Such capture of molecules (cations) in the hollows may permit molecular recognition, and is of interest from the viewpoint of receptor ability of $\{Mo_{36}\}$.

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References and Notes

1 A. Müller, J. Meter, E. Krickemeyer, and E. Diemann, *Angew. Chem., Int. Ed. Engl.*, **35**, 1206 (1996).
2 A. Müller, E. Krickmeyer, H. Bögge, M. Schmidtmann, C. Beugholt, P. Kögerler, and C. Lu, *Angew. Chem., Int. Ed.*, **37**, 1220 (1998).
3 A. Müller, E. Krickmeyer, H. Bögge, M. Schmidtmann, and F. Peters, *Angew. Chem., Int. Ed.*, **37**, 3359 (1998).
4 A. Müller, S. Q. N. Shah, H. Bögge, and M. Schmidtmann, *Nature*, **397**, 48 (1999).
5 A. Müller, C. Beugholt, H. Bögge, and M. Schmidtmann, *Inorg. Chem.*, **39**, 3112 (2000).
6 A. Müller, E. Beckmann, H. Bögge, M. Schmidtmann, and A. Dress, *Angew. Chem., Int. Ed.*, **41**, 1162 (2002).
7 K. H. Tytko, B. Schönfeld, B. Buss, and O. Glemser, *Angew. Chem., Int. Ed.*, **12**, 330 (1973).
8 K. H. Tytko and B. Schönfeld, *Z. Naturforsch.*, **30b**, 471 (1975).
9 I. Pault-Böschen, *J. Chem. Soc., Chem. Commun.*, **1979**, 780.
10 B. Krebs and I. Paulat-Böshen, *Acta. Crystallogr.*, **B38**, 1710 (1982).
11 Because of tiny size of crystals, coprecipitation of aggregates, and ease of dehydration, it was difficult to obtain enough amounts of samples with homogeneous stoichiometry for compositional analysis. Analytical results obtained for some compounds are given separately as supplemental data.

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