Research Article

Hybrid Layered Crystal Comprising Polyoxometalate and Surfactant Synthesized from Reduced Mo-Blue Species

Keisuke Mikurube, 1 Kimiko Hasegawa, 2 Haruo Naruke, 3 and Takeru Ito 1

1 Department of Chemistry, School of Science, Tokai University, 4-1-1 Kitakaname, Hiratsuka 259-1292, Japan
2 X-Ray Research Laboratory, Rigaku Corporation, 3-9-12 Matsubara-cho, Akishima 196-8666, Japan
3 Chemical Resources Laboratory, Tokyo Institute of Technology, 4259-RI-23 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

Correspondence should be addressed to Takeru Ito; takeito@keyaki.cc.u-tokai.ac.jp

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1. Introduction

Crystalline layered materials are superior to soft layered materials with respect to the structural stability and homogeneity. The two-dimensional anisotropy of layered materials leads to the emergence of properties such as electronic conductivity or intercalation [1–4], while the precise control of the layered periodicity and component arrangement is required. Inorganic-organic hybrid materials have wider options to select compositions and structures owing to organic components than purely inorganic compounds. Hybrid crystals composed of conductive organic molecules and inorganic anions have been reported [5–7].

Surfactant molecules to self-assemble into lamellar phase are an effective organic component as a structure-directing reagent for layered structures [8–10]. The layered distance can be controlled by changing the length of long alkyl chains. Polyoxometalate anions (POMs) having various physicochemical properties [11–17] can be used as inorganic component, which enables to design the composition, structures, and functions of hybrid layered crystals. Surfactant-POM hybrid layered crystals have been rarely reported [18–28] rather than surfactant-POM hybrid materials [29–33].

Surfactant-POM hybrid layered crystals can be synthesized by direct cation-exchange reaction, in which cationic surfactants are added to aqueous POM solution [18, 19, 24–27]. Another strategy uses precursor surfactant-POM hybrid crystals as synthetic starting material [21–23]. In this precursor method, the reaction of isopolymolybdate anions isomerize or react with the solvent during the recrystallization process to give other types of surfactant-POM hybrid crystals having different compositions and structures [21–23].

Isopolymolybdate can form several types of dark-blue reduced species, so-called "molybdenum-blue" (Mo-blue) species [15, 16]. These Mo-blues are relatively stable and have various structural diversity. After gradual oxidation, the Mo-blues change to conventional isopolymolybdate (colorless or pale yellow). The reoxidation of the Mo-blue species can be employed for the syntheses of surfactant-POM hybrid crystals [20]. Using Mo-blue species as starting precursor
material provides another strategy to control of compositions and structures of surfactant-POM hybrid crystals.

We report here a synthesis of surfactant-POM hybrid crystal by using Mo-blue species as starting precursor material. The Mo-blue species and hexadecylypyridinium (C_{16}py) cation formed hybrid materials (C_{16}py-Mo-blue). The gradual oxidation of the C_{16}py-Mo-blue resulted in the formation of C_{16}py-octamolybdic acid hybrid crystal, [C_{16}H_{33}N(C_{16}H_{12}O_{2})][\beta-H_{3}Mo_{6}O_{24} \cdot 2C_{2}H_{5}OH (C_{16}py-H_{2}Mo_{6})], which was the first example of proton-containing surfactant-polyoxomolybdate hybrid crystal.

2. Experimental

All chemical reagents were obtained from commercial sources. C_{16}py-Mo-blue hybrid was prepared as follows; Na_{2}MoO_{4} \cdot 2H_{2}O (2.6 g, 11 mmol) was dissolved in H_{2}O (10 mL), and the pH level was adjusted to 3.0–4.5 with 6 M HCl. To the colorless acidified solution was added solid ascorbic acid (0.06 g, 0.3 mmol) as reducing reagent. After stirring for 10 min. Obtained dark-blue precipitates (C_{16}py-Mo-blue) were washed by water/ethanol solution followed by drying in dark place. IR (KBr disk) for C_{16}py-Mo-blue: 953 (m), 908 (m), 876 (m), 845 (m), 791 (m), 764 (m), 661 (s), 644 (m), 625 (s), and 599 (s) cm\(^{-1}\).

C_{16}py-H_{2}Mo_{6} was synthesized by using gradual oxidation of C_{16}py-Mo-blue. 0.10 g of C_{16}py-Mo-blue was dispersed in hot ethanol/N,N-dimethylformamide (15 mL, 2:1 (v/v)), and the supernatant was kept at 293 and 288 K to give colorless needles of C_{16}py-H_{2}Mo_{6}. Dimethylamine molecules formed by the decomposition of N,N-dimethylformamide probably adsorbed to the crystals of C_{16}py-H_{2}Mo_{6} employed for the elemental analysis. Anal. for C_{16}py-H_{2}Mo_{6}: Calcld for C_{20}H_{59}N_{5}Mo_{6}O_{26}: C, 29.31; H, 4.92; N, 2.97%. Found: C, 29.11; H, 4.43 N, 2.96%. IR (KBr disk) for C_{16}py-H_{2}Mo_{6}: 943 (s), 914 (s), 837 (m), 723 (m), 687 (w), 656 (m), 552 (w), and 519 (w) cm\(^{-1}\).

IR spectra (as KBr pellet) were recorded on a Horiba FT-710 spectrometer. Powder X-ray diffraction (XRD) patterns were measured with a Rigaku Geigerflex RAD-2X diffractometer by using Cu Kα radiation (λ = 1.54056 Å) at ambient temperature.

Single crystal X-ray diffraction measurements for C_{16}py-H_{2}Mo_{6} were made on a Rigaku VariesMax with RAPID imaging plate area detector using CuKα radiation (crystal-to-detector distance: 127.40 mm) at Rigaku Corporation. Diffraction data were collected for a needle crystal (0.16 × 0.08 × 0.04 mm). The structure was solved by direct methods using SHELXS97 [34] and expanded using Fourier techniques. The refinement procedure was performed by the full-matrix least squares using SHELXL97 [34]. All calculations were performed using the CrystalStructure [35] software package. Empirical absorption correction was performed for the observed data. All nonhydrogen atoms were refined anisotropically. H atoms of C_{16}py cation were refined isotropically, and H atoms of ethanol C atoms were located in calculated positions. H atoms of H_{2}Mo_{6} and hydroxyl group in the ethanol were not included in the refinement procedure. CCDC-922099.

3. Results and Discussion

Polyoxomolybdate is well known to form reduced Mo-blue species [14–16]. The dark-blue precipitates were isolated from reduced polyoxomolybdate solution by adding C_{16}py cation. The IR spectrum of the precipitates (Figure 1(a)) revealed the presence of C_{16}py cation (1400–1600 and 2800–3200 cm\(^{-1}\) range). The IR bands in the 400–1200 cm\(^{-1}\) range were similar to those typical for Mo-blue nanorings [36, 37], indicating the formation of C_{16}py-Mo-blue hybrids. The Mo-blue species are gradually oxidized to form conventional polyoxomolybdate anion, which means that C_{16}py-Mo-blue works as starting material for the C_{16}py-POM hybrid crystals. Here colorless crystals of C_{16}py-H_{2}Mo_{6} were reproducibly synthesized using the C_{16}py-Mo-blue hybrid during the recrystallization process. The IR spectra of C_{16}py-H_{2}Mo_{6} exhibited similar pattern in the 400–1200 cm\(^{-1}\) range to that of β-octamolybdate [β-[Mo_{6}O_{24}]^{3+}, β-Mo_{6}O_{24}] anion (Figure 1(b)). The molecular structure was confirmed by X-ray structure analysis as described below. However, single broad band in the 600–800 cm\(^{-1}\) range for the usual β-Mo_{8} species [38, 39] was split into two bands for C_{16}py-H_{2}Mo_{6}, suggesting the presence of attaching protons to β-Mo_{8} anion (see below).

Powder X-ray diffraction pattern of C_{16}py-H_{2}Mo_{6} measured at ambient temperature (Figure 2(a)) was almost the same in the peak position as the pattern calculated from the results of single crystal X-ray analysis (Figure 2(b)). This indicates that C_{16}py-H_{2}Mo_{6} was obtained as a single phase. Slight differences in the peak intensity and position of the patterns will be owing to the difference in the measurement temperature (powder: ambient temperature, single crystal:...
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Figure 2: Powder X-ray diffraction patterns of C_{16}py-H_2Mo_8 from (a) observed data measured at ambient temperature and (b) calculated data using the structure obtained by single-crystal X-ray diffraction.

Table 1: Crystallographic data for C_{16}py-H_2Mo_8.

<table>
<thead>
<tr>
<th>Chemical formula</th>
<th>C_{16}H_{36}Mo_8N_2O_{28}</th>
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<tbody>
<tr>
<td>Formula weight</td>
<td>1882.69</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2_1/c (No. 14)</td>
</tr>
<tr>
<td>a (Å)</td>
<td>20.3302(4)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>8.24345(15)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>21.6976(15)</td>
</tr>
<tr>
<td>β (°)</td>
<td>116.534(8)</td>
</tr>
<tr>
<td>V (Å^3)</td>
<td>3253.3(2)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>μ (Cu Kα) (mm^{-1})</td>
<td>12.870</td>
</tr>
<tr>
<td>Number of reflections measured</td>
<td>36637</td>
</tr>
<tr>
<td>Number of independent reflections</td>
<td>5941</td>
</tr>
<tr>
<td>R_{int}</td>
<td>0.0405</td>
</tr>
<tr>
<td>Number of parameters</td>
<td>531</td>
</tr>
<tr>
<td>R (I &gt; 2σ(I))</td>
<td>0.0327</td>
</tr>
<tr>
<td>wR_2 (all data)</td>
<td>0.0777</td>
</tr>
</tbody>
</table>

The crystals of C_{16}py-H_2Mo_8 contained no water of crystallization to which proton can be attached. These results show the presence of two separate protons located to O4 (Figure 3(a)), supported by the IR spectrum of C_{16}py-H_2Mo_8 as mentioned above. Thus, the composition of C_{16}py-H_2Mo_8 was revealed to be [C_{5}H_{5}N(C_{16}H_{33})]_2[β-H_2Mo_8O_{26}]-2C_{2}H_{5}OH. This is the first surfactant-polyoxomolybdate hybrid crystals to comprise protons, while sodium cation has been introduced in the surfactant-polyoxomolybdate hybrid crystals [21, 22]. The reduced Mo-blue species tend to contain protons for the charge compensation, which may result in the formation of proton-containing surfactant-POM hybrid crystals. The C_{16}py-H_2Mo_8 hybrid crystal containing isopolyoxometalate probably does not behave as a strong acid, being different from heteropoly acids (heteropolyoxometalates comprising protons as counter cations) [11, 41]. C_{16}py-H_2Mo_8 possibly exhibits moderate proton conductivity in the intermediate temperature region over 373 K as observed in another surfactant-POM hybrid layered crystal [42].
Figure 4: (a) Molecular arrangements in the inorganic layers of C_{16}py-H_{2}Mo_{8}. The short contacts including C–H⋯O hydrogen bonds are represented in broken lines. (b) Molecular arrangements of C_{16}py-H_{2}Mo_{8} at the interface between the β-H_{2}Mo_{8} inorganic and C_{16}py organic layers. The hexadecyl groups and ethanol molecules are omitted for clarity.

Table 2: C–H⋯O hydrogen bonds in C_{16}py-H_{2}Mo_{8}.

<table>
<thead>
<tr>
<th>Symmetry codes:</th>
<th>C–H (Å)</th>
<th>H⋯O (Å)</th>
<th>C⋯O (Å)</th>
<th>C–H⋯O (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{5}–H_{5}⋯O_{8}</td>
<td>0.96(6)</td>
<td>2.84(6)</td>
<td>3.722(6)</td>
<td>152(5)</td>
</tr>
<tr>
<td>C_{6}–H_{6}B⋯O_{8}</td>
<td>0.81(7)</td>
<td>2.92(7)</td>
<td>3.726(8)</td>
<td>175(6)</td>
</tr>
<tr>
<td>C_{7}H⋯H_{7}B⋯O_{8}</td>
<td>0.92(4)</td>
<td>2.75(4)</td>
<td>3.641(5)</td>
<td>165(4)</td>
</tr>
<tr>
<td>C_{2}B⋯H_{2}⋯O_{9}</td>
<td>0.89(5)</td>
<td>2.62(5)</td>
<td>3.450(7)</td>
<td>156(4)</td>
</tr>
<tr>
<td>C_{9}B⋯H_{9}B⋯O_{9}</td>
<td>0.97(3)</td>
<td>3.05(3)</td>
<td>3.993(5)</td>
<td>163(3)</td>
</tr>
<tr>
<td>C_{2}I⋯H_{2}I⋯O_{12}</td>
<td>0.95(5)</td>
<td>2.66(5)</td>
<td>3.536(6)</td>
<td>153(5)</td>
</tr>
<tr>
<td>Between β-H_{2}Mo_{8} and ethanol</td>
<td>C_{22}′⋯H_{22}A⋯O_{3}</td>
<td>0.989(4)</td>
<td>2.139(2)</td>
<td>3.097(5)</td>
</tr>
</tbody>
</table>

Symmetry codes: 1−x,−y,−z; 2−1+x,y; z; 3−x,1−y,−z; 4−1−x,−0.5+y,−0.5−z; 5x,0.5−y,−0.5+z.

The crystal packing of C_{16}py-H_{2}Mo_{8} consisted of alternating inorganic β-H_{2}Mo_{8} monolayers and organic C_{16}py bilayers (Figure 3(b)). The hexadecyl chains of C_{16}py interdigitated in the C_{16}py bilayers. The inorganic monolayers were composed of β-H_{2}Mo_{8} and ethanol molecules of crystallization. Such alternate stacking of inorganic and organic layers was similar to that of most POM-surfactant hybrid crystals [18–28]. The periodicity of the layers was 18.2 Å. All C–C bonds in the hexadecyl chains showed anti conformation as observed in a hybrid crystal of C_{16}py and hexamolybdate [24].

However, the molecular arrangement in the inorganic layer was quite different from that for other C_{16}py-POM hybrid layered crystal [21–25]. The hydrophilic heads of C_{16}py usually penetrated into the POM inorganic layers, and the pyridine rings of C_{16}py interacted to form a π–π stacking pair or were located in the adjacent positions [21–25]. On the contrary in C_{16}py-H_{2}Mo_{8}, the hydrophilic heads of C_{16}py were completely excluded from the β-H_{2}Mo_{8} inorganic layers (Figure 4(a)). β-H_{2}Mo_{8} anions and ethanol molecules of crystallization had short contacts (the distance between two atoms shorter than the sum of van der Waals radii) including one C–H⋯O hydrogen bond (Table 2), which forms a densely packed anionic layer. This two-dimensional anionic layer has no space for the penetration of the pyridine rings (Figure 4(b)), and the interdigitated C_{16}py bilayers were sandwiched by the β-H_{2}Mo_{8} anionic layers (Figure 3(b)).

C_{16}py-H_{2}Mo_{8} had C–H⋯O hydrogen bonds [43] (Table 2). The C–H⋯O hydrogen bonds between β-H_{2}Mo_{8} and C_{16}py were 3.45–3.99 Å in C–O distance. The mean value was 3.67 Å, similar to the mean C⋯O distances (~3.6 Å) in other C_{16}py-POM hybrid crystals [21, 22, 24].
These hydrogen bonds as well as electrostatic interaction between C_{16}py and β-H_{2}Mo_{8} would stabilize the layered crystal structure of C_{16}py-H_{2}Mo_{8} with rigid packing.

4. Conclusions

A hybrid layered crystal, [(C_{5}H_{12}N(C_{14}H_{25}))][β-H_{2}Mo_{8}O_{26}·2C_{2}H_{5}OH (C_{16}py-H_{2}Mo_{8})], was successfully synthesized as single phase by using Mo-blue species as starting precursor material. C_{16}py-H_{2}Mo_{8} consisted of β-octamolybdate anion with two protons (β-H_{2}Mo_{8}), being the first example of proton-comprising surfactant-polyoxomolybdate hybrid crystals. The β-H_{2}Mo_{8} anions and ethanol molecules of crystallization formed two-dimensional anionic layer, which sandwiched interdigitated bilayers of C_{16}py cation. The hydrophilic head of C_{16}py did not attend to form the inorganic β-H_{2}Mo_{8} layers. Such protonated surfactant-polyoxomolybdate hybrid crystals would be promising for a new class of proton-conducting materials.

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References


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