Inorganic–Organic Hybrid Layered Crystal Composed of Polyoxomolybdate and Surfactant with π Electrons

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A polyoxometalate layered crystal containing surfactant with π electrons was successfully prepared by using hexadecylpyridinium (C_{16}py). X-ray single-crystal structure analysis revealed that monolayers of hexamolybdate (Mo_6) and bilayers of C_{16}py were stacked alternately. The hexadecyl chains of the C_{16}py in the bilayer interdigitated each other. The pyridine rings were inserted into the monolayers of the Mo_6 to form the inorganic layers together with the Mo_6 anions.

Layered materials are composed of two-dimensional strata of compounds, and its distinct anisotropy often gives rise to electronic conductivity, semiconductivity, and intercalation.[1–3] The emergence of interesting properties requires precise control of the layered structure such as the component arrangement or layer periodicity. Crystalline layered materials are superior to soft layered materials with respect to the structural stability and homogeneity. Hybrid crystals consisting of conductive organic molecules and inorganic anions have been investigated.[4]

An effective method for the preparation of hybrid layered crystals is to use surfactant molecules, which work as a structure-directing reagent for lamellar structures.[5] The layer distance can be easily controlled by changing the length of long alkyl chains. Polyoxometalate (POM) anions are promising as an inorganic component owing to their various physicochemical properties[6] and can be selected to design the composition and functions of hybrid layered crystals. POM–surfactant hybrid layered crystals have characteristics of both POM and layered materials, which can exhibit novel properties. Several POM–surfactant hybrid materials have been prepared to date.[7] However, POM–surfactant layered crystals are rare, where all of the surfactants used contain only saturated alkyl groups.[8–11]

Here, we report the preparation and structure of layered crystals of $[C_5H_5N(C_{16}H_{33})]_2[Mo_6O_{19}]$ (**1**) composed of hexamolybdate (Mo_6) and hexadecylpyridinium (C_{16}py). To the best of our knowledge, this is the first POM–surfactant hybrid crystal containing a surfactant with π electrons.

Compound **1** was synthesized by a modified procedure in the literature.[12] To 5 mL of aqueous solution of $Na_2MoO_4{\cdot}2H_2O$ (1.25 g, 5.2 mmol) was added 6 M HCl (1.5 mL, 8.7 mmol) with vigorous stirring. After 1 min, a water/ethanol (10 mL, 1:1 (v/v)) solution of $C_{16}pyCl{\cdot}H_2O$ (0.64 g, 1.8 mmol) was added to form a white precipitate. This suspension was heated at 60–80 °C for 15 min with stirring, then filtered, and dried with suction. The resulting product was dispersed in acetonitrile and heated to obtain a clear yellow supernatant, from which thin yellow plates of **1** were obtained by evaporation of the solvent (yield: 14% based on Mo).[13]

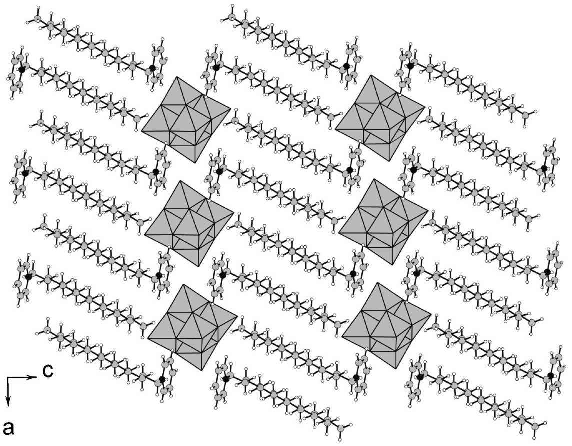

Figure 1. Crystal packing of **1** (C: gray, N: black, H: white; Mo_6 anions in gray polyhedra).

Figure 1 shows the crystal packing of **1** revealed by X-ray structure analysis.[14] The crystal packing consists of alternating inorganic monolayers of Lindqvist-type hexamolybdate (Mo_6) and organic bilayers of C_{16}py cations. The periodicity between the inorganic and organic layers is 16.6 Å. The hydrophobic hexadecyl chains of C_{16}py interdigitate in the bilayers of C_{16}py, and all C–C bonds have trans conformation without bending. On the other hand, the hydrophilic heads of C_{16}py face the Mo_6 anions with the pyridine rings inserted into the Mo_6 monolayers.

Viewed along the *c* axis, the inorganic monolayer of Mo_6 is composed of Mo_6 anions and pyridine rings paired through π–π stacking (Figure 2a). The vertical pyridine ring separation is 4.07 Å (Figure 2b), which is relatively long and suggests the presence of weak π–π stacking interaction.[15] At the interface between Mo_6 and C_{16}py layers, there are four C–H···O hydrogen bonds[16,17] per Mo_6 anion (Figure 3). Two of them were formed between the terminal methyl group of the C_{16}py hexadecyl tail and the terminal oxygen of Mo_6: $C21^{ii}–H38^{ii}\cdots O10$ and $C21^{iii}–H38^{iii}\cdots O10^{i}$ (3.719 Å, 173.4°; i: $1-x$, $1-y$, $1-z$; ii: x, $-2+y$, $-1+z$; iii: $1-x$, $3-y$, $2-z$). Another pair was formed between the pyridine ring of C_{16}py and the bridging oxygen of Mo_6: $C5^{iv}–H5^{iv}\cdots O2$ and $C5^{v}–H5^{v}\cdots O2^{i}$ (3.596 Å, 154.5°; i: $1-x$, $1-y$, $1-z$; iv: $1-x$, $2-y$, $1-z$; v: x, $-1+y$, z). The latter hydrogen bonds are slightly shorter than those (3.7–4.0 Å) in the crystals of Mo_6 and tetrabutylammonium,[18] possibly due to the presence of the surfactant with π electrons.[19] These shorter hydrogen bonds as well as electrostatic interaction between C_{16}py and Mo_6 are believed to stabilize the layered crystal structure of **1**, which has more rigid packing and no water or acetonitrile of crystallization.

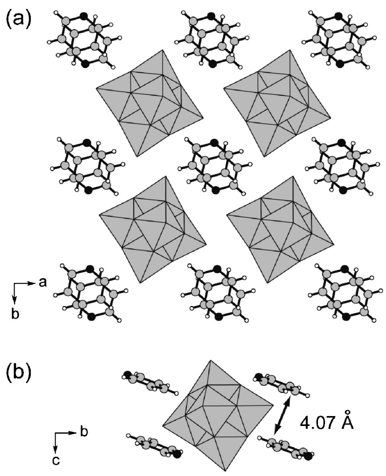

Figure 2. Molecular arrangements in the Mo_6 inorganic layer viewed along (a) c axis and (b) a axis. Atoms of hexadecyl chains are omitted for clarity.

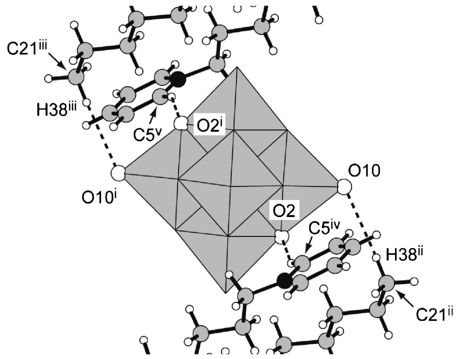

Figure 3. Molecular structure of **1** at the interface between the Mo_6 inorganic and C_{16}py organic layers. Hydrogen bonds are indicated by dotted lines. The labels of H5^{iv} and H5^{v} are omitted for clarity. Symmetry codes: (i) $1-x$, $1-y$, $1-z$; (ii) x, $-2+y$, $-1+z$; (iii) $1-x$, $3-y$, $2-z$; (iv) $1-x$, $2-y$, $1-z$; (v) x, $-1+y$, z.

In conclusion, we prepared the first POM hybrid layered crystal of $[C_5H_5N(C_{16}H_{33})]_2[Mo_6O_{19}]$ (**1**) containing a surfactant with π-electron moieties. The layered structure consisted of the interdigitated bilayer of the surfactant and the POM monolayer with the pyridine rings inserted. The C–H···O hydrogen bonds at the interface between POM and surfactant layers are thought to stabilize the crystal structure of **1**.

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13 Anal. Calcd for $C_{42}H_{76}N_2Mo_6O_{19}$: C, 33.9; H, 5.1; N, 1.9%. Found: C, 33.5; H, 4.6; N, 1.8%. IR (KBr disk): 957 (s), 790 (s) cm^{-1}.

14 Crystal data for **1**: $C_{42}H_{76}N_2Mo_6O_{19}$, $M_r = 1488.69$, triclinic, space group $P\bar{1}$, $a = 8.934(11)$, $b = 9.006(10)$, $c = 16.59(2)$ Å, $\alpha = 88.89(5)$, $\beta = 88.73(5)$, $\gamma = 88.59(5)°$, $V = 1334(3)$ Å^3, $Z = 1$, $T = 173$ K, $D_{calcd} = 1.854$ g/cm^3, $\mu = 1.439$ mm^{-1}, $F(000) = 746$, crystal description, $0.25 \times 0.07 \times 0.01$ mm^3, platelet, yellow. Diffraction data for **1** were collected on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphite monochromatized Mo Kα radiation ($\lambda = 0.7107$ Å) at 173 K. Of 12364 reflections collected ($2\theta_{max} = 55.0°$), 5953 reflections were unique ($R_{int} = 0.062$). Lorentz polarization effects and numerical absorption corrections (the programs *Numabs* and *Shape*) were applied to the intensity data. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms on C atoms were located in calculated positions. The structure was solved by direct method (*SHELXS*97) and refined (*SHELXL*97) based on 5953 all reflections and 314 parameters to $R_1 = 0.0425$ ($I > 2\sigma(I)$) and $wR_2 = 0.1144$ (all reflections). All calculations were performed using the *CrystalStructure* crystallographic software package. CCDC-721363.

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