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Polyoxomolybdate–Surfactant Hybrid Layered Crystal with Unusually Long Periodicity

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An inorganic–organic hybrid crystal was synthesized by using polyoxomolybdate and hexadecylpyridinium surfactant. The unit cell was monoclinic having quite a long cell dimension ($b = 75.0111(14)$ Å). The crystal structure was formed by alternative stacking of β-octamolybdate bilayers and interdigitated hexadecylpyridinium bilayers with layered periodicity of 3.75 nm, which is the largest value for polyoxometalate–surfactant hybrid crystals.

Polyoxometalate cluster anions have various physicochemical properties and behave as electron acceptors, luminescent moieties, magnetic components, or catalysts.[1–3] Polyoxometalates can be organized by structure-directing surfactants[4–6] to construct inorganic–organic hybrid materials[7] and layered crystals.[8–16] These polyoxometalate–surfactant hybrids can allow fine tuning of structure and function. Polyoxometalate–surfactant layered crystals with high crystalline order are promising for conducting materials as observed in precedential inorganic–organic hybrid conductors.[17–19]

Octamolybdate anion ($Mo_8O_{26}{}^{4-}$, Mo_8) has several isomers such as α-type or β-type,[20–24] and the type of isomer affects the formulae and structures of the Mo_8 and hexadecylpyridinium (C_{16}py) hybrid layered crystals.[14] One of the hybrid crystals is composed of β-type Mo_8 (β-Mo_8) with a formula of $[C_5H_5N(C_{16}H_{33})]_3Na[\beta\text{-}Mo_8O_{26}]\cdot CH_3CN$ (**1**).[14] This contains infinite one-dimensional chains consisting of β-Mo_8 and Na^+, which can potentially behave as conducting molecular wire. Such β-Mo_8–Na^+ chains may be used as a connecting component to build a molecular circuit on a solid surface. Therefore, these one-dimensional β-Mo_8–Na^+ chains should be precisely arranged in three-dimensional bulk crystals before the application to two-dimensional surfaces. In addition, layered structure with long periodicity enables effective separation of the potentially conductive β-Mo_8–Na^+ layers by the insulating C_{16}py layers.

We report here an unprecedented type of hybrid crystals **2** containing β-Mo_8 and C_{16}py. The crystal of **2** contained the same structural component of one-dimensional β-Mo_8–Na^+ chain as in **1**. However, the packing of the β-Mo_8–Na^+ chain was different, which leads to a crystal structure with quite long periodicity for **2**.

The hybrid crystals of **2** were synthesized by using the hybrid crystal containing α-type Mo_8 (α-Mo_8) and C_{16}py.[14] The C_{16}py–α-Mo_8 crystals were dissolved in acetonitrile as starting material.[25] A crucial difference between the formation of **2** and **1** is the presence of Na^+ and ethanol. The α-Mo_8 anions are thought to isomerize into β-Mo_8 anions,[20,21] which reprecipitate with C_{16}py to form the C_{16}py–β-Mo_8 crystals of **2**.

IR spectra,[25] elemental analyses,[25] and X-ray structure analysis[26,27] revealed the composition of **2** to be $[C_5H_5N(C_{16}H_{33})]_3Na[\beta\text{-}Mo_8O_{26}]\cdot CH_3CN\cdot C_2H_5OH$. The counter cations are three C_{16}py and one Na^+ per β-Mo_8 of 4− charge, the same as **1**. The difference in the composition between **1** and **2** is the presence of ethanol as solvent of crystallization. **2** contains one ethanol as well as one acetonitrile, while **1** has only one acetonitrile. The unit cell of **2** is monoclinic, and the length of b axis (75.0111(14) Å) is quite long compared with other surfactant crystals.[28] As shown in Figure 1, **2** consists of alternate stacked β-Mo_8 inorganic layers and C_{16}py organic layers with periodicity of 37.5 Å, which is much larger than **1** (18.6 Å)[14] and the largest among all other polyoxometalate–surfactant crystals.[8–16]

The organic layers consist of intedigitated C_{16}py bilayers. All C–C bonds except one C–C bond (C48–C49) have anti conformation. The hydrophilic heads of C_{16}py penetrate into the β-Mo_8 inorganic layers as observed in other C_{16}py–polyoxomolybdate crystals.[12,14]

The inorganic layers are composed of infinite chains of β-Mo_8 connected by Na^+ cations (Figure 1) as observed in **1**[14] and other β-Mo_8 salts.[29,30] The one-dimensional β-Mo_8–Na^+ chains have almost the same structure as those in **1**. However, the packing of the β-Mo_8–Na^+ chains is quite different (Figure 2). Figures 2a and 2b are projections along the direction of the β-Mo_8–Na^+ chains. In the crystal of **2**, the β-Mo_8–Na^+ chains arrange in a bilayer (Figures 1 and 2a). Such bilayer structure in the polyoxometalate–surfactant hybrid crystals is rare.[13] The C_{16}py tail is tilted by 17.5° from the normal of the *ac* plane which is parallel to the β-Mo_8 inorganic layer (Figures 1 and 2a). On the other hand, the β-Mo_8–Na^+ chains in **1** form a monolayer structure (Figure 2b), which is typical for the polyoxometalate–surfactant crystals.[8–16] The tilt angle between the C_{16}py tail and the β-Mo_8 inorganic layer is 59.7° (Figure 2c). The bilayer structure of β-Mo_8–Na^+ chains and smaller tilt angle of the C_{16}py tail will result in the layered crystal of **2** with unusually long periodicity.

The inorganic bilayers of **2** are composed of β-Mo_8–Na^+ anionic chains, C_{16}py cations, and acetonitrile molecules (solvent of crystallization). The space between the β-Mo_8–Na^+ chains is filled by the hydrophilic moiety of C_{16}py and acetonitrile molecules, which are located in the vicinity of Na^+ cations. Two pyridine rings containing N1 and N2 are not parallel (angle: 23.2°), but slightly overlapped, suggesting the presence of weak π–π stacking interaction (distance between

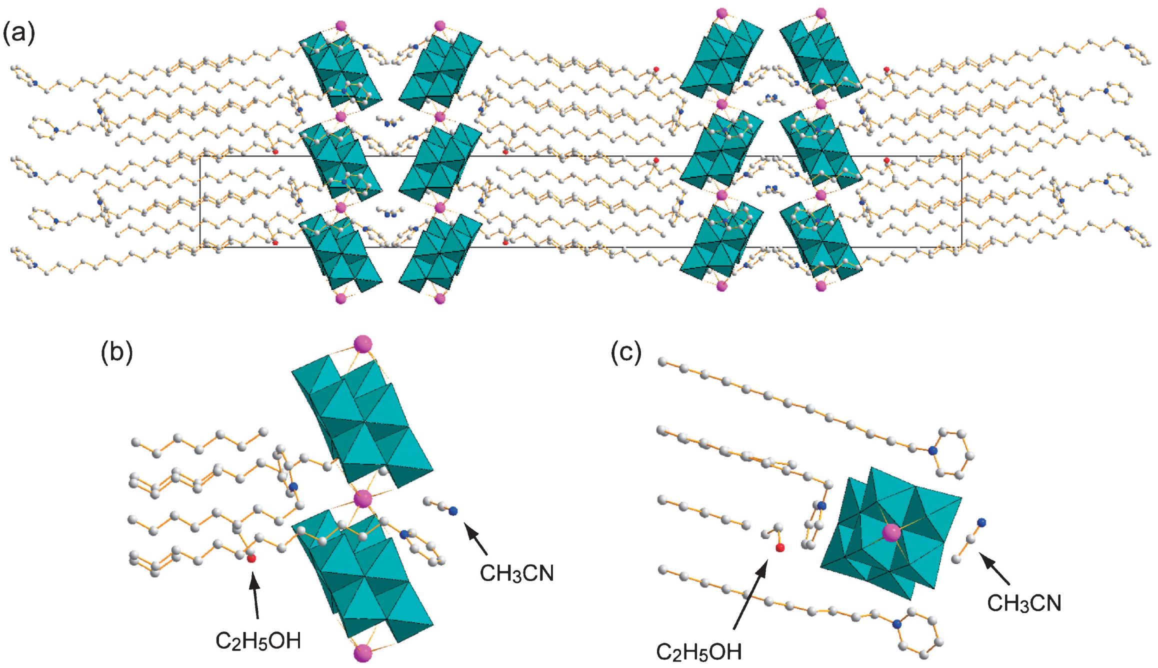

Figure 1. Crystal structure of **2** (C: gray, N: blue, O: red, Na: pink; β-Mo$_8$ in polyhedral representations). Hydrogen atoms are omitted for clarity: (a) packing diagram along *c* axis, (b) local structure along *c* axis, and (c) local structure along *a* axis.

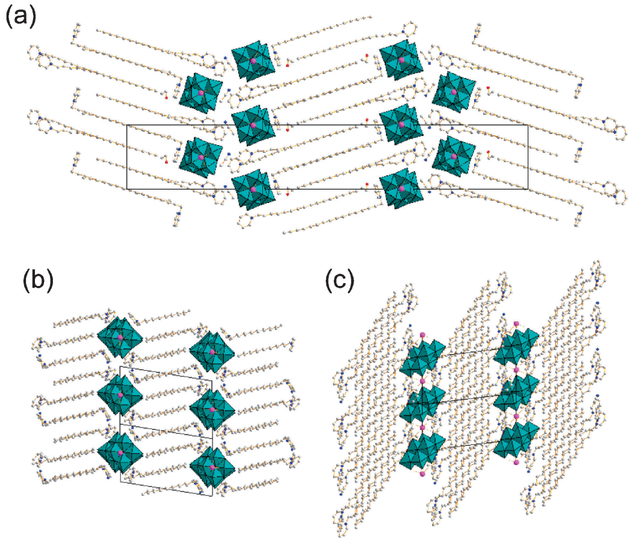

Figure 2. Crystal packing of C$_{16}$py–β-Mo$_8$ hybrids (C: gray, N: blue, O: red, Na: pink; β-Mo$_8$ in polyhedral representations). Hydrogen atoms are omitted for clarity: (a) **2** along *a* axis, (b) **1** along [1$\bar{1}$0] direction,[14] and (c) **1** along [110] direction.[14]

pyridine rings: 3.37–4.34 Å). Besides, the pyridine rings with N1 interact with acetonitrile molecules. The ethanol molecules are located at the interface between the β-Mo$_8$ and C$_{16}$py bilayers, outside the inorganic bilayers.

The formation of **2** seems to require the presence of Na$^+$ and ethanol. As described above, **2** contains ethanol together with acetonitrile as solvent of crystallization, which probably causes the drastic difference in the packing of the β-Mo$_8$–Na$^+$ chains. The crystals of **2** were obtained in several days,[25] while the formation of **1** takes over several months.[14] **2** precipitates faster than **1** and is possibly a metastable phase. However, recrystallization of **2** from acetonitrile did not yield the crystals of **1** but the C$_{16}$py–α-Mo$_8$ crystals by means of the isomerization from β-Mo$_8$ to α-Mo$_8$.[20,21]

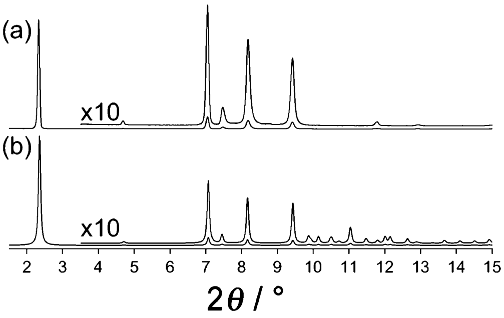

Figure 3. Powder X-ray diffraction patterns of **2** from (a) observed data measured at 93 K and (b) calculated data using the structure obtained by single-crystal X-ray diffraction. λ(Cu Kα) = 1.542 Å.

Powder X-ray diffraction[31] of **2** measured at 93 K (Figure 3a) approximates to the pattern calculated from the results of single-crystal X-ray analysis (Figure 3b). This indicates that **2** is formed as a single phase, while **1** is obtained as a mixture with the C$_{16}$py–α-Mo$_8$ crystals.[14] **2** is stable as crystalline material with the β-Mo$_8$ molecular structure retained, although the solvents of crystallization seem lost in the air.

In the crystal structure of **2**, there are several C–H···O hydrogen bonds[32,33] between β-Mo$_8$ and C$_{16}$py or solvent of crystallization. The C···O distances of the hydrogen bonds are 3.22–3.96 Å (mean value: 3.61 Å). These values are similar to those for **1**, which has C–H···O hydrogen bonds only between β-Mo$_8$ and C$_{16}$py.

In conclusion, we have reported a inorganic–organic hybrid crystal composed of β-type octamolybdate and hexadecylpyridinium, $[C_5H_5N(C_{16}H_{33})]_3Na[\beta\text{-}Mo_8O_{26}]\cdot CH_3CN\cdot C_2H_5OH$ (**2**). **2** had quite long layered periodicity, and different structure from another C_{16}py–β-Mo_8 crystal **1**. **2** contained bilayers of the β-Mo_8–Na^+ chains, while **1** was formed by monolayers of the β-Mo_8–Na^+ chains. The addition of ethanol to the mother liquor induces the drastic change in the arrangement of the β-Mo_8–Na^+ chains. The functions such as conductivity can be controlled by changing the molecular arrangement in the polyoxometalate–surfactant hybrid crystals.

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25 Syntheses of **2**: Hot acetonitrile solution of C_{16}py–α-Mo_8,[14] to which saturated ethanol solution of NaCl was added, was kept at 315 K for a day and then at room temperature. After several days, colorless fine needles of **2** were obtained. The crystals of **2** were efflorescent, and the elemental composition of **2** was calculated for the formula without solvent of crystallization. Anal. Calcd for $C_{63}H_{114}N_3NaMo_8O_{26}$: C, 35.69; H, 5.42; N, 1.98; Na, 1.08%. Found: C, 35.60; H, 5.21; N, 2.01; Na, 1.22%. IR (KBr disk): 941 (s), 910 (s), 837 (m), 712 (s), 677 (m), 555 (w), 525 (m), 482 (w), 418 (m) cm^{-1}.

26 a) X-ray diffraction data for **2** were collected with a Rigaku VariMax with RAPID imaging plate area detector using Cu Kα radiation (crystal-to-detector distance: 127.40 mm) at Rigaku Corporation. Since the crystals of **2** were damaged by long irradiation of the strong X-ray beam, the measurements were performed within 8 h. Diffraction data were collected for a fine crystal ($0.18 \times 0.04 \times 0.02\,mm^3$) and processed with PROCESS-AUTO.[26b] A structure was solved by direct methods using SIR92[26c] and refined by the full-matrix least-squares using SHELXL97.[26d] H atom of hydroxy group in the ethanol was not included in the refinement. All calculations were performed using the CrystalStructure[26e] software package. b) *PROCESS-AUTO*, Rigaku Corporation, Akishima, Tokyo, **2002**. c) A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *J. Appl. Crystallogr.* **1994**, *27*, 435. d) G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112. e) *CrystalStructure 3.8*, Rigaku/MSC, The Woodlands, TX, **2006**.

27 Crystal data for **2**: $C_{67}H_{123}N_4NaMo_8O_{27}$, $M_r = 2207.20$, monoclinic, space group $P2_1/c$, $a = 9.36665(17)$, $b = 75.0111(14)$, $c = 12.5538(9)$ Å, $\beta = 106.921(7)°$, $V = 8438.5(6)$ Å^3, $Z = 4$, $T = 93$ K, $\mu = 10.094\,mm^{-1}$. 79047 reflections measured, 15232 reflections independent ($R_{int} = 0.1587$). $R_1 = 0.0798$ ($I > 2\sigma(I)$), $wR_2 = 0.1826$ (all data). CCDC-822743.

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