

# Geometric Change in Layered Copper Dodecanesulfate

Young-Duk Huh\*, Seok-Soon Kweon, Ji-Hyun Kim, and June-Won Hyun<sup>†</sup>

Department of Chemistry, Institute of Nanosensor and Biotechnology, Dankook University, Seoul 140-714, Korea

<sup>†</sup>Department of Applied Physics, Institute of Nanosensor and Biotechnology, Dankook University, Seoul 140-714, Korea

## ABSTRACT

The layered structure of copper dodecanesulfate has been synthesized. X-ray power diffraction patterns indicate that interlayer distances of three different phases change drastically. A monolayer structure of the hydrated form of copper dodecanesulfate at 30°C transforms to a bilayer structure as a dehydrated form at 150°C.

**Key words** : Layered structure, Monolayer/bilayer phase transition

## Introduction

Two-dimensional layered hybrid inorganic/organic compounds are an important class of materials currently receiving considerable attention(1-7). Layered materials offer two-dimensional expandable interlayer space for organizing guest species. Layered hybrid inorganic/organic compounds can be obtained by intercalating of organic species into layered inorganic materials while maintaining the structural features of the inorganic frame. The basal spacings of the intercalated compounds have been determined from X-ray diffraction patterns and the arrangement of the intercalated species can be discussed by the basal spacings and the size of the guest species.

Layered transition metal soaps are very appealing model compounds as molecular-based magnets(8-12). Since the intercalated organic guests caused some structural change in the inorganic frame, distinguished magnetic properties of transition metal soaps were observed. There have been several reports on monolayer/bilayer phase transition of alkyl chains for layered hybrid inorganic/organic compounds. It is important to understand the mechanism of mono-

layer/bilayer phase transition due to its functionalities of biological membranes and liquid crystals, Tolbert *et al.* reported the control of inorganic layer thickness in iron oxide and surfactant composites(13). Awaga *et al.* reported the structural transformation and drastic magnetic change in a intercalated copper hydroxy compounds(14). A reversible monolayer/bilayer phase transition occurs as a result of soaking in methanol and acetonitrile. In the present work, three different layered forms of copper dodecanesulfate were synthesized. We report a thermo-induced monolayer/bilayer phase transition in copper dodecanesulfate compound.

## Experimental

Sodium dodecylsulfate and copper nitrate hemipentahydrate were obtained from Aldrich and used without further purification. The hydrated copper dodecanesulfate was synthesized by titration of an aqueous solution of 0.2M  $C_{12}H_{25}SO_4Na$  to an aqueous solution of 0.1M  $Cu(NO_3)_2 \cdot 2.5H_2O$ . The precipitate was aged at 10°C for 3 days, filtered, washed with decarboxylated water, and air dried. The precipitation is performed at 10°C to discourage formation of copper oxides during the titration. Elementary analysis was carried out by CHNS analysis (CE Instrument EA 1112 series). Combustion analysis for C, H, N, and S provided the

\* Corresponding author :

Young-Duk Huh

Tel : 82-2-709-2409

Fax : 82-2-792-9269

E-mail : ydhuh@dankook.ac.kr

following stoichiometry for the copper dodecanesulfate compound  $\text{Cu}(\text{H}_2\text{O})_2(\text{C}_{12}\text{H}_{25}\text{SO}_4)_2 \cdot 0.5\text{H}_2\text{O}$ . Anal. calcd. (found) for  $\text{Cu}(\text{H}_2\text{O})_2(\text{C}_{12}\text{H}_{25}\text{SO}_4)_2 \cdot 0.5\text{H}_2\text{O}$  : C, 45.1 (43.2); H, 8.6 (9.1); N, 0.0 (0.0); S, 10.0 (8.8). Thermogravimetric analyses (TA Instruments TGA 2050) were performed in a nitrogen atmosphere using a heating rate of  $10^\circ/\text{min}$ . DSC thermogram was obtained using a TA Instruments SDT 2960. Powder X-ray diffraction patterns were obtained on Rigaku diffractometer with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). Infrared spectra were obtained in  $4000\text{--}400 \text{ cm}^{-1}$  range using a Bomem DA8-12 FT-IR.

## Results and Discussion

Thermogravimetric and calorimetric measurements have been performed to understand the phase transition behaviors of copper dodecanesulfate. Figure 1 shows the TGA curve of copper dodecanesulfate compound. In the TGA, five distinct mass loss regions around  $50^\circ\text{C}$ ,  $130^\circ\text{C}$ ,  $250^\circ\text{C}$ ,  $350^\circ\text{C}$ , and  $770^\circ\text{C}$  are seen. The first one at  $50^\circ\text{C}$  is due to the dehydration of interlayer water content. The second one at  $130^\circ\text{C}$  is due to the dehydration of coordinated  $\text{H}_2\text{O}$  of  $\text{Cu}(\text{H}_2\text{O})_2(\text{C}_{12}\text{H}_{25}\text{SO}_4)_2$ . The calculated and measured mass losses are 7.0% and 6.7%. The third weight loss is observed at higher temperature in the range  $250^\circ\text{C}$  which corresponds to decomposition of dodecanesulfate groups. The fourth weight loss is step to form copper oxysulfide compound.

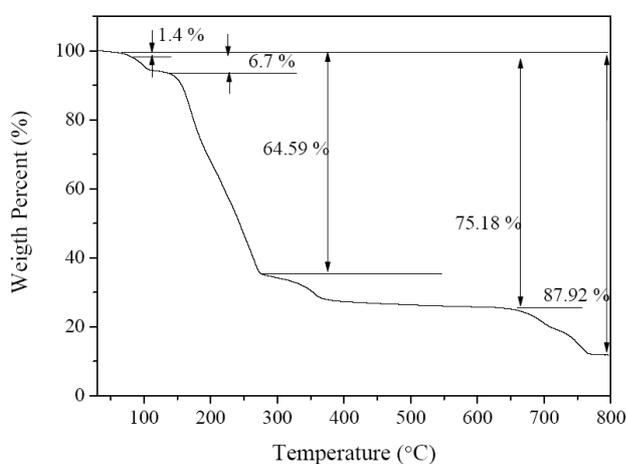


Fig 1. TGA curve of copper dodecanesulfate compound.

The last step above  $770^\circ\text{C}$  is to form  $\text{Cu}_3\text{O}_2$ . The calculated and measured mass losses are 88.4% and 87.9%. Figure 2 shows the DSC curve of copper dodecanesulfate compound. On the DSC graph, three transition peaks are monitored at  $51^\circ\text{C}$ ,  $127^\circ\text{C}$ , and  $206^\circ\text{C}$  which correspond to dehydration of interlayer water, coordinated water, and decomposition of intercalated organic dodecanesulfate, respectively.

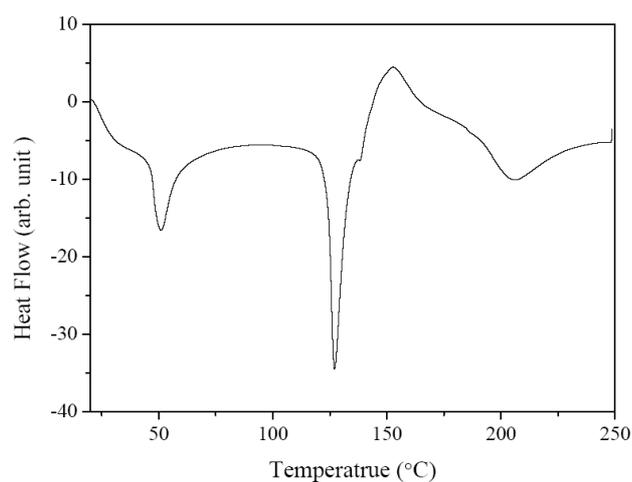


Fig 2. DSC curve of copper dodecanesulfate compound.

Figure 3 shows FT-IR spectra of copper dodecanesulfate at three different temperatures. As shown in figure 3(A), the broad absorption band in the range  $3200\text{--}3600 \text{ cm}^{-1}$  is the signature of water as a hydroxy stretching vibrational mode. A band as a hydroxy bending vibrational mode oc-

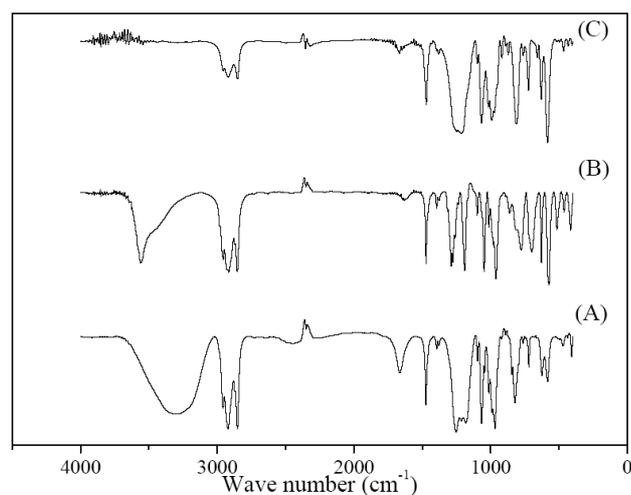
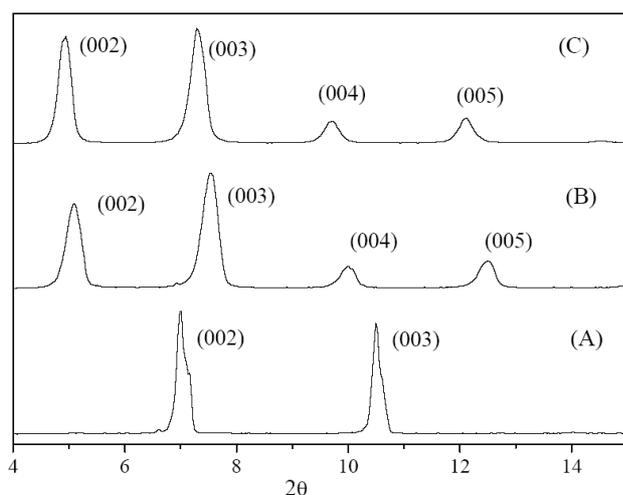


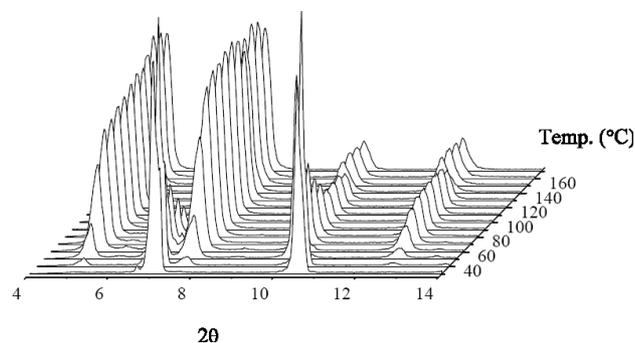
Fig 3. FT-IR spectra of copper dodecanesulfonate obtained at (a)  $30^\circ\text{C}$ , (b)  $100^\circ\text{C}$ , and (c)  $150^\circ\text{C}$ .

curs at  $1470\text{ cm}^{-1}$ . For the compound at  $100^\circ\text{C}$  as in figure 3(B), the intensity of broad band in the range  $3200\text{--}3600\text{ cm}^{-1}$  is decreased and band at  $1470\text{ cm}^{-1}$  is almost disappeared. It indicates that the interlayer water is lost for the copper dodecanesulfonate at  $100^\circ\text{C}$ . For the dehydrated form of copper dodecanesulfonate as in figure 3(C), the bands in the range  $3200\text{--}3600\text{ cm}^{-1}$  and at  $1470\text{ cm}^{-1}$  are completely disappeared. It suggest the compound has no water. These results confirm the TGA and DSC data.

Figure 4 shows the X-ray diffraction patterns and Miller indices of the copper dodecanesulfonate at three different temperatures. There are series of  $(00\ell)$  reflections with an equivalent interval, indicating a layered structure in it. The X-ray diffraction data were collected in the  $2\theta$  range of  $4\text{--}15^\circ$ . As shown in the figure 4, the  $(001)$  peaks which are in the  $2\theta$  range below  $4^\circ$  cannot be obtained. The basal spacing of 4(A), 4(B), and 4(C) were calculated to be  $24.7\text{ \AA}$ ,  $35.3\text{ \AA}$ , and  $36.5\text{ \AA}$  from the periodicity in the pattern, respectively. It indicate that the copper dodecanesulfate compound has three different layered structures at various temperature ranges. X-ray diffraction patterns of the layered structure of copper dodecanesulfate compound at various temperatures are obtained as in figure 5. Three different layered structures are existed. In the low temperature range of  $30\text{--}80^\circ\text{C}$ , the layer distance is  $24.7\text{ \AA}$  for a hydrated interlayered water and coordinated water form. In the intermediate



**Fig 4.** X-ray diffraction patterns and Miller indices of copper dodecanesulfonate obtained at (a)  $30^\circ\text{C}$ , (b)  $100^\circ\text{C}$ , and (c)  $150^\circ\text{C}$ .



**Fig 5.** X-ray diffraction patterns versus temperature ( $30^\circ\text{C}\text{--}170^\circ\text{C}$ ).

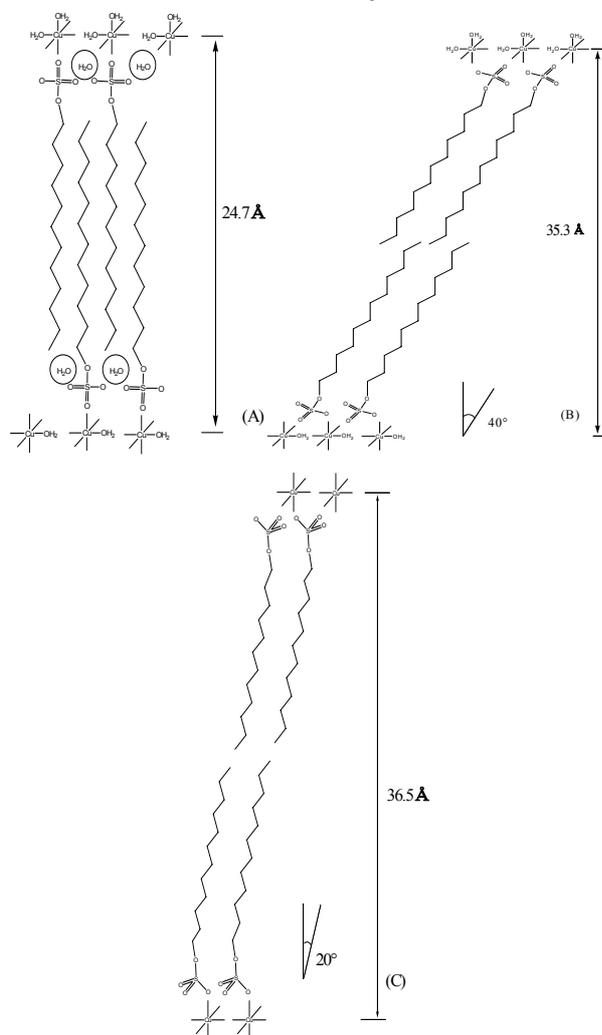
temperature range of  $50\text{--}130^\circ\text{C}$ , the layer distance is  $35.3\text{ \AA}$  for a coordinated water form of the compound. For the dehydrated form, the layer distance is  $36.5\text{ \AA}$  at high temperature range of  $130\text{--}170^\circ\text{C}$ .

Layered materials offer two-dimensional expandable interlayer space for organizing guest species. Layered hybrid inorganic/organic compounds have intercalated structures of organic species into layered inorganic materials while maintaining the structural features of the inorganic frame. The phase transition due to the orientation of organic species results in change of the layer distance. The geometry for orientation of intercalated organic compound can be obtained from the basal spacing of the intercalated compound and the size of the organic compound. The geometry for orientation of intercalated organic compound also results in monolayer/bilayer phase transition of alkyl chains for layered hybrid inorganic/organic compounds.

The thickness of inorganic layer of  $\text{Cu}(\text{H}_2\text{O})_2$  is unknown yet. Tolbert *et al.* measured the thickness of the inorganic layer of  $\text{Fe}(\text{H}_2\text{O})_6$ . In the case of inorganic layer of  $\text{Fe}(\text{H}_2\text{O})_6$ , six waters are coordinate to iron ion. However, only two waters are coordinated to copper ion in inorganic layer of  $\text{Cu}(\text{H}_2\text{O})_2$ . We assume that the two waters located to along z-axis in inorganic layer of  $\text{Cu}(\text{H}_2\text{O})_2$ . Then, the layer thickness of  $\text{Cu}(\text{H}_2\text{O})_2$  is almost equal to that of  $\text{Fe}(\text{H}_2\text{O})_6$ . The thickness of the inorganic layer of  $\text{Fe}(\text{H}_2\text{O})_6$  is  $6.5\text{ \AA}$ (13). Since the difference between the van der Waals radii of copper ion ( $0.72\text{ \AA}$ ) and iron ion ( $0.74\text{ \AA}$ ) is negligible, we used the same value of the inorganic layer for copper alkylsulfate system(15).

In the low temperature range of  $30\text{--}80^\circ\text{C}$ , the layer distance is  $24.7\text{ \AA}$  and the gallery height occupied by dodeca-

nesulfate is 18.2 Å. We calculated the size of dodecanesulfate of 18.7 Å by using a Alchemy program. The radius of the gallery occupied by dodecanesulfate and its size is  $r = (18.2)/(18.7) = 0.97$ . The completely interdigitated monolayer and noninterdigitated bilayer with the aliphatic chain normal to the plane of the inorganic layer should produce values of 1.0 and 2.0, respectively. The hydrated of the interlayered water and coordinated water of copper dodecanesulfonate is composed of interdigitated monolayer. The axis of dodecanesulfonate is perpendicular to the inorganic layer surface. Figure 6(A) shows a schematic diagram for the structure of compound at low temperature range. In intermediate tem-



**Fig 6.** Schematic presentation of structural change for copper dodecanesulfonate in temperature range of (A) 30°C-80°C, (B) 50°C-130°C, and (C) 140°C-170°C.

perature range of 50-130°C, the layer distance and gallery height is 35.3 Å and 28.8 Å. The radius of the gallery occupied by dodecanesulfonate is  $r = (28.8)/(18.7) = 1.54$ . It indicate the compound has a bilayer structure with tilted angle of 40°  $\{40 = \cos^{-1}[28.8/(18.7 \times 2)]\}$  as shown in figure 6(B).

In the high temperature range of 140-170°C with layer distance of 36.5 Å, there is no water in the inorganic layer. The copper ion is directly connected with oxygen atom of the sulfate group. Therefore, the thickness of the inorganic layer is equal to the diameter of copper ion (1.4 Å). The gallery height occupied by dodecanesulfate is 35.1 Å. The radius of the gallery occupied by dodecanesulfate group is  $r = (35.1)/(18.7) = 1.87$ . The complete bilayer with the aliphatic chain normal to the plane of the inorganic layer should produce value of 2.0. Therefore, the dehydrated form is composed of almost complete bilayer with tilted angle of 20°  $\{20 = \cos^{-1}[35.1/(18.7 \times 2)]\}$ . The schematic diagram is shown in figure 6(C).

We observed the thermal induced structural change of layered copper dodecanesulfate compound. The three different structures result from the geometric change of the dodecanesulfate group and inorganic frame. In the low temperature range, the compound has interlayer water and coordinated water as a complete monolayer structure. By dehydration of the interlayer water, the compound has a tilted bilayer structure in the intermediate temperature range. At high temperature, the compound has the dehydrated form with almost complete bilayer structure. Upon dehydration, two main changes are observed. The loss of water molecules cause the headgroups (sulfate groups) to pack much more closely together, possibly allowing for better chelation of the copper ions by the sulfate headgroups. This close packing of the headgroups is not compatible with the monolayer observed in the hydrated compounds, so the tails rearrange to form a bilayer structure.

## Conclusions

We observed the thermal induced structural change of layered copper dodecanesulfate compound. The dehydration process occurs with increasing temperature. The different structures result from the geometric change of the dodeca-

nesulfate group and inorganic frame at three temperature ranges. A monolayer structure at the low temperature range was changed to the tilted bilayer structure by dehydration of the interlayer water at the intermediate temperature range. At high temperature, the compound has a complete bilayer structure as the dehydrated form.

### Acknowledgement

This work was supported by a grant from Ministry of Science and Technology of Korea through Proton Accelerator User Program (No. M102KS010001-02K1901 -01810).

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(Received May 3, 2004; Accepted Aug 18, 2004)