COMMUNICATION

ChemComm
www.rsc.org/chemcomm

A series of long-chain lamellar hydrated copper(II) alkylsulfonates with different chain molecular assemblies

Seong-Hun Park† and Cheol Eui Lee*

Institute for Nano Science, Korea University, Seoul 136-701, Korea. E-mail: rscel@korea.ac.kr; Fax: 82-2-923-2682; Tel: 82-2-3290-3098

Received (in Columbia, MO, USA) 18th March 2003, Accepted 23rd May 2003
First published as an Advance Article on the web 18th June 2003

Reaction of copper(II) salts with *n*-alkylsulfonate anions yields light blue lamellar $Cu(C_nH_{2n+1}SO_3)_2 \cdot zH_2O$ displaying distinct (mono/bi-layer) chain packing with increasing alkyl chain lengths; This may be attributed to the amphiphilic nature of the surfactants, *i.e.*, the hydrophilic sulfonate head groups, mediating the coordination, and H-bonding interactions, and the hydrophobic alkyl chains.

Currently, there are numerous well studied examples of 'inorganic–organic' lamellar solids.[1] Widely studied classes in this area include clays, metal chalcogenides, and metal oxides as well as the metal phosphates and the phosphonates. Traditionally, networks sustained either by directional non-covalent interactions in organic systems[2] or by coordinate covalent bonds in coordination polymers[3] represent the two primary classes of crystal engineering, which have mainly been developed separately.[4] However, the ability to design and control the assembly of coordination networks through both coordination and H-bonding interactions has been of great interest in recent years.[5] By employing organic ligands with H-bonding functionalities combined with coordination sites for the transition metals, bridges have been built between the two main streams of crystal engineering.[6] The use of different organic groups changes the size and hydrophobic nature of the interlayer region and physical properties of the material. Sulfonation of the organic groups has been attempted in the past to create ion-exchange capabilities like those found in inorganic layered compounds such as the α-zirconium phosphate. Despite the strong analogy to the phosphonate groups,[7] the coordination chemistry of the sulfonates has been studied to a very limited extent. Examples which have been reported to date with silver(I)[8] and various alkali,[9] alkaline earth,[10] or transition metal[11–12] organosulfonates typically exhibit varying degrees of hydration, as would be expected for more weakly bonding ligands, but invariably, the networks all adopt two-dimensional structures except for the barium compounds.[13]

Owing to the weak coordination strength of the sulfonates toward the transition metal ions, most of the reported transition metal sulfonates prepared in aqueous solution were formed by segregation of aquametal complex cations and sulfonate anions. Herein, we present a family of previously unrecognized layered complexes. To our knowledge, there is no layered inorganic–organic system with a long-chain sulfonate anion. In this study, we have synthesized lamellar Cu(II) alkylsulfonates with the general formula $Cu(C_nH_{2n+1}SO_3)_2 \cdot zH_2O$ [$CuSO_3$-C*n*], where $z = 4$ (for $n = 10$ and 12; group (I)) or 2 (for $n = 14$, 16, and 18; group (II)). The purpose was to document the coordination chemistry of the alkylsulfonates toward divalent transition metal ions, as well as the nature of inorganic–organic lamellar materials derived from the metal sulfonates.

The $CuSO_3$-C*n* compounds may be generated by the addition of the aqueous sodium alkylsulfonate to a solution of $CuCl_2$ in water. Concentration of this solution results in the precipitation of $CuSO_3$-C*n*, in very good yields, as a light blue solid.‡ Elemental analyses and TGA data§ confirmed the composition of the $CuSO_3$-C*n* materials.

All the compounds show a lamellar structure as is evident from the powder XRD patterns exhibiting, in the low 2θ range, intense (00l) reflections, up to at least the third harmonic (Fig. 1(a)). The change in the alkyl chain packing can be understood through analysis of the variation in the fundamental layer spacing (d_{001}) with the alkyl chain length.[14] The *d*-spacing plotted against the number of carbon atoms in the alkylsulfonates for group (I) and (II) compounds is presented in Fig. 1 (b), which indicates a slightly greater slope for the group (II) samples (slope = 1.298 Å per carbon atom), compared to the group (I) materials (slope = 1.257 Å per carbon atom). The group (I) materials are thus identified to be composed of interdigitated alkyl chains all arranged normal to the layers, whereas the group (II) materials are of a non-interdigitated bilayer structure with a tilt angle of 31°. The intercept of the layer spacing *versus* the carbon chain length plot can be assigned to the thickness of the inorganic layers plus the sulfonate headgroup. The different *y*-intercepts of the two groups suggest the different coordination environments around the copper(II) ions.

The structures were solved from the X-ray powder diffraction data. Pattern indexing (DICVOL91) yielded monoclinic cells for both of them. PowderSolve[15] was used to determine the possible arrangements and conformations of the molecular fragments in the unit cell, and systematic absences were consistent with the *Pc* space group for all the compounds. The crystal structures¶ of both of the two groups are layered stuctures shown in Fig. 2. The crystal structures consist of alternating polar layers of the hydrated copper(II) ions inter-

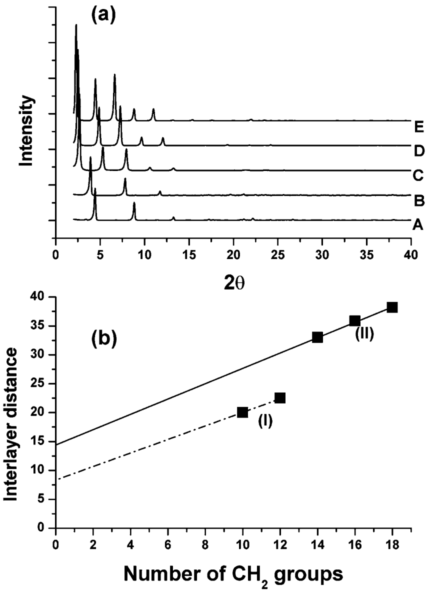

Fig. 1 (a) XRD pattern and (b) dependence of the interlayer distance on the carbon number of the lamellar copper alkanesulfonates (A–E for $n = 10$, 12, 14, 16, and 18).

---

† Present address: Nano Material Team, Korea Basic Science Institute (KBSI) at Daejeon.

DOI: 10.1039/b303106c

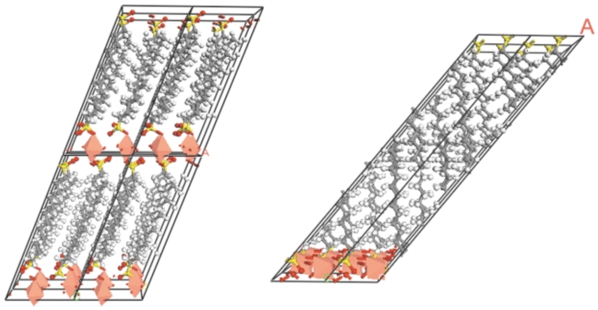

Fig. 2 Schematic crystal structures of the lamellar copper alkanesulfonates. (Left: group (I), right: group (II)). The solid lines represent a unit cell.

linked by hydrogen bonds and non-polar layers of perfectly aligned alkyl chains. The hydrated Cu(II) ion for group (I) is octahedrally coordinated with four O atoms of equatorial water and two O atoms of the axial monodentate sulfonate groups, whereas that for group (II) is octahedrally coordinated with two water and two bidentated alkylsulfonate groups. The structure for group (I) is very closely related to that of the triclinic copper dodecylsulfate tetrahydrate system.[16]

It is interesting that the two group compounds have distinct lattice dimensions.‖ Of the two groups, the group (II) compounds possess smaller lattice dimensions of the *bc* plane, whereas the parameter *a* undergoes an abrupt increase, indicating distinct chain packing – monolayer and bilayer structures for the group (I) and the (II) compounds, respectively. This mono-/bi-layer alkyl chain packing change may be attributed to the cooperative amphiphilic nature of the surfactants, *i.e*., both the hydrophilic sulfonate head groups, mediating the coordination and H-bonding interactions, and the hydrophobic alkyl chains.

In summary, we have synthesized a novel two-dimensional inorganic/organic lamellar structure with long-chain *n*-alkylsulfonate ligands. The resulting structure is depicted as a layer of coordinated copper(II) ions, the aqua and sulfonate ligands competing with the alkyl chains to form different (mono-/bilayer) packing with increasing alkyl chain lengths. This system may be anice candidate for the study of model biomembranes.

We wish to thank the KISTEP (National Research Laboratory) and the BK21 program for funding.

Notes and references

‡ $CuSO_3$-C*n* were made by mixing of 20 mL of diluted aqueous solutions of sodium *n*-alkylsulfonates, $C_nH_{2n+1}SO_3Na$ (n = 10, 12, 14, 16, 18; c = 0.01–0.005 mol L^{-1}), with 20 mL of 0.01 mol L^{-1} $CuCl_2\cdot 2H_2O$. $C_nH_{2n+1}SO_3Na$ (n = 16, 18) solutions were not soluble at this concentration at room temperature; thus, these surfactants and copper solutions were mixed at slightly elevated temperature (~50 °C). Shortly after mixing, a light blue precipitate began to form. The precipitate was filtered, washed with deoxygenated water, and dried under vacuum.

§ Elemental analyses are in agreement with calculated values: $CuSO_3$-C*10*: obs (calc) N: (0.0); C: 40.6509 (41.53978); H: 8.8095 (8.71485); S: 11.2546 (11.08996)%. $CuSO_3$-C*12*: obs (calc) N: (0.0); C: 44.4126 (45.43909); H: 9.4067 (9.21514); S: 10.0572 (10.10913)%. $CuSO_3$-C*14*: obs (calc) N: 0.0423 (0.0); C: 51.6812 (51.38604); H: 9.662 (9.54848); S: 10.3199 (9.79902)%. $CuSO_3$-C*16*: obs (calc) N: (0.0) ; C: 54.5169 (54.08982); H; 10.0474 (9.92931); S: 9.5533 (9.02529)%. $CuSO_3$-C*18*: obs (calc) N: (0.0); C: 56.6369 (56.39787); H: 10.4054 (10.2544); S: 8.8599 (8.36481)%.

TGA data: TGA of group (I) reveals the loss of 2 mol H_2O at 67, 57 °C (n = 10,12), followed by the loss of 2 mol H_2O at 112, 128 °C (n = 10,12) respectively. On the other hand, TGA of group (II) reveals the only loss of 2 mol H_2O at 113, 125, and 125 °C (n = 14,16,18) respectively.

¶ The crystal structure, shown in Fig. 2, was obtained by profile (Pawley) refinement in Material Studio v2.2 platform, however, a complete Rietveld refinement was not done.

‖ X-ray powder diffraction data were collected on a MacScience diffractometer (MXP3A-HF) using a CuKα radiation [λ = 1.5418 Å; step size = 0.026°(2θ); angular range 2–90°(2θ)]. X-ray diffraction patterns fully indexed monoclinic symmetry for $CuSO_3$-C*n*: n = 10, a = 22.9093(5), b = 5.28242(5), c = 10.0219(5) Å, β = 118.945°, V = 1061.31 Å^3, Z = 2; n = 12, a = 24.3764(5), b = 5.04063(5), c = 10.7321(5) Å, β = 112.148°, V = 1221.37 Å^3, Z = 2; n = 14, a = 43.2351(5), b = 5.21562(5), c = 7.14246(5) Å, β = 130.273°, V = 1228.84 Å^3, Z = 2; n = 16, a = 47.4858(5), b = 5.21342(5), c = 7.12992(5) Å, β = 129.404°, V = 1363.89 Å^3, Z = 2; n = 18, a = 51.7568(5), b = 5.19753(5), c = 7.10588(5), β = 128.634°, V = 1493.20 Å^3, Z = 2.

1 G. Alberti and U. Costantino, in *Comprehensive Supramolecular Chemistry*, ed. J. L. Atwood, J. E. D. Davies, D. D. MacNicol and F. Vögtle, Elsevier Science, New York, 1996, **vol. 7**, ch. 1, pp 1–24.

2 G. R. Desiraju, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2311.

3 G. F. Swiegers and T. J. Malefetse, *Chem. Rev.*, 2000, **100**, 3483.

4 M. J. Zaworotko, *Angew. Chem.*, 1998, **37**, 1211.

5 D. Braga, F. Grepioni and G. R. Desiraju, *Acc. Chem. Res.*, 2000, **33**, 601; D. Braga and F. Grepioni, *Chem. Rev.*, 1998, **98**, 1375; J. C. MacDonald, P. C. Dorrestein, M. M. Oilley, M. M. Foote, J. L. Lundburg, R. W. Henning, A. J. Schultz and J. L. Manson, *J. Am. Chem. Soc.*, 2000, **122**, 11692; M. Munakata, L. P. Wu, M. Yamamoto, T. Kuroda-Sowa and M. Maekawa, *J. Am. Chem. Soc.*, 1996, **118**, 3117; A. D. Burrows, D. M. P. Mingos, A. J. P. White and D. J. Williams, *Chem. Commun.*, 1996, 97; J. C. M. Rivas and L. Brammer, *New J. Chem.*, 1998, 1315.

6 Y.-B. Dong, M. D. Smith, R. C. Layland and H.-C. Z. Loye, *J. Chem. Soc., Dalton Trans.*, 2000, 775.

7 G. Cao, H.-G. Hong and T. E. Mallouk, *Acc. Chem. Res.*, 1992, **25**, 420; M. E. Thompson, *Chem. Mater.*, 1994, **6**, 1168; D. Grohol, F. Ging and A. Clearfield, *Inorg. Chem.*, 1999, **38**, 751and the references cited therein. D. M. Poojary, B. Zhang and A. Clearfield, *J. Am. Chem. Soc.*, 1997, **119**, 12550; D. M. Poojary, B. Zhang, P. Bellinghausen and A. Clearfield, *Inorg. Chem.*, 1996, **35**, 4942.

8 G. K. H. Shimizu, G. D. Enright, C. I. Ratcliffe, K. F. Preston, J. L. Reid and J. A. Ripmeester, *Chem. Commun.*, 1999, 1485; G. K. H. Shimizu, G. D. Enright, C. I. Ratcliffe, G. S. Rego, J. L. Reid and J. A. Ripmeester, *Chem. Mater.*, 1998, **10**, 3282; G. K. H. Shimizu, G. D. Enright, C. I. Ratcliffe and J. A. Ripmeester, *Chem. Commun.*, 1999, 461; N. J. Melcer, G. D. Enright, J. A. Ripmeester and G. K. H. Shimizu, *Inorg. Chem.*, 2001, **40**, 4641; S. K. Mäkinen, N. J. Melcer, M. Parvez and G. K. H. Shimizu, *Chem. Eur. J.*, 2001, **7**, 5176; A. P. Côte, M. J. Ferguson, K. A. Khan, G. D. Enright, A. D. Kulynych, S. A. Dalrymple and G. K. H. Shimizu, *Inorg. Chem.*, 2002, **41**, 287.

9 B. J. Gunderman and P. J. Squattrito, *Inorg. Chem.*, 1994, **33**, 2924; B. J. Gunderman and P. J. Squattrito, *Inorg. Chem.*, 1995, **34**, 2399; A. Martin, D. Parrish, A. A. Pinkerton, B. J. Gunderman and P. J. Squattrito, *Z. Anorg. Allg. Chem.*, 2001, **627**, 206.

10 A. P. Côte and G. K. H. Shimizu, *Chem. Commun.*, 2001, 251; S. A. Dalrymple and G. K. H. Shimizu, *Chem. Eur. J.*, 2002, **8**, 3010.

11 E. J. Kosnic, E. Lynn McClymont, R. A. Hodder and P. J. Squattrito, *Inorg. Chim. Acta*, 1992, **201**, 143; A. J. Shubnell, E. J. Kosnic and P. J. Squattrito, *Inorg. Chim. Acta*, 1994, **216**, 101; B. J. Gunderman, I. D. Kabell, P. J. Squattrito and S. N. Dubey, *Inorg. Chim. Acta*, 1997, **258**, 237.

12 C.-H. Chen, J. Cai, X.-L. Feng and X.-M. Chen, *J. Chem. Crystallogr.*, 2001, **31**, 271; J. Cai, C.-H. Chen, X.-L. Feng, C.-Z. Liao and X.-M. Chen, *J. Chem. Soc., Dalton Trans.*, 2001, 2370; J. Cai, C.-H. Chen, C.-Z. Liao, J.-H. Yao, X.-P. Hu and X.-M. Chen, *J. Chem. Soc., Dalton Trans.*, 2001, 1137.

13 J. O. Yu, A. P. Côte, G. D. Enright and G. K. H. Shimizu, *Inorg. Chem.*, 2001, **40**, 582.

14 A. I. Kitaigorodskii, *Organic Chemical Crystallography*, Consultants Bureau, New York, 1955.

15 G. E. Engel, S. Wilke, K. D. M. Harris and F. J. J. Leusen, *J. Appl. Cryst.*, 1999, **32**, 1169.

16 C. S. Bruschini, M. G. B. Drew, M. J. Hudson and K. Lyssenko, *Polyhedron*, 1995, **14**, 3099.