Synthesis and Structure of a New Layered Organic-inorganic Hybrid Compound Containing Unique Chain of CuI

Hao-guo Zhu, Zhi Yu, Hu Cai, Xiao-zeng You,* Jagadese J. Vittal,† Geoe-kheng Tan†
Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, P.R. China
†*Department of Chemistry, National University of Singapore, Lower Kent Ridge Road 119260, Singapore*

(Received December 14, 1998; CL-980923)

Synthesis and X-ray crystal structure of a novel iodocuprate(I) compound $(C_{16}H_{19}N_2)_2\ _\infty^1[Cu_5I_7]$ was reported. The unique CuI chains which result from the tetrahedron CuI_4 and pseudo trigonal pyramid CuI_3 through sharing edge are presented in the iodocuprate(I).

Low-dimensional organic-inorganic hybrid compounds have increasing attracting in recent times.[1,2] The composite systems are involved in various fundamental as well as more applied studies related to their transport,[1a] optical,[1b,1c] magnetic,[1b] or structural properties. In hybrid compound systems, The inorganic component structures have demonstrated a wide range of possibilities through influence of the size, shape and charge distribution of the associated organic components. The iodocuprate(I) demonstrates the wide diversity of crystal structure through varying organic ions, while in the solid state this chemistry is dominated by 4-coordination, significant numbers of 3- and 2-coordinated complexes are also known.[3-5] Herein we obtained an interesting compound $(C_{16}H_{19}N_2)_2\ _\infty^1[Cu_5I_7]$ (1) by controlling content of iodine ions through formation of iodoplumbate in solution, and its synthesis and structure was reported.

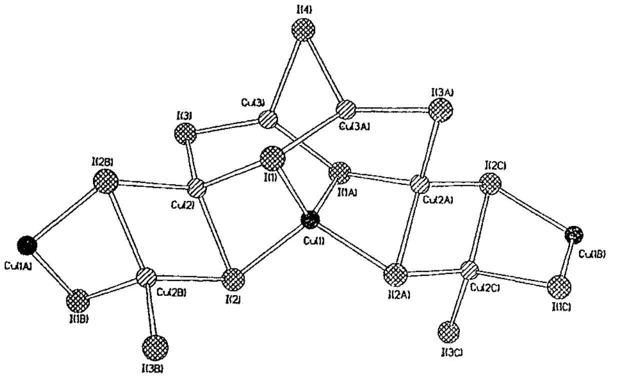

Figure 1. ORTEP view of the building block of $_\infty^1[Cu_5I_7]$ in the crystal **1**.

Compound (**1**) was synthesized from one-pot reaction involving CuI, NaI, 2-[P-(Dimethylamino)styryl]-pyridine-methiodide $(C_{16}H_{19}N_2)I$ and PbI_2 in a 1:1:1:1 molar ratio refluxed for 4 h in acetonitrile, followed by filtration while the solution cooled, the filtrate was allowed to stand for several weeks under 15 °C, the dark-red hexagonal block crystals of (**1**) were obtained.[6] The crystal structure of the compound,[7] $(C_{16}H_{19}N_2)_2\ _\infty^1[Cu_5I_7]$, contains infinite one-dimensionally linked anionic partial structures, which is depicted in Figure 1. In this case condensation of the building block $[Cu_5I_7]$ through common edge leads to one-dimensional ribbons, which are arranged around 2_1 screw axis to form helices in Figure 2. This polymeric anion contains several highly interesting features, the most extraordinary of which is local environment for the Cu(3) atom. The Cu(3) atom was located in a surrounding of I(1), I(1A), I(3) and I(4), but in order to form the stable polyanions, the distance(3.142 Å) between Cu(3) and I(1) atoms was very long, in comparison with 2.98 Å.[8] So it was only coordinated by three I atoms with two short Cu-I distances: 2.505, 2.587 Å, and a long Cu-I distance of 2.654 Å, which is longer than that of Cu-I atoms in trigonal planar coordination of Cu(I), therefore it becomes distorted pseudo trigonal pyramidal geometry [I(3)-Cu(3)-I(1A), 115.31°; I(3)-Cu(3)-I(4), 123.24°; I(4)-Cu(3)-I(1A), 107.95°]. The Cu(3)-Cu(3A) distance(2.552 Å) is comparable to the distance observed for Cu metal (Cu-Cu distance in metallic copper: 2.556 Å), and slightly longer than that found in the anion $Cu_2I_5^{3-}$(Cu-Cu distance: 2.538 Å),[4a] which consists of the CuI_3 trigonal-plane and the CuI_4 tetrahedron through common edge. While the local environment for the Cu(3) atom is analogous to what was observed Cu atoms in the $[Cu_4I_6]^{2-}$,[4d] but its Cu-Cu distance was longer(Cu-Cu distance: 2.74 Å), and so its Cu atom still kept trigonal-planar coordinated geometry. It was well known that Cu^I can have trigonal-planar or tetrahedral coordination in the polyanions, to the best of our knowledge, $(C_{16}H_{19}N_2)_2\ _\infty^1[Cu_5I_7]$ was first example of Cu(I) in both pseudo trigonal pyramidal and tetrahedral geometry in polyanions.[9] Due to the Cu(3) and Cu(3A) interaction, the building block $[Cu_5I_7]$, which was built up by the trigonal bipyramid of iodine containing Cu(3) and Cu(3A) atoms with the tetrahedron CuI_4 through sharing edge, was different from the $[Cu_5I_7]^{2-}$ anion, which was composed of the five face-to-face linked iodine tetrahedron of the pentagonal bipyramid containing Cu^I ions with C_{5h} symmetry.[4c]

Because the Cu(3) coordination sphere is pseudo trigonal pyramid geometry, it led to the tetrahedron of the corner-shared Cu(2) to be distorted with three long and one short Cu-I distance(2.761, 2.688, 2.678, 2.621 Å, respectively), and the Cu(2)-Cu(3) and Cu(2)-Cu(2A) distance(2.847 and 2.724 Å) were longer than that of the anions $_\infty^1[CuI_2]^-$, $_\infty^1[Cu_2I_3]^-$, $_\infty^1[Cu_3I_4]^-$ with the same edge-sharing CuI_4 tetrahedron.[5] The distance of Cu(1) with Cu(2), Cu(3) was 3.043 and 3.029 Å respectively, which was comparable to that of other related compounds. However, the stabilization of the helical chain conformation was involved in Cu(1), its trans edge-shared tetrahedron supports the buildup of the helical chain, and the spiral curve advances with Cu(1A) —·— Cu(1) —·— Cu(1B) as a twofold rotation axis in Figure 2, such type of structure is quite rare.

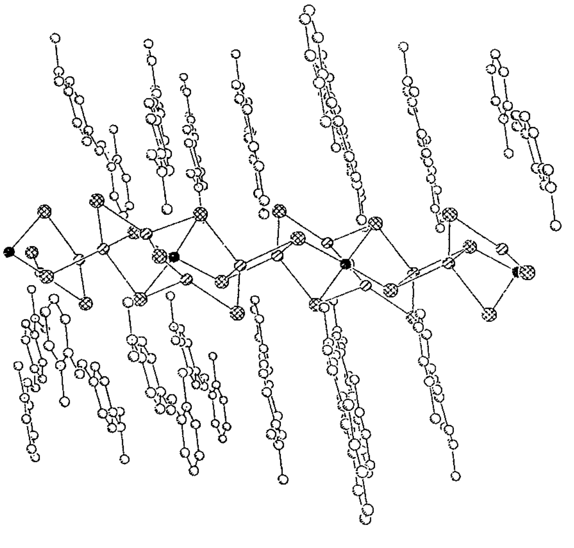

Figure 2. Ball and stick representations of $(C_{16}H_{19}N_2)_2\ _{\infty}^{1}[Cu_5I_7]$, viewed down the b axis, showing Cu(1) as the twofold rotation axis.

The individual $_{\infty}^{1}[Cu_5I_7]^-$ chain is parallel to C-axis, the plane of the organic cation is parallel to ab-plane and the polymeric anions intercalated between the organic cation layers. The one-dimensional chains are weakly held together by Van der Waals interaction forming the extended solid state structure. The solid did not show conductivity by routine four-probe electric resistivity measurements. There are two absorption peaks at 289 and 363 nm in solution, so the iodoplumbate was formed by adding PbI_2, and it controlled the content of iodine ions. Although it is not clear that how the organic components influence the formation of the structure in organic-inorganic hybrid compounds, these examples such as the structural changes from $[(C_3H_7)_4N]_2[Cu_5I_7]$ to $(C_{16}H_{19}N_2)_2\ _{\infty}^{1}[Cu_5I_7]$ and from $(C_{16}H_{19}N_2)_2\ _{\infty}^{1}[Cu_5I_7]$ to $[PyH]_2\ _{\infty}^{3}[Cu_5Br_7]$[10] suggest that the mild conditions could provide an opportunity to obtain new solid state compounds in which unusual structure and coordination spheres are achieved in organic-inorganic hybrid compounds.

We thank the National Natural Science Foundation of China and the Science Foundation of Jiangsu Province for financial support. JJV would like thank the National University of Singapore for funding(RP970618).

References and Notes

1 a) D. B. Mitzi. S. Wang. C. A. Feild. C. A. Chess and A. M. Guloy. *Science*. **267**. 1473(1995). b) P. G. Lacroix. R. Clement. K. Nakatani. J. Zyss and I. Ledoux. *Science*. **263**. 658(1994). c) T. Ishihara. *J. Lumin.*. **60 / 61**. 269(1994).

2 D. Hagrman. C. Zubieta. D. J. Rose. J. Zubieta and R. C. Haushalter. *Angew. Chem., Int. Ed. Engl.*. **36**. 873(1997).

3 B. J. Hathaway. "In Comprehensive Coordination Chemistry". 1st ed. by G. Wilkson. Pergamon Press. New York. 1987.

4 a) K. P. Bigalke. A. Hans and H. Hartl. *Z. Anorg. Allg. Chem.*. **563**. 96(1988). b) H. Hartl. *Angew. Chem., Int. Ed. Engl.*. **26**. 927(1987). c) H. Hartl and F. Mahdjour-Hassan-Abadi. *Angew. Chem., Int. Ed. Engl.*, **23**. 378(1984). d) N. P. Rath and E. M. Holt. *J. Chem. Soc., Chem. Commun.*. **1985**. 665.

5 a) H. Hartl and I. Brudgam. *Z. Naturforsch. B*. **44**. 936(1989). b) H. Hartl and F. Mahdjour-Hassan-Abadi. *Z. Naturforsch, B*. **39**. 149(1984). c) H. Hartl and F. Mahdjour-Hassan-Abadi. *Angew. Chem., Int. Ed. Engl.*. **33**. 1841(1994).

6 Found: C 22.16. H 2.20. N 3.21%: Calcd for **1**: C 22.80. H 2.26. N 3.32%. Without PbI_2. the crystal $(C_{16}H_{19}N_2)CuI_2$ was obtained. Found: C 34.2. H 3.42. N 5.07%: Calcd for $(C_{16}H_{19}N_2)CuI_2$: C 34.50. H 3.41, N 5.03%.

7 The crystal data for **1**: Fw=1684.66. monoclinic. space group C2/c, a=23.6448(5) Å. b=13.5973(3) Å. c=14.3840(3) Å; β=111.35°. V=4307.2(2) $Å^3$. Z=4. F(000)=3096. μ(Mo-K_α)=7.474 mm^{-1}. D_c=2.598 g/cm^3. R1=0.0338. wR2=0.0726.

8 L. I. Victoriano. M. T. Garland. A. Vega and C. Lopez. *Inorg. Chem.*. **37**. 3060(1998).

9 D. M. Young. U. Geiser. A. J. Schultz and H. H. Wang. *J. Am. Chem. Soc.*. **120**. 1331(1998).

10 L. Y. Y.Chan. S. Geller and P. M. Skarstad. *J. Solid State Chem.*. **25**. 85(1978).