

## RAPID COMMUNICATION

# An Unusual Organic–Inorganic Chain-like Hybrid Complex [(CuCl)<sub>2</sub>(*o*-phen)]<sub>∞</sub> (*o*-phen=*o*-phenanthroline)

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A novel organic–inorganic hybrid complex [(CuCl)<sub>2</sub>(*o*-phen)]<sub>∞</sub> **1** (*o*-phen=*o*-phenanthroline) has been hydrothermally synthesized and structurally characterized by elemental analyses, XPS spectrum, TG analysis, and single-crystal X-ray diffraction. Compound **1** crystallizes in the monoclinic system, space group *P*2<sub>1</sub>/*n*, *a* = 3.7285(7) Å, *b* = 19.603(4) Å, *c* = 16.757(3) Å, β = 95.83(3)°, *V* = 1218.4(4) Å<sup>3</sup>, *Z* = 4, λ(MoKα) = 0.71073 Å (*R*(*F*) = 0.0643 for 2559 reflections). Data were collected on an *R*-axis RAPID diffractometer at 293 K in the range of 1.60 < θ < 27.48°. The title compound exhibits a one-dimensional chain-like scaffolding constructed by the unusual [Cu<sub>3</sub>Cl<sub>3</sub>] hexagon motifs by sharing opposite edges. Only Cu(1) sites of the [Cu<sub>3</sub>Cl<sub>3</sub>] hexagon are coordinated with N donors of *o*-phen groups. Furthermore, the three-dimensional supermolecular architecture is formed by C–H...Cl hydrogen bonds between *o*-phen groups and CuCl chains. © 2002 Elsevier Science (USA)

**Key Words:** organic–inorganic hybrid; copper halide; hydrothermal synthesis; chain-like structure; hexagon motifs.

### INTRODUCTION

Organic–inorganic hybrid copper halides have received extensive attention in recent years owing to their great fundamental and practical interest. The architectures of copper halides can be tuned at the molecular level so as to possess unusual electronic properties, various components and potential applications in areas of molecular adsorp-

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tion, catalysis, electromagnetism, and photochemistry (1–15). It is therefore vital to design and synthesize novel organic–inorganic hybrid copper halides to explore their various properties. A recent advance in this system is to design the coordination frameworks of copper halides by the incorporation of various organic structure-directing agents. More recently, owing to the introduction of hydrothermal technique and various N-containing organic templating agents, a variety of novel organic–inorganic hybrid copper halides have been isolated with one-dimensional (1D) chain-like (5, 6) and two-dimensional (2D) layerlike structures (3, 9). Up to date, the basic copper halide skeletons of these complexes generally exhibit several geometrical motifs: cyclic Cu<sub>2</sub>X<sub>2</sub> dimeric (9), cubane tetrameric (12), zigzag polymeric (12), and “stair step” oligomeric (9) structures. It is noteworthy that the introduction of new organic templating agents always leads to the dramatic structural change of the basic inorganic phases (3), which has well been exemplified by the reports of Zubietta *et al.* (3, 4, 8) and Willett *et al.* (2, 14, 15).

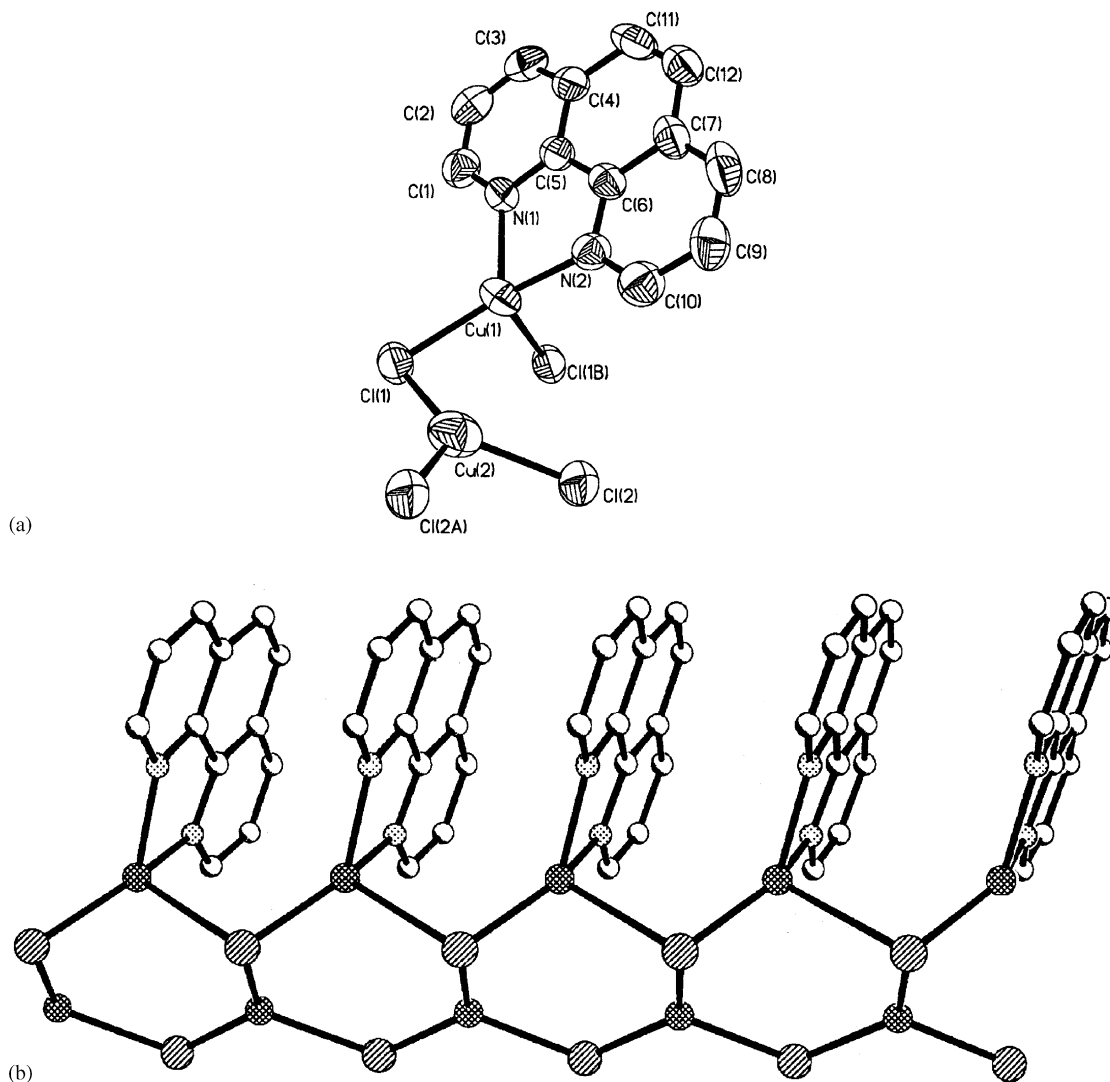
In this communication, we first studied the copper halides—*o*-phenanthroline (*o*-phen) system with the help of hydrothermal technique and report a novel copper chloride—*o*-phen coordination compound [(CuCl)<sub>2</sub>(*o*-phen)]<sub>∞</sub> **1**. Complex **1** exhibits a 1D chain-like scaffolding, which contains unusual [Cu<sub>3</sub>Cl<sub>3</sub>] hexagon motifs by sharing opposite edges. Only Cu(1) sites of the hexagon units are coordinated with two N donors of *o*-phen groups. To our knowledge, such basic *o*-phen—copper chloride skeleton has not been reported hitherto. Furthermore, an interesting 3D supermolecular architecture is formed via the C–H...Cl hydrogen bonds between adjacent organic *o*-phen groups and inorganic copper chloride phases.

## EXPERIMENT

*Hydrothermal Synthesis**General Procedures*

All chemicals were commercially purchased and used without further purification. Elemental analyses (C, H, and N) were performed on a Pekin-Elmer 2400 CHN elemental analyzer. Cu was determined by a Leaman inductively coupled plasma (ICP) spectrometer. ESR spectrum was recorded on a Japanese JES-FE3AX spectrometer at 298 K. XPS analysis was performed on a VG ESCALAB MK II spectrometer with an  $MgK\alpha$  (1253.6 eV) achromatic X-ray source. The vacuum inside the analysis chamber was maintained at  $6.2 \times 10^{-6}$  Pa during the analysis. TG analysis was performed on a Perkin-Elmer TGA7 instrument in flowing  $N_2$  with a heating rate of  $10^\circ C \text{ min}^{-1}$ .

A mixture of  $CuCl_2 \cdot 2H_2O$ ,  $CuCl$ , *o*-phen, and  $H_2O$  with the molar ratio of 1:1:1.6:445 was stirred for 20 min, sealed in a 15 mL polyfluoroethylene-lined stainless-steel bomb, and kept at  $170^\circ C$  under autogenous pressure for 3 days. After cooling to room temperature, yellow chunk crystals of **1** were isolated in ca. 50% yield (based on Cu) by mechanical separation from a green amorphous solid. The crystals of **1** were washed several times with distilled water and dried in air. The pH value of the solution changed from 6 to 1, which indicated that HCl was produced during the hydrothermal reaction process. Elemental analyses found: C, 37.94%; H, 2.26%; Cu, 33.52%; N, 7.23%; Calc. for  $C_{12}H_8Cl_2Cu_2N_2$  **1**: C, 38.11%; H, 2.13%; Cu, 33.60%; N, 7.41%.



**FIG. 1.** (a) ORTEP drawing of the unsymmetrical structural unit of **1** (50% probability ellipsoids) and the atom labeling scheme. (b) View of the 1D chain structure of **1** extending along the *a*-axis. The hydrogen atoms of the *o*-phen group are omitted for clarity. Selected bonds lengths (Å): Cu(1)–N(2), 2.017(7); Cu(1)–N(1), 2.100(7); Cu(1)–Cl(1), 2.219(3); Cu(1)–Cl(1B), 2.701(3); Cu(2)–Cl(1), 2.208(3); Cu(2)–Cl(2), 2.329(3); Cu(2)–Cl(2A), 2.227(3).

## X-Ray Crystallography

The structure of compound **1** was determined by single-crystal X-ray diffraction. Crystallographic data are as follows:  $C_{12}H_8Cl_2Cu_2N_2$ , monoclinic,  $P2_1/n$ ,  $a = 3.7285(7) \text{ \AA}$ ,  $b = 19.603(4) \text{ \AA}$ ,  $c = 16.757(3) \text{ \AA}$ ,  $\beta = 95.83(3)^\circ$ ,  $V = 1218.4(4) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_{\text{cal}} = 2.062$ ,  $\lambda (\text{MoK}\alpha) = 0.71073 \text{ \AA}$ . A yellow single crystal was mounted inside a glass fiber capillary. Data were collected on an  $R$ -axis RAPID IP diffractometer. Empirical absorption correction was applied. The structure was solved by the direct method and refined by full-matrix least squares on  $F^2$  using the SHELXL 97 software (16). All of the nonhydrogen atoms were refined anisotropically. All the hydrogen atoms were located from difference Fourier maps. A total of 9494 (2559 unique,  $R_{\text{int}} = 0.0286$ ) reflections were measured. Structure solution and refinement based on 2559 independent reflections with  $I > 2\sigma(I)$  and 163 parameters gave  $R_1 (wR_2) = 0.0643 (0.2322)$   $\{R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ;  $wR_2 = \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}\}$ . Crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates, and isotropic displacement parameters are available in supplementary crystallographic data Table 1–5.

## RESULTS AND DISCUSSION

The single-crystal X-ray diffraction analysis reveals that the structure of  $[(\text{CuCl})_2(o\text{-phen})]_\infty$  consists of copper(I) chloride chains with  $o$ -phen groups coordinated directly on the Cu(1) sites of the skeleton. There are two crystallographically unique Cu atoms in the asymmetrical structural unit, as shown in Fig. 1(a). The Cu(1) site exhibits a distorted tetrahedral coordination geometry with two N donors provided by the chelating  $o$ -phen ligand and two Cl donors. The average distance of Cu(1)–N bonds is  $2.059 \text{ \AA}$ , while Cu(1)–Cl bonds are in the range of  $2.219(3)$ – $2.701(3) \text{ \AA}$ . The angles of the Cu(1) site vary from  $81.3(3)^\circ$  to  $143.1(2)^\circ$ . The Cu(2) site adopts a slightly distorted triangular planar geometry by the coordination with three Cl donors. The Cu(2)–Cl average distance is  $2.255 \text{ \AA}$  and the Cl–Cu(2)–Cl angles are  $109.84(13)$ ,  $119.10(11)$ , and  $130.33(12)$ , respectively. Chlorine atoms Cl(1) and Cl(2) bridge the Cu sites in  $\mu_3$  and  $\mu_2$  modes, respectively. Therefore, a basic  $[\text{Cu}_3\text{Cl}_3]$  hexagon was formed in the structure of **1**. Only Cu(1) sites are coordinated with two N donors of the  $o$ -phen groups (see Fig. 1(b)). To our knowledge, such basic skeleton unit

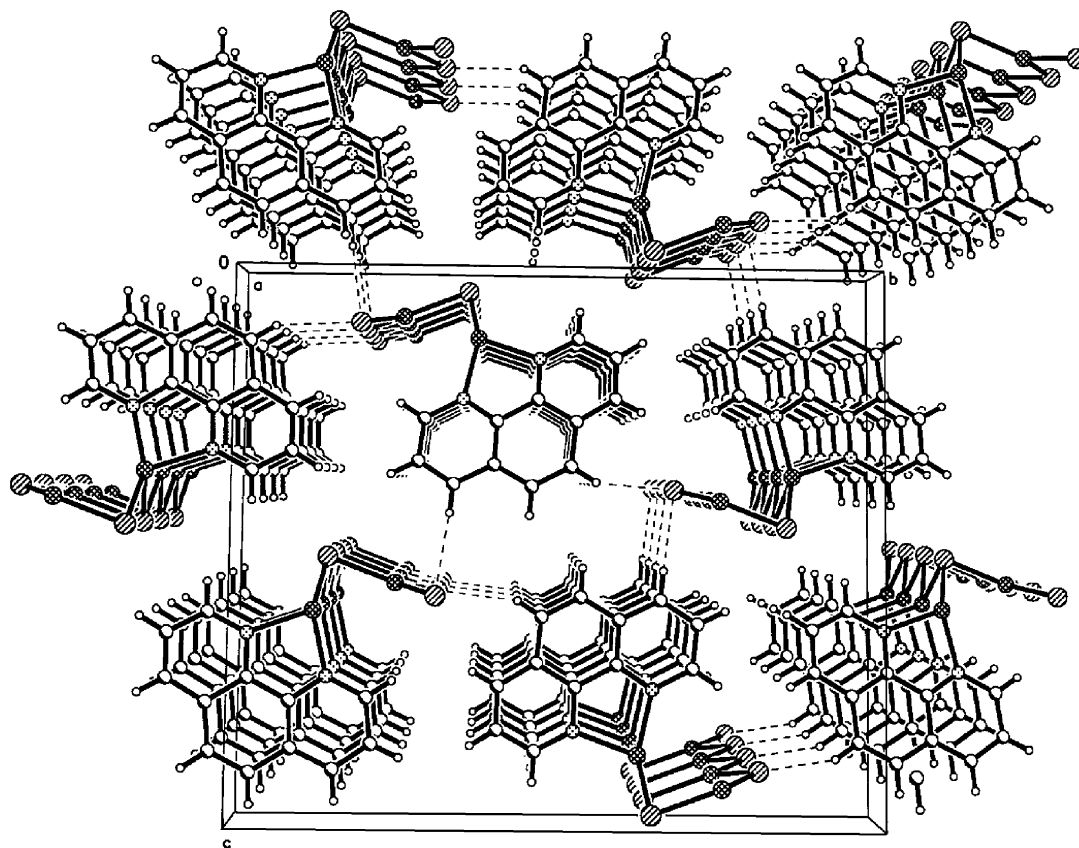


FIG. 2. View of the stacking arrangement of **1** along  $a$ -axis.

combined with *o*-phen groups has never been reported. The only similar compound is  $[(\text{CuCl})_2(\text{C}_{10}\text{H}_7\text{N}_3)]$ , in which all Cu sites of one  $[\text{Cu}_3\text{Cl}_3]$  hexagon are coordinated with N donors of the organic dipyrido[1,2-*a*:2',3'-*d*]imidazole group (6).

The basic  $[\text{Cu}_3\text{Cl}_3]$  hexagon building blocks of **1** form an infinite chain by sharing opposite edges. In the chain-like structure of **1**, there exist two typical CuCl zigzag chains, which are linked with each other via the  $\mu_3$ -Cu and  $\mu_3$ -Cl. The angle between two zigzag chains is  $92.37^\circ$ . When *o*-phen groups are coordinated to Cu(1) sites, two H atoms of *o*-phen rings are activated by Cl anions of adjacent chains at suitable distances and angles (17). As shown in Fig. 2, C atoms in the *o*-phen ring form double hydrogen bonds with the  $\mu_3$ -Cl of adjacent chains. Thus, the  $[(\text{CuCl})_2(\textit{o}\text{-phen})]_\infty$  chains are propagated into 3D architectures through the C–H...Cl hydrogen bonds. A statistical analysis based on CSD suggests that C–H...Cl contacts are within the range 2.7–3.0 Å (18). In this case, the C–H...Cl distance is 2.793–2.906 Å, which is in accordance with the statistical analysis. Furthermore, the C–H...Cl bond angles of **1** exhibit directionality with the range of  $153.39$ – $170.61^\circ$ , which further proves that the C–H...Cl hydrogen bonds are available in the structure of **1**.

It is interesting that *o*-phen components play double roles in the structure of **1**. The one is acting as ligand covalently linked to the copper halide chain. The adjacent phen rings are parallel to each other and cause significant  $\pi$ – $\pi$  stacking interactions with the center-to-center and interplanar distances of 3.728 and 3.457 Å, respectively. Therefore, the 1D copper chloride chain is highly strengthened by the strong  $\pi$ – $\pi$  interactions. The other role is acting as the donors of hydrogen bonding which leads to the generation of 3D supermolecular architecture. To our knowledge, 3D supermolecular structures that generated from 2D layers through hydrogen bonds are common phenomena in the chemistry of coordination polymers (19, 20); however, such 3D supermolecular architectures constructed by 1D chains are rare.

No signal has been found in the ESR spectrum, which confirms that all copper atoms in **1** are  $\text{Cu}^{\text{I}}$ . This is also proved by X-ray photoelectron spectra (XPS) measurement of **1** in the energy region of  $\text{Cu}2p_{1/2}$  and  $\text{Cu}2p_{3/2}$ . The XPS spectrum gives two peaks (the higher is at 932.4 eV) as shown in Fig. 3, attributable to  $\text{Cu}^{\text{I}}$ .

Thermogravimetric analysis proves that **1** possesses high thermal stability. In the TG curve of **1**, there exists only one weight loss stage. From  $20^\circ\text{C}$  to  $330^\circ\text{C}$ , compound **1** is stable. In the temperature range of  $330$ – $640^\circ\text{C}$ , the weight loss is 68.10%, corresponding to the release of *o*-phen and  $\text{Cl}_2$ . The whole weight loss (68.10%) is in good agreement with the calculated value (66.40%).

In conclusion, a new copper chloride—*o*-phen coordination complex  $[(\text{CuCl})_2(\textit{o}\text{-phen})]_\infty$  **1** has been hydrother-

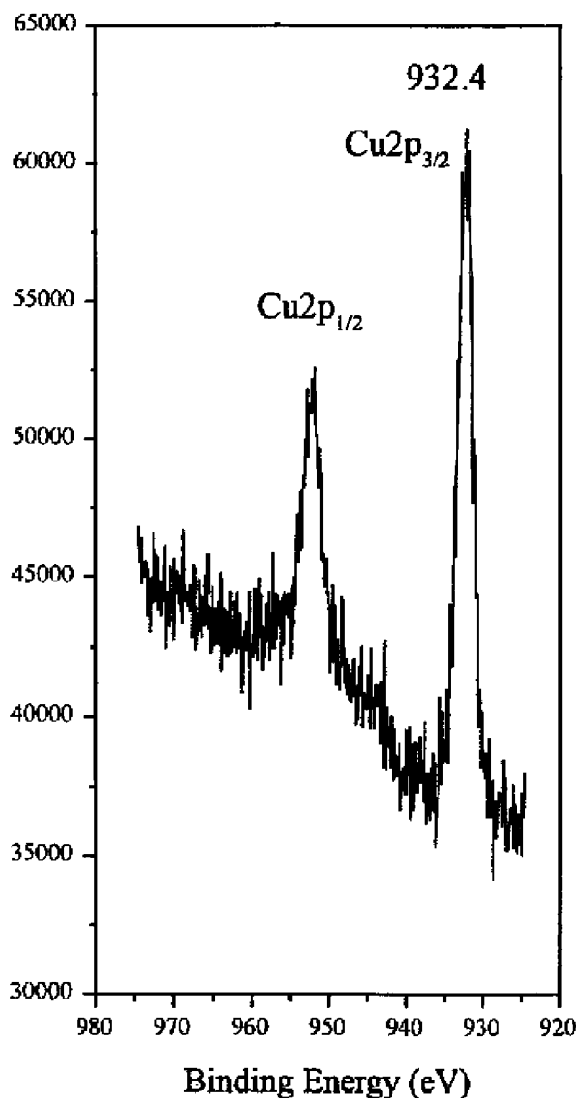


FIG. 3. X-ray photoelectron spectra (XPS) of **1**.

mally synthesized in the present work. Complex **1** exhibits an organic–inorganic hybrid 1D chain-like scaffolding constructed by the unusual  $[\text{Cu}_3\text{Cl}_3]$  hexagon motifs via sharing opposite edges. The *o*-phen groups are coordinated directly to the Cu(1) sites of copper chloride framework with the N donors. The roles of *o*-phen group are discussed. The successful isolation of **1** further confirms the function of organic structure-directing agents for “tailoring” the microstructures of copper halide. Owing to the C–H...Cl hydrogen bonds, 1D copper halide coordination polymer chain in this case is propagated into 3D architectures.

#### ACKNOWLEDGMENT

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