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Note

A novel three-dimensional hybrid framework based on fishbone-like copper halide inorganic units

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Abstract

A novel inorganic–organic hybrid cuprous chloride, $Cu_2^ICl(IN)$ (IN^- = isonicotinate ion) **1**, has been hydrothermally synthesized and structurally characterized by the elemental analyses, IR spectrum, TG analysis and the single crystal X-ray diffraction. The structure of **1** exhibits a three-dimensional network built up from unusual fishbone-like copper(I) chloride ribbons bridged by linear isonicotinato ligands. Its luminescent property was also investigated.

Keywords: Hydrothermal synthesis; Crystal structure; Copper chloride; Isonicotinate

1. Introduction

Copper halides have been subjected to a vast number of studies due to their structural diversity, originating from the polymerizing metal-halogen-based subunits, that give rise to a variety of applications, e.g., in molecular adsorption, catalysis, electromagnetism, and photochemistry [1–3]. In particular, polymeric structures based on copper halide units bridged by organic species received increasing interest by reason of the fact that the architectures of copper halides can be tuned at the molecular level so as to design and control, at least partly, the molecular structures of the final products [4–8], especially, when the so-called secondary build blocks (SBUs) concept was brought forward and extended by Yaghi and co-workers [9–12]. Previous studies have shown the tendency of Cu(I) to form one-dimensional (1-D) ribbon like structural motifs with halogens (X = Cl or Br) under hydrothermal conditions [4,5,13–15], which can be considered as optional candidates for the construction of interesting polymeric frameworks by using them as structural SBUs. Our current research aim is the creative synthesis of desired novel solid materials through extending such 1-D motif into higher dimensions (two-dimensional 2-D or three-dimensional 3-D) via appropriate bridging ligands.

Given this consideration, a noticeable linear tridentate ligand isonicotinate ion, which has recently shown interesting properties in constructing extended structures with copper atoms and other SBUs [16–18], captured our attention. The IN^- contains both a pyridyl group and a carboxylate group in the opposite position of an aromatic ring. It can connect metal ions with its one nitrogen donor and one or two oxygen donors. Several intriguing high-dimensional structures have been obtained in which the isonicotinato ligands display various coordination fashions and abilities [19–22]. On the other hand, isonicotinato ligand possesses negative charge which may dramatically influence the inorganic copper halide adducts by breaking the charge balance between Cu^+ and X^- in contrast to the neutral organic molecules (for example, the widely used organonitrogen ligands [5,6,8,13]), and a new copper halide subunit may be thus acquired.

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In this paper, we report a novel 3-D inorganic–organic hybrid cuprous chloride, $Cu_2^ICl(IN)$ (IN^- = isonicotinate ion) **1**, which is built from new 1-D fishbone-like $\{Cu_2Cl\}_n^+$ ribbons bridged by isonicotinato ligands. To the best of our knowledge, the fishbone-like copper(I) chloride moiety presented in **1** has never been documented before.

2. Experimental

2.1. General procedures

All chemicals purchased were of reagent grade and used without further purification. The hydrothermal reactions were performed in 20 ml Teflon-lined stainless steel vessels under autogenous pressure with a filling capacity of ≈60%. Water used in the reactions is distilled water. Elemental analyses (C and N) were performed on a Perkin–Elmer 2400 CHN Elemental Analyzer. Cu was determined by a Leaman inductively coupled plasma (ICP) spectrometer. IR spectrum was recorded in the range 400–4000 cm^{-1} on an Alpha Centaurt FT/IR spectrophotometer using KBr pellets. TG analysis was performed on a Perkin–Elmer TGA7 instrument in flowing N_2 with a heating rate of 10 °C min^{-1}. Photoluminescence spectra were measured using a FL-2T2 instrument (SPEX, USA) with 450-W Xenon lamp monochromatized by double grating (1200 g/mu).

2.2. Synthesis of $Cu_2^ICl(IN)$ (*1*)

Compound **1** was originally prepared via a self-assembly process under mild hydrothermal condition from the reaction of CuCl, isonicotinic acid, NaCl, and H_2O in a molar ratio of 2:1:1:555 at 140 °C for four days. After slow cooling to room temperature, the resulting orange needles of **1** were collected as a major phase (32% yield on Cu) together with a small quantity of blue block crystals, and then filtered off, washed with distilled water, and dried at ambient temperature. The needles were manually selected for structural determination and further characterization. *Anal.* Calc. for **1**: C, 25.32; N, 4.92; Cu, 44.65. Found: C, 25.19; N, 4.83; Cu, 44.92%. IR (KBr) ν/cm^{-1}: 3033w, 1585s, 1547s, 1227s, 1055w, 858w, 764m, 765m, 700s and 527w (Fig. S1).

In order to obtain pure phase product of **1**, several parallel experiments have been done thereafter. It was found that the uniform adducts of **1** could be successfully isolated when the reaction pH values were adjusted to 2.0–3.0 by HCl solution, whereas the reaction time played a less important role that was proved by some successful reactions with heating time between 3 days and 5 days.

2.3. X-ray crystallography

The data were collected on a Rigaku R-AXIS RAPID IP diffractometer at 293 K using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and oscillation scans technique in the range of $3.74° < \theta < 25.47°$. Empirical absorption correction was applied. A total of 5795 (1397 unique, $R_{int} = 0.1284$) reflections were measured. The structure was solved by direct methods using the program SHELXS-97 [23] and refined by full-matrix least-squares methods on F^2 using the SHELXL-97 [24] program package. All of the non-hydrogen atoms were refined anisotropically. Positions of the hydrogen atoms attached to carbon atoms were fixed at their ideal positions. Structure solution and refinement based on 1397 independent reflections with $[I > 2\sigma(I)]$ on 0 restraint and 110 parameters gave R_1 (wR_2) = 0.0560 (0.1175). A summary of the crystallographic data and structural determination for compound **1** is provided in Table 1. Selected bond lengths and angles are listed in Table 2.

Table 1
Crystal data and structure refinement for compound **1**

Empirical formula	$C_6H_4ClCu_2NO_2$
Formula weight	284.63
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a (Å)	19.065(4)
b (Å)	3.7262(7)
c (Å)	10.572(2)
Volume (Å^3)	751.0(3)
Z	4
Goodness-of-fit on F^2	1.119
Final *R* indices $[I > 2\sigma(I)]$	R_1[a] = 0.0560, wR_2[b] = 0.1175
Indices (all data)	R_1[a] = 0.0763, wR_2[b] = 0.1245

[a] $R_1 = \sum \||F_o| - |F_c|\| / \sum |F_o|$.
[b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1/2}$.

Table 2
Selected bond lengths (Å) and angles (°) for compound **1**[a]

Cu(1)–N(1)	1.988(5)	Cu(2)–O(1)#1	1.902(5)
Cu(1)–Cl(1)	2.2875(19)	Cu(2)–O(2)#2	1.902(4)
Cu(1)–Cl(1)#3	2.3622(19)	Cu(2)–Cl(1)	2.7156(19)
Cu(1)–Cl(1)#4	2.625(2)		
N(1)–Cu(1)–Cl(1)	125.90(17)	O(1)#1–Cu(2)–O(2)#2	172.2(2)
N(1)–Cu(1)–Cl(1)#3	112.27(16)	O(1)#1–Cu(2)–Cl(1)	91.67(16)
Cl(1)–Cu(1)–Cl(1)#3	106.51(8)	O(2)#2–Cu(2)–Cl(1)	96.01(16)
N(1)–Cu(1)–Cl(1)#4	98.60(19)	Cl(1)#5–Cu(1)–Cl(1)#4	104.48(7)
Cl(1)–Cu(1)–Cl(1)#4	106.69(7)		

[a] Symmetry transformations used to generate equivalent atoms: #1 $x - 1/2$, $-y + 5/2$, $-z + 1$; #2 $-x + 5/2$, $-y + 2$, $z + 1/2$; #3 x, $y + 1$, z; #4 $-x + 2$, $y + 1/2$, $-z + 1/2$.