Influence of synthesis condition on product formation: hydrothermal auto-oxidated synthesis of five copper halides with ratio of Cu(I)/Cu(II) in 1:1, 2:1, 3:1, 4:1 and 1:0

Shuai Zhang [a], Yanning Cao [a], Hanhui Zhang [a,b,*], Xiaochuan Chai [a], Yiping Chen [a], Ruiqing Sun [a]

[a] Department of Chemistry, Fuzhou University, Fuzhou, Fujian 350002, PR China
[b] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, The Chinese Academy of Sciences, Fuzhou, Fujian 350002, PR China

ABSTRACT

The hydrothermal synthesis and structural characterization of five copper iodides derived from chelated ligands, 1, 10-phenanthroline (phen), ethylenediamine (en) and 1, 3-propanediamine, are reported. Except monovalent copper compound **1** ((phen)Cu$_3$I$_3$ **1**), other four compounds ([Cu(phen)$_2$I][CuI$_2$] **2**, [Cu(phen)$_2$I][Cu$_3$I$_4$] **3**, [Cu(en)$_2$][Cu$_4$(phen)$_2$I$_6$] **4** and [Cu(1, 3-propanediamine)$_2$]$_2$[CuI$_2$]$_2$ **5**) are mixed-valent Cu(I)–Cu(II) compounds by partially auto-oxidated from Cu(I). Supramolecular frameworks of these compounds can be assembled by C/N–H⋯I hydrogen bonds, Cu(I)–Cu(I) interaction, weak Cu–I *semi*coordinate interaction, C–H⋯π and π–π stacking interactions. It's noteworthy that we find hydrothermal synthesis under higher pH value, higher synthesis temperature and longer reaction time can obtain higher ratio of Cu(I)/Cu(II) copper iodides and organic ligand with lower steric hinderance is prone to coordinated with divalent copper to form cation unit. Finally, the fluorescent study shows **1** exhibits intense orange–red luminescence with long lifetime at 293 K and more intense emission and longer lifetime at 77 K. Moreover, the room temperature EPR spectra of above five compounds not only show the valence of copper but demonstrate the coordination environment of Cu(II) centre.

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1. Introduction

Nowadays, the synthesis of inorganic–organic hybrid materials has attracted more and more people's attention, in which the research on metal-oxo cluster has gone through a long period with many vanadium-oxo clusters [1,2], molybdenum-oxo clusters [3,4], tungsten-oxo clusters [5] and hetero-polyacid clusters [6–8]. Though as a burgeoning field, metal-haloid cluster has aroused chemists' much attention for the reasons as follows: monovalent copper compounds showing strong fluorescence [9] and electrical-conductivity [10], divalent copper compounds displaying magnetic property [11] and mixed-valent Cu(I)–Cu(II) copper compounds with biological importance [12] and electronic properties [13]. So, Cu(I) halides have been widely employed as inorganic components in the construction of inorganic–organic hybrid coordination polymers [14,15]. It's known to all that Cu(II) halides have the tendency to be reduced to Cu(I) in the presence of organic species, particularly the compounds containing activated pyridine ring are involved [16,17]. Compared with chlorine (Cl) and bromine (Br), iodine (I) behaves more versatile bridging

modes ranging from μ_1- to μ_7-I [18–22], which can exhibit rhomboid dimers [23], zigzag chains [24], double-stranded ladders [16], cubane-like and stepped Cu$_4$I$_4$ tetramers [25,26], hexagonal grid chains [27], Cu$_6$I$_6$ hexamers including banded ribbons [28], Cu$_6$I$_6$ cores [27] and Cu$_6$I$_6$ clusters with two copper atoms in trigonal coordination environment etc. [15]. In comparison with coordination bonds, supramolecular interactions (hydrogen bond [29], C–H⋯π and π–π stacking interactions [30,31], metal–metal interaction [32] and weak coordinative interaction etc. [33]) can construct diversiform structure with novel topologies and potential application in host-guest chemistry, catalysis etc. [34]. Then, taking the advantages of forementioned factors, we are interested in obtaining mixed-valent Cu(I)–Cu(II) copper iodides originating from CuI by auto-oxidation under hydrothermal condition [35]. Herein, we have successfully combined phen, en and 1, 3-propanediamine with copper iodides to build five inorganic–organic hybrid compounds under similar hydrothermal conditions, which assemble to supramolecular architecture by various supramolecular interactions. Except monovalent compound **1**, other four are mixed-valent Cu(I)–Cu(II) compounds (with the ratio of Cu(I)/Cu(II) in 1:1, 3:1, 4:1, 2:1, respectively) by partially auto-oxidated from Cu(I). Meanwhile, we find that hydrothermal synthesis under higher pH value, higher synthesis temperature and longer reaction time can get

* Corresponding author at: Department of Chemistry, Fuzhou University, Fuzhou, Fujian 350002, PR China. Tel.: +86 591 87893235; Fax: +86 591 87893239.
E-mail address: zhanghh1840@hotmail.com (H. Zhang).

higher ratio of Cu(I)/Cu(II) copper iodide compounds and organic ligand with lower steric hinderance is prone to coordinated with divalent copper to form the cation unit, all of which are beneficial to our future design and synthesis via hydrothermal method to some extent. Besides single crystal X-ray diffraction (XRD) analysis, these five compounds are characterized by elemental analyses, powder XRD analysis, IR spectra, ultraviolet-visible diffuse reflection integral spectra (UV-vis DRIS), fluorescent spectra and EPR spectra analysis. The fluorescent study shows **1** exhibits intense orange–red luminescence with long lifetime ($\tau = 1.25\,\mu s$) at 293 K and more intense emission and longer lifetime ($\tau = 6.95\,\mu s$) at 77 K. Moreover, the room temperature EPR spectra of above five compounds not only show the valence of copper but demonstrate the coordination environment of Cu(II) centre.

2. Experimental

2.1. General procedures

All analytical regent grade chemicals were commercially purchased and used without purification. The elemental analyses of C, H, and N were performed with an Elementar Vario EL III elemental analyzer. The powder XRD patterns of solid-state samples were recorded on a PANalytical X' pert Pro diffractometer equipped with Cu-$K\alpha$ radiation ($\lambda = 0.1541$ nm) at room temperature. The IR spectra were recorded with a Perkin-Elmer Spectrum 2000 FT-IR spectrometer in the range of 400–4000 cm^{-1} using the KBr pellet technique. UV-Vis DRIS was measured by a Perkin-Elmer Lambda 900 UV-Vis spectrometer with BaSO$_4$ as the reference sample. The solid-state fluorescent spectra were recorded on an Edinburgh Instrument FL/FS-920 fluorescent spectrometer using Xe lamp for steady fluorescent and H$_2$ nanose-

cond flash lamp for transient fluorescence. EPR spectra of compounds **1**, **3**, **4** and **5** were recorded on a Bruker EMX-10/12 spectrometer at room temperature with a frequency modulation of 100 KHz except compound **2** recorded on a Bruker ER-420 spectrometer.

2.2. Synthesis of compounds

Synthesis of (phen)Cu$_3$I$_3$ **1**: The aqueous solution (2 cm^3) of CuI (0.19 g, 1 mmol) and NaI (0.30 g, 2 mmol) was stirred with adding [Mn(phen)$_2$I$_2$] (0.07 g, 0.1 mmol) and ethanol (1 cm^3). [Mn(phen)$_2$I$_2$] was prepared in advance according to the Ref. [36]. Then the mixture was stirred for another 30 min and pH value was adjusted to 5.8 with drops of 10% HCl and 10% NaOH solution. Finally, the mixed solution was sealed in a 15 cm^3 Teflon-lined stainless autoclave and heated at 170 °C for 4 d under autogenous pressure and then cooled to room temperature unaffectedly. Red rod crystals of **1** suitable for X-ray analysis were obtained in about 41% yield (based on Cu). Anal. calc for C$_{12}$H$_8$Cu$_3$I$_3$N$_2$: C, 19.18; H, 1.07; N, 3.73 wt%; found: C, 19.20; H, 1.04; N, 3.81 wt%. IR (KBr, cm^{-1}): 3042 (vw), 1616 (w), 1574 (w), 1502 (m), 1418 (s), 1134 (w), 834 (s), 761 (w), 722(s), 632 (vw).

Synthesis of [Cu(phen)$_2$I][CuI$_2$] **2**: The synthesis method of **2** was similar to that of **1** except that pH was adjusted to 6.0 with 10% HCl and 10% NaOH solution and the reaction temperature of 150 °C instead. Black thick sheet crystals of **2** were obtained in about 34% yield (based on Cu). Anal. calc for C$_{24}$H$_{16}$Cu$_2$I$_3$N$_4$: C, 33.20; H, 1.86; N, 6.45 wt%; found: C, 33.42; H, 1.83; N, 6.37 wt%. IR (KBr, cm^{-1}): 3042 (vw), 1619 (w), 1579 (w), 1514 (m), 1422 (s), 1138 (w), 843 (s), 775 (w), 718(s), 643 (w).

Synthesis of [Cu(phen)$_2$I][Cu$_3$I$_4$] **3**: The synthesis sources of **3** were the same as that of **1** except pH = 7.4 without adjusting. And the mixture was sealed in 15 cm^3 autoclave and heated at 130 °C for 2 d under autogenous pressure. Black square block crystals of **3**

Table 1
Crystallographic data for compounds **1**, **2**, **3**, **4** and **5**

Compounds	1	2	3	4	5
Empirical formula	C$_{12}$H$_8$Cu$_3$I$_3$N$_2$	C$_{24}$H$_{16}$Cu$_2$I$_3$N$_4$	C$_{24}$H$_{16}$Cu$_4$I$_5$N$_4$	C$_{14}$H$_{16}$Cu$_{2.50}$I$_3$N$_4$	C$_3$H$_{10}$Cu$_{1.50}$I$_2$N$_2$
Formula mass	751.52	868.19	1249.07	779.86	423.24
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	P-1	P-1	$P2_1/c$	P-1	P-1
A (Å)	4.1844(8)	7.8881(16)	14.081(4)	8.297(6)	6.896(6)
b(Å)	13.460(3)	9.5501(19)	9.424(5)	9.424(5)	8.685(8)
c (Å)	15.998(3)	17.346(4)	16.146(5)	13.985(6)	9.016(6)
α (deg)	113.74(3)	85.75(3)	90.00	83.46(2)	110.42(3)
β (deg)	92.58(3)	77.75(3)	113.957(12)	79.90(2)	98.87(3)
γ (deg)	98.12(3)	77.10(3)	90.00	64.82(2)	110.39(3)
V (Å^3)	811.3(3)	1244.3(4)	2909.9(16)	973.3(9)	450.4(6)
Dc (g/cm^3)	3.076	2.317	2.851	2.661	3.121
Z	2	2	4	2	2
$F(000)$	680	810	2276	719	383
λ (Mo$K\alpha$) (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
θ Range (deg)	3.06–27.48	3.09–27.48	3.12–27.48	3.29–27.48	3.28–27.48
Limiting indices	$-5 \leqslant h \leqslant 5$, $-17 \leqslant k \leqslant 17$, $-20 \leqslant l \leqslant 20$	$-10 \leqslant h \leqslant 9$, $-12 \leqslant k \leqslant 11$, $-22 \leqslant l \leqslant 22$	$-16 \leqslant h \leqslant 18$, $-18 \leqslant k \leqslant 18$, $-20 \leqslant l \leqslant 17$	$-10 \leqslant h \leqslant 10$, $-10 \leqslant k \leqslant 12$, $-18 \leqslant l \leqslant 18$	$-8 \leqslant h \leqslant 8$, $-11 \leqslant k \leqslant 11$, $-11 \leqslant l \leqslant 11$
Goodness-of-fit on F^2	1.132	1.039	1.036	1.018	1.049
Collected reflections	7907	11853	27550	9620	4477
Independent reflections (R_{int})	3627(0.0270)	5537(0.0417)	6544(0.0391)	4417(0.0275)	2042(0.0854)
Observed reflections ($I>2\sigma$ (I))	3044	4037	5327	3983	1811
Final R factors ($I>2\sigma$ (I))	R_1[a] = 0.0329, wR_2[b] = 0.0760	R_1 = 0.0379, wR_2 = 0.0676	R_1 = 0.0295, wR_2 = 0.0613	R_1 = 0.0240, wR_2 = 0.0567	R_1 = 0.0472, wR_2 = 0.1100
Final R factors (all data)	R_1 = 0.0416, wR_2 = 0.0791	R_1 = 0.0625, wR_2 = 0.0753	R_1 = 0.0418, wR_2 = 0.0645	R_1 = 0.0278, wR_2 = 0.0581	R_1 = 0.0503, wR_2 = 0.1123
Largest diff. map peak and hole e Å^{-3}	1.043 and −1.237	0.856 and −0.682	1.634 and −1.599	0.757 and −0.849	1.579 and −2.311

[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

[b] $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_0^2)^2]\}^{1/2}$.