



NOTE

Solvothermal Synthesis, Characterization and Crystal Structure of Mixed-Valent Complex $[\text{Cu(I)(phen)}_2]_2 \cdot 2[\text{Cu(II)(phen)}_2\text{I}] \cdot 3\text{I}$

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The solvothermal reaction of copper(I) iodide and 1,10-phenanthroline (phen) in ethanol solution in presence solution of HI yielded the mixed-valent Cu(I)-Cu(II) compound, namely $[\text{Cu(I)(phen)}_2]_2 \cdot 2[\text{Cu(II)(phen)}_2\text{I}] \cdot 3\text{I}$. The crystallizing sample was characterized by elementary analysis. Its structure was determined by single crystal X-ray diffraction experiment. The compound crystallizes in the monoclinic system and adopts a centrosymmetric space group of $P2_1/c$, with $a = 1.6175(3)$ nm, $b = 1.8659(4)$ nm, $c = 2.3025(5)$ nm, $\alpha = 90^\circ$, $\beta = 108.708(2)^\circ$, $\gamma = 90^\circ$, $V = 6.582(2)$ nm³, $Z = 4$, $D_c = 1.924$ g cm⁻³, $F(000) = 3664$, $\mu = 3.36$ mm⁻¹. The asymmetric unit contains one $[\text{Cu(I)(phen)}_2]^+$ cation, two $[\text{Cu(II)(phen)}_2\text{I}]^+$ cations and three I⁻ anions. Each Cu(I) cation is tetrahedrally coordinated by four nitrogen atoms from two bidentate chelating phen ligands. The coordinate polyhedra of two Cu(II) cations are both trigonal bipyramid, which are composed of four nitrogen atoms from two phen and one iodine atom.

Key Words: Solvothermal synthesis, Mixed-valent, Copper-iodide complex.

In the past decades, the syntheses of inorganic-organic hybrid materials have attracted more and more attentions^{1,2}. The research on metal halide compounds has aroused people's much attention for such reasons as: monovalent copper compounds showing strong fluorescence³, divalent copper compounds as magnetic materials⁴ and mixed-valent Cu(I)-Cu(II) copper compounds with biological⁵ and electronic properties⁶. In fact, the Cu(I) halides have been widely researched due to their significant value for functional materials. Recently, there have been a number of reports for copper(I) or copper(II)-iodide or mixed-valent Cu(I)-Cu(II) complexes with 1,10-phenanthroline (phen) as a coligand⁷⁻¹³. In virtue of its strong chelation to copper and some benefits for functional materials, we are interested in 1,10-phenanthroline as a coligand and have synthesized a novel monovalent copper compound Cu(I)(phen) previously¹⁰. Here, we report the synthesis and crystal structure of a mixed-valent compound $[\text{Cu(I)(phen)}_2]_2 \cdot 2[\text{Cu(II)(phen)}_2\text{I}] \cdot 3\text{I}$ (**1**).

All chemicals were obtained from commercial sources and used as received. Elemental analysis for C, H and N were performed on an Elementar Vario MICRO analytic instrument.

Synthesis of $[\text{Cu(I)(phen)}_2]_2 \cdot 2[\text{Cu(II)(phen)}_2\text{I}] \cdot 3\text{I}$ (1**):** The compound **1** was synthesized by a solvothermal reaction from Cu(I) and 1,10-phenanthroline. A mixture of Cu(I) (76

mg, 0.4 mmol), some drops of 45 % HI and phen·H₂O (160 mg, 0.8 mmol) in 12 mL ethanol was put into a Parr Teflon-lined autoclave (25 mL) and heated at 403 K for 3 days. After cooling down to room temperature, some black prism crystals of compound **1** were obtained (yield 103 mg, 40.7 % based on Cu(I)). Anal. calcd. for C₇₂H₄₈N₁₂I₅Cu₃: C, 45.36; H, 2.54; N, 8.82. Found: C, 45.89; H, 2.79; N, 8.22.

Single crystal structure determination: X-ray intensity data for **1** were collected on a black prism crystal (0.15 mm × 0.15 mm × 0.22 mm) at 293(2) K on a Rigaku RAXIS-RAPID CCD area detector diffractometer using graphite monochromated MoK_α radiation ($\lambda = 0.071075$ nm). The structure was solved using direct methods and refined by full-matrix least-squares techniques. All non-hydrogen atoms were assigned anisotropic displacement parameters in the refinement. All hydrogen atoms were added at calculated positions and refined using a riding model. The structure was refined on F² using SHELXTL-97 software package^{14,15} without any unusual events. The selected bond lengths and bond angles are gathered in Table-1.

We have synthesized the mixed-valent copper complex $[\text{Cu(I)(phen)}_2]_2 \cdot 2[\text{Cu(II)(phen)}_2\text{I}] \cdot 3\text{I}$ (**1**) (Fig. 1). The compound crystallizes in the orthorhombic system. It is worthy of note that compound **1** crystallizes in a monoclinic system and adopts

TABLE-1
SELECTED BOND LENGTHS (nm) AND
ANGLES (°) OF THE COMPOUND 1

Cu1-N1	0.1991(5)	Cu1-N2	0.2085(5)
Cu1-N3	0.2102(5)	Cu1-N4	0.1993(5)
Cu1-I2	0.2719(1)	Cu2-N5	0.2075(5)
Cu2-N6	0.1996(5)	Cu2-N7	0.2123(5)
Cu2-N8	0.1999(4)	Cu2-I4	0.2677(1)
Cu3-N9	0.2057 (5)	Cu3-N10	0.2047(5)
Cu3-N11	0.2079 (5)	Cu3-N12	0.2027(5)
N1-Cu1-N2	81.5(2)	N1-Cu1-N3	97.7(2)
N1-Cu1-N4	176.2(2)	N2-Cu1-N3	120.7(2)
N2-Cu1-N4	95.8(2)	N3-Cu1-N4	81.3(2)
N1-Cu1-I2	92.1(2)	N2-Cu1-I2	128.7(1)
N3-Cu1-I2	110.6(1)	N4-Cu1-I2	91.7(2)
N5-Cu2-N6	81.4(2)	N5-Cu2-N7	117.2(2)
N5-Cu2-N8	95.0(2)	N6-Cu2-N7	98.0(2)
N6-Cu2-N8	175.3(2)	N7-Cu2-N8	81.0(2)
N5-Cu2-I4	130.6(1)	N6-Cu2-I4	93.3(1)
N7-Cu2-I4	112.2(1)	N8-Cu2-I4	91.3(2)
N9-Cu3-N10	81.5(2)	N9-Cu3-N11	138.1(2)
N9-Cu3-N12	111.9(2)	N10-Cu3-N11	106.0(2)
N10-Cu3-N12	151.1(2)	N11-Cu3-N12	81.5(2)

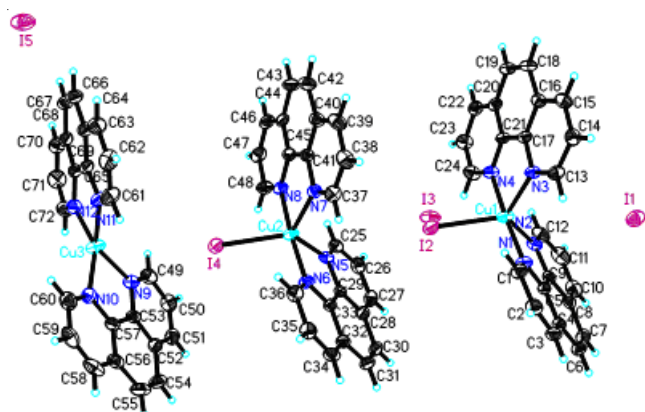


Fig. 1. Structure and labeling of the compound 1, with displacement ellipsoids drawn at the 30 % probability level and H atoms shown as small spheres of arbitrary radii

a centrosymmetric space group of $P2_1/c$. The asymmetric unit contains one $[\text{Cu(I)(phen)}_2]^+$ cation, two $[\text{Cu(II)(phen)}_2\text{I}]^+$ cations and three Γ^- anions. Each Cu(I) cation is tetrahedrally coordinated by four nitrogen atoms from two bidentate chelating phen ligands. The Cu-N bond lengths range from 0.2027 (5) to 0.2079 (5) nm, which are similar to that found in other $[\text{Cu(I)(phen)}_2]^+$ cation^{13,16-21}. The coordinate polyhedra of two Cu(II) cations are both trigonal bipyramid, which are composed of 4 nitrogen atoms from 2 phen and 1 iodine atom. The Cu(I) bond lengths are 0.2677 (1) and 0.2719 (1) nm, which are similar to that found in other copper(II)-iodide complexes¹¹⁻¹³. And the Cu-N bond lengths range from 0.1991 (5) to 0.2123 (5) nm, which are similar to that found in other $[\text{Cu(II)(phen)}_2\text{I}]^+$ cation¹¹⁻¹³. There are some π - π stacking interactions between adjacent phen ligands and some C-H...I hydrogen bonds between phen ligands and Γ^- anions. Subsequently, the compound is characterized as a supramolecular structure with some channels along c axis. The anions of I3 and I5 just fill in the channels (Fig. 2).

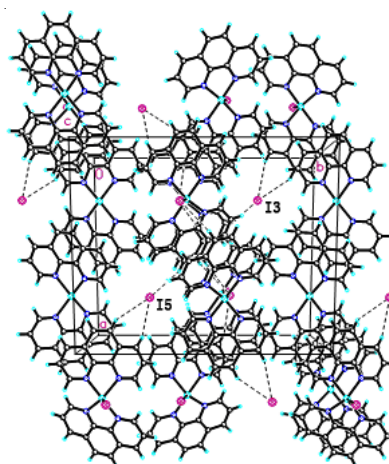


Fig. 2. Packing diagram viewed along the c-direction

Conclusion

In conclusion, we have synthesized the mixed-valent title complex $[\text{Cu(I)(phen)}_2] \cdot 2[\text{Cu(II)(phen)}_2\text{I}] \cdot 3\text{I}$. And it is characterized as a supramolecular structure constructed through weak π - π stacking interactions and C-H...I hydrogen bonds.

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