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Hydrothermal Synthesis and Crystal Structure of $Cu_3I_3(C_{12}H_8N_2)_2$

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In 1985, Healy *et al.* described the structural characterization of the 1:1 adducts of copper(I) bromide and iodide with 1,10-phen($C_{12}H_8N_2$) under ambient conditions: the bromide is ionic $[CuL_2]^+[BrCuBr]^-$, while the iodide is dimeric $[LCuI_2CuL]$ [1,2]. At present, we have investigated simple CuI-KI-phen-H_2O system. Now, we present structural characterization of trinuclear copper(I) halide cluster $Cu_3I_3phen_2$ obtained by hydrothermal synthesis.

The crystal structure of $Cu_3I_3phen_2$ is displayed in Figure 1. It is a non-centrosymmetric trinuclear neutral cluster. There are two crystallographically independent monovalent copper ions, Cu(1) and Cu(2), occurring in a 4-, and 3-fold coordinate site, respectively. Cu(1) atom in the tetrahedral site is coordinated to two bridging io-

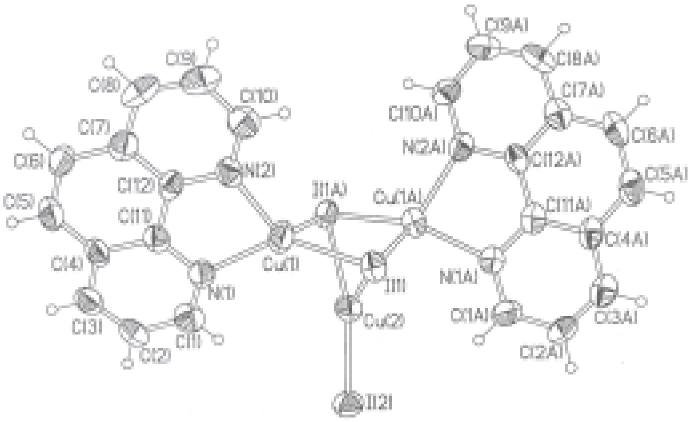

Figure 1. The structure of $Cu_3I_3phen_2$.

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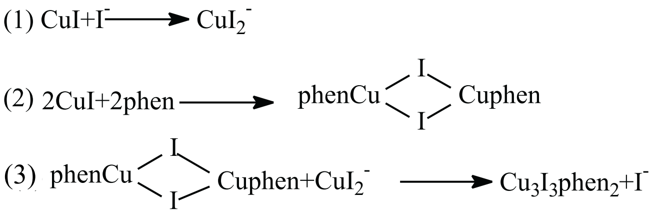
dide ions I^- and two N atoms in the 1,10-phen molecule. The Cu–I bonds range from 2.5911(13) Å to 2.7384(15) Å and the Cu(1)–N distances are 2.050(8)–2.069(7) Å. Cu(2) atom with a slightly distorted triangular planar geometry is coordinated to two bridging and one terminal iodide ions I^-. The terminal Cu(2)–I(2) distance, 2.4338(19) Å is slightly shorter than the bridging Cu(2)–I(1) distances, 2.6956(12) Å. The rhomb comprising four atoms Cu(1), Cu(1)#, I(1), I(1)# may be planar or folded about the bridging halide atoms. Here it is folded and the CuI_2Cu core displays a fold angle of 164°. Each 1,10-phen ligand in the compound is not perpendicular to the plane, which consists of adjacent three atoms in the CuI_2Cu core, the dihedral angles are 73.8 and 106.2°, respectively. The tetrahedrally coordinated copper is quite distorted with I–Cu–I angle of 102.72(4)° and I–Cu–N angles of 135.9(2) and 120.6(2)°. The I(2)–Cu(2)–I(1) and I(1)–Cu(2)–I(1)# angles for the triangular copper are 129.44(3) and 101.13(6)°, respectively. The Cu(1)–Cu(2) distance is short [2.5483(18) Å], the shortest non-bonded copper-copper contact in an oligonuclear complex appears to be the distance of 2.45 Å observed in $[\{Cu(PhN{=}NPh)\}_2]$ [3]. Four atoms Cu(2), I(1), I(1)# and I(2) are in a plane.

As far as large numbers of copper(I) halide framework structures so far determined are concerned, the trinuclear species are very rare, till now only one has been reported namely $Cu_3X_3L_2$ (X = Cl, Br, I, L = $CH_2(PPH_2)_2$) [4].

The title compound was constructed *via* self-assembly under mild hydrothermal conditions. Reactions of CuI (0.30 g), 1,10-phen (0.31 g), KI (0.66 g) and H_2O in the mole ratio 1:1:2.5:300 in a 30 mL Teflon-lined autoclave at 150° for 5 days afforded red rhombic crystals suitable for X-ray diffraction studies. The yield was 25% based on the CuI. The balance equations may be written as



(1) $CuI + I^- \longrightarrow CuI_2^-$

(2) $2CuI + 2phen \longrightarrow phenCu\genfrac{}{}{0pt}{}{\diagup I \diagdown}{\diagdown I \diagup}Cuphen$

(3) $phenCu\genfrac{}{}{0pt}{}{\diagup I \diagdown}{\diagdown I \diagup}Cuphen + CuI_2^- \longrightarrow Cu_3I_3phen_2 + I^-$

The title structure was solved by direct methods and refined by full-matrix least-square techniques. Non-H atoms were refined anisotropically to convergence. The H atoms were treated using a riding model. The crystal data and selected parameters are given in Tables 1–3*.

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* Crystallographic data have been deposited with the Cambridge Crystallographic Data Center (CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK) as deposition No. 164222.

Table 1. Crystal data and structure refinement for Cu_2I_3phen$_2$.

Empirical formula	$C_{12}H_8Cu_{1.50}I_{1.50}N_2$
Formula weight	465.86
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, *C*2/*c*
Unit cell dimensions	a = 10.0495(8) Å, α = 90°
	b = 15.0351(12) Å, β = 94.105(2)°
	c = 16.8237(12) Å, γ = 90°
Volume, *Z*	2535.5(3) Å^3, 8
Calculated density	2.441 g/cm^3
Absorption coefficient	6.168 mm^{-1}
F(000)	1736
Crystal size	0.14 × 0.14 × 0.08 mm
θ range for data collection	2.43 to 23.22°
Limiting indices	$-11 \le h \le 11$, $-16 \le k \le 16$, $-16 \le l \le 18$
Reflections collected/unique	6074/1807 [R(int) = 0.1488]
Completeness to θ = 23.22	99.9%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1807/0/155
Goodness-of-fit on F^2	0.940
Final R indices [$I > \sigma(I)$]	R_1 = 0.0440, wR_2 = 0.0884
R indices (all data)	R_1 = 0.0623, wR_2 = 0.0948
Largest diff. peak and hole	1.079 and –0.851 e. Å^{-3}

Table 2. Selected geometric parameters (Å,°).

I(1)–Cu(1)	2.5911(13)
I(1)–Cu(2)	2.6956(12)
I(1)–Cu(1)#1	2.7384(15)
I(2)–Cu(2)	2.4338(19)
Cu(1)–N(2)	2.050(8)
Cu(1)–N(1)	2.069(7)
Cu(1)–Cu(2)	2.5483(18)
Cu(1)–I(1)–Cu(2)	57.59(3)
Cu(1)–I(1)–Cu(1)#1	76.40(4)
Cu(2)–I(1)–Cu(1)#1	55.93(3)
N(2)–Cu(1)–N(1)	82.2(3)
N(2)–Cu(1)–Cu(2)	174.8(2)
N(1)–Cu(1)–Cu(2)	102.2(2)

Table 1 (continuation)

N(2)–Cu(1)–I(1)	111.64(19)
N(1)–Cu(1)–I(1)	135.9(2)
Cu(2)–Cu(1)–I(1)	63.26(3)
N(2)–Cu(1)–I(1)#1	120.6(2)
N(1)–Cu(1)–I(1)#1	105.0(2)
Cu(2)–Cu(1)–I(1)#1	61.19(3)
I(1)–Cu(1)–I(1)#1	102.72(4)
I(2)–Cu(2)–Cu(1)	139.68(4)
Cu(1)#1–Cu(2)–Cu(1)	80.64(8)
Cu(1)–Cu(2)–I(1)#1	62.89(5)
I(2)–Cu(2)–I(1)	129.44(3)
Cu(1)–Cu(2)–I(1)	59.14(4)
I(1)#1–Cu(2)–I(1)	101.13(6)

Symmetry transformations used to generate equivalent atoms: #1 –x, y, –z + 1/2.

Table 3. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for $Cu_3I_3phen_2$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
I(1)	1964(1)	7062(1)	2986(1)	42(1)
I(2)	0	9819(1)	2500	52(1)
Cu(1)	623(1)	6908(1)	1620(1)	53(1)
Cu(2)	0	8201(1)	2500	67(1)
N(1)	658(7)	7507(5)	514(4)	41(2)
N(2)	1222(7)	5823(5)	1000(4)	40(2)
C(1)	350(10)	8322(7)	274(6)	52(2)
C(2)	339(9)	8594(6)	–522(6)	46(2)
C(3)	637(9)	7990(7)	–1079(6)	50(3)
C(4)	978(9)	7118(6)	–866(5)	42(2)
C(5)	1332(10)	6454(7)	–1409(6)	55(3)
C(6)	1677(9)	5595(7)	–1159(6)	52(3)
C(7)	1670(8)	5369(6)	–334(5)	43(2)
C(8)	2015(9)	4525(7)	–33(7)	54(3)
C(9)	2012(9)	4354(6)	746(7)	54(3)
C(10)	1595(9)	5020(7)	1239(6)	48(2)
C(11)	967(8)	6891(6)	–50(5)	39(2)
C(12)	1290(8)	6011(6)	214(5)	36(2)

Data collection: *SMART* [5]. Cell refinement: *SMART.* Data reduction: *SAINT* [5]. Program(s) used to solve structure: *SHELXS-97* [6]. Program(s) used to refine structure: *SHELXL*-97 [7]. Molecular graphics: *SHELXP-97*. Software used to prepare material for publication: *SHELXTL* [8].

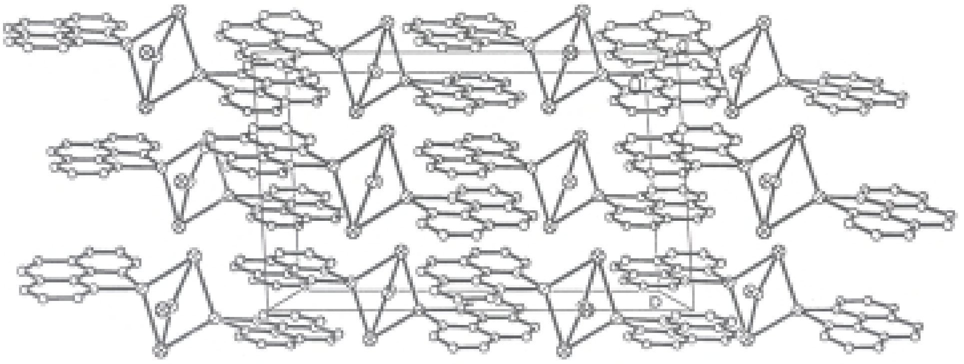

Figure 2. Packing diagram of $Cu_3I_3phen_2$.

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