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Crystal structure of iodobis(1,10-phenanthroline-κ^2N,N')-copper(II) iodo-(μ_2-iodo)copper(I) — octasulfur (2:1), $[CuI(C_{12}N_2H_8)_2]_2[Cu_2I_4] \cdot S_8$

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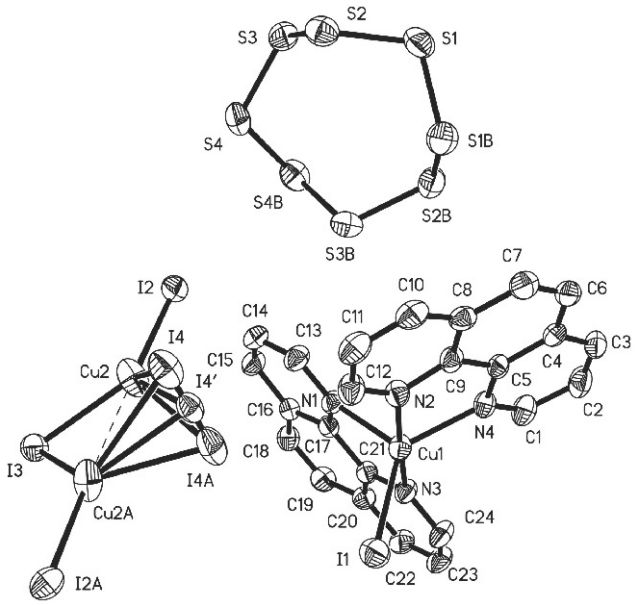

Abstract

$C_{24}H_{16}Cu_2I_3N_4S_4$, orthorhombic, *Pccn* (no. 56), a = 23.109(6) Å, b = 15.246(4) Å, c = 17.005(4) Å, V = 5991.2 Å^3, Z = 8, $R_{gt}(F)$ = 0.077, $wR_{ref}(F^2)$ = 0.232, T = 293 K.

Source of material

A mixture of $Cu(OAc)_2 \cdot H_2O$ (40 mg, 0.2 mmol), $NaS_2CN(C_6H_5)_2$ (45 mg, 0.2 mmol), phen (1,10-phenanthroline, 40 mg, 0.2 mmol) and $NaI \cdot 2H_2O$ (37 mg, 0.2 mmol) was stirred in dimethylformamide (20 mL) at 50 °C in air for about one day. The vapor of *i*-PrOH was diffused slowly into the resulting solution, and after about one month black prism-shaped crystals were obtained.

Experimental details

All non-hydrogen atoms were refined anisotropically. The H atoms were positioned geometrically and refined as riding atoms with d(C—H) = 0.93 Å, U_{iso}(H) = 1.2 U_{eq}(C). The highest peak (3.04 e Å^{-3}) and the deepest hole (–1.93 e Å^{-3}) in the difference Fourier map are located 0.04 Å and 0.60 Å from the atoms I3 and I1, respectively. The high residual values may be a result of the disorder at I4.

Discussion

Organonitrogen ligands, such as 1,10-phenanthroline (phen), 2,2′-bipyridine, 4,4′-bipyridine and their derivatives with suitable spacers have been extensively used in the construction of coordination complexes. They not only are versatile ligands for coordination bonding but can also form weak interactions, such as aromatic π–π stacking interactions, C–H···π interactions and hydrogen bonding which are important supramolecular forces enhancing the stability of the complexes in both solution and solid states [1-5].

The title crystal structure consists of $[Cu(II)I(phen)_2]^+$cations, dinuclear $(Cu(I)_2I_4)^{2-}$ anions and S_8 molecules. In the $[Cu(II)I(phen)_2]^+$ cations, the Cu1 atom is bivalent, which is found in a similar compound [6]. It is bonded to one I atom and four N atoms from two different phen molecules in a distorted trigonal bipyramid fashion with the distances d(Cu—I) = 2.691(2) Å and d(Cu—N) = 1.991(6)-2.138(6) Å. In the dinuclear $[Cu(I)_2I_4]^{2-}$ anion, the Cu2 atom is univalent, and the I4 atom is split into two sites, I4 and I4' with occupancies of 0.443 and 0.114. Cu2 atoms are coordinated by two μ_2 and one terminal I atom in triangle fashion with the Cu—I distances ranging from 2.503(2) to 2.571(2) Å. Two triangles are connected by common edge (I3, I4) to form the dinuclear structural anion with the distance d(Cu···Cu) = 2.700(3) Å showing the existence of weak interaction. The $[Cu(II)I(phen)_2]^+$ cations are joined by face-to-face π–π interactions between ring $R1$ (N1/C13-C17) and adjacent symmetry-related ring $R2$ (C16-C19), $R3$ (N4/C1-C5) and adjacent symmetry-related ring $R4$ (C4-C9) with dihedral angles of 1.58° and 0.94°, centroid-to-centroid distances of 3.554(5) Å and 3.625(5) Å, and plane-to-plane distances of 3.445 Å and 3.405 Å [7], respectively, to give rise to cation chains along (001).

Table 1. Data collection and handling.

Crystal:	black prism, size 0.12 × 0.22 × 0.46 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	48.13 cm^{-1}
Diffractometer, scan mode:	Rigaku Mercury CCD diffractometer, ω
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	34804, 5168
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4475
$N(param)_{refined}$:	347
Programs:	PLATON [7], SHELXS-97, SHELXL-97, SHELXTL [8]

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Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1A)	8*e*	0.3925	0.3902	0.3168	0.078
H(2A)	8*e*	0.3755	0.3143	0.4337	0.087
H(3A)	8*e*	0.4461	0.3083	0.5273	0.078
H(6A)	8*e*	0.5464	0.3528	0.5732	0.076
H(7A)	8*e*	0.6289	0.4285	0.5496	0.079
H(10A)	8*e*	0.6874	0.5316	0.4578	0.076
H(11A)	8*e*	0.6949	0.5987	0.3379	0.085
H(12A)	8*e*	0.6159	0.6017	0.2547	0.080

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(13A)	8*e*	0.6109	0.4341	0.1732	0.073
H(14A)	8*e*	0.6337	0.3594	0.0573	0.083
H(15A)	8*e*	0.5626	0.3301	–0.0328	0.073
H(18A)	8*e*	0.4559	0.3498	–0.0736	0.068
H(19A)	8*e*	0.3655	0.3937	–0.0421	0.072
H(22A)	8*e*	0.2959	0.4649	0.0568	0.073
H(23A)	8*e*	0.2846	0.5360	0.1738	0.078
H(24A)	8*e*	0.3630	0.5575	0.2551	0.075

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	8*e*		0.49383(4)	0.51808(8)	0.25086(5)	0.0396(6)	0.0704(7)	0.0415(6)	–0.0022(4)	–0.0027(3)	0.0009(4)
Cu(2)	8*e*		0.74863(6)	0.6615(1)	0.12356(8)	0.096(1)	0.081(1)	0.0615(9)	–0.0315(7)	–0.0168(6)	0.0118(6)
I(1)	8*e*		0.48363(3)	0.69386(5)	0.24684(4)	0.0847(6)	0.0676(5)	0.0731(5)	0.0033(3)	0.0018(3)	0.0040(3)
I(2)	8*e*		0.74656(2)	0.49749(4)	0.12956(4)	0.0557(5)	0.0745(5)	0.0625(5)	0.0047(2)	0.0013(2)	0.0172(3)
I(3)	4*c*		¾	¾	–0.00510(5)	0.0664(6)	0.0625(5)	0.0456(5)	0.0068(3)	0	0
I(4)	8*e*	0.443(2)	0.7881(1)	0.7321(1)	0.24689(8)	0.118(2)	0.067(1)	0.0488(9)	–0.013(1)	–0.0074(8)	–0.0051(6)
I(4')	4*c*	0.114(4)	¾	¾	0.2488(4)	0.076(6)	0.048(4)	0.036(4)	–0.004(4)	0	0
S(1)	8*e*		0.7820(1)	0.2030(2)	0.4652(2)	0.100(2)	0.088(2)	0.056(1)	0.016(1)	–0.004(1)	0.013(1)
S(2)	8*e*		0.8436(1)	0.2391(2)	0.3851(2)	0.067(2)	0.078(2)	0.076(2)	–0.002(1)	–0.016(1)	0.002(1)
S(3)	8*e*		0.8259(1)	0.1698(2)	0.2848(2)	0.078(2)	0.062(1)	0.076(2)	0.012(1)	0.012(1)	–0.005(1)
S(4)	8*e*		0.7943(1)	0.2569(2)	0.2047(2)	0.092(2)	0.074(2)	0.053(1)	–0.008(1)	0.013(1)	0.006(1)
N(1)	8*e*		0.5286(2)	0.4469(4)	0.1534(4)	0.036(3)	0.064(4)	0.045(3)	0.004(3)	0.000(3)	0.003(3)
N(2)	8*e*		0.5661(3)	0.5222(4)	0.3144(4)	0.044(3)	0.061(4)	0.050(4)	–0.007(3)	–0.002(3)	0.003(3)
N(3)	8*e*		0.4212(3)	0.5020(4)	0.1895(4)	0.039(3)	0.070(4)	0.045(3)	0.006(3)	0.002(3)	–0.001(3)
N(4)	8*e*		0.4691(3)	0.4331(4)	0.3434(4)	0.042(3)	0.056(3)	0.048(4)	–0.008(3)	0.004(3)	–0.005(3)
C(1)	8*e*		0.4208(4)	0.3898(6)	0.3556(6)	0.050(5)	0.082(6)	0.064(5)	–0.011(4)	0.007(4)	–0.011(4)
C(2)	8*e*		0.4106(4)	0.3428(6)	0.4257(6)	0.068(6)	0.070(5)	0.079(7)	–0.013(4)	0.030(5)	–0.002(5)
C(3)	8*e*		0.4523(4)	0.3396(6)	0.4811(6)	0.074(6)	0.061(5)	0.061(5)	0.004(4)	0.026(5)	0.009(4)
C(4)	8*e*		0.5045(4)	0.3829(5)	0.4694(5)	0.060(4)	0.047(4)	0.046(4)	0.014(3)	0.011(3)	–0.008(3)
C(5)	8*e*		0.5108(3)	0.4289(5)	0.3989(4)	0.054(4)	0.046(4)	0.036(4)	0.005(3)	0.009(3)	–0.007(3)
C(6)	8*e*		0.5505(4)	0.3835(6)	0.5263(5)	0.077(6)	0.072(5)	0.042(4)	0.026(5)	0.005(4)	–0.002(4)
C(7)	8*e*		0.5997(4)	0.4286(6)	0.5120(5)	0.070(5)	0.088(6)	0.038(4)	0.022(5)	–0.010(4)	–0.012(4)
C(8)	8*e*		0.6082(3)	0.4767(5)	0.4404(5)	0.052(4)	0.058(4)	0.045(4)	0.013(3)	–0.004(3)	–0.009(3)
C(9)	8*e*		0.5632(4)	0.4763(5)	0.3837(4)	0.053(4)	0.056(4)	0.040(4)	0.004(3)	0.005(3)	–0.007(3)
C(10)	8*e*		0.6573(3)	0.5271(6)	0.4218(6)	0.040(4)	0.079(6)	0.070(6)	0.003(4)	–0.013(4)	–0.012(5)
C(11)	8*e*		0.6611(4)	0.5694(7)	0.3517(6)	0.043(4)	0.085(6)	0.084(7)	–0.006(4)	–0.002(4)	–0.017(5)
C(12)	8*e*		0.6139(4)	0.5685(7)	0.3005(6)	0.053(5)	0.085(6)	0.063(5)	–0.009(4)	0.003(4)	0.005(4)
C(13)	8*e*		0.5817(4)	0.4219(6)	0.1373(5)	0.045(4)	0.085(6)	0.053(5)	0.010(4)	–0.001(3)	–0.002(4)
C(14)	8*e*		0.5958(4)	0.3770(6)	0.0667(6)	0.049(4)	0.084(6)	0.074(6)	0.020(4)	0.013(4)	0.013(5)
C(15)	8*e*		0.5540(4)	0.3599(5)	0.0134(6)	0.059(5)	0.058(5)	0.065(5)	0.007(4)	0.015(4)	–0.005(4)
C(16)	8*e*		0.4968(3)	0.3883(5)	0.0292(5)	0.050(4)	0.049(4)	0.049(4)	0.001(3)	0.006(3)	0.008(3)
C(17)	8*e*		0.4869(3)	0.4306(5)	0.1010(4)	0.044(4)	0.048(4)	0.041(4)	0.000(3)	0.001(3)	0.007(3)
C(18)	8*e*		0.4492(4)	0.3762(6)	–0.0251(5)	0.059(5)	0.065(5)	0.047(4)	–0.006(4)	0.000(4)	–0.003(4)
C(19)	8*e*		0.3955(4)	0.4026(6)	–0.0064(5)	0.058(5)	0.067(5)	0.054(5)	–0.002(4)	–0.013(4)	–0.001(4)
C(20)	8*e*		0.3834(3)	0.4441(5)	0.0671(5)	0.048(4)	0.055(4)	0.053(4)	0.000(3)	–0.004(3)	0.002(3)
C(21)	8*e*		0.4289(3)	0.4577(5)	0.1192(4)	0.037(3)	0.051(4)	0.043(4)	–0.003(3)	–0.002(3)	0.003(3)
C(22)	8*e*		0.3275(3)	0.4741(6)	0.0896(5)	0.037(4)	0.080(5)	0.064(5)	0.005(4)	–0.008(4)	0.004(4)
C(23)	8*e*		0.3209(3)	0.5158(7)	0.1587(6)	0.033(4)	0.093(6)	0.070(6)	0.009(4)	0.001(4)	–0.004(5)
C(24)	8*e*		0.3686(3)	0.5287(7)	0.2075(5)	0.042(4)	0.092(6)	0.053(5)	0.009(4)	0.004(3)	–0.014(4)

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References

1. Janiak, C.: A critical account on π–π stacking in metal complexes with aromatic nitrogen-containing ligands. J. Chem. Soc., Dalton Trans. (2000) 3885-3896.
2. Ye, B.-H.; Tong, M.-L.; Chen, X.-M.: Metal-organic molecular architectures with 2,2′-bipyridyl-like and carboxylate ligands. Coord. Chem. Rev. **249** (2005) 545-565.
3. Fan, L.-Q.; Wu, J.-H.; Lin, J.-M.; Huang, Y.-F.: Synthesis and crystal structure of a new Cu(II) dithiocarbamate complex CuI(prdtc)(phen). Chin. J. Struct. Chem. **28** (2009) 580-584.
4. Fan, L.-Q.; Wu, J.-H.; Lin J.-M.; Huang, Y.-F.: Synthesis, crystal structure and characterization of a new coordination polymers from the self-assembly of $CoCl_2$ salt and flexibel ligand 1,3-bis(4-pyridyl)propane. Chin. J. Struct. Chem. **29** (2010) 1484-1498.
5. Fan, L.-Q.; Wu, J.-H.; Huang, Y.-F.; Lin, J.-M.: Synthesis, strucuture and characterization of a new trinuclear magnetic semiconductor $PbI_4[Cu(Me_2dtc)(bipy)]_2$. Solid State Sci. **12** (2010) 558-562.
6. Latham, K.; Mensforth, E. J.; Rix, C. J.; White, J. M.: Synthesis of supramolecular metallo-amin-oxy acid systems *via* crystal disassembly/reassembly. CrystEngComm **11** (2009) 1343-1351.
7. Spek, A. L.: Single-crystal structure validation with the program PLATON. J. Appl. Crystallogr. **36** (2003) 7-13.
8. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.