Crystal structure of bis(1,10-phenanthroline)copper(I) dichlorocuprate(I), $[\text{Cu}(\text{C}_{12}\text{H}_8\text{N}_2)_2][\text{CuCl}_2]$

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Abstract

$\text{C}_{24}\text{H}_{16}\text{Cl}_2\text{Cu}_2\text{N}_4$, monoclinic, $C12/c1$ (no. 15), $a = 19.709(3)$ Å, $b = 14.830(3)$ Å, $c = 15.208(3)$ Å, $\beta = 103.096(2)^\circ$, $V = 4329.5$ Å³, $Z = 8$, $R_{\text{gt}}(F) = 0.027$, $wR_{\text{ref}}(F^2) = 0.089$, $T = 273$ K.

Source of material

The hydrothermal reaction of copper(II) dichloride (0.5 mmol) 1,10-phenanthroline (0.5 mmol) and *N*-benzenesulfonyl-L-glutamic acid (1 mmol) in an aqueous solution (12 mL) was carried out in a Teflon-lined stainless steel reactor. The mixture was heated at 165 °C for three days, and then slowly cooled down to room temperature. A dark green solution was formed. Dark green prismatic crystals of the title complex were grown from the solution by slow evaporation for about six days and isolated (yield 48 %).

Discussion

Crystal structures of bis-chelated transition-metal 1,10-phenanthroline (phen) complexes containing the $\text{Cu}(\text{phen})_2^+$ fragment have been extensively studied during last two decades [1–11]. However, complexes containing $\text{Cu}(\text{phen})_2^+$ and $\text{Cu}(\text{Cl}_2)^-$ subunits simultaneously have not been reported. During our investigation of the self-assemblies of metal ion and mixed ligands (1,10-phenanthroline and *N*-benzenesulfonyl-L-glutamic acid), we did not obtain the expected compound, but, instead, dark green prismatic crystals of bis(1,10-phenanthroline)copper(I) dichlorocuprate(I), grew from the above solution on slow evaporation. The new complex has been characterized by single-crystal diffraction analysis. The crystal structure of the title compound is composed of discrete $[\text{Cu}(\text{phen})_2]^+$ cations and $[\text{CuCl}_2]^-$ anions. The coordination environments of the two copper ions are different. The central Cu1 ion is four-coordinated by the nitrogen do-

nors from two bidentate phen ligands, forming two five-membered chelated rings. The two rings are not in a good planarity with a dihedral angle of 48.1°. The four Cu1—N bond lengths are in the range of 2.057(2) Å – 2.092(2) Å with an average value of 2.0745 Å, which are significantly longer than the averaged Cu(I)—N distances of $\text{Cu}(\text{phen})_2^+$ subunits in other compounds: $[\text{Cu}(\text{phen})_2][\text{ClO}_4]$ (2.049 Å) [2], $[\text{Cu}(\text{phen})_2]\text{I}$ (2.044 Å) [6], $[\text{Cu}(\text{phen})_2][\text{CuBr}_2]$ (2.039 Å) [2]. The central Cu2 ion is two-coordinated by two chlorine atoms with Cu2—Cl bond lengths are 2.0882(9) Å and 2.0958(9) Å, respectively, the angle of Cl—Cu—Cl is 178.75(3)°, which are close to those in the complex $[\text{Cu}(\text{II})(\text{phen})_2\text{Cl}][\text{Cu}(\text{I})\text{Cl}_2]$ [9]. In the arrangement of the unit cell, there exist orderly aromatic ring stacking interactions between phen ligands among the molecules of the complex. Six phen atoms (C1, C2, C3, C4, C12, N1) form weak π - π stacking with other phen atoms (C7', C8', C9', C10', C11', N2') in a neighboring molecule with centroid distance of 3.785 Å and dihedral angle of 3.7°. Such stacking expands along the *c* axis to form a one-dimensional chain structure. The *N*-benzenesulfonyl-L-glutamic acid obviously acts as reducing agent in the reduction of Cu(II)/Cu(I). The mechanistic details of the redox process are not completely clear. A similar phenomenon has been observed for the formation of $\text{Cu}(\text{II})(\text{phen})_2\text{Cl} \cdot \text{Cu}(\text{I})\text{Cl}_2$ [10].

Table 1. Data collection and handling.

Crystal:	dark green prism, size 0.18 × 0.34 × 0.35 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	22.32 cm ⁻¹
Diffractometer, scan mode:	Bruker SMART CCD, ϕ/ω
$2\theta_{\text{max}}$:	55°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	14321, 4943
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3875
$N(\text{param})_{\text{refined}}$:	353
Programs:	SHELXS-97 [12], SHELXL-97 [13]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(1)	8f	0.353(1)	0.344(2)	0.002(2)	0.067(6)
H(2)	8f	0.284(1)	0.472(2)	−0.034(2)	0.090(8)
H(3)	8f	0.330(1)	0.610(2)	0.010(2)	0.063(6)
H(5)	8f	0.437(1)	0.701(1)	0.087(2)	0.061(6)
H(6)	8f	0.553(2)	0.704(2)	0.165(2)	0.077(8)
H(8)	8f	0.659(1)	0.616(2)	0.249(2)	0.082(8)
H(9)	8f	0.712(1)	0.480(2)	0.285(2)	0.080(7)
H(10)	8f	0.650(1)	0.350(2)	0.237(1)	0.055(6)
H(13)	8f	0.355(1)	0.243(2)	0.158(1)	0.056(6)
H(14)	8f	0.296(1)	0.116(2)	0.172(2)	0.068(7)

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Table 2. Continued

Atom	Site	x	y	z	U _{iso}
H(15)	8f	0.347(1)	-0.023(2)	0.166(2)	0.069(7)
H(17)	8f	0.449(1)	-0.110(2)	0.134(2)	0.064(6)
H(18)	8f	0.561(1)	-0.105(2)	0.113(2)	0.063(6)

Table 2. Continued

Atom	Site	x	y	z	U _{iso}
H(20)	8f	0.663(1)	-0.019(2)	0.083(1)	0.063(6)
H(21)	8f	0.714(1)	0.120(2)	0.073(2)	0.078(7)
H(22)	8f	0.649(1)	0.249(2)	0.078(1)	0.056(6)

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Cu(1)	8f	0.50167(1)	0.29671(2)	0.12114(2)	0.0575(2)	0.0293(1)	0.0803(2)	-0.00075(9)	0.0111(1)	-0.0008(1)
Cu(2)	8f	0.79877(1)	0.29842(2)	0.25853(2)	0.0502(2)	0.0433(2)	0.0942(2)	0.0005(1)	0.0137(1)	0.0072(1)
Cl(1)	8f	0.79085(4)	0.30201(4)	0.39311(5)	0.0757(4)	0.0589(4)	0.0914(4)	-0.0088(3)	0.0122(3)	0.0149(3)
Cl(2)	8f	0.80467(4)	0.29321(4)	0.12275(5)	0.0797(4)	0.0638(4)	0.0994(5)	-0.0123(3)	0.0294(3)	-0.0047(3)
N(1)	8f	0.43502(8)	0.4020(1)	0.0667(1)	0.0477(8)	0.0417(8)	0.0523(8)	-0.0031(6)	0.0044(6)	-0.0023(7)
N(2)	8f	0.56378(7)	0.40442(9)	0.1740(1)	0.0445(7)	0.0334(7)	0.0528(8)	0.0007(6)	0.0078(6)	0.0032(6)
N(3)	8f	0.44047(8)	0.18961(9)	0.1409(1)	0.0458(8)	0.0352(8)	0.0563(9)	0.0006(6)	0.0089(6)	-0.0055(6)
N(4)	8f	0.56660(8)	0.19073(9)	0.1013(1)	0.0474(8)	0.0347(8)	0.0600(9)	0.0008(6)	0.0107(7)	0.0036(6)
C(1)	8f	0.3691(1)	0.4010(2)	0.0194(2)	0.055(1)	0.059(1)	0.063(1)	-0.011(1)	0.0012(9)	-0.010(1)
C(2)	8f	0.3290(1)	0.4784(2)	-0.0024(2)	0.043(1)	0.084(2)	0.060(1)	0.003(1)	-0.0018(9)	0.002(1)
C(3)	8f	0.3575(1)	0.5606(2)	0.0222(1)	0.049(1)	0.062(1)	0.058(1)	0.012(1)	0.0087(8)	0.011(1)
C(4)	8f	0.42681(9)	0.5658(1)	0.0720(1)	0.0455(9)	0.046(1)	0.049(1)	0.0076(8)	0.0129(7)	0.0068(8)
C(5)	8f	0.4615(1)	0.6487(1)	0.1009(2)	0.062(1)	0.036(1)	0.077(1)	0.0109(9)	0.016(1)	0.0067(9)
C(6)	8f	0.5281(1)	0.6498(1)	0.1498(2)	0.063(1)	0.032(1)	0.085(1)	-0.0030(9)	0.014(1)	-0.0008(9)
C(7)	8f	0.56560(9)	0.5678(1)	0.1758(1)	0.0484(9)	0.0364(9)	0.056(1)	-0.0044(7)	0.0123(8)	-0.0014(8)
C(8)	8f	0.6343(1)	0.5649(2)	0.2284(2)	0.053(1)	0.047(1)	0.071(1)	-0.0118(9)	0.0056(9)	-0.007(1)
C(9)	8f	0.6660(1)	0.4838(2)	0.2501(1)	0.044(1)	0.061(1)	0.064(1)	-0.0027(9)	-0.0011(9)	0.002(1)
C(10)	8f	0.6292(1)	0.4058(1)	0.2224(1)	0.048(1)	0.045(1)	0.062(1)	0.0066(8)	0.0040(8)	0.0108(9)
C(11)	8f	0.53285(8)	0.4852(1)	0.1494(1)	0.0416(8)	0.0335(8)	0.0429(8)	0.0004(7)	0.0108(7)	0.0028(6)
C(12)	8f	0.46246(8)	0.4839(1)	0.0941(1)	0.0418(8)	0.0362(9)	0.0419(9)	0.0007(7)	0.0108(7)	0.0006(7)
C(13)	8f	0.3758(1)	0.1894(1)	0.1536(2)	0.050(1)	0.046(1)	0.069(1)	0.0016(9)	0.0128(9)	-0.0121(9)
C(14)	8f	0.3391(1)	0.1111(2)	0.1615(2)	0.045(1)	0.062(1)	0.067(1)	-0.0056(9)	0.0139(9)	-0.008(1)
C(15)	8f	0.3693(1)	0.0298(2)	0.1559(1)	0.051(1)	0.051(1)	0.062(1)	-0.0133(9)	0.0076(9)	-0.0022(9)
C(16)	8f	0.43715(9)	0.0261(1)	0.1399(1)	0.0490(9)	0.0374(9)	0.0449(9)	-0.0056(7)	0.0018(7)	-0.0020(7)
C(17)	8f	0.4729(1)	-0.0560(1)	0.1315(1)	0.061(1)	0.034(1)	0.062(1)	-0.0058(9)	0.0030(9)	0.0011(8)
C(18)	8f	0.5380(1)	-0.0556(1)	0.1162(1)	0.060(1)	0.0322(9)	0.062(1)	0.0064(8)	0.0033(9)	-0.0014(8)
C(19)	8f	0.57302(9)	0.0273(1)	0.1071(1)	0.0494(9)	0.0393(9)	0.0426(9)	0.0064(8)	0.0019(7)	0.0013(7)
C(20)	8f	0.6407(1)	0.0319(2)	0.0911(1)	0.056(1)	0.051(1)	0.059(1)	0.0147(9)	0.0116(9)	0.0043(9)
C(21)	8f	0.6696(1)	0.1136(2)	0.0830(2)	0.049(1)	0.063(1)	0.072(1)	0.009(1)	0.0203(9)	0.010(1)
C(22)	8f	0.6310(1)	0.1916(1)	0.0874(2)	0.053(1)	0.047(1)	0.072(1)	-0.0015(9)	0.0175(9)	0.0120(9)
C(23)	8f	0.53859(9)	0.1090(1)	0.1133(1)	0.0439(9)	0.0336(8)	0.0405(8)	0.0010(7)	0.0039(6)	-0.0002(6)
C(24)	8f	0.47006(8)	0.1085(1)	0.1320(1)	0.0425(8)	0.0343(9)	0.0385(8)	-0.0004(7)	0.0011(6)	-0.0025(6)

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