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catena-Poly[[bis(μ-1,10-phenanthrolin-2-olato-κ^3*N*,*N*′:*O*)dicopper(I,II)(*Cu*—*Cu*)]-μ-chloro-copper(I)-μ-chloro]

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In the crystal structure of the title compound, $[Cu_3(C_{12}H_7N_2O)_2Cl_2]_n$, the mixed-valence Cu^{I}/Cu^{II} cation and the cuprate(I) anion both lie on centres of inversion. The O atom of one half of the planar *N,N*′-chelated dinuclear copper cation binds to the Cu atom of the other half; the geometry around the metal atom is square-planar, owing to the symmetry-related metal atom at a distance of 2.3945 (5) Å. The dinuclear cations are bridged through the anions to form an infinite linear chain.

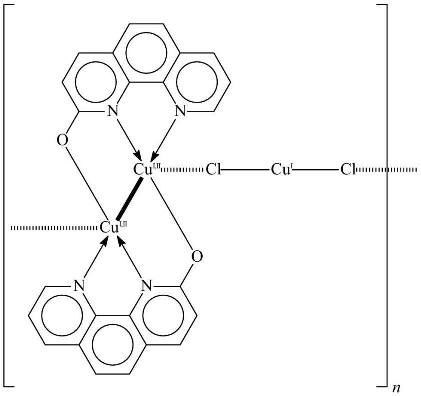
Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.004 Å
R factor = 0.032
wR factor = 0.091
Data-to-parameter ratio = 15.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Quantum chemical computations on the metal derivatives of 2-hydroxy-1,10-phenanthroline, which exists in the solid state in the keto form, suggest that their photoluminescent properties arise from the organic ligand, such properties being governed by the manner of binding of the deprotonated heterocycle (Zheng *et al.*, 2003). Among the metal complexes that have been crystallographically authenticated are the copper compounds bis[(1,10-phenanthrolin-2-olato)copper], which has the metal atoms in a +1 oxidation state, and $[(C_{12}H_7N_2O)_2Cu]_2(C_8H_4O_4)$, which has them in +1 and +2 oxidation states. Bis[(1,10-phenanthrolin-2-olato)copper] exists in three forms (Zhang, Tong & Chen, 2002; Zhang, Tong, Gong *et al.*, 2002); the Cu^{I}—Cu^{I} distance [2.679 (3) Å in the α form, 2.661 (2) Å in the β form and 2.673 (2) Å in the γ form] is decreased [2.497 (1) Å] in the monohydrate, which is a black Cu^{I}—Cu^{I} compound that was obtained hydrothermally from copper(II) nitrate, 1,10-phenanthroline and 4-aminobenzoic acid in sodium hydroxide solution (Lu *et al.*, 2004). The Cu—Cu distance [2.3945 (5) Å] in the present mixed-valence cation, which has a dichlorocuprate(I) counter-anion (Fig. 1), is significantly shorter, and is even shorter than the 2.56 Å separation in metallic copper (Sidorenko *et al.*, 2001).



(I)

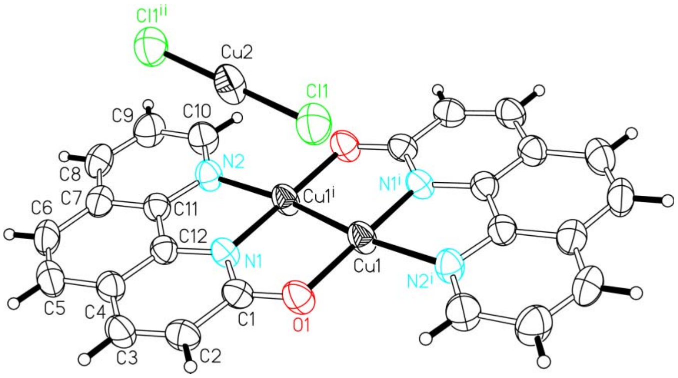


Figure 1
ORTEPII (Johnson, 1976) plot of (I). Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as spheres of arbitrary radii. [Symmetry code: (i) $-x, 1-y, 1-z$; (ii) $1-x, 1-y, 1-z$].

In the centrosymmetric cation, because the two Cu atoms are crystallographically equivalent, assigning a +1 oxidation state to one and a +2 oxidation state to the other is not possible. The cation should be considered as being disordered, with equal occupancies of both species. In fact, the valence is more probably intermediate, with the extra electron being shared between the metal atoms; the intermediate valence is indicated by a $Cu^{I,II}$ label in the scheme.

In the literature on copper(I) and copper(II) compounds, distances shorter than this have been reported occasionally, *e.g.* 2.369 (1) Å in tris(trimethylsilyl)silyldicopper bromolithium tetrahydrofuran trisolvate (Heine *et al.*, 1993), 2.391 (3) Å in lithium di-2,6-mesitylphenyldiiododicuprate tetrahydrofuran trisolvate (Hwang & Power, 1999), 2.426 (5) Å in the double cubane-type aqua ion $[(H_2O)_9Mo_3S_4CuCuS_4Mo_3(H_2O)_9]^{8+}$ (Shibahara *et al.*, 1988), 2.449 (1) Å in [2,7-bis(dibenzylamino)methyl)-1,8-naphthyridine](triphenylmethylcarboxylato)(trifluoromethanesulfonato)dicopper trifluoromethanesulfonate (He & Lippard, 2000) and 2.4712 (2) Å in dichlorotetrakis(di-2-pyridylamido)tricopper (Pyrka *et al.*, 1991). The distance is shorter than that [2.497 (1) Å] found in $[(C_{12}H_7N_2O)_2Cu^I]_2\cdot H_2O$; the overall conformation of the cation is similar to that of this Cu^I compound; however, this compound is stacked such that the Cu^I atom of one molecule interacts weakly with that of an adjacent molecule at 3.6676 (3) Å (Lu *et al.*, 2004).

The $Cu^{I,II}$ atom of the cation interacts with the Cl atom of the linear dichlorocuprate(II) anion, the long interaction giving rise to the formation of a chain that runs along the *a* axis of the triclinic cell (Fig. 2). The anion also lies on a special position of $\overline{1}$ site symmetry. Adjacent chains are linked by a weak C—H$\cdots$Cl [C8$\cdots$Cl1^{iii} = 3.629 (3) Å; symmetry code: (iii) $x, y, z-1$] interaction into a layer. The Cambridge Structural Database (Version 5.26; Allen, 2002) lists 48 examples of discrete Cu^ICl_2 anions; most of the these adopt a linear shape. Bis(tetramethylenediamine)copper(I) (Engelhardt *et al.*, 1984; Garbauskas *et al.*, 1986), bis(2,2′-bipyridyl)copper(I) (Skelton *et al.*, 1991), bis(2,4,6-trimethylpyridyl)copper(I) (Healy *et al.*, 1989) and tetrakis(trimethylphosphine)copper(I) (Chi *et al.*, 1992; Margraf *et al.*, 2004) dichlorocuprates are some of the examples that also feature copper in the cation. The database does not, however, list any example of a copper(II) dichlorocuprate(I) or a mixed-valence copper(I)/copper(II) dichlorocuprate(I). The deep blue colour of the title compound is different from the colour of other mixed-valence copper compounds, and may be a consequence of the influence of the anion.

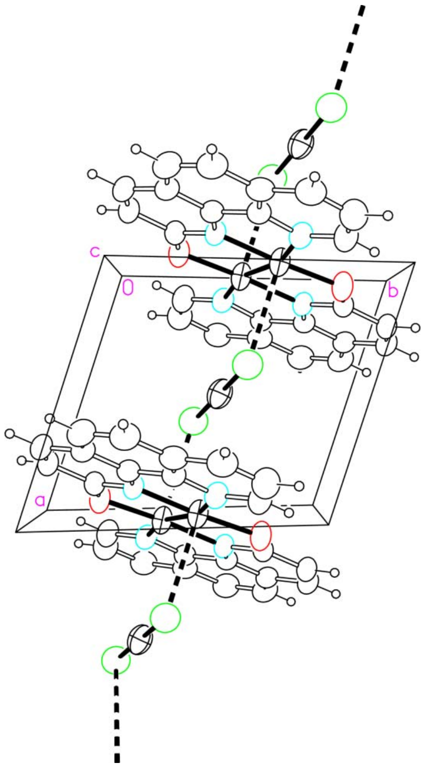


Figure 2
ORTEPII (Johnson, 1976) plot of the chlorine-bridged chain structure in (I).

Experimental

Copper(II) chloride dihydrate (0.17 g, 1 mmol), 1,10-phenanthroline hydrate (0.20 g, 1 mmol) and water (10 ml) were placed in a 23 ml Teflon-lined stainless steel Parr bomb. No sodium hydroxide was used in the synthesis. The bomb was then heated at 433 K for 3 d. After the bomb had cooled slowly to room temperature at a rate of 5 K h^{-1}, deep-blue, almost black, crystals were isolated from the solution in about 50% yield. Under diffuse yellow light, the crystals are light green. Only a few crystals of the compound were obtained in this reaction.

Crystal data

$[Cu_3(C_{12}H_7N_2O)_2Cl_2]$
$M_r = 651.91$
Triclinic, $P\overline{1}$
$a = 7.0588$ (6) Å
$b = 8.3638$ (6) Å
$c = 10.5690$ (8) Å
$\alpha = 112.301$ (1)°
$\beta = 94.096$ (1)°
$\gamma = 104.930$ (1)°
$V = 547.73$ (7) Å^3
$Z = 1$
$D_x = 1.976$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2232 reflections
$\theta = 2.7$–28.1°
$\mu = 3.16$ mm^{-1}
$T = 295$ (2) K
Block, dark blue
0.28 × 0.26 × 0.19 mm

Data collection

Bruker SMART APEX area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
$T_{\min} = 0.374$, $T_{\max} = 0.585$
4698 measured reflections
2407 independent reflections
2155 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.017$
$\theta_{\max} = 27.5°$
$h = -9 \rightarrow 9$
$k = -10 \rightarrow 10$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.091$
$S = 1.01$
2407 reflections
160 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0614P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.40$ e Å^{-3}
$\Delta\rho_{\min} = -0.30$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—Cl1	2.8947 (8)	Cu1—N2$^{\text{i}}$	2.048 (2)
Cu1—O1	1.894 (2)	Cu2—Cl1	2.1009 (7)
Cu1—N1$^{\text{i}}$	1.908 (2)		
Cl1—Cu1—O1	90.51 (6)	O1—Cu1—N2$^{\text{i}}$	99.69 (7)
Cl1—Cu1—N1$^{\text{i}}$	93.70 (6)	N1$^{\text{i}}$—Cu1—N2$^{\text{i}}$	83.80 (8)
Cl1—Cu1—N2$^{\text{i}}$	100.65 (6)	Cl1—Cu2—Cl1$^{\text{ii}}$	180
O1—Cu1—N1$^{\text{i}}$	173.96 (7)		

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $1-x, 1-y, 1-z$.

H atoms were placed in calculated positions (C—H = 0.93 Å) and included in the refinement in the riding-model approximation, with U_{iso}(H) values set at 1.2 times U_{eq}(C).

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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