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Two polymorphs of bis(1,10-phenanthroline-κ^2N,N')copper(I) iodide

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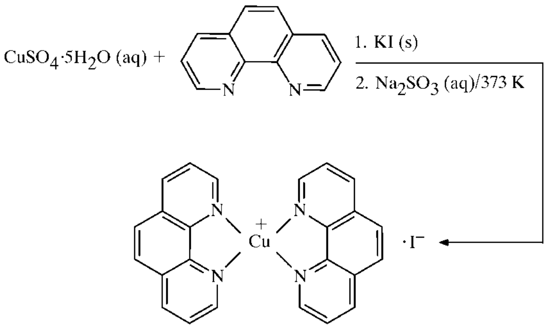
The title complex, $[Cu(C_{12}H_8N_2)_2]I$, (I), has been crystallized in two polymorphic forms, both containing four-coordinate copper. Both forms are orthorhombic, with form (I*a*) crystallizing in the primitive space group *Pban* and form (I*b*) in the *c*-centred space group *Ccca*. In (I*a*), the complex cation and the I^- anion both have 222 crystallographic symmetry, and in (I*b*), the complex cation has approximate 222 symmetry, with the I^- counter-ion distributed over three special positions.

Comment

Bis(1,10-phenanthroline-κ^2N,N')copper(I) iodide, (I), and other halo-forms have been prepared and employed in the preparation of a range of halo(amine)copper organophosphonate materials. The latter are the subject of a forthcoming publication and will not be discussed in detail here. However, the phosphonates themselves produced unexpected supramolecular structures, in which it was believed that compound (I) and the organophosphonic acid were unchanged and had merely produced an associated structure through favourable opportunities for π–π and hydrogen-bonding interactions. Thus, the structural observations made with regard to the resulting phosphonates prompted us to investigate the structure of (I).

There appear to be conflicting views concerning the structure of (I). These relate to the nature of the coordination of the I^- ion and the question of whether it is bound, producing a five-coordinate Cu^I centre, or whether the Cu atom is four-coordinate, with the I^- ion forming part of an ionic matrix. The majority of Cu^I complexes are four-coordinate and, indeed, (I) was originally thought to be ionic (Jardine *et al.*, 1970), because it gave conducting solutions in nitrobenzene (equivalent conductance of 30.8 mho in 10^{-3} *M* solution). However, there are exceptions to this four-coordinate rule, for example, the corresponding five-coordinate dafone complex, (II) (Kulkarni *et al.*, 2002; see Fig. 1).

Single-crystal structural analysis confirms that (I) is an ionic compound and that it exists in at least two polymorphic forms, (I*a*) and (I*b*). Both polymorphs are orthorhombic, with form (I*a*) crystallizing in space group *Pban* and form (I*b*) in *Ccca*. In polymorph (I*a*), the copper complex and the I^- ion both have crystallographic 222 symmetry, with the Cu and I atoms occupying 222 sites (Fig. 2*a*). In polymorph (I*b*), the copper complex has approximate 222 symmetry, with the I^- ion distributed over a twofold site and two 222 sites (Fig. 2*b*). There are significant differences in the geometry about the Cu atom in the two forms. Whilst each Cu atom is four-coordinate, the dihedral angle between the two planes made up of the Cu and the two phenanthroline N atoms is 43.30 (4)° in form (I*a*) and 61.80 (4)° in form (I*b*). Thus, the geometry of (I*a*) is midway between square-planar and tetrahedral, and the geometry of (I*b*) is closer to tetrahedral.



(I)

The packing diagrams for the two polymorphs are shown in Figs. 3(*a*) and 3(*b*). Both crystals contain ribbons of $[Cu(C_{12}H_8N_2)_2]^+$ cations, together with unassociated I^- counter-ions, which are positioned in the voids. The copper complex cations are associated with their identical neighbours through stacking of the phenanthroline aromatic rings in an 'offset' manner. This occurs to maximize attractive electrostatic interactions between the positively charged σ frameworks and the negatively charged π electrons, and has been observed for a number of similar systems (Hunter, 1994; Nord, 1985). The minimum distance between overlapping phenanthroline rings is approximately 3.550 Å in form (I*a*) and in the range 3.414–3.707 Å in form (I*b*); the angle between phenanthroline ring planes in the latter is 4.40 (4)°.

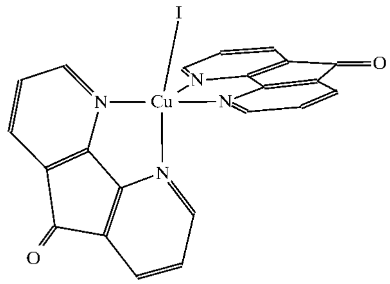


Figure 1
The trigonal–bipyramidal coordination of bis(dafone)copper(I) iodide, (II) (Kulkarni *et al.*, 2002).

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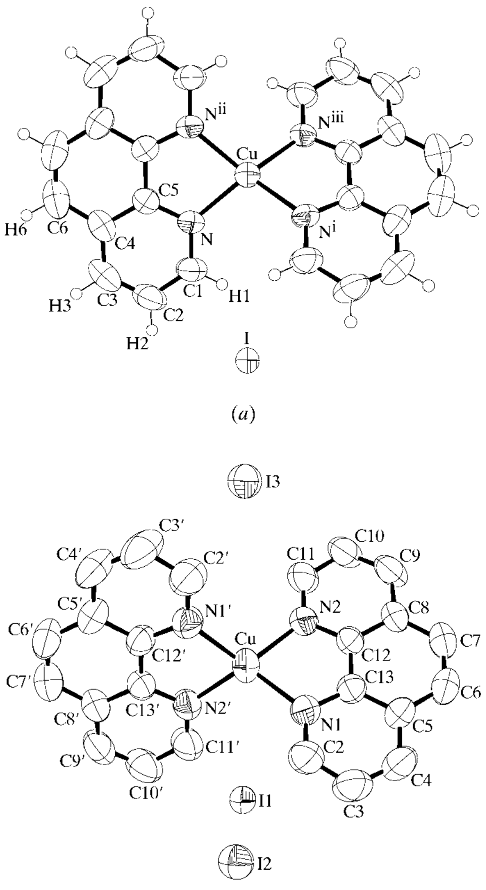
The bonding about the Cu atom in both (I*a*) and (I*b*) is typical of this class of compounds (Jardine *et al.* 1970). Phenanthroline ligands generally form four-coordinate complexes with Cu^I ions, due to steric interactions between the α-H atoms of the amine ligand (Simmons *et al.*, 1987). Therefore, if a $[Cu(C_{12}H_8N_2)_2]^+$ cation takes a quasi-square-planar stereochemistry, the four N atoms are expected to have a flattened tetrahedral disposition and the $N^i—Cu—N^{ii}$ or $N—Cu—N^{iii}$ angles should be in the range 150–160° [symmetry codes: (i) $x, \frac{1}{2} - y, 2 - z$; (ii) $\frac{3}{2} - x, \frac{1}{2} - y, z$; (iii) $\frac{3}{2} - x, y, 2 - z$], with no significant differences between the four Cu—N distances (Murphy, Murphy *et al.*, 1997; Murphy, Nagle *et al.*, 1997). This is the case in (I*a*). However, the corresponding angles (N1—Cu—N1′ and N2—Cu—N2′) in (I*b*) are considerably smaller, at approximately 138°, and the Cu—N distances (Tables 1 and 2) are all slightly different.

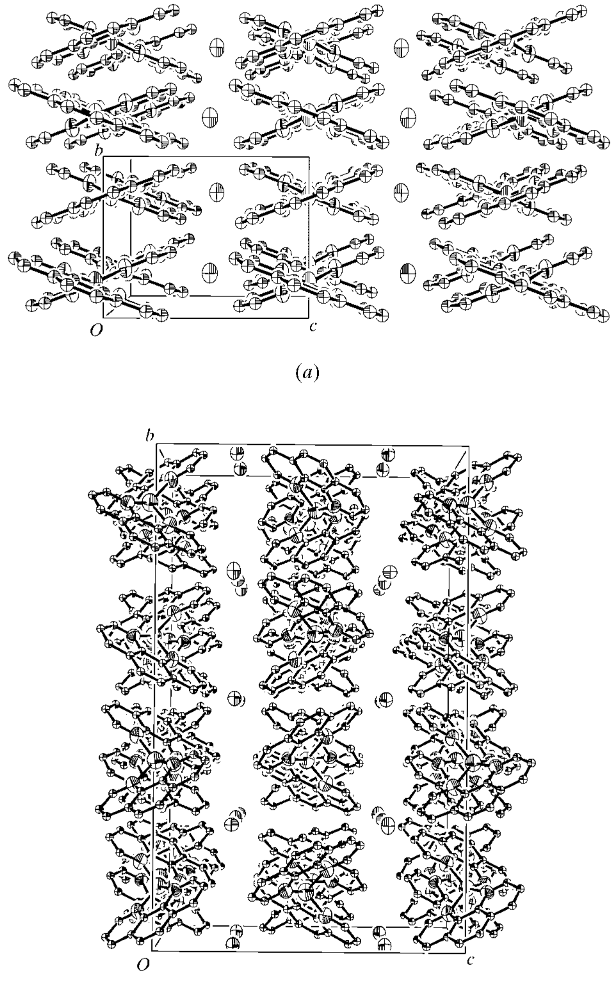
Other Cu^I complexes with bidentate amine ligands show different structures. The corresponding dafone complex, (II) (Fig. 1), has trigonal–bipyramidal coordination about the Cu atom, coordinating two dafone molecules and an I^- ion. The N atoms of the dafone ligand have a larger 'bite' size (2.99 Å) compared with phenanthroline (2.65 Å), and the ligand can expand the coordination number from four to five because it does not have the steric strain normally associated with phenanthroline in metal complexes (Kulkarni *et al.*, 2002). By comparison, the analogous Cu^{II} derivative, $[CuI(C_{12}H_8N_2)_2]I{\cdot}H_2O$ (Nagle & Hathaway, 1991), has a distorted trigonal–bipyramidal copper centre which bonds to four N atoms from two phenanthroline molecules and an I^- ion.



(*a*)

(*b*)

Figure 2
Views of the molecular units of (*a*) polymorph (I*a*) and (*b*) polymorph (I*b*). The symmetry codes are as given in Table 1. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.



(*a*)

(*b*)

Figure 3
Packing diagrams (viewed along the *a* axis) for (*a*) polymorph (I*a*) and (*b*) polymorph (I*b*), showing the distribution of the I^- ions within the ionic matrix and the π–π interactions between the phenanthroline rings.

Experimental

Compound (I) was synthesized according to the procedure of Tartarini (1933). Solid 1,10-phenanthroline monohydrate (1.80 g) was added to an aqueous solution of copper(II) sulfate pentahydrate (1.25 g, 50 ml). Solid potassium iodide (2 g) was added to this stirred solution, which turned a mustard-yellow colour. The solution was diluted with sodium sulfite (12.6 g, 250 ml) and brought to the boil, after which a purple precipitate was deposited. The solid was filtered off, washed with water and dried over P_2O_5 prior to recrystallization from ethanol.

Polymorph (I*a*)

Crystal data

$[Cu(C_{12}H_8N_2)_2]I$
$M_r = 550.85$
Orthorhombic, *Pban*
$a = 14.215\ (4)$ Å
$b = 7.458\ (2)$ Å
$c = 9.493\ (3)$ Å
$V = 1006.4\ (5)$ Å^3
$Z = 2$
$D_x = 1.817$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1677 reflections
$\theta = 2.9\text{–}26.7°$
$\mu = 2.64$ mm^{-1}
$T = 293\ (2)$ K
Plate, black
0.30 × 0.15 × 0.05 mm

Data collection

Bruker SMART APEX area-detector diffractometer
φ and ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.526$, $T_{\max} = 0.876$
5578 measured reflections
1178 independent reflections
892 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.031$
$\theta_{\max} = 27.5°$
$h = -18 \rightarrow 18$
$k = -9 \rightarrow 9$
$l = -12 \rightarrow 7$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.119$
$S = 1.24$
1178 reflections
70 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0406P)^2 + 0.9045P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.20$ e Å^{-3}
$\Delta\rho_{\min} = -0.32$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for polymorph (I*a*).

C1—N	1.306 (5)	N—Cu	2.008 (3)
C5—N	1.347 (5)		
N—C1—C2	123.6 (5)	C1—N—Cu	130.8 (3)
N—C5—C4	123.0 (4)	C5—N—Cu	111.9 (3)
N—C5—C5$^{\rm i}$	116.9 (2)	N$^{\rm i}$—Cu—N	82.28 (19)
C4—C5—C5$^{\rm i}$	120.1 (3)	N$^{\rm ii}$—Cu—N	106.80 (19)
C6$^{\rm i}$—C6—C4	121.8 (3)	N$^{\rm iii}$—Cu—N	147.7 (2)
C1—N—C5	117.1 (4)		

Symmetry codes: (i) $x, \frac{1}{2} - y, 2 - z$; (ii) $\frac{3}{2} - x, \frac{1}{2} - y, z$; (iii) $\frac{3}{2} - x, y, 2 - z$.

Polymorph (I*b*)

Crystal data

$[Cu(C_{12}H_8N_2)_2]I$
$M_r = 550.85$
Orthorhombic, *Ccca*
$a = 16.2547\ (7)$ Å
$b = 29.4171\ (13)$ Å
$c = 18.1262\ (8)$ Å
$V = 8667.3\ (7)$ Å^3
$Z = 16$
$D_x = 1.689$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1677 reflections
$\theta = 1.4\text{–}28.8°$
$\mu = 2.45$ mm^{-1}
$T = 293\ (2)$ K
Block, dark purple
0.4 × 0.3 × 0.3 mm

Data collection

Bruker SMART APEX area-detector diffractometer
φ and ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.375$, $T_{\max} = 0.484$
49 326 measured reflections
5435 independent reflections
2945 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.030$
$\theta_{\max} = 28.8°$
$h = -22 \rightarrow 21$
$k = -38 \rightarrow 39$
$l = -23 \rightarrow 23$

Table 2
Selected geometric parameters (Å, °) for polymorph (I*b*).

C2′—N1′	1.333 (4)	C13—N1	1.366 (3)
C2—N1	1.323 (4)	C13′—N2′	1.363 (3)
C11—N2	1.329 (4)	N1′—Cu	2.037 (2)
C11′—N2′	1.320 (4)	N1—Cu	2.032 (2)
C12—N2	1.361 (3)	N2′—Cu	2.038 (2)
C12′—N1′	1.358 (3)	N2—Cu	2.048 (2)
N1′—C2′—C3′	123.0 (3)	C2—N1—C13	117.3 (3)
N1—C2—C3	123.6 (3)	C2—N1—Cu	131.1 (2)
N2—C11—C10	123.9 (3)	C13—N1—Cu	111.46 (19)
N2′—C11′—C10′	122.9 (3)	C11′—N2′—C13′	117.7 (3)
N2—C12—C8	122.7 (3)	C11′—N2′—Cu	130.9 (2)
N2—C12—C13	117.3 (3)	C13′—N2′—Cu	111.3 (2)
N1′—C12′—C5′	122.8 (3)	C11—N2—C12	117.3 (3)
N1′—C12′—C13′	117.2 (3)	C11—N2—Cu	131.3 (2)
N1—C13—C5	123.0 (3)	C12—N2—Cu	111.27 (19)
N1—C13—C12	117.5 (2)	N1—Cu—N1′	137.28 (10)
N2′—C13′—C8′	122.8 (3)	N1—Cu—N2′	114.46 (10)
N2′—C13′—C12′	117.4 (3)	N1′—Cu—N2′	82.27 (10)
C2′—N1′—C12′	117.5 (3)	N1—Cu—N2	82.33 (9)
C2′—N1′—Cu	130.7 (2)	N1′—Cu—N2	111.48 (11)
C12′—N1′—Cu	111.7 (2)	N2′—Cu—N2	138.73 (10)

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.107$
$S = 0.98$
5435 reflections
274 parameters
H-atom parameters constrained
$w = 1/[s^2(F_o^2) + (0.0406P)^2 + 6.4435P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.37$ e Å^{-3}
$\Delta\rho_{\min} = -0.25$ e Å^{-3}

H atoms were treated as riding, with C—H distances of 0.93 Å. The highest electron-density peak for (I*a*) is about 1 Å from the I$^-$ ion.

For both compounds, data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXTL* (Bruker, 2001). For (I*a*), program(s) used to refine structure: *SHELXTL*. For (I*b*), program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). For both compounds, molecular graphics: *SHELXTL* and *ZORTEP* (Zsolnai, 1994).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1392). Services for accessing these data are described at the back of the journal.

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