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Structure of Bis(1,10-phenanthroline)copper(II) Bis(hexafluorophosphate)

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Abstract. $[Cu(C_{12}H_8N_2)_2][PF_6]_2$, (I), $M_r = 713.89$, monoclinic, $C2/c$, $a = 17.594$ (4), $b = 12.603$ (3), $c = 12.539$ (3) Å, $\beta = 111.90$ (2)°, $V = 2579.72$ Å^3, $Z = 4$, D_m(flotation) $= 1.810$ (6), $D_x = 1.83$ Mg m^{-3}, λ(Mo $K\alpha$) $= 0.71069$ Å, $\mu = 1.017$ mm^{-1}, $F(000) = 1420$, room temperature, $R = 0.049$ for 1723 unique observed reflections. The crystal contains $[Cu(phen)_2]^{2+}$ cations (phen = 1,10-o-phenanthroline) and $[PF_6]^-$ anions. The cation involves a compressed tetrahedral CuN$_4$ chromophore and lies on a crystallographic twofold axis of symmetry. The two independent anions are also in special positions of twofold symmetry, with near octahedral stereochemistry, and with the shortest Cu···F distances > 2.75 Å, they are too long even for weak semi-coordination.

Introduction. The compressed tetrahedral CuN$_4$ chromophore is of only limited occurrence in the coordination chemistry of the Cu^{II} ion involving simple neutral chelate N ligands (Hathaway & Billing, 1970; Hathaway, 1987). It was first

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Table 1. *Fractional atomic coordinates and thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq} (Å^2)
Cu	0.50000	0.69435 (7)	0.25000	0.0301 (5)
N(1)	0.5856 (2)	0.7207 (3)	0.1862 (3)	0.040 (2)
C(1)	0.5807 (3)	0.7668 (4)	0.0880 (4)	0.051 (3)
C(2)	0.6493 (3)	0.7856 (4)	0.0613 (5)	0.059 (3)
C(3)	0.7252 (3)	0.7518 (5)	0.1344 (5)	0.059 (3)
C(4)	0.7327 (3)	0.7009 (4)	0.2380 (4)	0.046 (3)
C(5)	0.8077 (3)	0.6598 (5)	0.3188 (5)	0.057 (3)
C(6)	0.8109 (3)	0.6151 (5)	0.4187 (5)	0.057 (3)
C(7)	0.7397 (3)	0.6097 (4)	0.4482 (4)	0.043 (3)
C(8)	0.7393 (3)	0.5700 (5)	0.5525 (5)	0.056 (3)
C(9)	0.6679 (3)	0.5714 (5)	0.5725 (4)	0.056 (3)
C(10)	0.5966 (3)	0.6119 (4)	0.4902 (4)	0.047 (3)
C(11)	0.6655 (3)	0.6489 (4)	0.3694 (4)	0.037 (2)
C(12)	0.6615 (3)	0.6905 (4)	0.2621 (4)	0.038 (2)
N(2)	0.5947 (2)	0.6503 (3)	0.3902 (3)	0.038 (2)
P(1)	0.50000	−0.01287 (18)	0.25000	0.0511 (12)
F(1)	0.5526 (2)	0.8949 (3)	0.3300 (3)	0.082 (3)
F(2)	0.4422 (3)	1.0742 (4)	0.1726 (4)	0.114 (4)
F(3)	0.5548 (4)	0.9854 (5)	0.1778 (6)	0.202 (6)
P(2)	0.50000	0.38512 (16)	0.25000	0.0498 (11)
F(4)	0.4638 (2)	0.4771 (3)	0.3053 (3)	0.090 (3)
F(5)	0.4648 (3)	0.2977 (3)	0.3087 (4)	0.116 (3)
F(6)	0.4175 (3)	0.3872 (4)	0.1419 (4)	0.101 (3)

Table 2. *Selected bond lengths* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

Cu—N(1)	1.979 (4)	Cu—N(2)	1.998 (4)
P(1)—F(1)	1.588 (4)	P(2)—F(4)	1.600 (3)
P(1)—F(2)	1.563 (4)	P(2)—F(5)	1.575 (4)
P(1)—F(3)	1.550 (5)	P(2)—F(6)	1.573 (4)
Cu···F(1)	2.75 (2)	Cu···F(4ⁱ)	2.95 (2)
N(2)—Cu—N(1)	83.8 (1)	N(2)—Cu—N(2')	147.7 (1)
N(1)—Cu—N(1')	160.7 (1)	N(1)—Cu—N(2')	101.6 (1)
F(2)—P(1)—F(1)	175.5 (3)	F(5)—P(2)—F(4)	90.8 (2)
F(3)—P(1)—F(1)	90.9 (3)	F(6)—P(2)—F(4)	88.4 (2)
F(3)—P(1)—F(2)	92.8 (4)	F(6)—P(2)—F(5)	91.0 (2)
F(1)—P(1)—F(1')	85.9 (3)	F(4)—P(2)—F(4')	87.1 (3)
F(2)—P(2)—F(2')	90.9 (4)	F(5)—P(2)—F(5')	91.2 (3)
F(3)—P(3)—F(3')	78.4 (3)	F(6)—P(2)—F(6')	178.1 (3)

Symmetry code: (i) $x, y, 1 - z$; (') $1 - x, y, \frac{1}{2} - z$.

recognized in [Cu(dpyam)₂][ClO₄]₂ (Johnson, Beineke & Jacobson, 1971) and more recently in [Cu(bpy)₂][PF₆]₂ (Foley, Tyagi & Hathaway, 1984), where dpyam = 2,2'-dipyridylamine and bpy = 2,2'-bipyridyl. As the phen, bpy and dpyam ligands represent a sequence of increasingly flexible chelate nitrogen ligands, the crystal structure of (I) has been determined in order to assess the effect of the rigidity of the phen ligand on the dihedral angle of the compressed tetrahedral CuN₄ chromophore.

Experimental. (I) was prepared by mixing a boiling solution of Cu(NO₃)₂.3H₂O (0·24 g, 1 mmol), phen (0·30 g, 1·5 mmol) in ethanol/water (1:1 v/v, 100 ml), and KPF₆ (0·46 g, 2·5 mmol) in hot water (50 ml); a greenish-blue precipitate was deposited immediately. Recrystallization from hot methanol solution yielded dark green crystals of (I). Found: C, 40·20; H, 2·25; N, 7·64; Cu, 8·60%. Calculated for C₂₄H₁₆CuF₁₂N₄P₂: C, 40·38; H, 2·26; N, 7·85; Cu, 8·90%.

The unit-cell data (25 reflections, θ 3–25°) and intensities for (I) were collected on a Philips PW 1100 diffractometer, with graphite-monochromatized Mo $K\alpha$ radiation. Reflections with $3\cdot0 < \theta < 25°$ in one quadrant were examined in the ω–2θ scan mode, with a constant scan speed of $0\cdot05° \text{ s}^{-1}$, and a variable scan width of $(0\cdot7 + 0\cdot1\tan\theta)°$. 1777 observed reflections were collected [$I > 2\cdot5\sigma(I)$] (h, −19–19, k, 0–14, l, 0–14) and yielded 1723 unique reflections. Lorentz and polarization corrections were applied, but no correction was made for absorption. The structure was solved by the SHELX76 direct methods (Sheldrick, 1976) and

difference Fourier techniques, and refined with 197 parameters, $N/P = 8\cdot75$, by full-matrix least-squares minimization of $\Sigma w(|F_o| - |F_c|)^2$, with anisotropic temperature factors on all the non-H atoms. The positions of the H atoms were calculated geometrically and the H atoms were then constrained to ride on the adjacent C atoms, assuming a C—H distance of 1·08 Å, and a fixed U_{iso} of 0·07 Å^2. The refinement converged with the maximum shift/e.s.d. < 0·002, with a refined weighting scheme, $w = k[\sigma^2(F_o) + g(F_o)^2]^{-1}$ with $k = 2\cdot034$ and $g = 0\cdot00025$. $R = 0\cdot049$ and $wR = 0\cdot057$. The maximum and minimum residual electron densities were 1·14 and $-0\cdot42 \text{ e Å}^{-3}$. Complex atomic scattering factors embedded in SHELX76 (Sheldrick, 1976) were employed and those for Cu were taken from (Cromer & Waber, 1974). All calculations were carried out with SHELX76 (Sheldrick, 1976), XANADU (Roberts & Sheldrick, 1979), CHEM-X (Davies, 1980) and PUBTAB (Hendrick, 1980) on the UCC mainframe IBM 4341 and VAX 11/780 computers. Final atomic coordinates and equivalent isotropic temperature factors are given in Table 1.* Selected bond lengths and angles are given in Table 2. Fig. 1 shows the molecular structure of (I) and the atom-numbering scheme used.

Discussion. The structure contains a [Cu(phen)₂]²⁺ cation and two independent [PF₆]⁻ anions, all three lying on special positions of twofold symmetry, Fig. 1. The structure of the cation involves a four coordinate CuN₄ chromophore, with a compressed tetrahedral stereochemistry and with the compression down the crystallographic twofold axis, which is

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parallel to the *b* axis, and perpendicular to the mean plane of the CuN₄ unit. The phen ligands are symmetry related and symmetrically bonded. The Cu—N(1) and Cu—N(2) distances of 1·979 (4) and 1·998 (4) Å, respectively, are not significantly different, mean 1·989 (4) Å. They involve a bite angle [N(1)—Cu—N(2)] of 83·8 (1)°, clearly less than 90° and involve a dihedral angle of 40·1°, between the symmetry related N(1)—Cu—N(2) planes. There are no unusual bond lengths or bond angles in the phen ligand, the pyridine rings are nearly planar (r.m.s.d. 0·017 and 0·001 Å, respectively) and inclined at an angle of 6·9°. The dihedral angle between the mean planes of the symmetry related phen ligands is 50·1°, significantly different from the angle of 40·1° between the N(1)—Cu—N(2) planes. The $[PF_6]^-$ anions have approximately octahedral stereochemistry with an acceptable mean P—F distance of 1·568 (5) Å and mean F—P—F angle of 88·7 (4)°, but with some exceptional values associated with some high thermal parameters for the F atoms (Frenz & Ibers, 1972). The relatively high residual electron density of 1·14 e Å^{-3} in (I) is also associated with the $[PF_6]^-$ anions. The $[PF_6]^-$ anions are positioned above and below the plane of the CuN₄ chromophore, with the closest approach to the Cu atom being 2·75 (2) Å to F(1) and 2·95 (2) Å to F(4), longer than the upper limit of 2·4 Å for semi-coordination, (Procter, Hathaway & Nicholls, 1968). Consequently, the stereochemistry of (I) is best described as compressed tetrahedral.

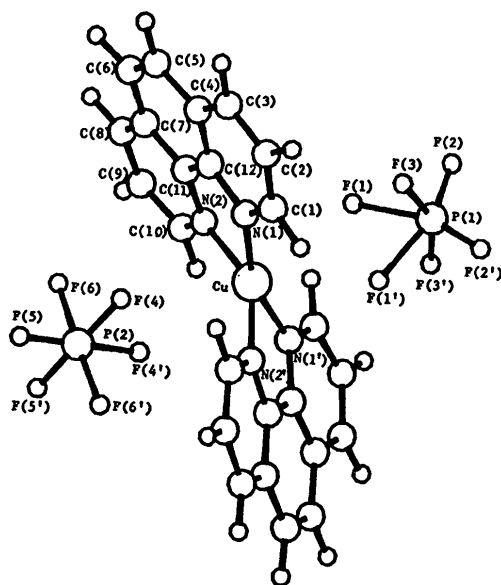The molecular structure of (I) is comparable to the compressed tetrahedral structure of $[Cu(bpy)_2][PF_6]_2$

Fig. 1. The molecular structure of $[Cu(phen)_2][PF_6]_2$ and the atom-numbering scheme used.

(II) (Foley *et al.*, 1984), with a mean Cu—N distance of 1·985 (11) Å and CuN₂ plane dihedral angle of 42·1°. This dihedral angle is significantly lower than that of 55·6° in $[Cu(dpyam)_2][ClO_4]_2$ (III) (Johnson *et al.*, 1971). The comparability in the molecular structures of (I) and (II) is reflected in the similarity of their electronic reflectance spectra, namely, 14 500, 17 200 (sh) cm^{-1} and 15 040 16 950 (sh) cm^{-1}, respectively. Both of which are significantly different from the three *d–d* bands observed in the polarized single-crystal spectrum of (III) (Dudley, Hathaway & Hodgson, 1972) at 10 400, 13 500 and 15 700 cm^{-1}. The present structure suggests that the chelate function of the phen ligand is comparable to that of the bpy ligand and significantly different from that of the more flexible dpyam ligand.

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