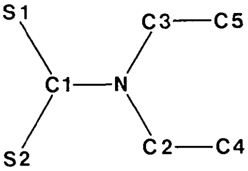

Fig. 2. Denotations of the atoms in the dithiocarbamate ion.

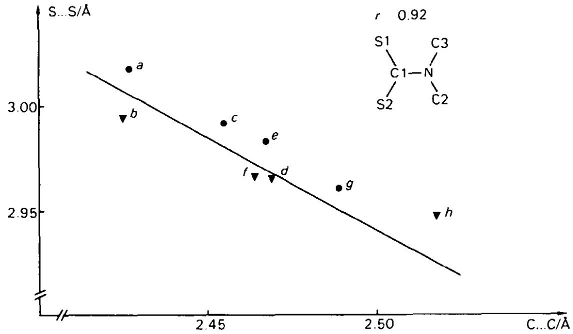

Fig. 3. $S(1)\cdots S(2) = f[C(2)\cdots C(3)]$. Circles represent Na^+ and triangles Li^+ compounds. Data are taken from (*a*) Albertsson *et al.* (1980); (*b*) Ymén (1983*a*); (*c*) Oskarsson & Ymén (1983); (*d*) Ymén (1983*b*); (*e*) Mereiter & Preisinger (1983); (*f*) this paper; (*g*) Ymén (1984) and (*h*) Oskarsson & Ymén (1984). Point (*b*) was excluded from the calculation of the correlation coefficient, *r*, for reasons discussed by Oskarsson & Ymén (1984). Points (*d*) and (*f*) represent $LiS_2CN(CH_3)_2.4H_2O$ and $LiS_2CN(C_2H_5)_2.3H_2O$ respectively.

[1·460(4) and 1·469(2) Å respectively]. These parameters are important for the intramolecular steric interference and their combined effect is reflected in the distance $C(2)\cdots C(3)$, which only differs by 0·005 Å in the two compounds. It has been proposed previously that the steric interactions are reflected in the distance $S(1)\cdots S(2)$ as a function of the distance $C(2)\cdots C(3)$ (Oskarsson & Ymén, 1984). The steric interference increases as the distance $C(2)\cdots C(3)$ increases (Fig. 3). As expected the points for $LiS_2CN(CH_3)_2.4H_2O$ and $LiS_2CN(C_2H_5)_2.3H_2O$ almost coincide in the middle of the graph, showing that the intramolecular steric interference in these two ligands is of similar strength (further support is provided by the two points observed for the corresponding Na^+ compounds).

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Acetatobis(1,10-phenanthroline)copper(II) Tetrafluoroborate, $[Cu(C_{12}H_8N_2)_2(C_2H_3O_2)]BF_4$

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Abstract. $M_r = 569{\cdot}81$, triclinic, $P\bar{1}$, $a = 15{\cdot}087\,(3)$, $b = 10{\cdot}615\,(2)$, $c = 8{\cdot}443\,(2)$ Å, $\alpha = 106{\cdot}43\,(2)$, $\beta = 76{\cdot}67\,(2)$, $\gamma = 109{\cdot}40\,(2)^\circ$, $U = 1209{\cdot}37$ Å^3, $Z = 2$, $D_m = 1{\cdot}52\,(5)$, $D_x = 1{\cdot}564$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 9{\cdot}22$ cm^{-1}, $F(000) = 577{\cdot}98$, $T = 296$ K. Final $R = 0{\cdot}036$ for 3287 unique observed reflections. The structure involves $[Cu(phen)_2(O_2CCH_3)]^+$ cations and BF_4^- anions; the cation

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involves a *cis*-$CuN_2N_2'OO'$ chromophore with a square-pyramidal distortion to give a (4+1+1*) stereochemistry with asymmetric coordination of the acetate group at Cu—O distances of 1·996 (2) and 2·670 (3) Å respectively.

Introduction. The title compound (1) represents one of a series of four cation-distortion isomers (Ray, Hulett, Sheahan & Hathaway, 1978) of the $[Cu(phen)_2(O_2CCH_3)]^+$ cation (Clifford, Counihan, Fitzgerald, Seff, Simmons, Tyagi & Hathaway, 1982; Simmons, Seff, Clifford & Hathaway, 1983).

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å²) *for the non-*H *atoms with e.s.d.'s in parentheses*

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Cu	0·26290 (2)	0·16920 (4)	0·04476 (4)	0·0404 (2)
N(1)	0·1767 (2)	0·2909 (3)	0·1303 (3)	0·046 (1)
C(1)	0·1822 (2)	0·3975 (3)	0·2595 (4)	0·059 (2)
C(2)	0·1194 (3)	0·4771 (4)	0·3032 (5)	0·066 (2)
C(3)	0·0493 (2)	0·4464 (4)	0·2090 (5)	0·064 (2)
C(4)	0·0405 (2)	0·3328 (3)	0·0720 (4)	0·050 (2)
C(5)	−0·0326 (2)	0·2881 (4)	−0·0309 (5)	0·062 (2)
C(6)	−0·0399 (2)	0·1743 (4)	−0·1543 (5)	0·061 (2)
C(7)	0·0248 (2)	0·0930 (3)	−0·1887 (4)	0·049 (2)
C(8)	0·0174 (2)	−0·0305 (4)	−0·3085 (4)	0·058 (2)
C(9)	0·0824 (3)	−0·1012 (4)	−0·3290 (4)	0·056 (2)
C(10)	0·1541 (2)	−0·0491 (3)	−0·2296 (4)	0·051 (2)
C(11)	0·0986 (2)	0·1366 (3)	−0·0942 (4)	0·041 (1)
C(12)	0·1062 (2)	0·2580 (3)	0·0382 (4)	0·044 (2)
N(2)	0·1633 (2)	0·0669 (2)	−0·1139 (3)	0·043 (1)
N(3)	0·3497 (2)	0·0482 (2)	−0·0634 (3)	0·041 (1)
C(13)	0·3347 (2)	−0·0767 (3)	−0·0427 (4)	0·051 (2)
C(14)	0·3996 (3)	−0·1525 (3)	−0·1168 (5)	0·061 (2)
C(15)	0·4813 (3)	−0·0978 (4)	−0·2134 (5)	0·061 (2)
C(16)	0·4990 (2)	0·0348 (3)	−0·2375 (4)	0·049 (2)
C(17)	0·5832 (2)	0·1020 (4)	−0·3369 (5)	0·063 (2)
C(18)	0·5972 (2)	0·2283 (4)	−0·3570 (5)	0·060 (2)
C(19)	0·5286 (2)	0·3035 (3)	−0·2783 (4)	0·046 (2)
C(20)	0·5393 (2)	0·4354 (3)	−0·2942 (4)	0·054 (2)
C(21)	0·4701 (2)	0·4981 (3)	−0·2142 (4)	0·057 (2)
C(22)	0·3898 (2)	0·4285 (3)	−0·1210 (4)	0·051 (2)
C(23)	0·4457 (2)	0·2409 (3)	−0·1794 (3)	0·039 (1)
C(24)	0·4306 (2)	0·1045 (3)	−0·1600 (3)	0·040 (1)
N(4)	0·3767 (2)	0·3033 (2)	−0·1029 (3)	0·040 (1)
C(25)	0·2767 (2)	0·1627 (3)	0·3501 (4)	0·045 (2)
C(26)	0·2984 (3)	0·2053 (4)	0·5242 (4)	0·065 (2)
O(1)	0·3225 (2)	0·2397 (2)	0·2525 (3)	0·051 (1)
O(2)	0·2142 (2)	0·0550 (3)	0·3081 (4)	0·076 (2)
B(1)	−0·2159 (3)	0·4466 (4)	0·2835 (5)	0·057 (2)
F(1)	−0·1953 (2)	0·3416 (2)	0·3186 (3)	0·091 (2)
F(2)	−0·1466 (2)	0·5674 (2)	0·3272 (4)	0·087 (2)
F(3)	−0·2203 (2)	0·4195 (3)	0·1156 (3)	0·084 (2)
F(4)	−0·3027 (2)	0·4582 (2)	0·3736 (3)	0·081 (1)

Table 2. *Selected bond lengths* (Å) *and angles* (°)

Cu—N(1)	2·010 (2)	Cu—N(2)	2·062 (2)
Cu—N(3)	2·025 (2)	Cu—N(4)	2·218 (2)
Cu—O(1)	1·996 (2)	Cu—O(2)	2·670 (3)
C(25)—O(1)	1·252 (4)	C(25)—O(2)	1·238 (4)
N(2)—Cu—N(1)	81·3 (1)	N(3)—Cu—N(1)	174·6 (1)
N(3)—Cu—N(2)	95·1 (1)	N(4)—Cu—N(1)	97·6 (1)
N(4)—Cu—N(2)	103·5 (1)	N(4)—Cu—N(3)	79·1 (1)
O(1)—Cu—N(1)	92·4 (1)	O(1)—Cu—N(2)	160·5 (1)
O(1)—Cu—N(3)	92·2 (1)	O(1)—Cu—N(4)	95·7 (1)
O(1)—Cu—O(2)	53·9 (2)	O(1)—C(25)—O(2)	122·7 (3)

Experimental. (1) was prepared by mixing 0·01 mol $[Cu(OH_2)_6](BF_4)_2$ and 0·01 mol NaO_2CCH_3 both in 60 ml 1:2 aqueous ethanol, and adding 0·022 mol 1,10-phenanthroline (phen) in 60 ml 1:2 aqueous ethanol; solution was boiled, filtered, and allowed to stand and turquoise-green crystals of $[Cu(phen)_2(O_2CCH_3)]BF_4.2H_2O$ were deposited; recrystallization from a 5:1 acetonitrile/2,2-dimethoxypropane solution kept at 273 K for a few days yielded turquoise-green crystals of (1), dimensions 0·3 × 0·3 × 0·4 mm. Found: C 55·20, H 3·45, Cu 11·20, N 9·98%; calculated for $C_{26}H_{19}BCuF_4N_4O_2$: C 54·80, H 3·36, Cu 11·15, N 9·83%. D_m measured by flotation. Intensities collected on a Philips PW 1100 diffractometer with graphite-monochromated Mo $K\alpha$ radiation. 3345 reflections with $3·0 < \theta < 30°$ in one quadrant (h ±17, k ±12, l 0–10), θ–2θ scans, constant scan speed $0·05°s^{-1}$, variable scan width $(0·7 + 0·1 \tan\theta)°$; 3287 unique reflections $[I > 2·5\sigma(I)]$. Lorentz and polarization corrections, no correction for absorption. Structure solved by Patterson and Fourier techniques and refined by full-matrix least squares, $\sum w(|F_o| - |F_c|)^2$ minimized, 342 parameters varied, anisotropic temperature factors for all non-H-atoms; positions of H atoms calculated geometrically and 'floated' on adjacent atoms (C—H 1·08 Å) with a fixed temperature factor of 0·07 Å². $(\Delta/\sigma)_{\max} < 0·002$. Refined weighting scheme, $w = k[\sigma^2(F_o) + g(F_o)^2]$ with $k = 1·00$ and $g = 0·00147$; $R = 0·036$, $R_w = 0·0538$. Max. residual electron density 0·47 e Å^{-3}. Complex atomic scattering factors employed, those for Cu corrected for anomalous dispersion (Cromer & Mann, 1968; Cromer & Liberman, 1970). All calculations carried out with *SHELX*76 (Sheldrick, 1976), *XANADU* (Roberts & Sheldrick, 1975), *PLUTO* (Motherwell, 1976) and *PUBTAB* (Henrick, 1980) on an IBM 4341 and VAX 11/780 computer.

Discussion. Final atomic coordinates and equivalent isotropic temperature factors are given in Table 1.* Selected bond lengths and angles are in Table 2. Fig. 1 shows the molecular structure of (1), the atom-numbering scheme and the packing arrangement.

The structure of (1) consists of $[Cu(phen)_2(O_2CCH_3)]^+$ cations and BF_4^- anions, with no evidence for semi-coordination of the BF_4^- anions to the copper(II) cations. There are no unusual features in the bond lengths or bond angles of the phen ligands (Frenz & Ibers, 1972; Nishigaki, Yoshioka & Nakatsu, 1978);

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* Lists of structure factors, anisotropic temperature factors, calculated H-atom coordinates, and full bond-length, bond-angle and mean-plane data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38939 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

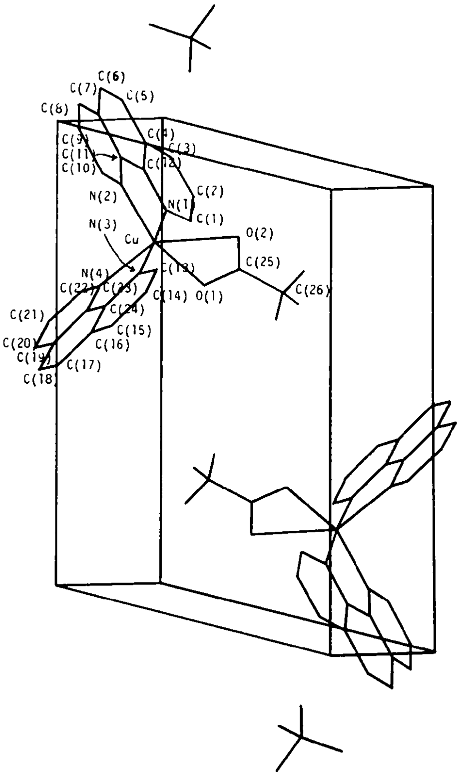

Fig. 1. The molecular structure of $[Cu(phen)_2(O_2CCH_3)]BF_4$, the atom-numbering scheme used and the molecular packing (excluding H atoms).

both are essentially planar with angles of twist of the pairs of pyridine groups 6·5 (10) and 0·3 (10)° for the two phen ligands. The BF_4^- anion forms a well defined tetrahedron, mean bond length 1·377 Å and mean bond angle 109·6°, in good agreement with previous results (Sutton, 1965), with no evidence for disorder, and the F atoms have reasonable temperature factors (Stynes & Ibers, 1971).

The stereochemistry of the $[Cu(phen)_2(O_2CCH_3)]^+$ cation is basically five-coordinate with a CuN_4O chromophore, but with the second O atom of the acetate group occupying the sixth coordination position at a distance >2·6 Å, to give a (4+1+1*)-type coordination (Hathaway, 1973; Hathaway, Ray, Kennedy, O'Brien & Murphy, 1980). The CuN_4OO' chromophore involves short $Cu-N_{ax}$ distances, mean 2·018 Å and longer $Cu-N_{eq}$ distances, mean 2·140 Å. There is a significant difference between the two equatorial Cu—N distances, with ΔN {= [Cu—N(4)] − [Cu—N(2)]} 0·156 Å. There is even greater asymmetry in the Cu—O distances ΔO {= [Cu—O(2)] − [Cu—O(1)]} 0·674 Å, with the long Cu—O(2) and Cu—N(4) distances *trans* to each other. This (4+1+1*)-type stereochemistry has been previously observed in $[Cu(bpy)_2(O_2CCH_3)]X$, where $X = ClO_4^-.H_2O$ and BF_4^-, with ΔN and ΔO values of 0·112 and 0·176 Å, and 0·617 and 0·805 Å, respectively (Hathaway *et al.*, 1980). In the four cation-distortion isomers of the $[Cu(phen)_2(O_2CCH_3)]^+$ cation (Clifford *et al.*, 1982), the structure of (1) represents the most extreme asymmetric coordination of the acetate group. The acetate group in (1) is reasonably planar (r.m.s.d. 0·0030 Å), and the C—O distances, mean 1·245 Å, are not significantly different as previously observed (Simmons *et al.*, 1983), despite the asymmetry in the two Cu—O distances, $\Delta O = 0{\cdot}674$ Å. In addition the near spherical symmetry of the thermal parameters of the O(1) and O(2) [see deposited material and Fig. 3 in Simmons *et al.* (1983)] suggests that the structure of (1) represents a *near* static extreme of the fluxional CuN_4O_2 chromophore of the $[Cu(phen)_2(O_2CCH_3)]X$ series of cation-distortion isomers (Clifford *et al.*, 1982).

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