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The Crystal Structure of Bis(ethylenediamine)copper(II) Fluoroborate

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The crystal structure of bis(ethylenediamine)copper(II) fluoroborate, $\text{Cu(en)}_2(\text{BF}_4)_2$, has been determined from three-dimensional X-ray diffraction data. Crystals are triclinic with space group $P\bar{1}$ and cell dimensions: $a = 7.42$, $b = 8.22$, $c = 5.92$ Å, $\alpha = 100^\circ 54'$, $\beta = 105^\circ 12'$, $\gamma = 106^\circ 0'$. The structure was refined by Fourier and full-matrix least-squares methods on 978 observed reflexions to $R = 15.3\%$.

The copper ion has the usual distorted octahedral coordination with four N atoms in an approximately square planar arrangement with Cu-N distances of 2.02 and 2.03 Å, and two F atoms completing the distorted octahedron at the longer distance of 2.56 Å. The ethylenediamine molecules are twisted relative to the plane containing the Cu and N atoms, with one C atom 0.40 Å above the plane, and the other 0.32 Å below the plane. The fluoroborate ions are distorted from tetrahedral symmetry.

Experimental

Violet coloured crystals in the form of platelets elongated in the c direction were kindly supplied by Dr. B. J. Hathaway (University of Essex).

For the purposes of X-ray analysis, a crystal of maximum dimensions 0.2 mm was used. Three-dimensional Weissenberg data were collected for the crystal rotating about its a and c axes, allowing the observations of 978 independent reflexions. Intensities were

Table 1. *Final coordinates and standard deviations*

	x/a	y/b	z/c	$\sigma(x/a)$	$\sigma(y/b)$	$\sigma(z/c)$
Cu	0.0000	0.0000	0.0000	—	—	—
N(1)	0.0555	0.2454	0.2130	0.002	0.002	0.002
N(2)	0.2729	0.0965	-0.0253	0.002	0.002	0.002
C(1)	0.2740	0.3373	0.2899	0.002	0.002	0.003
C(2)	0.3451	0.2924	0.0666	0.002	0.002	0.003
B	0.7714	0.2046	0.6282	0.003	0.002	0.003
F(1)	0.6649	0.2076	0.7936	0.002	0.002	0.002
F(2)	0.9393	0.3514	0.7186	0.002	0.002	0.002
F(3)	0.6657	0.1990	0.4111	0.002	0.001	0.002
F(4)	0.8281	0.0576	0.6039	0.002	0.001	0.002

Table 2. *Final temperature factor parameters*

	B	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu		2.32	1.29	2.72	0.57	0.75	0.30
N(1)	5.25 Å ²						
N(2)	5.04						
C(1)	5.39						
C(2)	5.59						
B	5.40						
F(1)		5.96	4.19	7.00	2.62	3.53	2.25
F(2)		5.28	3.09	7.20	0.78	-0.22	1.57
F(3)		4.86	3.32	5.05	2.29	0.35	1.21
F(4)		5.29	3.34	5.58	2.80	2.53	1.98

measured visually and converted to $|F|^2$ and $|F|$ by applying Lorentz and polarization corrections. No corrections were made for absorption or extinction.

Crystal data



Triclinic, $a = 7.42$, $b = 8.22$, $c = 5.92$, all ± 0.02 Å

$\alpha = 100^\circ 54'$, $\beta = 105^\circ 12'$, $\gamma = 106^\circ 0'$, all $\pm 30'$

$U = 321.3 \text{ \AA}^3$, $z = 1$, $D_m = 1.84 \text{ g.cm}^{-3}$, $D_c = 1.85 \text{ g.cm}^{-3}$.

$F(000) = 179$; Cu $K\alpha$, $\lambda = 1.542$ Å; $\mu = 33 \text{ cm}^{-1}$.

No absent reflexions. Space group $P1$ or $P\bar{1}$. $P\bar{1}$ is indicated from structure analysis.

Structure analysis

A negative pyroelectric test indicated a centre of symmetry, although statistical tests (Howells, Phillips & Rogers, 1950) on projection data were inconclusive. The space group was therefore initially assumed to be $P\bar{1}$, implying a centre of symmetry in the molecule. The copper atom was placed at the origin of the unit cell, and approximate coordinates for the remaining atoms were obtained from Patterson and heavy atom electron density projections. The atomic positions and isotropic temperature factors were initially refined by electron density projections, and then by least-squares analysis on full three-dimensional data with a block diagonal program written by G.S.D. King on an IBM 1620 computer. A weighting scheme

$$w = 1/(0.5 \times A|F| + B|F|^2),$$

was employed, and scattering factors for Cu, F, N, C and B were those due to Hanson, Herman, Lea &

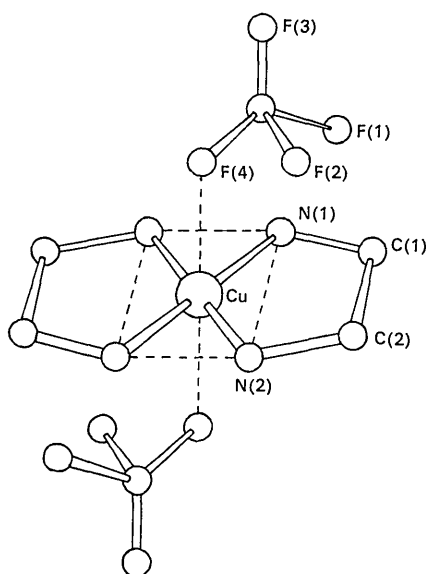


Fig. 1. The molecular structure of $\text{Cu}(\text{en})_2(\text{BF}_4)_2$.

Skillman (1964). Reflexions too weak to be observed were omitted. After several refinement cycles the structure converged, with a reliability index $R = 17.7\%$. Two cycles with the space group $P1$ did not improve R and showed no tendency to destroy the centre of symmetry, thus confirming the space group as $P\bar{1}$. A three-dimensional difference synthesis indicated some anisotropy in the copper and fluorine atoms. Further refinement was carried out with the Busing, Levy & Hunt full-matrix least-squares program on the IBM 7090 computer at Imperial College, London. Scattering factors for Cu^+ obtained from *International Tables for X-ray Crystallography* were corrected for the real part of anomalous dispersion, and anisotropic temperature factors were introduced for the copper and fluorine atoms. Layers were rescaled from the observed and calculated structure factors. After five cycles, the refinement converged with $R = 15.3\%$. A three-dimensional difference synthesis showed no features which could be interpreted, and agreement analysis of the observed and calculated structure factors showed no systematic sources of disagreement. The final atomic parameters and their standard deviations are set out in Tables 1 and 2. The observed and calculated structure factors are listed in Table 3.

Discussion

A representation of the structure is shown in Fig. 1 and the interatomic distances and angles are quoted in Table 4. The copper atom is surrounded by a tetragonally distorted octahedron, with four nitrogen atoms at 2.02 and 2.03 Å, and two fluorine atoms from approximately tetrahedral fluoborate ions at 2.56 Å.

The Cu–N distances are similar to those obtained for other complexes of this type (Brown & Lingafelter, 1965; Komiyama & Lingafelter, 1964; Pajunen, 1967), and correspond to a normal covalent bond. The ethylenediamine molecule is in the *gauche* configuration, with one carbon atom 0.40 Å above the plane containing the Cu and N atoms, the other carbon atom being 0.32 Å below it.

The Cu–F distance of 2.56 Å compares with the values of 1.93 and 2.27 Å in CuF_2 (Billy & Haendler 1957). In view of the stereochemistry and position of the F atom, it seems probable that there is some weak interaction between the two atoms and the term ‘semi-coordination’ has been used to describe such an interaction (Brown, Lee, Melsom, Hathaway, Procter & Tomlinson, 1967).

The BF_4^- ion forms a distorted tetrahedron with B–F distances of 1.36, 1.30, 1.39 and 1.40 Å. Spectroscopic evidence for the distortion is discussed in a previous paper (Brown *et al.*, 1967), although the precise causes of the distortion are not obvious. There are numerous approaches between fluorine atoms and carbon and nitrogen atoms in the range 3.1 to 3.3 Å, and these represent the closest intermolecular contacts. These distances are too long for hydrogen bonding. It is assumed that the combined effect of these contacts

Table 4. Bond lengths and angles and their standard deviations

	Bond length	σ		Bond angle	σ
B—F(1)	1.41 Å	0.03 Å	F(1)—B—F(2)	108.5°	1.5°
B—F(2)	1.37	0.02	F(1)—B—F(3)	112.2	1.8
B—F(3)	1.30	0.03	F(1)—B—F(4)	110.6	1.7
B—F(4)	1.38	0.03	F(2)—B—F(3)	110.2	1.8
Cu—N(1)	2.02	0.01	F(2)—B—F(4)	108.2	1.7
Cu—N(2)	2.03	0.01	F(3)—B—F(4)	107.1	1.5
Cu—F(4)	2.56	0.01 (5)	N(1)—Cu—N(2)	86.4	0.5
C(1)—N(1)	1.48	0.02	N(1)—Cu—F(4)	94.6	0.5
C(2)—N(2)	1.49	0.02	N(2)—Cu—F(4)	93.1	0.5
C(1)—C(2)	1.56	0.03	Cu—N(1)—C(1)	106.7	1.1
			Cu—N(2)—C(2)	108.4	1.1
			N(1)—C(1)—C(2)	108.3	1.1
			N(2)—C(2)—C(1)	106.9	1.4
			Cu—F(4)—B	116.3	1.5

and the semi-coordinated bond result in the distortion of the BF_4^- ion.

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The Rigid-Body Vibrations of Molecules in Crystals II. Application of the Schomaker-Trueblood Analysis

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The rigid-body motions of nine non-centrosymmetric molecules, examined in a previous paper with use of the Cruickshank analysis, have been re-analysed by the Schomaker-Trueblood technique, which takes account of correlation between translation and libration. Detailed results are given for 1-methylthymine and phenylcyclobutenedione to illustrate the improvement that results, and it is concluded that the rigid-body model is widely applicable. It is also pointed out how the full Schomaker-Trueblood analysis permits the rigidity of parts of molecules to be examined, and the advantages of such an approach are stressed.

Introduction

In an earlier paper (Burns, Ferrier & McMullan, 1967*a*) hereinafter referred to as I, the anisotropic temperature parameters of seventeen molecular crystals were analysed in terms of rigid-body motions as suggested by Cruickshank (1956). Criteria were proposed on the basis of which it could be decided whether or not the rigid-body model adequately accounted for the atomic thermal parameters obtained from the usual least-squares refinement. An atom-by-atom comparison was then used to classify the seventeen molecules roughly in order of their rigidity. Since then it has been shown (Schomaker & Trueblood, 1968) that the Cruickshank analysis is incomplete for molecules that do not possess a centre of symmetry, since in such cases correlation between translation and libration cannot be neglected.

Of the seventeen structures analysed in I, eight (numbered consecutively 2 through 9 in Table 1 of I*) have centrosymmetric molecules and are therefore unaffected. The remaining nine molecules have been re-analysed by the Schomaker-Trueblood (briefly, S-T) technique. It is a striking confirmation of the need for the full S-T analysis that of the molecules classified as unequivocally rigid in I, only *N*-acetylglycine was non-centrosymmetric.

Procedure

The S-T analysis gives values of the comparison parameters that are independent of the origin and orien-

* In the case of *cis,cis*-1,2,3,4-tetraphenylbutadiene only half of the molecule was shown by mistake, although the analysis was carried through referred to the centre of the whole molecule as origin.