The Crystal Structure of Monoaquabis(1,10-phenanthroline)copper(II) Tetrafluoroborate $[Cu(H_2O)(phen)_2](BF_4)_2$

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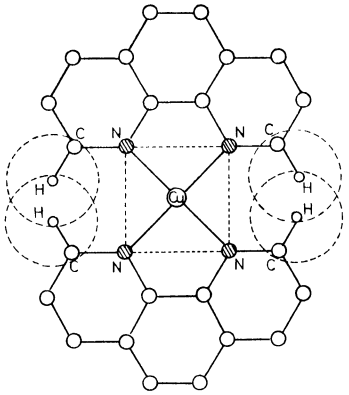
The crystal of the title compound is monoclinic, with $a=19.099(6)$, $b=8.100(3)$, $c=16.177(5)$ Å, $\beta=100.54(5)°$, the space group of C2/c, and $Z=4$. The structure was determined from the counter data and was refined to $R=0.083$ for 1736 non-zero reflections. The coordination geometry of the copper atom is best described as a distorted trigonal bipyramid, in which the equatorial plane is composed of Cu, two N, and water O atoms, and the axial positions are occupied by two N atoms. The complex has a crystallographically imposed twofold axis which passes through the copper and the water oxygen atoms at the equatorial plane. The two phenanthroline ligands are related with each other by this axis.

In bis(bipyridine) and bis(phenanthroline)copper(II) complexes, the $Cu(chelate)_2^{2+}$ (chelate=bpy or phen) group is unable to assume a coplanar disposition about the copper atom because of the steric repulsions between the hydrogen atoms of these two chelates(I). Therefore, it has been shown that the bis(bipyridine)copper(II) complexes take a variety of stereochemistries, a distorted trigonal bipyramid[1-5] and *cis*-[6] and *trans*-distorted octahedra,[7,8] while the structure of the bis(phenanthroline)copper(II) complexes has not yet been investigated in detail.[9,10] As a part of our structural studies of such complexes, a single-crystal X-ray analysis has been carried out on $[Cu(H_2O)(phen)_2](BF_4)_2$.



I

Experimental

The green crystals of $[Cu(H_2O)(phen)_2](BF_4)_2$ were prepared by a method similar to that used for the preparation of the corresponding nitrate;[9] they were then recrystallized from a water-methanol mixture. Found: C, 46.93; H, 2.96; N, 9.31%. Calcd for $Cu(phen)_2(BF_4)_2\cdot H_2O$: C, 46.83; H, 2.95; N, 9.10%.

Preliminary X-ray photographs taken with Cu$K\alpha$ radiation showed a Laue symmetry of 2/m, with systematic absences of hkl for $h+k=2n+1$ and $h0l$ for $l=2n+1$. The space group is either C2/c or Cc; the former was confirmed by a successful refinement of the structure.

A crystal with dimensions of $0.35\times0.36\times0.38$ mm was mounted on a glass fiber for data collection. The unit-cell dimensions were determined by a least-squares fit using 21 θ-values measured accurately on a diffractometer. Crystal data: $[Cu(H_2O)(phen)_2](BF_4)_2$, $M.W.=615.6$, monoclinic, $a=19.099(6)$, $b=8.100(3)$, $c=16.177(5)$ Å, $\beta=100.54(5)°$, $U=2460.5$ Å^3, $Z=4$, $D_c=1.66$, $D_m=1.64$ g cm^{-3}, Mo$K\alpha$ radiation($\lambda=0.71069$ Å), μ(Mo$K\alpha$)$=10.1$ cm^{-1}, space group C2/c.

The intensity data with $6°\leqq2\theta\leqq60°$ were collected at room temperature by the ω-2θ scan technique on a Philips PW1100 four-circle diffractometer using graphite-monochromated Mo$K\alpha$ radiation, a scan speed of $0.03°$ s^{-1}, a scan width of $(1.0+0.2\tan\theta)°$, and two 10-s background counts. Three standard reflections ($\bar{2}04$, $0\bar{2}0$, and 604), monitored every 4 h throughout the data collection, showed no significant variation in intensity. A total of 1736 intensities with $I_{top}-2\sqrt{I_{top}}\geqq I_{back}$ were classified as observed; I_{top} is the intensity(counts/s) measured at the top of the peak, and I_{back} is the mean background intensity(counts/s) obtained from the preliminary background measurement for 5 s on each side of the peak. The intensity data were processed with the computer program of Hornstra and Stubbe.[11] No absorption correction was made.

Structure Determination

The positions of the copper atoms were determined from a three-dimensional Patterson map, the space group being assumed to be C2/c. The structure was solved by the heavy-atom technique, and the positional and thermal parameters were refined by the block-diagonal least-squares method. The minimized function was $\Sigma w(F_o-|F_c|)^2$. A weighting scheme of the type suggested by Hughes[14] was applied using $w=1.0$ for $F_o\leqq F_{max}$ and $w=(F_{max}/F_o)^2$ for $F_o>F_{max}$; $F_{max}=31.0$ was found to be optimum. The atomic scattering curves were taken from Ref. 15. The initial refinement was carried out with isotropic thermal parameters. The thermal parameters of all the atoms except those of the BF_4^- ion converged at 3—5 Å^2, while those of the B and F atoms were found to be unusually large. In the subsequent refinement, the anisotropic thermal parameters were used for the Cu, C, N, and O atoms, but not for the B and F atoms. The R value was reduced to 0.116. Although introduction of anisotropic temperature factors for the B and F atoms as well as the other atoms reduced the R value further to 0.087, some of the F–B–F bond angles were found to be far from the tetrahedral angle (109°28′). In order to investigate carefully the electron-density distribution for the BF_4^- anion, we calculated a difference Fourier map in which the electron

TABLE 1. ATOMIC PARAMETERS AND THEIR STANDARD DEVIATIONS

OC indicates the occupancy factor of the atom in a distorted arrangement.

Atom	*x*	*y*	*z*	*B*/Å²	*OC*
Cu	0.0	0.0703(2)	0.25	a)	
O	0.0	−0.2060(10)	0.25	a)	
N(1)	0.0953(3)	0.0549(8)	0.3232(3)	a)	
N(2)	−0.0279(3)	0.1633(8)	0.3567(4)	a)	
C(1)	0.1555(4)	−0.0034(11)	0.3038(5)	a)	
C(2)	0.2180(4)	−0.0128(12)	0.3641(5)	a)	
C(3)	0.2184(4)	0.0399(10)	0.4438(5)	a)	
C(4)	0.1565(4)	0.1010(10)	0.4655(4)	a)	
C(5)	0.1514(5)	0.1628(12)	0.5477(5)	a)	
C(6)	0.0904(5)	0.2253(12)	0.5641(5)	a)	
C(7)	0.0271(4)	0.2296(10)	0.5007(4)	a)	
C(8)	−0.0402(5)	0.2894(12)	0.5140(5)	a)	
C(9)	−0.0962(5)	0.2875(12)	0.4497(6)	a)	
C(10)	−0.0893(4)	0.2231(12)	0.3704(5)	a)	
C(11)	0.0954(3)	0.1077(8)	0.4026(4)	a)	
C(12)	0.0302(4)	0.1675(9)	0.4204(4)	a)	
B(1a)	0.1727(6)	−0.4639(15)	0.3195(7)	2.9(0.2)	0.6
B(1b)	0.1468(11)	−0.4875(28)	0.3158(13)	3.5(0.3)	0.4
F(1a)	0.1237(7)	−0.3850(16)	0.2622(8)	8.3(0.3)	0.6
F(1b)	0.1538(12)	−0.3702(30)	0.2501(14)	10.2(0.5)	0.4
F(2a)	0.2338(8)	−0.3906(19)	0.3440(10)	10.2(0.4)	0.6
F(2b)	0.1712(19)	−0.3950(21)	0.3898(11)	7.5(0.4)	0.4
F(3a)	0.1423(9)	−0.4932(20)	0.3914(10)	10.5(0.4)	0.6
F(3b)	0.0810(17)	−0.5450(36)	0.3040(20)	13.4(0.8)	0.4
F(4a)	0.1875(6)	−0.6125(14)	0.2911(7)	7.1(0.2)	0.6
F(4b)	0.1877(10)	−0.6186(26)	0.3142(12)	9.1(0.5)	0.4
H(C1)	0.160(2)	−0.047(6)	0.243(3)	4.0	
H(C2)	0.260(3)	−0.058(7)	0.348(3)	4.0	
H(C3)	0.260(3)	0.025(7)	0.485(3)	4.0	
H(C5)	0.195(3)	0.187(7)	0.596(4)	4.0	
H(C8)	−0.041(3)	0.330(7)	0.566(3)	4.0	
H(C10)	−0.133(3)	0.225(7)	0.318(4)	4.0	
H(O)	0.030(3)	−0.281(7)	0.257(4)	4.0	

a) Anisotropic thermal factors are listed in Table 2.

TABLE 2. ANISOTROPIC THERMAL FACTORS[a] ($\times 10^4$) FOR THE NON-HYDROGEN ATOMS IN THE COMPLEX CATION

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	18.0(0.3)	171(2)	27.8(0.4)	0	−1.3(0.5)	0
O	28(2)	141(14)	67(4)	0	−3(5)	0
N(1)	21(1)	135(10)	33(2)	−8(7)	2(3)	−13(8)
N(2)	22(2)	153(11)	35(2)	15(7)	5(3)	10(8)
C(1)	20(2)	185(14)	48(4)	1(9)	0(4)	−28(12)
C(2)	22(2)	201(15)	49(4)	17(9)	1(4)	10(13)
C(3)	22(2)	179(17)	51(4)	0(9)	−13(4)	42(12)
C(4)	28(2)	155(15)	33(3)	−21(8)	−7(4)	19(9)
C(5)	37(3)	210(17)	30(3)	−36(11)	−6(4)	9(11)
C(6)	37(3)	203(17)	35(3)	−33(11)	−1(5)	19(12)
C(7)	32(2)	171(14)	30(3)	−17(9)	14(4)	16(10)
C(8)	46(3)	227(18)	33(3)	17(13)	26(5)	5(12)
C(9)	43(3)	214(18)	45(4)	50(13)	30(6)	7(13)
C(10)	29(2)	230(18)	39(3)	45(11)	11(4)	39(12)
C(11)	21(2)	105(11)	34(3)	−11(7)	−1(3)	22(8)
C(12)	27(2)	116(12)	31(3)	−13(8)	4(4)	6(9)

a) The anisotropic thermal factors are of the form: $\exp\{-(h^2B_{11}+k^2B_{22}+l^2B_{33}+hkB_{12}+hlB_{13}+klB_{23})\}$.

density due to the complex cation was eliminated. Figure 3 shows the resulting electron-density distribution, which can virtually account for the two azimuthally different BF_4^- ions in a statistical distribution. The weights of 0.6 and 0.4 for the BF_4^- ion with the subscript a and that with b(Fig. 3) were found to be optimum in view of the *R* value. Seven of the nine crystallographically independent hydrogen atoms could be located on the difference Fourier map calculated at this point. These seven hydrogen atoms were included in the final refinement, with an isotropic thermal parameter of 4.0 Å^2. The final *R* value was 0.083 for 1736 observed reflections. All the parameter shifts were less than 0.1σ in the final cycle of the refinement. The atomic coordinates and thermal parameters are listed in Tables 1 and 2. The observed and calculated structure factors are preserved at the Chemical Society of Japan(Document Number 7812). The computer programs used in the calculations were as follows: RSSFR-5[12] (Fourier synthesis), HBLS-V[13] (least-squares calculation), and DAPH[13] (interatomic distances and angles, least-squares plane, and coordinates of the H atoms). All the computations were carried out on a NEAC2200—700 computer at Osaka University.

Results and Discussion

The crystal is composed of the $[Cu(H_2O)(phen)_2]^{2+}$ cations and the tetrafluoroborate anions. The bond lengths and angles, with their estimated standard deviations, are given in Table 3.

Figure 1 shows a schematic drawing of the complex cation. There is a twofold axis which passes through the copper and the water-oxygen atoms and which relates the two phenanthroline ligands with each other. The central copper atom is surrounded by the four nitrogen atoms of the two phenanthroline ligands and one water-oxygen atom. The two Cu–N distances of 1.985(6) and 2.041(7) Å in the chelate ring are appreciably different. The Cu–O bond is 2.238(8) Å long.

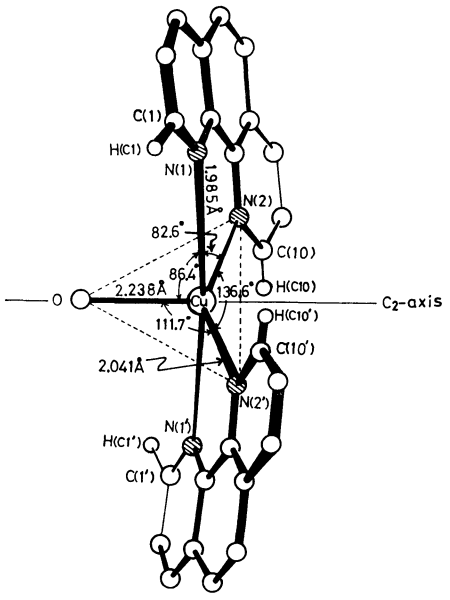
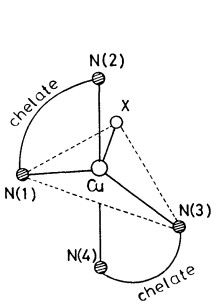
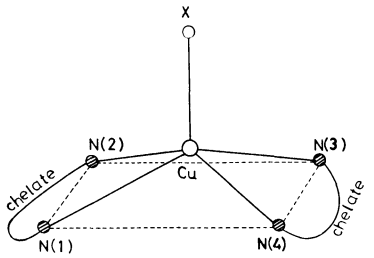


Fig. 1. A schematic drawing of the complex cation $[Cu(H_2O)(phen)_2]^{2+}$.

Among possible configurations for the five-coordinate complex, a trigonal-bipyramidal arrangement, II, and a square-pyramidal one, III, may be considered to be common in the $[Cu(chelate)_2X]^{n+}$ cations(chelate= phen or bpy).



II



III

Several complexes with a II trigonal-bipyramidal stereochemistry have been found in $[Cu(bpy)_2X]^{n+}$-type complexes (X=I, NH_3, Cl, $CS(NH_2)_2$, and Cu^ICl_2).[1-5] As has been suggested by Stephens *et al.*, it is characteristic that the four Cu–N(bpy) distances in all those complexes except $[Cu(bpy)_2I]^+$ fall into two sets: the axial Cu–N(bpy) distances range from 1.96 to 2.00 Å and are significantly shorter (0.06—0.12 Å) than the equatorial ones. The N(1)–Cu–N(3) angle in the equatorial plane has been shown to be in the range of 109—123° in those complexes.[1-5]

On the other hand, a complex with a square-pyramidal stereochemistry, III, has not yet been found in the bis(phenanthroline)- and bis(bipyridine)copper(II) complexes. However, it has been recently shown that, when the two bipyridine ligands are coordinated to a copper atom in a square-planar arrangement, they must be twisted out of the central copper atom, in opposite directions about their individual C_2-axis by 15—20° towards a tetrahedral stereochemistry, because of the steric repulsions between the hydrogen atoms of the bipyridine ligands in the square-coplanar Cu-$(bpy)_2^{2+}$ moiety(I).[7,8] Therefore, if a $[Cu(phen)_2X]^{n+}$ cation takes a square-pyramidal stereochemistry(III), the four nitrogen atoms of the $Cu(phen)_2^{2+}$ moiety in the basal plane should have a flattened tetrahedral disposition. Therefore, the N(1)–Cu–N(3) or N(2)–Cu–N(4) angle in III is presumably in the range of 150—160°. However, there must be no significant difference between the four Cu–N(phen) distances.

Judging from the details described above, the coordination geometry about the copper atom should be described as a distorted trigonal-bipyramid, because the two Cu–N distances for a given phenanthroline ligand are significantly different(Cu–N(1)=1.985(6) and Cu–N(2)=2.041(7) Å); the axial positions are occupied by N(1) and N(1'), while the Cu, N(2), N(2'), and O atoms lie on the trigonal plane. The angle of N(2)–Cu–N(2') in the trigonal plane is 137°; this value is, however, considerably larger than those (108—123°) found in the trigonal-bipyramidal complexes.[1-5] The

Table 3. Bond distances (l/Å) and angles (φ/°), with their estimated standard deviations in parentheses[a)]

Cu-N(1) = 1.985(6)	B(1a)-F(1a) = 1.35(2)
Cu-N(2) = 2.041(7)	B(1a)-F(2a) = 1.31(2)
Cu-O = 2.238(8)	B(1a)-F(3a) = 1.41(2)
N(1)-C(1) = 1.33(1)	B(1a)-F(4a) = 1.34(2)
N(1)-C(11) = 1.35(1)	B(1b)-F(1b) = 1.45(3)
N(2)-C(10) = 1.32(1)	B(1b)-F(2b) = 1.42(3)
N(2)-C(12) = 1.37(1)	B(1b)-F(3b) = 1.32(4)
C(1)-C(2) = 1.40(1)	B(1b)-F(4b) = 1.32(3)
C(2)-C(3) = 1.36(1)	C(1)-H(C1) = 1.05(5)
C(3)-C(4) = 1.39(1)	C(2)-H(C2) = 0.97(6)
C(4)-C(5) = 1.44(1)	C(3)-H(C3) = 0.95(6)
C(4)-C(11) = 1.40(1)	C(5)-H(C5) = 1.06(6)
C(5)-C(6) = 1.34(1)	C(8)-H(C8) = 0.91(6)
C(6)-C(7) = 1.44(1)	C(10)-H(C10) = 1.07(6)
C(7)-C(8) = 1.43(1)	O-H(O) = 0.83(6)
C(7)-C(12) = 1.41(1)	
C(8)-C(9) = 1.35(1)	O···F(1a) = 2.75(2)
C(9)-C(10) = 1.41(1)	O···F(1b) = 3.22(3)
C(11)-C(12) = 1.41(1)	
N(1)-Cu-N(2) = 82.6(3)	C(4)-C(5)-C(6) = 121.4(9)
N(1)-Cu-N(2′) = 100.1(3)	C(4)-C(11)-C(12) = 120.8(6)
N(1)-Cu-O = 86.4(3)	C(5)-C(6)-C(7) = 121.1(9)
N(2)-Cu-O = 111.7(3)	C(6)-C(7)-C(8) = 124.4(8)
Cu-N(1)-C(11) = 112.9(5)	C(6)-C(7)-C(12) = 118.7(8)
Cu-N(1)-C(1) = 128.1(6)	C(7)-C(12)-C(11) = 119.9(7)
Cu-N(2)-C(10) = 130.9(6)	C(7)-C(8)-C(9) = 119.3(9)
Cu-N(2)-C(12) = 110.1(5)	C(8)-C(7)-C(12) = 116.9(8)
C(1)-N(1)-C(11) = 118.9(7)	C(8)-C(9)-C(10) = 120.8(9)
C(10)-N(2)-C(12) = 119.0(7)	F(1a)-B(1a)-F(2a) = 117(1)
N(1)-C(1)-C(2) = 121.2(8)	F(1a)-B(1a)-F(3a) = 108(1)
N(1)-C(11)-C(4) = 122.3(6)	F(1a)-B(1a)-F(4a) = 111(1)
N(1)-C(11)-C(12) = 116.9(6)	F(2a)-B(1a)-F(3a) = 108(1)
N(2)-C(10)-C(9) = 121.4(9)	F(2a)-B(1a)-F(4a) = 106(1)
N(2)-C(12)-C(7) = 122.6(7)	F(3a)-B(1a)-F(4a) = 106(1)
N(2)-C(12)-C(11) = 117.5(6)	F(1b)-B(1b)-F(2b) = 102(2)
C(1)-C(2)-C(3) = 120.1(9)	F(1b)-B(1b)-F(3b) = 100(2)
C(2)-C(3)-C(4) = 119.8(8)	F(1b)-B(1b)-F(4b) = 112(2)
C(3)-C(4)-C(5) = 124.3(8)	F(2b)-B(1b)-F(3b) = 104(2)
C(3)-C(4)-C(11) = 117.7(7)	F(2b)-B(1b)-F(4b) = 110(2)
C(5)-C(4)-C(11) = 118.0(7)	F(3b)-B(1b)-F(4b) = 99(2)

a) Estimated standard deviations are right-adjusted to the last digit of the preceding number. The atom with the prime is related by a twofold symmetry to the corresponding unprimed atom.

Table 4. Least-squares planes and deviations of atoms from the plane (l/Å)

The equation of the plane is of the form $AX+BY+CZ+D=0$, where X, Y, Z, and D are measured in Å units. (The atoms marked by * are not included in the least-squares calculation.)

a) Phenanthroline ligand

$0.2954X+0.9161Y-0.2711Z+0.7571=0$

N(1)	0.026	N(2)	−0.038	C(1)	0.034	C(2)	0.004
C(3)	−0.016	C(4)	−0.025	C(5)	−0.021	C(6)	0.014
C(7)	0.018	C(8)	0.012	C(9)	0.016	C(10)	−0.012
C(11)	0.006	C(12)	−0.010	Cu*	−0.018	H(C1)*	0.050
H(C10)*	0.024						

b) Plane formed by Cu, N(2), and O atoms: $-0.8942X+0.0000Y-0.4477Z+1.1184=0$

c) Plane formed by Cu, N(1), and N(2) atoms: $0.2710X+0.9227Y-0.2743Z+0.7658=0$

d) Plane formed by Cu, N(1), and O atoms: $0.5880X-0.0000Y-0.8089Z+3.6511=0$

N(1)–Cu–O angle is 86.4°, and the N–Cu–N angle in the chelate ring is 82.8°.

On the basis of our previous X-ray examination of $[Cu(H_2O)(phen)_2](NO_3)_2$,[9] which was performed by the use of photographic data, the $[Cu(H_2O)(phen)_2]^{2+}$ cation was assigned a trigonal-bipyramidal structure, in which the axial and equatorial Cu–N distances were 1.99(1) and 2.03(1) Å respectively. Although the unit-cell dimensions of the $[Cu(H_2O)(phen)_2](BF_4)_2$ are different from those of the nitrate salt, the disposition of anions around the cation in the former resembles that in the latter; that is, these two crystal structures are roughly in agreement with each other. In the complex cation, there is no significant difference in the Cu–N distances, while the Cu–O distances are 2.18(1) Å in the NO_3^- salt and 2.238(8) Å in the BF_4^- salt, a difference of about 0.06 Å. However, the e.s.d. in the NO_3^- salt might be underestimated because it is based on photographic data. Therefore, we may regard the coordination geometries of these two complexes as essentially identical.

The phenanthroline ligands are planar within a maximum deviation of 0.04 Å(Table 4). The angle between the best planes of these two phenanthroline ligands is 47°. The H(C1)···H(C10′) distance is 2.43 Å; this value is equal to the sum of the van der Waals radii of the hydrogen atoms (Fig. 2). The bond lengths and angles agree with the values usually found in Cu(II)–phen complexes.[9,10,16,17] However, it is noted that the distances of C(2)–C(3), C(5)–C(6), and C(8)–C(9) are shorter than the others by 0.03—0.10 Å; such a trend has also been observed in the Cu(II)–phen complexes.

The arrangement of tetrafluoroborate ions is linked to the coordinated water molecules through O–H···F hydrogen bonding (O···F(1a)=2.75 Å) (Fig. 3). The B–F bond distances range from 1.32 to 1.45 Å, and the F–B–F angles, from 99 to 117°.

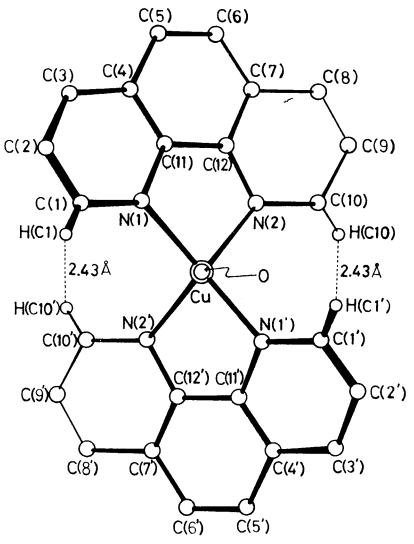


Fig. 2. The b axis projection of the complex cation $[Cu(H_2O)(phen)_2]^{2+}$.

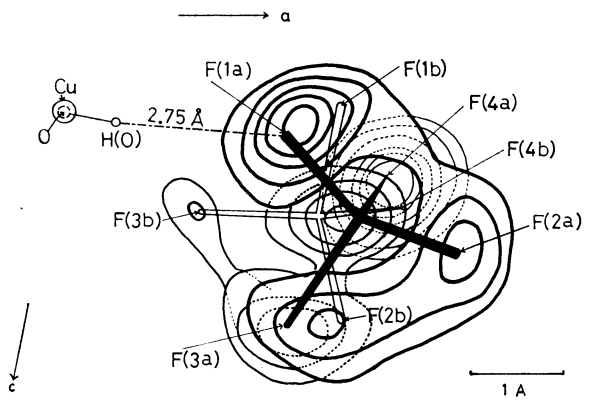


Fig. 3. The electron-density distribution of the disordered BF_4^- ion(O-H···F(BF_4^-) hydrogen bond, ——). The contours are at an arbitrary interval.

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References

1) G. A. Barclay, B. F. Hoskins, and C. H. L. Kennard, *J. Chem. Soc.*, **1963**, 5691.
2) F. S. Stephens, *J. Chem. Soc., Dalton Trans.*, **1972**, 1350.
3) F. S. Stephens and P. A. Tucker, *J. Chem. Soc., Dalton Trans.*, **1973**, 2293.
4) M. B. Ferrari, A. B. Corradi, G. G. Fava, C. G. Palmieri, M. Nardelli, and C. Pelizzi, *Acta Crystallogr., Sect. B*, **29**, 1808 (1973).
5) J. Kaiser, G. Brauer, and F. A. Schröder, *J. Chem. Soc., Dalton Trans.*, **1974**, 1490.
6) I. M. Procter and F. S. Stephens, *J. Chem. Soc. A*, **1969**, 1248.
7) H. Nakai, *Bull. Chem. Soc. Jpn.*, **44**, 2412 (1971).
8) M. B. Ferrari, G. G. Fava, and C. Pelizzi, *J. Chem. Soc., Chem. Commun.*, **1977**, 8.
9) H. Nakai and Y. Deguchi, *Bull. Chem. Soc. Jpn.*, **48**, 2557 (1975).
10) O. P. Anderson, *Inorg. Chem.*, **14**, 730 (1975).
11) J. Hornstra and B. Stubbe, PW1100 Data Processing Program, Philips Research Laboratories, Eindhoven, Holland.
12) T. Sakurai, The Universal Crystallographic Computing System(I), The Crystallographic Society of Japan(1967), p. 19.
13) T. Ashida, The Universal Crystallographic Computing System-Osaka, The Computation Center, Osaka University (1973), pp. 55, 63.
14) E. W. Hughes, *J. Am. Chem. Soc.*, **63**, 1737 (1941).
15) "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham (1962), p. 202.
16) D. L. McFadden and A. T. McPhail, *J. Chem. Soc., Dalton Trans.*, **1975**, 1993.
17) O. P. Anderson, *J. Chem. Soc., Dalton Trans.*, **1973**, 1237.