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The Crystal Structure of Tetra(pyridine oxide)copper(II) Fluoroborate

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The crystal and molecular structure of tetra(pyridine oxide)copper(II) fluoroborate $Cu(PyO)_4(BF_4)_2$ have been determined from three-dimensional X-ray diffraction data. The crystals are dark green in colour, monoclinic, space group $P2_1/c$, and the unit-cell dimensions are $a=9{\cdot}59$ Å, $b=14{\cdot}30$ Å, $c=10{\cdot}69$ Å, $\beta=122°0'$. The structure was refined by Fourier and full-matrix least-squares methods on 1019 independent observed reflexions to $R=9{\cdot}1\%$. The structure is centrosymmetrical about the copper. The four pyridine oxide molecules are bonded to the copper and form a 'swastika' arrangement. The oxygen atoms from the four pyridine oxide molecules form a square planar arrangement around the copper, with Cu–O bond lengths of 1·91 and 1·93 Å. The planes through the heterocyclic rings make an angle of 82·8° with each other, and the rings are inclined at 89·9° and 78·9° respectively to the square plane of copper and oxygen atoms. The fluoroborate ions are almost tetrahedral, and occupy approximately octahedral positions round the copper. There is no coordination between fluoroborate and copper since no fluorine atoms are in favourable geometric positions and the closest fluorine to copper approach is 3·34 Å.

Experimental

A sample was kindly provided by Dr B. J. Hathaway (University of Essex). The crystals were dark green in colour, and were in the form of hexagonal plates. Three-dimensional Weissenberg data were collected for a crystal of maximum dimension 0·4 mm, rotating about its b and c axes. 1019 independent reflexions were observed photographically. Intensities were measured visually and were converted to $|F^2|$ and $|F|$ by applying Lorentz and polarization corrections. No corrections were made for absorption or extinction.

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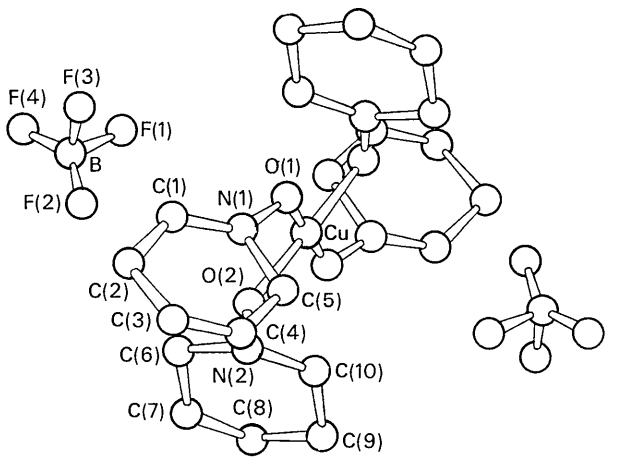

Fig. 1. The environment of the copper atom.

Crystal data

$Cu(C_5H_5NO)_4(BF_4)_2$, $M=617{\cdot}6$.

Monoclinic, $a=9{\cdot}59$, $b=14{\cdot}30$, $c=10{\cdot}69$ all $\pm 0{\cdot}02$ Å, $\beta=122°0' \pm 30'$.

$U=1243{\cdot}3$ Å^3, $Z=2$, $D_m=1{\cdot}71$ g.cm^{-3}, $D_c=1{\cdot}649$ g.cm^{-3}, $F(000)=622$, Cu $K\alpha$, $\lambda=1{\cdot}542$ Å, $\mu=22{\cdot}1$ cm^{-1}

Absent reflexions $h0l$ when l is odd, $0k0$ when k is odd;

Space group $P2_1/c$

Structure analysis

In view of the similarity in cell dimensions, space group and X-ray intensities between $Cu(PyO)_4(BF_4)_2$ and $Cu(PyO)_4(ClO_4)_2$ (Lee, Brown & Melsom, 1969), it was assumed that the two had basically the same structure Accordingly, structure factors were calculated for the fluoroborate structure with the use of atomic coordinates obtained from the perchlorate refinement. The copper atom was included as Cu^+ and its scattering factors were obtained from *International Tables for X-ray Crystallography* (1962). The scattering factors for the remaining atoms were those of Hanson, Herman, Lea & Skillman (1964). The first value of the reliability index R was 24·0% based on the 1019 observed reflexions. Positional parameters and isotropic temperature factors were refined initially on an IBM 1620 computer by use of a block diagonal least-squares program written by G. S. D. King (Union Carbide Ltd.). All reflexions were given unit weights.

The final part of the refinement was carried out on the SRC Atlas computer at Chilton, with the use of full-matrix least-squares program in the X-ray 63 system. The same scattering factors were used as previously, but those for Cu^+ were modified by applying both real and imaginary parts of dispersion corrections.

The final weighting scheme used was

$$w = \frac{1}{2A + |F_o| + \frac{2}{B}|F_o|^2}$$

with chosen values of $A=7{\cdot}0$ and $B=100$. Anisotropic thermal motion was allowed initially for copper atoms and later for the fluorine atoms as well. It was noted from the correlation matrix when $R=10{\cdot}1\%$, that there was some dependence between the x and z coordinates of each atom, so in the final stages alternate cycles of least-squares refinement were carried out in which the x or z coordinates were not allowed to refine. Convergence occurred giving a final agreement factor of $R=9{\cdot}1\%$. The final atomic parameters are given in Tables 1 and 2, the observed and calculated structure factors are given in Table 3, and agreement analysis is shown in Table 4.

Discussion

A view of the structure is shown in Fig. 1, and the principal bond lengths and angles together with their standard deviations are given in Tables 5 and 6. The structure is basically the same as the crystal structure of $Cu(PyO)_4(ClO_4)_2$ (Lee, Brown & Melsom, 1969) with BF_4^- replacing ClO_4^- in the lattice. Oxygen atoms from four pyridine oxide molecules are involved in square planar coordination with the copper. The four pyridine oxide molecules are in the same 'swastika' arrangement as in the perchlorate structure, and bond lengths and angles in them do not differ significantly. The planes

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	—	—	—
F(1)	−0·2420	0·0207	−0·3874	0·0015	0·0008	0·0014
F(2)	−0·1563	0·1644	−0·3689	0·0011	0·0009	0·0010
F(3)	−0·3006	0·1291	−0·2667	0·0011	0·0009	0·0009
F(4)	−0·4204	0·1374	−0·5045	0·0010	0·0009	0·0009
B	−0·2841	0·1139	−0·3828	0·0021	0·0015	0·0019
N(1)	0·0985	0·1825	0·0914	0·0010	0·0007	0·0009
N(2)	0·2271	−0·0082	−0·0918	0·0010	0·0007	0·0010
O(1)	0·0090	0·1156	0·0966	0·0010	0·0006	0·0008
O(2)	0·1763	0·0449	−0·0173	0·0010	0·0007	0·0009
C(1)	0·0336	0·2420	−0·0287	0·0014	0·0010	0·0014
C(2)	0·1275	0·3077	−0·0371	0·0016	0·0011	0·0014
C(3)	0·2903	0·3208	0·0767	0·0015	0·0010	0·0015
C(4)	0·3531	0·2620	0·1966	0·0016	0·0011	0·0015
C(5)	0·2568	0·1918	0·2027	0·0015	0·0010	0·0014
C(6)	0·1745	0·0166	−0·2281	0·0015	0·0010	0·0014
C(7)	0·2301	−0·0313	−0·3067	0·0016	0·0011	0·0015
C(8)	0·3375	−0·1026	−0·2404	0·0017	0·0012	0·0015
C(9)	0·3890	−0·0757	−0·0954	0·0018	0·0012	0·0016
C(10)	0·3311	−0·0757	−0·0189	0·0015	0·0010	0·0014

Table 2. *Final temperature factor parameters*

	B (Å^2)	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu		4·22	2·83	4·77	−0·44	3·27	−0·78
F(1)		12·61	6·78	15·60	2·18	9·09	1·79
F(2)		7·52	10·46	8·59	−1·54	5·04	−0·31
F(3)		8·43	13·57	5·73	−2·33	4·56	−2·74
F(4)		5·41	11·38	5·90	2·14	2·27	2·04
B	5·20						
N(1)	3·45						
N(2)	3·66						
O(1)	4·19						
O(2)	4·70						
C(1)	3·97						
C(2)	5·00						
C(3)	4·86						
C(4)	4·97						
C(5)	4·31						
C(6)	4·46						
C(7)	5·03						
C(8)	5·73						
C(9)	5·96						
C(10)	4·56						

Table 3. *Observed and calculated structure factors*

h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc
0	4	0	24.8	27.0	0	13	1	16.2	16.5	-2	11	1	23.6	24.4	1	15	2	9.9	9.6	2	13	3	19.7	17.5	-8	7	3	18.2	23.8
0	6	0	94.1	94.2	0	14	1	11.3	8.5	-2	17	1	13.3	12.8	1	16	2	13.4	10.9	2	14	3	9.9	8.3	-9	1	3	12.1	13.3
0	8	0	52.0	59.2	0	15	1	15.7	13.8	-3	1	1	44.5	49.7	1	2	2	58.9	66.0	2	15	3	7.3	7.1	-9	2	3	12.9	-12.1
0	10	0	36.2	36.4	0	17	1	12.5	12.3	-3	2	1	2.4	1.8	0	7	2	5.9	-6.3	3	1	3	12.1	10.6	-9	3	3	10.6	12.6
0	12	0	19.5	18.2	1	1	1	85.5	90.8	-3	3	1	22.3	22.4	0	8	2	18.9	16.9	3	2	3	26.7	-29.6	-9	4	3	6.1	6.7
0	16	0	22.6	19.3	1	2	1	31.1	-34.2	-3	4	1	37.6	-39.6	0	10	2	11.6	15.2	3	3	3	34.9	36.1	-1	0	4	41.4	-36.7
1	2	0	40.7	43.4	1	3	1	89.0	94.2	-3	5	1	29.7	30.9	0	11	2	24.4	-9.4	3	4	3	5.0	-2.9	0	0	4	60.1	60.4
1	3	0	103.3	112.9	1	5	1	40.3	38.0	-3	7	1	32.2	30.4	0	12	2	18.3	18.9	3	6	3	15.6	16.1	1	0	4	32.0	29.2
1	4	0	87.7	88.3	1	6	1	4.3	-6.5	-3	9	1	23.2	24.5	0	13	2	8.0	-6.6	3	7	3	13.9	15.1	2	0	4	17.0	15.6
1	5	0	27.1	-28.7	1	7	1	39.8	41.0	-3	10	1	9.2	-10.2	0	14	2	13.9	13.2	3	9	3	28.5	26.0	3	0	4	11.7	11.9
1	6	0	59.5	56.7	1	8	1	19.2	-16.4	-3	11	1	22.6	24.6	0	15	2	5.7	6.0	3	10	3	10.2	-8.3	0	1	4	10.6	10.3
1	7	0	32.4	-27.9	1	9	1	45.0	44.7	-3	12	1	8.7	-7.7	0	16	2	15.6	14.5	3	12	3	7.6	7.4	0	2	4	42.8	38.6
1	8	0	21.2	20.5	1	10	1	11.0	-10.2	-3	13	1	20.1	17.0	0	18	2	6.3	7.1	3	13	3	15.3	15.1	0	3	4	33.9	-30.9
1	9	0	24.4	26.5	1	11	1	12.1	13.9	-3	15	1	11.0	10.7	0	2	2	35.2	41.3	4	1	3	19.9	19.5	0	4	4	35.4	34.7
1	10	0	29.1	29.2	1	13	1	20.2	17.4	-3	17	1	7.8	7.4	0	3	2	25.9	-31.4	4	2	3	15.6	18.5	0	5	4	15.6	11.7
1	11	0	6.9	8.5	1	16	1	6.1	7.0	-4	1	1	57.8	59.0	3	0	2	11.9	4.8	4	3	3	16.5	16.7	0	7	4	8.7	-9.3
1	12	0	18.6	18.4	1	17	1	13.4	12.4	-4	2	1	28.4	-29.0	-1	3	2	10.2	10.6	4	5	3	19.3	22.1	0	8	4	18.9	18.5
1	15	0	13.2	10.1	2	1	1	51.8	46.2	-4	3	1	23.9	26.5	-1	4	2	58.5	70.0	4	6	3	9.4	10.0	0	11	4	8.6	-6.8
1	16	0	14.8	13.1	2	2	1	61.5	-63.3	-4	4	1	8.8	-8.7	-1	5	2	19.1	20.8	4	7	3	20.4	18.1	0	12	4	13.5	13.2
1	18	0	5.4	7.0	2	3	1	53.8	52.6	-4	5	1	37.1	37.5	-1	7	2	4.5	5.2	4	9	3	8.9	7.8	1	2	4	45.8	46.0
2	1	0	64.8	-64.1	2	4	1	8.8	-10.8	-4	6	1	18.7	-21.2	-1	9	2	8.9	7.6	5	1	3	14.5	15.7	1	4	4	80.9	84.7
2	2	0	33.4	-27.7	2	5	1	39.2	38.4	-4	7	1	39.9	45.1	-1	10	2	19.0	20.3	5	2	3	6.1	-6.5	1	5	4	7.7	-9.2
2	3	0	65.8	-66.3	2	7	1	40.0	44.2	-4	8	1	14.9	-16.8	-1	12	2	17.1	17.5	5	3	3	16.2	15.5	1	6	4	13.2	14.1
2	4	0	2.1	-2.1	2	8	1	6.9	-8.3	-4	9	1	37.7	36.8	-1	16	2	14.1	12.3	5	5	3	25.9	27.5	1	7	4	12.0	-12.0
2	5	0	10.5	11.7	2	9	1	33.4	35.1	-4	11	1	20.5	16.5	-2	2	2	27.6	27.5	5	6	3	13.8	14.2	1	8	4	19.9	21.0
2	6	0	5.1	-7.6	2	11	1	19.3	16.9	-4	13	1	16.4	12.6	-2	3	2	24.1	-21.7	5	11	3	9.7	10.3	1	9	4	10.8	-9.6
2	8	0	38.6	40.8	2	13	1	9.5	9.2	-4	15	1	11.9	12.7	-2	4	2	4.1	-7.3	6	5	3	11.9	11.6	1	10	4	15.4	12.4
2	9	0	3.0	3.0	2	15	1	8.4	7.3	-4	17	1	5.9	7.9	-2	7	2	26.4	30.0	-1	2	3	58.4	-53.2	1	11	4	8.1	-9.3
2	10	0	12.0	12.9	2	16	1	8.2	6.2	-5	1	1	50.0	55.2	-2	8	2	48.4	54.2	-1	3	3	57.2	48.2	1	12	4	10.1	10.0
2	11	0	9.8	-8.7	2	17	1	8.8	8.1	-5	3	1	31.7	34.4	-2	10	2	31.5	30.9	-1	4	3	26.2	25.2	1	14	4	11.0	10.3
2	12	0	13.6	15.2	3	1	1	44.1	43.6	-5	5	1	17.9	18.2	-2	11	2	10.0	-7.7	-1	5	3	52.9	46.9	2	1	4	26.5	-28.6
2	14	0	13.2	12.9	3	2	1	27.2	-26.8	-5	6	1	10.7	12.2	-2	12	2	14.1	10.3	-1	6	3	9.4	-10.5	2	2	4	24.9	23.5
2	16	0	11.9	10.4	3	3	1	6.7	-8.2	-5	7	1	18.7	20.0	-2	14	2	10.3	7.4	-1	7	3	37.0	41.0	2	3	4	15.4	-19.1
2	18	0	6.0	7.5	3	4	1	8.8	9.3	-5	8	1	10.2	-10.5	-2	16	2	12.7	12.0	-1	9	3	21.9	23.3	2	4	4	36.8	35.6
3	1	0	5.1	-5.7	3	5	1	3.2	-2.2	-5	9	1	38.5	37.0	-3	7	2	27.1	29.8	-1	10	3	10.0	10.6	2	5	4	10.0	11.7
3	2	0	2.2	1.6	3	6	1	15.8	13.9	-5	11	1	13.5	12.7	-3	8	2	40.9	46.2	-1	11	3	10.4	13.4	2	6	4	24.2	29.5
3	3	0	5.6	3.5	3	7	1	19.1	20.9	-5	15	1	9.0	7.7	-3	9	2	15.5	-17.5	-1	12	3	24.2	-23.2	2	8	4	18.0	19.8
3	4	0	14.3	-11.2	3	9	1	36.0	35.2	-6	1	1	22.5	24.9	-3	10	2	27.6	33.4	-1	13	3	10.2	11.8	2	10	4	9.9	12.0
3	5	0	34.4	-33.3	3	10	1	8.6	6.7	-6	3	1	29.1	33.4	-3	11	2	10.2	-7.5	-2	2	3	80.2	-76.4	2	12	4	14.0	12.8
3	6	0	18.7	-16.8	3	11	1	12.6	13.2	-6	4	1	13.4	-15.1	-3	12	2	27.9	29.3	-2	3	3	13.7	-14.2	2	14	4	10.9	8.8
3	8	0	51.5	52.0	3	13	1	12.1	11.9	-6	6	1	27.4	23.9	-3	14	2	18.8	15.5	-2	4	3	57.5	54.1	3	1	4	6.6	5.1
3	9	0	6.4	-5.9	3	15	1	11.4	11.3	-6	7	1	13.9	11.1	-3	16	2	13.3	11.3	-2	5	3	77.9	75.7	3	4	4	8.8	9.9
3	10	0	22.2	24.5	3	17	1	6.4	5.9	-6	8	1	9.4	8.3	-3	4	2	68.9	75.2	-2	6	3	11.2	9.0	3	8	4	16.8	13.7
3	11	0	8.6	-6.9	4	1	1	11.6	11.0	-6	9	1	9.1	10.7	-3	2	2	83.6	87.5	-2	7	3	37.8	35.1	3	12	4	15.1	16.0
3	12	0	19.0	18.9	4	2	1	18.9	20.3	-7	2	1	8.3	8.4	-4	7	2	11.2	-12.8	-2	8	3	4.9	-5.9	3	13	4	6.9	6.1
3	13	0	8.7	-8.7	4	3	1	10.6	7.4	-7	3	1	26.5	25.6	-4	8	2	39.2	40.0	-2	9	3	18.0	19.5	3	14	4	7.0	8.8
3	14	0	10.4	9.4	4	4	1	13.4	14.2	-7	7	1	13.2	13.2	-4	9	2	9.7	7.9	-2	11	3	33.0	35.0	4	4	4	17.3	17.1
3	16	0	11.5	11.4	4	5	1	20.4	23.7	-7	9	1	14.3	12.2	-4	10	2	23.0	20.9	-2	12	3	12.6	-14.1	4	7	4	12.4	10.9
4	1	0	30.7	-27.9	4	7	1	18.2	14.1	-8	1	1	19.5	18.9	-4	11	2	10.5	-9.3	-2	13	3	9.9	13.7	4	8	4	8.9	9.1
4	2	0	64.9	64.8	4	8	1	10.3	6.9	-8	4	1	8.4	7.3	-4	12	2	24.9	24.9	-2	15	3	14.9	16.0	4	12	4	7.3	8.3
4	3	0	29.8	35.2	4	9	1	22.1	20.0	-8	7	1	16.4	15.3	-4	16	2	10.0	9.9	-3	1	3	45.1	42.6	5	2	4	10.3	11.4
4	4	0	46.3	48.7	4	11	1	12.3	13.0	-8	9	1	16.2	15.7	-5	8	2	20.9	21.9	-3	2	3	10.1	7.8	5	4	4	16.3	17.4
4	5	0	16.5	19.8	4	13	1	16.0	14.2	-8	12	1	5.8	-6.5	-5	11	2	12.2	-11.8	-3	3	3	4.0	-2.2	5	6	4	17.8	15.7
4	6	0	26.8	26.2	5	1	1	26.6	27.8	-9	1	1	14.9	12.2	-5	13	2	6.7	6.3	-3	4	3	6.9	-7.6	-1	2	4	29.8	25.1
4	8	0	40.1	38.8	5	2	1	19.9	-21.0	-9	2	1	6.8	-8.5	-7	10	2	13.6	11.4	-3	5	3	62.3	59.8	-1	3	4	15.9	-15.6
4	10	0	27.6	26.5	5	3	1	22.9	27.3	-9	5	1	9.6	8.9	-7	8	2	22.8	25.2	-3	6	3	20.9	20.2	-1	4	4	49.4	45.4
4	12	0	10.8	10.7	5	5	1	21.8	20.4	-9	7	1	9.4	8.1	-7	6	2	12.6	12.6	-3	7	3	16.1	17.0	-1	5	4	33.4	31.4
5	1	0	12.8	-9.9	5	6	1	17.1	18.1	-9	9	1	6.4	5.9	-7	3	2	10.1	-8.3	-3	9	3	30.4	30.9	-1	6	4	32.3	28.2
5	2	0	53.9	51.2	5	7	1	25.7	23.5	-10	1	1	6.6	5.8	-8	8	2	15.6	15.1	-3	11	3	37.5	38.7	-1	7	4	29.6	31.4
5	3	0	7.5	6.7	5	8	1	11.5	10.2	-10	7	1	5.6	5.5	-8	10	2	13.6	14.9	-3	12	3	8.4	11.0	-1	8	4	18.6	17.1
5	4	0	37.5	35.5	5	9	1	16.8	14.7	6	4	2	17.6	19.2	-9	8	2	11.1	9.1	-3	13	3	17.7	20.6	-1	9	4	17.3	16.1
5	5	0	18.6	18.5	5	10	1	7.1	-6.5	6	6	2	12.3	9.6	-9	10	2	10.4	9.8	-3	14	3	7.5	5.6	-1	10	4	13.0	13.2
5	6	0	19.8	19.8	5	11	1	9.1	7.3	6	7	2	14.7	11.4	0	1	3	78.0	74.6	-4	1	3	50.2	45.5	-1	12	4	14.2	16.9
5	8	0	34.8	37.2	5	15	1	4.9	6.3	5	6	2	7.2	6.1	0	2	3	29.2	-25.8	-4	2	3	21.7	-22.4	-1	14	4	7.7	10.4
5	9	0	14.8	15.2	6	1	1	37.9	39.9	5	7	2	16.3	15.0	0	3	3	79.4	79.5	-4	3	3	58.5	55.8	-2	2	4	28.8	25.2
5	11	0	9.0	9.5	6	2	1	7.3	4.9	5	8	2	26.8	29.0	0	4	3	3.6	4.7	-4	4	3	40.3	-37.7	-2	3	4	34.8	32.1
6	2	0	19.9	23.9	6	3	1	16.2	16.5	4	7	2	11.8	11.9	0	5	3	38.6	35.1	-4	5	3	26.4	26.8	-2	4	4	72.7	65.4
6	4	0	16.5	14.9	6	4	1	8.3	-5.7	4	8	2	28.4	35.2	0	6	3	26.9	25.7	-4	6	3	36.8	37.5	-2	5	4	25.2	24.5
6	7	0	20.9	20.4	6	7	1	17.7	14.1	4	10	2	10.5	9.8	0	7	3	19.3	17.1	-4	7	3	31.5	33.1	-2	6	4	44.3	44.3
6	8	0	17.7	15.8	6	9	1	13.9	14.2	4	11	2	11.6	-10.6	0	8	3	9.0	7.7	-4	8	3	7.3	5.4	-2	7	4	26.5	22.0
6	9	0	7.0	-7.1	7	3	1	16.2	15.6	4	12	2	13.9	12.2	0	9	3	13.3	14.2	-4	9	3	32.8	35.0	-2	8	4	38.2	40.4
6	12	0	9.0	8.7	7	5	1	13.1	9.9	4	14	2	10.8	8.5	0	10	3	7.0	-7.2	-4	11	3	16.9	17.4	-2	9	4	14.9	17.5
7	4	0	6.6	-5.1	7	9	1	10.4	8.2	3	7	2	9.6	8.7	0	13	3	16.4	18.3	-5	1	3	24.6	24.2	-2	10	4	18.1	18.5
7	5	0	10.2	-9.5	-1	3	1	39.4	-39.3	3	8	2	16.5	15.1	1	1	3	49.3	47.9	-5	3	3	58.1	60.8	-2	12	4	25.2	26.5
7	6	0	13.0	14.6	-1	4	1	24.9	25.4	3	9	2	13.4	11.6	1	2	3	10.5	10.1	-5	4	3	22.1	-22.0	-2	13	4	9.1	9.5
7	8	0	11.6	10.1	-1	5	1	39.2	38.1	3	10	2	13.2	10.0	1	3	3	17.2	18.2	-5	5	3	28.4	33.5	-2	14	4	15.0	13.8
7	9	0	13.7	-14.3	-1	6	1	12.9	11.3	3	11	2	6.1	-6.4	1	4	3	5.8	-4.2	-5	6	3	5.2	3.9	-3	1	4	12.0	-9.7
7	10	0	10.3	9.3	-1	7	1	52.9	49.2	3	12	2	16.8	14.5	1	5	3	21.4	22.3	-5	7	3	12.1	12.9	-3	2	4	47.0	43.3
8	4	0	10.0	9.6	-1	8	1	31.5	31.9	3	14	2	12.1	11.2	1	6	3	11.4	9.8	-5	10	3	16.8	-17.1	-3	3	4	45.4	-39.7
8	5	0	8.3	-9.4	-1	9	1	22.5	26.7	2	8	2	34.6	39.5	1	7	3	35.8	38.5	-6	1	3	40.4	43.3	-3	4	4	46.7	41.8
8	6	0	9.3	10.6	-1	10	1	10.1	11.5	2	10	2	13.8	15.6	1	8	3	9.0	9.3	-6	2	3	12.7	12.5	-3	5	4	22.9	17.1
9	1	0	6.2	-5.1	-1	11	1	19.3	20.0	2	11	2	6.9	7.2	1	9	3	13.5	14.9	-6	4	3	15.9	-19.2	-3	6	4	42.9	46.4
9	2	0	7.1	8.4	-1	15	1	11.7	11.1	2	12	2	15.8	15.4	1	13	3	19.3	15.8	-6	5	3	17.4	19.2	-3	7	4	19.0	-17.6
9	3	0	3.3	2.8	-1	17	1	11.6	12.7	2	13	2	12.2	9.6	2	1	3	22.8	-22.7	-7	1	3	18.2	19.2	-3	8	4	20.9	21.1
9	4	0	8.7	6.0	-1	18	1	4.2	-3.5	2	14	2	10.4	7.0	2	2	3	11.9	-11.4	-7	3	3	20.6	25.2	-3	9	4	6.9	9.8
0	3	1	99.0	100.1	-2	1	1	66.8	67.9	2	15	2	10.4	7.3	2	3	3	58.3	58.0	-7	4	3	10.9	-8.9	-3	10	4	22.6	27.3
0	5	1	21.1	19.3	-2	2	1	3.7	-5.8	2	16	2	9.6	7.3	2	4	3	16.8	-18.3	-7	5	3	11.2	12.2	-3	11	4	6.6	-9.8
0	6	1	1.2	0.8	-2	3	1	46.3	-41.8	1	7	2	12.1	-11.8	2	5	3	24.5	24.0	-7	6	3	16.3	18.5	-3	12	4	24.0	27.8
0	7	1	13.1	15.0	-2	4	1	14.5	14.8	1	8	2	47.7	50.3	2	6	3	4.9	-4.3	-7	7	3	20.6	25.1	-3	14	4	13.7	13.8
0	8	1	16.2	18.3	-2	5	1	42.9	41.8	1	9	2	7.7	6.0	2	7	3	8.7	8.4	-7	9	3	18.0	20.8	-4	1	4	30.5	-31.2
0	9	1	38.1	35.4	-2	6	1	47.3	46.0	1	10	2	21.7	25.0	2	8	3	6.0	6.4	-8	1	3	14.6	14.0	-4	3	4	45.3	-41.7
0	10	1	7.7	7.6	-2	7	1	24.0	29.0	1	11	2	8.0	-5.6	2	9	3	26.7	28.2	-8	3	3	28.2	29.5	-4	4	4	15.5	17.1
0	11	1	17.5	19.8	-2	9	1	29.3	31.5	1	12	2	17.4	17.0	2	11	3	14.6	15.2	-8	4	3	8.3	7.6	-4	5	4	16.7	-14.4
0	12	1	10.8	-8.7	-2	10	1	11.1	-14.2	1	14	2	13.3	10.4	2	12	3	5.8	-3.7	-8	5	3	13.1	11.2	-4	6	4	43.5	49.5

Table 3 (*cont.*)

h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc
-4	7	4	22.1	-19.4	4	11	5	7.4	7.3	4	0	-2	67.0	64.5	10	1	-7	15.9	12.9	2	2	7	12.6	13.5	0	4	6	28.7	32.0
-4	9	4	5.3	-5.8	5	5	5	13.7	13.4	5	0	-2	72.6	70.2	11	1	-7	8.7	8.3	2	2	6	10.2	9.7	1	4	6	17.1	20.7
-4	10	4	15.1	12.8	-1	1	5	12.1	9.0	6	0	-2	15.1	14.6	3	1	-8	11.2	-13.8	3	2	2	16.5	15.3	1	4	2	67.5	58.5
-4	11	4	6.7	-8.4	-1	2	5	6.7	8.6	7	0	-2	26.4	27.0	6	1	-8	8.6	-8.4	4	2	2	28.0	27.7	0	4	2	43.8	38.3
-5	1	4	11.4	-10.2	-1	3	5	26.6	22.0	9	0	-2	13.4	11.0	7	1	-8	7.9	-7.5	5	2	2	19.7	22.4	1	5	-6	12.8	-13.8
-5	2	4	16.7	15.1	-1	4	5	26.6	22.9	10	0	-2	9.9	11.1	1	1	-9	16.6	19.2	6	2	2	15.3	15.3	4	5	-6	12.4	-13.3
-5	3	4	19.4	-16.8	-1	5	5	27.9	26.8	1	0	-4	37.8	-36.7	2	1	-9	16.5	10.8	2	3	-6	10.7	9.3	5	5	-6	12.0	-11.3
-5	4	4	36.3	33.5	-1	6	5	12.9	10.3	2	0	-4	41.2	42.2	4	1	-9	10.5	13.5	3	3	-6	19.7	16.8	1	5	-7	19.8	20.8
-5	5	4	18.5	19.7	-1	7	5	27.9	28.8	3	0	-4	75.8	82.5	5	1	-9	39.4	34.6	4	3	-6	11.8	-11.0	2	5	-7	27.9	29.0
-5	6	4	17.5	19.6	-1	8	5	13.9	15.3	4	0	-4	30.1	29.6	6	1	-9	32.6	26.0	5	3	-6	8.8	-7.1	3	5	-7	16.4	23.0
-5	9	4	10.3	-12.1	-1	9	5	18.9	18.1	5	0	-4	19.5	21.1	8	1	-9	17.6	16.7	6	3	-6	10.4	10.0	4	5	-7	23.4	24.4
-6	1	4	16.6	15.9	-1	10	5	12.9	15.3	6	0	-4	26.0	22.9	9	1	-9	19.8	17.7	9	3	-6	10.5	7.4	5	5	-7	28.7	29.7
-6	2	4	53.5	56.0	-2	2	5	37.2	-37.8	7	0	-4	35.8	34.7	10	1	-9	15.9	14.2	1	3	-7	21.2	23.8	6	5	-7	16.8	16.9
-6	3	4	5.4	-3.3	-2	3	5	59.3	56.3	11	0	-4	9.8	7.8	11	1	-9	15.9	13.5	2	3	-7	34.2	37.4	7	5	-7	30.7	27.2
-6	4	4	36.7	41.2	-2	4	5	44.5	44.6	1	0	-6	21.2	22.7	7	1	-11	12.1	9.5	3	3	-7	17.2	17.6	8	5	-7	26.3	22.3
-6	5	4	13.2	14.7	-2	5	5	32.7	32.6	2	0	-6	32.5	30.2	8	1	-11	17.0	16.2	4	3	-7	21.4	19.8	9	5	-7	14.8	14.2
-6	6	4	18.5	16.0	-2	6	5	20.7	23.7	3	0	-6	20.3	-21.5	9	1	-11	15.8	15.3	5	3	-7	32.3	35.6	10	5	-7	16.1	14.6
-6	7	4	6.4	8.6	-2	7	5	16.5	16.5	4	0	-6	4.8	-5.7	10	1	-11	12.8	11.3	6	3	-7	17.4	15.3	11	5	-7	9.5	9.3
-6	8	4	9.2	12.9	-2	8	5	8.8	-11.3	5	0	-6	67.6	66.1	11	1	-11	7.4	8.4	7	3	-7	26.5	31.4	3	5	-8	8.2	8.4
-6	9	4	11.4	13.6	-2	9	5	22.1	24.4	6	0	-6	35.4	32.8	5	2	-12	11.4	12.1	8	3	-7	21.0	22.5	5	5	-8	12.1	-12.5
-6	10	4	23.0	22.3	-3	2	5	5.3	4.5	7	0	-6	1.2	-0.6	6	2	-12	11.4	10.8	9	3	-7	11.3	10.8	6	5	-9	12.7	13.3
-7	2	4	28.4	32.9	-3	3	5	48.8	45.1	8	0	-6	9.7	9.1	7	2	-12	9.4	9.5	10	3	-7	10.1	10.7	7	5	-9	23.0	21.4
-7	3	4	6.2	-7.3	-3	4	5	18.3	-16.4	9	0	-6	20.0	16.8	8	2	-12	14.0	14.5	11	3	-7	10.3	12.0	10	5	-9	18.4	17.2
-7	4	4	24.5	28.1	-3	5	5	50.8	55.0	1	0	-8	11.5	9.4	9	2	-12	9.5	10.0	4	3	-9	13.4	16.7	9	5	-11	13.7	12.8
-7	5	4	7.2	7.0	-3	6	5	26.9	-29.0	5	0	-8	26.5	29.3	8	2	-11	8.0	5.8	5	3	-9	36.0	36.6	10	5	-5	15.6	13.2
-7	6	4	33.2	36.2	-3	7	5	15.9	13.0	6	0	-8	40.8	38.9	5	2	-10	27.6	25.2	6	3	-9	27.9	29.9	11	5	-5	8.8	10.0
-7	7	4	14.3	18.8	-4	1	5	49.2	45.0	7	0	-8	28.5	28.4	6	2	-10	10.9	12.7	8	3	-9	6.2	-6.9	2	5	-2	25.2	-22.0
-7	8	4	13.4	19.5	-4	2	5	3.1	-2.1	10	0	-8	13.6	11.2	8	2	-10	14.6	14.1	9	3	-9	10.4	11.6	4	5	-2	40.1	39.6
-8	1	4	11.3	11.1	-4	3	5	15.9	4.2	11	0	-8	8.4	8.2	9	2	-10	20.0	17.0	10	3	-9	18.6	16.1	5	5	-2	18.5	-17.7
-8	2	4	11.4	13.7	-4	4	5	41.1	-38.6	3	0	-10	13.7	14.7	10	2	-10	15.3	13.9	5	3	-8	8.8	-8.0	6	5	-2	17.3	-16.5
-8	4	4	23.7	25.6	-4	5	5	47.9	57.4	4	0	-10	10.5	10.7	1	2	-9	16.6	-16.5	6	3	-8	11.5	-11.9	7	5	-2	7.2	-8.0
-9	1	4	9.0	7.5	-4	7	5	28.3	29.8	5	0	-10	36.2	32.3	4	2	-9	6.9	-7.4	8	3	-5	17.9	19.1	8	5	-2	9.6	-8.2
-9	2	4	12.3	15.4	-5	1	5	29.0	29.6	6	0	-10	10.5	12.0	5	2	-9	12.2	-11.2	9	3	-5	15.9	16.5	5	5	2	8.2	-8.7
-9	3	4	8.3	-7.9	-5	2	5	12.0	11.4	7	0	-10	3.5	2.1	6	2	-9	10.9	10.4	10	3	-5	14.2	16.7	4	5	2	16.7	20.9
-10	1	4	8.3	-11.8	-5	3	5	37.4	38.8	8	0	-10	18.1	13.6	7	2	-9	9.3	-6.9	11	3	-5	11.6	12.0	3	5	2	9.8	-8.3
0	1	5	18.1	18.5	-5	4	5	9.0	-9.7	9	0	-10	20.4	19.3	8	2	-9	16.5	-13.2	3	3	-2	72.9	62.7	3	5	7	14.1	14.8
0	2	5	13.3	-11.2	-5	5	5	37.5	39.0	10	0	-10	15.6	14.1	1	2	-8	21.9	25.2	4	3	-2	19.0	15.1	2	5	7	11.6	13.0
0	3	5	50.9	48.7	-5	6	5	14.4	18.0	11	0	-10	11.5	10.3	2	2	-8	20.5	19.0	5	3	-2	23.4	21.9	2	5	2	8.9	-6.8
0	4	5	12.7	8.7	-6	1	5	38.5	42.4	9	0	-12	11.6	11.4	3	2	-8	21.3	25.2	1	3	2	37.7	-35.4	1	5	2	28.8	25.3
0	5	5	33.4	30.4	-6	3	5	27.3	32.3	10	0	-12	13.7	12.8	4	2	-8	19.5	20.9	0	3	7	23.9	24.8	0	5	7	10.1	11.5
0	6	5	6.1	6.3	-6	5	5	26.9	27.6	5	0	-12	12.8	7.7	5	2	-8	25.9	25.8	0	3	6	9.2	12.0	0	5	2	40.3	46.8
0	8	5	9.6	9.5	-7	1	5	12.6	16.3	11	1	-5	14.7	14.6	6	2	-8	24.2	28.3	2	3	2	7.2	-7.4	1	6	-6	20.2	21.0
0	11	5	13.8	16.1	-7	3	5	25.2	30.7	3	1	-5	20.2	23.4	7	2	-8	12.3	12.4	3	3	2	7.8	7.5	2	6	-6	32.7	38.7
1	1	5	42.9	40.9	-7	5	5	30.5	33.0	2	1	-5	2.8	-3.3	8	2	-8	12.8	15.2	4	3	2	8.8	-9.6	3	6	-6	19.2	17.4
1	2	5	12.1	-11.8	0	0	2	96.1	97.7	2	1	-4	33.6	-33.1	9	2	-8	19.5	17.9	1	4	-6	33.9	36.1	4	6	-6	18.5	21.6
1	3	5	32.8	32.1	0	0	4	63.4	60.4	1	1	-3	76.2	69.0	10	2	-8	15.9	13.7	2	4	-6	14.3	16.8	5	6	-6	34.1	39.4
1	4	5	15.8	12.5	0	0	8	23.0	22.8	2	1	-3	26.4	28.6	11	2	-8	18.2	14.8	3	4	-6	40.8	45.1	6	6	-6	32.2	30.2
1	5	5	19.9	22.9	0	0	10	15.3	18.1	3	1	-2	33.8	28.1	12	2	-8	7.8	9.2	4	4	-6	39.7	43.0	7	6	-6	30.7	28.0
1	6	5	6.2	-5.3	2	0	0	82.0	-75.7	4	1	-2	41.9	-38.8	1	2	-7	11.8	-14.0	5	4	-6	26.1	25.6	8	6	-6	20.9	21.4
1	7	5	23.6	23.9	3	0	0	69.4	65.8	6	1	-2	12.8	12.8	2	2	-7	14.3	-19.5	6	4	-6	46.1	45.6	9	6	-6	16.4	14.7
1	8	5	14.9	-15.3	4	0	0	33.9	38.5	0	1	8	19.0	23.7	3	2	-7	16.3	-16.7	7	4	-6	22.9	19.5	10	6	-6	8.6	11.8
1	9	5	12.3	12.8	5	0	0	36.5	41.6	0	1	6	10.2	12.0	4	2	-7	23.1	24.0	5	4	-7	11.7	-13.0	5	6	-7	11.1	13.4
2	1	5	9.2	6.3	6	0	0	24.4	27.4	1	1	2	20.9	-24.1	5	2	-7	15.9	-14.3	6	4	-7	12.2	-11.0	7	6	-7	10.7	-9.9
2	2	5	12.1	11.0	7	0	0	23.0	24.8	1	1	8	14.5	17.7	6	2	-7	9.6	-6.5	1	4	-8	17.0	19.3	5	6	-8	26.7	27.4
2	3	5	40.8	44.7	8	0	0	13.1	12.1	1	1	7	16.8	16.6	8	2	-7	15.9	-15.1	2	4	-8	31.8	31.5	6	6	-8	36.6	32.7
2	4	5	18.4	-21.3	9	0	0	9.4	10.1	1	1	6	12.7	17.8	1	2	-6	18.6	21.1	5	4	-8	29.2	26.4	7	6	-8	26.7	25.2
2	5	5	26.3	27.3	1	0	2	113.8	124.9	2	1	2	19.8	-20.3	2	2	-6	38.7	37.8	6	4	-8	20.3	21.0	8	6	-8	15.6	14.7
2	6	5	8.3	-8.2	2	0	2	91.1	97.6	2	1	6	11.7	13.3	3	2	-6	27.5	27.4	7	4	-8	10.8	11.8	9	6	-8	11.3	12.8
2	7	5	25.4	22.3	5	0	2	23.2	21.5	3	1	2	8.8	-9.5	4	2	-6	26.9	27.1	10	4	-8	15.6	13.8	10	6	-8	11.0	12.2
2	8	5	2.6	2.1	6	0	2	13.7	12.9	4	1	2	13.4	-15.2	5	2	-6	45.9	40.7	9	4	-10	14.7	11.6	9	6	-10	14.6	15.0
2	9	5	9.5	11.7	7	0	2	15.8	18.1	5	1	2	5.2	7.0	7	2	-6	13.5	13.9	9	4	-6	17.6	14.6	10	6	-10	11.1	13.6
2	13	5	13.4	16.1	8	0	2	4.9	6.9	6	1	3	16.6	17.0	9	2	-6	13.8	16.6	10	4	-6	20.5	18.1	7	6	-5	14.9	-9.5
3	1	5	8.9	7.7	1	0	4	23.7	29.2	1	1	-6	24.9	-27.6	10	2	-6	24.2	24.7	11	4	-6	9.0	9.9	6	6	-5	13.5	-11.8
3	3	5	15.0	14.7	2	0	4	17.6	15.6	2	1	-6	6.1	-9.1	11	2	-6	18.5	16.5	6	4	-5	7.5	-7.5	8	6	-4	16.7	17.1
3	4	5	14.8	-18.1	3	0	4	13.3	11.9	3	1	-6	37.5	38.1	9	2	-5	11.5	9.6	4	4	-2	66.5	57.7	8	6	-3	7.7	-6.0
3	5	5	9.9	9.1	5	0	4	15.7	14.4	5	1	-6	6.5	-5.1	4	2	-2	32.3	33.8	5	4	-2	14.4	-14.9	2	6	-2	28.6	24.8
3	6	5	16.5	15.0	6	0	4	19.8	19.1	6	1	-6	14.8	-14.2	5	2	-2	22.8	21.1	6	4	-2	18.9	21.7	3	6	-2	49.0	46.9
3	7	5	9.3	7.1	2	0	6	26.8	28.3	7	1	-6	20.0	-18.0	6	2	-2	30.6	29.9	7	4	-2	14.1	13.5	4	6	-2	37.8	40.4
3	8	5	7.6	5.2	3	0	6	15.0	12.4	1	1	-7	7.0	8.3	7	2	-2	21.5	21.7	8	4	-2	17.2	14.2	5	6	-2	27.1	26.5
3	9	5	8.4	9.0	1	0	8	11.0	10.4	2	1	-7	14.0	13.2	8	2	-2	24.1	21.3	5	4	2	14.7	16.7	8	6	-2	17.3	16.1
3	10	5	6.4	-4.3	2	0	8	13.8	14.6	3	1	-7	35.2	38.4	9	2	-2	13.5	12.9	4	4	2	21.9	25.8	0	6	2	39.4	39.1
3	11	5	9.5	9.9	3	0	8	10.0	9.1	4	1	-7	21.4	20.6	11	2	-4	11.8	10.5	3	4	6	22.7	24.4	1	6	2	36.5	35.1
3	12	5	6.6	6.8	1	0	10	9.3	13.0	5	1	-7	7.6	8.1	10	2	-4	7.5	10.2	3	4	2	26.6	24.6	2	6	2	30.1	31.4
3	13	5	6.7	8.5	1	0	-2	23.2	16.8	6	1	-7	37.5	39.2	0	2	6	17.3	17.0	2	4	6	18.1	22.4	2	6	6	14.8	15.8
4	2	5	16.4	15.8	2	0	-2	91.9	104.4	7	1	-7	9.7	13.1	0	2	8	15.9	19.6	2	4	2	32.7	38.4	3	6	2	17.1	18.1
4	5	5	13.6	11.6	3	0	-2	51.8	50.9	9	1	-7	16.1	16.0	1	2	6	19.3	23.0	1	4	8	13.1	14.2					

through the heterocyclic rings make an angle of 82·8° to each other, and are inclined at 89·9° and 78·9° to the square plane of copper and oxygen atoms. The Cu–O distances of 1·91 Å and 1·93 Å compare with the Cu–O distances of 1·92 Å and 1·93 Å in $Cu(PyO)_4(ClO_4)_2$ (Lee, Brown & Melsom, 1969) 1·89 Å and 1·90 Å in bis-(*N*-t-butylsalicylaldiminato) copper(II)] (Cheeseman, Hall & Waters, 1966); 1·90 Å in bis(salicylaldiminato)copper(II) (Baker, Hall & Waters, 1966); 1·91 Å and 1·94 Å in copper ethyl acetoacetate (Barclay & Cooper, 1965); and agrees with the normal single bond value of 1·94 Å (Pauling, 1960).

The angles Cu–O(1)–N(1) and Cu–O(2)–N(2) are greater than tetrahedral (116·7° and 118·6° respectively). This may be explained by the repulsive force between O(1)–N(2), and the similar one between O(2)–N(1) exceeding the repulsions between lone pairs of electrons on the oxygen atoms. On the other hand, Abrahams (1956) has noted that two-bonded oxygen usually has a bond angle which is tetrahedral or less,

Table 4. *Agreement analysis*

F_{obs}	R	sin θ	R	Layer	R
0–5	39·5%	0·00–0·10	–	*hk*0	7·1%
5–10	20·9	0·10–0·20	9·7%	*hk*1	7·8
10–15	15·0	0·20–0·30	10·3	*hk*2	11·7
15–20	14·8	0·30–0·40	8·0	*hk*3	7·8
20–25	14·4	0·40–0·50	11·7	*hk*4	10·2
25–30	11·9	0·50–0·60	16·7	*hk*5	9·9
30–35	11·0	0·60–0·70	14·9	*h*0*l*	8·2
35–40	10·4	0·70–0·80	14·7	*h*1*l*	11·3
40–45	7·9	0·80–0·90	11·9	*h*2*l*	9·3
45–50	8·3	0·90–1·00	18·3	*h*3*l*	10·0
50–55	7·9			*h*4*l*	10·8
55–60	7·6			*h*5*l*	9·4
60–65	4·6			*h*6*l*	8·8
65–70	4·4				
70–75	6·9				
75–80	6·6				
80–85	7·7				
85–90	12·9				
90–95	5·1				
95–100	9·5				

Table 5. *Bond lengths and their standard deviations*

	Distance	σ
Cu —O(1)	1·93 Å	0·008 Å
Cu —O(2)	1·91	0·010
O(1)–N(1)	1·31	0·013
O(2)–N(2)	1·36	0·012
N(1)–C(1)	1·38	0·010
N(1)–C(5)	1·35	0·011
N(2)–C(6)	1·31	0·006
N(2)–C(10)	1·31	0·015
C(1)–C(2)	1·34	0·021
C(2)–C(3)	1·39	0·014
C(3)–C(4)	1·38	0·013
C(4)–C(5)	1·39	0·021
C(6)–C(7)	1·39	0·018
C(7)–C(8)	1·35	0·021
C(8)–C(9)	1·40	0·008
C(9)–C(10)	1·42	0·020
B —F(1)	1·40	0·024
B —F(2)	1·36	0·023
B —F(3)	1·35	0·014
B —F(4)	1·31	0·012

Table 6. *Bond angles and their standard deviations*

	Angle	σ
O(1)–Cu—O(2)	88·4°	0·4°
Cu —O(1)—N(1)	116·7	0·6
Cu —O(2)—N(2)	118·6	0·7
O(1)–N(1)—C(1)	120·5	0·7
O(1)–N(1)—C(5)	119·5	0·7
C(1)–N(1)—C(5)	120·0	1·0
N(1)–C(1)—C(2)	120·5	0·8
C(1)–C(2)—C(3)	121·3	0·9
C(2)–C(3)—C(4)	117·7	1·3
C(3)–C(4)—C(5)	120·8	0·9
C(4)–C(5)—N(1)	119·7	0·8
O(2)–N(2)—C(6)	116·8	1·0
O(2)–N(2)—C(10)	117·3	0·5
C(6)–N(2)—C(10)	125·7	1·0
N(2)–C(6)—C(7)	119·5	1·1
C(6)–C(7)—C(8)	118·9	0·7
C(7)–C(8)—C(9)	120·0	1·3
C(8)–C(9)—C(10)	118·9	1·4

Table 6 (*cont.*)

	Angle	σ
C(9)–C(10)–N(2)	117·0	0·6
F(1)–B —F(2)	104·4	1·5
F(1)–B —F(3)	111·3	1·3
F(1)–B —F(4)	111·3	1·1
F(2)–B —F(3)	110·6	1·1
F(2)–B —F(4)	109·8	1·3
F(3)–B —F(4)	109·3	1·5

but an exception occurs if the attached groups are aromatic, when the bond angles are nearer to 120°, implying an approach to sp^2 hybridization.

The fluoroborate ions occupy approximately octahedral positions relative to the square plane around the copper, with closest approaches to the copper of 3·34 Å and 3·53 Å from F(3) and F(1) respectively. This compares with a Cu–F distance of 2·56 Å in $Cu(en)_2(BF_4)_2$ (Brown, Lee & Melsom 1968) where a weak form of bonding termed 'semi-coordination' has been proposed (Brown, Lee, Melsom, Hathaway, Procter & Tomlinson, 1967). The Cu–F approaches in the present complex are too large for there to be any bonding of this type, and this is confirmed by the fact that no fluorine atom is favourably positioned to form an octahedral complex. Semi-coordination has been to result in considerable distortion of the polyanion tetrahedron in both $Cu(en)_2(BF_4)_2$ (Brown, Lee & Melsom, 1968), and $Cu(en)_2(ClO_4)_2$ (Pajunen, 1967). Where there is no semi-coordinated bond as in $Cu(PyO)_4(ClO_4)_2$ and $Cu(PyO)_4(BF_4)_2$ much less distortion is to be expected, and this has been observed to be the case in $Cu(PyO)_4(ClO_4)_2$ (Lee, Brown & Melsom, 1969).

In $Cu(PyO)_4(BF_4)_2$ the B–F bond lengths vary from 1·38 Å to 1·40 Å with an average value of 1·35 Å. This average value is appreciably shorter than the value of 1·40 Å reported for KBF_4 (Bellanca & Sgarlata, 1951)

and 1·43 Å in $RhBF_4$ and NH_4BF_4 (Pendred & Richards, 1955). The sum of the single bond covalent radii of boron and fluorine (Pauling, 1960) is 1·53 Å, and if this is corrected for partial ionic character arising from differences in electronegativity (Schomaker & Stevenson, 1941) the predicted value becomes 1·37 Å in good agreement with our observed value. Although the bond B–F (4) appears to be significantly shortened, the reason for this is not apparent and it is unlikely that the spread of values is meaningful. The mean F–B–F bond angle is 109·5°, with a range of values from 104° to 111°.

Despite the fluorine atoms having high temperature factors, three-dimensional difference syntheses have provided no evidence of disorder of the BF_4^- ion. Examination of the anisotropic temperature factors of the fluorine atoms reveal that the atoms F(2), F(3) and F(4) are vibrating most along the b^* direction whilst F(1) is vibrating most in the a^*c^* plane. This is consistent with distorting modes of vibration rather than libration of the whole ion, although small angular oscillations of the ion are not precluded.

The BF_4^- ion is involved in a large number of interatomic contacts between 3·1 Å and 3·5 Å. Those contacts with different 'molecules' are given in Table 7, whilst those within the same 'molecule' are given in Table 8. Equations for the molecular planes and the distances of the atoms from them are given in Table 9.

Table 7. *Intermolecular distances less than* 3·5 Å

	Distance	Symmetry operation applied to second atom
C(4)–F(4)	3·28 Å	1
C(5)–F(4)	3·12	1
C(3)–F(3)	3·43	2
C(3)–F(4)	3·37	2
C(3)–C(7)	3·42	3
C(1)–F(2)	3·37	3
N(1)–F(2)	3·47	3
F(2)–C(1)	3·37	4
C(7)–C(3)	3·42	4
F(2)–N(1)	3·47	4
F(3)–C(3)	3·43	5
F(4)–C(3)	3·37	5
F(4)–C(9)	3·48	6
C(2)–F(1)	3·48	6
C(3)–F(1)	3·39	6
F(4)–C(4)	3·29	7
F(4)–C(5)	3·12	7
F(1)–C(7)	3·34	8
F(4)–C(8)	3·26	8
C(7)–F(1)	3·34	8
C(8)–F(4)	3·26	8
F(1)–C(2)	3·48	9
F(1)–C(3)	3·39	9
C(9)–F(4)	3·48	9

Key to symmetry operations

1. $x+1, \quad y, \quad z+1$
2. $x+1, \frac{1}{2}-y, \quad \frac{1}{2}-z$
3. $x, \frac{1}{2}-y, \quad \frac{1}{2}+z$
4. $x, \frac{1}{2}-y, \quad z+\frac{1}{2}$
5. $x-1, \frac{1}{2}-y, \quad z-\frac{1}{2}$
6. $-x, y+\frac{1}{2}, -z-\frac{1}{2}$
7. $x-1, \quad y, \quad z-1$
8. $-x, \quad -y, \quad -z-1$
9. $-x, y-\frac{1}{2}, -z-\frac{1}{2}$

Table 8. *Non-bonded contacts less than* 3·5 Å *within the asymmetric unit*

	Distance
F(1)–F(2)	2·18 Å
F(1)–F(3)	2·27
F(1)–F(4)	2·24
F(2)–F(3)	2·23
F(2)–F(4)	2·19
F(3)–F(4)	2·17
F(1)–C(6)	3·41
F(2)–C(1)	3·28
F(2)–C(6)	3·43
F(3)–Cu	3·34
F(3)–C(1)	3·27
F(3)–O(1)	3·42
N(1)–Cu	2·77
N(1)–C(2)	2·36
N(1)–C(3)	2·76
N(1)–C(4)	2·37
N(1)–O(2)	2·59
N(2)–Cu	2·83
N(2)–C(7)	2·34
N(2)–C(8)	2·69
N(2)–C(9)	2·33
O(1)–C(1)	2·34
O(1)–C(5)	2·29
O(1)–O(2)	2·67
O(2)–C(1)	3·11
O(2)–C(5)	2·94
O(2)–C(6)	2·28
O(2)–C(10)	2·28
C(1)–C(4)	2·73
C(1)–C(5)	2·37
C(2)–C(3)	2·38
C(2)–C(4)	2·37
C(2)–C(5)	2·74
C(3)–C(5)	2·40
C(6)–C(8)	2·37
C(6)–C(9)	2·73
C(6)–C(10)	2·33
C(7)–Cu	3·46
C(7)–C(9)	2·39
C(7)–C(10)	2·77
C(8)–C(10)	2·43

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Table 9. *Equations to planes*

Atoms in plane	Equations of planes
N(1), C(1), C(2), C(3), C(4), C(5)	$-5{\cdot}97x+9{\cdot}13y+7{\cdot}63z=1{\cdot}77$
N(2), C(6), C(7), C(8), C(9), C(10)	$6{\cdot}66x+9{\cdot}10y-0{\cdot}90z=1{\cdot}52$
Cu, O(1), O(2)	$2{\cdot}15x-5{\cdot}82y+6{\cdot}76z=0{\cdot}00$

x, y and z refer to fractional coordinates of the unit cell axes a, b and c.

Distances of atoms from planes

	Distance from first plane		Distance from second plane
N(1)	0·00 Å	N(2)	0·00 Å
C(1)	−0·01	C(6)	0·01
C(2)	0·01	C(7)	−0·01
C(3)	0·00	C(8)	0·00
C(4)	−0·01	C(9)	0·01
C(5)	0·01	C(10)	−0·01

Angles between planes and lines

Ring N(1)···C(5) to ring N(2)···C(10)	= 82·8°
Ring N(1)···C(5) to square plane Cu, O(1), O(2)	= 89·9
Ring N(2)···C(10) to square plane Cu, O(1), O(2)	= 78·9
Line through C(1) and C(5) to line through C(6) and C(10)	= 19·9

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Oxido Steroids. II. The Crystal and Molecular Structure of 11β,12β-Dibromo-3α,9-oxidocholanic Acid Methyl Ester

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The crystal structure of 11β,12β-dibromo-3α,9-oxidocholanic acid methyl ester has been analyzed and refined from three-dimensional intensity data to an R index of 0·14 for 2884 reflections. This steroid crystallizes from acetone in the orthorhombic space group $P2_12_12_1$ with unit-cell dimensions $a=11{\cdot}005$, $b=31{\cdot}383$, and $c=7{\cdot}133$ Å. The A ring is boat-shaped and the rings B and C are chair-shaped. The D ring is a distorted half-chair. The structural features of this molecule are discussed in comparison with those of its epimer 11β,12α-dibromo-3α,9-oxidocholanic acid methyl ester.

Introduction

11β,12β-Dibromo-3α,9-oxidocholanic acid methyl ester, $C_{25}H_{38}O_3Br_2$ (Fig. 1), is the second oxido steroid whose structure has been investigated in this laboratory. The other compound which was reported earlier is the 11β,12α-dibromo epimer of the above derivative (Gopalakrishna, Cooper & Norton, 1969). This derivative is a co-product of the 11β,12α-dibromo epimer formed in the process of bromination of 3α, 9-oxido-Δ^{11}-cholanic acid methyl ester (Mattox, Turner, Engel, McKenzie, McGuckin & Kendall, 1946). Both these epimers have the same stereochemical features, except that in one of them the bromine atom attached to C(12) is in the α-configuration and in the other it is

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