Reactions of Bis-(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)copper(II) with Pyrazine and the Crystal Structures of the 1 :1 and 2 :1 Complexes

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Reaction of $Cu(hfac)_2,H_2O$ [hfac = $(CF_3CO)_2{\cdot}CH$] with equimolar amounts of pyrazine (pyz) in carbon tetrachloride gave the 1 : 1 complex (I) $Cu(hfac)_2(pyz)$. Recrystallisation from hot carbon tetrachloride gave (I) together with (II) $[Cu(hfac)_2]_2(pyz)$. A 1 : 2 mixture of reactants gave $Cu(hfac)_2(pyz)_2$.

Three-dimensional crystal structure analyses were carried out on (I) and (II). The structures were solved from diffractometer data by the heavy-atom method and refined by least squares to R 0·58 [(I), 742 reflections] and 0·081 [(II), 956 reflections]. (I) is a linear co-ordination polymer, with $Z = 1$ in a triclinic unit cell with $a = 11{\cdot}228(6)$, $b = 6{\cdot}821(4)$, $c = 6{\cdot}742(7)$ Å, $\alpha = 109°\ 06'(5')$, $\beta = 103°\ 27'(3')$, $\gamma = 95°\ 12'(2')$, space group $P\bar{1}$. The copper is six-co-ordinated and occupies a crystallographic centre of symmetry; the two chelating hfac rings give Cu–O 1·924 and 2·004(7) and the pyrazine rings give Cu–N 2·529(9) Å. Each pyrazine ring bridges two copper atoms related by the translation [0,1,1].

The 2 : 1 complex (II), is monoclinic, with $Z = 2$ in a unit cell with $a = 10{\cdot}750(5)$, $b = 6{\cdot}761(10)$, $c = 23{\cdot}732(12)$ Å, $\beta = 93°\ 04'(1')$, space group $P2_1/c$. The centre of the pyrazine ring is on a crystallographic centre of symmetry and the five-co-ordinated copper atoms are not required to have any symmetry; in fact the co-ordination is square pyramidal, with mean base Cu–O bonds 1·94(1) Å. The copper atom is displaced 0·241 Å from the basal plane towards the nitrogen atom, Cu–N 2·250(17) Å.

In both complexes the bond lengths within the ligands are in the usual ranges.

THE reaction of 1,4-diazabicyclo[2,2,2]octane (ted) with aquobis-(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)copper(II) $[Cu(hfac)_2(H_2O)]$ gave $Cu(hfac)_2(ted)$, $Cu(hfac)_2(ted)_2$, and $[Cu(hfac)_2]_2(ted)$.[1] The structure of the 1 : 1 complex was determined and showed that the ted molecule bridges two copper atoms, and that the tetragonally distorted octahedral geometry for the copper is completed by the two chelating hfac ligands. An unusual feature of the structure was the long axial Cu–N bond [2·566(7) Å]. Usually the long bond is to the oxygen, not nitrogen, as in dinitratobis(pyrazine)copper(II).[2]

A possible explanation of the long Cu–N bond in $Cu(hfac)_2(ted)$ is the interaction between the ted hydrogen atoms with the hfac ring system. To test this we have used a different ligand, pyrazine (pyz), made several complexes with it from $Cu(hfac)_2(H_2O)$ and determined the crystal structures of two of them.

$Cu(hfac)_2(H_2O)$ reacts with pyz to give a variety of products according to the ratio of the reactants. $Cu(hfac)_2(H_2O)$ gave $Cu(hfac)_2(pyz)_2$ as green crystals from stoicheiometric (1 : 2) reaction in carbon tetrachloride. The crystals slowly dulled on standing and it is probable that loss of volatile pyz occurs. A white powdery material, obtained in slight yield, is probably pyrazinium hydrochloride formed through an accompanying hydrolysis reaction (1). This is analogous to the reaction of quinuclidine with $Cu(hfac)_2(H_2O)$ in CCl_4 which gives green crystals of $Cu(hfac)_2$(quinuclidine) together with quinuclidinium hydrochloride.[3]

$$Cu(hfac)_2(H_2O) + pyz \xrightarrow{CCl_4} Cu(hfac)_2(pyz)_2 + [pyzH^+][Cl^-] \quad (1)$$

When allowed to react in equimolar ratio in carbon tetrachloride, $Cu(hfac)_2(H_2O)$ and pyz gave green flakes of $Cu(hfac)_2(pyz)$. Recrystallisation from hot carbon tetrachloride gave green laths of the 1 : 1 complex, together with green rods which were shown by X-ray analysis to be $[Cu(hfac)_2]_2(pyz)$. It is probable that these products are formed by the reaction sequence (2) the excess of pyz volatilising from the solution.

$$Cu(hfac)_2(H_2O) + pyz \longrightarrow Cu(hfac)_2(pyz) \xrightarrow{heat} [Cu(hfac)_2]_2(pyz) + pyz \quad (2)$$

The i.r. spectra of the complexes may be compared with those of the $Cu(hfac)_2$–(ted) complexes (see Table 1). The crystal structures of the 1 : 1 and 2 : 1 complexes (I) and (II) have been determined.

Description of the Structure of $Cu(hfac)_2(pyz)$ (I).—The complex $Cu(hfac)_2(pyz)$ forms a linear co-ordination polymer with the $Cu(hfac)_2$ moieties bridged by pyz rings. It crystallises as apple green laths in the triclinic system. There is one formula unit per unit cell and the space group

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[1] R. C. E. Belford, D. E. Fenton, and M. R. Truter, *J.C.S. Dalton*, 1972, 2208.

[2] A. Santoro, A. D. Mighell, and C. W. Riemann, *Acta Cryst.*, 1970, **B26**, 979.

[3] D. E. Fenton, unpublished observations.

TABLE 1

I.r. spectra (cm^{-1}) with assignments [a]

Complex	Nature	νC=O (ν_2)	νC=C (ν_3)	νC=O (ν_4)	νC=C (ν_5)	Ring def.	δ_sCF_3
$Cu(hfac)_2(ted)$	*trans*-O_h [b]	1640	1558	1532	1253	678	593
$Cu(hfac)_2(pyz)$	*trans*-O_h	1639	1553	1526	1248	677	590
$Cu(hfac)_2(ted)_2$	*cis*-O_h? [b]	1649	1548	1526	1253	666	
$Cu(hfac)_2(pyz)_2$		1644	1549	1530	1250	665	579
$[Cu(hfac)_2]_2(ted)$		1640	1560	1530	1252	678	598
$[Cu(hfac)_2]_2(pyz)$	Square pyramidal	1638	1558	1528	1249	676	595

[a] K. Shobatake and K. Nakamoto, *J. Chem. Phys.*, 1968, **49**, 4792. [b] Ref. 1.

is $P\bar{1}$ so that the copper atoms and the centres of the pyz rings are on centres of symmetry, the relative positions found being (0,0,0) and (0,½,½) respectively. The designations of the atoms are shown in Figure 1 which shows part of the chain polymer; the arrangement in the unit cell is shown in Figure 2. Atomic co-ordinates are in Table 2, bond lengths and angles in the $Cu(hfac)_2$ moiety are displayed in Figure 3, others are in Table 3.

The mean plane of the hfac entity (Table 4) includes the copper atom and none of the chelate ring atoms are found to deviate significantly from the plane. The pyz ring is also planar within the estimated standard deviations. Although the CF_3 groups may adopt any angle about the $C–C(F)_3$ bond, each is found with one fluorine approximately in, and the other two equidistant from, the plane of the chelate ring. They differ in orientation so that F(12) is as close as possible to O(1) while F(52) is as far as possible from O(2) (Figures 1 and 2).

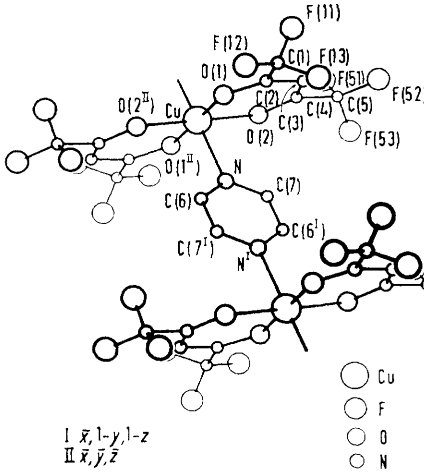

FIGURE 1 A portion of the infinite-chain polymer showing the designations of the atoms in the crystal chemical unit, and those of some atoms related by symmetry given Roman numeral superscripts corresponding to I, a centre of symmetry at 0,½,½ and II, a centre of symmetry at 0,0,0. The pyrazine ring can be seen to bridge the copper atoms at 0,0,0 and 0,1,1

The bonds and angles of the hfac ring agree closely with those previously reported for the ligand in similar environments. Even an anomalously short bond, involving an atom with highly correlated parameters [in this case C(1)–F(12)] has been noted [4,5] and attributed [5] to deficiencies in the calculated model.

The bond lengths and angles of the pyz system agree with those observed in $[Cu(hfac)_2]_2(pyz)$ and $Cu(NO_3)_2$-(pyz) [2] and are in the ranges expected for similar delocalised systems.

The chains of $[Cu(hfac)_2(pyz)]_\infty$ are held by van der Waals' contact in the *b* and *c* directions (Table 5) but along the *a* axis the only contacts <3·1 Å are between H(3) and fluorine.

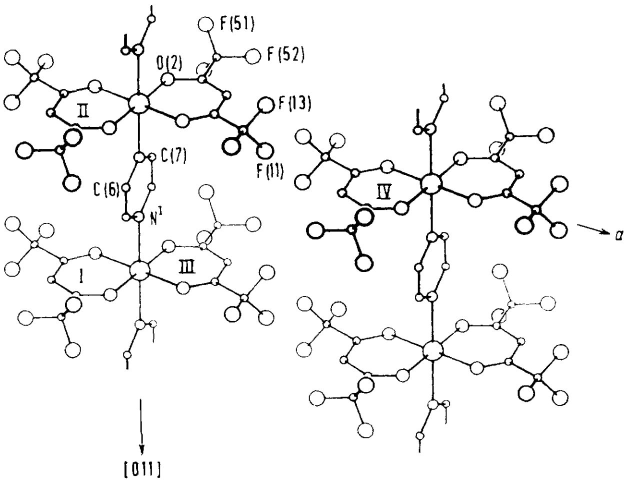

FIGURE 2 A view of the contents of more than one complete unit cell, with the origin in the top left-hand corner, the ***a*** axis runs to the right, and the [011] axis down the page. Roman numeral superscript III corresponds to a molecule at *x*, *y* + 1, *z* + 1, and IV to one at 1 − *x*, −*y*, −*z*

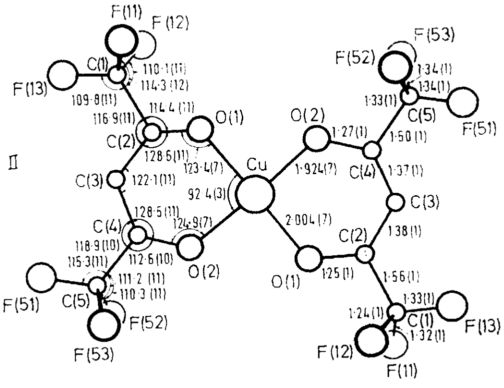

FIGURE 3 A diagram of the $Cu(hfac)_2$ entity showing bond lengths (Å) in the crystal chemical unit, and bond angles (°), in the centrosymmetrically related unit II as found in $Cu(hfac)_2$-(pyz). Numbers in parentheses are the standard deviations in the least significant digits. The diagram does not show the orientation of the CF_3 groups found in the structure

Environment of Copper in $Cu(hfac)_2(pyz)$.—The co-

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[4] M. R. Truter and B. L. Vickery, *J.C.S. Dalton*, 1972, 395.

[5] M. Elder, *Inorg. Chem.*, 1968, **8**, 2103.

ordination sphere of copper contains three pairs of significantly different bonds; in the equatorial plane the copper–oxygen bonds are 1·924(7) and 2·004(7) Å, and in the axial direction the copper–nitrogen distance is 2·529(9) Å. While Jahn–Teller distortion can be invoked to explain the appearance of four short equatorial and two long axial bonds [6] there is no simple explanation for the statistically significant (8σ) difference in the copper–oxygen(equatorial) distances. The symmetric carbon–oxygen and carbon–carbon bonds of the hfac rings indicate that the system is delocalised and therefore that the copper–oxygen contacts should be chemically equivalent. There is a difference in the environment of the oxygen atoms (Table 5), O(1) having more contacts to fluorine and O(2) more contacts to hydrogen, and it may be that the metal–oxygen distances are subject to variation by such subtle effects. There are many examples in the literature of statistically significant, but not readily explicable, differences in bond lengths, such as three pairs of copper–oxygen distances in $[Cu(H_2O)_6](ClO_4)_2$,[7] in $M_2^I[Cu(H_2O)_6](SO_4)_2$,[8] and in $CuBa_2(HCO_2)_6,4H_2O$;[9] the six chemically equivalent copper–oxygen

TABLE 2

(*a*) $Cu(hfac)_2(pyz)$ fractional atomic co-ordinates ×10⁴. Here, and throughout the paper, numbers in parentheses are the standard deviations in the least significant digits

	x/*a*	*y*/*b*	*z*/*c*
Cu	0	0	0
O(1)	1500(6)	1559(10)	−325(12)
O(2)	1005(6)	−1126(10)	1938(12)
C(1)	3608(13)	2854(22)	119(24)
C(2)	2590(10)	1498(16)	589(19)
C(3)	3000(10)	429(17)	1971(18)
C(4)	2190(10)	−779(17)	2534(18)
C(5)	2709(12)	−1877(21)	4053(23)
F(11)	4351(7)	1663(12)	−739(14)
F(12)	3191(7)	3891(15)	−1011(17)
F(13)	4376(7)	4190(12)	1990(14)
F(51)	2285(6)	−3966(10)	3107(13)
F(52)	3944(5)	−1618(10)	4685(12)
F(53)	2311(6)	−1280(12)	5856(12)
N	−12(7)	3207(13)	3213(15)
C(6)	−461(10)	4877(19)	2951(20)
C(7)	451(10)	3378(18)	5278(20)
H(3)	3924(54)	430(92)	2622(103)
H(6)	−835(54)	4845(91)	1310(105)
H(7)	728(55)	2117(87)	5579(105)

(*b*) Vibration parameters (×10³ Å²). (i) Anisotropic parameters, in the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	38(1)	59(2)	67(2)	4(1)	15(1)	32(1)
F(11)	95(6)	94(6)	132(8)	9(5)	67(6)	20(5)
F(12)	71(5)	201(10)	238(12)	14(6)	32(6)	187(10)
F(13)	92(6)	91(6)	131(8)	−14(5)	40(5)	24(6)
F(51)	69(5)	65(5)	125(7)	11(4)	8(5)	41(5)
F(52)	44(4)	96(6)	106(6)	6(4)	4(4)	52(5)
F(53)	79(5)	119(6)	69(6)	18(4)	21(4)	43(5)

(ii) Isotropic parameters in the form $\exp(-8\pi^2U_{iso}\sin^2\theta/\lambda^2)$

Cu	U_{iso}
O(1)	55(2)
O(2)	57(2)
C(1)	74(4)
C(2)	57(3)
C(3)	58(3)
C(4)	52(3)
C(5)	67(4)
N	54(3)
C(6)	61(3)
C(7)	59(3)
H(3)	95(39)
H(6)	115(42)
	92(37)

TABLE 3

(*a*) Intramolecular bond lengths (Å)

(i) Co-ordinate bonds

$Cu(hfac)_2(pyz)$		$[Cu(hfac)_2]_2(pyz)$	
Cu–O(1)	2·004(7)	Cu–O(1)	1·96(1)
Cu–O(2)	1·924(7)	Cu–O(2)	1·93(1)
Cu–N	2·529(9)	Cu–O(1′)	1·93(1)
		Cu–O(2′)	1·96(1)
		Cu–N	2·25(2)

(ii) Pyrazine bonds

N–C(6)	1·33(1)	N–C(6)	1·38(2)
N–C(7)	1·33(1)	N–C(7)	1·33(2)
C(6)–C(7^{I})	1·38(2)	C(6)–C(7^{I})	1·36(4)

(iii) Hydrogen distances

H(3)–C(3)	1·02(6)	H(3)–C(3)	0·88(15)
H(6)–C(6)	1·08(6)	H(3′)–C(3′)	0·97(15)
H(7)–C(7)	1·00(6)	H(6)–C(6)	0·88(17)
		H(7)–C(7)	0·95(15)

(*b*) Intramolecular angles (°)

(i) Co-ordinate angles

O(1)–Cu–O(2)	92·4(3)	O(1)–Cu–O(2)	91·1(5)
O(1)–Cu–N	89·4(3)	O(1′)–Cu–O(2′)	91·5(5)
O(2)–Cu–N	90·5(3)	O(1)–Cu–N	99·7(5)
		O(2)–Cu–N	96·3(6)
		O(1′)–Cu–N	95·6(6)
		O(2′)–Cu–N	96·7(6)
		O(2)–Cu–O(2′)	85·8(5)
		O(1)–Cu–O(1′)	88·1(5)

(ii) Pyrazine angles

N–C(6)–C(7^{I})	121(1)	N–C(6)–C(7^{I})	122(2)
N–C(7)–C(6^{I})	123(1)	N–C(7)–C(6^{I})	122(2)
C(6)–N–C(7)	115(1)	C(6)–N–C(7)	116(2)
Cu–N–C(6)	122·0(8)	Cu–N–C(6)	120(1)
Cu–N–C(7)	122·8(8)	Cu–N–C(7)	124(1)
C(7^{I})–C(6)–H(6)	120(4)	C(7^{I})–C(6)–H(6)	127(10)
C(6^{I})–C(7)–H(7)	117(4)	C(6^{I})–C(7)–H(7)	119(10)

(iv) Angles of hfac moiety in $[Cu(hfac)_2]_2(pyz)$

Cu–O(1)–C(2)	126(1)	Cu–O(1′)–C(2′)	126(1)
Cu–O(2)–C(4)	124(1)	Cu–O(2′)–C(4′)	126(1)
O(1)–C(2)–C(3)	128(2)	O(1′)–C(2′)–C(3′)	125(2)
O(2)–C(4)–C(3)	130(2)	O(2′)–C(4′)–C(3′)	128(2)
C(2)–C(3)–C(4)	119(2)	C(2′)–C(3′)–C(4′)	123(2)
C(1)–C(2)–C(3)	117(2)	C(1′)–C(2′)–C(3′)	120(2)
C(3)–C(4)–C(5)	118(2)	C(3′)–C(4′)–C(5′)	116(2)
C(2)–C(1)–F(11)	113(2)	C(2′)–C(1′)–F(1′1)	117(2)
C(2)–C(1)–F(12)	109(2)	C(2′)–C(1′)–F(1′2)	112(2)
C(2)–C(1)–F(13)	113(2)	C(2′)–C(1′)–F(1′3)	111(2)
C(4)–C(5)–F(51)	110(2)	C(4′)–C(5′)–F(5′1)	110(2)
C(4)–C(5)–F(52)	116(2)	C(4′)–C(5′)–F(5′2)	112(2)
C(4)–C(5)–F(53)	114(2)	C(4′)–C(5′)–F(5′3)	115(2)
F(11)–C(1)–F(12)	105(2)	F(1′1)–C(1′)–F(1′2)	107(2)
F(11)–C(1)–F(13)	109(2)	F(1′1)–C(1′)–F(1′3)	107(2)
F(12)–C(1)–F(13)	107(2)	F(1′2)–C(1′)–F(1′3)	102(2)
F(51)–C(5)–F(52)	104(2)	F(5′1)–C(5′)–F(5′2)	104(3)
F(51)–C(5)–F(53)	106(2)	F(5′1)–C(5′)–F(5′3)	106(3)
F(52)–C(5)–F(53)	105(2)	F(5′2)–C(5′)–F(5′3)	109(3)
O(1)–C(2)–C(1)	114(2)	O(1′)–C(2′)–C(1′)	115(2)
O(2)–C(4)–C(5)	112(2)	O(2′)–C(4′)–C(5′)	116(2)

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[6] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' Interscience, London, 2nd edn., 1966.

[7] N. V. Mani and S. Ramazeshan, *Z. Krist.*, 1961, **115**, 97.

[8] D. J. Robinson and C. H. L. Kennard, *Cryst. Struct. Comm.*, 1972, **1**, pp. 185, 189.

[9] R. V. G. Sundara Rao, K. Sundaramma, and G. Sivasankaro Rao, *Z. Krist.*, 1958, **110**, 231.

distances in tris[bis(di-isopropylphosphonato)methane]-copper(II) perchlorate,[10] Cu(ipcp), range from 2·067(2) to 2·111(2) Å, *i.e.* $>15\sigma$, but not in a way which could be ascribed to Jahn–Teller effects. Copper–nitrogen bonds in three pairs, 2·031, 2·226, and 2·450(7) Å were found in $\mathrm{Cu(bipy)_3(ClO_4)_2}$ (bipy = 2,2′-bipyridyl).[11] Comparison of a series of complexes with *N*-substituted *o*-hydroxy-acetophenone imines[12] showed differences in Cu–O (and in Cu–N) bond lengths of 15σ but again no correlation with geometrical or chemical features. The axial copper–nitrogen bond in $\mathrm{Cu(hfac)_2(pyz)}$, like that in $\mathrm{Cu(hfac)_2}$-(ted), is 0·5 Å, *i.e.* $>50\sigma$, longer than the equatorial bonds.

TABLE 4

Planes through various groups of atoms. The equations refer to orthogonal axes with $a' = a + b\cos\gamma + c\cos\beta$, $b' = b\sin\gamma + c(\cos\alpha - \cos\beta\,.\,\cos\gamma)/\sin\gamma$, and $c' = V/(ab\sin\gamma)$.

Distances from the planes ($\times 10^3$ Å) are in square brackets; those for atoms included in the calculation of the equation are italicised

(*a*) $\mathrm{Cu(hfac)_2(pyz)}$

Plane (1): $0{\cdot}282x' - 0{\cdot}551y' - 0{\cdot}785z' = 0$

[*O(1) −7, O(2) −5, C(2) 1, C(3) 5, C(4) −1,* Cu 0, C(1) −22, C(5) −6, F(11) 1020, F(12) − 114, F(13) −1040, F(51) 1051, F(52) 35, F(53) +1078]

Plane (2): $0{\cdot}902x' + 0{\cdot}432y' - 0{\cdot}001z' + 0{\cdot}030 = 0$

[*N −3, C(6) 3, C(7) 3, centre of symmetry at (0,½,½) 0,* Cu 30]

Angles between planes (1) and (2) 89·0°

(*b*) $\mathrm{[Cu(hfac)_2]_2(pyz)}$

Plane (3): $0{\cdot}490x' + 0{\cdot}596y - 0{\cdot}637z' + 1{\cdot}301 = 0$

[*O(1) 8, O(2) 4, C(2) −20, C(3) 22, C(4) −15,* Cu −153, F(11) 1108, F(12) −916, F(13) 199, F(51) −1324, F(52) 539, F(53) 317, C(1) 121, C(5) −106]

Plane (4): $0{\cdot}063x' + 0{\cdot}621y - 0{\cdot}781z' + 1{\cdot}540 = 0$

[*O(1′) 13, O(2′) −5, C(2′) −21, C(3′) 15, C(4′) −1,* Cu 31, F(1′1) 29, F(1′2) −1184, F(1′3) 826, F(5′1) −1321, F(5′2) 361, F(5′3) 486, C(1′1) −92, C(5′) −79]

Plane (5): $0{\cdot}219x' + 0{\cdot}622y - 0{\cdot}751z' + 1{\cdot}781 = 0$

[O(1) −38, O(2) 39, O(1′) 38, O(2′) −39, Cu 241, N 2490]

Plane (6): $-0{\cdot}963x' + 0{\cdot}258y - 0{\cdot}083z' - 0{\cdot}782 = 0$

[*N 18, C(6) −10, C(7) −14, centre of symmetry at (0,½,0) 0,* Cu − 89]

Angles between planes: (3)–(4) 26·1°
(3)–(5) 17·0
(4)–(5) 9·1
(5)–(6) 89·3

The reason for there being more contacts from O(2) to hydrogen is that the pyrazine ring lies so that the C(6) ··· C(7) direction is at 8·5° from the O(2)–Cu–O(2^{II}) direction, giving H(6) ··· O(2) 2·71 Å, and H(7) ··· O(2) 2·82 Å. It is to repulsion caused by contacts of this type that we previously attributed the elongation of the copper–nitrogen bond.[1] We now think this is not the explanation, partly because such repulsion could be relieved by a different orientation of the pyrazine ring, and partly because of the recently reported results on *trans*-bis-(ω-nitroacetophenonato)bis-(2-methylpyridine)-copper(II).[13] Although the methyl group should give greater steric hindrance than hydrogen the copper–nitrogen bond is short [2·004(5) Å] while the copper–oxygen bonds are 1·991(3) to the carbonyl oxygen and 2·252(5) Å to the nitro-oxygen.[13] In bis-(ω-nitroaceto-phenonato)copper(II)[13] itself the copper–oxygen bonds differ by $<1\sigma$ so the long copper–oxygen bond in the 2-methylpyridine adduct is not the result of the chemical difference in the oxygen atoms but is an example of the usual effect in 2N,4O-systems.

TABLE 5

Selected non-bonding interactions $<3{\cdot}1$ Å

$\mathrm{Cu(hfac)_2(pyz)}$		$\mathrm{[Cu(hfac)_2]_2(pyz)}$	
(*a*) Intramolecular			
O(1) ··· F(12)	2·59	O(1) ··· F(11)	2·73
O(1) ··· F(53)	3·06	O(1) ··· F(12)	2·80
O(2) ··· F(51)	2·72	O(2) ··· F(51)	2·90
O(2) ··· F(53)	2·75	O(2) ··· F(52)	2·66
		O(1′) ··· F(1′2)	2·80
		O(1′) ··· F(1′3)	2·69
		O(2′) ··· F(5′1)	3·01
		O(2′) ··· F(5′2)	2·60
(*b*) Intermolecular			
O(1) ··· F(51$^{\mathrm{V}}$)	3·06	O(2) ··· F(52$^{\mathrm{III}}$)	3·02
		O(2′) ··· F(52$^{\mathrm{III}}$)	3·08
F(11) ··· F(53$^{\mathrm{VI}}$)	2·87	F(11) ··· F(1′3$^{\mathrm{II}}$)	2·84
F(11) ··· F(52$^{\mathrm{VI}}$)	3·06	F(52) ··· F(12$^{\mathrm{IV}}$)	2·94
F(13) ··· F(51$^{\mathrm{V}}$)	2·90	F(5′1) ··· F(53$^{\mathrm{III}}$)	3·09
F(13) ··· F(52$^{\mathrm{V}}$)	3·00	F(5′2) ··· F(1′2$^{\mathrm{IV}}$)	3·10
H(3) ··· F(11$^{\mathrm{IV}}$)	2·80	H(3′) ··· F(11$^{\mathrm{V}}$)	3·05
H(3) ··· F(52$^{\mathrm{IX}}$)	2·52	H(3′) ··· F(1′1$^{\mathrm{VII}}$)	3·92
		H(3) ··· F(5′1$^{\mathrm{VI}}$)	3·06
		H(3′) ··· F(13$^{\mathrm{V}}$)	3·05
H(6) ··· F(51$^{\mathrm{II}}$)	2·88	H(6) ··· O(1′)	2·66
H(6) ··· F(12$^{\mathrm{X}}$)	2·84	H(6) ··· O(1$^{\mathrm{II}}$)	2·71
H(6) ··· O(1$^{\mathrm{X}}$)	2·86	H(6) ··· O(1′$^{\mathrm{II}}$)	3·00
H(6) ··· O(2$^{\mathrm{II}}$)	2·71	H(6) ··· F(11$^{\mathrm{II}}$)	3·06
H(7) ··· F(12$^{\mathrm{VII}}$)	3·00	H(7) ··· O(2)	2·82
H(7) ··· O(1$^{\mathrm{VII}}$)	2·86	H(7) ··· O(1$^{\mathrm{IV}}$)	2·72
H(7) ··· O(2)	2·82	H(7) ··· O(1′$^{\mathrm{IV}}$)	3·07
H(7) ··· O(2$^{\mathrm{VIII}}$)	3·01	H(7) ··· F(12$^{\mathrm{IV}}$)	2·57
		Cu ··· F(51$^{\mathrm{III}}$)	3·09

Roman numeral superscripts correspond to the following transformations to the co-ordinates given in Tables 2 and 6 as *x*, *y*, *z*

I	$-x, 1-y, 1-z$	I	$-x, 1-y, -z$
II	$-x, -y, -z$	II	$-x, -y, -z$
III	$x, 1+y, 1+z$	III	$-x, y-\frac{1}{2}, \frac{1}{2}-z$
IV	$1-x, -y, -z$	IV	$x, 1+y, z$
V	$x, 1+y, z$	V	$x-1, y, z$
VI	$x, y, z-1$	VI	$1+x, y, z$
VII	$x, y, z+1$	VII	$-x-1, -y, -z$
VIII	$-x, -y, 1-z$		
IX	$1-x, -y, 1-z$		
X	$-x, 1-y, -z$		

Both ted[14] and pyz have good donor properties, so poor chemical interactions do not seem to explain the long axial bonds. Other nitrogen donor molecules with $\mathrm{Cu(hfac)_2}$ have produced different geometrical effects. With two aromatic nitrogen atoms in *cis*-positions, *i.e.* $\mathrm{Cu(hfac)_2(bipy)}$[15] and $\mathrm{Cu(hfac)_2(py)_2}$ (py = pyridine)[16]

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[10] P. T. Miller, P. G. Lenhert, and M. D. Joesten, *Inorg. Chem.*, 1973, **12**, 218.

[11] O. P. Anderson, *J.C.S. Dalton*, 1972, 2597.

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[13] M. Bonamico, G. Dessy, V. Fares, and L. Scaramuzza, *J.C.S. Dalton*, 1972, 2477.

[14] J. V. Quagliano, A. K. Banerjee, V. L. Goedken, and L. M. Vallarino, *J. Amer. Chem. Soc.*, 1970, **92**, 3482.

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there are four short bonds, the copper–nitrogen and the -oxygen *trans* to these and two long copper–oxygen bonds with a tendency to asymmetry in the hfac ring. With two chelating nitrogen ligands the hfac may be forced to a unidentate form as in Cu(hfac)$_2$(*NN*-dimethylethylenediamine).[17]

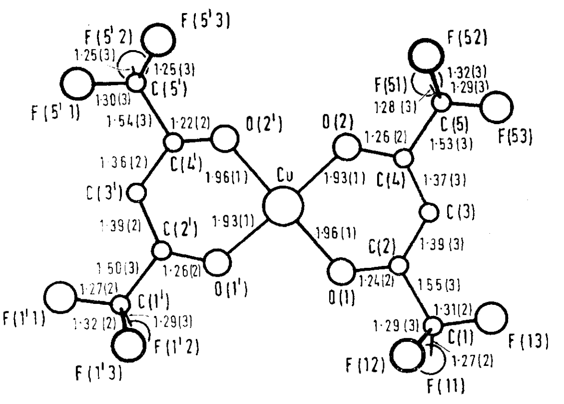

FIGURE 4 A diagram of the Cu(hfac)$_2$ entity showing the designations of the atoms and the bond lengths (Å) found in [Cu(hfac)$_2$]$_2$(pyz). It does not present the observed orientation of the CF$_3$ groups

Description of the Structure of [Cu(hfac)$_2$]$_2$(pyz) (II).—The compound [Cu(hfac)$_2$]$_2$(pyz) crystallises in the monoclinic system, space group $P2_1/c$ with two formula units in the unit cell. It forms a discrete molecule with the two Cu(hfac)$_2$ entities linked by the pyz ring which lies about the centre of symmetry at (0,$\frac{1}{2}$,0). Figure 4 shows the designation of atoms and bond lengths in the Cu(hfac)$_2$ entity and Figure 5 shows the structure as a whole and the designations of the pyz atoms.

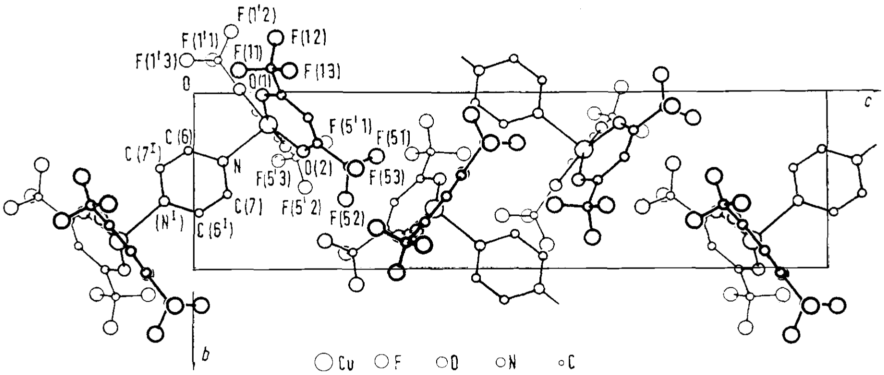

FIGURE 5 The structure projected on the (100) plane showing the designations of atoms in the pyrazine ring, those with superscript I are related to those in Table 6 at *x*, *y*, *z* by $-x$, $1-y$, $-z$. The fluorine atoms in the crystal chemical unit are labelled. One unit cell is outlined

The dimensions of the two independent hfac systems agree internally and are comparable to previously determined results.[1] The distribution of the twelve independent carbon–fluorine bond lengths gives a standard deviation about the mean (1·287 Å) of 0·026 Å. The mean plane of each hfac ring was calculated (Table 4). The copper atom is close to the plane of the primed ring [plane (4)] and 0·153 Å from the other one. In both, one CF$_3$ group is oriented to have one atom in the plane [F(13) and F(1'1)] as far as possible from the oxygen atoms O(1) and O(1'). The other CF$_3$ groups are oriented so that one carbon–fluorine bond is approximately normal to the corresponding plane [F(51) and F(5'1)] and on the opposite side to the copper.

The bond lengths and angles in the pyrazine ring, Table 3, and its planarity [Table 5, plane (6)] are as expected within the standard deviation. All standard deviations are higher than the corresponding ones in Cu(hfac)$_2$(pyz) because in this structure the co-ordinates of the copper atom are parameters.

Environment of Copper in [Cu(hfac)$_2$]$_2$(pyz).—The copper atom is five-co-ordinated in a distorted square pyramid being 0·24 Å from the basal plane through the oxygen atoms (Table 4) towards the apical nitrogen atoms. The copper–oxygen bond lengths, mean 1·94(1) Å are equal within their standard deviations (Figure 4) and the copper–nitrogen bond length 2·25(2) Å (Table 3) is significantly greater than that found in square-planar environments.[18] Factors affecting the relative stability of trigonal bipyramidal, square pyramidal, and distorted square pyramidal geometries include the possibility of π-bonding and crystal-packing forces.[19] As shown in Table 5, the crystal packing is fairly uniform for all the oxygen atoms, and unlikely to affect the geometry. Considerable π-bonding favours a square pyramid with the metal in the basal plane, but for a weak ligand-field the distorted geometry as found here is more stable.[20] The displacement is within the usual range, *e.g.*, 0·266 in bis-(*o*-hydroxyacetophenonato)-(4-methylpyridine)copper(II) [21] and 0·20 Å in bis(acetylacetonato)quinolinecopper(II).[22] In a complex having a unidentate nitrogen

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[17] M. A. Bush and D. E. Fenton, *J. Chem. Soc.* (*A*), 1971, 2446.

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[19] B. F. Hoskins and F. D. Whillans, *Co-ordination Chem. Rev.*, 1973, **9**, 365.

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[22] P. Jose, S. Ooi, and Q. Fernando, *J. Inorg. Nuclear Chem.*, 1969, **31**, 1971.

in the basal plane, bis(acetylacetonato)(4-aminopyridine)copper(II), the copper atom displacement is still 0·22 Å.[23]

Comparison of square-pyramidal copper(II) complexes [18] shows that in general, despite the displacement, the fifth-ligand bond length is 0·2—0·6 Å greater than the in-plane ligands, yet shorter than the equivalent axial bonds in tetragonal octahedral complexes. This pattern is followed in $[Cu(hfac)_2]_2(pyz)$, the copper–nitrogen bond being significantly shorter than the copper–nitrogen bonds in $Cu(hfac)_2(pyz)$ 2·529 Å or in $Cu(hfac)_2(ted)$ 2·566(7) Å; [1] the difference between the Cu–N(pyz) and Cu–N(ted) bond lengths is of the correct magnitude and direction to be the result of sp^2 and sp^3 hybridisation of nitrogen.

The closest approach to copper in the sixth axial position is $F(51^{III})$ at 3·09 Å (Table 5) giving the $N{-}Cu \cdots F(51^{III})$ angle 174°. This can be seen in Figure 5 from F(51) to the glide related copper atom at $(\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z)$.

EXPERIMENTAL

I.r. spectra were measured as Nujol mulls or KBr discs on a Perkin-Elmer 457 spectrophotometer.

Preparation of Complexes.—Aquobis(hexafluoroacetylacetonato)copper(II) was prepared by the method of ref. 24. Reactions were carried out in air.

Bis(hexafluoroacetylacetonato)(pyrazine)copper(II), (I). Aquobis(hexafluoroacetylacetonato)copper(II) (1 mmol) and pyz (1 mmol) were warmed together in carbon tetrachloride. On cooling light green flakes were formed, and shown by analysis to be the 1 : 1 species (I). The flakes were recrystallised from hot carbon tetrachloride to give two types of crystals; apple green laths and emerald green rods. The *laths* were separated from the mixture and shown by analysis to be (I) (Found: C, 30·1; H, 1·1; N, 5·0; *M*, (*X*-ray), 548. $C_{14}H_6CuF_{12}N_2O_4Cu$ requires C, 29·8; H, 1·1; N, 5·2%; *M*, 557·5).

Tetrakis(hexafluoroacetylacetonato)-μ-pyrazine-dicopper(II), (II). The emerald green rods were separated from the mixture in the previous preparation but insufficient crystals were obtained for analysis. Initially the crystals were thought to be a second crystal habit of the 1 : 1 species. The *X*-ray molecular weight was found to be 1035, corresponding to the formula $C_{24}H_8F_{24}N_2O_8Cu_2$. The compound is thought to have been formed by loss of pyz during recrystallisation.

Bis(hexafluoroacetylacetonato)bis(pyrazine)copper(II). Aquobis(hexafluoroacetylacetonato)copper(II) (1 mmol) was warmed with pyz (2 mmol) in carbon tetrachloride for 30 min. On cooling green *crystals* of the complex were formed; these slowly became opaque when set aside (Found: C, 32·8; H, 1·6; N, 8·5. $C_{18}H_{10}CuF_{12}N_4O_4$ requires C, 33·8; H, 1·6; N, 8·8%).

X-*Ray Diffraction Measurements.*—The procedures for both compounds were similar. That for (I) is described here with variations for (II) in square brackets.

A crystal *ca.* 0·1 × 0·2 × 1·0 mm [0·1 × 1·0 × 0·1 mm] was mounted in a quartz capillary on a Stoe goniometer head. Unit cell dimensions and their standard deviations were determined by a least-squares fit [25] to the setting angles of 19 [17] reflections which had been manually optimised on a Picker four-circle diffractometer.

Crystal Data.—$C_{14}H_6CuF_{12}N_2O_4$, (I) $M = 557·5$, Triclinic, $a = 11·228(6)$, $b = 6·821(4)$, $c = 6·742(7)$ Å, $\alpha = 109°\ 06'(5')$, $\beta = 103°\ 27'(3')$, $\gamma = 95°\ 12'(2')$, $U = 466·7$ Å^3, D_m (flotation) $= 1·95$, $Z = 1$, $D_c = 1·98$, $F(000) = 273$. Space group $P\bar{1}$ determined by structure analysis. Mo-K_α (Zr-filtered) radiation, $\lambda(K_{\alpha1}) = 0·70930$, $\lambda(K_{\alpha2}) = 0·71359$ Å (1 Å $\equiv 10^{-10}$m); μ(Mo-K_α) $= 11$ cm^{-1}, no absorption correction applied.

[$C_{24}H_8Cu_2F_{24}N_2O_8$, (II) $M = 1035$, Monoclinic, $a = 10·750(5)$, $b = 6·761(10)$, $c = 23·732(12)$, $\beta = 93°\ 04'(1')$, $U = 1722$ Å^3, D_m (flotation) $= 1·96$, $Z = 2$, $D_c = 1·99$, $F(000) = 1008$. Space group $P2_1/c$. μ(Mo-K_α) $= 12$ cm^{-1}, no absorption correction applied.]

Intensity measurements were obtained with the crystal mounted along the *c* [*b*] axis. Observations, in the range $\sin\theta/\lambda \leqslant 0·60$ [0·54] were made in the hkl, $\bar{h}kl$, $h\bar{k}l$, $\bar{h}\bar{k}l$ [hkl and $\bar{h}kl$] octants with the scintillation counter through a pulse-height discriminator. The θ—2θ scan mode was used at 0·5° min^{-1} from 0·5° below the $K_{\alpha1}$ peak to 0·5° above the $K_{\alpha2}$ peak; background counts of 25 s were taken at each end of the scan. Three reference reflections, (5$\bar{4}$4), ($\bar{1}\bar{6}$3), and ($\bar{2}$02) [(300), (808), and (323)], measured every 50 reflections were used to place all observations on a common scale. The observations were processed to give a set of intensities for which I, the net intensity was $> 3\sigma(I)$ as defined by $\sigma^2(I) = [c + 0·25(t_c/t_b)^2(B_1 + B_2)]$ where c is the total integrated count obtained in time t_c and B_1 and B_2 are background counts each obtained in time t_b. Lorentz and polarisation factors were applied and square roots taken to give 742 [987] values from 1800 [2346] original observations for $|F_{hkl}|$.

Structure Determination of (I).—The compound $Cu(hfac)_2(pyz)$ crystallised with one molecule in the unit cell. In the centrosymmetric space group $P\bar{1}$ the molecule is required to have $\bar{1}$ symmetry, with the copper atom and the pyz ring occupying $\bar{1}$ sites. In the non-centrosymmetric space group $P1$ the molecule need have no symmetry.

A Patterson synthesis [25] was computed from which the positions of two oxygen, three ring-carbon, and five fluorine atoms were obtained with a copper atom at the origin. Structure factors were calculated in $P\bar{1}$; a subsequent Fourier synthesis [25] showed the remaining fluorine atom together with the nitrogen atom. The isotropic thermal parameters of the thirteen atoms were refined over one cycle, structure factors were calculated and R was 0·28. The second Fourier synthesis showed the remaining four carbon atoms. The pyz ring was found to lie about the centre of symmetry at $(0,\frac{1}{2},\frac{1}{2})$. Block-diagonal least-squares were used to refine all positional parameters and isotropic temperature factors; R fell to 0·12 over four cycles. A difference-Fourier synthesis showed residual peaks around the copper and fluorine atoms, indicating anisotropic temperature factors for these atoms. After three cycles R was calculated as 0·08. A difference-Fourier synthesis showed broad peaks in the three regions where hydrogen atoms were expected. The positional parameters of all twenty atoms, together with the isotropic temperature factors of oxygen, nitrogen, and carbon, and anisotropic temperature factors of copper and fluorine atoms, were refined using block-diagonal least-squares. After three cycles R was 0·06.

To obtain more realistic standard deviations a final cycle

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[23] G. W. Bushnell, *Canad. J. Chem.*, 1971, **49**, 555.

[24] R. L. Belford, A. E. Martell, and M. Calvin, *J. Inorg. Nuclear Chem.*, 1956, **2**, 11.

[25] *X*-RAY ARC, IBM 1130 Program System, for details see P. R. Mallinson and M. R. Truter, *J.C.S. Perkin II*, 1972, 1818.

of full-matrix least-squares was calculated on the IBM 360 computer with the program NUCLS.[26] The function minimised was $R' = \Sigma w(|F_o| - |F_c|)^2$, where the weighting function w was adjusted to give reasonably constant average values of R' in different ranges of $|F_o|$ and $\sin\theta/\lambda$. The final scheme was $w = [\sigma^2_{\text{counting}}(-3{\cdot}46 + 0{\cdot}8|F_o| - 0{\cdot}3|F_o|^2)]^{-1}$; this gave R 0·058 and weighted R' 0·064. The maximum shift was 0·26σ.

Because hfac is normally a symmetrical chelating ligand we re-examined the structure analysis to see if the apparent difference in Cu–O distances was the result of error. The possibility of misindexing of the crystal data was eliminated, as was solution in space group $P1$. Although the final difference-Fourier synthesis had shown no indications of anisotropic vibration of the oxygen atoms, a refinement was attempted with anisotropic parameters for the oxygen atoms; the refined parameters showed no significant anisotropy. Absorption corrections were calculated for several planes, these confirmed that no corrections were necessary.

Final observed and calculated structure factors for (I) and (II) are listed in Supplementary Publication No. SUP 20838 (17 pp., 1 microfiche).[*] They were obtained from the parameters in Table 2 with scattering-factor curves for neutral copper, carbon, nitrogen, oxygen, and fluorine from ref. 27, for hydrogen from ref. 28, and anomalous dispersion curves for copper from ref. 29.

Bond lengths and angles with their standard deviations were calculated with the program ORFFE.[30] Mean planes (with estimated standard deviations) were calculated for the molecule on a IBM 1130 computer.[25]

The carbon–fluorine bond, C(1)–F(12), is much shorter than the others; the full-matrix least-squares showed four sets of F(12) parameters to have high correlation coefficients, namely y–z 0·6328, β_{22}–β_{23} 0·7924, β_{33}–β_{23} 0·7954, and β_{12}–β_{13} 0·6459. The greater uncertainty is reflected in the higher standard deviations for this atom (Table 2).

Structure Determination of (II).—With only two molecules of $[\mathrm{Cu(hfac)_2}]_2\mathrm{(pyz)}$ in the unit cell, space group $P2_1/c$, the molecule must occupy a symmetry site $\bar{1}$, with half a molecule in the asymmetric unit. A patterson synthesis [25] was calculated and solved for one copper at −0·055, 0·165, 0·125 and four oxygen atoms. Structure factors were calculated and a Fourier synthesis computed;[25] this showed six ring-carbon and three fluorine atoms. Structure factors were calculated assuming isotropic temperature factors for the thirteen atoms; a second Fourier analysis showed all remaining non-hydrogen positions. The pyz ring was found to be perpendicular to the plane of the Cu(hfac)$_2$ moiety, and to lie about the centre of symmetry at $(0,\frac{1}{2},0)$.

The positional and isotropic thermal parameters for all thirty atoms were refined using block-diagonal least-squares; over three cycles R dropped to 0·12. A difference synthesis showed residual peaks around the copper and fluorine atoms, suggesting anisotropic thermal vibration. Block-diagonal least-squares refined positional parameters, isotropic temperature factors for oxygen, nitrogen, and carbon, and anisotropic temperature factors for copper and fluorine atoms, to give R 0·10. Hydrogen atom positions were calculated, assuming C–H 0·95 Å, and trigonal symmetry about the carbon atoms.

TABLE 6

(*a*) Fractional co-ordinates (× 10⁴) for $[\mathrm{Cu(hfac)_2}]_2\mathrm{(pyz)}$

	x/a	y/b	z/c
Cu	−557(2)	1683(4)	1170(1)
O(1)	897(11)	−31(19)	1115(5)
O(2)	296(11)	3240(23)	1755(5)
C(1)	2834(23)	−1564(46)	1299(10)
C(2)	1832(20)	−33(35)	1446(8)
C(3)	2157(20)	1312(35)	1873(8)
C(4)	1331(18)	2782(30)	1997(8)
C(5)	1651(26)	4113(42)	2503(11)
F(11)	3114(18)	−1473(32)	788(7)
F(12)	2399(13)	−3334(27)	1360(8)
F(13)	3852(14)	−1438(30)	1624(8)
F(51)	1105(18)	3501(36)	2939(6)
F(52)	1288(18)	5978(27)	2449(7)
F(53)	2825(14)	4197(26)	2649(7)
O(1′)	−1504(12)	−223(21)	716(5)
O(2′)	−2084(12)	2925(21)	1414(5)
C(1′)	−3158(24)	−2027(46)	305(10)
C(2′)	−2676(18)	−343(31)	664(8)
C(3′)	−3510(20)	946(32)	905(8)
C(4′)	−3148(20)	2442(30)	1264(8)
C(5′)	−4199(27)	3600(52)	1529(12)
F(1′1)	−4325(11)	−2072(26)	187(6)
F(1′2)	−2848(14)	−3718(23)	522(7)
F(1′3)	−2603(15)	−2084(24)	−182(6)
F(5′1)	−4511(18)	2736(32)	1991(8)
F(5′2)	−3860(15)	5291(31)	1686(9)
F(5′3)	−5175(15)	3756(32)	1225(8)
N	−236(14)	3785(24)	457(6)
C(6)	−299(16)	3126(36)	−93(7)
C(7)	87(18)	5662(33)	532(8)
H(3)	2839	1142	2090
H(3′)	−4400	722	860
H(6)	−624	1936	−110
H(7)	202	6167	904

(*b*) Vibration parameters (× 10³ Å²)

(i) Anisotropic

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	37(1)	40(1)	32(1)	0(2)	3(1)	−4(2)
F(11)	174(17)	171(20)	135(14)	110(17)	89(13)	29(16)
F(12)	84(10)	74(11)	220(18)	3(13)	29(11)	−5(15)
F(13)	78(11)	143(17)	226(19)	50(13)	−50(12)	−105(16)
F(51)	191(18)	211(23)	85(11)	−119(19)	50(12)	−77(16)
F(52)	144(15)	101(16)	146(15)	19(12)	−34(12)	−70(13)
F(53)	79(11)	153(18)	141(13)	19(10)	−51(10)	−89(12)
F(1′1)	44(8)	127(15)	149(12)	−13(10)	−36(8)	−41(12)
F(1′2)	110(12)	62(12)	136(13)	−18(10)	−34(10)	−5(10)
F(1′3)	140(13)	92(13)	90(10)	−37(11)	1(10)	−54(10)
F(5′1)	159(16)	184(24)	137(14)	111(16)	86(13)	60(14)
F(5′2)	80(12)	124(17)	237(22)	−5(11)	34(13)	−96(17)
F(5′3)	94(13)	182(21)	173(16)	89(14)	−29(12)	−82(16)

(ii) Isotropic

	U_{iso}		U_{iso}		U_{iso}
O(1)	46(4)	O(1′)	49(4)	N	40(4)
O(2)	50(3)	O(2′)	55(4)	C(6)	44(5)
C(1)	66(6)	C(1′)	69(7)	C(7)	47(6)
C(2)	48(6)	C(2′)	38(5)	H(3)	125(99)
C(3)	54(6)	C(3′)	50(6)	H(3′)	41(63)
C(4)	45(6)	C(4′)	47(6)	H(6)	60(60)
C(5)	71(8)	C(5′)	75(8)	H(7)	12(34)

In early refinements counting statistics were used in the weighting scheme; an analysis of the average R' over ranges of $|F_o|$ showed an unequal distribution. The analysis also showed very poor agreement between planes with low $|F_o|$

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[*] See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue.

[26] NUCLS, IBM 360 full-matrix least-squares program by R. J. Doedens and J. A. Ibers.

[27] 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962, pp. 202—212.

[28] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1955, **42**, 3175.

[29] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[30] Northwestern University version of the Busing–Levy–Martin ORFFE program run on the University College IBM 360 computer.

values. During the final cycle of refinement 31 planes with $|F_c| < 10{\cdot}0$ were omitted.[24] The weighting scheme $w = (48{\cdot}6 - 1{\cdot}18|F_o| + 0{\cdot}0084|F_o|^2)^{-1}$ was found to give the most satisfactory weighting analysis and was therefore used in the final cycle of least-squares and calculation of standard deviations.

Two cycles of full-matrix least-squares were calculated on an IBM 360 computer using NUCLS.[26] 956 Planes were used in the refinement of all atomic positional parameters, isotropic temperature factors of oxygen, nitrogen, carbon, and hydrogen atoms, and anisotropic temperature factors of copper and fluorine atoms. The final R was 0·081 and R' 0·078. The maximum shift observed was 0·23σ (for one of the hydrogen atoms).

Final observed and calculated structure factors were obtained from the parameters in Table 6, with the same scattering factor curves as for (I).

Bond lengths and angles with their estimated standard deviations, were calculated with the program ORFFE.[30] The bond lengths of the hfac entities are shown in Figure 4 and the remaining bond lengths of the molecule and all bond angles are listed in Table 3.

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