Reactions of 1,4-Diazabicyclo[2,2,2]octane with Bis-(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)copper(II) and the Crystal Structure of the 1 : 1 Complex

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Reaction of $(hfac)_2Cu(H_2O)$ [hfac = $(CF_3{\cdot}CO)_2{\cdot}CH$] with equimolar amounts of $N(CH_2{\cdot}CH_2)_3N$ (ted), in benzene gave $(hfac)_2Cu(ted)$. A 1 : 2 mixture gave $Cu(hfac)_2(ted)_2$, which had an i.r. spectrum consistent with *cis*-octahedral geometry. An attempt to make a $tedH^+$ derivative from $Cu(hfac)_2(H_2O)$, hfac, and ted (1 : 1 : 1) gave $[Cu(hfac)_2]_2(ted)$; this composition was confirmed by preliminary *X*-ray diffraction measurements. A second species lost benzene of crystallisation to give an amorphous green product characterised by i.r. as probably containing an $(hfac)^-$ anion and the $tedH^+$ cation acting as a unidentate ligand to copper in $Cu(hfac)_2$.

Reaction of $(CF_3COCHCOCH_3)_2Cu$ with ted gave a 1 : 1 complex. A three-dimensional crystal structure analysis on $Cu(hfac)_2(ted)$ was carried out. Full-matrix least-squares refinement on 832 diffractometer observations gave *R* 0·06. *Z* = 2 in an orthorhombic unit cell having *a* = 16·148, *b* = 8·428, *c* = 7·743 Å and space group *Pnnm*. The copper and two β-diketonates lie in a plane of symmetry, the ligands are related by a two-fold axis, giving square-planar co-ordination about copper with Cu–O 1·958 and 1·954 Å. The fifth and sixth axial positions are occupied by nitrogen atoms at 2·566 Å. The ted molecule bridges two copper atoms separated by *c*, one nitrogen atom being co-ordinated to each copper. As the *c* axis is a two-fold axis of symmetry the molecules of base are disordered; two sets of sites related by 180° rotation about the *c* axis are 50% occupied by methylene carbon atoms. Bond lengths and angles in the ligand molecules are as expected.

THE co-ordinative saturation of metal(II) acetylacetonates may be achieved through their addition of Lewis bases.[1] Unidentate ligands lead, in general, to axial ligation as in *trans*-bis-(pentane-2,4-dionato)bispyridinecobalt(II), or -nickel(II);[2,3] although a *cis*-octahedral geometry is reported for bis-(pentane-2,4-dionato)bis(pyridine *N*-oxide)nickel(II).[4] An *X*-ray crystal structure analysis of bis-(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)bipyridyl copper(II), $[Cu(hfac)_2(bipy)]$, established *cis*-octahedral geometry,[5] and we have shown that bidentate, and potentially chelating ligands react to give, presumably, similar products.[6] An excess of diamine leads to the preparation of 1 : 2 complexes in which the diketonate anion is unidentate.[7] Co-ordinative saturation may also be achieved through addition of the diketonate anion.[8] Progressive trifluoromethylation of the acetylacetone has been shown to increase the affinity of the central metal atom for ligation.[9]

We have extended our study of the reaction of bidentate ligands with metal(II) hfacs to include a rigid

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[1] D. P. Graddon, *Co-ordination Chem. Rev.*, 1969, **4**, 1.

[2] R. C. Elder, *Inorg. Chem.*, 1968, **7**, 1117.

[3] R. C. Elder, *Inorg. Chem.*, 1968, **7**, 2316.

[4] W. D. Horrocks, jun., D. H. Templeton, and A. Zalkin, *Inorg. Chem.*, 1968, **7**, 1552.

[5] M. V. Veidis, G. H. Schreiber, T. E. Gough, and G. J. Palenik, *J. Amer. Chem. Soc.*, 1969, **81**, 1859.

[6] D. E. Fenton, R. S. Nyholm, and M. R. Truter, *J. Chem. Soc.* (*A*), 1971, 1577.

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

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

[9] L. L. Funck and T. R. Ortolano, *Inorg. Chem.*, 1968, **7**, 567.

molecule 1,4-diazabicyclo[2,2,2]octane, [$N(CH_2{\cdot}CH_2)_3N$, triethylenediamine, or ted]. The reaction of $Cu(hfac)_2$-(H_2O) with this ligand gave a variety of products according to the ratio of the reactant. The reaction of bis-(1,1,1-trifluoropentane-2,4-dionato)copper(II) with ted gave only a 1 : 1 complex and no isolable species were obtained from bis(acetylacetonato)copper-(II) and ted. There may be interactions in solution but in the same conditions as used for the hexafluoro-derivative no solid products were isolated.

The Complex $Cu(hfac)_2(ted)$.—$Cu(hfac)_2(H_2O)$ gave $Cu(hfac)_2(ted)$ as an amorphous yellow-green product on evaporation of benzene, or ethanolic solutions of equimolar amounts of the constituents. Slow recrystallisation from carbon tetrachloride gave acicular yellow-green needles.

We have determined the crystal structure of this compound as part of a study of the (hfac)–Cu linkage in various environments.[6-8]

The crystals are orthorhombic with space group *Pnnm* and $Z = 2$. This results in a highly symmetrical structure with the copper atoms at sites having $2/m$ symmetry: if one is at 0,0,0 the other is at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$.

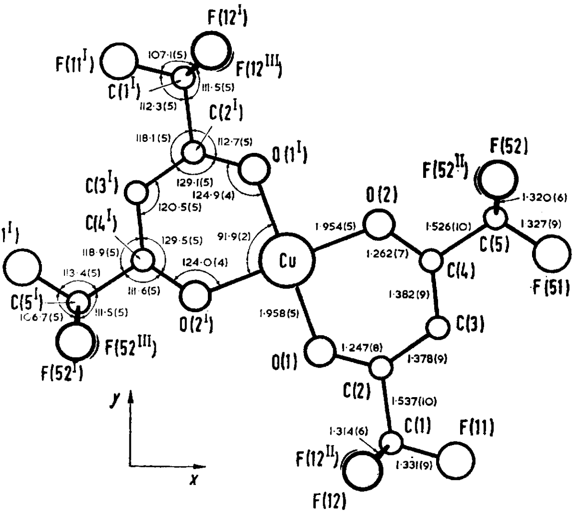

FIGURE 1 The $Cu(hfac)_2$ part of the molecule showing the designations of the atoms. Roman numeral superscripts have the following meanings with reference to the crystal chemical unit at *x*, *y*, *z*:

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

The crystallographic *x* and *y* directions are indicated. All atoms are at $z = 0$ except for F(12) and F(52); the mirror-related atoms F(12^{II}) and F(52^{II}) are shown slightly displaced. Bond lengths (Å), with standard deviations in the least significant digit in parentheses, are shown for the crystal chemical unit while bond angles are displayed on the ligand related to it by the two-fold axis

For the copper atom at 0,0,0 the hfac rings lie in the mirror plane at $z = 0$ as shown in Figure 1, which also gives the designations of the atoms in the $Cu(hfac)_2$ moiety. Each copper atom is also co-ordinated by two nitrogen atoms from different ted molecules; these molecules lie with the nitrogen atoms along the *c* axis (Figure 2) and bridge the copper atoms separated by one repeat unit along *z*.

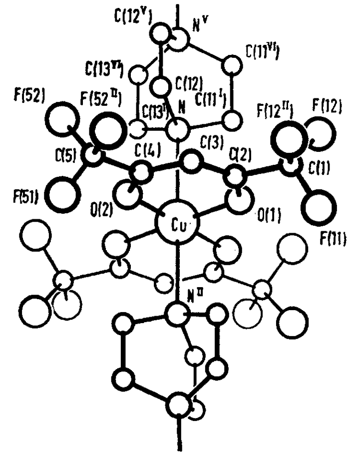

FIGURE 2 The environment of one copper atom. For each molecule of ted only one orientation is shown with the corresponding designations of the atoms. N^{II} and N^{V} are separated by one translation along *c*

There are two ted molecules in the unit cell so their centres must occupy sites of $2/m$ symmetry as found at $0,0,\frac{1}{2}$ and $\frac{1}{2},\frac{1}{2},0$. This means that for each molecule, with the nitrogen atoms lying on the *c* axis, the six carbon atoms can be related in pairs by the plane of symmetry but an individual molecule does not have a two-fold axis of symmetry along the *c* axis. In fact, the two-fold symmetry is the result of disorder, two orientations of the molecule are found, each 50% occupied. This is illustrated in Figure 2 by showing the ted molecules on opposite sides of the copper atom oriented in different directions. The effect in the structure as a whole is shown in Figure 3.

Structure of $Cu(hfac)_2(ted)$.—Agreement between independently determined values for the dimensions of $Cu(hfac)_2$ is good (Figure 1), an analysis for error in the C–F bonds from the spread about the mean, 1·323 Å, gives 0·007 Å suggesting that the standard deviations have not been underestimated in our crystallographic procedures. All the bond lengths within the ligand agree with those reported previously for delocalised chelated hfac ligands, *e.g.* in Hhfac;[10] in $CsY(hfac)_4$;[11] in (π-C_5H_5)$Zr(hfac)_3$;[12] and in *NNN'N'*-tetramethyl-1,8-diaminonaphthalene$^+Cu(hfac)_3^-$,[8] and the isomorphous magnesium derivative.

Again the dimensions of the ted molecule (Table 1) are those to be expected for bonds involving carbon and nitrogen atoms, both in a state of sp^3 hybridisation. They also agree with those reported for benzyl-lithium

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[10] A. L. Andreassen, D. Zebelman, and S. H. Bauer, *J. Amer. Chem. Soc.*, 1972, **93**, 1148.

[11] M. J. Bennett, F. A. Cotton, P. Legzdins, and S. J. Lippard, *Inorg. Chem.*, 1968, **7**, 1770.

[12] M. Elder, *Inorg. Chem.*, 1969, **8**, 2103.

ted[13] in which the ted molecule bridges two lithium atoms.

The environment of the copper atom is of particular interest. Tetragonally distorted octahedral geometry for copper has frequently been observed.[14] An unusal feature of the present complex is that the long axial bonds are the Cu–N bonds [2·566(7) Å], while the Cu–O bonds [mean 1·956(7)], are slightly shorter than usual. These Cu–O distances are significantly shorter than the equatorial Cu–O distances [2·015(5) Å] observed[8] in the complex anion $Cu(hfac)_3^-$ in which the symmetrical ligand environment is tetragonally distorted, [Cu–O(axial) 2·176(7) Å]. In the square planar complexes bis-(pentane-2,4-dionato)copper(II)[15] and bis-(3-methylpentane-2,4-dionato)copper(II)[16] the Cu–O bond lengths are 1·921 and 1·908 Å.

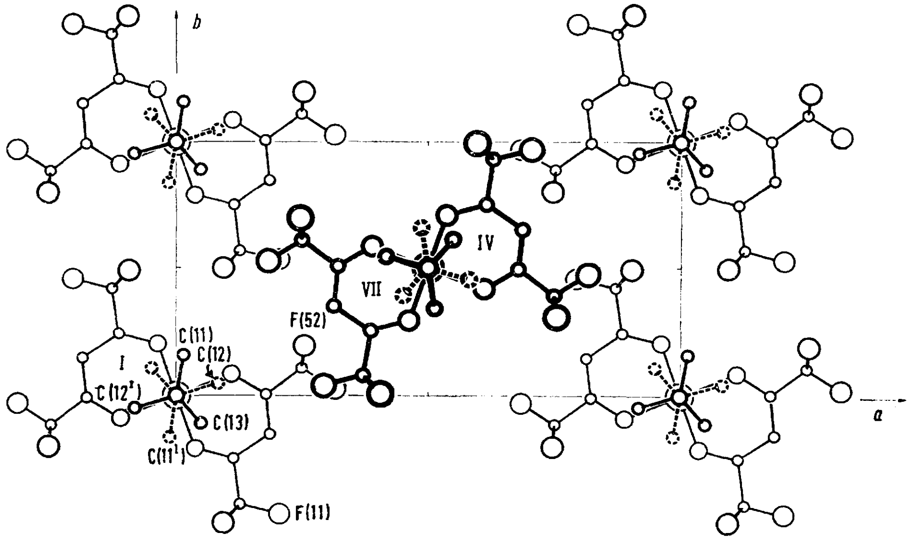

FIGURE 3 The structure projected down the *c* axis. For the ted molecules full and broken lines indicate the two possible orientations; C(11), C(12^I), and C(13) correspond to one molecule and C(11^I), C(12), and C(13^I) to the other

TABLE 1

Dimensions involving the ted part of the molecule with standard deviations in parentheses

(*a*) Bond lengths (Å)

N–C(11)	1·48(1)	C(11)–C(11^V)	1·55(3)
N–C(12)	1·47(1)	C(12)–C(12^V)	1·53(2)
N–C(13)	1·45(1)	C(13)–C(13^V)	1·53(3)
N–Cu	2·566(7)		

C–H distances assumed to be 0·95 Å

(*b*) Bond angles (°)

Cu–N–C(11)	110·8(6)	C(11)–N–C(13)	111·1(8)
Cu–N–C(12)	111·4(5)	C(11)–N–C(12^I)	105·4(8)
Cu–N–C(13)	111·8(5)	C(13)–N–C(12^I)	106·0(8)
N–C(11)–C(11^V)	110·8(9)		
N–C(12)–C(12^V)	111·3(8)		
N–C(13)–C(13^V)	111·8(9)		

In simple covalent compounds r_N is *ca.* 0·05 Å > r_O. A variety of Cu–O and Cu–N bond lengths have been reported where both oxygen and nitrogen are ligand atoms in planar four-co-ordinate complexes or in the equatorial plane of octahedral complexes. For thirteen *N*-substituted-bis(salicylaldiminato)copper(II) complexes the weighted mean values[17] were Cu–N **1·969** and Cu–O **1·893** Å, a difference of 0·076 Å.

Usually the long axial bond is to oxygen not nitrogen. For example in dinitratobis(pyrazine)copper(II),[18] a linear co-ordination polymer with the Cu–N ··· N–Cu chain axis lying perpendicular to the planes containing the Cu atoms and nitrate groups; the bond lengths are Cu–N 1·984(4) Å, with two Cu–O of 2·010(4) and two of 2·490(5) Å. In $(hfac)_2$(*NN*-dimethylethylenediamine)$_2$copper(II),[7] there are four nitrogen atoms, with Cu–N 1·989 and 2·064 Å, and the two axial bonds are to oxygen, Cu–O 2·793 Å.

TABLE 2

Distances < 3·0 Å from hydrogen atoms on ted to atoms in the chelate ring. Hydrogen atoms are designated H(*n*1) or H(*n*2) where *n* is the number of the corresponding carbon atom

H(131) ··· O(1)	2·79	H(122) ··· O(2)	2·84
H(111) ··· O(2)	2·98	H(121) ··· C(4)	2·94
H(121) ··· O(2)	2·97		

One possible explanation for the very long Cu–N bond in $Cu(hfac)_2$(ted) is the interaction of the ted hydrogens with the hfac ring. If the nitrogen formed a shorter bond with copper the hydrogens would also move closer to the ring system. The 'nearest neighbour' distances of hydrogens given in Table 2 are

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[13] S. P. Patterman, I. L. Karle, and G. D. Stucky, *J. Amer. Chem. Soc.*, 1970, **92**, 1150.

[14] For a review, see B. J. Hathaway and D. E. Billing, *Coordination Chem. Rev.*, 1970, **5**, 143.

[15] L. Dahl, personal communication, as reported in ref. 16.

[16] I. Robertson and M. R. Truter, *J. Chem. Soc.* (*A*), **1967**, 309.

[17] G. Marongiu and E. C. Lingafelter, *Acta Cryst.*, 1971, **B27**, 1195.

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

maximum values because the hydrogen positions were calculated assuming a C–H 0·95 Å, as commonly found by *X*-ray techniques.[19]

In the benzyl-lithium compound[13] there was some evidence for partial disorder of the ted. We are unable to explain the 50% occupation of two sites; our calculations show the interaction of hydrogen atoms with the chelate ring would be the same for all orientations and apparent free rotation might be expected.

1 : 2 *Complexes*.—The 1 : 2 complexes are prepared by stoicheiometric reaction in benzene or ethanol. Recrystallisation of $Cu(hfac)_2(ted)_2$ from carbon tetrachloride gave garnet red crystals. These readily sublimed as red flakes at 100°, leaving a greenish residue. When set aside in air the crystal slowly gave a greenish amorphous solid having an i.r. spectrum identical with that of $Cu(hfac)_2(ted)$. The visible spectra of both the 1 : 1 and 1 : 2 complexes of ted and $Cu(hfac)_2$ in CCl_4 gave identical spectra having a maximum at 14·4 kK.

TABLE 3

Infra-red spectra (cm^{-1}), with assignments

Complex	Nature	νC=O (ν_2)	νC=C (ν_3)	νC=O (ν_4)	νC=C (ν_5)	Ring def.	δsCF$_3$
Li(hfac)	Polymeric? [a]	1660	1560	1534	1257	667	588
Li(hfac)(tmed) (Solid)		1660	1540	1540	1268	667	584
Li(hfac)(tmed) (Benzene)	Monomer [a]	1660	1530	1530	1258		580
$Cu(hfac)_2(H_2O)$		1640	1560	1534	1255	680	600
$Cu(hfac)_2(bipy)$	*cis-O$_h$* [b]	1652 (broad)	1550	1525	1260	665	
$Cu(hfac)_2(tmed)$		1653	1543	1520	1255	665	588
$Cu(hfac)_3^-(tmndH^+)$	*O$_h$* [c]	1648	1553	1530	1260	672	589
$Cu(hfac)_2(dmed)_2$	' Unidentate [d] hfac '	1670	1259		1252	659	570
$Cu(hfac)_2(ted)$	*trans-O$_h$*	1640	1558	1532	1253	678	593
$[Cu(hfac)_2]_2(ted)$		1640	1560	1530	1252	678	598
$Cu(hfac)_2(ted)_2$		1649	1548	1526	1253	666	
$Cu(hfac)_2(tedH{\cdot}hfac)_2$		$\left.\begin{matrix}1665\\1640\end{matrix}\right\}$	1545	1540	1253	$\left.\begin{matrix}678\\659\end{matrix}\right\}$	$\left.\begin{matrix}600\\575\end{matrix}\right\}$
$(tedH)^+(hfac)^-$	' Ionic '	1666				658	578
$(tmndH)^+(hfac)^-$	' Ionic '	1665	1560, 1550	1530	1248	658	573

[a] K. Shobatake and K. Nakamoto, *J. Chem. Phys.*, 1968, **49**, 4792. Ref. 5. [c] Ref. 8. [d] Ref. 7. tmed = Tetramethylethylenediamine; dmed = *NN*-dimethylethylenediamine.

The diffuse reflectance spectra of the 1 : 1 and 1 : 2 complexes were different; $Cu(hfac)_2(ted)$ showed a maximum at 13·6 kK, and $Cu(hfac)_2(ted)_2$ gave a broad envelope with inflexions at 12·5, 15·5, and 19·3 kK. The mass spectrum of the red flakes showed no evidence for the parent peak, giving a superposition of the spectra of $Cu(hfac)_2$ and the ligand.

The ' single ' crystals of the 1 : 2 complex exhibited twinning and disorder and no deductions could even be made about the molecular symmetry by *X*-ray methods.

Hathaway[20] has suggested that $Cu(hfac)_2(pyridine)_2$ might exist in the *cis*-octahedral form. Possibly $Cu(hfac)_2(ted)_2$ has this, or a nonorthogonal arrangement. Low-temperature n.m.r. studies of bis-(4-picoline) adducts of bis-(β-diketonato)nickel complexes have indicated the increasing presence of *cis*-isomers when tfacH and hfacH replace acacH as the β-diketone.[21] It is also possible to envisage a polymeric lattice of Cu(ted), giving four nitrogen atoms per copper, and having the $hfac^-$ anion at long axial positions. The i.r. spectrum of the complex is different from that of $Cu(hfac)_2(ted)$, suggesting that it does not have a ***trans***-octahedral structure. ν(C⋅O) occurs at 1649 cm^{-1} which is not consistent with the presence of an anionic or losely held hfac [ν(C⋅O) 1665—1675 cm^{-1}][6,7] but is more like the values observed for the *cis*-octahedral complexes [ν(C⋅O) 1650 cm^{-1}].[6] Further indications are ν(C⋅C) 1548 cm^{-1} and the ring deformation at 666 cm^{-1}; these are more compatible with chelated, *cis*-octahedral species (Table 3).

Other Complexes.—The reaction of 1,8-(dimethylamino)naphthalene (tmnd) with hfacH and $Cu(hfac)_2(H_2O)$ gave the complex $(tmndH^+)Cu(hfac)_3^-$.[22] A similar reaction of ted, hfacH, and $Cu(hfac)_2(H_2O)$ in benzene gave two crystalline products, green needles and small green ' chunks '. The latter became opaque when set aside and the chemical analysis indicates loss of benzene.

The green needles showed only one ν(C⋅O) in the i.r. and were identical with similar crystals obtained in minor yield from the preparation of $Cu(hfac)_2(ted)$. The analytical data, and preliminary *X*-ray measurements suggest that this complex is $[Cu(hfac)_2]_2(ted)$. Reaction in stoicheiometric amounts gave only traces of the complex.

The analysis of the second species, when amorphous, corresponded to $Cu(hfac)_2(tedH{\cdot}hfac)_2$. The i.r. spectrum showed ν(C⋅O) at 1665 and 1640 cm^{-1}, and two deformations at 678 and 659 cm^{-1}, so that two independent hfac entities, one covalent, one ionic could be

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[19] See, *e.g.*, M. A. Bush and G. A. Sim, *J. Chem. Soc.* (*A*), 1970, 605.

[20] R. J. Dudley and B. J. Hathaway, *J. Chem. Soc.* (*A*), 1970, 2794.

[21] R. W. Kluiber, R. Kukla, and W. D. Horrocks, jun., *Inorg. Chem.*, 1970, **9**, 1319.

[22] D. E. Fenton, B. L. Vickery, and M. R. Truter, *Chem. Comm.*, 1971, 93.

present, and we suggest an octahedral complex of $Cu(hfac)_2$ in which ($tedH^+$) co-ordinates to $Cu(hfac)_2$ through its available donor nitrogen.

The reaction of $Cu(tfac)_2$ with ted gave only $Cu(tfac)_2(ted)$ illustrating the effect of trifluoromethylation on co-ordinative saturation. With $Cu(acac)_2$, no isolable species were obtained. The reactions were carried out under the same conditions as for $Cu(hfac)_2$.

EXPERIMENTAL

I.r. spectra were measured as Nujol mulls or KBr discs on a Perkin-Elmer 457 spectrophotometer. Visible, and diffuse reflectance spectra were recorded on a Unicam SP 500 spectrophotometer.

Preparation of Complexes.—Bis(hexafluoroacetylacetonato)(aquo)copper(II) was prepared by the method of ref. 23. Reactions were carried out in air. (*a*) Bis(hexafluoroacetylacetonato)(triethylenediamine)copper(II). Bis(hexafluoroacetylacetonato)(aquo)copper(II) (1 mmol) and 1,4-diazabicyclo[2,2,2]octane (triethylenediamine) (1 mmol) were warmed together in carbon tetrachloride for 30 min. On cooling acicular, *yellow-green crystals* of the complex grew (Found: C, 32·5; H, 2·4; Cu, 10·6; N, 4·7%; *M* (osmometry in benzene) 577, (*X*-ray) 605. $C_{26}H_{14}CuF_{12}N_2O_4$ requires C, 32·2; H, 2·5; Cu, 10·8; N, 4·6%; *M*, 590). If the preparation was carried out in benzene or ethanol solutions crystals grew slowly and became opaque when set aside. In these preparations traces of crystalline material remained which gave the same i.r. spectrum as $[Cu(hfac)_2]_2(ted)$.

(*b*) Bis(hexafluoroacetylacetonato)bis(triethylenediamine)copper(II). Bis(hexafluoroacetylacetonato)(aquo)copper(II) (1 mmol) was warmed with triethylenediamine (2 mmol) in benzene, or ethanol for 30 min. On cooling garnet red crystals of the complex were obtained. These slowly went opaque, and subsequent recrystallisation from carbon tetrachloride gave a crystalline form. The complex was sublimed, at aspirator pressure, on gentle warming to give *red flakes* of the complex (Found: C, 37·6; H, 3·7; Cu, 9·8; N, 7·9%; *M* (*X*-ray) 671. $C_{22}H_{26}CuF_{12}N_4O_4$ requires C, 37·1; H, 3·9; Cu, 9·1; N, 7·7%; *M*, 702).

(*c*) Bis(trifluoroacetylacetonato)(triethylenediamine)copper(II) was prepared by method (*a*) in benzene–ethanol solution. Yellow-green needles grew, which became opaque to give a green powder (Found: C, 39·9; H, 4·3; Cu, 12·9; N, 5·4. $C_{16}H_{20}CuF_6N_2O_4$ requires C, 39·8; H, 4·2; Cu, 13·2; N, 5·8%). The reaction of bis(acetylacetonato)copper(II) with excess of triethylenediamine in benzene–ethanol gave a green solution. On evaporation $Cu(acac)_2$ was recovered.

(*d*) The reaction of bis(hexafluoroacetylacetonato)(aquo)copper(II) (1 mmol), hexafluoroacetylacetone (1 mmol), and triethylenediamine (1 mmol) in benzene, or benzene–ethanol, gave on slow evaporation green *rods* (*A*) and pale green diamond-shaped *plates* (*B*). (i) $[Cu(hfac)_2]_2(ted)$, (*A*), (Found: C, 29·0; H, 1·5; Cu, 11·5; N, 2·6%; *M* (*X*-ray) 1087. $C_{26}H_{16}Cu_2F_{24}O_8N_2$ requires C, 29·2; H, 1·5; Cu, 11·9; N, 2·6%; *M* 1068). (ii) Plates of $Cu(hfac)(tedH{\cdot}hfac)_2$ (*B*) slowly became opaque when set aside and the analytical data indicated loss of benzene (Found: C, 44·2; H, 3·4; N, 4·4. $C_{26}H_{28}CuF_{24}N_4O_8$ with 3 molecules of benzene requires C, 44·8; H, 3·4; N, 4·1%). (iii) $Cu(hfac)_2(tedH{\cdot}hfac)_2$, (amorphous), (Found: C, 33·9; H, 2·5; N, 5·2. $C_{26}H_{28}CuF_{24}N_4O_8$ requires C, 34·3; H, 2·5; N, 5·0%).

Determination of the Crystal Structure of $Cu(hfac)_2(ted)$

An acicular crystal 0·1 × 0·1 × 0·3 mm was mounted in Araldite on a rigid support * on a Picker four-circle diffractometer. The unit-cell dimensions and their standard deviations were determined by a least-squares fit [24] to the setting angles of 12 reflections which had been carefully centred.

Crystal Data.—$C_{16}H_{14}CuF_{12}N_2O_4$, $M = 589{\cdot}5$, Orthorhombic, $a = 16{\cdot}148(18)$, $b = 8{\cdot}428(9)$, $c = 7{\cdot}743(9)$ Å, $U = 1053{\cdot}6$ Å^3, D_m (by flotation) $= 1{\cdot}9$, $Z = 2$, $D_c = 1{\cdot}85$, $F(000) = 586$. Space group *Pnnm* determined by structure analysis. Mo-K_α (Zr-filtered) radiation, $\lambda(K_{\alpha1}) = 0{\cdot}70930$, $\lambda(K_{\alpha2}) = 0{\cdot}71359$ Å (1 Å $\equiv 10^{-10}$m). μ(Mo-K_α) $= 12$ cm^{-1}; no absorption correction applied.

For intensity measurements the crystal was set in a random orientation with respect to the goniometer axes to minimise the risk of double reflection. Observations were made on the hkl and $\bar{h}\bar{k}l$ octants with a scintillation counter through a pulse-height discriminator out to $2\theta = 60°$. 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 103, 013, and 040 were measured every 50 reflections and used to put all observations on the same scale. The observations were processed [24] to give a set of intensities for which I, the net intensity, was $> 3\sigma(I)$ where $\sigma^2(I) = [C + 0{\cdot}25\,(t_c/t_b)^2(B_1 + B_2)]$ 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 764 values from 1808 original observations for $|F_{hkl}|$.

Structure Determination.—Systematic absences of reflections, $0kl$ with $k + l$ odd and $h0l$ with $h + l$ odd corresponded to space groups $Pnn(2)$ and *Pnnm*. In the former the copper atom must lie on a two-fold axis, a condition easily satisfied by a $Cu(hfac)_2$ molecule; the ted ligand must also lie on a two-fold axis which is possible if the axis passes through the centre of one C–C bond. In *Pnnm* the two formula units per cell must have $2/m$ symmetry, which is possible for a strictly planar $Cu(hfac)_2$ but not for ted, so the non-centrosymmetric space group seemed more probable and only the hkl reflections were used to solve the structure.

A Patterson synthesis was computed [24] and showed the atoms of the β-diketonate lying with the copper atom in the plane $w = 0$ with two pairs of fluorine atoms related by the (Patterson) plane of symmetry at $w = 0$. Along the w axis at 0,0,0·3 was another atom, presumably the

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* Support designed by R. H. B. Mais and P. G. Owston, Imperial Chemical Industries Ltd.

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

[24] '*X*-RAY ARC,' IBM 1130 programme system for crystallography, B. L. Vickery, D. Bright, and P. R. Mallinson. Cell dimensions from PICK 3, W. C. Hamilton's programme (adapted by D. B.). Data reduction PRED (by B. L. V.). Fourier summation FODAP, A. Zalkin's programme (adapted by D. B.). Block-diagonal least-squares, BLOK (by B. L. V.). Bond lengths and angles with standard deviations, BOND (by P. R. M.). Interatomic contacts including symmetry and translational relations, BANGL (by D. B.).

nitrogen of ted. This meant that the N $\cdots$ N direction of the ted molecule was occupying a two-fold axis so must be disordered in either space group. In fact the arrangement was strongly indicative of the space group *Pnnm* with Cu(hfac)$_2$ lying on the mirror plane at $z = 0$ and the ted lying along the z axis with its mirror plane on the crystallographic one at $z = \frac{1}{2}$.

Structure factors were calculated in *Pnnm* with the copper, the one nitrogen, and the eleven β-diketonate atoms. A subsequent Fourier synthesis clearly showed six peaks instead of the three expected for the CH$_2$ groups attached to one nitrogen; they appeared to be well resolved, suggesting half occupation of each site rather than complete rotation to give the two-fold symmetry. With these $\frac{1}{2}$ carbon atoms included, structure factors were calculated, R was 0·28. Four cycles of isotropic refinement by full-matrix least-squares reduced R to 0·134.

At this stage the 1818 observations for $\bar{h}\bar{k}\bar{l}$ were processed to give $|F_{\bar{h}\bar{k}\bar{l}}|$ and these values averaged with those for $|F_{hkl}|$, all the observations with $I \geqslant 0$ were included, giving 1650 altogether. A further test was applied and planes for which $|F_{\text{mean}}| < (\sigma F_{hkl} + \sigma F_{\bar{h}\bar{k}\bar{l}})$ were rejected so that in the final cycle 832 were used. Refinement was continued by block-diagonal least-squares [24] allowing for anisotropic vibration for copper and fluorine and reduced R to 0·068. Hydrogen atoms were included in positions calculated to give C–H 0·95 Å, for H(3) to complete a trigonal arrangement about C(3), and for the other hydrogens to complete tetrahedral arrangements about C(11)—(13). They were assigned isotropic vibration parameters and their parameters were not refined. The function refined in least-squares was $R' = \Sigma w(|F_o| - |F_c|)^2$ where the weighting function w was adjusted to give reasonably constant average values for R' in different ranges of $\sin\theta/\lambda$ and of $|F_o|$. The final scheme was $w = 1/(\sigma_{\text{counting}} + 0{\cdot}01|F_o| + 0{\cdot}0001F_o{}^2)^2$. Refinement converged at R 0·060. To obtain more realistic standard deviations we then carried out a final cycle of full-matrix refinement on the CDC 6600 computer with the programme NUCLS.[25] This gave R 0·060, *i.e.* 0·052 for the 626 planes with $h + k + l$ even and 0·097 for the 206 planes with $h + k + l$ odd. A difference-Fourier map was computed and its highest peak was 0·65 eÅ^{-3} near the copper. There was no evidence to suggest that the ted was rotating, *i.e.* the half-occupancy of the two sites for the methylene carbon atoms was satisfactory.

Final observed and calculated structure factors, listed in Supplementary Publication No. SUP 20474 (8 pp., 1 microfiche), were obtained from the parameters in Table 4 with scattering factors for copper corrected for the real part of the anomalous dispersion, carbon, nitrogen, oxygen, and fluorine from ref. 26 and for hydrogen from ref. 27.

TABLE 4

(*a*) Fractional co-ordinates and isotropic vibration parameters, exp − ($B \sin^2\theta/\lambda^2$), with standard deviations in parentheses, except where the parameter was fixed

	x/a	y/b	z/c	B/Å^2
Cu	0·0	0·0	0·0	
O(1)	0·0416(3)	−0·2182(6)	0·0	3·35(9)
O(2)	0·1121(3)	0·0870(5)	0·0	3·19(9)
C(1)	0·1293(5)	−0·4367(10)	0·0	4·21(16)
C(2)	0·1163(4)	−0·2561(8)	0·0	3·19(13)
C(3)	0·1853(4)	−0·1599(9)	0·0	3·35(14)
C(4)	0·1770(4)	0·0033(9)	0·0	2·89(11)
C(5)	0·2550(5)	0·1057(10)	0·0	4·05(16)
F(51)	0·3244(3)	0·0218(6)	0·0	
F(52)	0·2579(2)	0·1990(4)	0·1368(5)	
F(11)	0·2091(3)	−0·4760(6)	0·0	
F(12)	0·0957(2)	−0·5034(4)	0·1363(5)	
N	0·0	0·0	0·3315(8)	3·53(10)
C(11)	0·0190(7)	0·1602(17)	0·3995(19)	5·8(3)
C(12)	0·0824(7)	0·0397(13)	0·4008(17)	4·6(2)
C(13)	0·0564(7)	−0·1176(16)	0·4012(17)	5·3(3)
H(3)	0·24	−0·21	0·00	4·0
H(111)	0·07	0·20	0·35	4·0
H(112)	−0·02	0·24	0·35	4·0
H(121)	0·12	−0·03	0·36	4·0
H(122)	0·10	0·14	0·36	4·0
H(131)	0·04	−0·22	0·36	4·0
H(132)	0·11	−0·10	0·36	4·0

(*b*) Anisotropic vibration parameters (Å^2 × 10^3) * of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	284(5) *	310(6)	602(8)	25(7)	0	0
F(11)	59(3)	45(3)	177(7)	19(2)	0	0
F(12)	105(3)	52(2)	89(3)	3(2)	10(2)	25(2)
F(51)	37(2)	69(4)	140(5)	−6(2)	0	0
F(52)	69(2)	80(2)	80(3)	−20(2)	−9(2)	−27(2)

* Cu parameters × 10^4.

Bond lengths and their standard deviations were calculated with the programme ORFFE,[25] bond angles and their standard deviations and the intermolecular distances with the programmes BOND and BANGL.[24]

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* For details see Notice to Authors in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

[25] Northwestern University versions of the Busing–Levy ORFLS and ORFFE programmes run on the University of London CDC 6600 computer.

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

[27] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.