défini faisant un angle de 1,3° avec le plan bissecteur des cycles (Tableau 6).

La liaison S—S a une longueur de 2,010 (5) Å qui est voisine de celle trouvée dans le composé (V) (2,04 Å) et donc nettement supérieure à la longueur de la liaison S—S de (VI) (1,71 Å). Cette longueur est comparable à celle trouvée dans des ponts S—S, par exemple dans $[Ti(C_5H_5)_2(S_5)]$ où les longueurs S—S sont voisines de 2,06 Å (Epstein, Bernal & Kopf, 1971) ou dans des groupes S_2 bidentés sur le même métal tel que dans $[Mo_2(S_2)_6]^{2-}$ où leur longueur est de 2,043 (5) Å (Muller, Nolte & Krebs, 1978) et même dans un complexe étudié par Meunier & Prout (1979) où il existe un cycle Mo_2S_2 dans lequel les deux atomes de soufre sont à 2,019 (3) Å. Ces longueurs sont intermédiaires entre celle de l'ion S_2^{2-} (2,12 Å dans CoS_2; Elliott, 1960) et celle de la molécule S_2 à l'état vapeur dans son état fondamental ${}^3\Sigma_g^-$ (1,887 Å; Meyer, 1976).

La liaison latérale Nb—S(1) [2,515 (2) Å] a une longueur identique aux liaisons Nb—S entre CS_2 et Nb dans (I) et (III), par contre la liaison centrale Nb—S(2) [2,432 (3) Å] est nettement plus courte. Cette différenciation peut être comparée aux deux liaisons 'σ—π' Nb—(C_2H_4) de (IV), la liaison centrale Nb—C proche de la liaison σ Nb—C_2H_5 étant plus courte que l'autre.

La liaison σ Nb—CH_3 a quasiment la même longueur dans (I) et (II): 2,346 (8) et 2,327 (11) Å. Cette longueur est légèrement plus grande que dans le cas du groupe éthyl (IV): 2,316 Å, et du groupe σ-allyl (III): 2,309 (31) Å.

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The Structure of the 2:1 Complex of Bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)copper(II) with 1,4-Diazabicyclo[2.2.2]octane

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Abstract

Three-dimensional X-ray crystal-structure analysis has shown that the 2:1 complex, systematically named in the title, consists in the solid of discrete molecules of formula corresponding to the stoichiometry, *viz* $[Cu(C_5HF_6O_2)_2]_2(C_6H_{12}N_2)$, $C_{26}H_{16}Cu_2F_{24}N_2O_8$. In a monoclinic crystal having dimensions $a = 22{\cdot}854$ (6), $b = 25{\cdot}548$ (4), $c = 12{\cdot}601$ (2) Å, $\beta = 92{\cdot}26$ (2)° and space group $I2/c$ there are eight of these formula units, two independent sets of four molecules. Each molecule lies on a twofold axis of symmetry: for one set this axis

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passes through Cu—N···N—Cu and the CH_2 groups of the base are disordered; for the other set this axis passes through the centre of one C—C bond of the base. Full-matrix refinement reduced R to 0·073 for 3189 observed structure amplitudes measured on a four-circle diffractometer. Each copper atom is coordinated by four oxygen atoms, mean Cu—O = 1·952 (7) Å in the base plane and displaced by 0·25 Å from this plane towards a nitrogen atom, mean Cu—N = 2·256 (7) Å, at the apex of a square pyramid.

Introduction

During a systematic study of coordinative saturation of copper β-diketonates, Belford, Fenton & Truter (1972, hereafter BFT 1), reported the reactions between a bidentate but non-chelating nitrogen ligand 1,4-diazabicyclo[2.2.2]octane (also known as triethylenediamine, *i.e.* ted) and bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)copper(II), *i.e.* $(hfac)_2Cu$. Products were obtained with $(hfac)_2Cu$:ted stoichiometries of 1:1, 1:2 and 2:1. The crystal structure of the 1:1 compound (BFT 1) showed it to consist of a linear polymer formed by ted molecules bridging adjacent copper atoms which occupied sites of $2/m$ symmetry and were chelated by two $F_3CCOCHCOCF_3^-$ anions. We now report the structure of the 2:1 complex for comparison with the 1:1 complex and with the 2:1 and 1:1 complexes of $(hfac)_2Cu$ with pyrazine $C_4H_4N_2$ (Belford, Fenton & Truter, 1974, hereafter BFT 2).

Experimental

Preliminary X-ray photographs gave the space group and approximate cell dimensions. To preserve the convenient β angle close to 90° the non-standard body-centred cell was retained for collection of intensities and the structure analysis.

Crystal structure

$C_{26}H_{16}Cu_2F_{24}N_2O_8$, M_r = 1067·5. Monoclinic, a = 22·854 (6), b = 25·548 (4), c = 12·601 (2) Å, β = 92·26 (2)°, U = 7351·4 Å^3, D_m (flotation) = 1·93 Mg m^{-3}, Z = 8, D_c = 1·93 Mg m^{-3}, $F(000)$ = 4192. Space group $I2/c$ by structure analysis (non-standard setting of $C2/c$), equivalent positions $\pm(x,y,z;\ x,-y,\tfrac{1}{2}+z;\ \tfrac{1}{2}+x,\tfrac{1}{2}+y,\tfrac{1}{2}+z;\ \tfrac{1}{2}+x,\tfrac{1}{2}-y,z)$. λ(Mo $K\bar{\alpha}$) = 0·71069 Å, μ(Mo $K\alpha$) = 1·325 mm^{-1}. No absorption correction was applied.

Crystals were green needles; one 0·1 × 0·1 × 0·8 mm was mounted in Araldite on a quartz fibre and 3440 observations were collected first with a Picker card-controlled four-circle diffractometer, during a period of intermittent faults. Later, 4805 diffraction intensities for $3\cdot0 \le 2\theta \le 45°$ were remeasured, more reliably, on an Enraf–Nonius CAD-4 diffractometer with monochromated Mo $K\alpha$ radiation. The ω–2θ scan was used with the angle $(0\cdot9 + 0\cdot35\tan\theta)°$; the reflections $\bar{3}70$ and $23\bar{3}$ were measured every hour and showed no change in intensity with time.

Structure solution

Systematic absences of reflections correspond to space groups Ic or $I2/c$. With eight formula units in the cell no molecular symmetry would be required in the latter and there would be two independent formula units per equivalent position in the former. Statistical methods indicated that the centrosymmetric space group was correct.

From the first data set, interpretation of the three-dimensional Patterson synthesis was not straightforward. A separation of about 7·5 Å would correspond to a Cu–ted–Cu bridge as in the 1:1 complex. A strong peak at 0,0·28,0 (not a relation required by symmetry) gave a separation of 7·2 Å along the unique

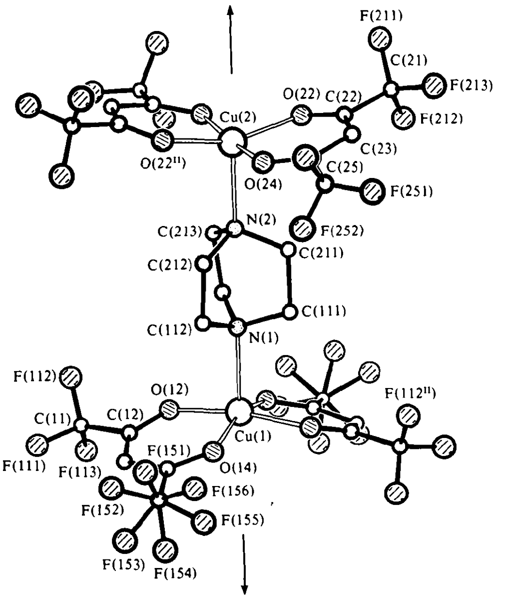

Fig. 1. A view of the Cu(1)—Cu(2) molecule showing the numbering of the atoms. Cu(1), N(1), Cu(2) and N(2) lie on a twofold axis shown by the arrow which relates the β-diketonates about each copper atom, the related atoms having designations with a superscript II. For the triethylenediamine molecule one orientation is shown, including designations of the carbon atoms which have three digits; the first is that of the nitrogen atom, the second is 1 and the third distinguishes the three independent atoms. The other orientation is obtained by rotation of 180° about the N···N direction. The trifluoromethyl group of C(15) is disordered and both sets of positions are shown. Hydrogen atoms are omitted; those on the β-diketonates are H(13) and H(23); those of the methylene groups are designated by three digits and the letter A or B; the digits are the same as those of the carbon atom to which they are attached.

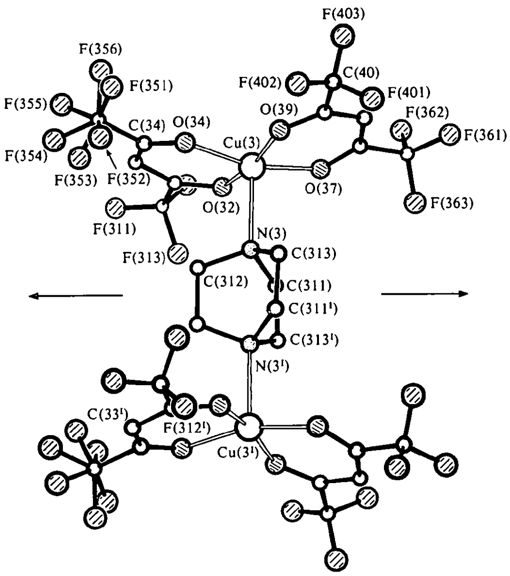

Fig. 2. The Cu(3) molecule with designations of the atoms; the two copper atoms are related by the twofold axis, shown by an arrow, and the rest of the molecule similarly to give the atoms with the superscript I. The hydrogen atoms are not shown; those on the β-diketonates are H(33) and H(38); those on the methylene groups are designated on the same principles as in the legend to Fig. 1.

axis and indicated that two copper atoms sharing a disordered ted molecule could be situated on the twofold axis. This arrangement with two independent copper atoms Cu(1) and Cu(2), Fig. 1, would account for four molecules in the unit cell.

Electron-density maps phased from copper atoms alone did not yield any sensible ligand details. Approaches by direct methods, using our suite of programs for the IBM 1130 computer (XRAY ARC, 1973), also failed to show definitive ligand fragments. However, comparison of inter-peak vectors, calculated from E maps, with Patterson map peaks, eventually led to a consistent set of coordinates for three copper sites. The third site, for Cu(3), corresponds to the second 2:1 molecule (Fig. 2), situated on a twofold axis which passes through the centre of one C—C bond of the ted molecules and relates Cu(3) and Cu(3^{I}). Fragments of some ligands were imagined in the E map and, using these, most of the atoms of the complex were located in subsequent electron-density maps.

Some of the fluorine atoms could not be satisfactorily resolved and it was at this stage that the second data set was measured. From examination of all the trifluoromethyl-group regions, with electron-density and difference maps, and subsequent refinement (*SHELX*; Sheldrick, 1976) with the second data set, it was concluded that (*a*) two of these groups [of C(21) and C(36)] were well behaved with normal vibration parameters, (*b*) two groups [of C(15) and C(35)] each showed six distinct fluorine sites, each with *ca* 50% occupancy, and (*c*) the remaining four groups were probably best described as ordered, but having rather large anisotropic thermal parameters. Figs. 1 and 2 show the designations of the atoms including the alternative sets for the trifluoromethyl groups on C(15) and C(35).

The copper and fluorine atoms in the ordered trifluoromethyl groups were allowed anisotropic vibration parameters. Hydrogen atoms were included with C—H distances of 1·08 Å and isotropic vibration parameters 0·01 Å^2 greater than those of the carbon atoms to which they were attached.

It was necessary to refine the parameters of the two molecules in alternate cycles with the scale factor in every cycle; thus correlations within molecules have been allowed for and those between neglected. Correlation coefficients greater than 0·6 were found among the vibration parameters of individual fluorine atoms and between the x and z coordinates of F(402).

The scattering factor curve for Cu^{2+} was from *International Tables for X-ray Crystallography* (1974); for the other atoms, the values incorporated in the refinement program *SHELX* (Sheldrick, 1976) were used.

A final electron-density difference synthesis showed as the highest peak 0·95 e Å^{-3} in a disordered trifluoromethyl group. Refinement was discontinued with R at 0·073 (R' 0·072) with unit weights for 3189 observed structure amplitudes (those for 200, 020 and 402 were omitted as were 1613 with $I < 2\sigma_I$).

Results and discussion

Final atomic coordinates are in Table 1.* Bond lengths and some bond angles are given in Table 2.

Mean values for the bond lengths within the β-diketone rings with the standard deviations calculated from the spread about the mean are C—O 1·265 (13), C—C 1·37 (1) and C—C(F) 1·52 (2) Å [this last includes the value of 1·58 (2) Å for C(34)—C(35)] suggesting that the e.s.d.'s from the correlation matrix are not seriously underestimated. For the C—F bonds in the ordered groups the mean is 1·28 Å with a standard deviation of ±0·03 Å. The apparent mean for the disordered groups is 1·32 Å; these fluorine atoms were given isotropic vibration parameters and their C—F distance agrees with the standard value (*Tables of Interatomic Distances and Configuration in Molecules and Ions*, 1965). We have not attempted to correct for 'riding motion' for the

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and intermolecular contacts have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35514 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates* ($\times 10^4$) *and isotropic vibration parameters*, U_{iso} ($\times 10^3$ Å^2), *with, in parentheses, the standard deviations in the least significant figures*

The percentage site-occupation factor (SOF) is given where it is less than 100.

	x	y	z	U_{iso}	SOF (%)
Cu(1)	0	3015 (1)	−2500	–	
Cu(2)	0	5793 (1)	−2500	–	
N(1)	0	3889 (4)	−2500	41 (3)	
C(111)	−608 (10)	4095 (9)	−2655 (20)	63 (6)	50
C(112)	165 (12)	4089 (9)	−1446 (20)	72 (7)	50
C(113)	371 (14)	4068 (11)	−3321 (24)	91 (9)	50
C(211)	−570 (11)	4706 (10)	−2801 (22)	74 (7)	50
C(212)	137 (12)	4706 (10)	−1447 (20)	76 (7)	50
C(213)	439 (13)	4682 (11)	−3240 (24)	90 (9)	50
N(2)	0	4906 (4)	−2500	39 (3)	
C(11)	1787 (7)	2769 (6)	−1870 (13)	84 (4)	
F(111)	2121 (4)	2665 (6)	−1044 (10)	–	
F(112)	1986 (4)	3172 (4)	−2262 (11)	–	
F(113)	1874 (4)	2394 (5)	−2492 (11)	–	
C(12)	1141 (5)	2808 (4)	−1633 (9)	59 (3)	
O(12)	837 (3)	2947 (3)	−2434 (6)	60 (2)	
C(13)	970 (5)	2700 (5)	−636 (10)	68 (3)	
C(14)	386 (5)	2743 (4)	−365 (9)	58 (3)	
O(14)	−37 (3)	2871 (3)	−966 (6)	58 (2)	
C(15)	228 (7)	2624 (6)	769 (12)	88 (4)	
F(151)	242 (10)	3018 (8)	1358 (15)	116 (6)	50
F(152)	628 (9)	2822 (7)	1494 (14)	107 (6)	50
F(153)	550 (9)	2228 (8)	1191 (15)	117 (6)	50
F(154)	135 (9)	2131 (7)	904 (14)	104 (5)	50
F(155)	−331 (9)	2466 (9)	838 (16)	127 (7)	50
F(156)	−279 (8)	2851 (8)	1057 (15)	106 (5)	50
C(21)	−1439 (6)	6153 (5)	−4611 (10)	68 (3)	
F(211)	−1200 (4)	6546 (3)	−5113 (6)	–	
F(212)	−1425 (4)	5745 (4)	−5251 (6)	–	
F(213)	−1989 (3)	6275 (4)	−4492 (6)	–	
C(22)	−1115 (4)	6029 (4)	−3576 (8)	50 (3)	
O(22)	−568 (3)	5942 (3)	−3667 (5)	53 (2)	
C(23)	−1417 (5)	6019 (4)	−2657 (9)	59 (3)	
C(24)	−1149 (4)	5910 (4)	−1679 (8)	46 (3)	
O(24)	−612 (3)	5833 (3)	−1468 (5)	46 (2)	
C(25)	−1532 (5)	5851 (5)	−742 (10)	62 (3)	
F(251)	−2059 (3)	5800 (7)	−941 (7)	–	
F(252)	−1386 (5)	5470 (5)	−141 (9)	–	
F(253)	−1461 (6)	6220 (5)	−83 (10)	–	
Cu(3)	3617·9 (5)	4509·4 (5)	1088 (1)	–	
N(3)	4496 (3)	4505 (3)	1982 (6)	38 (2)	
C(311)	4953 (4)	4765 (4)	1356 (9)	56 (3)	
C(312)	4697 (4)	3967 (4)	2228 (9)	56 (3)	
C(313)	4463 (5)	4792 (4)	3015 (8)	55 (3)	
C(31)	4274 (6)	3601 (5)	−1401 (10)	66 (3)	
F(311)	4321 (6)	3123 (3)	−1627 (9)	–	
F(312)	4088 (5)	3847 (5)	−2218 (7)	–	
F(313)	4802 (4)	3766 (6)	−1305 (8)	–	
C(32)	3932 (4)	3725 (4)	−429 (8)	50 (3)	
O(32)	3954 (3)	4208 (3)	−177 (5)	49 (2)	
C(33)	3664 (5)	3322 (5)	76 (9)	63 (3)	
C(34)	3380 (5)	3407 (5)	990 (9)	58 (3)	
O(34)	3323 (3)	3826 (3)	1519 (6)	58 (2)	
C(35)	3074 (7)	2935 (6)	1560 (13)	95 (5)	
F(351)	2652 (8)	3068 (6)	2144 (15)	97 (5)	50
F(352)	3189 (9)	2956 (8)	2640 (16)	116 (6)	50
F(353)	3459 (8)	2747 (8)	2244 (16)	110 (6)	50
F(354)	3328 (9)	2486 (8)	1341 (17)	120 (6)	50
F(355)	2955 (8)	2559 (7)	850 (14)	98 (5)	50
F(356)	2523 (8)	2953 (7)	1377 (15)	107 (5)	50
C(36)	3523 (5)	6086 (5)	55 (10)	62 (3)	
F(361)	3270 (4)	6517 (3)	406 (6)	–	
F(362)	3331 (4)	6021 (3)	−937 (6)	–	
F(363)	4088 (3)	6174 (3)	18 (7)	–	
C(37)	3394 (4)	5606 (4)	726 (8)	47 (2)	
O(37)	3686 (3)	5207 (3)	448 (5)	52 (2)	
C(38)	3013 (4)	5646 (4)	1525 (8)	51 (3)	
C(39)	2904 (4)	5241 (4)	2198 (8)	48 (3)	
O(39)	3115 (3)	4786 (3)	2168 (5)	53 (2)	
C(40)	2486 (6)	5323 (5)	3085 (10)	67 (3)	
F(401)	2632 (5)	5723 (5)	3654 (9)	–	
F(402)	2463 (6)	4961 (5)	3740 (10)	–	
F(403)	1981 (4)	5414 (7)	2774 (8)	–	

ordered fluorines for which the anisotropic vibrational motion yielded shortened C—F lengths. Individual values for C—C—F and F—C—F angles are not quoted. For the ordered groups C—C—F ranges from 110 to 117° with an e.s.d. of 1·3° while F—C—F ranges from 101 to 109° with an e.s.d. of 1·4°. For disordered groups the ranges are 106–115 (e.s.d. 1·4) and 100–116° (e.s.d. 1·7°) for C—C—F and F—C—F respectively.

The mean planes through various groups of atoms are given in Table 3. Planes (*a*)–(*d*) are those of the four *β*-diketonate skeletons, calculated allowing for weighting according to the standard deviations in the coordinates of the atoms; some of the exocyclic carbon atoms are significantly out of the planes. For the fluorine atoms which lie close to the planes there are two possible positions, one having the O—C—C—F conformation *trans* and the other *cis*; of the six such fluorine atoms in Table 3, only F(402) gives the *cis* conformation as shown in Fig. 2; the *trans* conformation gives fairly close H···F contacts, Table 4.

The three independent copper atoms have essentially the same environment: a square pyramid with the oxygen atoms, mean Cu—O = 1·952 (7) Å, in the base and a nitrogen atom, mean Cu—N = 2·256 (7) Å, at the apex. The Cu—O distances are close to 1·96 (1) Å, the value obtained for Cu—O in 4 + 1 or 4 + 2 coordination in a survey (Kawamura, Kawahara & Iiyama, 1978) of accurately determined inorganic complexes of copper.

Table 3 also shows the deviations of the copper atoms from the planes through the four oxygen atoms; for Cu(1) and Cu(2), the normal to this plane necessarily coincides with the Cu—N bonds; the Cu(3)—N(3) bond is 4·8 (2)° to the normal plane (*e*). Angles (*c*)–(*d*), (*a*)–(a^{ii}) and (*b*)–(b^{ii}) give the bowing at each copper atom.

Although the angles round the nitrogen atoms N(1) and N(2) do not differ significantly from 109·5°, the more accurate values round N(3) show a significant trend in the direction expected for a lone pair of electrons occupying the orbital directed towards copper; the mean Cu—N(3)—C angle at 111·3 (5)° is 3·7 (8)° larger than the mean C—N(3)—C angle. Several aspects of the geometry show that there is no preferred orientation of the ted groups with respect to the hfac ligands, and that it is unlikely that the Cu—N bond length

Table 2. *Bond lengths* (Å) *and angles* (°)

Bond lengths

(*a*) Round the copper atoms

	$n = 1$	$n = 2$	$n = 3$
Cu(*n*)—N(*n*)	2·233 (11)	2·268 (11)	2·262 (7)
Cu(*n*)—O(*n*2)	1·919 (7)	1·960 (7)	1·955 (7)
Cu(*n*)—O(*n*4)	1·973 (7)	1·949 (6)	1·957 (7)

Cu(3)—O(37)	1·963 (7)
Cu(3)—O(39)	1·949 (7)

(*b*) In the *β*-diketones

	$n = 1$	$n = 2$	$n = 3$
F(*n*11)—C(*n*1)	1·29 (2)	1·32 (2)	1·26 (2)
F(*n*12)—C(*n*1)	1·24 (2)	1·32 (2)	1·26 (2)
F(*n*13)—C(*n*1)	1·26 (2)	1·31 (2)	1·28 (2)
C(*n*2)—C(*n*1)	1·52 (2)	1·51 (2)	1·51 (2)
C(*n*2)—O(*n*2)	1·25 (1)	1·28 (1)	1·27 (1)
C(*n*2)—C(*n*3)	1·36 (2)	1·37 (2)	1·37 (2)
C(*n*3)—C(*n*4)	1·39 (2)	1·38 (2)	1·36 (2)
C(*n*4)—O(*n*4)	1·25 (1)	1·26 (1)	1·27 (1)
C(*n*4)—C(*n*5)	1·52 (2)	1·51 (2)	1·58 (2)
F(*n*51)—C(*n*5)	1·25 (3)	1·23 (2)	1·28 (3)
F(*n*52)—C(*n*5)	1·37 (2)	1·27 (2)	1·38 (3)
F(*n*53)—C(*n*5)	1·35 (3)	1·26 (2)	1·30 (3)
F(*n*54)—C(*n*5)	1·29 (3)		1·32 (3)
F(*n*55)—C(*n*5)	1·35 (3)		1·33 (2)
F(*n*56)—C(*n*5)	1·36 (3)		1·27 (2)

F(361)—C(36)	1·33 (1)	C(38)—C(39)	1·37 (1)
F(362)—C(36)	1·32 (1)	C(39)—O(39)	1·26 (1)
F(363)—C(36)	1·31 (1)	C(39)—C(40)	1·51 (2)
C(36)—C(37)	1·53 (2)	F(401)—C(40)	1·29 (2)
C(37)—O(37)	1·27 (1)	F(402)—C(40)	1·24 (2)
C(37)—C(38)	1·36 (1)	F(403)—C(40)	1·23 (2)

(*c*) In the triethylenediamine molecules

N(1)—C(111)	1·49 (2)	N(2)—C(211)	1·44 (3)
N(1)—C(112)	1·46 (3)	N(2)—C(212)	1·44 (3)
N(1)—C(113)	1·44 (3)	N(2)—C(213)	1·51 (3)
C(111)—C(211)	1·57 (3)	N(3)—C(311)	1·49 (1)
C(112)—C(212)	1·58 (3)	N(3)—C(312)	1·48 (1)
C(113)—C(213)	1·58 (4)	N(3)—C(313)	1·50 (1)
		C(311)—C(313$^{\mathrm{I}}$)	1·53 (1)
		C(312)—C(312$^{\mathrm{I}}$)	1·52 (1)

Bond angles

(*a*) Round the copper atoms, e.s.d. 0·3° unless stated

	$n = 1$	$n = 2$
N(*n*)—Cu(*n*)—O(*n*2)	95·2 (2)	101·1 (2)
N(*n*)—Cu(*n*)—O(*n*4)	100·8 (2)	93·0 (2)
O(*n*2)—Cu(*n*)—O(*n*4)	91·2	91·1
O(*n*2)—Cu(*n*)—O(*n*4$^{\mathrm{II}}$)	86·8	87·8
O(*n*2)—Cu(*n*)—O(n2$^{\mathrm{II}}$)	169·6	157·7
O(*n*4)—Cu(*n*)—O(*n*4$^{\mathrm{II}}$)	158·5	174·1

N(3)—Cu(3)—O(32)	92·0	O(32)—Cu(3)—O(34)	91·5
N(3)—Cu(3)—O(34)	99·5	O(37)—Cu(3)—O(39)	90·9
N(3)—Cu(3)—O(37)	97·3	O(32)—Cu(3)—O(37)	89·0
N(3)—Cu(3)—O(39)	101·0	O(34)—Cu(3)—O(39)	84·8
		O(32)—Cu(3)—O(39)	166·9
		O(34)—Cu(3)—O(37)	163·2

(*b*) In the *β*-diketone rings, e.s.d. 1° unless stated

	$n = 1$	$n = 2$	$n = 3$
C(*n*1)—C(*n*2)—O(*n*2)	112	114·0 (9)	112·9 (9)
C(*n*1)—C(*n*2)—C(*n*3)	119	119	118
O(*n*2)—C(*n*2)—C(*n*3)	129	127	129
C(*n*2)—C(*n*3)—C(*n*4)	122	122	121
C(*n*3)—C(*n*4)—O(*n*4)	127	128	130
C(*n*3)—C(*n*4)—C(*n*5)	119	117·9 (9)	120
C(*n*5)—C(*n*4)—O(*n*4)	115	114·2 (9)	110
Cu(*n*)—O(*n*2)—C(*n*2)	125·5 (7)	126·0 (6)	124·9 (6)
Cu(*n*)—O(*n*4)—C(*n*4)	125·5 (7)	125·8 (6)	124·2 (7)

C(36)—C(37)—O(37)	112·1 (9)		
C(36)—C(37)—C(38)	119·4 (9)	C(38)—C(39)—C(40)	119
O(37)—C(37)—C(38)	128	C(40)—C(39)—O(39)	113·8 (9)
C(37)—C(38)—C(39)	123	Cu(3)—O(37)—C(37)	124·2 (6)
C(38)—C(39)—O(39)	127	Cu(3)—O(39)—C(39)	126·3 (7)

(*c*) In the ted molecules

Cu(1)—N(1)—C(111)	110·6 (9)	Cu(2)—N(2)—C(211)	110·9 (10)
Cu(1)—N(1)—C(112)	110·5 (10)	Cu(2)—N(2)—C(212)	110·7 (11)
Cu(1)—N(1)—C(113)	108·5 (12)	Cu(2)—N(2)—C(213)	112·3 (11)
C(111)—N(1)—C(112)	101·6 (15)	C(211)—N(2)—C(212)	106·2 (16)
C(111)—N(1)—C(113)	111·6 (16)	C(211)—N(2)—C(213)	108·7 (16)
C(112)—N(1)—C(113)	114·0 (16)	C(212)—N(2)—C(213)	108·0 (16)
N(1)—C(111)—C(211)	108·0 (17)	N(2)—C(211)—C(111)	112·1 (18)
N(1)—C(112)—C(212)	109·9 (18)	N(2)—C(212)—C(112)	111·1 (18)
N(1)—C(113)—C(213)	109·1 (22)	N(2)—C(213)—C(113)	110·5 (22)
Cu(3)—N(3)—C(311)	111·1 (5)	N(3)—C(311)—C(313$^{\mathrm{I}}$)	111·2 (6)
Cu(3)—N(3)—C(312)	111·9 (5)	N(3)—C(312)—C(312$^{\mathrm{I}}$)	111·4 (8)
Cu(3)—N(3)—C(313)	110·9 (5)	N(3)—C(313)—C(311$^{\mathrm{I}}$)	111·0 (7)
C(311)—N(3)—C(312)	107·9 (7)		
C(311)—N(3)—C(313)	107·5 (7)		
C(312)—N(3)—C(313)	107·3 (6)		

is affected by interaction between the ted and hfac groups. As shown in Table 4, the H···O contacts are more than 2·6 Å. In the Cu(1)···Cu(2) molecule, not only are half the ted molecules effectively rotated by 60° about the orientation shown in Fig. 1, but there is no necessary relation between the relative orientations of the hfac groups on Cu(1) and Cu(2) and, in fact, they are approximately staggered. The projections of, for example Cu(2)—O(22) and of Cu(1)—O(14$^{\mathrm{II}}$) on the plane normal to the twofold axis are at 45°; this can also be expressed in terms of the dihedral angles C(13)—Cu(1)···Cu(2)—C(23$^{\mathrm{II}}$), 44·4 (3)°, and for the other molecule two independent values C(33)—Cu(3)···Cu(3$^{\mathrm{I}}$)—C(33$^{\mathrm{I}}$), −42·5 (3)°, and C(38)—Cu(3)···Cu(3$^{\mathrm{I}}$)—C(38$^{\mathrm{I}}$), −44·1 (3)°.

Longer axial than equatorial bonds are normally found for square-pyramidal complexes of d^9 cations and various theoretical treatments predict (Burdett, 1979) this even if the ligands are chemically identical. If only d orbitals are considered, an axial–Cu–equatorial angle of 90° would be expected, but hybridization of p_z and d_{z^2} leads to a more stable arrangement (Elian & Hoffmann, 1975) with this angle greater than 90° as found here, Table 2. The differences between the N—Cu—O angles, while statistically significant, do not correlate with variations in the Cu—O distances, or in the C—O bond lengths.

The unusual feature of the complexes formed by ted and by pyrazine is the occupation by nitrogen of the axial site. Many examples are known of adduct

Table 3. *Mean planes through various groups of atoms*

Distances of atoms less than ±0·5 Å from the plane (×10³ Å); those excluded from calculation of the plane are indicated by †. Equations are in the form $lx' + my' + nz' + d = 0$ where x', y' and z' refer to orthogonal axes parallel to the crystallographic a, b and c^* axes.

	l	m	n	d
(*a*)	−0·1309	−0·9594	−0·2495	6·7268
(*b*)	−0·1451	−0·9800	−0·1358	14·1281
(*c*)	−0·8271	0·1693	−0·5357	5·5609
(*d*)	−0·7367	−0·2752	−0·6175	10·2062
(*e*)	−0·8254	−0·0097	−0·5644	7·4135

(*a*) C(11) −21(16), C(12) 5(11), O(12) 1(7), C(13) 14(12), C(14) 1(11), O(14) −2(7), C(15) −9(16), Cu(1)† 105(8), F(111)† −120(20)

(*b*) C(21) −44(13), C(22) −12(10), O(22) 41(7), C(23) −37(11), C(24) −13(10), O(24) −32(6), C(25) 109(13), Cu(2)† 33(9), F(213)† −186(16), F(251)† 444(20)

(*c*) C(31) −73(13), C(32) 11(10), O(32) 19(6), C(33) 24 (11), C(34) 19(11), O(34) −28(7), C(35) 32(17), Cu(3)† −16(9), F(311)† −225(17)

(*d*) C(36) −46(12), C(37) 11(10), O(37) 7(7), C(38) 32(10), C(39) 1(10), O(39) −10(7), C(40) −10(13), Cu(3)† 137(8), F(361)† −184(14), F(402)† −201(16)

(*e*) O(37) 31(7), O(39) −33(7), O(32) −31(6), O(34) 33(7), Cu(3)† −251(4)

(*f*) O(12), O(14), $O(12^{II})$, $O(14^{II})$, Cu(1)† −271(4)

(*g*) O(22), O(24), $O(22^{II})$, $O(24^{II})$, Cu(2)† 240(4)

Angles between normals to planes (°), e.s.d.'s 0·2–1·3 °

(*a*)–(*f*)	16·4	(*a*)–(a^{II})	32·8
(*b*)–(*g*)	11·5	(*b*)–(b^{II})	23·0
(*c*)–(*e*)	10·5	(*c*)–(*d*)	26·7
(*d*)–(*e*)	16·4	(*c*)–(c^{I})	19·5
(*a*)–(b^{II})	27·5	(*d*)–(d^{I})	32·0

Table 4. *Intramolecular contacts* (Å) H···O <2·85 Å, H···F <2·40 Å

E.s.d.'s are 0·01 Å for H···O and 0·02 Å for H···F with hydrogen atoms allocated the e.s.d of the corresponding carbon atoms.

H(111*A*)···$O(12^{II})$	2·68	H(211*A*)···O(24)	2·70
H(112*A*)···O(14)	2·75	H(212*A*)···$O(22^{II})$	2·78
H(113*A*)···O(12)	2·60	H(212*B*)···O(24)	2·80
H(113*B*)···$O(14^{II})$	2·81	H(213*A*)···$O(24^{II})$	2·64
H(13)···F(111)	2·33	H(23)···F(213)	2·31
		H(23)···F(251)	2·39
H(311*A*)···O(32)	2·73	H(33)···F(311)	2·37
H(311*B*)···O(37)	2·69	H(38)···F(361)	2·32
H(312*A*)···O(34)	2·84		
H(313*B*)···O(39)	2·82		

formation by bis(*β*-diketonato)copper complexes with nitrogen compounds yielding complexes with the nitrogen atoms in the favoured sites, while one oxygen atom of a *β*-diketonate occupies a destabilized site, having a longer Cu···O bond than the other or even being displaced from the coordination sphere altogether as in $(Me_2NCH_2CH_2NH_2)_2(hfac)_2Cu$ (Bush & Fenton, 1971). From a publication (*Bond Index to the Determination of Inorganic Crystal Structures*, 1969–1977) listing the shortest bond distance of each kind in a structure we have located five other examples having a minimum Cu—N distance greater than 2·20 Å in pyramidal compounds with basal oxygen atoms and an apical nitrogen; two of these are binuclear complexes formed by 1,3,5-triketones and having pyridine as the nitrogen ligand. Cu—N distances are 2·32 Å in bis(heptanetrionato)bis(pyridine)dicopper(II) (Blake & Fraser, 1974), and 2·27 (1) Å in bis(1-phenyl-1,3,5-hexanetrionato)bis(pyridine)dicopper(II) (Lindvedt, Glick, Tomlonovic, Gavel & Kuszaj, 1976). Two are quinoline adducts of carboxylates (Sletten & Lie, 1976), the Cu—N distances being 2·24 Å in the acetate and 2·21 Å in the chloroacetate. The other example provides three independent copper atoms in the hydrated complex with guanosine 5′-monophosphate (Simonov, Ivanov, Ablov, Milkova & Malinovskii, 1976); the Cu—N distances are 2·203, 2·233 and 2·287 Å.

There is one six-coordinated example, the hydrated complex of copper perchlorate with riboflavin (Garland & Fritchie, 1974); four oxygen atoms occupy the equatorial plane and the N(5) atoms of two riboflavin molecules are at 2·43 and 2·39 Å in the fifth and sixth positions. In all the examples the nitrogen atom is sp^2 hybridized; a longer bond for six than for five coordination was found (BFT 2) by direct comparison in the $Cu(hfac)_2$pyrazine complexes, 2·529 (9) and 2·250 (17) Å respectively. Change in hybridization of the nitrogen atom from sp^2 to sp^3 gives a small (~0·03 Å) increase in the effective radius, as shown, for example, by comparison of the six-coordinated distances for pyrazine (BFT 2) and ted (BFT 1); such an effect is not shown by the five-coordinated complexes and this may be because it is counterbalanced by the interaction with the sixth position in the crystal.

There is a similarity in the packing of the 2:1 complexes in that the 90° angle between the Cu(1)···Cu(2) and the Cu(3)···$Cu(3^{I})$ directions is matched by an angle of 78° between the Cu···Cu directions of glide-related molecules in the pyrazine complex (BFT 2), but there is a difference in detail. In the pyrazine complex one fluorine atom in a glide-related molecule occupies a 'sixth' position at 3·09 Å from the copper atom, whereas none of the three copper atoms in the present structure has a neighbour at less than 3·4 Å around the 'sixth' position. Intermolecular distances less than 4·0 Å to copper are described in Fig. 3.

The listing of other intermolecular distances has been deposited.* Packing is dominated by F···F contacts;

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* See previous footnote.

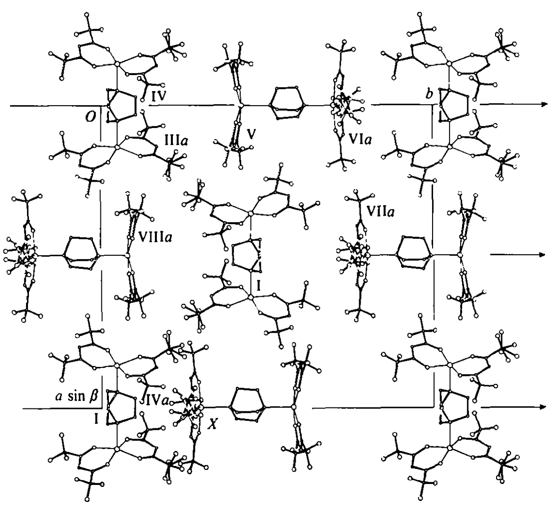

Fig. 3. Part of the structure, hydrogen atoms omitted, projected down the *c* axis. Roman numerals are defined below. With one exception, at *X*, the molecules shown have *z* coordinates for copper atoms in the range zero to +0·4. Thus the crystal chemical unit (c.c.u.) of Table 1 for the Cu(1)···Cu(2) molecule is omitted, being beneath the one marked at V and VI*a* with severe overlap in this projection; the c.c.u. translated by one unit along the *a* axis is shown at *X*. The possible additional contacts (Å) to the Cu atoms are Cu(1)···F(311$^{\mathrm{III,IV}}$) 3·49 (1), as Cu(1$^{\mathrm{X}}$)···F(311$^{\mathrm{IV}a}$)*; Cu(2)···F(151$^{\mathrm{V,VI}}$) 3·42 (2); Cu(2)··· F(156$^{\mathrm{V,VI}}$) 3·95 (2); Cu(3)···F(251$^{\mathrm{V}}$) 3·646 (8)*; and Cu(3)··· F(401$^{\mathrm{VI}}$) 3·78 (1). Contacts marked with an asterisk are shown; the others involve molecules which overlap in this projection. Roman numerals correspond to the following equivalent positions relative to the *x*,*y*,*z* coordinates in Table 1:

(I)	$1-x$,	y,	$\frac{1}{2}-z$	(I*a*)	$1-x$,	y,	$-\frac{1}{2}-z$
(II)	$-x$,	y,	$-\frac{1}{2}-z$	(II*a*)	$-x$,	y,	$\frac{1}{2}-z$
(III)	$\frac{1}{2}-x$,	$\frac{1}{2}-y$,	$-\frac{1}{2}-z$	(III*a*)	$\frac{1}{2}-x$,	$\frac{1}{2}-y$,	$\frac{1}{2}-z$
(IV)	$-\frac{1}{2}+x$,	$\frac{1}{2}-y$,	z	(IV*a*)	$\frac{1}{2}+x$,	$\frac{1}{2}-y$,	z
(V)	$-x$,	$1-y$,	$-z$	(V*a*)	$-x$,	$1-y$,	$-1-z$
(V*b*)	$1-x$,	$1-y$,	$-z$				
(VI)	x,	$1-y$,	$-\frac{1}{2}+z$	(VI*a*)	x,	$1-y$,	$\frac{1}{2}+z$
(VII)	$\frac{1}{2}-x$,	$-\frac{1}{2}+y$,	$-z$	(VII*a*)	$\frac{1}{2}-x$,	$\frac{1}{2}+y$,	$-z$
(VIII)	$-\frac{1}{2}+x$,	$\frac{1}{2}+y$,	$-\frac{1}{2}+z$	(VIII*a*)	$\frac{1}{2}+x$,	$-\frac{1}{2}+y$,	$\frac{1}{2}+z$

there is no evidence for cooperative ordering among the possible sites for the fluorine atoms on C(15) and/or C(35); none is involved in unacceptably short contacts. There are a few contacts between hydrogen atoms of ted ligands in one molecule and fluorine atoms of another; the minimum, 2·52 (2) Å, is larger than the sum of the van der Waals radii; the only hydrogen–hydrogen contact less than 2·6 Å is 2·43 (9) Å from H(311*A*) to H(311$B^{\mathrm{V}a}$), the molecule related by a centre of symmetry at $\frac{1}{2},\frac{1}{2},0$.

The relatively looser packing in the ted than in the pyrazine complex is reflected in the volume occupied per molecule, 918 compared with 861 Å^3, clearly not attributable to additional space occupied by the ted molecules which are essentially within the cylinder defined by the fluorine atoms.

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