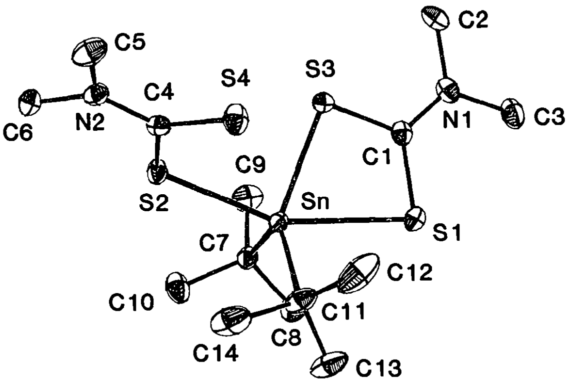

Fig. 1. Drawing of di(*tert*-butyl)bis(*N*,*N*-dimethyldithiocarbamato)-tin(IV) (50% probability thermal ellipsoids) along with the atom-numbering scheme. H atoms are omitted for clarity.

From X-ray studies the dithiocarbamate ligands act as anisobidenate in most of the mono- and diorganotin(IV) dithiocarbamate complexes (Morris & Schlemper, 1978, 1979; Harrison & Mangia, 1976; Lokaj, Kallö, Kettmann, Vrábel & Rattay, 1986; Wei, Kumar Das & Sinn, 1985; Lindley & Carr, 1974; Kimura, Yasuoka, Kasai & Kakudo, 1972; Furue, Kimura, Yasuoka, Kasai & Kakudo, 1970) whereas they behave as monodentate in most of the triorganotin dithiocarbamate complexes (Kumar Das, Wei & Sinn, 1985; Sheldrick & Sheldrick, 1970), except for the di(*tert*-butyl)tin complex of ethylenebis(dithiocarbamate) (Jung, Sohn & Ibers, 1986), where a geometry around the Sn atom similar to the present one was found. The steric effect of the two bulky *cis*-*tert*-butyl ligands may be responsible for the five-coordination of the Sn center in these compounds, although in diphenylbis(*N*,*N*-diethyldithiocarbamato)tin(IV), where the phenyl ligands are *cis*, the Sn center is six-coordinate (Lindley & Carr, 1974).

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The Structure of the Mixed-Ligand Compound [{Bis(1-pyrazolylmethyl)amine}(pyrazole)(tetrafluoroborato)copper(II)] Tetrafluoroborate

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Abstract. $[Cu(C_8H_{11}N_5)(C_3H_4N_2)(BF_4)](BF_4)$, $M_r = 482\cdot44$, triclinic, $P\bar{1}$, $a = 8\cdot489$ (1), $b = 8\cdot829$ (2), $c = 13\cdot189$ (4) Å, $\alpha = 100\cdot02$ (2), $\beta = 106\cdot19$ (2), $\gamma = 96\cdot42$ (1)°, $V = 921\cdot34$ Å^3, $Z = 2$, $D_x = 1\cdot74$ g cm^{-3}, λ(Cu $K\bar{\alpha}$) = $1\cdot54178$ Å, $\mu = 26\cdot4$ cm^{-1}, $F(000) = 482$, $T = 293$ K, final $R = 0\cdot040$ for 1712

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Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* (Cu^{II} Å$^2 \times 10^2$, *others* Å$^2 \times 10$) *of the non-hydrogen atoms*

$B_{eq} = \frac{8}{3}\pi^2 \mathrm{trace}\, \tilde{U}$.

	x	*y*	*z*	B_{eq}
Cu(01)	6212 (1)	2675 (1)	7573 (1)	321 (2)
N(02)	7707 (5)	2229 (5)	8965 (3)	32 (1)
C(10)	6708 (7)	1857 (7)	9650 (5)	38 (2)
N(11)	5298 (5)	2668 (4)	9444 (3)	31 (1)
N(12)	4768 (5)	3069 (4)	8476 (3)	31 (1)
C(13)	3388 (7)	3642 (6)	8481 (5)	38 (2)
C(14)	3019 (7)	3583 (7)	9429 (5)	44 (2)
C(15)	4253 (8)	2970 (7)	10017 (5)	40 (2)
C(20)	8622 (7)	999 (7)	8664 (5)	42 (2)
N(21)	8977 (5)	1234 (5)	7684 (4)	37 (1)
N(22)	7924 (5)	1910 (5)	6999 (3)	36 (1)
C(23)	8514 (8)	1895 (7)	6162 (5)	45 (2)
C(24)	9885 (9)	1207 (8)	6305 (6)	55 (2)
C(25)	10156 (7)	780 (7)	7267 (6)	50 (2)
N(31)	4228 (7)	4444 (5)	6151 (4)	50 (2)
N(32)	4759 (5)	3081 (5)	6254 (3)	34 (1)
C(33)	3863 (8)	2111 (7)	5334 (5)	52 (2)
C(34)	2812 (9)	2827 (9)	4681 (6)	69 (2)
C(35)	3071 (9)	4313 (9)	5210 (6)	70 (2)
B(40)	10944 (9)	3838 (8)	11707 (6)	43 (2)
F(41)	10069 (4)	4585 (4)	10989 (3)	85 (1)
F(42)	10394 (6)	4040 (6)	12562 (4)	130 (2)
F(43)	10748 (4)	2346 (4)	11240 (4)	97 (2)
F(44)	12573 (4)	4553 (4)	12019 (3)	68 (1)
B(50)	3894 (9)	8676 (8)	7254 (6)	41 (2)
F(51)	4722 (5)	7472 (4)	7418 (3)	92 (2)
F(52)	3498 (4)	9228 (4)	8175 (3)	63 (1)
F(53)	2554 (5)	8215 (5)	6398 (3)	98 (2)
F(54)	4950 (5)	9827 (4)	7077 (3)	80 (1)

significant reflections. The Cu^{II} ion has square-pyramidal coordination: two azole N atoms and one amine N atom of the bis(1-pyrazolylmethyl)amine ligand (am2p) and one azole N atom of pyrazole form the square base, with an F atom of one of the tetrafluoroborate anions in the apical position. The Cu—N distances are in the narrow range of 1·948 (4)–2·050 (4) Å; the Cu—F distance is 2·517 (3) Å. The coordinated tetrafluoroborate ion is also hydrogen bonded, through one of the other F atoms, to an N-hydrogen of a pyrazole molecule; this in turn is bound to another copper ion forming chains of cations parallel to **b**. The second BF^{4-} anion is hydrogen bonded to the amine N-hydrogen of the am2p ligand. The three pyrazole rings are planar. The two pyrazole groups, which are part of the ligand am2p, are almost coplanar.

Table 2. *Bond lengths* (Å), *bond angles* (°) *and hydrogen-bond data*

Cu(01)—N(02)	2·050 (4)	N(22)—C(23)	1·332 (6)
Cu(01)—N(12)	1·951 (4)	C(23)—C(24)	1·354 (8)
Cu(01)—N(22)	1·948 (4)	C(24)—C(25)	1·351 (9)
Cu(01)—N(32)	1·948 (4)	N(31)—N(32)	1·347 (5)
Cu(01)—F(54^{i})	2·517 (3)	N(31)—C(35)	1·327 (7)
N(02)—C(10)	1·452 (6)	N(32)—C(33)	1·328 (7)
N(02)—C(20)	1·467 (6)	C(33)—C(34)	1·351 (3)
C(10)—N(11)	1·448 (6)	C(34)—C(35)	1·337 (9)
N(11)—N(12)	1·354 (5)	B(40)—F(41)	1·348 (7)
N(11)—C(15)	1·336 (6)	B(40)—F(42)	1·329 (8)
N(12)—C(13)	1·328 (6)	B(40)—F(43)	1·324 (7)
C(13)—C(14)	1·379 (7)	B(40)—F(44)	1·370 (7)
C(14)—C(15)	1·346 (7)	B(50)—F(51)	1·354 (6)
C(20)—N(21)	1·450 (7)	B(50)—F(52)	1·372 (7)
N(21)—N(22)	1·351 (5)	B(50)—F(53)	1·325 (7)
N(21)—C(25)	1·336 (6)	B(50)—F(54)	1·374 (7)

N(02)—Cu(01)—N(12)	81·9 (2)	Cu(01)—N(22)—N(21)	113·1 (3)
N(02)—Cu(01)—N(22)	81·8 (2)	Cu(01)—N(22)—C(23)	141·5 (4)
N(02)—Cu(01)—N(32)	179·0 (2)	N(21)—N(22)—C(23)	105·2 (5)
N(12)—Cu(01)—N(22)	162·3 (2)	N(22)—C(23)—C(24)	110·6 (6)
N(12)—Cu(01)—N(32)	97·4 (2)	C(23)—C(24)—C(25)	106·6 (6)
N(22)—Cu(01)—N(32)	98·9 (2)	N(21)—C(25)—C(24)	107·1 (6)
N(02)—Cu(01)—F′(54)	86·9 (2)	N(32)—N(31)—C(35)	111·8 (5)
N(12)—Cu(01)—F′(54)	89·4 (2)	Cu(01)—N(32)—N(31)	125·3 (3)
N(22)—Cu(01)—F′(54)	83·0 (2)	Cu(01)—N(32)—C(33)	130·7 (4)
N(32)—Cu(01)—F′(54)	92·5 (2)	N(31)—N(32)—C(33)	103·2 (4)
Cu(01)—N(02)—C(10)	109·7 (3)	N(32)—C(33)—C(34)	112·0 (6)
Cu(01)—N(02)—C(20)	108·1 (3)	C(33)—C(34)—C(35)	105·9 (6)
C(10)—N(02)—C(20)	114·3 (4)	N(31)—C(35)—C(34)	107·1 (6)
N(02)—C(10)—N(11)	108·5 (4)	F(41)—B(40)—F(42)	107·6 (6)
C(10)—N(11)—N(12)	118·6 (4)	F(41)—B(40)—F(43)	108·9 (6)
C(10)—N(11)—C(15)	130·5 (5)	F(41)—B(40)—F(44)	107·1 (5)
N(12)—N(11)—C(15)	110·4 (4)	F(42)—B(40)—F(43)	112·3 (6)
Cu(01)—N(12)—N(11)	113·7 (3)	F(42)—B(40)—F(44)	108·6 (6)
Cu(01)—N(12)—C(13)	141·3 (4)	F(43)—B(40)—F(44)	112·1 (6)
N(11)—N(12)—C(13)	105·0 (4)	B(40)—F(41)—H(02)	119·0 (1)
N(12)—C(13)—C(14)	111·1 (5)	F(51)—B(50)—F(52)	108·3 (5)
C(13)—C(14)—C(15)	105·1 (5)	F(51)—B(50)—F(53)	110·1 (6)
N(11)—C(15)—C(14)	108·3 (5)	F(51)—B(50)—F(54)	107·6 (5)
N(02)—C(20)—N(21)	107·0 (4)	F(52)—B(50)—F(53)	112·0 (6)
C(20)—N(21)—N(22)	118·8 (4)	F(52)—B(50)—F(54)	109·2 (5)
C(20)—N(21)—C(25)	130·5 (5)	F(53)—B(50)—F(54)	109·5 (5)
N(22)—N(21)—C(25)	110·6 (5)	B(50)—F(51)—H(31)	139·0 (1)

N(02)—F(41)	3·102 (5)	N(31)—F(51)	2·814 (6)
N(02)—H(02)	0·84 (5)	N(31)—H(31)	0·82 (5)
H(02)—F(41)	2·42 (5)	H(31)—F(51)	2·07 (5)
N(02)—H(02)—F(41)	139·0 (5)	N(31)—H(31)—F(51)	151·0 (5)

Symmetry position: (i) *x*, *y*−1, *z*.

Introduction. The tetradentate nitrogen donor ligand tris(1-pyrazolylmethyl)amine forms several coordination compounds with transition metal salts (Driessen & Wiesmeijer, 1987). However, in the infrared spectrum of its compound with copper(II) tetrafluoroborate, absorption bands due to N—H or O—H vibrations are present. From the elemental analysis of this compound it is clear that neither water nor ethanol is present. These results point strongly to a partial hydrolysis of the ligand and to the presence of pyrazole itself. In addition, the pattern of the fluoroborate infrared bands indicates either coordination of the anions to the metal ion or participation in hydrogen bonding. To gain insight into the precise stereochemistry of this mixed-ligand copper(II) fluoroborate compound the crystal structure has been determined.

Experimental. Blue crystal, grown from ethanol at room temperature, with approximate dimensions 0·36 × 0·34 × 0·34 mm. Enraf–Nonius CAD-4 four-circle diffractometer, graphite-monochromatized Cu *Kα*. Cell constants from setting angles of 24 reflections; 13 < θ < 15°. Corrections for Lorentz and polarization effects. Absorption correction applied (transmission coefficients 0·879 to 1·093). $\theta_{max} = 60°$, *h*: −9 to 9, *k*: −9 to 9, *l*: 0 to 14. Standard reflections $\bar{2}1\bar{2}$, $\bar{1}1\bar{3}$, $21\bar{3}$, intensity variation 1·8%. 2861 measured reflections, 2719 independent, $R_{\rm int} = 0{\cdot}034$, 1007 with $I < 2\sigma(I)$ were classified as unobserved. Direct methods. F used in LS refinement. All H atoms found in difference Fourier maps. Least-squares refinement of positional and non-hydrogen anisotropic thermal parameters; fixed isotropic thermal factor of 5·0 Å^2 for the H atoms. $S = 1{\cdot}847$, $w = 1/\sigma^2(F)$, $R = 0{\cdot}040$, $wR = 0{\cdot}039$. $(\Delta/\sigma)_{\rm max} < 0{\cdot}20$. Max., min. $\Delta\rho$ excursions in final difference synthesis 0·39, −0·31 e Å^{-3}. Scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). Leiden University Computer (IBM 3083); *MULTAN* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and programs written or modified by S. Gorter, R. A. G. de Graaff and E. W. Rutten-Keulemans.

Discussion. Positional parameters and equivalent isotropic thermal parameters for the non-hydrogen atoms are listed in Table 1.* Bond distances and intramolecular bond angles for the non-H atoms are listed in Table 2. An *ORTEP* projection (Johnson, 1965) of the asymmetric unit of Cu(am2p)(pz)(BF$_4$)$_2$, where am2p is bis(1-pyrazolylmethyl)amine and pz is pyrazole, and the atomic labelling are given in Fig. 1.

The Cu$^{\rm II}$ ion is in a square-pyramidal environment of four N atoms and one F atom. The two azole N atoms and the amine N atom of the am2p ligand and the azole N atom of the pyrazole ligand form the base of the pyramid. An F atom of one of the tetrafluoroborate anions is in the apical position. The Cu—N distances are in the narrow range of 1·948 (4)–2·050 (4) Å (see Table 2). The rather long Cu—F distance of 2·517 (3) Å indicates semi-coordination of the F atom, which is substantiated by the coplanarity of the Cu ion and the four N atoms of the base of the square pyramid. The bite of the am2p ligand is rather restricted as shown by the N(02)—Cu—N(22) and the N(02)—Cu—N(12) angles of *ca* 82° (see Table 2), which is not uncommon for this type of ligand (Driel, Driessen & Reedijk, 1985). This restriction is compensated by the N(32)—Cu—N(22) and the N(32)—Cu—N(12) angles which are *ca* 98°.

The tetrafluoroborate ion, which is semi-coordinated to the copper ion, is also hydrogen bonded, through one of the other F atoms, to the N-hydrogen of a pyrazole molecule; this in turn is bound to another Cu ion, and so results in a chain-like structure with the chains lying along the b axis. The second fluoroborate anion is hydrogen bonded to the amine N-hydrogen of the am2p ligand. This is consistent with the infrared spectrum of this compound where N—H stretching absorptions are encountered at 3260 cm^{-1} (pyrazole N—H) and at 3360 cm^{-1} (amine N—H) (Nakamoto, 1978). The position of the latter band indicates moderately strong hydrogen bonding of the pyrazole to the fluoroborate ion (Bellamy & Owen, 1969).

The three pyrazole rings are planar. The two pyrazole groups which are part of the am2p ligand, are almost coplanar (dihedral angle of 4° between ring planes). There is no intermolecular stacking of the aromatic rings. The packing of the molecules is dictated by normal van der Waals contacts and the H bonding noted above.

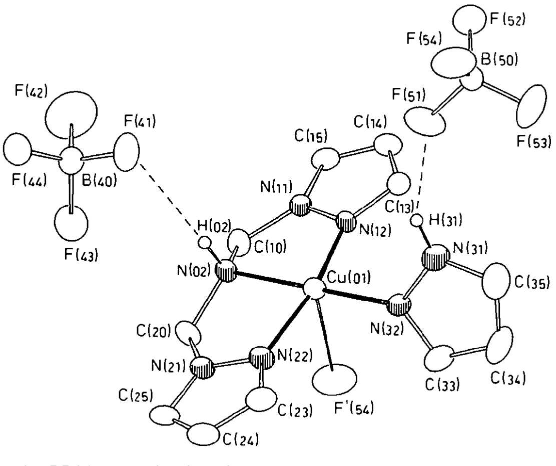

Fig. 1. *ORTEP* projection (Johnson, 1965) and atomic labelling of the molecular entity Cu(am2p)(pz)(BF$_4$)$_2$. For clarity the H atoms are omitted, except for those which take part in hydrogen bonding.

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* Lists of H-atom coordinates, anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44299 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.