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Intra- and inter-molecular hydrogen bonding interactions in $[Cu(en)(py)_2(FBF_3)_2]$ {en = 1,2-diaminoethane, py = pyridine}

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Abstract—The crystal and molecular structures of $[Cu(py)_2(en)(FBF_3)_2]$ (py = pyridine; en = 1,2-diaminoethane) **1** have been determined at 298 and 120 K. It comprises discrete molecular units based on *cis*-distorted tetragonally elongated octahedral copper(II). Strong equatorial bonds are formed by one bidentate en {Cu···N = 2.017 Å} and two monodentate py {Cu···N = 2.020 Å} ligands, while two monodentate tetrafluoroborate anions form weak axial bonds {Cu···F = 2.567 Å}. The location of the anion, which exhibits no disorder even at room temperature, is supported by an intramolecular N—H···F hydrogen bond {N···F = 3.193 Å, N···H = 0.88 Å, H···F = 2.42 Å, N—H—F = 146°}. A literature search has revealed similar intramolecular N—H···X interactions in all other structurally characterised copper(II) complexes containing equatorially coordinated 1,2-diaminoethane and axially located tetrafluoroborate or perchlorate {$[Cu(en)_2(FBF_3)_2]$ **2** and $[Cu(en)L(H_2O)(OClO_3)](ClO_4)$ (L = 2,2′-bipyridine **3** or 1,10-phenanthroline **4**)}. Temperature has limited effect on the structure of **1**, the weaker interactions being affected most. The most significant changes are contractions in the Cu···F axial interaction (1.22%), the intramolecular hydrogen bonds (2.64%) and the intermolecular hydrogen bonds (1.96%) which link the molecules to give a two-dimensional motif. © 1997 Elsevier Science Ltd

Keywords: copper(II); tetrafluoroborate; 1,2-diaminoethane; ethylenediamine; intramolecular hydrogen bonding.

Although the significance of intermolecular hydrogen bonding has long been recognised in biological chemistry [1] and crystal engineering [2] and more recently in the generation of inorganic supramolecular arrays [3], intramolecular interactions have received scant attention. In a recent communication [4], we argued that, in $[Cu(bipy)(cnge)_2(FBF_3)_2]$ {bipy = 2,2′-bipyridine, cnge = 2-cyanoguanidine}, axial coordination of tetrafluoroborate to *cis*-distorted tetragonally elongated octahedral copper(II) was supported by the formation of an intramolecular N—H···F bond between an equatorially located 2-cyanoguanidine amine functionality and a tetrafluoroborate fluorine (Fig. 1). To assess the catholicity of this assertion, we have initiated a programme to synthesise diverse complexes with the potential for intramolecular

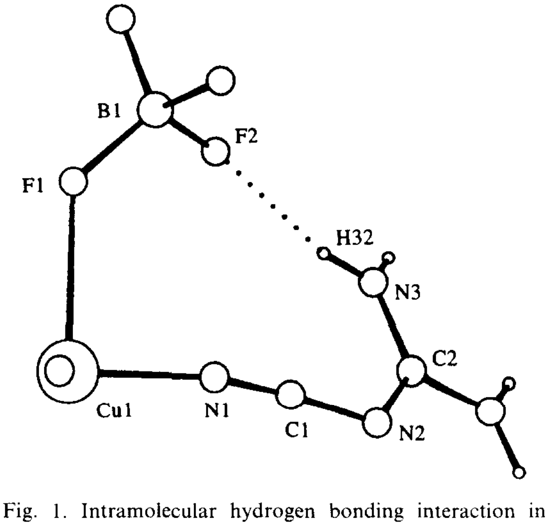

Fig. 1. Intramolecular hydrogen bonding interaction in $[Cu(2,2'\text{-bipy})(cnge)_2(FBF_3)_2]$ {N···F = 2.99, N···H = 0.87, H···F = 2.13 Å, N—H—F = 167°}.

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N—H···F bond formation. In this paper, we report the preparation and structural characterisation of $[Cu(en)(py)_2(FBF_3)_2]$ {en = 1,2-diaminoethane (ethylenediamine), py = pyridine} **1**. 1,2-diaminoethane was chosen as its amino groups are directly coordinated to the metal centre, rendering them much less flexible hydrogen bonding donors than those in cnge. The conclusions of a re-examination of previously disclosed structural data for $[Cu(en)_2(FBF_3)]_2$ **2** [5], and for the related perchlorates, $[Cu(en)L(H_2O)(OClO_3)](ClO_4)$ {L = bipy **3** or 1,10-phenanthroline (phen) **4**} [6] and $[Cu(Me_4en)(tfmh)](ClO_4)_2$ (tfmh = 1,1,1-trifluoro-6-methyl-2,4-heptanedionate) **5** [7] are also reported.

EXPERIMENTAL

Preparation of $[Cu(en)(py)_2(FBF_3)_2]$

Copper(II) tetrafluoroborate (Aldrich Chemical Company Ltd; $Cu(BF_4)_2 \cdot xH_2O$, $x = 3.4$ by copper analysis; 2.18 g, 7.3 mmol) in acetonitrile (50 cm^3) was added to a mixture of py (Aldrich Chemical Company Ltd; 0.58 g, 7.3 mmol) and en (Aldrich Chemical Company Ltd; 0.44 g, 7.3 mmol) in acetonitrile (50 cm^3). An immediate colour change was observed from blue to purple. After stirring the solution for 16 h, a purple powder was isolated by reduction in solvent volume followed by addition of Et_2O. It was purified by recrystallisation from MeCN and Et_2O. The product (1.22 g, 2.68 mmol; 73% [based on pyridine]) was characterised as $[Cu(en)(py)_2(FBF_3)_2]$ using elemental analyses, magnetic measurements and IR spectroscopy. Carbon, nitrogen and hydrogen analyses (microanalysis) and copper analyses (atomic absorption spectroscopy) were carried out in the University of Nottingham Chemistry Department by Mr T.J. Spencer and Mr M. Guyler, respectively. Analysis: found (calc. for $C_{12}H_{18}N_4B_2CuF_8$): C, 31.4 (31.7); H, 4.4 (4.0); N, 12.3 (12.3); Cu, 13.8 (14.0). Magnetic susceptibility data {$\mu_{eff} = 1.76\ \mu B$ (*ca.* 19×10^{24} J T^{-1})} were measured by the Gouy method. Infrared spectra {ν/cm^{-1}: 2924s, 2845s, 1610s, 1540s, 1470m, 1291m, 1085–1035s, br, 704s} were obtained on a Perkin Elmer PE983G spectrometer as KBr pressed pellets.

X-ray crystallography

Crystals suitable for X-ray diffraction experiments were obtained by slow diffusion of Et_2O into a satu-

Table 1. Data collection parameters and crystallographic data for $[Cu(en)(py)_2(FBF_3)_2]$

	298 K	120 K
Formula	$C_{12}H_{18}N_4B_2CuF_8$	$C_{12}H_{18}N_4B_2CuF_8$
M	455.46	455.46
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/c$
a (Å)	7.551(1)	7.479(1)
b (Å)	17.165(2)	16.939(2)
c (Å)	14.107(1)	13.889(1)
β (°)	100.804(3)	100.21(1)
Z	4	4
U (Å^3)	1795.95	1731.69
μ_{calc} (cm^{-1})	12.99	13.47
D_c (g cm^{-3})	1.68	1.75
D_m (g cm^{-3})	1.70	—
(flotation : bromoform/hexanes)		
$F(000)$	916	916
Crystal dimensions (mm^3)	0.42 × 0.65 × 0.18	0.215 × 0.18 × 0.07
Radiation	Mo-K_α (0.71073 Å)	Mo-K_α (0.71073 Å)
Index ranges	$-8 \leqslant h \leqslant 8$	$-8 \leqslant h \leqslant 8$
	$0 \leqslant k \leqslant 19$	$0 \leqslant k \leqslant 18$
	$0 \leqslant l \leqslant 16$	$0 \leqslant l \leqslant 15$
Reflections collected	3842	3779
Reflections (unique)	1397 ($R_{int} = 0.0607$)	1352 ($R_{int} = 0.0894$)
Reflections {data with $I > 2\sigma(I)$}	1229	1012
Number of parameters	159	159
Data/parameter ratio	8.79	8.50
R (all data)	0.0485	0.0478
R_w (all data)	0.1083	0.0917
R {data with $I > 2\sigma(I)$}	0.0444	0.0368
ρ_{min}, ρ_{max} (e Å^{-3})	−0.452, 0.312	−0.452, 0.543
(Δ/σ)max	0.0505	0.0717

rated solution of the product in MeCN. Small regularly shaped crystals were selected and mounted in Lindemann tubes for preliminary study. Oscillation and Weissenberg photographs gave preliminary dimensions for a monoclinic ($a = 7.58$ Å, $b = 17.00$ Å, $c = 14.03$ Å, $\beta = 98°$, $U = 1791$ Å^3) unit cell with space group *Cc* or *C*2/*c*. Diffraction data were collected at 298 K and 120 K using a Delft Instruments FAST TV area detector situated at the window of a rotating anode generator operating at 50 kV 10 mA (298 K) or 50 kV 35 mA (120 K) with a molybdenum anode [8]. For both temperatures, more than one hemisphere of data was collected. The data were corrected for Lorentz and polarisation effects as well as absorption effects (DIFABS [9]). Crystal data, together with details of both diffraction experiments, are listed in Table 1.

The structure was solved by direct methods (SIR92 [10]) and hydrogen atoms located from difference Fourier syntheses (CRYSTALS [11]). It was refined by full matrix least squares methods on F^2 using all data, anisotropic displacement parameters for non-hydrogen atoms and isotropic displacement parameters for hydrogen atoms (CRYSTALS [11]). The final cycle of refinement, with unit weights, gave R indices of 0.0485 (298 K) and 0.0478 (120 K). Full details of the structure solutions are given in Table 1. Structure diagrams were generated using the CAMERON suite of programs [12].

RESULTS AND DISCUSSION

Molecular structure of [Cu(py)$_2$(en)(FBF$_3$)$_2$] (**1**)

The molecular structure of **1** is shown in Fig. 2; selected interatomic distances and angles are given in Table 2. It comprises discrete molecular units based on a *cis*-distorted tetragonally elongated octahedral coordination geometry. The copper atom is located on a crystallographic two-fold axis which also bisects the C—C bond of the en ligand. Strong Cu···N equatorial bonds are formed by one bidentate en and two monodentate py ligands, while two monodentate tetrafluoroborate anions form weak Cu···F axial bonds (Table 2). The anion, which exhibits no disorder even at room temperature, is held in position by an intramolecular N(1)—H(101)···F(2) hydrogen bond (Table 3), somewhat longer than that in [Cu(bipy)(cnge)$_2$(FBF$_3$)$_2$] (Table 3) [4]. Despite the weakness of the Cu···F interaction and the intramolecular

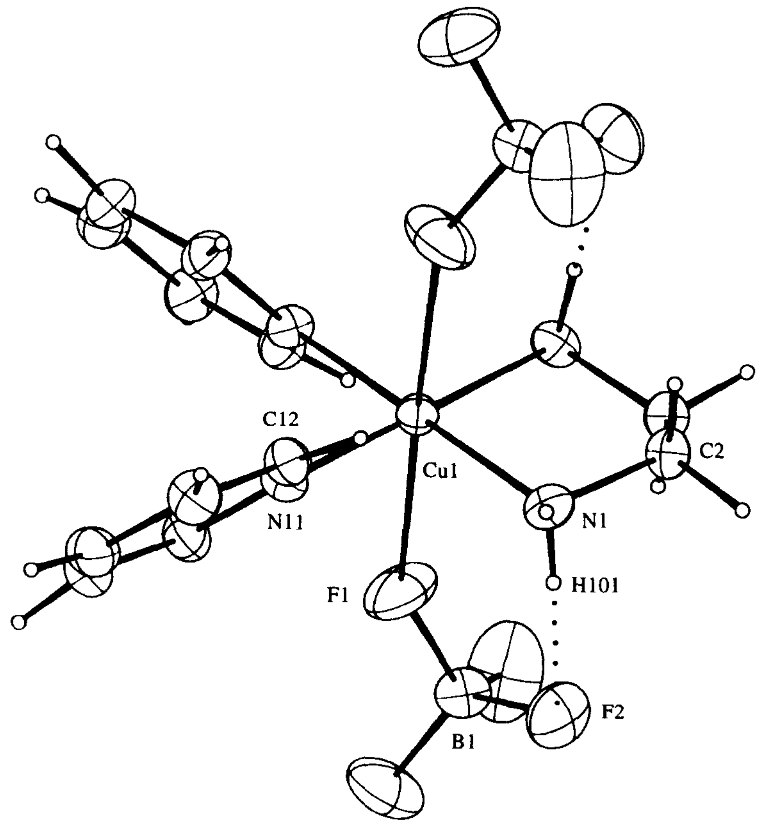

Fig. 2. Molecular structure of [Cu(en)(py)$_2$(FBF$_3$)$_2$] showing the intramolecular hydrogen bonding interaction {N(1)—H(101)···F(2): N···F = 3.19, N···H = 0.88, H···F = 2.42 Å, N—H—F = 146°}.

Table 2. Interatomic distances (Å) and angles (°) in [Cu(en)(py)$_2$(FBF$_3$)$_2$]

Temperature	298 K	120 K		298 K	120 K
Copper coordination sphere					
Cu(1)—N(1)	2.017(4)	2.013(3)	N(1)—Cu(1)—N(1^a)	84.6(2)	84.0(2)
Cu(1)—N(11)	2.020(4)	2.014(3)	N(1)—Cu(1)—N(11)	176.2(2)	175.4(1)
Cu(1)—F(11)	2.567(3)	2.536(2)	N(1)—Cu(1)—N(11^a)	93.3(2)	93.5(1)
			N(11)—Cu(1)—N(11^a)	89.0(2)	89.3(1)
			F(1)—Cu(1)—N(1)	90.5(2)	90.5(1)
			F(1)—Cu(1)—N(1^a)	88.6(2)	89.3(1)
			F(1)—Cu(1)—N(11)	92.6(2)	93.4(1)
			F(1)—Cu(1)—N(11^a)	88.2(2)	86.8(1)
			F(1)—Cu(1)—F(1^a)	178.8(2)	179.7(1)
Ethylenediamine					
N(1)—C(2)	1.477(6)	1.479(5)	N(1)—C(2)—C(2^a)	107.7(3)	107.5(3)
C(2)—C(2^a)	1.54(1)	1.495(8)			
			Cu(1)—N(1)—C(2)	109.4(3)	109.0(3)
Pyridine rings					
N(11)—C(12)	1.349(6)	1.342(5)	N(11)—C(12)—C(13)	122.4(5)	122.2(4)
C(12)—C(13)	1.382(7)	1.375(6)	C(12)—C(13)—C(14)	118.9(6)	119.1(4)
C(13)—C(14)	1.384(8)	1.377(6)	C(13)—C(14)—C(15)	119.5(5)	119.0(4)
C(14)—C(15)	1.374(8)	1.380(6)	C(14)—C(15)—C(16)	118.9(5)	118.8(4)
C(15)—C(16)	1.397(7)	1.365(6)	C(15)—C(16)—N(11)	121.9(5)	123.0(4)
C(16)—N(11)	1.348(6)	1.338(5)	C(16)—N(11)—C(12)	118.4(4)	118.1(3)
			Cu(1)—N(11)—C(16)	121.3(3)	122.1(3)
			Cu(1)—N(11)—C(12)	120.1(3)	119.8(3)
Tetrafluoroborate anions					
B(1)—F(1)	1.398(6)	1.397(5)	F(1)—B(1)—F(2)	107.8(4)	108.4(3)
B(1)—F(2)	1.383(6)	1.387(5)	F(1)—B(1)—F(3)	108.5(5)	108.7(4)
B(1)—F(3)	1.372(7)	1.386(5)	F(1)—B(1)—F(4)	110.0(5)	110.2(3)
B(1)—F(4)	1.369(6)	1.368(5)	F(2)—B(1)—F(3)	109.7(4)	108.9(3)
			F(2)—B(1)—F(4)	110.8(5)	110.5(4)
			F(3)—B(1)—F(4)	110.0(5)	110.0(4)
			Cu(1)—F(1)—B(1)	142.2(3)	140.0(2)

^{a}Symmetry relationship: $1-x$, y, $1.5-z$.

N—H ··· F contact, the anion does not adopt a symmetrical tetrahedral geometry, the B ··· F distance to the coordinated fluorine being considerably longer than those to the other three fluorines of which the intramolecularly hydrogen bonded one is the longest (Table 2). IR spectral data do not support the loss of symmetry as there is no apparent loss of degeneracy of the triply degenerate ν(B ··· F) mode (T$_2$) of tetrahedral BF$_4^-$

Intermolecular hydrogen bonding interactions in the crystal structure of **1**

The intramolecular N(1)—H(101) ··· F(2) hydrogen bond is one component of a bifurcated interaction based on H(101); the second is an intermolecular contact to the F(2) atom of a centrosymmetrically related molecule. The other amino hydrogen atom is involved in a regular intermolecular N(1)—H(102) ··· F(4) interaction to an adjacent molecule. The two intermolecular contacts effectively link the molecules of **1** in a two-dimensional structure as shown in the packing diagram (Fig. 3); interatomic distances and angles are listed in Table 3.

Although the structure differs little with temperature, it is the weaker interactions which are affected most. All three hydrogen bonded contacts are affected by cooling, the bifurcated hydrogen bonds contracting by 2.64% (intramolecular) and 1.96% (intermolecular) and the regular one by 0.5%. These contractions, together with a shortening in the Cu ··· F axial interaction (1.22%), result in a density decrease of 4.2% (from 1.75 to 1.68 g cm^{-3}).

Table 3. Hydrogen bonding contacts in various (1,2-diaminoethane)tetrafluoroboratocopper(II) and (1,2-diaminoethane)perchloratocopper(II) complexes including $[Cu(en)(py)_2(FBF_3)_2]$

N—H···X	Symmetry of X	N—X (Å)[a]	N—H (Å)	H—X (Å)[a]	NHX (°)[a]	HXY (°)[a]
$[Cu(en)(py)_2(FBF_3)_2]$						
298 K						
N(1)—H(101)···F(2)	$(1-x, y, 1.5-z)$	3.193(6)	0.88(7)	2.42(7)	146(6)	112(1)
N(1)—H(101)···F(2)	$(x, -y, 0.5-z)$	3.215(6)	0.88(7)	2.48(7)	141(6)	127(1)
N(1)—H(102)···F(4)	$(-x, y, 1.5-z)$	3.017(6)	1.02(7)	1.99(7)	180(5)	161(1)
120 K						
N(1)—H(101)···F(2)	$(1-x, y, 1.5-z)$	3.111(4)	0.82(5)	2.41(5)	144(4)	112(1)
N(1)—H(101)···F(2)	$(x, -y, 0.5-z)$	3.153(4)	0.82(5)	2.49(5)	139(4)	127(1)
N(1)—H(102)···F(4)	$(-x, y, 1.5-z)$	3.002(4)	0.78(5)	2.23(5)	169(4)	157(1)
$[Cu(bipy)(cnge)_2(FBF_3)_2]$						
N(3)—H(32)···F(2)	Intra	2.99	0.87	2.13	167	156
$[Cu(en)_2(FBF_3)_2]$						
N(1)—H(11)···F(2)	Inter	3.36	1.0	2.43	154	85
N(1)—H(12)···F(1)	Intra	3.19	1.0	2.42	133	88
N(1)—H(12)···F(2)	Intra	3.20	1.0	2.42	134	89
N(4)—H(41)···F(1)	Intra	3.15	1.0	2.36	136	108
N(4)—H(41)···F(3)	Inter	3.12	1.0	2.38	131	147
N(4)—H(42)···F(3)	Inter	3.22	1.0	2.51	153	94
$[Cu(phen)(en)(H_2O)(OClO_3)](ClO_4)$						
N(4)—H(14)···O(1)	Intra	3.03	0.91	2.19	152	118
$[Cu(2,2'\text{-bipy})(en)(H_2O)(OClO_3)](ClO_4)$						
N(4)—H(10)···O(2)	Intra	3.04	0.94	2.24	142	127

[a] For tetrafluoroborates X = F, Y = B; for perchlorates X = O, Y = Cl.

Hydrogen bonding in (1,2-diaminoethane) tetrafluoroboratocopper(II) and (1,2-diaminoethane) perchloratocopper(II) complexes

Although the number of structurally characterised tetrafluoroboratocopper(II) complexes is limited, the anion invariably occupies the weakest binding sites, e.g., the axial positions of either a square based pyramid [13] or a tetragonally elongated octahedron [5,14,15]. The structure of **1** supports our earlier assertion [4] that axial coordination of tetrafluoroborate is supported by intramolecular bonding interactions. To assess the generality of the argument we have searched the literature for structural data on (1,2-diaminoethane)tetrafluoroboratocopper(II) complexes. As only one was found, $[Cu(en)_2(FBF_3)_2]$ (**2**) [5] we also searched for (1,2-diaminoethane) perchloratocopper(II) complexes as tetrafluoroborato and perchlorato complexes are often isomorphous (e.g., $[Cu(py)_2(en)X_2]$ [16] and $[Cu(2,2'\text{-bipy})_2X_2]$ [15], X = FBF_3 or $OClO_3$). The structures of two related complexes, $[Cu(en)L(H_2O)(OClO_3)](ClO_4)$ {L = bipy **3** or 1,10-phenanthroline (phen) **4**} have been reported recently [6].

In the original paper reporting the structure of **2** [5], hydrogen locations were not considered. Their calculated positions, however, do suggest that intramolecular hydrogen bonding interactions do occur. They are shown diagrammatically in Fig. 4(a) and listed in Table 3. The greater number of interactions listed in Table 3 for **2** results from its crystallographically independent amino moieties; those in **1** are related by two-fold symmetry axes. There are three N—H···F intramolecular interactions in **2**, two of which {those involving H(12)} are bifurcated; they have similar N···F interatomic distances (3.15–3.20 Å) to that in **1** (3.193 Å). Three intermolecular contacts also occur (Table 3), two of which are bifurcated {those involving H(41)}. As for **1**, the intermolecular contacts in **2** link the molecules in a two-dimensional structure. They are, however, considerably weaker, the shortest N···F distance in **2** (3.12 Å) being considerably longer than that in **1** (3.02 Å).

Intramolecular N—H···O bonds also occur in the

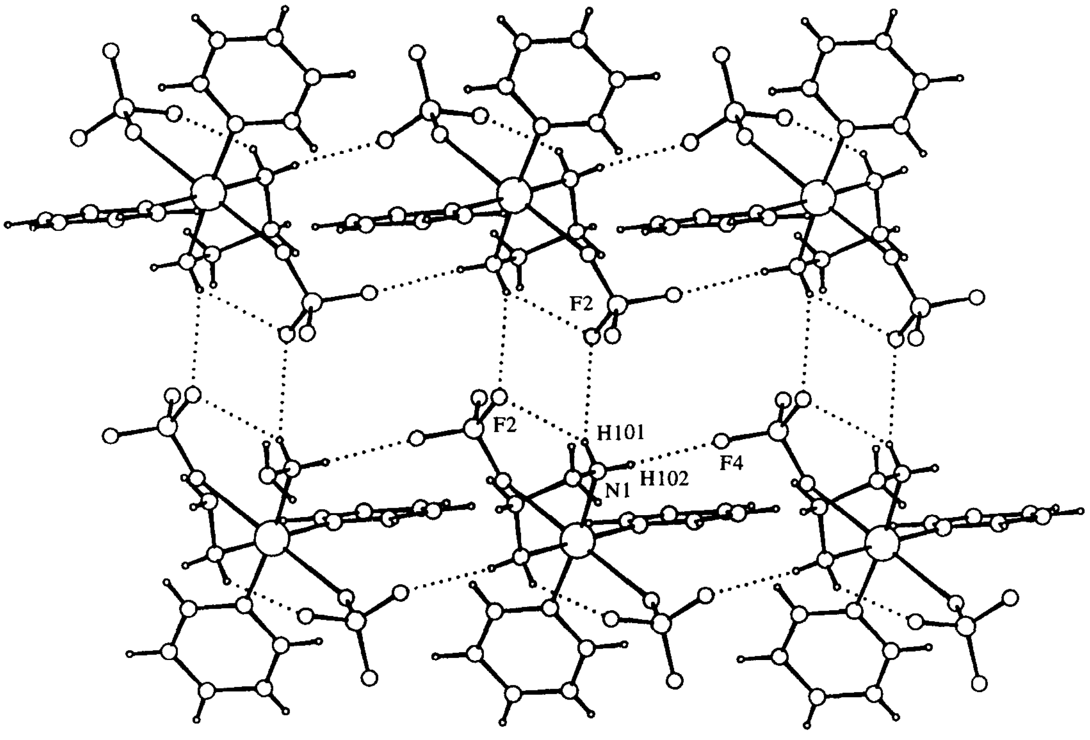

Fig. 3. Packing diagram for the crystal structure of $[Cu(en)(py)_2(FBF_3)_2]$ showing the intermolecular hydrogen bonding interactions {N(1)—H(101)···F(2): N···F = 3.22, N···H = 0.88, H···F = 2.48 Å, N—H—F = 141°; N(1)—H(102)···F(4): N···F = 3.02, N···H = 1.02, H···F = 1.99 Å, N—H—F = 180°}.

perchloratocopper(II) complexes, **3** and **4**. They are depicted in Figs 4(b) and 4(c) and listed in Table 3. Although the strength of the copper(II)-perchlorate coordination differs markedly {Cu···O = 2.75 Å (in **3**), 2.91 Å (in **4**)}, the supporting hydrogen bonds are very similar {N···F = 3.03 (in **3**), 3.04 Å (in **4**), Table 3}. They are somewhat shorter than those in **1** and **2**, probably owing to the fact that, unlike the latter, they are not bifurcated.

If these intramolecular hydrogen bonding interactions are of real significance, the anions in analogous *N,N,N′,N′*,-tetramethyl-1,2-diaminoethane (Me_4en) complexes should exhibit different coordination behaviour. The structure of a typical complex, $[Cu(Me_4en)(tfmh)](ClO_4)_2$ **5** [7] is shown in Fig. 4(d). The perchlorate anion is located above the copper(II) square planar coordination sphere in a pseudo-bidentate chelating mode {Cu···O(3) = 2.83 Å, Cu···O(5) = 3.05 Å}. Neither oxygen subtends angles close to 90° at the copper suggesting that the interaction is electrostatic, rather than coordinative.

CONCLUSION

Intramolecular N—H···X (X = F or O) interactions invariably occur between equatorially coordinated 1,2-diaminoethane and axially located tetrafluoroborate or perchlorate in copper(II) complexes. The geometry of the contact and the length of the copper–anion interaction are mutually interdependent; weak hydrogen bonds correlate with relatively short Cu···X contacts and vice-versa. For **1** (Cu···F = 2.57 Å) and **2** (Cu···F = 2.56 Å), the intramolecular N—H···F interactions form part of bifurcated hydrogen bonds with relatively low N—H—F angles and long N···F distances; for **3** (Cu···O = 2.75 Å) and **4** (Cu···O = 2.91 Å), regular N—H···O interactions with near linear N—H—O angles and shorter N···O distances are formed. These interactions are, however, somewhat weaker than that in $[Cu(bipy)(cnge)_2(FBF_3)_2]$, presumably owing to the restricted flexibility of the amino moieties of coordinated en compared with those of cnge.

Atomic coordinates, thermal parameters, a complete list of interatomic distances and angles, and observed and calculated structure factors have been deposited with the editor as supplementary material.

Acknowledgements—We thank Professor M. B. Hursthouse and the EPSRC Crystallography Service for X-ray data collection and the EPSRC for a maintenance grant (to J.S.).

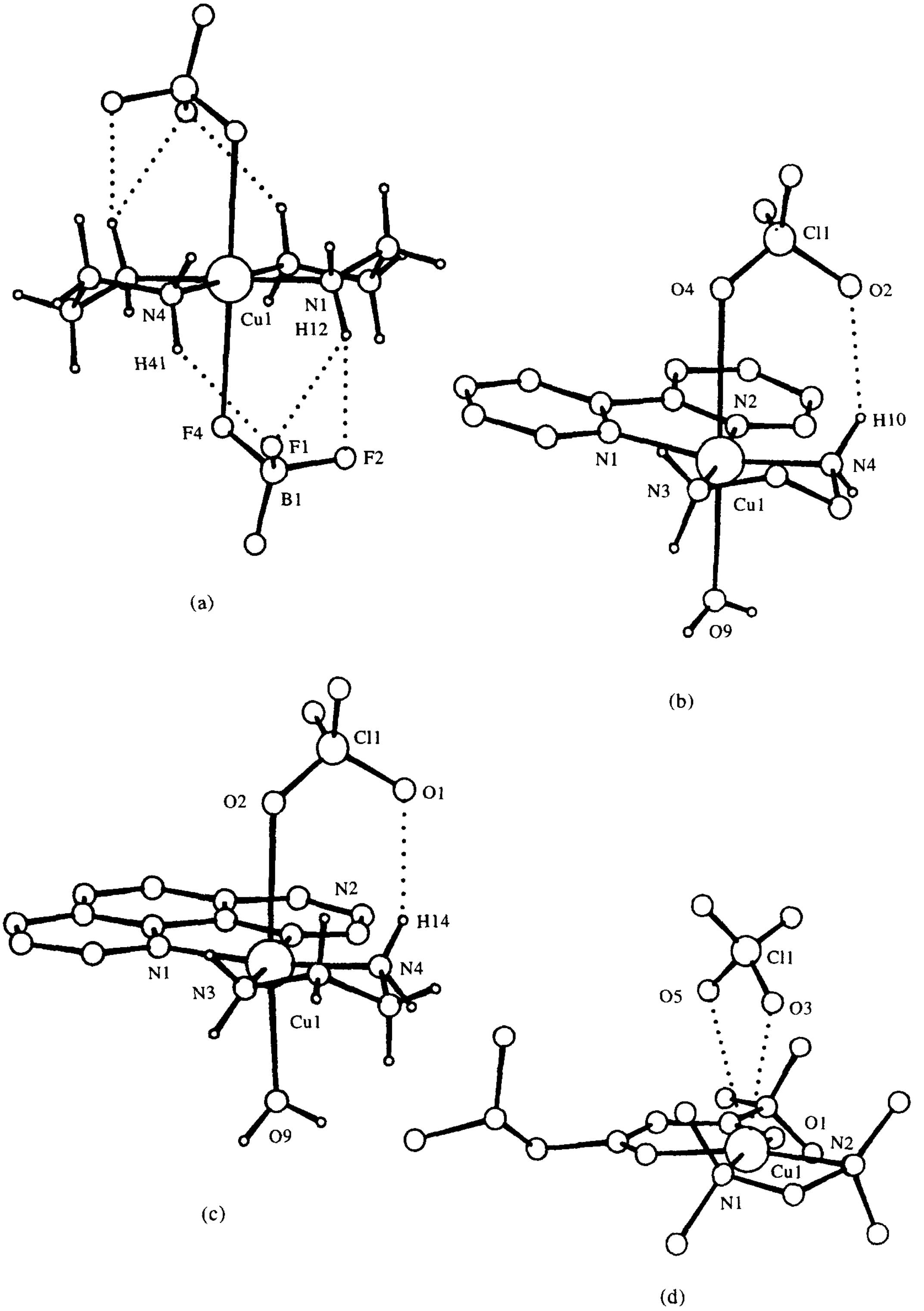

Fig. 4. Intramolecular hydrogen bonding interactions in (a) $[Cu(en)_2(FBF_3)_2]$ {N(1)—H(12)···F(1): N···F = 3.19, N···H = 1.0, H···F = 2.42 Å, N—H—F = 133°; N(1)—H(12)···F(2): N···F = 3.20, N···H = 1.0, H···F = 2.42 Å, N—H—F = 134°; N(4)—H(41)···F(1): N···F = 3.15, N···H = 1.0, H···F = 2.36 Å, N—H—F = 136°}, (b) $[Cu(en)(phen)(H_2O)(OClO_3)]^+$ {N···F = 3.03, N···H = 0.91, H···F = 2.19 Å, N—H—F = 152°}, (c) $[Cu(en)(2,2'\text{-bipy})(H_2O)(OClO_3)]^+$ {N···F = 3.04, N···H = 0.94, H···F = 2.24 Å, N—H—F = 142°} and (d) the molecular structure of $[Cu(Me_4en)(tfmh)](ClO_4)_2$.

REFERENCES

1. Creighton, T. E., *Proteins: Structure, and Molecular Properties*, 2nd. Ed., W. H. Freeman, New York, 1993.
2. Desiraju, G. R., *Crystal Engineering: The Design of Organic Solids*, Elsevier, Amsterdam, 1989; Desiraju, G. R., *Perspectives in Supramolecular Chemistry*, Wiley, Chichester, 1996; Desiraju, G. R., *Angew. Chem., Int. Ed. Engl.*, 1995, **34,** 2311.
3. Burrows, A. D., Chan, C.-W., Chowdhry, M. M., McGrady, J. E. and Mingos, D. M. P., *Chem. Soc. Rev.*, 1995, **24,** 329; Zaworotko, M. Z., *Chem. Soc. Rev.*, 1994, **23,** 283; Chowdhry, M. M., Mingos, D. M. P., White, A. J. P. and Williams, D. J., *J. Chem. Soc., Chem. Commun.*, 1996, 899; Burrows, A. D., Mingos, D. M. P., White, A. J. P. and Williams, D. J., *J. Chem. Soc., Chem. Commun.*, 1996, 97; Chan, C.-W., Mingos, D. M. P., White, A. J. P. and Williams, D. J., *J. Chem. Soc., Chem. Commun.*, 1996, 81; Munakata, M., Wu, L. P., Yamamoto, M., Kureda-Sowa, T. and Maekawa, M., *J. Am. Chem. Soc.*, 1996, **118,** 3117.
4. Batsanov, A. S., Hubberstey, P. and Russell, C. E., *J. Chem. Soc., Dalton Trans.*, 1994, 3189.
5. Brown, D. S., Lee, J. D. and Melson, B. G. A., *Acta Cryst.*, 1968, **B24,** 730; Brown, D. S., Lee, J. D., Melson, B. G. A., Hathaway, B. J., Proctor, I. M. and Tomlinson, A. A. G., *Chem. Comm.*, 1967, 369.
6. Su, C.-C., Lin, Y.-L., Liu, S.-J., Chang, T.-H., Wang, S.-L. and Liao, F.-L., *Polyhedron*, 1993, **12,** 2687.
7. Heunnen, G. W. J., Numan, M., Tsiamis, C. and Kavounis, C. A., *Z. Anorg. Allg. Chem.*, 1995, **621,** 1270.
8. Darr, J. A., Drake, S. R., Hursthouse, M. B. and Malik, K. M. A., *Inorg. Chem.*, 1993, **32,** 5704.
9. Walker, N. and Stewart, D., *Acta Cryst.*, 1983, **A39,** 158.
10. Altomare, A., Cascarano, G., Giacovazzo, C. and Guagliardi, A., *J. Appl. Cryst.*, 1993, **26,** 343.
11. Watkin, D. J., Prout, C. K., Carruthers, J. R. and Betteridge, P. W., *CRYSTALS*, Issue 10, Chemical Crystallography Laboratory, University of Oxford, 1996.
12. Watkin, D. J., Prout, C. K. and Pearce, L. J., *CAMERON*, Chemical Crystallography Laboratory, University of Oxford, 1996.
13. Martens, C. F., Schenning, A. P. H. J., Feiters, M. C., Heck, J., Beurskens, G., Beurskens, P. T., Steinwender, E. and Nolte, R. J. M., *Inorg. Chem.*, 1993, **32,** 3029.
14. Bouwman, E., Day, R., Dreissen, W. L., Tremel, W., Krebs, B., Wood, J. S. and Reedijk, J., *Inorg. Chem.*, 1988, **27,** 4614; Kindberg, B. L., Griffith, E. H. and Amma, E. L., *J. Chem. Soc., Chem. Commun.*, 1977, 461; Baker, E. N. and Norris, G. E., *J. Chem. Soc., Dalton Trans*, 1977, 877; Vezzosi, I. M., Zanoli, F. A., Battaglia, L. P. and Corradi, A. B., *Inorg. Chim. Acta*, 1985, **105,** 13; Wu, L. P., Kinery, M. E. and Hathaway, B. J., *Acta Crystallogr.*, 1992, **C48,** 35; Velthuizen, W. C., Haasnoot, J. G., Kinneging, A. J., Rietmeijer, F. J. and Reedijk, J., *J. Chem. Soc., Chem. Commun.*, 1983, 1366.
15. Foley, J., Kennefick, D., Phelan, D., Tyagi, S. and Hathaway, B. J., *J. Chem. Soc., Dalton Trans.*, 1983, 2333; Nakai, H., *Bull. Chem. Soc. Japan*, 1983, **56,** 1637.
16. Su, C.-C., Lin, Y.-L., Wang, S.-L. and Chou, W.-C., *Transition Met. Chem.*, 1993, **18,** 113.