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Intramolecular Hydrogen-bonding Stabilisation of Tetrafluoroborate Co-ordination to Copper(II): Crystal Structure of (2,2'-Bipyridine)bis(2-cyanoguanidine)bis-(tetrafluoroborato)copper(II)

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(2,2'-Bipyridine)bis(2-cyanoguanidine)bis(tetrafluoroborato)copper(II), in which tetrafluoroborate co-ordination is stabilised by an intramolecular N–H···F hydrogen bond, has been isolated from aqueous solution and structurally and spectroscopically characterised.

The factors influencing the formation of transition-metal complexes of weakly co-ordinating anions have yet to be fully identified. Whereas those complexes of the early and middle transition metals which act as precursors of strong organometallic Lewis acids are only formed in the absence of ligands of stronger co-ordinating ability,[1] the more classical complexes of the later transition metals can be isolated in the presence of more strongly co-ordinating ligands.[2–5] It may be surmised that additional interactions (*e.g.*, hydrogen bonding, bidentate bridging ligation) are required to support anion co-ordination in the latter complexes. Herein, we report the isolation and the structural and spectroscopic characterisation of $[Cu(bipy)(cnge)_2(FBF_3)_2]$ **1** (bipy = 2,2'-bipyridine and cnge = 2-cyanoguanidine), in which tetrafluoroborate co-ordination is supported *via* intra- and inter-molecular hydrogen bonds.

The BF_4^- anion has a notoriously weak σ-donor ability,[1] and few transition-metal complexes with BF_4^- as a ligand are known. In the copper(II) complexes,[2–7] distorted owing to the Jahn–Teller effect, the BF_4^- anion always occupies the most remote sites, *e.g.* the axial positions of either the tetragonal pyramid[6] or the tetragonally elongated octahedron;[2–7] copper–fluorine interatomic distances of 2.38 Å in pyramidal[6] and 2.47–2.69 Å in octahedral[2–7] complexes have been reported.

Treatment of an aqueous solution (25 cm^3) of $[Cu(H_2O)_6][BF_4]_2$ (2.76 g, 8.0 mmol) containing cnge (1.01 g, 12.0 mmol) with an acetonitrile solution (25 cm^3) of bipy (0.32 g, 2.0 mmol) gave a blue solution which was gently heated on a steam bath for 30 min. Deep purple crystals (hexagonal plates) were isolated (yield 0.5 g, 45%) from the mother-liquor upon standing for 24 h. Elemental analysis, magnetochemistry, IR and UV/VIS spectroscopy and FAB mass spectrometry showed them to have the formulation of **1**.†

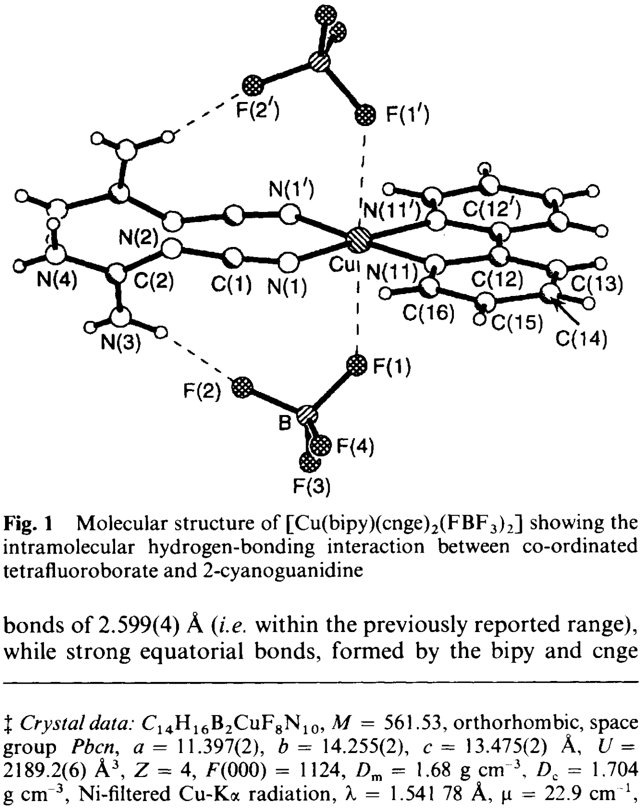

Fig. 1 Molecular structure of $[Cu(bipy)(cnge)_2(FBF_3)_2]$ showing the intramolecular hydrogen-bonding interaction between co-ordinated tetrafluoroborate and 2-cyanoguanidine

The structure of compound **1** (Fig. 1) was determined by single-crystal X-ray diffraction.‡ The copper atom is located on a crystallographic two-fold axis and has (4 + 2) co-ordination. Two monodentate BF_4^- ligands form weak (axial) Cu···F bonds of 2.599(4) Å (*i.e.* within the previously reported range), while strong equatorial bonds, formed by the bipy and cnge

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† Found (Calc.) for **1**: C, 29.90 (29.95); H, 2.85 (2.85); N, 24.70 (24.95%); μ_{eff} = 1.88 μ_B (*ca.* 19 × 10^{-24} J T^{-1}). UV/VIS spectrum (in ethanol): λ_{max} 710 nm, ε 3930 dm^3 mol^{-1} m^{-1}. Mass spectrum: principal peaks, *m/z* 303 {$[Cu(bipy)(cnge)]^+$}, 231 {$[Cu(cnge)_2]^+$}, 219 {$[Cu(bipy)]^+$}, 147 {$[Cu(cnge)]^+$}.

‡ *Crystal data:* $C_{14}H_{16}B_2CuF_8N_{10}$, *M* = 561.53, orthorhombic, space group *Pbcn*, *a* = 11.397(2), *b* = 14.255(2), *c* = 13.475(2) Å, *U* = 2189.2(6) Å^3, *Z* = 4, *F*(000) = 1124, D_m = 1.68 g cm^{-3}, D_c = 1.704 g cm^{-3}, Ni-filtered Cu-Kα radiation, λ = 1.541 78 Å, μ = 22.9 cm^{-1}, crystal size 0.18 × 0.40 × 0.47 mm. Enraf-Nonius CAD4 diffractometer, 2θ/ω scan mode with varied ψ, corresponding to maximum transmission, 2θ < 50°, 1299 total and 1132 unique data, R_{int} = 0.023. The structure was solved by Patterson and Fourier methods using SHELXS 86[8] and refined by full-matrix least squares using SHELXL 93[9] (on F^2 of 1131 reflections, with Chebyshev weighting scheme). All non-hydrogen atoms were refined with anisotropic displacement parameters for all atoms. All hydrogen atoms were located by Fourier difference syntheses and their positions refined (with U_{iso} fixed to 1.2 × U_{eq} of the carrying atom). Refinement converged to *R* = 0.061, *R'* = 0.124 for all data and 'conventional' *R* = 0.043 for 910 data with $|F| > 4\sigma(F)$; residual $\Delta\rho_{max}$ = 0.64, $\Delta\rho_{min}$ = −0.28 e Å^{-3}. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallograhic Data Centre, see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

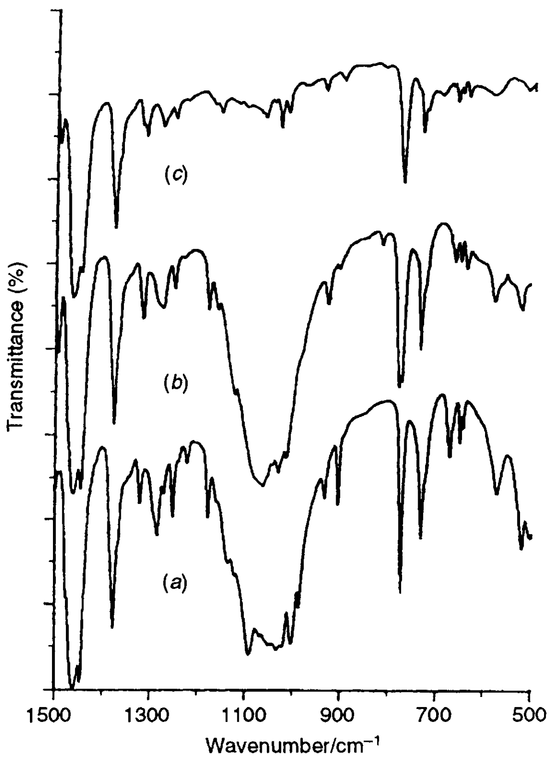

Fig. 2 IR spectra (Nujol mull; KBr windows; 500–1500 cm^{-1}) of (*a*) $[Cu(bipy)(cnge)_2(FBF_3)_2]$ **1**, (*b*) $[Cu(bipy)_2(cnge)][BF_4]_2$ **2** and (*c*) $[Cu(bipy)(cnge)Br_2]$ **3**

ligands {*d*[Cu ··· N(11)] 1.983(5) and *d*[Cu ··· N(1)] 1.931(5) Å}, differ only by the difference of the N(sp^2) and N(sp) radii. The tetrafluoroborate anion, which exhibits no disorder, is held in position by an intramolecular N(3)–H(32) ··· F(2) hydrogen bond to an adjacent cnge molecule [*d*(N ··· F) 2.99(1), *d*(N ··· H) 0.87(8), *d*(H ··· F) 2.13(9) Å; N–H–F 167(7)°]. To our knowledge, this represents the first example of a co-ordinated tetrafluoroborate of this type. Two other cnge hydrogen atoms also form intermolecular hydrogen bonds [N(4)–H(41) ··· F(4), *d*(N ··· F) 2.94(1) Å; N(4)–H(42) ··· N(2), *d*(N ··· N) 3.07(1) Å]. The fourth cnge hydrogen atom [H(31)] does not participate in any way.

Compound **1** is also the first example of a *cis*-located bis(cnge) complex of copper(II). All previously structurally characterised mononuclear copper(II)–cnge complexes have *trans*-located cnge molecules coplanar with the copper equatorial plane.[10] To accommodate the two cnge molecules in *cis* positions they are inclined by 59.4(2)° to the equatorial plane of the copper atom. This arrangement also facilitates the formation of the intramolecular bond.

Notwithstanding the rather long Cu ··· F(1) interatomic distance (2.599 Å) which exceeds that required for 'semi-co-ordination' as defined by Hathaway and co-workers,[11] this bonding affects the geometry of the BF_4^- ligand, in which the B ··· F distances decrease in the sequence: *d*[B ··· F(1)] 1.388(8) Å (co-ordination to copper), *d*[B ··· F(2)] 1.379(8) Å (intramolecular hydrogen bond), *d*[B ··· F(4)] 1.358(8) Å (intermolecular hydrogen bond) and *d*[B ··· F(3)] 1.336(8) Å (no hydrogen bond), indicating the presence of a Cu ··· F interaction.

The IR spectra of $[Cu(bipy)(cnge)_2(FBF_3)_2]$ **1**, $[Cu(bipy)_2(cnge)][BF_4]_2$ **2** and $[Cu(bipy)(cnge)Br_2]$ **3** (Fig. 2) confirm the absence of tetrahedral symmetry for the BF_4^- anion. Significant differences occur in the B–F stretching region (900–1100 cm^{-1}); in all other respects the spectra are virtually identical. Structurally, the anion has C_s local symmetry; reduction of symmetry from T_d to C_s should result in splitting of the triply degenerate ν(B–F) mode (T_2) into three singly degenerate modes ($2A' + A''$). Although some weak bipy bands (1012 and 1033 cm^{-1}) present in the spectrum of compound **3** are superimposed on the ν(B–F) absorption bands of **1** and **2**, it is clear that the single band at 1061 cm^{-1} in the spectrum of **2**, which contains non-co-ordinated BF_4^-,[12] is split in the spectrum of **1** to give two peaks at 1035 and 1089 cm^{-1}. Furthermore an extra peak appears for **1** at 906 cm^{-1}. This loss of degeneracy is consistent with reduced symmetry (C_{3v}, C_{2v} or C_s).[1c,2b,3a,7b]

Interestingly, the IR spectrum of compound **1** in a pressed KBr pellet differs from that shown in Fig. 2, but is reminiscent of a mixture of **3**, free cnge and KBF_4. This implies partial decomposition of **1** by reaction (1), indicating the high lability

$$[Cu(bipy)(cnge)_2(FBF_3)_2] + 2KBr \longrightarrow [Cu(bipy)(cnge)Br_2] + cnge + 2KBF_4 \quad (1)$$

of the BF_4^- anion as a ligand in this system.

The formation of compound **1** clearly shows that the hydrogen-bonding capabilities of ligands must be carefully assessed if co-ordination by tetrafluoroborate and other weakly co-ordinating anions is to be avoided.

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