The Structure of $Cu(en)_2(BF_4)_2$ and an Infrared Spectral Criterion for "Semi-co-ordinated" Polyanions

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THE use of infrared spectroscopy as a technique for determining whether or not a polyanion, present in a co-ordination complex, is co-ordinated to a transition-metal ion, is now well established in the case of the sulphate,[1] perchlorate,[2] and tetrafluoroborate[3] ions. Co-ordination lowers the symmetry of the anion ($T_d \rightarrow C_{3v}$) and results in the splitting of the degenerate modes, ν_3 and ν_4, of the free ion, and in the previously infrared-forbidden modes ν_1 and ν_2, becoming infrared-allowed.

The tetrafluoroborate anion is not a strong co-ordinating anion, as the terminal atoms are highly electronegative fluorine atoms, and there is no crystallographic evidence to indicate that it may act in this way. The infrared spectrum (Figure 1), of Cu(en)$_2$(BF$_4$)$_2$ recorded as a Nujol mull, shows some evidence of splitting of ν_3, over and above that of the free ion, and 30—40% relative intensity (ν_1/ν_3 and ν_2/ν_4) in the infrared-forbidden modes ν_1 and ν_2. Recorded as Nujol mulls the relative intensities are reproducible in all the complexes examined (see later). These results suggest that the tetrafluoroborate ions in this complex may be involved in co-ordination to the copper(II) ions. To verify this, the *X*-ray crystal structure has been determined. The crystals are triclinic [space group $P\bar{1}$ (no. 2)] with $a = 7{\cdot}42$, $b = 8{\cdot}22$, $c = 5{\cdot}92$ Å, $\alpha = 100°54'$, $\beta = 105°12'$, $\gamma = 106°0'$, $Z = 1$. Using Patterson and Fourier techniques, with copper at 0,0,0, all atoms except hydrogen were located, and refined by a full-matrix least-squares method. The structure is shown in Figure 2. The reliability index, *R*, for 979 independent reflections estimated visually is at present 15·3%. The copper ion is in a tetragonally distorted octahedral environment with four nitrogen atoms, from ethylenediamine molecules, in an approximately square-planar configuration, and two fluorine atoms from the tetrafluoroborate groups in the tetragonal positions. The tetrafluoroborate ion is slightly distorted from tetrahedral symmetry. The bond lengths and angles, and their estimated standard deviations are listed in the Table. Full details of the structure will be published elsewhere.

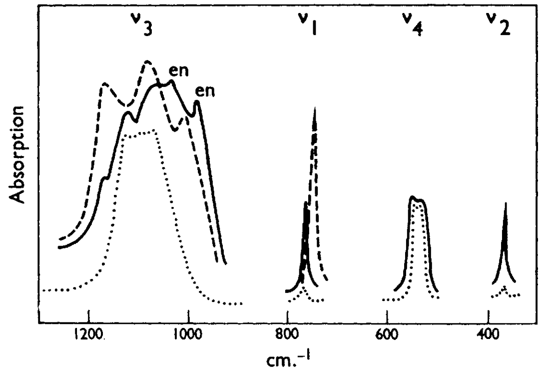

FIGURE 1. *The infrared spectra of* Cu(en)$_2$(BF$_4$)$_2$(——), KBF$_4$ (· · · ·),[4] *and* Me$_3$SnBF$_4$ (- - -),[3] (en = *bands arising from ethylenediamine*).

The molecular structure of Cu(en)$_2$(BF$_4$)$_2$ is thus very similar to Cu(en)$_2$(NO$_3$)$_2$[5] with square-coplanar Cu(en)$_2$ cations and the anions occupying definite positions on the tetragonal axis. In neither structure is there any evidence that the anions are rotating, but in both cases there is crystallographic evidence of a small, but significant distortion of the anions (from their free-ion symmetry), when present in the long tetragonal position. In Cu(en)$_2$(NO$_3$)$_2$ the distortion involves a movement of the central nitrogen 0·062 Å ($\sigma = 0{\cdot}009$ Å) out of the plane of the three oxygen atoms. It is suggested that it is this small distortion of the anions in a tetragonal position that is responsible for the 30—40% intensity of ν_1 and ν_2 of the tetrafluoroborate ion in Cu(en)$_2$(BF$_4$)$_2$ and the slight splitting (over and above that which occurs in the free ion) of ν_3. These results suggest that when a polyatomic anion occupies the long tetragonal position in an otherwise square-coplanar complex of copper(II) with an atom at a distance of 2·5—2·6 Å it must not be considered as nonbonding but very weakly co-ordinated, enough to produce the slight distortions of the anions seen above, but not sufficient to produce the gross distortion and full lowering of symmetry which occurs when these anions are involved as fully co-ordinated groups.[1–3] We suggest the term "semi-co-ordination" to describe this intermediate type of bonding.

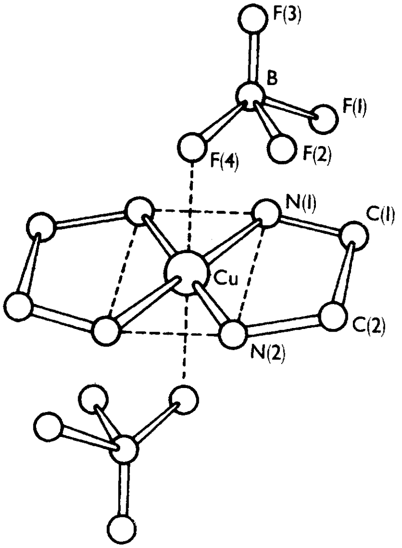

FIGURE 2. *The molecular structure of* Cu(en)$_2$(BF$_4$)$_2$.

The infrared spectra of Cu(en)$_2$(ClO$_4$)$_2$[6] and Cu(en)$_2$SO$_4$ also show evidence of semi-co-ordination of the perchlorate and sulphate ions respectively and suggests that these anions occupy definite positions along the tetragonal axes. The infrared

TABLE

	Bond length	σ		Bond angle	σ
B–F(1)	1·41 Å	0·03 Å	F(1)–B–F(2)	108·5°	1·5°
B–F(2)	1·37	0·02	F(1)–B–F(3)	112·2	1·8
B–F(3)	1·30	0·03	F(1)–B–F(4)	110·6	1·7
B–F(4)	1·38	0·03	F(2)–B–F(3)	110·2	1·8
Cu–N(1)	2·02	0·01	F(2)–B–F(4)	108·2	1·7
Cu–N(2)	2·03	0·01	F(3)–B–F(4)	107·1	1·5
Cu–F(4)	2·56	0·015			

evidence for semi-co-ordination is not restricted to square-coplanar complexes of ethylenediamine, but also occurs in the tetrafluoroborates, perchlorates, and sulphates of the cations $Cu(NH_3)_4^{2+}$,[7] $Cu(py)_4^{2+}$, $Cu(CH_3CN)_4^{2+}$,[8] and $Cu(pyO)_4^{2+}$ [pyO = pyridine 1-oxide] and establishes that in all of these complexes the copper(II) ion environment is tetragonal rather than square-coplanar. The infrared criterion for semi-co-ordination is of value in establishing whether or not these weakly co-ordinating polyanions are involved in the fifth and sixth ligand positions surrounding the copper(II) ion. Thus the infrared spectra[7] of $[Cu(NH_3)_5](BF_4)_2$ and $[Cu(en)_2NH_3](BF_4)_2$ show that the anions present are ionic or at the most occupy a position greater than 2·6 Å from the copper(II) ion along the tetragonal direction, suggesting that in both of these complexes the copper(II) ion is five-co-ordinate.

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