Crystal and Molecular Structure of Aquobis(ethylenediamine)(tetrafluoroborato)nickel(II) Tetrafluoroborate. A *cis*-Octahedral Nickel(II) Complex with a Co-ordinated Tetrafluoroborate Ion

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Both an aquo- $[Ni(en)_2(H_2O)(BF_4)](BF_4)$ (I), and a bisaquo-complex (II) $[Ni(en)_2(H_2O)_2](BF_4)_2$, may be obtained from aqueous solutions. The electronic spectra and easy loss of water from (II) suggest a *trans*-octahedral structure, and similar data for (I) indicate the presence of a *cis*-octahedral structure, and hence of a co-ordinated BF_4^- ion. This has been confirmed by a crystal structure analysis. Crystals of (I) are orthorhombic, space group $P2_12_12_1$ with $a = 7{\cdot}831(10)$, $b = 13{\cdot}118(10)$, $c = 13{\cdot}541(10)$ Å, and $Z = 4$. The structure was solved by use of three-dimensional *X*-ray diffraction methods from visually estimated data and refined by least-squares techniques to *R* 8·2% for 1267 independent non-zero reflections. The ethylenediamine ligands are in a *cis*-arrangement about the metal ion and are in a gauche configuration. The remaining two octahedral positions are occupied by a water molecule and a fluorine atom of a BF_4^- ion, with Ni–F 2·12 Å. There is strong hydrogen bonding between the hydrogens of the water molecule, a fluorine atom from a bonded tetrafluoroborate, and a further fluorine atom from a nonbonded BF_4^- ion. Solid-state electronic spectra of (I) show that BF_4^- lies slightly higher than H_2O in the spectrochemical series. Complex (II) in solution shows an electronic spectrum attributable to a *cis*-$[Ni(en)_2(H_2O)_2]^{2+}$ species, whilst (I) gives a spectrum which appears to be more characteristic of a *cis*-$[NiN_2O_4]$chromophore than of $[NiN_4O_2]$. This suggests that, in the latter, there is a labilizing effect of the two atoms (O and F) on the two nitrogen atoms of the ethylendiamine *trans* to them.

THE existence of *cis–trans* isomers of bisaquobis(ethylenediamine)nickel(II) ion, $[Ni(en)_2(H_2O)_2]^{2+}$, has not been confirmed. On the basis of differences in the electronic spectra, $[Ni(en)_2(H_2O)_2](ClO_4)_2$ was assigned[1] a *trans*-octahedral structure and $[Ni(en)_2(H_2O)_2][BPh_4]_2$ a *cis*-structure.[2] The former compound readily loses both water molecules (over P_2O_5 or on gentle heating) while the latter could not be dehydrated. In contrast other authors maintain that the tetraphenylborate easily loses its water molecules and assigned a *trans*-structure, although different preparative procedures were used.[3]

The present paper reports a further investigation of this system, but using BF_4^- as the anion. We found that two different aquo-complexes could be prepared, one of which, the mono-aquo-complex, proved to have a co-ordinated BF_4^- ligand.

EXPERIMENTAL

Bisaquobis(ethylenediamine)nickel(II) *Bis(tetrafluoroborate)*, (II).—Ethylenediamine (1·2 g, 0·02 mol) was slowly added to a solution of freshly prepared recrystallized (3 times from water) $[Ni(H_2O)_6](BF_4)_2$ (3·65 g, 0·01 mol) dissolved in water (10 ml). The deep blue solution was filtered, isopropyl alcohol (10 ml) added, and the mixture left at 0 °C for 5 days. The violet crystals were dried in air (Found: C, 12·5; H, 4·2; N, 14·3; Ni, 15·0. Calc. for $C_4H_{20}B_2F_8N_4NiO_2$: C, 12·35; H, 5·2; N, 14·4; Ni, 15·1%). The same compound was obtained by adding a solution of freshly prepared $Ni(en)_3(BF_4)_2$ (2 mol) first dried at 100 °C, to one of $[Ni(H_2O)_6](BF_4)_2$ (1 mol), and isolating as before.

Aquobis(ethylenediamine)(tetrafluoroborato)nickel(II) *Tetrafluoroborate*, (I).—During several of the preparations of the bisaquo-complex, addition of a large excess of isopropyl alcohol, or of a few seed crystals of $Ni(en)_2Cl_2$ led to a pale blue crystalline mass being precipitated after some days at 0 °C (Found: C, 13·2; H, 5·0; N, 15·2. Calc. for $C_4H_{18}B_2F_8N_4NiO$: C, 12·95; H, 4·9; N, 15·1%). The preparation is not easily reproducible but sufficient was obtained for physical measurements. A small quantity of the compound was also obtained on seeding a solution of $Ni(en)_2(BF_4)_2$ dissolved in acetone containing a few drops of methanol with a few crystals of $Ni(en)_2Cl_2$. Presumably the anhydrous form slowly takes up a water molecule present as impurity in the methanol. The preparation is similar to that giving the 'anhydrous blue perchlorate' assigned a structure containing bidentate ClO_4^- ion[2].

Bis(ethylenediamine)nickel(II) *Bistetrafluoroborate*, (III).—The bisaquo-complex lost two molecules of water when heated at 50 °C or if left over P_2O_5 in an air oven (wt. loss: 9·0%, calc. for two H_2O: 9·3%; Found: C, 13·5; H, 4·6; N, 15·8. Calc. for $C_4H_{16}B_2F_8N_4Ni$: C, 13·6; H, 4·6; N, 15·9%). The immediate product is a brown mass, which gives an orange powder on grinding.

The aquo-complex (I) lost the molecule of water only with difficulty: 85 °C *in vacuo* for *ca.* 6 h (wt. loss: 5·3%; calc. for one H_2O: 5·1%).

Physical Measurements.—Electronic spectra were recorded on Beckman DK 1A and Shimadzu MPS 50L spectrophotometers as reflectance, Nujol mulls and occasionally single crystals for increased resolution of the bands. I.r. spectra were recorded on a Perkin-Elmer 521 spectrophotometer.

The unit-cell dimensions of a single crystal of (I) were determined, by a modified version of Christ's method,[4] from a zero-layer Weissenberg photograph taken about the *a* axis with Cu-K_{α_1} radiation ($\lambda = 1{\cdot}5406$ Å), and precession photographs taken about the *b* axis with Cu-K_α radiation ($\lambda = 1{\cdot}5418$ Å).

Crystal Data for $[Ni(en)_2(H_2O)(BF_4)](BF_4)$.—$C_4H_{18}B_2F_8N_4NiO_2$, $M = 370{\cdot}53$, blue orthorhombic prisms, $a = 7{\cdot}831 \pm 0{\cdot}01$, $b = 13{\cdot}118 \pm 0{\cdot}01$, $c = 13{\cdot}541 \pm 0{\cdot}01$ Å, $U = 1391$ Å^3, $D_m = 1{\cdot}78 \pm 0{\cdot}01$ (by flotation), $Z = 4$, $D_c =$

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[1] H. Glazer and P. Pfeiffer, *J. prakt. Chem.*, 1939, **153**, 300.

[2] M. E. Farago and J. M. James, *Chem. Comm.*, 1965, 470; M. E. Farago, J. M. James, and V. C. G. Trew, *J. Chem. Soc.* (*A*), 1967, 820.

[3] J. H. Nelson and R. O. Ragsdale, *Inorg. Nuclear Chem. Letters*, 1967, **3**, 585.

[4] A. Mazzone, A. Vaciago, and M. Bonamico, *Ricerca sci.*, 1963, **33**, (IIA), 1113.

1·77, $F(000) = 739·2$, $\mu(\text{Cu-}K_\alpha) = 28·9\ \text{cm}^{-1}$. Space group $P2_12_12_1$ (D_2^4, No. 19), from systematic absences. The intensities of 1267 independent reflexions above background were collected from the layers 0—6*kl* (*ca.* 68% of those possible with Cu-K_α radiation). Intensities were estimated visually from sets of multiple-film equi-inclination photographs. Corrections for Lorentz and polarization effects, and for spot extension [5] were applied, but absorption was not allowed for. Independent layer scales were refined during the isotropic structure refinement.

TABLE 1

Positional (× 10^4) and thermal parameters * with estimated standard deviations in parentheses

	x/a	y/b	z/c	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Ni	1831(2)	1008(1)	3527(1)	106(3)	−13(3)	3(2)	50(1)	−5(1)	32(1)
O	−952(9)	970(7)	3363(5)	128(16)	−24(16)	−28(11)	89(5)	−28(9)	58(4)
N(1)	1845(13)	2590(5)	3408(5)	197(21)	24(15)	17(16)	49(4)	−2(6)	43(4)
N(2)	2143(12)	1076(6)	1977(5)	231(20)	−6(19)	12(12)	57(4)	3(7)	30(3)
N(3)	1792(13)	−583(6)	3624(5)	218(23)	−32(16)	13(17)	49(4)	−14(6)	42(4)
N(4)	4468(11)	824(6)	3828(6)	108(20)	7(15)	−26(13)	73(6)	−10(8)	56(4)
F(1)	1242(9)	1084(6)	5055(4)	205(14)	−48(16)	11(10)	99(5)	−12(7)	44(3)
F(2)	3347(12)	1120(7)	6247(6)	332(24)	28(20)	−189(19)	89(5)	−22(10)	112(6)
F(3)	926(13)	1856(8)	6601(6)	346(25)	−77(25)	79(17)	184(11)	−118(12)	67(5)
F(4)	2622(14)	2563(6)	5507(5)	503(30)	−177(20)	−140(18)	84(5)	27(7)	67(4)
B(1)	1997(19)	1628(8)	5838(7)	187(29)	41(22)	15(19)	53(6)	2(9)	45(5)
C(1)	1703(26)	2565(9)	2361(8)	517(50)	60(33)	25(30)	57(6)	29(10)	52(6)
C(2)	2485(28)	2186(10)	1727(9)	643(67)	27(35)	120(34)	62(7)	47(11)	58(7)
C(3)	3413(18)	−908(8)	4096(8)	280(34)	26(24)	−44(22)	53(6)	7(10)	63(6)
C(4)	4831(16)	−262(9)	3680(8)	106(25)	76(21)	−14(19)	92(8)	1(12)	69(7)
F(5)	−3404(23)	−1247(20)	5764(15)	499(53)	−454(72)	−228(53)	414(32)	343(43)	257(19)
F(6)	−1079(21)	−1173(13)	5242(9)	589(44)	144(50)	257(33)	260(17)	31(22)	121(9)
F(7)	−1526(22)	−1114(19)	6823(8)	588(49)	390(77)	−61(28)	489(33)	21(24)	71(6)
F(8)	−2023(39)	203(12)	5698(18)	1293(115)	340(66)	−430(91)	131(12)	−146(27)	320(23)
B(2)	−2002(19)	−794(11)	5946(8)	112(28)	−21(26)	−1(20)	95(10)	−12(12)	56(6)

* The exponential coefficients b_{ij} given are defined by: $T = \exp[10^{-4}(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hk + b_{23}kl)]$.

RESULTS

Determination and Refinement of the Structure.—The nickel atom and the six atoms co-ordinated to it were located from a three-dimensional Patterson synthesis computed using the full set of observed independent terms. The co-ordinates of the other atoms, except hydrogen, were found from a three-dimensional Fourier synthesis phased on the contribution of those already found. Atomic positional and isotropic thermal parameters ($\bar{B} = 3·5$ Å^2, by Wilson's method) were refined by several cycles of 4 × 4 block-diagonal least squares. The function minimized was $\Sigma w(|F_o| - k|F_c|)^2$. After isotropic refinement R was 0·13. Refinement was continued using anisotropic thermal parameters until convergence was achieved and final shifts in atomic parameters were $< 0·2\sigma$, at which stage the final R was 0·082. The weighting scheme: $w = (a + bF_o + cF_o^2)^{-1}$ where $a = 3·00$, $b = 1·00$, and $c = 0·007$, was used throughout refinement. Final atomic parameters with standard deviations are in Table 1. Calculated and observed structure factor tables based on final atomic parameters are listed in Supplementary Publication No. SUP 20407 (6 pp., 1 microfiche).* Interatomic distances and angles within the crystal chemical unit, together with standard deviations are shown in Table 2. Figure 1 shows the structure of the crystal chemical unit projected on the [111] plane together with the labelling of atoms.

Calculations.—Intensity corrections, scaling, Wilson plots, Fourier syntheses, and interatomic distances and angles were calculated with programs by Domenicano and Vaciago.[6] Programs of Albano *et al.*[7] were used for structure-factor calculations and least-squares refinement, and a program by R. Spagna [8] for calculation of least-squares planes. Atomic scattering factors were taken from ref. 9 and corrections were applied for the anomalous dispersion of Ni.[10]

Spectra.—Figure 2 shows the i.r. spectra of the three

TABLE 2

Bond lengths (Å) and angles (°) with their standard deviation in parentheses

(*a*) Distances

Ni–N(1)	2·08(1)	C(1)–C(2)	1·38(2)
Ni–N(2)	2·12(1)	C(3)–C(4)	1·51(2)
Ni–N(3)	2·09(1)		
Ni–N(4)	2·12(1)	B(1)–F(1)	1·41(1)
Ni–O	2·19(1)	B(1)–F(2)	1·37(1)
Ni–F(1)	2·12(1)	B(1)–F(3)	1·36(1)
		B(1)–F(4)	1·39(1)
N(1)–C(1)	1·47(1)	B(2)–F(5)	1·27(3)
N(2)–C(2)	1·52(2)	B(2)–F(6)	1·30(2)
N(3)–C(3)	1·48(2)	B(2)–F(7)	1·31(2)
N(4)–C(4)	1·47(2)	B(2)–F(8)	1·35(2)
$F(4^{X}) \cdots O$	2·70(1)	$F(7^{VIII}) \cdots O$	2·88(1)

(*b*) Angles

O–Ni–F(1)	83·3(3)	F(3)–B(1)–F(4)	105·5(9)
N(1)–Ni–N(2)	83·1(3)	F(5)–B(2)–F(6)	99·2(15)
N(3)–Ni–N(4)	83·6(4)	F(5)–B(2)–F(7)	105·7(16)
F(1)–B(1)–F(2)	112·5(9)	F(5)–B(2)–F(8)	113·2(20)
F(1)–B(1)–F(3)	115·0(12)	F(6)–B(2)–F(7)	112·6(15)
F(1)–B(1)–F(4)	110·6(8)	F(6)–B(2)–F(8)	101·3(16)
F(2)–B(1)–F(3)	106·0(9)	F(7)–B(2)–F(8)	122·5(18)
F(2)–B(1)–F(4)	106·7(11)		

Roman numerals as superscript refer to the equivalent transformations relative to the reference molecule at x, y, z:

VIII $x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$ IX $-x - \frac{1}{2}, -y, z - \frac{1}{2}$

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

[5] D. C. Phillips, *Acta Cryst.*, 1954, **7**, 746.

[6] A. Domenicano and A. Vaciago, unpublished work.

[7] V. Albano, A. Domenicano, and A. Vaciago, *Gazzetta*, 1966, **96**, 922.

[8] R. Spagna, unpublished work.

[9] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[10] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

complexes and Table 3 solid-state and solution electronic spectra. The solid-state spectra of the complexes are very different (Figure 3). Complex (III) shows only a single relatively intense band at 22·0 kK exactly as for the corresponding perchlorate,[2] as expected for a diamagnetic square planar [NiN$_4$] chromophore. Compound (II) has a band at 8·7 kK with a shoulder at *ca.* 9·3 kK followed by an indistinct band and shoulder at 13·5 and 14·3 kK respectively, and further more intense bands at 18·2 and 29·0 kK. The spectrum is almost identical with that found for the analogous bisaquoperchlorate compound,[2] although we prefer a different assignment of the bands. Since the water molecules are expected to be weaker donors than the ethylenediamine, a situation similar to that in Ni(py)$_4$X$_2$ (X = Cl or Br; py = pyridine) [11] might be expected. In fact the spectra are very similar for these two sets of complexes. Thus the band at 8·7 is assigned to ($^3T_{2g}$) $E_g \leftarrow {}^3B_{1g}$, that at 13·5 to ($^3T_{2g}$) $^3B_{2g} \leftarrow {}^3B_{1g}$ and the shoulder at 14·3 and band at 18·2 kK to the $^3A_{2g}$ and ^3E_g components, respectively, of $^3T_{1g}$. This gives, using a rough pseudo-octahedral calculation, *B ca.* 1 kK and $^3T_{1g}(O_h) \leftarrow {}^3B_{1g}$ *ca.* 29·0 kK. A further band at 29·0 kK is, indeed, found, although no splitting could be discerned. The remaining shoulders are assigned to singlet–triplet transitions. The spectrum is that expected for a *trans*-octahedral [Ni(en)$_2$(H$_2$O)$_2$]$^{2+}$ species.

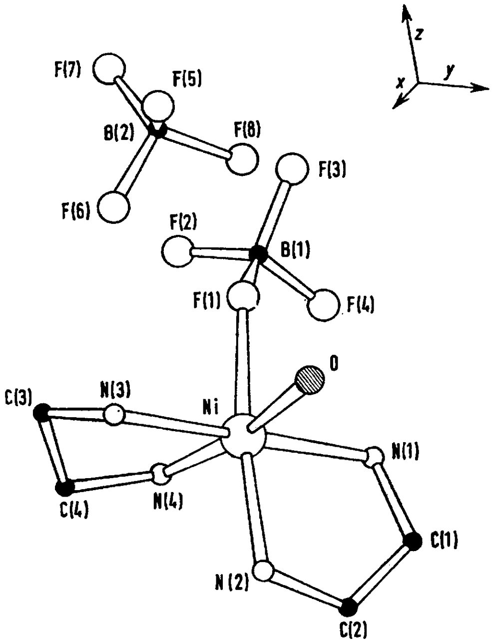

FIGURE 1 [Ni(en)$_2$(H$_2$O)(BF$_4$)](BF$_4$) Molecule seen along the [111] direction, showing the numbering system

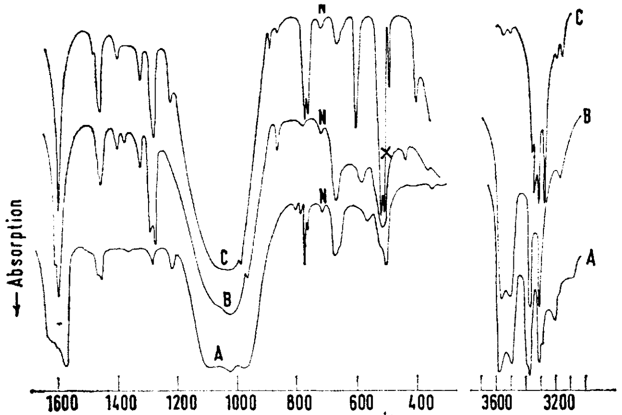

FIGURE 2 I.r. spectra between 3000—3600 cm^{-1} (Fluorolube) and 300—1600 cm^{-1} (peaks marked N due to Nujol mull). A, (I); B, (II); and C, (III). A cross marks reproducible barely resolved shoulder at *ca.* 512 cm^{-1} on the split ν_4(BF$_4^-$) band

(I) has a reflectance spectrum showing only three bands, at 11·0, 17·8, and 28·4 kK.

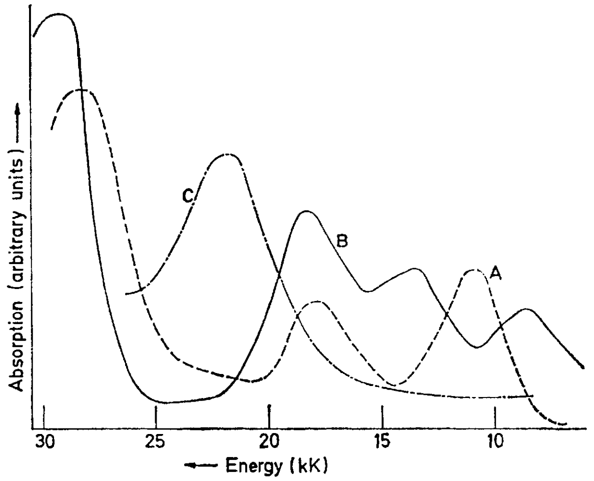

FIGURE 3 Reflectance spectra: A, (I); B, (II); and C, (III)

TABLE 3

Electronic spectra (kK)

(*a*) Solution [a]				
	$^3T_{2g} \leftarrow {}^3A_{2g}$	$^3T_{1g}(F) \leftarrow {}^3A_{2g}$	$^3T_{1g}(P) \leftarrow {}^3A_{2g}$	
[Ni(en)$_2$(H$_2$O)$_2$]-(ClO$_4$)$_2$	10·6 [7·1]	17·7 [5·7]	28·1 [9·1]	
[Ni(en)$_2$(H$_2$O)$_2$]-(BF$_4$)$_2$	10·8 [6·8] [b]	17·8 [5·7]	28·1 [8·9]	
[Ni(en)$_2$(H$_2$O)(BF$_4$)]-(BF$_4$)	10·4 [7·0]	16·3 [5·2]	27·2 [9·3]	
(*b*) Reflectance and Nujol mull [c]				
[Ni(en)$_2$(H$_2$O)$_2$](BF$_4$)$_2$ [d]	8·7 (9·3)	13·5 (14·3)	18·2	29·0
[Ni(en)$_2$(H$_2$O)(BF$_4$)]-(BF$_4$)		11·0	17·8	28·4
[Ni(en)(H$_2$O)$_4$](NO$_3$)$_2$	10·5	16·3		27·8
Ni(en)$_2$(BF$_4$)$_2$		22·0		

[a] $\varepsilon_{max.}$ in square brackets (l mol^{-1} cm^{-1}). [b] Energy not easily specified owing to very close singlet–triplet transition. [c] Shoulder in parentheses. [d] See text for possible assignment.

DISCUSSION

Description of the Structure of (I).—In (I) the nickel atom is in a distorted octahedral environment consisting of four nitrogen atoms at 2·08—2·12 Å, an oxygen atom at 2·19 Å, and a fluorine atom from a BF$_4^-$ ion at 2·12 Å (see Figure 1). There is a hydrogen bond (O–H · · · F 2·88 Å) between fluorine atom F(7$^{\rm VIII}$) (see Table 2) of the non-bonded BF$_4^-$ ion and the co-ordinated water molecule. The water molecule also forms a second, stronger hydrogen bond (O–H · · · F 2·70 Å) with F(4$^{\rm IX}$), of the co-ordinated BF$_4^-$ ion. The ethylenediamine molecules are thus in a *cis*-arrangement about the metal ion, and are both in the gauche configuration. C(1) And C(2) are

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[11] D. A. Rowley and R. S. Drago, *Inorg. Chem.*, 1967, **6**, 1092.

0·27 and 0·23 Å from the plane containing Ni, N(1), and N(2). C(3) And C(4) are 0·34 and 0·36 Å, from the plane containing Ni, N(3), and N(4). The gauche configuration has been found to be the most common one to date for complexes $[M(en)_3]^{n+}$ of Ni^{II}, Cu^{II}, Cr^{III}, and Co^{III}.[12]

The Ni–F distance of 2·12 Å may be compared with those of 1·97 and 2·02 Å in NiF_2.[13] The Ni–N distances are in the range found for other ethylenediamine complexes of Ni^{II}.[14] However, the data are not sufficiently accurate to be able to say clearly that the difference between Ni–N *trans* to the co-ordinated O and F atoms (2·12 Å) and the others (2·08 and 2·09 Å) is significant. The Ni–O distance of 2·19 Å is significantly longer than in other nickel complexes, *e.g.* $[Ni(en)(H_2O)_4](NO_3)_2$ (Ni–O 2·10 Å)[15] and $[Ni(H_2O)_2(stien)_2]$ $(Cl_2CH{\cdot}CO_2)_2$,$2H_2O$ (Ni–O 2·12 Å) (stien = 1,2-diphenylethylenediamine).[16] Since there is no steric hindrance present this argues that the two hydrogen bonds are sufficiently strong to ' hold ' the oxygen atoms away from the nickel atom, thus greatly weakening the Ni–O bond.

The two distorted tetrahedral BF_4^- ions have B–F distances of 1·36—1·41 Å (co-ordinated) and 1·27—1·35 Å (free ion). In the latter, the fluorine atoms have high temperature-factors (mean 15 $Å^2$) but three-dimensional difference-Fourier syntheses showed no evidence for the presence of disorder. Presumably the high temperature-factors are caused by eventual distortion of modes of vibration and/or libration of the whole ion. This may also explain the (probably only apparent) shortening of the B–F bond lengths in the free ion.

Although there have been many reports of co-ordination of ClO_4^- ion to transition-metal ions,[17] mainly based on not unambiguous i.r. evidence, there are fewer reports of co-ordination of BF_4^- ion.[18] I.r. spectral data have been used to suggest a fully co-ordinated BF_4^- ion in Me_3SnBF_4,[19] but the only crystallographic evidence to date is the long-bonded, ' semi-co-ordinate ', $Cu{-}FBF_3$ distance of 2·56 Å in $Cu(en)_2(BF_4)_2$.[20] $[Ni(en)_2(H_2O)(BF_4)](BF_4)$ is therefore the first example of what might be considered a ' normal ' co-ordinated BF_4^- ion.

I.r. and Electronic Spectra.—The i.r. evidence for a unidentate BF_4^- ion in (I) is ambiguous. Although the ν_1 (765 cm^{-1}) mode is visible and ν_4 (516 and 521sh cm^{-1}) is split, ν_2, activated by co-ordination and expected to be present at *ca.* 355 cm^{-1}, is not clearly observable. However, there are signs of splitting of the ν_3 mode at 1050 cm^{-1} as expected for a unidentate BF_4^- (Figure 2). The shoulder at 763 cm^{-1} may be due to the ν_1 mode of the free BF_4^- ion. These ambiguous i.r. spectra suggest caution in the use of anion i.r. spectra when both co-ordinated and free anion may be present simultaneously. The spectra of the bis-aquo-complex show that BF_4^- ions are not co-ordinated. Despite the square-planar type electronic spectrum, the anhydrous complex gives an i.r. spectrum showing obvious signs of splitting of the ν_4 mode (518 and 523 cm^{-1}) and high intensity of the ν_1 mode (760 and 765 cm^{-1}) and a possible ν_2 mode at *ca.* 355 cm^{-1}. The fact that there are two ν_1 bands and a shoulder at *ca.* 512 cm^{-1} indicates a weakly co-ordinated BF_4^- ion with a second BF_4^- ion in a different co-ordination environment. This is not unambiguous, however, since the ν(NH) region shows hydrogen bonding to be present and the lowering of symmetry of the BF_4^- ion from T_d may be caused by strong hydrogen bonding $N{-}H \cdots FBF_3^-$.

The three bands in the solid-state spectrum of (I) may be assigned to the transitions $^3T_{2g} \leftarrow {}^3A_{2g}$ (11·0 kK), $^3T_{1g}(F) \leftarrow {}^3A_{2g}$ (17·8 kK), and $^3T_{1g}(P) \leftarrow {}^3A_{2g}$ (28·4 kK) of an approximately O_h environment. A single-crystal spectrum with polarized light confirms that this is not too drastic an approximation, each band being split by no more than 0·4 kK. It may be noticed that the energy of the first band is higher than that in aqueous solutions of $[Ni(en)_2(H_2O)_2](ClO_4)_2$ and $[Ni(en)_2(H_2O)_2](BF_4)_2$, (Table 3), where a *cis*-structure appears to be present. This places BF_4^- ion in a slightly higher position than water in the spectrochemical series, with $Dq \simeq 1{\cdot}15$ kK (interpolating from the ' average environment rule '[21]), a value considerably different from that of fluoride ion, *e.g.* in $KNiF_3$, which has $Dq \simeq 0{\cdot}73$ kK.[21]

(I) And (II) show different behaviour in aqueous solution. Compound (II) gives a spectrum characteristic of a *cis*-octahedral $[NiN_4O_2]$, but (I), while still showing a solution spectrum of a *cis*-species, has bands which are sensibly shifted to lower energies (Table 3). It appears that a different chromophore is present in solution and the spectrum is, indeed, very similar to that of $[Ni(en)(H_2O)_4](NO_3)_2$ shown in Table 3 for comparison. This suggests that in aqueous solution an ethylenediamine molecule is free or that both ethylenediamine molecules are unidentate and mutually *cis*.

The implication is that the difference in Ni–N distances found in the structure analysis is, in fact, real and the oxygen and fluorine bonding atoms labilize the nitrogen atoms *trans* to them.

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