Crystal and Molecular Structure of Racemic *cis*-α-$[CoL(NO_2)_2][BF_4]$ and *cis*-α-$[CoL(NO_2)_2][BF_2O]$ (L = 3,6-dithiaoctane-1,8-diamine), a Compound containing an Anion Newly isolated in Crystalline Form†

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Two compounds crystallized as racemates from the same crystallization batch, derived from a water solution of $[CoL(NO_2)_2][BF_4]$ **1** (L = 3,6-dithiaoctane-1,8-diamine) which had stood for several weeks at 21 °C. The crystals have totally different morphology and were manually separated: **1**, orthorhombic, space group $Pca2_1$, $Z = 8$, $a = 12.811(3)$, $b = 12.213(6)$, $c = 18.906(8)$ Å, $R = 0.0433$, $R' = 0.0481$ for 1498 unique reflections; *cis*-α-$[CoL(NO_2)_2][BF_2O]$ **2**, monoclinic, space group $P2_1/n$, $Z = 4$, $a = 8.054(4)$, $b = 13.833(4)$, $c = 12.564(8)$ Å, $\beta = 105.26(4)°$, $R = 0.0491$, $R' = 0.0578$ for 2022 unique reflections. In both compounds the organic ligand is quadridentate with two *trans*-axial nitrogen and two *cis* sulfur donor atoms located *trans* to the two basal NO_2 ligands. Likewise, in both, the counter anion is hydrogen bonded to the terminal NH_2 hydrogens. Complex **2** contains the BF_2O^- anion which had, heretofore, not been isolated in crystalline form. In both cases the cations are in the *cis*-α configuration, having $\Lambda(\delta\lambda\lambda)$ and $\Delta(\lambda\lambda\delta)$ pairs as the asymmetric units of **1** and **2**.

It was reported[1-4] that *cis*-α-$[Co(trien)(NO_2)_2]X$ [trien = triethylenetetramine (3,6-diazaoctane-1,8-diamine), X = Cl or I] crystallize as conglomerates the structures and absolute configurations of which were established. These investigators noted that the halide counter ions were bonded to the hydrogens of the secondary NH groups in the basal plane of the cation, while the $CoNO_2$ oxygens were hydrogen bonded to the terminal(axial) NH_2 hydrogens. Examination of the NO_2^- and NO_3^- derivatives revealed racemic crystals in which the counter anions were hydrogen bonded to the terminal NH_2 hydrogens, thus blocking access to these hydrogens by the $CoNO_2$ oxygens. These results suggested that intramolecular $NO_2\cdots H{-}N$ hydrogen bonds between the nitrile ligand oxygens and the axial H_2N hydrogens, as well as interionic halide $\cdots$ HN hydrogen bonds with the basal plane(secondary) hydrogens, influence the crystallization pathway. In order to test the importance of the hydrogen bonding in the basal plane, the complexes *cis*-α-$[CoL(NO_2)_2]X$ (L = 3,6-dithiaoctane-1,8-diamine, X = Cl or ClO_4)[5] were prepared and an examination of the crystallization behaviour revealed both to be racemates. An independent study of the bromide[6] revealed it also to crystallize as a racemate. In order further to test the role of the charge-compensating anion in the dithiaoctane series, we prepared the tetrafluoroborate derivative which, on long standing in a water solution, unexpectedly produced crystals of both the BF_4^- and the OBF_2^- derivatives. Here, we also discuss the time dependence of the ^{19}F and ^{11}B NMR spectra of these ions, as well as their equilibrium with free fluoride anions.

Experimental

Synthesis and Crystal Growth.—The complex *cis*-α-$[CoL(NO_2)_2]Cl$ was prepared as described by Worrell and Bush.[7,8] The BF_4^- salt was prepared by adding a solution of $AgBF_4$ to a solution of the chloride (mol ratio 1 : 1), filtering off the AgCl and allowing the mother-liquor to crystallize at room temperature (*ca.* 21 °C). Reddish brown crystals of both **1** and the BF_2O^- salt **2** were formed and while those of **2** were a definite minority their morphology was so obviously different that it was easy to select individual crystals of each under the microscope. They were examined in the diffractometer and found to belong to different crystal systems and space groups. The combined X-ray analysis and the ^{19}F and ^{11}B NMR spectra of the two anions clearly show their chemical composition.

NMR Spectra.—The NMR spectra were obtained with a Nicolet NT-300 widebore instrument equipped with a Libra data station, references were external KF(aq) and $BF_3\cdot OEt_2(aq)$, no corrections were made for susceptibility. A complete analysis of the spectra is given in the Discussion. Fresh D_2O solutions of complex **1** produced ^{19}F and ^{11}B peaks essentially identical with those of a separate solution of $NaBF_4$ in the same medium. However, on long standing (5 d), additional ^{19}F and ^{11}B peaks occurred while the intensity of the original BF_4^- ones diminished. After 10 d the ^{19}F and ^{11}B peaks due to three separate substances were observable which were identified from their multiplicity and shifts as BF_4^-, $BF_3(OH)^-$ and BF_2O^-. The NMR peaks due to the first and third species can be observed immediately from a solution prepared with the crystalline material from which the crystal structures were determined.

X-Ray Crystallography.—The crystals of complexes **1** and **2** employed were of about the same size and fairly uniform (*e.g. ca.* 0.3 mm on edge). Data for both were collected with an Enraf-Nonius CAD-4 diffractometer operating with the TEXRAY 230 modification[9] of the SDP Plus software package.[10] The crystal was centred with data in the $18 \leqslant 2\theta \leqslant 32°$ range and examination of the cell constants and Niggli matrix[11] clearly showed **1** and **2** to crystallize in primitive orthorhombic and monoclinic space groups, the systematic absences of which indicated the former belong to $Pca2_1$ or $Pcam$ (non-standard form of $Pbcm$) while the latter belongs, unambiguously, to space group $P2_1/n$. The $F(hkl)_{obs}$ sets were corrected for absorption using empirical curves derived from ψ scans[9,10] of suitable reflections. The scattering curves were taken from ref. 12.

The three most probable MULTAN[13] solutions of complex **1**

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Transactions*, 1995, Issue 1, pp. xxv–xxx.

in space group *Pbcm* were unacceptable since: (*a*) the highest peak, presumably a Co, was located at (0.2981, 0.1827, $\frac{1}{4}$; a mirror plane) which is impossible for the cation to occupy, unless disordered, and not necessary in the polar space group; (*b*) the second highest peak, located at a general position, was half the intensity of the first, despite the fact that it should be the other independent Co atom; (*c*) if there is a Co at a mirror plane and one at a general position, *z* would be 12, which is impossible since the density would then be 2.816 g cm^{-3}, which it is not; (*d*) neither of the two highest peaks of the MULTAN solution had any ligands around them, which is not normal for a good data set. Using space group $Pca2_1$ instead, the structure was smoothly solved by MULTAN, which revealed the two Co atoms and many of the lighter ones. After refinement of the scale factor and the positional and isotropic thermal parameters, a Fourier-difference map showed the anions and many of the remaining atoms of the cations. The missing atoms were found in subsequent difference maps. The structure of **2** was routinely solved by the Patterson method. In both cases, hydrogen atoms were added to the cation at idealized positions (C–H and N–H 0.95 Å). Details of the data collection and processing are summarized in Table 1. The BF_4^- anions have the usual, large, amplitudes of thermal motion, which were a lesser problem with the anion of **2**. In both cases, the cations are very well behaved thermally.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results

The quality of the structural refinements is very good in both cases, as attested by the data in Table 1. The structural analysis for complex **1** reveals two cations as the asymmetric unit and, as is frequently the case, they are imperfectly related to one another by a non-crystallographic symmetry operation. Fig. 1 shows the relationship between the two cations the chiroptical symbols of which are, Λ(δλλ) and Λ(δλλ), demonstrating that these cations could not possibly have crystallized in the space group *Pbcm* since in the centrosymmetric case they would be related by an inversion centre, an impossible situation since they share the same chiroptical symbol. A packing diagram for the unit-cell contents of **1** is given in Fig. 2, projected down the *a* axis.

In the case of complex **2** the space group was unambiguous. The contents of the asymmetric unit are given in Fig. 3 and a packing diagram in Fig. 4. Final positional parameters for **1** and **2** are given in Tables 2 and 3, bond lengths and angles in Tables 4 and 5.

Discussion

The asymmetric unit of complex **1** is illustrated in Fig. 1, which shows that the configurations of the two independent cations, Co(1) and Co(2) (torsion angles 39.8, −52.2 and −55.0 and 41.3, −54.3 and −34.5°) are not enantiomeric to one another. In neither case does the chiroptical symbol Λ(δλλ) correspond to the lowest possible conformational energy of a *cis*-α cation, for which the symbol would be Δ(λδλ) or Λ(δλδ). Such a conformational behaviour differs from that previously found in the case of the chloride and the perchlorate.[5] In the former the asymmetric unit also contained a pair of cobalt atoms where the chiroptical symbol for Co(1) was Λ(δλδ) (torsion angles 42.3, −33.9 and 48.3°) and that for Co(2) was Δ(λδλ)

Table 1 Crystallographic data for complexes **1** and **2***

	1	**2**
Formula	$C_6H_{16}BCoF_4N_4O_4S_2$	$C_6H_{16}BCoF_2N_4O_5S_2$
M	418.08	396.08
Crystal symmetry	Orthorhombic	Monoclinic
Space group	$Pca2_1$ (no. 29)	$P2_1/n$ (no. 14)
a/Å	12.811(3)	8.054(4)
b/Å	12.213(6)	13.833(4)
c/Å	18.906(8)	12.564(8)
β		105.26(4)
U/Å^3	2958.05	1350.48
Z	8	4
D_c/g cm^{-3}	1.877	1.948
F(000)	1654	852
No. of unique data	2877	2652
No. of unique data with $I < 3\sigma I$	1498	2022
μ/cm^{-1}	14.914	16.141
R	0.0433	0.0491
R'	0.0481	0.0578

* Details in common: 18 °C; λ(Mo-Kα) 0.710 73 Å; $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{\frac{1}{2}}$.

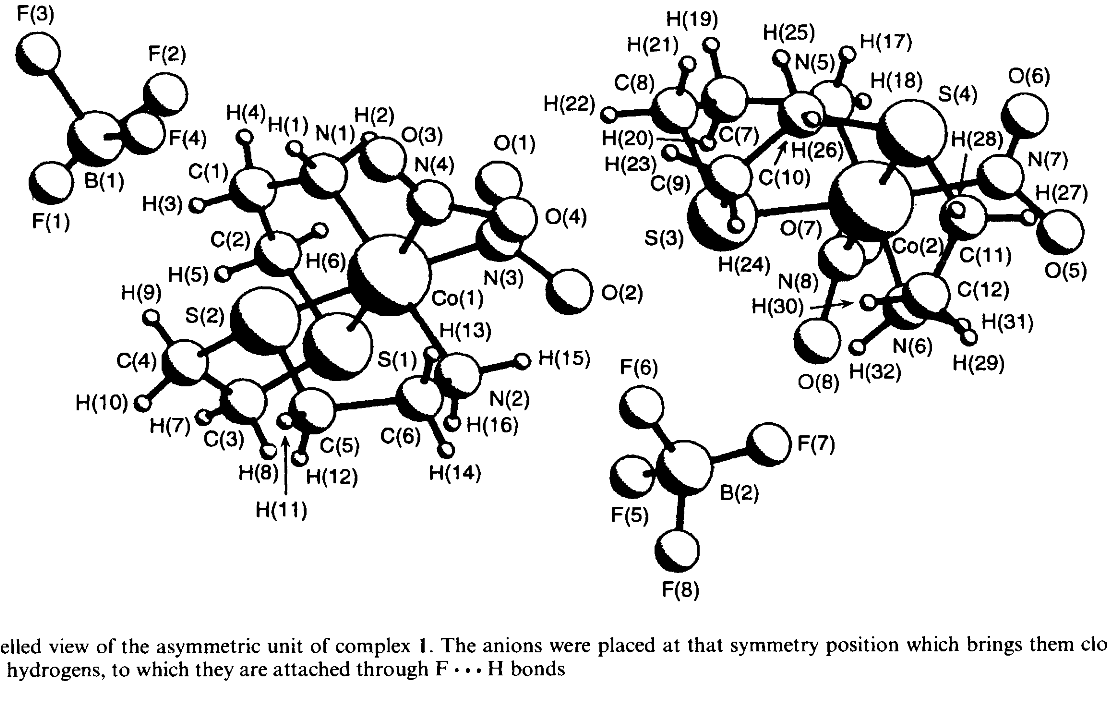

Fig. 1 A labelled view of the asymmetric unit of complex **1**. The anions were placed at that symmetry position which brings them closest to the terminal NH_2 hydrogens, to which they are attached through F ⋯ H bonds

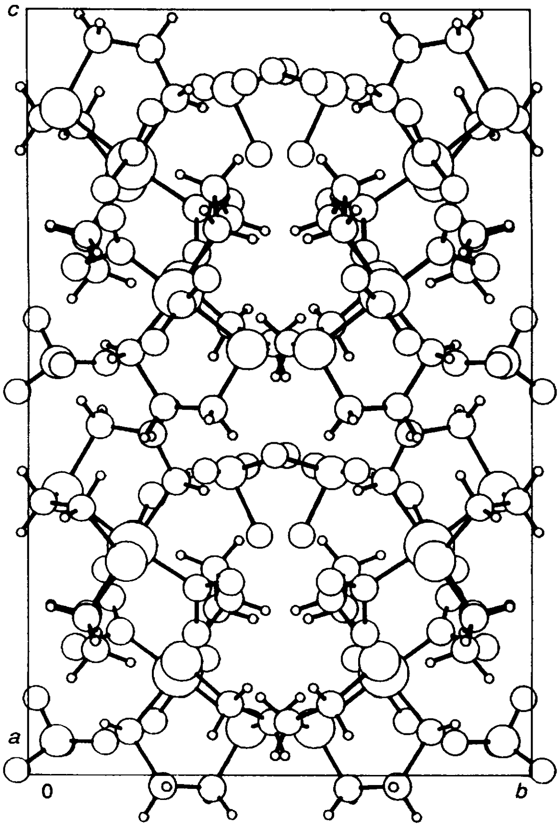

Fig. 2 Projection down *a* of the packing of the cations and anions in the lattice of complex **1**. The cations on the left-hand half of the cell are homochiral and are related to one another by the screw axis along *c*. The cation placed at the lowest left-hand side of the cell, near $b = 0.2$ and $c = \frac{1}{3}$, is Co(1); that near $b = \frac{1}{3}$ and $c = \frac{1}{8}$ is Co(2). Finally, note the mirror plane at $b = \frac{1}{2}$, showing the enantiomorphic relationship between the two halves of the unit cell

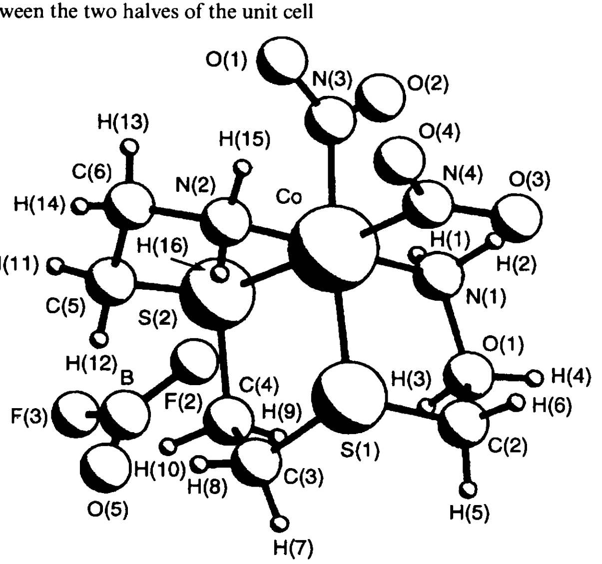

Fig. 3 A labelled view of the asymmetric unit of complex **2**. Note the configuration and conformational symbol for this cation is Λ(δλλ). The anion was also placed at that symmetry position which brings it closest to the terminal NH_2 hydrogens, to which it is attached through a F(2) • • • H(16) bond

(torsion angles −27.1, 39.8 and −42.1°); the cations of the preresolved perchlorate[5] were characterized by the chiroptical symbol $(+)_{546}$-Λ(δλδ) (torsion angles 42.8, −39.7 and 41.1°). Finally, in *cis*-α-$(-)_{589}$-Λ(δλδ)[Co(trien)$(NO_2)_2$]Cl·H_2O the torsion angles are 42.59, −40.39 and 39.31°.[1-3]

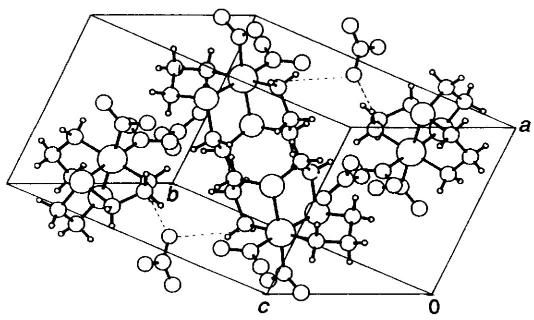

Fig. 4 Packing of the cations and anions in the lattice of complex **1**. The cations on the left-hand side of the cell are of the same chirality and are related to one another by the screw axis; in turn they are related to those on the right-hand side by the inversion centre

In complex **2** the cations in the asymmetric unit are characterized by the chiroptical symbol Λ(δλλ), or its enantiomorph. Thus, all three cations studied herein share the same chiral symbol, and all previous comments concerning the cations of **1** apply here equally well. We suggest that the conformational differences are related to the nature, and hydrogen bonding abilities, of the charge-compensating anions. In **1** and **2** the hydrogen bonds to the amines are NH • • • F bonds, in the chloride and perchlorate[5] they are NH • • • O or NH • • • Cl bonds, the last two being weaker than the former. Finally, we note that there is a considerable variation in the magnitudes of the torsion angles in **1** and **2**; this, no doubt, is the result of the bridging nature of the two fluoroborate anions, the changes of the C–S–C angles in the basal plane and the increased Co–S distance which results in ring strain. We have already discussed this phenomenon in two papers dealing with related species,[5,14] and the interested reader is referred to those for details of the chemical consequences of changing N- for S-donor ligands.

In combination with our previous results[1-5] it is clear that the crystallization pathway selected by a number of anion derivatives of the *cis*-α-[CoL$(NO_2)_2$]$^+$ cation produces racemic crystals, as we had expected.[5] Interestingly, in all cases the anion is hydrogen bonded to the terminal NH_2 moieties as shown in Figs. 1 and 3, the anions being placed in the symmetry position which brings them closest to the cations.

It was demonstrated earlier[4] that the increased Rh–N distances *cis*-α-[Rh(trien)$(NO_2)_2$]Cl, as compared with the cobalt analogue, led to a diminished hydrogen-bond interaction between the NO_2 oxygens and the terminal NH_2 hydrogens which, in turn, resulted in racemic crystals. At the time those results were published[4] it was noted that the location, and hydrogen-bonding behaviour, of the chloride anion in the rhodium complex was different from that found in crystals of *cis*-α-[Co(trien)$(NO_2)_2$]X (X = Cl or I) in that the strongest hydrogen bonds formed by the anions were to the terminal-(axial) NH_2 hydrogens, thus blocking hydrogen bonding by the NO_2 oxygens. Later, we observed[5] that the absence of secondary(basal plane) NH hydrogens, caused by sulfur substitution, produces the same result; *e.g.* the anions migrate to the axial NH_2 hydrogens and diminish the strength of the nitro ligand O • • • H–N interactions since any such bonding would lead to bifurcated hydrogens, known to form considerably weaker hydrogen bonds.[15] Moreover, one would expect a degree of steric hindrance and of coulombic repulsion between the anions and the non-bonded electron pairs of the NO_2 oxygens, which, consequently, would weaken further the intramolecular hydrogen bonds. The same observations apply here.

The results obtained for the *cis*-α-[Co(trien)$(NO_2)_2$]$^+$, *cis*-α-[Rh(trien)$(NO_2)_2$]$^+$ and the *cis*-α-[CoL′$(NO_2)_2$]$^+$ [L′ = $NH_2(CH_2)_2S(CH_2)_2S(CH_2)_2NH_2$] analogues were presented earlier.[1-5,16,17] Those obtained here are in full accord with previous suggestions concerning the effects of intra- and inter-

Table 2 Positional parameters and their estimated standard deviations (e.s.d.s) for complex **1**

Atom	*x*	*y*	*z*
Co(1)	0.182 9(2)	0.204 7(2)	0.303
S(1)	0.190 6(3)	0.066 3(2)	0.374 9(2)
S(2)	0.363 8(3)	0.193 9(3)	0.282 4(2)
O(1)	−0.018(1)	0.245(1)	0.370 4(6)
O(2)	−0.031 2(9)	0.153 5(9)	0.271 6(6)
O(3)	0.232(1)	0.401 0(7)	0.255 3(6)
O(4)	0.112 9(9)	0.333(1)	0.188 7(5)
N(1)	0.200(1)	0.291 6(9)	0.388 7(5)
N(2)	0.164 9(8)	0.117(1)	0.213 4(6)
N(3)	0.023(1)	0.209(1)	0.319 3(7)
N(4)	0.175(1)	0.334 3(7)	0.247 3(5)
C(1)	0.241(1)	0.245(1)	0.451 1(6)
C(2)	0.198(2)	0.141(2)	0.462 9(6)
C(3)	0.326(2)	0.029(2)	0.362(1)
C(4)	0.410 4(9)	0.105(1)	0.353 7(6)
C(5)	0.362(1)	0.115 5(9)	0.208 8(7)
C(6)	0.253(1)	0.133(1)	0.168 1(7)
Co(2)	0.682 2(2)	0.295 3(1)	0.136 27(9)
S(3)	0.865 4(3)	0.303 8(3)	0.152 5(2)
S(4)	0.690 0(4)	0.433 2(4)	0.062 6(2)
O(5)	0.484 7(9)	0.248(1)	0.072 3(6)
O(6)	0.463 0(8)	0.352(1)	0.156 1(6)
O(7)	0.616(1)	0.164 4(9)	0.234 9(7)
O(8)	0.723(1)	0.093(1)	0.171 0(7)
N(5)	0.6667(9)	0.374 3(8)	0.220 7(5)
N(6)	0.6992(8)	0.201(1)	0.058 2(6)
N(7)	0.5233(9)	0.302 1(9)	0.122 0(5)
N(8)	0.6748(9)	0.182(1)	0.191 5(8)
C(7)	0.764(1)	0.370(1)	0.272 2(6)
C(8)	0.863(1)	0.400(1)	0.233 6(7)
C(9)	0.905(2)	0.400(2)	0.095(1)
C(10)	0.829(1)	0.484(1)	0.070 8(7)
C(11)	0.687(1)	0.365(1)	−0.016 6(7)
C(12)	0.733(2)	0.267(2)	−0.0138(9)
B(1)	0.492(3)	0.399(5)	0.400(2)
F(1)	0.549(1)	0.350(1)	0.402 2(7)
F(2)	0.393 4(8)	0.432(1)	0.409 0(7)
F(3)	0.551(1)	0.512(1)	0.422 8(8)
F(4)	0.499(1)	0.458(1)	0.316 8(4)
B(2)	0.502(1)	−0.057(1)	0.045 7(6)
F(5)	0.524(2)	−0.016(2)	0.103(1)
F(6)	0.561(1)	−0.153(1)	0.044 0(8)
F(7)	0.393(2)	−0.067(2)	0.042(1)
F(8)	0.544(1)	0.022(1)	0.006 6(6)

Table 3 Positional parameters and their e.s.d.s for complex **2**

Atom	*x*	*y*	*z*
Co	0.195 77(9)	0.261 96(5)	0.606 48(6)
S(1)	0.449 9(2)	0.300 7(1)	0.726 0(1)
S(2)	0.322 6(2)	0.249 5(1)	0.467 6(1)
O(1)	−0.093 3(6)	0.154 5(4)	0.503 5(4)
O(2)	−0.116 6(6)	0.302 0(4)	0.460 2(4)
O(3)	0.048 5(6)	0.343 0(3)	0.763 2(4)
O(4)	0.042 4(6)	0.189 3(3)	0.762 2(4)
N(1)	0.155 6(6)	0.401 7(3)	0.580 2(4)
N(2)	0.238 8(6)	0.123 2(3)	0.629 4(4)
N(3)	−0.031 2(6)	0.235 6(4)	0.511 5(4)
N(4)	0.083 3(6)	0.265 5(4)	0.726 2(4)
C(1)	0.303 7(8)	0.467 6(4)	0.624 9(5)
C(2)	0.410 0(8)	0.428 5(4)	0.734 5(5)
C(3)	0.604 1(7)	0.290 7(5)	0.643 9(5)
C(4)	0.528 8(8)	0.306 9(5)	0.521 3(5)
C(5)	0.386 4(8)	0.123 1(5)	0.484 8(5)
C(6)	0.261 6(9)	0.069 4(5)	0.532 6(5)
B	0.163 5(7)	0.460 3(4)	0.299 7(4)
O(5)	0.280 1(7)	0.489 8(4)	0.373 5(4)
F(2)	0.030 8(6)	0.431 5(4)	0.318 7(4)
F(3)	0.176 6(7)	0.457 5(4)	0.204 8(4)

molecular interactions on the crystallization pathway selected by these substances. The accidental isolation of the anion BF_2O^- was a welcome and unexpected bonus. It was known to be capable of existence from the microwave, vapour-phase study of $BF_2(OH)$ by Takeo and Curl;[18] however, its isolation in crystalline form from water solutions had not been accomplished until now.

The BF_2O^- *Anion.*—The anion is planar, as shown by the equation of the best plane through all the atoms (and deviations thereof). The distances of the three moieties attached to the central B atoms do not differ very much, and it is essentially impossible to differentiate between O and F with the X-ray data, as we found out by permuting labels. Consequently, the arbitrary decision was made that the atoms with the shortest hydrogen bond would be fluoride. Unfortunately, the only sure method of making an unequivocal assignment is *via* neutron diffraction which is capable of differentiating between O and F; however, the crystals are too small for this technique to be applied. In the microwave study of Takeo and Curl[18] an unequivocal assignment was made since their compound had a hydrogen attached to the oxygen which helped in the identification. We felt that the likelihood of having multiple bonding between oxygen and boron would tend to shorten this B–O oxygen bond; consequently, the element with the shortest bond to boron was considered to be the oxygen. We believe this is a reasonable assignment.

NMR Spectra.—As noted in the foregoing, aqueous solutions of *cis*-α-$[CoL(NO_2)_2][BF_4]$ yield crystals of the tetrafluoroborate complex and of another salt, shown by X-ray crystallography to be BF_2O^-. The transformation of the BF_4^- anion into BF_2O^- is unexpected because ionic tetrafluoroborates are ordinarily resistant to hydrolysis.[19] Moreover, this appears to be the first structurally characterized example of a compound containing the trigonal-planar BF_2O^- anion, so we carried out NMR studies of the precursor complex in aqueous solution seeking to identify the source of the BF_2O^- complex.

The ^{19}F NMR spectra obtained on fresh aqueous solutions of the tetrafluoroborate complex exhibit a sharp singlet (δ −148.4, reference $CFCl_3$ *), consistent with the literature value for BF_4^-, δ −149.[20] Samples were held at room temperature and three more sets of spectra were obtained over about 4 weeks. After 1 week two additional signals at δ −141.6 (br s) and −127.3 (s) had appeared [Fig. 5(*a*)]. The shift of the former corresponds closely to that reported for $BF_3(OH)^-(aq)$ [δ −140.5 (1 : 1 : 1 : 1 q, J = 14.3 Hz)[21]] even though the quartet was not resolved in the spectra of our somewhat turbid solutions. The shift of the latter signal does not match either that reported for $BF_2(OH)_2^-(aq)$, δ −132.2 (s),[21] or that for $BF(OH)_3^-$ + F^-, δ −116.8 to 119.8 [variable owing to fluoride exchange; no signal for $BF(OH)_3^-$ alone was observed by earlier workers[21]]. Its position shifted toward lower field over the ensuing period [Fig. 5(*b*)] leading us tentatively to assign the signal to $BF(OH)_3^-$ + F^- since a shift downfield would be expected as the concentration of fluoride increased during hydrolysis of BF_4^-. Over this period the signals for BF_3OH^-/F^- and $BF_3(OH)^-$ grew in intensity relative to the BF_4^- peak, consistent with the expectation of increasing fluoride concentration.

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* The chemical shift was measured relative to external KF in D_2O and the values converted so as to be relative to $CFCl_3$ by employing δ −120 for the shift of $F^-(aq)$.[20] No corrections for volume susceptibility or concentration effects were made.

Table 4 Bond distances (Å) and angles (°) for complex **1** with e.s.d.s in parentheses

Co(1)–S(1)	2.235(4)	O(3)–N(4)	1.11(2)	Co(2)–N(8)	1.79(2)	C(7)–C(8)	1.46(3)
Co(1)–S(2)	2.248(6)	O(4)–N(4)	1.34(2)	S(3)–C(8)	1.96(2)	C(9)–C(10)	1.50(3)
Co(1)–N(1)	1.975(12)	N(1)–C(1)	1.41(2)	S(3)–C(9)	1.72(2)	C(11)–C(12)	1.37(3)
Co(1)–N(2)	2.052(13)	N(2)–C(6)	1.40(2)	S(4)–C(10)	1.819(12)	B(1)–F(1)	0.93(6)
Co(1)–N(3)	1.98(2)	C(1)–C(2)	1.46(3)	S(4)–C(11)	1.737(14)	B(1)–F(2)	1.29(5)
Co(1)–N(4)	1.970(10)	C(3)–C(4)	1.43(3)	O(5)–N(7)	1.26(2)	B(1)–F(3)	1.67(5)
S(1)–C(2)	1.92(2)	C(5)–C(6)	1.55(2)	O(6)–N(7)	1.17(2)	B(1)–F(4)	1.75(5)
S(1)–C(3)	1.73(3)	Co(2)–S(3)	2.369(5)	O(7)–N(8)	1.11(2)	B(2)–F(5)	1.23(2)
S(2)–C(4)	1.854(14)	Co(2)–S(4)	2.188(5)	O(8)–N(8)	1.34(2)	B(2)–F(6)	1.42(2)
S(2)–C(5)	1.72(2)	Co(2)–N(5)	1.899(12)	N(5)–C(7)	1.54(2)	B(2)–F(7)	1.34(2)
O(1)–N(3)	1.18(2)	Co(2)–N(6)	1.918(15)	N(6)–C(12)	1.66(2)	B(2)–F(8)	1.36(2)
O(2)–N(3)	1.32(2)	Co(2)–N(7)	1.962(14)				
S(1)–Co(1)–S(2)	90.9(2)	Co(1)–N(1)–C(1)	119.1(9)	N(7)–Co(2)–N(8)	93.8(6)	F(2)–B(1)–F(3)	95(4)
S(1)–Co(1)–N(1)	86.9(4)	O(3)–N(4)–O(4)	118(1)	N(5)–Co(2)–N(6)	173.2(6)	F(2)–B(1)–F(4)	91(3)
S(1)–Co(1)–N(2)	94.0(4)	N(1)–C(1)–C(2)	113(1)	C(10)–S(4)–C(11)	105.9(8)	F(3)–B(1)–F(4)	81(3)
S(1)–Co(1)–N(3)	88.2(5)	S(1)–C(2)–C(1)	110(1)	Co(2)–N(5)–C(7)	116(1)	F(5)–B(2)–F(6)	107(1)
S(1)–Co(1)–N(4)	175.0(4)	S(1)–C(3)–C(4)	121(2)	Co(2)–N(6)–C(12)	110(1)	Co(1)–N(2)–C(6)	110(1)
S(2)–Co(1)–N(1)	94.2(5)	S(2)–C(4)–C(3)	106(1)	Co(2)–N(7)–O(5)	117(1)	Co(1)–N(3)–O(1)	124(1)
S(2)–Co(1)–N(2)	85.8(4)	S(2)–C(5)–C(6)	109(1)	Co(2)–N(7)–O(6)	125(1)	Co(1)–N(3)–O(2)	112(1)
S(2)–Co(1)–N(3)	177.6(5)	N(2)–C(6)–C(5)	110(1)	O(5)–N(7)–O(6)	119(1)	O(1)–N(3)–O(2)	123(2)
S(2)–Co(1)–N(4)	90.4(5)	S(3)–Co(2)–S(4)	90.2(4)	Co(2)–N(8)–O(7)	129(1)	Co(1)–N(4)–O(3)	123(1)
N(1)–Co(1)–N(2)	179.1(6)	S(3)–Co(2)–N(5)	88.4(4)	Co(2)–N(8)–O(8)	120(1)	Co(1)–N(4)–O(4)	117(1)
N(1)–Co(1)–N(3)	88.0(6)	S(3)–Co(2)–N(6)	90.8(4)	O(7)–N(8)–O(8)	109(2)	Co(2)–S(3)–C(8)	96.5(7)
N(1)–Co(1)–N(4)	88.2(5)	S(3)–Co(2)–N(7)	175.2(4)	N(5)–C(7)–C(8)	108(1)	Co(2)–S(3)–C(9)	104.2(7)
N(2)–Co(1)–N(3)	92.1(6)	S(3)–Co(2)–N(8)	90.6(4)	S(3)–C(8)–C(7)	104(1)	Co(2)–S(4)–C(10)	104.1(1)
N(2)–Co(1)–N(4)	90.9(6)	S(4)–Co(2)–N(5)	98.7(4)	S(3)–C(9)–C(10)	122(2)	Co(2)–S(4)–C(11)	100.4(7)
N(3)–Co(1)–N(4)	90.7(6)	S(4)–Co(2)–N(6)	88.1(4)	S(4)–C(10)–C(9)	111(1)	C(8)–S(3)–C(9)	93(1)
Co(1)–S(1)–C(2)	97.8(7)	S(4)–Co(2)–N(7)	86.0(4)	S(4)–C(11)–C(12)	115(1)	F(5)–B(2)–F(7)	107(1)
Co(1)–S(1)–C(3)	100.1(7)	S(4)–Co(2)–N(8)	177.4(4)	N(6)–C(12)–C(11)	113(2)	F(5)–B(2)–F(8)	94(1)
C(2)–S(1)–C(3)	102(1)	N(5)–Co(2)–N(7)	89.6(6)	F(1)–B(1)–F(2)	155(6)	F(6)–B(2)–F(7)	115(1)
Co(1)–S(2)–C(4)	102.3(5)	N(5)–Co(2)–N(8)	86.3(6)	F(1)–B(1)–F(3)	105(3)	F(6)–B(2)–F(8)	116(1)
Co(1)–S(2)–C(5)	99.4(7)	N(6)–Co(2)–N(7)	91.7(6)	F(1)–B(1)–F(4)	107(5)	F(7)–B(2)–F(8)	114(1)
C(4)–S(2)–C(5)	103.6(8)	N(6)–Co(2)–N(8)	86.9(7)				

Table 5 Bond distances (Å) and angles (°) for complex **2**

Co–N(1)	1.973(2)	O(3)–N(4)	1.230(3)
Co–N(2)	1.959(2)	O(4)–N(4)	1.225(2)
Co–N(3)	1.936(2)	N(1)–C(1)	1.489(3)
Co–N(4)	1.950(2)	N(2)–C(6)	1.479(3)
S(1)–C(2)	1.805(2)	C(1)–C(2)	1.517(3)
S(1)–C(3)	1.817(2)	C(3)–C(4)	1.517(3)
S(2)–C(4)	1.804(2)	C(5)–C(6)	1.497(4)
S(2)–C(5)	1.819(2)	B–O(5)	1.204(3)
O(1)–N(3)	1.221(3)	B–F(2)	1.221(3)
O(2)–N(3)	1.224(3)	B–F(3)	1.226(2)
N(1)–Co–N(2)	178.5(8)	Co–N(4)–O(3)	120.7(2)
N(1)–Co–N(3)	89.7(8)	Co–N(4)–O(4)	119.2(2)
N(1)–Co–N(4)	90.9(8)	O(3)–N(4)–O(4)	120.0(2)
N(2)–Co–N(3)	90.4(9)	N(1)–C(1)–C(2)	109.2(2)
N(2)–Co–N(4)	90.6(8)	S(1)–C(2)–C(1)	111.2(2)
N(3)–Co–N(4)	85.7(8)	S(1)–C(3)–C(4)	114.5(2)
C(2)–S(1)–C(3)	105.5(1)	S(2)–C(4)–C(3)	113.4(2)
C(4)–S(2)–C(5)	100.1(1)	S(2)–C(5)–C(5)	109.1(2)
Co–N(1)–C(1)	117.2(1)	N(2)–C(6)–C(6)	108.8(2)
Co–N(2)–C(6)	115.3(2)	O(5)–B–F(2)	120.4(2)
Co–N(3)–O(1)	121.6(2)	O(5)–B–F(3)	120.7(2)
Co–N(3)–O(2)	119.5(2)	F(2)–B–F(3)	118.9(2)
O(1)–N(3)–O(2)	118.9(2)		

After no further changes were evident in the spectra, aqueous KF was added to one sample in order to look for evidence of fluoride exchange with the fluoroborate species in solution. Since BF_4^- and $BF_3(OH)^-$ are reported to undergo fluoride exchange very slowly under conditions similar to those used here,[21] the fact that the resonances at δ −148.4 and −141.6 were essentially unchanged upon introduction of F^-(aq) [Fig. 5(*c*)] supports their assignments. The signal attributed to $BF(OH)_3^-/F^-$ broadened and shifted toward δ −120, the shift of free F^-(aq),[20] as expected for a $BF(OH)_3^-/F^-$ resonance in the presence of an excess of fluoride. Since earlier workers detected separate ^{19}F NMR resonances for $BF_2(OH)_2^-$ and F^- at 27 °C,[21] our spectra appear to lack a signal for $BF_2(OH)_2^-$ suggesting that *cis*-α-[CoL(NO$_2$)$_2$][BF$_2$(OH)$_2$] precipitates under these conditions leading, after dehydration of the diol anion,* to formation of *cis*-α-[CoL(NO$_2$)$_2$][BF$_2$O] crystals.

Seeking to confirm the assignments, we also obtained ^{11}B NMR spectra of the *cis*-α-[CoL(NO$_2$)$_2$][BF$_4$] solutions. In spectra of fresh solutions only a broad singlet was observed at δ −1.52 which compares reasonably well to the value of δ − 1.8 ± 0.5 reported for NH_4BF_4(aq).[22] After 1 week the spectrum exhibited an additional weak, broad multiplet at approximately δ +0.3 ($J \approx 15$ Hz). Literature reports of the ^{11}B NMR spectrum of Na[BF$_3$(OH)] describe a broad, partially resolved quartet ($J = 12.7$ Hz) *upfield* from the resonance of BF_4^- by 1.74 ppm.[23] A later recomputation of the shift relative to $BF_3{\cdot}OEt_2$ listed a value of δ −3.6 for Na[BF$_3$(OH)].[22] Since this seemed inconsistent with our spectra an authentic sample of Na[BF$_3$(OH)] was prepared using the literature procedure[21] except that addition of alcohol to precipitate the product was omitted. The ^{11}B NMR spectrum of the product consisted of a broad quartet at δ 0.22 ($J = 14.8$ Hz) relative to $BF_3{\cdot}OEt_2$ (Fig. 6), which compares reasonably well with the ^{11}B quartet seen at δ +0.3, along with the resonance of BF_4^-. No explanation for the difference observed from the reported shift of Na[BF$_3$(OH)] is apparent, but the multiplicity, the coupling constant and the correspondence of the signal to the ^{19}F resonance of $BF_3(OH)^-$ strongly support the assignment.

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* The $BF_2(OH)_2^-$ ion can be regarded as a hydrated form of the trigonal BF_2O^- ion observed in the crystal structure determination. Formation of the trigonal species probably happens upon crystallization [*i.e.* $BF_2(OH)_2^- \longrightarrow BF_2O^- + H_2O$].

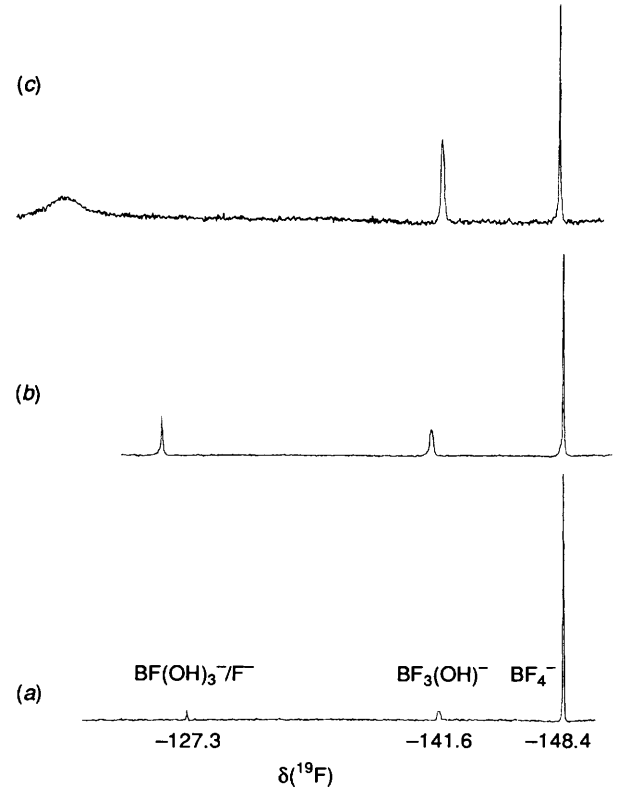

Fig. 5 Fluorine-19 NMR spectra of *cis*-α-[CoL(NO$_2$)$_2$][BF$_4$](aq) (*a*) after about 1 week, (*b*) after about 3 weeks and (*c*) after the addition of NaF(aq)

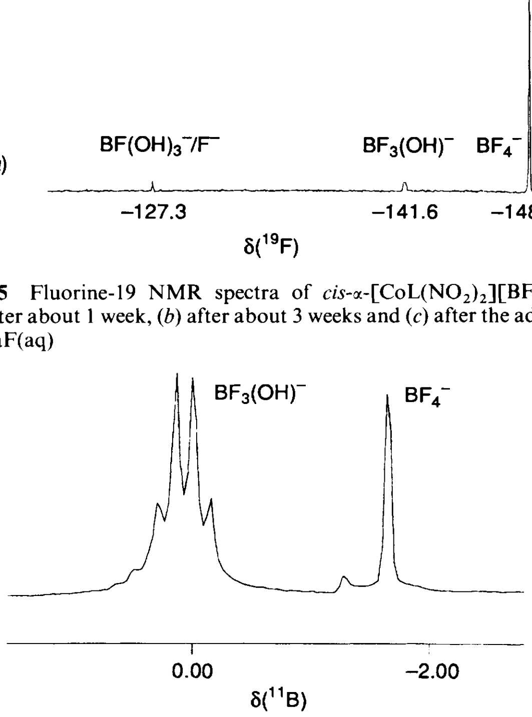

Fig. 6 The ^{11}B NMR spectrum of Na[BF$_3$(OH)] and NaBF$_4$ prepared from B(OH)$_3$, NaF and HF according to the procedure in ref. 21

The third ^{11}B resonance to appear was a small, broad singlet at δ −1.0, which is assigned to BF(OH)$_3$$^-$ as per the discussion of the ^{19}F spectra above. The absence of observable ^{11}B–^{19}F coupling is expected owing to the rapid fluoride exchange proposed for this species.[21] The third peak shifted upfield with time presumably as a consequence of the increasing fluoride concentration. Although we have not proven that the third peak does not represent BF$_2$(OH)$_2$$^-$, the assignments made are consistent with the absence of that resonance due to removal of the ion from solution by precipitation of its cobalt complex.

Since hydrolysis of alkali-metal tetrafluoroborates is very slow,[19] the more facile hydrolysis of our tetrafluoroborate complex was unexpected. In retrospect, however, the crystallization of *cis*-α-[CoL(NO$_2$)$_2$][BF$_2$O] probably promotes the hydrolysis by shifting the complex fluorohydroxoborate equilibria away from BF$_4$$^-$.[21] Treatment of NaBF$_4$ with CaCO$_3$ in boiling water similarly removes fluoride from the equilibrium enhancing the yield of Na[BF$_3$(OH)].[23]

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