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Studies on Macrocyclic Complexes Derived from *vic*-Dioximes.
IX*. The Crystal Structure of N,N-Dimethylpiperidinium Iodobis(difluoroborondimethylglyoximato)nickelate(II).
The Product from the Reaction of Bis(difluoroborondimethylglyoximato)nickel(II) with Piperidine and Iodomethane

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The reaction of bis(difluoroborondimethylglyoximato)nickel(II) and iodomethane with piperidine in acetone yields the deep-red, diamagnetic N,N-dimethylpiperidinium iodobis(difluoroborondimethylglyoximato)nickelate(II) salt. The salt $C_{15}H_{28}B_2F_4IN_5O_4Ni$*, crystallises in the monoclinic space group* $P2_1/c$ *with dimensions* a = 9.885(5), b = 19.042(6), c = 13.156(4) Å, β = 103.4(1)° *and* Z = 4. *The structure was refined to* R = 0.077 *for 1684 photographic reflexions using least-squares calculations. The structure consists of discrete N,N-dimethylpiperidinium and iodobis(difluoroborondimethylglyoximato)nickelate(II) ions. In the anion the macrocycle encompasses the base of a square-based pyramid [average Ni–N 1.87(1) Å] with the nickel atom being displaced 0.19 Å from the* N_4*-basal plane towards the apical iodine atom [Ni–I 2.842(2) Å]. Both glyoxime fragments of the macrocycle are closely planar with a dihedral angle between their planes of 8°. The axial fluorine atoms are in a* cis*-configuration. The piperidine ring of the cation adopts a chair conformation.*

Introduction

Cob(I)aloximes and like complexes, which mimic vitamin B_{12}, have been shown to be very powerful nucleophiles as evidence by Co–CH_3 bond formation in the presence of iodomethane and a suitable N-heterocyclic base [1]. Since bis(difluoroborondimethylglyoximato)nickel(II), $Ni(dmgBF_2)_2$, is isoelectronic with its Co(I) analogue its reaction with those species was investigated [2]. On the addition of the bases imidazole or piperidine intense-red species form in solution from which deep-red diamagnetic products are isolated. The varying stoichiometries of the compounds and that a like solution colour is obtained on the reaction of $Ni(dmgBF_2)_2$ and sodium iodide in acetone suggests that unlike Co(I) simple addition of –CH_3 and a base molecule to the metal atom in *trans*-positions does not occur but rather there is some interaction between the parent macrocycle and the iodide ion. The crystal structure of the compound derived from the reaction of $Ni(dmgBF_2)_2$ and iodomethane with piperidine has been undertaken to determine the nature of the product.

Experimental

The compound may be prepared by the controlled addition of piperidine to an acetone solution of $Ni(dmgBF_2)_2$ and iodomethane. However a more convenient method is to add N,N-dimethylpiperidinium iodide, freshly prepared by the addition of iodomethane to piperidine in acetone, to a hot acetone solution of $Ni(dmgBF_2)_2$. Deep-red diamagnetic crystals form on standing. Table I gives the details

TABLE I. Proton Magnetic Resonance Data.

Chemical Shift^a			
1.75 (m)	[1.9]	–CH_2–CH_2–CH_2–	(2H)
2.0 (m)^b			(4H)
2.22 (s)	[12.2]	C–CH_3	(12H)
3.38 (s)	[5.9]	N–CH_3	(6H)
3.66(t)	[3.8]	–CH_2–N–CH_2–	(4H)

^{a}Chemical shifts are given in p.p.m. relative to tetramethylsilane with relative intensites in square brackets; s = singlet, t = triplet, m = unresolved multiplet. ^{b}Partly obscured by solvent (d_6-acetone) impurity.

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*Part VIII, F. S. Stephens and R. S. Vagg, *Inorg. Chim. Acta, 51,* 163 (1981).

TABLE II. Final Atomic Coordinates (fractional × 10^4) with Estimated Standard Deviations in Parentheses.

	x	*y*	*z*
Ni	4649(2)	1324(1)	2287(1)
Ni(1)	3862(2)	−34(1)	1464(1)
N(11)	2989(12)	1506(7)	2672(9)
N(12)	5181(13)	1061(8)	3692(10)
N(21)	4212(15)	1763(7)	980(9)
N(22)	6425(13)	1340(7)	2026(8)
C(11)	2859(17)	1331(9)	3583(12)
C(12)	4243(17)	1086(9)	4225(12)
C(21)	5205(20)	1816(9)	467(12)
C(22)	6538(17)	1546(8)	1108(11)
C(M11)	1527(19)	1338(13)	3972(15)
C(M12)	4421(23)	878(12)	5349(12)
C(M21)	5059(20)	2072(9)	−634(12)
C(M22)	7842(17)	1568(11)	718(12)
O(11)	1821(12)	1726(7)	1976(9)
O(12)	6447(11)	808(7)	4148(8)
O(21)	2899(12)	1962(7)	485(8)
O(22)	7576(11)	1043(7)	2663(7)
B(1)	2054(21)	2254(14)	1215(14)
B(2)	7605(25)	1138(12)	3802(16)
F(11)	810(10)	2405(7)	591(8)
F(12)	2746(12)	2819(6)	1723(8)
F(21)	8767(10)	772(7)	4286(7)
F(22)	7698(13)	1846(6)	4040(8)
N	844(20)	4225(9)	2976(13)
C(1)	606(34)	3509(20)	3365(24)
C(2)	−861(45)	3360(14)	3231(32)
C(3)	−1614(31)	3384(27)	2150(38)
C(4)	−1411(25)	4083(33)	1718(18)
C(5)	112(31)	4290(16)	1848(17)
C(MN1)	2356(29)	4316(15)	3023(31)
C(MN2)	426(37)	4760(25)	3635(35)

of the NMR spectrum recorded on a Varian XL-200 spectrometer.

Crystal Data. $C_{15}H_{28}B_2F_4IN_5O_4Ni$, M_r = 625.7, Monoclinic, a = 9.885(5), b = 19.042(6), c = 13.156(4) Å, β = 103.4(1)°, U = 2408.9 Å^3, D_m = 1.75 (by flotation), Z = 4, D_c = 1.725 Mg m^{-3}, $F(000)$ = 1248, μ(Mo-K$_\alpha$) = 2.17 mm^{-1}. Systematic absences; $h0l$ if $l \neq 2n$ and $0k0$ if $k \neq 2n$, space group $P2_1/c$ (No. 14).

The compound crystallises as hexagonal-shaped plates elongated in the c direction and lying on the (100) face. Cell parameters were determined from precession photographs using Mo-K_α radiation. Intensities were estimated visually from precession photographs for the layers 0–3kl and h0–5l. They were corrected for Lorentz and polarisation effects but not for absorption or extinction. The structure factors were placed on a common scale by internal correlation and 1684 non-zero unique reflexions were obtained. Scattering factors were taken from 'International Tables for X-Ray Crystallography' [3]. All calculations were carried out on a UNIVAC 1106 computer with programmes written by F.S.S.

Structure Determination. The structure was solved by the heavy-atom method and refined by a full-matrix least-squares procedure in which $\Sigma w\Delta^2$ was minimised. Weights for each reflexion, w, were initially unity and in the final stages given by $w = (4.8 + 0.048|F_o| + 0.0072|F_o|^2)^{-1}$. Refinement was terminated when the maximum shift in any parameter was <0.1 σ. The final R was 0.077 and R' [$=(\Sigma w\Delta^2/\Sigma w|F_o|^2)^{1/2}$] was 0.105. A final difference map showed a maximum density of 0.9 eÅ^{-3} being located about the iodine atom. The final atomic parameters are given in Tables II and III.

TABLE III. Final Anisotropic Thermal Parameters (×10^4) in the Form $\exp -(h^2b_{11} + k^2b_{22} + l^2b_{33} + 2hkb_{12} + 2hlb_{13} + 2klb_{23})$ with Estimated Standard Deviations in Parentheses.

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Ni	68.9(19)	28.8(7)	42.0(10)	0.5(18)	19.3(12)	0.5(7)
I	144.7(20)	33.9(4)	104.4(11)	−17.7(10)	44.9(12)	−17.4(5)
N(11)	67(13)	27(4)	51(8)	0(10)	14(9)	−5(5)
N(12)	82(14)	30(4)	57(8)	−20(11)	24(10)	−3(5)
N(21)	105(17)	25(4)	44(7)	3(11)	29(10)	4(5)
N(22)	88(14)	28(4)	41(7)	2(11)	36(9)	−1(5)
C(11)	94(18)	26(5)	69(11)	−20(14)	30(12)	−11(7)
C(12)	89(17)	32(6)	55(10)	−16(13)	38(11)	9(6)
C(21)	146(25)	26(5)	44(9)	−3(14)	26(13)	0(6)
C(22)	103(19)	17(4)	58(9)	−10(13)	35(12)	−5(6)
C(M11)	125(23)	53(9)	86(13)	−14(19)	70(15)	7(10)
C(M12)	184(30)	49(7)	41(9)	13(17)	19(14)	14(7)
C(M21)	141(24)	32(6)	57(10)	11(14)	43(14)	17(6)
C(M22)	106(19)	39(6)	59(10)	4(15)	53(12)	2(7)

(continued on facing page)

TABLE III. *(continued)*

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
O(11)	86(13)	41(5)	75(8)	10(10)	7(9)	5(5)
O(12)	93(13)	39(4)	50(6)	14(10)	27(8)	7(4)
O(21)	104(14)	44(5)	57(7)	14(10)	11(9)	7(5)
O(22)	90(12)	38(4)	42(6)	1(9)	13(8)	−2(4)
B(1)	98(23)	52(9)	48(10)	−39(19)	37(14)	−7(9)
B(2)	102(26)	36(7)	63(12)	18(19)	13(16)	14(8)
F(11)	103(11)	67(6)	87(7)	26(10)	19(8)	21(6)
F(12)	129(14)	36(3)	91(8)	2(9)	21(9)	0(4)
F(21)	96(11)	57(5)	66(6)	19(9)	15(7)	8(5)
F(22)	138(16)	37(3)	92(8)	−24(9)	41(9)	−11(4)
N	151(25)	36(6)	92(12)	−7(17)	24(15)	−14(7)
C(1)	183(40)	82(17)	165(28)	−8(32)	5(29)	61(18)
C(2)	353(79)	29(7)	245(23)	−11(28)	107(50)	25(14)
C(3)	184(43)	131(26)	249(45)	−111(34)	146(40)	−123(30)
C(4)	146(33)	243(46)	70(15)	−138(35)	27(18)	5(20)
C(5)	260(46)	74(13)	87(16)	18(27)	49(23)	39(12)
C(MN1)	141(32)	40(9)	296(42)	−5(25)	26(33)	22(17)
C(MN2)	234(52)	112(20)	284(48)	−49(34)	125(44)	−127(27)

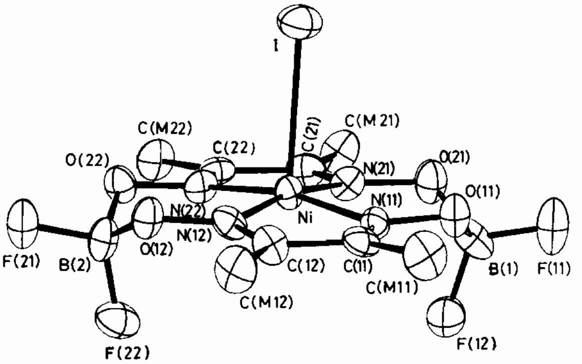

Fig. 1. A perspective drawing of the $[Ni(dmgBF_2)_2I]^-$ anion together with the labelling of the atoms. Thermal ellipsoids are drawn to include 35% probability.

A list of observed and calculated structure factors has been deposited with the Editor.

Discussion

The compound consists of discrete N,N-dimethylpiperidinium and iodobis(difluoroborondimethylglyoximato)nickel(II) ions. Figure 1 shows a perspective drawing of the anion and its atomic labelling scheme [4]. The packing of the ions in the lattice together with the atomic labelling scheme for the cation is shown in Fig. 2. The interion contact distances <3.5 Å are given in Table IV.

The bond lengths and angles within the ions are given in Table V. The piperidine ring adopts a chair conformation, the dihedral angles between the plane of the 'seat' (Table VI, plane 7) and the two three-atom planes (planes 8 and 9) being 53 and 50° and between the latter two planes 3°. The dimensions within the cation are in accord with those previously reported for the piperidinium ion [5].

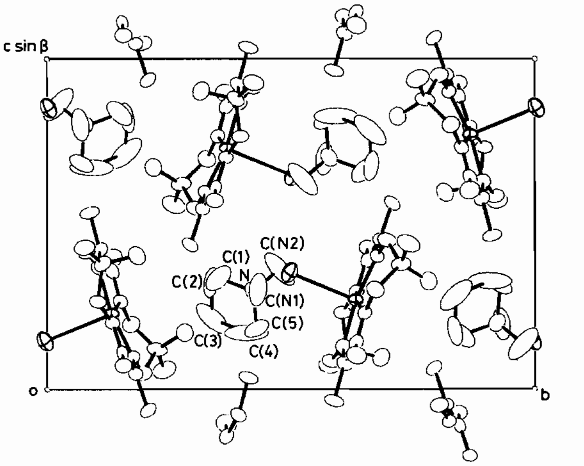

Fig. 2. The packing of the ions in the lattice together with the atomic labelling for the cation.

In the anion the macrocycle encompasses the base of a square-based pyramid with the nickel atom being displaced 0.19 Å from the N_4-basal plane (Table VI, plane 1) towards the apical iodine atom. Both glyoxime fragments of the macrocycle are closely planar (Table VI, planes 2 and 3) and the dihedral angle between their planes is 8°. The axial fluorine atoms are in a *cis* configuration with a F···F separation of 5.46 Å, which is similar to that found in the parent dimer [6]. The average Ni–N distance of

TABLE IV. Interion Contact Distances (A) <3.5 A with Estimated Standard Deviations in Parentheses.

C(M11)···F(21$^{\mathrm{I}}$)	3.05(2)	F(21)···C(4$^{\mathrm{VI}}$)	3.26(4)	O(22)···C(MN1$^{\mathrm{VII}}$)	3.41(3)
C(M22)···F(11$^{\mathrm{II}}$)	3.38(2)	O(21)···C(1$^{\mathrm{V}}$)	3.28(4)	F(11)···C(2$^{\mathrm{V}}$)	3.48(4)
C(M11)···F(11$^{\mathrm{III}}$)	3.39(2)	F(21)···C(5$^{\mathrm{VI}}$)	3.33(3)	F(22)···C(2$^{\mathrm{II}}$)	3.49(4)
C(M12)···O(12$^{\mathrm{IV}}$)	3.43(2)	F(11)···C(1$^{\mathrm{V}}$)	3.37(4)	F(21)···C(5$^{\mathrm{VII}}$)	3.49(3)
C(M21)···F(22$^{\mathrm{V}}$)	3.43(2)	F(12)···C(MN1)	3.39(4)		

Roman numerals as superscripts refer to the following equivalent positions relative to atoms at x, y, z:

I	$x-1,\ y,\ z$	IV	$1-x,\ -y,\ 1-z$	VII	$1-x, y-½, ½-z$
II	$1+x,\ y,\ z$	V	$x, ½-y, z-½$		
III	$x, ½-y, ½+z$	VI	$1+x, ½-y, ½+z$		

TABLE V. Bond Lengths and Angles with Estimated Standard Deviations in Parentheses.

a) Distances (Å)

Ni–I	2.842(2)		
Ni–N(11)	1.86(1)	Ni–N(21)	1.87(1)
Ni–N(12)	1.87(1)	Ni–N(22)	1.87(1)
N(11)–C(11)	1.28(2)	N(21)–C(21)	1.32(2)
N(12)–C(12)	1.29(2)	N(22)–C(22)	1.30(2)
C(11)–C(12)	1.51(2)	C(21)–C(22)	1.48(2)
C(11)–C(M11)	1.52(2)	C(21)–C(M21)	1.50(2)
C(12)–C(M12)	1.50(2)	C(22)–C(M22)	1.49(2)
N(11)–O(11)	1.36(2)	N(21)–O(21)	1.35(2)
N(12)–O(12)	1.36(2)	N(22)–O(22)	1.37(2)
B(1)–O(1)	1.47(3)	B(2)–O(21)	1.47(2)
B(1)–O(12)	1.52(2)	B(2)–O(22)	1.50(2)
B(1)–F(11)	1.34(2)	B(2)–F(21)	1.37(2)
B(1)–F(12)	1.37(3)	B(2)–F(22)	1.38(3)
N–C(MN1)	1.49(3)	C(1)–C(2)	1.45(4)
N–C(MN2)	1.46(3)	C(2)–C(3)	1.45(5)
N–C(1)	1.49(4)	C(3)–C(4)	1.48(7)
N–C(5)	1.50(3)	C(4)–C(5)	1.53(4)

b) Angles (°)

I–Ni–N(11)	95.3(4)	I–Ni–N(21)	94.1(4)
I–Ni–N(12)	97.0(5)	I–Ni–N(22)	97.5(4)
N(11)–Ni–N(12)	81.1(6)	N(21)–Ni–N(22)	81.4(6)
N(11)–Ni–N(21)	97.9(6)	N(12)–Ni–N(22)	97.2(5)
N(11)–Ni–N(22)	167.2(6)	N(12)–Ni–N(21)	168.9(6)
Ni–N(11)–O(11)	123(1)	Ni–N(21)–O(21)	124(1)
Ni–N(11)–C(11)	120(1)	Ni–N(21)–C(21)	118(1)
O(11)–N(11)–C(11)	117(1)	O(21)–N(21)–C(21)	118(1)
Ni–N(12)–O(12)	124(1)	Ni–N(22)–O(22)	124(1)
Ni–N(12)–C(12)	117(1)	Ni–N(22)–C(22)	118(1)
O(12)–N(12)–C(12)	119(1)	O(22)–N(22)–C(22)	117(1)
N(11)–C(11)–C(12)	109(1)	N(21)–C(21)–C(22)	111(1)
N(11)–C(11)–C(M11)	127(2)	N(21)–C(21)–C(M21)	127(2)
C(12)–C(11)–C(M11)	124(1)	C(22)–C(21)–C(M21)	122(2)
N(12)–C(12)–C(11)	113(1)	N(22)–C(22)–C(21)	112(1)
N(12)–C(12)–C(M12)	126(2)	N(22)–C(22)–C(M22)	127(2)

(continued on facing page)

TABLE V. *(continued)*

C(11)–C(12)–C(M12)	121(1)	C(21)–C(22)–C(M22)	121(1)
N(11)–O(11)–B(1)	115(1)	N(12)–O(12)–B(2)	115(1)
N(21)–O(21)–B(1)	114(1)	N(22)–O(22)–B(2)	112(1)
O(11)–B(1)–O(21)	112(2)	O(12)–B(2)–O(22)	115(2)
F(11)–B(1)–F(12)	115(2)	F(21)–B(2)–F(22)	113(2)
F(11)–B(1)–O(11)	107(1)	F(21)–B(2)–O(12)	106(1)
F(11)–B(1)–O(21)	105(1)	F(21)–B(2)–O(22)	103(2)
F(12)–B(1)–O(11)	110(1)	F(22)–B(2)–O(12)	111(2)
F(12)–B(1)–O(21)	108(1)	F(22)–B(2)–O(22)	109(2)
C(MN1)–N–C(1)	109(2)	N–C(1)–C(2)	112(3)
C(MN1)–N–C(5)	106(2)	C(1)–C(2)–C(3)	113(3)
C(MN2)–N–C(1)	110(3)	C(2)–C(3)–C(4)	109(3)
C(MN2)–N–C(5)	113(3)	C(3)–C(4)–C(5)	114(3)
C(MN1)–N–C(MN2)	108(2)	C(4)–C(5)–N	109(2)
C(1)–N–C(5)	110(2)		

TABLE VI. Least-Squares Planes Data.

a) Least-squares planes and their equations given by $lX' + mY' + nZ' - p = 0$ where X' Y' and Z' are orthogonal coordinates (Å) derived with respect to the orthogonal axes a', b, c. Deviations (Å) of relevant atoms from the planes are given in square brackets.

	l	*m*	*n*	*p*
Plane (1): N(11), N(12), N(21), N(22)	0.2381	0.9230	0.3023	4.1736
[N(11), N(22) 0.013; N(12), N(21) –0.013; Ni –0.19; I – 3.03]				
Plane (2): O(11), N(11), C(11), C(12), N(12), O(12)	0.2750	0.9345	0.2259	4.0694
[O(11) –0.023; N(11) 0.040; C(11) –0.029; C(12) 0.022; N(12) 0.018; O(12) –0.028; Ni –0.04; C(M11) –0.18; C(M12) 0.02]				
Plane (3): O(21), N(21), C(21), C(22), N(22), O(22)	0.2125	0.9118	0.3514	4.0141
[O(21) –0.025; N(21) 0.021; C(21) <0.001; C(22) –0.008; N(22) 0.045; O(22) –0.034; Ni –0.08; C(M21) –0.08; C(M22) 0.01]				
Plane (4): N(12), N(21), I	0.9327	–0.1596	–0.3233	3.1373
[Ni 0.001]				
Plane (5): N(12), N(21), N(11)	0.2516	0.9209	0.2977	4.2068
[Ni –0.181]				
Plane (6): N(12), N(21), N(22)	0.2245	0.9249	0.3068	4.1134
[Ni –0.181]				
Plane (7): N, C(2), C(3), C(5)	–0.5761	0.7295	0.3687	6.7788
[N, C(3) –0.005; C(2), C(5) 0.005; C(1) –0.66; C(4) 0.63]				
Plane (8): C(1), N, C(2)	0.0287	0.3791	0.9249	3.7465
Plane (9): C(4), C(3), C(5)	–0.0026	0.4200	0.9075	5.6131

b) Dihedral angles (°) between relevant planes

1–2	4.9	4–5	90.5	6–7	53.1
1–3	3.2	4–6	92.1	6–8	50.0
2–3	8.2	5–6	1.7	7–8	3.1

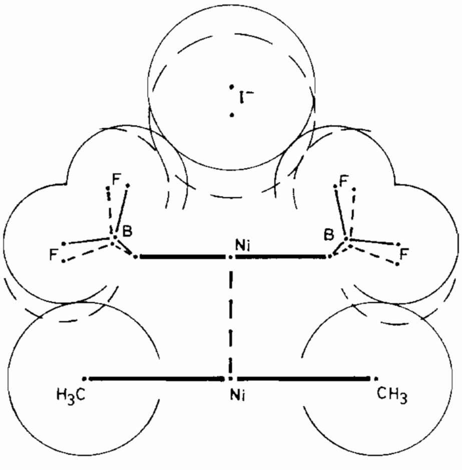

Fig. 3. Scaled drawing of the steric interactions between the iodide ion and the parent dimer $[Ni(dmgBF_2)_2]_2$. Van der Waals and ionic radii are taken from reference [10]. The full lines represent the situation in which the axial F···F separation is that of the parent (5.46 A) and the broken lines a separation of 1.0 A greater.

1.87(1) Å is the same as that in the parent and all other dimensions of the macrocycle are in accord with those found in the parent [6]. The Ni–I distance of 2.842(2) Å is considerably longer than reported values of 2.55–2.65 Å in five-coordinate nickel(II) complexes [7, 8] and in particular that of 2.649(3) Å to the apical iodine atom in the square-based pyramidal cation $\{Ni[\phi_2P(CH_2)_2S(CH_2)_3S(CH_2)_2P\phi_2]I\}^+$ [8]. Further the distance is only 0.04–0.06 Å shorter than those found in octahedral nickel(II) complexes [9]. This suggests that, on the basis of bond length alone, the interaction between the nickel and iodine atoms is far weaker than normally observed in five coordinate complexes. In fact, the coordination of the iodine atom would seem to have had little effect on the macrocycle except to raise the nickel atom slightly from the molecular plane. However, as its coordination number is increased the effective radius of the nickel atom can only expand in the tetragonal direction. This suggests that the 'apparently' long Ni–I distance approximates the minimum interatomic distance permitted under such conditions.

That the iodide ion does not form an adduct similar to those of the N-bases [2], in which the dimeric nature of the parent is retained, must be a consequence of a steric effect which would arise on it approaching the *cis* axial fluorine atoms. The initial interaction of the iodide ion and a moiety of the parent macrocycle would most likely be a long range (>4.0 Å) electrostatic attraction between the negatively charged iodide ion and the nickel atom. The latter would act as a positive centre resulting from the metal to ligand π-bonding and the electron withdrawing effects of the BF_2 groups, in particular. Figure 3 shows a scaled diagramatic representation of the steric interactions assuming accepted values for the appropriate radii [10]. The first position shows the closest allowable approach of the iodide ion to the nickel atom (~4.5 Å) in which the axial F···F separation is that found in the parent dimer [6]. As the iodide ion closes on the nickel atom so the axial fluorine atoms must move apart with the consequence that the equatorial fluorine atoms move nearer to the methyl groups of the other moiety of the parent. The second position represented is that when the F···F separation has been increased by 1.0 Å. Equatorial fluorine atom–methyl group repulsions are evident and the iodide ion is only 0.75 Å closer to the nickel atom. As the iodide ion comes even closer to the nickel atom the steric repulsions between the two moieties of the parent would become so great that the dimer is cleaved and in that moiety to which the iodide coordinates the originally axial fluorine atoms adopt equatorial positions.

Other anions, such as hydroxide and chloride ions, similarly form intensely coloured species in non-aqueous reaction solutions. The nature of these interactions is being studied further.

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