Inorganica Chimica Acta, 43 (1980) 77–82

Studies on Macrocyclic Complexes Derived from *vic*-Dioximes. Part VI*. The Crystal and Molecular Structure of the 1:1 Adduct of Benzimidazole with Bis(difluoroborondimethylglyoximato)nickel(II)

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Received April 23, 1980

The 1:1 adduct of benzimidazole with bis(difluoroborondimethylglyoximato)nickel(II) is monoclinic, space group C2/c, a = 10.108(3), b = 20.450(6), c = 19.235(6) Å, β = 92.5(1)°, Z = 8. The structure was refined to R = 0.078 for 2504 photographic reflexions. The structure consists of discrete $[Ni(dmg\text{-}BF_2)_2]_2$ *dimer units, which have space group imposed* $2(C_2)$ *symmetry, and benzimidazole molecules. The benzimidazole molecules are hydrogen-bonded to each other forming chains parallel to c that are incorporated in sheets centred about y = 0 and ½. The* $[Ni(dmg\text{-}BF_2)_2]_2$ *dimer units are sandwiched between the sheets of benzimidazole molecules such that there are π–π interactions between the dmg fragments of the macrocycles and the benzimidazole rings. The Ni atoms are coordinated to four N atoms of a closely planar macrocycle [average Ni–N 1.848(6) Å, N–Ni–N 83.0(3) and 97.0(3)°]. The Ni···Ni separation is 3.358(2) Å.*

Introduction

Bis(difluoroborondimethylglyoximato)nickel(II), $Ni(dmg\text{-}BF_2)_2$, forms diamagnetic 1:1 adducts with N-bases [1] and the crystal structures of the 4,4′-bipyridine [2] and aniline [3] adducts have shown that the dimeric nature of the parent [4] is retained with co-ordination of the bases through the N atoms in axial positions to the Ni atoms. Benzimidazole also forms a 1:1 diamagnetic adduct and its structure was undertaken to ascertain the bonding mode of the base.

Experimental

Crystal Data

$C_{15}H_{18}B_2F_4N_6O_4Ni$, M = 502.7, Monoclinic, a = 10.108(3), b = 20.450(6), c = 19.235(6) Å, β = 92.5(1)°, U = 3972.3 Å^3, D_m = 1.68 (by flotation), Z = 8, D_c = 1.680 g cm^{-3}, $F(000)$ = 2048, $\mu(\text{Mo-K}_\alpha)$ = 10.6 cm^{-1}. Systematic absences: hkl if $h + k \neq 2n$ and $h0l$ if $l \neq 2n$, space group Cc (No. 9) or $C2/c$ (No. 15).

The adduct crystallises as dark amber diamond-shaped plates lying on the (001) face. Cell parameters were determined from precession photographs using Mo-K$_\alpha$ radiation. Intensities were estimated visually from precession photographs for the layers 0–3 about [100], 0–5 about [010] and 0–4 about [110]. 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 2504 non-zero unique reflexions were obtained. Scattering factors were taken from 'International Tables for X-Ray Crystallography' [5]. All calculations were carried out on a UNIVAC 1106 computer with programmes written by F.S.S.

A three dimensional Patterson synthesis indicated that the space group is $C2/c$ with the Ni atoms lying on two-fold axes. The structure was solved by the heavy-atom method and refined by least-squares in which $\Sigma w\Delta^2$ was minimised. Weights were initially unity and in the final stages $w = (15.0 + 0.5|F_o| + 0.02|F_o|^2)^{-1}$. After isotropic refinement a difference map indicated the approximate positions for 17 of the 18 hydrogen atoms. The positions of these atoms were optimised, assuming C–H to be 1.0 Å, and they were included in the calculations but not refined. The anisotropic refinement was carried out in three block matrices; (*1*) the overall scale and thermal parameter, (*2*) the parameters for the Ni dimer unit and (*3*) the parameters for the benzimidazole molecule. Refinement was terminated when the maximum shift in any parameter was <0.1σ. The final R was 0.078 and R' $[=(\Sigma w\Delta^2/\Sigma w|F_o|^2)^{1/2}]$ was 0.107. A final difference map showed no features >|1.4|eÅ^{-3} and these were associated with the Ni atoms. The final atomic parameters are given in Tables I, II and III. A list of observed and calculated structure factors has been deposited with the Editor.

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*Part V, reference [2].

TABLE I. Final Atomic Coordinates (fractional $\times 10^4$) with Estimated Standard Deviations in Parentheses.

	x/a	y/b	z/c		x/a	y/b	z/c
Ni(1)	0	1386.6(6)	2500	C(M22)	−3470(8)	2920(4)	3554(5)
Ni(2)	0	3028.7(6)	2500	B(1)	2111(9)	1142(5)	1385(4)
N(11)	137(7)	1407(3)	3460(3)	B(2)	−2530(9)	3238(5)	1491(5)
N(12)	1835(6)	1389(3)	2583(3)	F(11)	3069(5)	1263(3)	921(2)
N(21)	179(6)	3026(3)	3467(3)	F(12)	1898(5)	487(2)	1481(2)
N(22)	−1768(6)	3006(3)	2672(3)	F(21)	−3562(5)	3059(3)	1057(2)
O(11)	892(6)	1465(3)	1115(2)	F(22)	−2421(6)	3901(2)	1570(3)
O(12)	2663(5)	1430(3)	2055(2)	C(1)	2066(8)	−273(5)	4495(4)
O(21)	−1329(6)	2977(3)	1155(3)	C(2)	872(8)	−330(5)	4130(4)
O(22)	−2774(5)	2926(3)	2166(3)	C(3)	821(8)	−367(5)	3406(5)
C(11)	1335(9)	1433(4)	3748(4)	C(4)	1959(8)	−368(4)	3031(4)
C(12)	2352(8)	1424(3)	3213(4)	C(5)	3151(7)	−297(4)	3397(3)
C(21)	−927(9)	3006(4)	3779(4)	C(6)	3214(7)	−240(4)	4123(3)
C(22)	−2100(7)	2983(4)	3312(4)	N(1)	4436(6)	−264(3)	3172(3)
C(M11)	1652(10)	1497(5)	4502(4)	N(2)	4534(7)	−172(4)	4331(3)
C(M12)	3810(8)	1467(5)	3389(5)	C(7)	5184(8)	−183(4)	3752(4)
C(M21)	−1008(9)	2992(5)	4554(4)				

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

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Ni(1)	61(1)	19.7(3)	14.8(3)	0	5.9(5)	0
Ni(2)	57(1)	18.4(3)	16.4(3)	0	15.2(5)	0
N(11)	93(7)	21(2)	19(1)	−4(3)	9(3)	0(1)
N(12)	68(6)	29(2)	20(1)	0(3)	12(2)	1(1)
N(21)	85(6)	22(2)	21(2)	−2(3)	12(3)	−2(1)
N(22)	79(6)	19(1)	17(1)	0(3)	6(2)	0(1)
O(11)	101(6)	30(2)	20(1)	6(3)	16(2)	4(1)
O(12)	74(5)	32(2)	21(1)	−5(3)	13(2)	2(1)
O(21)	84(6)	32(2)	21(1)	5(3)	9(2)	−1(1)
O(22)	64(5)	30(2)	24(1)	−8(2)	4(2)	2(1)
C(11)	101(9)	21(2)	23(2)	−6(4)	−2(3)	−2(2)
C(12)	81(7)	16(2)	26(2)	−5(4)	2(3)	−1(1)
C(21)	108(9)	18(2)	22(2)	1(4)	19(3)	−2(2)
C(22)	75(7)	20(2)	23(2)	−2(3)	14(3)	−1(2)
C(M11)	142(11)	32(3)	21(2)	−1(5)	−5(4)	−1(2)
C(M12)	69(8)	31(3)	36(3)	1(4)	−8(4)	4(2)
C(M21)	122(10)	36(3)	21(2)	−8(5)	18(4)	−1(2)
C(M22)	82(8)	28(3)	35(3)	3(4)	33(4)	1(2)
B(1)	84(9)	23(2)	21(2)	0(4)	16(3)	1(2)
B(2)	68(8)	25(2)	29(2)	6(4)	7(4)	4(2)
F(11)	115(6)	38(2)	27(1)	−13(3)	31(2)	−1(1)
F(12)	96(5)	21(1)	34(1)	−1(2)	9(2)	−1(1)
F(21)	82(5)	52(2)	27(1)	−7(3)	−1(2)	5(1)
F(22)	142(7)	25(1)	42(2)	13(3)	28(3)	7(1)
C(1)	86(8)	36(3)	21(2)	7(4)	11(3)	−1(2)
C(2)	78(8)	31(3)	30(2)	6(4)	15(3)	−1(2)
C(3)	60(7)	38(3)	32(2)	5(4)	−10(3)	−2(2)
C(4)	98(8)	31(2)	20(2)	11(4)	8(3)	−5(2)
C(5)	72(6)	22(2)	18(1)	3(3)	11(3)	1(1)
C(6)	70(6)	23(2)	18(1)	−2(3)	−1(3)	−1(1)
N(1)	77(6)	26(2)	21(2)	−1(3)	8(3)	−2(1)
N(2)	90(7)	36(2)	23(2)	−2(4)	−3(3)	−3(2)
C(7)	65(7)	28(2)	32(2)	3(4)	2(3)	−2(2)

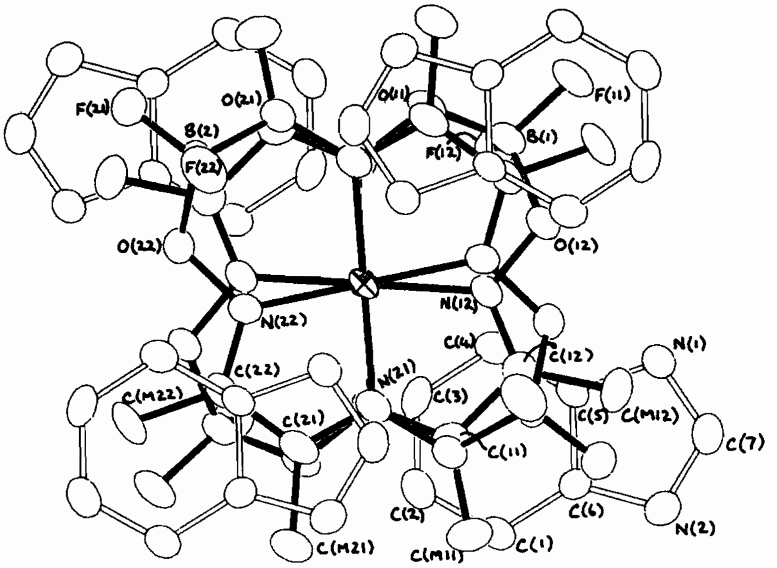

Fig. 1. A drawing of the $[Ni(dmg\text{-}BF_2)_2]_2$ dimer unit and the orientation of the benzimidazole rings to it. The atom labelling system is given and thermal ellipsoids are drawn to include 35% probability.

TABLE III. Hydrogen Atom Parameters (Coordinates: Fractional $\times 10^3$).*

	x/a	y/b	z/c
H(1)	220	−25	498
H(2)	25	−34	433
H(3)	7	−56	328
H(4)	175	−36	246
H(7)	599	−15	379
H(111)	152	197	467
H(112)	101	123	472
H(113)	254	135	446
H(121)	441	115	299
H(122)	396	113	380
H(123)	416	196	338
H(211)	−113	253	470
H(212)	−174	344	464
H(213)	−24	310	475
H(221)	−376	330	390
H(222)	−376	251	368
H(223)	−390	309	314

*For all H atoms $B = 6.0$ Å^2.

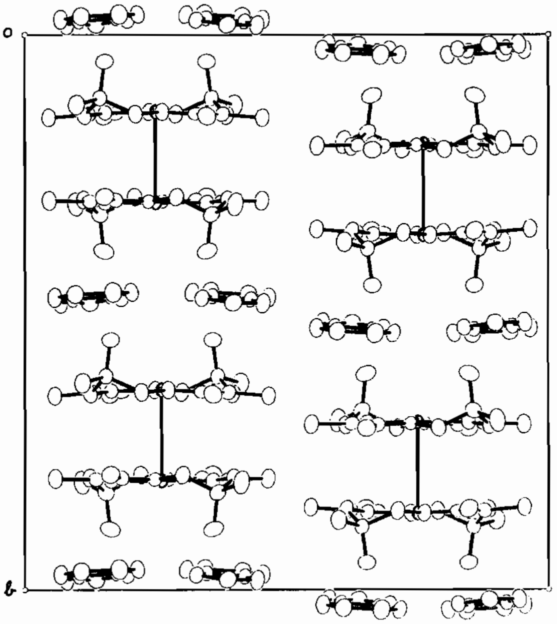

Fig. 2. The packing of the molecules in the crystal.

Results and Discussion

The crystal structure consists of discrete $[Ni(dmg\text{-}BF_2)_2]_2$ dimer units and benzimidazole molecules. The dimer units have space group imposed $2(C_2)$ symmetry with the Ni$\cdots$Ni directions aligned along b. Figure 1 shows the dimer unit and the orientation of the benzimidazole molecules to it [6]. The packing in the lattice is shown in Fig. 2. The bond lengths and angles are listed in Table IV and mean-plane calculations are given in Table V.

The bond lengths and angles in the benzimidazole molecule are in accord with those previously reported [7] with the exception that there is no distinction between the N atoms in the present determination. The individual molecules are hydrogen-bonded to each other *via* symmetry related N atoms [Table VI(b)] forming chains parallel to c that

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

(a) *Distances* (Å)

Ni(1)····Ni(2) 3.358(2)

	n = 1	n = 2
Ni(n)–N(n1)	1.845(6)	1.861(6)
Ni(n)–N(n2)	1.855(6)	1.832(6)
N(n1)–O(n1)	1.356(7)	1.347(7)
N(n2)–O(n2)	1.348(8)	1.388(8)
N(n1)–C(n1)	1.311(10)	1.229(9)
N(n2)–C(n2)	1.293(9)	1.289(8)
C(n1)–C(n2)	1.487(11)	1.457(11)
C(n1)–C(Mn1)	1.477(10)	1.496(10)
C(n2)–C(Mn2)	1.501(11)	1.486(10)
B(n)–O(n1)	1.473(11)	1.499(10)
B(n)–O(n2)	1.501(10)	1.478(10)
B(n)–F(n1)	1.368(9)	1.357(10)
B(n)–F(n2)	1.369(10)	1.359(11)

C(1)–C(2)	1.375(11)	C(6)–C(1)	1.391(10)
C(2)–C(3)	1.394(11)	C(5)–N(1)	1.389(8)
C(3)–C(4)	1.384(11)	C(6)–N(2)	1.383(9)
C(4)–C(5)	1.376(11)	C(7)–N(1)	1.331(10)
C(5)–C(6)	1.401(8)	C(7)–N(2)	1.319(10)

(b) *Angles* (°)*

	n = 1	n = 2
N(n1)–Ni(n)–N(n2)	83.3(3)	82.7(3)
N(n1)–Ni(n)–N(n2^{I})	96.7(3)	97.3(3)
N(n1)–Ni(n)–N(n1^{I})	177.4(3)	179.7(3)
N(n2)–Ni(n)–N(n2^{I})	179.7(3)	177.1(3)
Ni(n)–N(n1)–O(n1^{I})	125.4(2)	125.7(1)
Ni(n)–N(n1)–C(n1)	116.9(5)	114.6(6)
O(n1^{I})–N(n1)–C(n1)	117.4(5)	119.3(5)
Ni(n)–N(n2)–O(n2)	125.9(5)	124.6(4)
Ni(n)–N(n2)–C(n2)	116.1(5)	118.1(5)
O(n2)–N(n2)–C(n2)	117.5(6)	116.8(6)
N(n1)–C(n1)–C(n2)	111.1(6)	114.3(6)
N(n1)–C(n1)–C(Mn1)	125.2(8)	123.3(8)
C(n2)–C(n1)–C(Mn1)	123.7(7)	122.4(7)
N(n2)–C(n2)–C(n1)	112.6(7)	110.4(7)
N(n2)–C(n2)–C(Mn2)	124.4(7)	126.0(8)
C(n1)–C(n2)–C(Mn2)	123.0(7)	123.6(6)
B(n)–O(n1)–N(n1^{I})	113.6(4)	115.8(4)
B(n)–O(n2)–N(n2)	113.8(6)	114.9(6)
O(n1)–B(n)–O(n2)	113.6(6)	113.2(7)
F(n1)–B(n)–F(n2)	112.7(7)	113.1(7)
F(n1)–B(n)–O(n1)	107.0(6)	104.7(7)
F(n1)–B(n)–O(n2)	110.6(7)	109.8(7)
F(n2)–B(n)–O(n1)	104.0(7)	105.7(7)
F(n2)–B(n)–O(n2)	108.8(6)	110.3(7)

C(6)–C(1)–C(2)	118.4(6)	C(1)–C(6)–N(2)	132.2(6)
C(1)–C(2)–C(3)	120.5(7)	C(4)–C(5)–N(1)	131.0(6)
C(2)–C(3)–C(4)	121.8(7)	N(1)–C(5)–C(6)	107.7(6)
C(3)–C(4)–C(5)	117.5(6)	C(5)–C(6)–N(2)	107.4(6)
C(4)–C(5)–C(6)	121.3(6)	C(5)–N(1)–C(7)	104.5(6)
C(5)–C(6)–C(1)	120.4(7)	C(6)–N(2)–C(7)	105.3(6)
		N(1)–C(7)–N(2)	115.1(7)

*For Roman numeral superscripts refer to footnote of Table VI.

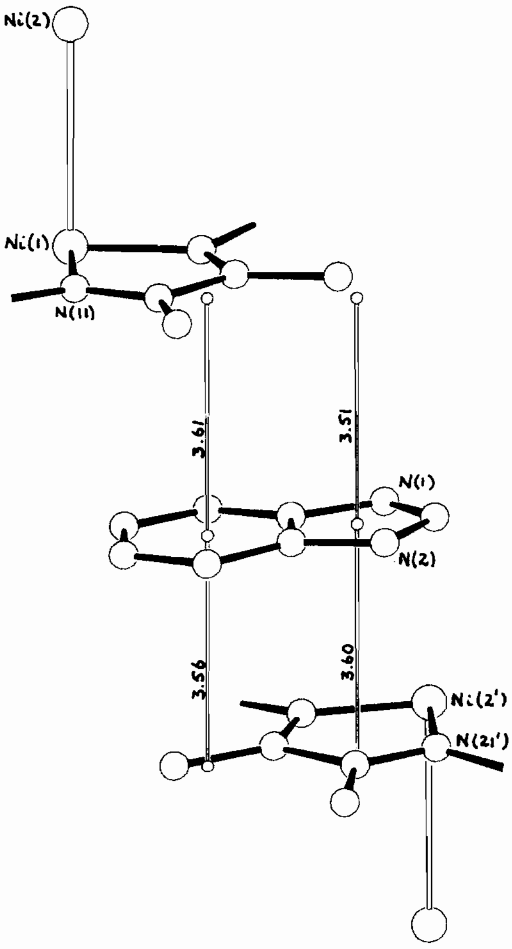

Fig. 3. The orientation of a benzimidazole molecule relative to the glyoxime moieties of neighbouring dimer units. The centroids of the two rings of the benzimidazole are shown projected onto the glyoxime planes.

are incorporated in sheets centred about y = 0 and ½.

The [Ni(dmg-BF$_2$)$_2$]$_2$ dimer units are sandwiched between the sheets of benzimidazole molecules such that the dmg fragments of the macrocycles lie directly over parts of benzimidazole rings. Contact distances [Table VI (a, ii)] and the fact that the planes of atoms concerned are nearly parallel (Table V, benzim/dmg (1) 3.8°, benzim/dmg (2) 4.8°) suggest that a π–type interaction between the benzimidazole and dmg rings exists. Similar

TABLE V. Least-squares Planes and their Equations given by $lX' + mY' + nZ' - p = 0$ where X', Y' and Z' are Orthogonal Coordinates Related to X, Y and Z by $X' = X \sin\beta$, $Y' = Y$, $Z' = Z + X \cos\beta$. Deviations (A) of Most Relevant Atoms from the Planes are given in Square Brackets.*

	l	*m*	*n*	*p*
Plane (1): N(11), N(12), N(11$^{\mathrm{I}}$), N(12$^{\mathrm{I}}$) [N(11) 0.02; N(12) −0.02; Ni(1) −0.02; O(11) 0.14; O(12) 0.06; C(11) 0.07; C(12) 0.05; C(M11) 0.20; C(M12) 0.14]	0.0000	1.0000	0.0000	2.8592
Plane (2): N(21), N(22), N(21$^{\mathrm{I}}$), N(22$^{\mathrm{I}}$) [N(21) 0.02; N(22) −0.02; Ni(2) 0.03; O(21) −0.08; O(22) −0.18; C(21) −0.02; C(22) −0.07; C(M21) −0.05; C(M22) −0.20]	0.0000	1.0000	0.0000	6.1684
Plane (3): C(1)–(7), N(1), N(2) [C(1) 0.02; C(2) < |0.01|; C(3) −0.03; C(4), C(5) 0.01; C(6) < |0.01|; C(7) −0.02; N(1) 0.01; N(2) −0.01]	0.0803	−0.9943	0.0701	1.2973
Plane (4): O(11$^{\mathrm{I}}$), N(11), C(11) C(M11), C(M12), C(12), N(12), O(12) [O(11$^{\mathrm{I}}$) 0.06; N(11) −0.05; C(11) −0.04; C(M11) 0.03; C(M12) 0.01; C(12) −0.03; N(12) −0.05; O(12) 0.06; Ni(1) 0.01; C(1) −3.59; C(2) −3.66; C(3) −3.68; C(4) −3.67; C(5) −3.58; C(7) −3.41; N(1) −3.41]	−0.0198	0.9990	−0.0407	2.6476
Plane (5): O(21$^{\mathrm{I}}$), N(21), C(21) C(M21), C(M22), C(22), N(22), O(22) [O(21$^{\mathrm{I}}$) −0.09; N(21) 0.05; C(21) 0.04; C(M21) 0.01; C(M22) −0.06; C(22) 0.03; N(22) 0.07; O(22) −0.06; Ni(2) 0.06; C(3$^{\mathrm{II}}$) 3.47; C(4$^{\mathrm{II}}$) 3.43; C(5$^{\mathrm{II}}$) 3.54; C(6$^{\mathrm{II}}$) 3.65; C(7$^{\mathrm{II}}$) 3.71; N(1$^{\mathrm{II}}$) 3.57]	−0.0312	0.9995	−0.0021	6.1178

*For Roman numeral superscripts refer to footnote of Table VI.

TABLE VI. Contact Distances (A).*

(a) *Contacts suggesting π–π interactions*

(i) *Intra-dimer units <3.5* A

O(11)····C(21$^{\mathrm{I}}$)	3.16	N(11)····N(21)	3.31
O(21)····C(11$^{\mathrm{I}}$)	3.16	N(12)····N(22$^{\mathrm{I}}$)	3.34
O(22)····C(12$^{\mathrm{I}}$)	3.19	O(12)····O(22$^{\mathrm{I}}$)	3.41
O(12)····C(22$^{\mathrm{I}}$)	3.30	N(12)····O(22$^{\mathrm{I}}$)	3.31
O(11)····C(22$^{\mathrm{I}}$)	3.50	N(22)····O(12$^{\mathrm{I}}$)	3.40
O(21)····C(M11$^{\mathrm{I}}$)	3.29	N(21)····O(11$^{\mathrm{I}}$)	3.48
O(22)····C(M12$^{\mathrm{I}}$)	3.32	N(11)····O(21$^{\mathrm{I}}$)	3.50
O(11)····C(M21$^{\mathrm{I}}$)	3.38	N(21)····C(11)	3.50
O(12)····C(M22$^{\mathrm{I}}$)	3.38		

(ii) *Dimer-benzimidazole <3.80* A

C(M12)····N(1)	3.62	C(22)····C(5$^{\mathrm{II}}$)	3.53
C(12)····C(5)	3.63	C(22)···C(4$^{\mathrm{II}}$)	3.54
C(M11)····C(1)	3.64	C(M22)····C(3$^{\mathrm{II}}$)	3.59
C(M12)····C(5)	3.67	N(21)····N(1$^{\mathrm{II}}$)	3.62
N(12)····C(4)	3.69	N(22)····C(4$^{\mathrm{II}}$)	3.64
N(11)····C(3)	3.70	C(21)····C(5$^{\mathrm{II}}$)	3.66
C(12)····C(4)	3.70	C(M22)····C(3$^{\mathrm{II}}$)	3.68
C(M12)····C(7)	3.70	N(21)····C(7$^{\mathrm{II}}$)	3.70
C(11)····C(2)	3.71	N(22)····C(5$^{\mathrm{II}}$)	3.74
C(11)····C(3)	3.77	C(21)····N(1$^{\mathrm{II}}$)	3.75
		C(21)····C(6$^{\mathrm{II}}$)	3.76
		C(M21)····C(6$^{\mathrm{II}}$)	3.78

(b) *Intermolecular <3.40* A

N(2)····N(2$^{\mathrm{III}}$)	2.79	F(22)····C(4$^{\mathrm{VIII}}$)	3.26
N(1)····N(1$^{\mathrm{IV}}$)	2.87	F(12)····C(3$^{\mathrm{IX}}$)	3.27
F(22)····C(7$^{\mathrm{V}}$)	3.02	F(12)····C(7$^{\mathrm{IV}}$)	3.30
C(M11)····F(21$^{\mathrm{V}}$)	3.14	F(12)····F(22$^{\mathrm{X}}$)	3.32
C(M22)····F(21$^{\mathrm{VI}}$)	3.14	C(M12)····F(11$^{\mathrm{IV}}$)	3.39
C(M21)····F(11$^{\mathrm{VII}}$)	3.21		

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

I	$\bar{x}, y, \frac{1}{2} - z$
II	$x - \frac{1}{2}, \frac{1}{2} + y, z$
III	$1 - x, \bar{y}, 1 - z$
IV	$1 - x, y, \frac{1}{2} - z$
V	$\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$
VI	$-\frac{1}{2} - x, y, \frac{1}{2} - z$
VII	$x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$
VIII	$x - 1, y, z$
IX	$\bar{x}, y, \frac{1}{2} - z$
X	$\frac{1}{2} + x, y - \frac{1}{2}, z$

arguments have been used in the structures of substituted-aniline adducts of cobaloxime [8] and the 1:1 aniline adduct of Ni(dmg-BF$_2$)$_2$ [3] even though the planes of the rings concerned are not parallel to one another. Figure 3 shows the orientation of a benzimidazole molecule relative to moities of neighbouring dimer units. As Figures 1 and 3 indicate the interaction of a benzimidazole molecule is different for a given moiety of a dimer unit; that with the Ni(1) moiety involves the six-membered ring whereas, that with the Ni(2) moiety involves essentially the imidazole ring. In this latter arrangement the hydrogen-bond [N(1)···N(1^{IV})] between symmetry related imidazole rings lies directly (3.38 Å) above the Ni(2) atom and in order to accommodate the rings the separation of the two axial F atoms of the macrocycle concerned is increased from 5.46, 5.50 Å in the parent [4] to 5.94 Å. This value is similar to that of 5.92 Å found in the 1:1 4,4′-bipyridine adduct [2] in which the pyridyl rings co-ordinate in axial positions to the Ni atoms. The longer hydrogen bond between the N(1) atoms is almost certainly a consequence of the steric interactions. The separation of the axial F atoms of the second moiety (5.60 Å) is also increased relative to the parent but indicates that the steric interactions are much less.

The dimeric nature of the planar parent Ni(dmg-BF_2)$_2$ with a *cis* conformation of the BF_2 groups [4] is maintained in this structure. The bond lengths and angles within the moieties of the dimer agree well with those reported in similar structures [2–4]. The Ni atoms are only slightly out of the four N atom coordination planes (0.02, 0.03 Å) with the deviation of each Ni atom away from the centre of the dimer. This contrasts with the parent in which the deviations (0.03, 0.01 Å) are both in the same axial direction. The Ni···Ni separation of 3.358 Å is significantly longer than that of 3.207 Å in the parent but markedly less than that of 3.654 Å [3] and 3.909 Å [2] when N-bases are co-ordinated. As observed in similar structures [2–4] there are close C···O contacts [Table VI (a, i)] which indicate that π–π type interactions between macrocycles in the dimer unit are maintained.

If in the dimer the Ni···Ni interaction is the predominant bonding factor then it would be expected that the separation of these atoms in the present structure should be unchanged from that found in the parent. On the other hand, if the π–π macrocycle interactions are the major force, with the Ni atom essentially acting to maintain planarity, then any other π–interaction would serve to lessen that between macrocycles. The results of the present determination support the latter explanation.

With the retention of the dimer structure it is not surprising that benzimidazole does not co-ordinate since it has been reported in reference to Vitamin B_{12} that steric effects resulting from such co-ordination require a marked distortion from planarity in the corrin macrocycle [9]. Such loss of planarity has been observed in the 1:1 *o*-phenanthroline adduct of bis(difluoroborondiphenylglyoximato)-nickel(II) [10] which is monomeric and has a distorted octahedral environment about the Ni atom.

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