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Studies on Macrocyclic Complexes Derived from *vic*-Dioximes. Part V*. The Crystal and Molecular Structure of the 1:1 Adduct of 4,4'-Bipyridine with Bis(difluoroborondimethylglyoximato)nickel(II)

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The 1:1 adduct of 4,4'-bipyridine with bis(difluoroborondimethylglyoximato)nickel(II) is orthorhombic, space group I222, a = *10.108(5),* b = *13.929(5),* c = *15.687(5)* Å, Z = *4. The structure was refined to* R = *0.080 for 835 photographic reflexions. The structure consists of* $Ni(dmgBF_2)_2$ *dimer units bridged by 4,4'-bipyridine molecules forming polymeric chains parallel to* c. *The remaining 4,4'-bipyridine molecule per dimer unit acts as a solvate and is also aligned along* c. *The Ni atom is co-ordinated to four N atoms of the closely planar macrocycle* [*average, Ni–N 1.85(1)* Å, *N–Ni–N 80.0(6) and 98.6(6)°*] *and a 4,4'-bipyridine N atom* [*Ni–N 2.35(1)* Å] *forming an irregular square pyramid. The Ni atom is 0.20* Å *out of the plane of the equatorial N atoms and the Ni···Ni separation in the dimer units is 3.909(3)* Å. *The 4,4'-bipyridine molecules are non-planar, the pyridyl rings being rotated by 34 and 40° about the 4,4'-bond for the coordinated and solvate molecules respectively.*

Introduction

Bis(difluoroborondimethylglyoximato)nickel(II), $Ni(dmgBF_2)_2$, has been shown to be dimeric both in the solid state [1] and in solution [3]. Monodentate bases form 1:1 adducts in solution [5] and the solid state [3, 4] with the retention of the dimeric nature of the parent. We have isolated with 4,4'-bipyridine 1:1 and 1:2 adducts both of which are diamagnetic. Since 4,4'-bipyridine cannot act as a multidentate ligand the 1:2 compound can be envisaged with the bipyridine bridging dimeric $Ni(dmgBF_2)_2$ units. Several structural possibilities are feasible for the 1:1 compound and hence we undertook the structural investigation here reported.

Experimental

Crystal Data: $C_{18}H_{20}B_2F_4N_6O_4Ni$, M_r = 540.7, Orthorhombic, a = 10.108(5), b = 13.929(5), c = 15.687(5) Å, U = 2208.6 Å^3, D_m = 1.62 (by flotation), Z = 4, D_c = 1.626 g cm^{-3}, $F(000)$ = 1104, μ(Mo-K$_\alpha$) = 9.5 cm^{-1}. Systematic absences h, k, l if $h + k + l \neq 2n$, Space group $I222$ (No. 23), $I2_12_12_1$ (No. 24), $Imm2$ (No. 45) or $Immm$ (No. 71).

The complex crystallises as deep-red [001] elongated hexagonal prismatic plates, with [100] the prismatic axis, on the addition of 4,4'-bipyridine dihydrate to a warm acetone solution of $Ni(dmgBF_2)_2$. 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], 0–4 about [010] and 0–5 about [110]. They were corrected for Lorentz and polarisation effects but no correction for absorption or extinction was applied. The structure factors were placed on a common scale by internal correlation, and 835 non-zero unique reflexions were obtained. Scattering factors were taken from *International Tables for X-ray Crystallography* [6]. All calculations were carried out on a UNIVAC 1106 computer with programmes written by F.S.S.

From the systematic absences the space group is $I222$, $I2_12_12_1$, $Imm2$ or $Immm$. With four $Ni(dmgBF_2)_2$(4,4'-bipy) units per cell each space group imposes symmetry requirements on the formula unit, the first two groups impose 2, the third m and the fourth mm. Of these the last is unlikely. The three-dimensional Patterson synthesis indicated the space group to be $I222$ which was subsequently confirmed by the successful analysis.

The structure was solved by the heavy-atom method and refined by full matrix-least squares in which $\Sigma w\Delta^2$ was minimised. Weights were initially unity and in the final stages $w = (10.0 + 0.1|F_o|)^{-1}$. Reflexions were omitted from a refinement cycle if $|F_c| < 0.3|F_o|$. After isotopic refinement a difference

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*Parts I–IV may be taken as references [1]–[4].

TABLE I. Final Atomic Co-ordinates with Estimated Standard Deviations in Parentheses (Fractional × 10^4).

	x/a	*y/b*	*z/c*
Ni	0	0	1246(2)
N(11)	1812(11)	−128(9)	1106(7)
N(12)	−122(15)	1314(8)	1127(6)
N(2)	0	0	2243(21)
N(3)	0	5000	4526(9)
B	2245(22)	1569(14)	1402(12)
F(1)	2083(13)	1496(9)	2293(6)
F(2)	3186(10)	2225(7)	1188(9)
O(11)	2701(11)	626(8)	1069(9)
O(12)	976(15)	1914(9)	1036(11)
C(11)	2276(17)	−975(14)	1017(12)
C(12)	−1249(21)	1694(16)	1012(12)
C(M11)	3713(19)	−1173(16)	930(14)
C(M12)	−1478(22)	2752(14)	906(13)
C(21)	−340(15)	781(10)	3172(8)
C(22)	−331(17)	820(9)	4050(8)
C(23)	0	0	4526(9)
C(31)	1019(25)	4729(25)	1802(16)
C(32)	1142(27)	4707(15)	942(15)
C(33)	0	5000	486(18)

map indicated approximate positions for all 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 refinement was terminated when the change in minimisation function was <0.05%. 832 reflexions were included in the final cycle. The final R, based on 835 reflexions, was 0.080 and $R'[=(\Sigma w\Delta^2/\Sigma w|F_o|^2)^{1/2}]$ was 0.091. A final difference map showed no features >|0.7|eÅ^{-3}. The final atomic parameters are given in Tables I, II and III. A lists of observed and calculated structure factors has been deposited with the Editor.

TABLE III. Hydrogen Atom Parameters (Co-ordinates: fractional × 10^3).

	x/a	*y/b*	*z/c*
H(111)	421	−65	77
H(112)	380	−167	53
H(113)	410	−141	140
H(121)	−65	306	72
H(122)	−173	294	147
H(123)	−223	289	49
H(21)	−60	137	282
H(22)	−54	145	437
H(31)	178	437	218
H(32)	199	452	62

For all hydrogen atoms B = 6.0 Å^2.

Results and Discussion

The structure consists of Ni(dmgBF$_2$)$_2$ dimer units bridged by 4,4′-bipyridine molecules forming polymeric chains parallel to c. The remaining 4,4′-bipyridine molecule acts as a solvate which is also aligned along c. The bond lengths and angles are given

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

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Ni	78(3)	34(1)	21(1)	−2(3)	0	0
N(11)	66(11)	24(7)	36(5)	−12(11)	3(7)	12(6)
N(12)	28(12)	55(7)	19(4)	−27(10)	−10(10)	−3(4)
N(2)	133(22)	34(8)	14(5)	23(25)	0	0
N(3)	183(48)	314(58)	76(17)	134(57)	0	0
B	107(26)	44(10)	36(9)	5(16)	3(13)	−2(8)
F(1)	171(16)	85(8)	36(4)	−17(12)	−16(8)	−4(5)
F(2)	104(12)	66(6)	76(7)	−39(8)	5(9)	9(7)
O(11)	66(13)	55(6)	48(7)	−19(9)	−2(8)	−6(6)
O(12)	121(15)	52(7)	40(7)	16(10)	−23(9)	2(6)
C(11)	68(19)	61(11)	28(7)	−8(14)	0(10)	−2(7)
C(12)	120(29)	70(13)	19(7)	50(16)	−7(12)	7(8)
C(M11)	97(23)	83(15)	66(12)	21(15)	21(14)	7(11)
C(M12)	149(27)	57(11)	55(10)	28(16)	10(14)	8(9)
C(21)	101(25)	37(7)	22(5)	1(11)	−3(8)	2(5)
C(22)	134(28)	30(7)	17(4)	−2(11)	11(9)	1(4)
C(23)	70(20)	44(10)	14(5)	−23(28)	0	0
C(31)	134(30)	171(40)	63(12)	−4(27)	−18(16)	8(16)
C(32)	194(37)	72(16)	67(12)	−19(19)	29(18)	14(10)
C(33)	107(32)	61(16)	84(16)	−29(39)	0	0

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

(a) *Distances* (Å)*

Ni···Ni^{I} 3.909(3)

Ni–N(11)	1.85(1)	Ni–N(12)	1.84(1)
Ni–N(2)	2.35(1)	C(11)–C(12^{II})	1.44(3)
N(11)–C(11)	1.28(2)	N(12)–C(12)	1.27(2)
C(11)–C(M11)	1.49(2)	C(12)–C(M12)	1.50(3)
N(11)–O(11)	1.38(2)	N(12)–O(12)	1.40(2)
O(11)–B	1.49(2)	O(12)–B	1.49(2)
B–F(1)	1.41(2)	B–F(2)	1.36(2)
N(2)–C(21)	1.32(1)	N(3)–C(31)	1.30(3)
C(21)–C(22)	1.38(2)	C(31)–C(32)	1.35(3)
C(22)–C(23)	1.40(1)	C(32)–C(33)	1.42(3)
C(23)–C(23^{III})	1.49(2)	C(33)–C(33^{IV})	1.52(4)

(b) *Angles* (°)*

N(11)–Ni–N(12)	98.6(6)	N(11)–Ni–N(12^{II})	80.0(6)
N(11)–Ni–N(11^{II})	166.4(5)	N(12)–Ni–N(12^{II})	168.4(5)
N(2)–Ni–N(11)	96.8(4)	N(2)–Ni–N(12)	95.8(3)
Ni–N(11)–O(11)	125(1)	Ni–N(12)–O(12)	123(1)
Ni–N(11)–C(11)	118(1)	Ni–N(12)–C(12)	119(1)
O(11)–N(11)–C(11)	117(1)	O(12)–N(12)–C(12)	117(1)
N(11)–C(11)–C(12^{II})	112(1)	N(12)–C(12)–C(11^{II})	111(1)
N(11)–C(11)–C(M11)	123(2)	N(12)–C(12)–C(M12)	124(2)
C(M11)–C(11)–C(12^{II})	125(1)	C(M12)–C(12)–C(11^{II})	125(1)
N(11)–O(11)–B	117(1)	N(12)–O(12)–B	117(1)
O(11)–B–O(12)	115(1)	F(1)–B–F(2)	112(2)
O(11)–B–F(1)	109(1)	O(12)–B–F(1)	108(2)
O(11)–B–F(2)	107(2)	O(12)–B–F(2)	107(1)
Ni–N(2)–C(21)	120(1)	C(31)–N(3)–C(31^{V})	116(3)
C(21)–N(2)–C(21^{II})	119(1)	N(3)–C(31)–C(32)	128(3)
N(2)–C(21)–C(22)	122(1)	C(31)–C(32)–C(33)	115(3)
C(21)–C(22)–C(23)	120(1)	C(32)–C(33)–C(32^{V})	119(3)
C(22)–C(23)–C(22^{II})	116(1)	C(32)–C(33)–C(33^{IV})	120(3)
C(22)–C(23)–C(23^{III})	122(1)		

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

I $x, \bar{y}, \bar{z}$
II $\bar{x}, \bar{y}, z$
III $x, \bar{y}, 1-z$
IV $x, 1-y, \bar{z}$
V $\bar{x}, 1-y, z$

in Table IV. Figure 1 shows the polymeric unit and the labelling of atoms [7]. The packing in the crystal is shown in Fig. 2. The arrangement of the Ni(dmg BF$_2$)$_2$ dimer units in the cell is similar to that in the parent with the exception that the stacking distance between units is increased by the bridging bipyridine molecules. It is this separation which creates a hole between dimer units sufficiently large to accommodate solvate 4,4′-bipyridine molecules. The intermolecular contact distances <3.5 Å are given in Table V.

The space group imposes 222 (D_2) symmetry points midway between the Ni···Ni of the dimer units and the centres of the 4,4′-bonds of the bipyridine rings. The dimeric nature of the parent Ni(dmg BF$_2$)$_2$ and the conformation of the moieties relative to one another [1] is retained on co-ordination of the base in axial positions forming square-pyramidal

TABLE V. Contact Distances (Å) < 3.5 Å*.

O(12)···C(12^{VI})	3.24	F(2)···C(22^{VII})	3.13
O(12)···C(M12^{VI})	3.30	F(2)···C(21^{VII})	3.31
O(11)···C(11^{I})	3.34	F(1)···C(M12^{VII})	3.35
O(11)···C(M11^{I})	3.39	F(1)···C(31^{VIII})	3.43
N(11)···N(11^{I})	3.49	F(2)···C(M11^{IX})	3.48

*Roman numeral superscripts I–V are as defined in Table IV.

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

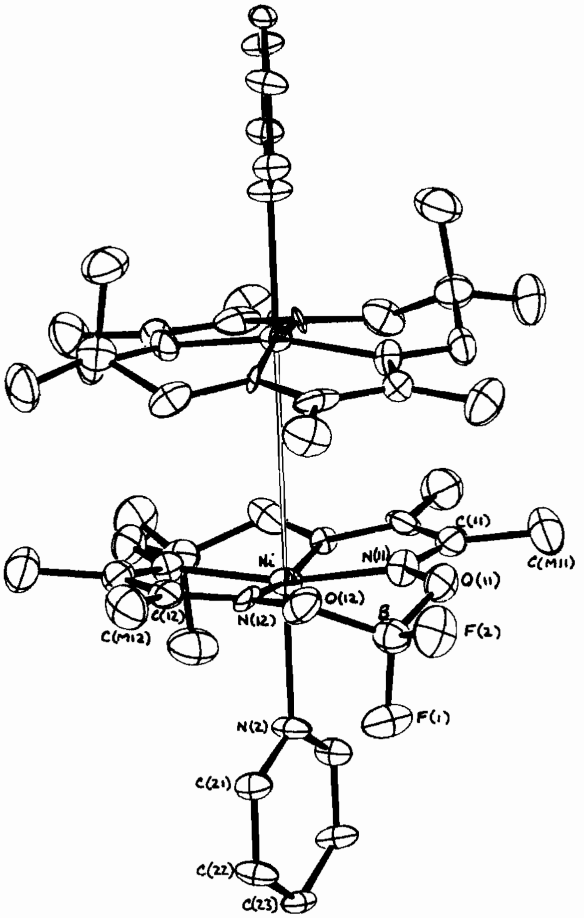
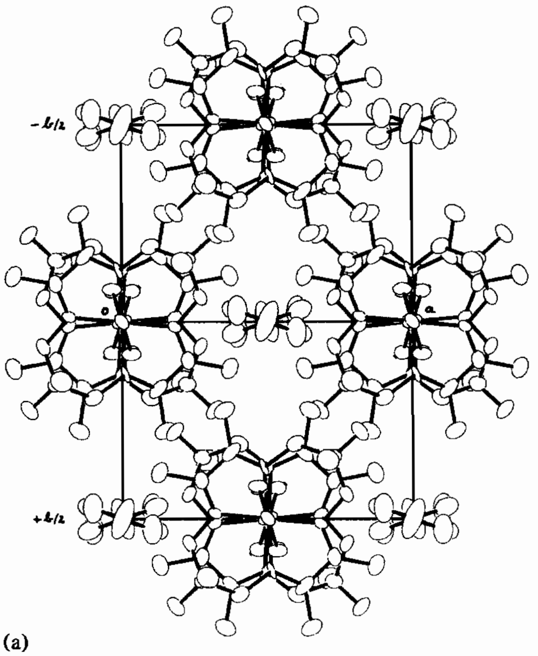
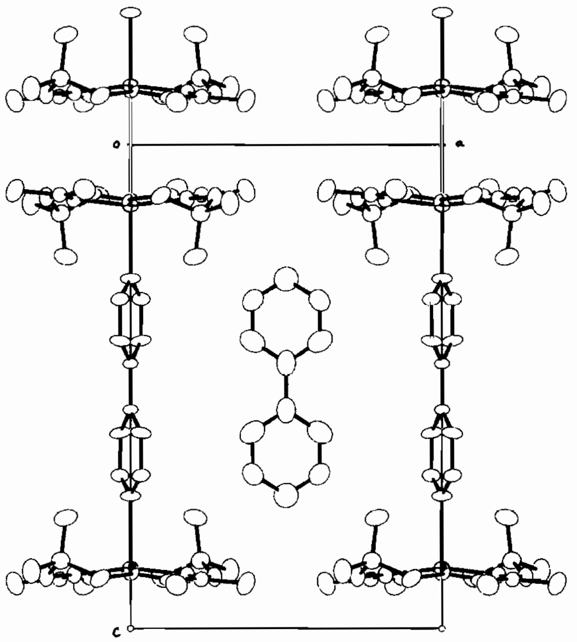


Fig. 1. A perspective drawing of the $\{(4,4'\text{-bipy})[\text{Ni(dmg BF}_2)_2]_2\}_n$ chain molecular unit with the labelling of the atoms. Thermal ellipsoids are drawn to include 35% probability.



(a)



(b)

Fig. 2. The packing in the crystal. (a) Projected down c and (b) projected down b with only the polymeric chains and solvate molecule centred at b = 0 shown for clarity.

environments about the Ni atoms. The Ni atom is displaced 0.20 Å from the equatorial co-ordination plane (Table VI) towards the pyridyl N atom and this results in a small angular distortion of the macrocyclic rings from the planarity observed in the parent structure even though the bond lengths are unchanged. The pyridyl Ni–N length of 2.35 Å is considerably shorter than the corresponding distances (2.72 and 2.60 Å) in the aniline adduct [4] and this shortening is accompanied by a lengthening of the Ni···Ni separation from 3.654 Å [4] to 3.909 Å. Unlike the aniline adduct which changes to the M–L–M stacking arrangement [8], the bipyridyl adduct retains the M–M arrangement of the parent.

Even though the separation of the Ni atoms in the dimer units is large the close packing of the two macrocycles is retained. The C···O contacts of 3.24 and 3.34 Å (Table V) are slightly longer than the corresponding values in the parent (3.13–3.17 Å) [1] and the aniline adduct (3.15–3.25 Å) [4]. The separation between the planes containing the four oxygen atoms of one moiety with the plane containing the four carbon atoms of the other (Table VI) is 3.24 Å which is in accord with the predicted spacing of about 3.2 Å for the close packing of organic ligands in these type of complexes [8].

The bond lengths and angles in the bipyridine molecules are in good agreement with those reported in structures of 4,4′-bipyridylium salts [9]. However

TABLE VI. Least-squares Planes and Their Equations Given by $lX + mY + nZ - p = 0$ where X, Y, and Z are the Co-ordinates in Å. Deviations (Å) of the Most Relevant Atoms from the Planes are Given in Square Brackets. Roman Numeral Superscripts are as Defined in Table IV.

Plane (1): N(11), N(12), N(11^{II}), N(12^{II})	0.0000	0.0000	1.0000	1.7514
[N(11) −0.02; N(12) 0.02; Ni 0.20; N(2) 2.56; O(11) −0.07; O(12) −0.13; C(11), C(12) −0.16; C(M11) −0.29; C(M12) −0.33; B 0.45; F(1) 1.85; F(2) 0.11]				
Plane (2): Ni, N(11), N(12^{II})	0.1096	−0.0938	0.9895	1.9344
[O(11) −0.06; C(11) 0.02; C(M11) 0.07; C(12^{II}), C(M12^{II}) < |0.01|; O(12^{II}) −0.18]				
Plane (3): N(2), C(21), C(22), C(23), C(22^{II}), C(21^{II})	−0.9569	−0.2905	0.0000	0.0000
[C(21) 0.01; C(22) −0.01]				
Plane (4): N(3), C(31), C(32), C(33), C(32^{IV}), C(31^{IV})	0.3384	0.9410	0.0000	6.5536
[C(31) < |0.01|; C(32) < 0.01]				
Plane (5): C(11), C(12), C(11^{II}), C(12^{II})	0.0000	0.0000	1.0000	1.5914
[C(11) 0.005; C(12) −0.005; N(11) 0.14; N(12) 0.17; O(11) 0.09; O(12) 0.03; C(M11) −0.13; C(M12) −0.18; Ni 0.36; N(2) 2.72]				
Plane (6): O(11), O(12), O(11^{II}), O(12^{II})	0.0000	0.0000	1.0000	1.6513
[O(11) 0.03; O(12) −0.03; N(11) 0.08; N(12) 0.12; C(11), C(12) −0.06; C(M11) −0.19; C(M12) −0.23; Ni 0.30; N(2) 2.66]				

unlike the 4,4′-bipyridylium ion which is planar in those structures [9] the pyridyl rings of the 4,4′-bipyridine molecules in the present study are rotated with respect to one another by 34 and 40° about the 4,4′-bonds for the co-ordinated and solvate molecules respectively.

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