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Studies on Macrocyclic Complexes Derived from *vic*-Dioximes. XII*. The Crystal Structure of the π-Sandwich Compound Formed between Anthracene and Bis(difluoroboronmethylglyoximato)nickel(II)

FREDERICK S. STEPHENS and ROBERT S. VAGG

School of Chemistry, Macquarie University, North Ryde, N.S.W. 2113, Australia

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The 1:1 adduct of anthracene with bis(difluoroboronmethylglyoximato)nickel(II) is triclinic, space group $P\bar{1}$, a = *7.448(6),* b = *7.780(7),* c = *9.366(8)* Å, α = *91.4(1),* β = *92.5(1),* γ = *92.1(1)°,* Z = *1. The structure was refined to* R = *0.075 for 1250 photographic reflexions by full-matrix least-squares methods. The planar macrocycle [average Ni–N 1.850(10)* Å *and N–Ni–N 82.4(3)°] and the anthracene molecule each have a space group imposed centre of symmetry. The planes of the macrocycle and anthracene molecule are nearly parallel and close intermolecular contacts indicate* π–π *interactions between the molecules which give rise to chains of alternately stacked molecules aligned along* a*. The stacking is such that molecules lie approximately in the* $(2\bar{1}1)$ *series of planes with an interplanar spacing of 3.17* Å*. The reduction of this separation compared with that previously reported for the adduct of the analogous dimethylglyoximato compound results from a diminished steric influence of the substituent methyl groups.*

Introduction

Bis(difluoroborondimethylglyoximato)nickel(II), $Ni(dmgBF_2)_2$, has been shown to form in the solid state π-sandwich compounds with planar tricyclic organic molecules in which one-dimensional stacking of alternate molecules is observed [1, 2]. The precise orientation of the organic molecules relative to the macrocyclic plane and hence the degree of π–π interaction allowed between them is influenced clearly by steric interactions with not only the axial fluorine atoms but the methyl groups of the glyoxime residues. Bis(difluoroboronmethylglyoximato)nickel(II), $Ni(mgBF_2)_2$, which can adopt either a *cis*- or *trans*-configuration, forms such an adduct with anthracene and its crystal structure, here reported, has been undertaken to investigate in particular the structural influence of the methyl groups.

Experimental

The compound was obtained as ruby-red crystals from the reaction of bis(difluoroboronmethylglyoximato)nickel(II) with excess anthracene in acetone solution.

Crystal Data: $C_{20}H_{18}B_2F_4N_4O_4Ni$, Mr = 534.7, Triclinic, a = 7.448(6), b = 7.780(7), c = 9.366(8) Å, α = 91.4(1), β = 92.5(1), γ = 92.1(1)°, U = 541.7 Å^3, Z = 1, D_c = 1.639 Mg m^{-3}, $F(000)$ = 272, μ(Mo-K$_\alpha$) = 0.97 mm^{-1}. Space group $P1$ (No. 1) or $P\bar{1}$ (No. 2).

The compound crystallizes as plates lying on the (010) face and with [100] elongation. Cell parameters were determined from precession photographs using Mo-K$_\alpha$ radiation. Intensities were estimated visually from precession photographs for the layers 0–2 about [010], [011] and $[01\bar{1}]$ and 0–3 about [001]. They were corrected for Lorentz and polarisation effects but not for absorption or extinction. The observed structure factors were placed on a common scale by internal correlation to yield a data set of 1250 non-zero unique reflexions which were used in subsequent calculations.

With Z = 1 the centric space group requires both molecules of the adduct to possess a centre of symmetry and this is evident from the three-dimensional Patterson synthesis. 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 minimized. The weight for each reflexion in the final stages was given by $w = (0.25 + 0.13|F_o| + 0.0006|F_o|^2)^{-1}$. Hydrogen atom positions of the methyl group were located from a difference map and the remainder were calculated assuming the appropriate geometry of the carbon atoms with C–H = 1.0 Å. These atoms were included in the refinement process but their parameters were not permitted to vary. Refinement was terminated when the maximum shift in any parameter was $<0.1\sigma$. The final value for R was 0.075 and for R' $[=(\Sigma w\Delta^2/\Sigma w|F_o|^2)^{1/2}]$ was 0.104. A final difference map showed no unusual features with a maximum density of |0.71| eÅ^{-3} associated with the nickel atom.

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*Part XI is reference [2].

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

	x	y	z
Ni	0	0	0
N(1)	−616(10)	−320(10)	−1922(8)
N(2)	715(9)	−2248(9)	−193(8)
O(1)	1469(9)	−857(8)	2773(7)
O(2)	1541(9)	−3158(8)	833(6)
C(1)	308(12)	1803(10)	2518(9)
C(2)	−540(11)	2921(11)	1481(9)
C(M)	719(14)	2324(12)	4021(10)
B	1035(14)	−2694(13)	2321(11)
F(1)	2093(8)	−3643(7)	3224(6)
F(2)	−776(7)	−3064(7)	2467(6)
C(3)	4240(14)	1387(16)	−671(14)
C(4)	4784(14)	1564(16)	764(13)
C(5)	4600(15)	3193(19)	1512(16)
C(6)	5131(19)	3299(22)	2939(19)
C(7)	5860(16)	1911(27)	3676(16)
C(8)	6079(14)	352(22)	2920(13)
C(9)	5550(13)	184(18)	1500(13)

TABLE III. Hydrogen Atomic Coordinates (fractional × 10^3).*

	x	y	z
H(M1)	201	271	406
H(M2)	−7	327	430
H(M3)	52	131	464
H(2)	−95	409	173
H(3)	368	238	−116
H(5)	410	419	101
H(6)	499	441	348
H(7)	622	202	472
H(8)	662	−63	342

*For hydrogen atoms B = 4.0 Å^2.

Neutral-atom scattering factors were taken from International Tables for X-ray Crystallography [3]. All calculations were performed on a UNIVAC 1106 computer with programmes written by F.S.S. The final atomic parameters are given in Tables I–III. A list of

TABLE II. 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	136(3)	95(3)	36(2)	9(2)	4(2)	−9(2)
N(1)	165(14)	153(13)	44(8)	−4(11)	−17(9)	30(9)
N(2)	151(14)	126(12)	53(8)	5(11)	2(9)	34(9)
O(1)	211(14)	140(11)	74(8)	1(10)	−32(9)	22(8)
O(2)	215(14)	146(11)	61(8)	42(10)	6(8)	18(8)
C(1)	203(19)	116(13)	39(9)	−18(13)	9(11)	8(10)
C(2)	166(18)	116(14)	73(11)	−13(12)	−5(12)	6(11)
C(M)	272(25)	166(17)	61(11)	−38(16)	12(13)	−17(12)
B	184(22)	133(17)	60(12)	21(16)	−30(14)	17(13)
F(1)	285(15)	179(10)	100(8)	65(10)	−31(9)	24(8)
F(2)	212(12)	173(10)	126(9)	−20(9)	46(8)	−1(8)
C(3)	174(21)	258(25)	151(19)	8(19)	−14(16)	49(19)
C(4)	148(19)	292(27)	127(16)	13(18)	−3(15)	1(19)
C(5)	181(23)	353(34)	176(22)	16(22)	31(18)	−26(23)
C(6)	253(31)	354(38)	228(29)	18(27)	55(25)	−93(27)
C(7)	153(24)	563(55)	173(23)	−15(28)	41(19)	−86(31)
C(8)	143(21)	504(44)	92(14)	3(24)	−25(14)	66(23)
C(9)	99(17)	336(29)	140(17)	−13(18)	−15(14)	58(20)

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

(a) Distances (Å)*

Ni–N(1)	1.846(7)	Ni–N(2)	1.854(7)
N(1)–O(1)	1.383(9)	N(2)–O(2^{I})	1.348(9)
O(1)–B	1.500(12)	O(2)–B	1.499(12)
B–F(1)	1.377(11)	B–F(2)	1.382(12)
N(1)–C(1)	1.302(10)	N(2)–C(2)	1.303(10)
C(1)–C(2)	1.458(13)	C(1)–C(M)	1.472(12)

(continued on facing page)

TABLE IV. *(continued)*

C(3)–C(4)	1.388(17)	C(3^{II})–C(9)	1.449(17)
C(4)–C(5)	1.448(17)	C(7)–C(8)	1.408(21)
C(5)–C(6)	1.376(20)	C(8)–C(9)	1.372(15)
C(6)–C(7)	1.409(23)	C(9)–C(4)	1.415(17)
(b) Angles (°)*			
N(1)–Ni–N(2)	82.4(3)	N(1)–Ni–N(2^{I})	97.6(3)
Ni–N(1)–O(1)	125.3(5)	Ni–N(2)–O(2^{I})	126.0(5)
Ni–N(1)–C(1)	117.8(6)	Ni–N(2)–C(2)	115.5(6)
O(1)–N(1)–C(1)	116.8(7)	O(2^{I})–N(2)–C(2)	118.2(7)
N(1)–C(1)–C(2)	110.4(7)	N(2)–C(2)–C(1)	113.7(7)
C(2)–C(1)–C(M)	123.3(8)	N(1)–C(1)–C(M)	126.3(8)
N(1)–O(1)–B	113.6(6)	N(2)–O(2)–B	114.2(6)
O(1)–B–O(2)	114.6(8)	F(1)–B–F(2)	111.9(8)
O(1)–B–F(1)	104.7(6)	O(2)–B–F(1)	106.2(8)
O(1)–B–F(2)	109.6(5)	O(2)–B–F(2)	109.8(7)
	C(9^{II})–C(3)–C(4)	122.6(11)	
C(3)–C(4)–C(5)	119.6(10)	C(3^{II})–C(9)–C(8)	122.5(13)
C(3)–C(4)–C(9)	121.0(11)	C(3^{II})–C(9)–C(4)	116.5(11)
C(9)–C(4)–C(5)	119.4(12)	C(4)–C(9)–C(8)	121.1(13)
C(4)–C(5)–C(6)	117.6(14)	C(9)–C(8)–C(7)	120.3(14)
C(5)–C(6)–C(7)	122.9(13)	C(8)–C(7)–C(6)	118.8(13)

*Roman numeral superscripts refer to the following equivalent positions relative to atoms at x, y, z: I $-x$, $-y$, $-z$; II $1-x$, $-y$, $-z$.

TABLE V. 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' and c where a' lies in the bc plane. Deviations (Å) of Relevant Atoms from the Planes are given in Square Brackets.*

	l	m	n	p
Plane (1): Ni, N(1), N(2), O(1), O(2) C(1), C(2), C(M), N(1^{I}), N(2^{I}), O(1^{I}), O(2^{I}), C(1^{I}), C(2^{I}), (CM^{I}) [N(1) −0.020; N(2) 0.043; O(1) 0.025; O(2) 0.004; C(1) −0.007; C(2) −0.013; C(M) −0.001; B −0.62; F(1) −0.39; F(2) −1.96]	0.9027	0.3215	−0.2861	0.0000
Plane (2): C(3), C(4), C(5), C(6), C(7) C(8), C(9), C(3^{II}), C(4^{II}), C(5^{II}), C(6^{II}), C(7^{II}), C(8^{II}), C(9^{II}) [C(3) −0.022; C(4) −0.012; C(5) 0.017; C(6) 0.005; C(7) −0.012; C(8) <0.001; C(9) −0.002]	0.9132	0.2789	−0.2972	3.4041

*For superscript notation see footnote Table IV.

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

Discussion

The bond lengths and angles are given in Table IV. Each molecule of the adduct possesses a space group imposed centre of symmetry and hence for the macrocycle the methyl groups and the axial fluorine atoms are each in a *trans* configuration. The bonding parameters of the macrocycle are in accord with those of the parent Ni(dmgBF$_2$)$_2$ [4] and its adducts [2 and references therein]. Similarily the anthracene molecular geometry agrees well with that previously reported [1, 5].

The parallel relationship of the closely planar Ni(mgBF$_2$)$_2$ macrocycle to the plane of the anthracene molecule (Table V, planes 1 and 2 intersecting at 2.5°) is shown projected in Fig. 1 together with the atom labelling scheme [6]. Table VI(b) gives the close intermolecular contacts and Fig. 2 shows the packing in the lattice in which molecules stack alternately in chains directed along a. This stacking

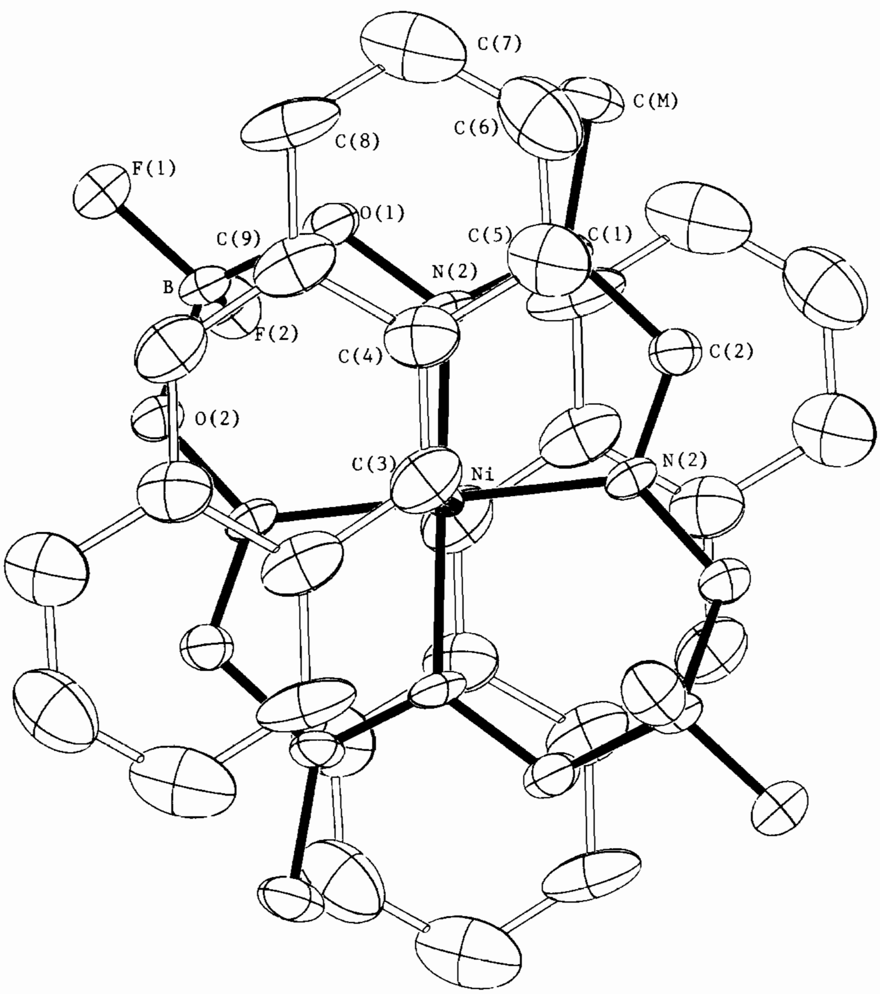

Fig. 1. The orientation of the anthracene molecule relative to the Ni(mgBF$_2$)$_2$ molecule. The atom labelling scheme is included and thermal ellipsoids are drawn to include 35% probability.

TABLE VI. Interatomic Contact Distances (Å) with Estimated Standard Deviations in Parentheses.*

a) Contacts <3.6 Å Suggesting π–π Interactions

	Interatomic Distances	Perpendicular Distance of Relevant Atom from	
		Macrocycle Plane	Anthracene Plane
C(I)···C(8^{III})	3.346(16)	3.33	3.31
O(2)···C(4^{II})	3.387(12)	3.31	3.29
Ni···C(3)	3.389(11)	3.38	3.40
O(1)···C(9)	3.391(13)	3.37	3.37
O(2)···C(3^{II})	3.395(12)	3.33	3.29
N(2)···C(4^{III})	3.442(12)	3.31	3.36
N(1)···C(4)	3.446(13)	3.41	3.36
N(2)···C(9^{III})	3.447(14)	3.34	3.36
C(2)···C(8^{III})	3.495(17)	3.33	3.27
C(1)···C(5)	3.512(15)	3.50	3.31
O(1)···C(8)	3.522(14)	3.39	3.37
C(2)···C(7^{III})	3.528(17)	3.28	3.27
C(1)···C(7^{III})	3.534(16)	3.28	3.31
C(2)···C(9^{III})	3.545(15)	3.34	3.27
N(1)···C(8^{III})	3.546(14)	3.33	3.36
C(2)···C(6^{III})	3.577(16)	3.21	3.27

b) Non-Bonding Contact Distances <3.5 Å

C(2)···F(2^{IV})	3.249(11)	C(M)···F(1^{IV})	3.376(11)

(continued on facing page)

TABLE VI. *(continued)*

C(M)···F(2^{V})	3.324(11)	F(1)···C(7^{VII})	3.440(18)
F(2)···C(3^{I})	3.340(13)	O(2)···C(2^{VI})	3.449(10)
F(1)···C(6^{VI})	3.357(18)		

*For Roman numeral superscripts refer to footnote Table IV and: III $x-1, y, z$; IV $x, 1+y, z$; V $-x, -y, 1-z$; VI $x, y-1, z$; VII $1-x, -y, 1-z$.

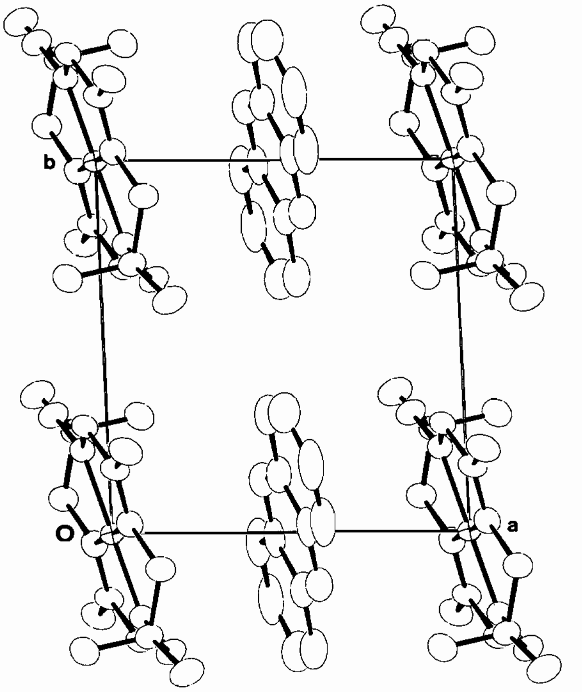

Fig. 2. The packing of the molecules in the crystal.

is such that the molecules lie approximately on the $(21\bar{1})$ series of planes with an interplanar separation of 3.17 Å. This spacing is significantly closer than that observed in the Ni(dmgBF$_2$)$_2$ adducts of 3.36 Å for anthracene [1] and 3.33 Å for phenazine [2] and may represent a generally closer stacking arrangement allowed by the fewer methyl groups present in the Ni(mgBF$_2$)$_2$ derivative.

As in the latter structures the contact distances given in Table VI(a) indicate that π-type interactions exist between the macrocycle and the organic molecule. The orientation of the anthracene molecule relative to the macrocycle is similar to that found in the corresponding Ni(dmgBF$_2$)$_2$ structure [1] but with the central ring more closely aligned in projection with the six-membered ring of the macrocycle; in the two structures the respective rings are rotated away from parallel alignment by 13.5 and 25.5° respectively. In all three adducts investigated thus far there are close contacts between the axial fluorine atom, F(2^{I}), directed towards the organic molecule and C–H groups of that molecule. These contacts involve either or both of the 5- and 10-positions of the linear tricyclic system. For the Ni(dmgBF$_2$)$_2$ (anthracene) structure [1] these are to C(3) at 3.485(7) and to C(8^{II}) at 3.386(8) Å with corresponding F···H distances of 2.69 and 2.57 Å, whereas for the phenazine adduct [2] only that to C(8^{II}) of 3.415(10) Å with an F···H of 2.51 Å is observed. In the present structure that to C(3) is 3.340(13) and to C(8^{II}) is 3.637 Å with F···H of 2.52 and 2.91 Å respectively. The shorter F···H distances observed in these structures are considerably less than the sum of the minimum van der Waals radii of 2.70 Å for the two atoms [7], and suggest that there is some attractive interaction between those hydrogen atoms and the fluorine atom. Thus the precise orientation of the organic molecule relative to the macrocycle in these structures, and hence the degree of π–π interaction allowed between them, would seem to be a compromise between minimizing steric effects of the methyl groups and maintaining some F···H interaction.

In both Ni(dmgBF$_2$)$_2$ adducts the dihedral angle between the two molecular planes represents a rotation of the organic molecule around its major axis with respect to the macrocycle plane thus reducing the steric effects between the methyl group, C($M2^{I}$), and the carbons atoms C(5^{II}) and C(6^{II}). Further, for the phenazine adduct the lack of a hydrogen atom on the nitrogen atom in the '10-position' permits the ring system to slip relative to the macrocycle in order to increase the overlap with the six-membered ring of the macrocycle; the larger dihedral angle observed between the two molecular planes most likely reflects an increased methyl interaction resulting from this slip. The lack of a methyl group on carbon atom C(2) in the present structure allows the organic molecule to pivot about C(3) and the ensuing steric effects between C(6) and the methyl group are relieved by a small rotation about the minor axis of the organic molecule relative to the macrocycle plane.

The differences between the crystal structures of the anthracene adducts of Ni(dmgBF$_2$)$_2$ [1] and Ni(mgBF$_2$)$_2$ clearly rely on the steric influence of the methyl group substituents. The reduction in the methyl substituents allows the anthracene molecule to approach more closely the macrocyclic plane, thus suggesting an increase of π–π interaction between the molecules. We are looking further at the effects of substituent changes in this and related systems.

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