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Studies on Macrocyclic Complexes Derived From *vic*-Dioximes. VIII*. The Crystal Structure of the π-Sandwich Compound between Bis(difluoroborondimethylglyoximato)nickel(II) and Anthracene

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The 1:1 adduct of anthracene with bis(difluoroborondimethylglyoximato)nickel(II) is monoclinic, space group $P2_1/n$, *a* = *7.773(11), b* = *15.681(19), c* = *9.579(11)* Å, β = *96.0(2)°, Z* = *2. The structure was refined to* R = *0.093 for 1948 photographic reflexions. The two molecules each have a space group imposed centre of symmetry and the Ni(dmg-*$BF_2)_2$ *molecule has the axial fluorine atoms in a* trans-*configuration. The anthracene and macrocycle molecules are nearly parallel and their close relative orientation indicates that a* π–π *interaction between them exists. This effectively gives rise to chains of molecules aligned along* a *with continuous* π–π *interaction in that direction.*

Introduction

Bis(difluoroborondimethylglyoximato)nickel(II), Ni(dmgBF$_2$)$_2$ exists in both solid [1] and solution [2] as a dimer. The bonding between the moieties can be represented by two extremes; on one hand a predominantly Ni···Ni interaction and on the other a π–π interaction in which the nickel atoms act essentially to maintain the planarity of the macrocycle. Support for the latter description comes from the crystal structure of the 1:1 benzimidazole adduct [3] in which this N-heterocyclic molecule does not coordinate but a π–π interaction with the dmg fragments between neighbouring dimer units is suggested. In addition the crystal structure of the 1:1 adduct of aniline [4], in which the parent dimer is retained on coordination of the aniline nitrogen atom to the nickel, indicates that some π-interaction between the macrocycle and the phenyl ring of the base is also present. In order to obtain conclusive evidence for the π–π hypothesis attempts were made to prepare adducts with molecules that contain no potential coordinating atoms. Anthracene forms such an adduct and we report here its crystal structure analysis.

Experimental

The method of preparation of the adduct is similar to that described for the 1:1 base adducts [5]. The dark red-brown diamagnetic crystals form on standing from a solution in which there is no obvious colour change on addition of the anthracene. Thermogravimetric studies on the adduct show a weight loss at 185–195 °C of 31.0% (Calc. for $C_{14}H_{10}$ loss: 31.7%) leaving yellow [Ni(dmgBF$_2$)$_2$]$_2$ as residue. A 200 MHz proton NMR study shows a slight increased shielding effect of the methyl protons (4.4 Hz) when anthracene is added to a D$_6$-acetone solution of the parent.

Crystal Data

$C_{22}H_{22}B_2F_4N_4O_4Ni$, M_r = 562.8, Monoclinic, a = 7.773(11), b = 15.681(19), c = 9.579(11) Å, β = 96.0(2)°, U = 1161.2 Å^3, Z = 2, D_c = 1.609 Mg m^{-3}, $F(000)$ = 576, μ(Cu–K_α) = 1.81 mm^{-1}. Systematic absences; $h0l$ if $h + 1 \neq 2n$ and $0k0$ if $k \neq 2n$, space group $P2_1/n$ (non-std. No. 14).

The adduct crystallises as elongated hexagonal-shaped plates lying on the (011) face and with [100] elongation. Cell parameters were determined from oscillation and Weissenberg photographs using Cu–K_α radiation. Intensities were estimated visually from equi-inclination Weissenberg photographs for the layers 0–4kl, h0–4l and hk0–3. 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 1948 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.

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*Part VII, Ref. [5].

TABLE I. Final Atomic Coordinates (fractional, $\times 10^4$) for Non-hydrogen Atoms with Estimated Standard Deviations in Parentheses.

	x	y	z
Ni	0	0	0
N(1)	640(6)	184(3)	1911(4)
N(2)	−906(6)	1088(3)	108(4)
O(1)	1590(5)	−372(2)	2766(4)
O(2)	1845(5)	−1503(2)	974(4)
C(1)	236(7)	921(3)	2409(5)
C(2)	−714(7)	1453(3)	1330(6)
C(M1)	652(9)	1179(4)	3891(6)
C(M2)	−1374(9)	2320(4)	1637(7)
B	1328(9)	−1285(4)	2383(6)
F(1)	2444(5)	−1728(2)	3334(4)
F(2)	−367(4)	−1506(2)	2462(4)
C(3)	4020(7)	710(3)	−464(6)
C(4)	4709(7)	668(3)	922(6)
C(5)	4481(9)	1340(4)	1908(7)
C(6)	5175(10)	1268(5)	3287(8)
C(7)	6134(9)	541(5)	3765(7)
C(8)	6395(9)	−111(5)	2862(7)
C(9)	5710(8)	−61(3)	1417(6)

TABLE III. Hydrogen Atomic Parameters (coordinates: fractional $\times 10^3$).[a]

	x	y	z
H(3)	334	122	−81
H(5)	381	187	160
H(6)	502	175	396
H(7)	664	50	478
H(8)	708	−64	320
H(11)	125	173	365
H(12)	146	77	440
H(13)	−42	144	420
H(21)	−157	239	266
H(22)	−246	239	100
H(23)	−53	278	135

[a] For all hydrogen atoms $B = 5.0$ Å^2.

Since the cell contains only two formula units the adduct molecules must each possess a centre of symmetry. 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 given by $w = (1.0 + 0.1|F_o| + 0.004|F_o|^2)^{-1}$. After isotropic refinement a difference map indicated the 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 subsequent calculations but not refined. The anisotropic refinement for all non-hydrogen atoms was terminated when the maximum shift in any parameter was $<0.1\sigma$. The final R was 0.093 and $R'[= (\Sigma w\Delta^2/\Sigma w|F_o|^2)^{1/2}]$ was 0.130. A final difference map showed no positive densities >0.6 eÅ^{-3}. 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.

TABLE II. Final Anisotropic Thermal Parameters ($\times 10^4$) 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	132.4(24)	28.0(5)	69.5(14)	−0.2(8)	−0.4(14)	0.2(5)
N(1)	91(8)	17(1)	44(4)	−5(3)	−10(5)	3(2)
N(2)	77(7)	18(2)	43(4)	3(3)	−5(4)	4(2)
O(1)	120(7)	22(2)	54(4)	2(3)	−40(4)	2(2)
O(2)	111(7)	25(2)	59(4)	16(3)	−16(4)	5(2)
C(1)	78(8)	24(2)	46(5)	−1(3)	−3(6)	2(2)
C(2)	72(8)	19(2)	61(5)	−5(3)	4(6)	−4(2)
C(M1)	138(11)	41(3)	59(6)	−1(5)	−9(7)	−18(3)
C(M2)	143(11)	23(2)	90(7)	6(4)	15(8)	−11(3)
B	111(11)	24(2)	48(6)	−2(4)	−7(7)	10(3)
F(1)	165(8)	34(2)	77(4)	17(3)	−34(4)	14(2)
F(2)	107(6)	33(2)	95(4)	−9(2)	10(4)	10(2)
C(3)	93(9)	22(2)	67(6)	9(4)	0(6)	3(3)
C(4)	88(9)	22(2)	74(6)	−9(4)	16(6)	−5(3)
C(5)	159(13)	29(2)	108(8)	−5(5)	40(9)	−23(4)
C(6)	161(13)	50(3)	94(8)	−29(6)	29(9)	−33(4)
C(7)	125(11)	60(4)	67(7)	−31(6)	16(8)	−12(4)
C(8)	131(12)	46(3)	64(7)	−10(5)	−1(8)	1(3)
C(9)	92(9)	27(2)	67(6)	−10(4)	6(7)	2(3)

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

Distances (Å)[a]			
Ni–N(1)	1.868(4)	Ni–N(2)	1.852(4)
N(1)–O(1)	1.360(6)	N(2)–O(2^{I})	1.369(5)
O(1)–B	1.486(7)	O(2)–B	1.488(7)
B–F(1)	1.378(7)	B–F(2)	1.372(7)
N(1)–C(1)	1.302(7)	N(2)–C(2)	1.298(7)
C(1)–C(M1)	1.479(7)	C(2)–C(M2)	1.493(7)
	C(1)–C(2)	1.466(7)	
C(3)–C(4)	1.380(8)	C(3^{II})–C(9)	1.398(8)
C(4)–C(5)	1.440(8)	C(7)–C(8)	1.369(10)
C(5)–C(6)	1.378(11)	C(8)–C(9)	1.432(8)
C(6)–C(7)	1.412(12)	C(9)–C(4)	1.435(8)
Angles (°)[a]			
N(1)–Ni–N(2)	82.4(2)	N(1)–Ni–N(2^{I})	97.7(2)
Ni–N(1)–O(1)	124.3(3)	Ni–N(2)–O(2^{I})	124.9(3)
Ni–N(1)–C(1)	116.5(4)	Ni–N(2)–C(2)	116.7(3)
O(1)–N(1)–C(1)	119.0(4)	O(2^{I})–N(2)–C(2)	118.3(3)
N(1)–C(1)–C(2)	111.7(4)	N(2)–C(2)–C(1)	112.7(4)
N(1)–C(1)–C(M1)	123.9(5)	N(2)–C(2)–C(M2)	124.8(5)
C(2)–C(1)–C(M1)	124.4(5)	C(1)–C(2)–C(M2)	122.5(5)
N(1)–O(1)–B	114.6(4)	N(2^{I})–O(2)–B	113.8(3)
O(1)–B–O(2)	113.8(5)	F(1)–B–F(2)	112.2(5)
O(1)–B–F(1)	105.2(5)	O(2)–B–F(1)	105.8(5)
O(1)–B–F(2)	109.7(5)	O(2)–B–F(2)	110.1(5)
	C(9^{II})–C(3)–C(4)	121.6(5)	
C(3)–C(4)–C(5)	122.3(6)	C(3^{II})–C(9)–C(8)	121.6(5)
C(3)–C(4)–C(9)	119.9(5)	C(3^{II})–C(9)–C(4)	118.5(5)
C(9)–C(4)–C(5)	117.8(6)	C(4)–C(9)–C(8)	119.8(6)
C(4)–C(5)–C(6)	120.4(7)	C(9)–C(8)–C(7)	120.3(6)
C(5)–C(6)–C(7)	121.2(6)	C(8)–C(7)–C(6)	120.4(6)

[a] Roman numerals as superscripts refer to the following equivalent positions relative to atoms at x, y, z: I, $-x, -y, -z$; II, $1 - x, -y, -z$.

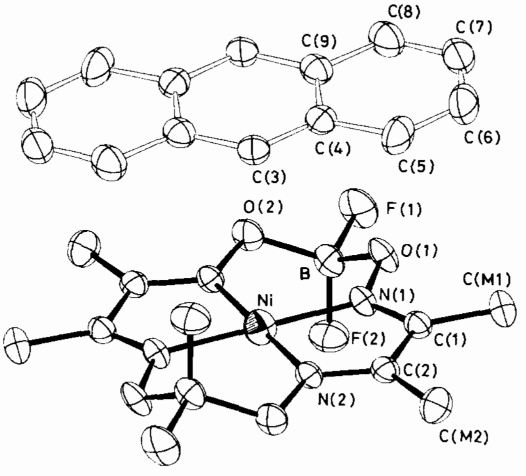

Fig. 1. A perspective drawing of the 1:1 adduct with the labelling of the atoms. The centroid of each molecule is at a centre of symmetry in the unit cell. Thermal ellipsoids are drawn to include 50% probability.

Discussion

The bond lengths and angles are given in Table IV. Figure 1 shows a perspective drawing of the 1:1 adduct together with the atom labelling [7]. Each molecule in the adduct possesses a space group imposed centre of symmetry. The closely planar macrocycle of the Ni(dmgBF$_2$)$_2$ molecule is almost parallel to the plane of the anthracene ring (Table V, planes 1 and 2, intersecting at 2.9°). The packing of the molecules in the cell is shown in Fig. 2. Non-bonding intermolecular contact distances <3.5 Å are given in Table VI(b).

The bond dimensions within the anthracene molecule show trends similar to those reported in crystalline anthracene [8]. The parent dimer [Ni(dmgBF$_2$)$_2$]$_2$ molecule is cleaved on formation of the adduct and the monomer adopts the more symmetrical conformation with the axial fluorine atoms in a *trans* configuration. All bond lengths and angles within the monomer are in good

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 (Å) of Relevant Atoms from the Planes are given in Square Brackets.[a]

	l	*m*	*n*	*p*
Plane (1): Ni, N(1), N(2), O(1), O(2), C(1), C(2), C(M1), C(M2), N(1^{I}), N(2^{I}), O(1^{I}), O(2^{I}), C(1^{I}), C(2^{I}), C(M1^{I}), C(M2^{I})	−0.8581	−0.4007	0.3212	0.0000
[N(1) 0.031; N(2) −0.026; O(1) −0.011; O(2) −0.027; C(1) <|0.001|; C(2) −0.011; C(M1) 0.007; C(M2) −0.007; B 0.63; F(1) 0.43; F(2) 1.96]				
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})	0.8362	0.4470	−0.3177	3.3613
[C(3) -0.020; C(4) −0.008; C(5) 0.010; C(6) 0.007; C(7) −0.004; C(8) −0.011; C(9) 0.004]				

[a] For superscript notation see footnote Table IV.

TABLE VI. Intermolecular Contact Distances (Å) with Estimated Standard Deviations in Parentheses.[a]

a) Contacts <3.6 Å Suggesting π–π Interactions

	Interatomic Distances	Perpendicular Distance of Relevant Atom from	
		Macrocycle Plane	Anthracene Plane
Ni···C(3)	3.390(6)	3.36	3 36
C(1)···C(5)	3.447(9)	3.34	3.29
C(1^{I})···C(8^{II})	3.463(9)	3.44	3.43
N(1)···C(4)	3.479(7)	3.38	3.38
N(1)···C(5)	3.493(8)	3.34	3.38
N(2^{I})···C(9^{II})	3.525(7)	3.43	3.48
O(2)···C(3^{II})	3.529(7)	3.53	3.47
O(1)···C(4)	3.543(7)	3.38	3.40
N(1^{I})···C(8^{II})	3.544(8)	3.44	3.34

b) Non-bonding Contact Distances <3.5 Å

F(2)···C(M2^{III})	3.318(7)	F(1)···C(7^{V})	3.431(8)
F(1)···C(5^{IV})	3.375(8)	F(2^{I})···C(3)	3.485(7)
F(2^{I})···C(8^{II})	3.386(8)	F(2)···C(5^{IV})	3.487(8)
F(1)···C(M2^{IV})	3.398(7)		

[a] For Roman numeral superscripts see footnote Table IV and III, $-\frac{1}{2} - x$, $y - \frac{1}{2}$, $\frac{1}{2} - z$; IV, $\frac{1}{2} - x$, $y - \frac{1}{2}$, $\frac{1}{2} - z$; V, $1 - x$, $-y$, $1 - z$.

agreement with those found in the parent dimer molecule [1].

Figure 3 shows the orientation of the molecules projected onto the plane of the macrocycle. The contact distances given in Table VI(a) indicate that π-type interactions between the anthracene molecules and the macrocycle exists. The orientation of the anthracene molecule is constrained by the axial fluorine atom F(2). In order to gain maximum overlap with a dmg fragment the ring pivots about C(3) and the degree of such pivoting is determined by the F(2)···C(8) contact. This orientation also gives overlap with two of the N–O groups. Such a situation is a composite of the two possible orientations found for the aromatic rings in aniline/cobaloxime complexes [9]. The effect of π-bonding between the parallel molecules is to give rise to chains of molecules aligned along *a* with a continuous π–π interaction in that direction (see Fig. 2). The range of perpendicular distances of 3.34–3.55 Å from the anthracene ring to the macrocycle plane, and the closest atom–atom contact of 3.39 Å, are

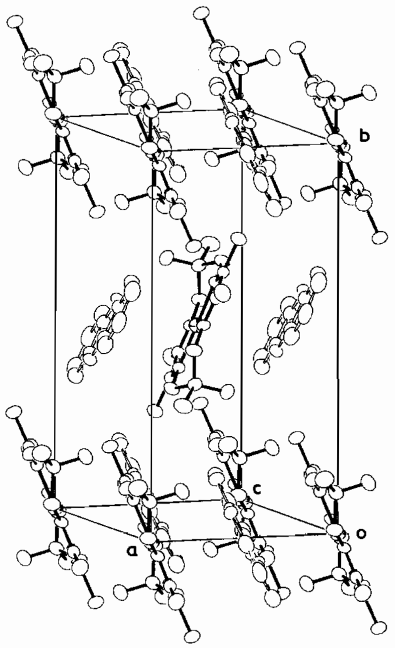

Fig. 2. The packing of molecules in the crystal.

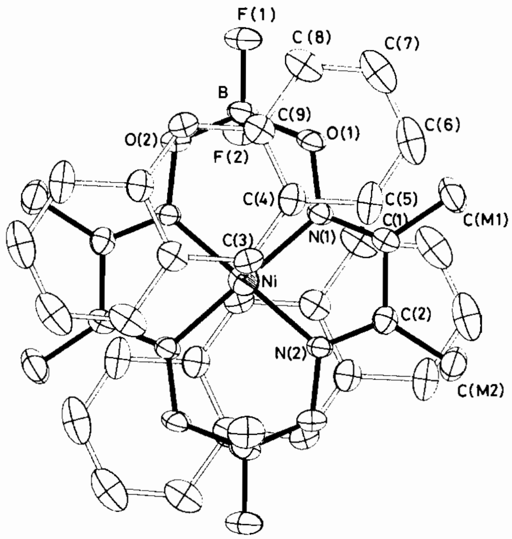

Fig. 3. The orientation of the anthracene molecules with respect to the $Ni(dmgBF_2)_2$ molecule.

each less than the corresponding values of 3.50–3.60 Å and 3.53 Å found in the structure of the benzimidazole adduct [3] in which a dimeric nature is retained. These interplanar distances are significantly less than the accepted non-bonded contact of 3.54 Å between aromatic systems [10]. The π–π interaction observed here is analogous to that proposed by Grigg *et al.* [11] for metalloporphyrin–nitroaromatic sandwich complexes.

The development of a π–π interaction between anthracene and the parent dimer, similar to that of the benzimidazole adduct, is unlikely due to steric hindrance effects which would be associated with the *cis*-axial fluorine atoms. The initial interaction between the anthracene molecules and the macrocycle, however, must be sufficient to cause rupture of the dimer. This could be viewed as a displacement reaction, and reinforces the argument that the self-association of the macrocycle moieties is predominantly of π–π character.

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