

The Crystal and Molecular Structure of 1,10-Phenanthrolinebis(difluoroborondiphenylglyoximato)nickel(II)–Diacetone

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The structure of the title compound has been refined to R 0.085 for 2008 photographic intensities. The crystals are monoclinic, space group $C2/c$, with $a = 20.577$ (36), $b = 10.756$ (24), $c = 20.130$ (42) Å, $\beta = 94.1$ (1)°, $Z = 4$. The complex has imposed 2 (C_2) symmetry. The planarity of the macrocyclic parent complex, bis(difluoroborondiphenylglyoximato)nickel(II), is destroyed by the *cis* coordination of the 1,10-phenanthroline giving rise to a distorted octahedral environment about Ni: the Ni–N distances are 2.007 (6), 2.106 (8) Å for the glyoxime and 2.114 (7) Å for the phenanthroline ligand. The acetone molecules occupy holes in the crystal lattice.

Introduction

A series of complexes $[\text{Ni}(\text{F}_2\text{BON:CR.CR':NO})_2]$ with $R = R' = \text{H}$, CH_3 , C_6H_5 and $R = \text{H}$, $R' = \text{CH}_3$ have been obtained by the addition of $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ to the parent glyoximates (Stephens, Vagg & Watton, 1977). The structure of the complex with $R = R' = \text{CH}_3$ has been reported (Stephens & Vagg, 1977) and has shown the two dimethylglyoximate ligands to be bridged by BF_2 groups, replacing the hydrogen bonds present in the parent glyoximate, and creating a planar macrocyclic structure. These BF_2 -substituted complexes, unlike their parent glyoximates, form numerous adducts with N-base ligands (Stephens, Vagg & Watton, 1977), in general, 1:2 adducts with monodentate bases such as pyridine and 1:1 adducts with bidentate bases such as 1,10-phenanthroline.

The 1:1 adducts with 1,10-phenanthroline are of interest; 1,10-phenanthroline can only coordinate *cis* and hence a distortion of the planar macrocycle is necessary. It has been suggested (Ablov & Samus, 1975) that similar complexes of conjugated planar macrocyclic ligands would resist bending or folding and as a consequence they have been used as models for biological systems. Two possible configurations about the metal atom could arise from the adduct formation, a distorted octahedron or a trigonal prism; the latter would require the least distortion from planarity of the macrocycle. An analysis of the 1,10-phenanthroline adduct for the complex with $R = R' = \text{phenyl}$ has been undertaken to determine the molecular structure.

Experimental

Crystal data

$\text{C}_{46}\text{H}_{40}\text{B}_2\text{F}_4\text{N}_6\text{O}_6\text{Ni}$, $M_r = 929.2$, monoclinic, $a = 20.577$ (36), $b = 10.756$ (24), $c = 20.130$ (42) Å, $\beta =$

94.1 (1)°, $U = 4443.9$ Å³, $D_m = 1.40$ (by flotation), $Z = 4$, $D_c = 1.389$ g cm⁻³, $F(000) = 1920$, $\mu(\text{Mo } K\alpha) = 4.0$ cm⁻¹. Systematic absences: hkl if $h + k \neq 2n$ and $h0l$ if $l \neq 2n$, space group Cc or $C2/c$.

The paramagnetic complex crystallizes as orange-red plates on the addition of 1,10-phenanthroline to an acetone solution of bis(difluoroborondiphenylglyoximato)nickel(II). Cell parameters were determined from precession photographs taken with Mo $K\alpha$ radiation. Intensities were estimated visually from the layers 0–6 precessing about [100], 0–5 about [001] and 0–7 about [101]. Reflexions were corrected for Lorentz and polarization effects but no correction for absorption or extinction was applied. 2644 non-zero reflexions were recorded and after internal correlation yielded 2008 unique reflexions.

Scattering factors were taken from *International Tables for X-ray Crystallography* (1962). All calculations were carried out on a Univac 1106 computer with programs written by FSS.

Structure determination

From the systematic absences the space group is Cc or $C2/c$. A Patterson synthesis indicated the centrosymmetric space group and this was confirmed by the successful analysis. The Patterson map yielded the position of the Ni atom and the complete solution was obtained by Fourier synthesis.

Refinement was carried out by least squares in which the function minimized was $\Sigma w\Delta^2$. The weight, w , was initially unity and in the final refinement given by $w = (15.0 + 0.7|F_o| + 0.007|F_o|^2)^{-1}$. For this latter scheme the mean values of $w\Delta^2$ for ranges of increasing $|F_o|$ were almost constant. Reflexions for which $|F_c| < 0.35|F_o|$ were omitted.

Initial refinement used a full-matrix procedure in

Table 1. Final atomic coordinates (fractional; $\times 10^4$ for non-hydrogen atoms, $\times 10^3$ for hydrogen atoms) with estimated standard deviations in parentheses

	x	y	z		x	y	z
Ni	0	1408 (1)	2500	C(22)	-1983 (4)	4267 (8)	1779 (5)
O(11)	342 (3)	2732 (6)	1208 (3)	C(23)	-2626 (5)	4700 (10)	1724 (6)
N(11)	-128 (4)	2581 (6)	1664 (4)	C(24)	-3118 (5)	3924 (12)	1841 (7)
C(111)	-717 (4)	2755 (7)	1449 (5)	C(25)	-3012 (5)	2685 (11)	1964 (7)
C(222)	-1182 (4)	2517 (7)	1970 (5)	C(26)	-2376 (5)	2216 (9)	2004 (5)
N(22)	-948 (3)	1864 (6)	2458 (4)	O(31)	-1462 (8)	-177 (12)	1174 (7)
O(22)	-1265 (3)	1870 (5)	3044 (3)	C(31)	-1717 (7)	-1034 (16)	853 (10)
F(1)	-1074 (3)	4023 (5)	3174 (3)	C(32)	-1806 (10)	-2284 (18)	1157 (13)
F(2)	-1415 (3)	2829 (6)	4022 (3)	C(33)	-1980 (13)	-886 (20)	107 (11)
B	-1039 (5)	2884 (9)	3481 (6)	H(1)	21	79	102
N(1)	50 (3)	-109 (6)	1837 (4)	H(2)	23	-121	31
C(1)	127 (6)	-113 (9)	1191 (6)	H(3)	17	-302	78
C(2)	173 (6)	-1203 (11)	808 (7)	H(6)	14	-438	199
C(3)	145 (7)	-2283 (12)	1089 (8)	H(12)	-32	473	80
C(4)	77 (6)	-2377 (10)	1804 (8)	H(13)	-77	566	-23
C(5)	34 (5)	-1225 (7)	2150 (6)	H(14)	-164	456	-85
C(6)	31 (8)	-3505 (9)	2165 (7)	H(15)	-202	267	-50
C(11)	-938 (4)	3228 (7)	772 (5)	H(16)	-161	176	57
C(12)	-696 (4)	4313 (9)	534 (5)	H(22)	-159	479	170
C(13)	-929 (5)	4796 (10)	-57 (6)	H(23)	-274	563	160
C(14)	-1430 (5)	4209 (11)	-429 (5)	H(24)	-357	425	186
C(15)	-1668 (5)	3111 (11)	-199 (6)	H(25)	-342	215	198
C(16)	-1434 (5)	2599 (9)	404 (5)	H(26)	-230	129	213
C(21)	-1861 (4)	3022 (8)	1914 (4)				

which positional and individual isotropic thermal parameters were refined. After three cycles the positions of the H atoms of the aromatic rings were calculated, assuming C-H = 1.0 Å, and in subsequent calculations their contributions were included.

Final refinement was with anisotropic thermal parameters for all non-hydrogen atoms. Owing to the large number of parameters (295) it was necessary to refine in block matrices; the five matrices contained the parameters for (1) the overall scale and thermal parameters, (2) the Ni atom, the phenanthroline ring and the atoms of the BF₂-glyoxime fragment, (3) and (4) the two phenyl rings and (5) the acetone molecule. Refinement was terminated when the maximum shift in any parameter was $< 0.15\sigma$. 2002 reflexions were included in the final cycle. The final value for *R*, based on 2008 reflexions, was 0.085 and for *R'* = $(\sum w\Delta^2/\sum w|F_o|^2)^{1/2}$, 0.113. A final difference map showed maximum positive electron density of 0.8 e Å⁻³ around the Ni atom.

Final atomic coordinates are given in Table 1.*

Discussion

Fig. 1 shows the geometry of the complex (Johnson, 1965) and the labelling of the atoms. The packing of the

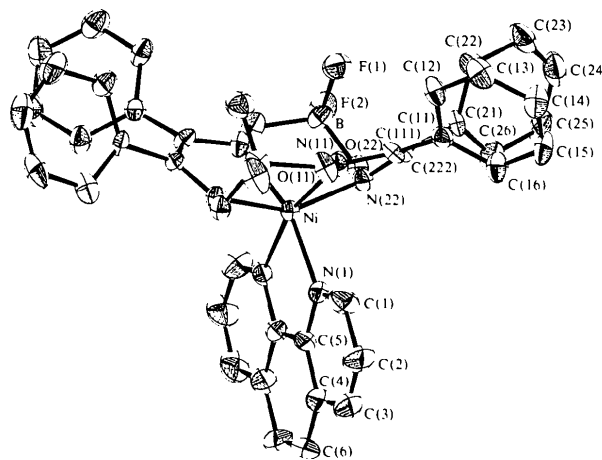


Fig. 1. A perspective drawing of the complex and the labelling of the atoms. Thermal ellipsoids are scaled to include 35% probability.

molecules is shown in Fig. 2. The molecules are held together by van der Waals forces with the acetone molecules occupying holes in the crystal lattice. The closest approach of any atom of the complex to an acetone molecule is from F(2) at $(x, -y, z - \frac{1}{2})$ to C(33), 3.29 Å. There are four other interatomic contacts less than 3.5 Å; C(13) to F(2) at $(x, 1 - y, z - \frac{1}{2})$ (3.27 Å), C(23) to O(22) at $(-\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z)$ (3.32 Å), C(14) to F(2) at $(x, 1 - y, z - \frac{1}{2})$ (3.37 Å) and C(24) to O(22) at $(-\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z)$ (3.43 Å).

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32650 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

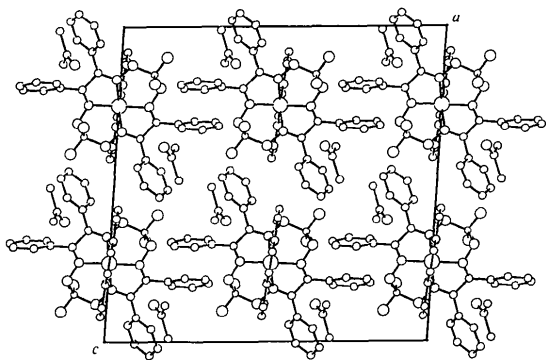
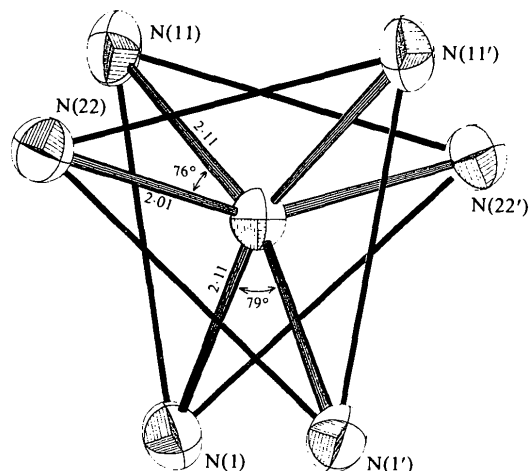


Fig. 2. The packing of the molecules in the crystal.

The bond distances and angles are given in Table 2. The molecule has imposed 2 (C_2) symmetry. The environment about Ni is a distorted octahedron (Fig. 3), the angles between the plane NiN(11)N(22) and the planes NiN(11')N(22') and NiN(1)N(1') both being 74° .

The Ni–N distances are typical of those observed in octahedral Ni^{II} complexes with N ligands (*Tables of Interatomic Distances and Configuration in Molecules*


 Fig. 3. The octahedral environment about the Ni atom; the angle between the two trigonal planes illustrated is 1.9° .

and Ions, 1958, 1965): those to the glyoxime N atoms (2.106, 2.007 Å) are markedly longer than the corresponding distances of 1.85–1.87 Å found in the square planar structures of Ni glyoximates (Stephens & Vagg, 1977; Bowers, Banks & Jacobson, 1972; Calleri,

Table 2. Bond lengths and angles with estimated standard deviations in parentheses

Atoms marked with a prime are related to those at (x, y, z) by the twofold axis at $(0, y, \frac{1}{2})$.

(a) Distances (Å)

Ni–N(11)	2.106 (8)	Ni–N(22)	2.007 (6)
Ni–N(1)	2.114 (7)	C(111)–C(222)	1.49 (1)
N(11)–O(11)	1.39 (1)	N(22)–O(22)	1.39 (1)
N(11)–C(111)	1.27 (1)	N(22)–C(222)	1.27 (1)
C(111)–C(11)	1.50 (1)	C(222)–C(21)	1.50 (1)
C(11)–C(12)	1.37 (1)	C(21)–C(22)	1.39 (1)
C(12)–C(13)	1.35 (1)	C(22)–C(23)	1.40 (1)
C(13)–C(14)	1.38 (1)	C(23)–C(24)	1.34 (2)
C(14)–C(15)	1.37 (1)	C(24)–C(25)	1.37 (2)
C(15)–C(16)	1.39 (1)	C(25)–C(26)	1.40 (1)
C(16)–C(11)	1.39 (1)	C(26)–C(21)	1.39 (1)
N(1)–C(1)	1.32 (1)	B–F(1)	1.37 (1)
C(1)–C(2)	1.41 (1)	B–F(2)	1.38 (1)
C(2)–C(3)	1.30 (2)	B–O(11')	1.53 (1)
C(3)–C(4)	1.46 (2)	B–O(22)	1.46 (1)
C(4)–C(5)	1.43 (1)	C(31)–O(31)	1.22 (2)
C(5)–N(1)	1.36 (1)	C(31)–C(32)	1.49 (2)
C(4)–C(6)	1.42 (2)	C(31)–C(33)	1.57 (2)
C(5)–C(5')	1.43 (2)		
C(6)–C(6')	1.37 (2)		

 (b) Angles ($^\circ$)

N(1)–Ni–N(1')	79.0 (3)	N(11)–Ni–N(22)	75.8 (3)
N(1)–Ni–N(11)	88.1 (3)	N(1)–Ni–N(22)	104.7 (3)
N(1)–Ni–N(11')	163.3 (3)	N(1)–Ni–N(22')	97.1 (3)
N(11)–Ni–N(11')	106.4 (3)	N(22)–Ni–N(22')	151.7 (3)
N(11)–Ni–N(22')	87.3 (3)		
Ni–N(11)–O(11)	123 (1)	Ni–N(22)–O(22)	119 (1)
Ni–N(11)–C(111)	115 (1)	Ni–N(22)–C(222)	119 (1)
O(11)–N(11)–C(111)	117 (1)	O(22)–N(22)–C(222)	118 (1)
N(11)–O(11)–B'	115 (1)	N(22)–O(22)–B	112 (1)

Table 2 (cont.)

N(11)–C(111)–C(222)	112 (1)	N(22)–C(222)–C(111)	114 (1)
N(11)–C(111)–C(11)	125 (1)	N(22)–C(222)–C(21)	124 (1)
C(222)–C(111)–C(11)	122 (1)	C(111)–C(222)–C(21)	122 (1)
C(111)–C(11)–C(12)	121 (1)	C(222)–C(21)–C(22)	121 (1)
C(111)–C(11)–C(16)	119 (1)	C(222)–C(21)–C(26)	119 (1)
C(12)–C(11)–C(16)	120 (1)	C(22)–C(21)–C(26)	120 (1)
C(13)–C(12)–C(11)	121 (1)	C(23)–C(22)–C(21)	120 (1)
C(14)–C(13)–C(12)	120 (1)	C(24)–C(23)–C(22)	120 (1)
C(15)–C(14)–C(13)	119 (1)	C(25)–C(24)–C(23)	122 (1)
C(16)–C(15)–C(14)	122 (1)	C(26)–C(25)–C(24)	120 (1)
C(11)–C(16)–C(15)	118 (1)	C(21)–C(26)–C(25)	119 (1)
Ni–N(1)–C(1)	130 (1)	C(3)–C(4)–C(6)	125 (1)
Ni–N(1)–C(5)	113 (1)	C(5)–C(4)–C(6)	119 (1)
C(1)–N(1)–C(5)	117 (1)	C(4)–C(5)–C(5')	120 (1)
C(2)–C(1)–N(1)	124 (1)	N(1)–C(5)–C(5')	118 (1)
C(3)–C(2)–C(1)	120 (1)	C(4)–C(6)–C(6')	121 (1)
C(4)–C(3)–C(2)	120 (1)	F(1)–B–F(2)	112 (1)
C(5)–C(4)–C(3)	116 (1)	O(11')–B–O(22)	115 (1)
N(1)–C(5)–C(4)	123 (1)	F(1)–B–O(11')	107 (1)
O(31)–C(31)–C(32)	122 (2)	F(1)–B–O(22)	113 (1)
O(31)–C(31)–C(33)	122 (2)	F(2)–B–O(11')	103 (1)
C(32)–C(31)–C(33)	116 (2)	F(2)–B–O(22)	106 (1)

Table 3. Least-squares planes and their equations given by $lX' + mY' + nZ' - p = 0$ where X' , Y' and Z' are orthogonal coordinates related to the atomic coordinates X , Y and Z by $X' = X \sin \beta$, $Y' = Y$, $Z' = Z + X \cos \beta$

Deviations (Å) of the most relevant atoms from the planes are given in square brackets.

	l	m	n	p
Plane (1): Ni, N(11), C(111), C(222), N(22)	0.1871	0.8428	0.5047	3.8726
[Ni –0.06, N(11) 0.12, C(111) –0.13, C(222) 0.04, N(22) 0.02, O(11) –0.06, O(22) 0.52, B 1.96]				
Plane (2): C(111), N(11), C(11), C(222)	0.0820	0.9465	0.3120	3.6489
[C(111) –0.021, N(11) 0.008, C(11) 0.007, C(222) 0.006]				
Plane (3): C(222), N(22), C(21), C(111)	0.3171	0.8302	0.4585	3.3785
[C(222) –0.002; N(22), C(21), C(111) 0.001]				
Plane (4): N(11), O(11), C(111), Ni	0.1591	0.8481	0.5055	3.8640
[N(11) 0.15; O(11), C(111) –0.06; Ni –0.04]				
Plane (5): N(22), O(22), C(222), Ni	0.3187	0.8958	0.3097	2.8824
[N(22) –0.13; O(22), C(222) 0.05; Ni 0.03]				
Plane (6): N(1), C(1)–C(6)	0.9941	0.0081	0.1084	0.5149
[N(1) –0.014, C(1) 0.002, C(2) 0.001, C(3) –0.004, C(4) 0.014, C(5) 0.012, C(6) –0.011, Ni 0.04]				
Plane (7): C(11)–C(16)	–0.6794	0.5158	0.5219	3.9769
[C(11) 0.005, C(12) 0.001, C(13) –0.008, C(14) 0.011, C(15) –0.007, C(16) –0.001, C(111) 0.03]				
Plane (8): C(21)–C(26)	0.0849	0.2031	0.9755	4.3549
[C(21) 0.007, C(22) 0.009, C(23) –0.023, C(24) 0.021, C(25) –0.005, C(26) –0.009, C(222) 0.03]				

Ferraris & Viterbo, 1967; Murmann & Schlemper, 1967; Williams, Wohlaue & Rundle, 1959). The formation of an octahedral stereochemistry with the *cis* coordination of the phenanthroline ligand considerably distorts the macrocyclic ligand from the planarity found in an analogous parent complex, bis(difluoroborondimethylglyoximate)nickel(II) (Stephens & Vagg, 1977). The five-membered glyoximate coordination ring deviates from planarity [plane (1), Table 3]; the two glyoxime C atoms are trigonally planar [planes (2) and (3), Table 3] whereas the N atoms show a trend towards a pyramidal environment [planes (4) and (5), Table 3]. In the present structure the C–N distances (1.39 Å) are in good agreement with the corresponding values (1.38–1.40 Å) in glyoxime (Calleri, Ferraris & Viterbo, 1966; Merritt & Lanterman, 1952), in contrast to the shorter values (1.34–1.35 Å) found in bis(glyoximate)nickel(II) complexes. With the exception of the C–N distances and the glyoxime bite angle [N(11)–Ni–N(22) 75.8°] the bond lengths and angles within the glyoxime ligand are in good agreement with the corresponding values in related complexes. The smaller bite angle in the present structure is a consequence of the longer Ni–N distances.

The phenyl rings and the phenanthroline ligand exhibit the expected planarity [planes (6)–(8), Table 3] and the bond lengths and angles within the rings are in good agreement with reported values (*Tables of Interatomic Distances*, 1958, 1965).

From thermodynamic studies of the 1:1 adducts of the parent macrocyclic complexes with bases Graddon & Siddiqi (1976) concluded that for the adducts the macrocyclic ligand would not permit the lengthening of the in-plane Ni–N bonds commensurate with the formation of high-spin species. The results of this

structure determination show this conclusion to be incorrect and further would cast some doubt on the validity (Ablov & Samus, 1975) of using this system as a model for rigidly planar biological macrocyclic chelates.

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The Crystal and Molecular Structure of the Methanesulphonamide of Morpholine (MSM): C₅H₁₁NOSO₂

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The structure of MSM has been determined by single-crystal X-ray diffraction techniques. The crystals are orthorhombic, space group $P2_12_12_1$, with cell parameters $a = 13.207$, $b = 10.078$ and $c = 5.7318$ Å; $Z = 4$. The structure was solved with the heavy-atom method and successive Fourier syntheses. It was further refined by a least-squares technique to a final R value of 0.055 for 1051 observed reflexions, measured on an automatic four-circle diffractometer. The hetero-ring shows a chair conformation with the N-SO₂-CH₃ group in the equatorial position. There are no intermolecular distances shorter than the sum of the van der Waals radii.

Introduction

The conformational equilibrium of piperidine (1) has been the subject of prolonged controversy. At present, however, there seems to be a satisfactory settlement in favour of the NH-equatorial form for the gas phase (Cook *et al.*, 1973). This conclusion appears to apply equally to a variety of C-substituted piperidines in which a ring CH₂ group in position 3 or 4 has been

replaced by O, S or N-H. Such a replacement in the position would not be expected to disturb greatly the equilibrium behaviour. In the present work the resolution of the crystal structure of *N*-methanesulphonylmorpholine was undertaken, following the suggestion of Dr Moreno-Mañas, in order to determine the conformation of the N-SO₂-CH₃ group.

Experimental

Crystals of MSM are transparent and colourless. Accurate cell parameters were determined by least-squares calculations from 26 θ values measured on a single-crystal X-ray diffractometer with Mo $K\alpha$ radiation. Systematic absences are compatible with the

