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Macrocyclic Nickel(II) Complexes: Spectroscopic Studies and Crystal Structure of Bis(difluoroboron-alpha-furilglyoximato)nickel(II)

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Abstract

Bis (difluoroboron - α - furilglyoximato) nickel (II), $C_{20}H_{12}O_8N_4B_2F_4Ni$, was prepared by cyclization of its hydrogen-bonded precursor with $BF_3{\cdot}OEt_2$. The compound crystallizes in the space group $P2_1/c$ with $a = 11.162(2)$, $b = 5.569(2)$, $c = 19.527(3)$ Å, $\beta = 100.08(1)°$, $U = 1195.1(3)$ Å^3, and $Z = 2$. The structure was refined to an R value of 0.033 using 2371 unique reflections collected with a CAD4-SDP diffractometer system. Unlike the corresponding planar macrocyclic as well as hydrogen-bonded dimethylglyoximates, the title compound neither dimerizes nor exhibits columnar stacked structure. The 14-member macrocycle is planar except the B atoms, and no metal–metal interactions are observed in this compound. The complexation and cyclization reactions were investigated using spectral data. The structure is compared with other macrocyclic complexes.

Introduction

Although spectroscopic data confirmed complexation as well as cyclization reactions in α-furilglyoximates, questions about dimerization, short range metal–metal interactions, geometric configuration and general packing pattern of the molecules in the crystal lattices cannot be answered on the basis of spectroscopic results [1, 2]. Our crystal structure determination [3] of $[Pd(Hafdo)_2]$ revealed a columnar stacked arrangement in this complex similar to bis(dimethylglyoximates) of nickel(II) and palladium(II) which are known [4] to exhibit uni-directional electrical conduction properties. The Pd–Pd distance in $[Pd(Hafdo)_2]$ was 3.465(4) Å compared to 3.207(6) Å for Ni–Ni distance in $[Ni(Hdmg)_2]$ [5].

In order to investigate macrocyclization of α-furilglyoximates, substitution of O–H–O by O–BF_2–O in the nickel(II)-, palladium(II)- and platinum(II)-α-furilglyoximates was carried out and suitable crystals of $[Ni(BF_2afdo)_2]$ were obtained for diffraction studies [1]. The present paper reports the spectroscopic results for $[M(BF_2afdo)]$, M = Ni(II) Pd(II) and Pt(II) and the crystal structure determination of $[Ni(BF_2afdo)_2]$. This study was undertaken to ascertain the packing pattern in the macrocycles as compared to their uncyclized counterparts. Much of the current interest in these chelates centers on their use as chemical models for biological systems [7] such as vitamin B_{12}, their oxygen transport functions [8] and their semiconducting properties in the solid state [4].

Experimental

Macrocyclization was carried out by adding dropwise a freshly distilled solution of $BF_3{\cdot}OEt_2$ to a suspension of the corresponding uncyclized complex in methylene chloride. A brick red precipitate was formed which was washed with ether, dried under vacuum and crystallized from acetone solution. The UV–Vis spectra were recorded on a Beckman ACTA MVII spectrophotometer in DMSO and the infrared spectra on a Perkin-Elmer 180 spectrophotometer using KBr pellets. The spectroscopic data are given in Table I. A rectangular piece cut from a long needle-shaped crystal was used for diffraction data. The details of structure determination are given in earlier papers [3, 9]. The crystal data, structure solution and refinement parameters are listed in Table II. The final atomic coordinates and the B_{eq} values are given in Table III. See also 'Supplementary Material'.

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TABLE I. Spectroscopic Data for [$Ni(BF_2afdo)_2$] and Related Compounds

	λ_{max} (cm^{-1})	$\epsilon_{max} \times 10^4$ ($LM^{-1}\ cm^{-1}$)		
(a) UV–Vis absorptions				
[$Ni(Hafdo)_2$]^a	37040 22730	9.74 1.29		
[$Ni(BF_2afdo)_2$]	37040 22940	41.01 0.36		
[$Pd(BF_2afdo)_2$]	36760 26320	41.01 3.58		
[$Pt(BF_2afdo)_2$]	35090 23810	3.19 1.81		
	C=N	N–O	B–O	B–F
(b) Infrared spectra (cm^{-1})				
[$Ni(Hafdo)_2$]^a	1500	1212, 1125		
[$Ni(BF_2afdo)_2$]	1465	1160, 1120	1210, 880	1040, 930
[$Pd(BF_2afdo)_2$]	1460	1170, 1120	1225, 870	1070, 980
[$Pt(BF_2afdo)_2$]	1460	1120	1240, 870	1060, 990

^{a}Ref. 3.

TABLE II. Crystal Data and Structure Solution and Refinement Parameters for [$Ni(BF_2afdo)_2$]

Formula	$C_{20}H_{12}O_8N_4B_2F_4Ni$
Formula wt	592.7
Crystal shape	rectangular
Crystal dimensions (mm)	0.13 × 0.10 × 0.37
a (Å)	11.162(2)
b (Å)	5.569(2)
c (Å)	19.527(3)
β (°)	100.08(1)
U (Å^3)	1195.1(3)
Space group	$P2_1/c$
Z	2
D(calc.) (g cm^{-3})	1.707
D(meas.) (g cm^{-3})	1.710(3)
λ(Mo Kα) (Å)	0.71073
F(000)	506
Temperature	23 ±2°
Method of density measurement	flotation
Diffractometer used	CAD4-SDP82
Intensity measurement method	$\omega-2\theta$
No. and 2θ range of	25
Reflections for lattice constants	$2\theta > 22°$
Absorption coefficient (cm^{-1})	8.98
Maximum transmission (%)	99.80
Minimum transmission (%)	95.64
Maximum value of $(\sin\theta)/\lambda$	1.193
Range of h, k and l	$0 \rightarrow 13, 0 \rightarrow 16, -23 \rightarrow 23$
Standard reflections	333, 3-1-7, 0-4-4
Intensity variation in standards	< 1.5%
No. of reflections measured	2671
No. of unique reflections	2371
No. of observed reflections	1480
Criterion for observed reflections	$I > 2\sigma(I)$
Method used to solve structure	heavy atom
Use of F or F^2 magnitudes in LS	F^2, full-matrix LS
Method of locating H-atoms	ΔF map
No. of parameters refined	205
Values of (a) R	0.033
(b) R_w	0.038
Value of w in weighing scheme	$1/\sigma^2$
Ratio of max. LS shift to error	0.08
Std. Dev. observation of unit wt.	1.204
Secondary extinction corrections	not used
Maximum height in final ΔF map	0.041 e/Å^3
Source of $\Delta f'$ and $\Delta f''$ values	International Tables
Computer programs used	SDP82

Results and Discussion

Spectroscopic Evidence for Complexation and Macrocyclization

In the UV–Vis region all H_2afdo complexes exhibited [1] a strong broad maximum around 36 700 to 39 000 cm^{-1} similar to the maximum observed in H_2dmg complexes [10] and assigned [11] to a $\pi-\pi^*$ transition from deprotonated free ligand. The ϵ_{max} values for the 37 040 cm^{-1} band are generally higher for the macrocycles than their uncyclized counterparts. This is perhaps due to the absence of metal–metal interactions in the former as compared to the latter which are either dimeric or exhibit columnar stacking. In the stacked structures such as [$Pd(Hafdo)_2$], the interlocking of furan groups from the adjacent molecules enhances

TABLE III. Positional Coordinates for [Ni(BF_2afdo)$_2$]

Atom	x/a	y/b	z/c	B_{eq} (Å^2)
Ni	0.0	0.0	0.0	2.164(9)
N(1)	−0.1400(2)	0.1228(4)	0.0247(1)	2.17(5)
N(2)	−0.0232(2)	−0.2362(5)	0.0628(1)	2.45(5)
O(1)	−0.1972(2)	0.3266(4)	−0.0025(1)	2.81(4)
O(2)	0.0533(2)	−0.4227(4)	0.0824(1)	3.01(4)
O(3)	−0.3774(2)	−0.1619(4)	0.0934(1)	3.85(5)
O(4)	−0.1956(2)	−0.2357(4)	0.2003(1)	3.76(5)
F(1)	−0.2277(2)	0.1876(4)	−0.1165(1)	4.83(5)
F(2)	−0.2407(2)	0.5880(4)	−0.0925(1)	5.37(4)
C(1)	−0.1940(2)	−0.0056(6)	0.0657(1)	2.26(5)
C(2)	−0.1153(2)	−0.2098(5)	0.0954(1)	2.35(6)
C(3)	−0.3155(2)	0.0369(5)	0.0782(2)	2.64(6)
C(4)	−0.3878(3)	0.2312(7)	0.0759(2)	3.96(8)
C(5)	−0.4999(3)	0.1493(8)	0.0908(2)	4.94(9)
C(6)	−0.4895(3)	−0.0846(8)	0.1010(2)	4.73(9)
C(7)	−0.1311(2)	−0.3484(6)	0.1554(1)	2.59(6)
C(8)	−0.0910(3)	−0.5634(6)	0.1817(2)	3.03(7)
C(9)	−0.1345(3)	−0.5916(7)	0.2445(2)	3.85(7)
C(10)	−0.1956(3)	−0.3932(8)	0.2537(2)	4.34(8)
B	−0.1831(3)	0.3767(8)	−0.0753(2)	3.18(7)
HC4	−0.368(2)	0.379(5)	0.065(1)	2.8(6)
HC5	−0.570(3)	0.232(7)	0.093(2)	7(1)
HC6	−0.544(3)	−0.200(6)	0.112(2)	5.2(9)
HC8	−0.049(3)	−0.659(5)	0.162(1)	3.4(7)
HC9	−0.123(3)	−0.726(7)	0.274(2)	5.7(9)
HC10	−0.237(3)	−0.346(7)	0.290(2)	6.1(9)

Hydrogen atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $B_{eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$. Numbers in parentheses in this and all subsequent tables represent estimated standard deviation in the last digit.

the metal–metal interactions which in turn stabilizes dimeric or columnar chain structures in solution as well as in the solid state. In the macrocycles the interlocking is hindered by the out-of-plane BF_2 groups preventing metal–metal interactions. The absence of such interactions results in an increase in the solubility and the molar absorptivity of the macrocycles.

In the infrared spectra, a broad intense –OH band at 3300–3000 cm^{-1} in the free ligand disappeared on complex formation. A shift of about 40 cm^{-1} in the ν(C=N) towards the lower frequency as compared to the free ligand indicated *N*-coordination. A broad absorption at 1300 cm^{-1} characteristic of the short intramolecular hydrogen bonding, its disappearance upon $BF_3 \cdot OEt_2$ treatment with concomitant appearance of ν(B–F) and ν(B–O) absorptions [6] around 1050, 980 and 1220, 870 cm^{-1}, respectively, indicated formation of macrocycles.

Unit Cell Packing of [Ni(BF_2afdo)$_2$]

In the unit cell of [Ni(BF_2afdo)$_2$], the Ni atoms in the adjacent molecules are at a distance of 5.669(2) Å which is markedly longer than Pd–Pd separation of 3.465(4) Å in [Pd(Hafdo)$_2$] [3]. Contrasting [Pd(Hafdo)$_2$] and several dimeric [Ni(BF_2dmg)$_2$] complexes [13–16], the [Ni(BF_2afdo)$_2$] monomers do not form columnar chains excluding any possibilities of having uni-directional electrical conduction properties which were predicted [3] for the [Pd(Hafdo)$_2$] and were experimentally observed [4] in several short hydrogen bonded vic-glyoximates.

Molecular Structure of [Ni(BF_2afdo)$_2$]

A perspective view of the macrocycle is shown in Fig. 1. The site symmetry for the Ni atom is square planar (D_{4h}). In contrast to the planar [Pd(Hafdo)$_2$] molecule, the B atoms in [Ni(BF_2afdo)$_2$] are displaced 0.693(4) Å out of the plane of the macrocyclic ring. The substitution of the bridged hydrogen atoms by the BF_2 groups, removed planarity of the molecule normally required for columnar stacking. Non-planar arrangement favours dimerization or formation of monomeric species. The furan moieties are planar and are free to rotate about the C(1)–C(3) or C(2)–C(7) axes relative to the macrocycle plane. In the case of [Pd(Hafdo)$_2$] the furan moieties on adjacent molecules were interlocked and nearly coplanar to the macrocyclic ring similar to the interlocked methyl groups in [M(Hdmg)$_2$] complexes [12]. The non-bonding distance between the furan oxygen atoms, O(3) and O(4) is 2.669(4) Å and the atoms are positioned across each other without being involved in any intra- or inter-molecular bonding.

Except for the non-bonding metal–metal distance, all intramolecular distances and angles (Table IV) in the [Ni(BF_2afdo)$_2$] are in agreement with those observed in [Pd(Hafdo)$_2$] and other macrocyclic complexes listed in Table V. The average N–O and C=N distances agree with the corresponding distances in most of the vic-glyoximates (Table V).

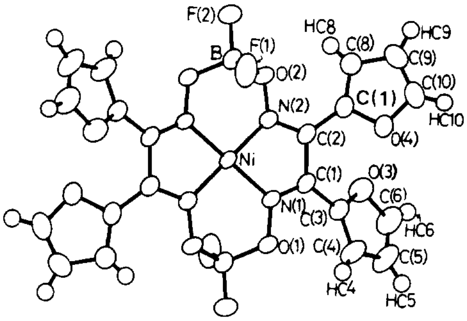

Fig. 1. ORTEP drawing (45% probability ellipsoid) of [Ni(BF_2afdo)$_2$] molecule showing labelling scheme and thermal vibration of atoms.

TABLE IV. Distances and Angles in $[Ni(BF_2afdo)_2]$

(a) Bonding distances (Å)

Ni–N(1)	1.845(2)	Ni–N(2)	1.847(2)
N(1)–O(1)	1.363(3)	N(2)–O(2)	1.357(3)
N(1)–C(1)	1.298(3)	N(2)–C(2)	1.309(3)
C(1)–C(3)	1.440(3)	C(2)–C(7)	1.440(4)
O(3)–C(3)	1.363(3)	O(4)–C(7)	1.378(3)
O(3)–C(6)	1.356(4)	O(4)–C(10)	1.363(4)
C(3)–C(4)	1.344(4)	C(7)–C(8)	1.345(4)
C(4)–C(5)	1.408(5)	C(8)–C(9)	1.403(4)
C(5)–C(6)	1.318(6)	C(9)–C(10)	1.324(5)
O(1)–B	1.484(4)	O(2)–B	1.501(4)
F(1)–B	1.366(4)	F(2)–B	1.353(4)
C(1)–C(2)	1.490(4)	C(8)–HC(8)	0.87(4)
C(4)–HC(4)	0.89(3)	C(9)–HC(9)	0.94(4)
C(5)–HC(5)	0.91(4)	C(10)–HC(10)	0.94(4)
C(6)–HC(6)	0.93(4)		

(b) Bonding angles (°)

N(1)–Ni–N(2)	82.34(9)	N(1)–Ni–N(2)	97.66(9)
Ni–N(1)–O(1)	124.6(2)	Ni–N(2)–O(2)	125.3(2)
Ni–N(1)–C(1)	117.6(2)	Ni–N(2)–C(2)	117.2(2)
C(1)–N(1)–O(1)	117.5(2)	C(2)–N(2)–O(2)	117.2(2)
C(7)–O(4)–C(10)	105.2(3)	C(3)–O(3)–C(6)	106.1(3)
N(2)–C(2)–C(1)	110.8(2)	N(2)–C(2)–C(7)	123.6(3)
C(1)–C(2)–C(7)	125.4(2)	O(3)–C(3)–C(1)	115.6(3)
O(3)–C(3)–C(4)	109.6(3)	C(2)–C(1)–C(3)	124.6(3)
C(1)–C(3)–C(4)	134.8(3)	C(3)–C(4)–C(5)	106.5(3)
C(4)–C(5)–C(6)	106.9(3)	O(3)–C(6)–C(5)	110.9(4)
O(4)–C(7)–C(8)	109.7(3)	O(4)–C(7)–C(2)	115.1(3)
C(2)–C(7)–C(8)	135.1(3)	C(7)–C(8)–C(9)	107.0(3)
N(1)–C(1)–C(3)	124.6(3)	N(1)–C(1)–C(2)	110.7(3)
N(1)–O(1)–B	114.1(2)	N(2)–O(2)–B	114.4(3)
C(8)–C(9)–C(10)	106.8(3)	O(4)–C(10)–C(9)	111.4(3)
O(1)–B–F(2)	106.1(3)	F(1)–B–F(2)	114.5(3)
O(2)–B–F(2)	106.9(3)	O(1)–B–F(1)	109.2(3)
O(2)–B–F(1)	109.7(3)	O(1)–B–O(2)	112.8(3)

The Ni–N distance also agrees with the corresponding distance in other nickel(II) macrocycles. In uncyclized $[Pd(Hafdo)_2]$ complex the Pd–N distance is significantly longer (about 0.1 Å) than the Ni–N distance, probably an effect of molecular constraints.

The 82.34(9)° chelate angle in the present complex agrees with 83.3(9)° observed in $[Ni(BF_2dmg)_2]$ and differs from 79.4(2)° observed in $[Pd(Hafdo)_2]$. The average CNO angle of 117.3(2)° in the present compound is 2° to 6° smaller than that observed in $[Ni(BF_2dmg)_2]$ and $[Pd(Hafdo)_2]$. The angles around the B atoms averaged to 109.9(3)° as expected for tetrahedral geometry. The average NOB angle of 114.3(2)° is slightly larger than the regular tetrahedral angle. The non-bonding intramolecular BF_2 bridged O---O distance of 2.486(3) Å is close to the O---O separation of 2.46(2) Å in $[Ni(BF_2dmg)_2]$ and is shorter than the hydrogen bridged O---O distance of 2.583(4) Å in $[Pd(Hafdo)_2]$.

The most important features of spectroscopic and X-ray structure analysis of $[Ni(BF_2afdo)_2]$ are: (a) the lack of columnar stacking (hence absence of metal–metal interactions), as compared to $[Pd(Hafdo)_2]$, $[M(Hdmg)_2]$ (where M = Ni(II), Pd(II) and Pt(II)) and several 1:1 adducts of $[Ni(Hdmg)_2]$, (b) the dissimilarity in packing requirements of methyl and furan groups in the macrocycles as compared to the uncyclized complexes of H_2afdo and H_2dmg, and (c) the formation of monomeric species on macrocyclization of H_2afdo complexes in contrast to dimerization in the H_2dmg complexes.

Supplementary Material

Anisotropic thermal parameters in the form of *U* values, structure factors tables and LS planes tables are available on request.

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TABLE V. Comparison of some Important Distances in $[Ni(BF_2afdo)_2]$ with Related Complexes

Compound	M–M	O---O	M–N	N–O	C=N	Reference
$[Pd(Hafdo)_2]$	3.465(4)	2.583(4)	1.972(5)	1.352(4)	1.305(6)	3
$[Ni(BF_2dmg)_2]$	3.207(6)	2.46(2)	1.87(1)	1.35(2)	1.29(3)	13
$[Ni(BF_2dmg)_2L]$[b]	3.358(2)	–	1.848(6)	1.352(7)	1.302(9)	15
$[Ni(BF_2dmg)_2L[$[c]	3.654(2)	–	1.867(6)	1.381(8)	1.297(10)	16
$[Ni(BF_2dmg)_2L]$[d]	3.909(3)	–	1.85(1)	1.39(2)	1.28(2)	14
$[Ni(BF_2afdo)_2]$	5.669(2)	2.486(3)	1.846(2)	1.361(3)	1.304(3)	a

[a] Present work. [b] L = benzimidazole. [c] L = aniline. [d] L = 4,4′-bipyridine.

References

1 A. Khan, *M.S. Thesis,* College of Graduate Studies, University of Petroleum and Minerals, Dhahran, Saudi Arabia, December 1985.

2 I. V. Khoroshun, N. N. Proskina, O. A. Bologa and Zh. Yu. Vaisbein, *Russ. J. Inorg. Chem., 26,* 696 (1981).

3 M. S. Hussain, S. A. A. Al-Hamoud, M. Z. El-Faer and A. Khan, *J. Coord. Chem., 14,* 91 (1985).

4 T. W. Thomas and A. E. Underhill, *Chem. Soc. Rev.,* 99 (1972).

5 L. E. Godycki and R. E. Rundle, *Acta Crystallogr., 6,* 487 (1953).

6 G. N. Schrauzer, *Chem. Ber., 95,* 1438 (1962).

7 J. M. Pratt and P. J. Graig, *Adv. Organomet. Chem., 11,* 331 (1973).

8 G. McLendem and A. E. Martall, *Coord. Chem. Rev., 19,* 1 (1976).

9 E. O. Schlemper, R. K. Murmann and M. S. Hussain, *Acta Crystallogr., Sect. C,* (1987), in press.

10 K. Burger, I. Ruff and F. Ruff, *J. Inorg. Nucl. Chem., 27,* 179 (1965).

11 J. Csaszar and K. Fugedi, *Acta Chim. Hung., 32,* 451 (1962).

12 M. S. Hussain, B. E. V. Salinas and E. O. Schlemper, *Acta Crystallogr., Sect. B, 35,* 628 (1979).

13 F. S. Stephens and R. S. Vagg, *Acta Crystallogr., Sect. B, 33,* 3159 (1977).

14 F. S. Stephens and R. S. Vagg, *Inorg. Chim. Acta, 42,* 139 (1980).

15 F. S. Stephens and R. S. Vagg, *Inorg. Chim. Acta, 43,* 77 (1980).

16 R. S. Vagg and E. C. Watton, *Acta Crystallogr., Sect. B, 34,* 2715 (1978).