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# Studies on Macrocyclic Complexes Derived from *vic*-Dioximes.
# Part VII*. Bis(difluoroboronglyoximato)nickel(II) Complexes and their Reactions with Nitrogenous Bases

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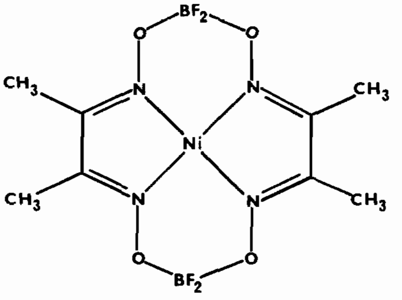
*A number of complexes of the form* $[Ni(F_2BON{:}CR{\cdot}CR'{:}NO)_2]$ *where* $R = R' = H$, $CH_3$ *or* $C_6H_5$ *and* $R = H$, $R' = CH_3$ *have been obtained by the addition of* $BF_3{\cdot}O(C_2H_5)_2$ *to the parent nickel(II) glyoximates. The products isolated on reaction of these complexes with monodentate and bidentate nitrogenous bases have been characterized by microanalysis, visible, NMR and mass spectral data and by thermal and magnetic studies. In the main stable diamagnetic 1:1 adducts are obtained with the monodentate bases and paramagnetic 1:1 complexes with the bidentates chosen. The central metal atom may be displaced from the macrocycle using 1,2-diaminoethane with resultant salt formation, and an interesting reaction with iodomethane in the presence of base is reported. Postulates of metal stereochemistry are made with reference to earlier reported crystal structures. The type of adduct formed appears to be influenced by the choice of glyoxime substituents (R and R').*

## Introduction

Schrauzer [1] first reported the reaction of $BF_3$ with bis(dimethylglyoximato)nickel(II) to yield the yellow planar macrocyclic complex Ni(dmg-$BF_2$), (I). He noted that its reaction with pyridine, piperidine or ammonia resulted in the formation of unstable 2:1 adducts, presumed to be six-coordinate, that retained the diamagnetic character of the parent. From solution studies, in which evidence only for 1:1 adduct formation was obtained, Graddon and Siddiqi [2] noted that adduct stability appeared not to depend on the formation of new Ni–N σ-bonds, and concluded that the main forces holding the adducts together would be van der Waals interactions or metal–ligand $d_\pi \rightarrow p_\pi$ bonding.



(I)

Our own studies have shown the parent macrocycle $Ni(dmgBF_2)_2$ to be dimeric both in the solid state [3] and in solution [4]. This dimeric nature is retained on 1:1 adduct formation with both aniline [4, 5] and 4,4'-bipyridine [6], where Ni–N σ-bonding is apparent, and with benzimidazole [7] in which case no Ni–N (ligand) bond exists but rather a π–π interaction alone between the planar molecules is suggested. Reaction of the diphenyl-substituted analogue $Ni(dpgBF_2)_2$ with 1,10-phenanthroline results in severe distortion of the macrocycle, accompanied by an increase in the Ni–N (glyoxime) bond lengths, with consequent formation of a high-spin six-coordinate monomeric 1:1 adduct [8].

The structural chemistry of these complexes would appear to be unique, and their modes of adduct formation quite various. We now report in detail the isolation and characterization of a series of these and other such adducts with a number of substituted glyoximates. Throughout the paper the following abbreviations have been used in the formulae to represent the bases.

| | |
|---|---|
| an | : aniline |
| benzim | : benzimidazole |
| 2,2'-bipy | : 2,2'-bipyridine |
| 4,4'-bipy | : 4,4'-bipyridine |
| 4-clan | : 4-chloroaniline |
| en | : 1,2-diaminoethane (ethylenediamine) |
| im | : imidazole |
| $imCH_3$ | : N-methylimidazolium cation |
| $2\text{-}NH_2py$ | : 2-aminopyridine |
| 4-mean | : methylaniline |

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*Part VI is reference [7].

*o*-phd : 1,2-diaminobenzene (*o*-phenylenediamine)
*o*-phen : 1,10-phenanthroline
pip : piperidine
pip$CH_3$ : N-methylpiperidinium cation

## Experimental

### *Physical Measurements and Analyses*

Magnetic moments were determined at room temperature using a Newport Single Temperature Gouy Balance (Model SM-12). Visible spectra were recorded in the range 400–1000 nm on a Carl-Zeiss PMQII spectrophotometer with an RA reflectance attachment calibrated against magnesium oxide. Thermogravimetric studies were carried out on a Stanton-Redcroft balance (Model TG-750) in conjunction with a direct-readout recorder. Nuclear Magnetic Resonance spectra were recorded on a Bruker WH90 spectrometer at the University of Surrey, and are reported in parts per million downfield from an internal standard of tetramethylsilane. Mass spectra were recorded on an AEI MS12 electron impact source mass spectrometer. Carbon, hydrogen, nitrogen and halide were determined in the C.S.I.R.O. Microanalytical Laboratory, Melbourne, Australia or by the Microanalytical Service, Department of Chemistry, University of Surrey. Nickel was determined by volumetric titration with EDTA [9].

### *Synthesis of Compounds*

#### *(a) Starting Materials*

Glyoxime, dimethylgyloxime, diphenylglyoxime and the bases were commercial grade chemicals used as obtained. Methylglyoxime was prepared by the reaction of methylglyoxal with acidified hydroxylamine hydrochloride [10]. Bis(glyoximato)-bis(methylglyoximato)-, bis(dimethylglyoximato)- and bis(diphenylglyoximato)nickel(II) were each prepared by reaction of the appropriate dioxime with an ammoniacal solution of nickel sulphate or acetate.

#### *(b) Parent Macrocyclic Chelates*

A suspension of each of the nickel-glyoximates in either dichloromethane or chloroform was reacted with borontrifluoride-diethyletherate according to the method of Schrauzer [1] to yield the following products.

##### *Bis(difluoroboronglyoximato)nickel(II) monohydrate, $Ni(gBF_2)_2 \cdot H_2O$*

The initial product was recrystallised from acetone/chloroform to yield a bright yellow microcrystalline solid. *Anal.* Found: C, 13.9; H, 1.9; N, 15.3%. Calcd. for $C_4H_6B_2F_4N_4O_5Ni$: C, 13.9; H, 1.7; N, 16.2%. On prolonged standing the monohydrate form is unstable, the colour slowly changing to blue-green. Dehydration of the compoud is easily attained by gentle heating (Wt. loss: 5.0%; Calcd.: 5.2%), the resultant anhydrous form being quite stable.

##### *Bis(difluoroboronmethylglyoximato)nickel(II), $Ni(mgBF_2)_2$*

Recrystallization from acetone yielded a bright-yellow microcrystalline solid. *Anal.* Found: C, 20.6; H, 2.2; N, 15.7; Ni, 16.0%. Calcd. for $C_6H_8B_2F_4N_4O_4Ni$: C, 20.2; H, 2.3; N, 15.7; Ni, 16.5%.

##### *Bis(difluoroborondimethylglyoximato)nickel(II), $Ni(dmgBF_2)_2$*

Recrystallization from acetone yielded long yellow needles.*Anal.* Found: C, 25.1; H, 3.1; N, 14.8; Ni, 15.4%. Calcd. for $C_8H_{12}B_2F_4N_4O_4Ni$: C, 25.1; H, 3.1; N, 14.6; Ni, 15.3%.

##### *Bis(difluoroborondiphenylglyoximato)nickel(II) monohydrate; $Ni(dpgBF_2)_2 \cdot H_2O$*

Recrystallization from dichloromethane yielded small orange/yellow needles. *Anal.* Found: C, 51.5; H, 3.4; N, 8.7; Ni, 9.1%. Calcd. for $C_{28}H_{22}B_2F_4N_4O_5Ni$: C, 51.6; H, 3.4; N, 8.6; Ni, 9.0%. The complex may be dehydrated by gentle heating (Wt. loss: 2.8%; Calcd. 2.8%), although unlike the unsubstituted analogue the monohydrate form is quite stable on prolonged standing. *Anal.* Found: C, 53.4; H, 3.6; N, 8.6%. Calcd. for $C_{28}H_{20}B_2F_4N_4O_4Ni$: C, 53.2; H, 3.2; N, 8.8%.

#### *(c) 1:1 Base Adducts*

The compounds $Ni(gBF_2)_2$(*o*-phen), $Ni(mgBF_2)_2$(*o*-phen), $Ni(dmgBF_2)_2$(*o*-phen), $Ni(dpgBF_2)_2$(*o*-phen)$\cdot 6H_2O$, $Ni(mgBF_2)_2$(2,2′-bipy)$\cdot 0.5H_2O$, $Ni(dmgBF_2)_2$(4,4′-bipy), $Ni(dmgBF_2)_2$(an), $Ni(dmgBF_2)_2$(2-$NH_2$py), $Ni(dmgBF_2)_2$(4-mean), $Ni(dmgBF_2)_2$(*o*-phd), $Ni(dpgBF_2)_2$(*o*-phd), and $Ni(dmgBF_2)_2$(benzim) were all prepared by reaction of an excess of the appropriate base with a warm solution of the macrocyclic parent in either chloroform, acetone, acetonitrile or dichloromethane as solvent. In general crystalline products were obtained on standing which were filtered off, washed with a minimum quantity of solvent and air-dried. The use of anhydrous acetone as solvent in the reaction of $Ni(dpgBF_2)_2$ with 1,10-phenanthroline resulted in the formation of an orange/red diacetone solvate species of $Ni(dpgBF_2)_2$(*o*-phen) [8].

$Ni(dmgBF_2)_2$(en) was prepared by the slow dropwise addition of a stoichiometric quantity of 1,2-diaminoethane in acetonitrile to a warm solution of $Ni(dmgBF_2)_2$ in the same solvent.

TABLE I. Analyses of Base Adducts (a check on % base is provided in Table III).

| Complex | % Found | | | | % Calcd. | | | |
|---|---|---|---|---|---|---|---|---|
| | C | H | N | Other | C | H | N | Other |
| Ni(gBF$_2$)$_2$(*o*-phen) | 37.5 | 2.2 | 16.5 | | 37.8 | 2.4 | 16.5 | |
| Ni(mgBF$_2$)$_2$(*o*-phen) | 40.2 | 3.1 | 15.3 | Ni: 10.8 | 40.3 | 3.0 | 15.7 | Ni: 10.9 |
| Ni(dmgBF$_2$)$_2$(*o*-phen) | 42.7 | 4.0 | 15.1 | | 42.5 | 3.6 | 14.9 | |
| Ni(dpgBF$_2$)$_2$(*o*-phen)·6H$_2$O | 51.8 | 4.3 | 9.3 | Ni: 7.0 | 52.2 | 4.4 | 9.1 | Ni: 6.4 |
| Ni(mgBF$_2$)$_2$(2,2′-bipy)·0.5H$_2$O | 36.6 | 3.3 | 16.3 | Ni: 10.6 | 36.8 | 3.3 | 16.1 | Ni: 11.2 |
| Ni(dmgBF$_2$)$_2$(en) | 27.3 | 4.6 | 18.7 | Ni: 13.4 | 27.1 | 5.0 | 18.9 | Ni: 13.2 |
| Ni(dmgBF$_2$)$_2$(an) | 35.3 | 4.1 | 14.5 | | 35.2 | 4.0 | 14.7 | |
| Ni(dmgBF$_2$)$_2$(*o*-phd) | 34.0 | 4.1 | 17.0 | | 34.1 | 4.1 | 17.1 | |
| Ni(dpgBF$_2$)$_2$(*o*-phd) | 54.8 | 4.0 | 11.8 | | 55.1 | 4.1 | 11.3 | |
| Ni(dmgBF$_2$)$_2$(4,4′-bipy) | 39.4 | 4.5 | 14.6 | | 40.0 | 3.7 | 15.5 | |
| [Ni(dmgBF$_2$)$_2$]$_2$(4,4′-bipy) | 33.9 | 3.7 | 15.1 | Ni: 12.3 | 33.8 | 3.5 | 15.1 | Ni: 12.7 |
| Ni(dmgBF$_2$)$_2$(4-mean) | 36.9 | 4.4 | 13.4 | | 36.6 | 4.3 | 14.2 | |
| Ni(dmgBF$_2$)$_2$(2-NH$_2$py) | 32.6 | 3.8 | 17.5 | | 32.6 | 3.8 | 17.6 | |
| Ni(dmgBF$_2$)$_2$(benzim) | 36.2 | 3.6 | 16.8 | Ni: 11.0 | 35.8 | 3.6 | 16.7 | Ni: 11.7 |
| Ni(dmgBF$_2$)$_2$(4-clan)$_4$ | 42.5 | 4.2 | 12.2 | Cl: 15.6 | 42.9 | 4.0 | 12.5 | Cl: 15.8 |
| Ni(dpgBF$_2$)$_2$(im)·H$_2$O | 51.5 | 4.0 | 13.8 | Ni: 7.1 | 51.9 | 3.8 | 14.2 | Ni: 7.5 |
| [Ni(en)$_3$][(dmgBF$_2$)$_2$] | 29.6 | 6.4 | 24.5 | Ni: 9.8 | 29.8 | 6.4 | 24.8 | Ni: 10.4 |
| [Ni(en)$_3$][(mgBF$_2$)$_2$]·1.5H$_2$O | 25.5 | 6.3 | 24.3 | Ni: 10.6 | 25.6 | 6.3 | 24.8 | Ni: 10.4 |
| (imCH$_3$)Ni(dmgBF$_2$)$_2$I | 25.3 | 3.7 | 14.7 | | 25.1 | 3.4 | 14.7 | |
| (pipCH$_3$)$_2$Ni(dmgBF$_2$)$_2$I$_2$ | 29.6 | 5.0 | 9.9 | Ni: 7.0<br>I: 32.4 | 28.6 | 4.8 | 10.0 | Ni: 7.0<br>I: 30.3 |

### *(d) Other Complexes*

*[Ni(dmgBF$_2$)$_2$]$_2$(4,4′-bipy)*

The 1:1 addition of 4,4′-bipyridine dihydrate to Ni(dmgBF$_2$)$_2$ in warm acetone solution resulted in red/brown microcrystals of 1:2 stoichiometry.

*Ni(dmgBF$_2$)$_2$(4-clan)$_4$*

The reaction of Ni(dmgBF$_2$)$_2$ with an excess of 4-chloroaniline in acetone yielded dark red crystals of the above formula.

*Ni(dpgBF$_2$)$_2$(im)$_2$·H$_2$O*

This complex crystallised readily from the reaction of an excess of imidazole in acetone with Ni(dpgBF$_2$)$_2$ in warm dichloromethane.

*[Ni(en)$_3$] [(dmgBF$_2$)$_2$] and [Ni(en)$_3$] [(mgBF$_2$)$_2$]·1.5H$_2$O*

These two mauve microcrystalline salts were prepared by the addition of an excess of 1,2-diaminoethane to a warm solution of the appropriate macrocyclic parent in either chloroform or dichloromethane. The products, which precipitated immediately in quantitative yield, were filtered off, washed with the solvent followed by diethylether and air dried.

*(imCH$_3$)Ni(dmgBF$_2$)$_2$I and (pipCH$_3$)$_2$Ni(dmgBF$_2$)$_2$I$_2$*

To a mixture of Ni(dmgBF$_2$)$_2$ and iodomethane in warm acetone or acetonitrile was added imidazole in acetone. An immediate deep-red colour was produced. The solution was filtered to remove any white crystalline N-methylimidazolium iodide which had formed. The solution was reduced in volume, 60–80 petroleum ether added and the mixture allowed to stand. The very deep-red needle crystals of (imCH$_3$)Ni(dmgBF$_2$)$_2$I which formed were filtered off, washed with a minimum of acetone/ether solvent mixture and air dried. (pipCH$_3$)$_2$Ni(dmgBF$_2$)$_2$I$_2$ was prepared by an analogous method. In this case the piperidine addition resulted in an immediate exothermic reaction with precipitation of some N-methylpiperidinium iodide.

The results of elemental analyses on the products are given in Table I.

## **Results and Discussion**

The tendency to form base adducts, and the stabilities of the resultant solid products, was observed to vary both with differences in the base chosen and in the glyoxime substituent. The complexes reported

TABLE II. Properties of Macrocyclic Complexes.

| Complex | Appearance | Mag. Mom. (B.M.) | Known or Proposed Structure |
|---|---|---|---|
| $Ni(gBF_2)_2 \cdot H_2O$ | yellow needles | diam. | sq. planar |
| $Ni(mgBF_2)_2$ | yellow needles | diam. | sq. planar |
| $Ni(dmgBF_2)_2$ | yellow needles | diam. | sq. planar, dimeric [3] |
| $Ni(dpgBF_2)_2 \cdot H_2O$ | yellow/orange needles | diam. | sq. planar |
| $Ni(gBF_2)_2$(*o*-phen) | v. pale green | 3.61 | distorted octahedral monomer |
| $Ni(mgBF_2)_2$(*o*-phen) | grey/green | 3.00 | distorted octahedral monomer |
| $Ni(dmgBF_2)_2$(*o*-phen) | buff | 3.30 | distorted octahedral monomer |
| $Ni(dpgBF_2)_2$(*o*-phen)$\cdot 6H_2O$ | orange-red | 3.26 | distorted octahedral monomer [8] |
| $Ni(mgBF_2)_2$(2,2'-bipy)$\cdot 0.5H_2O$ | brown | 3.05 | distorted octahedral monomer |
| $Ni(dmgBF_2)_2$(en) | red | 2.97 | octahedral monomer or chain |
| $Ni(dmgBF_2)_2$(an) | scarlet plates | diam. | sq. pyramidal, dimeric [5] |
| $Ni(dmgBF_2)_2$(*o*-phd) | dark red needles | diam. | sq. pyramidal, dimeric |
| $Ni(dpgBF_2)_2$(*o*-phd) | dark red-brown | diam. | sq. pyramidal |
| $Ni(dmgBF_2)_2$(4,4'-bipy) | deep red plates | diam. | sq. pyramidal dimeric chain [6] |
| $[Ni(dmgBF_2)_2]_2$(4,4'-bipy) | red-brown | diam. | sq. pyramidal, dimeric chain |
| $Ni(dmgBF_2)_2$(4-mean) | scarlet | diam. | sq. pyramidal, dimeric |
| $Ni(dmgBF_2)_2(2\text{-}NH_2py)$ | dark orange | diam. | sq. pyramidal, dimeric |
| $Ni(dmgBF_2)_2$(benzim) | dark amber crystals | diam. | sq. planar, dimeric [7] |
| $Ni(dmgBF_2)_2(4\text{-clan})_4$ | dark red | diam. | sq. pyramidal, dimeric |
| $Ni(dpgBF_2)_2(im)_2 \cdot H_2O$ | purple | 3.22 | octahedral monomer |
| $[Ni(en)_3][(dmgBF_2)_2]$ | pink-mauve | 3.02 | octahedral salt |
| $[Ni(en)_3][(mgBF_2)_2] \cdot 1.5H_2O$ | pale mauve | 2.99 | octahedral salt |
| $(imCH_3)Ni(dmgBF_2)_2I$ | v. deep red needles | diam. | indefinite |
| $(pipCH_3)_2Ni(dmgBF_2)_2I_2$ | red-black crystals | diam. | indefinite |

in detail in this paper are each stable as solids over prolonged periods of time. Several others similarly isolated proved to be quite unstable in the solid form resulting in loss of base and reversion to the parent macrocycle. In general these complexes were characterized solely by their magnetic properties and thermal analysis of base composition. Where considered appropriate some will be referred to in the text for comparative purposes.

The physical appearance and magnetic properties of each of the stable complex products are given in Table II, together with proposed metal stereochemistries. The yellow diamagnetic parent macrocycles may be taken as planar, each possibly dimeric in nature as demonstrated in the dimethyl-substituted compound [3, 4], with water acting only as a solvate molecule in the two monohydrate complexes. The mass spectrum of each of these complexes shows a strong signal attributable to the parent, with no evidence for dimeric character in the gaseous state.

The reaction of each of these macrocycles with 1,10-phenanthroline yields a 1:1 adduct which is

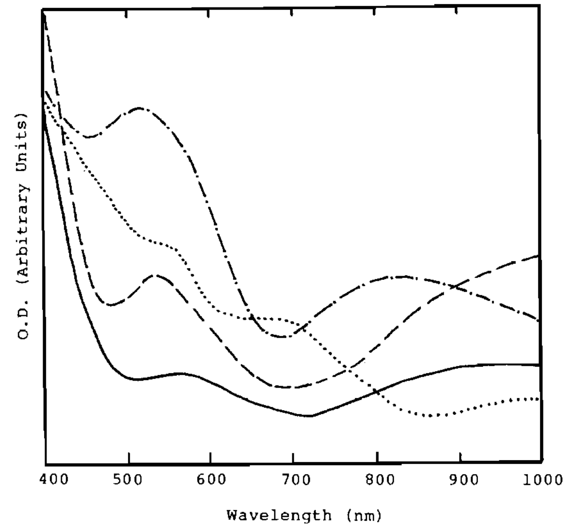


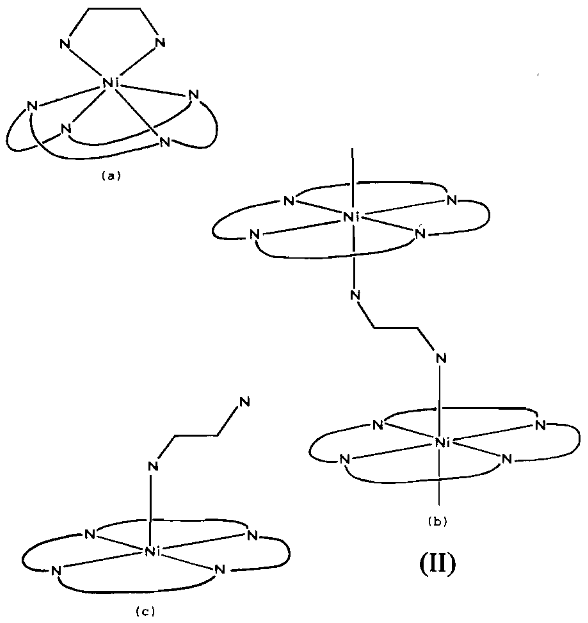
Fig. 1. Diffuse reflectance spectra of *o*-phen adducts. (———) $Ni(gBF_2)_2$(*o*-phen); (········) $Ni(mgBF_2)$(*o*-phen); (– – –) $Ni(dmgBF_2)_2$(*o*-phen); (–·–·–) $Ni(dpgBF_2)_2$(*o*-phen)$\cdot 6H_2O$.

TABLE III. Results of Thermogravimetric Studies.

| Complex | Temp. Range (°C) | Volatile Product | Wt. Loss (%) | | Residue Colour |
|---|---|---|---|---|---|
| | | | Calcd. | Found | |
| $Ni(gBF_2)_2$(*o*-phen) | 220–240<br>(rapid) | *o*-phen | 35.4 | 36.0 | black |
| $Ni(mgBF_2)_2$(*o*-phen) | 200–280 | *o*-phen | 33.5 | 33.5 | black |
| $Ni(dmgBF_2)_2$(*o*-phen) | 240<br>(rapid) | *o*-phen | 31.9 | 31.9 | black |
| $Ni(dpgBF_2)_2$(*o*-phen)$\cdot 6H_2O$ | 80–140 | $6H_2O$ | 11.6 | 10.7 | red |
| | 220–250 | *o*-phen | 19.4 | 20.5 | black |
| $Ni(mgBF_2)_2$(2,2′-bipy)$\cdot 0.5H_2O$ | 90–120 | ½ $H_2O$ | 1.7 | 2.0 | pale brown |
| | 180–300<br>(slow) | 2,2′-bipy | 29.9 | 29.0 | brown |
| $Ni(dmgBF_2)_2$(en) | 180–250 | en | 13.6 | 14.0 | grey |
| $Ni(dmgBF_2)_2$(an) | 115–160 | an | 19.5 | 19.4 | yellow |
| $Ni(dmgBF_2)_2$(*o*-phd) | 150–220 | *o*-phd | 22.0 | 21.7 | yellow |
| $Ni(dpgBF_2)_2$(*o*-phd) | 150–190 | *o*-phd | 14.6 | 17.0 | dark orange |
| $Ni(dmgBF_2)_2$(4,4′-bipy) | 130–150 | ½ 4,4′-bipy | 14.4 | 14.0 | brown |
| | 160–200 | ½ 4,4′-bipy | 14.4 | 14.0 | yellow |
| $[Ni(dmgBF_2)_2]_2$(4,4′-bipy) | 170–200 | 4,4′-bipy | 16.9 | 16.8 | yellow |
| $Ni(dmgBF_2)_2$(4-mean) | 105–170 | 4-mean | 21.8 | 22.5 | yellow |
| $Ni(dmgBF_2)_2$(2-$NH_2$py) | 120–150 | 2-$NH_2$py | 19.7 | 19.2 | yellow |
| $Ni(dmgBF_2)_2$(benzim) | 205–220 | benzim | 23.5 | 22.4 | yellow |
| $Ni(dmgBF_2)_2$(4-clan)$_4$ | 60–160 | 4-clan | 57.0 | 58.0 | yellow |
| $Ni(dpgBF_2)_2(im)_2\cdot H_2O$ | 40–60 | $H_2O$ | 2.3 | 3.0 | purple |
| | 85–180 | 2 im | 17.3 | 17.2 | orange/yellow |
| $[Ni(en)_3][(dmgBF_2)_2]$ | 100–110 | ½ en | 5.3 | 5.6 | pink |
| | 120–170 | 2 en | 21.3 | 21.4 | orange |
| | 180–230 | ½ en | 5.3 | 6.0 | black |
| $[Ni(en)_3][(mgBF_2)_2]\cdot 1.5H_2O$ | 40–100 | $1.5H_2O$ + ½ en | 10.1 | 9.6 | pink |
| | 115–185 | 2 en | 21.3 | 22.0 | brown |
| | 200–260 | ½ en | 5.3 | 5.6 | black |

paramagnetic. With 2,2′-bipyridine $Ni(mgBF_2)_2$ was the only parent observed to react, the product being the paramagnetic 1:1 complex $Ni(mgBF_2)_2$(2,2′-bipy)$\cdot 0.5H_2O$. The controlled addition of 1,2-diaminoethane to $Ni(dmgBF_2)_2$ results also in the like adduct $Ni(dmgBF_2)_2$(en). Each of these compounds shows absorption in the visible-spectral range (Fig. 1), and six-co-ordination is readily concluded. For *o*-phen and 2,2′-bipy this necessarily would be attained by addition of the bidentate base in *cis*-positions above the macrocyclic plane, leading to severe molecular distortions and an increase in the ionic radius of the metal atom on changing to the high-spin state. Such a form (IIa) already has been structurally characterized in the *o*-phen adduct of $Ni(dpgBF_2)_2$ [8]. It is most likely that a similar coordination mode exists in $Ni(dmgBF_2)_2$(en), although bridging of monomer units to form a polymeric octahedral chain (IIb) or a high-spin 5-coordinate species involving only monodentate function of en (IIc) remain alternative structural possibilities. Upon heating to remove the base (Table III) each of these compounds returns not to the yellow parent complex but rather to amorphous material of like formula.

Schrauzer [1] first observed the formation of diamagnetic labile 2:1 adducts with the monodentate amines pyridine, piperidine and ammonia. We have isolated several like complexes with volatile monodentate amines and each of the parent macrocycles. $Ni(dpgBF_2)_2$ forms 2:1 adducts of relatively low lability with pyridine and similar N-heterocycles, whereas analogous adducts with a lower degree of glyoxime substitution are quite labile. An analysis of the rate of base loss for these compounds generally shows two equal and distinct



(II)

steps, implying that one base molecule is more firmly held than the other.

Use of the non-volatile bifunctional base 4,4'-bipyridine leads to two interesting products, of general formulae $Ni(dmgBF_2)_2(4,4'\text{-bipy})$ and $[Ni(dmgBF_2)_2]_2(4,4'\text{-bipy})$. Considering the pyridine moieties in 4,4'-bipy as individual monodentate groups these complexes would correspond to 2:1 and 1:1 base adducts respectively. The crystal structure of the former complex had recently been reported [6], and shows each Ni atom to be five-coordinate with 4,4'-bipyridine bridging dimer units of the parent. The remaining half 4,4'-bipyridine per formula unit acts solely as a solvate, occupying channels in the crystal lattice. Presumably a similar bonding mode exists in the other 4,4'-bipyridine compound, but with a crystal lattice not requiring solvation. Thermal analysis of the solvated form (Table III) shows the base to be lost in two steps, the latter corresponding to decomposition of the non-solvated complex. These results imply that the 2:1 base adducts thought originally [1] to be examples of six-coordinate low-spin nickel(II) in fact may be 1:1 adducts in base-solvated form. This conclusion would be in full accord with results from solution studies [2].

The reaction of $Ni(dmgBF_2)_2$ with substituted anilines generally leads to stable deeply coloured 1:1 adducts that are diamagnetic (Table II). Apart from charge-transfer no absorption is observed for these complexes in the visible region (Fig. 2). The X-ray structure determination of the unsubstituted aniline compound [5] shows addition of two molecules of aniline to each end of the dimeric parent to have occurred. Each nickel atom is five-coordinate, and the structure appears to gain additional stability from a π–π interaction between parts of the macrocycles and the phenyl rings of the base. A like interaction had been postulated earlier for substituted-aniline adducts of cobaloximes [11]. Similar stereochemistries are now proposed for each of the diamagnetic adducts here reported. The potentially bidentate base 1,2-diaminobenzene appears to act solely as a monodentate, whilst 2-aminopyridine also would most likely coordinate through the amino group alone. The 4:1 adduct with 4-chloroaniline probably contains three base molecules per formula unit in a solvated form. This is supported by the compound's thermal properties, where initial melting to yield a deep-red liquid is followed by loss of base to yield the yellow parent macrocycle.

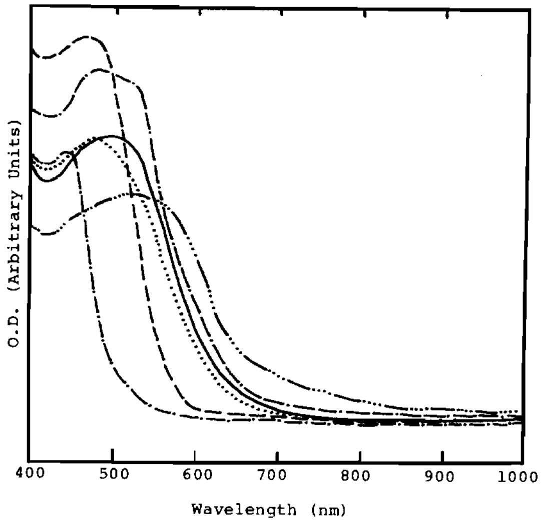


Fig. 2. Diffuse reflectance spectra of $Ni(dmgBF_2)_2$ and its substituted aniline adducts. (—·—·—) $Ni(dmgBF_2)_2$; (·······) $Ni(dmgBF_2)_2$(an); (··—··—··) $Ni(dmgBF_2)_2$(*o*-phd); (———) $Ni(dmgBF_2)_2$(4-mean); (– – – –) $Ni(dmgBF_2)_2$(2-$NH_2$py); (·— —·— —·) $Ni(dmgBF_2)_2$(4-clan).

The sole paramagnetic product obtained with a monodentate base, namely the imidazole adduct $Ni(dpgBF_2)_2(im)_2\cdot H_2O$, would appear to be the only example of a 2:1 octahedral adduct. Again analogous complexes were not obtained with a lower degree of glyoxime substitution. Presumably the compound is similar in structure to that of $Fe(dmgH)_2(im)_2\cdot 2CH_3OH$ [12], and might reflect to some extent the weak π-acceptor strength found in the imidazole ring [13]. Some distortion in the macrocycle may be necessary to accommodate the change to higher spin state.

The sterically hindered base benzimidazole forms a very interesting 1:1 adduct with $Ni(dmgBF_2)_2$. The complex has been shown [7] to contain dimeric macrocyclic units associated with the planar N-heterocycle not by Ni–N bond formation but rather by π–π interaction alone. Such a structure supports

TABLE IV. Proton Magnetic Resonance Data.

| Compound | Chemical Shift$^a$ $(CD_3)_2CO$ | [Relative Intensity] $(CD_3)_2SO$ | Assignment | |
|---|---|---|---|---|
| $Ni(dmgBF_2)_2$ | 2.29(s)$^b$ | 2.15(s) | C–$CH_3$ | (12H) |
| $Ni(dmgBF_2)_2$ + NaI | 2.07(s) | 2.10(s) | C–$CH_3$ | (12H) |
| $(imCH_3)Ni(dmgBF_2)_2I$ | 2.17(s) [11.8] | 2.16(s) [12.2] | C–$CH_3$ | (12H) |
| | 4.10(d) [3.3] | 3.84(s) [3.0] | N–$CH_3$ | (3H) |
| | 7.73(s) [1.8] | 7.65(s) [1.9] | N–CH–CH–N | (2H) |
| | 9.24(d) [0.9] | 8.99(d) [0.9] | N–CH–N | (1H) |
| $(pipCH_3)_2Ni(dmgBF_2)_2I_2$ | 1.73(q) [6.3]<br>2.0 (m) [5.2] | 1.5–1.8 (m) [12.0] | –$CH_2$–$CH_2$–$CH_2$– | (12H) |
| | 2.18(s) [12.4] | 2.15(s) [11.7] | C–$CH_3$ | (12H) |
| | | 2.74(s) [2.8] | N–H | (2H) |
| | 3.38(s) [6.1] | 3.06(s) [6.2] | N–$CH_3$ | (6H) |
| | 3.38(m) [4.2]<br>3.66(t) [3.7] | 3.32(t) [8.2] | –$CH_2$–N–$CH_2$– | (8H) |

$^a$Chemical Shifts in ppm relative to tetramethylsilane. $^b$s = singlet, d = doublet, t = triplet, q = quintet, m = unresolved multiplet.

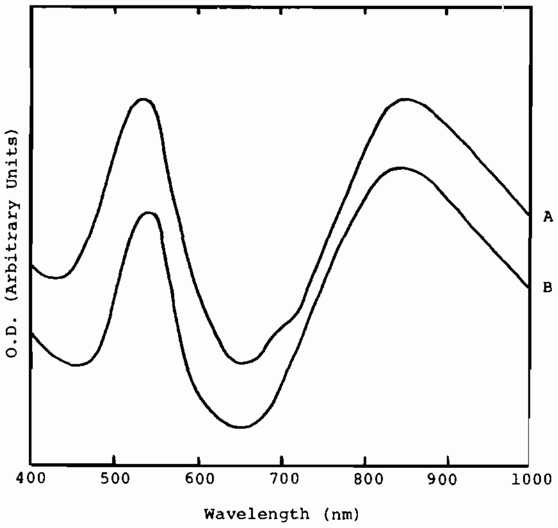


Fig. 3. Diffuse reflectance spectra of $[Ni(en)_3]^{2+}$ salts. A, $[Ni(en)_3][(dmgBF_2)_2]$; B, $[Ni(en)_3][(mgBF_2)_2]\cdot1.5H_2O$.

the postulation of a similar interaction occurring in the aniline adducts, and may account for the fact that those solid adducts are the most stable isolated with simple monodentates so far.

The reaction of the nickel-macrocycles with an excess of 1,2-diaminoethane leads to the immediate displacement of the metal atom by that base. The pale mauve salts $[Ni(en)_3][(dmgBF_2)_2]$ and $[Ni(en)_3][(mgBF_2)_2]\cdot1.5H_2O$ have solid-state visible spectra (Fig. 3) characteristic of the octahedral $[Ni(en)_3]^{2+}$ cation [14]. Their thermal decomposition patterns (Table III) show several steps that are attributable to loss of en, and their magnetic properties also indicate normal high-spin nickel(II). In these compounds the 14-membered macrocyclic ring must be present in a dianionic non-coordinated form, and the salts could be viewed as the final product resulting from initial severe distortions from planarity enforced by *cis*-bidentate function of the base [8].

As mimics of vitamin $B_{12}$ chemistry square-planar cob(I)aloximes and like complexes have been shown to be very powerful nucleophiles, evidenced by Co–$CH_3$ bond formation in the presence of iodomethane and a suitable N-heterocyclic base [15]. Since the parent Ni(II)-macrocycles described above would be isoelectronic with their Co(I) analogues it was considered of interest to investigate their reaction with those species. The addition of imidazole to a mixture of $Ni(dmgBF_2)_2$ and $CH_3I$ led immediately to the formation of an intense-red species in solution from which was isolated a solid product of empirical formula $Ni(dmgBR_2)_2(CH_3I)(im)$. Use of piperidine however yielded a deep red solid product of empirical formula $Ni(dmgBF_2)_2(CH_3I)_2(pip)_2$. Both compounds are diamagnetic and details of their NMR spectra, together with an interpretation, are given in Table IV. Similar deeply-coloured complexes were obtained with $Ni(dpgBF_2)_2$, although these compounds are not yet characterized.

The different stoichiometries of the compounds suggest that unlike Co(I) simple addition of –$CH_3$ and a base molecule to the metal atom in *trans* positions has not occurred. However the immediate colour formation in solution also would seem to negate the possibility of the complexes being derived solely from solid state effects similar to the solvation described earlier. In fact a like solution colour is obtained on reaction of $Ni(dmgBF_2)_2$ and sodium iodide in acetone. Thus the compounds would appear to be salts derived from the interaction of the parent macrocycle with iodide ion, and have been formulated as such in Tables I–IV. The determination of the site of that interaction, and its effect on the parent, await the results of further study.

In general our investigations thus far indicate that adduct formation with these macrocyclic chelates is largely dependent on the $\pi$-donor/acceptor abilities of the base, vindicating to some extent the conclusions of Graddon and Siddiqi [2]. The formation of strong Ni–N (base) $\sigma$-bonds might be expected to lead to an increase in the Ni····Ni separation of the dimeric parent to the point where octahedral 2:1 paramagnetic monomers result. The results of our continuing studies on these systems will form the basis of future communications.

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