

Alkoxy Boron-Bridged 14-Membered Macrocyclic Compounds of Nickel(II) with 1,1,8,8-Tetraalkoxy-1,8-dibora-4,5,11,12-tetrafuryl-3,6,10,13-tetraaza-2,7,9,14-tetraoxacyclotetradeca-3,5,10,12-tetraene

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A series of 14-membered alkoxyboron-bridged macrocyclic complexes of nickel(II) of the type NiL where L = 1,1,8,8-tetraalkoxy-1,8-dibora-4,5,11,12-tetrafuryl-3,6,10,13-tetraaza-2,7,9,14-tetraoxacyclotetradeca-3,5,10,12-tetraene have been prepared by adopting an *in situ* procedure using nickel(II) chloride, 1,2-difuryl ethane-1,2-dionedioxime and boric acid. The alkoxy groups have been derived from the solvent molecules. All the complexes are spin paired, crystalline and intense coloured solids. Infrared and electronic spectra show that they are isostructural and possess a nearly square planar configuration.

Key Words: Macrocycles, Nickel(II), Spectral study, Boron capping.

INTRODUCTION

In recent years, the chemistry of synthetic complexes containing macrocyclic ligands has commanded a great deal of attention^{1,2}. A part of the motivation for expanding considerable effort in the field has come from the continuing hope that a significantly more complete understanding of the chemistry of the naturally occurring macrocycles will be forthcoming from investigations of the synthetic ones^{3,4}.

We in continuation of our earlier interests in the field⁵⁻⁸, report a series of complexes of nickel(II) of the type NiL with the title ligand L (Fig. 1)

EXPERIMENTAL

All the chemicals used were BDH E.Merck or S. Merck reagents. 1,2-Difuryl-ethane-1,2-dionedioxime were prepared following literature procedures and their melting points agreed well with the reported values^{5,6}. All the compounds have been prepared under similar experimental condition and the preparation of one of the compounds is described here as an example.

1,1,8,8-Tetraethoxy-1,8-dibora-4,5,11,12-tetrafuryl-3,6,10,13-tetraaza-2,7,9,14-tetraoxacyclotetradeca-3,5,10,12-tetraene nickel(II): A mixture of

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$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (2.4 g, 0.01 mol), 1, 2-difurylthane-1,2-dione dioxime (2.6 g, 0.02 mol) and 40 mL of dry ethanol was stirred and refluxed for *ca.* 0.5 h on a water bath whereupon the solution gradually turned yellow and the colour deepened on slow addition of *ca.* 2.0 g of borax in small quantities during reflux. The solution thus obtained was allowed to concentrate by slow evaporation at room temperature over a period of several hours when a yellow crystalline product was obtained. It was filtered off, washed with small quantities of ethanol and recrystallized from acetonitrile. Yield was nearly 50%. Hydroxy, methoxy, ethoxy, isopropoxy and *n*-butoxy boron compounds were prepared using water, methanol, ethanol, iso-propanol and *n*-butanol, respectively as the solvent. Nickel in the complexes (Table-1) was analyzed at our laboratory using the standard procedure⁷. C, H and N analyses were done at CDRI, Lucknow. The analytical data are in good agreement with the reported formulae, NiL . IR spectra of the complexes were recorded in the range 4000-250 cm^{-1} on a Beckman spectrophotometer.

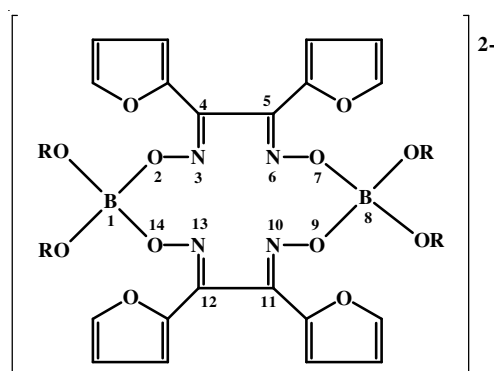


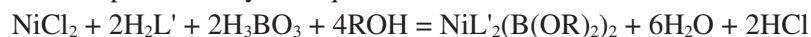
Fig. 1. R = H, CH₃, C₂H₅, C₃H₇ⁱ, C₄H₉ⁿ

TABLE-1
ANALYTICAL, COLOUR AND ELECTRONIC SPECTRAL DATA OF $\text{NiL}^{1,2}$

Complex	Colours	Elemental analysis (%): Found (Calcd.)				λ_{max} (cm^{-1})
		M	C	N	H	
NiL , R = H	Yellow	10.05 (10.08)	54.66 (54.70)	9.55 (9.57)	2.70 (2.73)	20750 b, 30100 s
NiL ; R = CH ₃	Deep brown	9.10 (9.20)	57.36 (57.41)	7.76 (7.80)	3.71 (3.74)	20400 b, 20200 s
NiL , R = C ₂ H ₅	Yellow	8.42 (8.46)	59.65 (59.68)	9.35 (9.38)	4.55 (4.59)	20600 b, 31000 s
NiL , R = C ₃ H ₇	Orange	7.80 (7.83)	61.58 (61.62)	7.39 (7.43)	5.28 (5.31)	20300 b, 30300 s
NiL , R = C ₄ H ₉	Violet	7.25 (7.29)	64.23 (64.27)	9.10 (9.15)	5.90 (5.93)	20500 b, 30200 s

RESULTS AND DISCUSSION

Preparation of the compounds: The reaction taking place in the synthesis of alkoxy boron-bridged macrocyclic compounds using nickel(II) chloride, furildioxime and boric acid molecules, one nickel(II) ion and four solvent molecules participate and it can be represented by the equation:



where $\text{H}_2\text{L} = 1,2\text{-difurylethane-1,2-dione dioxime}$; $\text{R} = \text{H}, \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7^i$ or C_4H_9^a .

Both hydrogen ion and water, which are formed during the reaction, besides the macrocyclic compounds, have a considerable effect on the reaction. The concentration of water has to be kept at the minimum by using dry alcohols in order to prevent contamination of one compound with another which may be formed on account of the *trans*-esterification reaction. It is also essential to maintain an optimum acidity in the reaction mixture for effective-cyclization. This has been achieved by adding small amounts of borax, so that the progress of the reaction is controlled by the addition of borax or sodium acetate. The metal ions undoubtedly play a pivotal role in the reaction process by binding the dioxime moieties in an anti-configuration and place the oxygen atoms of the oxime groups in suitable geometrical positions for reaction with the boron containing molecules.

Infrared spectra: Some striking differences between the IR spectra of the ligand 1,2-difurylethane-1,2-dione dioxime and their nickel(II) macrocyclic compounds have been observed with regard to sharpness, intensity and position of important vibrational bands such as $\nu(\text{C-N})$, $\nu(\text{N-O})$ and $\nu(\text{B-O})$, which provide valuable information for elucidation of the structures. However, it is significant to note that there is an overall similarity in the spectra of all the macrocyclic compounds. This indicates that the compounds possess similar structures.

The oximes and the *bis*(dioximato)nickel (II) complexes exhibit a broad and smooth band at 3200 cm^{-1} which is assigned to $\nu(\text{O-H})$ mode of the hydrogen bonded oximes. In the macrocyclic compounds, this band completely disappears clearly implying the breakdown of O-H bonds during the reaction of the oximes with boric esters; however the hydroxy compounds show characteristic band due to $\nu(\text{O-H})$. A sharp and intense band in the region $1660\text{-}1580 \text{ cm}^{-1}$ is observed for all the compounds which has been assigned to $\nu(\text{C-N})$. It is observed that the $\nu(\text{C-N})$ mode in all the compounds appears at a higher frequency with reduced intensity as compared to that in the free oximes^{2,4}.

All the compounds show two intense and sharp bands in the region $1240\text{-}1225$ and $1100\text{-}1060 \text{ cm}^{-1}$ which have been attributed to $\nu(\text{N-O})$ vibrations. These bands like the $\nu(\text{C-N})$ vibration also appear at higher frequencies in the complexes to their positions in the free oximes and these results are consistent with the earlier findings³.

Besides the above mentioned general similarity between the spectra of complexes of the series with the ligand L, an additional group of four bands appear in the spectra of the ligand L and its complexes which have been assigned to the furyl ring vibration. They appear at *ca.* $1590, 1570, 1500$ and 1440 cm^{-1} .

The most striking features in the spectra of the compounds is the appearance of intense, sharp and clearly identifiable bands in the region 1200-780 cm^{-1} which are absent in the spectra of the free oximes and *bis*-dioximato metal complexes. The bands appear at *ca.* 1190, 1000 and 790 cm^{-1} and have been assigned to the B-O stretching vibrations. A sharp band with medium intensity has been observed in the spectra of all the macrocycles in the range 470-465 cm^{-1} . This has been assigned to $\nu(\text{M-N})$.

The ligand L is coordinated to the nickel(II) ion in a tetradentate manner through the nitrogen atoms so as to fully encircle the metal ion. The electronic spectra and magnetic moments, which are described in the following paragraphs are consistent with the planar structure (Fig. 2) of the compounds.

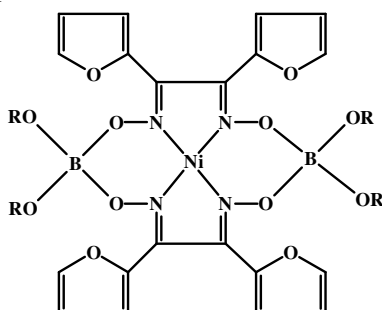


Fig. 2. R = H, CH₃, C₂H₅, C₃H₇ⁱ, C₄H₉ⁿ

Magnetic susceptibility measurements were carried out by the Gouy method using Hg[Co(CNS)₄] as a calibrant. All the compounds were found to be diamagnetic with the spin singlet, ¹A_{1g}, as the ground state. Their electronic spectra, recorded using a Beckman spectrophotometer, are dominated by intense bands in the visible and UV regions. The spectra consist of a broad band in the region 20000-22000 cm^{-1} and can be interpreted in terms of a planar structure (Fig. 2). The width of the spectral band manifests⁸ that the band represent a group of two to three transitions, the overlapping transition being ¹A_{2g}←¹A_{1g}, ¹B_{2g}←¹A_{1g} and ¹E_g←¹A_{1g}. The more intense bands observed beyond 30,000 cm^{-1} are believed to arise from M→L(π^*) charge-transfer transition.

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