

Macrocyclic Metal Complexes: Part VII—Spectral & Electrochemical Studies on Nickel(II) Complexes of Fluoro-boro-bridged Tetra-, Quinque- & Hexa-dentate Macrocyclic Ligands

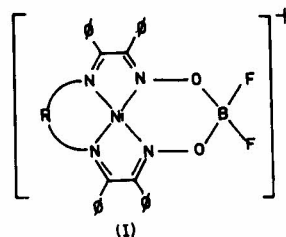
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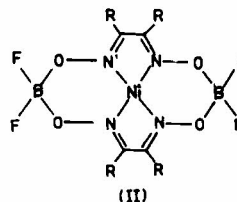
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Nickel(II) macrocyclic complexes of the type $[\text{NiL}^1 \text{--}^5 \text{BF}_2] \text{BF}_4$, where L^1 to L^5 are respectively $(\text{Ph}_4[13]\text{tetraeneN}_4)^-$, $(\text{Ph}_4[14]\text{tetraeneN}_4)^-$, $(\text{Ph}_4[13]\text{benzopentaeneN}_4)^-$, $(\text{Ph}_4[16]\text{tetraeneN}_5)^-$ and $(\text{Ph}_4[19]\text{tetraeneN}_6)^-$ have been synthesized by the action of boron trifluoride on NiLH_2Cl_2 where LH_2 represents the corresponding dioxime ligands. Structures of the complexes have been elucidated on the basis of analytical data and IR and electronic spectral, and magnetic moment studies. Polarographic studies carried out in 80% aq. DMF at $\mu = 0.1 \text{ M}$ (NaClO_4) show a quasi-reversible redox wave accompanied by one-electron transfer for all these complexes. The E_1 values for the cyclopean complexes are observed to be the most anodic amongst the macrocyclic complexes of nickel(II) known so far; this fact has been explained on the basis of their ligand field stabilization energies. The electrochemical behaviour of the series of fluoro-boro complexes, $\text{NiL}(\text{BF}_2)_2$, where L represents dimethylglyoximate, difurilglyoximate, benzildioximate and acetylacetonedioximate ions has been studied under similar conditions. In sharp contrast, these complexes show two-step one-electron reduction processes. It seems that stabilization of the formal state Ni^0 or Ni^I , in case the reduction is ligand based anion radical formation (during the second step of reduction) arises on account of a high degree of unsaturation due to incorporation of a pair of electrophilic $>\text{BF}_2$ groups at the bridge heads coupled with α -diimine groups that favour the dative M-N π -bonding interactions.

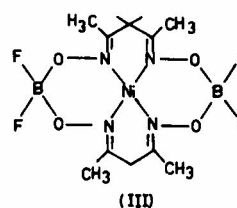
A variety of structurally modified ligands¹ have been used to prepare macrocyclic complexes. The richness of studies engulfing structural, spectral, thermodynamic and electrochemical²⁻⁵ aspects has greatly added to our knowledge specially with regard to similar naturally occurring systems. We have described recently a series of tetra-, quinque- and hexa-aza coordinated nickel(II) macrocyclic complexes⁶ with the ligands, $(\text{Me}_4[13]\text{tetraeneN}_4\text{O}_2\text{BF}_2)^-$, $(\text{Me}_4[13]\text{benzopentaeneN}_4\text{O}_2\text{BF}_2)^-$, $(\text{Me}_4[14]\text{tetraeneN}_4\text{O}_2\text{BF}_2)^-$, $(\text{Me}_4[16]\text{tetraeneN}_5\text{O}_2\text{BF}_2)^-$ and $(\text{Me}_4[19]\text{tetraeneN}_6\text{O}_2\text{BF}_2)^-$, henceforth called Me_4 cyclopeans. In continuation of our earlier studies, we report here the synthesis, characterization and electrochemical redox behaviour of a new series of tetra-, quinque- and hexa-aza coordinated macrocyclic complexes of nickel(II) with the cyclopean ligands, L^1 to L^5 {I, $\text{L}^1 = 1,1$ -difluoro-4,5,10,11-tetraphenyl-1-bora-3,6,9,12-tetraaza-2,13-dioxocyclotrideca-3,5,9,11-tetraenate, abbreviated $(\text{Ph}_2[13]\text{N}_4\text{O}_2\text{BF}_2)^-$, $\text{L}^2 = 1,1$ -difluoro-4,5,11,12-tetraphenyl-1-bora-3,6,10,13-tetraaza-2,14-dioxocyclotetradeca-3,5,10,12-tetraenate, abb. $(\text{Ph}_4[14]\text{N}_4\text{O}_2\text{BF}_2)^-$, $\text{L}^3 = 1,1$ -difluoro-4,5,10,11-tetraphenyl-7,8-benzo-1-bora-3,6,9,12-tetraaza-2,13-dioxocyclotrideca-3,5,7,9,11-pentaenate, abb. $(\text{Ph}_4[13]\text{benzoN}_4\text{O}_2\text{BF}_2)^-$, $\text{L}^4 = 1,1$ -difluoro-4,5,13,14-tetraphenyl-1-bora-3,6,9,12,15-penta-



- L^1 , $\text{R} = (\text{CH}_2)_2$
- L^2 , $\text{R} = (\text{CH}_2)_3$
- L^3 , $\text{R} = \text{C}_6\text{H}_4$
- L^4 , $\text{R} = (\text{CH}_2)_2\text{NH}(\text{CH}_2)_2$
- L^5 , $\text{R} = (\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2$



$\text{R} = \text{CH}_3, \text{C}_6\text{H}_5, \text{C}_4\text{H}_9\text{O} (\text{furyl})$



aza-2,16-dioxocyclohexadeca-3,5,12,14-tetraenate, abb. $(\text{Ph}_4[16]\text{N}_5\text{O}_2\text{BF}_2)^-$, $\text{L}^5 = 1,1$ -difluoro-4,5,16,17-tetraphenyl-1-bora-3,6,9,12,15,18-hexaaza-2,19-dioxocyclononadeca-3,5,15,17-tetraenate, abb. $(\text{Ph}_4[19]\text{N}_6\text{O}_2\text{BF}_2)^-$, henceforth called Ph_4 cyclopeans. The electrochemical behaviour of the earlier reported⁷ fluoro-boro macrocyclic complexes of L^6 to L^9 (II) and (III) has also been studied. Since the macrocyclic complexes of the latter series are formed by bridging dioximes with $>\text{BF}_2$ groups, henceforth they are called FBOX ligands. The macrocyclic ligands of the present series L^1 to L^5 have similar α -diimine structures on the back bone of the macrocyclic ring but differ in substituents, phenyl groups replacing the methyl groups present in the ligands of earlier series⁶. It is expected that the Ph_4 cyclopeans would provide a weaker ligand field on account of the presence of electrophilic phenyl group, and would stabilize metal ions in low oxidation states.

The parent precursor complexes, NiLH_2Cl_2 which have been used as the intermediates for the preparation of macrocyclic complexes of cyclopean ligands are reported here for the first time; but their methyl analogs with nickel(II) and other metal ions are known^{8,9}.

Materials and Methods

Ethylenediamine, propylenediamine, benzil, diethylenetriamine and boron trifluoride were BDH reagents while triethylenetraamine, *o*-phenylenediamine were Reidel reagents. Benzil monoxime was prepared according to the prescribed procedure¹⁰.

The ligands L^{10}H_2 to L^{14}H_2 where $\text{L}^{10}\text{H}_2 = 1,8$ -dihydroxyimino-1,2,7,8-tetraphenyl-3,6-diazoocta-2,6-diene, $\text{L}^{11}\text{H}_2 = 1,9$ -dihydroxyimino-1,2,8,9-tetraphenyl-3,7-diazonona-2,7-diene, $\text{L}^{12}\text{H}_2 = 1,8$ -dihydroxyimino-1,2,7,8-tetraphenyl-4,5-benzo-3,6-diazoocta-2,6-diene, $\text{L}^{13}\text{H}_2 = 1,11$ -dihydroxyimino-1,2,10,11-tetraphenyl-3,6,9-triazaundeca-2,9-diene and $\text{L}^{14}\text{H}_2 = 1,14$ -dihydroxyimino-1,2,13,14-tetraphenyl-3,6,9,12-tetraazatetradeca-2,12-diene were prepared by following similar procedures. The method adopted for L^{10}H_2 is given below.

Benzilmonoxime (4.5 g, 0.02 mol) was treated with ethylene-diamine (0.6 g, 0.01 mol) at room temperature when the reaction took place with evolution of heat and the product liquified. The reaction product solidified in about 10-15 min. The product was powdered and recrystallized from ethanol. The melting points of L^{10}H_2 , L^{11}H_2 , L^{12}H_2 , L^{13}H_2 and L^{14}H_2 were 80°, 88°, 85°, 125° and 115° respectively. Analytical data agree with the formulae.

All the nickel(II) complexes of the type, NiLH_2Cl_2 were prepared by adopting similar procedure. A

typical preparation (for $\text{NiL}^{10}\text{H}_2\text{Cl}_2$) is given below:

$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (2.4 g, 0.01 mol) dissolved in ethanol was treated with L^{10}H_2 (4.74 g, 0.01 mol) taken in ethanol. The solution was allowed to stand when red crystals were formed. They were filtered, washed with ethanol, ether and dried.

The cyclopean complexes were isolated by the action of freshly distilled boron trifluoride on the above precursor complexes in an ethereal medium. A typical preparation (NiL^1BF_4) is given below:

$\text{NiL}^{10}\text{H}_2\text{Cl}_2$ (5.04 g, 0.01 mol), was suspended in ether and boron trifluoride (freshly distilled, 3 ml) was added dropwise while stirring till the red colour transformed to yellow. After allowing to stand for 4 hr a yellow crystalline product was obtained; it was filtered, washed with ether and dried *in vacuo*. The analytical data are given in Table 1.

The preparations of the macrocyclic complexes NiL^{6-9} and their spectral properties have been described earlier⁷. Physical measurements were done as reported earlier¹¹.

Results and Discussion

The bright red nickel(II) complexes, NiLH_2Cl_2 , on reaction with boron trifluoride transform to yellow or orange coloured fluoro-boro-bridged macrocyclic complexes. The tetra-coordinated complexes of L^1 , L^2 and L^3 are yellow while the penta- and hexa-coordinated complexes of L^4 and L^5 are orange in colour. The reaction of boron trifluoride with the oxime oxygen atoms is facilitated by the right geometrical disposition of these atoms according to coordination template effect¹². The mechanism of the cyclization process probably follows the sequence of reactions given in Scheme 1.

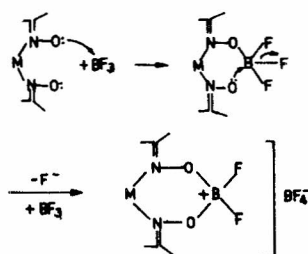
Infrared spectra

A broad band appears at 3400 (bands positions in cm^{-1}) for the series of NiLH_2Cl_2 complexes due to $\nu\text{O}-\text{H}$ of the $-\text{NOH}$ groups involved in intramolecular hydrogen bonding. Another band near 1700 is attributed to the deformation vibrations of $-\text{NOH}$ groups. In the cyclopean complexes these bands disappear due to the rupture of the $\text{O}-\text{H}$ bonds. The NiL^4BF_4 and NiL^5BF_4 complexes and their respective precursors show a band of medium intensity near 3080 associated with stretching vibrations of secondary NH groups and another band near 1330 due to $\nu\text{C}-\text{N}^{13}$. The bands near 3000 have been assigned to $\nu\text{C}-\text{H}$.

In the region 1600-1450 the IR spectra of the precursors show five to six bands, two weak bands at 1600 and 1580 and three strong bands are observed near 1550, 1500 and 1450 cm^{-1} . In the macrocyclic complexes, the pair of high frequency strong bands are observed to be most affected. Of these two, the higher

Table 1—Analytical Data of the Complexes

Complexes	Colour	Found (Calc.) %					μ_{eff} (B.M.)
		Metal	N	C	H	Cl	
NiL ¹⁰ H ₂ Cl ₂ (NiC ₃₀ H ₂₆ N ₄ O ₂ Cl ₂)	Red	9.75 (9.80)	9.24 (9.30)	59.55 (59.60)	4.26 (4.30)	11.68 (11.79)	3.2
NiL ¹¹ H ₂ Cl ₂ (NiC ₃₁ H ₂₈ N ₄ O ₂ Cl ₂)	Red	9.50 (9.57)	8.98 (9.09)	60.12 (60.19)	4.49 (4.53)	11.43 (11.52)	3.18
NiL ¹² H ₂ Cl ₂ (NiC ₃₄ H ₂₆ N ₄ O ₂ Cl ₂)	Red	9.15 (9.07)	8.72 (8.61)	62.48 (62.52)	3.95 (3.98)	10.98 (10.92)	3.1
NiL ¹³ H ₂ Cl ₂ (NiC ₃₂ H ₃₁ N ₅ O ₂ Cl ₂)	Reddish brown	9.24 (9.14)	10.80 (10.85)	59.49 (59.53)	4.47 (4.49)	11.12 (11.00)	3.1
NiL ¹⁴ H ₂ Cl ₂ (NiC ₃₄ H ₃₆ N ₆ O ₂ Cl ₂)	Reddish brown	8.52 (8.55)	12.08 (12.17)	59.11 (59.13)	5.19 (5.21)	10.19 (10.28)	3.15
(Ni(Ph ₄ [13]N ₄ O ₂ BF ₂)BF ₄) (NiC ₃₀ H ₂₄ N ₄ O ₂ B ₂ F ₆)	Yellow	8.92 (8.84)	8.41 (8.39)	52.37 (52.40)	3.45 (3.49)	—	2.5
(Ni(Ph ₄ [14]N ₄ O ₂ BF ₂)BF ₄) (NiC ₃₁ H ₂₆ N ₄ O ₂ B ₂ F ₆)	Yellow	8.75 (8.66)	8.25 (8.22)	54.59 (54.62)	3.77 (3.81)	—	2.45
(Ni(Ph ₄ [13]benzoN ₄ O ₂ BF ₂)BF ₄) (NiC ₃₄ H ₂₄ N ₄ O ₂ B ₂ F ₆)	Yellow	8.30 (8.25)	7.88 (7.83)	56.98 (57.06)	3.28 (3.35)	—	2.52
(Ni(Ph ₄ [16]N ₅ O ₂ BF ₂)BF ₄) (NiC ₃₂ H ₂₉ N ₅ O ₂ B ₂ F ₆)	Orange	8.28 (8.30)	9.90 (9.85)	53.95 (54.08)	3.96 (4.08)	—	2.5
(Ni(Ph ₄ [19]N ₆ O ₂ BF ₂)BF ₄) (NiC ₃₄ H ₃₄ N ₆ O ₂ B ₂ F ₆)	Orange	7.88 (7.83)	11.20 (11.15)	54.12 (54.18)	4.46 (4.51)	—	2.54



Scheme 1

energy band shifts to ~ 1620 as a band of medium intensity; the lower energy band moves down by $20\text{--}30\text{ cm}^{-1}$. From these characteristic features, it is believed that these two bands originate from $C\equiv N$ vibrations of the azomethine and imino-oxime groups.

Strong bands observed at 1210 and 1140 are due to $\nu N-O$ for the $NiLH_2Cl_2$ and macrocyclic complexes respectively. The spectra of macrocyclic complexes show several additional bands in the region $1400\text{--}800\text{ cm}^{-1}$. They exhibit three $\nu B-O$ bands near 1375, 1200 and 800^{14} and three bands near 1055, 1020 and 950 which have been assigned to BF stretching vibrations of $>BF_2$ and BF_4^- groups⁶.

Electronic spectra and magnetic properties

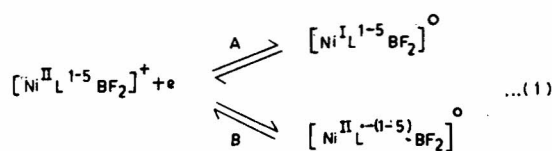
In sharp contrast to the earlier series of tetra-, penta- and hexa-aza macrocyclic complexes, which were either fully diamagnetic or partly paramagnetic (for penta- and hexa-aza complexes), the present series of

macrocyclic complexes have magnetic moments in the range 2.5–2.6 B.M. below the normal range observed for spin-free nickel(II) complexes. Nevertheless, they show a spin triplet ground term for the metal ion and indicate a weaker interaction of the macrocyclic rings. Their electronic spectra show bands near 20,000, 25,000 and 30,000. The former two bands have been assigned to the transitions ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ under octahedral approximations; these bands tail to low energy region and the weak band due to transition ${}^3A_{2g} \rightarrow {}^3T_{2g}$ is hidden under them and are discernible only in a few cases. The intense band at 30,000 is associated with charge transfer transitions.

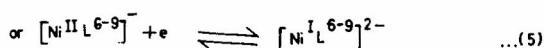
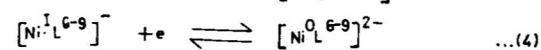
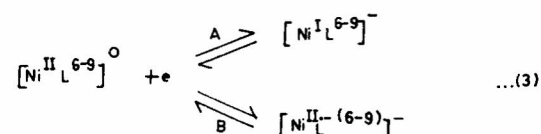
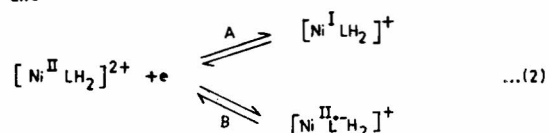
Electrochemical studies

The electrochemical data in 80% aq. DMF and at $\mu = 0.1\text{ M}$ (sodium perchlorate) for the macrocyclic complexes $[NiL^{1-5}]^+$, their respective parent complexes ($NiL^{10-14}H_2Cl_2$) and for the FBOX macrocyclic complexes (NiL^{6-9}) are shown in Table 2. The cyclopean complexes and their respective precursors undergo quasi-reversible one-electron reduction process at the DME at a moderate negative potential (versus SCE). The current potential profile at DME is typically S-shaped and the plot of $\log i/i_d - i$ versus E is linear indicating that the reduction process is diffusion controlled¹⁵. The redox mechanism corresponds to the reactions as given by Eqs. (1) and (2). But the redox behaviour of the FBOX nickel(II) macrocyclic complexes (NiL^{6-9}) are exciting and

unusual. They exhibit a two step redox process and each step is accompanied by one-electron transfer as shown in Eqs. 3-5.



and



The influence of structural and electronic parameters on the electrochemical redox behaviour of a range of quadridentate N_4 macrocyclic complexes of nickel(II) has been studied^{4,16}. The redox behaviour is a composite function of a range of factors such as ring size, ring substituents, degree and type of unsaturation, charge type and coordination number¹⁷⁻²⁰. The one electron reduction products of a variety of macrocycles exist as either d^9 nickel(I) complexes or metal(II) stabilized anion radicals depending upon the nature of the ligand unsaturation. The reduction products have been characterized by ESR spectral studies in a few cases. In the case of neutral complexes, the ESR spectra fall into two kinds. For complexes of saturated ligands or for those containing isolated imine groups, axial asymmetric spectra are observed with $g_{\perp} < g_{\parallel}$. Such spectra unambiguously suggest the presence of Ni(I) (d^9) species. On the other hand for complexes possessing α -diimine moieties, isotropic ESR spectra are observed without any, hyperfine splitting and the g value corresponds to that of a free electron. The implications of this are that the unpaired electron in each of these complexes is delocalized over the whole ligand framework. In view of the presence of a pair of α -diimine groups in all the complexes of the present series except L^9 , the one-electron reduction product for the $\text{Ph}_4\text{cyclopean}$ complexes and the reduction product in the first step for FBOX systems can be better explained by path B in Eqs. (1), (2) and (3) as nickel(II) coordinated to a stabilized neutral and anion radical for the cyclopeans and FBOX ligands respectively. In a

Table 2—Polarographic Data of the Complexes

Complex	$E_{\frac{1}{2}}$	Complex	$E_{\frac{1}{2}}$ (V)
$\text{NiL}^{10}\text{H}_2\text{Cl}_2$	-0.580	$[\text{NiL}^1\text{BF}_2]\text{BF}_4$	-0.501
$\text{NiL}^{11}\text{H}_2\text{Cl}_2$	-0.640	$[\text{NiL}^2\text{BF}_2]\text{BF}_4$	-0.525
$\text{NiL}^{12}\text{H}_2\text{Cl}_2$	-0.639	$[\text{NiL}^3\text{BF}_2]\text{BF}_4$	-0.527
$\text{NiL}^{13}\text{H}_2\text{Cl}_2$	-0.645	$[\text{NiL}^4\text{BF}_2]\text{BF}_4$	-0.658
$\text{NiL}^{14}\text{H}_2\text{Cl}_2$	-0.678	$[\text{NiL}^5\text{BF}_2]\text{BF}_4$	-0.690
Complex	E_1^1 (V)	E_1^2 (V)	
NiL^6	-0.90	-1.25	
NiL^7	-0.88	-1.11	
NiL^8	-0.87	-1.25	
NiL^9	-0.875	-1.30	

recent electrochemical investigation on Ni(II) schiff base macrocyclic complexes containing iminopyridine function a similar metal-stabilized ligand radical species has been proposed²¹.

The $E_{\frac{1}{2}}$ values for the 13- and 14-membered quadridentate $\text{Ph}_4\text{cyclopean}$ complexes are more anodic than those of their respective parent complexes (Table 2). However, on increased coordination with secondary NH groups in the 16- and 19-membered macrocyclic ligands with pyramidal and approximately octahedral geometries, the $E_{\frac{1}{2}}$ values are drastically altered and attain a higher cathodic value with respect to their parent complexes. This can be explained on the basis of the electrostatic or covalent effects. Nucleophilic attack of the secondary amine groups enhances the electronic charge on the metal ion and aids in a cathodic shift in the $E_{\frac{1}{2}}$ value.

Of considerable interest is a comparison of the $E_{\frac{1}{2}}$ values for $\text{Ph}_4\text{cyclopean}$, $\text{Me}_4\text{cyclopean}$, FBOX and related tetraene nickel(II) macrocyclic complexes¹⁷⁻²⁰. In the earlier paper on $\text{Me}_4\text{cyclopeans}$ we have suggested that the $E_{\frac{1}{2}}$ values are governed by the electrostatic forces of the macrocyclic structure and denticity of the cyclic ligands. Data obtained during the present investigations throw light on the relative ligand field energies of the macrocyclic ligands. The ligand field energy is a composite function of σ and π M-L interactions and the d -electron configuration of the metal ion. Examination of spectral and magnetic properties suggest that the tetraene N_4 macrocycles can be arranged in order of decreasing ligand field stabilisation energy as: tetraene $\text{N}_4 \approx \text{Me}_4\text{cyclopeans} > \text{FBOX} > \text{Ph}_4\text{cyclopeans}$ and for the tetraene N_5 or N_6 ligands as: $\text{Me}_4\text{cyclopeans} > \text{Ph}_4\text{cyclopeans}$.

The magnitude and range of $E_{\frac{1}{2}}$ values vary considerably for different systems and shift in the cathodic direction with increasing ligand field energy. The σ and π M-L interactions depend upon factors like macrocyclic ring cavity and substituents on ligand frame. On account of the four phenyl group substituents and their electron withdrawing nature

coupled with α -diimine groups, the E_1 values for the $\text{Ph}_4\text{cyclopeans}$ are most anodic amongst those of the nickel(II) macrocyclic complexes and the overall match is good.

$\text{Ni}^{\text{I}}/\text{Ni}^{\text{O}}$ or $\text{Ni}^{\text{II}}/\text{Ni}^{\text{I}}$ couple for FBOX macrocycle

For FBOX series of ligand macrocyclic complexes, a facile second step reduction is observed that does not occur for the cyclopean nickel(II) complexes in the range zero to -2.0 V studied. It would be useful to discuss this aspect of the redox process to gain insight into the redox phenomena.

As evidenced from this work and several earlier reports, the E_1 values for $\text{M}^{n+1}/\text{M}^{n+}$ couple greatly depend upon structural modifications of the macrocyclic ligands. For FBOX system the second redox wave is attributed to the redox couple $\text{Ni}(\text{I})/\text{Ni}^{\text{O}}$ or $\text{Ni}^{\text{II}}/\text{Ni}^{\text{I}}$ and a formal change of metal ion electron configuration from d^9 to d^{10} or from d^8 to d^9 respectively. For stabilization of Ni^{O} or Ni^{I} , a higher degree of unsaturation or electronegativity has to be incorporated into the ligand system in order to get Ni^{O} or Ni^{I} macrocyclic complexes in solution. The introduction of a pair of electronegative bridge heads and the overall planarity of the ligands satisfy these requirements. The stabilization is achieved through coordination of imine nitrogen atoms, and extended dative M-N π -interaction provided by the α -diimine groups. A more definite conclusion would be possible from a study of the electrochemical behaviour of $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ couple that is analogous to $\text{Ni}^{\text{I}}/\text{Ni}^{\text{O}}$ couple in respect of d -electron configurations for these system of ligands. Investigations on copper(II) complexes are in progress and the results will be communicated in due course.

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