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A series of macrocyclic complexes of nickel(II) has been synthesised by the action of formaldehyde on bis(benzilmonohydrazone)diimine nickel(II) complexes. The macrocycles and the precursors have the spin singlet ground state, are square planar in structure and show one ligand field band near 19,000 cm⁻¹. The complexes show one electron reduction in two discrete steps with $E_{1/2}$ values in the ranges -0.33 to -0.55 V and -1.53 V to -1.63 V respectively. The $\Delta E_{1/2}$ values have been examined thermodynamically for each macrocycle and the precursor, and $\Delta E_{1/2}$ values between the macrocycle (Cy') and its corresponding precursor (L). The analysis suggests formation of ligand anion radical in the first step and a reduced metal-ligand anion radical complex in the second step.

Research on diverse aspects of macrocyclic complexes has evoked considerable interest in recent years⁴⁻¹⁵. In a recent communication¹⁶ we had reported a series of square planar macrocyclic complexes of nickel(II) isolated through the reaction of α- and β-diketones with Ni(II) complexes of 1,4,6,8,11-pentaazaundecane(I). The complexes undergo metal-based one-electron one-step reversible reduction and the redox potentials correlate with the ligand field strengths of the macrocycles. In continuation of this work, we have prepared new macrocyclic complexes of nickel(II) with the object of studying the effect of variation in the ligand field on the redox behaviour and to promote a ligand based reduction. It was thought that macrocyclic ligands with wider electron delocalisation, particularly those coupled with α-diimine functions, would be able to promote ligand based electron transfer.

Benzilmonohydrazone was chosen as the basic structural component so that its intact carbonyl function could be condensed with an amine group to get a new series of complexes containing the open chain ligands. In situ condensation of benzilmonohydrazone in presence of Ni(II) ion has been carried out with 1,2-diaminoethane, 1,3-diaminopropane and 1,2-diaminopropane to get the series of nickel(II) complexes with the ligands bis(benzilmonohydrazone)-ethylenediimine, (L¹); bis(benzilmonohydrazone)-1,3-propylenediimine, (L²); and bis(benzilmonohydrazone)-1,2-propylenediimine, (L³) respectively. The ligand for the fourth complex, bis(benzilmonohydrazone)-1,2-phenylenediimine, (L⁴), isolated by using 1,2-diaminobenzene, is of benzenoid type.

The terminal uncoordinated $-\text{NH}_2$ groups of L¹⁻⁴ are in appropriate geometrical orientations to undergo further condensation with formaldehyde leading to the formation of the macrocyclic complexes (see Fig. 1) 2,3,8,9-tetraphenyl-1,4,7,10,11,13-hexaazacyclotrideca-1,3,7,9-tetraene, [Ph₄[13]tetraeneN₄(N₂)], (Cy¹); 2,3,9,10-tetraphenyl-1,4,8,11,12,14-hexaazacyclotetradeca-1,3,8,10-tetraene, [Ph₄[14]tetraeneN₄(N₂)], (Cy²); 5-methyl-2,3,8,9-tetraphenyl-1,4,7,10,11,13-hexaazacyclotrideca-1,3,7,9-tetraene, [MePh₄[13]tetraeneN₄(N₂)], (Cy³) and 2,3,8,9-tetraphenyl-5,6-benzo-1,4,7,10,11,13-hexaazacyclotetradeca-1,3,5,7,9-pentaene, [Ph₄bzo[13]-pentaeneN₄(N₂)], (Cy⁴) respectively.

Materials and Methods
Benzil used was obtained from Loba Chemicals
and hydrazine hydrate was a BDH reagent. The diamines, viz., 1,2-diaminoethane, 1,3-diaminopropane, 1,2-diaminopropane and 1,2-diaminobenzene were E. Merck reagents. Methanol was refluxed and distilled over lime before use. Benzilmonohydrazone was prepared according to a known procedure.

The precursor complexes of $L^{1-4}$ were prepared by following similar procedures and a typical procedure is provided here.

\[
\{\text{Bis}(\text{BMH})\text{ethylenediamine}}\text{nickel(II) perchlorate}, \\
NiC_{31}H_{28}N_{6}(\text{ClO}_4)_2
\]

Benzilmonohydrazone (BMH) (1.1 g; 5 mmol) was dissolved in 50 ml of methanol. To the refluxing solution of BMH, nickel(II) perchlorate hexahydrate (0.9 g; 2.5 mmol) in 75 ml of methanol was added, followed by the addition of the diamine (1,2-diaminoethane; 0.15 g; 2.5 mmol) when the green colour of solution changed to reddish orange. The reflux was continued for 8 hr. The contents were cooled to $\sim 0^\circ\text{C}$ and allowed to stand for 24 hr when an yellow coloured product was obtained. It was filtered and washed with absolute methanol followed by ether and dried in vacuo.

\[
\text{Found: Ni, 7.92; N, 11.28; Cl, 9.43. Calc.: Ni, 7.95; N, 11.32; Cl, 9.57%}. 
\]

Two alternative procedures were tried to synthesise the macrocyclic complexes: (i) isolation of the precursor complex followed by the acid catalysed reaction with formaldehyde for cyclisation, and (ii) acid catalysed \textit{in situ} reaction of nickel(II) benzilmonohydrazone and formaldehyde followed by reaction with the diamine. Under dilute conditions, the same macrocyclic complex was obtained as the final product irrespective of the route of preparation. However, we have adopted the latter procedure to isolate the macrocycles ($C_y^{1-4}$). A typical preparation is described below.

\[
(2,3,8,9\text{-Tetraphenyl-1,4,7,10,11,13-hexaaazacyclotrideca-1,3,7,9-tetraene})\text{nickel(II) perchlorate}, \\
NiC_{31}H_{28}N_{6}(\text{ClO}_4)_2
\]

A methanolic solution of benzilmonohydrazone (1.1 g; 5 mmol) and nickel(II) perchlorate hexahydrate (0.9 g; 2.5 mmol) dissolved in methanol (100 ml) were refluxed. The resulting solution was treated with an aqueous solution of formaldehyde (0.075 g; 2.5 mmol). Two drops of perchloric acid were added to catalyze the reaction. It was further refluxed for 6 hr when the colour of the solution changed from yellow to green. 1,2-Diaminoethane (0.15 g; 2.5 mmol) was added slowly and the reflux was continued for 8 hr. The product started appearing in the reaction vessel during the period of reflux and there was a change in colour of the solution from green to red. The deep red solid was filtered and washed with methanol, followed by ether. Then it was dried in vacuo. [Found: Ni, 7.92; N, 11.28; Cl, 9.43. Calc.: Ni, 7.95; N, 11.32; Cl, 9.57%].

Analytical results of other complexes of $L^{1-4}$ and $C_y^{1-4}$ agreed satisfactorily with the formulae of the complexes shown in Table 1.

Physical measurements were done following procedures described earlier.

\section*{Results and Discussion}

The precursor complexes $MLX_2$ ($i$ = 1 to 4) are
Table 1 - Electronic spectral and polarographic data of the nickel(II) complexes of the precursor L and macrocycles Cy

<table>
<thead>
<tr>
<th>Complexes</th>
<th>( ^1A_{2g} \rightarrow {^1}A_{1g} ) (cm(^{-1}))</th>
<th>CT band (cm(^{-1}))</th>
<th>(-E_{1/2} (V))</th>
<th>(-E_{1/2} (V))</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiL(^{(1)})(ClO(_4))(_2)</td>
<td>19,000</td>
<td>28,900</td>
<td>0.49</td>
<td>1.59</td>
</tr>
<tr>
<td>NiL(^{(1)})Br(_2)</td>
<td>19,400</td>
<td>28,800</td>
<td>0.49</td>
<td>1.58</td>
</tr>
<tr>
<td>NiL(^{(1)})I(_2)</td>
<td>19,200</td>
<td>28,900</td>
<td>0.48</td>
<td>1.58</td>
</tr>
<tr>
<td>NiL(^{(1)})(ClO(_4))(_2)</td>
<td>19,200</td>
<td>30,300</td>
<td>0.50</td>
<td>1.65</td>
</tr>
<tr>
<td>NiL(^{(1)})Br(_2)</td>
<td>19,100</td>
<td>29,200</td>
<td>0.50</td>
<td>1.62</td>
</tr>
<tr>
<td>NiL(^{(1)})I(_2)</td>
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<td>28,900</td>
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<td>28,900</td>
<td>0.50</td>
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<td>1.58</td>
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<tr>
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<tr>
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<td>29,800</td>
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<tr>
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</tr>
<tr>
<td>NiCy(^{(1)})(ClO(_4))(_2)</td>
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<tr>
<td>NiCy(^{(1)})I(_2)</td>
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<td>0.36</td>
<td>1.57</td>
</tr>
<tr>
<td>NiCy(^{(1)})(ClO(_4))(_2)</td>
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<td>29,800</td>
<td>0.42</td>
<td>1.62</td>
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<tr>
<td>NiCy(^{(1)})Br(_2)</td>
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<td>29,800</td>
<td>0.41</td>
<td>1.60</td>
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<tr>
<td>NiCy(^{(1)})I(_2)</td>
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<td>0.35</td>
<td>1.62</td>
</tr>
<tr>
<td>NiCy(^{(1)})(ClO(_4))(_2)</td>
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<td>NiCy(^{(1)})Br(_2)</td>
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<td>1.57</td>
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<tr>
<td>NiCy(^{(1)})I(_2)</td>
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<td>NiCy(^{(1)})(ClO(_4))(_2)</td>
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<td>29,400</td>
<td>0.42</td>
<td>1.62</td>
</tr>
<tr>
<td>NiCy(^{(1)})Br(_2)</td>
<td>18,900</td>
<td>28,500</td>
<td>0.42</td>
<td>1.60</td>
</tr>
<tr>
<td>NiCy(^{(1)})I(_2)</td>
<td>19,000</td>
<td>28,900</td>
<td>0.41</td>
<td>1.57</td>
</tr>
</tbody>
</table>

either yellow or brown in colour and the macrocyclic complexes MCy\(_{X_2}\) \((i=1\) to \(4)\) are all deep red. They are all diamagnetic in character implying a planar structure.

The asymmetric and symmetric vibrations for the primary amine \((\text{NH}_2)\) group of benzilmonohydrazzone appear as a triplet around 3380, 3260 and 3180 cm\(^{-1}\). The \(\nu(C=O)\) of benzil \((-1650\) cm\(^{-1}\)) suffers a red shift and appears at \(-1625\) cm\(^{-1}\) in benzilmonohydrazzone. Another sharp band noticed at \(-1610\) cm\(^{-1}\) in benzilmonohydrazzone is due to the \(\nu(\text{C} \equiv \text{N})\) vibrations, the \(\text{C} \equiv \text{N}\) group originating from the reaction of benzil with hydrazine. In the case of open chain \{bis-(benzilmonohydrazone)diimine\}nickel(II) complexes, the \(\nu(C=O)\) stretching band disappears corroborating the reaction of the carbonyl groups of benzilmonohydrazzone with the \(-\text{NH}_2\) groups of the respective diamines. The observation of a single \(\nu(C \equiv \text{N})\) stretching band implies that the two kinds of imine \((\text{C} \equiv \text{N})\) groups do not significantly differ in their vibrational energies. The \(\text{NH}_2\) stretching frequencies appear at \(-3380, -3260\) and \(-3170\) cm\(^{-1}\) as a triplet while the deformation mode appears at \(-1530\) cm\(^{-1}\) and no significant change in the structure of the spectra is noticed in these regions. The bands due to \(\text{NH}_2\) wagging vibrations appear in the region 760 cm\(^{-1}\).

The most notable feature of the spectra of the macrocycles is the disappearance of the \(\text{NH}_2\) stretching and deformation vibrations. A lone band appears near 3265 cm\(^{-1}\) that originates from the stretching vibrations of secondary \(\text{NH}\) groups\(^{18,19}\) and is an unequivocal indicator of the macroyclic structure. The \(\nu(\text{C} \equiv \text{N})\) band observed at \(-1610\) cm\(^{-1}\) in the open chain complexes shifts to the higher frequency region in the macrocycles \((1650 \text{ cm}^{-1})\) indicating higher stability due to macrocyclic effect through \(\pi\) electron charge-transfer from metal to the ligand\(^{20}\). The \(\nu M - \text{N} \) mode occurs at \(-465\) and \(-500 \text{ cm}^{-1}\) in the precursor and macrocyclic complexes respectively\(^{21}\).

The electronic spectra of the precursors and macrocycles are dominated by two intense bands, one in the visible region near 19000 cm\(^{-1}\) and the other in the UV region near 29000 cm\(^{-1}\) (Table 1). The low frequency band has a lower intensity than that of the latter band and has been assigned to the transition \(^{1}A_{2g} - ^{1}A_{1g}\) under a square planar environment for the nickel(II) ion. The more intense band \((28000-31000 \text{ cm}^{-1})\) is believed to be due to charge transfer transition.

Spectra of several nickel(II) saturated macrocycles and unsaturated macrocycles containing \(\alpha\)-diimine, isolated imines, dienes and tetraenes in the spin state \(S=0\) have been reported\(^{22}\). A majority of these complexes shows a single ligand field band in the range 21000-23500 cm\(^{-1}\), and in a few cases a charge transfer band beyond 33000 cm\(^{-1}\) is observed. Only in a few complexes like \([\text{Ni}(N\text{-Me}_{2}[14\text{-}ane-N])\text{ClO}_{4}]_2\) a low energy ligand field band is observed\(^{23,24}\) in the vicinity of 19000 cm\(^{-1}\). The reported complexes contain either methyl groups or methyl groups in combination with functions like acetyl or benzoyl as pendants on the macro-ring. The present complexes constitute a unique group exhibiting low energy ligand field transitions which may be due to the electron withdrawing phenyl groups pendant on the ligand frame in conjugation with \(\alpha\)-diimine groups.

Polarographic data of the precursors and the macrocyclic complexes studied in DMF-water mixture \((80:20, \text{v/v})\) and at an ionic strength of 0.1 M (tetraethylammonium perchlorate) at DME are given in Table 1. All the complexes undergo diffusion-
controlled quasireversible two-step one-electron reduction. Cyclisation has a profound effect on the redox behaviour, particularly on the first redox step. Studies on the redox behaviour of several nickel(II) complexes in spin state zero show that most of the complexes undergo one-step one-electron reduction and the $E_{1/2}$ values lie in the range $-0.4$ to $-1.6$ V. In a few cases, a second step of reduction occurs and $E_{1/2}$ values are highly cathodic, mostly lying in the range $-1.8$ to $-2.0$ V.

An inspection of the present electrochemical data shows that the values of thermodynamic parameters $E_{1/2}$ for the precursor complexes of $L^1$-4 lie within a close range but for the complexes of $L^4$ the value is more cathodic, the shift being caused by the in-built benzo group in the macrocyclic ring. Such an effect exerted by the benzo group was observed in one of our earlier studies also. Further, the first step of reduction of the macrocyclic complexes is relatively more facile and less cathodic with respect to the corresponding step in present precursors. However, within the series of macrocycles, the $E_{1/2}$ values for $Cy^{1-4}$ are more anodic than that for $Cy^4$. The cathodic shift for the latter again implies that the effect of the benzo-group predominates in the $Cy^4$ macrocycles.

The $E_{1/2}$ values show that the second step of reduction is more facile compared to that for many known complexes (loc cit). The $E_{1/2}$ values for $Cy^{1-4}$ do not significantly differ from the $E_{1/2}$ values of the respective precursors, $L^1-4$. On the other hand, the redox process for $Cy^4$ is more cathodic with respect to that for $L^4$ complexes. For the present series of macrocycles, the $E_{1/2}$ value for $Cy^4$ is most cathodic indicating pronounced stability for the 14-membered macrocycle, a fact well established through several investigations.

An examination of the $E_{1/2}$ values in the series, based on the parameteric equations (i) and (ii), offers valuable information and suggests the mode of the redox mechanism.

$$\Delta E_{1/2} = (E_{1/2}^L - E_{1/2}^Cy)$$

where $i = 1, 2$ and $j = 1, 2, 3, 4$.

The results can be clearly seen pictorially from the horizontal bar diagram presented for the bromide complexes for $L^1-4$ and $Cy^{1-4}$ in Fig. 2. The broken line indicates the change in $E_{1/2}$ of the macrocycle with respect to its precursor.

The redox processes can be considered to be either predominantly ligand-based or metal-based as depicted in the expressions (a), (b), (c) and (d) in Scheme 1.

$$[Ni^{II}L]^2^- + e^- \rightarrow [Ni^{III}L]^+ \quad \ldots \quad (a)$$
$$[Ni^{II}L]^2^- + e^- \rightarrow [Ni^{III}L^-]^+ \quad \ldots \quad (b)$$
$$[Ni^{II}L^-] + e^- \rightarrow [Ni^{III}L^-] \quad \ldots \quad (c)$$
$$[Ni^{II}L^-]^+ + e^- \rightarrow [Ni^{II}L]$$.  \quad \ldots \quad (d)$$

Scheme 1

The $E_{1/2}$ values (Eq. (i) and Fig. 2) for the precursor and its daughter macrocycle are of the order of $-110$ mV and $-120$ mV respectively. The parallelism is suggestive of similar redox behaviour of the macrocycles and the respective precursors (Fig. 2). The $\Delta E_{1/2}$ values (Eq. (ii) and Fig. 2) for the first step of reduction differ widely ranging from 90 to 150 mV for $j = 2, 1, 3$ and 4 and suggest that this step of the redox process is predominantly ligand-based as proposed in path-b. The presence of $\alpha$-diamine groups augmented by resonating phenyl groups is favourable for such a process. However, for the second step the $E_{1/2}$ values lie over a narrow range $-1.54$ to $-1.58$ V and no appreciable difference exists in the $E_{1/2}$ values of the macrocycle and the corresponding precursor which are of the order of only 10 to 30 mV. This means that this step of reduction is no longer a major function of the ligand structure and the reduction is believed to follow path (c) where a univalent metal-anion radical ligand complex is formed, i.e., this redox process is mostly metal-based. The high reduction potential for the 14-membered macrocycles strengthens this conclusion. Stabilisation of a lower valent metal ion-ligand anion radical complex requires a high degree of unsaturation and electron affinity for the complex system which appears to be achieved for the present complexes through the coordination of imine nitrogen atoms and extended dative metal ligand $\pi$ in-
interaction provided by the \( \alpha \)-diimine groups in concert with the phenyl groups.

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References