Template synthesis and spectral speciation of nickel(II) macrocyclic complexes derived from 4-methyl-2,6-di(formyl/benzoyl)phenol and diamines

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Received 10 September 1998; revised 3 December 1998

Nickel(II) macrocyclic complexes [Ni(L)Cl₂]·2H₂O (1, 2) have been synthesized from the nickel(II)-directed condensation of 4-methyl-2,6-diformylphenol (1) or 4-methyl-2,6-dibenzoylphenol (2) with diamines [ethylenediamine(a), 1,3-diaminopropane (b) and o-phenylenediamine (c)] in ethanol in high yields. These complexes are monomeric, non-electrolytes and paramagnetic indicating a distorted octahedral geometry around nickel, which is supported by IR, electronic, ESR and magnetic susceptibility measurements.

There is discernible growth in interest in the synthesis of macrocyclic products using the metal ion template procedure. There are recent reports of mononuclear and binuclear nickel(II) macrocyclic complexes. The structure-function relationship in nickel macrocycles vis-à-vis natural systems is a subject of considerable importance. Recent studies of metal-selenium (M-Se) interactions in the active site of the [FeNiSe] hydrogenases aroused further interest in synthesizing and studying their nickel complexes. We recently reported the template synthesis, characterization, electrochemical and catalytic behaviour of oxovanadium(IV) and Cu(II) macrocyclic complexes. As part of our ongoing study of the coordination chemistry of the macrocyclic ligands, we herein report the template synthesis and spectral speciation of the monomeric nickel(II) macrocyclic complexes.

Experimental

All chemicals used were of reagent grade and used as received. Published methods were used to synthesize 4-methyl-2,6-diformylphenol and 4-methyl-2,6-dibenzoylphenol. Ethylenediamine, 1,3-diaminopropane and o-phenylenediamine and nickel chloride hexahydrate were obtained from Aldrich and Merck. Solvents were purified by standard methods.

Synthesis of complexes [Ni(L)Cl₂]·2H₂O [1a-1c]

To a boiling solution of NiCl₂·6H₂O (2 mmol) and 4-methyl-2,6-diformylphenol (0.45 g, 4 mmol) in ethanol (20 cm³), an ethanolic solution of diamine (4 mmol) [ethylenediamine(a), 1,3-diaminopropane(b) and o-phenylenediamine(c)] was added slowly with constant stirring and the mixture was boiled under reflux for 4 h when a light brown compound was separated out. The product was filtered off, washed with ethanol and dried in air. The yields were 70 - 78%.

Synthesis of complexes [Ni(L)Cl₂]·2H₂O [2a-2c]

These complexes were prepared by a similar procedure as described above employing 4-methyl-2,6-dibenzoylphenol and diamines in the presence of NiCl₂·6H₂O in a 2:2:1 molar ratios, respectively in 75 - 80% yields.

The IR spectra (4000-200 cm⁻¹) were recorded on a Perkin-Elmer 883 spectrophotometer with KBr/CsI pellets. The electronic spectra in MeOH solution were obtained with a Shimadzu UV-160A recording spectrophotometer. The ESR spectra were recorded on a Varian E-112 spectrometer operating in the X-band region at 77K (liquid nitrogen temperature). Room temperature magnetic susceptibility measurements were performed with an EG & G PAR 155 vibrating sample magnetometer. A digital conductivity meter DCM 900 was used for conductivity measurements in DMF. Elemental analyses were performed on a Carlo Erba 1106 elemental analyzer.

Results and discussion

The template condensation of 4-methyl-2,6-di(formyl/benzoyl)phenol with various diamines in the presence of NiCl₂·6H₂O in ethanol yields light brown compounds of composition [Ni(L)Cl₂]·2H₂O [1-2]. The elemental analyses values were found to be in close agreement with the calculated values for the molecular formulae assigned to these complexes (Table 1). The molar conductance values for these complexes are fairly low compared with

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Indian Journal of Chemistry
Table I - Characterization data of the complexes

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<th>Complex</th>
<th>Found (Calc.) %</th>
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<tr>
<td></td>
<td>C</td>
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<tr>
<td>([\text{Ni}(L)\text{Cl}]_2\text{H}_2\text{O} (1a))</td>
<td>49.15 (48.93)</td>
</tr>
<tr>
<td>([\text{Ni}(L)\text{Cl}]_2\text{H}_2\text{O} (1b))</td>
<td>50.78 (50.56)</td>
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<tr>
<td>([\text{Ni}(L)\text{Cl}]_2\text{H}_2\text{O} (1c))</td>
<td>56.40 (56.64)</td>
</tr>
<tr>
<td>([\text{Ni}(L')\text{Cl}]_2\text{H}_2\text{O} (2a))</td>
<td>65.15 (65.43)</td>
</tr>
<tr>
<td>([\text{Ni}(L')\text{Cl}]_2\text{H}_2\text{O} (2b))</td>
<td>66.50 (66.69)</td>
</tr>
<tr>
<td>([\text{Ni}(L'')\text{Cl}]_2\text{H}_2\text{O} (2e))</td>
<td>69.10 (68.96)</td>
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the values reported for 1:1 electrolytes, suggesting that former non-electrolytes are consistent with the presence of coordinated chlorines. The IR spectra of 1 and 2 show one band in the 305 - 319 cm⁻¹ region assignable to v(Ni-Cl) vibrations characteristic of terminal chlorines in a trans configuration in an octahedral arrangement of the ligands around the metal ion. The absorption bands in the 1570-1582 cm⁻¹ region are assignable to the v(C=N) stretching vibration. The appearance of a strong band in the 1535-1550 cm⁻¹ region is due to the v(C=O) vibration of the phenol which assumes partial double bond character as a consequence of delocalisation of the double bonds in the chelate rings containing C=N linkages. A phenyl ring vibration observed at 1610 cm⁻¹ in 1 and 2 but no absorption band associated with -NH stretch at 3260 cm⁻¹ could be detected. All the complexes show a broad band ~3400 cm⁻¹ due to water molecules.

The electronic spectra of 1 and 2 in MeOH solution exhibit two bands in the 11300-11500 and 17300-17600 cm⁻¹ regions which may be assigned to \(\alpha_2 \rightarrow \gamma_1\) transitions respectively suggesting an octahedral geometry around nickel(II) ion. Strong absorption at higher frequencies preclude observation of other possible ligand field transitions.

The ESR spectra of nickel(II) complexes were recorded both in polycrystalline and in MeOH glass at 77K. ESR data \((g_{\alpha} = 2.00)\) suggesting the presence of an unpaired electron in the complex.

The magnetic susceptibilities of nickel(II) complexes in the solid state were determined by the vibrating sample magnetometer at room temperature. The experimental magnetic moments of all complexes lie within the 2.90-3.06 BM range, which are higher than the spin-only value of 2.83 BM. Magnetic moment data reveal only a small orbital contribution to the predicted spin-only value and the monomeric nature of the complexes. Based on analytical, spectral and magnetic evidences, complexes 1 and 2 can be assigned a monomeric octahedral geometry around nickel with NiN₂O₂ core and two chlorine atoms in trans position (Structure I).

It is interesting to observe that the condensation reactions of 4-methyl-2,6-di(formyl/phenyl)phenol with various diamines in the presence of Cu²⁺, VO²⁺ and Ni²⁺ ions resulted in the formation of a monomeric octahedral geometry around the metal ion.
Acknowledgement

The authors thank the CSIR, New Delhi, for financial support and the RSIC, IIT, Madras for providing facilities for recording ESR and magnetic susceptibility measurements.

References