Physicochemical studies of (o-vanillin thiosemicarbazonato)-nickel(II) chelate

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Summary
Five- and six-membered rings result from the chelation of nickel(II) by the dibasic tridentate Schiff base ligand, o-vanillin thiosemicarbazone (o-VTSC), a new chelate prepared and characterized. The structural results are discussed in the light of spectroscopic and other data.

Introduction
The number and diversity of sulphur-nitrogen chelating agents used to prepare new coordination compounds, have increased recently(1,2) and the pronounced biological activity of the metal chelates has created considerable interest(3). The complexes formed with transition metals and uranium with thiosemicarbazones and their analogues have been described earlier(4-6). In this paper the results of the i.r., u.v.-vis. spectroscopic investigations, molar conductance, t.g.a. and n.m.r. data on the nickel chelate of o-VTSC are reported.

Experimental

Materials
o-vanillin-thiosemicarbazide (SISCO), Ni(OAc)2 4H2O (E. Merck) and the reagent grade solvent DMF and EtOH were used as supplied.

Physical measurements
Carbon, hydrogen and nitrogen content were analysed at the RSIC, Central Drug Research Institute, Lucknow, India, and nickel content in the laboratory at Jabalpur, India. 1H n.m.r. spectra of the ligand and chelate were recorded on a WH-270 FTNMR spectrometer equipped with an ASPECT 2000 computer at Bangalore, India. The i.r. spectra were recorded on a Perkin-Elmer model 1430 in the 4000-200 cm-1 range using CsI pallets and the electronic spectrum on a Pye-Unicam SP 8-100 spectrophotometer.

Magnetic susceptibilities were measured by Gouy's method using Hg[Co(SCN)4] as a calibrant. The conductivity measurements were made on a direct reading Toshniwal conductivity bridge employing a 10-3M solution of the chelate in DMF. T.g.a. were made at RSIC Nagpur employing DuPont Instrument.

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Nickel(II)-o-VTSC chelate

The Schiff base ligand o-VTSC (0.005 mol, 1.13 g) was prepared by condensation of o-vanillin with an equimolar ratio of thiosemicarbazide(6) dissolved in 1:1 DMF-EtOH (100 cm3) and added to an aqueous solution of Ni(OAc)2 (0.005 mol, 1.24 g). The mixture was boiled under reflux for 6 h and cooled overnight, after which a brown precipitate formed. This was removed by filtration, washed thoroughly several times with EtOH and Et2O, and finally dried. The chelate was insoluble in H2O, EtOH, MeOH and common organic solvents, but soluble in polar solvents such as DMF, DMSO and Dioxan. The product was recrystallized from DMF; m.p. > 360°C.

The chelate is formed in a 1:1 stoichiometry, having the formula [Ni(o-VTSC)H2O], as revealed by microanalytical data (Table I).

Results and discussion

i.r. spectral studies

I.r. spectral data of the ligand and the chelate exhibit characteristic bands as shown in Table 2. The ligand is present in the thione form in the solid state and enolizes in solution during chelation. A specific band (azomethine) at 1580 cm-1 confirms the formation of the Schiff base by condensation of o-vanillin with thiosemicarbazide(6). The coordination sites are as follows. (a) Phenolic oxygen: absence of a ν(OH) band at ca. 3420 cm-1 in the complex spectrum and the ν(C=O) shift by 20-25 cm-1 to higher wavenumber clearly indicate the deprotonation and subsequent coordination of o-VTSC via phenolic oxygen. The presence of a ν(M=O) band in the far i.r. region at ca. 590 cm-1 further confirms this bonding site. (b) Azomethine nitrogen: the positive ν(C=N) shift by 10 cm-1 to 1580 cm-1 in the ligand and the higher shift of ν(N=O) at ca. 1050 cm-1 is observed. New bands appear due to the chelate [ν(C=N=N=N=) skeleton] at ca. 1530 cm-1 and ν(M=O) at ca. 365 cm-1 further confirming the participation of azomethine nitrogen(7). (c) Thiolic sulphur atom: absence of ν(C=S) band in the spectrum of the chelate at 1480 cm-1 and presence of new band due to ν(C=S) and ν(Ni-O) at 850 and 580 cm-1 respectively confirm that coordination occurs through the thiolic sulphur atom(8). (d) Coordinated water: presence of ν(OH), δ(H2O) and γ(H2O) in the i.r. spectrum of chelate at 3420, 960 and 650 cm-1 shows the presence of coordinated H2O in the complex(9). The ―OCH3 group does not take part in coordination as the ν(OCH3) band observed at ca. 2800 cm-1 in the ligand remains unaltered on chelation(10).
Table 1. Analytical, conductance and magnetic data for o-VTSC chelate.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Found (Calcd.)(%)</th>
<th>M</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>$\Lambda_{\text{m}}$</th>
<th>$\mu_{\text{eff}}$ (B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-VTSC</td>
<td>-</td>
<td>48.1</td>
<td>5.0</td>
<td>18.7</td>
<td>-</td>
<td>-</td>
<td>(48.0) (4.9) (18.7)</td>
</tr>
<tr>
<td>[Ni(o-VTSC).H2O]</td>
<td>20.1</td>
<td>37.0</td>
<td>3.4</td>
<td>14.3</td>
<td>3.83</td>
<td>2.23</td>
<td>(20.8) (36.1) (3.7)</td>
</tr>
</tbody>
</table>

*Molar conductance, measured in ca. 10^-3 M DMF solution and expressed in ohm^-1 cm^2 mol^-1*, **VTSC = o-Vanillinthiosemicarbazone: C_{9}H_{11}N_{3}O_{2}S.**

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is found to be 2.30 B.M., which is intermediate of tetrahedral (3.2-4.1 B.M.) and square planar (diamagnetic) complexes, suggesting that this chelate shows the rare phenomenon of spin-state equilibrium between the spin-free tetrahedral and the spin-paired square planar configurations. This rules out the possibility of octahedral geometry where magnetic moment values lie in the range 2.9-3.3 B.M. Similar high spin-low spin equilibrium has been noticed in the nickel(II) complex formed with a macrocyclic tetradentate ligand derived from 2-aminobenzaldehyde by Busch et al. (1a). The $D_{4h}$ symmetry is preferred rather than $O_{h}$ for the complex and a singlet-triplet equilibrium may occur.

Table 2. Prominent i.r. spectral data (cm^-1) for o-VTSC and Ni—o-VTSC chelate.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu$(NH)</th>
<th>$\nu$(C=N)</th>
<th>$\nu$(C=N-N=C)</th>
<th>$\nu$(N-N)</th>
<th>$\nu$(C:S)</th>
<th>$\nu$(C-S)</th>
<th>$\nu$(M-O)</th>
<th>$\nu$(M-S)</th>
<th>$\nu$(M-N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[o-VTSC]</td>
<td>3130</td>
<td>1580</td>
<td>-</td>
<td>1050</td>
<td>1460</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$v$(H2O) ca. 3480, $\delta$(H2O) ca. 1660 and $\gamma$(H2O) at ca. 680 cm\(^{-1}\) in the chelate.

Electronic spectra and magnetic susceptibilities

In the electronic spectrum of o-VTSC, three intense maxima are observed at 235, 268 and 350 nm due to $n-\pi^*$, $\pi-\pi^*$ and $\sigma-\sigma^*$ transitions, respectively. The latter two bands show blue shift by 40-60 nm in the brown coloured nickel(II) chelate. The three bands observed at 420, 570 and 870 nm are assigned as $^1B_{2g}$- $^1A_{1g}$, $^1A_{2g}$- $^1A_{1g}$ and $^1E_g$- $^1A_{1g}$ transitions, respectively.

The magnetic moment of monomeric Ni—o-VTSC chelate is found to be 2.30 B.M., which is intermediate of tetrahedral (3.2-4.1 B.M.) and square planar (diamagnetic) complexes, suggesting that this chelate shows the rare phenomenon of spin-state equilibrium between the spin-free tetrahedral and the spin-paired square planar configurations. This rules out the possibility of octahedral geometry where magnetic moment values lie in the range 2.9-3.3 B.M. Similar high spin-low spin equilibrium has been noticed in the nickel(II) complex formed with a macrocyclic tetradentate ligand derived from 2-aminobenzaldehyde by Busch et al. (1a). The $D_{4h}$ symmetry is preferred rather than $O_{h}$ for the complex and a singlet-triplet equilibrium may occur.

Table 3. H\(^1\) n.m.r. spectral data of o-VTSC and its nickel(II) chelate.

<table>
<thead>
<tr>
<th>Nuclei</th>
<th>Chem shift (p.p.m.) nickel(II) chelate</th>
<th>Chem shift (p.p.m.) o-VTSC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatic protons</td>
<td>6.45(t), 6.9(d)</td>
<td>6.75(t), 6.95(d), 7.55(d)</td>
</tr>
<tr>
<td>Alkene-CH</td>
<td>7.9</td>
<td>8.4</td>
</tr>
<tr>
<td>Alkene-NH(_2)</td>
<td>6.35</td>
<td>7.9, 8.1</td>
</tr>
<tr>
<td>Alkene-OCH(_3)</td>
<td>3.75</td>
<td>3.80</td>
</tr>
<tr>
<td>Alkene-OH</td>
<td>-</td>
<td>11.4</td>
</tr>
<tr>
<td>Alkene-NH</td>
<td>-</td>
<td>9.2</td>
</tr>
</tbody>
</table>

Figure 1. T.g.a. of Ni—o-VTSC complex.

Electronic spectra and magnetic susceptibilities

In the electronic spectrum of o-VTSC, three intense maxima are observed at 235, 268 and 350 nm due to $n-\sigma^*$, $\sigma-\sigma^*$ and $\pi-\pi^*$ transitions, respectively. The latter two bands show blue shift by 40-60 nm in the brown coloured nickel(II) chelate. The three bands observed at 420, 570 and 870 nm are assigned as $^1B_{2g}$- $^1A_{1g}$, $^1A_{2g}$- $^1A_{1g}$ and $^1E_g$- $^1A_{1g}$ transitions, respectively.

The magnetic moment of monomeric Ni—o-VTSC chelate is found to be 2.30 B.M., which is intermediate of tetrahedral (3.2-4.1 B.M.) and square planar (diamagnetic) complexes, suggesting that this chelate shows the rare phenomenon of spin-state equilibrium between the spin-free tetrahedral and the spin-paired square planar configurations. This rules out the possibility of octahedral geometry where magnetic moment values lie in the range 2.9-3.3 B.M. Similar high spin-low spin equilibrium has been noticed in the nickel(II) complex formed with a macrocyclic tetradentate ligand derived from 2-aminobenzaldehyde by Busch et al. (1a). The $D_{4h}$ symmetry is preferred rather than $O_{h}$ for the complex and a singlet-triplet equilibrium may occur.

$^1H$ n.m.r. spectra

$^1H$ n.m.r. spectra of Ni—o-VTSC chelate were recorded and the spectral lines assigned for all protons with the help of the deuterium exchanged spectrum. The chemical shift values are given in Table 3. The disappearance of $-NH$ and $-OH$ proton signals in the spectrum clearly shows the sites of coordination with nickel. Also the aromatic protons signals at 6.95 and 7.55 p.p.m. of the ligand have shifted to 6.70 p.p.m., the proton at 6.75 shifted to 6.45 p.p.m. Olefinic CH shifted from 8.4 p.p.m. in the ligand to 7.9 p.p.m. The $-NH_2$ and $-OCH_3$ have shifted from 8.0 to 6.35 p.p.m. and 3.8 to 3.75 p.p.m., respectively. The results are in agreement with the proposed structure (Figure 2).

Conclusions

The ligand o-VTSC behaves as a dibasic tridentate ligand towards nickel(II) and the three bonding sites are confirmed to be phenolic oxygen, azomethine nitrogen and thiolo sulphur atom based on spectral, magnetic and t.g.a.