SPECTRAL CHARACTERIZATION OF Ni (II) TETRA SELENIAZIDE COMPLEX : MASS & I.R. SPECTRA

GOVIND KUMAR GUPTA and S. P. S. JADON*

Department of Chemistry, S. V. College, ALIGARH – 202001 (U.P.) INDIA

ABSTRACT

A grayish black complex of Ni(II) seleniazide was synthesized by refluxing equimolar ratio of Se$_4$N$_3$Br and NiCl$_2$ (dehydrated). On the basis of quantitative estimations and Mass Spectrum, the complex is formulated as (Se$_4$N$_3$)$_4$NiCl$_2$. The comparative I.R. spectral data suggested the quadridentated coordinated linkage of Se$_4$N$_3$ to Ni atoms.

Key words: Spectral characterization, Ni (II) Seleniazide, Mass spectra, IR Spectra.

INTRODUCTION

The formation of complex Se$_4$N$_3$Br with Mn (II) & Fe (III) have been reported$^{1,2}$. Since both Se and N have electron pair in spare to donate any metal atom or ion. In continuation of the present work, the complex of Se$_4$N$_3$Br with Ni(II) synthesized and its investigations are being reported herewith.

EXPERIMENTAL

Se$_4$N$_4$ was prepared by the ammonination of Se$_2$Cl$_2$ as reported$^{4-6}$. Se$_4$N$_3$Br was synthesized by the reaction of dry HBr gas on Se$_4$N$_4$ dissolved in CCl$_4$. The excess of Br was removed by washing with CCl$_4$. The red coloured product (Se$_4$N$_3$Br) was finally washed with alcohol, ether and dried. The complex of Se$_4$N$_3$Br with dehydrated NiCl$_2$ was prepared by refluxing equimolar ratio of both in DMF for 6-8 h. The greyish black mass, produced, was separated by filtration washed subsequently with DMF, alcohol, ether, dried and stored in vacuum desiccator. The qualitative analysis for Ni, Se, Br and Cl ions were done and bromide ions were found absent. Se and Ni were estimated by using thiourea and

*Author for correspondence; E-mail: sps_jadon@yahoo.co.in
dimethyl glyoxime respectively as described. The mass and I.R. spectra consequently recorded on Jeol SX-102 (FAB) and Shimadzeu 8201 PC (4000-400 cm⁻¹) from CDRI Lucknow.

RESULTS AND DISCUSSION

The complex of Se₄N₃Br with NiCl₂ is grayish black. The qualitative estimations showed absence of bromine in it. The quantitative estimations, based, on classical methods were done and the analytical data; % found (cal.) –Se 80.921 (80.89), N 10.755 (10.751), Ni 3.758 (3.756), Cl 4.545 (4.543) and mol. wt. 1562 (1562.6) g/mole formulated the complex as (Se₄N₃)₄NiCl₂, which is supported by its mass Spectrum (Fig. 1, Table 1).

Table 1: Mass and I.R. spectral data of nickle complex

<table>
<thead>
<tr>
<th>m/z</th>
<th>Mass data</th>
<th>I.R. Spectral data</th>
<th>Force constant</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fragments</td>
<td>Vibrations (cm⁻¹)</td>
<td>Bands</td>
</tr>
<tr>
<td>91</td>
<td>Se–N (M–2)</td>
<td>670.3</td>
<td>Se–N→Ni</td>
</tr>
<tr>
<td>149</td>
<td>Se–N→Ni  (M–3)</td>
<td>768.7</td>
<td>Se–N</td>
</tr>
<tr>
<td>235</td>
<td>Se–N₂→NiCl₂ (M–2)</td>
<td>1062.0 (trip, b)</td>
<td>Br–Se–N→Ni</td>
</tr>
<tr>
<td>339</td>
<td>Se₃–N₃→Ni (M+1)</td>
<td>1380.7 (d, b)</td>
<td>Br–Se–N→Ni</td>
</tr>
<tr>
<td>413</td>
<td>Se₄N₃→Ni (M–3)</td>
<td>1623.3</td>
<td>Se–N→Ni</td>
</tr>
<tr>
<td>576</td>
<td>Se₄N₃NiCl-Se–N (M+3)</td>
<td>2362.0</td>
<td>Se–N</td>
</tr>
<tr>
<td>598</td>
<td>Se₄N₃NiCl₂ (M+3)</td>
<td>2919.3</td>
<td>Se–N</td>
</tr>
<tr>
<td>688</td>
<td>Se₄N₃NiCl₂-Se₂N₃</td>
<td>3414.9</td>
<td>Se–N</td>
</tr>
<tr>
<td>960</td>
<td>(Se₄N₃)₂–Ni–Se₂N₂ (M–1)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Cont…
<table>
<thead>
<tr>
<th>Mass data</th>
<th>I.R. Spectral data</th>
</tr>
</thead>
<tbody>
<tr>
<td>m/z</td>
<td>Fragments</td>
</tr>
<tr>
<td>1028</td>
<td>((\text{Se}_4\text{N}_3)_2\text{NiCl} \cdots \text{Se}_2\text{N}_2) (M+3)</td>
</tr>
<tr>
<td>1057</td>
<td>((\text{Se}_4\text{N}_3)_2\text{NiCl} \cdots \text{Se}_2\text{N}_3) (M-3)</td>
</tr>
<tr>
<td>1155</td>
<td>((\text{Se}_4\text{N}_3)_2\text{NiCl} \cdots \text{Se}_2\text{N}_3) (M+2)</td>
</tr>
<tr>
<td>1194</td>
<td>((\text{Se}_4\text{N}_3)_3\text{NiCl} \cdots \text{N}_2) (M-3)</td>
</tr>
<tr>
<td>1312</td>
<td>((\text{Se}_4\text{N}_3)_3\text{NiCl} \cdots \text{Se}_2\text{N}_3) (M+1)</td>
</tr>
<tr>
<td>1528</td>
<td>((\text{Se}_4\text{N}_3)_4\text{NiCl}) (M+2)</td>
</tr>
</tbody>
</table>

Fig. 1: Mass spectrum of complex
Showing the prominent mass line at m/z 1528 for \((\text{Se}_4\text{N}_3)_4\text{NiCl}\) fragment having 35 mass for Cl less than its mol.wt. (1562 g/mol.). The appearance of the other mass lines according to the various fragments shown in Table 1 may be explored by the FAB fragmentation technique as mentioned below:

\[(\text{Se}_4\text{N}_3)_4\text{NiCl}_2 \quad m/z = 1562 \]
\[\text{−Se}_3\text{N} \]
\[(\text{Se}_4\text{N}_3)_3\text{NiCl}_2 \quad m/z = 1312 \text{ (M+1)} \]
\[\text{−Se}_3\text{N} \quad \text{m/z = 598 (M+3)} \]
\[\text{−N−Se} \quad \text{m/z = 1528 (M+2)} \]
\[\text{−N} \quad \text{m/z = 1155 (M+2)} \]
\[\text{−N} \quad \text{m/z = 1057 (M-3)} \]
\[\text{−Se}_2\text{N}_2 \quad \text{m/z = 1028 (M+3)} \]
\[\text{−Se}_2\text{N}_2 \quad \text{m/z = 688} \]
\[\text{−Se}_2\text{N}_2\text{Cl}_2 \quad \text{m/z = 413 (M-3)} \]
\[\text{−Se}_2\text{N}_2 \quad \text{m/z = 235 (M-2)} \]

\[(\text{Se}_4\text{N}_3)_3\text{NiCl}_2 \quad m/z = 1528 \quad \text{M+2} \]
\[\text{−Se}_3\text{N} \quad \text{m/z = 1155 (M+2)} \]
\[\text{−N} \quad \text{m/z = 1057 (M-3)} \]
\[\text{−Se}_2\text{N}_2 \quad \text{m/z = 688} \]
\[\text{−Se}_2\text{N}_2\text{Cl}_2 \quad \text{m/z = 413 (M-3)} \]

\[\text{−Se}_2\text{N}_2 \quad \text{m/z = 235 (M-2)} \]

\[\text{−Se}_2\text{N}_2 \quad \text{m/z = 149 (M-3)} \]

\[\text{−Se}_2\text{N}_2 \quad \text{m/z = 235 (M-2)} \]

\[\text{−Se}_2\text{N}_2 \quad \text{m/z = 149 (M-3)} \]

\[\text{−Se}_3\text{N} \quad \text{m/z = 598 (M+3)} \]

\[\text{−N} \quad \text{m/z = 1528 (M+2)} \]

\[\text{−N} \quad \text{m/z = 1155 (M+2)} \]

\[\text{−N} \quad \text{m/z = 1057 (M-3)} \]

\[\text{−Se}_2\text{N}_2 \quad \text{m/z = 688} \]

\[\text{−Se}_2\text{N}_2\text{Cl}_2 \quad \text{m/z = 413 (M-3)} \]

\[\text{−Se}_2\text{N}_2 \quad \text{m/z = 235 (M-2)} \]

\[\text{−Se}_2\text{N}_2 \quad \text{m/z = 149 (M-3)} \]

\[\text{−Se}_3\text{N} \quad \text{m/z = 598 (M+3)} \]

\[\text{−N} \quad \text{m/z = 1528 (M+2)} \]

\[\text{−N} \quad \text{m/z = 1155 (M+2)} \]

\[\text{−N} \quad \text{m/z = 1057 (M-3)} \]

\[\text{−Se}_2\text{N}_2 \quad \text{m/z = 688} \]

\[\text{−Se}_2\text{N}_2\text{Cl}_2 \quad \text{m/z = 413 (M-3)} \]

\[\text{−Se}_2\text{N}_2 \quad \text{m/z = 235 (M-2)} \]

\[\text{−Se}_2\text{N}_2 \quad \text{m/z = 149 (M-3)} \]

\[\text{−Se}_3\text{N} \quad \text{m/z = 598 (M+3)} \]

\[\text{−N} \quad \text{m/z = 1528 (M+2)} \]

\[\text{−N} \quad \text{m/z = 1155 (M+2)} \]

\[\text{−N} \quad \text{m/z = 1057 (M-3)} \]

\[\text{−Se}_2\text{N}_2 \quad \text{m/z = 688} \]

\[\text{−Se}_2\text{N}_2\text{Cl}_2 \quad \text{m/z = 413 (M-3)} \]

\[\text{−Se}_2\text{N}_2 \quad \text{m/z = 235 (M-2)} \]

\[\text{−Se}_2\text{N}_2 \quad \text{m/z = 149 (M-3)} \]

\[\text{−Se}_3\text{N} \quad \text{m/z = 598 (M+3)} \]

\[\text{−N} \quad \text{m/z = 1528 (M+2)} \]

\[\text{−N} \quad \text{m/z = 1155 (M+2)} \]

\[\text{−N} \quad \text{m/z = 1057 (M-3)} \]

\[\text{−Se}_2\text{N}_2 \quad \text{m/z = 688} \]

\[\text{−Se}_2\text{N}_2\text{Cl}_2 \quad \text{m/z = 413 (M-3)} \]

\[\text{−Se}_2\text{N}_2 \quad \text{m/z = 235 (M-2)} \]

\[\text{−Se}_2\text{N}_2 \quad \text{m/z = 149 (M-3)} \]

\[\text{−Se}_3\text{N} \quad \text{m/z = 598 (M+3)} \]

\[\text{−N} \quad \text{m/z = 1528 (M+2)} \]

\[\text{−N} \quad \text{m/z = 1155 (M+2)} \]

\[\text{−N} \quad \text{m/z = 1057 (M-3)} \]

\[\text{−Se}_2\text{N}_2 \quad \text{m/z = 688} \]

\[\text{−Se}_2\text{N}_2\text{Cl}_2 \quad \text{m/z = 413 (M-3)} \]

\[\text{−Se}_2\text{N}_2 \quad \text{m/z = 235 (M-2)} \]

\[\text{−Se}_2\text{N}_2 \quad \text{m/z = 149 (M-3)} \]

\[\text{−Se}_3\text{N} \quad \text{m/z = 598 (M+3)} \]

\[\text{−N} \quad \text{m/z = 1528 (M+2)} \]

\[\text{−N} \quad \text{m/z = 1155 (M+2)} \]

\[\text{−N} \quad \text{m/z = 1057 (M-3)} \]

\[\text{−Se}_2\text{N}_2 \quad \text{m/z = 688} \]

\[\text{−Se}_2\text{N}_2\text{Cl}_2 \quad \text{m/z = 413 (M-3)} \]

\[\text{−Se}_2\text{N}_2 \quad \text{m/z = 235 (M-2)} \]

\[\text{−Se}_2\text{N}_2 \quad \text{m/z = 149 (M-3)} \]
To through light on the bonding and geometry of the complexes its I.R. spectrum recorded in KBr is compared to that of ligand and interpritated as per litlature. The sharp frequency at 670.2 cm\(^{-1}\) in the I.R. of ligand has shortned and brodened in the I.R. of complexes, due to the linkage of Se-N band to Ni-atom similarly a prominant peak at 761.2 cm\(^{-1}\) in the I.R. of ligand has deleted in the I.R. of complexes. The three prominant vibration 929.3, 1043.8 and 1215.5 cm\(^{-1}\) in the I.R. spectrum of ligand have coupled to form a broad tripled at 1062.0 cm\(^{-1}\) in the I.R. spectrum of complex, suggesting that Se\(_4\)N\(_3\) group of the ligand has coordinative to Ni atom. The bands at 1422.0, 1520.0 and 1652.1 cm\(^{-1}\) in the I.R. of ligand have also mixed in the I.R. of complex showing a broad, condensed, dublet at 1380.7 cm\(^{-1}\) along with a new assignment for Se=\(\rightarrow\)Ni at 1623.3 cm\(^{-1}\). This view of coordinate linkage is also supported by the broad peake at higher region of I.R. of complex comparative to that of ligand. The I.R. spectrum of complex expounds that Se\(_4\)N\(_3\)^\(-\) has quadridentedly coordinative to Ni atom in the complex. The values of the force constant K calculated (Table 1) by using the following equation (loc.cit.)

\[
\bar{v} = \frac{1}{2\pi \mu} \sqrt{\frac{k}{\mu}} = 5.3 \times 10^{-12} \sqrt{\frac{k}{\mu}}
\]

Where \(\bar{v}\) = frequency and \(\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} + \frac{1}{m_3} + \ldots\)

Also sustained the aforesaid view of quadridentative linkage in the complex as shown by Fig. 3 having tetrahedral geometry.

![Fig. 2 (a): IR Spectrum of Ligand](image-url)
Fig. 2 (b): IR Spectrum of complex

Fig. 3: Structure of the complex, \((\text{Se}_4\text{N}_3)_4\text{NiCl}_2\)

ACKNOWLEDGMENT

Authors wish to thank to the Director, C. D. R. I., Lucknow to provide instrumental facilities.

REFERENCES


Accepted: 20.04.2014