



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

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ABSTRACT

A grayish black complex of Ni(II) seleniazide was synthesized by refluxing equimolar ratio of $\text{Se}_4\text{N}_3\text{Br}$ and NiCl_2 (dehydrated). On the basis of quantitative estimations and Mass Spectrum, the complex is formulated as $(\text{Se}_4\text{N}_3)_4\text{NiCl}_2$. The comparative I.R. spectral data suggested the quadridentated coordinated linkage of Se_4N_3 to Ni atoms.

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

INTRODUCTION

The formation of complex $\text{Se}_4\text{N}_3\text{Br}$ 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 $\text{Se}_4\text{N}_3\text{Br}$ with Ni(II) synthesized and its investigations are being reported herewith.

EXPERIMENTAL

Se_4N_4 was prepared by the ammoniation of Se_2Cl_2 as reported⁴⁻⁶. $\text{Se}_4\text{N}_3\text{Br}$ was synthesized by the reaction of dry HBr gas on Se_4N_4 dissolved in CCl_4 . The excess of Br was removed by washing with CCl_4 . The red coloured product ($\text{Se}_4\text{N}_3\text{Br}$) was finally washed with alcohol, ether and dried. The complex of $\text{Se}_4\text{N}_3\text{Br}$ 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

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dimethyl glyoxime respectively as described⁷. 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 $\text{Se}_4\text{N}_3\text{Br}$ with NiCl_2 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 $(\text{Se}_4\text{N}_3)_4\text{NiCl}_2$, which is supported by its mass Spectrum (Fig. 1, Table 1).

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

Mass data		I.R. Spectral data		
m/z	Fragments	Vibrations (cm^{-1})	Bands	Force constant $\text{K} \times 10^5 \text{ dyns cm}^{-2}$
91	Se–N (M–2)	670.3	Se–N→Ni	3.1590
149	Se–N→Ni (M–3)	768.7	Se–N	4.1545
235	Se–N ₂ –NiCl ₂ (M–2)	1062.0 (trip, b)	Br–Se–N→Ni	6.9059
339	Se ₃ –N ₃ –Ni (M+1)	1380.7 (d, b)	Br–Se–N→Ni	11.6728
413	Se ₄ N ₃ → Ni (M–3)	1623.3	Se–N→Ni	18.5273
576	$\begin{array}{c} \text{N} \\ \downarrow \\ \text{Se}_4\text{N}_3\text{---NiCl---Se---N} \\ \uparrow \\ \text{N} \end{array}$ (M+3)	2362.0	Se–N	39.2261
598	$\begin{array}{c} \text{Se---N} \\ \downarrow \\ \text{Se}_4\text{N}_3\text{---NiCl}_2 \\ \uparrow \\ \text{N} \end{array}$ (M+3)	2919.3	Se–N	59.9201
688	Se ₄ N ₃ –NiCl ₂ –Se ₂ N ₃	3414.9	Se–N	81.9919
960	(Se ₄ N ₃) ₂ –Ni–Se ₂ N ₂ (M–1)			

Cont...

Mass data		I.R. Spectral data		
m/z	Fragments	Vibrations (cm ⁻¹)	Bands	Force constant K × 10 ⁵ dyns cm ⁻²
1028	$\begin{array}{c} \text{N} \\ \downarrow \\ (\text{Se}_4\text{N}_3)_2\text{-NiCl-}\text{Se}_2\text{N}_2 \text{ (M+3)} \\ \uparrow \\ \text{N} \end{array}$			
1057	$\begin{array}{c} \text{N} \\ \uparrow \\ (\text{Se}_4\text{N}_3)_2\text{-NiCl}_2\text{-}\text{Se}_2\text{N}_3 \text{ (M-3)} \\ \uparrow \\ \text{N} \end{array}$			
1155	$\begin{array}{c} \text{N} \\ \downarrow \\ (\text{Se}_4\text{N}_3)_2\text{-NiCl}_2\text{-}\text{Se}_2\text{N}_3 \text{ (M+2)} \\ \uparrow \\ \text{N} \end{array}$			
1194	(Se ₄ N ₃) ₃ -NiCl-N ₂ (M-3)			
1312	(Se ₄ N ₃) ₃ -NiCl ₂ -SeN ₂ (M+1)			
1528	(Se ₄ N ₃) ₄ -NiCl (M+2)			

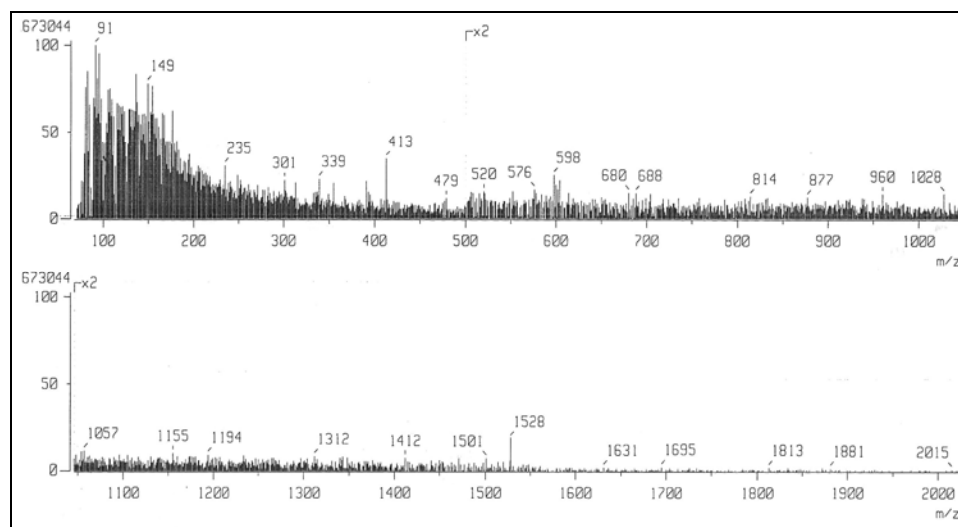
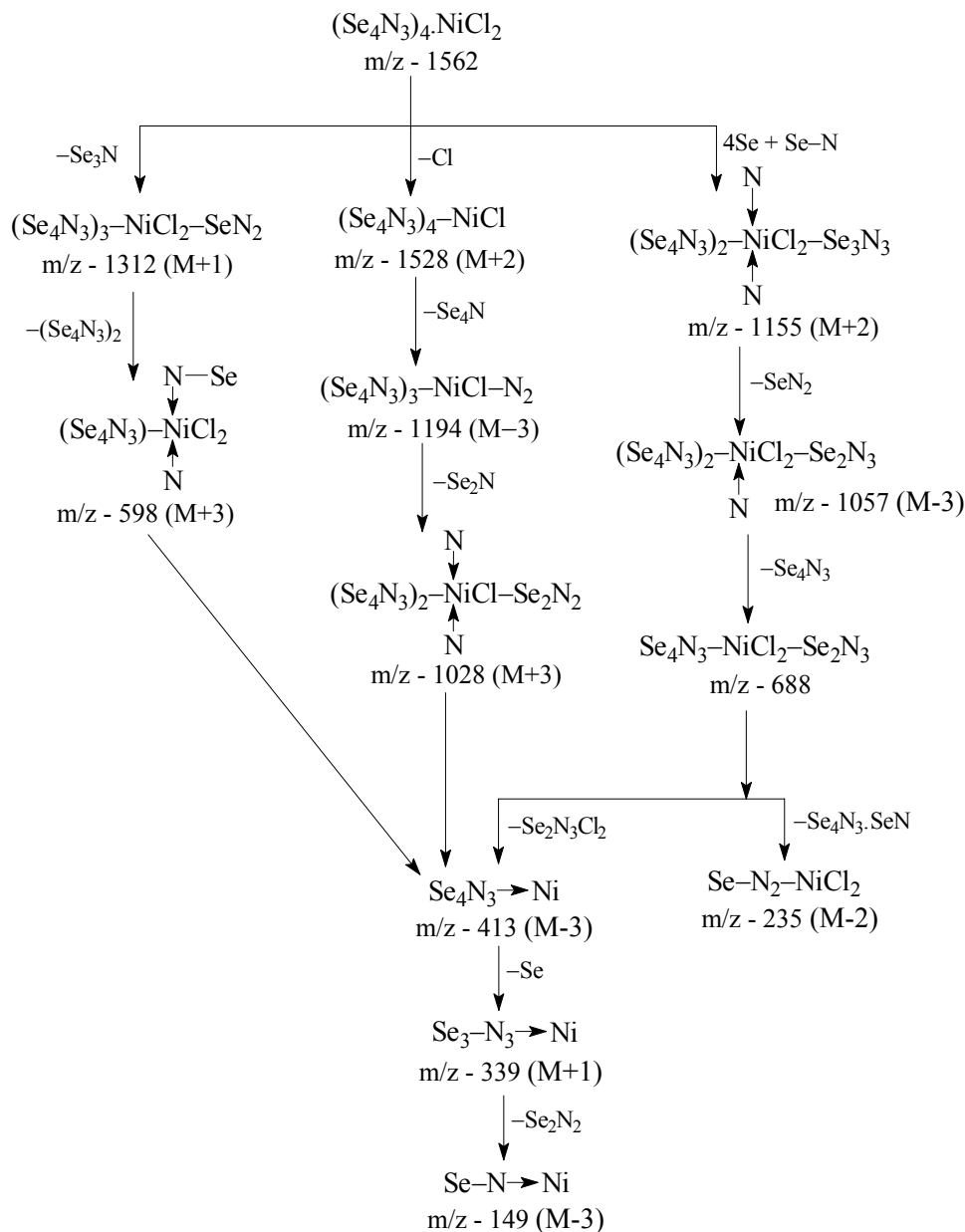


Fig. 1: Mass spectrum of complex

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:



Scheme 1

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 interpreted as per literature³. 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 prominent peak at 761.2 cm^{-1} in the I.R. of ligand has deleted in the I.R. of complexes. The three prominent 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_4N_3 group of the ligand has coordinated 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-N→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 comprative to that of ligand. The I.R. spectrum of complex expounds that Se_4N_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.)

$$\bar{\nu} = \frac{1}{2\pi\pi} \sqrt{\frac{k}{\mu}} = 5.3 \times 10^{-12} \sqrt{\frac{k}{\mu}}$$

Where $\bar{\nu}$ = frequency and $\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} + \frac{1}{m_3} + \dots$

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

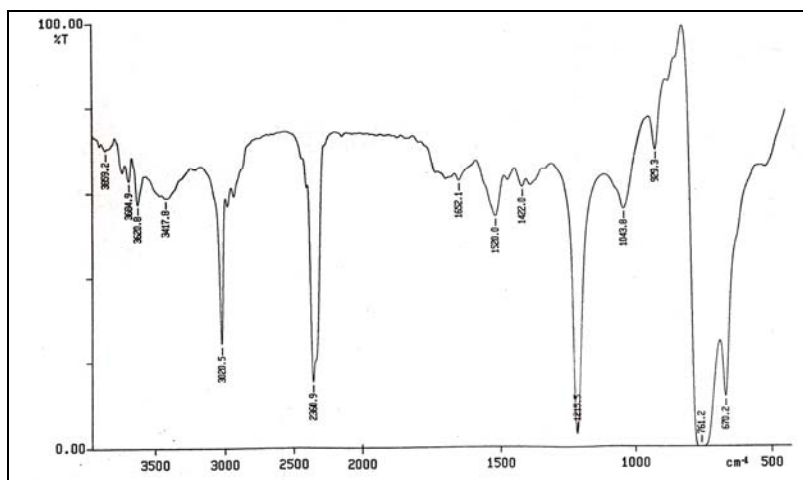


Fig. 2 (a): IR Spectrum of Ligand

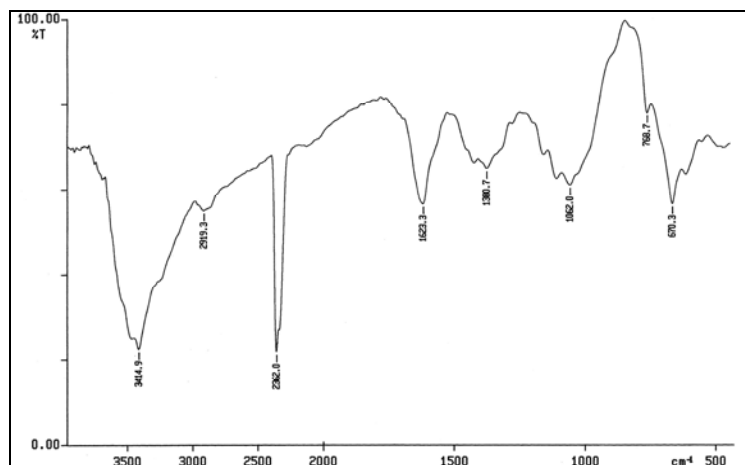


Fig. 2 (b): IR Spectrum of complex

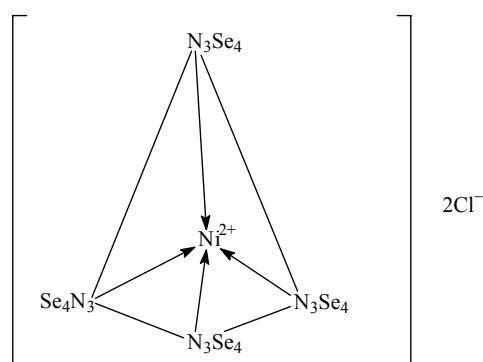


Fig. 3: Structure of the complex, $(\text{Se}_4\text{N}_3)_4\text{NiCl}_2$

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