

Characterization of the Reaction Product of $\text{Se}_4\text{N}_3\text{Cl}$ and Phenyl Hydrazine by ^1H NMR

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$\text{Se}_4\text{N}_3\text{Cl}$ was mixed with phenyl hydrazine in equimolar ratio and refluxed in non-polar solvent. The product formed was analyzed quantitatively, as well as mass, IR, electronic and ^1H NMR spectrometrically and assigned as $(\text{Se}_4\text{N}_3)_2\text{—N—NH—C}_6\text{H}_5$.

Key Words: ^1H NMR, Phenyl hydrazine, $\text{Se}_4\text{N}_3\text{Cl}$.

INTRODUCTION

The complexes of Se_4N_4 with AlBr_3 , SF_6 and tungsten compounds have been reported^{1–9}. The halogenated adducts of Se_4N_4 such as SeN_2Cl_2 , $\text{Se}_3\text{N}_3\text{Cl}$ and $\text{Se}_4\text{N}_3\text{Cl}$ have also been synthesized^{10, 11}. In this paper, the synthesis and characterization of the reaction product of $\text{Se}_3\text{N}_3\text{Cl}$ with phenyl hydrazine has been reported.

EXPERIMENTAL

Se_4N_4 was synthesized^{12, 13} by passing dry NH_3 into SeCl_2 dissolved in CCl_4 kept in an ice bath. The orange needle shaped crystalline solid obtained was treated with acetyl chloride to get $\text{Se}_4\text{N}_3\text{Cl}$, which was mixed with phenyl hydrazine in equimolar ratio using DMF as solvent and refluxed for about 24 h. The red coloured product formed was filtered, washed subsequently with DMF, Et_2OH and Et_2O and stored *in vacuo*.

Mass, IR, UV and ^1H NMR spectra of the compound were carried out on JEOL SX-102 (FAB), Shimadzu 8201 PC (4000–400 cm^{-1}), Perkin-Elmer Lambda-15 (200–800 nm) and Bruker DRX-300 (300 MHz) respectively.

RESULTS AND DISCUSSION

The chemical data of the reaction product, % found (calcd.), as Se 76.57 (76.79), N 13.55 (13.61), C 8.72 (8.75), H 0.84 (0.85) and m.w. 826 (823), formulated the compound as $(\text{Se}_4\text{N}_3)_2\text{—N—NH—C}_6\text{H}_5$, which is supported by the mass lines observed in its mass spectrum at m/z 179, 391, 469, 559 and 824 for $\text{Se}_2\text{—N}_3$, $\text{Se}_4\text{N}_3\text{—NH—NH}_2$ ($M + 2$), $\text{Se}_4\text{N}_3\text{—NH—NH—C}_6\text{H}_5$ ($M + 3$), $\text{Se}_4\text{N}_3\text{—NH—NH—C}_6\text{H}_5\text{—Se—N}$ and $(\text{Se}_4\text{N}_3)_2\text{—N—NH—C}_6\text{H}_5$ ($M + 2$) fragments, respectively.

The vibrations found in its IR spectrum (Table-1) from 474.1 to 830.4 cm^{-1} are due to Se—N bands¹⁴ and Se—N ring, while the frequencies in higher region from 3339.4 to 1302.7 cm^{-1} are on account of N—H and δ N—H bands. The remaining

assignments at 912.5 cm^{-1} for $\text{C}_6\text{H}_5\text{—NH}_2$ and $1142.0\text{—}1001.9\text{ cm}^{-1}$ for Se—N—H groups are present, inferring that Se_4N_3 ion has linked to phenyl hydrazine through its N atom in place of C atom of C_6H_5 group, forming the compound as follows:

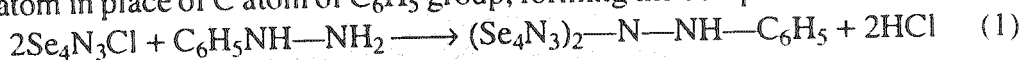


TABLE-I
IR (cm^{-1}) SPECTRAL DATA OF THE REACTION PRODUCT

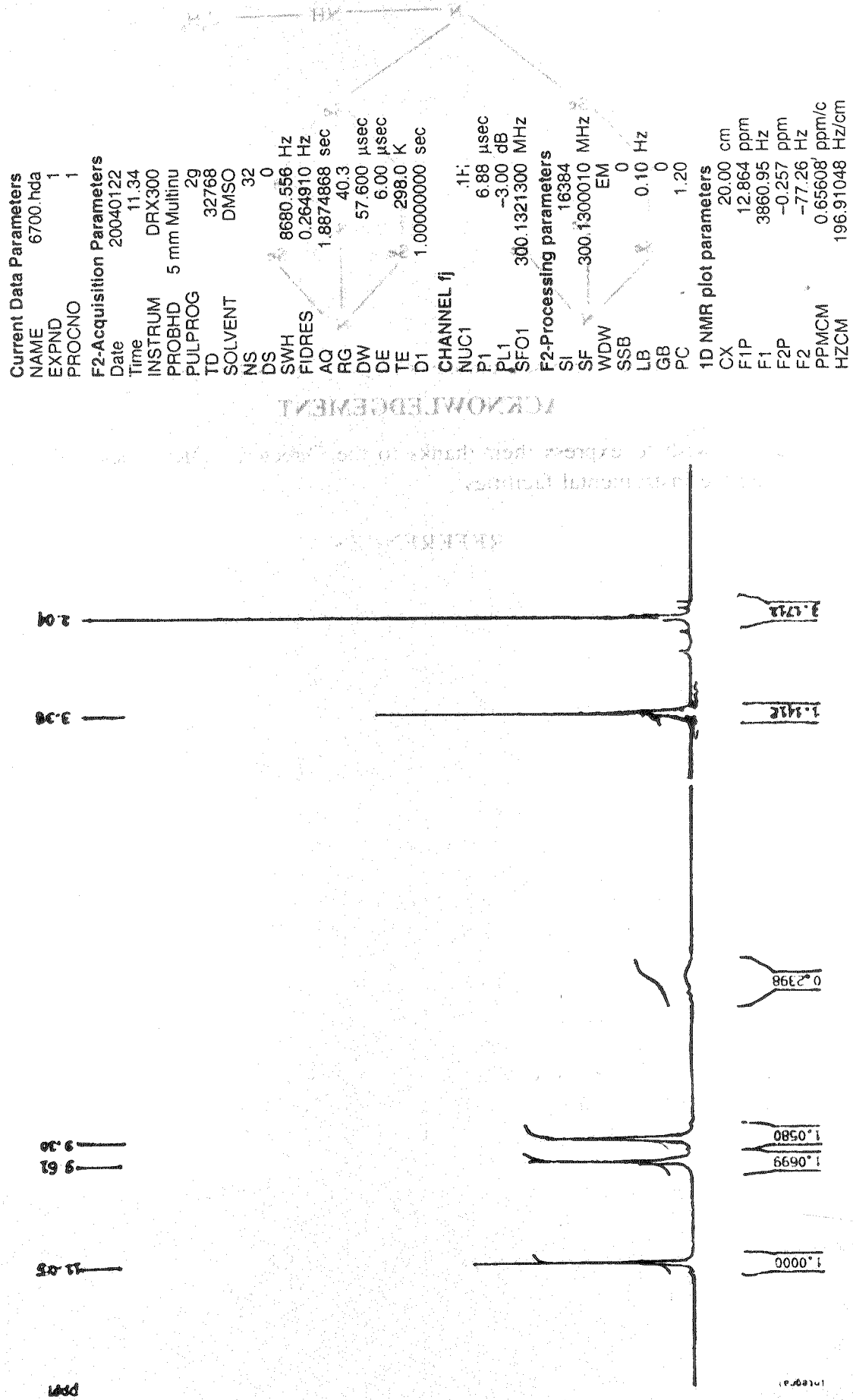
S.No.	Vibrations (cm^{-1})	Band assigned	Force constant (N/m^2)
1.	474.1 (s)	$\nu(\text{Se—N})$	1.567
2.	508.8 (s)	$\nu(\text{Se—N})$	1.805
3.	539.5 (s)	$\nu(\text{Se—N})$	2.456
4.	646.7	$\nu(\text{Se—N})$	2.915
5.	724.7 (b)	$\nu(\text{Se—N ring})$	3.660
6.	830.4 (s)	$\nu(\text{Se—N ring})$	4.806
7.	912.5 (s)	$\nu(\text{C}_6\text{H}_5\text{—NH}_2)$	3.039
8.	1001.9 (s)	$\nu(\text{Se—N—H})$	6.937
9.	1060.0 (s)	$\nu(\text{Se—N—H})$	7.765
10.	1142.0 (b)	$\nu(\text{Se—N—H})$	9.011
11.	1369.5–1302.7 (qu. B)	$\nu(\text{N—H})$	9.282
12.	1421.7	$\nu(\text{N—H})$	1.105
13.	1511.4	$\nu(\text{N—H})$	1.171
14.	1620.1	$\nu(\text{N—H})$	1.346
15.	2364.9	$\nu(\text{N—H})$	3.238
16.	3184.3	$\nu(\text{N—H})$	5.870
17.	3339.4	$\nu(\text{N—H})$	5.719

These vibrations are compared to the frequencies of $\text{Se}_4\text{N}_3\text{Cl}$ and the occurrence of single and double bonds is confirmed by the values of force constants calculated.

Two bands have appeared at $\nu_1 = 256.8$ and $\nu_2 = 571.0$ nm in its electronic spectrum out of which the former assignment is due to charge transfer transition, *i.e.*, ionic environment suggesting the ionic nature of the product. The latter band is corresponding to $d\pi\text{—}p\pi$ transition of Se_4N_3^+ ring present in the compound. The values of oscillator strength, ' f ' = 2.53×10^{-5} and 3.596×10^{-5} are also according to spin-allowed Laporte forbidden transition, showing the linkage of $\text{Se}_4\text{N}_3\text{Cl}$ and $\text{C}_6\text{H}_5\text{NH—NH}_2$ in the product with the evolution of HCl. The values of band gap energy ($\Delta E_g = 0.805$ eV) and number of conducting electrons ($N_c = 3.57 \times 10^5$) indicate the conductive character of the compound.

^1H NMR spectrum (Fig. 1) consists signals at chemical shift, δ 2.04 ppm along with two shouldered signals on each side due to five (0.5) protons of C_6H_5 group, while single signal at chemical shift δ 3.38 ppm is on account of N—NH band. A swollen signal (triplet) and other signals at δ 9.30, 9.61 and 11.05 ppm are according to Se—N bands of two Se_4N_3 rings linked to N—NH group of phenyl hydrazine with the elimination of 2HCl mol. as expressed by eqn. (1) and the structure of the reaction product, Fig. 2.

Fig. 1. 1H NMR spectrum of the compound



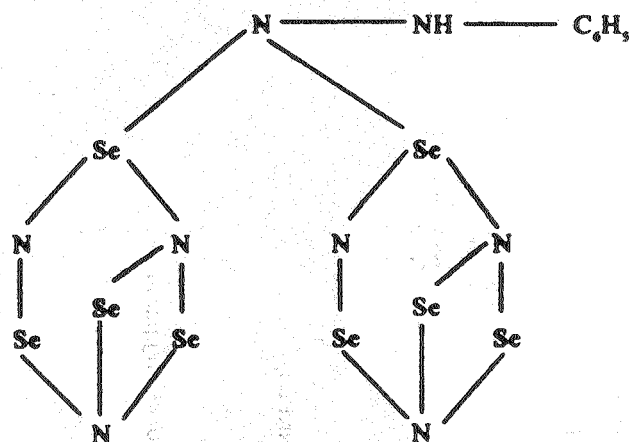


Fig. 2. Proposed structure of $(\text{Se}_4\text{N}_3)_2\text{—N—NH—C}_6\text{H}_5$

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