

Coordination of Heptasulphaimide (S_7NH) with $SiCl_4$

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ABSTRACT :

Reaction of heptasulphaimide (S_7NH) with $SiCl_4$ leads to the formation of quadridentate complex, $[(S_7NH)_2 SiCl_4]$, without the evolution of HCl in non-polar solvent. Its mass, i.r., uv, e.p.r. and 1H NMR spectra inferred its O_h symmetrical geometry along with paramagnetism and hydrogen bonding in it.

Introduction :

Various complexes of S_7NH with metallic salts of Fe, Co, Ni, Cu, Ru, Au, Pt, and Pd have been reported¹⁻³. Bergmann⁴ has prepared the Titanocene complex, $[(Cp)_2 Ti S_7NH]$ and $[(Cp)_2 Ti S_7NCH_3]$, containing bridging Sulfur-bond.

Experimental :

Heptasulfaimide, (S_7NH) was recovered from the ether extract, as

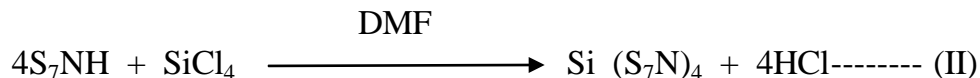
By product during the synthesis of $S_4N_4^5$, as yellow flat plates. Water free Aldrich chemicals were used through out the work. The equimolar solutions of S_7NH and $SiCl_4$, dissolved in DMF separately are mixed and refluxed for 12 hrs at 150^0C till the cream coloured product was precipitated. The mass obtained was filtered, washed successively with DMF, ethanol and ether to remove S_7NH if remained unreacted then dried and stored in vacuo.

Quantitative estimations for constituent elements and molecular weight determination were done as described in Vogel's text book⁶. The mass spectrum was recorded on 'Micro Mass Quattro-II' triple quadrupole Spectrometer at 20-25 Volt, while Shimadzu FTIR model 201 P.C. ($400 - 4000\text{ cm}^{-1}$) and Perkin-Elmer Lambda -15 ($200 - 800\text{ nm}$), Spectrometers were used for I.R. and electronic spectra (uv) respectively. The E.P.R. and $^1H.N.M.R.$ spectra of the complex were carried out subsequently on varians E-X-4 band (DPPH) and F.T.N.M.R. model DPX-200 (DMSO as solvent) spectrometers at 300^0K .

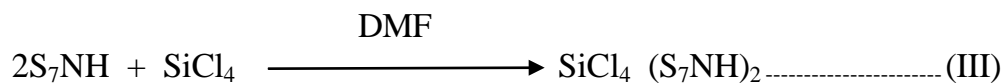
Result and Discussion :

The reaction of heptasulfaimide (S_7NH) being ionic in nature, with $SiCl_4$ may be either (I) or (II).





But on testing the evolution of HCl with Ammonia, no fumes were observed, showing the absence of HCl and analytical data; % found (cal.), S 68.8 (69.15), N 4.30 (4.32), Si 4.28 (4.30), Cl 21.80 (21.90), H 0.30 (0.30) and mol. Wt. 651.6 (648.0), formulate it $(S_7NH)_2 \cdot SiCl_4$, suggesting that ionic replacement between $SiCl_4$ and S_7NH has not occurred and the reaction may be as scheme (III), not according to route (I) and (II).



This view is also supported by its mass spectrum (table-1) in which mass lines (m/z) at 208 for S_6NH (M+1), 238 for S_7N , 289/291 for $SiCl_2 - S_6$, 498 for $S_5 - SiCl_2 - S_7NH$ and 511 due to $NS_5 - SiCl_2 - S_7N$ fragments have observed, inferring the presence of S_7NH molecule in the complex and having the aforesaid molecular formula.

The vibrations, found in its i.r. spectrum (table-1) are interpreted on the basis of available literature⁷. The frequencies at 751.1 (wb) & 800 - 828 (b) cm^{-1} due to $S - S \rightarrow Si$ and 905 - 940 (b) & 965(b) cm^{-1} for $S - N \rightarrow Si$ bands have been

occurred, explaining that S_7NH has linked to $SiCl_4$ quadridentatively through its both S and N atoms, forming O_h complex. The other peaks in higher region are according to S – N – H & N – H groups as present in the ligand, S_7NH .

Only one band at 207.2 nm, which is due to charge transfer transition caused by ionic nature of S_7NH was found in its electronic spectrum (table-2). The absence of $\pi\pi^*$ transition also indicate the coordination of S_7NH to $SiCl_4$. This is opinionated by the values of oscillator strength, 'f' and 'Dq' for the Spin-Allowed Laporte - Forbidden transition due to 'Td' symmetry⁸ of Si atom, which has changed to O_h symmetry during the coordination of S_7NH and $SiCl_4$. The values of band gap energy and number of conducting electrons (N_c) expound the electrical conductivity of the complex.

E.P.R. spectrum of the complex possess hyperfine splitting with four prominent peaks (table-2), caused by 'H' atoms, inferring the linkage of S_7NH to $SiCl_4$ without elimination of HCl. The values of μ_{eff} (in the range 1.70 – 1.74 B.M.) and magnetic susceptibility, X_A of the order 10^{-3} suggest the paramagnetism and presence of unpaired electrons in the complex, on account off 'Hydrogen Bonding' in it. The values of $g_{av} > 2.0$ are according to vacant 'd' energy shell of Si atom to accept electron pairs for coordination, while $g_{av} = 2.003$ are due to free electron present in it. The value for number of unpaired electron is also one, which upholds aforesaid view. If the complex formation has occurred through reaction (I) and (II), no signal should be appeared in its e.p.r. spectrum on account of covalent character of Si

atoms.

¹H N.M.R. spectrum (fig.-1) of the complex, graphed, consists two sets of three strong signals at δ 2.476, 2.712, 2.881 and 7.507, 7.949 & 8.159 ppm for two 'H' atoms linked to 'N' atoms of S₇NH adjacent to two doublets at δ 3.167, 3.399 and δ 8.9 – 9.10 ppm for N-H bands arranged symmetrically, opposite to each other with Si centred atom, as expressed by its geometrical structure, fig.-2.

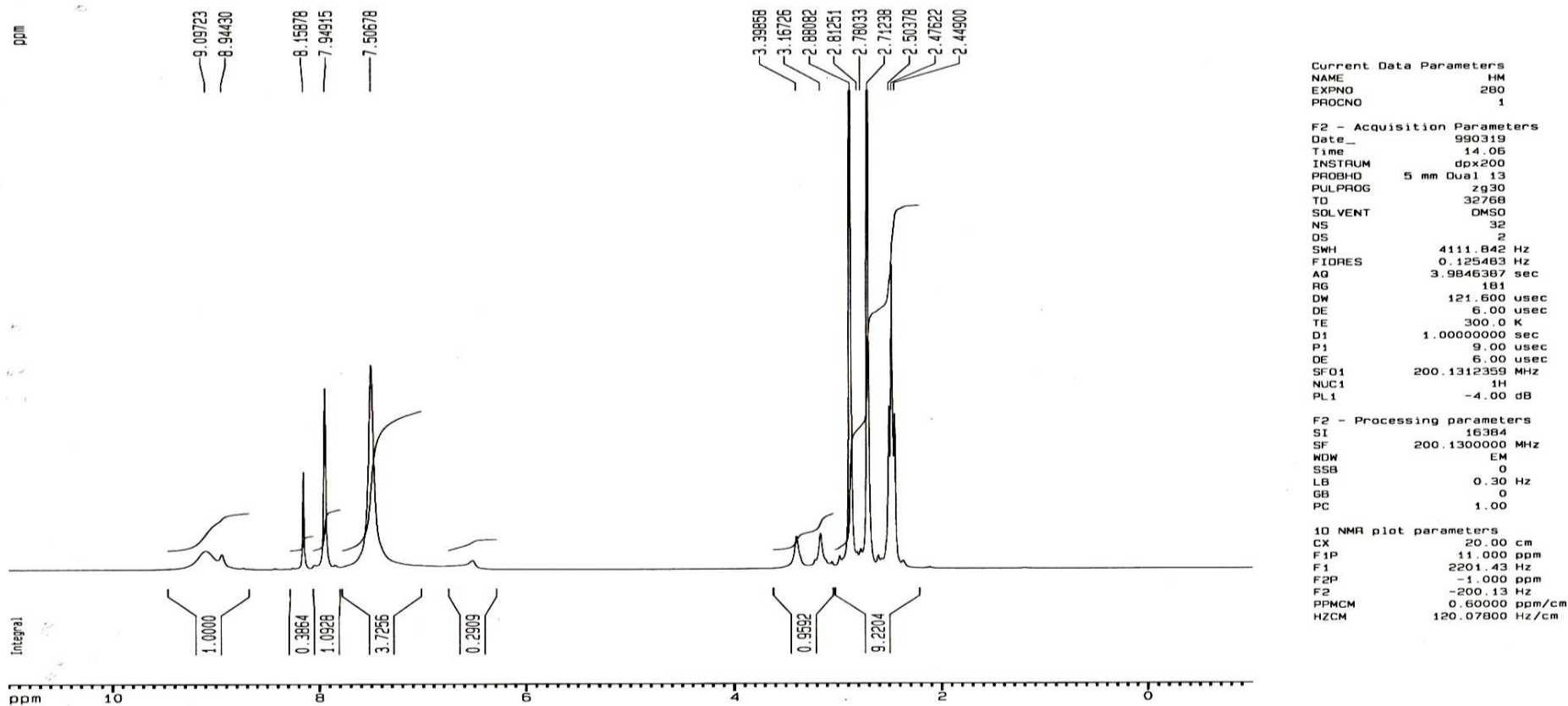


Fig.-1 :¹H N.M.R. spectrum of the complex of Heptasulphaimide(S₇NH) with SiCl₄

Table-1

Mass and I.R. spectra of the complex (S₇NH)₂.SiCl₄

S.No.	Mass parameters		I.R. Spectral data	
	m/z	Fragments	Vibrations (Cm ⁻¹)	Bands Assigned
1	208	S ₆ NH (M+1)	400.0(s)	Si –Cl
2	238	S ₇ N	427.7 (s)	S – S
3	289/291	SiCl ₂ - S ₆	757.1 (wb)	S – S → Si
4	324	SiCl ₂ - S ₇	800-828 (b)	S – S → Si
5	372	SiCl ₃ - S ₇ N	905-940 (b)	S – N → Si
6	436	S ₂ - SiCl ₃ - S ₇ N (M-1)	965.0 (b)	S – N → Si
7	453	S ₃ - SiCl ₃ - S ₇	1225 (s)	S – N → H
8	498	S ₅ - SiCl ₂ - S ₇ N	1295 (s)	S – N → H
9	511	NS ₅ - SiCl ₂ - S ₇ N	1338.5 (s)	S – N → H
10		-	2278.5 (s)	δ N – H
11		-	2476.4 (s)	δ N – H
12		-	2864.1 (s)	δ N – H

Table-2

Electronic and E.P.R. spectra of $(S_7NH)_2 \cdot SiCl_4$

S. No.	Electronic data (u v)		E.P.R. Parameters				
			Magnetic Field (Gauss)	g_{av}	μ_{eff} (BM)	X_A $\times 10^{-3}$	n
1	Bands (nm)	207.2 C.T.	3028(b)	1.964	1.701	1.21	1
2	Oscillator Strength 'f'	5.698×10^{-3} Td \rightarrow O _h	3265	1.994	1.724	1.29	1
3	Dq (cm ⁻¹)	482.6	3325(s)	2.004	1.736	1.27	1
4	Band gap energy ΔE_g (e.v.)	0.598	3376(s)	2.003	1.734	1.25	1
5	(Nc)	2.85×10^{29}					

Conclusion :

The results infer that heptasulfaimide (S_7NH) has coordinated in quadridentate manner to $SiCl_4$ without elimination of HCl gas, forming the complex, $(SiCl_4)_2 \cdot SiCl_4$ having paramagnetic character, electrical conductivity and O_h geometrical array as fig.-2.

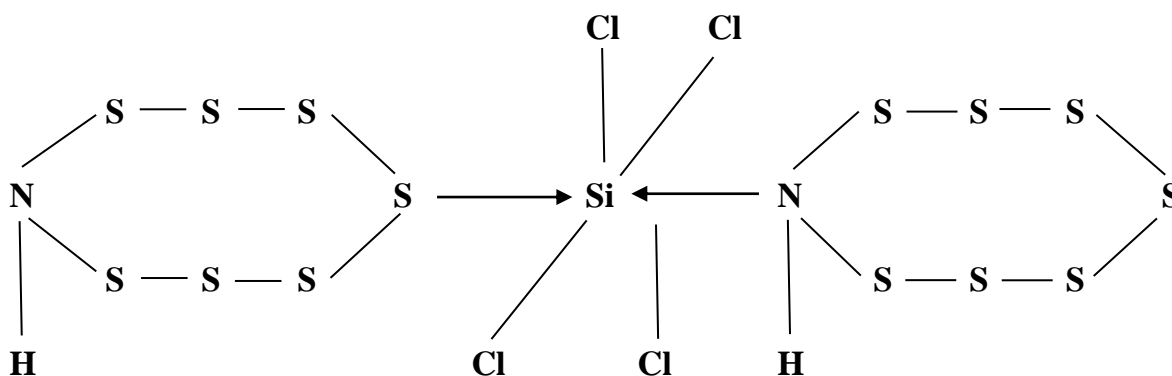


Fig.-2

Proposed structure of the complex of Heptasulphaimide (S_7NH) with $SiCl_4$

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