

Spectroscopic investigation of the reaction product of tetrathiazylidihydrofluoride ($S_4N_4H_2F_2$) with Hg (II) Chloride

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Abstract

The reaction of tetrathiazylidihydrofluoride ($S_4N_4H_2F_2$) with $HgCl_2$ was carried out in organic medium. The product obtained was characterized on the basis of IR, UV, EPR, Mass and 1H NMR spectra and is formulated as $[S_3N_4H_2F_2HgCl]_x$ where $x = 3.28$

Key words: Tetrathiazylidihydrofluoride, N-coordinated complex, hydrogenbonding.

Introduction

The synthesis of halocyclothiazenes like $(NSCl)_3$, S_4N_3Cl , $S_3N_2Cl_2$, S_3N_2Br have been reported¹⁻⁵. The preparation of sulphur-nitrogen fluorine compounds have been developed rapidly⁶⁻⁸. The preparation of $S_4N_4H_2F_2$ and its complexes with Si(IV), Sn(II), Ti(III) and Zr(IV) have been described⁹⁻¹¹. In view of this the reaction of $S_4N_4H_2F_2$ with $HgCl_2$ in non aqueous solvent leading to formation of metal complex and its spectrometric investigation are being presented here.

Experimental

Tetrathiazylidihydrofluoride¹² was

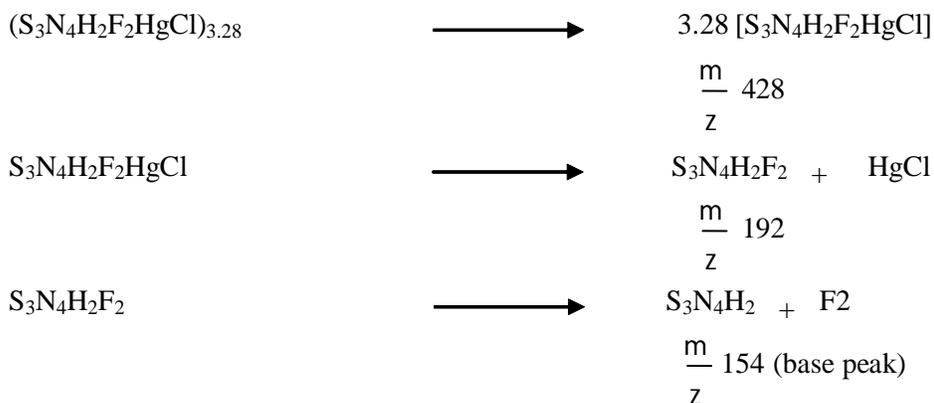
prepared by passing dry hydrogen fluoride gas (H_2F_2) into benzene solution of S_4N_4 ¹³ at 290 K with constant mechanical stirring for 5 hours till it was red. The reddish yellow mass was separated followed by washing with benzene to remove unreacted S_4N_4 and dried in Vacuo. 0.1 m.mol (0.224 g) of $S_4N_4H_2F_2$ and 0.1 m.mol (0.271 g) of $HgCl_2$ were dissolved separately in 50 ml ethanol. The two solutions were mixed and the reaction mixture was refluxed for about 24 hours. The white precipitate formed was separated by filtration and washed with ethanol to remove unreacted reactants, if any and then dried in vacuo. The complex was analysed qualitatively and quantitatively using gravimetric technique¹⁴. The molecular weight was determined by Rast method using camphor as solvent. IR (400-4000 cm^{-1}), UV (200-800 nm)

and EPR spectra of the complex were recorded subsequently on IFS-66 VFT-IR, UV-VIS-NIR and EPRX/Q band spectrometer at room temperature. Mass and ^1H NMR spectrum were recorded on a Jeol SX 102 (FAB) and Bruker DRX-300 spectrometer respectively.

Result and Discussion

The white coloured product obtained by the reaction of $\text{S}_3\text{N}_4\text{H}_2\text{F}_2$ with HgCl_2 is insoluble in benzene, CCl_4 , CHCl_3 but soluble in highly polar solvents like acetone and DMSO. It decomposes above 260°C to blackish solid. Analytical data: S 22.43, N 13.08, H 0.46, F

8.87, Hg 46.86, Cl 8.30 and m.w 1407 g/mol reveal the formula as $[\text{S}_3\text{N}_4\text{H}_2\text{F}_2\text{HgCl}_2]_{3.28}$. The mass spectrum shows the prominent lines at m/z 89, 107, 136, 154, 192, 428 due to $(\text{S-N})\text{H}_2\text{F}_2$ ($M+3$), 3Cl , S_3N_3 , $\text{S}_3\text{N}_4\text{H}_2$ (base peak), $\text{S}_3\text{N}_4\text{H}_2\text{F}_2$ and $\text{S}_3\text{N}_4\text{H}_2\text{F}_2$ fragments respectively along with other peaks at m/z 227, 289, 305, 383, 539, 1036, 1282, 1316, 1407 for the fragments of the complex are presented in Table 1. The formation and composition of the complex may be proved by the fragment formed, during the decomposition of $(\text{S}_3\text{N}_4\text{H}_2\text{F}_2\text{HgCl}_2)_{3.28}$ and indicating the prominent lines for the various fragments as explained below:



The formation of $(\text{S}_3\text{N}_4\text{H}_2\text{F}_2\text{HgCl})_{3.28}$ is also supported by the IR spectrum presented in Table 2. From these results, it is inferred that $\text{S}_3\text{N}_4\text{H}_2\text{F}_2$ has coordinated to HgCl through N-coordinated S-N bonds, in free ligand the vibration in the range $640\text{-}940\text{ cm}^{-1}$ (S-N) shifted to higher frequencies ($686\text{-}1033\text{ cm}^{-1}$) explaining that $\text{S}_3\text{N}_4\text{H}_2\text{F}_2$ has bidentately coordinated to HgCl via antipodal N atoms of $\text{S}_3\text{N}_4\text{H}_2\text{F}_2$ ring as shown in Fig. 1

The electron spectrum of the complex

reveals two peaks at 200-232 nm (Flat band, $\epsilon=10$) and 245 nm; the former peak is due to charge transfer transition explaining the ionic form of HgCl and $\text{S}_3\text{N}_4\text{H}_2\text{F}_2$ while latter fragment is due to $p\Pi - p\Pi$ transitions of $\text{S}_3\text{N}_4\text{H}_2\text{F}_2$ ring which is coordinated to HgCl . This view is also supported by the values of frequency ratio $\nu_1/\nu_2 < 1$. The value of oscillator strength f , 1.58×10^{-4} expresses the presence of spin allowed laporte forbidden transition inferring the spin orbital coupling that is formation of

L \longrightarrow M coordinated complex.

EPR spectrum of the complex shows a narrow peak of high intensity. The value of g_{\parallel} (1.981) $<$ 2 supports the coordination, while value of g_{\perp} (2.0578) is for free electron present on the sulphur atom of the complex. The values of magnetic moment μ_{eff} 1.71 BM and magnetic susceptibility χ_A 1.21×10^{-3} confirms the presence of unpaired electron and supports the hydrogen bonding in the complex as already evidenced by IR spectral data.

To confirm the geometrical structure of the reaction product of S₃N₄H₂F₂ with HgCl₂ its ¹H NMR spectrum is recorded. It has two signals at chemical shift δ 1.998 and 2.879 ppm for the NH group of S₃N₄H₂F₂ ring. The other signals in the range δ 6.378 - 6.506 ppm are due to hydrogen bonded N-H groups. The signals at δ 6.633 and 6.826 ppm are due to two antipodal N-H groups indicating coordination of HgCl by antipodal N atoms of N-H group of S₃N₄H₂F₂ ring.

On the basis of aforesaid studies the geometrical array of the complex may be proposed to be shown in Fig. 1

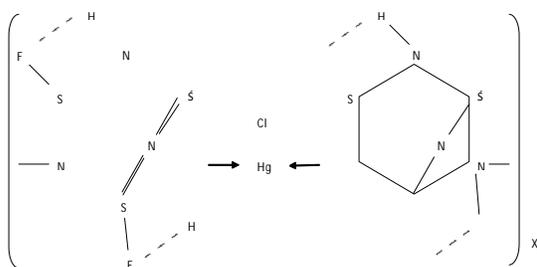


Fig.1. Proposed structure of (S₃N₄H₂F₂HgCl)_x where x = 3.28

Table 1. Mass spectral data of the complex

m/z	Bands assigned
89	(S-N)H ₂ F ₂
107	3 Cl
136	S ₃ N ₃
154	S ₃ N ₄ H ₂ (Base peak)
227	S ₃ N ₄ H ₂ F ₂ Cl
289	(S-N)H ₂ F ₂ Hg
305	(S-N)H ₂ F ₂ Hg N-H
383	(S-N)H ₂ F ₂ NH
487	(S ₃ N ₄ H ₂ F ₂ HgCl) (S-N)
539	(S ₃ N ₄ H ₂ F ₂ HgCl) (S-N) ₂
569	(S ₃ N ₄ H ₂ F ₂ HgCl) (N-S-N) ₂
617	(S ₃ N ₄ H ₂ F ₂ HgCl) (S ₂ N ₂ F)
671	(S ₃ N ₄ H ₂ F ₂ HgCl) (S ₃ N ₃ H ₂ F ₂)
767	(S ₃ N ₄ H ₂ F ₂ HgCl) (S ₃ N ₄ H ₂ F ₂) (S-F-S)
1036	(S ₃ N ₄ H ₂ F ₂) ₃ HgCl (S-N) H ₂ F ₂
1282	(S ₃ N ₄ H ₂ F ₂ HgCl) ₂ (S ₃ N ₄ H ₂ F ₂) (S ₃ N ₄)
1316	(S ₃ N ₄ H ₂ F ₂ HgCl) ₂ (S ₃ N ₄ H ₂ F ₂) (S ₃ N ₄) (NH ₂ F)
1407	(S ₃ N ₄ H ₂ F ₂ HgCl) ₃ (S ₃ N ₄) M-1

Table 2 IR Spectral data of the complex

ν cm ⁻¹		Assignment
Ligand	Complex	
S ₃ N ₄ H ₂ F ₂	[S ₃ N ₄ H ₂ F ₂ HgCl] _{3.28}	
-	499	Hg-N
640	686	S-N \longrightarrow Hg
719	-	S-N
920	-	S-N
930	-	S-N
940	1033	S-N \longrightarrow Hg
1220	1133	N-S-N
1392	-	N-S-N
1655	1613	N-H
2010	1919	N-H
31800-3500(b)	3526(b)	N-H
	3584(b)	N-H } (hydrogen bonded)

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