Original Article

Bulletin of Pure and Applied Sciences.
Vol.38 C (Chemistry), No.1, 2019: P.84-88
Print version ISSN 0970 4620
Online version ISSN 2320 320X
DOI 10.5958/2320-320X.2019.00009.8
http://www.bpasjournals.com/chemistry/

Spectroscopic investigation of the reaction product of tetrathiazyldihydridofluoride ($S_4N_4H_2F_2$) with Cd(II) Chloride

Abstract
The reaction of tetrathiazyldihydridofluoride ($S_4N_4H_2F_2$) with Cd(II) Chloride was carried out in organic medium the product obtained was characterized on the basis of IR, UV, EPR, Mass and ^{1}H NMR Spectra and is formulated as $(S_3N_4H_2F_2CdCl)_x$ where x=2.32

Keywords: Tetrathiazyldihydrofluoride, hydrogen-bonding, semiconductor

Ishanki Sharma[1]
Hemant Kumar Sharma[2*]

Author Affiliations
[1]Department of chemistry, Jawaharlal Nehru Rajkeeya Mahavidyalaya (J.N.R.M), Port Blair -744104, Andaman and Nicobar Islands, India
E-mail: ishanki013@gmail.com
[2]Associate Professor and Head, Department of chemistry, Jawaharlal Nehru Rajkeeya Mahavidyalaya (J.N.R.M), Port Blair -744104, Andaman and Nicobar Islands, India
E-mail: hemantsharmapb@gmail.com

***Corresponding Author**
Hemant Kumar Sharma, Associate Professor and Head, Department of chemistry, Jawaharlal Nehru Rajkeeya Mahavidyalaya (J.N.R.M), Port Blair -744104, Andaman and Nicobar Islands, India.

E-mail: hemantsharmapb@gmail.com

Received on 20.02.2019
Accepted on 18.03.2019

1. Introduction

The synthesis of halocyclothiazeneslike $(NSCl)_3$, $S_4N_3Cl_3$, $S_3N_2Cl_2$, S_3N_2Br (Zborilova, 1979; Glemser, 1976; Goehring 1960) have been described. Synthesis and characterization of tetrathiazyltetrafluoride and tetrathiazyldifluoride ($N_4S_4F_2$) (Banister, 1975; Glemser, 1976; and Mewsetal, 1975) have been investigated. Chelating behavior of $N_4S_4F_4$ with BF_3 and AsF_5 (Glemser, 1972; and Mews, 1976) tetrathiazyldihydridofluoride with Ti(III), Zr(IV), Si(IV), Sn(II), Ni(II), Hg(II) and Cu(II) (sharmaetal. 1986, 1994, 1989, 2009, 2016) have been reported. In view of this the reaction of tetrathiazyldihydrofluoride ($S_4N_4H_2F_2$) with $CdCl_2$ in non-aqueous solvent leading to the formation of metal complex and spectroscopic investigation are being presented here. The structure of tetrathiazyldihydrofluoride is depicted in Fig.1

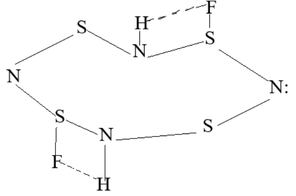

Figure 1: Structure of tetrathiazyldihydrofluoride

2. Materials and Methods

Tetrasulphurtetranitride (S_4N_4) was prepared (Goehring, 1960) by passing dry ammonia gas through Sulphurmonochloride (S_2Cl_2) in CCl_4. The ratio 1:10 of S_2Cl_2 and CCl_4 was taken for carrying out the reaction. The various steps of reaction are as under:

$2\ S_2Cl_2 + 4\ NH_3 \rightarrow NSCl + 3NH_4Cl + 3S$
$2\ NSCl + S_2Cl_2 \rightarrow [S_3N_2Cl]^+\ Cl^- + SCl_2$
$3\ [S_3N_2Cl]^+Cl^- + S_2Cl_2 \rightarrow 2[S_4N_3]^+\ Cl^- + 3SCl_2$
$[S_4N_3]^+\ Cl^- + 2\ SCl_2 + 4NH_3 \rightarrow S_4N_4 + 3NH_4Cl + S_2Cl_2$

The orange yellow mass formed was separated followed by washing with H_2O, CCl_4 and CS_2 to remove unreacted NH_4Cl, S_2Cl_2 and S. The formed product was extracted from 1, 4-dioxane and fractionally crystallized from benzene. The orange needle type crystal melted at 178°C.

Tetrathiazyldihydrofluoride (Jadon,1986) was prepared by passing dry hydrogen fluoride gas to benzene solution of S_4N_4 at 298K with constant mechanical stirring for about 5h till a reddish yellow precipitate was obtained. The reddish yellow mass was separated by filtration and successively washed with ethanol and ether. It was dried and stored in vacuo.

1m. mol. (0.224g) of $S_4N_4H_2F_2$ with 1m. mol. (0.183g) of $CdCl_2$were dissolved separately in 50mL ethanol. The two solutions were mixed and the reaction mixture was refluxed for about 24h. 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 analyzed qualitatively and quantitatively using gravimetric technique (Vogel, 1978).The molecular weight was determined by Rast method using camphor as solvent.IR (400-4000 cm^{-1}), UV (200-800 nm), 1^{H} NMR and mass spectrum of the complex was recorded subsequently on IFS-66, VFT-IR, UV-VIS-NIR, Jeol SX 102 (FAB) and Bruker DRX-300 spectrometer respectively. EPR spectrum of the complex was recorded on EPR X/Q band spectrometer at room temperature.

3. Results and Discussion

The white colored product obtained by the reaction of $S_4N_4H_2F_2$ with $CdCl_2$ is insoluble in water, ethanol, benzene, carbon tetrachloride but soluble in highly polar solvents like $CHCl_3$, acetone, and DMSO. It melts at 298°C. Analytical data % found S 28.24, N 16.48, H 0.59, F 11.18, Cd 33.07, Cl 10.44 and molecular weight 789 g/mol. reveals the molecular formula as $[S_3N_4H_2F_2CdCl]_{2.32}$. The mass spectrum shows prominent lines at m/z 89, 102, 107, 136, 157 due to $(S\text{-}N)H_2F_2$, S_2F_2, $(S\text{-}N)Cl_2$, S_3N_3 (M+2) and S_3N_3F (base peak) fragments respectively along with other peaks at m/z 209, 225, 227, 267, 279, 303, 305,391 ,796 for the fragments of complex presented in table1.

Table 1: Mass spectral data of the complex

m/z	Bands Assigned
89	$(S\text{-}N)H_2F_2$
102	S_2F_2
107	$(S\text{-}N)Cl_2$
136	S_3N_3 (M+2)
157	S_3N_3F (Base peak)
192	$S_3N_4H_2F_2$
209	$(S_3N_4H_2)\ (NH_2F)\ (HF)$
225	$(S_3N_4H_2)\ (NH_2F)\ (HF)\ (NH_2)$
227	$(S_3N_4H_2)\ (NH_2F)\ (HF)\ (NH_2)\ H_2$
267	$(S_3N_4H_2)\ (NH_2F)_2\ (HF)_2\ (H_2)$ (M+1)
279	$(S_3N_4H_2)\ (NH_2F)_2\ (NHF)\ (HF)(H)$

303	$S_3N_4F_2Cd$
305	$S_3N_4H_2F_2Cd$
391	$(S_3N_4H_2F_2CdCl)$ (S-F)
680	$(S_3N_4H_2F_2CdCl)_2$
782	$(S_3N_4H_2F_2CdCl)_2$ $(S\text{-}F)_2$
796	$(S_3N_4H_2F_2CdCl)_2$(N-S-F) (S-F)

The mechanism for the formation of the complex may be explained on the basis of mass fragmentation of the complex as:

$S_4N_4H_2F_2CdCl_2 \rightarrow S_3N_4H_2F_2CdCl + SCl$
$S_3N_4H_2F_2CdCl \rightarrow S_3N_4H_2F_2 + CdCl$
m/z 192
$S_3N_4H_2F_2 \rightarrow S_3N_3F + NH_2F$
m/z 157
$S_3N_4H_2F_2CdCl + (S\text{-}N)H_2F_2 \rightarrow (S_3N_4H_2F_2CdCl)(S\text{-}F) + NH_2F$
m/z 391
$(S_3N_4H_2F_2CdCl)(S\text{-}F) \rightarrow (S_3N_4H_2F_2CdCl)_2(S\text{-}F)_2$
m/z 391 m/z 782
$(S_3N_4H_2F_2CdCl)_2(S\text{-}F)_2 \rightarrow (S_3N_4H_2F_2CdCl)_2 + S_2F_2$
m/z 782 m/z 680
$(S_3N_4H_2F_2CdCl)_2 + NH_2F + S_2F_2 \rightarrow (S_3N_4H_2F_2CdCl)_2\ (N\text{-}S\text{-}F)\ (S\text{-}F) + HF + H$
m/z 680 m/z 796

The formation of $(S_3N_4H_2F_2CdCl)_{2.32}$ is also supported by the I.R spectrum presented in Table 2 and it is found that frequencies 618 and 704 cm^{-1} are assigned for two S-N→Cd bands. The vibrations 1119 and 1366 cm^{-1} correspond to two S-coordinated S-N-F groups. The assignments at 1582 and 1622 cm^{-1} are due to two N-H groups. I.R spectrum clearly indicates that $S_3N_4H_2F_2$ has quadridentately coordinated to CdCl via. antipodal N and S atom of $S_3N_4H_2F_2$ ring as shown in Fig. 2.

Table 2: I.R spectral data of the complex

ν cm^{-1}		**Assignment**
Ligand $S_4N_4H_2F_2$	**Complex $(S_3N_4H_2F_2CdCl)_2$**	
-	480	Cd-CN
640(bs)	618(s)	S-N→Cd
719(s)	704(s)	S-N→Cd
920(s)	_	S-N
930(s)	_	S-N
940(s)	_	S-N
1220(bs)	1119(s)	N-S→Cd | F
1392(s)	1366(ws)	N-S→Cd | F
1655(s)	1582(s)	N-H
_	1622(s)	N-H
2010(s)	1946(ws)	N-H
_	3544(s)	N-H
3180-3500(b)	3629(b)	N-H(hydrogen bonded)

The electronic spectrum of the complex shows two peaks at 229 and 261 nm having molar extinction coefficient 3.9. The former peak is due to charge transfer transition explaining the ionic form of CdCl and $S_3N_4H_2F_2$ while latter peak is due to *pπ-pπ* transition of $S_3N_4H_2F_2$ ring which is coordinated to CdCl. This view is also supported by the value of frequency ratio $\nu_1/\nu_2<1$. The value of oscillator strength f, $4.50x10^{-5}$ expresses the presence of spin allowed laporte forbidden transition inferring the spin orbital coupling that is formation of L→M coordinated complex. The value of band gap energy (ΔE, 0.66eV) calculated from electronic spectrum indicate the semi conductive nature of the complex.

EPR spectrum of the complex shows a symmetric broad peak of high intensity, indicating presence of unpaired electron. The value of $g_{||}$(1.9668)<2 supports the coordination while value of $g_{\perp}$(2.0895) is for free electron present on N and S atom of the complex. The values of magnetic moment 1.74 B.M and magnetic susceptibility χ_A 2.04x 10^{-3} confirmed the presence of unpaired electron and supports Hydrogen bonding and semi conductivity of the complex as already evidenced by I.R and electronic spectral data.

To confirm the geometrical structure of the reaction product of $S_4N_4H_2F_2$ with $CdCl_2$ its ^1H N.M.R spectrum is recorded in $CDCl_3$. It has two signals at chemical shift δ1.251-1.561 (multiplet) and 3.730-3.731 ppm (doublet) for antipodal NH proton of $S_3N_4H_2F_2$ ring indicating coordination of CdCl through antipodal N atoms. The signals at δ7.726-7.277 ppm (multiplet) is due to hydrogen bonded N-H protons.

On the basis of aforesaid studies the geometrical array of the complex may be proposed to be shown in Fig. 2.

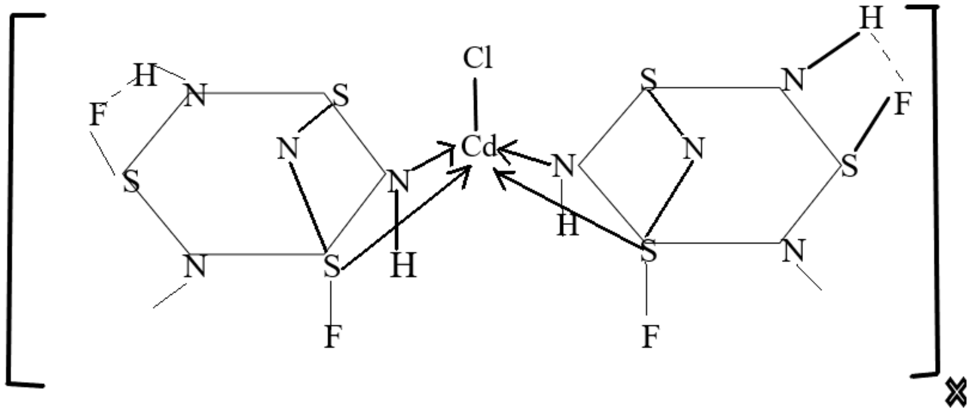

Fig 2: Proposed structure of $(S_3N_4H_2F_2CdCl)_x$,where x=2.32

4. References

1. Zborilova, Vonl and Gebauer (1979) Einneuer Typ Von Thiazylhalogenierung Von schwefeltetranitrid., P.Z.anorg.allg. Chem. 4485-10
2. Glemser O. (1976) Recent Investigation on cyclic Sulfur – Nitrogen halogen compounds. Z. Naturforsch B31b 610-619
3. Goehring M.B(1960) Inorganic Synthesis Vol.6, Interscience New York pp 124
4. Banister A, (1975) Inorganic Chemistry vol. 2 MTP International Review of Science pp41.
5. Glemser O. and Mews R. (1972) Sulfur – Nitrogen Fluorine compounds Adv. Inorg. Chem, Radio Chem. 14 : 333-390
6. Mews R, Wagner D. L. and Glemser O. (1975) Uber Reaktianen Von cyclo Thiazylhalogeniden nut Lewis – Säuren. Z. Anorg. Allg. Chem. 412 : 148-154
7. Mews R (1976) Nitrogen – Sulfur Fluorine ions. Adv. Inorg. Chem. Radio Chem. 19 : 185-237

8. Sharma H.K, Yadav A.K and Jadon S.P.S (1986) Characterization of the complexes of Ti (III) and Zr (IV) with Tetrathiazylhydrofluoride by U.V, E.P.R and XRD spectra. Rev. Roum. dechim31(3) : 305-308
9. Sharma H.K (1994) Synthesis and Characterization of polymeric complexes of Si (IV) with tetrathiazyldihydrofluoride by I.R, U.V, EPR, and XRD spectroscopy. Bangladesh J. Sciind. Res. 29(1): 34-40
10. Sharma H.K (1989) Characterization of polymeric complexes of Sn(II) with tetrathiazyldihydrofluoride by I.R, U.V, EPR, and XRD spectroscopy. Curr. Sci, 58(12)679
11. Sharma H.K (2009) Spectroscopic Characterization of reaction product of tetrathiazyldihydrofluoride ($S_4N_4H_2F_2$) with Ni(II) Chloride Bangladesh J. Sciind. Res. 44(4) 485-487.
12. Sharma H.K and Kumar Pramod (2016) Spectroscopic Investigation of the reaction product of Tetrathiazyldihydrofluoride ($S_4N_4H_2F_2$) with Cu(II) Chloride. J. Chem. & Cheml. Sci. 6(9): 817-820
13. Jadon S.P.S (1986) Synthesis and Investigations of the new adduct of S_4N_4Curr. Sci. 55: 781-782