Spectroscopic Characterization of Reaction Product of Tetrathiazyldihydrofluoride ($S_4N_4H_2F_2$) with Ni (II) Chloride

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Abstract

Ni(II) chloride reacts with tetrathiazyldihydrofluoride in an organic medium to give solid composition of the complex ($S_4N_4H_2F_2$)$_2$ NiCl$_2$. The complex has been shown by physicochemical methods to be bidentated N-coordinated complex having distorted $O_h$ geometry and paramagnetic character.

Key Words: Tetra sulphur tetranitride, Tetrathiazyl dihydrofluoride, N- coordinated complex

Introduction

Synthesis and characterization of tetrathiazyldetrafluoride (Banister, 1975, Glemser 1976 and Mews et al. 1975) and tetrathiazyldifluoride ($N_4S_4F_2$) (Zborilova and Gebauer, 1979) have been described. Chelating behaviour of ($N_4S_4F_2$) with BF$_3$ and AsF$_3$, (Glemser, 1972, Mews 1976) tetrathiazyl dihydrofluoride with Ti(III), Zr(IV), Si(IV) and Sn (II) (Sharma et al 1986, 1994, 1989, 2006) have been reported. The complexing reaction of tetrasulphurtetranitride $S_4N_4$ with Ni(II) chloride in ethanol showed a series of compounds to be formed (Piper, 1958).

$$\text{NiCl}_2 + S_4N_4 \rightarrow \text{EtOH} \rightarrow \text{Ni(HN}_2\text{S}_2\text{)}_2 \text{NiS}_3\text{N}_2\text{H} + \text{NiS}_6\text{N}_2$$

The protons in Ni($H_N_2S_2$)$_2$ molecule are fairly acidic and consequently derivatives are readily obtainable.

$$\text{Ni (HN}_2\text{S}_2\text{)}_2 + \text{CH}_3\text{Li} \rightarrow \text{Ni(CH}_3\text{N}_2\text{S}_2\text{)}_2$$

In view of this the reaction of tetrathiazyldihydrofluoride ($S_4N_4H_2F_2$) with NiCl$_2$ in non-aqueous solvent leading to the formation of metal complex and spectrometric investigations are being reported here. The structure of tetrathiazyldihydrofluoride is depicted in Fig.1.

Materials and Methods

$S_4N_4$ was prepared (Goehring, 1960) by passing dry ammonia gas through sulphur monochloride ($S_2Cl_2$) 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 the reaction are as under:

$$2\text{S}_2\text{Cl}_2 + 4 \text{NH}_3 \rightarrow \text{NSCl} + 3\text{NH}_4\text{Cl} + 3\text{S}$$

$$2\text{NSCl} + \text{S}_2\text{Cl}_2 \rightarrow [\text{S}_3\text{N}_2\text{Cl}]^+ \text{Cl}^- + \text{SCl}_2$$

$$3[\text{S}_3\text{N}_2\text{Cl}]^+ \text{Cl}^- + \text{S}_2\text{Cl}_2 \rightarrow 2[\text{S}_4\text{N}_3]^+ \text{Cl}^- + 3\text{SCl}_2$$

$$[\text{S}_4\text{N}_3]^+ \text{Cl}^- + 2\text{SCl}_2 + 4\text{NH}_3 \rightarrow \text{S}_4\text{N}_4 + 3\text{NH}_4\text{Cl} + \text{S}_2\text{Cl}_2$$

Fig. 1. Structure of Tetrathiazyldihydrofluoride.
The orange yellow mass formed was separated followed by washing with H₂O, CCl₄ and CS₂ to remove unreacted NH₄Cl, S₂Cl₂ and S. The formed product was extracted from the crude reaction products and fractionally crystallized from benzene. The orange crystals melted at 178°C.

Tetrathiazyl dihydrofluoride (Jadon, 1986) was prepared by passing dry hydrogen fluoride gas to benzene solution of S₄N₄ at 298K with constant mechanical stirring for about 4-5 hours till a reddish yellow precipitate was obtained. The reddish yellow mass was separated by filtration and successively washed with alcohol and ether. It was dried and stored in vacuo.

The reaction of tetrathiazyl dihydrofluoride (TTADHF) with NiCl₂ was carried out in DMF solution by refluxing for 24 h. the light green mass was formed, separated by filtration and washed with DMF followed by ether, dried and stored in vacuo. The molecular weight was determined by viscosity method using ethanol as standard solvent. IR (400-4000 Cm⁻¹), UV (200-800nm) and EPR spectra of complex were recorded subsequently on IFS-66 VFT-IR, UV-VIS-NIR and EPR X/Q band spectrometer at room temperature.

Results and Discussion
The light green complex obtained by the reaction of S₄N₄H₂F₂ with NiCl₂ is soluble in water and ethanol. It decomposes above 190°C. Analytical data % found (calculated): S 44.31(44.32), N 19.40(19.39), H 0.69(0.69), F 13.15(13.15), Ni 10.15(10.16), Cl 12.30(12.29) and m.w. 578 formulate the composition of complex as (S₄N₄H₂F₂)₂NiCl₂ explaining that two rings have linked to NiCl₂ molecule. The vibrations observed in the IR spectrum of the complex are compared to that of TTADHF (Table.I) and it is found that frequencies 568 and 895 cm⁻¹ are for two S-N ←→ Ni bands, while assignment at 801 cm⁻¹ is assignable to free S-N band. The frequencies 1174 and 1415 cm⁻¹ corresponds to two N-S-F groups. The vibrations 1598 and 2262 cm⁻¹ are due to hydrogen bonding between two N-H and fluoride F⁻ ions. A shift to the lower energy region of bands 568 and 895 cm⁻¹ due to S-N vibrations in the complex relative to those in the free ligand indicate the coordination of NiCl₂ through antipodal N atoms.

In the electronic spectrum two bands 27777, 29761 and third band as a shoulder at 37037 cm⁻¹ are observed. The former two bands may be due to absorption corresponding to 3ₐ₂₂(F) ←→ 3₉₁₂(F) and 3ₐ₂₂(F) ←→ 3₉₁₂(P) transitions. The third shoulder band can be assigned to charge transfer transition confirming the hydrogen bonding and lone pair of electrons on N atom of S₄N₄H₂F₂. This view is also supported by value of frequency ratios v₂/v₁= 1.07(1~2). The computed value of oscillator strength f, (1.66x10⁻⁴) suggests the spin allowed laporte forbidden transitions. The transition 3ₐ₂₂(F) ←→ 3₉₂₂(F) was found absent indicating the distortion from O₉ geometry.

The EPR spectrum of the complex shows five equally spaced peaks (I=1 for N) having intensities ratio 2:3:1:2:3. This can be explained by the fact that when a molecule containing n equivalent nuclei then (2nI+1) lines of equal spacing result. Appearance of five lines in the EPR spectrum indicates that n should be equal to 2. These two nuclei correspond to two Nitrogen nuclei located in the immediate vicinity of Ni ion. As the intensities are identical, hyperfine splitting of two antipodal N atoms arise in the vicinity of single atomic nucleus Ni. Five identical lines of equal spacing, values of hyperfine coupling constant A_N(15G), A_Ni(95G) and g∥<2 found in the EPR spectrum of the complex suggest the coordination of Ni ion through antipodal N atoms. The value of g_L2.184>2 indicates the distortion in the complex from O₉ geometry. The values of magnetic moment μ_eff 1.90 BM, magnetic susceptibility χ_A 1.49x10⁻³ confirm the presence of unpaired electron, indicating hydrogen bonding and paramagnetism in the complex. Since the structure of tetrathiazyl dihydrofluoride reported, the geometrical array of the complex may be proposed to be shown in Fig.2.

Table. I. IR spectral data of the ligand and its complex

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<tr>
<th>Ligand S₄N₄H₂F₂ cm⁻¹</th>
<th>Complex S₄N₄H₂F₂ NiCl₂</th>
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References


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