

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

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Abstract

Ni(II) chloride reacts with tetrathiazylidihydrofluoride 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

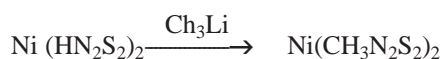
Introduction

Synthesis and characterization of tetrathiazyltetrafluoride (Banister, 1975, Glemser 1976 and Mews *et al.* 1975) and tetrathiazyl difluoride ($N_4S_4F_2$) (Zborilova and Gebauer, 1979) have been described. Chelating behaviour of ($N_4S_4F_4$) 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).



The protons in $Ni(HN_2S_2)_2$ molecule are fairly acidic and consequently derivatives are readily obtainable.



In view of this the reaction of tetrathiazylidihydrofluoride ($S_4N_4H_2F_2$) with $NiCl_2$ in non aqueous solvent leading to the formation of metal complex and spectrometric investigations are being reported here. The structure of tetrathiazylidihydrofluoride 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:

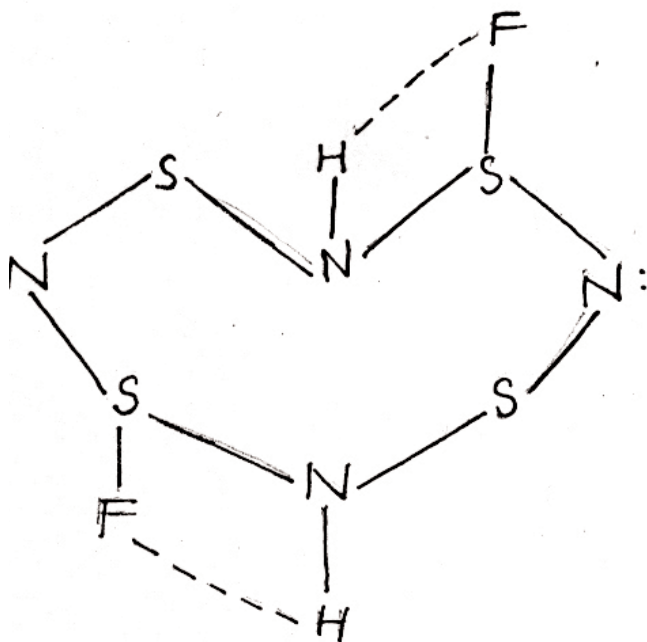
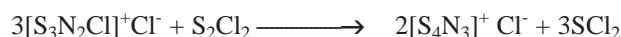
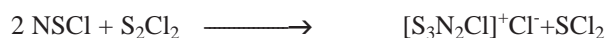
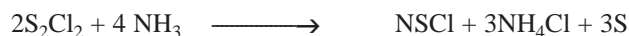


Fig. 1. Structure of Tetrathiazylidihydrofluoride.

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^oC.

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 (400-400^o 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^oC. 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)₂ NiCl₂ 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

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

Ligand S ₄ N ₄ H ₂ F ₂ cm ⁻¹	Complex S ₄ N ₄ H ₂ F ₂ NiCl ₂	Assignments
640	568	S-N-----Ni
719	----	S-N
798	801	S-N Free
920	895	S-N -----Ni
930	-----	S-N
940	-----	S-N
1220	1174	N-S-F
1392	1415	N-S-F
1655	1598	N-H
2010	2262	N-H
3180-3500(b)	3306(b)	SN-H

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 3_{A_{2g}}(F) → 3_{T_{1g}}(F) and 3_{A_{2g}}(F) → 3_{T_{1g}}(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 3_{A_{2g}}(F) → 3_{T_{2g}}(F) was found absent indicating the distortion from O_h 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_⊥ 2.1844>2 indicates the distortion in the complex from O_h 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.

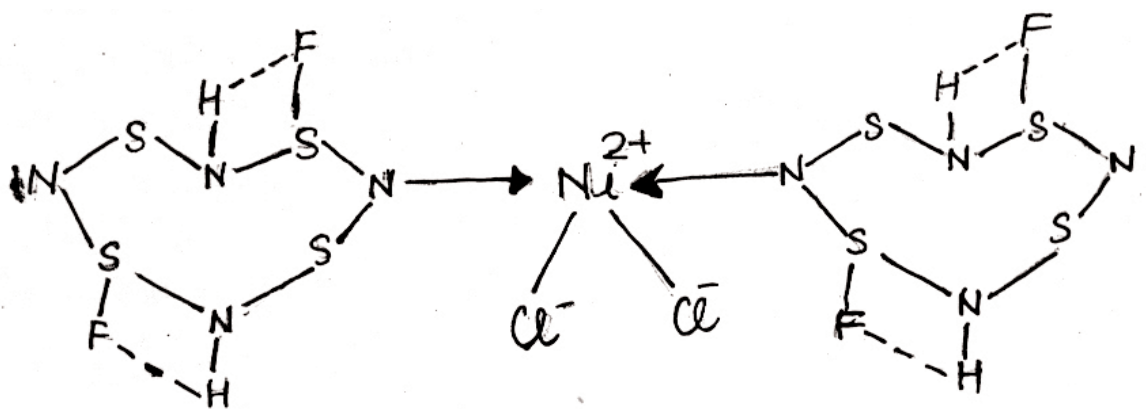


Fig. 2. Structure of $(S_4N_4H_2F_2)_2NiCl_2$

References

- Banister A, (1995) Inorganic Chemistry vol. 2 MTP International Review of Science pp 41.
- Glemser O. (1976) Recent Investigation on cyclic Sulfur - Nitrogen halogen compounds. *Z. Naturforsch B31b* 610 - 619.
- Glemser O. and Mews R. (1972) Sulfur - Nitrogen Fluorine compounds *Adv. Inorg. Chem, Radio Chem.* **14**: 333 - 390.
- Goehring M.B., (1960) Inorganic Synthesis vol. 6, Interscience New York, pp 124.
- Jadon S. P. S. (1986) Synthesis and Investigations of the new adduct of S_4N_4 . *Curr. Sci.* **55**: 781 - 782.
- Mews R, Wagner D. L. and Glemser O. (1975) Über Reaktionen von cyclo Thiazyl halogeniden mit Lewis - Säuren. *Z. Anorg. Allg. Chem* **412**: 148 - 154.
- Mews R. (1976) Nitrogen - Sulfur Fluorine ions. *Adv. Inorg. Chem. Radio Chem.* **19**: 185 - 237.
- Piper T. S. (1958) The Reaction of Tetrasulfurtetranitride with Nickel Chloride. *J. Am. Chem. Soc.* **80**: 30 - 32.
- 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 UV, EPR and XRD spectra. *Rev. Roum. dechim* **31**(3): 305 - 308.
- Sharma H. K. (1994) Synthesis and Characterization of polymeric complexes of Si (IV) with tetrathiazylhydrofluoride by IR, UV, EPR and XRD spectroscopy. *Bangladesh J. Sci ind. Res.*, **29**(1): 34 - 40.
- Sharma H. K. (1989) Characterization of the polymeric complex of Sn (II) with tetrathiazylhydrofluoride by IR, UV, EPR and XRD spectroscopy. *Curr. Sci.* **58**(12) 679.
- Sharma H. K. (2006) Effect of pressure and temperature on complex of Zr (IV) tetrathiazylhydrofluoride (TTADHF). *Ultra Science* **18**(3): 371 - 374
- Zborilova L. and Gebauer P. (1979) Ein neuer Typ von Thiazyl halogeniden als Zwischenprodukt der Halogenierung von Schwefeltetranitrid. *Z. Anorg. Allg. Chem.* **448**: 5 - 10.

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