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Synthesis, Characterization and Antimicrobial Studies of Adducts of Thiotrithiazyl Chloride with Hydrazine and Phenyl Hydrazine

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New adducts of thiotrithiazyl chloride with hydrazine and phenyl hydrazine have been synthesized and characterized on the basis of elemental, mass electronic, IR, NMR and ESR spectral studies. The adducts was screened against the gram-ve bacteria, *E.coli* and *S. typhimurium* and fungi, *C. albicans* and *C. neoformans*. The both hydrazine and phenyl hydrazine adducts are found to be active against the fungi *C. albicans* and the bacteria *E. coli* and *S. typhi* except *C. neoformans*.

Key Words: Thiotrithiazyl chloride, Synthesis, Adduct, Antimicrobial, Hydrazine, Phenyl hydrazine.

INTRODUCTION

Nitrogen and sulphur compounds and their derivatives[1-3] are generally found active against the bacteria and fungi and used as medicines *e.g.*, sulpha drugs and azides[4-6]. Thiotrithiazyl chloride is a stable cyclic derivative of tetrasulphurtetranitride[7]. The antimicrobial studies of the adducts of urea[8] and thiourea with thiotrithiazyl chloride have already been carried out.

In the present communication, the synthesis, characterization and antimicrobial studies of the new adducts of thiotrithiazyl chloride with hydrazine and phenyl hydrazine are being reported.

EXPERIMENTAL

All the chemicals used are of AR grade. S_4N_3Cl was synthesized by the reaction of S_4N_4 with acetyl chloride as reported[9]. The elemental analyses was done using CHN microanalyzer and also gravimetrically using standard methods[10]. Mass spectrum was recorded on Jeol SX102 (FAB) mass spectrometer. Infra red spectrum was recorded on Shimadzu 8201 PC IR/Hitachi spectrophotometer (range 4000-400 cm^{-1}). The electronic spectrum was recorded on Perkin Elmer Lambda 15UV/vis spectrophotometer (200-860 nm). The ^1H NMR spectrum was recorded on Bruker DRX 300 MHz spectrometer. The melting point was determined on electrical melting point apparatus and was uncorrected.

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Preparation of an adduct of S_4N_3Cl with hydrazine (H): To a solution of S_4N_3Cl in DMF, was added liquid hydrazine hydrate in equimolar ratio with constant shaking. The reaction mixture was refluxed for 6 h on a steam bath. This solution was kept over night. A white coloured precipitate settled which was filtered, washed with ethanol and dried *in vacuo*.

Preparation of an adduct of S_4N_3Cl with phenyl hydrazine (PH): Phenyl hydrazine was dissolved in 30 mL of DMF. To this solution, equimolar DMF solution of S_4N_3Cl was mixed. The resulting mixture was refluxed on steam bath for 6 h. A brown coloured precipitate was obtained which was filtered, washed with ethanol and dried *in vacuo*.

The antimicrobial activity of newly synthesized adducts was evaluated by filter paper disc diffusion method[11].

The bacteria and fungi were incubated at 37 ºC in agar-agar pepton-media for their growth. A media prepared by same process using yeast (0.5 mg), NaCl (30 mg) and glucose (0.25 g) was placed in sterilized petri dishes and was divided into four equal parts along with a hole at the centre for control. A thin layer of test organisms after their growth was coated on the surface of petri dish media. The adducts synthesized, were dissolved in DMSO to make stock solution of 3 mg/mL concentration. Circular disc of equal size were cut from Whatmann filter paper no. 42 and sterilized in an autoclave for 1 h. Filter paper disc soaked in 0.1 mL of the test solution were placed in different parts of petri dishes containing cultured media along with DMSO as control in the central hole. The petri dishes were again incubated at 37 ºC to study the inhibition of the bacteria. The inhibition zones were measured in mm. The adducts were studied at three different concentrations *i.e*., 10, 50 and 100 ug/mL.

RESULTS AND DISCUSSION

The analytical data for the adducts are given in Table-1. The analytical data shows that both hydrazine and phenylhydrazine forms 1:1 adducts with S_4N_3Cl. On the basis of elemental analysis and mass spectrum the adducts H and PH was formulated as S_4N_3 NHNH S_4N_3 and $(S_4N_3)_2NNHC_6H_5$, respectively.

TABLE-1
ANALYTICAL DATA OF THE ADDUCTS

Compound	m.w. found. (calcd.)	Found (calcd.) (%)			
		C	H	N	S
Hydrazine	370 (371)	–	0.54 (0.53)	30.27 (30.18)	69.18 (69.00)
Phenyl hydrazine	446 (445)	18.14 (18.28)	1.34 (1.35)	23.11 (23.33)	57.39 (57.91)

The FAB mass spectrum of adduct H shows the fragment ion peak at m/z = 357 corresponding to the fragment $S_4N_3NHNHS_4N_2$ (M + 1). The other important peaks

at m/z = 405, 389, 241, 257 and 199 correspond to the (S_4N_3) NHNH-S (M + 3), $S_4N_3NNS_4N_2$-S(M + 3), $S_4N_3NNSN_2$ (M + 1), S_4N_3NNSN (M - 3) and S_4N_3NHN. The adduct PH shows the peaks at m/z = 399, 366 244 and 199 corresponding to fragments $C_6H_5NHNS_3N_2S_4N_3$ (M - 1), $C_6H_5NHNS_2N_2S_4N_3$ (M - 2), S_4N_3NHNSN (M - 1) and S_4N_3NHN.

The infrared spectra of adduct H exhibits the bands at 618, 1117, 1404 and 980 cm^{-1} which may be assigned to ν(S-S), ν(S-N), ν(S=N) and ν(N-N), respectively. The band at 3130 cm^{-1} is assigned to ν(N-H). IR spectrum of adduct PH shows the broad bands at 487, 670, 1170 and 1404 cm^{-1} corresponding to ν(S-Cl), ν(S-S), ν(S-N) and ν(S=N) str., respectively. The absence of band at 489 cm^{-1} due to (S-Cl) str. in the adducts shows the linking through sulphur of thiotrithiazyl ring.

The electronic spectrum of hydrazine adduct shows the bands at 34482 and 38461 cm^{-1} which are assigned to intraligand d_π-p_π charge transfer transition with in thiotrithiazyl ring. The bands at 42016 and 48076 cm^{-1} is assigned to n-σ* transition between the S_4N_3Cl ring and nitrogen atom of hydrazine. The electronic spectrum of phenyl hydrazine adduct displays bands at 37764 cm^{-1} which may be due to intra ligand charge transfer with in the adduct.

EPR Spectrum of hydrazine adduct at room temperature yield a broad signal with g_{av} value of 1.921 and μ_{eff} = 1.663 BM showing the paramagnetic nature of the adduct. EPR spectrum of phenyl hydrazine adduct shows no EPR signal indicating the diamagnetic nature of the adduct.

^1H NMR spectrum of the hydrazine adduct shows a multiplet signal between δ: 7.304-7.187 ppm due to the presence of S_4N_3NH proton. The two triplet signals between δ: 3.510-3.40 and 2.543-2.498 ppm may be assigned to the two groups of S_4N_3 and NH protons differing in their arrangement. ^1H NMR spectrum of phenyl hydrazine adduct exhibits a singlet at δ: 7.381 ppm assigned to the protons of C_6H_5 group which are all symmetric. The signal at δ: 2.506 ppm is due to S_4N_3NH proton but the signal is poorly resolved due to excessive interaction between phenyl hydrazine and S_4N_3Cl.

The data of antibacterial and antifungal screening is reported in Table-2. The effectiveness of the synthesized adducts were tested against the bacteria *E. coli*, *S. typhi* and fungi *C. albicans* and *C. neoformans*.

TABLE-2
ANTIMICROBIAL ACTIVITY OF THE ADDUCTS

Adducts	Concentration (μg/mL)	Antibacterial activity zone of inhibition (mm)		Antifungal activity zone of inhibition (mm)	
		E. coli	*S. typhi*	*C. albicans*	*C. neoformans*
Hydrazine	100	18	15	12	00
	50	02	09	07	00
	10	08	07	03	00
Phenyl hydrazine adduct	100	18	00	17	12
	50	15	00	12	08
	10	06	00	08	04

The data (Table-2) indicate that inhibition increases with concentration and activity of the adducts is found to be maximum at 100 µg/mL. The results showed that both hydrazine and phenyl hydrazine adducts are equally effective against bacteria *E. coli* and fungi *C. albicans* whereas former adduct is ineffective against fungi *C. neoformans* and latter against bacteria *S. typhi*. Thus both the adducts of hydrazine and phenyl hydrazine may be used in 100 µg dose for the treatment of skin inflammation, mouth infection, disease of vagina, cancer, AIDS, *etc.*, caused by *C. albicans* fungi.

Conclusion

Spectral data suggest that both hydrazine and phenyl hydrazine are linked to the electropositive sulphur of the thiotrithiazyl ring through their nitrogen atom. Following structures are proposed to the hydrazine adduct (Fig. 1) and phenyl hydrazine adduct (Fig. 2).

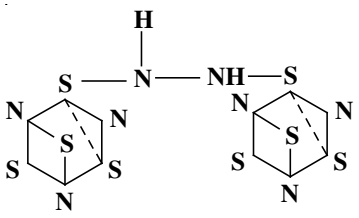

Fig. 1. (H): Structure of an adduct $[(S_4N_3NHNHS_4N_3]$

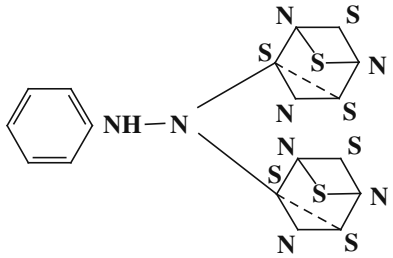

Fig. 2. (PH): Structure of an adduct $[(C_6H_5NHN(S_4N_3)_2]$

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