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Spectral Investigation of the Complex of $S_3N_3Cl_3$ With $Th(NO_3)_4.4H_2O$

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ABSTRACT

The complex of trithiazyl trichloride ($S_3N_3Cl_3$) was synthesized with $Th(NO_3)_4.4H_2O$ and formulated as-$[S_3N_3Cl_3Th(NO_3)_4.4H_2O]_{1.5}$ on the basis of mass spectral and chemical data, while IR, UV, EPR and XRD patterns showed that $S_3N_3Cl_3$ had co-ordinated quadridentatively with Th atom having diamagnetic nature and triclinic structure.

KEYWORDS : Trithiazyl trichloride ($S_3N_3Cl_3$), Tetra Sulphur Tetra Nitride (S_4N_4), Thorium (Th)

1. INTRODUCTION

$S_3N_3Cl_3$ (trithiazyl trichloride) was prepared by the chlorination of S_4N_4 in a non aqueous solvent by Nelson method [1]. Various author reported the formation of the complexes of $S_3N_3Cl_3$ with Cu^{2+},$ThCl_4$,Cu(II), $ZrOCl_2.2H_2O$, Zn(II), Cd(II) and Hg(II) [1-6] In the present paper, the investigations done for the complex of $S_3N_3Cl_3$ with $Th(NO_3)_4.4H_2O$ are being reported.

2. EXPERIMENTAL DETAILS

First tetrasulphur tetranitride (S_4N_4) was prepared by the reaction of NH_4Cl on S_2Cl_2 in non polar solvent kept in an ice bath.S_4N_4 was formed according to the following reaction-

$$S_2Cl_2 \xrightarrow{NH_3} S_4N_4$$

By passing chlorine into S_4N_4 solution, adduct of S_4N_4 - trithiazyl trichloride was synthesized. The mass formed was separated and dried in air. To prepare complex of Th with $S_3N_3Cl_3$, $S_3N_3Cl_3$ solution was mixed with the solution of Th compounds and the resultant solution was refluxed on a hot plate for 20 hours. The product (complex), thus obtained was separated, washed by suitable solvent, dried over fused $CaCl_2$ and stored.

Quantitative estimations for constituent elements of the complex were done gravimetrically as well as spectrometrically. The molecular weight was determined by Rast's method. I. R. spectrum of the complex was recorded on Perkin Elmer 337 infrared spectrometer in the range of 4000-400 cm^{-1} using Nujol Mull technique at room temperature. Electronic spectrum was graphed on UV 260 spectrometer in the range of wavelength 200nm-900nm. EPR and XRD spectra were recorded subsequently on JEOL (RE-2X)X band ESR spectrometer (Japan) in magnetic field range 0-8000 Gauss at 300 K temperature and Philips XRD Modal No. PW 3710, by using CuK_α source of radiation (λ=1.54056A0) at room temperature in the range of 2Θ from 7 to 70^0 respectively.

3. RESULTS AND DISCUSSION

The complex of $S_3N_3Cl_3$ with thorium nitrate was analyzed for its constituent elements along with its molecular weight. Analytical data of the complex: % found (calculated)- S 12.07 (12.05); N 12.32 (12.30); Cl 13.39 (13.37); O 32.18 (32.14); H 1.0 (1.00); Th 29.17 (29.23) and molecular weight found (calculated)- 1193.04 (1194.75) g/mole assigned it as $[S_3N_3Cl_3Th(NO_3)_4.4H_2O]_{1.5}$. To come at a definite molecular structure of the complex, the results of instrumental analysis done were as follows

3.1Mass Spectral Analysis

The fragments according to the mass lines were noted against each M/Z ratio. The mass lines for M/Z ratio at 120, 139, 155, 207, 227, 279, 307, 391, 403, 424, 443, 460, 474, 485, 498, 511, 544 and 600 were on account of $(N\text{-}S\text{-}N)_2$, $(S\text{-}N)_3$, $(N\text{-}S\text{-}N)_2$ Cl, $S_3N_3Cl_2$, $(S_2\text{-}N\text{-}Cl)_2$, S_5N_6Cl, $S_3N_3Cl_3$, $(S_3N_2Cl_2)_2$, $SN_3ClTh(NO_3)$, S_4N_2ClTh, $SNCl_2Th(NO_3)$, S_2NCl_2 $Th(NO_3).H_2O$,$(S\text{-}N\text{-}Cl)_2Th(NO_3).H_2O$, $(S\text{-}N_2\text{-}Cl)_2Th(NO_3)$, $S_3N_4ClTh(NO_3).H_2O$,$[\text{-}S\text{-}Th(NO_3)_4]$, $S_2NCl_2Th(NO_3).H_2O$,$(S\text{-}N_2\text{-}Cl)_2Th(NO_3)_2.3H_2O$ fragments present in the complexes.

The mass spectrum of complex also possesses mass peaks at 391 for $(S_3N_2Cl_2)_2$, 403 for SN_3Cl $Th(NO_3)$, 443 for S_2NCl_2 $Th(NO_3)$ suggesting that $Th(NO_3)$ had linked with $S_3N_3Cl_3$ ring while mass lines at 460 for S_2NCl_2 $Th(NO_3).H_2O$, 474 for $(S\text{-}N\text{-}Cl)_2$ $Th(NO_3).H_2O$, 498 for S_3N_4Cl Th $(NO_3).H_2O$, 589 for $S_2N_3Cl_2$ $Th(NO_3)_2.3H_2O$ indicate that one $S_3N_3Cl_3$ ring had been linked with $Th(NO_3)_4.4H_2O$ during the reaction.

3.2 I. R. spectral studies

The frequencies found in its I.R. spectrum are shown in table-1. Due to the lack of lower region facility the presence of metal ions could not be detected while its mass spectrum shows the presence of metal cations along with their anions. The vibrations at 662(d) $cm^{-1}$and 886(d) cm^{-1} which are due to the presence two S.N ----> M bands indicating that two N and two S atoms of $S_3N_3Cl_3$ ring had co-ordinated to thorium atom of thorium nitrate quadridentatidly. The vibration at 1064 (s) cm^{-1} was due to free S-N band. The vibrations from 1100 (s) cm^{-1} -1440 (s) cm^{-1} and at 2117(s) cm^{-1} were due to N-S-Cl band. The vibrations at 1499(s) cm^{-1} and 1685 (b-d) cm^{-1} were corresponding to N-O group. The vibrations at 2320 (s) cm^{-1} and 2508(s) cm^{-1} were for two distorted S coordinated N-S bond suggesting the co-ordination of S-N bands through its S atom to thorium atom forming a quadridentated complex. The other vibrations from 2871(s) cm^{-1}- 3839(s) cm^{-1} were due to OH groups showing the presence of water molecule of thorium nitrate.

Table-1: I.R. spectral data of the complex

S.No.	Vibrations cm^{-1}	Transmittance (%)	Band assignment	Force constant (K x 10^5 dyne/cm)
1	662.0(d)	4.40	N-S----->M	2.52
2	866.0(d)	52.78	S-N--->M	4.32
3	1064.0(s)	22.59	S-N	6.52
4	1100.0(s)	1.82	N-S-Cl	5.46
5	1256.0(s)	12.49	N-S-Cl	7.12
6	1392.0(s)	0.29	N-S-Cl	8.75
7	1413.0(s)	6.38	N-S-Cl	9.01
8	1440.0(s)	7.66	N-S-Cl	9.36
9	1499.0(s)	15.52	N-O	9.92
10	1685.0(b-d)	-0.14	N-O	12.53
11	2117.0(s)	62.18	N-S-Cl	20.23
12	2320.0(s)	64.51	δN-S	30.98
13	2508.0(s)	65.74	δN-S	36.21
14	2871.0(s)	20.75	O-H	3.26
15	2932.0(s)	11.76	O-H	3.40
16	3451.0(s)	1.25	O-H	4.71
17	3839.0(s)	60.30	O-H	5.82

3.3 Electronic Spectrum

The electronic spectrum of the complex had two bands out of which the lower band at 28248.59 cm^{-1} corresponds to p_π- d_π transition of $S_3N_3Cl_3$ ring. The higher band at 33112.58 cm^{-1} was due to charge

transfer transition as confirmed by the frequency ratio $v_1/v_2 = 1.72<2$. In the complex the spin orbital coupling was not taking place because the value of oscillator strength was of the order of 10^{-6} for spin forbidden leporte forbidden transition. The low value of Dq and high value of electron repulsion parameter 'B' were also in accordance with co-ordination linkage between thorium nitrate and trithiazyl chloride forming a quadridentated complex with absence of ^2E_g <-- $^2T_{2g}$ transitions which were generally found in thorium complexes. The values of band gap energy (ΔE_g) and no. of conduction electrons (table-2) suggest its conductive nature.

Table -2: U.V. Spectral data of the complex

Band assignment, nm(cm^{-1})	**Molar absorptivity** ε	v_1/v_2	Dq (cm^{-1})	Band gap energy ΔE_g(ev)	No. of conductive electrons (n_c)	Oscillator strength (f)	B
302 (33112.58)	0.399					$3.31x10^{-6}$	1921.83
354 (28248.9)	**0.181**	**1.72**	**486.40**	**0.30**	**$2.46x10^{24}$**	$1.18x10^{-6}$	1511.97

3.4 E. P. R. Spectrometric Investigations

There was no peak observed in the E.P.R. spectra of the complex suggesting that this complex was diamagnetic in nature with incomplete f and d shells in Thorium to co-ordinate with trithiazyl chloride resulting the formation of quadridentated complex of thorium nitrate, while $S_3N_3Cl_3$ is paramagnetic in nature. This indicates the change in bonding of $S_3N_3Cl_3$ with donation of electron pairs to Th.

3.5 X RAY Diffractometric Studies

In XRD spectrum of the complex, a strong peak at $44.62^0(2\Theta)$ of high intensity for metal atom having one peak of its right side at $64.95^0(2\Theta)$ due to $S_3N_3Cl_3$ ring were observed. The other peaks were for the other parts of the ring. The value of $\sin^2\Theta$, hkl, "d", axial ratio and axial angles (Table 3 and 4) were corresponding to triclinic geometry of the complex in which one $S_3N_3Cl_3$ ring had co-ordinated to $Th(NO_3)_4.4H_2O$ through metal atom(Fig-1). Thus Th atom of $Th(NO_3)_4.4H_2O$ was quadricientated co-ordinated by one $S_3N_3Cl_3$ ring.

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Table -3: XRD Pattern of the complex

S.No.	2Θ(deg.)	**$Sin^2\Theta$**	$(h^2+k^2+l^2)Q$	hkl	d (A^0)	d_{hkl}(A^0)
1	9.260	0.0065	1x0.0065	100	9.5450	9.5450
2	13.093	0.1140	2x0.0065	110	6.7568	6.7558
3	15.00	0.1305	3x0.0056	111	5.9025	5.9429
4	20.514	0.1718	5x0.0063	210	8.6450	8.6799
5	21.764	0.1888	6x0.0059	211	8.1597	8.1879
6	27.588	0.2384	9 x0.0065	221	6.4620	6.3694
7	28.82	0.2488	10 x0.0061	310	8.8640	8.6421
8	31.172	0.2607	11 x0.0065	311	8.8640	8.6421
9	32.348	0.2785	13 x0.0060	320	8.2974	8.2740
10	42.936	0.3659	21 x0.0064	421	8.4207	8.4044
11	44.455	0.3783	24 x0.0060	422	8.1446	8.1194
12	46.00	0.3907	25 x0.0061	430	7.8862	7.8891
13	51.764	0.4265	29 x0.0065	432	7.0587	7.0965

Table -4: XRD Pattern of the complex

S. No.	a_0(A^0)	b_0(A^0)	c_0(A^0)	α(deg.)	β(deg.)	γ (deg.)
1	9.5541	7.8040	5.0374	86.256	125.272	148.127
2	19.1082	33.7567	43.9261	153.880	131.633	68.936
3	28.6623	50.6348	65.8891	151.165	128.993	66.511
4	29.8326	23.8637	20.1469	93.545	125.814	136.392
5	38.5138	30.8079	26.0095	92.678	124.760	135.294
6	39.4495	31.5564	26.6414	92.554	124.611	135.177

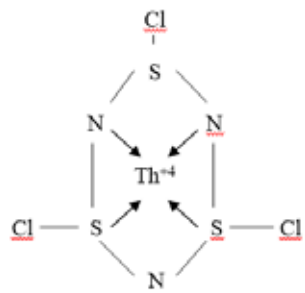

Fig.1: Proposed Structure of the Complex $S_3N_3Cl_3Th^{+4}$

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