XRD PATTERN OF THE COMPLEX OF TETRATHIAZYL DIHYDROFLUORIDE (TTADHF) WITH Th (IV)

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ABSTRACT :

The complex of tertrathiazyl Dihydrofluoride ($S_4N_4H_2F_2$) with $ThCl_4$ was synthesised and investigated with the help of various Physico-Chemical methods. The chemical data and its molecular weight have assigned it as $S_4N_4H_2F_2.ThCl_4$, which has octadentated Th^{+4} ion having hexagonal geometrical structure. The complex has been found paramagnetic and semicoductive in nature.

INTRODUCTION :

Halogenated derivatives of S_4N_4[1] such as $S_4N_4Cl_4$, $S_4N_4F_4$ and S_4N_3Cl etc. have been prepared[2-15]. It has been revealed that trimer and tetramer are non planar cyclic structure. The synthesis of a new adduct of S_4N_4 as TTADHF ($S_4N_4H_2F_2$) was reported[16]. Since TTADHF has cyclic structure and loan pairs of electrons similar to S_4N_4 and $S_4N_4H_4$, the complex with Th (IV) is prepared and its studies are presented herewith.

MATERIAL AND METHODS :

Tetrathiazyl Dihydrofluride was synthesised as reddish yellow solid, by mixing H_2F_2 into benzene solution of S_4N_4 with constant stirring for 4 to 6 hrs. To prepare the complex, 2 gm of $S_4N_4H_2F_2$ dissolved in DMF (100ml) was mixed to equimolar DMF solution to $ThCl_4$ and refluxed for 24 hrs. The change in colour and formation of a solid mass indicate the complex formation. The product was separated, washed with DMF followed by ether, dried and stored in Vacuo.

The quantitative estimation for constituent elements were done gravimetrically and atomic absorption spectrometrically. Its molecular weight was determined by the Rast's method. I.R. and electronic spectra of the complex was determined on Perkin-Elmer-337 (KBr) and double beam 4 bond spectrometer at 300^0 K, using DPPH as internal standard, while X-Ray-diffraction spectrum was carried out on XRD-C, SGP-3 single beam GM-11 diffractometer using FeK_α as source of radiation ($\lambda = 1.573A^0$).

RESULTS AND DISCUSSION :

For the confirmation of structure of the complex, the results obtained are analysed. The chemical data for the constituent elements, found (Cal%) as, Th 38.33 (38.79), S 21.50 (21.44), N 9.18 (9.36), Cl 23.45 (23.70), H 0.3 (0.34) and F 6.18 (6.35) are according to its molecular formula $S_4N_4H_2F_2.ThCl_4$ which is also supported by its molecular weight, found 597.86 (Cal. 598.15). The complex is cream coloured compound having m.p. 273^0C.

The I.R. spectrum data (table-1) of the complex are compared with that of ligand ($S_4N_4H_2F_2$) and it is observed that four (N-S-N→M) coordinated vibrations at 462, 470, 520 and 585 cm^{-1} and four (S-N-S→M) frequencies at 450, 670, 748 and 780 cm^{-1} have

been found expressing the eight coordination number of Th^{+4} ion in the complex. The frequencies at 720 cm^{-1} and in the region 910 to 1080 cm^{-1} are for free S-N bands while virabtions in the range of 1100 to 1300 cm^{-1} and onwards (Table-1) are corresponding to N-S-F and N-H bands present in the complex. The broad peak 3350 to 3590 cm^{-1} is due to hydrogen bonding in the complex. The values, determined for the force constant ($K_\alpha 10^5$ dyns/cm^2) suggest the presence of S-N single bond except free S=N bands in the complex.

Only two peaks at 24271 (υ_1) and 32051 cm^{-1} (υ_2) have been observed in the electronic spectrum of the complex. The band at 32051 cm^{-1} is due to charge transfer transition in the complex showing the presence of Th^{+4} and Cl^{-1} ions. This view is also get weightage by the frequency ration $\upsilon_1/ \upsilon_2 = 0.76 < 1$. The values of oscillator strength 'f' 1.78 x 10^{-5} and 7.86 x 10^{-4}, Dq 778 cm^{-1}, B (electron repulson parameter) 1296.4 cm^{-1}, Dq/B 0.60, Eg (band gap energy) 0.96 e.v. and $\lambda\alpha$ (conductivity) 7.268 x 10^{-17} mhos, have been calculated from its spectrum infering spin allowed transition with its semiconductive nature. The assignment at 24271 cm^{-1} is due to $^3T_{1g}$ (F)$\rightarrow$ $^3T_{2g}$ (F) transition in Thorium ion.

The disappearance of other two transitions, which generally occur in $ThCl_4$, indicates the formation of coordination bond between lignad and Th^{+4} ion.

The EPR spectrum of the complex has broad peak with small blurred peaks in lower part expressing paramagnetic nature of the complex and octadentated coordination in the complex (fig.-1). The values of $g_{av} = 1.957$, found from its spectrum, confirms the presence of unoccupied energy shells in Th^{+4}ion to accept electron pair for octadentated coordination ($g_{av} = 2.3003$ for normal atom). The values of $\mu_{eff} = 1.695$ BM and magnetic susceptibility $X_A = 1.87$ x 10^{-3}, calculated, show the presence of unpaired electron and paramagnetism in it. The value of spin orbital coupling constant (λs) computed as

$$g_{av} = 2 \left(1 - \frac{4\lambda s}{10 \, Dq} \right)$$

and found as $\lambda s = 41.62$ cm^{-1} ascertain the coordination between $S_4N_4H_2F_2$ and $ThCl_4$.

To elustrate the geometrical array of the complex, its X-ray powder diffraction pattern, recorded is interpretated and from the values of $Sin^2\theta$, 'd', I/I_0 and miller indices (table-2), the axial ratio a_0, b_0 and c_0 are computes as

$$\frac{a_0}{b_0} = \frac{sin\theta_1}{Sin\theta_2} \; ; \qquad \frac{b_0}{c_0} = \frac{sin\theta_3}{sin\theta_4} ; \qquad \frac{c_0}{a_0} = \frac{sin\theta_5}{sin\theta_6}$$

Where $sin\theta_1$, 100-110, $sin\theta_2 = Sin$ 110-200 and So on.

The axial angle 'ϕ' between two planes can also be calculated as :

$$Cos\ \phi \ = \ \frac{hh' \ + \ kk' \ + \ ll'}{[h^2 + k^2 + l^2] \ \times \ [(h')^2 + (k')^2 + (l')^2)]}$$

The values of axial ratio found as $a_0 = b_0 = 9.311$ A^o, $c_0 = 10.406$ A^o; the axial angles $\alpha = \beta = 90^o$ and $\gamma = 116^0\,36'$ are for the distorted hexagonal geometrical structure of octadentated thorium (IV) complex as expressed by fig.1.

Table–1
I.R. SPECTRUM DATA OF THE COMPLEX

Vibrations (cm^{-1})		Bonds Assigned	Force Constant (K x 10^5 dyns/ cm^{-1})
S$_4$N$_4$H$_2$F$_2$	Complex		
	450 (S)	S-N-S→M	1.165
	462 (S)	N-S-N→M	
	470	N-S-N→M	
	520	N-S-N→M	
540 (S)	----	S-N	
	585	N-S- N→M	
600 (S)			
	618 (WS)		
625 (S)	-----	S-N	
640 (S)	-----	S-N	
660 (S)	-----	S-N	
	670 (S)	S-N-S→M	
719 (S)			
	720 (S)	S-N	2.98
	748 (S)	S-N-S→M	
	780 (S)	S-N-S→M	
790 (S)			
	910		4.766
940 (S)	940 (S)	Free S-N	5.194
	950		
	970		6.225
1012 (S)	1012 (S)		
1040	1040 (S)		
1080	1070-1080 (b)		
1105	1152 (S)	N-S-F	5.338
	1190 (S)	N-S-F	5.8655
1220	1242-1262 (b)		
1394	1392	N-H	1.483
1655	1640-1730 (b)		1.651
3180 (b)	3350-3550 (b)	N-H	2.295
	3590	H-bonding (H….F)	

Table – 2

X-ray powder diffraction pattern of the complex $(ThCl_4.S_4N_4H_2F_2)$

$\theta_{(0)}$	$Sin^2\,\theta$	h k l	I/I_0	$D(A^o)$	q x $(h^2+ k^2+ l^2)$
4.75	0.006857	1 0 0	68	11.6957	1 x 0.006857
6.10	0.01129	1 1 0	40	9.1145	2 x 0.005645
9.40	0.02667	2 0 0	26	5.9308	4 x 0.006668
14.65	0.06366	2 2 1	55	3.8299	9 x 0.007107
15.85	0.07459	3 1 0	39	3.5466	10 x 0.007459
17.70	0.05244	3 2 0	19	3.1860	13 x 0.007111
12.75	0.12550	3 3 0	100	2.7340	18 x 0.006972
23.80	0.16280	4 2 2	10	2.3909	24 x 0.006783
24.45	0.17130	4 3 0	6	2.3402	25 x 0.006852
26.65	0.20120	4 3 2	6	2.1596	29 x 0.006938
30.20	0.2530	4 4 2	14	1.9286	36 x 0.007028
31.95	0.2800	4 4 3	5	1.8330	41 x 0.006829

$$q_{av} = \ 0.006854$$
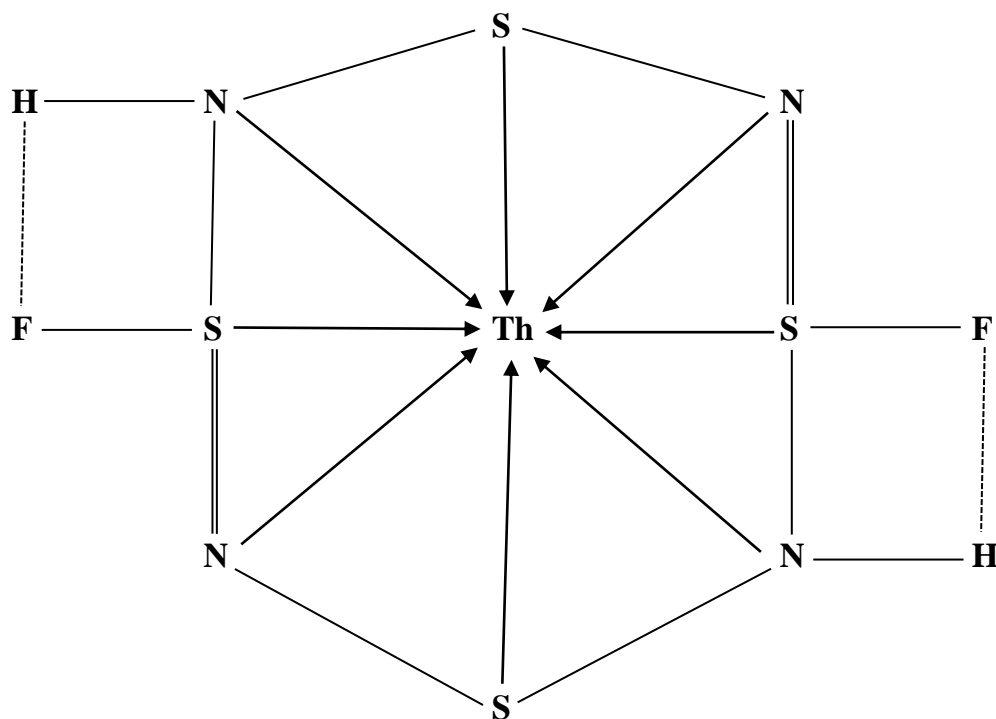
Figure -1 : Proposed structure of the complex of Tetra thi azyl dihydrofluoride (TTADHF) with Th (IV)

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