

Spectral analysis of the reaction product of FeSO_4 with Trithiazyltrichloride

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ABSTRACT: Trithiazyltrichloride was prepared by passing dry chlorine gas in the solution of Tetrasulphurtetranitride in CS_2 at 0°C . The formed trithiazyltrichloride was investigated and used as a ligand (L) to prepare its complex with FeSO_4 . The reaction product was obtained after refluxing FeSO_4 with tri-thiazyltrichloride in DMF for 8 hour at 35°C . The obtained polymer product was analyzed with the help of Mass, IR, Electronic, EPR and XRD diffraction spectra. The formulated complex $(\text{FeSO}_4 \text{S}_3\text{N}_3\text{Cl}_3)_5$ is found to be iron bridged tetra-dentate co-ordinate pentamer and paramagnetic with triclinic geometrical structure.

Keywords: Synthesis, Trithiothiazyltrichloride, Ferrous Sulfate DMF, polymer.

INTRODUCTION:

Trithiazyltrichloride ($\text{S}_3\text{N}_3\text{Cl}_3$)⁽¹⁻³⁾ is a compound of S_4N_4 ⁽⁴⁾ has complexation tendency due to lone pair electron donor N and S atoms. Its complexes with AlCl_3 ⁽⁵⁾ and ThCl_4 ⁽⁶⁾ (CuSO_4)⁽⁷⁾ have been reported. The reaction of $\text{S}_3\text{N}_3\text{Cl}_3$ with Lewis acids like SbCl_5 , SbF_5 , AsF_6 and BCl_3 give ionic compounds⁽⁸⁾ of type $\text{X}_2\text{N}_3\text{S}_3^+(\text{Cl})$. The transition metal complexes of type $\text{N}(\text{S} \text{Cl})_2 \text{M}^+\text{X}^-$ have also reported by Alange⁽⁹⁾ et.al. $\text{S}_3\text{N}_3\text{Cl}_3$ react with $\text{Mo}(\text{CO})_6$ give $\text{MoS}_3\text{N}_3\text{Cl}_3$ was studied by Kineth⁽¹⁰⁾. The spectral investigation of the complex $(\text{S}_3\text{N}_2\text{Cl}_3\text{FeSO}_4)_5$ from the reaction of $\text{S}_3\text{N}_3\text{Cl}_3$ with FeSO_4 is reported here in.

EXPERIMENTAL

S_4N_4 , starting material in this work was prepared by passing dry NH_3 gas in S_2Cl_2 in CCl_4 . $\text{S}_3\text{N}_3\text{Cl}_3$ was synthesized by passing dry Cl_2 gas in the solution of S_4N_4 in CS_2 at 0°C . $(\text{S}_3\text{N}_3\text{Cl}_3\text{FeSO}_4)_5$ was prepared by refluxing equal molar ratio of $\text{S}_3\text{N}_3\text{Cl}_3$ with FeSO_4 in DMF. The yellowish colored product was separated by filtration and washed with DMF, alcohol ether and stored in vacuum desiccator for different analysis. The quantitative estimation of complex was done by standards methods as well as by mass spectrometry which was carried out on mass spectrometer model no. 7070F, using E.I. operations at 0°K . The molecular weight of the complex was determined by Rast's method using camphor as solvent. The electronic spectrum was recorded on Varian VIS 2390, spectrophotometer. FTIR and EPR spectra of the complex were recorded on Nicolet FTIR and X-E, 4 band EPR (at LNT) spectrophotometer respectively. XRD spectrum of the complex was recorded on XRD -6 SPG-3 single chasis model 11GM 11 diffractometer by using Fe K_α as source of radiations of the wavelength 1.948 \AA at 50 kVp / 10 Mo by plate dispersion method.

Analytical data, found % S=32.30, N=10.60, Cl=26.84, Fe=14.09, calculated % S= 32.32, N=10.66, Cl=26.86, Fe=14.10 and molecular weight 1979.60(calculated=1980.85) g/m are good agreement with suggested molecular formula.

The chemical data of the complex was obtained from its quantitative estimation indicate its empirical formula as $\text{S}_3\text{N}_3\text{Cl}_3 \text{FeSO}_4$, while the molecular weight determined by Rast's method 1979.60 g/ m suggests its pentamer and hence its molecular formula may be assigned as $(\text{S}_3\text{N}_3\text{Cl}_3 \text{FeSO}_4)_5$.

The mass lines in the FAB mass spectrum of the complex is given in the table-1 show the presence of the fragments at m/z 77,83, 98, 110, 145 and 299 for S-N-S, N-S-Cl, SO_4 , S-N-S-Cl, $\text{S}_2\text{N}_3\text{Cl}$ and $\text{S}_3\text{N}_3\text{Cl}_3\text{Fe}^{++}$ respectively. From the fragments, the molecular weight and molecular formula assigned resembles to the molecular formula determined by the chemical data of the complex, inferring that complex is pentamer possessing $\text{S}_3\text{N}_3\text{Cl}_3\text{FeSO}_4$ unit in it.

To elucidate the stereochemistry of the complex, electronic spectrum of the complex was carried out in the range of 200-800 nm. The electronic spectrum of the complex has two signals at 208 nm and 320 nm suggest charge transfer transition between Fe^{++} and SO_4^{--} ions and ${}^4\text{E}_g - \text{A}_{1g}(\text{G})$ transitions. The lower frequency transitions, ${}^4\text{T}_{1g} - {}^6\text{A}_{1g}$ and ${}^4\text{T}_{1g} - {}^4\text{T}_{2g}$ may disappeared due to coordination of trithiazyltrichloride ring S or N atoms to Fe^{++} ions during the complex formation. The value of oscillator strength f is in order of 10^{-4} for the complex inferred that transitions are spin allowed Laporte forbidden. It is also supported by the lower value of Dq given in the table -2. The band gap energy for the

complex 5.53 eV suggest that it is good conductor of electricity. This view has been further confirmed by the high value of conducting electrons and conductivity $\lambda_{\infty} = 1.66 \times 10^{24}$ (mhos) (table-2).

The IR spectrum of the complex possesses bands at 822, 846, 980, 1002 nm and 1090-1141 (b, w) 1378-1383 cm^{-1} (duplet) for N-S-Cl polymer, (N-S-Cl)_x are consistent with those cited in literature⁽⁹⁾. The peaks at 612, 687, 775, 805 cm^{-1} are due to S-N-M, N-S-M, Cl-M and SO_4^{2-} ions in the complex. The other signals at 1484, 1577, 1651, 1733 cm^{-1} corresponds to N-S and S-N assignments. The symmetric peaks at 2292 and 2340 cm^{-1} due to N-S-Cl coordinated to FeSO_4 tetra-dentate with iron bridging complex formation. The value of force constant calculated from the spectrum by equation

$$\nu = 5.3 \times 10^{-12} \sqrt{(k/\mu)}$$

Subsequently in order 2.6×10^{-5} and 6.30×10^{-5} dyne/ cm^2 show the presence of the S_3N_3 ring in the complex, while the higher value of force constant 30-32 dyne/ cm^5 infer the coordination of $\text{S}_3\text{N}_3\text{Cl}_3$ with FeSO_4 .

EPR spectrum of the complex has shown three signals (table-3) at 4740, 4842 and 4940 gauss. The bands at 4740 and 4842 are indicating the presence of charge transfer transitions between SO_4^{2-} , Cl^- and Fe^{++} ions. The oxidation of ferrous to ferric ions is taking place during the complex formation reaction and polymerization as below



The other peak at 4940 gauss infers $3d^5$ electronic configuration and paramagnetic of complex. The value of $U_{\text{eff}} = 5.98$ suggests the divalent Fe ion in the complex, which is change during the reaction of $\text{S}_3\text{N}_3\text{Cl}_3$ with FeSO_4 . The low value of Hamiltonian constant suggests the paramagnetic and spin orbital coupling and coordinate linkage in the complex.

For the determination of geometrical structure of the complex, XRD spectrum was recorded 2θ range of $3^\circ - 40^\circ$. The value of d , $\sin 2\theta$, miller indices and intensity ratio were calculated. The peaks observed are according to free S-N bands, repetition of similar peaks supports the polymerization in the complex. The high value of intensity ratio indicate that complex is more than 60 % crystalline in nature.

From the values of $\sin^2 2\theta$, d , axial distance and axial angles were determined. The values found are as under for the complex –

$$a_0 = 3.626 \text{ \AA}, \quad b_0 = 5.129 \text{ \AA}, \quad c_0 = 4.187 \text{ \AA},$$

$$\alpha = 35.26^\circ, \quad \beta = 54.74^\circ, \quad \gamma = 45^\circ$$

On the basis above studies the complex has triclinic geometrical structure. Propose structure of the complex is given below.

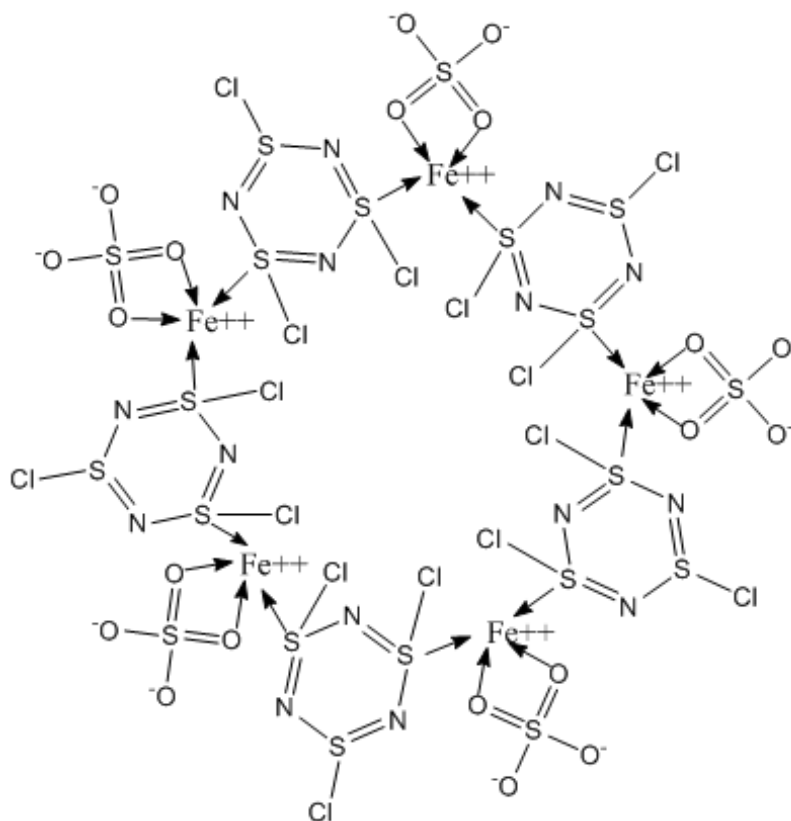


Fig . 1

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Table 1- F. T. I. R. SPECTRAL DATA OF THE COMPLEX.

S. No.	Frequencies(cm^{-1})	Band assigned	Force constant $\text{K} \times 10^5 \text{ Dyne/cm}^{-1}$
1	612.10	N-S-M	2.15
2	687.14	S-N-M	2.71
3	775.00(d)	S-O-M	3.45
4	805(t)	N-S-Cl	3.73
5	822(b)	$\text{SO}_4^{2-} \text{ Cl}^-$	3.88
6	846.10	S-N	4.11
7	980.89	S-N	5.50
8	1002.16	S-N	5.79
9	1090-1141.69	S-N	5.66
10	1378-1383(d)	S-N	8.58
11	1484.45	$\text{S}_3\text{-N}_3$ ring	9.93
12	1570.59	$\text{S}_3\text{-N}_3 \cdot \text{Cl}_2$	11.11
13	1577.11	N-S-Cl	11.21
14	1582.50	N-S-Cl	11.28
15	1651.00	S-N-Cl	12.29
16	1700.00	S-N-Cl	13.08
17	1733.87	S-N	17.03

Table 2- EPR spectral data of the complex

S.No.	Magnetic field (Gauss)	g_z	$g_x = g_y$	g_{av}	μ_{eff} (B.M.)	Magnetic suscepability $\chi_A \times 10^{-3}$
1	4740	1.366	1.894	1.681	6.1	6.06
2	4842	1.339	1.904	1.66	5.98	5.81
3	4940	1.3115	1.567	1.388	1.850	5.58

Table 3- XRD pattern of the complex

S.N.	2θ	$\text{Sin}\theta$	hkl	d (A°)	I/I ₀
1	1.85	0.03228	110	30.17	45.45
2	2.20	0.03839	110	25.37	45.45
3	2.67	0.04658	200	41.82	45.45
4	3.25	0.05669	211	34.36	54.54
5	3.65	0.06366	220	30.00	63.63
6	3.95	0.06869	221	28.28	61.36



7	4.32	0.07533	311	37.32	72.27
8	4.75	0.08281	320	35.25	68.18
9	5.30	0.09237	322	31.63	72.27
10	5.85	0.1019	331	28.67	77.27
11	6.15	0.1071	332	27.21	68.18
12	6.50	0.1146	430	33.99	90.90
13	6.80	0.1184	431	32.90	77.27
14	7.10	0.1236	432	31.52	77.27
15	7.60	0.1323	441	29.44	81.81
16	8.70	0.1513	443	25.75	81.81
17	9.00	0.1564	444	24.91	77.27
18	9.45	0.1641	543	29.68	72.27
19	9.75	0.1693	552	28.77	72.27
20	10.00	0.1736	553	28.05	86.36
21	10.33	0.1792	554	27.18	72.27
22	11.30	0.1959	555	24.86	100.00
23	11.60	0.2011	654	29.06	77.27
24	12.25	0.2127	655	27.47	68.18
25	12.92	0.2236	665	26.16	77.27
26	13.85	0.2394	666	24.41	77.27
27	14.80	0.2555	766	26.68	63.63
28	15.00	0.2689	776	25.36	59.09
29	16.30	0.2806	777	24.30	59.09
30	17.15	0.2848	877	27.36	63.36
31	17.95	0.3081	887	25.29	54.54
32	18.15	0.3115	888	25.01	54.54
33	18.95	0.3247	987	26.99	54.54
34	19.40	0.3321	988	26.40	54.54

$$a_0 = 3.626 \text{ A}^\circ, b_0 = 5.129 \text{ A}^\circ, c_0 = 4.187 \text{ A}^\circ, \alpha = 35.26^\circ, \beta = 54.74^\circ \text{ and } \gamma = 45^\circ$$