

Mass, FTIR, EPR and XRD Spectral Studies of the Complex of CuSO₄ with Trithio Thiazyl Trichloride

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Abstract: The trithioazyltrichloride was prepared, studied and used as a ligand (L) to prepare its complex with CuSO₄. The complex was investigated with the help of Mass, FTIR, EPR and XRD diffraction spectra. The formulated complex (S₃N₂Cl₂CuSO₄)₃ is found to be a quadridentated and paramagnetic with triclinic geometrical structure.

Keywords: Synthesis, Trithiothiazyltrichloride, copper sulphate, DMF.

I. INTRODUCTION

S₃N₃Cl₃⁽¹⁻³⁾ is a halogenated derivative of S₄N₄⁽⁴⁾ has complexation tendency due to N and S donor atoms. Its complexes with AlCl₃⁽⁵⁾ and ThCl₄⁽⁶⁾ have been reported. The reaction of S₃N₃Cl₃ with Lewis acids like SbCl₅, SbF₅, AsF₆ and BCl₃ give ionic compounds⁽⁷⁾ of type X₂N₃S₃^{+(Cl)}. The transition metal complexes of type N(SCl)₂M⁺X⁻ have also reported by Alange⁽⁸⁾ et.al. S₃N₃Cl₃ react with Mo(CO)₆ give MoS₃N₃Cl₃ was studied by Kineth⁽⁹⁾. The spectra investigation of the complex (S₃N₂Cl₂CuSO₄)₃ from the reaction of S₃N₃Cl₃ with CuSO₄ is reported here in.

II. EXPERIMENTAL

S₄N₄, starting material in this work was prepared by passing dry NH₃ gas in S₂Cl₂ in CCl₄. S₃N₃Cl₃ was synthesized by passing dry Cl₂ gas in the solution of S₄N₄ in CS₂ at 0° c. (S₃N₂Cl₂CuSO₄)₃ was prepared by refluxing equimolar ratio of S₃N₃Cl₃ with CuSO₄ in DMF. The brackish 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 Å⁰ at 50 kvp / 10 Mo by plate dispersion method.

III. RESULT AND DISCUSSION

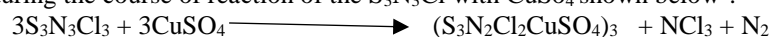
The complex of S₃N₃Cl₃ with CuSO₄ is insoluble in most of the solvents and do not melt up to 400⁰. Its analytical data, found % S=36.11, N= 7.89, Cl=20.00, Cu=17.98. (Cal)% S=36.10, N=7.50, Cl=20.03, Cu=18.05 and molecular weight, 1066.30 (cal=1063.50) g/mole are good agreement with the suggested molecular formula (S₃N₂Cl₂.CuSO₄)₃.

Mass spectral studies of the complex show peaks due to (57 M/e) N₄⁺, (64 M/e) Cu⁺⁺, (69 M/e) S⁺- Cl, (78 M/e) Cu⁺ N, (80 M/e) CuO, (97 M/e) CuS, (83 M/e) N=S⁺-Cl, (97 M/e) Cu⁺ S, (105 M/e) S₂⁺N₃, (129 M/e) S₂⁺N₂Cl, (149 M/e) N⁺S₂Cl₂, 257 Cl S₃ N₂ Cu⁺⁺ cation along with sulphate ion as an unit of its molecular formula (S₃N₂Cl₂Cu⁺⁺ SO₄⁻).

The two bands are present in the electronic spectrum of the complex. The band at 200nm is shown charge transfer transition between Cu⁺⁺ and SO₄⁻ ions, which is also indicated by mass spectrum. The charge transfer transition is also confirmed by frequency ratio $\nu/\nu_0 = 0.80 \leq 1$, the band at 320nm shows $\pi - \pi^*$ transitions of the ligand S₃ N₂ Cl₂. The band for ²T_g -²E_g transition of Cu⁺⁺ is not appear in the spectrum suggest that CuSO₄ co-ordinated to S₃ N₂ Cl₂ in the complex. The co-ordination is also supported by the values of oscillator strength $f_s = 3.1 \times 10^{-4}$ for the spin allowed laporte forbidden transitions, confirming exchange of electron pairs to Cu⁺⁺ with the formation of the complex. The value of E_g = 5.166 eV and its conductivity $\lambda_{\infty} = 1.33 \times 10^{24}$ (mhos) indicate that it is good conductor

In FTIR spectrum the presence of fragment are also confined by the bands at 426.14 (S), 461.52, 479 (V), 479 and 620 cm⁻¹ are due to coordinated N-S-M, S-O-M and SO₄⁻² ions. The free S-N bands appear at 620, 638, 673, 744, 797, 833,

868, 974 cm^{-1} . The bands at 698 cm^{-1} for S-N, 1322 cm^{-1} and 1014 cm^{-1} for N-S-Cl or trimer (N-S-Cl)₃ are consistent with those reported. The symmetric bands at 1116, 1151 cm^{-1} are due to N-S-Cl or Cl-S-N linkage to Cu^{++} ions. The shifting of frequencies infers the change in $\text{S}_3\text{N}_3\text{Cl}$ ring and its linkage to CuSO_4 . The calculated value of force constant from the equation $\nu = 5.3 \times 10^{-12} \sqrt{(k/\mu)}$ subsequently in order 1.6×10^5 and 6.12×10^5 dyne / cm^2 show the presence of single S-N and double S=N bond in $\text{S}_3\text{N}_2\text{Cl}_2$ ring. While the higher value of force constant ($K = 59$ or 70×10^5 dyne / cm^2) confirms the coordination of $\text{S}_3\text{N}_3\text{Cl}$ ring with CuSO_4 . FTIR spectrum of the complex has supported the Cu^{++} , bridged coordination of CuSO_4 with $\text{S}_3\text{N}_3\text{Cl}$. Above points of FTIR and mass spectra are confirmed that $\text{S}_3\text{N}_3\text{Cl}_3$ cyclic ring contraction take place during the course of reaction of the $\text{S}_3\text{N}_3\text{Cl}$ with CuSO_4 shown below:-



The EPR spectrum of complex is shown three prominent signals at 5650, 6275 and 6925 gauss. The signals at 5650 and 6925 G are broad indicating the presence of charge transfer transition between $\text{Cu}^{++}\text{SO}_4^{--}$ and d^9 electronic configuration of Cu^{++} ion which can take electron pairs to form coordinated complex. The value of μ_{eff} and magnetic susceptibility χ_A found as $\chi_A = 1/T (\mu_{\text{eff}} / 2.828)^2$. The EPR spectral data in table-2 are also confirming to d^9 electronic configuration of Cu^{++} with the presence of single unpaired electron and its paramagnetic. The sharp and narrow high intensity peak 6275 G in the EPR spectrum indicating that exchange of electron pairs has occurred in the complex $(\text{S}_3\text{N}_3\text{Cl}_2\text{CuSO}_4)_3$ between CuSO_4 and $\text{S}_3\text{N}_3\text{Cl}$ ligand. The proposed structure of the complex is given in Fig-1.

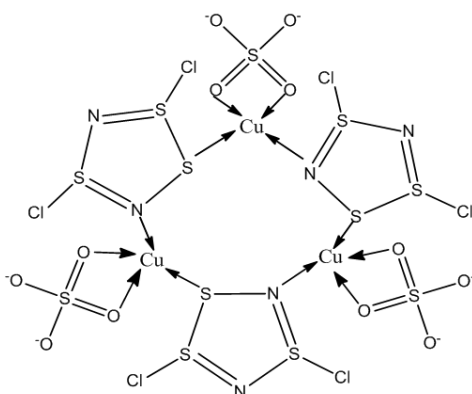


Fig -1 Proposed structure of the complex $(\text{S}_3\text{N}_2\text{Cl}_2\text{CuSO}_4)_3$

XRD spectrum of the complex was recorded in 2θ range of 3° to 40° . The value of d , $\text{Sin}^2 \theta$, miller indices and intensity ratio was calculated (Table-3). The high Value of intensity ratio indicate that complex is more than 50% crystalline in nature. From the values of $\text{Sin}^2 \theta$ and d , the axial distance and axial angles were determined. The found values are given as below $a_0 = 3.54 \text{ \AA}$, $b_0 = 5.008 \text{ \AA}$, $c_0 = 4.085 \text{ \AA}$, $\alpha = 35.29^\circ$, $\beta = 54.78^\circ$ and $\gamma = 45^\circ$. This data suggest that atoms of the complex are arranged in triclinic geometrical pattern with polymeric chain.

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

S. No.	Frequencies(cm ⁻¹)	Band assigned	Force constant Kx10 ⁵ Dyne/cm ⁻¹
1	426.14	N-S-M	1.045
2	461.52	S-N-M	1.101
3	479.21	S-O-M	1.322
4	514.59	N-S-Cl	1.510
5	620.73	SO ₄ ⁻	
6	638.42	S-N	2.35
7	673.89	S-N	2.62
8	744.56	S-N	3.19
9	797.69	S-N	3.31
10	833.07	S-N	3.62
11	868.45	S-N	3.95
12	974.59	S-N	5.03
13	1116.11	N-S-Cl	6.67
14	1151.50	N-S-Cl	7.12
15	1611	S-N	14.96
16	3221.5	S-N	59.78
17	3486.87	S-N	70.03

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 susceptability χ _A × 10 ⁻³
1	5650	1.142	1.894	1.681	2.241	3.631
2	6275	1.029	1.904	1.66	2.218	3.593
3	6925	0.932	1.567	1.388	1.850	2.597

Table 3- XRD pattern pf the complex

S.No.	2θ	Sinθ	Hkl	d (A°)	I/I _o
1	1.80	0.03141	110	31.00	45.45
2	2.20	0.03459	111	28.20	45.45
3	2.65	0.04623	200	42.13	45.45
4	3.20	0.05582	211	34.90	54.54
5	3.62	0.0631	220	30.88	63.63
6	3.92	0.0683	221	28.53	63.63
7	4.20	0.07498	311	38.97	72.27
8	4.70	0.08193	320	35.66	72.27
9	5.25	0.09150	322	31.93	72.27
10	5.80	0.1010	331	28.93	77.27
11	6.10	0.1062	332	27.51	72.27
12	6.45	0.1114	430	34.97	77.27
13	6.75	0.1175	431	33.15	86.36
14	7.05	0.1227	432	31.75	86.36
15	7.20	0.1253	441	31.09	86.36
16	7.55	0.1339	442	29.53	90.90
17	8.45	0.1469	443	26.51	90.90
18	9.00	0.1564	444	25.20	100
19	9.40	0.1633	543	29.81	88.18
20	10.00	0.1736	553	28.05	95.45



DOI: [10.17148/IARJSET.2021.8608](https://doi.org/10.17148/IARJSET.2021.8608)

21	10.30	0.1788	554	27.23	86.36
22	11.25	0.1950	555	24.97	86.36
23	11.55	0.2000	654	29.22	90.90
24	12.00	0.2079	655	28.10	100
25	12.20	0.2113	664	27.69	95.45
26	12.90	0.2232	665	26.18	95.45
27	13.70	0.2368	666	24.67	90.90
28	14.75	0.2546	766	26.77	77.27
29	15.85	0.2731	777	24.96	77.27
30	16.25	0.2798	877	27.85	63.63
31	17.10	0.940	887	26.50	63.63
32	17.90	0.3073	888	25.35	59.09
33	18.20	0.3123	987	28.10	54.54
34	18.90	0.3239	988	27.06	54.54
35	19.35	0.33133	998	26.45	54.54
36	19.75	0.33791	999	25.94	45.45

$a_0 = 3.54 \text{ A}^\circ$, $b_0 = 5.008 \text{ A}^\circ$, $c_0 = 4.085 \text{ A}^\circ$, $\alpha = 35.29^\circ$, $\beta = 54.78^\circ$ and $\gamma = 45^\circ$