JSIANE : Vol. 3, Issue 4, 2023, Page 61-66 ISSN (Online) 2583-2093

Journal of Science Innovations and Nature of Earth

Journal homepage : www.jsiane.com

SPECTROSCOPIC STUDIES OF COMPLEX COMPOUND OF ZINC WITH LIGAND OF THIO-TRITHIAZYLCHLORIDE AND TYROSINE

Veena Chauhan
Department of Chemistry, D. S. College, Aligarh, (U.P.)India
Corresponding Author E-mail: veenachauhanchem@gmail.com

Abstract

Tetrasulphur tetranitride, S_4N_4 has been recognised as an extremely versatile reagent for the preparing of sulphur nitrogen compounds via the reaction of both organic as well as inorganic species. Reaction with transition metal species result in the formation of a number of complex compounds. Reaction of thio- trithiazylchloride with tyrosine amino acid gave the new ligand. The spectroscopic studies of the reaction product of this new ligand with zinc oxide are reported in this paper on the basis of IR, UV, NMR and X- ray spectra.

Keywords : thio-trithiazylchloride, Zinc, tyrosine, Spectroscopic, ligand

Received 13.09.2023 **Revised 19.10.2023** **Accepted 25.12.2023**

Experimental

All the chemicals used for the synthesis of adduct of thio-trithiazylchloride with amino acid tyrosine were of analytical grade. The used solvents in the synthesis of adduct were purified by standard methods. The elemental analysis was carried out using CHN micro-analyser and also gravimetrically methods. Mass spectrum was recorded on Jeol-SX-102 (FAB) mass Spectrometer. The UV and IR were recorded on Perkin-Elmer Lambda 15 UV/ VIS spectrophotometer and Shimadzu 8201 PC IR Hitachi spectrophotometer respectively. NMR spectrum was recorded on Brucker DRX-300 NMR spectrometer.

XRD spectrum was carried out on Philips PW 3710 spectrometer using Cu- α as a source of radiation (λ=1.5405A^o) in 2Θ range 20-90 at S.AI.F. Nagpur, Maharastra.

Preparation of the complex compound –Tetrasulfur tetranitride and thiotrithiazylchloride were prepared by known procedures. The synthesized ligand of thio-trithiazylchloride with tyrosine and zinc oxide was dissolved separately in DMF, after mixing the both solution in refluxing flask, the mixture was refluxed 8 hrs. The resulting product was filtered, washed with alcohol and ether kept in vacuum. The complex of novel ligand with Zn (II) is colourless solid, insoluble in organic solvents and water but found to be soluble in polar organic solvents DMF and DMSO. This complex is very stable and does not melt up to 300 ^{0}C. On the basis of quantitative estimations, its molecular weight was found to be 762.0 g /mol. The qualitative analysis of the complex was done. The test for chloride ion was found to be negative. To deduce the structure, geometrical array and magnetic properties the following spectral studies were carried out and discussed in detail.

Mass spectrum- The FAB mass spectrum was recorded **(Fig.1 Table.1)**. The peaks at m/z = 136, 154,289 and 307 have been assigned to the matrix m- nitrobenzyl alcohol. The mass spectrum shows the peaks at m/z =583, 460, 273, 232, 165 corresponding to the fragments S_4N_3NHCH (COO) $CH_2C_6H_4$OHZnS_4N_3.(M–1), S_4N_3NHCH(COO)$CH_2C_6H_4$OHZnSN(M1) S_2N_2NHCH (COO) $CH_2C_6H_4$OH(M-2), SNNHCH(COO)$CH_2C_6H_4$OH, $S_3N_3NHCH_2$.The mass line at m/z=762 in the mass pattern supported its molecular weight and its molecular formula(Table-1).

The formation of various fragments may be concluded molecular formula of the complex

[$(S_4N_3NHCH\ (COO)\ CH_2C_6H_4OH)_2Zn$]

IR Spectrum –

The ligand **(Fig.2Table.2)** shows IR bands at 668, 1119, 1402 and 2359 cm^{-1} assigned to S– N, N – S, S – N, COO^- and NH respectively. In the complex, the band at 1402 cm^{-1} gets observed in IR of ligand, bifurcated into the bands at 1397 and 1458 cm^{-1} showing the coordination of S – N band of the ring. The band at 1007 cm^{-1} has been also show ring coordination through nitrogen atom to metal. The band at 1615cm^{-1} shows the coordination of COO group through oxygen atom of ligand to the metal. The band at 2359 shifted to 2364cm^{-1}is due to the coordination of N atom of amino group of the ligand. . Additional bands at 455 cm^{-1} and 617cm $^{-1}$ are due to $M \leftarrow O$ and $M \leftarrow N$ bonding.
(Cm $^{-1}$)

U.V. spectrum - The UV spectrum of the complex **(Fig .3 Table.3)** displays bands at 36764cm^{-1} and34246 cm^{-1} which may be assigned to the charge transfer between ligand to the metal(L→M) and the intra ligand charge transfer in S_4N_3 ring respectively. The band at 48543cm^{-1} may be due to the n → π* transition in the adduct .On the basis of the bands octahedral geometry may be proposed for the complex. The values of B, β, δ, C % calculated shows the ionic character of the different bonds in the complex. The values of 10Dq, band gap energy (Eg), number of conducting electrons and electrical conductivity indicated its semi conductive nature. The values of oscillator strength'f' of the order of 10^{-4} show the transitions to be Spin Allowed and Laporte Forbidden.

***E.P.R. spectrum* -** The E.P.R. spectrum was recorded at room temp , **(Fig 4).** no signals shown expounding the diamagnetic nature of the complex.

***^{1} H NMR* spectrum–** The multiple signals between 1.150 – 3.420ppm is slightly downfield due to the coordination of nitrogen atoms of two S_4N_3rings of the ligand to metal atom. The two doublets between ∂ 6.610-6.6996 ppm and 7.092-7.636 due to two asymmetric phenolic groups in the complex and two signals between 7.927 - 8.219ppm has appeared showing the coordination of nitrogen atom of NH groups of ligand **(Table.4 Fig.5).**

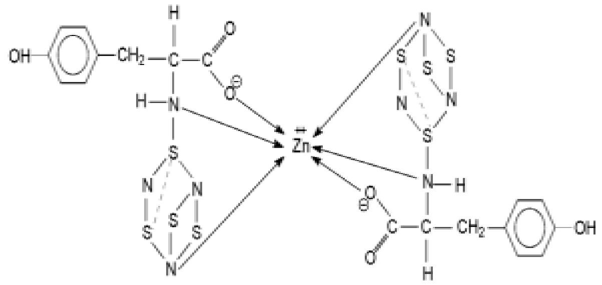
***XRD Analysis*-** The powdered X-Ray diffraction pattern of the complex **(Fig.6 Table.5**) is recorded which shows that, the values of d_{hkl} calculated is in close agreement with the theoretical values. The values of axial distances 228 (a_0 = 21.20Å, b_0 = 21.20Å, c_0 = 25.96.Å) and axial angles (α = 90.00°, β, = 90.00°, γ = 120.00°) explains the hexagonal geometrical array of the complex.

Conclusion

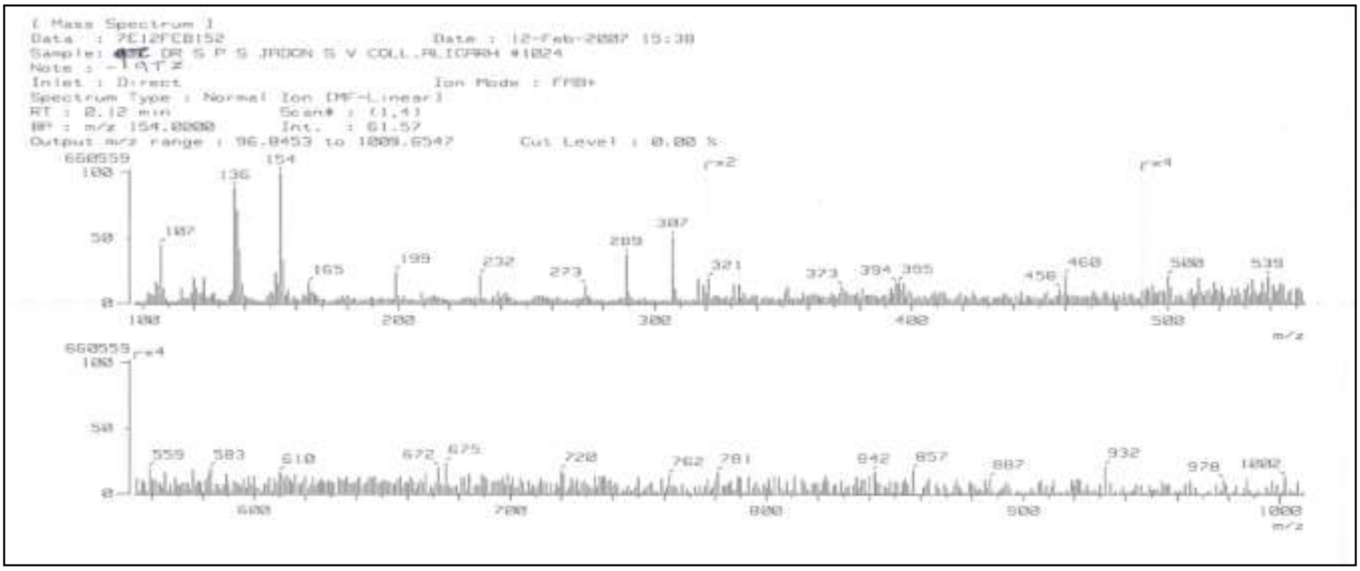
On the basis of FAB Mass spectrum of the complex was formulated as [(S4N3NHCH (COO) CH2C6H4OH)2 Zn] and the molecular weight was found to be 763.0 g/mol.

The I.R. spectrum confirms the coordination of thiotrithiazyl rings through nitrogen atom of the ligand to the Zn (II) atom. The N – atom of NH group and O-atom of carboxylate group of ligand are also involved in coordination. On basis of U.V., EPR and XRD analysis, the complex was found to be octahedral with hexagonal geometrical arrangement of atoms. At high resolution in1HNMR two sets of signals between 6.610-6.690ppm and 6.694-7.902ppm for two asymmetric phenolic groups present in the complex.

The coordination may be shown as:



Proposed structure of the complex (TC_1)



```
[ Mass Spectrum ]
Data  : 7E12FEB152                    Date : 12-Feb-2007 15:30
Sample: DR S P S JADON S V COLL.ALIGARH #1024
Note  : -TAT2
Inlet : Direct                        Ion Mode : FAB+
Spectrum Type : Normal Ion [MF-Linear]
RT : 2.12 min            Scan# : (1,4)
BP : m/z 154.0000        Int.  : 61.57
Output m/z range : 96.8453 to 1009.6547      Cut Level : 0.00 %
```

Fig 1; Mass spectrum of the complex (TC1)

Table 1: Mass Spectral data of the complex (TC1)

m/z ratio	Fragment assigned
165	$S_3N_3NHCH_2$
232	$SNNHCH(CH_2C_6H_4OH)$
273	$S_2N_2NH(COO)(CH_2C_6H_4OH)(M-1)$
395	$S_4N_3NHCH(COOSN)(CH_2C_6H_4OH)$
460	$S_4N_3NHCH(COO)(CH_2C_6H_4OH)Zn\ SN$
539	$S_4N_3NHCH(COO)(CH_2C_6H_4OH)ZnS_3N_3(M-1)$
583	$S_4N_3NHCH(COO)(CH_2C_6H_4OH)ZnS_4N_3(M-1)$
610	$S_4N_3\text{-}NH\text{-}CH(COO)(CH_2C_6H_4OH)Zn\text{-}S_4N_3\text{-}N{=}CH_2$
671	$\{S_4N_3NH\text{-}CH_2(COO)\}_2(CH_3)(CH_2C_6H_4OH)Zn$ (M+1)
762	$[S_4N_3NH\text{-}CH(COO)(CH_2C_6H_4OH)]_2\ Zn$ (M-1)

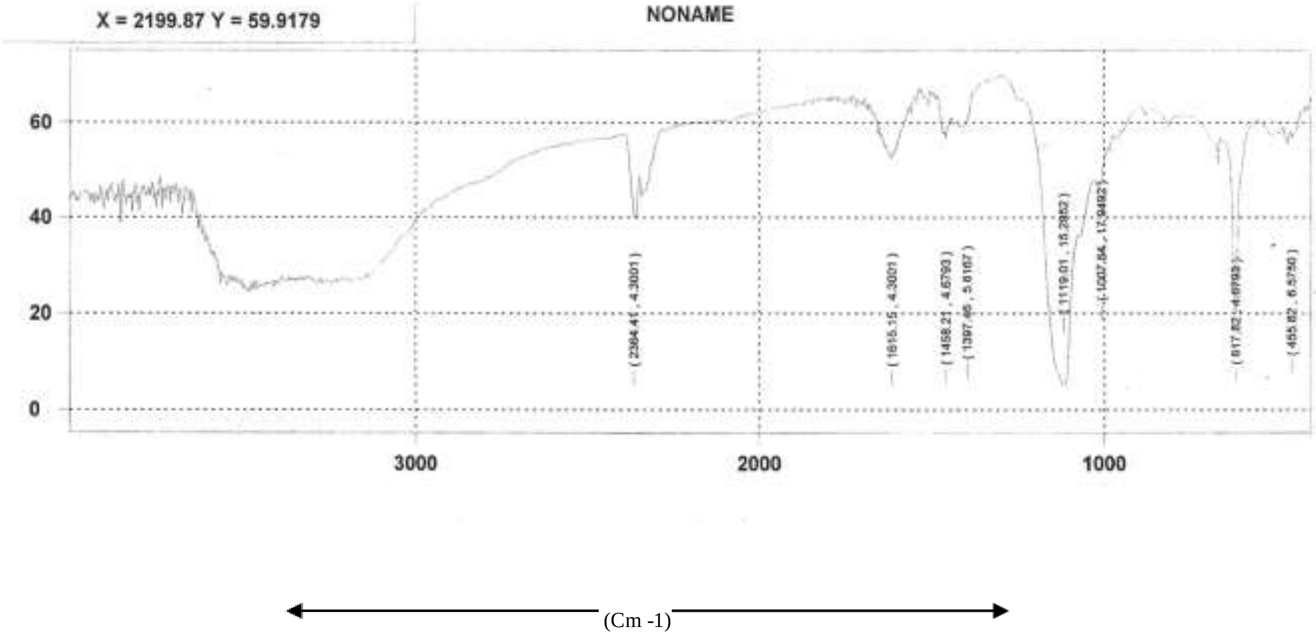


Fig. 2; IR Spectrum of the complex(TC$_1$)

Table 2 : IR Spectral data of the Complex (TC$_1$)

Vibrational Frequencies (cm^{-1})	**Band assigned**	**Force constant Kx10^{5}dynes/cm^2**
455(s)	υ_{M-O}	1.45
617(w)	υ_{M-N}	2.66
1007 (sh)	S – S str.	710
1119(s)	S– N bonded	8.77
1397 (sh)	N–S bonded.	13.68
1458(m)	S–N bonded inS$_4$N$_3$ring	15.10
1615(br)	$^{\nu}$COOof bonded	18.53
2365 (w)	H-N bonded	39.17

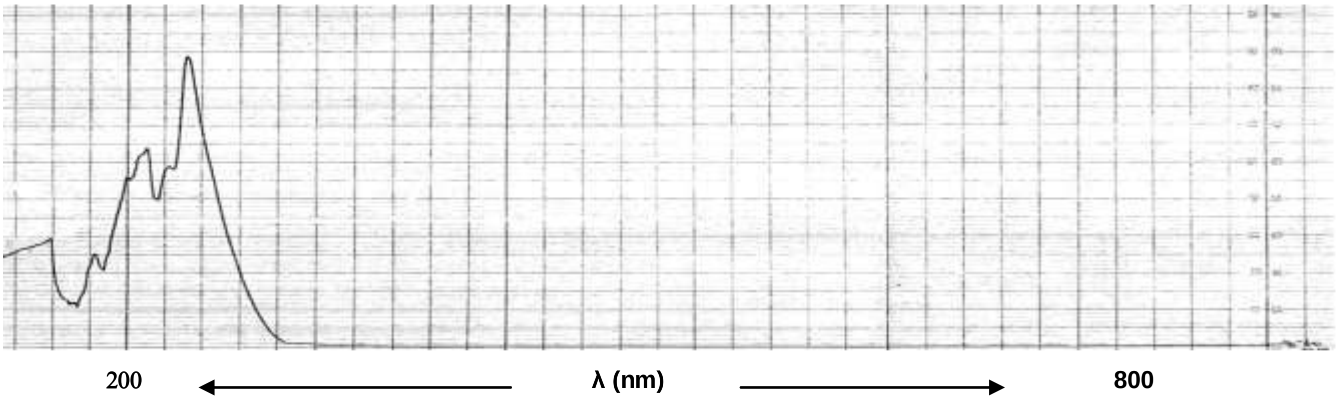
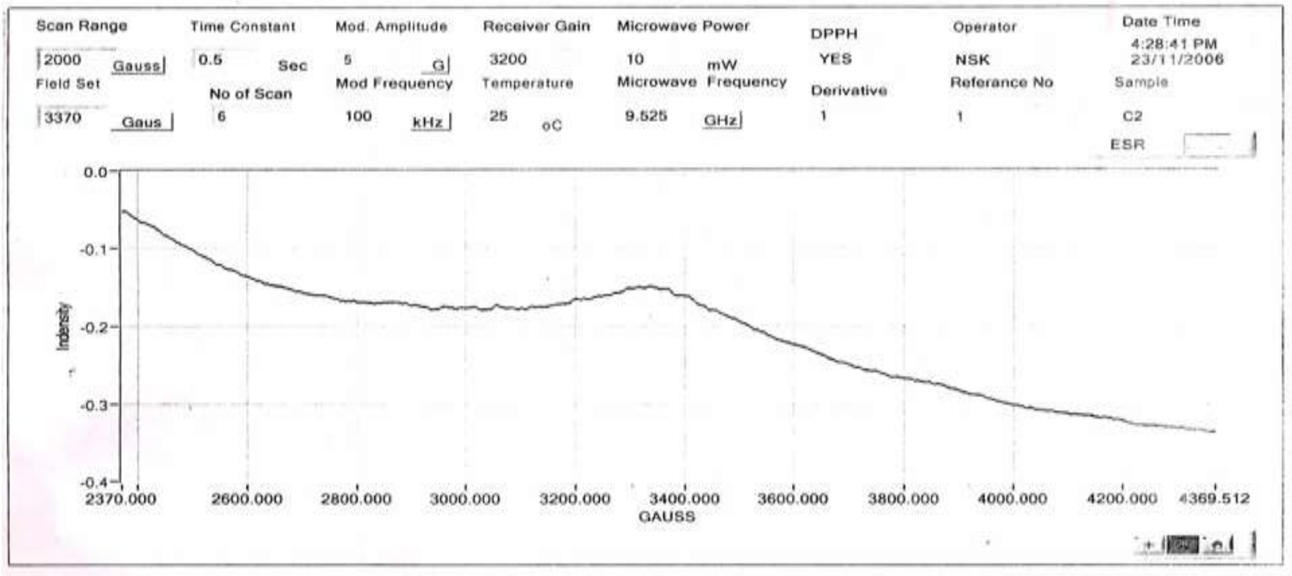


Fig 3:U.V. Spectrum of the Complex(TC$_1$)

Table 3 : U.V. Spectral data of the complex (TC_1)

Band Position nm (cm^{-1})	Molar absorptivity ($\varepsilon \times 10^3$)	ν_1/ν_2	10Dq (cm^{-1}) $\nu_2 - \nu_1$	$\Delta\nu_{1/2}$	B	β	Band gap energy ΔEg (ergs)eV	No. of conducting electrons $n_c \times 10^{17}$	Oscillator Strength (f) × 10^{-4}	δ_c % covalency	Electrical conductivity $\sigma \times 10^{-7}$
206	0.251	1.320	11779	1885	942.5	0.77	1.46	0.84	20.43	29.8	0.63
(48543)							(2.33×10^{-12})				
272	0.346	1.073	2518	4029	2014.5	1.66	0.316	3.95	60.22	39.7	1.41
(36764)							(0.5×10^{-12})				
392	0.667	1.073	2518	3920	1960	1.41	0.316	3.95	12.95	29.02	
(34246)							(0.5×10^{-12})				



← H (Guass) →

Fig.4 :E.P.R. Spectrum of the complex(TC_1)

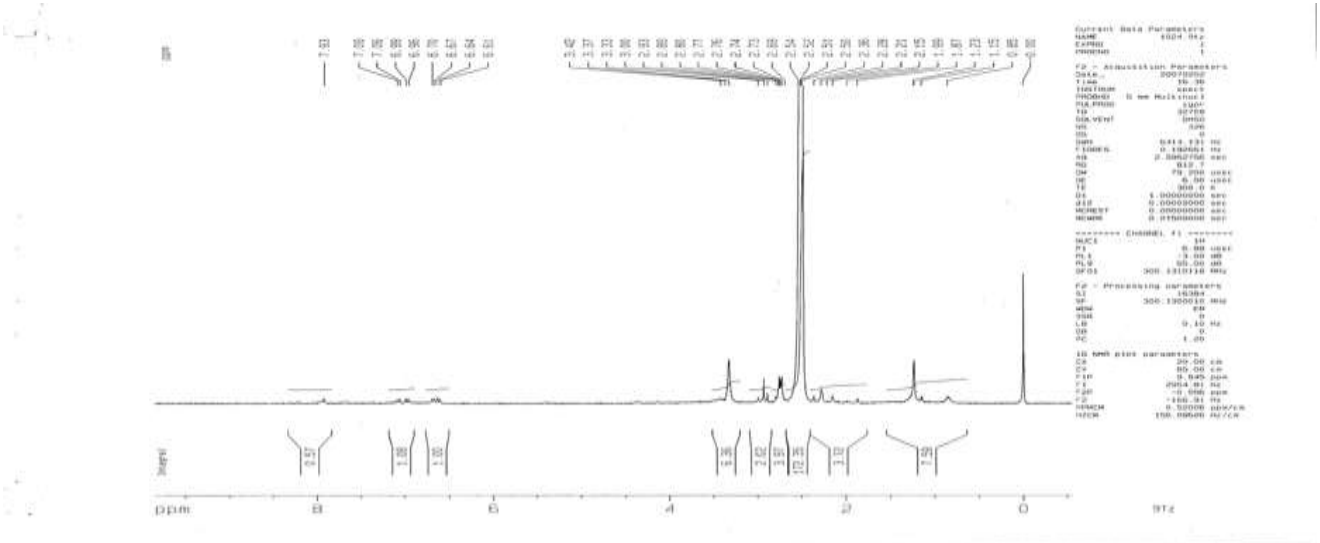


Fig.5(a); ^{1}HNMR Spectrum of the complex(TC_1)

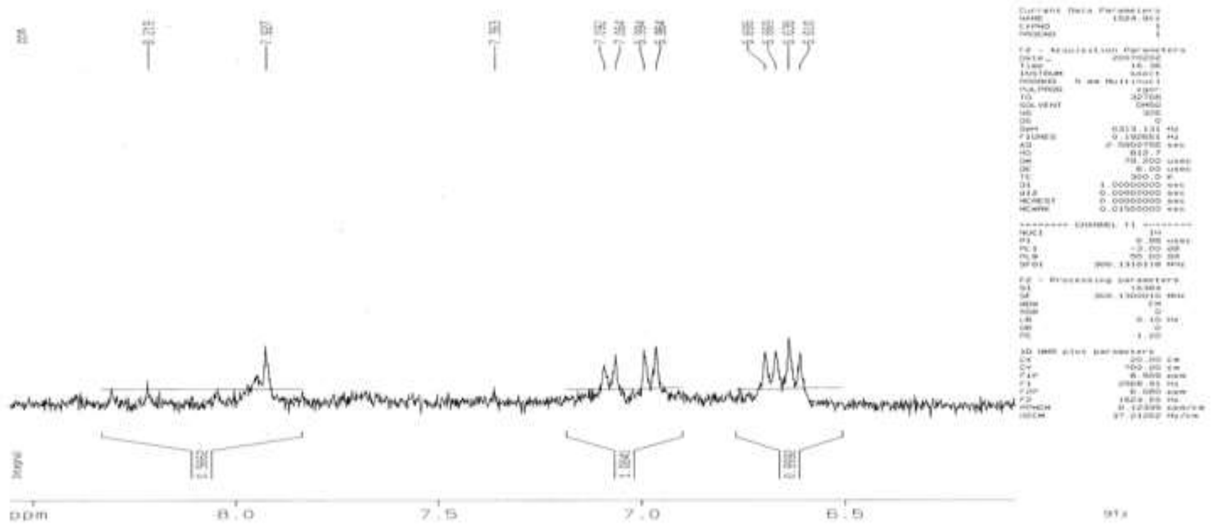


Fig.5(b);^{1}HNMR Spectrum of the complex(TC$_1$)

Table 4:^{1}H NMR spectral data of the Complex (TC$_1$)

Frequency (MHz)	**Chemical shift δ (ppm)**	**τ =10-δ (ppm)**	**Coupling Constt (J) Hz**
255	0.85	9.15	
345	1.15	8.85	90.00
645	2.15	7.85	300.00
1026	3.42	6.58	381.00
1983	6.61	3.39	957.00
2097	6.99	3.01	114.00
2118	7.06	2.94	21.00
2397	7.93	2.07	261.00

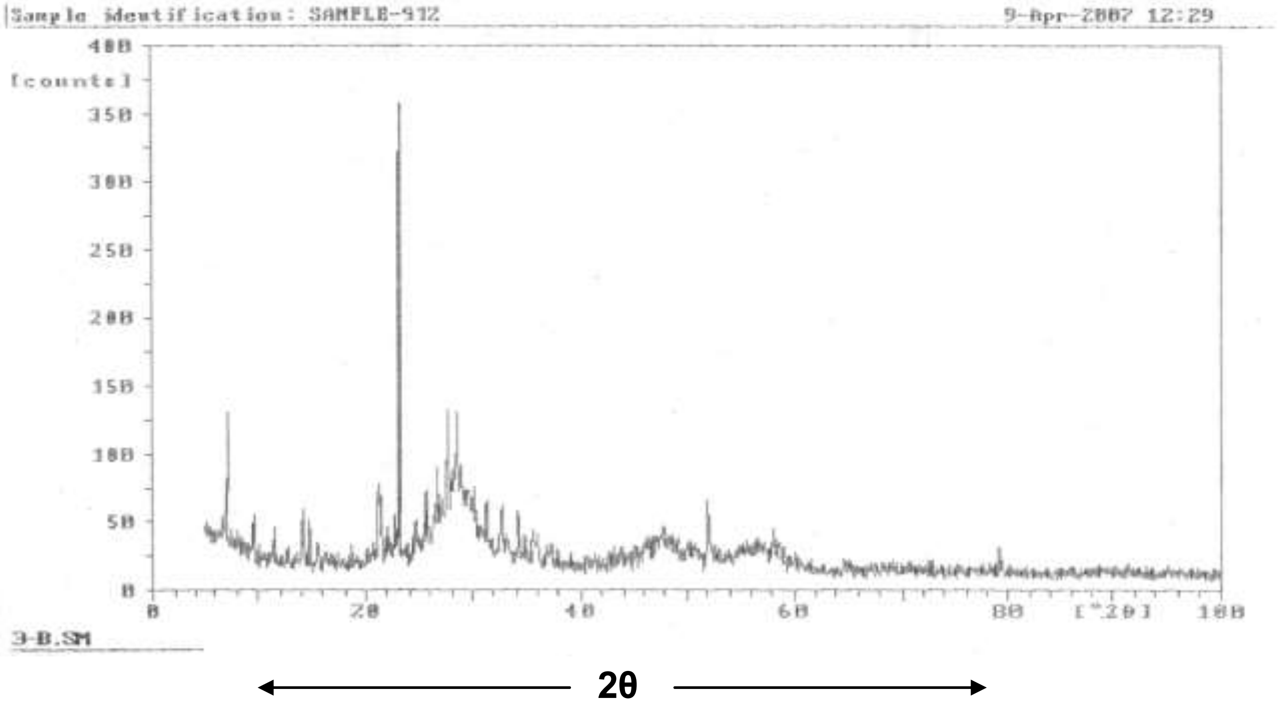


Fig.6; XRD Spectrum of the complex(TC$_1$)

Table 5: XRD (Powder) pattern of the complex (TC_1)

2θ (^{0})	$\sin^2\theta$	$Q\times(h^2+k^2+l^2)$	hkl	d_{nkl} (obs) (Å)	d_{hkl}(theor) (Å)
7.030	0.00107	0.00107(1)	100	12.5637	12.5637
14.065	0.00213	0.00106(2)	110	6.3915	6.2935
21.140	0.00320	0.00106(3)	111	4.1992	4.1990
21.36	0.00323	0.00107(3)	111	4.1564	4.1567
22.62	0.00342	0.00114(3)	111	3.9277	3.9275
23.030	0.00348	0.00116(3)	111	3.8587	3.8567
25.780	0.00389	0.00129(3)	111	3.4529	3.4528
26.63	0.00401	0.00133(3)	111	3.3446	3.3452
27.665	0.00417	0.00139(3)	111	3.2218	3.2222
28.630	0.00431	0.00143(3)	111	3.1154	3.1142
30.175	0.00454	0.00151(3)	111	2.9666	2.9588
31.355	0.00471	0.00157(3)	111	2.8505	2.8500
32.155	0.00492	0.00169(3)	111	2.7318	2.7313
34.235	0.00573	0.00143(4)	111	2.6170	2.6166

Q_{av} = 0.00132 a_o = 21.20 Å b_o = 21.20 Å c_o = 25.96 Å α = 90.01^o β = 90.00^o γ = 120.00^o

References

R.C.Paul, C.L. Arora , J. Kishore and K. C. Malhotra; The nature of tetrasulphur tetranitride with Lewis Acids ;Aust. J. of Chem, (1971), 24,1637-1641.

M. Goehring., H. Hohenschutz , and R.,J.Appel, Adduct of Tetrasulphur Tetranitride with sulphur trioxide ; Nature , (1954) 96, 678 -681.

K. J.Wynne, and W. L. Jolly; Adduct of Tetrasulphur tetranitride with Borontrichloride; Inorg. Chem. (1967), 6,107-110.

P. J. Ashley and E. G. Torrible; IR spectra of the adduct of Tetraphlfur tetranitride with metal halides; Canad. J. Chem. (1969), 47, 2587-2591.

A. Singh and S. P. S. Jadon; Synthesis and characterization of zinc complexes of Bis(thiotrithiazyl) thioureate ; Int. J. Chem. Sci.; 2007, 5(2) , 769-775.

V. Chauhan and S. P. S. Jadon ; Mass and NMR spectra of the complex N-Thiotrithiazyl O-Thiotrithiazyl phenylalaniate with zinc.; Int. J. Chem. Sci.;2010 , 8(3) 1699-1704.

S. S. Yadav and S. P. S. Jadon; Spectroscopic investigation of the reaction product of Thiotrithiazylchloride with mercuric chloride; J. Indian Chem. soc. ;2002 , 79 . 751-753.

V. Chauhan and S. P. S. Jadon ; Spectroscopic studies of novel adduct of Thiotrithiazylchloride with 2-amino -3-phenylpropanoic acid; 2017,15, 110-114.

K. Nakamato, Infra Red and Raman Spectra of Coordination Compounds 3rd Ed. Wilay Publication Sciences New York 1978.

B. N. Figgis and J. Lewis; Modern Coordination Chemistry,; Wiley Inter Sciences

New York 1967.