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Spectral Investigation of the Complex of $S_3N_3Cl_3$ with $ZrOCl_2 \cdot 2H_2O$

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The complex of trithiazyl trichloride ($S_3N_3Cl_3$) synthesised with $ZrOCl_2 \cdot 2H_2O$ is formulated as $(S_3N_3Cl_3)_2ZrOCl_2 \cdot 2H_2O$, on the basis of mass spectral and chemical data, While IR, UV, EPR and XRD patterns have expressed that $S_3N_3Cl_3$ has coordinated hexadentatively with Zr atom having sandwich type structure, paramagnetic nature and triclinic geometrical array.

INTRODUCTION

Nelson[1] prepared $S_3N_3Cl_3$ (trithiazyl trichloride) by the chlorination of S_4N_4[2] in a nonaqueous solvent. Glemser *et al.*[3] and Patton[4] reported that $S_3N_3Cl_3$ dissociate into monomeric form (NSCl) on heating. Alange *et al.*[5] have also prepared the complexes of $S_3N_3Cl_3$ with transition metal compounds, yielding $N(SCl_2)^+MX^-_{n+1}$ ionic compounds. Jadon[6,7] reported the formation of the complexes of $S_3N_3Cl_3$ with Cu^{2+} and $ThCl_4$ under varying conditions and suggested that complexes are metal bridged coordinated complexes, in place of ionic. In the present paper the investigations done for the complex of $S_3N_3Cl_3$ with $ZrOCl_2 \cdot 2H_2O$, are being reported.

RESULTS AND DISCUSSION

The complex of $S_3N_3Cl_3$ with $ZrOCl_2 \cdot 2H_2O$ was prepared by refluxing DMF solution of both (taken in equimolar proportion) for 24 h and analysed for its constituent elements along with its molecuar weight. Analytical data of the complex: % found (cal.): S 27.27 (27.30): N 11.93 (11.95): Cl 40.34 (40.39): O 6.81 (6.83): H 0.54 (0.57): Zr 12.95 (12.97) and molecular weight found (cal.): 703.36 (703.20) g/mole are according to its molecular formula $(S_3N_3Cl_3)_2$ $ZrOCl_2 \cdot 2H_2O$. To come at a definite molecular structutre of the complex, the results of instrumental analysis done are as follows:

Mass Spectral Analysis: The mass spectrum of the complex possesses mass peaks at M/Z ratio 339 for $S_3N_2Cl \cdot ZrOCl_2$, 355 for $S_2N_3Cl_2 \cdot ZrOCl_2$, 369 for $(S_2NCl)_2 \cdot ZrOCl_2$ and 383 for $(S_2N_2Cl)_2 \cdot ZrOCl_2$ suggesting that $ZrOCl_2$ is linked with $S_3N_3Cl_3$ ring, while the mass peaks for M/Z ratio at 467 for $(S_2N_2Cl)_2 \cdot ZrOCl_2 \cdot 2H_2O$, 551 for $S_5N_5Cl_3 \cdot ZrOCl_2 \cdot 2H_2O$ and 577 for $S_5N_7Cl_3 \cdot ZrOCl_2 \cdot 2H_2O$ indicate that two $S_3N_3Cl_3$ rings have coordinated with $ZrOCl_2 \cdot 2H_2O$ during reaction, inferring the molecular weight and molecular formula of the complex as mentioned above.

IR Spectral Studies: The frequencies found in its IR spectrum are given in Table-1. Due to the lack of the 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 556 cm^{-1}, 661 cm^{-1} and 866 cm^{-1} for S—N → M indicate that three N atoms of one $S_3N_3Cl_3$ ring have coordinated to zirconium atom. Bands in 1392–1094 cm^{-1} region are for S—N—Cl groups. The vibrations from 2505–2274 cm^{-1} are due to three distorted N–S bands, indicating the coordination of another $S_3N_3Cl_3$ ring to zirconium atom through its N atom. The vibrations in 3475–2863 cm^{-1} region are due to OH groups, showing the presence of water molecule of $ZrOCl_2 \cdot 2H_2O$.

TABLE-1
IR SPECTRAL DATA OF THE COMPLEX

S.No.	Vibrations $cm^{-1}(\bar{\nu})$	% T Transmittance	Assignment of bands	Force constant {k × 10^5 dyne/cm)
1.	556.0 (b)	31.54	S—N → M	1.779
2.	661.0 (s)	1.99	S—N → M	2.515
3.	866.0 (s)	47.28	S—N → M	4.317
4.	1094.0 (s)	–0.09	N—S—Cl	5.403
5.	1257.0 (s)	3.29	N—S—Cl	7.132
6.	1392.0 (s)	0.09	N—S—Cl	8.747
7.	2274.0 (s)	64.36	δ—N—S	29.767
8.	2323.0 (s)	62.59	δ—N—S	31.064
9.	2505.0 (s)	62.23	δ—N—S	36.122
10.	2863.0 (s)	7.61	O—H	3.239
11.	3072.0 (s)	42.66	O—H	3.729
12.	3475.0 (b)	4.14	O—H	4.772

Electronic Spectrum: The electronic spectrum of the complex has two bands, out of which the lower band at 26595 cm^{-1} corresponds to P_π–d_π transition of $S_3N_3Cl_3$ ring. The higher band at 32258 cm^{-1} due to charge transfer transition is also confirmed by the frequency ratio $\nu_1/\nu_2 = 1.213 < 2$. The value of oscillator strength $f = 9.138 \times 10^{-6}$ expresses spin forbidden, Leporte forbidden transition and exchange of electrons from L → M with spin orbital coupling. Low value of Dq and high value of electron repulsion parameter 'B' are also in accordance with coordination of trithiazyl trichloride to zirconyl chloride with the formation of hexadentated complex with absence of $^3T_{1g}(F) \rightarrow {}^3A_{2g}(F)$, $^3T_{1g}(F) \rightarrow {}^3T_{2g}(F)$ and $^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$ transitions as found in Zr complexes generally. The values of band gap energy (ΔEg) and number of conduction electrons (Table-2) suggest its conductive nature.

TABLE-2
UV SPECTRAL DATA FOR COMPLEX, $(S_3N_3Cl_3)_2 \cdot ZrOCl_2 \cdot 2H_2O$

Assignment of bands, nm (cm^{-1})	Molar Absorptivity ε	ν_1/ν_2	Dq (cm^{-1})	Band gap energy ΔEg (eV)	Number of conductive electrons (n_c)	Oscillator strength (f)	B
310 (32258)	1.0519	1.213	566.232	0.351	1.62×10^{25}	9.138×10^{-6}	2010.94
376 (26595)	0.4355					4.99×10^{-6}	2654.79

EPR Spectrometric Investigation: EPR spectrum of the complex shows only a broad peak of low intensity expressing paramagnetic nature of the complex. The values of various tensors determined as $g_{av} = 1.771$ $\mu_{eff} = 1.1525$ BM and $\chi_A = 0.5536 \times 10^{-3}$ CGS infers that zirconium atom has empty 'd' energy shell to accept electron pairs from the ligand, $S_3N_3Cl_3$ to form hexadentated complex. The value of number of unpaired electrons, found to be 1, may be due to the hydrogen bonding in the complex. The values of χ_A and μ_{eff} indicate the paramagnetic character of complex, while the ligand $S_3N_3Cl_3$ was found to be diamagnetic in nature.

X-Ray Diffractometric Studies: In XRD spectrum of the complex, a strong peak at 44.62°(2θ) of high intensity for metal atom having two peaks to its both sides at 38.4° (left) and at 64.95° (right) due to $S_3N_3Cl_3$ rings are observed. The other peaks are for the other parts of the ring. The value of $\sin^2\theta$, hkl, 'd' axial ratio and axial angles (Tables 3 and 4) are corrosponding to triclinic geometry of the complex, in which two $S_3N_3Cl_3$ rings have coordinated to $ZrOCl_2 \cdot 2H_2O$ through metal bridging forming sandwich type structure as shown by Fig. 1. Thus Zr atom of $ZrOCl_2 \cdot 2H_2O$ is hexadentatively coordinated by two $S_3N_3Cl_3$ rings for which six S—N bands and four angle sets have been found (Table-4), expressing linkage of distorted $S_3N_3Cl_3$ rings to Zr atom in triclinic structure of the complex.

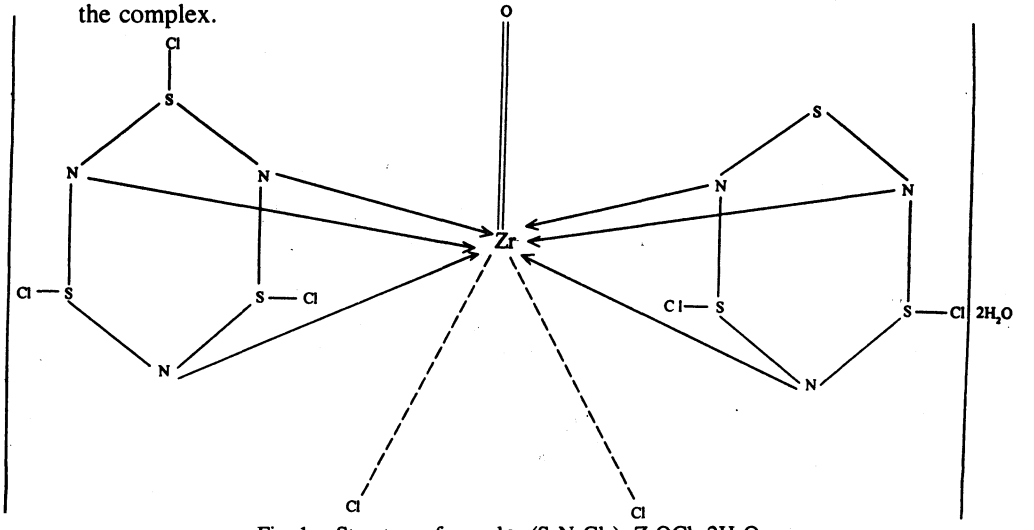

Fig. 1. Structure of complex $(S_3N_3Cl_3)_2 \cdot ZrOCl_2 \cdot 2H_2O$

TABLE-3
XRD PATTERN OF COMPLEX

S.No.	2θ (degrees)	$\sin^2\theta$	$(h^2+k^2+l^2)Q$	hkl	d (Å)	d_{hkl} (Å)
1.	9.650	0.0071	(1) (.0071)	100	9.1591	9.1414
2.	13.675	0.0142	(2) (.0071)	110	6.4730	6.4649
3.	16.615	0.0209	(3) (.0070)	111	5.3310	5.3156
4.	19.408	0.0284	(4) (.0071)	200	9.1374	9.1415
5.	21.446	0.0347	(5) (.0069)	210	8.2737	8.2941
6.	24.112	0.0436	(6) (.0073)	211	7.3746	7.3610
7.	29.110	0.0632	(9) (.0070)	221	6.1304	6.1377
8.	31.168	0.0721	(10) (.0072)	310	8.6033	8.6112
9.	35.578	0.0933	(13) (.0072)	320	7.5640	7.5532
10.	38.450	0.1084	(16) (.0068)	400	9.3660	9.3410
11.	44.615	0.1441	(20) (.0072)	420	8.1168	8.1194
12.	48.526	0.1688	(24) (.0070)	422	7.4980	7.5171
13.	54.998	0.2132	(29) (.0074)	432	6.6734	6.6512
14.	57.350	0.2302	(32) (.0072)	440	6.4217	6.4190
15.	59.408	0.2455	(35) (.0070)	531	7.7728	7.7810
16.	61.466	0.2610	(38) (.0069)	532	7.5385	7.5214
17.	64.950	0.2883	(41) (.0070)	540	7.1734	7.1891
18.	67.346	0.3074	(42) (.0073)	541	6.9450	6.9555
19.	68.552	0.3172	(45) (.0070)	542	6.8384	6.8622

TABLE-4
X-RD PATTERN OF COMPLEX

S.No.	a_0 (Å)	b_0 (Å)	c_0 (Å)	α (degrees)	β (degrees)	γ (degrees)
1.	9.16	7.48	4.10	79.2	126.50	153.8
2.	18.28	14.92	8.20			
3.	18.33	13.66	6.70	54.7	142.10	162.3
4.	27.23	21.11	9.53			
5.	36.83	29.66	12.30	62.7	133.03	161.6
6.	36.06	26.82	58.30	151.4	158.30	41.6
7.	46.20	34.36	74.72			

EXPERIMENTAL

Trithiazyl trichloride was prepared by Nelson's method *(loc. cit.)* by chlorination of S_4N_4 in CS_2, kept in ice-cold bath for 8–10 h. The sky-blue coloured mass obtained was separated, washed and dried. Formation of $S_3N_3Cl_3$ is confirmed by its melting point 168°C.

To prepare the complex, definite quantity of $S_3N_3Cl_3$ (0.5 g) and $ZrOCl_2 \cdot 2H_2O$ (0.5 g) were dissolved in DMF separately and the solutions was mixed and refluxed for about 24 h unless change in colour of the solution appeared, indicating the formation of complex. The mass formed was filtered, washed with DMF followed by alcohol and after that it was dried and stored over fused $CaCl_2$.

Quantitative estimations for constituent elements of the complex were done gravimetrically as well as spectrometrically. The molecular weight was determined by Rast's method. IR 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 200 nm–900 nm. 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 Model No. PW 3710, by using CuK_α as source of radiation ($\lambda = 1.54056$ Å) at room temp in the range of 2θ from 7 to 70° respectively.

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REFERENCES

1. J. Nelson and H.G. Heal, *Inorg. Nucl. Chem. Lett.*, **6**, 429 (1970).
2. M.B. Goehering, *Quart. Rev.*, **10**, 437 (1956).
3. O. Glemser and J. Wiegner, *Inorg. Nucl. Chem. Letter*, **7**, 623 (1974).
4. R.L. Patton and W.L. Jolly, *Inorg. Chem.*, **9**, 1079 (1979).
5. (a) G.C. Alange, B.J. Bell and A.J. Banister, *J. Chem. Soc. Dalton Trans.*, 2399 (1972); (b) G.C. Alange, *Inorg. Nucl. Chem. Lett*, **13**, 175 (1978).
6. S.P.S. Jadon, *Asian J. Chem.*, **12**, 1139 (2000).
7. ——— , *J. Bangladesh Acad. Science*, **24**, 135 (2000).

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