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Synthesis and Characterisation of the Complexes of $S_3N_3Cl_3$ with $ThCl_4$ under Varying Conditions

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The complexes of $S_3N_3Cl_3$ with $ThCl_4$ were synthesised at normal and high temperature and pressure. Their chemical data have assigned these complexes C_1 and C_2 respectively as $S_3N_3Cl_3 \cdot ThCl_4$, and trimer $(S_3N_3Cl_3 \cdot ThCl_4)_3$ out of which the former has hexadentated Th^{4+} while the latter complex has bidentated Th^{4+} bridging between $S_3N_3Cl_3$ units. This is supported by their electronic and EPR spectra which express that these complexes are of paramagnetic and good conductive nature subsequently with distorted hexagonal and triclinical geometrical array.

INTRODUCTION

The formation of various halogenated derivatives of S_4N_4,[1] such as $S_4N_4F_4$, S_4N_4Br, S_3N_3Cl and $S_3N_3F_3$ has been reported[2–10]. Meuwsen[11], Schroeder (*loc. cit.*), Cohen *et al.*[12] and Nelson (*loc. cit.*) have also prepared $S_3N_3Cl_3$ (trithiazyl trichloride) by the chlorination of S_4N_4 in a nonaqueous solvent. Patton[13] and Glemser[14] have expressed that $S_3N_3Cl_3$ dissociate into monomeric form (NSCl) on heating and it forms ionic compounds[15] with $AlCl_3$ as $N(SCl)_2^+AlCl_4^-$. Glemser *et al.*[16,17] have suggested that trithiazyle trichloride reacts with Lewis' acids such as $SbCl_5$, SbF_5 and AsF_5 etc. to form ionic compounds as $S_3N_3^+ \cdot MCl_6^-$ which probably possesss the $S_3N_3Cl_3$ cyclic ring[18]. Knneth *et al.*[15] (*loc. cit.*) have prepared complexes of the type $MoS_3 \cdot N_3Cl_3$ by the reaction of $Mo(CO)_6$ with $S_3N_3Cl_3$. In the present paper trithiazyl trichloride is used as donor to synthesise its complex with $ThCl_4$ and to study it under varying conditions of pressure and temperature.

RESULTS AND DISCUSSION

The complexes of trithiazyle trichloride, $S_3N_3Cl_3$ with $ThCl_4$, prepared at normal temperature and pressure and at 373 K and 1.75×10^5 dynes/cm^2 pressure are termed as complexes C_1 and C_2 which are analysed for their constituent elements along with their molecular weights. The results (Table-1) are according to their molecular formulae $S_3N_3Cl_3 \cdot ThCl_4$ and $(S_3N_3Cl_3 \cdot ThCl_4)_3$ respectively for the complexes C_1 and C_2.

TABLE-1
ANALYTICAL DATA OF THE COMPLEXES OF $S_3N_3Cl_3$ WITH $ThCl_4$ AT VARYING TEMPERATURE

Complex	m.w. found (cal.) gm/mol	m.p. (°C)	Colour	% Analysis, found (calcd.)			
				Th	S	N	Cl
$S_3N_3Cl_3 \cdot ThCl_4$ (C_1)	620 (621.44)	218	white	37.54 (37.51)	15.50 (15.52)	6.80 (6.79)	40.21 (40.17)
$(S_3N_3Cl_3 \cdot ThCl_4)_3$ (C_2)	1852 (1851)	297 d	brown	36.50 (36.90)	1672 (16.10)	7.05 (7.00)	40.23 (40.05)

The frequencies for $S_3N_3Cl_3$ and complexes C_1 and C_2 found in their IR spectra are noted in Table-2. Being non-availability of lower region the frequencies for Cl^- and Th^{4+} have not appeared in their IR spectra. The vibrations at 445, 480, 510 cm^{-1} for S—N→M and 530, 600 and 615 (s) cm^{-1} for N—S→M appear in the spectrum of the complex C_1. It means $S_3N_3Cl_3$ ring has coordinated hexadentedly to Th^{4+} through three N-coordinated S—N bonds and three S-coordinated S—N bonds, as shown in Fig. 1. The other frequencies in IR spectrum of complex C_1 are as in the IR spectrum of ligand $S_3N_3Cl_3$. The IR spectrum of the complex C_2 is also compared with IR spectra of $S_3N_3Cl_3$ and complex C_1. Three N-coordinated bands at 490 (s), 520, 590 (s) cm^{-1} and three

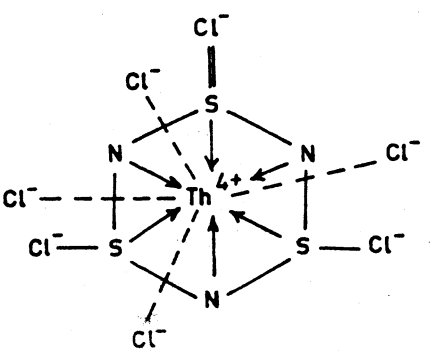

Fig. 1 Proposed structure of $S_3N_3Cl_3 \cdot ThCl_4$ complex

S-coordinated bands at 625, 650 (s) and 670 (s) cm^{-1}, which are in higher region than that of complex C_1, are found. The molecular formula of complex C_2 indicates that it is a trimer of complex C_1 and each Th^{4+} is bidented bridged between two $S_3N_3Cl_3$ rings coordinated by each S and N atoms of the ring as expressed by Fig. 2. From this it is concluded that the complex C_1 assigned as $S_3N_3Cl_3 \cdot ThCl_4$ has polymerised during heat treatment under high pressure changing entirely in all respects of properties and structure, as a trimer of it. On heating under high temperature and pressure the hexadented thorium of

complex C_1 has changed into bidented thorium forming trimer. The other vibrations (Table-2) are for N—S—Cl at 1130–1170, 1190, 1230–1275 cm^{-1} in both complexes.

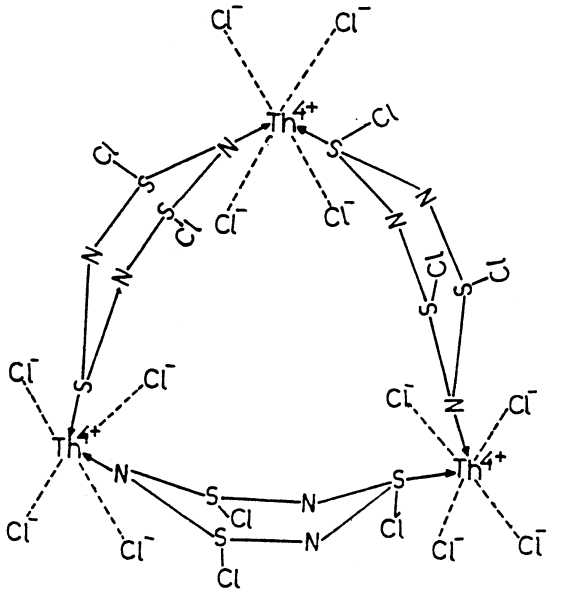

Fig. 2 Proposed structure of $(S_3N_3Cl_3 \cdot ThCl_4)_3$

The electronic spectra of both complexes C_1 and C_2 have three bands out of which the lower band at 14970 cm^{-1} for complex C_1 and at 14814 cm^{-1} for complex C_2 are corresponding to p_π–d_π transition of $S_3N_3Cl_3$ ring.

The bands found at higher region at 35971 and 37037 cm^{-1} for complex C_1 and C_2 respectively are according to charge transfer transition caused by the presence of Th^{4+} and Cl^- ions. The presence of charge transfer transition in both complexes is also confirmed by the frequency ratio $\nu_2/\nu_3 = 0.46$ and $0.44 < 1$. The middle one band in the complexes is for $^3T_{1g}(F) \longrightarrow 3T_{2g}(F)$ transition of thorium (Th^{4+}) ion. The other transitions $^3T_{1g}(F) \longrightarrow {}^3A_{2g}(F)$ and $^3T_{1g}(F) \longrightarrow {}^3T_{2g}(P)$, which must be present in the complex, are absent, showing that coordination has occurred. The values of oscillator strength 'f' calculated as

$f = 4.32 \times 10^{-19} \times E_{max} \times \Delta\nu_{1/2}$and noted in Table-3, suggest that both complexes possess spin allowed Laporte forbidden transitions. The values determined for band gap energy (ΔEg) and conductivity are for their semi-conductive natures.

TABLE-2
IR SPECTRAL DATA OF $S_3N_3Cl_3$ AND ITS COMPLEXES WITH $ThCl_4$

$S_3N_3Cl_3$ cm^{-1}	Frequencies for complex C_1 (in cm^{-1})	Bands assigned	Frequencies for complex C_2 (cm^{-1})	Bands assigned
	445 (s)			
	480 (s)	S—N→M	490 (s)	S—N→M
	510 (s)		520 (s)	S—N→M
	530 (s)		590 (s)	S—N→M
	600 (s)	N—S→M		
	615 (s)			
700 (ws)	702 (vs)		625 (s)	N—S→M
715 (ws)	720 (vs)		650 (s)	N—S→M
725 (s)	740 (s)		670 (s)	N—S→M
748 (s)	808 (s)	free S—N	720 (s)	S—N
760 (s)	845 (s)		752 (vs)	
780 (s)	890 (vs)		880–900 (b)	
805 (s)	955 (vs)		920 (b)	
	990 (vs)		950 (b)	S—N
840 (s)	1025 (vs)		970 (wb)	
862 (ws)	1070 (s)			
890 (vs)				
908 (s)	1130–1150 (b)	N—S→M	1035 (vw)	N—S—Cl
925 (s)	1190 (s)		1080 (s)	N—S—Cl
960 (s)	1230 (s)	N—S—Cl	1150–1170 (b)	N—S—Cl
	1250 (s)		1188 (s)	N—S—Cl
970 (s)			1250–1262 (b)	N—S—Cl
980 (s)			1275 (wb)	N—S—Cl
990 (s)				
1010 (s)				
1040 (ws)				
1080 (ws)				
1110 (s)				

EPR spectrum of each complex recorded shows only a broad peak of high intensity. The values of various tensors determined as $g_{av} = 1.8723$, $\mu_{eff} = 1.621$ and $\chi_A = 1.0865 \times 10^{-3}$ for the complex C_2 while $g_{av} = 1.9934$, $\mu_{eff} = 1.726$ and $\chi_A = 1.232 \times 10^{-3}$ for the complex C_2, infer that thorium atom in both complexes has empty shells to accept electron pair to form coordinated complex because $g_{av} = 2.3003$ is for free electron in neutral atom. The values of μ_{eff} and magnetic susceptibility suggest the presence of unpaired electrons and their paramagnetic nature. The broadness of lower part of the peak expresses that combination of various small hyperfine peaks due to unpaired electrons due to $5f^1$, $6s^2p^6$ configuration of Th^{4+} ion is occurring. The upper part of peak is narrow which has indicated the exchange of electron pair forming coordinate bond. The distribution of electrons, calculated by the equation

$$\frac{n_g}{n_0} = e^{-g\,BeHo/Kt}$$

is 12.12% and 4.01% for complexes C_1 and C_2 corresponding to coordination numbers 6 and 2 of thorium in complexes C_1 and C_2 respectively, as expressed by Figs. 1 and 2, This view has also been supported by their IR spectra.

TABLE-3
ELECTRONIC SPECTRA OF THE COMPLEX

Complex	Assignments (cm^{-1})	Oscillator strength 'f'	Dq/B	Band gap energy (eV)	Conductivity $\times 10^{-4}$ (mhos)
C_1	35971 (ν_3)	2.943×10^{-3}			
	1666 (ν_2)	3.801×10^{-5}	0.60	0.21	3.04
	14970 (ν_1)	8.920×10^{-4}			
C_2	37037 (ν_3)	2.864×10^{-3}			
	16393 (ν_2)	5.759×10^{-4}	0.59	0.19	1.94
	14814 (ν_1)	1.102×10^{-3}			

From X-ray powder diffraction patterns of both complexes, Miller indices, intensity ratio and value of d(Å) (Tables-4 and 5) are determined. The values of axial ratios are $a_0 = 3.862$, $b_0 = 3.153$ and $c_0 = 1.7266$ Å and axial angles are $\alpha = 90°$, $\beta = 135°$ and $\gamma = 120°$ for the complex C_1 and according to distorted hexagonal array because of normal hexagonal structure a_0 must be equal to b_0 and $\alpha = \beta = 90°$. The axial ratios for complex C_2 are $a_0 = 5.3770$, $b_0 = 7.6060$ and $c_0 = 6.5877$ Å while the axial angles are $\alpha = 137.1°$, $\beta = 74.38°$ and $\gamma = 137.1°$ corresponding to triclinical geometry. From these data, it is confirmed that hexadented thorium (Fig. 1) has changed into bidentated thorium bridging under high pressure and temperature forming trimer of the geometrical structure (Fig. 2).

TABLE-4
X-RAY POWDER DIFFRACTION PATTERN OF THE COMPLEX C_1

Q	$\sin^2\theta$	hkl	I/I_0	d (Å) (observed)	$q \times (h^1 + k^2 + l^2)$
14.60	0.06351	100	24	3.8428	1×0.066351
20.75	0.12550	110	100	2.2778	2×0.062750
25.75	0.18870	111	4	2.2897	3×0.062900
30.15	0.25220	200	9	1.9286	4×0.063100
34.10	0.31430	210	5	1.7278	5×0.062860
37.85	0.37650	211	18	1.5769	6×0.062750
45.00	0.50000	220	3	1.3686	8×0.062500
48.75	0.56530	221	1	1.2995	9×0.062810
					$q_{av} = 0.0629$

TABLE-5
X-RAY POWDER DIFFRACTION PATTERN OF THE COMPLEX C_2

Q	$\sin^2\theta$	hkl	I/I_0	d (Å) (observed)	$q \times (h^1 + k^2 + l^2)$
14.60	0.0635	110	49	3.8296	2×0.03175
18.80	0.1039	111	20	2.9980	3×0.03463
20.75	0.1255	200	100	2.2778	4×0.03138
25.75	0.1887	211	6	2.2255	6×0.03145
30.25	0.2538	220	22	1.9225	8×0.03173
34.25	0.3167	310	8	1.7211	10×0.03167
38.00	0.3790	311	35	1.5912	11×0.03446
					$q_{av} = 0.03244$

EXPERIMENTAL

Trithiazyl trichloride, $S_3N_3Cl_3$ was prepared by Nelson's method (*loc. cit*), by the chlorination of S_4N_4 in CS_2 kept in ice-cold bath for about 6–8 h. The sky-blue coloured mass separated was washed and dried. $S_3N_3Cl_3$ is confirmed by its m.p. = 168°C, molecular weight and IR spectrum.

To prepare the complexes, $S_3N_3Cl_3$ and $ThCl_4$, dissolved in DMF separately, were mixed in equimolar ratio and the resultant was refluxed for about 24 h. The change in colour of the solution indicates the complex formation. The white mass formed was filtered, washed with DMF followed by ether, dried and stored *in vacuo*. The complex thus formed is termed as C_1 half of which was treated at 373 K and 1.75×10^5 dyne/cm^2 pressure in an autoclave was put in a sealed tube and for about 72 h. It was found that the complex C_1 changed entirely into a new complex C_2 in all respects, *i.e.*, colour, odour, m.p., solubility, etc.

Quantitative estimations for constituent elements of the complexes

C_1 and C_2 were done gravimetrically as well as spectrometrically, using Bausch and Lomb Spectronic-21 spectrophotometer. S and Th were estimated subsequently at 250 and 545 nm by well known methods[19] The molecular weights were determined by Rast's camphor process. IR spectra of the complexes on KBr discs in the range of 400 to 4000 cm^{-1} were recorded on Perkin-Elmer grating spectrometer-337 model, while for electronic spectra, double beam Galford spectrophotometer having the range 200 to 800 nm was used.

EPR and XRD spectra were recorded on Varians X-E-4 band spectrometer at 300 K by using DPPH as internal standard and on XRD-6, SGP-3, single chassis GM-11 diffractometers respectively; Fe-K_α was used as source of radiation (λ = 1.937 Å) at 50 KVP/10 Ma using Plat dispersion method.

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