Asian Journal of Chemistry Vol. 17, No. 2 (2005), 1221–1225

Spectral Characterization of the Complex of Heptasulfaimide with $SnCl_2$

U.K. TRIPATHI†, S.C. TRIPATHI† and S.P.S. JADON*
Department of Chemistry, S.V. College, Aligarh-202 001, India
E-mail: sps_jadon@yahoo.co.in

Mass, IR, electronic, EPR and ^1H NMR spectral investigations of the complex of heptasulfaimide (S_7NH) with $SnCl_2$ suggested its formula as $(S_7NH)_2 \cdot SnCl_2$. On the basis of quantitative estimations, the complex has O_h geometrical structure along with its paramagnetic and conductive nature.

Key Words: Heptasulfaimide, $SnCl_2$, Complex.

INTRODUCTION

Complexes of heptasulfaimide (S_7NH) with several transitional metals have been reported[1–5]. Bergmann[6] also studied Ti complexes and assigned them as $[(Cp)_2TiS_7NH]$ and $[(Cp)_2TiS_7N(CH_3)]$.

EXPERIMENTAL

Doubly distilled Aldrich AnalaR grade chemicals were used. S_7NH was obtained[7] as byproduct during the synthesis of S_4N_4. S_7NH (0.5 g) and $SnCl_2$ (0.5 g) dissolved in ethanol separately, were mixed and refluxed for 24 h at 150°C till chocolate coloured mass was precipitated. The product was separated, washed successively with ethanol and ether to remove unreacted S_7NH and $SnCl_2$, dried and stored in vacuum over fused $CaCl_2$.

The qualitative and quantitative estimations of constituents were done as described previously[8]. Mass, IR and electronic spectra of the complex were recorded, subsequently on Micro-Mass Quatro-II, Shimadzu FTIR model 201 PC (4000–400 cm^{-1}) and Perkin-Elmer-Lambda-15 (200–800 nm) spectrometers, respectively, while EPR and ^1H NMR spectra were carried out on Varian E-X-4 band and FT NMR mode DPX-200 (DMSO solvent) spectrometers at 300 K. XRD pattern was graphed on Philips model PW-1130 X-ray diffractometer (CuK_α, $\lambda = 1.5405$ Å).

---

†Department of Chemistry, J.M.V. Ajeetmal, Etawah (U.P.), India.

RESULTS AND DISCUSSION

Analytical data of the complex: % found (calcd.) are as Sn 17.75 (17.70), Cl 10.60 (10.65), S 66.90 (66.85), N 4.20 (4.15), H 0.28 (0.30) and m.w. 662.4 (667.8). The mass, IR, electronic and EPR spectral parameters have been enlisted in Tables 1 and 2. The chemical shift δ and coupling constant J are calculated from its ^1H NMR spectrum (Fig. 1), while the values of Miller Indices, hkl, $\sin^2\theta$ and d, determined from its X-ray powder diffraction pattern, are mentioned in Table-3.

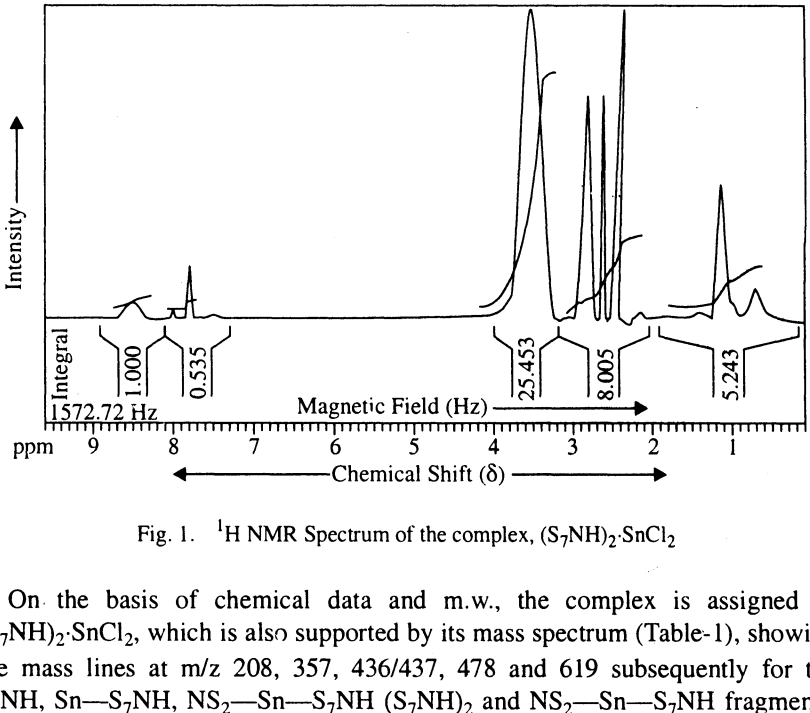

Fig. 1. ^1H NMR Spectrum of the complex, $(S_7NH)_2{\cdot}SnCl_2$

On the basis of chemical data and m.w., the complex is assigned as $(S_7NH)_2{\cdot}SnCl_2$, which is also supported by its mass spectrum (Table-1), showing the mass lines at m/z 208, 357, 436/437, 478 and 619 subsequently for the S_6NH, Sn—S_7NH, $NS_2\text{—}\underset{\substack{|\\ Cl}}{Sn}\text{—}S_7NH$ $(S_7NH)_2$ and $NS_2\text{—}\underset{\substack{|\\ Cl}}{Sn}\text{—}S_7NH$ fragments, suggesting that two molecules of S_7NH have coordinated to one molecule of $SnCl_2$ as:

$$2S_7NH + SnCl_2 \longrightarrow (S_7NH)_2{\cdot}SnCl_2 \qquad (1)$$

The evolution of HCl was tested by NH_3 gas and found negative explaining the absence of ionic displacement as:

$$2S_7NH + SnCl_2 \longrightarrow Sn(S_7N)_2 + HCl \qquad (2)$$

The coordination of S_7NH to $SnCl_2$ is inferred by the frequencies at 422.14 and 540.0 cm^{-1} for two S—S → Sn; 773.8 and 928.6 cm^{-1} for two S—N → Sn bands observed in its IR spectrum (Table-1). The other vibrations in higher region are due to S—N—H and δN—H bands. These IR results indicate that two molecules of S_7NH have linked quadridentatively to $SnCl_2$ through its S and N atoms, forming O_h geometry.

TABLE-1
MASS AND IR SPECTRA OF THE COMPLEX $(S_7NH)_2 \cdot SnCl_2$

S.No.	Mass parameters		IR spectral data	
	m/z	Fragments	Vibrations (cm^{-1})	Bands assigned
1.	208	S_6NH (M + 1)	405.00 (s)	S—S
2.	237	S_7N— (M - 1)	422.40 (s)	S—S → Sn
3.	324/325	Sn—S_6N	540.00 (b)	S—S → Sn
4.	357	Sn—S_7NH	773.80 (b)	S—N → Sn
5.	372	N—SnCl—S_7NH (M + 1)	928.60 (b)	S—N → Sn
6.	404	NS—SnCl—S_7NH (M - 1)	1325.0 (d)	S—N—H
7.	436/437	NS_2—SnCl—S_7NH	1521.7 (s)	S—N—H
8.	478	$(S_7NH)_2$	1640.0 (s)	S—N—H
9.	579	NS_6—SnCl—S_7NH	1705.0 (s)	S—N—H
10.	619	NS_7—SnCl—S_7NH	2964.4 (s)	δ (N—H)
11.	—	—	3363.6 (s)	δ (N—H)
12.	—	—	3448.5 (s)	δ (N—H)

Three peaks are found in the electronic spectrum (Table-2) of the complex. Out of these, the former two assignments according to 6.0066 and 5.4323 eV indicate ionization due to charge transfer transition, inferring the ionic nature of S_7NH and $SnCl_2$ in the complex. This view is upheld by the values of oscillator strength of the order of 10^{-4} for spin-allowed Laport-forbidden transition with $T_d \rightarrow O_h$ symmetry[9] and different Dq values from free Sn^{2+} ion. The last band at 39062 cm^{-1} (4.8437 eV for the absence of ionic environment) is on account off pπ-dπ transition of S_7NH ring. The values of band gap energy ($\Delta E = 0.59–1.16$) expound semiconductivity of the complex.

TABLE-2
ELECTRONIC AND E.P.R. SPECTRA OF $(S_7NH)_2 \cdot SnCl_2$

S.No.	Electronic data				E.P.R. Parameters			
	Bands (nm)	$f \times 10^{-4}$	Dq (cm^{-1})	ΔE (eV)	Magnetic field (gauss)	g_{av}	μ_{eff} (BM)	$\chi_A \times 10^{-3}$ (esu)
1.	48440 (ν_1, C.T.)	45.75	937.8	1.16	2260	1.965	1.70	1.21
2.	43809 (ν_2, C.T.)	26.49	463.1	0.57	2615	1.971	1.71	1.24
3.	39062 (ν_3, pπ-dπ)	2.75	474.7	0.59	3153	1.977	1.70	1.22
4.	—	—	—	—	3205	1.984	1.72	1.23

The EPR spectrum of the complex possesses prominent four peaks, further blurring due to H atom hyperfining, expressing paramagnetic character of the complex. This opinion is also supported by the values of magnetic moment, μ_{eff} = 1.70–1.72 B.M. and magnetic susceptibility χ_A of the order 10^{-3} esu. The values of $g_{av} < 2$ (Table-2) are according to vacant energy shell in Sn atom to accept electron pairs to form quadridentative complex with S_7NH, as shown by Fig. 2.

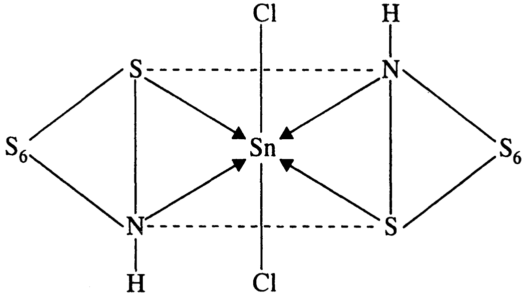

Fig. 2. Structure of $(S_7NH)_2\cdot SnCl_2$

The appearance of the signals in ^{1}H NMR spectrum infers the presence of H atoms in the complex without the loss of HCl. ^{1}H NMR spectrum of the complex consists two sets of doublets at δ 0.65, 1.10 ppm and δ 7.75, 8.05 ppm opposite to each other with the centred two sets of three signals (Fig. 1), explaining that N—H groups of two S_7NH molecules have symmetrically coordinated to $SnCl_2$ in transverse position as shown by its geometrical structure (Fig. 2).

From the X-ray power diffraction pattern of the complex recorded over 2θ range 15–18°, the values of hkl and d (Å), calculated (Table-3) are in close agreement to theoretical ones. The values of axial ratios a_0 = 4.6488 Å, b_0 = 5.3683 Å, c_0 = 3.2867 Å and axial angles α = β = 90°, γ = 120° are according to $a_0 \neq b_0 \neq c_0$, α = β = 90°, γ = 120° for monoclinic geometrical packing of O_h unit cells.

TABLE-3
XRD PATTERN OF THE COMPLEX $(S_7NH)_2\cdot SnCl_2$

S.No.	2θ (°)	$\sin^2 \theta$	hkl	d (Å)	
				Observed	Theoretical
1.	19.08	0.02747	100	4.6473	(4.6474)
2.	27.16	0.05513	110	3.2860	(3.2804)
3.	33.80	0.08451	111	2.6831	(2.6496)
4.	39.12	0.11209	200	2.3237	(2.3007)
5.	43.68	0.13839	210	2.1129	(2.0705)
6.	48.36	0.16778	211	1.8517	(1.8805)
7.	55.78	0.21881	220	1.6431	(1.6200)
8.	59.68	0.24759	300	1.4964	(1.5080)
9.	63.64	0.27643	310	1.4696	(1.4609)
10.	67.00	0.30463	311	1.3911	(1.3915)
11.	69.96	0.32866	222	1.3416	(1.3452)
12.	73.40	0.35716	320	1.2889	(1.2888)

ACKNOWLEDGEMENTS

The authors wish to express thanks to the Director, CDRI Lucknow and the Chairman, RSIC, IIT Kanpur for providing instrumental facilities to UKT.

REFERENCES

1. C. Dommingo and J.M. Orza, *Spectrochim. Acta*, **34A**, 1033 (1978).
2. H.G. Fernanadez, H. Coudame and M.A. Pindit, *Phosphorus, Sulfur, Silicon Relat. Elem.*, **41**, 405 (1986).
3. C.C. Wang, Y.Y. Hong, H.U. Chun and Y. Hong, *Inorg. Chim. Acta*, **23**, 3331 (1992).
4. H.G. Fernandez, G. Madelenin, R. Freymann and C.R. Scandes, *Acad. Sci. Ser.*, **292**, 1393 (1981); **296**, 61 (1983).
5. T. Chivers and M. Hojo, *Inorg. Chem.*, **23**, 2738 (1984).
6. K. Bergemann, M. Kustos, P. Krueger and R. Steudil, *Angew. Chem.*, **34**, 1330 (1995).
7. M.B. Goehring and W.L. Jolly, *Inorg. Chem.*, **1**, 76 (1962).
8. A.I. Vogel, A Text Book of Quantitative Inorganic Analysis, Longmans (1967).
9. B.N. Figgs, Introduction to Ligand Fields, Wiley Eastern, New Delhi (1974).

(*Received*: 25 August 2004; *Accepted:* 19 January 2005) AJC-4070