

NOTE

X-Ray Diffraction Pattern of the Complex of Heptasulfaimide with Sn(IV)

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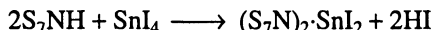
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On refluxing SnI_4 with S_7NH , Sn^{4+} is reduced to Sn^{2+} with the formation of $(\text{S}_7\text{N})_2\text{SnI}_2$ as confirmed by its mass and IR spectra. The values of axial ratios and axial angles determined from its XRD pattern suggest monoclinic packing of its unit lattice.

Key Words: X-Ray diffraction, Heptasulfaimide, Sn(IV).

Ionic as well as coordinated compounds of S_7NH with organic and metallic salts have been reported^{1,9}, suggesting the linkage of S_7NH through its S and N atoms with sulfur bridging in the complex.

Quantitative estimations, m.w. (848.5 g mol^{-1}) and fragments $\text{S}_4\text{—SnI}_2\text{—S}_7\text{N}$ and $\text{NS}_6\text{—SnI}_2\text{—S}_7\text{N}$ at m/z 738 and 818 found in its mass spectrum, infer its m.f. as $(\text{S}_7\text{N})_2\text{SnI}_2$, explaining that S_7NH has reduced SnI_4 during the reaction as follows:



This ionic displacement is also confirmed by carrying out the reaction in ethanol. The vibrations at 484 (b, w) , 513 (b) cm^{-1} , for two $\text{S—S} \rightarrow \text{Sn}$; $650\text{--}750 \text{ (b)}$, 966 (b) cm^{-1} for two $\text{S—S} \rightarrow \text{Sn}$ and in higher region for N—S bands, observed in its IR spectrum, indicate quadridentative linkage of S_7N group to Sn atom, forming O_h complex. The O_h geometry is supported by the values of oscillator strength 'f' of the order of 10^{-4} for spin-allowed Laporte forbidden transition with $\text{T}_d \rightarrow \text{O}_h$ symmetry¹⁰ as shown by its proposed structure, (Fig. 1).

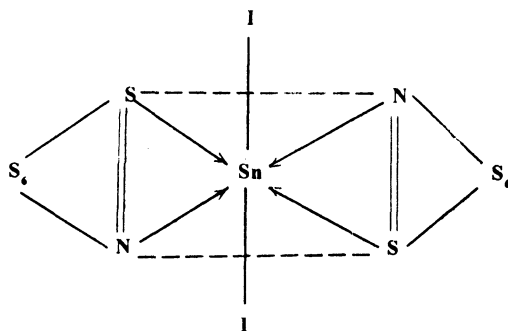


Fig. 1

From XRD pattern of the complex recorded in 2θ range from 5 to 50° (Table-1) $\sin^2 \theta$, hkl and 'd' are calculated. The values of 'd' observed resemble the theoretical ones, upholding the previous discussion about the structure of the complex. The values of axial ratios: $a_0 = 11.3247 \text{ \AA}$, $b_0 = 9.2456 \text{ \AA}$ and $c_0 = 5.6614 \text{ \AA}$; axial angles: $\alpha = 83.97^\circ$, $\beta = 25.54^\circ$ and $\gamma = 150.03^\circ$ determined from its XRD spectrum, are according to $a_0 \neq b_0 \neq c_0$ and $\alpha \neq \beta \neq \gamma$ for triclinic geometry of unit cell as expressed by Fig. 1.

TABLE-1
XRD PATTERN OF THE COMPLEX $(S_7N)_2 \cdot SnI_2$

S.No.	2θ ($^\circ$)	$\sin^2 \theta$	hkl	'd' (\AA)	
				Observ.	(Theor.)
1.	7.80	0.0046	100	11.3247	(11.3256)
2.	11.40	0.0098	110	7.7550	(7.7555)
3.	13.60	0.0140	111	6.5053	(6.5053)
4.	15.60	0.0184	200	5.6773	(5.6755)
5.	19.20	0.0278	211	4.6202	(4.6187)
6.	22.20	0.0371	220	4.0021	(4.0008)
7.	23.58	0.0417	300	3.7710	(3.7697)
8.	25.02	0.0469	310	3.4885	(3.5559)
9.	26.12	0.0511	311	3.4097	(3.4086)
10.	28.40	0.0602	320	3.1410	(3.1400)
11.	33.50	0.0830	411	2.6735	(2.6726)
12.	39.80	0.1159	500	2.2636	(2.2629)
13.	42.99	0.1343	520	2.1023	(2.1021)
14.	43.80	0.1391	521	2.0656	(2.0651)
15.	46.06	0.1530	532	1.9695	(1.9689)
16.	49.58	0.1759	620	1.8376	(1.8369)

Doubly distilled, Aldrich make chemicals of AnalaR grade were used. S_7NH was recovered as a byproduct from ether extract during the synthesis of S_4N_4 .¹¹ To get better yield, dry NH_3 was passed in excess after the appearance of solomon red colour of S_4N_4 formed in CCl_4 . The equimolar mixture of S_7NH and SnI_4 , dissolved in DMF separately, was refluxed for 24 h at $150^\circ C$. The brown coloured product obtained, was separated, washed with DMF followed by ethanol and ether, dried and stored *in vacuo* over fused $CaCl_2$.

The quantitative estimations for constituent elements were done as described¹². Mass, IR and XRD spectra of the complex were graphed subsequently on Jeol SX-102 (FAB), Shimadzu 8201 PC spectrometers from CDRI Lucknow and Philips Model No. PW 1130/00 x-ray diffractometer using CuK_α as source of radiation ($\lambda = 1.5410 \text{ \AA}$) from IIT Kanpur.

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