

hydrogen diffusion in the presence of thiourea as an inhibitor; details have been described earlier<sup>4</sup>. During the electrolysis, hydrogen liberated at the nickel wire (cathode) diffuses into it slowly. Such hydrogenated wires, lose the mobile part of hydrogen within 7–8 h while retaining the trapped hydrogen in the lattice. This is indicated by the fact that the outgassed sample does not attain its original values of thermo-emf<sup>4</sup>, resistivity<sup>5</sup>, rigidity<sup>6</sup>, etc. We thus have two sets of samples: (i) differently annealed samples, cold-worked to various degrees (number of cycles of winding–unwinding around a rod under a load of 1 kg), (ii) samples subjected to cathodic hydrogen diffusion and subsequent outgassing of the mobile part of hydrogen.

Figure 1 shows the variation in resistivity with the number of cycles of cold work for samples annealed at different temperatures. Figure 2 shows the resistivity variation after hydrogenation and outgassing. Two salient features are clear from these figures: (i) samples annealed at 290° and 600°C show a different behaviour from the rest (figure 2); 290°C is close to the strain recovery temperature (300°C), while 600°C is the recrystallization temperature, (ii) after hydrogen treatment the samples tend to attain a saturation value of resistivity.

If hydrogen ions are trapped in the lattice vacancies, the medium becomes electrically more homogeneous. As the amount of cold working is increased, the number of defects created increases and so does the amount of hydrogen that can be trapped. The sample shows a tendency to achieve a saturation value in its resistivity.

The effect of annealing on the shape of the *d*-band has been reported<sup>7</sup> earlier on the basis of thermo-electric studies. The process of cold work affects the shape of the *d*-band to the same extent in the different annealed samples. In the present case cold work affected resistivity in different annealed samples to different extents; it is the hydrogen diffusion that tends to restore the disturbed values. Thermo-emf is a property dependent on the shape of the *d*-band, but resistivity is dependent on the number and distribution of lattice defects. The effect of hydrogen diffusion seems to be to smoothen out the effect of vacancies which trap hydrogen.

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## CHARACTERIZATION OF THE POLYMERIC COMPLEX OF Sn(II) WITH TETRATHIAZYL DIHYDROFLUORIDE BY IR, UV AND EPR SPECTROSCOPY

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SYNTHESIS and investigations of tetrathiazyl dihydrofluoride (TTADHF) and its complexes with Ti(III) and Zr(IV) have been reported<sup>1,2</sup>. The preparation and studies of the complex of SnCl<sub>2</sub> with TTADHF are presented here.

TTADHF was prepared by mixing dry H<sub>2</sub>F<sub>2</sub> into a benzene solution of S<sub>4</sub>N<sub>4</sub> synthesized by Goehring's method<sup>3</sup>. To prepare the complex, DMF solutions of SnCl<sub>2</sub> and TTADHF were mixed together in equimolar ratio and refluxed for about 24 h. The brownish-red product formed was separated and washed with DMF till the washings were colourless. It was dried and stored *in vacuo*. For estimations, the complex was analysed qualitatively and quantitatively by atomic absorption spectroscopy and gravimetrically<sup>4</sup>. Molecular weight was determined by viscosity method. IR (KBr Pellet) and UV (reflectance) spectra were obtained on Perkin Elmer 257 and VSU-22 spectrometers respectively. The EPR spectrum was recorded on X-E-4 band EPR spectrometer at 300 K.

The complex is hard. It does not melt but decomposes above 400 C, and is insoluble in benzene and alcohol. The molecular formula was determined from its molecular weight, which was found to be 1646.5. Chemical analysis: % found S, 31.05; N,

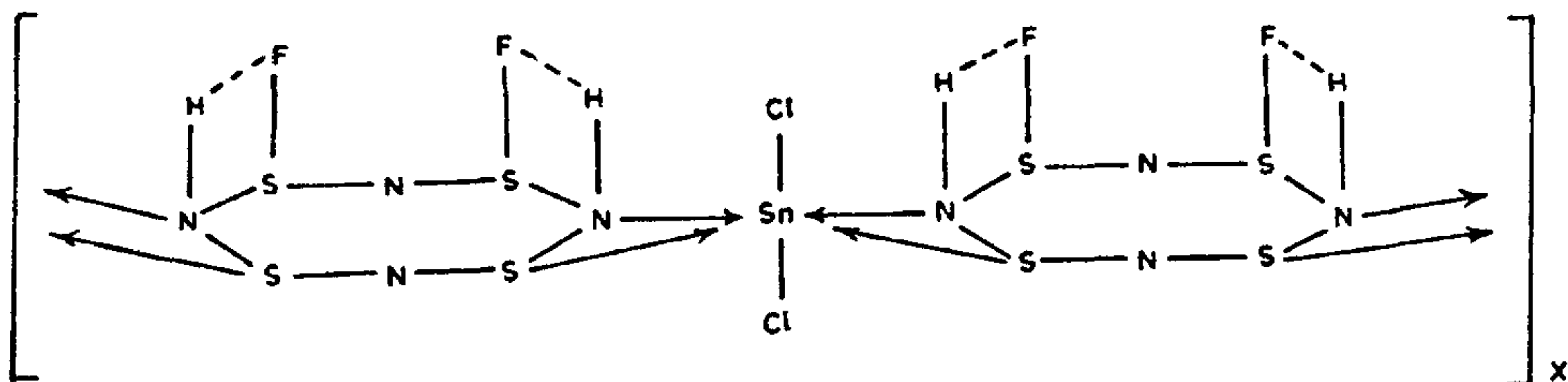


Figure 1. Proposed structure of  $[S_4N_4H_2F_2SnCl_2]_x$  (where  $X=4.21$ ).

13.12; H, 0.49; F, 9.22; Sn, 28.89; Cl, 17.23. Thus the molecular formula of the complex is assumed to be  $[S_4N_4H_2F_2SnCl_2]_{4.21}$ .

The IR spectrum of the complex shows strong bands at  $840$  and  $990\text{ cm}^{-1}$  for the two S–N bonds possessing a co-ordinated S atom. The vibrations  $1020$  and  $1060\text{ cm}^{-1}$  correspond to the two S–N bonds with a co-ordinated N atom. The frequencies  $1120$  and  $1230\text{ cm}^{-1}$  correspond to the two N–S–F groups in the complex. The vibration  $1360$ – $1660$ ,  $3100$ – $3400$ (b)  $\text{cm}^{-1}$  indicates the presence of S–N–H group. The latter band,  $3100$ – $3400$ (b)  $\text{cm}^{-1}$ , is broad, indicating hydrogen bonding in the complex. Thus  $S_4N_4H_2F_2$  acts as a tetradentate chelating agent, co-ordinating through S and N of TTADHF cyclic ring, and a polymeric complex is formed (figure 1).

The electronic spectrum shows two peaks, at  $26,315$  ( $\nu_1$ ) and  $40,816$  ( $\nu_2$ )  $\text{cm}^{-1}$ ; the former is due to  $p\pi \rightarrow d\pi$  transition and the latter indicates charge transfer. Presence of charge transfer is also supported by the value  $\nu_2/\nu_1=1.55$  ( $1\sim 2$ ). The computed values for oscillator strength ( $f$ ,  $1.38 \times 10^{-5}$ ), energy gap ( $\Delta E$ ,  $1.79\text{ eV}$ ) and conductivity ( $\lambda_{\infty}$ ,  $2.9 \times 10^{-11}\text{ mho.cm}^{-1}$ ) suggest the spin-allowed Laporte forbidden transition and semiconductive nature of the complex.

The EPR spectrum of the complex shows a narrow peak of high intensity, and other peaks are blurred, indicating the presence of unpaired electrons. The narrowness of the main peak and blurring of the other peaks also suggest the transfer of electrons from S and N atoms of TTADHF to Sn atom of  $SnCl_2$ . This implies a co-ordinate bond and polymerization of the  $S_4N_4H_2F_2SnCl_2$  unit to a tetramer, with quadridentate bridging of each unit through the Sn atom. The values of magnetic moment  $\mu_{\text{eff}}$ ,  $1.72\text{ BM}$ , and magnetic susceptibility  $\chi_A$ ,  $1.86 \times 10^{-3}$ , confirm the presence of unpaired electron, indicating

hydrogen bonding, semiconductivity and paramagnetism in the complex. The values of  $g_{\parallel}$  ( $1.981$ ),  $g_{\perp}$  ( $1.985$ ) and  $A_H$  ( $66\text{ gauss}$ ), which indicate empty shell and electron transfer, also support the co-ordination. The lower value of spin orbital coupling constant ( $\lambda_s$ ,  $25.97\text{ cm}^{-1}$ ) indicates slight spin orbital coupling.

Since the structure of TTADHF has been reported, the geometrical array of the complex, which is a tetradentate co-ordinated tetramer, may be proposed to be as shown in figure 1.

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## BENTHIC FORAMINIFERA AS BATHYMETRIC INDICATORS

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STUDIES on benthic foraminiferal distributions in continental margin sediments of some parts of the world have been carried out by several workers<sup>1-4</sup>. Bathymetric distribution of foraminifera in the continental margin of Visakhapatnam, east coast of India ( $17^{\circ}43'\text{ N}$ ,  $83^{\circ}15'\text{ E}$ ), has been reported earlier<sup>5</sup>.