necessary to reflux the mixture for nearly two hours and then concentrate slowly to separate the product. The adducts thus formed were collected by filtration, washed with small volumes of methanol followed by ether and finally dried *in vacuo*.

Analysis of cobalt was carried out by fusion with potassium pyrosulphate, oxidation by hydrogen peroxide and iodimetric titration. Estimation of nitrogen was done by Kjeldahl's method.

The electronic and IR spectral measurements and magnetic susceptibility determinations at room temperature (~300K) were carried out as described earlier[12]. Thermal decomposition of finely powdered samples were carried out in a derivatograph (MOM, Hungarian Optical Works, Budapest) in the temperature range 30-1000° at a furnace heating rate of 10° per minute.

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Some Thiocyanate Compounds of Tin

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Conductometric and potentiometric titrations of $SnCl_2$ with KSCN (equimolar solutions) indicate the formation of the compound $[Sn(OH)_2(SCN)]$ Cl at pH below 4. However at formality ratio of 1:2 ($SnCl_2$: KSCN) the titration curves reveal the formation of the compound $[Sn(SCNH)(SCN)]$ Cl at pH 2, which gets deprotonated to $[Sn(SCN)_2]$ on raising the pH to 3. This has been attributed to the generation of HNCS ($pK_a = 2.5$) at pH around 2. At pH around 5 the change

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in formality ratio is almost without any effect on the composition and structure of the compound $[Sn(SCN)(OH)]$ formed due to the hydrolysis of $[Sn(OH_2)_3]^{2+}$ to the hydroxytin cation $[Sn(OH_2)_2(OH)]^+$ which combines with NCS- to form a neutral covalent compound $[Sn(SCN)(OH)]$. IR data show that these compounds contain both Sn-NCS and Sn-SCN linkages, which is likely due to the affinity of sulphur for the formation of two single bonds instead of one double bond. This gets support from the great tendency of Sn(II) to attain the maximal possible coordination number, which is achieved by polymerization of the above mentioned thiocyanate compounds formed in the form of dimers $[Sn(OH_2)(SCN)]_2Cl_2$; $[Sn(SCN)_2]_2$; $[Sn(SCNH)(SCN)]_2$ Cl_2 and $[Sn(SCN)(OH)]_2$. X-ray data have been presented in support of the formation of these compounds.

THE mode of coordination of thiocyanate with non-transition elements has not been investigated much. The chief interest of earlier workers has been the assignments of IR absorption bands particularly due to M—S or M—N bonding but the assignments are not unequivocal[1-4] and conflicting conclusions have been reported[1-4]. This prompted us to study the compounds formed by the reaction of $SnCl_2$ and KSCN in different molar ratios and pH values by conductometric and potentiometric titrations, molecular conductance, infrared, X-ray and elemental analysis.

All the reagents used were of AR or equivalent grade. Infrared spectra were recorded on Unicam UP 1000 and UR-10 infrared spectrophotometers. X-Ray diffraction powder data for the complexes were obtained with a Siphret diffractometer using Cu K_α radiation with nickel filter ($\lambda = 1.542$ Å) according to the method described in the literature[5,6]. Conductivity was measured with a Beckman conductivity bridge, model RC-16B2 using a cell having a cell constant of 0.675. The potentiometric studies were carried out with a Tinsley potentiometer type 3387 B according to the methods described in the literature[7,8].

Conductometric titrations were carried out at different pH values. At pH values 2.0 and 3.0, the inflections in the curves correspond to the $SnCl_2$: KSCN formality ratios of 1:1 and 1:2 while the titration curve at pH 5.0 shows only the inflection corresponding to the ratio 1:1. Similar results are obtained in the potentiometric titrations. The elemental analyses of the compounds isolated at these ratios, given in Table 1, suggest that they have the compositions: $[Sn(OH_2)(NCS)]Cl$; $[Sn(SCN)_2]$ at pH 2.0 and 3.0 respectively and $[Sn(SCN)(OH)]$ at pH 5.0. The molar conductances of these compounds are given in Table 2. The interpretation of the results based on the available literature[7], indicates that thiocyanatotin(II) formed at pH 2 or 3 and formality ratio of $SnCl_2$: KSCN = 1:1 dissociates into a total number of 3 ions. On the other hand, the compound formed from the formality ratio of $SnCl_2$: KSCN = 1:2 and at pH 2 has a molar conductance which is indicative of its dissociation into 15 ions with the exception of H+ or OH-. The compound formed at pH 3 and formality ratio 1:2 behaves as a non-

TABLE 1 — ELEMENTAL ANALYSES OF COMPOUNDS FORMED IN THE REACTION OF $SnCl_2$ WITH KSCN AT DIFFERENT FORMALITY RATIOS AND pH VALUES

pH	$SnCl_2$: KSCN	Sn (%)	S (%)	Species formed
2	1:1	68·52	16·05	$[Sn(SCN)]^+$
2	1:2	51·21	27·26	$[Sn(SCNH)(SCN)]^+$
2	1:3	51·21	27·26	—
3	1:1	68·64	16·83	$[Sn(SCN)]^+$
3	1:2	51·08	27·91	$[Sn(SCN)_2]$
3	1:3	51·13	28·01	—
5	1:1	60·53	16·38	$[Sn(SCN)(OH)]$
5	1:2	60·58	16·42	—
5	1:3	60·44	16·30	—

TABLE 2 — MOLAR CONDUCTANCE OF COMPOUNDS FORMED AND ISOLATED IN THE REACTION OF $SnCl_2$ WITH KSCN AT DIFFERENT FORMALITY RATIOS AND pH VALUES

$SnCl_2$: KSCN	Λ_M at different formality (concentrations of the compounds corrected for dilution and pH)		
	0·1 F	0·01 F	0·001 F
	pH 2		
1:1	184	204	271
1:2	574	793	958
1:3	589	791	955
	pH 3		
1:1	186	201	275
1:2	—	—	—
1:3	—	—	—
	pH 5		
1:1	169	206	269
1:2	177	203	271
1:3	181	204	274

electrolyte in solution. The abnormally high molar conductance of the former and low conductance of the latter may be understood if we remember that the pseudohalide ion SCN⁻ undergoes hydrolysis in solution with the formation of hydrothiocyanic acid, HNCS at pH below 2·5 (ref. 9). However, HNCS is still capable of acting as a bidentate ligand (S, N donor). Consequently, the compound with abnormally high molar conductance seems to contain hydrothiocyanic acid as a ligand. The complex dissociates into $2H^+$ and $2Cl^-$ and is changed to a neutral covalent compound (Eq. 1):

$$[Sn(SCNH)(SCN)]_2Cl_2 \rightarrow [Sn(SCN)_2]_2 + 2Cl^- + 2H^+ \quad ...(1)$$
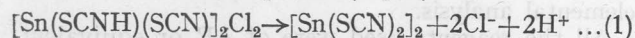
This possibility seems quite feasible due to the formation of such a compound (1b) at pH 2 and the formality ratio 1:2 ($SnCl_2$: KSCN). This, also, gets support from the extreme low molar conductance of thiocyanatotin(II) formed under the same conditions but at pH 3·0 (structures 1b and 1c). At pH 3, hydrothiocyanic acid dissociates into H^+ and SCN⁻. The SCN⁻ so obtained forms with Sn(II) a neutral covalent compound, $[Sn(SCN)_2]$, which polymerizes to the dimer (1c) having the composition $[Sn(SCN)_2]_2$.

At pH around 5 $[Sn(OH_2)_3]^{2+}$ undergoes hydrolysis with the formation of hydroxycation $[Sn(OH_2)_2(OH)]^+$ which reacts with SCN⁻ anion to form a neutral covalent compound $[Sn(SCN)(OH)]$ which polymerizes to the dimer (1d) due to the reasons mentioned previously. Since SCN⁻ and OH⁻ are covalently bonded to Sn(II), the molar conductance of this compound is extremely low (Table 2).

Infrared data of these compounds indicate that all thiocyanatotin(II) compounds exhibit two ν C—N around 2090 and 2058 cm⁻¹ and two ν C—S around 845 cm⁻¹. Accordingly, these compounds contain both Sn—NCS and Sn—SCN linkages[10]. This gets support from the fact that the sulphur atom has a tendency to form fewer double bonds than nitrogen atom[11,12]. The sulphur atom possesses an affinity to form two single bonds rather than one double bond. Consequently, $[Sn(NCS)_2]$ and $[Sn(SCN)]Cl$ instead of being formulated as monomers with one S=C double bond should be formulated as 1b-c without double bonds.
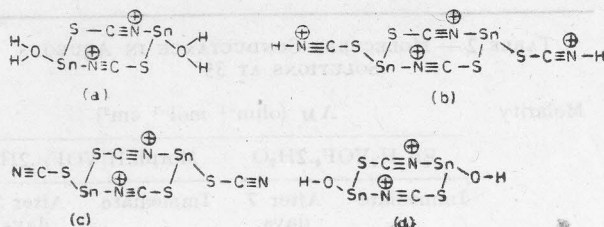
The medium to weak absorption bands at 547 and 505 cm⁻¹ are indicative of the formation of Sn—N linkages, since it is well established[10,11] that

ν Sn—N appears in the region 527-466. This is consistent with the known tendency of Sn(II) to form predominantly covalent bonds with the donor atoms of the ligands, which is greatest when the donor atom is a non-metal from group V through group VII.

A comparison of the IR data of thiocyanatotin(II) compounds formed at different formality ratios of $SnCl_2$: KSCN and pH values reveal that all of them are dimers. Thus, $[Sn(OH_2)(SCN)]_2Cl_2$, $[Sn(SC\overset{+}{N}H)(SCN)]_2Cl_2$, $[Sn(SCN)_2]_2$ and $[Sn(SCN)(OH)]_2$ are formed at pH 2 and formality ratios ($SnCl_2$: KSCN) of 1:1, 1:2; at pH 3 and formality ratio 1:2; at pH 5 and formality ratio of 1:1, respectively. At pH below 4 change in pH is almost without any effect on the composition and structure of thiocyanatotin(II) formed from the reactions of $SnCl_2$ and KSCN at formality ratio 1:1. Consequently, the reaction of $SnCl_2$ with KSCN at formality ratio 1:1 and pH 2 or 3 gives one and the same compound. The appearance of new absorption bands at 2560 and 1990 cm⁻¹ in the case of thiocyanate compounds formed at pH 2 and formality ratio of 1:2 and their disappearance on raising the pH to 3 may be due to the fact that SCN⁻ undergoes hydrolysis to hydrothiocyanic acid, HNCS with $pK_a = 2·5$ (ref. 9). It follows that at pH below 2·5 HNCS molecules exist in solution. However, as mentioned earlier HNCS is still capable of acting as a bidentate ligand (S, N donor). It is to be noted that the change in formality ratio of KSCN: $SnCl_2$ is almost without any effect on the coordination number of Sn(II), which is usually three. This may be due to the fact that Sn atom like other elements tends to attain the maximal coordination number[8-13]. On the other hand, the energy difference of the outer s and p orbitals of Sn atom is large, which reduces the possibilities of sp^3-hybridization[13]. Consequently, it seems likely that s electrons of the,

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Sn atom in thiocyanate derivatives do not participate in the sp^3 hybridization, i.e. the Sn-NCS, Sn-SCN, Sn-OH bonds are formed by pure p-electrons. This explains why the ratio of SCN⁻ : Sn in thiocyanate compounds does not exceed 3 : 1, and pyramidal rather than planar spatial configurations of most of Sn(II) compounds. This has been confirmed by the Mössbauer spectra[13]. Moreover, there are some indications that tin can function as trivalent both in organic and in inorganic compounds[14,15]. Since the oxidation state of tin and electroneutrality principle[11] have a decisive influence on its coordination number, it will bind two SCN groups to give a neutral compound. The attainment of the maximal possible coordination number of three by Sn(II) is achieved by polymerization.

X-Ray diffraction data demonstrate the distinctive nature of thiocyanate compounds of Sn(II) formed at pH values 2, 3 and 5 and formality ratios 1 : 1 and 1 : 2 (SnCl₂ : KSCN) = 2. Their diffraction patterns were obtained and their interplanar spacings calculated. The unit cell of complexes (**1a, 1b, 1c** and **1d**) have the following parameters: $a = 11.53$, 12.96, 10.98, and 11.23 Å; $b = 9.01$, 8.51, 7.74, and 9.04 Å; $c = 7.42$, 7.93, 6.98, and 7.32 Å. $\alpha = 106°31'$, $109°05'$, and $107°91'$; $\beta = 79°57'$, $102°75'$, $108°75'$, and $184°61'$; $\gamma = 101°41'$, $51°49'$, $81°49'$ and $76°65'$. These compounds have the triclinic symmetry and belong to the space group with the $P1$ and $P1m$ symmetry. The rotation diffraction pattern and the expanded layer-line diagrams clearly reveal the $C' = C/2$ pseudo-period. The chosen unit cell contains six formula units. The projections of the Patterson function in the xy and xz planes do not reveal peaks corresponding to the interatomic Sn-Sn distance. The absolute magnitude of this distance is about 4.73 Å, which is much more than the distance in metallic tin (2.80 Å). The ability of the complex to undergo self-association in solutions to form dimer (**1b**) is consistent with this conclusion.

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Oxofluorovanadates(IV)

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The preparations of oxotetrafluorovanadates(IV) of protonated ethylenediamine, benzidine, hydrazine and oxotrifluorovanadates(IV) of quinoline, tetramethylammonium, 2-aminopyridine, propylenediamine and morpholine are reported. The results of conductance measurements, TGA, ion exchange study, magnetic susceptibility measurements and IR spectra of the compounds are given and discussed.

THE literature[1-6] survey shows that oxofluorovanadates(IV) are of three types containing $(VOF_5)^{3-}$, $(VOF_4)^{2-}$ and $(VOF_3)^-$ ions. The yet unknown oxotetrafluorovanadates(IV) containing organic base cations have been reported here along with several new oxotrifluorovanadates(IV).

Vanadium(IV) fluoride trihydrate, $VOF_2.3H_2O$ was prepared by the reduction of vanadium pentoxide by ethanol in the presence of hydrofluoric acid (40%) on a water-bath followed by evaporation to a viscous liquid and then drying in a desiccator containing H_2SO_4.

For the estimation of vanadium the compound was fused with sodium carbonate, extracted with water and vanadium estimated using Mohr's salt solution and potassium dichromate[8]. From such a separate fusion fluorine was estimated gravimetrically as PbClF after separating vanadium as silver vanadate[9]. Nitrogen was estimated by semimicro Dumas' method.

Magnetic susceptibilities were measured by Guoy method and the diamagnetic corrections were done as described by Figgis and Lewis[10]. The TGA of the compounds were carried out on a manually operated apparatus, the rate of heating being 2°/min. The IR spectra were recorded on a Perkin-Elmer apparatus in KBr pellet in the region 4000-