Reactions of (SCN)\textsubscript{2} with SnX\textsubscript{4} (X = Br, I)

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From the reaction between (SCN)\textsubscript{2} and SnI\textsubscript{4} a compound is formed the formula of which is ISn(NCS)\textsubscript{3}-I\textsubscript{2}, in which I\textsubscript{2} molecules form charge-transfer complexes with thiocyanate groups. ISn(NCS)\textsubscript{3} can be isolated from this compound. Both compounds were characterised by means of elemental analyses and UV-visible, IR and \textsuperscript{119}Sn Mössbauer spectra, and a polymer structure with thiocyanate bridges was deduced. The equilibrium constant was calculated for the reaction:

ISn(NCS)\textsubscript{3}-I\textsubscript{2}(solid)+CS\textsubscript{2}=ISn(NCS)\textsubscript{3}(solid)+I\textsubscript{2}(solution) \quad K = 2.2 \pm 0.3 \times 10^{-3} \text{ mol} \textsuperscript{-1},

and it was found that the two solid compounds form a single phase. SnBr\textsubscript{4} forms an unstable addition compound with (SCN)\textsubscript{2}, which decomposes even below 0 °C.

Introduction

In a previous paper [1] we reported on the study of the reaction between (SCN)\textsubscript{2} and SnCl\textsubscript{4}, where it was observed that the thiocyanogen molecule stabilises by forming a bridge between two tin atoms. With the formation of the addition compound \nu_{CN} increases from 2160 and 2171 cm\textsuperscript{-1} [2, 3] to 2201 and 2209 cm\textsuperscript{-1}, respectively. The present paper describes the study of the reaction between (SCN)\textsubscript{2} and SnX\textsubscript{4} (X = Br, I). It was found that SnI\textsubscript{4} due to the greater oxidising power of (SCN)\textsubscript{2} in comparison to that of I\textsubscript{2} displays a behaviour completely different from that of the other tin tetrahalides.

Results and Discussion

The reaction between SnBr\textsubscript{4} and (SCN)\textsubscript{2} yields a yellow solid which is unstable at room temperature and decomposes even at temperatures below 0 °C giving rise to (SCN)\textsubscript{2} and SnBr\textsubscript{4}. On the other hand, it was found to be stable in CS\textsubscript{2} solution at room temperature for at least 24 h. The solid contains (SCN)\textsubscript{2} and can oxidise iodide ions to I\textsubscript{2}. The SnBr\textsubscript{4} probably forms an unstable addition compound with (SCN)\textsubscript{2}, hence displaying a similar behaviour to that described for BX\textsubscript{3} (X = F, Cl) [4].

The reaction between (SCN)\textsubscript{2} and SnI\textsubscript{4} produces a highly hygroscopic, brown compound the formula of which is ISn(NCS)\textsubscript{3}-I\textsubscript{2}, and which upon contact with various solvents gives off I\textsubscript{2}. The following reaction takes place:

\[ 2\text{SnI}_4+3(\text{SCN})_2\rightarrow 2\text{ISn(NCS)}_3\text{I}_2+\text{I}_2 \quad (1) \]

If the ISn(NCS)\textsubscript{3}-I\textsubscript{2} is washed with warm CS\textsubscript{2} until no more I\textsubscript{2} is liberated, a yellow compound ISn(NCS)\textsubscript{3} is formed.

The I\textsubscript{2} molecule in ISn(NCS)\textsubscript{3}-I\textsubscript{2} remains united by means of the formation of a charge-transfer complex with a thiocyanate group bonded to the tin atom: Sn—NCS…\textsubscript{I}, which is similar to charge-transfer complexes with other thiocyanate groups [5]. Fig. 1 shows the UV and visible spectra of ISn(NCS)\textsubscript{3}-I\textsubscript{2} and ISn(NCS)\textsubscript{3} in the solid state. It can be observed that there are two bands in the ISn(NCS)\textsubscript{3}-I\textsubscript{2} spectrum which do not appear in the ISn(NCS)\textsubscript{3} spec-

Fig. 1. UV/Visible Spectra.

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trum. These bands at 352 and 503 nm are assigned to the charge-transfer band and to the \( \pi^* \rightarrow \sigma^* \) transition of the \( \text{I}_2 \) molecule, respectively. (The location of these bands was found by analysing the spectrum through Gaussian analysis with a BIGAUSS program.) The small shift in the \( \text{I}_2 \) band with regard to its value in the gas phase (520 nm) indicates that the bonding of the \( \text{I}_2 \) molecule with the thiocyanate groups is weak, thus explaining why \( \text{I}_2 \) is lost upon contact with solvents.

The Mössbauer parameters of both compounds at liquid \( \text{N}_2 \) temperature can be seen in Table I. The similarity in the Mössbauer spectra confirms a very similar environment of the tin atoms in both compounds. This fact was expected, as the formation of charge-transfer bonds between \( \text{I}_2 \) and thiocyanate groups does not affect the first coordination sphere of the tin atoms. The surprisingly low isomer shift value indicates a polymeric structure with high coordination number, probably six, of the tin atoms, which is reached through bridging thiocyanate groups. The slightly lower isomer shift value in \( \text{ISn(NCS)}_3 \cdot \text{I}_2 \) suggests a greater electronegativity of the SCN groups joined to the \( \text{I}_2 \). Table I shows the characteristic bands of the thiocyanate groups, of \( \text{ISn(NCS)}_3 \cdot \text{I}_2 \) and \( \text{ISn(NCS)}_3 \), respectively, which were assigned in the IR spectra. Because of the differences between the IR spectra of both compounds the bands at 2095 cm\(^{-1} \) (v\( \text{CN} \)), 816 cm\(^{-1} \) (v\( \text{CS} \)), 445 and 430 cm\(^{-1} \) (\( \delta \text{NCS} \)) were assigned to the NCS group linked to the \( \text{I}_2 \) in the \( \text{ISn(NCS)}_2 \cdot \text{I}_2 \) compound. The remaining bands, which are very close in both compounds, should be assigned to the bridging SCN groups. Due to the low frequency at which the stretching vibrations v\( \text{CN} \) appear, these bridges might be of any type other than that of M–SCN–M [6–8]. An example of this can be observed in the compound (LiNCS)\(_4\), in which the thiocyanate groups act as a triple bridge through the N atom, where v\( \text{CN} \) appears at 2022 and 1993 cm\(^{-1} \) [9].

The equilibrium constant of the reaction

\[
\text{ISn(NCS)}_3 \cdot \text{I}_2(s) + \text{CS}_2 \rightleftharpoons \text{ISn(NCS)}_3(s) + \text{I}_2(sl)
\]

\( s = \text{solid}, \text{sl} = \text{solution} \)

has been determined at 15 °C, by stirring different quantities of \( \text{ISn(NCS)}_3 \cdot \text{I}_2 \) with different volumes of \( \text{CS}_2 \) and measuring the absorbance of the \( \text{I}_2 \) solution at 518.5 nm, once equilibrium was achieved. As this is a heterogeneous reaction, two possibilities exist:

a) The solids do not form solid solutions between themselves, in which case their activities equal one and the equilibrium constant equals the \( \text{I}_2 \) concentration.

b) The solid compounds form a single phase, in which case their activities are not equal to one, but are proportional to their molar fraction, and the following expression can easily be deduced:

\[
\text{K} = \frac{\text{V}^2}{(1000\text{N} - \text{VC})}
\]

where V = volume of solution (ml), N = number of initial moles of \( \text{ISn(NCS)}_3 \cdot \text{I}_2 \) and C = molar concentration of \( \text{I}_2 \) measured experimentally.

If (a) holds true, the \( \text{I}_2 \) concentration will be the same in all measurements, whilst if (b) applies, the constant calculated from formula (3) should be practically equal in every case.

It is observed, in Table II, that the iodine concentration varies in the different samples, whilst the con-

### Table I. IR and Mössbauer\(^a\) data.

<table>
<thead>
<tr>
<th>Compound</th>
<th>IR [cm(^{-1})](^b)</th>
<th>Mössbauer(^c) [mms(^{-1})]</th>
<th>( \delta \text{(NCS)} )</th>
<th>( \Delta )</th>
<th>( \Gamma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{ISn(NCS)}_3 \cdot \text{I}_2 )</td>
<td>2095 vs, 816 m</td>
<td>2030 sh, 788 sh</td>
<td>2000 vs, 763 sh</td>
<td>( \approx ) 1980 sh</td>
<td>470 w, b</td>
</tr>
<tr>
<td>( \text{ISn(NCS)}_3 )</td>
<td>2058 vs, vb, 794 sh</td>
<td>( \approx ) 1985 sh</td>
<td>760 w</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\( ^a \) At liquid \( \text{N}_2 \) temperature; \( ^b \) vs = very strong, m = medium, w = weak, sh = shoulder; \( ^c \) vb = very broad, b = broad; \( ^\delta \) isomer shift, \( ^\Delta \) = Quadrupole splitting, \( ^\Gamma \) = Half width, Incertitude of the parameters ± 0.03 mms\(^{-1}\).

### Table II. Equilibrium constant of the Reaction:

\[
\text{ISn(NCS)}_3 \cdot \text{I}_2(s) + \text{CS}_2 \rightleftharpoons \text{ISn(NCS)}_3(s) + \text{I}_2(sl)
\]

\( s = \text{solid}, \text{sl} = \text{solution} \)

\( N = \text{number of initial moles of ISn(NCS)}_3 \cdot \text{I}_2 \), \( V = \text{volume of solution (ml), C = I}_2 \) concentration, \( K \): constant calculated from \( K = \frac{V^2}{1000(N - VC)} \).

\( ^a \) s = solid, sl = solution; \( ^b \) N = number of initial moles of \( \text{ISn(NCS)}_3 \cdot \text{I}_2 \), V = volume of solution (ml), C = I\(_2\) concentration, K: constant calculated from K = V\(^2\)/(1000 N - VC).
stant calculated by equation (3) coincides with its average value, within the range of experimental error, which shows that ISn(NCS)$_3$I$_2$ and ISn(NCS)$_3$ form a single phase. The average value of the resulting equilibrium constant, calculated according to bibliography [10], is $K = 2.2 \pm 0.3 \times 10^{-3}$ mol l$^{-1}$.

Because of the low I$_2$ concentrations found, see Table II, the following approximations used in the calculation can be considered reasonable: i) to consider the I$_2$ concentration equal to its activity, ii) to assume that the density of the solutions is equal to that of the pure solvent [11].

During the preparation of ISn(NCS)$_3$I$_2$, according to reaction (1) I$_2$ is liberated. In order to eliminate this I$_2$ two possible methods can be followed: either to wash the solid with solvent or to use a vacuum extraction. In the former case, reaction (2) would take place and hence the purity of the product would be diminished. In the second case, the pressure plays a critical role. In order to quantify this point, it is necessary to know the value of the equilibrium constant of the following reaction:

$$\text{ISn(NCS)}_3\cdot\text{I}_2\text{(s)} \rightleftharpoons \text{ISn(NCS)}_3\text{(s)} + \text{I}_2\text{(g)} \quad (4)$$

which is calculated by means of the following thermodynamic cycle:

$$\begin{align*}
\text{CS}_2 & \\
\text{ISn(NCS)}_3\cdot\text{I}_2\text{(s)} & \rightleftharpoons \text{ISn(NCS)}_3\text{(s)} + \text{I}_2\text{(sl)} \quad K \\
\frac{1}{K_1} & \quad \text{CS}_2 \rightleftharpoons K_3 \\
\text{ISn(NCS)}_3\text{(s)} + \text{I}_2\text{(g)} & \rightleftharpoons \text{ISn(NCS)}_3\text{(s)} + \text{I}_2\text{(s)} \quad K_2
\end{align*}$$

From bibliographic data on the vapour pressure of I$_2$ at 15 °C [12—14] and on I$_2$ solubility in CS$_2$, at the same temperature [15,16], it is found that $K_2 = 7.7 \pm 0.6$ torr$^{-1}$ and $K_3 = 0.67 \pm 0.03$ mol l$^{-1}$, and hence $K_1 = K/K_2K_3 = 4.3 \pm 1.1 \times 10^{-4}$ torr. Given that (4) is a heterogeneous reaction in which the two solid compounds form a single phase, the molar fraction of ISn(NCS)$_3$-I$_2$ in equilibrium can be calculated, depending on the pressure, as indicated in Table III. The most suitable pressure for eliminating any I$_2$ liberated during reaction (1) is around 10$^{-1}$ torr. At higher pressures, the I$_2$ is not eliminated, whose vapour pressure at 15 °C is 0.13 torr [12—14], and at lower pressures the purity of the compound is considerably decreased, see Table III, due to reaction (4) taking place in greater proportion.

### Table III. Molar fraction of ISn(NCS)$_3$-I$_2$ with regard to pressure.

<table>
<thead>
<tr>
<th>Pressure (torr)</th>
<th>10$^{-1}$</th>
<th>10$^{-2}$</th>
<th>10$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar fraction ($\times 100$)</td>
<td>99.6</td>
<td>95.9</td>
<td>69.9</td>
</tr>
</tbody>
</table>

### Experimental

All manipulations were carried out in an inert atmosphere to prevent any hydrolysis of the compounds. SnBr$_4$, SnI$_4$ and (SCN)$_2$ were prepared using previously described methods [17]. Sn and S were determined gravimetrically as SnO$_2$ and BaSO$_4$, respectively. Iodine was determined potentiometrically using AgNO$_3$.

The Mössbauer spectra were obtained with a conventional spectrometer working in constant-acceleration mode. A standard source of Ca$^{119}$SnO$_3$ was used in transmission geometry, filtering the $\gamma$ radiation with a Pd (50 $\mu$m) foil filter. Velocity calibration was performed with the four inner lines of a $\alpha$-Fe foil, using the alternative side of the transducer.

The isomer shifts are referred to BaSnO$_3$ at room temperature. A normal copper sample holder with beryllium windows was immersed in a liquid nitrogen flow cryostat, with the temperature stability better than ±0.5 °K. At least 1 E6 baseline counts were accumulated for each spectrum. Spectra were computed using a constrained non-linear regression program [18], allowing all parameters to vary, except the condition of equal width for each doublet.

The UV-visible spectra were recorded on a Cary Model 17 instrument, using Nujol mulls between NaCl windows.

IR spectra were recorded on a Perkin-Elmer, Model 325, in the range of 4000—200 cm$^{-1}$, using Nujol mulls between CsI windows.

### SnBr$_4$ reaction with (SCN)$_2$

A solution of 5.30 g (12.1 mmol) of SnBr$_4$, recently distilled, in 15 ml of dry CS$_2$, was dropped with constant stirring into a solution of (SCN)$_2$ (150 g, 12.9 mmol) in dry CS$_2$ (30 ml) cooled to −15 °C (ice and common salt). The yellow tone of the (SCN)$_2$ solution is increased. The solution is stirred at room temperature for 24 h without any change being observed. The solvent is eliminated in vacuum, whilst the substance is cooled to −15 °C, and a yellow solid remains. When the compound is allowed to reach room temperature, it polymerises, even below 0 °C, giving rise to red (SCN)$_2$ and releasing SnBr$_4$. If the yellow solid is brought into contact with a CsI crystal (IR windows), the characteristic violet colour of I$_2$
immediately appears. Due to its instability, the yellow solid could not be characterised.

**Preparation of ISn(NCS)$_3$.$I_2$**

The same procedure was carried out as in the previous paragraph, using 2.32 g (20 mmol) of (SCN)$_2$ and 7.95 g (12.7 mmol) of SnI$_4$. The solution immediately turned violet and a solid appeared, which was filtered, quickly washed with CS$_2$ at $-15^\circ$C and vacuum dried. The vacuum (10$^{-1}$ torr) was maintained until no further I$_2$ was released. A brown solid was produced with low yield. The compound rapidly hydrolysed upon contact with the atmosphere; and with carbon sulphide, carbon tetrachloride, benzene, chloroform, nitrobenzene, tetrahydrofurane and acetone it releases I$_2$ and leaves an insoluble residue. The release of the I$_2$ molecule in nitrobenzene is practically quantitative as demonstrated by the cryoscopic measurements: experimental molecular weight = 636 ± 64 (calculated = 674). Point of fusion: decomposes at around 89 $^\circ$C.

C$_3$I$_3$N$_3$S$_3$Sn
Calcd I 56.51 S 14.28 Sn 17.62,
Found I 55.01 S 14.56 Sn 17.60.

1.01 g (1.5 mmol) of ISn(NCS)$_3$.$I_2$ were washed with hot CS$_2$ until the solution no longer contained I$_2$, a yellow hygroscopic solid remained. The yield was practically quantitative. The solid was found to be insoluble in all solvents in which SnI(NCS)$_3$.$I_2$ releases I$_2$. Point of fusion: decomposes at around 135 $^\circ$C.

C$_3$IN$_3$S$_3$Sn
Calcd I 30.23 S 22.91 Sn 28.27,
Found I 29.62 S 23.17 Sn 27.96.

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