Etherate and Pyridine Compounds of Mixed Complex Halo Acids of Indium(III) with Thiocyanate

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Ether, Pyridine, Thiocyanate, Indium

The preparation, for the first time, of ether and pyridine compounds of mixed complex halo acids of indium(III) with thiocyanate is described.

The study of the chemical and physical properties of these acids and the UV and IR spectra of the pyridine compounds are also reported and discussed.

Complex salts of various metals with pseudo-halides (CN\(^-\), SCN\(^-\)) are known as well as the corresponding free acids, for example, H\(_3\)Co(CN)\(_6\), H\(_3\)Cr(SCN)\(_6\) etc. 1-3.

Simple and mixed complex salts of halo acids of indium with organic Lewis bases, of the types H[InX\(_4\)] \(\cdot\) aB and H[InX\(_2\)X'] \(\cdot\) aB, (where X, X' are different halides and B various organic bases such as ether, pyridine, aniline and quinoline) have been prepared and studied4-6. Also mixed complex halo acids of various metals with thiocyanate, among them those of indium, H[InCl\(_3\)] \(\cdot\) 2 Et\(_2\)O and H[InBr\(_3\)]SCN \(\cdot\) 2 Et\(_2\)O, have been prepared7.

In the present work the preparation and study of ether and pyridine compounds of mixed complex haloacids of indium(III) with thiocyanate are reported.

I. Preparation of the etherate mixed complex haloacid H[InI\(_3\)]SCN \(\cdot\) 4 Et\(_2\)O

This compound was prepared, by a method analogous to that of etherohalogenosis8, as follows:

Anhydrous salts of KSCN and KHSO\(_4\) in powder form were placed in ether containing traces of moisture. By the reaction of these salts hydrogen thiocyanide is produced and in this way hydrothiocyanic ether is formed. The traces of moisture are needed for the formation of a concentrated solution on the surface of the salt crystals, thus aiding the start and satisfactory yield of the formation of HSCN.

The hydrothiocyanic ether was kept at 0–5 °C for 24–48 h, to prevent decomposition and polymerization of HSCN. To this ether was added chemically pure, anhydrous InI\(_3\). A vigorous reaction took place with a simultaneous red-brown coloration of the ether solution. At the end of the reaction and after removal of the excess ether by pumping, a liquid was obtained of oily nature and density ca. 1.8 g \(\cdot\) cm\(^{-3}\). For the identification of this product it was decomposed by water in a closed flask yielding a solution of hydrogen ions, cationic indium, iodide and thiocyanate ions and ether.

The hydrogen ion was determined potentiometrically using a pH-meter model 26, Radiometer, Copenhagen, and glass and calomel electrodes. Indium was determined gravimetrically with hydroxyquinoline. The sum of iodide and thiocyanate was determined by potentiometric titration with a solution 0.1 N AgNO\(_3\) using a Corning potentiometer, model 12, and sulfide and calomel electrodes. This determination was verified by the Volhard method. The amount of ether was calculated by difference of weight.

The results of the analysis are given in the Table I.

Table I. Results of the analysis.

<table>
<thead>
<tr>
<th>Formula</th>
<th>Color</th>
<th>H:In:I:SCN:Et(_2)O</th>
</tr>
</thead>
<tbody>
<tr>
<td>H[InI(_3)]Scn (\cdot) 4 Et(_2)O</td>
<td>Red-brown</td>
<td>1.00:1.13:3.02:1.00:3.90</td>
</tr>
</tbody>
</table>

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II. Preparation of compounds of the formula

\[ H[InX_3SCN] \cdot 4 \text{Pyr} \]

(where \( X = \text{Cl}, \text{Br}, \text{I} \) and \( \text{Pyr} = \text{pyridine} \))

The pyridine compounds were prepared by reacting pure pyridine with freshly prepared etherate complex halo acid and simultaneous replacement of the ether molecules by pyridine. The reaction is vigorous and exothermic. The excess of pyridine was removed from the compounds by placing them in a vacuum desiccator over concentrated sulfuric acid and intermittent pumping. The crystalline compounds thus obtained had the odor of pyridine, were insoluble in water and nonpolar solvents but soluble in acetone, dimethylsulfoxide, acetic acid, and dilute (2N) nitric acid.

The compounds were analyzed as follows:

Hydrogen was determined by dissolving a definite amount of the compound in dimethylsulfoxide and titrating potentiometrically with a 0.1 N NaOH solution. The analysis was checked by conductometric measurements.

Indium was determined by dissolving the compounds in 2 N CH₃COOH and precipitating indium with 8-hydroxyquinoline.

Pyridine was determined by dissolving the compounds in glacial acetic acid and titrating potentiometrically with a 0.1 N HCIO₄ solution using glass and calomel electrodes. To the test solution a small amount of mercuric acetate had been added and in the calomel electrode the saturated KCl solution was replaced by a methanolic one.

The sum of the halide and thiocyanate ions in each compound was determined potentiometrically as well as by the Volhard method, the solvent being dilute (2 N) nitric acid. The determination of thiocyanate in the presence of chloride was done with KIO₃ by the Andrews method. The determination of bromide in the presence of thiocyanate was done by dissolving the compound in sulfuric acid and adding a strong oxidizing agent (i.e., K₂Cr₂O₇ or KMnO₄).

By heating then the above mixture in a distillation apparatus the thiocyanate ions are oxidized to HCN (or other products) collected in a NaOH trap, while the bromide ions are oxidized to elemental bromine which, by distillation, is collected in a vessel containing an excess of KI solution and the liberated iodine is titrated with a 0.1 N Na₂S₂O₃ solution in the presence of starch or carbon tetrachloride. The results of these analyses are shown in Table II.

III. Analysis of IR and UV spectra of the pyridine compounds

The IR spectra of the pyridine compounds were obtained with a Perkin-Elmer, model 577 spectrophotometer with the sample in the form of KBr pellets. The IR spectrum shows absorption bands in the region 3220–2850 cm⁻¹, at 2070, 1630, 1605, 1535, 1475, 1445, 1327 cm⁻¹, in the region 1400 to 1050 cm⁻¹, at 875, 695 cm⁻¹ in the region 1050 to 600 cm⁻¹ and at 425 cm⁻¹. In addition, the compound H[InCl₃SCN] · 4 Pyr gives an absorption band at 275 cm⁻¹.

Table II. Results of the analysis.

<table>
<thead>
<tr>
<th>Formula</th>
<th>Color</th>
<th>Mole ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( H : \text{In} : \text{X} : \text{SCN} : \text{Pyr} )</td>
</tr>
<tr>
<td>H(InCl₃SCN) · 4 Pyr</td>
<td>Rose</td>
<td>1.05 : 1.00 : 3.01 : 1.00 : 4.05</td>
</tr>
<tr>
<td>H(InBr₃SCN) · 4 Pyr</td>
<td>Cream</td>
<td>1.00 : 1.10 : 3.05 : 1.00 : 4.02</td>
</tr>
<tr>
<td>H(InI₃SCN) · 4 Pyr</td>
<td>Brown</td>
<td>1.00 : 1.13 : 3.07 : 1.00 : 3.98</td>
</tr>
</tbody>
</table>

\( \text{X} = \text{Cl}, \text{Br}, \text{I} \) and \( \text{Pyr} = \text{pyridine} \).
Table III. Values of the extinction coefficients.

<table>
<thead>
<tr>
<th>λ (nm)</th>
<th>H(InCl₃SCN) · 4 Pyr</th>
<th>Values of $\epsilon$ (mole⁻¹ cm⁻¹)</th>
<th>H(InBr₃SCN) · 4 Pyr</th>
<th>H(InI₃SCN) · 4 Pyr</th>
</tr>
</thead>
<tbody>
<tr>
<td>242</td>
<td>12,206</td>
<td>8,850</td>
<td></td>
<td></td>
</tr>
<tr>
<td>246</td>
<td>13,809</td>
<td>9,832</td>
<td>17,394</td>
<td></td>
</tr>
<tr>
<td>252</td>
<td>15,368</td>
<td>10,890</td>
<td>18,810</td>
<td></td>
</tr>
<tr>
<td>258</td>
<td>15,706</td>
<td>11,211</td>
<td>19,802</td>
<td></td>
</tr>
<tr>
<td>264</td>
<td>12,206</td>
<td>8,789</td>
<td>18,300</td>
<td></td>
</tr>
</tbody>
</table>

symmetric stretching vibration (commonly referred as $\nu$CN)\textsuperscript{15}.

The absorption band at 695 cm\textsuperscript{-1} is assigned to C–S stretching frequency and shows a Me–S bond\textsuperscript{16}.

The absorption band at 425 cm\textsuperscript{-1} is assigned to NCS bending vibration and shows S-bonded thiocyanate complex, thus excluding a N-bonded thiocyanate complex\textsuperscript{17}.

The band at 878 cm\textsuperscript{-1} is the first overtone of $\delta$(NCS)\textsuperscript{18}. Finally, the absorption band at 275 cm\textsuperscript{-1} in the spectrum of $\text{H[InCl}_3\text{SCN]}$ · 4 Pyr is probably due to the In–Cl-bond.

The UV spectra of the pyridine compounds were taken with an OPTICA CF 4R UV spectrophotometer in the region 220–320 nm, using solutions of these compounds in absolute ethanol and in concentrations of the order 10\textsuperscript{-5} M. The spectra show absorption maxima at 242, 246, 252, 258 and 264 nm. The values of the extinction coefficients, $\epsilon$, for all the compounds are shown on Table III.

The observed absorption maxima belong to pyridine and are due to $\pi$-$\pi^*$ electronic transition\textsuperscript{19} which is the known benzenoid absorption; it appears at 260 nm and splits in the 238, 239, 246, 251, 258 and 264 nm when the spectrum of pyridine is taken in ethanol\textsuperscript{20}. The rather high values of $\epsilon$ for these compounds as compared to the corresponding ones of pyridine and the slight shifts of the absorption maxima suggest complexation.

On the basis of the analysis, IR and UV spectra the following structure for these compounds is proposed.

$$\text{[InX}_3\text{SCN(Pyr)]}_2^+ - \text{[Pyr} ... \text{H} ... \text{Pyr}]^+$$

where the negatively charged group constitutes the inner sphere of the complex while in the outer sphere the two remaining molecules of pyridine form a hydrogen bridge with their nitrogen atoms and the hydrogen ion. To the anion an octahedral structure is assigned since it is known that indium-(III) shows a great tendency of forming octahedral complexes.

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