Metal Derivatives of Antimony Thiocarboxylates: Part III-Complexes of Silver(I), Thallium(I), Aluminium(III), Chromium(III), Iron(III), Oxozirconium (IV) & Thorium(IV) with Antimony Hydrogen Bis(thioiglycollate)

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Complexes of Ag(I), TI(I), Al(III), Cr(III), Fe(III), oxozirconium (IV) and Th(IV) with antimony hydrogen bis(thioiglycollate) have been prepared and characterized on the basis of elemental analyses, infrared (far and near) and electronic spectral data and magnetic susceptibility measurements. The carboxylate group has been suggested to be bidentate and bridging in the complexes. The formation constants of Al(III) and Cr(III) complexes have also been determined potentiometrically.

In continuation of our studies on the metal derivatives of antimony thiocarboxylates1-4, we report here the syntheses and characterization of the complexes of antimony hydrogen bis(thioiglycollate) with Ag(I), TI(I), Al(III), Cr(III), Fe(III), oxozirconium(IV) and Th(IV). Formation constants of Al(III) and Cr(III) complexes have also been calculated.

All the chemicals used in the present investigation were of AR grade. The ligand, antimony hydrogen bis(thioiglycollate), was prepared and purified according to known methods8-8.

For the formation constant studies, the solutions of metal nitrates (AR grade) were prepared in doubly distilled water. The solutions of the ligand, antimony hydrogen bis(thioiglycollate) and sodium perchlorate (Riedel) were prepared by dissolving the requisite quantities in conductivity water.

Preparation of the complexes—To a hot aqueous solution of the ligand was added slowly and with constant stirring, an aqueous solution of metal ion. A precipitate was obtained on mixing which was filtered immediately and washed successively with hot water, ethanol and ether. It was then dried in vacuo at 60°.

In case of TI(I), Al(III) and Cr(III) complexes, 0.1N NaOH solution of the ligand was used for the precipitation of the complexes.

IR spectra (4000-250 cm⁻¹) were recorded in nujol on a Beckman IR-20 spectrophotometer. Magnetic susceptibility measurements were carried out on a Gouy balance. The diffused reflectance spectra were recorded on SP-700 ultraviolet and visible spectrophotometer using MgO as the reference.

A Philips pH meter (PR 9405 M) with a glass calomel electrode assembly was used, calibrating it as usual1-2.

The stoichiometries of the complexes have been established on the basis of elemental analyses (Table 1). The complexes are insoluble in common polar and non-polar organic solvents and do not melt even up to 300°C.

IR spectra of the complexes showed the presence of νas COO and νs COO in the region 1560-1540 and 1380-1360 cm⁻¹ respectively showing a decrease in frequency by 175-195 cm⁻¹ compared with the positions in the free ligand. This decrease suggests that the ligand acts as a bridging chelating ligand in which both the oxygen atoms of the carboxylate group take part in coordination9. The asymmetric bidentate bridging nature of the carboxylate group in the present complexes is consistent with the results obtained in the case of CaCu(OAc)₄.6H₂O10 (Δν = 180 cm⁻¹).

The zirconium complex shows a sharp band around 890 cm⁻¹ due to νZr = O mode. It was suggested by Komissarova et al.9 that the bridging Zr=O-Zr groups should absorb below 900 cm⁻¹ and they observed a band around 850 cm⁻¹ for Zr-O-Zr group in zirconyl acetate.

Bands at 575, 542, 450 and 362 cm⁻¹ in the spectra of aluminium complex could be assigned to νAl-O bond11 while a medium sharp band at 475 cm⁻¹ in the iron(III) complex is probably due to νFe - O11.

The magnetic susceptibility measurements indicated the Ag(I), TI(I), Al(III), OZr(IV) and Th(IV) complexes to be diamagnetic. The diffused reflectance spectrum of the Th(IV) complex did not show any band in the visible region. These complexes are highly insoluble in common solvents. Therefore, on the basis of elemental analyses, IR data, diamagnetism and insolubility of the complexes, a polymeric structure could be assigned to these complexes12.

The magnetic moment of the Cr(III) complex was found to be 3.86 B.M. corresponding to three unpair-

<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour</th>
<th>Found(Calc.), %</th>
</tr>
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<tbody>
<tr>
<td>[Ag(C₃H₅O₃S₂Sb)]</td>
<td>Pale-yellow</td>
<td>27.46 (12.73)</td>
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<tr>
<td></td>
<td></td>
<td>26.32 (11.72)</td>
</tr>
<tr>
<td>[TI(C₃H₅O₃S₂Sb)]</td>
<td>Light-yellow</td>
<td>31.25 (18.67)</td>
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<tr>
<td></td>
<td></td>
<td>58.15 (9.48)</td>
</tr>
<tr>
<td>[Cr(C₃H₅O₃S₂Sb)]</td>
<td>Light-blue</td>
<td>5.28 (15.18)</td>
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<tr>
<td></td>
<td></td>
<td>5.38 (15.18)</td>
</tr>
<tr>
<td>[Fe(C₃H₅O₃S₂Sb)]</td>
<td>Light-yellow</td>
<td>6.02 (13.94)</td>
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<tr>
<td></td>
<td></td>
<td>6.42 (13.94)</td>
</tr>
<tr>
<td>[Al(C₃H₅O₃S₂Sb)]</td>
<td>white</td>
<td>2.31 (14.81)</td>
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<tr>
<td></td>
<td></td>
<td>2.31 (14.81)</td>
</tr>
<tr>
<td>[ZrO(C₃H₅O₃S₂Sb)]</td>
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<td>13.71 (12.89)</td>
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<td></td>
<td>12.80 (13.40)</td>
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<tr>
<td>[Th(C₃H₅O₃S₂Sb)]</td>
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<td>17.43 (13.00)</td>
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<td></td>
<td></td>
<td>16.14 (13.36)</td>
</tr>
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</table>

Table 1—Analytical Data of the Complexes

Metal C H
ed electrons within the expected range of octahedral Cr(III) complexes. The electronic spectrum of Cr(III) complex showed bands at 710, 475 and 370 nm. The spectrum is typical of octahedral coordination. Thus, on the basis of above facts, octahedral polymeric structure could be proposed for the Cr(III) complex.

Low magnetic moment of Fe(III) complex (3.60 B.M.) suggested spin-spin coupling between unpaired electrons of the neighboring iron atoms. Polynuclear Fe(III) complexes have been reported to have similar \( \mu_{\text{eff.}} \) values (3.65-4.43 B.M.). The electronic spectrum of Fe(III) complex showed three bands at 680, 590 and 360 nm which could be attributed to the transitions, \( A_{1g} \rightarrow 4T_{1g}(^4G) \), \( A_{1g} \rightarrow 4T_{2g}(^4P) \) and \( A_{1g} \rightarrow 4T_{2g}(^4D) \) respectively. Thus, the analytical data, insolubility, high m.p., magnetic moment, electronic spectrum and the presence of bridging carboxylate groups suggested an octahedral structure for the iron(III) complex.

Formation constants of the Al(III) and Cr(III) complexes—The formation constants have been determined using Calvin-Bjerrum pH titration technique as modified by Irving and Rossotti. The dissociation constant of the ligand antimony (III) against CO was determined by the technique as modified by Irving and Rossotti. Formation constants of the complexes with other metal ions as precipitation started from the very beginning.

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References