

## FORMATION OF ANTIMONITES AND THIOANTIMONITES OF COBALT AS A FUNCTION OF pH

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■ **ABSTRACT:** The precise nature of the reaction of cobalt chloride with antimonite anions (pH 11.4 and 8.1) and thioantimonite anions (pH 1.0, 8.9 and 6.8) have been investigated by means of electrometric techniques involving pH and conductometric titrations. The well-defined breaks and inflections in the titration curves provide cogent evidence for the formation of ortho-antimonite ( $3\text{CoO}\cdot\text{Sb}_2\text{O}_3$ ), ortho-thioantimonite ( $3\text{CoS}\cdot\text{Sb}_2\text{S}_3$ ) and pyro-thioantimonite ( $2\text{CoS}\cdot\text{Sb}_2\text{S}_3$ ) of cobalt in the vicinity of pH 7.6, 7.9 and 6.5, respectively. Analytical investigations of the compounds have also been carried out which substantiate the results of the electrometric study.

■ **KEYWORDS:** Antimonites; thioantimonites; cobalt; electrometric study.

### Introduction

Antimony is not used in industry in the unalloyed state to any extent. Its main use in the metallic state is as a constituent of many alloys, to which it imparts certain desired properties, such as expansion on solidification, increased hardness, and corrosion resistance.<sup>4</sup> The electrodeposition of antimony alloys employ antimonites and thioantimonites in alkaline media.<sup>14,15</sup> The electrodeposits of antimony alloys are generally brittle and stressed and do not adhere well to the metal basis. So far the baths developed have very little practical applications. The properties of antimony and its cheapness would perhaps make electrodeposited antimony very useful, if a reasonably satisfactory plating baths were developed. The problem in the electrodeposition bath seems to be due to complicated aqueous solution chemistry of antimony. The anionic species of antimony change with the pH of the bath.

The problems in electrodeposition baths of antimony alloys and insufficient data on the chemistry of oxy- and thioanionic compounds of Sb(III) lead the author to

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investigate them. It should, however, be noted that the interest in the chemistry of ternary compounds of antimony is recently increasing due to their probable use as semiconductors.<sup>2</sup>

The chemistry of antimony is complicated.<sup>5,17</sup> A variety of simple and complex antimonites are obtainable.<sup>18</sup> Because of the weakness of the acidic properties of antimony sesquioxide, the sesquioxide antimonites are subject to extensive hydrolysis in aqueous solutions.<sup>18</sup> It has also been reported<sup>13</sup> that investigations on antimony are made difficult by the fact that sometimes it appears as Sb(III) and as Sb(V) in the same compound. The antimony compounds are formally similar, but because of the tendency of antimony to form five or six bonds, the species in aqueous solutions of similar arsenic and antimony compounds may be different.<sup>1</sup>

In earlier publications, the results on different thioanion formation of W(VI), As(III)<sup>8</sup> and Sb(III),<sup>11</sup> and the formation and composition of antimonates and thioantimonates of uranyl<sup>19</sup> and cadmium<sup>10</sup> have been reported. In view of the interesting results obtained, it was considered worthwhile to realize similar investigations on the reaction between cobalt(II) and different antimonite<sup>12</sup> and thioantimonite anions.<sup>11</sup>

## Material and methods

Merck's extra-pure reagents,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{SbCl}_3$ ,  $\text{KOH}$ ,  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  and hydrochloric acid were used, and the solutions were prepared in fresh distilled water. The sodium ortho-thioantimonite,  $\text{Na}_3\text{SbS}_3$ , solution was prepared by digesting carefully one mole of a synthesized sample of  $\text{Sb}_2\text{S}_3$  with three moles of  $\text{Na}_2\text{S}$ . The concentration of the stock solution was further checked by determining antimony as sulfide<sup>19a</sup> and sulfur by wet process.<sup>19b</sup> The pH variations of the thioantimonite solution were made by gradual addition of hydrochloric acid.<sup>11</sup> Similarly, potassium ortho-antimonite,  $\text{K}_3\text{SbO}_3$ , was prepared by digesting a synthesized sample of  $\text{Sb}_2\text{O}_3$  with the required amount of  $\text{KOH}$ . Dilute hydrochloric acid was used for pH variation of the ortho-antimonite solution.<sup>12</sup>

The pH measurements were carried out by using a Metrohm Herisau (Switzerland) pH-meter and Schott Gerate glass combination electrode. The conductance of the solutions were measured by employing a Metrohm conductometer Mod. E518 and a titration cell Mod. E645. 25 ml of titre solution was taken in the cell each time and thermostated at  $25 \pm 0.1^\circ\text{C}$ . Using different concentrations of the reactants, a series of glass electrode and conductometric titrations was performed. Observed pH changes were plotted as a function of the volume of the titrant added. The inflections obtained by the curves were confirmed by the pronounced maxima in  $\text{d}^2\text{pH}/\text{dV}^2$  and zero in  $\text{d}^3\text{pH}/\text{dV}^3$  graphs. Differential plots of only one system (Figures 1 and 2, curves F and G) are given for the sake of brevity. The end-point in conductometric titrations

were located graphically. Only a limited number of experimental points are shown in the curves to maintain legibility and to avoid overlapping. The electrometric titration results on the formation of antimonites and thioantimonites of cobalt are summarized in Table 1.

Table 1 - Summary of results of electrometric titrations. Volume of titre solution taken in the cell = 25 ml

Molarity of solutions	Equivalence points (ml)			Formula supported			
	Calculated from	Observed from	Conductance				
CoCl <sub>2</sub>	K <sub>3</sub> SbO <sub>3</sub>	Direct titrations	Figures 1 and 2	curve 1			
			M/60		2.25	2.25	3CoO.Sb <sub>2</sub> O <sub>3</sub>
			M/80		2.00	1.98	
			M/2000		1.88	1.85	
CoCl <sub>2</sub>	M/1000	Reverse titrations	Figures 1 and 2	curve 2			
			M/8000		2.78	2.80	3CoO.Sb <sub>2</sub> O <sub>3</sub>
			M/1250		2.60	2.65	
			M/1500		2.78	2.78	
CoCl <sub>2</sub>	Na <sub>3</sub> SbS <sub>3</sub>	Direct titrations	Figures 3 and 4	curve 1			
			M/20		1.88	1.85	3CoS.Sb <sub>2</sub> S <sub>3</sub>
			M/30		2.25	2.20	
			M/900		2.08	2.10	
CoCl <sub>2</sub>	M/20	Reverse titrations	Figures 3 and 4	curve 2			
			M/160		2.08	2.10	3CoS.Sb <sub>2</sub> S <sub>3</sub>
			M/250		2.00	2.00	
			M/350		2.38	2.35	
CoCl <sub>2</sub>	Na <sub>4</sub> Sb <sub>2</sub> S <sub>5</sub>	Direct titrations	Figure 5	curve 1			
			M/20		2.00	2.00	2CoS.Sb <sub>2</sub> S <sub>3</sub>
			M/30		1.88	1.86	
			M/1000		2.50	2.50	
CoCl <sub>2</sub>	M/40	Reverse titrations	Figure 5	curve 2			
			M/250		2.00	2.00	2CoS.Sb <sub>2</sub> S <sub>3</sub>
			M/350		2.14	2.15	
			M/450		2.22	2.25	

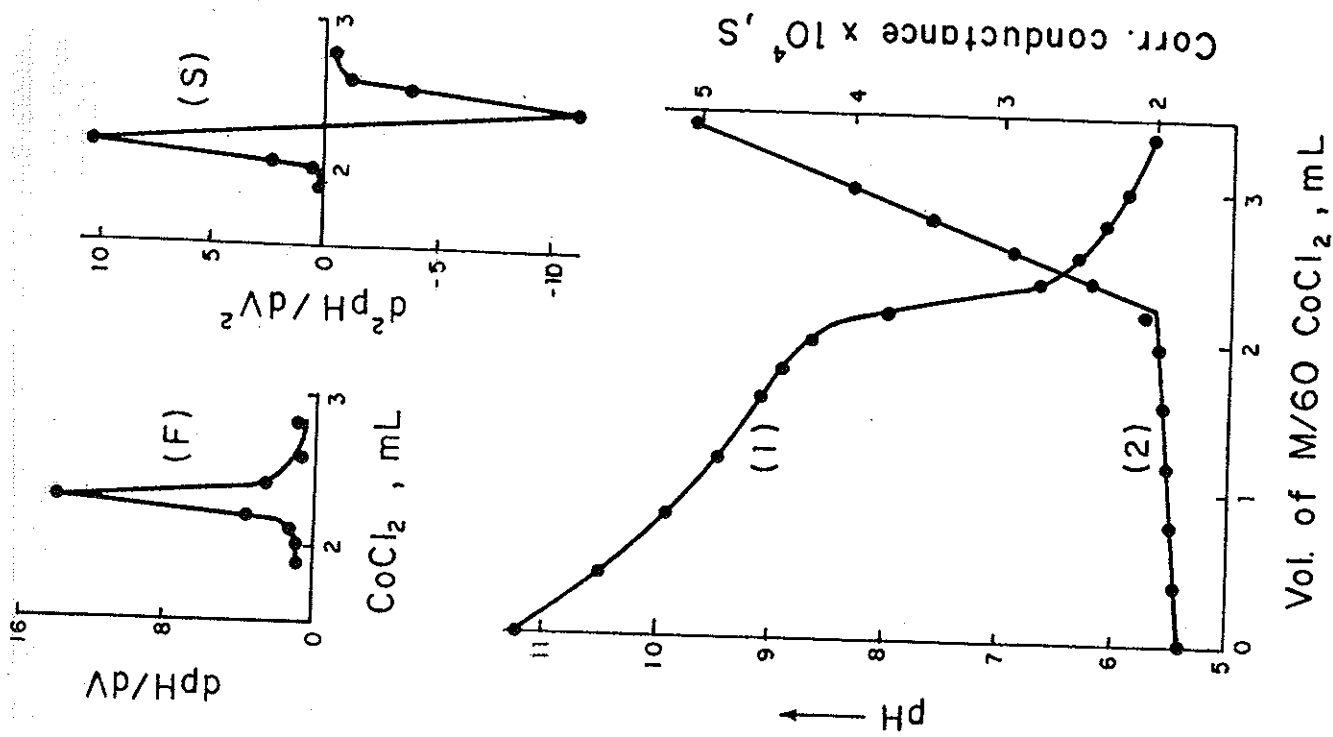


FIGURE 1 - Direct titrations of ortho-antimonite (M/60  $\text{CoCl}_2$  vs. M/1000  $\text{K}_3\text{SbO}_3$ ), (1) pH; (2) conductometric; (F) first derivative; and (S) second derivative.

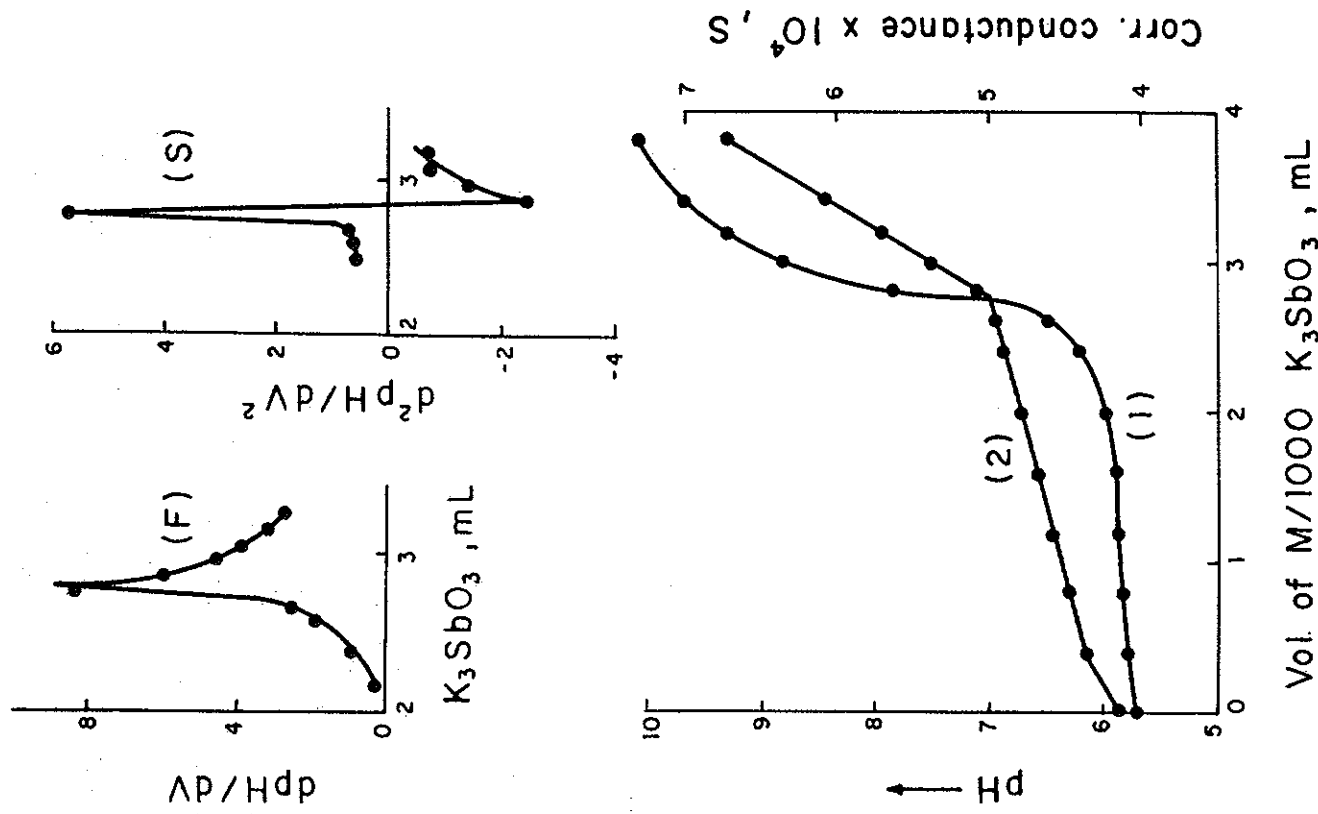


FIGURE 2 - Reverse titrations of ortho-antimonite (M/1000  $\text{K}_3\text{SbO}_3$  vs. M/60000  $\text{CoCl}_2$ ), (1) pH; (2) conductometric; (F) first derivative; and (S) second derivative.

The precipitates obtained at the end-points of the titrations were also analyzed to substantiate the electrometric results. The different thioantimonites of cobalt were prepared by mixing stoichiometric amount of cobalt chloride solution with the respective sodium thioantimonite solution. Similarly the cobalt ortho-antimonite was precipitated by interaction of cobalt chloride with potassium ortho-antimonite. The precipitates obtained were washed several times with aqueous ethanolic 10% (v/v) solution and dried completely in vacuum desiccator. A known amount (2 g) of each of these dried precipitates was digested with conc. HNO<sub>3</sub> (15 ml) to dryness on a steam bath. The treatment was repeated twice. The residue was dissolved in minimum quantity of hydrochloric acid and then antimony was determined as sulfide<sup>18a</sup> and cobalt as anthranilate.<sup>18c</sup> Sulfur in the cobalt thioantimonites was determined gravimetrically by wet process.<sup>18b</sup> The results are shown in Table 2.

Table 2 - Summary of analytical results of the precipitates

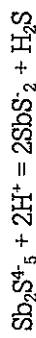
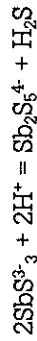
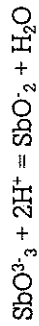
Proposed formula of the compound	Mode of synthesis	Analysis %: Found (Calculated)		
		Co	Sb	S
3CoO.Sb <sub>2</sub> O <sub>3</sub>	Analysis of the ortho-antimonite precipitates			
	Direct*	34.27(34.24)	47.12(47.16)	
-	Reverse**	34.22	47.19	
	Analysis of the ortho-thioantimonite precipitates			
3CoS.Sb <sub>2</sub> S <sub>3</sub>	Direct	28.90(28.86)	39.71(39.74)	31.38(31.40)
	Reverse	28.83	39.76	31.44
2CoS.Sb <sub>2</sub> S <sub>3</sub>	Analysis of the pyro-thioantimonite precipitates			
	Direct	22.61(22.59)	46.63(46.66)	30.70(30.73)
	Reverse	22.56	46.70	30.77

\* Direct - cobalt chloride solution added to potassium ortho-antimonite solution.

\*\* Reverse - potassium ortho-antimonite solution added to cobalt chloride solution.

## Results and discussion

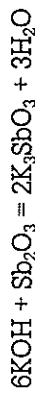
A recent study by the author on acidification of alkali metal antimonites<sup>13</sup> and thioantimonites<sup>11,12</sup> shows the existence of two different antimonite (SbO<sub>3</sub><sup>3-</sup>, SbO<sub>2</sub>) and three thioantimonite (SbS<sub>3</sub><sup>3-</sup>, Sb<sub>2</sub>S<sub>5</sub><sup>4-</sup>, SbS<sub>2</sub><sup>2-</sup>) species. The stepwise formation of these anions by gradual addition of acid to the ortho form may be represented as follows:



The non-existence of Sb<sub>2</sub>O<sub>6</sub><sup>4-</sup> corresponding to Sb<sub>2</sub>S<sub>5</sub><sup>4-</sup> is in agreement with the results reported by Ferrin.<sup>6</sup>

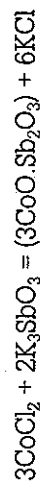
## Cobalt antimonites

The solution of potassium ortho-antimonite (pH 11.4) was prepared by digesting carefully a synthesized sample of Sb<sub>2</sub>O<sub>3</sub> in a solution of KOH of required strength.



Potassium meta-antimonite (pH 8.1) was prepared by addition of hydrochloric acid to potassium ortho-antimonite solution in the molar ratio 2:1.

The pH and conductometric investigations of the reaction between the solution of cobalt chloride and potassium ortho-antimonite are illustrated in Figures 1 and 2. An examination of the results of these titrations reveals that the reaction can be successfully followed by using either of the reactants as titrant (Table 1). In the direct pH titrations (Figure 1, curve 1), when cobalt chloride solution (pH 5.5) was added from the microburette to K<sub>3</sub>SbO<sub>3</sub> solution (pH 11.4) in the cell, the pH of the latter shows gradual decrease with a marked downward jump in pH at the stoichiometric end-point, which corresponds to the formation and precipitation of cobalt ortho-antimonite, 3CoO.Sb<sub>2</sub>O<sub>3</sub>, in the vicinity of pH 7.6. In case of inverse titrations (Figure 2, curve 1), when K<sub>3</sub>SbO<sub>3</sub> solution was used as titrant, a sharp upward jump in pH was observed at 3:2 molar ratio of Co<sup>2+</sup>:SbO<sub>3</sub><sup>3-</sup>, confirming the formation of the same compound, cobalt ortho-antimonite, in accordance with the following equation:



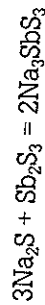
The inflections obtained by the pH titration curves were further confirmed by the pronounced maxima in dpH/dV and zero in d<sup>2</sup>pH/dV<sup>2</sup> graphs (Figures 1 and 2, curves F and S).

Conductometric titrations between the solutions of cobalt chloride and potassium ortho-antimonite (Figures 1 and 2, curve 2) provide well-defined breaks at the stoichiometric point for the formation of cobalt ortho-antimonite, confirming the formation of the same compound as indicated by the pH study.

The electrometric titrations between cobalt chloride and potassium meta-anthimonite failed to give any dependable results. This may be ascribed to the soluble nature of the product, the small difference in pH values of the reactants and the presence of potassium chloride in appreciable amounts, preventing the occurrence of a break in titration curves.

### Cobalt thioantimonites

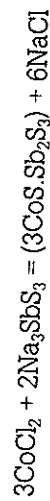
The solution of sodium ortho-thioantimonite (pH 12.0) was prepared by digesting analyzed sample of antimony trisulfide in sodium sulfide solution of required strength.



Sodium pyro-thioantimonite (pH 8.9) and meta-thioantimonite (pH 6.8) were prepared by progressive additions of hydrochloric acid to sodium ortho-thioantimonite solutions in the molar ratios 1:1 and 2:1, respectively.<sup>11</sup>

Figures 3 and 4 illustrate the curves of the pH and conductometric titrations performed between the solutions of sodium ortho-thioantimonite and cobalt chloride. In the direct titrations (Figure 3, curve 1), when cobalt chloride solution (pH 5.5) was added from the microburette to the alkali ortho-thioantimonite solution (pH 12.0), a sharp fall in pH was noted with an inflection at the molar ratio of  $\text{Co}^{2+}:\text{SbS}_3^{3-}$  as 3:2 in the vicinity of pH 7.9, corresponding to the stoichiometry for the formation of cobalt ortho-thioantimonite,  $3\text{CoS}\cdot\text{Sb}_2\text{S}_3$ .

In reverse titrations (Figure 4, curve 1), when  $\text{Na}_3\text{SbS}_3$  solution was added to the cobalt chloride solution, the pH first increased very slowly, but at the end-point it gave a jump corresponding to the formation of the same compound in accordance with the following equation:



Employing similar concentrations of the reactants, both direct (Figure 3, curve 2) and reverse (Figure 4, curve 2) conductometric titration between cobalt chloride and sodium ortho-thioantimonite gave well-defined breaks at 3:2 molar ratio of  $\text{Co}^{2+}:\text{SbS}_3^{3-}$ , confirming the formation of cobalt ortho-thioantimonite. In direct titrations, when cobalt chloride solution was added from the microburette to the solution of alkali ortho-thioantimonite, a decrease in conductance was observed (due to removal of  $\text{SbS}_3^{3-}$  ion in the form of precipitate) till the stoichiometric end-point after which conductance increased with the increase in ionic concentration. In case of reverse titrations, as comparatively more mobile sodium ions are introduced in the cell, the conductance values show a gradual increase from the very beginning.

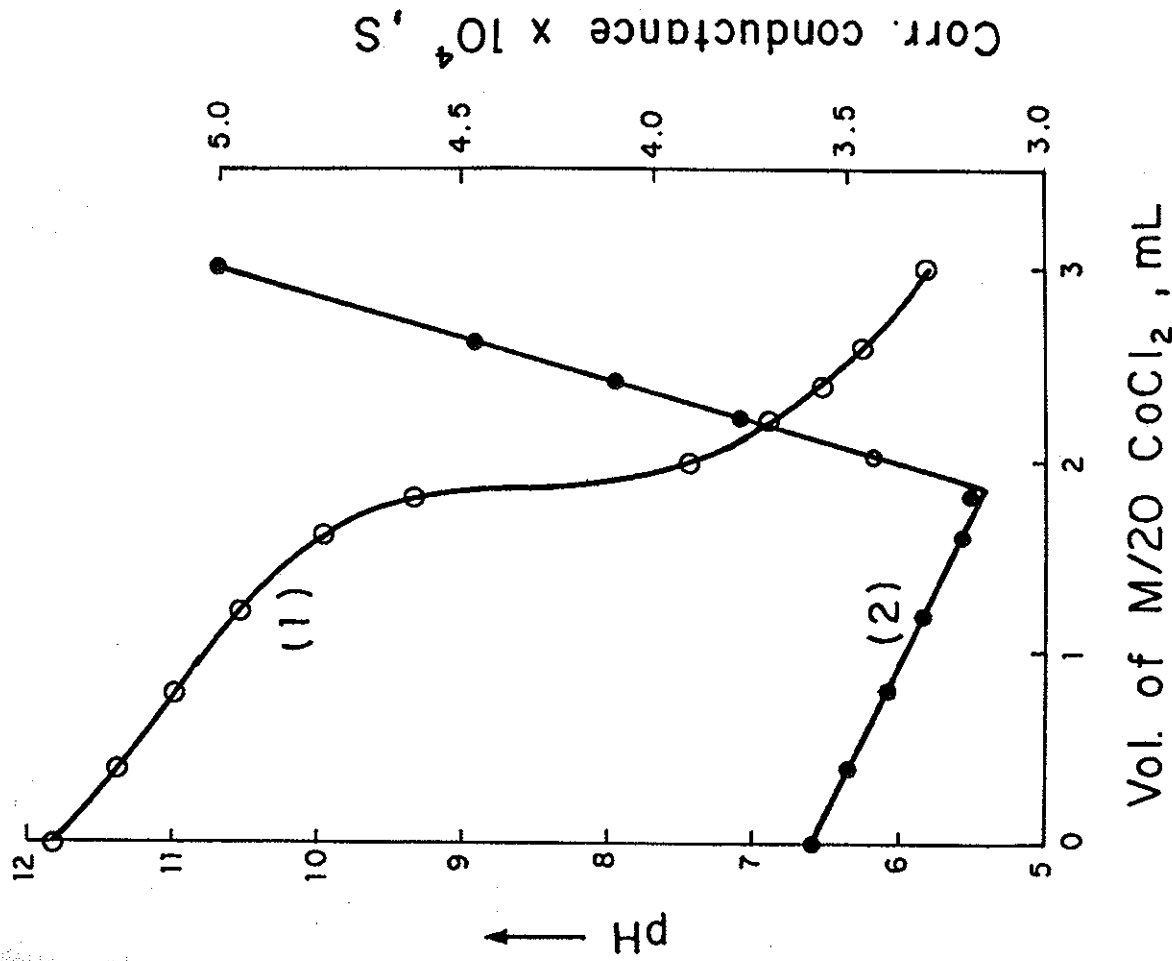


FIGURE 3 - Direct titrations of ortho-thioantimonite (M/20 CoCl<sub>2</sub> vs. M/400 Na<sub>3</sub>SbS<sub>3</sub>). (1) pH; (2) conductometric.

Figure 5 illustrates the changes occurring in conductance values when the titration between the solutions of cobalt chloride and sodium pyro-thioantimonite are performed. The direct (curve 1) and reverse (curve 2) titration curves provide well-defined breaks at the point where the molar ratio of  $\text{Co}^{2+}:\text{Sb}_2\text{S}_5^{4-}$  is 2:1, which corresponds to the stoichiometry for the formation of  $2\text{CoS} \cdot \text{Sb}_2\text{S}_3$  in the neighbourhood of pH 6.5 (Table 1). The reaction can be represented by the following equation:

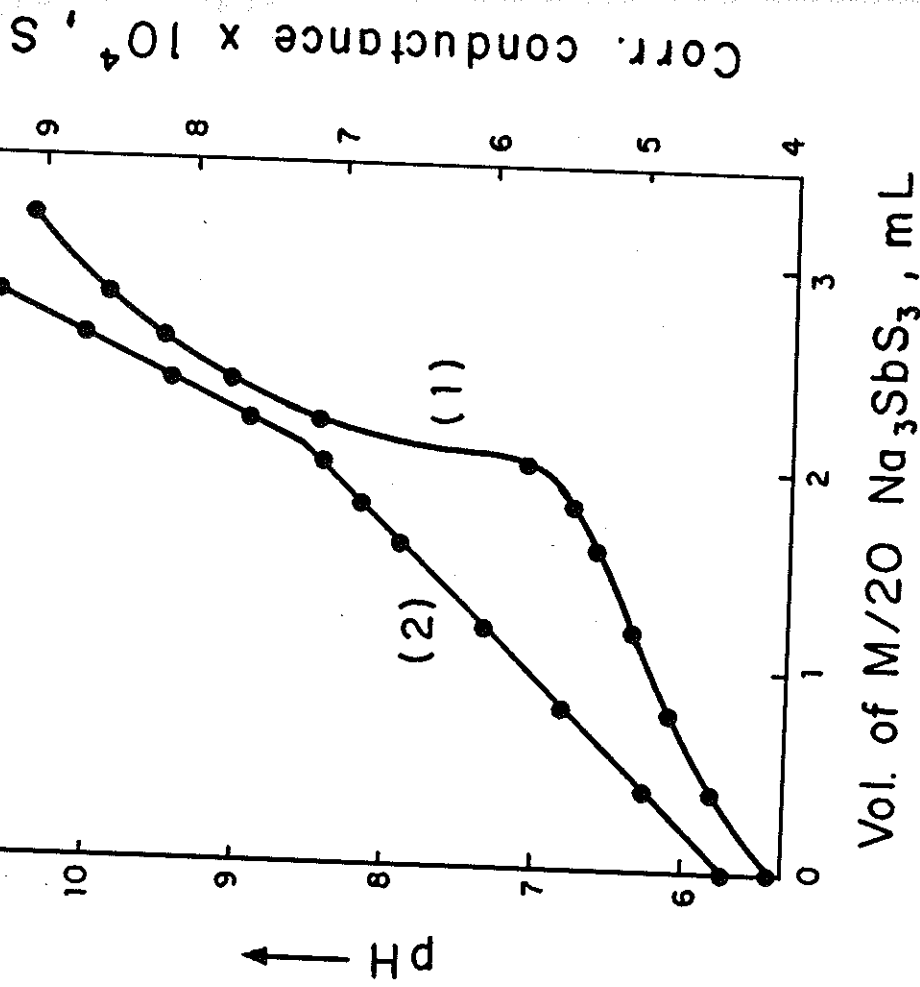


FIGURE 4 - Reverse titrations of ortho-thioantimonite (M/20  $\text{Na}_3\text{SbS}_3$  vs. M/160  $\text{CoCl}_2$ ). (1) pH; (2) conductometric.

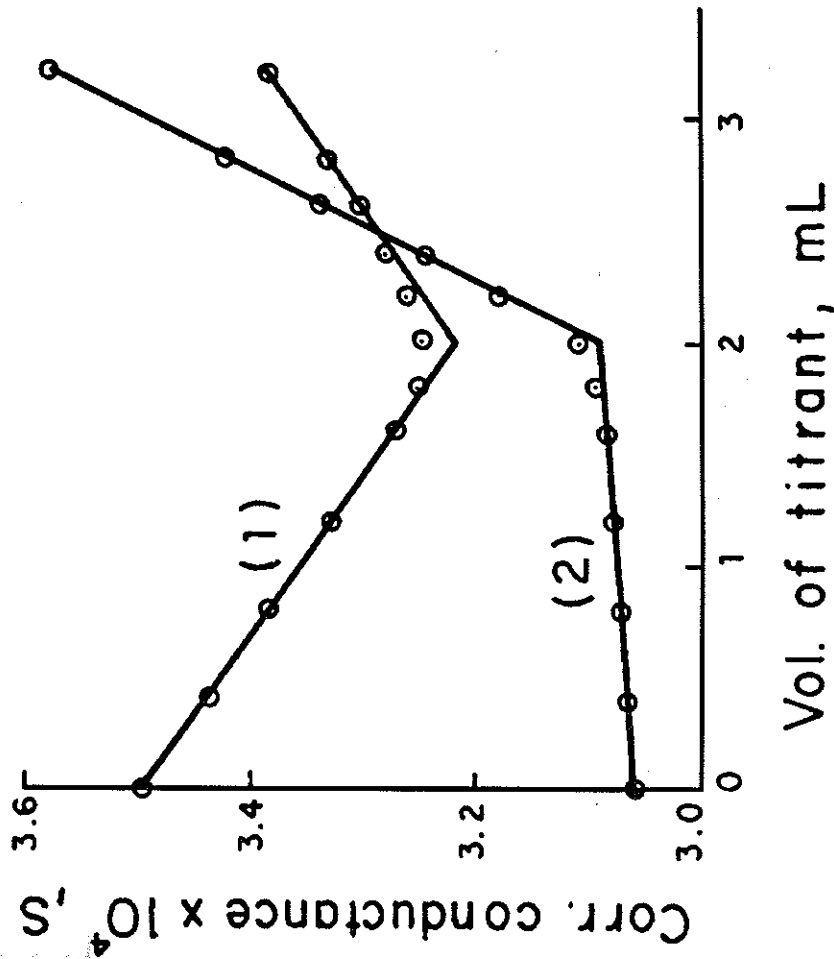


FIGURE 5 - Direct and reverse conductometric titrations of pyro-thioantimonite (curve 1: M/20  $\text{CoCl}_2$  vs. M/500  $\text{Na}_2\text{Sb}_2\text{S}_5$ ; curve 2: M/40  $\text{Na}_2\text{Sb}_2\text{S}_5$  vs. M/250  $\text{CoCl}_2$ ).

The pH investigations on the pyro-thioantimonite system was - also carried out but the titration curves - did not give any sharp inflection to throw any light on the formation of cobalt pyro-thioantimonite which may be ascribed to the close pH values of the reactants.

Investigations on the reaction of cobalt chloride with sodium meta-thioantimonite failed to give any dependable results. The reasons may be similar to those acting in case of the meta-antimonite.

The precipitates obtained at the end-points of the titrations of cobalt chloride with the antimonite and thioantimonite anions were also analyzed by the classical methods. The results obtained (Table 2) confirm those obtained by the electrometric study. The analytical results obtained were also confirmed by atomic absorption spectroscopy.

The present electrometric and analytical investigations confirm the formation and precipitation of cobalt ortho-antimonite  $3\text{CoO} \cdot \text{Sb}_2\text{O}_3$  and cobalt ortho- $3\text{CoS} \cdot \text{Sb}_2\text{S}_3$  and pyro- $2\text{CoS} \cdot \text{Sb}_2\text{S}_3$  thioantimonites, in the neighbourhood of pH 7.6, 7.9, and 6.5, respectively. As the structure of these molecules is not known, they are represented as double compounds, the way usually adopted for such compounds.<sup>3,18</sup>

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PRASAD, S. Formação de antimonitos e tioantimonitos de cobalto em função do pH. *Ecl. Quím.* (São Paulo), v.20, p.35-47, 1995.

RESUMO: A natureza precisa da reação de cloreto de cobalto com os ânions de antimonito (pH 11,4 e 8,1) e de tioantimonito (pH 12,0; 8,9 e 6,8) foi investigada por meio de técnicas eletrométricas envolvendo titulações condutométricas e potenciométricas entre os reagentes. Os pontos finais obtidos a partir de inflexões acentuadas e patamares nas curvas de titulações fornecem evidências convincentes sobre a formação de orto-antimonito ( $3\text{CoO} \cdot \text{Sb}_2\text{O}_3$ ), orto-tioantimonito ( $3\text{CoS} \cdot \text{Sb}_2\text{S}_3$ ) e piro-tioantimonito ( $2\text{CoS} \cdot \text{Sb}_2\text{S}_3$ ) de cobalto nas vizinhanças do pH 7,6; 7,9 e 6,5, respectivamente. Também foram realizadas investigações analíticas sobre os precipitados obtidos, que comprovam os resultados dos estudos eletrométricos.

PALAVRAS-CHAVE: Antimonitos; tioantimonitos; cobalto; estudo eletrométrico.

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