

## Complex Formation of Chromium(III) with Thioglycollic Acid

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The interaction between chromium(III) and thioglycollic acid has been investigated by spectrophotometric and potentiometric methods. The complex-formation is extremely slow at room temperature, but occurs at a reasonable rate when the reactants are heated above 60°C. In alkaline solutions a blue-green complex with the formula  $\text{Cr}(\text{SCH}_2\text{COO})_3^{3-}$  is formed. The absorption curve of the complex exhibits two maxima at 476 and 632 nm, respectively, and the molar extinction coefficient at either maximum is 202. In acidic medium a mixture of various chromium complexes is obtained upon heating the reactants. At low pH values two red complexes with formulas  $\text{Cr}(\text{SCH}_2\text{COOH})_2^{2+}$  and  $\text{Cr}(\text{SCH}_2\text{COOH})_2^+$  are predominant, whereas the formation of the yellow-green complex  $\text{Cr}(\text{SCH}_2\text{COO})_2^-$  is favoured in less acidic solutions. No pH value or concentration of the reactants was found at which only one of these complexes is formed.

Thioglycollic acid (mercaptoacetic acid) forms stable complexes with several metals. The formation and composition of the complexes formed with iron,<sup>1,2</sup> molybdenum,<sup>3</sup> cobalt,<sup>4,5</sup> nickel,<sup>5,6</sup> zinc,<sup>5,7,8</sup> lead,<sup>7,8</sup> manganese,<sup>5</sup> mercury,<sup>8,9</sup> silver,<sup>8</sup> and cadmium<sup>8</sup> are reported in the literature, and thioglycollic acid has been recommended as a powerful masking agent in spectrophotometric analysis<sup>10,11</sup> and in complexometric titrations.<sup>12</sup>

The reaction between thioglycollic acid (designated in this paper as TGA) and chromium(III) was first reported by Mayr and Gebauer<sup>13</sup> who pointed out that chromium could not be precipitated quantitatively in alkaline medium when TGA was used as masking agent for iron. According to Bhuchar,<sup>14</sup> a chromium-TGA complex is easily formed when the reactants are heated on a hot plate. He claims that a violet complex is obtained upon heating an acidic solution of chromium and excess TGA, and that a green complex is formed when pH of the solution is increased above 6.

The existence of chromium-TGA complexes has not been confirmed by other investigators, and the present work was carried out in order to investigate the complex formation of chromium with TGA and to determine the composition of the complexes.

## EXPERIMENTAL

*Apparatus.* A Beckman DB recording spectrophotometer with 1.000 cm glass cells was used for the absorbance measurements. The pH of all solutions was measured with a Beckman Zeromatic pH-meter using glass and calomel electrodes. Potentiometric pH-titrations were performed in a water-jacketed beaker, and the temperature of the solution was kept constant  $\pm 0.2^\circ\text{C}$  during the titration by means of a circulating pump. Effective stirring was obtained with a magnetic stirrer.

*Materials.* Thioglycolic acid (80 % in water) was obtained from E. Merck AG, Germany. The acid was purified by vacuum distillation as described by Leussing and Koltzoff.<sup>15</sup> The fraction collected boiled at  $111-113^\circ\text{C}$  at 18 mm pressure. The distilled acid was stored at  $0^\circ\text{C}$ , and the bottle in which it was kept was flushed with pure nitrogen during and after the removal of samples. Stock solutions of chromium, approximately 0.1 M, were prepared from reagent grade chromium(III) chloride (British Drug House) and chromium(III) perchlorate (G. F. Smith Chem. Co.) and standardized by oxidation with persulphate followed by iodometric titration. Standard 0.5 M potassium hydroxide was prepared by dissolving reagent grade potassium hydroxide in  $\text{CO}_2$ -free water and standardized by potentiometric titration. The remaining chemicals were of reagent grade and were used without further purification.

## RESULTS AND DISCUSSION

*Standardization of dilute TGA solutions.* Standard 0.1 M solution of TGA was prepared by diluting a known weight of the distilled acid with air-free water. The solution was standardized by iodometric titration as described by Leussing and Koltzoff.<sup>15</sup> According to Lucas and King<sup>16</sup> too high results are obtained when the titration is performed at temperatures above  $0^\circ\text{C}$ . We observed, however, practically no effect of the temperature in the range  $0-40^\circ\text{C}$ , provided the solution was freshly prepared. The titer of the TGA solution was also checked by alkalimetric titration using phenolred as indicator and by potentiometric end-point detection. All iodometric and alkalimetric titrations agreed within 0.2 % and showed that the concentrated redistilled TGA was 99.8 % pure and that it was stable for months.

*Decomposition of dilute TGA solutions.* Dilute TGA solutions are oxidized by air<sup>17</sup> and the rate of oxidation increases with increasing temperature<sup>18</sup> and pH of the solution.<sup>19</sup> During the present investigation we observed that pure, dilute solutions of TGA are decomposed slowly even when they are stored in nitrogen atmosphere. The titer of a 0.1 M TGA solution decreased about 1 % a week. One of the decomposition products, hydrogen sulphide, could easily be detected a few days after preparation of the solution. Similar results have been reported by Hellström<sup>20</sup> and Mayr and Gebauer.<sup>1</sup> The decomposition of TGA is probably autocatalytic. We observed that the decomposition rate decreased markedly when the decomposition products were removed from the atmosphere above the solution. Thus, when the bottle in which the dilute TGA was kept, was flushed with pure nitrogen every day, the titer decreased less than 0.1 % a week. Further experiments showed that the rate of the autocatalytic decomposition in inactive atmosphere is of the same order of magnitude as the rate of oxidation in air. Consequently, when a standard TGA solution is stored for some time, it is very important to flush the flask at least once a day with pure nitrogen.

The rate of oxidation of TGA increases rapidly in the presence of certain metals.<sup>18,21,22</sup> Iodometric titrations of TGA in absence and presence of chro-

mium(III) showed that chromium does not have a similar catalytic effect at any pH value or temperature below 100°C.

*Spectrophotometry.* Preliminary experiments indicated that the reaction between chromium and TGA is extremely slow at room temperature, but the reaction rate increases rapidly with increasing temperature and excess of reagent. In alkaline solutions a precipitate of chromium hydroxide was formed which dissolved upon heating, provided excess TGA was present. The colour of the complex formed was very dependent on pH of the solution. At pH 3 a grey colour was obtained which turned to red at lower pH values and to green when pH was increased above 4.

Absorption curves of chromium/TGA mixtures recorded at different pH values are given in Fig. 1. The solutions were prepared by mixing chromium with 50 times excess of TGA and adjusting pH to desired value by addition of potassium hydroxide or hydrochloric acid. The solutions were then diluted to 100 ml and heated 2 h on a water bath. After cooling to room temperature the pH of the solutions was checked and the extinctions measured against distilled water. At pH values above 10 a precipitate was formed even in the presence of 50 times excess TGA, and the investigation was therefore restricted to lower pH values.

As indicated in Fig. 1 the absorption curves exhibit two maxima at all pH values. At pH values above 7 and below 2.5, the wavelength at both maxima is constant, independent of pH of the solution. In the pH range 2.5–7, however, both maxima are shifted to longer wavelengths with increasing pH of the solution, and the extinction at both maxima increases with increasing pH and reaches a limiting value at pH 7.

The effect of varied excess of TGA on the absorption curves was also investigated. Several experiments showed that at a given pH value in the

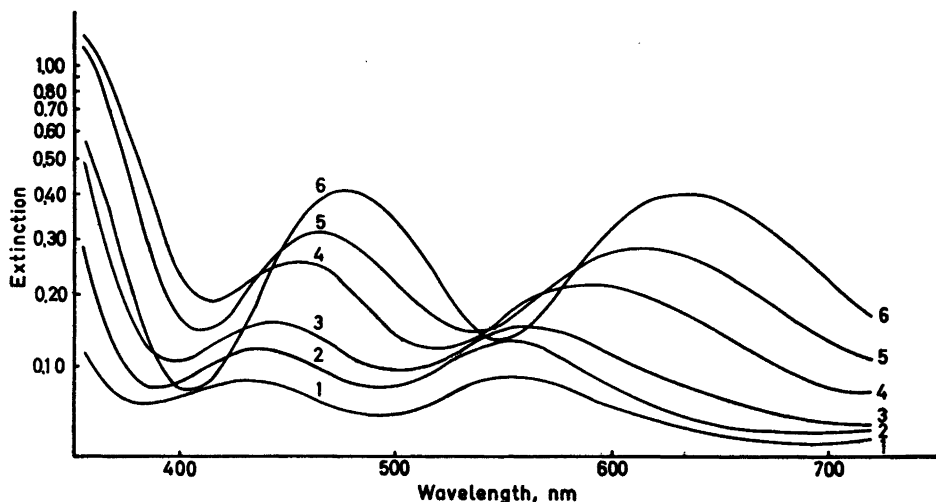


Fig. 1. Absorption curves of  $2 \times 10^{-3}$  M chromium and 0.1 M TGA at different pH values. Curve 1: pH 1.5, 2: pH 2.5, 3: pH 3.0, 4: pH 4.0, 5: pH 5.0 and 6: pH 7–10.

range 2.5–7, the extinctions increased and the maxima shifted to longer wavelength with increasing excess of reagent. At pH values below 2.5 and above 7.0, however, the absorption curves were not affected when the concentration of TGA was increased from 20 to 150 times that of chromium.

The above experiments indicate that a mixture of two complexes with different composition are formed in the pH range 2.5–7. The composition of the complexes was investigated by the method of continuous variation.<sup>23</sup> The experiments were restricted to pH values below 4, because the lack of excess TGA resulted in the formation of chromium hydroxide at higher pH values. No suitable buffer was found at these low pH values. Organic acids and even sulphate and acetate ions interfered in the complex formation between chromium and TGA, when the latter was not present in a large excess. The lack of a suitable buffer made the preparation of the solutions extremely difficult, because the extinctions are very dependent on pH of the solution in acidic medium (Fig. 1). Chromium perchlorate and TGA were mixed in different ratios and the solutions, containing a constant total concentration of reactants, were heated on a water bath for 2 h. During the heating, the pH of the solutions decreased as a result of the complex formation. The pH could not be adjusted to desired value after cooling to room temperature, because equilibrium between the reactants could only be obtained in a reasonable time at higher temperatures. A lot of various mixtures, each of them with a presumed right pH value, were prepared, the pH was checked after cooling to room temperature, and solutions in which the pH disagreed by more than  $\pm 0.05$  unit, were discarded.

The extinctions of each of the remaining solutions were measured against a blank with the same pH and containing the same amount of chromium, and the difference extinction,  $Y$ , plotted against the mole ratio,  $C_{\text{TGA}}/(C_{\text{TGA}} + C_{\text{Cr}})$ . The result of two series at pH 2.20 and 3.40, respectively, is given in Fig. 2. The Job's curve obtained at pH 3.40 showed a maximum at the mole ratio 0.65, which is close to the expected value for a complex with two ligands. The maximum on the curves obtained in the pH range 2.00–2.40, however, occurred at the mole ratios 0.59–0.62 which is in between the theoretical values for complexes with one and two ligands, respectively. Typical S-formed curves were observed at low mole ratios, indicating the presence of a complex with more than one ligand. On the other hand, the slope of the curves at mole ratios close to zero has a finite value and indicates that a 1:1 complex also exists in these acidic solutions.<sup>24</sup> The shape of the Job's curves indicates an equilibrium between two complexes at low pH values. Curves plotted from extinctions measured at wavelengths apart from the maximum (*i.e.* 520, 570, 600, and 625 nm) did, however, not show any marked shift of the maximum, indicating that the absorption maxima of the two complexes must be close to each other.

The existence of a mixture of two complexes in acidic medium was confirmed by the molar ratio method.<sup>25</sup> The solutions were prepared as described above and the extinctions were measured at 546 and 600 nm, respectively. A few curves are plotted in Fig. 3. It is evident from the figure that relatively weak complexes are formed between chromium and TGA. The S-formed shape of curve I indicates the presence of a complex with two ligands at pH 3.40,

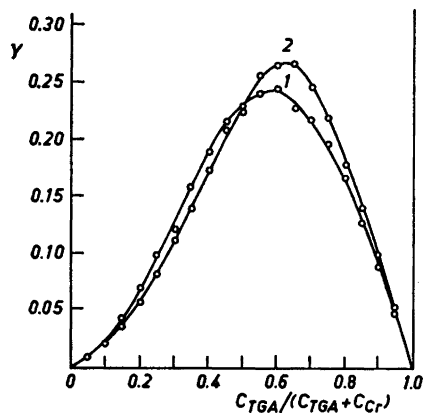


Fig. 2. Continuous variation curves for the system chromium-TGA at pH 2.20 (curve 1) and pH 3.40 (curve 2). Constant sum of concentrations  $C = C_{Cr} + C_{TGA} = 1.57 \times 10^{-2}$  M. Extinctions measured at 546 nm.

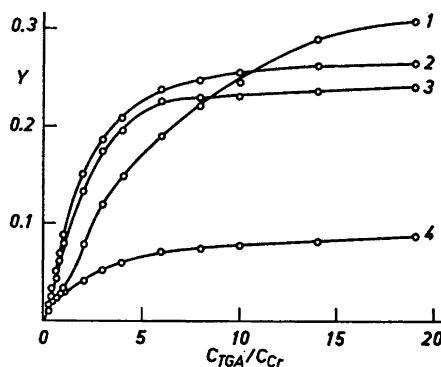
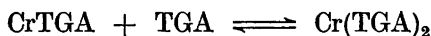


Fig. 3. Molar ratio curves for the system chromium-TGA at pH 3.40 (curves 1 and 2) and pH 2.20 (curves 3 and 4). Extinctions measured at 600 nm (curves 1 and 4) and 546 nm (curves 2 and 3).

whereas the slope of curve 2 at low TGA concentrations indicates that a 1:1 complex also is present in the same solution.<sup>26,27</sup> The lack of an inflexion point and the slopes of the curves 3 and 4 indicate that a complex with one ligand predominates at pH 2.20. As stated above, the absorption maximum is shifted to longer wavelengths with increasing excess of reagent in the pH range 2.5–7 and explains the increase in the extinction values of curve 1 at high TGA concentrations.

The spectrophotometric experiments indicate that the following equilibrium exists at pH values below 4 (charge signs are omitted).



The equilibrium is shifted to the right upon increasing the total TGA concentration or by increasing the pH of the solution. No pH value or concentration of reactants was found at which only one complex was present. Consequently, the so-called "straight line methods"<sup>26,28,29</sup> failed in the attempt to ascertain the composition of the complexes. Moreover, the wavelength of the absorption maxima and the extinction coefficients of each of the two complexes could not be determined.

**Potentiometry.** The complex formation in alkaline solutions was investigated by potentiometric titration using carbonate-free potassium hydroxide as titrant. The titration of the acid alone and of mixtures with chromium/TGA ratios 1:2, 1:5, and 1:10 were performed at 60°C. The initial volume of the solutions (100 ml) and the ionic strength (0.1 M KCl) were kept constant in all titrations. The solutions were heated for 2 h on a waterbath before the titration and the titration was performed very slowly at 60°C in order to ensure complete reaction between each addition of the titrant. During the heating on a waterbath the red colour of the chromium/TGA complexes was

developed. Upon addition of alkali, the colour turned to yellow-green at pH 4 and to blue-green when pH was increased above 7.

Titration curves of the 1:5 and 1:10 mixtures showed two inflexions, corresponding to the addition of two and three equivalents, respectively, of alkali per mole of chromium (Fig. 4). The titration curve of the 1:2 mixture showed only a single inflexion after the addition of two equivalents of alkali, and chromium hydroxide was precipitated at higher pH values.

The average number of ligand bound per mole of chromium (designated by  $\bar{n}$ ) was calculated from the titration curves using the method of Bjerrum.<sup>30</sup>  $\bar{n}$  was calculated from:

$$\bar{n} = \frac{C_{\text{TGA}} - ([\text{H}_2\text{A}] + [\text{HA}^-] + [\text{A}^{2-}])}{C_{\text{Cr}}} \quad (1)$$

where  $C_{\text{TGA}}$  and  $C_{\text{Cr}}$  denote the total concentration of TGA and chromium, respectively,  $[\text{A}^{2-}]$  the concentration of the ligand  $^-\text{SCH}_2\text{COO}^-$ , and  $[\text{HA}^-]$  the concentration of  $\text{HSCH}_2\text{COO}^-$ . The concentration of  $\text{A}^{2-}$  at several points on the titration curve was calculated from the dissociation constants of TGA and the equation:

$$2 C_{\text{TGA}} = 2 [\text{H}_2\text{A}] + [\text{HA}^-] + [\text{H}^+] + a C_{\text{TGA}} - [\text{OH}^-] \quad (2)$$

where  $a$  denotes the number of mole of base added per mole TGA. The dissociation constants of TGA at 60°C ( $\text{p}K_c = 3.48$  and  $9.62$ , respectively) were calculated from the titration curve of the acid in absence of chromium.<sup>31</sup>

The calculated values of  $\bar{n}$  are plotted against the negative logarithm of  $[\text{A}^{2-}]$  in Fig. 5. The formation curve exhibits inflexion points at  $\bar{n} = 1.5$  and  $\bar{n} = 2.5$ , indicating that 1:2 and 1:3 complexes with  $\text{A}^{2-}$  as ligand are formed. The 1:2 complex has a yellow-green colour and it is only formed at pH values above 4. Hence, this complex is not identical with the red 1:2 complex formed at lower pH values. The presence of complexes with  $^-\text{SCH}_2\text{COOH}$  as ligand

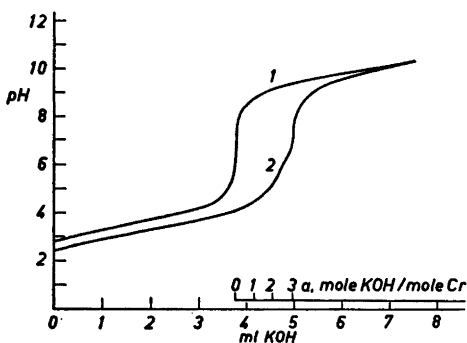


Fig. 4. Potentiometric titration curves of  $2 \times 10^{-2}$  M TGA in absence (curve 1) and in presence (curve 2) of  $2 \times 10^{-3}$  M chromium.

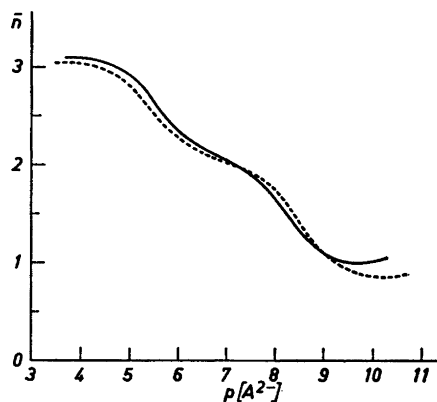


Fig. 5. Formation curve for the chromium-TGA system with  $\text{A}^{2-}$  as ligand. Chromium/TGA ratio 1:10 (full curve) and 1:5 (dashed curve).

was not taken into account in the calculation of  $C_{TGA}$  from eqn. 2. Hence, the fact that the formation curve does not approach zero at high  $pA^{2-}$  values, must be due to the formation of complexes with  $^{-}SCH_2COOH$  as ligand at low pH values, and the over-all formation constant could not be calculated from the formation curve.

*The moving boundary method.* The spectrophotometric and potentiometric experiments indicate that the formula of the complexes formed at pH values above 4 is  $CrA_2^{-}$  and  $CrA_3^{3-}$ , respectively, and that a mixture of the two complexes  $Cr(HA)_2^{+}$  and  $Cr(HA)_2^{2+}$  is formed at lower pH values. All the complexes are coloured and the charge type could therefore easily be confirmed by measuring the migration of the various species in an electric field. The experiments were carried out using an apparatus described by Burton.<sup>32</sup>

The solution to be tested was placed in the bottom of a U-formed tube and the limbs of the tube were filled with an approximately 0.1 M uncoloured electrolyte of the same pH as that of the test solution. Two platinum electrodes were placed at a convenient level in the two limbs and connected to a 130 V DC source. When the circuit was completed, the boundary moved toward the cathode or the anode depending on the charge sign of the coloured species. The solutions to be tested were prepared by mixing chromium with a 50 times excess of TGA, adjusting pH to desired value and heating on a waterbath for 2 h. The ionic strength was made slightly higher than that of the uncoloured electrolyte by adding potassium chloride. The greater density of the coloured solution prevented turbulence and mixing of the solutions, and a very distinct boundary was obtained.

The experiments showed that the yellow-green and blue-green complexes formed at pH 4 and 8, respectively, moved toward the anode, whereas the red complexes formed at lower pH values, moved toward the cathode. It is evident from these experiments that the green complexes are negatively charged, and that the red complexes are carrying a positive charge.

### CONCLUSION

Chromium(III) reacts easily with TGA when the temperature of the solution is increased above 60°C. In the pH range 7–10 a complex with the formula  $Cr(SCH_2COO)_3^{3-}$  is formed. The complex has a blue-green colour and absorption maxima at 632 and 476 nm, respectively. The molar extinction coefficient at either maximum is 202. In slightly acidic solutions (pH 4) a yellow-green complex with formula  $Cr(SCH_2COO)_2^{-}$  is formed. This complex has a well defined absorption maximum at 590 nm and a less distinct maximum at 420–460 nm. At pH values below 4 a red colour is obtained upon heating a mixture of chromium and TGA. The red colour is due to a mixture of two complexes with the formulas  $Cr(SCH_2COOH)_2^{2+}$  and  $Cr(SCH_2COOH)_2^{+}$ .

In the pH range 2.5–7 the following equilibrium exists:



At temperatures above 60°C the equilibrium is rapidly obtained and it is shifted to the right upon increasing pH of the solution or by increasing the

excess of the TGA. At room temperature the equilibrium is not affected by increasing the excess of TGA. Variation of pH of the solution has, however, a marked effect even at room temperature. Thus, the blue-green colour of the  $\text{Cr}(\text{SCH}_2\text{COO})_3^{2-}$  complex formed at pH 8, turned red upon addition of hydrochloric acid, and the red colour of acidic solutions turned to green when pH was increased above 8. The equilibrium is, however, only obtained upon heating the solutions.

The yellow-green complex  $\text{Cr}(\text{SCH}_2\text{COO})_2^-$  appeared to be more inert at room temperature than the other complexes. This complex was obtained upon heating the reactants in a solution of pH 4, and it was preferably formed in more concentrated solutions. After cooling to room temperature, the colour of this complex did not change upon adjusting pH to 1 or to 9. Iodometric titration of the acidified solution showed that about 1.6 mole TGA per mole chromium did not react with iodine. Similar titrations of the red complexes and of the blue-green complex showed that practically all TGA in these complexes reacts with iodine when pH of the solutions is adjusted to 1–2.

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