Studies of Complexes of the Transition Metals. II. Cobalt Complex with Dithioloxalate

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Studies of Complexes of the Transition Metals. II. Cobalt Complex with Dithioloxalate[1]

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Abstract. The cobalt (II) ion and dithioloxalate ion form a complex which is stable in a water solution and highly colored. The complex was studied by means of spectrophotometric methods in the visible region. By using the method of continuous variation of Job and the method of varying mole ratio, the composition of the complex was found to be that of three moles of ligand to one mole of cobalt. The overall formation constant of the complex was determined by the method of varying mole ratio and by successive dilutions of stoichiometric proportions of ligand and metal. The ionic strength of these solutions was kept constant at 0.1, and the measurements were made at room temperature. It was assured that the cobalt (III) complex was not present in the studies by oxidizing a cobalt (II) complex and determining its spectrum. The results of this research indicate that the cobalt complex with dithioloxalate is more stable than the corresponding oxygen complex.

Dithioloxalate forms a highly colored complex with nickel (Deskin, 1958) and with cobalt (Robinson and Jones, 1912). In this investigation it was desired first to find the formula for the cobalt complex in dilute solution, and then to determine the formation constant. Since the complex was stable in a water solution, spectrophotometric methods seemed advantageous.

<center>EXPERIMENTAL</center>

Materials

The dithioloxalic acid dipotassium salt employed was Eastman Kodak Company white label. It was analyzed for potassium after drying in a desiccator by a method of precipitation using sodium tetraphenylboron as a precipitating agent (Chem. Analyst, 1953). The analysis gave a value of 38.84 percent, and the calculated value is 39.39 percent. The dithioloxalic acid dipotassium salt was also analyzed for sulfur by the method of Paar bomb fusion (Paar Manual No. 121), followed by precipitation as $BaSO_4$. The value obtained by these determinations was 30.14 percent, and the calculated value is 34.02 percent.

The cobalt (II) solution that was used was prepared from reagent grade cobalt chloride and standardized electrolytically. All solutions were made by diluting the original solution.

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Solutions

All of the solutions of the complex ions were prepared from freshly boiled distilled water. The pH of the solutions was adjusted to 4.0 ± 0.5 by the use of a Beckman pH meter, which was standardized by means of a standard buffer. Reagent grade potassium chloride was added to adjust the total ionic strength to 0.1.

Absorption Spectra

All of the measurements were made on a Beckman model DU Quartz spectrophotometer, using a tungsten lamp and Corex cells with a path length of 10.00 ± 0.01 mm. These readings were taken at room temperature.

EXPERIMENTAL RESULTS

Composition of the Complex

In order to determine the molecular formula of the complex, the method of continuous variation devised by Job (1928; 1936), and the method of varying mole ratio (Yoe and Jones, 1944) were used. A typical plot for the method of continuous variation is shown in Figure 1.
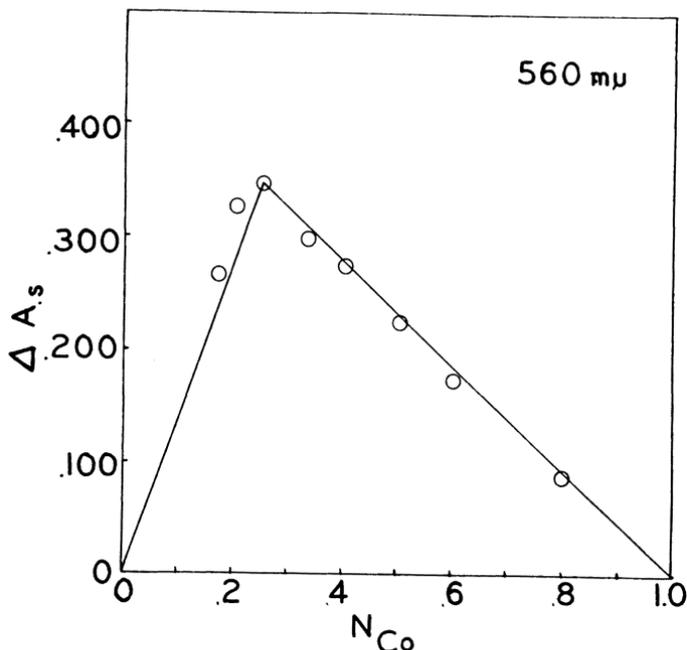

Figure 1. Continuous variation plot for the cobalt-dithioloxalate complex.

When the difference between the observed absorbence and the calculated absorbence ($\triangle A_s$) was plotted against mole fraction of cobalt, it was found that a complex containing three moles of dithio-

loxalate to one mole of cobalt was formed. In order to alleviate any instability of the solutions during the determinations, each of the solutions was made, the pH adjusted, and the spectrophotometric measurements taken before preparing the next solution.

By using the method of varying mole ratio, the value of a three to one complex was verified, the complex being formed at the place where the graph leveled to a constant value. Figure 2 is a typical plot obtained for the cobalt dithioloxalate complex. It was found
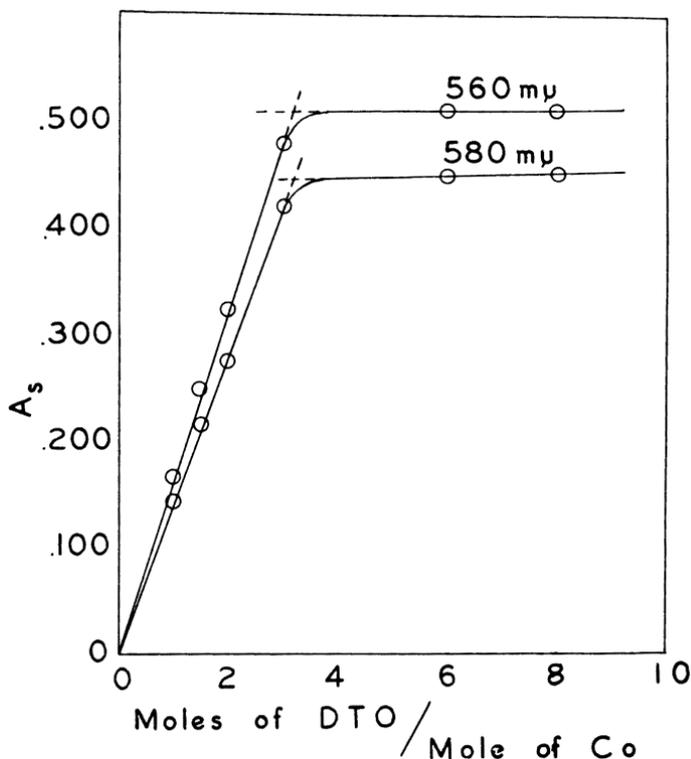
Figure 2.   Varying mole ratio plot for the cobalt-dithioloxalate complex.

necessary to make corrections for the absorbence due to dithiolox-alate when present in large excess.

Formation Constants[2]

The method of varying mole ratio can also be used to give a value for the formation constant. If it is assumed that the association is complete when the ligand is in excess, the molar absorbency index for the complex at one particular wave length can be evaluated.

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[2]These are the concentration formation constants.

Then the concentration of the complex at various points on the graph below the three to one ratio may be obtained. In this work, the values obtained for the formation constants by this method were used as qualitative guides to the values reported.

The other method used to obtain formation constants involved successive dilutions of a solution containing the stoichiometric concentration of three moles of ligand to one mole of metal ion (Turner and Anderson, 1949; Foley and Anderson, 1949). By using both the graphs of continuous variation and successive dilutions, a series of pairs of solutions could be selected having equal absorbence (and thus essentially equal concentration of complex), but different concentrations, of reagents.

From the equation:

$$K_f = \frac{\alpha}{\left[Co_1^{+2} - \alpha\right]\left[DTO_1^{-2} - 3\alpha\right]^3} = \frac{\alpha}{\left[Co_2^{+2} - \alpha\right]\left[DTO_2^{-2} - 3\alpha\right]^3}$$

the concentration of the complex at equilibrium was evaluated, and hence the formation constant. The formation constants at different wave lengths are given in Table 1.

Table 1
Concentration Formation Constants at 25° C

At 560 mμ:			
A_s	$[Co^{+2}]$	$[DTO^{-2}]$	log K_f
0.325	3.60×10^{-4} M	8.40×10^{-4} M	11.5
0.300	4.20×10^{-4}	7.80×10^{-4}	11.3
0.290	4.50×10^{-4}	7.50×10^{-4}	10.9
0.225	6.12×10^{-4}	5.88×10^{-4}	11.6
		Mean	11.4
At 580 mμ:			
A_s	$[Co^{+2}]$	$[DTO^{-2}]$	log K_f
0.290	3.60×10^{-4} M	8.40×10^{-4} M	10.7
0.268	4.20×10^{-4}	7.80×10^{-4}	10.8
0.202	6.12×10^{-4}	5.88×10^{-4}	11.5
		Mean	11.0

Since the peak for the complex was not too well defined, both 560 mμ and 580 mμ were used for these studies. To assure the absence of the cobalt (III) complex in our studies, a solution of the cobalt (II) complex was prepared using stoichiometric quantities. This solution was oxidized, and visual inspection showed a change in color from yellowish-brown to blood red. Spectra measurements confirmed a change in the spectrum with a change in the oxidation state of cobalt.

DISCUSSION

The equilibrium constants given in the table refer to the reaction:

$$Co^{+2} + 3 \ DTO^{-2} \leftrightarrows Co(DTO)_3^{-4}, \text{ where the } K_f \text{ given in the}$$

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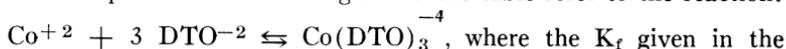1959]   COMPLEXES OF TRANSITION METALS   193

table is for the product of $(k_1 k_2 k_3)$. It is interesting to make comparisons of this complex to other complexes containing five membered rings.

The overall formation constant $(k_1 k_2 k_3)$ for the cobalt oxalate complex is log $K_f = 9.7$ (Sartori, 1934), which is less than that of the cobalt dithioloxalate complex. This is analogous to the comparison between the nickel dithioloxalate complex and the nickel oxalate complex, which have values for their formation constants of log $K_f = 9.43$ (Deskin, 1958) and log $K_f = 6.51$ (Barney, *et al.*, 1951), respectively. This indicates that the coordinating ability of the dithioloxalate grouping is greater than that of the oxalate grouping. These values for the nickel complexes cannot be compared on an absolute scale with those for the cobalt complexes, since the formation constants for nickel are for the product of $(k_1 k_2)$.

The cobalt ethylenediammine complex has been studied and found to have a log $K_f = 13.69$ (Edwards, 1950). This value is also the overall constant $(k_1 k_2 k_3)$ as above. This value is greater than the value for the cobalt dithioloxalate complex. The nickel ethylenediammine complex was found to have a log $K_f = 14.06$ (Bjerrum, 1941), greater than the formation constant for the nickel dithioloxalate complex (log $K_f = 9.43$). The order of magnitude of the aforementioned complexes can possibly be explained in terms of basicity. The nitrogen atom is more basic than the sulfur atom, and the sulfur atom is more basic than the oxygen atom, which might explain the order of magnitude of the formation constants.

The cobalt glycinate complex has been found to have a formation constant $(k_1 k_2 k_3)$ log $K_f = 10.81$ (Tanford and Shore, 1953), which is about the same order of magnitude as the cobalt dithioloxalate complex.

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