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## Studies of Complexes of the Transition Metals IV. Cobalt Complex with Dithiomalonate<sup>1</sup>

RONALD L. BRUBAKER and WILLIAM A. DESKIN<sup>2</sup>

*Abstract.* The cobalt (II) ion and the dithiomalonate ion form a complex which is reasonably stable in aqueous solution and highly colored. Studies were conducted by means of spectrophotometric methods in the visible region. The composition of the complex and the overall formation constant were determined using the method of continuous variation of Job and successive dilutions of stoichiometric proportions of the ligand and metal. All measurements were made at room temperature with the solutions kept at a constant ionic strength of 0.1. The results indicate the composition of the complex to be that of three moles of ligand to one mole of cobalt. The formation constant obtained is lower than that of the cobalt dithioloxalate complex, indicating that the six membered ring is less stable than a similar five membered ring.

The dithiomalonate ion forms a highly colored complex with nickel (Deskin, 1958) and with cobalt (Robinson and Jones, 1912). It was the purpose of this research to determine the molecular formula and the overall formation constant of the cobalt dithiomalonate complex in dilute solution. Since the aqueous solution is highly colored and reasonably stable it seemed advantageous to use a spectrophotometric method.

### EXPERIMENTAL

**Materials.** A cobalt (II) solution was prepared from Mallinckrodt AR grade cobalt chloride and standardized electrolytically.

The dithiomalonic acid dipotassium salt was not commercially available. It was prepared by adding malonyl chloride to ethanethiol and slowly heating the solution to remove hydrogen chloride and the excess reagents. The resulting dithiomalonic acid diethyl ester was dissolved in alcohol. A solution of potassium hydrosulfide in alcohol was added to the ester and the mixture was allowed to stand. The mixture was shaken on a mechanical shaker for some time to insure the completion of the reaction. The precipitate which formed during this operation was removed by filtration, and the remaining solution was seeded and allowed to stand. The precipitate which then formed was washed with alcohol and dried in a vacuum desiccator. Analyses of the compound were carried out. Potassium was

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determined by the sodium tetraphenylboran method (Chem. Analyst, 1953). The analysis gave a value of 36.01 percent, and the calculated value is 36.82 percent. An analysis for sulfur was conducted by the Paar fusion method (Paar Manual No. 121), followed by precipitation as barium sulfate. The value obtained for this analysis was 30.28 percent, and the calculated value is 30.20 percent.

**Solutions.** Solutions of the dithiolmalonate were prepared daily. All solutions used for measurements were prepared from the standard solutions by volumetric dilution with freshly boiled distilled water, using a solution of Baker Analyzed Reagent grade potassium chloride to adjust the ionic strength of the solutions to 0.1. The pH of these solutions was adjusted to  $4.0 \pm 0.2$ , using a Beckman pH meter.

**Absorption Measurements.** All absorption measurements were made on a Beckman model DU Quartz spectrophotometer, using a tungsten lamp and Corex cells with a path length of  $10.0 \pm 0.01$  mm. All readings were made at room temperature.

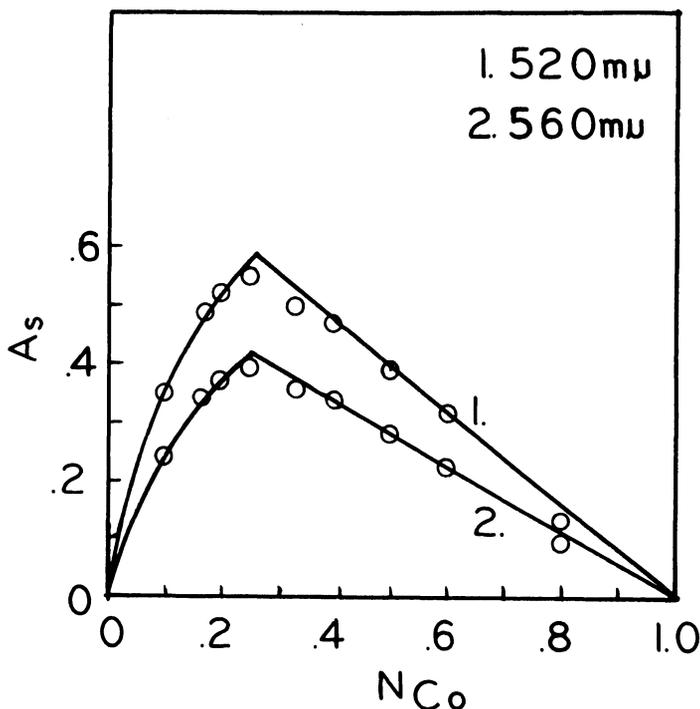


Figure 1. Continuous variation plot for the cobalt-dithiolmalonate complex.

## 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) was used. The figure shows a plot of the experimental data obtained from an average of several determinations. The plotted absorption was corrected for the very small absorption of the cobalt (II) ion at the wavelengths studied. The spectrum of dithiolmalonate showed no significant absorption in the region under consideration. The absorption was plotted against the mole fraction of cobalt (II), and the maximum absorption was observed to occur at a mole fraction corresponding to a mixture of three moles of dithiolmalonate to one mole of cobalt. In order to obtain maximum stability it was necessary to allow the solutions to come to equilibrium for a short period of time before measurements were made.

**Formation Constant.** The concentration formation constant was determined using the plot shown and a plot of the absorption vs. the concentration of the cobalt ion in a 3:1 mixture of the reagents. This plot was prepared by successive dilutions of a solution containing the stoichiometric proportions of three moles of ligand to one mole of metal ion (Turner and Anderson, 1949; Foley and Anderson, 1949). From these two plots a series of pairs of solutions could be selected which had equal absorption (and thus essentially equal concentration of the complex) but different concentrations of the reagents. The following equation was used for calculations:

$$K_f = \frac{\alpha}{[\text{Co}_1^{+2} - \alpha] [\text{DTM}_1^{-2} - 3\alpha]^3} = \frac{\alpha}{[\text{Co}_2^{+2} - \alpha] [\text{DTM}_2^{-2} - 3\alpha]^3}$$

Using the concentrations of cobalt (Co) and dithiolmalonate (DTM) obtained from the plots, the equation was solved for alpha (the concentration of the complex) and from this the formation constant was evaluated.

The formation constant was determined principally at 520  $m\mu$ , since this wavelength gave optimum conditions for accuracy. Measurements were also made at 560  $m\mu$  and 600  $m\mu$  and were used to confirm the results obtained. The results of calculations using the plots obtained at 520  $m\mu$  are summarized in Table 1. It will be noted that points chosen on the right side of the plot gave less consistent results than those on the left side. Although there is little conclusive evidence, it is possible that the deviation of the results taken from the points on the right side of the plot may be due to the formation of small amounts of a 1:1 or 2:1 complex. This is very unlikely to occur under the conditions present on the left side of the curve, as there is a large excess of the ligand. The

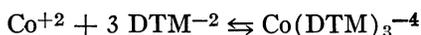
**Table 1**  
Concentration Formation Constants at 25° C.

A <sub>s</sub>	Right side		log K <sub>f</sub>
	[Co+2]	[DTM <sup>-2</sup> ]	
0.400	1.44 x 10 <sup>-3</sup>	1.56 x 10 <sup>-3</sup>	9.22
0.350	1.65 x 10 <sup>-3</sup>	1.56 x 10 <sup>-3</sup>	9.76
0.300	1.84 x 10 <sup>-3</sup>	1.16 x 10 <sup>-3</sup>	10.30
0.250	2.03 x 10 <sup>-3</sup>	0.97 x 10 <sup>-3</sup>	10.89
	Left side		
0.400	0.37 x 10 <sup>-3</sup>	2.63 x 10 <sup>-3</sup>	9.15
0.350	0.29 x 10 <sup>-3</sup>	2.63 x 10 <sup>-3</sup>	9.25
0.300	0.23 x 10 <sup>-3</sup>	2.77 x 10 <sup>-3</sup>	9.33
0.250	0.17 x 10 <sup>-3</sup>	2.83 x 10 <sup>-3</sup>	9.41
		Mean	9.66

mean value obtained at 560 mμ is 9.55, and at 600 mμ it is 9.71. These values are in relatively good agreement with the mean at 520 mμ. The overall mean value of all the calculations is 9.66, the same value as obtained at 520 mμ.

#### DISCUSSION

The equilibrium constant determined refers to the reaction:



where K<sub>f</sub> is the product of (k<sub>1</sub>k<sub>2</sub>k<sub>3</sub>). It is interesting to compare the results obtained to the results reported for some other complexes.

Unfortunately, the overall formation constant (k<sub>1</sub>k<sub>2</sub>k<sub>3</sub>) of the cobalt malonate complex has not been reported. However, it can be predicted to be considerably less than three times 3.72, the value reported by Stock and Davies (1949) for log k<sub>1</sub>. It could be expected that the value would be somewhat less than the value obtained for the dithiolmalonate complex. The work of Christoffersen and Deskin (1959) indicated that the co-ordinating ability of sulfur in the cobalt dithioxalate complex, log K<sub>f</sub> = 11.0, is greater than the coordinating ability of oxygen in the cobalt oxalate complex, log K<sub>f</sub> = 9.7 (Sartori, 1934). As the formation of a complex depends on the ability of the donor atom to donate a pair of electrons to establish a coordinate bond, it would be expected that under similar conditions sulfur, which is a stronger base than oxygen, would form the more stable complex.

A second comparison of the results obtained to the work of Christoffersen and Deskin indicates that the five membered ring of the dithioloxalate complex is more stable than the six membered ring of the dithiolmalonate complex. This can be explained in terms of the bond strain due to the distortion of the normal bond angles of the carbon atom, which is less for a five membered ring in an un-conjugated system than for a six membered ring. This lends sup-

port to the work of Deskin (1958) with these ligands and the nickel (II) ion, for which the same order of stability was observed for the five and six membered rings.

Data on other ligands which form six membered rings with the cobalt (II) ion are very sparse. The formation constant ( $k_1k_2$ ) for cobalt 1,3-aminopropionic acid was reported by Albert (1950). From his value ( $\log\beta_2 \sim 7$ ) it might be predicted that the overall constant ( $k_1k_2k_3$ ) is of the same order of magnitude as that of the dithiolmalonate complex, since the structures are roughly similar and the 1,3-aminopropionic acid has as donor atoms a more basic nitrogen atom and a less basic oxygen atom.

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