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Studies of Complexes of the Transition Metals. V. Copper Complex with Dithiolmalonate¹

WILLIAM A. DESKIN² AND PERRY L. WEIGEL

Abstract. The copper (II) ion and the dithiolmalonate ion form a complex with an absorption maximum in the ultraviolet region (275 $m\mu$) of the spectrum. The formula of the complex was determined by the methods of varying mole ratio and continuous variation and was found to be $\text{Cu}(\text{DTM})_2 \cdot 2$. The formation constant of the complex was determined by the method of continuous variation and successive dilutions of the stoichiometric proportions of Cu^{+2} and DTM^{-2} . All measurements were made at room temperature with the pH of solutions adjusted at 5.0 ± 0.2 . The ionic strength was controlled at 0.1 by the addition of potassium sulfate.

The dithiolmalonate ion forms complexes with nickel (Deskin, 1958) and cobalt (Brubaker and Deskin, 1960). Earlier work by Robinson and Jones (1912) indicated complexes were also formed by other transition metal ions, including copper (II). The purpose of this research was to determine the molecular formula and the formation constant for the copper dithiolmalonate complex in dilute aqueous solution. A spectrophotometric method was chosen as this complex exhibited an absorption maximum in the near ultraviolet.

EXPERIMENTAL

Materials

A copper (II) solution was prepared from reagent grade cupric sulfate and standardized electrolytically. All solutions were made by diluting the original solution.

The dithiolmalonic acid dipotassium salt (from the work of Brubaker and Deskin, 1960) was prepared by the addition of malonyl chloride to ethanethiol while slowly heating the solution to remove HCl and excess reagents. A solution of potassium hydrosulfide in alcohol was added to the ester and the mixture was allowed to stand. After the precipitate was obtained it was washed in alcohol and dried in a vacuum desiccator. The compound was then analyzed for potassium and sulfur. The experimental results were 36.01% potassium and 30.28% sulfur as compared to the calculated values of 36.82% and 30.20%, respectively.

Solutions

Each solution was prepared with freshly boiled distilled water.

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Before each measurement the dithiolmalonate solution was prepared, the ionic strength was controlled at 0.1 with potassium sulfate, the pH was adjusted to 5.0 ± 0.2 , and the solution was then immediately spectroanalyzed.

Absorption Measurements

The absorption measurements were made on a Beckman model DU Quartz spectrophotometer, using a hydrogen lamp and silica cells with a path length of 10.00 ± 0.01 mm. All readings were made at room temperature.

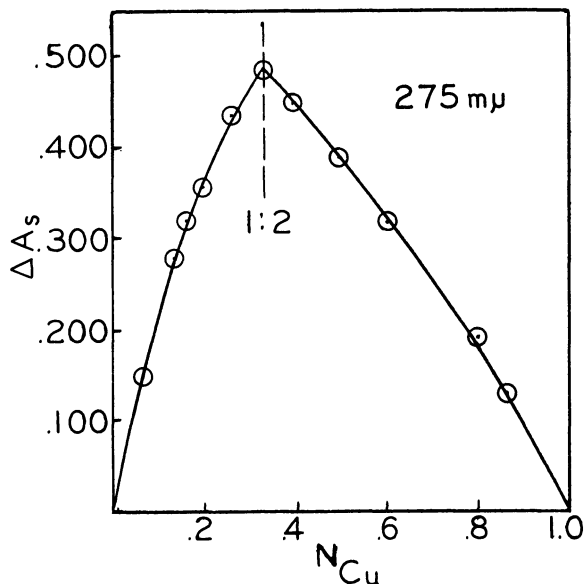


Figure 1. Continuous variation plot for the copper-dithiolmalonate complex.

EXPERIMENTAL RESULTS

Molecular Formula

The molecular formula was determined by the varying mole ratio method (Yoe and Jones, 1944) and was confirmed by the method of continuous variation (Job, 1928, 1936). Figure 1 shows a plot of the experimental data. There was a considerable correction for the absorption of DTM in the ultraviolet region. This was determined by running spectra of DTM in different concentrations and plotting the spectra. Both methods show the formation of a complex with a 2:1 mole ratio of DTM to Cu. In Figure 1, ΔA_s was plotted against mole fraction of Cu.

Formation Constant

The concentration formation constant was determined by com-

binning Figure 1 with a plot of the absorbance of solutions which were dilutions of the stoichiometric proportions of ligand and copper ion in a ratio of 2:1. 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 reagents. The following equation was used for calculations:

$$K_f = \frac{X}{[\text{Cu}_1^{+2} - X] [\text{DTM}_1^{-2} - 2X]^2} = \frac{X}{[\text{Cu}_2^{+2} - X] [\text{DTM}_2^{-2} - 2X]^2}$$

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

The formation constant was determined at 275 m μ and at 300 m μ . The results are given in Table 1. The overall mean value for log K_f was found to be 10.12.

DISCUSSION

The equilibrium constant, K_f, that has been determined refers to the reaction:

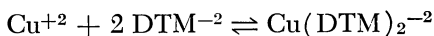


Table 1. Concentration Formation Constants at 25° C.

A _s	[M ₁]	[L ₁]	[M ₂]	[L ₂]	Log K _f	Log K _f
	x 10 ⁵	x 10 ⁵	x 10 ⁵	x 10 ⁵	(M ₁ &L ₁)	(M ₂ &L ₂)
300m μ						
.130	2.10	12.97	2.83	5.66	9.53	9.87
.133	2.10	12.90	2.90	5.80	10.13	9.97
.137	2.18	12.82	2.98	5.96	9.97	9.99
.141	2.25	12.75	3.07	6.14	10.51	9.99
.144	2.33	12.67	3.14	6.28	9.93	9.97
.148	2.40	12.60	3.22	6.44	10.28	10.00
.152	2.48	12.52	3.29	6.58	10.37	10.03
.155	2.55	12.45	3.36	6.72	10.06	10.01
.158	2.63	12.37	3.43	6.86	9.68	9.94
.161	2.70	12.30	3.52	7.04	10.14	9.62
			Mean		10.06	9.94
275m μ						
.265	2.03	12.97	2.56	5.12	10.10	10.48
.273	2.10	12.90	2.64	5.28	10.13	10.47
.306	2.40	12.60	2.95	5.90	10.29	10.51
.322	2.55	12.45	3.11	6.22	9.87	10.42
.380	10.35	4.65	2.71	5.42	10.14	10.40
.276	10.43	4.57	2.67	5.34	9.93	10.26
.268	10.58	4.42	2.58	5.16	9.92	10.29
.263	10.65	4.35	2.54	5.08	10.18	10.45
			Mean		10.07	10.41

and is the product of k_1k_2 for the stepwise formation. Several interesting comparisons may be made with complexes of probably similar structure or ring size.

This complex may be compared with the copper malonate complex. Log K_f for the copper malonate complex has been reported by Davies (1935) to be 8.15 for the 1:2 complex. Ligands that contain sulfur atoms as donors generally form stronger bonds with transition metals than do oxygen atoms. This may be due to the lower electronegativity of sulfur, resulting in the sulfur-containing ligand being more basic. Dwyer and Sargeson (1959) also ascribe this increased stability to the ability of the sulfur to form double bonds.

A second comparison may be made when one considers the copper dithioloalate complex. In the complex with the dithioloalate a six-membered ring is formed, whereas with dithioloalate a five-membered ring is formed. For unconjugated systems, the five-membered ring (copper dithioloalate, $\log \beta_3 = 13.5$) is more stable than a six-membered ring (copper dithioloalate). This has previously been shown to hold for complexes of nickel and cobalt with DTO and DTM (Brubaker and Deskin, 1960).

Other ligands that form six-membered rings which may be compared include 1,3-diaminopropane ($\log K_f = 16.94$; Irving, 1954) and β -alanine ($\log K_f = 12.89$; Li and Doody, 1954). In the case of the greater basicity of the diamine one would expect a more stable complex to be formed. β -alanine, containing a nitrogen donor and an oxygen donor, is intermediate in strength between the more basic diamine and the dithioloalate.

Another interesting fact that should be pointed out is that copper (II) form a 1:2 complex with DTM and was observed to form a 1:3 complex with DTO under about the same conditions, pH 4-5. This may be due to a steric effect in that there is not enough room for three of the larger DTM ions around the copper ion.

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