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Formation Constants for Dithiooxalate Complexes

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The formation constants have been determined for the dithiooxalate complexes of copper (II) and palladium (II) with potassium dithiooxalate. Earlier studies have shown that nickel (II), palladium (II) and platinum (II) form square planar complexes with this ligand. Subsequent work has shown that copper (II) also forms a planar complex with potassium dithiooxalate.

The pH of the solution was adjusted to 9.0 and the absorbance was measured. Spectra suggest that mixed ethylenediamine-dithiooxalate complexes are not formed. The solutions were assumed to contain the species M(en)$_2^{2+}$, Men$_2^{2+}$, en, M(dto)$_2^{2-}$ and dto$_2^{-}$. The extinction coefficients of these species are known and the formation constants of M(en)$_{n}^{2+}$ are available. This information, together with knowledge of the total concentration of metal, ethylenediamine, and dithiooxalate, allows one to solve for the value of $\beta_2$ for the dithiooxalate complex. The calculations were made using a program written for the IBM 1130.

RESULTS AND DISCUSSION

The formation constant was determined for copper (II) with the dithiooxalate ligand. Spectral measurements were made at 396 nm for a series of solutions where the concentrations of the ligands were varied over a five-fold range. The equilibration reaction

$$\text{Cu}^{2+} + 2 \text{dto}^{2-} = \text{Cu}^{2+} + 2 \text{dto}^{2-}$$

was approached from both directions. The results of some 20 measurements gave for $\text{Cu}^{2+}$ and $\text{dto}^{2-}$, $\log \beta_2 = 20.0 \pm 0.2$. The extinction coefficient for $\text{Cu}^{2+}$ is 8900 1 mole$^{-1}$ cm$^{-1}$.

In the study of the palladium (II) complex with dithiooxalate, it was found that we could only study the equilibrium from one direction. The equilibrium

$$\text{Pd}^{2+} + 2 \text{dto}^{2-} = \text{Pd}^{2+} + 2 \text{dto}^{2-} + 2 \text{en} + 2 \text{ts}^{-}$$

proceeded at a reasonable rate. The reverse reaction, in which the palladium (II) complex with dithiooxalate exchanges with ethylenediamine, did not proceed rapidly enough to make quantitative measurements for the formation constants. Some solutions were still changing in absorbance after 24 hours, and over this period of time the dithiooxalate ligand was decomposing.

The results of some 20 solutions in which the potassium salt of dithiooxalate was added to the palladium (II) complex of ethylenediamine (equation 3) gave a log $\beta_2$ for $\text{Pd}^{2+}$ and $\text{dto}^{2-}$ of 29. The extinction coefficient at 380 nm for $\text{Pd}^{2+}$ is 6700 1 mole$^{-1}$ cm$^{-1}$. However, it should be pointed out that this method is based on a reliable value for the formation constant of $\text{Pd}^{2+}$ and $\text{dto}^{2-}$ (6). Some early work (7) reports a log $\beta_2$ of 26.9. Subsequent research on the $\text{Pd}^{2+}$ complex set a lower limit on $\log K_2$ of 20 and reports $\log K_2 = 18.4$. In our work we require a value for $K_2$ of $\geq 10^{18.4}$.

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for log $\beta_2$ for the Pd(dto)$_2^{2-}$ complex. This is most interesting in that it is thermodynamically one of the most stable complexes which has been reported.

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**LITERATURE CITED**