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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) at a constant ionic strength of 0.2 *M* (sodium perchlorate). The following values are reported: for the $Cu(dto)_2^{2-}$ complex log $\beta_2 = 20.0 \pm 0.2$, for the $Pd(dto)_2^{2-}$ complex log $\beta_2 = 28.9 \pm 0.5$.

Recent studies in our laboratories have been made to determine the formation constants for complexes of copper (II) and palladium (II) with potassium dithiooxalate. Earlier studies (1) have shown that nickel (II), palladium (II) and platinum (II) form square planar complexes with this ligand. Subsequent work (2) has shown that copper (II) also forms a planar complex with potassium dithiooxalate.

EXPERIMENTAL

The metal salts used in this research were reagent grade. The solutions were prepared using distilled water which had been passed through a mixed bed ion exchange column. Solutions of the metal salts were analyzed by standard gravimetric methods. The ionic strength of all solutions was adjusted to 0.2 *M* by addition of the appropriate amount of sodium perchlorate. Ethylenediamine was purified by refluxing with zinc dust and distilled. Potassium dithiooxalate, K_2dto (Eastman Kodak) was purified by a published method (3). The salt bis-ethylene-diaminepalladium (II) p-toluenesulphonate, $Pd(en)_2(ts)_2$, was prepared by a published method (4). Anal. calcd. for $C_{18}H_{30}N_4O_6S_2Pd$: Pd, 18.7. Found: Pd, 18.4.

Spectra

All spectra were recorded on a Beckman DK-2A spectrophotometer.

Formation Constants

The β_2 values of the metal dithiooxalate complexes were determined in water at 25° and an ionic strength of 0.2 *M* (sodium perchlorate). The method (5) used was a competitive reaction between ethylenediamine and dithiooxalate for coordination sites on the metal ion. Concentrations of the species in the reaction were adjusted

$$M(en)_2^{2+} + 2\ dto^{2-} = M(dto)_2^{2-} + 2\ en \qquad (1)$$

so that the equilibration reaction proceeded only part way. 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+}, 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 (6). This information, together with knowledge of the total concentration of metal, ethylenediamine, and dithiooxalate, allows one to solve for the value of β_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

$$Cu(en)_2^{2+} + 2\ dto^{2-} = Cu(dto)_2^{2-} + 2\ en \qquad (2)$$

was approached from both directions. The results of some 20 measurements gave for $Cu(dto)_2^{2-}$, log $\beta_2 = 20.0 \pm 0.2$. The extinction coefficient for $Cu(dto)_2^{2-}$ is 8900 l 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

$$Pd(en)_2(ts)_2 + 2\ dto^{2-} = Pd(dto)_2^{2-} + 2\ en + 2\ ts^{-} \quad (3)$$

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 β_2 for $Pd(dto)_2^{2-} = 29$. The extinction coefficient at 380 nm for $Pd(dto)_2^{2-}$ is 6700 l mole^{-1} cm^{-1}. However, it should be pointed out that this method is based on a reliable value for the formation constant of $Pd(en)_2^{2+}$. Some early work (7) reports a log β_2 of 26.9. Subsequent research on the $Pd(en)_2^{2+}$ complex (4) sets a lower limit on log K_1 of 20 and reports log $K_2 = 18.4$. In our work we require a value for K_2 and β_2. For the above calculation of log β_2 for the $Pd(dto)_2^{2-}$ complex, we have used the value reported by Jørgensen (4) for K_2 and the β_2 of Mellor and Maley (7). Thus our value is certainly a lower limit. Using the values of Jørgensen to set a lower limit for β_2, our value would be greater than 40

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for log β_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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