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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 β_2 = 20.0 ± 0.2, for the Pd(dto)_2^2- complex log β_2 = 28.9 ± 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 of the metal salts were analyzed by a published method (3). The salt bis-ethylene-diaminopalladium (II) p-toluenesulphonate, Pd(en)_2^2 ts^- was prepared by a published method (4). Anal. Calcd. for C_{18}H_{30}N_{4}O_{6}S_{2}Pd: 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^- = M(dto)_2^2- + 2 en

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)_2^2+ 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^- = Cu(dto)_2^2- + 2 en

was approached from both directions. The results of some 20 measurements gave for Cu(dto)_2^2-, log β_2 = 20.0 ± 0.2. The extinction coefficient for Cu(dto)_2^2- 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 equilibration from one direction. The equilibrium

Pd(en)_2^2 + 2 dto^- = Pd(dto)_2^2^- + 2 en + 2 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 β_2 for Pd(dto)_2^2^- = 29. The extinction coefficient at 380 nm for Pd(dto)_2^2^- 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 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_2 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 $\beta_2$ 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