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Synthesis and Characterization of a Mixed Ligand Complex of Copper(I) with 2,9-Dimethyl-1,10-phenanthroline and Cyanide

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Abstract

Copper(I) reacts with cyanide and 2,9-dimethyl-1,10-phenanthroline, (dmp), to form the mixed ligand complex, $Cu(dmp)(CN)_2^-$, which can be extracted from aqueous solutions into chloroform as an ion association complex with the tetrabutylammonium ion, $(C_4H_9)_4N^+$. Orange–red crystals of the ion association complex have been isolated and the single crystal X-ray structure of the complex has been determined. The mixed ligand complex is formed by the reaction of $Cu(dmp)_2^+$ with CN^- or by the reaction of $Cu(CN)_4^{3-}$ with dmp. The displacement constant, K_{d_1} for the reaction: $Cu(CN)_4^{3-} + dmp \rightleftharpoons Cu(dmp)(CN)_2^- + 2\ CN^-$ has been determined. The calculated value for the displacement constant K_{d_2}, for the reaction: $Cu(dmp)(CN)_2^- + dmp \rightleftharpoons Cu(dmp)_2^+ + 2\ CN^-$, cannot be reconciled with the observation that dmp readily displaced two cyanide ions from the mixed ligand complex.

Introduction

The spectrophotometric determination of copper(I) is a well-established method that is based on the formation of the orange–yellow complex, $Cu(dmp)_2^+$, ($\lambda_{max} = 457$ nm; $\epsilon = 7000$ l mol^{-1} cm^{-1} at 457 nm) where dmp is the bidentate ligand 2,9-dimethyl-1,10-phenanthroline [1, 2]. It was observed that the addition of small amounts of CN^- to an aqueous solution of $Cu(dmp)_2^+$ decreased the absorbance of the solution at 457 nm, presumably due to the displacement of one of the bidentate ligands by CN^- and the formation of the mixed ligand complex, Cu(dmp)(CN). Initial attempts to exploit this reaction for the determination of low levels of CN^- in ethanol–water solutions were successful, in the range of 0.5–10 ppm CN^- [3]. The mixed ligand complex has been synthesized either by the reaction of CuCN with dmp or by the reaction of CN^- with $Cu(dmp)^+$. An X-ray structure determination [4] has shown that Cu(dmp)(CN) consists of a one-dimensional zig-zag chain of copper(I) linked by the ambidentate ligand, CN^-. Each copper(I) is four-coordinate; two of the coordination positions in the distorted tetrahedron are occupied by the nitrogen atoms of the chelating agent, dmp, and the two remaining positions by a carbon atom and a nitrogen atom from two CN^- groups.

On the basis of the above reactions, it was suggested that it should be possible to determine the concentration of copper(I) in electroless copper plating baths by the reaction of dmp with the copper(I) species that are present in these plating solutions [5]. The addition of CN^- to the plating solution stabilizes the copper(I) as $Cu(CN)_2^-$ and the reaction of dmp with $Cu(CN)_2^-$ should result in the formation of a stable mixed ligand complex of copper(I), CN^- and dmp. It was decided, therefore, to investigate the reaction of $Cu(CN)_2^-$ with dmp and to establish the conditions under which the mixed ligand complex, if formed, could be extracted into an organic solvent [6]. It was evident that under the conditions that were employed in the electroless plating of copper, the $Cu(CN)_2^-$ species is present in relatively low concentrations and that it would be necessary to carry out a preconcentration of the copper(I) complex before attempting to determine the copper(I) complex in solution. The method that was selected was the extraction of the mixed ligand complex of copper(I), CN^- and dmp, $Cu(dmp)(CN)_2^-$, as an ion association complex with a tetrabutylammonium salt. The copper(I) complex is concentrated into a small volume in the extraction step; hence the concentration levels of copper(I) that can be determined are lowered by at least a factor of 100. In order to establish the feasibility of the proposed analytical method we have synthesized the ion association complex, $(C_4H_9)_4N[Cu(dmp)(CN)_2]$ and investigated its properties.

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Experimental

Synthesis of $(C_4H_9)_4N[Cu(dmp)(CN)_2]$

A 1:1 aqueous methanol solution (15 ml) containing 8 mmol of tetrabutylammonium hydroxide, $(C_4H_9)_4NOH$, was cooled to 0 °C, and HCN gas, prepared by the reaction of NaCN with H_2SO_4, was passed through this cooled solution with the aid of a nitrogen gas stream. After about 15 min, 4.5 mmol (0.41 g) of CuCN and 4.5 mmol (0.94 g) of 2,9-dimethyl-1,10-phenanthroline, (dmp), were added to the solution and the mixture was stirred with the aid of a magnetic stirrer for about 30 min until all the solid material had dissolved. The resulting yellow solution was extracted with 30 ml of chloroform. Upon the addition of 200 ml of cyclohexane to this extract, a dark red oil which was formed was separated, dried in a stream of nitrogen gas and dissolved in 30 ml of chlorobenzene. The oil was reprecipitated when 150 ml of benzene was added. This procedure of dissolution in chlorobenzene and precipitation by the addition of benzene was repeated several times to purify the reaction product. Finally, the dark red oil ($\approx$3 g) was covered with a 1:1 mixture of chlorobenzene and benzene, and upon standing for a few hours, orange–red crystals were formed in the layer of the dark red oil.

An alternative method was devised for the synthesis of the ion association complex. Perchloric acid (2 ml 2 M) was added to 4 ml of methanolic Bu_4NOH (1 M) and 4 ml of aqueous KCN was added to the reaction mixture. The $KClO_4$ that was formed was separated by filtration and 3 mmol CuCN (0.27 g) and 3 mmol of dmp (0.62 g) were added to the filtrate and stirred for about 1 h until all the CuCN had dissolved. Twenty ml of water was added to the reaction mixture and the ion association complex, $Bu_4N\cdot[Cu(dmp)(CN)_2]$ was extracted with 30 ml of chloroform. The dark red oil that was obtained by the addition of cyclohexane to the chloroform solution was washed repeatedly with benzene. The oil was dissolved in chlorobenzene and upon the addition of benzene, orange–red crystals of the ion association complex were obtained. These crystals were stored in a benzene solution of $Bu_4N\cdot CN$, prepared by the reaction of $Bu_4N\cdot OH$ with $HClO_4$ and KCN. Degradation of the crystals by the loss of HCN from the crystal surface was prevented by storing the crystals in this manner.

Crystal Data and Structure Determination

Red crystals of the ion association complex, $(C_4H_9)N^+\cdot Cu(dmp)(CN)_2^-\cdot 3H_2O$, $M_r = 620.2$, were obtained by slow cooling of a solution of the complex and tetrabutylammonium cyanide in a benzene–chlorobenzene solution. A crystal was mounted in a glass capillary with a small crystal of sodium cyanide. Sodium cyanide and water vapor in the capillary maintained a low vapor pressure of HCN around the crystal which prevented deterioration of the single crystal. A Nicolet-Syntex $P2_1$ diffractometer was used for the data collection with Mo Kα radiation ($\lambda = 0.71073$ Å). The lineshapes of the different spots indicated that there was a flaw in the crystal, the linewidths, however, were less than 0.3°. The cell constants were determined from 25 reflections in the range $21° < 2\theta < 30°$; $a = 11.225 \pm 0.002$, $b = 24.970 \pm 0.004$, $c = 13.267 \pm 0.002$ Å, $V = 3590.4$ Å^3; space group $P2_1/n$, ($h0l$:$h + l = 2n$ and $0k0$:$k = 2n$) $D_m = 1.17$ g cm^{-3}, $D_c = 1.15$ g cm^{-3}. The $2\theta/\theta$ scan method with a variable scan rate from 2° to 8°/min was used to collect the data ($h = 0$ to 10, $k = 0$ to 24, $l = -12$ to 12). Three standard reflections that were collected after every 46 reflections had a standard deviation of 0.6%. The linear absorption coefficient was 6.4 cm^{-1}. An absorption correction was not attempted. Of the 3720 reflections that were collected, 3153 were unique and not systematically absent.

The Patterson method was used to determine the positions of the copper atoms and one of the dimethylphenanthroline nitrogen atoms. The remaining carbons and nitrogens were found with successive difference maps. Most of the remaining electron density is probably due to partially occupied interstitial water molecules. The position of the hydrogen atoms were calculated assuming either a trigonal or tetrahedral coordination about the carbon atoms with a C–H bond distance of 0.95 Å. A full-matrix least-squares refinement of 166 parameters was carried out with 1811 reflections greater than 3σ. The copper atom was refined anisotropically. The hydrogen coordinates were not refined. With two oxygen atoms included interstitially at unit occupation, $R = 0.124$ and $R_w = 0.172$.

The infrared spectrum of the ion association complex in KBr was obtained with a Perkin-Elmer Model 398 infrared spectrophotometer. The frequencies (cm^{-1}) of the principal bands are: 3420(vs, broad); 3040(vw); 3020(vw); 2920(vs); 2600(s); 2084(shoulder); 2066(vs); 1630(m); 1570(m); 1490(s); 1475(s); 1450(s); 1370(m); 1350(m); 1140(m); 1020(m); 850(s); 720(m); 680(m); 550(m).

Reaction of $Cu(dmp)_2^+$ *with* CN^-

A standard solution of $Cu(dmp)_2^+Cl^-$, (2.50×10^{-4} M) was prepared by the reduction of $CuCl_2\cdot 2H_2O$ with copper metal in the presence of dmp in a 1:1 aqueous methanol solution. Aliquots of this standard solution were mixed in varying proportions with a 2.50×10^{-4} M solution of KCN in 1:1 aqueous methanol, and the absorption spectra of the resulting solutions were recorded. The decrease in the absorbance at 458 nm with the increase in the mole fraction of CN^-, $n_{CN^-}/(n_{CN^-} + n_{Cu^+})$, as shown in Fig. 1 corresponds to the decrease in

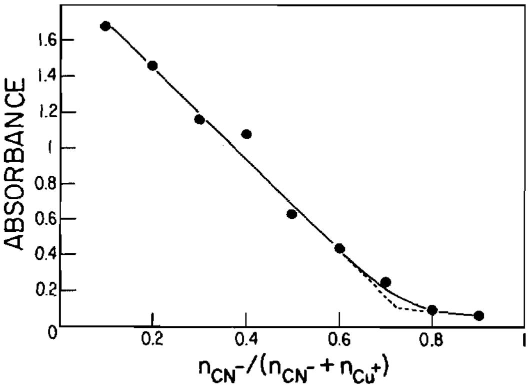

Fig. 1. Variation of the absorbance at 458 nm with the mole fraction of CN^- in 1:1 aqueous methanol solutions.

the concentration of $Cu(dmp)_2^+$. The complex that is formed (eqn. (1)) has a copper(I):CN^- mole ratio of 1:2.

$$Cu(dmp)_2^+ + 2CN^- \rightleftharpoons Cu(dmp)(CN)_2^- + dmp \quad (1)$$

Reaction of $Cu(CN)_4^{3-}$ with dmp

Solutions of $Cu(CN)_4^{3-}$ (2.50×10^{-3} M) and dmp (2.50×10^{-3} M), in 1:1 aqueous methanol were mixed in varying ratios. The absorption spectra of the resulting solutions, in each of which the total concentration of CN^- was 1.50×10^{-2} M, were recorded. A plot of the absorbance at 375 nm *versus* the mole fraction of dmp, $n_{dmp}/(n_{dmp} + n_{Cu^+})$, is shown in Fig. 2. The increase in the absorbance at 375 nm corresponds to an increase in the concentration of $Cu(dmp)(CN)_2^-$.

Results and Discussion

The mixed ligand complex of copper(I), dmp and CN^-, $Cu(dmp)(CN)_2^-$, was isolated as an ion association complex with the tetrabutylammonium ion, $(C_4H_9)_4N^+$. The orange–red crystals of the ion association complex are soluble in alcohols and halogenated hydrocarbons and can be extracted very efficiently with chloroform from aqueous solutions. The orange–red crystals decompose readily in air or in aqueous solutions with the loss of HCN and the formation of the insoluble copper(I) complex, Cu(dmp)(CN), which has been synthesized and characterized previously [4]. The loss of HCN can be minimized if the orange–red crystals of the ion association complex are formed in a chloroform solution containing tetrabutylammonium cyanide.

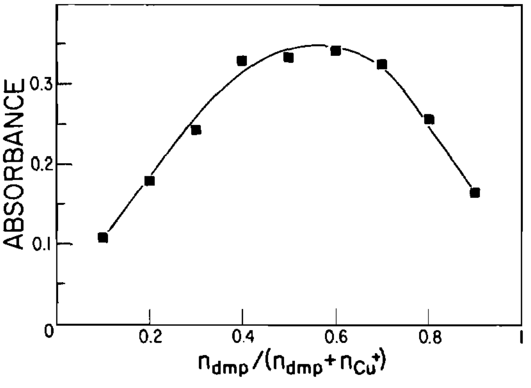

Fig. 2. Variation of the absorbance at 375 nm with the mole fraction of dmp in 1:1 aqueous methanol solutions. The total concentration of CN^- in each solution is 1.50×10^{-2} M.

The structure of the copper(dmp)$(CN)_2^-$ anion is shown in Fig. 3. Table I contains bond lengths and bond angles for the anion only. Figure 4 shows the relative position of the copper complex to the tetrabutylammonium cation. Figure 5 is a stereo view of the unit cell. The Cu(I) in $Cu(dmp)(CN)_2^-$ exists in a distorted tetrahedral environment consisting of two dimethylphenanthroline nitrogens and two cyanide carbons. The bond lengths in the copper complex are very similar to those found for the polymeric $[Cu(dmp)(CN)]_n$. The N(1)–Cu–N(10) bond angle is 78.3° which is similar to the value of 79.1° that was found for the monocyano complex.

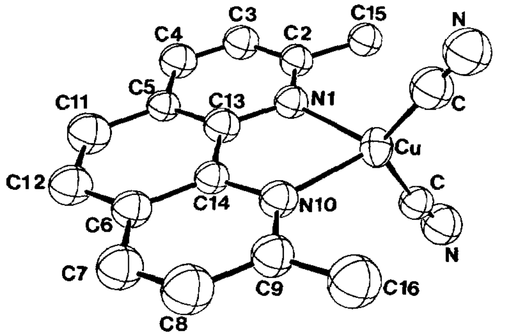

Fig. 3. ORTEP plot of $Cu(dmp)(CN)_2^-$.

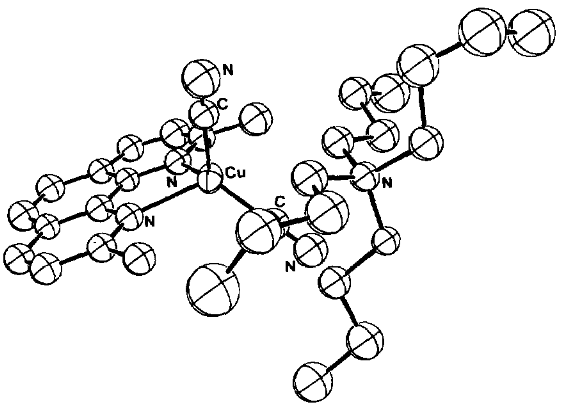

Fig. 4. ORTEP plot of the ion association complex $[Cu(dmp)(CN)_2^-] \cdot N(C_4H_9)_4^+$.

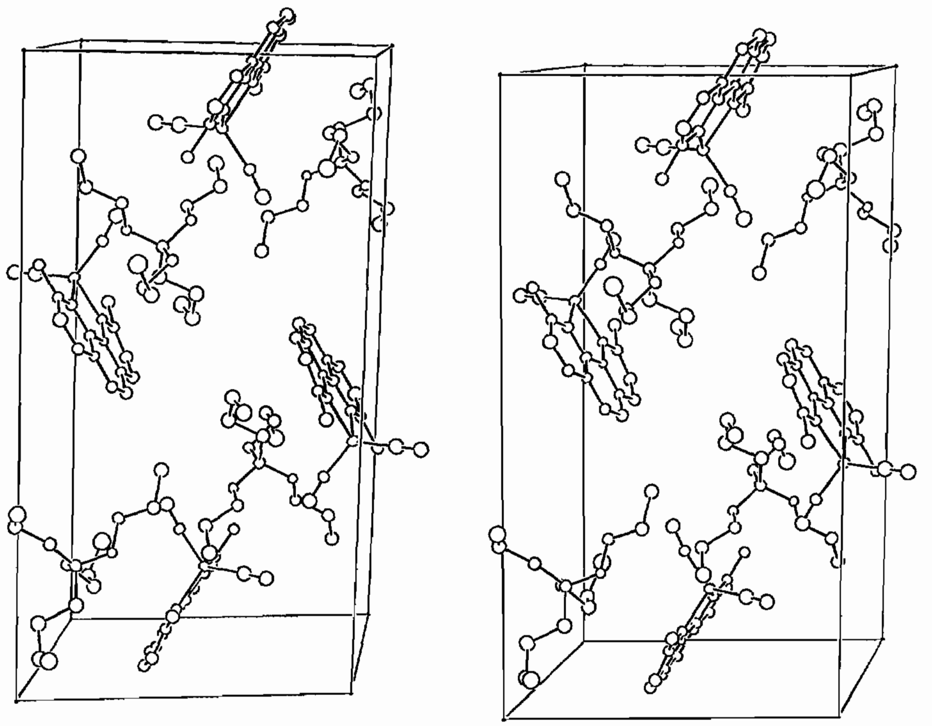

Fig. 5. Stereo view of the monoclinic unit cell.

The most substantial difference between the two coordination spheres is the angle between the cyano groups. For the dicyano complex the C–Cu–C angle is 126°, while the angle between the ambidentate cyanides in the monocyano complex is 119°. The presence of the tetrabutylammonium ion with the dicyano complex probably results in very different packing forces between the anionic copper complex and the tetrabutylammonium cation. The dihedral angle between the plane containing the two cyano groups and the dimethylphenanthroline is 78.7°. This angle is not substantially different from the value of 84.1° found in $[Cu(dmp)(CN)]_n$.

TABLE I. Bond Lengths (Å) and Angles (°) in [Cu(dmp)-(CN)] and $[Cu(dmp)(CN)_2^-]$

	$[Cu(dmp)(CN)]_n$[a]	$[Cu(dmp)(CN)_2]^-$
Cu–N(1)	2.121	2.12
Cu–N(10)	2.131	2.15
Cu–C	1.897	1.93, 1.98
Cu–N	2.008	
C–N	1.15	1.13, 1.15
N(1)–Cu–N(10)	79.1	78.3
N(1)–Cu–C	125.9	103, 118
N(1)–Cu–N	107.5	
N(10)–Cu–C	116.0	109, 113
C–Cu–C		126
C–Cu–N	111.9	

[a] The values for $[Cu(dmp)(CN)]_n$ are taken from ref. 4.

The arrangement of butyl groups around the central N is that of a slightly distorted tetrahedron. The C–N–C angles range from 103° to 113°. The C–C–N angles range from 113 to 115° and the remaining C–C–C angles are between 107° and 119°.

Copper(I) in the presence of CN^- and dmp can be extracted from an aqueous solution with a chloroform solution of tetrabutylammonium bromide, $Bu_4N \cdot Br$. Before extraction, the aqueous solution has an absorption maximum at 360 nm. In methanol, this absorption maximum shifts to 375 nm and in chloroform, the maximum shifts to 405 nm (Fig. 6).

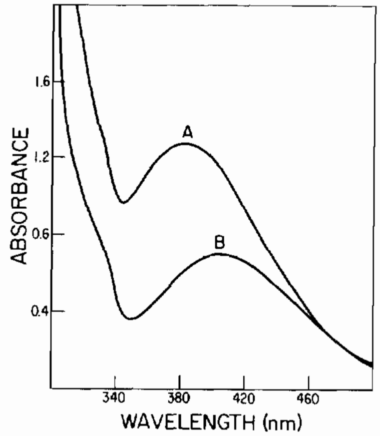

Fig. 6. Absorption spectrum of the ion association complex $Bu_4N[Cu(dmp)(CN)_2]$ (7.26×10^{-4} M): A, in chloroform; B, in methanol containing 3% *v*/*v* chloroform.

The orange–red crystals of the ion association complex, $Bu_4N^+ \cdot [Cu(dmp)(CN)_2^-]$ have the identical maxima in methanol and chloroform solutions. The large shifts in the absorption maxima may be caused by variations in the number and type of molecules that are coordinated to the copper(I) in the different solvents.

The continuous variation method that was employed for investigating the reaction of $Cu(dmp)_2^+$ with CN^- showed that the ratio, copper(I):CN^- was 1:2 in the mixed ligand complex that was formed (Fig. 1). When the reaction of $Cu(dmp)_2^+$ with dmp was investigated by the same method (Fig. 2) the ratio, copper(I):dmp, was approximately 1:1. The broad maximum and hence the uncertainty in the location of the maximum and the corresponding mole fraction can be attributed to the presence of several competing equilibria in solution. The principal equilibrium however, that is established in solution is

$$Cu(CN)_4^{3-} + dmp \rightleftharpoons Cu(dmp)(CN)_2^- + 2CN^- \qquad (2)$$

and the equilibrium constant for this displacement reaction is given by

$$K_{d_1} = \frac{[Cu(dmp)(CN)_2^-]\,[CN^-]^2}{[Cu(CN)_4^{3-}]\,[dmp]} \qquad (3)$$

The two cyanide ions in the mixed ligand complex can also be displaced by dmp

$$Cu(dmp)(CN)_2^- + dmp \rightleftharpoons Cu(dmp)_2^+ + 2CN^- \qquad (4)$$

and the equilibrium constant for this displacement reaction is given by

$$K_{d_2} = \frac{[Cu(dmp)_2^+]\,[CN^-]^2}{[Cu(dmp)(CN)_2^-]\,[dmp]} \qquad (5)$$

The value of K_{d_1} can be obtained from the results shown in Fig. 2. At the maximum in the continuous variation plot (Fig. 2)

$$[Cu(dmp)(CN)_2^-] = \frac{0.334}{1750} \qquad (6)$$

where 1750 l mol^{-1} cm^{-1} is the molar absorptivity of the mixed ligand complex at 375 nm and 0.334 is the absorbance of the solution when the mole fraction of dmp, $n_{dmp}/(n_{dmp} + n_{Cu^+})$, is 0.5, or the copper(I):dmp mole ratio is 1:1. The mass balance equations for dmp, copper(I) and CN^- are

$$[dmp] = 0.5 \times 2.50 \times 10^{-3} - [Cu(dmp)(CN)_2^-] = 1.06 \times 10^{-3}\ M \qquad (7)$$

$$[Cu(CN)_4^{3-}] = 0.5 \times 2.50 \times 10^{-3} - [Cu(dmp)(CN)_2^-] = 1.06 \times 10^{-3}\ M \qquad (8)$$

$$[CN^-] = 1.50 \times 10^{-2} - 4[Cu(CN)_4^{3-}] - 2[Cu(dmp)(CN)_2^-] = 1.04 \times 10^{-2}\ M \qquad (9)$$

Hence, the value of K_{d_1} (eqn. (3)), obtained from eqns. (6)–(9) is 0.02. The uncertainty in this equilibrium constant of ±0.01 is dependent on the uncertainty in the location of the maximum in Fig. 2.

It is of interest to examine the overall formation constants that have been reported for the copper(I) complexes, $Cu(CN)_4^{3-}$ and $Cu(dmp)_2^+$. The values of $\log \beta_4$ that have been reported for the tetracyano complex of copper(I) vary between 28 and 31 [7, 8]. The value of $\log \beta_2$ that has been reported for the formation of the bis complex of dmp and copper(I) in 50% *v*/*v* dioxane–water is 19.1. On the basis of these values, the calculated value for the overall displacement constant, K_d, for the reaction

$$Cu(CN)_4^{3-} + 2dmp \overset{K_d}{\rightleftharpoons} Cu(dmp)_2^+ + 4CN^- \qquad (10)$$

lies between 10^{-9} and 10^{-12}. This estimated value of K_d is much too small and cannot be reconciled with the following experimental observations: the mixed ligand complex, $Cu(dmp)(CN)_2^-$ is formed by the displacement of two cyanide ions in the complex, $Cu(CN)_4^{3-}$, by dmp, and the equilibrium constants for this displacement reaction was found to be 0.02 ± 0.01. The ligand, dmp, will also readily displace the remaining cyanide ions from the mixed ligand complex

$$Cu(dmp)(CN)_2^- + dmp \overset{K_{d_2}}{\rightleftharpoons} Cu(dmp)_2^+ + 2CN^-$$

This displacement constant must, therefore, be large and must be much greater than the values $10^{-9}/(0.02 \pm 0.01) = 5 \times 10^{-8}$, or $10^{-12}/(0.02 \pm 0.01) = 5 \times 10^{-11}$, that are calculated from K_{d_1} and K_d. From this work, it may be concluded that the formation constant of the bis complex of dmp and copper(I) must be much greater than $10^{19.1}$.

Acknowledgement

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References

1 G. F. Smith and W. H. McCurdy, *Anal. Chem., 24,* 371 (1952).

2 A. A. Schilt, 'Analytical Applications of 1,10-Phenanthroline and Related Compounds', Pergamon Press, Oxford, 1969.

3 N. Scott, *Ph.D. Dissertation,* University of Arizona, 1984.

4 G. O. Morpugo, G. Dessy and V. Fares, *J. Chem. Soc., Dalton Trans.*, 785 (1984).

5 S.U.R. Contract No. 446, IBM Corp., Endicott, N.Y. 13760, 1984.

6 E. Shemesh, *M.S. Thesis,* University of Arizona, 1986.

7 S. Suzuki, *Sci. Reports Res. Inst., A5,* Tohoku University, 1953.

8 B. R. James and R. J. P. Williams, *J. Chem. Soc.*, 2007 (1961).