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A Study on the Complexation of Copper(II) Ion with 2,2-Bis(hydroxymethyl)-2,2′,2″-nitrilotriethanol in Aqueous Solution

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The complex formation from Cu(II) ion and 2,2-bis(hydroxymethyl)-2,2′,2″-nitrilotriethanol (Bistris) in aqueous solution has been studied potentiometrically and spectrophotometrically. Bistris (L) coordinates to Cu(II) as tridentate. The complex CuL^{2+} undergoes deprotonation in neutral and basic media. The deprotonated complexes involve metal-alcoholate coordinate bond in stable chelate structures.

Introduction

Tris(hydroxymethyl)aminomethane (Tris) and bis(2-hydroxyethyl)imino-tris(hydroxymethyl)methane (Bistris) are used extensively as buffer materials in the studies of biochemical systems. Bistris was first synthesized in 1966.[1] The thermodynamic parameters of Bistris have been reported.[2~4] The stability constants of complexes formed by the combination of the neutral Bistris and some transition and nontransition metal ions have been determined by potentiometric and spectrophotometric methods by Scheller *et al.*[5] The complex formation from Bistris and alkaline earth metals have been studied by Sigel *et al.*[6]

However, the complex formation between Bistris and metal ions where the hydroxyl proton of the coordinated ligand is displaced by the metal has not been investigated. In the present study, the various complexes formed from Bistris and Cu(II) ion in wide pH ranges have been studied potentiometrically and spectrophotometrically.

Experimental

Bistris used in this study was the '99+ %' grade from Aldrich Chemical Company. It was dried for 24 hours at 80 ℃ before use. All the other chemicals used were of reagent grade. The Cu(II) nitrate solution was standardized by complexometry. Twice-recrystalized potassium nitrate was used to maintain ionic strength.

In all experiments the hydrogen ion activity was measured with Orion Research EA-940 expandable ion analyzer and Ross 81-01 combination electrode. The pH meter was calibrated with phthalate and phosphate buffers. The hydrogen ion concentration was obtained from the measured pH by using the activity coefficient at the ionic strength used here.[7] The hydroxide ion concentration was obtained by using the value of 13.78 for pKw of water.[8]

Solutions of Bistris and hydrochloric acid were titrated with standard sodium hydroxide solution in the presence and absence of Cu(II) ion. All titrations were carried out at 25 ℃ using 50 mL test solutions. The ionic strength was kept at 0.1 M with KNO_3. The titrant was 0.966 M NaOH. A 2-mL Gilmont buret was used. The electronic absorption spectra were taken with Perkin Elmer Model 551S spectro-

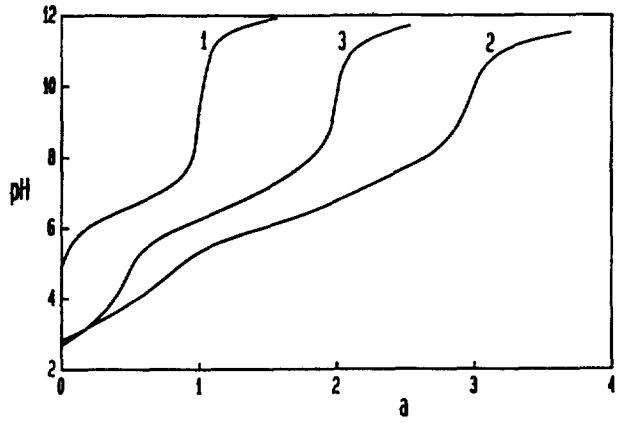

Figure 1. Potentiometric equilibrium curves of Bistris and its Cu(II) complex systems. The initial concentrations are: Curve 1: 20.0 mM in Bistris and 19.8 mM in HCl. Curve 2: 9.89 mM in $Cu(NO_3)_2$, 10.0 mM in Bistris and 9.93 mM in HCl. Curve 3: 9.89 mM in $Cu(NO_3)_2$, 20.0 mM in Bistris and 19.8 mM in HCl.

photometer using 1-cm quartz cells. In Figure 1 and elsewhere, 'a' is the number of moles of NaOH added from the buret divided by the number of moles of HCl initially present in the solution.

Results and Discussion

The Bistris-HCl equilibrium curve is shown in Figure 1, Curve 1. In the reaction

$$HL^+ \rightleftharpoons H^+ + L \qquad K_a=[H^+][L]/[HL^+]$$

L represents the neutral Bistris. The value of K_a obtained from this curve is given in Table 1. The values reported for pK_a are 6.46,[1] 6.48[2,3] and 6.41[9] at zero ionic strength, and 6.56 at 0.1 and 6.72 at 1.0 ionic strength,[5] all at 25 ℃. It is seen from Figure 1, Curve 1, that no proton dissociates from Bistris itself even at very high pH.

The 1 : 1 and 1 : 2 Cu(II)-Bistris titration curves are shown in Figure 1, Curves 2 and 3, respectively. The final inflection points of these curves do not fall at the same 'a' value as Curve 1. This indicates that additional protons are dissociated from the complex. The reactions taking place between Cu(II) and Bistris in these solutions are shown below.

$$Cu^{2+} + L = CuL^{2+} \qquad K_1=[CuL^{2+}]/[Cu^{2+}]/[L]$$
$$CuL^{2+} = CuLH_{-1}^{+} + H^+ \qquad K_{1A}=[CuLH_{-1}^{+}][H^+]/[CuL^{2+}]$$
$$CuLH_{-1}^{+} = CuLH_{-2} + H^+ \qquad K_{1B}=[CuLH_{-2}][H^+]/[CuLH_{-1}^{+}]$$

In these expressions the negative subscript to H indicates the number of protons removed from the complex CuL^{2+}.

The constant K_1 was evaluated from the 1 : 1 Cu(II)-Bistris data (Figure 1, Curve 2) in the early part and is given in Table 1. The same value was obtained from the 1 : 2 data (Figure 1, Curve 3). The complex CuL_2^{2+} did not appear to form in any appreciable amount even in the 1 : 2 Cu(II)-Bistris system. The Bjerrum plot ($\bar{n}$ *vs.* log[L]) was distorted above $\bar{n}=1$. The shape was very much like those in Figure 1 of ref. 10 for Ni(II)-Tris systems indicating protolytic reactions of the complex $NiTris^{2+}$. Instead of second Bistris

Table 1. Equilibrium constants for the reactions of Bistris with proton and Cu(II) ion.*

K	Log K	
	H^+	Cu^{2+}
K_1	6.50	5.13
K_{1A}		−5.77
K_{1B}		−7.48

*At 25° and μ=0.10 with KNO_3.

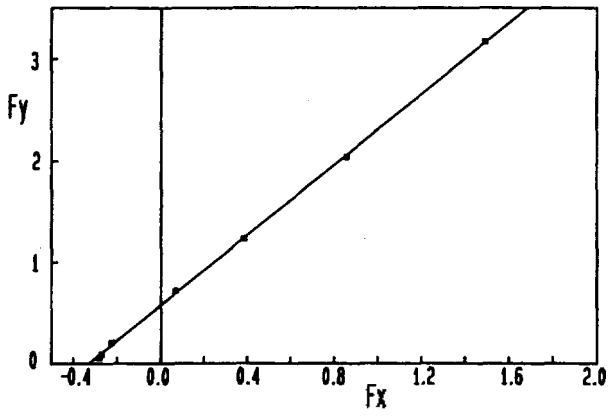

Figure 2. Determination of K_{1A} and K_{1B} for the 1 : 1 Cu(II)-Bistris system by eq. (2). $F_x=|(S-T_L+[L])[H^+]/(S+T_M-T_L+[L])|10^7$. $F_y=|(T_M-S+T_L-[L])[H^+]^2/(T_M+S-T_L+[L])|10^{13}$

L coordinating to the complex CuL^{2+}, protons are being released from this complex as the pH is increased.

The buffer regions beyond $a=1$ in the 1 : 1 and beyond $a=0.5$ in the 1 : 2 systems indicate that the complex CuL^{2+} acts as an acid. Here, the concentration of the aquo Cu^{2+} ion would be very small compared to those of other Cu(II) species. Therefore, the aquo Cu^{2+} ion concentration is initially neglected and the following equations are set up.

$$T_M=[CuL^{2+}]+[CuLH_{-1}^{+}]+[CuLH_{-2}]$$
$$T_L=[HL^+]+[L]+[CuL^{2+}]+[CuLH_{-1}^{+}]+[CuLH_{-2}]$$
$$T_H=[HL^+]+[H^+]-[OH^-]-[CuLH_{-1}^{+}]-2[CuLH_{-2}]$$

In these equations, T_M, T_L and T_H stand for the total concentrations of Cu(II), Bistris and acidic proton, respectively. From these, eqs. (1) and (2) may be obtained.

$$[L]=(T_L-T_M)/([H^+]/K_a+1) \qquad (1)$$

$$\frac{(T_M-S+T_L-[L])[H^+]^2}{T_M+S-T_L+[L]}=K_{1A}\left[\frac{(S-T_L+[L])[H^+]}{T_M+S-T_L+[L]}\right]+K_{1A}K_{1B} \qquad (2)$$

where

$$S=2T_M+T_H-[H^+]+[OH^-]$$

The constants K_{1A} and K_{1B} were evaluated from the plot of eq. (2). Using the constants K_a, K_1, K_{1A} and K_{1B}, the concentrations of all species were calculated at each point. Subtracting the calculated aquo Cu^{2+} ion concentration from T_M gives a new term T_M'. Now T_M' is used in place of T_M in

eqs. (1) and (2) and eq. (2) is plotted again. This process was repeated. The fourth and final plot is shown in Figure 2. The values of the constants from this plot are given in Table 1. The 1 : 2 data (Figure 1, Curve 3) were treated in the same way and gave practically the same values.

The pK_a of Bistris, Tris and ammonia are 6.50 (Table 1), 8.11[11] and 9.29,[11] respectively. Therefore the basicity decreases in the order ammonia>Tris>Bistris; this is expected to be the order of the metal-ligand coordinate bond strength.

The formation constants (Log K_1) for $CuNH_3^{2+}$, $CuTris^{2+}$ and $CuBistris^{2+}$ are 4.12[11], 3.95[11] and 5.13 (Table 1), respectively. The values for the first two are comparable in spite of the fact that ammonia is much more basic than Tris (by more than 1 log unit). This is because, in $CuTris^{2+}$, one of the hydroxy oxygens of the ligand is also coordinated to the metal forming a chelate structure. The basicity of Bistris is much lower than that of Tris (by more than 1.5 log unit). However, the stability of $CuBistris^{2+}$ is much greater than that of $CuTris^{2+}$ (by more than 1 log unit). This certainly indicates that additional hydroxy oxygen of the ligand is coordinated to the metal in $CuBistris^{2+}$. Therefore, Bistris binds Cu(II) as terdentate at least. Water molecules and/or some of the remaining hydroxyl groups of Bistris are believed to occupy the remaining coordinate positions.

Curve 1 of Figure 1 shows that the hydroxyl proton of Bistris does not dissociate in the absence of metal ion. When Cu(II) ion is added to this solution, in addition to the nitrogen, some of the hydroxyl groups of the ligand also coordinate the metal. This makes these hydroxyl protons more acidic and, on addition of sodium hydroxide, these protons are dissociated (Curves 2 and 3 of Figure 1). The resultant alcoholate group forms a strong bond to the metal and stable chelate structures are obtained. The value of K_{1A} for Cu(II)-Bistris is larger than that for Cu(II)-Tris[11] just as the value of K_1 is. Thus, $CuBistris^{2+}$ is stronger acid than $CuTris^{2+}$. Additional coordination groups in Bistris not only increase K_1 but also facilitate the release of hydroxyl proton from the complex.

The visible absorption spectra of Cu(II)-Bistris systems are shown in Figure 3. Spectrum 1 is that of aquo Cu^{2+} ion. Spectrum 2 corresponds to the point $a=1$, Curve 2 of Figure 1. Spectrum 3, corresponding to the point $a=0.5$, Curve 3 of Figure 1, is nearly the same as Spectrum 2. This is because CuL^{2+} is the main metal species in both solutions. Spectrum 5 corresponds to the midpoint between the two inflection points of Curve 2 of Figure 1. Spectrum 7 corresponds to the final inflection point of Curve 2 of Figure 1 and is entirely due to $CuLH_{-2}$. Spectra 4 and 6 correspond to the buffer region at $0.5<a<2$ of Curve 3 of Figure 1. Spectrum 8 is identical with Spectrum 7. This confirms the potentiometric finding that the metal species at the final inflection point of Curve 3 of Figure 1 is also $CuLH_{-2}$. Using the constants in Table 1, the concentrations of all complexes in the spectral solutions for Figure 3 were calculated. The molar absorbance of each complex was calculated using eq. 3 by solving simultaneous equations for different values of 'a'.

$$A=\varepsilon_1[Cu^{2+}]+\varepsilon_2[CuL^{2+}]+\varepsilon_3[CuLH_{-1}^{+}]+\varepsilon_4[CuLH_{-2}] \quad (3)$$

In eq. 3, ε_1, ε_2, ε_3 and ε_4 represent the molar absorbances of Cu^{2+}, CuL^{2+}, $CuLH_{-1}^{+}$ and $CuLH_{-2}$, respectively. The

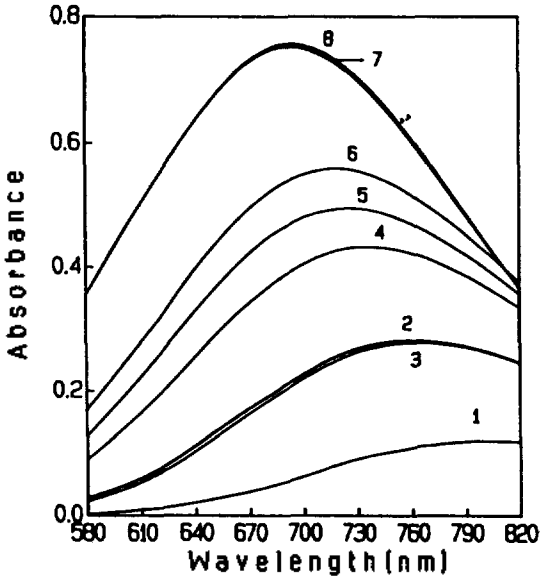

Figure 3. Visible absorption spectra of Cu(II)-Bistris systems. All solutions are 10.3 mM in $Cu(NO_3)_2$ and 10.3 mM in Bistris (Curves 2, 5, 7), 20.6 mM in Bistris (Curves 3, 4, 6, 8), 9.94 mM in HCl (Curve 3), 10.3 mM in NaOH (Curves 5, 6), and 20.6 mM in NaOH (Curves 7, 8). Curve 1 is for aquo Cu^{2+} ion.

values of maximum molar absorbances ($M^{-1}cm^{-1}$) and the corresponding wavelengths (nm) of the d-d transition are: Cu_{aq}^{2+}, 12, 800; CuL^{2+}, 21, 780; $CuLH_{-1}^{+}$, 55, 728; and $CuLH_{-2}$, 73, 695. The value of ε_{max} increases with shift of the band maximum toward shorter wavelengths as the coordination and/or deprotonation increases. The shift in λ_{max} with increase in ε_{max} is especially pronounced in going from CuL^{2+} to $CuLH_{-1}^{+}$. This is due to the formation of the strong chelate structure of the complex with metal-alcoholate bond. The negatively charged alcoholate oxygen atom in $CuLH_{-1}^{+}$ would form much stronger bond with the metal than would the neutral hydroxy oxygen atom in CuL^{2+}.

In the reaction between metal ion and N-hydroxyethylethylenediamine,[12] the hydrogen of the hydroxy group becomes more acidic when the hydroxy oxygen is coordinated to the metal and dissociates in basic medium. The IR spectra[13] of solid Cu(II) complexes of aminoalcohols showed that the hydroxyl proton of the ligand is dissociated and the site is occupied by the metal. The X-ray data[14] for Ni(II) triethanolamine complex showed that the ligand is terdentate and that the metal-triethanolamine oxygen distance is shorter than the metal-water oxygen distance. This indicates that the former bond is stronger than the latter and that the hydroxyl hydrogen of triethanolamine is more acidic than the water hydrogen. Therefore, when this complex reacts with sodium hydroxide, the hydroxyl hydrogen of triethanolamine would dissociate before the hydrogen of the coordinated water molecule. Proton NMR studies[15] of Cu(II) triethanolamine complex showed that the proton peak of methylene group of the ligand becomes broader as the pH is raised. This has been interpreted as indicating that the hydroxy oxygen is deprotonated and coordinated to the metal forming a chelate. The visible spectrophotometric[16] and ESR[17] studies of Cu(II) complexes of ethanolamines in aqueous solutions

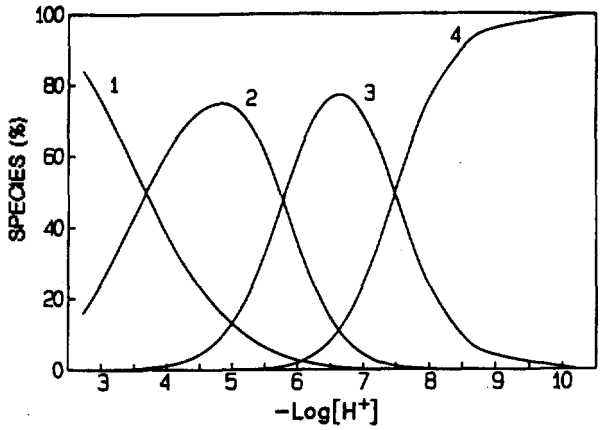

Figure 4. Complex species distribution. Curve 1-Cu^{2+}. Curve 2-CuL^{2+}. Curve 3-$CuLH_{-1}^{+}$. Curve 4-$CuLH_{-2}$

showed deprotonation of the hydroxyl groups and formation of stable chelate rings. The ESR and CD studies of Cu(II) complexes of D-glucosamine[18] and of Cu(II) complexes of the reaction products[19] of D-glucose with amino acids indicated that one of the sugar hydroxy groups is deprotonated and coordinated to the Cu(II). The X-ray studies[20] of crystal Cu(II) complexes of Tris showed coordination of deprotonated hydroxyl group; both Tris and monodeprotonated Tris are coordinated to Cu(II) as bidentate through the nitrogen and the hydroxyl/deprotonated oxygen atom in square planar geometry. The study[20] also showed that, in the Cu(II) complex containing both Tris and deprotonated Tris, the Cu-alcoholate oxygen bond is shorter than the Cu-hydroxy oxygen bond. This indicates that the former bond is stronger than the latter, as expected from the negative charge on the alcoholate oxygen atom. The results of Cu(II)-Bistris complexes are in agreement with those of the related aminoalcohol complexes of Cu(II).

Finally, the distribution of the complex species in solution is shown in Figure 4. This was obtained from the equilibrium constants in Table 1 and the experimental conditions for the 1 : 1 Cu(II)-Bistris system (Figure 1, Curve 2). The complex species distribution can also be plotted against the 'a' value. These curves were very similar to those in Figure 4. The curves in Figure 4 show that the proportions of CuL^{2+} and $CuLH_{-1}^{+}$ are highest at $-\log[H^+]$ values of 4.81 and 6.63, respectively. At high pH, nearly all the Cu(II) exists as $CuLH_{-2}$. Similar results were also obtained for the 1 : 2 Cu(II)-Bistris system.

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