

Copper(II) Complexation by 2-((3-((2-Hydroxy-1,1-di(hydroxymethyl)ethyl)amino)propyl)amino)- 2-(hydroxymethyl)-1,3-propanediol in Aqueous Solution

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The complex formation from Cu(II) ion and 1,3-bis(tris(hydroxymethyl)methylamino)propane (bistrispropane) in aqueous solution has been studied potentiometrically and spectrophotometrically. Bistrispropane (btp) coordinates to Cu(II) as multidentate. In the btp (L) complex CuL^{2+} , two of the hydroxyl oxygen atoms as well as the amine nitrogens of the ligand are coordinated. In neutral and weakly acidic media, one of the coordinated hydroxyl groups is deprotonated. In basic media, an additional hydroxyl group undergoes deprotonation. The equilibrium constants for the formation of CuL^{2+} , CuLH_{-1}^{+} , and CuLH_{-2} have been determined. The nature of the coordinate bonds has been deduced from the potentiometric data and the spectra of these complexes.

Introduction

The compound 1,3-bis(tris(hydroxymethyl)methylamino)propane ('bistrispropane') is used extensively in biochemical research as a buffer material along with some other hydroxyamines such as bis(2-hydroxyethyl)imino-tris(hydroxymethyl)methane (bistris) and tris(hydroxymethyl)aminomethane (tris) since the pK_a values of these aminoalcohols lie in the vicinities of physiological pH range. These compounds are also good complexing agents because they all contain hydroxyl groups in addition to amine nitrogen. Biological systems usually contain metal ions. Therefore, metal complexes of these buffer compounds are formed in biochemical systems containing metal ions when these materials are used to control the pH.

The complexing properties of bistris have been investigated in neutral pH range¹⁻³ and also in extreme pH values.³ The equilibrium constants of complexes formed from tris and various metal ions have been reported.⁴ Bistrispropane (btp) was first synthesized in 1944⁵ but its complexing properties have not been investigated quantitatively although its chelate complex of Cu(II) has been employed in analytical detection of btp.⁶ In the present study, the complex formation from Cu(II) ion and btp has been investigated potentiometrically and spectrophotometrically in wide pH ranges.

Experimental

Reagents. Bistrispropane used in this study was the '99%+' grade from Aldrich Chemical Company. It was dried for 24 hours at 140 °C in a vacuum oven before use. The copper(II) nitrate used was the '99.999%' grade also from Aldrich. The sodium hydroxide (Titrisol ampules) and hydrochloric acid were both Merck p.a. grade and their stock solutions were standardized by the usual methods. Potassium nitrate (Merck p.a.) was recrystallized twice. It was used to maintain ionic strength of the test solutions.

The stock solution of Cu(II) nitrate was standardized by complexometry using Na_2EDTA (Merck p.a.). Aliquots of the metal stock solution were also passed through the acid

form of Amberlite IR-120 cation exchange resin (Fluka) and the effluent solutions were titrated with the standard NaOH solution. The Cu(II) concentration determined by this indirect method agreed with the result of the complexometry within about 0.1%.

Measurements. In all potentiometric titrations, the hydrogen ion activity was measured with an Orion Research EA-940 Expandable Ion Analyzer with a Ross 81-01 combination pH electrode. The instrument was calibrated with phthalate and phosphate buffers. The hydrogen ion concentration was obtained from the measured pH by using the activity coefficient calculated by the Davies equation⁷ at the ionic strength employed here. The hydroxide ion concentration was obtained by using the value of 13.778 for pK_w of water.⁸ In the present study, pH refers to the hydrogen ion activity as measured by the glass electrode and $-\log[\text{H}^+]$ or $p[\text{H}]$ refers to the hydrogen ion concentration.

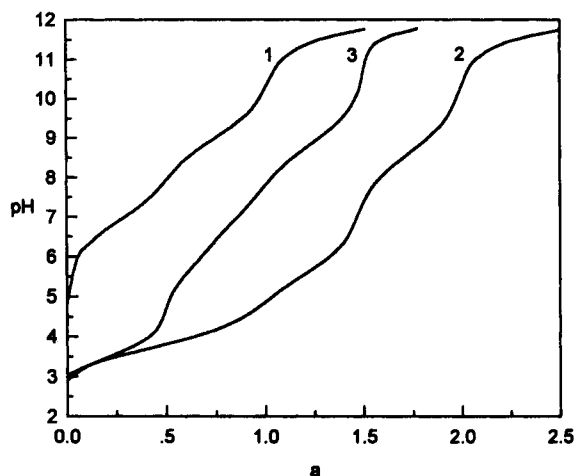
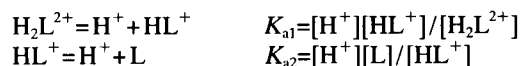


Figure 1. Potentiometric equilibrium curves of bistrispropane and its Cu(II) complex systems. The initial concentrations are: Curve 1: 10.40 mM in btp and 20.80 mM in HCl. Curve 2: 10.04 mM in $\text{Cu}(\text{NO}_3)_2$, 10.40 mM in btp, and 20.80 mM in HCl. Curve 3: 10.04 mM in $\text{Cu}(\text{NO}_3)_2$, 20.80 mM in btp, and 41.60 mM in HCl. a = number of moles of NaOH added/number of moles of HCl initially present.

Solutions of btp and hydrochloric acid in the absence and presence of Cu(II) ion were titrated with standard sodium hydroxide solution (1.012 M) using a 2-mL Gilmont buret. All titrations were carried out using 50 mL test solutions at 25.0 ± 0.1 °C. The ionic strength of the test solutions was kept constant at 0.1 M with KNO_3 . Before the start of the titration, nitrogen gas was passed through the test solution for 30 minutes; the titration was carried out under nitrogen atmosphere by passing the gas over the solution. The nitrogen gas had previously been passed through sodium hydroxide pellets and then distilled water. The electronic absorption spectra were taken with Shimadzu UV-3101PC spectrophotometer using 2-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 test solution. It is the experimental base-to-acid molar ratio.

Results and Discussion

Bistrispropane. The btp-HCl equilibrium titration curve is shown in Figure 1, Curve 1. There are 2 inflection points in this curve. The first, at $a=0.5$, corresponds to HL^+ and the second, at $a=1$, corresponds to L, where L represents the neutral btp.



The following equation may be derived for this system.

$$\begin{aligned} [\text{H}^+]^2 &\left(\frac{2T_L}{T_H - [\text{H}^+] + [\text{OH}^-]} - 1 \right) \\ &= [\text{H}^+] \left(1 - \frac{T_L}{T_H - [\text{H}^+] + [\text{OH}^-]} \right) K_{a1} + K_{a1}K_{a2} \end{aligned}$$

where T_L and T_H represent analytical concentrations of btp and ionizable hydrogen, respectively.

The plot of this equation for the data in the middle part of Curve 1 of Figure 1 gave linear relationship and the values of the two constants were obtained, $\text{p}K_{a1}=6.75$ and $\text{p}K_{a2}=8.89$. Using these values as the initial estimates, more accurate values of the constants were obtained by the PKAS fortran program⁹ which gives the overall protonation constants ($\beta_{011}=1/K_{a2}$ and $\beta_{012}=1/(K_{a1}K_{a2})$). The titration data

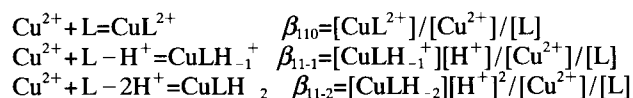
Table 1. Equilibrium constants for the reaction of bistrispropane with proton and Cu(II) ion^a

Log β , LogK	H ⁺	Cu ²⁺
β_{011}	8.89	
β_{012}	15.64	
K_{a1}	-6.75	
K_{a2}	-8.89	
β_{110}		10.57
β_{1-1}		5.12
β_{1-2}		-3.29
K_{1A}		-5.45
K_{1B}		-8.41

^aAt 25 °C and I=0.1 with KNO_3 . $K_{a1}=\beta_{011}/\beta_{012}$, $K_{a2}=1/\beta_{011}$, $K_1=\beta_{110}$, $K_{1A}=\beta_{1-1}/\beta_{110}$, $K_{1B}=\beta_{1-2}/\beta_{1-1}$.

in the buffer region of $a=0.15$ to 0.83 were used in these calculations. The final values of these constants are given in Table 1. They are actually the same as those obtained by the graphical method. The values of the constants reported are $\text{p}K_{a1}=6.88^{10}$ at 35 °C and in 0.5 M NaCl and $\text{p}K_{a1}=6.8$ and $\text{p}K_{a2}=9$ at 20 °C.¹¹ It is seen from Figure 1, Curve 1, that no proton dissociates from btp itself even at very high pH. The lower basicities of both nitrogens in btp compared with the corresponding nitrogens in propylenediamine⁴ (pn) are a direct result of the presence of the hydroxyl groups in btp.

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



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

In the 1:1 system (Figure 1, Curve 2) there are a weak inflection at $a=1$ and strong inflections at $a=1.5$ and 2. This shows that the formation of CuL^{2+} and acid dissociation of the complex occur in slightly overlapping steps around $a=1$, whereas the deprotonated complexes CuLH_{-1}^+ and CuLH_{-2} are formed in distinctly different pH regions. The 1:2 system (Figure 1, Curve 3) also shows 3 inflections, two strong ones at $a=0.5$ and 1.5 and a weak one at $a=1$. The first indicates formation of CuL^{2+} as the major species and the last suggests formation of CuLH_{-2} also as the major species. The faint middle one indicates formation of intermediate species.

Identical formation curve (\bar{n} vs. $\log[\text{L}]$) was obtained up to $\bar{n}=1$ for both the 1:1 and 1:2 systems. The value of β_{110} was obtained graphically from the data for Curve 2 at $a<0.7$ and also from Curve 3 at $a<0.4$. This value ($\log \beta_{110}=10.59$) was used later as the initial value in the accurate evaluation of all complex formation constants by the computer program BEST.⁹ The formation curve above $\bar{n}=1$ for the 1:2 system was somewhat unusual casting doubt as to whether CuL_2^{2+} is formed. Hydrolytic reaction of CuL^{2+} or both reactions may occur in this region. Attempts to calculate β_{120} by graphic method and later by the BEST⁹ and the SCOGS¹² programs all failed. Therefore, it was concluded that no appreciable amount of CuL_2^{2+} is formed.

These results suggest that, in the 1:1 system, the complexes CuL^{2+} , CuLH_{-1}^+ and CuLH_{-2} are formed at $a=1$, 1.5 and 2, respectively, as the major species. In this system at $1<a<1.5$, mass balance equations are set up for T_M , T_L , and T_H , where T_M stands for the total concentration of Cu(II), and T_L and T_H have the same meaning as previously described. Using the values of K_{a1} , K_{a2} , and β_{110} obtained above, these equations are solved for β_{1-1} . The constant β_{1-2} was evaluated in the region $1.5<a<2$ in a similar fashion. Using these values of the constants as the initial estimates, all the overall formation constants were evaluated simultaneously by the BEST⁹ program from data for the whole titration

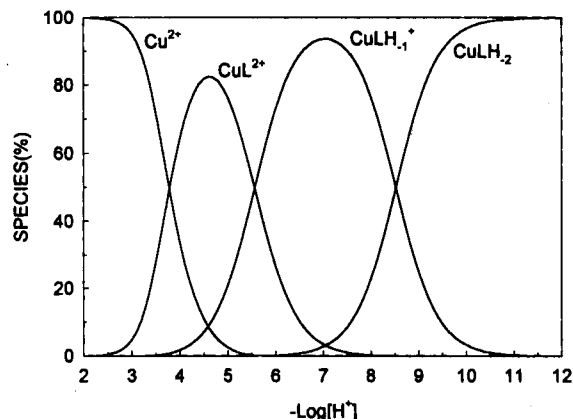


Figure 2. Distribution of the complex species in the Cu(II)-btp 1:1 system. Total Cu(II) concentration 10.04 mM and total btp concentration 10.40 mM.

curve except the extreme ends. For the 1:1 system, the data for $0.1 < a < 1.9$ were used; for the 1:2 system, $0.1 < aw < 1.4$. The formation constants are given in Table 1.

In addition to the major species initially predicted from the shapes of the curves of Figure 1, inclusion of the dinuclear species $\text{Cu}_2\text{L}_2^{4+}$ and $\text{Cu}_2\text{L}_3^{4+}$ in the model as minor species gave better results. However, it was unclear whether these were actually present in the solution or they simply appeared in the mathematical process of minimizing σ_{pH} in the calculation.

In the 1:2 system, introduction of $\text{Cu}_2\text{L}_3^{4+}$ in the computation improved the σ fit. Other species were also tried with improvements in the σ fit. Again, however, there was no direct evidence for their existence. A small error in the stoichiometries of experimental solutions does not affect significantly the formation constants of the major species but could lead to wrong conclusions regarding minor species. In both the 1:1 and 1:2 systems, the formation constants of the major species were practically not affected by whether or not the minor species were included in the calculation.

The distribution of the metal species in the 1:1 system was calculated using the constants in Table 1 by the SPE⁹ program and is shown in Figure 2 as a function of $\text{p}[\text{H}]$. The distribution diagram for the Cu(II)-btp 1:2 system is similar to that of the 1:1 system, even though the experimental stoichiometries are quite different in the two systems. This is because the same major species are formed in the two solutions.

In the complex CuL^{2+} the two nitrogens and two hydroxyl oxygens, one from each end of the ligand, are believed to occupy the four sites in the plane. Two of the remaining hydroxyl groups or water molecules probably occupy the axial positions. When alcoholic groups are attached to amines, their complex stability generally increases.^{4,13} The overall protonation constant (β_{012}) of a polyamine is a measure of its total basicity and therefore a measure of its complex stability or the metal-ligand bond strength. The value of $\log\beta_{012}$ is 19.32⁴ for pn and 15.64 (Table 1) for btp. The complex stability is $\log K_1=9.66^4$ for $\text{Cu}(\text{pn})^{2+}$ and 10.57 (Table 1) for $\text{Cu}(\text{btp})^{2+}$. Thus, the total basicity of btp is 3.7 log unit lower than pn but the stability of $\text{Cu}(\text{btp})^{2+}$ is 0.9 log unit higher than $\text{Cu}(\text{pn})^{2+}$. This shows that some of the hydroxyl oxygens of btp are also coordinated to the metal

in $\text{Cu}(\text{btp})^{2+}$.

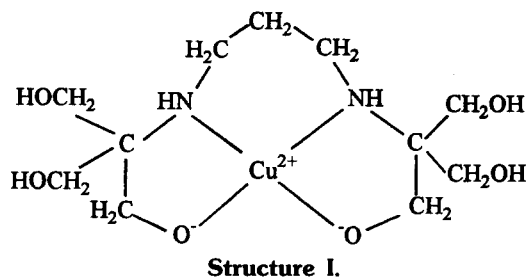
For *N*-(2-hydroxyethyl)-1,3-propylenediamine⁴ (hpn) the constants are $\log\beta_{012}=18.43$ and $\log K_1=10.42$ (25 °C, $I=0$) for $\text{Cu}(\text{hpn})^{2+}$. Thus, the basicity of btp is 2.8 log unit lower than hpn but the complex stability is 0.15 log unit higher for $\text{Cu}(\text{btp})^{2+}$ than for $\text{Cu}(\text{hpn})^{2+}$. This shows that at least two hydroxyl groups are coordinated to the metal in addition to the two nitrogen atoms in $\text{Cu}(\text{btp})^{2+}$. The hydroxyl group coordination is also apparent when the protonation constants and the Cu(II) complex formation constants are compared between pn and hpn.

When the ligand forms only an isolated chelate ring, *i.e.*, if the ligand is bidentate, generally 5-membered chelate ring is more stable than 6-membered¹⁴ as illustrated by a comparison of the data for ethylenediamine (en) and pn. The total basicity for en is smaller than that for pn but the Cu(II) complex stability is larger for en than for pn.

When fused chelate rings are formed by polydentate ligands, the situation is more complicated. The overall protonation constant, $\log\beta_{014}$, of triethylenetetramine (2,2,2-tet), 1,4,8,11-tetraazaundecane (2,3,2-tet), and 1,5,9,13-tetraazatridecane (3,3,3-tet) are 28.67, 31.67, and 36.03, respectively.⁴ On the other hand, the Cu(II) complex formation constant, $\log K_1$, of 2,2,2-tet, 2,3,2-tet, and 3,3,3-tet are 20.05, 23.20, and 17.05, respectively.⁴ These complexes have 5-5-5, 5-6-5, and 6-6-6 membered chelate rings, respectively. The 2,3,2-tet complex is the most stable. This has been interpreted in terms of steric strain¹⁵ in the middle ring which is less strained in 6-membered than in 5-membered ring. This arises from the difference in the 'bite' distance between the two middle nitrogen atoms of the ligands. The steric strain decreases by alternation of the ring size, 5-6-5. The higher stability of the 2,3,2-tet complex over the 2,2,2-tet complex is also partly due to increase in the total ligand basicity in 2,3,2-tet compared to 2,2,2-tet. However, the ligand basicity alone can not explain the difference in the complex stability. This is apparent when 3,3,3-tet is included in the comparison. In the complex $\text{Cu}(2,3,2\text{-tet})^{2+}$, the CuN_4 unit is nearly planar and the 5-6-5 fused chelate rings take the stable gauche-chair-gauche conformations.¹⁶ In some Cu(II)-polyaminoalcohol complexes which have the similar 5-6-5 fused chelate rings, an X-ray investigation of the crystal structure showed that the 6-membered ring is in chair conformation and the 5-membered rings are in gauche form.¹⁷

The basicity of *N,N*-bis(2-hydroxyethyl)ethylenediamine (bishen) is $\log\beta_{012}=15.50$ and is about the same as for btp. The stability of $\text{Cu}(\text{bishen})^{2+}$ is $\log K_1=9.68$; thus, that of $\text{Cu}(\text{btp})^{2+}$ is 0.9 log unit higher. It is believed that the chelate structures of these polyaminoalcohol complexes are similar to those of the tetraamine complexes^{15,16} of corresponding ring sizes: $\text{Cu}(\text{btp})^{2+}$ and $\text{Cu}(\text{bishen})^{2+}$ have fused 5-6-5 and 5-5-5 membered chelate rings, respectively. Therefore, the extra stability of $\text{Cu}(\text{btp})^{2+}$ over $\text{Cu}(\text{bishen})^{2+}$ is a direct result of the steric strain in the 5-membered middle ring of the latter being relieved in the 6-membered middle ring of the former. The greater stability of $\text{Cu}(\text{btp})^{2+}$ may also indicate additional hydroxyl group coordination at the weak axial positions.

The structure of $\text{Cu}(\text{btp})^{2+}$ is believed to resemble that¹⁶ of $\text{Cu}(2,3,2\text{-tet})(\text{ClO}_4)_2$ with the positions of the two end ni-



trogens in the latter occupied by hydroxyl groups in the former, and the axial positions occupied by the two oxygen atoms of the perchlorate ions in the latter occupied by two additional hydroxyl or water oxygen atoms in the former. Accordingly, the 5-6-5 fused chelate rings in $\text{Cu}(\text{btp})^{2+}$ are believed to be in the gauche-chair-gauche conformations.

In going from pn to hpn to btp, the total basicity decreases but the Cu(II) complex stability increases. This trend is in line with the stability increase associated with the alternation of the size of the fused chelate rings between 5- and 6-membered rings. On the other hand, in the series en to hen to bishen, the total basicity decreases, and their Cu(II) complex stability also decreases. Here, the trend is associated with the increase in steric strain when the same, 5-membered, chelate rings are fused into multiple rings of the same size.

Deprotonation. Some aminoalcohol complexes of Cu(II) and Ni(II) undergo deprotonation of the coordinated hydroxyl groups in neutral or basic media, simultaneously resulting in the formation of a bond between the metal and the negatively charged alkoxide oxygen atom. In the Cu(II) complexes of bistris³ and tris⁴ the deprotonation reaction starts to occur at about pH 6 and continues at higher pH. For the Cu(II)-btp complexes the first deprotonation occurs around pH 5.5; the second just above pH 8. Deprotonation does not change the chelate ring size. The proposed structure of CuLH_{-2} is given in Structure I.

$\text{Cu}(\text{btp})^{2+}$ is a substantially stronger acid than $\text{Cu}(\text{bishen})^{2+}$. The deprotonation constants are $\text{p}K_{1A}=5.45$ for the former and 7.15 for the latter. This suggests that the coordinate bond between the ethanolic oxygen and the metal ion is stronger in the former than in the latter. In other words, the induction effect of Cu(II) in withdrawing the electronic charge from the coordinated hydroxyl oxygen atom is greater in $\text{Cu}(\text{btp})^{2+}$ than in $\text{Cu}(\text{bishen})^{2+}$ and thus the ligand hydroxyl group of btp is more readily deprotonated. The second deprotonation constant of $\text{Cu}(\text{btp})^{2+}$ is also greater than that of $\text{Cu}(\text{bishen})^{2+}$; $\text{p}K_{1B}=8.41$ for the former and 9.37 for the latter. These differences probably arise from the difference in the nature of the chelate rings in the two complexes.

It is also interesting to compare Cu(II)-btp with Cu(II)-bistris.³ $\text{Cu}(\text{btp})^{2+}$ is a slightly stronger acid than $\text{Cu}(\text{bistris})^{2+}$; $\text{p}K_{1A}=5.45$ vs. 5.77. But the second deprotonation constant of the btp complex is considerably smaller than that of the bistris complex; $\text{p}K_{1B}=8.41$ vs. 7.48. In this case the two aminoalcohol complexes can not be directly compared because btp is a diamine whereas bistris is a monoamine. The Cu(II)-bistris complex has two fused 5-membered chelate rings whereas the Cu(II)-btp complex has three fused, 5-6-5 membered, chelate rings. The two coordinated hydroxyl

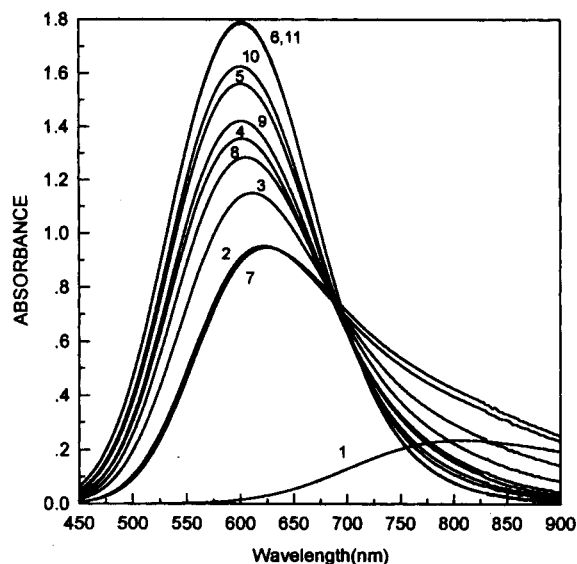


Figure 3. Visible absorption spectra of Cu(II)-bistrispropane systems. All solutions are 10.04 mM in $\text{Cu}(\text{NO}_3)_2$. And 10.40 mM in btp (Curves 2, 3, 4, 5, 6), 20.80 mM in btp (Curves 7, 8, 9, 10, 11), 20.80 mM in HCl (Curve 7), 10.05 mM in HCl (Curve 8), 5.21 mM in NaOH (Curve 3), 10.42 mM in NaOH (Curve 4, 10), 15.59 mM in NaOH (Curve 5), and 20.80 mM in NaOH (Curve 6, 11).

groups in $\text{Cu}(\text{bistris})^{2+}$ are located trans to each other and therefore are far apart. On the other hand, in $\text{Cu}(\text{btp})^{2+}$, they must be located at adjacent positions cis to each other. Therefore, after the first coordinated hydroxyl group is deprotonated, the resulting negatively charged alkoxide oxygen atom could form an intramolecular hydrogen bond to the proton of the second coordinated hydroxyl group. This will make the second deprotonation more difficult. Therefore the second deprotonation constant of $\text{Cu}(\text{btp})^{2+}$ would be smaller than that of $\text{Cu}(\text{bistris})^{2+}$ as observed.

Spectra. The visible absorption spectra of the Cu(II)-btp complexes are shown in Figure 3. Spectrum 1 is that of the aqua Cu^{2+} ion. Spectrum 2, 3, 4, 5 and 6 correspond to Curve 2 of Figure 1 at $a=1, 1.25, 1.5, 1.75$ and 2, respectively. Spectrum 7, 8, 9, 10 and 11 correspond to Curve 3 of Figure 1 at $a=0.5, 0.75, 1, 1.25$ and 1.5, respectively. Spectra 2 and 7 are almost identical supporting the potentiometric finding that CuL^{2+} is the major species at both the first inflection points of Curves 2 and 3 of Figure 1. Spectrum 4 corresponds to the second inflection point of Curve 2 of Figure 1 and is almost entirely due to CuLH_{-1}^{+} . The fact that Spectrum 3 is almost exactly halfway between Spectra 2 and 4 shows that CuL^{2+} and CuLH_{-1}^{+} are the only species present in any appreciable extent in this region. Spectrum 6 corresponds to the final inflection point of Curve 2 of Figure 1 and is entirely due to CuLH_{-2} . Again Spectrum 5 is almost exactly halfway between Spectra 4 and 6. This shows that no species other than CuLH_{-1}^{+} and CuLH_{-2} is present in any measurable extent in this region. Spectra 8, 9 and 10 correspond to the sloping buffer region of Curve 3 of Figure 1. Spectrum 11 corresponds to the final inflection point of Curve 3 of Figure 1 and is identical with Spectrum 6. This again supports the potentiometric finding that the complex species at the final inflection

Table 2. Molar absorbances of complexes

Species	λ_{\max} (nm)	ϵ_{\max} ($M^{-1}cm^{-1}$)
Cu^{2+}_{aq}	802	12
$Cu(btp)^{2+}$	622	46
$Cu(btpH_{-1})^+$	602	67
$Cu(btpH_{-2})$	600	89
$Cu(pn)^{2+}$	652	46
$Cu(pn)_2^{2+}$	570	106

btp=bistrispropane, pn=propylenediamine.

points of Curves 2 and 3 of Figure 1 are identical ($CuLH_{-2}$).

The concentrations of the complexes present in each of the spectral solutions were calculated using the constants in Table 1 by the SPE⁹ program. The molar absorbances of the complexes were calculated in a manner similar to the case of the bistris complexes.³ The values of the maximum molar absorbances ($M^{-1}cm^{-1}$) and the corresponding wavelengths (nm) of the complexes are given in Table 2. As in the case of the Cu(II)-bistris complexes,³ the value of the maximum molar absorbance increases with shift of the band maximum toward shorter wavelengths as the coordination and/or deprotonation increases.

With the bistris complexes, the most pronounced spectral shift was observed at the first deprotonation.³ With the Cu(II)-btp complexes, however, the spectral shift upon deprotonation is rather small compared with that accompanying the formation of the complex CuL^{2+} from the aquo Cu^{2+} ion. The difference arises from the two nitrogen atoms in btp which form strong chelate structure even before any deprotonation occurs. In Table 2 are also given the spectral data for Cu(II) complexes of pn for comparison. The absorption maximum for $Cu(btp)^{2+}$ occurs at a considerably shorter wavelength than that of $Cu(pn)^{2+}$. This again indicates additional coordination (hydroxyl group coordination) in $Cu(btp)^{2+}$ over $Cu(pn)^{2+}$. This is in agreement with the potentiometric equilibrium results that showed that $Cu(btp)^{2+}$ is a stronger complex than $Cu(pn)^{2+}$.

Table 2 also gives spectral data for $Cu(pn)_2^{2+}$. It appears that the four nitrogen atoms in the two pn ligands exert stronger ligand field than the two nitrogen atoms and the two negatively charged oxygen atoms in the deprotonated btp complex $CuLH_{-2}$. Structurally the btp complexes CuL^{2+} , $CuLH_{-1}^+$, and $CuLH_{-2}$ all resemble $Cu(2,3,2-tet)^{2+}$ which

absorbs at even shorter wavelength, 525 nm.¹⁵ This shows that the amine nitrogen coordination gives stronger bond than even the negatively charged alkoxide oxygen bond to Cu(II).

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