Copper(II) Complexes of *N,N'*-Bis(β-carbamoylethyl)trimethylenediamine in Aqueous Solution

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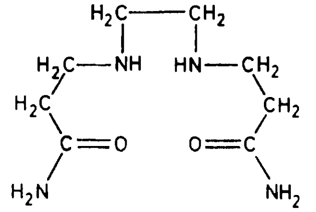
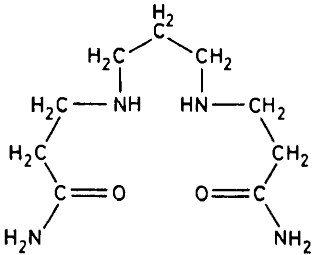
The interactions of the title ligand (bctn) with copper(II) in aqueous solution have been investigated by potentiometric and spectrophotometric techniques. The two protonation constants of the ligand at 25 °C and 0.2 mol dm^{-3} Na[NO$_3$] are $10^{9.29}$ and $10^{7.06}$ dm^3 mol^{-1}. Quantitative equilibrium studies of the stepwise reactions which precede the formation of [Cu(bctn)]$^{2+}$ and the Cu–O to Cu–N bond rearrangements at the two amide sites are described in detail. Electronic spectra of the copper(II) chelates formed have been recorded and are discussed.

IN our earlier spectrophotometric and potentiometric studies of copper(II) complexes of *N,N'*-bis(β-carbamoylethyl)ethylenediamine, bcen,[1] it was shown that copper(II) can induce ionization of the amide protons after combination with this ligand. In order to investigate the effect of chelate-ring size upon equilibrium constants, the detailed stepwise reactions which precede the formation of the copper(II) complex of *N,N'*-bis(β-carbamoylethyl)trimethylenediamine, bctn, and the Cu–O to Cu–N bond rearrangements at the two amide sites have now been studied by potentiometric and spectrophotometric techniques.



bcen



bctn

EXPERIMENTAL

Materials.—The ligand was prepared from propane-1,3-diamine (16.6 cm^3, 0.2 mol) and acrylamide (28.4 g, 0.4 mol) in acetonitrile (100 cm^3) by heating under reflux for 2 h. The solution was cooled and the product filtered off, washed with cold chloroform, recrystallized from chloroform, and dried in air, m.p. 101—103 °C (Found: C, 49.55; H, 9.20; N, 25.85. Calc. for $C_9H_{20}N_4O_2$: C, 50.0; H, 9.30; N, 25.9%). The compound was 99.9% pure as determined by titration with standard base.

The salt $Cu[ClO_4]_2 \cdot 6H_2O$ was recrystallized from water and standardized by titration with ethylenediaminetetraacetate. A saturated solution of sodium hydroxide (reagent grade) was prepared to precipitate sodium carbonate. A sample of this was diluted with freshly boiled, distilled, deionized water and stored in a Nalgene Teflon bottle. It was standardized against weighed amounts of potassium hydrogenphthalate.

Measurements.—For pH measurements a Radiometer PHM 64 equipped with a GK 2401 B combined electrode was used. The pH was standardized with NBS buffers and the readings were corrected to give the hydroxide-ion concentration. The hydrogen-ion concentration in 0.2 mol dm^{-3} Na[NO$_3$] solution is calculated from $-\log[H^+] = pH - 0.14$.

Appropriate aliquots of standard solutions of ligand or ligand and metal were titrated with a standard sodium hydroxide solution. In all titrations the ionic strength was maintained relatively constant by using 0.20 mol dm^{-3} Na[NO$_3$] as supporting electrolyte. The solutions were protected from air by a stream of humidified prepurified nitrogen and were maintained at 25.0 ± 0.05 °C during measurements. The equilibrium constants were obtained by a linear least-squares fit of the data by using an IBM 1130 computer. A Cary 17 spectrophotometer with a thermostatted cell compartment was used to record absorption spectra.

RESULTS AND DISCUSSION

Protonation Constants.—A potentiometric titration of the nitrate salt of diprotonated bctn with standard base yielded the experimental data shown as the smooth curve 1 in Figure 1. In this Figure *a* represents the number of mols of hydroxide ion added per mol of bctn present in the solution. Equation (1) is obtained from the usual mass- and charge-balance relationships, where

$$1/K_1{}^{H} = AK_2{}^{H} + B$$

$$A = \frac{[H^+]^2(ac_{H_nL} + [H^+] - [OH^-])}{[OH^-] - [H^+] + (2 - a)c_{H_nL}}$$

$$B = \frac{[H^+]\{(a-1)c_{H_nL} - [OH^-] + [H^+]\}}{[OH^-] - [H^+] + (2 - a)c_{H_nL}} \qquad (1)$$

c_{H_nL} is the total concentration of ligand. *A* and *B* were calculated from several sets of values of *a* and [H$^+$] taken from curve 1. The values of $K_1{}^{H}$ and $K_2{}^{H}$ obtained by using Schwarzenbach's method[2] are listed in Table 1 along with corresponding values reported for bcen.[1] The relative abundances for $NH_2COCH_2CH_2NH_2CH_2CH_2CH_2NH_2CH_2CH_2CONH_2{}^{2+}$ (H_2L^{2+}), $NH_2COCH_2CH_2NH_2$-

$CH_2CH_2CH_2NHCH_2CH_2CONH_2^+$ (HL^+), and $NH_2COCH_2CH_2NHCH_2CH_2CH_2NHCH_2CH_2CONH_2$ (L) as a function of pH at 25.0 °C and $I = 0.20$ mol dm^{-3} (Na[NO$_3$]) are shown in Figure 2.

For bctn the value of the protonation constant K_2^H is less than that of K_1^H as might have been expected on the basis of both statistical factors [3] and of electrostatic repulsion between the hydrogen ion and the protonated ligand. For each stage of protonation the constants K_1^H and K_2^H lie in the order bctn > bcen. This sequence can be related to the different inductive effects of the constituent groups in the ligands. The values of K_1^H and K_2^H of bctn are all significantly lower than the corresponding constants of propane-1,3-diamine,[4] in accord with the base-weakening effect of the neighbouring amide group.[5]

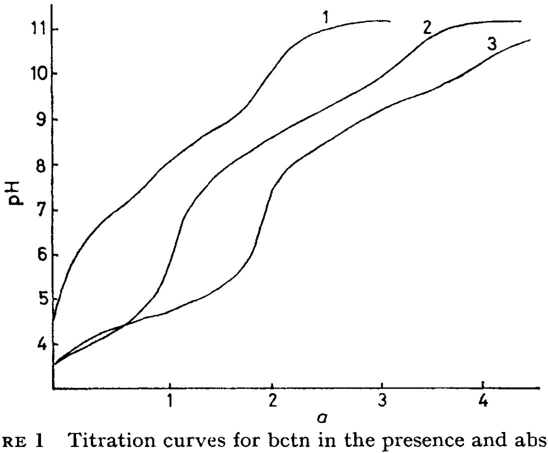


FIGURE 1 Titration curves for bctn in the presence and absence of Cu^{2+} at 25 °C and in 0.2 mol dm^{-3} Na[NO$_3$]. Test solution: (1) 20.0 cm^3, 0.010 16 mol dm^{-3} [H$_2$bctn][NO$_3$]$_2$; (2) 20.0 cm^3, 0.009 78 mol dm^{-3} Cu[NO$_3$]$_2$ and 0.0196 mol dm^{-3} [H$_2$bctn][NO$_3$]$_2$; (3) 20.0 cm^3, 0.009 78 mol dm^{-3} Cu[NO$_3$]$_2$ and 0.009 81 mol dm^{-3} [H$_2$bctn][NO$_3$]$_2$. Titrant 0.390 2 mol dm^{-3} Na[OH]; a = number of mols of Na[OH] added per mol of ligand

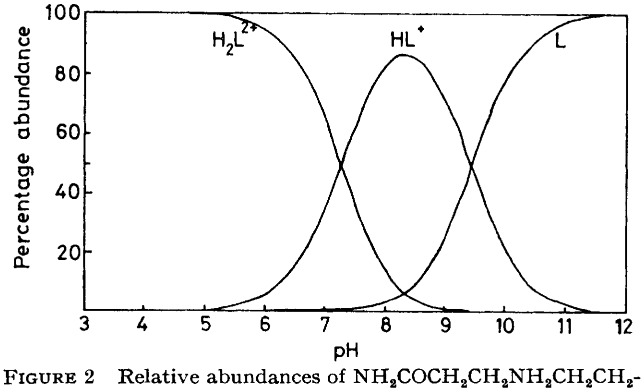


FIGURE 2 Relative abundances of $NH_2COCH_2CH_2NH_2CH_2CH_2CH_2NH_2CH_2CH_2CONH_2^{2+}$ (H_2L^{2+}), $NH_2COCH_2CH_2NH_2CH_2CH_2CH_2NHCH_2CH_2CONH_2^+$ (HL^+), and $NH_2COCH_2CH_2NHCH_2CH_2CH_2NHCH_2CH_2CONH_2$ (L) as a function of pH at 25.0 °C and $I = 0.20$ mol dm^{-3} (Na[NO$_3$])

Copper(II) *Complex*.—Job's method of continuous variations was adopted for the determination of the composition of the complex. The result indicated that copper(II) forms a 1 : 1 complex with bctn.

Equilibrium constants. The titration curves for copper(II)-bctn systems are shown in Figure 1 (curves 2 and 3). The reactions are fast. During titration the colour of the solutions gradually changed from blue to deep blue and finally to violet. For the 1 : 1 copper(II)–bctn solution (curve 3) a definite break at $a = 2$ is seen. In the first (sloping) buffer region the two protons attached to the amine groups of the ligand are dissociated by the copper(II) ion. In the second (sloping) buffer region the two amide protons are dissociated in overlapping steps.

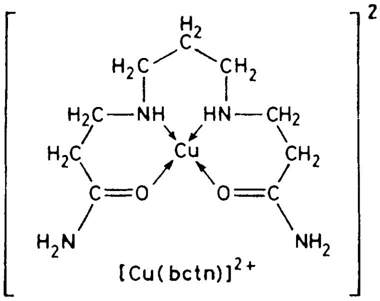
The equilibria (2)—(4) were found to describe the reactions of copper(II) with bctn, where L represents the

$$Cu^{2+} + L \rightleftharpoons [CuL]^{2+};\ K_f = [CuL^{2+}]/[Cu^{2+}][L] \quad (2)$$

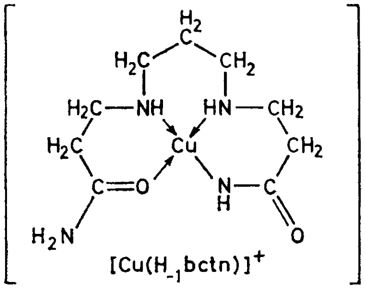
$$[CuL]^{2+} \rightleftharpoons [CuH_{-1}L]^+ + H^+;\ K_A = [CuH_{-1}L^+][H^+]/[CuL^{2+}] \quad (3)$$

$$[CuH_{-1}L]^+ \rightleftharpoons [CuH_{-2}L] + H^+;\ K_B = [CuH_{-2}L][H^+]/[CuH_{-1}L^+] \quad (4)$$

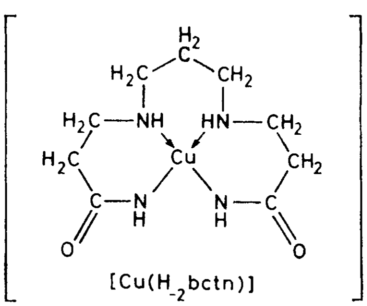
unprotonated ligand, bctn, and the negative subscript to H represents the number of amide protons removed from the complex. The three complexes $[CuL]^{2+}$, $[CuH_{-1}L]^+$, and $[CuH_{-2}L]$ are shown below.



$[Cu(bctn)]^{2+}$



$[Cu(H_{-1}bctn)]^+$



$[Cu(H_{-2}bctn)]$

Below $a = 2$ for the 1 : 1 titration (or below $a = 1$ in the 1 : 2 titration) only the formation of $[CuL]^{2+}$, equation

(2), takes place. For this reaction, equations (5)—(9) are obtained from the usual mass-balance and charge-balance relationships, where $c_{\mathrm{H}_n\mathrm{L}}$ and c_{M} are the total concentrations of ligand and metal species, respectively.

$$\log K_{\mathrm{f}} = \log \frac{\bar{n}}{1-\bar{n}} - \log[\mathrm{L}] \qquad (5)$$

$$[\mathrm{L}] = (2c_{\mathrm{H}_n\mathrm{L}} - ac_{\mathrm{H}_n\mathrm{L}} + [\mathrm{OH}^-] - [\mathrm{H}^+])/\alpha' \qquad (6)$$

$$\bar{n} = (c_{\mathrm{H}_n\mathrm{L}} - \alpha[\mathrm{L}])/c_{\mathrm{M}} \qquad (7)$$

$$\alpha' = 2K_1^{\mathrm{H}}K_2^{\mathrm{H}}[\mathrm{H}^+]^2 + K_1^{\mathrm{H}}[\mathrm{H}^+] \qquad (8)$$

$$\alpha = K_1^{\mathrm{H}}K_2^{\mathrm{H}}[\mathrm{H}^+]^2 + K_1^{\mathrm{H}}[\mathrm{H}^+] + 1 \qquad (9)$$

The stability constant, K_{f}, obtained by using equation (5) is listed in Table 1 along with the corresponding value reported for $[\mathrm{Cu(bcen)}]^{2+}$.[1]

TABLE 1

Equilibrium constants for the interaction of bctn and bcen [a] with copper(II) at 25.0 ± 0.1 °C and $I = 0.2$ mol dm^{-3} (Na[NO$_3$])

Equilibrium quotient, K	L = bctn	L = bcen [a]
$K_1^{\mathrm{H}} = [\mathrm{HL}^+]/[\mathrm{H}^+][\mathrm{L}]$ [b]	$10^{9.29}$	$10^{8.81}$
$K_2^{\mathrm{H}} = [\mathrm{H_2L}^{2+}]/[\mathrm{H}^+][\mathrm{HL}^+]$ [b]	$10^{7.06}$	$10^{5.84}$
$K_{\mathrm{f}} = [\mathrm{CuL}^{2+}]/[\mathrm{Cu}^{2+}][\mathrm{L}]$ [b]	$10^{10.33}$	$10^{12.62}$
$K_{\mathrm{A}} = [\mathrm{CuH_{-1}L}^+][\mathrm{H}^+]/[\mathrm{CuL}^{2+}]$ [c]	$10^{-8.67}$	$10^{-8.12}$
$K_{\mathrm{B}} = [\mathrm{CuH_{-2}L}][\mathrm{H}^+]/[\mathrm{CuH_{-1}L}^+]$ [c]	$10^{-10.13}$	$10^{-9.45}$

[a] Ref. 1. [b] In units of dm^3 mol^{-1}. [c] In units of mol dm^{-3}.

It is interesting to compare the protonation constants and stability constants for the copper(II)–bctn and –bcen systems. The value of $K_1^{\mathrm{H}}K_2^{\mathrm{H}}$ for bctn is 100 times larger than the corresponding value for bcen, while the value of K_{f} for $[\mathrm{Cu(bctn)}]^{2+}$ given in Table 1 is about 100 times smaller than the corresponding constant for $[\mathrm{Cu(bcen)}]^{2+}$.[1] These differences are mainly attributed to steric constraints in the three linked six-membered rings of $[\mathrm{Cu(bctn)}]^{2+}$ which are relieved by the presence of a middle five-membered ring in the bcen complex. Analogous to the copper(II) complex of the linear tetraamine *N,N'*-bis(3-aminopropyl)propane-1,3-diamine,[6,7] the extremely large strain in the three consecutive six-membered rings hinders the formation of $[\mathrm{Cu(bctn)}]^{2+}$ to a significant extent, and an alternating sequence of five- and six-membered rings increases complex stability.[8]

Reactions (3) and (4) take place in the region from $a = 2$ to 4 of the 1 : 1 titration curve (or in the region from $a = 1$ to 3 of the 1 : 2 titration curve). For these reactions the relationship between K_{A} and K_{B} is as in equation (10). A and B were calculated from several sets of values of a, $[\mathrm{H}^+]$, c_{M}, and $c_{\mathrm{H}_n\mathrm{L}}$ taken from each of the titration curves.

$$1/K_{\mathrm{A}} = AK_{\mathrm{B}} + B$$

$$A = \frac{(2-a)c_{\mathrm{H}_n\mathrm{L}} + 2c_{\mathrm{M}} - [\mathrm{H}^+] + [\mathrm{OH}^-] - \alpha'[\mathrm{L}]}{[\mathrm{H}^+]^2(ac_{\mathrm{H}_n\mathrm{L}} - 2c_{\mathrm{H}_n\mathrm{L}} + [\mathrm{H}^+] - [\mathrm{OH}^-] + \alpha'[\mathrm{L}])}$$

$$B = \frac{(a-2)c_{\mathrm{H}_n\mathrm{L}} - c_{\mathrm{M}} + [\mathrm{H}^+] - [\mathrm{OH}^-] + \alpha'[\mathrm{L}]}{[\mathrm{H}^+]\{(2-a)c_{\mathrm{H}_n\mathrm{L}} - [\mathrm{H}^+] + [\mathrm{OH}^-] - \alpha'[\mathrm{L}]\}}$$

$$[\mathrm{L}] = (c_{\mathrm{H}_n\mathrm{L}} - c_{\mathrm{M}})/\alpha \qquad (10)$$

The values of K_{A} and K_{B}, obtained by using Schwarzenbach's method,[2] are listed in Table 1 along with corresponding values reported for the copper(II)–bcen system.[1] The relative equilibrium constants for these two systems indicate that the steric strains in the three consecutive six-membered rings hinder not only the formation of the complex $[\mathrm{Cu(bctn)}]^{2+}$, but also the Cu–O to Cu–N bond rearrangements at the two amide sites.

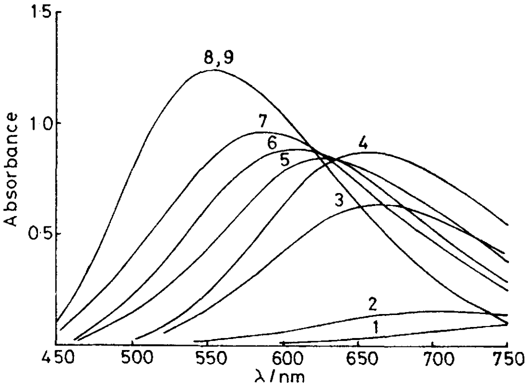


FIGURE 3 Visible absorption spectra of copper(II)–bctn solutions. All solutions contain 0.009 78 mol dm^{-3} Cu[NO$_3$]$_2$, 0.009 81 mol dm^{-3} [H$_2$bctn][NO$_3$]$_2$, and 0.20 mol dm^{-3} Na[NO$_3$]. The pH values of the solutions are: (1) 6.23; (2) 3.41; (3) 4.86; (4) 6.54; (5) 7.31; (6) 8.54; (7) 9.31; (8) 11.96; and (9) 12.10

Above $a = 4$ for the 1 : 1 solution and above $a = 3$ for the 1 : 2 solution the titration curves are the same as those calculated assuming no further reaction between $[\mathrm{CuH_{-2}L}]$ and hydroxide ion.

Electronic spectra. The absorption spectra of copper(II)–bctn solutions are shown in Figure 3. As the concentration of base is increased the band maximum increases in intensity (curves 2—4). Curve 4, at $a = 2$, is almost entirely due to the species $[\mathrm{CuL}]^{2+}$. As the base concentration is further increased beyond $a = 2$ (curves 5—7) the band maximum shifts to shorter wavelengths. That curve 8 is identical with 9 confirms the potentiometric observation that no further reaction takes place between $[\mathrm{CuH_{-2}L}]$ and OH$^-$.

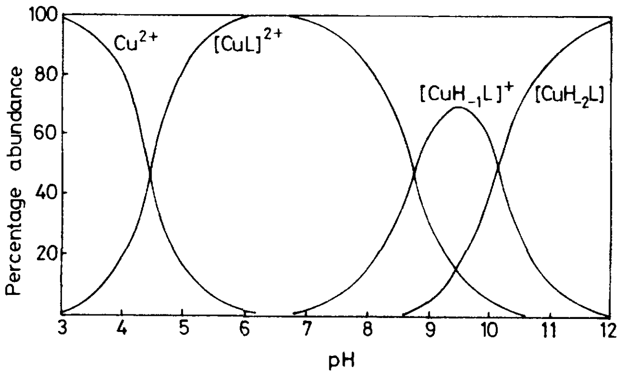


FIGURE 4 Degree of formation of copper(II)–bctn complexes in 1 : 1 metal-to-ligand solution

Using the various equilibrium constants in Table 1, the degree of formation of each copper(II)–bctn species in a 1 : 1 solution can be calculated and is shown in Figure 4.

TABLE 2

Absorption maxima for copper(II) complexes in the visible region

Species	$\lambda_{max.}$/nm
$[Cu(bctn)]^{2+}$	658
$[Cu(H_{-1}bctn)]^{+}$	595
$[Cu(H_{-2}bctn)]$	555
$[Cu(bcen)]^{2+}$	645 *
$[Cu(H_{-1}bcen)]^{+}$	580 *
$[Cu(H_{-2}bcen)]$	535 *

* Ref. 1.

From this Figure, the concentrations of all species present in the solution (the spectrum of which is in Figure 3) can be calculated. Then, with equation (11), the spectra

$$A = l(\varepsilon_{Cu^{2+}}[Cu^{2+}] + \varepsilon_{CuL^{2+}}[CuL^{2+}] + \varepsilon_{CuH_{-1}L^{+}}[CuH_{-1}L^{+}] + \varepsilon_{CuH_{-2}L}[CuH_{-2}L]) \quad (11)$$

in Figure **3** can be resolved into their components. The absorption characteristics of all species so obtained are shown in Figure **5** and in Table **2**, along with the reported values for the copper(II)–bcen system. As in the case of copper(II)–*N,N'*-diglycylethylenediamine,[9] the potentiometric and spectrophotometric observations of copper(II)–bctn solutions indicate that it is the amide protons, not those of co-ordinated water molecules, which are dissociated. Evidence in support of this was obtained from i.r. spectroscopic studies of these complexes in solution.[10] In view of the similarity of the ligands btcn and bcen, we may expect that the corresponding complexes would have absorption maxima of similar wavelengths. The wavelength for each of the copper(II)–bctn complexes is slightly larger than that of the corresponding copper(II)–bcen species. These differences reflect the distorted planar structures of the copper(II)–bctn complexes. In general, the lower the degree of distortion from a square-planar structure, the smaller is $\lambda_{max.}$. The distortions are mainly attributed to the large steric constraints in the three linked six-membered chelate rings. The fact that the equilibrium constants K_f, K_A, and K_B for the copper(II)–bctn system are significantly smaller than those for copper(II)–bcen lends support to this view.

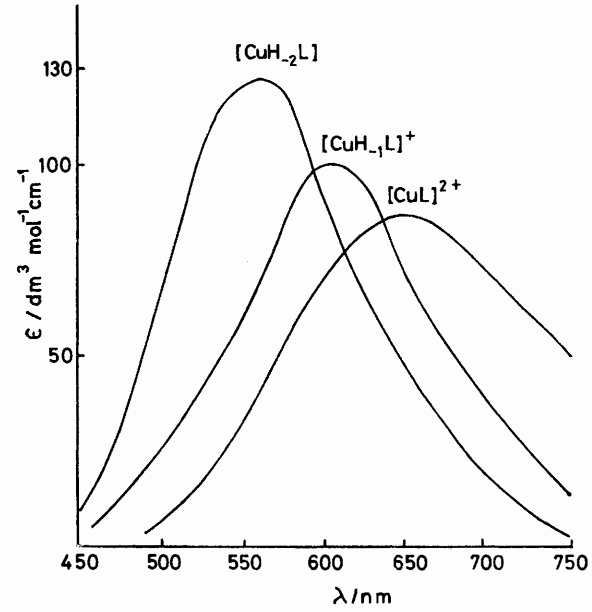


FIGURE 5 Molar absorbances of the various copper(II)–bctn complexes in the visible region

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