Copper(II) Complexes of *N,N'*-Bis(2-carbamoylethyl)ethylenediamine in Methanol–Water

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The interactions of the *N,N'*-bis(2-carbamoylethyl)ethylenediamine (bcen) with copper(II) in 50 wt.% methanol–water have been investigated by a potentiometric technique. The two protonation constants of the ligand at 25.0 ± 0.1 °C and 0.10 mol dm^{-3} NaClO$_4$ are $10^{8.50}$ and $10^{5.05}$ dm^3 mol^{-1}. The formation of $[\mathrm{Cu(bcen)}]^{2+}$ and the Cu–O to Cu–N bond rearrangements at the two amide sites of this complex have been studied quantitatively under the same conditions. Solvent effects on the protonation constants of the ligand and on the equilibrium constants of these reactions are discussed.

Previously, we reported thermodynamic studies of copper(II) complexes of diamino-diamides in aqueous solution.[1–4] Complexation of copper(II) with such ligands is accompanied by ionization of the co-ordinated amide groups, and Cu–O to Cu–N bond rearrangements at the two amide sites occur with increasing pH. The result of an *X*-ray crystallographic study[5] have shown unequivocally the displacement of the amide protons in the solid $[\mathrm{CuH_{-2}bcen}]$[bcen = *N,N'*-bis(2-carbamoylethyl)ethylenediamine] and the co-ordination of the resulting negatively charged amide groups to the metal ion.

In order to investigate the solvent effects on the equilibrium constants of the above reactions, the formation of the copper(II) complex of bcen and the Cu–O to Cu–N bond rearrangements at the two amide sites of this complex in 50 wt. % methanol–water as solvent have been studied by a potentiometric technique.

Experimental

Reagents.—The ligand, bcen, was the same as that reported previously.[1,3] All other chemicals used were of GR grade from Merck or Fluka.

Measurements.—For pH measurements a Radiometer PHM64 equipped with a GK2401B combined electrode was used. The pH was standardized with a specific solvent composition, 50 wt. % methanol–water. The oxalate buffer (0.01 mol dm^{-3} oxalic acid + 0.01 mol dm^{-3} ammonium hydrogenoxalate) and succinate buffer (0.01 mol dm^{-3} succinic acid + 0.01 mol dm^{-3} lithium hydrogensuccinate) were prepared in the same solvent. The hydrogen-ion and hydroxide-ion concentrations in 0.10 mol dm^{-3} NaClO$_4$ were calculated from $-\log[\mathrm{H^+}] = \mathrm{pH} - 0.13$ and $-\log[\mathrm{OH^-}] = 13.97 - \mathrm{pH}$.[6]

Appropriate aliquots of standard solutions of ligand or ligand and metal ion were titrated with a standard CO$_2$-free sodium hydroxide solution prepared by following the method of Rorabacher *et al.*[6] In all titrations the ionic strength was maintained constant by using 0.10 mol dm^{-3} NaClO$_4$ as supporting electrolyte. The solutions were protected from air by a stream of humidified prepurified nitrogen which had first been bubbled successively through two towers containing solvent of identical composition to the titration solution in order to facilitate saturation of the gas with the solvent vapour and thereby minimize evaporation. The temperature was controlled at 25.0 ± 0.1 °C during measurements. The equilibrium constants were obtained by a linear least-squares fit of the data by using an Apple II microcomputer.

Results and Discussion

Protonation Constants.—The potentiometric titration curve of the perchlorate salt of diprotonated bcen with standard base is shown in the Figure. The values of the protonation constants of bcen, K_1^{H} and K_2^{H}, in 50 wt. % methanol–water are listed in the Table together with values reported for this ligand in

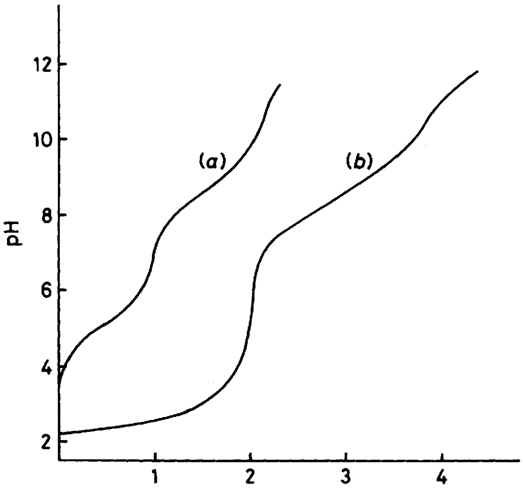


Figure. Titration curves for bcen in the presence and absence of Cu$^{\mathrm{II}}$ in 50 wt. % methanol–water and 0.10 mol dm^{-3} NaClO$_4$ at 25.0 ± 0.1 °C. Test solutions: (*a*) 21.5 cm^3 of 0.009 30 mol dm^{-3} [H$_2$bcen][ClO$_4$]$_2$; (*b*) 23.1 cm^3 of 0.005 19 mol dm^{-3} [H$_2$bcen][ClO$_4$]$_2$ and 0.004 81 mol dm^{-3} Cu[ClO$_4$]$_2$. Titrant: 0.1004 mol dm^{-3} NaOH in 50 wt. % methanol–water; *a* = number of mols of NaOH added per mol of ligand

Table. Basicity constants for bcen and equilibrium constants for its copper(II) complexes in 50 wt. % methanol–water at 25.0 ± 0.1 °C and *I* = 0.10 mol dm^{-3} (NaClO$_4$)

wt. % CH$_3$OH	log K_1^{H}	log K_2^{H}	log K_f	log K_A	log K_B
0	8.78	5.82	12.58	−8.08	−9.33
	±0.04	±0.03	±0.07	±0.05	±0.04
50	8.50	5.05	12.92	−7.23	−9.13
	±0.03	±0.03	±0.04	±0.04	±0.04

aqueous solution. The protonation constants for bcen in 50 wt. % methanol are smaller than those in aqueous solution. This trend is in accord with those found for ammonia, aniline, methylamine, and a few polyamines.[6] The general patterns of the protonation constants for amines and polyamines have been interpreted in terms of electrostatic effects,[7] base solvation, and proton solvation as a function of the solvent composition.[6] The solvent effect[8] upon K_2^H is more pronounced than upon K_1^H. This effect arises from the increased electrostatic repulsion between an approaching proton and the positively charged sites of the protonated species and is a function of the dielectric constant.

Equilibrium Constants for the Interactions of Copper(II) *with bcen.*—The complexation reactions of copper(II) with bcen in 50 wt. % methanol–water are fast. During titration the colour of the solutions changed from blue to deep blue and finally to violet. The titration curve for the 1:1 copper(II)–bcen system is shown in the Figure, curve (*b*). 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 (1)—(3) were found to describe the reactions of copper(II) with bcen, where L represents the unprotonated ligand, bcen, and the negative subscript to H represents the number of amide protons lost from the ligand. The three complexes $[CuL]^{2+}$, $[CuH_{-1}L]^+$, and $[CuH_{-2}L]$ are shown opposite.

$$Cu^{2+} + L \rightleftharpoons [CuL]^{2+};\ K_f = [CuL^{2+}]/[Cu^{2+}][L] \quad (1)$$

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

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

Below $a = 2$ for the 1:1 titration only the formation of $[CuL]^{2+}$ takes place. The stability constant for this complex in 50 wt. % methanol–water solution is given in the Table. Reactions (2) and (3) take place in the region from $a = 2$ to 4. For these reactions the relationship between K_A and K_B is as in equation (4). The values of A and B were calculated from several sets of values of a, $[H^+]$, c_M, and c_{H_nL} taken from each titration curve. The values of K_A and K_B, obtained by using Schwarzenbach's method,[9] are listed in the Table. Above $a = 4$ for the 1:1 solution the titration curve is as calculated assuming no further reaction between $[CuH_{-2}L]$ and hydroxide ion.

$$1/K_A = AK_B + B \quad (4)$$

$$A = \frac{(2 - a)c_{H_nL} + 2c_M - [H^+] + [OH^-] - \alpha'[L]}{[H^+]^2(ac_{H_nL} - 2c_{H_nL} + [H^+] - [OH^-] + \alpha'[L])} \quad (5)$$

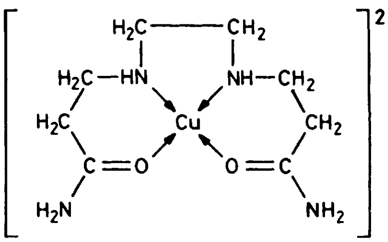
$$B = \frac{(a - 2)c_{H_nL} - c_M + [H^+] - [OH^-] + \alpha'[L]}{[H^+]\{(2 - a)c_{H_nL} - [H^+] + [OH^-] - \alpha'[L]\}} \quad (6)$$

$$[L] = (c_{H_nL} - c_M)/\alpha \quad (7)$$

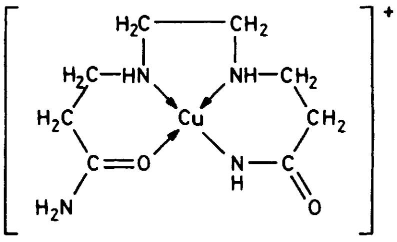
$$\alpha = K_1^H K_2^H [H^+]^2 + K_1^H [H^+] + 1 \quad (8)$$

$$\alpha' = 2K_1^H K_2^H [H^+]^2 + K_1^H [H^+] \quad (9)$$

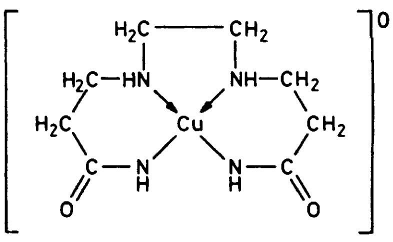
The stability constant value for $[Cu(bcen)]^{2+}$ in 50 wt. % methanol–water is about two times larger than that in aqueous solution. In general, the value of a stability constant is strongly influenced by the solvation energy of the metal ion. As expected from the Born equation, the solvation energy of a metal ion increases with increasing dielectric constant of the solvent. The sequence for the stability constants of $[Cu(bcen)]^{2+}$ in water and in 50 wt.% methanol–water is consistent with this expectation.[10]



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



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



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

It is interesting to note that the protonation constants of bcen in 50 wt. % methanol–water are smaller than those in aqueous solution, while the stability constant for $[Cu(bcen)]^{2+}$ in 50 wt. % methanol–water is larger than that in aqueous solution. These results imply the analytically significant possibility that Cu^{II} may compete more successfully with the proton for the ligand in 50 wt. % methanol–water than is the case in aqueous solution.

The deprotonation constants for $[Cu(bcen)]^{2+}$ and $[Cu(H_{-1}bcen)]^+$, K_A and K_B, in 50 wt. % methanol–water are larger than those in aqueous solution. This trend is consistent with the relative basicities of these solvents.[11] The addition of methanol provides a larger number of basic water molecules through a breakdown of the complex water structure, resulting in a slightly higher basicity for 50 wt. % methanol–water relative to pure water.[12]

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