Hydration and Structure of Some Copper(II) Ethylenediaminetetra-acetate and Aminocarboxylate Complexes in Aqueous Solution

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THERE is little definitive evidence as to the number and identity of the donor atoms in multidentate ligands bound to metal ions in solution. Speculation, based on thermodynamic data, as to the number of binding sites in *e.g.* polyaminocarboxylate and polyamine ligands has been rife for two decades.[1] We have recently demonstrated methods for locating binding sites based upon differential proton relaxation[2] and differential contact shifts[3] in bound ligands. It is also possible to determine the number of water molecules bound to certain co-ordinated metal ions by studying the proton relaxation of water.

Consider a ligand A (charge omitted for simplicity) in stepwise equilibrium with the complexes $BA_n(H_2O)_{x_n}$ $(0 \leqslant n \leqslant N)$ of a paramagnetic metal ion $B(H_2O)_{x_0}$ in aqueous solution. The fraction of total metal ions in each complex is denoted by α_n, the (mean) proton relaxation time of the aquo-ligands in each complex by T_n and the relaxation time of water outside the primary hydration spheres by T_W. We define a variable

$$\rho = 1 - \frac{\lim\limits_{\alpha_0 \to 1} (1/T_{BA}) - 1/T_{BA}}{1/T_B - \lim\limits_{B \to 0} (1/T_B)} \qquad (1)$$

in terms of observable proton relaxation times of water, T_B and T_{BA}, containing the same total concentration, B, of free and co-ordinated metal ions respectively. Combination of the Bloembergen equation[4] and the law of mass action yields

$$\rho = \frac{\sum\limits_{n=0}^{n=N} \alpha_n x_n \, (1/T_n - 1/T_W)}{x_0 \, (1/T_0 - 1/T_W)} \qquad (2)$$

at high frequencies. For systems in which $T_W \gg T_n$ for complexes with $x_n \neq 0$, equation (2) approximates closely to

$$\rho = \frac{T_0}{x_0} \sum_{n=0}^{n=N} \alpha_n x_n / T_n \qquad (3)$$

Using a Perkin Elmer 60 Mc./sec. spectrometer, values of ρ at 34° were obtained from line widths. Corresponding values of α_n were calculated[5] from the stoicheiometry, pH, and stability constants.[6] Equation (3) was solved for the N parameters $(T_0 x_n / T_n x_0)$ by standard methods.[5]

On the reasonable assumption[4,7] that the relaxation times are determined solely by the nuclear spin–electron spin dipole–dipole relaxation

$$T_0/T_n = (g_n/g_0)^2 (\tau_n/\tau_0) \, (r_0/r_n)^6 \qquad (4)$$

where r_n is the appropriate mean distance from the metal ion to the protons in bound water in $BA_n(H_2O)_{x_n}$. Values of the g factors were taken from the literature.[8] The correlation times, τ_n, were assumed to be rotational tumbling times: various models indicate that these are proportional to the product of the volume of the species and bulk viscosity.[9] At low concentrations of metal ion and ligand, the viscosity is invariant. The ratios (τ_n/τ_0) were calculated from the appropriate crystal packing volumes on the assumption that the Kitaigorodskii packing coefficients[10] are equal. Hence values of $(x_n/x_0)\,(r_0/r_n)^6$ were obtained.

With x_0 as 6 for Cu^{II},[11] values of (r_0/r_n) were obtained for integral values of x_n. On the assumption that crystallographically determined $Cu–OH_2$ bond lengths[12–14] for axial and equatorial aquo-ligands place approximate limits on the permissible value of (r_0/r_n), a unique value of x_n could be selected for each system. (The assumption that bond lengths in crystals and in solution are approximately equal is justified, in so far as the ratio of distances from Cu^{II} to the Me– and $–CH_2–$ protons in crystalline[13] bismethoxyacetatocopper(II) dihydrate is $1{\cdot}14_3$ and that found in solution by differential proton relaxation[2] is 1·16.)

Some Cu^{II} α- and β-aminocarboxylate systems (glycine, α- and β-alanine, sarcosine, and *NN*-dimethylglycine) were studied as controls, as there is little reason to doubt that $x_1 = 4$ and $x_2 = 2$. Application of the above procedure to bisglycinatocopper(II), for example, implies one aquo-ligand with $Cu–OH_2 = 1{\cdot}8_5$ Å, or two at a mean distance of 2·3 Å, or three at 2·6 Å. Of these possibilities only the bisaquo-complex is compatible with known bond lengths,[12–14] and a $Cu–OH_2$ separation of 2·3 Å implies two axial water molecules.

For all the α- and β-amino-acid systems studied,

TABLE

		$[CuA(H_2O)_4]^+$				$[CuA_2(H_2O)_2]$		
		$Cu–OH_2$ in Å				$Cu–OH_2$ in Å		
Ligand	r_0/r_1[a]	Solution	Crystal	Position[b] of H_2O	r_0/r_2[a]	Solution	Crystal	Position[b] of H_2O
Glycine	$0{\cdot}99_6$	2·12		2A + 2E	$0{\cdot}94_5$	2·29		2A
α-Alanine	$0{\cdot}97_8$	2·18		2A + 2E	$0{\cdot}92_7$	2·34		2A
β-Alanine	$0{\cdot}98_4$	2·16	2·20[c]	2A + 2E	$0{\cdot}94_9$	2·26	2·43[d]	2A
Sarcosine	$0{\cdot}98_4$	2·16		2A + 2E	$0{\cdot}94_8$	2·28		2A
NN-Dimethylglycine								
Complex	$0{\cdot}96_8$	2·21		2A + 2E	$0{\cdot}91_4$	2·39		2A
$[Cu(EDTA)(H_2O)]^{2-}$	1·03	2·03	2·08[c]	E				
$Cu(HEDTA)(H_2O)_2]^-$	1·01	2·08		2E				

[a] Calculated assuming r_0 is equal to the appropriate mean of axial and equatorial Cu–H distances[14] in the hexa-aquo-ions in crystals.

[b] A = axial; E = equatorial.

[c] Mean axial and equatorial value for Cu^{II} (amino)carboxylates and peptides.[12,13]

[d] Mean axial value for Cu^{II} (amino)carboxylates and peptides.[12,13]

[e] In $[Ni(H_2EDTA)(H_2O)]$, isomorphous[15] with the Cu^{II} complex.

we find $[CuA_2(H_2O)_2]$ with two axial water molecules and $[CuA(H_2O)_4]^+$ with four water molecules at a distance compatible with two axial and two equatorial aquo-ligands (see Table). Provided that the co-ordination number of Cu^{II} remains six throughout, the organic ligands are bidentate in solution. The long axial $Cu–OH_2$ bonds for *NN*-dimethylglycine are consistent with models, which indicate that $N–Me_2$ groups will obstruct the approach of water.

With $(EDTA)^{4-}$ and its monoprotonated form $(HEDTA)^{3-}$ as ligands, we find $[Cu(EDTA)(H_2O)]^{2-}$ and $[Cu(HEDTA)(H_2O)_2]^-$. In both, the water is equatorial, as in crystalline[15] $[Cu(H_2EDTA)(H_2O)]$. Again provided that the co-ordination number of Cu^{II} in these complexes remains six, as in the crystalline complex and as is implied by the visible spectra, EDTA is a pentadentate ligand and HEDTA a tetradentate ligand, owing to strain in the CuNN plane.[15] It appears to have escaped notice that the stability constant of the HEDTA complex is slightly less than that of the mono-NTA complex,[6] in which the ligand is at most tetradentate.

For the triglycylglycine system at high pH, recalculation of the data of Falk *et al.*,[16] with the correct value of τ_0/τ_1, suggests that $x = 2$ with $Cu–OH_2 = 2{\cdot}2$ Å. In crystalline[12] disodium triglycylglycinatocuprate(II) decahydrate, all four nitrogen atoms bind the Cu^{II} ion, but the carboxyl group does not.

This method is being applied to a wide variety of systems.

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