Axial Ligation Constants of Copper(II) Macrocyclic Tetra-amine Complexes

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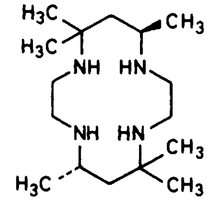
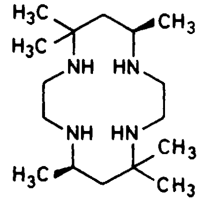
The effect of solvent on the axial ligation constants of red (*C-meso-* and red (*C-rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane)copper(II) complexes with Cl^-, Br^-, I^-, and N_3^- in dimethylformamide, dimethyl sulphoxide, methanol, and water has been studied by spectrophotometric techniques. The sequence for the axial ligation constants varies in the order $K_{H_2O} \ll K_{dmso} < K_{dmf} < K_{MeOH}$. A linear relationship between the relative free energies of solvation for the anions in organic and aqueous solvents and the relative free energies of ligand addition to copper(II) macrocyclic complexes in these solvents was obtained.

Previously, we have reported the equilibrium constants for the formation of adducts of copper(II) macrocyclic tetra-amine complexes with anionic ligands in aqueous solution represented by the general equation (1). Here L is the macrocyclic ligand *C-meso* (L^1) or *C-rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane (L^2).[1-3] These ligation constants can be quantitatively correlated by use of the Edwards equation,[4] $\log K/K_0 = \alpha E + \beta H$, where E is a redox factor and H is a proton basicity factor of the anionic ligands.[4-7] It is still not clear what effect the solvent has on these ligation constants. To help clarify the situation, the equilibria of these reactions in dimethylformamide (dmf), dimethyl sulphoxide (dmso), and methanol (MeOH) were studied by spectrophotometric methods.

$$[CuL]^{2+} + X^- \overset{K}{\rightleftharpoons} [CuLX]^+ \qquad (1)$$



L^1



L^2

Experimental

Reagents.—The macrocyclic ligands L^1 and L^2 were prepared by the procedures described by Hay *et al.*[8] The salts red $[CuL^1][ClO_4]_2$ [9] (Found: C, 35.0; H, 6.65; Cl, 13.0; N, 10.35. Calc. for $C_{16}H_{36}Cl_2CuN_4O_8$: C, 35.15; H, 6.60; Cl, 13.0; N, 10.25%) and red $[CuL^2][ClO_4]_2$ [10] (Found: C, 35.05; H, 6.85; Cl, 13.1; N, 10.35%) were prepared as described previously. All other chemicals used in this work were of GR grade from Merck.

Instrumentation.—A Cary 17 spectrophotometer with a thermostatted cell compartment was used to record absorption spectra. The temperature was maintained within ±0.1 °C. Equilibrium constants were obtained by a linear least-squares fit of the data on an IBM 1130 computer.

Table 1. Axial ligation constants of copper(II) macrocyclic tetra-amine complexes with various anions in organic or aqueous * solution at 25.0 °C

X^-	Red $[CuL^1]^{2+}$ In dmf	In dmso	In MeOH	In water
(*a*)				
Cl^-	1.3×10^4	1.2×10^4	3.8×10^4	1.5
Br^-	4.6×10^3	1.6×10^3	3.5×10^4	2.3
I^-	9.3×10^2	1.2×10^2	1.8×10^4	3.0
N_3^-	9.7×10^3	2.1×10^3	4.5×10^4	4.0
	Red $[CuL^2]^{2+}$			
(*b*)				
Cl^-	1.1×10^4	8.9×10^3	2.9×10^4	1.8
Br^-	6.4×10^3	2.1×10^3	2.7×10^4	3.2
I^-	1.5×10^3	2.2×10^2	2.1×10^4	6.5
N_3^-	1.1×10^4	2.6×10^3	4.0×10^4	8.6

* See ref. 1.

Results and Discussion

The equilibrium constant for the reaction of red $[CuL^1]^{2+}$ or red $[CuL^2]^{2+}$ and anionic ligand was determined by measuring the apparent absorbance, $\varepsilon_{app.}$, at 600 nm, which had a linear dependence on $(\varepsilon_{app.} - \varepsilon_{CuL})/[X^-]$ in accordance with equation (2). The value of $[X^-]$ was calculated by an iterative procedure in which an estimated value of K_X was used to calculate values of $[X^-]$ and then these were used to obtained a new value of K_X until the least-squares deviation in the plot of $\varepsilon_{app.}$ *vs.* $-(\varepsilon_{app.} - \varepsilon_{CuL})/[X^-]$ reached a minimum value. The equilibrium constants in dmf, dmso, and MeOH determined in this work are compiled in Table 1, along with those for aqueous solutions reported in earlier studies for comparison.[1-3,5-7]

$$\varepsilon_{app.} = -\frac{1}{K_X} \cdot \frac{\varepsilon_{app.} - \varepsilon_{CuL}}{[X^-]} + \varepsilon_{CuLX} \qquad (2)$$

The following trends in Table 1 are particularly noteworthy: (1) for each of these reactions, the sequence for the axial ligation constants is $K_{H_2O} \ll K_{dmso} < K_{dmf} < K_{MeOH}$; (2) for

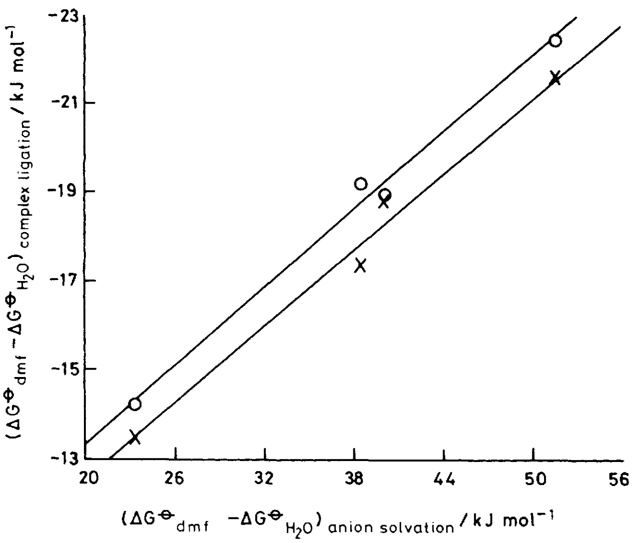


Figure 1. Plot of $(\Delta G^\ominus_{dmf} - \Delta G^\ominus_{H_2O})_{complex\ ligation}$ against $(\Delta G^\ominus_{dmf} - \Delta G^\ominus_{H_2O})_{anion\ solvation}$ at 25 °C: ○, red $[CuL^1]^{2+}$; ×, red $[CuL^2]^{2+}$

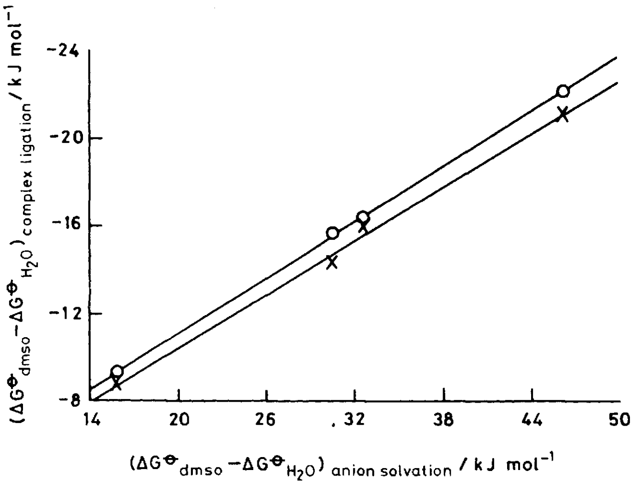


Figure 2. Plot of $(\Delta G^\ominus_{dmso} - \Delta G^\ominus_{H_2O})_{complex\ ligation}$ against $(\Delta G^\ominus_{dmso} - \Delta G^\ominus_{H_2O})_{anion\ solvation}$ at 25 °C: key as in Figure 1

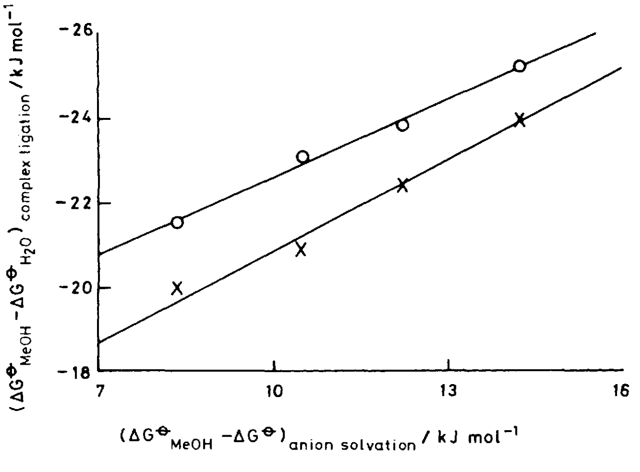


Figure 3. Plot of $(\Delta G^\ominus_{MeOH} - \Delta G^\ominus_{H_2O})_{complex\ ligation}$ against $(\Delta G^\ominus_{MeOH} - \Delta G^\ominus_{H_2O})_{anion\ solvation}$ at 25 °C: key as in Figure 1

Table 2. Values (kJ mol^{-1}) of $(\Delta G^\ominus_{org} - \Delta G^\ominus_{H_2O})_{anion\ solvation}$* and $(\Delta G^\ominus_{org} - \Delta G^\ominus_{H_2O})_{complex\ ligation}$ of copper(II) macrocyclic tetraamine complexes with various anions at 25.0 °C

		$(\Delta G^\ominus_{dmf} - \Delta G^\ominus_{H_2O})_{ligation}$	
X^-	$(\Delta G^\ominus_{dmf} - \Delta G^\ominus_{H_2O})_{solvation}$	Red $[CuL^1]^{2+}$	Red $[CuL^2]^{2+}$
Cl^-	51.5	−22.4	−21.6
Br^-	40.2	−18.8	−18.8
I^-	23.4	−14.2	−13.5
N_3^-	38.5	−19.3	−17.7

		$(\Delta G^\ominus_{dmso} - \Delta G^\ominus_{H_2O})_{ligation}$	
	$(\Delta G^\ominus_{dmso} - \Delta G^\ominus_{H_2O})_{solvation}$	Red $[CuL^1]^{2+}$	Red $[CuL^2]^{2+}$
Cl^-	46.0	−22.2	−21.1
Br^-	32.6	−16.2	−16.0
I^-	15.9	−9.2	−8.7
N_3^-	30.5	−15.5	−14.2

		$(\Delta G^\ominus_{MeOH} - \Delta G^\ominus_{H_2O})_{ligation}$	
	$(\Delta G^\ominus_{MeOH} - \Delta G^\ominus_{H_2O})_{solvation}$	Red $[CuL^1]^{2+}$	Red $[CuL^2]^{2+}$
Cl^-	14.2	−25.1	−24.0
Br^-	12.1	−23.8	−22.4
I^-	8.4	−21.5	−20.0
N_3^-	10.5	−23.1	−20.9

* See ref. 11.

each of these copper(II) macrocyclic complexes, the ligation tendency for the anions varies in the order $I^- < Br^- < N_3^-$, Cl^- in dmf and dmso, the tendency in MeOH being very similar, while in water it varies as $Cl^- < Br^- < I^- < N_3^-$.

In general, the value of the ion-association constant for a given equilibrium is strongly influenced by the dielectric constant of the medium. As expected from the electrostatic theory, the force acting between $[CuL]^{2+}$ and X^- increases with decreasing dielectric constant of the solvents. The above sequence for the equilibrium constant is consistent with this expectation.

The different ligation tendencies in these solvents indicate that the equilibrium constants depend significantly on the extent of solvation of the anions, and lead us to think that there may be a relationship between the relative free energies of solvation for these anionic ligands in organic and aqueous solvents, $(\Delta G^\ominus_{org} - \Delta G^\ominus_{H_2O})_{anion\ solvation}$,[11] and the relative free energies of ligand addition to copper(II) macrocyclic complexes in these solvents, $(\Delta G^\ominus_{org} - \Delta G^\ominus_{H_2O})_{complex\ ligation}$. Values of these quantities are compiled in Table 2, and the linear relationships between them are shown in Figures 1—3.

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