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The Chelate Effect in Complexes with Ethanolamine

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A glass electrode study of the complexes of ethanolamine (L) with Cu(II), Ni(II), Co(II), Mn(II), and Zn(II) has been carried out. It is shown that the higher values of logK reported for Cu(II) by previous workers are in error because of the presence of deprotonated species such as $Cu(LH_{-1})$ *in their solutions. A 0.1* M $LHNO_3$ *background electrolyte was used to suppress these deprotonation reactions, and at 25 °C* $\log K_1 = 4.50$, $\log K_2 = 4.05$, *and* $\log K_3 = 3.33$ *were obtained. The reaction constant for the process* $CuL_3^{2+} \rightleftharpoons CuL_2(LH_{-1})^+ + H^+$ *was found to be −8.2. The d–d spectra of the Cu(II) complexes in solution were used to support the interpretation that this was the process occurring in solution rather than the addition of a fourth L to give* CuL_4^{2+} *as suggested by previous workers. For Ni(II) and Co(II), no evidence of deprotonation of the coordinated ligands was found, and here* $\log K_1 = 3.05$, $\log K_2 = 2.25$, *and* $\log K_3 = 1.85$ *were obtained for Ni(II), and* $\log K_1 = 2.20$ *and* $\log K_2 = 1.33$ *were obtained for Co(II). The precipitation of hydroxide did not allow the obtaining of a complete titration curve for Zn(II) and Mn(II), but* $\log K_1 = 2.41$ *and 0.81 respectively were calculated from the curves obtained. The stability of the ethanolamine complexes was discussed in relation to correlations for the chelate effect that were obtained previously.*

Introduction

The alcoholic hydroxyl group is a particularly interesting donor group in coordination chemistry, because it is related to water in the same way as the alkylamine group in glycine or ethylenediamine is related to ammonia. For reactions studied in aqueous solution, coordination of a hydroxyl group produces a chelate effect with unusual properties. If the donor abilities of the oxygen in water and the chelated hydroxyl group were identical, and steric effects, which have been shown to be important [1], are neglected for the moment, two important considerations would remain. Firstly, in the usual standard state, *i.e.* the one molar standard state, there are 55.5 times as many water molecules as ligand molecules, which, without the chelate effect, would mean that a water molecule would be attached with a probability 55.5 times greater than that of the alcoholic group. Thus, one finds that for the coordination of methanol to Cu(II), $\log K_1$ in molarity units is −1.48 [2], not much larger than the −1.74, *i.e.* −log55.5, expected from this consideration alone. For chelated hydroxyl groups, the chelate effect counters this unfavourable contribution, leading to weak, but important, stabilisation. This is seen in that an unsubstituted alkylamine such as ethylamine precipitates the hydroxide when added to cupric solutions because of the steric hindrance to coordination cuased by the alkyl group. The coordination of the hydroxyl group in ethanolamine considerably reduces this steric strain (it replaces an adjacent coordinated water molecule, and it is with these that the steric interference occurs) and stable complexes result. The second consideration, the chelate effect, can be reasonably well accounted for [3] in a simple quantitative fashion on the basis of Adamson's [4] proposals concerning the origin of the chelate effect. In simple terms, in the unsual molarity standard reference state, the concentration of the chelate effect. In simple terms, in the unusual actually 55.5 *M* at infinite dilution. This results in different units, $dm^3\ mol^{-1}$ for the $\log K_1$ of the chelate, and $dm^6\ mol^{-2}$ for the $\log\beta_2$ of coordination of the two unidentate ligands, when the usual comparisons are made so as to illustrate the chelate effect. The difficulty of the units can be overcome by expressing $\log\beta_n$ in dimensionless mole fraction units [4]. This has the mathematical consequence of equation 1 for constants that are expressed on the usual molarity scale [3]. For a bidentate ligand such as

$$\log K_1(\text{polydentate}) = \log\beta_n(\text{unidentate}) + \\ + (n-1)\log 55.5 \qquad (1)$$

ethanolamine, n equals 2, so that a stabilisation due to the chelate effect of log55.5 would be expected. In the absence of steric and inductive effects, which were found to be important [2, 3], one would expect

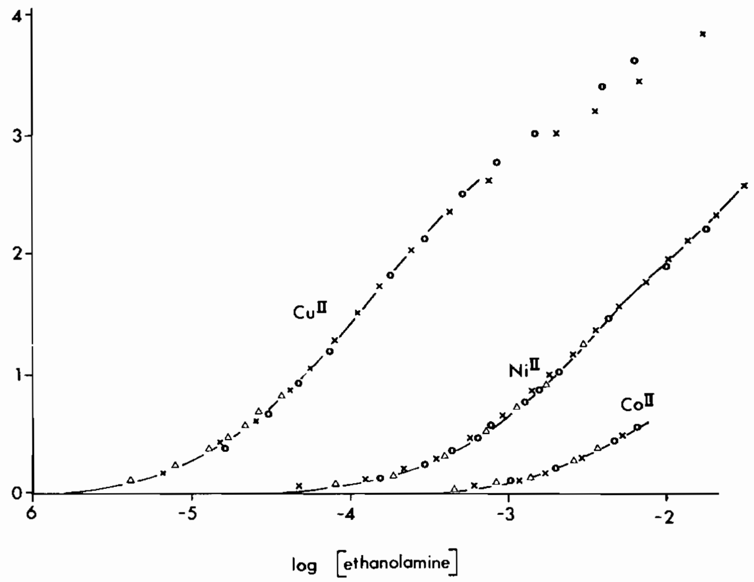

Fig. 1. Plot of $\bar{n}$ *versus* log[ethanolamine] for Cu^{II}, Ni^{II}, and Co^{II}. Initial metal ion concentrations; Cu(II) 0.0184 *M* (△), 8.8 × 10^{-3} *M* (○), 4.2 × 10^{-3} *M* (×); Ni(II) 3.3 × 10^{-2} *M* ( ), 2.5 × 10^{-2} *M* ( ), 1.65 × 10^{-2} *M* ( ); Co(II) 2.5 × 10^{-2} *M* ( ), 1.65 × 10^{-2} *M* ( ), 8.8 × 10^{-3} *M* ( ).

consideration 1 to be cancelled out by consideration 2. That is to say, the destabilisation of the alcoholic hydroxyl group coordination by log55.5 in the usual standard state caused by the great preponderance of solvent molecules is exactly cancelled when the alcoholic group is part of a chelate because of the favourable contribution of log55.5 associated with the chelate effect. We thus expect the chelated alcoholic hydroxyl group on this basis to cause no extra stabilisation for the amine group in ethanolamine. Any alteration in stability as compared with ammonia can thus be discussed in terms of the inductive effect of the bridging ethylene group [3], somewhat modified by steric effects [4].

In terms of the model of the chelate effect for amines discussed previously [3], we would expect the $\log K_1$ for Cu(II) with ethanolamine to be given simply by $\log K_1(NH_3)$ (which is [5] 4.1) multiplied by the inductive effect factor (1.152), *i.e.* 4.72. The values for $\log K_1$ for complexes of ethanolamine reported in the literature are highly variable [5], ranging for Cu(II), for example, from $\log K_1$ equals 4.7 [6] to 5.7 [7]. In order to resolve this problem, and allow a better analysis of the chelate effect in complexes of ethanolamine, we have undertaken a glass electrode study of the ethanolamine complexes of Cu(II), Ni(II), Zn(II), Co(II), and Mn(II).

Experimental

Stock solutions of the metal nitrates were prepared from the A.R. salts, and standardised by titration with EDTA [8]. Ethanolamine (Fluka, *puriss*) was weighed out to make up a stock solution, and standardised with nitric acid. The purity was found to be greater than 99 percent judged by the weight of amine taken. Potentials were recorded on a Radiometer PHM64 pH meter. The cell and other apparatus were as described previously [9]. The approach used was to titrate x ml of 0.033 *M* metal nitrate plus y ml of 0.1 *M* HNO_3, where x plus y equals 20 ml, with 0.2 *M* ethanolamine in 0.1 *M* HNO_3. This produces an ionic strength of 0.1, with the background salt being mainly ethanolammonium nitrate, which, as discussed below, is essential for preventing deprotonation of the alcoholic hydroxyl group of the coordinated ethanolamine. A value of x equals zero gives one the pK_a determination, the pK_a of ethanolamine being found in this work (mean of three titrations) to be 9.451 ± 0.005 in 0.1 *M* $HOCH_2CH_2NH_3NO_3$ at 25 °C. Variation of x and y allows one at low x to have a high background of ethanolammonium ions, while at low y one has a low background concentration of the latter ions but a high metal concentration. Varying the x and y and checking the resulting $\bar{n}$ *versus* log[L] curves ([L] = free ligand concentration) for superimposability allows one to check for deprotonation of the coordinated ligand, and also any polymerisation equilibria that might occur. The logK values for the metal complexes were calculated from the $\bar{n}$ *versus* log[L] curves by a small computer program which took trial values of logK from log[L] at $\bar{n}$ at 0.5, 1.5, and 2.5, and then refined these by an iterative method

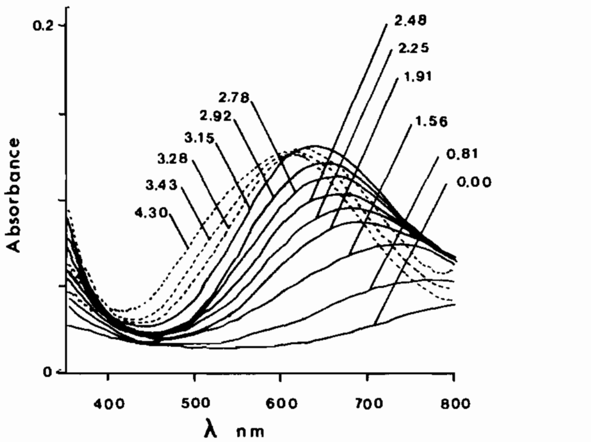

Fig. 2. Electronic spectra of 2.211 × 10^{-3} *M* Cu^{2+} solutions with $\bar{n}$ values indicated. The latter were calculated from the constants determined in this paper. T = 25 °C and μ = 0.1. The isosbestic point after $\bar{n}$ = 3.0 occurs at 614 nm, and is associated with deprotonation of a coordinated ethanolamine ligand at higher $\bar{n}$ values.

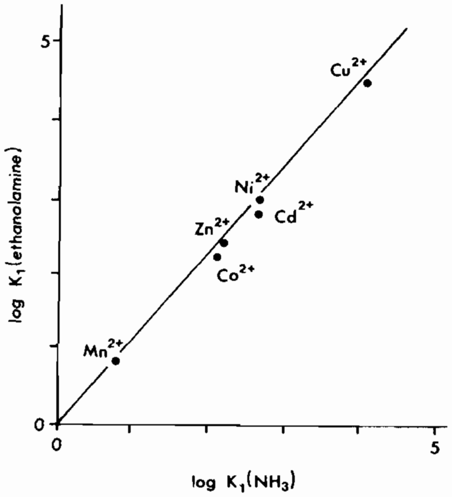

Fig. 3. Relationship between $\log K_1$ (ethanolamine) and $\log K_1$ (NH_3) for a variety of metal ions. The solid line drawn in has a slope of 1.152, which is the inductive effect factor discussed in reference 3.

to achieve as close a fit as possible to the experimental curve.

Results and Discussion

In Fig. 1 is shown the experimental plots of $\bar{n}$ *versus* log[L] for Cu(II) and Ni(II). For Cu(II) below $\bar{n}$ equals 2.5, very good superimposability is obtained, which means that below this no dimers occur, and the ligand is not being deprotonated. Above $\bar{n}$ equals 2.5, divergence of the $\bar{n}$ *versus* log[L] curve occurs as the concentration of background LH^+ ion varies, which suggests that this release of a proton does not correspond to coordination of a fourth ethanolamine molecule to Cu(II) as suggested [7, 10], but rather to removal of a proton from the hydroxyl group of an ethanolamine group already coordinated to Cu(II) to give the complex $[Cu(HOCH_2CH_2NH_2)_2NH_2CH_2CH_2O]^+$. The $\bar{n}$ *versus* log[L] curve for Cu(II) can be well accounted for below $\bar{n}$ equals 2.5 by $\log K_1$ = 4.50, $\log K_2$ = 4.05, and $\log K_3$ = 3.33 (solid line). This is in reasonable agreement with the work of Sklenskaya and Karapetyansk [6] of $\log K_1$ = 4.7, $\log K_2$ = 3.8 and $\log K_3$ = 2.9 taking into consideration the higher ionic strength (0.43 *M* $LHNO_3$) used in their study. Figure 2 shows the variation in the visible spectrum of Cu(II) as the ratio of ligand to metal ion is varied. The change is a smooth progression until the ratio exceeds 3:1, when a clear change in the direction of spectral shift occurs as more ligand is added, suggesting that there is no longer a smooth replacement of water by ethanolamine molecules, but something different, such as the suggested deprotonation of an already coordinated ethanolamine. In their extensive study of copper(II) ethanolamine complexes at higher pH, Fisher and Hall [11] showed that all of the hydroxyl groups on the bis-ethanolamine complex were deprotonated in the absence of added ethanolammonium nitrate. It seems most likely, therefore, that the higher logK values found [7, 10] without a high background concentration of $LHNO_3$ reflect a certain level of deprotonation of the coordinated ligands, and are therefore in error. In this study, if the complex at $\bar{n}$ above 3.0 involves deprotonation, a logK for the process of −8.2, ±0.1 can be

$$CuL_3 \rightleftharpoons CuL_2(LH_{-1}) + H^+ \qquad (2)$$

obtained from the titration curves. The fact that a consistent value for this constant can be obtained from three separate titration curves shows that the proposal that the process involved is that in equation 2 must be correct.

For Ni(II) and Co(II), the curves were superimposable over the whole accessible range, and constants in reasonable agreement with those obtained by other workers [6, 12, 13] were calculated from the formation curves, namely $\log K_1$ = 3.05, $\log K_2$ = 2.25, and $\log K_3$ = 1.85 for Ni(II), and $\log K_1$ = 2.20, $\log K_2$ = 1.33 for Co(II). The titrations with the Zn(II) were plagued by precipitation of hydroxide, which must relate to the high acidity of the Zn(II) ion coupled with its small affinity for ethanolamine. The highest $\bar{n}$ values obtained before precipitation set in were about 0.15, and from these a value of $\log K_1$ = 2.41 was obtained. The surprisingly high

$\log K_1 = 3.7$ reported [7] for Zn(II) must reflect hydroxide formation, or else deprotonation of the coordinated ligand. Titrations were carried out for Mn(II), and $\log K_1 = 0.81$ could be calculated from the titration curve which unfortunately did not exceed $\bar{n}$ equals 0.1 before hydroxide precipitation commenced.

In Fig. 3 is shown a plot of $\log K_1$ (ethanolamine) *versus* $\log K_1$ (NH_3). The line drawn in has a slope of 1.152, which is that expected on the basis of the simple model [3] of the chelate effect discussed above. The slightly lower slope which would be obtained from a best-fit line drawn through the experimental points possibly relates to the lower basicity of the nitrogen in ethanolamine ($pK_a = 9.45$) as compared with a polyamine such as ethylenediamine ($pK_a = 9.9$). Figure 3 suggests that the chelate effect in complexes of ethanolamine is very simply analysed. Empirical force field calculations [1] on the very similar ethylenediamine complexes have shown that for Ni(II) there is an increase of 0.61 kcal mol^{-1} in the strain energy, U, of the ligand on forming the $[Ni(en)(H_2O)_4]^{2+}$ complex. One would expect the increase in U to be very similar for the chelated ethanolamine molecule. Equation 1 does not explicitly take into account the increase in U on complex formation. It does so fortuitously [1] because the term in λ which is the stepwise decrease in $\log K_n$ (NH_3) as n increases, exactly matches the unfavourable contribution from the increase in U on coordination. The increase in U was not included in our initial discussion of the chelate effect in complexes of ethanolamine, and the fact that Fig. 3 shows that it has not made itself apparent suggests that this unfavourable contribution is probably counterbalanced by the increased basicity of the alcoholic oxygen as compared with that in the water molecule displaced on coordination. It will be necessary to extend the study to complexes of other hydroxyethyl substituted amines such as diethanolamine and triethanolamine to obtain a better analysis of the relative importance of inductive and strain effects in the ethanolamine-type chelate ring. On the practical level, a simple correlation such as that in Fig. 3 allows for the prediction that hydroxy-ethyl substitution should not lead to stabilities of ethanolamine complexes that are much higher than those of the ammines, so that the reported $\log K_1 = 7.56$ [10] for the lead(II) complex of ethanolamine must be regarded with suspicion, as it leads to a $\log K_1$ (NH_3) of about 6.7 for lead (II). This is rather unlikely in view of the estimated [12] value of $\log K_1$ (NH_3) = 1.6, and the fact that it would lead to a highly stable hydrolysis-resistant ammine complex of lead(II) in aqueous solution, which is not observed.

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