COORDINATION BY 2-PYRIDYLMETHYL-2'-AMINOETHYLAMINE

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Abstract -- The synthesis of the tridentate ligand 2-pyridylmethyl-2'-aminoethylamine is described. The infrared and NMR spectral characteristics and the corresponding trihydrochloride and dipicrate are also reported. The stepwise proton dissociation constants and stability constants with Cu(II) have been determined potentiometrically at 25°C and at an ionic strength of 0.10 in KNO₃. The highest order complex is two. The first ligand is involved as a tridentate chelate while the second ligand is monodentate in its coordination.

INTRODUCTION

THE SYNTHESIS of 2-pyridylmethyl-2'-aminoethylamine (aminoethylaminomethyl pyridine; AEAMP) described herein by reaction of 2-chloroethylamine



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with excess 2-aminomethyl pyridine avoids the use of 2-chloromethyl pyridine (a serious vesicant and lachrymator) which is required in the synthesis described by Hoyer[1]. The infrared and NMR spectral characteristics of AEAMP and data for the corresponding dipicrate which are reported here have not been previously reported. Hoyer's coordination work with Cu(II) was performed at 20°C and in 0.10 M KCl. The work herein described was carried out at 25°C and in 0.10 M KNO₃.

Of particular significance, however, is the fact that the geometrical structure of the Cu(II) complex which is supported by our data differs considerably from the structure reported by Hoyer. Also the absence of direct supporting experimental data in Hoyer's work makes it difficult to accept his suggested structure.

EXPERIMENTAL

Procedure

All measurements were made with a Metrohm Hereassau 388 Research pH meter with Beckman calomel and E-2 glass electrodes. Standard buffer solutions at pH 4.01 and 7.00 were used for standardization of the potentiometric apparatus. All solutions were 0.10 M in KNO₃, the temperature was 25°C, and a nitrogen atmosphere was maintained. The titrant was standard CO₂-free KOH.

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1. E. Hoyer, Chem. Ber. 93, 2475 (1960).

Systems of varying concentrations and varying ligand to metal ion ratios were investigated in order to detect any concentration effects.

The proton dissociation constants and the complex formation constants were obtained by treatment of the potentiometric data using the method of Bjerrum[2]. All calculations leading to the results reported here have been performed by use of a set of eight previously described digital computer programs[3]. The reliability of the final constants was in each case varified by generation of a theoretical formation curve which was compared for agreement with the corresponding experimental formation curve.

The NMR spectra were obtained with a Varian Associates A-60A spectrometer using carbon tetrachloride as solvent and tetramethylsilane as the internal reference. A Perkin-Elmer Model 521 spectrophotometer was used for infrared spectra. Melting points were determined with the Thomas-Hoover instrument. Elemental analyses and molecular weight determinations were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Two 12 g samples of 2-chloroethylamine monohydrochloride were neutralized individually with saturated aqueous K_2CO_3 . After removal of the precipitated KCl, the free base solution was added with rapid stirring to a solution of 44 g of 2-aminomethyl pyridine in an equal volume of ethanol. The reaction mixture was then refluxed for 2 hr. The ethanol was removed by rotary evaporation, the residue poured onto crushed ice, and the mixture neutralized with 25% KOH followed by the addition of excess KOH pellets. The dark orange-brown solution was extracted several times with CHCL₃. After drying with anhydrous MgSO₄ and removal of the CHCl₃, the residue was distilled under vacuum. After one distillation the product was yellow in color and yielded a poor NMR spectrum. Double redistillation gave a nearly colorless non-viscous liquid in 40 per cent yield. The compound had a boiling point at 0·1 mm of 85°C, an n_D^{25} of 1·5369, and was readily soluble in water, alcohol, and chloroform. The NMR spectrum was excellent showing peaks at τ 1·44–3·12 (aromatic protons), 6·18 and 7·35 (methylene protons), and 8·67 (amine protons) with area ratios of 4:2:4:3, in agreement with theory.

Anal. Calcd. for $C_8H_{13}N_3$: C, 63.56; H, 8.66; N, 27.77; M.W. 151. Found: C, 63.37; H, 8.70; N, 27.95; M.W. 151.

The trihydrochloride was formed and recrystallized out of ethanol saturated with dry HCl and had a melting point of 217°C.

Anal. Calcd. for C₈H₁₃N₃. 3HCl: C, 39·85; H, 6·14; N, 16·12; Cl, 40·88. Found: C, 39·93; H, 6·25; N, 16·17; Cl, 40·69.

The dipicrate was likewise formed out of ethanol and melted at 137°C. Anal. Calcd. for $C_{20}H_{19}N_8O_{14}$; C, 39·42; H, 3·14; N, 20·69. Found: C, 39·53; H, 3·39; N, 20·46.

DISCUSSION

The acid dissociation constants and the complex stability constants for AEAMP and the analogous aliphatic ligand diethylenetriamine (DIEN) are listed in Table 1. Experimental and theoretical formation curves which were obtained in this study are shown in Fig. 1. The stepwise nature of the reactions is

Table 1. Acid dissociation constants and Cu(II) stability constants for AEAMP and DIEN

Ligand	pK1	pK2	pK3	log K ₁	log K ₂	Reference
AEAMP	1.84	5.91	9.54	14.60	5.50	Present study
AEAMP (20°)	2.33	5.74	9.78	14.6	4.9	[1]
DIEN (20°)	3.70	8.88	9-94	15.84	4.79	[4]

2. J. Bjerrum, Metal Ammine Formation in Aqueous Solution. Haase. Copenhagen (1957).

3. J. K. Romary, A. C. Andrews and D. L. Donnelly, J. inorg. nucl. chem. 29, 1805 (1962).

4. G. H. McIntyre, Jr., B. P. Block and W. C. Fernelius, J. Am. chem. Soc. 81, 529 (1959).



Fig. 1. Experimental and theoretical formation curves at 25° C and 0.10 M KNO₃ for 2-pyridylmethyl-2'-aminoethylamine coordination with Cu(II) where X = ligand and proton dissociation curves where X = hydrogen ion. Solid curves are from experimental data; open circles and triangles are theoretical points generated by the constants reported in Table 1.

clearly illustrated. As might be expected considering the basicity differences involved and the greater steric limitations imposed upon AEAMP as a result of the fixed relative positions of the heteronitrogen and the adjacent carbon, the 1:1 complex of AEAMP is significantly less stable than that for DIEN. On the other hand the 2:1 complex stabilities are of the same order of magnitude.

Of much greater importance, however, is the enormous decrease in the strength of coordination of the second ligand. Hoyer has proposed that both the first and second ligand are chelated in a tridentate manner leading to a distorted octahedral configuration and a coordination number of six for the Cu(II) ion. The diminished value for $\log K_2$ was attributed to the effect of distortion in the second ligand. Other explanations are also possible.

Assuming a maximum coordination number of four, one could propose that the first ligand is bound through all three nitrogens. Then under the influence of the second ligand, one of the nitrogen-metal bonds with the original ligand is broken followed by coordination of the second ligand through two nitrogen atoms leaving both chelated in a bidentate configuration. Also assuming a coordination number of four, the observed stabilities could be explained by tridentate chelation of the first ligand and *monodentate* coordination of the second ligand.

In an attempt to answer this question the titrations shown in Fig. 2 were made. Curve A is the titration of (protonated) AEAMP itself while Curve B is the titration of a solution containing a 1:1 mole ratio of ligand to Cu(II). It is observed that for the first order complex the ligand is coordinated tridentate with the two five-member chelate rings leading to a very stable complex.

Curve C shows the titration of a solution containing a 2:1 mole ratio of AEAMP to Cu(II). The shift of curve C away from curve A corresponds to the *overall* formation of the 2:1 complex. To draw attention to the coordination of the *second* ligand alone the dotted curve D is shown. Curve D was obtained by



Fig. 2. Potentiometric titration of 2-pyridylmethyl-2'-aminoethylamine under the conditions: A, 0.005 M ligand (protonated); B, 0.005 M ligand and 0.005 M Cu(II); C, 0.01 M ligand and 0.005 M Cu(II); D, data of curve C replotted to illustrate mono-dentate coordination of second ligand.

replotting the data of curve C after correction of the a values to eliminate the effect of the first ligand. That is, the pH at a = 1.5 on curve C corresponds, stoichiometrically, to the beginning of the titration of the second ligand and is thus transposed to a value of a = 0 on curve D. Likewise, the pH at a = 2 is transposed to a = 1 etc. This procedure, of course, leads to the most meaningful results only in those cases where the coordination of the first ligand is substantially complete prior to the beginning of the coordination of the second ligand. From curve D it is observed that the titration of the *second* ligand, in the presence of the already formed 1:1 complex, exactly follows the titration of the ligand itself until well past the beginning of the removal of the second proton indicating negligible coordination through these sites. During the neutralization of the third proton, however, significant coordination is occurring as evidenced by the departure of curve D from curve A. (A larger separation between pK_2 and pK_3 would have provided for a more idealized superposition of curve D upon curve A until a = 2). These results indicate that for the second ligand there is negligible coordination until the third nitrogen site becomes involved in a monodentate fashion. This structure agrees with that based upon enthalpies proposed by Fernelius for DIEN and Cu(11).

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