Coordination Studies: Dipyridylamine and 3,3′-iminobispropylamine

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Introduction

The research reported is part of a continuing study of the coordination of amines with copper (II) and nickel (II) ions, with particular emphasis on the nature of the ions, their stability in solution, and the effect of structural features on stability.

The formula of dipyridylamine (pyridine, 2,2′ iminodi-), first prepared in 1914 by Chichibabin and Zeide (3), suggests several possible centers of coordination. Coordination through the nitrogen atoms of the two pyridine rings would produce a six-membered ring structure. If the secondary amine position were also involved, two four-membered rings could be present, but the steric factors make this unlikely. Coordination at one position only is also possible.

To compare the effect of ring size, 3,3′-iminobispropylamine (3,3′-diaminodipropylamine) was chosen, since diethylenetriamine (2,2′-diaminodiethylamine) has been investigated previously (6). The coordination of this compound has been examined recently by Hares, Fernelius, and Douglas (4). Our work in progress at the same time has attacked the problem by different methods.

Theoretical

Spectrophotometric measurements may be used to establish that coordination takes place, to establish conformity to Beer's Law, and to obtain the formula of the ions present by the method of continuous variation of Job (5) and the spectrophotometric titration method of Yoe and Jones (7).

Application of the pH titration method developed so extensively after introduction by Bjerrum (4) often provides an excellent method for the study of coordination of this type. However, insolubility of the complex ion is often a limiting factor. Mixed solvents, especially water-dioxane introduced by Calvin and Wilson (2), have been used to increase the solubility of the ions. Determination of the acid dissociation constants for the protonated amines under comparable conditions of ionic strength is necessary as preliminary. With this information, measurement of the pH of solutions containing known concentrations of metal ion, acid, and coordinating agent gives data for calculation of the equilibrium constant.

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Experimental

The dipyridylamine was purchased from the Reilly Tar and Chemical Co. and the 3,3′-iminobispropylamine from the Mathiesen Company.

The dipyridylamine was recrystallized from hot water. The white needles were dissolved in purified dioxane and the solution standardized by potentriometric titration in approximately 50% water-dioxane mixture.

Dioxane was purified by refluxing for 8 hours with 10% by weight of 1 N HCl, drying over NaOH, and distillation over sodium.

The 3,3′-iminobispropylamine was purified by distillation at 20 mm. Hg pressure. Solutions were standardized by titration with nitric acid using methyl orange as indicator.

Standard solutions of cupric nitrate, nickel nitrate and nitric acid were prepared from reagent grade chemicals and standardized by the usual procedures.

The spectrophotometric titration was performed by preparation of solutions of constant concentration of metal ion and multiples of this value for the amine concentration. The optical density was measured at the wave length of maximum absorption.

For the continuous variation measurements, a series of solutions at constant total concentration was prepared, with the concentrations varied from 0.01 molar in metal ion to 0.01 molar in amine. The optical density of the solutions was measured at the wave length of maximum absorption.

Spectrophotometric measurements were made with a Beckman model DU instrument.

The acid dissociation constants of 3,3′-iminobispropylamine (3,3′-diaminodipropylamine) were determined from pH measurements of a series of solutions containing 0.1 M barium chloride, 1.0 M potassium nitrate, 0.094 M nitric acid and amine concentration in the ranges 0.034 to 0.043 M, 0.056 to 0.076 M, and 0.105 to 0.155 M. The pH measurements were made at 30° C. ± 0.2° C. with a Beckman model G pH meter standardized against Beckman buffer solutions.

Discussion of Results

3,3′-iminobispropylamine

The acid dissociation constants of 3,3′-iminobispropylamine were found to have pK values of 8.15, 9.75, and 10.75 at 30° C. These values are almost the same as those determined by Hares, Fernelius and Douglas: 8.02, 9.70, 10.70. The present values were determined at a higher ionic strength and are reported since conditions were not identical.

The wave length of maximum absorption of the copper (II) complex ion was found to be 590 mμ. At this wave length the amine may be used as a colorimetric reagent for copper. Both the spectrophotometric titration and continuous variation methods indicate that two moles of amine per mole of copper are present in the ion. Evidence for a 1:1 ratio of

copper and the amine is obtained in the titration, but the 2:1 ratio seems more stable. This does not agree with Hares, Fernelius and Douglas who report a formation constant only for the 1:1 ratio.

With nickel (II) ions a maximum absorption is found at 570 mμ. Spectrophotometric data indicate both a 1:1 and 2:1 ratio of amine to nickel ions.

2,2′-dipyridylamine

The absorption curve of 2,2′-dipyridylamine with copper (II) ions shows peaks at 420 mμ and 660 mμ. The absorption at 420 mμ is obscured in the presence of amine, so the longer wave length was used in this investigation. The color of this ion in water-dioxane solution is green. Continuous variation data at 660 mμ give a coordination number of two for this ion.

The color of the ion of nickel and dipyridylamine is not intense, but does show maximum absorption at 560 mμ and at 900 mμ. Spectrophotometric data gave evidence of a coordination number of two for the ion formed with nickel. For this ion a 50% mixture of ethanol and water can be used as the solvent.

Further research of the coordination of this amine with copper is proceeding.

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