

two strong NC bands is in accord with the expected  $C_{3v}$  symmetry of the molecule. The relatively high mean frequency ( $2156 \text{ cm.}^{-1}$ ) suggests that back acceptance by the isonitriles is not great. This then would require that the CO engage in con-

siderable back acceptance, and the rather low CO frequency ( $1923 \text{ cm.}^{-1}$ ) is in accord with this view.

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[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORIES OF BROWN UNIVERSITY, PROVIDENCE, RHODE ISLAND]

## Coördination Compounds of Labile Metals with Ethylenimine

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Ethylenimine (aziridine) forms coördination compounds with labile metal ions similar to those formed by ammonia and primary amines. Complexes with divalent copper, nickel, cobalt, manganese and mercury have been isolated and identified. The formation constants of complexes with copper, zinc, silver and mercury ions in aqueous solution have been measured by the Bjerrum method. The temperature dependence of ethylenimine ionization is expressed by the equation:  $pK_a = 2438 \left(\frac{1}{T}\right) - 0.244$ , whence  $\Delta H^\circ = 11.6 \text{ kcal./mole}$ .

### Introduction

No data have been found in the literature to indicate that work on coordination compounds containing ethylenimine as a ligand has been carried out. This is presumably a result of the well-known instability of the ethylenimine ring. It is only with the advent of the kinetic data on ring opening<sup>1,2</sup> that stability conditions have become sufficiently defined to encourage synthetic work on such unusual reactions of the ethylenimines.

The aim of this research was to find out: (1) what types of complexes are possible, (2) the stability of the ethylenimine ring when bonded to a metal and (3) the strength of the resulting metal-to-nitrogen bond. With the use of special precautions, complexes of ethylenimine with several transition metals have been prepared and identified, and the Bjerrum method has been applied in four cases to determine the formation constants of these complexes. Definite conclusions on these research aims have been reached.

### Experimental and Results<sup>3</sup>

**A. Reagents.**—The ethylenimine was prepared either by the method of Wenker<sup>4</sup> or was a commercial product. It was dried over sodium and distilled from this metal just before use; boiling point,  $55.5^\circ$ .

All the salts and solvents used in the preparation of complexes were of reagent grade. The solution of mercuric nitrate was prepared from mercuric oxide plus the equivalent amount of nitric acid in  $2N$  sodium nitrate. The mercury concentration was determined by titration with thiocyanate. The stock solution of  $5N$  sodium nitrate was prepared from reagent grade salt and tested for neutrality. The nitric acid solutions were standardized with a solution of sodium hydroxide of known normality. Distilled water was used through all the preparations.

**B. Preparation and Properties of Cu(II) Complexes.**  
**1. Tetraethylenimine Copper(II) Nitrate.**  $[\text{Cu}(\text{C}_2\text{H}_5\text{N})_4](\text{NO}_3)_2$ .—*Prep.* 1.4 g. of Az were dissolved in 1.5 ml. of ethanol and cooled in ice. A solution of 0.5 g. of cupric nitrate trihydrate in the same solvent was then added drop

by drop. The flask was left in ice for half an hour. The violet, crystalline precipitate thus formed was filtered by suction, washed once with cold ethanol and redissolved at R.T. in ethanol containing a few drops of Az. The complex was recrystallized by adding ether and cooling in ice. The precipitate was filtered and washed successively with a cold dilute solution of Az in ethanol, cold ethanol and finally with anhydrous ether. It was dried in a vacuum desiccator over KOH pellets.

*Anal.* Calcd.: C, 26.70; H, 5.60; N, 23.34. Found: C, 26.27; H, 5.45; N, 23.28.

**Properties.**—M.p.,  $142^\circ(\text{d})$ . The compound is soluble in water and polar solvents, insoluble in ethyl ether and benzene. Aqueous solutions of this and of the following copper-complexes are decomposed by boiling or by the addition of mineral acids.

**II. Tetraethylenimine Copper(II) Sulfate Hydrate.**  $[\text{Cu}(\text{C}_2\text{H}_5\text{N})_4]\text{SO}_4 \cdot 1.5 \text{ H}_2\text{O}$ .—*Prep.* 3 g. of finely powdered cupric sulfate pentahydrate were dissolved in a solution of 3.5 g. of Az in 4 ml. of water cooled in ice. The solution was filtered, ethanol added until precipitation began and precipitation completed by cooling in ice for 1 hr. The deep blue crystals were collected on a filter and redissolved in the minimum amount of water at R.T. After addition of a few drops of Az, the complex was recrystallized by addition of ethanol and cooling, filtered by suction and washed successively with a solution of Az in ethanol, ethanol and ether. It was dried in a vacuum desiccator over KOH.

*Anal.* Calcd.: C, 26.77; H, 6.46; N, 15.61; S, 8.93. Found: C, 26.81; H, 6.88; N, 15.31; S, 8.79.

**Properties.**—M.p.,  $132^\circ(\text{d})$ . The compound is very soluble in water and methanol, slightly soluble in ethanol and acetone, insoluble in ether and benzene.

**III. Tetraethylenimine Copper(II) Iodide.**<sup>5</sup>  $[\text{Cu}(\text{C}_2\text{H}_5\text{N})_4]\text{I}_2$ .—*Prep.* 0.3 g. of finely powdered cupric acetate was dissolved in a mixture of 1.2 g. of Az in 2 ml. of water. By addition of a saturated solution of 1 g. of potassium iodide in water, a violet crystalline precipitate was formed at once. This was filtered by suction, dissolved in a concentrated solution of Az in water and recrystallized by addition of a concentrated solution of potassium iodide in water. The precipitate was filtered and washed with a cold dilute solution of Az in water, taking care not to pass air through the solid, and dried "in vacuo" over KOH.

*Anal.* Calcd.: C, 19.61; H, 4.11; I, 51.80. Found: C, 19.60; H, 4.21; I, 51.58.

**Properties.**—M.p.,  $120^\circ(\text{d})$ . Treatment with ethanol or ether decomposes the compound, leaving a brown solid or solution. The solid complex can be kept unchanged for a long time in a closed container, if protected from air and humidity.

**IV. Tetraethylenimine Copper(II) Bromide.**  $[\text{Cu}(\text{C}_2\text{H}_5\text{N})_4]\text{Br}_2$ .—The preparation is similar to the one used for

(1) W. G. Barb, *J. Chem. Soc.*, 2564, 2577 (1955).

(2) J. E. Harley, C. E. O'Rourke, L. B. Clapp, J. O. Edwards and B. C. Lawes, *THIS JOURNAL*, **80**, 3458 (1958).

(3) Analyses were performed by the Microchemical Laboratory, Massachusetts Institute of Technology. The symbol Az for ethylenimine (aziridine) will be used. R.T. Stands for room temperature (about  $23^\circ$ ).

(4) H. Wenker, *THIS JOURNAL*, **56**, 2328 (1936).

(5) See F. Ephraim and R. Linn, *Ber.*, **46**, 3746 (1913-1914) for  $[\text{Cu}(\text{CH}_2\text{NH}_2)_4]\text{I}_2$ .

copper nitrate, except that methanol was used in the place of ethanol.

*Anal.* Calcd.: C, 24.28; H, 5.09; N, 14.16. Found: C, 24.27; H, 5.26; N, 13.76.

*Properties.*—Violet crystals; m.p., 125°(d). The compound is soluble in water and polar solvents, insoluble in ether and benzene.

V. Tetraethylenimine Copper(II) Chloride  $[\text{Cu}(\text{C}_2\text{H}_5\text{N})_4]\text{Cl}_2$ .—The preparation is identical to that used for the copper bromide complex.

*Anal.* Calcd.: C, 31.32; H, 6.57; N, 18.21. Found: C, 30.80; H, 7.09; N, 17.61.

*Properties.*—M.p. 135°(d). The complex is soluble in water and polar solvents, insoluble in ether and benzene. The vapor pressure of Az is much higher for this solid than for the bromide and iodide. The fact that the analyses gave results lower than calculated is probably due to this greater instability.<sup>6</sup>

#### C. Preparation and Properties of Ni(II) Complexes.

I. Hexaethylenimine Nickel(II) Nitrate.  $[\text{Ni}(\text{C}_2\text{H}_5\text{N})_6](\text{NO}_3)_2$ .—*Prep.* 2 g. of nickel nitrate hexahydrate were dissolved in the minimum amount of water and added dropwise into a solution of 2.6 g. of Az in 1 ml. of water cooled in ice. The precipitation of the crystalline, blue-violet complex was complete in a few minutes. The precipitate was filtered by suction, washed once with ethanol and recrystallized by dissolving in water at R.T., adding 1 g. of Az and cooling in ice. The crystals were then filtered, washed with cold ethanol and dried in a vacuum desiccator over KOH pellets.

*Anal.* Calcd.: C, 32.67; H, 6.85; N, 25.40. Found: C, 32.46; H, 6.67; N, 25.63.

*Properties.*—M.p., 160–162°(d). The complex is soluble in water, slightly soluble in methanol, insoluble in ethanol, acetone and ether. The aqueous solutions of this and of the following nickel-complexes are decomposed by boiling or by the addition of mineral acids.

II. Tetraethylenimine Nickel(II) Sulfate.  $[\text{Ni}(\text{C}_2\text{H}_5\text{N})_4]\text{SO}_4$ .—*Prep.* This very soluble complex must be prepared from a very concentrated solution.

1 g. of nickel sulfate was dissolved in the minimum amount of water and the solution was filtered. To the filtrate cooled in ice in a large excess of Az was added drop by drop, about 3 g., or until precipitation was obtained. The flask was left for 2 hr. in the refrigerator. The pale violet powder was filtered by suction and redissolved in methanol. 1 g. of Az was added to the solution cooled in ice and the complex was recrystallized by careful addition of ether. The solid was filtered, washed with a dilute solution of Az in ether, then with ether and dried in a vacuum desiccator over KOH.

*Anal.* Calcd.: C, 29.38; H, 6.17; N, 17.14. Found: C, 29.30; H, 6.62; N, 17.99.

*Properties.*—This compound does not melt but when heated gradually loses Az, leaving nickel sulfate. In the capillary tube the decomposition (the color is the index) is not yet complete at 200, but almost so at 300°. The complex is very soluble in water, methanol and ethanol, slightly soluble in acetone, insoluble in ether.

III. Hexaethylenimine Nickel(II) Iodide.  $[\text{Ni}(\text{C}_2\text{H}_5\text{N})_6]\text{I}_2$ .—The preparation is similar to that used for the nickel nitrate complex.

*Anal.* Calcd.: C, 25.24; H, 5.29; N, 14.72. Found: C, 25.04; H, 5.04; N, 13.90.

*Properties.*—Violet crystals; m.p., 180–182°. Moderately soluble in water, insoluble in water in the presence of an excess of Az and in organic solvents.

IV. Hexaethylenimine Nickel(II) Bromide.  $[\text{Ni}(\text{C}_2\text{H}_5\text{N})_6]\text{Br}_2$ .—By addition of anhydrous Az to a concentrated aqueous solution of nickel bromide were obtained violet crystals of a complex containing slightly less than six moles of Az per nickel atom.

*Anal.* Calcd.: C, 30.22; H, 6.34; N, 17.62. Found: C, 29.65; H, 6.28; N, 16.52.

*Properties.*—M.p., 183°. Very soluble in water, soluble in ethanol and acetone, insoluble in ether.

(6) M. Straumanis and A. Cirulis, *Z. anorg. u. allgem. Chem.*, **230**, 80 (1937). These authors prepared an analogous complex with ethylamine, having similar instability at room temperature.

IV. Tetraethylenimine Nickel(II) Chloride.  $[\text{Ni}(\text{C}_2\text{H}_5\text{N})_4]\text{Cl}_2$ .—The preparation is similar to that used for the copper bromide complex. The compound was obtained in the form of pale violet crystals.

*Anal.* Calcd.: C, 31.84; H, 6.68; N, 18.56. Found: C, 31.54; H, 6.94; N, 18.27.

*Properties.*—M.p., 181–182° (with partial decomposition). The complex is very soluble in water and methanol, slightly soluble in ethanol and acetone, insoluble in ether.

#### D. Preparation and Properties of Co(II) Complexes.

*General.*—Analogous to the behavior of the amino-cobaltous complexes, the coordination compounds of the Co(II) salts with ethylenimine, although relatively stable toward O<sub>2</sub> in the dry state, are slowly oxidized in the air when moist or in solution, the iodide being more stable in this respect than the chloride. The aqueous solutions are decomposed by boiling or by the addition of mineral acids.

I. Hexaethylenimine-Cobalt(II) Iodide.  $[\text{Co}(\text{C}_2\text{H}_5\text{N})_6]\text{I}_2$ .—*Prep.* 0.3 g. of cobaltous acetate tetrahydrate was added to a solution of 1.2 g. Az in 3 ml. of water cooled in ice. When the solid had dissolved completely, the iodide was precipitated by the addition of 3 ml. of a concentrated aqueous solution of potassium iodide. The pink powder was filtered by suction and washed with a little cold water. The compound thus obtained contained traces of a greenish matter. It was dissolved in 20 ml. of water, the insoluble green compound was removed by filtration, the filtrate was cooled and 1 g. of Az was added drop by drop. By the addition of 0.5 ml. of the potassium iodide solution, the iodide precipitated in the form of small pink crystals. These were filtered, washed with a cold solution of Az in water and dried in a vacuum desiccator over KOH.

*Anal.* Calcd.: C, 25.24; H, 5.30; N, 14.72. Found: C, 24.84; H, 5.36; N, 14.34.

*Properties.*—M.p., 140°(d). The compound is soluble in water, insoluble in organic solvents.

II. Tetraethylenimine-Cobalt(II) Chloride.  $(\text{Co}(\text{C}_2\text{H}_5\text{N})_4)\text{Cl}_2$ .—*Prep.* An excess of Az was added to a solution of cobalt chloride in methanol. The complex was obtained in the form of a pink microcrystalline powder by addition of ether and recrystallized from methanol-ether.

*Anal.* Calcd.: C, 31.80; H, 6.67; N, 18.54. Found: C, 32.56; H, 6.69; N, 17.67.

*Properties.*—M.p., 140°(d). The compound is very soluble in water, methanol and ethanol, insoluble in ether and has a high vapor pressure of Az.

A sample of this complex, heated in the vacuum at 60–70°, turned into a blue, ethylenimine-containing compound. This is believed to be the *trans*- $[\text{CoCl}_2(\text{C}_2\text{H}_5\text{N})_2]$  complex, by the analogy with the corresponding ammonia-complex<sup>7</sup> but was not analyzed on account of the difficulty of purification.

#### E. Preparation and Properties of Mn(II) Complexes.

I. Pentaethylenimine-Manganese(II) Iodide.  $[\text{Mn}(\text{C}_2\text{H}_5\text{N})_5]\text{I}_2$ .—*Prep.* To a solution of 0.6 g. manganous iodide in 10 ml. of water cooled in ice was added drop by drop 1.5 g. Az. By rubbing the walls of the flask with a rod a crystalline precipitate was obtained, brownish due to oxidation.<sup>8</sup> This was filtered by suction, washed with a little cold water and redissolved in water at R.T. The solution was filtered and the complex was recrystallized by adding 1 g. of Az and cooling in ice; it was filtered by suction, washed with a cold aqueous solution of Az, with a little cold water and dried in a vacuum desiccator over KOH.

*Anal.* Calcd.: C, 22.92; H, 4.81; N, 13.36. Found: C, 22.68; H, 4.98; N, 13.17.

*Properties.*—M.p., 132–33° (d). The complex is soluble in water, slightly soluble in methanol, insoluble in acetone and ether. The aqueous solutions of the manganous complexes are decomposed by boiling, by the addition of mineral acids or by prolonged exposure to atmospheric oxygen.

II. Tetraethylenimine-Manganese(II) Chloride.  $[\text{Mn}(\text{C}_2\text{H}_5\text{N})_4]\text{Cl}_2$ .—*Prep.* 2 g. of Az were added to a solution of 1 g. of manganous chloride in 5 ml. of methanol cooled in ice. By rubbing the walls of the flask with a rod a crystalline white precipitate was formed. This was filtered by suction, washed with cold methanol and redissolved in methanol at R.T. The solution was filtered, cooled in ice and 1 g. Az was added. The crystallization was rendered

(7) W. Biltz and B. Fetkenheuer, *Z. anorg. Chem.*, **89**, 97 (1914).

complete by addition of ether. The complex was filtered by suction, washed with a 50:50 mixture of methanol-ether containing a few drops of Az, then with ether and dried in a vacuum desiccator over KOH.

*Anal.* Calcd.: C, 32.24; H, 6.76; N, 18.80. Found: C, 31.80; H, 6.56; N, 18.68.

*Properties.*—Decomposition point, 135°. Very soluble in water and methanol, soluble in ethanol and acetone, insoluble in ether.

**F. Preparation and Properties of Hg(II) Complexes.**  
**I. Diethylenimine-Mercury(II) Nitrate**  $[\text{Hg}(\text{C}_2\text{H}_5\text{N})_2](\text{NO}_3)_2$ .—*Prep.* A solution of 3 g. of mercuric nitrate in 5 ml. of water plus 1 ml. of conc. nitric acid was added drop by drop to a solution of 1.4 g. of Az in 25 ml. 50% sodium nitrate cooled in ice. A white precipitate, consisting of brilliant sheets, was obtained. This was filtered by suction, washed successively with a 40% aqueous sodium nitrate solution, a little water, a dilute solution of Az in ethanol, finally with anhydrous ether and dried in a vacuum desiccator over KOH.

*Anal.* Calcd.: C, 11.69; H, 2.45; N, 13.64. Found: C, 11.49; H, 2.41; N, 12.99.

*Properties.*—M.p. 150° (d). The compound is not hygroscopic and was insoluble in all the usual solvents. Therefore it could not be recrystallized. Vapor pressure negligible.

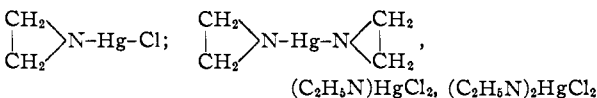
**II. Reaction of Ethylenimine with Mercury (II) Iodide.**—*Prep.* 4.54 g. (0.01 mole) of mercuric iodide were added in small portions to a solution of 0.86 g. (0.02 mole) of Az in 20 ml. of ether cooled in ice. The solid dissolved with an exothermic reaction and a colorless solution was formed. The last portions of mercuric iodide dissolved with difficulty; at this stage a few more drops of Az were added. The solution was filtered and the ether evaporated "in vacuo." A white crystalline compound, possibly the di-ethylenimine complex, was thus obtained. It was suspended in petroleum ether (30–60° fraction), filtered by suction and washed with a little petroleum ether. The solid was not stable and rapidly turned into an insoluble yellowish amorphous compound, which was not analyzed.

**III. Ethylenimine-Mercury(II) Bromide.**  $\text{Hg}(\text{C}_2\text{H}_5\text{N})\text{Br}_2$ .—*Prep.* A solution of 0.3 g. of Az in 3 ml. of acetone was added drop by drop to a solution of 2.5 g. of mercuric bromide in acetone cooled in ice. The white, brilliant sheets were collected on a fritted glass filter, washed with acetone, then with ether and dried in a vacuum desiccator over KOH.

*Anal.* Calcd.: C, 5.95; H, 1.25; N, 3.47. Found: C, 6.06; H, 1.39; N, 3.18.

*Properties.*—Volatile with decomposition at 115°. Insoluble in water, acetone and ether. Soluble in an excess of ethylenimine and in dilute acids.

**IV. Reaction of Ethylenimine with Mercury(II) Chloride.** *Observations.*—By addition of Az to an aqueous solution of mercuric chloride a white, amorphous precipitate was obtained. The analysis gave the results: C, 10.52; H, 2.00; N, 5.95, with a carbon-to-nitrogen ratio equal to 2.05:1. These percentages cannot be explained with a single formula, and the solid was believed to be a mixture of several ethylenimine complexes and ethylenimido compounds, such as



It is known that solutions of mercuric chloride with ammonia give similarly complex mixtures of indefinite composition, containing also oxy- and hydroxy radicals. The so-called "infusible white precipitate,"  $\text{HgNH}_2\text{Cl}$ , can be obtained in a fairly pure state by careful control of the experimental conditions. Presumably on account of the lower basicity of the ethylenimine nitrogen, no analogous compound with the ethylenimine could be isolated, but by operating at high concentration of chloride ions and by lowering the basicity of the solution with the addition of hydrochloric acid, a complex containing 1 mole Az per mole mercuric chloride was obtained, as shown below.

**V. Ethylenimine-Mercury(II) Chloride.**  $(\text{C}_2\text{H}_5\text{N})\text{HgCl}_2$ .—*Prep.* A mixture of 3 g. of mercuric chloride and 6 g. of potassium chloride was dissolved in a solution of 1.5 ml. of conc. hydrochloric acid in 25 ml. of water. The

solution was added dropwise through a filter to a solution of 1.4 g. of Az and 2 g. of potassium chloride in 18 ml. of water cooled in ice. The white, crystalline precipitate was filtered by suction, washed with a cold solution of Az in water, then with ethanol and dried in a vacuum desiccator over KOH.

*Anal.* Calcd.: C, 7.64; H, 1.60; N, 4.45; Cl, 22.54. Found: C, 7.94; H, 1.87; N, 4.25; Cl, 21.71.

*Properties.*—M.p., 153°(d). This compound was insoluble in all the common solvents and in acid and basic solutions.

**G. Complexes with Some Other Cations. I. Silver.**—Silver chloride dissolved in an excess of anhydrous Az yielding a colorless solution. By the addition of water, ethanol or ether the silver chloride reprecipitated and was redissolved by the addition of enough Az to shift the equilibrium toward the complex formation. The complex could not be isolated.

Silver nitrate similarly dissolved in an excess of anhydrous Az, giving a colorless solution. A complex was precipitated in the form of colorless sheets by the addition of anhydrous ether. The crystals were filtered by suction and washed with ether but proved not to be stable, being deliquescent and having a high vapor pressure of ethylenimine.

**II. Zinc.**<sup>8</sup>—Both zinc iodide and zinc chloride gave in ethanol solution white crystalline complexes, with coordination number between 4 and 5 and high vapor pressure of Az.

**III. Cadmium.**<sup>8</sup>—Cadmium iodide and chloride gave similarly poor complexes, with coordination number about two and high vapor pressure of Az.

**IV. Lead.**<sup>8</sup>—Lead (II) chloride and nitrate gave white insoluble complexes, which in vacuum or in air lost all their Az inside 1 or 2 hr.

**H. Temperature Dependence of Ethylenimine Ionization.**—Basicity constants for ethylenimine have been measured recently by several authors.<sup>9</sup> It was here considered interesting, even if only indirectly related (see below) with our study of the ethylenimine complexes, to study the variation of the basicity constant with temperature in the range from 15 to 30°.

The equation used was

$$pK_a = pH + \log [\text{Az H}^+]/[\text{Az}] + \log f^* \quad (1)$$

where  $f^*$  expresses the activity of the ions in the solution. By mixing calculated amounts of ethylenimine and perchloric acid solutions of known normality, an exactly half-neutralized solution 0.005 *N* in both Az and  $\text{AzH}^+$  was obtained. At this dilution the activity coefficients can be considered unity, and equation 1 becomes:  $pK_a = pH$ . The experimental points are shown in Fig. 1. A straight line was obtained, and the dependence of  $pK_a$  from the temperature is expressed by the equation

$$pK_a = 2438 \left( \frac{1}{T} \right) - 0.244,$$

thus the value of  $\Delta H^\circ$  is 11.6 kcal./mole<sup>-1</sup>.

Other runs were made at a 0.05 *N* concentration in Az and  $\text{AzH}^+$ . In this case the activity coefficients are not unity, but the points obtained lie on a straight line parallel to the one previously obtained. The two lines coincide if in equation 1 is introduced the correction for an activity coefficient  $f^* = 0.87$ .

The values found are in good agreement with those reported in the literature,<sup>9</sup> which cover different conditions of temperature and concentration yet are not complete studies in themselves.

**I. Equilibrium Constant Experiments. I. Procedure.**—The pH measurements were made with a glass electrode and a Beckman model G pH meter. The meter was adjusted for asymmetry and temperature and was standardized against a Reference Buffer Solution ( $pH = 7.00 \pm 0.01$  at 25°) furnished by the Hartmann-Leddon Co.

The ethylenimine solutions were prepared shortly before use, by dissolving a weighed amount in ice-cold water in a

(8) See F. Ephraim, *Z. physik Chem.*, **83**, 196 (1913), for data on the corresponding ammonia complexes.

(9) (a) C. E. O'Rourke, L. B. Clapp and J. O. Edwards, *THE JOURNAL*, **78**, 2159 (1956); (b) E. J. Shepherd and J. A. Kitchener, *J. Chem. Soc.*, 2448 (1956); (c) G. J. Buist and H. J. Lucas, *THE JOURNAL*, **79**, 6157 (1957); see other literature in the given references.

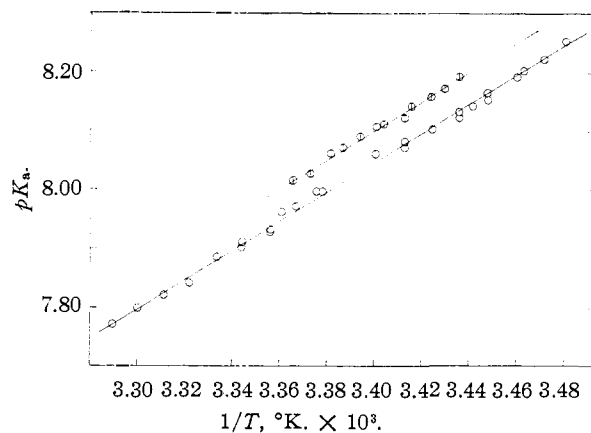


Fig. 1.—Variation with the temperature of the negative logarithm of the acid dissociation constant of ethylenimine: ⊙, in 0.05 *N* solution in Az and AzH<sup>+</sup>; O, in 0.005 *N* solution in Az and AzH<sup>+</sup>.

volumetric flask and diluting to volume. The exactly neutralized solutions of ethylenimine-nitric acid were all prepared immediately before use in the following way: The Az was weighed and dissolved in ice-cold water; the solution was slowly added to the equivalent amount of standardized nitric acid kept ice-cold in a volumetric flask and cold water was added to volume; the neutrality of the solution was tested by comparing its pH with the theoretical one at that temperature, calculated from the formula

$$pH = 7 - \frac{1}{2} \log C - \frac{1}{2} pK_b$$

where *C* is the salt concentration; then the calculated amount of acid or base was added until complete neutralization was reached.

All the ethylenimine-containing solutions were kept in an ice bath until use.

The acid dissociation constant of Az was measured independently for each run in solutions of nearly the same ionic strength as the solutions containing the complex-forming metal ion, in three individually prepared samples. It was noted that at a temperature of 25° and in a 0.1 *N* concentration of nitric acid (*i.e.*, ethyleniminium ion) hydrolysis took place, as evidenced by the non-constant values of the *K<sub>a</sub>* obtained. At lower temperatures, especially in the range 15–17°, the values of *pK<sub>a</sub>* were constant over a period of 1 hr., within the limits of experimental error. The samples were therefore prepared from cold (about 10°) ethylenimine and Az-nitric acid solutions and thermostated in a water-bath at a temperature between 14 and 16°. Each pH measurement was rechecked at least once, and the actual temperature at every measurement was read on a thermometer immersed in the sample, with an accuracy of ± 0.1°.

All the results were reproducible at the same concentration and temperature. The function of the sodium nitrate was merely to provide a medium of approximately constant ionic strength. The correction for hydrogen ion concentration was introduced in the case of the most acid solutions (as with the mercuric ion). None of the solutions gave any precipitation of a complex, but deposits of metallic silver and mercury were formed from the corresponding solutions after remaining for a few days at R.T.

II. An Example of an Equilibrium Constant Determination.—Data for a typical experiment are summarized in Table I. The values of log *K<sub>a</sub>* were deduced from the expression

$$\log K_a = -pH + \log [Az] - \log [AzH^+]$$

The average value found, in this example 9.73, was used to calculate the concentration of free ethylenimine present at equilibrium, by means of the equation

$$\log [Az] = \log K_a + \log [AzH^+] + pH$$

The negative of the value thus found is *p*[Az], which is the negative logarithm of the concentration of free imine. The calculated values of *p*[Az] are listed in the last column of Table I.

TABLE I  
GLASS ELECTRODE MEASUREMENTS IN SILVER NITRATE SOLUTIONS

[NaNO <sub>3</sub> ] = 1.0 M; [AzH <sup>+</sup> ] = 0.1 M. <i>T</i> = 16.5°				
[AgNO <sub>3</sub> ]	[Az]	pH	$\bar{n}$	<i>p</i> [Az]
0.02	0.006	6.06	0.270	3.21
.02	.012	6.38	.546	2.97
.02	.018	6.48	.82	2.79
.02	.024	6.62	1.09	2.65
.02	.030	6.75	1.35	2.52
.02	.036	6.92	1.58	2.35
.02	.042	7.11	1.75	2.16
.02	.048	7.30	1.86	1.97
.02	.054	7.43	1.98	1.84
.02	.060	7.58	1.98	1.69
..	.012	7.35	8.27	9.73
..	.036	7.83	8.27	9.73
..	.054	8.01	8.28	9.72
			<i>pK<sub>a</sub></i>	log <i>K<sub>a</sub></i>

According to the method of Bjerrum,<sup>10</sup> the values of  $\bar{n}$  (the average number of moles of Az attached to one mole of the metal ion) can be calculated directly from the equation

$$\bar{n} = \frac{C_{Az} - [Az]}{C_M}$$

where *C<sub>Az</sub>* represents the total ligand concentration and *C<sub>M</sub>* the total concentration of metal ion, whether complexed or not.

The values of  $\bar{n}$  were then plotted on a large scale graph versus *p*[Az], and from the loci of the points thus obtained were drawn the formation curves.

III. Tetraethylenimine Cupric Ion.—Measurements were made both in the absence and in the presence of sodium nitrate. The corresponding formation curves were found to be parallel and are shown in Fig. 2. The upper curve

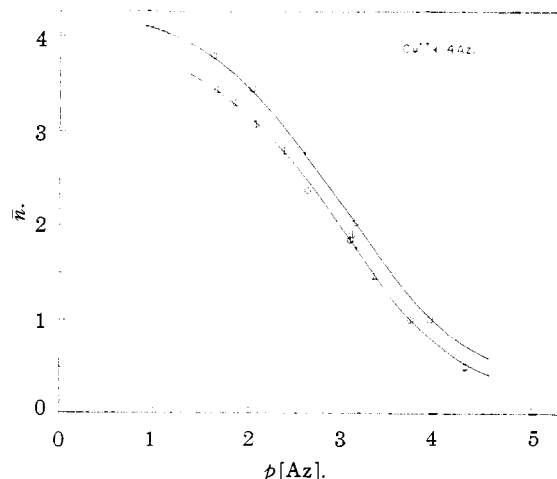


Fig. 2.—The formation curves for the tetraethylenimine cupric ion: ⊙, in 0.2 *N* AzH<sup>+</sup> at 20.5°; O, in 1.0 *N* NaNO<sub>3</sub> and 0.1 *N* AzH<sup>+</sup> at 16°.

was used for the calculation of the complexity constants. Following the Bjerrum method, two sets of temporary constants were calculated. The two methods are in brief

- (A) The use of *p* [Az] at all half  $\bar{n}$  values
- $$\log k_n = p[Az]_{\bar{n} = n - 1/2}$$

These values of log *k<sub>n</sub>* are read directly on the graph.

- (B) The use of the expression

$$\log k_n = p[Az]_{\bar{n} = 2} + \log \left( \frac{5 - \bar{n}}{\bar{n}} x^{5 - 2\bar{n}} \right)$$

(10) J. Bjerrum, "Metal Amine Formation in Aqueous Solution," Haase and Son, Copenhagen, 1941; p. 21.

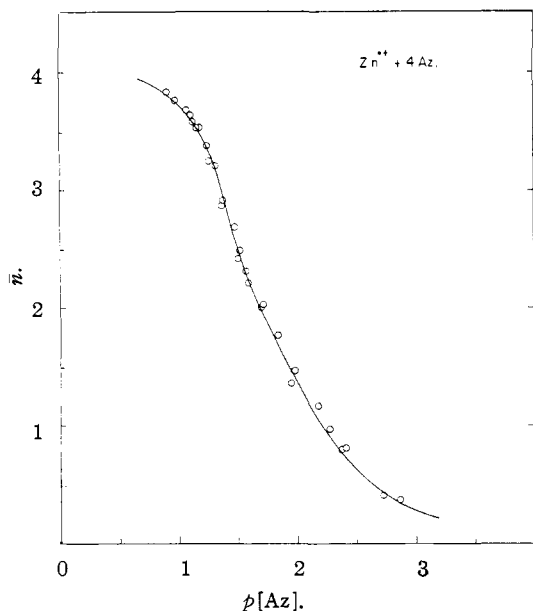


Fig. 3.—The formation curve for the tetraethylenimine zinc ion in 0.1 *N* AzH<sup>+</sup> and 1*N* NaNO<sub>3</sub> at 15.5°.

The  $p[\text{Az}]$  value at the midpoint of the curve is read from the graph; the value of the "spreading factor"  $x$  is calculated from the midpoint slope, by means of the equation given in the book by Bjerrum at p. 31, by successive approximation.

For the cupric ion-Az system the slope was found to be  $\Delta = 0.575$ , whence  $x = 1.54$ .

The temporary constants were then approximated with an expression derived from the "formation function" of the system. The calculated temporary and final constants are given in Table II.

TABLE II

CONSECUTIVE COMPLEXITY CONSTANTS FOR TETRAETHYLENIMINE CUPRIC ION IN 1*N* NaNO<sub>3</sub> AND 0.1 *N* AzH<sup>+</sup> AT 16°

	Method A	Method B	Log $k_n$ (final)
Log $k_1$	4.475	4.288	4.366
Log $k_2$	3.490	3.488	3.438
Log $k_3$	2.750	2.762	2.744
Log $k_4$	1.925	1.962	2.095
Log $K_4$	12.640	12.500	12.643

IV. Tetraethylenimine Zinc Ion.—Measurements were made in solutions of 0.1 normal AzH<sup>+</sup> and 1*N* sodium nitrate. The formation curve is shown in Fig. 3. From a midpoint slope  $\Delta = 1.124$  was calculated the spreading factor  $x = 0.925$ . Two sets of temporary constants were calculated by the methods A and B, and the values from A were used for the successive approximation. As in the case of the zinc-ammonia complexes,<sup>10</sup> the approximation formulas do not converge, possibly because of the small value of the spreading factor. The values in the last column of Table III give the results of six successive approximations.

TABLE III

CONSECUTIVE COMPLEXITY CONSTANTS FOR TETRAETHYLENIMINE ZINC COMPLEX IN 0.1 *N* AzH<sup>+</sup> AND 1 *N* NaNO<sub>3</sub> AT 15.5°

	(A)	(B)	Log $k_n$ (final)
Log $k_1$	2.60	2.18	2.44
Log $k_2$	1.90	1.83	1.79
Log $k_3$	1.50	1.53	0.98
Log $k_4$	1.16	1.18	2.02
Log $K_4$	7.16	6.72	7.23

V. Diethylenimine Silver Ion.—The formation curve is shown in Fig. 4. In the case where the maximum co-

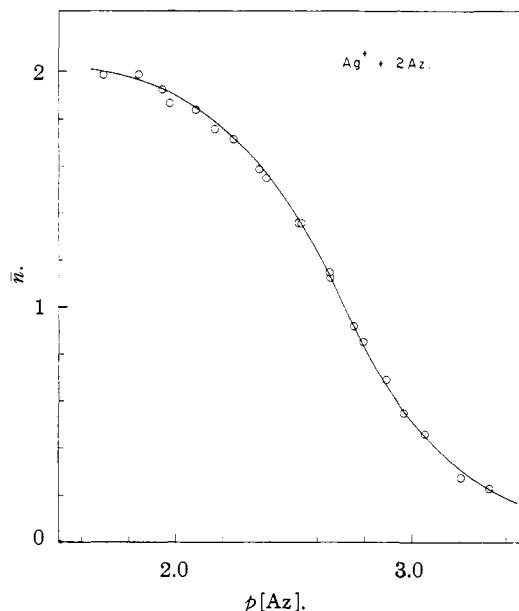


Fig. 4.—The formation curve for the diethylenimine silver ion in 0.1 *N* AzH<sup>+</sup> and 1*N* NaNO<sub>3</sub> at 16.5°.

ordination number is 2, no approximation is needed. The spreading factor is given by the equation:  $x = 1/\Delta - 1$  and was here found to be:  $x = 0.251$ ,  $\Delta$  being equal to 0.799.

By combining the two equations

$$\log K_2 = \log k_1 k_2 = 2p[\text{Az}]_{n-1}$$

and

$$k_1/k_2 = 4x^2$$

the complexity constants were calculated to be

$$\log k_1 = 2.40, \log k_2 = 3.00, \log K_2 = 5.40$$

in 0.1 *N* AzH<sup>+</sup> and 1.0 *N* NaNO<sub>3</sub> at 16.5°.

VI. Diethylenimine Mercuric Ion.—The formation of a tetraimine complex taking place at Az-concentration higher than 0.1 *N* was not investigated as difficulties in handling became too great even at low temperatures. The formation curve for the diethylenimine complex is shown in Fig. 5. The midpoint slope was 0.326 and the spreading factor  $x = 2.07$ . This very high value, favoring the monoimine complex, is in agreement with the fact that only a mono-complex was isolated with mercuric chloride and bromide.

The complexity constants in 0.3 *N* AzH<sup>+</sup> and 1.0 *N* NaNO<sub>3</sub> were found to be

$$\log k_1 = 5.48; \log k_2 = 4.24; \log K_2 = 9.72$$

### Discussion

The observations and conclusions made were:

(1) The nitrogen of the ethylenimine acts as a typical amine nitrogen in forming bonds to metal ions.

(2) The bonding is quite similar to that in ammonia and amino complexes, as the colors, vapor pressures and other properties show remarkable parallelism.

(3) The maximum coordination number is the same as for the ammonia complexes, but the steric effect of the ring prevents in several cases the attainment of such a number. In Table IV our results are compared with these obtained by Ephraim<sup>5</sup> with methyl- and ethylamine.

From the data in Table IV, it appears that the steric properties of aziridine fall between those of methylamine and ethylamine. This conclusion is supported by the complexing data found with silver

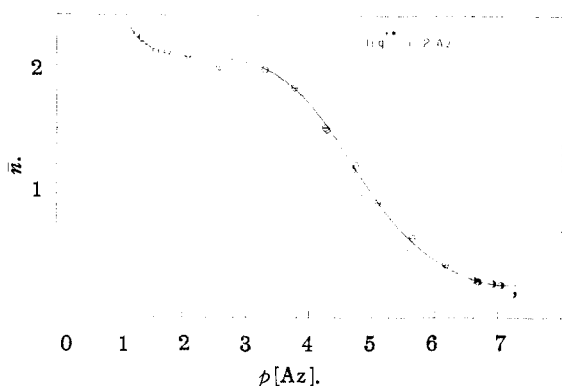


Fig. 5.—The formation curve for the diethylenimine mercuric ion: O, in 0.1*N* AzH<sup>+</sup> and 1*N* NaNO<sub>3</sub> at 15°; ⊙, in 0.3*N* AzH<sup>+</sup> and 1*N* NaNO<sub>3</sub> at 15°; ●, in 1*N* NaNO<sub>3</sub> and variable (AzH<sup>+</sup>), without addition of free Az.

ion. From comparison with the linear free energy plots of Bruehlman and Verhoek<sup>11</sup> ethylenimine appears to complex more strongly than expected for a secondary amine of comparable ionization constant. The spreading factor  $\alpha$  for complexes with silver ion is also low, being comparable to that found for primary amines rather than secondary amines.<sup>11</sup> Thus, all of the available data indicate that the nitrogen of aziridine is little affected in its chemistry by the steric properties of the balance of the three-membered ring.

(4) The ethylenimine ring is quite stable when bonded to a metal in a solid complex. Complexes were stored in a closed container for several months without appreciable change in color and properties.

(11) R. J. Bruehlman and F. H. Verhoek, *THIS JOURNAL*, **70**, 1401 (1948).

TABLE IV<sup>a</sup>  
COORDINATION NUMBERS OF AMINE COMPLEXES

	MeNH <sub>2</sub>	Et-NH <sub>2</sub>	Az
NiI <sub>2</sub>	6	6	6
NiBr <sub>2</sub>	6	4-6	6
NiCl <sub>2</sub>	6	4	4
MnI <sub>2</sub>	6	4 <sup>b</sup>	5
MnCl <sub>2</sub>	6	4	4

<sup>a</sup> The cobalt salts behave similarly; Copper had in all cases the coordination number four. <sup>b</sup> 6 at *T* well below 0°.

Only those with higher vapor pressure (as the chlorides) were gradually losing ethylenimine but apparently without opening of the ring. The presence of metal ions in the Az-solution did not appear to cause a significantly more rapid ring opening.

(5) The strength of the metal-to-nitrogen bond was found in all cases to be lower than that of the corresponding ammonia-complexes. It is not surprising that Az forms weaker complexes, in view of its lower basicity to protons than ammonia. The formation curves have the same shape as those reported by Bjerrum for the ammonia-complexes, to which they are approximately parallel. In the case of mercury, the curve is here much flatter, showing a higher relative stability of the mono-complex; the reason for this is not presently known.

It must be pointed out that all the investigated complexes were formed with metal ions belonging to the "rapid replacement" class. The results of the work on metals whose coordination spheres are "inert" to replacement, namely Cr(III) and Co(III), will be reported in a future publication.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE PENNSYLVANIA STATE UNIVERSITY, UNIVERSITY PARK, PENNSYLVANIA]

## Stability Relationships Among the Rare Earth Dipicolinates

BY INGMAR GRENTHE<sup>1</sup>

RECEIVED JULY 13, 1960

Step-wise stoichiometric formation constants have been determined for the complexes between copper, yttrium, the rare earths and the dipicolinate ion. The measurements have been made in an aqueous perchlorate medium of the ionic strength  $\mu = 0.5 M$  at a temperature of 20°.

### Introduction

Complex formation between various metal ions and the dipicolinate ion has been studied earlier.<sup>2,3</sup> These measurements now have been extended to include the rare earths and yttrium. It was impossible to use the familiar *pH* method for the determination of the formation constants, because of the low basicity of the dipicolinate ion and because of its very high affinity for the metal ions being studied.

The copper-dipicolinate system was determined by e.m.f. measurements of the concentration of free

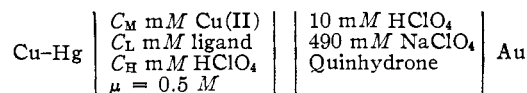
(1) Department of Chemistry, University of Lund, Lund, Sweden.

(2) R. M. Tichane and W. E. Bennet, *THIS JOURNAL*, **79**, 1293 (1957).

(3) G. Anderegg, *Helv. Chim. Acta*, **43**, 414 (1960).

central ion, [Cu<sup>+2</sup>], in the solutions of complexes, by means of a copper amalgam electrode. When the complexity of this system was known, that of the others could be determined by a competition method.<sup>4</sup>

**Calculation of Complexity Constants from Measurements of [Cu<sup>+2</sup>] = [M] with the Copper Amalgam Electrode.** 1. Cu<sup>+2</sup>-dipic<sup>-2</sup>.—Experimentally, the e.m.f., *E*, of cells of the following type was measured



(4) I. Leden, *Acta Chem. Scand.*, **6**, 971 (1952).