and by the presence of water vapor; under the more severe conditions of treatment, this change is accompanied by a decrease in the number of catalytic centers without substantial change in their nature.

4. Some possible mechanisms for the formation of ethylene have been considered in the light of the reaction kinetics, and the ether intermediate theory in its simplest form has been shown to be inapplicable.

5. Changes of activity with use have been explained as the result of changes in the water content of the surface, rather than in surface area.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEW HAMPSHIRE]

Copper(II) and Nickel(II) Complex Ions of Hydroxyethylethylenediamine

BY JEAN L. HARVEY,[1] CHARLES I. TEWKSBURY AND HELMUT M. HAENDLER

Complex ions formed by the action of multidentate amines on metal ions are of considerable interest structurally. In a previous article Haendler[2] reported the formation of copper(II) and nickel(II) complex ions with diethylenetriamine, $H_2N(CH_2)_2NH(CH_2)_2NH_2$. Subsequently, Breckenridge[3] isolated specific complexes of this amine and of hydroxyethylethylenediamine (2-(2-aminoethylamine)-ethanol), $H_2N(CH_2)_2NH(CH_2)_2OH$ (abbreviated "hn"). The work on diethylenetriamine led to the conclusion that it probably behaved as a tridentate ligand, a conclusion supported by polarographic studies by Laitinen, *et al.*,[3a] and that the copper and nickel complexes were structurally similar.

Using hydroxyethylethylenediamine, however, Breckenridge was able to isolate copper complexes with a copper:hn ratio of 1:1 and 1:2 from 95% ethanol and a single nickel complex with a nickel:hn ratio of 1:3 from absolute ethanol. Spectrophotometric methods have now been applied to the study of the ions formed in water solution by copper(II) and nickel(II) ions and this amine. It has been found that copper forms the complex ions $[Cu(hn)]^{++}$, $[Cu(hn)_2]^{++}$ and $[Cu(hn)_4]^{++}$, and that nickel forms the ions $[Ni(hn)]^{++}$ and $[Ni(hn)_2]^{++}$.

The results for copper are compatible with the structures suggested by Breckenridge. In $[Cu(hn)]^{++}$ and $[Cu(hn)_2]^{++}$, the amine probably acts as a bidentate ligand, the coördinating power of the hydroxyl group being slight. The shape of the spectral curves for $[Cu(hn)_4]^{++}$ indicates low stability of the ion, consistent with a non-chelated structure involving four primary amine groups. The complex is apparently stable only in solution.

Attempts to identify the ions formed between copper(II) and diethanolamine (2,2′-dihydroxydiethylamine), $HO(CH_2)_2NH(CH_2)_2OH$ (abbreviated "den"), indicate that there are ions with copper:den ratios of both less than 1:3 and greater than 1:3. If the amine were coördinated through both the amine and hydroxyl groups, a ratio of 1:2 would be the maximum expected. No ratio greater than 1:3 could be expected if coördination were through the hydroxyl groups only. It is thus probable that the diethanolamine is coordinated only through the secondary amine group. The ions are stable only in the presence of excess amine, indicating lower coördinating power than with primary amine groups. This supports the proposal that only primary amine groups are involved in the 1:4 ion of hydroxyethylethylenediamine and that both amine groups participate in the formation of 1:1 and 1:2 ions.

The $[Ni(hn)]^{++}$ and $[Ni(hn)_2]^{++}$ are assumed to be similar in structure. No evidence could be found of an ion corresponding to $[Ni(hn)_3]Cl_2$ isolated by Breckenridge. There is evidence, however, that the solvent affects the coördinating power of the amine. Mann[4] reported that only two moles of diaminopropanol would coördinate to nickel in water solution. The compound $[Ni(hn)_2]HgI_4$ has been prepared by reaction in

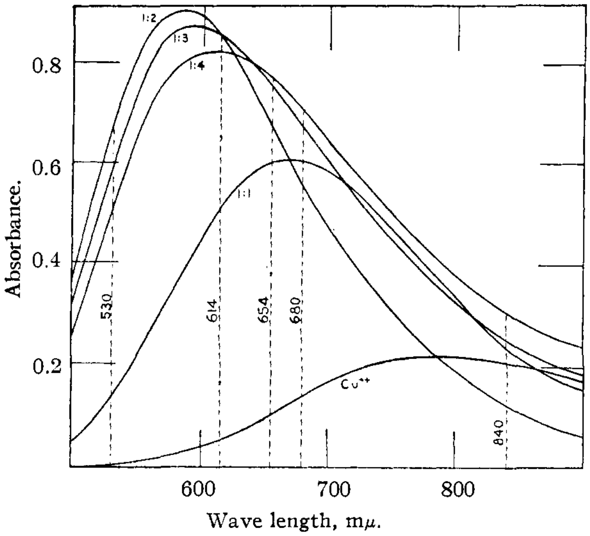

Fig. 1.—The absorption spectra of solutions of Cu^{++} and hn.

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[1] This paper represents in part a thesis presented by J. L. Harvey to the University of New Hampshire in partial fulfillment of the requirements for the degree of Master of Science.

[2] Haendler, THIS JOURNAL, **64**, 686 (1942).

[3] Breckenridge, *Can. J. Research*, **B26**, 11 (1948).

[3a] Laitinen, *et al.*, THIS JOURNAL, **71**, 1550 (1949).

[4] Mann, *J. Chem. Soc.*, 2904 (1927).

water solution, using an amount of amine in excess of that needed for the 1:3 compound.

Experimental

Determination of composition was made by the method of continuous variations, as described by Vosburgh and Cooper.[5] Maxima of curves obtained by plotting the amount of ligand solution (x) against the difference (Y) between observed absorbance and that calculated for no reaction give directly the compositions of the ions present, if both components are in solutions of equimolar concentration.

All absorption spectra were measured with the Beckman DU Spectrophotometer, using 1-cm. Corex cells. Measurements were made directly in terms of absorbance.[6]

Hydroxyethylethylenediamine was purified by vacuum distillation, b. p. 130.5° at 11 mm. Solutions of the amine were standardized against hydrochloric acid, using brom thymol blue. Diethanolamine was also distilled, b. p. 155–157° at 12 mm.

Copper(II) Complex Ions.—A 0.100 *M* copper(II) ion solution was prepared from copper(II) acetate monohydrate, used without further purification. Five drops of 6 *M* acetic acid per liter was added to prevent hydrolysis. The absorption spectra were measured for solutions 0.010 *M* in copper ion and, in addition, 0.010, 0.020, 0.030, 0.040 and 0.060 *M* in hydroxyethylethylenediamine, corresponding to molar ratios of 1:1, 1:2, 1:3, 1:4 and 1:6. The spectra are shown in Fig. 1. The 1:6 curve closely resembled the 1:4 curve.

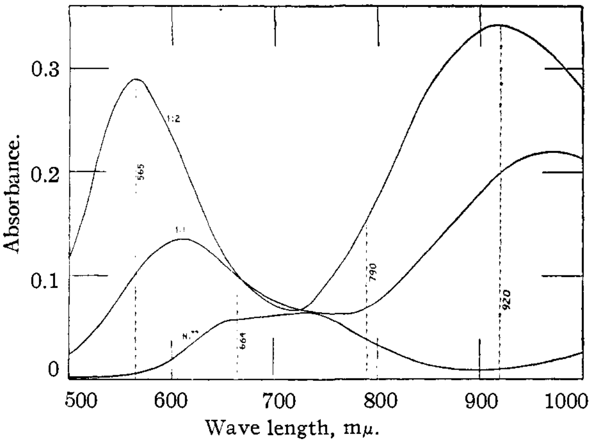

Fig. 3.—The absorption spectra of solutions of Ni^{++} and hn.

Further measurements were made at 530, 614, 654, 668, 680 and 840 mμ, using variable amounts of 0.010 *M* solutions. The *Y* curves are shown in Fig. 2. The maxima indicate the presence of the ions $[Cu(hn)]^{++}$, $[Cu(hn)_2]^{++}$ and $[Cu(hn)_4]^{++}$.

Nickel(II) Complex Ions.—A 0.667 *M* nickel (II) sulfate solution was prepared from the hexahydrate, which had been treated for removal of cobalt.[7] Five drops of 3 *M* sulfuric acid per

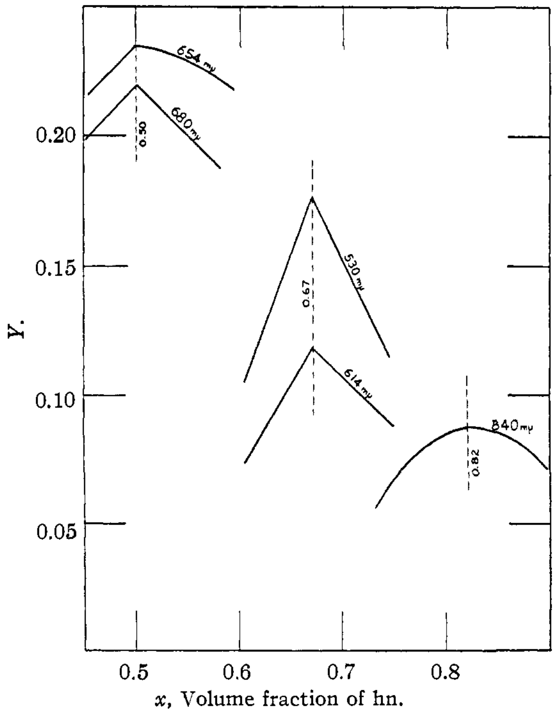

Fig. 2.—*Y* curves for mixtures of (1 − x) volumes of 0.010 *M* Cu^{++} and x volumes of 0.010 *M* hn solutions.

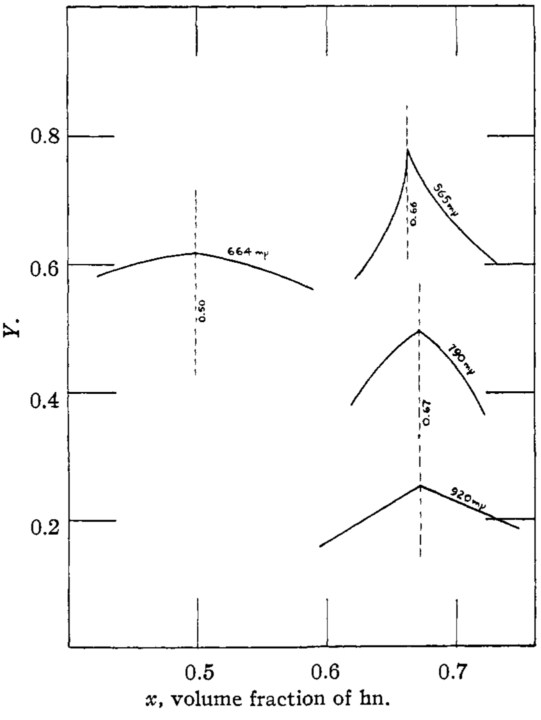

Fig. 4.—*Y* curves for mixtures of (1 − x) volumes of 0.334 *M* Ni^{++} and x volumes of 0.334 *M* hn solutions.

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[5] Vosburgh and Cooper, THIS JOURNAL, **63**, 437 (1941).

[6] Mellon, *Anal. Chem.*, **21**, 3 (1949).

[7] Deakin, Scott and Steele, *Z. physik. Chem.*, **69**, 126 (1909).

liter was added. A 0.667 *M* amine solution was used. By dilution, solutions 0.067 *M* in nickel ion and of the proper amine concentration for ratios of 1:1, 1:2, 1:3, 1:4 and 1:6 were prepared. The absorption spectra of these solutions are shown in Fig. 3. The spectra of the 1:3, 1:4 and 1:6 ratios are almost identical to the 1:2 curve.

The *Y* curves were obtained from measurements at 565, 664, 790 and 920 mμ, using 0.334 *M* solutions. These curves, Fig. 4, show the presence of the ions $[Ni(hn)]^{++}$ and $[Ni(hn)_2]^{++}$.

The compound $[Ni(hn)_2]HgI_4$ was prepared by adding an excess of a solution of mercury(II) iodide in excess potassium iodide to a mixture of nickel sulfate and hydroxyethylethylenediamine. The pale blue-violet precipitate was washed with dilute amine solution and with ethanol. Nickel was determined as anthranilate, after removal of mercury with hydrogen sulfide, and mercury was determined as $[Cu(en)_2]HgI_4$.[8]

Anal. Calcd. for $[Ni(hn)_2]HgI_4$: Ni, 6.02; Hg, 20.6. Found: Ni, 6.09, 5.92; Hg, 20.1, 20.2.

Copper(II) Complex Ions of Diethanolamine.—The absorption spectra were measured for solutions 0.010 *M* in copper ion and containing diethanolamine in ratios of 1:3, 1:4, 1:6 and 1:8. The spectra are shown in Fig. 5. The 1:8 curve resembled the 1:6. Solutions of lower ratio could not be prepared because of precipitation of hydroxide. The 1:3 solution hydrolyzed slowly. Uncorrected *Y* curves for the higher values of *x* are shown in Fig. 6. The maximum at 0.82 suggests the 1:4 ion for the measurement at 530 mμ. At the other wave lengths the absence of maxima indicate that the ions formed are less than 1:3.

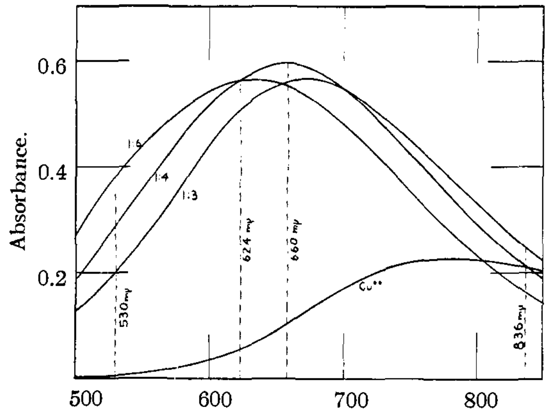

Fig. 5.—Absorption spectra of solution of Cu^{++} and diethanolamine.

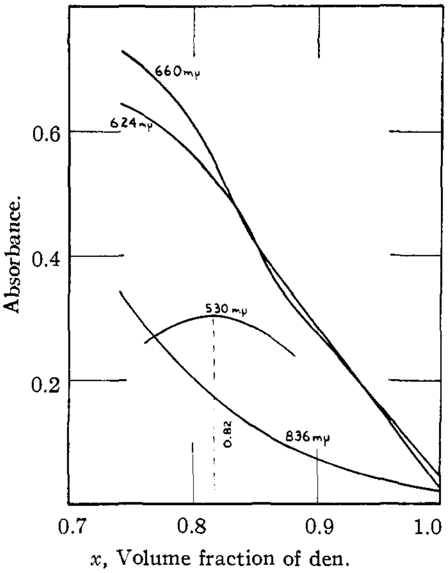

Fig. 6.—Absorption spectra for mixtures of (1 − *x*) volumes of 0.010 *M* Cu^{++} and *x* volumes of 0.010 *M* diethanolamine.

Summary

Complex formation between copper(II) and nickel(II) ions and hydroxyethylethylenediamine has been studied spectrophotometrically.

The presence of the ions $[Cu(hn)]^{++}$, $[Cu(hn)_2]^{++}$, $[Cu(hn)_4]^{++}$, $[Ni(hn)]^{++}$ and $[Ni(hn)_2]^{++}$ has been shown.

DURHAM, NEW HAMPSHIRE RECEIVED JUNE 18, 1949

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[8] Spacu and Suciu, *Z. anal. Chem.*, **77**, 334 (1929).