$$-\frac{d \ln [\text{complex}]}{dt} = K(k_2 + k_3[\text{H}^+])$$

with $K = k_1/k_{-1}$. The observed rate equation has this form.

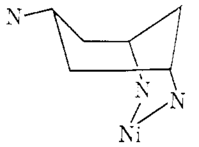
The actual stereochemistry of the intermediate containing two Ni–N bonds is important in assessing the credibility of the assumption upon which the rate law is based. Breakage of the first Ni–N bond necessarily forces one of the remaining six-membered rings into an unstable boat conformation. The conformational change in **1** was achieved by rotation within the cyclohexane ring across a potential barrier which should be about 10 kcal mol^{-1} by analogy with other cyclohexanes.[6] The triaxial conformation of the cyclohexane ring is retained in **2**, but a conformational change has occurred within the metal-containing ring. The potential barrier for this process is unknown. We cannot, therefore, easily rule out either **1** or **2** on the basis of energetics, and it is possible that they both play a role in the dissociative process. Nevertheless, both **1** and **2** contain nonbonded contacts which will cause either of them to be highly unstable. These repulsive forces are best relieved by returning to the tridentate form of the ligand, and re-forming the Ni–N bond should be a very favorable process. The assumption which was used in obtaining the rate equation at least seems plausible due to this reason, and, in addition, the less-than-normal ability[4] of the acid to scavenge the partially dissociated ligands is explicable now.

TABLE II

RATE CONSTANTS AND ACTIVATION PARAMETERS

Temp, °C	10^4k, sec^{-1}	10^4k_H, M^{-1} sec^{-1}
25.00	1.30	1.39
34.73	3.35	5.02
44.42	9.53	14.5
E_a, kcal mole^{-1} [a]	19.3 ± 0.9	22.7 ± 0.8
$\Delta S^{\ddagger}$, cal deg^{-1} mol^{-1}	−13.5 ± 3.1	−2.0 ± 2.8

[a] Errors are standard deviations obtained by the method of least squares.



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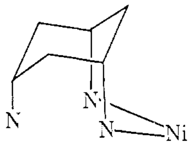

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Acknowledgment.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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Preparation-Controlled Forms of Copper(II) and Nickel(II) Ethylenediaminetetraacetato Complex Diprotic Acids

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Dihydrogen ethylenediaminetetraacetatoaquocopper(II), $CuYH_2 \cdot H_2O$, has been studied by several groups of investigators, but several discrepancies persist regarding its structure and properties. We have evidence that two forms exist, a monohydrate and an anhydrous species, depending upon the method of preparation. Slow crystallization by evaporation at 40° in a vacuum oven produces the dark blue monohydrate. Rapid crystallization from solution supersaturated at boiling temperature or by addition to excess ethanol produces the anhydrous compound. The analogous nickel(II) compounds are formed by similar treatments, and preliminary work indicates two forms also for zinc and cobalt(II). Manganese(II) appears to have only one form.

Brintzinger and Hesse[1] prepared a greenish blue copper(II) EDTA compound that was shown by analysis to be the anhydrous $CuYH_2$. This compound did not lose weight until decomposition set in above 200°. They concluded that the structure was the square-planar complex. Kirschner[2] prepared the monohydrate, $CuYH_2 \cdot H_2O$, in which he proposed quadridentate complexation by the ligand because of the equal intensities of the antisymmetric stretching frequencies of the coordinated carboxylate groups and the uncoordinated carboxylic acid groups. Smith and Hoard[3] and Garvan[4] examined $CuYH_2 \cdot H_2O$ by X-ray diffraction and infrared spectroscopy. Both found the copper(II) compound to be isomorphous with $NiYH_2 \cdot H_2O$ and concluded that the ligand is quinquedentate and the structure octahedral. Bhat and Iyer[5] prepared a compound that analysis indicated to be the monohydrate but which showed no weight loss until melting followed by decomposition above 238°. Martynenko, *et al.*,[6,7] studied the copper(II)–EDTA system and concluded that there are no less than four species, including the monohydrate, an unstable anhydrous form, a stable anhydrous form, and a dehydrated form. The monohydrate was crystallized from solutions of the complex acid less that 0.1 M, and the

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(5) T. R. Bhat and R. K. Iyer, *J. Inorg. Nucl. Chem.*, **29**, 179 (1967).

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TABLE I

ELEMENTAL ANALYSES OF THE COPPER(II) AND NICKEL(II) COMPLEX ACIDS[a]

Compound	% C		% N		% H		% Cu		% Ni	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$CuYH_2$	33.95	34.14	7.91	7.92	3.98	4.02	17.96	18.04	...	...
$CuYH_2 \cdot H_2O$	32.30	32.10	7.53	7.37	4.33	4.27	17.09	17.30	...	...
$NiYH_2$	34.42	34.69	8.02	7.80	4.04	4.28	...	...	16.82	16.57
$NiYH_2 \cdot H_2O$	32.73	32.53	7.63	7.47	4.39	4.28	...	...	15.99	16.14

[a] Determined by Galbraith Laboratories, Knoxville, Tenn.

anhydrous forms were crystallized from solutions greater than 0.1 *M*. They concluded that the ligand is tridentate and that the water of the hydrated form is in the coordination sphere of the metal in either a tetrahedral or a square-planar complex.

Experimental Section

Preparation of the Complexes.—The copper(II) complex acids were prepared by a method similar to that of Pfeiffer and Schmitz,[8] by reaction of freshly prepared copper(II) hydroxide with a stoichiometric amount of ethylenediaminetetraacetic acid, H_4Y. The anhydrous light blue form, $CuYH_2$, is precipitated by boiling the solution until the solid acid begins to form and then cooling rapidly or by pouring the hot concentrated solution into a large excess of 95% ethanol. The hot concentrated solution evidently is supersaturated, as precipitation is practically complete within 2 min. The monohydrated dark blue form, $CuYH_2 \cdot H_2O$, is prepared by slow evaporation at 40° in the vacuum oven over a period of hours. Both forms can be reprecipitated by the same methods used for their initial preparation. Each can be converted to the other form by use of the appropriate crystallization method. Mixtures of the two species tend to form at intermediate crystallization rates and are difficult to recognize.

The nickel(II) complex acids were prepared by the method of Smith and Hoard[3] by reaction of freshly precipitated nickel hydroxide and H_4Y and also by reaction of H_4Y with nickel carbonate. The monohydrate, $NiYH_2 \cdot H_2O$, precipitates upon crystallization from aqueous solution and tends to be the predominant form. The anhydrous form, $NiYH_2$, is prepared by pouring a hot concentrated solution of the complex acid into a large excess of acetone. The anhydrous form is stable at ordinary humidities, but immediately converts to the monohydrate upon contact with water.

Two forms were also observed for the complex acids of zinc and cobalt(II), but only one form was observed for manganese(II). These compounds have not been further characterized.

The elemental analyses for the copper(II) and nickel(II) complex acids are shown in Table I. From titration data, the pK_a values were found to be 3.39 for $CuYH_2$ and 3.27 for $CuYH_2 \cdot H_2O$, although there is undoubtedly one one species in solution. From the neutralization equivalents, the formula weight for the anhydrous compound was found to be 338 (theoretical 354), and that of the monohydrate to be 362 (theoretical 372). The magnetic moments of both copper(II) compounds were found to be 1.93 BM.

Absorption Spectra.—The infrared spectra of the copper(II) complex acids in potassium bromide pellets are very similar to those obtained by previous workers. The antisymmetric stretching frequencies of the protonated and nonprotonated carboxylate groups occur at approximately the same frequencies in both complex acids. The nonprotonated carboxylate bands are slightly more intense in each case. The ionized carboxylate peak occurs at 1606 cm^{-1} in the monohydrate and at 1613 cm^{-1} in the anhydrous form. The protonated carboxylate peak occurs at 1736 cm^{-1} in the monohydrate and at 1750 cm^{-1} in the anhydrous compound. A sharp water band, which is absent in the anhydrous compound, occurs at 3590 cm^{-1} in the monohydrate. A weak, broad O–H band centered at about 3450 cm^{-1} appears in the spectra of both compounds.

Aqueous solutions of both copper(II) species exhibit identical ultraviolet and visible absorption spectra. There is a peak at 239 mμ, with a shoulder at 269 mμ and a weak d–d transition peak at approximately 738 mμ.

Smith and Hoard[3] and Garvan[4] have discussed the infrared absorption spectra of what was evidently the monohydrate nickel(II) complex acid, $NiYH_2 \cdot H_2O$. Garvan noted the presence of a coordinated water peak at 3606 cm^{-1}. The only essential difference in our absorption spectra of the monohydrate and anhydrous forms is the presence of the water band at 3594 cm^{-1}.

Thermal Analyses.—Both differential thermal analysis (dta) and thermogravimetric analysis (tga) were made of the copper(II) complex acids. With the anhydrous compound $CuYH_2$, the dta showed an endotherm beginning at 231° closely followed by a more intense endothermic peak beginning at about 245°. Bhat and Iyer[5] attributed the first event to melting and the second to decomposition of the carboxylate groups. A further weight loss beginning at about 360° was attributed to decomposition of the ethylenediamine segment of the ligand. With the monohydrate compound, $CuYH_2 \cdot H_2O$, the dta showed an endothermic event beginning at 132°. This accompanied a weight loss beginning at 145° corresponding to the loss of one water molecule. After that weight loss, the thermal behavior of the remaining compound resembled that of the anhydrous complex acid.

The dta curve for the anhydrous nickel(II) complex acid, $NiYH_2$, shows no thermal events until about 305°. From that temperature until about 425°, two major and several minor decomposition peaks appear. For the monohydrate complex acid, $NiYH_2 \cdot H_2O$, the dta curve is quite similar to that of the anhydrous compound, except for a peak probably corresponding to water loss beginning at about 230°.

Ultraviolet Photolysis.—A Hanovia high-pressure mercury arc lamp using Vycor and nickel oxide filters was used to irradiate the complex acids. Photosensitivity was measured by the increase in the carbon dioxide band at 2340 cm^{-1} in the manner described by Lambert, Godsey, and Seitz.[9] Irradiation of approximately 0.005 mmol of the monohydrate and anhydrous copper(II) complex acids in 200-mg potassium bromide pellets showed the anhydrous complex acid to be slightly photosensitive. This was the only observable change in the spectra. The copper(II) and nickel(II) monohydrate complex acids were found to be essentially nonphotosensitive.

Results and Discussion

The preparation of the anhydrous and monohydrate forms of both the copper(II) and nickel(II) complex acids depends upon the rate of crystallization from aqueous solution. This may be a general characteristic of the first transition series of metals, as two forms were also observed for the corresponding cobalt(II) complex acid, as well as for zinc.

Our results are consistent with an octahedral structure containing quinquedentate EDTA for the monohydrate complex acids of both copper(II) and nickel(II).

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This was also the structure proposed by Smith and Hoard[3] and Garvan[4] for these compounds. A square-planar structure containing quadridentate EDTA is favored for the anhydrous copper(II) complex acid. Stuart–Briegleb models indicate severe steric strain for either four-coordinate tetrahedral or five-coordinate trigonal-bipyramidal or square-pyramidal structures. As Smith and Hoard[3] and Lind, Lee, and Hoard[10] have observed, protonation does not protect a carboxyl group from coordination with the metal. Thus a coordinated carboxyl group could also provide an acidic proton in solution.

Two of the forms proposed by Martynenko, *et al.*,[6,7] for the copper(II) complex acids appear to be the monohydrate and anhydrous forms reported here. Since the infrared spectra of our anhydrous form and that of the monohydrate form dehydrated at 210° were identical, we conclude that there are not two distinct stable anhydrous species. Our methods of preparation did not permit observation of their proposed unstable anhydrous form. In any case, tetrahedral structures for these complex acids do not seem plausible.

We propose that the anhydrous form, which is precipitated quickly from solution, is derived from the solution species. This form would be octahedral with the ligand occupying equatorial sites and two easily lost water molecules occupying the axial positions. When the rate of precipitation is slow, rearrangement occurs to incorporate a water molecule in the equatorial plane of the octahedral structure which also contains the two amine nitrogens and a carboxyl oxygen. This is the structure determined by Smith and Hoard[3] for the nickel(II) monohydrate complex acid which is isomorphous with the copper(II) monohydrate. In this structure, the coordinated water gains added stabilization through intermolecular hydrogen bonding to two carboxyl oxygens in neighboring molecules of the solid complex acid. Thus the formation of two distinct forms of the complex acid for each metal is controlled by the rate of crystallization from solution (preparation controlled). Their formation is also indirectly controlled by the steric restrictions imposed by the chelating ligand (ligand controlled). If this is the case, then similar forms might be predicted for metal cations of similar size and charge.

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