tris(thiobenzoato)chromium(III) and assigned this as excitation to a state arising from both charge transfer and an excited ligand state.

The reaction of bis(thiocarboxylato)nickel(II) compounds with a large excess of pyridine or some picolines resulted in the isolation of bright green crystalline complexes of the general formula $Ni(RCOS)_2 \cdot 2L$, where $R = CH_3$ and L = py, β-pic, or γ-pic; or $R = C_6H_5$ and L = py, α-pic, β-pic, or γ-pic. Reactions involving bis(thiopropionato)nickel(II) resulted in decomposition of the compound to nickel sulfide, and no complexes were obtained. Infrared spectra of the complexes (Table I) suggest that the thiocarboxylic acids are behaving as bidentate or bridging ligands, although, since the lowering of $\nu(C{=}O)$ is not as great as is observed for the bis(thiocarboxylato)nickel(II) compounds, the type of coordination may be different from that found for the latter compounds. Furlani, *et al.*,[6] concluded that tris(thiobenzoato)chromium(III) contains bidentate thiocarboxylates although no infrared data were quoted for this compound. Room-temperature magnetic properties (Table II) suggest the nickel ion is in an octahedral environment, with a triplet ground state. Further evidence to support this conclusion is obtained from the reflectance spectra (Table III). The following transitions are assigned for nickel(II) in O_h symmetry: ν_1, $\sim$9500 cm^{-1}, $^3A_{2g} \rightarrow {}^3T_{2g}$; ν_2 $\sim$11,500 cm^{-1}, $^3A_{2g} \rightarrow {}^1E_g$; ν_3, $\sim$16,500 cm^{-1}, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$; ν_4, $\sim$26,000 cm^{-1}, $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ plus charge transfer.

Thus the reaction of these nitrogen donor ligands with the bis(thiocarboxylato)nickel(II) compounds breaks down the dimeric structure to produce complexes probably containing bidentate thiocarboxylates Attempts to remove the pyridine ligands by heating under vacuum above the boiling point of the ligand for several hours resulted in a change from bright green to the red-brown characteristic of the original dimeric species. However, reproducible analyses were not obtained for these products and prolonged heating finally led to complete decomposition to nickel sulfide.

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Dissociation Reactions of the Amide Protons of N,N′-Diglycylethylenediaminenickel(II). Kinetics of Octahedral–Square-Planar Conversion[1]

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The kinetics of the transition of nickel(II)–N,N′-diglycylethylenediamine (DGEN) complexes from the paramagnetic octahedral form to the diamagnetic square-planar form, which accompanies the dissociation of the amide hydrogens from the ligand, have been studied spectrophotometrically. The rate is given by $d[NiH_{-2}L]/dt = k[OH^-][NiL^{2+}] + k'[OH^-] \cdot [NiL_2{}^{2+}]$ where L represents the neutral ligand DGEN, $NiH_{-2}L$ is the fully deprotonated yellow complex, and k and k' are 3.3×10^2 and 2.5×10^2 sec^{-1} M^{-1}, respectively, at 25.3° and an ionic strength of 1.0 M. The mechanisms of the reactions are discussed. Evidence is presented for the simultaneous dissociation of the two peptide protons proposed previously on the basis of potentiometric equilibrium studies.

Introduction

The amide hydrogens in polypeptides may be displaced by nickel(II)[2-4] as well as by copper(II)[2,5-7] ions. Direct evidence for amide proton displacement was obtained from aqueous (D_2O) infrared spectra for complexes in solution[4,6,7] and from X-ray crystallographic studies for complexes in the solid state.[8] In these deprotonated peptide complexes, the metal ion is coordinated to the nitrogen of the peptide groups both in solution and in the solid state. The nickel(II) complexes of polypeptides in which the peptide protons are displaced are yellow, diamagnetic, and square planar.[3,4,9,10] The displacement of the peptide hydrogens is slow[3,4] and all of the peptide hydrogens in the ligand seemed to be released simultaneously,[4,10] or nearly simultaneously, to give the final completely deprotonated forms in one-step neutralization reactions.

In a recent publication,[11] the equilibria involved in the formation of N,N′-diglycylethylenediamine (DGEN) complexes of nickel(II) and copper(II) have been described. It was found that this synthetic peptide-like ligand behaves in a manner similar to that

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[1] This investigation was supported by a research grant from the Robert A. Welch Foundation.

[2] A. R. Manyak, C. B. Murphy, and A. E. Martell, *Arch. Biochem. Biophys.*, **59**, 373 (1955).

[3] R. B. Martin, M. Chamberlin, and J. T. Edsall, *J. Am. Chem. Soc.*, **82**, 495 (1960).

[4] M. K. Kim and A. E. Martell, *ibid.*, **89**, 5138 (1967).

[5] H. Dobbie and W. O. Kermack, *Biochem. J.*, **59**, 246, 257 (1955).

[6] A. E. Martell in "Recent Topics in Coordination Chemistry," S. Misumi and K. Ueno, Ed., Special Publication No. 84, Nankodo Publishing Co., Japan, 1968, p 47.

[7] M. K. Kim and A. E. Martell, *J. Am. Chem. Soc.*, **88**, 914 (1966).

[8] H. C. Freeman in "The Biochemistry of Copper," J. Peisach, P. A. Isen, and W. E. Blumberg, Ed., Academic Press, Inc., New York, N. Y., 1966.

[9] R. Mathur and R. B. Martin, *J. Phys. Chem.*, **69**, 668 (1965).

[10] M. K. Kim and A. E. Martell, *J. Am. Chem. Soc.*, **91**, 872 (1969).

[11] K. S. Bai and A. E. Martell, *ibid.*, **91**, 4412 (1969).

reported for the peptides: the two amide hydrogens are displaced by these metal ions. With nickel(II), both protons seem to be displaced simultaneously at a pH of about 8 and a yellow complex is formed; visible–near-infrared spectra indicated that this complex is diamagnetic. It was also found that, whereas the amide proton displacement reaction is very fast with copper(II), the reaction with nickel(II) is quite slow.

There are several instances in which geometrical transitions were reported to be involved in reactions of complexes of this metal ion.[12-16] In the present study, the rates and mechanism of displacement of the amide protons in DGEN by nickel(II) and the resulting transition in the coordination sphere of the metal from the blue octahedral to the yellow planar form are investigated.

Experimental Section

Reagents.—The ligand DGEN was synthesized by the method of Cottrell and Gill,[17] the compound being isolated as the dihydrochloride salt. It was 99.8% pure as determined by potentiometric titration with standard base. Solutions of nickel(II) chloride were standardized by titration with EDTA in the usual manner. Reagent grade boric acid and sodium borate were recrystallized twice from aqueous solutions. Morpholine (Fisher) was distilled twice. About equivalent amounts of this distilled liquid base and concentrated hydrochloric acid were mixed slowly in isopropyl alcohol in the cold; the salt was recrystallized twice from isopropyl alcohol to which a small amount of water was added. Trimethylamine hydrochloride (Eastman) was recrystallized three times from ethanol–ether solution.

Equilibrium Data.—A Beckman Research Model 101900 pH meter was used for all measurements of hydrogen ion concentrations. The pH meter–electrode system was standardized in terms of hydrogen ion concentration with standard solutions of acetic acid–sodium acetate buffers, hydrochloric acid, and sodium hydroxide, at an ionic strength of 1.0 *M* adjusted with potassium chloride, employing the data of Harned and Owen.[18] Procedures for potentiometric titration were described previously.[11] For equilibrium titrations, Beckman No. 39000 glass and No. 39071 calomel electrodes were used. For the measurements of the hydrogen ion concentrations of the spectral solutions, a Beckman No. 39013 combination electrode was employed. The equilibrium constants pertinent to this research were evaluated in the manner described previously[11] and are listed in Table I. The complexity constants of DGEN are all slightly greater than those obtained in 0.10 *M* ionic strength with potassium nitrate.[11] Under the present experimental conditions, no evidence was found for the formation of NiL_3^{2+} or any "mixed" complexes containing both the neutral and the deprotonated ligands in solutions of metal–ligand molar ratios of up to 1:5.

Kinetic Measurements.—In kinetic experiments involving metal ion complexes, it is expedient to maintain the pH of the solution constant in order to simplify the calculations. For this purpose, buffer solutions of boric acid, morpholine, and trimethylamine were employed. Tris(hydroxymethyl)aminomethane was found to be unsatisfactory because of its extensive interaction with nickel(II) ion.[19] The stock solutions (0.1–0.2 *M*) of the blue nickel(II)–DGEN complex were prepared by mixing stoichiometric ratios of solutions of metal chloride and ligand. To this solution, sodium hydroxide was added to bring the value of *a* just under 2 so that there would be practically no free acid or ammonium protons which otherwise might later alter the buffer pH somewhat. Under these conditions, most of the metal ion and the ligand are combined as NiL^{2+}, as calculations based on the data in Table I would readily show.

TABLE I
PROTONATION CONSTANTS OF DGEN AND EQUILIBRIUM CONSTANTS INVOLVING NICKEL(II)–DGEN COMPLEXES

K^a	Log K
$K_1 = [NiL^{2+}]/[Ni^{2+}][L]$	5.65
$K_2 = [NiL_2^{2+}]/[NiL^{2+}][L]$	3.16
$K_{1AB} = [NiL^{2+}]/[NiH_{-2}L][H^+]^2$	16.50

[a] At 25° and μ = 1.0 *M*, adjusted with KCl; log K_1^H = 8.39 and log K_2^H = 7.71 for DGEN. L = neutral DGEN.

Absorption spectra for kinetic measurements were taken with a Cary Model 14 recording spectrophotometer using 1.00-cm cells. The reactions were initiated by adding small amounts (0.10 ml in most runs) of the blue complex stock solution to a buffer solution (usually 2.70 ml) adjusted with KCl such that the final ionic strength will always be 1.0 *M*. In all cases, the buffer concentration was at least 100 times that of the complex, and in many runs a large part of the ionic strength was contributed by the ionic species of the buffer itself.

The reaction was followed by measuring absorbance as a function of time at 415 mμ, the wavelength of maximum absorption (ϵ 217) of the planar complex. At this wavelength, the molar absorbances of the blue species are all very small, the ϵ values being about 3 for both Ni_{aq}^{2+} and NiL^{2+} and zero for NiL_2^{2+}.[11] At the end of the absorbance measurements, the hydrogen ion concentrations of the solutions were determined. The pH change during reaction was found to be negligible and less than 0.03 unit in most cases. The rates of formation of the yellow complex were determined by plotting log $(A_\infty - A)$ *vs.* time. A typical example of such first-order plots is given in Figure 1. The first-order rate constant at constant pH, k_{obsd}, was obtained from the slope of the curve.

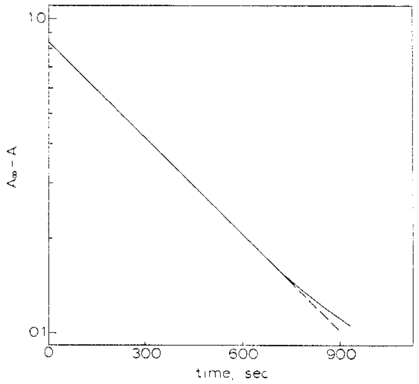

Figure 1.—First-order conversion of the blue, octahedral complex NiL^{2+} to the yellow, planar from $NiH_{-2}L$; $[NiL^{2+}]$ = 0.00395 *M* at t = 0 and $-\log [H^+]$ = 8.63, at 25.3° and μ = 1.0 adjusted with KCl.

Results

In applying the first-order rate expression $\log (A_\infty - A_t)/(A_\infty - A_0) = -k_{obsd}t/2.303$ to the observed absorbance–time data obtained at constant pH (Figure 1), it was assumed that the formation of NiL^{2+} from aquonickel ion and the ligand is much faster than the subsequent reaction of its conversion to the yellow form, so that all the nickel ion and the ligand exist

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(12) R. G. Wilkins, *J. Chem. Soc.*, 4521 (1957).

(13) D. W. Margerum, T. J. Bydalek, and J. J. Bishop, *J. Am. Chem. Soc.*, **83**, 1791 (1961).

(14) R. K. Murmann, *ibid.*, **84**, 1349 (1962).

(15) R. K. Murmann, *Inorg. Chem.*, **2**, 116 (1963).

(16) N. W. H. Ma, D. A. White, and R. B. Martin, *ibid.*, **6**, 1632 (1967).

(17) T. L. Cottrell and J. E. Gill, *J. Chem. Soc.*, 129 (1947).

(18) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd ed, Reinhold Publishing Corp., New York, N. Y., 1958, pp 483, 523, 578.

(19) K. S. Bai and A. E. Martell, *J. Inorg. Nucl. Chem.*, **31**, 1697 (1969).

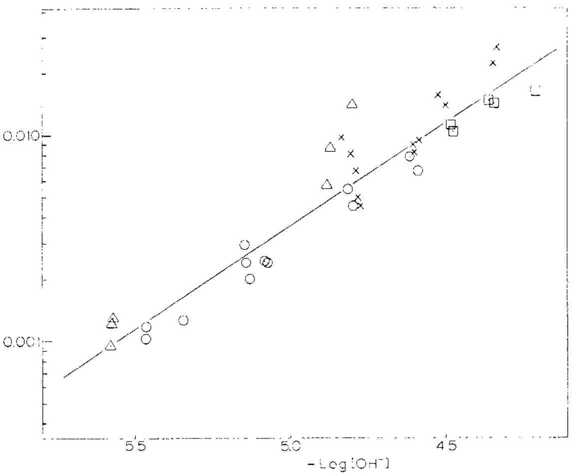

Figure 2.—Observed first-order rate constants as a function of pH. Buffers: ◬, borate; ⊙, morpholine; ⊡, trimethylamine, ×, from Table II.

as the blue octahedral complex NiL^{2+} at the onset ($t = 0$) of its conversion to the yellow complex. The validity of this assumption was qualitatively observed in earlier work.[11] The paramagnetic complexes of nickel(II) are generally labile,[20] and thus many of their reactions are quite rapid, although slower than those of the corresponding complexes of such other metals as copper(II) and zinc(II).[20] Eigen and Wilkins[21] listed a number of reactions of octahedral nickel(II) complexes and their rate constants, including some data for glycine–peptide complexes. These data show that the octahedral nickel(II) complexes are generally formed very rapidly when compared with the slow rates such as observed in the present work.

The linearity of the first-order plot in Figure 1 also indicates that the above assumption is valid. Thus

$$Ni_{aq}^{2+} + L \rightleftharpoons NiL^{2+} \xrightarrow{k_{obsd}} NiH_{-2}L + 2H^+ \qquad (1)$$

and the rate is given by

$$\frac{d[NiH_{-2}L]}{dt} = -\frac{d[NiL^{2+}]}{dt} = k_{obsd}[NiL^{2+}] \qquad (2)$$

where k_{obsd} is a function of the acidity of the solution. To determine the relationship between k_{obsd} and pH, the reactions were carried out at various pH values and the results are shown in Figure 2. In calculating the hydroxide ion concentrations from the measured hydrogen ion concentrations, the concentration constant of water at 1.0 M ionic strength ($pK_w = 13.77$) calculated from the data of Harned and Owen[18] was used.

Above pH about 9.7, the reaction is too fast to be followed by the conventional techniques employed in the present work. Below pH about 8.7 the reaction does not go to completion; the rate constants obtained below this pH are those calculated from initial parts of the reactions. No appreciable dependence of the rate on buffer concentration was observed. The relatively large deviation of the points obtained in borate buffer at higher pH may be due to variations of ionic strength resulting from the presence of polymeric forms of borate at the high concentrations employed. The linearity of the curve in Figure 2, which extends for about 1.5 pH units with a unit positive slope, indicates a rate law of the form

$$k_{obsd} = k[OH^-] \qquad (3)$$

where the second-order rate constant k is evaluated to be $3.3 \times 10^2\ sec^{-1}\ M^{-1}$.

The first-order dependence on hydroxide ion concentration of the overall rate of formation of the square-planar complex from the octahedral form, $d[NiH_{-2}L]/dt = k[OH^-][NiL^{2+}]$, indicates that abstraction of the first peptide hydrogen (eq 4) is rate determining and the second peptide hydrogen is released relatively rapidly (eq 5). The intermediate species, $NiH_{-1}L^+$, is therefore concluded to be unstable and readily converted to the final product, $NiH_{-2}L$. This conclusion is consistent with the previous observation in equilibrium studies[11] that $NiH_{-1}L^+$ does not exist in appreciable concentrations.

$$NiL^{2+} + OH^- \xrightarrow{k} NiH_{-1}L + H_2O \qquad (4)$$

$$NiH_{-1}L^+ + OH^- \xrightarrow{fast} NiH_{-2}L + H_2O \qquad (5)$$

According to eq 1 and 2, the rate equation for constant pH may also be expressed as $d[NiH_{-2}L]/dt = k_{obsd}K_1[Ni^{2+}][L]$. Thus, at constant pH, the reaction should be first order in both the metal ion and the ligand. The metal:ligand ratio was varied (because of the possibility of formation of nickel hydroxide, the concentration of the metal ion must not be greater than that of the ligand). Under the conditions of excess ligand, however, NiL_2^{2+} is also present in the reaction system (see Table I). By measuring the initial reaction rates at different initial concentrations of the reactants, the values of k_{obsd} were calculated from the equilibrium concentrations of all species present and eq 2. The values of k_{obsd} so calculated did not fall along the line in Figure 2 but were all much above the line. This suggests that NiL_2^{2+} also may be a reactant undergoing the transition reaction. The reaction rate is therefore expressed by

$$\frac{d[NiH_{-2}L]}{dt} = -\left[\frac{d[NiL^{2+}]}{dt} + \frac{d[NiL_2^{2+}]}{dt}\right] = k_{obsd}[NiL^{2+}] + k'_{obsd}[NiL_2^{2+}] \qquad (6)$$

Using the molar absorbance of $NiH_{-2}L$, the data in Table I, the initial concentrations of the reactants, the pH, and the absorbance values of the absorbance–time curves, the concentrations of all species were calculated at all points on the latter curve. It was found that, under the present experimental conditions, the concentrations of free nickel ion were always negligible (less than 0.1% of total nickel). Therefore, decrease in total concentration of the blue complexes

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(20) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley and Sons, New York, N. Y., 1967, p 145.

(21) M. Eigen and R. G. Wilkins in "Mechanisms of Inorganic Reactions," Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965.

was always equal to increase in the yellow complex, which gives eq 6. This equation rearranges to

$$\frac{\mathrm{d}A/\mathrm{d}t}{\epsilon l[\mathrm{NiL}^{2+}]} = k_{\mathrm{obsd}} + k'_{\mathrm{obsd}}K_2[\mathrm{L}] \qquad (7)$$

where ϵ is the molar absorbance and l is the length of the light path. The values of $\mathrm{d}A/\mathrm{d}t$ were estimated from the slopes of the absorbance–time curves, and the concentrations were calculated as mentioned above. The two first-order rate constants, k_{obsd} and k'_{obsd}, were then obtained from eq 7. These rate constants are given in Table II.

The values of k_{obsd} in Table II are also shown in Figure 2, where it is seen that these points now fall along the line obtained previously from systems containing only NiL^{2+} as the reactant. By plotting the values of k'_{obsd} against log $[\mathrm{OH}^-]$, the rate constant for the reaction of $\mathrm{NiL_2}^{2+}$ with hydroxide ion was estimated to be $k' = 2.5 \times 10^2$ sec^{-1} M^{-1}. The complete rate equation is therefore

$$\frac{\mathrm{d}[\mathrm{NiH_{-2}L}]}{\mathrm{d}t} = k[\mathrm{OH}^-][\mathrm{NiL}^{2}]^{+} + k'[\mathrm{OH}^-][\mathrm{NiL_2}^{2+}] \qquad (8)$$

TABLE II
FIRST-ORDER RATE CONSTANTS OBTAINED WITH VARYING METAL:LIGAND RATIOS[a]

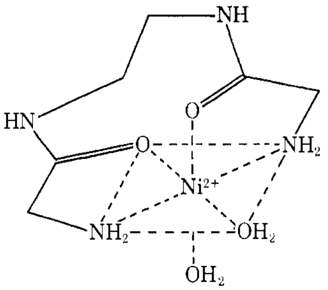
No.	T_{M}, M	T_{L}, M	$-$Log $[\mathrm{H}^+]$	k_{obsd}, sec^{-1}	k'_{obsd}, sec^{-1}
1	0.00395	0.01148	8.97	0.0080	0.0057
2	0.00616	0.01255	8.94	0.0098	0.0040
3	0.00395	0.01148	8.99	0.0048	0.0042
4	0.00308	0.01255	9.00	0.0045	0.0037
5	0.00303	0.01233	9.19	0.0093	0.0072
6	0.00606	0.01233	9.17	0.0080	0.0050
7	0.00395	0.00847	8.99	0.0067	0.0032
8	0.00395	0.01148	9.17	0.0088	0.0065
9	0.00616	0.01255	9.25	0.0160	0.0087
10	0.00395	0.00847	9.27	0.0140	0.0095
11	0.00395	0.00847	9.44	0.0270	0.0140
12	0.00395	0.01148	9.43	0.0220	0.0160

[a] At 25.3° and $\mu = 1.0$ with KCl. T_{M} and T_{L} represent the total concentrations of nickel and the ligand, respectively. Numbers 1 and 2 are from borate buffers, 3–8 from morpholine buffers, and 9–12 from trimethylamine buffers.

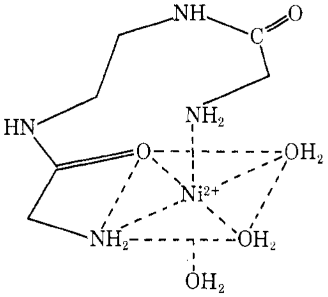
Discussion

Although the overall stoichiometric reaction requires 2 mol of hydroxide ions/mol of the blue complexes, only one of them is involved in the rate-determining step. The attack of the first hydroxide ion on one of the two peptide groups is slow and the reaction of a second hydroxide ion with the second peptide group is fast.

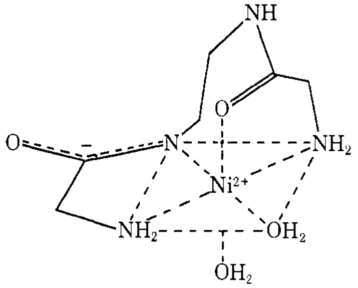
The coordinate bonding arrangement in which both amino and carbonyl oxygen atoms are bound, with the pairs of donors bridged with an improbable, *i.e.*, weak nine-membered, ring is believed to be similar to that suggested (Ia). The first hydrogen ion that is released must come from the coordinated peptide groups because in the absence of nickel ion the peptide hydrogens are not dissociated even at very high pH. The electron withdrawal of the positive nickel ion from the coordinated oxygen of I would polarize the H–N bond of the peptide, thus facilitating its cleavage by the hydroxide ion. As has been observed for a similar Cu(II)-promoted displacement of an amide proton in triglycine,[22] the proton may be released before or after rearrangement to nitrogen coordination, as illustrated by arrangement of donor groups on the left side of II.



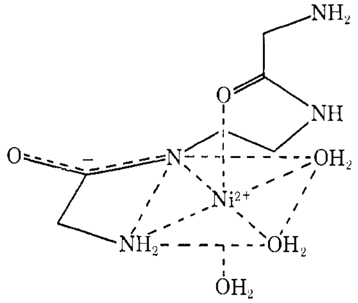
Ia, NiL^{2+} (tetradentate)



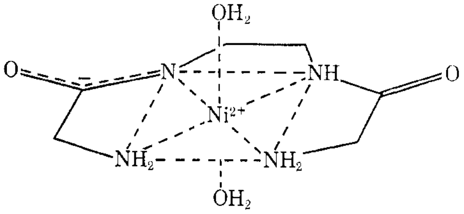
Ib, NiL^{2+} (terdentate)



IIa, $\mathrm{NiH_{-1}L}^+$ (tetradentate)



IIb, $\mathrm{NiH_{-1}L}^+$ (terdentate)



IIc, $\mathrm{NiH_{-1}L}^+$ (unstable intermediate)

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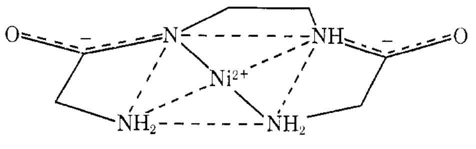
(22) G. K. Pagenkopf and D. W. Margerum, *J. Am. Chem. Soc.*, **90**, 6963 968).

If rearrangement occurs prior to deprotonation, to give a form of I analogous to II, the intermediate would be highly unstable relative to I (*i.e.*, it would have a very low probability of formation), but subsequent deprotonation would be extremely rapid. It is conceivable that deprotonation of I could take place prior to rearrangement, through the catalytic effect of the metal ion, with subsequent shift of the coordinate bond from carbonyl oxygen to carbonyl nitrogen, to give II. These two alternative sequences cannot, with the data available, be distinguished from each other, or from a concerted reaction involving simultaneous rearrangement and deprotonation. Since these processes are currently indistinguishable, the concerted reaction is proposed as a working hypothesis.

The analogous reaction of peptide proton dissociation in copper(II)–triglycine is very fast although the rate is slower than normal acid–base reactions.[22] It was proposed that the rearrangement of the coordinate bond from oxygen to nitrogen (neutral or negative), not proton transfer (subsequent or prior), is the rate-determining step in this case. Any difference in the strengths of the metal–peptide oxygen bonds (or metal–neutral nitrogen bonds) for copper(II) and nickel(II) would not be very significant because both bonds are very weak. The rearrangement of the coordinate bond and the dissociation of the peptide protons in NiL^{2+} are expected to take place at roughly the same rates as those for the analogous copper(II)–triglycine complex (CuL^+).

In any case the partially rearranged, probably distorted octahedral intermediate, II, would have its second (protonated) amide group favorably oriented for the subsequent rearrangement–deprotonation step, since it would be directed around the perimeter of the developing square-planar coordination sphere of the metal ion because of the trigonal nature of the negative coordinated nitrogen atom. Formula IIb shows a configuration in which the second nitrogen is favorably disposed for deprotonation and coordination. Other conformations are of course possible, but would probably not differ very much in energy. If these structures resemble the reaction intermediates, it would not be surprising to find the second deprotonation and N-coordination step to give the final product III, more rapid than the reaction from I to II, as is observed.



III, $NiH_{-2}L$ (planar)

The fact that the 2:1 complex NiL_2^{2+} is also a reactant indicates that the second coordinated ligand molecule is released after the rate-determining step. The fact that k' (assigned to NiL_2^{2+}) is smaller than k indicates that the reaction of the 2:1 complex with OH^- takes place less readily than does the 1:1 complex, reflecting the stronger catalytic effect of the metal ion on the ligand in the 1:1 complex. The electronic interaction between metal ion and ligand would be expected to be less when the interaction takes place with two ligands rather than one. This effect is sufficient to more than overbalance the statistical effect of the two ligand molecules, which acting alone would make k' larger than k.

The fact that displacement of the first peptide proton is slow and that of the second is fast is in accord with the results of the equilibrium studies previously reported,[11] which indicated the absence of sufficient amounts of the intermediate $NiH_{-1}L^+$ to be detected by potentiometric measurement of hydrogen ion concentration or by spectral measurement. While the failure to obtain an equilibrium constant for this intermediate is not proof of its complete absence, it is estimated that its maximum concentration could not be much greater than 1% of the total metal chelate species present. Thus the equilibrium studies provide an independent indication that the first deprotonation is much slower than the second. These results are similar to those reported[4,10] for the nickel(II)–polyglycine complexes (tri- and tetraglycine), wherein all peptide protons seem to be displaced simultaneously.[23] The lack of appreciable concentrations of partially deprotonated nickel(II)–peptide complexes contrasts the behavior of the corresponding Cu(II) complexes, which have been shown[7,11] to form in a stepwise fashion. On this basis it would be expected that the rate of formation of the approximately planar diamagnetic, yellow, fully deprotonated Ni(II) complexes, $NiH_{-n}L$, of tri- and tetraglycine would also be first order in hydroxide ion concentration.

It is of interest to consider possible structures of the blue Ni(II) complexes initially formed and the intermediates that must be formed, though probably at quite low concentrations, in the course of conversion to the final fully deprotonated product. For the initial complex, NiL^{2+}, an octahedral structure is suggested for which Ia illustrates one of several possible arrangements of donor groups. While Ib allows a regular or nearly regular arrangement of donor atoms about the metal ion, one of the carbonyl oxygens is not coordinated, and there is a very large chelate ring. Other arrangements such as Ia are possible and perhaps more probable, with both carbonyl oxygens and both amino nitrogens coordinated, although the octahedral arrangement would be somewhat distorted.

It may be seen that the reversal of the position of the coordinated amide group in going from I to II, with the loss of a proton, directs the remaining less strongly coordinated portion of the ligand closer to some of the remaining coordination sites of Ni(II), thus making carbonyl oxygen coordination somewhat easier.

[23] Note Added in Proof.—Recent further potentiometric and magnetic equilibrium studies of the Ni(II)–triglycine system (A. Kaneda and A. E. Martell, to be published) demonstrate the formation of a small amount of $NiH_{-1}L$ in the conversion of NiL^+ to $NiH_{-2}L^-$. The amount of the intermediate formed is, however, many times less than the amount predicted on purely statistical grounds.

If this happens, however, in such a manner that the second amino group is also coordinated as in IIa, the amide nitrogen would be directed away from the position to which it eventually becomes coordinated. Thus IIa is the more stable intermediate that must rearrange to IIb before the next deprotonation and coordination change to negative amide nitrogen can occur. In spite of these complications, the step II to III is faster than I to II.

It is interesting that none of the more stable intermediates IIa and IIb resembles the planar structure indicated by III. A tetragonal structure, with two water molecules spaced above and below the plane somewhat farther away than the other four donors, is also possible. The fact that the second step is faster than the first is probably the result of the fact that the negative amide nitrogen atom that is first to be deprotonated holds the remaining donor groups of the ligand in a position that allows a fairly close average approach to the coordination sphere of the metal ion. Thus it is seen that the steric arrangement of the first two strongly coordinated groups in $NiH_{-1}L^+$ increases the probability of the formation of the conformer IIc, which may be considered the immediate precursor for the second deprotonation step. This is not the situation in the conversion of I to II, however, since the carbonyl oxygen is coordinated in a five-membered ring that includes a strongly coordinated partner. Thus it seems that the relative rates of the successive deprotonation reactions may be logically related to the probable structures of the complexes present in solution, and the more rapid rate of the second deprotonation reaction seems quite reasonable.

Finally, it is seen that the rate of the second deprotonation of the 2:1 complex NiL_2^{2+} to give $NiH_{-2}L$ would not be as rapid as for the 1:1 complex, since dissociation of the second ligand would be necessary before IIc could be formed. On this basis, therefore, one might expect higher concentrations of intermediates such as $Ni(H_{-1}L)L^+$ in both equilibrium and kinetic systems containing amide (and peptide) donor groups. In the presence of excess ligand, therefore, the conversion to III may easily occur in two steps, with partially deprotonated 2:1 complexes as intermediates.

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A New Synthetic Route to Macrocyclic Nickel(II) Complexes with Uninegative, Schiff-Base Ligands

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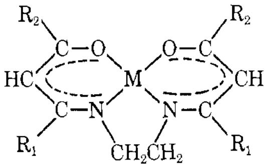
Two series of nickel(II) complexes containing uninegative, macrocyclic Schiff-base ligands have been prepared *via* simple condensation reactions. Characterization of the new compounds Ni(AT)X and Ni(TAT)X, where AT is 11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-10,12-diene, TAT is 11-methyl-13-(trifluoromethyl)-1,4,7,10-tetraazacyclotrideca-10,12-diene, and X^- is Br^-, I^-, SCN^-, NO_3^-, BF_4^-, or PF_6^-, is discussed. Derivatives of Ni(AT)X and Ni(TAT)X are the first macrocyclic metal complexes to be synthesized by reaction of both oxygen atoms of a β-diketone (enol form) with both terminal $-NH_2$ groups of a polyamine. The cyclization reaction is predominant, even in the preparation of Ni(TAT)X complexes, where it requires condensation at a carbonyl oxygen atom adjacent to a normally deactivating trifluoromethyl group.

Introduction

The condensation of amines with β-diketones and β-keto aldehydes to form β-keto amines and the use of β-keto amines as ligands in the preparation of metal complexes are well known. A review[2] of work in this area shows that many investigations have been concerned with the formation and structure of tetradentate metal complexes (I) derived from various diamines and β-diketones.



I

The effect of trifluoromethyl groups at positions R_1 and R_2 on directing the course of the Schiff-base condensation and the normal bis(keto amine) stoichiometry of the ligands should be mentioned, as they are particularly relevant to the work presented here.

Dipole moment studies on the condensation products of trifluoroacetylacetone with diamines[3,4] and the resulting metal complexes[5,6] have shown that condensa-

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(2) R. H. Holm, G. W. Everett, Jr., and A. Chakravorty, *Progr. Inorg. Chem.*, **7**, 83 (1966).

(3) D. J. McCarthy and A. E. Martell, *J. Am. Chem. Soc.*, **78**, 264 (1956).

(4) R. J. Hovey and A. E. Martell, *ibid.*, **82**, 364 (1960).

(5) R. J. Hovey and A. E. Martell, *ibid.*, **82**, 2697 (1960).

(6) P. J. McCarthy and A. E. Martell, *ibid.*, **78**, 3106 (1956).