

Notes

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Proton-Transfer Reactions of Cyano(glycylglycylglycinato)nickelate(II) and Cyano(glycylglycinamido)nickelate(II)

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Nickel(II) and copper(II) facilitate the ionization of amide protons upon complexation with short-chain polypeptides^{1,2} resulting in square-planar complexes which, in the case of nickel, are spin paired. Studies of proton-transfer reactions of these complexes³⁻⁹ have shown that some reactions are subject to general acid catalysis³⁻⁵ whereas others⁶ only react with H_3O^+ . A general mechanism has been proposed to account for the different reactivity patterns.⁶

Nickel(II) triglycine ($NiH_2\text{-}2glyglygly^-$) and nickel(II) diglycinamide ($NiH_2\text{-}2glygla^-$) form 1:1 mixed complexes with cyanide ion.^{10,11} These complexes are square planar with polypeptide nitrogens occupying three of the coordination sites and cyanide occupying the fourth.

In this paper we report the kinetics of proton transfer to $NiH_2\text{-}2glyglyglyCN^{2-}$ and $NiH_2\text{-}2glyglaCN^-$. The rates of these reactions are considerably slower than the corresponding reactions with $NiH_2\text{-}2glyglygly^-$ and $NiH_2\text{-}2glygla^-$ indicating kinetic stabilization of the complex by CN^- ion.

Experimental Section

Reagents. Nickel(II) perchlorate stock solution was prepared from the twice recrystallized salt. The solution was standardized by EDTA titration using murexide indicator. Solutions of triglycine and diglycinamide were prepared from the chromatographically pure solid (Mann Research Laboratories, New York, N.Y., and Fox Chemical Co., Los Angeles, Calif.). These solutions were used shortly after preparation. Ionic strength was maintained with sodium perchlorate. Acetate, phosphate, malonate, and tris(hydroxymethyl)aminomethane buffers were prepared from the recrystallized salts. The desired pH for each buffer was obtained through the addition of sodium hydroxide or perchloric acid. Sodium cyanide was prepared from the twice recrystallized salt and standardized by the argentimetric method.

The nickel(II) complexes were prepared fresh for each series of kinetic measurements. The procedure for preparation of the complexes involved the mixing of nickel(II) and polypeptide solutions so there was at least a 100% excess of ligand. The pH of the resulting solution was slowly adjusted to about 10. At this pH the amide protons are ionized. A stoichiometric amount of sodium cyanide was then added. In the case of triglycine the mixed complex $NiH_2\text{-}2glyglyglyCN^{2-}$ formed instantaneously. For diglycinamide, however, complete formation required about 1 hr, depending upon how much excess diglycinamide was present. The absorption maxima and molar absorptivities for $NiH_2\text{-}2glyglyglyCN^{2-}$ are λ_{max} 410 nm and ϵ 174 $M^{-1} cm^{-1}$ and for $NiH_2\text{-}2glyglaCN^-$ they are λ_{max} 405 nm and ϵ 170 $M^{-1} cm^{-1}$. The pK_a values for the mixed complexes appear comparable to the parent complexes. The complexes are completely formed at the concentration levels utilized in these experiments. The pH values were converted to $-\log [H^+]$ by subtracting 0.10.¹²

Kinetic Measurements. The proton-transfer reactions were initiated by pH jump. A typical kinetic run involved the rapid addition (by syringe) of 0.5–1.0 ml of buffer to 50.0 ml of nickel complex solution of pH 10. The nickel complex concentrations were $7 \times 10^{-6} M$, $\mu = 0.10 F$ ($NaClO_4$). Buffer solutions were fairly concentrated, $\sim 1.0 F$, in order to have sufficient buffer capacity to maintain a constant pH throughout the reaction. Buffer concentrations in the reaction solution ranged from 0.005 to 0.05 F . Upon addition of the buffer

Table I. Observed Rate Constants for Decomposition of $NiH_2\text{-}2glyglyglyCN^{2-}$ and $NiH_2\text{-}2glyglaCN^-$ Complexes

$NiH_2\text{-}2glyglaCN^-$			$NiH_2\text{-}2glyglyglyCN^{2-}$		
$-\log [H^+]$	$10^4 k_{obsd}, sec^{-1}$	Buffer ^a	$-\log [H^+]$	$10^3 k_{obsd}, sec^{-1}$	Buffer ^a
5.05	380	Ac	5.01	68.5	Ac
5.65	97.5	M	5.61	21.6	Ac
6.17	28.2	M	6.20	7.15	M
6.33	21.5	M	6.81	3.66	M
6.94	4.85 ^b	P	7.99	2.76	T
7.07	5.78	M	8.34	3.36	T
8.02 ^c	2.30	T	8.41 ^c	2.83	T
8.18	1.27	T			
8.35 ^c	0.92	T			
8.42 ^c	0.96	T			
8.52 ^c	1.03	T			

^a Ac = acetate, M = malonate, P = phosphate, T = tris(hydroxymethyl)aminomethane. ^b Rate constant obtained by extrapolating phosphate concentration to zero. ^c EDTA concentration $10^{-4} M$, $T = 25.0^\circ$, $\mu = 0.10 F$ ($NaClO_4$).

Table II. Rate Constants for the Decomposition of Selected Nickel-Peptide Complexes

Complex	k_d, sec^{-1}	$k_H, M^{-1} sec^{-1}$	Ref
$NiH_2\text{-}2glyglyglyCN^{2-}$	2.7×10^{-3}	6.9×10^3	This work
$NiH_2\text{-}2glyglaCN^-$	8.0×10^{-5}	4.3×10^3	This work
$NiH_2\text{-}2glyglygly^-$	5.0×10^{-2}	2.0×10^5	3
$NiH_2\text{-}2glyglygly^{2-}$	1.6×10^{-5}	7.1×10^4	6
$NiH_2\text{-}2glygla^-$		3.3×10^4	6

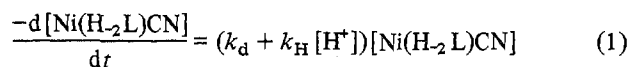
the pH of the reaction solution changed to that of the buffer and remained constant throughout the reaction. The reactions were independent of buffer concentration except for phosphate.

The decay of the complexes was monitored spectrophotometrically at 246 nm for $NiH_2\text{-}2glyglaCN^-$ and 245 nm for $NiH_2\text{-}2glyglyglyCN^{2-}$. Both complexes exhibit absorption maxima at these wavelengths. All reactions obeyed pseudo-first-order kinetics. Rate constants were calculated from the plots of $\ln(A - A_\infty)$ vs. time. Each reported rate constant is the average of at least two kinetic runs.

EDTA was used to scavenge the reactions at the higher pH values. In all cases the rate was independent of EDTA concentrations. The reactions also exhibited no dependence upon bicarbonate, oxygen, or buffer concentration except phosphate. In some cases a slight increase in rate was observed when a higher concentration of buffer has to be used to maintain constant $-\log [H^+]$. This influence is believed due to an increase in ionic strength.

Results

The decomposition of $NiH_2\text{-}2glyglyglyCN^{2-}$ and $NiH_2\text{-}2glyglaCN^-$ was studied at a number of $-\log [H^+]$ values. The observed pseudo-first-order rate constants are listed in Table I and a plot of $\log k_{obsd}$ vs. $-\log [H^+]$ is shown in Figure 1. A rate equation consistent with the observed kinetics and pH profile is shown in eq 1, where L is triglycine (glyglygly)



or diglycinamide (glygla); charges are omitted. Reactions that are consistent with the observed pH dependence are shown in eq 2 and 3. The observed pseudo-first-order rate constant



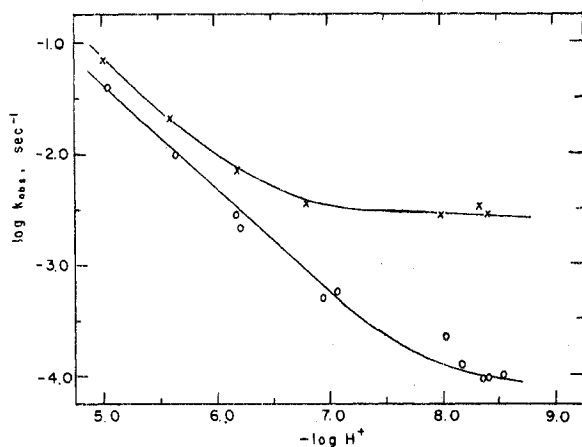


Figure 1. Decomposition rate for $\text{NiH-2glyglyglyCN}^{2-}$ and NiH-2glyglylaCN^- at different hydrogen ion concentrations ($T = 25.0^\circ$, $\mu = 0.10$ F (NaClO_4)): X, $\text{NiH-2glyglyglyCN}^{2-}$; o, NiH-2glyglylaCN^- .

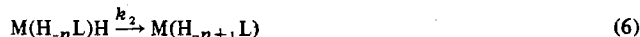
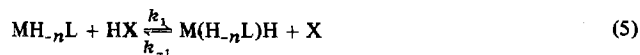
is the sum of the two terms shown in eq 4. The solid lines

$$k_{\text{obsd}} = k_d + k_H[\text{H}^+] \quad (4)$$

in Figure 1 are calculated using the rate constants listed in Table II. Two-term rate equations have been observed for other similar systems.³

Discussion

The transfer of protons to deprotonated nickel-polypeptide complexes can be general acid or specific hydrogen ion catalyzed.^{3,6} A general mechanism (eq 5 and 6) has been



proposed to account for the different reactivity patterns.⁶

Two cases are particularly applicable to the kinetics observed in this study. Under conditions where the concentration of the intermediate, $\text{M}(\text{H}_n\text{L})\text{H}$, is small and $k_2 \gg k_{-1}[\text{X}]$, general acid catalysis will be observed. This fits the kinetic data observed for NiH-2glyglygly^- and CuH-2glyglygly^- . The other case also has negligible intermediate concentrations; however, $k_2 \ll k_{-1}[\text{X}]$. This fits the data for $\text{NiH-3glyglygly}^{2-}$ and NiH-3glyglyla^- over a wide pH range.

When cyanide ion adds to NiH-2glyglygly^- , it probably replaces the bound carboxylate group. Cyanide coordination generates a stronger ligand field which results in increased stability of the intermediate $\text{Ni}(\text{H-2glyglyglyCN})\text{H}$ and a change in the relative magnitude of $k_{-1}[\text{X}]$ and k_2 . With $k_{-1}[\text{X}] \gg k_2$ the system becomes specific hydrogen ion catalyzed and in essence involves preequilibrium followed by Ni-N(amide) bond breakage. This fits the data from pH 5 to pH 9, Figure 1. The rate constant k_H from eq 3 is equal to K_1k_2 as defined in eq 5 and 6. Both systems, $\text{NiH-2glyglyglyCN}^{2-}$ and NiH-2glyglylaCN^- , are interpreted in the same manner. One would predict a loss of hydrogen ion dependence at low pH values. As the hydrogen ion concentration increases, the concentration of the intermediate will become an ever-increasing fraction of nickel total. When complete conversion has occurred, $k_{\text{obsd}} = k_2$. Rapid-mixing techniques are required to verify this prediction.

Table II lists the rate for the mixed cyanide complexes and other similar complexes. The stabilization imparted by cyanide coordination is sizable as reflected by the decrease in the respective rate constants. Cyanide is more effective than the addition of another gly residue in decreasing the rate. It is

somewhat surprising that k_d for $\text{NiH-2glyglyglyCN}^{2-}$ is not smaller.

An alternate mechanism to the one presented here is the dissociation of CN^- followed by subsequent reaction with hydrogen ion or dissociation to form products. With this mechanism the rate reduction is due to the fact that a small fraction of the nickel is present as reactant. There are three points that can be made to discount this mechanism. (1) The reactions obey pseudo-first-order kinetics. During the course of reaction cyanide concentration is changing; thus if it is factor in the rate equation, one probably would not observe first-order dependence. (2) Considering the triglycine system, the same percentage decrease should be observed in k_H and k_d as one goes from NiH-2glyglygly^- to $\text{NiH-2glyglyglyCN}^{2-}$ since both will be dependent upon the fraction of nickel present as the mixed triglycine-cyanide complex. The decrease in k_H is a factor of 29 and in k_d is a factor of 18.5. These are probably different within experimental error. (3) Triethylenetetramine (trien) reacts with $\text{NiH-2glyglyglyCN}^{2-}$ through a two-path mechanism.¹³ One of these paths is trien independent and has a rate constant of $2.3 \times 10^{-3} \text{ sec}^{-1}$, very similar in magnitude to k_d for the triglycine-cyanide system. These three points taken by themselves are not sufficient to reject the predissociation mechanism; however, together they provide good evidence that the cyanide mixed complexes are the reactive species.

Registry No. NiH-2glyglylaCN^- , 53290-91-8; $\text{NiH-2glyglyglyCN}^{2-}$, 51194-58-2.

References and Notes

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On the Base Strengths of (ω -Methoxyalkyl)trichloro- and (ω -Methoxyalkyl)trimethylsilanes

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Infrared base strength measurements have been used to determine the proton affinity of such donor atoms as oxygen,¹⁻⁷ nitrogen,⁷⁻¹² and sulfur⁷ which are bound directly to group 4 metal atoms. These results are among the studies which have indicated that the properties of some organosilicon compounds are affected in a manner which is not evident in the carbon analogs.¹³ One such effect may be an interaction between the vacant 3d orbitals of silicon and a lone pair of electrons on a directly bonded donor atom,¹³ hyperconjugation ($\sigma-\pi$