value of 54.1° found in TiS_2. Comparison of curves a and b shows that electron filling of the t_{2g} subbands decreases the θ value slightly, which is a reflection of the fact that the bottom portion of the t_{2g} subbands is low in energy for small θ (see Figures 1 and 2). Consequently, electron filling of the t_{2g} subbands itself cannot be responsible for the Ib → Ia phase transition, so that the cause for this transition must be associated with ionic interactions of Na^+ cations with sulfur layers of TiS_2 slabs. It is worth noting that no phase transition such as Ib → Ia is present in intercalation of TiS_2 with alkali metal atoms other than sodium.[1,2b,10]

Concluding Remarks

It is often assumed that intercalation of a layer compound does not modify slabs of the host. That this is not necessarily the case was strongly suggested by the work of Molinie et al.[2h] on Na_xTiS_2. The present study shows that the abrupt change in the ^{23}Na Knight shifts at the boundary of phases Ib and Ia is due primarily to the flattening of a TiS_2 slab beyond the critical a_{cr} value of 3.50 Å. (Note that the larger the a value, the more flattened is a TiS_2 slab.) This structural change brings about an abrupt increase not only in $n(e_f)$ but also in the anisotropy of electron distribution around Ti^{4+}. Can we expect such a drastic change in electronic structure for other alkali-metal intercalations in TiS_2? In the first-stage compound of various A_xTiS_2 (A = Li, K, Rb, Cs), the a value is found to increase gradually with x.[10] However, in none of those systems, does the maximum a value exceed the critical value a_{cr} = 3.50 Å. Therefore an abrupt change in band electronic structure such as the one observed for the Ib → Ia phase transition in Na_xTiS_2 is not expected for other alkali-metal intercalations in TiS_2.

In the present study we have considered only ideal stoichiometric TiS_2, but nonstoichiometric situations arise in the form of $Ti_{1+y}S_2$ (usually $y \simeq 0.005$). This nonstoichiometry would lead to slightly populated d-block bands in the absence of sodium intercalation, which might slightly change the phase boundaries of Na_xTiS_2 but not the conclusions of the present study.

Acknowledgment. This work was in part supported by the Camille and Henry Dreyfus Foundation through a Teacher-Scholar Award to M.-H.W.

Registry No. TiS_2, 12039-13-3; sodium titanium sulfide, 12624-30-5.

---

(10) Bichon, J.; Danot, M.; Rouxel, J. *C. R. Seances Acad. Sci., Ser. C* **1973**, *276*, 1283.
(11) Ammeter, J. H.; Bürgi, H.-B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686.
(12) Richardson, J. W.; Nieuwpoort, W. C.; Powell, R. R.; Edgell, W. E. *J. Chem. Phys.* **1962**, *36*, 1057.

Contribution from the Department of Chemistry,
Montana State University, Bozeman, Montana 59717-0001

Reaction of Triethylenetetramine with Nickel(II) *N*,*N*′-Diglycylethylenediamine

JON P. STORVICK and GORDON K. PAGENKOPF*

Received June 30, 1983

The reaction of triethylenetetramine with nickel(II) *N*,*N*′-diglycylethylenediamine, $NiH_{-2}DGEN$, proceeds through $trien_t$-dependent and -independent pathways. The rate constants for the trien species cannot be resolved, but their ratios are $k_{HT}/k_T = 0.63$ and $k_{H_2T}/k_T = 0.046$. The rate constant for the dissociation of a terminal amine group from nickel(II) is 0.08 s^{-1}. The reaction is specific hydrogen ion dependent with a rate constant $k_{H_3O} = 8.5 \times 10^3\ M^{-1}\ s^{-1}$.

Complexation of short-chain polypeptides by nickel(II) enhances the acidity of the amide protons, and as a consequence many nickel(II) complexes have been prepared in water solution that are of square-planar configuration with coordinated imide groups.[1–6] *N*,*N*′-Diglycylethylenediamine (DGEN) forms a complex of this configuration provided the pH of the solution is 8 or greater.[6] Coordination of DGEN to nickel is through the two terminal amine groups and through the two deprotonated amide nitrogens.

The transfer of Ni(II) and Cu(II) from short-chain polypeptide complexes to other multidentate ligands such as ethylenediaminetetraacetate may proceed through a variety of pathways.[7–9] These routes include solvent assisted, direct replacement, and proton-transfer limited that may or may not be general-acid catalyzed. The variation in reactivity patterns is dependent upon steric interactions within the substrate complex and the replacing ligand in addition to the relative lability of the leaving groups.[10,11]

This study involves the transfer of Ni(II) from *N*,*N*′-diglycylethylenediamine to triethylenetetramine (trien). The reaction proceeds through $trien_t$-dependent and -independent pathways. The $trien_t$ dependence is not the same as that observed in other systems.

Experimental Section

Diglycylethylenediamine was synthesized by the method of Gill and Cottrell;[12] the melting point of the dihydrochloride salt was 246 °C. A stock nickel solution, 0.0991 M, was prepared from twice-recrystallized $Ni(ClO_4)_2$ and standardized by EDTA titration. Ionic strength was maintained at 0.10 M with $NaClO_4$. Sodium borate was used to maintain constant pH, and the pH values were converted to hydrogen ion concentration with the extended Debye–Hückel relationship.

Solutions of $NiH_{-2}DGEN$ were prepared by dissolving an analytically weighed portion of DGEN in water followed by addition of an aliquot of Ni(II) stock solution. The solution was bubbled with nitrogen to remove dissolved oxygen before the pH was slowly adjusted to a value greater than 9. The solutions were always prepared fresh and kept under nitrogen. A 50% excess of DGEN was maintained.

Triethylenetetramine solutions were prepared from the recrystallized disulfate salt. Standardization was achieved spectrophotometrically, using Cu(II) at pH 4.8 (acetate buffer). These solutions were also kept

---

(1) Bai, K. S.; Martell, A. E. *J. Am. Chem. Soc.* **1969**, *91*, 4412.
(2) Bai, K. S.; Martell, A. E. *Inorg. Chem.* **1970**, *9*, 1126.
(3) Martin, R. B.; Chamberlain, M.; Edsall, J. T. *J. Am. Chem. Soc.* **1960**, *82*, 495.
(4) Kim, M. K.; Martell, A. E. *J. Am. Chem. Soc.* **1967**, *89*, 5138.
(5) Billo, E. J.; Margerum, D. W. *J. Am. Chem. Soc.* **1970**, *92*, 6811.
(6) Pearson, R.; Pagenkopf, G. K. *Inorg. Chem.* **1978**, *17*, 1799.
(7) Pagenkopf, G. K.; Margerum, D. W. *J. Am. Chem. Soc.* **1968**, *90*, 6963.
(8) Paniago, E. B.; Margerum, D. W. *J. Am. Chem. Soc.* **1972**, *94*, 6704.
(9) Billo, E. J.; Smith, G. F.; Margerum, D. W. *J. Am. Chem. Soc.* **1971**, *93*, 2635.
(10) Pagenkopf, G. K.; Margerum, D. W. *J. Am. Chem. Soc.* **1970**, *92*, 2683.
(11) Hauer, H.; Dukes, G. R.; Margerum, D. W. *J. Am. Chem. Soc.* **1973**, *95*, 3515.
(12) Cottrell, T. L.; Gill, J. E. *J. Chem. Soc.* **1947**, 129.

0020-1669/85/1324-1827$01.50/0

Table I. Concentrations and k_{obsd} for the Reaction of $trien_t$ with NiH_2DGEN

$10^4 \times [NiH_{-2}DGEN]_0$, M	pH	$10^3 \times [trien]_t$, M	10^3k_{obsd}, s^{-1}	10^3k_{obsd}(calcd), s^{-1}
6.00	3.45	15.2	4200 ± 410	3630
6.00	3.72	15.2	1810 ± 240	1960
6.00	4.07	15.2	886 ± 53	876
6.00	4.52	15.2	272 ± 27	310
6.00	4.95	15.2	92.5 ± 9.5	115
6.00	5.53	15.2	29.8 ± 2.6	31.3
5.71	5.80	14.4	16.7 + 0.8	16.5
5.71	6.04	14.4	11.3 + 0.8	16.5
5.71	6.04	14.4	11.3 + 0.6	9.82
5.71	6.32	14.4	6.45 + 0.20	5.47
6.61	6.57	8.98	3.39 ± 0.03	3.29
6.20	6.62	11.8	3.43 ± 0.10	3.10
5.66	6.67	15.4	3.48 ± 0.11	2.96
4.96	6.70	20.2	3.48 ± 0.07	2.98
6.34	7.85	8.86	1.07 ± 0.03	1.06
5.87		11.5	1.32 ± 0.05	1.29
5.29		14.8	1.53 ± 0.07	1.57
4.53		19.0	1.88 ± 0.05	1.92
6.90	8.45	5.78	1.41 ± 0.03	1.34
6.34		8.86	1.79 ± 0.07	1.88
5.87		11.5	2.32 ± 0.07	2.35
4.76		17.7	3.31 ± 0.08	3.43
7.21	8.94	4.03	2.10 ± 0.05	1.78
6.61		7.38	3.35 ± 0.07	2.99
6.10		10.2	3.98 ± 0.15	4.00
3.66		12.7	4.72 ± 0.09	4.88
6.61		3.88	1.68 ± 0.08	1.73
6.10		5.37	2.27 ± 0.15	2.27
5.66		6.64	2.73 ± 0.10	2.73
5.29		7.75	3.02 ± 0.04	3.13
6.90	9.35	6.07	4.20 ± 0.13	3.99
6.34		9.30	5.92 ± 0.41	5.89
5.87		12.1	7.17 ± 0.35	7.49
5.29		15.5	8.48 ± 0.48	9.40
5.15[a]		8.86	5.15	5.63
25.0		100	47.6 ± 3.6	45.1
25.0		150	58.8 ± 2.4	59.3
25.0		200	65.9 ± 8.1	70.3
25.0		250	79.7 ± 3.5	79.2
5.29	9.89	14.8	12.3 ± 1.1	13.3
5.87		11.5	10.6 ± 0.6	10.5
5.34		8.86	8.43 ± 0.14	8.31
6.90		5.78	5.47 ± 0.14	5.62

[a] Single run.

under nitrogen. The trien pK_a values used to resolve the rate constant ratios are $pK_{a(HT)} = 9.74$, $pK_{a(H_2T)} = 9.08$, and $pK_{a(H_3T)} = 6.56$.[13]

The reaction of $NiH_{-2}DGEN$ with $trien_t$ was monitored at 410 nm ($\epsilon = 220\ M^{-1}\ cm^{-1}$), using 5-cm cells and a Varian 634 spectrophotometer. A Durham stopped-flow spectrophotometer was used for the low-pH (<5.8) and high-$trien_t$ conditions. Temperature was maintained at 25.0 °C. Pseudo-first-order kinetics were observed when the $trien_t$ concentration was a factor of 10 greater than the Ni(II) concentration. The reported rate constants were obtained from least-squares fit to plots of $-\ln (A - A_\infty)$ vs. time and are the averages of at least three runs. Extrapolation of absorbance readings to zero time agreed with the expected values, and the reaction was not influenced by the addition of excess DGEN. The resolved rate constants were obtained by using nonlinear least-squares fitting.[14]

Results

The reaction of $NiH_{-2}DGEN$ with $trien_t$ was studied over the pH range of 3.45–9.89. When the $trien_t$ concentration is significantly greater than the $NiH_{-2}DGEN$ concentration, pseudo-first-order kinetics are observed in agreement with eq 1. As long

$$\text{rate} = -d[NiH_{-2}DGEN]/dt = k_{obsd}[NiH_{-2}DGEN] \quad (1)$$

as the pH is greater than approximately 7.7 an increase in the $trien_t$ concentration results in an increase in k_{obsd}. The increase is not linear however, with the dependence decreasing as the concentration increases. The data were summarized in Table I. A reaction sequence consistent with this observation is shown in eq 2 and 3. Application of the steady-state approximation to

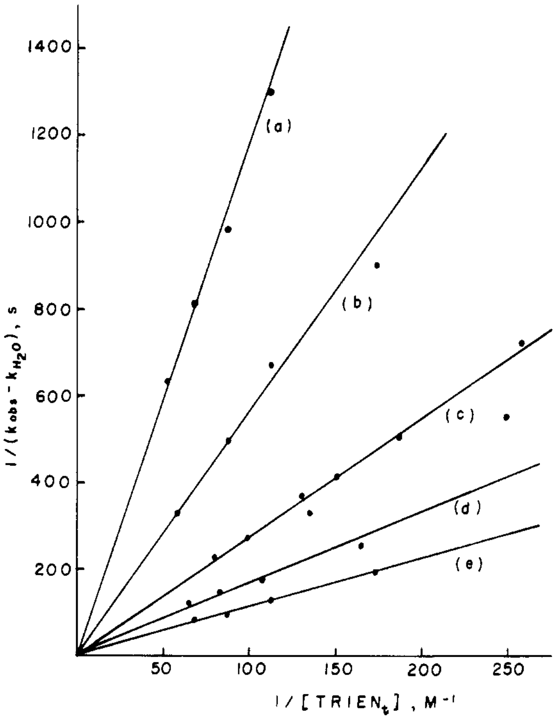


Figure 1. Verification of the relationship between the observed rate constant and the $trien_t$ concentration (eq 6): (a) pH 7.85; (b) pH 8.45; (c) pH 8.94; (d) pH 9.35; (e) pH 9.89.

$$NiH_{-2}DGEN \xrightarrow{k_{H_2O}} \text{products} \quad (2)$$

$$NiH_{-2}DGEN \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (NiH_{-2}DGEN)^* \xrightarrow[trien_t]{k_2} \text{products} \quad (3)$$

$(NiH_{-2}DGEN)^*$ provides the rate equation (4). The observed

$$\text{rate} = \frac{-d[NiH_{-2}DGEN]}{dt} = \left\{k_{H_2O} + \frac{k_1k_2[trien_t]}{k_{-1} + k_2[trien_t]}\right\}[NiH_{-2}DGEN] \quad (4)$$

rate constant under pseudo-first-order conditions is equal to (5)

$$k_{obsd} = k_{H_2O} + \frac{k_1k_2[trien_t]}{k_{-1} + k_2[trien_t]} \quad (5)$$

and rearrangement provides eq 6. A value of $k_{H_2O} = 2.1 \times 10^{-4}$

$$\frac{1}{(k_{obsd} - k_{H_2O})} = \frac{k_{-1}}{k_1k_2[trien_t]} + \frac{1}{k_1} \quad (6)$$

s^{-1} has been reported in a separate study.[6] This value was obtained from extrapolation, and for these studies a value of $3 \times 10^{-4}\ s^{-1}$ provides better agreement between the data and eq 6. A plot of $1/(k_{obsd} - k_{H_2O})$ vs. $1/[trien_t]$ is shown in Figure 1.

The intercept from Figure 1 is equal to 6.22 s, and thus $k_1 = 0.16\ s^{-1}$. As is evident by the data listed in Table I the reaction rate increases as the pH is increased from 7.7 to 9.8 and also increases as the pH decreases from 7.7 to 3.45. The increase in rate at the higher pH values indicates that the least protonated $trien_t$ species are the most reactive. The $trien_t$ dependent rate constant k_2 cannot be resolved into the contributions from the three $trien_t$ species present in this pH range since the slopes from Figure 1 provide k_{-1}/k_2. The relative values for trien, $Htrien^+$ and H_2trien^{2+} have been obtained from the ratios of the slopes in Figure 1; they are $k_{HT}/k_T = 0.63$ and $k_{H_2T}/k_T = 0.046$. These values

---

(13) Sillen, L. G.; Martell, A. E. *Spec. Publ.—Chem. Soc.* **1964**, *No. 17*; **1971**, *No. 25*.

(14) Howald, R. A. "LLJAC Program", Montana State University, private communication, 1983.

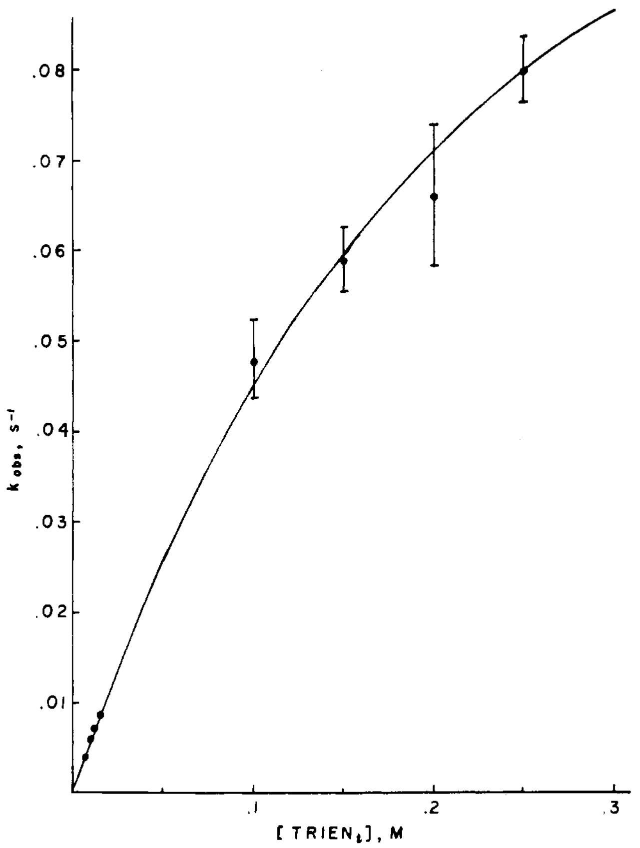


Figure 2. k_{obsd} vs. [trien$_t$] (pH 9.35). The solid line is predicted from the rate constants listed in Table II.

Table II. Rate Constants for the Reaction of trien$_t$ with $NiH_{-2}DGEN$

const	value
k_1	$0.16 \pm 0.02\ s^{-1}$
k_{-NH_2R}	$0.08 \pm 0.01\ s^{-1}$
k_{H_3O}	$(8.5 \pm 1.5) \times 10^3\ M^{-1}\ s^{-1}$
k_{H_2O}	$(3.0 \pm 0.5) \times 10^{-4}\ s^{-1}$
k_{-1}/k_T	0.129 ± 0.003 M
k_{-1}/k_{HT}	0.206 ± 0.004 M
k_{-1}/k_{H_2T}	2.80 ± 0.08 M
k_{HT}/k_T	0.63 ± 0.03
k_{H_2T}/k_T	0.046 ± 0.002
k_{HT}/k_{H_2T}	13.7 ± 1.3

were calculated by using the respective α values and all possible linear combinations. Comparison of observed and predicted rate constants at pH 9.35 is shown in Figure 2.

As the pH decreases from 7.7, the trien$_t$ dependence is lost. The observed rate constant increases, exhibiting a linear dependence upon hydrogen ion concentration. This is consistent with the reaction given in eq 7. Graphical evaluation provides $k_{H_3O} = 8.5 \times 10^3\ M^{-1}$. The agreement between the observed rate constants and the predicted values is shown in Figure 3. The rate constants are summarized in Table II.

$$NiH_{-2}DGEN + H_3O^+ \xrightarrow{k_{H_3O}} \text{products} \qquad (7)$$

Discussion

trien Reactivity. The reaction of $NiH_{-2}DGEN$ with trien$_t$ does not follow the general reactivity pattern that has been observed for other complexes such as $NiH_{-2}GGG^-$,[9] $CuH_{-2}GGG^-$,[10] and $NiH_{-2}GGhis^-$.[15] For the triglycine complexes the nucleophilic pathway is subject to steric interactions but in general maintains an integral order over the range of trien$_t$ concentrations studied. The kinetic lability of the $NiH_{-2}GGhis^-$ complex is much smaller by comparison, and correspondingly the rate constant is reduced.[15] This complex is also subject to proton-assisted decomposition.

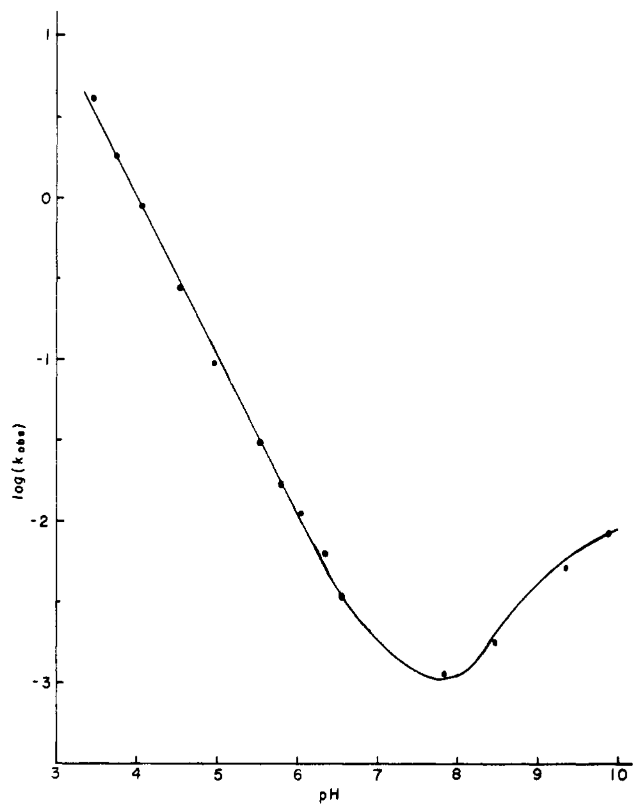


Figure 3. Dependence of k_{obsd} on pH ([trien$_t$] = 8.86×10^{-3} M). The solid line is calculated by 5 and 7 and the constants listed in Table II.

The loss of integral dependence upon trien$_t$ concentration in the transfer of Ni(II) from DGEN to trien$_t$ is due to the protective action exerted by the two terminal amine groups and the rigidity of the terminal chelate rings. In the reaction with $NiH_{-2}GGG^-$ the carboxylate donor is sufficiently labile to provide an equatorial position for coordination to an amine donor of trien. For the $NiH_{-2}DGEN$ complex the amine donors are not as labile, and in addition, k_{-1}, the rate constant for the closing of the chelate ring, is comparable to k_2[trien$_t$] (see eq 2 and 3). This balance accounts for the variable trien$_t$ dependence. The rate constant k_1, as designated in eq 3, is equal to twice the value for the breakage of the bond between nickel and the terminal amine groups, $k_1/2 = k_{-NH_2R}$. This results from two equivalent pathways to form the steady-state species. The extrapolated value of k_1 equals $0.16\ s^{-1}$. This value is much smaller than the values observed for the dissociation of nonchelated amines from high-spin nickel(II). For example[16] the constant for NH_3 dissociation is $7.1\ s^{-1}$ and for $EtNH_2$ is $13.3\ s^{-1}$. This difference could be due in part to the spin states, with the low-spin Ni(II) being less labile. The constants for the opening of Ni–en chelate rings are comparable[17,18] (0.11–$0.13\ s^{-1}$), and thus the spin states may not play a critical role.

The rate constant value for trien reacting with $(NiH_{-2}DGEN)^*$ can be approximated from data obtained in other studies. The rate constant for the reaction of trien with nickel triglycine[9] ($NiH_{-2}GGG^-$) is $1.7 \times 10^4\ M^{-1}\ s^{-1}$. The reactive intermediate, $(NiH_{-2}DGEN)^*$, is believed to have one of the terminal amine groups dissociated from nickel, and thus it is similar to the diglycylamide complex ($NiH_{-2}GGa$). The value of k_2 (eq 3) for trien should be larger for $(NiH_{-2}DGEN)^*$ than it is for the triglycine complex by an amount equal to the stability imparted to

---

(15) Bannister, C. E.; Raycheba, J. M. T.; Margerum, D. W. *Inorg. Chem.* **1982**, *21*, 1106.

(16) Rorabacher, D. B.; Melendez-Cepeda, C. A. *J. Am. Chem. Soc.* **1971**, *93*, 6071.

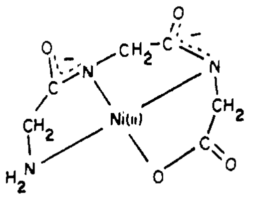
(17) Read, R. A.; Margerum, D. W. *Inorg. Chem.* **1981**, *20*, 3143.

(18) Read, R. A.; Margerum, D. W. *Inorg. Chem.* **1983**, *22*, 3447.

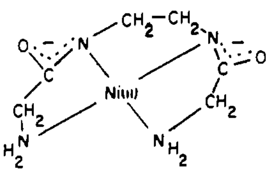
$NiH_{-2}GGG^-$ through coordination of the carboxylate group. Comparison of the thermodynamic stability[19] of $NiH_{-2}GGG^-$ and $NiH_{-2}GGa$ indicates this factor should be $10^{1.5}$, and thus the predicted value of k_T for $(NiH_{-2}DGEN)^*$ is 5×10^5 M^{-1} s^{-1}.

The ratio of k_{-1}/k_T is 0.129 M, which provides an estimated value of 6×10^4 s^{-1} for k_{-1}. Coupling this value with k_{-NH_2R} (k_{-1}/k_{-NH_2R}) yields an estimated chelate stability constant of 10^6. This value is significantly greater than the value of 10^5 obtained by comparison of the stabilities[13] of $Ni(OH_2)_5NH_3^{2+}$ and $Ni(OH_2)_4en^{2+}$ but is comparable to the value obtained upon comparison to $Ni(OH_2)_5EtNH_2$; the enhanced stability may be due primarily to the small value of k_{-NH_2R}.

The structures of $NiH_{-2}GGG^-$ and $NiH_{-2}DGEN$ are depicted by I and II. At this time there is no evidence for polypeptides unwrapping from the amine terminal position in any of the nucleophilic replacement reactions.[9,10,15] The presence of the deprotonated linkage in the chelate ring that is being broken adds sizable kinetic stability to the system.



I



II

In $NiH_{-2}DGEN$ this grouping is present on both sides of the complex, and correspondingly a change in $trien_t$ reactivity pattern is observed. When the planar NCO unit is part of the chelate ring that must be disrupted and twisted out of the way to permit coordination to the incoming group, there is one less bond for free rotation. This reduces the rate of the process. For the triglycine and glycylglycylhistidine complexes, the deprotonated groupings are not part of the most labile chelate ring and the complexes exhibit first-order $trien_t$ dependence. Shifting the deprotonated group to the terminal chelate ring in $NiH_{-2}DGEN$ complex adds rigidity to the chelate ring and reduces the rate of amine nitrogen dissociation by a factor of approximately 100.

The relative ratios of the trien species rate constants $k_T/k_{HT}/k_{H_2T}$ of 1.0/0.63/0.046 are typical of the values observed when these ligands react through nucleophilic displacement processes. This also indicates that H_2trien^{2+} is not acting as a general acid.

Proton Transfer. The rate constants for reaction of $NiH_{-2}DGEN$ and other square-planar polypeptide complexes with H_3O^+ are summarized in Table III. The largest k_{H_3O} value is exhibited by the nickel–triglycine complex, and this complex is believed to be the only one proceeding through an "inside" protonation mechanism. Inside protonation refers to addition of a proton to an imide nitrogen during the rate-determining step as opposed to "outside" protonation where the proton attaches to a carbonyl oxygen. The reactions of four of these complexes with H_3O^+ involve transfer of a proton to a terminal imide group. The relative rates are sensitive to ligand field stabilization, with the strongest field complex reacting slowest. It is not surprising that the tetraglycine and triglycineamide complexes react more rapidly than $NiH_{-2}DGEN$ since the terminal amine groups in DGEN provide protection. As with the $trien_t$ reactions, the presence of the imide linkages in the terminal chelate rings imparts kinetic stability and reduces the rate constant.

Table III. Dissociation and Protonation Rate Constants for Similar Nickel(II) Complexes

complex	k_{H_2O}, s^{-1}	k_{H_3O}, M^{-1} s^{-1}	ref
$NiH_{-2}DGEN$	3×10^{-4}	8.5×10^3	this work
$NiH_{-2}GGG^-$	5×10^{-2}	2×10^5	5
$NiH_{-2}GGH^-$	8×10^{-5}	3×10^4	15
$NiH_{-3}GGGG^{2-}$	1.6×10^{-5}	7.1×10^4	8
$NiH_{-3}GGGa^{2-}$		3.3×10^4	8
$NiH_{-2}GGG(CN)^{2-}$	2.7×10^{-3}	6.9×10^3	20
$NiH_{-2}GGa(CN)^-$	8×10^{-5}	4.3×10^3	20
$NiH_{-3}GGGGa$		2.5×10^2	21

The protonation rate constant, $k_{H_3O} = 10^{3.9}$ M^{-1} s^{-1}, is less than that observed for other analogous complexes (see Table III). In $NiH_{-3}G_4^{2-}$ and $NiH_{-3}G_4a^-$,[19] the proton is going to terminal coordination sites and correspondingly the rate should be greater than that observed for the complexes where a terminal protective group is present. In the $NiH_{-2}GGa^-$ complex the carbonyl oxygen that is protonated is not a part of the chelate ring that is breaking. The increased kinetic stability of $NiH_{-2}DGEN$ toward reaction with H_3O^+ parallels that observed in the trien reaction where the planar NCO group in the breaking chelate plays a large role. Substitution of CN^- for the fourth coordination site increases the ligand field stabilization and markedly reduces the rate constant for the reaction with H_3O^+.

The solvent-assisted pathway, eq 2, is believed to involve transfer of a proton from coordinated water.[15] A stronger ligand field presumably reduces the out-of-plane interaction and correspondingly the values of k_{H_2O}. This may be evident, but other parameters such as ring strain, trans effect, and the charge of the complex play a role; thus, changes in k_{H_3O} and k_{H_2O} are not parallel.

In summary, the presence of the imide linkage in the chelate ring that is breaking during the reaction with $trien_t$ may impart sufficient stability to alter the reactivity pattern. This configuration also favors the outside protonation mechanism.

Registry No. trien, 112-24-3.

---

(19) Dorigatti, T. F.; Billo, E. J. *J. Inorg. Nucl. Chem.* **1975**, *37*, 1515.

(20) Pagenkopf, G. K.; Brice, V. T. *Inorg. Chem.* **1975**, *14*, 3118.

(21) Raycheba, J. M. T.; Margerum, D. W. *Inorg. Chem.* **1980**, *19*, 497.