sorption disappeared also by a second rate law with $2k \simeq 4 \times 10^7\ M^{-1}\ \text{sec}^{-1}$ and is therefore attributed to $Ni^{III}(NH_3)_q$. The specific rates of reactions 11 and 12 could not be determined separately but for the combined reactions $2k/\epsilon = (2.5 \pm 1)10^6$, which means that the rates of these reactions approach the diffusion-controlled limit. A possible contribution of the reaction

$$Ni^{I}(NH_3)_p + NH_2 + H_2O \longrightarrow Ni^{II}(NH_3)_n + (p - n + 1)NH_3 + OH^- \quad (13)$$

to the fast decay cannot be ruled out.

It is concluded that this study clearly indicates that a trivalent ammino-nickel complex is formed by the oxidation of $Ni^{II}(NH_3)_n$ by NH_2 radicals. The mechanism of formation and disappearance of this trivalent complex resemble those of the $Cu^{III}(NH_3)_q$ complex.[20] It is of special interest to note that NH_2 radicals are strong enough oxidizing agents to cause the oxidation of these complexes.

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CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, NUCLEAR RESEARCH CENTRE-NEGEV, BEER-SHEVA, ISRAEL,
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Trivalent Nickel. II. A Pulse Radiolytic Study of the Formation and Decomposition of the Ethylenediamine and Glycine Complexes in Aqueous Solution

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The reaction of hydroxyl radicals with divalent nickel complexes, with ethylenediamine and glycine as ligands, yields unstable intermediates. These unstable intermediates are shown to be complexes of trivalent nickel. The specific rates of formation and decomposition as well as the spectra of these complexes were measured as functions of pH and divalent complex concentration. The mechanism of the reactions involved is discussed and compared with the behavior of the corresponding copper complexes.

Complexes of trivalent nickel with different aliphatic amine compounds have been shown to be stable in the solid state and in solution in different organic solvents.[1-6] These complexes are known to decompose in aqueous solutions. It has also been suggested that the $Ni^{III}(en)_3$, en = ethylenediamine, is formed as an intermediate in the electrocatalytic oxidation of ethylenediamine on Pt electrodes in aqueous solutions.[7] The redox potential of the couple $Ni^{II}(en)_3$–$Ni^{III}(en)_3$, as estimated from these experiments, is lower than 0.9 V. Furthermore, the results indicated that the rate determining step in the electrocatalytic process is the decomposition of the trivalent complex.[7]

We have decided to study, by the pulse radiolytic technique, in detail the mechanism of formation and decomposition of $Ni^{III}(en)_3$. As the results indicated that $Ni^{III}(en)_3$ is more stable than $Cu^{III}(en)_2$[8] we decided to study also the properties of $Ni^{III}Gly_3$, Gly = glycine, and compare them with the corresponding copper complex. It was found that the decomposition reaction of $Ni^{III}Gly_3$ obeys a second-order rate law and not a first-order rate law as has been reported for the corresponding copper complex.[8]

Experimental Section

All solutions were prepared from triply distilled water. Glycine AR grade was supplied by Merck and ethylenediamine sulfate purum, enH_2SO_4, was supplied by Fluka. All other chemicals used were of AR grade. The procedure of preparation of samples, irradiation, observation of the optical changes, and evaluation of the results has been identical with that described in the preceding paper.

Results

The composition of unbuffered solutions containing different concentrations of $NiSO_4$ and enH_2SO_4 in the range of 8–10 was calculated from the concentrations used and from the average values of the stability constants for these complexes as obtained from the literature.[9] In these calculations it has been assumed that all the ethylenediamine is in its basic form though its pK values are 7.0 and 10.0. The measurements were carried out above pH 8.0 and it is expected that when one end of the ligand gets complexed the other end becomes more acidic, and due to the high tendency for chelation it also will get complexed. This approximation in the calculations seems justified within the error limit of our measurements. Similar calculations were carried out also for the nickel–glycine solutions. In the latter case, due to the high pK of the amine group, pK = 9.7, all measurements were carried out at pH 10.0.

The specific rates of reaction of the free ligands ethylenediamine and glycine with OH radicals were determined by competition between reaction 1 or 2

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TABLE I

SPECTROSCOPIC DATA FOR $\mathrm{Ni^{III}(en)_{\mathit{n}}}$ AND $\mathrm{Ni^{III}Gly_{\mathit{n}}}$[a]

$[\mathrm{Ni^{2+}}]$, M	[en], M	[Gly], M	pH	$\epsilon_{\mathrm{obsd}}{}^{300}$,[b] M^{-1} cm^{-1}	$\epsilon_{\mathrm{cor}}{}^{300}$[c]	$\epsilon_{\max}$, M^{-1} cm^{-1}	$\lambda_{\max}$, nm
	1×10^{-3}		10.0	Small			
1×10^{-4}	3×10^{-4}		8.5	1100	1300		280 ± 5
1×10^{-3}	3×10^{-3}		8.5	1700	1700		295 ± 5
2×10^{-5}	6×10^{-5}		10.0	1000	1540		280 ± 5
1×10^{-4}	3×10^{-4}		10.0	1360	1800		
1×10^{-3}	3×10^{-3}		10.0	1900	1900	2000	295 ± 5
		1×10^{-3}	10.0	190[d]	190		255 ± 10
3×10^{-4}		9×10^{-4}	10.0	590[d]	880		285 ± 10
2×10^{-3}		6×10^{-3}	10.0	850[d]	1050	2800	285 ± 10

[a] All solutions were N_2O saturated. [b] The error limit on $\epsilon_{\mathrm{obsd}}{}^{300}$, the observed absorption coefficient, at 300 nm is ±20%. [c] $\epsilon_{\mathrm{cor}}{}^{300}$ is the corrected absorption coefficient of $\mathrm{Ni^{III}L_{\mathit{n}}}$ at 300 nm. The corrections were introduced due to partial hydroxyl radical scavenging by the free ligands. [d] Measured at 350 nm.

TABLE II

THE SPECIFIC RATES OF REACTION OF THE HYDROXYL RADICAL WITH DIVALENT NICKEL COMPLEXES[a]

$[\mathrm{Ni^{2+}}]$, M	[en], M	pH ± 0.1	$[\mathrm{en}]_\mathrm{f}$,[b] M	$[\mathrm{NCS^-}]$, M	k_{obsd},[c] M^{-1} sec^{-1}	k_{cor},[d] M^{-1} sec^{-1}
5×10^{-5}	1.5×10^{-4}	8.0	3×10^{-5}	2×10^{-4}	1.6×10^{9}	1.1×10^{9}
3×10^{-4}	9×10^{-4}	8.0	1×10^{-4}	2×10^{-4}	1.5×10^{9}	1.3×10^{9}
2×10^{-4}	6×10^{-4}	8.5	8×10^{-5}	7×10^{-5}	9.5×10^{9}	7.5×10^{9}
5×10^{-4}	1.5×10^{-3}	8.5	1.3×10^{-4}	7×10^{-5}	1.2×10^{10}	1.0×10^{10}
1×10^{-3}	3×10^{-3}	8.5	2×10^{-4}	7×10^{-5}	1.3×10^{10}	1.2×10^{10}
3×10^{-4}	9×10^{-4}	8.5	1×10^{-4}	2×10^{-4}	9.2×10^{9}	7.5×10^{9}
1×10^{-3}	3×10^{-3}	8.5	2×10^{-4}	2×10^{-4}	1.4×10^{10}	1.3×10^{10}
2×10^{-3}	6×10^{-3}	8.5	6×10^{-4}	2×10^{-4}	1.35×10^{10}	1.2×10^{10}
2×10^{-4}	6×10^{-4}	9.0	8×10^{-5}	7×10^{-5}	1.3×10^{10}	1.0×10^{10}
5×10^{-4}	1.5×10^{-3}	9.0	1.3×10^{-4}	7×10^{-5}	1.5×10^{10}	1.2×10^{10}
1×10^{-3}	3×10^{-3}	9.0	2×10^{-4}	7×10^{-5}	1.1×10^{10}	1.0×10^{10}
2×10^{-3}	6×10^{-3}	9.0	6×10^{-4}	7×10^{-5}	1.3×10^{10}	1.1×10^{10}
2×10^{-4}	6×10^{-4}	10.0	8×10^{-5}	7×10^{-5}	1.5×10^{10}	1.1×10^{10}
5×10^{-4}	1.5×10^{-3}	10.0	1.3×10^{-4}	7×10^{-5}	1.3×10^{10}	1.0×10^{10}
3×10^{-4}	9×10^{-4}	10.0	1×10^{-4}	2×10^{-4}	1.7×10^{10}	1.3×10^{10}
1×10^{-3}	3×10^{-3}	10.0	2×10^{-4}	2×10^{-4}	1.9×10^{10}	1.7×10^{10}
	[Gly], M		$[\mathrm{Gly}]_\mathrm{f}$, M			
2×10^{-4}	6×10^{-4}	10.0	1.4×10^{-4}	2×10^{-4}	2.3×10^{10}	1.4×10^{10}
5×10^{-4}	1.5×10^{-3}	10.0	2.6×10^{-4}	2×10^{-4}	1.5×10^{10}	9.1×10^{9}
6×10^{-4}	1.8×10^{-3}	10.0	3.1×10^{-4}	2×10^{-4}	2.1×10^{10}	1.1×10^{10}
8×10^{-4}	3×10^{-3}	10.0	6.0×10^{-4}	2×10^{-4}	1.9×10^{10}	1.3×10^{10}

[a] All solutions were O_2 saturated. The measurements were carried out at 500 nm. The pulse intensity was 200 rads/pulse. [b] The calculated concentration of free ligand in the solutions (see text). [c] The observed specific rate of reaction, error limit ±15%. [d] The corrected specific rate of reaction, corrected for the contribution of the reaction of hydroxyl radicals with the free ligand, error limit ±20%.

and reaction 3[10] at different pH's. (The results reported are for the total specific rate of reaction of OH radicals with the free ligands. In alkaline solutions, pH >10, some hydrogen abstraction from NH_2 groups might occur.[10b]) Oxygen-saturated solutions

$$\mathrm{OH + NH_2CH_2CH_2NH_2 \longrightarrow H_2O + NH_2CHCH_2NH_2} \quad (1)$$

$$\mathrm{OH + NH_2CH_2CO_2^- \longrightarrow H_2O + NH_2CHCO_2^-} \quad (2)$$

$$\mathrm{OH + NCS^- \longrightarrow NCS + OH^-;} \quad k_3 = 2.0 \times 10^{10}\ M^{-1}\ \mathrm{sec}^{-1} \quad (3)$$

$$\mathrm{NCS + NCS^- \rightleftarrows (NCS)_2^-} \quad (4)$$

containing different concentrations of NCS^- and ligands were irradiated. The absorption due to $(NCS)_2^-$ at 500 nm was followed. The results, calculated by assuming $k_3 = 2.0 \times 10^{10}\ M^{-1}\ \mathrm{sec}^{-1}$ [11] are $k_1 = (5.3 \pm 1.0) \times 10^{8}\ M^{-1}\ \mathrm{sec}^{-1}$, $k_1 = (4.5 \pm 1.0) \times 10^{9}\ M^{-1}\ \mathrm{sec}^{-1}$, $k_1 = (6.0 \pm 1.0) \times 10^{9}\ M^{-1}\ \mathrm{sec}^{-1}$, and $k_1 = (1.0 \pm 0.2) \times 10^{10}\ M^{-1}\ \mathrm{sec}^{-1}$ at pH 8.0, 8.5, 9.0, and 10.0, respectively. The pH effect on k_1 is in accordance with the expected effect of deprotonation of the amino group on the rate of abstraction of the α hydrogen atom.[11b] For the case of glycine $k_2 = (9.7 \pm 2.0) \times 10^{9}\ M^{-1}\ \mathrm{sec}^{-1}$ at pH 10.0 was obtained. The latter value is somewhat higher than other values reported in the literature.[12]

The spectra of the transients formed by pulse radiolyzing N_2O-saturated solutions containing $2 \times 10^{-5}\ M$ $NiSO_4$ and $6 \times 10^{-5}\ M$ enH_2SO_4 or $1 \times 10^{-3}\ M$ $NiSO_4$ and $3 \times 10^{-3}\ M$ enH_2SO_4 at pH 8.5 and 10.0 were measured. The results are summarized in Table I. It is evident from the results that the position of the absorption band is not affected by the change in pH but depends slightly on the concentration of the nickel and ethylenediamine. The shift to the red with the increase in the complex concentration suggests that the absorption band of $\mathrm{Ni^{III}(en)_3}$ is somewhat shifted to the red relatively to the $\mathrm{Ni^{III}(en)_2}$ absorption band. No transient absorption in the same region was observed when N_2O-saturated solutions containing only $1 \times 10^{-3}\ M$ enH_2SO_4 in the same pH range were irradiated.

The absorption spectrum of the transient formed by irradiating an N_2O-saturated solution containing 1 ×

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10^{-3} *M* $NiSO_4$ and 3×10^{-3} *M* glycine at pH 10 was measured. The results are summarized in Table I. A transient is observed also in N_2O-saturated solutions containing only glycine at pH 10.0. However, in this case $\lambda_{max} = 255 \pm 5$ nm as compared to $\lambda_{max} = 290 \pm 10$ nm for the nickel-containing solutions.

The absolute molar extinction coefficients were determined by the ferrocyanide method.[13] The yield of Ni^{III} formed was calculated from the relative rates of reaction of OH radicals with the free ligands and the complexes (see below) and from the calculated solution compositions.

The specific rates of reaction of the divalent nickel complexes with hydroxyl radicals were measured by the NCS^- competition technique.[10a,11a] The results were corrected for the contribution of the reaction of the hydroxyl radicals with the free ligands present in the solutions. The latter concentrations were calculated as described before. The results are summarized in Table II.

The specific rate of disappearance on the $Ni^{III}(en)_n$ and $Ni^{III}Gly_n$ complexes formed in N_2O-saturated solutions was measured. Both reactions were found to obey a second-order rate law. The specific rates for these disappearance reactions as functions of pH and complex concentration are summarized in Tables III and IV. The relative large error limit on the results is due to the large pH effect on the rates. From the results three effects can be seen. (a) The rate of the disappearance reaction increases with the increase in pH. (b) The rate of disappearance increases with increase in the [ligand]/[$NiSO_4$] ratio. (c) The rate of disappearance decreases with increasing concentration of the complex (at constant [ligand]/[$NiSO_4$] ratio).

TABLE III

THE SPECIFIC RATE OF THE DISAPPEARANCE REACTION OF $Ni^{III}(en)_n$[a]

[Ni], *M*	[en], *M*	pH ± 0.1	2*k*, M^{-1} sec^{-1}
2×10^{-5}	6×10^{-5}	9.2	5.2×10^{6}
2×10^{-5}	6×10^{-5}	9.5	1.1×10^{7}
2×10^{-5}	6×10^{-5}	10.0	2.5×10^{7}
2×10^{-5}	8×10^{-5}	9.0	6.2×10^{6}
2×10^{-5}	1×10^{-4}	9.8	2.1×10^{7}
5×10^{-5}	1.5×10^{-4}	8.5	2.3×10^{6}
5×10^{-5}	1.5×10^{-4}	9.0	2.1×10^{6}
5×10^{-5}	1.5×10^{-4}	9.5	2.4×10^{6}
5×10^{-5}	1.5×10^{-4}	10.0	5.2×10^{6}
5×10^{-5}	2×10^{-4}	8.5	4.9×10^{6}
5×10^{-5}	2×10^{-4}	9.0	6.3×10^{6}
5×10^{-5}	2×10^{-4}	9.5	9.6×10^{6}
5×10^{-5}	2×10^{-4}	10.0	2.3×10^{7}
1×10^{-4}	3×10^{-4}	10.0	4.3×10^{6}
1×10^{-4}	4×10^{-4}	8.5	1.5×10^{6}
1×10^{-4}	4×10^{-4}	9.0	1.7×10^{6}
1×10^{-4}	4×10^{-4}	9.5	6.9×10^{6}
1×10^{-4}	4×10^{-4}	10.0	4.3×10^{7}
3×10^{-4}	9×10^{-4}	9.0	2.3×10^{6}
3×10^{-4}	9×10^{-4}	9.5	2.7×10^{6}
3×10^{-4}	9×10^{-4}	10.0	5.3×10^{6}
1×10^{-3}	1×10^{-3}	8.5	6.2×10^{5}
1×10^{-3}	1×10^{-3}	9.0	2.1×10^{6}
1×10^{-3}	1×10^{-3}	9.5	3.2×10^{6}
5×10^{-4}	1.5×10^{-3}	10.0	3.0×10^{6}
1×10^{-3}	4×10^{-3}	8.5	7.8×10^{4}
1×10^{-3}	4×10^{-3}	9.0	2.5×10^{5}
1×10^{-3}	4×10^{-3}	9.5	5.0×10^{5}
1×10^{-3}	4×10^{-3}	10.0	2.0×10^{6}

[a] All solutions were N_2O saturated. The pulses used were of 1200 and 400 rads/pulse. Measurements were carried out at 300 nm. The accuracy is ±20%.

TABLE IV

THE SPECIFIC RATE OF THE DISAPPEARANCE REACTION OF $N^{III}Gly_n$[a]

[Ni], *M*	[Gly], *M*	pH ± 0.1	2*k*, M^{-1} sec^{-1}
1×10^{-4}	3×10^{-4}	8.9	4.2×10^{9}
3×10^{-4}	9×10^{-4}	8.9	3.2×10^{9}
1×10^{-3}	3×10^{-3}	8.9	1.6×10^{9}
2×10^{-3}	6×10^{-3}	8.9	2.2×10^{9}
1×10^{-4}	3×10^{-4}	10.0	8.5×10^{9}
3×10^{-4}	9×10^{-4}	10.0	5.8×10^{9}
1×10^{-3}	3×10^{-3}	10.0	7.2×10^{9}

[a] All solutions were N_2O saturated. The pulses used were of 1200 and 2100 rads/pulse. Measurements were carried out at 350 nm. The accuracy is ±20%.

The disappearance reaction of the transients formed by pulse radiolyzing Ar-saturated solutions containing different concentrations of nickel and ethylenediamine was studied. It was found that, in parallel to the nickel–ammonia system,[13] the disappearance reaction might be divided into two parts, both of which obey a second-order rate law. The first reaction is fast with $2k/\epsilon_{300} = (5 \pm 2) \times 10^5$ whereas the second reaction is much slower with rates similar to those observed in the N_2O-saturated solutions (depending on pH and solution concentration).

Discussion

It is evident from the results that hydroxyl radicals oxidize amine complexes of nickel. The spectra of the oxidized complexes are very similar to that of $Ni^{III}(NH_3)_n$[13] having a maximum at 285 ± 10 nm. If the site of oxidation would be on the ligand one would expect different spectra for the amine, ethylenediamine, and glycine complexes. Furthermore, the spectra obtained for the ammonia and ethylenediamine complexes are very different from those obtained by the oxidation of the free ligands with OH radicals. It is concluded therefore, that the site of oxidation of the amine complexes of nickel by hydroxyl radicals is on the central nickel cation. The data seem to be insufficient for determining the transition causing this absorption band. We have no explanation for the lack of a pH effect, or for the effect of *n* on the location of the absorption peak of $Ni^{III}(en)_n$. Furthermore, we have no explanation for the large difference between the measured spectra and those reported for cyclic amine complexes of trivalent nickel in acetonitrile.[4] In the latter case absorption bands around 300 nm were also observed but with much higher extinction coefficients and with a second band at ~400 nm and a band due to a d–d transition at ~650 nm.

The specific rates of reaction of the hydroxyl radicals with the nickel complexes show a marked dependence on pH (Table II). In this respect the results are very similar to those reported for the copper–amine systems.[8] The results do not indicate a different rate for the oxidation of $Ni(en)_2^{2+}$ and $Ni(en)_3^{2+}$. However, due to the large error limit on the results the existence of small differences between these rates cannot be ruled out. (The large error is due to the strong pH dependence and to the large corrections introduced in the calculation for the contribution of reaction with the free ligands.) No formation of trivalent nickel was ob-

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[13] See preceding paper: J. Lati and D. Meyerstein, *Inorg. Chem.*, **11**, 2393 (1972).

served below pH 7.5. Under these conditions most of the nickel is not complexed and all the OH radicals reacted with the free ligand. No formation of trivalent nickel could be observed, in the 260–400 nm range, also in neutral solutions containing no ligands. It has to be concluded that most probably Ni^{2+}_{aq} is not oxidized by OH radicals, or that the rate of the latter reaction is too slow to be observed under our experimental conditions. This difference between the behavior of Cu^{2+}_{aq} explains why no effect of Ni^{2+} ions on the radiolysis of ethylenediamine solutions at pH 4 was observed.[14]

The disappearance reaction of $Ni^{III}(en)_n$ was found to obey a second-order rate law. The products of the decomposition reaction of the trivalent complexes were not measured as it was found that the kinetics of the disappearance reaction changed after several pulses. The products have therefore to be measured at concentration levels of less than 1×10^{-5} *M*. It is believed, however, that the products are mainly NH_2CH_2CHO and NH_3 which were shown to be the major products after extensive oxidation of ethylenediamine complexes.[14] The possibility that an imine is produced as an intermediate cannot be ruled out. The increase in the specific rates of disappearance with increasing pH are believed to be caused by one of the following factors. (a) It is plausible that the $Ni^{III}(en)_n$ complexes behave as acids in basic solutions, *i.e.*

$$Ni(en)_2(H_2O)_2^{3+} + OH^- \rightleftharpoons Ni(en)_2(H_2O)(OH)^{2+} + H_2O \quad (5)$$

or

$$Ni^{III}(en)_n^{3+} + OH^- \rightleftharpoons Ni^{III}(en)_{(n-1)}(NHCH_2CH_2NH_2)^{2+} + H_2O \quad (6)$$

Similar basic forms of different amine complexes of trivalent cations are known.[9] It might be argued that the disappearance reaction

$$2Ni^{III}(en)_n \xrightarrow{H_2O} Ni(en)_n^{2+} + Ni(en)_{(n-1)}^{2+} + NH_2CH_3CHO + NH_3 \quad (7)$$

is faster for the basic forms of the complexes. (b) It is possible that at high pH's the equilibrium reaction

$$Ni^{III}(en)_n + OH^- \rightleftharpoons Ni(en)_n^{2+} + OH \quad (8)$$

begins to contribute to the mechanism. This equilibrium might affect the rate of disappearance either through the reactions

$$OH + NH_2CH_2CH_2NH_2 \longrightarrow NH_2\dot{C}HCH_2NH_2 + H_2O \quad (9)$$

$$NH_2\dot{C}HCH_2NH_2 + Ni^{III}(en)_n \xrightarrow{H_2O} Ni(en)_n^{2+} + NH_3 + NH_2CH_2CHO \quad (10)$$

or *via*

$$OH + Ni^{III}(en)_n \longrightarrow Ni(en_{(n-1)})^{2+} + NH_3 + NH_2CH_2CHO \quad (11)$$

From the effect of the concentration of free ethylenediamine on the specific rate of disappearance of $Cu^{III}(en)_2$ it was possible to suggest[8] that the effect of pH on this reaction is due to the equilibrium

$$Cu^{III}(en)_2 + OH^- \rightleftharpoons Cu(en)_2^{2+} + OH \quad (12)$$

In the present system due to the smaller stability constants for the $Ni(en)_n^{2+}$ complexes, all the solutions contained free ligand, and a change in its concentration affected the mechanism by changing the reacting species (see below). We were, therefore, unable to prove which mechanism causes the increase in the specific rate of reaction 7, although through analogy with the copper system we believe that the equilibrium reaction 8 causes the pH effect.

The increase in the specific rate of the disappearance reaction with the increase in the ratio of ligand to nickel concentration is believed to be due to the competition between reactions 9 and 13.

$$OH + Ni(en)_n^{2+} \rightleftharpoons Ni^{III}(en)_n^{3+} \quad (13)$$

The radicals formed in reaction 9 react with the trivalent nickel according to reaction 10 thus increasing the observed rate of disappearance of the trivalent nickel complex.

The decrease in the specific rate of the disappearance reaction with the increase of complex concentration at constant pH and ligand to nickel concentration ratio is believed to be due to two causes. (a) The higher the complex concentration the lower is the ratio of free ligand to nickel concentration thus inhibiting reactions 9 and 10. (b) As the results seem to indicate that the above reason does not explain all the effect observed, we believe that reaction 7 is slower for $Ni^{III}(en)_3$ than for $Ni^{III}(en)_2$. As even in the solutions containing 1×10^{-3} *M* Ni^{2+} and 4×10^{-3} *M* en about 5% of the trivalent nickel is formed as $Ni^{III}(en)_2$, part of the latter might be converted into $Ni^{III}(en)_3$ due to the higher stability of the trivalent complex; the observed specific rates 1×10^5 M^{-1} sec^{-1} and 2.0×10^6 M^{-1} sec^{-1} at pH 8.5 and pH 10.0 are upper limits for the specific rates of disappearance of $Ni^{III}(en)_3$. The difference between the reactivity of $Ni(en)_3^{3+}$ and $Ni^{III}(en)_2^{3+}$ might stem from the difference in the electron tunneling probability through ethylenediamine and water as ligands. This suggestion is in accordance with the mechanism suggested in order to explain the results obtained in a study of the electrocatalytic oxidation of ethylenediamine in the presence of nickel ions in aqueous solutions.[7]

An experiment to plot the disappearance kinetics of the trivalent complex at pH 8.5 as a first-order reaction indicates that this reaction is slower than 1.0×10^0 sec^{-1}. It is therefore concluded that the upper limit for the specific rate of the intramolecular oxidation of the ligand by the central cation is lower than 1.0×10^0 sec^{-1}. This is in agreement with the fact that different complexes of trivalent nickel with aliphatic amines are stable as solids and as solutes in several organic solvents.[1-6] The complexes are believed to be unstable in aqueous solutions due to the extra stabilization of H^+ formed in the decomposition reaction of the trivalent complexes in water.

The disappearance kinetics of the $Ni^{III}Gly_n$ complexes formed in N_2O-saturated solutions also were found to obey a second-order rate law (Table IV). The specific rates of reaction in this case increase also with increasing pH and decrease with increase in the divalent complex concentration. The reasons for these effects are believed to be similar to those suggested for the ethylenediamine complexes. It is of interest to note the difference in behavior between the $Ni^{III}Gly_n$ and the $Cu^{III}Gly_2$ complexes;[8] the latter decomposes *via* an

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intramolecular first-order rate determining step. It is believed that this difference is due to the lower redox potential of the amine complexes of trivalent nickel as compared with that of the corresponding copper complexes.[4,7,15,16] However, it is found also for the trivalent nickel that complexes with amino acids as ligands are less stable than complexes with ethylenediamine.

One might be tempted to suggest that tetravalent nickel complexes are formed as intermediates in the second-order disappearance reactions of the trivalent complexes. Tetravalent nickel complexes with oxides and fluorides are known. The formation of a tetravalent nickel complex with ethylenediamine has been suggested as one explanation for some observations in the corresponding electrochemical system.[7] However, no kinetic or spectroscopic evidence for the formation of such an intermediate was found in this study.

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Aquation Kinetics of the Aquoammine Complexes of Palladium(II)[1]

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Upon treatment with excess aqueous $HClO_4$, $Pd(NH_3)_4{}^{2+}$ is converted through four consecutive steps to $Pd(OH_2)_4{}^{2+}$. Correlation of observed rate constants with actual mechanistic steps is based primarily on reconstruction of the absorption spectra of the intermediate species; it was thus found that the rate constants decrease steadily from one step to the next. At 50°, $\mu = 1$, rate constants found are respectively 0.020, 0.008, 9.2×10^{-3}, and 2.2×10^{-4} sec^{-1}. Activation enthalpies range from 21 to 24 kcal/mol and activation entropies from +4 to −4 eu. Substituent effects are compared with those in chloride-containing complexes and with those for the reverse reactions.

Introduction

As a logical continuation of previous kinetic studies[2-6] in the chloroammine complexes of palladium(II), we have investigated the rates of substitution of ammonia by water in the aquoammine series. Acidification of $Pd(NH_3)_4{}^{2+}$, in the absence of complexing anions, results in stepwise aquation

$$Pd(NH_3)_4{}^{2+} + nH^+ + nH_2O = nNH_4{}^+ + Pd(NH_3)_{4-n}(OH_2)_n{}^{2+} \quad (1)$$

The rate of the first step of this equation is obtained from the chloride-independent term in the rate law for chloride substitution.[3-5] Rasmussen and Jørgensen,[7] incidental to their equilibrium studies in the palladium ammine–hydrogen ion system, have given approximate values at 20 and 25° for the first rate constants of the two steps of eq 1. Coe and Lyons[8] have shown clearly that the second step leads to the formation of a preponderance of the cis isomer of $Pd(NH_3)_2(OH_3)_2{}^{2+}$.

Although it has been asserted that only two steps of eq 1 take place,[3,8] graphical analysis[9] of our preliminary data at room temperature showed three components—*i.e.*, three steps—in an 8-hr run. Moreover, when the systems were allowed to stand for several days or when runs were conducted at elevated temperatures, the final systems yielded a spectrum very similar to that reported[7] for $Pd(OH_2)_4{}^{2+}$: maximum absorbance at 380 nm with a molar absorptivity of about 80 cm^2 mmol^{-1}. We thus conclude that eq 1 proceeds through four consecutive steps, ultimately to form tetraaquopalladium(II) ion.

Experimental Section

Materials.—Solutions of $Pd(NH_3)_4(ClO_4)_2$ were prepared[3] by the addition of the stoichiometric quantity of silver perchlorate to a solution of $Pd(NH_3)_4Cl_2$, prepared from *trans*-$Pd(NH_3)_2Cl_2$ as described previously.[10]

Equipment.—Absorbance measurements were made with either a Beckman Model DU (manual operation) or a Model DK-1A (recording) spectrophotometer, using silica cells with thermostated cell holders which controlled actual cell temperature.

Kinetics.—All runs were carried out in 1.0 *M* perchloric acid (ionic strength 1.0). Runs were initiated by injecting the palladium solution into the acid, appropriate concentrations being used to allow for the volumes of reagents. Absorbance–time readings were continued until virtually all change had ceased. For the majority of runs a stable infinite-time absorbance (A_∞) could be obtained.

Each run was carried out at a fixed wavelength in the range 300–420 nm. The use of several wavelengths at each temperature assisted in the assignment of rate constants to the mechanistic steps as is discussed below.

A few runs at 25° were carried out in 10-cm absorbance cells at 0.443 m*M* Pd(II); all the remainder made use of 5.33 m*M* Pd(II) in 1-cm cells.

Results

Treatment of the Data.[11]—In a number of runs the

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[11] For supplementary material (specific kinetic data) order document NAPS-01810 from ASIS National Auxiliary Publications Service, c/o CCM Information Corp., 909 3rd Ave., New York, N. Y. 10022; remitting $2.00 for microfiche or $5.00 for photocopies. Advance payment is required. Make check payable to: CCMIC-NAPS.