complexes are compared. Thus, while e_σ and e_π of pyridine are significantly different from those of pyrazole and 2-methylimidazole, the parameters obtained for the chloride and bromide complex of each amine are very similar, and what differences do occur can probably be ascribed to slight changes in the Ni–N bond lengths.

The order of σ-antibonding power of the ligands (assuming average values for the halide ions) is 2-methylimidazole $\sim$ pyrazole $>$ pyridine $>$ thiourea $>$ chloride $>$ bromide, while the π-antibonding order is 2-methylimidazole $\sim$ pyrazole $>$ thiourea $>$ pyridine $\sim$ chloride $>$ bromide. These series represent the σ- and π-donor properties of the ligands toward nickel(II) at what are probably their usual bond distances. It is interesting that pyridine behaves as a comparatively weak π donor. For pyridine $e_\pi/e_\sigma \approx 0.125$, while for the other in-plane ligands this ratio is 0.2–0.25. The magnitude of e_π depends upon interactions with empty antibonding ligand orbitals as well as with filled bonding orbitals.[14] The former interactions produce a negative contribution to e_π, so that it is possible that the small value of e_π for pyridine is due to the presence of comparatively low-lying π-antibonding orbitals in this ligand. However, as has been mentioned, if the π-bonding effect of the amine groups is not symmetrical about the Ni–N bond directions, it is possible that e_π has been somewhat overestimated for 2-methylimidazole and pyrazole.

The separation between the e_g and t_{2g} orbitals in an octahedral complex is given[14] by $\Delta = 3e_\sigma - 4e_\pi$. The metal ion in $N(CH_3)_4NiBr_3$ is surrounded by a distorted octahedral array of bridging bromide ions at a mean Ni–Br distance of 2.56 Å.[30] The relevant overlaps using the $(Ni^+)(Br^-)$ wave functions[27] are $S_\sigma = 0.0766$ and $S_\pi = 0.0291$, and using eq 2 with the mean value of $K = 448$ kK found for the three bromide complexes a value of $\Delta = 6.4$ kK is estimated for $N(CH_3)_4NiBr_3$, which compares well with the value of $\Delta = 6.3$ kK observed experimentally.[30] The bonding parameters found for the terminal bromide groups in the complexes studied here are therefore in good agreement with the Δ value in the octahedral nickel bromide chromophore containing bridging halide ions.

Conclusions

The angular overlap model apparently provides a useful framework within which to interpret the excited-state energies of tetragonally distorted nickel halide complexes. It will be interesting to see whether this model can be extended to similar complexes with other metal ions and also to compounds with ligands such as $-NO_2$ and $-CN$ which are expected to have quite different bonding properties from those discussed here.

Acknowledgments.—The author is grateful to Dr. D. M. L. Goodgame for a gift of samples of bromotetrakis(2-methylimidazole)nickel(II) bromide and chlorotetrakis(2-methylimidazole)nickel(II) chloride and to Dr. A. Skapski and Dr. D. M. L. Goodgame for communicating the results of the crystal structure determination prior to publication. The receipt of an Imperial Chemical Industries Fellowship for 1968–1970 and a Queen Elizabeth II Fellowship for 1971 is gratefully acknowledged.

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CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, NUCLEAR RESEARCH CENTRE-NEGEV, BEER-SHEVA, ISRAEL,
AND THE UNIVERSITY OF THE NEGEV, BEER-SHEVA, ISRAEL

Trivalent Nickel. I. A Pulse Radiolytic Study of the Formation and Decomposition of the Ammoniacal Complex in Aqueous Solution

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The oxidation of the $Ni^{II}(NH_3)_n$ complex by NH_2 radicals in aqueous solutions yields an unstable trivalent nickel complex. The specific rate of this reaction is 1×10^7 M^{-1} sec^{-1}. The absorption spectrum of the trivalent complex was measured. The mechanism of disappearance of the trivalent complex is *via* a second-order reaction with $2k \leq 3.5 \times 10^7$ M^{-1} sec^{-1}. The specific rate of the reaction $OH + NH_3 \rightarrow NH_2 + H_2O$ at pH 11.3 is 2.4×10^7 M^{-1} sec^{-1}. The specific rate of oxidation of hydrazine by the trivalent nickel complex is 4×10^6 M^{-1} sec^{-1}.

The preparation of different trivalent nickel complexes, both in the solid state and in solutions in organic solvents has been recently described.[1-14] On the other hand it has been argued that in many of these complexes the oxidation site is on the ligands and not on the central nickel ion.[15,16] It seems to us that enough evidence

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exists in the literature to prove that at least the oxidized form of nickel complexes with saturated aliphatic amines do contain a central nickel ion in its trivalent oxidation state.[1,2,7,8]

All the known trivalent nickel complexes are unstable in aqueous solutions, with the possible exception of the dioxime complexes in strong alkaline solutions.[17] However, it has been suggested that trivalent nickel complexed to ethylenediamine is formed as an intermediate in the electrocatalytic oxidation of ethylenediamine on platinium electrodes.[18] As the half-wave potential of the latter oxidation wave is less positive than that for the corresponding copper complex,[19] we hoped that the chemical properties of trivalent ammino-nickel complexes might also be studied by the pulse radiolytic method.[20]

We have decided to study first the absorption spectrum, and the mechanism of formation and decomposition of the ammoniacal complex of trivalent nickel. The reason for this choice is that it is highly unlikely that a site of oxidation other than on the nickel ion exists in this complex. The results clearly indicate the formation of an unstable oxidized complex.

Experimental Section

All solutions were prepared from triply distilled water and AR grade reagents. The procedure of preparation of the samples, irradiation, observation of the optical changes, and calculation of the specific rate constants have been identical with those described earlier in detail.[21,22] The pulse radiolytic experiments were carried out using 0.1–1.3 μsec, 5 MeV, 200 mA pulses from the linear accelerator at the Hebrew University of Jerusalem. The dose per pulse has been (1–10) × 10^{19} eV $l.^{-1}$. The formation and disappearance of the intermediates were followed at 300 nm unless otherwise stated, the irradiation cell was 4 cm, and the analyzing light traveled three times through the cell.

The absolute molar absorption coefficients were determined by pulse radiolyzing, under exactly identical conditions, a standard solution, the solution to be analyzed, and the standard solution once again. The standard solution chosen was 1×10^{-3} *M* $K_4Fe(CN)_6$ saturated with N_2O. The yield of $Fe(CN)_6^{3-}$ was assumed to be 5.5, though a somewhat higher yield is possible,[23] and $\epsilon_{4200}(Fe(CN)_6^{3-})$ 1000 M^{-1} cm^{-1} was used. (The yields of the intermediates were calculated from the known yields of the primary radicals formed and their known specific rates of reaction with the solutes.) The accuracy of ε thus determined was ±15%.

Results and Discussion

The radiolysis of water may be described by

$$H_2O \xrightarrow{\gamma,e^-} e^-_{aq},\ H,\ OH,\ H_2,\ H_2O_2,\ H_3O^+ \qquad (1)$$

the yields of the products in neutral solutions being: $G_{e^-_{aq}} = 2.6$, $G_{OH} = 2.65$, $G_H = 0.6$, $G_{H_2O_2} = 0.75$, and $G_{H_2} = 0.45$. (The "*G* value" is defined as the number of molecules of product formed by the absorption of 100 eV by the sample.) N_2O-saturated solutions were used in order to suppress the reactions of e^-_{aq} and to increase the yield of OH radicals. The hydrated electron reacts with N_2O according to[24,25]

$$N_2O + e^-_{aq} \xrightarrow{k_2} N_2 + O^-;\ k_2 = 5.6 \times 10^9\ M^{-1}\ sec^{-1} \qquad (2)$$

$$O^- + H_2O \rightleftarrows OH + OH^- \quad pK_{OH} = 11.8 \pm 0.2 \qquad (3)$$

In neutral and alkaline solutions saturated with N_2O, 2×10^{-2} *M*, the yield of OH is therefore increased to $G_{OH} \simeq 5.5$. (A somewhat higher yield is plausible due to the effect of N_2O on G_{H_2}.[23])

Solutions containing (1–10) × 10^{-4} *M* $NiSO_4$ and 0.67 *M* NH_3 at pH = 11.3 ± 0.1 and saturated with N_2O have been irradiated. The formation of a transient absorbing species with a half-life of several milliseconds was observed. The spectrum of this transient, $\lambda_{max} = 295 \pm 5$ nm, $\epsilon_{max} = 1400 \pm 300\ M^{-1}\ cm^{-1}$, which is believed to be $Ni^{III}(NH_3)_q$ (see below) is shown in Figure 1. [The subscript *q* is used as the number of the ligands in the product complex and is unknown. It is assumed that all the forms of $Ni^{II}(NH_3)_n$ existing in the solution, which are mainly *n* = 4, 5, and 6, react with the same rate constants. This is naturally an approximation, thus the observed specific rate constant for this reaction is a weighted average of the specific rate constants of the three reactions occurring. The subscript *n* is used for the reactant and the subscript *q* for the products though no evidence for a change in *n* during the reactions was obtained.] The study could not be extended beyond 260 nm due to the absorption by the solution. Nearly no transients were formed in solutions containing only 0.67 *M* NH_3 at pH 11.3 ± 0.1. The latter transients also disappeared within about 100 μsec.

The specific rate of reaction of e^-_{aq} with $N^{II}(NH_3)_n$ in 0.67 *M* NH_3 solutions saturated with Ar was mea-

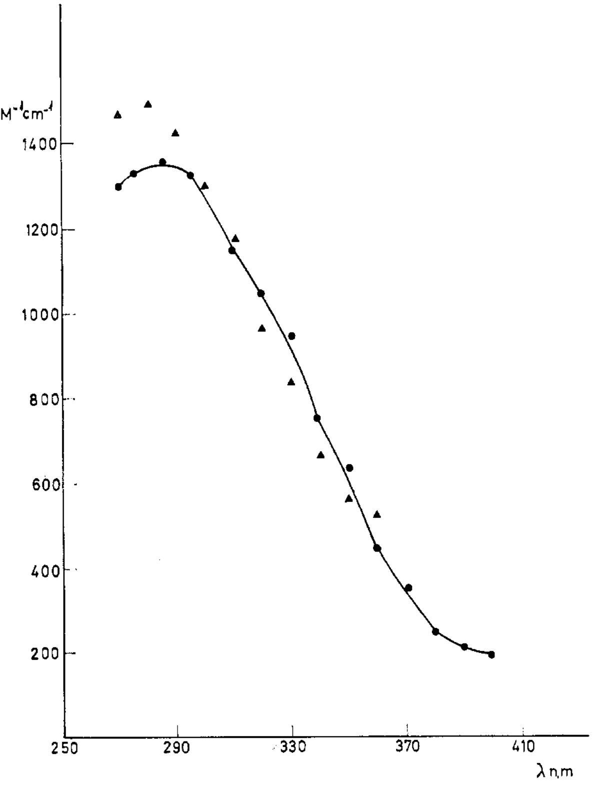

Figure 1.—Absorption spectrum of $Ni^{III}(NH_3)_q$. All solutions contained 0.67 *M* NH_3 at pH 11.3 ± 0.1 and were N_2O saturated. The dose was 900 rads/pulse: ▲, 2×10^{-5} *M* $NiSO_4$; ●, 1×10^{-3} *M* $NiSO_4$.

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sured by following the kinetics of disappearance of e^-_{aq} at 575 nm.

$$\mathrm{Ni^{II}(NH_3)_n + e^-_{aq} \longrightarrow Ni^{I}(NH_3)_p} \quad (4)$$

The specific rate constant for this reaction was found to be $k_4 = (8.4 \pm 1.2) \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}$. Therefore, in a solution containing $(1–10) \times 10^{-4}\ M$ $NiSO_4$ and saturated with N_2O less than 8% of the e^-_{aq} react *via* reaction 4. Furthermore, this reaction should be over within less than 0.1 μsec, due to the high N_2O concentration. The formation of the transient on the other hand was relatively slow, the half-times of reaction observed being longer than 70 μsec. It has to be concluded that the transient observed is not the product of reaction 4.

It is also higly unlikely that the intermediate is formed by a reaction of H atoms with the solute, due to the following reasons. (a) The yield of H atoms under the conditions studied is less than 10% of the radical yield. Therefore the extinction coefficient measured for this intermediate, see below, would be much larger than that measured for $Ni^I(NH_3)_p$, see below, the most probable product of this reaction. (b) H atoms are known not to react with $Ni^{2+}{}_{aq}$[26] and there is no reason to assume that NH_3 ligands would enhance this reaction. (c) The half-life time of H atoms in solution at pH 11.30, due to the reaction $OH^- + H \rightarrow e^-_{aq} + H_2O$[24] is less than 10 μsec, whereas the intermediate was formed much slower.

The relative long reaction half-time for the formation of the transient seemed also to exclude the possibility that it is formed *via* the reaction

$$\mathrm{OH + Ni^{II}(NH_3)_n \longrightarrow Ni^{III}(NH_3)_q + OH^- + (n - q)NH_3} \quad (5)$$

as the reaction

$$\mathrm{OH + OH \longrightarrow H_2O_2};\ 2k_6 = 1 \times 10^{10}\ M^{-1}\ \mathrm{sec}^{-1}\ {}^{24} \quad (6)$$

would effectively compete under these conditions with reaction 5. It seemed plausible that the reaction

$$\mathrm{NH_2 + Ni^{II}(NH_3)_n + H_2O \longrightarrow Ni^{III}(NH_3)_q + (n - q + 1)NH_3 + OH^-} \quad (7)$$

leads to the formation of the intermediate observed.

We have measured, therefore, by competition with NCS^-,[27] the specific rate of the reaction

$$\mathrm{OH + NH_3 \longrightarrow NH_2 + H_2O} \quad (8)$$

or

$$\mathrm{O^- + NH_3 \longrightarrow NH_2 + OH^-} \quad (8a)$$

$k = (2.7 \pm 0.4) \times 10^7\ M^{-1}\ \mathrm{sec}^{-1}$ has been obtained by this method. The measurements were carried out at pH 11.3. $k_{\mathrm{OH+NCS^-}} = 2.0 \times 10^{10}\ M^{-1}\ \mathrm{sec}^{-1}$ [28] has been used and corrected for the portion of O^- present at pH 11.3, $pK(OH) = 11.8 \pm 0.2$, which reacts significantly slower with NCS^-.[27]

We have checked this result by measuring k_8 also by competition with CH_3OH. The effect of NH_3 on the amount of CH_2O^- formed at pH 11.3 was measured and $k_{\mathrm{OH+CH_3OH}} = 5 \times 10^8\ M^{-1}\ \mathrm{sec}^{-1}$ was used.[24] This method yielded $k_8 = (2.0 \pm 0.4) \times 10^7\ M^{-1}\ \mathrm{sec}^{-1}$. It is concluded that $k_8 = (2.4 \pm 0.6) \times 10^7\ M^{-1}\ \mathrm{sec}^{-1}$. It has to be pointed out that k_8 has been measured at pH 11.3 ± 0.1 and no attempt was made to measure the relative contributions of reactions 8 and 8a. The measurement of these relative contributions is complicated due to the lack of an absorption of the NH_2 radicals in the region studied and the effects of the OH radical dissociation on its specific rates of reaction with NCS^- and CH_3OH.[24]

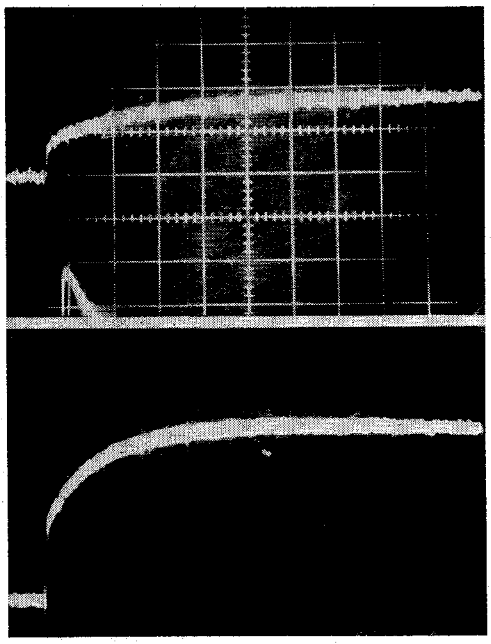

Figure 2.—Oscilloscope traces recording the formation of $Ni^{III}(NH_3)_q$. Pulse intensity 5×10^{19} eV/pulse. Abscissa 50 μsec/div, ordinate 50 mV/div, total light intensity 800 mV. Solution composition 0.67 M NH_3, pH 11.3 ± 0.1, N_2O saturated: top, $5 \times 10^{-4}\ M$ $NiSO_4$; bottom, $1 \times 10^{-3}\ M$ $NiSO_4$.

The value obtained in this study for k_8 is somewhat smaller than $k_8 = 7 \times 10^7\ M^{-1}\ \mathrm{sec}^{-1}$ reported in the literature.[29] The reasons for this disagreement are not clear as neither the pH nor the concentrations of NH_3 used were reported. We could not follow reaction 7 by observing the disappearance of the absorption due to NH_2 at 530 nm because of its very small extinction coefficient ($\epsilon_{525}{}^{\max} = 75\ M^{-1}\ \mathrm{cm}^{-1}$).[29]

It is clear, therefore, that in 0.67 M NH_3 solutions at pH 11.3 all the OH radicals react *via* reaction 8 within less than 1 μsec. The formation of the transient, which has a half-time of over 70 μsec (Figure 2), can therefore not be due to reaction 5. It is suggested that the transient is formed by reaction 7. The specific rate of reaction 7 was measured, the results are summarized in Table I. The results indicate a decrease in "k_7" with increasing concentration of $NiSO_4$, which is accompanied by a parallel increase in the final optical density due to the transient. This increase is believed to be due to the competition between reaction 7 and reaction 9, for which the specific rate of reaction $2k_9 = 3.5 \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}$ has been reported.[29]

$$\mathrm{NH_2 + NH_2 \longrightarrow H_2NNH_2} \quad (9)$$

More evidence supporting this competition will be given below. The increase in the optical density due to the transients when the $NiSO_4$ concentration is

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TABLE I

THE EFFECT OF $NiSO_4$ CONCENTRATION ON THE SPECIFIC RATES OF FORMATION AND DISAPPEARANCE OF $Ni^{III}(NH_3)_q$[a]

$[NiSO_4]$, M	Optical density[b]	k_7, M^{-1} sec^{-1} [c]	$2k_{10}$, M^{-1} sec^{-1} [d]
5×10^{-5}	0.006	3.6×10^8	3.0×10^8
1×10^{-4}	0.012	1.5×10^8	2.8×10^8
2×10^{-4}	0.023	6.8×10^7	2.3×10^8
5×10^{-4}	0.048	2.2×10^7	9.6×10^7
1×10^{-3}	0.093	1.0×10^7	5.2×10^7
2×10^{-3}	0.140	9.9×10^6	3.5×10^7

[a] All solutions contained 0.67 M NH_3 at pH 11.3 ± 0.1 and were N_2O saturated. The pulse intensity was 5×10^{19} eV l.$^{-1}$. [b] Values for a typical set of experiments. The optical density given is of the plateau formed after the formation reaction ended. [c] The observed specific rates of reaction without correction for the contribution of reaction 9. The error limit is ±15%. [d] The observed specific rates of reaction without correction for the contribution of the reaction with hydrazine (see text).

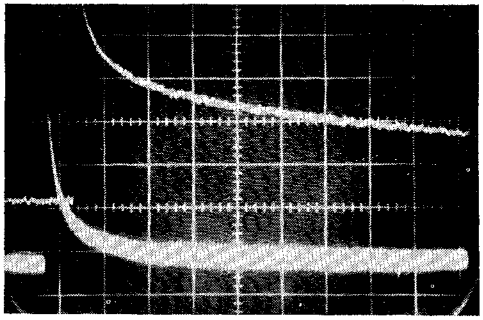

Figure 3.—Oscilloscope trace recording the disappearance of $Ni^{III}(NH_3)_q$ in Ar-saturated solutions. Pulse intensity 5×10^{19} eV/pulse. Solution composition is 0.67 M NH_3, 1×10^{-3} M $NiSO_4$, with pH 11.3 ± 0.1, Ar saturated. Total light intensity 800 mV. Upper trace: abscissa 50 μsec/div, ordinate 100 mV/div. Lower trace: abscissa 5 msec/div, ordinate 20 mV/div.

increased from 1 to 2×10^{-3} M is probably due, at least in part, to an increase in the yield of $Ni^I(NH_3)_p$ formed in reaction 4. It will be shown below that $\epsilon_{300}[Ni^I(NH_3)_p] > \epsilon_{300}[Ni^{III}(NH_3)_q]$. It is concluded that $k_7 = (1.0 \pm 0.2) \times 10^7$ M^{-1} sec^{-1}. The results do not rule out the possibility that reaction 5 also contributes to the formation of $Ni^{III}(NH_3)_q$. If the rate of reaction 5 is higher than 5×10^9 M^{-1} sec^{-1} it is expected to compete with reaction 7 when the $NiSO_4$ concentration exceeds 5×10^{-4} M. We could not check this point by decreasing the NH_3 concentration due to precipitation of nickel hydroxide. The results do, however, indicate that reaction 5 is fast; this is deduced from the increase in the absorption formed during the pulse when the $NiSO_4$ concentration is increased (Figure 2). This increase in absorption is larger than that expected to originate from the parallel increase in the yield of $Ni^I(NH_3)_p$.

We believe, therefore, that it might be concluded that the precursor or the transient observed is the NH_2 radical. We tried to estimate the maximum absorption coefficient of the $Ni^{III}(NH_3)_q$ complex by comparing the absorption formed at 300 nm due to it in solutions of $(1–2) \times 10^{-3}$ M $NiSO_4$ and 0.67 M NH_3, saturated with N_2O, with that formed in a 1×10^{-3} M $K_4Fe(CN)_6$ solution also saturated with N_2O at 420 nm. The measurements are complicated by the contribution of $Ni^I(NH_3)_p$ to the absorption at 300 nm. The absorption coefficient of the latter complex was determined by following the absorption formed within 10 μsec from the pulse, in solutions saturated with Ar and containing $(2–10) \times 10^{-5}$ M $NiSO_4$ and 0.67 M NH_3 as $\epsilon_{300}[Ni^I(NH_3)_p] = 2000 \pm 400$ M^{-1} cm^{-1}. The value of $\epsilon_{300}[Ni^I(NH_3)_p]$ was used to correct the contributions of the monovalent nickel complex to the absorption formed in N_2O-saturated solutions. $\epsilon_{300}[Ni^{III}(NH_3)_q] = 1300 \pm 300$ M^{-1} sec^{-1} has been thus determined.

The mechanism of disappearance of the $Ni^{III}(NH_3)_q$ complex formed in N_2O-saturated solutions was studied. It was found that the reaction obeys a second-order rate law. The specific rates of reaction measured are summarized in Table I. The results clearly indicate a decrease in the specific rate of reaction with the increase in $NiSO_4$ concentration. As the ammonia concentration in all cases was much higher than the nickel concentration the increase in the latter is not expected to change the composition of the $Ni^{III}(NH_3)_q$ complex. The only effect of the increase in the nickel concentration seems to be a decrease in the hydrazine yield due to the competition between reactions 7 and 9. (A rough calculation shows that the decrease in k_7 with the increase in Ni^{2+} concentration is in agreement with the expected values based on k_7 and k_9.[29]) It seemed therefore plausible that the increased rate of disappearance is due to a reaction between the trivalent nickel complex and hydrazine. We have measured the effect of added hydrazine on the mechanism of disappearance of the $Ni^{III}(NH_3)_q$ complex. The solutions used contained $(1–2) \times 10^{-3}$ M $NiSO_4$, $(1–5) \times 10^{-4}$ M H_2NNH_2, 0.67 and M NH_3 and were N_2O saturated. (These solutions were stable and over 90% of the hydrazine is uncomplexed.)[30] It was found that under these conditions the disappearance mechanism was changed to pseudo first order, the specific rate of reaction being $k_{Ni^{III}(NH_3)_q + H_2NNH_2} = (4 \pm 1) \times 10^6$ M^{-1} sec^{-1}. This result explains the effect of nickel concentration on the rate of disappearance of the trivalent nickel complex. It is concluded that the reaction

$$2Ni^{III}(NH_3)_q \longrightarrow 2Ni^{II}(NH_3)_n + \text{oxidation products} \quad (10)$$

(probably H_2O_2 or H_2NNH_2) has a specific rate of reaction $2k_{10} < 3.5 \times 10^7$ M^{-1} sec^{-1} at pH 11.3 ± 0.1. It is plausible that $Ni^{II}(NH_3)_q + Ni^{IV}(NH_3)_t$ are the primary products in reaction 10. $Ni^{IV}(NH_3)_t$ is, however, unstable in aqueous solutions, and no spectral evidence for its formation as an intermediate was obtained; we prefer therefore not to derive any conclusions concerning the detailed mechanism of reaction 10. An experiment to plot the disappearance reaction of the $Ni^{III}(NH_3)_q$, formed in N_2O-saturated solutions, as a first-order reaction indicates that this reaction is slower than 2×10^2 sec^{-1}. It is therefore concluded that the oxidation of the solvent H_2O or of the NH_3 ligand by the Ni(III) central atom is slower than 2×10^2 sec^{-1}.

The disappearance of the transients formed in Ar-saturated solutions is also governed by a second-order rate law but is much faster. The mechanism under these conditions is believed to be a combination of the reactions

$$Ni^I(NH_3)_p + Ni^{III}(NH_3)_q \longrightarrow 2Ni^{II}(NH_3)_n \quad (11)$$

$$2Ni^I(NH_3)_p \longrightarrow Ni^0 + Ni^{II}(NH_3)_n + (2p - n)NH_3 \quad (12)$$

as after the fast initial disappearance reaction about 25% of the absorption remained (Figure 3). This ab-

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sorption disappeared also by a second rate law with $2k \simeq 4 \times 10^7\ M^{-1}\ \mathrm{sec}^{-1}$ and is therefore attributed to $\mathrm{Ni^{III}(NH_3)}_q$. 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

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

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 $\mathrm{Ni^{II}(NH_3)}_n$ by $\mathrm{NH_2}$ radicals. The mechanism of formation and disappearance of this trivalent complex resemble those of the $\mathrm{Cu^{III}(NH_3)}_q$ complex.[20] It is of special interest to note that $\mathrm{NH_2}$ 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,
AND THE UNIVERSITY OF THE NEGEV, BEER-SHEVA, ISRAEL

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 $\mathrm{Ni^{III}(en)_3}$, 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 $\mathrm{Ni^{II}(en)_3}$–$\mathrm{Ni^{III}(en)_3}$, 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 $\mathrm{Ni^{III}(en)_3}$. As the results indicated that $\mathrm{Ni^{III}(en)_3}$ is more stable than $\mathrm{Cu^{III}(en)_2}$[8] we decided to study also the properties of $\mathrm{Ni^{III}Gly_3}$, Gly = glycine, and compare them with the corresponding copper complex. It was found that the decomposition reaction of $\mathrm{Ni^{III}Gly_3}$ 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, $\mathrm{enH_2SO_4}$, 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 $\mathrm{NiSO_4}$ and $\mathrm{enH_2SO_4}$ 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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