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Oxidation of Ascorbate by Ni(III) Complexes with Tetraaza-macrocyclic Ligands in Neutral Aqueous Solutions. A Pulse-Radiolysis Study

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Oxidation of Ascorbate by Ni(III) Complexes with Tetraaza-macrocyclic Ligands in Neutral Aqueous Solutions. A Pulse-Radiolysis Study

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The mechanisms and kinetics of oxidation of ascorbate, AH^-, by $Ni(III)L^i_{aq}$ and by $L^iNi(III)(HPO_4)_2^-$ complexes (L^1 = *meso*-(5,12)-7,7,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; L^2 = 1,8-dimethyl-1,3,6,8,10,13-hexaazacyclotetradecane) in neutral aqueous solutions have been investigated.

The oxidation of ascorbate by the $L^iNi(III)(HPO_4)_2^-$ and $Ni(III)L^1_{aq}$ proceeds *via* two consecutive reactions well separated in time. The products of the first reaction are the $A^{\cdot-}$ radical anion and the corresponding Ni(II) complex. The oxidations by the $L^iNi(III)(HPO_4)_2^-$ complexes proceed *via* the outer sphere mechanism, whereas the detailed mechanism of reaction of $Ni(III)L^1_{aq}$ cannot be determined. The rate of reaction decreases with the increase in the concentration of phosphate, thus indicating that $L^iNi(III)(HPO_4)(H_2O)^+$ and $L^iNi(III)OH^{2+}$ are stronger oxidizing agents than $L^iNi(III)(HPO_4)_2^-$.

The oxidation of ascorbate by $Ni(III)L^2_{aq}$ proceeds *via* three consecutive reactions which are well separated in time. Thus the results clearly point out that this process occurs *via* the inner sphere mechanism. The first transient observed is tentatively identified as $L^2(H_2O)Ni(II)(A^{\cdot-})^{2+}$, *i.e.*, an unexpected complex of the ascorbate anion radical. Also in this process the last transient observed is the $A^{\cdot-}$ anion radical. The stabilization of the ascorbyl radical in a transient complex might be of biological significance.

Keywords: Ascorbate; Nickel(III); Oxidation; Mechanism; Ascorbyl radial

INTRODUCTION

Ascorbic acid, a moderate reducing agent, is commonly considered as one of the most important anti-oxidant agents in the aqueous phase in biological systems. The biological protective properties of ascorbate against radical damage is due to the efficiency of ascorbate as a radical scavenger and the relative low reactivity of the radical anion $A^{\cdot-}$ formed in these reactions.

Metal complexes are increasingly implicated as having essential functions in many biological processes, especially in those involving radicals. Therefore the reaction of a variety of metal complexes with ascorbic acid was studied [1–8]. Most studies aimed at elucidating the electron transfer steps between the metal complexes and ascorbate were carried out at low pH-s where

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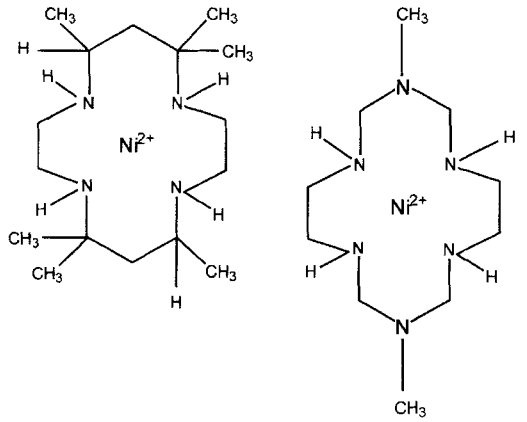
the metal ions: Fe^{3+}; Cu^{2+}; Mn^{3+} and Ni^{3+} are relatively stable. Very few studies were carried out near the neutral, physiological, pH [9].

Nickel is known to occur as a redox active central cation in a number of biological systems. In some of them the nickel has a planar coordination sphere, where the ligating atoms are nitrogen, sulfur and oxygen [10]. Synthetically produced Ni(II) complexes with macrocyclic ligands may therefore serve as a good models to the biological systems.

The Ni(II) complexes with macrocyclic ligands offer a wide range of redox potentials. However, relatively few studies concerning the kinetics and mechanisms of reaction of the corresponding Ni(III) complexes with reducing substrates were reported. McAuley *et al.*, showed using the stopped flow technique that Ni(III) complexes with tetraaza macrocyclic ligands (cyclam, *meso*-hexamethylcyclam, rac-hexamethylcyclam) oxidize ascorbic acid, hydroquinone and catechol in acidic media *via* single electron transfer reactions which proceed *via* the outer sphere mechanism [11a]. Banerjee *et al.* showed that ascorbate is oxidized also by $[Ni(III)L^3]^{2+}$, $[Ni(III)L^4]^{2+}$ and $[Ni(IV)L^5_2]^{2+}$, (HL^3 = 15-amino-3-methyl-4, 7, 10, 13-tetraazapentadec-3-en-2-oneoxime; H_2L^4 = 3,14-dimethyl-4,7,10,13-tetraazahexadec-3,13-diene-2,15-dionedioxime, HL^5 = 6-amino-3-methyl-4-aza hex-3-en-2-oneoxime), in the pH range 2.5-8.2, *via* the outer-sphere mechanism [11b]. In a recent study it was shown that the precipitate formed on the electrode upon electropolymerizing 1,5,8,12-tetraaza-2,4,9,11-tetramethylcyclotetradecinatonickel(II) on glassy carbon electrodes produces electrodes which electrocatalyze the oxidation of ascorbate in neutral aqueous solutions in the presence of phosphate anions [11c].

It seemed therefore of interest to study the kinetics and mechanisms of reaction of $Ni(III)L^1$ and $Ni(III)L^2$, Schemes 1, with ascorbate at neutral pH's in the presence and absence of axial stabilizing ligands using the fast kinetic technique of pulse-radiolysis. The results clearly demonstrate that the mechanism of reaction changes upon slight changes in the complex structure.



L^1 L^2

SCHEME 1 The nickel macrocyclic complexes herein studied.

EXPERIMENTAL

Materials

L-ascorbic acid (A.R.-Sigma) and all other reagents were of A.R. grade and were used as received. The *meso*-stereo-isomers of the free ligand (L^1) and the perchlorate salt of its nickel(II) complex – $Ni(II)L^1(ClO_4)_2$ were prepared according to the literature procedure [12]. $Ni(II)L^2(ClO_4)_2$ was prepared by template synthesis as previously described [13].

The solutions were handled by the syringe technique; pH determinations were carried out by immersing the glass electrode into the syringe while N_2O was bubbled through the solutions. A fresh stock solution of ascorbate was prepared every few hours by dissolving the solid in previously deaerated solutions. Aliquots of the ascorbate solution were injected into syringes containing deaerated solutions of all other solutes required for the experiment. All solutions containing $[Ni(II)L^1_{aq}]^{2+}$ were at pH 6.0 and those containing $[Ni(II)L^2_{aq}]^{2+}$ at pH 7.0. All experiments were carried out at room temperature (22 ± 1)°C.

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Irradiations

Pulse-radiolysis experiments were carried out using the Varian 7715 linear electron accelerator of the Hebrew University of Jerusalem. The pulse duration was 0.1–1.5 μs with a 200 mA current of 5 MeV electrons. The dose per pulse was 3–30 Gy. Irradiations were carried out in a 4 cm spectrosil optical cell, the analyzing light passing three times through the cell. A 150 W Xenon arc provided the analyzing light. The experimental setup was identical to that described earlier in detail [14].

For dosimetry an N_2O-saturated solution containing 1×10^{-3} M KSCN was used. The yield of $(SCN)_2^{\cdot -}$ was measured by using $\varepsilon_{475} = 7600\,M^{-1}cm^{-1}$ and the dose per pulse was calculated assuming $G(SCN)_2^{\cdot -} = 6.0$ [15] and an optical path of 12.3 cm. The dose per pulse was set so that the initial radical concentration was 2–20 μM. The value of the molar extinction coefficients calculated from the dosimetry measurements carry an error limit of ± 15% due to the scatter of the pulse intensity and uncertainties in G values.

Production of the $Ni(III)L^i(HPO_4)_2^-$ Complexes

These complexes were prepared in neutral N_2O saturated solutions containing: $(5-100) \times 10^{-5}$ M $Ni(II)L^{i\,2+}$, 5×10^{-3} M HCO_2^- and 0.02–0.3 M $H_nPO_4^{(3-n)-}$ *via* the following reaction sequence:

$$H_2O \xrightarrow{e^-} e_{aq}^-(2.65); H(0.60); OH(2.65); H_2(0.45); H_2O_2(0.75) \quad (1)$$

Where the values in brackets give the relative yields of the primary products.

$$e_{aq}^- + N_2O \rightarrow N_2 + {}^{\cdot}OH + OH^- \qquad k_2 = 8.7 \times 10^9\,M^{-1}s^{-1}\ [16] \quad (2)$$

$$HCOO^- + H^{\cdot}/{}^{\cdot}OH \rightarrow COO^{\cdot -} + H_2/H_2O\ k_3(H^{\cdot}/{}^{\cdot}OH) = 2.5/2.9 \times 10^8/10^9\,M^{-1}s^{-1}\ [16] \quad (3)$$

$$[Ni(II)L_{aq}^i]^{2+} + e_{aq} \rightarrow [Ni(I)L_{aq}^i]^+ \quad k_4(L^1) = 5.6 \times 10^{10}\,M^{-1}s^{-1}\ [17]$$
$$k_4(L^2) = \text{unknown but probably} \geq 10^{10}\ [16] \quad (4)$$

$$[Ni(II)L_{aq}^i]^{2+} + COO^{\cdot -} \rightarrow [Ni(I)L_{aq}^i]^+ + CO_2\ k_5(L^1) = 5.7 \times 10^9\,M^{-1}s^{-1}\ [17]\ k_5(L^2) = (1.5 \pm 0.3) \times 10^8\,M^{-1}s^{-1}(\text{this study}) \quad (5)$$

$$[Ni(I)L_{aq}^i]^+ + N_2O + H_2O \rightarrow [Ni(III)L_{aq}^i]^{3+} + 2OH^- + N_2\ k_6(L^1) = 3.9 \times 10^7 M^{-1}s^{-1}\ [17]$$
$$k_6(L^2) = (4.5 \pm 0.9) \times 10^7 M^{-1}s^{-1}(\text{this study}) \quad (6)$$

$$[Ni(III)L_{aq}^i]^{3+} + 2H_nPO_4^{(3-n)-} \leftrightarrow [Ni(III)L^i(HPO_4)_2]^- + (2n-2)H^+$$
$$K_7(L^1) = 2.3 \times 10^8\,M^{-2}\ [18a]$$
$$K_7(L^2) = 2.3 \times 10^7\,M^{-2}\ [19] \quad (7)$$

Thus all the primary radicals are transformed into the desired tervalent complexes.

Production of the $Ni(III)L^i_{aq}$ Complexes

As formate is also a good ligand of the tervalent complexes [18a, 19] the preparation of these complexes was performed *via* reactions (1), (2) and (8).

$$[Ni(II)L_{aq}^i]^{2+} + {}^{\cdot}OH \rightarrow [Ni(III)L_{aq}^i]^{3+} + OH^-$$
$$k_8(L^1) = 1.5 \times 10^9\,M^{-1}s^{-1}[20]$$
$$k_8(L^1) = 1.8 \times 10^9\,M^{-1}s^{-1}(\text{this study, measured indirectly by competition with } (SCN)_2^{\cdot -}) \quad (8)$$

This sequence has the disadvantage that some of the hydroxyl radicals react directly with ascorbate, yielding some $A^{\cdot -}$ radicals. In order of decreasing the yield of $A^{\cdot -}$ radicals thus formed $[Ni(II)L_{aq}^{2\,2+}] \geq 2[AH^-]$ and $[Ni(II)L_{aq}^{1\,2+}] \geq 5[AH^-]$ was maintained throughout this study, taking in account that $k(AH^- + {}^{\cdot}OH) = 4 \times 10^9\,M^{-1}s^{-1}$ [11a].

RESULTS AND DISCUSSION

Oxidation of Ascorbate by $[Ni(III)L^{i}(HPO_4)_2]^-$

The $[Ni(III)L^{i}(HPO_4)_2]^-$ complexes at neutral pHs are relatively long lived species [18,19]. When low concentrations of ascorbate are added to solutions of these complexes the life time of the tervalent nickel complexes is shortened considerably and two consecutive processes well separated in time are observed, Figure 1. The first process observed in both systems (L^1 and L^2) obeys a first order rate law, the rate of which depends linearly on the concentration of ascorbate, Figure 2. The rates of reaction thus obtained are summed up in Table I. The product of the first reaction observed is identified as the $A^{\cdot -}$ radical anion due to the following reasons:

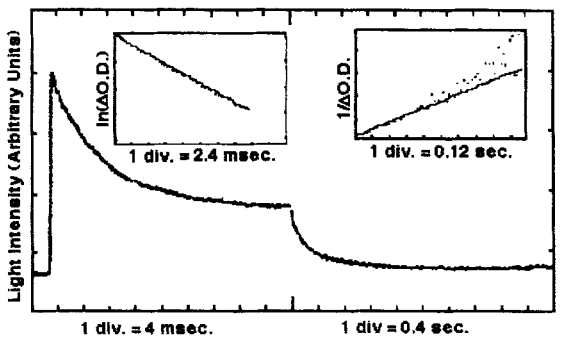

FIGURE 1 Oxidation of ascorbate by $(Ni(III)L^1(HPO_4^{2-})_2)^-$. Solution composition: 1×10^{-3}M ascorbate; 1×10^{-3}M NiL^{12+}; 5×10^{-3}M HCOONa; 0.02M phosphate; N_2O saturated; pH 7.0. Measured at 300nm; Pulse intensity 25Gray/pulse.

(A) Its absorption spectrum has $\lambda_{max} = 360$nm. *i.e.*, identical with the known spectrum of the $A^{\cdot -}$ radical anion [11a].

(B) The kinetics of its disappearance obey a second order rate law with a rate constant fitting the known rate of the reaction [11a]:

$$2A^{\cdot -} + H^+ \rightarrow AH^- + A$$
$$k_9 = (1.2 \pm 0.3) \times 10^6\ M^{-1}s^{-1} \qquad (9)$$

Therefore it is concluded that the first reaction observed is the oxidation of ascorbate by the

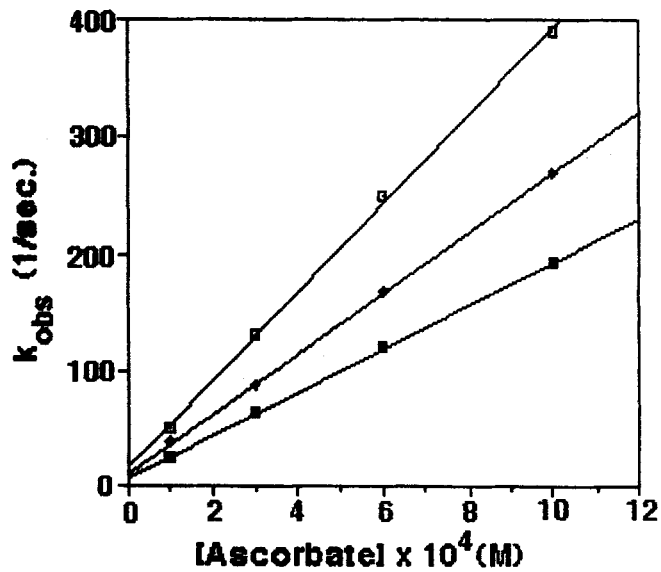

FIGURE 2 Dependence of the observed rate of the first process on the ascorbate concentration, the case of $[Ni(III)L^1(HPO_4^{2-})_2]^-$. Solution composition: 1×10^{-3}M NiL^{12+}; 5×10^{-3}M HCOONa; N_2O saturated; pH 7.0, ⊡ 0.02M phosphate, ◆ 0.04M phosphate, ■ 0.08M phosphate, * At high concentrations of ascorbate the ratio $[Ni(II)L^1{}_{aq}{}^{2+}] \geq 5[AH^-]$ could not be maintained as already mentioned, though the results obtained still fit the linear dependence described.

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nickel(III) complexes:

$$[Ni(III)L^i(HPO_4)_2]^- + AH^- \rightarrow [Ni(II)L^i(HPO_4)_2]^{2-} + A^{\cdot -} + H^+$$
$$k_{10} = \text{see Table I} \qquad (10)$$

The $[Ni(II)L^i(HPO_4)_2]^{2-}$ is unstable and decomposes into $[Ni(II)L^i]^{2+} + 2HPO_4^{2-}$.

The dependence of the rate of reaction on the phosphate concentration suggests that the complexes: $[Ni(III)L^i_{aq}]^{3+}$,[1] and $[Ni(III)L^i(HPO_4)(H_2O)]^+$ are stronger oxidizing agents than $[Ni(III)L^i(HPO_4)_2]^-$ in accordance with expectations. However the fact that the rates of reaction increase less than linearly with $[phosphate]^{-1}$ points out that the complexes $[Ni(III)L^i(HPO_4)_2]^-$ are major participants in these oxidation reactions.

The results thus suggest (ruling out the possibility that a hepta-coordinated intermediate is formed, which is improbable due to the bulkiness of the reactants involved) that the mechanism of reaction involves an outer sphere electron transfer step. Using the Marcus cross correlation ($E_{1/2}[Ni(III)L^i(HPO_4)_2]^-/Ni(II)L^i = 0.90\,V$ at 0.04 M phosphate [19]; and 0.77 V at 0.03 M phosphate [18a, 19] for L^1 and L^2 respectively,; $E°(AH^-/A^{\cdot -}) = 0.68\,V$ [11a]; $k_{22}(AH^-/A^{\cdot -}) = 1 \times 10^4 M^{-1}s^{-1}$ [11a] and $k_{12} = k_{10}$ (see Tab. I) one obtains for the self exchange rates of the nickel complexes the following values:

$$k_{11}([Ni(III)L^1(HPO_4)_2]^-/[Ni(II)L^1]^{2+}) = (9.3 \pm 1.9) \times 10^3 M^{-1}s^{-1}$$
$$k_{11}([Ni(III)L^2(HPO_4)_2]^-/[Ni(II)L^2]^{2+}) = (2.5 \pm 0.5) \times 10^3 M^{-1}s^{-1}$$

These values are in good agreement with those previously reported for octahedral complexes of tervalent nickel with tetra-aza-macrocyclic and with linear ligands [11b, 25].

TABLE I Dependence of the rates of reaction on phosphate concentration

[Phosphate] (M)	k (M^{-1} sec^{-1})
NiL^1	
0.02	3.8×10^5
0.04	2.6×10^5
0.08	1.9×10^5
NiL^2	
0.03	5.3×10^4
0.30	3.3×10^4

Oxidation of Ascorbate by $[Ni(III)L^i_{aq}]^{3+}$ Complexes

A. The Case of $[Ni(III)L^1_{aq}]^{3+}$

When $[Ni(III)L^1_{aq}]^{3+}$ is reduced by ascorbate ions in the absence of a stabilizing axial anionic ligand also two consecutive processes, well separated in time, are observed. The first process obeys a first order rate law with a rate constant depending linearly on the concentration of ascorbate. The product of this reaction is identified as the radical anion $A^{\cdot -}$. The first reaction observed is therefore:

$$[Ni(III)L^1_{aq}]^{3+} + AH^- \rightarrow [Ni(II)L^1_{aq}]^{2+} + A^{\cdot -} + H^+$$
$$k_{10a} = (4.9 \pm 0.6) \times 10^6 M^{-1}s^{-1} \qquad (10a)$$

The results in this system do not enable a decision concerning the question whether reaction (10a) proceeds *via* the outer- or the inner-sphere mechanisms as less steric hindrance is involved and the ligand exchange rate of the Jahn-Teller distorted tervalent low spin nickel complexes is relatively high [26]. If it is assumed

[1] It should be noted that in neutral solutions $[Ni(III)L^i_{aq}]^{3+}$ is probably $[Ni(III)L^i(OH)]^{2+}$ or $[Ni(III)L^i(OH)_2]^+$ or $[Ni(III)L^i(OH)(H_2O)]^{2+}$ [26, 27]. The exact nature of these complexes in neutral solution can unfortunately not be elucidated *via* potentiometric measurements, as suggested by one of the reviewers, as these tervalent nickel complexes are short lived in neutral solutions [18a, 20, 24, 26, 27].

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that reaction (10a) proceeds *via* the outer-sphere mechanism then k_{11}, the self exchange rate for the nickel complex can be calculated in an analogous manner to the previous section. (using: $E°([Ni(III)L^1_{aq}]^{3+}/[Ni(II)L^1_{aq}]^{2+} = 0.94\,V$ [24] – after correcting to pH 7.0; $E°(AH^{\cdot}/A^{-}) = 0.68\,V$ [11a]; $k_{22}(AH^{\cdot}/A^{-}) = 1 \times 10^4\,M^{-1}s^{-1}$; $k_{12} = k_{10a} = (4.9 \pm 0.6) \times 10^6\,M^{-1}s^{-1}$). Thus k_{11} ($[Ni(III)L^1_{aq}]^{3+}/([Ni(II)L^1_{aq}]^{2+}) = 3.0 \times 10^5\,M^{-1}\,s^{-1}$ is obtained. This rate constant is by at least one order of magnitude higher than those obtained for the phosphate complexes and those reported for a variety of Ni(III) complexes in the literature [25]. This result might indicate that reaction (10a) proceeds *via* the inner-sphere mechanism, see next section. However one should remember that all the other values were obtained for Ni(III) complexes with an octahedral coordination sphere whereas $[Ni(III)L^1_{aq}]^{3+}$ might have another coordination sphere, probably a square pyramidal [26, 27].

B. The Case of $[Ni(III)L^2_{aq}]^{3+}$

When $[Ni(III)L^2_{aq}]^{3+}$ is reduced by ascorbate ions in the absence of a stabilizing axial anionic ligand three consecutive processes, well separated in time, are observed, Figure 3. (No information regarding the nature of $[Ni(III)L^2_{aq}]^{3+}$ in neutral aqueous solutions is available, however as all complexes of L^2 are similar to those of cyclam one can assume that this is so also in the present case, for the cyclam complex it was proposed that the tervalent complex is an octahedral one with one hydroxo ligand at this pH [27].) The first process during which the typical absorption band of Ni(III) complexes disappears, Figure 4, obeys a first order rate law with a rate depending linearly on the concentration of ascorbate, Figure 5. The second process obeys a first order rate law the rate of which is independent of the concentration of all solutes present. The last transient is again identified as the radical anion $A^{\cdot -}$. These results clearly point out that in this system the redox process occurs via the inner-sphere

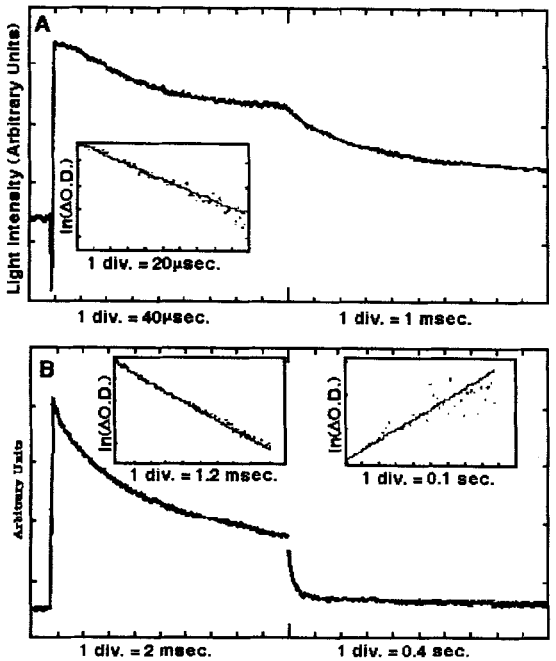

FIGURE 3 Oxidation of ascorbate by $[Ni(III)L^2_{aq}]^{3+}$. Solution composition: 4×10^{-4}M ascorbate; 1×10^{-3}M; $NiL^{2\,2+}$; N_2O saturated; pH 6.0, Measured at 300 nm; Pulse intensity 25 Gray/pulse, A. The first two processes attributed to reactions (15) and (16). B. The second and third processes observed attributed to reactions (16) and (9).

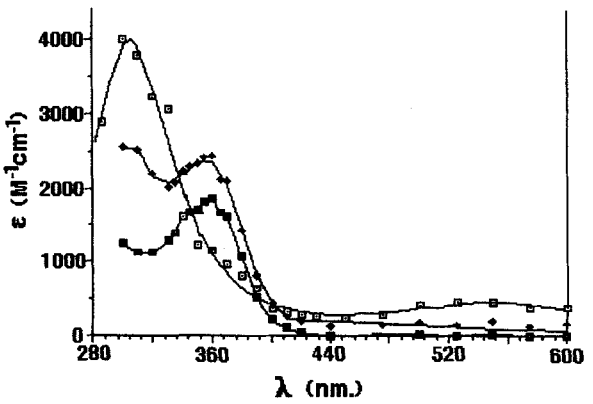

FIGURE 4 The UV-vis spectra of the intermediates obtained when $[Ni(III)L^2_{aq}]^{3+}$ oxidizes ascorbate. Solution composition: 4×10^{-4}M ascorbate; 1×10^{-3}M; NiL^{22+}; N_2O saturated; pH 6.0, □ First intermediate – measured 40 μsec. after the pulse, ◆ Second intermediate – measured 0.2 msec. after the pulse, ■ Third intermediate – measured 20 msec. after the pulse.

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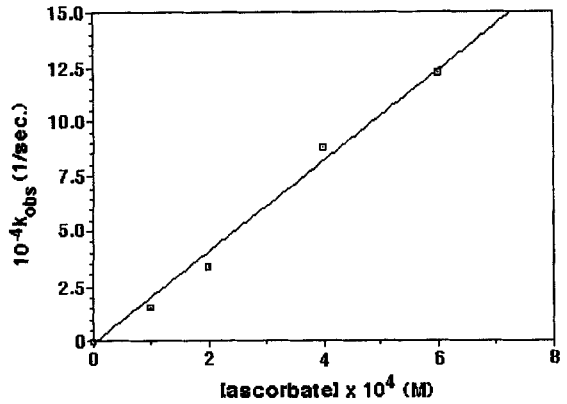

FIGURE 5 Dependence of the observed rate of the first process on the ascorbate concentration, the case of $[Ni(III)L^2_{aq}]^{3+}$. Solution composition: 1×10^{-3} M $NiL^{1\,2+}$; 5×10^{-3} M HCOONa; N_2O saturated; pH 6.0.

mechanism. Two alternative mechanisms can be proposed:

$$[Ni(III)L^2_{aq}]^{3+} + AH^- \rightarrow [L^2Ni(III)A]^+_{aq} + H^+ \qquad (13)$$
$$k_{13} = (2.1 \pm 0.5) \times 10^8 M^{-1}s^{-1}$$

$$[L^2Ni(III)A]^+_{aq} \rightarrow [Ni(II)L^2_{aq}]^{2+} + A^{\cdot -} \qquad (14)$$
$$k_4 = (5.0 \pm 1.0) \times 10^2 s^{-1}$$

$$2A^{\cdot -} + H^+ \rightarrow AH^- + A \qquad (9)$$
$$k_9 = (1.2 \pm 0.3) \times 10^6 M^{-1}s^{-1}$$

$$[Ni(III)L^2_{aq}]^{3+} + AH^- \rightarrow [L^2Ni(II)(A^{\cdot -})]^+_{aq} + H^+ \qquad (15)$$
$$k_{15} = (2.1 \pm 0.5) \times 10^8 M^{-1}s^{-1}$$

$$[L^2Ni(II)(A^{\cdot -})]^+_{aq} \rightarrow [Ni(II)L^2_{aq}]^{2+} + A^{\cdot -} \qquad (16)$$
$$k_{16} = (5.0 \pm 1.0) \times 10^2 s^{-1}$$

$$2A^{\cdot -} + H^+ \rightarrow AH^- + A \qquad (9)$$
$$k_9 = (1.2 \pm 0.3) \times 10^6 M^{-1}s^{-1}$$

SCHEME 3

The kinetic data do not allow differentiating between these two possibilities. However the spectrum of the second transient, Figure 4, differs significantly from those of all known Ni(III) complexes with tetraaza-macrocyclic ligands [25] and is similar to that of the radical anion $A^{\cdot -}$, Figure 4 [22]. It is therefore tempting to propose that Scheme 3 fits the mechanism of the oxidation of ascorbate by $[Ni(III)L^2_{aq}]^{3+}$. Thus it is proposed that the second transient observed is the unexpected complex $[L^2Ni(II)(A^{\cdot -})]^+_{aq}$ with the anion radical as an axial ligand.

In view of these results and the observation that $k_{11}([Ni(III)L^1_{aq}]^{3+}/([Ni(II)L^1_{aq}]^{2+})$ is significantly larger than expected it is reasonable to propose that also reaction (10a) proceeds *via* the inner-sphere mechanism but that in this system the rate of the ligand exchange step, the reaction equivalent to reaction (16) is faster than the rate of formation of $[L^1Ni(II)(A^{\cdot -})]^+_{aq}$.

CONCLUDING REMARKS

Several general conclusions seem to emerge from this study:

(1) The results clearly point out that phosphate as an axial ligand slows down considerably the rate of oxidation of ascorbate by the tervalent complexes studied. The effect is larger for $[Ni(III)L^2_{aq}]^{3+}$ than for $[Ni(III)L^1_{aq}]^{3+}$. Phosphate as a ligand also changes the mechanism of reaction from inner-sphere to outer-sphere at least in the case of $[Ni(III)L^2_{aq}]^{3+}$.

(2) The detection of $A^{\cdot -}$ as the product in all systems studied indicates that the rate of reduction of the tervalent complexes by it, is not significantly faster than the rate of oxidation of ascorbate by the same complexes.

(3) The observation of the tnsient complex $[L^1Ni(II)(A^{\cdot -})]^+_{aq}$ is relatively long lived

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suggests that the ascorbyl radical, $A^{\cdot -}$, might be stabilized by a variety of transition metal complexes. This finding, if correct, might be of biological significance.

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