Inorg. Chem. **1982**, *21*, 1837–1845 **1837**

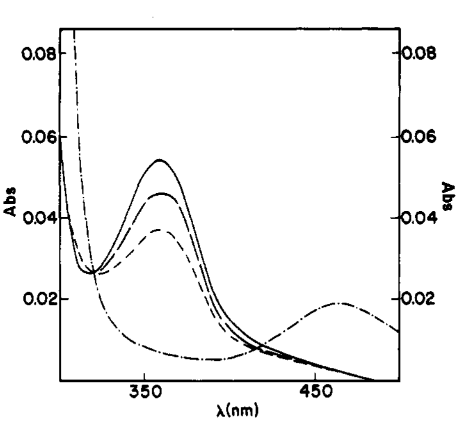


Figure 5. Differential spectra after γ-ray irradiations of 1.8×10^{-4} M $Ni^{II}(CR+4H)$ and N_2O-saturated solutions at various pHs: (—) pH 10; (– –) pH 5.5; (- - -) pH 3.2; (–·–) spectrum of the starting material. Dosage = 8 krd; optical path = 1 cm.

complex at 360 nm and the absorption recorded after irradiation of N_2O-saturated solutions with a given dose. There must then be a contribution to this yield from both the ligand radical intermediate as well as the Ni(III) species. Addition of ·OH to the pyridine in reaction 4 provides no feasible pathway for generation of $Ni^{II}(CR+2H)$. It appears more likely then that hydrogen abstraction occurs essentially in position 2 or 12 (see Introduction); such ligand radicals could then disproportionate to give the $Ni^{II}(CR+2H)$ complex. At lower pH (neutral or acidic solution), the yield for Ni^{II}-(CR+2H) is lower than that at pH 10. This loss may be attributable to competitive reactions: ligand degradation or demetalation, for example, when the formation of the ligand radical from the Ni^{III} species is decreased by the increasing acidity of the solution.[4]

Conclusion

Both spectroscopic and kinetic data given here provide evidence that two types of initial intermediates, Ni(III) macrocyclics or Ni(II) ligand radicals, may be produced by ·OH attack on the group of CR complexes investigated. With use of differential reactivity toward oxygen it has been shown that, in the case of $Ni^{II}(CR\text{-}2H)$ and $Ni^{II}(CR+4H)$, ·OH attack can produce more than one type of intermediate in competing reactions. In the case of $Ni^{II}(CR+4H)$, product spectra suggest increased ring unsaturation best explained by formation of a ligand radical via hydrogen abstraction. The product spectra from ·OH reaction with $Ni^{II}(CR)$ do not suggest a similar pathway. The metal center oxidation is consistent with an inner-sphere mechanism, and the mode of attack on the complex appears to be influenced by the related parameters of ligand unsaturation and solvent binding in the axial positions.

Acknowledgment. The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-2237 from the Notre Dame Radiation Laboratory.

Registry No. $Ni^{II}(CR)(H_2O)_2$, 36515-22-7; $Ni^{II}(CR\text{-}2H)$, 47023-96-1; $Ni^{II}(CR+4H)$, 53537-59-0; ·OH, 3352-57-6.

Contribution from the Radiation Laboratory,
University of Notre Dame, Notre Dame, Indiana 46556

Chemical Kinetics of Nickel(III) Macrocyclic Complexes. Pulse Radiolysis Study of $Ni^{II}(CR+4H)$, $Ni^{II}(CR)$, and $Ni^{II}(CR\text{-}2H)$ in Aqueous Solutions of Br^- and CNS^-

P. MORLIERE and L. K. PATTERSON*

Received April 2, 1981

Oxidation of three closely related nickel(II) macrocyclic complexes $Ni^{II}(CR\text{-}2H)$, $Ni^{II}(CR)$, and $Ni^{II}(CR+4H)$ via anion radical reaction has been investigated by pulse radiolysis methods. While the initial oxidation products follow the form $Ni^{III}(L)(X^-)(H_2O)$, in agreement with previous studies (L = macrocyclic ligand; X^- = Br^-, SCN^-), pH- and anion-concentration-dependent behavior provides evidence indicating subsequent formation of several other complexes $Ni^{III}(L)(X^-)_2$, $Ni^{III}(L)(OH^-)(H_2O)$, $Ni^{III}(L)(OH^-)$, and $Ni^{III}(L)(OH^-)_2$. The kinetics for interconversion among these species have been measured and are found in several cases to exhibit reversible behavior. In those cases the associated equilibrium constants have been determined. The formation of $Ni^{III}(L)(X^-)_2$ may be seen to depend on the degree of macrocyclic unsaturation and character of the anion. With the exception of the fully unsaturated CR-2H ligand, $Ni^{III}(L)(OH^-)$ and $Ni^{III}(L)(OH^-)(H_2O)$ and $Ni^{III}(L)(OH^-)_2$ decay via ligand radical formation at neutral pH and higher. Steady-state radiolysis results indicate introduction of an additional double bond into the ligand. At low pH, anion-substituted Ni(III) species return almost quantitatively to their parent Ni(II) complexes.

Introduction

There are now several papers in the literature which report the oxidation of Ni(II) complexes by anion radicals, principally $Br^{-}{}_{2}$.[1-4] Such work has, to a degree, been motivated by increased interest in the chemistry of complexes exhibiting unstable oxidation states;[5] certain catalytic reactions as well as some biological processes are thought to involve intermediates with highly oxidized metal centers.[6]

The mechanism initiated by such oxidation has been shown to be complicated by the interaction of anion and central metal which extends well beyond the initial electron-transfer step. For example, in a recent report from our laboratory[4] con-

---

(1) Marathamuthu, P.; Patterson, L. K.; Ferraudi, G. *Inorg. Chem.* **1978**, *17*, 3157. (b) Ferraudi, G.; Patterson, L. K. *J. Chem. Soc., Chem. Commun.* **1977**, 755.

(2) Whitburn, M. D.; Laurence, G. S. *J. Chem. Soc., Dalton Trans.* **1979**, *1*, 139.

(3) Jaacobi, M.; Meyerstein, D.; Lilie, J. *Inorg. Chem.* **1979**, *18*, 429.

(4) Morliere, P.; Patterson, L. K. *Inorg. Chem.* **1981**, *20*, 1458.

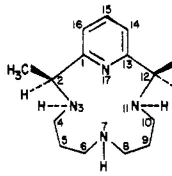
(5) Levason, W.; McAuliffe, C. A. *Coord. Chem. Rev.* **1974**, *12*, 151.

(6) Meyerstein, D. *Acc. Chem. Res.* **1978**, *11*, 43 and references therein.

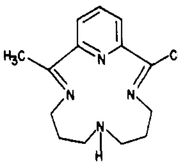
0020-1669/82/1321-1837$01.25/0

cerning Br^-_2 oxidation of $Ni^{II}(CR+4H)$ and subsequent chemistry of the $Ni^{III}(CR+4H)(H_2O)(Br^-)$ intermediates in acidic solution, it was shown that this species is in equilibrium with the fully aquated species, giving an equilibrium constant of 360 M^{-1}. As a consequence of this behavior the dominant species at low [Br^-], $Ni^{III}(CR+4H)(H_2O)_2$, disappears via a ligand radical with first-order decay, while at high [Br^-] the monobromo species disappears by second order to give a product not wholly characterized. Additionally, the binding of the anion markedly influences the behavior of absorption bands in the visible region, bands which reflect the symmetry of the complex. Ni(III) complexes like the parent compounds[7,8] may be characterized by a planar ligand; the remaining axial sites afford possible sites for anion binding. From such binding, alterations in symmetry can certainly occur. Further, the reaction mechanisms for the Ni(III) complexes reveal some pH dependence which may be most reasonably explained by a substitution of OH^- at the axial position for anions occupying those sites.

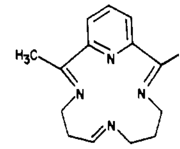
The overall redox chemistry in the macrocyclic complexes gives considerable evidence of dependence both on the nature of the anion radical and on the structure of the macrocyclic ligand. Here we present a comparative study of Ni(II) complexes involving three related ligands which differ by the degree of ring unsaturation: CR = 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene; CR-2H = 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,6,11,13,15-hexaene; CR+4H = 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene, α isomer.



CR+4H



CR



CR-2H

In aqueous solutions these Ni(II) complexes may or may not coordinate with the solvent. They are reported as a high-spin octahedral $Ni^{II}(CR)(H_2O)_2$, a low-spin square-planar $Ni^{II}(CR-2H)$, and a mixture of $Ni^{II}(CR+4H)(H_2O)_2$ with $N^{II}(CR+4H)$ in a ratio of about 1/1 at room temperature.[8] For brevity they will be written as $Ni^{II}(L)$. The degree to which water is bound at the central metal can be shown to correlate with rates of attack by anion radicals. The different anion radicals Br^-_2 and $(CNS)^-_2$ have been used; they differ markedly as oxidizers and as ligands.

This study has been directed toward characterizing the overall reaction mechanism in terms of (1) equilibrium behavior $Ni^{III}(L)(X^-)$ and aquated species, (2) transitions from planar to distorted ligand symmetry, (3) replacement of X^- by OH^- at the central metal ion, and (4) final product formation. It may be readily seen in the intercomparisons of these systems and the Br^-_2–$Ni^{II}(CR+4H)$ case[4] that the various processes within the overall oxidation mechanism can vary markedly with the choice of anion and ligand.

Experimental Section

Radiolytic Procedure. Optical pulse radiolysis measurements were made with a computerized system previously described.[9] Absorbance data are presented in dimensions of an extinction coefficient by the parameter $\Delta\epsilon'$ calculated from the expression

$$\Delta\epsilon' = (\mathrm{Abs})K/GD$$

where Abs is the absorbance for a given pulse, D the dose, and G the radiolytic yield. K is a calibration factor, chosen such that $\Delta\epsilon'$ for the $(SCN)^-_2$ anion radical in the same cell is equal to 7600 M^{-1} cm^{-1} at 472 nm in N_2O-saturated solutions containing 10^{-2} M SCN^-, with the assumption $G_{(SCN)^-_2} = 6.1$.[10] Static irradiations were performed with a ^{60}Co source calibrated by Fricke dosimetry.[11]

Material and Synthesis. The complexes were prepared as the perchlorate salts[12,13] $Ni^{II}(L)(ClO_4)_2$ according to literature procedures. Three recrystallizations were carried out from distilled water. The electronic and infrared spectra are in good agreement with data previously reported.[8,13] Other materials were of reagent grade and were used without further purification. Water for the radiolysis experiments and synthesis was obtained from a Milli-R015 Millipore filtering system. In the pH range 5–9, phosphate buffer was used, the pH being adjusted by addition of perchloric acid or sodium hydroxide; pH values outside this range were obtained with perchloric acid and sodium hydroxide.

Results and Discussion

Formation of Br^-_2 and $(SCN)^-_2$ Radicals via Water Radiolysis. The products of water radiolysis, their yields, and their redox character have been previously discussed.[14] As in earlier work the conversion of e_{aq}^- into an equivalent yield of ·OH to produce essentially a one radical system was achieved by reaction with N_2O.[4] The conditions for avoiding loss of primary e_{aq}^- to H^+ and Ni(II) are the same as previously discussed.[4] The reactivity of the complexes to e_{aq}^- shows limited variation throughout the series $k_{e_{aq}^-+Ni^{II}L} = 3.8 \times 10^{10}$, 4.5×10^{10}, and 5.2×10^{10} M^{-1} s^{-1} where L = CR+4H, CR, and CR-2H, respectively).[15]

In solutions containing X^- anions (X^- = SCN^- or Br^-), X^-_2 anion radicals are formed via reaction 1, which occurs with

$$X^- + \cdot OH \rightarrow XOH^- \qquad (1a)$$

$$X^- + XOH^- \rightarrow X^-_2 + OH^- \qquad (1b)$$

rate constants of $k_1 \simeq 10^9$ M^{-1} s^{-1} for Br^- and 10^{10} M^{-1} s^{-1} for SCN^- at pH <11.[16] As the reaction of ·OH radical with the nickel(II) complexes ($k_{\cdot OH+Ni^{II}(L)} = 4.5 \times 10^9$, 6.0×10^9, and 7.1×10^9 M^{-1} s^{-1} for L = CR, CR-2H, and CR+4H, respectively)[17] may compete with reaction 1, ratios of [X^-]/[$Ni^{II}(L)$] sufficiently large must be used to obtain stoichiometric formation of X^-_2 from ·OH radicals via reaction 1. At small concentrations in X^- ([X^-] ≈ (1–2) × 10^{-3} M) requiring corresponding small $Ni^{II}(L)$ concentrations, low doses were used to avoid loss of X^-_2 by the competing bimolecular disproportionation of X^-_2 ($2k_{X^-_2+X^-_2} \approx 2.5 \times 10^9$ and 3.5×10^9 M^{-1} s^{-1} for X^- = SCN^- and Br^-, respectively[17]).

In N_2O-saturated solutions, the X^-_2 yield will depend to some extent on the concentrations of X^- acting as ·OH spur scavenger.[19] Such dependences are taken into account here in the determination of both spectral and kinetic parameters. Hence in nitrous oxide saturated solutions containing X^- ions, and under conditions described above, the only radicals able to react with the nickel(II) macrocyclic complexes are X^-_2 and

---

(7) Karn, J. H. Ph.D. Dissertation, The Ohio State University, 1966.

(8) Barefield, E. K. Ph.D. Dissertation, The Ohio State University, 1969.

(9) Patterson, L. K.; Lilie, J. *Int. J. Radiat. Phys. Chem.* **1974**, *6*, 129.

(10) Schuler, R. H.; Patterson, L. K.; Janata, E. *J. Phys. Chem.* **1980**, *84*, 2088.

(11) Sehested, K. In "Manual on Radiation Dosimetry"; Holm, N. W., Berry, R. J., Eds.; Marcel Dekker: New York, 1970; p 313.

(12) Karn, J. W.; Busch, D. H. *Inorg. Chem.* **1969**, *8*, 1149.

(13) Barefield, E. K.; Lovecchio, F. V.; Tokel, N. E.; Ochiai, E.; Busch, D. H. *Inorg. Chem.* **1972**, *11*, 283.

(14) Matheson, M. S.; Dorfman, L. M. "Pulse Radiolysis"; MIT Press: Cambridge, MA, 1969.

(15) Personal determination of the rate constants in neutral N_2-saturated solutions containing 10^{-1} M *tert*-butyl alcohol.

(16) Farhataziz; Ross, A. B. *Natl. Stand. Ref. Data Ser.* (*U.S. Natl. Bur. Stand.*) **1979**, *NSRDS-NBS 59*.

(17) Personal determination of the rate constants in N_2O-saturated solutions: submitted for publication.

(18) Ross, A. B.; Neta, P. *Nat. Stand. Ref. Data Ser.* (*U.S. Natl. Bur. Stand.*) **1979**, *NSRDS-NBS 65*.

(19) Schuler, R. H.; Hartzell, A. L.; Behar, B. *J. Phys. Chem.* **1981**, *85*, 192.

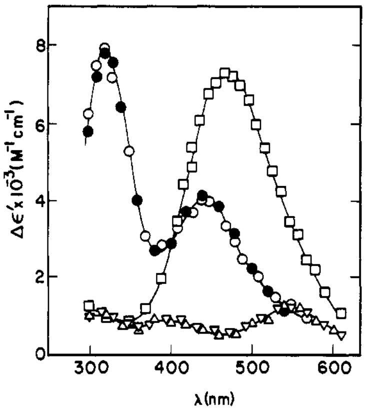


Figure 1. Transient spectra produced by $(SCN)^-_2$ oxidation of $Ni^{II}(CR+4H)$ in N_2O-saturated solution: $[SCN^-] = 2 \times 10^{-3}$ M, $[Ni^{II}(CR+4H)] = 10^{-4}$ M. The spectra were recorded at various intervals after the pulse and have been assigned: $(SCN)^-_2$ (□) t = 0.4 μs, pH 4.7; $Ni^{III}(CR+4H)(H_2O)(SCN^-)$ (●) t = 15 μs, pH 6.0, unbuffered solutions; $Ni^{III}(CR+4H)(H_2O)(SCN^-)$ (○) t = 15 μs, pH 4.7; d-$Ni^{III}(CR+4H)(OH^-)$ (△) t = 15 μs, pH 9.6; d-$Ni^{III}(CR+4H)(OH^-)$ (▽) t = 3 ms, pH 6.0, unbuffered solutions.

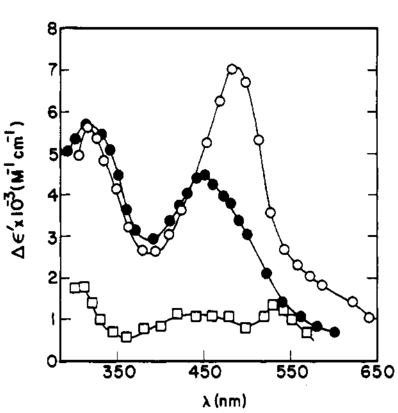


Figure 2. Transient spectra produced by $(SCN)^-_2$ oxidation of $Ni^{II}(CR)$ in N_2O-saturated solution: $[Ni^{II}(CR)] = 1.5 \times 10^{-4}$ M. The spectra were recorded at various intervals after the pulse and have been assigned: $Ni^{III}(CR)(H_2O)(SCN^-)$ (●) t = 25 μs, pH 3.2, $[SCN^-] = 2 \times 10^{-3}$ M; $Ni^{III}(CR)(SCN^-)_2$ and $Ni^{III}(CR)(H_2O)(SCN^-)$ mixture (○) t = 500 μs, pH 3.2, $[SCN^-] = 5 \times 10^{-3}$ M; d-$Ni^{III}(CR)(OH^-)$ (□) t = 3 ms, pH 6.7, $[SCN^-] = 2 \times 10^{-3}$ M.

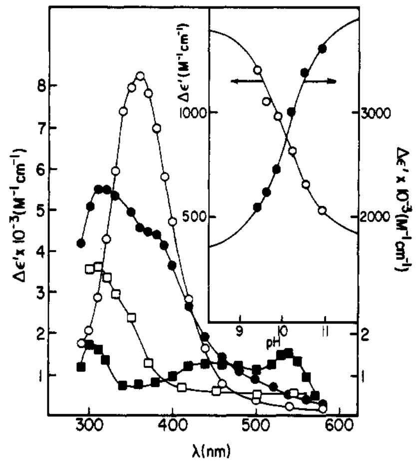


Figure 3. Transient spectra produced by Br^-_2 oxidation of $Ni^{II}(CR)$ in N_2O-saturated solution, $[Br^-] = 10^{-2}$ M, $[Ni^{II}(CR)] = 1.5 \times 10^{-4}$ M. The spectra were recorded at various intervals after the pulse and have been assigned: Br^-_2 (○) t = 0.8 μs, pH 5; $Ni^{III}(CR)(H_2O)(Br^-)$ (●) t = 30 μs, pH 5; d-$Ni^{III}(CR)(OH^-)$ (■) t = 14 ms, pH 6.7; $Ni^{III}(CR)(OH^-)_2$ (□) t = 25 μs, pH 10.8. Insert: pH dependence of the absorption recorded after reaction 3; λ = 530 nm (○) and λ = 310 nm (●). The curves were calculated for $K_4 = 8 \times 10^3$ M^{-1} (see text).

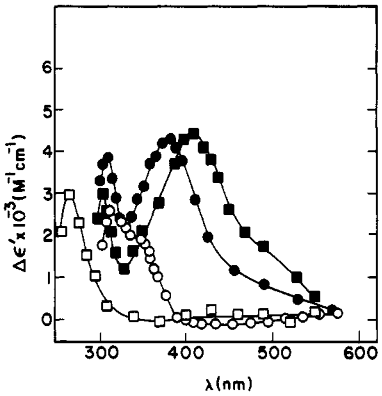


Figure 4. Transient spectra produced by Br^-_2 oxidation of $Ni^{II}(CR-2H)$ in N_2O-saturated solutions: $[Ni^{II}(CR-2H)] = (2.5–5.0) \times 10^{-5}$ M. The spectra were recorded at various intervals after the pulse and have been assigned: $Ni^{III}(CR-2H)(H_2O)(Br^-)$ (●) t = 25 μs, pH 3.2, $[Br^-] = 2.5 \times 10^{-3}$ M; $Ni^{III}(CR-2H)(Br^-)_2$ (■) t = 500 μs, pH 3.2, $[Br^-] = 10^{-2}$ M; $Ni^{III}(CR-2H)(H_2O)(OH^-)$ (○) t = 300 μs, pH 8,7, $[Br^-] = 5 \times 10^{-3}$ M; $Ni^{II}(CR-2H) + Br^-_3$ (□) t = 30 ms, pH 3.2, $[Br^-] = 10^{-2}$ M.

·H with relative yields ~10/1.[14]

In presence of X^-, these Ni(II) complexes are found to coordinate one X^- ion to give the monothiocyanato or the monobromo complexes. For these three complexes, the affinity of Br^- toward the nickel(II) complexes is low;[20] when concentrations in Br^- lower than 2×10^{-2} M are used, less than 20% of the complexes coordinate with Br^- anion. For SCN^- the affinity is a little higher[20] and the complexation is limited to about 20%, with SCN^- concentrations lower than 5×10^{-3} M.

Formation of Initial Intermediates via Oxidation by Anion Radicals. In the pH range 3–9, the first observed reaction is the disappearance of X^-_2 and simultaneous formation of initial transient oxidation product, whose spectrum is unaffected by acid concentrations over the range of our measurements. The spectra associated with this step in each system are reported in Figures 1–5. This reaction may be written as eq 2. The

$$Ni^{II}(L) + X^-_2 \xrightarrow{H_2O} Ni^{III}(L)(X^-)(H_2O) + X^- \qquad (2)$$

literature to date[1-4] on Br^-_2 oxidation of macrocyclic complexes indicates that the initial species following electron transfer to the anion radical involve the anion X^-, indeed, $Ni^{III}L(Br^-)(H_2O)$. The presence of a band in the near-UV without any accompanying band which might be assigned to a d–d transition may best be interpreted as characteristic of planar hexacoordinated species. This spectral behavior is similar to that observed in acetonitrile where similar nickel(III) complexes are hexacoordinated.[21]

By contrast to the Br^- containing systems, it was observed immediately following $(SCN)^-_2$ oxidation that the initial transient exhibits, in addition to the UV band, a intense well-defined absorption at 450 nm (Figures 1, 2, and 5). These differing spectra for oxidation of the same complex strongly suggest involvement of the anion in the initial transient. The course of each reaction of the form indicated by equation 2 was monitored by following changes in the optical absorption at various wavelengths under pseudo-first-order conditions ($[Ni^{II}(L)] \gg [X^-_2]$) and by changing the $Ni^{II}(L)$ concentra-

---

(20) Equilibrium constant $K_{Br^-} \approx$ 10–15 M^{-1} and $K_{SCN^-} \approx$ 40–60 M^{-1}, depending on the ligand, were determined by absorption spectroscopy.

(21) Olson, D. C.; Vasilevskis, J. *Inorg. Chem.* **1969**, *8*, 1611.

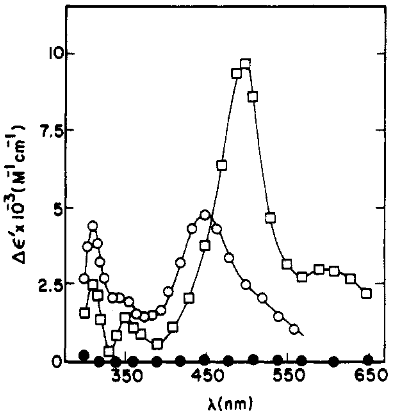


Figure 5. Transient spectra produced by $(SCN)^-_2$ oxidation of Ni^{II}(CR-2H) in N_2O-saturated solutions: pH 7 (phosphate buffer = 10^{-4} M), [Ni^{II}(CR-2H)] = 10^{-4} M. The spectra were recorded at various intervals after the pulse and have been assigned: Ni^{III}(CR-2H)(H_2O)(SCN^-) (○) t = 6 μs, [SCN^-] = 10^{-3} M; Ni^{III}(CR-2H)$(SCN^-)_2$ (□) t = 300 μs, [SCN^-] = 5 × 10^{-3} M; Ni^{II}(CR-2H) (●) t = 7.5 ms, [SCN^-] = 10^{-2} M.

Table I. Rate Constants (M^{-1} s^{-1}) for Reactions of Br^-_2 and $(SCN)^-_2$ with Ni(II) Macrocyclic Complexes[a, b]

oxidizing radical	Ni^{II}(CR+4H)	Ni^{II}(CR)	Ni^{II}(CR-2H)
Br^-_2	8.0 × 10^9	1.6 × 10^9	1.1 × 10^{10}
$(SCN)^-_2$[c]	6.3 × 10^9	1.4 × 10^9	1.0 × 10^{10}

[a] All solutions were N_2O saturated. [b] pH 4. [c] Monitored at 540 nm.

tions. The rate constants for Br^-_2 oxidation via reaction 2 are found to be independent of both pH and wavelength. In $(SCN)^-_2$ oxidation, however, the rate constants are independent of the solution acidity but differ slightly with the analyzing wavelength. The rate constants for anion radical reaction are given in Table I. At 450 nm, the rate constants are 15–25% lower than those determined in the near-UV or the red region, depending on the ligand. It may be suggested that the growth of the band at 450 nm reflects a second slightly slower process which overlaps the initial oxidation process. A rapid exchange of the coordinating atom from nitrogen to sulfur in the SCN^- ligand may be associated to this "second step". Coordination of the sulfur atom anion to the metal center, allowing π-bonding interaction, could contribute to the modifications in the energy of the d orbitals,[22] leading to a low-energy charge-transfer transition. Such isomerization linkages for thiocyanate ion have been previously mentioned for platinum complexes.[22] For $(SCN)^-_2$ oxidation, the rate constants given in Table I were determined at 540 nm where the absorption of the Ni(III) species is low. As may be seen in Table I, for each complex the reactivity is lower for $(SCN)^-_2$ than for Br^-_2. Also for each ligand system, these initial rate constants may be seen to parallel the degree of axial water coordination mentioned above.[8,12,13] The highest rate constant is obtained for Ni^{II}(CR-2H), whose axial positions are free of bound H_2O, and the lowest is obtained for Ni^{II}(CR), which is fully coordinated by the solvent. This dependence is also strongly suggestive of attack at the axial position. Additionally the low-spin state of CR-2H would be expected to exhibit a lower activation energy in radical attack than the high-spin CR system. Such configuration may contribute to the observed difference in rate constants.

Decay of Ni^{III}(CR)(SCN^-)(H_2O), Ni^{III}(CR)(Br^-)(H_2O), and Ni^{III}(CR+4H)(SCN^-)(H_2O) in Neutral and Basic Solutions. The production of Br^-_2, and subsequently Ni^{III}(L)(X^-)(H_2O), via reaction 1 provides an equivalent concentration of OH^-.

In neutral and unbuffered solutions these three transients decay, as did Ni^{III}(CR+4H)(Br^-)(H_2O), by second-order processes whose rate constants are independent of X^- concentration. At higher pH these decays show dependence on [OH^-] (Table II). This behavior is best described by reaction 3, suggested earlier,[4] with "d-" indicating a distorted complex.

$$Ni^{III}(L)(X^-)(H_2O) + OH^- \rightarrow d\text{-}Ni^{III}(L)(OH^-) + H_2O + X^- \quad (3)$$

The spectrum recorded following Ni^{III}(CR+4H)(SCN^-)(H_2O) decay is essentially that of the distorted d-Ni^{III}(CR+4H)(OH^-) transient observed after the decay of Ni^{III}(CR+4H)(Br^-)(H_2O) and may also be attributed to a distorted complex following the arguments previously given[4] (see Figure 1). The spectrum recorded following disappearance of Ni^{III}(CR)(SCN^-)(H_2O) is also comparable to the decay product of Ni^{III}(CR)(Br^-)(H_2O) (see Figures 2 and 3) and exhibits the visible absorption due to d–d transitions in an unsymmetrical complex. It appears that the presence of the two ligand double bonds in the CR ligand compared to CR+4H does not block deformation of the complex.

With addition of buffer to solution (pH 5.2–8.7), the kinetics become first order, but the rate constants are not completely linear with [OH^-] (see Table II). Further rate constants somewhat dependent on wavelength (when X^- = SCN^-) were observed. Though the buffer is clearly involved in formation of d-Ni^{III}(L)(OH^-), no evidence for additional intermediates was seen and no concentration dependence of rate constants on buffer or X^- at the levels used could be detected. We were not able to further elucidate the mechanism of buffer interaction.

The initial intermediates in reaction 3 Ni^{III}(CR+4H)(SCN^-)H_2O, Ni^{III}(CR)(Br^-)(H_2O), and Ni^{III}(CR)(SCN^-)(H_2O) are unstable in basic solution and not observed at pH ≳9. However, as pH was increased (9.5 ≤ pH ≤ 10.8) marked modifications in d-Ni^{III}(CR)(OH^-) spectra were observed. Absorption in the near-UV band increases with a simultaneous loss of absorption in the visible region. This dependence on [OH^-] follows a relationship of the form $\Delta\epsilon' = (\alpha + \beta\gamma[OH^-])/(1 + \gamma[OH^-])$, generally indicative of an equilibrium process. The implied reversibility is consistent with eq 4. Indeed the calculated curve with $\alpha = \Delta\epsilon'$[d-Ni^{III}(CR)(OH^-)], $\beta = \Delta\epsilon'$[Ni^{III}(CR)$(OH^-)_2$], and $\gamma = K_4$ associated with absorption vs. [OH^-] is presented in Figure 3 and yields an equilibrium constant K_4 = 8 × 10^3 M. The relative instability of the distorted complex d-Ni^{III}(CR)(OH^-) due to the unsaturation in the ring favors a transformation to the apparently symmetric configuration, Ni^{III}(CR)$(OH^-)_2$ associated to the symmetry of the axial positions. The decrease of the visible absorption along with increasing UV absorption is consistent with this return to a pseudooctahedral configuration.

$$d\text{-}Ni^{III}(CR)(OH^-) + OH^- \rightleftharpoons Ni^{III}(CR)(OH^-)_2 \quad (4)$$

Failure to observe such a process with the CR+4H ligand may be due to differences in the stability of the distorted species or in the less favorable binding of Ni^{III}(CR+4H) to ligands at the axial sites.

Decay of the Intermediates d-Ni^{III}(CR+4H)(OH^-), d-Ni^{III}(CR)(OH^-), and Ni^{III}(CR)$(OH^-)_2$ in Basic Solutions. The mechanism shown in eq 5–7 for the decay of Ni(III) macro-

$$[Ni^{III}(L)]^{3+} + OH^- \rightarrow [Ni^{III}(L\text{-}H)]^{2+} + H_2O \quad (5)$$

$$[Ni^{III}(L\text{-}H)]^{2+} \rightarrow [Ni^{II}(L\text{-}H)]^{2+} \quad (6)$$

$$2[Ni^{II}(L\text{-}H)]^{2+} \rightarrow [Ni^{II}(L)]^{2+} + [Ni^{II}(L\text{-}2H)]^{2+} \quad (7)$$

---

[22] Huheey, J. P. "Inorganic Chemistry"; Harper and Row: New York, 1972; and references therein.

Table II. Rate Constants for the Formation of the Distorted d-Ni^{III}(L)(OH$^-$) Intermediates in Neutral Solutions[a]

pH	ligand	10^4[Ni^{II}(L)], M 10^3[Br$^-$], M	10^3[SCN$^-$], M	10^4[phosphate], M	10^4[borate], M	λ, nm	k
5.2	CR	1	2	2		320	1.4×10^3 s^{-1}
5.2	CR	1	2	2		450	8.9×10^2 s^{-1}
5.2	CR	1	5	2		320	1.2×10^3 s^{-1}
5.2	CR	1	5	2		450	9.3×10^2 s^{-1}
6.0	CR	1.5	3			320	4.6×10^9 M^{-1} s^{-1}
6.0	CR	1.5	3			320	4.6×10^9 M^{-1} s^{-1}
6.0	CR	1.5	6			320	4.6×10^9 M^{-1} s^{-1}
6.0	CR	1.5	6			450	3.7×10^9 M^{-1} s^{-1}
6.7	CR	1	2	2		320	3.7×10^3 s^{-1}
6.7	CR	1	2	2		450	2.6×10^3 s^{-1}
6.7	CR	1	2	10		320	4.4×10^3 s^{-1}
6.7	CR	1	2	10		450	2.4×10^3 s^{-1}
6.7	CR	1	5	10		320	3.7×10^3 s^{-1}
6.7	CR	1	5	10		450	2.5×10^3 s^{-1}
8.7	CR	2	4		2	320	2.3×10^4 s^{-1}
8.7	CR	2	4		10	320	2.2×10^4 s^{-1}
6.0	CR+4H	1	3			320	2.1×10^{10} M^{-1} s^{-1}
6.0	CR+4H	1	3			450	2.3×10^{10} M^{-1} s^{-1}
6.0	CR+4H	1	6			320	2.0×10^{10} M^{-1} s^{-1}
6.0	CR+4H	1	6			450	1.9×10^{10} M^{-1} s^{-1}
7	CR+4H	1	2	1		320	1.3×10^5 s^{-1}
7	CR+4H	1	2	1		450	1.1×10^5 s^{-1}
8.7	CR+4H	1	2		1	320	2.0×10^5 s^{-1}
8.7	CR+4H	1	2			320	2.5×10^5 s^{-1}
4.8	CR	1	10			320	1.6×10^2 s^{-1}
4.8	CR	1	10	2		320	3.5×10^2 s^{-1}
5.1	CR	1.5	10	2		320	7.4×10^2 s^{-1}
5.1	CR	1.5	10	4.5		320	7.9×10^2 s^{-1}
5.1	CR	1.5	10	11		320	8.0×10^2 s^{-1}
6.0	CR	1.5	5			320	7.4×10^9 M^{-1} s^{-1}
6.0	CR	1.5	10			320	7.6×10^9 M^{-1} s^{-1}
6.7	CR	1.5	10	2		320	5.3×10^3 s^{-1}
7.0	CR	1.0	10	2		320	6.3×10^3 s^{-1}
8.7	CR	2.0	5		1	320	4.3×10^4 s^{-1}
8.7	CR	2	5		5	320	4.5×10^4 s^{-1}
8.7	CR	2	10		5	320	4.7×10^4 s^{-1}
8.8	CR	1.5	10			320	5.3×10^4 s^{-1}
8.8	CR	1.5	10	2		320	5.3×10^4 s^{-1}

[a] All solutions were N_2O saturated.

cyclic complexes via ligand radical in basic solution has been suggested in some form by various workers[1-3] and reported earlier for the CR+4H system.[4] The initial deprotonation of an amino function in this scheme was found to be much slower than subsequent steps 6 and 7. Decays of d-Ni^{III}(CR+4H)(OH$^-$) generated by (SCN)$^-_2$ oxidation increase in proportion to OH$^-$ concentration, and the resulting overall rate constant k_5 is equal to 1.5×10^7 M^{-1} s^{-1}. This value is equal to that determined for oxidation by Br$^-_2$, demonstrating, along with spectral evidence, that the distorted species is the same whether oxidation occurs through Br$^-_2$ or (SCN)$^-_2$. After static irradiations by γ rays of N_2O-saturated solutions containing 2×10^{-3} M SCN$^-$ and 2×10^{-4} M Ni^{II}(CR+4H), the recorded differential spectrum shows the absorption band at 360 nm, characteristic of the Ni^{II}(CR+2H) complex,[13] in agreement with the suggested mechanism. In the case of the CR ligand, two initial steps for ligand radical formation are possible:

$$[\text{d-Ni}^{III}(\text{CR})(\text{OH}^-)]^{2+} + \text{OH}^- \rightarrow [\text{Ni}^{III}(\text{CR-H})(\text{OH}^-)]^+ + H_2O \quad (8)$$

$$[\text{Ni}^{III}(\text{CR})(\text{OH}^-)_2]^+ + \text{OH}^- \rightarrow [\text{Ni}^{III}(\text{CR-H})(\text{OH}^-)_2]^0 + H_2O \quad (9)$$

Since the decay of the species is much slower than the establishment of equilibrium 4, the experimental rate constant k_{exptl} is equal to $(k_8[\text{OH}^-] + k_9K_4[\text{OH}^-]^2)/(1 + K_4[\text{OH}^-])$. With use of the equilibrium constant K_4 equal to 8×10^3 M calculated above, the expression $(k_{\text{exptl}}[1 + K_4[\text{OH}^-]])/[\text{OH}^-]$ was plotted as a function of OH$^-$ concentration. A good linear relationship is obtained leading to $k_8 = 2.5 \times 10^6$ M^{-1} s^{-1} and $k_9 = 1.0 \times 10^5$ M^{-1} s^{-1} (see Figure 6). It first may be noted that the deprotonation of the ligand CR in the distorted species is less facile than for the ligand CR+4H. Second, the deprotonation of the distorted d-Ni^{III}(CR)(OH$^-$) is much easier than the deprotonation of the undistorted Ni^{III}(CR)(OH$^-$)$_2$. In the undistorted species the presence of two OH$^-$ ions in the axial positions may decrease the positive charge of the metal center, providing a lower acidity for the coordinated amino group. Static irradiations by γ rays of solutions containing 10^{-2} M Br$^-$ and 2×10^{-4} M Ni^{II}(CR)(H$_2$O)$_2$ and saturated by N_2O were performed at various pH. Differential spectra recorded after irradiation are fully consistent with the formation of the Ni^{II}(CR-2H) complex. Particularly in neutral solution a quantitative yield was obtained, in agreement with the suggested mechanism of (5)-(7).

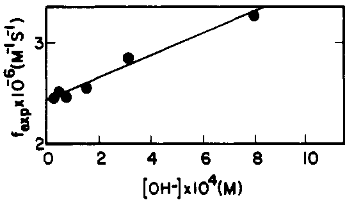


Figure 6. Determination of the rate constants k_8 and k_9 associated with the experimental decay of d-Ni^{III}(CR)(OH$^-$) and Ni^{III}(CR)(OH$^-$)$_2$ mixtures in basic solutions: $f_{\text{exp}} = k_{\text{exptl}}[1 + K_4[\text{OH}^-]]/[\text{OH}^-]$ (see text).

Decay of the Intermediate Ni^{III}(CR-2H)(Br$^-$)(H$_2$O) in Neutral Solution. Due to the high degree of unsaturation

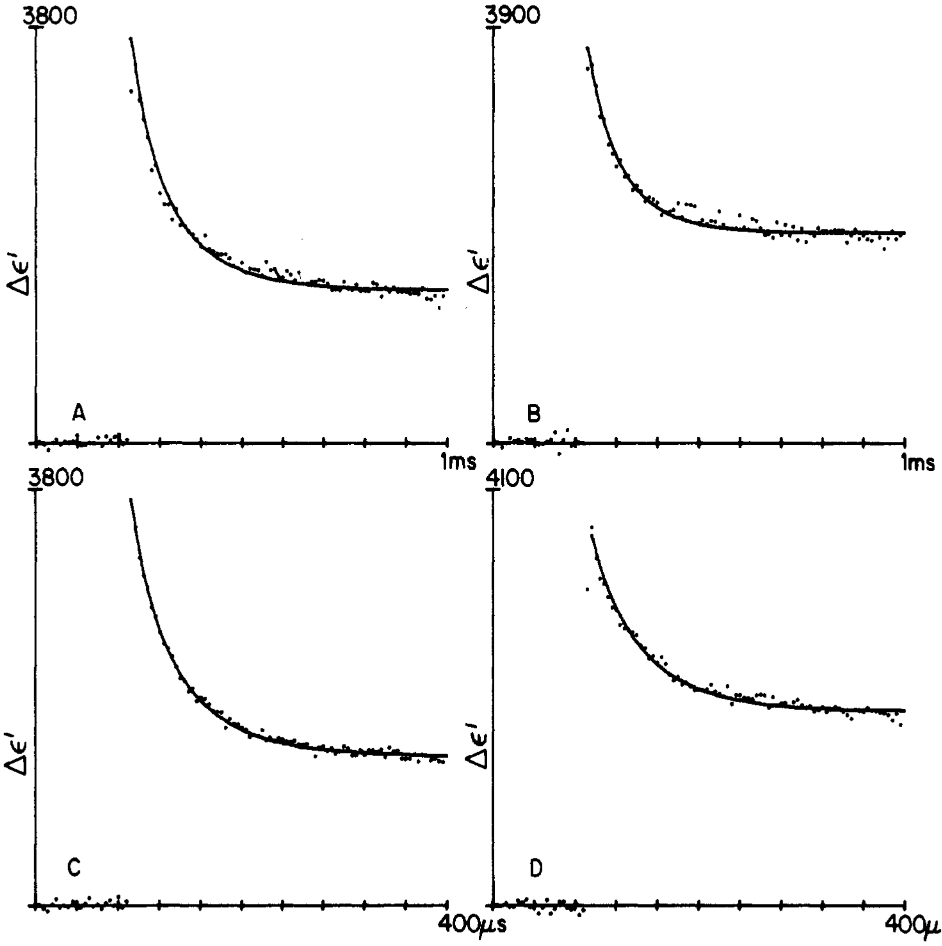


Figure 7. Experimental decay in N_2O-saturated unbuffered solutions of the intermediate $Ni^{III}(CR\text{-}2H)(H_2O)(Br^-)$ for various doses and Br^- concentrations. The curves are calculated from the rate law for reaction 10: (A) $[Ni^{III}(CR\text{-}2H)(H_2O)(Br^-)]_0 = 1.75 \times 10^{-6}$ M, $[Br^-] = 2 \times 10^{-3}$ M, $k_{10} = 4.3 \times 10^9$ M^{-1} s^{-1}, $k_{-10} = 8.5 \times 10^5$ M^{-1} s^{-1}; (B) $[Ni^{III}(CR\text{-}2H)(H_2O)(Br^-)]_0 = 1.3 \times 10^{-6}$ M, $[Br^-] = 6 \times 10^{-3}$ M, $k_{10} = 4.5 \times 10^9$ M^{-1} s^{-1}, $k_{-10} = 6.0 \times 10^5$ M^{-1}; (C) $[Ni^{III}(CR\text{-}2H)(H_2O)(Br^-)]_0 = 3.4 \times 10^{-6}$ M; $[Br^-] = 6 \times 10^{-3}$ M, $k_{10} = 5.0 \times 10^9$ M^{-1} s^{-1}, $k_{-10} = 6.0 \times 10^5$ M^{-1} s^{-1}; (D) $[Ni^{III}(CR\text{-}2H)(H_2O)(Br^-)] = 2.1 \times 10^{-6}$ M, $[Br^-] = 10^{-2}$ M, $k_{10} = 5.0 \times 10^9$ M^{-1} s^{-1}, $k_{-10} = 6.0 \times 10^5$ M^{-1} s^{-1}.

already present in the (CR-2H) ligand, the decay of the Ni^{III} intermediate may not be expected to proceed as do the CR and CR+4H complexes. At pH 8.7, in borate buffered solutions, the intermediate $Ni^{III}(CR\text{-}2H)(Br^-)(H_2O)$ decays by a first-order process and we observe the formation of second intermediate whose spectrum is reported in Figure 4. A comparable spectrum has been observed in oxidation of the complex $Ni^{II}(CR\text{-}2H)$ by ·OH radicals in neutral solutions, and it is reasonable to suggest that this reaction involves the formation of the intermediate $Ni^{III}(CR\text{-}2H)(OH^-)(H_2O)$. One may suggest that the presence of an additional nonconjugated double bond in the macrocyclic ring compared to CR will block any deformation of the complex; indeed we do not observe any low-energy transition similar to those exhibited by the other complexes. Since OH^- and $Ni^{III}(CR\text{-}2H)(H_2O)(Br^-)$ are produced in same quantity in neutral unbuffered solutions, second-order kinetics are again expected for reaction 10.

$$Ni^{III}(CR\text{-}2H)(H_2O)(Br^-) + OH^- \rightarrow Ni^{III}(CR\text{-}2H)(OH^-)(H_2O) + Br^- \quad (10)$$

Indeed dose-dependent second-order decays were observed for this process. However, the absorption plateau at 390 nm following decay is not negligible even though $Ni^{III}(CR\text{-}2H)(OH^-)(H_2O)$ does not absorb at this wavelength. Further, this plateau was found to increase with Br^- concentration and decreases with the dose. The spectrum at the end of this reaction may be interpreted as mixtures of $Ni^{III}(CR\text{-}2H)(H_2O)(OH^-)$ and $Ni^{III}(CR\text{-}2H)(H_2O)(Br^-)$. This data clearly indicates that reaction 10 is an equilibrium. From the remaining absorption at the end of reaction 10, for various doses ($D \approx 0.2$–0.6 krd) and various Br^- concentration ($[Br^-] = (1$–$10) \times 10^{-3}$ M), an equilibrium constant, K_{10}, is determined from

$$K = \frac{(\Delta\epsilon'_1 - \Delta\epsilon')(\Delta\epsilon'_1 - \Delta\epsilon'_2)[Br^-]}{(\Delta\epsilon' - \Delta\epsilon'_2)C_0}$$

where $\Delta\epsilon'_1$ and $\Delta\epsilon'_2$ represent the extinction coefficients of $Ni^{III}(CR\text{-}2H)(Br^-)(H_2O)$ and $Ni^{II}(CR\text{-}2H)(OH^-)(H_2O)$, respectively, and C_0 represents the initial concentration of $Ni^{III}(CR\text{-}2H)(H_2O)(Br^-)$ and also the initial OH^- concentration. A set of seven experiments at various dose and Br^- concentrations leads to a value $K_{10} = 7.2 \times 10^3$. According to the rate law for reaction 10

$$-d[Ni^{III}(L)(H_2O)(Br^-)]/dt = k_{10}[Ni^{III}(L)(H_2O)(Br^-)] \times [OH^-] - k_{-10}(C_0 - [Ni^{III}(L)(H_2O)(Br^-)])[Br^-]$$

good fits of kinetic data were obtained leading to values of $k_{10} \approx 4.7 \times 10^9$ M^{-1} s^{-1} and $k_{-10} \approx 6.9 \times 10^5$ M^{-1} s^{-1}, i.e., an equilibrium constant $K_{10} = k_{10}/k_{-10} \approx 6.8 \times 10^3$ in good agreement with the value taken from absorption data above. Examples of these fits are given in Figure 7. At pH lower than 7, the equilibrium is expected to be deplaced toward the formation of $Ni^{III}(CR\text{-}2H)(Br^-)(H_2O)$. However, at pH 5.5, in phosphate buffer solution, we are still able to observe a partial formation of $Ni^{III}(CR\text{-}2H)(OH^-)(H_2O)$ and it is again

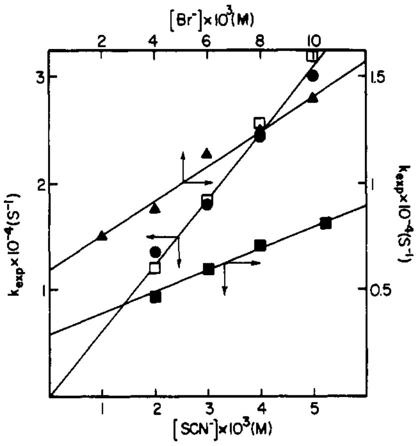


Figure 8. Plots of the experimental first-order rate constant for formation of Ni^{III}(L)(X$^-$)$_2$ vs. X$^-$ concentration in N$_2$O-saturated solution: (●) X$^-$ = SCN$^-$, L = CR-2H, pH 3.2; (□) X$^-$ = SCN$^-$, L = CR-2H, pH 7; (■) X$^-$ = SCN$^-$, L = CR, pH 3.2; (▲) X$^-$ = Br$^-$, L = CR-H, pH 3.2.

clear that buffer strongly interacts in the formation of this complex. At pH >9 the parent compound, Ni^{II}(CR-2H), proved unstable and no studies were conducted under these conditions.

Additional Reactions of Ni^{III}(CR)(X$^-$)(H$_2$O) and Ni^{III}(CR-2H)(X$^-$)(H$_2$O) Intermediates. There are several systems in which the behavior of Ni(III) intermediates is far different from any reported above. In neutral or acidic solution, Ni^{III}(CR-2H)(SCN$^-$)(H$_2$O) appears to undergo a transformation which leads to a species not easily compared to those discussed above. Its spectrum is reported in Figure 5. As may be seen, this transient is accompanied by a large increase in the absorption at 500 nm, with very little change in the near-UV region. This behavior appears to be unique among all cases of the anion radical oxidation[1,2] either here or in the literature studies of stable nickel(III) macrocyclic complexes in presence of SCN$^-$.[23] The course of this reaction was monitored at 500 nm under conditions of very low dose ($D \leq$ 0.1 krd) to avoid interference from the subsequent second-order process. This reaction of Ni^{III}(CR-2H)(SCN$^-$)(H$_2$O) obeys first-order kinetics; and as may be seen on Figure 8, the rate constants are proportional to SCN$^-$ concentration. The linear dependence of the first-order rate constants on SCN$^-$ concentration and the high extinction coefficient at 500 nm precluding a d–d transition suggest the formation of the dithiocyanato complex Ni^{III}(CR-2H)(SCN$^-$)$_2$ as per reaction 11 with a high equilibrium constant of formation, in agreement

$$\mathrm{Ni^{III}(CR\text{-}2H)(SCN^-)(H_2O) + SCN^- \rightleftarrows Ni^{III}(CR\text{-}2H)(SCN^-)_2 + H_2O} \quad (11)$$

with the absence of any apparent intercept in the plot. This is also consistent with the fact that only small additional increases of absorbance at 500 nm are observed with increasing SCN$^-$ concentrations. From this very small variation, we can estimate K_{11} to be equal to about 3000 M^{-1}. At pH 7, the resulting value k_{11} is equal to 6.0 × 10^6 M^{-1} s^{-1}.

The substitution by the second SCN$^-$ ion is accompanied by a shift toward the red of the lowest energy charge-transfer band. In acidic solution, the same reaction is observed leading to the same intermediate. At pH 3.2 the rate constant k_{11} is equal to 6.0 × 10^6 M^{-1} s^{-1}, a value which is identical with that determined in neutral solutions. In order to obtain the behavior observed here (i.e., no variation in $\Delta\epsilon'_{500}$ with [SCN$^-$] at the end of reaction 11 and a linear dependence of k_{11} on [SCN$^-$]) it is necessary to have the equilibrium constant of the potential competing process (eq 12) be very high, e.g., 2 orders of magnitude greater than K_{11}.

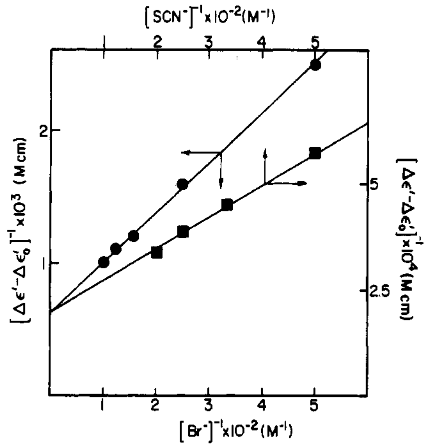


Figure 9. Plots of $(\Delta\epsilon' - \Delta\epsilon_0)^{-1}$ vs. [X$^-$]$^{-1}$ for the spectrophotometric determination of the equilibrium constants for the formation of Ni^{III}(L)(X$^-$)$_2$ in acidic solutions (pH 3.2): (■) X$^-$ = SCN$^-$, L = CR, λ = 480 nm; (●) X$^-$ = Br$^-$, L = CR-2H, λ = 400 nm.

$$\mathrm{Ni^{III}(CR\text{-}2H)(H_2O)_2 + SCN^- \rightleftarrows Ni^{III}(CR\text{-}2H)(H_2O)(SCN^-) + H_2O} \quad (12)$$

In acidic solution, the behavior of Ni^{III}(CR)(SCN$^-$)(H$_2$O) is very similar to that for the CR-2H complex. No reactions of distortion analogous to (3) dependent on [OH$^-$] are expected, and we are able to observe again a conversion of the Ni^{III}(CR)(SCN$^-$)(H$_2$O) proportional to [SCN$^-$] which increases the absorption at 500 nm (see Figure 2). The plot of experimental rate constants vs. [SCN$^-$] is given in Figure 8, suggesting, as with reaction 11, process 13. From the slope

$$\mathrm{Ni^{III}(CR)(SCN^-)(H_2O) + SCN^- \rightleftarrows Ni^{III}(CR)(SCN^-)_2 + H_2O} \quad (13)$$

of the plot k_{exptl} vs. [SCN$^-$], we may set k_{13} = 1.0 × 10^6 M^{-1} s^{-1} and from the intercept k_{-13} = 3.0 × 10^3 s^{-1}. Then the equilibrium constant of formation of the dithiocyanato complex is equal to about 330 M^{-1}. Unlike the Ni^{II}(CR-2H)/SCN$^-$ system one may allso determine this equilibrium constant from the changes in the optical spectrum at the end of this second reaction for various SCN$^-$ concentrations. In Figure 9 is given the plot $(\Delta\epsilon' - \Delta\epsilon'_0)^{-1}$ vs. [SCN$^-$]$^{-1}$ taken at the end of this second reaction where $\Delta\epsilon'_0$ represents the absorbance of Ni^{III}(CR)(SCN$^-$)(H$_2$O) and $\Delta\epsilon'$ the absorbance for the mixture of mono- and dithiocyanato complexes. The linearity of this plot indicates coordination of the second SCN$^-$ ion and leads to an equilibrium constant equal to about 270 M^{-1}, a value which is very comparable to that determined from kinetic data. A spectrum reflecting a mixture of Ni^{III}(CR)(SCN$^-$)$_2$ and Ni^{III}(CR)(SCN$^-$)(H$_2$O) is included in Figure 2, and a shift similar to that observed with the CR-2H ligand toward the red of the low-energy charge-transfer band may be seen. The good linearity of both plots from kinetic or spectroscopic data lead us to the conclusion that equilibrium 14 is not interfering.

$$\mathrm{Ni^{III}(CR)(H_2O)_2 + SCN^- \rightleftarrows Ni^{III}(CR)(SCN^-)(H_2O) + H_2O} \quad (14)$$

Then as in the case of Ni^{III}(CR-2H)(H$_2$O)(SCN$^-$), the equilibrium constant K_{14} must be at least 2 orders of magnitude higher than K_{13}.

In acidic solution, no formation of Ni^{III}(CR+4H)(SCN$^-$)$_2$ is observed, indicating a very low equilibrium constant for the

---

(23) Haines, R. I.; McAuley, A. *Inorg. Chem.* **1980**, *19*, 719.

Table III. Rate Constants (M^{-1} s^{-1}) for the Second-Order Decay of $Ni^{III}(L)(X^-)(H_2O)$ and $Ni^{III}(L)(X^-)_2$ in Acidic Solutions[a] (pH 3.2)

X^-	$Ni^{III}(CR+4H)(X^-)(H_2O)$	$Ni^{II}(CR)(X^-)(H_2O)$	$Ni^{III}(CR)(X^-)_2$	$Ni^{III}(CR-2H)(X^-)(H_2O)$	$Ni^{III}(CR-2H)(X^-)_2$
Br^-	*b*	1.1×10^7	*c*	6.9×10^7	2.8×10^8
SCN^-	6.5×10^5	5.0×10^7	1.6×10^8	*c*	3.7×10^8

[a] All solutions were N_2O saturated. [b] Reference 4. [c] Not observed.

formation of the dithiocyanato complex. We also do not observe any formation of $Ni^{III}(CR+4H)(H_2O)_2$; hence, the equilibrium constant of formation for the monothiocyanato complex must be at least on the order of several thousands units.

In acidic solutions we were able to observe equilibrium 15,

$$Ni^{III}(CR-2H)(Br^-)(H_2O) + Br^- \rightleftarrows Ni^{III}(CR-2H)(Br^-)_2 + H_2O \quad (15)$$

and the spectrum of the dibromo complex is reported in Figure 4. Both plots (k_{15} vs. $[Br^-]$ and $(\Delta\epsilon'_\infty - \Delta\epsilon'_0)^{-1}$ vs. $[Br^-]^{-1}$) (see Figures 8 and 9) agree with the complexation of a second Br^- ion and lead to values $k_{15} \approx 8.0 \times 10^5$ M^{-1} s^{-1}, $k_{-15} \approx 6 \times 10^3$ s^{-1}, and an equilibrium constant $K_{15} \approx 140$ M^{-1}. In acidic solution, the intermediate $Ni^{III}(CR)(Br^-)(H_2O)$ does not undergo a second Br^- coordination or a substitution of Br^- by the solvent in the range of Br^- concentration used ($[Br^-] = (2-10) \times 10^{-3}$ M). From all the results, it appears that SCN^- is a better ligand than Br^- in these systems, as expected from the position of SCN^- in the spectrochemical series. The most interesting feature is that the tendency to coordinate a first or second SCN^- or Br^- ion increases in the order CR+4H < CR < CR-2H, i.e., with the degree of unsaturation in the ligand.

Decays of $Ni^{III}(L)(X^-)(H_2O)$ and $Ni^{III}(L)(X^-)_2$ in Acidic Solutions. From the dependence of reactions 5–7 on $[OH^-]$, decays via ligand radical are highly unfavorable in acidic solutions; all the complexes $Ni^{III}(L)(X^-)(H_2O)$ or $Ni^{III}(L)(X^-)_2$ decay by second-order processes. In an earlier report,[4] we mentioned a dose-dependent decay of $Ni^{III}(CR+4H)(Br^-)(H_2O)$ in acidic solution, but due to the low rate constant for this reaction, allowing a competing deprotonation of the ligand, we were unable to draw any conclusions concerning the mechanism. In the systems discussed above, the decays were fast enough to observe clear second order-reaction, exhibiting good dose dependence of the half-life and no competition with ligand deprotonation. No reaction via a ligand radical is expected with the ligand CR-2H since it is already fully unsaturated. In all cases this second-order reaction involves uniform decay of the absorption in the whole spectral region (λ = 300–550 nm), and, as may be seen on Figure 5 in the case of $Ni^{II}(CR-2H)(SCN^-)$, the remaining transient absorption is negligible at the end of the reaction. Similar behavior was observed with the other ligand systems although quantitative spectra of weakly absorbing transients were not obtainable at long time with our pulse radiolysis monitoring system. The data, however, clearly indicate a return to the starting material without any significant loss. This observation is confirmed by γ-ray experiments described below. With $Ni^{III}(CR+4H)(SCN^-)(H_2O)$ and $Ni^{III}(CR)(Br^-)(H_2O)$, the second-order rate constant is independent of SCN^- or Br^- or $Ni^{II}(L)$ concentration. With the systems $Ni^{III}(CR-2H)/Br^-$, $Ni^{III}(CR-2H)/SCN^-$, and $Ni^{III}(CR)/SCN^-$, a slight dependence on the anion concentration alone is observed over the ranges used; $[Br^-] = (2-10) \times 10^{-3}$ M, $[SCN^-] = (2-5) \times 10^{-3}$ M. This dependence is not unexpected since equilibria involving different axially coordinated Ni(III) species were observed, and the reactivity of these species will vary to some degree.

In earlier reports,[2,3] second-order decay of other Ni(III) macrocyclic complexes in acidic solutions were observed. The mechanisms of eq 16–18 and of eq 19 and 20 were suggested,

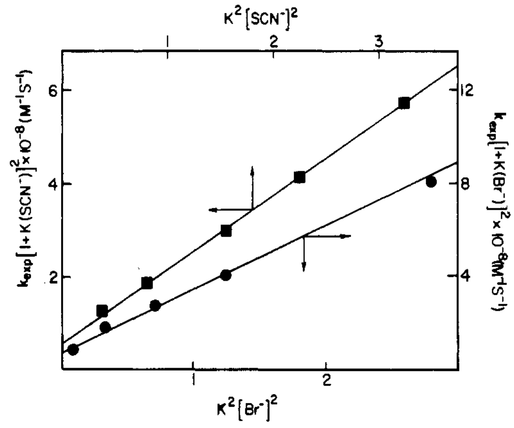


Figure 10. Dependence of the experimental second-order rate constants on $[X^-]^2$ for the last decay observed in acidic solution (reaction 23) (pH 3.2) for $Ni^{III}(L)(X^-)(H_2O)/Ni^{III}(L)(X^-)_2$ systems: (●) $X^- = Br^-$, L = CR-2H, $K = 140$ M^{-1}; (■) $X^- = SCN^-$, L = CR, $K = 300$ M^{-1} (see text).

$$Ni^{III}(L)(X^-) \rightleftarrows Ni^{III}(L) + X^- \quad (16)$$

$$Ni^{III}(L)(X^-) + X^- \rightleftarrows Ni^{II}(L) + X^-_2 \quad (17)$$

$$Ni^{III}(L) + X^-_2 \rightarrow Ni^{II}(L) + X_2 \quad (18)$$

$$Ni^{III}(L) + Br^- \rightarrow Ni^{II}L + \cdot Br \quad (19)$$

$$\cdot Br + Ni^{III}(L) \rightarrow Ni^{II}(L') + Br^- + H_3O^+ \rightarrow Ni^{II}(L) + HOBr \quad (20)$$

which exhibit some similarities, in agreement with a linear dependence of the experimental second-order rate constant on $[Br^-]$ concentration and a linear dependence on $[Ni^{II}(L)]^{-1}$. The systems in the present work differ completely. Indeed we do not observe any linear dependence with $[X^-]$ or $[Ni^{II}(L)]^{-1}$. From this one may conclude that $\cdot X$ or X^-_2 are not responsible for this observed second-order reaction. The mechanism of eq 21 and 22 may be suggested, step 21 being

$$2Ni^{III}L(X^-)(H_2O) \rightarrow Ni^{II}(L) + Ni^{III}(L)(H_2O)(X^-_2) + H_2O \quad (21)$$

$$Ni^{III}L(X^-_2)(H_2O) \rightarrow Ni^{II}(L) + X_2 + H_2O \quad (22)$$

the rate-limiting one, in agreement with observation. In the presence of nickel(III) species involving equilibria similar to (16) and (17), reactions 23 and 24 are implied, and the experimental rate constant k_{exptl} is equal to $(k_{21} + k_{23}K^2 \cdot [X^-]^2)/(1 + K[X^-])^2$, where K is the equilibrium constant of formation for $Ni^{III}(L)(X^-)_2$ from $Ni^{III}(L)(X^-)(H_2O)$. With

$$2Ni^{III}(L)(X^-)_2 \rightarrow Ni^{II}(L) + Ni^{III}L(X^-_2)(X^-) + X^- \quad (23)$$

$$Ni^{III}(L)(X^-_2)(X^-) \rightarrow Ni^{II}(L) + X_2 + X^- \quad (24)$$

the equilibrium constants K_{13} and K_{15} previously determined, linear plots of $k_{exptl}[1 + K(X^-)]^2$ vs. $K^2[X^-]^2$ were obtained (see Figure 10). The rate constants for these second-order

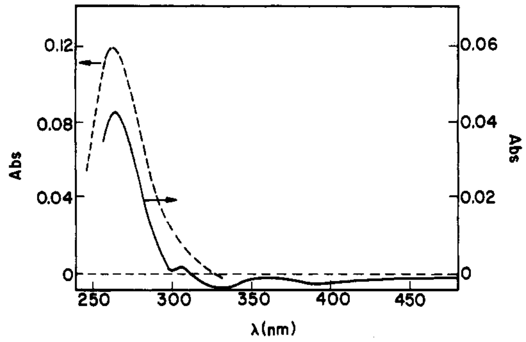


Figure 11. Differential spectra recorded after γ irradiation of N_2O-saturated solutions containing 10^{-4} M Ni^{II}(CR-2H), 10^{-2} M Br^- (—), 10^{-1} M Br^- (- - -): pH 3.2; dose ≈ 3 krd.

reactions are reported in Table III. An alternative mechanism may be considered with the limiting step of eq 25, requiring

$$Ni^{III}(L)(X^-)(H_2O) + Ni^{III}(L)(X^-)(H_2O) \rightarrow Ni^{II}(L) + Ni^{IV}(L)(X^-)(H_2O) + H_2O + X^- \quad (25)$$

a redox potential Ni^{III}/Ni^{IV} lower than that for Ni^{II}/Ni^{III}. Termination steps such as eq 26 and 27 must be rejected since

$$Ni^{IV}(L)(X^-)(H_2O) \rightarrow Ni^{III}(L)(H_2O) + X\cdot \quad (26)$$

$$Ni^{IV}(L)(X^-)(H_2O) + X^- \rightarrow Ni^{III}(L)(H_2O) + X^-_2 \quad (27)$$

the production of $X\cdot$ or X^-_2 will introduce a dependence on $[Ni^{II}(L)]$ in the rate law. Furthermore, production of nickel(III) species in reactions 26 and 27 does not allow second-order kinetics to be observed. In agreement with experimental data, the fast termination steps might be eq 28 and 29.

$$Ni^{IV}(L)(X^-)(H_2O) + X^- \rightarrow Ni^{III}(L)(X^-_2)(H_2O) \quad (28)$$

$$Ni^{IV}(L)(X^-_2)(H_2O) \rightarrow Ni^{II}(L) + X_2 + H_2O \quad (29)$$

Although there are some reports of Ni(IV) complexes such a mechanism remains very speculative. However, in order to determine whether X_2 is a product of reaction, N_2O saturated solutions containing 10^{-4} M Ni^{II}(CR-2H) and 10^{-2} Br^- were irradiated by γ rays. About 20% of the starting material was converted, and a differential spectrum was recorded after irradiation. In the 300–600-nm region, the differential absorption is very low and we are able to observe a bleaching of only about 10% of the converted material. Ninety percent of the converted material returns to the starting material in agreement with reactions 21–24. In the UV region we observe a well-defined band with a maximum absorption at 265 nm (see Figure 11). This band is attributable to the species Br^-_3 formed from reaction 30. After γ irradiations with 10^{-1} M

$$Br_2 + Br^- \rightleftarrows Br^-_3 \quad (30)$$

Br^- the differential absorption at 265 nm increases in agreement with equilibrium 30 (see Figure 11). However, no quantitative determinations can be made since Br_2 is able to undergo additional reactions with water, but clearly there is compelling evidence for X_2 production in the disappearance of $Ni^{III}(L)(X^-)(H_2O)$ or $Ni^{III}L(X^-)_2$ in acidic solutions.

Conclusion

In this report, we have examined the kinetics of $(SCN)^-_2$ and Br^-_2 interaction with three related Ni(II) macrocyclic complexes over wide ranges of anion concentration, pH, and reaction time. As such, the work extends considerably previous studies of unstable aqueous Ni(III) complexes and touches upon a number of processes not considered earlier. The reaction rates in the first step, for example, have been shown to correlate not with the double-bond character of the macrocyclic ligand but rather with the degree of aquation at sites axial to the ligand in the parent Ni(II) complex. This data strongly suggests displacement of the bound water and X^-_2 attack at the same sites. Additionally the low-spin state of CR-2H would be expected to exhibit a lower activation energy in radical attack than the high-spin CR system. Such configuration may contribute to the observed difference in rate constants.

The variations of anion concentration and pH used have shown the chemistry of initial oxidation products $Ni^{III}(L)(X^-)(H_2O)$ to be indeed complex. However, except for the final steps involving regeneration of divalent nickel, most behavior subsequent to $Ni^{III}(L)(X^-)(H_2O)$ formation may be understood in terms of interdependent competition among X^-, OH^-, and H_2O for axial ligand sites. Such a scheme provides pathways for generating intermediates of the form $Ni^{III}(L)(X^-)_2$, $Ni^{III}(L)(OH^-)_2$, and $Ni^{III}(L)(OH^-)(H_2O)$. Additionally, from spectral evidence indicating low-energy d–d transitions in the visible and behavior in systems previously investigated there is evidence for formation of $Ni^{III}(L)(OH^-)$, which gives evidence for an asymmetric structure. It may be seen from the data presented that these species are not all observed in each system. Their occurrence follows a pattern dependent on the nature of X^-, the degree of unsaturation in the ligand, pH, and kinetics of degradation to Ni(II) products. (a) While $Ni^{III}(L)(CNS^-)_2$ can occur from L = CR or CR-2H, $Ni^{III}(CR\text{-}2H)(Br^-)_2$ is the only dibromo complex seen. Measurements of *K* for the mono- and dithiocyanato complexes confirms the greater stability of $Ni^{III}(CR\text{-}2H)(X^-)_2$. (b) Each of the species d-$Ni^{III}(L)(OH^-)$, $Ni^{III}(L)(OH^-)_2$, or $Ni^{III}(L)(OH^-)(H_2O^-)$, whose generation is dependent on the character of the macrocyclic ligand, may be formed either through a bromide or thiocyanate precursor. (c) In agreement with earlier studies, d-$Ni^{III}(L)(OH^-)$ can occur only when deformation of the macrocyclic ring is allowed; i.e., no such species is observed with CR-2H.

Degradation via ligand radical at neutral or higher pH to produce Ni^{II}(L-2H) is dependent on the number of ligand sites available for deprotonation, the rate constant for radical formation in the Ni(CR+4H) system being greater than that for Ni(CR) and disappearing entirely for Ni(CR-2H), which degrades by an undetermined mechanism. By contrast, at acid pH the rate constant for return of $Ni^{III}(L)(X^-)(H_2O)$ to the parent material follows the trend CR-2H > CR > CR-4H.

Acknowledgment. The authors wish to thank Dr. P. Neta for helpful discussion. The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-2207 from the Notre Dame Radiation Laboratory.

Registry No. Ni^{II}(CR+4H), 53537-59-0; $Ni^{II}(CR)(OH_2)_2$, 36515-22-7; Ni^{II}(CR-2H), 47023-96-1; Br_2^-, 12595-70-9; $(SCN)_2^-$, 34504-17-1; $Ni^{III}(CR)(OH^-)$, 80864-65-9; $Ni^{III}(CR+4H)(OH^-)$, 76011-07-9; $Ni^{III}(CR)(OH^-)_2$, 80864-66-0; $Ni^{III}(CR+4H)(SCN^-)(H_2O)$, 80864-67-1; $Ni^{III}(CR)(Br^-)(H_2O)$, 80864-68-2; $Ni^{III}(CR)(SCN^-)(H_2O)$, 80864-69-3; $Ni^{III}(CR)(SCN^-)_2$, 80864-70-6; $Ni^{III}(CR\text{-}2H)(Br^-)(H_2O)$, 80864-58-0; $Ni^{III}(CR\text{-}2H)(SCN^-)(H_2O)$, 80864-57-9; $Ni^{III}(CR\text{-}2H)(OH^-)(H_2O)$, 80864-56-8; $Ni^{III}(CR\text{-}2H)(Br^-)_2$, 80878-11-1; $Ni^{III}(CR\text{-}2H)(SCN^-)_2$, 80864-59-1.