Reaction of *trans*-Dichlorobis(ethylenediamine)nickel(III) in Aqueous Hydrochloric Acid

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Abstract

Both EPR and electronic absorbance spectroscopy have been used to follow the disappearance of $[Ni^{III}(en)_2Cl_2]^+$ in aqueous HCl solutions. The rate of Ni(III) reduction is influenced by both the H^+ and Cl^- concentrations, although the rate is not linear with respect to the concentration of either species. A mechanism is proposed in which the first step in the reaction is the proton-induced chelate ring opening which is followed by the reduction of Ni(III) by chloride ions. In the presence of H_2SO_4 the coordinated Cl^- ions are rapidly replaced by HSO_4^- ions and the resulting complex is much more stable, even in a 6 N acid solution.

Introduction

The decomposition of nickel(III) complexes involving a number of macrocyclic ligands has been studied in detail [1, 2]. By contrast, the decomposition kinetics for $[Ni^{III}(en)_2Cl_2]^+$ complexes, which were synthesized at an early date [3], have not been determined in aqueous solution. The present work is an extension of the chemistry of $[Ni^{III}(en)_2Cl_2]^+$ in a type-Y zeolite where residual water appears to play a role in the reduction of Ni(III) [4].

The mechanism for the decomposition of nickel(III) macrocycles varies significantly with respect to pH. In more basic solutions (pH > 3) the reduction of the metal ion is believed to proceed with the formation of a radical intermediate on the ligand [1, 2]. This reaction may be described as a proton abstraction by the base, with the concomitant reduction of the nickel(III). At low pH the reduction of nickel(III) is achieved by the oxidation of halide ions, including Cl^-, which presumably become part of the inner coordination sphere [1].

Using pulse radiolysis studies Lati and Myerstein [5] also observed that the rate of disappearance of $Ni^{III}(en)_n$ increased with increasing pH. They attributed this pH effect, in part, to the reaction:

$$Ni^{III}(en)_n + OH^- \rightleftarrows Ni^{II}(en)_n + OH\cdot \qquad (1)$$

In the present study the kinetic analysis has been restricted to the acidic region where the reaction rates were sufficiently slow to measure. Both UV and EPR spectroscopy were used to follow the reduction of the nickel(III) complex. In addition, the stepwise exchange of chloride ligands with bisulfate ligands was observed by both types of spectroscopy.

Experimental

The $[Ni^{III}(en)_2Cl_2]Cl$ was prepared according to the method of Babaeva *et al.* [3]. Chlorine was bubbled through a saturated solution of $[Ni^{II}(en)_2]Cl_2$ in absolute methanol for several min. The resulting brownish yellow microcrystals were filtered, washed with absolute methanol, and dried in air. The crystals which were mainly $[Ni^{III}(en)_2Cl_2]Cl\cdot HCl\cdot 2H_2O$ were further washed with a 1:1 solution of H_2O and concentrated HCl and then again with anhydrous methanol. The purified material was $[Ni^{III}(en)_2(Cl_2]$-Cl. *Anal.* calcd. for $[Ni^{III}(en)_2Cl_2]$: Ni, 20.42; N, 19.52; Cl, 36.75; C, 16.73; H, 5.23. Found: Ni, 20.32; N, 19.39; Cl, 37.60; C, 16.65; H, 5.73. The EPR and infrared spectra were obtained in the solid state after mixing the pure compound with KCl ($[Ni^{III}(en)_2Cl_2]Cl$:KCl = 1:40).

In a typical kinetic run 1 mg of $[Ni^{III}(en)_2Cl_2]Cl$ was dissolved at 25 °C in 5 ml of an aqueous solution (7.0×10^{-4} M). The solution (0.5 ml) was placed in a 4 mm diameter EPR tube and frozen at 77 K. The solution was subjected to 2 freeze-thaw cycles, under vacuum, in order to remove dissolved air. Since a well resolved EPR spectrum was not observed at room temperature, it was necessary to keep the sample at 25 °C for a specified period and then to cool the sample for an EPR analysis. In order to minimize the error in the time at 25 °C the sample was warmed as rapidly as possible to this temperature. The UV spectra were much more straightforward to obtain since the entire process could be carried out at 25 °C. A cell of 5 mm path length was used for this purpose.

Infrared spectra were obtained at 25 °C using a Perkin-Elmer 580B spectrophotometer. The sample was in the form of a self-supporting wafer. A Varian

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2300 spectrophotometer was used to record the UV spectra. The EPR spectra were obtained using a Varian E-6S X-band spectrometer. A phosphorous-doped silicon standard was the reference for determination of both g values and spin concentrations. Absolute spin concentrations, calculated by double integration of the derivative spectra, are accurate to *ca.* ±25%, but relative spin concentrations for a sequence of spectra are considerably more accurate.

Results and Discussion

EPR Spectra

The EPR spectrum of solid $[Ni^{III}(en)_2Cl_2]Cl$, shown in Fig. 1a for comparison purposes, has been previously reported [4, 6]. This spectrum is characterized by $g_{\parallel} = 2.019$ and $g_{\perp} = 2.184$ with no resolved hyperfine splitting. The Ni^{III} spin concentration determined from the spectra was 68% of the total nickel in the sample. Even considering a possible error of ±25% in the spin concentration, the Ni^{III} ions which contribute to the spectrum are less than total nickel in the sample. This discrepancy suggests that another complex may be present in the sample. The electronic spectrum likewise indicates the presence of an impurity in the $[Ni^{III}(en)_2Cl_2]Cl$ crystals (see below).

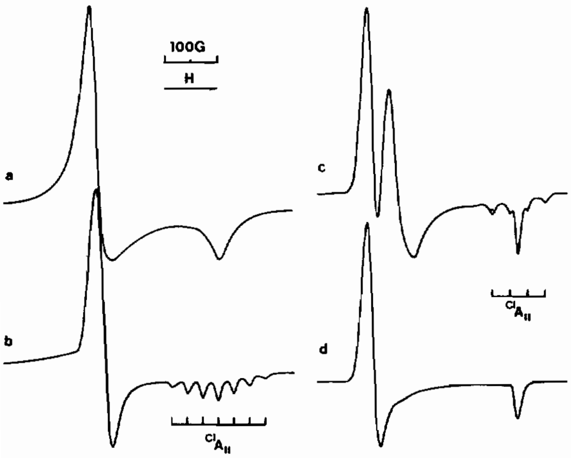


Fig. 1. EPR spectra of $Ni^{III}(en)_2$ complexes: (a) $[Ni^{III}(en)_2Cl_2]Cl$ in the solid state, diluted by mixing with KCl; (b) $[Ni^{III}(en)_2Cl_2]^+$ in a solution of 1 N HCl; (c) a mixture of $[Ni^{III}(en)_2(HSO_4)Cl]^+$ and $[Ni^{III}(en)_2(HSO_4)_2]^+$ in a solution of 1 N H_2SO_4; and (d) $[Ni^{III}(en)_2(HSO_4)_2]^+$ in a solution of 6 N H_2SO_4.

When the Ni^{III} complex was dissolved in 1 N HCl the spectrum depicted in Fig. 1b was observed. This spectrum is similar to that reported by Larin *et al.* [7, 8], although the value of $g_{\perp} = 2.165 \pm 0.002$ (Table I) is outside the expected limits of error for the value of 2.185 ± 0.003 determined by Larin *et al.* [8]. The discrepancy probably results from the method used in determining g values from polycrystalline data. Larin *et al.* [8] used the position of the maximum in the derivative spectrum to calculate the value of $g_{\perp}$; whereas, simulations of polycrystalline spectra show that a point upfield from the maximum should be used. The latter, of course, gives rise to a smaller value for $g_{\perp}$. As noted previously the spectrum is characteristic of a low-spin d^7 ion in axial symmetry ($g_{\perp} > g_{\parallel} \cong 2.0$) [4].

Seven hyperfine lines, resulting from two equivalent chlorine atoms (I = 3/2), are clearly evident in the spectrum of Fig. 1b. A hyperfine splitting of 29.5 G is in good agreement with the value reported for this complex in a Y-type zeolite. The hyperfine splitting did not change with pH, nor did it change as the complex decayed with time.

At pH values ≧ 1.0 a symmetric line with $g_{\perp} = 2.123$ was observed as shown in Fig. 2b. This spectrum is not due to a $\Delta m_s = \pm 2$ transition of an S = 1 species (*e.g.* spin coupled Ni(III) complexes) since no half-field transition was observed. As mentioned in the introduction, the base-promoted reduction of Ni(III) macrocyclic amines is believed to proceed through a radical intermediate [2]:

$$\mathrm{Ni^{III}N}{\leq}\mathrm{H} + \mathrm{B} \longrightarrow \mathrm{Ni^{II}N}\dot{<} + \mathrm{BH^+} \quad (2)$$

These radicals have g values of *ca.* 2.037 and $a_N = 29.2$ G. The shift from the free electron g value is attributed to the contribution of metal orbitals to the molecular orbital which contains the unpaired electron [2]. In view of the influence of pH on the spectrum in Fig. 2b it seems likely that radicals also

TABLE I. EPR Parameters for Ni(III) Complexes.

Complex/Solvent	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}^{Cl}$, G	Ref.
$[Ni^{III}(en)_2Cl_2]^+$/aq HCl	2.017	2.165	30	This work
$[Ni^{III}(en)_2Cl_2]^+$/aq HCl	2.020	2.185	32	7
$[Ni^{III}(en)_2Cl_2]Cl$, solid	2.019	2.184		This work
$[Ni^{III}(en)_2Cl_2]Cl$, solid	2.020	2.20		6
$[Ni^{III}(en)_2(HSO_4)_2]^+$/6 N H_2SO_4	2.019	2.212		This work
$[Ni^{III}(en)_2(HSO_4)_2]^+$/aq H_2SO_4	2.020	2.256		7
$[Ni^{III}(en)_2(HSO_4)Cl]^+$/1 N H_2SO_4	2.018	2.180	33	This work

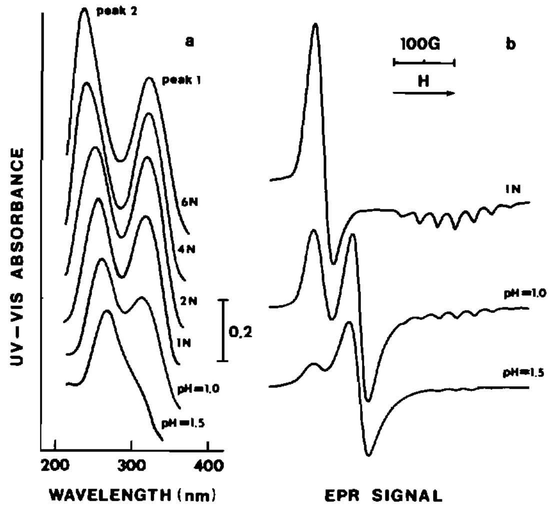


Fig. 2. Variation in EPR spectra and UV-visible absorbance as a function of HCl concentration.

are formed by reaction (2), but the influence of the metal ion in shifting the g value is even more pronounced since the en ligands are smaller. The overall line width is consistent with the presence of nitrogen and proton hyperfine interaction. In the following kinetic experiments the contribution of the symmetric line was included in determining the concentration of Ni(III), although the integral of the symmetric line never contributed more than 20% to the overall integral.

Upon dissolving $[Ni^{III}(en)_2Cl_2]Cl$ in 1 N and 6 N H_2SO_4 solutions the spectra depicted in Figs. 1c and d, respectively, were observed. The spectrum of Fig. 1c confirms the presence of two species; one is a complex in which one chlorine ligand has been replaced by a HSO_4^- ion and the other is a complex in which both chlorine ligands have been replaced. Larin *et al.* [8] reported a similar ligand replacement when $[Ni^{III}(en)_2Cl_2]Cl$ was dissolved in HNO_3.

Electronic Spectra

As shown in Fig. 2a, the electronic absorbance spectra of $[Ni^{III}(en)_2Cl_2]^+$ in HCl solutions are characterized by bands in the range 316 to 322 nm (peak 1) and 237 to 266 nm (peak 2). At pH > 1.5 peak 1 was not observed. There is no correlation between the behavior of peaks 1 and 2, therefore they are attributed to different species. By contrast, as will be shown in the subsequent section, peak 1 and the EPR spectrum of the $[Ni^{III}(en)_2Cl_2]^+$ complex behave in an analogous manner with respect to time and changes in pH. Thus, peak 1 is assigned to $[Ni^{III}(en)_2Cl_2]^+$. The nickel(III) absorbance is typically in the 300–400 nm range [9, 10], although in pulse radiolysis studies of $Ni^{III}(en)_n$ complexes Lati and Meyerstein [5] observed a λ_{max} at 280–290 nm. The spectrum of nickel(III) complexes in this region has been assigned to metal–ligand charge transfer [9, 10]. Based upon the spin concentration determined by EPR and the electronic absorbance a value of $\epsilon = 1.8\ (\pm 0.1) \times 10^4$ L mol^{-1} cm^{-1} has been calculated. This value is somewhat greater than those of similar complexes which typically are in the range of 2×10^3–1.5×10^4 L mol^{-1} cm^{-1} [9].

The origin of peak 2 is unknown, although it does not correlate with EPR spectrum of the $[Ni^{III}(en)_2Cl_2]^+$ complex. No absorbance was noted in the region of 550 nm, which is the position of the radical intermediates, formed during the decay of the Ni(III) macrocyclic amines [1, 2].

In both 1 N and 6 N H_2SO_4 solutions maxima in the absorbance were observed at 264 nm and 208 nm with a shoulder at about 350 nm. The peak at 264 nm is the dominant feature in the spectrum. Although the electronic spectra were not studied relative to the EPR spectrum of the Ni^{III} complex, by analogy we assign the 264 nm band to the $[Ni^{III}(en)_2(HSO_4)_2]^+$ complex.

Reaction Kinetics

Previous results have shown that the stability of Ni(III) amines strongly depends on the pH of the solution and such factors as the presence of halide ions [1]. At high pH the reduction of Ni(III) is generally very rapid, and presumably occurs via a concerted proton abstraction from a ligand and Ni(III) reduction, as previously mentioned [1, 2]. At low pH, in the absence of a sufficient concentration of free base, other reactions must prevail, such as the oxidation of halide ions by the Ni(III). Our results confirm these observations: at pH > 2 the decay of the Ni(III) complex was too rapid to follow by our technique, at pH ≅ 1 the complex was reasonably stable in solution, and at lower pH values, which were accompanied by greater chloride ion concentrations, the decay rate increased.

The results obtained with increasing concentrations of HCl are depicted in Fig. 3. Considering the complications involved in obtaining the EPR spectra at 77 K, the agreement between the EPR and absorbance data is good. A plot of the logarithm of the absorbance versus time yielded straight lines for solutions which were 1 N–6 N in HCl. The rate constants, listed in Table II, are a nonlinear function of the HCl concentration.

In an attempt to separate the effects of $[H^+]$ and $[Cl^-]$ on the decay rate the HCl concentration was fixed at 1 N, and the decay was followed after adding KCl to the solution. In the absence of KCl the half-life was 28 min. After making the solution 1 N in K^+ (2 N in Cl^-) the half-life decreased to 20 min, but upon further addition of KCl no significant changes in half-life were observed. This result suggests that both protons and chloride ions are responsible for the reduction of Ni(III).

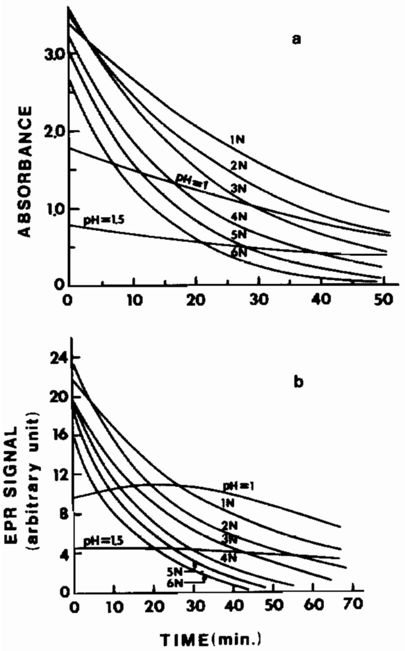


Fig. 3. Reaction of $[Ni^{III}(en)_2Cl_2]^+$ as a function of HCl concentration: (a) UV-visible spectra; (b) EPR spectra.

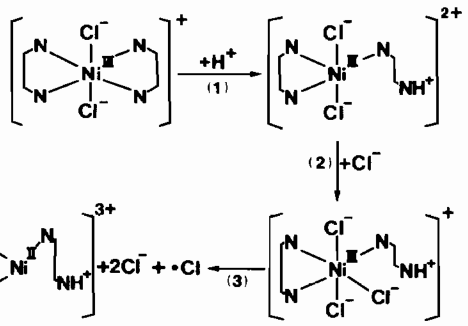
TABLE II. Kinetic Data for HCl-Promoted Dissociation of $[Ni^{III}(en)_2Cl_2]^{+a}$.

[HCl] (N)	$t_{1/2}$ (min)	$k \times 10^4$ (s^{-1})
1	27	4.3
2	21	5.5
3	17	6.8
4	13	8.9
5	11	10.5
6	9	12.8

[a] Rate data obtained at 25 °C from absorbance.

The synergistic role of protons and chloride ions is further illustrated by experiments in which the acid was H_2SO_4. Even in 6 N H_2SO_4 there was no observable decrease in Ni(III) concentration over a period of 2 h and only a 20% decrease over a period of 6 h. Obviously the replacement of Cl^- ions by HSO_4^- ions in the complex, and the replacement of Cl^- ions by HSO_4^- and SO_4^{2-} ions in solution had a marked effect on the stability of the Ni(III) complex. The reduction of Ni(III) in the $[Ni^{III}(en)_2(HSO_4)Cl]^+$ complex in the 1 N H_2SO_4 solution likewise was slow. This observation suggests that Cl^- ions from solution, rather than the Cl^- ions coordinated along the *z* direction of the complex, are responsible for the reduction step.

These phenomena may be understood in terms of an acid-assisted oxidation of Cl^- by Ni(III). Whitburn *et al.* [1] have demonstrated that Ni(III) is a powerful oxidant which is capable of oxidizing Cl^-, Br^-, SCN^- and N_3^-. The observed kinetic and spectroscopic results can be reasonably well described by the mechanism of Scheme 1, provided the rate constants for steps one and two are approximately equal, and both are slow compared with step 3.



Scheme 1.

At the lower chloride concentrations step 2 would be limiting and the rate of decomposition of the original complex would depend upon chloride concentration. At greater chloride concentrations (>2 N) step 1 would be rate limiting and the overall rate would become independent of chloride concentration. For this mechanism to be reasonable the rate constant for chelate ring opening upon protonation of $[Ni^{III}(en)_2Cl_2]^+$ must be on the order of 5×10^{-4} s^{-1} in 1 N HCl, which is considerably slower than the value of $k = 0.2$ s^{-1} which has been reported for the protonation of $[Ni^{II}(en)]^{2+}$ [11]. The slower rate of protonation and ring opening in the $Ni^{III}(en)_2$ complexes is supported by the stability of $[Ni^{III}(en)_2(HSO_4)_2]^+$ in strong acid media.

The fate of the •Cl is uncertain; however, it probably recombines to form Cl_2 and also attacks the en ligand. The reduction of Ni(III) is not reversible in the sense that the decay half-life in the presence of 760 torr Cl_2 was the same as that observed under vacuum.

The rather unusual curves observed for the solutions at pH = 1 and 1.5 deserve further comment. The slower long-term decay may be explained by the effects of the H^+ and Cl^- as proposed in scheme I. The small initial concentration of the Ni(III) complex, however, is surprising. It is possible that the dissolution of the solid $[Ni^{III}(en)_2Cl_2]Cl$ increases the local pH to the point (pH ≈ 2) where a rapid base-promoted reaction occurs. In fact, when the system was not stirred the initial loss of Ni(III) complex was even more dramatic.

Conclusions

trans-Dichlorobis(ethylenediamine)nickel(III) is moderately stable in aqueous HCl solutions over a narrow range of concentrations around pH = 1.5. At higher pH values the complex decomposes rapidly, presumably because of hydroxide attack on the ligand along with the reduction of Ni(III). At lower pH values both the presence of protons and chloride ions becomes important. Acid promoted chelate ring opening followed by the oxidation of Cl^- is believed to occur. In H_2SO_4 solutions Cl^- ligand replacement results in a much more stable complex.

Acknowledgement

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