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Complexation of a Nickel(III) Macrocyclic Complex by Sulfate Ion. A Pulse Radiolytic Study

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The kinetics of oxidation of Ni^{II}[*meso*-Me_6[14]aneN_4] (NiL^{2+}) to Ni(III) by OH radical and subsequent complexation by sulfate ion have been studied in acidic aqueous media at 22 °C and $\mu = 0.01$–0.3 M by the pulse radiolytic technique. Results indicate that NiL^{3+} hydrolyzes with a $pK = 3.7 \pm 0.2$ but that, at least up to pH 5.2, substitution by SO_4^{2-} occurs only on the unhydrolyzed species with a rate constant of 1×10^6 M^{-1} s^{-1} at $\mu = 0.03$ M. The equilibrium constant for sulfate complexation is 3.0×10^4 M^{-1} at $\mu = 0.03$ M and the product of the reaction is identical with the stable $NiLSO_4^+$ species produced by the electrochemical oxidation of NiL^{2+} in sulfate media. The results demonstrate the stabilization of Ni^{III} by sulfate complexation.

Introduction

In recent years, a large number of complexes have been prepared containing transition metals in uncommon oxidation states by chemical, electrochemical, and pulse radiolytic techniques.[2,3] Trivalent nickel complexes, for example, have been prepared and identified in the presence of stabilizing ligands such as EDTA,[4] a variety of nitrogen macrocycles,[5,6] and peptides.[7] Ni(III) complexes with nitrogen macrocyclic ligands are generally stable for long periods only in aprotic solvents, and kinetic studies involving Ni(III) in aqueous media have so far been concerned primarily with the formation and decay of the trivalent state.[8–11]

We have recently found, however, that in the presence of both a macrocyclic ligand and high excesses of polyvalent anion (for example, sulfate) nickel(III) solutions can be prepared which are indeed stable in water.[12] One such complex, Ni^{III}[*meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane](H_2O)SO_4^+ (Ni^{III}[Me_6[14]aneN_4](H_2O)SO_4^+ or more simply $NiLSO_4^+$), has been characterized, and mildly acidic solutions containing 0.1 M SO_4^{2-} stored for over 1 year show no significant signs of decomposition.[12]

In the present work, we have employed the pulse radiolytic technique to study the kinetics of oxidation of NiL^{2+} to $Ni^{III}L$ by hydroxyl radicals and the subsequent complexation kinetics for the formation of stable $NiLSO_4^+$. Equilibrium data for the latter reaction and for hydrolysis of NiL^{3+} have also been determined. The effect of ionic strength on the complexation rate has been studied to give further insight into the nature of the reacting species.

Experimental Section

Materials. The meso stereoisomers of the free ligand[13] and the perchlorate salt of the nickel(II) complex $NiL(ClO_4)_2$[14] were prepared according to the methods of Busch and co-workers. Chemical analyses of samples prepared in this laboratory were in good agreement with calculated analyses. Spectra of solutions of the complex prepared by us and provided by Professor Busch for comparison were virtually identical with each other, before and after oxidation. Kinetic experiments with complexes from the two sources yielded good agreement except that a slow reaction of small amplitude followed complexation by sulfate with some of our preparations. We interpret this difference as being due to a small amount of another isomer of NiL^{2+} since elemental analyses and the final spectrum of $Ni^{III}LSO_4^+$ were as predicted. The results reported here are, within experimental error, independent of the source of $NiL(ClO_4)_2$.

All other chemicals were of AR grade. $NaClO_4$ for ionic strength adjustment was prepared from NaOH and $HClO_4$. All water used was triply distilled.

Concentration ranges employed in this study were $[NiL^{2+}] = 1 \times 10^{-5}$–$4 \times 10^{-4}$ M and $[SO_4^{2-}] = 3 \times 10^{-5}$–0.1 M.

Procedure. The optical pulse radiolysis studies were carried out at the electron accelerator at the Hebrew University of Jerusalem. Pulses of 5-MeV electrons, 200 mA, and 0.05–0.3-μs duration were employed. The dose per pulse was 200–1000 rd (1 rd = 6.24×10^{13} eV g^{-1}).

Preparation of solutions and irradiation were performed as previously described.[15] All experiments were at room temperature, 22 ± 2 °C. Optional data was stored in digital form and processed in a Nova 1200 minicomputer linked to a Tektronix 1401 video terminal with hard-copy output. First-order plots were linear through up to 5 half-lives, and replicate determinations were generally within ±5% of each other. For the complexation reaction, kinetic results proved to be independent of dose per pulse. However, most runs were performed at a constant dose of ~1000 rd so that final optical densities could be used to determine equilibrium constants. Spectral measurements were referenced to the absorbance at 420 nm of a 10^{-3} M $Fe(CN)_6^{4-}$ solution which received a pulse identical with that of the NiL^{2+} solution ($\epsilon_{420} = 1000$ for $Fe(CN)_6^{3-}$).

The yields of primary products of pulse radiolysis in N_2O-saturated solutions at low pH are summarized by eq 3 and 4 of ref 10. From the discussion therein it may be seen that the OH radical is the only important reactant under the experimental conditions and that there is no significant reduction of $Ni^{II}L$.

Results and Treatment of Data

General Observations and Product Spectra. When N_2O-saturated solutions of $NiL(ClO_4)_2$ react with the OH radical in the presence of SO_4^{2-}, two widely separated consecutive reactions are observed which we attribute to the oxidation of NiL^{2+} to NiL^{3+} (eq 1) followed by complexation by sulfate (eq 2). At very high SO_4^{2-} concentration, the second product was found to be stable over a period of several weeks at pH 3 but decomposed within a few seconds at pH 11. At lower sulfate concentrations the second product is less stable, decomposing within several minutes at 3.0 < pH < 5.0. However, we did not study the decomposition kinetics in detail, as our experimental setup does not enable measurements at times longer than 2 min. UV–visible spectra of the two products were determined at pH 3 and are shown in Figure 1. The observed spectrum of NiL^{3+} is independent of whether or not sulfate ion is present and is similar to that reported by Patterson et al.[9b] for the same system at pH 5.

$$NiL^{2+} + OH\cdot \xrightarrow{k_1} NiL^{3+} + OH^- \qquad (1)$$

$$NiL^{3+} + SO_4^{2-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} NiLSO_4^+ \qquad (2)$$

The spectrum of the final product is virtually identical in all respects with that reported earlier for electrochemical preparations of the $NiLSO_4^+$ ion.[12b]

Kinetics of NiL^{2+} Oxidation. The initial oxidation of NiL^{2+} to trivalent nickel (eq 1) is a very rapid reaction which obeys first-order kinetics under all conditions employed in the study.

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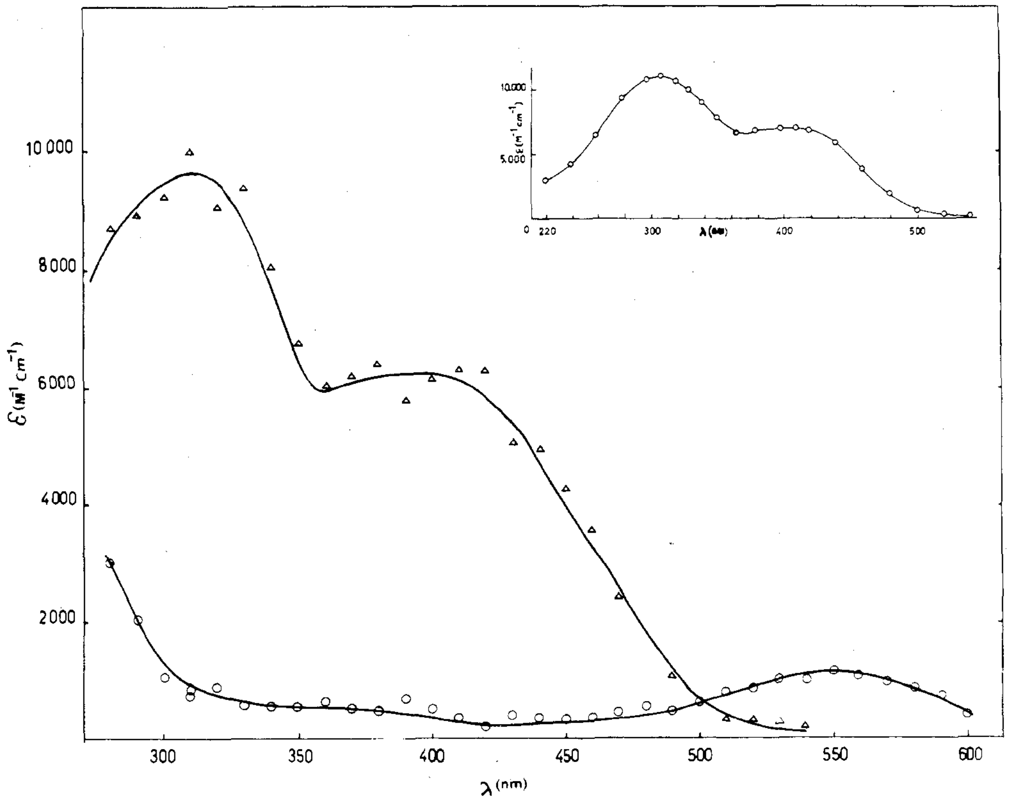

Figure 1. UV–visible spectra of NiL^{3+} (○) and $NiLSO_4^+$ (△) at pH 3 and 22 °C. Insert: spectrum of electrochemically produced $NiLSO_4^+$.[12]

Table I. Equilibrium Quotient for $NiLSO_4^+$ Formation[a]

pH[b]	3.20	3.20	3.55	4.10	4.70	5.20
μ, M[c]	0.30	0.03	0.03	0.03	0.03	0.03
$10^{-3}Q$, M^{-1}	3.0 ± 0.2	25 ± 5	22 ± 2	12 ± 2	3.3 ± 0.4	1.0 ± 0.2
pK_H^{calcd}		3.9	4.0	3.9	4.0	3.7

[a] 22 ± 2 °C, $[SO_4^{2-}] = 3 \times 10^{-5}$–$1 \times 10^{-2}$ M, $[Ni(III)]_{total} \approx 3 \times 10^{-6}$ M. [b] ±0.02 pH unit before radiolysis. [c] Adjusted with $NaClO_4$.

The observed rate constant is independent of sulfate ion concentration, pH, and wavelength of monitoring light and is first order in $[NiL^{2+}]$. The second-order rate constant for this process is $k_1 = (1.5 \pm 0.5) \times 10^9\ M^{-1}\ s^{-1}$, in good agreement with the result reported by Patterson et al.[9] for oxidation in the absence of SO_4^{2-}.

Formation Constant for $NiLSO_4^+$. Hydrolysis of NiL^{3+}. For lower concentrations of SO_4^{2-}, the limiting optical density at 320 nm (near the absorption maximum for $NiLSO_4^+$) was observed to increase with $[SO_4^{2-}]$ in a manner consistent with the formation of a single complex as shown by eq 2. An equilibrium quotient was calculated for each set of conditions by referencing the observed absorbance to the limiting absorbance obtained at very high SO_4^{2-} concentrations and to the absorbance of uncomplexed NiL^{3+} produced in the initial oxidation reaction. Table I gives the average value, Q, for this quotient for a variety of acidities and two ionic strengths. Each determination is the result of experiments at four to six different SO_4^{2-} concentrations with extra weighting, when possible for conditions where between 20 and 80% of the Ni(III) is complexed. Initial $[NiL^{2+}]$ was 1×10^{-4} M for all experiments and identical pulse intensities were used for each series. It can be seen from Table I that at ionic strength $\mu = 0.03$ M the apparent stability quotient decreases steadily with increasing pH. This variation can be adequately described by assuming that the rapid hydrolysis of NiL^{3+} (eq 3) competes

$$NiL^{3+}(aq) \underset{}{\overset{K_H}{\rightleftharpoons}} NiLOH^{2+} + H^+ \qquad (3)$$

with the formation of the nickel(III)–sulfate complex. Thus

Table II. Complexation Results at $\mu = 0.03$ M

pH	$10^{-5}k_A$, $M^{-1}\ s^{-1}$	k_B, s^{-1}
3.20	6.7	120
3.57	3.9	60
4.10	1.1	45
4.72	0.31	35
5.20	0.24	20
3.2[a]	0.65	130

[a] $\mu = 0.3$ M.

the equilibrium quotient Q is related to the stability constant K for reaction 2 and K_H by

$$Q = \frac{[NiLSO_4^+]}{[Ni^{III}]_T[SO_4^{2-}]} = \frac{K}{1 + K_H/[H^+]} \qquad (4)$$

where $[Ni(III)]_T$ represents the sum of the hydrolyzed and unhydrolyzed forms. We estimate the limiting value of $Q = K = (3.0 \pm 0.5) \times 10^4\ M^{-1}$ at $\mu = 0.03$ M and from this value and eq 4 calculate a pK_H for each set of experiments in Table I. The agreement is quite good (last line of Table I) and leads to a value of $pK_H = 3.9 \pm 0.2$ (deviation includes the effect of errors in Q). Since at pH 5.2 the overall oxidation reaction can be recast as

$$NiL^{2+} + OH\cdot \rightarrow NiLOH^{2+} \qquad (1')$$

the pH of the system did not change during the initial oxidation nor was there an appreciable change during complex formation except possibly at the highest $[SO_4^{2-}]$ at pH 5.2.

Kinetics of $NiLSO_4^+$ Formation. The kinetics of $Ni^{III}L$ complexation by sulfate ion were studied under the conditions described in the previous section. At constant pH and μ the reaction obeys a first-order rate law with an observed rate constant k_0 which is independent of pulse intensity and varies linearly with sulfate concentration

$$k_0 = k_A[SO_4^{2-}] + k_B \qquad (5)$$

This relationship is demonstrated in Figure 2. Values of the

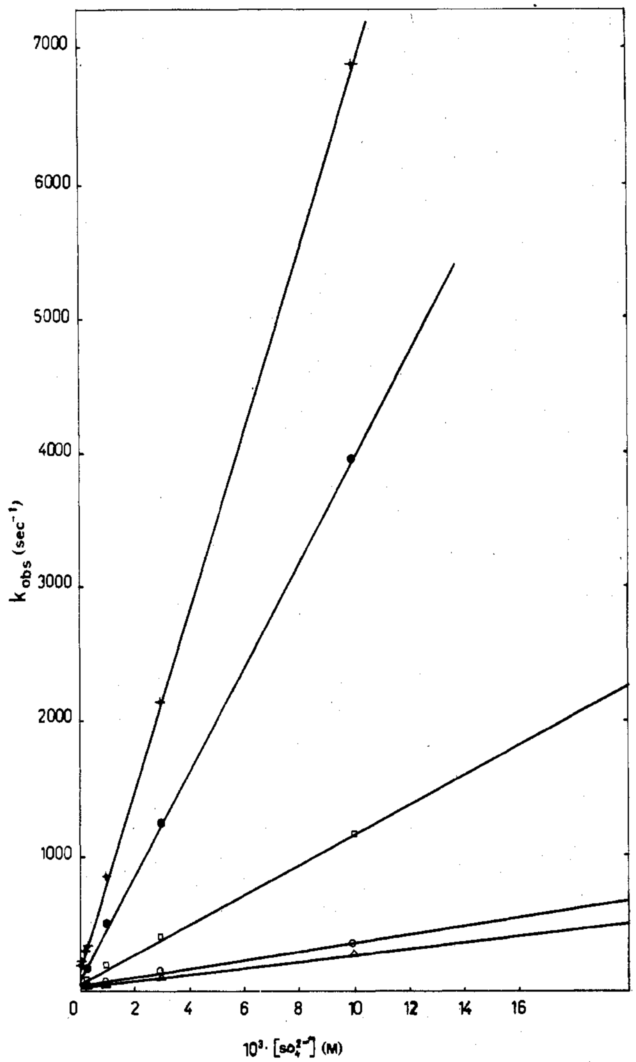

Figure 2. Dependence of k_o on $[SO_4^{2-}]$ at μ = 0.03 M and 22 °C. Key: (+) pH 3.20, (●) pH 3.57, (□) pH 4.10, (○) pH 4.72, (△) pH 5.20.

parameters k_A and k_B are given in Table II. Although eq 5 has the form expected for the reversible reaction indicated in eq 2, the ratio k_A/k_B agrees with the values of Q in Table I only at pH 5.2 and is 4–5 times smaller for each of the other sets of data. This difference appears to be too large to be attributed to experimental error in the determination of k_B. In addition, blank solutions containing no sulfate show a small absorbance change at 320 nm which has a first-order rate constant similar (<3 times) to the observed value of k_B and like k_B decreases with increasing pH. Analysis of this situation leads to the following conclusions: (i) the $[SO_4^{2-}]$-dependent parameter k_A can be related to the forward rate constant k_2; (ii) there is a form of $Ni^{III}L$ which forms slowly compared to the rate of Ni(II) oxidation or Ni(III) hydrolysis; (iii) this minor species (perhaps a conformational isomer of NiL^{3+}) reacts rapidly enough with SO_4^{2-} to provide an alternate path for complex formation. Sample calculations taking account of the constraints imposed by the principle of detailed balance[16] indicate that this path could be responsible for a contribution to k_o which, having the form $(a + b[SO_4^{2-}])/(c + d[SO_4^{2-}])$, varies only slightly with $[SO_4^{2-}]$ and is of the proper magnitude to explain values of k_B larger than those expected for k_{-2}.[17]

Figure 2 demonstrates a dependence of k_A on pH. This variation can be explained by the presumption that the hydrolyzed species $NiLOH^{2+}$ has a reactivity with sulfate which is negligible compared to that of NiL^{3+}. The ratio k_A/k_2 then becomes equal to the fraction of total Ni(III) in the unhydrolyzed form, and the hydrolysis constant K_H can be determined from eq 6 where the quantity in parentheses is equal to $[NiLOH^{2+}]/[NiL^{3+}]$.

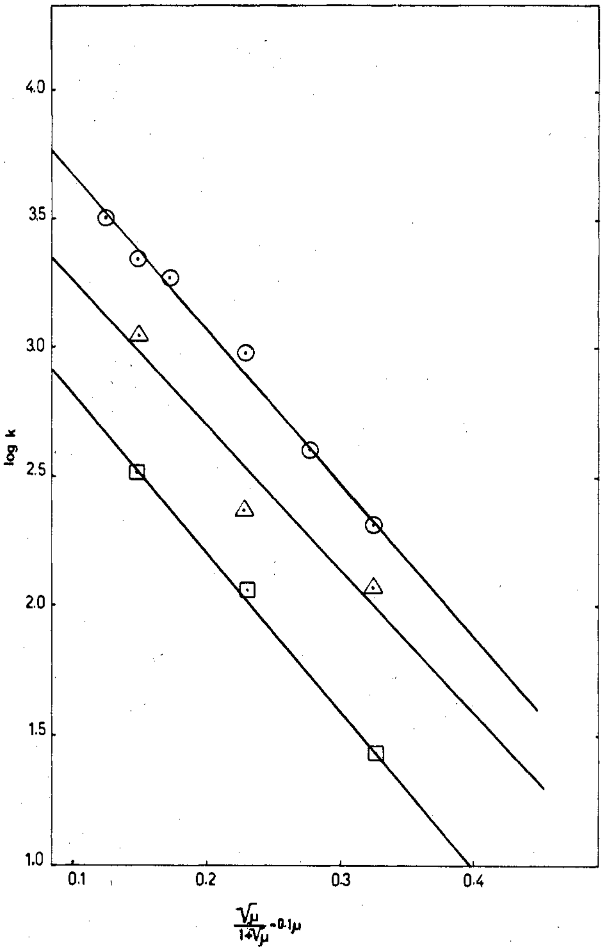

Figure 3. Ionic strength dependence for complex formation. The rate constant, k, is the observed rate constant for $[SO_4^{2-}] = 3 \times 10^{-3}$ M corrected for k_B. Key: (□) pH 4.7, (△) pH 4.1, (○) pH 3.2.

$$K_H = [H^+]\left(\frac{1 - k_A/k_2}{k_A/k_2}\right) \qquad (6)$$

Analysis of eq 6 for the data of Figure 2 leads to values of $k_2 = (1.0 \pm 0.2) \times 10^6$ M^{-1} s^{-1} and pK_H = 3.5 ± 0.3 M^{-1} at μ = 0.03 M.

This determination of pK_H is in reasonably good agreement with the value obtained from final absorbances. In view of larger uncertainties in rate constant determinations and the kinetic complexities noted above, we feel that the average value of pK_H = 3.7 adequately explains both the kinetic and equilibrium results.

The foregoing analysis presumes that NiL^{3+} is the only reacting species throughout the pH range of our experiments even though it is a minor species at higher pH. The variation of k_A with ionic strength[18] was studied at pH 3.2, pH 4.1, and pH 4.7. Plots of log k_A vs. $\mu^{1/2}/(1 + \mu^{1/2})$ have slopes of about −5.5 for the three sets of experiments. For oppositely charged ions at high ionic strength, values somewhat less negative than the charge product $-Z_AZ_B$ are common.[19] The ionic strength variation is displayed in Figure 3 as plots of log k_{obsd} vs. $\mu^{1/2}/(1 + \mu^{1/2}) - 0.1\mu$. The last term helps correct for ion pairing.[20,21] The slopes of the three plots in Figure 3 are all very close to −6.0, indicating that even at higher pH, k_A is due to the reaction between tripositive NiL^{3+} and dinegative SO_4^{2-} with no significant contribution of a path involving $NiLOH^{2+}$.

Discussion

The oxidation of Ni(II) to Ni(III) by hydroxyl radicals is a phenomenon for which a number of specific examples exist,[4,9-11] including previous studies of the Ni[Me$_6$[14]aneN$_4$]system.[9,11] The rate constant $k_1 = (1.5 \pm 0.5) \times 10^9$ M^{-1} s ($\mu = 0.3$ M) is similar to that found in the earlier work.

The demonstration from both spectral and kinetic data that Ni[Me$_6$[14]aneN$_4$]$^{3+}$ hydrolyzes with an average pK_H of 3.7 is consistent with the earlier observation that Ni^{III}[Me$_6$-[14]dieneN$_4$]$^{3+}$ has a pK = 3.45.[10,22] Acid dissociation constants for a series of five cobalt(III) macrocycles tabulated by Endicott[23] are all in the range pK_1 = 2.7–4 with Co^{III}-[Me$_6$[14]aneN$_4$] the most acidic. The enhanced acidity of trivalent metal ions over the +2 state is well established,[24] and the relatively high acidities of these macrocyclic complexes seems quite reasonable. Further hydrolysis at higher pH is also plausible (pK_2 = 6.4 for CoL^{3+}).[24]

Patterson et al.[9] interpret the slope of +3 of the ionic strength dependence for the conproportionation reaction between the Ni^{III}- and Ni^{I}-4,11-diene complexes as an indication that Ni(III) is not hydrolyzed at pH 5. The ionic strength and pH dependence for SO$_4^{2-}$ complexation (Figures 2 and 3) indicate that in our system NiLOH^{2+} is the principal species at this pH but that NiL^{3+} is the reacting form of Ni(III). The fact that ionic strength effects are similar for the forward rate constant and the equilibrium quotient (cf. the first two entries in Table I with Figure 3) is as expected.[21]

The strong absorption bands in the near-UV of NiLSO$_4^+$ are most probably due to ligand-to-metal charge-transfer processes. It is of interest to note that the absorption band of NiL^{3+} at 550 nm, which is most probably due to a d–d transition, disappears upon complexation with sulfate.

The value of $k_2 = 1 \times 10^6$ M^{-1} s^{-1} indicates a marked lability for the axial water molecules on NiL^{3+}. Preliminary experiments with phosphate (at pH 5) also indicate rapid replacement of an axial water molecule. If we presume that reaction 2 proceeds by a dissociative-type mechanism in which ion-pair formation between NiL^{3+} and SO$_4^{2-}$ (eq 7) has an

$$\mathrm{NiL(H_2O)_2^{3+} + SO_4^{2-}} \overset{K_{\mathrm{ip}}}{\rightleftharpoons} \mathrm{[NiL(H_2O)_2^{3+},SO_4^{2-}]} \qquad (7)$$

equilibrium constant, K_{ip}, of about 90,[26] we obtain a first-order rate constant of $k_{\mathrm{ex}} = 1.1 \times 10^4$ s^{-1} for water exchange on NiL^{3+}. As would be expected, this rate is less than the rates of ligand exchange measured for several macrocyclic complexes of isoelectronic d^7 Co(II).[26]

The potential of 0.850 V vs. NHE observed for the anodic oxidation of NiL^{2+} in the presence of sulfate ion[12] can be combined with the formation constant at μ = 0.3 M (Table I) to give an estimate of +1.1 V for the redox potential of NiL^{3+}. This is in good agreement with the potential reported by Lovecchio et al.[6] in acetonitrile. A similar correlation has been observed for Ni[Me$_6$[14]diene]$^{3+}$ which has a redox potential of +1.34 V in water.[10]

Finally, this work shows that the stabilization of Ni(III) macrocyclic complexes, previously demonstrated by electrochemical oxidation of NiL^{2+} in the presence of SO$_4^{2-}$, can be achieved by a two-step process in which the unstable Ni(III) intermediate reacts directly with sulfate. The value of $K = 3 \times 10^4$ is similar to values found for sulfate complexation with other trivalent metals.[24] This value is over 300 times greater than would be expected for contact ion-pair formation between 3+ and 2− charges[25] and, taken together with the marked spectral changes and the dramatic stabilization of the trivalent state by sulfate, provides sufficient evidence for true inner-sphere complex formation.

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Registry No. NiL^{2+}, 70850-81-6; NiL^{3+}, 70850-82-7; SO$_4^{2-}$, 14808-79-8; NiLSO$_4^+$, 70850-83-8.

References and Notes

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