species, which enhances collisional interaction. The large effect seen for phenyl substitution may be due to favorable orbital overlap in the formation of the Cl^--associated transition state.

Ground-state quenching of $^2T_1/^2E$ results in a diminution in the population of the states and must result in a diminution of the quantum yields of the various processes that arise from $^2T_1/^2E$. Φ_{rx}, for example, would be expected to decrease with increasing [Cr(III)] in 1.0 M NaCl inasmuch as $\Phi_{rx} = {}^2k_{rx}{}^2\tau$ and ${}^2\tau = 1/({}^2k_0 + {}^2k_g[\mathrm{Cr(III)}])$. It is easily seen that a plot of $1/\Phi_{rx}$ vs. [Cr(III)] is predicted to be linear with a slope of ${}^2k_g/{}^2k_{rx}$ and an intercept of ${}^2k_0/{}^2k_{rx}$; the slope/intercept ratio represents ${}^2k_g/{}^2k_0$. It is also clear that the maximum effect will be seen for those complexes with a combination of large values of ${}^2k_g$ and low values of ${}^2k_{rx}$. Unfortunately, a low value of ${}^2k_{rx}$ implies a low value of Φ_{rx} rendered even lower by ground-state quenching. The low value of Φ_{rx} becomes more uncertain; the large value of $1/\Phi_{rx}$ has very large error limits. As a result, although we have determined Φ_{rx} as a function of [Cr(III)] for 11 complexes over a concentration range of greater than an order of magnitude, only three complexes show the effect outside of experimental error. Figure 4 illustrates the data for the 5-Br(phen), 5-Ph(phen), and 4,7-Ph_2phen complexes, which have the largest values of ${}^2k_g$. Comparison of the slope/intercept ratios from Figure 4 with the values of ${}^2k_g$ and ${}^2\tau_0$ from Table I shows agreement of the values within a factor of 3. Considering the errors involved in the data and the extrapolations, such agreement must be considered to be quite good.

Registry No. $Cr(bpy)_3^{3+}$, 15276-15-0; $Cr(4,4'\text{-}Me_2bpy)_3^{3+}$, 58220-56-7; $Cr(4,4'\text{-}Ph_2bpy)_3^{3+}$, 58220-56-7; $Cr(phen)_3^{3+}$, 15276-16-1; $Cr(5\text{-}Cl(phen))_3^{3+}$, 51194-62-8; $Cr(5\text{-}Br(phen))_3^{3+}$, 51194-64-0; $Cr(5\text{-}Me(phen))_3^{3+}$, 51194-70-8; $Cr(5\text{-}Ph(phen))_3^{3+}$, 51194-60-6; $Cr(5,6\text{-}Me_2phen)_3^{3+}$, 51261-67-7; $Cr(4,7\text{-}Me_2phen)_3^{3+}$, 51194-72-0; $Cr(4,7\text{-}Ph_2phen)_3^{3+}$, 69178-81-0; $Cr(3,4,7,8\text{-}Me_4phen)_3^{3+}$, 51194-74-2.

Contribution from the Departments of Chemistry, Ben Gurion University of the Negev, Beer-Sheva, Israel, the Nuclear Research Center Negev, Beer-Sheva, Israel, and the University of Rhode Island, Kingston, Rhode Island

Difference in the Stabilities of the Diastereoisomers of the Tervalent Nickel Complex with 5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane in Sulfate- and Perchlorate-Containing Aqueous Solutions. An Electrochemical and Pulse Radiolysis Study

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The electrochemical oxidation of two isomers of the complex of divalent nickel with *rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane in aqueous solutions containing perchlorate and sulfate was studied. These oxidations are less reversible than that of the analogous meso complex. Furthermore the kinetic stabilization of the tervalent meso complex by sulfate, through the formation of $NiL(SO_4)_2^-$, is ca. 5000 times larger than that of the racemic complexes. The oxidation of a racemic complex by hydroxyl radicals was studied. The pK_H of the axial water bound to the tervalent nickel complex thus formed is 3.7. The stability constant for complexation by the first sulfate is 2200 M^{-1}, i.e., ca. one order of magnitude less than that observed for the corresponding meso complex. The rate-determining step in the anation by sulfate of the tervalent racemic complex is an isomerization of the latter, the rate of which is independent of sulfate concentration. The reasons for the large differences in properties of these diastereoisomers are discussed. The decomposition of several tervalent nickel complexes in alkaline media is first-order in hydroxide ion concentration. Kinetic salt effects on this reaction indicate that at pH 10.0 the tervalent complexes have the formula $NiLOH^{2+}$ for L = the racemic and meso isomers as well as for the corresponding hexamethyl[14]diene ligand and $NiL(OH)_2^+$ for L = cyclam. This means that in the latter complex the tervalent nickel is in an octahedral environment whereas in the former ones it is pentacoordinated.

We have recently reported that axial ligation of sulfate and other anions to several tervalent nickel complexes with tetraaza macrocyclic ligands lengthens considerably the lifetime of the tervalent nickel complexes in slightly acidic aqueous solutions.[2,3] A detailed study indicated that in concentrated sulfate solutions the stabilization is due to the equilibrium reaction

$$NiL^{3+} + 2SO_4^{2-} \rightleftarrows NiL(SO_4)_2^- \qquad (1)$$

where $k_1 \sim 10^5\ M^{-2}$ and $5 \times 10^6\ M^{-2}$ for L = L_1 = 1,4,8,11-tetraazacyclotetradecane and L = L_2 = *meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, respectively.[4,5] However, whereas the addition of 0.5 M Na_2SO_4 to NiL_2^{3+} at pH 1.6 lengthens the half-life of the tervalent nickel from ~1.2 min to ≥1 year, the addition of the same sulfate concentration to NiL_1^{3+} increases its lifetime only from ~10 h to ~5 days.[6] These results indicate that $NiL_2(SO_4)_2^-$ decomposes only via $NiL_2(H_2O)_2^{3+}$ whereas $NiL_1(SO_4)_2^-$ decomposes by oxidation of the ligand L_1, without loss of the axial sulfates.[4,7]

These very different effects of sulfate on the properties of otherwise very similar complexes seemed to indicate that steric factors considerably affect the chemical properties of these tervalent nickel complexes. We decided therefore to study the

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[†] Dr. Gregory Ginzburg passed away August 5, 1981.

(1) (a) Ben-Gurion University of the Negev. (b) University of Rhode Island. (c) Nuclear Research Centre Negev.

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(7) A small contribution of $NiL_2(SO_4)(H_2O)^+$ to the decomposition reaction cannot be ruled out.

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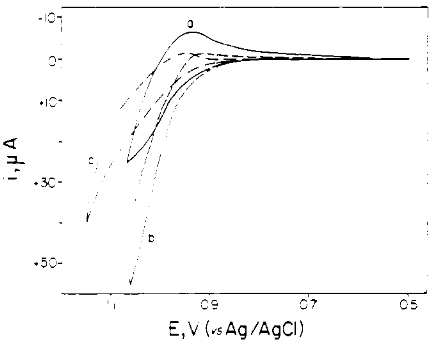

Figure 1. Cyclic voltammograms of 5 × 10^{-4} M NiL^{2+} in 0.3 M NaClO$_4$ at pH 2.0: 1.2-cm^2 Au anodes and 11.2 mV/s scan rate. The current is corrected for the contribution of the supporting electrolyte: (a) NiL$_2^{2+}$; (b) α-NiL$_3^{2+}$; (b) α-NiL$_3^{2+}$; (c) β-NiL$_3^{2+}$.

properties of the tervalent nickel complex with L$_3$ = *rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane in the presence and absence of sulfate.

During the present study reports appeared on the different properties of NiL$_1^{3+}$ and NiL$_4^{3+}$, where L$_4$ = 1,4,7,11-tetraazacyclotetradecane.[8] Those results also indicated that steric factors contribute considerably to the properties of tervalent nickel complexes though naturally the difference between the ligands studied there is larger than that of those reported here.[8] Furthermore, reports appeared on the effect of the stereoisomerization of the bonding of the hydrogens to the nitrogens on the physical and chemical properties of divalent copper complexes with tetraaza macrocyclic ligands.[9]

Experimental Section

Materials. The complexes NiL$_1$(ClO$_4$)$_2$, NiL$_2$(ClO$_4$)$_2$, and NiL$_5$(ClO$_4$)$_2$ were identical with those used in earlier studies.[2-6] (L$_5$ = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene). NiL$_3$(ClO$_4$)$_2$ was prepared by reduction of NiL$_5$(ClO$_4$)$_2$ with Raney nickel, and isomer separation was done according to the procedure described in the literature.[10] Thus the α form of NiL$_3^{2+}$ was obtained. This form is stable only in acidic solutions and in neutral and slightly acidic solutions is transformed into the thermodynamically more stable β form.[10] The transition was followed spectrophotometrically. Only fresh solutions of the α isomer at pH <2 were used.

All other compounds were AR grade and were used without further purification. Triple-distilled water was used throughout this study.

Electrochemical Experiments. The setup used was identical to that described earlier in detail.[5,6] All potentials quoted are vs. an Ag/AgCl reference electrode.

Pulse Radiolysis Experiments. 0.1–1.5-μs 200-mA pulses of 5-MeV electrons from the linear accelerator at the Hebrew University of Jerusalem were used. The dose per pulse was 100–3000 rd. The cell was a 4-cm cell with an optical path length of 12.5 cm. The details of the setup in Jerusalem and the techniques used to evaluate the results were reported earlier in detail.[3,6]

Results and Discussion

Cyclic voltammograms of the three isomers NiL$_2^{2+}$, α-NiL$_3^{2+}$, and β-NiL$_3^{2+}$ in perchlorate media at pH 2.0 are plotted in Figure 1. For all three isomers the electrochemical oxidation process is clearly irreversible. Only for the meso isomer, NiL$_2^{2+}$, was a reduction wave observed on the back scan. An experiment to prepare α-NiL$_3^{3+}$ or β-NiL$_3^{3+}$ by preparative electrochemical oxidation at 1.2 or 1.4 V failed though NiL$_2^{3+}$ can be prepared under these conditions.[4]

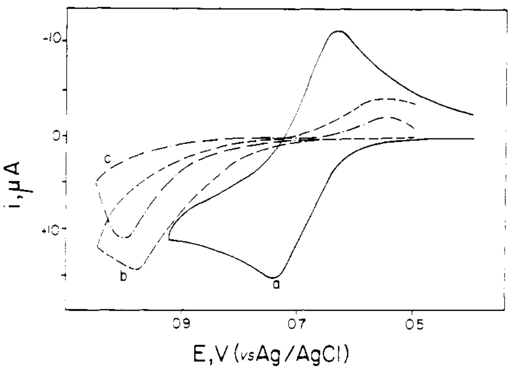

Figure 2. Conditions as in Figure 1 but 0.1 M Na$_2$SO$_4$ supporting electrolyte instead of the perchlorate.

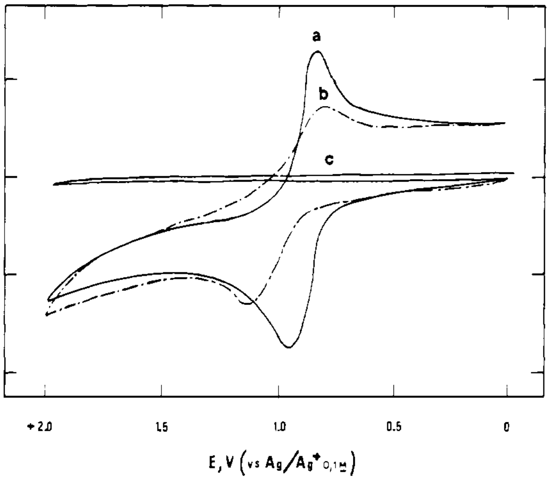

Figure 3. Cyclic voltammograms in CH$_3$CN, 0.1 M (C$_4$H$_9$)$_4$NClO$_4$; scan rate 11.2 mV/s: (a) 4.7 × 10^{-3} M NiL$_2$(ClO$_4$)$_2$, (b) 3 × 10^{-3} M α-NiL$_3$(ClO$_4$)$_2$, (c) supporting electrolyte only.

Cyclic voltammograms of the three isomers in sulfate-containing media are plotted in Figure 2. For all three complexes the electrochemical process is irreversible under the experimental conditions $\Delta E_p > 60$ mV. For NiL$_2^{2+}$ the anodic and cathodic (measured relative to the extended base line) peak currents are equal. For α- and β-NiL$_3^{2+}$ the cathodic current is considerably smaller than the anodic one. As the lifetime of α- and β-Ni^{III}L$_3$ in 0.1 M Na$_2$SO$_4$ at pH 2.0 is much longer than the scan time (see below), this result indicates that the electrochemical oxidation of α- and β-NiL$_3^{2+}$ to α- and β-Ni^{III}L$_3$[11] is accompanied by other Faradaic processes, i.e., the oxidation of the ligand. This suggestion is in accord with the observation that NiL$_3^{3+}$ cannot be formed in aqueous solutions by preparative electrochemical oxidation in perchlorate media though the lifetime of NiL$_3^{3+}$ in this medium is similar to that of NiL$_2^{3+}$ (see below), which can be prepared electrochemically,[2,4,5] and similar anodic currents are observed in both systems.

Measurements in 0.5 M Na$_2$SO$_4$ and at slow scan rates, 2.2 mV/s, indicate that $E_{1/2}$ in these solutions is ca. 750 mV for α- and β-NiL$_3^{2+}$ and 640 mV for NiL$_2^{2+}$. This result indicates that the stability constant for the equilibrium reaction shown in eq 2 is at most two orders of magnitude smaller than K_1

$$\alpha\text{- or }\beta\text{-NiL}_3^{3+} + n\text{SO}_4^{2-} \rightleftarrows \alpha\text{- or }\beta\text{-NiL}_3(\text{SO}_4)_n^{3-2n} \qquad (2)$$

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[11] The notation α- and β-NiL$_3^{3+}$ indicates that those are the oxidation products of α- and β-NiL$_3^{2+}$ without indicating that no configurational changes occurred during the oxidation process.[12]

Table I. Half-Life Time for the Decomposition of $NiL(SO_4)_n^{3-2n}$ in 0.1 M Na_2SO_4, pH 2.0

complex	approx half-life, h	complex	approx half-life, h
$NiL_1(SO_4)_2^-$	120	α-$NiL_3(SO_4)_2^-$	3
$NiL_2(SO_4)_2^-$	9000	β-$NiL_3(SO_4)_2^-$	2

$\sim 5 \times 10^6$ M^{-2} for NiL_2^{3+}.[12] K_2 will be even larger if the redox potential of α- or β-NiL_3^{2+} in 0.3 M $NaClO_4$ is higher than that of NiL_2^{2+}. As $K_3 = 250$ at $\mu = 0.3$ M (see eq 3),

$$\beta\text{-}NiL_3^{3+} + SO_4^{2-} \rightleftarrows \beta\text{-}NiL_3SO_4^{+} \qquad (3)$$

we have to conclude that $n = 2$ in eq 2 as was found also for other NiL^{3+} complexes, where L = L_1, L_2, and L_5.[4,5] The cyclic voltammograms of NiL_2^{2+} and α-NiL_3^{2+} in CH_3CN media were studied, and these are shown in Figure 3. The results indicate that the oxidation of NiL_2^{2+} under these conditions is irreversible, the peak separation being slightly over 60 mV. However, the oxidation peak potential of α-NiL_3^{2+} is considerably shifted to a more positive potential whereas the reduction of α-NiL_3^{3+}, back scan, is faster (i.e., the peak separation is considerably larger than 60 mV). These results suggest an intervention of a rate-determining chemical reaction prior to the electron transfer in the oxidation process of α-NiL_3^{2+}, which shifts the oxidation peak strongly.

α- and β-$NiL_3(SO_4)_n^{3-2n}$ were synthesized by preparative electrochemical oxidation in 0.1 M Na_2SO_4 at pH 2.0. The spectra of these complexes are similar to those of $NiL_2(SO_4)_2^-$.[2,5] However the lifetimes of the complexes under these conditions differ considerably, as can be seen in Table I. These results indicate that the decomposition reactions of α- and β-$NiL_3(SO_4)_2^-$ do not require the loss of the two sulfates prior to the oxidation of the ligand. In this respect the complexes α- and β-$Ni^{III}L_3$ resemble $Ni^{III}L_1$[4,6] and differ from their isomer $Ni^{III}L_2$.[4]

Homogeneous Oxidation of β-NiL_3^{2+} by Hydroxyl Radicals. In order to obtain further information on the factors affecting the oxidation of the racemic isomer β-NiL_3^{2+} and the properties of the tervalent complex obtained, we decided to study the reaction

$$\cdot OH + \beta\text{-}NiL_3^{2+} \rightarrow \beta\text{-}Ni^{III}L_3 \qquad (4)$$

and the properties of the tervalent product complex in perchlorate and sulfate media by the pulse radiolysis technique. The parallel study for NiL_2^{2+} was reported,[3] and the reactions of α-NiL_3^{2+} cannot be studied as pH ≥ 3 is required if one wants to transform the hydrated electrons into hydroxyl radicals via

$$e^-_{aq} + N_2O \rightarrow N_2 + \cdot OH + OH^-_{aq} \qquad k = 8.7 \times 10^9\ M^{-1}\ s^{-1}\ {}^{13} \qquad (5)$$

as

$$e^-_{aq} + H_3O^+ \rightarrow H \qquad k = 2.2 \times 10^{10}\ M^{-1}\ s^{-1}\ {}^{13} \qquad (6)$$

The rate of reaction 4 was measured by following the rate of appearance of the absorption spectrum a in Figure 4; $k_4 = (3 \pm 1) \times 10^9$ M^{-1} s^{-1}. The formation of this transient is followed by two consecutive processes obeying first-order rate laws.

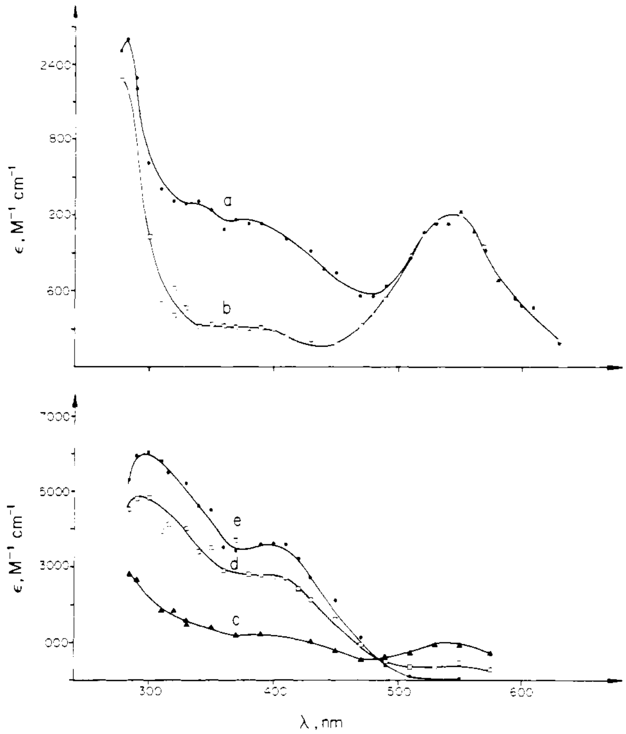

Figure 4. Absorption spectra of $Ni^{III}L_3$ complexes formed by the oxidation of NiL_3^{2+} with hydroxyl radicals. Solutions contained 1×10^{-4} M $NiL_3(ClO_4)_2$ at pH 3.2 and were saturated with N_2O. Pulse intensity was 1000 rd/pulse. Curves are shown for 0.3 M $NaClO_4$ solutions (a) 6 μs after the pulse and (b) 10 ms after the pulse, Curves are shown for 0.1 M Na_2SO_4 solutions (c) 10 μs after the pulse, (d) 7 ms after the pulse, and (e) 9 s after the pulse.

The first of these reactions has a rate of $(2.6 \pm 0.6) \times 10^3$ s^{-1} and causes a considerable decrease of the absorption in the near-UV without affecting the absorption band with the maximum at 550 nm (Figure 4, curve b). The latter observation indicates that the two first intermediates formed are tervalent nickel complexes, and it is suggested that the reaction observed is a rearrangement, isomerization, reaction, which causes a change in the conformation of the ligand. Similar processes were reported for $Ni^{III}L_2$[3] and other tervalent nickel complexes.[14,15] This isomerization reaction is much faster than that of α-NiL_3^{2+} into β-NiL_3^{2+}, but an increase in the rate is expected due to the higher acidity of the N–H bond in the tervalent complex.

The second first-order process observed causes the disappearance of all absorption bands at $\lambda > 300$ nm and is therefore attributed to the oxidation of the ligand by the central tervalent nickel. The rate of this reaction is $k \sim 0.04$ s^{-1} in the pH range 3.0–6.0.

When the same experiments are repeated in sulfate-containing solutions, the first reaction observed is again reaction 4. Thus the spectrum of the first transient observed in the sulfate-containing solution, Figure 4 curve c, is identical to that observed in the perchlorate solution, Figure 4 curve a. The formation of β-$Ni^{III}L_3$ in sulfate-containing solutions is followed by two first-order processes after which the absorption spectra d and e in Figure 4 are observed. The latter product is stable on the time scale of the pulse radiolysis experiment, several minutes, and its absorption spectrum is identical with that of β-$NiL_3(SO_4)_2^-$ produced electrochemically.

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(12) This comparison is formally justified only if $n = 2$. However as the change in $\Delta E°$ clearly points out that $n > 1$ and as $n \leq 2$ due to the number of coordination sites available, the treatment is correct. We cannot obtain an exact value of K_2 as we have only a lower limit for the redox potential of NiL_3 in perchlorate media.

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Table II. Rates of Reaction Observed in Sulfate-Containing Solutions

$[SO_4^{2-}]$, M	pH	k_1,[a] s^{-1}	k_2,[b] s^{-1}
10^{-2}	3.0	120 ± 20	3.0 ± 1.0
2×10^{-3}	3.0	60 ± 10	1.0 ± 0.2
5×10^{-4}	3.0	67 ± 5	1.0 ± 0.4
10^{-2}	5.0	15 ± 5	0.6 ± 0.2
2×10^{-3}	5.0	21 ± 8	0.6 ± 0.2

[a] Rate of the reaction causing the change in the spectrum from curve c to curve d in Figure 4. [b] Rate of the reaction causing the change in the spectrum from curve d to curve e in Figure 4.

Though the formation of β-$NiL_3(SO_4)_2^-$ from β-$Ni^{III}L_3$ clearly involves reactions with sulfate, the rates of the reactions observed are independent of sulfate concentration, as shown in Table II. The rates of these reactions are also independent of ionic strength. Thus the kinetics of complexation of β-$Ni^{III}L_3$ by sulfate is different in nature from that reported earlier for the meso isomer $Ni^{III}L_2$.[3] These results are not surprising if one remembers that β-$Ni^{III}L_3$ isomerizes with a rate of 2.6×10^3 s^{-1} and if one assumes that complexation by sulfate occurs only after isomerization. The latter assumption is reasonable if complexation by sulfate occurs only for a nickel in an octahedral environment, as required for the formation of β-$NiL_3(SO_4)_2^-$, as a model of β-$Ni^{III}L_3$ clearly indicates that due to steric hindrance the nickel can be only pentacoordinated. Thus we conclude that the isomerization of β-$Ni^{III}L_3$ is the rate-determining step in its complexation by sulfate. This conclusion is in accord also with the observation that the electrochemical oxidation of β-NiL_3^{2+} in sulfate media is irreversible under conditions where that of NiL_2^{2+} is reversible.

The equilibrium constant of reaction 3 can be determined from the effect of low sulfate concentrations on the absorption due to the large difference in the absorption coefficients of the three forms of the tervalent complex (Figure 4). The results gave identical values when calculated at the end of the first reaction observed, curve d, or the second reaction observed, curve e. These results seem to indicate that the second reaction observed is an isomerization reaction of β-$NiL_3SO_4^+$, which has little effect on the stability constant of sulfate complexation. The equilibrium constant values measured at $\mu = 0.03$ M depend on the pH of the solution; K_3 (observed) = 2000, 800, 350, and 150 M^{-1} at pH 3.0, 3.8, 4.4, and 5.0, respectively. From these values we calculate $K_3 = 2200 \pm 50$ M^{-1} and $pK_H = 3.7 \pm 0.2$ for the hydrolysis reaction

$$\beta\text{-}NiL_3^{3+} \rightleftarrows \beta\text{-}NiL_3OH^{2+} + H_3O^+ \qquad (7)$$

At $\mu = 0.3$ M, $K_3 = 250 \pm 50$ M^{-1} was similarly obtained. These results indicate that the stability constant for the complexation of the first sulfate to β-NiL_3^{3+} is over an order of magnitude smaller than that observed for its isomer NiL_2^{3+}.[3]

Coordination Numbers of $Ni^{III}L$ Complexes. It was suggested that the absorption of $Ni^{III}L$ complexes at 550 nm is due to a distortion of the complex resulting in the nickel atom being out of the plane defined by the four nitrogen atoms of the ligand.[3,14,15] Such a conformation requires that the nickel will be pentacoordinated. On the other hand all the anions that stabilize the tervalent nickel complex form octahedral complexes of the type $Ni^{III}LX_2$.[4] The latter complexes have indeed no absorption band around 550 nm.[4] We decided to check the coordination number of the $Ni^{III}L$ complexes in the absence of stabilizing anions by an independent technique.

For all the tervalent nickel complexes studied we find that the rate of decomposition of the complex in alkaline solutions, $9.0 \leq pH \leq 11.0$, is first order in OH^-:

$$Ni^{III}L + OH^- \rightarrow Ni^{II}L' + H_2O \qquad (8)$$

The detailed mechanism of reaction 8 is most probably[14,16,17]

$$Ni^{III}L + OH^- \rightleftarrows Ni^{III}(L\text{-}H) + H_2O \qquad (9)$$

followed by

$$Ni^{III}(L\text{-}H) \xrightarrow{+Ox} Ni^{II}L' \qquad (10)$$

where (L-H) represents the ligand L that lost one of the protons bound to the nitrogens. The pK of reaction 9 is clearly above 11.0. The rate of reaction 8 is 1.5×10^5 M^{-1} s^{-1} for $L = L_1$, 2.2×10^4 M^{-1} s^{-1} for $L = L_2$, 2.7×10^4 M^{-1} s^{-1} for $L = L_3$, and 1.2×10^3 M^{-1} s^{-1} for $L = L_5$, at $\mu = 0.3$ M.

The observation that the rate of the decomposition of the tervalent nickel complexes is first order in hydroxide enables the determination of the charge of $Ni^{III}L$ by the use of the kinetic salt effect. Thus we determined that the charge on $Ni^{III}L$ for $L = L_2$, L_3, or L_5 at pH 10.0 is +2 whereas it is +1 for $L = L_1$. This result indicates that at this pH exist $NiLOH^{2+}$ for $L = L_2$, L_3, or L_5 and $NiL_1(OH)_2^+$. As it is difficult to envisage a nonhydrolyzed water molecule bound to a tervalent nickel center at pH 10, we suggest that the results point out that the $NiLOH^{2+}$ complexes, $L = L_2$, L_3, or L_5, are pentacoordinated whereas $NiL_1(OH)_2^{2+}$ is octahedral. This conclusion is in accord with the observation that for L_2,[3,15] L_3, and L_5[14] the isomerization reaction of the $Ni^{III}L$ formed in reaction 4 in neutral solutions causes an increase, or no change, in the absorption band at 550 nm whereas it causes a decrease of this band for $Ni^{III}L_1$.[6]

Concluding Remarks

The results obtained in this study confirmed our feeling that the chemical properties of tervalent nickel complexes with tetraaza macrocyclic ligands depend strongly on steric factors. Thus the properties of the $Ni^{III}L_3$ complexes differ considerably from those of their isomer $Ni^{III}L_2$. The difference in the kinetics of the electrochemical oxidation process stems mainly from the fact that the formation of $NiL_3(SO_4)_2^-$ requires an isomerization, change in the conformation of the ligand, whereas $NiL_2(SO_4)_2^-$ retains the conformation of the divalent complex.[4]

The difference in the kinetic stabilization of the tervalent nickel complexes by sulfate seems to stem from several sources.

(a) The stability constant for the ligation of sulfate to $Ni^{III}L_3$, K_1, is smaller than the analogous value for $Ni^{III}L_2$.[4] However as the ratio of K_1 for the two complexes is smaller than 10^2 and the ratio of the stabilizing effect is $\sim 5 \times 10^3$, this cannot be the only factor causing the difference in the kinetic stabilization. (The lifetimes of $Ni^{III}L_2$ and $Ni^{III}L_3$ in perchlorate media at $3 \leq pH \leq 6$ are very similar; see above and ref 3 and 15.)

(b) The decomposition reactions of the $Ni^{III}L$ complexes are believed to involve a proton abstraction by a base from the Ni^{III}-N-H groups.[14,16,17] The acidity of these protons is expected to decrease when an anion is axially coordinated to the nickel. The smaller stability constant for the ligation of sulfate to NiL_3^{2+} than to NiL_2^{3+} suggests also that the acidity of these protons is larger in $NiL_3(SO_4)_n^{3-2n}$ than in $NiL_2(SO_4)^{3-2n}$.

(c) Finally steric factors might affect the rates of decomposition of the $NiL(SO_4)_n^{3-2n}$ complexes. Thus it is plausible that the base has to reach the Ni^{III}-N-H group and steric hindrance might slow down this reaction. This might be the reason why sulfate has only a small kinetic stabilizing effect in the case of $Ni^{III}L_1$ though K_1 in this case is similar to that for $Ni^{III}L_2$.[4,6] A second factor that causes the large differences in the kinetic stabilization of the latter might be that as the final stage in the decomposition reaction is the formation of an imine group of the type

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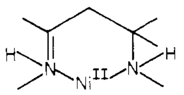
(16) Barefield, K.; Mocella, M. T. *J. Am. Chem. Soc.* **1975**, *97*, 4238.
(17) Meyerstein, D. *Acc. Chem. Res.* **1978**, *11*, 43.



it is required that the hydrogen to be lost on the C–H group will be with the right configuration relative to the nitrogen. This is always the case for $Ni^{III}L_1$, as there are two hydrogens on the carbon, and might not be the case for $Ni^{III}L_2$ and $Ni^{III}L_3$. This factor might also contribute to the differences observed in the stabilization caused by sulfate of the latter two complexes.

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Registry No. NiL_2^{2+}, 47105-35-1; α-NiL_3^{2+}, 51372-00-0; β-NiL_3^{2+}, 51371-74-5; α-$NiL_3(SO_4)_2^-$, 78821-58-6; β-$NiL_3(SO_4)_2^-$, 78739-34-1.

Notes

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Novel Peroxo Complexes of Uranium Containing Organic Ligands

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Peroxo complexes of molybdenum and tungsten are attracting interest as oxidants in organic synthesis.[1-5] As uranium somewhat resembles the group 6B elements, it was of interest to discover whether it would form analogous peroxo complexes which contain organic moieties. The preeminence of the UO_2 grouping distinguishes uranium from molybdenum and tungsten, however, and this factor may have hitherto prevented the generation of peroxo complexes from uranyl salts and organic reagents. The present paper describes the isolation and characterization of novel mono- and diperoxo complexes. These are found to be unusually stable, and they are relatively unreactive. they are the first reported examples of peroxo complexes of uranium which contain organic moieties.

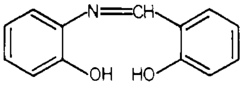
Experimental Section

The organic reagents (Eastman) were used as supplied.

Purification of Solvents. Spectrograde acetone was dried by cooling in the presence of NaI to form crystals of $(CH_3)_2CONaI$. The acetone was recovered by warming to 30 °C and then distilling. Other solvents were simply distilled.

Preparation of UCl_4. The compound formed when CCl_4 vapor entrained in a stream of dry N_2 was passed over U_3O_8 in a tube held at 500 °C for 2.5 h.

Preparation of Schiff Bases. *N*-(2-Hydroxyphenyl)salicylidenimine is identified hereafter as L. A solution of 2-aminophenol (0.1 mol, 10.9 g) in a 1:1 mixture of benzene and ethanol (100 mL) was added to a solution of salicylaldehyde (0.1 mol, 12.2 g) in benzene (20 mL). The resulting mixture was boiled for 3 min and then cooled in an ice–salt bath whereupon bright reddish yellow crystals formed. these were separated, washed several times with hot ethanol, and dried in vacuo over magnesium perchlorate; yield 16.1 g. Recrystallization was from methanol. Anal. Calcd for $C_{13}H_{11}NO_2$: C, 73.23; H, 5.16. Found: C, 73.22; H, 5.16.



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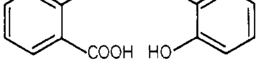

L′

N-(2-Carboxyphenyl)salicylidenimine is identified hereafter as L′. This was obtained when a solution of 2-aminobenzoic acid (0.1 mol, 13.7 g) in a 1:1 mixture of benzene and ethanol (100 mL) was added to a solution of salicylaldehyde (0.1 mol, 12.2 g) in benzene (20 mL). The resulting solution was heated on a steam bath for 5 min and then cooled in an ice–salt bath. Yellow crystals were separated and washed with benzene and ethanol; yield 17.0 g. Recrystallization was from methanol. Anal. Calcd for $C_{14}H_{11}NO_3$: C, 69.70; H, 4.56. Found: C, 69.7; H, 4.55.

Preparation of Complexes. The complexes and their elemental analyses are listed in Table I. Complexes of U(IV) were prepared by addition of a stoichiometric quantity of the ligand to UCl_4 in acetone. Two different approaches were used to synthesize peroxo complexes. Peroxo complexes containing multidentate ligands were prepared by adding H_2O_2 (50%) to solutions of the U(IV) intermediates in methanol (compound **13**) or a 1:1 mixture of acetone and methanol (compounds **14–17**). When U(IV) adducts of the unidentate ligands were dissolved in boiling acetone or methanol prior to the addition of H_2O_2, the product was $UO_4{\cdot}4H_2O$. However, complexes containing monodentate ligands were successfully converted to peroxo complexes of U(VI) by moistening the crystals in succession with acetone and H_2O_2 (50%) and warming.

Analyses. Uranium was determined gravimetrically.[8] Methanolic solutions of the peroxo complexes were titrated with Ce(IV) to determine the number of active oxygen atoms present.[9] The titrations (Table II) indicated that complexes **10–12** and **13–17** are di- and monoperoxo complexes, respectively.

Infrared spectra (Nujol mulls) were recorded with a Pye Unicam SP1100 or a Beckman IR-20 spectrophotometer. Spectra between 1500 and 200 cm^{-1} for some complexes were obtained with a Perkin-Elmer 283 spectrophotometer. Raman spectra of the solids were obtained with a Spectra-Physics Model 125A He–Ne laser operated at 50–60 mW. The 6328-Å line was used, and the spectra were calibrated by means of the neon lines. Proton and ^{13}C NMR spectra were obtained with Varian T-60 and FT-80 spectrophotometers. Tetramethylsilane was employed as internal standard.

Results and Discussion

Complexes of Uranium(IV). Several complexes which served as precursors of the peroxo compounds are described below. Compounds **2** and **3** have been reported previously.[6,7] The U(IV) complexes were soluble in almost all of the polar solvents tried, and the electrical conductivities of 5×10^{-4} M solutions in nitromethane or nitrobenzene indicated that all of the complexes were undissociated.

Infrared data are shown in Table III. Complex **1** shows a decrease in ν(N–O) compared to the value for free pyridine

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