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The Methyl(cyclam)nickel(III) Dication in Aqueous Solutions: Determination of the Equilibrium Constant of Homolysis, Kinetics of O_2 Insertion, and Methyl Transfer to Cr^{2+}_{aq}

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The reaction of methyl radicals with LNi^{2+}, L = cyclam, proceeds via $LNi^{2+} + {}^{\bullet}CH_3 \rightleftharpoons L(H_2O)Ni^{III}\text{–}CH_3^{2+}$, $K = 1.1 \times 10^7$ M^{-1}, ${}^{\bullet}CH_3 + L(H_2O)Ni^{III}\text{–}CH_3^{2+} \rightarrow LNi^{2+} + C_2H_6$. In the presence of dioxygen $L(H_2O)Ni^{III}\text{–}CH_3^{2+}$ decomposes via homolysis followed by $O_2 + {}^{\bullet}CH_3 \rightarrow {}^{\bullet}O_2CH_3$ and ${}^{\bullet}O_2CH_3 + LNi^{2+} \rightarrow L(H_2O)Ni^{III}\text{–}O_2CH_3^{2+}$. $L(H_2O)Ni^{III}\text{–}CH_3^{2+}$ reacts with $Cr(H_2O)_6^{2+}$ via $L(H_2O)Ni^{III}\text{–}CH_3^{2+} + Cr(H_2O)_6^{2+} \rightarrow LNi^{2+} + (H_2O)_5Cr^{III}\text{–}CH_3^{2+}$. The kinetics of these reactions and the properties of the new intermediates are discussed, and their relevance as models for biological systems is pointed out.

Introduction

σ-Bonded organometallic complexes are key intermediates in many important industrial processes, in biochemical reactions, and in organic synthesis. Though many of these processes, especially the biochemical ones, occur in aqueous solutions, little is known about the chemistry of these complexes in this medium. This is due to the short life time of these complexes in water. In the past, mainly Cr^{III} and Co^{III} complexes of the type $L_xM^n\text{–}R$ (R = alkyl, substituted alkyl, aralkyl, etc.; L = H_2O, macrocyclic ligand) have been studied due to their relative stability.[1] Recently it was shown that pulse radiolysis is a powerful technique for the study of the properties of short-lived intermediates of this type.[2] Indeed we could study the properties of analogous complexes of Mn^{III},[3] Fe^{III},[3,4] Cu^{III},[5] and Cu^{II}.[6]

Despite the extensive chemistry of organonickel complexes[7] little was known until recently about the chemistry of alkylnickel species in aqueous solutions.[8] This is surprising as interest in organonickel chemistry was enhanced by the detection and isolation of four types of nickel-containing enzymes since 1975.[9] In three of them, hydrogenase, methyl coenzyme M reductase and acetyl-CoA-cleaving CO dehydrogenase, nickel is believed to be selected for the biological analogues of industrial catalytic processes (i.e., H_2 splitting, reductive desulfurization, carbonylation) due to its unique combination of redox and coordination properties. The proposed enzyme chemistry for at least the two latter classes is closely related to organonickel chemistry: (a) reductive desulfurization of methyl thioether to methane through a $LNi^{II}\text{–}CH_3$ (L = tetrahydrocorphin) followed by protonolysis; (b) reversible CO insertion in a $Ni\text{–}CH_3$ complex.[10] Certain hydrogenases were shown to contain paramagnetic centers attributable to the less common Ni(III) (d^7, low spin) state.[9a,11]

Recently the discovery that relatively long-lived nickel(I) macrocyclic complexes can be prepared in aqueous solutions[12] led to the synthesis of $(tmc)Ni^{II}\text{–}R^+$ and the study of the chemical properties of these complexes. (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane).[13] It was suggested[14] that $(tmc)Ni^{III}\text{–}R^{2+}$ is formed as a short-lived intermediate during one of the routes of decomposition of $(tmc)Ni^{II}\text{–}R^+$. The results indicated that $(tmc)Ni^{III}\text{–}R^{2+}$ decomposes via homolysis. The only known example for a true organonickel(III) species is an aralkyl complex of the type $Ni(NCN')X_2$ (NCN' = $C_6H_3(CH_2NMe_2)_2$-*o,o'*, an extremely stabilizing ligand for high oxidation states),[15] which is relatively stable in aqueous solutions.

We decided to try to study the properties of $L(H_2O)Ni^{III}\text{–}CH_3^{2+}$ (where L = cyclam = 1,4,8,11-tetraazacyclotetradecane) by following the reaction of methyl-free radicals with LNi^{2+} using the pulse-radiolysis technique. Indeed we were able to study the kinetics of formation and decomposition of the first example of an alkylnickel(III) complex of this type. The existence of compounds of this type is therefore further evidence for the possibility that Ni(III)–C σ-bonded species are intermediates not only in organonickel chemistry but also in enzyme chemistry.

Experimental Section

Materials. All solutions were prepared from AR grade chemicals and from distilled water further purified by passing through a milli Q Millipore setup; final resistivity > 10 MΩ/cm. $Cr(H_2O)_6^{2+}$ solutions for the scavenging experiments were prepared as described elsewhere.[16] $Ni(cyclam)(ClO_4)_2$ was prepared according to literature methods.[17] N_2O was first bubbled through a scrubbing bottle, containing VSO_4 in dilute H_2SO_4 over Zn amalgam, to remove traces of oxygen before saturating the sample under study.

Techniques. Solutions were handled by the syringe technique. pH determinations of solutions containing $Cr(H_2O)_6^{2+}$ were carried out by immersing the glass electrode into the syringe, while N_2O or He was bubbled through the solutions.

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Pulse-radiolysis experiments were carried out at the linear electron accelerator facility of the Hebrew University of Jerusalem; 0.5–1.5 μs, 5 MeV, and 200 mA pulses were used. The dose per pulse was in the range 1000–3000 rad/pulse. This technique was used to measure the specific rates of formation and decomposition of the methylnickel(III) complex as well as to measure its absorption spectrum. The experimental setup and the techniques used for evaluating the results have been described elsewhere in detail.[2a,18]

γ irradiations were carried out by using a ^{60}Co source with a dose rate of 3300 rad/min. The yield of gaseous products, methane and ethane, was determined by gas chromatography. (The error is ±10% of the experimental value.) The gas samples were taken through a rubber septum with a gastight syringe and were separated on a Poropak column by using a Varian 3700 TCD gas chromatograph, calibrated with the necessary standards.

Slow consecutive reactions were recorded with a HP 8452 A diode-array spectrophotometer. For these experiments N_2O-saturated solutions were irradiated in a 6-cm-long Suprasil spectrophotometric cell.

The alkylnickel complex, $L(H_2O)Ni^{III}–CH_3^{2+}$, was obtained by the reaction of $Ni^{II}(cyclam)^{2+}$ with $^{\bullet}CH_3$ radicals, which are produced by the reaction of $^{\bullet}OH$ radicals with $(CH_3)_2SO$:[19]

$$^{\bullet}OH + (CH_3)_2SO \rightarrow (CH_3)_2SOOH \quad k_1 = 7.0 \times 10^9\ M^{-1}\ s^{-1} \quad (1)$$

$$(CH_3)_2SOOH \rightarrow CH_3SOOH + {}^{\bullet}CH_3 \quad k_2 = 1.5 \times 10^7\ s^{-1} \quad (2)$$

$$LNi^{2+} + {}^{\bullet}CH_3 \rightarrow L(H_2O)Ni^{III}–CH_3^{2+} \quad (3)$$

$^{\bullet}OH$ radicals are the major products of the radiolysis of N_2O-saturated (2.2×10^{-2} M) dilute aqueous solutions (pH >3), summed up in the following equations:

$$H_2O \xrightarrow{\gamma,\, e^-} e^-_{aq}, {}^{\bullet}OH, {}^{\bullet}H, H_2, H_2O_2, H_3O^+, OH^- \quad (4)$$

(Yields of products: $G(e^-_{aq}) = 2.65$, $G(OH) = 2.65$, $G(H) = 0.60$, $G(H_2) = 0.45$, and $G(H_2O_2) = 0.75$.)[20]

$$N_2O + e^-_{aq} \xrightarrow{H_2O} N_2 + {}^{\bullet}OH + OH^- \quad k_5 = 8.7 \times 10^9\ M^{-1}\ s^{-1}\ {}^{21} \quad (5)$$

The following reactions have to be considered in choosing the best conditions for the specific experiments:

$$e^-_{aq} + H^+ \rightarrow {}^{\bullet}H \quad k_6 = 2 \times 10^{10}\ M^{-1}\ s^{-1}\ {}^{20} \quad (6)$$

$$^{\bullet}OH + LNi^{2+} \rightarrow OH^- + L(H_2O)_2Ni^{3+} \quad k_7 = 2 \times 10^9\ M^{-1}\ s^{-1},\ \text{at pH } 3^{22} \quad (7)$$

$$^{\bullet}CH_3 + {}^{\bullet}CH_3 \rightarrow C_2H_6 \quad k_8 = 1.6 \times 10^9\ M^{-1}\ s^{-1}\ {}^{23} \quad (8)$$

$$Cr(H_2O)_6^{2+} + {}^{\bullet}CH_3 \rightarrow (H_2O)_5Cr^{III}–CH_3^{2+} \quad k_9 = 2.4 \times 10^8\ M^{-1}\ s^{-1}\ {}^{24} \quad (9)$$

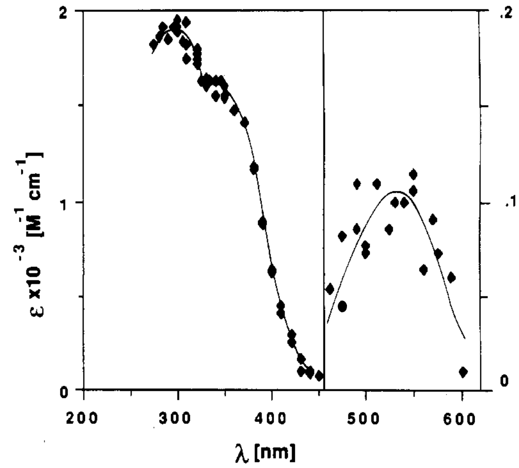

Figure 1. UV/vis spectrum of pulse radiolytically generated $L(H_2O)$-$Ni^{III}–CH_3^{2+}$ from N_2O-saturated aqueous solutions (pH 3) of LNi^{2+} (5×10^{-4} M) and $(CH_3)_2SO$ (0.1 M).

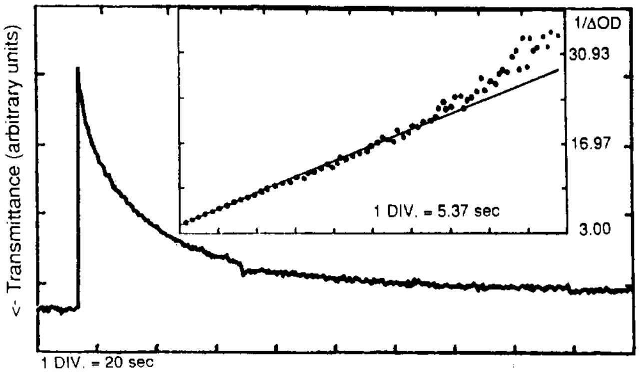

Figure 2. Decay of the absorption (at 300 nm) due to $L(H_2O)Ni^{III}–CH_3^{2+}$ and a second-order plot (insert) (LNi^{2+} (1×10^{-3} M), $(CH_3)_2SO$ (0.1 M), pH 3).

Table I. Decomposition of $L(H_2O)Ni^{III}–CH_3^{2+}$ at pH 3

$[LNi^{2+}]$, M	$10^4[Cr_{aq}^{2+}]$, M	$10^5[O_2]$, M	$10^{-4}k_{obs}$,^{a} $M^{-1}\ s^{-1}$	k_{obs},^{b} s^{-1}
2×10^{-4}			3.6	
5×10^{-4}			1.2	
1×10^{-3}			0.6	
1×10^{-3}	2			19.0
1×10^{-3}	3			25.0
1×10^{-3}	4			30.5
1×10^{-3}	6			60.5
1×10^{-3}	8			81.0
2×10^{-4}	3			22.5
6×10^{-4}	3			23.6
5×10^{-4}		traces		9.3^c
5×10^{-4}		2.5		12.7
5×10^{-4}		5		21.5
5×10^{-4}		10		30.7
2.5×10^{-4}		5		29.2
10×10^{-4}		5		12.7

^{a} k_{obs} of reactions obeying a second-order rate law. ^{b} k_{obs} of reactions obeying a first-order rate law. ^{c} The fit of the first-order plot in this case was not perfect.

Results and Discussion

When N_2O-saturated solutions containing 0.1 M $(CH_3)_2SO$, 1×10^{-3} M $HClO_4$, and $(1–10) \times 10^{-4}$ M $NiL(ClO_4)_2$ are irradiated by a short electron pulse from the linear accelerator, the formation of a relatively long-lived species is observed. As traces of oxygen sometimes caused the formation of a second transient (vide infra), spectral data and kinetics were evaluated only from the second and third pulses delivered to the sample. The kinetics of the formation (vide infra) indicate that it is produced in a reaction between LNi^{2+} and a free radical formed by the radiation. As the primary radicals formed by the radiation are transformed under the experimental conditions via reactions 5, 1, and 2 into $^{\bullet}CH_3$ radicals, and as C_2H_6 is the final product (vide infra) and L is a saturated ligand with no free nonbonding electrons, one has to conclude that the transient complex observed is $L(H_2O)$-$Ni^{III}–CH_3^{2+}$ formed according to eq 3. As most tervalent nickel–cyclam complexes are octahedral,[25] including the hydroxo

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complex,[26] we assume that an aquo ligand is also added in reaction 3.

UV/Vis Spectrum of Ni(cyclam)–CH_3^{2+}. The UV/vis spectrum of $L(H_2O)Ni^{III}–CH_3^{2+}$ corrected for the absorption of the starting material is plotted in Figure 1. The spectrum resembles that of other complexes of $L(H_2O)_2Ni^{3+}$ [22] though the molar absorption coefficients are somewhat smaller and the two UV bands are shifted to lower wavelengths.[22]

Kinetics of Ni(cyclam)–CH_3^{2+} Formation. The kinetics of formation of $[L(H_2O)Ni^{III}–CH_3]^{2+}$ were studied in the 300–360-nm range, and shown to obey a pseudo-first-order rate law. The observed rate is proportional to $[LNi^{2+}]$ and independent of wavelength and $[H^+]$ in the pH range 3–10 (higher H^+ concentrations were not used because of the competing reaction 6). From the $[LNi^{2+}]$ dependence the specific rate of reaction $k_3 = (6.5 \pm 0.7) \times 10^8$ M^{-1} s^{-1} was derived.

Kinetics of Decomposition. The methylnickel complex decomposes in the 100-s range. The kinetics of the disappearance of the absorption of $L(H_2O)Ni^{III}–CH_3^{2+}$ at pH 3 obey second-order kinetics in the absence of scavengers; a typical example is shown in Figure 2. The observed rates of reaction are inversely proportional to $[LNi^{2+}]$ (see Table I). It should be noted that the absorption at the end of this reaction is nearly identical with that prior to the pulse. These kinetic results and the observation that ethane is quantitatively formed from the methyl radicals (vide infra) prove that the observed reactions are

$$LNi^{2+} + {}^{\bullet}CH_3 \rightleftharpoons L(H_2O)Ni^{III}–CH_3^{2+} \tag{10}$$

$${}^{\bullet}CH_3 + L(H_2O)Ni^{III}–CH_3^{2+} \rightarrow LNi^{2+} + C_2H_6 \tag{11}$$

Assuming steady-state conditions for the $^{\bullet}CH_3$ radicals, the mechanism is satisfactorily described by the following rate law:

$$-\frac{d[L(H_2O)Ni^{III}–CH_3^{2+}]}{dt} = \frac{2k_{11}k_{-10}[L(H_2O)Ni^{III}–CH_3^{2+}]^2}{k_{10}[LNi^{2+}] + k_{11}[L(H_2O)Ni^{III}–CH_3^{2+}]} \tag{12}$$

If $k_{10}[LNi^{2+}] \gg k_{11}[L(H_2O)Ni^{III}–CH_3^{2+}]$, this rate law is reduced to

$$-\frac{d[L(H_2O)Ni^{III}–CH_3^{2+}]}{dt} = \frac{2k_{11}[L(H_2O)Ni^{III}–CH_3^{2+}]^2}{K_{10}[LNi^{2+}]} \tag{13}$$

Plotting the observed rate of decomposition, k_{obs}, vs $1/[LNi^{2+}]$ yields a straight line that passes through the origin, thus indicating that the approximation made is justified. From the slope of this line the quotient $2k_{11}/K_{10} = 7.0 \pm 0.7$ s^{-1} is calculated. (If the ethane is formed via reaction 8, a linear dependence of k_{obs} on $1/[LNi^{2+}]^2$ is expected, and if it is formed via $2L(H_2O)Ni^{III}–CH_3^{2+} \rightarrow 2LNi^{2+} + C_2H_6$, no dependence of k_{obs} on $[LNi^{2+}]$ is expected.)

Whereas the known organonickel(II) species decompose in aqueous solutions via heterolysis,[8,13] homolysis is expected[14] for the organonickel(III) complexes due to the higher stability of the 2+ oxidation state. In this respect the $L(H_2O)Ni^{III}–CH_3^{2+}$ complex can be compared to related organocobalt(III) species,[1] which also undergoes homolysis although their kinetic stability is considerably higher (they are usually readily isolable; the highest reported rate constant for the homolysis is $k = 9.4 \times 10^{-2}$ s^{-1} at 25 °C[27]).

Homolytic Insertion of Dioxygen into the Nickel–Carbon σ-Bond. It was noted that in some samples the formation of $L(H_2O)Ni^{III}–CH_3^{2+}$ in the first pulse was followed by a reaction that causes an increase, and not a decrease, in the absorption due to the product. In these samples the kinetics observed after the second and third pulse were identical with those described above. This result suggests that the observed increase in absorption is due to dioxygen impurities. In order to check this hypothesis, solutions containing low concentrations of dioxygen were irradiated. The concentration of dioxygen was kept low enough so that $k_{10}[LNi^{2+}] > k_{14}[O_2]$ was maintained.

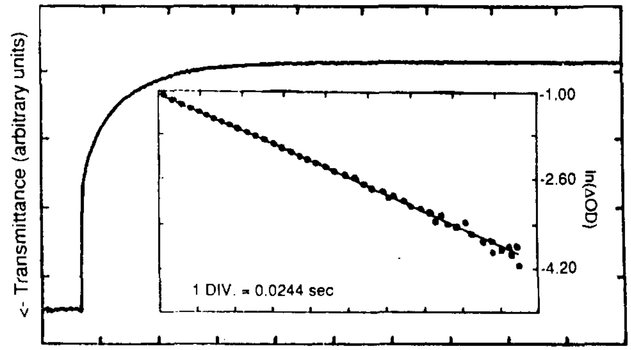

Figure 3. Increase of the absorption (at 300 nm) due to formation of $L(H_2O)Ni^{III}–OOCH_3^{2+}$ in the presence of oxygen and a first-order plot (insert) (LNi^{2+} (5×10^{-4} M), $(CH_3)_2SO$ (0.1 M), O_2 (2.5×10^{-5} M), pH 3).

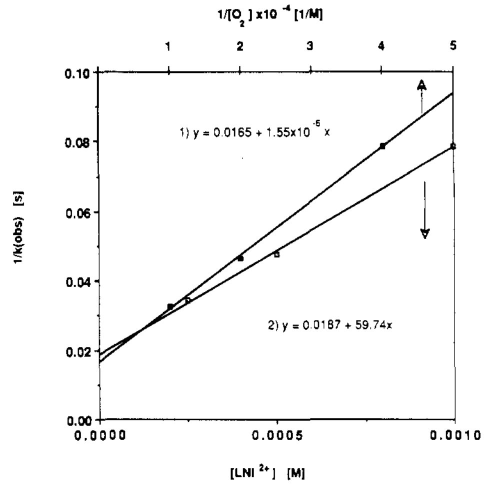

Figure 4. Dependence of $1/k_{obs}$ for the insertion reaction on $[LNi^{2+}]$ at constant $[O_2] = 5 \times 10^{-5}$ M and on $1/[O_2]$ at constant $[LNi^{2+}] = 5 \times 10^{-4}$ M. All solutions contained 0.1 M $(CH_3)_2SO$ at pH 3.0. Wavelength of observation: 300 nm.

Under these conditions the decomposition reaction of $L(H_2O)Ni^{III}–CH_3^{2+}$ is indeed replaced by a process obeying a first-order rate law, which causes an increase in the absorption due to the product formed; see for example Figure 3. The observed rate of this process, Table I, increases when $[O_2]$ increases and decreases when $[LNi^{2+}]$ increases. These results suggest that the following scheme describes the observed process:

$$LNi^{2+} + {}^{\bullet}CH_3 \rightleftharpoons L(H_2O)Ni^{III}–CH_3^{2+} \tag{10}$$

$$O_2 + {}^{\bullet}CH_3 \rightarrow {}^{\bullet}O_2CH_3 \quad k_{14} = 4.7 \times 10^{9}\,{}^{28} \tag{14}$$

$${}^{\bullet}O_2CH_3 + LNi^{2+} \rightarrow L(H_2O)Ni^{III}–O_2CH_3^{2+} \tag{15}$$

If this scheme describes the observed process, it is expected to obey the following rate law:

$$-\frac{d[L(H_2O)Ni^{III}–CH_3^{2+}]}{dt} = \frac{k_{14}k_{-10}[O_2][L(H_2O)Ni^{III}–CH_3^{2+}]}{k_{10}[LNi^{2+}] + k_{14}[O_2]} \tag{16}$$

i.e.

$$\frac{1}{k_{obs}} = \frac{K_{10}[LNi^{2+}]}{k_{14}[O_2]} + \frac{1}{k_{-10}}$$

In Figure 4 $1/k_{obs}$ is plotted vs $[LNi^{2+}]$ and vs $1/[O_2]$. From the

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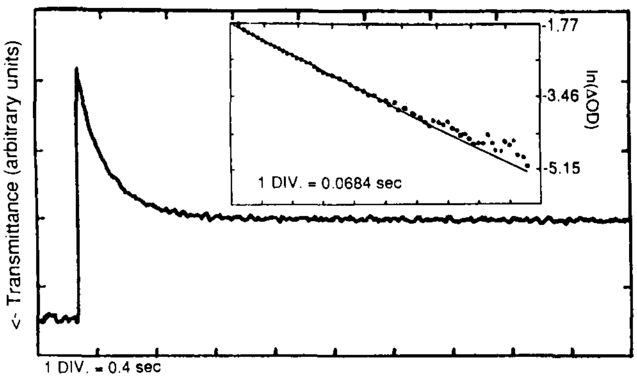

Figure 5. Decay of the absorption (at 300 nm) due to the formation of $(H_2O)_5Cr-CH_3^{2+}$ in the presence of chromous and a first-order plot (insert) (LNi^{2+} (1×10^{-3} M), $(CH_3)_2SO$ (0.1 M), Cr^{2+}_{aq} (1×10^{-4} M), pH 3).

intercepts in the figure, $k_{-10} = 57 \pm 6$ s^{-1} is calculated. From this value and $k_{10} = (6.5 \pm 0.7) \times 10^8$ M^{-1} s^{-1}, $K_{10} = 1.1 \times 10^7$ M^{-1} is derived. From the slopes of the lines in Figure 4, $K_{10}/k_{14} = (3.05 \pm 0.1) \times 10^{-3}$ s^{-1} is calculated, and hence $k_{14} = 3.7 \times 10^9$ M^{-1} s^{-1}. The latter value is in very good agreement with the literature value for k_{14},[28] thus proving that the suggested reaction scheme indeed describes the observed process. From the value for the equilibrium constant and from $2k_{11}/K_{10} = 7.0 \pm 0.7$ s^{-1} $2k_{11} = 8 \times 10^7$ M^{-1} s^{-1} for the reaction of methyl radicals with the methylnickel complex also can be calculated.

The spectrum of $L(H_2O)Ni^{III}-O_2CH_3^{2+}$ resembles that of other tervalent nickel complexes. The molar extinction coefficients of this complex, $\epsilon_{300} = 15\,000$ M^{-1} cm^{-1} and $\epsilon_{350} = 11\,000$ M^{-1} cm^{-1}, are considerably higher than those reported for other LNi^{III} complexes.[22] The complex $[L(H_2O)Ni^{III}-O_2CH_3]^{2+}$ decomposes photochemically by the analyzing light. When an irradiated sample is kept in the dark and taken to a spectrophotometer, its spectrum after ~4 min is similar to that of $L(H_2O)Ni^{3+}$ at the same pH,[22] indicating that $L(H_2O)Ni^{III}-O_2CH_3^{2+}$ decomposes via

$$L(H_2O)Ni^{III}-O_2CH_3^{2+} \xrightarrow{H^+} L(H_2O)_2Ni^{3+} + HO_2CH_3 \quad (17)$$

in analogy to similar Mn(III) and Co(III) complexes.[29]

Methyl Transfer to the Chromous Ion. When $Cr(H_2O)_6^{2+}$ is added to solutions containing LNi^{2+} and $(CH_3)_2SO$ at such concentrations that the methyl radicals react with LNi^{2+} and not with $Cr(H_2O)_6^{2+}$, the rate of decomposition of $L(H_2O)Ni^{III}-CH_3^{2+}$ is enhanced; see for example Figure 5. In this case a residual absorbance remains, the spectrum of which is identical with that of $(H_2O)_5Cr^{III}-CH_3^{2+}$.[1a,24] The kinetics of the decomposition of $L(H_2O)Ni^{III}-CH_3^{2+}$ under these conditions obey a pseudo-first-order rate law, the observed rate being proportional to $[Cr(H_2O)_6^{2+}]$ and independent of $[LNi^{2+}]$. The results are summed up in Table I. These results point out that the reaction occurring is

$$L(H_2O)Ni^{III}-CH_3^{2+} + Cr(H_2O)_6^{2+} \rightarrow LNi^{2+} + (H_2O)_5Cr^{III}-CH_3^{2+} \quad (18)$$

which does not proceed via an initial homolysis of the Ni–carbon bond. Thus the mechanism of reaction 18 is analogous to that of $Cr(H_2O)_6^{2+}$ with a large number of alkylcobalt(III) compounds.[1] From the observed rate constants, Table I, $k_{18} = 1.1 \times 10^5$ M^{-1} s^{-1} is calculated. This specific rate of reaction is about 3 orders of magnitude higher than those reported for the fastest alkyl-transfer reactions from organocobalt complexes,[1] probably due to the higher redox potential of the Ni(III) complex.

Product Analysis. Steady-state irradiations of solutions containing 1×10^{-3} M NiL^{2+} and 0.1 M $(CH_3)_2SO$ at pH ~3 in the ^{60}Co γ-source yielded the gaseous products methane (<5%) and ethane (~90%). Blanks, containing 0.1 M $(CH_3)_2SO$ at pH 3, produced ca. 15% methane and 85% ethane. (all values are ±10% of the percentages).

After the decomposition of the methylnickel intermediate only small spectral changes due to Ni^{III}cyclam[22] and a product with an absorption maximum at 276 nm are observed. Immediate changes (start of measurements ca. 5 min after irradiations) can be attributed to the small contribution of reaction 7; indeed the yield of $NiL(H_2O)_2^{3+}$ at this stage is less than 0.5% of the free radical yield. Slow consecutive reactions were due to the reaction of $Ni(cyclam)^{2+}$ with H_2O_2, as verified by comparison to irradiations in the absence of $(CH_3)_2SO$ or by mixing $Ni(cyclam)^{2+}$ with H_2O_2.

Concluding Remarks

The results obtained in this study point out that relatively stable complexes with a nickel(III)–carbon σ-bond can be formed when appropriate ligands are used. The stability constant for the complexation of methyl free radicals to NiL^{2+} is similar to that of its complexation to $(N(CH_2CO_2)_3)Co(H_2O)_2^{-}$[30] and considerably larger than that of its complexation to $(N(CH_2CO_2)_3)Mn(H_2O)_2^{-}$[3] and to $(N(CH_2CO_2)_3)Fe(H_2O)_2^{-}$[3] but considerably smaller than that of its complexation to CoL^{2+}.[31] This result clearly indicates that the metal–carbon bond strengths in these systems are not directly correlated to the redox potential of the complex. The relatively high value of the stability constant for the nickel complex points out that indeed analogous complexes might be formed as transients in biological systems.

The homolytic dioxygen insertion reaction observed is the first for which a full kinetic analysis was carried out, though this mechanism has been shown to occur in several systems containing cobalt complexes.[1c,32] It might be a good model for analogous processes of biological significance, e.g. the lipoxygenation of fatty acids by soybean lypoxygenase via transients with Fe–carbon σ bonds.[33]

The transient complex $L(H_2O)Ni^{III}-O_2CH_3^{2+}$ is expected to be a powerful three-electron-oxidizing agent with a relatively long lifetime. As such it might be an interesting model to some P-450 catalyzed reactions and analogous processes. We plan therefore to study the chemical properties of this complex, which is easily attainable in aqueous solutions.

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