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Electron Paramagnetic Resonance Studies of Nickel(III)–Oligopeptide Complexes

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Oxidation of nickel(II)–oligopeptide complexes in aqueous solution yields paramagnetic products. Electron paramagnetic resonance spectra are consistent with nickel(III) in a tetragonal geometry with four donor groups from the oligopeptide in the equatorial plane and two axially bound water molecules. The unpaired electron is located in an orbital which has a large amount of d_{z^2} character although broadening effects attributed to hyperfine splitting from equatorial nitrogens are observed. The magnitude of the equatorial g value increases as the strength of the equatorial donor increases in the order N^-(peptide) > $-NH_2$ > imidazole ≃ $-CO_2^-$. Nickel(III) glycylglycylglycinamide, $Ni^{III}(H_{-3}G_3a)$, forms two complexes with ammonia (with stability constants of 2×10^7 and 60 M^{-1}) in which NH_3 replaces first one and then the second axially bound water molecule. These complexes stabilize nickel(III) relative to nickel(II), shifting the electrode potential (vs. NHE) of 0.83 V for $Ni^{III}(H_{-3}G_3a)$ to 0.29 V in 1.0 M ammonia solution. Nickel(III) complexes with five or more nitrogen donors are slower to undergo self-decomposition reactions. The initial nickel(III)–oligopeptide complexes also are stabilized by chelation of a second oligopeptide to form bis complexes with five nitrogen donors.

Introduction

Oxidation of nickel(II)–oligopeptide complexes by electrochemical or chemical methods gives products which have been characterized as nickel(III) complexes.[1] The characterization has included extensive cyclic voltammetric studies,[2] UV–visible spectroscopic and circular dichroism[3] measurements, and preliminary electron paramagnetic resonance investigations. Kinetic behavior has also been examined.[1,4]

In the present work, electron paramagnetic resonance is used to show that the electron has been removed from the metal center so that the unpaired electron is associated with nickel(III) rather than with a coordinated nitrogen or carbon radical. Interpretation of the spectra indicates that the initial oxidation products are tetragonal with a nearly square-planar arrangement of the peptide donors. Evidence is presented for additional, more stable nickel(III) species with axial nitrogen coordination.

Experimental Section

The chromatographically pure oligopeptides glycylglycylglycine (G_3, Sigma Chemical Co.), glycylglycylglycylglycine (G_4, Biosynthetika), glycylglycylglycylglycylglycine (G_5, Biosynthetika), glycylglycyl-L-histidine (G_2his, Vega-Fox Chemical Co.), and glycylglycylglycinamide (G_3a, Vega-Fox Chemical Co.) were used as supplied. A stock solution of $Ni(ClO_4)_2$, prepared by the action of $HClO_4$ on $NiCO_3$, was twice recrystallized from water and standardized by titration with EDTA. Stock solutions of $NaClO_4$ were prepared by the addition of $HClO_4$ to Na_2CO_3 and were standardized gravimetrically after boiling to remove excess CO_2.

Solutions of nickel(II) peptides were prepared by the reaction of 5% excess ligand with $Ni(ClO_4)_2$. The fully deprotonated complexes (i.e., with three peptide or amide nitrogens coordinated for G_3a, G_4, and G_5 and with two peptide nitrogens coordinated with G_3 and G_2his) were formed by addition of NaOH to give pH 10.5 at equilibrium. Unless otherwise stated, the ionic strength was maintained constant at 0.10 M using $NaClO_4$ as background electrolyte.

Electrochemical oxidation was achieved using a flow system[5] with a graphite powder working electrode packed in a porous-glass column and wrapped with a platinum wire auxiliary electrode. In general the fully deprotonated form of the complex (10^{-3} M) was oxidized at a potential (measured against Ag|AgCl) 200 mV above the $E°$ value[2] using a flow rate of 1.5 mL min^{-1}. The solution collected from the electrolysis column was at pH 5–6, where the rate of decomposition of the oxidized complexes is relatively slow. The $Ni^{III}(H_{-3}G_3a)$ species is the least stable of the trivalent peptide complexes (by an order of magnitude) and has a half-life at 23 °C of about 200 s at pH 6.

The EPR spectra of magnetically dilute aqueous glasses containing nickel(III)–peptide complexes (<10^{-3} M) were measured at -150 ± 5 °C using a Varian E-109 X-band EPR system modulated at 100 kHz. The electrochemically generated nickel(III)–peptide complexes at pH 6 were quenched in liquid nitrogen at time intervals ranging from 15 s to several hours after formation. Samples from the reactions in borate buffer (pH 8.6) and in buffered ammonia solutions at various pH values were quenched rapidly in liquid nitrogen. Depending on the experiment, the initial nickel(III) concentration varied from 10^{-6} to 10^{-4} M.

Table I. Relative Broadening Parameters Used in Calculating the Aqueous Glassy EPR Spectra of Nickel(III)–Oligopeptide ($T = -150$ °C)

Complex	W_{xx}	W_{yy}	W_{zz}
$Ni^{III}(H_{-2}G_3)$	1.75	2.50	1
$Ni^{III}(H_{-2}G_2his)$	1.68	3.89	1
$Ni^{III}(H_{-3}G_4)^-$	5.97	2.50	1
$Ni^{III}(H_{-3}G_5)^-$	5.97	2.43	1
$Ni^{III}(H_{-3}G_3a)$	5.88	2.94	1
$Ni^{III}(H_{-2}G_3a)(H_{-1}G_3a)$	3.26	3.26	1
$Ni^{III}(H_{-3}G_3a)NH_3$	4.33	4.33	1
$Ni^{III}(H_{-3}G_3a)(NH_3)_2$	4.00	4.00	1

Magnetic field values were measured relative to DPPH. A spectrum matching procedure[6] was employed to obtain g values and hyperfine coupling constants. This entailed the generation of calculated curves from estimated g values and broadening parameters until the best fit with the experimental curve was obtained. In general, the fits were excellent although discrepancies were observed at the extremes. These discrepancies may be ascribed to deviations from Gaussian line shapes[7] which were used throughout the calculations.

The relative broadening parameters, W, used for each g value are shown in Table I, where W is a function of the peak–peak half-width of the derivative signal.[6] Broadening parameters were used instead of terms for hyperfine interaction. In one case, hyperfine coupling of 15–20 G from four nonequivalent nitrogen donors was included in the calculation (at great expense) and gave the same broadening without resolution of the hyperfine splitting.

Quoted g_{zz} values are precise to ±0.1%. The precision of g_{xx} and g_{yy} decreases approximately as the inverse of the broadening parameters. Hyperfine coupling constants are accurate to ±1 G.

Equilibrium measurements for solutions containing more than one paramagnetic species were obtained from the ratio of EPR signals. The line shapes of the signals for the individual complexes were superimposed to obtain a sum which corresponded to the observed signal in the mixture.

Results and Discussion

The Metal Ion Oxidation State. Electron paramagnetic resonance studies of aqueous glasses containing the immediate products of the controlled oxidation of nickel(II)–oligopeptide complexes reveal species which have a single unpaired electron. Representative spectra are given in Figure 1. These spectra suggest species which are, to a first approximation, axially symmetric with g_{xx}, g_{yy} > g_{zz}. However, Figure 1a and c clearly shows $g_{xx} \neq g_{yy}$. Anisotropic g values were calculated using a spectrum matching procedure[6] which required small differences between the values of g_{xx} and g_{yy} to obtain the correct curve shapes. Derived g values are presented in Table II.

In all cases the average g values are in excess of 2.18 indicating that the unpaired electron is associated primarily with

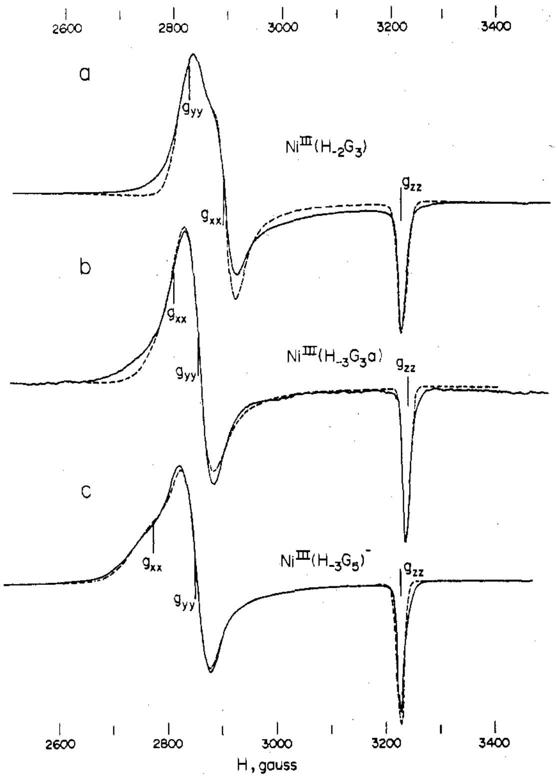


Figure 1. EPR spectra (—, experimental; ---, calculated) for Ni(III)–peptide complexes in magnetically dilute aqueous glasses at −150 °C: (a) $Ni^{III}(H_{-2}G_3)$, 10^{-4} M, pH 6, 9.084 GHz; (b) $Ni^{III}(H_{-3}G_3a)$, 10^{-4} M, pH 6, 9.082 GHz; (c) $Ni^{III}(H_{-3}G_5)^-$, 10^{-4} M, pH 6, 9.083 GHz.

Table II. Best Fit g Values for Aqueous Glassy Spectra of Nickel(III)-Oligopeptide Complexes at −150 °C

Complex	g_{xx}	g_{yy}	g_{zz}	g_{av}
$Ni^{III}(H_{-2}G_3)$	2.242	2.295	2.015	2.184
$Ni^{III}(H_{-2}G_2his)$	2.256	2.278	2.015	2.183
$Ni^{III}(H_{-3}G_4)^-$	2.297	2.278	2.010	2.195
$Ni^{III}(H_{-3}G_5)^-$	2.340	2.278	2.011	2.210
$Ni^{III}(H_{-3}G_3a)$	2.310	2.281	2.006	2.199

the nickel ion in these complexes.[8] If ligand oxidation had occurred, the paramagnetic product would be a nitrogen- or carbon-centered radical complex of nickel(II). Such species would be expected[8,9] to exhibit all three g values close to the spin-only value of 2.002. The large orbital contribution to paramagnetism actually observed suggests that the unpaired electron is located primarily on the metal ion consistent with the trivalent oxidation state.

The Geometry of Nickel(III)–Oligopeptide Complexes. For the cases studied, the nickel(II) complexes can be regarded as truly square planar[10] and the redox reversibility suggests that the immediate oxidation products have similar structures. Thus, the cyclic voltammetric values of $E°$ for a given nickel–peptide complex are constant over a pH range of 6.5–10.5 while the peak current response decreases with decreasing pH because of loss of the fully deprotonated peptide complexes of nickel(II).[2] This behavior is confirmed again for G_3a where an $E°$ value of 0.83 ± 0.01 V (vs. NHE) is found from pH 6.0 to 8.6. Furthermore, the EPR spectra (−150 °C) are unchanged over this pH range. These results indicate that the trivalent complex is $Ni^{III}(H_{-3}G_3a)$ as opposed to a species with fewer N^- groups or with more OH^- groups coordinated to the nickel.

Consideration of a simplified energy diagram, Scheme Ic, indicates that for low-spin d^7 nickel(III) in a square-planar arrangement, the unpaired electron would be located in an orbital with a large amount of d_{xy} character. The g values are predicted[11] by the approximate expressions in eq 1–3,

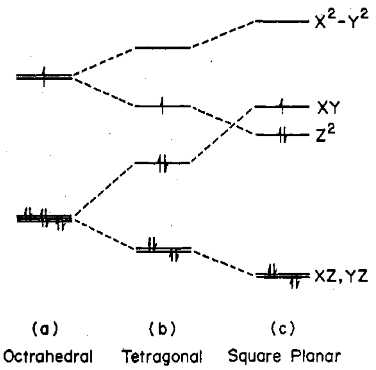
$$g_{xx} = 2 - \frac{2\lambda}{\Delta E_{xy-xz}} \tag{1}$$

$$g_{yy} = 2 - \frac{2\lambda}{\Delta E_{xy-yz}} \tag{2}$$

$$g_{zz} = 2 - \frac{8\lambda}{\Delta E_{xy-(x^2-y^2)}} \tag{3}$$

where λ, the spin–orbit coupling constant, is negative (−715 cm^{-1} in the free ion)[11] and the formalism ΔE_{xy-xz} represents the energy required to couple the d_{xy} ground state with an excited state in which the electron is in a d_{xz} orbital. This would require $g_{zz} > g_{xx}, g_{yy}$ but this is inconsistent with the experimental observations.

Scheme I. Simplified Energy Level Diagram for Low-Spin d^7 Nickel(III)^a



^{a} Extent of axial binding decreases from left to right.

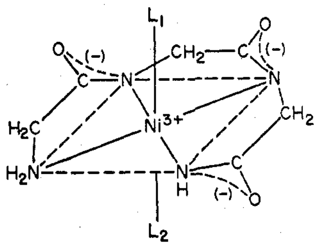
The EPR results are best described by a tetragonally distorted octahedral geometry, Scheme Ib, with the electron in an orbital which has a large amount of d_{z^2} character. The predicted g values are given by the approximate expressions[11] in eq 4–6. This yields $g_{xx}, g_{yy} > g_{zz}$ as observed. The structure

$$g_{xx} = 2 - \frac{6\lambda}{\Delta E_{z^2-yz}} \tag{4}$$

$$g_{yy} = 2 - \frac{6\lambda}{\Delta E_{z^2-xz}} \tag{5}$$

$$g_{zz} = 2 \tag{6}$$

proposed for these complexes is illustrated for $Ni^{III}(H_{-3}G_3a)$ in structure **1a** and includes axially bound water molecules.



1a, $L_1 = H_2O$, $L_2 = H_2O$
b, $L_1 = NH_3$, $L_2 = H_2O$
c, $L_1 = NH_3$, $L_2 = NH_3$

Although both square planar[13,14] and tetragonally distorted octahedral[8,13–19] geometries have been observed previously for nickel(III), the latter is the most common. In a number of cases, hyperfine coupling from axial donors has been observed.[13,14,16] Hence, it is reasonable to include water in the axial positions in structure **1a**.

The reduction potentials of the mono(oligopeptide)nickel(III) complexes vary relatively little with changes in the ligand structure.[2] This suggests that little crystal field stabilization energy is gained when an electron is removed from nickel(II). Indeed, the small dependence of $E°$ on crystal field stabilization energy led to the postulate that trivalent complexes of nickel peptides were tetragonal rather than square planar.[2] Further support for a tetragonal structure was derived from the effect of bulky alkyl substituents on the electrode potentials.[2] The present EPR data confirm this postulate.

Effect of Equatorial Donor Atoms. Values of g_{xx} and g_{yy} are sensitive to the nature of the equatorial donor atoms. One of the equatorial axes has the same donor atoms (an amine nitrogen and a deprotonated peptide nitrogen) for all the complexes and one g value (g_{yy}) is nearly constant (2.283 ± 0.012). Equatorial axes with two deprotonated peptide nitrogens have g values (g_{xx}) larger while those with a single deprotonated peptide nitrogen and either a carboxylate group or an imidazole nitrogen (Im) have lower values. It is not clear why the g_{xx} values for $Ni^{III}(H_{-3}G_4)^-$ and for $Ni^{III}(H_{-3}G_5)^-$ differ as much as they do, but it may be related to distortions in the G_5 complex due to interaction of the metal center with the free carboxylate group.[3]

The general trend in g values reflects the trend in donor strength[20] of the groups (7) as evaluated from spectroscopic

$$>N^- > -NH_2 > -Im \sim -CO_2^- \qquad (7)$$

shifts in the d–d absorption maxima of copper(II)–polypeptide complexes and changes in the electrode potentials of copper(II)–copper(III) redox couples.[2] As the strength of the equatorial binding increases, the value of g_{xx} increases and reflects the similar coordination behavior of copper(II) and nickel(III) toward these biologically important ligands.

Hyperfine Coupling from Equatorially Bound Nitrogens. It should be noted from Figure 1 and the data in Table I that considerable broadening of the EPR spectra in the g_{xx}, g_{yy} region is required to obtain the proper peak intensities. Hyperfine splitting from equatorially bound nitrogens could not be resolved. However, calculations show that splittings from nonequivalent nitrogen nuclei as large as 20 G would not be detectable in the broad absorption envelope. The broadening increases with donor strength. Hyperfine coupling to nitrogen of this magnitude is not inconsistent with the proposed nickel(III) formulation.[13,14]

Axial Binding of NH_3. In the case of $Ni^{III}(H_{-3}G_3a)$, the nature of the tetragonal distortion was investigated using ammonia as a probe. As the concentration of ammonia in solutions of $Ni^{III}(H_{-3}G_3a)$ is increased, two new paramagnetic species are detected. The EPR spectra of aqueous glasses containing these species are presented in Figure 2. Both spectra are similar in form to the spectrum of $Ni^{III}(H_{-3}G_3a)$ with $g_\perp > g_\parallel(g_{zz})$ but show hyperfine splitting in the $g_\parallel$ region. The g_{xx} and g_{yy} values are approximately equal and are not resolved.

Figure 2a suggests a species which has a single nitrogen nucleus ($I = 1$) bound in an axial position. It is not possible for one nitrogen donor from the equatorial peptide ligand to shift its coordination to an axial position.[10] Structure **1b** is proposed for the complex which behaves as if it were in equilibrium with $Ni^{III}(H_{-3}G_3a)$. A plot of the percent complex against ammonia concentration (Figure 3) gives a value of 2 × 10^7 M^{-1} for the stability constant in eq 8. The initial

$$Ni^{III}(H_{-3}G_3a) + NH_3 \rightleftarrows Ni^{III}(H_{-3}G_3a)(NH_3) \qquad (8)$$

temperature was 23 °C and the solutions freeze within 2 s after quenching. Hence the equilibrium constant is approximate because the relaxation time is not known for the negative temperature jump.

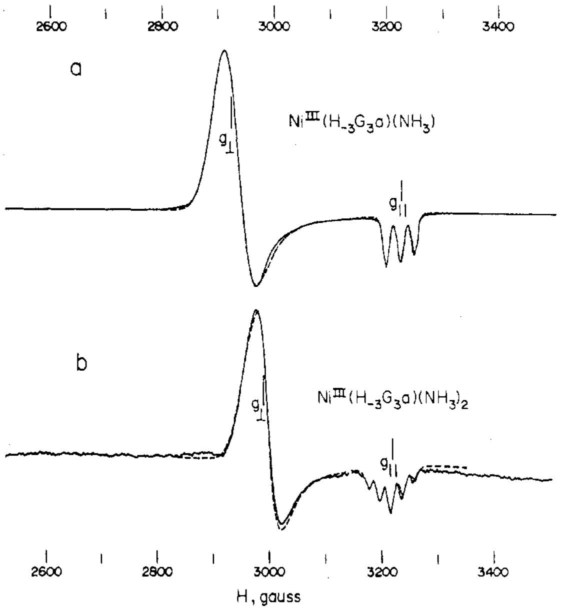


Figure 2. EPR spectra (—, experimental; ---, calculated) for ammonia adducts to $Ni^{III}(H_{-3}G_3a)$ in magnetically dilute aqueous glasses at −150 °C: (a) $Ni^{III}(H_{-3}G_3a)(NH_3)$ formed from 10^{-4} M $Ni^{III}(H_{-3}G_3a)$ and 2 M $[NH_3]_T$ at pH 5.1, 9.079 GHz; (b) $Ni^{III}(H_{-3}G_3a)(NH_3)_2$ formed from 10^{-5} M $Ni^{III}(H_{-3}G_3a)$ and 2 M $[NH_3]_T$ at pH 9.9, 9.081 GHz.

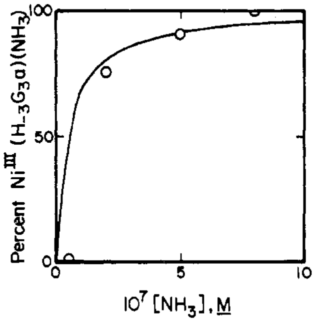


Figure 3. Plot of percent $Ni^{III}(H_{-3}G_3a)(NH_3)$ as a function of free ammonia concentration ($[Ni^{III}(H_{-3}G_3a)]_T \simeq 10^{-5}$ M, $[NH_3]_T = 2.3 \times 10^{-2}$ M, pH 4–6, [2-(*N*-morpholino)ethanesulfonic acid] = 1 × 10^{-2} M).

A second molecule of ammonia may add to give the proposed complex shown in structure **1c** whose EPR spectrum is presented in Figure 2b. The spectrum indicates that when two ammonia molecules are present, they are bound in equivalent axial positions. A stability constant of 60 M^{-1}, Figure 4, is evaluated for eq 9. Derived g values and hyperfine

$$Ni^{III}(H_{-3}G_3a)(NH_3) + NH_3 \rightleftarrows Ni^{III}(H_{-3}G_3a)(NH_3)_2 \qquad (9)$$

coupling constants are presented in Table III.

Hyperfine splitting from axially bound ammonia molecules provides strong supporting evidence that the geometry of nickel(III)–peptide complexes is tetragonal. As the extent of axial coordination increases, the energy of the d_{z^2} orbital increases relative to the d_{xy}, d_{yz} and causes a reduction in the g_{xx}, g_{yy} values. The $g_\perp$ values are also less sensitive to differences in the donors in the equatorial plane and $g_{zz} \simeq g_{yy}$, but the spectra still show broadening as a result of unresolved hyperfine splitting.

As the binding in the axial direction increases, there is a trend in g_{zz} from 2.006 in $Ni^{III}(H_{-3}G_3a)(H_2O)_2$ to 2.011 in $Ni^{III}(H_{-3}G_3a)(H_2O)(NH_3)$ to 2.019 in $Ni^{III}(H_{-3}G_3a)(NH_3)_2$. This may be explained by an increase in the vibronic mixing of the d_{z^2} and $d_{x^2-y^2}$ ground states as the complex approaches octahedral geometry.[21]

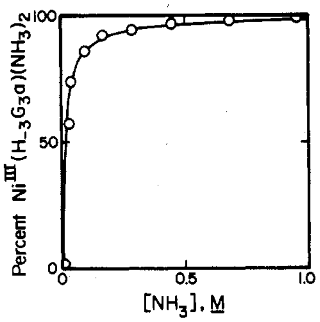


Figure 4. Plot of percent $Ni^{III}(H_{-3}G_3a)(NH_3)_2$ as a function of free ammonia concentration ($[Ni^{III}(H_{-3}G_3a)]_T \simeq 10^{-5}$ M, $[NH_3]_T = 2.0$ M, pH 8–10).

Table III. Hyperfine Coupling Constants and *g* Values for Complexes of $Ni^{III}(H_{-3}G_3a)$ Which Show Axial Coordination of Nitrogen. Data Refer to Magnetically Dilute Aqueous Glasses at −150 °C

Complex	$g_\perp (g_{xx} \simeq g_{yy})$	$g_\parallel (g_{zz})$	a_{zz}, G
$Ni^{III}(H_{-3}G_3a)(NH_3)$	2.217	2.011	23.4
$Ni^{III}(H_{-3}G_3a)(NH_3)_2$	2.178	2.019	19.0
$Ni^{III}(H_{-2}G_3a)(H_{-1}G_3a)$	2.196	2.023	21.3

The large difference in stability constants for addition of the fifth and sixth nitrogen donors to $Ni^{III}(H_{-3}G_3a)$ shows a strong preference for five nitrogen donors. This can be compared with the constants for addition of the fifth and sixth ammonia molecules to give $Co(NH_3)_6^{3+}$. The stepwise constants are 1.1×10^5 and 3.2×10^4 M^{-1}, respectively.[22,23] The low-spin d^6 cobalt(III) prefers octahedral geometry whereas the d^7 nickel(III) shows a preference for a square-pyramidal arrangement of donors. Square-pyramidal geometry is also common with low-spin d^7 cobalt(II).[24,25]

The stepwise stability constants for the fifth and sixth ligands to give high-spin d^8 $Ni(NH_3)_6^{2+}$ are only 6.5 and 1.4 M^{-1}, respectively.[22,23] Low-spin d^8 complexes such as $Ni^{II}(H_{-3}G_3a)^-$ show a preference for square-planar geometry. We found no spectrophotometric evidence for complexation of ammonia to $Ni^{II}(H_{-3}G_3a)^-$ at its absorption maximum (408 nm) even in 4.5 M ammonia solutions. This was investigated with a stopped-flow spectrometer because of the displacement of the peptide by NH_3. An upper limit for the stability constant of 2×10^{-2} M^{-1} was evaluated assuming that 10% conversion would have been detected.

Complexes of nickel(III) which show strong axial coordination are both thermodynamically and kinetically more stable than those in which the axial donor is water. Since the *E*° value for eq 10 is 0.83 V, the *E*° values for eq 11 and 12 in

$$Ni^{III}(H_{-3}G_3a) + e^- \rightleftarrows Ni^{II}(H_{-3}G_3a)^- \tag{10}$$

$$Ni^{III}(H_{-3}G_3a)(NH_3) + e^- \rightleftarrows Ni^{II}(H_{-3}G_3a)^- + NH_3 \tag{11}$$

$$Ni^{III}(H_{-3}G_3a)(NH_3)_2 + e^- \rightleftarrows Ni^{II}(H_{-3}G_3a)^- + 2NH_3 \tag{12}$$

1.0 M $[NH_3]$ can be calculated to be 0.40 and 0.29 V, respectively. Direct electrochemical measurement of these potentials has not proved possible because the reductions are irreversible and are complicated by a slow displacement of the equatorial oligopeptide by ammonia. Also at high pH the $Ni^{III}(H_{-3}G_3a)$ complex undergoes rapid self-redox reactions.

The complex $Ni^{III}(H_{-3}G_3a)(NH_3)$ was fully formed when 10^{-5} M $Ni^{III}(H_{-3}G_3a)$ was allowed to react for 15 s in a solution containing 2×10^{-2} M total ammonia in 10^{-2} M 2-(*N*-morpholino)ethanesulfonic acid buffer at pH 4 ($[NH_3]_{free} \simeq 10^{-6}$ M) before quenching. Assuming a half-life less than 5 s, a second-order rate constant greater than 10^4 M^{-1} s^{-1} is evaluated for axial substitution of $Ni^{III}(H_{-3}G_3a)$. Axial substitution rates are not known for other metal–peptide complexes. Although there have been many kinetic studies of nucleophiles with nickel(II)– and copper(II)–peptides, the reactions involve displacement of equatorial groups.[26-29]

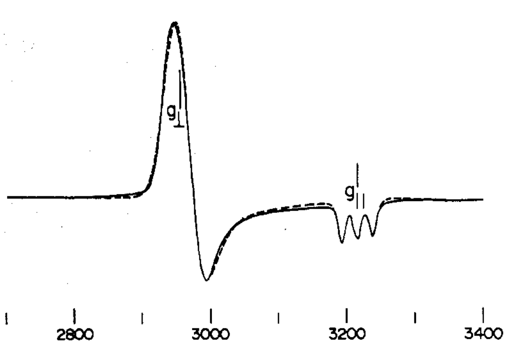
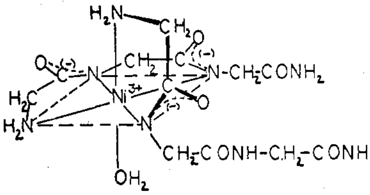


Figure 5. EPR spectrum of the proposed $[Ni^{III}(H_{-2}G_3a)(H_{-1}G_3a)]$ complex (—, experimental; - - -, calculated) in a magnetically dilute aqueous glass at −150 °C: $[Ni(III)]_T \simeq 2.5 \times 10^{-3}$ M, pH 6, 9.081 GHz.

One consequence of the enhanced stability of axially bound complexes of nickel(III) is observed when solutions of $Ni^{III}(H_{-3}G_3a)$ are allowed to decay. In borate buffer, pH 8.6, the half-life for decomposition of $Ni^{III}(H_{-3}G_3a)$ is around 5 s. However, an EPR signal, Figure 5, from a more stable complex with a half-life of 10^4 s is observed at longer times. The signal is enhanced by addition of free G_3a and indicates an axially symmetric complex with $g_\perp = 2.196$ and $g_\parallel = 2.023$. Hyperfine splitting corresponds to a single nitrogen bound in the axial position, with $a_\parallel = 21.3$ G and is comparable to that of the ammonia complexes. Similar spectra with identical *g* values and hyperfine coupling constants are observed when the ligand is G_3 or G_4. This suggests chelation of a second oligopeptide as in structure **2**. An EPR spectrum similar to Figure 5 was reported[1] for $Ni^{III}(H_{-3}G_3a)$ but in fact the spectrum corresponds more closely to the proposed bis complex, $Ni^{III}(H_{-2}G_3a)(H_{-1}G_3a)$, which has a much longer lifetime than the mono complex under the experimental condition (pH 9.5).



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The rates of formation of the bis complexes are much slower than the formation of the ammonia adducts. Intermediates, which were detected by EPR, suggest that axial binding is rapid and that ring closure involving replacement of a donor in the equatorial plane is the rate-determining step. Hence the second G_3a molecule is believed to be chelated and we assume the coordination is that shown in structure **2**.

Conclusions

Oxidation of square-planar nickel(II)–oligopeptide complexes give nickel(III) species which are proposed to have a tetragonally distorted octahedral geometry with four donors from the oligopeptide groups in the equatorial plane and coordination of solvent in the axial positions. The EPR spectra of the nickel(III) complexes are sensitive to the nature of the equatorial donor atoms. As the donor strength decreases in the order $>N^- > -NH_2 > Im \sim -CO_2^-$, the equatorial *g* value decreases.

One axial solvent molecule may be displaced by NH_3 to form a very strong complex with five nitrogen donors. Substitution of the second solvent molecule is less favorable.

The oxidizing power of nickel(III) decreases upon adduct formation and the kinetic stability is greatly increased. This enhanced kinetic and thermodynamic stability of nickel(III) with five or more nitrogen donors suggests that nickel(III) could be expected to form in biological systems.[30] It is known[4] that $Ni^{II}(H_{-3}G_4)^{2-}$ will react with oxygen to give nickel(III) and we believe that bis(peptide)nickel(III) complexes would form readily to give a relatively stable reservoir of oxidizing power.

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Registry No. $Ni^{III}(H_{-2}G_3)$, 60165-86-8; $Ni^{III}(H_{-2}G_2his)$, 12170-35-3; $Ni^{III}(H_{-3}G_4)^-$, 34722-98-0; $Ni^{III}(H_{-3}G_5)^-$, 34740-00-6; $Ni^{III}(H_{-3}G_3a)$, 60108-87-4; $Ni^{III}(H_{-2}G_3a)(H_{-1}G_3a)$, 66172-40-5; $Ni^{III}(H_{-3}G_3a)NH_3$, 66172-39-2; $Ni^{III}(H_{-3}G_3a)(NH_3)_2$, 66172-44-9.

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Carbon-13 Nuclear Magnetic Resonance, Infrared, and Equilibrium Studies of *cis*- and *trans*-$W(CO)_4(CS)L$ Complexes

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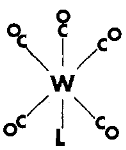
Complexes of the formula *trans*-$W(CO)_4(CS)L$, II, were prepared from *trans*-$W(CO)_4(CS)I^-$ by halide abstraction with silver(I) ion followed by addition of a ligand L (L = $P(OC_6H_5)_3$, $P(OCH_3)_3$, $P(C_6H_5)_3$, $P(4\text{-}CH_3C_6H_4)_3$, $P(n\text{-}C_4H_9)_3$, $4\text{-}CH_3C_5H_4N$, CNC_6H_{11}). Upon mild heating, the pure trans isomers were converted to equilibrium mixtures of *cis*-$W(CO)_4(CS)L$, III, and trans complexes. Equilibrium constants for these mixtures were determined by ^{13}C NMR and were found to be related to the π-acceptor capacity of L. Analysis of IR and ^{13}C NMR data collected from these complexes and their $W(CO)_5L$, I, analogues permits comparisons of bonding and spectroscopic properties of CO and CS. Correlations were found for k(CO) of II with k(cis CO) of I, k(CS) of II and III with k(cis CO) of I, k(cis CO) of I with δ(cis CO) of I, k(CO) of II with δ(CO) of II, k(CS) of III with δ(CS) of III, δ(CO's cis to L) and δ(CS) of III with δ(cis CO) of I, and δ(CO) of II with δ(cis CO) of I. The comparisons demonstrate the "charge-buffering effect" of CS, which in these complexes appears to be based largely on the strong π-acceptor capability of CS.

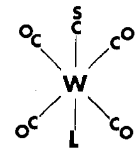
Introduction

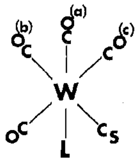
A number of ^{13}C NMR studies of transition-metal carbonyl complexes have been recently published.[2,3] Results obtained on various substituted derivatives have been related to the charge-donor ability of substituent ligands and to M–CO σ and π bonding. However, there are few data in the literature on the ^{13}C NMR spectra of transition-metal thiocarbonyl complexes.[4,5] One purpose of this study was to gather ^{13}C NMR data on the CS group in a class of metal carbonyl compounds containing the CS ligand and another ligand which was systematically varied. Analysis of both δ(CS) and δ(CO) values, together with infrared results for the ν(CO) and ν(CS) modes, was expected to yield information about the bonding properties of the thiocarbonyl group.

Results and Discussion

A. Preparation and Characterization of Complexes. Thermal CO substitution in $W(CO)_5(CS)$ by PPh_3 has been previously found to afford mixtures of cis and trans isomers of $W(CO)_4(CS)(PPh_3)$ (II and III, L = PPh_3), which do not appear to be separable by fractional crystallization or column chromatography.[6] By use of silver(I) ion to abstract the halide ion from *trans*-$W(CO)_4(CS)I^-$ in a coordinating solvent, followed by addition of a ligand L, II is obtained[6,7] (eq 1).


I


II



III

$$trans\text{-}W(CO)_4(CS)I^- + Ag^+ \xrightarrow[-AgI]{L} trans\text{-}W(CO)_4(CS)L \qquad (1)$$

This method has now been used with a variety of ligands to prepare pure trans products, which have been characterized by IR and ^{13}C NMR spectra (Tables I and III). For direct