Force Constants. The initial Urey–Bradley force constants were transferred from the following compounds: $H_2PO_4^-$,[22] PS_4^{3-},[23] $Ni(S_2CSC_2H_5)_2$,[24] and $Ni(S_2COC_2H_5)_2$.[25] The force constants that were used to give the best fit with the observed frequencies are collected in Table II.

Nickel(II) forms four-membered chelate rings with dithiophosphates, dithiocarbamates, and xanthates. The anomalous properties of the four-membered chelate rings in the dithiophosphate complexes can be attributed to the presence of the large phosphorus atom with available d orbitals. The Ni–S bond in the four-membered ring containing a phosphorus atom is more prone to disruption than the Ni–S bond in the corresponding ring systems in which the phosphorus is replaced by a carbon atom.[24-26] The Ni–S distances that have been determined by x-ray crystallographic techniques do not reflect these bonding differences in the chelate rings. For instance, the Ni–S distance in bis(ethylxanthato)nickel(II) is 2.23 Å and in bis(*O,O'*-dimethyldithiophosphato)nickel(II) it is 2.222 Å. It might be deduced from these bond distances that the Ni–S bond in the dithiophosphate complex is somewhat stronger than the Ni–S bond in the xanthate complex and that the dithiophosphate complex of nickel(II) is more stable than the xanthate complex. The force constants, however, imply correctly that the xanthate is much more stable than the dithiophosphate. The bond distances in these metal chelates are quite insensitive to variations in metal–ligand bonding. The interpretation of subtle but significant variations in x-ray crystallographic bond parameters in terms of the electronic structures of these systems can be quite misleading.

Registry No. $Ni(DMP)_2$ (salt form), 25764-05-0; $Ni(DMP)_2$ (coordination form), 15844-04-9; $Ni(DMP\text{-}d_6)_2$ (salt form), 61812-69-9; $Ni(DMP\text{-}d_6)_2$ (coordination form), 61813-20-5; $Pt(DEP)_2$ (salt form), 31596-89-1; $Pt(DEP)_2$ (coordination form), 37583-01-0; $Ni(DEP)_2$ (salt form), 3911-05-5; $Ni(DEP)_2$ (coordination form), 16743-23-0.

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Electrode Potentials of Nickel(III,II)–Peptide Complexes

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Standard electrode potentials from 0.96 to 0.79 V are determined for a series of 30 $Ni^{III,II}$–peptide couples in aqueous solution. The values of $E°$ decrease with the number of deprotonated peptide groups and can increase with bulky C substituents depending upon their position in the amino acid residues. Histidine-containing peptide complexes have relatively high electrode potentials. Ligand effects on the values of $E°$ are much smaller for the nickel peptides than for the corresponding copper peptides, which is indicative of the relative advantages in ligand field stabilization of d^8 vs. d^9 and d^7 electronic configurations in the square-planar and tetragonal environments of the peptide complexes.

Introduction

A number of trivalent nickel complexes with nitrogen donors have been prepared in nonaqueous solution[1-5] or in the solid state.[6,7] The formation of Ni(III) complexes with several pyridine oxime ligands in nonaqueous solution prompted the proposal of some qualitative criteria for ligands which stabilize complexes of Ni(III) rather than Ni(IV).[8] In addition, an extensive series of tetraaza macrocyclic nickel complexes in acetonitrile has been used to quantitatively correlate potentials of the $Ni^{III,II}$ couples with the nature of the ligands.[2] Characterization of trivalent nickel complexes in aqueous solution until recently has been limited to transient species,[9] although there is a preliminary report of a relatively stable Ni^{III}–EDTA complex.[10]

We have recently prepared and characterized several relatively stable nickel(III)–peptide complexes in aqueous solution.[11] In the present work a more extensive series of nickel peptides is electrochemically oxidized and characterized in aqueous solution. The electrode potentials have been measured for 30 $Ni^{III,II}$–peptide complexes in order to determine what factors affect the relative thermodynamic stability of the divalent and trivalent oxidation states. The changes in the values of $E°$ for the nickel complexes with changes in the nature of ligands are compared with the results obtained from a similar study of copper–peptide complexes.[12] A correlation between the visible absorption maxima of the divalent complexes and the electrode potentials is used to explain the differences in the relative stability of the oxidation states for the two metal–peptide systems.

Experimental Section

The wavelengths of the visible absorption maxima of the fully deprotonated Ni(II) complexes of the peptides and peptide amides used are listed in Table I. The commercial sources for the chromatographically pure peptides also are given. The following ab-

Table I. Properties of the Nickel–Peptide Complexes

Nickel peptides	Ligand source	λ_{max} ($Ni^{III}L$),[a] nm	Δ,[b] mV	$E°$,[c] V
		Tripeptides[d]		
GGG	*g*	430	81	0.85
AAA	*h*	426	87	0.84
AGG	*h*		78	0.85
VGG	*i*	428	79	0.85
IGG	*j*	428	73	0.85
LGG	*i*	428	71	0.85
GGA	*h*	430	70	0.85
GGL	*h*	429	74	0.87
GGF	*k*		89	0.89
GGV	*i*	430	78	0.89
GGI	*h*	430	70	0.89
GGβA	*i*		79	0.84
GLG	*h*	430	72	0.86
LLL	*i*		95	0.87
		Histidine-Containing Peptides[d,f]		
GGhis	*k*	425	90	0.96
GGhisG	*h*	424	100	0.95
asp-ala-his-lys	*h*	420	145	0.94
		Tetrapeptides[e]		
G_3AOCH_3	*h*	416	75	0.84
G_3A	*h*	418	95	0.82
A_4	*h*	414	101	0.82
AG_3	*h*	408	99	0.80
G_4	*h*	411	98	0.79
		Peptide Amides and Higher Order Peptides[e]		
G_4a	*k*	410	73	0.84
G_3a	*i*	408	80	0.83
VGGa	*i*	411	75	0.83
GGAa	*k*	408	75	0.82
G_5	*h*	410	87	0.83
A_5	*h*	413	88	0.83
G_4AOCH_3	*h*	410	83	0.83
G_6	*h*		78	0.83

[a] Visible absorption maximum of the fully deprotonated Ni(II) complex. [b] Peak potential separation indicating reversibility of the electrode reaction (Δ = 59.5 mV for a one-electron couple which is completely reversible electrochemically). [c] Determined by cyclic voltammetry at 100 mV s^{-1} with a carbon-paste working electrode, at $[NiL]_T = 2 \times 10^{-3}$ M, pH 9.6, 25 °C, $\mu = 0.10$ M ($NaClO_4$); $E°$ vs. NHE. [d] $E°$ value for $Ni^{III}(H_{-2}L) + e^- \rightleftarrows Ni^{II}(H_{-2}L)^-$. [e] $E°$ value for $Ni^{III}(H_{-3}L)^{(n+1)+} + e^- \rightleftarrows Ni^{II}(H_{-3}L)^{n+}$. [f] pH 8.2. [g] Sigma Chemical Co. [h] Biosynthetika. [i] Vega-Fox Chemical Co. [j] Bachem Inc. [k] Cyclo Chemical Co.

breviations are used for the amino acid residues of the peptides: glycyl, G; L-alanyl, A; β-alanyl, βA; L-valyl, V; L-leucyl, L; L-isoleucyl, I; L-phenylalanyl, F; L-histidyl, his; L-aspartyl, asp; L-lysyl, lys. The methyl esters of G_3A and of G_4A also were used. Peptide amides such as triglycinamide are designated by G_3A.

Solutions of the nickel(II)–tripeptide complexes were prepared by the reaction of 100% excess ligand with $Ni(ClO_4)_2$ solutions (standardized by EDTA titration). The peptide ligand was used in 5–10% excess of the nickel in all other complexes. The pH was adjusted using NaOH. All of the reactant solutions were adjusted to an ionic strength of 0.10 M with $NaClO_4$ (prepared from Na_2CO_3 and $HClO_4$).

Ultraviolet and visible absorption measurements were obtained using a Cary 14 spectrophotometer and pH measurements were obtained using a Radiometer PHM26 pH meter. Electrochemical oxidation was performed with a flow system in which the electrode arrangement included a graphite powder working electrode packed in a porous-glass column, wrapped externally with a Pt-wire electrode.[13] This electrochemical system was thermostated at 2–5 °C in order to minimize decomposition of the Ni(III) complex while on the electrode column. In general the pH of millimolar solutions of nickel(II) peptides was adjusted in order that the fully deprotonated form of the complex was oxidized at a potential about 200 mV above its value of $E°$ at a flow rate of 1 mL min^{-1}. The oxidized complex was collected in a pH 5 buffer solution in order to minimize decomposition. Molar absorptivities were determined for the electrochemically generated

Table II. Characteristic Absorption Bands of Nickel(III)–Peptide Complexes

Nickel(III) peptide	λ_{max}, nm (ϵ, M^{-1} cm^{-1})
$H_{-3}G_3a$	325 (5360 ± 150), 235 (10 700 ± 500)
$H_{-3}GGAa$	325 (5820 ± 100), 238 (11 300 ± 600)
$H_{-3}G_5$	325 (5820 ± 130), 240 (11 300 ± 400)
$H_{-3}G_4$	327 (5240 ± 240), 250 sh[a]
$H_{-2}GGG$	340 (4500 ± 150), 250[a]
$H_{-2}VGG$	340 (4330 ± 100), 254 (10 200 ± 400)
$H_{-2}AAA$	345 (4270 ± 200), 260 (10 600 ± 300)
$H_{-2}GGV$	355 (4740 ± 100), 255 (11 300 ± 600)

[a] Molar absorptivity not determined due to decomposition of the complex.

nickel(III)–peptide complexes by measuring the absorbance changes in a 1-cm cell upon the addition of aliquots of standardized hydroquinone solutions. The EPR spectra of the electrochemically generated Ni(III) complexes were recorded at liquid nitrogen temperatures (frozen aqueous solutions, $[NiL]_T = 2 \times 10^{-2}$ M) with an X-band E-9 Varian EPR spectrometer. The *g* values were calculated using the signal of di-*tert*-butyl nitroxide recorded under the same conditions as the standard.[14]

Cyclic voltammetry was performed at 25 °C with a three-electrode system consisting of a carbon-paste working electrode, a platinum-wire auxiliary electrode, and a saturated NaCl calomel reference electrode. Voltammograms were generated using a Bioanalytical Systems Inc. CV-1 instrument and recorded on a Hewlett-Packard HP703513 X-Y recorder. Preconditioning of the carbon-paste electrode by cycling between the potential limits of the solvent was necessary to obtain quasi-reversible current–potential curves. The uncomplexed ligand did not contribute to the background current. Solutions of nickel ion in basic solution and in the absence of peptide ligand gave a weak signal in the region of interest, but its peak shape and current–potential response behavior on the carbon-paste electrode were distinct from the response curves of the nickel–peptide complexes. The $E°$ values were determined as the midpoint between the peak potentials. The electrode potentials were obtained from an average of at least three separate cyclic voltammetric measurements and have a reproducibility of ±5 mV. All the $E°$ values are given in terms of standard electrode potentials (V) vs. NHE.

Results

The nickel complexes of the peptides and peptide amides are oxidized electrochemically to the corresponding Ni(III) species in aqueous solution. Oxidation causes a change in the visible absorption spectrum from the low-intensity d–d absorption band of the Ni(II) complexes, centered near 420 nm, to an intense charge-transfer band near 330 nm. A second characteristic charge-transfer band is found near 250 nm. Table II lists the absorption maxima and molar absorptivities for some of the nickel(III) peptides. As expected, the energy of these bands increases as the electron-donor strength of the ligand increases[15] from doubly deprotonated to the triply deprotonated complexes. In general these complexes decompose over a period of several hours at pH 5, 25 °C. At the higher values of pH, where the cyclic voltammetry measurements were made, decomposition occurs over a period of several minutes.

Electrochemical analyses by cyclic voltammetry were used to determine the electrode potentials of a series of nickel–peptide complexes. Figure 1 shows the current–voltage response obtained in aqueous solution at a scan rate of 100 mV s^{-1} for the Ni–AGG complex. The initial solution contains only the divalent complex which generates the oxidation wave (negative current), while the trivalent complex, which is formed, generates the reduction wave (positive current). This current response curve is representative of all the complexes. The separation of anodic and cathodic peaks was 70–90 mV in all but a few cases and peak current ratios were near unity. Slight variations in the values of the peak potentials with different scan rates were observed, although the midpoint of

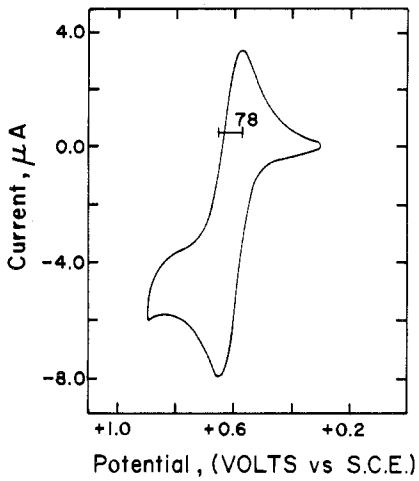

Figure 1. Cyclic voltammogram of $[Ni(H_{-2}AGG)]^-$ in aqueous solution at a carbon-paste electrode at $[NiAGG]_T = 2.0 \times 10^{-3}$ M, $\mu = 0.10$ M ($NaClO_4$), 25 °C, and scan rate = 100 mV s^{-1}; $E° = 0.85$ V vs. NHE.

the peak potentials did not vary. These features are indicative of quasi-reversible electrochemical behavior[16] and the midpoint between the oxidation peak and the reduction peak is a reasonable estimate of the electrode potential of the $Ni^{III,II}$–peptide couples. Similar methods were used to measure the $E°$ values for $Cu^{III,II}$–peptide complexes[12] and the reliability of the potentials measured by cyclic voltammetry for the copper peptides was confirmed by redox equilibria measurements with $Ir^{IV,III}Cl_6^{2-,3-}$. Table I lists the standard electrode potentials for Ni(III)–Ni(II) couples with a series of peptide complexes. The peak potential separations are also listed as an indication of the reversibility of the electrochemical process.

The values of $E°$ for a given nickel–peptide complex are constant over the pH range of 6.5–10.5, while the peak current response decreases with decreasing pH. This peak current response is expected with the acid–base equilibrium of the nickel(II) peptides offsetting the redox equilibrium as shown for NiGGG in eq 1 The constant value of $E°$ over the wide

$$Ni^{II}(H_{-2}GGG)^- \overset{E°}{\rightleftharpoons} Ni^{III}(H_{-2}GGG) + e^- \quad (1)$$

$$2H^+ \downarrow\uparrow$$

$$NiGGG^+$$

pH range indicates that the acid–base equilibration is slow compared to the electron-transfer rate and the electrochemical scan rate. One of the major factors which contributes to this slow transfer of the first proton to the peptide nitrogen in $Ni^{II}(H_{-2}GGG)^-$ is the necessity of electronic and structural rearrangement for the transition from square-planar to octahedral complexes.[17] At the lower pH values the doubly deprotonated complex is oxidized preferentially, since $NiGGG^+$ has a much higher potential. Slow proton-transfer reactions are typical for the other nickel(II) tripeptides and are even slower for the triply deprotonated tetrapeptide complexes.[18,19] Therefore, the values of $E°$ reported in Table I are believed to be an accurate measurement of the redox reaction involving the fully deprotonated complexes.

Discussion

The nickel–peptide complexes have strong in-plane donors which tend to stabilize the trivalent state of nickel. The triply deprotonated complex of nickel tetraglycine has an amine nitrogen and three deprotonated peptide nitrogens bound to the metal. The crystal structure of the Ni(II) complex shows that the metal ion and the four nitrogen atoms are nearly coplanar and the complex is described as truly square-planar.[20] Electrochemical oxidation of $Ni^{II}(H_{-3}G_4)^{2-}$ results in the Ni(III) complex. The EPR spectrum of the trivalent nickel complex obtained at liquid nitrogen temperatures is similar to the spectra obtained for many of the nickel(III)–tetraaza macrocyclic complexes[2,3,6] with $g_\perp$ greater than the $g_\parallel$. This is consistent with the unpaired electron in the d_{z^2} orbital for d^7 Ni(III). The magnitude of $g_\perp$ (2.268) for nickel(III) tetraglycine and the relative magnitude of $g_\perp$ compared to $g_\parallel$ indicate that the nickel complex is no longer square-planar after oxidation but assumes a tetragonal geometry in the higher oxidation state.[3,5,6] Similar anisotropic g values were determined for the nickel(III)–pentaglycine complex ($g_\perp$ = 2.272). [The value of $g_\perp$ previously reported by us[11] for the triglycinamide complex has been redetermined and the initial value is 2.273 rather than 2.166.] The other nickel–peptide complexes are also expected to be square-planar in the divalent state and tetragonal in the trivalent state.

The values of $E°$ for the $Cu^{III,II}$–peptide complexes were found to be highly dependent upon the nature of the ligands.[12] On the other hand the values of $E°$ for the $Ni^{III,II}$–peptide complexes are much less sensitive to changes in the nature of the ligands. The relative thermodynamic stability of the divalent vs. the trivalent nickel complexes can be affected by the type of coordinating groups and by the presence of bulky C substitutents in the amino acid residues. Whereas the relatively large variation in electrode potential of the copper peptides could be attributed to the large gain in crystal field stabilization energy (CFSE) for the transition from d^9 Cu(II) to d^8 Cu(III), the smaller changes in the values of $E°$ for similar ligand changes are consistent with a smaller gain in CFSE for the transition from d^8 Ni(II) to d^7 Ni(III).

Effect of Coordinating Groups on $E°$. On the whole, the peptide amides, the tetrapeptides, and the higher order peptides listed in Table I have slightly lower potentials than the tripeptides. These triply deprotonated complexes have similar coordination to that of nickel tetraglycine. The fully deprotonated tripeptides have only two deprotonated peptide nitrogens, along with an amine nitrogen and a carboxylate group bound to nickel. The deprotonated peptide group is higher in the spectrochemical series than either amine or the carboxylate group.[21] Its strong electron-donor properties should help stabilize the trivalent oxidation state as was seen in the copper complexes.[12,22] This stabilization does occur with the nickel complexes, but the magnitude of the effect (20–60 mV) is much smaller than with the copper complexes.

Ligands with histidine as the third amino acid residue have an amine nitrogen, two deprotonated peptide nitrogens, and an imidazole nitrogen bound to nickel. Although the imidazole group is higher in the spectrochemical series than the carboxylate group,[21] the values of $E°$ of the histidine-containing peptides were greater than for the tripeptide complexes. High potentials also were found for the same complexes of copper and were attributed to a combination of the relative effects of cumulative ring strain and π back-bonding.[12] A comparison of the electrode potentials for the nickel complexes of GGA and GGβA indicates that the reduction in cumulative ring strain in the 5,5,6-membered ring system of the GGhis complex is less important in influencing the electrode potential than the presence of the imidazole group and the subsequent influence of π back-bonding on the divalent nickel complex.

Effect of C Substituents on $E°$. The presence of C substituents on the ligands markedly lowered the electrode potentials for the copper peptides.[12] Although bulky substituents can influence the value of $E°$, there is an increase in the electrode potential rather than a decrease. In both metal systems the presence of these substituents seems to favor the d^8 form of the complex. The nickel complex of GGV has an electrode potential 40 mV higher than that of the GGG

complex. This increase in the value of $E°$ can be attributed to the interaction of the bulky substituent with axial solvation as in the case of the nickel macrocyclic complexes.[2] Such interactions would be more likely in the trivalent complex where oxidation of the metal ion causes contraction of the equilibrium bond distances and where EPR evidence indicates that the geometry of the oxidized complex is tetragonal. As expected the highly branched C substituents are the most effective in increasing the potential. The electrode potential of the GGA complex is the same as that of GGG, while the values of $E°$ increase by 20 mV with the GGL complex and by 40 mV with more highly branched substituents in the GGV and GGI complexes. This steric effect is positionally dependent. When the substituents are on the amino-terminal residue of the peptide (as in VGG) the value of $E°$ for the nickel complex does not differ from that of the GGG complex, but when the substituent is on the carboxylate end of the tripeptide (as in GGV) the value of $E°$ is 40 mV higher. Steric interaction with the amide oxygen of the preceding residue causes greater axial disposition of side chains in non-amino-terminal residues than in the amino-terminal residue, allowing for the differences in axial interaction.[23,24] The presence of alkyl substituents on the nickel–tetraaza macrocyclic complexes in acetonitrile showed much larger increases in the value of $E°$ attributed to interaction with axial solvation.[2] The moderate increases in the value of $E°$ for the $Ni^{III,II}$–peptide complexes may indicate that the C substituents of the peptides have a lesser degree of axial interaction than the macrocyclic substituents or that such nonbonding interactions are more pronounced in acetonitrile solutions than in aqueous solution.

A Comparison of the Effect of the CFSE on $E°$ for Nickel and Copper Complexes. Our previous work showed that the relative gain in the CFSE for the transition from d^9 Cu(II) to d^8 Cu(III) was an important factor in the overall stabilization of the trivalent oxidation state.[12] This gain in the CFSE is due to the contributions from the change in electronic configuration,[25] as well as the increase in the charge of the metal ion.[26] A similar analysis of the nickel peptides indicates that the change in the CFSE is much smaller and therefore causes a smaller difference between the thermodynamic stability of the divalent and trivalent oxidation states.

An indication of the CFSE can be obtained from the energy of the d–d transitions. The visible spectra of the nickel(II)–peptide complexes show a single absorption band which envelopes three d–d transitions. The order of increasing energy of the d orbitals for the square-planar d^8 nickel complexes is considered to be $xy \sim yz < z^2 < xy < x^2 - y^2$, with the corresponding transitions $A_{2g} \leftarrow A_{1g} < B_{1g} \leftarrow A_{1g} < E_{1g} \leftarrow A_{1g}$.[24] For this series of Ni(II) complexes the absorption maxima vary between 430 and 407 nm, while the shape of the band remains the same. The relationship between $\bar{\nu}_{max}$ for the nickel(II) peptides and the values of $E°$ is shown in Figure 2. The correlation indicates that the values of $E°$ decrease slightly as the CFSE increases. An explanation for this inverse relationship is presented by the simplified energy level diagram shown in Figure 3. The total CFSE of the divalent complex is given by Δ, while the CFSE of the trivalent complex is $x\Delta$. With a net gain in the CFSE for the transition from Ni(II) to Ni(III) (i.e., $x > 1$) the value of $E°$ decreases as the CFSE of the divalent complex increases. The relationship between Δ and $E°$ can be expressed by eq 2. Since Δ is related to $\bar{\nu}_{max}$,

$$E° = (1 - x)\Delta + E' \qquad (2)$$

the value of x can be calculated from the plot in Figure 2 using the following relationships. CD data on the nickel peptides indicate that a good estimate for the value of $10Dq$ is $0.9\bar{\nu}_{max}$.[24] With the CFSE of square-planar Ni(II) estimated to be

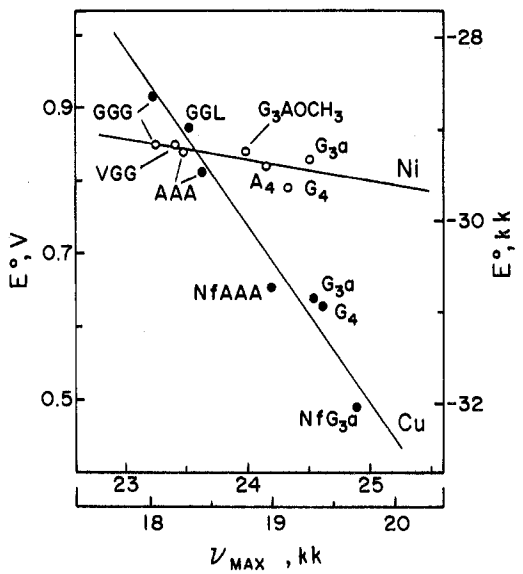

Figure 2. Electrode potentials (V vs. NHE) as a function of the divalent metal peptide d–d absorption maxima (10^3 cm^{-1}). Upper abscissa for nickel and lower abscissa for copper. Right-hand ordinate gives $E°$ in terms of $cm^{-1} \times 10^3$ (eq 4).

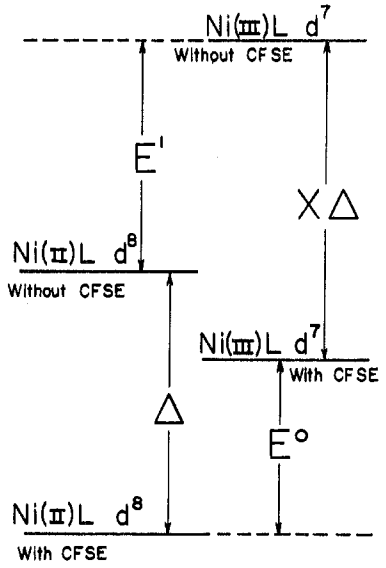

Figure 3. Relative energy-level diagram of $Ni^{III,II}$–peptide couples. Ni(II) CFSE is given by Δ and Ni(III) CFSE is $x\Delta$.

$24.56Dq$,[25] the value of Δ is related to $\bar{\nu}_{max}$ by eq 3. The value

$$\Delta = (24.56/10)0.9\bar{\nu}_{max} \qquad (3)$$

of $E°$ can be expressed in terms of μm^{-1} relative to the ionization of hydrogen (eq 4),[27] rather than in volts vs. NHE.

$$^1/_2H_2(g) + H_2O(aq) \rightleftarrows H_3O^+(aq) + e^-(vacuum) \quad -3.6\,\mu m^{-1} \qquad (4)$$

Using the slope of the plot between $\bar{\nu}_{max}$ of the divalent nickel complex and $E°$ (μm^{-1}) as shown in Figure 2, the value of x is determined from eq 2 to be 1.1 for the $Ni^{III,II}$–peptide couples. The analysis assumes that E' is independent of ligand effects over the limited energy range of these Ni(II) complexes. In square-planar $Ni^{III,II}$ complexes the CFSE can be estimated to increase by a factor of 1.1 due to the change in the electronic configuration[25] and by an additional factor of 1.4–1.8 due to the change in the charge of the metal ion.[26] The combination of these effects gives a value of 1.7 ± 0.2 for x, which is higher than the experimentally determined value of x. This is further evidence that the trivalent complexes of the nickel peptides are no longer square-planar.

A similar relationship between the visible absorption maxima of the copper(II) peptides and their values of $E°$ (also shown in Figure 2) indicates that the CFSE increases by a factor of 2.8 for the transition from Cu(II) to Cu(III).[12] The magnitudes of these relationships reflect the relative advantages in ligand field stabilization of d^8 vs. d^9 and d^7 electronic configurations in the square-planar or tetragonal environment of the peptide complexes.

Conclusions

A comparison of the potentials for copper and nickel peptides shows that while the triply deprotonated complex of G_3a has a $Cu^{III,II}$ potential 0.19 V less than the corresponding $Ni^{III,II}$ potential, the $Cu^{III,II}$ potential of the doubly deprotonated complex of GGG is 0.7 V greater than the corresponding $Ni^{III,II}$ potential. The reverse ordering of potentials can be attributed to the relative magnitude of the gain in the CFSE for the transition from the divalent to the trivalent oxidation state in these two metal ions. Whereas the potentials of the copper peptides are very sensitive to the nature of the ligands due to a substantial gain in CFSE for the transition from d^9 Cu(II) to d^8 Cu(III), the potentials of the nickel peptides change very little with changes in the nature of the ligands due to only a small gain in CFSE for the transition from d^8 Ni(II) to d^7 Ni(III).

Some of these Ni(II) peptides react with molecular oxygen in neutral solution and result in the decomposition of the ligand.[28-30] Small amounts of nickel(III) peptide are formed as intermediates in these reactions. The amount of trivalent nickel formed after a short induction period approaches the concentration expected from the redox equilibrium between the $Ni^{III,II}$ complex and the four-electron oxygen to water couple. Since the present study indicates that there is little variation in potential with changes in the nature of the ligand, other Ni(III) complexes may be attainable under similarly mild conditions. Very little is known about nickel in biological systems, although it appears to be an essential metal[31] and the enzyme jack bean urease has recently been shown to contain nickel.[32] The accessibility and relative stability in aqueous solution of nickel(III)–peptide complexes indicate that the trivalent state of nickel should be considered an attainable oxidation state for biological redox reactions and other nickel-catalyzed reactions.

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Registry No. $Ni^{II}(H_{-2}GGG)^-$, 31011-65-1; $Ni^{II}(H_{-2}AAA)^-$, 19330-36-0; $Ni^{II}(H_{-2}AGG)^-$, 19330-35-9; $Ni^{II}(H_{-2}VGG)^-$, 62029-58-7; $Ni^{II}(H_{-2}IGG)^-$, 62006-74-0; $Ni^{II}(H_{-2}LGG)^-$, 62006-75-1; $Ni^{II}(H_{-2}GGA)^-$, 19330-49-5; $Ni^{II}(H_{-2}GGL)^-$, 62006-76-2; $Ni^{II}(H_{-2}GGF)^-$, 62006-77-3; $Ni^{II}(H_{-2}GGV)^-$, 62006-78-4; $Ni^{II}(H_{-2}GGI)^-$, 62006-79-5; $Ni^{II}(H_{-2}GG\beta A)^-$, 62057-41-4; $Ni^{II}(H_{-2}GLG)^-$, 62006-80-8; $Ni^{II}(H_{-2}LLL)^-$, 62006-81-9; $Ni^{II}(H_{-2}GGhis)^-$, 62006-82-0; $Ni^{II}(H_{-3}GGhisG)^{2-}$, 62006-83-1; $Ni^{II}(H_{-3}asp\text{-}ala\text{-}his\text{-}lys)^{2-}$, 62006-84-2; $Ni^{II}(H_{-3}AOCH_3)^-$, 62006-85-3; $Ni^{II}(H_{-3}G_3A)^{2-}$, 62006-86-4; $Ni^{II}(H_{-3}A_4)^{2-}$, 62006-66-0; $Ni^{II}(H_{-3}AG_3)^{2-}$, 62006-67-1; $Ni^{II}(H_{-3}G_4)^{2-}$, 39016-92-7; $Ni^{II}(H_{-3}G_4a)^-$, 34722-99-1; $Ni^{II}(H_{-3}G_3a)^-$, 34722-97-9; $Ni^{II}(H_{-3}VGGa)^-$, 62006-68-2; $Ni^{II}(H_{-3}GGAa)^-$, 62015-50-3; $Ni^{II}(H_{-3}G_5)^{2-}$, 62005-78-1; $Ni^{II}(H_{-3}A_5)^{2-}$, 62005-81-6; $Ni^{II}(H_{-3}G_4AOCH_3)^-$, 62005-80-5; $Ni^{II}(H_{-3}G_6)^{2-}$, 62005-79-2; $Ni^{III}(H_{-3}G_3a)$, 60165-87-9; $Ni^{III}(H_{-3}GGAa)$, 62006-69-3; $Ni^{III}(H_{-3}G_5)^-$, 60108-88-5; $Ni^{III}(H_{-3}G_4)^-$, 60165-88-0; $Ni^{III}(H_{-2}GGG)$, 60165-86-8; $Ni^{III}(H_{-2}VGG)$, 62006-70-6; $Ni^{III}(H_{-2}AAA)$, 62006-71-7; $Ni^{III}(H_{-2}GGV)$, 62006-72-8.

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