Table II. Assignment of the Absorption Maxima to the Electronic Transitions of the Complex $[Cu(phen)_2H_2O](NO_3)_2$[a]

Transition[b]	Obsd	Calcd[c]
$^2A(^2A_1') \rightarrow {}^2A(^2E')$	12	11.4-11.7
$^2B(^2E')$	12.8	12.9-13.4
$^2B(^2E'')$		14.9-15.3
$^2A(^2E'')$	15	15

[a] All the values are expressed in 10^3 cm^{-1}. [b] The energy levels are labeled according to the C_2 symmetry group; in parentheses are the symmetry labels of the D_{3h} symmetry group. [c] $e'_\sigma{}^O = 0.95 \pm 0.05$, $e'_\pi{}^O = e'_\pi{}^O = -0.25$, $e'_\sigma{}^{N(1)} = 6$, $e'_\pi{}^{N(1)} = 0.15 \pm 0.1$, $e'_\sigma{}^{N(2)} = 5.4$, $e'_\pi{}^{N(2)} = (1.3 \pm 0.2) \times 10^3$ cm^{-1}, $e'_{\pi_s}{}^{N(1)}/e'_{\pi_c}{}^{N(1)} = 0.15$, $e'_{\pi_s}{}^{N(2)}/e'_{\pi_c}{}^{N(2)} = 0.02$.

correspond to the $g_\perp$ value of pure D_{3h} symmetry, can be easily reproduced as a consequence of the ground-state eigenfunction. This suggests that, although the values of the fitting parameters may not be satisfactory to a chemical sense, they can however reproduce nicely the experimental observables. The chemical meaning of the ligand field parameters is an open problem,[27] and particularly in the case of the copper(II) complexes it is not uncommon to find values of the parameters which do not appeal to the chemical sense[28] but are however useful, at least in a bookkeeping sense, to interpret the spectra.

Conclusions

In the present work accurate experimental techniques allowed the determination both of the principal values and directions of the **g** and ϵ tensors. Contrary to the findings of Hitchman[13] the two tensors were not found appreciably misaligned.

Although the number of experimental data was large, it was not sufficient to determine the values of the parameters of the AOM, and some additional assumptions had to be made. This result is quite general, and although recently the use of the magnetic parameters (**g**, χ, etc.) has been advocated,[29] it appears that the determination of the parameters can be obtained only by introduction of ad hoc assumptions (ζ and k isotropic, etc.).

An important result of our calculations is that no fit of the experimental data could be obtained transferring the values of the parameters from different complexes,[21] a fact that had not happened for other low-symmetry chromophores[30] but which seems now to be fairly general for trigonal-bipyramidal copper(II) complexes.

Acknowledgment. Thanks are due to Professor L. Sacconi and to Professor I. Bertini for helpful discussions.

Registry No. $[Cu(phen)_2H_2O](NO_3)_2$, 57572-96-0.

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Circular Dichroism of Copper and Nickel Tetra- and Pentapeptide Complexes

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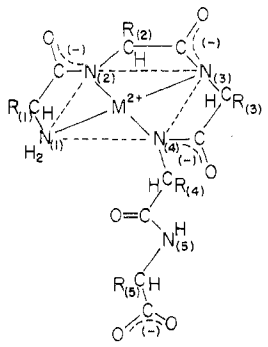
Asymmetric centers located one or two amino acid residues beyond the planar chelate ring structure in copper(II) and nickel(II) oligopeptide complexes still contribute to the visible circular dichroism of the metal ion chromophore. The triply deprotonated tetrapeptide complexes of A_4, V_4, G_3A, and G_3AOCH_3 and pentapeptide complexes of A_5, G_4A, and G_4AOCH_3 (where G is glycine, A is L-alanine, V is L-valine, and OCH_3 is the methyl ester) are compared with the CD behavior of tripeptide complexes. Intramolecular hydrogen bonding and weak axial coordination are proposed to account for the required vicinal interactions between the metal ion center and the asymmetric centers in the fourth and fifth amino acid residues in the peptides. The metal ions increase the rates of hydrolyses of the pentapeptide esters but do not affect the tetrapeptide esters. The CD spectra of copper(III) and nickel(III) oligopeptide complexes also are reported.

Introduction

The circular dichroism (CD) of copper(II) and nickel(II) complexes with optically active di- and tripeptides has been studied.[1-5] In the present work we address the question of what happens to the visible CD spectra in complexes of tetrapeptides, pentapeptides, and their methyl esters as the optically active center is moved down the peptide chain away from the site of chelation to these metal ions. Circular dichroism in the complexes arises from the vicinal interaction of the metal ion chromphoric center and the carbon atom asymmetric center in the peptide residue. Therefore, the CD signal would be expected to decrease sharply as these two centers are separated. Nevertheless, we find significant CD signals for Cu(II) and Ni(II) complexes even when the optically active center is five atoms away from the metal ion (in terms of the square-planar coordination sites). Thus, when the carbon atom next to $R_{(5)}$

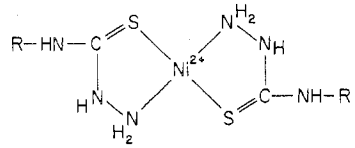
in structure I is the only asymmetric center present in the



I. $M(H_{-3}PENTAPEPTIDE)^{2-}$

complex, there still is an appreciable CD signal. Our data with various complexes suggest that there are preferred modes of association of the "free" oligopeptide chain with the metal-chelated, square-planar portion of the complex, so that the two centers are in vicinal positions.

It has been shown that chelation is not necessary to produce measurable circular dichroism in a metal ion chromophore under the influence of an asymmetric carbon. However, relatively few systems containing a monodentate optically active ligand have been studied.[6-9] The $Co^{III}(NH_3)_5L^*$ complexes (where L^* represents an optically active monodentate aminocarboxylate ligand) generally have a larger circular dichroism signal when L^* is bound through a primary amino nitrogen rather than through a negatively charged carboxylate oxygen. In each case the asymmetric center is located in an α position relative to the coordinating function. Thus, when an additional carbon atom is included between the donor atom and optically active carbon of the ligand the CD signal has a weaker rotational strength. In a study of the carbonyl chromophore in compounds such as $C_2H_5{*}CH(CH_3)(CH_2)_nCHO$ and $C_2H_5{*}CH(CH_3)(CH_2)_nCOCH_3$ the observed optical rotation becomes negligible when n is 3 or greater.[10] Square-planar nickel(II) thiosemicarbazide complexes (structure II) have been used to show the effect of



II. Ni(II)-BIS (THIOSEMICARBAZIDE)

separation of the optically active center from a metal chromophoric center. An asymmetric carbon located four atoms away from the nickel ion (R = *s-sec*-butyl) shows a substantial vicinal effect, but no measurable CD is produced when the active carbon is moved one atom farther away from the metal ion chromophore (R = *s*-2-methylbutyl).[11]

Contributions to the optical activity by asymmetric carbon atoms in square-planar copper(II) and nickel(II) peptide complexes have been characterized previously.[2-5] Important effects are attributed to the nature of the donor atoms in chelate rings formed by optically active amino acid residues[5] and to the position of the asymmetric center relative to the metal ion.[2,3,5] In addition, the CD signal generated by a tripeptide complex composed of three alkyl-substituted optically active amino acids is an additive function of the individual contribution from the corresponding monosubstituted tripeptide complexes.

In the present study the oligopeptide complexes were prepared such that the triply deprotonated species were formed in solution in order to maintain similar donor atoms in the chelate rings around the metal center.[12-15] In each case the metal is bound by an amino-terminal nitrogen and three deprotonated peptide nitrogens, represented by the formulas $M^{II}(H_{-3}L)^{2-}$ or $M^{II}(H_{-3}LOCH_3)^-$, where M is copper(II) or nickel(II), HL denotes a peptide ligand, and $HLOCH_3$ is the methyl ester of a peptide ligand. Thus, a comparison among the various peptide complexes can be made since the metal ion is always coordinated through one amino terminal nitrogen (N_1) and three deprotonated peptide nitrogens (N_2, N_3, N_4). A generalized structure for a pentapeptide complex is shown in structure I. The effects of locating an asymmetric carbon outside the chelate rings in complexes of longer peptides are compared to the results obtained using optically active tripeptide ligands.

Crystal structures of $Ni^{II}(H_{-3}G_4)^{2-}$ and $Cu^{II}(H_{-3}G_4)^{2-}$ show the above coordination and also demonstrate that direct axial interaction of the free carboxylate group of tetrapeptide ligands with the metal center is not possible.[16-18] The crystal structure of $Cu^{II}(H_{-3}G_5)^{2-}$ shows similar coordination of the metal ion; although the terminal carboxyl group of the *pentapeptide* ligand can reach an axial coordination position of the Cu^{II}, it appears to be hydrogen bonded to the terminal amino group in the crystalline state of $Na_2Ni(H_{-3}G_5)\cdot 4H_2O$.[19] In solution the complexes in the present study all possess approximate square-planar geometry as evidenced by the nature of the absorption and CD spectra of the Cu(II) and Ni(II) species. However, additional axial coordination as well as hydrogen bonding interactions is possible.

In the course of this work it became evident that the Cu(II) and Ni(II) complexes of G_3AOCH_3 and G_4AOCH_3 undergo slow hydrolysis resulting in the formation of $M^{II}(H_{-3}G_3A)^{2-}$ and $M^{II}(H_{-3}G_4A)^{2-}$. The hydroxide ion catalyzed hydrolyses of the Ni(II) and Cu(II) complexes of G_3AOCH_3 proceed at rates comparable to those of free peptide ligands. The pentapeptide ester complexes react about a factor of 10 faster than the corresponding tetrapeptide analogues denoting the possibility of a weak interaction between the metal ion and carboxyl terminal amino acid residue in agreement with the vicinal effects evident in the complexes of G_4A. Strong interactions between either Co(III) or Cu(II) and peptide ester functions result in greatly accelerated rates.[20-24]

Complexes with deprotonated peptide nitrogens have recently been shown to stabilize copper and nickel in the +3 oxidation state in aqueous solution.[25-28] Using selected peptide ligands the CD spectra were obtained for $Cu^{III}(H_{-3}L)^-$ and $Ni^{III}(H_{-3}L)^-$ complexes.

Experimental Section

Circular dichroism measurements were made using a Cary Model 61 circular dichroism spectropolarimeter or a Cary Model 60 spectropolarimeter with CD attachment. Absorption spectra were recorded using a Cary Model 14 or Cary Model 15 spectrophotometer. All spectral measurements were made with 2.00-cm cells except as indicated. Sample solutions were freshly prepared each day using aliquots of standardized (vs. EDTA) $Cu(ClO_4)_2$ or $Ni(ClO_4)_2$ with a 5–10 mole % excess of peptide ligand to ensure complete formation of the complex. The pH of the M(II) solutions was adjusted to a value of about 10.8 by addition of NaOH. Ionic strength was maintained at 0.1 M by addition of $NaClO_4$. The copper(III) and nickel(III) peptide complexes were prepared electrochemically from the corresponding metal(II) complexes utilizing a flow system containing a graphite powder working electrode packed in a porous glass column, wrapped externally with a Pt wire electrode.[26,27,29]

The values of the molar absorptivity, ϵ, and of $\Delta\epsilon$ ($\epsilon_l - \epsilon_r$)[30-32] for the copper and nickel complexes were obtained using concentrations ranging from 3×10^{-4} to 6×10^{-3} M. The CD measurements were shown to follow a Beer's law relation.

The oligopeptides used in this study (obtained from Biosynthetika) were A_4, A_5, V_4, G_3A, and G_4A and the methyl esters G_3AOCH_3 and G_4AOCH_3, where G is glycine, A is L-alanine, and V is L-valine. Analyses were carried out to detect the presence of potential interfering peptide ligands in each oligopeptide sample. Peptide separations were

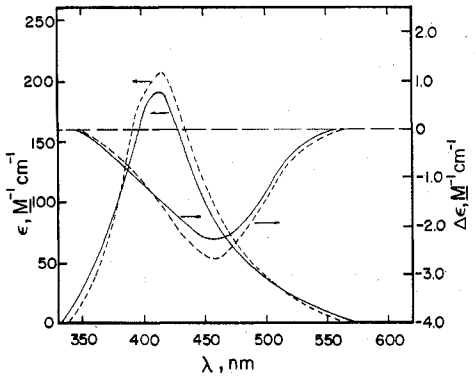


Figure 1. Absorption and circular dichroism spectra of $Ni^{II}(H_{-3}A_4)^{2-}$ (---) and $Ni^{II}(H_{-3}A_5)^{2-}$ (–): pH 10.8, 25 °C, μ = 0.1 M ($NaClO_4$).

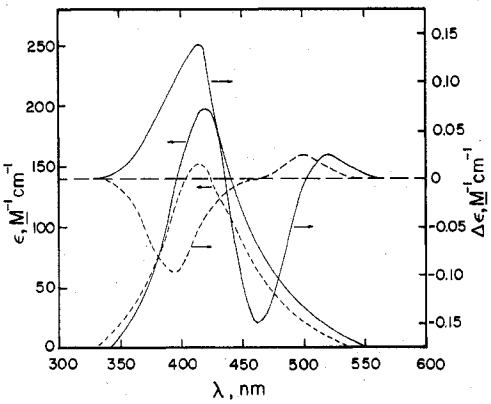


Figure 2. Absorption and circular dichroism spectra of $Ni^{II}(H_{-3}G_3A)^{2-}$ (–) and $Ni^{II}(H_{-3}G_3AOCH_3)^{-}$ (---): pH 10.8, 25 °C, μ = 0.1 M ($NaClO_4$).

performed by ion-exchange methods[33,34] using a Varian Aerograph high-pressure liquid chromatograph (Model 4100) equipped with a differential refractometer detector (Waters Associates Model R401). In addition, peptide analysis was accomplished using a Beckman Model 120B amino acid analyzer modified to a Model 121. The esterified peptides were found to contain 2–3 mole % of hydrolyzed peptide while all other peptides were found to be a least 99.5% homogeneous.

The rate of peptide–methyl ester hydrolysis was measured at 25.0 °C by the change in the CD signal. The rate expression found was

$$\frac{-d[M^{II}(H_{-3}LOCH_3)^-]}{dt} = k_{obsd}[M^{II}(H_{-3}LOCH_3)^-]$$

where k_{obsd} depends on the pH.

Results and Discussion

$Ni^{II}(H_{-3}L)^{2-}$, $Ni^{II}(H_{-3}LOCH_3)^-$. The absorption and circular dichroism spectra of $Ni^{II}(H_{-3}A_4)^{2-}$ and $Ni^{II}(H_{-3}A_5)^{2-}$ are shown in Figure 1. The tetra-L-alanine complex exhibits a larger CD signal than $Ni^{II}(H_{-3}A_5)^{2-}$ although an additional asymmetric center is included in the pentapeptide. Corresponding spectra of $Ni^{II}(H_{-3}G_3A)^{2-}$ and $Ni^{II}(H_{-3}G_3AOCH_3)^-$ are presented in Figure 2. Both positive and negative contributions to the CD result from locating the alanyl residue immediately outside the chelate rings with the optically active carbon bound to a trigonal deprotonated peptide nitrogen.

The Cu^{II}- and $Ni^{II}(H_{-2}$tripeptide$)^-$ complexes with one or more L-amino acid residues exhibit only negative CD in the visible region.[2-5] When the asymmetric center is located adjacent to a deprotonated peptide nitrogen, but is not included in a chelate ring (as in $M^{II}(H_{-3}G_3A)^{2-}$), the rotational strengths are diminished by factors of about 3–5 relative to the tripeptide complexes, $M^{II}(H_{-2}GAG)^-$ and $M^{II}(H_{-2}GGA)^-$.

For the tetrapeptide complex, changing the carboxylate group to a methyl ester has large effects on the CD signal

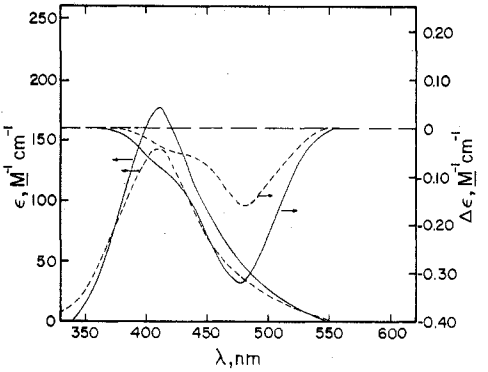


Figure 3. Absorption and circular dichroism spectra of $Ni^{II}(H_{-3}G_4A)^{2-}$ (–) and $Ni^{II}(H_{-3}G_4AOCH_3)^-$ (---): pH 10.8, 25 °C, μ = 0.1 M ($NaClO_4$).

Table I. Spectral Characteristics of Nickel(II) and Copper(II) Oligopeptide Complexes

	Cu(II)		Ni(II)	
L	CD, $\Delta\epsilon$ (λ_{max})	ABS, ϵ (λ_{max})	CD, $\Delta\epsilon$ (λ_{max})	ABS, ϵ (λ_{max})
		$M^{II}(H_{-3}L)^{2-}$		
G_4		145 (520)[a]		186 (410)
G_3A[b]				190 (409)[b]
A_4	−1.27 (530)	159 (515)	−2.80 (457)	210 (414)
A_5	−1.01 (523)	158 (515)	−2.20 (475)	190 (415)
V_4	−1.20 (540)	138 (523)		
G_3A	+0.14 (490)	133 (523)	+0.14 (410)	198 (419)
	−0.05 (625)		−0.15 (465)	
			+0.03 (520)	
G_4A	−0.16 (550)	150 (510)	−0.32 (475)	180 (410)
	+0.02 (460)			
		$M^{II}(H_{-3}L)^-$		
G_3AOCH_3	+0.17 (545)	150 (525)	−0.095 (395)	154 (415)
			+0.03 (505)	
G_4AOCH_3	−0.13 (540)	151 (510)	−0.16 (480)	143 (410)

[a] W. L. Koltun, R. H. Roth, and F. R. N. Gurd, *J. Biol. Chem.*, 228, 124 (1963). [b] T. F. Dorigatti and E. J. Billo, *J. Inorg. Nucl. Chem.*, 37, 1515 (1975).

(Figure 2). The positive CD signal found at 400 nm for $Ni^{II}(H_{-3}G_3A)^{2-}$ becomes negative for $Ni^{II}(H_{-3}G_3AOCH_3)^-$, other bands are missing or are shifted, and the total rotational strength[32] is about a factor of 2 smaller.

The CD influence of the alanyl residue at the carboxyl terminal position of a pentapeptide is shown in Figure 3. In this case the asymmetric center has four atoms between it and the Ni(II) chromophore. The G_4A complex has only negative $\Delta\epsilon$ values and the $\Delta\epsilon$ magnitude at ~470 nm is twice that of G_3A. However, the overall rotational strength is about the same since G_3A also has a positive $\Delta\epsilon$. The G_4AOCH_3 complex has a smaller CD signal than the G_4A complex. The magnitudes of the CD spectra for G_4AOCH_3 and G_3AOCH_3 are similar but their characteristics are different.

The absorption spectra of all the square-planar nickel(II) oligopeptide complexes studied have a λ_{max} in the 409–419-nm region with molar absorptivities of 143–210 M^{-1} cm^{-1}. The individual characteristics of the absorption and CD spectra for the nickel(II) oligopeptides are listed in Table I.

$Cu^{II}(H_{-3}L)^{2-}$, $Cu^{II}(H_{-3}LOCH_3)^-$. As in the case of the Ni(II) complexes the CD of $Cu^{II}(H_{-3}A_4)^{2-}$ shows a larger negative maximum than $Cu^{II}(H_{-3}A_5)^{2-}$. The absorption and CD spectra of the G_3A and G_3AOCH_3 complexes are shown in Figure 4. A positive (490 nm) and negative (~625 nm) peak is noted for the G_3A complex while only a broad positive maximum (545 nm) occurs for $Cu^{II}(H_{-3}G_3AOCH_3)^-$. Both complexes show comparable rotational strengths. The spectra of $Cu^{II}(H_{-3}G_4A)^{2-}$ and $Cu^{II}(H_{-3}G_4AOCH_3)^-$ are presented in Figure 5. Similar to the analogous Ni(II) complexes a

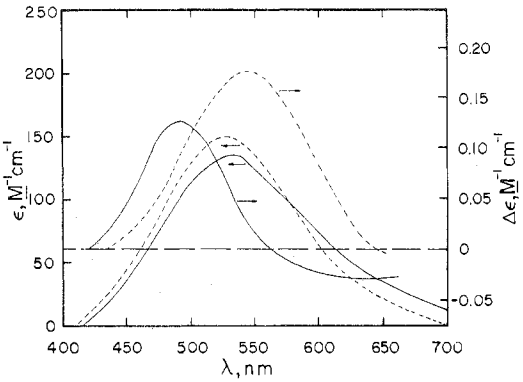


Figure 4. Absorption and circular dichroism spectra of $Cu^{II}(H_{-3}G_3A)^{2-}$ (–) and $Cu^{II}(H_{-3}G_3AOCH_3)^-$ (---): pH 10.8, 25 °C, μ 0.1 M ($NaClO_4$).

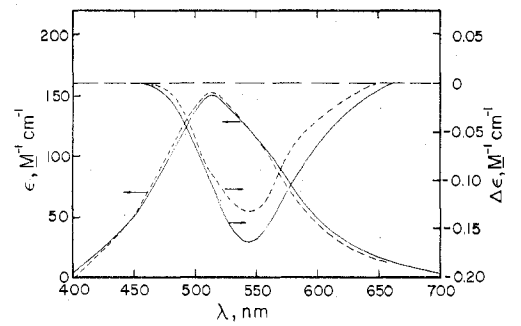


Figure 5. Absorption and circular dichroism spectra of $Cu^{II}(H_{-3}G_4A)^{2-}$ (–) and $Cu^{II}(H_{-3}G_4AOCH_3)^-$ (---): pH 10.8, 25 °C, μ = 0.1 M ($NaClO_4$).

Table II. Observed First-Order Rate Constants (25.0 °C, μ = 0.1 M) for the Hydrolyses of Copper(II) and Nickel(II) Oligopeptide Methyl Ester Complexes

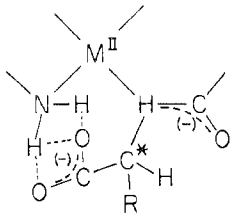
Complex	pH	$10^4 k_{obsd}$, s^{-1}
$Ni(H_{-3}G_4AOCH_3)^-$	10.0	2.3
$Ni(H_{-3}G_4AOCH_3)^-$	10.7	7.1
$Ni(H_{-3}G_4AOCH_3)^-$	11.0	13.0
$Ni(H_{-3}G_3AOCH_3)^-$	10.8	1.3
$Cu(H_{-3}G_4AOCH_3)^-$	10.8	~13
$Cu(H_{-3}G_3AOCH_3)^-$	10.8	1.0

negative CD band is observed; however, the Cu(II) complex of the esterified peptide ligand exhibits only slightly reduced intensity. The absorption spectra show λ_{max} values ranging from 510 to 525 nm for these complexes with molar absorptivities of 133–159 M^{-1} cm^{-1}, consistent with square-planar Cu(II) species. The spectral characteristics of the individual Cu(II) complexes are given in Table I.

$M^{II}(H_{-3}LOCH_3)^-$ Hydrolysis. Figure 7 shows the changes in CD spectra during the hydrolysis of the $Ni^{II}(H_{-3}G_3AOCH_3)^-$ complex. The rate constants for the hydrolyses of various metal(II) peptide ester complexes are given in Table II. The observed rate constants show a hydroxide ion dependence. The rates of hydrolyses of the square-planar nickel(II) and copper(II) tetrapeptide methyl esters are comparable to those of free peptide esters,[20,35] indicating negligible metal ion catalysis. However, the rates for the pentapeptide esters are a factor of 5–13 faster than those of the tetrapeptide esters suggesting an effect produced by weak axial interaction in the pentapeptides. Previous results show very effective metal ion catalysis for complexes in which an ester group can interact in a favorable metal ion coordination position.[21-24] Thus, in-plane Cu(II) catalysis results in an enhancement of 10^4 relative to uncomplexed peptide ester hydrolysis.[21] The smaller degree of enhancement in the present case indicates weaker coordinative interactions of the pentapeptide esters with the axial positions of the metal ions.

Assignment of d–d Spectral Transitions. For copper(II) and nickel(II) tripeptide complexes of the type $M^{II}(H_{-2}L)^-$ the spacing of the 3d orbitals in order of increasing energy is $xz \sim yz < z^2 < xy < x^2 - y^2$ for Ni(II)[3] and $xz \sim yz < xy < z^2 < x^2 - y^2$ for Cu(II)[2] where x and y are directed along the metal–donor bonds. By replacing one negatively charged oxygen donor with a deprotonated peptide nitrogen in the case of the tetra- or pentapeptide complexes, it is assumed that the relative positions of these levels remain the same, although the spacing between the levels would be affected by the stronger ligand field created by four nitrogen donors. In the D_{4h} symmetry group the two magnetic dipole allowed one-electron d–d transitions for the Cu(II) and Ni(II) complexes in order of increasing energy are $d_{x^2-y^2} \rightarrow d_{xy}$ and $d_{x^2-y^2} \rightarrow d_{xy} \sim d_{yz}$. The $d_{x^2-y^2} \rightarrow d_{z^2}$ transition is magnetic dipole forbidden and should not significantly contribute to the observed circular dichroism.[36-38] The degenerate d_{xz}, d_{yz} orbitals may be split to yield a transition containing two components if a deviation from strictly square-planar geometry occurs.[2] In $Ni^{II}(H_{-3}G_3A)^{2-}$ a transition centered at ~450 nm accounts for the main rotational strength and is split into approximately equal positive and negative contributions. A similar splitting of a CD band for $Ni^{II}(L\text{-}Cys)_2^{2-}$ has been attributed to nondegenerate d_{xz}, d_{yz} orbitals.[3] Using that assignment for the 450-nm band of $Ni^{II}(H_{-3}G_3A)^{2-}$, the remaining lower energy circular dichroism at 520 nm would then result from the $d_{x^2-y^2} \rightarrow d_{xy}$ transition. In the corresponding $Cu^{II}(H_{-3}G_3A)^{2-}$ complex a positive maximum occurs at 490 nm ($\Delta\epsilon$ = 0.14 M^{-1} cm^{-1}) with a small negative peak at ~625 nm. As seen with the Ni(II) complex, the proposed higher energy $d_{x^2-y^2} \rightarrow d_{xz}, d_{yz}$ transition yields more intense CD. By replacing G_3A with its methyl ester analogue the nature of the functional group next to the asymmetric carbon is changed. This affects the observed CD in both the Cu(II) and Ni(II) complexes. $Ni^{II}(H_{-3}G_3AOCH_3)^-$ shows a smaller rotational strength compared to the G_3A complex with one higher energy transition at 395 nm ($\Delta\epsilon$ = –0.095 M^{-1} cm^{-1}) and a lower energy transition at ~505 nm ($\Delta\epsilon$ = + 0.03 M^{-1} cm^{-1}). Similarly, the CD of the bis complex of Ni(II) using cysteine methyl ester ligands does not show a splitting of the band corresponding to the d_{xz}, d_{yz} transition.[3] In that case the removal of the splitting was attributed to the reduced tendency of the ester function to bind in the axial position of the complex as was proposed with the carboxylate group of a cysteine ligand.

Discussion of Ligand Conformations in Solution. For the metal tetrapeptide complexes, interactions of the negatively charged carboxylate group with the hydrogen atoms of the amino terminal nitrogen (stucture III) may account for the

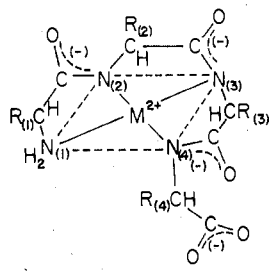


III

significantly different CD spectra of $M^{II}(H_{-3}G_3A)^{2-}$ and $M^{II}(H_{-3}G_3AOCH_3)^-$. The IR frequency of the carboxylate function in solution is similar for $Ni^{II}(H_{-3}G_4)^{2-}$ (1560 cm^{-1}) and $Cu^{II}(H_{-3}G_4)^{2-}$ (1557 cm^{-1}) but is significantly different from the frequency observed for an uncoordinated peptide carboxylate (1597 cm^{-1}). This has been attributed[39] to "the influence of the negative charges of the ligand donor groups on the electron density in the uncoordinated carboxylate

group". The intramolecular interactions suggested in structure III involve the carboxyl terminal residue and may explain this phenomenon as well as the CD.

It is proposed that the Ni(II) G_3A complex (structure IV)

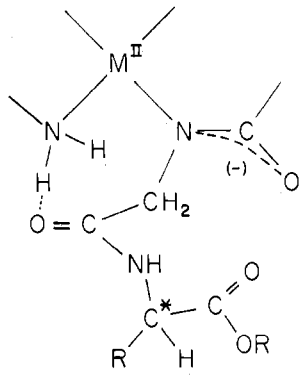


IV. M(H_{-3}TETRAPEPTIDE)$^{2-}$

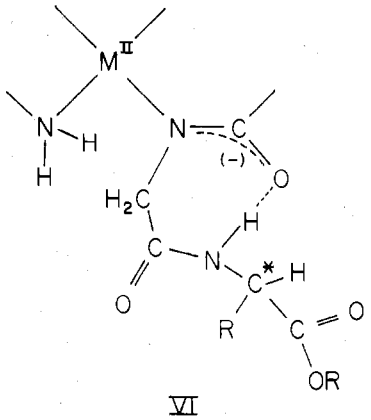
is truly square-planar while the Cu(II) species is somewhat distorted. In the crystalline state for $Cu^{II}(H_{-3}G_4)^{2-}$, Cu(II) is slightly displaced relative to the N_2–N_4 plane.[26] This should be an important factor in determining the conformation of the carboxyl terminal residue (R_4) and the extent of interactions involving the carboxylate group in solution. For nickel(II) tripeptide and cysteine complexes the CD bands involving the d_{xz}, d_{yz} orbitals appear to be the most sensitive to ligand conformation.[3] The difference in character of the CD bands (attributed to d_{xz}, d_{yz} orbitals) for $Ni^{II}(H_{-3}G_3A)^{2-}$ (Figure 2) and for $Cu^{II}(H_{-3}G_3A)^{2-}$ (Figure 4) may be caused by a difference in the conformation of the asymmetric center related to the degree of planarity of the complex.

In the pentapeptide complexes, $Ni^{II}(H_{-3}G_4A)^{2-}$ and $Cu(H_{-3}G_4A)^{2-}$, the terminal carboxylate group is able to move directly into an apical position above or below the complex plane. Rotational strengths for these complexes are comparable to those observed for the G_3A complexes although the optically active carbon is five atoms distant from the metal(II) ion chromophore. The $M^{II}(H_{-3}G_4AOCH_3)^-$ complexes produce CD signals similar in shape to those from the corresponding G_4A species; however, the relative magnitudes of the CD signals of $M^{II}(H_{-3}G_4A)^{2-}$ and $M^{II}(H_{-3}G_4AOCH_3)^-$ are different for Cu(II) and Ni(II). The $\Delta\epsilon$ of the Ni(II) complex shows a decrease by a factor of 2 in going from the G_4A ligand to the methyl ester derivative whereas with Cu(II) only a factor of 1.2 is observed. Although electrostatic interactions are not possible with the esterified peptide ligands, the $\Delta\epsilon$ values of -0.16 M^{-1} cm^{-1} (475 nm) for $Ni^{II}(H_{-3}G_4AOCH_3)^-$ and -0.13 M^{-1} cm^{-1} (540 nm) for $Cu^{II}(H_{-3}G_4AOCH_3)^-$ indicate that vicinal effects are transmitted by the asymmetric carbon. The esterified peptide fragment must be oriented in a biased position near the metal(II) center. Free rotation around the bonds of atoms which are involved in producing vicinal effects on a chromophore will tend to create a cancellation of the perturbations causing the CD signal.[40]

Intramolecular hydrogen bonding may be important in determining the conformational preference evident in the $M^{II}(H_{-3}G_4A)^{2-}$ and $M^{II}(H_{-3}G_4AOCH_3)^-$ complexes. Using molecular models, several intramolecular interactions which may serve to enhance the vicinal effects in these species are possible. In addition to the electrostatic attraction of the carboxylate group of G_4A to the metal(II), the peptide oxygen of the fourth amino acid residue can hydrogen bond at the amino terminus (N_1) of the coordinated peptide (structure V). Also, the peptide hydrogen of the fifth amino acid residue may interact with the partially negatively charged peptide oxygen of the fourth amino acid residue as shown in structure VI.



V



VI

Although it is difficult to show in drawings, the space-filling models indicate that the latter two hydrogen-bonding interactions could occur simultaneously. The esterified pentapeptide ligand also may bind to metal centers via the carbonyl oxygen of the ester function.[21-23] When this group is axially coordinated the hydrogen bonding shown in structure V is sterically still possible and could be combined with hydrogen bonding between the peptide hydrogen of the fifth amino acid residue and the deprotonated peptide nitrogen of the fourth amino acid residue. Hence, multiple points of interaction may occur between the "free" oligopeptide chain and the rest of the complex, helping to make particular conformations more stable. At present we cannot specify which interactions occur but can state that one or more must occur to give the observed CD behavior.

Intramolecular electrostatic ligand–ligand interactions have been shown[41] to enhance the rotational strength in various mixed ligand Cu(II) complexes where the position of the active carbon remains fixed relative to the metal center and ligand–ligand interactions serve to increase the overall rigidity of the complex in solution. A factor of 2 enhancement in observed vs. expected $\Delta\epsilon$ values was noted. Similar effects produced by intramolecular electrostatic and hydrogen-bonded interactions are proposed to explain the observed magnitude of the $\Delta\epsilon$ in the nickel(II) and copper(II) pentapeptide complexes in the present work.

The penta-L-alanine complexes of Cu(II) and Ni(II) show a decreased CD intensity compared to the tetra-L-alanine analogues. Since a predominantly negative CD signal results from the $M^{II}(H_{-3}G_4A)^{2-}$ complexes, the reason for the decreased $\Delta\epsilon$ value for $M^{II}(H_{-3}A_5)^{2-}$ lies in a large positive effect produced by the fourth amino acid residue (R_4) of the *pentapeptide*. Both $Cu^{II}(H_{-3}G_3A)^{2-}$ and $Ni^{II}(H_{-3}G_3A)^{2-}$ show a substantially positive CD signal. In the pentapeptide complexes a preferred orientation of the carboxyl terminal fragment may alter the position of the fourth amino acid relative to the metal center compared to the conformation it

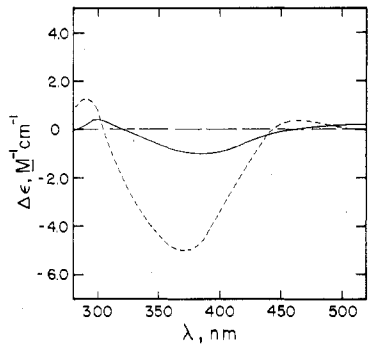


Figure 6. Circular dichroism spectra of $Cu^{III}(H_{-3}A_5)^-$ (---) and $Ni^{III}(H_{-3}A_5)^-$ (–): pH ~7, 25 °C, μ = ~0.01 M.

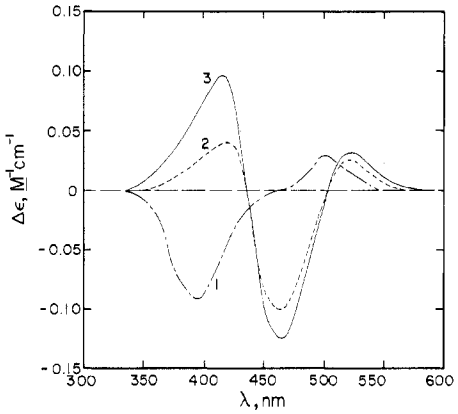


Figure 7. Change in circular dichroism signal with time showing hydrolysis of $Ni^{II}(H_{-3}G_3AOCH_3)^-$: 25 °C, pH 10.8, μ = 0.1 M ($NaClO_4$); (- · -) t = 0 (1), (---) t = 3 h (2), (–) t = 6 h (3).

would assume as the terminal amino acid in a tetrapeptide complex and produce an enhanced positive CD.

$Cu^{III}(H_{-3}L)^-$, $Ni^{III}(H_{-3}L)^-$. In these complexes one spectral feature is a charge-transfer band at 365 nm with molar absorptivities of 5500–7500 M^{-1} cm^{-1} depending on the nature of the peptide.[27] Typical CD spectra of a copper(III) and nickel(III) peptide are presented in Figure 6. Both metals produce a negative contribution centered at ~380 nm with the Cu(III) complex yielding a much larger CD signal than the Ni(III) species. It is interesting to note that the characteristic CD bands arising from the d–d transitions at ~470 nm for the nickel(II) peptides appear as a small positive maximum in this region for the d^8 copper(III) oligopeptide complexes. Some of the pertinent features of the absorption and circular dichroism spectra of various copper(III) and nickel(III) peptide complexes are presented in Table III.

The CD signals produced by the copper(III) and nickel(III) oligopeptide complexes result from the ligand-to-metal charge-transfer band centered at 365 nm. The λ_{max} values of the CD spectra are between 370 and 385 nm for these trivalent metal ion species. The large molar absorptivities of the complexes which arise from an electric-dipole-allowed transition cause the measurement of the CD to be difficult. Only the highly substituted tetra- and pentapeptides yielded measurable CD signals. For copper(III) peptides, the $\Delta\epsilon$ values reflect an increase in the number of amino acid residues in the peptide as well as the nature of the substituent. On the other hand, similar CD signals are noted when comparing the Ni(III) complexes of A_4 and A_5. (Attempts to form a nickel(II) tetravaline complex resulted in the formation of nickel(II) hydroxide species.) The reasons for the differences in rotational strength among the various metal(III) oligopeptide complexes are not clear at this time.

A possible application of circular dichroism measurements lies in the study of the equilibria and kinetics of redox reactions involving metal oligopeptide complexes (eq 1). In this case

$$M^{III}(L^*) + M^{II}(L) \rightleftarrows M^{II}(L^*) + M^{III}(L) \quad (1)$$

M can be either a copper or nickel ion, L^* represents an optically active deprotonated peptide ligand, and L is a non-optically-active deprotonated peptide ligand. Thus, the electron transfer between the substitution-inert M(III) and the M(II) complexes may be followed by changes in the visible CD signal. This is especially advantageous since $M^{III}(L^*)$ and $M^{III}(L)$ often exhibit nearly identical absorption spectra.

Table III. Spectral Characteristics of the Copper(III) and Nickel(III) Oligopeptide Complexes

L	CD $\Delta\epsilon$ (λ_{max})[d]	Absorption ϵ (λ_{max})
	$Cu^{III}(H_{-3}L)^-$	
G_4[a]		7120 (365)
G_5[a]		7670 (365)
A_4[b]	−3.7 (380)	5360 (365)
A_5	−5.0 (370)	~5000 (365)
V_4	−7.6 (385)	~5000 (365)
	$Ni^{III}(H_{-3}L)^-$	
G_3a[c]		5360 (320)
A_4	−0.9 (385)	~4500 (320)
A_5	−0.9 (385)	~4500 (320)

[a] Reference 27. [b] F. P. Bossu and K. L. Chellappa, private communication. [c] Reference 26. [d] Calculated using 1.00-cm cell.

Conclusion

The visible circular dichroism of copper(II) and nickel(II) tetra- and pentapeptide complexes containing asymmetric carbon atoms located outside the normal square-planar chelate ring structures have been characterized. A carboxyl terminal L-alanyl residue in a triply deprotonated tetrapeptide complex, $M^{II}(H_{-3}G_3A)^{2-}$, exhibits both positive and negative CD in contrast to the copper(II) and nickel(II) L-alkyl-substituted tripeptide complexes which produce only negative CD in the visible spectral region. The pentapeptide complexes ($M^{II}(H_{-3}G_4A)^{2-}$) show mainly negative CD signals. The $\Delta\epsilon$ values suggest that axial and/or intramolecular hydrogen bonded interactions occur between the terminal peptide fragment and the rest of the complex. Such interactions would allow the vicinal effect of the L-alanyl residue to be transmitted more effectively by reducing the distance from the asymmetric carbon to the metal(II) center and increasing the rigidity of the complex. A significant electrostatic effect of a negatively charged carboxylate function is reflected in the CD of the Ni(II) complexes since the methyl ester derivatives of G_4A and G_3A produce a factor of 2 decrease in the CD signal. However, only a small decrease is noted in the rotational strength of $Cu^{II}(H_{-3}LOCH_3)^-$ compared to $Cu^{II}(H_{-3}L)^{2-}$. The $\Delta\epsilon$ values of the metal(II) ester peptide complexes indicate that the carboxylterminal residue prefers an orientation allowing effective vicinal effects even in the absence of a charged carboxylate function.

This work shows that metal ions can cause CD signals from d–d transitions for asymmetric centers which are not involved in chelation or are not immediately adjacent to the main coordination donors. The possibility of CD arising from hydrogen bonding of the peptide chain to a metal peptide segment must be kept in mind in the interpretation of results for other systems.

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Registry No. $Cu^{II}(H_{-3}A_4)^{2-}$, 62959-95-9; $Cu^{II}(H_{-3}A_5)^{2-}$, 62905-80-0; $Cu^{II}(H_{-3}V_4)^{2-}$, 62959-94-8; $Cu^{II}(H_{-3}G_3A)^{2-}$, 62882-76-2; $Cu^{II}(H_{-3}G_4A)^{2-}$, 62882-75-1; $Ni^{II}(H_{-3}G_4)^{2-}$, 39016-92-7; $Ni^{II}(H_{-3}A_4)^{2-}$, 62006-66-0; $Ni^{II}(H_{-3}A_5)^{2-}$, 62882-74-0; $Ni^{II}(H_{-3}G_3A)^{2-}$, 62006-86-4;

$Ni^{II}(H_{-3}G_4A)^{2-}$, 62882-73-9; $Cu^{II}(H_{-3}G_3AOCH_3)^-$, 62882-66-0; $Cu^{II}(H_{-3}G_4AOCH_3)^-$, 62882-65-9; $Ni^{II}(H_{-3}G_3AOCH_3)^-$, 62006-85-3; $Ni^{II}(H_{-3}G_4AOCH_3)^-$, 62882-64-8; $Cu^{III}(H_{-3}A_5)^-$, 62882-63-7; $Cu^{III}(H_{-3}V_4)^-$, 62959-93-7; $Ni^{III}(H_{-3}A_4)^-$, 62882-62-6; $Ni^{III}(H_{-3}A_5)^-$, 62882-61-5.

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Paramagnetic M(I) Complexes Generated by the Electrochemical Reduction of M(II) Nickel, Palladium, and Platinum 1,2-Dithiolates

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The electrochemical reduction of square-planar nickel, palladium, and platinum complexes of the maleonitriledithiolate (mnt) ligand have been investigated. In each case, reduction of the $M^{II}(mnt)_2^{2-}$ species in nonaqueous solvents proceeded by a one-electron process, shown to be reversible by cyclic voltammetry and ac polarography. ESR spectra obtained for $Pd(mnt)_2^{3-}$ and nickel-61 enriched $Ni(mnt)_2^{3-}$ were consistent with the formulation of these species as d^9 metals with the unpaired electron in an orbital consisting of contributions from the d_{xy} metal orbital and in-plane sulfur orbitals. More covalency is found in the palladium complex than in the nickel complex. The reduction of $Pt(mnt)_2^{2-}$ proceeds by two successive one-electron processes. Arguments based on these data are presented which suggest a ground state for $Pt(mnt)_2^{3-}$ which may be different from its Ni or Pd analogue.

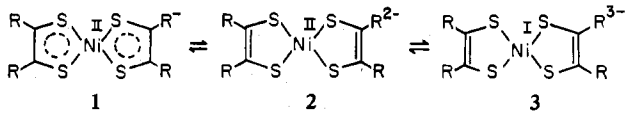
Introduction

Although metal(I) complexes of nickel, palladium, and platinum have been proposed as intermediates in a number of reactions,[1-5] direct experimental evidence and isolation of such complexes have been rare. In fact, most known Ni(I) complexes and all isolated Pd(I) and Pt(I) complexes are binuclear in nature, giving diamagnetic metal–metal bonded or ligand-bridged bimetallic species.[6] In previous communications[7-9] we have established the existence of mononuclear d^9 complexes of Ni, Pd, and Pt produced by the reversible one-electron reduction of d^8 metal dithiolate complexes. In this paper we offer a fuller exposition of both the voltammetric data and electron spin resonance (ESR) results on these reduced complexes.

Naturally, ESR spectroscopy, so successfully employed in the study of d^9 copper complexes, is a powerful tool for study of the electronic structures of the nickel group d^9 complexes. Therefore, it is somewhat surprising that even in the case of nickel, for which a respectable number of d^9 complexes are now known,[10] very little ESR work has been reported. Besides our earlier report on $Ni(mnt)_2^{3-}$[7] and the work of Busch and co-workers on reduced nickel macrocyles,[11] only signals from trapped Ni(I), arising from x irradiation of $Ni(CN)_4^{2-}$[12] and nickel-doped glasses,[13] have been reported. Two other studies, in which signals from nickel(I) impurities in ternary chalcopyrites and ZnSe were observed,[14,15] are apparently the only ones reporting ^{61}Ni hyperfine splittings (^{61}Ni, $I = {}^3/_2$, 1.2% abundance). In this paper we report the ^{61}Ni-enriched ESR spectrum of $Ni(mnt)_2^{3-}$.

In contrast to nickel, stable paramagnetic d^9 complexes of Pd and Pt are apparently unknown. Several papers have appeared in which Pd(II) complexes were irradiated and studied by ESR at 77 °K,[16-20] but the signals ascribed to Pd(I) disappeared upon warming of the matrix. A similar study involving irradiation of K_2PtCl_4 resulted in several platinum-containing radicals, including a signal attributed to $[PtCl_4]^{3-}$,[21] and $[PtBr_6]^{5-}$ has been postulated as the photolysis product of Pt(II) in AgBr matrices.[22]

In this work we have studied the electrochemical reduction of dianions of the square-planar metal(II) 1,2-dithiolate complexes $M(mnt)_2^{2-}$ (**2**, R = CN). In addition to providing



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