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Dipeptide Complexes of Cobalt(II) and Cobalt(III)[1]

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Received June 29, 1970

Cobalt(II) ion promotes ionization of amide hydrogens near pH 10 in dipeptides to yield 2:1 complexes with four nitrogen and two carboxylate oxygen donors. Complexes of 18 dipeptides yield four d–d transitions at 1250, 1000, 610, and 480 nm. The first and third bands are assigned to the low-spin and the second and fourth to the high-spin components of octahedral complexes. Magnetic susceptibility and extensive titration results are consistent with the high-spin–low-spin equilibrium. Large side chains in the carboxyl terminal residue provide steric inhibition to amide hydrogen ionization and oxygenation of the Co(II) complexes. Side chains in both residues of the dipeptide usually yield the same sign for the circular dichroism of 2:1 Co(II) and Co(III) complexes. In both kinds of complexes the magnitude of the CD consists of nearly independent and additive contributions from each amino acid residue.

Introduction

In an earlier study from the laboratory, dealing with oxygenation and oxidation of cobalt(II) chelates, special attention was paid to their properties in scrupulously oxygen-free solutions. It was observed that Co(II) promoted the deprotonation of the peptide nitrogen of dipeptides such as glycylglycine. The resulting bis-dipeptide chelate exhibited an unusual visible–near-infrared absorption spectrum consisting of three maxima rather than the two expected for a high-spin octahedral Co(II) complex. The additional band at 610 nm was accounted for by postulating an equilibrium between high- and low-spin states in the octahedral bis-dipeptide complex. Support for this interpretation was the observed intermediate value of 4.1 BM for the magnetic susceptibility.[2] The spectral properties of the 2:1 dipeptide complexes are recognizably different from spectra of tetrahedral Co(II) complexes.[3]

There are several reasons for this further study of cobalt(II) dipeptide complexes in which the generality of the above observations is tested. Metal ion promoted amide hydrogen ionization in dipeptides had not been previously verified for Co(II). The spectrum and proposed structure of the bis-dipeptide complex of cobalt(II) is unusual. Finally it was suggested that oxygenation of Co(II) complexes proceeds by a low-spin Co(II) intermediate.[2]

The 24 dipeptides used in the present investigation are of wide structural variety in order to test the high-spin–low-spin hypothesis and to see how general is promotion of the ionization of dipeptide amide hydrogens by Co(II). We also report the circular dichroism of some of the dipeptide complexes of Co(II) and the Co(III) oxidation products obtained by oxygenation. The dipeptides chosen were selected as a test of the applicability of regional rules to account for the sign and magnitude of the optical activity induced in the ligand field bands of metal ions by optically active ligands.

Experimental Section

All materials were weighed out as required, to avoid problems of solution instability. Analytical reagent grade $Co(NO_3)_2 \cdot 6H_2O$ and dipeptides of the highest available commercial purity were used. Equivalent weights were checked by potentiometric titration. Distilled water was degassed immediately before use.

Titrations were carried out at room temperature (24°) in an airtight reaction vessel, under a nitrogen atmosphere. The nitrogen was purified by passage through vanadium(II) chloride scrubbers.[4] Removal of any trace of oxygen is critical for titrations involving cobalt(II). A Beckman Zeromatic pH meter and associated Sargent S-30070-10 miniature combination glass–calomel electrode were used to measure pH. Ligand and metal ion concentrations were generally 0.50 and 0.025 *M*, respectively. This 20:1 molar ratio of ligand to metal ion was required to prevent precipitation of cobalt(II) hydroxide. All acid ionization constants were obtained at 0.575 *M* ionic strength and 24° and are hybrid constants consisting of activity of hydrogen ion and concentrations of other components.

Absorption spectra were recorded on a Cary 14R spectrophotometer. Circular dichroism was measured using a Durrum-Jasco ORD-UV-5 recording spectropolarimeter with a circular dichroism attachment. All spectral measurements were carried out at 24° and under a nitrogen atmosphere for solutions containing Co(II). Circular dichroism results are reported as differential molar absorptivities between left and right circularly polarized light, $\Delta\epsilon$. All molar absorptivities are based upon the molar concentration of cobalt ion.

Results

Oxygen-free solutions containing a dipeptide and cobalt(II) in a 20:1 molar ratio fall into two classes according to their titration and spectral behavior on the addition of base. Both classes of dipeptides show an indistinct end point, near pH 10, at 1.0 equiv of NaOH added per mole of neutral dipeptide, corresponding to neutralization of the ammonium group. The end point occurs at 2.0 equiv if an additional side-chainacidic group such as carboxylic acid or phenolic is present. Up to this end point the solution is pale pink with absorption maxima at about 1100 nm ($\epsilon \sim 5$) and about 500 nm ($\epsilon \sim 15$), typical of octahedral high-spin Co(II) complexes.

For class I dipeptides, addition of more NaOH reveals a second, distinct end point at 1.1 (or 2.1) equiv, corresponding to the ionization of one additional hydrogen ion from each of two dipeptides bound to a given Co(II). An average pK_a of 10.10 ± 0.05 was measured for this ionization by titrating a solution containing a 10:1 molar ratio of glycylglycine to Co(II). Accompanying this second ionization is a color change to green or green-blue, depending on the extent to which intense absorption in the ultraviolet extends into the visible. The color is fully developed by pH 12. For 18 class I dipeptides, the spectra recorded at pH 12 are remarkably similar with absorption maxima at about 1250 nm ($\epsilon \sim 4$), 1000 nm ($\epsilon \sim 10$), 610 nm ($\epsilon \sim 24$), and 480 nm ($\epsilon \sim 15$). The visible spectrum, which is not appre-

(1) This research was supported by a grant from the National Science Foundation.

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ciably affected by changes in temperature or solvent, has been given previously as a figure.[2]

The absorption spectra of solutions containing glycylglycine and Co(II) in a 20:1 molar ratio were studied in detail as a function of pH from 9.0 to 12.1. With increase in pH a maximum develops at 1000 nm and the absorption at 505 nm decreases; calculation at both wavelengths using five solutions of pH in the above range yields $pK_a = 10.53 \pm 0.02$. Increase in pH also produces a maximum at 610 nm where analysis of six solutions yields $pK_a' = 10.68 \pm 0.02$. Differences between these values and the potentiometric titration value mentioned above are discussed in the next section.

Class I dipeptides include, in addition to glycylglycine, the glycyl-L-amino acids with α-alanine, α-amino-*n*-butyric acid, serine, aspartic acid, glutamic acid, phenylalanine, and tyrosine as the L-amino acid; also included are the L-aminoacylglycines of sarcosine, α-alanine, valine, leucine, isoleucine, serine, and phenylalanine, together with L-alanyl-L-alanine, L-alanyl-D-alanine, and L-phenylalanyl-L-phenylalanine.

Class II dipeptides yield precipitates after the addition of 1.0 equiv of NaOH to a solution containing dipeptide and Co(II) in a 20:1 molar ratio. No blue-green color or second end point is observable. Such dipeptides include glycyl-β-alanine, β-alanylglycine, and, where an α-amino acid residue is present, only the glycyl-L-amino acids of sarcosine, valine, leucine, and isoleucine.

As they are too complex to present in tabular form, circular dichroism curves for a set of alanyl and phenylalanyl bis-dipeptide complexes of Co(II) are shown in Figures 1 and 2. The spectra were recorded at about

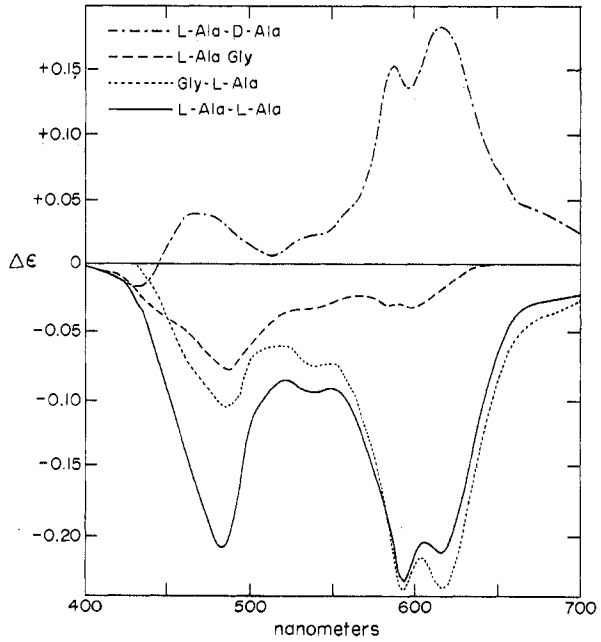

Figure 1.—Circular dichroism of alanyl bis-dipeptide complexes of cobalt(II) at pH 11.8.

pH 11.8 in oxygen-free solutions 0.025 *M* in Co(II) and 0.50 *M* in dipeptide. The absorption spectra of the green-blue solutions containing $Co^{II}(dipeptide^{2-})_2^{2-}$ are mentioned above.

Upon bubbling oxygen into these green-blue solutions, first the brown color of oxygenated complexes

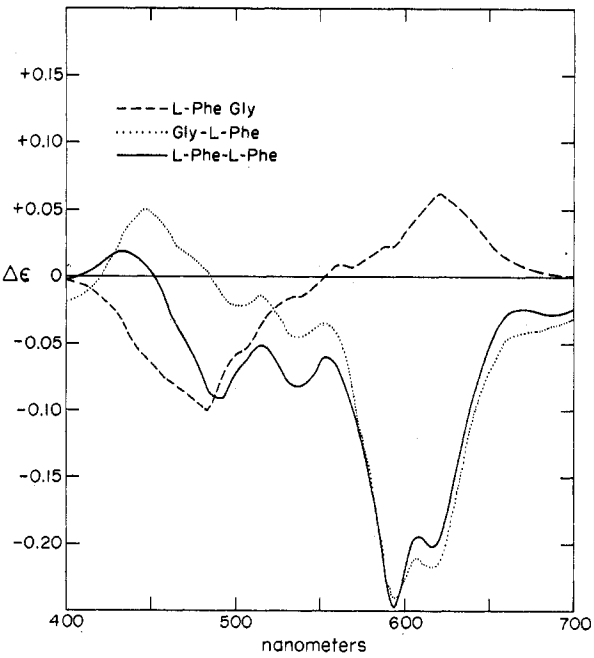

Figure 2.—Circular dichroism of phenylalanyl bis-dipeptide complexes of cobalt(II) at pH 11.8.

and finally the wine red color of $Co^{III}(dipeptide^{2-})_2^-$ complexes are observed.[2] The relatively uncomplicated visible circular dichroism and absorption spectra of these final solutions are presented in Table I. In most cases the oxygenated complexes were formed in several minutes followed by a slower conversion to Co(III) complexes requiring several hours. However, for glycyl-L-phenylalanine and glycyl-L-tyrosine, the green-blue solutions turned brown more slowly. The slow conversion and the variable molar absorptivities in Table I indicate that the solutions may contain mixtures of Co(III) complexes.

TABLE I
VISIBLE CIRCULAR DICHROISM OF Co(III) BIS-DIPEPTIDE COMPLEXES

	Circular dichroism		Molar absorptivity[d]
	375–410 nm	500–515 nm	(~520 nm)
Gly-L-Ala	−0.39	−1.72	310
L-AlaGly	+0.82	−2.37[a]	392
L-Ala-L-Ala	+0.29	−3.48	326
L-Ala-D-Ala	+1.08	+0.62[b]	340
Gly-L-Phe	−0.63	−2.55	258
L-PheGly	+0.78	−2.54[c]	386
L-Phe-L-Phe	+0.28	−5.22	248

[a] +0.07 at 592 nm. [b] At 535 nm. [c] +0.73 at 578 nm. [d] In addition to the maximum near 520 nm, all the complexes display an absorption peak at 380–450 nm with ε 130–210.

Discussion

At low pH, oxygen-free solutions, containing a dipeptide and cobalt(II) in a 20:1 molar ratio, exhibit absorption spectra characteristic of octahedral high-spin Co(II) complexes. The dipeptides, such as glycylglycine and glycylsarcosine, are weakly chelated to Co(II) through amino nitrogen and carbonyl oxygen atoms. The liberation of one additional proton from each of two glycylglycine molecules coordinated to each cobalt(II), as the pH is raised, but the absence of such ionization for glycylsarcosine, indicates that deprotona-

tion of the amide nitrogen occurs in glycylglycine. Each complex then contains two glycylglycine molecules which are tridentate, being bound *via* amino and deprotonated amide nitrogens and a carboxylate oxygen. The planarity of the amide linkage enforces a near-D_{2d} (actually C_2) structure on the bis-dipeptide complex. This structure has been found in the X-ray studies of nickel(II)[5] and cobalt(III)[6,7] complexes of deprotonated glycylglycine.

Upon replacement of oxygen donors by deprotonated amide nitrogens of glycylglycine, two bands in the cobalt(II) spectrum shift to shorter wavelengths, reflecting the greater ligand field strength of nitrogen. The $^4T_{1g} \rightarrow {}^4T_{2g}$ (in O_h) transition shifts from 1100 to 1000 nm and the $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition from 500 to 480 nm. The new bands which appear at 1250 and 610 nm upon amide hydrogen ionization are assigned to the $^2E_g \rightarrow {}^2T_{1g}$, $^2T_{2g}$ and $^2E_g \rightarrow {}^2A_{1g}$ transitions, respectively, in a low-spin octahedral complex. These assignments are consistent with the Tanabe–Sugano diagram[8] at a Dq/B value of 1.4 (previously calculated from the high-spin components),[2] where the $^4T_{1g}$ level is lower than ^2E_g. The favoring of the high-spin species is also indicated by the intermediate magnetic susceptibility value of 4.1 BM for the $[Co^{II}(GlyGly^{2-})_2]^{2-}$ complex in solution, a result which suggests an equilibrium between spin states with about 70% of the high-spin and 30% of the low-spin form.[2] The most significant change in structure which occurs in the equilibrium is the Co(II)–donor atom bond distances. Despite the wide variation in side chains of the dipeptides studied, the ligand field spectra of all of the Co(II) complexes containing two ligands with deprotonated amide nitrogens are virtually identical.

Amide hydrogen ionizations occurring in the formation of 2:1 dipeptide–cobalt(II) complexes may be represented as

$$Co(HL)_2 \underset{}{\overset{K_1}{\rightleftharpoons}} Co(HL)(L)^- \overset{K_2}{\rightleftharpoons} CoL_2^{2-}(h)$$
$$\overset{K_3}{\rightleftharpoons} CoL_2^{2-}(l)$$

where the low-spin complex, $CoL_2^{2-}(l)$, occurs only when there are two amino and two amide nitrogen donors. Acid ionization constants for removal of amide hydrogens are

$$K_1 = (H^+)[Co(HL)(L)^-]/[Co(HL)_2]$$
$$K_2 = (H^+)[CoL_2^{2-}(h)]/[Co(HL)(L)^-]$$
$$K_3 = (H^+)[CoL_2^{2-}(l)]/[Co(HL)(L^-)]$$

where parentheses represent activities and brackets concentrations.

For complexes with two amide hydrogens removed, the concentration ratio of the high- to low-spin forms is $[CoL_2^{2-}(h)]/[CoL_2^{2-}(l)] = K_2/K_3$. Growth of the 610-nm absorption peak is a measure of the concentration of low-spin complex so that $pK_3 = 10.68$. Unfortunately pK_2 cannot be calculated as the absorption at both 505 and 1000 nm is determined by a mixture of several species with uncertain weightings. However, the smaller value of $pK_a = 10.53$ determined at the last two wavelengths qualitatively indicates a preponderance of high-spin complex which is consistent with the 70% high spin–30% low spin magnetic susceptibility result.

In a separate set of experiments, acid ionization constants for amide deprotonation were determined from the oxygenation reaction of the 2:1 glycylglycine–cobalt(II) complex.[2,9] The two amide ionizations were resolved into $pK_1' = 9.85$ and $pK_3' = 10.15$, where $pK_1' = pK_1$ in terms of the above formulation. Since all of the complexes with two ionized amide hydrogens are in the low-spin form after oxygenation, the value of $pK_3 - pK_3' = -\log \alpha$, where α is the low-spin fraction of 2:1 complexes containing two ionized amide hydrogens. Hence $100\alpha = 30\%$, in excellent agreement with the independent estimate from magnetic susceptibility. The less than statistical difference observed for the successive ionizations in the oxygenation reaction, $pK_3' - pK_1'$, occurs not just because of the change to the low-spin state, as the oxygenation reaction contributes by converting all doubly ionized complexes to the low-spin form.

The mean ionization constant determined by potentiometric titration in oxygen-free solutions is $(K_1(K_2 + K_3))^{1/2}$ where $K_2 + K_3 = (H^+)([CoL_2^{2-}(h)] + [CoL_2^{2-}(l)])/[Co(HL)(L)^-]$. From the values above the average pK_a, for ionization of two amide hydrogens from the 2:1 glycylglycine–cobalt(II) complex is calculated as 10.1, in agreement with the value observed directly by titration. Thus experimental observation of five different amide hydrogen ionization constants with pK_a values of 9.85–10.68 does not reflect experimental error but rather provides support for the above ionization scheme with an equilibrium between the favored high-spin and low-spin cobalt(II) complexes, of 2− charge, in oxygen-free solutions. The variation in observed ionization constants cannot be explained by any scheme which accounts for the four absorption bands by splitting of ^4T states in a high-spin only complex due to descent from octahedral symmetry. The deprotonated amide nitrogen is more effective in promoting spin pairing in Ni(II)[10] and Co(II) complexes than is indicated by simple consideration of its ligand field strength.

Of the four divalent transition metal ions known to promote amide hydrogen ionization in glycylglycine, the order of increasing effectiveness (with a pK_a in parentheses) is Co(II) (~10) < Ni(II) (~9.5)[10] < Cu(II) (~4)[11,12] < Pd(II) (~3)[13] with the value for Co(III) uncertain. Despite repeated proposals to the contrary, the most basic site in an amide linkage is the carbonyl oxygen so that protonation[14] and metal ion coordination[15] occur at that atom. However, after amide deprotonation the most basic site is the nitrogen

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atom where either protonation or metal ion coordination takes place.[15] When either protonation or complexation has occurred at an ionized amide nitrogen, the carbonyl oxygen becomes the basic center. Consequently, when an inert cobalt(III) complex is formed by coordination at the ionized amide nitrogen, any rapid protonation occurs at the carbonyl oxygen.[7,16] References 7 and 14–16 provide extensive nmr and X-ray support for the above conclusions, which we have consistently held.[2,10,13]

Class II dipeptides show no detectable amide hydrogen ionization under the experimental conditions. Three subclasses appear according to the reasons for lack of observable amide deprotonation: glycylsarcosine possesses a methyl group instead of an amide hydrogen, the dipeptides containing β-alanine must form six- as well as five-membered chelate rings in order to be tridentate, and glycylamino acid dipeptides with side chains that are bulky or branched at the β carbon in the carboxyl terminal residue provide steric interactions with the amide carbonyl oxygen that appear to inhibit amide hydrogen ionization. In contrast to the Co(II) complex of glycylsarcosine which does not seem to oxygenate or oxidize under any conditions, the complexes of glycyl-L-valine and glycyl-L-leucine undergo very slow oxygenation and subsequent oxidation.

Metal ion promoted amide hydrogen ionizations occur at 0.55 and 0.85 pK_a unit higher in the copper(II) complexes of glycyl-L-leucine[11] and glycyl-L-valine,[12] respectively, than in the glycylglycine complex. The nickel(II)-promoted amide hydrogen ionization of glycyl-L-valine occurs at least 1 pK_a unit higher than that for glycylglycine.[10] No inhibition of amide hydrogen ionizations occurs for the Ni(II) complexes of L-leucylglycine and L-valylglycine.[10] The pK_a values for ammonium deprotonation of amino acids and dipeptides with bulky amino terminal groups are not markedly different from those for glycine and glycylglycine. These comparisons suggest that steric effects are responsible for the inhibited amide hydrogen ionizations in metal ion–dipeptide complexes. Since only one dipeptide molecule is involved in each copper(II) complex, the steric effects need not involve interaction between two dipeptide ligands. In contrast to side chains in the amino terminal position, those in the carboxyl terminal position of a tridentate dipeptide chelate undergo steric repulsion with the amide carbonyl oxygen forcing the side chains into a quasiaxial position.[17] The resulting steric strain on the preferably planar amide linkage may account for inhibited amide hydrogen ionizations in glycylamino acids with bulky side chains. Interaction between two dipeptide ligands might provide an additional source of steric inhibition of amide hydrogen ionization in the 2:1 dipeptide complexes of Ni(II) and Co(II).

The amide hydrogen ionization is inhibited by a factor of less than 10 in the copper(II) complex of glycyl-L-valine. Because it reduces the number of nitrogen donors below the minimum of 4 probably required for efficient oxygenation and oxidation of cobalt(II) complexes of dipeptides, inhibition of amide hydrogen ionization is expected to reduce the rate of oxidation by a factor of at least 10. However, oxidation of the cobalt(II) complex of glycyl-L-valine is 10^3 times slower than for glycylglycine. Examination of space-filling molecular models reveals severe steric hindrance to oxygenation of a 2:1 dipeptide–cobalt(II) complex, by detachment of one bound carboxylate, when this carboxylate residue contains a bulky side chain. Thus the slow rate of oxidation of the cobalt(II) complex of glycyl-L-valine is ascribed to steric effects of the bulky carboxyl terminal residue which both inhibits amide hydrogen ionization and limits access of oxygen to form an oxygenated complex. Intermediate oxygenation rates observed for ligands like glycyl-L-phenylalanine are ascribed solely to limitation of oxygen access to the metal ion as no inhibition of amide hydrogen ionization is noted.

Circular dichroism results were obtained to ascertain the applicability of regional rules for describing optical activity in octahedral-type complexes with near-D_{2d} symmetry. The CD results presented in Figures 1 and 2 and Table I permit a partial test in three different kinds of complexes: high-spin Co(II) from 400 to 520 nm and low-spin Co(II) from 520 to 700 nm in Figures 1 and 2 and Co(III) in Table I. According to the band assignments suggested in the second paragraph of the Discussion, both high- and low-spin Co(II) complexes possess magnetic dipole allowed transitions at and above 1000 nm, beyond the long-wavelength limit of the CD instrument. Regional rules apply to the sum of optical activity over the entire d–d manifold.[18] Therefore application to the partial CD spectra of the Co(II) complexes in Figures 1 and 2 must be made with reservations, the final interpretation awaiting CD measurements up to 1300 nm. Since the CD results for the Co(III) complexes listed in Table I include, in addition to the $^1A_{1g} \rightarrow {}^1T_{2g}$ transition near 390 nm, the only spin and magnetic dipole allowed transition $^1A_{1g} \rightarrow {}^1T_{1g}$ in O_h at 520 nm, conclusions may be reached with more assurance. Of all the bands reported in Figures 1 and 2 and Table I, only for the 480-nm band in the Co(II) complexes and the 520-nm band in the Co(III) complexes does the dissymmetry ratio $\Delta\epsilon/\epsilon$ sometimes exceed 0.01, consistent only with their assignments to magnetic dipole allowed transitions in the parent octahedral group.

If the Z axis is chosen so as to pass through both amide nitrogens in the 2:1 dipeptide–metal ion complexes, the D_{2d} regional rule is a quadrant rule where the pseudoscalar function is represented by $x^2 - y^2$.[19] According to this regional rule, amino terminal and carboxyl terminal side chains of the dipeptide complexes composed of L-amino acids project into regions of opposite sign. For the complexes containing one asymmetric unit per dipeptide, this prediction is borne out by only the high- and low-spin phenylalanyl dipeptide complexes of Co(II) shown in Figure 2. The prediction is not obeyed by the alanyl dipeptide complexes of Figure 1 nor any Co(III) complexes listed in Table I. Therefore, the D_{2d} quadrant rule does not seem to be applicable to these complexes and a mixed-sector rule is required. The octahedral O_h sector rule[19] does accommodate the results, but the distance dependence is high.

Inspection of the areas under the curves in Figures 1 and 2 reveals that dipeptides with two asymmetric resi-

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dues give Co(II) complexes whose CD magnitudes are the sums of the two complexes containing one corresponding asymmetric residue per dipeptide. For example, in Figure 1 for both the 400–520- and 520–700-nm regions the area under the curve for L-alanyl-L-alanine approximates the sum of the areas under the curves for L-alanylglycine and glycyl-L-alanine. The area under the curve for L-alanyl-D-alanine equals the difference in areas between those for L-alanylglycine and glycyl-L-alanine. Excellent agreement is obtained between magnitudes calculated from sums and observed values for the Co(III) complexes of Table I except for the 535-nm band of L-alanyl-D-alanine where the sign is reversed. Though the agreement between calculated and observed magnitudes is poor, sign agreement is obtained if the CD over both Co(III) transitions is considered together. Scaling of the CD magnitudes of the Co(III) complexes so that all values refer to a complex with a molar absorptivity of 400 near 520 nm improves the agreement between calculated and observed values for alanyl dipeptides but worsens the agreement for phenylalanyl dipeptides. Excepting the one Co(III) complex mentioned above, we conclude that the magnitude of the optical activity through four ligand field transitions in both cobalt(II)– and cobalt(III)–dipeptide complexes consists of nearly independent and additive contributions from each amino acid residue. Similar conclusions have been reached for tetragonal peptide complexes of nickel(II), palladium(II), and copper(II) where a hexadecant regional rule appears to apply.[13,20]

Unless their formation is highly stereoselective, solutions of the 2:1 dipeptide complexes of both Co(II) and Co(III) will contain a mixture of diastereomers when at least one amino acid residue is asymmetric. While stereoselectivity in the labile Co(II) complexes is only thermodynamic, that in the inert Co(III) complexes may also contain kinetic contributions originating from differential rates of oxygenation. The additivity observed for the CD magnitudes indicates either that equivalent amounts of two diastereomers are present for any one set of dipeptides or that diastereomers exhibit similar CD magnitudes. Preliminary nmr results on solutions show two isomers present in approximately a 2:1 molar ratio for both the L-alanylglycine– and L-phenylalanylglycine–cobalt(III) complexes. Examination of space-filling molecular models reveals that the thermodynamically favored diastereomer possesses side chains directed toward the carboxylate oxygen rather than the amino nitrogen of the other dipeptide in a 2:1 complex. The identical 2:1 ratios for the dipeptides with a small methyl and a large benzyl side chain suggest a kinetic rather than a thermodynamic origin for stereoselectivity. As noted above experimentally it is observed that oxygenation is inhibited in dipeptide complexes containing large or branched side chains in the carboxyl terminal residue. This inhibition might produce lower yields which may account for the low values of the molar absorptivities at 520 nm in the Co(III) complexes of dipeptides with carboxyl terminal side chains. Because of the proximity of the side chains on one dipeptide with the carboxylate oxygen that is released upon oxygenation on the other, the thermodynamically favored diastereomer is not the more active kinetically. The kinetically more active diastereomer, with the side chains directed toward the amino nitrogen of the other dipeptide, leaves the approach to the carboxylate oxygens relatively unhindered. Mixed DL-dipeptides of necessity contain side chains hindering the approach of oxygen molecules, accounting for their observed[21] slower rate of oxidation compared to that of their LL counterparts.

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Oxalatotetramines of Cobalt(III)

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Received May 25, 1970

The syntheses, resolution, electronic structures, and stereochemistry of mixed-ligand complexes of cobalt(III) with the dianion of oxalic acid and ammonia, ethylenediamine (en), 1,3-diaminopropane (tn), triethylenetetramine (trien), 3,7-diaza-1,9-diaminononane (2,3,2-tet), and 4,7-diaza-1,10-diaminodecane (3,2,3-tet) are reported. The instability of cobalt(III) complexes with 4,8-diaza-1,11-diaminoundecane (3,3,3-tet) indicates that the complexes $Co(NH_3)_4ox^+$, $Co(en)_2ox^+$, $Co(tn)_2ox^+$, α-*cis*-$Co(trien)ox^+$, β-*cis*-$Co(trien)ox^+$, β-*cis*-$Co(2,3,2\text{-tet})ox^+$, and α-*cis*-$Co(3,2,3\text{-tet})ox^+$ comprise the complete series of oxalatotetramine complexes with unsubstituted amines.

Introduction

The complexes oxalato(tetraammine)cobalt(III), $Co(NH_3)_4ox^+$, oxalatobis(ethylenediamine)cobalt(III), $Co(en)_2ox^+$, oxalatobis(1,3-diaminopropane)cobalt(III), $Co(tn)_2ox^+$, oxalatotriethylenetetraminecobalt(III), $Co(2,2,2\text{-tet})ox^+$, oxalato-4,7-diaza-1,10-decanediaminecobalt(III), $Co(3,2,3,\text{-tet})ox^+$, and oxalato-3,7-diaza-1,9-nonanediaminecobalt(III), $Co(2,3,2\text{-tet})ox^+$, comprise a complete series of mixed-ligand oxalatotetraminecobalt(III) ions. Though numerous other complexes are doubtless formed with N- and C-substituted derivatives of these ligands and with cyclic tetramines,