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# Synthesis and Spectral Characterization of the Mixed-Ligand Complexes [*N*-(2-Pyridylmethyl)-L-aspartato][amino acidato]cobalt(III), Co(PLASP)(AA)

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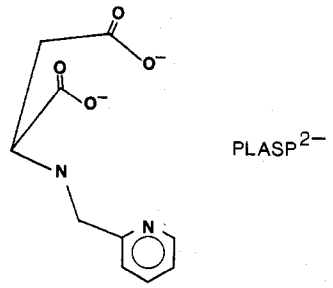
A series of mixed-ligand cobalt(III) complexes of the form Co(PLASP)(AA), where $PLASP^{2-}$ is the tetradentate ligand *N*-(2-pyridylmethyl)-L-aspartate and $AA^-$ is a bidentate amino acidate ligand, were prepared from Co(II) and Co(III) reactants. For the amino acidates glycinate, α-aminoisobutyrate, L-alaninate, L-threoninate, L-prolinate, D- and L-asparaginate, D- and L-phenylalaninate, and D-, L-, and D,L-valinate only the facial $Co^{III}N_3O_3$ isomer, in which the β-$CO_2^-$ group of $PLASP^{2-}$ is coordinated trans to the pyridyl group of $PLASP^{2-}$, was isolated. The bidentate amino acidate is coordinated with its amino group trans to the α-$CO_2^-$ of $PLASP^{2-}$ and its α-$CO_2^-$ group trans to the secondary amino nitrogen of $PLASP^{2-}$. The CD spectra of the Co(PLASP)(AA) complexes were resolved into contributions from the optically active portion of the amino acidate chelate ring (*Y*) and from the rest of the molecule (*X*). The latter contribution is constant for all the complexes studied. Proton NMR spectra of the complexes are also explained in terms of the conformation of the amino acidate chelate ring. In addition, visible and $^{13}C$ NMR spectra of the complexes are discussed.

## Introduction

Nickel(II) and copper(II) complexes of *N*-(2-pyridylmethyl)-L-aspartate, $PLASP^{2-}$, stereoselectively coordinate




$PLASP^{2-}$

optically active amino acidates, $AA^-$, in forming M(PLASP)$(AA)^-$ complexes.[1] In order to investigate the structure of mixed complexes containing $PLASP^{2-}$ and $AA^-$ ligands, the kinetically inert cobalt(III) complexes of the type Co(PLASP)(AA) were prepared. In the present study, $AA^-$ is one of the following amino acidates: glycinate ($Gly^-$), α-aminoisobutyrate (α-$AIBA^-$), L-alaninate (L-$Ala^-$), L-threoninate (L-$Thr^-$), L-prolinate (L-$Pro^-$), D-, L-, or D,L-valinate ($Val^-$), D- or L-asparaginate ($AsN^-$), and D- or L-phenylalaninate ($Phe^-$).

Previously we reported the X-ray structure of a complex of this type, [Co(PLASP)(L-Phe)]·$3H_2O$.[2] This $Co^{III}N_3O_3$ complex was found to have a facial structure in which the three coordinated oxygen (or nitrogen) atoms occupy one triangular face of the coordination octahedron, and the pyridyl group of $PLASP^{2-}$ is coordinated trans to the β-$CO_2^-$ group of $PLASP^{2-}$ (Figure 1a).[2] We proposed that this geometry was due to a combination of electronic, structural, and steric factors. It was of interest to prepare other Co(PLASP)(AA) complexes to establish their geometries and to seek trends in their UV–visible, CD, and NMR spectra.

## Experimental Section

**Materials.** All amino acids were purchased from Aldrich and Eastman Kodak and were used without further purification. The ligand $PLASPH_2$ was prepared as previously reported.[2]

**Preparation of the [*N*-(2-pyridylmethyl)-L-aspartato][amino acidato]cobalt(III), Co(PLASP)(AA), Complexes.** The method of preparation and purification (see below) of each Co(PLASP)(AA) complex is given in Table I. Elemental analyses and yields of each product are also given in that table.

**Method A.** This procedure in which excess hydrogen peroxide is used to oxidize Co(II) to Co(III) in the presence of $PLASP^{2-}$ and $AA^-$ has been described previously.[2] All reactions were carried out by using 10 mmol of $PLASP^{2-}$, 10 mmol of $AA^-$, and 10 mmol of $CoSO_4·7H_2O$ except in the preparation of [Co(PLASP)(L-Thr)]·$^1/_2H_2O$ which was carried out by using 5 mmol each of $PLASP^{2-}$, $AA^-$, and $CoSO_4·7H_2O$. All products were purified by using column chromatography on either aluminum oxide (acidic or neutral) or Dowex 50W-X8 in the $Na^+$ form. A typical column size was 2.5 × 60 cm. The solvent used for purification on alumina was either water or a water–ethanol mixture, while water was used as the solvent for purifications on Dowex 50W-X8. The product was the second band off the columns and was preceded by a brown band containing decomposition products, unreacted ligands, and salts. The product isolated by column chromatography was further purified by dissolving the complex in a minimum of water and adding a volume of methanol or ethanol equal to 4–5 times the volume of water to force precipitation. The complexes [Co(PLASP)(L-Phe)]·$3H_2O$, [Co(PLASP)(D-Phe)]·$2H_2O$, and [Co(PLASP)(D-Ala)] were purified in either of two ways. The first was by recrystallization from water of the reddish solid obtained by concentrating the reaction mixture under vacuum. The second was by column chromatography. The complex [Co(PLASP)(L-Phe)]·$H_2O$ was precipitated by dissolving the [Co(PLASP)(L-Phe)·$3H_2O$ complex in water and then adding a volume of ethanol equal to 4–5 times the volume of water. Anal. Calcd for $C_{19}H_{20}N_3O_6Co·H_2O$: C, 49.25; H, 4.75; N, 9.07. Found: C, 49.13; H, 4.73; N, 9.01.

**Method B, Preparation of [Co(PLASP)(L-Val)].** $PLASPH_2$ (1.12 g, 5 mmol), L-ValH (0.89 g, 5 mmol), $Na_3[Co(CO_3)_3]·3H_2O$ (1.82 g, 5 mmol), and activated carbon were placed in a flask, and 50 mL of water was added. The solution began foaming, and a purple color became visible. Next, 15 mL of 1 N $H_2SO_4$ was added, and more foaming occurred. The solution was stirred overnight, filtered, and reduced under vacuum to 3–5 mL. This solution was placed on an acidic alumina column (2.5 × 65 cm) and eluted with 40:60 $EtOH/H_2O$. The large reddish pink band containing the product was collected and concentrated to 1–2 mL, and 125 mL of methanol was added to force out the product.

**Method C, Preparation of [Co(PLASP)(D,L-Val)].** $PLASPH_2$ (0.56 g, 2.5 mmol), D,L-ValH (0.30 g, 2.5 mmol), $CoSO_4·7H_2O$ (0.70 g, 2.5 mmol), and 5 mL of 1 N NaOH were dissolved in 50 mL of water, and $PbO_2$ (0.35 g, 1.5 mmol) was added. The solution was heated (50–60 °C) for 1 h. Next, 2.5 mL of 1 N $H_2SO_4$ was added, and the solution was filtered. The solution was concentrated under reduced pressure to 1–2 mL and placed on a column (1.9 × 40 cm) of DowexW-X8 in the $Na^+$ form. The first band off the column contained decomposition and anionic products. The second reddish pink band containing the product was collected and reduced to ~5 mL, and 100 mL of ethanol was added to force out the product.

**Method D.** The ligands $PLASPH_2$ (0.56 g, 2.5 mmol) and AAH (2.5 mmol) and $CoSO_4·7H_2O$ (0.70 g, 2.5 mmol) were placed in 10 mL of water. Next 7.5 mL of 1 N NaOH was added to give a brown solution of pH 9. The solution was stirred for 5 min, and activated carbon (0.1 g) was added. Then a solution of $K_2S_2O_8$ (0.4 g, 1.5 mmol)

(1) Nakon, R.; Rechani, P. R.; Angelici, R. J. *Inorg. Chem.* **1973**, *12*, 2431.
(2) Meiske, L. A.; Jacobson, R. A.; Angelici, R. J. *Inorg. Chem.* **1980**, *19*, 2028.

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Table I. Synthesis, Purification, and Elemental Analysis of Co(PLASP)(AA) Complexes

| complex | method of prepn | column support | chromatography solvent | % yield | formula | % C calcd | % C found | % H calcd | % H found | % N calcd | % N found |
|---|---|---|---|---|---|---|---|---|---|---|---|
| [Co(PLASP)(Gly)] | A | neutral alumina | 50:50 MeOH/$H_2O$ | 9 | $C_{12}H_{14}N_3O_6Co$ | 40.57 | 40.76 | 3.94 | 4.17 | 11.83 | 11.83 |
| [Co(PLASP)(L-Ala)] | A | neutral alumina | $H_2O$ | 19 | $C_{13}H_{16}N_3O_6Co$ | 42.29 | 42.18 | 4.34 | 4.51 | 11.39 | 11.40 |
| [Co(PLASP)(α-AIBA)]·$H_2O$ | A | neutral alumina | 50:50 EtOH/$H_2O$ | 18 | $C_{14}H_{18}N_3O_6Co\cdot H_2O$ | 41.91 | 42.15 | 4.99 | 5.22 | 10.48 | 10.35 |
| [Co(PLASP)(L-Thr)]·$1^1/_2H_2O$ | A | neutral alumina | 40:60 EtOH/$H_2O$ | 18 | $C_{14}H_{18}N_3O_7Co\cdot 1^1/_2H_2O$ | 39.45 | 39.57 | 4.93 | 4.77 | 9.86 | 9.81 |
| [Co(PLASP)(L-Pro)]·$1^1/_2H_2O$ | A | Dowex | $H_2O$ | 26 | $C_{15}H_{18}N_3O_6Co\cdot 1^1/_2H_2O$ | 42.66 | 42.38 | 4.98 | 5.19 | 9.95 | 9.90 |
| | D | Dowex | $H_2O$ | 40 | | | | | | | |
| [Co(PLASP)(LVal)] | A | neutral alumina | 40:60 EtOH/$H_2O$ | 34 | $C_{15}H_{20}N_3O_6Co$ | 45.35 | 45.41 | 5.04 | 4.90 | 10.58 | 10.60 |
| | B | acidic alumina | 40:60 EtOH/$H_2O$ | 14 | | | | | | | |
| [Co(PLASP)(D-Val)] | A | neutral alumina | 40:60 EtOH/$H_2O$ | 9 | $C_{15}H_{20}N_3O_6Co$ | 45.35 | 45.16 | 5.04 | 5.10 | 10.58 | 10.52 |
| [Co(PLASP)(D,L-Val)] | A | neutral alumina | 40:60 EtOH/$H_2O$ | 30 | $C_{15}H_{20}N_3O_6Co$ | 45.35 | 44.91 | 5.04 | 5.24 | 10.58 | 10.26 |
| | C | Dowex | $H_2O$ | 33 | | | | | | | |
| [Co(PLASP)(L-AsN)]·$H_2O$ | D | Dowex | $H_2O$ | 36 | $C_{14}H_{17}N_4O_7Co\cdot H_2O$ | 39.08 | 39.09 | 4.42 | 4.57 | 13.03 | 13.04 |
| [Co(PLASP)(D-AsN)]·$^1/_2H_2O$ | D | Dowex | $H_2O$ | 11 | $C_{14}H_{17}N_4O_7Co\cdot {}^1/_2H_2O$ | 39.91 | 40.08 | 4.27 | 4.51 | 13.30 | 13.19 |
| [Co(PLASP)(L-Phe)]·$3H_2O$ | A | neutral alumina | $H_2O$ | 18 | $C_{19}H_{20}N_3O_6Co\cdot 3H_2O$ | 45.70 | 45.59 | 5.21 | 5.33 | 8.41 | 8.37 |
| [Co(PLASP)(D-Phe)]·$2H_2O$ | A | neutral alumina | $H_2O$ | 8 | $C_{19}H_{20}N_3O_6Co\cdot 2H_2O$ | 47.41 | 47.26 | 4.99 | 4.15 | 8.73 | 8.69 |

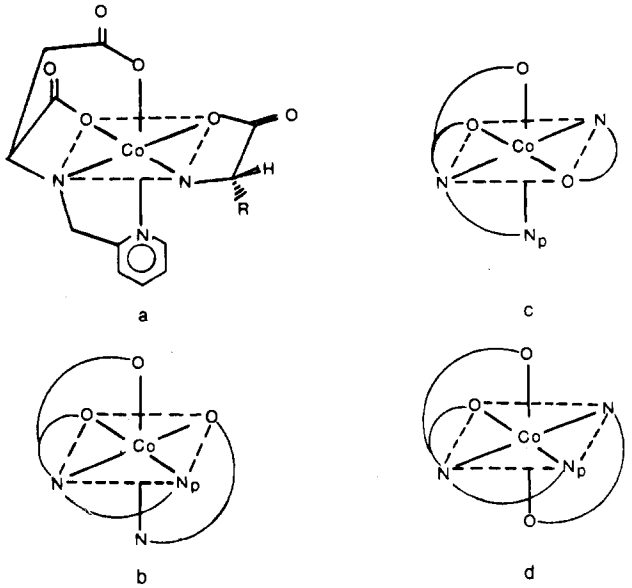


**Figure 1.** The four possible isomers of Co(PLASP)(L-AA) complexes: (a) *fac* β-$CO_2^-$, (b) *fac* α-$CO_2^-$, (c) *mer* β-$CO_2^-$, and (d) *mer* α-$CO_2^-$.

in 15 mL of water was added. The reaction mixture was heated for 1 h at ~60 °C and filtered to give a deep purple solution. The solution was reduced to 5–10 mL and placed on a column (2.5 × 65 cm) of Dowex 50W-X8 in the $Na^+$ form. The first band off the column contains anionic and decomposition products while the second reddish pink band contains the desired product. This second band was collected and reduced to ~5 mL. The product was precipitated by addition of ethanol. Separation of the two diastereomers Co(PLASP)(L-AsN) and Co(PLASP)(D-AsN) was achieved by placing the reaction mixture (after reduction to 5–10 mL) on a Dowex 50W-X8 column in the $Na^+$ form. Upon elution with water, three bands formed with the first band off the column containing decomposition and anionic products, the second containing the [Co(PLASP)(L-AsN)]·$H_2O$ diastereomer, and the third band containing the [Co(PLASP)(D-AsN)]·$^1/_2H_2O$ diastereomer.

**Spectra.** Visible and CD spectra were recorded in water at room temperature by using a Jasco ORD/UV/CD-5 spectrometer. The

**Table II.** Visible Absorption Maxima for Co(PLASP)(AA) Complexes in Water

| compd | λ, nm | ε, $cm^{-1}$ $M^{-1}$ | λ, nm | ε, $cm^{-1}$ $M^{-1}$ |
|---|---|---|---|---|
| [Co(PLASP)(Gly)] | 515 | 223 | 370 | 137 |
| [Co(PLASP)(L-Ala)] | 512 | 230 | 370 | 146 |
| [Co(PLASP)(α-AIBA)]·$H_2O$ | 511 | 222 | 370 | 136 |
| [Co(PLASP)(L-Thr)]·$1^1/_2H_2O$ | 511 | 233 | 368 | 134 |
| [Co(PLASP)(L-Pro)]·$1^1/_2H_2O$ | 517 | 211 | 373 | 138 |
| [Co(PLASP)(L-Val)] | 510 | 229 | 368 | 132 |
| [Co(PLASP)(D-Val)] | 513 | 230 | 371 | 137 |
| [Co(PLASP)(D,L-Val)] | 513 | 201 | 370 | 120 |
| [Co(PLASP)(L-AsN)]·$H_2O$ | 513 | 199 | 371 | 122 |
| [Co(PLASP)(D-AsN)]·$^1/_2H_2O$ | 513 | 220 | 371 | 128 |
| [Co(PLASP)(L-Phe)]·$H_2O$ | 513 | 228 | 369 | 138 |
| [Co(PLASP)(L-Phe)]·$3H_2O$ | 512 | 226 | 368 | 142 |
| [Co(PLASP)(D-Phe)]·$2H_2O$ | 512 | 232 | 369 | 136 |

$^1H$ NMR spectra were recorded in 99.7% deuterium oxide at room temperature on a JEOL FX90Q Fourier transform NMR spectrometer, using *tert*-butyl alcohol (δ 1.23) as an internal standard. The peak positions are given in ppm downfield from $Me_4Si$. The $^{13}C$ NMR spectra also were recorded at room temperature on the above NMR spectrometer in either 99.7% deuterium oxide or 70% aqueous $H_3PO_4$, using 1,4-dioxane (67.0 ppm downfield from $Me_4Si$) as an internal standard.

## Results and Discussion

Figure 1 shows the four possible geometric isomers of the Co(PLASP)(L-AA) complex. The structures in Figure 1a,b have a facial arrangement of oxygen atoms. Reversing the coordination of the amino acidate, $AA^-$, in Figure 1a,b, gives the two meridional isomers shown in Figure 1c,d. The four isomers in Figure 1 are denoted as *fac* β-$CO_2^-$, *fac* α-$CO_2^-$, *mer* β-$CO_2^-$, and *mer* α-$CO_2^-$ with the terms β-$CO_2^-$ and α-$CO_2^-$ being used to denote which $CO_2^-$ group of $PLASP^{2-}$ is coordinated trans to the pyridyl group.

**Visible Spectra of the Co(PLASP)(AA) Complexes.** The visible spectra of the Co(PLASP)(AA) complexes in water exhibit two symmetrical peaks (Table II) with maxima at 513 ± 4 and 370 ± 3 nm, which are comparable to those of various facial $Co^{III}N_3O_3$ complexes containing amino acidates reported

**Table III.** Circular Dichroism Maxima and Minima for Co(PLASP)(AA) Complexes in Water[a]

| complex | band I | | | | band II | | | |
|---|---|---|---|---|---|---|---|---|
| | λ | Δε | λ | Δε | λ | Δε | λ | Δε |
| [Co(PLASP)(Gly)] | 544 | +0.94 | 495 | +0.56 | 370 | −0.06 | 345 | +0.07 |
| [Co(PLASP)(L-Ala)] | 546 | +0.68 | 500 | +0.46 | 375 | +0.25 | 359 | +0.25 |
| [Co(PLASP)(α-AIBA)]·$H_2O$ | 545 | +0.81 | 495 | +1.17 | 370 | −0.13 | 340 | +0.09 |
| [Co(PLASP)(L-Thr)]·$1^1/_2H_2O$ | 560 | +0.38 | 486 | +0.39 | 382 | +0.19 | 355 | +0.26 |
| [Co(PLASP)(L-Pro)]·$1^1/_2H_2O$ | 555 | +0.58 | 490 | +1.16 | 385 | +0.29 | 358 | +0.36 |
| [Co(PLASP)(L-Val)] | 560 | +0.31 | 488 | +0.63 | 380 | +0.18 | 355 | +0.25 |
| [Co(PLASP)(D-Val)] | | | 520 | +2.07 | 372 | −0.38 | 332 | +0.06 |
| [Co(PLASP)(D,L-Val)] | 538 | +0.91 | 500 | +1.08 | 375 | −0.10 | 340 | +0.11 |
| [Co(PLASP)(L-AsN)]·$H_2O$ | 545 | +0.70 | 495 | +1.01 | 375 | +0.36 | 355 | +0.34 |
| [Co(PLASP)(D-AsN)]·$^1/_2H_2O$ | | | 504 | +1.24 | 375 | −0.41 | 332 | +0.08 |
| [Co(PLASP)(L-Phe)]·$3H_2O$ | 560 | +0.36 | 485 | +0.31 | 385 | +0.18 | 360 | +0.20 |
| [Co(PLASP)(D-Phe)]·$2H_2O$ | | | 505 | +1.68 | 375 | −0.27 | 338 | +0.10 |

[a] Units for Δε are $cm^{-1}$ $M^{-1}$; units for λ are nm.

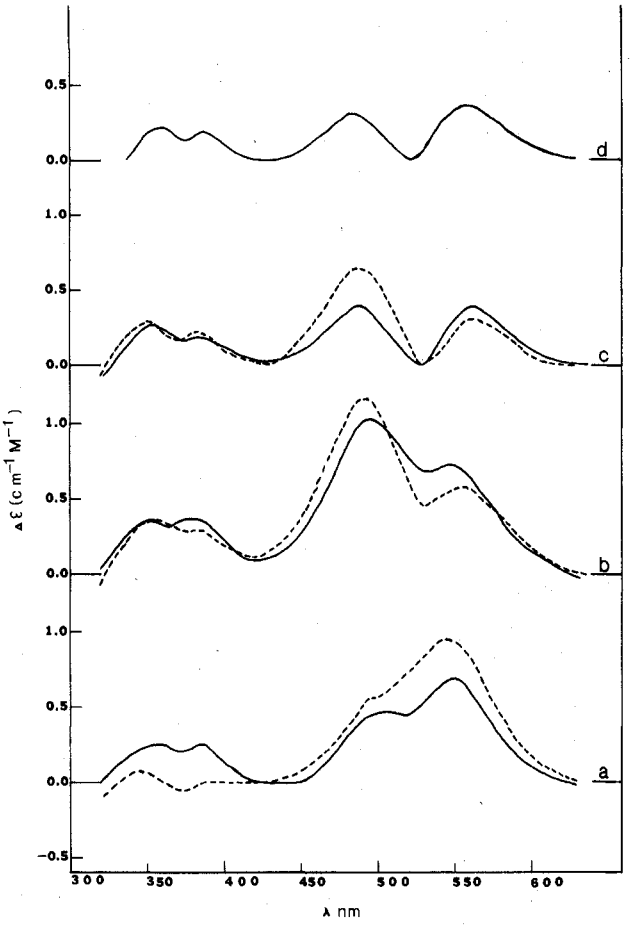


**Figure 2.** CD spectra for (a) [Co(PLASP)(Gly)] (---) and [Co(PLASP)(L-Ala)] (—), (b) [Co(PLASP)(L-Pro)]·$1^1/_2H_2O$ (---) and [Co(PLASP)(L-AsN)]·$H_2O$ (—), (c) [Co(PLASP)(L-Val)] (---) and [Co(PLASP)(L-Thr)]·$1^1/_2H_2O$ (—), and (d) [Co(PLASP)(L-Phe)]·$3H_2O$ (—).

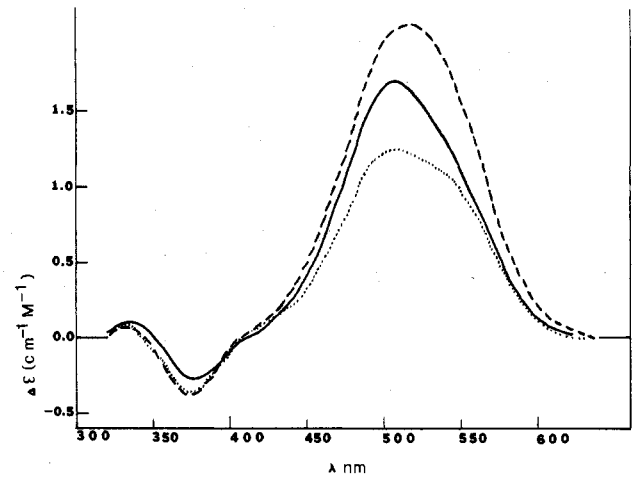


**Figure 3.** CD spectra for [Co(PLASP)(D-Val)] (--), [Co(PLASP)(D-Phe)]·$2H_2O$ (—), and [Co(PLASP)(D-AsN)]·$^1/_2H_2O$ (···).

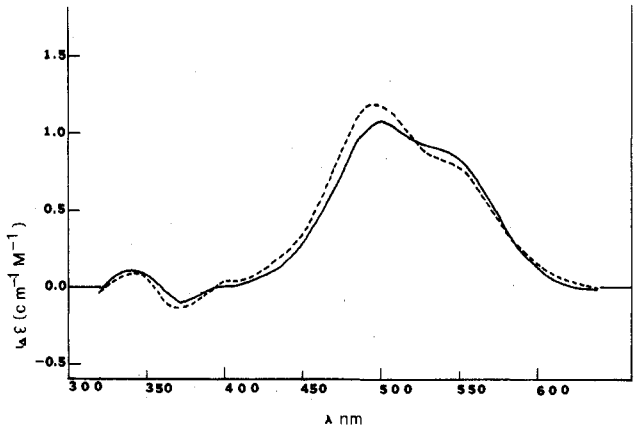


**Figure 4.** CD spectra for [Co(PLASP)(α-AIBA)]·$H_2O$ (---) and [Co(PLASP)(D,L-Val)] (—).

previously.[3-5] (The spectrum of the Co(PLASP)(L-Phe)·$3H_2O$ complex is shown in Figure 5 of ref 2.) Since the absorption maxima and extinction coefficients for the complexes listed in Table II are so similar, the arrangement of the ligands around the Co(III) in all of these complexes is probably the same. This is consistent with $^{13}C$ NMR studies of these complexes which show the $^{13}C$ chemical shifts of the coordinated ligand $PLASP^{2-}$ to remain nearly identical in all of the Co(PLASP)(AA) complexes (see below). Therefore, on the basis of the visible and $^{13}C$ NMR spectra of the Co(PLASP)(AA) complexes and the previously reported X-ray structure[2] of [Co(PLASP)(L-Phe)]·$3H_2O$, all of the complexes listed in Table II are assigned the facial structure in which the pyridine is coordinated trans to the β-$CO_2^-$ group of $PLASP^{2-}$ (Figure 1a). Further evidence for this assignment is given by the circular dichroism spectra of the complexes and will be considered next.

**Circular Dichroism Spectra of the Co(PLASP)(AA) Complexes.** The circular dichroism spectra of the various Co(PLASP)(AA) complexes in water are shown in Figures 2–4,

(3) Watabe, M.; Onuki, K.; Yoshikawa, S. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 687.
(4) Douglas, B. E.; Yamada, S. *Inorg. Chem.* **1965**, *4*, 1561.
(5) Denning, R. G.; Piper, T. S. *Inorg. Chem.* **1966**, *5*, 1056.

and the numerical values for their minima and maxima are given in Table III. Each circular dichroism spectrum can be divided into two major bands, with band I occurring in the 485–560-nm range and band II occurring from 330 to 385 nm; these bands occur in the regions of the visible spectrum where these complexes absorb.

Based upon the general shapes of bands I and II, the CD spectra of the Co(PLASP)(AA) complexes can be divided into three groups. For the first group, containing the Co(PLASP)(L-AA) and Co(PLASP)(Gly) complexes, both bands I and II (Figure 2) consist of two positive peaks, with the exception of band II of the glycinate complex which has a small negative and a small positive peak. The intensities of the peaks in band I vary considerably from one L-amino acidate to another, while the intensities of the peaks in band II remain fairly constant.

The second group consists of the Co(PLASP)(D-AA) complexes (Figure 3), in which band I is a single broad positive peak which also varies in intensity from one D-amino acidate to another. Band II consists of a small positive peak and a larger negative peak which, as in the case of the L-$AA^-$ complexes, does not vary greatly in intensity from one D-$AA^-$ to another.

Band I of the third group, containing only [Co(PLASP)($\alpha$-AIBA)]·$H_2O$ and Co(PLASP)(D,L-Val) (Figure 4), consists of two positive peaks which are similar to those of band I of the L-$AA^-$ complexes. However, band II which is similar to band II of the D-$AA^-$ complexes (Figure 3) consists of a negative and a positive peak. Since the Co(PLASP)(AA) complexes in the three groups mentioned above have the same basic structures, differing only at the $\alpha$-carbon of the amino acidate, differences in their CD peak intensities and shapes must be related to the differences at the $\alpha$-carbon of the amino acidates.

Previous work by various authors has shown that CD spectra of several cobalt(III) complexes containing optically active ligands can be separated into a configurational effect (the contribution to the CD spectrum from the spatial position of the chelate rings) and a vicinal effect (the contribution from an asymmetric ligand).[4,6-10] Similar arguments may be applied here to explain the differences in the CD spectra of the Co(PLASP)(AA) complexes. These spectra for the Co(PLASP)(AA) where $Y$ is the effect on CD associated with a change in the optical activity of (or substitution at) the amino acidate $\alpha$-carbon, and an $X$ contribution, where $X$ is the effect on the CD associated with the rest of the complex.

Thus the value of $\Delta\epsilon$ at a given wavelength in the CD spectrum of a Co(PLASP)(AA) complex may be expressed as eq 1. If it is assumed that $Y_D = -Y_L$, then one obtains eq

$$X + (Y_D \text{ or } Y_L) = \text{CD[Co(PLASP)(D-AA or L-AA)]} \quad (1)$$

2. Using CD data for pairs of Co(PLASP)(D-AA) and Co-

$$X = \{\text{CD[Co(PLASP)(L-AA)]} + \text{CD[Co(PLASP)(D-AA)]}\}/2 \quad (2)$$

(PLASP)(L-AA) complexes, $X$ values have been calculated for complexes where $AA^-$ = $Val^-$, $Phe^-$, and $AsN^-$.

The above treatment implies that $X$ values for all Co(PLASP)(AA) complexes are the same. That this is substantially the case is shown in Figure 5. From eq 2, it follows that the CD spectrum of Co(PLASP)(D,L-Val) should also be the same as that of the calculated $X$ values. This is verified in Figure 4. The presence of equal amounts of diastereomers in the Co(PLASP)(D,L-Val) complex is confirmed by its proton NMR spectrum (see below). Finally, it should be noted that the CD spectrum of the complex Co(PLASP)($\alpha$-AIBA) containing a nonoptically active amino acidate is essentially the same as that of Co(PLASP)(D,L-Val) (Figure 4) and that of the calculated $X$ terms (Figure 5). These results support the assumption that the $X$ contribution is essentially the same in all of these complexes.

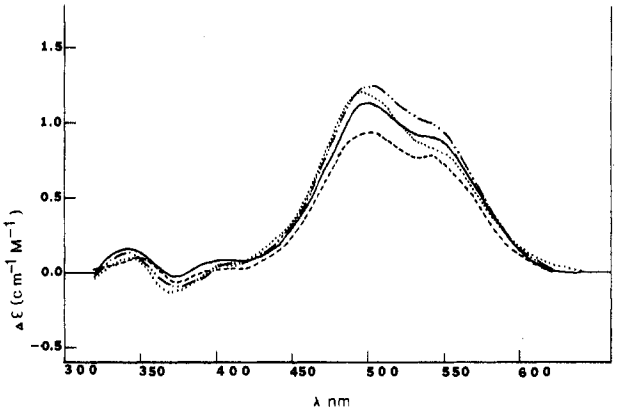


**Figure 5.** CD spectrum for [Co(PLASP)($\alpha$-AIBA)]·$H_2O$ (···) and calculated $X$ terms from {[Co(PLASP)(L-Val)] + [Co(PLASP)(D-Val)]}/2 (-·-·-), {[Co(PLASP)(L-AsN)]·$H_2O$ + [Co(PLASP)(D-AsN)]·$^1/_2H_2O$}/2 (—), and {[Co(PLASP)(L-Phe)]·$3H_2O$ + [Co(PLASP)(D-Phe)]·$2H_2O$}/2 (---).

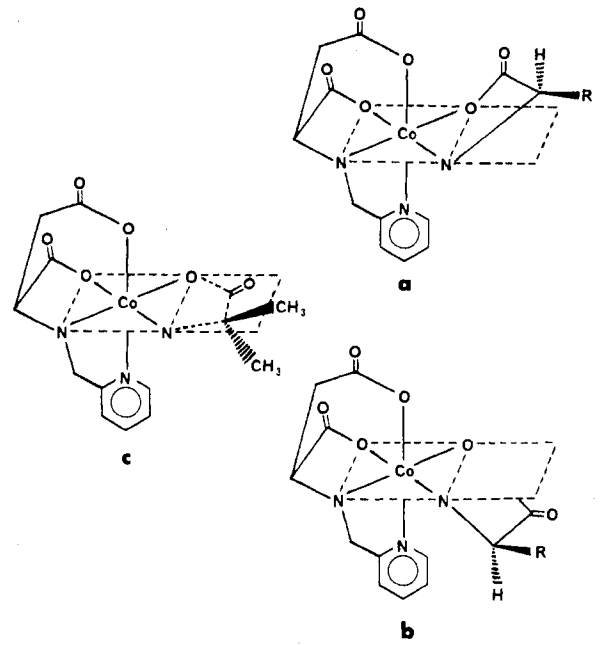


**Figure 6.** Possible $AA^-$ chelate ring conformations in (a) Co(PLASP)(L-AA), (b) Co(PLASP)(D-AA), and (c) Co(PLASP)($\alpha$-AIBA) complexes.

The $Y$ terms, however, depend, as expected, upon the chirality and the nature of the R group at the optically active amino acidate $\alpha$-carbon. These factors may also be expected to be important for determining the geometry of the $AA^-$ chelate ring. In order to accommodate a bulky R group in the favorable equatorial position, an L-amino acidate should adopt the conformation shown in Figure 6a, while a D-amino acidate should adopt the conformation shown in Figure 6b. It should be noted that the L-$Phe^-$ chelate ring in solid [Co(PLASP)(L-Phe)]·$3H_2O$ adopts the conformation shown in

(6) Koine, N.; Sakota, N.; Hidaka, J.; Shimura, Y. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 1583.
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Table IV. $^1$H Chemical Shifts of Various Co(PLASP)(AA) Complexes and $PLASPH_2$ in 99.7% $D_2O$[a]

| | PLASP$^{2-}$ | | | | | | AA$^-$ | | |
|---|---|---|---|---|---|---|---|---|---|
| AA$^-$ | δ(α-H) | δ(β-H)[b] | δ($CH_2$-py)[c] | δ(*o*-py) | δ(*m*-py) | δ(*p*-py) | δ(α-H) | δ(β-H) | δ(γ-H) |
| α-AIBA$^-$ | 3.95 q | 3.07 m | 5.21 d, 4.48 d | 8.21 d | 7.60 m | 8.07 t | | 1.23 s, 1.51 s | |
| Gly$^-$ | 3.94 q | 3.08 m | 5.19 d, 4.46 d | 8.24 d | 7.60 m | 8.08 t | 3.61 d,[d] 3.27 d | | |
| L-Val$^-$ | 3.95 q | 3.07 m | 5.24 d, 4.48 d | 8.21 d | 7.59 m | 8.07 t | 3.69 d | 2.27 m | 0.94 d, 0.70 d |
| D-Val$^-$ | 3.94 q | 3.06 m | 5.24 d, 4.51 d | 8.11 d | 7.60 m | 8.07 t | 3.36 d | 2.30 m | 0.96 d, 0.89 d |
| D,L-Val$^-$ | 3.94 m | 3.06 m | 5.24 d, 4.49 d, 4.47 d | 8.20 d, 8.11 d | 7.58 m | 8.06 t | 3.68 d, 3.36 d | 2.27 m | 0.95 d, 0.70 d,[e] 0.88 d |
| L-Pro$^-$ | 3.97 q | 3.09 m | 5.31 d, 4.52 d | 8.29 d | 7.64 m | 8.10 t | 4.18 m | 2.9-1.2 m[f] | |
| L-Thr$^-$ | 3.97 q | 3.09 m | 5.23 d, 4.42 d | 8.18 d | 7.56 m | 8.04 t | 3.63 d | 4.36 m | 1.20 d |
| L-AsN$^-$ | 3.94 m | 3.09 m | 5.21 d, 4.46 d | 8.29 d | 7.56 m | 8.06 t | 3.94 m | 2.85 d | |
| D-AsN$^-$ | 3.94 q | 3.07 m | 5.23 d, 4.48 d | 8.18 d | 7.60 m | 8.08 t | 3.69 q | 2.84 m | |
| L-Phe$^-$ | 3.93 q | 3.1 m | 5.29 d, 4.48 d | 7.87 d | 7.47 m | 8.00 t | 4.1 m | 3.1 m | 7.24 m[g] |
| D-Phe$^-$ | 3.91 q | 3.1 m | 5.30 d, 4.44 d | 8.19 d | 7.52 m | 8.04 t | 3.65 | 3.4 m | 7.34 m[g] |
| $PLASPH_2$ | 4.03 t | 3.01 d | 4.50 s | 8.62 d | 7.56 m | 8.01 t | | | |

[a] The center of each peak (or peaks) is given, and the multiplicity is given by s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. [b] The multiplet consists of two overlapping AB quartets. [c] The coupling constant for the doublets given in this column is 18 Hz. [d] $J$ = 17 Hz. [e] The relative areas for the γ-methyl groups are a total of 3 for the doublets at 0.95 and 0.88 and 1 for the doublet at 0.70. The coupling constant for each doublet is 7 Hz. [f] This region includes the β, γ, and δ protons of the prolinate ligand. [g] The peak given is for all the phenyl protons of the phenylalaninate ligand.

Figure 6a.[2] If the amino acidate has two groups of the same size attached to the α-carbon as in α-aminoisobutyrate ($H_2NC(CH_3)_2CO_2^-$), the amino acidate could either adopt a planar conformation as in Figure 6c or equilibrate between the two structures in Figure 6a,b. Thus, the observed CD spectrum for Co(PLASP)(α-AIBA) should be a good approximation for *X* since the *Y* contribution will be averaged to either zero due to equilibration between the two structures in Figure 6a,b or zero due to the planar (no net *Y*) nature of the α-AIBA$^-$ chelate ring. This appears to be a reasonable approximation since, as noted above, the CD spectrum of the α-AIBA$^-$ complex is essentially the same as that of the Co(PLASP)(D,L-Val) complex and that of the calculated *X* terms.

Calculations of the *Y* terms for the Val$^-$, Phe$^-$, and AsN$^-$ diastereomers with use of eq 1 and on the assumption that *X* is equal to the observed CD spectrum of the [Co(PLASP)(α-AIBA)] complex are given in Figure 7. Examination of these curves shows that to a first approximation, the assumption that $Y_D = -Y_L$ in formulating eq 2 is valid. Since the degree of bending of an L-amino acidate chelate ring from the coordination plane as in Figure 6a should be equal but opposite in direction to a D-amino acidate chelate ring as in Figure 6b, *Y* may represent the contribution of the amino acidate chelate ring bending to the overall CD spectrum. It should be noted that if any steric interaction or hydrogen bonding is present in one diastereomer (such as Co(PLASP)(L-AA)) and not in the other (such as Co(PLASP)(D-AA)), then $Y_D$ may not be equal to $-Y_L$. This may occur in the Co(PLASP)(D- and L-AsN$^-$) complexes (Figure 7a) where the β-amide group is polar and capable of hydrogen bonding with other polar groups of the complex. A similar interaction has been established in the related D-Co(en)$_2$(L-glutamate)$^+$ complex.[11a]

In addition to *Y* terms calculated from eq 1 and 2 for complexes with AA$^-$ = Val$^-$, Phe$^-$, and AsN$^-$, these terms were also calculated for L-Ala$^-$, L-Pro$^-$, L-Thr$^-$, and Gly$^-$ with use of eq 1 on the assumption that the *X* terms are equal to the CD spectrum of Co(PLASP)(α-AIBA); these *Y* terms are shown in Figure 8. The basic shape of the *Y* curves of all the Co(PLASP)(L-AA) complexes is essentially the same (Figures 7 and 8). This conclusion also includes the nonoptically active Gly$^-$, which suggests that the Gly$^-$ chelate ring has the conformation adopted by the L-amino acidates (Figure 6a). It also indicates that the AA$^-$ ligand need not be optically active in order to contribute a *Y* term to the spectrum. This suggests that it is the chelate ring conformation which is important in determining the magnitude of *Y* in the Co(PLASP)(AA) complexes. Further evidence for the conformation (or bending) of the chelate rings is given in the discussion of the $^1$H NMR spectra of the Co(PLASP)(AA) complexes.

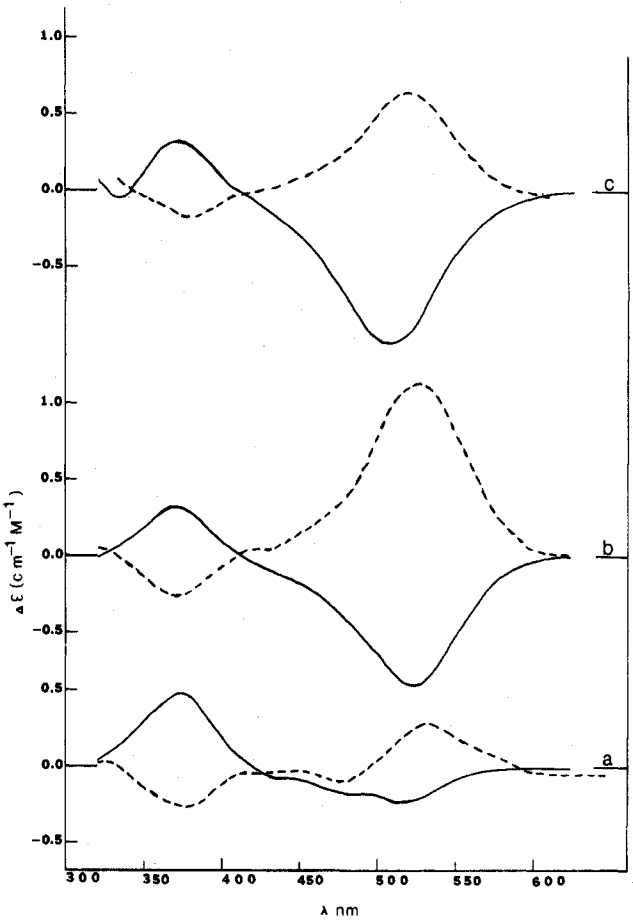


**Figure 7.** *Y* terms calculated by [Co(PLASP)(AA)] − [Co(PLASP)(α-AIBA)]·$H_2O$ for (a) D-AsN$^-$ (---) and L-AsN$^-$ (—), (b) D-Val$^-$ (---) and L-Val$^-$ (—), and (c) D-Phe$^-$ (---) and L-Phe$^-$ (—).

**$^1$H NMR Spectra of the Co(PLASP)(AA) Complexes.** The $^1$H NMR spectra of the various Co(PLASP)(AA) complexes and $PLASPH_2$ in 99.7% deuterium oxide are given in Table

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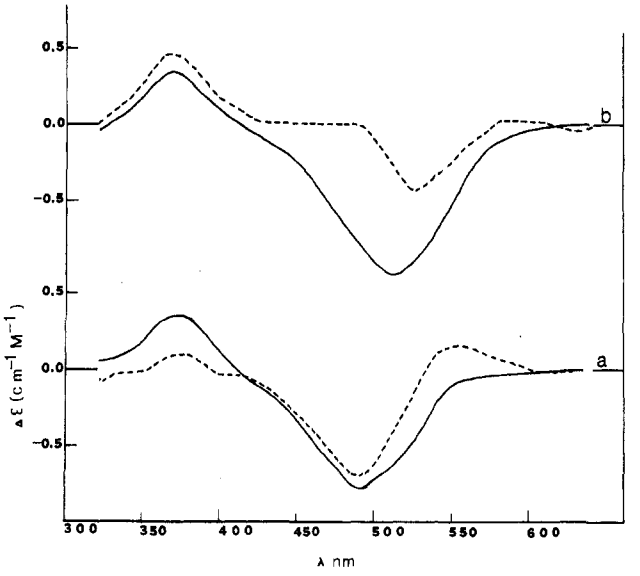


**Figure 8.** *Y* terms calculated by [Co(PLASP)(AA)] - [Co(PLASP)(α-AIBA)]·$H_2O$ for (a) $Gly^-$ (---) and L-$Ala^-$ (—) and (b) L-$Pro^-$ (---) and L-$Thr^-$ (—).

IV. The chemical shifts of the coordinated $PLASP^{2-}$ ligands (with the exception of the ortho pyridyl proton which will be considered later) are nearly identical and are not affected by the amino acidate present in the complex.

In general the α proton of the coordinated $PLASP^{2-}$ occurs as a quartet at δ 3.95 while the β-methylene protons occur as two overlapping quartets (arising from an ABX pattern) centered at δ 3.1. The pyridyl methylene protons appear as two doublets centered at δ 5.25 and 4.46 with a coupling constant of 18 Hz. This coupling constant is similar to those reported for the methylene protons of cobalt(III) complexes containing ligands such as $^-O_2CCH_2NHCH_2CO_2^-$, $IMDA^{2-}$.[10,11b] The pyridyl protons of the coordinated $PLASP^{2-}$ exhibit a complex pattern (Figure 9) which is similar to the splitting observed for 2-picoline.[12] The meta protons occur as a multiplet (an overlapping doublet and triplet) centered at δ 7.5–7.6 while the para proton occurs as a triplet centered at δ 8.05. The ortho proton occurs as a doublet whose position varies from δ 7.87 to 8.29.

A comparison of the chemical shifts for the ortho pyridyl protons in Figure 9 reveals that the shifts of the various D-amino acidate complexes remain fairly constant (δ 8.11–8.19) while the shifts of certain L-amino acidate complexes are slightly deshielded when compared to the D-amino acidates; also the shifts of the L-amino acidate complexes do not remain constant (δ 8.29–7.87). These differences in chemical shifts for all the complexes can be accounted for if the direction of chelate ring bending and the size and type of R group are considered. In the D analogues (Figure 6b) the chelate ring is bent downward and toward the ortho proton while in the L analogues (Figure 6a) the chelate ring is bent upward and away from the ortho proton. Thus the α-carboxylate of the amino acidate is closer to the ortho proton in the D analogues, giving rise to a greater amount of shielding relative to the L-amino acidates. The variation in the chemical shift of the ortho proton in the L-amino acidate complexes may be attributed to the presence of a bulky R group in the vicinity of the ortho pyridyl proton. The shielding of the ortho pyridyl proton in the L-$Phe^-$ complex presumably is due to the orientation of the phenyl group which has been shown by an X-ray structure to be in a shielding position in the solid state.

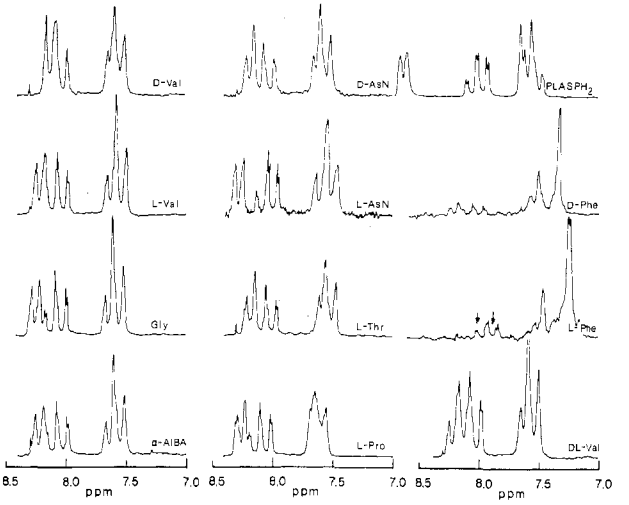


**Figure 9.** Proton NMR for the pyridyl protons of $PLASPH_2$ and various Co(PLASP)(AA) complexes in 99.7% $D_2O$.

Although the $PLASP^{2-}$ protons (with the exception of the ortho pyridyl proton) in the different Co(PLASP)(AA) complexes do not vary, there are considerable differences in the chemical shifts of the amino acidate protons of the enantiomers of $Val^-$, $AsN^-$, and $Phe^-$, of the glycinate protons, and of the α-$AIBA^-$ methyl protons. In general, the α protons of the L-amino acidates occur at lower fields than those of the D analogues. This is presumably due to the positioning of the α-protons of the D-amino acidates over the pyridine π cloud. Likewise the glycinate proton at δ 3.27 and the methyl group of α-$AIBA^-$ at δ 1.23 can be assigned to those protons pointing over the pyridyl ring while the glycinate proton at δ 3.61 and the α-$AIBA^-$ methyl at δ 1.51 can be assigned to those directed away from the pyridine group. Although a similar trend is not seen for the β protons of the amino acidates, the γ protons of L-$Val^-$ and the phenyl protons of L-$Phe^-$ are upfield from their D analogues. Both L-$Val^-$ and D-$Val^-$ have a γ-methyl group at δ 0.95, but in L-$Val^-$ (which has its R group near the pyridyl ring) the second γ-methyl group is shielded (δ 0.70) more than the corresponding γ-methyl group (δ 0.89) of D-$Val^-$ (which has its R group away from the pyridyl ring). This trend is the same for L-$Phe^-$ where the phenyl group is close to the pyridyl ring and thus shielded (δ 7.24) when compared to the D-$Phe^-$ phenyl group (δ 7.34). The smaller difference in chemical shifts between the γ protons of D- and L-$Val^-$ as compared to their α-proton difference is presumably due to the greater distance from the pyridyl ring to these γ protons.

**$^{13}C$ NMR Spectra of the Co(PLASP)(AA) Complexes.** The $^{13}C$ NMR spectra for $PLASPH_2$, $PLASPNa_2$, and the various Co(PLASP)(AA) complexes in $D_2O$ or 70% $H_3PO_4$ are given in Table V. The chemical shifts of the $PLASP^{2-}$ ligand remain constant in all complexes and do not seem to be affected by the type of amino acidate used. This is consistent with assigning the same structure (Figure 1a) to all the various Co(PLASP)(AA) complexes isolated. The α-$CO_2^-$ carbon resonances of the chelated $PLASP^{2-}$ ligand in $D_2O$ were observed to fall in the range 183.0–183.3 ppm while the β-$CO_2^-$ carbon resonances fall in the range 176.6–177.1 ppm. The α-carbon resonances occur in the range 68.4–68.5 ppm and the β-carbon resonances occur at 59.0–59.2 ppm. The above assignments are consistent with the chemical shifts for cobalt complexes containing aspartic acid previously reported.[13,14] The pyridyl methyl carbons fall in the range 37.7–38.0 ppm

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(14) Yasui, T.; Ama, T. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 3171.

Table V. $^{13}C$ NMR of the Co(PLASP)(AA) Complexes in $D_2O$[a]

| | PLASP$^{2-}$ | | | | | PLASP$^{2-}$ | | | | | AA$^-$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| complex | α-$CO_2^-$ | β-$CO_2^-$ | α-C | β-C | py-C-N | 1 | 2 | 3 | 4 | 5 | α-$CO_2^-$ | α-C | β-C | γ-C |
| [Co(PLASP)(Gly)] | 183.1 | 177.0 | 68.4 | 59.0 | 37.8 | 165.2 | 150.1 | 141.6 | 126.0 | 122.9 | 185.6 | 46.8 | | |
| [Co(PLASP)(α-AIBA)]·$H_2O$ | 183.0 | 176.8 | 68.5 | 59.2 | 38.0 | 165.4 | 149.6 | 141.6 | 126.1 | 123.1 | 189.9 | 61.4 | 27.6, 27.5 | |
| [Co(PLASP)(L-Thr)]·$1^1/_2H_2O$ | 183.0 | 177.0 | 68.5 | 59.2 | 37.7 | 165.3 | 150.2 | 141.5 | 125.6 | 122.5 | 184.8 | 66.8 | 63.7 | 18.8 |
| [Co(PLASP)(L-Pro)]·$1^1/_2H_2O$ | 183.0 | 176.9 | 68.6 | 59.1 | 38.0 | 164.7 | 149.8 | 141.7 | 126.3 | 123.6 | 187.1 | 66.3 | 50.0 | 29.3, 26.0 |
| [Co(PLASP)(L-Val)] | 183.0 | 176.9 | 68.5 | 59.2 | 37.9 | 165.5 | 149.7 | 141.6 | 126.0 | 122.8 | 186.0 | 63.9 | 30.2 | 18.1, 15.7 |
| [Co(PLASP)(D-Val)] | 183.1 | 176.6 | 68.4 | 59.2 | 38.0 | 165.4 | 149.7 | 141.5 | 126.1 | 123.1 | 186.1 | 63.4 | 30.0 | 18.6, 16.0 |
| [Co(PLASP)(D,L-Val)] | 183.0, 183.2 | 177.0, 176.7 | 68.5 | 59.2 | 37.9 | 165.5, 165.4 | 149.7 | 141.5 | 126.0 | 122.9, 123.1 | 186.0, 186.1 | 63.7, 63.4 | 30.2, 29.9 | 18.0, 18.5, 15.7, 15.9 |
| [Co(PLASP)(L-AsN)] | 183.2 | 177.1 | 68.5 | 59.1 | 37.9 | 165.0 | 150.9 | 141.5 | 125.4 | 122.5 | 185.0 | 54.9 | 35.6 | 175.2 |
| [Co(PLASP)(D-AsN)] | 183.3 | 176.9 | 68.4 | 59.1 | 37.9 | 165.4 | 149.9 | 141.6 | 126.2 | 123.1 | 185.0 | 55.3 | 37.6 | 174.8 |
| [Co(PLASP)(α-AIBA)]·$H_2O$[b] | 183.1 | 180.4 | 67.5 | 59.4 | 36.8 | 164.9 | 149.7 | 142.9 | 127.2 | 123.9 | 191.0 | 63.0 | 27.8, 27.3 | |
| [Co(PLASP)(L-Ala)][b] | 183.1 | 180.7 | 67.6 | 59.4 | 36.6 | 164.6 | 149.8 | 142.9 | 127.4 | 123.9 | 188.1 | 55.2 | 18.5 | |
| [Co(PLASP)(L-Phe)]·$3H_2O$[b] | 183.3 | 180.2 | 67.9 | | 38.7 | 164.7 | 150.0 | 142.7 | 127.4 | 123.8 | 187.1 | | | 135.2,[c] 129.8 |
| [Co(PLASP)(D-Phe)]·$2H_2O$[b] | 182.9 | 180.5 | 67.6 | | 37.3 | 163.9 | 148.6 | 141.9 | 127.1 | 123.4 | 186.3 | | | 134.1,[c] 130.2 |
| $PLASPH_2$ | 174.8 | 172.4 | 58.5 | 50.5 | 34.7 | 150.1 | 148.9 | 140.2 | 125.4 | 125.2 | | | | |
| $PLASPNa_2$ | 181.2 | 180.1 | 61.5 | 52.6 | 41.8 | 157.9 | 148.8 | 138.6 | 123.6 | 123.4 | | | | |

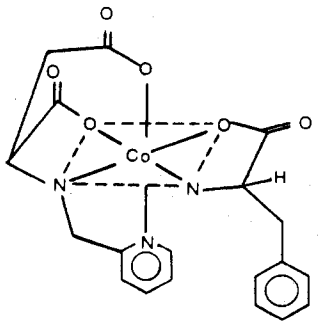
[a] The chemical shifts are given downfield from $Me_4Si$ with dioxane used as an internal reference at 67.0 ppm. [b] In 70% aqueous $H_3PO_4$. [c] Phenyl ring carbon resonances.

while the pyridyl carbons range from 122.5–165.5 ppm and are assigned further in Table V. Spectra of the less soluble complexes containing Ala$^-$ and Phe$^-$ were obtained in 70% $H_3PO_4$ and are similar to the $^{13}C$ spectra of the more soluble complexes in $D_2O$. The largest difference occurs in the chemical shift of the β-$CO_2^-$ carbon of the PLASP$^{2-}$ ligand. This change in the β-$CO_2^-$ carbon resonance may be due to some protonation of the β-$CO_2^-$ group by the $H_3PO_4$ solvent.

The α-$CO_2^-$ and α-carbon resonances of the coordinated amino acidates vary considerably and range from 184.8 to 189.9 ppm and from 46.8 to 66.8 ppm, respectively, and agree with previously reported values for chelated α-amino acidates.[15] The β and γ (or phenyl) carbons are assigned in Table V and also agree with previously reported values.[16]

## Conclusion

In a previous paper we reported the crystal structure for [Co(PLASP)(L-Phe)]·$3H_2O$ as



and suggested that this facial $Co^{III}N_3O_3$ structure was due to a favorable combination of electronic, structural, and steric factors.[2] The coordination of the tetradentate PLASP$^{2-}$ ligand with its pyridyl group trans to the β-$CO_2^-$ group of PLASP$^{2-}$ gives the least strained bond angle around the secondary amino nitrogen and thus is presumably favored structurally over the more strained structure (Figure 1b,d) in which the pyridyl group is trans to the α-$CO_2^-$ group of PLASP$^{2-}$. There were results in the literature to suggest that coordination of the L-Phe$^-$ amino acidate to give a facial isomer is electronically favored over a meridional $Co^{III}N_3O_3$ structure. Finally it was suggested that coordination of the L-Phe$^-$ ligand was sterically favored when compared to a D-amino acidate since the α-carbon of the L-Phe$^-$ chelate ring is pointing up and away from the pyridyl ring.

From the present study it appears that the D or L configuration of the amino acidate does not play a large role in determining the overall geometry of the Co(PLASP)(AA) complexes since the same isomer (Figure 1a) was isolated for both enantiomers of Val$^-$, Phe$^-$, and AsN$^-$. Thus, only electronic and structural factors seem to have a major role in determining the overall geometry of the Co(PLASP)(AA) complexes.

**Acknowledgment.** The authors thank the National Institute of General Medical Sciences for support of this research through Grant GM12626. We thank the National Science Foundation for support of the purchase of the JEOL FX90Q NMR spectrometer.

**Registry No.** Co(PLASP)(Gly), 75046-10-5; Co(PLASP)(L-Ala), 75046-11-6; Co(PLASP)(α-AIBA), 75046-12-7; Co(PLASP)(L-Thr), 75046-13-8; Co(PLASP)(L-Pro), 75059-66-4; Co(PLASP)(L-Val), 75046-14-9; Co(PLASP)(D-Val), 75082-19-8; Co(PLASP)(DL-Val), 75082-20-1; Co(PLASP)(L-AsN), 75046-15-0; Co(PLASP)(D-AsN), 75109-28-3; Co(PLASP)(L-Phe), 75109-62-5; Co(PLASP)(D-Phe), 75082-21-2; $PLASPH_2$, 41203-01-4; $PLASPNa_2$, 75045-92-0; $Na_3[Co(CO_3)_3]$, 23311-39-9.

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(16) Horsley, W.; Sternlicht, H.; Cohen, J. S. *J. Am. Chem. Soc.* **1970**, *92*, 680.