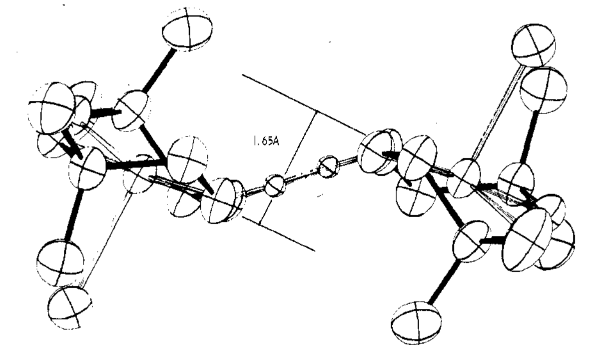

Figure 5. View of the dinuclear cation $[Cu(MepH)(Mep)(H_2O)]_2^{2+}$, showing the "step" arrangement.

results are presented in Table IX.

The hydrogen-bonded complexes $[Cu(EtaH)(Eta)]_2^{2+}$, $[Cu(MepH)(Mep)(H_2O)]_2^{2+}$, and $[Cu(DiimH)]_2$ have very similar structures although in $[Cu(MepH)(Mep)(H_2O)]_2^{2+}$ the coordination of copper is square pyramidal and the other compounds exhibit square-planar coordination. Magnetic and structure parameters are listed in Table X. The two coordination planes (*xy* planes of copper atoms) of each dimer are parallel as a result of a center of inversion, but the separation of these two planes varies from 0.22 Å in one of the $[Cu(DiimH)]_2$ units to 1.65 Å in $[Cu(MepH)(Mep)(H_2O)]_2^{2+}$. The hydrogen-bonded O–O distances also show considerable variation from the 2.31 Å of $[Cu(DiimH)]_2$ to the 2.52 Å of $[Cu(MepH)(Mep)(H_2O)]_2^{2+}$.

Although the strongest antiferromagnetic coupling corresponds to the shortest hydrogen-bonded oxygen–oxygen distance, there is no direct correlation between these parameters for the three compounds; no correlation of the coupling constants with the copper–copper distances or the separation of the coordination planes is apparent for the series of compounds. It is probable that a number of factors, including coordination geometry of copper and additional weak hydrogen bonds, affect the magnitude of the coupling and additional examples of this type of structure are needed for an understanding of these factors.

Acknowledgment. This work was partially supported by NSF Grant GP-20885. The help of the Office of Computer Services, Georgia Institute of Technology, with computations is appreciated.

Registry No. $[Cu(EtaH)(Eta)]_2(NO_3)_2$, 73522-88-0; $[Cu(MepH)(Mep)]_2(NO_3)_2 \cdot 2H_2O$, 73496-14-7; $[Cu(Eph)_2]_3$, 73522-29-9.

Supplementary Material Available: A listing of calculated and observed structure factors (25 pages). Ordering information is given on any current masthead page.

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Synthesis, Spectral Characterization, and Molecular Structure of [*N*-(2-Pyridylmethyl)-L-aspartato](L-phenylalaninato)cobalt(III) Trihydrate, [Co(PLASP)(L-Phe)]·3H$_2$O

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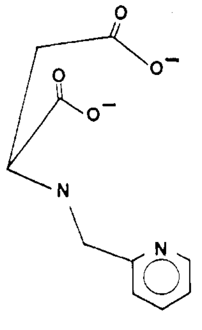
The new $Co^{III}N_3O_3$ complex $[Co(PLASP)(L\text{-}Phe)] \cdot 3H_2O$ was prepared by the oxidation of Co(II) to Co(III) in the presence of *N*-(2-pyridylmethyl)-L-aspartic acid, $PLASPH_2$, and L-phenylalanine, L-Phe. The crystal and molecular structure of the complex, determined by three-dimensional X-ray analysis, established that of the four possible geometrical isomers, the only isomer isolated was a facial isomer in which the β-COO$^-$ and the pyridine groups of PLASP^{2-} are mutually trans. The compound crystallizes in the orthorhombic space group $P2_12_12_1$, with $a = 9.821$ (3) Å, $b = 23.069$ (4) Å, $c = 9.564$ (2) Å, and $Z = 4$. The structure was solved by the heavy-atom method and refined by full-matrix least-squares procedures to a final R factor of 0.059. The geometry around the cobalt atom is distorted octahedral, with the PLASP^{2-} ligand being tetradentate and the L-phenylalaninate ligand bidentate. In addition to the crystal structure, the ^1H NMR and visible spectra of [Co(PLASP) (L-Phe)]·3H$_2$O are discussed.

Introduction

Studies in this laboratory have shown that metal complexes of certain asymmetric tetradentate ligands exhibit stereoselective effects in coordinating optically active amino acids.[1,2] In order to better understand these effects, we have synthesized a series of mixed complexes of the type Co(PLASP)(AA), where PLASP^{2-} is the dianion of the tetradentate *N*-(2-pyridylmethyl)-L-aspartic acid ligand and AA$^-$ is the anion of one of the following amino acids: D- or L-phenylalanine, D-, DL-, or L-valine, L-alanine, L-threonine, L-proline, glycine, and α-aminoisobutyric acid.[3] Although there are four possible geometrical isomers (Figure 1) of these complexes, only one was isolated for all the amino acids listed above. The visible spectra of these complexes, when compared to the spectra of various $Co^{III}N_3O_3$ complexes reported in the literature support a facial arrangement of the oxygen (or nitrogen) atoms around



PLASP^{2-}

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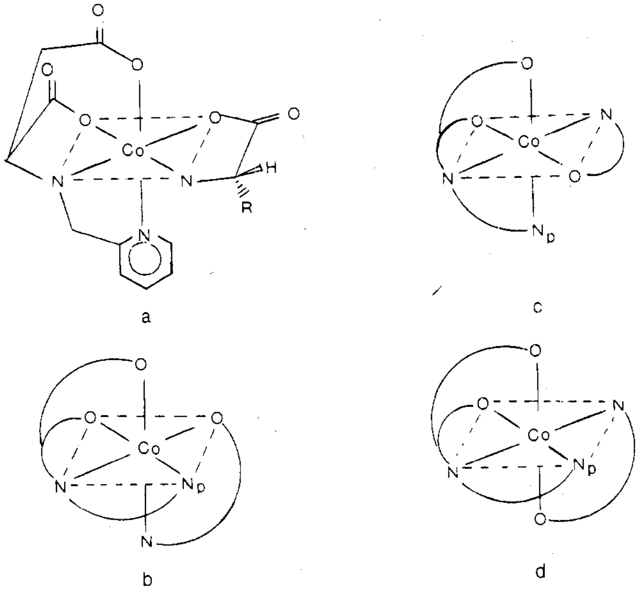

Figure 1. Four possible geometrical isomers of Co(PLASP)(AA): (a) *fac*-β-CO_2^- trans to py, (b) *fac*-α-CO_2^- trans to py, (c) *mer*-β-CO_2^- trans to py, and (d) *mer*-α-CO_2^- trans to py.

the cobalt (Figure 1a,b).[4-6] Since the visible and ^1H NMR spectra do not fully determine the type of facial isomer present, an X-ray structure analysis of [Co(PLASP)(L-Phe)]·3H_2O was undertaken. The synthesis and spectra of this complex are also reported herein.

Experimental Section

Preparation of *N*-(2-Pyridylmethyl)-L-aspartic Acid, PLASPH_2. The synthesis given below is an improvement over that reported previously.[1] To a slurry of L-aspartic acid (53.2 g, 400 mmol) in 150 mL of water was added 4 M NaOH at room temperature until the pH reached 9.7–9.8. The pH increased to 10.1–10.2 after the solution was placed in an ice bath. Next a solution of 2-pyridinecarboxaldehyde (21.4 g, 200 mmol) in 20 mL of water was added dropwise over a period of 1 h to give a pH of 9.6. After the solution was stirred for an additional hour, $NaBH_4$ (3.1 g, 80 mmol) dissolved in 20 mL of water was added dropwise over 30 min. The pH of the solution was slowly brought back to 9.6 with 6 M HCl. The solution was then stirred for 2 h, and more $NaBH_4$ (3.1 g, 80 mmol) in 20 mL of water was added dropwise. After being stirred overnight, the solution was brought to pH 3.2 with 6 M HCl, and the unreacted aspartic acid was filtered off. The solution volume was reduced under vacuum until a solid formed. This solid was filtered; continued reduction of the filtrate gave additional fractions of solid. Each solid fraction was treated with 500–600 mL of boiling methanol and filtered. The methanol solutions were combined and taken to dryness under vacuum. The resulting impure PLASPH_2 was dissolved in 300 mL of water and placed on a 3.6 × 60 cm column of Dowex 50W-X8 (50–100 mesh) ion-exchange resin in the H^+ form. After the column was washed with 2 L of water, the product was eluted off with 0.4 M NH_4OH, and 18-mL fractions were collected. The fractions with a pH between 3 and 4.5 were combined and reduced under vacuum to 100 mL. Next, 500 mL of absolute ethanol was added and the solution placed in a freezer at −10 °C overnight. Twenty-three grams of product was obtained with another 2 g of product obtained by reducing the solution and adding absolute ethanol a second time. The total yield was 25 g (57%).

Preparation of [*N*-(2-Pyridylmethyl)-L-aspartato](L-phenylalaninato)cobalt(III) Trihydrate, [Co(PLASP)(L-Phe)]·3H_2O. To a solution of *N*-(2-pyridylmethyl)-L-aspartic acid (2.24 g, 10 mmol) and NaOH (0.74 g, 18.5 mmol) in 30 mL of water was added a solution of $CoSO_4·7H_2O$ (2.81 g, 10 mmol) and 1.4 mL of 30% H_2O_2. The resulting dark red-brown solution was stirred for 10 min, and a solution of L-phenylalanine (1.65 g, 10 mmol) and NaOH (0.16 g, 4 mmol) in 45 mL of water was added. The solution initially turned dark brown and slowly turned purple over a period of 1.5 h. After the solution was stirred overnight, 1 mL of 30% H_2O_2 in 10 mL of water was added to ensure complete oxidation of the Co(II) to Co(III). This was followed by the addition of 2.5 mL of 1 N H_2SO_4. The solution was heated to 45 °C for 1 h and filtered. The filtrate was carefully reduced under vacuum to a 50-mL volume. Half of this solution was placed on a 4.5 × 45 cm alumina column and eluted with water to give a brown band consisting of decomposition products and a red band containing the product. This red solution was reduced under vacuum to 100 mL and left standing for several days to give red-violet crystals suitable for X-ray analysis. The crystals were filtered and dried under vacuum. The yield of [Co(PLASP)(L-Phe)]·3H_2O was 16%. Anal. Calcd for [Co(PLASP)(L-Phe)]·3H_2O, $C_{19}H_{20}N_3O_6Co·3H_2O$: C, 45.70; H, 5.21; N, 8.37. Found: C, 45.59; H, 5.33; N, 8.41.

Spectra. The visible spectra were recorded in water at room temperature by using a Jasco ORD/UV/CD-5 spectrophotometer. The ^1H NMR spectra were measured by using a Varian Associates HA-100 spectrometer in 99.7% deuterium oxide vs. *tert*-butyl alcohol (δ 1.23) as an internal standard and trifluoroacetic acid as an external lock. Because of its low solubility in water, the ^1H NMR of [Co(PLASP)(L-Phe)]·3H_2O was accumulated by using a Nicolet Instrument Corp. Model 535 Signal Averager. The chemical shifts are reported in ppm downfield from Me_4Si.

Crystal Data. The crystals were obtained directly from the preparation in the form of red prismatic bars. A crystal with approximate dimensions of 0.1 × 0.2 × 0.4 mm was mounted on the end of a glass fiber, long dimension along the fiber axis, with epoxy glue and the fiber subsequently placed in a standard goniometer head. The goniometer was placed on an automatic four-circle X-ray diffractometer, and three initial ω-oscillation photographs were taken at various χ and φ settings by using a Polaroid cassette. From these photographs 12 independent reflections were selected, and their coordinates[5] were input to the automatic indexing program ALICE.[7] The reduced cell and reduced-cell scalars that resulted from ALICE indicated an orthorhombic crystal system. The ω-oscillation photographs around each of the three axes subsequently taken verified the presence of *mmm* Laue symmetry. The observed layer line spacings agreed with the spacings predicted for the cell by the indexing program. A least-squares refinement of the lattice constants was based on the ±2θ measurements of 15 high-angle reflections on a previously aligned four-circle diffractometer (graphite-monochromated Mo Kα radiation, λ = 0.709 54 Å) at 25 °C, yielded *a* = 9.821 (3), *b* = 23.069 (4), and *c* = 9.564 (2) Å. The observed density is 1.5 g/cm^3 by the flotation method, and the calculated density is 1.53 g/cm^3.

Collection and Reduction of X-ray Intensity Data. Data were collected at room temperature by using an automated four-circle diffractometer designed and built in the Ames Laboratory.[8] An ω-step-scan technique was used to measure all data within a 2θ sphere of 50° ((sin θ)/λ = 0.596 Å^{-1}) in two octants. For a check on the electronic and crystal stability, the intensities of three standard reflections were remeasured every 75 reflections. The intensities of these standard reflections did not vary significantly during the collection of 4445 reflections. Examination of the data revealed systematic extinctions for *h*00, *h* = 2*n* + 1, 0*k*0, *k* = 2*n* + 1, and 00*l*, *l* = 2*n* + 1, thus uniquely determining the space group to be $P2_12_12_1$.

The measured intensity data were corrected for Lorentz–polarization effects, but no absorption correction was made since the minimum and maximum transmission factors were 0.84 and 0.92 (μ = 8.84 cm^{-1}). The estimated variance in each intensity was calculated by $\sigma_I^2 = C_T + K_tC_B + (0.03C_T)^2 + (0.03C_B)^2$ where C_T and C_B represent the total and background counts, respectively, K_t is a counting time constant, and the factor 0.03 represents an estimate of nonstatistical errors. The estimated standard deviations in the structure factors were calculated by the method of finite differences.[9] Equivalent reflections were averaged and yielded 1993 reflections with $|F_o| > 3\sigma_{F_o}$ which were retained for use in subsequent calculations.

Solution and Refinement of the Structure. The position of the cobalt atom was obtained by analysis of a sharpened three-dimensional

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Table I. Final Atomic Parameters

(a) Final Positional Parameters ($\times 10^4$) and Their Estimated Standard Deviations (in Parentheses)[a]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Co	4407 (1)	51264 (4)	5229 (1)	C4	3220 (9)	6246 (4)	4527 (10)
O1	5252 (6)	5575 (2)	6664 (6)	C5	7015 (8)	5188 (4)	3929 (11)
O2	6362 (7)	6408 (2)	6951 (7)	C6	6972 (7)	4658 (3)	4786 (10)
O3	3063 (5)	5712 (2)	4925 (6)	C7	8061 (9)	4286 (4)	4874 (12)
O4	2262 (7)	6580 (3)	4403 (9)	C8	7966 (10)	3802 (4)	5763 (11)
O5	3144 (5)	4771 (2)	6458 (5)	C9	6758 (10)	3709 (4)	6485 (10)
O6	1095 (5)	4373 (3)	6508 (7)	C10	5695 (9)	4087 (3)	6332 (9)
O7	5833 (10)	4273 (5)	1997 (14)	C11	2107 (8)	4528 (3)	5860 (8)
O8	−429 (8)	6354 (4)	4648 (9)	C12	2169 (8)	4454 (3)	4285 (8)
O9	7833 (10)	7230 (3)	5461 (11)	C13	1904 (8)	3838 (3)	3797 (10)
N1	5663 (7)	5505 (2)	3980 (7)	C14	2922 (9)	3399 (3)	4291 (9)
N2	5779 (6)	4550 (3)	5496 (6)	C15	3933 (10)	3190 (4)	3353 (12)
N3	3537 (6)	4686 (3)	3782 (7)	C16	4883 (12)	2786 (5)	3781 (14)
C1	5845 (8)	6019 (3)	6207 (9)	C17	4879 (11)	2579 (4)	5098 (17)
C2	5837 (8)	6101 (3)	4630 (10)	C18	3881 (10)	2784 (4)	6079 (14)
C3	4634 (9)	6468 (3)	4152 (10)	C19	2929 (10)	3195 (4)	5658 (10)

(b) Final Thermal Parameters ($\times 10^4$) and Their Estimated Standard Deviations (in Parentheses)[b]

atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	54 (1)	9.0 (0.2)	59 (1)	0 (0.3)	7 (1)	0.5 (0.4)
O1	80 (7)	14 (1)	64 (6)	−5 (2)	−1 (5)	−1 (2)
O2	130 (9)	17 (1)	123 (9)	−21 (3)	−9 (8)	−10 (3)
O3	71 (6)	11 (1)	107 (8)	4 (2)	−3 (6)	5 (2)
O4	99 (8)	16 (1)	246 (15)	13 (3)	22 (10)	17 (4)
O5	55 (5)	16 (1)	60 (6)	−4 (2)	2 (5)	1 (2)
O6	56 (6)	26 (2)	104 (8)	−6 (3)	29 (6)	−4 (3)
O7	256 (18)	46 (3)	388 (25)	−13 (7)	−107 (19)	59 (8)
O8	153 (10)	45 (2)	141 (11)	−22 (4)	−11 (11)	−6 (5)
O9	221 (13)	20 (2)	330 (20)	−13 (4)	76 (16)	8 (5)
N1	66 (7)	9 (1)	84 (8)	4 (3)	11 (8)	−1 (2)
N2	53 (7)	12 (1)	73 (8)	−3 (2)	−1 (6)	−2 (2)
N3	55 (7)	13 (1)	56 (7)	−7 (2)	5 (6)	−3 (2)
C1	61 (9)	14 (2)	76 (9)	1 (3)	−7 (8)	0 (3)
C2	76 (9)	11 (1)	93 (10)	−1 (3)	−1 (9)	−3 (3)
C3	90 (10)	13 (2)	103 (11)	−1 (3)	−10 (10)	5 (3)
C4	96 (10)	13 (2)	81 (11)	8 (3)	−3 (9)	1 (4)
C5	73 (9)	18 (2)	142 (13)	7 (4)	37 (10)	7 (4)
C6	55 (7)	14 (1)	93 (10)	4 (3)	−5 (9)	−6 (4)
C7	91 (10)	32 (2)	134 (14)	18 (4)	17 (12)	0 (5)
C8	85 (10)	18 (2)	127 (13)	14 (4)	−12 (10)	0 (4)
C9	114 (12)	15 (2)	93 (11)	4 (4)	−38 (11)	4 (4)
C10	87 (10)	11 (1)	93 (10)	6 (3)	−9 (10)	−3 (3)
C11	66 (9)	10 (1)	75 (9)	3 (3)	14 (8)	0 (3)
C12	48 (8)	14 (2)	57 (8)	1 (3)	5 (7)	0 (3)
C13	58 (8)	12 (1)	112 (11)	−5 (3)	−15 (9)	−4 (3)
C14	77 (9)	13 (2)	98 (11)	−7 (3)	11 (9)	−3 (3)
C15	112 (12)	20 (2)	162 (16)	2 (4)	45 (12)	−12 (5)
C16	125 (14)	20 (2)	206 (21)	10 (5)	27 (15)	−8 (6)
C17	136 (14)	16 (2)	220 (20)	7 (4)	1 (16)	−10 (6)
C18	98 (11)	19 (2)	213 (19)	−1 (4)	−24 (14)	12 (6)
C19	91 (10)	14 (2)	127 (13)	−6 (4)	−11 (10)	11 (4)

[a] The positional parameters are presented in fractional unit cell coordinates. [b] The β_{ij} are defined by $T = \exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

Patterson function. The remaining atoms were found by successive structure factor[10] and electron density map calculations.[11] Before final refinement, it was observed that large reflections suffered from secondary extinctions effects. These effects were corrected by the approximation $I_o' = I_o/(1 + gI_c)$, where *g* was computed from seven of the largest reflections. The positional parameters for all the nonhydrogen atoms and their anisotropic thermal parameters were refined by a full-matrix least-squares procedure[10] minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma_F{}^2$, to a final conventional residual index of $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.059$. The scattering factors used were those of Hanson et al.[12] modified for the real part of anomalous dispersion.[13]

The final positional and thermal parameters are given in Table I. The standard deviations were calculated from the inverse matrix of the final least-squares cycle.[14] Bond lengths and angles are given in Tables II and III. A listing of the structure factors is available as supplementary material.

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Table II. Interatomic Distances (Å) and Their Estimated Standard Deviations (in Parentheses)

Co–O1	1.909 (5)	C10–N2	1.34 (1)
Co–O3	1.911 (5)	C6–C7	1.37 (1)
Co–O5	1.896 (5)	C7–C8	1.41 (1)
Co–N1	1.926 (6)	C8–C9	1.39 (1)
Co–N2	1.910 (6)	C10–C9	1.37 (1)
Co–N3	1.919 (6)	C11–O5	1.295 (9)
C1–O1	1.257 (9)	C11–O6	1.225 (9)
C1–O2	1.253 (9)	C12–C11	1.52 (1)
C4–O3	1.298 (9)	C13–C12	1.52 (1)
C4–O4	1.22 (1)	C12–N3	1.523 (9)
C1–C2	1.52 (1)	C14–C13	1.50 (1)
C2–C3	1.52 (1)	C14–C15	1.42 (1)
C2–N1	1.518 (9)	C14–C19	1.39 (1)
C5–N1	1.52 (1)	C15–C16	1.38 (1)
C3–C4	1.52 (1)	C16–C17	1.34 (2)
C5–C6	1.47 (1)	C17–C18	1.44 (2)
C6–N2	1.377 (9)	C18–C19	1.39 (1)
O4–O8	2.70 (1)	O7–N3	2.98 (1)
O2–O9	2.78 (1)	O7[a]–O8[b]	2.70 (1)
O9–O4[c]	2.808 (1)	O8[d]–O9	2.76 (1)
O6–N1[e]	2.98 (1)		

[a] Symmetry operation: $x, y, 1 + z$. [b] Symmetry operation: $^1/_2 - x, 1 - y, ^1/_2 + z$. [c] Symmetry operation: $^1/_2 + x, 1^1/_2 - y, 1 - z$. [d] Symmetry operation: $1 + x, y, z$. [e] Symmetry operation: $^1/_2 - x, 1 - y, ^1/_2 + z$.

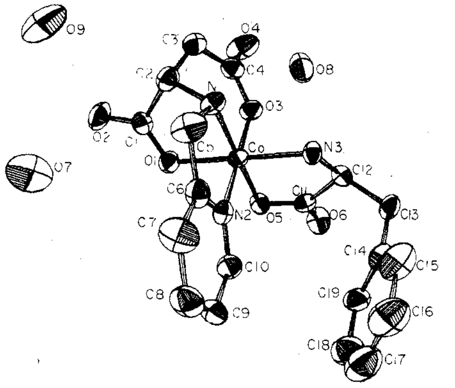

Figure 2. Structure of [Co(PLASP)(L-Phe)]·3H_2O.

Results and Discussion

Table III. Bond Angles (Deg) and Their Estimated Standard Deviations (in Parentheses)

O1–Co–O3	91.5 (2)	N1–C2–C3	107.1 (7)
O1–Co–O5	94.2 (2)	C1–C2–C3	111.8 (7)
O1–Co–N1	85.5 (2)	C2–C3–C4	116.6 (7)
O1–Co–N2	88.6 (2)	O3–C4–O4	122.4 (8)
O3–Co–O5	87.0 (2)	O3–C4–C3	119.9 (7)
O3–Co–N1	91.6 (2)	O4–C4–C3	117.7 (7)
O3–Co–N3	87.5 (3)	N1–C5–C6	110.9 (6)
O5–Co–N2	94.5 (3)	N2–C6–C5	116.7 (7)
O5–Co–N3	85.8 (2)	N2–C6–C7	121.2 (8)
N1–Co–N2	86.9 (3)	C5–C6–C7	122.1 (8)
N1–Co–N3	94.5 (3)	C6–C7–C8	118.8 (9)
N2–Co–N3	92.4 (3)	C7–C8–C9	118.6 (8)
O1–Co–N3	179.0 (3)	C8–C9–C10	120.0 (8)
O3–Co–N2	178.5 (3)	C9–C10–N2	121.7 (8)
O5–Co–N1	178.5 (3)	O5–C11–O6	122.8 (7)
Co–O1–C1	113.2 (5)	O5–C11–C12	117.1 (7)
Co–O3–C4	129.2 (5)	O6–C11–C12	120.1 (8)
Co–O5–C11	115.3 (5)	N3–C12–C11	108.1 (7)
Co–N1–C2	103.2 (5)	N3–C12–C13	112.4 (6)
Co–N1–C5	111.2 (5)	C11–C12–C13	113.8 (7)
Co–N2–C10	126.3 (5)	C12–C13–C14	114.9 (7)
Co–N2–C6	114.1 (5)	C13–C14–C15	119.7 (8)
Co–N3–C12	110.5 (5)	C13–C14–C19	121.9 (8)
C2–N1–C5	110.6 (6)	C15–C14–C19	118.4 (9)
C6–N2–C10	119.5 (7)	C14–C15–C16	121 (1)
O1–C1–O2	125.1 (8)	C15–C16–C17	121 (1)
O1–C1–C2	116.3 (7)	C16–C17–C18	120 (1)
O2–C1–C2	118.5 (8)	C17–C18–C19	120 (1)
N1–C2–C1	107.1 (7)	C14–C19–C18	120 (1)

Description and Discussion of the Structure. The crystal structure of [Co(PLASP)(L-Phe)]·3H_2O consists of discrete molecules having a slightly distorted octahedral coordination geometry around the cobalt atom. All three waters (O7, O8, O9) of hydration provide crystalline stability by forming strong hydrogen bonds between complexes in neighboring unit cells and asymmetric units. The various hydrogen bonds are given in Table II. Strong interactions occur between the carboxylate oxygen, O2, the water molecule, O9, and the carboxylate oxygen, O4, of a neighboring asymmetric unit ($^1/_2 + x, 1^1/_2 - y, 1 - z$). Other hydrogen bonding interactions connecting various asymmetric units involve a series of three hydrogen bonds such as O4 $(1 + x, y, z)$···O8$(1 + x, y, z)$···O9···O2. Additional crystalline stability is provided by the weaker hydrogen bond between O6 and N1 of an adjacent unit ($^1/_2 - x, 1 - y, ^1/_2 + z$). The atoms are labeled as shown in Figure 2. A stereographic view of the unit cell and adjacent moieties of [Co(PLASP)(L-Phe)]·3H_2O is presented in Figure 3.

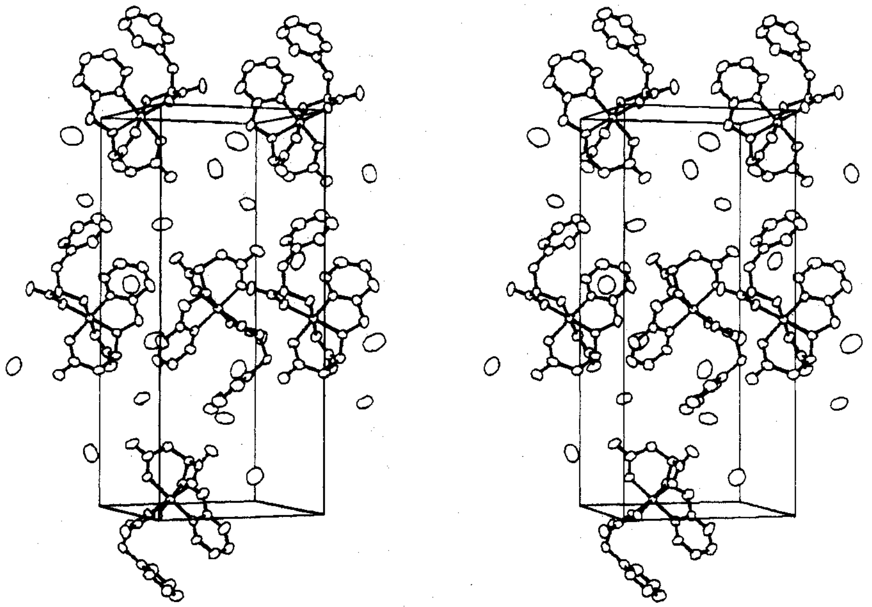

Figure 3. Stereoscopic view of the unit cell with the *a* axis horizontal and the *b* axis vertical.

The coordination about the cobalt atom can be considered to be facial, since the three carboxylic oxygens (O1, O3, O5) occupy one triangular face of the coordination octahedron and the three nitrogen atoms (N1, N2, N3) occupy another face. The L-aspartic acid portion of the $PLASP^{2-}$ ligand is facially coordinated to the cobalt atom through its α-amino nitrogen (N1), α-carboxylate oxygen (O1), and β-carboxylate oxygen (O3). This mode of coordination is similar to that found for various bis(L-aspartato)cobalt(III) complexes previously reported in the literature.[15,16] The *N*-(2-pyridylmethyl) group is attached to the cobalt atom through the pyridine nitrogen (N2) and occupies a position trans to the β-carboxylate oxygen (O3). The bidentate amino acid, L-phenylalanine, occupies the two remaining coordination sites about the cobalt atom. The α-amino nitrogen (N3) of phenylalanine is coordinated to the cobalt in a position trans to the α-carboxylate oxygen (O1) of $PLASP^{2-}$, and its α-carboxylate oxygen (O5) is attached trans to the secondary nitrogen (N1) of the $PLASP^{2-}$ ligand. The absolute configuration about the cobalt atom was assigned by using optically active amino acids of known configuration in the synthesis of the complex.

The bond distances observed within the $PLASP^{2-}$ and L-Phe^{-} ligands are comparable to average values found in structures of other complexes containing aspartic acid,[15,16] phenylalanine,[17] and pyridine[18-20] ligands. For the β-carboxylate of $PLASP^{2-}$ and the α-carboxylate of L-Phe^{-}, two different C–O bond distances are observed. The C-O distances (C4–O3 = 1.298 (9) Å; C11–O5 = 1.295 (9) Å) for the coordinated oxygen atoms are significantly longer than those (C4–O4 = 1.22 (1) Å; C11–O6 = 1.225 (9) Å) for the uncoordinated "carbonyl-type" oxygen atoms, as observed in other cobalt(III) complexes containing coordinated amino acids.[21-25] On the other hand, the C–O distances of both the coordinated (C1–O1 = 1.257 (9) Å) and the uncoordinated (C1–O2 = 1.253 (9) Å) oxygen atoms appear to be equal in the α-carboxylate group of $PLASP^{2-}$. This has been noted before in the literature.[26]

The bond distances Co–N1 (1.926 (6) Å), Co–N3 (1.919 (6) Å), Co–O1 (1.909 (5) Å), Co–O3 (1.911 (5) Å), and Co–O5 (1.896 (5) Å) are similar to the cobalt secondary amino nitrogen,[21,24,27-30] cobalt primary amino nitrogen,[31-34] and cobalt carboxylate oxygen[15,16,21-29,31-35] distances found in other cobalt(III) complexes containing polyamines, amino acids, and amino polycarboxylates. The cobalt–pyridine bond distance (Co–N2 = 1.910 (6) Å) compares closely with the Co(III)–N(sp^2) distances reported for other Co(III) complexes containing coordinated pyridine and imidazole.[20,24,34]

Table IV. Equations of Least-Squares Planes[a]

atom	D^b	atom	D
Plane 1: O1–O5–N1–N3			
$0.6535X + 0.7414Y - 0.1524Z - 5.1979 = 0$			
Co	−0.0204	C1	0.4416
O1	−0.0038	C2	0.8186
O5	0.0038	C3	2.2862
N1	0.0037	C4	2.7593
N3	−0.0038	C11	0.3408
N2	−1.9250	C12	0.4040
		C13	−0.4084
Plane 2: (pyridine ring) C6–C7–C8–C9–C10–N2			
$0.3482X + 0.5403Y + 0.7660Z - 11.70 = 0$			
N2	−0.0078	N1	0.0322
C5	0.0620	C10	−0.0011
C6	0.0146	Co	0.0453
C7	−0.0122	O3	0.0934
C8	0.0033	O5	0.0713
C9	0.0032		
Plane 3: O5–C11–O6–C12			
$-0.4144X + 0.9013Y - 0.1260Z - 7.8600 = 0$			
Co	0.3751	O6	0.0031
O5	0.0028	C12	0.0023
C11	−0.0083	N3	−0.0113
Plane 4: (phenyl ring) C14–C19			
$0.6169X + 0.7373Y + 0.2755Z - 8.6903 = 0$			
C13	−0.0087	C17	−0.0048
C14	−0.0084	C18	−0.0023
C15	0.0014	C19	0.0089
C16	0.0052		

[a] Planes are defined as $C_1X + C_2Y + C_3Z + C_4 = 0$ where *X, Y,* and *Z* are Cartesian coordinates. [b] *D* is the distance (Å) of the given atom from the fitted plane.

The deviations of the bond angles around the cobalt atom from ideal octahedral geometry range from 1.5 to 4.5°. The greatest deviations from 90° occur for the angles contained in the three five-membered chelate rings, O1–Co–N1, 85.5 (2)°, N1–Co–N2, 86.9 (3)°, and O5–Co–N3, 85.8 (2)°, and the angles in the same plane as a five-membered ring, N1–Co–N3, 94.5 (3)°, O1–Co–O5, 94.2 (2)°, and O5–Co–N2, 94.5 (3)°. The O–Co–N bond angles of the five-membered "glycinate-type" rings are consistent with angles reported for other Co(III) amino acid complexes.[15-35] The smallest angular deviation from ideal geometry is for the O1–Co–O3 (91.5 (2)°) angle contained in the six-membered ring of the $PLASP^{2-}$ ligand, and this value is consistent with those reported for bis(aspartato)cobalt(III) complexes.[15,16]

The largest deviation of the cobalt atom out of a coordination plane occurs for the O1–O5–N1–N3 plane. The cobalt atom is displaced 0.02 Å out of this plane toward the pyridine nitrogen N2 (plane 1, Table IV). Also the distance from the cobalt to the plane defined by the pyridine ring is 0.045 Å and is somewhat shorter than the distances reported previously.[25] The coordination plane O3–N1–N2–O5–Co and the pyridine plane N2–C6–C7–C8–C9–C10 (plane 2, Table IV) are nearly parallel as demonstrated by the small dihedral angle of 1.60° between these two planes. Additional evidence of the near parallelism of the pyridine and O3–N1–N2–O5–Co planes is

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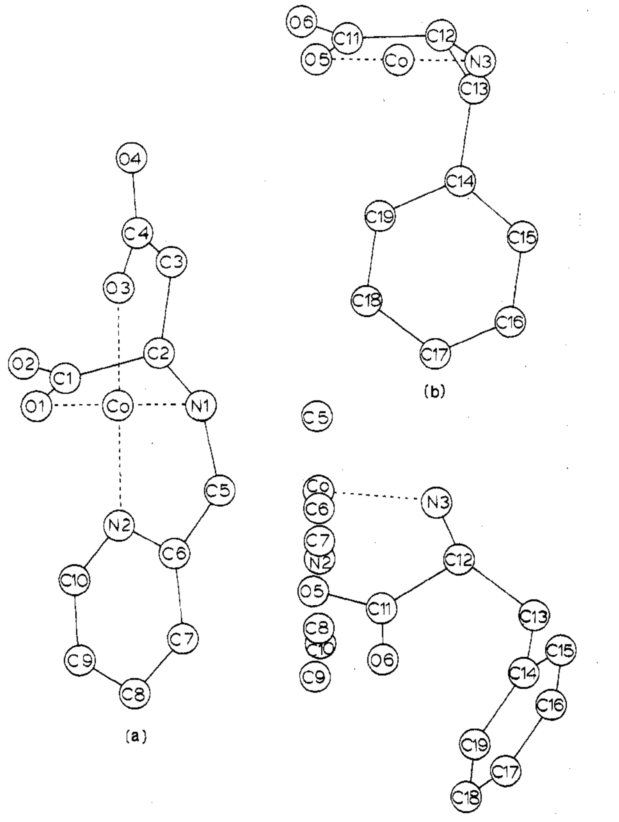

Figure 4. Projections of various parts of [Co(PLASP)(L-Phe)]·3H$_2$O: (a) PLASP^{2-}, (b) L-Phe$^-$ chelate ring, and (c) the pyridine and phenyl rings as viewed parallel to the pyridine ring.

the small deviation of N1 (0.03 Å), C5 (0.06 Å), O3 (0.09 Å), and O5 (0.07 Å) out of the plane defined by the pyridine (plane 2, Table IV).

The five-membered glycinate ring of the PLASP^{2-} ligand is in an asymmetric-envelope conformation with the β-carbon (C3) in an axial position as shown in Figure 4a. The torsional angle, N1–C2–C1–O1, of 24.6° falls within the 0–30° range observed for other coordinated amino acids.[36]

In addition to the asymmetric carbons in the ligands, the coordination of the PLASP^{2-} ligand to the cobalt atom gives rise to an asymmetric secondary nitrogen, N1, which has the R absolute configuration. The configuration of the PLASP^{2-} chelate rings seems to produce little angular strain in the C2–N1–C5 bond angle (110.6 (6)°), which is close to the ideal tetrahedral value of 109.5°. This nearly ideal bond angle may possibly be used to explain why the pyridine coordinates trans to the β-COO$^-$ group of PLASP^{2-} instead of in the somewhat more strained position trans to the α-COO$^-$ group of PLASP^{2-}. This angular strain has been noted before for Co(III) complexes containing polydentate chelates such as iminodiacetic acid and ethylenediaminetetraacetic acid.[21,29]

The five-membered ring of the phenylalanine ligand is also coordinated to the cobalt atom in an asymmetric envelope configuration. This is shown in Figure 4b. The α-carbon, C12, is displaced out of the N1–N3–Co–O1–O5 plane in a direction away from the pyridine ring. This displacement of the α-carbon along with the bending of the chelate ring puts the phenyl, R group, in an equatorial position as opposed to an axial position with reference to the N1–N3–Co–O1–O5 plane. The atoms of the phenylalanine ligand (O5, C11, O6, C12, N3) are nearly planar, as demonstrated by a torsional angle of 1.43° (N3–C12–C11–O5 angle) and the fact that N3 deviates only 0.01 Å out of the O5–O6–C11–C12 plane (plane 3, Table IV). The phenyl group of the phenylalanine ligand is planar with the largest deviation from planarity being 0.009 Å (plane 4, Table IV). The dihedral angle between the planes defined by the pyridine and phenyl rings is 34.5°, and the closest distance between the two rings is 3.46 (1) Å (for C17···C9). The phenylalanine ligand does not appear to interact sterically with any part of the PLASP^{2-} ligand. The spacial relationship between the pyridine and phenyl rings is shown in Figure 4c.

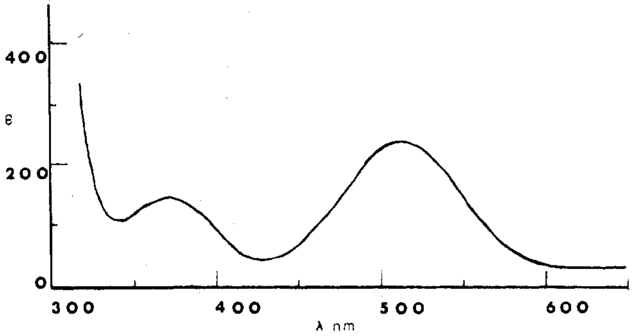

Figure 5. Visible spectrum of [Co(PLASP)(L-Phe)]·3H$_2$O.

Discussion of Spectra. In the ^{1}H NMR spectrum of the free ligand, PLASPH$_2$, the α-proton of the aspartic acid portion of the molecule occurs as a triplet centered at δ 4.03, and the β-protons of the aspartic acid portion occur as a doublet centered at δ 3.01. The methylene protons of the pyridylmethyl group occur as a singlet centered at δ 4.50, while the pyridyl protons occur as a doublet centered at δ 8.62 for the ortho proton, a triplet centered at δ 8.01 for the para proton, and an overlapping doublet and triplet at δ 7.65–7.48 for the two meta protons.

The accumulated spectrum of the [Co(PLASP)(L-Phe)]·3H$_2$O complex in D$_2$O at room temperature gives a multiplet centered at δ 7.47 for the pyridyl meta protons, a doublet centered at δ 7.87 for the ortho proton, a triplet centered at δ 8.00 for the pyridyl para proton, a multiplet at δ 7.24 for the phenyl protons, and overlapping multiplets at 3.1 for the β-PLASP^{2-} and β-L-Phe$^-$ protons. The methylene protons of the pyridylmethyl fragment occur as two doublets centered at δ 4.48 and 5.29, with a coupling constant of 18 Hz. The α-proton of L-Phe$^-$ occurs as a multiplet centered at δ 4.10 while the α-proton of PLASP^{2-} occurs as a multiplet at δ 3.93.

The ^{1}H NMR spectrum of the Co complex supports a facial geometry around the cobalt ion. The splitting of the methylene protons of the pyridylmethyl group from a singlet into two doublets shows that the chemical environments on both sides of the plane formed by the coordinated –NH–CH$_2$–py group in the complex are different (i.e., on one side is a coordinated nitrogen and on the other is an oxygen).

The visible spectrum is given in Figure 5. The visible spectrum for the complex shows two symmetrical peaks at 371 nm (ϵ = 138 cm^{-1} M^{-1}) and 513 nm (ϵ = 226 cm^{-1} M^{-1}). This spectrum is very similar to those of facial Co^{III}N$_3$O$_3$ complexes of amino acids and their derivatives reported previously in the literature.[4-6]

Conclusion

Attempts to prepare the other isomers of Co(PLASP)(AA) complexes (Figure 1b,c,d) by other synthetic routes[3] have given only the facial isomer in which the pyridine is coordinated trans to the β-CO$_2^-$ group (Figure 1a). This may be due to a combination of electronic, structural, and steric factors. If the PLASP^{2-} ligand is considered first, there are two ways the pyridine nitrogen can coordinate as shown in Figure 1a,b. The difference in electronic factors between these two sites should

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[36] Hawkins, C. J. "Absolute Configuration of Metal Complexes"; Wiley-Interscience: New York, 1971, p 94.

be small, since the pyridine is coordinated trans to a CO_2^- group in both cases. Structurally these two sites are not equivalent. It has been noted before that polydentate ligands such as $^-O_2C-CH_2-NH-CH_2-CO_2^-$, $IMDA^{2-}$, can coordinate in two ways.[21,29,35] In the facial mode, the glycinate chelate rings are 90° to each other, and there is very little strain in the C–N–C angle. In the meridional mode the glycinate chelate rings are in the same plane. This type of coordination causes considerable strain in the C–N–C angle. Thus coordination of the pyridine trans to the β-CO_2^- group in Co(PLASP)(L-Phe) likewise gives the least strain at N1 and allows the rigid chelate ring Co–N1–C5–C6–N2 (along with the entire pyridine ring) to be planar.

If the coordination of the phenylalaninate ligand is considered next, there are two ways it can coordinate as shown in Figure 1a,c. Coordination as in Figure 1a would be electronically favored since the amino group is trans to oxygen (the carboxylate group). It has been noted before,[6,37,38] that amino groups avoid coordinating trans to each other, which would favor the structure in Figure 1a over that in Figure 1c. Additional support for facial coordination is given in an earlier theoretical account of bonding in transition-metal complexes which states that the most stable isomer for low-spin d^6 $ML_3L'_3$ complexes should be facial.[39] This appears to be the case in complexes where no steric interaction is evident. Also, coordination as in Figure 1a is sterically favored since the α-carbon of the phenylalaninate chelate ring is pointing up and away from the pyridine ring. This configuration of the L-Phe^- ring is determined by the bulky R group, $-CH_2-Ph$, which would favor the equatorial rather than axial position.

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Registry No. [Co(PLASP)(L-Phe)]·$3H_2O$, 73396-77-7; $PLASPH_2$, 41203-01-4; L-aspartic acid, 56-84-8; 2-pyridinecarboxaldehyde, 1121-60-4.

Supplementary Material Available: A table listing observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

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Coordination Chemistry of Microbial Iron Transport Compounds. 20. Crystal and Molecular Structures of Two Salts of *cis*- and *trans*-Tris(benzohydroximato)chromate(III)[1]

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The isolation of crystalline solids of *cis*- and *trans*-tris(benzohydroximato)chromate(III) salts is reported. The structures of both isomers have been determined by single-crystal X-ray diffraction, using automated counter data. Interisomerization of the neutral hydroxamato and anionic hydroximato complexes occurs via loss of a proton on the hydroxamate nitrogens. This deprotonation results in only small changes in the geometry of either the CrO_6 coordination polyhedron or the ligand. These results support a view of these complexes as rigid, octahedral complexes in which the hydroxamate ligand has substantial negative charge on both oxygen atoms and nearly full formation of a C=N double bond in the center of the ring. The Cr–O bond lengths average 1.955 (13) and 1.987 (12) Å for the *N*-hydroxyl and carbonyl oxygens in the trans isomers, while the corresponding distances in the cis isomer are 1.951 (4) and 1.965 (2) Å. The structures of the *cis*- and *trans*-tris(benzohydroximato)chromate(III) complexes were solved by direct phasing methods followed by full-matrix least-squares and Fourier techniques. Green-purple crystals of the cis isomer conform to space group $P\bar{3}c1$ with $a = 13.762$ (1) Å, $c = 26.238$ (2) Å, $V = 4304$ (2) Å^3, $Z = 4$, $\rho_{calcd} = 1.58$ g cm^{-3}, and $\rho_{obsd} = 1.57$ g cm^{-3}. Refinement using 2612 reflections with $F^2 > 3\sigma(F^2)$ gave $R = 4.39\%$ and $R_w = 6.45\%$. Green-purple crystals of the trans isomer conform to space group $P2_1/n$ with $a = 10.310$ (3) Å, $b = 11.208$ (2) Å, $c = 28.638$ (5) Å, $\beta = 93.65$ (2)°, $V = 3203$ (2) Å^3, $Z = 4$, $\rho_{calcd} = 1.44$ g cm^{-3}, and $\rho_{obsd} = 1.42$ g cm^{-3}. Refinement using 4617 reflections with $F^2 > 3\sigma(F^2)$ gave $R = 3.89\%$ and $R_w = 4.61\%$.

Introduction

The siderophores are low-molecular-weight compounds whose manufacture by microbes, in order to facilitate the uptake of ferric iron, we have described in previous papers in this series[1] and in recent reviews.[3] The most common functional groups in the siderophores are the hydroxamate group as in ferrichromes[4] and ferrioxamines[5] and the catecholate group as in enterobactin.[6] Replacing the ferric ion (high-spin d^5 system) by the chromic ion (d^3) produces inert complexes which may be used as chemical probes in studying the iron-transport mechanism in living systems.[7,8] Unlike the ferric

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