overlap populations of 0.50 and 0.55 for the NN and NS linkages, respectively. This value for the SN overlap suggests a strengthened single bond (cf. to the case of S_4N_4 where the overlap population is 0.49 and the case of $S_3N_3^-$ where it is 0.52). The charges of −0.027 for the terminal nitrogen, 0.012 for the central nitrogen, and 0.014 for sulfurs are much smaller in magnitude than in any of the symmetric NSN species mentioned above.

Discussion

The $S_4N_5^-$ species which has been offered (eq 1) as a possible source of N_2S has an NSN angle of 108°, an NS bond length of 1.62 Å,[6] and an NS overlap population of 0.38. This is rather similar to the species we have denoted by NSN90 with bond length 1.63 Å and NS overlap population of 0.41. Taking into account the channels sketched in Figure 1, one can estimate a barrier of this species to decomposition of about 9–15 kcal and a barrier for the NSN180 species of about 15–25 kcal.

The transformation of NSN90 → NSN180 involves the crossover of electrons from orbital $4a_1$ to the orbital $3b_2$. On the other hand the transformation of NSN90 to the decomposition channel involves the crossover of electrons from orbital $1a_2$ to the orbital $2b_1$. Both one-electron processes would require a perturbation with b_2 symmetry. Thus both of the transformations of NSN90 require the same one-electron perturbation. In the context of the location of NSN in the parent species, e.g., in $S_4N_5^-$, this would require that the perturbation be asymmetric with respect to a plane passing through the bridging nitrogen N_B and the two sulfur atoms below the N_4 plane (cf. eq 1). It is easy to see that $S_4N_5^-$ or an initial transition state would be symmetric to this symmetry element. Consequently there is some chance that NSN90 could be cleaved intact although the barrier to the decomposition channel is not large. Certainly the experimental work to date[1,2] which yields N_2 and S^0 (or S_8) suggests that for cleavage at ca. 80 °C the decomposition channel is readily accessible. However in less vigorous or in constrained environments (e.g., glasses) access to this channel may be more difficult.

Another a priori possibility for the decomposition of NSN is the asymmetrical distortion leading to NS + N products which should themselves be reactive; again we remark that production of N_2 and S in the experiments mentioned above does not seem to favor this path. A further alternative is the assymetric rearrangement of NSN to the apparently stable NNS. But since NNS has a relatively strong NS bond it would not seem likely that under these conditions linear NNS would be the precursor to the observed N_2 and S decomposition products. We have not probed the channels appropriate to these cases primarily because they are likely to involve a pathway requiring a judicious sequence of variations in all three parameters θ_{SNN}, R_{NS}, and R_{NN}.

Conclusions

Our calculations point to NNS as the lowest energy N_2S species. Further we have detected two metastable species NSN90 and NSN180 which are in an energy minimum to symmetric variation. For one of these metastable species, NSN90, there is a barrier of roughly 9–15 kcal to decomposition to N_2 + S.

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Synthesis and Spectral Characterization of *fac*- and *mer*-[*N*-(Carboxymethyl)-L-β-(2-pyridyl)-α-alaninato](D-threoninato)cobalt(III), [Co(*N*-Cm-L-Pyala)(D-Thr)], and the Molecular Structure of the *mer* Isomer

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Oxidation of Co(II) to Co(III) in the presence of *N*-(carboxymethyl)-L-β-(2-pyridyl)-α-alaninate (*N*-Cm-L-Pyala^{2-}) and D-threoninate (D-Thr$^-$) produced two isomers of the complex [Co(*N*-Cm-L-Pyala)(D-Thr)] which were easily separated on acidic alumina. On the basis of their visible spectra, one isomer was assigned a structure in which the nitrogen atoms are arranged meridionally around the cobalt, while the other was assigned to the only possible facial isomer. Of the three possible meridional isomers, the one isolated was assigned a structure in which the amino nitrogen of the D-Thr$^-$ ligand is coordinated trans to the pyridyl nitrogen of the *N*-Cm-L-Pyala^{2-} ligand. This assignment was based on the presence of a shoulder on the low-wavelength side of the 537-nm absorption observed in its visible spectrum. This geometry was confirmed by a three-dimensional X-ray analysis of *mer*-[Co(*N*-Cm-L-Pyala)(D-Thr)]·$^1/_2$$H_2O$. The compound crystallizes in the monoclinic space group $P2_1$ with a = 10.350 (4) Å, b = 10.339 (4) Å, c = 15.340 (6) Å, β = 92.98 (5)°, and Z = 4. The structure was solved by the heavy-atom method and refined initially by block-matrix least-squares and finally by full-matrix least-squares procedures to a final weighted R factor of 0.084. In addition to the crystal structure of *mer*-[Co(*N*-Cm-L-Pyala)(D-Thr)]·$^1/_2$$H_2O$, the ^1H NMR, visible, and CD spectra of both the *mer*- and *fac*-[Co(*N*-Cm-L-Pyala)(D-Thr)] isomers are discussed.

Introduction

Metal complexes of the two asymmetric tetradentate ligands *N*-(2-pyridylmethyl)-L-aspartate (PLASP^{2-}) and *N*-(carboxymethyl)-L-β-(2-pyridyl)-α-alaninate (*N*-Cm-L-Pyala^{2-}) exhibit stereoselective effects in coordinating optically active amino acidates (AA$^-$).[1,2] Stereoselectivity has also been found in

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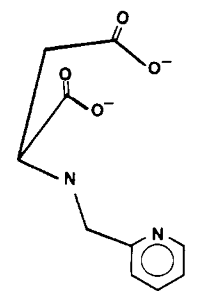
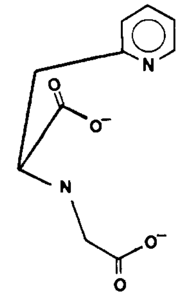
(1) Nakon, R.; Rechani, P. R.; Angelici, R. J. *Inorg. Chem.* **1973**, *12*, 2431.


PLASP^{2-}


N-Cm-L-Pyala^{2-}

the formation of their Co(III) complexes. Thus the only isolated isomer of the Co(PLASP)(AA) complexes is a facial isomer in which the pyridine nitrogen is coordinated trans to the β-carboxylate group of the PLASP^{2-} ligand.[3,4] This coordination geometry was ascribed to a combination of electronic, structural, and steric factors. For further investigation of these factors, a series of mixed complexes of the type Co(*N*-Cm-L-Pyala)(AA), where AA$^-$ is a potentially bidentate amino acidate, was prepared.

Comparison of the two ligands PLASP^{2-} and *N*-Cm-L-Pyala^{2-} shows that the pyridyl and β-CO$_2^-$ groups of PLASP^{2-} are interchanged in the *N*-Cm-L-Pyala^{2-} ligand. In view of the seemingly minor structural differences between these ligands, it was of interest to compare structures of their Co(III) complexes for the purpose of understanding the factors which contribute to the formation of the observed Co(III) complex isomers. For this reason, isomers of Co(*N*-Cm-L-Pyala)(AA) (Figure 1) were prepared and structurally characterized for comparison with the analogous Co(PLASP)(AA) and other related Co^{III}N$_3$O$_3$ complexes.[3-7]

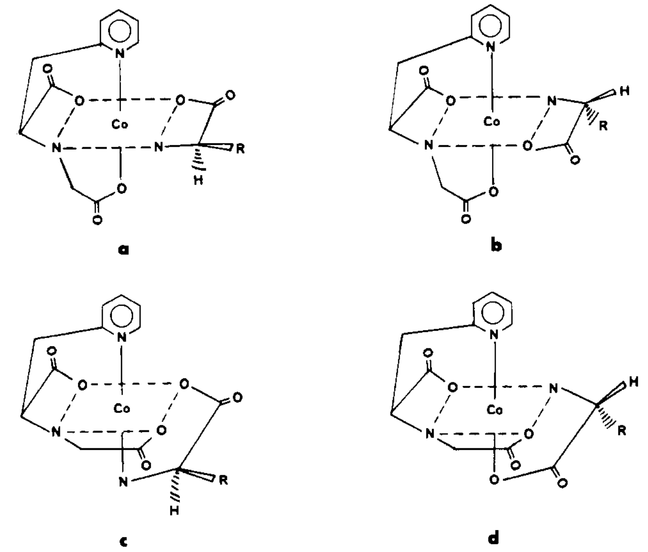


Figure 1. Four possible isomers of Co(*N*-Cm-L-Pyala)(D-AA): (a) *fac*, (b) *mer* *N*-Cm-CO$_2^-$, (c) *mer* AA$^-$ amino, and (d) *mer* AA$^-$CO$_2^-$.

Experimental Section

Purification of *N*-(Carboxymethyl)-L-β-(2-pyridyl)-α-alanine, *N*-Cm-L-PyalaH$_2$. The ligand *N*-Cm-L-PyalaH$_2$ was prepared as previously reported.[2] Its purification was performed by ion-exchange chromatography using Dowex 50W-X8 (50–100 mesh) in the H$^+$ form in a manner similar to that described previously for *N*-(2-pyridylmethyl)-L-aspartic acid.[4] Fractions with pH values between 2.8 and 4.0 were combined and reduced to near dryness. Absolute ethanol was added to precipitate additional product, and the resulting slurry was filtered. The product, *N*-Cm-L-PyalaH$_2$, was identified by comparing its melting point and ^{1}H NMR spectrum to those previously reported.[2]

Preparation of *fac*-[*N*-(Carboxymethyl)-L-β-(2-pyridyl)-α-alaninato](D-threoninato)cobalt(III) Hydrate, *fac*-[Co(*N*-Cm-L-Pyala)(D-Thr)]·H$_2$O, and *mer*-[*N*-(Carboxymethyl)-L-β-(2-pyridyl)-α-alaninato](D-threoninato)cobalt(III) Hemihydrate, [Co(*N*-Cm-L-Pyala)(D-Thr)]·$^1/_2$H$_2$O. To an aqueous solution containing D-threonine (0.30 g, 2.5 mmol), *N*-Cm-L-PyalaH$_2$ (0.56 g, 2.5 mmol) and 6 mL of 1.0 N NaOH in 20 mL of water was added a solution of CoSO$_4$·7H$_2$O (0.70 g, 2.5 mmol) and 3 mL of 5% H$_2$O$_2$ (aqueous) in 15 mL of water. The reaction mixture was stirred overnight at room temperature to give a purple solution. This solution was filtered and reduced to ~10 mL under vacuum, giving a reddish pink precipitate which was later identified as the facial isomer. The facial isomer was filtered off, and the remaining solution was placed on a column (1.7 × 55 cm) of acidic alumina (120 mL). The column was eluted with 40:60 EtOH/H$_2$O to give two bands. The purple meridional isomer along with other impurities was not adsorbed on the column and eluted as band I. The less soluble facial isomer was retained on the column and slowly moved down the column as band II. Band II was reduced to near dryness under vacuum, yielding the facial isomer as a reddish pink solid which was removed by filtration and washed with 95% ethanol. Band I was reduced to dryness under vacuum, dissolved in 3–4 mL of water, loaded on a column (1.5 × 65 cm) of Dowex 50W-X8 (100–200 mesh) in the Na$^+$ form, and eluted with water to give two bands. The first was light brown and contained decomposition products along with Na$_2$SO$_4$. The second band which contained the purple meridional isomer was reduced to dryness under vacuum and dissolved in 2 mL of H$_2$O. The solution was filtered through glass wool into a 10-mm NMR tube. After the solution stood for several days, crystals began to form. These were filtered and found to be suitable for X-ray analysis. A second batch of crystals was obtained by addition of 95% EtOH to the filtrate. The total yield of the facial isomer was 145 mg (15%), and that of the meridional isomer was 56 mg (6%). Anal. Calcd for *fac*-[Co(*N*-Cm-L-Pyala)(D-Thr)]·H$_2$O, C$_{14}$H$_{18}$N$_3$O$_7$Co·H$_2$O: C, 40.30; H, 4.80; N, 10.07. Found: C, 40.36; H, 5.14; N, 10.05. Calcd for *mer*-[Co(*N*-Cm-L-Pyala)(D-Thr)]·$^1/_2$H$_2$O, C$_{14}$H$_{18}$N$_3$O$_7$Co·$^1/_2$H$_2$O: C, 41.19; H, 4.66; N, 10.30. Found: C, 41.87; H, 4.79; N, 10.30.

Spectra. Visible and circular dichroism spectra were recorded in water at room temperature with use of a Jasco ORD/UV/CD-5 spectrophotometer. Proton NMR spectra of the meridional and facial isomers and the free ligand *N*-Cm-L-PyalaH$_2$ were recorded at room temperature on a Jeol FX-90Q spectrometer in 99.7% deuterium oxide with *tert*-butyl alcohol (δ 1.23) as an internal reference and deuterium oxide as an internal lock. The peak positions (δ) are given in ppm downfield from Me$_4$Si.

Crystal Data. The crystals were obtained as red-violet elongated hexagonal plates in the manner described above. A crystal of approximate dimensions 0.08 × 0.2 × 0.25 mm (μ = 11.4 cm^{-1} for Mo Kα radiation) was mounted on a glass fiber. The fiber was then positioned on a goniometer head, and three preliminary ω-oscillation photographs were taken at various χ and Φ settings on an automated four-circle diffractometer. From these photographs 10 independent reflections were selected, and their coordinates were input to the automatic indexing program ALICE.[8] The resulting reduced cell and reduced-cell scalars indicated $P2_1$ (monoclinic) symmetry which was subsequently verified by three axial ω-oscillation photographs. The layer spacings observed in these photographs agreed within experimental error with those predicted for this cell by the indexing program. The lattice constants were determined by least-squares refinement based on the $\pm 2\theta$ measurements of 12 high-angle reflections on a previously aligned diffractometer (Mo Kα radiation, λ = 0.709 54 Å) at 27 °C using a graphite monochromator with λ determined via an aluminum powder standard. The constants are a = 10.350 (4) Å, b = 10.339 (4) Å, c = 15.340 (6) Å, β = 92.98 (5)°, V = 1639

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(2) Bedell, S. A.; Rechani, P. R.; Angelici, R. J.; Nakon, R. *Inorg. Chem.* **1977**, *16*, 972.

(3) Meiske, L. A.; Jacobson, R. A.; Angelici, R. J. *Inorg. Chem.* **1980**, *19*, 2028. Meiske, L. A.; Angelici, R. J. *Ibid.* **1980**, *19*, 3783.

(4) Meiske, L. A.; Jacobson, R. A.; Angelici, R. J. Abstract, 14th Midwest Regional Meeting, of the American Chemical Society, Oct 1978.

(5) Douglas, B. E.; Yamada, S. *Inorg. Chem.* **1965**, *4*, 1561.

(6) Watabe, M.; Onuki, K.; Yoshikawa, S. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 687; **1976**, *49*, 1845.

(7) Watabe, M.; Onuki, K.; Yoshikawa, S. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 1354.

(8) Jacobson, R. A. *J. Appl. Crystallogr.* **1976**, *9*, 115.

(1) Å^3, and Z = 4. The observed density is 1.6 g/cm^3 by the flotational method, and the calculated density is 1.65 g/cm^3 for $Z = 4$ with use of the above cell constants.

Collection and Reduction of X-ray Intensity Data. The data were collected at 27 °C with an automated four-circle diffractometer (using graphite-monochromated Mo Kα radiation) designed and built at Ames Laboratory and previously described by Rohrbaugh and Jacobson.[9] All the data (3468 reflections) in the hkl and $\bar{h}\bar{k}l$ octants within a 2θ sphere of 50° ((sin θ)/λ = 0.596 Å^{-1}) were measured with use of an ω step-scan technique.

For electronic and crystal stabilities to be monitored, the intensities of three standard reflections were measured after every 75 reflections. These standard reflections did not change significantly throughout the entire data collection period. Systematic absences of the type 0k0, $k = 2n + 1$, coupled with statistical indications for the absence of a center of symmetry uniquely indicated space group $P2_1$, with two symmetry unrelated molecules per asymmetric unit.

The measured intensity data were corrected for Lorentz and polarization effects. Since a scan around the goniometer axis showed all measured intensities to be within 6%, no absorption corrections were made on the measured intensity data.

The estimated variance in each intensity was calculated by $\sigma_I^2 = C_T + K_t C_B + (0.03C_T)^2 + (0.03C_B)^2$, where C_T and C_B represent total and background count, 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 factor amplitudes were calculated by the method of finite differences.[10] Of the 3468 reflections collected, 3285 independent reflections had $I_0 \geq 3\sigma_I$ and were used in the structure solution and refinement.

Solution and Refinement of the Structure. The positions of the two cobalt atoms in the asymmetric unit were obtained by analysis of a sharpened three-dimensional Patterson function. The remaining atoms were found by successive structure factor[11] and electron density map calculations.[12] The positional parameters for all nonhydrogen atoms and their anisotropic thermal parameters were refined by a block-matrix least-squares procedure[13] to a weighted R factor of 0.085. The final refinement of parameters was by a full-matrix least-squares procedure,[11] minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma_F^2$, to a conventional discrepancy factor of $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.084$. The scattering factors were those of Hanson et al.,[14] modified for the real and imaginary parts of anomalous dispersion.[15]

The solution and refinement of the structure were completed without attempting to refine the absolute configuration of the ligands. The configurations of chiral atoms in the complex were based on the known configurations of N-Cm-L-PyalaH$_2$[1] and D-threonine used in the synthesis of the complex.

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.[16] Bond lengths and angles are given in Tables II and III.

Results and Discussion

Description and Discussion of the Structure. Each asymmetric unit of the crystal contains two molecules of [N-(carboxymethyl)-L-β-(2-pyridyl)-α-alaninato](D-threoninato)cobalt(III) and one molecule of water. In each complex molecule, the cobalt atom is octahedrally coordinated to three oxygen and three nitrogen atoms (Figure 2). Since the bond distances and angles listed in Tables II and III do not differ significantly for the two complex molecules, only those for molecule 1 will be discussed below. The digits 1 or 2 directly following either Co, O, N, or C refer to molecule 1 or molecule 2 in the asymmetric unit.

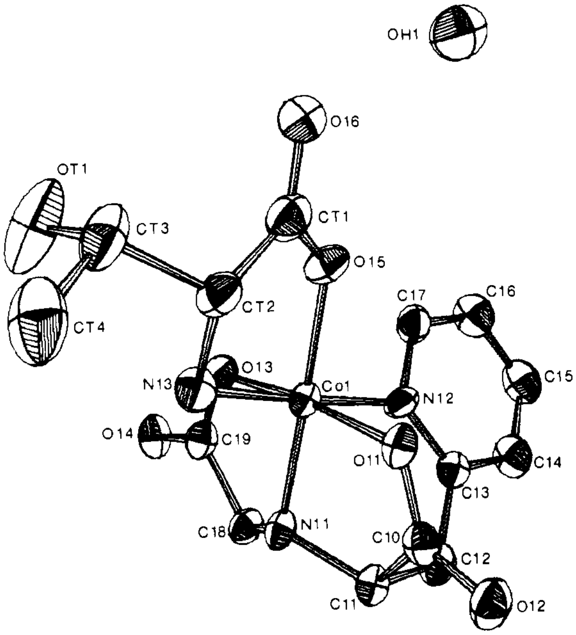

Figure 2. ORTEP drawing of [Co(N-Cm-L-Pyala)(D-Thr)]·$^1/_2$H$_2$O.

The coordination around the cobalt atom is considered to be meridional since the three carboxylate oxygens (O11, O13, O15) lie in a plane which is perpendicular to the plane of the three nitrogens (N11, N12, N13). The L-β-(2-pyridyl)-α-alaninate fragment of N-Cm-L-Pyala^{2-} is facially coordinated to the cobalt through its α-carboxylate oxygen (O11), its secondary α-amino nitrogen (N11), and its pyridine nitrogen (N12) in a manner similar to that reported for the bis[D-β-(2-pyridyl)-α-alaninato]nickel(II) and -cobalt(III) complexes.[17,18] The remaining N-(carboxymethyl) oxygen (O13) is coordinated to the cobalt in a position trans to the α-carboxylate oxygen, O11. The bidentate amino acidate, D-threoninate, occupies the two remaining coordination sites, with its α-amino nitrogen (N13) coordinated to the cobalt trans to the pyridine nitrogen (N12) of N-Cm-L-Pyala^{2-} and its α-carboxylate oxygen (O15) trans to the α-amino nitrogen (N11) of N-Cm-L-Pyala^{2-}. This structure (Figure 1c) in which the pyridine is coordinated trans to the amino nitrogen of the D-threoninate ligand confirms the structure predicted on the basis of its visible spectrum (see next section). The term meridional isomer used throughout the remainder of this paper will apply to this isomer (Figure 1c).

The bond distances and bond angles observed for the L-β-(2-pyridyl)-α-alanine, L-Pyala, fragment of N-Cm-L-Pyala^{2-} agree quite well with those reported for the M(D-Pyala)$_2$ complexes, where M is Ni(II) or Co(III).[17,18] The bond distances and angles found in the N-(carboxymethyl)group agree with those reported for bis(iminodiacetato)cobaltate(III).[19] The observed bond distances and angles in the D-

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(9) Rohrbaugh, W. J.; Jacobson, R. A. *Inorg. Chem.* **1974**, *13*, 2535.

(10) Lawton, S. L.; Jacobson, R. A. *Inorg. Chem.* **1968**, *7*, 2124.

(11) Busing, W. R.; Martin, K. O.; Levy, H. A. "ORFLS, A Fortran Crystallographic Least Squares Program", U.S. Atomic Energy Commission Report ORNL-TM-305; Oak Ridge National Laboratory: Oak Ridge, Tenn., 1962.

(12) Hubbard, C. A.; Quicksall, C. O.; Jacobson, R. A. "The Fast Fourier Algorithm and the Programs ALFF, ALFFDP, ALFFPROJ, ALFFT and FRIEDEL", U.S. Atomic Energy Commission Report IS-2625; Iowa State University and Institute for Atomic Research: Ames, Iowa, 1971.

(13) Lapp, R. L.; Jacobson, R. A. "ALLS, A Generalized Crystallographic Least Squares Program", U.S. DOE Report; Iowa State University and Ames Laboratory: Ames, Iowa, 1979.

(14) Hanson, H. P.; Herman, F.; Lea, J. D.; Skillman, S. *Acta Crystallogr.* **1960**, *17*, 1040.

(15) Templeton, D. H. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1962; Vol. III, Table 3.3.2C, pp 215–216.

(16) Busing, W. R.; Martin, K. O.; Levy, H. A. "ORFFE, A Fortran Crystallographic Function and Error Program", U.S. Atomic Energy Commission Report ORNL-TM-306; Oak Ridge National Laboratory: Oak Ridge, Tenn., 1964.

(17) Ebner, S. R.; Helland, B. J.; Jacobson, R. A.; Angelici, R. J. *Inorg. Chem.* **1980**, *19*, 175.

(18) Ebner, S. R.; Jacobson, R. A.; Angelici, R. J. *Inorg. Chem.* **1979**, *18*, 765.

(19) Corradi, A. B.; Palmieri, C. G.; Nardelli, M.; Pellinghelli, M. A.; Tani, M. E. V. *J. Chem. Soc., Dalton Trans.* **1973**, 655.

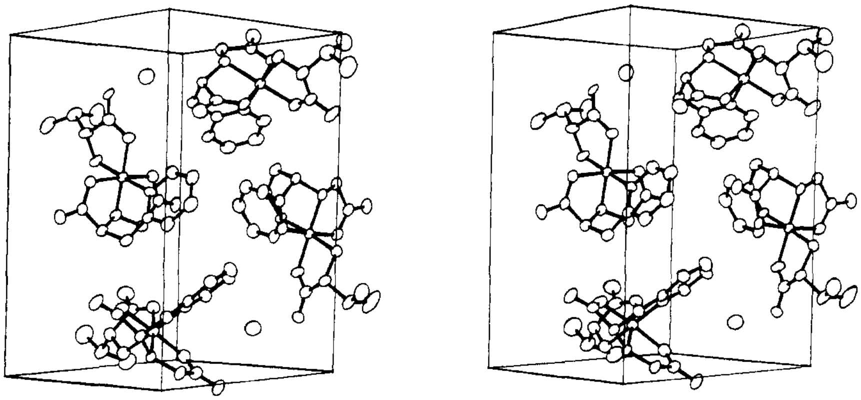

Figure 3. Stereographic view of the [Co(*N*-Cm-L-Pyala)(D-Thr)]·$^1/_2H_2O$ unit cell as viewed across the edge (*c* axis) of the cell.

threoninate ligand are similar to those reported for L-threonine and bis(L-threoninato)copper(II).[20-22] The three CO_2^- groups each contain one short and one long C–O bond. The C–O distances for the three coordinated oxygens (C10–O11 = 1.29 (1) Å, C19–O13 = 1.28 (1) Å, CT1–O15 = 1.30 (1) Å) and the C–O distances for the shorter uncoordinated "carbonyl-type" oxygens (C10–O12 = 1.24 (1) Å, C19–O14 = 1.24 (1) Å, CT1–O16 = 1.21 (1) Å) correspond well with those found in other amino acidato cobalt(III) complexes.[3,18,23-26]

The bond distances Co1–N11 (1.911 (7) Å), Co1–N13 (1.946 (7) Å), Co1–O11 (1.882 (6) Å), Co1–O13 (1.900 (6) Å), and Co1–O15 (1.898 (5) Å) are comparable to cobalt(III) secondary amino nitrogen,[3,26,27] cobalt(III) primary nitrogen,[18,26,28] and cobalt(III) carboxylate oxygen[3,18,26,29] distances found in cobalt(III) complexes of polyamines, amino acids, and amino polycarboxylates. The cobalt pyridine nitrogen bond distance (Co1–N12 = 1.970 (6) Å) is equal (within experimental error) to the Co–N pyridine bond distances reported for $Co(D\text{-}Pyala)_2^+$.[18]

The bond angles around the cobalt atom deviate significantly from ideal octahedral geometry with the smallest deviation being 0.4° and the greatest being 6.2°. The three angles O11–Co1–N11 (86.6 (3)°), O13–Co1–N11 (87.3 (3)°), and O15–Co1–N13 (83.8 (3)°) contained in the three five-membered chelate rings are consistent with other values reported for cobalt(III) complexes containing "glycinate-type" chelate rings.[3,18,23-29] The angle N11–Co1–N12 (89.1 (3)°) contained in the six-membered chelated ring of the *N*-Cm-L-Pyala^{2-} ligand is consistent with values reported for $Co(D\text{-}Pyala)_2^+$ [18] and other Co(III) complexes containing six-membered rings.[30,31] There is considerable deviation from the ideal value of 180° for the O11–Co1–O13 (173.8 (3)°) bond angle. This distortion seems to be due to the formation of two five-membered chelate rings (Co1–O11–C10–C12–N11 and Co1–N11–C18–C19–O13) in the same plane. Chelation of O11, N11, and O13 meridionally pulls O11 and O13 toward N11 and distorts the coordination plane (formed by O11, N11, O13, and O15). Additional evidence of angular strain caused by the formation of the two five-membered chelate rings is found in the C11–N11–C18 (120.7 (6)°) bond angle which is severely distorted from the ideal tetrahedral value of 109.5°. Similar angular strain and distortions have been reported previously for Co(III) complexes containing EDTA, IMDA, and related ligands.[23,26,29]

The cobalt atom does not deviate significantly (greatest deviation is 0.03 Å) from any of the three coordination planes defined by N13–O13–N12–O11, N11–O11–O15–O13 and N11–N12–O15–N13. The distance from the cobalt atom to the plane defined by the pyridine ring is 0.20 Å and is similar to the distances previously reported.[18] The least-squares plane of the pyridine ring is not coincident with either the O11–N12–O13–N13 plane or the O15–N12–N11–N13 plane (planes 2 and 3, Table IV). The dihedral angle between the pyridine plane and the O11–N12–O13–N13 plane is 60.6° while the angle between the pyridine plane and the O15–N12–N11–N13 plane is 30.1°.

The two five-membered chelate rings (Co1–N11–C11–C10–O11 and Co1–N11–C18–C19–O13) of the tetradentate ligand *N*-Cm-L-Pyala^{2-} exist in an asymmetric envelope configuration which has been noted before for other bidentate amino acidato metal complexes.[32,33] The carbon atoms C11 and C18 are displaced in the same direction due to constraints placed on the two chelate rings by the facial coordination of the L-Pyala fragment and the configuration around the nitrogen. The facial coordination of the L-Pyala fragment causes C12 to be in an axial position when referenced to the N11–O13–O15–O11 plane and C11 to be displaced a greater distance from the O13–Co1–O11 plane than C18. Additional evidence of the axial position of C12 is seen in the O11–C10–C11–C12 torsional angle of 89.7° and a displacement of 2.21 Å for C12 above the O11–N11–O13 plane (plane 4, Table IV). The torsional angles O11–C10–C11–N11 (28.6°) and O13–C19–C18–N11 (20.6°) fall within the 0–30° range observed for other coordinated amino acids.[33]

The D-threoninate chelate ring Co1–N13–CT2–CT1–O15 also exists in an asymmetric envelope configuration, which allows the R group to be in an equatorial position when referenced to the N13–Co1–O15 plane. The 0.15-Å displacement of CT3 from the N13–Co1–O15 plane also supports an equatorial position for CT3 (plane 5, Table IV). The O15–CT1–CT2–N13 torsional angle of 17.2° is within the range noted above.

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[20] Ramanadham, M.; Sikka, S. K.; Chidambaram, R. *Pramana* **1973**, *1*, 247.

[21] Amirthalingam, V.; Muralidharan, K. V. *Pramana* **1975**, *4*, 83.

[22] Shoemaker, D. P.; Donohue, J.; Shoemaker, V.; Corey, R. B. *J. Am. Chem. Soc.* **1950**, *72*, 2328.

[23] Halloran, L. J.; Caputo, R. E.; Willett, R. D.; Legg, J. I. *Inorg. Chem.* **1975**, *14*, 1762.

[24] Anderson, B. F.; Buckingham, D. A.; Gainsford, G. J.; Robertson, G. B.; Sargeson, A. M. *Inorg. Chem.* **1975**, *14*, 1658.

[25] Liu, C. F.; Ibers, J. A. *Inorg. Chem.* **1969**, *8*, 1911.

[26] Voss, K. E.; Angelici, R. J.; Jacobson, R. A. *Inorg. Chem.* **1978**, *17*, 1922.

[27] Buckingham, D. A.; Cresswell, P. J.; Dellaca, R. J.; Dwyer, M.; Gainsford, G. J.; Marzilli, L. G.; Maxwell, I. E.; Robinson, W. T.; Sargeson, A. M.; Turnbill, K. R. *J. Am. Chem. Soc.* **1974**, *96*, 1713.

[28] Gillard, R. D.; Payne, N. C.; Robertson, G. B. *J. Chem. Soc. A* **1970**, 2579.

[29] Weakliem, H. A.; Hoard, J. L. *J. Am. Chem. Soc.* **1959**, *81*, 549.

[30] Oonishi, I.; Shibata, M.; Marumo, F.; Saito, Y. *Acta Crystallogr., Sect. B* **1973**, *B29*, 2448.

[31] Oonishi, I.; Sato, S.; Saito, Y. *Acta Crystallogr., Sect. B* **1975**, *B31*, 1318.

[32] Freeman, H. C. *Adv. Protein Chem.* **1967**, *22*, 258.

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

Table I. Final Atomic Parameters

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

	x	y	z		x	y	z
Co1[b]	1596 (1)	0	4115.3 (7)	Co2	4394 (1)	472 (1)	8741.2 (7)
O11	1543 (5)	1804 (5)	4272 (4)	O21	3945 (6)	1903 (6)	8031 (4)
O12	1360 (6)	3273 (6)	5329 (4)	O22	4646 (7)	3893 (7)	7776 (4)
O13	1548 (6)	−1835 (6)	4069 (4)	O23	4952 (6)	−859 (6)	9533 (4)
O14	1293 (6)	−3529 (5)	4936 (5)	O24	6656 (7)	−1351 (7)	10423 (5)
O15	2113 (5)	135 (6)	2950 (3)	O25	3186 (6)	−578 (6)	8082 (4)
O16	1449 (7)	753 (10)	1611 (4)	O26	1098 (7)	−746 (9)	7704 (5)
OT1	−1324 (9)	−889 (9)	2063 (7)	OT2	−586 (7)	205 (10)	8964 (6)
N11	1020 (7)	−134 (7)	5275 (4)	N21	5532 (7)	1592 (7)	9412 (4)
N12	3397 (6)	−41 (8)	4596 (4)	N22	5839 (7)	−11 (8)	8009 (4)
N13	−142 (7)	123 (7)	3573 (4)	N23	2917 (7)	866 (8)	9432 (5)
C10	1451 (8)	2133 (8)	5077 (6)	C20	4745 (9)	2847 (9)	8148 (5)
C11	1530 (8)	1051 (9)	5748 (6)	C21	5939 (8)	2574 (8)	8767 (5)
C12	2955 (9)	855 (10)	6053 (6)	C22	7005 (9)	2108 (8)	8215 (6)
C13	3853 (8)	439 (9)	5364 (5)	C23	6833 (8)	770 (8)	7807 (5)
C14	5159 (8)	467 (11)	5576 (6)	C24	7741 (9)	365 (10)	7233 (6)
C15	6045 (9)	−26 (12)	5007 (7)	C25	7709 (11)	−880 (11)	6912 (7)
C16	5579 (9)	−526 (11)	4213 (6)	C26	6723 (11)	−1718 (10)	7156 (7)
C17	4267 (8)	−549 (9)	4024 (6)	C27	5785 (10)	−1222 (10)	7697 (6)
C18	1350 (9)	−1448 (8)	5609 (6)	C28	6524 (9)	810 (8)	9893 (6)
C19	1393 (8)	−2352 (9)	4817 (6)	C29	6039 (9)	−565 (9)	9978 (6)
CT1	1245 (9)	552 (10)	2369 (6)	CT5	1989 (9)	−299 (9)	8184 (6)
CT2	−69 (9)	791 (9)	2728 (5)	CT6	1682 (9)	616 (10)	8903 (6)
CT3	−1232 (10)	489 (11)	2091 (6)	CT7	621 (8)	172 (11)	9472 (6)
CT4	−2432 (10)	1091 (13)	2403 (8)	CT8	842 (13)	−1164 (13)	9852 (8)
OH1	4082 (8)	888 (7)	1224 (5)				

(b) Final Thermal Parameters with Their Estimated Standard Deviations (in Parentheses)[c]

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co1	1.91 (4)	1.58 (4)	1.89 (4)	−0.11 (3)	−0.33 (31)	−0.04 (4)
O11	2.4 (3)	1.5 (2)	2.7 (3)	−0.1 (2)	−0.3 (2)	0.2 (2)
O12	2.7 (3)	1.8 (3)	4.1 (3)	−0.1 (2)	0.1 (3)	−0.6 (2)
O13	2.8 (3)	2.3 (3)	2.9 (3)	0.1 (2)	−0.3 (2)	−0.5 (2)
O14	2.6 (3)	1.2 (2)	5.1 (4)	0.0 (2)	−0.1 (3)	0.4 (2)
O15	2.8 (2)	3.0 (3)	2.0 (2)	0.3 (2)	−0.5 (2)	−0.3 (2)
O16	4.2 (3)	9.0 (6)	2.0 (3)	0.1 (4)	−0.4 (3)	1.1 (3)
OT1	5.8 (5)	4.0 (4)	10.4 (7)	0.5 (4)	−4.8 (4)	−2.9 (4)
N11	2.7 (3)	1.4 (3)	2.4 (3)	−0.4 (3)	−0.4 (3)	0.0 (3)
N12	2.4 (3)	2.7 (3)	2.0 (3)	−0.2 (3)	−0.2 (2)	−0.6 (3)
N13	2.7 (3)	2.2 (3)	2.3 (3)	−0.5 (3)	−0.4 (3)	0.8 (3)
C10	1.5 (3)	2.1 (3)	2.9 (4)	0.0 (3)	−0.1 (3)	0.2 (3)
C11	2.1 (3)	2.1 (3)	2.5 (4)	−0.1 (3)	−0.2 (3)	0.1 (3)
C12	2.5 (3)	3.1 (4)	2.7 (4)	0.0 (3)	−0.6 (3)	0.1 (3)
C13	2.4 (3)	2.3 (3)	2.4 (3)	−0.1 (3)	−0.3 (3)	0.5 (3)
C14	1.8 (3)	4.3 (4)	3.8 (4)	0.0 (3)	−0.5 (3)	−0.1 (4)
C15	2.3 (3)	4.0 (4)	4.7 (5)	0.1 (4)	−0.2 (3)	0.6 (4)
C16	2.3 (3)	4.4 (3)	3.5 (5)	0.2 (3)	−0.3 (3)	0.7 (4)
C17	2.3 (3)	3.0 (4)	3.3 (4)	−0.3 (3)	0.1 (3)	−0.4 (3)
C18	3.0 (4)	1.8 (3)	2.6 (4)	−0.1 (3)	−0.1 (3)	0.0 (3)
C19	2.0 (4)	2.4 (4)	3.2 (4)	0.0 (3)	−0.3 (3)	0.0 (4)
CT1	3.6 (4)	2.7 (3)	2.7 (4)	−0.3 (3)	−0.3 (3)	−0.3 (4)
CT2	3.0 (3)	3.1 (5)	2.1 (3)	−0.4 (3)	−0.6 (3)	−0.1 (3)
CT3	3.4 (4)	4.0 (4)	3.6 (4)	−0.6 (4)	−1.9 (4)	−0.2 (4)
CT4	2.6 (4)	5.3 (6)	5.8 (6)	−0.3 (4)	−1.9 (4)	1.3 (5)
OH1	5.8 (4)	3.4 (3)	3.9 (3)	0.6 (3)	0.0 (3)	0.0 (3)
Co2	2.65 (4)	1.77 (4)	2.06 (4)	−0.05 (2)	−0.14 (3)	−0.17 (4)
O21	2.9 (3)	2.7 (3)	2.5 (3)	−0.6 (1)	−0.8 (2)	−0.1 (2)
O22	4.4 (3)	2.7 (3)	3.7 (3)	0.6 (3)	−0.6 (3)	1.3 (3)
O23	3.5 (3)	2.1 (3)	3.1 (3)	−0.2 (3)	0.6 (3)	0.0 (2)
O24	4.7 (3)	2.6 (3)	4.0 (3)	1.1 (3)	−0.4 (3)	1.4 (3)
O25	3.6 (3)	3.0 (3)	3.0 (3)	−0.1 (3)	−0.1 (3)	−0.7 (3)
O26	3.8 (3)	5.9 (4)	3.9 (3)	−0.5 (3)	−1.3 (3)	−1.9 (3)
OT2	3.6 (3)	7.4 (6)	6.8 (5)	−0.2 (4)	−1.4 (3)	−0.5 (4)
N21	2.2 (3)	1.9 (3)	2.1 (3)	0.4 (2)	−0.2 (3)	0.3 (2)
N22	3.8 (3)	1.8 (3)	1.9 (3)	0.0 (3)	0.0 (3)	0.1 (3)
N23	2.2 (3)	3.3 (3)	3.0 (3)	0.0 (3)	−0.3 (3)	−0.6 (3)
C20	3.0 (4)	2.3 (4)	2.2 (3)	0.6 (3)	0.0 (3)	−0.1 (3)
C21	2.9 (3)	1.5 (3)	2.0 (3)	0.1 (3)	−0.3 (3)	0.3 (3)
C22	3.0 (4)	2.0 (3)	2.5 (4)	0.3 (3)	0.1 (3)	−0.4 (3)
C23	1.8 (3)	2.6 (4)	2.3 (4)	0.5 (3)	−0.2 (3)	0.4 (3)
C24	3.1 (4)	3.3 (4)	2.8 (4)	0.4 (3)	−0.3 (3)	−0.4 (3)
C25	4.0 (4)	3.8 (5)	3.5 (5)	1.1 (4)	0.3 (4)	−0.5 (4)
C26	4.5 (5)	3.8 (5)	3.3 (4)	1.2 (4)	0.0 (4)	−0.7 (4)
C27	4.9 (5)	2.4 (4)	2.8 (4)	0.9 (4)	0.1 (4)	−0.4 (3)

Table I (*Continued*)

(b) Final Thermal Parameters with Their Estimated Standard Deviations (in Parentheses)[c]

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C28	3.3 (4)	1.4 (4)	2.9 (4)	0.3 (3)	−0.4 (3)	0.5 (3)
C29	3.2 (4)	2.3 (3)	2.3 (4)	0.3 (3)	0.0 (3)	0.6 (3)
CT5	3.5 (4)	3.0 (5)	2.6 (4)	−0.9 (3)	−0.7 (3)	0.0 (3)
CT6	2.6 (3)	3.5 (4)	3.1 (4)	0.4 (3)	−0.4 (3)	−1.0 (4)
CT7	2.1 (3)	5.3 (6)	3.9 (4)	0.3 (4)	−0.6 (3)	0.4 (4)
CT8	6.0 (6)	4.1 (6)	4.7 (6)	−0.6 (5)	0.1 (5)	1.3 (5)

[a] The positional parameters are presented in fractional unit cell coordinates. [b] The *y* positional parameter was not varied. [c] The B_{ij} are defined by $T = \exp\{-^1/_4(h^2B_{11}a^{*2} + k^2B_{22}b^{*2} + l^2B_{33}c^{*2} + 2hkB_{12}a^*b^* + 2hlB_{13}a^*c^* + 2klB_{23}b^*c^*)\}$.

Table II. Bond Distances (Å) for *mer*-[Co(*N*-Cm-L-Pyala)(D-Thr)]·$^1/_2$H$_2$O with Their Estimated Standard Deviations (in Parentheses) and Possible Hydrogen Bonding Contracts (Å)

Co1–O11	1.882 (6)	Co2–O21	1.881 (6)
Co1–O13	1.900 (6)	Co2–O23	1.906 (6)
Co1–O15	1.898 (5)	Co2–O25	1.907 (6)
Co1–N11	1.911 (7)	Co2–N21	1.913 (7)
Co1–N12	1.970 (6)	Co2–N22	1.981 (7)
Co1–N13	1.946 (7)	Co2–N23	1.948 (8)
C10–O11	1.29 (1)	C20–O21	1.29 (1)
C10–O12	1.25 (1)	C20–O22	1.22 (1)
C19–O13	1.28 (1)	C29–O23	1.32 (1)
C19–O14	1.24 (1)	C29–O24	1.22 (1)
CT1–O15	1.30 (1)	CT5–O25	1.29 (1)
CT1–O16	1.21 (1)	CT5–O26	1.24 (1)
CT3–OT1	1.43 (1)	CT7–OT2	1.44 (1)
C10–C11	1.52 (1)	C20–C21	1.54 (1)
C11–C12	1.54 (1)	C21–C22	1.50 (1)
C11–N11	1.51 (1)	C21–N21	1.49 (1)
C12–C13	1.51 (1)	C22–C23	1.53 (1)
C13–C14	1.37 (1)	C23–C24	1.39 (1)
C13–N12	1.34 (1)	C23–N22	1.36 (1)
C14–C15	1.40 (1)	C24–C25	1.38 (1)
C15–C16	1.39 (1)	C25–C26	1.40 (1)
C16–C17	1.37 (1)	C26–C27	1.41 (1)
C17–N12	1.39 (1)	C27–N22	1.34 (1)
C18–C19	1.54 (1)	C28–C29	1.52 (1)
C18–N11	1.49 (1)	C28–N21	1.47 (1)
CT1–CT2	1.51 (1)	CT5–CT6	1.50 (1)
CT2–CT3	1.54 (1)	CT6–CT7	1.51 (1)
CT2–N13	1.47 (1)	CT6–N23	1.50 (1)
CT3–CT4	1.49 (2)	CT7–CT8	1.51 (2)
OH1–O16	2.82 (1)	O26–OT2	2.78 (1)
OH1–N23[a]	2.95 (1)	N13–OT1	2.77 (1)
OH1–O24[a]	3.03 (1)	N13–O12[b]	2.88 (1)
OH1–O22[b]	2.85 (1)	N13–O14[c]	2.98 (1)
N11–O14[c]	2.92 (1)	N11–O12[b]	3.07 (1)

[a] Symmetry operation *x*, *y*, *z* − 1. [b] Symmetry operation −*x*, *y* − $^1/_2$, 1 − *z*. [c] Symmetry operation −*x*, $^1/_2$ + *y*, 1 − *z*.

The meridional coordination of O11, N11, and O13 gives rise to an asymmetric secondary nitrogen which has the *S* absolute configuration. This configuration is opposite to the *R* configuration found in the other diastereomer, *fac*-[Co(*N*-Cm-L-Pyala)(D-Thr)]·H$_2$O (Figure 1a).

The asymmetric units are linked to each other by hydrogen bonds (Table II), but there are no hydrogen bonds between the molecules in the same asymmetric unit. Figure 3 gives a stereographic view down the *c* axis of the molecular packing in the crystal lattice.

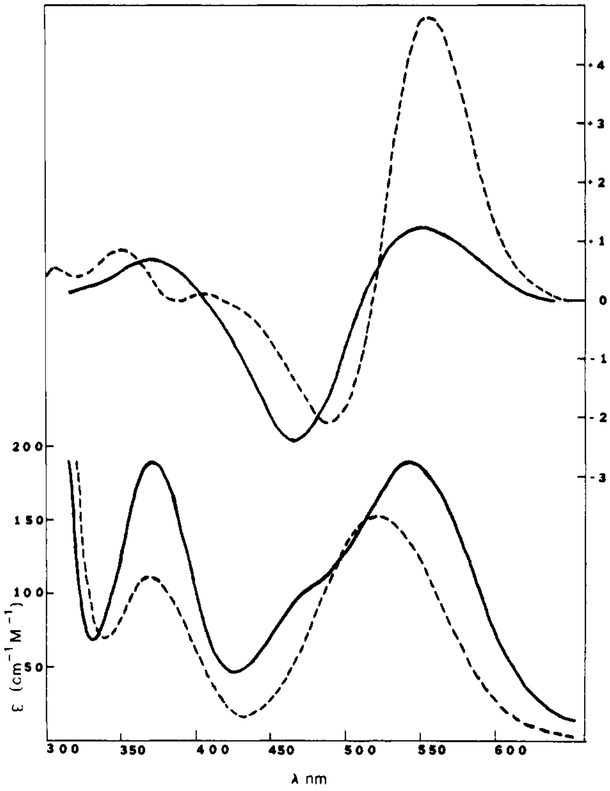

Figure 4. Visible (lower) and circular dichroism (upper) spectra of (—) *mer*-[Co(*N*-Cm-L-Pyala)(D-Thr)]·$^1/_2$H$_2$O (—) and *fac*-[Co(*N*-Cm-L-Pyala)(D-Thr)]·H$_2$O (---).

Discussion of Spectra. The visible spectrum of *fac*-[Co(*N*-Cm-L-Pyala)(D-Thr)]·H$_2$O with its two symmetrical peaks at 520 (ϵ = 153 cm^{-1} M^{-1}) and 367 nm (ϵ = 113 cm^{-1} M^{-1}) is characteristic of other facial Co^{III}N$_3$O$_3$ complexes reported previously.[3-7] Since only one of the four possible isomers of Co(*N*-Cm-L-Pyala)(D-Thr) is facial, the structure in Figure 1a is assigned to *fac*-[Co(*N*-Cm-L-Pyala)(D-Thr)]·H$_2$O. The visible spectrum of *mer*-[Co(*N*-Cm-L-Pyala)(D-Thr)]·$^1/_2$H$_2$O given in Figure 4 (maxima at 542 nm, ϵ = 188 cm^{-1} M^{-1} and 371 nm, ϵ = 189 cm^{-1} M^{-1}) is typical of previously reported meridional Co^{III}N$_3$O$_3$ complexes.[3-7] The position of the shoulder at 470 nm (ϵ = 100 cm^{-1} M^{-1}), which is on the high-energy side of the peak at 542 nm, is characteristic of complexes containing pyridine or imidazole coordinated trans to an amino group.[7,18] On the basis of the position of the shoulder, the meridional isomer can be assigned the structure in Figure 1c, which is that found in the X-ray analysis.

The CD spectra of *fac*- and *mer*-Co(*N*-Cm-L-Pyala)(D-Thr) are given in Figure 4. The overall shape of the CD spectrum of *fac*-[Co(*N*-Cm-L-Pyala)(D-Thr)]·H$_2$O is nearly identical with those of the cis-N,cis-O$_5$ Co(*N*-Cm-L-Asp)(AA) complexes, where the ligands are *N*-(carboxymethyl)-L-aspartate (*N*-Cm-L-Asp^{3-}) and D-amino acidates, reported by Bernauer.[34] The major difference is that the *N*-Cm-L-Pyala^{2-} mixed cobalt(III) complexes have a $\Delta\epsilon$ which is almost twice those of the *N*-Cm-L-Asp^{3-} analogues.[34] Thus, it seems that substitution of a carboxylate group with a pyridine group increases the $\Delta\epsilon$ of the CD spectrum. A similar increase has been noted before for complexes containing pyridine and imidazole.[35] The CD spectrum of the *mer*-[Co(*N*-Cm-L-Py-

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(34) Colomb, G.; Bernauer, K. *Helv. Chim. Acta* **1977**, *60*, 459.

Table III. Bond Angles (Deg) for *mer*-[Co(*N*-Cm-L-Pyala)(D-Thr)]·$^1/_2$H$_2$O with Their Estimated Standard Deviations (in Parentheses)

	molecule 1	molecule 2
O1–Co–O3	173.8 (3)	174.2 (3)
O1–Co–O5	93.4 (3)	90.3 (3)
O1–Co–N1	86.6 (3)	87.9 (3)
O1–Co–N2	90.4 (3)	92.4 (3)
O1–Co–N3	87.6 (3)	88.5 (3)
O3–Co–O5	92.6 (3)	95.5 (3)
O3–Co–N1	87.3 (3)	86.3 (3)
O3–Co–N2	90.9 (3)	88.1 (3)
O3–Co–N3	91.5 (3)	91.4 (3)
O5–Co–N1	178.2 (3)	176.9 (3)
O5–Co–N2	92.7 (3)	92.8 (3)
O5–Co–N3	83.8 (3)	84.0 (3)
N1–Co–N2	89.1 (3)	89.8 (3)
N1–Co–N3	94.4 (3)	93.4 (3)
N2–Co–N3	175.8 (3)	176.7 (3)
Co–O1–CO	112.9 (5)	112.2 (5)
Co–O3–C9	112.7 (6)	112.7 (6)
Co–O5–CT1	116.7 (5)	
Co–O5–CT5		114.6 (6)
Co–N1–C1	105.7 (5)	104.0 (5)
Co–N1–C8	108.1 (5)	109.3 (5)
Co–N2–C3	127.1 (6)	125.7 (6)
Co–N2–C7	113.8 (5)	114.8 (7)
Co–N3–CT2	108.6 (5)	
Co–N3–CT6		109.9 (5)
O1–CO–O2	123.9 (8)	124.6 (8)
O1–CO–C1	116.7 (7)	115.9 (7)
O2–CO–C1	119.3 (8)	119.5 (8)
O3–C9–O4	123.8 (9)	122.9 (9)
O3–C9–C8	117.7 (8)	116.6 (8)
O4–C9–C8	118.5 (8)	120.4 (8)
O5–CT1–O6	124.4 (9)	
O5–CT5–O6		122.2 (9)
O5–CT1–CT2	113.9 (7)	
O5–CT5–CT6		118.2 (8)
O6–CT1–CT2	121.7 (8)	
O6–CT5–CT6		119.6 (9)
N1–C1–CO	105.6 (6)	106.7 (7)
N1–C1–C2	110.2 (7)	113.3 (7)
N1–C8–C9	107.4 (7)	109.4 (7)
N2–C3–C2	121.4 (7)	121.3 (7)
N2–C3–C4	120.8 (8)	120.8 (8)
N2–C7–C6	121.7 (8)	122 (1)
N3–CT2–CT1	109.4 (7)	
N3–CT6–CT5		107.4 (7)
N3–CT2–CT3	112.8 (8)	
N3–CT6–CT7		111.3 (7)
CO–C1–C2	108.7 (7)	107.4 (7)
C1–N1–C8	120.7 (6)	119.4 (7)
C1–C2–C3	116.2 (7)	116.6 (7)
C2–C3–C4	117.6 (8)	117.8 (8)
C3–C4–C5	121.0 (9)	120.4 (9)
C3–N2–C7	118.9 (7)	119.5 (8)
C4–C5–C6	118.3 (8)	119.0 (9)
C5–C6–C7	119.2 (9)	117.8 (9)
CT1–CT2–CT3	115.0 (8)	
CT5–CT6–CT7		114.9 (9)
CT2–CT3–CT4	110.3 (9)	
CT6–CT7–CT8		113.6 (9)
CT2–CT3–OT1	105.7 (8)	
CT6–CT7–OT2		108.5 (8)
CT4–CT3–OT1	112 (1)	
CT8–CT7–OT2		110 (1)

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

atom	D^b	atom	D
Plane 1 (Pyridine Ring): N12–C13–C14–C15–C16–C17			
$-0.0886X - 0.9012Y + 0.4230Z - 2.746 = 0$			
Co1	0.197	C14	−0.002
N12	−0.009	C15	−0.004
C11	−0.101	C16	−0.008
C12	0.151	C17	0.010
C13	0.005		
Plane 2: O11–N12–O13–N13			
$-0.4022X - 0.0766Y + 0.9123Z - 5.240 = 0$			
Co1	−0.020	O13	0.079
O11	0.083	N13	−0.082
N12	−0.080		
Plane 3: O15–N12–N11–N13			
$0.0109X + 0.9966Y + 0.0823Z - 0.5523 = 0$			
Co1	−0.019	N11	−0.019
O15	−0.020	N13	0.019
N12	0.020		
Plane 4: O11–N11–O13			
$0.9371X - 0.0235Y + 0.3483Z - 3.413 = 0$			
Co	0.023	C10	0.272
O11	0.000	C11	0.683
O13	0.000	C12	2.210
N11	0.000	C18	0.505
N12	1.992	C19	0.205
Plane 5: N13–Co1–O15			
$0.0302X + 0.9956Y + 0.0885Z - 0.5979 = 0$			
Co1	0.000	CT1	0.325
N13	0.000	CT2	0.577
O15	0.000	CT3	0.145
O16	0.437	CT4	0.769
OT1	−1.280		

[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.

ala)(D-Thr)]·$^1/_2$H$_2$O complex cannot be compared to its *N*-Cm-L-Asp^{3-} analogue because the corresponding isomer of the mixed-ligand cobalt^{III}(*N*-Cm-L-Asp)(AA) complex has not been reported.

The proton NMR spectrum of the D-threoninate fragment of the facial isomer consists of a doublet at δ 1.27 for the γ-methyl protons, a multiplet at δ 4.4 for the β-methine proton, and a doublet at δ 3.54 for the α proton. The *N*-Cm-L-Pyala^{2-} portion of the facial isomer consists of a multiplet at δ 3.9 for the β-methylene and α protons, two doublets at δ 3.60 and 4.33 with J = 18 Hz for the *N*-(carboxymethylene) protons, an overlapping doublet and triplet at δ 7.46 for the meta pyridyl protons, a triplet at δ 7.98 for the para pyridyl proton, and a doublet at δ 8.12 for the ortho proton of pyridine.

The proton NMR spectrum of the D-threoninate ligand of the meridional isomer exhibits a doublet at δ 1.37 for the γ-methyl protons, a multiplet at δ 4.4 for the β-methine proton, and a doublet which overlaps the *N*-(carboxymethyl) singlet at δ 3.62 for the α proton. The *N*-Cm-L-Pyala^{2-} fragment consists of a broad singlet at δ 3.62 for the *N*-(carboxymethylene) protons, a multiplet at δ 4.00 for the β-methine and α-protons, an overlapping doublet and triplet at δ 7.61 for the meta pyridyl protons, a triplet at δ 8.07 for the para pyridyl proton, and a doublet at δ 8.99 for the ortho pyridyl proton.

Comparison of the ^{1}H NMR spectra for the facial and meridional isomers reveals that the two spectra are very similar, with the major differences being in the splitting of the *N*-(carboxymethyl) protons and in the chemical shifts of the ortho pyridyl protons. The splitting of the *N*-(carboxymethyl) protons in *fac*-[Co(*N*-Cm-L-Pyala)(D-Thr)]·H$_2$O is similar to the two doublets reported previously for the *N*-(pyridylmethyl) protons of the *fac*-Co(PLASP)(AA) complexes. Comparison of the ortho pyridyl proton (doublet at δ 8.69) of the free ligand *N*-Cm-L-PyalaH$_2$ to the ortho pyridyl proton (doublet at δ 8.12) of the facial isomer and to the ortho pyridyl proton

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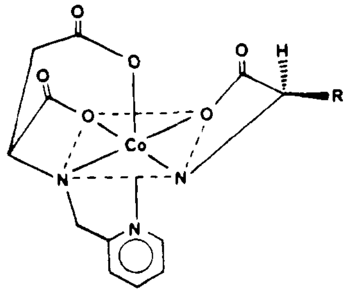
(35) Ebner, S. R.; Angelici, R. J. *Inorg. Chem.* **1980**, *19*, 1031.



fac-Co(PLASP)(AA)

(doublet at δ 8.99) of the meridional isomer shows the ortho pyridyl proton of the facial isomer to be shifted upfield (shielded) while the proton of the meridional isomer is shifted downfield (deshielded). This shielding and deshielding is presumably due to the magnetic anisotropy of the D-threoninate carboxylate group. In the facial isomer, the ortho proton is positioned over the D-Thr$^-$ carboxylate plane and is shielded while in the meridional isomer, the ortho proton is nearly in the plane of the D-Thr$^-$ carboxylate group and is deshielded. It may be noted that since the $^-O_2CC(R)N(H)CH_2CO_2^-$ portion of the *N*-Cm-L-Pyala^{2-} ligand resembles the tridentate ligand IMDA^{2-}, $^-O_2CCH_2N(H)CH_2CO_2^-$, the ^{1}H NMR spectra reported above for the facial and meridional isomers of Co(*N*-Cm-L-Pyala)(D-Thr) are also comparable to the cis (facial coordination of IMDA^{2-}) and trans (meridional coordination of IMDA^{2-}) isomers of [Co(IMDA)(dien)]$^+$ reported by Legg and Cooke.[36]

Conclusion

Previously we reported that for a series of Co(PLASP)(AA) complexes the only isomer isolated was the *fac*-Co(PLASP)(AA) isomer shown in the Discussion of Spectra.[3,4] However for the Co(*N*-Cm-L-Pyala)(AA) complexes reported herein, two isomeric forms, one facial and one meridional, were isolated. Since the donor groups in the PLASP^{2-} and *N*-Cm-L-Pyala^{2-} ligands are essentially identical, electronic differences between the two ligands are unlikely to account for the different geometries of their cobalt(III) complexes. However, the flexibility of the group attached to the amino nitrogen differs significantly. The *N*-(carboxymethyl) chelate ring of *N*-Cm-L-Pyala^{2-} which has only one sp^2 carbon and an sp^3 oxygen (Co1–O13–C19 bond angle is 112.7°) coordinated to the cobalt is flexible and capable of coordinating trans to both the pyridyl group and the α-carboxylate group of the *N*-Cm-L-Pyala^{2-} ligand. This has been reported previously for Co(III) complexes containing ethylenediaminetetraacetic acid and iminodiacetic acid.[23,26,29] On the other hand, the *N*-(pyridylmethyl) chelate ring of PLASP^{2-} which has two sp^2 centers, one at carbon and the other at the coordinated pyridine nitrogen, is less flexible and therefore less capable of coordinating in the more strained position trans to the α-carboxylate group of the PLASP^{2-} ligand. Thus the difference in angular strain in the *N*-Cm-L-Pyala^{2-} and PLASP^{2-} ligands accounts for the geometries of their Co(III) complexes. The effects of electronic and steric factors on the overall geometry of the facial and meridional isomers of Co(*N*-Cm-L-Pyala)(AA) will be discussed in greater detail in a later paper.

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Registry No. *mer*-[Co(*N*-Cm-L-Pyala)(D-Thr)]·$^1/_2H_2O$, 77058-78-7; *fac*-[Co(*N*-Cm-L-Pyala)(D-Thr)], 77027-86-2.

Supplementary Material Available: A table listing observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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(36) Legg, J. I.; Cooke, D. W. *Inorg. Chem.* **1966**, *5*, 594.