Cu···Cl = 3.02 Å, θ = 91.5°). Since J is not expected to be extremely sensitive to θ, we can reasonably compare the two exchange constants, −12 and −13.4 K, respectively, based only on the coordination geometry. Thus, the distortion from planar coordination present in $CuCl_2 \cdot 2(CH_2)_4SO$ (but not in $CuCl_2 \cdot 2py$) causes a decrease in the antiferromagnetic coupling. This is not surprising since, with the lobes of the $d_{x^2-y^2}$ orbital not pointing directly at the chlorine atoms, lower electron density is anticipated at the bridging chlorine and thus less exchange of spin information. Likewise, the dimethylglyoxime complex $[(DMG)CuCl_2]_2$ has nearly identical bridging geometry (Cu–Cl = 2.24 Å, Cu···Cl = 2.70 Å, θ = 88°) except for the 0.3-Å shortening of the long Cu–Cl bond. Yet this shortening has the effect of changing the interaction from antiferromagnetic to ferromagnetic ($J/k = -12$ vs. +4.4 K)! Finally, we note that the linear-chain arrangement in $CuCl_2 \cdot 2(CH_3)_2SO$ leads to weak antiferromagnetic interaction ($J/k = -4.8$ K).[14] In this salt, a monobridged superexchange pathway exists, with θ = 144.6°.

Summary

We have shown that discrete $Cu_2Cl_4(C_4H_8SO)_4$ dimers exist in the solid state in the 2:1 $(CH_2)_4SO$–$CuCl_2$ salt. The coordination geometry, approximately square pyramidal, contains three chlorine and two oxygen atoms. Copper atoms within the dimer are linked by a pair of asymmetrical Cu–Cl···bridges, leading to antiferromagnetic coupling with a singlet–triplet separation of 24 K.

Acknowledgment. We thank C. P. Landee for assistance with the susceptibility measurements and R. Wong for the EPR measurements. The work was supported by NSF.

Registry No. $Cu_2Cl_4((CH_2)_4SO)_4$, 68876-53-9.

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

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Preparation, Structure, and Spectral Characterization of Bis[D-β-(2-pyridyl)-α-alaninato]cobalt(III), $Co(D\text{-}Pyala)_2^+$

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Received July 21, 1978

The complex $[Co(D\text{-}Pyala)_2]NO_3 \cdot {}^1/_2H_2O$ was prepared by reaction of Co(II) or Co(III) with D-$H_2NCH(CH_2C_5H_4N)CO_2^-$, D-$Pyala^-$, the tridentate analogue of histidine. It was established by an X-ray crystal study of the complex that of the three possible isomeric forms, the most stable was that in which the carboxylate groups of the two ligands are mutually trans. This structure contrasts with that of the predominant isomer of the histidinate complex $Co(L\text{-}his)_2^+$, in which the imidazole groups are mutually trans. Infrared, ^1H NMR, visible, ORD, and CD spectra of $Co(D\text{-}Pyala)_2^+$ are discussed and are entirely consistent with the solid-state structure.

Introduction

The synthetic amino acid β-(2-pyridyl)-α-alanine, $^+H_3NCH\text{-}(CH_2C_5H_4N)CO_2^-$ (PyalaH), is a tridentate analogue of histidine with a pyridine group in place of the imidazole. In earlier work, it was shown that $Pyala^-$ binds to transition-metal ions to form $M(Pyala)_2$ with some enantioselectivity depending upon the chirality of the $Pyala^-$ ligand.[1] Where the ligand is present as only one enantiomer, e.g., D-$Pyala^-$, the octahedral $M(D\text{-}Pyala)_2$ complexes may exist in three geometric isomeric forms (Figure 1). In the present study, we prepared the Co(III) complex $Co(D\text{-}Pyala)_2^+$ for the purpose of establishing the most stable isomer of this complex.

All three isomers of the $Co(ligand)_2^+$ complexes have been isolated for the tridentate ligands L-histidinate[2,3], L-2,3-diaminopropionate,[4] and L-2,4-diaminobutyrate.[5] The trans-imidazole isomer was the major structural form of $Co(L\text{-}his)_2^+$. It was suggested that because of steric hindrance the imidazole groups prefer to occupy trans positions in octahedral $M(his)_2$ complexes.[6] Because of the similarity of $Pyala^-$ to his^-, $Co(D\text{-}Pyala)_2^+$ might be expected to prefer the trans-pyridyl structure. However, as reported herein, the trans-carboxylate structure is the most stable form. This complex was fully characterized by its IR, ^1H NMR, visible, ORD, and CD spectra.

Experimental Section

Materials. Racemic β-(2-pyridyl)-α-alanine (PyalaH) was prepared and resolved as described previously.[7] $[Co(NH_3)_4CO_3]NO_3$,[8a] $[Co(NH_3)_6](NO_3)_3$,[8b] and $Na_3[Co(CO_3)_3] \cdot 3H_2O$[8c] were prepared according to literature methods.

Preparation of Bis[D-β-(2-pyridyl)-α-alaninato]cobalt(III) Nitrate Hemihydrate, $[Co(D\text{-}Pyrala)_2]NO_3 \cdot {}^1/_2H_2O$. $[Co(NH_3)_4CO_3]NO_3$ (0.75 g, 3.0 mmol) and D-PyalaH (1.00 g, 6.0 mmol) were dissolved in 40 mL of distilled water, and 0.3 g of activated charcoal was added. The solution was stirred at 85 °C for 20 h. The charcoal was filtered from the hot solution and washed with boiling water. The filtrate and wash solution were combined and evaporated to dryness. The glassy solid that formed was redissolved in a minimum of 80:20 $MeOH$–H_2O and

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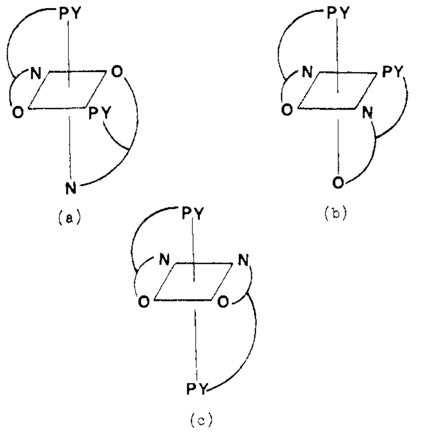

Figure 1. The three possible isomers of $Co(D\text{-}Pyala)_2^+$ ion: (a) trans carboxylate, (b) trans amino, and (c) trans pyridyl.

loaded on a column (2.25 × 70 cm) of basic alumina (200 mL). The bands were eluted with 80:20 MeOH–H_2O at 1 drop/4 s. Of the bands which separated, only one contained more than a few milligrams of material when evaporated to dryness. This component eluted first from the column and was red-violet in color. After the solution was evaporated to 1 mL, 9 mL of methanol was added. This was allowed to stand overnight, and red-violet crystals formed. They were filtered from the solution and vacuum-dried. The yield was 44%. Anal. Calcd for $[Co(C_8H_9N_2O_2)_2]NO_3\cdot{}^1/_2H_2O$: C, 41.75; H, 4.16; N, 15.21. Found: C, 41.55; H, 4.13; N, 15.39.

No crystals could be isolated from the other bands eluted from the column. NMR, visible, and CD spectra indicated that these components were not isomers of $Co(D\text{-}Pyala)_2^+$.

The complex was also prepared by adding $Co(NO_3)_2\cdot 6H_2O$ (0.87 g, 3.0 mmol) to 50 mL of water containing D-PyalaH (1.0 g, 6.0 mmol) and NaOH (6.0 mmol). After 15 min of stirring, 0.5 mL of 30% H_2O_2 was added. The solution was allowed to stand for 2 h and then was evaporated to dryness. The solid formed was dissolved in 80:20 MeOH–H_2O and chromatographed as above. The yield of the trans-carboxylate $[Co(D\text{-}Pyala)_2]NO_3\cdot{}^1/_2H_2O$ was 19%.

In a preparation similar to that above $[Co(NH_3)_6](NO_3)_3$ (1.04 g, 3.0 mmol), D-PyalaH (1.0 g, 6.0 mmol), and NaOH (6.0 mmol) were dissolved in 50 mL of water. Activated charcoal (0.5 g) was added, and the solution was stirred at 60 °C for 2 h. The charcoal was filtered from the hot solution and the filtrate was evaporated to dryness. The residue was dissolved in 80:20 MeOH–H_2O and chromatographed as described above. The trans-carboxylate $[Co(D\text{-}Pyala)_2]NO_3\cdot{}^1/_2H_2O$ was the only isomer isolated. The yield based on total cobalt was 24%.

Freshly prepared $Na_3[Co(CO_3)_3]\cdot 3H_2O$ (0.54 g, 1.5 mmol) was added to a solution of D-PyalaH (1.0 g, 3.0 mmol) and HNO_3 (6.0 mmol) in 50 mL of H_2O. After the initial foaming subsided, 0.5 g of activated charcoal was added. The solution was heated to 60 °C for 2 h and then stirred at ambient temperature for 16 h. The charcoal was filtered from the solution and washed with hot water until the filtrate was colorless. The solution was evaporated to dryness, dissolved in 80:20 MeOH–H_2O, and chromatographed as described previously. One band formed and was identified as trans-carboxylate $[Co(D\text{-}Pyala)_2]NO_3\cdot{}^1/_2H_2O$. The yield was 53% (based on total Co).

Spectra. The infrared spectrum was recorded on a KBr disk using a Beckman IR 4250 spectrophotometer. The visible, optical rotatory dispersion, and circular dichroism spectra were recorded at room temperature using a Jasco ORD/UV/CD-5 spectrophotometer. The ^1H NMR spectrum was measured on a Varian Associates HA-100 spectrometer in 99.7% deuterium oxide vs. *tert*-butyl alcohol (δ 1.23) as an internal standard.

Crystal Data. A crystal of dimensions 0.1 × 0.1 × 0.5 mm was mounted on a glass fiber with Duco cement and subsequently attached to a standard goniometer head. From four preliminary ω-oscillation photographs taken on an automated four-circle X-ray diffractometer at various χ and ϕ settings, nine independent reflections were selected and their coordinates were input to the automatic indexing program ALICE.[9] The resulting reduced cell and reduced-cell scalars indicated an orthorhombic crystal system. Orthorhombic *mmm* symmetry was confirmed by inspection of the three axial ω-oscillation photographs. Observed layer line separations agreed well with those predicted for the cell by the indexing program.

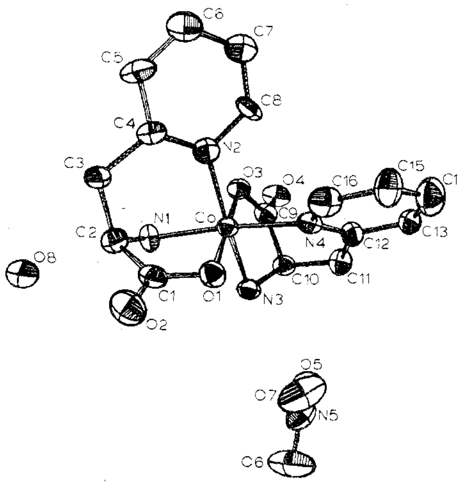

Figure 2. Structure of $[Co(D\text{-}Pyala)_2]NO_3\cdot{}^1/_2H_2O$.

A least-squares refinement of the lattice constants based on the $\pm 2\theta$ measurements of 13 reflections on a previously aligned four-circle diffractometer (graphite-monochromated Mo Kα radiation, λ 0.709 54 Å) at 25 °C, yielded a = 9.248 (1), b = 18.439 (4), and c = 21.697 (5) Å.

Collection and Reduction of X-ray Intensity Data. Data were collected at 25 °C using an automatic four-circle diffractometer designed and built in the Ames Laboratory.[10] All data in two octants and within a 2θ sphere of 50° ($(\sin\theta)/\lambda = 0.596$ Å^{-1}) were measured using an ω step–scan technique.

As a general check on electronic and crystal stability, the intensities of three standard reflections were remeasured every 75 reflections. These standards did not vary significantly throughout the entire data collection period. A total of 4168 reflections were recorded in this manner. Examination of the data revealed systematic absences for hkl, $h + k = 2n + 1$, and $00l$, $l = 2n + 1$, thus uniquely defining the space group as $C222_1$.

The measured intensities were corrected for Lorentz and polarization effects, but no absorption correction was made (μ = 10.24 cm^{-1}). The minimum and maximum transmission factors were 0.88 and 0.92. 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 count, respectively, K_t is a counting time constant, and the factor 0.03 represents an estimate of nonstatistical errors. The standard deviations in the structure factor amplitudes were obtained by the method of finite differences.[11] Equivalent reflections for which $|F_o| > 3\sigma F_o$ were retained and averaged. This yielded 1646 independent reflections which were used in subsequent calculations.

Solution and Refinement of the Structure. The position of the cobalt atom was obtained by analysis of a three-dimensional Patterson function. The remaining atoms were found by successive structure factor[12] and electron density map calculations.[13] The positional parameters for all nonhydrogen atoms and their anisotropic thermal parameters were refined by a full-matrix least-squares procedure,[12] minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma_F^2$, to a final conventional residual index of $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.062$. Examination of observed and calculated structure factors revealed no appreciable extinction effects. The scattering factors used were those of Hanson et al.,[14] modified for anomalous dispersion.[15]

The solution and refinement of the structure were completed without attempting to refine the absolute configuration of the cation. The final structure of the optically active cation was based on the known[1] configuration of D-Pyala$^-$.

The final positional and thermal parameters are listed in Table I. The standard deviations were calculated from the inverse matrix of the final least-squares cycle.[16]

Description and Discussion of the Structure

The crystal structure consists of discrete bis[D-β-(2-pyridyl)-α-alaninato]cobalt(III) cations, $Co(D\text{-}Pyala)_2^+$, and nitrate anions. The atomic labeling of the structure is shown in Figure 2. The cobalt atom is coordinated to the carboxylate

Table I. Final Atomic Parameters

(a) Final Positional Parameters and Their Estimated Standard Deviations (in Parentheses)[a]

atom	x	y	z
Co	5598.6 (11)	2547.4 (5)	4002.0 (5)
O1	4385 (7)	2760 (3)	3327 (3)
O2	3367 (8)	3699 (4)	2846 (3)
O3	6748 (6)	2351 (3)	4707 (2)
O4	6919 (7)	1599 (4)	5499 (3)
O5	1675 (9)	848 (4)	4691 (3)
O6	9722 (10)	1063 (6)	4218 (5)
O7	1761 (11)	1254 (6)	3773 (4)
O8[b]	3364 (13)	5000	5000
N1	4952 (9)	3469 (4)	4331 (3)
N2	7316 (8)	3055 (4)	3672 (3)
N3	4082 (8)	2016 (4)	4435 (3)
N4	6053 (8)	1627 (4)	3580 (3)
N5	1038 (11)	1058 (5)	4221 (5)
C1	4090 (10)	3450 (5)	3271 (4)
C2	4734 (10)	3931 (5)	3771 (4)
C3	6147 (11)	4274 (5)	3578 (5)
C4	7422 (10)	3760 (5)	3513 (4)
C5	8732 (11)	4060 (6)	3325 (5)
C6	9971 (13)	3639 (6)	3272 (5)
C7	9868 (11)	2908 (6)	3442 (4)
C8	8550 (9)	2637 (5)	3639 (4)
C9	6272 (10)	1823 (5)	5051 (4)
C10	4885 (10)	1483 (5)	4831 (4)
C11	5273 (11)	818 (5)	4445 (4)
C12	6021 (10)	961 (5)	3834 (4)
C13	6578 (11)	356 (5)	3536 (5)
C14	7149 (14)	437 (6)	2949 (5)
C15	7069 (13)	1095 (5)	2660 (4)
C16	6525 (13)	1685 (6)	2984 (4)

(b) Final Thermal Parameters (×10^4) and Their Estimated Standard Deviations (in Parentheses)[c]

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	47.9 (12)	15.0 (3)	10.3 (2)	0.7 (6)	−1.2 (4)	−0.3 (2)
O1	74 (7)	20 (2)	13 (1)	4 (3)	−3 (3)	−1 (1)
O2	104 (9)	30 (2)	17 (2)	10 (4)	−5 (4)	5 (2)
O3	60 (7)	20 (2)	12 (1)	0 (3)	−3 (2)	1 (1)
O4	84 (9)	36 (3)	12 (1)	1 (4)	−4 (3)	6 (2)
O5	122 (11)	41 (3)	19 (2)	5 (5)	2 (4)	6 (2)
O6	100 (13)	65 (5)	50 (4)	−15 (6)	−18 (6)	24 (4)
O7	192 (15)	69 (5)	15 (2)	−54 (8)	6 (5)	−2 (2)
O8	114 (16)	37 (4)	36 (4)	0	0	−2 (3)
N1	95 (10)	14 (2)	12 (2)	7 (4)	2 (4)	0 (2)
N2	74 (10)	21 (2)	11 (2)	−1 (4)	4 (3)	0 (2)
N3	55 (9)	19 (2)	16 (2)	0 (4)	−1 (3)	2 (2)
N4	53 (9)	21 (2)	12 (2)	1 (4)	0 (3)	−1 (2)
N5	125 (14)	27 (3)	22 (2)	−22 (5)	4 (5)	0 (2)
C1	50 (11)	21 (3)	14 (2)	2 (4)	3 (4)	3 (2)
C2	69 (12)	20 (3)	13 (2)	−4 (5)	−1 (4)	1 (2)
C3	54 (12)	18 (3)	26 (3)	−1 (5)	10 (5)	6 (2)
C4	59 (11)	22 (3)	12 (2)	−6 (5)	−1 (4)	2 (2)
C5	69 (13)	30 (4)	20 (3)	−17 (6)	0 (5)	4 (3)
C6	92 (13)	34 (4)	17 (2)	−3 (6)	1 (5)	1 (3)
C7	87 (13)	30 (3)	13 (2)	−2 (6)	1 (4)	0 (2)
C8	47 (9)	25 (3)	17 (2)	13 (5)	3 (4)	−5 (2)
C9	68 (12)	21 (3)	13 (2)	3 (5)	4 (4)	4 (2)
C10	65 (10)	19 (3)	14 (2)	0 (5)	−2 (4)	3 (2)
C11	106 (15)	19 (3)	14 (2)	−1 (5)	0 (5)	2 (2)
C12	72 (12)	16 (2)	15 (2)	3 (5)	−2 (4)	−1 (2)
C13	71 (12)	23 (3)	19 (2)	2 (5)	−5 (5)	−10 (2)
C14	154 (19)	30 (4)	23 (3)	10 (7)	−11 (7)	−10 (3)
C15	147 (18)	25 (3)	13 (2)	2 (6)	−2 (5)	−7 (2)
C16	99 (14)	33 (4)	12 (2)	−5 (6)	−5 (5)	−3 (2)

[a] The positional parameters are presented in fractional unit cell coordinates (×10^4). [b] The y and z positional parameters were not varied. [c] The β_{ij} are defined by $T = \exp\{-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})\}$.

oxygen atom, the amino nitrogen atom, and the pyridine nitrogen atom of each D-Pyala$^-$ ion in a slightly distorted octahedral arrangement. The configuration may be termed trans carboxylate according to the convention noted in the Introduction (Figure 1).

The interatomic distances and angles are given in Tables II and III. A comparison between the two D-Pyala$^-$ groups shows that corresponding bond lengths and angles do not differ significantly. (The difference in each case is less than 3 times the standard deviation.) The bond distances observed within the ligands compare quite well with those for similar groups in either (D-histidinato)(L-histidinato)cobalt(III) bromide[17] or carbonatotetrakis(pyridine)cobalt(III) perchlorate.[18] Two types of C–O distances in the carboxylate groups are evident.

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

Co-O1	1.887 (6)	Co-O3	1.898 (5)
Co-N1	1.938 (7)	Co-N3	1.952 (7)
Co-N2	1.978 (7)	Co-N4	1.973 (7)
O1-C1	1.31 (1)	O3-C9	1.30 (1)
O2-C1	1.23 (1)	O4-C9	1.21 (1)
O1-O2	2.230 (9)	O3-O4	2.214 (8)
C1-C2	1.52 (1)	C9-C10	1.51 (1)
N1-C2	1.50 (1)	N3-C10	1.50 (1)
C2-C3	1.51 (1)	C10-C11	1.53 (1)
C3-C4	1.52 (1)	C11-C12	1.52 (1)
C4-C5	1.39 (1)	C12-C13	1.39 (1)
C5-C6	1.39 (2)	C13-C14	1.39 (1)
C6-C7	1.40 (1)	C14-C15	1.37 (1)
C7-C8	1.39 (1)	C15-C16	1.39 (1)
C8-N2	1.38 (1)	C16-N4	1.37 (1)
N2-C4	1.35 (1)	N4-C12	1.35 (1)
N5-O5	1.24 (1)	O5-O6	2.12 (1)
N5-O6	1.22 (1)	O5-O7	2.13 (1)
N5-O7	1.24 (1)	O6-O7	2.15 (1)
N1-O8	3.497 (9)		
N3-O5	3.15 (1)		
N3-O7	2.94 (1)		

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

O1-Co-O3	177.2 (3)		
N1-Co-N4	172.1 (3)	N3-Co-N2	171.4 (3)
O1-Co-N1	85.4 (3)	O3-Co-N3	85.4 (3)
O1-Co-N2	95.7 (3)	O3-Co-N4	95.2 (3)
O1-Co-N3	92.9 (3)	O3-Co-N1	92.5 (3)
O1-Co-N4	86.8 (3)	O3-Co-N2	86.1 (3)
N1-Co-N2	88.1 (3)	N3-Co-N4	86.9 (3)
N1-Co-N3	92.4 (3)	N2-Co-N4	93.9 (3)
Co-O1-C1	113.5 (6)	Co-O3-C9	114.5 (5)
Co-N1-C2	104.0 (5)	Co-N3-C10	104.4 (5)
Co-N2-C4	127.4 (6)	Co-N4-C12	126.1 (6)
Co-N2-C8	114.8 (6)	Co-N4-C16	116.1 (6)
O1-C1-O2	123.2 (9)	O3-C9-O4	123.2 (8)
O1-C1-C2	114.9 (8)	O3-C9-C10	114.7 (7)
O2-C1-C2	121.9 (8)	O4-C9-C10	122.1 (8)
C1-C2-N1	107.4 (7)	C9-C10-N3	109.2 (7)
N1-C2-C3	110.3 (8)	N3-C10-C11	109.1 (7)
C1-C2-C3	112.6 (8)	C9-C10-C11	108.0 (8)
C2-C3-C4	115.9 (7)	C10-C11-C12	116.5 (7)
C3-C4-N2	121.4 (8)	C11-C12-N4	121.7 (8)
C3-C4-C5	117.1 (8)	C11-C12-C13	115.8 (8)
C4-C5-C6	121.3 (9)	C12-C13-C14	118.8 (9)
C5-C6-C7	117 (1)	C13-C14-C15	120 (1)
C6-C7-C8	119 (1)	C14-C15-C16	118.9 (9)
C7-C8-N2	122.9 (9)	C15-C16-N4	122.1 (9)
C8-N2-C4	117.7 (8)	C16-N4-C12	117.7 (8)
N2-C4-C5	121.4 (9)	N4-C12-C13	122.3 (8)
O5-N5-O6	119 (1)	O5-N5-O7	119 (1)
O6-N5-O7	122 (1)		

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

atom	D[b]	atom	D
Plane 1: N2-C4-C5-C6-C7-C8			
$0.22919X + 0.23315Y + 0.94504Z - 10.4 = 0$			
N2	−0.0056	C2[c]	0.0266
C4	−0.0061	C3[c]	0.0778
C5	0.0149	Co[c]	0.0887
C6	−0.0120		
C7	0.0004		
C8	0.0085		
Plane 2: N4-C12-C13-C14-C15-C16			
$0.91075X + 0.19490Y + 0.36406Z - 8.47207 = 0$			
N4	0.0387	C10[c]	−0.0085
C12	−0.0269	C11[c]	−0.2256
C13	−0.0105	Co[c]	0.3201
C14	0.0357		
C15	−0.0234		
C16	−0.0136		
Plane 3: N5-O5-O6-O7			
$0.00542X + 0.93598Y + 0.35201Z - 5.05479 = 0$			
N5	0.0002		
O5	0		
O6	0		
O7	0		

[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. [c] These atoms were not included in the calculation of the plane.

The C–O distances of the coordinated oxygen atoms (1.31 (1) and 1.30 (1) Å) are significantly longer than those in the uncoordinated "carbonyl-type" oxygen atoms (1.23 (1) and 1.21 (1) Å), as has been observed in other amino acid complexes.[19-21] The Co–N(amino) and Co–O bond distances are comparable to those found in other cobalt(III) complexes,[17,19-21] and the Co–N(pyridine) bond distances are similar to those reported in other cobalt(III) structures.[18,32] The corresponding N(amino)–Co–N(pyridine), N(amino)–Co–O, and N(pyridine)–Co–O bond angles for the two ligands differ only slightly (up to 1.2°). Distortions from ideal octahedral geometry are apparent by comparison of angles around the cobalt atom. Deviations from 90° occur for all angles and range from 1.9 to 5.7°. These differences are best explained by considering the constraints imposed upon the coordination geometry by the chelate ring sizes. The small angles (both 85.4 (3)°) in the five-membered amino acidate chelate rings are consistent with other values reported for cobalt(III) complexes.[19-31] The six-membered rings have the smallest deviations from 90° as was also found for the (D-histidinato)(L-histidinato)cobalt(III) ion.[17] The pyridine rings seem to repel each other, as suggested by the expansion of the O1–Co–N2, O3–Co–N4, and N4–Co–N2 angles and contraction of the N2–Co–O3 and N4–Co–O1 angles.

A small difference in the bonding of the two D-Pyala^- ions is seen when considering the pyridine rings. The distances from the cobalt atom to the least-squares planes of the pyridine rings are 0.09 and 0.32 Å (Table IV). Also the Co–N2 and Co–N4 bonds make angles of 2.6 and 9.3° with the plane of their respective pyridine rings. Similar displacements of the cobalt atom with respect to the plane of the ring have been observed in other pyridine-containing cobalt(III) complexes.[18,33] The dihedral angle between the least-squares planes of the two pyridine rings is 53.2°. Neither of these least-squares planes is coincident with the plane defined by N1–N2–N3–N4–Co. The dihedral angles between N1–N2–N3–N4–Co and the planes of the rings are 33.7° (for the ring containing N2) and 39.8° (for the ring containing N4).

The nitrate ion has average N–O distances of 1.23 (1) Å and average O–N–O angles of 120 (1)°, all of which are normal for this ion.

The water molecule, O8, forms no close contacts to the rest of the structure. The nearest approach of the oxygen atom O8 is to the amino nitrogen N1. This distance (3.497 (9) Å) is considerably longer than the sum of the van der Waals radii for an N···O contact (3.07 Å).[34]

Hydrogen bonding does not appear to play a major role in stabilizing this crystal structure. Neither the closest contacts nor the associated angles indicate anything but very weak hydrogen bonding. The interaction most favorable for hydrogen-bond formation would be between N3 and O7 (2.94 (1) Å). However, the N5–O7–N3 angle is 98.6°, somewhat less than the 120° expected, and, more importantly, the assumption of an N–H bond length of 1.05 Å places the hydrogen a distance of 2.45 Å from O7.

The packing of the eight cations and anions in the unit cell is shown in Figure 3.

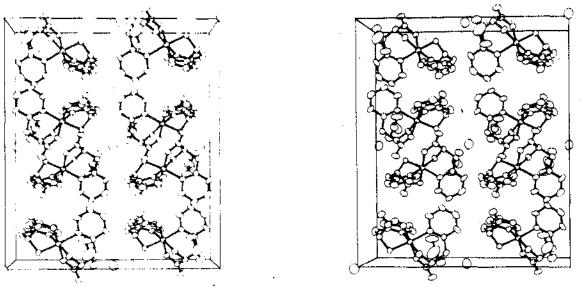

Figure 3. Stereoscopic view of the unit cell with the *b* axis horizontal and the *c* axis vertical.

Discussion

Attempts were made by several different methods to prepare all three isomers of Co(D-Pyala)$_2^+$. However, only the trans-carboxylate isomer (Figure 1a) was isolated from all preparative methods. These include mixing Co(II) salts with D-Pyala$^-$ and subsequently oxidizing the metal ion to Co(III) and reacting D-Pyala$^-$ with [Co(NH$_3$)$_4$CO$_3$]NO$_3$, [Co(NH$_3$)$_6$](NO$_3$)$_3$, or Na$_3$[Co(CO$_3$)$_3$]·3H$_2$O. In an attempt to isomerize the trans-carboxylate isomer, the complex was heated with charcoal in boiling water for 24 h. Only starting material and some decomposition products remained after this treatment. Similar treatment of an analogous complex, (D-aspartato)(L-2,4-diaminobutyrato)cobalt(III) produced an equilibrium mixture of isomers.[35] The three isomers of (L-histidinato)(iminodiacetato)cobalt(III) were found to isomerize in water without any catalysis at 80 °C.[36] Since trans-carboxylate Co(D-Pyala)$_2^+$ did not produce a mixture of isomers under similar conditions, we believe that this is the most stable form.

The infrared spectrum of trans-carboxylate [Co(D-Pyala)$_2$]NO$_3$·$^1/_2$H$_2$O exhibited strong NH$_2$ stretching absorptions at 3218 and 3100 cm^{-1}. The NH$_2$ deformation mode was observed at 1610 cm^{-1}. The intense CO$_2^-$ asymmetric stretching absorption appeared at 1670 cm^{-1}, compared to 1650 cm^{-1} reported for the bis(histidinato)cobalt(III) ion.[3] The presence of the nitrate anion was detected as a sharp peak at 1385 cm^{-1}.

The visible, ORD, and CD spectra of the trans-carboxylate isomer are given in Figure 4. These spectra are very similar to those of the analogous isomers of bis(L-2,3-diaminopropionato)cobalt(III) ion,[4] bis(L-2,4-diaminobutyrato)cobalt(III) ion,[5] and bis(L-histidinato)cobalt(III) ion.[2] The splitting in the lowest energy spin-allowed d–d band was used to assign the correct geometry to the complex before the crystal structure had been solved. Two components were seen in this band with the less intense shoulder appearing at shorter wavelengths as in the previously mentioned complexes.[2-5] The CD spectrum is very similar to the inverse of the spectra of the (L-histidinato)-, (L-2,3-diaminopropionato)-, and (L-2,4-diaminobutyrato)cobalt(III) complexes.[2,4,5] This result confirms the original assignment, which was based on the Clough–Lutz–Jirgenson rule,[1] of the D configuration to the free D-PyalaH ligand.

The ^{1}H NMR spectrum of the diamagnetic complex is consistent with its C_2 symmetry which implies two equivalent D-Pyala$^-$ groups. In free D-PyalaH, the α and β protons show an ABX pattern. The α proton occurs as four peaks of equal intensity centered at δ 4.13, and the β protons occur as three peaks centered at δ 3.33 with the lowest field peak being the most intense. Upon coordination to cobalt(III), the α proton is shifted upfield and the β protons are shifted downfield, as in the case of L-histidine. The shifts are such that both α and β protons absorb at δ 3.91 ppm and appear as a sharp singlet with no splitting. The position of the pyridine protons also differs from that observed in the uncoordinated ligand. The most noticeable shift occurs for the protons on carbons 8 and 16 in Figure 2. D-PyalaH shows a set of complex peaks assigned to this proton at 8.36–8.50 ppm, with the remaining pyridine protons at 7.22–7.89 ppm. Coordination in the trans-carboxylate structure shifts the C8 and C16 protons upfield to where they are no longer distinguishable from the other ring protons at 7.22–8.14 ppm. This shift is not unexpected when the structure of the complex is considered, since this proton occupies a position over the other pyridine ring and is thus shielded.

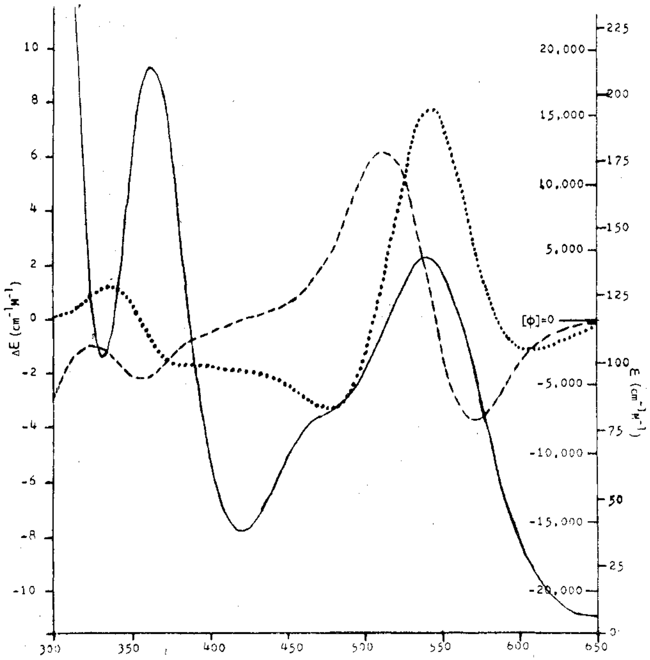

Figure 4. Absorption (—), molar rotation (···), and CD (---) spectra of trans carboxylate Co(D-Pyala)$_2^+$ ion in aqueous solution.

Conclusion

When L-histidine, L-2,3-diaminopropionic acid, or L-2,4-diaminobutyric acid is coordinated to cobalt(III), all three possible isomers are separated.[2-5] In the case of L-histidine the major isomer is the trans-imidazole isomer which accounted for more than 75% of the products.[2] Since the imidazole and pyridine rings are sterically very similar, the distribution of isomers based on repulsion of the rings alone was expected to be similar for Co(L-his)$_2^+$ and Co(D-Pyala)$_2^+$. However, we observe the formation of the trans-carboxylate isomer of Co(D-Pyala)$_2^+$ almost exclusively, and our other studies indicate that this is the thermodynamically most stable isomer. The reason for this stability may be related to the stabilities of similar amino acid–cobalt complexes. Thus only a small amount of the trans N isomer of bis(L-aspartato)cobalt(III) anion could be prepared.[37] Likewise, little of the analogous trans N isomer was found in the equilibrium mixtures of (D-aspartato)(L-2,4-diaminobutyrato)cobalt(III)[35] and (L-histidinato)(iminodiacetato)cobalt(III).[36] Only 6% of the trans-N(amino) isomer of Co(L-his)$_2^+$ and none of this isomer of Co(L-his)(D-his)$^+$ could be isolated.[2] Our results support these findings since the trans-amino isomer of Co(D-Pyala)$_2^+$ could not be isolated. This suggests that α-amino nitrogens avoid being trans to each other in all of these complexes.

Reasons for the absence of the trans-pyridyl isomer of Co(D-Pyala)$_2$ are not as obvious. Indeed, many factors may contribute to its instability. The weaker coordination of pyridine compared to imidazole (the difference in log K_f values for several transition metal ions is about 1.0) may cause the pyridine to preferentially assume a position trans to the amino nitrogen. The greater π-acceptor ability of the pyridine group trans to the strongly donating amino group may also add to the stability of the trans-carboxylate structure (Figure 1). Finally molecular models of the trans-pyridyl structure show that the α-hydrogen of the pyridine ring points into the π cloud of the carboxylate group of the other ligand. Repulsion between the α hydrogen and carboxylate group may also destabilize this structure. This repulsion would be much smaller in $Co(L\text{-}his)_2^+$, where the α-hydrogen of the smaller imidazole ring does not point directly into the π cloud of the carboxylate group. Thus, electronic as well as steric factors may be responsible for the destabilization of the trans-amino and trans-pyridyl structures.

Acknowledgment. The authors thank J. H. Benson and B. J. Helland for their assistance in collecting data. The major support of this research was provided by National Institutes of Health Research Grant GM12626.

Registry No. $[Co(D\text{-}Pyala)_2]NO_3\cdot{}^1/_2H_2O$, 68890-44-8; $[Co(NH_3)_4CO_3]NO_3$, 15040-52-5; $Co(NO_3)_2\cdot 6H_2O$, 10026-22-9; $[Co(NH_3)_6](NO_3)_3$, 10534-86-8; $Na_3[Co(CO_3)_3]\cdot 3H_2O$, 15684-40-9.

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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