

**Table X.** Bond Distances (Å) and Bond Angles (Deg) in the THF Ligand

O(7)-C(11)	1.49 (3)	C(11)-C(12)	1.37 (5)
O(7)-C(14)	1.42 (3)	C(12)-C(13)	1.44 (5)
		C(13)-C(14)	1.45 (4)
C(11)-O(7)-C(14)	105 (2)	C(12)-C(11)-O(7)	105 (3)
O(7)-C(14)-C(13)	113 (2)	U-O(7)-C(11)	128 (1)
C(14)-C(13)-C(12)	101 (3)	U-O(7)-C(14)	127 (2)
C(13)-C(12)-C(11)	116 (4)		

**Table XI.** Comparison of  $\text{UO}_2(\text{FAA})_2\text{THF}$  and  $\text{UO}_2(\text{FAA})_2\text{OP}(\text{OMe})_3$ , Bond Distances (Å)

	$\text{UO}_2(\text{FAA})_2\text{-THF}$	$\text{UO}_2(\text{FAA})_2\text{-OP}(\text{OMe})_3$
U-O(uranyl)	1.66	1.74
U-O(carbonyl)	2.38	2.40
U-O(THF or OP(OMe) <sub>3</sub> )	2.35	2.31
C-O(carbonyl)	1.30	1.25
C-C(ring)	1.35	1.36
C-C(CF <sub>3</sub> )	1.54	1.62
C-F	1.30	1.34

unusually large when compared with those in  $\text{UO}_2(\text{FAA})_2\text{OP}(\text{OMe})_3$ . The high thermal motions may be a consequence of some positional disorder. The main structural consequence is that there is uncertainty in the C-F distances which show a wide range of values from 1.06 to 1.66 Å although the average distance is reasonable.

**The THF Ligand.** Bond distances and bond angles for the THF ligand are given in Table X. The distances are similar to those in  $\text{Li}_4[\text{Mo}_2(\text{CH}_3)_8]\cdot 4\text{THF}$ <sup>26</sup> (average C-O = 1.44 Å, average C-C = 1.47 Å) although C(1)-C(12) is perhaps a little short. A least-squares plane through O(7), C(11), and C(14) was calculated as  $0.9894x + 0.050y - 0.1324z = 1.8538$ , and the angles between this plane and the  $\text{UO}_5$  pentagon were

(26) F. A. Colton, J. M. Troup, T. R. Webb, D. H. Williamson, and G. Wilkinson, *J. Am. Chem. Soc.*, **96**, 3824 (1974).

(27) G. Gordon and H. Taube, *J. Inorg. Nucl. Chem.*, **16**, 272 (1961).

calculated as 67.9° indicating that the THF ligand is tilted with C(11) toward O(6) and C(14) toward O(3).

**Comparison with  $\text{UO}_2(\text{FAA})_2\text{OP}(\text{OMe})_3$ .**<sup>11b</sup> Some points of comparison with  $\text{UO}_2(\text{FAA})_2\text{OP}(\text{OMe})_3$  have been noted above. In general the two molecules are very similar as can be seen from a comparison of average bond distances (Table XI). Most of the differences are within the experimental errors although the uranyl oxygen distances are somewhat short which probably reflects absorption errors. Residual peaks were found in the final difference Fourier in the vicinity of the uranium atom. The hfacac rings in both molecules are planar indicating delocalization and tilted in the same direction with respect to the  $\text{UO}_5$  pentagon. In the  $\text{OP}(\text{OMe})_3$  derivative both planes are equivalent and tilted by 22.5° compared with 18.9 and 13.2° in the THF compound. This tilting is not an unusual feature of chelated uranyl compounds, and tilting angles in the range 3-42° have been observed in other systems.<sup>24</sup> Both compounds show high thermal motion and disorder of the peripheral  $\text{CF}_3$  groups and consequently variations and uncertainties in the C-F distances.

### Summary

A THF adduct of  $\text{UO}_2(\text{FAA})_2$  with an unobstructed IR absorption band near 950  $\text{cm}^{-1}$  and vapor pressures of about 1 torr at 100 °C has been prepared. The compound sublimes as a unit and has considerable thermal stability as evidenced by its mass spectroscopic cracking pattern in which the  $\text{FAA}^-$  anions are lost more easily than THF. Its crystal structure has been determined and the compound has been further characterized by its UV-visible spectrum, NMR spectrum, and other physical tools which are generally consistent with the formulation  $\text{UO}_2(\text{FAA})_2\cdot\text{THF}$ . The excited-state lifetimes obtained are indicative of the suitability of compound 1 for isotope separations with a  $\text{CO}_2$  laser.

**Registry No.** 1, 69244-67-3.

**Supplementary Material Available:** Positional and thermal parameters (Table S-2) and calculated and observed structure factors (Table S-1) (10 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,  
Iowa State University, Ames, Iowa 50011

## Preparations and Spectral Characterizations of the $\beta$ -(2-Pyridyl)- $\alpha$ -alanine Complexes: $\text{Trans-Amino Co}(\text{D-Pyala})_2^+$ , Racemic *all-cis*- $\text{Co}(\text{D-Pyala})(\text{L-Pyala})^+$ , and $\text{Trans-Carboxylate Cr}(\text{D-Pyala})_2^+$

STEPHEN R. EBNER and ROBERT J. ANGELICI\*

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The trans-amino complex  $[\text{Co}(\text{D-Pyala})_2]\text{NO}_3\cdot 1\frac{1}{2}\text{H}_2\text{O}$  was prepared by reaction of  $\text{Co}(\text{II})$  with  $\text{D-H}_2\text{NCH}(\text{CH}_2\text{C}_5\text{H}_4\text{N})\text{CO}_2^-$ ,  $\text{D-Pyala}^-$ , and subsequent oxidation to form the  $\text{Co}(\text{III})$  complex. Isomerization of this complex to the more stable trans-carboxylate structure occurred in aqueous solution at room temperature. From the reaction of  $\text{D,L-Pyala}^-$  with  $\text{Co}(\text{III})$ , racemic *all-cis*- $[\text{Co}(\text{D-Pyala})(\text{L-Pyala})]\text{NO}_3\cdot\text{H}_2\text{O}$  was isolated. The greater stability of certain  $\text{Co}(\text{Pyala})_2^+$  isomers suggests that (1) amino groups avoid being trans to each other and (2) pyridyl groups avoid being trans to each other and prefer to be trans to an amino group. The reaction of  $\text{Cr}(\text{III})$  with  $\text{D-Pyala}^-$  produced a tris(amino acid) complex,  $\Delta\text{-fac-}[\text{Cr}(\text{D-Pyala})_3]\cdot\text{H}_2\text{O}$ , and a bis complex, trans-carboxylate  $[\text{Cr}(\text{D-Pyala})_2]\text{Cl}$ . Structural assignments of the  $\text{Co}(\text{III})$  and  $\text{Cr}(\text{III})$  complexes were based on their infrared,  $^1\text{H}$  NMR, visible, ORD, and CD spectra.

### Introduction

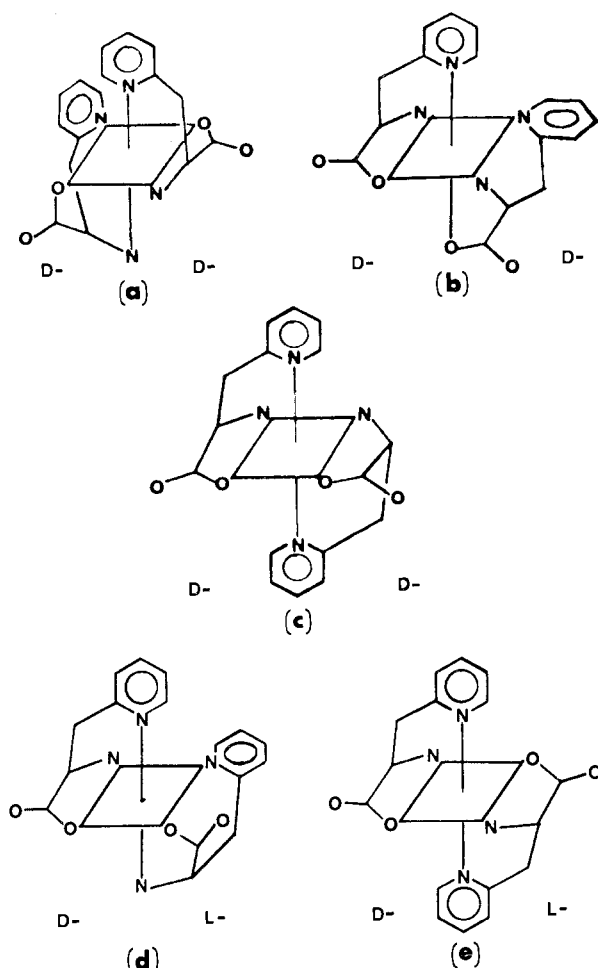
This study is part of an investigation into the origins of the stereoselectivity observed in the chelation of  $\beta$ -(2-pyridyl)- $\alpha$ -alanine,  $^+\text{H}_3\text{NCH}(\text{CH}_2\text{C}_5\text{H}_4\text{N})\text{CO}_2^-$ ,  $\text{PyalaH}$ , to transition-metal ions.<sup>1</sup> When the  $\text{Pyala}^-$  ligands are allowed to have either the D or L configuration, five different geometrical

isomers of the  $\text{M}(\text{Pyala})_2^+$  complexes are possible as indicated in Figure 1. Four of these, a-d, are optically active, and the fifth, e, is a meso complex.

Recently, the trans-carboxylate  $\text{Co}(\text{D-Pyala})_2^+$  complex (Figure 1a) was isolated and characterized.<sup>2</sup> It was suggested

(1) Rechani, P. R.; Nakon, R.; Angelici, R. J. *Bioinorg. Chem.* **1976**, *5*, 329.

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



**Figure 1.** The five possible geometrical isomers from the reaction of cobalt(III) with D,L-PyalaH: (a) trans carboxylate; (b) trans amino; (c) trans pyridyl; (d) all-cis; (e) all-trans.

that this form was the most stable isomer since several different methods of preparation produced this complex as the major species, and attempts to convert it to other isomers were unsuccessful. We have now separated and fully characterized a second isomer trans-amino  $\text{Co}(\text{D-Pyala})_2^+$  that was formed in very low yield in the preparation of the trans-carboxylate complex.

The complexes formed in the reaction of racemic ligand D,L-PyalaH have also been isolated and identified. The structures of the resulting complexes are compared with those reported for analogous complexes of histidine.<sup>3</sup> Finally, the more labile chromium(III) complexes of D-Pyala<sup>-</sup> have also been studied.

### Experimental Section

**Materials.** Racemic  $\beta$ -(2-pyridyl)- $\alpha$ -alanine was prepared and resolved as described previously.<sup>4</sup>

**Preparation of Trans-Amino Bis[D- $\beta$ -(2-pyridyl)- $\alpha$ -alaninato]cobalt(III) Nitrate,  $[\text{Co}(\text{D-Pyala})_2]\text{NO}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ .** The complex was prepared by adding  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (1.75 g, 6.0 mmol) to 20 mL of water containing D-PyalaH (2.0 g, 12.0 mmol) and NaOH (12.0 mmol). After the solution was stirred for 15 min,  $\text{PbO}_2$  (0.75 g, 3.1 mmol) was added, and the resulting mixture was heated to 70 °C for 1 h. The unreacted  $\text{PbO}_2$  was filtered from the solution, which was subsequently loaded on a column (1.8 × 42 cm) of Dowex 50W-X8 in the  $\text{Na}^+$  form. The column was washed with 200 mL

of water to remove ligand decomposition products. Elution with 0.1 M  $\text{NaNO}_3$  at 1 drop/2 s for 1 week gave three bands. The first complex eluted was trans-carboxylate  $\text{Co}(\text{D-Pyala})_2^+$  which was identified by its visible, circular dichroism, and  $^1\text{H}$  NMR spectra.<sup>2</sup> The yield was 46% on the basis of the  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  starting material.

The second band was evaporated to 10 mL and a layer of absolute ethanol (~20 mL) was added. The  $\text{NaNO}_3$  that precipitated from the aqueous phase as the layers diffused together was filtered from the solution. The filtrate was evaporated to 5 mL, and a layer of ethanol (~10 mL) was added once again. This caused precipitation of most of the remaining  $\text{NaNO}_3$ . The solution was filtered and evaporated to dryness, and the precipitate was dissolved in a minimum of boiling 95% ethanol. A layer of acetone (~15 mL) was floated on top of the ethanol solution. When the acetone was allowed to diffuse into the ethanol, red crystals precipitated. These were filtered from the solution and vacuum dried. The yield of the trans-amino complex was 4%. Anal. Calcd for  $[\text{Co}(\text{D-Pyala})_2]\text{NO}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ : C, 40.18; H, 4.43; N, 14.64; Co, 12.32. Found: C, 40.24; H, 4.45; N, 14.27; Co, 12.48.

Crystals were obtained from the third band, after removing the  $\text{NaNO}_3$  as described above, by evaporation of the solution to 1 mL, adding a layer of acetone, and cooling. Carbon, hydrogen, and nitrogen analyses of these crystals as well as their circular dichroism spectrum indicated that this complex was not an isomer of  $\text{Co}(\text{D-Pyala})_2^+$ , and it was not characterized further.

**Preparation of Racemic all-cis- $[\text{Co}(\text{D-Pyala})(\text{L-Pyala})]\text{NO}_3 \cdot \text{H}_2\text{O}$ .** This complex was prepared according to several different procedures. Those methods in which  $[\text{Co}(\text{NH}_3)_6](\text{NO}_3)_3$ ,  $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{NO}_3$  and  $\text{Na}_3[\text{Co}(\text{CO}_3)_3] \cdot 3\text{H}_2\text{O}$  were used as starting material have been reported previously,<sup>2</sup> and the only change was in using D,L-PyalaH instead of D-PyalaH. The method involving oxidation of cobalt(II) nitrate to the cobalt(III) complex was also similar to that reported,<sup>2</sup> but  $\text{PbO}_2$  (0.38 g, 1.6 mmol) was used as the oxidizing agent instead of hydrogen peroxide.

Separation of the isomeric cobalt(III) complexes was achieved chromatographically on basic alumina in 90:10 MeOH- $\text{H}_2\text{O}$ . After 8 h, three bands were eluted separately from the column. The first band was red-violet and was identified by its visible and  $^1\text{H}$  NMR spectra<sup>2</sup> as a racemic mixture of trans-carboxylate  $\text{Co}(\text{D-Pyala})_2^+$  and  $\text{Co}(\text{L-Pyala})_2^+$ . The lack of any optical activity in its circular dichroism spectrum verified the presence of equal amounts of the enantiomers  $\text{Co}(\text{D-Pyala})_2^+$  and  $\text{Co}(\text{L-Pyala})_2^+$ . The lowest yield, 7.6%, was obtained from the reaction solution in which cobalt(II) was oxidized to cobalt(III) with  $\text{PbO}_2$ . The highest yield, 10%, was isolated from the reaction of  $\text{Na}_3[\text{Co}(\text{CO}_3)_3] \cdot 3\text{H}_2\text{O}$  with D,L-PyalaH.

The third band was red and was identified by its visible and  $^1\text{H}$  NMR spectra as a racemic mixture of the trans-amino complex,  $\text{Co}(\text{D-Pyala})_2^+$  and  $\text{Co}(\text{L-Pyala})_2^+$ . Since the enantiomers were formed in equal amounts, no circular dichroism was observed. The yields of this complex were always very small (<1%).

The second band eluted from the column was red-violet and yielded the major product. The solution containing the red-violet complex was evaporated to a small volume (~1 mL), and a layer (2–3 mL) of ethanol was added. The crystals that formed were filtered, washed with 95% ethanol, and vacuum dried. The highest yield obtained of this all-cis- $[\text{Co}(\text{D-Pyala})(\text{L-Pyala})]\text{NO}_3 \cdot \text{H}_2\text{O}$  complex was 26% from the reaction of  $\text{Na}_3[\text{Co}(\text{CO}_3)_3] \cdot 3\text{H}_2\text{O}$  with D,L-PyalaH. The lowest yield, 20%, was isolated from the oxidation of cobalt(II) to cobalt(III) with  $\text{PbO}_2$ . The ratio of the yield of all-cis- $[\text{Co}(\text{D-Pyala})(\text{L-Pyala})]\text{NO}_3 \cdot \text{H}_2\text{O}$  to that of trans-carboxylate  $[\text{Co}(\text{D-Pyala})_2]\text{NO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$  and  $[\text{Co}(\text{L-Pyala})_2]\text{NO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$  was a constant, 2.6, for each reaction. Anal. Calcd for  $[\text{Co}(\text{C}_8\text{H}_9\text{N}_2\text{O}_2)_2]\text{NO}_3 \cdot \text{H}_2\text{O}$ : C, 40.95; H, 4.30; N, 14.92. Found: C, 41.22; H, 4.34; N, 14.92.

**Preparation of Tris(D- $\beta$ -(2-pyridyl)- $\alpha$ -alaninato)chromium(III) Monohydrate,  $[\text{Cr}(\text{D-Pyala})_3] \cdot \text{H}_2\text{O}$ , and Bis[D- $\beta$ -(2-pyridyl)- $\alpha$ -alaninato]chromium(III) Chloride,  $[\text{Cr}(\text{D-Pyala})_2]\text{Cl}$ .** The  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  (0.80 g, 3.0 mmol) and D-PyalaH (1.0 g, 6.0 mmol) were dissolved in 20 mL of water, and a methanol solution of  $(n\text{-Bu})_4\text{N}^+\text{OH}^-$  was added dropwise until the pH was 6.0. The green solution turned violet after being stirred for 2 h at 55 °C. This solution gave different products when treated in each of the following two ways:

(A) The aqueous solution was evaporated under reduced pressure to about 10 mL and allowed to stand at room temperature. After 3 days, pink crystals of  $[\text{Cr}(\text{D-Pyala})_3] \cdot \text{H}_2\text{O}$  formed. They were filtered from the solution and recrystallized from boiling water. Anal. Calcd

(3) Bagger, S.; Gibson, K.; Sorensen, C. S. *Acta Chem. Scand.* **1972**, *26*, 2503.

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

for  $\text{Cr}(\text{C}_5\text{H}_4\text{N}_2\text{O}_2)_3 \cdot \text{H}_2\text{O}$ : C, 50.97; H, 5.17; N, 14.86. Found: C, 50.89; H, 5.32; N, 14.66.

(B) The reaction solution was evaporated to dryness, and the solid was dissolved in methanol. This solution was chromatographed on basic alumina (125 mL, column  $1.9 \times 55$  cm) and eluted with methanol at 1 drop/2 s. One violet band formed and was eluted from the column after 6 h. The solution was evaporated to 5 mL and stored at  $-40^\circ\text{C}$ . Attempts to obtain crystals of the violet  $[\text{Cr}(\text{D-Pyala})_2]\text{Cl}$  complex were unsuccessful.

**Spectra.** The visible, optical rotatory dispersion, and circular dichroism spectra were recorded at room temperature by using a Jasco ORD/UV/CD-5 spectrophotometer. The  $^1\text{H}$  NMR spectra were recorded on a Varian Associates HA-100 spectrometer in 99.7% deuterium oxide vs. *tert*-butyl alcohol ( $\delta$  1.23 from  $\text{Me}_4\text{Si}$ ) as an internal standard. The infrared spectra of  $\text{Cr}(\text{D-Pyala})_3 \cdot \text{H}_2\text{O}$  as a KBr pellet and  $\text{Cr}(\text{D-Pyala})_2\text{Cl}$  in  $\text{D}_2\text{O}$  solution were recorded by using a Beckman IR4250 spectrophotometer.

## Results and Discussion

Coordination of  $\text{D-Pyala}^-$  to cobalt(III) can result in three geometrical isomers of the  $\text{Co}(\text{D-Pyala})_2^+$  complex. These isomers are labeled the *trans* carboxylate, *trans* amino, and *trans* pyridyl (Figure 1a-c). If racemic ligand  $\text{D,L-Pyala}^-$  is reacted with cobalt(III), five geometrical isomers are possible. Three of these (Figure 1a-c) are enantiomeric *D,D*- and *L,L*-pairs in which both ligands in the complex have the same absolute configuration. In the remaining two geometries (Figure 1d,e) the ligands must be of opposite chirality,  $\text{Co}(\text{D-Pyala})(\text{L-Pyala})^+$ . The all-*cis* complex exists in two enantiomeric *D,L*-forms, while the all-*trans* complex is not optically active.

**Trans-Amino  $[\text{Co}(\text{D-Pyala})_2]\text{NO}_3 \cdot 1/2\text{H}_2\text{O}$ .** The isolation and characterization of *trans*-carboxylate  $\text{Co}(\text{D-Pyala})_2^+$  (Figure 1a) has been reported.<sup>2</sup> The structural assignment was made by comparing the visible and CD spectra of *trans*-carboxylate  $\text{Co}(\text{D-Pyala})_2^+$  to the analogous isomer of bis(*L*-2,3-diaminopropionato)cobalt(III),<sup>5</sup> bis(*L*-2,4-diaminobutyrate)cobalt(III),<sup>6</sup> and bis(*L*-histidinato)cobalt(III).<sup>3</sup> Confirmation of the spectral assignment was made by an X-ray crystal structure analysis.<sup>2</sup>

A second isomer of  $\text{Co}(\text{D-Pyala})_2^+$  has now been isolated and identified as the *trans*-amino complex (Figure 1b). The visible, ORD, and CD spectra of this complex are shown in Figure 2. The splitting in the lowest energy spin-allowed *d-d* band is useful for assigning the correct geometry. Calculations based on the angular overlap model for  $\text{Co}(\text{L-His})_2^+$  predict that the shoulder in the *trans*-amino structure should occur on the long-wavelength side of the band system.<sup>7</sup> The *trans*-imidazole spectrum does not show any splitting. This suggests that the  $\text{Co}(\text{D-Pyala})_2^+$  complex reported here has the *trans*-amino structure.

In addition, the visible, ORD, and CD spectra of *trans*-amino  $\text{Co}(\text{D-Pyala})_2^+$  compare quite well with those of the *trans*-amino isomers of bis(*L*-2,3-diaminopropionato)cobalt(III),<sup>5</sup> bis(*L*-2,4-diaminobutyrate)cobalt(III),<sup>6</sup> and bis(*L*-histidinato)cobalt(III).<sup>3</sup> The CD spectrum especially aided in the structural assignment since the *trans*-amino and *trans*-imidazole  $\text{Co}(\text{L-His})_2^+$  spectra differ significantly. The CD spectrum of *trans*-amino  $\text{Co}(\text{D-Pyala})_2^+$  is similar to the inverse of the spectra of the (*L*-histidinato)-,<sup>3</sup> (*L*-2,3-diaminopropionato)-,<sup>5</sup> and (*L*-2,4-diaminobutyrate)cobalt(III)<sup>6</sup> *trans*-amino complexes.

The  $^1\text{H}$  NMR spectrum of the *trans*-amino  $\text{Co}(\text{D-Pyala})_2^+$  complex is consistent with its  $\text{C}_2$  symmetry which requires two equivalent *D-Pyala}^- groups. In free *D-PyalaH*, the  $\alpha$  proton was observed as four peaks of equal intensity centered at  $\delta$  4.13, and the  $\beta$  protons occurred as three peaks centered at  $\delta$  3.33*

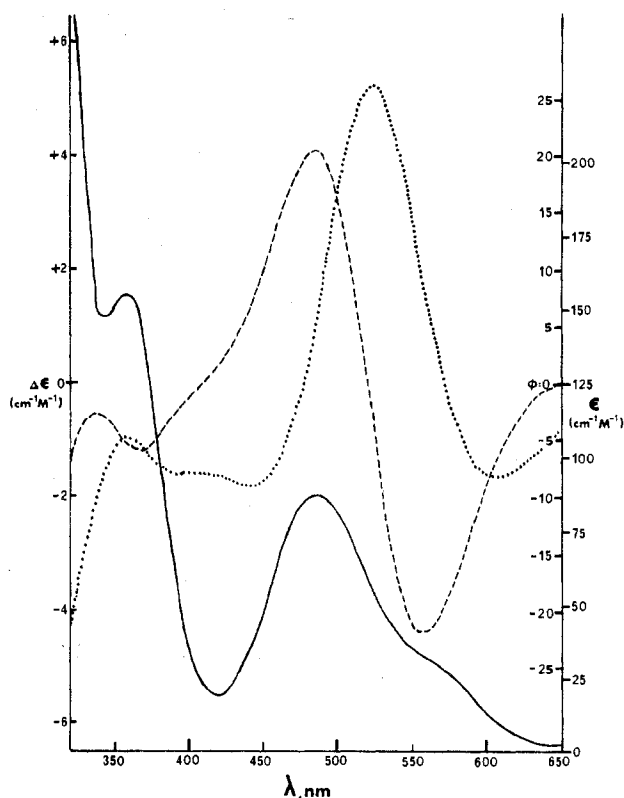


Figure 2. Absorption (—), molar rotation (···), and circular dichroism (---) spectra of *trans*-amino  $\text{Co}(\text{D-Pyala})_2^+$  in aqueous solution.

with the lowest field peak being the most intense. Upon deprotonation and coordination to cobalt(III) in the *trans*-amino structure, the  $\alpha$  proton was shifted upfield and the  $\beta$  protons were shifted downfield such that the  $\alpha$  and  $\beta$  proton patterns overlap. Four peaks of unequal intensity were observed from  $\delta$  3.97–4.22. This differs from the spectrum of the *trans*-carboxylate isomer which exhibited only a sharp singlet at  $\delta$  3.91.

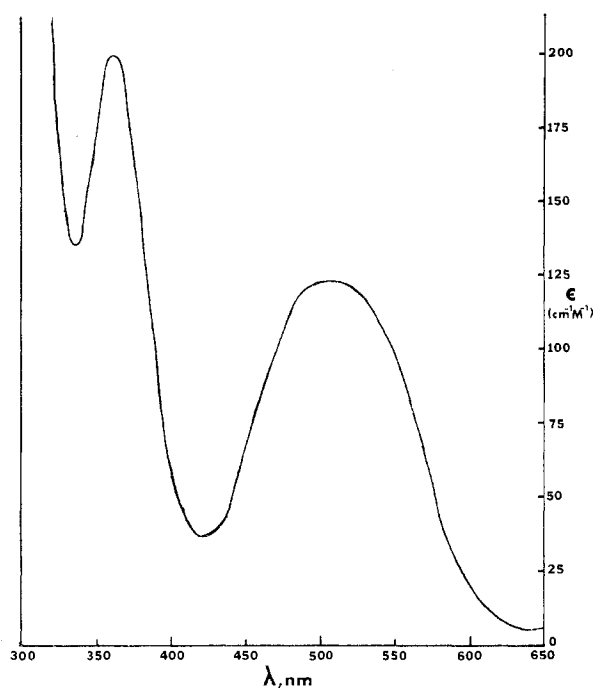
The peak positions in the aromatic region of the spectrum for the *trans*-amino complex differ from those of either the uncoordinated ligand or the *trans*-carboxylate isomer. The *D-PyalaH* showed peaks which resemble a doublet ( $\delta$  8.46), a triplet ( $\delta$  7.79), and an overlapping doublet and triplet ( $\delta$  7.22–7.44). The coordinated pyridine in the *trans*-amino complex showed the following pattern: overlapping triplet and doublet ( $\delta$  8.07), doublet ( $\delta$  7.66), and triplet ( $\delta$  7.34). These shifts can be compared with those observed for *trans*-carboxylate  $\text{Co}(\text{D-Pyala})_2^+$ : triplet ( $\delta$  7.99), doublet ( $\delta$  7.90), doublet ( $\delta$  7.62), and triplet ( $\delta$  7.40). Upon expansion further splitting can be observed in all three spectra due to coupling of nonadjacent hydrogens of the ring. The most easily assigned peak is that from the proton on the carbon adjacent to the pyridine nitrogen ( $\delta$  8.46 in the *D-PyalaH*). The doublet observed for this proton was shifted to 8.07 ppm in the *trans*-amino complex and to 7.90 ppm in the *trans*-carboxylate structure. These shifts parallel those reported for the analogous proton of histidine upon coordination to cobalt(III).<sup>3</sup>

**Racemic all-*cis*- $[\text{Co}(\text{D-Pyala})(\text{L-Pyala})\text{NO}_3 \cdot \text{H}_2\text{O}$ .** Three bands were separated from the reaction mixture by column chromatography when the racemic ligand, *D,L-Pyala}^-, was reacted with cobalt(III). The order of elution was racemic *trans*-carboxylate ( $\text{Co}(\text{D-Pyala})_2^+$  and  $\text{Co}(\text{L-Pyala})_2^+$ ), racemic all-*cis*- $\text{Co}(\text{D-Pyala})(\text{L-Pyala})^+$ , and racemic *trans*-amino ( $\text{Co}(\text{D-Pyala})_2^+$  and  $\text{Co}(\text{L-Pyala})_2^+$ ). The racemic all-*cis* complex (Figure 1d) was the major product of all the preparations.*

(5) Freeman, W. A.; Liu, C. F. *Inorg. Chem.* **1968**, *7*, 764.

(6) Freeman, W. A.; Liu, C. F. *Inorg. Chem.* **1970**, *9*, 1191.

(7) Schmidtke, H. H. *Chem. Phys. Lett.* **1969**, *4*, 451.



**Figure 3.** Absorption spectrum of racemic *all-cis*-Co(D-Pyala)(L-Pyala)<sup>+</sup> in aqueous solution.

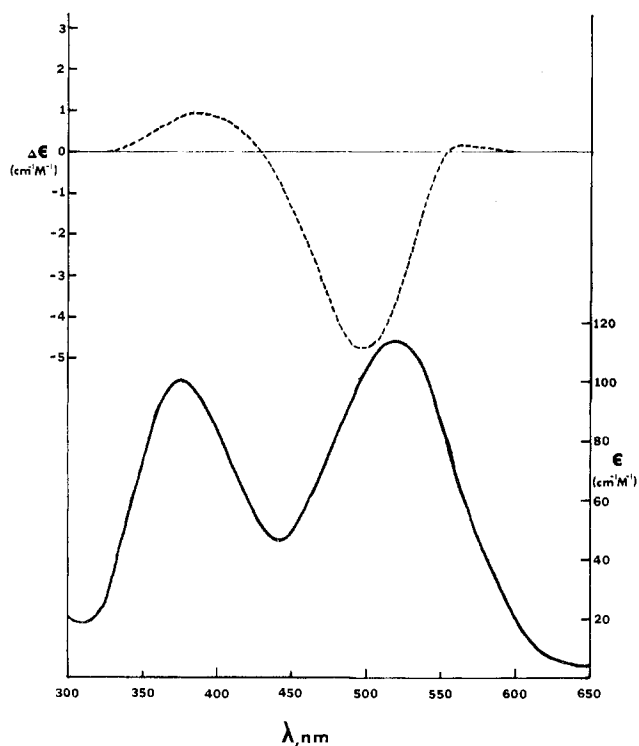
The visible spectrum of racemic *all-cis* [Co(D-Pyala)(L-Pyala)]NO<sub>3</sub>·H<sub>2</sub>O in water is shown in Figure 3. The broad band at 502 nm identifies the structure as being *all-cis* because of its similarity to the analogous histidinato complex.<sup>3</sup>

The <sup>1</sup>H NMR spectrum of the racemic *all-cis* complex is composed of two Pyala<sup>-</sup>-type spectra. This is not evident in the methine and methylene patterns since the chemical shift of all six of these protons is equal, and only one slightly broadened peak is observed at  $\delta$  3.91. However, the aromatic region consists of a number of patterns from which the presence of two different pyridine rings can be identified. The patterns observed for these protons (ignoring coupling of  $J < 2$  Hz) were doublet ( $\delta$  8.48), triplet ( $\delta$  8.09), triplet ( $\delta$  7.86), doublet ( $\delta$  7.67), doublet ( $\delta$  7.45), and triplet ( $\delta$  7.10).

**fac-[Cr(D-Pyala)<sub>3</sub>]·H<sub>2</sub>O and Trans-Carboxylate [Cr(D-Pyala)<sub>2</sub>]Cl.** When an aqueous solution of chromium(III) and D-Pyala<sup>-</sup> was left standing at room temperature, the tris(amino acid) complex, [Cr(D-Pyala)<sub>3</sub>]·H<sub>2</sub>O, precipitated. If an aqueous solution containing only trans-carboxylate Cr(D-Pyala)<sub>2</sub><sup>+</sup> was allowed to stand at room temperature for 3 days, precipitation of [Cr(D-Pyala)<sub>3</sub>]·H<sub>2</sub>O occurred also. Presumably, an equilibrium between the bis complex Cr(D-Pyala)<sub>2</sub><sup>+</sup> and the tris complex Cr(D-Pyala)<sub>3</sub> was established in solution, and because of its very low solubility (less than 1 mg/10 mL of H<sub>2</sub>O), [Cr(D-Pyala)<sub>3</sub>]·H<sub>2</sub>O precipitated.

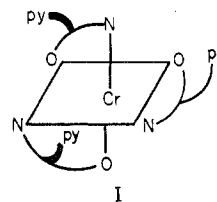
The infrared spectrum of [Cr(D-Pyala)<sub>3</sub>]·H<sub>2</sub>O is similar to that of other tris(amino acidato)chromium(III) complexes.<sup>8-10</sup> Stretching absorptions for -NH<sub>2</sub> are observed from 3130 to 3310 cm<sup>-1</sup>. The -NH<sub>2</sub> deformation frequency appears at 1600 cm<sup>-1</sup>, suggesting the amine groups are bonded to the chromium atom.<sup>10</sup> The asymmetric -CO<sub>2</sub> stretching mode occurs at 1660 cm<sup>-1</sup>, and the symmetric vibration is at 1382 cm<sup>-1</sup>.

The visible and circular dichroism spectra of the complex in Me<sub>2</sub>SO are given in Figure 4. The maxima and extinction coefficients are comparable to values reported for tris(amino acidato)chromium complexes isolated previously.<sup>8-13</sup> The



**Figure 4.** Absorption (—) and circular dichroism (---) spectra of  $\Lambda$ -*fac*-[Cr(D-Pyala)<sub>3</sub>]·H<sub>2</sub>O in Me<sub>2</sub>SO.

maxima for an aqueous solution of the complex are at 379 nm ( $\epsilon$  102 cm<sup>-1</sup> M<sup>-1</sup>) and 518 nm ( $\epsilon$  81 cm<sup>-1</sup> M<sup>-1</sup>). Because of the similarity of the circular dichroism spectra of [Cr(D-Pyala)<sub>3</sub>]·H<sub>2</sub>O to those of the tris(amino acidato)chromium(III) complexes reported previously,<sup>10</sup> the configuration of the complex can be assigned as  $\Lambda$ -*fac* as shown in structure I. The



circular dichroism spectrum of [Cr(D-Pyala)<sub>3</sub>]·H<sub>2</sub>O in H<sub>2</sub>O has maxima at 406 nm ( $\Delta\epsilon$  +0.24 cm<sup>-1</sup> M<sup>-1</sup>) and 517 nm ( $\Delta\epsilon$  -0.83 cm<sup>-1</sup> M<sup>-1</sup>).

The trans-carboxylate Cr(D-Pyala)<sub>2</sub><sup>+</sup> complex was separated from any decomposition products and any remaining tris complex by column chromatography on basic alumina in methanol. The complex was absorbed by cationic-exchange resins, suggesting that it is a charged species and not a neutral tris(amino acidato)chromium(III) complex. Storage of the purple trans-carboxylate complex in methanol at 0 °C prevented its conversion to [Cr(D-Pyala)<sub>3</sub>]·H<sub>2</sub>O. The infrared spectrum of trans-carboxylate Cr(D-Pyala)<sub>2</sub><sup>+</sup> showed a sharp peak at 1635 cm<sup>-1</sup>, indicating that both carboxylate groups are coordinated. The coordination of the four nitrogen donors is inferred by the positions of the maxima in the visible and circular dichroism spectra. These are comparable to the CrN<sub>4</sub>O<sub>2</sub> chromophore as described below.

Structural assignments can be made when both the *cis*-O and *trans*-O isomers of a CrN<sub>4</sub>O<sub>2</sub> complex are isolated, since

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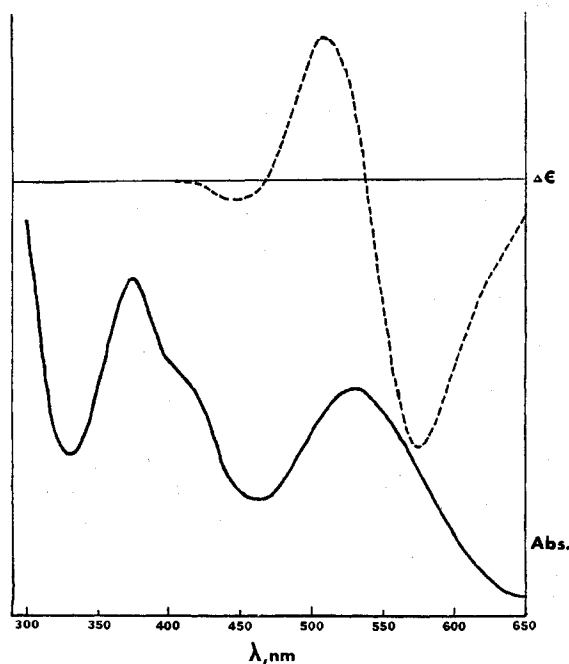


Figure 5. Absorption (—) and CD (---) spectra of trans-carboxylate  $\text{Cr}(\text{D-Pyala})_2^+$  in aqueous solution.

the *cis*-O isomer usually has maxima at higher energy than the *trans*-O isomer. In addition, the *trans*-O isomer may show a splitting of the  $A_{2g} \rightarrow T_{2g}$  band further supporting the structural assignments. This splitting was observed in  $\text{Cr}(\text{D-Pyala})_2^+$  (Figure 5) which leads to its assignment as *trans* carboxylate. The similarity of the spectra of *trans*-carboxylate  $\text{Cr}(\text{D-Pyala})_2^+$  ( $\lambda_{\text{max}}$  382, 420 (sh), 536 nm) and *trans*-O  $\text{Cr}(\text{en})_2(\text{OAc})_2^+$  ( $\lambda_{\text{max}}$  373, 420 (sh), 535 nm)<sup>14</sup> is further support for this structural assignment.

The CD spectrum of the complex supports the  $\text{Cr}(\text{D-Pyala})_2^+$  formulation since the curve differs from those of  $\text{Cr}(\text{amino acidato})_3$  and  $\text{Cr}(\text{amino acidato})_2(\text{H}_2\text{O})_2^+$  complexes.<sup>9,10,12</sup>

### Conclusion

Previously, we isolated and identified the *trans*-carboxylate isomer of  $\text{Co}(\text{D-Pyala})_2^+$ . Since this complex did not isomerize in the presence of charcoal at 80 °C to either the *trans*-amino or the *trans*-pyridyl structure, the *trans*-carboxylate configuration was presumed to be the most stable isomer.<sup>2</sup> The present study supports this conclusion, since *trans*-amino  $\text{Co}(\text{D-Pyala})_2^+$  isomerizes to the *trans*-carboxylate structure when left standing in water at room temperature for 3 weeks. Heating the *trans*-amino isomer at 80 °C for 12 h in the presence of activated charcoal gave a mixture of *trans* carboxylate to *trans* amino in a ratio of 14:1. Thus the percentage of each isomer present in the reaction solution decreases in the order *trans* carboxylate > *trans* amino > *trans* pyridyl. The greater stability of the *trans*-carboxylate isomer suggests that *amino groups avoid being trans to each other*. This conclusion was also reached by Watabe et al., who found only small amounts of the *trans*-N isomer in equilibrium mixtures

of (D-aspartato)(L-2,4-diaminobutyrate)cobalt(III)<sup>15</sup> and (L-histidinato)(iminodiacetato)cobalt(III).<sup>16</sup> Also, only a small amount of the analogous *trans*-N isomer of bis(L-aspartato)cobalt(III) anion could be prepared.<sup>17</sup> Finally, only 6% of the *trans*-N(amino) isomer of  $\text{Co}(\text{L-His})_2^+$  and none of this isomer of  $\text{Co}(\text{L-His})(\text{D-His})^+$  could be isolated.<sup>3</sup> The greater stability of the *trans*-carboxylate isomer as compared to the *trans*-pyridyl isomer also suggests that pyridyl groups avoid being *trans* to each other and prefer to be *trans* to an amino group. This suggestion is not documented by other work because few complexes containing only two pyridine groups have been studied. The reason for this may be the  $\pi$ -bonding ability of the pyridyl ligand which could accept electron density provided to the metal by the strongly  $\sigma$  donor *trans* amino group.

In the reactions of cobalt(III) with D,L-PyalaH, there was a preference for the formation of the all-*cis* isomer. Smaller amounts of the *trans*-carboxylate and *trans*-amino isomers were also isolated, but none of the *trans*-pyridyl or all-*trans* complex was found. The ratio of racemic all-*cis*- $\text{Co}(\text{D-Pyala})(\text{L-Pyala})^+$  to racemic *trans* carboxylate was 2.6:1 for all of the different preparations used. Thus, the all-*cis* structure seems to be the most stable complex formed. The absence of *trans*-amino groups and the presence of an amino group *trans* to a pyridyl in this isomer would be expected to contribute to its higher stability. The presence of *trans*-amino groups in the all-*trans* isomer may account for the lack of evidence for this isomer.

The greater stability of the all-*cis* structure compared to the *trans* carboxylate might either be attributed to the presence of two *trans*-aminopyridyl units or to a decrease in steric repulsion between the pyridine rings. Since the angle between the planes of the pyridine rings increases from about 30° in *trans* carboxylate to about 60° in all-*cis*, the repulsion between the pyridine groups is probably less in the all-*cis* complex than in the *trans*-carboxylate isomer.

As for  $\text{Co}(\text{D-Pyala})_2^+$ , the most stable isomer of  $\text{Cr}(\text{D-Pyala})_2^+$  appears to be the *trans* carboxylate. The reasons for this stability may be analogous to those suggested above for the  $\text{Co}(\text{D-Pyala})_2^+$  complexes. Evidence for  $\pi$  bonding from chromium(III) to pyridine has been reported<sup>18</sup> and may play a role in determining the preferred structure. The weak  $\sigma$ -donor ability and possible  $\pi$  bonding of the pyridine may favor a strong  $\sigma$  donor such as the amino nitrogen in a position *trans* to the pyridine.

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**Registry No.** *trans*-amino- $[\text{Co}(\text{D-Pyala})_2]\text{NO}_3$ , 73284-81-8; all-*cis*- $[\text{Co}(\text{D-Pyala})(\text{L-Pyala})]\text{NO}_3$ , 73284-83-0;  $\Delta$ -*fac*- $[\text{Cr}(\text{D-Pyala})_3]$ , 73117-39-2; *trans*-carboxylate- $[\text{Cr}(\text{D-Pyala})_2]\text{Cl}$ , 73175-02-7; *trans*-carboxylate- $[\text{Co}(\text{D-Pyala})_2]\text{NO}_3$ , 68890-43-7; *trans*-carboxylate- $[\text{Co}(\text{L-Pyala})_2]\text{NO}_3$ , 73117-40-5; *trans*-amino- $[\text{Co}(\text{L-Pyala})_2]\text{NO}_3$ , 73137-29-8.

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