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Preparation and Spectral Characterization of Some Mixed-Ligand Cobalt(III) Complexes of the Form [Co(L-Pyala)(A)], A = L-Histidinate, L- or D-Aspartate, or Iminodiacetate

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Mixed-ligand cobalt(III) complexes of the form [Co(L-Pyala)(A)], where A = L-histidinate, L- or D-aspartate, or iminodiacetate and L-Pyala$^-$ = L-$H_2NCH(CH_2C_5H_4N)CO_2^-$, were prepared from Co(III) and Co(II) reactants. Isolated isomers of each complex were assigned structures on the basis of their visible and circular dichroism spectra. The observed distribution of isomers suggests that in these complexes, as well as in previously reported Co(Pyala)$_2^+$ complexes, amino groups avoid being trans to each other; pyridyl groups also avoid being trans to each other but prefer to be trans to an amino group.

Introduction

The preparation and characterization of the most stable Co(Pyala)$_2^+$ complexes containing the optically active tridentate ligand β-(2-pyridyl)-α-alanine, $^+H_3NCH(CH_2C_5H_4N)CO_2^-$ (PyalaH), have been reported.[1,2] The most stable isomers were found to be all *cis*-Co(D-Pyala)(L-Pyala)$^+$ and trans-carboxylate Co(D-Pyala)$_2^+$. The absence or instability of the other possible isomers suggested that amino groups avoid being trans to each other and pyridyl groups also avoid being trans to each other. In addition, there was evidence to suggest that the most favorable position for the amino nitrogen atom was trans to a pyridine donor. These observations could not be completely rationalized by considering ligand steric interactions, which suggested that electronic factors such as σ-donor and π-acceptor abilities may play important roles in determining the most stable isomer of these cobalt(III) complexes.

We have now prepared and characterized a number of mixed-ligand complexes of the type Co(L-Pyala)(A), where *A* = L-histidinate, L- or D-aspartate, or iminodiacetate, in order to determine their preferred geometries and to understand the factors which contribute to these preferences.

Experimental Section

Materials. L-histidine, L- and D-aspartic acid, and iminodiacetic acid were purchased from Aldrich Chemical Co. Racemic β-(2-pyridyl)-α-alanine (PyalaH) was prepared and resolved as described previously.[3]

Isomers of [Co(L-Pyala)(L-His)]NO_3. To a hot solution (ca. 60 °C) containing L-PyalaH (0.5 g, 3.0 mmol), L-histidine (0.47 g, 3.0 mmol), and NaOH (0.24 g, 6.0 mmol) in 15 mL of water was added $Co(NO_3)_2 \cdot 6H_2O$ (0.87 g, 3.0 mmol). After the solution was mixed for 15 min, PbO_2 (0.36 g, 1.5 mmol) was added and the stirring and heating continued for 1 h. The solution was filtered, cooled to room temperature, and loaded on a column (2.4 × 80 cm, 350 mL) of Dowex 50W-X8 resin which was in the sodium form. Any uncharged or anionic species produced in the reaction were washed from the column with 250 mL of water. Separation of the Co(III) complexes was achieved by eluting with 0.05 M $NaNO_3$ at a rate of 1 drop/4 s. Eight colored bands formed: three red-violet, two red, and three orange in order of elution from the column. The first red-violet band was eluted after 12 days, and the last orange band, on the forty-second day. Each band was evaporated to 20 mL and a layer (100 mL) of absolute ethanol was added. As the two layers diffused together, $NaNO_3$ precipitated. The solution was filtered and evaporated to 5 mL and another layer (20 mL) of absolute ethanol added. More $NaNO_3$ precipitated from the solution as the layers mixed. The solution was filtered and evaporated to dryness under reduced pressure to give a solid. This solid was dissolved in D_2O and the ^1H NMR taken. Those spectra which contained either pyridine or imidazole protons in the aromatic region, but not both, were identified by matching their ^1H NMR, visible, and circular dichroism spectra with those reported for the isomers of Co(D-Pyala)$_2^+$ [1,2] and Co(L-His)$_2^+$.[4] In this way the following assignments were made (% yield based on Co(II) starting material in parentheses): band 1, trans-carboxylate Co(L-His)$_2^+$ (8.5); band 3, trans-carboxylate Co(L-Pyala)$_2^+$ (23.7); band 4, trans-imidazole Co(L-His)$_2^+$ (26.0); band 6, trans-amino Co(L-His)$_2^+$ (4.3); band 8, trans-amino Co(L-Pyala)$_2^+$ (3.0).

Two of the bands (2, 5) which showed peaks for both pyridine and imidazole protons in their ^1H NMR spectra were crystallized from 1 mL of water to which a layer of 9 mL of ethanol had been added. These were identified as I (band 2, yield 19.5%) and III (band 5, yield 3.5%). Complex II (band 7) could not be crystallized. Anal. Calcd for $[Co(C_8H_9N_2O_2)(C_6H_8N_3O_2)]NO_3 \cdot H_2O \cdot {}^1/_4C_2H_5OH$: C, 37.07; H, 4.40; N, 17.89. Found (I): C, 36.91; H, 4.34; N, 17.82. Anal. Calcd for $[Co(C_8H_9N_2O_2)(C_6H_8N_3O_2)]NO_3 \cdot 2H_2O$: C, 35.31; H, 4.44; N, 17.64. Found (III): C, 35.49; H, 4.01; N, 17.57.

Isomers of [Co(L-Pyala)(L-Asp)]. The mixture of isomers was obtained by a procedure similar to that described above by using L-aspartic acid instead of L-histidine. A column (1.8 × 70 cm, 175 mL) of Dowex 50X-X8 resin which was in the sodium form was used to separate the isomers. Three bands were eluted with water, while a fourth, consisting of the isomers of Co(L-Pyala)$_2^+$, stuck to the top of the column. The first band contained a mixture of the anionic bis(aspartato)cobalt(III) complexes, Co(L-Asp)$_2^-$.[5] The second (IV) and third (VI) bands, which were purple and red in color, proved to be two of the isomers of [Co(L-Pyala)(L-Asp)]. These bands were each separately evaporated to 2 mL under reduced pressure and a layer (10 mL) of absolute ethanol was added. As the two layers diffused together, crystals were formed. Anal. Calcd for $[Co(C_8H_9N_2O_2)(C_4H_5NO_4)] \cdot H_2O$: C, 38.62; H, 4.32; N, 11.26. Found (IV): C, 38.59; H, 4.83; N, 11.11. Anal. Calcd for $[Co(C_8H_9N_2O_2)(C_4H_5NO_4)] \cdot {}^3/_2H_2O$: C, 37.71; H, 4.48; N, 10.99. Found (VI): C, 37.85; H, 4.57; N, 11.24.

Isomers of [Co(L-Pyala)(D-Asp)]. These isomers were obtained by a method similar to that described above. Of the three possible isomers only two were isolated. The meridional isomer (VII) was eluted first from the column followed by the facial isomer (IX). Anal. Calcd for $[Co(C_8H_9N_2O_2)(C_4H_5NO_4)] \cdot H_2O \cdot {}^1/_4C_2H_5OH$: C, 39.02; H, 4.59; N, 10.92. Found (VII): C, 39.20; H, 4.89; N, 10.93. Anal. Calcd for $[Co(C_8H_9N_2O_2)(C_4H_5NO_4)] \cdot H_2O$: C, 38.62; N, 4.32; N, 11.26. Found (IX): C, 38.44; H, 4.61; N, 11.11.

Isomers of [Co(L-Pyala)(IMDA)]. The same procedure was used as described above. Only one of the three possible isomers was separated and crystallized (X). One of the two meridional isomers (XI) and the facial (XII) isomer were not obtained. Anal. Calcd for $[Co(C_8H_9N_2O_2)(C_4H_5NO_4)] \cdot {}^1/_2H_2O$: C, 39.58; H, 4.15; N, 11.54. Found (X): C, 39.83; H, 4.25; N, 11.64.

Alternate methods of preparation using either $[Co(NH_3)_4CO_3]NO_3$, $[Co(NH_3)_6](NO_3)_3$, or $Na_3[Co(CO_3)_3] \cdot 3H_2O$ with L-PyalaH and IMDA or L- or D-AspH_2 as starting materials were performed as

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

(2) Ebner, S. R.; Angelici, R. J., submitted for publication in *Inorg. Chem.*

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

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(5) Legg, J. I.; Neal, J. A. *Inorg. Chem.* **1973**, *12*, 1805. Hoggard, P. E.; Schmidtke, H. H. *Inorg. Chim. Acta* **1979**, *34*, 77.

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Table I. Product Yields in Various Preparations of Co(L-Pyala)(A) Mixed Complexes

		starting material			
ligand	product	$Co(NO_3)_2 \cdot 6H_2O$	$[Co(NH_3)_4CO_3]NO_3$	$[Co(NH_3)_6](NO_3)_3$	$Na_3[Co(CO_3)_3] \cdot 3H_2O$
L-aspartic acid	IV	21	21	26	22
	V	NO[a]	NO	NO	NO
	VI	24	NO	NO	2
D-aspartic acid	VII	19	21	28	26
	VIII	NO	NO	NO	NO
	IX	40	NO	12	3
iminodiacetic acid	X	47	62	36	46
	XI	NO	NO	NO	NO
	XII	NO	NO	NO	NO

[a] Not observed.

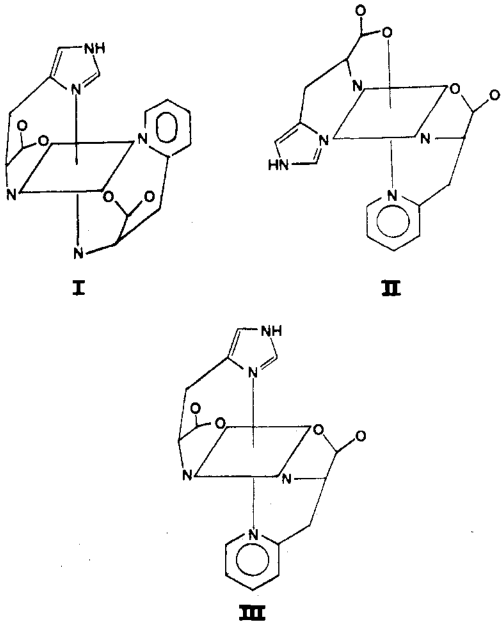

Figure 1. Isomers of Co(L-Pyala)(L-His)$^+$: I, trans carboxylate; II, trans amino; III, trans rings.

described previously.[1] The results are listed in Table I. Other products that also formed in these reactions included the isomers of Co(L-Pyala)$_2^+$, Co(L-Asp)$_2^-$, Co(D-Asp)$_2^-$, and Co(IMDA)$_2^-$.

Spectra. Visible and circular dichroism spectra were measured with a Jasco ORD/UV/CD-5 spectrophotometer in aqueous solution. The ^{1}H NMR spectra were recorded on a Varian Associates HA-100 spectrometer in 99.7% deuterium oxide vs. *tert*-butyl alcohol (δ 1.23) as an internal standard.

Results and Discussion

Isomers of [Co(L-Pyala)(L-His)]NO_3. The three isomers of Co(L-Pyala)(L-His)$^+$ are shown in Figure 1. All three of these complexes were separated by column chromatography from the analogous isomers of Co(L-Pyala)$_2^+$ and Co(L-His)$_2^+$. Only structures I and III could be obtained in crystalline form. The yield of each complex based on the number of moles of Co(II) starting material was as follows: I, 19.5; II, unknown; III, 3.5%. Of the nine structures that may form in the reaction mixture (three isomers for each of the following complexes: Co(L-Pyala)$_2^+$, Co(L-Pyala)(L-His)$^+$, and Co(L-His)$_2^+$) only one, trans-pyridyl Co(L-Pyala)$_2^+$, was not obtained. Previous attempts[1,2] to prepare this complex were also unsuccessful.

Structural assignments of the isomers of Co(L-Pyala)(L-His)$^+$ were based on the similarity of their visible and circular dichroism spectra to those of Co(L-Pyala)$_2^+$ and Co(L-His)$_2^+$. The visible spectra (Figure 2) are similar for analogous isomers with the extinction coefficients increasing within each series in the order Co(L-His)$_2^+$ < Co(L-Pyala)(L-His)$^+$ < Co(L-Pyala)$_2^+$. The band that appears at longer wavelength is not shifted by changing the ligand; however, the band in the high-energy region experiences a shift of about 10 nm when an imidazole nitrogen is replaced by a pyridine nitrogen donor in the coordination sphere of the cobalt(III) trans-carboxylate isomers: Co(L-His)$_2^+$, 344 nm; Co(L-Pyala)(L-His)$^+$, 354 nm; Co(L-Pyala)$_2^+$, 364 nm.

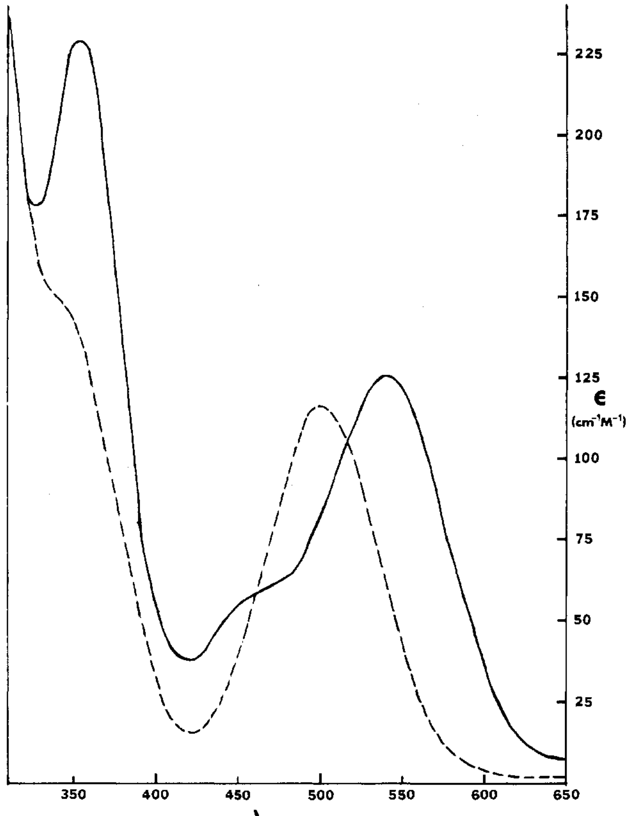

Figure 2. Visible spectra of I (—) and III (---).

Complex II has a visible spectrum similar to those of the trans-amino isomers[2] of Co(L-Pyala)$_2^+$ and Co(L-His)$_2^+$, in which the shoulder appears on the long wavelength side of the lower energy band. The maximum in the spectrum of II occurs at 487 nm with the shoulder at about 560 nm.

The circular dichroism spectrum of I (Figure 3) is similar to those of the trans-carboxylate isomers of Co(L-Pyala)$_2^+$[1] and Co(L-His)$_2^+$.[4] For these complexes, $\Delta\epsilon$ increases in the same order as was observed for the extinction coefficients in the visible spectra. There is a difference, however, in the CD spectrum of III compared to that observed for trans-imidazole Co(L-His)$_2^+$. A positive absorption appears at 538 nm followed by a negative peak at 478 nm for III, whereas trans-imidazole Co(L-His)$_2^+$ shows a negative band at 525 nm and a positive band at 475 nm. This change in the CD spectrum may be due

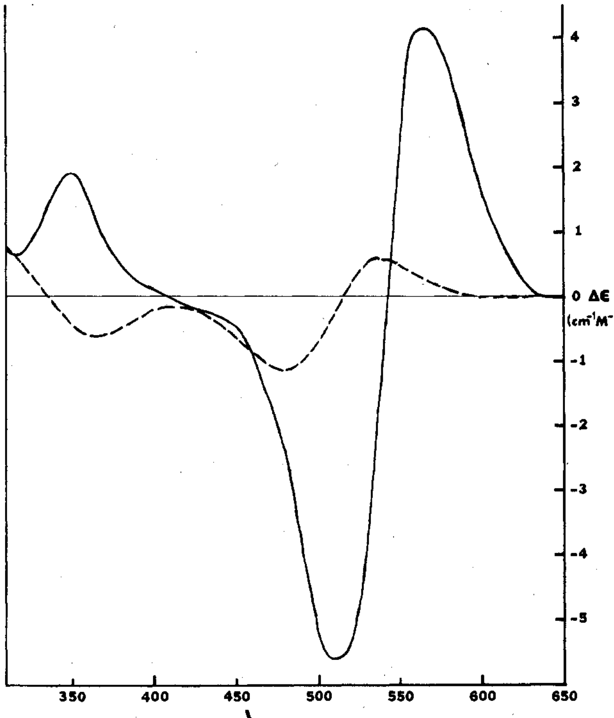

Figure 3. Circular dichroism of I (—) and III (- - -).

to the added asymmetry about the cobalt center caused by the substitution of a pyridine for an imidazole group. The difference in donor ability of these two nitrogen atoms (the difference in log K_f for several transition-metal ions is 1)[6] as well as the lesser strain in the aminopyridine chelate ring may account for these differences.

Interpretation of the ^{1}H NMR spectra of the Co(L-Pyala)(L-His)$^+$ complexes is difficult because of the large degree of overlap between the protons of each ligand. Structure I shows a number of complex patterns at (number of H's in parentheses) 3.48–3.64 (1), 3.84–4.04 (5), 7.27–7.67 (4), and 7.96–8.16 ppm (2). The imidazole protons, which can be distinguished from the pyridine peaks because their absorptions are sharper ($J \approx 1.5$ Hz), occur at 7.30 and 7.50 ppm. The analogous protons occur at 7.41 and 7.82 ppm in trans-carboxylate Co(L-His)$_2^+$, which has a structure similar to I. From an inspection of molecular models, the shift from 7.82 to 7.50 ppm in the proton on the carbon atom adjacent to the coordinated nitrogen atom of the imidazole ring may be rationalized. Because of the larger size of the pyridine ring, the imidazole proton is thrust deeper into the shielding region of the pyridine ring. The ethanol reported in the analysis of trans-carboxylate [Co(L-Pyala)(L-His)]NO$_3$·H$_2$O·$^1/_4$C$_2$H$_5$OH was observed as a triplet at 1.16 ppm, with the quartet which should be at 3.60 ppm overlapping with the ligand protons.

Structure II has complex patterns with much overlap between the protons of the ligands at 3.38–3.78 (2), 3.89–4.11 (2), 4.18–4.36 (2), 7.13–7.34 (2), 7.38–7.57 (1), 7.74–8.00 ppm (3). The imidazole protons fall within these complex patterns at 7.28 and 7.91 ppm. These protons occur at 7.26 and 7.93 ppm in trans-amino Co(L-His)$_2^+$.

Although the ^{1}H NMR spectrum of III is simpler in the aromatic region, the methine and methylene protons of the L-histidinate and L-Pyala$^-$ ligands overlap extensively. If small couplings ($J < 2$ Hz) are ignored, the spectrum of III is as follows: 3.41, singlet (2); 3.84, complex (4); 7.23, singlet (1); 7.62, triplet (2); 7.86, singlet (1); 7.89, triplet (1); 8.41 ppm, doublet (1). The absorptions at 7.23 and 7.86 ppm are assigned to the imidazole protons. The values reported[4] for the analogous protons in trans-imidazole Co(L-His)$_2^+$ were 7.31 and 7.93 ppm.

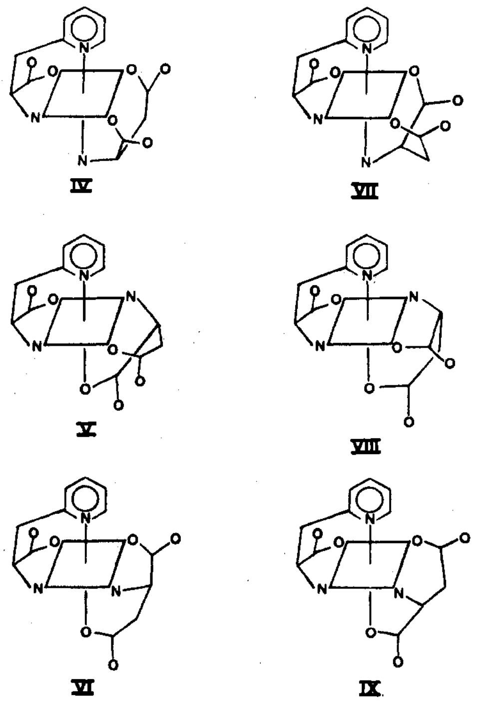

Figure 4. Isomers of [Co(L-Pyala)(L-Asp)]: IV, trans(O$_5$)cis(N$_5$); V, cis(O$_5$),trans(N$_5$); VI, L-*fac*. Isomers of [Co(L-Pyala)(D-Asp)]: VII, *mer*-cis(O$_5$), cis(N$_5$); VIII, trans(O$_5$),trans(N$_5$); IX, D-*fac*.

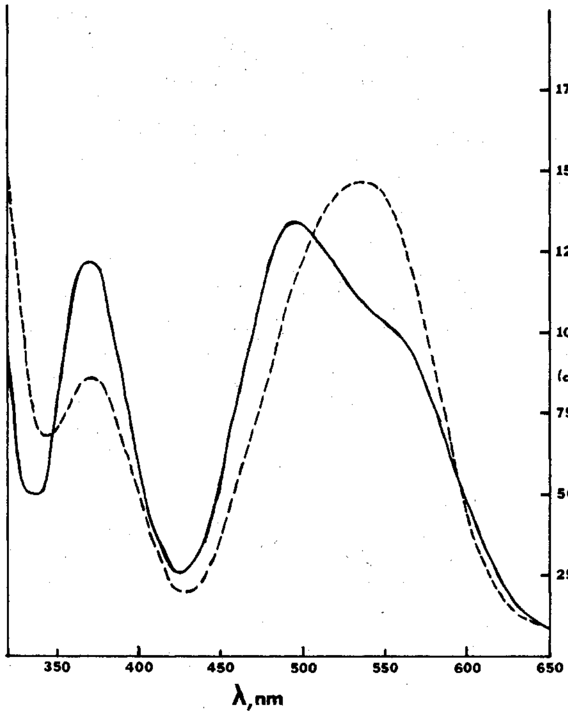

Figure 5. Visible spectra of IV (—) and VI (- - -).

Isomers of [Co(L-Pyala)(L-Asp)] and [Co(L-Pyala)(D-Asp)]. The possible isomers of [Co(L-Pyala)(L-Asp)] and [Co(L-Pyala)(D-Asp)] are shown in Figure 4. Both series of mixed complexes are composed of two meridional and one facial arrangement of nitrogen donor atoms about the cobalt(III) center. The isomers are denoted by considering the 5-membered glycinato N and O atoms. The two *mer* isomers for the

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(6) Sillen, L. G.; Martell, A. E. *Chem. Soc., Spec. Publ.* **1964**, *No. 17*, 25.

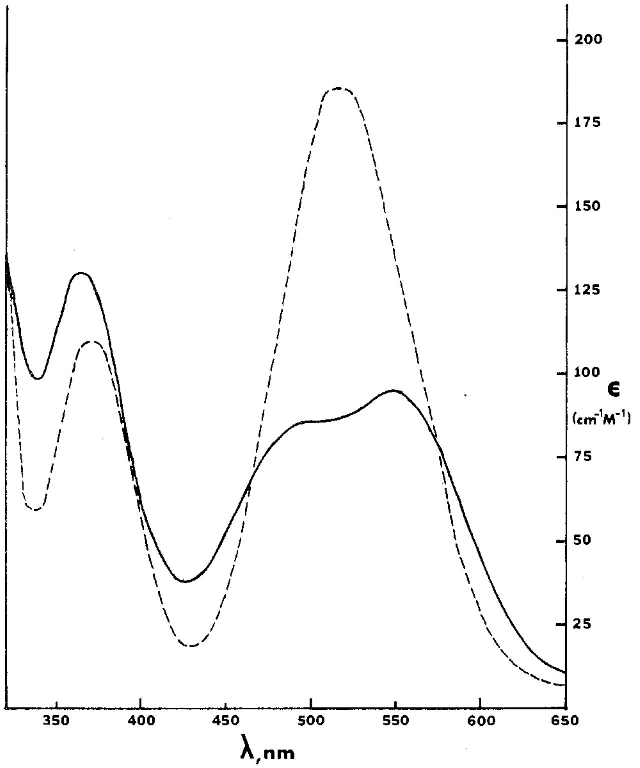

Figure 6. Visible spectra of VII (—) and IX (- - -).

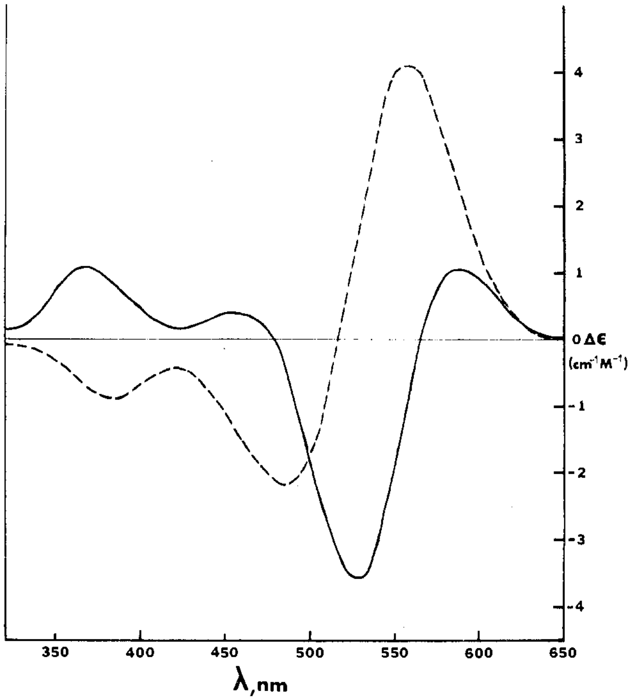

Figure 7. Circular dichroism of IV (—) and VI (- - -).

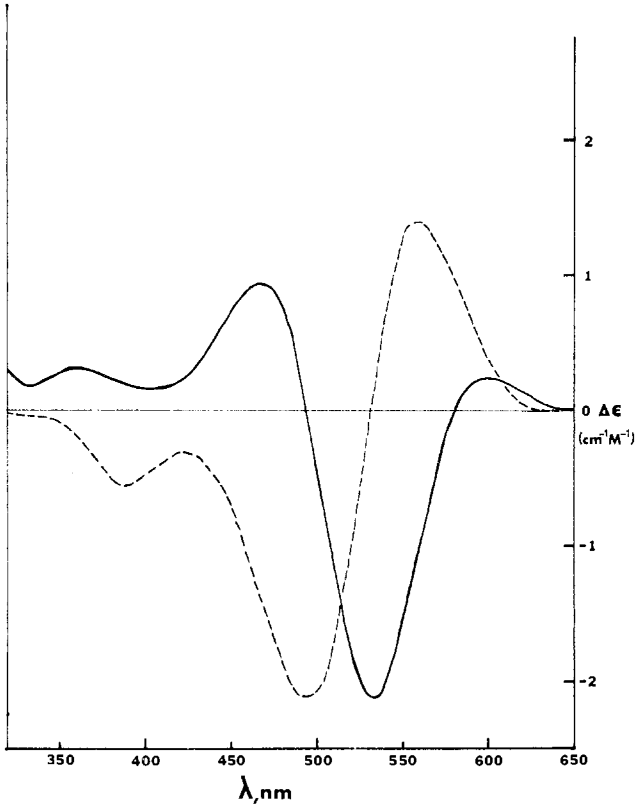

Figure 8. Circular dichroism of VII (—) and IX (- - -).

L-series are denoted by trans(O_5),cis(N_5) (IV) and cis(O_5),trans(N_5) (V). Similarly, the three isomers of [Co(L-Pyala)(D-Asp)] are designated by *mer*-cis(O_5),cis(N_5) (VII), trans(O_5),trans(N_5) (VIII), and *fac* (IX).

Figures 5 and 6 show the visible absorption spectra of the isolated complexes. These spectra may be compared to those for [Co(L-His)(L- or D-Asp)],[7] [Co(L-2,4-dba)(L- or D-Asp)],[8] and [Co(L-orn)(L- or D-Asp)].[9] The isomers of [Co(L-Pyala)(L-Asp)], IV and VI, are assigned as trans(O_5),cis(N_5) and *fac* because of the similarity of their visible spectra to those of the analogous isomers of the complexes of L-histidinato, L-2,4-diaminobutyrato, and L-ornithine. Likewise, VII and IX, which are isomers of [Co(L-Pyala)(D-Asp)] are assigned as *mer*-cis(O_5),cis(N_5) and *fac*.

Figures 7 and 8 show the CD spectra of IV, VI, VII, and IX. The CD spectrum of IV is similar to the reported spectra for the trans(O_5),cis(N_5) isomers of [Co(L-His)(L-Asp)],[7] [Co(L-2,4-dba)(L-Asp)],[10] and [Co(L-orn)(L-Asp)].[9] Likewise, the CD spectrum of VI can be compared to that of the facial isomers of the cobalt(III) complexes of L-histidinato, L-2,4-diaminobutyrato, and L-ornithine with L-aspartate. The two isomers of [Co(L-Pyala)(D-Asp)], VII and IX, can be assigned because of the similarity of their CD spectra to the *mer*-cis(O_5),cis(N_5) and *fac* isomers of previously reported analogues containing L-histidinate,[7] L-ornithinate,[9] or L-2,4-diaminobutyrate.[11]

The coordination of L-Pyala$^-$, in place of L-His, L-2,4-dba, and L-orn in the four complexes isolated, IV, VI, VII, and XI, caused an increase in the magnitude of the CD peaks. A positive band also appeared at about 580 nm in the CD spectra of the two meridional isomers, IV and VII, which was not present in the L-His, L-2,4-dba, or L-orn complexes.

The general similarity of the CD spectra of IV to VII and VI to IX seems to indicate that the arrangement of the donor atoms about the cobalt(III) center makes the major contribution to the CD spectra of these complexes. The absolute configuration of the aspartate anion makes only a minor contribution.

The ^{1}H NMR spectra of these isomers, IV, VI, VII, and IX, had overlapping complex patterns from 2.65 to 5.00,

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(7) Watabe, M.; Yano, H.; Yoshikawa, S. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 61.

(8) Watabe, M.; Onuki, K.; Yoshikawa, S. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 687.

(9) Watabe, M.; Onuki, K.; Yoshikawa, S. *Nippon Kagaku Kaishi* **1977**, *12*, 1833.

(10) Watabe, M.; Yoshikawa, S. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2185.

(11) Watabe, M.; Kawaai, S.; Yoshikawa, S. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1845.

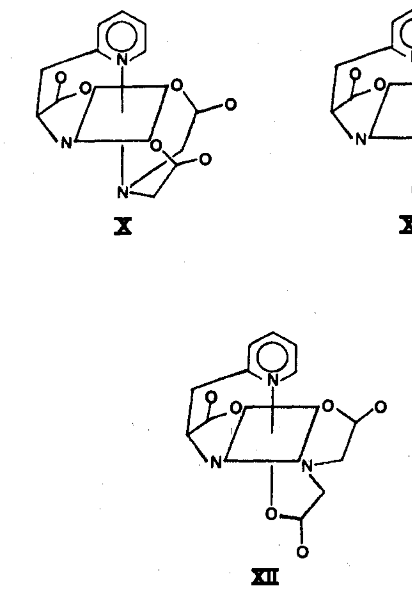

Figure 9. Isomers of [Co(L-Pyala)(IMDA)]: X, *mer*-cis(N); XI, trans(N); XII, *fac*.

corresponding to the two methine and four methylene protons of the two ligands. The aromatic region was less complex and is given as follows (the patterns reported are without considering small couplings, $J < 2$ Hz; t = triplet, d = doublet): (IV) 7.60 [t, d (2)], 8.07 [t (1)], 8.59 ppm [d (1)]; (VI) 7.44 [t, d (2)], 7.92 [t (1)], 8.18 ppm [d (1)]; (VII) 7.58 [t, d (2)], 8.05 [t (1)], 8.72 ppm [d (1)]; (IX) 7.40 [t, d (2)], 7.91 [t (1)]; 8.19 ppm [d (1)]. The ethanol which appeared in the analysis of VII was also detected in the ^{1}H NMR as a triplet at 1.16 ppm and a quartet at 3.60 ppm.

Isomer of [Co(L-Pyala)(IMDA)]. Figure 9 shows the three possible isomers of [Co(L-Pyala)(IMDA)]. The two meridional isomers, X and XI, are denoted cis(N) and trans(N) by considering the position of the amino group of L-Pyala$^-$ in relation to the nitrogen atom of IMDA.

Figure 10 shows the visible and circular dichroism spectra of the sole isomer of [Co(L-Pyala)(IMDA)] that was isolated. The absorption spectrum is similar to that reported for the cis(N) isomer of [Co(L-His)(IMDA)].[12] *cis(N)*-[Co(L-His)(IMDA)] and X have a shoulder on the high-energy side of the first absorption band which is characteristic of this isomer. The CD spectrum also compares favorably with that of the *cis(N)*-[Co(L-His)(IMDA)] complex. The coordination of the L-Pyala$^-$ ligand in place of L-His caused an increase in $\Delta\epsilon$ as was noted for the isomers of [Co(L-Pyala)(L-Asp)] and [Co(L-Pyala)(D-Asp)]. It appears that this increase in $\Delta\epsilon$ is due to the L-Pyala$^-$ ligand, since this is the only difference between the cis(N) isomers of [Co(L-Pyala)(IMDA)] and [Co(L-His)(IMDA)].

The ^{1}H NMR spectrum of *cis(N)*-[Co(L-Pyala)(IMDA)] exhibited the following absorptions: 3.51, d (1); 3.57, d (1); 3.74, s (3); 4.23, d (1); 4.34, d (1); 7.55, d, t (2); 8.01, t (1); 8.92 ppm, d (1). The doublets, 3.51, 3.57, 4.23, and 4.34 ppm, were assigned to the four protons of the IMDA ligand. The two protons on each carbon were inequivalent and, thus, split each other. The coupling constants, 17 and 18 Hz, were within the normal range observed for two protons on the same carbon split by each other. The singlet at 3.74 ppm consisted of both the α and β protons of the L-Pyala$^-$ ligand; no splitting was observed because the chemical shifts of these three protons were the same as was also found in trans-carboxylate Co(D-Pyala)$_2^+$.[1] The remaining peaks were assigned to the aromatic protons of the pyridine ring.

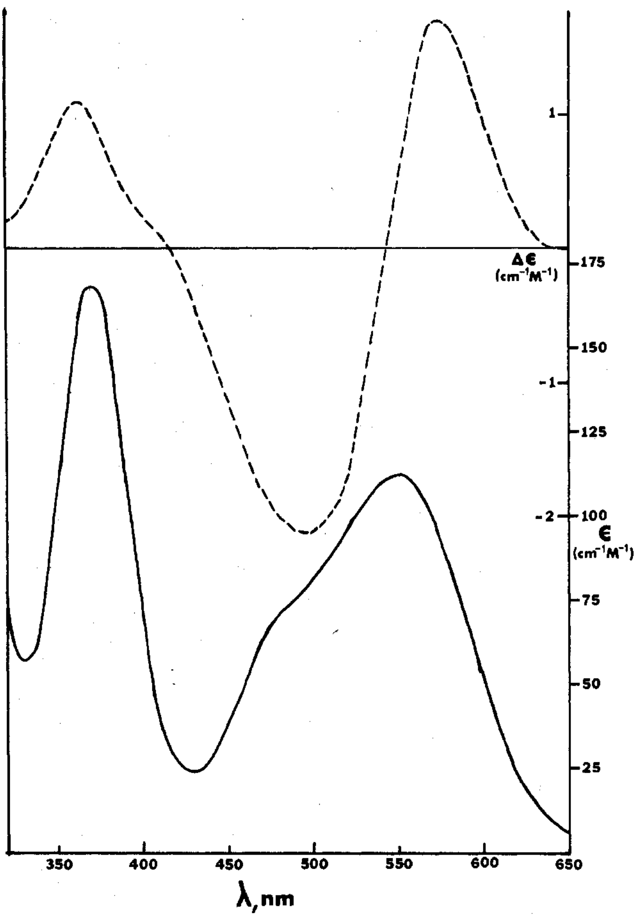

Figure 10. The visible (—) and circular dichroism (- - -) spectra of X.

Conclusion

As noted in the Introduction, it has been suggested previously[2] in discussing the stabilities of isomers of Co(D-Pyala)$_2^+$ and Co(D-Pyala)(L-Pyala)$^+$ that amino groups avoid being trans to each other and pyridyl groups avoid being trans to each other but prefer to be trans to an amino group. We find that these observations are also useful in understanding the major isomers formed in the preparations of the mixed-ligand complexes Co(L-Pyala)(A) described in this paper.

The major isomer isolated in the preparation of the mixed ligand complex Co(L-Pyala)(L-His)$^+$ was I. In this isomer the amino group of the histidine ligand occupies the position trans to the pyridine group of L-Pyala$^-$. Only low yields of II, in which the amino groups are trans, and III, in which the pyridine and imidazole donors are trans, were observed.

Table I shows product distributions found in preparations of the Co(L-Pyala)(A) complexes, where A = D- or L-aspartate or iminodiacetate. Although these are not necessarily thermodynamic isomer distributions, observations can be made concerning the products formed. The major isomer produced in most[13] of the reactions was that in which the amino group of L-Asp, D-Asp, or IMDA occupies the position trans to the pyridyl group. Complexes in which amino groups are mutually trans (V, VIII, and XI) were not observed in any of the reaction solutions.

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(13) Only preparations involving PbO$_2$ oxidation of Co(II) with L-Asp$^-$ and D-Asp$^-$ give a major product in which an amino group is not trans to the pyridyl (see Table I). It might be argued that oxidative preparations would be least likely to give a thermodynamic distribution of products.

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Registry No. I, 72905-42-1; II, 72983-35-8; III, 72937-78-1; IV, 72937-79-2; VI, 72937-80-5; VII, 72983-36-9; IX, 72905-31-8; X, 72905-32-9; trans-carboxylate Co(L-His)$_2^+$, 28696-52-8; trans-carboxylate Co(L-Pyala)$_2^+$, 72982-76-4; trans-imidazole Co(L-His)$_2^+$, 18744-92-8; trans-amino Co(L-His)$_2^+$, 24419-71-4; trans-amino Co(L-Pyala)$_2^+$, 72982-77-5; Co(NO$_3$)$_2$, 10141-05-6; [Co(NH$_3$)$_4$CO$_3$]NO$_3$, 15040-52-5; [Co(NH$_3$)$_6$](NO$_3$)$_3$, 10534-86-8; Na$_3$[Co(CO$_3$)$_3$], 23311-39-9.

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Palladium(II) Thiocyanate Organophosphorus Complexes[1]

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A series of seven complexes of the type L$_2$Pd(CNS)$_2$ [L = R$_n$P(C$_6$H$_5$)$_{3-n}$, n = 0–3, R = methyl and benzyl] have been prepared and investigated for geometrical and linkage isomerism. The complexes have been characterized from physical properties, infrared spectroscopy, and ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy. Most of the complexes are exclusively trans in CDCl$_3$ solution, the exceptions being L = (C$_6$H$_5$)$_3$P and (C$_6$H$_5$)$_2$PCH$_3$ which exhibit both cis and trans isomers. Infrared integrated intensity ratio studies in chloroform indicate the predominance of N-bonded isomers in every case, while NMR shows the presence of other possible linkage isomers for various complexes. An NMR shift reagent, Eu(fod)$_3$, was used to facilitate identification of the different linkage isomers in solution. The interrelation of geometrical and linkage isomerism for this series of complexes, as well as the factors influencing such, is discussed.

Introduction

The ambidentate bonding capability of the thiocyanate ion has been attracting much attention for at least the last decade. This ambidentate nature has been interpreted in terms of Pearson's "soft–hard" concepts,[3] antisymbiosis effects,[4] and π bonding.[5,6] Whatever the rationale, the thiocyanate ion is a chemical probe of molecular environment in that it responds to steric and electronic stimuli by bonding either through sulfur, through nitrogen, or in a bridging fashion. Much effort[7–21] has been expended toward understanding the importance and function of these stimuli in relation to the thiocyanate bonding mode in transition-metal complexes.

In the past, nickel(II), palladium(II), and platinum(II) have been preferentially employed in the majority of studies of this bonding behavior. Among these transition metals there exists a potential for several geometries. Many studies[11,13,15,20,21] have had the constraint of a bidentate neutral ligand, the nature of which, however, prohibits geometrical isomerism. The results of these studies, while valid in their own right, tend to paint an imcomplete picture of the various influences on linkage isomerism in nickel triad thiocyanate complexes. The L$_2$M(CNS)$_2$ complexes, where L is a monodentate neutral ligand, have the capacity for geometrical isomerism, which we feel should influence the thiocyanate bonding mode. With the work described in this paper we attempt to tackle the question of the interrelation of linkage and geometrical isomerism and the factors influencing each in L$_2$M(CNS)$_2$ complexes, specifically when M = Pd(II) and L is a series of monodentate phosphines.

Experimental Section

Reagents and Physical Measurements. Chemicals were reagent grade and were used as received from the manufacturer or were synthesized as described below. All solvents, when necessary, were dried by standard procedures and were stored over Linde 4-Å molecular sieves. All reactions involving phosphines were conducted in a nitrogen atmosphere. Melting points were determined on a Mel-temp melting point apparatus and are uncorrected. Satisfactory elemental analyses were performed by Chemalytics, Inc., Tempe, Ariz. 85282.

Infrared spectra were obtained on a Perkin-Elmer 599 spectrophotometer. Samples were studied as Nujol mulls between CsBr plates or as chloroform solutions in NaCl cells. Integrated intensities of the CN stretching absorptions were determined by literature methods.[22] Proton, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR were recorded at 99.54, 25.00, and 40.26 MHz, respectively, on a JEOL FX-100 spectrometer in Fourier transform mode. Proton and carbon chemical shifts are relative to internal Me$_4$Si while phosphorus chemical shifts are reported relative to external 85% H$_3$PO$_4$. Saturated CDCl$_3$ solutions for NMR were

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