In summary, the catalytically active species is best formulated as a rhodium(III) carbonyl dinitrosyl complex in which both nitrosyl ligands are bent. The catalyst reacts with NO to form a complex anionic rhodium nitrosyl, which in turn can serve as the catalyst precursor and which under anhydrous conditions with CO yields a relatively stable solution of the catalyst.

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Registry No. $[RhCl_2(CO)(NO)_2]^-$, 61752-34-9; $(AsPh_4)[Rh_2(NO)_2Cl_4]$, 61867-72-9; $(NMe_4)_2[Rh_2(NO)_2Cl_5]$, 61867-73-0; $(AsPh_4)[RhCl_2(CO)_2]$, 13986-82-8; $[RhCl(CO)_2]_2$, 14523-22-9; nitric oxide, 10102-43-9.

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(15) The analytical results, though not good, are best fit by the empirical formulas $(AsPh_4)[Rh_2(NO)_2Cl_4]$ and $(NMe_4)_2[Rh_2(NO)_2Cl_5]$. Anal. Calcd for $(AsPh_4)[Rh_2(NO)_2Cl_4]$, $C_{24}H_{20}AsCl_4N_2O_2Rh_2$: C, 36.44; H, 2.55; Cl, 17.93; N, 3.54. Found: C, 37.69; H, 2.80; Cl, 18.46; N, 3.37. Calcd for $(NMe_4)_2[Rh_2(NO)_2Cl_5]$, $C_8H_{24}Cl_5N_4O_2Rh_2$: C, 16.25; H, 4.09; Cl, 29.98; N, 9.47. Found: C, 17.94; H, 4.62; Cl, 31.73; N, 9.28. The species are diamagnetic.

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Stereoselective Binding of Optically Active Amino Acids by Nickel(II) and Copper(II) Complexes of *N*-Carboxymethyl-β-(2-pyridyl)-L-α-alanine

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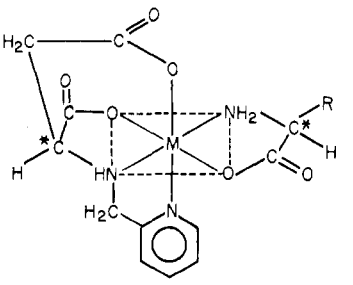
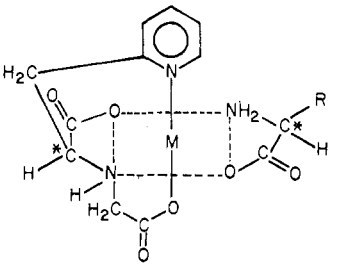
Previously we reported[2] the stereoselective binding of optically active amino acids by Ni(II) and Cu(II) complexes of *N*-(2-pyridylmethyl)-L-aspartic acid (*N*-pyr-L-Asp). The stronger preference of these complexes for L-amino acidates was rationalized by assuming that the resulting complex had geometry I. In this structure the L-amino acidates (as shown) would bind normally because the bulky R group would not encounter significant crowding from the carboxylate donor trans to the pyridine. On the other hand, the R group of D-amino acidates (where R and H interchange positions from the L form) would crowd the large pyridyl group thereby reducing the interaction between D-amino acidates and the metal ion.



I

For the purpose of testing this model further, we have synthesized a ligand *N*-carboxymethyl-β-(2-pyridyl)-L-α-alanine (Cm-L-Pyala) in which the pyridyl and carboxylate groups are essentially interchanged from those in *N*-pyr-L-Asp. By assuming a structure similar to I, we would expect Cm-L-Pyala^{2-} and an L-amino acidate to coordinate as follows:



II

In this case, steric crowding between the R side chain and the pyridyl group should reduce binding of the L-amino acidates as compared to their D enantiomers. Thus, the selectivity should be just the reverse of that found in the M(*N*-pyr-L-Asp) complexes.

The strength of the binding of D- and L-amino acidates (A^-) in these Cm-L-Pyala complexes was determined by measuring constants for the following equilibria:

$$(\text{Cm-L-Pyala})M + \text{L-}A^- \rightleftarrows (\text{Cm-L-Pyala})M(\text{L-A})^- \quad (K_L) \qquad (1)$$

$$(\text{Cm-L-Pyala})M + \text{D-}A^- \rightleftarrows (\text{Cm-L-Pyala})M(\text{D-A})^- \quad (K_D) \qquad (2)$$

The results of these studies are reported herein.

Experimental Section

Preparation of *N*-Carboxymethyl-β-(2-pyridyl)-L-α-alanine, Cm-L-PyalaH$_2$. Racemic β-(2-pyridyl)-α-alanine (PyalaH)) was prepared as described previously.[3] It was resolved by precipitation of L-Pyala-*d*-tartrate with *d*-tartaric acid as reported.[3] However, instead of using $HgCl_2$ to remove L-Pyala from the diastereomeric salt, 10.0 g (31.5 mmol) of L-Pyala-*d*-tartrate was dissolved in 100 ml of hot water. The resulting solution was passed through a column of 150 ml of Bio-Rad AG-3 weakly basic ion exchange resin in the basic form. The L-PyalaH was eluted with approximately 1 L of hot water. (Ninhydrin tests were negative on later fractions.) Evaporation of the solution yielded L-PyalaH which was recrystallized from 80% ethanol to give 4.65 g (89%).

The 4.65 g (28 mmol) of L-PyalaH was neutralized in 42 ml of water to pH 10 with 5 M LiOH. Separately, 4.67 g (32.8 mmol) of bromoacetic acid was dissolved in a minimum volume of water (~5 ml) and brought to pH 6 at 0 °C with 5 M LiOH. To the stirred L-Pyala solution at 60 °C was added slowly the bromoacetic acid solution. The pH 10 of the solution was maintained by adding 5 M LiOH as required. When the pH ceased changing (after ~30 min), the pH was reduced to 3 with concentrated HCl. After evaporation under reduced pressure, an oil remained. It was dissolved in 95% ethanol; after a few hours at room temperature solid Cm-L-PyalaH$_2$ precipitated. Recrystallization from hot methanol gave 3.0 g (48%) of Cm-L-PyalaH$_2$. It had a melting point of 178–180 °C and $[\alpha]_D^{25}$ +36.4 (*c* 0.35, H_2O). Anal. Calcd for $C_{10}H_{12}N_2O_4 \cdot 1.5H_2O$: C, 47.8; H, 6.01; N, 11.1. Found: C, 48.2; H, 6.14; N, 11.21. The proton NMR spectrum of Cm-L-PyalaH$_2$ in D_2O shows the following peaks: δ 7.85–8.90 multiplet, pyridine H's; δ 4.05–4.32 doublet of doublets,

Table I. Visible Spectra of M(Cm-L-Pyala) Complexes

Metal complex	λ_{max}, nm	ϵ_{max}, M^{-1} cm^{-1}
Cu(Cm-L-Pyala)	680	65
Cu(Cm-L-Pyala)(D-Phe)$^-$	655	75
Ni(Cm-L-Pyala)	610, 365	7.4, 12

methine H; δ 3.5–3.9, two overlapping doublets, both methylene H's.

Standardization of Solutions. Solutions of Cm-L-PyalaH_2 were standardized by potentiometric titration. The D- and L-amino acid solutions were standardized both by potentiometric titration in water and by titration with NaOH of an ethanol–H_2O solution to a phenolphthalein end point according to Greenstein and Winitz.[4] Solutions of Baker-analyzed $Cu(NO_3)_2 \cdot 3H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ were standardized by passing them through Dowex 50W-X8 strongly acidic cation-exchange resin and titrating the effluent acid with NaOH.[5]

Potentiometric Measurements. A Corning Digital 112 Research Model pH meter was used to determine hydrogen ion concentrations in all potentiometric titrations, which were carried out in a double-walled cell of 50 ml capacity. The temperature of all solutions was maintained at 25.00 ± 0.05 °C by circulation of thermostated water through the outer jacket of the cell. The titration vessel was fitted with Corning glass and calomel extension electrodes, a microburet delivery tube, and a nitrogen inlet tube. The glass electrode was calibrated in terms of –log [H^+] according to the procedure of Rajan and Martell[6] using HCl and NaOH solutions. The solutions were stirred with a magnetic stirrer. Ionic strengths of all solutions were maintained at 0.10 M by the addition of an appropriate amount of 1.0 M KNO_3. All titrations were performed at least in duplicate with most in triplicate.

The protonation constants of Cm-L-PyalaH_2, the formation constants (K_L and K_D, eq 1 and 2) of the mixed ligand (Cm-L-Pyala)M(A)$^-$ complexes, and the formation of the hydroxo complex (Cm-L-Pyala)M(OH)$^-$ were calculated from titration data using Bjerrum's method.[7] The amino acid protonation constants used in the calculations were obtained from the literature.[2,8] Only data from 20 to 80% of a buffer region were used in the calculations, and all calculations were performed on an IBM 360-65 digital computer (West Virginia University Computation Center). The low pH at which Cu^{2+} and Ni^{2+} complexation of Cm-L-Pyala occurs precludes the calculation of stability constants from the potentiometric data obtained here.

The mixed ligand amino acid complexes were studied by bringing together in solution equimolar amounts of the metal ion (1.3×10^{-3} M), the auxiliary ligand (Cm-L-PyalaH_2), and the amino acid followed by adjustment of the ionic strength to 0.10 M with KNO_3. Titrations were made with 0.11 M NaOH. It was necessary to include the equilibrium

$$\text{(Cm-L-Pyala)Cu} + \text{OH}^- \rightleftarrows \text{(Cm-L-Pyala)Cu(OH)}^- \quad (K_{OH}) \qquad (3)$$

in calculating values of K_L and K_D. The value of log K_{OH} was found to be 4.00 ± 0.01.

Visible Spectra. All spectra were recorded on a Cary-14 grating spectrophotometer. Measurements of equimolar (0.0514, 0.0257, 0.0128 M) metal–ligand aqueous solutions with sufficient base to neutralize ligand protons were taken at 25.00 ± 0.05 °C. Maxima and extinction coefficients are given in Table I. These solutions of Ni(Cm-L-Pyala) and Cu(Cm-L-Pyala) have λ_{max} values of 610 and 680 nm, respectively, which are considerably lower than values for the corresponding glycine complexes, Ni(Gly)$^+$ (650 nm)[9] and Cu(Gly)$^+$ (725 nm).[9] This indicates that more than one nitrogen-donor group is coordinated to the metal ion in the Cm-L-Pyala complexes. Therefore, these spectra support the expected coordination of the pyridine group in both complexes.

Results and Discussion

Protonation constants of the two protons of Cm-L-PyalaH_2 were found to be log $K_1' = 8.94 \pm 0.01$ and log $K_2' = 4.21 \pm 0.02$. The larger constant (log K_1') is similar to that found for other amino acids and corresponds to protonation of the secondary amino group. It is also nearly identical to that (8.95)[3] of its precursor β-(2-pyridyl)-α-alanine, $NH_2CH(CH_2C_5H_4N)CO_2^-$, Pyala. Log K_2' is somewhat larger than that (3.89) for Pyala, and like Pyala probably corresponds to protonation of the pyridine nitrogen.

Table II. Values[a] of log K_L, log K_D, and Δ for the Addition of Amino Acidates to Ni(Cm-L-Pyala) and Cu(Cm-L-Pyala) According to Equations 1 and 2

Metal ion	Amino acid[b]	log K_D[c]	log K_L[c]	Δ
Ni^{2+}	Valine ($CH(CH_3)_2$)	3.51	2.95	0.56
Ni^{2+}	Phenylalanine (CH_2Ph)	2.98	2.72	0.26
Ni^{2+}	Alanine (CH_3)	3.09	2.84	0.25
Ni^{2+}	Serine (CH_2OH)	2.92	2.71	0.21
Cu^{2+}	Phenylalanine (CH_2Ph)	3.72	3.59	0.13
Cu^{2+}	Valine ($CH(CH_3)_2$)	3.65	3.69	−0.04

[a] At 25.0 °C and 0.10 M ionic strength (KNO_3). [b] R side chain given in parentheses. [c] All error limits are ±0.02 except those of Ni-D-Phe and Ni-D-Ala, which were ±0.03, and Ni-D-Val and Ni-L-Ala, which were ±0.01.

Values of log K_L and log K_D for eq 1 and 2 are given in Table II. The values for Ni(Cm-L-Pyala) indicate that this complex preferentially binds D-amino acidates by a factor of up to 3.6 (for valine) as compared to their L enantiomers. As noted in the introductory section, this D-enantiomeric preference was expected on the assumption that the products have structure II. This structure also suggests that amino acids with the bulkiest R side chains (i.e., most branched at the β-carbon atom) should show the greatest selectivity. This trend is observed in fact as demonstrated by decreasing stereoselectivity (measured by Δ = log K_D − log K_L in Table II) with R in the order: $CH(CH_3)_2 > CH_2C_6H_5 \sim CH_2OH \sim CH_3$. The stereoselectivity ($\Delta = 0.56$) of Ni(Cm-L-Pyala) for D-valine is substantially larger than that ($\Delta = 0.08$)[2] of Ni(*N*-pyr-L-Asp), structure I, for L-valine. The stereoselectivity of Ni(Cm-L-Pyala) for other amino acidates is also larger than that of Ni(*N*-pyr-L-Asp).

Although Cu(Cm-L-Pyala) also preferentially binds the D enantiomer of phenylalanine, its stereoselectivity is smaller than that of the Ni(II) complex. With valine there appears to be no selectivity. The tendency of Cu(II) to form square planar, rather than octahedral, complexes as in structure II probably accounts for its reduced stereoselectivity, because all six donor atoms may not be coordinated to the Cu^{2+}.

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Registry No. Cu(Cm-L-Pyala), 61916-20-9; Ni(Cm-L-Pyala), 61916-21-0; Ni(Cm-L-Pyala)(D-Val)$^-$, 61916-22-1; Ni(Cm-L-Pyala)(L-Val)$^-$, 61950-36-5; Ni(Cm-L-Pyala)(D-Phe)$^-$, 61950-35-4; Ni(Cm-L-Pyala)(L-Phe)$^-$, 61916-10-7; Ni(Cm-L-Pyala)(D-Ala)$^-$, 61950-34-3; Ni(Cm-L-Pyala)(L-Ala)$^-$, 61916-09-4; Ni(Cm-L-Pyala)(D-Ser)$^-$, 61950-33-2; Ni(Cm-L-Pyala)(L-Ser)$^-$, 61916-08-3; Cu(Cm-L-Pyala)(D-Phe)$^-$, 61989-62-6; Cu(Cm-L-Pyala)(L-Phe)$^-$, 61916-07-2; Cu(Cm-L-Pyala)(D-Val)$^-$, 61990-17-8; Cu(Cm-L-Pyala)(L-Val)$^-$, 61916-06-1; L-PyalaH, 37535-51-6; bromoacetic acid, 79-08-3.

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