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Preparation and Characterization of the Copper(II) and Zinc(II) Complexes of D-β-(2-Pyridyl)-α-alaninate and Their Condensation Products with Acetone

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The complexes Cu(D-Pyala)$_2$·2H$_2$O and Zn(D-Pyala)$_2$ were prepared by stirring an aqueous solution of D-$^+H_3NCH(CH_2C_5H_4N)CO_2^-$, D-PyalaH, with Cu(OH)$_2$ or Zn(OH)$_2$. The IR, ^{1}H NMR, visible, and CD spectra of Cu(D-Pyala)$_2$·2H$_2$O in aqueous solution support a structure for the complex that contains cis-amino and cis-carboxylate groups with one pyridine group occupying an apical position, while the other pyridine group is not coordinated. An X-ray diffraction study has established this structure for the complex in the solid state. The ^{13}C and ^{1}H NMR and IR spectra of Zn(D-Pyala)$_2$ suggest tridentate chelation of both D-Pyala$^-$ ligands. The Cu(D-Pyala)$_2$·2H$_2$O, Zn(D-Pyala)$_2$, and Ni(D-Pyala)$_2$·2H$_2$O complexes condensed with two molecules of acetone to add a three-carbon bridge between the two amino groups. The resulting complexes contained a hexadentate ligand with amino and imino, two pyridyl, and two carboxylate donor groups. On the basis of their NMR, visible, and CD spectra, structures have been proposed for these complexes.

Introduction

Potentiometric studies have shown that β-(2-pyridyl)-α-alanine, $^+H_3NCH(CH_2C_5H_4N)CO_2^-$ (PyalaH), binds to transition-metal ions to form M(Pyala)$_2$ with a significant degree of enantioselectivity.[1] Formation constants for the binding of L-Pyala$^-$ or D,L-Pyala$^-$ with Cu(II), Ni(II), Co(II), and Zn(II), which were determined by potentiometric titration, showed that the mixed complexes M(L-Pyala)(D-Pyala) were more stable than the bis complexes M(L-Pyala)$_2$.

We have been investigating the origins of this stereoselective effect by considering the possible structures of the complexes and determining the most stable species. Previous investigations[2,3] have shown that the most stable complex of cobalt(III), Co(D-Pyala)$_2^+$, has the trans-carboxylate configuration (Figure 1a). The structure[4] of Ni(D-Pyala)$_2$·2H$_2$O was determined from X-ray diffraction data and was found to be the trans-amino isomer (Figure 1b). In this report, we extend these studies to include the D-Pyala$^-$ complexes of Cu(II) and Zn(II).

Experimental Section

Materials. Racemic β-(2-pyridyl)-α-alanine was prepared and resolved as described previously.[5] Zn(OH)$_2$ was prepared by the method of Dietrich and Johnston.[6] Cu(OH)$_2$ was prepared according to the literature method.[7] The preparation of Ni(D-Pyala)$_2$·2H$_2$O was reported previously.[4]

Preparation of Bis[D-β-(2-pyridyl)-α-alaninato]copper(II) Dihydrate, Cu(D-Pyala)$_2$·2H$_2$O. To an aqueous solution containing 1.0 g (6.0 mmol) of D-PyalaH in 20 mL of H$_2$O was added 3.0 mmol of freshly prepared Cu(OH)$_2$. The mixture was stirred at 80 °C for 2 h, after which the solution was deep blue. The unreacted Cu(OH)$_2$ was filtered from the solution, which was then evaporated under reduced pressure to 2 mL. A layer of absolute ethanol (38 mL) was floated on top of the aqueous phase, and the two layers were allowed to diffuse together. The blue crystals that formed were filtered from the mother liquor, washed with 1 mL of cold ethanol, and dried under vacuum. The mother liquor was blue-green. It was evaporated to dryness, and the solid that formed was dissolved in 5 mL of water. A yellow color was extracted from the aqueous phase with EtOAc (10 mL, twice) leaving a blue solution. The blue aqueous phase was evaporated under reduced pressure to 1 mL, and 19 mL of absolute ethanol was added. The two phases were allowed to diffuse together, and the resulting solution was cooled to −40 °C, which yielded more of the deep blue crystals. The yield of Cu(D-Pyala)$_2$·2H$_2$O based on the moles of Cu(II) in the starting material was 79.2%. Anal. Calcd for Cu(C$_8$H$_9$N$_2$O$_2$)$_2$·2H$_2$O: C, 44.70; H, 5.16; N, 13.03. Found: C, 44.76; H, 5.26; N, 13.01.

Preparation of Bis[D-β-(2-pyridyl)-α-alaninato]zinc(II), Zn(D-Pyala)$_2$. The ligand D-PyalaH (1.0 g, 6.0 mmol) was dissolved in 20 mL of H$_2$O, and Zn(OH)$_2$ (0.3 g, 3.0 mmol) was added. This solution was stirred at 60 °C for 16 h. The unreacted Zn(OH)$_2$ was filtered from the solution, which was then evaporated to 1 mL. A layer of absolute ethanol (19 mL) was added and allowed to diffuse into the aqueous phase. The white crystals that formed were filtered, washed with cold ethanol, and vacuum-dried. The yield of Zn(D-Pyala)$_2$, based on Zn(II) starting material, was 83%. Anal. Calcd for Zn(C$_8$H$_9$N$_2$O$_2$)$_2$: C, 48.56; H, 4.58; N, 14.16. Found: C, 48.39; H, 4.58; N, 14.18.

Preparation of Ni(aib-D-Pyala)·H$_2$O. Ni(D-Pyala)$_2$·2H$_2$O[4] (1.0 g, 2.4 mmol) was dissolved in 15 mL of methanol, 15 mL of acetone was added, and the solution was refluxed for 32 h. At the end of this period, the solution was colorless and a purple precipitate had formed. The solid was filtered, washed with cold water, and vacuum-dried. The yield of Ni(aib-D-Pyala)·H$_2$O was 98%. Anal. Calcd for [Ni(C$_{22}$H$_{26}$N$_4$O$_4$)]·H$_2$O: C, 54.24; H, 5.79; N, 11.50. Found: C, 54.34; H, 5.95; N, 11.37.

Preparation of Cu(aib-D-Pyala)·4$^1/_2$H$_2$O. Blue crystals of Cu(D-Pyala)$_2$·2H$_2$O (1.0 g, 2.4 mmol) were dissolved in 125 mL of methanol, and 10 mL of acetone was added. After refluxing for 92 h, the solution was evaporated to 2 mL, and 10 mL of acetone was floated on top of the colored phase. Blue-green crystals formed as the layers diffused together. These crystals were filtered from the mother liquor, washed with acetone, and redissolved in a minimum of 95% ethanol (~3 mL). A layer of acetone (10 mL) was added, and the phases were allowed to diffuse together, causing precipitation of the complex as deep blue crystals. The crystals were air-dried, because they lost their luster and became crumbly if dried under vacuum. Analysis of the vacuum-dried crystals indicated that four molecules of water had been lost. The yield of Cu(aib-D-Pyala)·4$^1/_2$H$_2$O was 55%. Anal. Calcd for Cu(C$_{22}$H$_{26}$N$_4$O$_4$)·4$^1/_2$H$_2$O: C, 47.60; H, 6.36; N, 10.09. Found: C, 47.45; H, 6.29; N, 10.16.

Preparation of Zn(aib-D-Pyala)·1$^1/_2$H$_2$O. After Zn(D-Pyala)$_2$ (1.0 g, 2.5 mmol) was dissolved in 10 mL of water, 10 mL of acetone was added and the solution was allowed to stand at room temperature. White crystals began forming after 4 days. More crystals were allowed to precipitate for 2 weeks, at which time the crystals were filtered from the solution. The fluffy white crystals were dissolved in boiling water and precipitated by cooling to 10 °C. The crystals were filtered from the mother liquor and dried under vacuum. The yield of Zn(aib-D-Pyala)·1$^1/_2$H$_2$O was 23%. Anal. Calcd for Zn(C$_{22}$H$_{26}$N$_4$O$_4$)·1$^1/_2$H$_2$O: C, 52.55; H, 5.81; N, 11.14. Found: C, 52.59; H, 5.74; N, 11.13.

Spectra. Infrared spectra were recorded in KBr disks or D$_2$O solutions with use of a Beckman IR 4250 spectrophotometer. Visible and circular dichroism spectra were recorded at room temperature with use of a Jasco ORD/UV/CD-5 spectrophotometer. The ^{1}H

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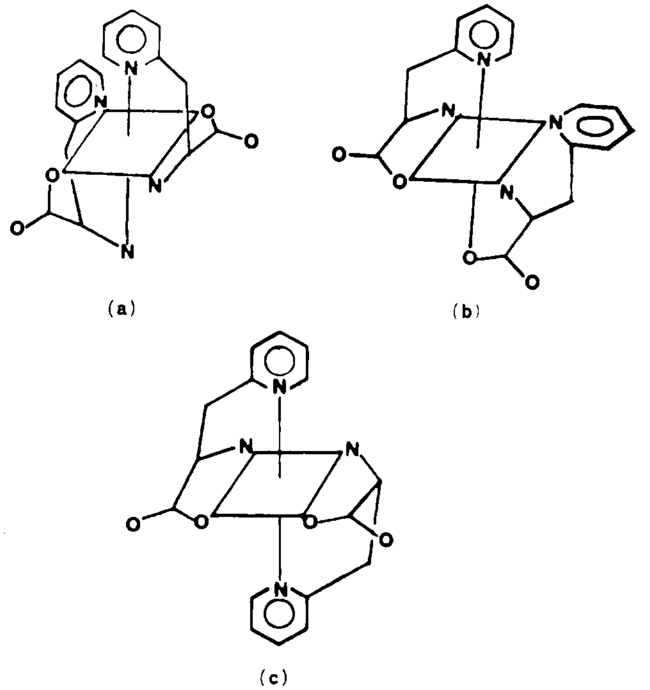

Figure 1. The three isomers of M(D-Pyala)$_2$: (a) trans carboxylate; (b) trans amino; (c) trans pyridyl.

NMR spectra were measured on a Varian Associates HA-100 spectrometer in 99.7% deuterium oxide vs. *tert*-butyl alcohol (δ 1.23) as an internal standard. The ^{13}C NMR spectrum was recorded on a JEOL FX90Q spectrometer in D_2O with dioxane (67.00 ppm) as an internal standard.

Crystal Data: Cu($C_8H_9N_2O_2$)$_2$·2H_2O, M_r = 429.91, orthorhombic $P2_12_12_1$, a = 5.877 (2) Å, b = 11.535 (2) Å, c = 28.09 (1) Å, V = 1904.2 Å^3, Z = 4, D_{calcd} = 1.50, Mo Kα radiation (λ = 0.71073 Å), μ = 12.3 cm^{-1}.

A single crystal of approximate dimensions 0.15 × 0.15 × 0.5 mm was mounted on a glass fiber and placed in a standard goniometer head. Data collection and unit cell determination were done on a Nonius CAD-4 diffractometer, at room temperature. Reflections in the *hkl* octant were collected up to 2θ = 50°, giving 1954 unique reflections with 1002 being observed ($I_o > 3\sigma(I)$). The intensity data were corrected for Lorentz and polarization effects; however, no absorption or extinction corrections were made.

The structure was solved by using a MULTAN direct methods in the "Enraf-Nonius Structure Determination Package".[8] Routine E-map and difference-map calculations revealed all non-H atoms. Attempts to refine the electron density difference-map positional parameters for the water oxygen atoms and six atoms of the uncoordinated pyridine ring led to very large isotropic temperature factors and unreasonable bond distances and angles. The positional parameters for these atoms, which are listed in Table I, were taken from the E map and not refined. Because it was not possible to distinguish nitrogen from carbon atoms in the uncoordinated pyridine ring, all of these atoms are labeled as carbons in Table I and Figure 4. Least-squares refinement using unit weights for all other atoms and refining the copper atom anisotropically gave R = 0.160 and R_w = 0.212. Final positional and thermal parameters in this structure (A) are listed in Table I.

Data were collected on a second crystal (structure B) as described above. Unit cell constants were a = 5.9011 (8) Å, b = 11.577 (1) Å, c = 27.753 (5) Å, V = 1896.0 Å^3, and μ = 18.7 cm^{-1}. Two octants of data were collected, giving 4400 reflections. Equivalent data were merged, giving 2626 unique reflections with an internal consistency R index of 0.038. Of these, 2029 were listed as observed ($I_o > 1\sigma(I)$). Intensities were corrected for Lorentz and polarization effects, but no absorption or extinction corrections were made.

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations (Structure A)

atom	x	y	z	β_{11}
Cu[a]	0.0250 (6)	0.1153 (3)	0.4211 (1)	0.0212 (9)
O1	−0.088 (3)	0.127 (2)	0.4868 (7)	5.3 (5)
O2	0.071 (5)	0.069 (2)	0.5561 (9)	8.0 (7)
O3	−0.262 (4)	0.090 (2)	0.3923 (8)	7.0 (6)
O4	−0.466 (5)	0.067 (2)	0.3290 (9)	8.6 (7)
O5[b]	0.139 (4)	0.403 (2)	0.3859 (7)	5.0 (0)
N1	0.335 (4)	0.152 (2)	0.4485 (8)	4.5 (6)
N2	0.127 (4)	−0.083 (2)	0.4314 (8)	4.4 (5)
N3	0.104 (5)	0.159 (2)	0.3551 (9)	6.2 (7)
C1	0.045 (5)	0.096 (3)	0.5120 (10)	5.0 (7)
C2	0.315 (6)	0.089 (3)	0.5034 (11)	5.9 (8)
C3	0.426 (6)	−0.031 (3)	0.4946 (11)	5.5 (8)
C4	0.308 (6)	−0.110 (3)	0.4578 (11)	5.2 (7)
C5	0.402 (6)	−0.232 (3)	0.4518 (11)	5.2 (8)
C6	0.289 (6)	−0.307 (3)	0.4240 (11)	5.4 (8)
C7	0.108 (6)	−0.273 (3)	0.4021 (11)	5.3 (8)
C8	0.030 (5)	−0.161 (2)	0.4058 (9)	4.3 (6)
C9	−0.278 (7)	0.095 (3)	0.3536 (13)	7.0 (10)
C10	−0.067 (6)	0.118 (3)	0.3245 (11)	6.2 (8)
C11	−0.117 (10)	0.182 (5)	0.2768 (19)	12.4 (17)
C12[b]	0.094 (0)	0.206 (0)	0.2500 (0)	5.0 (0)
C13[b]	0.147 (0)	0.113 (0)	0.2209 (0)	5.0 (0)
C14[b]	0.370 (0)	0.157 (0)	0.1895 (0)	5.0 (0)
C15[b]	0.436 (0)	0.258 (0)	0.1946 (0)	5.0 (0)
C16[b]	0.367 (0)	0.336 (0)	0.2199 (0)	5.0 (0)
C17[b]	0.187 (0)	0.309 (0)	0.2527 (0)	5.0 (0)

[a] The form of the anisotropic thermal parameter is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$. For the Cu atom, β_{22} = 0.0091 (3), β_{33} = 0.00234 (6), β_{12} = 0.001 (1), β_{13} = 0.0046 (5), and β_{23} = −0.0017 (3). [b] These atoms were not included in the least-squares calculations. The positional parameters were taken from an electron density difference map.

The structure was solved by using the program for crystal structure determination (SHELX-76) by George Sheldrick. All non-H atoms were found by E-map and difference-map calculations. The positional parameters for all atoms were refined and led to acceptable bond distances and angles; however the isotropic temperature factors for the uncoordinated pyridine ring atoms (C12–C17) were very large. It was not possible to distinguish the nitrogen from carbon atoms in this ring. The least-squares refinement converged to R = 0.169 and R_w = 0.195. Positional and thermal parameters, as well as bond distances and angles, are included in the supplementary material and labeled structure B.

Results and Discussion

Cu(D-Pyala)$_2$·2H_2O. The first and second stability constants, log K_1 and log K_2, for the interaction of D-Pyala$^-$ with copper(II) are 8.26 and 6.83,[1] respectively. The corresponding values for 2-(2-aminoethyl)pyridine are 7.3 and 5.6.[9] log K_1 and log K_2 values for phenylalanine are 7.93 and 6.90.[10] The larger value of log K_1 for D-Pyala$^-$ would seem to indicate that the first D-Pyala$^-$ ion chelates through all three groups, the amino and pyridine nitrogen atoms and the carboxylate oxygen atom. log K_2 for D-Pyala$^-$ is very close to that for phenylalanine, suggesting that the second D-Pyala$^-$ group may coordinate as a simple amino acid, through its amino nitrogen and carboxylate oxygen atoms.

The antisymmetric $-CO_2^-$ stretching frequency in D_2O for D-PyalaH was shifted from 1611 to 1570 cm^{-1} when the pD was raised to 10.0. These values are comparable to those reported for other amino acids of the forms $^+H_3N-C(R)H-CO_2^-$ and $NH_2-C(R)H-CO_2^-$, respectively.[11] Upon formation of the complex Cu(D-Pyala)$_2$ in D_2O, this band is shifted to 1598 cm^{-1}. This value is similar to others reported for bidentate amino acids coordinated to copper(II) through their amino and carboxylate groups.[11-13] Similar shifts have been

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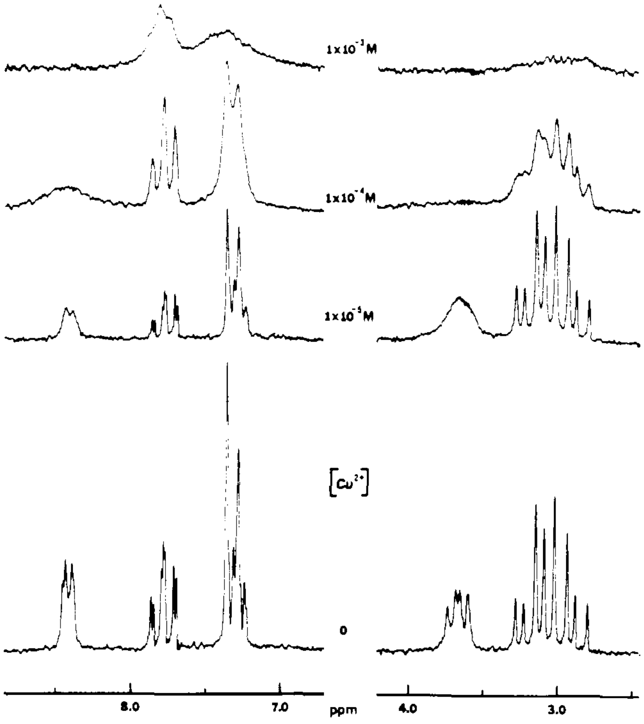

Figure 2. ^1H NMR spectra of D-PyalaH (0.4 M) at pD 10.0 in the presence of zero, 10^{-5}, 10^{-4}, and 10^{-3} M copper(II) ion.

reported for the copper(II)-L-histidine system ($^+NH_3$-C-(R)H-CO_2^-, pD = 2.5, 1622 cm^{-1}; NH_2-C(R)H-CO_2^-, pD = 10.2, 1578 cm^{-1}; coordinated $-NH_2$ and $-CO_2^-$, 1592 cm^{-1}).[14]

When the pyridyl ring nitrogen is complexed with a metal, the ring breathing mode shifts from about 995 (uncomplexed) to 1015 cm^{-1} (complexed).[15] The IR spectrum of D-PyalaH in KBr showed this band at 977 cm^{-1}. In the complex Cu(D-Pyala)$_2$·2H_2O, it was shifted to 1015 cm^{-1}, which may indicate coordination through the pyridine group.

The use of ^1H NMR spectroscopy for the elucidation of metal ion binding sites is a well-established technique.[16] The copper(II) ion, being paramagnetic, causes proton relaxation effects and selectively broadens the signals of protons near the binding sites. Since there is rapid exchange between complexes and free ligand, only a trace of paramagnetic copper(II) is used to cause the broadening of proton signals in proximity to the binding sites. Figure 2 shows the results obtained when increasing amounts of copper(II) were added to a D_2O solution of D-Pyala$^-$ at pD 10.0. The signal for the methine proton at 3.73 ppm (quartet, X portion of ABX spin pattern) was broadened by the addition of small amounts of copper(II). The initial line width for the quartet, measured at half-height, went from 16 Hz at zero copper(II) concentration to 22 Hz at 10^{-5} M copper(II). At 10^{-4} and 10^{-3} M copper(II), the peak was lost in the base line. The signal for the methylene protons, adjacent to the methine, was a pair of overlapping quartets at 3.08 ppm (AB portion of ABX spin pattern). These were broadened at the higher copper(II) concentrations due to a proximity effect. This is analogous to L-α-aminobutyric acid, where the signal for the β-methylene group was broadened in the presence of 2 × 10^{-4} M copper(II) at pD 7.6.[17]

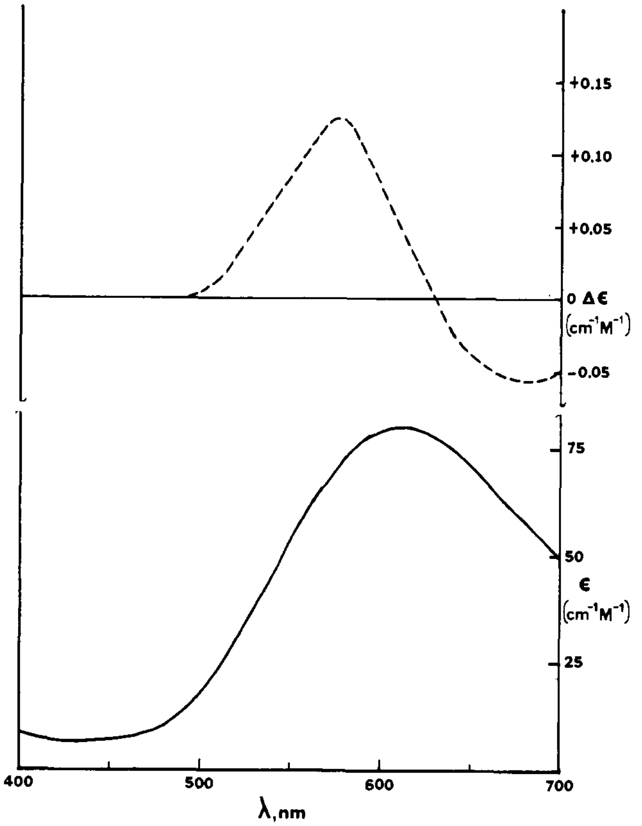

Figure 3. Visible (—) and CD (- - -) spectra of Cu(D-Pyala)$_2$·2H_2O in aqueous solution.

The signal for the α proton of the pyridine ring at 8.44 ppm (doublet, if small couplings ($J < 2$ Hz) are ignored) was broadened when small amounts of copper(II) were added. The initial line width for the doublet went from 9 Hz at zero copper(II) concentration to 13 Hz at 10^{-5} M copper(II) and 40 Hz at 10^{-4} M copper(II). The γ and β protons of the pyridine ring at 7.78 and 7.32 ppm, respectively, were only slightly broadened, as was observed for the methylene protons.

These results may be compared with those observed for (*S*)-β-(2-pyridylethyl)-L-cysteine, in which broadening of the α-methine group indicated glycine-type chelation through the amino and carboxylate groups, while the pyridyl nitrogen atom was eliminated as a binding site because the ring protons were not broadened even at 10^{-3} M copper(II) concentration.[15] However, the broadening of the α-methine and α-pyridine protons in the present case suggests that D-Pyala$^-$ is tridentate in binding to copper(II).

Further evidence regarding the structure of Cu(D-Pyala)$_2$ was provided by visible absorption and circular dichroism spectra, which are shown in Figure 3. Visible absorption spectra of 1:2 complexes of copper(II) and amino acids, which are bound through one amino nitrogen and one carboxylate oxygen atom, exhibit a maximum near 620 nm, as typified by L-alanine.[18] Displacement of an apical water molecule in Cu(gly)$_2$ with imidazole causes an increase in ϵ (45 to 62 cm^{-1} M^{-1}), with no change in the maximum.[19] The absorption maximum of Cu(D-Pyala)$_2$·2H_2O in aqueous solution (Figure 2) occurs at 613 nm with an ϵ of 85 cm^{-1} M^{-1}. The similarity between the maximum of Cu(D-Pyala)$_2$ and other bis(amino acidato)copper(II) complexes implies that two D-Pyala$^-$ ions bind through their amino nitrogen and carboxylate oxygen

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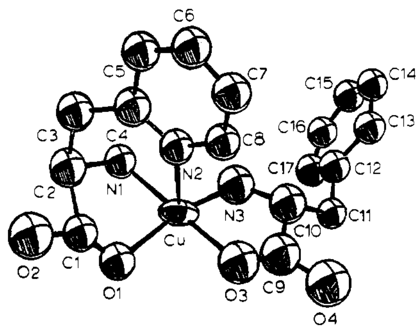
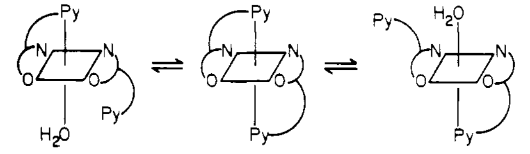


Figure 4. Structure of Cu(D-Pyala)$_2$·2H$_2$O. The water molecules are not shown.

atoms to form an N_2O_2 chromophore about the copper(II) center. The larger ϵ value for Cu(D-Pyala)$_2$ than for the bis(amino acidato)copper(II) complexes (ϵ values between 40 and 60 cm^{-1} M^{-1}) supports an apical interaction of the pyridine group with the copper(II) ion, which is consistent with the ^{1}H NMR studies.

The inverse of the CD spectra of bis(L-amino acidato)-copper(II) complexes shows a small negative peak ($\Delta\epsilon < -0.05$) around 700 nm and a more intense positive band with a maximum between 580 and 640 nm.[18,20–23] The CD spectrum of Cu(D-His)$_2$, which is equal to the inverse of the CD spectrum of Cu(L-His)$_2$, had a large negative maximum at 690 nm ($\Delta\epsilon = -0.52$) with a less intense positive peak at 570 nm ($\Delta\epsilon = +0.03$).[20] It was proposed that one histidinate was bound to copper(II) primarily through the amino and imidazole nitrogen atoms, with weaker apical chelation by the carboxylate group. The second histidinate was proposed to be bidentate and was coordinated to copper(II) through the amino nitrogen atom and carboxylate oxygen atom. The chelate plane was composed of one oxygen and three nitrogen donors. The CD spectrum of Cu(D-Pyala)$_2$·2H$_2$O in aqueous solution lies between that of the simple bidentate amino acids and the CD spectrum of Cu(D-His)$_2$. The positions of the maxima are similar to those of Cu(L-His)$_2$, but the intensities of the absorptions are much less.

The structure which best fits all of the spectral results is one in which one D-Pyala$^-$ ion is tridentate, while the second is bidentate (structure I). Exchange of the coordinated pyridine group could occur through an intermediate (structure II) in which both ligands become tridentate with a trans-pyridyl structure.



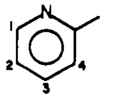
I II I

The crystal structure determination of Cu(D-Pyala)$_2$·2H$_2$O was undertaken in order to establish the configuration of the D-Pyala$^-$ ligands about the copper ion in the solid state. We were able to determine the configuration of the complex, but could not completely solve the structure because of difficulties in refining the atomic positions in the uncoordinated pyridine ring (atoms C12–C17).[24] The copper(II) ion is coordinated to the amino, carboxylate, and pyridine groups of one D-Pyala$^-$ and to the amino and carboxylate groups of the other D-Pyala$^-$ (Figure 4). Like the amino groups, the carboxylate groups are cis to each other in the base of the square pyramid while the pyridine group is in the apical position.

Table II. Selected Distances (Å) and Angles (Deg) for Cu(D-Pyala)$_2$·2H$_2$O (Structure A)

Cu–O1	1.97 (1)	Cu–O3	1.89 (1)
Cu–N1	2.02 (1)	Cu–N3	1.98 (1)
Cu–N2	2.38 (1)		
O1–Cu–O3	96.5 (5)	N1–Cu–N3	95.3 (6)
O1–Cu–N1	86.1 (5)	O3–Cu–N3	81.3 (6)
O1–Cu–N2	92.1 (5)	O3–Cu–N2	97.3 (5)
O1–Cu–N3	160.6 (5)	O3–Cu–N1	176.0 (6)
N1–Cu–N2	85.7 (5)	N3–Cu–N2	107.3 (5)

Table III. ^{1}H NMR Spectra of D-Pyala and Zn(D-Pyala)$_2$ in D$_2$O



	pyridine moiety				alanine moiety	
	1 (d)^a	2 (t)	3 (t)	4 (d)	CH	CH$_2$
D-PyalaH (pD 7.0)	8.44	7.28	7.78	7.32	4.12	3.38
D-Pyala$^-$ (pD 10.0)	8.44	7.28	7.78	7.32	3.73	3.22
Zn(D-Pyala)$_2$	8.11	7.18	7.78	7.25	3.87	3.35

^{a} First-order splitting ($J < 2$ Hz).

Selected bond distances and angles are given in Table II. The Cu–amino nitrogen (2.02 (1) and 1.98 (1) Å) and Cu–carboxylate oxygen (1.97 (1) and 1.89 (1) Å) distances are similar to those in previously reported structures.[25–29] The Cu–pyridine nitrogen bond length (2.38 (1) Å) compares with that of a pyridine molecule occupying the apical position of a square-pyramidal complex (2.308 (6) Å).[30]

The present structure may be contrasted with those of copper complexes containing the histidine ligand. In these complexes, the imidazole group occupies a strongly coordinating position, with the carboxylate group being either uncoordinated or weakly coordinated.[27,28,31] In Cu(D-Pyala)$_2$, the carboxylate groups are in the tightly bound square-planar positions, while one pyridine group is weakly coordinated in an apical position and one is not coordinated.

Zn(D-Pyala)$_2$. The first and second stability constants, log K_1 and log K_2, for the interaction of D-Pyala$^-$ with zinc(II) are 4.93 and 4.12,[1] respectively, whereas the values for phenylalanine are 4.29 and 4.1.[10] This suggests that at least one of the D-Pyala$^-$ ligands in Zn(D-Pyala)$_2$ is tridentate.

The infrared spectrum of Zn(D-Pyala)$_2$ was taken in D$_2$O as well as in a KBr disk. The asymmetric $-CO_2^-$ stretching frequency, which occurs at 1570 cm^{-1} for D-Pyala$^-$ in D$_2$O, was shifted to 1592 cm^{-1} upon complex formation with zinc(II). This shift is similar to that reported for the zinc(II) complex of D,L-alanine in D$_2$O (1575 cm^{-1}, deprotonated and uncoordinated; 1592 cm^{-1}, deprotonated and coordinated to Zn(II)).[11] In a KBr pellet, Zn(D-Pyala)$_2$ showed bands at 3360–3159 cm^{-1} for the coordinated NH$_2$ stretches and strong absorptions at 1611 and 1590 cm^{-1} corresponding to the $-NH_2$

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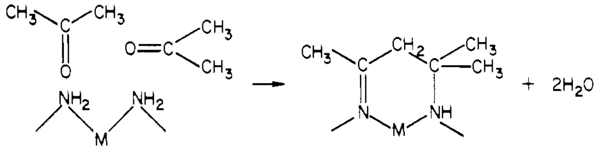
scissors and $-CO_2^-$ asymmetric stretching modes. These values are comparable to those reported for bis(amino acidato)-zinc(II) complexes in which the amino nitrogen and carboxylate oxygen atoms are coordinated.[32-34]

The ^{1}H NMR spectral data for D-PyalaH and its 2:1 zinc(II) complex in D_2O are presented in Table III. The alanine moiety of D-PyalaH at pD 7.0 and 10.0 consisted of an ABX pattern, with a quartet for the methine proton, and a pair of overlapping quartets for the methylene protons. The pyridine protons exhibited first- and second-order splitting, but the second-order coupling constants are only about 2 Hz. With second-order coupling being ignored, the spectra at pD 7.0 and 10.0 are designated as follows: 1, doublet; 2, triplet; 3, triplet; 4, doublet. Deprotonation results in an upfield shift of the C–H and CH_2 resonances due to inductive and magnetic anisotropic effects.[35] The methine proton, which is closest to the deprotonation site (the amino group), showed the largest upfield shift. The protons of the pyridine moiety were not affected by increasing the pD from 7.0 to 10.0 (pK_a is 3.89 for pyridine nitrogen).[1] In the zinc(II) complex, the pyridine resonances, particularly that of the α proton, lay upfield from those observed in the spectra of D-PyalaH and D-Pyala$^-$. This shift suggests that the pyridine nitrogen atom is coordinated to zinc(II). That the amino group is also coordinated is implied by noting that the alanine resonances lie between those observed for free D-PyalaH at pD 7.0 and 10.0, where the amino group is protonated and deprotonated, respectively. These shifts are similar to those observed when L-histidine coordinates to zinc(II).[11] Coordination of the amino and carboxylate groups is also supported by ^{13}C NMR data. The α-carbon and carboxylate carbon atoms were shifted from 57.25 and 182.01 ppm in D-Pyala$^-$ to 53.78 and 180.01 ppm, respectively, in Zn(D-Pyala)$_2$. A large change was also observed for the β-carbon atom upon coordination: 43.11 ppm in D-Pyala$^-$; 38.45 ppm in Zn(D-Pyala)$_2$. The pyridine ^{13}C resonances in the zinc(II) complex occurred at 158.12, 148.53, 139.76, 126.38, and 123.29 ppm.

The ^{13}C NMR, ^{1}H NMR, and IR spectra, as well as the formation constants for Zn(D-Pyala)$_2$, suggest tridentate chelation of the D-Pyala$^-$ ligands. Crystal structures of zinc(II) amino acid complexes have shown that the preferred geometry about the metal ion center is either regular or distorted octahedral.[36,37] The absence of any water in the crystals of Zn(D-Pyala)$_2$ suggests that the metal ion is coordinated to the amino nitrogen, pyridine nitrogen, and carboxylate oxygen atoms of each D-Pyala$^-$ ligand in the solid state. Although the spectral data imply that the same type of structure occurs in water, it is not possible to assign the structure to one of the three expected isomers (Figure 1).

Condensation Products. The direct condensation of metal–amine complexes with acetone has been investigated in depth by Curtis.[38] We find that the reaction of M(D-Pyala)$_2$ with acetone results in the formation of complexes in which a three-carbon bridge links amine and imine donor groups:



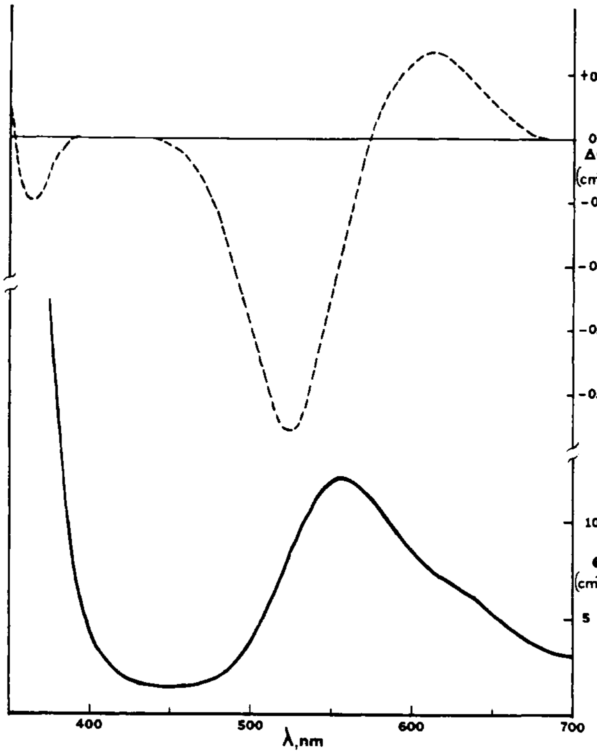
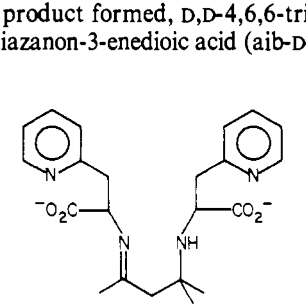
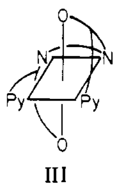


Figure 5. Visible (—) and CD (- - -) spectra of Ni(aib-D-Pyala)·H_2O in methanol.

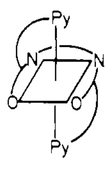
In the present case, the amino groups are part of the D-Pyala$^-$ ligand, and the product formed, D,D-4,6,6-trimethyl-2,8-bis-(2-picolyl)-3,7-diazanon-3-enedioic acid (aib-D-Pyala) is shown by



The two possible structures for M(aib-D-Pyala) are trans carboxylate (III) or trans pyridyl (IV).



III



IV

Ni(aib-D-Pyala)·H$_2$O. Only one N–H stretching band at 3200 cm^{-1} was observed in the infrared spectrum of Ni(aib-D-Pyala)·H_2O in a KBr disk, compared to the two absorptions at 3305 and 3260 cm^{-1} for the $-NH_2$ groups of Ni(D-Pyala)$_2$·2H_2O.[4] Other nickel(II) complexes containing an N–H group showed a similar band.[38,39] Three intense bands were observed at 1667, 1641, and 1595 cm^{-1} in the spectrum of Ni(aib-D-Pyala)·H_2O. In D_2O, the band at 1595 cm^{-1} remained unchanged, suggesting that this is the CO_2^- asymmetric stretching mode. The sharp band at 1667 cm^{-1} is most likely the coordinated imino stretch, since this compares favorably with that found for the condensation product of acetone with bis[2-(2-aminoethyl)pyridine)]bis(isothiocyanato)-

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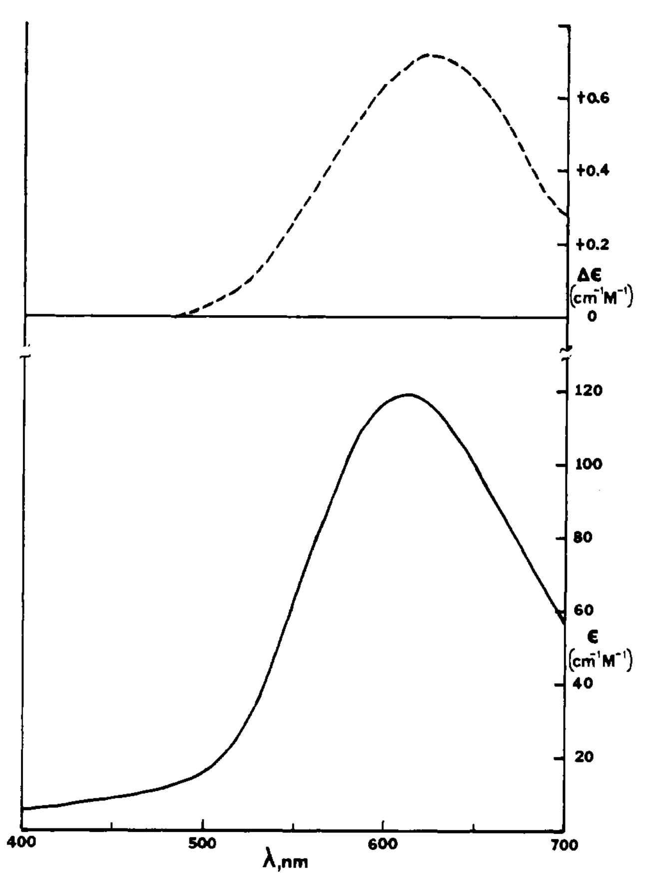


Figure 6. Visible (—) and CD (---) spectra of Cu(aib-D-Pyala)·$4^1/_2H_2O$ in methanol.

nickel(II),[40] at 1668 cm^{-1}. The band at 1641 cm^{-1} may be due to the water of crystallization.

The visible and CD spectra of Ni(aib-D-Pyala)·H_2O in methanol are given in Figure 5. The absorption maximum at 556 nm is similar to that observed for Ni(D-Pyala)$_2$·$2H_2O$, 563 nm and suggests that the same chromophore is present in both complexes, namely, NiN_4O_2. However, Ni(aib-D-Pyala)·H_2O has a more pronounced shoulder at about 630 nm than was observed in the spectrum of Ni(D-Pyala)$_2$·$2H_2O$.

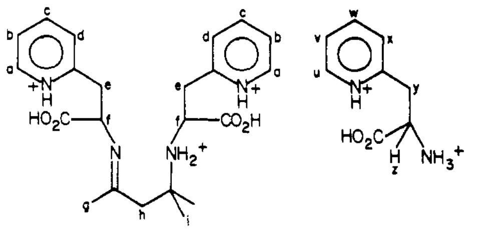
The circular dichroism spectrum of Ni(aib-D-Pyala)·H_2O showed a positive band at 614 nm and two negative bands at 535 and 374 nm. There are also three transitions in the CD spectrum of [Ni(D-Pyala)$_2$]·$2H_2O$, but the signs and intensities of these bands differ from those shown for Ni(aib-D-Pyala)·H_2O. This is probably due to a number of factors, including the addition of another chelate ring, formation of an asymmetric nitrogen, and most likely a different arrangement of donor atoms about the nickel center. Whether Ni(aib-D-Pyala)·H_2O has structure III or IV cannot be established on the basis of the spectral results.

Attempts to reduce the imino group with $NaBH_4$, $NaBH_3CN$, and Pd/C with H_2 in water or alcohol were unsuccessful.

Cu(aib-D-Pyala)·$4^1/_2H_2O$. Crystals of this complex lost four molecules of water when dried under vacuum. However, the infrared spectrum remained the same, implying that no change in coordination to the copper(II) ion occurred.

The infrared spectrum of Cu(aib-D-Pyala)·$4^1/_2H_2O$ in a KBr pellet has one N–H absorption at 3140 cm^{-1}. This band was observed at 3120 cm^{-1} in similar complexes prepared by Curtis.[39] Three bands were found in the C=N and CO_2^- region as was observed in the nickel(II) analogue. The absorption at 1662 cm^{-1} may be assigned to the C=N stretch by comparison with similar copper(II) complexes such as those prepared by Curtis[39] and Rastogi and Pachauri.[40] The band at 1598 cm^{-1} may be assigned to the $-CO_2^-$ asymmetric stretching mode since in D_2O this band remained unchanged. The band at 1635 cm^{-1} is of unknown origin and may be from the water of crystallization.

Table IV. ^1H NMR of D-PyalaH and Zn(aib-D-Pyala)·$1^1/_2H_2O$ in 1 M D_2SO_4/D_2O



shift, ppm	splitting (ignoring $J < 2$ Hz)[a]	no. of H's	assignt
	Zn(aib-D-Pyala)·$1^1/_2H_2O$		
1.43	s	6	i
2.26	s	3	g
3.18	s	2	h
3.78	d	4	e
4.62	c	2	f
8.05	t	2	b
8.09	d	2	d
8.63	t	2	c
8.79	d	2	a
	D-PyalaH$_3^{2+}$		
3.82	d	2	y
4.70	t	1	z
8.06	t	1	v
8.12	d	1	x
8.64	t	1	w
8.78	d	1	u

[a] s = singlet, d = doublet, t = triplet, c = complex.

The visible and CD spectra of Cu(aib-D-Pyala)·$4^1/_2H_2O$ in methanol are given in Figure 6. The absorption maximum, 614 nm, is nearly identical with that observed for Cu(D-Pyala)$_2$·$2H_2O$, 613 nm. However, the extinction coefficient for Cu(aib-D-Pyala)·$4^1/_2H_2O$ (119 cm^{-1} M^{-1}) is greater than that for Cu(D-Pyala)$_2$·$2H_2O$ (85 cm^{-1} M^{-1}).

The CD spectrum of Cu(aib-D-Pyala)·$4^1/_2H_2O$ differs from that of Cu(D-Pyala)$_2$·$2H_2O$ in both the shape of the curve and size of Δε. The reasons for this are probably similar to those given above for the nickel(II) complexes. The arrangement of the donor atoms about copper(II) in Cu(aib-D-Pyala) is not known.

Zn(aib-D-Pyala)·$1^1/_2H_2O$. The infrared spectrum of this complex in a KBr disk exhibited an NH stretch at 3212 cm^{-1}, which may be compared with the $-NH_2$ stretches observed for Zn(D-Pyala)$_2$ at 3360 and 3255 cm^{-1}. The C=N stretch occurred at 1666 cm^{-1}, and the asymmetric carboxylate stretch was at 1593 cm^{-1}. The infrared spectrum of the complex in D_2O showed the $-CO_2^-$ stretch at 1591 cm^{-1}, similar to that observed in the solid state.

The ^1H NMR spectrum of Zn(aib-D-Pyala)·$1^1/_2H_2O$ was taken in 1 M D_2SO_4 because of its low solubility in water and is reported in Table IV. The appearance of peaks at 1.43, 2.26, and 3.18 ppm indicated that the diacetone amino–imine bridge was present. The pyridine region for Zn(aib-D-Pyala) was quite different from that of Zn(D-Pyala)$_2$. The positions of the pyridine peaks in Zn(aib-D-Pyala) were similar to those of D-PyalaH$_3^{2+}$ in 1 M D_2SO_4, suggesting that the pyridyl group is protonated and not coordinated to Zn(II). It is not

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possible to determine if the remaining donor atoms are coordinated to Zn(II) in 1 M D_2SO_4. No structural assignment could be made from the data available.

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Registry No. Cu(D-Pyala)$_2$·2H_2O, 77846-71-0; Zn(D-Pyala)$_2$, 60478-55-9; Ni(aib-D-Pyala), 77827-46-4; Cu(aib-D-Pyala), 77827-47-5; Zn(aib-D-Pyala), 77827-48-6; Ni(D-Pyala)$_2$, 77827-49-7; acetone, 67-64-1.

Supplementary Material Available: Tables listing observed and calculated structure factors for structure A and structure B and bond distances and angles for both structures (16 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry and Ames Laboratory-USDOE,[1]
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Preparation of Some Dithiocarbene Complexes, $W(CO)_5[C(SR)_2]$, and Their Reactions with Nucleophiles

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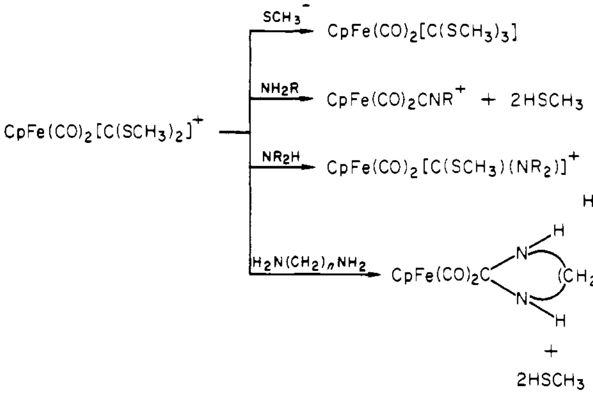
Received September 9, 1980

The reaction of $W(CO)_5CS$ with ^-SR (R = CH_3, C_2H_5, *i*-C_3H_7, *n*-C_4H_9, or *t*-C_4H_9) followed by alkylation of the resulting dithioester anion, $W(CO)_5[C(=S)SR]^-$, by R′I (R′ = CH_3 or C_2H_5) produces [bis(alkylthio)carbene]tungsten complexes, $W(CO)_5[C(SR)(SR')]$, in good yield. The substituted tetracarbonyl[bis(methylthio)carbene]tungsten complexes *cis*-$W(CO)_4[P(OCH_3)_3][C(SCH_3)_2]$ and *cis*-$W(CO)_4[P(OPh)_3][C(SCH_3)_2]$ are prepared by an analogous route using *cis*-$W(CO)_4L(CS)$, where L = $P(OCH_3)_3$ or $P(OPh)_3$. (Cyclic dithiocarbene)tungsten complexes may be prepared in a similar manner from $W(CO)_5CS$, $NaS(CH_2)_nSH$ (*n* = 2, 3, 4), and CH_3I to give $W(CO)_5\overline{CS(CH_2)_nS}$. The carbene complex $W(CO)_5\{C(SCH_3)[SFe(CO)_2Cp]\}$ (Cp = η^5-C_5H_5) is prepared by the reaction of $W(CO)_5[C(=S)(SCH_3)]^-$ with $CpFe(CO)_2(THF)^+$. Isocyanide complexes, $W(CO)_5CN$-R, are formed when $W(CO)_5[C(SCH_3)_2]$ reacts with primary amines, RNH_2, where R = CH_3, $(CH_2)_2CH_3$, CH_2Ph, C_6H_{11}, and $(CH_2)_2N(CH_3)_2$, or the diamine $NH_2(CH_2)_3NH_2$. When *cis*-$W(CO)_4[P(OPh)_3][C(SCH_3)_2]$ is reacted with NH_2CH_2Ph and $NH_2(CH_2)_3NH_2$, isocyanide complexes are also formed. The reaction of $W(CO)_5[C(SCH_3)_2]$ with secondary amines $NH(CH_3)_2$, $\overline{HN(CH_2)_2OCH_2CH_2}$, or $\overline{HN(CH_2)_4CH_2}$ yields (aminothiocarbene)tungsten complexes, $W(CO)_5[C(SCH_3)NR_2]$. The compound $[N(C_2H_5)_4{}^+][W(CO)_5CN^-]$ was formed from the reaction of $W(CO)_5[C(SCH_3)_2]$ with $[N(C_2H_5)_4{}^+][N_3{}^-]$.

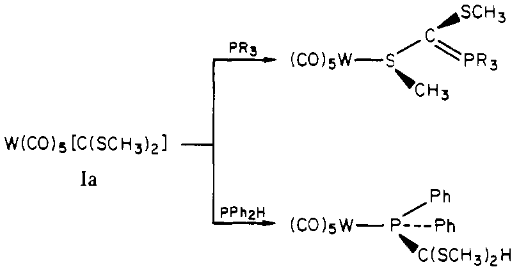
Introduction

It has been only recently that transition-metal complexes containing the dithiocarbene ligand $[C(SR)_2]$ have been isolated,[2-11] and only a few studies of their reactivity have been reported.[8,10,11] McCormick and Angelici[8,12] found that $CpFe(CO)_2[C(SCH_3)_2]^+$ (Cp = η^5-C_5H_5) reacts with mercaptides and amines according to eq 1.



(1)

Recently, we reported the preparation of $W(CO)_5[C(SCH_3)_2]$[11] and its remarkable reactions with secondary and tertiary phosphines (eq 2).



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(2)

We would now like to report the preparations of other [bis(alkylthio)carbene]pentacarbonyltungsten complexes, $W(CO)_5[C(SR)_2]$, and their reactions with amines and other nucleophiles.

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[1] Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This research was supported by the Assistant Secretary of Energy Research, Office of Energy Research, WPAS-KC-03-02-01.

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