absent (O3–N5 distance of 5.68 Å) as a result of the extended conformation for the side chain. These results agree with our original contention that in these systems varying the hydrogen bonding capability of the side chain will significantly alter that chain's conformation.

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Supplementary Material Available: A listing of structure factor amplitudes (2 pages). Ordering information is given on any current masthead page.

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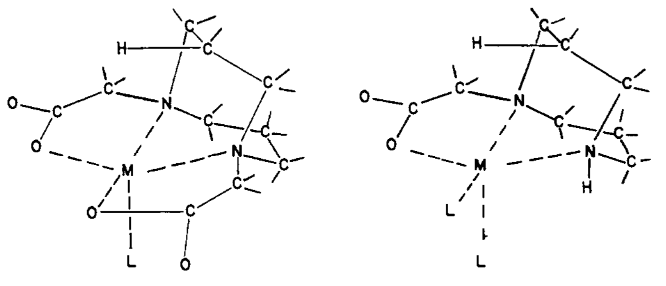
Five-Coordinate Amino Acid Complexes. Synthesis and Characterization of Nickel(II), Copper(II), and Zinc(II) Complexes of 1,5-Diazacyclooctane-*N*-monoacetic Acid

Michael H. West and J. Ivan Legg*

Contribution from the Department of Chemistry, Washington State University, Pullman, Washington 99163. *Received September 19, 1975*

Abstract: A new tridentate ligand, 1,5-diazacyclooctane-*N*-monoacetic acid (dacoma), has been synthesized. By comparison with the closely related ligand 1,5-diazacyclooctane-*N,N′*-diacetic acid (dacoda), dacoma is expected to restrict metal ions to a square pyramidal five-coordinate geometry. A close resemblance of the electronic absorption spectrum of Ni(II)-substituted carboxypeptidase A in the presence of an inhibitor to that of [Ni(dacoda)H_2O] has been demonstrated. Chelation of dacoma leads to a well-defined geometry in which the ligand occupies three planar sites with the remaining planar site and one apical site left free for additional coordination. The Ni(II), Cu(II), and Zn(II) complexes of dacoma were prepared and characterized by magnetic susceptibility measurements, x-ray powder-pattern analysis, visible absorption, and infrared spectroscopy as well as potentiometric pH titrations. By comparison with the solution spectrum of [Ni(dacoda)H_2O], $[\mathrm{Ni(dacoma)(H_2O)_2}]^+$ is shown to have a square pyramidal geometry. The Ni(II) and Zn(II) complexes of dacoma are isomorphous in the solid state, but the Cu(II) complex is not. Although Ni(II)- and Zn(II)-dacoma are not stable at basic pH's, $[\mathrm{Cu(dacoma)(H_2O)}]^+$ is quite stable over a wide pH range. The interaction of optically active amino acids with $[\mathrm{Cu(dacoma)H_2O}]^+$, which has two cis sites available for chelation, was examined as a function of pH by circular dichroism (CD) and visible absorption spectroscopy. Potentiometric pH measurements were used to determine formation constants for the ternary complexes. The L-amino acids were shown to chelate to $[\mathrm{Cu(dacoma)H_2O}]^+$ through an equatorial amino nitrogen and an apical carboxylate group. This study supports the observation that a biphasal CD spectrum with a lower energy, positive band which is dominant or comparable in intensity to a higher energy negative band is characteristic of this mode of amino acid chelation to Cu(II).

Five-coordinate complexes have seldom been prepared and studied under aqueous conditions due to their inherent instability in this solvent.[1] Averill et al. reported the synthesis of a series of five-coordinate, square pyramidal complexes stable in aqueous solution involving the tetradentate ligand, 1,5-diazacyclooctane-*N,N′*-diacetic acid (dacoda), Figure 1.[2]



M(dacoda)L M(dacoma)L$_2$

Figure 1. Metal complexes of 1,5-diazacyclooctane-*N*,*N*′-diacetic acid and 1,5-diazacyclooctane-*N*-monoacetic acid.

Molecular models predict that a methylene proton of the dacoda backbone should project over an axial ligating position preventing coordination at that site which would limit metal complexes of this ligand to a maximum coordination number of five. The geometry of [Ni(dacoda)(H_2O)]·$2H_2O$, determined by an x-ray crystal study, confirmed the predictions.[3] Spectral studies demonstrated that this geometry was maintained for the Ni(II) complex in solution as well as for the Co(II) and Zn(II) complexes.[2]

In addition to providing interest because of their unusual stereochemical features, the pentacoordinate nature of these complexes establishes a similarity with certain proteolytic metalloenzymes such as carboxypeptidase A (CPD). Rosenberg et al. recently noted the close resemblance of the electronic absorption spectrum of Ni(II)-substituted CPD in the presence of the inhibitor sodium β-phenylpropionate (βPP) to that of [Ni(dacoda)(H_2O)].[4] They concluded that Ni(II)CPD·βPP has the same donor sets as [Ni(dacoda)(H_2O)]. In addition, intermediates and products of CPD peptide and ester hydrolysis could include amino acids and peptides bound to the metal ion at the active site. Therefore, it was of direct interest to examine the binding of amino acids and peptides to metal ion complexes with the same basic structure as the dacoda complexes. For this purpose we have prepared a new ligand, 1,5-diazacyclooctane-*N*-monoacetic acid (dacoma), Figure 1, analogous to dacoda with the exception that only one acetate group is present.

Dacoma was expected to impose the same maximal, five-coordinate geometry found for dacoda complexes but leave two cis sites available for chelation of amino acids. Dacoma complexes with Ni(II), Cu(II), and Zn(II) were synthesized and characterized. Although the Ni(II)- and Zn(II)-dacoma complexes proved to be unstable in basic aqueous solution, Cu(II)-dacoma is quite stable, and its ternary complexes with optically active amino acids were extensively investigated by several techniques including circular dichroism (CD) and electronic absorption spectroscopy as well as potentiometric pH titrations.

Experimental Section

Materials and Standard Solutions. Sodium perchlorate from G. Frederick Smith was recrystallized from water and air-dried. Standardization of the $NaClO_4$ was accomplished by passing aliquots of the solution down a cation-exchange column in the H^+ form, Dowex 50W-X8, and titrating the displaced H^+ with standard NaOH solution.

Solutions of Cu(II) were prepared by dissolving $CuSO_4·5H_2O$, Baker, A.R., in deionized water. Standardization was carried out by titration with Na_2H_2EDTA, Mallinckrodt, A.R., at pH 7 using Eriochrome Black T (EBT) as an indicator.[5] The indicator was prepared by mixing intimately 1 part EBT per 200 parts NaCl with a mortar and pestle.

Standard dacoma solutions, prepared from pure analyzed dacoma·$^3\!/_2$HBr, were checked by potentiometric pH titration with NaOH.

Solutions of [Cu(dacoma)H_2O]ClO_4 were prepared from the pure solid and analyzed by spectrophotometry using the molar absorptivity of 118 M^{-1} cm^{-1} at 650 nm.

Sodium hydroxide and perchloric acid standards were prepared from 50% NaOH and concentrated $HClO_4$, Baker, A.R., respectively. The NaOH was standardized by titrating dried, weighed amounts of primary standard potassium acid phthalate, Mallinckrodt, A.R., using phenolphthalein as an indicator. The standardized NaOH was then used to titrate $HClO_4$.

All amino acids were used as received. The L-serine was purchased from Sigma, glycine from Eastman and Fisher Scientific, L-aspartic acid, L-alanine, and L-proline from Aldrich, and D-aspartic acid from Nutritional Biochemicals Corporation.

Titrations. All titrations were carried out at constant ionic strength of 0.1262 M $NaClO_4$. A Beckman Research pH meter in conjunction with a Corning Semi-Micro combination electrode having an Ag|AgCl internal reference was employed. To avoid $KClO_4$ precipitation at the electrode interface, the internal filling solution was 4.6 M NaCl. Prior to each titration, the pH meter was standardized at pH 4.01 and 10.00 using Coleman buffer solutions. Each titration was carried out on 4.0-ml samples in a cell thermostated at 25.0 °C. Before beginning the titration, nitrogen gas was bubbled through the solution and then passed over the surface of the solution during the titration to exclude CO_2. NaOH titrant was delivered with a precalibrated micrometer-driven 2.5-ml syringe (Hamilton Gastight no. 1002, 2.5 ml, Reno, Nevada). The micrometer head was purchased from Mitutoyo. Solutions were stirred during and after each addition of titrant but not during a pH measurement.

In determining the formation constant of [Cu(dacoma)(H_2O)]$^+$, the solution to be titrated was prepared from a standard Cu(II) solution and a slight molar excess (ca. 4%) of standard dacoma·$^3\!/_2$HBr solution. Similarly, the formation constant studies for the ternary complexes between [Cu(dacoma)H_2O]$^+$ and amino acids were carried out in the presence of an excess of amino acid varying from 1% for L-aspartic acid to 17% for glycine. The concentrations used for determining the pK_a values for the respective amino acids were identical with those employed in studying ternary complex formation. These initial concentrations were always in the vicinity of 0.01 M.

Calculations. Measured pH values were converted to hydrogen ion concentration, [H^+],

$$-\log\,[H^+] = pH + \log f_\pm$$

via the logorithm of the mean activity coefficient, $\log f_\pm$, having a value of −0.1121 calculated from the Davies equation,[6]

$$-\log f_\pm = 0.5Z_1Z_2\left[\frac{I^{1/2}}{1+I^{1/2}} - 0.30I\right]$$

where Z_1 and Z_2 are the charges (taken without regard for sign) on the cation and anion of the electrolyte used to maintain the ionic strength, I.

A value of 13.78 was employed for pK_w at 25 °C.[7] The pH and corresponding volume of NaOH titrant added during the titration were incorporated into a computerized curve-fitting routine derived by Dye and Nicely in order to calculate the desired equilibrium constants,[8]

$$[\mathrm{Cu(dacoma)(H_2O)}]^+ \xrightleftharpoons{K_{OH}} H^+ + [\mathrm{Cu(dacoma)(OH)}]$$

$$[\mathrm{Cu(dacoma)}]^+ + X^{-,2-} \xrightleftharpoons{K_X} [\mathrm{Cu(dacoma)(X)}]^{0,-}$$

where X = amino acid

$$Cu^{2+} + \mathrm{dacoma}^- \xrightleftharpoons{K_f} [\mathrm{Cu(dacoma)}]^+$$

In the computation of log K_X, the following species were considered: [Cu(dacoma)(H_2O)]$^+$, [Cu(dacoma)(OH)], [Cu(dacoma)(X)]$^{0,-}$, and the various protonated forms of the respective amino acids, X. The pK_{OH} was calculated from the titration data for the ternary systems. The formation constant for the binary system, K_f, was computed by including [Cu]$^{2+}$, [Cu(dacoma)(H_2O)]$^+$, [H_3dacoma]$^{2+}$, [H_2dacoma]$^+$, and [Hdacoma] in the calculations. For each data set the deviation between calculated and experimental volumes of titrant was minimized.

Physical Measurements and Instrumentation. Visible and near-infrared absorption spectra were recorded using a Cary Model 14 spectrophotometer. The circular dichroism spectra were obtained with a Jasco Model ORD/UV-5 with the Sproul Scientific SS 20 CD modification. Periodically the calibration of the CD was checked with a standard *d*-10-camphorsulfonic acid solution. A value of $\Delta\epsilon = 2.25$ was used for Eastman *d*-10-camphorsulfonic acid dried over P_2O_5 at 80 °C for several days.[9] All measurements were made using glass-stoppered 1-cm cells. Concentrations of the order of 5×10^{-3} M were employed for visible absorption and CD measurements.

X-Ray powder patterns were obtained using Cu Kα radiation. Magnetic susceptibility measurements were carried out by the Faraday technique using a Cahn RG automatic electrobalance and a Varian V4005 electromagnet. Infrared solution spectra (D_2O) were recorded on a Beckman IR 18-A spectrophotometer. All elemental analyses were performed by D. Harsh, Department of Chemistry, University of Idaho, Moscow, Idaho.

Preparation of 1,5-Diazacyclooctane-*N*-monoacetate Sesquihydrobromide, dacoma·3/2HBr. 1,5-Diazacyclooctane (daco) was prepared by the method of Buhle et al.[10] and isolated as the dihydrobromide, daco·2HBr.[11]

A stirred solution of 6.95 g (0.0500 mol) of bromoacetic acid in 25 ml of water, cooled in an ice-acetone bath, was neutralized slowly by dropwise addition of 2.10 g (0.0500 mol) of $LiOH·H_2O$ in 25 ml of water at such a rate that the temperature did not exceed 10 °C. Likewise, a solution of 13.80 g (0.0500 mol) of daco·2HBr in 25 ml of water in a two- or three-necked round-bottom flask, cooled in ice-acetone, was neutralized by dropwise addition of 4.2 g (0.10 mol) of $LiOH·H_2O$ in 25 ml of water. The bromoacetate solution was then added dropwise to the stirred daco solution maintaining the temperature below 10 °C followed by dropwise addition of 2.10 g (0.0500 mol) of $LiOH·H_2O$ in 25 ml of water. The flask was stoppered and stirred at room temperature (ca. 25 °C) for 2–3 days. The solution was then extracted with three 50-ml portions of methylene chloride to remove unreacted daco. Any dacoda was removed as Ba(dacoda) by addition of 2–3 ml of 1 M $BaBr_2$ solution followed by filtration of the white solid after stirring for ca. 1 h. The solution was neutralized with 48% HBr and concentrated in a rotary evaporator to ca. 20 ml.

The ligand was then isolated and desalted by gel permeation chromatography. The solution was loaded onto a column (94 × 4.5 cm) of Sephadex G-15 or G-10. During elution of the column with chloroform-saturated water, a light yellow band separated roughly into two bands. Just prior to elution of the first yellow band (ca. 3.5 h on G-15, and 2.5 h on G-10), fractions of 15–20 ml were taken for 1 to 1.5 h. A series of test tubes containing 3 ml of $CuCl_2$ (ca. 5 g/100 ml) was prepared and 2 drops of each fraction added to individual test tubes. Formation of a deep blue copper complex indicated presence of an amine. Two such constituents were identified in the eluate, corresponding roughly to the two yellow bands. Fractions corresponding to the two constituents were combined to give two solutions and evaporated to ca. 10 ml. Each solution was then adjusted to a pH of 1.5–2.0 with 48% HBr and evaporated under an air stream. The first eluted solution dried to a glaze. However, the second solution yielded crystals of varying shades of yellow (depending on impurities). The first band was not identified but could have been dacoda. Recrystallization by dissolution in a minimum amount of water at room temperature together with treatment with decolorizing charcoal followed by evaporation yielded colorless crystals which were washed with a little water and air-dried. Additional crystals were obtained by similar treatment of the filtrates. Depending upon the pH at which crystallization occurred, product with either 1.5 or 2 hydrobromides of crystallization was obtained. The composition can be determined either by elemental analysis or, more rapidly, by potentiometric pH titration with NaOH. Anal. Calcd for $C_8H_{16}N_2O_2·1.5HBr$: C, 32.73; H, 6.01; N, 9.54. Found: C, 32.69; H, 6.04; N, 9.25. Calcd for $C_8H_{16}N_2O_2·2HBr$: C, 27.29; H, 5.72; N, 7.96. Found: C, 27.33; H, 5.64; N, 7.89.

Preparation of dacoma Complexes. (a) Synthesis of 1,5-diazacyclooctane-*N*-monoacetato(monoaqua)copper(II) perchlorate, [Cu(dacoma)(H₂O)]ClO₄. A mixture of 0.452 g (1.35 mmol) of dacoma·2HBr and 0.561 g (2.71 mmol) of $AgClO_4$ dissolved in 10 ml of water was stirred for several minutes. After removal of the AgBr precipitate by filtration, 0.501 g (1.35 mmol) of $Cu(ClO_4)_2·6H_2O$ was added to the above filtrate resulting in a deep blue solution and a large reduction in pH. Addition of approximately 0.1 N NaOH to a pH near 7 produced a more intensely blue solution. Any excess bromide ion was precipitated by adding 1 M $AgClO_4$ in a dropwise fashion. Immediately after filtration of the AgBr, the volume of the solution was reduced in vacuo until deep blue crystals of $[Cu(dacoma)(H_2O)]ClO_4$ were obtained. The crystals were isolated by filtration and air-dried, and the filtrate was further reduced in volume to obtain a second crop of crystals. Recrystallization was effected from water. Anal. Calcd for $[Cu(C_8H_{15}N_2O_2)H_2O]ClO_4$: C, 27.28; H, 4.86; N, 7.95. Found: C, 27.41; H, 4.73; N, 7.76.

Table I. Magnetic Data for dacoma and Selected dacoda Complexes

Complex	$10^6\chi_g$(20 °C) ± s	μ_{eff}, μ_B
$[Ni(dacoma)(H_2O)_2]ClO_4$	12.54 ± 0.09	3.28
$[Cu(dacoma)(H_2O)]ClO_4$	4.27 ± 0.02	1.88
$[Ni(dacoda)(H_2O)]·2H_2O$[2]	13.09 ± 0.07	3.30
$[Cu(dacoda)]·3H_2O$[2]	3.94 ± 0.05	1.90

(b) Synthesis of 1,5-Diazacyclooctane-*N*-monoacetato(diaqua)zinc(II) Perchlorate, [Zn(dacoma)(H₂O)₂]ClO₄. The preparative procedure used was similar to that utilized for the copper(II) complex except that 0.509 g (1.52 mmol) of dacoma·2HBr, 0.599 g (3.04 mmol) of $AgClO_4$, and 0.567 g (1.52 mmol) of $Zn(ClO_4)_2·6H_2O$ were used. The pH reduction noted upon addition of solid $Zn(ClO_4)_2·6H_2O$ was small when compared to the corresponding change observed on addition of $Cu(ClO_4)_2·6H_2O$. Adjustments in pH were made with 1 M LiOH. The complex was isolated as transparent, colorless crystals. Anal. Calcd for $[Zn(C_8H_{15}N_2O_2)(H_2O)_2]ClO_4$: C, 25.82; H, 5.16; N, 7.53. Found: C, 26.11; H, 4.97; N, 7.38.

(c) Synthesis of 1,5-Diazacyclooctane-*N*-monoacetato(diaqua)nickel(II) Perchlorate, [Ni(dacoma)(H₂O)₂]ClO₄. To 0.295 g (1.01 mmol) of dacoma·3/2HBr, 10 ml (1.00 mmol) of 0.100 M $Ni(NO_3)_2$ solution prepared from $Ni(NO_3)_2·6H_2O$ was added with stirring. The acidic, pale green solution was neutralized with 1 M LiOH. As the pH was raised above 7, the solution became dark green with some accompanying precipitation of pale green $Ni(OH)_2$. Two milliliters of 0.631 M $NaClO_4$ were then added to provide an excess of perchlorate ion. After removal of $Ni(OH)_2$ by filtration, the solution was evaporated under vacuum overnight which resulted in the formation of dark green platelets which were removed by filtration and air-dried. Anal. Calcd for $[Ni(C_8H_{15}N_2O_2)(H_2O)_2]ClO_4$: C, 26.29; H, 5.25; N, 7.67. Found: C, 26.02; H, 5.12; N, 7.54.

Results and Discussion

Characterization of 1,5-Diazacyclooctane-*N*-monoacetic Acid and Its Complexes. The negative logarithms of the acidity constants (pK_a) for dacoma are pK_1 = 1.69 ± 0.01, pK_2 = 5.18 ± 0.01, and pK_3 = 11.75 ± 0.01 where pK_1 corresponds to ionization of the protonated acetate carboxylate group, and pK_2 and pK_3 refer to ionization of the protonated nitrogen atoms in the eight-membered ring of dacoma. The corresponding pK_a's for dacoda are (pK_1 too small to be determined) p$K_2 \simeq 2.00$, pK_3 = 4.80 ± 0.05, and pK_4 = 11.5 ± 0.1 at 25 °C in 0.1 M $NaClO_4$.[12] The Cu(II)-dacoma complex has a formation constant log K_f = 15.28 ± 0.05. An inflection point is found in the binary system corresponding to the addition of 2.5 mol of base per mole of Cu(II), preceded by a relatively low pH buffer zone.

Both the gram susceptibility and the magnetic moment at 293 K for the Ni(II)- and Cu(II)-dacoma complexes are reported in Table I. As can be seen from a comparison with the magnetic moments determined previously for the Ni(II)- and Cu(II)-dacoda complexes, these analogous compounds have very similar solid state magnetic moments. As previously noted neither of the magnetic moments is particularly diagnostic of a five-coordinate geometry.[2]

X-Ray powder patterns indicated that $[Ni(dacoma)(H_2O)_2]ClO_4$ and $[Zn(dacoma)(H_2O)_2]ClO_4$ have isomorphous structures. Averill et al. found that the Co(II), Ni(II), and Zn(II) complexes with dacoda were isomorphous but the corresponding Cu(II) complex was not.[2] This difference is most likely due to elongation of the Cu–H_2O bond in the Cu(II) complex, Figure 1. Whereas pK_a's for the axially bound water

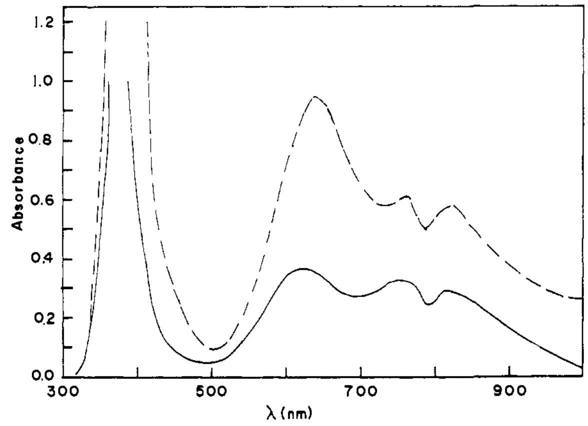


Figure 2. Aqueous solution absorption spectra of [Ni(dacoda)(H_2O)], —, and [Ni(dacoma)$(H_2O)_2$]$^+$, - -.

molecule in the dacoda complexes of Co(II), Ni(II), and Zn(II) could be readily determined, the pK_a of the axially coordinated water molecule in the Cu(II) complex is greater than 13 reflecting the weak interaction of the water molecule with Cu(II)-dacoda.[12] Since two cis sites are still available for ligation in dacoma complexes, coordination of two water molecules is possible. Unfortunately, the inherent instability of the Ni(II) and Zn(II) complexes in aqueous solution precluded determination of the pK_a values by potentiometric or spectrophotometric techniques. On the other hand the stability of the corresponding Cu(II) complex permitted the detection of an ionizable water molecule with pK_{OH} of 9.44 ± 0.07 as calculated from potentiometric data. An inflection point is apparent in the titration of [Cu(dacoma)(H_2O)]$^+$ with base. The water molecule is expected to be in the remaining planar position, a ligating site not available to water in the corresponding dacoda complex, Figure 1. The visible absorption spectrum shifted to higher energy and decreased slightly in intensity as base was added which is consistent with the ionization of an equatorially coordinated water molecule.[13] However, this system did not exhibit isosbestic behavior. Any axial solvent interaction would be weak.

The solution electronic absorption spectrum of [Ni(dacoma)$(H_2O)_2$]ClO_4 is very similar in both band position and relative intensities to that found for [Ni(dacoda)H_2O]·$2H_2O$, Figure 2. A square pyramidal geometry for the latter complex in the solid state was determined by an x-ray crystal study,[3] and good agreement between solid and solution state spectra confirmed this geometry in solution.[2] Hence, due to the close similarity between the solution visible absorption spectra of [Ni(dacoda)(H_2O)] and [Ni(dacoma)$(H_2O)_2$]$^+$, a five-coordinate, square pyramidal structure is proposed for the latter, Figure 1. Since powder patterns suggest that the Ni(II)- and Zn(II)-dacoma complexes are isomorphous, a square pyramidal structure is also quite probable for the Zn(II) compound.

Although the visible absorption spectra of [Ni(dacoda)(H_2O)] and [Ni(dacoma)$(H_2O)_2$]$^+$ are quite similar, the solution visible absorption spectrum of Cu(II)-dacoma is distinctly red-shifted compared to the Cu(II)-dacoda complex, Figure 3. Even though the set of donor atoms is similar in both instances, the quadridentate dacoda provides a stronger ligand field in the square plane for the Cu(II) than the tridentate dacoma. As Hopgood and Angelici reported earlier for a series of ternary complexes of amino acids and amino acid esters with Ni(II)- and Cu(II)-NTA (NTA = nitrilotriacetate), the principal absorption band, ν_{Cu}, of Cu(II) complexes is remarkably sensitive to donor atom variations while the lowest energy band, ν_{Ni}, of the corresponding Ni(II) complexes is relatively insensitive to such changes.[13] The molar absorptivity for the Cu(II)-dacoma complex is appreciably lower than for Cu(II)-dacoda, reflecting possibly reduced ring strain as well. The infrared solution spectrum shows the presence of a fully coordinated acetate group (1610 cm^{-1})[2] for [Cu(dacoma)-H_2O]$^+$ above pH 4.

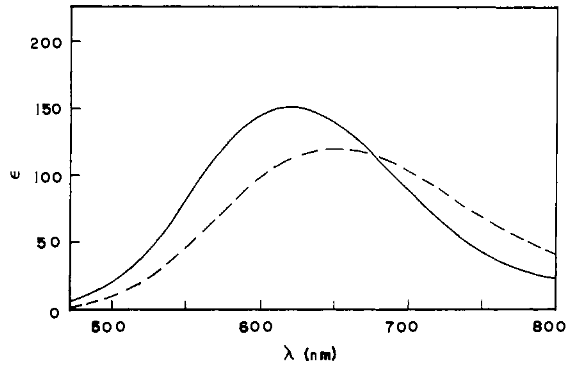


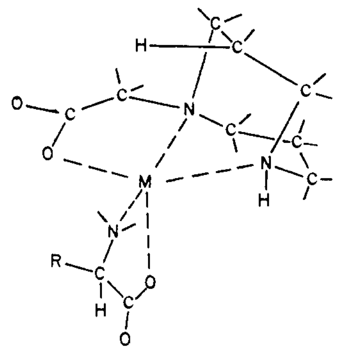
Figure 3. Aqueous solution absorption spectra of [Cu(dacoda)], —, and [Cu(dacoma)(H_2O)]$^+$, - -.

Table II. Circular Dichroism Data for Ternary Complexes of Amino Acids with Copper(II)-1,5-Diazacyclooctane-*N*-monoacetate

Amino acid	$\Delta\epsilon$ (λ_{max})	$\Delta\epsilon$ (λ_{max})	pH, max intens
L-ala	+0.151 (645)	−0.033 (543)	9.65
L-asp	+0.122 (660)	−0.057 (555)	9.60
L-pro	+0.073 (685)	−0.049 (585)	9.46-10.01
L-ser	+0.138 (625)	−0.029 (534)	9.83

Interaction of Amino Acids with Cu(II)-dacoma. Since dacoma is restricted to planar coordination and is expected to block coordination along one of the axial sites, Figure 1, the ligation sites available to a bidentate ligand are well defined in contrast to complexes involving flexible multidentate chelating agents. Although an unsymmetrical bidentate ligand such as an amino acid could coordinate to [Cu(dacoma)-(H_2O)]$^+$ in two distinct modes, the most probable mode is that of an equatorially coordinated amino nitrogen and apically coordinated carboxylate oxygen illustrated in Figure 4. A pseudo-plane of symmetry exists with respect to the chelate ring distribution of dacoma and the amino acid. Thus, the primary source of metal ion-associated optical activity is expected to be that which arises from the interaction of the asymmetric amino acid center with the ligand field transitions, the so-called vicinal effect. The magnitude of the circular dichroism (CD) $\Delta\epsilon$ values reported here are typical of vicinal effects found in Cu(II)-amino acid complexes.[14]

The interaction of optically active amino acids with [Cu(dacoma)(H_2O)]$^+$ resulted in a biphasal, pH dependent CD spectrum characterized by a long wavelength band with a positive maximum between 600 and 700 nm and a shorter wavelength negative band located between 500 and 600 nm, Figure 5. The rotatory strength, as measured by the area under the CD bands between 450 and 700 nm, was strongly net positive in every case with the exception of L-proline where the negative and positive bands were nearly equal in magnitude, Table II.[15] For all amino acids there was no observable CD spectrum up to a pH of 6. The intensity of both the positive and negative bands increased when the pH was raised, maximizing between pH 9.5 and 10, as illustrated for [Cu(dacoma)(L-ala)] in Figure 6. Above pH 10 the intensity of each band diminished appreciably. A corresponding change in the electronic absorption spectrum was observed over the same pH range. A red shift and an increase in intensity of the absorption spectrum



M(dacoma)(L-amino acid)

Figure 4. Proposed stereochemistry of [M(dacoma)(L-amino acid)].

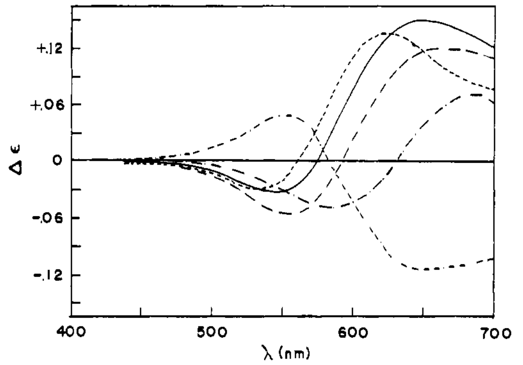


Figure 5. Circular dichroism spectra of various amino acid complexes with Cu(II)-dacoma: L-asp, – –; D-asp, • – – •; L-pro, – • – •; L-ser, - - -; L-ala, —.

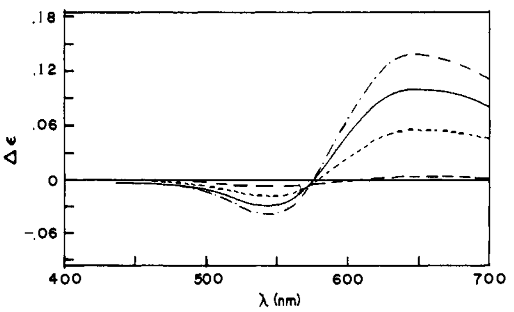


Figure 6. pH-Dependent circular dichroism spectra for L-alanine complexes with Cu(II)-dacoma: pH 6.11, – –; pH 7.48, - - -; pH 9.20, • – • –; pH 10.79, —.

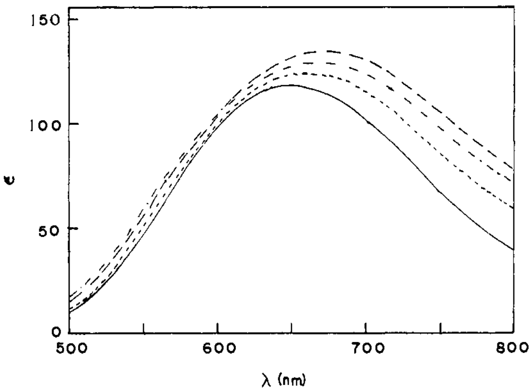


Figure 7. pH-Dependent absorption spectra for L-alanine complexes with Cu(II)-dacoma: pH 5.30, —; pH 7.79, - - -; pH 9.25, – –; pH 11.04, • – • –.

Table III. Amino Acid Ionization Constants (pK_a) and Formation Constants (log K_x) for Ternary Complexes of Various Amino Acids with Copper(II)-1,5-Diazacyclooctane-*N*-monoacetate at 25 °C and 0.1262 M $NaClO_4$

Amino acid	pK_a	Log K_x
gly	9.58 ± 0.01	4.63 ± 0.03
L-ala	9.75 ± 0.01	4.42 ± 0.02
L-asp	9.60 ± 0.01 3.53 ± 0.02	4.84 ± 0.03
D-asp	9.67 ± 0.01 3.51 ± 0.01	4.86 ± 0.06
L-pro	10.49 ± 0.01	4.68 ± 0.02
L-ser	9.15 ± 0.05	4.37 ± 0.07

was also observed upon addition of base to [Cu(dacoma)-$(H_2O)]^+$ and amino acid as illustrated for L-alanine in Figure 7. The red shift attained a maximum on the order of 25 nm at pH 10. These spectral changes, particularly the appearance of a circular dichroism spectrum, mark the formation of the ternary amino acid complex.

The potentiometric pH titration curves for the amino acids considered in this investigation exhibited a lower pH buffer zone in the presence of $[Cu(dacoma)(H_2O)]^+$, relative to its absence, due to coordination of the amino acid, as expected. There is not a large variation among the formation constants for the ternary complexes. Aspartic acid forms the strongest ternary complexes and L-serine the weakest with $[Cu(dacoma)(H_2O)]^+$, Table III.

It could be argued that the amino acid might be coordinated in the plane of Cu(II)-dacoma as a monodentate. However, several studies involving the coordination of optically active ligands as mono- and bidentates argue for chelation of the amino acid as opposed to complexation as a monodentate ligand in the Cu(II)-dacoma complexes. The very small $\Delta\epsilon$ value (+0.005) reported for coordination of L-lactic acid to $[Cu(dien)H_2O]^{2+}$ (dien = diethylenetriamine) as a monodentate through its carboxylate group should be noted.[16] A small, positive $\Delta\epsilon$ value for coordination of an optically active unidentate ligand to the cobalt(III) ion has been reported.[17] It has also been demonstrated for the tetraammine complex of Co(III) containing chelated *d*-tartrate ion that the observed rotational strength is larger than that found in pentaammine Co(III) containing unidentate *d*-tartrate ion.[18] Thus, the presence of a unidentate optically active ligand in a complex generates a weak CD spectrum in contrast to the bidentate, chelated ligand. The $\Delta\epsilon$ values observed for the Cu(II)-amino acid complexes were at least an order of magnitude greater than those reported for optically active ligands coordinated as monodentates.

The well-defined geometry imposed by the tridentate dacoma on a metal ion, and the consequent restriction imposed on the mode of chelation of amino acids, permits a detailed and informative comparison with other ternary amino acid copper complexes involving flexible multidentate chelating agents. A priori it would be expected that the amino group would coordinate in the square plane and the carboxylate in the apical position in Cu(II)-dacoma, Figure 4, since Cu(II) tends to form tetragonal complexes with strong field ligands coordinated in the plane.

A species with equatorially coordinated carboxylate group could form at lower pH where the amino acid amino group is still protonated. However, no circular dichroism spectrum was observed until the pH region was attained where deprotonation and subsequent coordination of the amino group occurs.

Recently, Murakami et al. studied a series of ternary complexes between optically active amino acids and [Cu(dien)-

$(H_2O)]^{2+}$ where the flexible triamine is expected to coordinate in the plane.[16] The visible absorption and CD spectra reported for the interaction of L-alanine and L-valine with [Cu(dien)-$(H_2O)]^{2+}$ are very similar to those observed in this study over the same pH range. In a prior report they presented aqueous (D_2O) infrared evidence for apical coordination of the L-alanine carboxylate group.[19] The asymmetric carbonyl stretching frequency for L-alanine was pH dependent and correlated well with the concentration of apically coordinated carboxylate in the ternary complex as determined by the intensity of the CD spectrum.

The net positive, biphasal CD spectrum observed for the amino acid Cu(II)–dacoma complexes in this study has been shown to occur also in bis(amino acid)–Cu(II) complexes where the amino acid is coordinated as a tridentate ligand through one apical and two in-plane coordination sites. Wilson et al. reported circular dichroism and electronic absorption spectra for bis(amino acid) complexes with Cu(II).[20] As expected the square planar complex, $[Cu(L\text{-}ala)_2]$, exhibits a net negative CD spectrum. However, L-asparagine can function as a tridentate ligand once the β-amide group deprotonates, and the corresponding bis complex with Cu(II) gave a net positive biphasal CD spectrum. In addition, apical coordination displaces the visible absorption band maximum toward longer wavelength as observed in this study (vide infra). Tridentate L-histidine also produces a net positive, biphasal CD spectrum in its two-to-one Cu(II) complex similar to that found for L-asparagine. In this case, the axial coordination sites are occupied by a carboxylate oxygen and an imidazole nitrogen.[21]

Hopgood and Angelici concluded that chelation of α-amino acids to $[Cu(NTA)]^-$ produced ternary complexes with a high degree of tetragonal distortion.[13] They demonstrated that the α-amino acid is chelated to the two cis sites available in the plane rather than binding along the tetragonal axis and the plane. In the former instance a net negative CD spectrum should result as observed for square planar bis(amino acid)-copper(II) complexes and in the latter a net positive, biphasal CD spectrum should be observed as found for [Cu(dacoma)-(amino acid)] in this study. A CD study of $[Cu(NTA)(L\text{-}ala)]^-$ in our laboratory demonstrated a dominant, negative CD band centered at 675 nm ($\Delta\epsilon = -0.03$) confirming Hopgood and Angelici's proposed structure for these ternary complexes.

Making the reasonable assumption that the relative orbital energies are $d_{x^2-y^2} \gg d_{z^2} > d_{xy} > d_{xz}, d_{yz}$,[22] the red shift in the spectra on chelation of the amino acid can be rationalized. Although a planar water is replaced by an amine nitrogen raising the energy of the half empty $d_{x^2-y^2}$ orbital and the d_{xy} orbital, chelation is expected to greatly increase the axial interaction thereby raising the energies of the d_{z^2} and d_{xz}, d_{yz} orbitals. The net effect is to lower the separation between the lower set of orbitals and the $d_{x^2-y^2}$ orbital, resulting in a shift to lower energy for the three expected transitions. Apical coordination by the amino group of the chelated amino acid would most likely give rise to a significantly larger red shift in the visible absorption spectrum relative to that observed for apical carboxylate group coordination.

The circular dichroism spectrum of $[Cu(dacoma)(L\text{-}pro)]^+$ is different from that of the other amino acid ternary complexes. The areas under the positive and negative CD bands were more nearly equal than for the other amino acids, Figure 5. In addition, the area of the positive band was the smallest for any amino acid in this study. Proline is unique in that it contains two potentially asymmetric atoms. Yasui proposed that for L-proline to act as a chelate the nitrogen donor must assume one configuration.[23,24] Chelation is expected only when the asymmetric carbon and nitrogen are in an *S,S* or *R,R*[25] configuration. An examination of molecular models for [Cu(dacoma)(L-pro)] confirmed Yasui's suggestion. Since an asymmetric nitrogen atom is directly coordinated to Cu(II), it could very well influence the observed optical activity to a greater extent than an asymmetric carbon atom removed from the metal chromophore by at least one atom. It has been demonstrated that coordinated asymmetric nitrogens make a significant contribution to the observed optical activity.[26] Furthermore, Yasui postulated that the vicinal effect due to the nitrogen atom was opposite to that attributed to the carbon atom. This correlates well with the small area under the positive CD band observed for the dacoma complex with L-proline. Hawkins and Wong found that $[Cu(L\text{-}pro)_2]$ gave a net positive CD spectrum in water in contrast to the results obtained for other square planar bis(amino acid) complexes of Cu(II).[14] They too invoked Yasui's proposal to explain their data.

Murakami et al. attribute the decreased CD intensity for both positive and negative bands at higher pH in [Cu(dien)-(amino acid)]$^+$ to apical coordination of hydroxide and displacement of the apical carboxylate group.[16] As the CD spectrum diminished the absorption spectrum blue shifted and decreased in intensity. The blue shift is consistent with removal of the chelate-induced strong axial perturbation (vide supra). We also found analogous spectral changes in this pH range, but competition of hydroxide ion for the in-plane coordination site with the α-amino group could equally well account for the observed changes by displacement of the amino acid from the ternary complex. The presence of an ionizable water molecule coordinated in the square plane as in the case of $[Cu(dacoma)H_2O]^+$ or $[Cu(dien)H_2O]^{2+}$ ($pK_{OH} = 8.62$)[27] makes this latter alternative feasible.

Summary

We have shown that amino acids chelate to [Cu(dacoma)-$H_2O]^+$ through a planar amino nitrogen and an apically coordinated carboxylate group. For these ternary complexes and other Cu(II)–amino acid complexes previously reported it would appear that a net positive, biphasal CD spectrum is diagnostic of this binding mode. The relatively rigid five-coordinate geometry imposed on metal ions by dacoma permits a concise structural analysis of the ternary complexes with amino acids in aqueous solution, an advantage not often present in other ternary systems. The knowledge derived from characterization of the dacoma complexes should be of assistance in determining the donor groups and geometry about a metal ion in the active site of metalloenzymes, as has already been demonstrated by Rosenberg et al. in their use of the dacoma analogue, dacoda, for their study of the metal ion environment in carboxypeptidase A.[4]

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Sulfur-Bridged Binuclear Iron(II) Complexes. Effect of Ligand Constraints on Their Physical Properties; Reactions with Carbon Monoxide and Alkyl Isocyanides

Kenneth D. Karlin and Stephen J. Lippard*

Contribution from the Department of Chemistry, Columbia University, New York, New York 10027.

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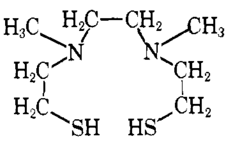
Abstract: The synthesis of the sulfur-bridged iron(II) complexes $(FeL)_2$ and $(FeL')_2$ is described. Differences in the steric constraints of the tetradentate N_2S_2 donor ligands *N,N'*-dimethyl-*N,N'*-bis(2-mercaptoethyl)ethylenediamine (LH_2) and *N,N'*-dimethyl-*N,N'*-bis(2-mercaptoethyl)-1,3-propanediamine ($L'H_2$) are reflected in the physical properties of the complexes. Magnetic and Mössbauer studies over a temperature range show both $(FeL)_2$ and $(FeL')_2$ to contain high spin iron(II) ($S = 2$) atoms which are antiferromagnetically coupled leading to an overall $S = 0$ ground state. The extent of coupling is substantially greater in $(FeL)_2$, however, which has a more constrained geometry and a shorter nonbonded iron–iron distance. The reversible reaction of $(FeL)_2$ with carbon monoxide to give crystalline $FeL(CO)_2$ is described. Analogous chemistry with alkyl isocyanides leads to $FeL(CNR)_2$, $R = CH_3$ or t-C_4H_9. Under the same conditions, $(FeL')_2$ does not react with these ligands. The similarity between the physical and chemical properties of $(FeL)_2$ and $[Fe(cys)_2]_n$, cys $= {}^-SCH_2CH(NH_3{}^+)(CO_2{}^-)$, is noted.

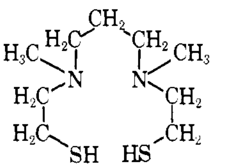
There has been much recent interest in the synthesis and characterization of iron-sulfur complexes.[1,2] The attention given to this area by coordination chemists stems largely from the recognition of redox active iron–sulfur cores in a wide variety of proteins.[3-7] Many of these proteins embody nFe-nS* units that release hydrogen sulfide upon mild acidification. Analogues of the iron-sulfur protein cores for $n = 2$ and $n = 4$ have been prepared and well characterized.[2] Other iron-sulfur proteins are known or thought to contain $Fe\text{-}SCH_2R$ linkages, in which the thiolate donor ligand is cysteine.[3,4] Iron cysteinate complexes have been studied, but definitive structural information is lacking.[8-13]

The studies described in the present series of papers[14-16] were undertaken with the objectives of (1) synthesizing iron sulfur complexes in which the sulfur donor ligand is saturated (i.e., $R\text{-}CH_2\text{-}S^-$) and with no additional stabilizing π acid ligands such as CO, $C_5H_5{}^-$, or a porphyrin ring; (2) producing high spin iron centers and, in the case of sulfur-bridged compounds, evaluating the magnetic exchange between the iron atoms; and (3) examining the effects of ligand constraints on the physical properties and chemical reactions of the iron complexes. The rationale underlying these objectives is described in part elsewhere.[1]

To achieve these aims, the ligands LH_2 and $L'H_2$ were synthesized. Geometric considerations suggested that high-spin complexes of L would be much more strained than those of L′, an expectation verified by subsequent x-ray structural investigations of iron and zinc complexes of these ligands.[17,18] In particular, the long iron–nitrogen bond lengths (2.2–2.35 Å) in high spin iron complexes of L produce angular strain in the five-membered ethylenediamine chelate ring of $(FeL)_2$ that is relieved in the analogous six-membered 1,3-propanediamine chelate ring of $(FeL')_2$ (Figure 1).[18]



LH_2



$L'H_2$

In the present paper we describe an improved synthesis of the ligands and their iron(II) complexes, magnetic and Mössbauer data that fix the oxidation and spin states, and reactions with carbon monoxide and alkyl isocyanides. Three subsequent papers report the results of a detailed magnetic analysis of $(FeL)_2$ and $(FeL')_2$,[14] the oxidative addition reaction of nitrosonium ion with $(FeL)_2$ and $(CoL)_2$ and the x-ray crystal structures of the products,[15] and the synthesis of mononuclear iron nitrosyl complexes together with the molecular structure determination of FeL(NO).[16]