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Transamination in the 2-Formylpyridine–Amino Acid–Metal Ion Systems. Stereochemistry of Zinc(II) and Copper(II) Complexes of *N*-(2-Pyridylmethylidene)amino Acids[1]

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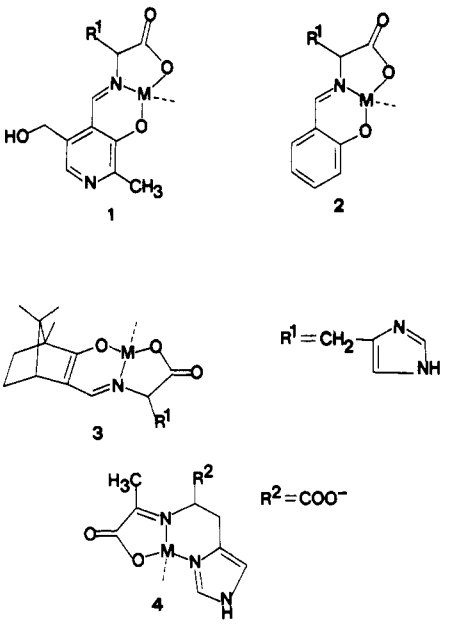
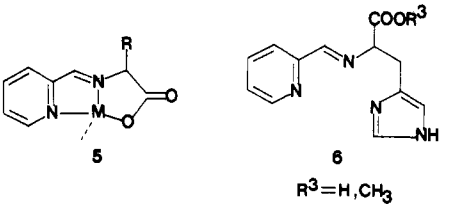
Zinc(II) or copper(II) ions promote the formation of the Schiff base between 2-formylpyridine and amino acids in neutral aqueous solution. The resulting aldimine complexes are unstable when the amino acids carry nonpolar side chains and undergo an easy aldimine → ketimine tautomerization, possibly flanked by other reactions that lead to complex mixtures of products. The reaction path has been established in the case of zinc(II) complexes, where aldimine formation and its subsequent decomposition can be followed through NMR, UV, and CD spectroscopy. The copper(II) systems are apparently more reactive than their zinc(II) analogues, since very little accumulation of the aldimine complex occurs in solution. The special reactivity of these vitamin B_6 model systems is ascribed to the formal positive charge of the complexes and the presence of two fused five-membered chelate rings. When the amino acid is histidine, the zinc(II)- and copper(II)–aldimine complexes are more stable and can be isolated in reasonably pure form. The relative stability of these histidine complexes is due to the adoption of a histamine-like chelation mode by the amino acid residue. This involves adjacent five- and six-membered chelate rings. The stereochemistry of these systems is discussed in relation to that of the other vitamin B_6 model systems.

Introduction

In previous papers we described the stereochemical properties of a variety of metal complexes of Schiff bases of amino acids derived from pyridoxal, salicylaldehyde, (+)-(hydroxymethylene)camphor, and pyruvic acid.[2-5] These systems have been considered for a long time as models for pyridoxal catalysis since they often reproduce some of the transformations of amino acids effected by pyridoxal-dependent enzymes.[6] Of particular importance are the chelates containing histidine residues since the rigid polydentate Schiff base ligands provide a useful frame to establish correlations between spectral properties of the complexes and mode of binding of the histidine residue. This is not usually possible for simple histidine complexes, where this potentially tridentate amino acid tends to form species with mixed chelation modes.[7,8] In the Schiff base chelates derived from histidine the glycine-like and histamine-like binding modes of the amino acid residue can be easily distinguished by circular dichroism.[2-4] The preference for either mode is apparently determined by the chelate ring type of the fused carbonyl residue, as it was found that in complexes derived from pyridoxal (**1**), salicylaldehyde (**2**), or (+)-(hydroxymethylene)camphor (**3**) the histidine residue chelates glycine-like, while in complexes derived from pyruvate (**4**) the histidine residue is bound histamine-like. These results



can be of some importance also in the coordination chemistry of histidine-containing peptides, where deprotonation of amide groups often leads to chelate ring systems similar to those of **1–4**, and need therefore to be confirmed for a larger set of compounds. The present investigation was initially aimed at determining the stereochemical properties of zinc(II) and copper(II) complexes of 2-formylpyridine imines with a series of L-amino acids (**5**) (including histidine), since Schiff base



chelates derived from 2-formylpyridine had never been reported before. Rather surprisingly we found that the systems derived from amino acids carrying nonpolar side chains are unstable and only complexes derived from imines of histidine or histidine methyl ester (**6**) could be isolated in reasonable purity. The reactivity of the systems 2-formylpyridine–L-amino acid–zinc(II) was therefore investigated in some detail to

(1) Coordination Modes of Histidine. 6. For part 5 see ref 7e.
(2) (a) Casella, L.; Gullotti, M. *J. Am. Chem. Soc.* **1981**, *103*, 6338–6347. (b) Casella, L.; Gullotti, M. *Ibid.* **1983**, *105*, 803–809.
(3) (a) Casella, L.; Gullotti, M. *Inorg. Chem.* **1981**, *20*, 1306–1308. (b) Casella, L.; Gullotti, M.; Rockenbauer, A., submitted for publication.
(4) Casella, L.; Gullotti, M.; Pacchioni, G. *J. Am. Chem. Soc.* **1982**, *104*, 2386–2396.
(5) (a) Casella, L.; Gullotti, M.; Pasini, A.; Rockenbauer, A. *Inorg. Chem.* **1979**, *18*, 2825–2835. (b) Casella, L.; Gullotti, M.; Pasini, A.; Visca, M. *Inorg. Chim. Acta* **1976**, *19*, L9–L13. (c) Casella, L.; Gullotti, M.; Pasini, A.; Ciani, G.; Manassero, M.; Sironi, A. *Ibid.* **1978**, *26*, L1–L2.
(6) (a) Snell, E. E., Braunstein, A. E., Severin, E. S., Torchinsky, Yu. M., Eds. "Pyridoxal Catalysis: Enzymes and Model Systems"; Interscience: New York, 1968. (b) Martell, A. E. *Met. Ions Biol. Syst.* **1973**, *2*, 208–263. (c) Holm, R. H. In "Inorganic Biochemistry"; Eichhorn, G. L., Ed.; Elsevier: New York, 1973; pp 1137–1167. (d) Pasini, A.; Casella, L. *J. Inorg. Nucl. Chem.* **1974**, *36*, 2133–2144. (e) Phipps, D. A. *J. Mol. Catal.* **1979**, *5*, 81–107.
(7) (a) Led, J. J.; Grant, D. M. *J. Am. Chem. Soc.* **1977**, *99*, 5845–5858. (b) Itabashi, M.; Itoh, K. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3131–3137. (c) Goodman, B. A.; McPhail, D. B.; Powell, H. K. J. *J. Chem. Soc., Dalton Trans.* **1981**, 822–827. (d) Hoggard, P. E. *Inorg. Chem.* **1981**, *20*, 415–420. (e) Casella, L.; Gullotti, M. *Ibid.* **1983**, *22*, 242–249. (f) Casella, L.; Gullotti, M. *J. Inorg. Biochem.* **1983**, *18*, 19–31.
(8) (a) Sundberg, R. J.; Martin, R. B. *Chem. Rev.* **1974**, *74*, 471–517. (b) Chow, S. T.; McAuliffe, C. A. *Prog. Inorg. Chem.* **1975**, *19*, 51–103. (c) Martin, R. B. *Met. Ions Biol. Syst.* **1979**, *9*, 2–39.

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establish the nature of the reaction products. These results are also presented here and discussed in relation to the reactivity of the other vitamin B_6 model systems.

Experimental Section

All reagents were of highest grade commercially available and used as received. D-Histidine methyl ester dihydrochloride was prepared as described previously.[4] Elemental analyses were from the microanalytical laboratory of the University of Milan. The proton NMR spectra were obtained with a Bruker WP-80 spectrometer operating at 80 MHz and using a pulsed Fourier transform technique. The internal reference standard used in D_2O solutions was sodium 3-(trimethylsilyl)propionate-d_4. The electronic, circular dichroism, and infrared spectra were recorded on a Beckman DK-2A, a Jobin-Yvonne Mark III, and a Nicolet MX-1 instrument, respectively. The EPR spectra were obtained on a Varian E-109 spectrometer operating at X-band frequencies. The magnetic moments of the copper(II) complexes were determined at 295 K with a Cahn 1000 electrobalance. Tetrakis(thiocyanato)mercury cobaltate was used as a susceptibility standard, and the diamagnetic corrections were estimated by measurements on the corresponding zinc(II) complexes and with use of the appropriate Pascal constants for the anions involved.[9]

Preparation of the Complexes.[10] The preparation of all the copper(II) complexes was carried out under nitrogen to prevent any possible oxidation of the ligands. the zinc(II) and copper(II) complexes derived from L- or D-histidine were obtained according to the following procedure. Equimolar amounts of 2-formylpyridine (2 mmol) and L- or D-histidine were stirred in absolute methanol (25 mL) for about 10 min at room temperature. Then zinc(II) nitrate hexahydrate, or copper(II) perchlorate hexahydrate (2 mmol), and methanolic sodium hydroxide (1.9 mmol) were added with stirring, giving a clear solution. Within a few hours a precipitate of the product formed. This was filtered, washed with small amounts of methanol and water, and dried under vacuum.

To obtain the derivatives of L- or D-histidine methyl ester, we reacted 2-formylpyridine (2 mmol) and free L- or D-histidine methyl ester (2 mmol) in absolute methanol (25 mL) for about 10 min. Then zinc(II) nitrate hexahydrate, or copper(II) perchlorate hexahydrate (2 mmol), was added with stirring. The complex Cu(pyc-D-hisOCH_3)$(ClO_4)_2$ precipitated from the reaction solution, while Zn(pyc-L-hisOCH_3)$(NO_3)_2$ precipitated by concentration to a small volume of the solution and addition of absolute ethanol. These products were filtered, washed with small amounts of methanol and water, and dried under vacuum. To obtain Cu(pyc-L-hisOCH_3)$(ClO_4)_2$, we concentrated the reaction solution to a small volume and chromatographed it on a Sephadex LH-20 column (2.5 × 30 cm, methanol as eluant). The single main fraction was collected and evaporated to dryness under vacuum.

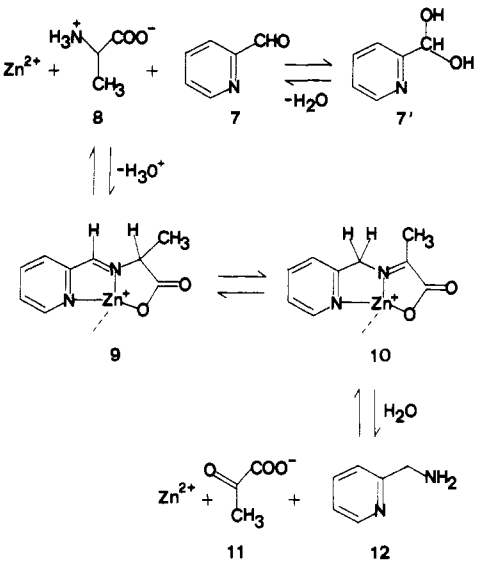
The complex Cu(pyc-L-his′) was obtained by mixing 2-formylpyridine (2 mmol) and L-histidine (2 mmol) in methanol (25 mL) and adding freshly prepared cupric hydroxide (2 mmol) with stirring. A brown precipitate slowly formed. This was filtered, washed with small amounts of methanol and water, and dried under vacuum. Elemental analyses of the zinc and copper complexes are collected in Table I.[11]

For the observation of the CD features of zinc(II) or copper(II) complexes of the 2-formylpyridine Schiff bases of nonpolar L-amino acids we prepared solutions of the metal salt (zinc(II) nitrate or copper(II) perchlorate) (1 mmol), 2-formylpyridine (1 mmol), the amino acid (1 mmol), and sodium hydroxide (1 mmol) in water (10 mL) under nitrogen. These were diluted 1:25 with degassed water immediately before recording of the spectra. The spectral data were collected within a few minutes after preparation of the solutions and are reported in Table V.

Results

The purpose of this investigation was to synthesize zinc(II) and copper(II) complexes of 2-formylpyridine imines with a series of L-amino acids (**5**) including those containing a histidine residue. Repeated preparations of complexes of type **5**, carried out in a variety of (mild) conditions, gave products with unsatisfactory chemical analyses except when the amino acid was histidine or histidine methyl ester. Since the materials isolated in these unsuccessful preparations were often completely optically inactive, we decided to investigate in some detail the reaction between 2-formylpyridine and amino acids in the absence and presence of metal ions to establish whether the special reactivity exhibited by these systems had to be related to complex formation.

Scheme I



The System 2-Formylpyridine–L-Amino Acid–Zinc(II) (1:1:1). Figure 1a shows the proton NMR spectrum of a 0.1 M solution of 2-formylpyridine and L-alanine in D_2O (pD ~5). The singlet signals at δ 9.99 and 6.05 are assigned to the free (**7**) and hdyrated (**7′**) forms of the aldehyde, respectively,[12] while the doublet (δ 1.51) and quartet (δ 3.82) signals are due to free L-alanine (**8**) (Scheme I). Upon addition of an equivalent amount of zinc(II) nitrate to this solution (pD ~5) the spectrum in Figure 1b is obtained. Aldimine formation is easily detected by the appearance of new signals for condensed L-alanine (doublet at δ 1.62 and quartet at δ 4.47, partially obscured by HDO) and for the azomethine proton of **9** (near δ 8.8, under the envelope of aromatic signals), while the free aldehyde proton signal is drastically reduced in intensity. The extent of aldimine formation increases on raising the pD of the solution and is accompanied by an increase in intensity of the resonances due to the azomethine and condensed L-alanine and by a corresponding decrease of the hydrated aldehyde signal near δ 6. At pD ~7, however, a broad signal centered at δ 2.45 appears and progressively increases in intensity with time (Figure 1c). This is accompanied by a reduction of the azomethine signal, the apparent H–D exchange of the α-CH proton of the alanine residue of **9** (resulting in a singlet signal for the methyl group of the Schiff base), and the appearance of a further singlet near δ 1.9. The NMR spectrum of the solution after approximately 3 h at pD ~7 is shown in Figure 1d. For longer reaction times (up to 24 h) the NMR spectra of this neutral solution show only changes in the relative intensities of the individual signals (those related to **9** being mostly affected) with a significant decrease in the overall integrated intensity of the aliphatic signals relative to that of the aromatic signals. The broad peak at δ 2.45 corresponds to the methyl groups of free (**11**) and

(9) Mabbs, F. E.; Machin, D. J. "Magnetism and Transition Metal Complexes"; Chapman and Hall: London, 1974; Chapter 1.

(10) Abbreviations used for the ligands: *N*-(2-pyridylmethylidene)amino acidato anion, pyc-aa; condensed amino acidato anion, aa; alaninate anion, ala; histidinate anion, his; histidine methyl ester, hisOCH_3. The primed symbol his′ refers to the dianionic species containing a deprotonated imidazole ring.

(11) Supplementary material.

(12) Pocker, Y.; Meany, J. E.; Nist, B. J. *J. Phys. Chem.* **1967**, *71*, 4509–4513.

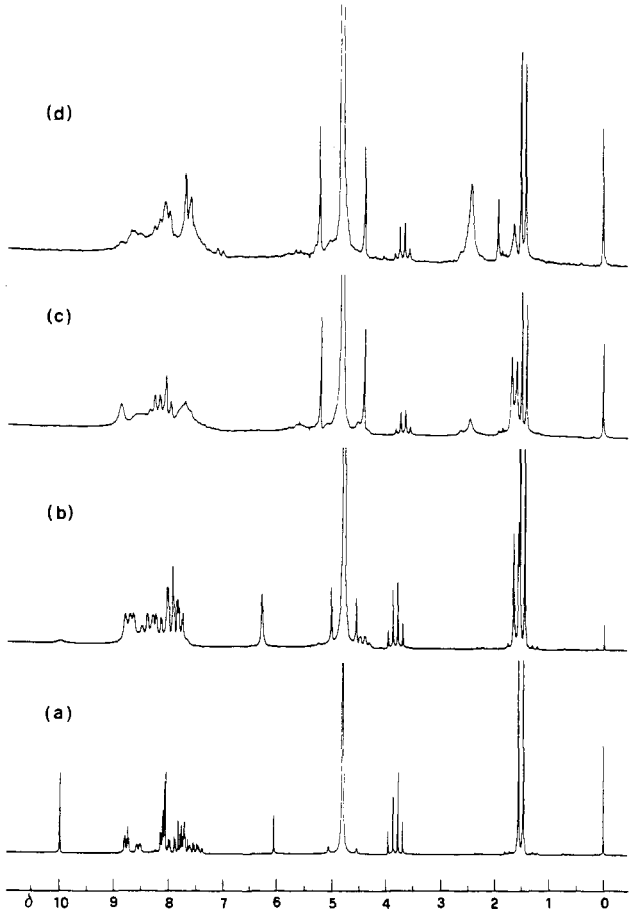


Figure 1. Proton NMR spectra of an equimolar solution of 2-formylpyridine and L-alanine in D_2O (concentration ~0.1 M): (a) after mixing of the reagents; (b) after the addition of an equimolar amount of $Zn(NO_3)_2 \cdot 6H_2O$ (pD ~5); (c) as in (b) at pD ~7; (d) as in (c) after ~3 h.

condensed (**10**) pyruvate residues,[13-15] resulting from the transamination sequence represented by the reaction **9** → **10** (Scheme I). These assignments were confirmed by recording NMR spectra of the system pyruvate–L-alanine–Zn(II) (1:1:1) with the same conditions as those described above. The signal near δ 1.9 may be related to the methyl group of hydrated pyruvate or, more likely, to that of dimeric pyruvate,[13] since its relative intensity seems to increase with time compared to that of the δ 2.45 peak. The lability of pyruvate or pyruvidene methyl groups to H–D exchange[14,15] accounts for the decrease in intensity of their NMR signals on prolonged standing of the solution. The methylene proton signal of the 2-(aminomethyl)pyridine residue of **10** and that of **12** are probably buried under the intense HDO signal. They can be detected as a low-field shoulder on the HDO signal in Figure 1d but occur as a separate broad signal centered near δ 5.1 in the NMR spectra of the products isolated in attempted preparations of Zn(pyc-L-ala)X. The spectra of these impure materials recorded immediately after dissolution in D_2O also contain an intense signal of the pyruvate methyl group, a negligible signal of the pyruvate dimer, and a doublet–quartet pattern typical for free alanine, while the aromatic signals are similar to those in Figure 1d.

Aldimine formation and its subsequent decomposition in the system 2-formylpyridine–L-alanine–zinc(II) can be followed also by electronic and CD spectroscopy. The spectra recorded

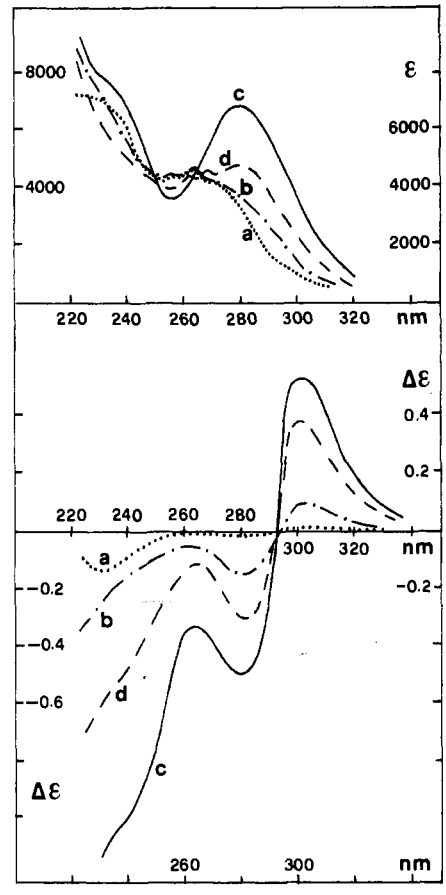


Figure 2. Electronic and CD spectra of an equimolar solution of 2-formylpyridine and L-alanine in water (concentration 0.1 M): (a) after mixing of the reagents (···); (b) after the addition of an equimolar amount of $Zn(NO_3)_2 \cdot 6H_2O$ (pH ~5) (-·-·); (c) as in (b) at pH ~7 (—); (d) as in (c) after ~3 h (---).

after dissolution of 2-formylpyridine and L-alanine (1:1) in water are shown in Figure 2a. The electronic spectrum is essentially that of free and hydrated 2-formylpyridine,[16] while the CD curve shows that the amount of aldimine is negligible. Adding an equivalent amount of zinc(II) nitrate to this solution (pH ~5) produces a shoulder on the low-energy tail of the UV band and significant CD activity between 340 and 260 nm, which can be related to aldimine formation (Figure 2b). When the pH of the solution is raised to ~7, the imine bands clearly develop in the UV (near 280 nm) and CD spectra (positive peak at 300 nm and negative peak at 280 nm), as shown by the curves in Figure 2c. However, all these UV and CD bands undergo a subsequent parallel decrease in intensity with time (~30% after approximately 3 h, Figure 2d) as a result of the aldimine decomposition reactions.

The dramatic changes undergone by the system 2-formylpyridine–L-alanine–zinc(II) are not reproduced by the metal-free system. The NMR and optical spectra of neutral aqueous solutions of 2-formylpyridine and L-alanine show almost negligible aldimine formation even after 24 h. The system 2-formylpyridine–L-valine–zinc(II) (1:1:1) behaves quite similarly to that of L-alanine, although both the transamination reaction[17] and the overall loss of optical activity of the solution occur at a slower rate than in the L-alanine system

(13) Leussing, D.; Standfield, C. K. *J. Am. Chem. Soc.* **1964**, *86*, 2805–2810.
(14) Gansow, O. A.; Holm, R. H. *J. Am. Chem. Soc.* **1968**, *90*, 5629–5631; **1969**, *91*, 5984–5993.
(15) Dempsey, A.; Phipps, D. A. *Inorg. Chim. Acta* **1979**, *36*, L425–L427.
(16) Nakamoto, K.; Martell, A. E. *J. Am. Chem. Soc.* **1959**, *81*, 5857–5863, 5863–5869.
(17) The β-CH proton signal of the α-ketoisovalerate residue (the transamination product of L-valine) occurs as a multiplet centered at δ 3.1 in the NMR spectra of neutral D_2O solutions of 2-formylpyridine–L-valine–zinc(II) (1:1:1). The α-CH and β-CH proton signals of the aldimine complex of L-valine occur at δ 4.23 (doublet) and δ 2.40 (multiplet), respectively.

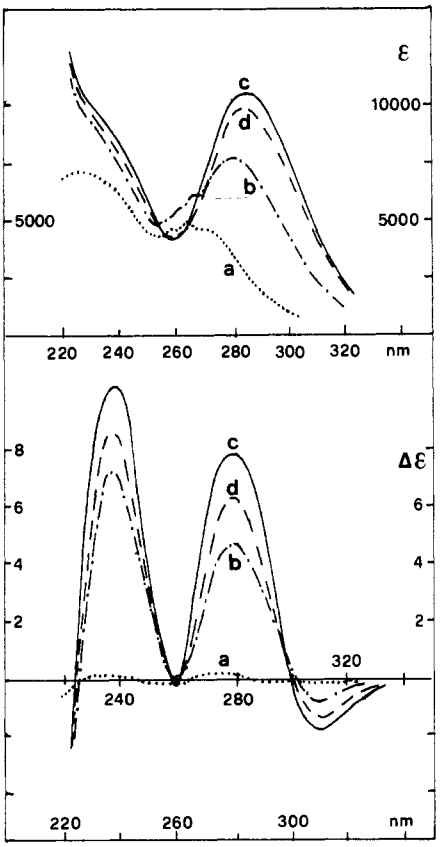


Figure 3. Electronic and CD spectra of an equimolar solution of 2-formylpyridine and L-histidine in water (concentration 0.1 M): (a) after mixing of the reagents (···); (b) after the addition of an equimolar amount of $Zn(NO_3)_2 \cdot 6H_2O$ (pH ~5) (-·-·); (c) as in (b) at pH ~7 (—); (d) as in (c) after ~24 h (---).

(we observed ~20% decrease in the intensity of the UV band at 284 nm and ~30% decrease in the CD activity of the bands at 305 and 288 nm in a neutral 0.1 M aqueous solution of the reagents after ~24 h). This agrees with previous results reported for a series of pyridoxal phosphate–L-amino acid–zinc(II) systems, where it was found that the presence of bulky side chains on the amino acid decreases the rate of transamination.[18] Neutral solutions of 2-formylpyridine–L-histidine–zinc(II) appear more stable than those of nonpolar L-amino acid. The proton NMR spectra of a solution of 2-formylpyridine–L-histidine–zinc(II) nitrate (1:1:1) in D_2O at pD ~7 show no major change within about 24 h. In particular, the reduction in intensity of the azomethine proton signal at δ 8.70 is almost negligible, while the (minor) changes observed for the complex multiplet between δ 2.8 and 4.5 (additional components may be buried under HDO), comprising the α-CH and β-CH_2 signals of the L-histidine residue, may be mainly due to H–D exchange undergone by the α-CH proton. This is confirmed by the relative optical stability of a neutral 0.1 M aqueous solution of 2-formylpyridine–L-histidine–zinc(II) (1:1:1). The UV (284 nm) and CD bands (310 and 281 nm) related to the zinc(II)–aldimine complex remain essentially unaffected within a few hours, and only after longer reaction times do nonnegligible reductions in the intensity of the UV (~10% after 24 h) and CD bands (~20% after 24 h) occur (Figure 3). These changes may be related to minor extents of transamination and transamination plus racemization reactions, respectively.

Zinc(II) and Copper(II) Complexes of Schiff Bases. The relative stability of the histidine aldimine complexes allowed the isolation of analytically pure chelates of this amino acid

(18) Hopgood, D. *J. Chem. Soc., Dalton Trans.* **1972**, 482–487.

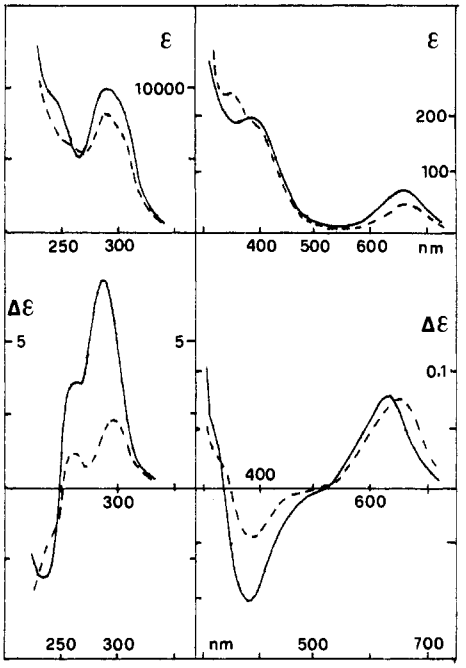


Figure 4. Electronic and CD spectra of (—) $Cu(pyc\text{-}L\text{-}his)ClO_4$ in water solution and (---) $Cu(pyc\text{-}L\text{-}hisOCH_3)(ClO_4)_2$ in methanol solution.

and of its methyl ester derivative by template synthesis. The perchlorate salts were routinely used in the syntheses of copper(II) complexes, while the nitrate salts were preferred in the case of the zinc(II) analogues for the higher solubility of the resulting complexes. The use of cupric hydroxide in the synthesis of the copper(II)–L-histidine complex led to the formation of the species Cu(pyc-L-his′), containing a deprotonated imidazole nucleus. The other copper(II) chelates were prepared from both L- and D-histidine derivatives. The Schiff base structure of the ligands in the chelates is confirmed by the presence of azomethine proton signals in the NMR spectra of $Zn(pyc\text{-}L\text{-}his)NO_3$ (at δ 8.70) and $Zn(pyc\text{-}L\text{-}hisOCH_3)(NO_3)_2$ (at δ 8.80) in D_2O and of strong imine ν(C=N) bands at 1630–1650 cm^{-1} in the solid-state IR spectra of all the complexes (Tables II[11] and III). These bands are flanked by the asymmetric carboxylate stretch, ν_{as}(COO), near 1600 cm^{-1},[19,20] in the IR spectra of complexes derived from histidine. The positions of the IR bands related to methyl ester or imidazole groups of histidine residues are similar to those reported recently for other Schiff base complexes of histidine.[2a,3a,4] The IR spectra of complexes containing perchlorate ions show a broad and featureless band near 1100 cm^{-1} that indicates these anions are not coordinated,[19] while it is more difficult to infer the mode of binding of nitrate ions from the IR spectra of the zinc complexes. We tentatively assign the broad band centered at 1360 cm^{-1} in the IR spectrum of $Zn(pyc\text{-}L\text{-}his)NO_3$ to ionic nitrate[21] and the bands near 1660 and 1320 cm^{-1} in the spectrum of $Zn(pyc\text{-}L\text{-}hisOCH_3)(NO_3)_2$ to coordinated nitrate.[19,21,22] Solution conductivity data at 10^{-3} M concentration indicate that both $Zn(pyc\text{-}L\text{-}his)NO_3$ (Λ_M = 128 cm^2 mol^{-1} in water) and $Zn(pyc\text{-}L\text{-}hisOCH_3)(NO_3)_2$ (Λ_M = 116 cm^2 mol^{-1} in methanol)[23] are 1:1 electrolytes.

(19) Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed.; Wiley-Interscience: New York, 1978; Chapter 3.
(20) Deacon, G. B.; Phillips, R. J. *Coord. Chem. Rev.* **1980**, *33*, 227–250.
(21) Rosenthal, M. R. *J. Chem. Educ.* **1973**, *50*, 331–335.
(22) (a) Lever, A. B. P.; Mantovani, E.; Ramaswamy, B. S. *Can. J. Chem.* **1971**, *49*, 1957–1964. (b) Casella, L.; Ibers, J. A. *Inorg. Chem.* **1981**, *20*, 2438–2448.
(23) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81–122.

Table III. Electronic and CD Spectra and Selected Infrared Data of Zinc(II) and Copper(II) Complexes of Histidine Schiff Bases

compd	solvent	UV-Vis λ_{max},[a] nm (ϵ)	CD λ_{max}, nm ($\Delta\epsilon$)	ν,[c] cm^{-1} [mode]
Zn(pyc-L-his)NO_3	H_2O	284 (8800) 268 sh (5400) 261 sh (4000) 240 sh (7000)	310 (−0.88) 281 (+4.82) 238 (+5.58)	3250 m [im ν(NH)]; 3140 m [im ν(CH)]; 1635 sh [ν(C=N)]; 1601 s, br [ν_{as}(COO), ν(ring)]; 1506 w [im ν(ring)]; 1360 s, br [$\nu(NO_3)$]
Zn(pyc-L-hisOCH$_3$)$(NO_3)_2$	CH_3OH	283 (5500) 268 sh (3500) 261 sh (2700) 235 sh (4600)	310 (−0.28) 280 (+1.83) 240 sh (+1.70)	3220 s, br [im ν(NH)]; 3142 s [im ν(CH)]; 1738 m, 1734 m [ν(C=O)]; 1662 s [$\nu(NO_3)$]; 1636 s [ν(C=N)]; 1605 s [ν(ring)]; 1510 sh [im ν(ring)]; 1318 s [$\nu(NO_3)$]
Cu(pyc-L-his)ClO_4	H_2O	660 (70) 383 (200) 291 (10 000) 245 sh (9500)	630 (+0.08) 386 (−0.10) 330 sh (+0.04) 288 (+7.11) 262 (+3.73) 235 (−3.18)	3218 w [im ν(NH)]; 3166 m, 3123 sh [im ν(CH)]; 1652 s [ν(C=N)]; 1603 vs, 1582 s [ν_{as}(COO), ν(ring)]; 1502 w [im ν(ring)]; 1402 m [ν_s(COO)]; 1100 vs, br [$\nu(ClO_4)$]
Cu(pyc-D-his)ClO_4	H_2O	659 (65) 385 (190) 290 (10 000) 245 sh (11 000)	630 (−0.08) 385 (+0.11) 330 sh (−0.04) 289 (−6.94) 262 (−3.38) 233 (+2.79)	3220 m, br [im ν(NH)]; 3167 m, 3148 m [im ν(CH)]; 1651 s [ν(C=N)]; 1601 vs, 1582 sh [ν_{as}(COO), ν(ring)]; 1505 w [im ν(ring)]; 1403 m [ν_s(COO)]; 1100 vs, br [$\nu(ClO_4)$]
Cu(pyc-L-hisOCH$_3$)$(ClO_4)_2$	CH_3OH	672 (45) 378 sh (200) 351 (235) 297 sh (7200) 289 (8500) 259 sh (5600)	645 (+0.08) 390 (−0.04) 330 sh (+0.02) 292 (+2.40) 258 (+1.05) 235 sh (−2.00)	3352 m, br [im ν(NH)]; 3156 w, 3130 w [im ν(CH)]; 1746 s [ν(C=O)]; 1645 s, 1623 m [ν(C=N)]; 1601 s, 1585 m [ν(ring)]; 1507 m [im ν(ring)]; 1100 vs, br [$\nu(ClO_4)$]
Cu(pyc-D-hisOCH$_3$)$(ClO_4)_2$	CH_3OH	670 (45) 368 (165) 296 sh (6000) 289 (7100) 259 sh (6000)	650 (−0.12) 392 (+0.05) 335 sh (−0.06) 291 (−4.62) 256 (−2.99) 235 sh (+0.64)	3326 m, br [im ν(NH)]; 3159 w, 3139 w [im ν(CH)]; 1733 vs [ν(C=O)]; 1649 s [ν(C=N)]; 1604 s, 1580 sh [ν(ring)]; 1508 m, [im ν(ring)]; 1090 vs, br [$\nu(ClO_4)$]
Cu(pyc-L-his′)	H_2O	385[b] (1500) 295 sh (4300) 260 (7500)		3150 m [im ν(CH)]; 1617 sh [ν(C=N)]; 1597 vs, br, 1570 sh [ν_{as}(COO), ν(ring)]; 1507 sh [im ν(ring)]

[a] sh = shoulder. [b] The electronic bands related to the d–d envelope occur as a broad and poorly defined shoulder on this band, between 600 and 700 nm. [c] Recorded as Nujol mulls. Abbreviations: im = imidazole, s = strong, m = medium, w = weak, br = broad, vs = very strong.

The electronic and CD spectra of the complexes are reported in Table III, and representative examples for the copper(II) chelates are given in Figure 4. The spectra of complexes derived from histidine were recorded in water, while those derived from histidine methyl ester were recorded in methanol solution. In general, the UV spectra exhibit an intense absorption band at 280–290 nm, which can be attributed to a $\pi \rightarrow \pi^*$ transition of the conjugated imine chromophore, and higher energy absorptions associated with pyridine ring transitions. Shoulders on these bands appear in the electronic spectra of most of the chelates and are often clearly resolved in the CD spectra. The spectra of copper(II) complexes exhibit additional weaker absorptions in the visible region, at 630–650 nm (d–d envelope) and at 350–400 nm (charge-transfer transitions). The CD spectra of the zinc(II) complexes display two bands of opposite sign, partially canceling each other, in correspondence with the UV band near 285 nm, and additional CD activity at higher energy. The CD spectra of the copper(II) complexes show single CD bands in correspondence with the absorption bands at 630–650, 350–400, and near 290 nm. It is important to note that, in each series, the spectra of complexes containing histidine or histidine methyl ester residues with the same absolute configuration display the same sign pattern of CD bands throughout the spectral region studied. This behavior is in contrast with that found for the corresponding complexes derived from pyridoxal, salicylaldehyde, or (+)-(hydroxymethylene)camphor[2–4] but agrees with that of the complexes derived from pyruvate.[4] The complex Cu(pyc-L-his′) is completely optically inactive. Also, an immediate loss of the optical activity of all the other copper(II) complexes of histidine or histidine methyl ester is obtained by dissolving them in pyridine.

Table IV. EPR Data[a] and Magnetic Moments[b] of Copper(II) Complexes of Histidine Schiff Bases

compd	g_c	$g_\perp$	$10^4\lvert A_\parallel\rvert$, cm^{-1}	μ_{eff}, μ_B
Cu(pyc-L-his)ClO_4	2.259	2.062	174	1.86
Cu(pyc-D-his)ClO_4	2.261	2.061	174	1.80
Cu(pyc-L-hisOCH$_3$)$(ClO_4)_2$	2.267	2.067	170	1.89
Cu(pyc-D-hisOCH$_3$)$(ClO_4)_2$	2.266	2.063	172	1.88
Cu(pyc-L-his′)	2.242	2.055	188	1.58

[a] Spectra recorded in frozen aqueous solution at −140 °C. A small amount of ethylene glycol was added to enhance the spectral resolution. [b] Measured on powder samples at 295 K.

The EPR spectra of the copper(II) complexes recorded in frozen aqueous solutions show the pattern typical for nearly tetragonal symmetry ($g_\parallel > g_\perp$), well-resolved parallel hyperfine structure, and large $A_\parallel$ values (Table IV). In general, the $g_\parallel$, $A_\parallel$, and $g_\perp$ values are in the range expected for N- or O-bonded Cu, and it can be observed that $g_\parallel$ decreases, while $A_\parallel$ increases, as the overall positive charge of the complex decreases, in accord with established trends.[24] In the case of Cu(pyc-L-his′) we did not detect the "half-field" $\Delta M = \pm 2$ transition near $g = 4$ observed for other imidazolate-bridged copper(II) complexes.[25] It is possible that the exchange

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Table V. Electronic and CD Spectra of 2-Formylpyridine–L-Amino Acid–Metal Ion Systems (1:1:1) in Neutral Aqueous Solution[a]

system[b]	UV λ_{max}, nm (ϵ)	CD λ_{max}, nm ($\Delta\epsilon$)
Zn-pyc-L-ala	282 (6700), 235 sh (7700)	304 (+0.54), 280 (−0.49), 235 sh (−1.13)
Zn-pyc-L-val	284 (6900), 236 (6200)	304 (+2.72), 288 (−1.26), 230 (−2.78)
Zn-pyc-L-phe	288 (6000), 238 (5000)	310 (+1.00), 282 (−6.62), 243 (−5.50)
Cu-pyc-L-ala	635 (60), 300 sh (1200), 288 sh (2000), 258[c] (5500), 235 (6400)	635 (−0.06), 390 (+0.01), 290 sh (−0.25), 235 (−1.10)
Cu-pyc-L-leu	680 (70), 302 sh (1100), 290 sh (1600), 258[c] (4000), 234 (4700)	670 (−0.11), 385 (+0.04), 300 sh (−0.50), 292 (−0.75)
Cu-pyc-L-val	650 (60), 302 sh (1100), 291 sh (1800), 258[c] (5000), 233 (5500)	620 (−0.14), 390 (+0.08), 300 sh (−0.40), 290 (−0.65), 258 (−0.72)
Cu-pyc-L-phe	690 (60), 305 sh (1600), 292 sh (2600), 258[c] (4200), 234 (5000)	660 (−0.20), 395 (−0.06), 305 sh (−1.57), 295 (−2.37)

[a] Recorded within a few minutes after mixing of the reagents; see Experimental Section. [b] The abbreviation M-pyc-L-aa comprises several species existing in equilibrium in solution for the ternary systems. Abbreviations: ala = alanine, val = valine, leu = leucine, phe = phenylalanine. [c] Shoulders on this band occur at 266 and 252 nm.

interacton mediated by the imidazolate group in this complex is weak or that in (aqueous) solution the imidazolate species is in equilibrium with monomeric hydroxo complexes. The magnetic moment of Cu(pyc-L-his′), though, is significantly reduced compared to that of the other copper(II) complexes (Table IV).

Since we were unable to obtain complexes derived from nonpolar L-amino acids in reasonable purity, we recorded electronic and CD spectra of neutral aqueous solutions of several 2-formylpyridine–L-amino acid–zinc(II) and -copper(II) (1:1:1) systems. Although these ternary systems are clearly unstable, we wanted to gain at least a qualitative description of the chiroptical properties of complexes of type **5**, containing a glycine-like bound L-amino acid residue. The spectral data were collected within a few minutes after mixing of the reagents, since appreciable reduction in intensity of the CD bands was observed when the solutions were allowed to stand, particularly in the case of the copper(II) systems. These data are summarized in Table V, and representative spectra are given in Figures 2 (zinc(II) complexes) and 5 (copper(II) complexes). Despite the fact that the visible CD spectra of the copper(II) systems are probably contributed by bands due to the binary copper(II)–L-amino acid systems,[26] we can reasonably assume that the CD bands near 300 nm (associated with the imine chromophore) and 390 nm (that we assign to a charge-transfer transition from the imine group to copper(II)) are determined by the species of structure **5**, since the UV absorption and CD bands of binary copper(II)–L-amino acid systems occur at much higher energy.[27]

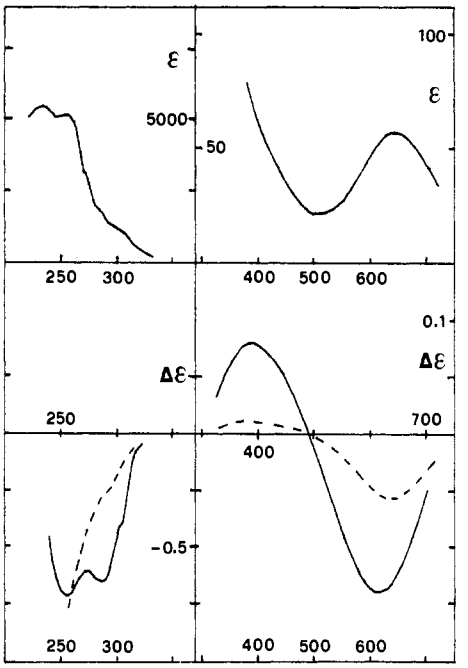
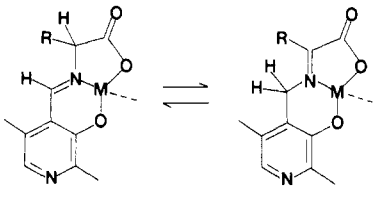


Figure 5. Circular dichroism spectra in neutral water solution of (—) 2-formylpyridine–L-valine–copper(II) (1:1:1) and (---) 2-formylpyridine–L-alanine–copper(II) (1:1:1). The electronic spectrum of the former system is also reported. The spectra were recorded within a few minutes after mixing of the reagents.

Discussion

The role of pyridoxal phosphate in biological transamination reactions is rather well established.[28] In nonenzymic systems, the minimum structural requirements for the occurrence of pyridoxal-mediated transaminations of amino acids are the presence of the 4-formyl group and the 3-hydroxyl substituent on the pyridine ring.[6,29] In general, however, these reactions are extremely slow in the absence of metal ions, and also for the metal ion containing systems the aldimine (**13**) → ketimine (**14**) conversion is slow under mild conditions,[18,30] since metal



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ions apparently stabilize the aldimine more than the ketimine form. By contrast, the reverse ketimine → aldimine process is relatively fast in systems containing metal ions[14,31] and occurs at appreciable rate also in metal-free systems.[32] In the absence of the 3-hydroxyl substitutent, quaternization of the pyridine ring nitrogen promotes efficient transamination of amino acids through the reactive dihydropyridine intermediate **16**.[33] This

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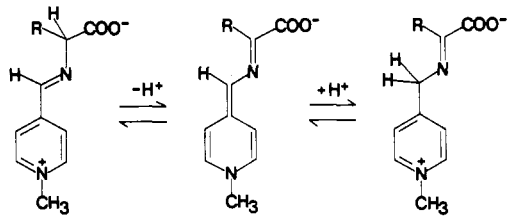

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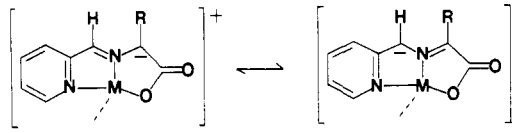
reaction has been recently exploited for the conversion of amines to carbonyl compounds on a preparative scale.[34] Imines of simple formylpyridines, however, effect this conversion only in the presence of strong oxidizing agents[35] or with use of a large excess of a strong base such as lithium diisopropylamide.[36] Condensation between 2-formylpyridine and amino acids is extremely slow in neutral aqueous solution. Metal ions promote the formation of the Schiff base, but the resulting systems undergo easy aldimine → ketimine tautomerization (possibly flanked by other reactions), especially when the amino acids carry nonpolar side chains, leading to complex mixtures of products. The copper(II) systems of type **5** are apparently more reactive than their zinc(II) analogues in these transformations. The UV absorption spectra of neutral solutions of 2-formylpyridine–L-amino acid–copper(II) (1:1:1) show that very little accumulation of the aldimine complex occurs in solution (Table V, Figure 5). The UV band associated with the imine chromophore (near 300 nm) always appears as a shoulder on the main absorption due to 2-formylpyridine (near 260 nm). Formation of some aldimine complex is more evident in the CD spectra, but the CD activity near 300 and 390 nm decreases rather rapidly with time. For instance, in the 2-formylpyridine–L-alanine–copper(II) system these 300- and 390-nm CD bands are almost completely extinguished after a reaction time of only 1 h (some residual CD activity near 630 nm is due to a small amount of copper(II)–L-alanine complex[26]). We believe that two factors determine the special reactivity of these systems: (i) the overall positive charge of complexes of the type M^{II}(pyc-L-aa)$^+$, which presumably favors α-C–H ionization to generate the species **18** ⇄ **19**, and (ii) the system of two fused five-membered



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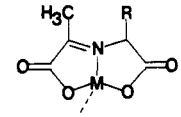
chelate rings, which appears to be somewhat strained, since it forces the azomethine proton and the α-carbon substituent in closer proximity than in a system such as **13** consisting of a five- and a six-membered ring. The enhancement of reactivity at the α-carbon atom with increase of the positive charge of the complex has been clearly demonstrated by comparative H–D exchange experiments and reactions with electrophiles of series of metal complexes with simple amino acids and amino acid–Schiff bases.[37] The existence of strain in systems containing two fused five-membered chelate rings has been recognized for complexes derived from pyruvate and amino acids (**20**)[32,38] and in other cases.[39] It is worth noting



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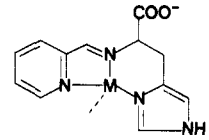
here that pyruvate, or other α-keto acids, can effectively replace pyridoxal in promoting metal ion catalyzed reactions of amino acids, including transamination.[15,32,40] The reactivity of systems of type **20**, though, is clearly lower than that of **5**, since the complexes derived from pyruvate are reasonably stable in neutral solution[4] and can resist conditions somewhat more drastic than those employed here for the 2-formylpyridine derivatives.[15,37c,40c,41] The higher reactivity of the latter complexes, therefore, is to be ascribed mainly to their positive charge. It appears that the systems 2-formylpyridine–amino acid–metal ion (particularly copper(II)) are the most efficient model systems for reproducing the biological transamination catalyzed by pyridoxal phosphate.

The existence of strain in systems of fused five-membered chelate rings has the important consequence of determining the adoption of the histamine-like, rather than glycine-like, chelation mode (**21**) by the histidine residues in the 2-



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formylpyridine complexes derived from this amino acid. The mode of histidine binding is easily inferred from the CD spectra of the complexes. The pattern of CD bands in the spectra of complexes derived from L-histidine is the same as that of complexes derived from L-histidine methyl ester and bears a mirror-image relationship to that of complexes containing nonpolar L-amino acid residues. This is readily deduced from the features of the CD spectra shown in Figures 2 and 3 for the zinc(II) complexes and in Figures 4 and 5 for the copper(II) complexes (see also Tables III and V). As we suggested previously,[2-4] the CD spectra of tridentate Schiff base chelates of amino acids are determined by the preferred conformation assumed by the amino acid chelate ring. This contains an axially disposed side chain and involves a chirality of sign λ for nonpolar L-amino acids and L-histidine residues bound glycine-like (e.g. **1–3**), while for L-histidine residues bound histamine-like (**4** and **21**) the disposition of the side chain is the same as for a nonpolar D-amino acid (δ conformation). The EPR spectra of the copper(II) complexes recorded in frozen aqueous solution support this interpretation, since the g values determined for species of type **21** (e.g. Cu(pyc-L-his)ClO_4 or Cu(pyc-L-hisOCH_3)$(ClO_4)_2$, CuN_3O core) are similar to those of the corresponding pyruvate complexes (**4**) recorded in pyridine (CuN_3O core) but lower than those observed for **4** in water or methanol (CuN_2O_2 core).[4] The consequences of the assumption of a histamine-like coordination mode by the histidine residues have been discussed previously in terms of the stereochemistry of vitamin B_6 model systems.[4] We note here that the racemization reaction un-

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dergone by the copper(II) complexes of *N*-(2-pyridylmethylidene)histidine in pyridine parallels that observed for the corresponding pyruvate complexes. This confirms our interpretation based on apical binding by the donor base, which causes a conformational inversion of the amino acid chelate ring to the conformation containing an equatorial side chain and an axial α-C–H bond,[4] and is in full agreement with Dunathan's prediction.[42] Racemization in pyridine is faster for complexes of type **21** than for those of type **4**. As for the reactions undergone by complexes of type **20** and **5**, the accelerating effect must be related to the presence of a higher positive charge.

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Registry No. **11**, 127-17-3; **12**, 3731-51-9; Zn(pyc-L-his)NO_3·H_2O, 86024-31-9; Zn(pyc-L-hisOCH_3)$(NO_3)_2$, 86045-51-4; Cu(pyc-L-his)ClO_4·H_2O, 86024-33-1; Cu(pyc-D-his)ClO_4·H_2O, 86087-49-2; Cu(pyc-L-hisOCH_3)$(ClO_4)_2$·H_2O, 86024-35-3; Cu(pyc-D-hisOCH_3)$(ClO_4)_2$·$HOCH_3$, 86024-37-5; Cu(pyc-L-his')·H_2O, 86024-38-6; Zn(pyc-L-ala)$^+$·H_2O, 86024-39-7; Zn(pyc-L-val)$^+$·H_2O, 86024-40-0; Zn(pyc-L-phe)$^+$·H_2O, 86024-41-1; Cu(pyc-L-ala)$^+$·H_2O, 86024-42-2; Cu(pyc-L-leu)$^+$·H_2O, 86024-43-3; Cu(pyc-L-val)$^+$·H_2O, 86024-44-4; Cu(pyc-L-phe)$^+$·H_2O, 86024-45-5; L-his, 71-00-1; D-his, 351-50-8; L-hisOCH_3, 1499-46-3; D-hisOCH_3, 17720-12-6; L-ala, 56-41-7; L-val, 72-18-4; L-phe, 63-91-2; L-leu, 61-90-5; 2-formylpyridine, 1121-60-4; α-ketoisovalerate, 759-05-7.

Supplementary Material Available: Listings of elemental analyses (Table I) and complete infrared data of zinc(II) and copper(II) complexes of histidine Schiff bases (Table II) (3 pages). Ordering information is given on any current masthead page.

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Ligand-to-Metal Charge-Transfer Spectra of Tetrahaloaurate(III) and *trans*-Dicyanodihaloaurate(III) Ions

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Electronic absorption and magnetic circular dichroism (MCD) spectra are reported for AuX_4^- (X = Cl^-, Br^-), *trans*-$Au(CN)_2X_2^-$ (X = Cl^-, Br^-, I^-), and *trans*-$Au(CN)_2BrY^-$ (Y = Cl^-, I^-) in acetonitrile solution. These complexes exhibit a number of intense bands in the vis–UV region that are assigned to ligand-to-metal charge transfer (LMCT) from occupied halide-based orbitals to the lowest energy σ^* orbital, which is primarily $5d_{x^2-y^2}$ localized on gold. A detailed model for LMCT in planar complexes of D_{4h} and D_{2h} symmetries that includes halide spin–orbit coupling and intermixing σ- and π-bonding orbitals of the same symmetry is presented and used to interpret the absorption and MCD spectra.

Introduction

The intense bands exhibited by many halo complexes in the UV region have been assigned as ligand-to-metal charge-transfer (LMCT) electronic transitions.[2] Such transitions involve excitation of electrons from occupied orbitals localized on the halide to an empty or partly filled orbital of predominantly metal character, commonly a metal d orbital. The LMCT transitions can thus be viewed as an incipient reduction of the metal with concomitant oxidation of the halide ligand and are therefore related to the redox properties of the metal ion and halide. The low-energy LMCT excited states are also of considerable interest in the understanding of photochemical reactions of halo complexes.[3,4]

The study of the LMCT process in square-planar complexes based on investigation of typical Pt(II) halo complexes has been complicated by the presence of allowed metal 5d → 6p transitions in the same energy region as LMCT. For example, both d → p and LMCT assignments have been given to the intense band system near 4.4 μm^{-1} in $PtCl_4^{2-}$.[5-9] In contrast, the halo complexes of isoelectronic Au(III) are expected to be free of such complications because the 5d–6p energy separation is larger than for Pt(II). This together with the red shift expected for LMCT as the metal oxidation state is increased from Pt(II) to Au(III) ensures a large separation between d → p and LMCT band systems in Au(III). The study of Au(III) halo complexes therefore provides an excellent opportunity to characterize the LMCT process in square-planar complexes. However, apart from the $AuCl_4^-$ and $AuBr_4^-$ ions,[5,10-12] there have been few halo Au(III) complexes investigated and none in any great detail. Consequently, motivated by our general interest in LMCT in square-planar complexes, we describe herein a detailed model for low-energy LMCT excited states for the D_{4h} AuX_4^- ions. The model, which includes both intermixing of σ and π ligand orbitals of the same symmetries and consideration of halogen spin–orbit coupling, is used to interpret the electronic absorption and magnetic circular dichroism (MCD) spectra for $AuCl_4^-$ and $AuBr_4^-$ that were obtained in acetonitrile solution. Although aqueous MCD spectra for these ions were reported earlier,[5] they have been carefully remeasured with high sensitivity here in acetonitrile. Also a low-temperature (ca. 15 K) MCD measurement was made for $HAuCl_4$ incorporated into a thin transparent poly(vinyl alcohol) (PVA) film. In addition the LMCT model generalized to D_{2h} symmetry is used to interpret

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(2) See for example: (a) Jørgensen,, C. K. "Absorption Spectra and Chemical Bonding in Complexes"; Addison-Wesley: Reading, MA, 1962. (b) Ballhausen, C. J.; Gray, H. B. In "Coordination Chemistry"; Martell, A. F., Ed.; American Chemical Society: Washington, DC, 1971; ACS Monogr. No. 168, p 3.
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