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Optical Rotatory Dispersion Studies of L-Histidine Chelation

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Optical rotatory dispersion studies were carried out on L-histidine in its several pH forms and in chelation with divalent transition metals. L-Histidine exhibits a positive Cotton effect with characteristics that vary as a function of pH. Upon chelation with the transition metals—Co(II), Ni(II), Cu(II), and Zn(II)—a reversal of the direction of rotation accompanied by a several-fold increase in molecular rotation, *i.e.*, a negative Cotton effect of greater amplitude, was observed. Addition of two equivalents of ethylenediaminetetraacetate, EDTA, regenerates the optical rotatory dispersion (ORD) curve of free L-histidine, and the methyl ester of L-histidine displays a positive Cotton effect in the presence of Co(II), Ni(II), and Zn(II). These reversals of rotation are discussed relative to the many-electron model of optical rotation of Jones and Eyring under the assumption that the carboxyl oxygens are physically distinct and that the sign of the Cotton effect due to the $n-\pi^*$ transition in the acyl moiety can be distinguished. Within this framework, the observed reversals of rotation can be explained. The reversal of the Cotton effect is interpreted as the result of a change in conformation—a change resulting in a conformation for the chelated histidine which was highly improbable for the free L-histidine in solution. These observations indicate the sensitivity of ORD to conformation and, hence, its utility in determination of conformation, but they add a note of caution to interpretations of absolute configuration. Copper-histidine complexes exhibit an optically active transition at about 247 $m\mu$ which was not found with the other three transition metals. Assuming that this absorption represents a charge transfer from the imidazole to the copper, the Jones and Eyring model may be applied to arrive at the correct sign of the observed Cotton effect.

Introduction

Optical rotatory dispersion, the rotation of plane-polarized light as a function of wave length, has been gaining prominence as a tool for the study of molecular stereochemistry. Optical rotatory studies have been successfully used to predict absolute configuration¹⁻³ about an asymmetric center, to determine conformation and structure of such complex molecules as the steroids⁴ by comparison with simpler compounds of known conformation, and to approximate per cent helicity of proteins.⁵⁻⁷

Due to their implication in biological systems, metal complexes of histidine and of its imidazole moiety have been extensively studied. Cobalt complexes of histidine and their molecular oxygen adducts were described by Hearon, Burk, and Schade⁸ where the biological significance of these species is discussed. As part of their characterization they reported the optical rotatory dispersion curve of di(histidino)cobalt through the absorption region of the metal chromophore, that is, from 440 to 700 $m\mu$. The absorption spectra of copper-histidine complexes from 230 to 290 $m\mu$,⁹ and the infrared spectra of zinc complexes of histidine and histidyl peptides^{10,11} have been determined. Using various methods, such as potentiometric and ion exchange, the formation constants of several transition metal-histidine complexes have been reported,^{12,13}

and the crystal and molecular structures of di(histidino)zinc(II) have been resolved by X-ray crystallography both as the dihydrate¹⁴ and the pentahydrate.¹⁵ Most recently cobalt-histidine complexes have been studied using nuclear magnetic resonance resulting in proposed structures of the forms this system takes in solution.¹⁶ It is the purpose of this work to examine the optical rotatory dispersion curves of L-histidine, free and in chelation, between 190 and 320 $m\mu$ and to interpret the striking results in terms of a current theory of optical rotation.

Experimental

The ORD curves were determined using the continuously recording Cary Model 60 spectropolarimeter which, when solvent and solute permit, can scan down to 185 $m\mu$. The specifications state that the polarimeter is sensitive to 0.4 mdeg. at 400 $m\mu$. This sensitivity decreases with increased absorption and is consequently a function of concentration, nature of solute and solvent, and wave length. The light source is a xenon arc lamp and the slit width was programmed to maintain a 15-Å. band width. The temperature of the sample cell was approximately 27°. Scan speeds from less than 1 up to 5 $m\mu$ /min. and a response time of 30 sec. for 98% response to a step increase in the optical activity were used.

pH readings were taken on the Beckman Zeromatic pH meter. L-Histidine and the methyl ester of L-histidine were obtained from Sigma Chemical Co. as the free base. All samples were run at 0.4 μ mole/ml., and when basic solutions were studied, the pH was adjusted from neutral or acidic pH to basic pH immediately before running. The pH chosen for the ORD curves was such that a single species predominates in solution. This was done by selecting the unbuffered pH regions of the titration curves. The aqueous solvent and solutions were repeatedly bubbled with nitrogen to remove troublesome gases and were stored under N₂.

Following the determination of the ORD curve for a histidine-metal chelate at a given pH, the disodium salt of EDTA was added to the sample, the pH was readjusted to that of the previous run, and the sample was rerun.

Results

L-Histidine in Its Various pH Forms.—The optical rotatory dispersion curves of L-histidine at four pH values are given in Fig. 1. The fraction of species

(1) E. U. Condon, W. Altar, and H. Eyring, *J. Chem. Phys.*, **5**, 753 (1937).

(2) J. G. Kirkwood, *ibid.*, **5**, 479 (1937); W. W. Wood, W. Fickett, and J. G. Kirkwood, *ibid.*, **20**, 561 (1952).

(3) W. Kuhn, *Naturwiss.*, **26**, 289 (1938); *Z. physik. Chem.*, **B31**, 23 (1935).

(4) C. Djerassi, "Optical Rotatory Dispersion," McGraw-Hill Book Co., Inc., New York, N. Y., 1960.

(5) C. Cohen, *Nature*, **175**, 129 (1955).

(6) J. T. Yang and P. Doty, *J. Am. Chem. Soc.*, **79**, 761 (1957).

(7) P. Urnes and P. Doty, *Advan. Protein Chem.*, **16**, 401 (1961).

(8) J. Z. Hearon, D. Burk, and A. L. Schade, *J. Natl. Cancer Inst.*, **9**, 337 (1949).

(9) J. T. Edsall, G. Felsenfeld, D. S. Goodman, and F. R. N. Gurd, *J. Am. Chem. Soc.*, **76**, 3054 (1954).

(10) G. Weitzel, F. Schneider, A-M. Fretzdorff, and H-E. Heyke, *Z. physiol. Chem.*, **307**, 14 (1957).

(11) G. Weitzel, F. Schneider, and A-M. Fretzdorff, *ibid.*, **307**, 23 (1957).

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(13) R. Leberman and B. R. Rabin, *Trans. Faraday Soc.*, **55**, 1669 (1959).

(14) R. H. Kretsinger, F. A. Cotton, and R. F. Bryan, *Acta Cryst.*, **16**, 651 (1963).

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(16) C. C. McDonald and W. D. Phillips, *J. Am. Chem. Soc.*, **85**, 3736 (1963).

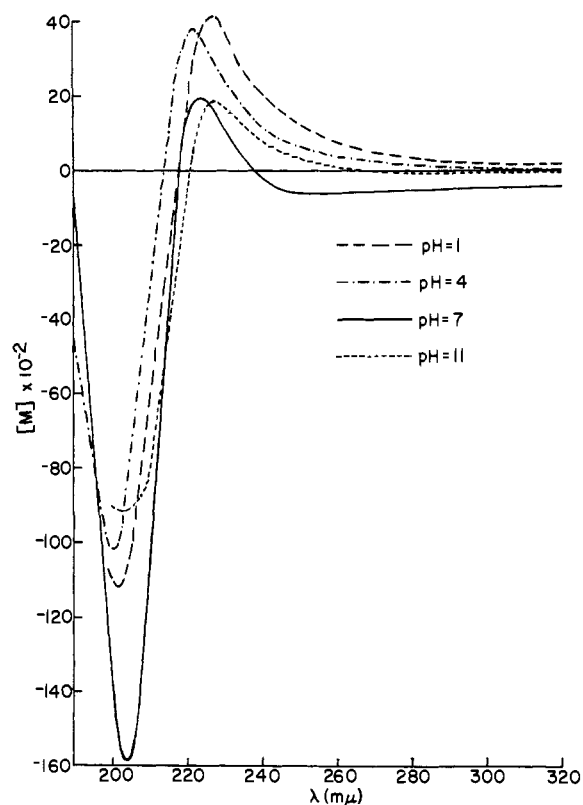


Fig. 1.—Rotatory dispersion curves of L-histidine at pH values which represent, as nearly as practicable, single species in solution.

present at these hydrogen ion concentrations may be calculated using the following pK values: COOH, 1.82; imidazolium, 6.00, $-\text{NH}_3^+$, 9.27; imidazole, 13.4. At pH 1.0, 87% of the histidine is in the totally protonated form (H_4A^{+2}); at pH 4, 99% contains the carboxylate anion (H_3A^+); at pH 7, 91% is as the zwitterion (H_2A); and at pH 11, 98% is as the HA^- species. All four species exhibit a positive Cotton effect, that is, the first extremum in order of decreasing wave length is positive. The most pronounced change is found when the pH is increased from 4 to 7. This increase results in the removal of a proton from the imidazolium moiety. It is noted that the ORD curve is displaced negatively and displays an increase in the amplitude of the Cotton effect. Both the negative displacement and the increase, in molecular rotation suggests to the authors that a bias has been added favoring one conformation.

ORD Curves of L-Histidine in Presence of Divalent Metal Ions.—The titration of L-histidine from pH 1 to 10 involves three proton functions—the carboxyl, the imidazolium, and the amino protons—in order of increasing pK , whereas the titration of L-histidine in the presence of equimolar amounts of any one of four divalent metal ions—Co(II), Ni(II), Cu(II), and Zn(II)—requires four equivalents of base to raise the pH from 1 to 10. The first proton titrated is that of the carboxyl group. The second and third proton functions have a common pK and are reported to be from the imidazolium and amino cations.^{9,16–18} The fourth proton is considered to be that of a coordinated water

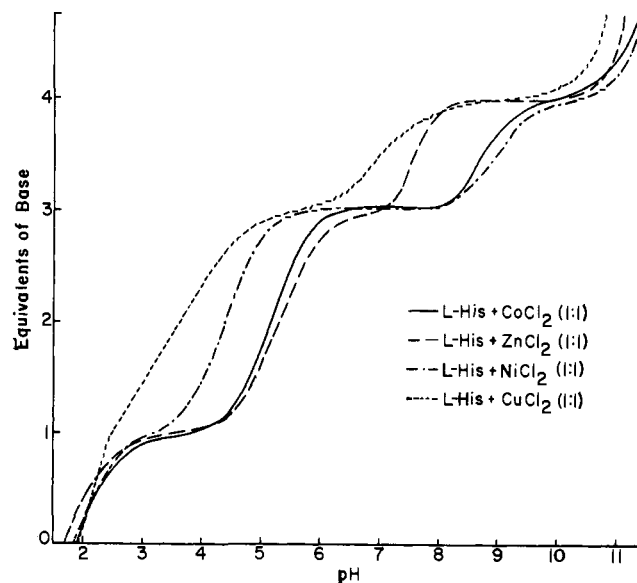


Fig. 2.—Titration curves of L-histidine in the presence of equimolar metal ion.

molecule.¹³ These titration curves, given in Fig. 2, dictate the pH at which the ORD curves are run.

The rotatory dispersion curves for the metal ion-histidine systems at the pH representing the first equivalence point exhibit positive Cotton effects of little variation and at only slight variance to that of the free L-histidine at its first equivalence point. However, if the rotatory dispersion curves are run at the pH representing the removal of an additional two protons, rather remarkable changes are observed. Negative Cotton effects of several-fold greater amplitudes are found (see Fig. 3–6). As may be seen by referring to these figures, the addition of two equivalents of EDTA to the metal-histidine system competitively regenerates positive Cotton effects of the form of free L-histidine at that pH. The copper-L-histidine system has a rotatory dispersion curve distinct from that of the other metal ions in that its curve contains additional rotation extrema at 235 and 257 $m\mu$. The curves of the methyl ester of L-histidine in the presence of equimolar metal ion are also reported in Fig. 3–6. It is noted that the positive Cotton effect is retained except in the case of Cu(II) where a negative Cotton effect is seen. Included in Fig. 3 and 4 are the curves obtained when there are two equivalents of histidine to one equivalent of Co(II) and of Ni(II), respectively.

Upon raising the pH such that the fourth proton function has been removed, rotatory dispersion curves are obtained which differ in amplitude and have small differences in form from those obtained at lower pH. This may be seen by comparing Fig. 7 with the preceding four figures. The cobalt-histidine system, however, does display a slight rotational extremum at 260 $m\mu$.

Cobalt is the only metal studied which exhibited an oxygen effect when complexes with histidine. Saturation with molecular oxygen at pH 7 shows but a slight Cotton effect at about 278 $m\mu$ with otherwise no change in the rotatory dispersion curve in the 190- to 320- $m\mu$ range. Rigorous exclusion of molecular oxygen from the L-histidinocobalt(II) complex at pH 10 resulted in the loss of the rotational extremum at 260 $m\mu$ (Fig. 7) with the generation of a curve almost super-

(17) R. B. Martin and J. T. Edsall, *J. Am. Chem. Soc.*, **80**, 5033 (1958).

(18) N. C. Li, T. L. Chu, C. T. Fujii, and J. M. White, *ibid.*, **77**, 859 (1955).

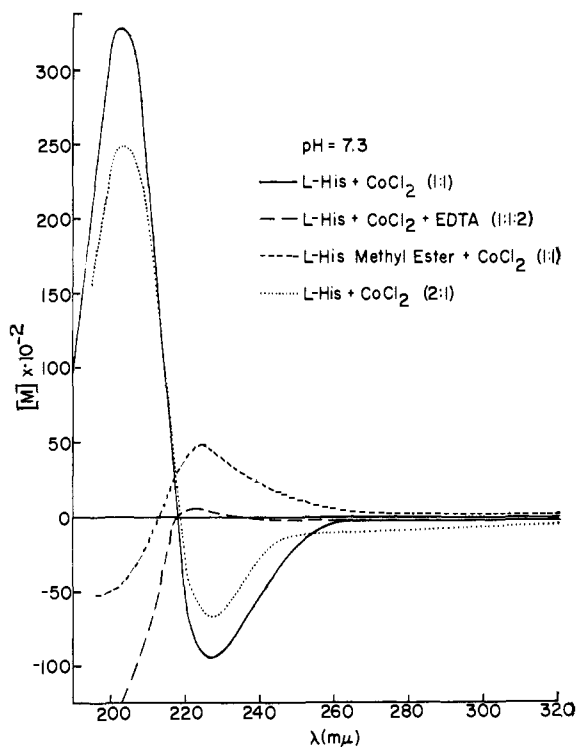


Figure 3.

impossible on that at pH 7. Saturation with oxygen showed a Cotton effect centering at 278 $m\mu$ with a molecular amplitude of 2000 and a negative displacement of the 227- and 207- $m\mu$ extrema. The curve in Fig. 7 represents about 35% of the O_2 effect. Subsequent purging with very pure nitrogen showed the effect to be reversible.

Discussion

It has been established by X-ray diffraction that histidine in di(histidino)zinc(II) complexes exists as a tridentate ligand in both the dihydrate and pentahydrate crystalline forms.^{14,15} Potentiometric and ion-exchange techniques have indicated that histidine, at the proper pH, also occurs as a tridentate ligand in solutions containing one of the metal ions: Co(II), Ni(II), Cu(II), or Zn(II).^{8,12,13} Reasoning that previous work on these complexes was not unambiguous, McDonald and Phillips¹⁶ have recently studied the cobalt(II)-histidine complexes using nuclear magnetic resonance and reported that a clear assignment of structures can be made which is in concurrence with the previously reported data. They reported 1:1 histidine-Co(II) complexes and 2:1 histidine-Co(II) complexes in the pH range of 4.5 to 10.5 in which histidine behaves as a tridentate ligand bound to the metal ion by the carboxylate, amino, and imidazole groups. They also reported that the relative abundance of these two complexes is a function of the histidine concentration. Leberman and Rabin¹³ list the formation constants for the mono- and dihistidino metal complexes from their own and other workers' data. The average values for the formation constants therein listed are given in Table I. As these formation constants are very large and differ by approximately 10^2 , except in the case of Zn(II), it can be seen that equivalent amounts of metal ion and histidine will give predominantly the monohistidino complexes and

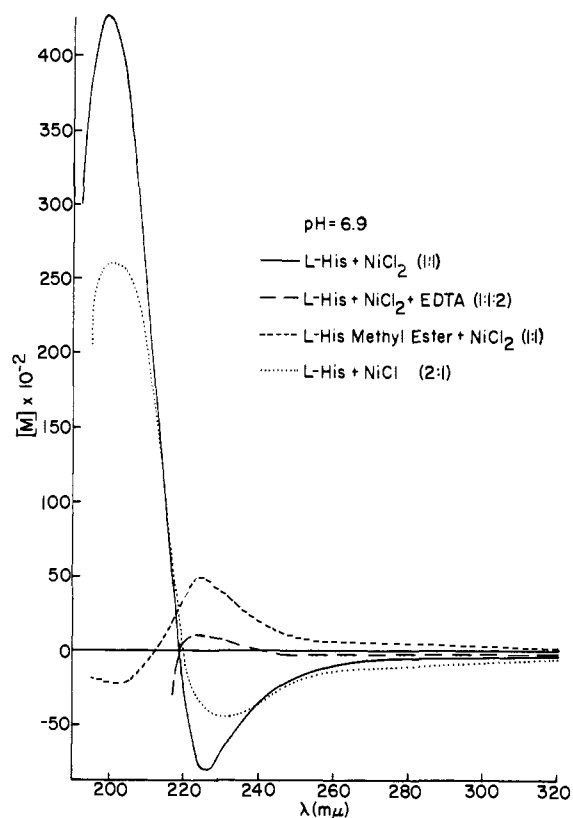


Figure 4.

that an equivalence of 2:1 would give predominantly the dihistidino complex, at the appropriate pH.

TABLE I

| Metal ion | log K_1 | log K_2 |
|-----------|-----------|-----------|
| Co(II) | 7.11 | 5.42 |
| Ni(II) | 8.74 | 6.94 |
| Cu(II) | 10.56 | 8.25 |
| Zn(II) | 6.88 | 5.70 |

The results herein reported may be interpreted by suitable application of the many-electron model of optical rotation of Jones and Eyring^{19,20} which is an extension of the one-electron theory of Condon, Altar, and Eyring.¹ The model is one of considering a distorted chromophoric ellipsoid, an ellipsoid made dissymmetric by the presence of vicinal groups. The potential for the chromophoric electron is written

$$V = \frac{1}{2}(k_1x^2 + k_2y^2 + k_3z^2) + Axyz$$

where it required that the force constants be unequal in order to have the necessary anisotropy. A right-handed coordinate system is used. The force constants are assigned such that $k_1 > k_2 > k_3$. This assignment provides the criteria for orientation of the coordinate system, that is, z would be the most polarizable direction, y the second most polarizable, and x the least polarizable. The $Axyz$ term introduces the dissymmetry and arises from the effect of vicinal groups on the motion of the chromophoric electron. If the vicinal group is positively charged, then the potential controlling the motion of the chromophoric electron is decreased in the direction of this group. The positive hole left by excitation of the chromophoric electron

(19) L. L. Jones and H. Eyring, *Tetrahedron*, **13**, 235 (1961).

(20) H. Eyring, L. L. Jones, and J. D. Spikes in "Horizons in Biochemistry," M. Kasha and B. Pullman, Ed., Academic Press, New York, N. Y., 1962, pp. 229-250.

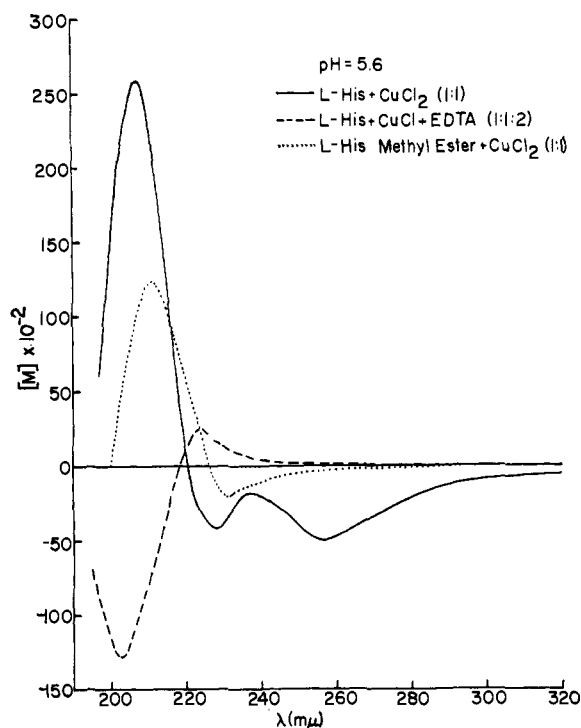


Figure 5.

causes the polarizable vicinal groups to feed electrons toward that hole, which is to say that the positive hole extends into this position. An apparent decrease in potential in the direction of polarizable groups would result. Thus, for positively charged groups and polarizable groups the perturbing term, $Axyz$, would be negative. The reverse would be true for negatively charged groups. Treating the chromophoric electron as a three-dimensional harmonic oscillator and choosing force constants and quantum numbers such that correct energies are obtained for the chromophore, it can be shown that the direction of rotation follows the sign of the parameter A .¹ Expanding the interaction of the chromophoric electron with the other charged particles in the molecule, it can be shown that the first terms which are of a symmetry allowing optical rotation are of the form $Axyz$.^{19,20}

In order to apply this model the following is required: The coordinate system must be properly oriented. For example, the most polarizable direction of a carbonyl chromophore would be along the carbon-oxygen bond axis, the second most polarizable direction would be in the plane of the sp^2 -hybridized system, and the least polarizable direction would be perpendicular to that plane. The axis directions are chosen to form a right-handed coordinate system. The sign of the Cotton effect due to the optically active transition of interest must be determined from the rotatory dispersion curve, and the contribution of the vicinal groups must be apparent and unambiguous as to sign.

In applying this model to the histidino complexes the assumptions are made that the carboxylate anion is sufficiently bound to the divalent metal ion to allow distinction of the two oxygens and to allow recognition of an acyl moiety which may be treated as the chromophore of interest, that the sign of the Cotton effect at the long wave length side of 220 $m\mu$ is controlled by this acyl chromophore, and that the methylene group and

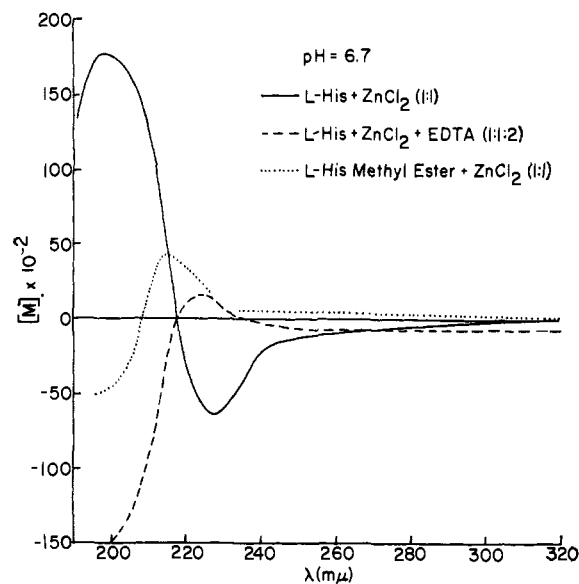


Figure 6.

the imidazole moiety are the polarizable vicinal groups resulting in the largest dissymmetric perturbations of the chromophoric ellipsoid.

On the basis of previous work on the complexes of amino acids and on considerations of rotatory strength, the aforementioned assumptions can be substantially justified. X-Ray diffraction studies of the di(histidino)zinc(II) complexes^{14,15} show the carboxyl oxygens to be physically distinct, that is, the bond angles and bond lengths are different for the two oxygens. Thus, it is reasonable to consider an acyl moiety. In these complexes there are four chromophores in which active transitions may occur—the metal ion, the amino, carboxyl, and imidazole groups. The metal ions have their absorption maxima in or near the visible range whereas the absorption maximum for the amino group is at 190 $m\mu$ or less so that these two groups would contribute only background rotation in the region of interest. However, the carboxyl and imidazole groups have overlapping absorption maxima. An absorption maximum for carboxyl is found in the range 205 to 225 $m\mu$ while that of the imidazole group is in the range 205 to 215 $m\mu$.^{21,22} Thus it is necessary to consider these groups in more detail.

The rotatory dispersion curves of L-lactic acid and L-alanine are given in Fig. 8; both exhibit positive Cotton effects. These molecules differ only in that the α -amino of L-alanine is replaced by an α -hydroxyl in L-lactic acid. Comparison of Fig. 8 and 1 shows that at acid pH all three molecules have very similar rotatory dispersion curves, the principal difference being an increased amplitude in the case of L-histidine in which a β -hydrogen of alanine has been replaced by the imidazole moiety. The long wave length chromophore in alanine and lactic acid can be assigned to the $n-\pi^*$ transition of the acyl moiety as the other chromophores—the hydroxyl of lactic acid, the protonated amino of alanine, and the $\pi-\pi^*$ transition in the carboxyl common to both molecules—do not have such long wave length transitions. Therefore, it can be assumed that a Cotton effect due to an $n-\pi^*$ transition

(21) G. Leandri, A. Mangini, F. Montanari, and R. Passarini, *Gazz. chim. ital.*, **85**, 769 (1955).

(22) D. B. Wetlaufer, *Advan. Protein Chem.*, **17**, 303 (1962).

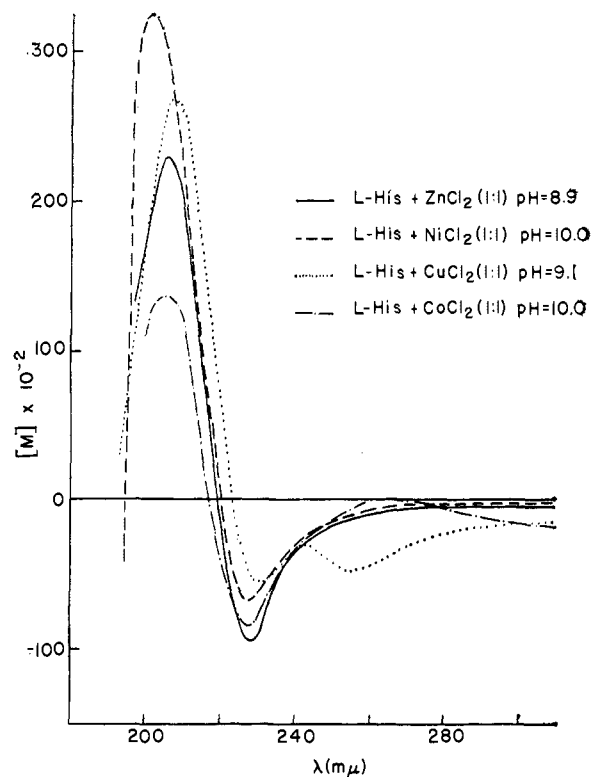


Figure 7.

in the acyl moiety of L-histidine does exist and, as a positive Cotton effect can be resolved by inspection (Fig. 9), it is reasonable to relate the two. Interpreting the L-histidine curve in light of those of L-alanine and L-lactic acid, one would be inclined to view imidazole as a vicinal group, increasing the amplitude, but not functioning as an optically active chromophore. Two additional considerations support this view.

Imidazole, though it is not apparent from observing its structure as classically written, is an aromatic, planar ring system.²³ Transitions in the phenyl group were found experimentally by Kuhn and Biller²⁴ to be of low rotational strength in methylphenylcarbinol. The phenyl system has been theoretically treated by Caldwell²⁵; his studies indicate low rotational strengths for this aromatic system, and that, where there are degenerate transitions, they appear to be of equal magnitude but opposite in sign, thereby canceling. The second consideration is that imidazole is removed from the asymmetric center by the CH₂ group. As there is a very steep dependence of rotational strength on distance, the contribution to rotation of transitions in imidazole would be further diminished. Consistent with comparison of rotatory dispersion curves of L-histidine to those of L-alanine and L-lactic acid, consistent with what is known of rotational strength of aromatic systems, and consistent with consideration of distance dependence, we can take the extremum at the long wave length side of 220 mμ to be due to the n-π* transition in the acyl moiety.

The coordinate system may be set up as indicated in complex I which shows L-histidine in tridentate chelation with a metal ion. The acyl group is treated just as the carbonyl group with the most polarizable direc-

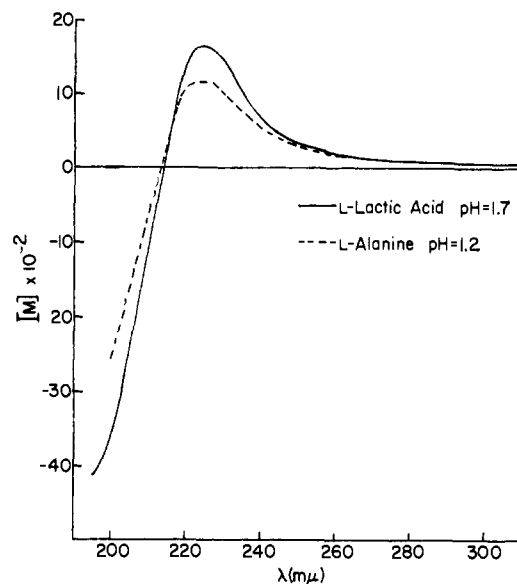
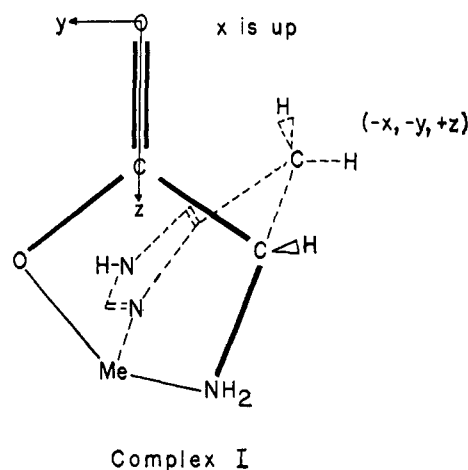


Fig. 8.—Rotatory dispersion curves of L-alanine and L-lactic acid which display the same form as that of L-histidine. These curves present evidence for an n-π* transition.

tion along the carbon-oxygen bond axis, the y-direction in the plane of sp²-hybridization, and the least



polarizable x-direction perpendicular to that plane. All the groups vicinal to the acyl group are now considered. The problem is to determine the dominant distortion of the chromophoric ellipsoid by these neighboring groups. Any group dissected by a plane will have contributions of opposing sign. If the group is bisected by a plane, its contributions will cancel. The farther removed a group is from any plane the larger will be its contribution. The oxygen, metal, and α-carbon atoms and amino group lie in the yz-plane and as they are divided by that plane they would give little or no contribution to the asymmetry. However, the methylene group, CH₂, is well displaced from any plane and yet resides near the acyl group. This CH₂ group would give the principal asymmetry. Its octant is -x, -y, +z, and as it is a polarizable group, the product *Axyz* is negative which means that *A* must be negative. Since the sign of rotation follows the sign of *A*, the extremum at the long wave length side of 220 mμ should be negative, as it is. The imidazole group, if not bisected by the xz-plane, lies more in the -y-direction in which case it would give the same contribution as the methylene group. There is

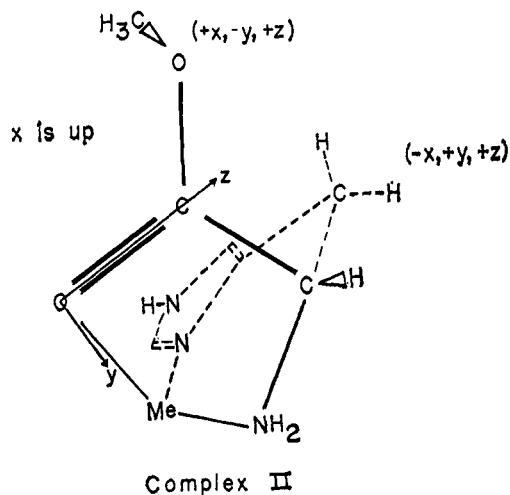
(23) M. Milone and E. Borello in "Advances in Molecular Spectroscopy," Vol. 2, A. Mangini, Ed., Macmillan Co., New York, N. Y., 1962, p. 885.

(24) W. Kuhn and H. Biller, *Z. physik. Chem.*, **B29**, 1 (1953).

(25) D. J. Caldwell, Ph.D. dissertation, Princeton University, 1962.

also the equation of the waters of coordination. Two of the three coordinating water molecules lie in the yz -plane *trans* to the oxygen and amino groups and would contribute little to the rotation. However, the third water is mainly in the $+x$ -, $+y$ - and $+z$ -directions. This would also give a negative A . Thus, a long wave length negative extremum is expected and is found in the L-histidino-metal complexes. However, it should be kept in mind that while the vicinal effect of imidazole has been considered, its effect as a chromophore has been assumed negligible. This assumption should be investigated experimentally in a comparable molecule.

The methyl ester of L-histidine, though it is in chelation with the transition metals,¹² gives a positive Cotton effect in the case of Co(II), Ni(II), and Zn(II). The acyl oxygen of alkyl esters is more electronegative than the alkyl oxygen. If there is any bias in the orientation of the ester group, the conformation given in complex II would be most favored; that is, the



negative acyl oxygen would be directed toward the divalent metal. In this conformation it is seen that the methylene and imidazole groups would constitute the dominant distortion. These groups are in the $-x$ -, $+y$ - and $+z$ -directions. Again, $Axyz$ is taken negative for these polarizable groups, which means that A is positive as the Cotton effect is seen to be all but Cu(II). The crystal field splitting energies of copper are such that it prefers a square-planar complex which may result in insufficient biasing of the ester group's orientation.

The foregoing discussion amounts to the application of an octant rule for which there is abundant experimental evidence.⁴ The early theoretical justification of an octant rule may be found in the work of Kauzmann, Walter, and Eyring²⁶ and of Condon, Altar, and Eyring.¹ A similar interpretation of the data is achieved by critical application of a detailed octant rule for magnetic transitions. Tinoco,²⁷ applying first-order perturbation theory to zero-order wave functions and assuming completely isolated groups, has arrived at a six-term expression for the rotational strength, R_A , of the A th transition in a molecule. This expression contains the previously obtained one-

(26) W. J. Kauzmann, J. E. Walter, and H. Eyring, *Chem. Rev.*, **26**, 339 (1940).

(27) I. Tinoco, *Advan. Chem. Phys.*, **4**, 113 (1962).

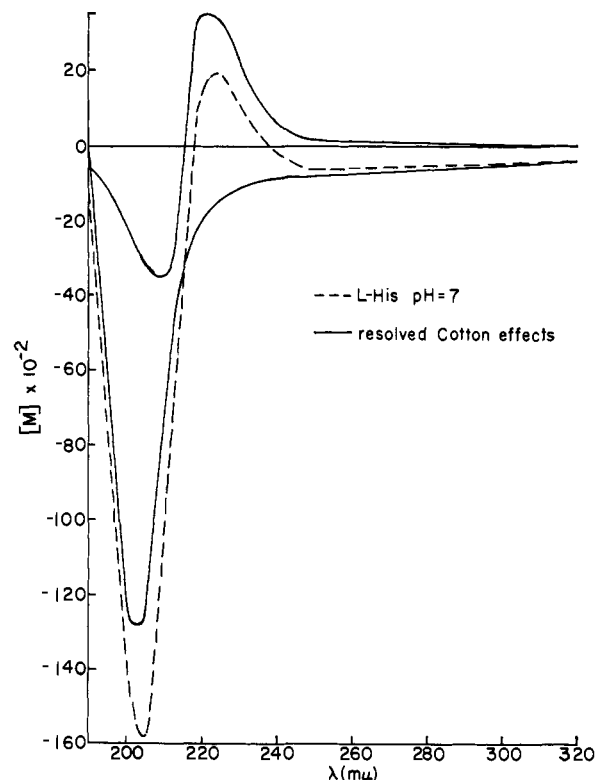


Fig. 9.—Rotatory dispersion curve of L-histidine resolved into two simple Cotton effects.

electron^{1,26} and coupled oscillator² terms. The first term listed by Tinoco has nonzero values only for inherently dissymmetric chromophores, and the sixth term is the electric-electric coupled oscillator term. Therefore, if one considers magnetic transitions in an inherently symmetrical chromophore, the remaining four terms determine the rotational strength of that transition and the sign of its Cotton effect. Caldwell and Eyring,²⁸ using explicit expressions for the perturbing potential, have shown that these four terms are proportional to the static charge, polarizability, and incomplete screening properties of the vicinal group and that for three of these terms the sign of the Cotton effect follows $-\gamma_x\gamma_y\gamma_z$, and that the fourth term has a $-\gamma_x\gamma_y$ sign dependence, where γ_x , γ_y , and γ_z are the direction cosines of the perturbing group. When the static charge of the vicinal group is positive, all three properties add with the same sign. When the static charge of the vicinal group is negative, this effect enters with a sign opposite to that of the polarizability and incomplete screening effects, and explicit evaluation of the magnitudes may be necessary to determine the sign of the Cotton effect. Applications of this octant rule to L-histidine-metal complexes yields the same interpretation as the Jones and Eyring model.

Copper is also unique in that its rotatory dispersion curve displays additional extrema. Edsall, *et al.*,⁹ have reported that copper-histidine complexes have an absorption maximum between 250 and 255 $m\mu$ which is not seen in either of the species alone and which is not found in zinc-imidazole and zinc-histidine systems while an absorption maximum is found with copper-imidazole complexes. This suggests that one is dealing with a charge transfer from imidazole to Cu(II). It is interesting to see how one might apply

(28) D. J. Caldwell and H. Eyring, *Rev. Mod. Phys.*, **35**, 577 (1963).

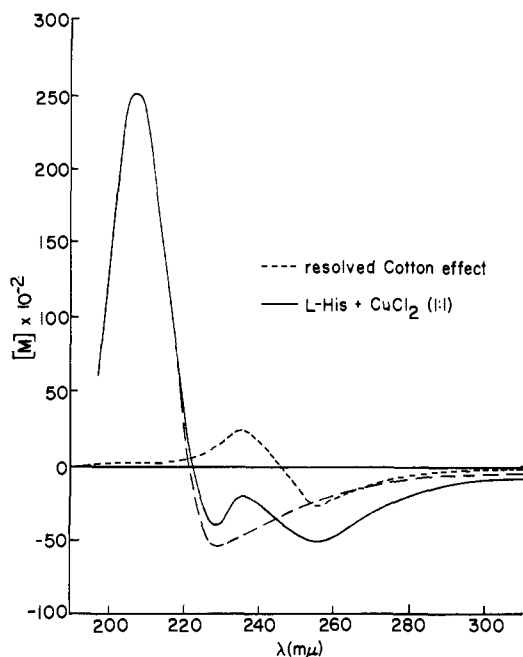
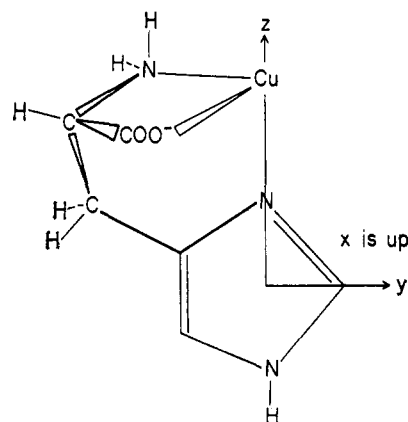


Fig. 10.—Rotatory dispersion curve of the L-histidine-copper complex resolved into a simple Cotton effect and a Cotton effect similar to those of the cobalt, nickel, and zinc complexes.

the many-electron model to this chromophoric electron. Looking at complex I (imidazole plane), it would be reasonable to take the most polarizable z -direction in the direction of charge transfer. The y -direction would be in the imidazole plane and the x -direction would be perpendicular to that plane. All of the groups lie in



Complex I (imidazole plane)

or very near a plane except the carboxylate anion which is clearly the principal perturbation of the "chromophoric ellipsoid." As it is a negative group, the product $Axyz$ would be positive in this direction, that is, the static charge effect is assumed to be dominant, and as xyz is negative, A must be negative, *i.e.*, a negative Cotton effect might be expected. Figure 10 shows that the curve for the L-histidinocopper(II) can be resolved into a curve similar to those of the other transition metals and a negative Cotton effect curve.

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Electron Paramagnetic Resonance Studies of the Electronic Structures of Bis(maleonitriledithiolato)copper(II), -nickel(III), -cobalt(II), and -rhodium(II) Complexes

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The electron paramagnetic resonance spectra of the low spin ($S = 1/2$) planar complexes $[\text{CuS}_4\text{C}_4(\text{CN})_4]^{-2}$, $[\text{CoS}_4\text{C}_4(\text{CN})_4]^{-2}$, $[\text{RhS}_4\text{C}_4(\text{CN})_4]^{-2}$, and $[\text{NiS}_4\text{C}_4(\text{CN})_4]^{-}$ have been obtained at room temperature in magnetically dilute single crystals of diamagnetic $(n\text{-Bu}_4\text{N})_2[\text{NiS}_4\text{C}_4(\text{CN})_4]$ and $(n\text{-Bu}_4\text{N})[\text{CuS}_4\text{C}_4(\text{CN})_4]$, respectively, whose crystal structures are known. It was found that the principal axes of the tensors g and A lie along the symmetry axes of the complex in the crystal, within experimental error. Calculations of g and A are made for several possible ground-state configurations of the metal ion in the complex and are compared with the experimental spin-Hamiltonian. The following probable ground-state hole configurations are deduced: $[\text{CuS}_4\text{C}_4(\text{CN})_4]^{-2}$, $|\epsilon\rangle$; $[\text{CoS}_4\text{C}_4(\text{CN})_4]^{-2}$, $[\text{NiS}_4\text{C}_4(\text{CN})_4]^{-}$, $|\epsilon^2y\rangle$; $[\text{RhS}_4\text{C}_4(\text{CN})_4]$, $|\epsilon^20\rangle$ ($\epsilon \equiv d_{xy}$, $y \equiv d_{yz}$, $0 \equiv d_{z^2-x^2}$, where the z -axis is perpendicular to the molecular plane and the y -axis bisects each ligand). Configurational excitation energies estimated from the spin-Hamiltonians are compared with the optical spectra, and assignments of certain observed electronic transitions are made.

Introduction

Paramagnetic resonance spectroscopy has been extensively utilized in the study of planar chelates of Cu(II), which have a d^9 -electron configuration.²⁻⁹

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We have recently reported on the synthesis and characterization of a series of planar four-coordinate complexes of transition metal ions of the 3d, 4d, and 5d groups which readily undergo oxidation-reduction reactions.¹⁰ These complexes are remarkable in that the geometry of the complex is unaffected by oxidation-reduction reactions, and one can obtain planar complexes containing the transition metal ions in a series of formal oxidation states. The object of this paper is to report on the results of paramagnetic resonance

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