the band at 16 670 cm^{-1} can be assigned either to both the transitions $^2B_{1g} \rightarrow {}^2E_g$ ($xz, yz \rightarrow x^2 - y^2$) and $^2B_{1g} \rightarrow {}^2A_{1g}$ ($z^2 \rightarrow x^2 - y^2$) or only to $^2B_{1g} \rightarrow {}^2E_g$ ($xz, yz \rightarrow x^2 - y^2$). The first suggestion is very possible since in $CuCl_4^{2-}$ the bands do occur respectively at ~14 300 and 8300 cm^{-1}. Higher energies for all these transitions are an indication of stronger ligand field provided by the isothiocyanate ligand. The other higher energy bands must be of charge-transfer origin.

We have further proof of this possibility through our INDO-MO calculation on this complex. The unrestricted Hartree-Fock scheme of the Roothan LCAO type at the INDO level of approximation has been used along with the parameterization scheme of Clack et al.[19] Other details on this nature of calculation are found elsewhere.[20] The two molecular species—planar $[Cu(NCS)_4]^{2-}$ and tetragonally elongated $[Cu(NCS)_4(SCN)_2]^{4-}$—were both studied to find out the effect of distant and bridging SCN groups on both the optical and EPR properties. Though no crystal structure is available on $[(C_2H_5)_4N]_2Cu(NCS)_4$, the bond distances[21] of $CuHg(SCN)_4$ were used in view of the high similarity of the optical absorption spectra of both complexes at least at room temperature. The calculations reveal the ground-state $^2B_{1g}$ for the complex ion with the one-electron molecular orbital ordering as $z^2 < xz, yz < xy < x^2 - y^2$ for both the species. The calculations were also performed for the excited states $^2B_{2g}$, ^2E_g, and $^2A_{1g}$. The calculated values found in Table II agree very well with the experimental ones. However, the calculated energy for $^2A_{1g}$ was found to be unreasonably large and hence not reported here. At least the first two transitions $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2E_g$ which are needed for the interpretation of EPR results have been found to be in excellent agreement, especially for the planar species.

So that the observed spin Hamiltonian parameters could be compared with the calculated ones, equations for $g_\parallel$, $g_\perp$, $A_\parallel$, and $A_\perp$ were derived by employing the complete set of MO coefficients including those of ligands as obtained from the INDO-MO results. Calculated transition energies, a spin-orbit coupling constant (λCu) of 817 cm^{-1}, a value of 0.34 for the Fermi contact term, β, a value of 402×10^{-4} cm^{-1} for P_{Cu} ($=g_n\beta_n g_e\beta_e\langle r^{-3}\rangle$), and all overlap values were also employed. Appropriate spin-orbit coupling constants for the ligand atoms[22] were also introduced. The calculated values given in Table I are in very good agreement with the experimental parameters of the planar complex except for $g_\parallel$. The agreement is even better in the case of the assumed tetragonal complex. The metal coefficients associated with the molecular orbitals b_{1g}, e_g, and b_{2g} are respectively 0.734, 0.969, and 0.953 for the planar complex and 0.756, 0.936, and 0.931 for the tetragonal symmetry as obtained from the INDO-MO calculations. All this tends to prove that the $Cu(NCS)_4^{2-}$ group is essentially planar with the possibility of weak coordination of the neighboring groups. Particular mention may be made of the observation from both theory and experiment that the four pseudohalide ligands are located in a square-planar fashion in this solid rather than its tetrahedral form. It is hoped that this may be borne out by the crystal structural investigation under progress. Yet another interesting observation pertains to the tetraethylammonium tetrakis(isocyanato)cuprate(II), which exhibits magnetic parameters similar to that of the isothiocyanates.

Registry No. $[(C_2H_5)_4N]_2Cu(NCS)_4$, 14127-40-3.

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Coordination Modes of Histidine. Circular Dichroism Study of Copper(II) Complexes of the Schiff Bases Derived from (1*R*)-3-(Hydroxymethylene)camphor and Histidine Derivatives

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Received September 9, 1980

The presence of histidine has been established in a large number of enzyme active centers,[1] and the histidyl residue is probably the most important metal-binding site in biological systems.[2,3] In addition, histidine appears to be involved in copper(II) transport in blood.[4] The investigation of the coordination mode of histidine and histidyl residues in metal complexes is thus very important for the elucidation of structures and functions of histidine-containing biological systems. The results of X-ray crystal and spectral studies of several metal complexes containing histidine[2,5] or histidyl residues[6] have shown that each of the three potential coordination sites of the amino acid can be used for bonding to metal ions, depending upon the pH, the presence of other ligands, and the coordination geometry of the metal ion. However, correlations between spectral and structural data are complicated by the apparent tendency of the histidine residues to form complexes with mixed chelation modes in solution. We report here the chiroptical properties of copper(II) complexes of the Schiff bases formed between (1*R*)-3-(hydroxymethylene)camphor and histidine derivatives (I).[7,8] In these complexes the contribution to the optical activity of glycine-like the histamine-like coordination modes of the histidine residues can be unambiguously established.

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(7) Abbreviations: (1*R*)-3-(hydroxymethylene)camphor anion = hmc; L- or D-histidinate anion = L- or D-his; L- or D-histidine methyl ester = L- or D-hisOCH_3; phenylalaninate anion = phe; glycinate anion = gly: amino acid anion = aa; histamine = him; N^τ-methylhistamine = himNCH_3; pyridine = py; acetate ion = OAc.
(8) The free ligands I and II undergo a tautomeric equilibrium in solution between the enamine and Schiff base forms. In the copper(II) complexes, however, the ligands are bound in the Schiff base form.[10]

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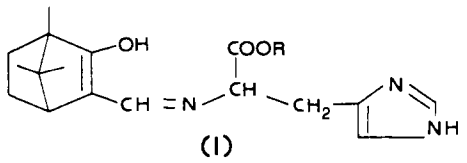
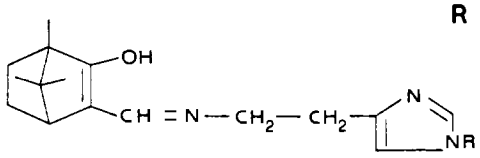


(I)

R = H, CH_3



(II)

Figure 1 shows the electronic and circular dichroism (CD) spectra of Cu(hmc-L-his) and Cu(hmc-D-his)·py[9] in chloroform solution. A quasi-enantiomeric behavior is exhibited by the CD spectra of the diastereoisomeric complexes in the range 300–800 nm, indicating that the absolute configuration of the amino acid is the ruling factor in determining the overall chirality of the complexes. This feature is common to the Cu(hmcaa) complexes and arises from the conformation adopted by the five-membered amino acid chelate ring.[10,11] When the amino acid has L absolute configuration, the amino acid chelate ring in Cu(hmc-L-aa) adopts a λ puckered conformation which gives rise to CD bands of negative sign in the 600–800-nm region of the spectrum, while the hmc chelate ring is almost planar. These distinctive conformational features have been established by the X-ray structural determination of Cu(hmc-L-phe).[11b] In Cu(hmc-L-his) and Cu(hmc-D-his), therefore, the histidine residue chelates glycine-like through the imine nitrogen and carboxylate oxygen donors. The imidazole nitrogen donor atom is also available for coordination in roughly an apical position or binding to a neighboring molecule. The EPR spectra of Cu(hmc-L-his) and Cu(hmc-D-his)·py in frozen chloroform solution (Figure 2) display a ligand field symmetry apparently lower than in the other Cu(hmcaa) complexes,[10] suggesting the tridentate binding mode for the histidine residues.[12]

The CD spectra of Cu(hmc-L-hisOCH_3)OAc and Cu(hmc-D-hisOCH_3)OAc display a rather interesting behavior (Figure 3). The spectra are still almost enantiomeric, indicating that it is the absolute configuration of the amino acid which dictates the chirality of the complexes. However, the signs of the Cotton effects are opposite to those of the Cu(hmcaa) complexes containing an amino acid with the same absolute configuration throughout the spectral range. Thus, for instance in the 600–800-nm region Cu(hmc-L-his) has negative and Cu(hmc-L-hisOCH_3)OAc positive CD activity. Although vicinal effects will probably give some contribution, the observed inversion of Cotton effects can be accounted for by conformational arguments. As inferred from their infrared spectra, in Cu(hmc-L-hisOCH_3)OAc and Cu(hmc-D-hisOCH_3)OAc the carbonyl groups of the amino acid ester residues are not coordinated to the metal ion (ν(C=O) at 1745 cm^{-1} is unshifted from the position in the free ligands). Therefore, in these complexes the histidine residue chelates only through the imine and imidazole nitrogen donors (histamine-like) and the side chain is in the same disposition as for the amino acids with the opposite absolute configuration.

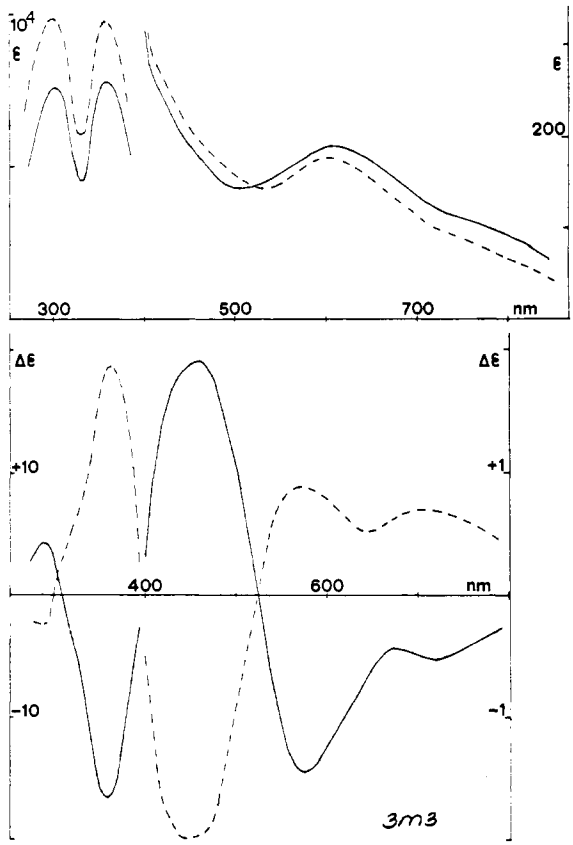


Figure 1. Electronic and circular dichroism spectra of Cu(hmc-L-his) (—) and Cu(hmc-D-his)·py (---) in chloroform solution.

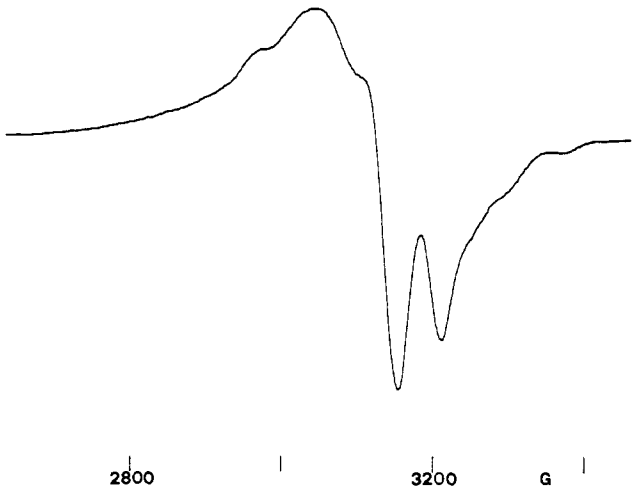


Figure 2. EPR spectrum of Cu(hmc-L-his) in frozen chloroform solution at −160 °C (ν = 9.073 GHz). The EPR spectrum of Cu(hmc-D-his)·py is very similar to that of Cu(hmc-L-his).

The chirality associated with the conformation of the six-membered histidine chelate ring bound through two nitrogen donors (δ in Cu(hmc-L-hisOCH_3)OAc) is thus opposite to that of the conformation adopted by the five-membered chelate ring of the amino acids with the same absolute configuration bound through one amino nitrogen and one carboxyl oxygen donors (λ in Cu(hmc-L-aa)[13]).

(9) The pyridine adduct Cu(hmc-D-his)·py was used instead of Cu(hmc-D-his) for the higher solubility in chloroform.
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(12) We are currently trying to obtain crystals of these complexes suitable for X-ray structural determination.
(13) We cannot explicitly mention a chirality of sign λ for Cu(hcm-L-his) (or δ for Cu(hmc-D-his)) because the histidine residue is probably coordinated as a tridentate chelate in these complexes. The problem of assigning a net chirality when a multidentate ligand has a branch with a ligating atom at its end and this branch is bonded to a nonligating atom has not been solved; see, for instance: Saito, Y. *Top. Stereochem.* **1978**, *10*, 95–174.

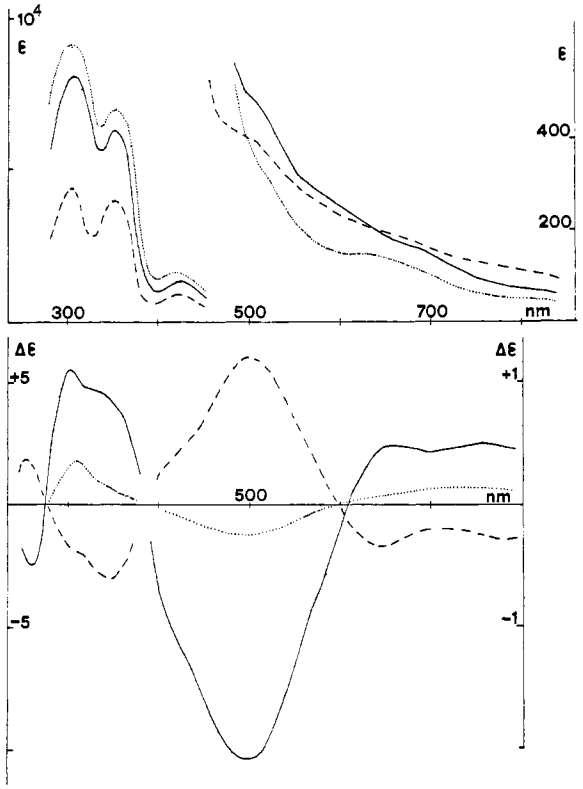

Figure 3. Electronic and circular dichroism spectra of Cu(hmc-L-hisOCH$_3$)OAc (—), Cu(hmc-D-hisOCH$_3$)OAc (---), and Cu(hmchimNCH$_3$)OAc (···) in chloroform solution.

The contribution of the chiral centers of the camphor moiety to the optical activity of the complexes is of only minor entity and can be evaluated by the low-intensity Cotton effects exhibited by the copper(II) complexes of the ligands II, i.e., Cu(hmchim)[14] and Cu(hmchimNCH$_3$)OAc. The CD spectra of these latter complexes display bands of the same sign pattern as Cu(hmc-L-hisOCH$_3$)OAc and Cu(hmc-D-his) (Figure 3). Therefore, the camphor chiral centers induce a chirality of sign δ in the six-membered, N–N bonded, chelate ring of the histamine derivatives. This accounts for the lower amplitude of the CD bands in Cu(hmc-D-hisOCH$_3$)OAc than in Cu(hmc-L-hisOCH$_3$)OAc. It can be noted that chirality of the same sign (δ) is induced by the camphor chiral centers also in the five-membered, N–O bonded, amino acid chelate ring of the Cu(hmcaa) complexes, as it has been found in the CD spectrum of Cu(hmcgly).[10]

Experimental Section

Elemental analyses were from the microanalytical laboratory of the University of Milano. Electronic and circular dichroism spectra were recorded on Beckman DK-2A and on Jobin-Yvonne Mark III instruments, respectively. Infrared spectra were recorded on a Perkin-Elmer 621 spectrophotometer. EPR spectra were recorded on a Varian E-109 spectrometer operating at X-band frequencies.

Preparation of the Complexes. Cu(hmc-L-his), Cu(hmc-D-his). Equimolar amounts of (+)-(hydroxymethylene)camphor and L- or D-histidine (1 mmol) were refluxed in anhydrous methanol (50 mL) for about 2 h. Cupric acetate (1 mmol) was then added to the hot solution, and green precipitates of the complexes readily formed. The products were collected by filtration, washed with a small amount of methanol–water (1:1), and dried under vacuum.

Cu(hmc-L-his)·H$_2$O. Anal. Calcd for $CuC_{17}H_{23}N_3O_4$: C, 51.43; H, 5.84; N, 10.59. Found: C, 51.53; H, 5.99; N, 10.23.

Cu(hmc-D-his)·CH$_3$OH. Anal. Calcd for $CuC_{18}H_{25}N_3O_4$: C, 52.61; H, 6.13; N, 10.23. Found: C, 53.00; H, 6.05; N, 10.17.

The pyridine adduct of Cu(hmc-D-his) was obtained by slow evaporation of a pyridine solution of the complex at room temperature.

Cu(hmc-D-his)·py. Anal. Calcd for $CuC_{22}H_{26}N_4O_3$: C, 57.70; H, 5.68; N, 12.24. Found: C, 56.94; H, 5.27; N, 11.91.

Cu(hmc-L-hisOCH$_3$)OAc, Cu(hmc-D-hisOCH$_3$)OAc, Cu(hmchimNCH$_3$)OAc. Equimolar amounts of (+)-(hydroxymethylene)camphor and free L- or D-histidine methyl ester, or *N*$^\pi$-methylhistamine[15] (1 mmol) (obtained from the corresponding hydrochloride salts and sodium methoxide in absolute ethanol) in methanol (50 mL) were refluxed for about 2 h. Cupric acetate (1 mmol) was then added to the warm solution. The solution was concentrated to a small volume and chromatographed on a Sephadex LH-20 (methanol as eluant). A single main fraction was obtained in each case. This was collected and evaporated to dryness under vacuum.

Cu(hmc-L-hisOCH$_3$)OAc·2H$_2$O. Anal. Calcd for $CuC_{20}H_{31}N_3O_7$: C, 49.13; H, 6.34; N, 7.59. Found: C, 49.83; H, 6.30; N, 7.27.

Cu(hmc-D-hisOCH$_3$)OAc·2H$_2$O. Anal. Calcd for $CuC_{20}H_{31}N_3O_7$: C, 49.13; H, 6.34; N, 7.59. Found: C, 49.56; H, 6.46; N, 7.31.

Cu(hmchimNCH$_3$)OAc·2H$_2$O. Anal. Calcd for $CuC_{19}H_{31}N_3O_5$: C, 51.30; H, 6.97; N, 9.45. Found: C, 51.96; H, 6.40; N, 9.42.

Cu(hmchim). Equimolar amounts of (+)-(hydroxymethylene)-camphor and free histamine (obtained from the dihydrochloride salt and sodium methoxide in absolute ethanol) (1 mmol) in anhydrous methanol (50 mL) were refluxed for about 2 h. Upon addition of cupric acetate (1 mmol) a brown precipitate immediately formed. This was collected by filtration, washed with methanol, and dried under vacuum. Anal. Calcd for $CuC_{16}H_{22}N_3O$: C, 57.22; H, 6.56; N, 12.52. Found: C, 57.42; H, 6.30; N, 12.57.

Acknowledgment. The authors thank the Italian CNR for financial support and Professor Renato Ugo for helpful discussions.

Registry No. Cu(hmc-L-his), 75847-55-1; Cu(hmc-D-his), 75880-25-0; Cu(hmc-D-his)·py, 75847-56-2; Cu(hmc-L-hisOCH$_3$)OAc, 75847-57-3; Cu(hmc-D-hisOCH$_3$)OAc, 75880-26-1; Cu(hmchimNCH$_3$)OAc, 75847-58-4; Cu(hmchim), 75847-59-5; (+)-(hydroxymethylene)camphor, 14681-31-3; D-histidine, 351-50-8; L-histidine, 71-00-1; L-histidine methyl ester, 1499-46-3; D-histidine methyl ester, 17720-12-6; *N*-methylhistamine, 501-75-7; histamine, 51-45-6.

(14) The complex containing a deprotonated imidazole, Cu(hmchim), was obtained as the derivative of histamine. This compound is probably polymeric and completely insoluble in chloroform. However its CD spectrum in pyridine is identical with that of Cu(hmchimNCH$_3$)OAc.

(15) Prepared according to: Durant, G. J.; Emmett, J. C.; Gannellin, C. R.; Roe, A. M.; Slater, R. A. *J. Med. Chem.* **1976**, *19*, 923–928.

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Thionitrosyl-Bridged Rhodium Complexes: Replacement of NO with NS from Transition-Metal Nitrosyl Complexes

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Received September 22, 1980

In recent years there has been considerable speculation about the synthetic and structural studies of metal–thionitrosyl complexes.[1-11] Current interest in the reactions of metal–

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