(3) Atwood, J. L.; Darensbourg, D. J. *Inorg. Chem.* **1977**, *16*, 2314.
(4) Darensbourg, D. J.; Kump, R. L. *Inorg. Chem.* **1978**, *17*, 2680.
(5) Gansow, O. A.; Kimura, B. Y.; Dobson, G. R.; Brown, R. A. *J. Am. Chem. Soc.* **1971**, *93*, 5922.
(6) Braterman, P. S.; Milne, D. W.; Randall, E. W.; Rosenberg, E. *J. Chem. Soc., Dalton Trans.* **1973**, 1027.
(7) Bodner, G. M.; Kahl, S. B.; Bork, K.; Storhoff, B. N.; Wuller, J. E.; Todd, L. J. *Inorg. Chem.* **1973**, *12*, 1071.
(8) Bodner, G. M.; Todd, L. J. *Inorg. Chem.* **1974**, *13*, 1335.
(9) Assignments are based on intensity ratios, relative magnitudes of P–C coupling constants, and spectral measurements on a stereospecifically labeled derivative.
(10) Todd, L. J.; Wilkinson, J. R. *J. Organomet. Chem.* **1974**, *77*, 1.
(11) There is some attenuation of these correlations for tungsten derivatives.
(12) Darensbourg, D. J.; Salzer, A. *J. Am. Chem. Soc.* **1978**, *100*, 4119.
(13) On the basis of kinetic evidence, these amine-displacement reactions proceed with essentially complete amine–molybdenum bond breaking.[2,14]
(14) Hyde, C. L.; Darensbourg, D. J. *Inorg. Chem.* **1973**, *12*, 1286.
(15) Kelly, J. M.; Bent, D. V.; Hermann, H.; Schulte-Frohlinde, D.; Koerner von Gustorf, E. *J. Organomet. Chem.* **1974**, *69*, 259.
(16) The related 16-electron group 6b metal derivative $[Cr(CO)_5]$ has an average characteristic inverse lifetime in CO-saturated cyclohexane solution of $\sim 3 \times 10^4$ s^{-1}.[17,18]
(17) Kelly, J. M.; Hermann, H.; Koerner von Gustorf, E. *J. Chem. Soc., Chem. Commun.* **1973**, 105.
(18) Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1975**, *97*, 3380.
(19) Darensbourg, D. J.; Baldwin, B. J., unpublished results.
(20) Darensbourg, D. J. *Inorg. Chem.* **1979**, *18*, 14.
(21) Ewen, J.; Darensbourg, D. J. *J. Am. Chem. Soc.* **1976**, *98*, 4317.
(22) Darensbourg, D. J.; Alejandro, L., unpublished results.

Contribution from the Istituto di Chimica Generale e Inorganica, Università di Milano, Milano, Italy, and the Central Research Institute for Chemistry of the Hungarian Academy of Science, Budapest, Hungary

Complexes with Diastereoisomeric Ligands. 1. Copper(II) Complexes with the Tridentate Schiff Bases of (1*R*)-3-(Hydroxymethylene)camphor or (1*R*)-2-(Hydroxymethylene)menthone and (*S*)- or (*R*)-Amino Acids

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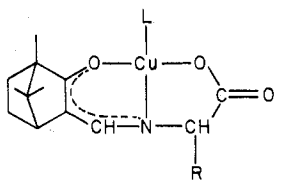
Copper(II) complexes with tridentate Schiff bases derived by the condensation of (+)-(hydroxymethylene)camphor or (+)-(hydroxymethylene)menthone with a series of (*S*)- and (*R*)-amino acids have been synthesized. Little interaction between the various chiral centers has been found and the conformation of the chelate rings depends mainly on the configuration of the α-carbon atom of the amino acid. ESR and electronic spectra results indicate that a competitive mechanism between the σ and π bondings, as well as between the different kinds of σ bondings of the complex, is operative. The variations of the *K* Fermi term are interpreted by considering an exchange polarization of the partially filled 4s orbital.

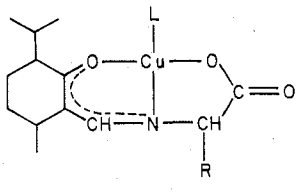
Introduction

The problem of stereoselectivity in the formation of complexes of amino acids with metal ions is still an open question and its understanding is still poor, although relevant effects have often been reported.[2] For instance ternary complexes of the type Cu(*S*-aa′)(*R*,*S*-aa″)[3] have been used to separate aa″ in its optical isomers[4] and some ligand reactions within the coordination sphere have been reported to proceed with a high chiral recognition. Some examples are decarboxylation of 2-amino-2-methylmalonic acid,[5] racemization of amino acids,[6] hydrolysis of amino acid esters,[7] and stereoselective formation of threonine vs. allothreonine.[8] In particular, metal complexes of amino acid Schiff bases have received little attention from the stereochemical[9] standpoint, though their importance as model systems of pyridoxal-dependent enzymes is well-known.[10]

We have therefore synthesized a series of copper(II) complexes with the Schiff bases formed between (1*R*)-3-(hydroxymethylene)camphor or (1*R*)-2-(hydroxymethylene)menthone and a series of (*R*)- or (*S*)-amino acids and studied their conformational properties with the hope of elucidating the behavior of a chiral amino acid in Schiff base chiral environment. The general formulas of the complexes are shown in structures I and II.



I



II

A detailed study of the electronic properties of this new class of compounds has also been carried out to have a deeper knowledge of the coordination and bonding properties of copper(II) complexes with tridentate amino acid Schiff bases. Until now only scattered reports have appeared on this subject.[11,12]

Some preliminary results on the conformational aspects have already appeared[13] and more recently the structure of a member of this class of compounds, namely, [*N*-[(+)-(hydroxymethylidene)camphorato]-(*S*)-phenylalaninato]copper(II), has been resolved.[14] This investigation has shown that the Schiff base has formed through the condensation of the formyl rather than the ketone group of (hydroxymethylene)camphor as was expected on the grounds of previous studies on the Schiff bases formed between the same β-diketone and optically active diamines.[15]

Experimental Section

Analyses (Table I) were from the microanalytical laboratory, the University of Milan. Molecular weights (in chloroform and pyridine) were determined at the Franz Pascher Microanalytisches Laboratorium, Bonn, West Germany. Magnetic moments were measured at 97 and 294 K with the Faraday method; the diamagnetic contribution was calculated with Pascal's constant. Infrared spectra were recorded on a Perkin-Elmer Model 621 spectrophotometer, electronic spectra were recorded on a Beckman DK-2A instrument equipped with a reflectance attachment, and a Varian NV 14 was used to record ^1H NMR spectra with Me_4Si as internal reference. CD spectra were recorded on a Jobin-Yvonne Mark III instrument; solid-state spectra were obtained on potassium bromide pellets of known concentration (weight of product/total weight) and of constant thickness (0.2 mm). ESR spectra were recorded in the atmosphere on a JEOL JES-ME-3X spectrometer with freshly prepared solutions and calibrated with Mn–MgO. Computer simulations of the spectra were carried out on

0020-1669/79/1318-2825$01.00/0

Table I

compd	mp, °C	analyses, % C calcd	C found	H calcd	H found	N calcd	N found	μ, μ_B at 97 K
KH(+)-hmc(*R*)-phe	dec	65.93	65.74	6.32	6.26	3.85	3.78	
KH(+)-hmc(*S*)-phe·1.5H_2O	93	61.32	61.20	6.95	7.10	3.68	3.56	
Cu(+)-hmcgly·H_2O[a]	310	49.29	49.42	6.00	6.31	4.42	4.37	1.7
Cu(+)-hmcgly·py	146	57.30	58.13	5.84	6.17	7.43	7.32	
Cu(+)-hmc(*S*)-leu·H_2O[b]	146	54.76	54.90	7.25	7.50	3.76	3.67	1.9
Cu(+)-hmc(*S*)-leu·PPh_3[c]	188	68.13	68.28	6.49	6.38	2.27	2.32	
Cu(+)-hmc(*R*)-leu·H_2O	215	54.76	54.00	7.25	7.57	3.76	3.67	
Cu(+)-hmc(*S*)-phe[d]	216	61.77	61.30	5.92	6.08	3.60	3.56	2.0
Cu(+)-hmc(*R*)-phe	206	61.77	61.21	5.92	5.93	3.60	3.56	2.0
Cu(+)-hmc(*S*)-val	225	56.39	56.26	6.75	6.56	4.11	3.96	
Cu(+)-hmc(*S*)-tyr·H_2O	154	56.80	56.40	5.92	6.40	3.31	3.25	1.8
[Cu(+)-hmc(*S*)-pro]$C_2H_3O_2$	dec	54.20	54.90	6.27	6.23	3.51	3.60	1.9
K[Cu(+)-hmc(*S*)-glu]·$2H_2O$	310	43.18	42.76	5.39	4.90	3.14	2.95	2.0
$[NH(C_2H_5)_3]$[Cu(+)-hmc(*S*)-glu]·$^1/_2CHCl_3$	131	50.83	50.60	6.87	6.82	5.27	4.92	
Cu(+)-hmc(*S*)-Dopa·H_2O·$^1/_2C_6H_{14}$	204	57.00	56.76	6.62	6.50	2.90	2.72	
Cu(+)-hmc(*SR*)-phe	192	61.77	61.38	5.92	5.93	3.60	3.61	1.9
Cu(±)-hmc(*S*)-phe·$4H_2O$	205	52.11	52.48	6.73	6.23	3.04	2.92	
Cu(±)-hmc(*R*)-phe·$4H_2O$	212	52.11	52.34	6.73	6.51	3.04	2.90	
Cu(+)-hmmgly·H_2O	*e*	48.98	49.28	6.60	6.98	4.40	4.42	1.9
Cu(+)-hmm(*S*)-leu[f]	252	57.22	57.27	7.58	7.74	3.93	4.03	2.0
Cu(+)-hmm(*R*)-leu	111	57.22	57.31	7.58	7.68	3.93	4.01	
Cu(+)-hmm(*S*)-phe	235	61.46	61.70	6.40	6.70	3.58	3.53	2.0
Cu(+)-hmm(*R*)-phe·H_2O	185	58.75	58.55	6.60	5.91	3.42	3.57	
Cu(acac)(*S*)-phe·H_2O	148	51.45	52.41	5.21	5.30	4.28	4.20	
Cu(sal)(*S*)-leu·C_2H_5OH	135	52.60	53.89	6.13	5.98	4.08	3.92	
Cu(sal)(*R*)-leu·H_2O	121	49.60	50.00	5.40	5.60	4.45	4.55	
Cu(sal)(*S*)-phe·1.5H_2O	195	53.70	53.84	4.47	4.28	3.92	3.83	2.0
Cu(sal)(*S*)-phe	202	58.09	58.00	3.93	4.05	4.24	4.17	

[a] Mol wt in chloroform 926 (calcd for trimer 949.5). [b] Mol wt in chloroform 1270 (calcd for trimer 1117.5); mol wt in pyridine 347 (calcd for monomer 372.5). [c] Mol wt in chloroform 526 (calcd for monomer 616.5). [d] Mol wt in chloroform 1115 (calcd for trimer 1165.5). [e] Mp 148 °C and 210 °C. Two different phases. [f] Mol wt in chloroform 1034 (calcd for trimer 1069.5); mol wt in pyridine 361 (calcd for monomer 356.5).

a CDC 3300 computer. Conductivity measurements were performed on a Philips conductometer, PR 9500. Reagent grade chemicals were used in this work. Known literature methods were used for the preparation of (+)-(hydroxymethylene)camphor[17] and (+)-(hydroxymethylene)menthone[18] and their optical rotation agreed with the literature values.

Potassium *N*-[(+)-(Hydroxymethylidene)camphor]-(*S*(*R*))-phenylalaninate. Equimolar amounts of (*S*)- or (*R*)-phenylalanine, (+)-(hydroxymethylene)camphor, and 0.1 N alcoholic potassium hydroxide were refluxed for about 1 h. The yellow solution was concentrated to dryness under reduced pressure. Molar conductivity of a 10^{-3} M methanol solution of the *S* derivative is 68 Ω^{-1} cm^2 at 25 °C, in agreement with a 1:1 electrolyte.[19]

[*N*-[(+)-(Hydroxymethylidene)camphorato]aminoacidato]copper (II). Equimolar amounts of (+)-hmcH and the proper amino acid (glycine, leucine, phenylalanine, valine, and proline) (3 mmol) were dissolved in 50 mL of absolute ethanol and refluxed. When necessary the minimum amount (5 mL) of water was added to ensure complete dissolution of the amino acid. After 2 h the heating was interrupted and an ethanol solution of copper(II) acetate (3 mmol in 50 mL) was added to the warm yellow solution of the Schiff base. If a blue precipitate was obtained, this was removed by filtration. After 1 day the solution was concentrated to 50 mL and allowed to stand until the complex precipitated. The green compound was recovered by filtration, washed with a small amount of ethanol–water (1:1), and dried under vacuum. The derivatives of (*R*)-amino acids were much more soluble in the solvent and a more effective concentration often followed by addition of small amounts of water was necessary to obtain a precipitate. Recrystallization of the crude product was carried out from ethanol (see Table I for elemental analyses). The proline derivative was purified by chromatography on potato starch with ethanol as eluent and it is a 1:1 electrolyte in 10^{-3} M Me_2SO solution (18 Ω^{-1} cm^2).

In the cases of tyrosine, dihydroxyphenylalanine, and glutamic acid, the complete dissolution of the amino acid was achieved on adding 1 mL of triethylamine. Only the glutamic acid derivative, however, was obtained as the triethylammonium salt and was purified by chromatography on potato starch with ethanol as eluent. The potassium salt of the glutamic acid derivative was obtained by carrying out the preparation with an equimolar amount of 0.1 N alcoholic potassium hydroxide. Both of the complexes of glutamic acid are 1:1 electrolytes (K[Cu(+)-hmc(*S*)-glu] Λ_M = 95 Ω^{-1} cm^2 in 10^{-3} M water; $[NH(C_2H_5)_3]$[Cu(+)-hmc(*S*)-glu] Λ_M = 26 Ω^{-1} cm^2 in 10^{-3} M Me_2SO).

[*N*-(+)-[(Hydroxymethylidene)menthonato]aminoacidato]copper(II). The glycine, leucine, and phenylalanine derivatives were prepared according to the standard method described above.

[*N*-(Acetylacetone iminato)-(*S*)-phenylalaninato]copper(II). This compound was prepared with the usual method in the presence of sodium hydrogen carbonate as a buffering agent. After filtration of the inorganic salt, the solution was taken to dryness and the product was purified by elution with chloroform on a potato starch column.

(*N*-Salicylideneaminoacidato)copper(II). They were prepared according to the method reported in the literature.[20] The phenylalaninatocopper(II) compound was dried by azeotropic distillation with benzene.

Results and Discussion

Characterization of the Compounds. In the general procedure of preparation the amino acid was refluxed in ethanol with (+)-hmcH or (+)-hmmH until a yellow solution was obtained; addition of copper(II) acetate to this solution yielded the desired compound. If the yellow solution was taken to dryness, an untreatable material was obtained. However in the case of (*S*)- and (*R*)-phe we isolated and characterized the monopotassium salt of the ligands KH(+)-hmc(*R*)-phe and KH(+)-hmc(*S*)-phe, a 1:1 electrolyte in methanol (see Experimental Section) and also soluble in nonpolar solvents such as tetrachloromethane. The ^{1}H NMR spectra of the compounds, recorded in CD_3OD and $CDCl_3$, show the existence in solution of three isomers and one isomer, respectively. By use of previous literature,[15,21] tentative assignments are given in Figure 1. It is likely that in chloroform the potassium ion is somewhat coordinated thus blocking the molecule in the

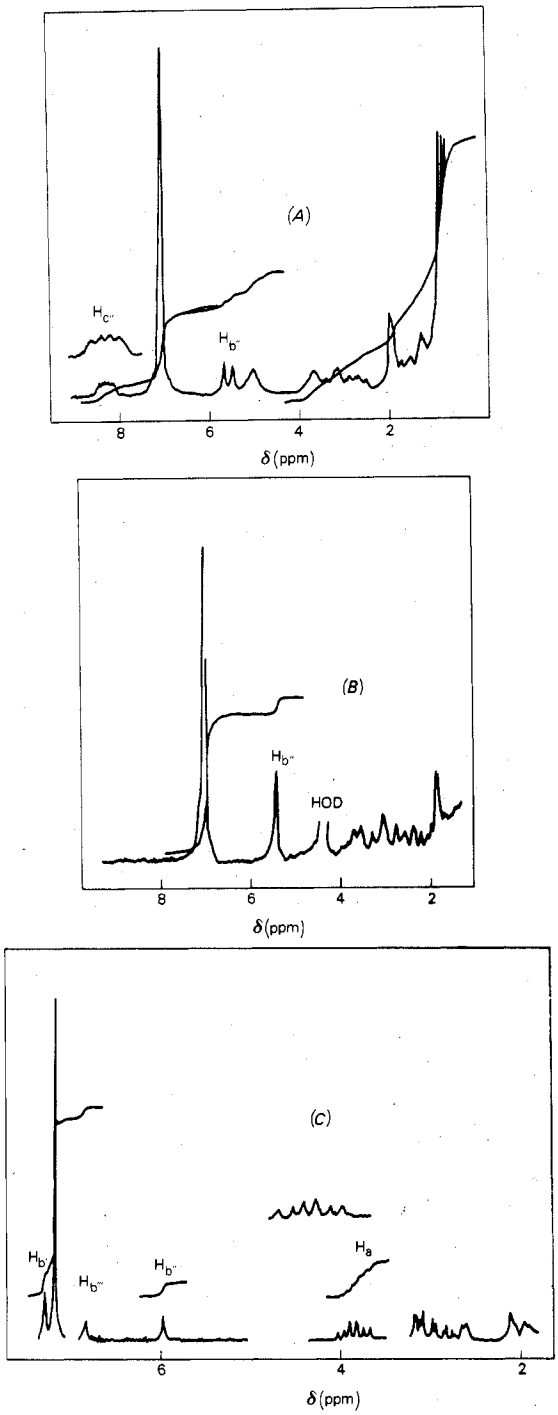
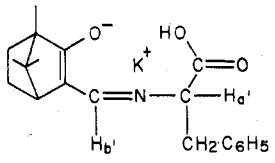
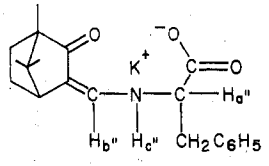


Figure 1. ^{1}H NMR spectra of KH(+)-hmc(*S*)-phe in chloroform-d_1 (A) before and (B) after addition of heavy water and in methanol-d_4 (C).

conformation III or IV, whereas in methanol, where the compounds are dissociated, the anti form of the enamine V can also be present.

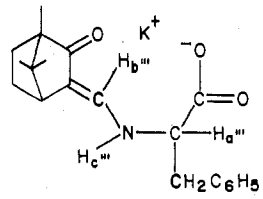


III



IV

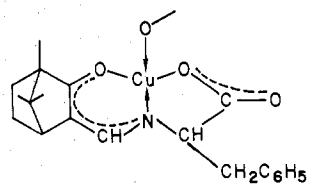
In chloroform the broad signal centered at δ 8.30 ppm is assigned to the c″ proton of IV coupled both with b″ and with



V

a″ protons, $J_{b''c''}$ = 13 Hz and $J_{a''c''}$ = 6 Hz. Proton b″ appears as a doublet centered at 5.55 ppm. The absence of other signals at low field and the correct integration ratios toward the phenyl protons are in accordance with the existence of only IV in chloroform solution. To confirm this assignment, we notice that on addition of D_2O the signal at 8.30 ppm disappears, whereas the 5.55-ppm doublet becomes a singlet. A further confirmation was obtained through spin-decoupling experiments: on irradiation of the 8.30-ppm signal the 5.55-ppm doublet becomes a singlet, whereas upon irradiation of the 5.55-ppm doublet the 8.30-ppm broad signal becomes a doublet. In methanol solution the spectrum is better resolved. Three singlets at low fields, namely, 5.97, 6.81, and 7.30 ppm of relative magnitude 0.25:0.25:0.50 with respect to the phenyl protons, are assigned to the b″, b‴, and b′ protons of the three tautomers IV, V, and III, respectively, in the equilibrium mixture. Moreover in this solvent the resonance of proton a on the α-carbon atom of the amino acid is well defined and it appears as two triplets centered at 3.81 and 3.90 ppm of relative magnitude 0.5:0.5 and assigned to the Schiff base III and enamine IV + V tautomers.

The electronic spectrum of KH(+)-hmc(*S*)-phe gives less information about the isomer distribution in solution: only one broad band at 2.995 μm^{-1} in chloroform and 3.090 μm^{-1} in methanol is present. A marked difference in the position of the absorption bands for the Schiff base and enamine forms was reported for *N*-salicylidenevaline in solution and other pyridoxal analogue Schiff bases with amino acids.[22] In these latter systems the red shift observed in the absorption bands of the enamine form was attributed to a larger extent of delocalization with respect to the Schiff base form, whereas in our case the equilibrium between the two forms does not involve a change in the extent of delocalization. At any rate no trace of free camphor at 3.860 μm^{-1} is detectable in solution. The fact that an enamine–Schiff base equilibrium is present in methanol solution, but only one isomer (the enamine) in chloroform, suggests that the equilibrium is controlled by extended hydrogen bonding and solvating ability of methanol vs. coordinating ability of the ligand toward the potassium ion. The preferred structure of the ligand coordinated to the potassium ion is therefore the enamine IV probably because of the lower stability of an *endo*cyclic double bond in III and of the higher acidity of the carboxyl group. When the ligand becomes dinegative and copper(II) substitutes potassium, a large delocalization occurs as was found in the X-ray structure of Cu(+)-hmc(*S*)-phe (VI).[14] The copper(II) is quasi-planar

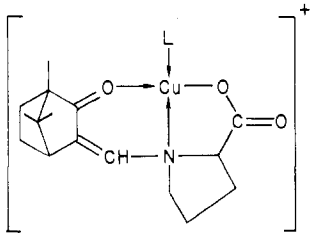


VI

four-coordinate, the fourth coordination position being filled by the oxygen atom of a carboxylate group of a nearby molecule thus giving rise to infinite chains. The other complexes of the series which crystallize with solvent molecules could also be five-coordinate in the solid state, probably with

a solvent molecule in the axial position as it has been reported for many amino acid–Schiff base–copper(II) complexes;[23] however, the structure of Cu(+)-hmc(*S*)-phe seems to suggest that the tendency to pentacoordination must not be overemphasized since the copper(II) ion is known to arrange in a variety of stereochemistries.[24,25] The molecular weights of some of the complexes (Table I) are in agreement with trimeric structures in chloroform to fulfill the coordination requirements of the copper ion, whereas in pyridine the polymeric structure is broken since the compounds were found to be monomers. Pyridine adducts of formula Cu(+)-hmcaa·py have been isolated in the solid state although here again the compounds could be polymers to achieve a possible pentacoordination of the copper(II) ion. The occurrence of a trimeric unit in compounds containing a water molecule, e.g., Cu(+)-hmc-(*S*)-leu·H_2O, would indicate that water is not strongly bound to copper. In fact the triphenylphosphine adduct Cu(+)-hmc(*S*)-leu·PPh_3 is a monomer in chloroform (Table I) showing that the phosphine molecule is sufficiently strong a base to break the association linkages in poor donor solvents. Unfortunately other phosphine adducts, e.g., Cu(+)-hmcgly·PPh_3, and pyridine adducts were not sufficiently soluble for molecular weight measurements to allow the complete settlement of this point.

With glutamic acid and proline, ionic 1:1 electrolyte complexes were obtained: the potassium and triethylammonium salts of [Cu(+)-hmc(*S*)-glu]$^-$ and the acetate of the proline derivative, namely, [Cu(+)-hmc(*S*)-pro]$C_2H_3O_2$. In this case only a pure enamine structure must be present because a secondary nitrogen atom is involved and the most likely structure of the complex is VII. It is likely that in VII



VII

tetracoordination is achieved by coordination of the acetate group, at least in the solid state and in chloroform solution. In donor solvents, competition between solvent molecules and the acetate group can occur, thus accounting for the observed conductivity (see Experimental Section).

Electronic and ESR Spectra. The magnetic moments of some of the compounds here reported are all in the normal range (1.70–2.04 μ_B) for simple spin doublet species and show no evidence of antiferromagnetism down to 97 K (Table I). These data are apparently in contrast with those of copper(II) complexes of similar tridentate Schiff bases of amino acid which, when anhydrous, show subnormal magnetic moments and, when containing coordinated water molecules, behave in a normal way and obey the Curie–Weiss law. In these latter compounds it has been suggested that the presence of the water molecule in the apical position prevents the close packing in the solid state of adjacent molecules to give antiferromagnetic coupling through a superexchange mechanism.[12b,20] As a matter of fact we have isolated the hydrated Cu(sal)(*S*)-phe·$1.5H_2O$ and Cu(acac)(*S*)-phe·H_2O with normal magnetic moments (~1.90 μ_B) whereas subnormal magnetic moments are reported for the anhydrous Cu(sal)(*S*)-phe as well as all the other anhydrous complexes of the series.[12a,20] By contrast no copper–copper interaction has been found either in Cu-(+)-hmc(*S*)-phe or in all the other (+)-(hydroxymethylene)camphor and (+)-(hydroxymethylene)menthone complexes even if anhydrous. This fact could be attributed to some steric hindrance of the bulky terpene moieties which prevents

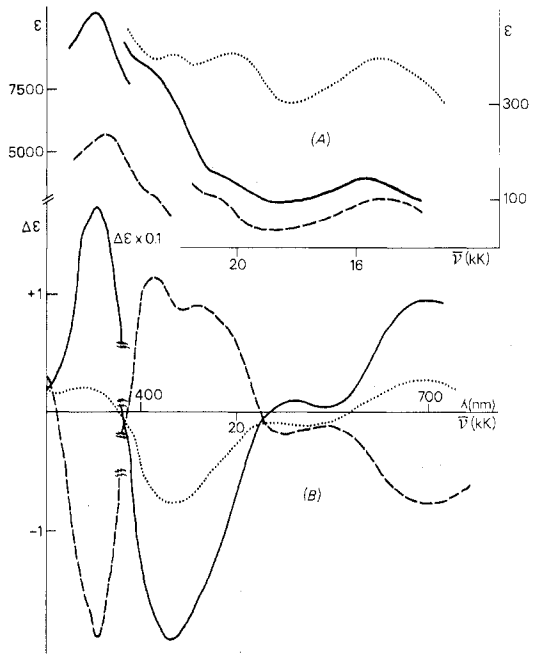


Figure 2. (A) Electronic spectra of Cu(+)-hmc(*S*)-phe in chloroform (—), pyridine (- - -), and the solid state (reflectance, ···). (B) CD spectra in chloroform of Cu(+)-hmc(*S*)-phe (- - -), Cu(+)-hmc(*R*)-phe (—), and Cu(+)-hmcgly (···).

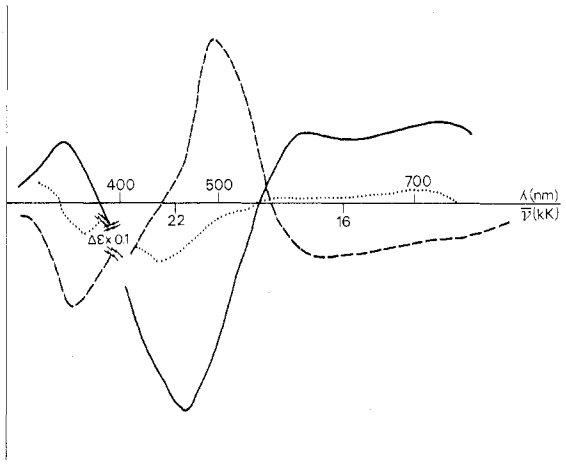


Figure 3. CD spectra in the solid state (KBr disks) of Cu(+)-hmc(*S*)-phe (- - -), Cu(+)-hmc(*R*)-phe (—), and Cu(+)-hmcgly (···).

a favorable packing in the solid state. As a matter of fact no packing of this kind has been found in the structure of Cu-(+)-hmc(*S*)-phe[14] although an infinite polymeric chain is present. The polymer chain is more or less broken in solution but the variation of molecular association is not accompanied by marked spectral changes: the electronic and CD spectra of the investigated compounds reveal a closely similar pattern in the solid state and in chloroform and pyridine solutions (Figures 2–4 and Tables II and III).

The analysis of ESR spectra can give a clue to resolve this contradiction. The ESR spectra (Table IV) taken in frozen solution show a pattern typical for tetragonal symmetry: well-resolved parallel hyperfine structure, slightly or not resolved perpendicular band with strong extra absorptions in the high-field region (Figures 5 and 6). Computer simulations proved that no significant rhombic distortion occurs, which is in accordance with the results of Yokoi,[26] who found that in frozen solution the effective symmetry of the ligand field tends to be higher than the symmetry of the ligand geometry. In a few cases we observed chloroform spectra of superimposed

Table II. Electronic Spectra

compd	solvent	$\bar{\nu}$, μm^{-1} (ϵ)
KH(+)-hmc(*S*)-phe·1.5H_2O	$CHCl_3$	2.995 (17 300)
	MeOH	3.090 (13 800)
Cu(+)-hmcgly·H_2O	$CHCl_3$	1.563 (128); 1.923 sh (120); 2.222 sh (285); 2.381 sh (309); 2.786 (9800); 3.279 (9900)
	py	1.550 (173); 2.128 sh (180); 2.326 sh (263); 2.778 (8560); 3.279 (7230)
	reflctn	1.570; 2.146 sh, br
Cu(+)-hmcgly·py	$CHCl_3$	1.724 (112); 2.000 sh (123); 2.273 sh (511); 2.532 sh (1304); 2.801 (7100); 3.322 (7320)
Cu(+)-hmc(*S*)-leu·H_2O	$CHCl_3$	1.563 (138); 2.392 sh (820); 2.793 (10 400); 3.300 (9050)
Cu(+)-hmc(*S*)-leu·PPh_3	$CHCl_3$	1.538 (39); 1.938 sh (44); 2.381 sh (308); 2.732 (2250); 3.236 sh (6500)
Cu(+)-hmmgly·H_2O	$CHCl_3$	1.577 (197); 2.212 sh (226); 2.967 (7170); 3.125 (7170)
	py	1.587 (170); 2.150 sh (108); 2.500 sh (770); 2.941 (8000)
Cu(acac)(*S*)-phe·H_2O	$CHCl_3$	1.613 (88); 2.326 sh (117); 3.145 (8000)
	Me_2SO	1.539 (86); 2.370 sh (113); 2.667 (390); 3.155 (6900)
Cu(sal)(*S*)-leu·C_2H_5OH	$CHCl_3$	1.618 (183); 2.165 sh (268); 2.725 (3600)
Cu(sal)(*S*)-phe·1.5H_2O	$CHCl_3$	1.563 (115); 2.179 sh (110); 2.710 (4300)

centers (Table IV) which are probably to ascribe to species of different molecular complexity in solution. No spin–spin exchange coupling between copper ions has ever been found in accordance with magnetic data. The ESR spectral parameters together with some computed quantities for some significant compounds are collected in Table IV. The variations of the g hyperfine parameters were interpreted by using the following rules characteristic of copper complexes:[26b] the covalencies of planar and axial bonds have opposite effects on the magnetic parameters; namely, the g factors and hyperfine parameters decrease when the planar bonds become more covalent[12b,37-31] (see, e.g., the series of chromophores O_4, O_2N_2, and N_4), while they increase when the axial bonds become more covalent[29,32-35] (donor solvents). The parameters $A_\parallel$ and partly $g_\parallel$ measured in methanol or chloroform solution of pyridine adducts, such as Cu(+)-hmcgly·py, are smaller

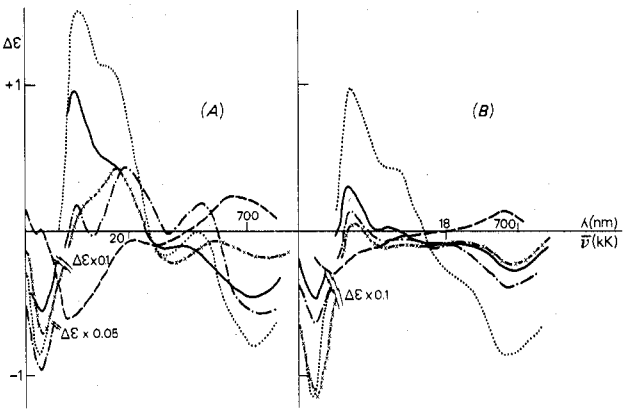


Figure 4. CD spectra in chloroform (A) and in pyridine (B) of a series of Cu(+)-hmc(*S*)-aa. The amino acid derivatives are leu (—), val (···), tyr (-···-), Dopa (- × - × -) and pro (- - -).

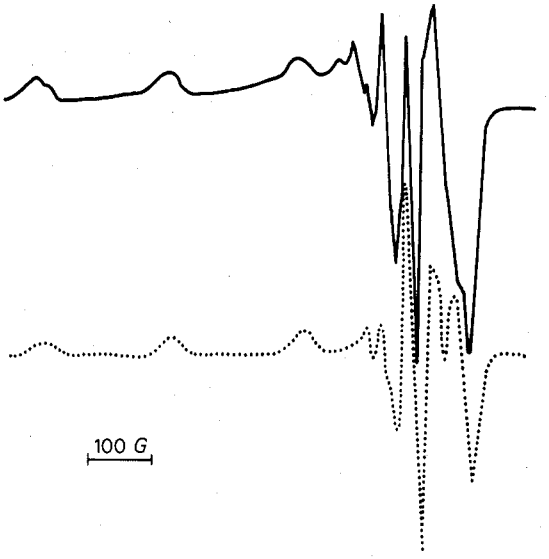


Figure 5. Experimental (top) and computer-simulated (bottom) spectra of Cu(+)-hmm(*S*)-leu in chloroform a 77 K. Simulation parameters are $g_\parallel = 2.23$, $g_\perp = 2.046$, $A_\parallel(^{63}Cu) = 192.9$ G, $A_\parallel(^{65}Cu) = 206.6$ G, $A_\perp(^{63}Cu) = 29.2$ G, $A_\perp(^{65}Cu) = 31.4$ G, and $a_N(1) = 8$ G. Additional small lines in the experimental spectrum are due to an additional center of low concentration.

compared not only to the case when no pyridine is present but also to that recorded in neat pyridine or Me_2SO, where another

Table III. Circular Dichroism Spectra

compd	solvent	$\bar{\nu}$, μm^{-1} ($\epsilon_l - \epsilon_d$)
Cu(+)-hmcgly·H_2O	$CHCl_3$	1.464 (+0.23); 1.754 (−0.10); 2.294 (−0.70); 2.890 (+1.87); 3.333 (+3.44)
	py	1.493 (+0.25); 2.247 (−0.83); 2.597 (−0.40); 2.801 (+1.40)
Cu(+)-hmc(*S*)-leu·H_2O	$CHCl_3$	1.418 (−0.46); 1.776 (−0.14); 2.174 sh (+0.52); 2.451 (+0.97); 2.857 (−5.50)
	py	1.449 (−0.23); 1.754 (−0.07); 2.439 (+0.32); 2.833 (−4.40)
Cu(+)-hmc(*R*)-leu·H_2O	$CHCl_3$	1.440 (+1.06); 1.800 (+0.12); 2.174 sh (−1.68); 2.364 (−2.31); 2.882 (+10.71)
	py	1.471 (+0.99); 1.740 sh (+0.27); 2.040 sh (−1.10); 2.336 (−1.75); 2.817 (+13.62)
Cu(+)-hmc(*S*)-phe	$CHCl_3$	1.422 (−0.71); 1.818 (−0.19); 2.183 (+0.89); 2.415 (+1.12); 2.833 (−18.73); 3.390 (+3.46)
	py	1.462 (−0.56); 1.754 (−0.13); 2.392 (+0.27); 2.801 (−14.70)
Cu(+)-hmc(*R*)-phe	$CHCl_3$	1.456 (+0.96); 1.808 (+0.08); 2.083 sh (−0.90); 2.342 (−1.80); 2.841 (+17.35)
	py	1.502 (+0.96); 1.724 (+0.27); 2.083 (−1.15); 2.326 (−1.47); 2.801 (+20.72)
Cu(±)-hmc(*S*)-phe·4H_2O	$CHCl_3$	1.429 (−0.72); 1.786 (−0.10); 2.082 sh (+0.93); 2.342 (+1.33); 2.833 (−14.70)
Cu(±)-hmc(*R*)-phe·4H_2O	$CHCl_3$	1.422 (+0.83); 1.786 (+0.17); 2.174 sh (−1.30); 2.336 (−1.47); 2.857 (+16.00)
Cu(+)-hmmgly·H_2O	$CHCl_3$	1.486 (+0.14); 1.754 (−0.14); 2.222 (+0.06); 2.817 (+0.12)
Cu(+)-hmm(*S*)-leu	$CHCl_3$	1.493 (−0.99); 1.862 (−0.56); 2.571 (+3.15); 2.950 (−13.22)
	py	1.460 (−0.87); 1.835 (−0.34); 2.062 sh (+0.07); 2.199 sh (+0.34); 2.481 (+1.40); 2.899 (−14.02)
Cu(+)-hmm(*R*)-leu	$CHCl_3$	1.511 (+0.62); 1.923 (+0.10); 2.222 sh (−0.36); 2.525 (−1.09); 2.941 (+6.15)
	py	1.471 (+0.48); 1.887 (+0.07); 2.469 (−0.40); 2.907 (+5.84)
Cu(+)-hmm(*S*)-phe	$CHCl_3$	1.515 (−1.00); 1.855 (−0.50); 2.222 sh (+1.39); 2.480 (+2.60); 2.915 (−10.60)
	py	1.471 (−0.88); 1.825 (−0.28); 2.222 sh (+0.20); 2.457 (+0.74); 2.882 (−22.41)
Cu(+)-hmm(*R*)-phe·H_2O	$CHCl_3$	1.520 (+0.63); 1.887 (+0.16); 2.222 sh (−0.43); 2.500 (−0.89); 2.924 (+11.60)
	py	1.475 (+0.48); 1.887 (+0.10); 2.451 (−0.30); 2.882 (+10.00)

Table IV. Magnetic Parameters and Molecular Orbital Coefficients of Some Complexes

compd	solvent	$g_{\parallel}$[a]	$g_{\perp}$[a]	$10^4A_{\parallel}$,[a] cm^{-1}	10^4K,[b] cm^{-1}	α^2 [c]	β_1^2 [d]	β^2 [e]	ϵ'^2 [f]
Cu(+)-hmcgly·H_2O	$CHCl_3$	*g*	*g*	*g*	118.0				
	MeOH	2.261	2.056	187.0	117.0	0.86	0.76	0.87	0.18
	Me_2SO	2.262	2.055	180.0	120.0	0.84	0.76	0.88	0.13
	py	2.240	2.054	183.0	112.0	0.85	0.70	0.85	0.22
Cu(+)-hmcgly·py	$CHCl_3$	2.241	2.055	175.0	119.0	0.76	0.87	0.97	0.03
	MeOH	2.240	2.051	178.0	114.0	0.79	0.84	0.87	0.13
	py	2.238	2.054	180.0	110.0	0.81	0.72	0.89	0.19
Cu(+)-hmc(*S*)-phe	$CHCl_3$	2.252	*h*	183.0	123.0	0.88	0.71		0.16
	MeOH	2.261	2.056	186.0	119.0	0.86	0.76	0.87	0.17
	Me_2SO	2.257	2.060	183.0	120.0	0.86	0.73	0.94	0.15
	py	2.249	2.051	178.0	113.0	0.82	0.74	0.84	0.16
Cu(+)-hmc(*R*)-phe	$CHCl_3$	2.258	2.054	183.0	123.0	0.87	0.74	0.84	0.14
	MeOH				119.0				
	Me_2SO	2.257	2.060	180.0	120.0	0.84	0.74	0.96	0.13
	py	2.249	2.052	178.0	114.0	0.82	0.74	0.85	0.16
[Cu(+)-hmc(*S*)-pro]$C_2H_3O_2$	$CHCl_3$	2.291	2.068	171.0	117.0	0.72	1.00	1.00	0.00
	MeOH	2.289	2.060	180.0	118.0	0.78	0.92	1.00	0.07
	Me_2SO	2.277	2.057	183.0	116.0	0.80	0.83	0.96	0.12
	py	2.276	2.059	182.0	121.0	0.82	0.80	0.96	0.10
Cu(sal)(*S*)-phe·H_2O	$CHCl_3$	2.269	*h*	182.0	122.0	0.83	0.80		0.10
	MeOH	2.266	2.054	185.0	121.0	0.84	0.79	0.88	0.12
	Me_2SO	2.260	2.064	187.0	116.0	0.87	0.73	0.99	0.21
	py	2.254	2.052	179.0	114.0	0.82	0.75	0.85	0.15

[a] Measured in frozen solution at 77 K. [b] Measured in liquid solution at around 60 °C. [c] See text. [d] Calculated from ΔE_{xy} (band I in the electronic spectra); when this was not available, the position of the band in $CHCl_3$ was used, after a downshift correction of 0.0 μm^{-1} for MeOH, 0.05 μm^{-1} for Me_2SO, and 0.04 μm^{-1} for py. See also ref 36-38. [e] Calculated from $\Delta E_{xz,yz} = 2.20$ μm^{-1}. See also ref 36-38. [f] Calculated from eq 3. [g] Superposition of centers, ambiguous assignment. [h] These data are missing because of the presence of a superposed singlet probably due to molecular associations.

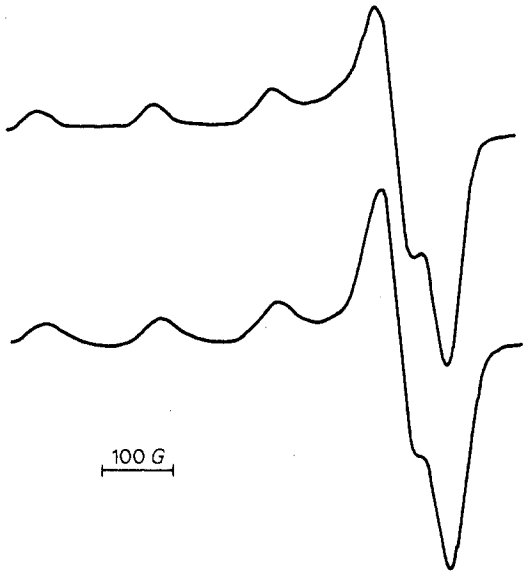


Figure 6. Experimental (top) and simulated (bottom) ESR spectra of Cu(+)-hmc(*S*)-phe in pyridine at 77 K. Simulation parameters are $g_{\parallel} = 2.252$, $g_{\perp} = 2.0506$, $A_{\parallel} = 177.5$ G, and $A_{\perp} = 8$ G.

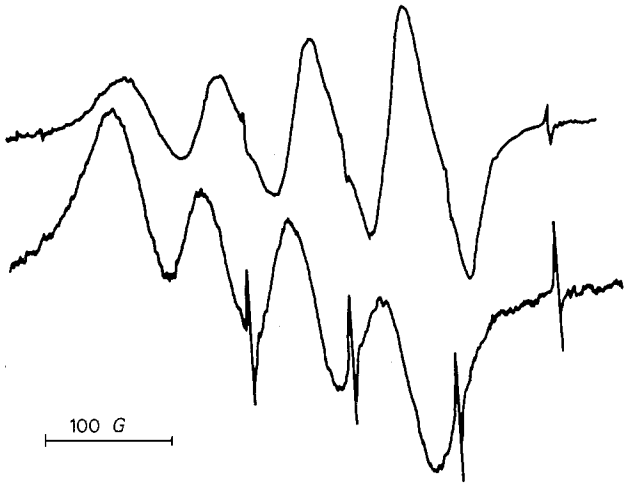


Figure 7. ESR spectra of Cu(+)-hmc(*S*)-val (top) and [Cu(+)-hmc(*S*)-pro]$C_2H_3O_2$ (bottom) in methanol at 60 °C. Marker lines of Mn:MgO are shown.

solvent molecule is likely to coordinate in an axial position. We conclude that coordination of a donor molecule in the plane gives rise to stronger planar covalency while additional axial coordination leads to a stronger axial bond and to a corresponding compensation of magnetic parameters. A similar compensational mechanism may explain the close similarity of electronic and CD spectra in the solid state and in chloroform and pyridine solutions; the shifts of the antibonding energy levels caused by replacement of an oxygen atom of a water molecule or of a carboxyl group of a neighbor unit by donor molecules can be compensated by the additional axial coordination. This assumption is in accordance with the observed variations of the first electronic band of Cu(+)-hmcgly: in chloroform this band is shifted from 1.563 to 1.724 μm^{-1} when one pyridine molecule replaces water, and it returns to 1.550 μm^{-1} when the spectrum is recorded in pyridine.

For the interpretation of the above described trends in terms of ligand field theory we follow the usual scheme.[36-38] We assume an effective tetragonal site symmetry and characterize the planar σ and π and the axial σ and π bonds between the 3d copper and ligand orbitals by the molecular orbital coefficients α, β_1, α_1, and β, respectively. The usual[36-38] expressions of the $g_{\parallel}$, $g_{\perp}$, $A_{\parallel}$, and $A_{\perp}$ spin Hamiltonian parameters and the typical constants of Cu^{2+} ions ($\lambda = -828$ cm^{-1}, $P = 0.036$ cm^{-1}, see ref 39) have been used. As the complexes under study possess rather similar structure, we approximate uniformly the small *f* corrections[38] to 0.04 and 0.067 in the expressions of *g* and *A*, respectively. Since the relation between the *K* Fermi term and the molecular orbital coefficients is rather uncertain,[29,30,33,34,39] we determined the value of *K* from the experimental data. For this purpose we calculated the isotropic g_{iso} and A_{iso} parameters from the liquid solution spectra at around 60 °C, where a well-resolved hy-

perfine pattern can be obtained (Figure 7) and derived K from the relation

$$K = -A_{iso} + P(g_{iso} - 2.0023)(1 + f) \quad (1)$$

where $f = 0.067$. The K values obtained are also included in Table IV.

In the derivation of different molecular orbital coefficients we applied the following procedure. First the parameter α was extracted from the respective $A_{\parallel} + K$ values, i.e., essentially from the dipole–dipole interaction. The advantage of this method is that we can avoid any uncertainty related to the assignment of electronic bands, with the drawback, however, that we have to combine spectral data extracted from different states of solutions (liquid and frozen). This enhances the experimental error to ~5%.

The β_1 and β bonding parameters can be calculated if ΔE_{xy} and $\Delta E_{xz,yz}$ are known from the electronic spectra. The common feature of the electronic spectra in the d–d region is the presence of a band at 1.450–1.660 μm^{-1} which is just resolved from the tail of a much more intense band at higher energy, probably charge transfer in origin, and the presence of shoulders at 1.9–2.2 μm^{-1} on the intense high-energy band. A careful observation of the CD spectra (Figures 2–4) shows that three bands are present in the d–d region (1.4–2.1 μm^{-1}). All the complexes of amino acids with the same absolute configuration (i.e., S) show two clearly defined bands having an opposite sign of the Cotton effect, namely, at ~1.450 μm^{-1}, band I, and ~2.1 μm^{-1}, band III (negative the former, positive the latter); a third band (negative) at intermediate energy, ~1.8 μm^{-1}, band II, is badly resolved. We carried out assignments of the above three bands by assuming reasonable limits for the molecular orbital coefficients, namely, $\alpha^2 \lesssim \beta_1^2 \lesssim \beta^2 \leq 1$; that is the in-plane σ bonding should be at least as covalent as π bondings. This condition leads to reasonable values of β_1 and β, if band I is assigned to ΔE_{xy} and band III to $\Delta E_{xz,yz}$. The assignment of band I to the transition $d_{x^2-y^2} \rightarrow d_{xy}$ harmonizes with the previously discussed shifts of this band in the electronic spectra of Cu(+)-hmcgly. The mono(pyridine) adduct forms stronger planar σ bonding than the water adduct, thus raising ΔE_{xy}; in donor solvents, as Me_2SO and pyridine, where solvent molecules coordinate also in the apical position, the formation of axial bonding weakens the planar bonding via a competitive mechanism between the in-plane and out-of-plane σ bondings, thus lowering ΔE_{xy}.

According to the above tentative assignment the most likely order of the copper d orbitals is $d_{x^2-y^2} > d_{xy} > d_{xz} \sim d_{yz}$, the position of d_{z^2} being not defined.[24,40] This picture can be further refined considering the shifts of CD bands in different solvents (see Figure 4). Band I and band II approach themselves passing from chloroform to pyridine solution; i.e., band II shifts to lower energy and band I to higher energy. The effect on band II may only be due to the lower Cotton effect displayed in pyridine by the intense band III, opposite in sign to the other two, with respect to chloroform. This is supported by the finding that the lowest energy band in the electronic spectrum, which is related to the CD band I occurs at higher energy (~1.5 μm^{-1}) than in the CD spectrum and is usually found at slightly lower energy in pyridine than in chloroform. The low-energy shift of band II is quite general in strong donor solvents (Table III) and seems therefore significant to us of an involvement of solvent coordination. We concluded from ESR evidence that pyridine and Me_2SO should also coordinate in axial position, and since this coordination raises most markedly the energy of the d_{z^2} orbital, we assign the band at ~1.8 μm^{-1} to the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition. The above interpretation would place the d_{z^2} orbital in the following ordering of the copper(II) d orbitals: $d_{x^2-y^2} > d_{xy} > d_{z^2} > d_{xz} \sim d_{yz}$.

The solvent effects, discussed earlier in connection with the variations of spin Hamiltonian parameters and the electronic spectra, can also be treated in terms of molecular orbital parameters. It can be seen from Table IV that in weakly donor solvents the supposedly planar pyridine coordination leads to stronger in-plane σ bonding (α^2 decreases) and, as a compensation, to weaker in-plane π bonding (β_1^2 increases). A similar competition can be recognized when the data for [Cu(+)-hmc(S)-pro]$C_2H_3O_2$ with those of the other complexes are compared. In the former case no π bonding occurs in weak donor solvents ($\beta_1^2 \approx \beta^2 \approx 1$), as can be expected for the tertiary nature of the nitrogen atom, while in the meantime the covalency of in-plane σ bonding is enhanced. In strong donor media the molecular orbital coefficients of complexes with Schiff bases and enamine structure become nearly equal (Table IV), which reveals that the simultaneous planar and axial donor coordination can effectively match the differences of the coordination bonds.

It can also be seen from Table IV that both the bonding and the magnetic parameters are rather close for the menthone, camphor, and salicylaldehyde derivatives thus meaning that the same delocalized π system in the six-membered chelate ring is provided in the three cases.

A comparison of α^2 and the K Fermi term in Table IV shows that the variation of K does not follow the widely accepted relation $K = \alpha^2 K_0$ suggested originally by Maki and McGarvey.[36] The deviation is particularly striking in the case of Cu(+)-hmcgly·py in different solvents where the opposite trend is observed. The failure of such a relationship was found by many authors,[29,30,33,34,39,41] but the proposed explanations are rather divergent.

We think that the decisive factor which influences the K vs. α^2 dependence is the exchange polarization between the unpaired d electron and the fractional electron pair in the 4s orbital. According to the calculations of Watson and Freeman[42] for the neutral copper atom with configuration $3d^9 4s^2$, the exchange polarization of 4s orbital (3.09 au) almost nullifies the net polarization of inner s orbitals (−3.78 au). In the case of our complexes the bonding orbital

$$\varphi_{a_{1g}}{}^{b} = \epsilon' 4s + \epsilon \varphi_L(z^2) \quad (2)$$

transfers charge to the 4s orbital. Then the Fermi term can be written as

$$K = \alpha^2(K_{1s} + K_{2s} + K_{3s} + \epsilon'^2 K_{4s}) \quad (3)$$

Since the Fermi constants derived by McGarvey[39] from the ESR data are slightly larger than the theoretical values obtained from the Hartree–Fock calculation,[42] we assumed $K_{1s} + K_{2s} + K_{3s} = 0.0185$ cm^{-1} and $K_{4s} = -0.015$ cm^{-1}. The ϵ'^2 values calculated by eq 3 are also given in Table IV. Though the uncertainty of this parameter is large, a tendency seems to be evident: when the in-plane σ bonding becomes weaker, the bonding between the 4s orbital and the ligand is stronger. This competition between the two types of σ bonding can explain why the isotropic hyperfine term varies in the opposite direction than would be expected either from chemical evidence or from the variation of g factors.

The line-width alteration in the ESR spectra in liquid solution can be used to obtain information on the molecular structure.[43] We used the amplitude ratio of the fourth and first lines (A_4/A_1) as a measure of line-width variation. Since the anisotropic magnetic parameters are only slightly different, this ratio will directly show the changes in rotational tumbling motion (Table V). At a given temperature and in a given solvent, the intrinsic viscosity being the same, the order of A_4/A_1 ratio will give the order of the effective hydrodynamic radius. It can be seen that in strong donor media, and partly in methanol, the Debye radius is not significantly affected by the nature of diketones (hmc, hmm, or sal) but depends

Table V. Ratio of the Amplitudes of the Fourth and First Hyperfine Lines in the Isotropic ESR Spectra

compd	in Me_2SO at 80 °C	in py at 60 °C	in MeOH at 60 °C	in $CHCl_3$ at 23 °C
Cu(+)-hmcgly·H_2O	3.1	2.8	2.0	
Cu(+)-hmcgly·py	3.1	2.7	3.3	3.4
Cu(+)-hmc(*S*)-phe	4.2	4.3	2.5	11.6
Cu(+)-hmc(*R*)-phe	4.0	4.0	2.6	8.3
Cu(+)-hmc(*S*)-val	3.9	3.0	2.7	6.2
Cu(+)-hmc(*S*)-tyr·H_2O	7.0	6.0	6.6	
[Cu(+)-hmc(*S*)-pro]$C_2H_3O_2$	1.9	2.4	1.0	6.4
Cu(+)-hmc(*S*)-Dopa·H_2O·$^1/_2C_6H_{14}$	8.7	10.8	4.5	4.6
Cu(+)-hmmgly·H_2O	3.1	2.7	1.9	3.5
Cu(+)-hmm(*S*)-leu	3.9	3.8	2.5	13.8
Cu(sal)(*S*)-phe	4.3	4.0	2.7	4.6
Cu(sal)(*S*)-phe·H_2O	5.3	3.8	3.3	13.7

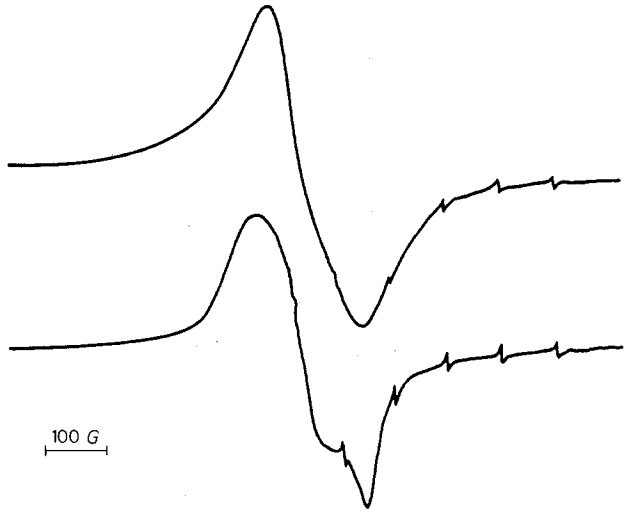
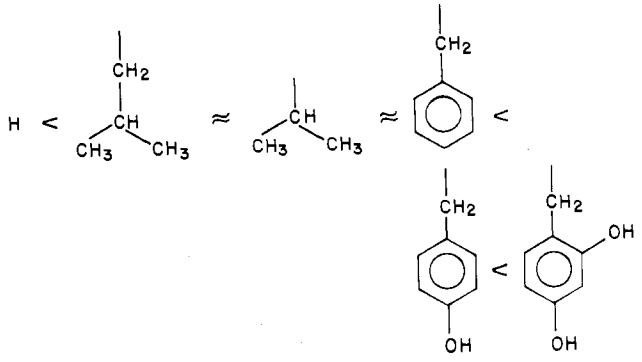


Figure 8. ESR spectra of undiluted powder samples at room temperature of the diastereoisomeric couple Cu(+)-hmc(*S*)-phe (top) and Cu(+)-hmc(*R*)-phe (bottom). Marker lines of Mn:MgO are shown.

strongly on the amino acid side chain. The hydrodynamic radius has been found to increase in the order:



In methanol a few deviations occur showing the role of additional coordinating agents (e.g., pyridine vs. water). It is noteworthy that [Cu(+)-hmc(*S*)-pro]$C_2H_3O_2$ has a markedly smaller radius compared to the Schiff base complexes; the reason is probably due to the fused-ring system leading to a more compact overall geometry. In chloroform we obtained anomalous ordering for A_4/A_1 showing the presence of molecular associations for Cu(+)-hmc(*S*)-phe, Cu(+)-hmm(*S*)-leu, and Cu(sal)(*S*)-phe·H_2O in agreement with the molecular weight measurements.

ESR spectra of undiluted powder samples were also recorded, but all the spectra fell into the uninformative "E" and "F" class in the Hathaway[44] classification. It is of interest, however, that the spectra of the diastereoisomers Cu(+)-hmc(*S*)-phe and Cu(+)-hmc(*R*)-phe show a different pattern (Figure 8) in this phase, though the spectra are nearly identical in any diluted sample. This can be explained by a different packing of neighboring molecules in the two diastereoisomers. We studied also the angular dependence of undiluted Cu(+)-hmc(*S*)-phe single crystals. The spectra consist of a broad singlet in any orientation; only position and width were found to change. The apparent crystal g values obtained are $g_\parallel' = 2.06$ and $g_\perp' = 2.155$. Assuming an inclination angle of 45° between the tetragonal axes of crystallographically nonequivalent molecules on the basis of X-ray data[14] (and also assuming that the effective tetragonal axis is parallel to the normal of the best CuO_3N plane), we obtained the molecular g values[44] as $g_\parallel = 2g_\perp' - g_\parallel' = 2.25$ and $g_\perp = g_\parallel' = 2.06$ in good agreement with the data of the frozen solutions.

The high-energy region of the electronic spectra consists of two intense absorptions at ~2.8 and 3.3 μm^{-1} which occur in all of the complexes (Table II), with the exception of [Cu(+)-hmc(*S*)-pro]$C_2H_3O_2$. The 2.8-μm^{-1} band may be assigned to a $\pi \rightarrow \pi^*$ transition originating in the ligand chromophore, the red shift observed compared to its position in the free ligand, i.e., KH(+)-hmc(*S*)-phe (2.995 μm^{-1} in chloroform, 3.090 μm^{-1} in methanol), being attributed to the increase of conjugation occurring upon coordination.[45] The 3.3-μm^{-1} band may probably be considered as a high-energy charge-transfer band (e.g., $\sigma \rightarrow$ d), on the basis of preceding assignments of other copper(II)–Schiff base complexes.[46] Finally the bands which often appear as shoulders at energies intermediate between the d–d and intraligand transitions can be assigned to lower energy charge-transfer transitions, although their intensity is not as high as could be expected.

Circular Dichroism Spectra. The general pattern of the CD spectra of Cu(+)-hmc(*S*)-aa and Cu(+)-hmm(*S*)-aa (Figures 2–4 and Table III) shows a rather broad negative band at about 1.5 μm^{-1}, a positive band at 2.5 μm^{-1}, and an intense negative one at 2.86 μm^{-1}. The spectra of the derivatives of (*R*)-amino acids are in an almost enantiomeric relationship with those of (*S*)-amino acids; the spectrum of the glycine derivative approaches the differences between the curves of the diastereoisomeric couples ((*S*)-phe, (*R*)-phe; (*S*)-leu, (*R*)-leu). [Cu(+)-hmc(*S*)-pro]$C_2H_3O_2$ presents a spectrum which, in all the ranges studied, is opposite to that of the other amino acids with the same absolute configuration.

Both vicinal[47,48] and conformational[47,49] effects have been proposed to explain the CD spectra of copper(II)–amino acid complexes for which a regional rule[49,50] based on a D_{4h} microsymmetry accounts for most of the observed spectra, although for copper complexes of N-substituted amino acids only conformational effects have been invoked.[51] Regional rules are based on a one-electron static perturbation, but in the presence of delocalized π systems as in the compounds presented in this paper, this model is no longer sufficient to account for the observed trends and conformational effects must also be considered. Moreover in the compounds here presented a D_{4h} microsymmetry is too rough an approximation because of the tetrahedral distortion observed in the reported

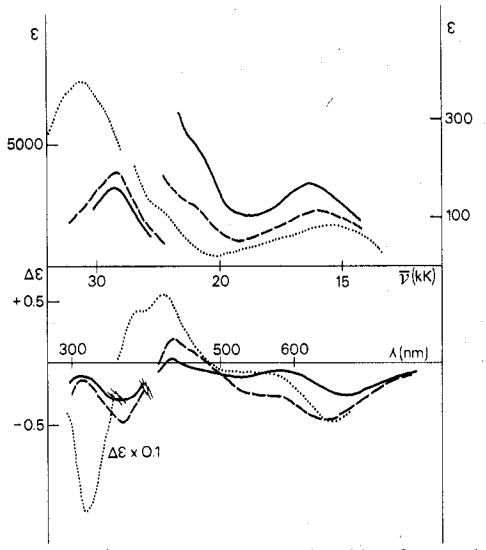
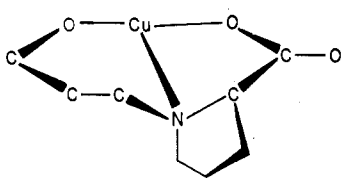


Figure 9. Electronic and CD spectra in chloroform solution of Cu(sal)(*S*)-leu (—), Cu(sal)(*S*)-phe (---), and Cu(acac)(*S*)-phe (···).

structure,[14] which is likely to occur in all the compounds. In Cu(+)-hmc(*S*)-phe the β-diketone chelate ring in the coordination macrocycle is planar whereas the five-membered amino acid ring adopts a λ puckered conformation with the benzyl group axial. It is therefore the configuration of the amino acid which dictates the conformation of the whole macrocycle formed by the two fused chelate rings. We propose on the basis of the following discussion that this conformation is responsible of the observed trends of the CD spectra. The similarity of the CD spectra of this compound in the solid state and in solution (see Figures 3 and 4) suggests that the λ conformation is maintained in solution. Moreover, since all the amino acids with the same absolute configuration display a rather similar CD pattern, it can be concluded that all the compounds here presented having an (*S*)-amino acid (with the exception of proline) adopt the same conformation (λ) of the five-membered chelate ring. On the contrary the complexes with (*R*)-amino acids must have an axial (δ) conformation since their CD spectra are almost enantiomeric of those of the corresponding (*S*)-amino acid compounds. This proposal is also supported by the fact that complexes of the same amino acid with other carbonyl compounds display rather similar spectra although different (menthone vs. camphor) or no (salicylaldehyde or acetylacetone) contribution to the overall chirality could be expected from the ketone (Figure 9). Also the spectra of Cu(±)-hmc(*S*)-phe and Cu(±)-hmc(*R*)-phe are not only enantiomeric but also superimposable on those of the corresponding derivatives of (+)-hmcH. Also the presence of other functional groups in the amino acid side chain does not alter the preferred conformation.

The (*S*)-proline derivative shows in the d–d region a CD pattern opposite to that of the other (*S*)-amino acid derivatives;[52] in this case the presence of a tetrahedral asymmetric nitrogen atom should distort the system of the camphor moiety from planarity. From models it appears that the least distortion occurs when the amino acid chelate ring is in a δ conformation (VIII). Although the nitrogen atom of proline



VIII

coordinates stereoselectively with an *S* configuration, the conformational features of the chelate rings are dictated by the presence of another substituent at the nitrogen atom as suggested by the structure of bis(*N*-benzylprolinato)copper(II).[53]

As for the contribution of the terpene moiety to the overall chirality it can be noted that Cu(+)-hmcgly and Cu(+)-hmmgly exhibit CD spectra which are almost an average of those of the diastereoisomeric pairs with two nearly isodichroic points at 1.89 and 2.60 μm^{-1} and display a sign pattern analogous to that of the complexes with (*R*)-amino acids. It is worth noting that the derivative of racemic amino acids (Cu(+)-hmc(*SR*)-aa) have CD spectra which are very similar to that of the glycine complex. From this evidence we tentatively conclude that the chiral centers of the camphor moiety induce a chirality in the five-membered chelate ring of glycine of sign δ. This induction, however, is not large enough to dictate the preferred conformation of the five-membered chelate ring when chiral amino acids substitute glycine. The chirality of the α carbon of the amino acid now becomes the ruling factor of the conformation of the whole coordination set. The minor contribution of the chiral centers of the camphor may exert a lowering of the absolute value of the ω angle (defined as the dihedral angle between (M–)OOC and CCN)[50] in the case of the (*S*)-amino acids (λ conformation) since these give CD spectra of lower intensity than the corresponding *R* isomers (δ conformation).

Another possibility is that, in solution, a dynamic conformational λ ⇌ δ equilibrium of the amino acid chelate ring can be present. The position of the equilibrium would be determined by the chiral centers of the terpene and the presence of substituents at the α-carbon atom of the amino acid. Such an equilibrium has been proposed for other metal complexes of quadridentate Schiff bases with optically active 1,2-diamines.[54] A separation of the four possible isomers of VOsal(±)-pn has also been reported.[55] Attempts to separate by chromatography the two possible λ and δ conformational isomers of Cu(+)-hmcgly were, however, unsuccessful.

By comparison of the CD spectra in the solid state and in different solvents it can be seen that the general pattern is maintained only with a lowering of the intensities of the bands passing from chloroform to more coordinating solvents (Me_2SO, py)(Figure 4 and Table III) whereas for instance inversions of sign have been reported for other copper(II) complexes both passing from the solid state to solution[50,56] or from chloroform to pyridine solution.[54b] These facts have been explained with an inversion of the conformation of the chelate rings, due to new steric repulsion arising from the change of the coordination number.[54b] In the compounds here presented it is likely that the conformation of the chelate ring is essentially modified by neither the probable presence of coordinated solvent molecules nor a different degree of molecular aggregation (polymeric in the solid state, trimeric in chloroform, and monomeric in pyridine).

Inspection of the CD spectra of the diastereoisomeric potassium salts of the ligand (KH(+)-hmc(*S*)-phe and KH-(+)-hmc(*R*)-phe) in methanol and chloroform suggests some additional rather interesting consideration. The CD spectra of the diastereoisomeric couple consist mainly of two bands at ~2.90 and 3.30 μm^{-1} (Figure 10). The high-energy band appears as a shoulder of the 3.0-μm^{-1} band in the electronic spectrum and is related to the chirality of the camphor asymmetric carbon atoms, as it is always positive, whereas the low-energy band must be related to the chirality of the amino acid moiety, its sign being positive for the (*R*)-phe and negative for the (*S*)-phe derivative. The magnitude of the Cotton effect depends on the contribution of isomers III, IV, and V present in solution. Therefore the spectra are difficult to rationalize but it is interesting to note that in chloroform, where only

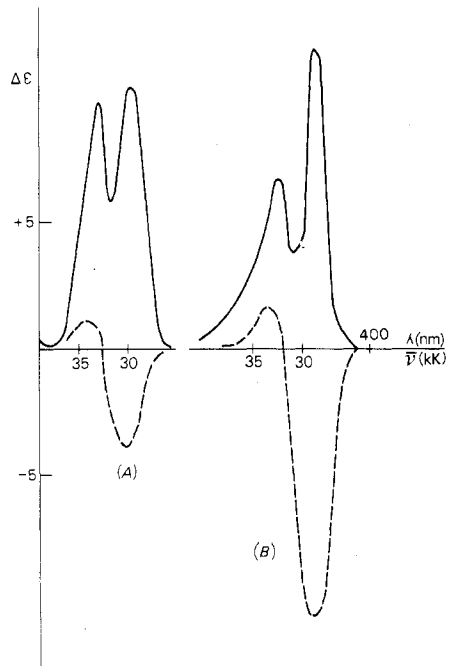


Figure 10. CD spectra in methanol (A) and in chloroform (B) of KH(+)-hmc(*S*)-phe (- - -) and KH(+)-hmc(*R*)-phe (—).

isomer IV exists, the ~2.9-μm^{-1} band has an enantiomeric behavior with respect to the absolute configuration of the amino acid. Since a similar behavior is shown by all the diastereoisomeric couples of the complexes here presented and since in IV the potassium ion is coordinated, we conclude that the enantiomeric relationship of the CD spectra is a conformational feature which arises solely from coordination.

Conclusions

It has been reported that in bis(aminoacidato)copper(II) complexes a number of different conformations varying from axial to envelope and to equatorial are thermodynamically equally possible provided the ω angle lies between −30 and +30°.[50] In the compounds here described this does not seem to be the case since, on the contrary, the amino acid prefers only the axial conformation which is so stable to dictate the main conformational feature of the whole coordination set. Such a relevant stereospecific effect is usually not observed in complexes of amino acid with apolar side chains and must be related to the presence of the Schiff base; it can be considered as an example of the more general case of square-planar complexes of Schiff bases of the type M(sal)((±)-diamine) where the substituents of the chiral carbon atom are axial rather than equatorial.[54b]

The reason for the inversion of the conformation from amino acids or diamine to their Schiff base complexes must be related to factors as increased rigidity, the presence of new coordination sites, and steric hindrance between the azomethine hydrogen atom and the substituent at the α-carbon atom.[14,54b] Coordination plays a rather important role, since, upon complex formation some degrees of freedom are lost, and the final conformation will depend both on the spatial orientation that the ligand must assume because of the geometrical requirements of the metal ion and on the degree of geometrical distortion undergone by the complex to meet the structural restriction of the ligand itself. The result of the subtle balance of these factors is, in the present case, a small tetrahedral distortion of the essentially planar geometry of the copper environment. The principal responsible of such a distortion is likely to be the bulkiness of the substituent R of the amino acid. This effect is difficult to evaluate quantitatively, but it is noteworthy that the amplitude of the Cotton effect of the 2.8-μm^{-1} band, related to the delocalized π system, roughly follows the order of the hydrodynamic radius (as inferred from ESR data) and that this depends on the nature of *R* and not on the diketone used.

The enantiomeric behavior of the circular dichroism spectra of the derivatives of (*R*)- and (*S*)-amino acids suggests two considerations. First any stereoselectivity in any reaction at the α-carbon atom in an amino acid–Schiff base–metal ion system, as in the pyridoxal potentiated enzymes, should have its origin from a chiral environment other than the Schiff base as the large apoenzyme, since a planar delocalized π system separates the chiral centers of the camphor from the α-carbon atom. A model example is the stereoselectivity of formation of threonine and allothreonine by condensation of acetaldehyde to potassium bis(*N*-salicylideneglycinato)cobaltate(III),[9b] where the chiral environment is provided by the octahedral cobalt complex and not by the Schiff base which is strictly planar. Although chiral Schiff bases have sometimes been used successfully,[9a,57] in the cases reported, no delocalized π systems were present or large chiral organic parts were attached to the carbonyl residue, and it could be that asymmetric through the space interactions provided the chiral environment.

In a complex of the type ML′L″ (where L′ and L″ are two chiral chelates and M is an intrinsically asymmetric metal center as the planar Cu(II) ion) the most favorable situations which give rise to a diastereoisomeric behavior are when the chiral centers are both in the chelate ring and/or when stereospecific interactions between L′ and L″ occur as in Cu(*R*-, *S*-glu)(*S*-arginine),[4] where electrostatic interactions between the side chains have been invoked to explain the observed stereoselectivity.

Only in the solid state do Cu(+)-hmc(*S*)-phe and Cu(+)-hmc(*R*)-phe become diastereoisomers because of the different crystal packings, which give rise not only to different solubility[14] but also to different ESR spectra of undiluted samples (Figure 8).

In diluted samples the spectra are similar and rather like those of all the other complexes here described, suggesting that, in solution, the ligand field symmetry is higher than the ligand geometry; i.e. the tetrahedral distortion, responsible of the observed Cotton effects, does not alter the essentially tetragonal symmetry of the ligand field. The electronic situation is the same for all the complexes, despite the difference of the ketone moiety (menthone, camphor, or salicylaldehyde), with the obvious exception of the proline derivative. It is interesting to note that the extended π system is not present in the potassium salt, as shown by NMR spectroscopy, but occurs only upon complexation and that, therefore, it is the formation of the complex that makes the enantiomeric behavior observed in solution possible.

Finally the tridentate ligand poses the problem of the saturation of the coordination sites of the copper ion. Tetracoordination can be achieved by water, a carboxylate group of another molecule, or pyridine. In donor solvents axial coordination is also possible; however, the observed increase of the values of $A_{\parallel}$ from Cu(+)-hmcgly·py in chloroform to Cu(+)-hmcgly·H_2O and to the pyridine solution of Cu(+)-hmcaa are in accordance with a decrease of covalency in the coordination plane and an increase in the axial coordination, with a corresponding compensation of the magnetic parameters. The same trend holds for the variation of the calculated molecular orbital parameters α^2 and β_1^2, related to in-plane σ bonding and π bonding, respectively, thus supporting the existence of a competitive mechanism between the σ and π bonding as well as the different (in-plane and axial) σ bondings.

The *K* Fermi constants, calculated from the isotropic parameters A_{iso} and g_{iso}, show an anomalous behavior and do not

follow the $K = \alpha^2 K_0$ approximation. An exchange polarization between the unpaired d electron and fractional $4s^2$ density seems to be important in this case as well as a competition between the strengths of the in-plane and axial σ bondings, which could explain why the isotropic hyperfine term varies in a direction opposite that which would be expected.

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Registry No. KH(+)-hmc(*R*)-phe, 70913-25-6; KH(+)-hmc(*S*)-phe, 70981-16-7; Cu(+)-hmcgly, 70940-73-7; Cu(+)-hmcgly·py, 70940-74-8; Cu(+)-hmc(*S*)-leu, 70940-75-9; Cu(+)-hmc(*S*)-leu·PPh_3, 70940-76-0; Cu(+)-hmc(*R*)-leu, 70981-70-3; Cu(+)-hmc(*S*)-phe, 71030-73-4; Cu(+)-hmc(*R*)-phe, 71030-72-3; Cu(+)-hmc(*S*)-val, 70940-77-1; Cu(+)-hmc(*S*)tyr, 70940-78-2; [Cu(+)-hmc(*S*)-pro]-$C_2H_3O_2$, 70940-79-3; K[Cu(+)-hmc(*S*)-glu], 70940-80-6; [NH-$(C_2H_5)_3$][Cu(+)-hmc(*S*)-glu], 71981-73-6; Cu(+)-hmc(*S*)-Dopa, 70982-60-4; Cu(+)-hmc(*SR*)-phe, 70940-81-7; Cu(±)-hmc(*S*)-phe, 70940-82-8; Cu(±)-hmc(*R*)-phe, 70940-83-9; Cu(+)-hmmgly, 70940-84-0; Cu(+)-hmm(*S*)-leu, 70940-85-1; Cu(+)-hmm(*R*)-leu, 70981-74-7; Cu(+)-hmm(*S*)-phe, 70940-86-2; Cu(+)-hmm(*R*)-phe, 71030-74-5; Cu(acac)(*S*)-phe, 70982-61-5; Cu(sal)(*S*)-leu, 38840-38-9; Cu(sal)(*R*)-leu, 70940-88-4; Cu(sal)-L-phe, 38840-37-8; Cu-(sal)-D-phe, 70940-87-3; (+)-hmcH, 14681-31-3; (+)-hmmH, 31527-09-0; gly, 56-40-6; (*R*)-leu, 328-38-1; (*S*)-leu, 61-90-5; (*R*)-phe, 673-06-3; (*S*)-phe, 63-91-2; (*S*)-val, 72-18-4; (*S*)-pro, 7005-20-1; (*S*)-tyr, 55520-40-6; (*S*)-Dopa, 59-92-7; (*S*)-glu, 56-86-0.

Supplementary Material Available: Electronic and circular dichroism spectra (extensions of Tables II and III) of all the compounds synthesized (7 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Università di Milano. (b) Hungarian Academy of Science.
(2) Dunlop, J. H.; Gillard, R. D. *Adv. Inorg. Chem. Radiochem.* **1966**, *9*, 185. Davankov, V. A.; Kurganov, A. A.; Rogozhin, S. V. *Russ. Chem. Rev. (Engl. Transl.)* **1974**, *43*, 764. Pasini, A.; Casella, L. *J. Inorg. Nucl. Chem.* **1974**, *36*, 2133. Brookes, G.; Pettit, L. D. *J. Chem. Soc., Chem. Commun.* **1974**, 813. Swash, J. L. M.; Pettit, L. D. *Inorg. Chim. Acta* **1976**, *19*, 19. Bedell, S. A.; Rechani, P. R.; Angelici, R. J.; Nakon, R. *Inorg. Chem.* **1977**, *16*, 972.
(3) Abbreviations used throughout this paper are hmc and hmm, (hydroxymethylene)camphor and (hydroxymethylene)menthone anions respectively; aa is an amino acid anion; the abbreviation for the anions of the particular amino acid are gly = glycine, leu = leucine, phe = phenylalanine, val = valine, tyr = tyrosine, pro = proline, glu = glutamic acid, and Dopa = dihydroxyphenylalanine.
(4) Sakurai, T.; Yamauchi, O.; Nakahara, A. *J. Chem. Soc., Chem. Commun.* **1976**, 553. Porter, S. K.; Angelici, R. J.; Clardy, J. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 21.
(5) Asperger, R. G.; Liu, C. F. *Inorg. Chem.* **1967**, *6*, 796. Job, R.; Bruice, T. C. *J. Chem. Soc., Chem. Commun.* **1973**, 332.
(6) Hirota, K.; Izumi, J. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2287.
(7) Leach, B. E.; Angelici, R. J. *J. Am. Chem. Soc.* **1969**, *91*, 6296.
(8) Murakami, M.; Takahashi, K. *Bull. Chem. Soc. Jpn.* **1959**, *32*, 308. Dabrowiak, J. C.; Cooke, D. W. *Inorg. Chem.* **1975**, *14*, 1305.
(9) (a) Kuzuhara, H.; Iwata, M.; Emoto, S. *J. Am. Chem. Soc.* **1977**, *99*, 4173. (b) Belokon', Yu. N.; Belikov, V. M.; Vitt, S. V.; Dolgaya, M. M.; Savel'eva, T. F. *J. Chem. Soc., Chem. Commun.* **1975**, *86*. Belokon', Yu. N.; Belikov, V. M.; Vitt, S. V.; Savel'eva, T. F.; Burbelo, V. M.; Bakhmutov, V. I.; Aleksandrov, G. G.; Struchkov, Yu. T. *Tetrahedron* **1977**, *33*, 2551.
(10) Snell, E. E.; Braunstein, A. E.; Severin, E. S.; Torchinsky, Y. M., Eds. "Pyridoxal Catalysis: Enzymes and Model Systems"; Interscience: New York, 1968. Holm, R. H. "Inorganic Biochemistry"; Eichorn, G. L., Ed.; Elsevier: New York, 1973; p 1137.
(11) Theriot, L. J.; Carlisle, G. O.; Hu, H. J. *J. Inorg. Nucl. Chem.* **1969**, *31*, 2891. Carlisle, G. O.; Theriot, L. J. *Ibid.* **1973**, *35*, 2093. Chow, S. T.; Johns, D. M.; McAuliffe, C. A. *Inorg. Chim. Acta* **1977**, *22*, 1. Wrobleski, J. T.; Long, G. J. *Inorg. Chem.* **1977**, *16*, 2752.
(12) (a) Carlisle, G. O.; Ganguli, K. K.; Theriot, L. J. *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 527. (b) Zyzyck, L. A.; Frummer, H.; Villa, J. F. *J. Inorg. Nucl. Chem.* **1975**, *37*, 1653.
(13) Casella, L.; Gullotti, M.; Pasini, A.; Visca, M. *Inorg. Chim. Acta* **1976**, *19*, L9.
(14) Ciani, G.; Manassero, M.; Sironi, A.; Casella, L.; Gullotti, M.; Pasini, A. *Inorg. Chim. Acta* **1978**, *26*, L1.
(15) Gullotti, M.; Pasini, A.; Fantucci, P.; Ugo, R.; Gillard, R. D. *Gazz. Chim. Ital.* **1972**, *102*, 855. Jensen, H. P.; Larsen, E. *Ibid.* **1977**, *107*, 143.
(16) We thank Dr. M. Gargano, the University of Bari, for performing the measurements.
(17) Bishop, A. W.; Claisen, L.; Sinclair, W. *Justus Liebigs Ann. Chem.* **1894**, *281*, 314.
(18) Bishop, A. W.; Claisen, L.; Sinclair, W. *Justus Liebigs Ann. Chem.* **1894**, *281*, 394.
(19) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.
(20) Carlisle, G. O.; Syamal, A.; Ganguli, K. K.; Theriot, L. J. *J. Inorg. Nucl. Chem.* **1972**, *34*, 2761.
(21) Jensen, H. P.; Larsen, E. *Acta Chem. Scand., Ser. A* **1975**, *29*, 157.
(22) Heinert, D.; Martell, A. E. *J. Am. Chem. Soc.* **1963**, *85*, 183.
(23) Ueki, T.; Ashida, T.; Sazada, Y.; Kakudo, M. *Acta Crystallogr.* **1967**, *22*, 870. Ueki, T.; Ashida, T.; Sazada, Y.; Kakudo, M. *Acta Crystallogr., Sect. B* **1969**, *25*, 328. Nakao, Y.; Sazaki, S.; Sakurai, K.; Nakahara, A. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 1536. Cutfield, J. F.; Hall, D.; Waters, T. N. *Chem. Commun.* **1967**, 785. Bentley, G. A.; Waters, J. M.; Waters, T. N. *Chem. Commun.* **1968**, 988.
(24) Hathaway, B. J.; Billing, D. E. *Coord. Chem. Rev.* **1970**, *5*, 143. Hathaway, B. J. *Struct. Bonding (Berlin)* **1973**, *14*, 49.
(25) Calligaris, M.; Nardin, G.; Randaccio, L. *Coord. Chem. Rev.* **1972**, *7*, 385.
(26) (a) Yokoi, H.; Otagiri, M.; Isobe, T. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2395. (b) Yokoi, H.; Sai, M.; Isobe, T.; Ohsawa, S. *Ibid.* **1972**, *45*, 2189.
(27) Adato, I.; Ben-Bassat, A. H. I.; Sarel, S. *J. Phys. Chem.* **1971**, *75*, 3828.
(28) Yokoi, H.; Isobe, T. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 2187.
(29) (a) Kuska, H. A.; Rogers, M. T. *J. Chem. Phys.* **1965**, *43*, 1744. (b) Kuska, H. A.; Rogers, M. T.; Drullinger, R. E. *J. Phys. Chem.* **1967**, *71*, 109.
(30) Chiang, T. C. *J. Chem. Phys.* **1968**, *48*, 1814.
(31) Swett, V. C.; Dudeck, E. P. *J. Phys. Chem.* **1968**, *72*, 1244.
(32) Adato, I.; Eliezer, I. *J. Chem. Phys.* **1971**, *54*, 1472. Antosik, S.; Brown, N. M. D.; McConnel, A. A.; Porte, A. L. *J. Chem. Soc. A* **1969**, 545.
(33) Yokoi, H.; Isobe, T. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 2054. Yokoi, H.; Sai, M.; Isobe, T. *Ibid.* **1970**, *43*, 1078.
(34) Zink, J. I.; Drago, R. S. *J. Am. Chem. Soc.* **1972**, *94*, 4550.
(35) Libutti, B. L.; Wayland, B. B.; Garito, A. F. *Inorg. Chem.* **1969**, *8*, 1510.
(36) Maki, A. H.; McGarvey, B. R. *J. Chem. Phys.* **1958**, *29*, 31.
(37) Kivelson, D.; Neiman, R. *J. Chem. Phys.* **1961**, *35*, 149.
(38) Gersmann, H. R.; Swalen, J. D. *J. Chem. Phys.* **1962**, *36*, 3221.
(39) McGarvey, B. R. *J. Phys. Chem.* **1967**, *71*, 51.
(40) Lever, A. B. P. "Inorganic Electronic Spectroscopy"; Elsevier: New York, 1968.
(41) Kuska, H. A. *J. Am. Chem. Soc.* **1975**, *97*, 2289.
(42) Watson, R. E.; Freeman, A. J. *Phys. Rev.* **1961**, *123*, 2027.
(43) Wilson, R.; Kivelson, D. *J. Chem. Phys.* **1966**, *44*, 154.
(44) Hathaway, B. J.; Tomlinson, A. A. *Coord. Chem. Rev.* **1970**, *5*, 1.
(45) Downing, R. S.; Urbach, F. L. *J. Am. Chem. Soc.* **1969**, *91*, 5977. Perry, S. J.; Quinn, R. S.; Dudek, E. P. *Inorg. Chem.* **1968**, *7*, 814.
(46) Waters, T. N.; Wright, P. E. *J. Inorg. Nucl. Chem.* **1971**, *33*, 359.
(47) Hawkins, C. J. In "Absolute Configuration of Metal Complexes"; Wiley-Interscience: New York, 1971; p 187.
(48) Tsangaris, J. M.; Martin, R. B. *J. Am. Chem. Soc.* **1970**, *92*, 4255.
(49) Wellman, K. M.; Mecca, T. G.; Mungall, W.; Hare, C. R. *J. Am. Chem. Soc.* **1968**, *90*, 805.
(50) Gollogly, J. R.; Hawkins, C. J.; Wong, C. L. *Inorg. Nucl. Chem. Lett.* **1970**, *6*, 215.
(51) Wilson, E. W., Jr.; Martin, R. B. *Inorg. Chem.* **1971**, *10*, 1197.
(52) A similar behavior has been found in the series of complexes bis[(*S*)-aminoacidato]copper(II) and has been interpreted on the basis of sector rules.[47]
(53) Aleksandrov, G. L.; Struchkov, Yu. T.; Kurganov, A. A.; Rogozhin, S. V.; Davankov, V. A. *J. Chem. Soc., Chem. Commun.* **1972**, 1328.
(54) (a) Pasini, A.; Gullotti, M. *J. Coord. Chem.* **1974**, *3*, 319. (b) Pasini, A.; Gullotti, M.; Ugo, R. *J. Chem. Soc., Dalton Trans.* **1977**, 346.
(55) Martin, D. F.; Ramaiah, K.; *J. Inorg. Nucl. Chem.* **1965**, *27*, 2027.
(56) Gillard, R. D.; Laurie, S. H.; Ugo, R. *J. Inorg. Nucl. Chem.* **1971**, *33*, 997.
(57) Hirota, K.; Izumi, Y.; *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2287. Yamada, S.; Oguri, T.; Shioiri, T. *J. Chem. Soc., Chem. Commun.* **1976**, 136.