Kinetic and Structural Trans Influence in (Glycinato)cobalt(III) Complexes? The above structural feature correlates nicely with the α-hydrogen-exchange rates of this compound, if we recall that the chelate rings Co(A)–N(A1)–C(A1)–C(A2)–O(A1) and Co(B)–N(B1)–C(B1)–C(B2)–O(B1) of Figure 3 correspond to the a chelate of I of Figure 1. Since the Co(A)–N(A1) and Co(B)–N(B1) bond distances are the shortest among the Co–N bonds, the electron-withdrawing effect of the central metal ion should be transmitted most effectively to these chelates, hence the greatest exchange rate at C(A1) or equivalently C(B1). Though this structure–reactivity correlation may be just fortuitous, it seems probable that the different exchange rates result, at least partially, from the structural trans influence.

It is often pointed out[22] that it is rather difficult to decide whether any bond-length variation is significant and therefore whether this can be attributed to effects of the lattice and the counteranion(s). The sample complex analyzed here crystallographically is a nonelectrolyte and carried no counteranions, and as such the lattice effects should be minimal. The possible occurrence of the structural trans influence in chelated glycinates seems to be found also in the recently reported crystal structure of *mer-cis*(*N*),*cis*(*O*)-[Co(gly)$_2$(eta)],[25] where eta = $H_2NCH_2CH_2O^-$. To avoid the lattice effects, we refer to only the electrically neutral complex. In this complex, the Co–N(glycinate) bond trans to oxygen is 1.924 (4) Å and that trans to nitrogen is 1.955 (5) Å.

To confirm the existence of structural trans influence and its correlation with the hydrogen-exchange rates, we are making the crystal structure analysis of the diastereoisomer formed by Λ-C_1-*cis*(*O*)-[Co(gly)$_2$(en)]$^+$ (complex IV of Figure 1) and the monohydrogen *d*-tartrate ion.[29]

Acknowledgments are made to Dr. A. Kobayashi, The University of Tokyo, for the gift of a computer program and to the Ministry of Education, Science, and Culture for a Grant-in-Aid for Scientific Research (B-547043). All the computations of the structure determination were carried out by a HITAC 8700 computer at the Hiroshima University Computer Center.

Registry No. *mer*-[Co($H_2NCH_2CO_2$)$_3$]·$2H_2O$, 80340-08-5.

Supplementary Material Available: Final anisotropic thermal parameters (Table II), intermolecular hydrogen bonds (Table IV), least-squares planes formed by the glycinato ligands (Table V), and a listing of observed and calculated structure amplitudes (7 pages). Ordering information is given on any current masthead page.

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Contribution from the Consiglio Nazionale delle Ricerche of Italy, Istituto di Chimica Generale e Inorganica, University of Modena, 41100 Modena, Italy, the Istituto di Chimica Generale, Centro di Studio per la Strutturistica Diffrattometrica del CNR, University of Parma, 43100 Parma, Italy, and the Istituto di Chimica, Facoltà di Medicina-Veterinaria, University of Bari, 70126 Bari, Italy

Synthesis and Spectroscopic and Magnetic Properties of Mixed-Ligand Complexes of Copper(II) with Imidazole and N-Protected Amino Acids. Crystal and Molecular Structure of Bis(hippurato)bis(imidazole)copper(II)

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Mixed-ligand complexes of the type $CuL_2(Im)_2$ (L = N-protected amino acidate = benzoylglycinate (hippurate), acetylglycinate (aceturate), *N*-acetyl- and *N*-benzoyl-DL-alaninate, *N*-acetyl- and *N*-benzoyl-β-alaninate and -leucinate; Im = imidazole) were synthesized and characterized by means of electronic, infrared, and EPR spectroscopies. For one of them, bis(hippurato)bis(imidazole)copper(II), the crystal structure was also determined by the single-crystal X-ray diffraction method. The compound crystallizes in the monoclinic space group $P2_1/c$ with two molecules in a unit cell of dimensions $a = 10.4863$ (4) Å, $b = 11.4758$ (3) Å, $c = 10.3410$ (4) Å, and $\beta = 102.234$ (1)°. Least-squares refinement of the 217 variables led to a value of the conventional R index of 0.041 for 1932 independent reflections having $I > 2\sigma(I)$. The structure consists of copper atoms lying on the center of symmetry, square-planar coordinated via two centrosymmetric imidazole nitrogens and carboxylic oxygens; two weak interactions (2.736 (4) Å) with uncoordinated carboxylic oxygens in the "out-of-plane" positions complete the coordination to a very distorted tetragonal bipyramid. Electronic and infrared spectra are consistent with this type of structure for all the complexes. The EPR spectra on finely ground polycrystalline samples are also consistent with an essentially $d_{x^2-y^2}$ ground state, except those of bis(amino acidato)bis(imidazole)copper(II) (amino acidate = hippurate and *N*-acetyl-β-alaninate), which are discussed in the light of the structural properties as due to the presence of magnetically unequivalent sites.

Introduction

So that the importance of mixed-ligand complexes in biological fluids could be understood, the mutual influence of two ligands bound to the same metal ion was investigated. In particular the ternary 2,2′-bipyridyl–Cu^{2+}–O and imidazole–Cu^{2+}–O ligand complexes[2–5] were found more stable than the corresponding binary complexes, Cu^{2+}–O ligand, since bipyridyl and imidazole enhance the affinity of Cu(II) for the oxygen donor sites of anionic ligands.[4] These studies have only been performed in solution and are lacking in respect of the disposal of the ligands around the metal ion and of the co-

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[1] (a) University of Modena. (b) University of Parma. (c) University of Bari.

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ordination geometry of the metal ion.

Although conscious of the possible structural differences of the complexes in the solution and in the solid state, a contribution to the explanation of these problems may be derived from the study of the same systems in the solid state. Therefore, we have now isolated in the solid state and investigated by means of spectroscopic, magnetic, and structural measurements some mixed complexes of copper(II) with ligands of biochemical interest as imidazole (Im) and some N-protected amino acids, which were previously found to act invariably as oxygen donor anionic ligands.[6]

These systems which contain the ligating moieties found in proteins such as imidazole and carboxylate groups may be also considered realistic model systems of many naturally occurring mixed-ligand complexes[7] in which these ligating groups reasonably appear to be present.[4]

Experimental Section

All chemicals were reagent grade and used as received.

Preparation of the Complexes. The bis(N-protected amino acidato)bis(imidazole)copper(II) complexes (N-protected amino acidate = benzoylglycinate (or hippurate), acetylglycinate (or aceturate), *N*-acetyl-*β*-alaninate, *N*-acetyl-DL-leucinate) were prepared by dissolving in methanol the bis(N-protected amino acidate)copper(II) salt (prepared as reported in ref 8,9a–c) and imidazole with a molar ratio of 1:2. With addition of isopropyl alcohol and with cooling the solution at 5 °C, violet crystalline compounds precipitated. Anal. Calcd for bis(hippurato)bis(imidazole)copper(II) ($C_{24}H_{24}CuN_6O_6$) C, 51.82; H, 4.35; N, 15.12. Found: C, 51.55; H, 4.40; N, 15.14. Mp: 220–224 °C dec. Calcd for bis(aceturato)bis(imidazole)copper(II) ($C_{14}H_{20}CuN_6O_6$): C, 38.91; H, 4.67; N, 19.47. Found: C, 39.21; H, 4.73; N, 19.52. Mp: 185–189 °C dec. Calcd for bis(*N*-acetyl-*β*-alaninato)bis(imidazole)copper(II) ($C_{16}H_{24}CuN_6O_6$): C, 41.76; H, 5.26; N, 18.28. Found: C, 41.56; H, 5.24; N, 18.02. Mp: 172–176 °C dec. Calcd for bis(*N*-acetyl-DL-leucinato)bis(imidazole)copper(II) ($C_{22}H_{36}CuN_6O_6$) C, 48.54; H, 6.67; N, 15.45. Found: C, 48.23; H, 7.00; N, 15.65. Mp: 228–231 °C dec. Bis(*N*-benzoyl-DL-alaninato)bis(imidazole)copper(II) and bis(*N*-benzoyl-DL-leucinato)bis(imidazole)copper(II) hydrate complexes were obtained by adding an excess of imidazole to a methanolic solution of the corresponding (N-protected amino acidato)copper(II) salts (prepared as reported in ref 9d) and by adding diethyl ether until complete precipitation of the blue powders was obtained. Anal. Calcd for $C_{26}H_{28}CuN_6O_6$ (first complex): C, 53.44; H, 4.83; N, 14.40. Found: C, 52.98; H, 4.83; N, 14.38. Mp: 215–219 °C dec. Calcd for $C_{32}H_{42}CuN_6O_7$ (second complex): C, 55.98; H, 6.17; N, 12.25. Found: C, 55.86; H, 6.14; N, 12.22. Mp: 115–119 °C dec. Bis(*N*-acetyl-DL-alaninato)bis(imidazole)copper(II) and bis(benzoyl-*β*-alaninato)bis(imidazole)copper(II) hydrate complexes were prepared by treating an ethanolic solution of the corresponding bis(N-protected amino acidato)copper(II) salts (prepared as reported in ref 9e,f) with an ethanolic solution of imidazole in a molar ratio of 1:2. The solution was slowly evaporated until a violet or blue compound, respectively, was separated. Anal. Calcd for $C_{16}H_{24}CuN_6O_6$ (first complex): C, 41.76; H, 5.26; N, 18.28. Found: C, 41.29; H, 5.38; N, 18.36. Mp: 256–261 °C dec. Calcd for $C_{26}H_{30}CuN_6O_7$ (second complex): C, 51.84; H, 5.02; N, 13.96. Found: C, 51.92; H, 5.05; N 13.97. Mp: 104–108 °C dec.

Table I. Crystal Data

mol formula	$C_{24}H_{24}CuN_6O_6$
mol wt	556.04
a	10.4863 (4) Å
b	11.4758 (3) Å
c	10.3410 (4) Å
β	102.234 (1)°
V	1216.16 (7) $Å^3$
Z	2
d_{calcd}	1.52 g cm^{-3}
space group	$P2_1/c$
cryst dimens	0.06 × 0.15 × 0.60 mm
radiation	Cu Kα (λ = 1.541 78 Å)
2θ limits	4–140°
abs coeff	16.8 cm^{-1}
$F(000)$	574 e
unique data used ($I > 2\sigma(I)$)	1932
no. of variables	217
R	0.041

Physical Measurements. The electronic spectra of the solid compounds were recorede as mull transmission spectra with a Shimadzu MPS 50L spectrophotometer. The infrared spectra were recorded with a Perkin-Elmer 180 spectrophotometer in KBr pellets and Nujol mull on KBr pellets as support in the 4000–250 cm^{-1} spectral range. The room-temperature magnetic moments were measured with the Gouy method with $Ni(en)_3S_2O_3$ as calibrant and correcting for diamagnetism with the appropriate Pascal constants. The low- and room-temperature EPR spectra were recorded on a JEOL PE-3X spectrometer. Quartz sample tubes were employed for polycrystalline sample. Spectra were calibrated with diphenylpicrylhydrazyl (DPPH, g = 2.0036) as a field marker.

X-ray Data Collection for Cu(Hippu)$_2$(Im)$_2$. Preliminary cell dimensions were determined from rotation and Weissemberg photographs; more accurate values were calculated by least-squares treatment of $(\theta, \chi, \varphi)_{hkl}$ angles measured on an "on-line" single-crystal Siemens AED automated diffractometer for 15 reflections. The refined constants and other relevant crystal data are given in Table I. The crystal was mounted with [001] axis along the φ axis of the diffractometer, and intensity data were collected with Ni-filtered Cu Kα radiation at a takeoff angle of 4°. The moving-counter-moving-crystal scan technique was employed with a drive speed related to the number of counts on the peak (lowest speed 2.5°/min). The intensity of a standard reflection was measured periodically and subsequently used for scaling; no significant change was observed in the intensity of this reflection during data collection. Measurements were made with the "five-points" technique for 2300 independent reflections; 1932 of these having $I > 2\sigma(I)$ were considered as observed and used in the analysis ($\sigma^2(I)$ = (total counts) + (0.01 × intensity)^2). The structure amplitudes were corrected for Lorentz and polarization effects and put on absolute scale by least squares. No correction for absorption was applied as the μr value is very low (0.09) and, with the assumption of cylindrical shapes for the crystal, the absorption correction coefficients are practically unvaried in the 0–70° θ range.

Solution and Refinement of the Structure. The structure was solved by the heavy-atom technique. Calculation of structure factors with the contribution of the copper atom, followed by Fourier synthesis, yielded a picture of the whole structure excluding the hydrogen atoms. The refinement was carried out isotropically and anisotropically by several full-matrix least-squares cycles to a R = 6.3%. At this stage $F_o - F_c$ map was computed, which revealed the hydrogen atom positions. The final R, after isotropic refinement of the hydrogen atoms, was 4.1%. The effects of anomalous dispersion were included in all structure factor calculations. No evidence for secondary extinction was found. The function minimized in the least-squares calculation was $\sum w|\Delta F|^2$. Atomic scattering factors were taken from ref 10 for Cu, O, N, and C and from ref 11 for hydrogen atoms. All the calculations were performed with a Cyber 76 Computer of Centro di Calcolo Interuniversitario dell'Italia Nord Orientale, Bologna, Italy,

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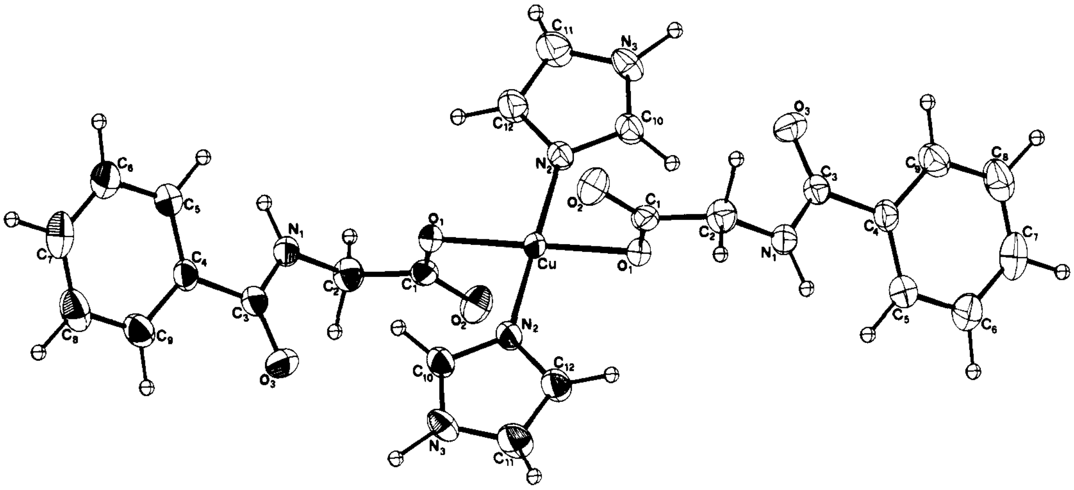

Figure 1. ORTEP drawing of the molecule showing the labeling scheme and thermal motion ellipsoids (40%) for nonhydrogen atoms. The spheres corresponding to the hydrogen atoms are on an arbitrary scale.

Table II. Final Fractional Atomic Coordinates (×10^4 for Nonhydrogen and ×10^3 for Hydrogen Atoms)

	x (σ)	y (σ)	z (σ)
Cu	0	5000	5000
O_1	1391 (3)	3909 (2)	4764 (3)
O_2	2637 (4)	5349 (3)	5707 (4)
O_3	3393 (4)	1991 (3)	6892 (3)
N_1	3522 (4)	2455 (3)	4804 (4)
N_2	−58 (3)	4246 (3)	6691 (3)
N_3	346 (4)	3021 (3)	8348 (4)
C_1	2501 (4)	4374 (3)	5211 (4)
C_2	3726 (5)	3683 (4)	5122 (5)
C_3	3435 (4)	1676 (4)	5759 (4)
C_4	3375 (4)	413 (4)	5379 (4)
C_5	2960 (5)	29 (4)	4080 (5)
C_6	2871 (6)	−1155 (5)	3789 (6)
C_7	3219 (6)	−1952 (5)	4807 (7)
C_8	3672 (6)	−1585 (5)	6101 (5)
C_9	3738 (5)	−403 (5)	6397 (5)
C_{10}	570 (5)	3275 (4)	7159 (4)
C_{11}	−451 (5)	3860 (5)	8676 (5)
C_{12}	−711 (5)	4610 (5)	7660 (5)
H_1	364 (4)	223 (4)	391 (4)
H_2	73 (4)	228 (4)	895 (4)
H_3	457 (4)	377 (4)	605 (4)
H_4	414 (4)	405 (4)	435 (4)
H_5	271 (4)	66 (4)	329 (4)
H_6	240 (4)	−139 (4)	279 (4)
H_7	314 (4)	−287 (4)	459 (4)
H_8	397 (4)	−222 (4)	688 (4)
H_9	416 (4)	−16 (4)	737 (4)
H_{10}	114 (4)	279 (4)	668 (4)
H_{11}	−84 (4)	387 (4)	938 (4)
H_{12}	−141 (4)	524 (4)	752 (4)

Table III. Bond Distances (Å) and Angles (Deg) with Esd's in Parentheses

Cu-O_1	1.976 (3)	C_5-C_6	1.391 (7)
Cu-O_2	2.736 (4)	C_6-C_7	1.384 (9)
Cu-N_2	1.964 (3)	C_7-C_8	1.387 (8)
O_1-C_1	1.275 (5)	C_8-C_9	1.389 (8)
O_2-C_1	1.227 (5)	C_4-C_9	1.400 (7)
C_1-C_2	1.529 (7)	N_2-C_{10}	1.332 (6)
N_1-C_2	1.453 (6)	N_3-C_{10}	1.332 (6)
N_1-C_3	1.349 (6)	N_3-C_{11}	1.364 (7)
C_3-O_3	1.236 (5)	C_{11}-C_{12}	1.341 (7)
C_4-C_3	1.500 (6)	N_2-C_{12}	1.392 (7)
C_4-C_5	1.393 (6)		
C_2-H_3	1.16 (5)	C_8-H_8	1.08 (5)
C_2-H_4	1.07 (5)	C_9-H_9	1.05 (5)
N_1-H_1	0.99 (5)	C_{10}-H_{10}	1.02 (5)
C_5-H_5	1.08 (5)	N_3-H_2	1.08 (5)
C_6-H_6	1.08 (5)	C_{11}-H_{11}	0.91 (5)
C_7-H_7	1.07 (5)	C_{12}-H_{12}	1.02 (5)
O_1-Cu-N_2	89.6 (2)	C_5-C_4-C_9	119.6 (8)
Cu-O_1-C_1	109.3 (4)	C_4-C_5-C_6	120.7 (9)
O_1-C_1-O_2	123.4 (7)	C_5-C_6-C_7	119.1 (10)
O_2-C_1-C_2	118.3 (8)	C_6-C_7-C_8	121.0 (10)
O_1-C_1-C_2	118.4 (8)	C_7-C_8-C_9	120.0 (10)
C_1-C_2-N_1	115.6 (7)	C_8-C_9-C_4	119.6 (9)
C_2-N_1-C_3	120.4 (8)	N_2-C_{10}-N_3	110.4 (6)
N_1-C_3-O_3	121.4 (8)	C_{10}-N_2-Cu	125.9 (3)
N_1-C_3-C_4	117.0 (8)	C_{10}-N_3-C_{11}	108.2 (8)
O_3-C_3-C_4	121.6 (8)	N_3-C_{11}-C_{12}	107.0 (7)
C_3-C_4-C_5	123.1 (9)	C_{11}-C_{12}-N_2	108.8 (7)
C_3-C_4-C_9	117.4 (8)	Cu-N_2-C_{12}	128.4 (3)
		C_{12}-N_2-C_{10}	105.7 (7)

Table IV. Cu-N Distances (Å) in Some Cu-Im Complexes

	complex	Cu-N(Im) dist	source
1	Cu(Hippu)$_2$(Im)$_2$	1.964 (3)	this work
2	Cu(Glygly-H)(Im)	1.96/1.94	26
3	Cu(Glyglygly-H)(Im)	1.95	26
4	[Cu(Ac-α-ala)$_2$(MeIm)$_2$]	1.959 (5)	27
5	[Cu(Im)$_4$]I$_2$	1.98-2.04	28
6	[Cu(Im)$_3$SO$_4$]	2.000 (5)-2.021 (5)	29
7	[CuBr$_2$(MeIm)$_2$]	1.953 (5)	30
8	[CuCl$_2$(MeIm)$_2$]	1.962 (4)-1.975 (5)	31

with the SHELX system of programs.[12] The final atomic coordinates are listed in Table II. A listing of the observed and calculated structure factors for the reflections used in the analysis and a table of thermal parameters are available in supplementary material.

Analysis. Nitrogen, carbon, and hydrogen were analyzed with a C. Erba Elemental Analyser Instrument Model 1106 by G. Pistoni.

Results and Discussion

Description of the Structure. The structure of the title compound consists of copper atoms, lying on the center of symmetry, square-planar coordinated via two centrosymmetric imidazole nitrogens and carboxylic oxygens. Two weak interactions (2.736 (4) Å) with uncoordinated carboxylic oxygens in the "out-of-plane" positions complete the coordination to very distorted tetragonal bipyramid. This situation, typical for carboxylate complexes, was found in bis(*N*-acetylglycinato)diaquacopper(II)dihydrate[6a] and in bis(*N*-acetyl-β-alaninato)diaquacopper(II)[9b] (Figure 1).

The structural features of the complex are given in Table III. The equatorial atoms $\mathrm{CuN_2O_1N_2^{i}O_1^{i}}$ (i = $\bar{x}$, $\bar{y}$, $\bar{z}$) are strictly coplanar, as required by the symmetry, the distortion of the coordination polyhedron being measured by the angle between the Cu–O_2 vector and the normal to coordination

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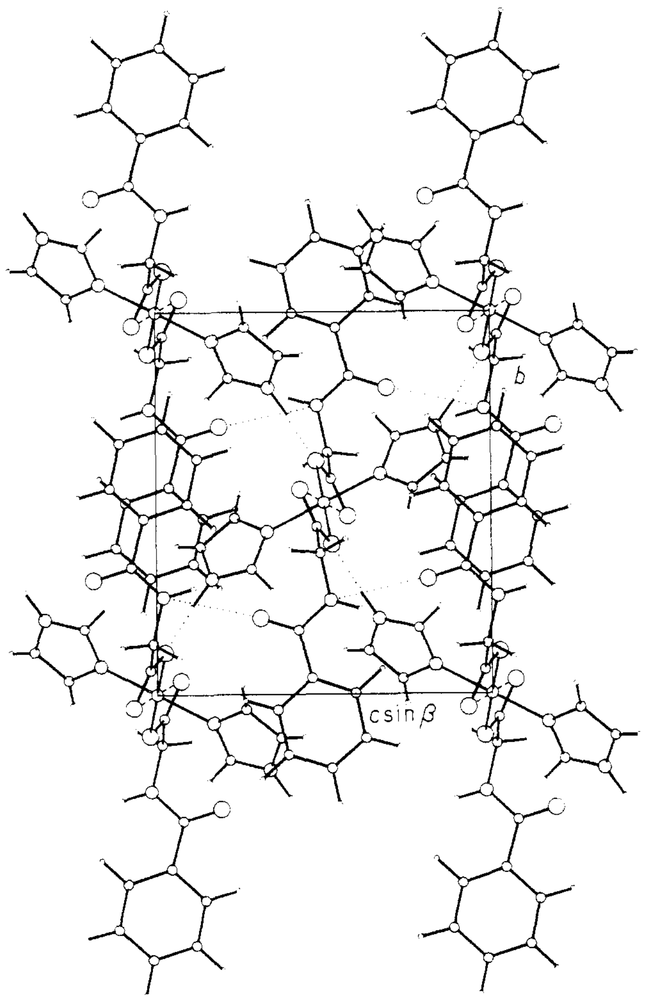

Figure 2. Projection of the structure along [100].

plane (37.2°). Some Cu–N(imidazole) distances are reported in Table IV. In the **1–4** complexes these are in average 1.96 Å, while in the **5–8** the same distances are about 2.00 Å. It appears that this reduced bond length observed in the mixed-ligand complexes supports the view of Siegel[2,13] concerning the importance of π back-bonding from Cu^{2+} to heteroatomic N bases in mixed-ligand complexes containing oxygen donors.

The equations of the best planes and the displacements of each atom are quoted in the supplementary material. The C_α–COO group is planar with the peptide nitrogen 0.29 Å out of this plane. The imidazole ring is practically normal to carboxylate and peptide groups (dihedral angles between these planes being 87.9 and 87.4°, respectively), while the dihedral angle between the imidazole and benzene ring is 48.0°. Also the imidazole ring is coplanar with the coordination plane: the copper atom is 0.05 Å out of imidazole ring and the dihedral angle between the coordination plane and imidazole is 9.23°.

Bond distances and angles in the imidazole ligand correspond well with those found in free imidazole at −150 °C[14] and with those reported for neutral ligand in other metal complexes.[15]

In the hippurate moiety the conformation is invariate with respect to that of hippuric acid[16] and that of copper(II) hippurate,[8] the dihedral angle between the phenyl ring and peptide moiety (24°) being comparable with corresponding values in hippuric acid (14°),[16] and in copper(II) hippurate (20 and 10°).[8] As shown in Table V, in which the most relevant torsion angles are quoted, the glycine moiety exhibits the "eclipsed" conformation, which is normal in amino acid molecules.

Table V. Torsion Angles (Deg)

$O_1C_1C_2N_1$	−13.2 (6)	$O_3C_3C_4C_9$	−22.5 (7)
$O_2C_1C_2N_1$	166.9 (4)	$O_3C_3C_4C_5$	156.5 (5)
$C_1C_2N_1C_3$	−82.1 (5)	$N_1C_3C_4C_9$	158.2 (4)
$C_2N_1C_3O_3$	7.4 (7)	$N_1C_3C_4C_5$	−22.8 (6)
$C_2N_1C_3C_4$	−173.3 (4)		

Table VI. Room-Temperature Electronic, Magnetic, and EPR Results of the Complexes in the Solid State[a]

	d-d transns, nm	μ_{eff}, μ_B	$g_\parallel$	$g_\perp$
$Cu(Hippu)_2(Im)_2$[b]	680 sh, 570	1.84		
$Cu(Acgly)_2(Im)_2$	680 sh, 565	1.84	2.219	2.055
$Cu(Bz\text{-}\alpha\text{-}ala)_2(Im)_2$	740 sh, 600	1.89	2.227	2.123–2.055
$Cu(Ac\text{-}\alpha\text{-}ala)_2(Im)_2$	690 sh, 565	1.81	2.202	2.059
$Cu(Bz\text{-}\beta\text{-}ala)_2(Im)_2\cdot H_2O$	780 sh, 670	1.84	2.310	2.059
$Cu(Ac\text{-}\beta\text{-}ala)_2(Im)_2$[b]	690 sh, 580	1.87		
$Cu(Bzleu)_2(Im)_2\cdot H_2O$	608	1.82	2.250	2.058
$Cu(Acleu)_2(Im)_2$[c]	670 sh, 560	1.93	2.246	2.016

[a] Abbreviations: Hippu = benzoylglycinate (hippurate) ion; Acgly = acetylglycinate (aceturate) ion; Bz- and Ac-α-ala = *N*-benzoyl- and *N*-acetyl-DL-alaninate ion; Bz- and Ac-β-ala = *N*-benzoyl- and *N*-acetyl-β-alaninate ion; Bzleu and Acleu = *N*-benzoyl- and *N*-acetyl-DL-leucinate ion; Im = imidazole. [b] Their *g* values are reported in the text. [c] $A_\parallel = 178 \times 10^{-4}$ cm^{-1}.

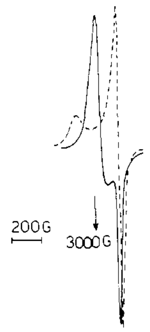

Figure 3. Exemplifying EPR spectra of $Cu(Hippu)_2(Im)_2$ and $Cu(Ac\text{-}\beta\text{-}ala)_2(Im)_2$ (—) complexes and Cu(amino acidato)$_2$(Im)$_2$ (- - -) complexes at room temperature.

In Figure 2 is reported the projection of the structure along the [100] axis. Packing is mainly determined by N–H···O hydrogen bonds involving peptidic nitrogen and peptidic oxygen of an adjacent molecule [$N_1 \cdots O_3^{ii}$ (ii = x, $^1/_2 - y$, $z - {}^1/_2$) = 3.053 (6) Å; N_1–$H_1 \cdots O_3^{ii}$ = 138.9°; $N_1 - H_1$ = 0.99 Å; $H_1 \cdots O_3^{ii}$ = 2.234 Å] and uncoordinated imidazole nitrogen and coordinated carboxylic oxygen [$N_3 \cdots O_1^{iii}$ (iii = x, $^1/_2 - y$, $^1/_2 + z$) = 2.751 (4) Å; N_3–$H_2 \cdots O_1^{iii}$ = 174.5°; N_3–H_2 = 1.08 Å; $H_2 \cdots O_1^{iii}$ = 1.67 Å].

Magnetic and Spectroscopic Properties. All the complexes present a "normal" room-temperature solid magnetic moment for an orbitally nondegenerate ground state (Table VI).

The polycrystalline EPR spectra of the complexes, except those of the benzoylglycinate (hippurate) and acetyl-β-alaninate complexes, are of axial type, showing experimental *g* values (Table VI) in the range expected for normal tetragonally elongated octahedral complexes with CuO_4N_2 chromophore,[6c,17,18] in perfect agreement with the structural results. The EPR spectra obtained for $Cu(Hippu)_2(Im)_2$ and $Cu(Ac\text{-}\beta\text{-}ala)_2(Im)_2$ complexes (Figure 3) are quite different from those normally found for tetragonally distorted octahedral

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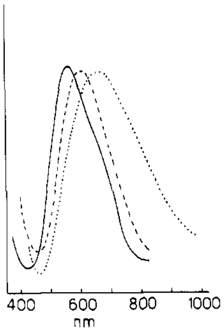

Figure 4. Exemplifying room-temperature solid electronic spectra of Cu(amino acidato)$_2$(Im)$_2$ (—), Cu(Bzleu)$_2$(Im)$_2$·H$_2$O (- - -), and Cu(Bz-β-ala)$_2$(Im)$_2$·H$_2$O (···) complexes.

copper(II) complexes, as they present axial "reversed" spectra with $g_\perp$ (2.154) greater than $g_\parallel$ (2.050) and $\langle g \rangle = 2.118$. Upon cooling of the samples, the intensity of the highest field increased slightly. An analysis based on the known crystal structure of the Cu(Hippu)$_2$(Im)$_2$ complex may suggest a resonable explanation of the observed spectrum, as it excludes the presence of stereochemistries giving rise to species with d_{z^2} ground state.[19,20] In our case, it is far more likely that the single ion ground state may be largely $d_{x^2-y^2}$ and that observed resonance is determined by magnetically inequivalent sites within the unit cell in an antiferromagnetic arrangement, as also previously reported for similar cases.[19-21] In the Cu(Hippu)$_2$(Im)$_2$ complex the angle between the O$_1$–O$_2$ planes of two sites is 133.43° and the relative orientations of the tetragonally elongated octahedra will determine the observed crystal g tensors. Molecular g values of 2.171 and 2.047 for $g_\parallel$ and $g_\perp$, respectively, for the Cu(Hippu)$_2$(Im)$_2$ complex may be calculated with the method reported in ref 20. These values agree well with the presence of a strong in-plane ligand field as found in other structurally known complexes having similar in-plane chromophore and bond distances.[22]

On these bases the EPR spectra of the Cu(Ac-β-ala)$_2$(Im)$_2$ complex may be also explained, although its molecular g values may not be calculated, as its crystal structure is not available.

The room-temperature solid electronic spectra of the complexes are all consistent with an essentially $d_{x^2-y^2}$ ground state. In fact, being very similar to each other with respect to d–d band shape and positions (Table VI and Figure 4) and similar to the spectrum of the structurally known Cu(Hippu)$_2$(Im)$_2$ complex, they are consistent with a tetragonally elongated ligand field with CuO$_4$N$_2$ chromophore.[6c,23] A lower tetragonal distortion in the hydrate complexes, which show a band maximum shift toward lower energies, may be associated with the presence of the water molecule which may influence, directly or indirectly, the coordination sphere of the metal ion: in the former case if directly linked to the copper(II) ion, in the latter it is responsible for a change in the hydrogen bonding determining the crystal packing.

The IR spectra of all the complexes show clear evidence of an "asymmetrical" bidentate coordination through the carboxylate group of the amino acids as the $\Delta\nu$ values (ν(OCO)$_{\mathrm{asym}}$ − ν(OCO)$_{\mathrm{sym}}$) of 190–210 cm^{-1} are in the range of that expected for this type of coordination,[24,25] and as in all the complexes the ν(OCO)$_{\mathrm{sym}}$ position is found at the same or lower energies than that of the corresponding alkali salts. This last fact was previously considered a very important prerequisite in a correct assignment of the way in which a carboxylate group may coordinate.[6c]

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Registry No. Cu(Hippu)$_2$(Im)$_2$, 80243-37-4; Cu(Acgly)$_2$(Im)$_2$, 80243-38-5; Cu(Bz-α-ala)$_2$(Im)$_2$, 80243-39-6; Cu(Ac-α-ala)$_2$(Im)$_2$, 80243-40-9; Cu(Bz-β-ala)$_2$(Im)$_2$, 80243-41-0; Cu(Ac-β-ala)$_2$(Im)$_2$, 80243-42-1; Cu(Bzleu)$_2$(Im)$_2$, 80243-43-2; Cu(Acleu)$_2$(Im)$_2$, 80243-44-3.

Supplementary Material Available: Tables of least squares planes and anisotropic thermal parameters and a listing of structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

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