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Synthesis and Spectroscopic and Structural Properties of Bis(*N*-acetyl-DL-tryptophanato)copper(II) Complex and Its Amine Adducts. Effect of Amines on the Amino Acid Coordination. Crystal and Molecular Structure of Diaquabis(*N*-acetyl-DL-tryptophanato)bis(pyridine)-copper(II)

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Abstract: A green compound of the type Cu(Actrp)$_2$·H$_2$O (Actrp = *N*-acetyl-DL-tryptophanate ion) and its aromatic and aliphatic heterocyclic amine adducts, Cu(Actrp)$_2$B$_2$ (B = pyridine (py), 3- and 4-methylpyridine (3- and 4-pic), *N*-methylpiperazine (NCH$_3$pipz), morpholine (morph), and piperidine (pipd)), Cu(Actrp)$_2$(py)$_2$(H$_2$O)$_2$, and Cu(Actrp)$_2$·pipz (pipz = piperazine), were prepared and characterized by means of low- and room-temperature magnetic and EPR measurements and room-temperature electronic and infrared spectroscopy. While Cu(Actrp)$_2$·H$_2$O shows physical properties indicating a binuclear configuration, all the aromatic heterocyclic amine adducts appear to possess a tetragonal configuration with CuO$_4$N$_2$ chromophore. For one of the latter complexes, diaquabis(*N*-acetyl-DL-tryptophanato)bis(pyridine)copper(II), the crystal structure was also determined by single-crystal X-ray diffraction methods. The complex crystallizes in the monoclinic space group *P*2$_1$/*c* with two molecules in a unit cell of dimensions *a* = 9.377 (6) Å, *b* = 19.341 (14) Å, *c* = 11.615 (7) Å, β = 123.2 (2)°, d_{calcd} = 1.41 g cm^{-3}, d_{measd} = 1.42 g cm^{-3}. Least-squares refinement of the 150 variables has led to a value of the conventional *R* index (on *F*) of 0.071 for 783 independent reflections having *F* > 4σ(*F*). The geometry about the copper atom, which is coordinated to two carboxylic oxygens and two pyridine nitrogen atoms, is completed to an elongated tetragonal bipyramid by two weak interactions with two water molecules. The Cu–N, Cu–O(amino acid), and Cu–O(water) distances are 1.95 (1), 2.02 (1), and 2.61 (1) Å, respectively, and the O(amino acid)–Cu–N angle is 87.9 (6)°. For the adducts of the aliphatic heterocyclic amines a square-planar geometry with CuO$_2$N$_2$ chromophore may be suggested. In all the complexes reported in this work the amino acid appears to coordinate the copper(II) ion only toward the carboxylate group. For the assignment of the way in which the carboxylate group coordinates, we suggest that the observation of the position of the ν(OCO)$_s$ is particularly relevant.

Introduction

Coordination chemists have been interested for many years in the donor properties of amino acids as models for metal–protein interaction.

The amino acids containing terminal *N*-acetyl residues are of particular interest not only because they are present in some natural proteins and peptides, but also because it is possible that an acetyl amino acid might be the starting unit in the biosynthesis of some peptide chains which grow by the stepwise addition of amino acyl residues to the acetylated N-terminal amino acid.[2] In particular *N*-acetyl-DL-tryptophan inhibits complex formation between pepsin and bovine serum albumin and also stabilizes serum albumin against denaturation by heat, urea, and guanidine salts and against isomerization at pH 4.[3]

N-Acetyltryptophan was furthermore found as a metabolite excreted in the urine by normal and cancer patients before and after tryptophan feeding. In particular it was reported that *N*-acetyl-D-tryptophan ingestion by man did not increase the amount of these metabolites excreted, while acetyl-L-tryptophan ingestion raised the urinary excretion but less than that observed for equimolar quantities of L-tryptophan or D-tryptophan. Langner and Edmonds have also shown that acetyl-D-tryptophan is poorly adsorbed.[4]

Having paid particular attention to the coordination properties of *N*-acetyl and *N*-benzoyl amino acids,[5] we have investigated in this paper the coordination behavior of *N*-acetyl-DL-tryptophan (hereafter abbreviated as ActrpH) toward the copper(II) ion and the effect of amines on the amino acid coordination.

All the synthesized compounds were characterized by means of electronic, infrared, and EPR spectroscopy and magnetic moment measurements, and for one of them, the only one of which more suitable crystals, although very thin, were obtained, the crystal structure was also determined.

This work also takes on great interest from the fact that the metal–tryptophanate systems have generally been poorly examined[6] and till now the crystal structure of only one tryptophanate, the glycyl-L-tryptophanatocopper(II) trihydrate,[7,8] is known.

Table I. Crystal Data for Cu(Actrp)$_2$(py)$_2$(H$_2$O)$_2$

molecular formula	C$_{36}$H$_{40}$CuN$_6$O$_8$
mol wt	748.3 amu
a	9.377(6) Å
b	19.341(14) Å
c	11.615(7) Å
β	123.2(2)°
V	1763(2) Å
Z	2
space group	$P2_1/c$ (from systematic absences)
crystal dimensions	0.07 × 0.04 × 0.26 mm
radiation	Cu Kα (λ = 1.5418 Å) (Ni filtered)
2θ limits	6–120°
temp	20 °C
absorption coefficient	13.42 cm^{-1}
unique data used ($F_o >$ $4\sigma(F_o)$)	783
number of variables	150
R	0.071

Experimental Section

All chemicals were reagent grade and used as received.

Preparation of Bis(*N*-acetyl-DL-tryptophanato)copper(II) Monohydrate, Cu(Actrp)$_2$·H$_2$O. The complex was prepared by direct reaction of ActrpH (2 mmol) and copper(II) hydroxide, freshly prepared (1 mmol), in water or by adding a methanolic copper(II) perchlorate hexahydrate (1 mmol) solution to a methanolic sodium *N*-acetyl-DL-tryptophanate (2 mmol) solution, obtained by mixing stoichiometric amounts of sodium hydroxide and ActrpH in methanol. From the green water or methanolic solution the green compound precipitated after some minutes. Anal. Calcd for C$_{26}$H$_{28}$CuN$_4$O$_7$: C, 54.26; H, 4.94; N, 9.80. Found: C, 54.79; H, 5.10; N, 9.18.

Preparation of Bis(*N*-acetyl-DL-tryptophanato)bis(pyridine)copper(II), Cu(Actrp)$_2$(py)$_2$. The compound was obtained by dissolving the Cu(Actrp)$_2$·H$_2$O complex in ethanol containing an amine excess and by adding diethyl ether. The final product is blue. Anal. Calcd for C$_{36}$H$_{36}$CuN$_6$O$_6$: C, 60.68; H, 5.10; N, 11.81. Found: C, 61.05; H, 5.11; N, 12.18.

Preparation of Bis(*N*-acetyl-DL-tryptophanato)bis(3-picoline)-copper(II), Cu(Actrp)$_2$(3pic)$_2$. This compound was prepared in a manner analogous to the pyridine adduct. The final product is blue. Anal. Calcd for C$_{38}$H$_{40}$CuN$_6$O$_6$: C, 61.63; H, 5.45; N, 11.36. Found: C, 61.88; H, 6.00; N, 11.21.

Preparation of Bis(*N*-acetyl-DL-tryptophanato)bis(4-picoline)-copper(II), Cu(Actrp)$_2$(4pic)$_2$. This compound was also prepared in a manner analogous to the pyridine adduct. The final product is blue. Anal. Calcd for C$_{38}$H$_{40}$CuN$_6$O$_6$: C, 61.63; H, 5.45; N, 11.36. Found: C, 61.95; H, 5.63; N, 11.42.

Preparation of Bis(*N*-acetyl-DL-tryptophanato)bis(morpholine)-copper(II), Cu(Actrp)$_2$(morph)$_2$. The compound was prepared in a manner analogous to the pyridine adduct. The final compound is lilac. Anal. Calcd for C$_{34}$H$_{44}$CuN$_6$O$_8$: C, 56.05; H, 6.09; N, 11.55. Found: C, 56.07; H, 6.11; N, 11.46.

Preparation of Bis(*N*-acetyl-DL-tryptophanato)monopiperazine-copper(II), Cu(Actrp)$_2$·pipz. The blue compound was prepared in a manner analogous to the pyridine adduct. Anal. Calcd for C$_{30}$H$_{36}$CuN$_6$O$_6$: C, 56.26; H, 5.67; N, 13.14. Found: C, 55.89; H, 6.01; N, 14.08.

Preparation of Bis(*N*-acetyl-DL-tryptophanato)bis(piperidine)-copper(II), Cu(Actrp)$_2$(pipd)$_2$. The complex was obtained by dissolving Cu(Actrp)$_2$·H$_2$O and an amine excess in methanol and by cooling the solution at 4–5 °C for some hours. The final product is lilac. Anal. Calcd for C$_{36}$H$_{48}$CuN$_6$O$_6$: C, 59.67; H, 6.68; N, 11.61. Found: C, 59.16; H, 6.74; N, 11.75.

Preparation of Bis(*N*-acetyl-DL-tryptophanato)bis(*N*-methylpiperazine)copper(II), Cu(Actrp)$_2$(NCH$_3$pipz)$_2$. The compound was obtained by mixing Cu(Actrp)$_2$·H$_2$O and an amine excess in 2-propanol and adding diethyl ether. The final product is lilac. Anal. Calcd for C$_{36}$H$_{50}$CuN$_8$O$_6$: C, 57.29; H, 6.68; N, 14.86. Found: C, 56.69; H, 7.05; N, 14.49.

Preparation of Diaquabis(*N*-acetyl-DL-tryptophanato)bis(pyridine)copper(II), Cu(Actrp)$_2$(py)$_2$(H$_2$O)$_2$. The compound was obtained by dissolving Cu(Actrp)$_2$·H$_2$O in water containing an excess of pyridine. By allowing the solution to stand for several days at room

temperature (about 20 °C), blue crystals separated. The compound was repeatedly recrystallized in a water–pyridine solution to obtain suitable crystals for X-ray analysis. Anal. Calcd for C$_{36}$H$_{40}$CuN$_6$O$_8$: C, 57.76; H, 5.39; N, 11.24. Found: C, 57.68; H, 5.42; N, 11.20.

Physical Measurements. The electronic spectra of the solid compounds were recorded as mull transmission spectra with a Shimadzu MPS 50L spectrophotometer. The infrared spectra were recorded with a Perkin-Elmer 180 spectrophotometer in KBr pellets in the 4000–250-cm^{-1} spectral range. The low- and room-temperature magnetic moments were measured with the Gouy method using Nien$_3$S$_2$O$_3$ 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 samples. Spectra were calibrated with diphenylpicrylhydrazyl (DPPH, g = 2.0036) as a field marker.

X-ray Data Collection for Cu(Actrp)$_2$(py)$_2$(H$_2$O)$_2$. Light blue crystals, marginally suitable for X-ray diffraction study, were prepared and recrystallized as described above. Preliminary cell dimensions were determined from rotation and Weissenberg photographs; successively these values were refined by least-squares using 2θ values of 15 high-angle reflections (120° < 2θ < 140°) accurately measured on an "on-line" single-crystal automated Siemens AED diffractometer using Cu Kα radiation (λ = 1.5418 Å). The refined cell constants and other relevant crystal data are given in Table 1. The crystal was mounted with the [001] axis along the φ axis of the diffractometer. Intensity data were collected using nickel-filtered Cu Kα radiation at a takeoff angle of 6°. 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). One reflection was measured after every 20 reflections as a check of alignment and crystal and instrument stability. No significant change in the measured intensities of these reflections was observed during data collection. Measurements were made with the "five-point technique" for 2470 independent reflections in the interval 6° < 2θ < 120°. Of these only 783 had $F > 4\sigma(F)$, the crystal being rather thin; these were considered as observed and used in the analysis.

The structure amplitudes were obtained after the usual Lorentz and polarization factors and put on absolute scale by least squares. No corrections for absorption were performed, as the μ_R value is very low (0.04), assuming a cylindrical shape for the crystal.

Solution and Refinement of the Structure. The structure was solved using the heavy-atom technique. A structure factor calculation with the contribution of the copper atom at the origin of the cell gave a conventional R = 43.2%. The successive Fourier synthesis revealed the positions of all nonhydrogen atoms, which were refined, first isotropically for all atoms and then anisotropically only for copper, oxygen, and nitrogen, by several full-matrix least-squares cycles to give R = 7.8%. The partial anisotropic refinement was assumed to have an acceptable value (5.9) for the ratio (no. observations)/(no. parameters). Only the hydrogen atoms of the water molecule were located in a difference map; the others were introduced in their geometrically calculated positions, which corresponded to positive regions of electron density. The final structure factor calculation with the contribution of the hydrogen atoms gave R = 7.1%. This result was considered satisfactory in view of the relatively low number of observations. The effects of the anomalous dispersion for Cu were included in all structure-factor calculations.

The function minimized was $\sum w|\Delta F|^2$ with unit weights, as the weighting scheme $w^{-1} = [\sigma^2(F_o) + |g|(F_o)^2]$ attempted with different g values gave unsatisfactory results. Atomic scattering factors were taken from ref 9 for Cu, O, N, and C, and from Stewart, Davidson, and Simpson[10] for H.

All the calculations were performed using the CYBER 76 of the Centro di Calcolo Interuniversitario dell'Italia Nord Orientale, Bologna, with the SHELX system of programs (Sheldrick 1976).[11] The final atomic coordinates are listed in Table IV. The large standard deviations are imputable to the small numbers of observations. 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 the supplementary material.

Analysis. Nitrogen, carbon, and hydrogen were analyzed with a Perkin-Elmer 240 elemental analyzer by Mr. Giuseppe Pistoni.

Results and Discussion

All the compounds are stable in air and soluble in methanol.

Table II. Room-Temperature Electronic, Magnetic, and EPR Results of the Complexes in the Solid State

	d–d transitions, $\times 10^3$ cm^{-1}	CT transitions	μ_{eff}, μ_B	dimer g_z	$g_\perp$	$\langle g \rangle^a$	$A_\parallel$, 10^4 cm^{-1}	donor atom set
			Type 1 Complexes					
{Cu(Actrp)$_2$·H$_2$O}$_2$	14.1	26.0 sh	1.29	2.427	2.190	2.269		O$_5$
					monomer			
				$g_\parallel$ 2.272	$g_\perp$ 2.028	2.093	136	
			Type 2 Complexes					
				$g_\parallel$	$g_\perp$	$\langle g \rangle^a$		
Cu(Actrp)$_2$(py)$_2$	15.4	26.3 sh	1.78	2.311	2.073	2.152	154	N$_2$O$_4$
Cu(Actrp)$_2$(py)$_2$(H$_2$O)$_2$	15.9		1.79	2.290	2.060	2.137	165	N$_2$O$_4$
Cu(Actrp)$_2$(3pic)$_2$	16.4	26.3 sh	1.84	2.312	2.068	2.149	165	N$_2$O$_4$
Cu(Actrp)$_2$(4pic)$_2$	17.1	26.3 sh	1.80	2.319	2.075	2.159	136	N$_2$O$_4$
			Type 3 Complexes					
Cu(Actrp)$_2$·pipz	17.2		1.70	2.146	2.041	2.076		N$_2$O$_2$
Cu(Actrp)$_2$(NCH$_3$pipz)$_2$	16.0 sh 19.8		1.80	2.236	2.058	2.117	172	N$_2$O$_2$
Cu(Actrp)$_2$(morph)$_2$	15.9 sh 20.0		1.70			2.075^b		N$_2$O$_2$
Cu(Actrp)$_2$(pipd)$_2$	16.0 sh 20.2		2.02	2.234	2.057	2.116	172	N$_2$O$_2$

^{a} $\langle g \rangle = (g_\parallel + 2g_\perp)/3$. ^{b} The spectrum is isotropic.

Table III. Experimental and Calculated Corrected Molar Susceptibilities and Magnetic Moments for the Bis(N-acetyl-DL-tryptophanato)copper(II) Monohydrate Complex
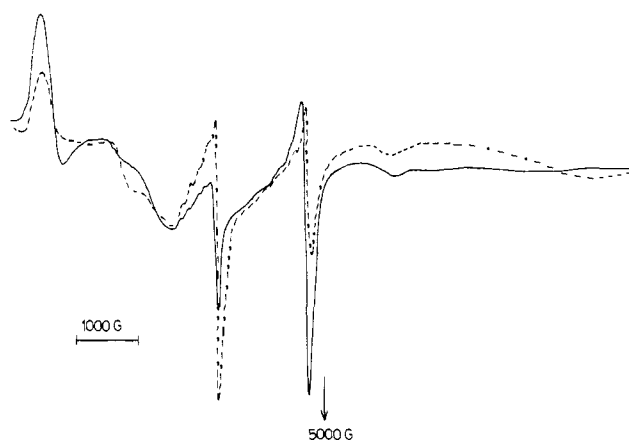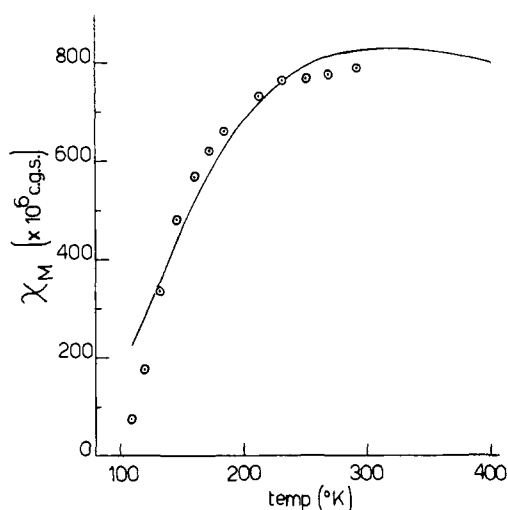
temp, K	exptl $10^6 \chi_M$	μ_{eff}	calcd $10^6 \chi_M$	μ_{eff}
109	79	0.26	226	0.44
119	178	0.41	282	0.52
132	336	0.60	358	0.61
146	473	0.75	439	0.72
160	570	0.86	514	0.81
172	622	0.93	573	0.89
185	662	0.99	628	0.96
212	731	1.12	718	1.10
230.5	759	1.19	761	1.18
250	765	1.24	793	1.26
269.5	776	1.30	813	1.32
291	788	1.36	825	1.39
300			828	1.41
325			829	1.47
350			823	1.52
375			813	1.56
400			800	1.60

Figure 1. EPR spectra of Cu(Actrp)$_2$·H$_2$O at 25 (——) and at -150 °C (---).

Figure 2. Variation of magnetic susceptibility with temperature of the Cu(Actrp)$_2$·H$_2$O complex: ⊙, experimental susceptibility; dashed line, calculated.

Colors, magnetisms, and EPR, infrared, and electronic spectra of the complexes are such as to divide the complexes into three types.

Type 1 Complexes. This group only contains the green bis(N-acetyl-DL-tryptophanato)copper(II) monohydrate for which, as it display magnetic and spectral characteristics (Table II) similar to those of the copper(II) acetate monohydrate and similar binuclear complexes,[12-16] the presence of analogous binuclear entities is indicated.

The EPR spectrum of this complex (Figure 1), which strongly resembles those of other binuclear complexes,[17,18] shows zero field splitting of 0.38 cm^{-1} and the presence of magnetic dilute copper(II) impurities, whose intensity of signal increases when the temperature decreases.

The corrected molar susceptibility varies with temperature (Table III and Figure 2), but no maximum in the curve is observed in the temperature range studied. However, the experimental data can also be fitted closely by the Bleaney–Bowers equation,[19] so that, following the procedure adopted by Martin et al.,[20] by using for the Landè splitting factor ($\bar{g} = [(g_\parallel^2 + 2g_\perp^2)/3]^{1/2}$ [21]) the EPR-determined value of 2.272 and for the temperature-independent paramagnetism ($N\alpha$) a value of 60 × 10^{-6} emu/mol, a 2J (exchange integral) value

of -351 ± 15 cm^{-1} may be calculated. This value indicates a relatively strong magnetic interaction between the two copper ions and falls in the range expected for dimeric copper(II) carboxylates.[18] From the calculated curve, with the parameters $2J = -351$ cm^{-1}, $\bar{g} = 2.272$, and $N\alpha = 60 \times 10^{-6}$ cgs units,
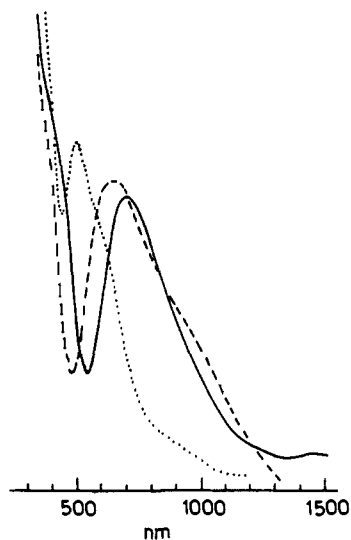
Figure 3. Exemplifying room-temperature solid electronic spectra of type 1 (—), type 2 (-··-), and type 3 (. . .) complexes.

Table IV. Fractional Coordinates ($\times 10^4$) for Cu, O, N, and C and ($\times 10^3$) for H(1) and H(2), with Estimated Standard Deviations in Parentheses

	x	y	z
Cu	0	0	0
O(1)	2482(14)	−43(8)	1092(11)
O(2)	3241(16)	14(9)	3278(13)
O(3)	8051(18)	−927(8)	3408(15)
O(4)	−164(20)	−358(8)	2095(14)
N(1)	4170(20)	1446(9)	−599(18)
N(2)	6508(19)	−361(8)	4088(16)
N(3)	−15(16)	−1014(7)	−431(12)
C(1)	5583(22)	1863(11)	1529(20)
C(2)	6394(27)	2387(12)	2533(25)
C(3)	6358(28)	3057(14)	2104(26)
C(4)	5593(27)	3225(13)	718(23)
C(5)	4743(25)	2722(10)	−30(21)
C(6)	4744(26)	2053(10)	108(23)
C(7)	4496(25)	879(11)	281(21)
C(8)	5390(24)	1141(11)	1579(20)
C(9)	6055(27)	734(11)	2883(22)
C(10)	5428(20)	−10(13)	2780(18)
C(11)	3582(22)	−2(14)	2366(21)
C(12)	7708(31)	−771(12)	4310(26)
C(13)	8793(29)	−1096(13)	5688(22)
C(14)	−1192(31)	−1444(12)	−409(23)
C(15)	−1289(32)	−2128(13)	−759(24)
C(16)	−268(28)	−2404(13)	−1161(23)
C(17)	859(27)	−1974(11)	−1202(22)
C(18)	1024(28)	−1273(12)	−818(21)
H(1)[a]	107	−44	282
H(2)[a]	−42	1	236

[a] Atoms are not refined.

a maximum in susceptibility at about 325 K is recognized (Figure 2).

Its electronic spectrum (Table II and Figure 3), which is also strictly similar to those of the other carboxylates,[14,16,17,22] presents a band at 26 000 cm^{-1}, as a shoulder, which is considered peculiar to these types of compounds.[14,16,17,23]

Type 2 Complexes. This group contains the blue Cu(Actrp)$_2$B$_2$ (B = py, 3pic, and 4pic) and Cu(Actrp)$_2$-(py)$_2$(H$_2$O)$_2$ adducts.

Description of the Structure of Cu(Actrp)$_2$(py)$_2$(H$_2$O)$_2$. As shown in Figure 4, the copper(II) atom lies on a symmetry center, coordinated by two carboxylic oxygens and two pyridine nitrogen atoms. Coordination is completed to an elongated
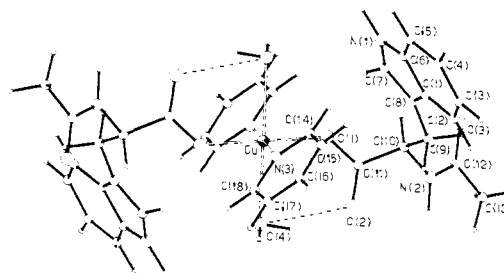

Figure 4. Projection of the coordination polyhedron.

Table V. Bond Distances and Angles with Esd's in Parentheses

Bond Distances (Å)			
Cu–O(1)	1.95(1)	C(2)–C(3)	1.38(4)
Cu–O(4)	2.61(1)	C(3)–C(4)	1.39(3)
Cu–N(3)	2.02(1)	C(4)–C(5)	1.40(3)
O(1)–C(11)	1.26(2)	C(5)–C(6)	1.38(3)
O(2)–C(11)	1.26(3)	C(7)–C(8)	1.36(3)
O(3)–C(12)	1.29(4)	C(8)–C(9)	1.51(3)
N(1)–C(6)	1.36(3)	C(9)–C(10)	1.53(3)
N(1)–C(7)	1.41(3)	C(10)–C(11)	1.52(3)
N(2)–C(10)	1.45(2)	C(12)–C(13)	1.49(3)
N(2)–C(12)	1.28(3)	C(14)–C(15)	1.37(3)
N(3)–C(14)	1.39(3)	C(15)–C(16)	1.38(4)
N(3)–C(18)	1.37(3)	C(16)–C(17)	1.37(4)
C(1)–C(2)	1.41(3)	C(17)–C(18)	1.41(3)
C(1)–C(6)	1.43(3)	O(4)–H(1)	0.87
C(1)–C(8)	1.41(3)	O(4)–H(2)	1.00

Bond Angles (deg)			
O(1)–Cu–N(3)	87.9(6)	C(1)–C(8)–C(7)	110(2)
Cu–O(1)–C(11)	132(1)	C(7)–C(8)–C(9)	126(2)
C(6)–N(1)–C(7)	112(2)	C(1)–C(8)–C(9)	124(2)
C(10)–N(2)–C(12)	112(2)	C(8)–C(9)–C(10)	119(2)
Cu–N(3)–C(18)	122(1)	N(2)–C(10)–C(9)	110(1)
Cu–N(3)–C(14)	118(1)	C(9)–C(10)–C(11)	110(2)
C(14)–N(3)–C(18)	120(2)	N(2)–C(10)–C(11)	111(2)
C(6)–C(1)–C(8)	107(2)	O(2)–C(11)–C(10)	120(2)
C(2)–C(1)–C(8)	134(2)	O(1)–C(11)–C(10)	115(2)
C(2)–C(1)–C(6)	118(2)	O(1)–C(11)–O(2)	124(2)
C(1)–C(2)–C(3)	119(2)	O(3)–C(12)–N(2)	124(2)
C(2)–C(3)–C(4)	122(2)	N(2)–C(12)–C(13)	119(2)
C(3)–C(4)–C(5)	121(2)	O(3)–C(12)–C(13)	117(2)
C(4)–C(5)–C(6)	118(2)	N(3)–C(14)–C(15)	120(3)
C(1)–C(6)–C(5)	122(2)	C(14)–C(15)–C(16)	122(3)
N(1)–C(6)–C(5)	132(2)	C(15)–C(16)–C(17)	118(3)
N(1)–C(6)–C(1)	105(2)	C(16)–C(17)–C(18)	122(2)
N(1)–C(7)–C(8)	106(2)	N(3)–C(18)–C(17)	119(2)
H(2)–O(4)–H(1)	104.1		

tetragonal bipyramid by two weak interactions (2.61 (1) Å) with water molecules forming intramolecular hydrogen bonds with the uncoordinated carboxylic oxygens (O(2) ··· H(2)O(4) 2.79 (2) Å). The peptide group is not involved in the coordination. The final interatomic distances and angles are given in Table V. Bond distances and angles in the tryptophanate ion are comparable with those found in other tryptophan derivatives.[24] The equations of the best planes and the displacements of atoms from the planes are listed in Table VI. As found in other tryptophan compounds, the indole part is planar, the maximum deviation being 0.02 Å. The C$^\alpha$–COO is planar and the amino nitrogen is −0.74 Å out of this plane. The indole ring forms an angle of 81.0° with the carboxylate plane and of 63.7° with the plane of the peptide group. The dihedral angle between carboxylate and peptide group is 139.1°.

The conformation of *N*-acetyltryptophan residue can be described using the torsion angles defined by the IUPAC-IUB Commission on Biochemical Nomenclature (1970). Table VII shows the torsion angles for some tryptophan derivatives. The values of the torsion angles are $\omega = 178.3°$, $\varphi = 139.5°$, $\chi^1 =$

Table VI. Least-Squares Planes[a]

atom	deviation, Å	equation of the plane
		Plane I. Carboxyl Group
O(1)	−0.002	$0.00884X + 0.99874Y − 0.04930Z =$
		$−0.11887$
O(2)	−0.003	
C(11)	0.018	
C(10)	−0.004	
N(2)	−0.743	
		Plane II. Peptide Group
C(10)	0.002	$−0.56079X − 0.76753Y − 0.31050Z =$
		$−2.67355$
N(2)	0.011	
C(12)	0.000	
C(13)	−0.013	
O(3)	0.002	
C(11)*	0.922	
C(9)*	−1.443	
		Plane III. Indole Ring
C(1)	0.013	$−0.98499X + 0.16180Y − 0.06019Z =$
		$−3.71820$
C(2)	−0.003	
C(3)	−0.003	
C(4)	−0.003	
C(5)	0.017	
C(6)	0.004	
C(7)	0.000	
C(8)	−0.007	
N(1)	−0.021	
		Plane IV. Pyridine Ring
N(3)	−0.001	$−0.20168X + 0.23556Y − 0.95070Z =$
		$−0.11556$
C(14)	0.009	
C(15)	−0.006	
C(16)	0.005	
C(17)	0.011	
C(18)	−0.007	

[a] Equation of the plane $AX + BY + CZ = D$ with respect to an orthogonal system, where X, Y, Z, and D are in Å. The asterisked atoms are not included in the plane.

166.2°, $\chi^{2.1} = −12.1°$, $\chi^{2.2} = 166.7°$, and $C'−C^\alpha−C^\beta−C^\gamma = −71.8°$. The $C^\beta−C^\gamma$ bond lies at gauche position to the $C^\alpha−COO^-$ and trans to the $C^\alpha−N$-acetyl. This conformation, in which the C^γ lies trans with respect to the nitrogen, is not found in other tryptophan derivatives. In N-acetyl-L-tryptophan[24] C^γ is gauche to N and trans to C', with respect to the $C^\alpha−C^\beta$ bond ($\chi^1 = −56.6°$ and $C'−C^\alpha−C^\beta−C^\gamma = 176.7°$). A similar conformation is found in gly-L-trp[25] and Ac-L-trp-OMe.[26] On the other hand, DL-tryptophan ethyl ester hydrochloride[27] has C^γ in gauche position to N and to C' ($\chi^1 = 68.22°$ and $C'−C^\alpha−C^\beta−C^\gamma = 54.1°$). This kind of conformation is found in aqua(glycyl)tryptophanatocopper(II) dihydrate.[7,8]

Packing of the molecules is shown in Figure 5, in which the projection of the structure along the a axis is illustrated. The N-acetyltryptophan molecules are connected by hydrogen bonds between the nitrogen atom of the indole ring and the acetyl oxygen atom N(1)-H(1$_N$)···O(3) $(1 − x, \bar{y}, \bar{z}) = 2.92$ (2) Å, (N(1)-Ĥ(1$_N$)···O(3) = 149.8°) and between the acetylic nitrogen and uncoordinated carboxylic oxygen N(2)-H(2$_N$)···O(2) $(1 − x, \bar{y}, 1 − z) = 3.01$ (2) Å, (N(2)-Ĥ(2$_N$) ···O(2) = 161.1°). The contact O(3)···O(4) $(1 − x, \bar{y}, \bar{z}) = 3.02$ (3) Å cannot be considered as a hydrogen bond.

Electronic and Magnetic Properties. The room-temperature solid electronic spectra of all the type 2 complexes show a band envelope centered at 15 390–17 090 cm⁻¹ (Figure 3, Table II), which is indicative of a tetragonally distorted ligand field, with CuO_4N_2 chromophore.[28,29] Their similarity with the spectrum
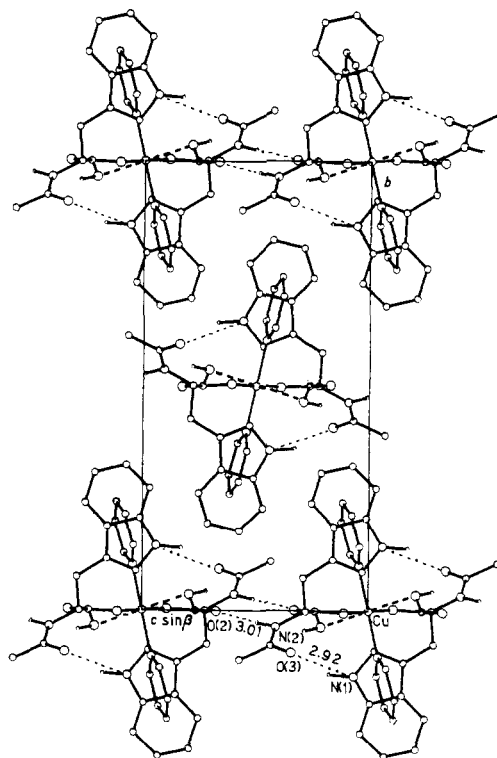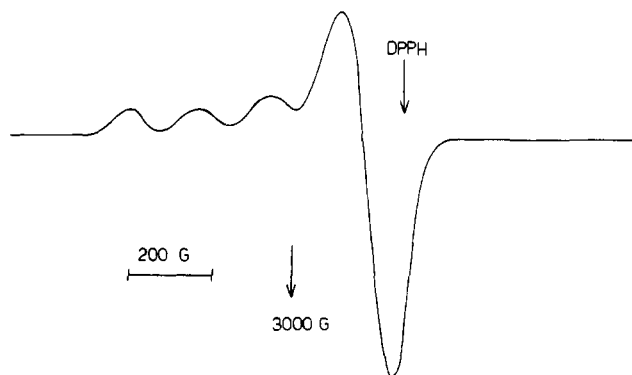

Figure 5. Projection of the structure along [100].

Figure 6. EPR spectrum of $Cu(Actrp)_2(py)_2(H_2O)_2$ complex at room temperature.

of the structurally known $Cu(Actrp)_2(py)_2(H_2O)_2$ complex confirms the tetragonal configuration of these complexes and the CuO_4N_2 chromophore. The shift of the d–d bands at higher energies in the order py < 3pic < 4pic agrees with the basicity of the amines.[30]

The EPR results obtained on polycrystalline samples are summarized in Table II (Figure 6). The values found for the parallel components of the g and A tensors, in agreement with the X-ray data for the $Cu(Actrp)_2(py)_2(H_2O)_2$ complex, with the electronic results, and with the literature,[31,32] confirm the presence of elongated tetragonal structures and of an O_4N_2 chromophore in all the type 2 complexes.

In the $Cu(Actrp)_2B_2$ complexes, with respect to the structurally known $Cu(Actrp)_2(py)_2(H_2O)_2$ complex, the absence of coordinated water molecules must be counterbalanced by the carboxylate group, which may act as bidentate.

Type 3 Complexes. This group contains all the adducts of the aliphatic heterocyclic amines.

Electronic and Magnetic Properties. The "lilac" complexes show "normal" room-temperature magnetic moments and two d–d bands in the 15 870–20 160-cm⁻¹ spectral range in the solid state (Table II). These complexes may be therefore considered to possess similar configurations.

Table VII. Torsion Angles (deg) in Some Tryptophan Derivatives[a]

	ω	ϕ	χ^1	$\chi^{2.)}$	$\chi^{2.2}$
acetyl-L-tryptophan (a)	172.9	−56.9	−59.2	116.5	−70.4
glycyl-L-tryptophan dihydrate (b)	−178.1	−72.9	−65.1	60.6	−122.3
acetyl-L-tryptophan methyl ester (c)	−176.5	−65.6	−64.7	88.0	−89.7
DL-tryptophan ethyl ester (d)			71.5	−83.5	96.1
aqua(glycyl)-L-tryptophanatocopper(II) dihydrate (e)	179.5	−165.7	56.5	80.6	−86.0
present work	178.3	139.5	166.2	−121	166.7

[a] (a) Reference 24; (b) ref 25; (c) ref 26; (d) ref 27; (e) ref 7 and 8.

Table VIII. More Relevant IR Bands

	$\nu(NH)_i$	$\nu(NH)_p$	$\nu(NH)_A$	$\nu(NH)_p$	$\nu(OCO)_a$	$\nu(OCO)_s$	$\Delta\nu$
ActrpH	3387 vs 3335 m	2970 mb		2970 mb	1710 vs	1235 vs	475
D-ActrpH	2525 vs 2474 m	2230 ms		2230 ms	1700 vs	1233 s	467
ActrpNa	3400 vs	3280 sb			1588 vs	1398 vs	190
D-ActrpNa	2530 vs 2435 sb	2440 s 2360 ms			1585 vs	1400 vs	185
Binuclear Complexes							
{Cu(Actrp)₂·H₂O}₂[a]	3428 s	3330 sb			1605 vs	1415 vs	191
Monodentate Amino Acid							
Cu(Actrp)₂(py)₂(H₂O)₂[a]	3400 sh 3310 s	3270 sh			1585 vs	1400 vs	185
Cu(Actrp)₂(NCH₃pipz)₂	3400 sh 3360 m	3270 ms	3220 m		1602 vs	1400 vs	202
Cu(Actrp)₂(morph)₂	3400 sh 3378 ms	3270 ms	3222 m		1600 vs	1402 vs	198
Cu(Actrp)₂(pipd)₂	3400 sh 3315 sh	3271 vs	3233 m		1601 vs	1401 vs	200
Bidentate Amino Acid							
Cu(Actrp)₂(py)₂	3400 mw	3275 s			1600 vs	1396 vs	204
Cu(Actrp)₂(3pic)₂	3400 mw	3275 s			1610 vs	1395 vs	215
Cu(Actrp)₂(4pic)₂	3402 mw	3268 s			1610 vs	1385 vs	225
Cu(Actrp)₂·pipz	3395 w	3260 s	3222 sh		1602 vs	1385 vs	217

[a] The bands at 3575, 3508 ms cm⁻¹ in Cu(Actrp)₂·H₂O and at 3545 ms cm⁻¹ in Cu(Actrp)₂(py)₂(H₂O)₂ may be attributed to the coordinated water molecules.

The position and shape of their transitions (Figure 3), similar to those of other complexes for which direct structural information is available from X-ray analyses,[33-36] are consistent with in-plane square-planar coordination, involving a O_2N_2 donor-atom set.

Their magnetic resonances (Table II) are also in agreement with these results. In fact, extensive studies on planar complexes, containing a CuO_2N_2 chromophore, have established that $g_\parallel$ and $A_\parallel$ values of 2.10-2.23 and 165-205 × 10⁻⁴ cm⁻¹, respectively, are to be expected.[36,37]

The red shift in the electronic spectra and greater $g_\parallel$ and $A_\parallel$ values of the type 2 complexes with respect to the type 3 complexes agree with the stereochemical change from tetragonal (type 2) to square planar (type 3). In fact, it has been a generally accepted rule that the g values decrease and energies increase as the planar ligand field becomes stronger, or as the axial ligand field becomes weaker.[38,39] This different behavior of the type 2 and 3 complexes depends on the basicity of the amines being greater for the aliphatic than for the aromatic heterocyclic amines, which causes stronger Cu–N bonds in the former than in the latter adducts.

The "blue" Cu(Actrp)₂·pipz complex shows an electronic spectrum suggesting an intermediate stereochemistry between type 2 and type 3 complexes. The rather narrow EPR line of its EPR spectrum with respect to the other complexes is suggestive of an electron delocalization due to the piperazine molecules "bridging" two copper(II) ions.[40,41]

Infrared Spectra. The IR spectra of all the complexes (Table VIII) are treated at the same time, being similar to each other, to that of the structurally known Cu(Actrp)₂(py)₂(H₂O)₂ complex, and to those of the alkali salts. This suggests that only the carboxylate group of the amino acid is involved in the metal coordination. On the other hand, the coordination of the amino acid toward oxygen atoms is also indicated by the EPR and electronic results.

The assignment of the N–H stretching vibrations of the indole ($\nu(NH)_i$) (3387 vs, 3335 m cm⁻¹) and of the peptide ($\nu(NH)_p$) (2970 mb cm⁻¹) groups of the amino acid is reasonable as in the solid state the NH of the peptide group is involved in intermolecular hydrogen bonding.[24] On complex formation these bands do not significantly change in position with respect to those of the sodium salt, excluding the participation of these groups in the metal coordination.

The amine coordination is demonstrated by the shift at lower energies of the NH stretching vibration ($\nu(NH)_A$ in Table VIII), in the aliphatic, and of the bands in the 800–500-cm⁻¹ region, in the aromatic heterocyclic amines, with respect to free amines.[42-46] The shape of these bands appears well resolved in the type 3 complexes, in which is also found a band at 3220–3233 cm⁻¹ assignable to NH stretching of the aliphatic heterocyclic amines. The lowering of these bands with respect to free amines[42,43] indicates that these amines are coordinated to the metal atom toward the nitrogen atom.

The coordination of the aromatic heterocyclic amine is demonstrated by the shift of the bands in the 800–500-cm⁻¹ region with respect to free amines.[44-46]

In the assignment of the way in which the carboxylate group coordinates, the trends in positions of and separation between the intense antisymmetric and symmetric carboxylate stretching vibrations[18,47] are considered of primary importance. This criterion in some cases is misleading, as is demonstrated by the small $\Delta\nu$ values ($\nu(OCO)_{as} - \nu(OCO)_s$) in the structurally known Cu(Actrp)₂(py)₂(H₂O)₂ (this work) and Ni(H₂O)₄(CH₃COO)₂[48,49] complexes, as the small separation in both the complexes derives from strong intramolecular hydrogen bonding between the uncoordinated carboxylate oxygen atoms and water molecules (O–O distances 2.79 and 2.619 Å, respectively).

The simultaneous examination of the position of the symmetric carboxylate stretching vibration, which is the band

directly connected with the oxygen atom linked to the copper(II) ion, together with $\Delta\nu$ separation, may help to prevent one from falling into this error.

In our complexes $\nu(OCO)_s$ appears at 1415 cm^{-1} in the binuclear Cu(Actrp)$_2\cdot$H$_2$O complex, in which the carboxylate group acts as a "bridging" bidentate, at 1400–1402 cm^{-1} in the type 3 complexes, and at 1385–1396 cm^{-1} in the type 2 complexes, in which the carboxylate group acts as monodentate and bidentate, respectively.

Theoretically $\nu(OCO)_s$ should be found at higher energies in bidentate carboxylate than in monodentate. The inversion in the experimental results depends upon the fact that the uncoordinated oxygen atom of the carboxylate group is always involved in strong intermolecular or intramolecular hydrogen bonding, which may be the real reason for the monodentate behavior of the carboxylate group.

Although the spectral range of $\nu(OCO)_s$ is very restricted, we suggest that in general for the compounds of the carboxylates and amino acids, which do not contain complicating donor side chains, values of $\nu(OCO)_s$ greater than $\sim$1414 cm^{-1} may be assumed as strongly indicative of bridging bidentate carboxylate, while values in the $\sim$1400–1414-cm^{-1} spectral range are indicative of monodentate and those lower than $\sim$1400 cm^{-1} of bidentate carboxylate. In particular in the case of bidentate coordination $\nu(OCO)_s$ appears at the same or lower energy than that of the corresponding alkali salts.

The experimental support for truly bidentate carboxylate coordination is small owing to the lack of structurally known compounds available ($\nu(OCO)_s$ at 1397 cm^{-1} [50] was found for the bis(N-acetylglycinato)copper(II) tetrahydrate[5d]). In the case of "bridging" bidentate coordination there is the support of a great number of literature data, as reported in ref 18.

In the case of monodentate coordination many experimental results confirm our suggestion. In fact $\nu(OCO)_s$ at 1413[48] and at 1400 cm^{-1} (this work) are found in the Ni(H$_2$O)$_4$-(CH$_3$COO)$_2$[49] and Cu(Actrp)$_2$(py)$_2$(H$_2$O)$_2$ complexes, respectively, in which the carboxylate acts as monodentate, and at 1405 cm^{-1} in the Ni(teta)(OAc)$_2$ complex, in which the carboxylate is almost certainly monodentate.[48] Furthermore, complexes of the type (NiL$_2$(H$_2$O)$_2$) (L = glycinate and α- and β-alaninate) and Zn(gly)$_2\cdot$H$_2$O, in which only one oxygen atom of the carboxylate group is involved in the metal coordination,[51] show $\nu(OCO)_s$ in the 1404–1414-cm^{-1} spectral range.[52,53]

Supplementary Material Available: A listing of the observed and calculated structure factors for the reflections used in the analysis and a table of thermal parameters (6 pages). Ordering information is given on any current masthead page.

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