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Spectroscopic and Structural Investigation of Two (2,2′-Bipyridyl)bis(N-protected-aminoacidato)copper(II) Complexes, Two Compounds Containing Truly CuN_2O_2 Chromophore

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The compounds of formula [Cu(bipy)(acleuO)$_2$] (1) and [Cu(bipy)(ts-β-alaO)$_2$] (2) (bipy = 2,2′-bipyridil, acleuO = N-acetyl-DL-leucinate anion, ts-β-alaO = N-tosyl-β-alaninate anion) were synthesized and characterized by means of spectroscopic and structural measurements. Complex (1) crystallizes in the monoclinic space group C2/c with cell parameters a = 17.465(4), b = 19.740(5), c = 9.080(2) Å, β = 115.0(1)° with Z = 4; complex (2) crystallizes in the triclinic space group P$\bar{1}$, with cell parameters a = 14.489(3), b = 14.308(3), c = 8.659(1) Å, α = 75.0(1), β = 74.6(1), γ = 66.6(1)°, Z = 2. Both structures were solved by conventional Patterson and Fourier methods and refined to R factors of 4.10 and 3.8% respectively. In both crystals the Cu atom is four-coordinated by the nitrogen atoms of a bipy molecule and two carboxylate oxygens of two N-protected aminoacid anions acting as unidentate ligands. The only significant difference between the coordination geometry of (1) and (2) is in the tetrahedral distortion of the coordination plane. Complex (2) is strictly planar, while in complex (1) the distortion expressed by the dihedral angle between the N(1)CuN(1′) and O(1)CuO(1′) planes is 20.8°. The electronic and EPR results agree with these different coordination geometries. The infra-red data are consistent with a truly monodentate carboxylate group. The spectroscopic results on a series of previously investigated [Cu(bipy)(N-protected aminoacidato)$_2$] complexes of unknown structures are discussed again in the light of the present structural reports.

Introduction

The accumulated information on the crystal structures of ternary copper(II) complexes with 2,2′-bipyridil (bipy) and O, or O, N or N donor ligands clearly shows that a somewhat distorted square-pyramidal geometry is preferred [1–9]. In these complexes the mutual influence of the four in plane donor atoms and the number of active sites on the second ligand is discriminating toward the choice of the apical ligand. With unidentate or bidentate ligands, the apical position is occupied by a water molecule [1–4], and even by much weaker coordinating species such as ethanol [8] and isopropanol [9]. This behavior was assigned to the stabilization effect of bipy on the equatorial ligands [8]. As a consequence, the axial ligand may be replaced by a different species with retention of the square-pyramidal geometry [8], or removed with formation of dehydrate complexes with coordination geometry change [8].

For the ternary anhydrous bipy complexes, which are easily formed by N-protected amino acids, the lack of structural data has prevented an unambiguous assignment of coordination geometry [10–16].

We have now separated suitable crystals for X-ray diffraction analysis of two different N-protected amino acids: N-acetyl-DL-leucine and N-tosyl-β-alanine (N-tosyl group is the 4-toluensulfonyl group) and report here their crystal and molecular structures. Furthermore, from comparison of their spectroscopic properties with those of previously investigated N-protected amino acidate–Cu(II)–bipy complexes [10–16] a more reliable assignment of the coordination geometry of the complexes of unknown structures may be derived.

Experimental

Preparations

Complex (1). This complex was prepared as reported in ref. 14. Recrystallization from ethanol and diethyl ether produces blue-violet crystals. *Anal.* Found: C, 55.2; H, 6.5; N, 10.0. $C_{26}H_{36}CuN_4O_6$ requires: C, 55.3; H, 6.4; N, 9.9%. Complex (2). The simple [Cu(ts-β-alaO)$_2$] complex was obtained by evaporation at room temperature of a water-

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methanol 1:1 solution of copper(II) acetate monohydrate and N-tosyl-β-alanine in a molar ratio of 1:2. The green complex was dissolved in methanol and an equimolar amount of solid bipy was added. Then diethyl ether was added to the solution, which was left at 4 °C overnight. The violet crystals separated were filtered off and rapidly washed with cold ethanol. *Anal.* Found: C, 50.9; H, 4.7; N, 7.9; S, 8.7. $C_{30}H_{32}CuN_4O_8S_2$ requires: C, 51.1; H, 4.6; N, 8.0; S, 9.1%.

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 or in nujol mull on KBr as support in 4000–250 cm^{-1} spectral range. The EPR spectra were recorded on a Jeol PE-3X spectrometer on polycrystalline samples using diphenylpicryhydrazyl (DPPH, g = 2.0036) as the calibrating field marker.

X-Ray Data Collection

Crystal Data for [Cu(bipy)(acleuO)$_2$] (*1*). $C_{26}H_{36}CuN_4O_6$, M = 564.1, Monoclinic, a = 17.465(4), b = 19.740(5), c = 9.080(2) Å, β = 115.0(1)°, U = 2837 Å^3, Space group $C2/c$, D_m = 1.30 g cm^{-3} (by flotation), Z = 4, D_c = 1.32 g cm^{-3}, F(000) = 1188, Cu-Kα radiation, λ = 1.54178 Å, μ(Cu-Kα) = 14.2 cm^{-1}, crystal dimensions 0.13 × 0.16 × 0.58 mm.

Crystal Data for [Cu(bipy)(ts-β-alaO)$_2$] (*2*). $C_{30}H_{32}CuN_4O_8S_2$, M = 703.96, Triclinic, a = 14.489(3), b = 14.308(3), c = 8.659(1) Å, α = 75.0(1), β = 74.6(1), γ = 66.6(1)°, U = 1565 Å^3, Space group $P\bar{1}$, D_m = 1.47 g cm^{-3} (by flotation), Z = 2, D_c = 1.49 g cm^{-3}, F(000) = 730, Cu-Kα radiation, λ = 1.54178 Å, μ(Cu-Kα) = 25.5 cm^{-1}, crystal dimensions 0.10 × 0.14 × 0.08 mm.

Intensity data for both crystals were collected at room temperature on an automated Siemens AED single-crystal computer controlled diffractometer with the ω–2θ scan technique up to $\theta \leqslant 60°$. The intensities of one standard reflection, monitored at 50-reflection intervals, showed no significant changes. All data were corrected for Lorentz and polarization effects but not for absorption in view of the low μR (0.10) (assuming cylindrical shape for the crystal) for complex (*1*), and because of the small and almost isotropic dimensions of the crystal (2). A total of 2037 and 5087 independent reflections were measured for (*1*) and (*2*) respectively; of these, 1317 and 3411 for (*1*) and (*2*) respectively with $I > 2\sigma(I)$ were denoted as observed and used in structure determination.

TABLE I. Atomic Coordinates, with Esds in parentheses, for [Cu(bipy)(acleuO)$_2$] (*1*).

Atom	x	y	z
Cu	0.0000	0.10899(5)	0.2500
N(1)	−0.0570(2)	0.0321(2)	0.1011(5)
C(1)	−0.1190(3)	0.0375(3)	−0.0516(6)
C(2)	−0.1610(4)	−0.0189(3)	−0.1375(7)
C(3)	−0.1394(4)	−0.0820(3)	−0.0686(7)
C(4)	−0.0749(4)	−0.0879(3)	0.0866(8)
C(5)	−0.0348(3)	−0.0303(2)	0.1670(6)
O(1)	0.0320(2)	0.1773(2)	0.4185(4)
O(2)	0.1538(2)	0.1746(2)	0.3959(4)
C(6)	0.1064(3)	0.1990(2)	0.4531(6)
C(7)	0.1342(3)	0.2596(2)	0.5687(6)
N(2)	0.2237(2)	0.2558(2)	0.6819(5)
C(8)	0.2498(4)	0.2108(3)	0.8015(7)
O(3)	0.2008(3)	0.1706(2)	0.8227(5)
C(9)	0.3430(4)	0.2107(4)	0.9126(7)
C(10)	0.1181(4)	0.3242(3)	0.4689(7)
C(11)	0.1319(4)	0.3901(3)	0.5639(8)
C(12)	0.0650(8)	0.4005(5)	0.6293(15)
C(13)	0.1312(6)	0.4489(3)	0.4553(11)

Solution and Refinement of the Structures

Complex (*1*). The structure was solved by conventional Patterson and Fourier methods, and refined isotropically by full-matrix least-squares calculation to R = 7.9%. The final anisotropic cycles of the refinement, including hydrogens at the calculated positions with variable isotropic thermal parameters, converged to R = 4.10 and R_w = 4.13%. The weighting scheme employed was $w = 1.0/\sigma^2(F_o) + 0.0062\ F_o^2)$; six reflections (110, $\bar{1}$11, 221, $\bar{4}$02, $\bar{5}$12, $\bar{1}$32) probably affected by secondary extinction or counting errors were excluded from the final refinement.

Complex (*2*). The structure was solved by conventional Patterson and Fourier methods; full-matrix least-squares refinement of positional and isotropic thermal parameters for all the non-hydrogen atoms led to convergence at R = 9.6%. At this stage the hydrogen atoms, then treated as fixed contributors, were added to the model at their calculated positions. Further full-matrix least-squares anisotropic refinement of non-hydrogen atoms improved the R and R_w factors to 3.8 and 4.0% respectively. The weighting scheme employed was $w = 1.85/(\sigma^2(F_o) + 0.0078\ F_o^2)$. Eight strong low-angle reflections were excluded from the final refinement as being probably affected by secondary extinction. For both complexes, complex neutral-atom scattering factors [17] were employed throughout; all the calculations were performed on a CDC Cyber 7600 computer using the SHELX-76 program package [18] and the ORTEP plotting program [19].

TABLE II. Atomic Coordinates with Esds in Parentheses for [Cu(bipy)(ts-β-alaO)$_2$] (*2*).

Atom	*x*	*y*	*z*
Cu	0.54970(4)	0.21114(4)	0.82122(6)
N(1)	0.4949(2)	0.1169(2)	0.7683(3)
C(1)	0.4078(3)	0.1448(3)	0.7145(5)
C(2)	0.3774(3)	0.0728(4)	0.6810(5)
C(3)	0.4370(3)	−0.0292(4)	0.7048(5)
C(4)	0.5277(3)	−0.0587(3)	0.7579(5)
C(5)	0.5554(3)	0.0154(3)	0.7886(4)
N(2)	0.6613(2)	0.0766(2)	0.8724(3)
C(6)	0.7443(3)	0.0634(3)	0.9267(4)
C(7)	0.8197(3)	−0.0317(3)	0.9539(5)
C(8)	0.8092(3)	−0.1157(3)	0.9249(6)
C(9)	0.7232(3)	−0.1042(3)	0.8692(5)
C(10)	0.6500(3)	−0.0067(3)	0.8446(4)
O(1)	0.4350(2)	0.3334(2)	0.7646(3)
O(2)	0.5378(2)	0.3345(2)	0.5267(3)
C(11)	0.4557(3)	0.3725(3)	0.6152(5)
C(12)	0.3715(3)	0.4680(3)	0.5552(5)
C(13)	0.3591(3)	0.4722(3)	0.3882(5)
N(3)	0.3537(2)	0.3740(2)	0.3719(4)
S(1)	0.2452(1)	0.3619(1)	0.3940(1)
O(3)	0.2682(2)	0.2559(2)	0.3853(4)
O(4)	0.1811(2)	0.4034(2)	0.5338(4)
C(14)	0.1883(3)	0.4375(3)	0.2240(5)
C(15)	0.2302(3)	0.4068(3)	0.0767(5)
C(16)	0.1844(3)	0.4618(4)	−0.0553(5)
C(17)	0.0978(3)	0.5496(3)	−0.0448(6)
C(18)	0.0533(4)	0.6099(4)	−0.1946(6)
C(19)	0.0574(4)	0.5786(3)	0.1022(8)
C(20)	0.1007(4)	0.5244(4)	0.2401(6)
O(5)	0.6163(2)	0.2883(2)	0.8784(3)
O(6)	0.4982(2)	0.2930(2)	1.0997(3)
C(21)	0.5718(3)	0.3162(3)	1.0160(4)
C(22)	0.6163(3)	0.3784(3)	1.0729(5)
C(23)	0.7125(3)	0.3090(3)	1.1423(4)
N(4)	0.6877(2)	0.2315(2)	1.2776(3)
S(2)	0.7772(1)	0.1276(1)	1.3392(1)
O(7)	0.7262(2)	0.0678(2)	1.4666(4)
O(8)	0.8406(2)	0.0848(2)	1.1996(4)
C(24)	0.8547(3)	0.1594(3)	1.4277(4)
C(25)	0.9606(3)	0.1180(3)	1.3832(4)
C(26)	1.0214(3)	0.1334(3)	1.4641(5)
C(27)	0.9796(3)	0.1894(3)	1.5890(5)
C(28)	1.0478(4)	0.2014(4)	1.6816(7)
C(29)	0.8743(3)	0.2321(3)	1.6297(5)
C(30)	0.8112(3)	0.2179(3)	1.5502(5)

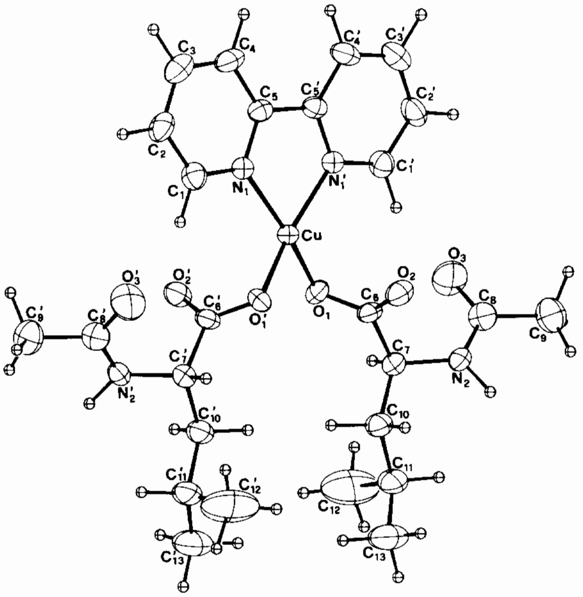

Fig. 1. ORTEP view of the [Cu(bipy)(acleuO)$_2$] complex showing the atom numbering and the thermal motion ellipsoids (40%) for the non-hydrogen atoms. The hydrogen atoms are represented as spheres of arbitrary radius.

Final fractional coordinates for non-hydrogen atoms of (*1*) and (*2*) are listed in Tables I and II, respectively.

Supplementary Data Available

(No. SUP... 26 pp): structure factors, thermal parameters, H-atoms coordinates and thermal parameters, least-squares planes, bond distances and bond angles involving carbon atoms.

Analysis

Nitrogen, carbon, hydrogen and sulfur were analyzed with a C. Erba Elemental Analyser Instrument Mod. 1106.

Results and Discussion

Description of the Structures

Drawings of the structures, showing the labelling scheme are given in Figs. 1 and 2. Selected bond

TABLE III. Selected Bond Distances (Å) and Bond Angles (deg) with Esds in Parentheses for [Cu(bipy)(acleuO)$_2$] (*1*).

Distances			
Cu–N(1)	1.996(4)	O(2)–C(6)	1.245(7)
Cu–O(1)	1.936(4)	C(7)–N(2)	1.465(6)
N(1)–C(1)	1.355(6)	N(2)–C(8)	1.325(7)
N(1)–C(5)	1.352(6)	C(8)–O(3)	1.240(8)
O(1)–C(6)	1.275(6)		

(continued overleaf)

TABLE III. *(continued)*

Angles

N(1)–Cu–N(1′)	81.0(2)	N(1)–C(5)–C(5′)	114.1(2)
O(1)–Cu–O(1′)	91.7(2)	O(1)–C(6)–O(2)	123.7(4)
O(1)–Cu–N(1)	163.6(2)	O(1)–C(6)–C(7)	115.2(5)
O(1)–Cu–N(1′)	95.7(2)	O(2)–C(6)–C(7)	120.9(5)
Cu–O(1)–C(6)	110.6(3)	C(7)–N(2)–C(8)	120.2(5)
Cu–N(1)–C(1)	125.9(3)	N(2)–C(7)–C(6)	121.1(4)
Cu–N(1)–C(5)	111.1(3)	N(2)–C(7)–C(10)	109.5(4)
N(1)–C(1)–C(2)	121.2(5)	N(2)–C(8)–C(9)	116.6(5)
N(1)–C(5)–C(4)	122.1(5)	O(3)–C(8)–C(9)	121.0(5)
C(1)–N(1)–C(5)	118.6(4)	O(3)–C(8)–N(2)	122.3(6)

Primed atoms are related to unprimed by the following symmetry transformation of the reference coordinates: –x, y, ½ – z.

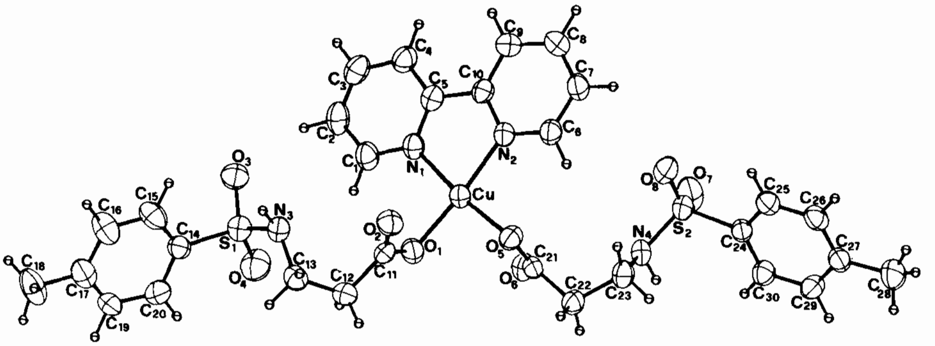

Fig. 2. ORTEP view of the [Cu(bipy)(ts-β-alaO)$_2$] complex showing the atom numbering and the thermal motion ellipsoids (40%) for the non-hydrogen atoms. The hydrogen atoms are represented as spheres of arbitrary radius.

TABLE IV. Selected Bond Distances (Å) and Bond Angles (deg) with Esds in Parentheses for [Cu(bipy)(ts-β-alaO)$_2$] *(2)*.

Distances

Cu–N(1)	2.005(4)	N(3)–S(1)	1.606(4)
Cu–N(2)	1.996(2)	S(1)–O(3)	1.436(3)
Cu–O(1)	1.934(2)	S(1)–O(4)	1.421(3)
Cu–O(5)	1.944(3)	S(1)–C(14)	1.768(4)
N(1)–C(1)	1.335(6)	O(5)–C(21)	1.277(4)
N(1)–C(5)	1.359(4)	O(6)–C(21)	1.233(5)
N(2)–C(6)	1.333(6)	C(23)–N(4)	1.467(5)
N(2)–C(10)	1.353(6)	N(4)–S(2)	1.613(3)
O(1)–C(11)	1.277(4)	S(2)–O(7)	1.442(3)
O(2)–C(11)	1.233(4)	S(2)–O(8)	1.425(3)
C(13)–N(3)	1.483(6)	S(2)–C(24)	1.759(5)

Angles

N(1)–Cu–N(2)	80.9(1)	C(13)–N(3)–S(1)	120.6(2)
N(1)–Cu–O(1)	93.1(1)	N(3)–S(1)–O(3)	105.7(2)
N(1)–Cu–O(5)	173.4(1)	N(3)–S(1)–O(4)	108.1(2)
N(2)–Cu–O(5)	92.5(1)	N(3)–S(1)–C(14)	108.4(2)
N(2)–Cu–O(1)	173.9(2)	O(3)–S(1)–C(14)	106.5(2)
O(1)–Cu–O(5)	93.6(1)	O(4)–S(1)–C(14)	107.5(2)
Cu–N(1)–C(1)	126.5(3)	S(1)–C(14)–C(15)	118.7(3)
Cu–N(1)–C(5)	114.7(3)	S(1)–C(14)–C(20)	121.0(4)
Cu–N(2)–C(6)	125.9(3)	O(5)–C(21)–O(6)	122.6(4)

(continued on facing page)

TABLE IV. *(continued)*

Cu–N(2)–C(10)	115.0(2)	O(5)–C(21)–C(22)	115.9(3)
Cu–O(1)–C(11)	109.5(2)	O(6)–C(21)–C(22)	121.5(3)
Cu–O(5)–C(21)	111.0(3)	C(22)–C(23)–N(4)	109.2(3)
C(5)–N(1)–C(1)	118.8(4)	C(23)–N(4)–S(2)	120.3(2)
N(1)–C(5)–C(10)	114.5(4)	N(4)–S(2)–O(7)	105.6(2)
C(10)–N(2)–C(6)	119.0(3)	N(4)–S(2)–O(8)	107.6(2)
C(5)–C(10)–N(2)	114.8(3)	N(4)–S(2)–C(24)	109.6(2)
O(1)–C(11)–O(2)	122.6(3)	O(7)–S(2)–C(24)	107.2(2)
O(1)–C(11)–C(12)	114.8(3)	O(8)–S(2)–C(24)	106.6(2)
O(2)–C(11)–C(12)	122.7(3)	S(2)–C(24)–C(25)	119.5(3)
C(12)–C(13)–N(3)	111.1(3)	S(2)–C(24)–C(30)	120.2(3)

distances and angles for (*1*) and (*2*) are listed in Tables III and IV, respectively. Remaining bond distances and bond angles are available as Supplementary material.

(*1*). The structure is built up of monomeric units of [Cu(bipy)(acleuO)$_2$] in which the Cu atom, which lies on the twofold axis, exhibits tetrahedrally distorted square-planar geometry. The N_2O_2 coordination occurs through the nitrogen atoms of the bipy ligand and two carboxylate oxygens from symmetry related N-acetyl-DL-leucinate anions, acting as unidentate ligands. The closest approaches to the octahedral sites about the metal ion are due to O(2) and O(2′) carboxylate oxygens. On the basis of the interatomic distance (2.764(2) Å) and of some interatomic angles (O(1)–Cu···O(2) = 52.9(2)°) we have considered this interaction out of range for even weak semi-coordination [1]. Otherwise the coordination geometry may be regarded as elongated octahedral with two off-the z-axis long Cu–O distances [20].

The deviations of the donor atoms from their mean plane within the ±0.25–0.27 Å range and the dihedral angle of 20.8° between the O(1)CuO(1′) and N(1)CuN(1′) planes both indicate a significant tetrahedral distortion of the basal square-planar coordination geometry.

The dimensions of the organic ligands compare well with those observed in N-protected amino acids- [21] or bipy- [1–9, 22, 23] copper complexes. The planar individual pyridine rings of the bipy molecule are twisted about the 2,2′ bond by 9.8°; this value is in the 0–13.4° previously observed range for this coordinated ligand [4, 22, 23].

The crystal packing is mainly due to a hydrogen bond interaction between the peptide nitrogen and the uncoordinated carboxylate O atom of an adjacent molecular unit [N(2)···O(2′) = 2.871(6) Å; H···O(2′) = 1.83 Å; ∠N(2)–H···O(2) = 161.3°; (′ = ½ – x, ½ – y, 1 – z)]; there are no other short van der Waals contacts.

(*2*). The crystal is composed of discrete molecular units of [Cu(bipy)(ts-β-alaO)$_2$] which show the Cu atom to be in a strictly square-planar coordination geometry. It is interesting to note that the metal binding by the organic ligands is the same as in the previous structure, and similarly the closest approaches to the axial octahedral sites about the metal atom are due to the uncoordinated carboxylate oxygens [Cu···O(2) = 2.704(2) Å, O(1)–Cu···O(2) = 53.6(1)°; Cu···O(6) = 2.751(3) Å, O(5)–Cu···O(6) = 52.6(1)°]. These axial non-bonding interactions could prevent a square-pyramidal pentacoordination about the metal atom, the most frequently observed one for ternary bipy and peptide or aminoacid copper(II) complexes [1–9]

A comparison between corresponding Cu-donor bond distances in the present complexes shows no significant differences; the somewhat short Cu–O bond distances [from 1.934 to 1.944 Å] could be due to the π-back bonding from the metal atom to the aromatic amine to which the increased stability of such ternary Cu^{2+} complexes [24] has repeatedly been attributed.

The only significant difference between the coordination geometry of the present complexes is in the tetrahedral distortion of the coordination plane. Unlike the structure of complex (*1*), in the structure of (*2*) the Cu and its donor atoms are nearly coplanar, with deviations from their mean plane ranging from –0.0017 to 0.0028 Å and a corresponding dihedral angle at the Cu atom of 0.3°.

In the [Cu(bipy)(NO$_2$)$_2$] complex, which possesses similar square-planar stereochemistry, the coordination plane presents a moderate tetrahedral distortion in the range ±0.13 Å [22].

Bond distances and angles within the organic ligands are normal. The individual pyridine rings of the bipy are planar within experimental error and twisted about the 2,2′ bond by 2.2°.

The crystal packing is mainly due to two hydrogen bond interactions involving the uncoordinated carboxylate oxygens and the amide groups of adjacent molecular units [N(3)···O(6)^{i} = 2.857(5) Å, H···O(6)^{i} = 1.95 Å, ∠N(3)–H···O(6)^{i} = 157.6°; N(4)···O(2)^{ii} = 2.858(5) Å, H···O(2)^{ii} = 1.96 Å,

TABLE V. Room-Temperature Electronic, EPR and Infrared Results for 2,2'-Bipyridil-bis(N-protected amino acidato)copper(II) Complexes.

	Complexes	d–d band maximum (cm^{-1})	$g_{\parallel}$	$g_{\perp}$	$\nu(OCO)_{as}$ (cm^{-1})	$\nu(OCO)_s$ (cm^{-1})	Ref.
1	$[Cu(bipy)(acleuO)_2]$	16670 14290sh	2.257	2.050	1600vs	1400vs	14, this work
2	$[Cu(bipy)(ts\text{-}\beta\text{-}alaO)_2]^a$	17600 14800sh	2.204	2.060	1600vs	1398vs	this work
3	$[Cu(bipy)(acvalO)_2]$	17200 14300sh	2.253	2.063	1582vs	1402vs	15
4	$[Cu(bipy)(bzglyO)_2]$	16670 14290sh			1602vs	1390vs	11
5	$[Cu(bipy)(ac\text{-}\alpha\text{-}alaO)_2]$	16390			1603vs	1405vs	13
6	$[Cu(bipy)(ac\text{-}\beta\text{-}alaO)_2]$	16300	2.212	2.087	1580vs	1400vs	16
7	$[Cu(bipy)(acglyO)_2]$	15750 13300sh			1608vs	1396vs	10
8	$[Cu(bipy)(bz\text{-}\beta\text{-}alaO)_2]$	15870			1588vs	1395s	12

[a] $\nu(SO_2)_{as}$ = 1328, 1320vs; $\nu(SO_2)_s$ = 1155vs; $\nu(SN)$ = 940s; $\delta(SO_2)$ = 570s; $\rho(SO_2)$ = 550vs (30).

$\angle N(4)–H\cdots O(2)^{ii}$ = 157.2°; (i = x, y, z − 1; ii = x, y, z + 1)].

Spectroscopic Results

The room temperature electronic data, the EPR parameters and the more relevant infrared bands for both the compounds are reported in Table V, together with the spectroscopic results on a series of structurally unknown [Cu(bipy)(N-protected amino acidato)$_2$]. The electronic and EPR data for (*1*) and (*2*) are within the range expected for CuN_2O_2 chromophore [25, 27] and the marked tetrahedral distortion from planarity of complex (*1*) with respect to complex (*2*) is reflected in its d–d band maximum and in the g-values; in fact the increasing tetrahedral distortion shifts the main absorption band to lower energy, as previously found in tetrachlorocuprates [26], and increases the g-values [25, 26]. The comparison of electronic and EPR results of complexes (*1*) and (*2*) with those of the other complexes of Table V suggests that the *3–6* complexes possess an approximately square-planar arrangement with CuN_2O_2 chromophore, while for the complexes *7* and *8* the shift to ≅15800 cm^{-1} may be more consistent with a square-pyramidal geometry [9].

In the infra-red spectra of (*1*) and (*2*) we may note that the same binding mode of carboxylate groups and the similarity in their hydrogen bonds justifies the strict similarity of ν(OCO) stretching frequencies. For the other complexes of Table V, the comparison of the stretching frequencies of carboxylate group with those of complexes (*1*) and (*2*) and with those of other structurally known complexes of the same N-protected amino acids [10, 21, 28, 29] strongly support a unidentate coordination of carboxylate group, thus reinforcing our assignment of a four-coordinated geometry with respect to the previously suggested tetragonal octahedral geometry.

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References

1 W. Fitzgerald, J. Foley, D. McSweeney, N. Ray, D. Sheahan, S. Tyagi, B. J. Hathaway and P. O'Brien, *J. Chem. Soc., Dalton Trans.*, 1117 (1982) and refs. therein.

2 K. Von Deuten and G. Klar, *Cryst. Struct. Commun., 9,* 479 (1980).

3 K. Aoki, *J. Chem. Soc., Chem. Commun.*, 600 (1977).

4 L. Antolini, G. Marcotrigiano, L. Menabue and G. C. Pellacani, *Inorg. Chem., 22,* 141 (1983) and refs. therein.

5 C. J. Neitzel and R. Desiderato, *Cryst. Struct. Commun., 4,* 333 (1975).

6 G. Nardin, L. Randaccio, R. P. Bonomo and E. Rizzarelli, *J. Chem. Soc., Dalton Trans.*, 369 (1980).

7 N. J. Ray and B. J. Hathaway, *Acta Crystallogr., B34,* 3224 (1978).

8 L. Antolini and L. Menabue, *Inorg. Chem.*, in press.

9 L. Antolini, L. P. Battaglia, A. Bonamartini Corradi, G. Marcotrigiano, L. Menabue, G. C. Pellacani and M. Saladini, *J. Chem. Soc., Dalton Trans.*, in press.

10 G. Marcotrigiano and G. C. Pellacani, *Can. J. Chem., 52,* 3607 (1974).

11 G. Marcotrigiano and G. C. Pellacani, *Z. Anorg. Allg. Chem., 413,* 171 (1975).

12 G. Marcotrigiano, L. Menabue and G. C. Pellacani, *Inorg. Chim. Acta, 19,* 133 (1976).

13 G. Marcotrigiano, L. Menabue and G. C. Pellacani, *J. Inorg. Nucl. Chem., 39,* 1897 (1977).

14 G. Marcotrigiano, L. Menabue, P. Morini and G. C. Pellacani, *Bull. Chem. Soc. Jpn., 52,* 3420 (1979).

15 G. Marcotrigiano, L. Menabue and G. C. Pellacani, *Inorg. Chim. Acta, 46,* 107 (1980).

16 L. Menabue, P. Prampolini, M.Saladini and P. Morini, *Inorg. Chim. Acta, 68,* 157 (1983).

17 'International Tables for X-Ray Crystallography, Vol. 4', Kynoch Press, Birmingham, 1974, pp. 99–101, 149–150.

18 G. M. Sheldrick, 'SHELX 76 Program for Crystal Structure Determination', University Chemical Laboratory, Cambridge, 1976.

19 C. K. Johnson, 'ORTEP' Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1965.

20 B. J. Hathaway, *Structure and Bonding, 14,* 49 (1973).

21 (a) L. P. Battaglia, A. Bonamartini Corradi, L. Menabue, G. C. Pellacani, P. Prampolini and M. Saladini, *J. Chem. Soc., Dalton Trans.*, 781 (1982) and refs. therein;
(b) L. Antolini, L. P. Battaglia, A. Bonamartini Corradi, G. Marcotrigiano, L. Menabue, G. C. Pellacani and M. Saladini, *Inorg. Chem., 21,* 1391 (1982) and refs. therein.

22 F. S. Stephens, *J. Chem. Soc. (A),* 2081 (1969).

23 B. J. Hathaway, *Coord. Chem. Rev., 41,* 423 (1982) and refs. therein.

24 H. Sigel, *Met. Ions Biol. Syst., 2,* 63 (1973) and refs. therein.

25 R. C. Rosenberg, C. A. Root, P. K. Rabenstein and H. B. Gray, *J. Am. Chem. Soc., 97,* 2092 (1975).

26 L. P. Battaglia, A. Bonamartini Corradi, G. Marcotrigiano, L. Menabue and G. C. Pellacani, *Inorg. Chem., 18,* 148 (1979).

27 Y. Mino, T. Ishida, N. Ota, M. Inoue, K. Nomoto, H. Yoshioka, T. Takemoto, Y. Sugiura and H. Tanaka, *Inorg. Chem., 20,* 3440 (1981).

28 G. Marcotrigiano, G. C. Pellacani, L. P. Battaglia and A. Bonamartini Corradi, *Cryst. Struct. Commun., 5,* 923 (1976).

29 L. P. Battaglia, A. Bonamartini Corradi, G. Marcotrigiano, L. Menabue and G. C. Pellacani, *Inorg. Chem., 20,* 1075 (1981).

30 L. Antolini, L. P. Battaglia, G. Battistuzzi Gavioli, A. Bonamartini Corradi, G. Grandi, G. Marcotrigiano, L. Menabue and G. C. Pellacani, *J. Am. Chem. Soc., 105,* 4327 (1983) and refs. therein.