Spectroscopic and electronic properties of mixed ligand aminoacidatocopper(II) complexes – Molecular structure of [Cu(4,7-dimethyl-1, 10-phenanthroline) (L-phenylalaninato)](ClO4)

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Spectroscopic and electronic properties of mixed ligand aminoacidatocopper(II) complexes
Molecular structure of [Cu(4,7-dimethyl-1,10-phenanthroline)(L-phenylalaninato)](ClO$_4$)

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Abstract

Mixed-ligand aminoacidatocopper(II) complexes of the types, [Cu(L-phe)(*NN*)](ClO$_4$)·nH$_2$O [L-phe=L-phenylalaninato; *NN*=2,2′-bipyridine (n=2), 1,10-phenanthroline (n=2), and 4,7-dimethyl-1,10-phenanthroline (dmphen, n=0)], [Cu(gly)(*NN*)](ClO$_4$)·nH$_2$O [gly=glycinato; *NN*=2,2′-bipyridine (n=1), 1,10-phenanthroline (n=0), neocuproine (n=0), and ethylenediamine (n=2)], and [Cu(L-ala)(*NN*)](ClO$_4$)·nH$_2$O [L-ala=L-alaninato; *NN*=2,2′-bipyridine (n=0), 1,10-phenanthroline (n=1), and neocuproine (n=2)], have been synthesized and characterized by elemental analyses, and IR, UV–Vis, CD, and EPR spectroscopic measurements. The molecular structure of [Cu(L-phe)(dmphen)](ClO$_4$) (**1**) has been determined by three-dimensional X-ray diffraction data. Complex **1** consists of discrete perchlorate anions and square planar cationic copper complexes. Based on the spectroscopic data, the structures of the complexes are either square pyramidal or square planar in solid state, whereas they are square pyramidal in solution. The sequence of d orbitals was assigned as $d_{xy} \gg d_{z^2} > d_{x^2-y^2} > d_{yz} > d_{xz}$ for the solution species as deduced from the Gaussian resolved electronic absorption and CD spectroscopic data. Both aminoacidato and heterocyclic diimine ligands do not participate in π-interactions in these complexes. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Aminoacidatodiiminecopper(II) complexes; X-ray structure; d–d spectra; Circular dichroism spectra; EPR spectra; Gaussian analysis

1. Introduction

The complexity of stereochemistry of Cu(II) complexes has well been documented [1], and many factors [2–4], such as ligand field stabilization energies, the Pauling electroneutrality principle, the Jahn–Teller effect, semicoordination, counter ion effects, steric effects, etc. have been invoked to account for the complicated structures. Correlation of frontier orbitals with stereochemistry of transition metal complexes has been demonstrated in the literature [5]. Indeed, the d orbital energy levels reflect directly the geometries and conformations of the complexes. For instance, the different orientations of the imidazole ligands in [Cu(imidazole)$_4$(NO$_3$)$_2$] [6] and [Cu(imidazole)$_4$(ClO$_4$)$_2$] [7] have been ascribed to the

imidazole π-donating ability [8] and accordingly the layouts of the d_π orbitals are different for these two complexes. It is, therefore, valuable to study the bonding properties of ligands in order to correlate with the stereochemistry of complexes. To this end, investigation on the relative energies of d_π orbitals should be very useful in elucidation of the extent of π-interactions between the central metal ion and the ligands.

We have previously studied the electronic structures of some mixed-ligand copper(II) complexes containing diimine ligands. The ethylenediamine (en) complexes, [Cu(diimine)(en)(H$_2$O)](ClO$_4$)$_2$ [9], have a regular sequence of d orbitals as usually observed for square pyramidal copper(II) complexes, namely, the non-bonding $d_{x^2-y^2}$ higher in energy than the potential d_π orbitals, d_{xz} and d_{yz}. No π-interaction was suggested for these complexes. In [Cu(diimine)(acetylacetonato)(ClO$_4$)] complexes [10], the non-bonding $d_{x^2-y^2}$ was found to be degenerate with one of the non-degenerate d_π orbitals.

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The rise of the d_π orbital was ascribed to the π-donating ability of the acetylacetonato ligand, while the diimines showed no π-interactions with the central copper ion. The 2-acetylpyrrolatocopper(II) complexes, [Cu(diimine)(2acpyr)$_2$] [11], exhibited a large separation of the d_{xz} and d_{yz} orbitals suggesting the diimines as π-donors. This is unusual because diimine ligands are generally known to be good π-acceptors [12,13]. It is desirable to provide additional experimental evidence to support the conclusions drawn from Gaussian analysis of the d–d absorption spectra. In this paper, we report analyses of both the d–d absorption and the CD spectra of some chiral aminoacidatodiiminecopper(II) complexes to substantiate the assignments of the electronic structures.

2. Experimental

2.1. Materials and preparations

Glycine (Aldrich), L-alanine (Aldrich), L-phenylalanine (Sigma), ethylenediamine (Fluka), 2,2'-bipyridine (Sigma), 1,10-phenanthroline (Sigma), neocuproine (Sigma), 4,7-dimethyl-1,10-phenanthroline (Aldrich), Cu(ClO$_4$)$_2$·6H$_2$O (Aldrich) and organic solvents are used as received.

(**Caution:** *Perchlorate complexes are potential explosives. Handling of these complexes must be in small quantity with great care*).

2.1.1. [Cu(L-phe)(dmphen)](ClO$_4$) (**1**) [14]

To a MeOH solution (10 ml) of Cu(ClO$_4$)$_2$·6H$_2$O (2.0 mmol), a MeOH solution (10 ml) of L-phenylalanine (2.0 mmol) and NaOH (2.0 mmol) was added, and after stirring for 5 min, dmphen (2.0 mmol) in MeOH (10 ml) was added. After reaction at room temperature for 30 min, the reaction mixture was added with diethyl ether and then refrigerated for a few days to give purple crystalline products. Yield, 75%. M.p. 164°C (dec.). IR (cm^{-1}): ν(N–H) 3258m 3235m; ν(COO) 1647s; δ[C–H(py)] 864s 826s 752m; δ(py) 421m; ν[Cu–N(dmphen)] 322m 303w; ν(ClO$_4$) 1094vs 625s. Found: C, 51.5; H, 4.2; N, 7.8. Calc. for C$_{23}$H$_{22}$N$_3$O$_6$ClCu: C, 51.6; H, 4.1; N, 7.9%. The single crystals suitable for X-ray structure determination were obtained by slow diffusion of diethyl ether to the reaction mixture.

2.1.2. [Cu(L-phe)(phen)](ClO$_4$)(H$_2$O)$_2$ (**2**)

This blue complex was prepared by the procedure as described above but using phen. Yield, 69%. M.p. 132°C (dec.). IR (cm^{-1}): ν(O–H) 3553m 3485m; ν(N–H) 3279m 3217m; ν(COO) 1620vs; δ[C–H(py)] 860s 766m; δ(py) 432mw; ν[Cu–N(phen)] 326mw 293w; ν(ClO$_4$) 1088vs 625s. Found: C, 47.0; H, 4.1; N, 7.4. Calc. for C$_{21}$H$_{22}$N$_3$O$_8$ClCu: C, 46.4; H, 4.1; N, 7.7%.

2.1.3. [Cu(L-phe)(bipy)](ClO$_4$)(H$_2$O)$_2$ (**3**)

This blue complex was prepared by the procedure as described above but using bipy. Yield, 71%. M.p. 148°C (dec.). IR (cm^{-1}): ν(O–H) 3400br m; ν(N–H) 3296m 3206m; ν(COO) 1632s; δ[C–H(py)] 764s 750m; δ(py) 417m; ν[Cu–N(bipy)] 306m 278w; ν(ClO$_4$) 1090vs 623s. Found: C, 44.0; H, 4.3; N, 7.8. Calc. for C$_{19}$H$_{22}$N$_3$O$_8$ClCu: C, 43.9; H, 4.3; N, 8.1%.

2.1.4. [Cu(gly)(phen)](ClO$_4$) (**4**) [15]

This blue complex was prepared by the procedure as described above but using glycine and phen. The blue precipitates from the reaction mixture were filtered and recrystallized from acetonitrile and diethyl ether. The product was dried at room temperature in vacuo over P$_4$O$_{10}$. Yield, 80%. M.p. 272°C (dec.). IR (cm^{-1}): ν(N–H) 3314mw 3259mw; ν(COO) 1586s; δ[C–H(py)] 847s 779m; δ(py) 432m; ν[Cu–N(phen)] 322m 293mw; ν(ClO$_4$) 1088vs 621s. Found: C, 39.8; H, 2.8; N, 9.8. Calc. for C$_{14}$H$_{12}$N$_3$O$_6$ClCu: C, 40.3; H, 2.9; N, 10.1%. Molar conductivity: 114 S cm^2 mol^{-1} in MeCN.

2.1.5. [Cu(gly)(bipy)](ClO$_4$)(H$_2$O) (**5**)

This blue complex was prepared by the procedure as described above but using bipy. Yield, 70%. M.p. 265°C (dec.). IR (cm^{-1}): ν(O–H) 3629br w; ν(N–H) 3337w 3284w; ν(COO) 1586s; δ[C–H(py)] 766s; δ(py) 411m; ν[Cu–N(bipy)] 326mw 293mw; ν(ClO$_4$) 1087vs 623s. Found: C, 34.7; H, 3.2; N, 9.9. Calc. for C$_{12}$H$_{14}$N$_3$O$_7$ClCu: C, 35.1; H, 3.4; N, 10.2%. Molar conductivity: 140 S cm^2 mol^{-1} in MeCN.

2.1.6. [Cu(gly)(neoc)](ClO$_4$) (**6**)

This green complex was prepared by the procedure as described above but using neoc. Yield, 65%. M.p. 213°C (dec.). IR (cm^{-1}): ν(N–H) 3323mw 3270mw; ν(COO) 1576s; δ[C–H(py)] 858s 779m; δ(py) 434mw; ν[Cu–N(neoc)] 341w 299m; ν(ClO$_4$) 1087vs 623s. Found: C, 42.4; H, 3.6; N, 9.1. Calc. for C$_{16}$H$_{16}$N$_3$O$_6$ClCu: C, 43.2; H, 3.6; N, 9.4%. Molar conductivity: 160 S cm^2 mol^{-1} in MeCN.

2.1.7. [Cu(gly)(en)](ClO$_4$)(H$_2$O)$_2$ (**7**)

This blue complex was obtained without recrystallization by the procedure as described above but using ethylenediamine. Yield, 55%. M.p. 201°C (dec). IR (cm^{-1}): ν(O–H) 3596w; ν(N–H) 3337ms 3289ms 3243ms; ν(COO) 1580s; ν[Cu–N(en)] 390m 338ms; ν(ClO$_4$) 1089vs 623s. Found: C, 15.2; H, 3.9; N, 12.1. Calc. for C$_4$H$_{16}$N$_3$O$_8$ClCu: C, 14.8; H, 4.7; N, 13.0%.

2.1.8. [Cu(L-ala)(phen)](ClO$_4$)(H$_2$O) (**8**)

This blue complex was prepared by the procedure as described above but using L-alanine and phen. Yield, 75%. M.p. 273°C (dec.). IR (cm^{-1}): ν(O–H) 3457w br; ν(N–H) 3296w 3232w; ν(COO) 1635s; δ[C–H(py)] 856s 785m;

δ(py) 432m; ν[Cu–N(phen)] 316m 291m; ν(ClO₄) 1080vs 621s. Found: C, 40.7; H, 3.4; N, 9.7. Calc. for C₁₅H₁₆N₃O₇ClCu: C, 40.1; H, 3.6; N, 9.4%. Molar conductivity: 124 S cm² mol⁻¹ in MeCN.

2.1.9. [Cu(L-ala)(bipy)](ClO₄) (9)

This blue complex was prepared by the procedure as described above but using L-alanine and bipy. Yield, 72%. M.p. 263°C (dec.). IR (cm⁻¹): ν(N–H) 3330w 3262w; ν(COO) 1610s; δ[C–H(py)] 774s; δ(py) 415m; ν[Cu–N(bipy)] 340m 320m; ν(ClO₄) 1082vs 621s. Found: C, 38.3; H, 3.3; N, 10.2. Calc. for C₁₃H₁₄N₃O₆ClCu: C, 38.3; H, 3.5; N, 10.3%. Molar conductivity: 136 S cm² mol⁻¹ in MeCN.

2.1.10. [Cu(L-ala)(neoc)](ClO₄)(H₂O)₂ (10)

This green complex was prepared by the procedure as described above but using L-alanine and neoc. Yield, 65%. M.p. 222°C (dec.). IR (cm⁻¹): ν(O–H) 3472m; ν(N–H) 3328mw 3296mw 3233mw; ν(COO) 1601s; δ[C–H(py)] 866s 783m; δ(py) 438mw; ν[Cu–N(neoc)] 291m; ν(ClO₄) 1082vs 621s. Found: C, 41.2; H, 4.4; N, 8.3. Calc. for C₁₇H₂₂N₃O₈ClCu: C, 41.2; H, 4.5; N, 8.5%. Molar conductivity: 158 S cm² mol⁻¹ in MeCN.

2.2. Physical measurements

Electronic spectra were recorded on a Hitachi model 3501 spectrophotometer equipped with an integrating sphere for reflectance measurements. Solid samples in some cases were measured as Nujol mulls on Whatman No. 1 filter paper. Circular dichroism spectra were recorded on JASCO J-720 and J-715 spectropolarimeters. Deconvolution of the visible absorption and CD spectra into Gaussian component bands was performed on a VAX 6510 computer using the profile-fitting program CUVFIT [16]. EPR spectra were obtained using Bruker EMX 10 and ER 200D spectrometers and calibrated with DPPH (g = 2.0037). IR spectra were recorded as Nujol mulls or KBr pellets on a BIO-RAD FTS-40 FTIR spectrometer. A Siemens SMART CCD diffractometer equipped with a normal focus, 3 kW sealed tube X-ray source was used for crystal data collection. Elemental analyses were carried out by the microanalysis laboratories of Taiwan University, Taipei.

2.3. Structure determination and refinement

Details of crystal data and intensity collection are summarized in Table 1. A crystal of complex **1** was selected for indexing and intensity data collection at 293 K in 1271 frames with increasing ω (width of 0.3° per frame). Unit cell dimensions were determined by a least-squares fit of 4357 reflections with 5 < 2θ < 50°. Absorption correction was based on 6619 symmetry-equivalent reflections (−23 ≤ h ≤ 20, −26 ≤ k ≤ 27, −6 ≤ l ≤ 7) using

Table 1
Summary of crystal data and processing parameters for **1**

[Cu(C₉H₁₀NO₂)(C₁₄H₁₂N₂)](ClO₄) (**1**)	
Color; habit: violet; columnar	μ = 1.133 mm⁻¹
Crystal size: 0.05 × 0.05 × 0.30 mm	λ = 0.71073 Å
Space group: P2₁2₁2; orthorhombic	Total refl. (unique): 12 713 (4823)
a = 18.052(1) Å	R_{int} = 5.69%
b = 21.381(1) Å	2θ range: 2.5 to 55.8°
c = 5.845(1) Å	R = 0.0489
V = 2256.0(8) Å³	R_w = 0.0473
Z = 4	Number of parameters: 318
ρ_{calc} = 1.576 g cm⁻³	Absolute structure: η = 1.06(7)

the SHELXTL-PC program package ($T_{min,max}$ = 0.702, 0.942). On the basis of systematic absences, statistics of intensity distribution, and successful solution and refinement of the structure, the space group was determined to be P2₁2₁2.

The structure was solved by direct methods using the SHELXTL-PC program package v.4.0 and refined by full-matrix least-squares on F values. Scattering form factors and anomalous dispersion correction terms were taken from the *International Tables for X-ray Crystallography* [17]. All hydrogen atoms included in the refinement were located in succeeding difference Fourier syntheses after the non-hydrogen atoms were refined anisotropically.

3. Results and discussion

3.1. Description of molecular structures

The molecular structure of the title complex is shown in Fig. 1. Selected bond lengths and angles are given in Table 2. The complex consists of discrete ClO₄⁻ anions and
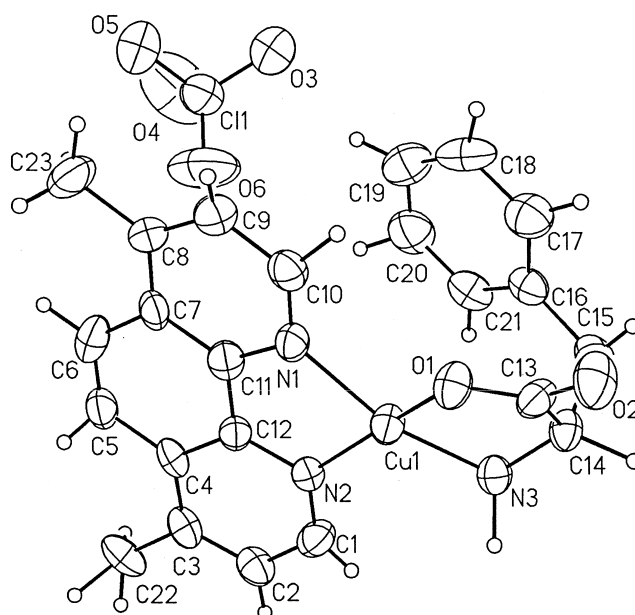

Fig. 1. Molecular structure of **1** with numbering scheme.

Table 2
Selected bond lengths (Å) and angles (°) for **1**

[Cu(L-phe)(dmphen)](ClO$_4$) (**1**)			
Cu(1)–N(1)	1.988(6)	Cu(1)–N(2)	1.992(6)
Cu(1)–N(3)	1.991(6)	Cu(1)–O(1)	1.916(5)
O(1)–Cu(1)–N(1)	93.5(2)	O(1)–Cu(1)–N(2)	166.1(2)
O(1)–Cu(1)–N(3)	85.6(2)	N(1)–Cu(1)–N(2)	82.6(2)
N(1)–Cu(1)–N(3)	162.8(3)	N(2)–Cu(1)–N(3)	102.1(2)

[Cu(L-phe)(dmphen)]$^+$ cations. Although the perchlorate O(3) lies at an axial site of 2.689 Å from the Cu(1), the [Cu(L-phe)(dmphen)]$^+$ is best considered as a square planar structure. This complex ion is somewhat distorted toward a tetrahedral structure; the deviations from the least-squares plane through the CuN$_3$O atoms are O(1) 0.2551, N(1) −0.2730, N(2) 0.2347, N(3) −0.2485 and Cu(1) 0.0317 Å. The gauche L-phe chelate has a λ conformation, with a torsion angle of 13° and an axial benzyl amino acid side chain. From a preliminary X-ray structure determination of [Cu(gly)(phen)](ClO$_4$) (**1**) [18], the discrete [Cu(gly)(phen)]$^+$ is square pyramidal with the gly and phen forming a basal plane and the glycinato carboxylate oxygen of a neighboring complex on the apical position with Cu–O of 2.237 Å. The basal atoms of the [Cu(gly)(phen)]$^+$ are nearly coplanar, while the copper atom lies above the plane by 0.0716 Å toward the axial oxygen. With the exception of the short Cu(1)–O(1) of 1.916(5) Å of the L-phe, the coordination bond lengths of the amino acid ligands are normal as compared with the literature values [19,20]. The mean Cu–N(diimine) distance of ~2.00 Å and the bite angle of ~82° for the diimine ligands are close to the corresponding average values for some phen copper(II) complexes [9,21,22]. The dimensions of **1** are in the normal ranges although the thermal parameters of the perchlorate O atoms are somewhat large.

3.2. Infrared, EPR and electronic spectroscopy

The infrared spectral data for the aminoacidate complexes are given in Section 2. Two medium to weak peaks appear in the region of ~3300 cm^{-1} for the N–H stretching of the aminoacidato groups. The medium N–H stretching peaks for the en complex also appear in this region. For those complexes containing H$_2$O molecules, the O–H stretching peaks were observed in the 3500 cm^{-1} region. These peaks are usually broad and weak suggesting water of crystallization in these complexes. The strong peaks appearing in the ~1600 cm^{-1} region were assigned for the ν(COO) but interfered by the ν(C=N) and δ(NH) peaks. The very strong broad peaks in the 1090 cm^{-1} region suggest the discrete perchlorate anions in agreement with the X-ray structure of **1**. The ν(Cu–O) and ν(Cu–N) of aminoacidate ligands may appear in the region of ~330 to ~430 cm^{-1}, as reported for [Cu(gly)$_2$] and [Cu(ala)$_2$]

complexes [23–25]. However, assignments for these peaks were not attempted because too many peaks appeared in this region. The Cu–N stretches for the diimines [26–28] were tentatively assigned in the 300 cm^{-1} region and somewhat higher frequency for the en.

The EPR, UV–Vis and CD spectral data are given in Table 3. Although the powder EPR spectra are of axial or axial–rhombic type [29], the glass spectra exhibit the fine structures of axial–rhombic spectral features, indicating that the complexes are essentially square pyramidal or square planar. The g_z values are much higher for the neoc complexes (**6**, **10**), whereas the hyperfine coupling constants, A_z(Cu), are much lower, suggesting tetrahedral distortion [30,31] of the basal plane for the neoc complexes, where steric congestion must be serious. For the en complex (**7**), extra sets of peaks were observed indicating decomposition of the complexes in solution and the glass spectrum was not analyzed. All of the complexes exhibit superhyperfine coupling in the g_y region. There appears approximately five-line nitrogen superhyperfine splitting for most of the complexes. The apparent separation of the g_x and g_y indicates the non-degeneracy of the d_{xz} and d_{yz} orbitals of the aminoacidato complexes.

All of the aminoacidatocopper(II) complexes exhibit the solid state LF band maximum in a range of 599 to 635 nm, except the neoc complexes (**6**, **10**), which appear at ~100 nm longer wavelengths. It is likely that these complexes are square pyramidal, except the square planar [Cu(L-phe)(dmphen)](ClO$_4$) with a λ_{max} at 599 nm. The LF band maxima suggest that the bonding strengths of the aminoacidato ligands increase as L-phe<L-ala<gly. In agreement with the EPR spectral data, the much lower λ_{max} values for the neoc complexes indicate that the basal planes are greatly distorted. In aqueous CH$_3$OH solution, the LF band maxima of most of the phen and bipy complexes are somewhat red-shifted. This could stem from the replacement of the axial anions or ligands by the solvent molecules, which is consistent with the results of conductivity measurements. The bidentate ligands are non-dissociative in aqueous CH$_3$OH solution, because the LF band maxima are virtually unaffected by addition of excess amounts of the bidentate ligands. The blue shift of the en complex (**7**) in aqueous CH$_3$OH is due to decomposition of the complexes as suggested from the EPR spectral data.

The $\pi\rightarrow\pi^*$ intraligand transitions appearing in the ~270 and ~220 nm regions for phen complexes (**2**, **4**, **8**) and ~310 and ~240 nm for bipy ones (**3**, **5**, **9**) are

Table 3
Electronic and CD spectral data for aminoacidatocopper(II) complexes

Compound[a]	UV–Vis[b] λ_{max} ($\varepsilon \times 10^3$), nm	CD[c] λ_{max} ($\Delta\varepsilon$), nm	EPR[d]
[Cu(L-phe)(dmphen)]-(ClO$_4$) (**1**)	599/refl. 609(0.076) 300sh(10.0) 275(45.3) 232(26.3)	592(−0.637) 800(+0.082)	g_z 2.237 (2.291) g_y 2.053 (2.070) g_x 2.005 (2.070) A_z^{Cu} 187; A_y^{N} 12
[Cu(L-phe)(phen)]-(ClO$_4$)(H$_2$O)$_2$ (**2**)	635/refl 617(0.075) 295(3.70) 274(11.5) 226(13.3)	598(−0.666) 804(+0.081)	g_z 2.241 (2.291) g_y 2.054 (2.070) g_x 2.007 (2.070) A_z^{Cu} 185; A_y^{N} 11
[Cu(gly)(phen)]-(ClO$_4$) (**4**)	611/mull; [660][e] 629(0.050); [620(0.049)][e] 293sh 272(29.1) 225(29.5)		g_z 2.224 (2.186) g_y 2.061 (2.110) g_x 2.009 (2.060) A_z^{Cu} 187; A_y^{N} 11
[Cu(L-ala)(phen)]-(ClO$_4$)(H$_2$O) (**8**)	621/mull 626(0.050) 272(34.9) 224(35.5)	550(−0.016) 690(+0.027)	g_z 2.217 (2.172) g_y 2.061 (2.113) g_x 2.004 (2.051) A_z^{Cu} 186; A_y^{N} 11
[Cu(L-phe)(bipy)]-(ClO$_4$)(H$_2$O)$_2$ (**3**)	622/refl. 606(0.072) 312(13.6) 301(13.3) 242(13.7)	591(−0.715) 779(+0.123)	g_z 2.235 (2.297) g_y 2.053 (2.090) g_x 2.003 (2.090) A_z^{Cu} 189; A_y^{N} 12
[Cu(gly)(bipy)]-(ClO$_4$)(H$_2$O) (**5**)	606/mull; [605–610][e] 611(0.050); [610(0.053)][e] 311(12.3) 300(12.9) 242(13.8)		g_z 2.231 (2.214) g_y 2.029 (2.063) g_x 2.008 (2.063) A_z^{Cu} 198;
[Cu(L-ala)(bipy)]-(ClO$_4$) (**9**)	611/mull 626(0.060) 310(19.6) 300(19.9) 240(20.1)		g_z 2.221 (2.235) g_y 2.051 (2.216) g_x 2.005 (2.216) A_z^{Cu} 197; A_y^{N} 12
[Cu(gly)(neoc)]-(ClO$_4$) (**6**)	710/mull 690(0.070) 274(22.3) 227(29.1)		g_z 2.265 g_y 2.060 (2.141) g_x 2.020 A_z^{Cu} 169;
[Cu(L-ala)(neoc)]-(ClO$_4$)(H$_2$O)$_2$ (**10**)	692/mull 697(0.070) 274(27.1) 227(34.5)	683(−0.070)	g_z 2.267 (2.231) g_y 2.066 (2.088) g_x 2.018 (2.041) A_z^{Cu} 169; A_y^{N} 13

[a] L-phe = L-phenylalaninato; gly = glycinato; L-ala = L-alaninato; phen = 1,10-phenanthroline; dmphen = 4,7-dimethyl-1,10-phenanthroline; bipy = 2,2′-bipyridine; neoc = neocuproine.

[b] Solution spectra measured in aqueous MeOH with ε in M^{-1} cm^{-1}.

[c] Measured in aqueous MeOH with $\Delta\varepsilon$ in M^{-1} cm^{-1}.

[d] X-band EPR spectra measured at 77 K in aqueous MeOH matrix with coupling constants in 10^{-4} cm^{-1}. Room temperature powder spectral data in parentheses.

[e] Ref. [15].

essentially not varied as compared with those of the corresponding ethylenediamine and acetylacetonate complexes [9,10]. Since no π-interactions have been suggested for the ethylenediamine complexes [9], there must be virtually no π-interactions participating in the diimine–copper bonds in the mixed ligand aminoacidato complexes.

The L-aminoacidatocopper(II) complexes exhibit CD spectral traces in the visible region with a typical pattern of an intense negative peak at ~600 nm and extended to positive $\Delta\varepsilon$ in the ~700 to ~800 nm region. The $\Delta\varepsilon$ values are much greater for the L-phe complexes than for the L-ala complexes. The [Cu(L-ala)(bipy)](ClO$_4$) (**9**) shows only very weak signals likely due to rapid racemization in solution.

3.3. Electronic structures and bonding properties

As evident from the EPR and the visible absorption spectral data, the complexes in solution are of square pyramidal structure with a CuN$_3$O basal plane and a loosely bound apical O atom of the solvent molecule. It is usually observed that the bonding abilities of O-donors are weaker than N-donors for copper(II) complexes. Although the Cu–N and Cu–O bonds of aminoacidato ligands are short, the aminoacidatodiimine copper(II) complexes in the present study exert weaker ligand field strengths than those complexes with a CuN$_4$ basal plane. In order to reveal the electronic structures and the bonding properties of these complexes, the solution LF spectra were deconvoluted into

Gaussian component bands. Starting from a set of four trial peaks, in accordance with the axial–rhombic EPR spectra, computer iteration processes were performed until a minimum value of the reliability factor, R [32], was reached. Each complex had an excellent fit with the R factor within 0.6%, and showed a resulting set of four Gaussian component peaks as illustrated in Fig. 2.

Basically, the CD spectrum in the visible region should be composed of the same component peaks of the corresponding visible absorption spectrum. Their peak positions and half-height widths are quite similar, but the areas are varying. Each of the component peaks of the CD spectrum may bear a positive or negative Cotton effect. It is therefore possible to fit the CD spectral contours by taking the component peaks of the absorption spectrum as a starting trial set. With the peak positions and half-height widths fixed and the areas varied at the early stages, performance of the computer iteration processes can be greatly facilitated. The positions and the half-height widths are then gradually allowed to vary to reach a minimum R value. Each of the L-phe complexes (**1**, **2**, **3**), which have large $\Delta\varepsilon$, had an excellent fit with the R value less than ~0.5%. The component peak positions and the half-height widths are in good agreement with those of the absorption spectrum as shown in Fig. 2. The peak positions along with the half-height widths and the relative peak areas are listed in Table 4. Because of the small $\Delta\varepsilon$, deconvolution

processes for the CD spectra of the L-ala complexes were not performed.

For square pyramidal bis-chelate copper(II) complexes with no π-interactions involved in the coordination bonds, such as [Cu(en)(phen)(H$_2$O)](ClO$_4$)$_2$ and [Cu(en)(bipy)(H$_2$O)](ClO$_4$)$_2$ complexes [9], the sequence of the d orbitals is expected to be $d_{xy} \gg d_{z^2} > d_{x^2-y^2} > d_{yz} > d_{xz}$. The coordinate system is defined with y lying parallel to the basal plane and along the vector from the central copper atom to the midpoint of the two nitrogen atoms of the heterocyclic chelate ring, with x orthogonal to y and lying in the basal plane through the copper atom, and with z orthogonal to x and y. Note the Gaussian components of the absorption and the CD spectra for the L-phe complexes (**1**, **2**, **3**). The agreement in peak positions and half-height widths is striking. Note also that for the absorption spectra, two intense peaks were resolved in the high energy region and two small peaks in the low energy region for all of the structurally similar complexes except the neocuproine ones (**6**, **10**).

In conclusion, the heterocyclic bidentate ligands did not participate in π-interactions in these square pyramidal aminoacidatocopper(II) complexes. The non-degeneracy of the d_{yz} and d_{xz} orbitals is due to the unsymmetrical geometry of the aminoacidato ligands or the possibility of π-donating of the carboxylate O atom [33]. It is therefore quite certain that the sequence of the d orbitals is the same
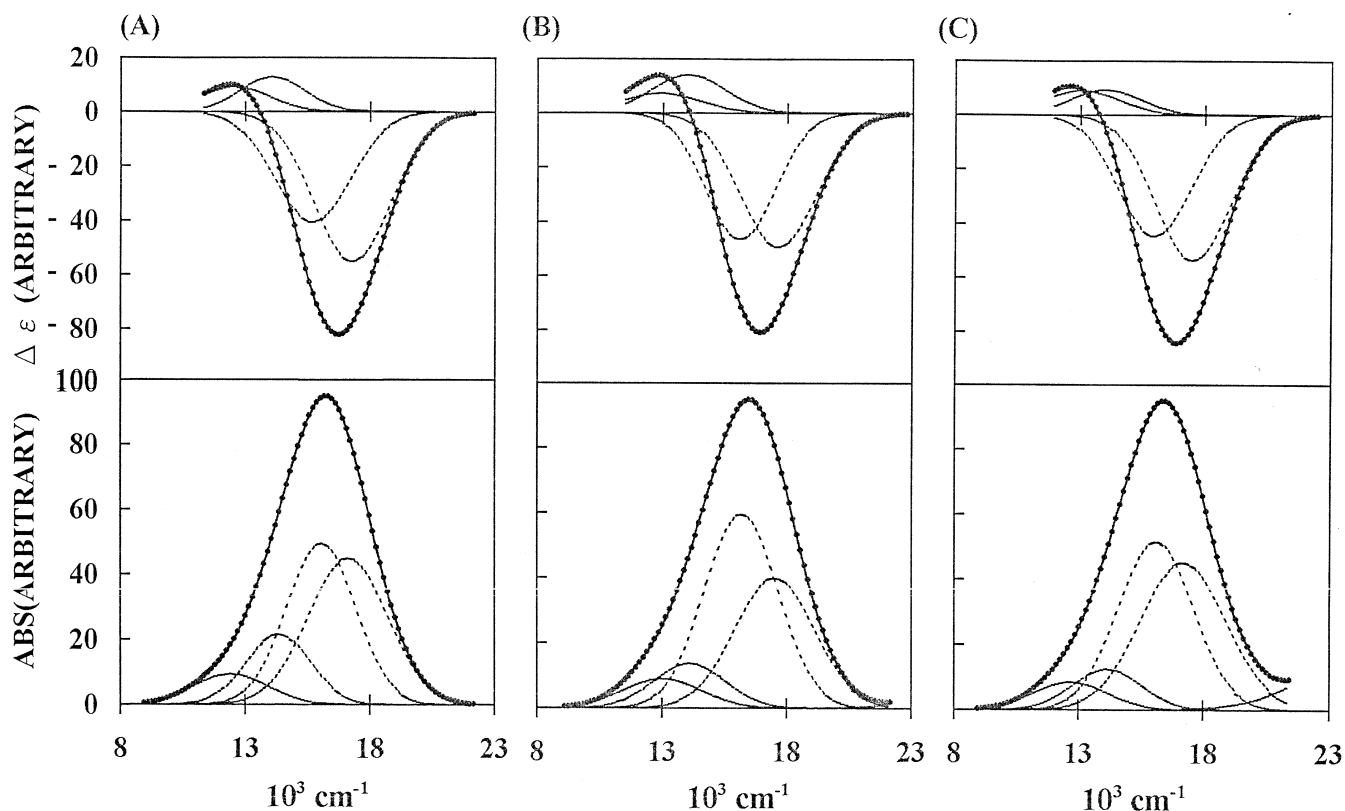

Fig. 2. Solution visible absorption and CD spectra and Gaussian line-shape analysis of: (A) [Cu(L-phe)(dmphen)](ClO$_4$) (**1**), $R=0.55\%$ (ABS), 0.54% (CD); (B) [Cu(L-phe)(phen)](ClO$_4$)(H$_2$O)$_2$ (**2**), $R=0.48\%$ (ABS), 0.41% (CD); (C) [Cu(L-phe)(bipy)](ClO$_4$)(H$_2$O)$_2$ (**3**), $R=0.60\%$ (ABS), 0.45% (CD).

Table 4

Gaussian component bands for the visible absorption and CD spectra of diimineaminoacidatocopper(II) complexes[a]

Band	$\nu(10^3\ cm^{-1})$	Area[b]	$\delta_{1/2}$[c] $(10^3\ cm^{-1})$	Assignment
[Cu(L-phe)(dmphen)](ClO$_4$) (1), R[d] = 0.55%; (0.54%)				
I	12.7; (13.0)	6.9; (+7.9)	3.50; (3.59)	d_{z^2}
II	14.2; (14.0)	9.3; (+7.5)	3.24; (3.34)	$d_{x^2-y^2}$
III	16.1; (16.0)	42.0; (−37.7)	3.54; (3.46)	d_{yz}
IV	17.2; (17.5)	41.8; (−46.9)	4.02; (3.57)	d_{xz}
[Cu(L-phe)(phen)](ClO$_4$)(H$_2$O)$_2$ (2), R = 0.48%; (0.41%)				
I	12.4; (12.6)	7.7; (+7.2)	3.49; (3.26)	d_{z^2}
II	14.3; (14.1)	15.3; (+9.3)	3.01; (3.03)	$d_{x^2-y^2}$
III	16.0; (15.7)	37.6; (−35.2)	3.25; (3.59)	d_{yz}
IV	17.1; (17.3)	39.4; (−48.3)	3.74; (3.64)	d_{xz}
[Cu(L-ala)(phen)](ClO$_4$)(H$_2$O) (8), R = 0.48%				
I	11.9	11.3	2.70	d_{z^2}
II	13.7	10.6	3.04	$d_{x^2-y^2}$
III	15.5	37.6	3.58	d_{yz}
IV	17.0	40.5	3.93	d_{xz}
[Cu(gly)(phen)](ClO$_4$) (4), R = 0.41%				
I	10.9	8.2	3.12	d_{z^2}
II	13.3	14.6	3.17	$d_{x^2-y^2}$
III	15.4	37.2	3.56	d_{yz}
IV	16.9	40.0	3.90	d_{xz}
[Cu(L-phe)(bipy)](ClO$_4$)(H$_2$O)$_2$ (3), R = 0.60%; (0.45%)				
I	13.0; (12.9)	8.5; (+6.7)	3.71; (3.77)	d_{z^2}
II	14.1; (14.0)	9.9; (+12.1)	3.39; (3.49)	$d_{x^2-y^2}$
III	16.2; (16.1)	40.4; (−37.3)	3.47; (3.27)	d_{yz}
IV	17.5; (17.6)	41.2; (−43.9)	3.74; (3.62)	d_{xz}
[Cu(L-ala)(bipy)](ClO$_4$) (9), R = 0.40%				
I	10.6	6.6	3.01	d_{z^2}
II	12.8	16.1	3.20	$d_{x^2-y^2}$
III	15.3	42.1	3.79	d_{yz}
IV	17.3	35.2	3.88	d_{xz}
[Cu(gly)(bipy)](ClO$_4$)(H$_2$O) (5), R = 0.30%				
I	11.2	9.9	3.35	d_{z^2}
II	13.4	11.7	3.02	$d_{x^2-y^2}$
III	15.6	39.2	3.65	d_{yz}
IV	17.2	39.2	3.85	d_{xz}
[Cu(L-ala)(neoc)](ClO$_4$)(H$_2$O)$_2$ (10), R = 0.46%				
I	9.4	11.8	2.56	d_{z^2}
II	12.1	28.1	3.83	$d_{x^2-y^2}$
III	14.2	32.7	3.36	d_{yz}
IV	16.4	27.4	3.21	d_{xz}
[Cu(gly)(neoc)](ClO$_4$) (6), R = 0.48%				
I	9.6	17.0	2.57	d_{z^2}
II	12.2	26.1	3.63	$d_{x^2-y^2}$
III	14.2	31.5	3.40	d_{yz}
IV	16.3	25.4	3.54	d_{xz}

[a] For abbreviations, see footnote (a) of Table 3. CD data shown in parentheses.
[b] Relative peak area in arbitrary scale based on a sum of 100.
[c] Half-eight width.
[d] Reliability factor defined as $R = \Sigma|y_{obs,i} - y_{calc,i}| / |\Sigma\ y_{obs,i}|$.

as those usually observed for square pyramidal copper(II) complexes, namely, $d_{xy}(d_{x^2-y^2}) \gg d_{z^2} > d_{x^2-y^2}(d_{xy}) > d_{yz} \geq d_{xz}$. We prefer a d_{xy} ground orbital here because the spectral behavior is similar for the aminoacid-atodiiminecopper(II) and the ethylenediaminediimine-copper(II) complexes. Finally, the CD spectra of the square pyramidal L-phe complexes, of which the gauche L-phe chelates are of λ conformation, have two positive component peaks of $d_{z^2} \to d_{xy}$ and $d_{x^2-y^2} \to d_{xy}$ transitions and two negative component $d_{yz} \to d_{xy}$ and $d_{xz} \to d_{xy}$ transitions.

Supplementary data

Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request quoting the deposition number 108442.

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