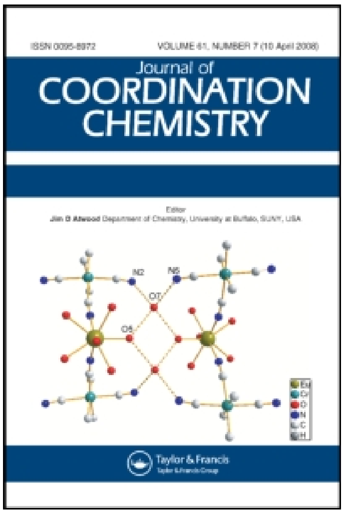

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Synthesis, Characterization and Crystal Structure of a Ternary Cu(II) Complex with 1,10-Phenanthroline and *l*-Leucinate

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SYNTHESIS, CHARACTERIZATION AND CRYSTAL STRUCTURE OF A TERNARY Cu(II) COMPLEX WITH 1,10-PHENANTHROLINE AND L-LEUCINATE

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The complex [Cu(L-Leu)(phen)(H_2O)]NO_3 has been synthesized and characterized by elemental analysis, molar conductivity, spectroscopic and X-ray diffraction methods, where phen = 1,10-phenanthroline and L-Leu = L-leucinate. The complex crystallizes in the triclinic space group $P\bar{1}$ with two molecules in a unit cell of dimensions $a = 7.288(4)$ Å, $b = 11.588(7)$ Å, $c = 12.349(3)$ Å, $\alpha = 86.388(10)^\circ$, $\beta = 76.175(11)^\circ$, $\gamma = 72.132(3)^\circ$, $V = 963.8(10)$ Å^3, $Z = 2$, $D_c = 1.564\,\text{g/cm}^3$, $\mu = 1.177\,\text{mm}^{-1}$, $F(000) = 470$, $R_1 = 0.0611$, and $wR_2 = 0.0711$. The copper(II) is ligated in a distorted square-pyramidal geometry by the two nitrogen atoms of phen and the amino nitrogen atom and one carboxylate oxygen atom from each independent L-Leu moiety in the basal plane, and one water oxygen at the apical position. A supramolecular configuration is formed from strong phen–phen stacking interactions between neighboring [Cu(L-leu)(phen)(H_2O)]$^+$ cations in the crystal.

Keywords: 1,10-Phenanthroline; L-Leucinate; Copper (II); Crystal structure

INTRODUCTION

Ternary metal complexes involving an aromatic amine as the primary ligand and various biomolecules, such as amino acids, peptides, nucleotides, nucleosides, etc. as secondary ligands, have attracted much attention over a number of years [1–4], because these ternary complexes can serve as useful models of metalloenzyme–substrate or metalloenzyme–inhibitor systems [5], and the antitumor mechanism of a new class of antitumor compounds with the general formula *cis*-[Pt(NH_3)$_2$(N-het)Cl] [6]. We have studied a series of ternary metal complexes containing an aromatic amine (bipy,

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phen, TATP, pdphen or pyridine-like ligands) and an amino acid (Gly, L-Phe, L-His, L-Met or L-Tyr) or a nucleotide (UTP or ATP) by UV–Vis, IR, ^{1}H NMR, ESR, X-ray diffraction or potentiometric pH titration methods, and which revealed intramolecular and intermolecular noncovalent interactions in the complexes, e.g. aromatic stacking, hydrogen bonding and hydrophobic interactions, and their structural dependence on the interactions, ligands and central metal ions [4,7–11]. As a continuation of our interest in this field we now describe the synthesis and structural characterization of $[Cu(L\text{-}Leu)(phen)(H_2O)]NO_3$ (L-Leu = L-leucinate group, phen = 1,10-phenanthroline).

EXPERIMENTAL

Synthesis

1,10-phenanthroline (1 mmol) and $Cu(NO_3)_2{\cdot}3H_2O$ (1 mmol) were dissolved in 25 mL of water with heating and stirring. To this solution was added dropwise a hot aqueous solution containing L-Leu (1 mmol). The pH was adjusted to 5 with dilute aqueous NaOH solution, and the mixture was filtered. The resulting solution was left in a desiccator with silica gel for three weeks until well-formed, blue single crystals were obtained. Anal Calcd. for $C_{17}H_{22}CuN_4O_7S$ (%): C, 41.67; H, 4.53; N, 11.44; Found: C, 41.78; H, 4.58; N, 11.36.

Physical Measurements

Elemental analyses (carbon, nitrogen and hydrogen) were performed on a Perkin-Elmer 240C microanalyzer, and the molar conductivity was measured in ethanol with a DDS-11A conductivity gauge. The infrared absorption spectrum in a KBr disk was recorded on a Nicolet 170SX spectrophotometer. The electronic absorption spectrum of the complex was measured in ethanol on a Pharmacia 4000 UV–Vis spectrophotometer at room temperature. The anisotropic X-band ESR spectra of the complex in the crystalline state were recorded on a Brucker ECS 106 spectrometer with a frequency modulation of 100 kHz at ambient temperature.

X-ray Structural Determination of the Complex

Details of the structure solution and refinement for the complex are shown in Table I.

A well-shaped crystal of the complex with approximate dimensions $0.50 \times 0.40 \times 0.11\,\mathrm{mm}^3$ was mounted on a Bruker Smart 1K CCD system diffractometer with graphite monochromated Mo K_α radiation at $\lambda = 0.71073$ Å. The SMART program was applied to search for diffraction peaks to determine cell parameters, and collected data were reduced using the SAINT+ program [12]. Absorption corrections were applied with the Siemens Area Detector ABSorption (SADABS) program [13].

The structure was solved by direct and Fourier methods, and refinements were carried out by full-matrix least-squares on F^2 with positional and anisotropic thermal parameters. The fractional atomic coordinates and anisotropic thermal parameters for non-hydrogen atoms were refined to convergence. All hydrogen atoms were placed in

TABLE I Crystal data and structure refinement for the complex [Cu (L-Leu)(phen)(H_2O)]NO_3

Formula	$C_{18}H_{22}CuN_4O_6$	
M	453.94	
Color	Blue	
Crystal size (mm^3)	0.50 × 0.40 × 0.11	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	$a = 7.288(0)$ Å	$\alpha = 86.388(10)^\circ$
	$b = 11.588(1)$ Å	$\beta = 76.175(11)^\circ$
	$c = 12.349(1)$ Å	$\gamma = 72.132(10)^\circ$
Volume (Å^3), Z	963.8(1), 2	
D_c (g/cm^3)	1.564	
μ(mm^{-1})	1.177	
F(000)	470	
Temperature (K)	293(2)	
θ range for data collection	1.70 to 27.05°	
Range of h, k, l	$-9 \leq h \leq 6$, $-14 \leq k \leq 13$, $-15 \leq l \leq 12$	
Reflections measured	6192	
Independent reflections	4083 ($R_{int} = 0.0279$)	
Completeness to $\theta = 27.05^\circ$	96.3 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	4083/0/300	
Max. and min. transmission	0.8814, 0.5905	
Parameters refined	272	
Goodness of fit on F^2	1.147	
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0611$, $wR_2 = 0.1532$	
R indices (all data)	$R_1 = 0.0711$, $wR_2 = 0.1613$	
Extinction	0.018(2)	
Mar. min. height in final ΔF map (e/Å^3)	0.758, −0.749	

calculated positions. Atomic scattering factors were taken from the International Tables for X-ray Crystallography [14]. All calculations were performed on a PC with the Siemens SHELXS97 [15] and SHELXL97 [16] program packages. Fractional atomic coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms are listed in Table II. The selected bond lengths and angles are collected in Table III.

RESULTS AND DISCUSSION

Elemental analysis of the title complex is in good agreement with the following formula: [Cu(L-Leu)(phen) (H_2O)]NO_3. The complex is soluble in water, methanol and ethanol, but not in ether and other low polarity organic solvents. Molar conductivity in ethanol with the complex approaching 1 : 1 electrolyte value [17] ($\Lambda = 76.32$ S cm^2/mol) supports this formulation.

Crystal Structure

The crystal is composed of [Cu(L-Leu)(phen)(H_2O)]$^+$ cations and nitrate anions, which are packed with each other by electrostatic and hydrogen-bonding interactions

TABLE II Fractional atomic coordinates ($\times 10^4$ Å) and equivalent isotropic displacement parameters *U*(eq) ($\times 10^3$ Å ^{2}) for the complex

Atom	*x*	*y*	*z*	*U*(eq)
Cu(1)	7157(1)	5995(1)	7901(1)	34(1)
C(1)	7271(8)	7910(5)	6101(4)	50(1)
C(2)	7383(9)	8310(5)	5000(5)	58(1)
C(3)	7511(8)	7527(6)	7377(4)	45(1)
C(4)	7530(7)	6334(5)	4461(4)	47(1)
C(5)	7638(8)	5443(6)	3689(4)	59(2)
C(6)	7638(8)	4311(6)	4002(4)	57(2)
C(7)	7489(7)	3960(5)	5148(4)	46(1)
C(8)	7457(8)	2812(5)	5559(5)	56(1)
C(9)	7287(8)	2574(5)	6669(5)	54(1)
C(10)	7171(7)	3487(4)	7377(4)	45(1)
C(11)	7378(6)	4818(4)	5929(4)	36(1)
C(12)	7400(6)	6017(4)	5582(4)	38(1)
N(1)	7300(6)	6785(3)	6386(3)	37(1)
N(2)	7228(5)	4586(3)	7024(3)	36(1)
O(1)	7381(5)	5035(3)	9230(3)	41(1)
O(2)	7490(6)	5124(3)	10989(3)	55(1)
C(13)	7515(7)	5574(4)	10058(4)	39(1)
C(14)	7697(13)	6849(5)	9864(4)	71(2)
C(15)	8353(18)	7354(8)	10586(9)	46(2)
C(15B)	6854(17)	7686(8)	10754(8)	42(2)
C(16)	7869(12)	8765(5)	10627(5)	67(2)
C(17)	9700(12)	8737(9)	10982(6)	97(3)
C(18)	6158(13)	9635(8)	11347(8)	103(3)
N(3)	7764(9)	7195(4)	8727(3)	60(1)
O(3)	853(9)	8225(5)	7625(5)	98(2)
O(4)	2690(20)	8964(19)	6535(18)	102(6)
O(5)	−330(20)	9754(11)	6590(14)	92(4)
O(7)	−1230(20)	9590(12)	7388(17)	112(5)
O(8)	1730(50)	9520(20)	6508(18)	171(14)
N(4)	815(10)	9074(4)	7004(4)	63(1)
O(6W)	3910(5)	6845(4)	8565(4)	53(1)

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE III Selected bond lengths (Å) and angles (°)

Cu(1)–O(1)	1.935(3)	Cu(1)–N(3)	1.984(4)
Cu(1)–N(2)	1.996(4)	Cu(1)–N(1)	2.024(4)
Cu(1)–O(6W)	2.233(4)	O(3)–N(4)	1.206(7)
O(4)–N(4)	1.322(17)	O(5)–N(4)	1.151(11)
O(7)–N(4)	1.399(15)	O(8)–N(4)	1.027(16)
O(1)–Cu(1)–N(3)	83.98(16)	O(1)–Cu(1)–N(2)	92.46(15)
N(3)–Cu(1)–N(2)	166.5(2)	O(1)–Cu(1)–N(1)	170.89(15)
N(3)–Cu(1)–N(1)	100.02(16)	N(2)–Cu(1)–N(1)	81.76(16)
O(1)–Cu(1)–O(6W)	91.73(16)	N(3)–Cu(1)–O(6W)	90.9(2)
N(2)–Cu(1)–O(6W)	102.24(16)	N(1)–Cu(1)–O(6W)	96.37(16)
C(1)–N(1)–Cu(1)	129.7(3)	C(12)–N(1)–Cu(1)	112.2(3)
C(10)–N(2)–Cu(1)	128.8(3)	C(11)–N(2)–Cu(1)	113.2(3)
C(13)–O(1)–Cu(1)	115.7(3)	O(2)–C(13)–O(1)	123.5(4)
O(2)–C(13)–C(14)	119.6(4)	O(1)–C(13)–C(14)	116.9(4)
C(15)–C(14)–N(3)	125.2(6)	N(3)–C(14)–C(13)	111.2(4)
C(14)–N(3)–Cu(1)	110.9(3)	O(8)–N(4)–O(5)	80.8(19)
O(8)–N(4)–O(3)	142(2)	O(5)–N(4)–O(3)	137.2(12)
O(8)–N(4)–O(4)	37(2)	O(5)–N(4)–O(4)	115.5(14)
O(3)–N(4)–O(4)	105.3(11)	O(8)–N(4)–O(7)	124(2)
O(5)–N(4)–O(7)	49.4(10)	O(3)–N(4)–O(7)	92.7(9)
O(4)–N(4)–O(7)	160.8(12)		

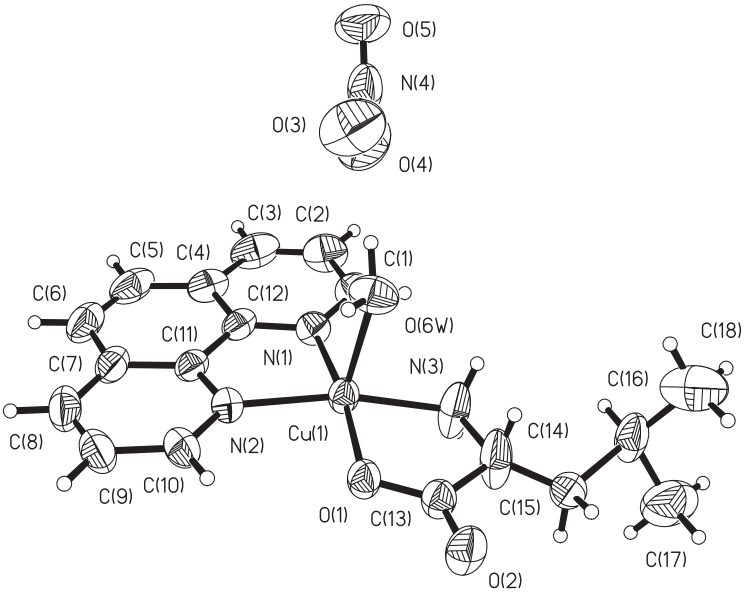

FIGURE 1 ORTEP plot showing the structure of the $[Cu(L\text{-}Leu)(phen)(H_2O)]^+$ cation and the atom-numbering scheme.

[N(3A)$\cdots$O(3) = 2.866(7) Å in $x+1$, y, z, O(6WB)$\cdots$O(3) = 2.772(7) Å, and O(6W)$\cdots$ O(2) in $-x+1$, $-y+1$, $-z+2$]. As shown in Fig. 1, the structure of the cation $[Cu(L\text{-}Leu)(phen)(H_2O)]^+$ is similar to that of the complex reported earlier [Cu(L-phe) (phen) $(H_2O)]^+$ [18]. Each central Cu(II) ion coordinates to the two nitrogen atoms of phen, and the amino nitrogen atom and one carboxylate oxygen atom of L-Leu in the equatorial positions (Cu(1)–O(1) = 1.935(3) Å, Cu(1)–N(1) = 2.024(4) Å, Cu(1)–N(3) = 1.984(4) Å, Cu(1)–N(2) = 1.996(4) Å); a water oxygen atom at an axial position (Cu(1)–O(6W) = 2.233(2) Å), completes the square-pyramidal geometry. N(1), N(2), N(3), O(1) and Cu atoms deviate by −0.0467, 0.0505, 0.0469, −0.0507 and −0.1810 Å, respectively, from the least-squares plane ($6.465x - 0.865y - 0.731z = 3.7118$) defined by the four ligating atoms N(1), N(2), N(3) and O(1), indicating that the five atoms are approximately coplanar. The bond lengths in the complex are comparable to the corresponding values found for [Cu(L-phe)(phen) $(H_2O)]^+$ (Cu–O = 1.927(6) Å, Cu–N = 1.968(9)–2.077(6) Å, Cu–O (w) = 2.213(10) Å). The square-pyramidal geometry around the central Cu(II) atom is severely distorted, the X–Cu–Z angles being 166.5(2) to 100.89(15)° where X and Z are any two atoms which lie *trans* to each other and the X–Cu–Y angles ranging from 81.76(7) to 100.02(7)° where X and Y are any atoms which lie *cis* to each other.

In the crystal of the complex, the phen–phen aromatic-ring stacking interactions (2.567 Å) between the neighboring [Cu(L-Leu) (phen)$(H_2O)]^+$ cations exist, which are significantly stronger than the aromatic-ring stacking interactions (3.0–3.6 Å) in the related ternary metal complexes [1,8,9]. This interaction is similar to the stacking interaction between neighboring DNA bases in the direction of the molecular axis in the DNA double helices [19], and makes the complex form a supramolecular configuration (Fig. 2).

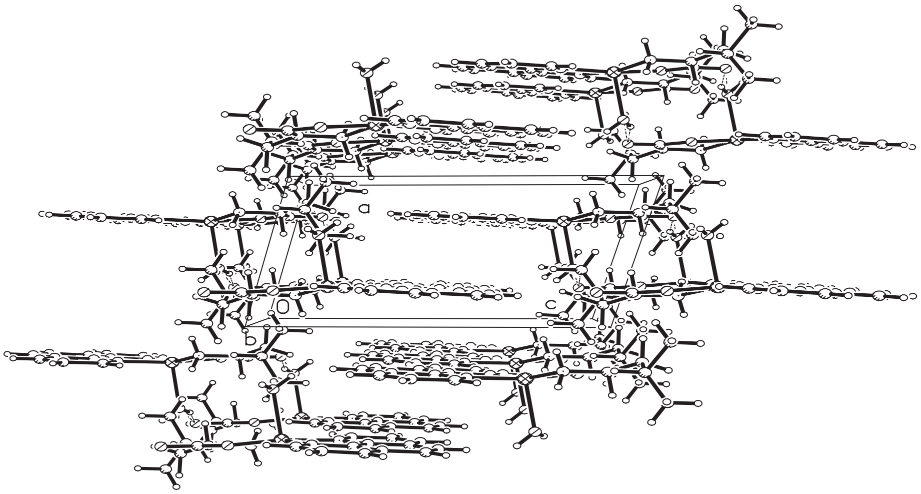

FIGURE 2 Packed view of the complex.

Infrared Absorption Spectrum

The infrared spectrum of the complex shows a strong and broad band at $3396\,\text{cm}^{-1}$, which is ascribed to the stretching mode of the coordinated water molecule. The bands at 3231 and $3135\,\text{cm}^{-1}$ can be attributed to the stretching vibration of the coordinated NH_2 group. The absence of any bands in the region $1750–1700\,\text{cm}^{-1}$ in the IR spectrum of the isolated complex suggests coordination of the COO^- group of L-leucinate to the metal ion. The bands at 1629 and $1392\,\text{cm}^{-1}$ arise from the antisymmetric and symmetric stretching vibrations of the coordinated carboxylate, respectively. The $\Delta\nu_{\text{co}_2}$ value ($\nu^{\text{as}}_{\text{co}_2} - \nu^{\text{s}}_{\text{co}_2} = 223\,\text{cm}^{-1}$) between the bands shows that the carboxylate is monodentate [16]. Thus, one can deduce that the monovalent anion of L-Leu is coordinated to the metal ion as a bidentate N,O-ligand, which is in agreement with the crystal structure mentioned above. The band at $1578\,\text{cm}^{-1}$ is assigned to the stretching vibration of the C=N group of the phen ligand and confirms its coordination to the metal ion. Furthermore, this band could also be ascribed to the deformation mode δ_{NH} of the N–H group belonging to the amino acid moiety [20].

Electronic Absorption Spectrum

The electronic absorption spectrum of the complex in aqueous solution presents four important absorption bands, in which the bands at 222 [$\varepsilon = 20900\,\text{L/(mol cm)}$], 271 [$\varepsilon = 20900\,\text{L/(mol cm)}$] and 295 [$\varepsilon = 95800\,\text{L/(mol cm)}$] can be attributed to the $\pi \rightarrow \pi^*$ transitions of the coordinated phen ligand, the broad and weak absorption band at 618 nm [$\varepsilon = 73\,\text{L/(mol cm)}$] to the $d \rightarrow d$ transition of the central Cu^{2+} ion, which is comparable to those for the related aromatic amine-Cu(II)-amino acid complexes [7–9].

Electron Paramagnetic Resonance Spectra

In order to yield more accurate crystal *g*-values, the single-crystal ESR spectrum for the complex was measured at room temperature.

The g-values of the complex are clearly anisotropic: $g_{\mathrm{I}}=2.152\,\mathrm{G}$, and $g_{\zeta}=2.073\,\mathrm{G}$. The molecular g-values ($>2.04\,\mathrm{G}$) and $g_{\mathrm{I}}>g_{\zeta}$ indicate a distorted square-based pyramidal copper environment (i.e., a $d_{x^2-y^2}$ ground state) [21], which is in agreement with the result obtained by X-ray diffraction.

Acknowledgments

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Supplementary Material

Full lists of crystallographic data are available from the author upon request.

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