Aliphatic Amino Acid–Metal Ion–Aromatic Amine Ternary Complexes. Crystal Structures of Aqua(L-leucinato)(1,10-phenanthroline)copper(II) Nitrate and Aqua(DL-leucinato)(1,10-phenanthroline)copper(II) Nitrate

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Abstract

The crystal structures of the two aliphatic amino acid–metal ion–aromatic diamine ternary complexes, [Cu(L-Leu)(*o*-phen)(H_2O)]NO_3 (**1**) and [Cu(DL-Leu)(*o*-phen)(H_2O)]NO_3 (**2**) (Leu = leucinato and *o*-phen = 1,10-phenanthroline), have been determined by X-ray diffraction. Complex **1** crystallizes in the triclinic space group $P\bar{1}$ with $a = 12.362(2)$, $b = 11.593(2)$, $c = 7.311(2)$ Å, $\alpha = 107.82(2)$, $\beta = 76.05(2)$, $\gamma = 93.62(2)°$, $Z = 2$, $D_{calc} = 1.557$ g cm^{-3}, and $R = 0.045$ for 3184 unique observed reflections. Complex **2** crystallizes in triclinic space group $P\bar{1}$ with $a = 12.368(4)$, $b = 11.608(4)$, $c = 7.280(3)$ Å, $\alpha = 107.16(3)$, $\beta = 75.98(3)$, $\gamma = 93.54(3)°$, $Z = 2$, $D_{calc} = 1.556$ g cm^{-3}, and $R = 0.052$ for 2579 unique observed reflections. The L-Leu complex (**1**) involves two crystallographically independent molecules, which are related by a pseudo center of symmetry except for the C^{β} atoms. Both the **1** and **2** structures are essentially identical, including the crystal packing mode, except for the existence of an exact crystallographic center of symmetry in **2**. In **2** the C^{β} atom of Leu is disordered at two positions corresponding to D- and L-configurations, respectively. In each complex, the copper atom is coordinated in a distorted square-pyramidal geometry by the bidentate Leu and *o*-phen ligands at the equatorial sites and water at an axial position. The isopropyl side chain of each Leu extends away from the aromatic ring system of *o*-phen, thus there is no intramolecular ligand–ligand interaction between them, in contrast to a ring–aliphatic hydrophobic interaction in solution for this ternary system. Factors affecting the formation of a folded structure having such an inter-ligand interaction are considered from the structural viewpoint.

Introduction

Non-covalent ligand–ligand interactions in mixed-ligand complexes have currently received much attention because they could mimic substrate–metal ion–enzyme interactions in the active center of enzymes [1], where substrate recognition processes and subsequent reactions proceed in highly specific manners involving intrinsic non-covalent interactions. These include ring–ring stacking [2–4], ring–aliphatic hydrophobic [2, 5], and electrostatic [6] interactions. Because of the great importance of stereochemistry in non-covalent interactions, X-ray diffraction studies have also been undertaken and indeed substantiated the ring–ring stacking interactions typically in the nucleotide–metal–aromatic diamine system [7] or in the amino acid–metal–aromatic diamine system [8]. On the contrary, however, X-ray evidence for the latter two non-covalent interactions is, to our knowledge, still lacking.

Fischer and Sigel have demonstrated in a solution study [5b] that an intramolecular hydrophobic interaction occurs between the aromatic ring system of an aromatic amine and the aliphatic side chain of leucine in the amino acid–metal–aromatic diamine ternary complex system, in which the two constituents are connected via a metal ion-bridge, though such a 'folded' structure exists in rather small amounts (about 13% for [Cu(Leu)(*o*-phen)]$^+$, where Leu = leucinato and *o*-phen = 1,10-phenanthroline). This led us to an X-ray study of the above ternary system in order to examine such an interaction or compare differences between the solution and the solid state structures. Furthermore, the detailed structural knowledge of amino acids and their metal complexes will be of great utility in structural studies of proteins and peptides. We report here crystal structures of the L-Leu–Cu^{2+}–*o*-phen (**1**) and the DL-Leu–Cu^{2+}–*o*-phen (**2**) ternary complexes. This is only the fourth [9a–c] crystal structure of a metal–leucine complex.

Experimental

Preparation of the Crystals

Complexes **1** and **2** were prepared by mixing L-leucine for **1** or DL-leucine for **2** (26 mg, 0.2

0020-1693/89/$3.50

mmol) dissolved in 3 ml of water and 1,10-phenanthroline (40 mg, 0.2 mmol) and $Cu(NO_3)_2$ (48 mg, 0.2 mmol) dissolved in 5 ml of water, and allowing the solutions to stand at room temperature. Crystals formed after two weeks.

X-ray Structure Determination

Cell parameters were determined on a Rigaku AFC-5 four-circle diffractometer with graphite-monochromated Mo Kα (λ = 0.71073 Å) from 20 high-order reflections in the ranges of $24 < 2\theta < 35°$ for **1** and $20 < 2\theta < 32°$ for **2**. A close similarity of the cell dimensions between **1** and **2** caused a doubt that **1** and **2** are the same compound, i.e. L-leucine in **1** isomerized into DL-leucine. CD measurements, however, denied this possibility, that is, **1** was optically active [CD_{max} (10^3 cm^{-1}) ($\Delta\epsilon$ (mol^{-1} dm^3 cm^{-1})) = 14.5 (+0.17)], while **2** was inactive. Details of the data collections together with structure refinements are summarized in Table 1. Intensities were corrected for LP effects but not for absorption.

The structures were solved by heavy-atom methods and refined with block-diagonal least-squares procedures. For **1**, non-centrosymmetric space group $P1$ was adopted because of the sole presence of optically active L-Leu. A Fourier synthesis phased by two copper atoms revealed that molecules lie nearly in the planes at $z \simeq \pm 1/4$ and that two independent Leu molecules are related by a pseudo center of symmetry. It appends a pseudo mirror symmetry to the structure and results in two possible positions for the C^{β} [C(3)] atom. One of them was chosen according to the known L-configuration, thus assigning the enantiomeric model. When this was done, another peak disappeared. For **2**, the centrosymmetric space group $P\bar{1}$ was first assumed. Interestingly, the situation for **2** was almost same as that for **1**. If one peak was accepted, however, the peak showed an unusual large thermal parameter

TABLE 1. Crystal and refinement data

Compound	**1**	**2**
Formula	$C_{18}H_{22}CuN_4O_6$	$C_{18}H_{22}CuN_4O_6$
Molecular weight	453.95	453.95
a (Å)	12.362(2)	12.368(4)
b (Å)	11.593(2)	11.608(4)
c (Å)	7.311(2)	7.280(3)
α (°)	107.82(2)	107.16(3)
β (°)	76.05(2)	75.98(3)
γ (°)	93.62(2)	93.54(3)
V (Å^3)	967.9(4)	968.8(7)
Space group	$P1$	$P\bar{1}$
Z	2	2
D_{calc} (g cm^{-3})	1.557	1.556
μ (cm^{-1})	11.71	11.70
Radiation used	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)
Crystal size (mm)	0.27 × 0.49 × 0.57	0.09 × 0.13 × 0.38
Temperature (K)	296	296
2θ Range measured (°)	0–50	0–50
Scan mode	ω–2θ	ω–2θ
Scan range (°)	1.5 + 0.5 tan θ	1.6 + 0.5 tan θ
Scan speed (2θ/min, °)	4	4
Background counting(s)	5	5
Transmission factors[a]	0.93–1.11	0.97–1.04
Data measured	3414	3424
Unique data used (m) $[F_o > 3\sigma(F_o)]$	3184	2579
H atoms	not refined	those of *o*-phen refined isotropically
No. variables (n)	524	304
Weighting scheme (w)	0 for 3 strong low-order reflecns 1 for others	0 for 1 strong low-order reflecn 1 for others
R[b]	0.045	0.052
R_w[b]	0.048	0.053
GOF[b]	1.04	1.20
$(\Delta\rho)_{max}$ (e Å^{-3})	0.65	0.65

[a] Ψ-Scan method; normalized to an average of unity. [b] $R = \Sigma||F_o| - |F_c||/\Sigma F_o$; $R_w = [\Sigma w(F_o - |F_c|)^2/\Sigma w F_o^2]^{1/2}$; $GOF = [\Sigma w(F_o - |F_c|)^2/(m - n)]^{1/2}$.

and another peak still appeared. So we deduced that C^{β} is disordered at two positions corresponding to D- and L-configurations, respectively. This situation was also encountered with alternative space group $P1$ (final R, R_w, and $GOF = 0.055$, 0.060, and 1.44, respectively, comparable with those for $P\bar{1}$ in Table 1, and some unreasonable bond angles about the disordered C(3) and C(3′), as discussed below), and thus we here adopt the space group $P\bar{1}$.

TABLE 2. Final atomic coordinates and equivalent isotropic temperature factors[a] for [Cu(L-Leu)(*o*-phen)(H_2O)]NO_3 (1)

	x	*y*	*z*	B_{eq} (Å^2)
Cu(A)	0.2900	0.4000	0.2200	2.4
O(1A)	0.4221(4)	0.4954(5)	0.2331(8)	2.8
O(2A)	0.5980(5)	0.4916(6)	0.2646(11)	4.4
N(1A)	0.3715(5)	0.2744(6)	0.2697(11)	3.2
C(1A)	0.5043(6)	0.4435(8)	0.2642(12)	2.9
C(2A)	0.4784(7)	0.3212(8)	0.3073(14)	3.5
C(3A)	0.5745(7)	0.2322(7)	0.1942(13)	3.4
C(4A)	0.5696(7)	0.1200(8)	0.2727(17)	4.2
C(5A)	0.5972(10)	0.1490(12)	0.4684(19)	5.8
C(6A)	0.6472(13)	0.0243(13)	0.1155(25)	7.8
N(11A)	0.1420(6)	0.3197(6)	0.2342(10)	3.0
N(12A)	0.2013(6)	0.5405(6)	0.2292(10)	2.8
C(11A)	0.1093(9)	0.2074(8)	0.2302(14)	4.0
C(12A)	−0.0020(7)	0.1707(8)	0.2363(12)	3.1
C(13A)	−0.0807(6)	0.2496(9)	0.2547(13)	3.3
C(14A)	−0.0517(7)	0.3679(8)	0.2572(11)	3.2
C(15A)	0.0585(6)	0.3966(7)	0.2455(11)	2.5
C(16A)	0.0919(6)	0.5183(8)	0.2434(11)	2.8
C(17A)	0.0156(6)	0.6012(7)	0.2541(10)	2.5
C(18A)	0.0588(9)	0.7152(9)	0.2484(13)	4.3
C(19A)	0.1662(9)	0.7426(7)	0.2330(14)	3.9
C(20A)	0.2367(7)	0.6511(8)	0.2259(13)	3.4
C(21A)	−0.1310(8)	0.4551(10)	0.2735(14)	4.4
C(22A)	−0.0976(7)	0.5670(10)	0.2692(13)	4.1
O(wA)	0.3584(5)	0.3122(5)	−0.1057(9)	3.7
N(13A)	0.1966(7)	0.0969(9)	0.5932(18)	6.5
O(11A)	0.2623(7)	0.1773(7)	0.5879(13)	6.1
O(12A)	0.2056(18)	0.0253(10)	0.4344(23)	19.7
O(13A)	0.1386(9)	0.0876(13)	0.7428(28)	15.1
Cu(B)	0.7097(1)	0.5990(1)	0.7885(2)	2.4
O(1B)	0.5774(4)	0.5028(5)	0.7576(8)	2.7
O(2B)	0.4013(5)	0.5158(5)	0.7644(9)	3.3
N(1B)	0.6279(6)	0.7096(8)	0.7094(15)	5.0
C(1B)	0.4924(7)	0.5570(6)	0.7663(12)	2.4
C(2B)	0.5068(6)	0.6917(7)	0.7747(13)	2.6
C(3B)	0.4396(7)	0.7349(7)	0.6658(13)	3.1
C(4B)	0.4443(8)	0.8732(8)	0.6939(21)	5.4
C(5B)	0.3993(9)	0.8909(9)	0.5280(18)	5.0
C(6B)	0.3749(12)	0.9534(10)	0.8921(18)	6.0
N(11B)	0.8627(5)	0.6766(6)	0.7767(10)	2.5
N(12B)	0.7975(5)	0.4577(6)	0.7821(9)	2.5
C(11B)	0.8879(7)	0.7910(8)	0.7779(13)	3.3
C(12B)	0.9940(10)	0.8369(10)	0.7600(17)	4.9
C(13B)	1.0779(11)	0.7604(11)	0.7512(15)	5.9
C(14B)	1.0554(7)	0.6339(9)	0.7518(12)	3.5
C(15B)	0.9415(6)	0.5996(8)	0.7643(11)	2.7
C(16B)	0.9064(7)	0.4819(7)	0.7695(11)	2.5
C(17B)	0.9874(8)	0.3915(10)	0.7514(13)	4.3
C(18B)	0.9466(9)	0.2749(8)	0.7574(14)	4.0
C(19B)	0.8327(9)	0.2574(9)	0.7753(14)	4.2
C(20B)	0.7591(8)	0.3478(7)	0.7923(13)	3.2
C(21B)	1.1332(6)	0.5434(11)	0.7441(14)	4.3
C(22B)	1.1012(8)	0.4279(10)	0.7441(15)	4.6
O(wB)	0.6460(6)	0.6811(5)	1.1127(9)	4.0
N(13B)	0.7949(7)	0.9085(5)	0.4321(13)	4.0
O(11B)	0.7360(10)	0.8232(9)	0.4189(18)	9.3
O(12B)	0.8260(17)	0.9631(8)	0.5752(25)	18.4
O(13B)	0.8359(8)	0.9308(13)	0.2792(20)	12.0

(continued)

TABLE 2. *(continued)*

[a] $B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}a_ia_j$.

TABLE 3. Final atomic coordinates and equivalent isotropic temperature factors[a] for [Cu(DL-Leu)(*o*-phen)(H_2O)]NO_3 (2)

	x	*y*	*z*	B_{eq} (Å^2)
Cu	0.2890(1)	0.4001(1)	0.2158(1)	2.7
O(1)	0.4213(3)	0.4951(3)	0.2382(5)	3.3
O(2)	0.5975(3)	0.4858(3)	0.2505(6)	4.1
N(1)	0.3716(4)	0.2757(4)	0.2657(8)	4.1
C(1)	0.5045(4)	0.4410(5)	0.2521(8)	3.1
C(2)	0.4828(5)	0.3158(5)	0.2807(11)	4.7
C(3)[b]	0.5733(6)	0.2268(7)	0.1835(12)	3.4
C(3′)[b]	0.5644(12)	0.2674(13)	0.3327(26)	3.0
C(4)	0.5643(5)	0.1187(5)	0.2732(12)	5.3
C(5)	0.5935(6)	0.1339(7)	0.4646(12)	6.8
C(6)	0.6436(8)	0.0269(7)	0.1098(13)	7.4
N(11)	0.1380(3)	0.3210(4)	0.2308(6)	2.9
N(12)	0.2015(3)	0.5411(4)	0.2242(6)	2.9
C(11)	0.1088(5)	0.2090(5)	0.2273(9)	3.8
C(12)	−0.0012(5)	0.1693(6)	0.2393(10)	4.7
C(13)	−0.0808(5)	0.2467(6)	0.2510(10)	4.7
C(14)	−0.0545(4)	0.3671(5)	0.2529(8)	3.7
C(15)	0.0575(4)	0.3995(5)	0.2412(7)	2.9
C(16)	0.0918(4)	0.5179(5)	0.2384(7)	3.0
C(17)	0.0145(5)	0.6045(5)	0.2503(8)	3.6
C(18)	0.0554(5)	0.7188(5)	0.2448(9)	4.4
C(19)	0.1660(5)	0.7420(5)	0.2293(9)	4.2
C(20)	0.2375(5)	0.6498(5)	0.2176(8)	3.5
C(21)	−0.1325(5)	0.4572(6)	0.2659(8)	4.6
C(22)	−0.1000(5)	0.5691(6)	0.2638(9)	4.8
O(w)	0.3544(3)	0.3188(3)	−0.1095(5)	4.0
N(13)	0.2031(4)	0.0931(4)	0.5776(9)	5.0
O(11)	0.2632(5)	0.1770(5)	0.5849(9)	7.5
O(12)	0.1946(10)	0.0293(6)	0.4271(14)	17.8
O(13)	0.1507(6)	0.0805(8)	0.7325(14)	13.1

[a] $B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}a_ia_j$. [b] The occupancy factors for C(3) and C(3′) are 0.68 and 0.32, respectively.

All non-hydrogen atoms were refined anisotropically for **1** and **2**, including the disordered C(3) and C(3′) in **2** with occupancy factors 0.68 and 0.32, respectively, estimated by their electron densities. All hydrogen atoms were added to the structures in the final cycles of refinements except those attached to minor disordered model. Final atomic coordinates with their e.s.d.s are listed in Tables 2 and 3. Neutral atomic scattering factors and anomalous dispersion corrections for Cu were taken from the International Tables for X-ray Crystallography [10]. All calculations were performed with the UNICS III program system [11] on a FACOM 780 computer.

Results

Complexes **1** and **2** both consist of discrete $[Cu(Leu)(o\text{-phen})(H_2O)]^+$ cations and nitrate anions. The L-Leu complex (**1**) involves two crystallographically independent molecules A and B, which are related by a pseudo center of symmetry except for the C^β atoms. The cationic structures of **1** and **2** with the atom-numbering scheme are shown in Figs. 1 and 2 and their crystal packings in Figs. 3 and 4, respectively. Interatomic distances and angles are listed in Table 4.

The structural features of **1** and **2** are fundamentally alike: the copper atom is coordinated in a distorted square-pyramidal geometry with the equatorial plane defined by a leucinato ligand through the carboxylate oxygen O(1) and the amino nitrogen N(1) atoms and a bidentate *o*-phen; the apical position is occupied by a water molecule. The equatorial coordination planes, from which the Cu atoms deviate towards the axial O atoms by 0.142(4) [A] and 0.201(4) [B] Å in **1** and 0.159(2) Å in **2**, show small tetrahedral distortions with the largest deviations of 0.065(5) [A] and 0.132(8) [B] Å in **1** and 0.047(3) Å in **2** for the amino nitrogens, resulting most probably from their hydrogen-bonding interactions with nitrate groups. The dimensions of the *o*-phen ligands compare well with those observed in the free molecule [12] and metal complexes [8, 13a–c]. In **1** the bond lengths and angles of the L-Leu ligand are as expected, but in **2** some unreasonable bond angles appear involving disordered C(3) and C(3′). We noticed that C(2) and C(4) also have unusual thermal vibrations perpendicular to the molecular plane. It suggests a certain disorder for these atoms, which may be responsible for the deviations from normal bond angles. The side chain of each leucinato ligand assumes the *trans*-CO_2 configuration [9a], i.e. the C^γ atom [C(4)] is *trans* to the carboxylate group with respect to the C^α–C^β bond: torsion angles C(1)–C(2)–C(3)–C(4) = 164.5(8)° [A] and 173.5(8)° [B] for **1** and 160.2(6)° for **2** and N(1)–C(2)–C(3)–C(4) = −69.8(10)° [A] and −63.7(10)° [B] for **1** and −64.1(8)° for **2**.

The crystal packings for both complexes are also similar; they are dominated by hydrogen-bonding interactions, self-stacking interactions of *o*-phen ligands, and hydrophobic self-interactions of isopropyl groups of Leu ligands. The water ligand donates a hydrogen atom to the carboxylate oxygen O(2) belonging to the neighbouring molecule and another to the nitrate oxygen O(11), which also accepts a hydrogen atom from the amino nitrogen of the molecule related by a translation along the *c* axis. Thus a nitrate anion links two complex cations through hydrogen bonds. The average ring–ring spacings of 3.47 and 3.42 Å for **1** and 3.46 and

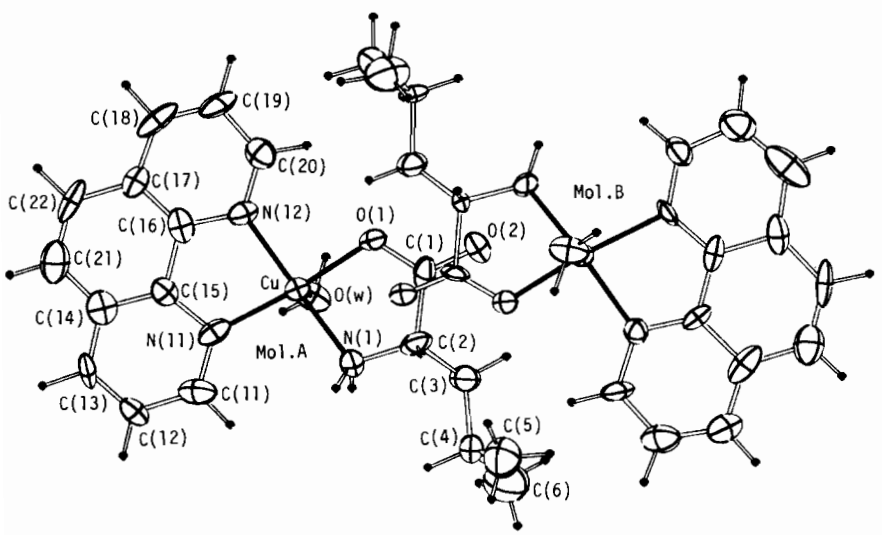

Fig. 1. Cationic structure of **1**. Two independent cations are labeled A and B, respectively.

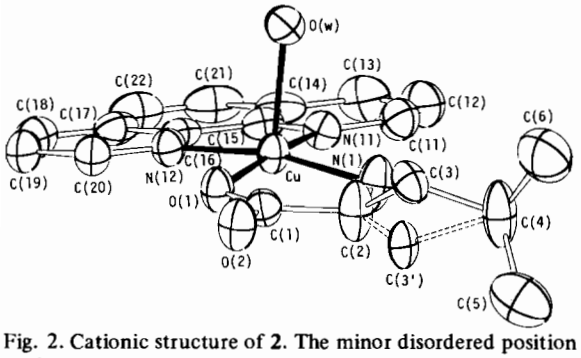

Fig. 2. Cationic structure of **2**. The minor disordered position C(3′) is denoted by broken line.

3.42 Å for **2** are comparable to those observed in other amino acid–metal ternary complexes involving *o*-phen [13a–c] or bipyridyl [13d]. The dihedral angle between the two *o*-phen ligands is 0.5(1)° in **1** but is 0° by symmetry in **2**. The shortest interatomic stacking distances are given in Table 4. The intermolecular van der Waals contacts exist between C(5) of the leucinato side chain and C(20) of the *o*-phen ring [3.65(2) and 3.78(1) Å in **1** and 3.78(1) Å in **2**]. The crystal packing seems to affect the conformation of the leucinato side chain, that is, the steric hindrance between the isopropyl group and neighboring *o*-phen ring-edges prohibits the

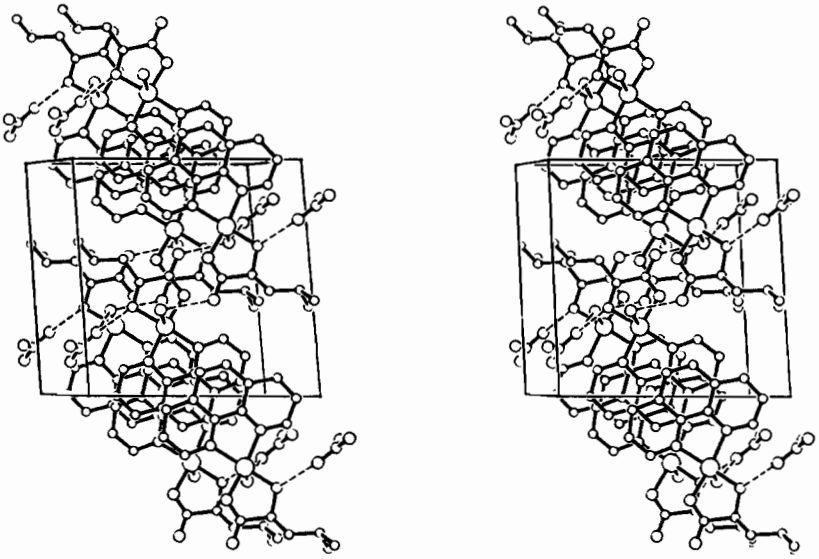

Fig. 3. A stereopair of the crystal packing for **1** viewed down the *c* axis with the *b* axis being horizontal and the *a* axis vertical. Broken lines denote hydrogen bonds.

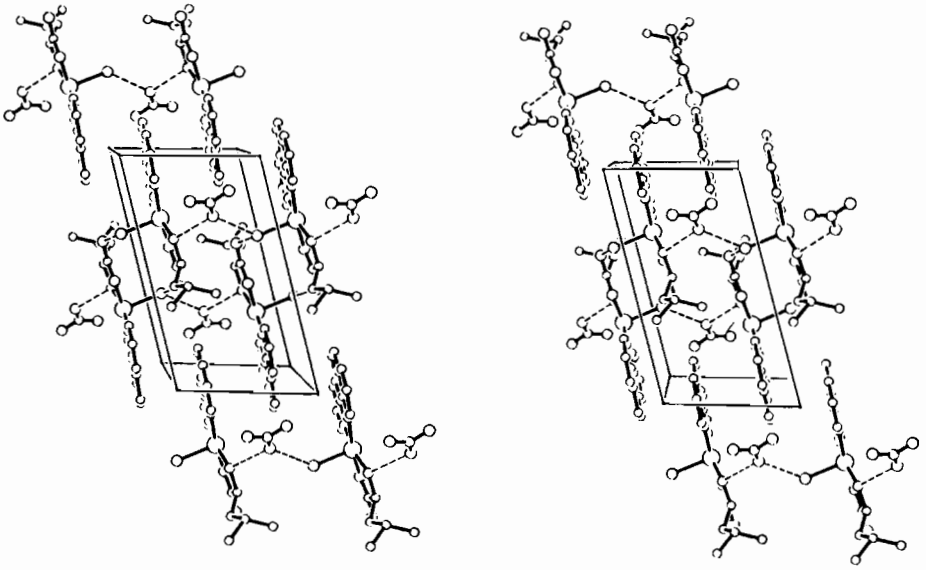

Fig. 4. A stereopair of the crystal packing for **2** viewed down the *b* axis with the *c* axis horizontal and the *a* axis vertical. Broken lines denote hydrogen bonds, and C(3′) is omitted.

TABLE 4. Interatomic distances (Å) and angles (°) in [Cu(L-Leu)(*o*-phen)(H_2O)]NO_3 (**1**) and [Cu(DL-Leu)(*o*-phen)(H_2O)]NO_3 (**2**)

	1		**2**
	Molecule A	Molecule B	
Coordination sphere			
Cu–O(1)	1.919(5)	1.940(5)	1.929(4)
Cu–N(1)	1.989(8)	1.975(11)	1.983(6)
Cu–N(11)	1.994(7)	2.036(6)	2.022(5)
Cu–N(12)	1.996(7)	2.005(7)	1.996(4)
Cu–O(w)	2.253(5)	2.226(6)	2.236(3)
O(1)–Cu–N(1)	86.5(3)	81.2(3)	84.8(2)
O(1)–Cu–N(11)	172.4(2)	169.7(2)	170.9(2)
O(1)–Cu–N(12)	92.2(3)	92.9(3)	92.4(2)
O(1)–Cu–O(w)	90.1(2)	93.7(2)	92.0(2)
N(1)–Cu–N(11)	97.9(3)	102.3(3)	99.3(2)
N(1)–Cu–N(12)	168.4(3)	162.5(3)	168.4(2)
N(1)–Cu–O(w)	88.0(3)	96.0(3)	89.5(2)
N(11)–Cu–N(12)	82.3(3)	81.0(3)	82.0(2)
N(11)–Cu–O(w)	96.2(2)	95.5(3)	96.2(2)
N(12)–Cu–O(w)	103.5(3)	100.9(3)	101.9(2)
C(1)–O(1)–Cu	114.9(5)	117.1(5)	115.9(4)
C(2)–N(1)–Cu	109.7(6)	109.0(7)	110.7(5)
C(11)–N(11)–Cu	133.0(7)	126.8(6)	130.3(4)
C(15)–N(11)–Cu	112.3(5)	112.6(5)	111.5(4)
C(16)–N(12)–Cu	114.1(6)	112.7(5)	113.2(4)
C(20)–N(12)–Cu	128.3(6)	127.7(6)	128.4(4)
Leucinato ligand			
C(1)–O(1)	1.31(1)	1.24(1)	1.278(7)
C(1)–O(2)	1.25(1)	1.20(1)	1.232(7)
C(1)–C(2)	1.54(1)	1.55(1)	1.53(1)
C(2)–N(1)	1.45(1)	1.48(1)	1.44(1)
C(2)–C(3)	1.52(1)	1.48(1)	1.47(1)
C(3)–C(4)	1.57(2)	1.55(1)	1.56(1)
C(4)–C(5)	1.48(2)	1.52(2)	1.48(1)
C(4)–C(6)	1.52(2)	1.54(2)	1.53(1)
C(2)–C(3′)			1.36(2)
C(3′)–C(4)			1.65(2)
O(1)–C(1)–O(2)	122.2(9)	127.2(7)	123.8(5)
O(1)–C(1)–C(2)	116.3(7)	116.0(7)	116.4(5)
O(2)–C(1)–C(2)	121.5(9)	116.8(7)	119.8(6)
C(1)–C(2)–N(1)	111.7(8)	106.2(6)	111.6(6)
C(1)–C(2)–C(3)	110.0(7)	115.5(7)	116.5(7)
N(1)–C(2)–C(3)	113.1(7)	113.3(8)	117.0(7)
C(2)–C(3)–C(4)	112.6(7)	115.3(8)	113.7(7)
C(3)–C(4)–C(5)	113.6(9)	105.7(9)	120.6(7)
C(3)–C(4)–C(6)	106.8(10)	115.5(10)	101.4(7)
C(5)–C(4)–C(6)	112.1(12)	108.3(9)	109.5(7)
C(1)–C(2)–C(3′)			116.5(10)
N(1)–C(2)–C(3′)			131.5(10)
C(2)–C(3′)–C(4)			114.3(13)
C(3′)–C(4)–C(5)			85.8(9)
C(3′)–C(4)–C(6)			129.8(9)
1,10-Phenanthroline ligand			
N(11)–C(11)	1.33(1)	1.34(1)	1.323(8)
N(11)–C(15)	1.38(1)	1.33(1)	1.365(7)
N(12)–C(16)	1.35(1)	1.34(1)	1.351(7)
N(12)–C(20)	1.33(1)	1.35(1)	1.323(7)

(continued)

TABLE 4. *(continued)*

	1		**2**
	Molecule A	Molecule B	
C(11)–C(12)	1.41(1)	1.38(1)	1.399(9)
C(12)–C(13)	1.33(1)	1.38(2)	1.345(10)
C(13)–C(14)	1.39(1)	1.48(2)	1.412(10)
C(14)–C(15)	1.37(1)	1.43(1)	1.401(8)
C(14)–C(21)	1.41(2)	1.45(2)	1.434(10)
C(15)–C(16)	1.45(1)	1.41(1)	1.418(8)
C(16)–C(17)	1.36(1)	1.45(1)	1.400(8)
C(17)–C(18)	1.40(1)	1.42(2)	1.399(9)
C(17)–C(22)	1.42(1)	1.43(1)	1.439(9)
C(18)–C(19)	1.33(1)	1.39(2)	1.361(9)
C(19)–C(20)	1.40(1)	1.39(1)	1.399(9)
C(21)–C(22)	1.34(2)	1.37(2)	1.339(10)
C(11)–N(11)–C(15)	114.8(8)	120.6(7)	118.1(5)
N(11)–C(11)–C(12)	122.3(9)	124.2(9)	122.7(6)
C(11)–C(12)–C(13)	120.7(8)	116.8(11)	119.3(6)
C(12)–C(13)–C(14)	119.7(8)	121.6(11)	120.6(7)
C(13)–C(14)–C(15)	116.5(9)	114.5(9)	116.5(6)
C(13)–C(14)–C(21)	122.3(8)	128.2(9)	125.4(6)
C(15)–C(14)–C(21)	121.2(9)	117.3(9)	118.2(6)
C(14)–C(15)–N(11)	126.0(8)	122.3(8)	122.8(5)
C(14)–C(15)–C(16)	117.8(8)	121.2(8)	120.3(5)
N(11)–C(15)–C(16)	116.2(7)	116.5(7)	116.9(5)
C(15)–C(16)–C(17)	120.7(7)	120.0(8)	120.7(5)
C(15)–C(16)–N(12)	115.1(8)	117.2(8)	116.4(5)
C(17)–C(16)–N(12)	124.2(8)	122.7(8)	122.9(5)
C(16)–C(17)–C(18)	115.1(8)	117.2(9)	117.1(6)
C(16)–C(17)–C(22)	119.0(8)	118.2(10)	117.9(6)
C(18)–C(17)–C(22)	126.0(9)	124.5(11)	125.0(6)
C(17)–C(18)–C(19)	123.6(10)	116.8(10)	120.0(6)
C(18)–C(19)–C(20)	116.4(9)	123.4(9)	119.1(6)
C(19)–C(20)–N(12)	123.1(8)	120.2(9)	122.5(6)
C(20)–N(12)–C(16)	117.6(8)	119.6(8)	118.4(5)
C(14)–C(21)–C(22)	119.7(9)	122.3(8)	121.5(7)
C(21)–C(22)–C(17)	121.6(10)	120.8(10)	121.4(7)
Nitrate anion			
N(13)–O(11)	1.20(1)	1.18(1)	1.19(1)
N(13)–O(12)	1.19(2)	1.18(2)	1.15(1)
N(13)–O(13)	1.19(2)	1.21(2)	1.20(1)
O(11)–N(13)–O(12)	111.0(13)	125.4(13)	120.4(9)
O(11)–N(13)–O(13)	122.7(12)	115.7(11)	117.0(8)
O(12)–N(13)–O(13)	126.0(13)	118.3(11)	122.6(10)
Hydrogen bonds[c]			
N(1)...O(11)	2.90(1)	2.86(2)	2.895(8)
O(w)...O(11)	2.79(1)^{i}	2.77(1)^{ii}	2.785(7)^{i}
O(w)...O(2)	2.78(1)^{i,b}	2.72(1)^{ii,a}	2.733(6)^{v}
Closest ring-stacking contacts between *o*-phen ligands[c]			
N(11)...C(22)	3.47(1)^{iii,b}	3.45(1)^{viii,a}	3.443(7)^{vi}
C(12)...C(18)	3.53(1)^{iii,b}	3.48(1)^{viii,a}	3.500(9)^{vi}
C(14)...C(16)	3.49(1)^{iii,b}	3.47(1)^{viii,a}	3.470(7)^{vi}
C(14)...C(18)	3.48(1)^{iv,b}	3.47(1)^{ix,a}	3.465(8)^{vii}
C(16)...C(22)	3.45(1)^{iv,b}	3.47(1)^{ix,a}	3.471(8)^{vii}

[c]On the right top of the data, the Roman numerals denote the symmetry code of the second atom, and [a] or [b] means that the second atom is from molecule A or B in **1**. Symmetry code: (i) $x, y, z-1$; (ii) $x, y, z+1$; (iii) $x-1, y, z$; (iv) $x-1, y, z-1$; (v) $1-x, 1-y, -z$; (vi) $-x, 1-y, 1-z$; (vii) $-x, 1-y, -z$; (viii) $x+1, y, z$; (ix) $x+1, y, z+1$.

trans-N configuration [9a] (C^{γ} is *trans* to the amino group). On the contrary, the *trans*-CO_2 conformation formed here has a double advantage: it allows no intermolecular constraint and more importantly, favorable hydrophobic self-interaction between aliphatic side chains. In turn, this hydrophobic self-interaction seems an important factor that affects the crystal packing and the conformation of the side chain adopted. In fact, a survey of the other crystal structures involving Leu [9, 14] shows that Leu seems to take the *trans*-N or -CO_2 rotamers so as to optimize such a hydrophobic interaction in the crystal lattice.

Discussion

Fischer and Sigel have proposed a structural model for a Leu–Cu^{2+}–*o*-phen complex in solution, where the isopropyl group of Leu is located above the aromatic ring system of *o*-phen [5b]. The X-ray analyses of the L-Leu– (1) and the DL-Leu–Cu^{2+}–*o*-phen (2) complexes reveal that the metal ion indeed bridges between the two constituents, but, contrary to our expectation, the side chain of Leu extends away from the *o*-phen ring. It seems of interest to consider here from a structural point of view which factor(s) is responsible for such a metal ion-bridge ligand–ligand interaction. We can see that, under a situation that the carboxylate and the amino groups occupy the equatorial coordination sites, such an interligand interaction is doubly unlikely for the Leu–M^{2+}–*o*-phen system. First, so far reported crystal structures containing Leu show that Leu takes the *trans*-N (13 examples, [9a, b, 14a–e]) or *trans*-CO_2 (7 examples [9a–c and this work]) configurations while it does not the *cis*-CO_2 configuration [9a] (C^{γ} is *cis* to both the carboxyl and amino groups) (no example), where only the *cis*-CO_2 configuration makes the folded structure possible. Second, this is a definitive reason: even if the leucinato ligand could adopt the *cis*-CO_2 configuration, the isopropyl group side chain is still too short to reach over the *o*-phen ring. This can be clearly visualized in Fig. 2 in ref. 8 ([Cu(L-tryptophanato)(*o*-phen)]$^+$) or in Fig. 1 in ref. 13a (Cu(L-aspartato)(*o*-phen)) by overlapping the Leu C^{γ} atom onto the corresponding atoms C(4) or C(16), respectively. Accordingly, it now becomes clear that, in order to achieve any isopropyl–*o*-phen ring interaction, the amino nitrogen must occupy the axial position of the coordination sphere, where the carboxylate oxygen locates at the equatorial site in agreement with a well known propensity [3a] that Cu^{2+} ion prefers oxygen to nitrogen as basal donors which are opposite to the aromatic diamine. This is completely in accord with the model of Fischer and Sigel (Fig. 4 in ref. 5b). However, we are now aware that we cannot expect such a metal–N axial bonding for these ternary complex systems in the solid state since both the carboxyl and amino groups are invariably involved in the equatorial coordination in all the known amino acid–metal–*o*-phen or –bipyridyl crystal structures [8, 13 and this work] (of course, this does not hold for the structure(s) in solution). To avoid this difficulty, therefore, an analogous system containing 2,2′,2″-terpyridine, which permits only one remaining site for the equatorial coordination, is now being examined, with a hope to substantiate a distinct structure which involves such an important ring–aliphatic hydrophobic interaction in the solid state.

Supplementary Material

Listings of the thermal parameters for the non-hydrogen atoms, the coordinates for hydrogen atoms, bond distances and angles involving hydrogen atoms, least-squares planes and close contacts, and of observed and calculated structure factors are available from the authors on request.

References

1 (a) H. Sigel and D. B. McCormick, *Acc. Chem. Res., 3* (1970) 201; (b) H. Sigel, B. E. Fischer and B. Prijs, *J. Am. Chem. Soc., 99* (1977) 4489.
2 S.-H. Kim and R. B. Martin, *J. Am. Chem. Soc., 106* (1984) 1707.
3 (a) H. Sigel, *Angew. Chem., Int. Ed. Engl., 14* (1975) 394; (b) H. Sigel, R. Malini-Balakrishnan and U. K. Haring, *J. Am. Chem. Soc., 107* (1985) 5137, and refs. therein.
4 (a) O. Yamauchi and A. Odani, *J. Am. Chem. Soc., 107* (1985) 5938; (b) O. Yamauchi, K. Tsujide and A. Odani, *J. Am. Chem. Soc., 107* (1985) 659; (c) O. Yamauchi and A. Odani, *Inorg. Chim. Acta, 100* (1985) 165.
5 (a) P. R. Mitchell, *J. Chem. Soc., Dalton Trans.*, (1979) 771; (b) B. E. Fischer and H. Sigel, *J. Am. Chem. Soc., 102* (1980) 2998; (c) H. Sigel, B. E. Fischer and E. Farkas, *Inorg. Chem., 22* (1983) 925.
6 (a) G. Brookes and L. D. Pettit, *J. Chem. Soc., Dalton Trans.*, (1977) 1918; (b) O. Yamauchi and A. Odani, *J. Am. Chem. Soc., 103* (1981) 391, and refs. therein.
7 (a) K. Aoki, *J. Am. Chem. Soc., 100* (1978) 7106; (b) K. Aoki, *J. Chem. Soc., Chem. Commun.*, (1979) 589; (c) P. Orioli, R. Cini, D. Donati and S. Mangani, *J. Am. Chem. Soc., 103* (1981) 4446; (d) W. S. Sheldrick, *Z. Naturforsch., Teil B, 37* (1982) 863.
8 K. Aoki and H. Yamazaki, *J. Chem. Soc., Dalton Trans.*, (1987) 2017.
9 (a) T. G. Fawcett, M. Ushay, J. P. Rose, R. A. Lalancette, J. A. Potenza and H. J. Schugar, *Inorg. Chem., 18* (1979) 327; (b) K. Prout, S. R. Critchley, E. Cannillo and V. Tazzoli, *Acta Crystallogr., Sect. B, 33* (1977) 456; (c) A. Bino, F. A. Cotton and P. E. Fanwick, *Inorg. Chem., 19* (1980) 1215.
10 *International Tables for X-ray Crystallography*, Vol. IV, Kynoch Press, Birmingham, 1974.
11 T. Sakurai and K. Kobayashi, *Rikagaku Kenkyusho Hokoku, 55* (1979) 69.

12 S. Nishigaki, H. Yoshioka and K. Nakatsu, *Acta Crystallogr., Sect. B, 34* (1978) 875.
13 (a) L. Antolini, L. P. Battaglia, A. B. Corradi, G. Marcotrigiano, L. Menabue, G. C. Pellacani, M. Saladini and M. Sola, *Inorg. Chem., 25* (1986) 2901; (b) L. Antolini, G. Marcotrigiano, L. Menabue, G. C. Pellacani, M. Saladini and M. Sola, *Inorg. Chem., 24* (1985) 3621; (c) X. Solans, L. Ruiz-Ramirez, A. Martinez, L. Gasque and J. L. Brianso, *Acta Crystallogr., Sect. C, 44* (1988) 628; (d) L. Antolini, G. Marcotrigiano, L. Menabue and G. C. Pellacani, *Inorg. Chem., 22* (1983) 141.
14 (a) M. M. Harding and R. M. Howieson, *Acta Crystallogr., Sect. B, 32* (1976) 633; (b) B. D. Blasio, C. Pedone and A. Sirigu, *Acta Crystallogr., Sect. B, 31* (1975) 601; (c) E. Subramanian, *Acta Crystallogr., 22* (1967) 910; (d) M. O. Chaney, O. Seely and L. K. Steinrauf, *Acta Crystallogr., Sect. B, 27* (1971) 544; (e) L. Golic and W. C. Hamilton, *Acta Crystallogr., Sect. B, 28* (1972) 1265.