be made, it is essential that one has a measure of the accuracy of the Mn–N–O angles found in [Mn(NO)$_2${P(OCH$_3$)$_2$C$_6$H$_5$}$_2$Cl]. The relative size, shape, and orientation of the thermal ellipsoids of the N and O atoms (Table VIII, Figure 2) show that the atoms are not disordered and that the thermal motion is physically reasonable; i.e., the ellipsoids of the O atoms are consistently larger than those of the N atoms, and the longest axes of the ellipsoids are perpendicular to the bonds while the shortest axes are parallel to the bonds. One may thus conclude that this particular deviation from linearity is real and not an artifact caused by either disorder or large thermal motion. However, the Mn–N–O groups in [Mn(NO)(CO)$_3$P(C$_6$H$_5$)$_3$], ν = 1712 cm^{-1},[2,4,15] and [Mn(NO)(CO)$_2${P(C$_6$H$_5$)$_3$}$_2$], ν = 1662 cm^{-1},[2,4,13] were reported to be linear (between 178 and 180°). A close examination shows that the NO groups of these molecules are almost certainly disordered in the crystals. We suggest that the disorder in these two mononitrosyl complexes obscures the true Mn–N–O geometry and that the Mn–N–O groups in all of these compounds are similar in nature, i.e., nonlinear, with a Mn–N–O angle of about 165°.

The molecular parameters reported here for [Mn(NO)$_2${P(OCH$_3$)$_2$C$_6$H$_5$}$_2$Cl], while being generally similar to those found in the triclinic form,[7] differ significantly in detail. A full paper describing the structure of this second polymorph has been submitted for publication in *Inorganic Chemistry.*

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Registry No. Mn(NO)$_2${P(OCH$_3$)$_2$C$_6$H$_5$}$_2$Cl, 68366-07-4.

Supplementary Material Available: A listing of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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Molecular Structures of the Copper–Amino Acid Complexes Bis(L-leucinato)copper(II) and Bis(D,L-2-aminobutyrato)copper(II)

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The crystal structures of the title complexes, Cu(L-leu)$_2$ and Cu(D,L-but)$_2$, have been determined by single-crystal three-dimensional X-ray techniques. Crystal data for the two complexes are as follows. Cu(L-leu)$_2$, Cu(H$_2$NCH(CO$_2$)CH$_2$CH(CH$_3$)$_2$)$_2$: space group $P2_1$; a = 9.725 (4), b = 5.127 (1), c = 14.689 (6) Å; β = 105.79 (3)°; d_{obsd} = 1.532 (5), d_{calcd} = 1.525 g/cm^3; Z = 2. Cu(D,L-but)$_2$, Cu(H$_2$NCH(CO$_2$)CH$_2$CH$_3$)$_2$: space group $P2_1/c$; a = 11.138 (6), b = 5.066 (1), c = 9.487 (6) Å; β = 92.15 (6)°; d_{obsd} = 1.66 (2), d_{calcd} = 1.662 g/cm^3; Z = 2. Full-matrix least-squares refinement of 1683 and 1552 reflections with $F^2 \geq 3\sigma(F^2)$ gave final values for R_F of 0.032 and 0.037 for Cu(L-leu)$_2$ and Cu(D,L-but)$_2$, respectively. Both structures consist of tetragonally coordinated Cu(II) ions arranged in isolated sheets. Equatorial N$_2$O$_2$ ligation is provided by trans coordination of two amino acids, while axial Cu–O ligation by two neighboring amino acids completes the metal coordination and links the CuL$_2$ units to form carboxylate-bridged sheets of Cu(II) ions. Intermolecular N–H···O hydrogen bonds further link the CuL$_2$ units within each sheet. Coordination of the polar ends of the amino acids with Cu(II) allows the nonpolar side chains to align, creating hydrophobic regions which are slightly different in both structures. Bond distances and angles within the coordination spheres are typical, while C–C–C bond angles at the hydrophilic–hydrophobic juncture are ~6° larger than the remaining C–C–C angles. These large angles are attributed to modest steric strain between the carboxylate, amino, and alkyl groups attached to the α carbon atom. The structures are compared with those of their free amino acids and those of other Cu(II) amino acid complexes.

Introduction

For some time, we have been interested in the structural, spectroscopic, and magnetic properties of Cu(II) and Co(II) complexes,[2-10] particularly those with sulfur-containing amino acid and amino acid derivative ligands. One goal of these studies has been to provide a series of well-characterized model compounds which would lead to a better understanding of the absorption spectra of type 1 Cu(II) proteins such as stellacyanin and plastocyanin and their Co(II)-substituted counterparts.

While examining the structure[9] of bis(L-methioninato)copper(II), a strong similarity was noted between the structure

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Table I. Crystal Data and Data Collection Details

	$Cu(L\text{-leu})_2$	$Cu(D,L\text{-but})_2$
formula	$Cu(C_6H_{12}NO_2)_2$	$Cu(C_4H_8NO_2)_2$
mol wt	323.90	267.79
a, Å	9.725 (4)	11.138 (6)
b, Å	5.127 (1)	5.066 (1)
c, Å	14.689 (6)	9.487 (6)
β, deg	105.79 (3)	92.15 (6)
space group	$P2_1$	$P2_1/c$
Z	2	2
no. of reflections used to determine cell constants	15	15
d_{calcd}, g/cm³	1.525	1.662
d_{obsd}, g/cm³	1.532 (5) (gradient)	1.66 (2) (flotation)
λ(Mo Kα), Å	0.710 69	0.710 69
monochromator	graphite cryst	graphite cryst
linear abs coeff, cm^{-1}	16.3	19.7
cryst dimensions, mm	0.22 × 0.83 × 0.04	0.25 × 0.45 × 0.10
abs factor range	1.04–1.56	1.21–1.58
diffractometer	Syntex $P2_1$	Syntex $P2_1$
data collection method	θ–2θ	θ–2θ
2θ limit, deg	60	60
temp, °C	23 (1)	23 (1)
scan rate,[a] deg/min	2	2
scan range, deg	$2\theta_{K\alpha_1} - 0.8$ to $2\theta_{K\alpha_2} + 0.85$	$2\theta_{K\alpha_1} - 0.8$ to $2\theta_{K\alpha_2} + 0.85$
no. of std reflections	3	3
variation in std intens	±3%	±2%
no. of unique data collected	2291	1741
no. of data used in refinement	1683 $[F^2 \geqslant 3\sigma(F^2)]$	1552 $[F^2 \geqslant 3\sigma(F^2)]$
data:parameter ratio	7.0	11.9
final R_F[b]	0.032	0.037
final R_{wF}[c]	0.036	0.046

[a] Background measurements were made at the beginning and end of each scan; the total time for background counting was equal to the scan time. [b] $R_F = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. [c] $R_{wF} = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2]^{1/2}$.

of the free ligand[11] and those of several metal complexes;[12–14] all were found to crystallize as double-layer sheet structures characterized by distinct hydrophobic and hydrophilic regions. This basic structure also encompasses a variety of other amino acids,[15] amino acid hydrohalides,[16–21] and metal derivatives,[12,22–25] particularly if the amino acid contains a nonpolar or slightly polar side chain. As part of a study designed to elucidate the effects of hydrogen bonding, side chain polarity, side chain configuration, and M(II) incorporation on the double layer structure, we have prepared anhydrous Cu(II) complexes of L-leucine and D,L-2-aminobutyric acid,[26] both of which contain nonpolar side chains. We report here the crystal structures of these complexes; electronic-spectral and magnetic properties of tetragonal Cu(II) ions arranged in double-layer sheet structures have been reported elsewhere.[9]

Experimental Section

Syntheses. Cu(II) complexes of D,L-2-aminobutyric acid and L-leucine were prepared readily by the urea hydrolysis technique. In a typical experiment, a solution of 0.431 g of $CuCl_2 \cdot 2H_2O$ (2.0 mmol), 0.525 g of L-leucine (4.0 mmol) or 0.412 g of D,L-2-aminobutyric acid (4.0 mmol), and 0.170 g of urea (2.0 mmol) in approximately 200 mL of water was filtered through a Millipore membrane (0.22 μm pore size) and maintained at 85 °C for 24 h. When the solution was cooled, the anhydrous complexes $Cu(D,L\text{-but})_2$ and $Cu(L\text{-leu})_2$ crystallized as six-sided blue plates which were separated from solution by filtration, washed with water, and air-dried.

Collection of Diffraction Data. Pertinent details regarding crystal data, intensity data collection, and refinement of the structures are collected in Table I. For $Cu(L\text{-leu})_2$, diffractometer examination of the reciprocal lattice led to the extinction $0k0$ ($k = 2n + 1$) which is consistent with space groups $P2_1$ and $P2_1/m$. The centrosymmetric space group $P2_1/m$ was rejected because the complex contained only L-leucine ligands. With $Cu(D,L\text{-but})_2$, systematic extinctions for $0k0$ ($k = 2n + 1$) and $h0l$ ($l = 2n + 1$) were observed, fixing the space group as $P2_1/c$.

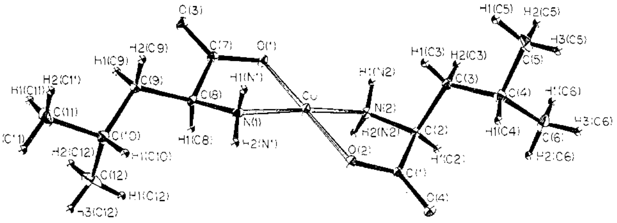

Figure 1. Molecular structure of $Cu(L\text{-leu})_2$ showing the atom numbering scheme.

Intensities I and $\sigma(I)$ were calculated from

$$I = (P - LB - RB)(SR)$$

$$\sigma(I) = (P + LB + RB)^{1/2}(SR)$$

where P is the peak count, LB is the "left" background count, RB is the "right" background count, and SR is the scan rate. Intensities were corrected for decay by applying average decay factors obtained from the standard reflections. All data were corrected for Lorentz, polarization, and absorption[27] effects; the polarization correction for the parallel–parallel mode of the Syntex $P2_1$ diffractometer was chosen assuming the monochromator crystal to be 50% perfect and 50% mosaic. Values of $\sigma(F_o^2)$ were computed from

$$\sigma(F_o^2) = (Lp)^{-1}(\sigma^2(I) + (0.03I)^2)^{1/2}$$

Solution and Refinement of the Structures.[28] **(a) $Cu(L\text{-leu})_2$.** Both structures were solved by direct methods using the program MULTAN 74[29] and refined using full-matrix least-squares techniques. Neutral-atom atomic scattering factors[30] were used in the refinements; both real and imaginary parts of the anomalous dispersion corrections were applied to Cu.[30] For $Cu(L\text{-leu})_2$, an E map, calculated using 152 phases from the starting set having the highest combined figure of merit, revealed all nonhydrogen atoms except two terminal methyl C atoms; these were located readily on a subsequent difference Fourier map. With all nonhydrogen scattering matter present, the initial agreement factor $R_F = \sum||F_o| - |F_c||/\sum|F_o|$ was 0.153.

Several cycles of isotropic refinement, based on F, led to convergence with $R_F = 0.088$; subsequent anisotropic refinement converged with $R_F = 0.045$. At this point, H atoms were added to the model. Methyl group H atoms were located[31] by placing tetrahedrally oriented H atoms 0.95 Å[32] from the appropriate C atom. These were rotated at 5° intervals until a best fit was obtained between calculated H positions and positive regions of a difference Fourier map. Methylene, methyne, and amine H atom positions were calculated assuming tetrahedral geometry and an N–H distance of 0.87 Å.[32] All 24 H atoms were located in regions of high electron density in the difference Fourier map. Hydrogen atoms were assigned temperature factors according to $B_H = B_N + 1$, where N is the atom to which H is bonded; these temperature factors were not refined.

A weighting scheme was chosen by an analysis of variance to make $|\Delta F|/\sigma$ independent of $|F_o|$. This led to the following assignments for $\sigma(F_o)$:

$$\sigma(F_o) = 1.964 - 0.023|F_o| \qquad |F_o| < 40.6$$

$$\sigma(F_o) = 0.544 + 0.012|F_o| \qquad 40.6 < |F_o| < 255.7$$

Several additional cycles of refinement of all coordinates and anisotropic temperature factors for all nonhydrogen atoms reduced R_F to 0.032 and $R_{wF} = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$ to 0.036. For the final cycle, all nonhydrogen parameter changes were within 0.4σ, where σ is the esd obtained from the inverse matrix. Five H-atom coordinates ($y_{H1(N1)}$, $y_{H2(N2)}$, $y_{H1(C9)}$, $y_{H3(C11)}$, and $z_{H1(C9)}$) showed changes within 1.5σ while the remaining H-atom coordinate changes were within 1σ. A final difference map showed a general background of approximately ±0.11 e/Å³. The largest positive peak (0.18 e/Å³) was smaller than the largest negative peak. Final atomic parameters are listed in Table II. Views of the complex and its packing are shown in Figures 1 and 2, respectively.

(b) $Cu(D,L\text{-but})_2$. An E map, calculated using 499 phases from the starting set having the highest combined figure of merit, revealed all nonhydrogen atoms. The initial agreement factor R_F, based on these coordinates, was 0.141. Isotropic, followed by anisotropic,

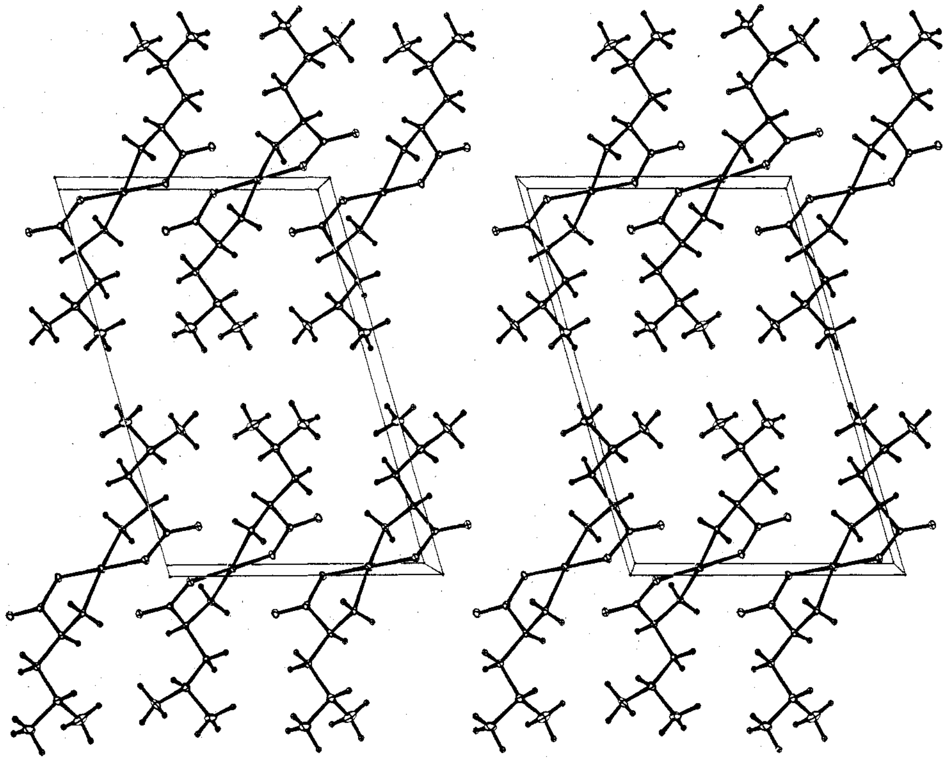

Figure 2. Stereoscopic packing diagram for Cu(L-leu)$_2$ viewed along *b*. The *a* axis is horizontal.

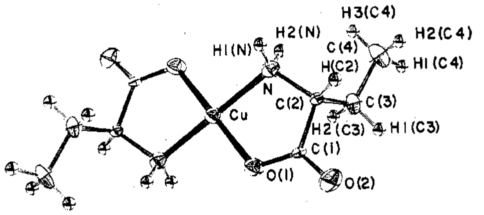

Figure 3. Molecular structure of Cu(D,L-but)$_2$ showing the atom numbering scheme.

refinement of all nonhydrogen atoms reduced R_F to 0.050.

Methyne and amine H atom coordinates were calculated as with Cu(L-leu)$_2$. For the methyl group, one H atom was located on a difference Fourier map, and the remaining two positions were calculated assuming tetrahedral geometry. Inclusion of these atoms with temperature factors assigned as $B_H = B_N + 1$ reduced R_F to 0.042. Anisotropic refinement of all nonhydrogen atoms and the coordinates of all H atoms led to convergence with $R_F = 0.037$ and $R_{wF} = 0.046$.

For the final cycles, weights $w = 1/\sigma^2$ were based on the following assignments, chosen by an analysis of variance:

$$\sigma(F_o) = 3.090 - 0.043|F_o| \qquad |F_o| \le 35.0$$

$$\sigma(F_o) = 1.148 + 0.015|F_o| \qquad 35.0 \le |F_o| < 80.0$$

$$\sigma(F_o) = 1.630 + 0.010|F_o| \qquad |F_o| \ge 80.0$$

A final difference Fourier map revealed a general background of ±0.24 e/Å^3 and no significant features; for the final cycle, all nonhydrogen parameter changes were within 0.2σ while all H-atom parameter changes were within 1σ. Final atomic parameters for Cu(D,L-but)$_2$, along with their estimated standard deviations, are given in Table III. Views of the complex and its packing are shown in Figures 3 and 4, respectively. Lists of observed and calculated structure factors for both structures are available.[33]

Description of the Structures and Discussion

The structures of Cu(L-leu)$_2$ and Cu(D,L-but)$_2$ consist of tetragonally coordinated Cu(II) ions arranged in isolated two-dimensional sheets. These sheets are parallel to the *ab* face in Cu(L-leu)$_2$ and to the *bc* face in Cu(D,L-but)$_2$. Trans coordination of two amino acid molecules per Cu(II) produces equatorial N_2O_2 ligand sets, while additional interactions with two carboxylate oxygen atoms from neighboring ligands [O(3′) and O(4′) in Cu(L-leu)$_2$ and O(2′) and O(2‴) in Cu(D,L-but)$_2$] give rise to weak apical Cu–O bonds which link the CuL$_2$ units to form carboxylate-bridged sheets of Cu(II) ions. The CuL$_2$ units are further linked within a sheet by "intermolecular" N–H···O hydrogen bonds (Table IV).

Both structures may be viewed as double layers containing two well-defined regions, one hydrophobic and one hydrophilic. The hydrophobic region is formed from the nonpolar side chains (*sec*-butyl in L-leucine and ethyl in D,L-butyrate). These face each other in the crystals and pack so as to minimize

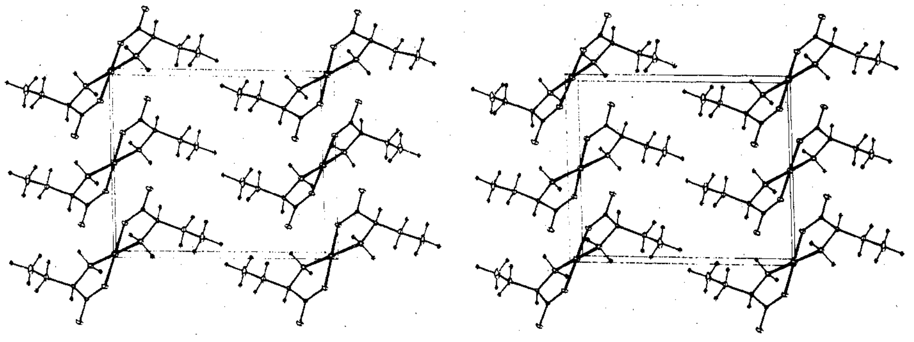

Figure 4. Stereoscopic packing diagram for Cu(D,L-but)$_2$ viewed along *b*. The *a* axis is horizontal.

Table II. Fractional Atomic Coordinates and Thermal Parameters[a] for Cu(L-leu)$_2$

atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.75369 (6)	0.9310	0.00796 (3)	42.7 (3)	18.0 (1)	26.7 (2)	19 (1)	−2.2 (2)	−16 (1)
O(1)	0.5786 (3)	1.1406 (8)	−0.0203 (2)	42 (3)	17 (1)	31 (1)	8 (6)	4 (2)	−14 (4)
O(2)	0.9293 (3)	0.7229 (8)	0.0361 (2)	47 (3)	16 (1)	29 (1)	5 (6)	5 (2)	−17 (4)
O(3)	0.3582 (3)	1.147 (1)	−0.1186 (2)	56 (4)	29 (2)	33 (1)	44 (7)	4 (2)	−9 (4)
O(4)	1.1580 (3)	0.735 (1)	0.1197 (2)	45 (3)	31 (2)	29 (1)	19 (7)	7 (2)	1 (4)
N(1)	0.6432 (4)	0.706 (1)	−0.0967 (3)	44 (4)	21 (2)	24 (2)	20 (7)	7 (2)	−10 (4)
N(2)	0.8704 (4)	1.1763 (9)	0.1038 (3)	49 (4)	14 (2)	24 (2)	−1 (7)	7 (2)	2 (4)
C(1)	1.0339 (5)	0.815 (1)	0.1018 (3)	50 (4)	15 (2)	22 (2)	−5 (7)	12 (2)	10 (4)
C(2)	0.9952 (4)	1.031 (1)	0.1628 (3)	37 (4)	18 (2)	24 (2)	−4 (7)	2 (2)	1 (4)
C(3)	0.9518 (4)	0.902 (1)	0.2468 (3)	51 (3)	20 (2)	22 (2)	2 (8)	8 (2)	−5 (5)
C(4)	1.0626 (5)	0.730 (1)	0.3130 (3)	80 (5)	35 (2)	29 (2)	54 (10)	12 (3)	17 (6)
C(5)	1.0002 (8)	0.599 (2)	0.3859 (4)	142 (8)	43 (3)	33 (2)	15 (13)	15 (4)	52 (7)
C(6)	1.1958 (6)	0.882 (2)	0.3636 (4)	67 (5)	85 (7)	47 (3)	1 (15)	−14 (3)	39 (12)
C(7)	0.4833 (5)	1.068 (1)	−0.0953 (3)	54 (4)	15 (2)	27 (2)	14 (8)	12 (2)	6 (5)
C(8)	0.5376 (4)	0.8791 (9)	−0.1593 (3)	40 (4)	15 (2)	24 (2)	−8 (6)	7 (2)	0 (4)
C(9)	0.4182 (4)	0.739 (1)	−0.2317 (3)	47 (4)	26 (2)	24 (2)	−1 (8)	7 (2)	−10 (5)
C(10)	0.4632 (5)	0.610 (1)	−0.3137 (3)	80 (5)	26 (2)	26 (2)	28 (9)	12 (2)	−1 (5)
C(11)	0.3365 (7)	0.466 (2)	−0.3771 (4)	124 (7)	47 (4)	42 (2)	22 (15)	6 (3)	−73 (10)
C(12)	0.5188 (9)	0.810 (2)	−0.3719 (5)	189 (11)	46 (3)	44 (3)	28 (17)	52 (5)	12 (9)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
H1(N1)	0.610 (7)	0.61 (2)	−0.070 (4)	2.8	H2(C6)	1.237 (9)	0.96 (2)	0.319 (6)	5.3
H2(N1)	0.695 (7)	0.62 (2)	−0.123 (5)	2.8	H3(C6)	1.266 (9)	0.78 (2)	0.406 (6)	5.3
H1(N2)	0.820 (7)	1.25 (2)	0.138 (4)	2.8	H1(C8)	0.587 (7)	0.98 (2)	−0.185 (5)	2.7
H2(N2)	0.892 (7)	1.31 (2)	0.068 (5)	2.8	H1(C9)	0.349 (7)	0.87 (2)	−0.252 (4)	3.0
H1(C2)	1.069 (7)	1.12 (2)	0.186 (5)	2.8	H2(C9)	0.383 (7)	0.60 (2)	−0.197 (5)	3.0
H1(C3)	0.871 (8)	0.83 (2)	0.227 (5)	3.0	H1(C10)	0.533 (7)	0.48 (2)	−0.289 (4)	3.4
H2(C3)	0.935 (8)	1.04 (2)	0.282 (5)	3.0	H1(C11)	0.272 (10)	0.58 (2)	−0.394 (6)	5.1
H1(C4)	1.099 (8)	0.60 (2)	0.287 (5)	4.0	H2(C11)	0.302 (9)	0.35 (2)	−0.345 (6)	5.1
H1(C5)	0.904 (9)	0.53 (2)	0.356 (6)	4.8	H3(C11)	0.360 (9)	0.41 (2)	−0.432 (6)	5.1
H2(C5)	0.986 (9)	0.74 (2)	0.424 (6)	4.8	H1(C12)	0.598 (9)	0.90 (2)	−0.342 (6)	5.5
H3(C5)	1.066 (8)	0.49 (2)	0.422 (5)	4.8	H3(C12)	0.537 (9)	0.74 (2)	−0.423 (7)	5.5
H1(C6)	1.176 (10)	1.00 (2)	0.400 (7)	5.3	H2(C12)	0.446 (9)	0.91 (3)	−0.396 (6)	5.5

[a] Values for β_{22} are $\times 10^3$; all other values are $\times 10^4$. The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table III. Fractional Atomic Coordinates and Thermal Parameters[a] for Cu(D,L-but)$_2$

atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0	$^1/_2$	0	59.0 (4)	17.5 (2)	51.1 (5)	−24 (1)	−16.2 (3)	25 (1)
O(1)	−0.0461 (2)	0.7072 (4)	−0.1662 (2)	59 (2)	17.2 (7)	48 (2)	−16 (3)	−8 (2)	9 (3)
O(2)	−0.1655 (2)	0.7026 (5)	−0.3604 (2)	77 (2)	30 (1)	52 (2)	−5 (4)	−16 (2)	38 (4)
N	−0.1202 (2)	0.2418 (5)	−0.0766 (3)	48 (2)	18.1 (9)	54 (2)	−9 (4)	−3 (2)	21 (4)
C(1)	−0.1324 (3)	0.6096 (6)	−0.2240 (3)	27 (2)	7 (1)	20 (3)	11 (4)	−1 (2)	10 (4)
C(2)	−0.1978 (3)	0.3676 (6)	−0.1877 (3)	27 (2)	11 (1)	35 (3)	−8 (4)	−8 (2)	20 (5)
C(3)	−0.3180 (3)	0.4471 (8)	−0.1329 (5)	20 (2)	20 (2)	95 (5)	−2 (5)	9 (3)	22 (7)
C(4)	−0.3986 (4)	0.2120 (12)	−0.1019 (8)	36 (3)	41 (3)	204 (10)	−44 (8)	18 (5)	92 (14)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
H1(N)	−0.160 (5)	0.17 (1)	−0.017 (6)	3.0	H2(C3)	−0.359 (5)	0.56 (1)	−0.209 (6)	3.3
H2(N)	−0.083 (5)	0.11 (1)	−0.112 (6)	3.0	H1(C4)	−0.474 (6)	0.28 (1)	−0.070 (7)	5.0
H(C2)	−0.221 (4)	0.22 (1)	−0.270 (5)	2.2	H2(C4)	−0.361 (6)	0.09 (1)	−0.038 (7)	5.0
H1(C3)	−0.300 (4)	0.58 (1)	−0.050 (6)	3.3	H3(C4)	−0.340 (6)	0.11 (1)	−0.196 (7)	5.0

[a] Values for β_{22} are $\times 10^3$; all other values are $\times 10^4$. The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

hydrophobic repulsions in a manner reminiscent of the packing of long-chain hydrocarbons.[34] The hydrophilic region contains the Cu(II) ions as well as the carboxylate and amine groups. Double layers of this type are common to many structures of amino acids[15] and metal amino acid derivatives[9,22-25] with nonpolar or slightly polar side chains.

The structural features of Cu(L-leu)$_2$ and of Cu(D,L-but)$_2$ are given in Tables V and VI, respectively. In Cu(D,L-but)$_2$, the equatorial CuN_2O_2 units are strictly coplanar as required by the center of symmetry; with Cu(L-leu)$_2$, modest deviations from planarity (±0.04 Å) are observed with O and N atoms on opposite sides of the least-squares plane (not shown). Equatorial bond distances and angles within the coordination sphere are typical. The Cu–N distances [1.996 (4) and 1.989 (4) Å for Cu(L-leu)$_2$; 1.990 (3) Å for Cu(D,L-but)$_2$] are equivalent to within experimental error and fall in the rather narrow range of 1.97–2.02 Å reported[35] for several tetragonally coordinated copper(II) bis(amino acid) complexes. The Cu–O (equatorial) bond lengths [1.960 (4) and 1.960 (3) Å for Cu(L-leu)$_2$; 1.947 (2) Å for Cu(D,L-but)$_2$] are also quite similar to each other and to those reported[36] (1.947–1.97 Å) for analogous complexes. For racemic Cu(D,L-but)$_2$, the Cu–O (axial) bond lengths (2.758 (3) Å) are equal, as required crystallographically, while with Cu(L-leu)$_2$, they are significantly different (2.629 (4) and 2.749 (4) Å). Typically, Cu–O (axial) bond lengths in bis(L-amino acid) complexes have been found[9,22,24,35e] to differ by ~0.1–0.2 Å.

The structures of the title complexes may be compared with those of their corresponding free amino acids. Both L-leucine[37] and D,L-2-aminobutyric acid[38] exist in the solid state as zwitterions held together in a trans arrangement by N–H···O hydrogen bonds to form two-dimensional double-layer sheet

Table IV. Possible Hydrogen Bonding Distances (Å) and Angles (deg) for Cu(L-leu)$_2$ and Cu(D,L-but)$_2$

donor (D)	hydrogen (H)	acceptor (A)	D–H···A	D···A	H···A	D–H
			Cu(L-leu)$_2$			
N(1)	H1(N1)	O(1) i^a	151 (7)	3.120 (6)	2.54 (7)	0.77 (8)
N(1)	H1(N1)	O(1) ii	133 (7)	3.230 (6)	2.54 (9)	0.77 (8)
N(1)	H1(N1)	O(3) ii	121 (7)	3.181 (5)	2.71 (6)	0.77 (8)
N(1)	H2(N1)	O(4) iii	147 (6)	3.167 (6)	2.44 (8)	0.83 (8)
N(2)	H1(N2)	O(3) ii	137 (6)	3.328 (6)	2.62 (8)	0.89 (8)
N(2)	H2(N2)	O(2) iv	156 (6)	3.079 (6)	2.21 (9)	0.93 (8)
N(2)	H2(N2)	O(2) iii	118 (6)	3.202 (5)	2.66 (7)	0.93 (8)
N(2)	H2(N2)	O(4) iii	117 (5)	3.232 (5)	2.70 (6)	0.93 (8)
			Cu(D,L-but)$_2$			
N	H1(N)	O(2) v	144 (5)	3.100 (4)	2.40 (6)	0.82 (6)
N	H2(N)	O(1) i	158 (5)	2.965 (4)	2.16 (6)	0.85 (6)
N	H2(N)	O(2) vi	114 (4)	3.266 (4)	2.82 (5)	0.85 (6)
N	H2(N)	O(1) vi	118 (4)	3.123 (4)	2.64 (5)	0.85 (6)

^{a} i = $x, y-1, z$; ii = $1-x, -\frac{1}{2}+y, -z$; iii = $2-x, -\frac{1}{2}+y, -z$; iv = $x, y+1, z$; v = $x, \frac{1}{2}-y, \frac{1}{2}+z$; vi = $-x, -\frac{1}{2}+y, -\frac{1}{2}+z$.

Table V. Bond Distances (Å) and Angles (deg) for Cu(L-leu)$_2$^{a}

	Distances		
Cu–N(2)	1.996 (4)	Cu–N(1)	1.989 (4)
Cu–O(2)	1.960 (4)	Cu–O(1)	1.960 (3)
Cu–O(4′)^b	2.749 (4)	Cu–O(3′)^c	2.629 (4)
C(1)–O(2)	1.286 (5)	C(7)–O(1)	1.288 (5)
C(1)–O(4)	1.233 (5)	C(7)–O(3)	1.239 (5)
C(1)–C(2)	1.536 (7)	C(7)–C(8)	1.538 (6)
C(2)–N(2)	1.486 (5)	C(8)–N(1)	1.476 (6)
C(3)–C(2)	1.555 (6)	C(9)–C(8)	1.525 (6)
C(4)–C(3)	1.521 (6)	C(10)–C(9)	1.538 (6)
C(4)–C(5)	1.523 (8)	C(10)–C(11)	1.518 (8)
C(4)–C(6)	1.522 (8)	C(10)–C(12)	1.525 (9)
	Angles		
N(2)–Cu–O(2)	84.2 (2)	O(4)–C(1)–C(2)	119.8 (4)
N(2)–Cu–O(1)	95.6 (2)	C(1)–C(2)–N(2)	108.2 (3)
N(2)–Cu–O(4′)	84.3 (1)	C(1)–C(2)–C(3)	108.6 (4)
N(2)–Cu–O(3′)	99.5 (1)	C(2)–C(3)–C(4)	117.1 (4)
N(2)–Cu–N(1)	174.6 (2)	C(3)–C(4)–C(5)	110.9 (4)
O(2)–Cu–O(4′)	92.1 (1)	C(3)–C(4)–C(6)	112.1 (6)
O(2)–Cu–O(3′)	92.9 (1)	C(5)–C(4)–C(6)	109.4 (5)
O(3′)–Cu–O(4′)	173.98 (7)	Cu–O(1)–C(7)	113.8 (3)
N(1)–Cu–O(1)	84.2 (2)	Cu–N(1)–C(8)	105.6 (3)
N(1)–Cu–O(2)	95.9 (2)	O(1)–C(7)–O(3)	124.4 (4)
N(1)–Cu–O(4′)	90.3 (2)	O(1)–C(7)–C(8)	114.8 (4)
N(1)–Cu–O(3′)	85.9 (2)	O(3)–C(7)–C(8)	120.8 (4)
O(1)–Cu–O(2)	179.7 (8)	C(7)–C(8)–N(1)	107.1 (3)
O(1)–Cu–O(4′)	87.7 (1)	C(7)–C(8)–C(9)	113.5 (4)
O(1)–Cu–O(3′)	87.3 (1)	C(8)–C(9)–C(10)	115.1 (4)
Cu–O(2)–C(1)	115.2 (3)	C(9)–C(10)–C(11)	109.5 (4)
Cu–N(2)–C(2)	108.2 (3)	C(9)–C(10)–C(12)	111.7 (5)
O(2)–C(1)–O(4)	124.5 (5)	C(11)–C(10)–C(12)	109.5 (5)
O(2)–C(1)–C(2)	115.6 (4)		

^{a} Distance and angle data are given for all nonhydrogen atoms. A list of bond distances and angles involving H atoms is available.[33] ^{b} The symmetry operation $2-x, \frac{1}{2}+y, \bar{z}$ relates O(4) and O(4′). ^{c} The symmetry operation $1-x, -\frac{1}{2}+y, \bar{z}$ relates O(3) and O(3′).

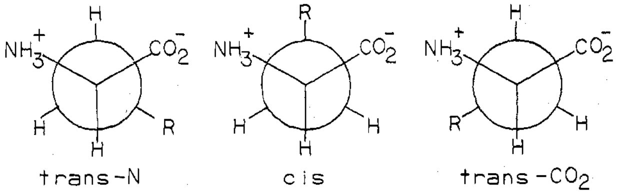

Figure 5. Trans-N, cis-CO$_2$, and trans-CO$_2$ amino acid rotamers.

structures similar to those of the title complexes. The effect of Cu(II) incorporation may be visualized in terms of Newman projections of the amino acid rotamers along the C(2)–C(3) bond axis (Figure 5). In the solid state, both L-leucine and D,L-2-aminobutyric acid have the trans-N configuration with the bulky side chain R "adjacent" to the carboxylate group.

Table VI. Bond Distances (Å) and Angles (deg) for Cu(D,L-but)$_2$^{a}

	Distances		
Cu–O(1)	1.947 (2)	C(1)–C(2)	1.532 (4)
Cu–N	1.990 (3)	C(2)–N	1.481 (4)
Cu–O(2′)^b	2.758 (3)	C(2)–C(3)	1.510 (5)
C(1)–O(1)	1.288 (4)	C(3)–C(4)	1.526 (6)
C(1)–O(2)	1.244 (4)		
	Angles		
N–Cu–N″ ^{c}	180	Cu–O(1)–C(1)	115.2 (2)
O(1)–Cu–O(1″)	180	Cu–N–C(2)	110.1 (2)
O(2′)–Cu–O(2‴)^d	180	O(2)–C(1)–O(1)	123.6 (3)
O(1)–Cu–N	84.55 (9)	O(2)–C(1)–C(2)	118.9 (3)
O(1)–Cu–N″	95.45 (9)	O(1)–C(1)–C(2)	117.4 (2)
O(2′)–Cu–N	94.7 (1)	C(1)–C(2)–N	108.7 (2)
O(2′)–Cu–N″	85.3 (1)	C(1)–C(2)–C(3)	110.3 (3)
O(2′)–Cu–O(1)	93.82 (8)	N–C(2)–C(3)	111.8 (3)
O(2′)–Cu–O(1″)	86.18 (8)	C(2)–C(3)–C(4)	113.2 (4)

^{a} Distance and angle data are given for all nonhydrogen atoms. A list of bond distances and angles involving H atoms is available.[33] ^{b} The symmetry operation $x, \frac{3}{2}-y, \frac{1}{2}+z$ relates primed and unprimed atoms. ^{c} The symmetry operation $-x, 1-y, -z$ relates doubly primed and unprimed atoms. ^{d} The symmetry operation $x, y-\frac{1}{2}, -\frac{1}{2}-z$ relates triply primed and unprimed atoms.

Table VII. Intramolecular Contacts (Å) Shorter Than 3.5 Å

Cu(L-leu)$_2$ (trans-N)		Cu(L-leu)$_2$ (trans-CO$_2$)		Cu(D,L-but)$_2$ (trans-CO$_2$)	
atoms	dist	atoms	dist	atoms	dist
C(3)···O(4)	3.206 (5)	C(9)···O(3)	2.829 (6)	C(3)···O(2)	3.082 (5)
C(3)···O(2)	3.177 (5)	C(10)···N(1)	3.229 (6)	C(3)···O(1)	3.328 (5)
C(4)···O(4)	3.218 (6)	C(12)···C(8)	3.098 (8)	C(4)···N	3.105 (6)
C(4)···C(1)	3.068 (6)				
C(6)···C(2)	3.155 (7)				

In contrast, the side chain assumes the trans-CO$_2$ configuration in Cu(D,L-but)$_2$ while, for Cu(L-leu)$_2$, with two unique ligands, one assumes the trans-CO$_2$ configuration and the second the trans-N configuration. We defer detailed analysis of these conformational changes in terms of dihedral angles to a future publication.

Examination of the C–C–C bond angles in the two complexes reveals unusually large C$^\alpha$–C$^\beta$–C$^\gamma$ angles at the juncture of the hydrophobic and hydrophilic regions. This is particularly evident in Cu(L-leu)$_2$ which shows both C(2)–C(3)–C(4) [117.1 (4)°] and C(8)–C(9)–C(10) [115.1 (4)°] approximately 6° larger, on average, than the remaining C–C–C angles. Such large angles could result from modest steric strain between the two regions or from electronic effects. If the origin is electronic, these effects are not mirrored in the C–C distances, which, for both structures, appear normal in the vicinity of C(2)–C(3)–C(4). As shown by the data in Table VII, both complexes exhibit several short[39] intramolecular distances. All of these short distances involve α, β, or γ carbon atoms and are consistent with the large angles observed. For example, in Cu(D,L-but)$_2$, a decrease in the C(2)–C(3)–C(4) angle by movement of C(3) or C(4) would require a decrease in an already short C(3)···O (carboxylate) or C(4)···N distance. Thus, we attribute the large C–C–C angles observed to steric strain between the carboxylate, amino, and alkyl groups attached to the α carbon atom. All the metal(II)–bis(amino acid) complexes (M = Cu, Zn, Cd) which crystallize in double-layer structures show large C^{α}–C^{β}–C^{γ} angles and have at least one amino acid in the trans-CO$_2$ configuration.[40]

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Supplementary Material Available: Listings of structure factor amplitudes and bond distances and angles involving H atoms for Cu(L-leu)$_2$ and Cu(D,L-but)$_2$ (18 pages). Ordering information is given on any current masthead page.

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