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(48) After this article was submitted, two related papers have appeared in the literature. One paper describes the crystal structure of the polymeric $[Co_2(H_2O)_4(5'\text{-UMP})_2]_n$, which also shows the "phosphate only" type of coordination for 5′-UMP [B. A. Cartwright, D. M. L. Goodgame, I. Jeeves, and A. C. Skapski, *Biochim. Biophys. Acta*, **477**, 195 (1977)]. In contrast, the crystal structure of the ternary complex $[Cu(5'\text{-IMP})(bpy)(H_2O)_2]\cdot NO_3\cdot H_2O$ [K. Aoki, *J. Chem. Soc., Chem. Commun.*, 600 (1977)] shows nucleotide–metal binding through the base (in this case, hypoxanthine) and not through the phosphate group.

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Molecular Structure and Magnetic Properties of *trans*-Bis(L-methioninato)copper(II), $Cu(C_5H_{10}NO_2S)_2$

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Received August 9, 1977

The crystal and molecular structure of bis(L-methioninato)copper(II), Cu(L-Met)$_2$, $Cu(C_5H_{10}NO_2S)_2$, has been determined from single-crystal three-dimensional x-ray data collected by counter methods. The compound crystallizes as elongated blue six-sided plates in the space group $P2_1(C_2^2$, No. 4) with $Z = 2$, $a = 9.487$ (5) Å, $b = 5.061$ (3) Å, $c = 15.563$ (8) Å, $\beta = 92.46$ (3)°, $d_{\text{calcd}} = 1.601$ g/cm^3, and $d_{\text{obsd}} = 1.60(1)$g/cm^3. Least-squares refinement of 1191 reflections having $F^2 \geq 3\sigma(F^2)$ gave a conventional R factor of 0.046. There are no discrete molecules in the crystal; it consists of isolated sheets of Cu(II) ions with tetragonal N_2O_4 ligand sets formed by trans coordination of two L-methionine molecules. Additional interactions with carboxylate ions from neighboring methionine molecules lead to two apical Cu–O bonds and link the Cu(II) ions to form a carboxylate-bridged sheet structure. The structure of Cu(L-Met)$_2$ is compared with that reported by others for racemic Cu(D,L-Met)$_2$. Infrared spectra and magnetic properties of both complexes are presented and discussed. Effective magnetic moments of the racemic complex fell in the range 1.85–1.90 μ_B at temperatures between 270 and 6.2 K and followed Curie law behavior. Similarly, effective magnetic moments of Cu(L-Met)$_2$ fell in the range 1.76–1.87 μ_B at temperatures between 270 and ~13.5 K; below 13.5 K, the magnetic moment steadily decreased to 1.65 μ_B at 4.2 K. ESR spectra of both polycrystalline complexes were measured at Q- and X-band frequencies over wide temperature ranges. Crystallographic similarities between the free methionine ligands and their complexes with Cu(II), Zn(II), and Cd(II) are presented and discussed.

Introduction

Our interest in the Cu(II) complexes of sulfur-containing ligands[2] and in the magnetic properties of carboxylate-bridged Cu(II) lattice structures[3] led us to investigate the Cu(II) complexes of D,L- and L-methionine. Other workers have shown that the CuN_2O_4 ligand set in the D,L complex consists of trans equatorial N_2O_2 bonding along with two apical bonds to carboxylate oxygen atoms of neighboring ligands.[4] Well-separated planar arrays of these bridged Cu(II) ions form the overall crystal structure. We are unaware of prior characterizations of bis(L-methioninato)copper(II), Cu(L-Met)$_2$. Our analysis of the infrared spectrum of this complex, using known spectral/structural guidelines,[5] indicated that the ligand might be bound to Cu(II) in the less common cis fashion. Further, the mode of ligand bonding could not be determined unambigously by preliminary ESR studies at X-band; although the expected axial spectra were observed for Cu(D,L-Met)$_2$, isotropic spectra were obtained with Cu(L-Met)$_2$. To determine the coordination geometry unambiguously, the crystal structure of Cu(L-Met)$_2$ has been determined and is reported here.

In the present work, both complexes are further characterized by ESR and infrared spectral measurements and by magnetic susceptibility studies over the 270–4.2 K temperature range. Lastly, a strong similarity between the crystal structures of certain free amino acids (such as L-methionine) and their complexes with divalent metal ions such as Cu(II), Zn(II), and Cd(II) is noted.

Experimental Section

Preparation of Complexes. The Cu(II) complex of either D,L- or L-methionine was prepared readily by the urea hydrolysis technique. In a typical experiment, a solution of 0.43 g of $CuCl_2\cdot 2H_2O$ (2.5 mmol), 0.75 g of D,L- or L-methionine (5.0 mmol), and 0.15 g of urea (2.5 mmol) in 25 mL of hot water was filtered through a Millipore membrane (0.22-μm pore size) and maintained at 80 °C for 48 h. The complexes crystallized as six-sided blue plates which were separated from the hot solution by filtration, washed with H_2O, and air-dried. Typical yields were ~70%. Anal. Calcd for Cu(Met)$_2$, $C_{10}H_{20}N_2O_4S_2Cu$: C, 33.37; N, 7.78; H, 5.60. Found for Cu(L-Met)$_2$: C, 32.43; N, 7.53; H, 5.96. Found for Cu(D,L-Met)$_2$: C, 33.30; N, 7.68; H, 5.59.

To facilitate ESR studies, Cu(II) was doped at the ~1 wt % level into Zn(Met)$_2$ lattices. Aqueous solutions containing 0.75 g (2.5 mmol) of either D,L- or L-methionine, 0.337 g (2.47 mmol) of $ZnCl_2$, and 0.004 g (0.02 mmol) of $CuCl_2.2H_2O$ were neutralized to pH ~7.5 with dilute aqueous NaOH, filtered while hot, and concentrated by evaporation at room temperature. The concentrated filtrates deposited pale blue crystalline products which were collected by filtration, washed with water, and dried in vacuo over P_2O_5.

Anal. Calcd for 1% Cu(Met)$_2$ in Zn(Met)$_2$, $C_{10}H_{20}N_2O_4S_2Zn$ (1% Cu): C, 33.20; N, 7.74; H, 5.57; Zn 17.89; Cu, 0.20. Found for 1% Cu/Zn(L-Met)$_2$: C, 33.16; N, 7.74; H, 5.39; Zn, 17.85; Cu, 0.32.

0020-1669/78/1317-0034$01.00/0

Table I. Crystal Data for Cu(L-Met)$_2$

a, Å	9.487 (5)	Z	2
b, Å	5.061 (3)	Extinction	$0k0$, $k = 2n + 1$
c, Å	15.563 (8)	Space group	$P2_1$
β, deg	92.46 (3)	μ	17.95 cm^{-1} (Mo Kα)
V, Å^3	746.6	λ, Å	0.71069 (Mo Kα, graphite monochromated)
d_{obsd}, g/cm^3	1.60 (1)		
d_{calcd}, g/cm^3	1.601		

Found for 1% Cu/Zn(D,L-Met)$_2$: C, 33.37; N, 8.03; H, 5.50; Zn, 18.03; Cu, 0.13.

Infrared Spectral Measurements. A Perkin-Elmer Model 225 spectrophotometer was used to obtain the infrared spectra of both complexes dispersed in KBr and in CsBr pellets. The absence of spectrally significant solute–matrix interactions was established by additional studies using mineral oil and perfluorocarbon mull techniques.

Magnetic Measurements. ESR spectra of powdered samples were recorded on a Varian E-9 X-band spectrometer and a Varian E-15 Q-band spectrometer operating at 9.1–9.5 and ~35 GHz, respectively. The X-band frequency was determined using a Hewlett-Packard Model 5240A 12.4-GHz digital frequency meter while the Q-band frequency was calibrated with DPPH ($g = 2.0036$). The magnetic field calibration for the Q-band spectrometer was with hydrogen nuclei when the magnet was used for wide-line NMR experiments. X-Band spectra were recorded at ~300, ~80, and 9 K with the lowest temperature measured using a calibrated carbon resistor. Q-Band spectra were taken at ~300 and ~110 K.

Variable-temperature (4.5–270 K) magnetic susceptibilities were measured with a Princeton Applied Research Model 150A vibrating-sample magnetometer operating at 12.7 kG. Powdered samples of the two complexes weighed 0.1100 and 0.3786 g for Cu(L-Met)$_2$ and Cu(D,L-Met)$_2$, respectively. The samples were calibrated with a sample of CuSO$_4$·5H$_2$O which was run over the entire temperature range. The temperature control and measurement was with a calibrated gallium–arsenide diode.

Observed molar susceptibility data were corrected for atomic diamagnetism (-186×10^{-6} cgs per copper ion) and for temperature-independent paramagnetism (61×10^{-6} cgs per copper ion). Atomic diamagnetism of the ligands was determined using Pascal's constants[6] and the observed diamagnetism of leucine.[7]

Crystal and X-Ray Data. A crystal of dimensions 0.2 × 0.5 × 0.08 mm was mounted parallel to the long dimension (b axis) in a sealed glass capillary. Preliminary Weissenberg and precession photographs revealed a monoclinic cell with the systematic absence $0k0$, $k = 2n + 1$. Although two space groups, $P2_1$ ($C_2{}^2$, No. 4) and $P2_1/m$ ($C_{2h}{}^2$, No. 11) are consistent with this extinction, the centrosymmetric space group, $P2_1/m$, was rejected initially because the complex contained an optically active ligand. (A solution of the complex in 8.6 N HCl exhibited an optical rotation of $[\alpha]_D{}^{23} = 24.3°$.) Subsequent solution and refinement of the structure confirmed the space group as $P2_1$.

Unit cell parameters (Table I) were determined by a least-squares analysis of the θ, χ, and ϕ values of 11 carefully centered reflections obtained using graphite-monochromated Mo Kα radiation and an Enraf-Nonius CAD-3 automated diffractometer. A density of 1.60 (1) g/cm^3 was measured by the density gradient method[8] using CCl$_4$ as the high-density medium and bromobenzene as the low-density medium; sucrose ($d = 1.588$ g/cm^3) and potassium hydrogen phthalate ($d = 1.636$ g/cm^3) were used as standards.[7] A θ–2θ scan over the range $3 \leq \theta \leq 30°$ was used to collect a total of 2525 reflections.[9] Of these, 1191 having $F^2 \geq 3\sigma(F^2)$ were used in the solution and refinement of the structure. The diffraction data were corrected for absorption effects.[10] Since the complex was prepared from L-methionine, no attempt was made to determine the absolute configuration by x-ray methods.

Solution and Refinement of the Structure.[11] Attempts at solving the structure by the heavy-atom method were only partially successful. Approximate Cu coordinates were obtained from an otherwise featureless normal sharpened Patterson map. Approximate sulfur coordinates could not be determined from the Patterson map because the relatively large temperature factors of the sulfur atoms caused the Cu–S vectors to be weak.

Solution of the structure was achieved by direct methods using the tangent formula.[12] Because of a pseudo-C centering condition indicated by the weakness of the $h + k = 2n + 1$ reflections, the structure factors were normalized in two groups: $h + k = 2n$ (even) and $h + k = 2n + 1$ (odd). A total of 303 reflections with $|E| \geq 1.3$ was input into the program MULTAN,[13] and a starting set was produced (Table II). An E map calculated with phases having the highest figure of merit revealed all the nonhydrogen atoms except the two terminal methyl carbon atoms and two methylene carbon atoms [C(5), C(5B), C(3B), C(4B)]. These atoms were located by the usual combination of Fourier and least-squares techniques. With all nonhydrogen scattering matter present, the initial agreement factor $R_F = \sum||F_o| - |F_c||/\sum|F_o|$ was 0.22.

Table II. Starting Set and Phases from MULTAN

hkl	Phase, deg		hkl	Phase, deg
12,0,0	360	from Σ_1 relationship	508	0
214	360		3,0,17	180
2,0,15	360		213	225
560	45	enantiomorph fixing	7,2,12	225

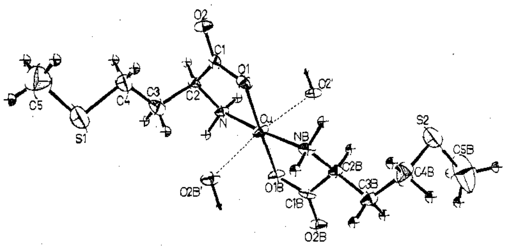


Figure 1. Molecular structure of Cu(L-Met)$_2$ showing the atom numbering scheme.

Isotropic refinement was initiated using atomic scattering factors from Cromer and Waber.[14] All atoms were treated as neutral species. Both real and imaginary parts of the anomalous dispersion correction were applied to Cu and S.[15] Initial refinement was based on F^2, and weights were set according to $w = 1/\sigma^2(F^2)$. After two cycles of full-matrix isotropic refinement, the overall value of R_F was 0.16; R_F was equal to 0.14 for reflections with $h + k = 2n$ and 0.19 for reflections with $h + k = 2n + 1$. It appeared that strong reflections with $h + k = 2n$ effectively blocked convergence of the weaker reflections with $h + k = 2n + 1$. A procedure similar to that of Leipoldt and Coppens[16] was used to effect convergence of those reflections. All reflections with $h + k = 2n + 1$ (about one-third of the total 3σ data) and approximately the same number of high-order weaker reflections with $h + k = 2n$ were used in the next two refinement cycles. Using these data, R_F fell to 0.12 and little difference was observed between the two classes of reflections. Subsequent refinement of positional and isotropic thermal parameters using all the data reduced R_F to 0.090. Two additional cycles of refinement with anisotropic thermal parameters for all nonhydrogen atoms reduced R_F to 0.065.

Further refinement was based on F. A weighting scheme, chosen by an analysis of variance,[11] led to the following assignments for $\sigma(F_o)$: $\sigma(F_o) = 1.10 - 0.029|F_o|$, $|F_o| \leq 18.4$; $\sigma(F_o) = 0.012 + 0.030|F_o|$, $|F_o| > 18.4$. Two cycles of refinement reduced R_F to 0.055 and $R_{wF} = [\sum w(F_o - F_c)^2/\sum wF_o{}^2]^{1/2}$ to 0.066. Idealized coordinates of the H atoms were calculated but not refined. The CH$_3$ groups were rotated at 20° intervals until all three H atoms were located in regions of positive electron density. The H atoms were added as a fixed atom contribution to the overall structure factor calculation, using isotropic temperature factors equal to those of the attached C atoms. Three additional cycles of refinement gave final values of $R_F = 0.046$ and $R_{wF} = 0.055$. For the last cycle, all parameter changes were within their estimated standard deviations. A final difference map showed a general background of approximately 0.4 e/Å^3 and revealed no significant features. Final atomic parameters, together with their estimated standard deviations, are given in Table III. A view of the structure showing the atomic numbering scheme is given in Figure 1. A list of observed and calculated structure factors is available.[17]

Description of the Structure

The structure consists of tetragonally coordinated Cu(II) ions (Figure 1) arranged in isolated sheets (Figure 2). The packing in the structure is shown in Figure 3. Trans coor-

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

Heavy Atom Coordinates

Atom	x (×10^4)	y (×10^3)	z (×10^4)	β_{11} (×10^4)	β_{22} (×10^3)	β_{33} (×10^4)	β_{12} (×10^3)	β_{13} (×10^4)	β_{23} (×10^4)
Cu	−2479 (1)	60.0	4933.3 (8)	43.8 (8)	14.2 (3)	24.3 (4)	−3.0 (3)	10.8 (5)	−14 (2)
S(1)	−2064 (5)	318 (1)	1272 (2)	198 (6)	86 (3)	49 (2)	−6 (1)	−47 (3)	91 (7)
S(2)	−2717 (4)	291 (1)	8430 (2)	158 (6)	87 (3)	39 (1)	−6 (1)	−33 (2)	0 (7)
O(1)	−843 (7)	267 (2)	4637 (4)	53 (10)	18 (5)	23 (2)	−3 (2)	−2 (4)	−5 (9)
O(1B)	−4142 (7)	−147 (2)	5240 (4)	45 (10)	10 (5)	32 (3)	0 (1)	8 (4)	−5 (9)
O(2)	1049 (7)	258 (2)	3845 (4)	48 (9)	16 (5)	40 (3)	0 (2)	4 (4)	4 (9)
O(2B)	−5919 (7)	−137 (2)	6124 (4)	44 (10)	28 (7)	33 (3)	−2 (2)	7 (4)	9 (11)
N	−1765 (8)	−199 (2)	4076 (5)	38 (9)	14 (4)	26 (3)	0 (2)	5 (4)	−9 (11)
NB	−3080 (9)	298 (3)	5851 (5)	36 (9)	11 (4)	25 (3)	0 (2)	−1 (4)	−13 (10)
C(1)	−105 (11)	171 (2)	4032 (6)	50 (12)	11 (5)	15 (4)	3 (2)	−2 (5)	18 (11)
C(1B)	−4747 (12)	−63 (3)	5897 (6)	27 (13)	13 (6)	30 (4)	1 (2)	−8 (5)	−2 (12)
C(2)	−762 (11)	−58 (2)	3528 (6)	44 (11)	18 (4)	19 (4)	−2 (2)	3 (5)	−8 (11)
C(2B)	−3867 (10)	142 (2)	6452 (6)	41 (10)	14 (4)	21 (3)	1 (1)	4 (4)	−9 (9)
C(3)	−1628 (11)	51 (4)	2729 (6)	94 (12)	46 (6)	26 (4)	−9 (3)	−10 (5)	−17 (22)
C(3B)	−4759 (9)	299 (2)	7065 (6)	63 (10)	21 (4)	27 (4)	1 (2)	7 (5)	−6 (12)
C(4)	−823 (14)	215 (3)	2131 (7)	134 (16)	43 (7)	29 (5)	−1 (3)	−17 (7)	29 (16)
C(4B)	−3864 (13)	465 (3)	7694 (7)	124 (16)	37 (6)	37 (5)	−4 (2)	11 (7)	−47 (15)
C(5)	−933 (21)	535 (6)	695 (9)	255 (31)	127 (18)	47 (6)	−14 (7)	4 (11)	11 (40)
C(5B)	−3947 (24)	144 (4)	9130 (10)	367 (44)	78 (13)	54 (7)	−15 (6)	−18 (14)	61 (27)

Hydrogen Atom Coordinates

Atom	x (×10^3)	y (×10^3)	z (×10^3)	B, Å^2	Atom	x (×10^3)	y (×10^3)	z (×10^3)	B, Å^2
H(N-1)	−264	−270	368	1.03	H(C4-1)	−1	95	187	4.76
H(N-2)	−121	−356	442	1.03	H(C4-2)	−43	390	247	4.76
H(NB-1)	−376	450	557	1.61	H(C4B-1)	−454	569	812	3.39
H(NB-2)	−215	379	618	1.61	H(C4B-2)	−347	635	736	3.39
H(C2)	6	−191	333	1.76	H(C5-1)	−31	662	114	7.75
H(C2B)	−311	31	684	1.82	H(C5-2)	−155	662	27	7.75
H(C3-1)	−250	171	295	2.96	H(C5-3)	−20	421	33	7.75
H(C3-2)	−212	−108	237	2.96	H(C5B-1)	−367	185	980	7.73
H(C3B-1)	−538	163	743	2.21	H(C5B-2)	−398	−70	905	7.73
H(C3B-2)	−546	428	669	2.21	H(C5B-3)	−487	248	893	7.73

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

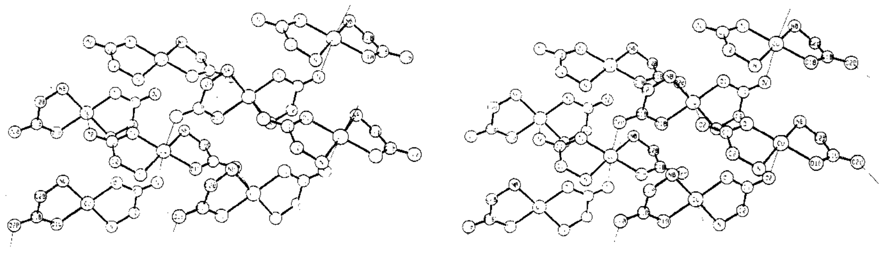


Figure 2. Stereoscopic view of the carboxylate-bridged layer structure in Cu(L-Met)$_2$.

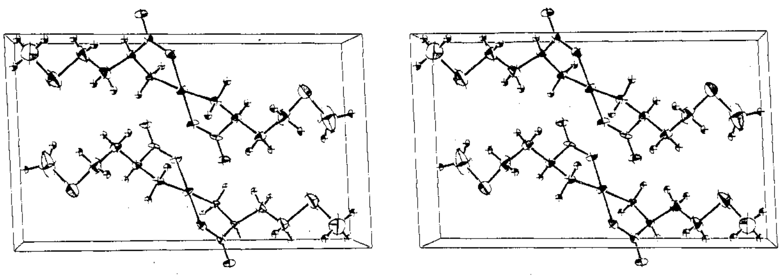


Figure 3. Stereoscopic packing diagram for Cu(L-Met)$_2$ viewed along *b*. The *c* axis is horizontal.

dination of two methionine molecules per Cu(II) produces an equatorial N_2O_2 ligand set. Additional interaction with two carboxylate oxygen atoms [O(2B′) and O(2′)] from neighboring methionine molecules gives rise to the apical bonds and links the Cu(II) species into a carboxylate-bridged sheet structure. The structural features of Cu(L-Met)$_2$ are given in Table IV, along with those reported[18] for Cu(D,L-Met)$_2$. The structural parameters of both complexes are comparable; many of the minor differences are a consequence of the center of symmetry present in the racemic complex structure. For example, in the present study, the O(1)–Cu–O(1B), N–Cu–NB, and O(2′)–Cu–O(2B′) bond angles were found to be 179.6 (4), 175.0 (3), and 173.7 (2)°, respectively. Corresponding angles in the racemic complex are required crystallographically to be 180°. Also, the bond distances in both complexes are similar. For example, the average value of the Cu–O(1) (1.944 (8) Å) and Cu–O(1B) (1.970 (8) Å) bond lengths compares favorably with the value of 1.951 (4) Å observed for the racemic complex. Similarly, values of the Cu–N (2.010 (10) Å) and Cu–NB (1.970 (10) Å) bond lengths and Cu–O(2′) (2.751 (7) Å) and Cu–O(2B′) (2.676 (8) Å) bond lengths span the respective values of 1.983 (5)

Table IV. Bond Distances (Å) and Angles (deg) in Cu(L-Met)$_2$ and Cu(D,L-Met)$_2$[a,b]

Atoms	Cu(L-Met)$_2$	Cu(D,L-Met)$_2$
Cu-O(1)	1.944 (8)	(1.951 (4))
Cu-O(1B)	1.970 (8)	(*1.951 (4)*)[b]
Cu-N	2.01 (1)	(1.983 (5))
Cu-NB	1.97 (1)	(*1.983 (5)*)
O(1)-C(1)	1.29 (1)	(1.274 (7))
O(1B)-C(1B)	1.27 (1)	(*1.274 (7)*)
O(2)-C(1)	1.23 (1)	(1.231 (7))
O(2B)-C(1B)	1.24 (1)	(*1.231 (7)*)
N-C(2)	1.49 (1)	(1.474 (8))
NB-C(2B)	1.46 (1)	(*1.474 (8)*)
C(1)-C(2)	1.52 (2)	(1.553 (9))
C(1B)-C(2B)	1.57 (2)	(*1.553 (9)*)
C(2)-C(3)	1.56 (2)	(1.502 (10))
C(2B)-C(3B)	1.52 (1)	(*1.502 (10)*)
C(3)-C(4)	1.48 (2)	(1.545 (13))
C(3B)-C(4B)	1.52 (2)	(*1.545 (13)*)
C(4)-S(1)	1.82 (1)	(1.806 (10))
C(4B)-S(2)	1.78 (1)	(*1.806 (10)*)
S(1)-C(5)	1.80 (2)	(1.785 (16))
S(2)-C(5B)	1.79 (2)	(*1.785 (16)*)
Cu-O(2′)	2.751 (7)	(2.713 (4))
Cu-O(2B′)	2.676 (8)	(*2.713 (4)*)
Cu···Cu′	5.338 (2)	(5.364)
O(1)-Cu-N	84.2 (4)	(84.1 (2))
O(1B)-Cu-NB	83.7 (4)	(*84.1 (2)*)[b]
O(1B)-Cu-N	96.3 (4)	(95.8 (2))
O(1)-Cu-NB	95.9 (4)	(*95.8 (2)*)
O(1)-Cu-O(1B)	179.6 (4)	(180.0)
N-Cu-NB	175.0 (3)	(*180.0*)
O(2′)-Cu-O(1)	95.0 (3)	(93.0 (2))
O(2′)-Cu-O(1B)	85.0 (3)	(*87.0 (1)*)
O(2′)-Cu-O(2B′)	173.7 (2)	(*180.0*)
O(2′)-Cu-N	85.7 (3)	(86.0 (2))
O(2′)-Cu-NB	89.3 (3)	(*94.0 (2)*)
O(2B′)-Cu-O(1)	89.1 (3)	(*87.0 (1)*)
O(2B′)-Cu-O(1B)	90.9 (3)	(*93.0 (2)*)
O(2B′)-Cu-N	99.5 (3)	(94.0 (2))
O(2B′)-Cu-NB	85.5 (3)	(*86.0 (2)*)
Cu-O(2′)-C(1′)	117.0 (6)	(117.3 (4))
Cu-O(2B′)-C(1B′)	119.4 (8)	(*117.3 (4)*)
Cu-O(1)-C(1)	115.8 (8)	(116.0 (4))
Cu-O(1B)-C(1B)	114.3 (8)	(*116.0 (4)*)
O(1)-C(1)-O(2)	123.8 (10)	(124.7 (6))
O(1B)-C(1B)-O(2B)	124.8 (12)	(*124.7 (6)*)
O(1)-C(1)-C(2)	116.0 (10)	(116.4 (5))
O(1B)-C(1B)-C(2B)	114.8 (10)	(*116.4 (5)*)
O(2)-C(1)-C(2)	120.1 (9)	(118.9 (5))
O(2B)-C(1B)-C(2B)	120.4 (9)	(*118.9 (5)*)
Cu-N-C(2)	108.0 (8)	(110.3 (4))
Cu-NB-C(2B)	107.9 (8)	(107.9 (8))
C(1)-C(2)-N	109.2 (8)	(108.3 (5))
C(1B)-C(2B)-NB	106.2 (8)	(*108.3 (5)*)
N-C(2)-C(3)	107.4 (8)	(112.9 (6))
NB-C(2B)-C(3B)	115.8 (9)	(*112.9 (6)*)
C(1)-C(2)-C(3)	109.4 (10)	(108.9 (6))
C(1B)-C(2B)-C(3B)	113.1 (8)	(*108.9 (6)*)
C(2)-C(3)-C(4)	115.5 (9)	(111.7 (7))
C(2B)-C(3B)-C(4B)	112.4 (9)	(*111.7 (7)*)
C(3)-C(4)-S(1)	106.7 (8)	(109.0 (7))
C(3B)-C(4B)-S(2)	116.7 (9)	(*109.0 (7)*)
C(4)-S(1)-C(5)	99.2 (7)	(102.1 (6))
C(4B)-S(2)-C(5B)	101.5 (8)	(*102.1 (6)*)

[a] Values for Cu(D,L-Met)$_2$ are from ref 18. Atoms marked by a prime are related to unmarked atoms by space group symmetry operations. [b] Italicized bond distances and angles are required crystallographically.

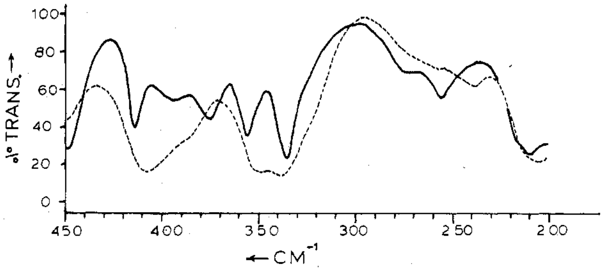


Figure 4. Infrared spectra of Cu(L-Met)$_2$ (solid line) and Cu(D,L-Met)$_2$ (dashed line) over the 450–200-cm^{-1} range. Both complexes were dispersed in mineral oil mulls contained between polyethylene plates.

and 2.713 (4) Å observed for the racemic complex. Least-squares planes for both structures are presented in Table V. The carboxylate groups effectively are planar in both structures. Modest distortions in the Cu(L-Met)$_2$ complex are evidenced by the observed puckering of the Cu, O(1), O(1B), N, NB unit. A further similarity between the structures of both Cu(II) complexes is that each unit cell contains two magnetically nonequivalent Cu(II) ions. These Cu(II) ions differ in the arrangement of their tetragonal axes which coincide with the direction of the apical O–Cu–O bonds. The resulting misalignment of these tetragonal axes is relevant to the ESR spectral studies (vide infra). Due to the nonlinearity of the O(2)–Cu–O(2B′) atoms, the misalignment in the unit cell of Cu(L-Met)$_2$ may be defined in two nearly equivalent ways. Based upon the angle between neighboring O(2′)–O(2B′) vectors, the misalignment is 68.83°; based upon the angle between neighboring Cu–O(2′) and Cu–O(2B′) vectors, it is 69.10°. The misalignment of the tetragonal axes in the unit cell of Cu(D,L-Met)$_2$ is 66.98° and is defined uniquely because the apical O–Cu–O group is linear.

Structural data reported here and elsewhere[2,18] show that the copper ions in both complexes are located in isolated sheets perpendicular to c^*. The minimum interlayer separation of copper ions is 15.563 Å in Cu(L-Met)$_2$ and 16.035 Å in Cu(D,L-Met)$_2$. Within layers, the minimum copper–copper separation is 5.061 Å in Cu(L-Met)$_2$ and 5.018 Å for the racemic complex. The ions within a layer are bridged through the carboxylate oxygen atoms which occupy the apical sites in the copper coordination spheres. In Cu(D,L-Met)$_2$, the copper atoms form a planar array of equal sided (5.364 Å) parallelograms; in Cu(L-Met)$_2$, the corresponding array is approximately planar (±0.01 Å) and has edge lengths of 5.338 and 5.423 Å.

Lastly, we note that the temperature factors of the atoms increase regularly in going from copper to the terminal methyl group of the ligand. In the final cycle of isotropic refinement (R_F = 0.090), sulfur temperature factors were found to be approximately four times as large as those of the copper atoms. On electron density maps, the sulfur atoms appeared as broad peaks with heights approximately equal to those of the ligand nitrogen and oxygen atoms; this accounts for the difficulty encountered in solving the structure by the heavy-atom method. Similar trends have been found for Cu(D,L-Met)$_2$.[18]

Results

Infrared-Spectral Results. The structure of Cu(L-Met)$_2$ was probed by an infrared spectral analysis prior to the crystallographic study. Both methionine complexes exhibited sharp NH$_2$ stretching modes at ~3390, ~3230, and ~3130 cm^{-1}. The NH$_2$ deformation mode in both materials was observed as a sharp shoulder (~1580 cm^{-1}) located next to the intense >C=O stretching mode at ~1620 cm^{-1}. These spectral congruencies indicated that the coordination structures of both complexes were comparable. In order to determine if this apparent similarity also included trans Cu(amino acid)$_2$ arrangements in both complexes, the low-energy infrared region (Figure 4) was examined in detail. According to established infrared/structural guidelines, a cis isomer should exhibit sym Cu–N and sym Cu–O vibrations in the 410–450 and 270–300 cm^{-1} spectral regions, respectively.[5] Both cis and trans isomers should exhibit asym Cu–N and asym Cu–O vibrations in the 470–500 and 320–350 cm^{-1} spectral regions, respectively.

Table V. Least-Squares Planes[a] and Deviations Therefrom for Cu(L-Met)$_2$ and Cu(D,L-Met)$_2$[b]

Equations of the Planes

Plane	*A*	*B*	*C*	*D*	Atoms defining plane
I	0.5259	−0.4787	0.7030	3.872	Cu, O(1), O(1B), N, NB
	(−0.5309	−0.4729	0.7032	0.0)	
II	−0.8251	0.4868	0.2868	2.439	C(1), C(2), C(3), C(4)
	(0.9039	0.1139	0.4123	2.551)	
III	0.0770	−0.7292	0.6800	6.038	C(1B), C(2B), C(3B), C(4B)
	(0.9039	0.1139	0.4123	−2.551)	
IV	0.4160	−0.6394	0.6466	3.339	O(1), C(1), C(2), O(2)
	(−0.4510	−0.6310	0.6313	0.2539)	
V	0.4008	−0.7413	0.5383	3.220	O(1B), C(1B), C(2B), O(2B)
	(−0.4510	−0.6310	0.6313	−0.2539)	

Deviations from the Planes

Plane	Atom	Dev, Å	Plane	Atom	Dev, Å
I	Cu	−0.03 (0.0)	IV	O(1)	0.00 (0.0)
	O(1)	−0.03 (0.0)		C(1)	0.01 (0.0)
	O(1B)	−0.04 (0.0)		C(2)	0.00 (0.0)
	N	0.04 (0.0)		O(2)	0.00 (0.0)
	NB	0.06 (0.0)			
II	C(1)	0.09 (0.04)	V	O(1B)	0.00 (0.0)
	C(2)	−0.22 (−0.05)		C(1B)	−0.01 (0.0)
	C(3)	0.33 (−0.10)		C(2B)	0.00 (0.0)
	C(4)	−0.20 (0.11)		O(2B)	0.00 (0.0)
III	C(1B)	0.05 (−0.04)			
	C(2B)	−0.06 (0.05)			
	C(3B)	−0.05 (0.10)			
	C(4B)	0.06 (−0.11)			

[a] Equations are expressed in the form $AX_0 + BY_0 + CZ_0 = D$ where X_0, Y_0, and Z_0 are Cartesian axes lying along bxc^*, b, and c^*, respectively. [b] Values for Cu(D,L-Met)$_2$ are given in parentheses and were derived from data given in ref 18.

More detailed isotopic substitution studies along with more complete normal-coordinate analyses indicate that these metal–ligand modes apparently have appreciable mixed character.[19,20] However, both complexes, as well as both free ligands, exhibited absorptions at ~270 cm^{-1} and in the 410–450 cm^{-1} region. The results suggested that either (a) Cu(L-Met)$_2$ also had a trans structure or (b) the sym Cu–N and sym Cu–O vibrations appropriate for a cis structure are coincident with ligand modes. A decisive choice among these alternatives would in our opinion have required detailed isotopic substitution studies along with normal-coordinate analyses.

The weak absorptions (not shown) of Cu(D,L-Met)$_2$ and Cu(L-Met)$_2$ at ~495 and ~475 cm^{-1}, respectively, are appropriate in energy for Cu–N modes. Further studies would be required to identify which of the two absorptions in the 335–356-cm^{-1} region (Figure 4) corresponds to the expected Cu–O mode.

The crystallographic study ruled out cis coordination as a source of the relative complexity of the Cu(L-Met)$_2$ infrared spectra in the 420–330-cm^{-1} region. The center of symmetry in the Cu(D,L-Met)$_2$ structure requires that both ligands have identical bond angles and distances. This crystallographic constraint is removed for the Cu(L-Met)$_2$ structure, and different bond distances and angles are observed within the crystallographically nonequivalent methionine residues. If the CO$_2$ fragment and the remainder of the ligand [(C(4)–S(1)–C(5)] are regarded as the bulky groups attached to the C(2)–C(3) ethane fragment, the conformations about the C(2)–C(3), C(3)–C(4), and C(4)–S(1) bonds are gauche, trans, and trans, respectively. In contrast, the C(2B)–C(3B), C(3B)–C(4B), and C(4B)–S(2) bonds have trans, gauche, and gauche conformations, respectively. Thus, the apparent complexity of the Cu(L-Met)$_2$ spectra may arise from the noncoincidence of deformation modes associated with the two nonequivalent methionine ligands.

Results of Magnetic Studies. The *g* values obtained from the ESR studies of polycrystalline Cu(L-Met)$_2$ and Cu(D,L-Met)$_2$ are listed in Table VI. The racemic complex exhibited rhombic spectra (not shown) at both Q-band and X-band frequencies. The appearance of these spectra was invariant to cooling the samples from ~300 to 110 K (Q-band) and from ~300 to ~9 K (X-band). In contrast, the X-band ESR spectrum of Cu(L-Met)$_2$ consists of an isotropic signal centered at $g = 2.139$. Cooling the sample to either ~80 or ~9 K did not result in either a changed appearance of the spectrum or significant shifts in the observed *g* value. We originally thought that the possibility of magnetic interactions between the Cu(II) ions and the magnetic nonequivalence of the two Cu(II) ions within the unit cell might give rise to these isotropic spectra.[21] However, the observation of isotropic spectra turned out to be a simple issue of instrumental resolution; rhombic spectra of Cu(L-Met)$_2$ were observed readily at Q-band frequencies and, as expected from our structural and magnetic studies (vide infra), were similar to the spectra obtained for the racemic complex.

Table VI. Measured *g* Values for Polycrystalline Cu(L-Met)$_2$ and Cu(D,L-Met)$_2$

	Cu(L-Met)$_2$	
Q-Band:	~300 K	2.056, 2.099, 2.204
	~100 K	2.057, 2.102, 2.204
X-Band:	~300 K	2.139
	~80 K	2.135
	~9 K	2.134
	Cu(D,L-Met)$_2$	
Q-Band:	~300 K	2.054, 2.106, 2.208
	~110 K	2.054, 2.105, 2.207
X-Band:	~300 K	2.052, 2.110, 2.210
	~80 K	2.049, 2.102, 2.208
	~9 K	2.049, 2.111, 2.203

Other workers also have observed rhombic ESR spectra for polycrystalline Cu(II) complexes of D,L-Methionine and other amino acids.[22] Two explanations for the rhombic spectra were considered: (a) the spectra result from the local Cu(II) coordination geometries; (b) the spectra arise from magnetic exchange interactions between crystallographically or mag-

Table VII. Representative[a] Observed Magnetic Susceptibilities (cgs × 10^3) and Effective Magnetic Moments (μ_B)

	Cu(L-Met)$_2$		Cu(D,L-Met)$_2$	
T, K	$\chi_M{}^b$	$\mu_{eff}{}^c$	$\chi_M{}^b$	$\mu_{eff}{}^c$
270	1.49	1.79	1.67	1.90
221	1.88	1.82	2.01	1.89
170	2.48	1.83	2.56	1.86
103	4.25	1.87	4.43	1.91
41.3	9.92	1.81	10.47	1.86
13.5	28.79	1.76	33.95	1.91
10.3	36.04	1.73	44.08	1.91
6.2	55.67	1.66	73.64	1.91
4.2	80.72	1.65		

[a] See ref 17 for complete data. [b] Includes a diamagnetic correction of −186 × 10^{-6} cgsu. [c] Calculated by the relationship $\mu = 2.828(\chi_M T)^{1/2}$.

netically nonequivalent Cu(II) ions and do not necessarily reflect the coordination geometries. ESR doping studies constitute an attractive vehicle for testing explanation (b) because of the near isomorphism of the Cu(L-Met)$_2$ and Zn(L-Met)$_2$ lattices (vide infra). Powder diffraction studies, which will be described elsewhere, suggest a near isomorphism between the corresponding racemic complexes as well. In contrast to the rhombic spectra obtained for the pure Cu(II) complexes, axial Q-band spectra were exhibited at 300 K by both zinc(II) methionine complexes doped with ca. 1% Cu(II). The parameters $g_\parallel = 2.273$, $g_\perp = 2.059$, and $A_\parallel$(Cu) = 172 G (av) were obtained in the Zn(L-Met)$_2$ host; the corresponding parameters of $g_\parallel = 2.277$, $g_\perp = 2.062$, and $A_\parallel$(Cu) = 164 G (av) were obtained from the doped racemic host lattice. Comparable parameters of $g_\parallel = 2.264 \pm 0.006$, $g_\perp = 2.057 \pm 0.002$, and $|A_\parallel| = (181 \pm 7) \times 10^{-4}$ cm^{-1} also were reported for seven copper(II) amino acid complexes dispersed in H_2O/CH_3OH glasses at 77 K.[22] Thus, the magnetic dilution achieved in the Cu-doped Zn(Met)$_2$ lattices resulted in ESR spectra which reflect the nearly axial metal ion coordination geometries. Consequently, the rhombic ESR spectra exhibited by the pure Cu(Met)$_2$ complexes may arise from a weak exchange interaction ($|J| \leq$ ca. 0.5 cm^{-1}) involving the carboxylate bridges. Such an exchange-induced averaging process may cause the observed *g* values to differ from the principal *g* values of the local Cu(II) ions. In order to explore this hypothesis further, single-crystal ESR studies of both the pure Cu(II) and doped complexes are needed.

As noted above, inter- and intralayer copper separations in both complexes are sufficiently large to preclude direct magnetic exchange interactions. The sole remaining mechanism for significant magnetic coupling is superexchange via the bridging carboxylate linkages. A polyatomic orbital pathway of this type was postulated to account for the small net ferromagnetism observed with Cu(L-Tyr)$_2$.[23] This latter complex contains tetragonal CuN$_2$O$_4$ chromophores which are structurally analogous to those observed for the title complex. However, the copper ions are joined by the carboxylate bridges into spiraling chains, rather than sheets.

Selected representative magnetic susceptibilities and moments of Cu(L-Met)$_2$ and Cu(D,L-Met)$_2$ are given in Table VII. Complete magnetic data are available.[17] The magnetism of the racemic complex corresponds to a simple Curie law behavior over the 270–6.2 K temperature range. Effective magnetic moments fell in the range 1.85–1.92 μ_B and exhibited no significant trends. The magnetism of Cu(L-Met)$_2$ exhibited simple Curie law behavior over the 270–13.5 K temperature range; effective magnetic moments fell in the range 1.76–1.87 μ_B. Below 13.5 K, the magnetic moment steadily decreased to a value of 1.65 μ_B at 4.2 K.

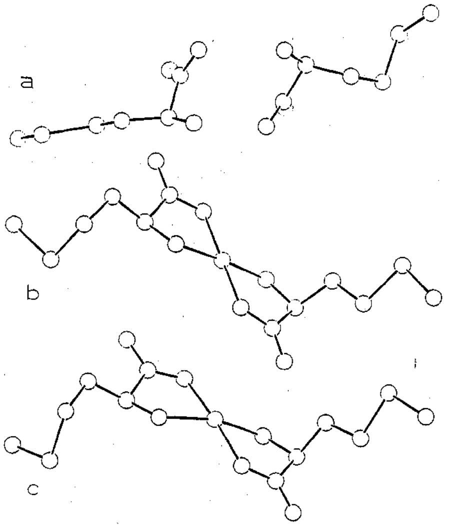


Figure 5. L-Methionine structures projected along *b*: (a) L-methionine; (b) Cu(L-Met)$_2$; (c) Zn(L-Met)$_2$.

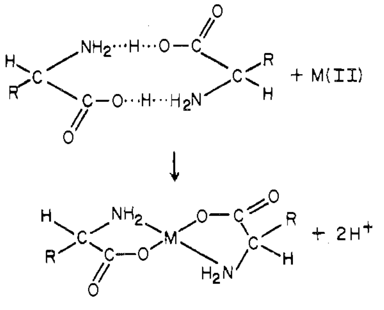
It is apparent that these carboxylate-bridged sheets of Cu(II) ions do not exhibit appreciable magnetic interactions. Two features of these carboxylate bridges may serve to attenuate the strong magnetic coupling displayed by the well-known dimeric Cu(II) carboxylates.[24] First, the carboxylate bridges in the dimers have syn–syn arrangements whereas those in the sheet structures are syn–anti. Secondly, the bridges in the dimers involve equatorial bonding positions exclusively whereas each Cu(II) ion in the sheet structures is magnetically linked to its neighbors via two long apical Cu–O bonds.

Structural Similarities between Methionine Complexes and Free Methionine. Both the title complex and free L-methionine crystallize in the same space group with similar cell dimensions and volume; this similarity extends to the Zn(II) and Cd(II) L-methionine complexes as well as the racemic ligand and its Cu(II) complex (Table VIII). To determine reasons for these similarities, we examined the packing of the free ligands and selected complexes; *b*-axis projections of the asymmetric units of L-methionine, Cu(L-Met)$_2$ and Zn(L-Met)$_2$ are shown in Figure 5.[29]

As with many free amino acids,[30] both L- and D,L-methionine exist in the solid state as zwitterions held together in a trans arrangement by hydrogen bonds (Figure 5a). Additional hydrogen bonding interactions join the zwitterions to form a double layer structure. Complex formation with a divalent metal ion may be viewed formally as a substitution process within the free ligand lattice

Table VIII. Crystallographic Data for Methionine and Its Complexes

	L-Met[25]	Cu(L-Met)$_2$	Cd(L-Met)$_2$[26]	Zn(L-Met)$_2$[27]	D,L-Met[28] (α-form)	Cu(D,L-Met)$_2$[4]
a, Å	9.498 (5)	9.487 (5)	9.73 (1)	9.437 (4)	9.76	9.482 (5)
b, Å	5.189 (5)	5.061 (3)	5.157 (5)	5.119 (2)	4.70	5.018 (4)
c, Å	15.318 (5)	15.563 (8)	15.53 (1)	15.731 (5)	16.70	16.035 (13)
β, deg	97.69 (10)	92.46 (3)	105.8 (1)	107.96 (2)	102	93.78 (4)
Space group	$P2_1$	$P2_1$	$P2_1$	$P2_1$	$P2_1/a$	$P2_1/a$
V, Å^3	748.2	746.6	749.8	722.9	749.3	761.3



R = $CH_3SCH_2CH_2$-

With L-methionine, the effect of Cu(II) or Zn(II) substitution is to rotate the carboxylate groups so that they are more nearly coplanar with the amino groups, consistent with the formation of metal–ligand bonds. To accomodate this structural change and pack efficiently, the side-chain conformation changes. The asymmetric units of Cu(L-Met)$_2$ and Zn(L-Met)$_2$ are quite similar to each other (Figure 5b,c) with only small differences in the conformations of the side chains. Perhaps the most striking observation is that the zinc ion in Zn(L-Met)$_2$ is forced to adopt an unusual tetragonal coordination geometry, presumably because of constraints imposed by the ligands.

Studies designed to examine the generality and implications of these structural similarities in amino acid and metal amino acid structures currently are being performed in our laboratories. Published data for free racemic α-amino-n-butyric acid[31] and its Cu(II) complex[32] suggest that the above methionine systems do not constitute an isolated example of this effect.

Acknowledgment. This research was supported by the Rutgers Computing Center and by a grant (AM16412) from the National Institutes of Health. Preliminary ESR measurements were made by Dr. Pu Sen Wang in the laboratory of Professor Edel Wasserman at Rutgers University. We thank Professor Derek Hodgson for a preprint of ref 27 in advance of publication.

Registry No. Cu(D,L-Met)$_2$, 15170-74-8; Cu(L-Met)$_2$, 64314-89-2; Zn(L-Met)$_2$, 40816-51-1; Zn(D,L-Met)$_2$, 64364-41-6.

Supplementary Material Available: Listings of structure factor amplitudes and observed magnetic susceptibilities and moments of Cu(D,L-Met)$_2$ and Cu(L-Met)$_2$ (8 pages). Ordering information is given on any current masthead page.

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