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Structural Characterization of Bis(L-methionato)zinc(II), Zn(L-met)₂

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The crystal and molecular structure of bis(L-methionato)zinc(II), Zn(L-met)₂, has been determined from three-dimensional x-ray counter data. The complex crystallizes in the monoclinic space group *P*2₁ with two formula units in a cell with dimensions *a* = 15.731 (5) Å, *b* = 5.119 (2) Å, *c* = 9.437 (4) Å, and β = 107.96 (2)°. Least-squares refinement of the structure led to a value of the conventional *R* factor (on *F*) of 0.055 for 1083 data with $F^2 > 2\sigma(F^2)$. The complex consists of Zn(met)₂ units linked by long-range Zn—O contacts of 2.240 (7) and 2.729 (7) Å into sheets lying approximately in the crystallographic *b*—*c* plane. There is slightly distorted octahedral geometry around each zinc center, the base plane being occupied by the amino nitrogen atom and one carboxyl oxygen atom from each independent methionine moiety. The remaining carboxyl oxygen atoms participate in long-range Zn—O interactions. The geometry of the methionine ligands is similar to that of uncomplexed L-methionine. Polymeric interactions in Zn(L-met)₂ are similar to those found in Cu(DL-met)₂ and Cd(L-met)₂.

Introduction

Metal poisoning has become an unpleasant side effect of our technologically advanced society. Caused mainly by industrial pollution and the use of metals in household and agricultural products,² metal poisoning has been treated effectively with chelating agents.³ Most commonly used in this capacity are ethylenediaminetetraacetic acid (EDTA),^{4,5} 2,3-dimercaptopropanol (BAL, for British Anti-Lewisite),^{6,7} and derivatives of cysteine such as β , β' -dimethylcysteine (penicillamine).⁸⁻¹⁰ The nature and extent of the binding of cysteine and its derivatives with transition metals have been the topics of considerable research,¹¹⁻²⁵ not only because of its importance in chelation therapy but also in catalysis.¹¹ Cysteine and penicillamine, which have been shown to occupy one, two, or three coordination sites depending on the metal, can form two five-membered and one six-membered chelate rings if they exhibit tridentate coordination. Tridentate methionine potentially forms one five-, one six-, and one seven-membered ring. However, no such metal complex of methionine has been isolated to date, and, in general, solid-state complexes of methionine are not as well characterized as those of cysteine and penicillamine. With Pt(II)¹⁸ and Pd(II)²³ methionine acts as a bidentate chelate bonding through sulfur and nitrogen with the carboxyl group protonated. With the

amino group but not the carboxyl group protonated, methionine coordinates to two different Hg(II) centers, one through sulfur and the other through both carboxyl oxygen atoms.²⁶ When neither the amino nor the carboxyl group is protonated and the metal is Cd(II)²⁷ or Cu(II),²² methionine again interacts with two metal centers. It coordinates through the amino nitrogen and one carboxyl oxygen to one center and through the other carboxyl oxygen to the second metal center. As was the case for cysteine and penicillamine, the mode of methionine binding also varies depending on the metal atom.

Zinc is a much less toxic metal than other group 2B metals²⁸ and has been shown to compete successfully with cadmium for protein binding sites.²⁹ Thus, zinc complexes are most useful in comparison with their cadmium analogues. In order both to further examine the effect of increased chelate ring size on the extent of methionine binding to metals and to compare it with the cadmium analogue, we undertook the x-ray structural analysis of Zn(L-met)₂.

Experimental Section

The complex was prepared by adding an aqueous solution of L-methionine to a suspension of freshly prepared Zn(OH)₂ in water so that the molar ratio of ligand to metal was 2:1. The reaction mixture was filtered and the filtrate allowed to evaporate until colorless plates precipitated. Anal. Calcd for ZnS₂O₄N₂C₁₀H₂₀: Zn, 18.07; N, 7.74;

C, 33.20; H, 5.57. Found: Zn, 18.21; N, 7.80; C, 33.30; H, 5.46. On the basis of Weissenberg and precession photography, the crystals were assigned to the monoclinic system, the systematic absences being $0k0$ for k odd. This is consistent with the space groups $P2_1$ (C_2^2) and $P2_1/m$ (C_{2h}^2), but since only L-methionine is present in the molecule, the space group is constrained to be the noncentrosymmetric choice $P2_1$. The cell constants, $a = 15.731$ (5) Å, $b = 5.119$ (2) Å, $c = 9.437$ (4) Å, and $\beta = 107.96$ (2)°, were obtained by least-squares methods from observations made at 22° using Mo $K\alpha_1$ radiation with the wavelength assumed to be 0.7093 Å.

Diffraction data were collected using a platelike crystal mounted roughly parallel to the crystallographic b axis. The faces and the separations between opposite pairs are as follows: (100) and (100), 0.0024 cm; (102) and (102), 0.0100 cm; (010) and (010), 0.0632 cm. Intensity data were collected on a Picker four-circle automatic diffractometer equipped with a graphite monochromator at a takeoff angle of 1.3°. Data were collected in the θ - 2θ scan mode at the rate of 0.5°/min from 0.85° below the $K\alpha_1$ peak position to 0.85° above the $K\alpha_2$ peak position with 20-s stationary-crystal, stationary-counter background counts at both ends of the scan.

A unique data set ($\pm h, k, l$) was collected having $2^\circ < 2\theta < 50^\circ$ (Mo $K\alpha$), beyond which there was very little intensity above background. A total of 1429 reflections were recorded, including several Friedel pairs. Three standard reflections were examined after every hundred reflections and showed no systematic decline as a function of exposure time.

The data were processed by the method of Ibers and co-workers³⁰ using their formula for the estimated standard deviation

$$\sigma(I) = [C + 0.25(t_s/t_o)^2(B_H + B_L) + p^2I^2]^{1/2}$$

the value of p being assigned as 0.05. The values of I and $\sigma(I)$ were corrected for Lorentz and polarization effects using the formula

$$\frac{1}{Lp} = \frac{2 \sin \theta}{\cos^2 2\theta_m + \cos^2 2\theta}$$

where θ_m , the monochromator angle, is 12°. The data were also corrected for absorption,³¹ the attenuation coefficient being 20.27 cm⁻¹; transmission coefficients for the data crystal were in the range 0.812–0.960. Of the 1429 recorded reflections, 1083 were independent and had intensities greater than 2 times their estimated standard deviations.

Solution and Refinement of Structure

All least-squares refinements in this analysis were carried out on F_o , the weights being taken as $4F_o^2/\sigma^2(F_o^2)$. In calculations of F_o , the atomic scattering factors for nonhydrogen atoms were taken from ref 32a and those for H from Stewart, Davidson, and Simpson.³³ The effects of the anomalous dispersion of Zn and S were taken into account in calculations of F_o ; the values of $\Delta f'$ and $\Delta f''$ were taken from ref 32b.

Examination of a three-dimensional Patterson function revealed the positions of zinc, one sulfur, and one oxygen atom. The presence of these correct positions in the least-squares refinement sufficiently phased the data so that the remaining nonhydrogen atoms could be located from subsequent difference Fourier syntheses.

After making certain that these atomic positions were consistent with the presence of an L-methionine moiety in the complex, the positions of the 19 nonhydrogen atoms were refined isotropically, which led to values of the agreement factors $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o^2)]^{1/2}$ of 0.126 and 0.140, respectively. Anisotropic refinement of these same atoms yielded $R_1 = 0.059$ and $R_2 = 0.066$. At this point an attempt was made to locate the hydrogen atoms from a difference Fourier synthesis. Since all 20 positions could not be unambiguously located, the hydrogen atoms were placed in calculated positions and assigned isotropic thermal parameters of 7.0 Å². The positions of the hydrogen atoms were calculated on the basis of tetrahedral geometry at both C and N atoms and C–H and N–H bond distances of 0.95 Å. A final least-squares calculation in which the nonhydrogen atoms were varied anisotropically and the hydrogen atoms were not varied yielded $R_1 = 0.055$ and $R_2 = 0.057$. The decision to not vary the hydrogen atoms was forced upon us by the paucity of reliable data. The present refinement involved 1083 data and 171 variables, and isotropic refinement of the hydrogen atoms would have increased the number of variables to 251 and reduced the number of observations per variable to 4.31; this was deemed

Table I. Fractional Coordinates for Zn(L-met)₂ with Standard Deviations in Parentheses

Atom	x	y	z
Zn	0.0160 (1)	0.0	0.2672 (1)
S(1)	-0.3462 (2)	-0.2024 (9)	0.1192 (3)
S(2)	0.3839 (2)	-0.3099 (9)	0.3612 (3)
O(11)	-0.1099 (4)	0.2647 (16)	0.5509 (6)
O(21)	-0.0190 (4)	0.2488 (14)	0.4113 (6)
O(12)	0.1113 (4)	-0.2073 (18)	-0.0688 (6)
O(22)	0.0389 (4)	-0.2176 (16)	0.1003 (6)
N(1)	-0.0960 (5)	-0.1974 (19)	0.2748 (7)
N(2)	0.1021 (5)	0.2497 (18)	0.2071 (7)
C(11)	-0.0876 (6)	0.1812 (22)	0.4424 (9)
C(21)	-0.1508 (5)	-0.0189 (31)	0.3341 (9)
C(31)	-0.2159 (6)	-0.1535 (24)	0.4016 (10)
C(41)	-0.2813 (6)	-0.3378 (25)	0.2945 (11)
C(M1)	-0.4119 (8)	0.0314 (42)	0.1747 (16)
C(12)	0.0977 (7)	-0.1258 (23)	0.0461 (10)
C(22)	0.1559 (6)	0.0963 (22)	0.1329 (9)
C(32)	0.2374 (6)	-0.0164 (35)	0.2556 (9)
C(42)	0.2974 (7)	-0.1896 (29)	0.1993 (10)
C(M2)	0.4440 (8)	-0.5278 (40)	0.2784 (13)
H(N1)	-0.1301	-0.2676	0.1785
H(N1')	-0.0793	-0.3566	0.3394
H(21)	-0.1846	0.0751	0.2536
H(31)	-0.1838	-0.2585	0.4895
H(31')	-0.2508	-0.0313	0.4326
H(41)	-0.2465	-0.4891	0.2773
H(41')	-0.3211	-0.4146	0.3457
H(M1)	-0.4388	0.0053	0.2475
H(M1')	-0.3772	0.1706	0.2010
H(M1'')	-0.4621	0.0525	0.0883
H(N2)	0.0694	0.3699	0.1399
H(N2')	0.1412	0.3213	0.2923
H(22)	0.1754	0.1948	0.0652
H(32)	0.2733	0.1182	0.3081
H(32')	0.2174	-0.1230	0.3244
H(42)	0.2642	-0.3402	0.1414
H(42')	0.3237	-0.1019	0.1347
H(M2)	0.4273	-0.7154	0.2707
H(M2')	0.4368	-0.4872	0.1772
H(M2'')	0.5059	-0.5380	0.3321

statistically unfavorable. No extinction correction was deemed necessary, and none was applied.

In the final cycle of least-squares, the fact that no atomic parameter underwent a shift of more than 0.10 times its estimated standard deviation was taken as evidence that the refinement had converged. The final difference Fourier showed ten high peaks ranging from 0.48 to 1.47 e Å⁻³ cylindrically situated around the Zn atom. In view of the crystal quality and the approximate nature of the absorption correction, this residual electron density is not entirely unexpected. No other peak in the Fourier map was higher than 0.43 e Å⁻³. The positional and thermal parameters derived from the final cycle of least-squares are presented in Tables I and II.

A list of observed and calculated structure amplitudes is available.³⁵

Description of the Structure

The structure consists of sheets of [Zn(L-met)₂] units which lie roughly in the crystallographic b - c plane, the individual units being linked by long-range Zn–O contacts as shown in Figure 1. The geometry around each Zn is roughly octahedral with four short and two long bonds, a configuration similar to that found in six-coordinate copper complexes.^{36–38} The associated distances and angles are given in Tables III and IV. The base plane of the octahedron is formed by nitrogen and oxygen atoms, N(1), O(21), N(2), and O(22), from the two independent methionine moieties. The chelating atoms are arranged in the trans configuration and the bonded distances are in the range of Zn–O and Zn–N distances in other zinc–amino acid complexes.^{39–43} The axial sites are occupied by carboxyl oxygen atoms O(11)' and O(12)' from two other molecules, the Zn–O(11)' and Zn–O(12)' distances being 2.240 (6) and 2.729 (7) Å, respectively. These distances compare with long-range Zn–O(carboxyl) distances in Zn–(DL-histidine)₂,³⁹ Zn(L-glutamate),⁴² and Zn(L-serine)₂.⁴³

Table II. Thermal Parameters for $\text{Zn}(\text{L-met})_2$

Atom	β_{11}^a	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Zn	0.0054 (1)	0.0292 (6)	0.0151 (2)	-0.0063 (3)	0.0068 (1)	-0.0120 (4)
S(1)	0.0043 (2)	0.0524 (20)	0.0115 (4)	-0.0006 (5)	-0.0004 (2)	-0.0029 (8)
S(2)	0.0051 (2)	0.0655 (25)	0.0122 (4)	0.0087 (6)	-0.0004 (2)	-0.0000 (9)
O(11)	0.0037 (4)	0.0224 (37)	0.0063 (8)	-0.0005 (10)	0.0022 (4)	-0.0011 (16)
O(21)	0.0033 (3)	0.0129 (34)	0.0061 (8)	-0.0006 (9)	0.0029 (4)	-0.0005 (14)
O(12)	0.0053 (4)	0.0365 (43)	0.0060 (8)	0.0019 (12)	0.0038 (5)	-0.0041 (18)
O(22)	0.0033 (3)	0.0184 (34)	0.0056 (8)	0.0000 (10)	0.0014 (4)	-0.0016 (16)
N(1)	0.0024 (4)	0.0185 (42)	0.0063 (10)	-0.0014 (11)	0.0011 (5)	-0.0043 (18)
N(2)	0.0021 (4)	0.0186 (44)	0.0063 (9)	0.0003 (11)	0.0011 (5)	-0.0005 (18)
C(11)	0.0036 (5)	0.0129 (45)	0.0041 (11)	0.0010 (13)	0.0013 (6)	0.0017 (20)
C(21)	0.0027 (4)	0.0176 (46)	0.0054 (10)	-0.0033 (16)	0.0018 (6)	-0.0026 (25)
C(31)	0.0031 (5)	0.0287 (54)	0.0065 (12)	-0.0029 (15)	0.0012 (6)	0.0007 (23)
C(41)	0.0029 (5)	0.0291 (57)	0.0118 (15)	-0.0001 (15)	0.0011 (8)	0.0003 (26)
C(M1)	0.0043 (6)	0.0456 (86)	0.0293 (27)	-0.0004 (26)	-0.0010 (11)	-0.0063 (53)
C(12)	0.0029 (5)	0.0175 (47)	0.0075 (13)	0.0032 (14)	0.0014 (7)	0.0061 (23)
C(22)	0.0030 (5)	0.0197 (52)	0.0048 (11)	0.0001 (12)	0.0018 (6)	0.0011 (19)
C(32)	0.0031 (5)	0.0387 (61)	0.0082 (13)	0.0033 (20)	0.0013 (7)	-0.0048 (33)
C(42)	0.0032 (5)	0.0417 (65)	0.0097 (14)	0.0035 (17)	0.0011 (7)	0.0000 (29)
C(M2)	0.0062 (7)	0.0557 (89)	0.0162 (19)	0.0056 (27)	0.0024 (10)	0.0071 (44)

^a The form of the thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The assumed isotropic temperature factor for all hydrogen atoms is 7.0 \AA^2 .

Table III. Interatomic Distances (Å) in $\text{Zn}(\text{L-met})_2$

Zn-O(21)	2.059 (6)	C(31)-C(41)	1.53 (1)
Zn-O(22)	2.049 (6)	C(41)-S(1)	1.79 (1)
Zn-N(1)	2.052 (8)	S(1)-C(M1)	1.76 (2)
Zn-N(2)	2.064 (8)	C(12)-O(12)	1.24 (1)
Zn-O(11)''	2.240 (6)	C(12)-O(22)	1.28 (1)
Zn-O(12)'	2.729 (7)	C(12)-C(22)	1.53 (1)
C(11)-O(11)	1.25 (1)	C(22)-N(2)	1.48 (1)
C(11)-O(21)	1.25 (1)	C(22)-C(32)	1.55 (1)
C(11)-C(21)	1.57 (1)	C(32)-C(42)	1.51 (2)
C(21)-N(1)	1.48 (1)	C(42)-S(2)	1.81 (1)
C(21)-C(31)	1.53 (1)	S(2)-C(M2)	1.79 (2)

Table IV. Interatomic Angles (deg) in $\text{Zn}(\text{L-met})_2$

O(21)-Zn-N(1)	82.7 (3)	O(21)-C(11)-C(21)	116.5 (7)
N(1)-Zn-O(22)	96.6 (3)	C(11)-C(21)-N(1)	108.9 (7)
O(22)-Zn-N(2)	80.8 (3)	N(1)-C(21)-C(31)	115.0 (12)
N(2)-Zn-O(21)	97.5 (3)	C(11)-C(21)-C(31)	113.2 (7)
O(11)''-Zn-N(1)	94.5 (3)	C(21)-C(31)-C(41)	113.9 (7)
O(11)''-Zn-O(22)	93.8 (3)	C(31)-C(41)-S(1)	116.6 (8)
O(11)''-Zn-N(2)	102.1 (3)	C(41)-S(1)-C(M1)	101.9 (6)
O(11)''-Zn-O(21)	94.2 (2)	Zn-O(22)-C(12)	115.4 (7)
O(12)'-Zn-N1	80.7 (3)	Zn-N(2)-C(22)	108.7 (7)
O(12)'-Zn-O(22)	92.1 (2)	O(12)-C(12)-O(22)	124.6 (11)
O(12)'-Zn-N(2)	82.9 (3)	O(12)-C(12)-C(22)	118.8 (9)
O(12)'-Zn-O(21)	79.9 (2)	O(22)-C(12)-C(22)	116.5 (8)
O(21)-Zn-O(22)	172.0 (3)	C(12)-C(22)-N(2)	108.2 (7)
N(1)-Zn-N(2)	163.3 (3)	N(2)-C(22)-C(32)	107.8 (7)
O(11)''-Zn-O(12)'	172.7 (2)	C(12)-C(22)-C(32)	110.1 (10)
Zn-O(21)-C(11)	114.2 (6)	C(22)-C(32)-C(42)	114.8 (7)
Zn-N(1)-C(21)	108.4 (7)	C(32)-C(42)-S(2)	107.0 (7)
O(11)-C(11)-O(21)	125.1 (9)	C(42)-S(2)-C(M2)	101.8 (5)
O(11)-C(11)-C(21)	118.3 (8)		

Thus, each Zn is bound to four methionine moieties while each methionine anion is associated with two Zn atoms. The coordination about a single zinc atom is shown in Figure 2.

The octahedral geometry around zinc is not severely distorted, the $\text{O}(11)''\text{-Zn-O}(12)'$ angle being $172.7 (2)^\circ$ and X-Zn-Y angles ranging from $79.9 (2)$ to $102.1 (3)^\circ$ where X and Y are any two atoms which lie cis to each other. The chelate bites, the $\text{O}(21)\text{-Zn-N}(1)$ and $\text{O}(22)\text{-Zn-N}(2)$ angles, of $82.7 (3)$ and $80.8 (3)^\circ$, respectively, force the other "in-plane" angles to differ from 90 and 180° . The trans atoms N(1) and N(2) lie 0.08 \AA below the best least-squares plane through the four ligating atoms while O(21) and O(22) lie 0.08 \AA above it. The Zn atom sits 0.22 \AA above the plane toward O(11)'.

The two five-membered chelate rings do not have perfect δ or λ conformations. The ring containing Zn, O(21), C(11),

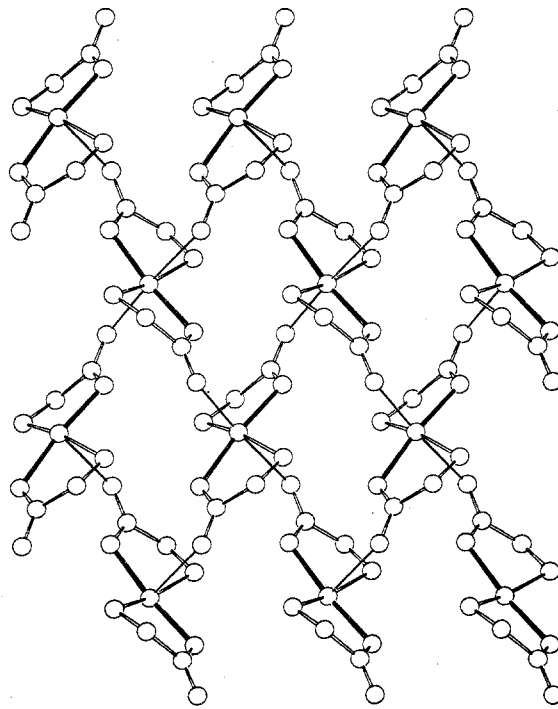


Figure 1. View of the polymeric nature of $\text{Zn}(\text{L-met})_2$ shown roughly in the b - c plane. The side-chain atoms C(31), C(41), C(M1), S(1), C(32), C(42), C(M2), and S(2) have been omitted for clarity.

C(21), and N(1) does exhibit a δ conformation, but C(21) is 0.42 \AA below the plane defined by O(21), Zn, and N(1) while C(11) is only 0.01 \AA above it. Thus it is more like an envelope with C(11), O(21), Zn, and N(1) in a plane and C(21) lying below it. The ring containing Zn, O(22), C(12), C(22), and N(2) almost adopts a λ conformation but C(12) and C(22) both lie above the plane defined by O(22), Zn, and N(2), with C(22) being much further away from the line. This ring seems to be in a conformation intermediate between an envelope and the classical λ . These conformational abnormalities are probably due to the partial double-bond character of the C(11)-O(21) and C(12)-O(22) bonds in the two rings.

Packing of the $\text{Zn}(\text{L-met})_2$ units is dominated by the two methionine ligands. In the solid-state structure of L-methionine,⁴⁴ there are two crystallographically independent methionine molecules which adopt different conformations, as is the case in $\text{Zn}(\text{L-met})_2$. The pertinent dihedral angles

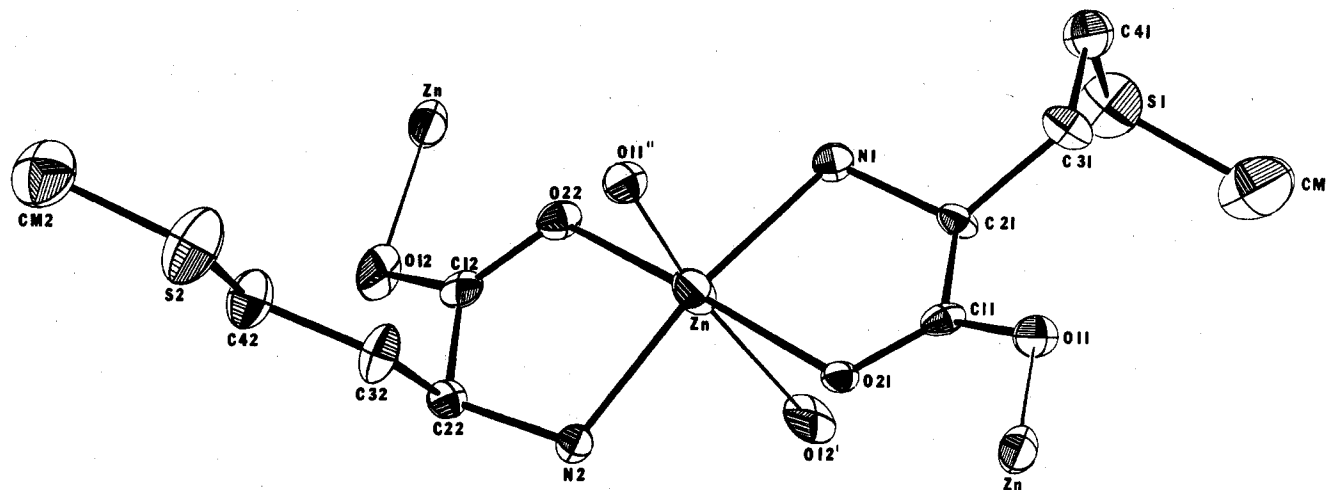
Figure 2. Coordination around one Zn center in $\text{Zn}(\text{L-met})_2$.

Table V

Dihedral Angles ^a (deg) in $\text{Zn}(\text{L-met})_2$ and L-methionine				
Angle	L-Methionine ^b		$\text{Zn}(\text{L-met})_2$ ^c	
	A	B	1	2
C(M)-S-C(4)-C(3)	179.7	73.6	-64.9	176.0
S-C(4)-C(3)-C(2)	174.2	73.6	-54.3	-177.3
C(4)-C(3)-C(2)-N	194.0	194.4	-57.0	177.3
C(4)-C(3)-C(2)-C(1)			176.8	59.4
C(3)-C(2)-C(1)-O(1)			-18.8	-92.6
C(3)-C(2)-C(1)-O(2)			162.5	86.2
N-C(2)-C(1)-O(2)			33.2	-31.4

State of Rotation

Axis	Type of rotn			
	L-met		Zn-met	
C(2)-C(3)	N ^d	N ^d	C(1) ^d	N ^d
C(3)-C(4)	Trans	Gauche	Gauche	Trans
C(4)-S	Trans	Gauche	Gauche	Trans

^a The dihedral angles presented for $\text{Zn}(\text{L-met})_2$ were calculated as positive when the far atom rotates anticlockwise relative to the near atom to be eclipsed. ^b Reference 43. ^c This work. ^d C(4) is trans to this atom.

and rotational states are given in Table V. The side-chain atoms in molecule A in L-methionine and ligand 2 in $\text{Zn}(\text{met})_2$ are extended in a nearly trans-planar conformation, while the side chains in molecule B and ligand 1 are severely folded. It has been suggested⁴³ that the two methionine moieties adopt different conformations in order to avoid short intermolecular S...C contacts. Indeed, there are no intermolecular contacts between sulfur and other atoms less than 3.5 Å in L-methionine or $\text{Zn}(\text{met})_2$, nor does S act as an acceptor in hydrogen-bond formation.

The hydrogen bonding in $\text{Zn}(\text{L-met})_2$ is much less extensive than in L-methionine. Many of the hydrogen bonds which link individual molecules into sheets in L-methionine are eliminated by long- and short-range coordination of the metal atom in $\text{Zn}(\text{L-met})_2$. Only one hydrogen atom on each nitrogen atom shows evidence of hydrogen bonding, the criterion used being that of Hamilton and Ibers.⁴⁵ The relevant distances and angles are given in Table VI. Atom H(N2) appears to participate in a bifurcated hydrogen bond, acting as a donor to the O(22) atoms on two different $\text{Zn}(\text{L-met})_2$ units. It is noteworthy that all hydrogen-bonding interactions take place within one layer and that all oxygen acceptor atoms are also tightly bound to zinc.

The structure of $\text{Zn}(\text{L-met})_2$ is similar to that of $\text{Cu}(\text{DL-met})_2$ ²² and $\text{Cd}(\text{L-met})_2$.²⁷ In all three complexes the methionine is deprotonated and is present as the monoanion. The

Table VI. Hydrogen Bonding

A-B...C	A...C, Å	B...C, Å	A-B-C, deg
N(1)-H(N1')...O(21) ^{I a}	2.97	2.44	112.07
N(2)-H(N2)...O(22) ^{II}	2.97	2.17	144.77
N(2)-H(N2)...O(22) ^{III}	3.07	2.42	127.22

^a Roman superscripts refer to atoms in the following positions: (I) $-x, y - 1/2, -z + 1$; (II) $x, y + 1, z$; (III) $-x, y + 1/2, -z$.

main differences in the complexes occur in the long-range M-O distances. In $\text{Cu}(\text{DL-met})_2$ copper lies on an inversion center which constrains the two axial Cu-O bonds to be identical; there are no such constraints on the Cd and Zn complexes. The axial Cd-O distances in $\text{Cd}(\text{L-met})_2$ differ by only 0.019 Å, while those in $\text{Zn}(\text{L-met})_2$ differ by 0.489 Å. The single-bond metallic radius of Cu is 0.075 Å less than that of Zn,⁴⁶ while the Cu-O(2) distance of 2.713 Å is only 0.016 Å shorter than the Zn-O(12)' distance of 2.729 Å. The Cd-O distances of 2.445 and 2.524 Å are similar to the Zn-O(11)' distances of 2.240 Å when the 0.164-Å difference in single-bond metallic radius⁴⁶ is taken into account. Thus, the long-range interactions in $\text{Zn}(\text{L-met})_2$ are stronger than those in $\text{Cu}(\text{DL-met})_2$, while the axial Cd-O interactions are intermediate in strength between the two long-range Zn-O interactions.

The mode of methionine binding in the platinum,¹⁸ palladium,²³ and mercury complexes²⁶ is different from that in $\text{Zn}(\text{L-met})_2$, the ligand being singly protonated in the first two and being a neutral zwitterion in the third. Since the charge on methionine varies, the difference in the mode of binding cannot be totally attributed to the change in metal ions, and comparisons between complexes are difficult.

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Supplementary Material Available: Listing of observed and calculated structure amplitudes (7 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of Tetrakis(bis(methylamino)carbene)platinum(II) Hexafluorophosphate, $[\text{Pt}(\text{C}(\text{NHMe})_2)_4](\text{PF}_6)_2$

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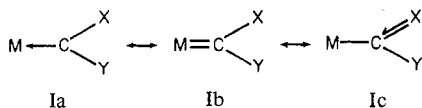
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The crystal and molecular structure of tetrakis(bis(methylamino)carbene)platinum(II) hexafluorophosphate, $[\text{Pt}(\text{C}(\text{NHMe})_2)_4](\text{PF}_6)_2$, has been determined from three-dimensional x-ray data collected by counter techniques. The compound crystallizes in the monoclinic space group $P2_1/c$ (C_{2h}^2). There are two formula units within a unit cell of dimensions $a = 8.480$ (4) Å, $b = 9.120$ (4) Å, $c = 17.530$ (9) Å, and $\beta = 96.37$ (1)°. The observed and calculated densities are 1.90 (1) and 1.906 g/cm³, respectively. The cationic complex has a crystallographically imposed inversion center and nearly ideal square-planar coordination. The average Pt–C bond length is 2.0466 (6) Å, corresponding to a Pt–C(sp²) single bond. The carbene ligands adopt the amphi configuration in which there exist two stereochemically distinct methyl groups, and the planes of the carbene ligands form angles of 81.8 and 77.1° with the coordination plane of the Pt(II) ion. The orientation of the carbene ligands is such that the complex possesses nearly C_{2h} symmetry. The equivalent C(carbene)–N bonds have an average length of 1.310 (3) Å indicative of significant double-bond character. The structural results thus confirm the importance of $p_\pi \rightarrow p_\pi$ dative bonding in stabilizing amino carbene ligands, and support the notion of hindered rotation about the carbene C–N bond proposed previously based on NMR studies.

Introduction

Since the initial report in 1964,² the field of transition metal–carbene complexes has become a major area of investigation. Several recent reviews document and summarize the developments in this area.^{3–5} The majority of carbene complexes reported to date contain at least one heteroatom (N, O, S) bonded to the carbene carbon which plays an important role in stabilizing the carbene moiety. This can be envisioned in terms of the resonance structures for the metal–carbene unit. Structure Ia corresponds to carbene coordination



while structures Ib and Ic depict stabilizing interactions through metal $d_\pi \rightarrow p_\pi$ back-bonding and dative π bonding between the heteroatom and the carbene carbon, respectively. X-ray structural results have shown the im-

portance of the latter interaction, which involves a filled p orbital of the heteroatom and the vacant p orbital of the sp²-hybridized carbene, through the observation of partial double-bond character in the carbene carbon–heteroatom bond length.^{3–5} NMR results have also demonstrated hindered rotation about this bond due to the π interaction.^{3–5} The existence of stabilization via structure Ic seriously questions the correctness of viewing these ligands as true carbenes, and alternate suggestions for naming and describing them have been presented by others.^{4–7}

A principal way in which coordinated carbenes containing a heteroatom have been synthesized involves nucleophilic attack on a coordinated carbonyl or isocyanide, resulting in the formation of alkoxy and amino carbenes, respectively. Usually in reactions of this type, one or at most two coordinated ligands are converted into carbene type ligands. However, in 1972 Miller and Balch reported the addition of methylamine to $\text{M}(\text{CNMe})_4^{2+}$ ($\text{M} = \text{Pt}, \text{Pd}$) to yield the intriguing percarbene complexes of $\text{M}(\text{C}(\text{NHMe})_2)_4^{2+}$ stoi-