

This structure is an example of the unusual situation of a nearly centrosymmetric molecule which crystallizes in a non-centrosymmetric space group. Another molecule which has a center of symmetry, but crystallizes in a non-centrosymmetric space group, is β -1:2:5:6-dibenzanthracene (Robertson & White, 1956). Biphenylene (Waser & Lu, 1944; Fawcett & Trotter, 1966) crystallizes in space group $P2_1/a$ with six molecules per unit cell. Two of the molecular centers fall on centers of symmetry, but the other four molecules are in general positions despite their apparent center of symmetry.

The equations of the least-squares planes through the benzene and cyclobutane rings and the deviations of the individual atoms from their respective planes are given in Table 6. The second benzene ring shows a slight degree of non-planarity.

A stereoscopic view down the b axis showing the packing of the molecules is given in Fig. 6. There are no short contacts between molecules. The shortest heavy-atom-to-hydrogen intermolecular distance is 2.73 Å between H(24) of the base molecule and C(15) of the molecule in equivalent position $x-\frac{1}{2}, -y+1, z$. The shortest hydrogen-to-hydrogen intermolecular

distance is 2.45 Å between H(32) of the base molecule and H(28) of the molecule in the equivalent position $x+\frac{1}{2}, -y, z$.

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The Crystal Structure of Bis(L-serinato)zinc*

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The crystal structure of bis(L-serinato)zinc, $ZnC_6H_{12}O_6N_2$, has been determined and refined by three-dimensional least-squares techniques. The crystals are monoclinic, space group $P2_1$, with $a=9.542$, $b=8.818$, $c=5.666$ Å and $\beta=96.7^\circ$. The final R value for 950 reflections is 0.036; the standard deviations are about 0.006 Å for the C, N and O atom positions. The compound is not isostructural with either the Ni or Cu complex of L-serine. The zinc coordination is intermediate between a square pyramid and a trigonal bipyramid with the first one being slightly favored. The two serine molecules have different conformations for the hydroxyl group; one serine molecule having the unusual *anti-gauche* conformation.

Introduction

The structure of the Zn chelate of L-serine was determined as one of a series of L-serine chelates (van der Helm & Franks, 1969; Van der Helm & Hossain, 1969) to obtain information about the relative influence of transition metal ions on the configuration of an amino acid. No two of the three complexes of serine thus far

determined are isomorphous. Zinc was chosen as one of the transition metal ions because its role in biological reactions has long been known.

Experimental

The compound bis(L-serinato)zinc was prepared by reacting two moles of L-serine with one mole each of zinc sulfate and barium hydroxide in a minimal amount of water. The barium sulfate produced was removed by centrifugation. The solution produced, which tended to become supersaturated, was then diluted about fifty times with absolute ethanol in order to ob-

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tain crystals suitable for use as seed crystals. When the seed crystals were obtained, a solution of the complex was equilibrated with a solution of diethyl ether and absolute ethanol and the seed crystals were used to grow crystals suitable for X-ray analysis. After two or three days, colorless hexagonally prismatic crystals of the compound appeared. The base plane is the 001 plane.

X-ray investigation of the crystals showed them to be monoclinic and the space group to be $P2_1$ (systematic absences: $0k0=2n+1$). Due to the presence of L-serine in the complex, the space group $P2_1/m$ could be excluded. The 2θ values of 29 reflections, measured at 22°C, were used to determine cell dimensions: $a=9.542 \pm 0.009$, $b=8.818 \pm 0.003$, $c=5.666 \pm 0.003$ Å and $\beta=96.72 \pm 0.06^\circ$ ($\lambda(\text{Cu } K\alpha)=1.5418$ Å). It should be noted that although the cell dimensions are within 4% of those of the copper complex with serine, these compounds are not isomorphous as were the copper and zinc complexes of glutamic acid (Gramaccioli & Marsh, 1966 and Gramaccioli, 1966). The F.W. for Zn(L-serine)_2 is 275.38 yielding a ρ_c of 1.93 g.cm⁻³. A density of 1.91 g.cm⁻³ was measured by the flotation method, thus there are two formula units per unit cell.

The integrated intensities were taken on a General Electric XRD-5 diffraction unit using the θ - 2θ scan method and nickel-filtered Cu $K\alpha$ radiation. The diffraction unit was equipped with a SPG Single Crystal Orienter, a scintillation counter, and pulse height analyzer.

The data crystal had the approximate dimensions of $0.24 \times 0.16 \times 0.16$ mm. All reflections with a 2θ below 140° were measured. Of the 950 reflections within this 2θ -limit, 13 did not show a peak on the recorder while scanning through their diffraction position. The intensities recorded for these 13 unobserved reflections were $\frac{1}{5}$ of the background intensity measured at the location of the reflection. Lorentz, polarization and absorption corrections ($\mu=39.6$ cm⁻¹) were applied to the data.

Structure determination

The location of the zinc atom was obtained from a sharpened Patterson synthesis. Further interpretation yielded two sets of locations for all carbon, nitrogen, and oxygen atoms. The two sets are related by the pseudo-mirror plane given by the Patterson function. One set showed the L-configuration for both the serine molecules and was taken as the trial structure.

Table 1. Positional parameters of hydrogen atoms

An isotropic temperature factor of 3.5 Å² was assigned to the hydrogen atoms.

	x	y	z
H[C(2A)]	-0.050	0.350	0.190
H(1)[N(A)]	0.200	0.260	0.240
H(2)[N(A)]	0.070	0.145	0.030
H(1)[C(3A)]	-0.120	0.180	-0.020
H(2)[C(3A)]	-0.100	0.060	0.210
H[O(3A)]	-0.280	0.320	0.037
H[C(2B)]	0.500	0.170	0.430
H(1)[N(B)]	0.390	0.165	0.710
H(2)[N(B)]	0.350	-0.010	0.770
H(1)[C(3B)]	0.650	0.070	0.810
H(2)[C(3B)]	0.710	0.010	0.530
H[O(3B)]	0.570	-0.140	0.910

The initial structure factor calculation had an $R = (\sum ||kF_o| - |F_c|| / |kF_o|)$ of 0.13. The structure was refined by block-diagonal least-squares computations using anisotropic temperature factors. At an R value of 0.06 the approximate positions of the hydrogen atoms were obtained from a difference Fourier synthesis. At this time all the observed amplitudes were corrected for anomalous dispersion (Patterson, 1963). The parameters of the zinc, carbon, nitrogen, and oxygen atoms were further refined by least squares until the parameter shifts were less than $\frac{1}{5}$ the calculated standard deviations. At this point another difference Fourier synthesis was calculated based on a structure

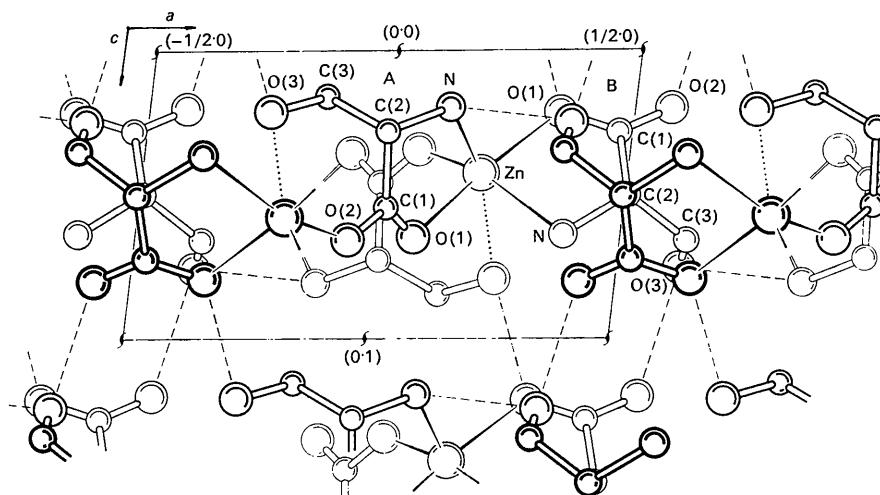


Fig. 1. A projection of the structure down the b axis.

Table 2. Final parameters

x , y and z are fractional coordinates. The temperature factor is expressed in the form:

$$\exp[-(b_{11}x^2 + b_{22}y^2 + b_{33}z^2 + b_{23}kl + b_{13}hl + b_{12}hk)]$$

The e.s.d.'s for the last digit are given in parentheses.

	x	y	z	b_{11}	b_{22}	b_{33}	b_{23}	b_{13}	b_{12}
Zn	0.19408 (6)	-0.0005 (2)	0.4234 (1)	0.0046 (1)	0.0068 (1)	0.0209 (2)	0.0100 (4)	0.0033 (2)	0.0012 (3)
O(1A)	0.0726 (4)	0.1288 (5)	0.6501 (6)	0.0074 (5)	0.0070 (6)	0.0117 (12)	0.0011 (14)	0.0008 (12)	0.0044 (9)
O(2A)	0.0630 (4)	0.3308 (5)	0.6578 (7)	0.0082 (5)	0.0079 (6)	0.0133 (13)	0.0025 (15)	0.0043 (13)	0.0046 (9)
C(1A)	0.0047 (8)	0.2367 (9)	0.5503 (9)	0.0046 (5)	0.0050 (8)	0.0120 (26)	0.0041 (25)	0.0017 (23)	0.0011 (11)
C(2A)	0.0022 (6)	0.2505 (7)	0.2749 (9)	0.0046 (6)	0.0067 (8)	0.0110 (18)	0.0012 (20)	0.0035 (17)	0.0010 (12)
N(A)	0.1197 (5)	0.1707 (6)	0.1936 (8)	0.0039 (5)	0.0094 (7)	0.0108 (14)	0.0036 (18)	0.0029 (13)	0.0021 (10)
C(3A)	0.1389 (6)	0.1716 (8)	0.1632 (10)	0.0046 (6)	0.0123 (10)	0.0143 (19)	0.0021 (25)	0.0027 (7)	0.0034 (14)
O(3A)	0.2574 (5)	0.2612 (7)	0.2033 (8)	0.0085 (6)	0.0242 (10)	0.0234 (16)	0.0199 (23)	0.0084 (15)	0.0170 (14)
O(1B)	0.3432 (4)	0.0872 (5)	0.2108 (8)	0.0062 (5)	0.0115 (7)	0.0244 (16)	0.0175 (18)	0.0023 (14)	0.0021 (10)
O(2B)	0.5736 (4)	0.1164 (6)	0.1957 (7)	0.0072 (5)	0.0136 (8)	0.0190 (14)	0.0011 (18)	0.0107 (14)	0.0046 (10)
C(1B)	0.4719 (6)	0.0628 (6)	0.2869 (10)	0.0062 (6)	0.0056 (7)	0.0139 (18)	0.0037 (19)	0.0038 (18)	0.0014 (11)
C(2B)	0.5018 (6)	0.0456 (6)	0.4954 (11)	0.0044 (5)	0.0063 (9)	0.0150 (16)	0.0024 (18)	0.0001 (15)	0.0005 (10)
N(B)	0.3782 (5)	0.0587 (5)	0.6285 (8)	0.0061 (6)	0.0081 (7)	0.0152 (16)	0.0011 (17)	0.0028 (15)	0.0016 (10)
C(3B)	0.6382 (5)	0.0098 (13)	0.6538 (10)	0.0060 (6)	0.0083 (9)	0.0225 (18)	0.0045 (36)	0.0023 (16)	0.0042 (22)
O(3B)	0.6293 (5)	0.1403 (7)	0.7538 (8)	0.0080 (6)	0.0092 (10)	0.0185 (16)	0.0039 (23)	0.0034 (15)	0.0070 (14)

factor calculation which did not include the hydrogen atom contributions. All hydrogen atom positions were confirmed and are given in Table 1. The maximum spurious peaks in the difference Fourier synthesis were -0.4 and $+0.3 \text{ e.}\text{\AA}^{-3}$. In a final Fourier synthesis the peak height for the Zn atom was $78 \text{ e.}\text{\AA}^{-3}$ while those for the hydrogen atoms varied between 0.6 and $1.4 \text{ e.}\text{\AA}^{-3}$. The final parameters for all non-hydrogen atoms are listed in Table 2. Observed and calculated structure factors are given in Table 3. The final R value for all 950 reflections is 0.036 .

The quantity minimized in the least-squares calculations was $\sum w(|kF_o| - |F_c|)^2$. The final weighting was $\sqrt{w} = |kF_o|/P$ if $|kF_o| \leq P$ and $\sqrt{w} = P/|kF_o|$ if $P < |kF_o|$, with $P = 15.0$ electrons. A logical routine, which determines the reflections to be included in the least-squares computations, was used (Van der Helm & Nicholas, 1970). The structure-factor least-squares and Fourier programs used were written by Ahmed (1966). The atomic scattering factors used for Zn^{2+} , O, N and C as well as the dispersive corrections for Zn were from *International Tables for X-ray Crystallography* (1962). The scattering factors for hydrogen atoms used were those of Stewart, Davidson & Simpson (1965).

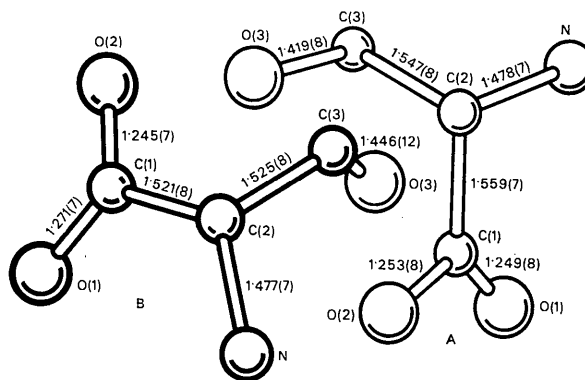


Fig. 2. Bond distances. The standard deviations for the last digit are given in parentheses.

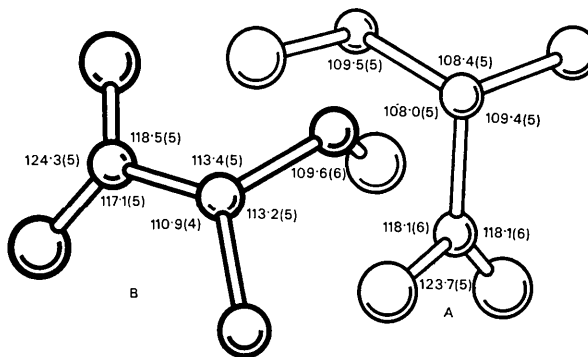


Fig. 3. Bond angles. The standard deviations for the last digit are given in parentheses.

Table 3. Observed and calculated structure factors

The listing shows $|10F_O|$ and $|10F_C|$. The reflections for which the intensity could not be distinguished from the background are indicated by a star.

K	FO	FC	ALPHA	K	FO	FC	ALPHA	K	FO	FC	ALPHA	K	FO	FC	ALPHA	K	FO	FC	ALPHA	K	FO	FC	ALPHA																				
0	170	178	65.20	1	179	183	65.20	2	187	192	65.20	3	195	200	65.20	4	203	208	65.20	5	211	216	65.20	6	219	224	65.20	7	227	232	65.20	8	235	240	65.20	9	243	248	65.20	10	251	256	65.20

Table 3 (cont.)

K	FD	FC	ALPHA	K	FD	FC	ALPHA	K	FD	FC	ALPHA	K	FD	FC	ALPHA	K	FD	FC	ALPHA	K	FD	FC	ALPHA				
0	266	263	180.00	0	100	99	0.0	0	202	206	0.0	0	90	94	180.00	0	131	128	0.0	1	88	83	266.53	3	169	180	263.21
1	119	113	93.87	1	116	113	93.87	1	105	107	94.24	1	105	107	94.24	1	120	122	109.28	1	88	83	266.53	3	169	180	263.21
2	176	180	136.48	2	164	165	276.65	2	161	167	340.84	2	161	167	340.84	2	75	77	365.01	11	11	11	-2	0	32	24	180.00
3	36	30	109.04	3	60	58	7.06	3	109	117	86.74	3	72	76	206.36	11	11	11	-2	0	29	23	180.00				
4	152	163	181.92	4	119	121	271.31	4	147	147	391.77	4	104	111	293.96	11	11	11	-2	1	85	90	271.90				
5	38	39	295.62					5	92	92	68.28	5	90	92	181.23	11	11	11	-2	2	33	31	180.00				

Description and discussion of the structure

A projection of the structure down the *b* axis is shown in Fig. 1. The bond lengths and bond angles in the two L-serine molecules are indicated in Figs. 2 and 3. In bis(L-serinato)copper(II) (Van der Helm & Franks, 1969) the dimensions of the two serine molecules were very similar. In the present structure this is not the case. This can be seen, for instance, in the difference in the C(1)–C(2) bond lengths and the significant difference in the C(1)–C(2)–C(3) bond angles. On the other hand the differences in the carboxylate groups are caused by the fact that both oxygen atoms of serine A, but only C(1)–O(1) of serine B, form complex bonds with zinc ions.

Both serine molecules are twisted about the C–C α [C(1)–C(2)] bond. The rotation is about +20° for serine A and –20° for serine B (Table 4). This rotation is of a similar magnitude to that observed in the nickel(II) chelate of L-serine (Van der Helm & Hossain, 1969), and about 2–3 times as large as those found in the copper(II) chelate. The conformation around the C α –C β [C(2)–C(3)] bond is different for the two serines. In D,L-serine (Shoemaker, Barieau, Donohue & Lu, 1953) the *gauche-gauche* conformation is observed for the N and carboxylate groups respectively with respect to the OH group. This same conformation is present in both serines in the copper(II) chelate of L-serine and is also observed in serine B of the present structure (Table 4). The *gauche-anti* conformation is observed in the nickel(II) chelate of L-serine, in which the conformational angle C(1)–C(2)–C(3)–O(3) is thus approximately 180°. Serine A in the present structure has the *anti-gauche* conformation which has not been observed previously; the N–C(2)–C(3)–O(3) angle is approximately 180° (Table 4).

Table 5. Least-squares planes

The equations of the planes are expressed in the form:

$$Ax + By + Cz = D$$

where *x*, *y* and *z* are fractional coordinates and *D* is the distance from the origin in Å. The method of Schomaker, Waser, Marsh & Bergman (1959) was used to calculate the least-squares planes.

Plane	A	B	C	D
1 O(1A), O(2A), C(1A), C(2A)	7.668	5.145	0.135	1.313
2 O(1B), O(2B), C(1B), C(2B)	0.636	6.859	–3.560	–1.136
3 O(1A), O(2A α), O(1B), N(B)	1.142	–6.173	3.882	2.129

A(1)		A(2)		A(3)	
O(1A)	–0.006 Å	O(1B)	0.006 Å	O(1A)	–0.317 Å
O(2A)	–0.006	O(2B)	0.006	O(2A α)	0.316
C(1A)	0.015	C(1B)	–0.016	O(1B)	–0.380
C(2A)	–0.004	C(2B)	0.005	N(B)	0.381
N(A)	0.509	N(B)	–0.458	Zn	–0.260
Zn	0.230	Zn	–0.251	N(A)	–2.294

Table 4. Configurational angles

	Serine A	Serine B
O(1) C(1) C(2) N	–23.3°	21.4°
O(2) C(1) C(2) N	–200.4	198.4
C(1) C(2) C(3) O(3)	71.9	–61.1
N C(2) C(3) O(3)	–169.7	66.4

The zinc ion is coordinated by the nitrogen and carboxylic oxygen atom [O(1)] of each serine molecule forming two five-membered chelate rings. The chelate rings are in the envelope conformation, *i.e.* the Zn and N atoms are displaced toward the same side from the least-squares planes calculated through the carboxyl groups (planes 1 and 2, Table 5). The zinc ion forms a fifth bond with O(2A) of a symmetry related serine molecule. The five bonds are of similar strength (Fig. 4), the two Zn–O(1) bonds having the longest distances. There is a sixth atom in the coordination sphere, O(3A), but the distance to the Zn ion (2.99 Å) indicates a negligible bond order. It shows, however, that the zinc ion can accommodate the oxygen atom in that location.

There are four significant differences between the metal surroundings in the Cu^{II} and Zn chelates of L-serine. If the Zn coordination, for the moment, is considered to be a square pyramid, with N(1B), O(1B), O(1A) and O(2A α) as the basal plane, the following differences can be pointed out: (1) The N(1) and O(1) atoms forming the two chelate rings occupy three points in the basal plane and the top of the pyramid. In the Cu chelate these atoms occupy the four points in the basal plane. (2) A least-squares plane calculated through the four atoms in the basal plane (plane 3, Table 5) show this plane to be tetrahedrally distorted. This distortion is about three times larger than in the Cu chelate. (3) The five bonds are of similar strength

Table 6. Bond angles in zinc surrounding

	Ideal square-pyramid	Observed	Ideal trigonal bipyramid
N(B) Zn O(2Aa)	160°	143.4°	120°
N(B) Zn O(1A)	88.4	90.7	90
N(B) Zn O(1B)	88.4	80.0	90
N(B) Zn N(A)	100	112.2	120
O(1A) Zn N(A)	100	79.6	90
O(1A) Zn O(2Aa)	88.4	99.7	90
O(1A) Zn O(1B)	160	167.7	180
N(A) Zn O(2Aa)	100	104.1	120
N(A) Zn O(1B)	100	96.3	90
O(1B) Zn O(2Aa)	88.4	92.6	90

The standard deviation of the observed bond angles is between 0.2 and 0.3°. The average deviations of the observed angles from ideal square-pyramid and trigonal bipyramid values are 9.1 and 10.9° respectively.

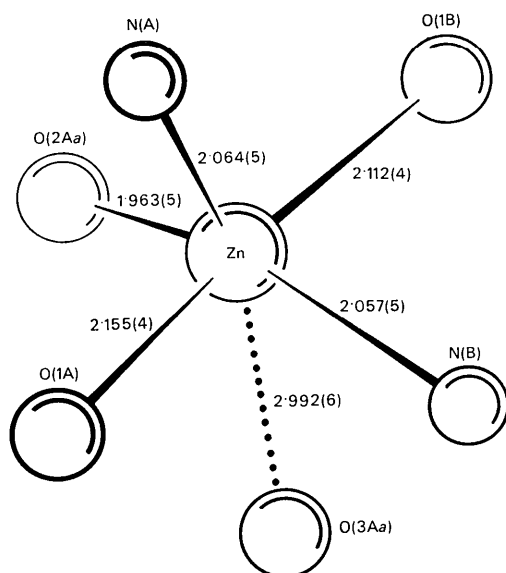


Fig. 4. Bond distances involving the zinc ion. The standard deviations for the last digit are given in parantheses.

in the present structure while in the Cu chelate one bond (2.36 Å) is significantly longer than the other four. (4) The space below the base of the pyramid is occupied by a hydroxyl oxygen atom, [O(3A)], where in the Cu compound this space is unoccupied. These differences together with the new conformation of serine A, mentioned before, make the similarity of the cell dimensions of the two compounds quite remarkable. These cell dimensions are $a = 9.54$ (9.92), $b = 8.82$ (8.41), $c = 5.67$ (5.65) Å and $\beta = 96.7$ (90.6)° (those for the Cu chelate are given in parentheses). The probable explanation for the similarity is thought to be the fact that an infinite column around the twofold screw axis is formed, in both compounds, by serines A, each of which is complexed to two metal ions.

Although it is possible to view the Zn surrounding as a square pyramid, it is also feasible to recognize it as a trigonal bipyramid with N(B), N(A) and O(2Aa) as the trigonal plane, and O(1A)–O(1B) as the axis. A comparison of the observed bond angles in the Zn surrounding with those of the 'ideal' square pyramid and trigonal bipyramid, suggested by Gillespie (1963), is given in Table 6. The interpretation as a square pyramid seems to be slightly favored. It is interesting to note, however, that theoretical calculations (Craig, Maccoll, Nyholm, Orgel & Sutton, 1954) predict the axial bonds in a trigonal bipyramid to be slightly longer (7–9%) as is observed in the present structure: the Zn–O(1) distances are elongated compared with the other three complex bonds to the zinc ion. On comparing the Cu^{II} and Zn chelates of glutamic acid (Gramaccioli & Marsh, 1966, Gramaccioli, 1966), L-serine and glycylglycylglycine (ggg) (Freeman, Robinson & Schoone, 1964; van der Helm & Nicholas, 1970), one has isomorphous structures for glutamic acid with square-pyramidal metal surroundings. For Cu^{II} this surrounding remains essentially the same going *via* L-serine to ggg, but for Zn it slowly changes to a trigonal bipyramid in this series. These changes

Table 7. Intermolecular distances

Hydrogen bonding					
Donor (X)	Acceptor (Y)	X–H...Y	X...Y		
O(3A)	O(1Bb)	170°	2.741 Å		
O(3B)	O(2Bc)	148	2.628		
N(A)	O(3Bd)	158	2.904		
N(B)	O(2Bd)	168	3.051		
N(B)	O(3Aa)	135	3.062		
N(A)	O(1Ae)	150	3.081		
Van der Waals contacts less than 3.5 Å					
C(3A)	O(1Bb)	3.442 Å	O(2A)	C(3Ac)	3.344
N(B)	O(3Bd)	3.422	C(3B)	O(2Bc)	3.390
C(2B)	O(3Bd)	3.288	O(1A)	C(2Aa)	3.439
O(1A)	C(2Aa)	3.439	C(2B)	O(3Bd)	3.288

The small letter in parentheses indicates that one of the following operations has to be applied to the coordinates given in Table 2.

<i>a</i>	– <i>x</i>	$y - \frac{1}{2}$	– <i>z</i> + 1
<i>b</i>	– <i>x</i>	$y + \frac{1}{2}$	– <i>z</i>
<i>c</i>	<i>x</i>	<i>y</i>	<i>z</i> + 1
<i>d</i>	– <i>x</i> + 1	$y + \frac{1}{2}$	– <i>z</i> + 1
<i>e</i>	<i>x</i>	<i>y</i>	<i>z</i> – 1

in behavior are probably related to the distinctly different biological functions of copper and zinc. Other bond angles involving zinc are Zn-N(A)-C(2A): 112.1, Zn-N(B)-C(2B): 111.9, Zn-O(1A)-C(1A): 114.8 and Zn-O(1B)-C(1B): 115.7°.

The hydrogen atoms were located from a difference Fourier synthesis, but their locations were not further refined. The covalent bond distances involving hydrogen vary between 1.02 and 1.16 Å.

The structure contains six hydrogen atoms which can form hydrogen bonds. All six seem to be involved in this type of bonding (Table 7), although only the first three seem to form strong hydrogen bonds. These three are indicated in Fig. 1 by dashed lines. All other intermolecular distances below 3.5 Å are also given in Table 7. The only atom showing considerable anisotropy is O(3A) with a value of 9.35 Å² for the temperature factor along the major axis.

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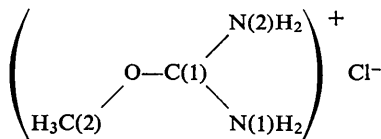
The Crystal and Molecular Structure of *O*-Methylisourea Hydrochloride

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The crystal structure of *O*-methylisourea hydrochloride



has been determined from a single-crystal X-ray study by photographic methods. The space group is $P2_12_12_1$, $a=9.43$ (2), $b=11.16$ (2), $c=5.01$ (1) Å, $Z=4$, $R=0.07$ for 522 observed reflections. Within the cation, bond distances are C(2)-O=1.44 (1), O-C(1)=1.33 (1), C(1)-N(1)=1.29 (1), C(1)-N(2)=1.32 (1) Å; bond angles are C(1)-O-C(2)=117 (1), N(1)-C(1)-O=123 (1), N(2)-C(1)-O=113 (1), N(1)-C(1)-N(2)=124 (1)°; and the angle between planes C(1)-O-C(2) and N(1)-C(1)-N(2)=4 (1)°. The structure is in general agreement with valence theory expectations of multiple bonds between C(1) and the atoms attached to it. The H atoms were located in difference syntheses and refined by least-squares. Each H atom bonded to N is linked in an approximately linear N-H...Cl hydrogen bond, with N...Cl distances of 3.16 (1), 3.23 (1), 3.25 (1) and 3.39 (1) Å.

The molecular structure of the *O*-methylisourea cation has been described (Edsall, 1943) as involving resonance among the bond arrangements

