# The Crystal Structure of Bis(L-serinato)copper(II)*

By Dick van der Helm and William A. Franks

*Chemistry Department, University of Oklahoma, Norman, Oklahoma 73069, U.S.A.*

The crystal structure of bis(L-serinato)copper(II), $CuC_6H_{12}O_6N_2$, has been determined and refined by three-dimensional least-squares techniques. The crystals are monoclinic, space group $P2_1$, with $a = 9.924$, $b = 8.413$, $c = 5.651$ Å and $\beta = 90.6°$. The final $R$ value for 946 reflections is 0.040; the standard deviations are about 0.006 Å for the light-atom positions. The compound is not isostructural with either the Ni or the Zn complex of L-serine. The copper surroundings are a square pyramid. Both serine molecules have the same configuration for the hydroxyl group, being the one found in DL-serine. The only influence of chelation of the serine molecules seems to be a small rotation of the amino group out of the plane of the acid group. All active protons are used for hydrogen bonding.

## Introduction

The structure of the $Cu^{II}$ chelate of L-serine was determined as one of a series of L-serine chelates to obtain information about the relative influence of transition metal ions on the configuration of an amino acid. None of the $Cu^{II}$, $Zn^{II}$ or $Ni^{II}$ complexes of L-serine are isomorphous. Another point of interest was the $Cu^{II}$ co-ordination, in view of the multitude of different $Cu^{II}$ surroundings which have been reported in the literature.

## Experimental

The compound bis(L-serinato) copper(II) was prepared by reacting L-serine, copper sulfate and barium hydroxide in the molar proportions of 2:1:1. Barium sulfate was removed by filtration. The resulting solution was about 0.05 $M$ in concentration of the complex. Crystals of the complex were obtained by diluting the solution 100 times with absolute ethanol. Blue crystalline rectangular plates appeared on standing for two or three days at room temperature. The plate face is the (001) plane while the crystals are elongated along the $b$ axis. Extinctions, using polarized light, of a crystal lying on its plate face were not sharp.

The preliminary X-ray investigation showed it to be unnecessary to recrystallize the original crop of crystals. The crystals are monoclinic and belong to the space group $P2_1$ (systematic absences: $0k0$, $k = 2n + 1$). The space group $P2_1/m$ is excluded because the compound contains L-serine. The $2\theta$-values of 26 reflections, measured at 22°C, were used in a least-squares calculation to determine the cell dimensions, which were calculated to be $a = 9.924 \pm 0.003$ Å, $b = 8.413 \pm 0.002$ Å, $c = 5.651 \pm 0.001$ Å and $\beta = 90.6° \pm 0.1°$. The F.W. for Cu(L-serine)$_2$ is 271.72 yielding $\varrho_c = 1.91$ g.cm$^3$ while $\varrho_o$ is 1.90 g.cm$^3$ measured by the flotation method. There are two formula units in the unit cell.

The crystals showed a rather large mosaic spread (1°). This observation, together with the fact that the monoclinic angle is to close to 90°, made it necessary to investigate the possibility of twinning. Four different crystals were mounted. The intensities of nine $h0l$ and corresponding $h0\bar{l}$ reflections were measured for each crystal. From the measurements the conclusion could be drawn that the twinning was necessarily less than 5% and therefore most likely not existent at all. No indication of twinning was observed in the subsequent structure investigation.

A crystal cut to dimensions $0.50 \times 0.17 \times 0.09$ mm was used as the data crystal. The integrated intensities were taken on a G.E.-X.R.D.-5 diffraction unit by the $\theta$–$2\theta$ scan method with Ni-filtered Cu $K\alpha$ radiation. The diffraction unit was equipped with an SPG Single Crystal Orienter, a scintillation counter and pulse height analyzer. All reflections with a $2\theta$-value below 140° were measured. Of the 946 reflections within this $2\theta$-limit, 10 were below the threshhold of observation. Lorentz, polarization and absorption corrections ($\mu = 36.43$ cm$^{-1}$) were applied to the data.

## Structure determination

The location of the copper 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 a pseudo-mirror plane. One set showed the L-configuration for both serine molecules and was taken as the trial structure.

The initial structure factor calculation had an $R(= \Sigma \, ||kF_o| - |F_c||/\Sigma \, |kF_o|$ of 0.20. The structure was refined by block-diagonal least-squares computations with anisotropic temperature factors, which led to an $R$ value of 0.06. Approximate positions of the hydrogen atoms were obtained from a difference-Fourier synthesis which was calculated at this stage of the refinement. At the same time all the observed amplitudes were corrected for anomalous dispersion (Patterson,

1963). The parameters of the copper, carbon, nitrogen and oxygen atoms were further refined by least-squares until the parameter shifts were less than $\frac{1}{3}$ the calculated standard deviations. At this point another difference-Fourier synthesis was calculated, based on a structure factor calculation wich did not include the hydrogen atom contributions and the hydrogen coordinates were revised. The location of the hydrogen atom attached to O(3 $A$) could not be ascertained from this map; the locations and peak heights of the other hydrogen atoms are given in Table 1. The maximum spurious peaks in the difference Fourier were $-1.0$ and $+1.2$ e.Å$^{-3}$ which occurred close to the position of the copper atom. The new hydrogen atom locations were included in more least-squares cycles but not refined. The refinement was completed when the shifts for all parameters became lower than $\frac{1}{3}$ the calculated standard deviations. The final weighting was $\sqrt{w} = |F_o|/P$ if $|F_o| \le P$, and $\sqrt{w} = P/|F_o|$ if $P < |F_o|$, with $P = 17.0$ electrons. The final parameters and their estimated standard deviations are shown in Table 2. All coordinate parameters were refined including the polar coordinate of the Cu atom. In a block-diagonal least-squares refinement of a structure in a polar space group it is not necessary to fix the coordinate of one of the atoms in the polar direction, because this least-squares matrix is not singular. Table 2, therefore, shows e.s.d.'s for the positional coordinates of all atoms. The $R$ value for all data is 0·040. A list of the observed and calculated structure factors is given in Table 3. A final electron density map is shown in Fig. 1. The peak heights (Table 4) are comparatively large, reflecting the relatively small temperature factors; electron counts of the peaks yielded the expected values. The atomic scattering factors used were from International Tables for X-ray Crystallography (1962), for Cu$^{2+}$, O, N and C. The scattering factors for hydrogen atoms used were those of Stewart, Davidson & Simpson (1965).

Table 1. *Positional parameters and peak heights of hydrogen atoms*

The parameters are expressed as fractions of cell edges. An isotropic temperature factor of 3·5 Å$^2$ was assigned to the hydrogen atoms. Parameters for H(O3$A$) are not shown (see text).

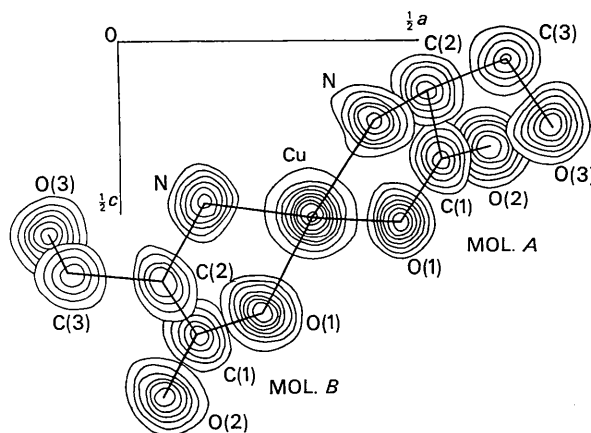| | $x$ ($\times 10^3$) | $y$ ($\times 10^3$) | $z$ ($\times 10^3$) | Peak heights |
|---|---|---|---|---|
| H(1)(N$A$) | 375 | 620 | 110 | 0·5 e.Å$^{-3}$ |
| H(2)(N$A$) | 490 | 640 | 260 | 0·4 |
| H(C2$A$) | 460 | 390 | $-020$ | 0·5 |
| H(1)(C3$A$) | 670 | 400 | $-080$ | 0·5 |
| H(2)(C3$A$) | 650 | 610 | $-090$ | 0·5 |
| H(1)(N$B$) | 120 | 500 | 340 | 0·7 |
| H(2)(N$B$) | 130 | 680 | 400 | 0·3 |
| H(C2$B$) | 110 | 700 | 800 | 0·5 |
| H(1)(C3$B$) | $-110$ | 610 | 810 | 0·3 |
| H(2)(C3$B$) | $-110$ | 690 | 580 | 0·4 |
| H(O3$B$) | $-170$ | 500 | 460 | 0·7 |



Fig. 1. Composite electron density map. First contour at 2 e.Å$^{-3}$. Contours around light atoms every 2 e.Å$^{-3}$ and around the Cu atom at every 10 e.Å$^{-3}$.

Table 2. *Parameters of copper, oxygen, nitrogen and carbon atoms bis(L-serinato)copper(II)*

Positional parameters are expressed as fractions of cell edges. Anisotropic temperature factors are expressed as

$$\exp\{-(h^2 b_{11} + k^2 b_{22} + l^2 b_{33} + klb_{23} + hlb_{13} + hkb_{12})\}.$$

Standard deviations are given in parentheses.

| | $x$ ($\times 10^4$) | $y$ ($\times 10^4$) | $z$ ($\times 10^4$) | $b_{11}$ ($\times 10^4$) | $b_{22}$ ($\times 10^4$) | $b_{33}$ ($\times 10^4$) | $b_{23}$ ($\times 10^4$) | $b_{13}$ ($\times 10^4$) | $b_{12}$ ($\times 10^4$) |
|---|---|---|---|---|---|---|---|---|---|
| Cu | 3182 (1) | 4999 (2) | 4861 (1) | 38 (1) | 46 (1) | 133 (2) | 39 (5) | 32 (2) | 18 (3) |
| O(1$A$) | 4667 (5) | 3448 (7) | 5018 (10) | 63 (6) | 79 (8) | 151 (16) | 71 (20) | 73 (16) | 73 (11) |
| O(2$A$) | 6169 (5) | 2188 (6) | 2780 (9) | 62 (5) | 53 (7) | 147 (17) | 9 (19) | 19 (14) | 33 (10) |
| C(1$A$) | 5356 (6) | 3282 (8) | 3147 (13) | 28 (6) | 45 (9) | 178 (23) | 5 (24) | $-1$ (18) | 22 (13) |
| C(2$A$) | 5103 (7) | 4503 (8) | 1150 (12) | 42 (6) | 52 (9) | 103 (20) | 11 (20) | 13 (18) | 4 (11) |
| N($A$) | 4202 (6) | 5785 (7) | 2088 (10) | 47 (6) | 35 (8) | 120 (18) | 10 (20) | $-10$ (16) | 2 (11) |
| C(3$A$) | 6419 (6) | 5125 (12) | 0223 (11) | 53 (6) | 52 (9) | 177 (19) | 2 (34) | 45 (18) | $-15$ (18) |
| O(3$A$) | 7180 (5) | 5791 (7) | 2098 (10) | 57 (6) | 78 (8) | 250 (20) | 5 (22) | $-49$ (16) | $-53$ (11) |
| O(1$B$) | 2403 (5) | 3960 (6) | 7615 (9) | 57 (5) | 62 (7) | 156 (16) | 60 (18) | 38 (14) | 27 (10) |
| O(2$B$) | 0747 (6) | 4153 (8) | 10186 (10) | 95 (7) | 107 (9) | 161 (17) | 72 (23) | 105 (18) | 22 (14) |
| C(1$B$) | 1313 (7) | 4585 (8) | 8367 (13) | 44 (7) | 73 (14) | 176 (22) | $-23$ (23) | 66 (19) | $-39$ (13) |
| C(2$B$) | 0714 (7) | 5956 (9) | 6901 (12) | 44 (7) | 70 (11) | 106 (20) | $-3$ (24) | 50 (18) | 4 (14) |
| N($B$) | 1388 (6) | 6002 (7) | 4571 (10) | 49 (6) | 37 (8) | 119 (18) | 22 (20) | 29 (16) | 22 (11) |
| C(3$B$) | $-0793$ (8) | 5895 (10) | 6737 (13) | 63 (8) | 61 (11) | 172 (24) | $-48$ (27) | 37 (21) | $-19$ (16) |
| O(3$B$) | $-1191$ (5) | 4496 (6) | 5537 (11) | 70 (6) | 63 (8) | 256 (20) | 21 (19) | $-91$ (18) | $-12$ (10) |

## Table 3. *Observed and calculated structure factors*

The listing shows for each reflection $k$, $|10F_o|$, $|10F_c|$ and the phase angle in degrees. The reflections for which the intensity could not be distinguished from the background are indicated by a star.

Column headers (repeated across the page): K   FO   FC   ALPHA

Table 3 (cont.)

Table 4. *Peak heights of copper, oxygen, nitrogen and carbon atoms*

| | | | |
|---|---|---|---|
| Cu | 82·0 e.Å⁻³ | O(3A) | 13·4 e.Å⁻³ |
| N(A) | 13·0 | O(3B) | 12·5 |
| N(B) | 13·4 | C(1A) | 10·6 |
| O(1A) | 14·7 | C(1B) | 10·3 |
| O(1B) | 15·4 | C(2A) | 10·2 |
| O(2A) | 13·9 | C(2B) | 9·9 |
| O(2B) | 13·5 | C(3A) | 10·1 |
| | | C(3B) | 9·4 |

## Discussion of the structure

The bond lengths and bond angles in the L-serine ligands are shown in Figs. 2 and 3. These values show a good consistency for the two independent L-serine ions. The averages of the bond lengths are given in Table 5 and compared with average values obtained from a large number of reported copper complexes of amino acids and peptides (Freeman, 1966), with the results from DL-serine (Shoemaker, Barieau, Donohue & Lu, 1953) and those from copper glutamate dihydrate (Gramaccioli & Marsh, 1966). A similar comparison for bond angles is given in Table 6. It can be concluded from the tabulated data that there are no significant changes in the bond lengths when serine is being chelated except for the expected small changes in the acid group. Some of the bond angles, however, in the present structure differ by more than 5σ from those reported for DL-serine, *i.e.* C(3)–C(2)–N and C(2)–C(3)–O(3) (Table 6). It is interesting to note that C(1)–C(2)–C(3) and the C(3)–C(2)–N angles are all larger than the tetrahedral angle. Furthermore both C(2)–C(3) distances are smaller than one would expect for a C(sp³)–C(sp³) bond.

Chelation of serine causes a small rotation around the C(1)–C(2) bond. In DL-serine the nitrogen atom is 0·05 Å out of the plane of the acid group, while in the present structure the nitrogen atoms are 0·16 Å and 0·31 Å removed from the planes through the acid groups (Table 8, planes 1 and 2). These observations correspond to rotations of 6·6° and 12·5°, respectively. The sense of rotation is clockwise on looking down from C(1) to C(2). The configuration around the C(2)–C(3) bond in both the serine molecules is similar to the one found in DL-serine (Shoemaker, *et al.* 1953) and L-serine phosphate (McCallum, Robertson & Sim,

1959). This particular configuration might be considered the least favorable of the three possible staggered configurations with the hydroxyl group close to both the carboxyl and amino groups. Fig. 4 shows a schematic drawing of the serine molecules viewed along the C(3)–C(2) bonds.
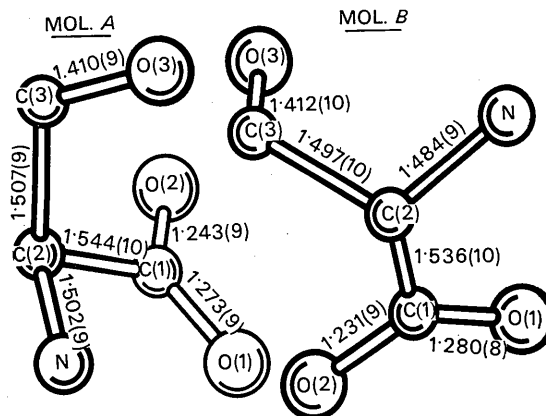


Fig. 2. Bond lengths in both serine ions. Number in parentheses is the estimated standard deviation of the last digit.
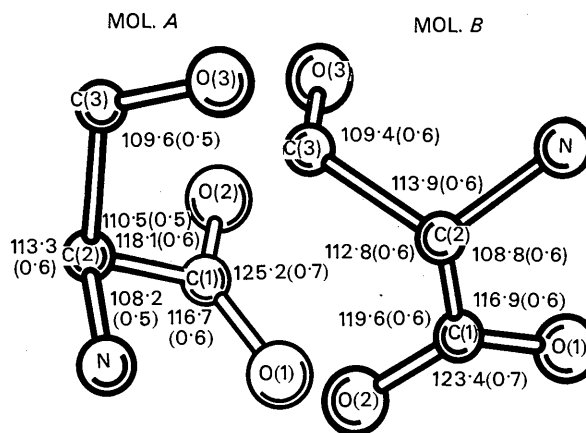


Fig. 3. Bond angles in both serine ions. Number in parentheses is the estimated standard deviation.

Table 5. *Comparison of bond lengths*

Column I: Average bond lengths of L-serine in bis(L-serinato)copper(II). Column II: Average bond lengths from a tabulation on several copper chelates of amino acids and peptides (Freeman, 1966). Column III: Results of DL-serine (Shoemaker *et al.* 1952). Column IV: Results from the structure of copper glutamate dihydrate (Gramaccioli & Marsh, 1966). Numbers in parentheses are estimated standard deviations of the last digit given.

| | I | II | III | IV |
|---|---|---|---|---|
| C(1)–C(2) | 1·540 (7) Å | 1·520 (5) Å | 1·528 (9) Å | 1·509 (6) Å |
| C(1)–O(1) | 1·276 (7) | 1·286 (7) | 1·268 (9) | 1·284 (6) |
| C(1)–O(2) | 1·237 (6) | 1·235 (5) | 1·261 (9) | 1·242 (6) |
| C(2)–N | 1·493 (6) | 1·482 (7) | 1·491 (9) | 1·486 (6) |
| C(2)–C(3) | 1·502 (7) | — | 1·513 (9) | — |
| C(3)–O(3) | 1·411 (7) | — | 1·425 (9) | — |
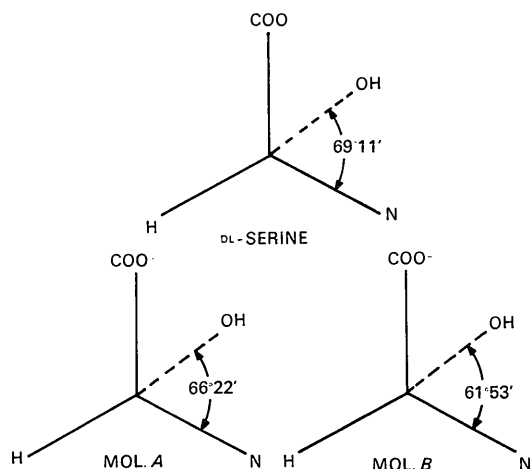
Fig. 4. Configuration of the hydroxyl group in DL-serine, L-serine A and L-serine B. View is along the C(3)–C(2) bond.
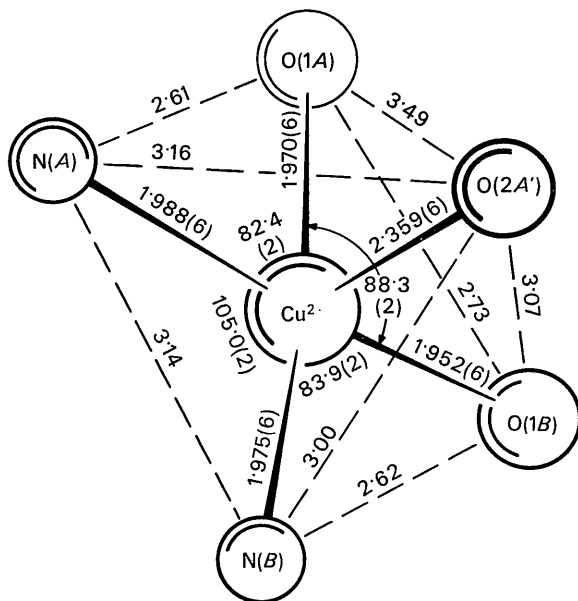
### Table 6. Comparison of bond angles

The column numbers refer to the sources given in Table 5. Numbers in parentheses are estimated standard deviations of the last digit given.

|  | I | III | IV |
|---|---|---|---|
| O(1)–C(1)–O(2) | 124·3 (5) | 125·3 | 124·3 |
| O(1)–C(1)–C(2) | 116·8 (4) | 117·4 | 117·5 |
| O(2)–C(1)–C(2) | 118·9 (4) | 117·2 | 118·2 |
| C(1)–C(2)–N | 108·5 (4) | 110·0 | 110·1 |
| C(1)–C(2)–C(3) | 111·7 (4) | 110·3 | 110·0 |
| C(3)–C(2)–N | 113·6 (4) | 111·1 | 111·3 |
| C(2)–C(3)–O(3) | 109·5 (4) | 112·0 | — |

The copper is coordinated to a carboxylic oxygen and the nitrogen of both L-serine ions to form two 5-membered chelate rings. Dimensions for those rings, if not shown in Figs. 2 and 3, are given in Table 7. These bond lengths and angles compare well with previously reported results. The rings are not flat. When least-squares planes are calculated for the carboxylic acid groups, it is observed that the Cu and N atoms are on opposite sides of these planes (Table 8).

### Table 7. Bond lengths and bond angles of chelate rings in bis(L-serinato)Cu$^{II}$

The columns A and B refer to the chelate rings formed by the serine molecules A and B respectively. Column C are average values tabulated by Freeman (1966). The numbers in parentheses are the estimated standard deviations for the last digit.

|  | A | B | C |
|---|---|---|---|
| Cu–O | 1·970 (5) Å | 1·952 (5) Å | 1·966 (12) Å |
| Cu–N | 1·988 (6) | 1·975 (6) | 1·996 (5) |
| O(1)–Cu–N | 82·4° (2) | 83·9° (2) | 84° |
| Cu–O(1)–C(1) | 116·4 (4) | 115·4 (4) | 120 (5) |
| Cu–N–C(2) | 110·4 (4) | 109·3 (4) | 111 |

The two serine residues are *cis* with respect to each other. The same configuration has been observed in bisglycinatocopper(II) hydrate (Tomita & Nitta, 1961; Freeman, Snow, Nitta & Tomita, 1964). The surroundings of the copper ion form a square pyramid which is shown in Fig. 5. The four atoms in the basal plane are a part of the two chelate rings and form strong bonds with the copper ion. These four atoms are not coplanar but form a very flattened tetrahedron. The copper ion is not in the center of this tetrahedron



Fig. 5. Surroundings of the copper ion. Standard deviations of last digit in parentheses.

### Table 8. Equations of some least-squares planes

Equations are expressed in the form $Ax + By + Cz = D$ where $D$ is expressed in Å, and $x$, $y$ and $z$ are fractional coordinates.

| Plane | Atoms in plane | A | B | C | D |
|---|---|---|---|---|---|
| 1 | O(1A) O(2A) C(1A) C(2A) | 7·194 | 4·814 | 2·121 | 6·086 |
| 2 | O(1B) O(2B) C(1B) C(2B) | 5·277 | 5·531 | 2·983 | 5·729 |
| 3 | O(1A) O(1B) N(A) N(B) | 4·074 | 5·870 | 3·291 | 5·694 |

| Atoms | Δ(1) | Atoms | Δ(2) | Atoms | Δ(3) |
|---|---|---|---|---|---|
| Cu | −0·360 Å | Cu | +0·166 Å | Cu | +0·137 Å |
| O(1A) | −0·005 | O(1B) | +0·001 | O(1A) | −0·117 |
| O(2A) | −0·005 | O(2B) | +0·001 | O(1B) | +0·116 |
| C(1A) | +0·014 | C(1B) | −0·004 | N(A) | +0·101 |
| C(2A) | −0·004 | C(2B) | +0·001 | N(B) | −0·101 |
| N(A) | +0·164 | N(B) | −0·313 |  |  |

but displaced towards the top of the square pyramid by 0·14 Å (Table 8). The serine molecule $A$ is bonded to two copper ions. The top of the pyramid is occupied by the carboxyl oxygen which is *trans* to the amino group of an $A$-type serine molecule. The fifth interaction is weaker than the first four. The sixth position is unoccupied, [O(2$B$), translated one unit in the negative **c** direction, is at 3·63 Å from the copper atom] where in the similar structure of bis(L-serinato)zinc(II) (van der Helm, Nicholas & Fisher, 1969) a hydroxyl oxygen is in this position (at 2·99 Å), forming a weak interaction with the metal ion. The *cis* configuration leads to a short non-bonded distance between O(1$A$) and O(1$B$) of 2·73 Å, which is significantly shorter than the 2·83 Å found between the two similar oxygens in the structure of bisglycinatocopper(II) hydrate (Freeman, Snow, Nitta & Tomita, 1964). The *cis* configuration is also present in the structure of diaquobis-(L-serinato)nickel(II) (van der Helm & Hossain, 1969) and the corresponding O–O distance in that case is 2·87 Å.

The principal axes of the thermal ellipsoids were determined and the magnitudes of their direction cosines with respect to the cell edges are listed in Table 9. The atoms of serine molecule $B$ have in general a slightly higher temperature movement than the same atoms in serine molecule $A$. This is probably correlated with the fact that serine $A$ forms a chelate ring with one copper and is also complexed to another copper ion whereas serine $B$ forms only a chelate ring. This can be seen in Fig. 6, which shows the molecular structure as viewed down the **b** axis. The two serine molecules are approximately related by a twofold axis lying in the basal plane of the copper surroundings and bisecting the angle N($B$)–Cu–N($A$). The protons available for hydrogen bonding (two on each nitrogen atom and one on each hydroxyl oxygen atom) are all being used (Table 10) to form bonds of similar strength. All oxygen atoms accept one hydrogen bond. The coordinate and hydrogen bonds form a three-dimensional network.

**Table 9. *Values of anisotropic temperature factors along the principal axes***

Values of the temperature factors (in Å²) along the major, intermediate and minor axes of the thermal ellipsoids are given together with the direction cosines of these axes with respect to the axes of the crystallographic unit cell.

|        | $B_i$ | $l_1$   | $l_2$   | $l_3$   |
|--------|-------|---------|---------|---------|
| Cu     | 2·20  | 0·539   | 0·464   | 0·697   |
|        | 1·25  | 0·777   | 0·047   | −0·636  |
|        | 1·04  | −0·324  | 0·884   | −0·332  |
| O(1$A$)| 4·07  | 0·666   | 0·604   | 0·431   |
|        | 1·43  | −0·226  | −0·397  | 0·892   |
|        | 1·13  | −0·711  | 0·691   | 0·136   |
| O(2$A$)| 2·75  | 0·884   | 0·403   | 0·225   |
|        | 1·83  | −0·212  | −0·102  | 0·974   |
|        | 1·24  | −0·416  | 0·909   | 0·009   |
| C(1$A$)| 2·28  | −0·020  | 0·037   | 0·999   |
|        | 1·57  | 0·620   | 0·784   | −0·023  |
|        | 0·80  | 0·784   | −0·619  | 0·030   |

**Table 9 (cont.)**

|        | $B_i$ | $l_1$   | $l_2$   | $l_3$   |
|--------|-------|---------|---------|---------|
| C(2$A$)| 1·72  | 0·846   | 0·383   | 0·361   |
|        | 1·47  | −0·475  | 0·858   | 0·203   |
|        | 1·24  | −0·242  | −0·343  | 0·910   |
| N($A$) | 1·90  | 0·941   | 0·001   | −0·350  |
|        | 1·51  | 0·333   | 0·198   | 0·918   |
|        | 0·98  | −0·068  | 0·980   | −0·185  |
| C(3$A$)| 2·68  | 0·656   | −0·124  | 0·738   |
|        | 1·79  | 0·608   | −0·498  | −0·625  |
|        | 1·34  | 0·448   | 0·858   | −0·256  |
| O(3$A$)| 3·64  | −0·550  | 0·365   | 0·757   |
|        | 2·74  | −0·428  | 0·649   | −0·624  |
|        | 1·26  | 0·716   | 0·668   | 0·192   |
| O(1$B$)| 2·95  | 0·639   | 0·510   | 0·569   |
|        | 1·75  | 0·756   | −0·280  | −0·600  |
|        | 1·27  | −0·141  | 0·813   | −0·563  |
| O(2$B$)| 4·58  | 0·792   | 0·391   | 0·460   |
|        | 2·89  | −0·473  | 0·879   | 0·071   |
|        | 1·33  | −0·386  | −0·274  | 0·885   |
| C(1$B$)| 3·07  | 0·580   | −0·508  | 0·631   |
|        | 1·93  | −0·068  | 0·749   | 0·659   |
|        | 1·01  | 0·812   | 0·425   | −0·409  |
| C(2$B$)| 2·14  | 0·794   | 0·268   | 0·537   |
|        | 1·97  | −0·186  | 0·962   | −0·199  |
|        | 0·96  | −0·579  | 0·058   | 0·820   |
| N($B$) | 2·25  | 0·829   | 0·330   | 0·442   |
|        | 1·35  | −0·485  | 0·024   | 0·879   |
|        | 0·89  | −0·278  | 0·944   | −0·177  |
| C(3$B$)| 2·98  | 0·711   | −0·394  | 0·574   |
|        | 2·00  | −0·699  | −0·304  | 0·655   |
|        | 1·45  | 0·078   | 0·867   | 0·491   |
| O(3$B$)| 4·14  | −0·620  | 0·121   | 0·782   |
|        | 1·94  | 0·753   | −0·184  | 0·623   |
|        | 1·75  | 0·219   | 0·975   | 0·021   |

**Table 10. *Hydrogen bonding***

| Donor ($D$) | Acceptor ($A$) | $\angle$ C–D–A |         |
|-------------|----------------|----------------|---------|
| N($A$)      | O(1$A$)        | 120°           | 2·99 Å  |
| N($A$)      | O(2$A$)        | 91             | 3·01    |
| N($B$)      | O(3$B$)        | 91             | 2·95    |
| N($B$)      | O(2$B$)        | 129            | 2·99    |
| O(3$A$)     | O(1$B$)        | 121            | 2·70    |
| O(3$B$)     | O(3$A$)        | 99             | 2·74    |

Although the packing below the square pyramid around the copper ions is rather open, there occur in this area two van der Waals interactions shorter than
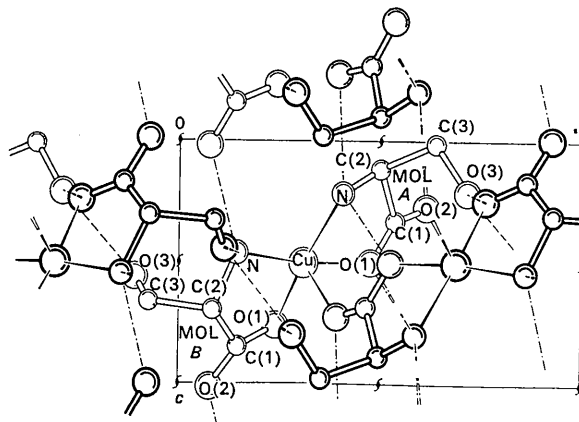


Fig. 6. Projection of the structure down the *b* axis.

3·5 Å: C(3A)–C(3B): 3·48 Å and N(A)–O(1B): 3·44 Å
(See Table 11). The other intermolecular distances be-
low 3·5 Å are also listed in Table 11.

Table 11. *Van der Waals interactions*

The atoms listed in the first column have the parameters given
in Table 2. The atoms in the second column are related by the
formulas given in column 3 to the parameters for the atoms
given in Table 2.

|        |        | Formula | Distance |
|--------|--------|---------|----------|
| N(A)   | O(1B)  | −c | 3·44 Å |
| C(2A)  | O(1B)  | +c | 3·36 |
| C(2B)  | O(2A)  | $1-x, y+\frac{1}{2}, 1-z$ | 3·27 |
| C(1B)  | O(2A)  | $1-x, y+\frac{1}{2}, 1-z$ | 3·39 |
| C(2A)  | O(2A)  | $1-x, y+\frac{1}{2}, 1-z$ | 3·40 |
| N(A)   | C(1A)  | $1-x, y+\frac{1}{2}, 1-z$ | 3·44 |
| C(2B)  | O(3B)  | $-x, y+\frac{1}{2}, 1-z$ | 3·32 |
| C(3A)  | C(3B)  | $-a-c$ | 3·48 |
| C(3B)  | O(3A)  | $-a$ | 3·29 |
| O(3A)  | O(1A)  | $1-x, y+\frac{1}{2}, 1-z$ | 3·33 |

The computer programs used in this work are listed
by van der Helm & Hossain (1969). The authors are
indepted to Dr F.R.Ahmed (1966) for the use of his
I.B.M. 360 programs, and to the Computing Center of
the University of Oklahoma for putting computer time
at their disposal.

**References**

AHMED, F. R. (1966). *Structure Factor Least Squares
NRC-10, Fourier for Distorted and Undistorted Nets,
NRC-8.* Ottawa: National Research Council.
FREEMAN, H. C., SNOW, M. R., NITTA, I. & TOMITA, K.
(1964). *Acta Cryst.* 17, 1463.
FREEMAN, H. C. (1966). In *The Biochemistry of Copper,*
p. 77. Ed. J. PEISACH, P. AISEN & W. E. BLUMBERG. New
York: Academic Press.
GRAMACCIOLI, C. M. & MARSH, R E. (1966). *Acta Cryst.*
21, 594.
*International Tables for X-ray Crystallography* (1962). Vol.
III, p. 202. Birmingham: Kynoch Press.
McCALLUM, G. H., ROBERTSON, J. M. & SIM, G. A.
(1959). *Nature, Lond.* 184, 1863.
PATTERSON, A. L. (1963). *Acta Cryst.* 16, 1255.
SHOEMAKER, D. P., BARIEAU, R. F., DONOHUE, J. & LU, C.
S. (1953). *Acta Cryst.* 6, 241.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965).
*J. Chem. Phys.* 42, 3175.
TOMITA, K. & NITTA, I. (1961). *Bull. Chem. Soc. Japan,* 34,
286.
VAN DER HELM, D. & HOSSAIN, M. B. (1969). *Acta Cryst.*
B 25, 457.
VAN DER, HELM, D., NICHOLAS, A. F. & FISCHER, C. G.
(1969). *Acta Cryst.* To be published.

# The Crystal Structure of Diaquobis(L-serinato)nickel(II)*

BY DICK VAN DER HELM AND M. BILAYET HOSSAIN

*Chemistry Department, University of Oklahoma, Norman, Oklahoma 73069, U.S.A.*

The crystal structure of diaquobis(L-serinato)nickel(II), $NiC_6H_{16}O_8N_2$, has been determined and refined
by three-dimensional least-squares techniques. The crystals are monoclinic, space group $C2$, with $a=$
7·776, $b=8·546$, $c=8·834$ Å and $\beta=101°31'$. The final $R$ value for 608 reflections is 0·043; the standard
deviations are about 0·006 Å for the non-hydrogen light-atom positions. The compound is not iso-
structural with either the Cu or the Zn complex of L-serine. The nickel environment is octahedral
and the ligands are attached *cis* to the metal ion. The serine molecule has a different configuration for
the hydroxyl group when compared with the one found in DL-serine. A fractional molecule of water of
crystallization is present in the structure.

## Introduction

The influence of transition metal ions on the confor-
mation of peptides and amino acids prompted the in-
vestigation of a series of chelates of L-serine. A pre-
liminary investigation showed the nickel compound to
crystallize in a different space group to the Cu and Zn
chelates, while the crystals apparently contained water
of crystallization or complexed water in contrast to the
non-hydrated Cu and Zn compounds.

---

## Experimental

The compound was prepared in aqueous solution by
adding proportional amounts of $NiSO_4$, $Ba(OH)_2$ and
L-serine to form $Ni(L\text{-serine})_2$. The $BaSO_4$ was sepa-
rated from the light blue solution by centrifugation.
Evaporation of the solution yielded a glass. After seve-
ral unsuccessful attempts, some crystalline material was
obtained from a 2-propanol–$H_2O$ solution. Subse-
quently an aqueous solution was equlibrated with an
ether–ethanol (2:1) mixture. Close to the saturation
point the solution was seeded with a few crystals. This
technique yielded a good crop of blue, well formed,