

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 below 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 indebted 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.

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

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The crystal structure of diaquobis(L-serinato)nickel(II), $\text{NiC}_6\text{H}_{16}\text{O}_8\text{N}_2$, 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 $\beta = 101^\circ 31'$. 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 isostructural 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 conformation of peptides and amino acids prompted the investigation of a series of chelates of L-serine. A preliminary 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-serine)_2 . The BaSO_4 was separated from the light blue solution by centrifugation. Evaporation of the solution yielded a glass. After several unsuccessful attempts, some crystalline material was obtained from a 2-propanol– H_2O solution. Subsequently an aqueous solution was equilibrated 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,

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thin crystal plates. The same experiment without the use of a seed-crystal was not successful.

The plate face proved to be the (001) plane and it had the shape of a parallelogram. The crystals viewed under the polarizing microscope showed sharp extinctions along the diagonals of the parallelogram when lying on the plate face. The plates are rather thin (<0.03 mm) and examination of a crystal lying on its edge showed it to be dark blue, opaque and laminar in appearance.

The 2θ values of 30 reflections were measured at 22°C on a General Electric SPG Single Crystal Orienter with Cu $K\alpha$ radiation ($\lambda=1.5418$ Å). The cell dimensions were calculated with a least-squares method from these 2θ values and are given in Table 1. The systematic absences (hkl , $h+k$ odd) are consistent with the monoclinic space groups $C2$, Cm and $C2/m$. Only $C2$, however, can accommodate L-serine, and it is therefore the space group which was assigned to the compound. The density was calculated on the basis of two Ni(L-serine) $_2 \cdot 2\text{H}_2\text{O}$ per unit cell and this value, together with the observed density, is shown in Table 1.

Table 1. *Crystal data*

$a = 7.776 \pm 0.002$ Å	$\rho_o = 1.783$ g.cm $^{-3}$
$b = 8.546 \pm 0.002$	$\rho_c = 1.737$ g.cm $^{-3}$
$c = 8.834 \pm 0.003$	F.W. = 300.90 g.F.U. $^{-1}$
$\beta = 101^\circ 31' \pm 13'$	F.U. = Ni(C $_3$ N $_3$ O $_3$ H $_6$) $_2 \cdot 2\text{H}_2\text{O}$
$V = 575.2$ Å 3	
$Z = 2$	

X-ray diffraction showed the crystals to have a large mosaic spread, ($\leq 10^\circ$) which was a maximum along c . By trial a crystal with a mosaic spread of about 2° was chosen for the measurement of the intensity data. The dimensions of the crystal were $0.59 \times 0.59 \times 0.032$ mm. The beam tunnel for the diffracted X-rays was removed during the intensity measurements to allow for the optical divergence caused by the mosaicity of the crystal. The aperture of the filter holder was increased for the same reason. Integrated intensities were measured on a G.E. X.R.D.-5 diffraction unit equipped with a scintillation counter and a pulse height analyzer using the θ - 2θ scan technique and Ni filtered Cu $K\alpha$ radiation. All reflections (608) with a 2θ -value below 145° were observed; 16 of these intensities were below the threshold of measurement. The intensities were corrected for the Lorentz and polarization factors, and for absorption ($\mu = 59.22$ cm $^{-1}$).

Structure determination and refinement

A sharpened Patterson map was computed. The only high peak other than the origin peak appeared at $0.50, 0.50, 0.00$, in agreement with the supposed location of Ni on the twofold axis. The peaks around the origin showed that the Ni-ion is surrounded octahedrally. The further interpretation of the heavy-light atom vectors visible in the Patterson map yielded the expected two possible locations for all C, N and O atoms,

one set forming the D-, the other the L-enantiomorph of serine. The latter set of locations was chosen as the trial structure.

The first structure factor calculation yielded an $R (= \sum ||kF_o| - |F_c| | / \sum |kF_o|)$ of 0.28. The refinement was done by block-diagonal least-squares using initially isotropic and later anisotropic temperature factors. The quantity minimized was $\sum w(|kF_o| - |F_c|)^2$. The observed structure amplitudes were corrected for anomalous dispersion as suggested by Patterson (1963). Intermediate difference-Fourier syntheses showed the approximate positions of the hydrogen atoms and a persistent indication of a fractional ($\frac{1}{2}$) molecule of water at the approximate position $0, \frac{1}{2}, 0$. Both these features were included in further refinements.

The parameters of the hydrogen atoms were not refined. The least-squares procedure was interrupted when all parameter shifts were less than $\frac{1}{3}$ the calculated standard deviations. A new difference Fourier synthesis was calculated using reflections with $\sin^2\theta \leq 0.55$. This Fourier synthesis was based on a structure factor calculation which did not include the hydrogen atom contributions. The final locations of the hydrogen atoms (Table 2) were determined from this map, which showed in addition 10-15 spurious peaks with heights between 0.3 and 0.6 e.Å $^{-3}$. The lowest negative electron density in the difference-Fourier was -0.7 e.Å $^{-3}$ at a location close to the nickel ion position. The refinement was finished with several cycles of least-squares until the parameter shifts were once again less than $\frac{1}{3}$ the calculated standard deviations. The final weighting scheme was $1/w = 1$ if $|F_o| \leq P$ and $1/w = P/|F_o|$ if $|F_o| > P$ ($P = 24.2$ electrons). The final parameters for all atoms except the hydrogens are given in Tables 3 and 4. Table 3 shows the estimated standard deviations for all positional coordinates in the polar direction (van der Helm & Franks, 1969). A composite electron density map is shown in Fig. 1. An interesting feature of this Fourier synthesis is the comparatively high electron densities at the atomic centers. The final R value is 0.043 for all data. The list of calculated and observed structure factors is presented in Table 5.

Table 2. *Positional parameters of the hydrogen atoms*

The identification in the first parentheses refers to the atom to which the hydrogen is bonded.

	x	y	z	Peak height
H(C2)	0.474	0.570	0.302	0.5 e.Å $^{-3}$
H(N)(1)	0.258	0.702	0.085	0.6
H(N)(2)	0.470	0.735	0.160	0.4
H(C3)(1)	0.082	0.638	0.279	0.5
H(C3)(2)	0.175	0.550	0.430	0.4
H(O3)	0.220	0.795	0.470	0.3
H(Ow)(1)	0.718	0.415	0.245	0.5
H(Ow)(2)	0.682	0.584	0.192	0.5

Discussion of the structure

The bonded and non-bonded distances in the octahedral environment of the nickel ion are given in Fig. 2.

The bond angles involving the metal ion are presented in Table 6. The metal environment is approximately octahedral. One cause of the distortion is the α -amino acid itself forming a 5-membered chelate ring using the carboxylic oxygen and nitrogen atoms. Additional distortion is caused by the *cis* configuration around the nickel ion, which results in non-bonded O–O and N–N distances along the edges of the octahedron instead of

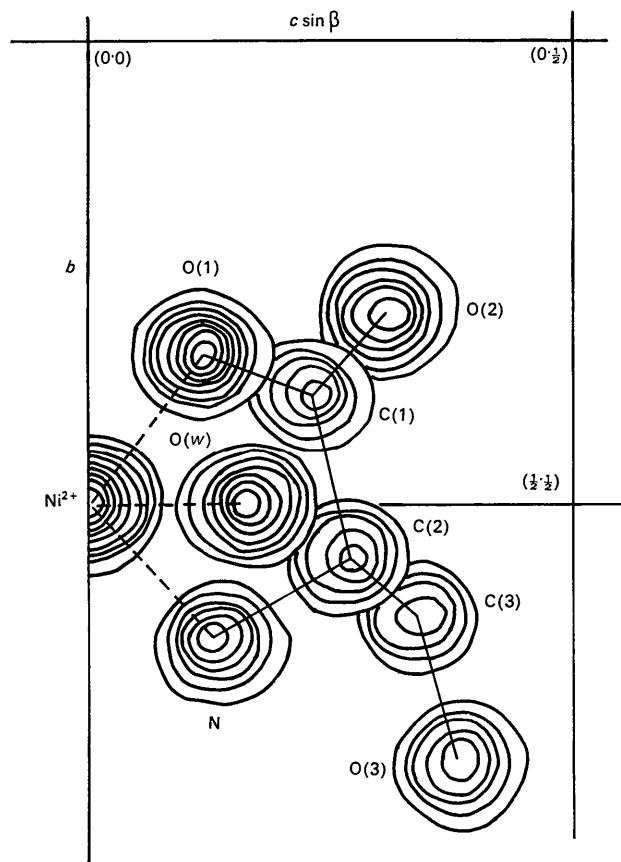


Fig. 1. Composite Fourier synthesis. Contours around all atoms start at $2 \text{ e.}\text{\AA}^{-3}$ and are drawn at intervals of $2 \text{ e.}\text{\AA}^{-3}$. Around the nickel ion the contours are at intervals of $10 \text{ e.}\text{\AA}^{-3}$.

Table 3. Positional parameters of nickel, oxygen, nitrogen and carbon atoms

The parameters are expressed as fractions of cell edges. The e.s.d. ($\times 10^4$) are given in parentheses. The occupancy of $O(w)$ was refined to 0.33 ± 0.04 .

	x	y	z
Ni	0.5000 (0)	0.5000 (2)	0.0000 (0)
O(1)	0.3879 (6)	0.3349 (5)	0.1107 (5)
O(2)	0.2513 (7)	0.2940 (6)	0.3067 (6)
O(3)	0.2476 (9)	0.7781 (6)	0.3900 (6)
N	0.3773 (7)	0.6452 (6)	0.1384 (6)
C(1)	0.3268 (8)	0.3830 (7)	0.2269 (7)
C(2)	0.3518 (9)	0.5556 (7)	0.2710 (7)
C(3)	0.2084 (10)	0.6205 (8)	0.3460 (9)
O(w)	0.7337 (5)	0.5021 (9)	0.1743 (4)
O(wf)	0.5000 (0)	0.9661 (29)	0.0000 (0)

N–O distances. The O–O distances (2.87 \AA) is appreciably smaller than the N–N distance (3.39 \AA), although not as short as the same distance in bis(L-serinato)copper(II) (2.73 \AA) (van der Helm & Franks, 1969). Several structures of nickel chelates of amino acids have been reported in the literature, but in only one case, the structure of bis(DL-histidino)nickel(II) hydrate (Fraser & Harding, 1967), have the nickel–ligand distances been accurately determined. The Ni–N distance (2.100 \AA) compares quite well with the same distance in the nickel complex of DL-histidine (2.106 \AA) and with other Ni–N distances in octahedral complexes as listed by Nardelli, Gasparri, Musatti & Manfredotti (1966). Of the two independent nickel–oxygen distances the Ni–O(w) length (2.135 \AA) is longer and the Ni–O(1) length (2.012 \AA) is much shorter than the value $2.08 \pm 0.02 \text{ \AA}$ listed in *International Tables for X-ray Crystallography* (1962a). The Ni–O(w) distance compares well with Ni–O(w) = 2.12 ± 0.05 and Ni–O = $2.13 \pm 0.01 \text{ \AA}$ given by Freeman (1967), and of 2.113 \AA found in the structure of DL-histidinonickel(II) hydrate (Fraser & Harding, 1967). The Ni–O(1) distance in the present structure seems to be significantly shorter than any of these values. The structure of nickel di- α -aminoisobutyrate tetrahydrate (Noguchi, 1962) has a small Ni–O distance of $2.01 \pm 0.05 \text{ \AA}$. None of the three basal least-squares planes, two of which are independent, can be called planar (planes 1 and 2, Table 7).

Table 4. Anisotropic temperature factor parameters of nickel, oxygen, nitrogen and carbon atoms

The anisotropic temperature factors are expressed as

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

The parameters and their standard deviations are multiplied by 10^4 .

	b_{11}	b_{22}	b_{33}	b_{23}	b_{13}	b_{12}
Ni	107 (1)	18 (1)	49 (1)	0 (0)	51 (2)	0 (0)
O(1)	135 (8)	24 (5)	55 (5)	-14 (8)	100 (11)	6 (10)
O(2)	220 (11)	41 (6)	82 (6)	-6 (10)	138 (14)	-54 (13)
O(3)	366 (17)	30 (6)	75 (6)	-14 (10)	177 (17)	2 (16)
N	135 (10)	29 (6)	74 (7)	15 (11)	110 (13)	-6 (12)
C(1)	116 (10)	27 (6)	63 (8)	0 (12)	65 (15)	7 (14)
C(2)	147 (12)	21 (6)	55 (7)	-3 (11)	59 (15)	0 (14)
C(3)	190 (14)	39 (7)	98 (9)	-4 (15)	117 (19)	-20 (18)
O(w)	137 (7)	47 (4)	73 (5)	-6 (18)	61 (9)	-15 (21)
O(wf)	432 (113)	53 (52)	242 (75)	0 (0)	-224 (136)	0 (0)

Table 5. Observed and calculated structure factors

Values listed are h, |10F_o|, |10F_c| and the phase angle in degrees. Intensities which could not be distinguished from the background are indicated by a star.

Table with multiple columns for Miller indices (h, k, l) and structure factor magnitudes (|10F_o|, |10F_c|) and phase angles. The table is organized into several sections based on the Miller indices, such as h k l = 0, h k l = ±1, h k l = ±2, etc.

Table 6. Bond angles involving nickel

The prime denotes atoms related by a 2-fold axis to the atomic positions given in Table 3. The angles have a standard deviation of 0.2°.

Table listing bond angles involving nickel atoms: O(1)-Ni-O(1') 90.9°, O(1)-Ni-N 80.8°, O(1)-Ni-N' 171.4°, O(1)-Ni-O(W) 88.1°, O(1)-Ni-O(W') 92.5°, N-Ni-N' 107.6°, N-Ni-O(W) 89.7°, N-Ni-O(W') 89.7°, O(W)-Ni-O(W') 179.1°.

The bond distances and bond angles for the ligand, with their standard deviations as calculated from the final least-squares cycle, are given in Figs. 3 and 4. The relative lengths of the C-O bonds in the carboxylic acid group are as expected in that the C-O distance of the oxygen atom bonded to the nickel ion is the longer one. The C(1)-C(2) and C(3)-O(3) distances are normal. The C(2)-C(3) distance (1.511 Å) is the same as that

found in DL-serine (Shoemaker, Barieau, Donohue & Lu, 1953), although one would expect it to be slightly longer. The C(2)-N distance (1.446 Å) is significantly shorter than the average value (1.49 ± 0.004 Å) calculated by Freeman (1967) for this distance in a series

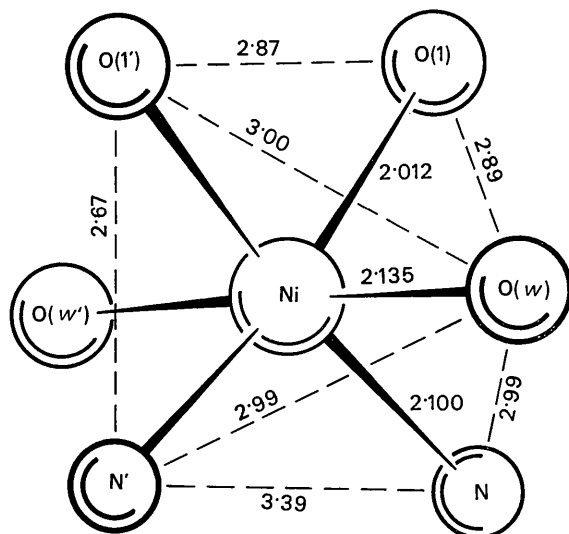


Fig. 2. Bonded and non-bonded distances in the octahedron. E.s.d.'s are 0.005 Å.

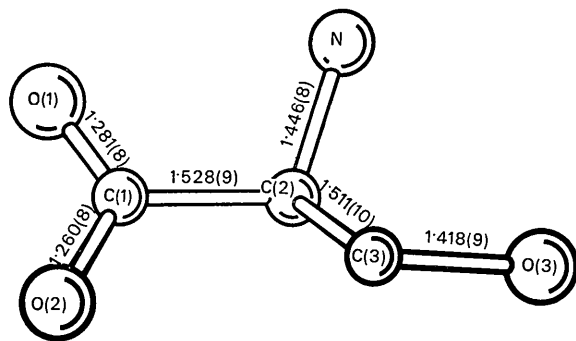


Fig. 3. Bond lengths in ligand. E.s.d.'s for the last digit are given in parentheses.

of metal chelates of amino acids, and also shorter than the C-N (α -amino group) distance in the nickel chelate of DL-histidine (Fraser & Harding, 1967) *i.e.* 1.48 Å. An equally short C-N distance (1.44 Å) is observed in the structure of glycylglycylglycinatocopper(II) chloride (Freeman, Robinson & Schoone, 1964). It is also interesting to note that in that same structure there is a short Cu-O distance, [1.93 Å to be compared with the average 1.966 ± 0.012 Å as tabulated by Freeman (1966)] which constitutes a similar pattern to that observed in the present structure in which a short Ni-O distance is observed. One is also tempted to correlate the short C-N distance in the present structure with the larger than tetrahedral angles around the C(2) atom. Similar positive deviations, however, are also found in the structures of the copper(II) and zinc(II) chelates of L-serine (van der Helm & Franks, 1969; van der Helm, Nicholas & Fisher, 1969), although they are not as large as in the present structure.

The chelation with nickel changes the configuration of the hydroxyl group if it is compared with DL-serine (Shoemaker, Barieau, Donohue & Lu, 1953) (Fig. 5). The hydroxyl group is opposite the carboxylic acid group rather than between the acid and amino groups. In addition the nitrogen is rotated slightly out of the plane of the acid group (plane 3, Table 7) where in DL-serine the nitrogen atom is only 0.05 Å out of this plane. The nitrogen atom is rotated clockwise by 22.3° out of the plane through the carboxyl group, looking down from C(1) to C(2). The 5-membered chelate ring is therefore not planar. The angles Ni-N-C(2) and Ni-O(1)-C(1) are 108.0° and 115.5° respectively.

The overall packing of the structure is shown in Fig. 6. The drawing does not show the fractional molecule of water, which in this projection would coincide with the nickel ion position. This feature of the structure, which was persistently observed in difference-Fourier syntheses, was included in the final refinement of the structure. Its final parameters are given in Table 3. The irregular occurrence of this water molecule of crystallization can possibly explain the high temperature factors which it shows. The occupancy factor is calculated to be 0.33 ± 0.04 , which if included in the density calculation, gives $\rho_c = 1.772$ g.cm $^{-3}$. It explains

Table 7. 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. The prime denotes atoms related by a 2-fold axis ($\frac{1}{2}, y, 0$) to the positions given in Table 3.

Plane	Atoms	A	B	C	D
1	O(1), O(1'), N, N'	5.3742	0.0000	5.0377	2.6871
2	O(1), O(w), N', O(w')	3.5563	-6.5208	-4.7600	-1.4142
3	O(1), O(2), C(1), C(2)	6.0127	-1.7924	3.8167	2.1519

Atoms	$\Delta(1)$	Atoms	$\Delta(2)$	Atoms	$\Delta(3)$
O(1)	-0.045 Å	O(1)	+0.083 Å	O(1)	+0.003 Å
O(1')	+0.045	O(w)	-0.080	O(2)	+0.003
N	+0.038	N'	+0.080	C(1)	-0.008
N'	-0.038	O(w')	-0.083	C(2)	+0.002
Ni	0.000	Ni	-0.068	N	-0.511
				Ni	-0.042

to a large extent therefore the discrepancy between the calculated and observed densities shown in Table 1. The fractional molecule of water has a total of 18 contacts below 3.50 Å with other atoms of the structure (Table 8). Only contacts with atoms C(1) are short: 2.99 Å. This cage probably maintains the experimentally observed stability of the crystal.

Table 8. Distances from fractional molecule of water

The locations used are those given in Table 3. The identification in parentheses specifies the operation which has to be performed.

$$\begin{aligned} (') &: \frac{1}{2}-x, y-\frac{1}{2}, -z \\ (') &: -x, y, -z \\ (') &: x-\frac{1}{2}, y+\frac{1}{2}, z. \end{aligned}$$

All distances occur twice. The second set is obtained after an operation of the 2-fold axis which passes through the origin.

O(wf)-O(1)	3.18 Å	O(wf)-C(3)	3.42 Å
O(wf)-O(2)	3.35	O(wf)-N'	3.22
O(wf)-N	3.32	O(wf)-O(w'')	2.83
O(wf)-C(1)	2.99	O(wf)-O(1''')	3.46
O(wf)-C(2)	3.34		

The structure consists of layers of molecules parallel to the (001) plane. The layer is held together by coordinate bonds and two hydrogen bonds of the water molecule which is complexed to the nickel ion. It is doubtful if the two contacts of the nitrogen atom (3.18 Å and 3.25 Å) with carboxylic oxygens can be called hydrogen bonds. If so, they are definitely weak bonds and therefore not shown in Fig. 6. The layers are packed together by means of a hydrogen bond between the hydroxyl oxygen atom and a carboxyl oxygen atom. The hydrogen bonding is summarized in Table 9. Large mosaic spread, especially in the [001] direction, was observed for all crystals. This is probably caused by the fact that the layers are bonded together in that direction by a hydrogen bond which has limited directional properties involving the hydroxyl hydrogen atom.

Table 9. Hydrogen bonds

X is the donor atom and Y the acceptor. The parameters of Table 3 are used. The identification in parentheses specifies the operation which has to be performed.

$$\begin{aligned} (') &: x+\frac{1}{2}, y-\frac{1}{2}, z \\ (') &: x+\frac{1}{2}, y+\frac{1}{2}, z \\ (') &: \frac{1}{2}-x, y+\frac{1}{2}, 1-z \\ (') &: \frac{1}{2}-x, y+\frac{1}{2}, -z \end{aligned}$$

X	Y	XY	XH	YH	$\angle XHY$
O(w)	O(3')	2.69 Å	1.00 Å	1.72 Å	164°
O(w)	O(2'')	2.75	0.84	2.09	138
O(3)	O(2''')	2.68	0.79	1.94	156
N	O(1''')	3.18	1.06	2.19	160
N	O(2'')	3.25	1.04	2.36	140

The lengths and orientations of the axes of the vibration ellipsoids are shown in Table 10. All the ellipsoids have their major axis roughly parallel to the *a* axis and their minor axis approximately parallel to the *b* axis, while the relative values of the major to

Table 10. 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_{i1}	l_{i2}	l_{i3}
Ni	2.51	0.938	0.000	0.151
	1.33	-0.345	0.000	0.989
	0.52	0.000	1.000	0.000
O(1)	3.38	0.864	-0.001	0.322
	1.18	-0.451	-0.447	0.847
	0.59	-0.225	0.894	0.424
O(2)	5.42	0.896	-0.158	0.228
	1.86	-0.368	0.261	0.948
	1.02	0.249	0.952	-0.222
O(3)	8.57	0.957	0.001	0.094
	1.72	-0.282	-0.248	0.964
	0.83	-0.073	0.969	0.247
N	3.55	0.792	0.014	0.440
	1.51	-0.574	0.361	0.835
	0.75	0.210	0.932	-0.330
C(1)	2.80	0.880	0.042	0.289
	1.61	-0.472	-0.055	0.957
	0.78	-0.064	0.998	0.041
C(2)	3.41	0.968	0.000	0.052
	1.54	-0.250	-0.043	0.998
	0.60	-0.011	0.999	0.042
C(3)	4.65	0.865	-0.069	0.315
	2.38	-0.494	0.060	0.948
	1.11	0.089	0.996	-0.035
O(w)	3.23	0.934	-0.104	0.148
	2.05	-0.347	-0.037	0.988
	1.34	0.084	0.994	0.053
O(wf)	14.70	-0.856	0.000	0.677
	4.53	0.517	0.000	0.736
	1.58	0.000	1.000	0.000

minor axes are surprisingly large. Both these features can be correlated with two separate observations: the occurrence of the fractional molecule of water and the large mosaicity of the crystals. It can be concluded that the disturbing effect of the former predominates.

Computations

The absorption corrections were calculated on an I.B.M. 1410 with a program written by Dr P.J.Schapiro. The Fourier and Patterson syntheses were carried

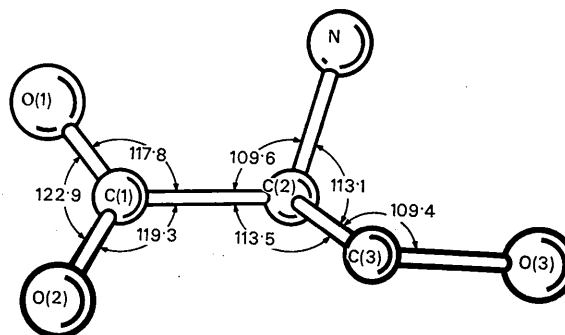


Fig. 4. Bond angles in ligand. E.s.d.'s are 0.6°.

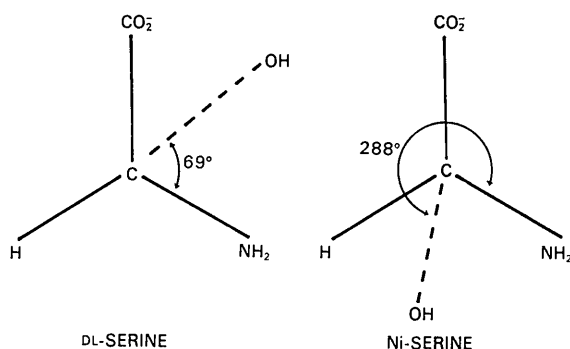


Fig. 5. Configuration of serine in DL-serine (A) and diaquo-bis(L-serinato)nickel(II) (B).

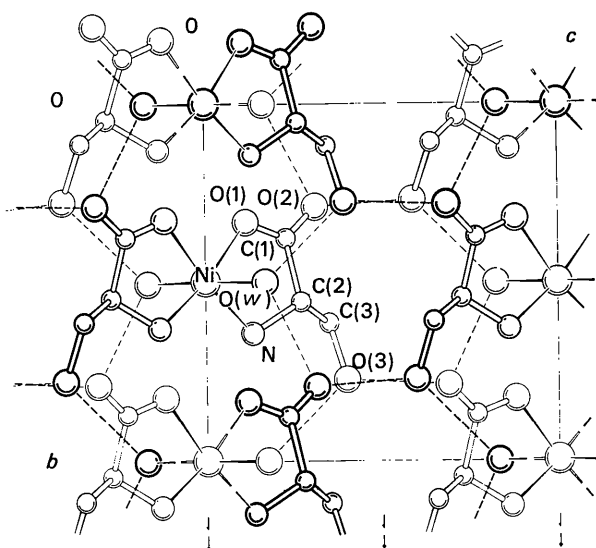


Fig. 6. Projection of the structure on a plane perpendicular to [100].

out on an IBM 1620 with a program written by King & van der Helm (1963), and on an IBM 360 with programs written by Ahmed (1966a) and Ahmed & Saunderson (1966). The structure factor-least squares computations were made on an IBM 1620 with a program written by van der Helm (1962) and adapted for card input-output by Rosenstein & Dutta (1964), and on an IBM 360 with a program written by Ahmed (1966b). Table 5 was prepared with a program written by Pippy (1967). All other computations were made with programs written in this laboratory.

The atomic scattering factors used were from *International Tables for X-ray Crystallography* (1962b), for the carbon, nitrogen and oxygen atoms and the nickel

ion. The oxygen atom in the carboxyl group complexed to the Ni-ion was taken as O⁻. The Af' for Ni using Cu $K\alpha$ radiation is given as -3.1 in *International Tables*, but it is assessed as an uncertain value due to the proximity of the absorption edge. During the refinement of the present structure this value was refined by least-squares methods and found to be -4.2 instead. The scattering factors for hydrogen atoms used were those of Stewart, Davidson & Simpson (1965).

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