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# Crystallographic Studies of Metal–Peptide Complexes. IX.* Disodium Bis(glycylglycinato)nickelate(II) Octahydrate and Disodium Bis(glycylglycinato)nickelate(II) Nonahydrate

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The structures of two glycylglycine complexes of $Ni^{II}$, disodium bis(glycylglycinato)nickelate(II) octahydrate and disodium bis(glycylglycinato)nickelate(II) nonahydrate, have been determined from three-dimensional X-ray counter data. The crystals of the octahydrate are monoclinic with $a = 27{\cdot}83$ (2), $b = 6{\cdot}19$ (1), $c = 13{\cdot}93$ (1) Å, $\beta = 121{\cdot}92$ (8)°, $Z = 4$ and space group $C2/c$. The crystals of the nonahydrate are triclinic with $a = 21{\cdot}33$ (1), $b = 5{\cdot}77$ (1), $c = 8{\cdot}79$ (1) Å, $\alpha = 99{\cdot}6$ (1), $\beta = 89{\cdot}5$ (1), $\gamma = 90{\cdot}1$ (1)°, $Z = 2$ and space group $P\bar{1}$. The positional and anisotropic thermal parameters for both structures have been refined by full-matrix least-squares methods. The final residual $R$, the number of independent observations, the number of unobservably weak reflections, and the mean e.s.d. of the positional parameters of the light atoms are: 0·047, 1859, 225 and 0·003 Å for the octahydrate, and 0·073, 3553, 682 and 0·006 Å for the nonahydrate respectively. The two types of crystals (which were formed simultaneously from the same mother liquor) contain the same anion, in which two mutually perpendicular glycylglycine residues act as tridentate ligands *via* their amino, peptide and carboxyl groups. The mean metal–ligand bond lengths are Ni–N(amino) = 2·14, Ni–N(peptide) = 1·99, and Ni–O(carboxyl) = 2·17 Å.

## Introduction

Previous papers in this series have described the structures of a number of $Cu^{II}$–peptide complexes. Two types of correlation have been established for these complexes (Freeman, 1967). Firstly, the order of the ligand-field effects of the main types of donor atoms present in peptides is N(amino) > N(peptide) > $OH_2$ > O(carboxyl) ≃ N(imidazole). Secondly, the stronger the ligand field of the four closest (equatorial) donor atoms is, the weaker are the bonds from a Cu atom to the axial donors.

In complexes of $Ni^{II}$ the properties which are affected by the ligand field include the magnetic character as well as the coordination geometry and the *d–d* transition energies. Octahedral and tetrahedral $Ni^{II}$ complexes are paramagnetic (high-spin) and generally blue/green; square-planar $Ni^{II}$ complexes are diamagnetic (low-spin) and generally yellow/orange. The transition from a high-spin octahedral configuration to a low-spin square-planar configuration may be caused by a tetragonal geometrical distortion, or by an electrostatic distortion (the replacement of one or more donor atoms by stronger-field donors). We are concerned particularly with the latter situation. The same ligand-field effects which cause a shift to shorter absorption wavelengths and lower coordination numbers among Cu–peptide complexes should cause transitions from high-spin octahedral to low-spin square-planar configurations among Ni–peptide complexes.

We embarked upon the present work in order to provide structural data to test the above hypothesis. A preliminary account of our results (Freeman, Guss & Sinclair, 1968) has already been used by other authors in the discussion of, for example, thermodynamic, spectroscopic and kinetic measurements on Ni–peptide complexes (Lim & Nancollas, 1971; Blair & Larsen, 1971; Margerum & Dukes, 1973). In this and the following paper (Freeman, Guss & Sinclair, 1978) we report, respectively, details of the structures of two complexes containing the bis(glycylglycinato)nickelate(II) ion† and two complexes containing the triglycylglycinatonickelate(II) ion.

## Experimental

Excess freshly precipitated and washed nickel hydroxide was added to a solution of glycylglycine (0·002 mol) in 1 *M* sodium hydroxide (1 ml). After removal of excess hydroxide, the two complexes were crystallized by the slow addition of a (1:1) mixture of methanol and acetone. The square blue plates and blue/green needles,

* Part VIII: Bear & Freeman (1976).

† Nomenclature: HGly-Gly$^{\pm}$ represents $^{+}NH_3CH_2CONHCH_2COO^{-}$, the zwitterion form of glycylglycine. The two complexes described in this paper are then $Na_2Ni(Gly\text{-}H_{-1}Gly)_2.8H_2O$ and $Na_2Ni(Gly\text{-}H_{-1}Gly)_2.9H_2O$ respectively. We also use the shorter forms $Na_2Ni(H_{-1}GG)_2.8H_2O$ and $Na_2(H_{-1}GG)_2.9H_2O$.

which formed simultaneously in different parts of the container, were subsequently shown to be $Na_2Ni(Gly\text{-}H_{-1}Gly)_2.8H_2O$ and $Na_2Ni(Gly\text{-}H_{-1}Gly)_2.9H_2O$ respectively. From its appearance, the latter compound corresponds to the complex isolated by Manyak, Murphy & Martell (1955) and described by them as $Na_2Ni(Gly\text{-}H_{-1}Gly)_2.10H_2O$. All diffraction measurements reported in this paper were made with Cu $K\alpha$ radiation [$\lambda(\text{Cu } K\alpha_1) = 1{\cdot}5405$ Å, $\lambda(\text{Cu } K\alpha_2) = 1{\cdot}5443$ Å] on an equi-inclination diffractometer.

## $Na_2Ni(Gly\text{-}H_{-1}Gly)_2.8H_2O$

### *Crystal data*

The complex crystallized with a monoclinic unit cell having $a = 27{\cdot}83$ (2), $b = 6{\cdot}19$ (1), $c = 13{\cdot}93$ (1) Å, $\beta = 121{\cdot}92$ (8)°, $V = 2037$ (8) Å$^3$, $D_m = 1{\cdot}66$ (2) (by flotation in $CHCl_3/CHBr_3$), $D_x = 1{\cdot}66$ g cm$^{-3}$, $Z = 4$ for FW 509·0, and $\mu(\text{Cu } K\alpha) = 24{\cdot}2$ cm$^{-1}$. The unit-cell dimensions were fitted by least squares to values of $\sin\theta$ for 13 high-angle reflections. The systematic absences ($hkl$ absent for $h + k = 2n + 1$, $h0l$ absent for $l = 2n + 1$) indicated that the space group was either $C2/c$ (centrosymmetric) or $Cc$ (noncentrosymmetric). The choice of the former is justified by the consistency of the structure refinement.

### *X-ray data*

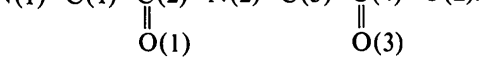
The data for this structure were recorded using one crystal of dimensions 0·10 × 0·21 × 0·12 mm, mounted parallel to the [010] direction. The intensity measurements were made with a partially automated Supper equi-inclination diffractometer (Freeman & Maxwell, 1969; Freeman, Guss, Nockolds, Page & Webster, 1970). Each reflection was measured by means of an $\omega$ scan at a constant rate of 0·05° s$^{-1}$. The counter aperture was 3°, and the scan range was either 2 or 3°. The intensity $I(hkl)$ of a reflection with integrated peak count $P$ and background counts $B_1$ and $B_2$ was given by $I = P - (B_1 + B_2)$, and its standard deviation by $\sigma(I) = [P + B_1 + B_2 + (0{\cdot}02P)^2 + 0{\cdot}05(B_1 + B_2)^2]^{1/2}$. 1859 independent reflections were measured. The rejection criterion for the 225 unobservably weak reflections (which were excluded from all subsequent calculations) was $I < 2\sigma(I)$. Standard Lorentz–polarization corrections were applied to produce a set of corrected structure amplitudes $F(hkl)$ and their standard deviations $\sigma(F) = (\text{Lp})^{1/2}\{[I + \sigma(I)]^{1/2} - I^{1/2}\}$. Absorption corrections were made by the Gaussian integration method of Coppens, Leiserowitz & Rabinovich (1965) using a (4 × 8 × 4) grid parallel to **a**, **b** and **c** respectively. The transmission factors were 0·74–0·82.

### *Solution and refinement*

The structure was solved by the use of standard Patterson and Fourier syntheses. The Ni atom was found to lie on a special position in space group $C2/c$, imposing a diad axis on the molecule. For the refinement, the function $\sum w(|F_o| - s|F_c|)^2$ was minimized by full-matrix least squares with the program *ORFLS* (Busing, Martin & Levy, 1962). The weights $w$ were given by $w = 1/\sigma^2(F)$.

Five cycles of refinement of the scale, positional and anisotropic thermal parameters resulted in a residual $R = \sum||F_0| - s|F_c||/\sum|F_0| = 0{\cdot}066$. A subsequent ($F_0 - F_c$) synthesis enabled the coordinates of the six H atoms bonded to C or N atoms to be determined. Inclusion of the 24 H atom parameters in the refinement reduced the residual to 0·057 – a significant decrease at the 95% confidence level (Hamilton, 1964). A further ($F_o - F_c$) synthesis using the new parameters enabled the remaining H atoms in the eight water molecules to be located. Continued refinement with the extra 32 variables once again resulted in a significant decrease of the residual to 0·047 for the observed reflections. The weighted residual $R_w = [\sum w(|F_o| - s|F_c|)^2/\sum wF_o^2]^{1/2}$ was 0·055. The isotropic thermal parameters, $B$, of the H atoms ranged from 1 (1) to 6 (2) Å$^2$. In the final cycle in which it was varied, no positional parameter changed by more than 0·04 e.s.d. for a nonhydrogen atom, or more than 0·3 e.s.d. for a H atom. The corresponding maximum changes in thermal parameters were 0·1 and 0·5 e.s.d. respectively. The final ($F_o - F_c$) synthesis showed no excursions of magnitude greater than 0·3 e Å$^{-3}$.

The atomic scattering factors used were those for $Ni^{2+}$, $Na^+$, C, O and N (Cromer & Waber, 1965) and H (Stewart, Davidson & Simpson, 1965). The real part of the correction for anomalous dispersion, −3·1 e (*International Tables for X-ray Crystallography*, 1962), was added to the $Ni^{2+}$ values over the entire range of $\sin\theta$. The values of the final positional parameters are listed in Table 1.* The peptide chain is labelled from the N(amino) end:




## $Na_2Ni(Gly\text{-}H_{-1}Gly)_2.9H_2O$

### *Crystal data*

The complex crystallized with a triclinic unit cell having $a = 21{\cdot}33$ (1), $b = 5{\cdot}77$ (1), $c = 8{\cdot}79$ (1) Å, $\alpha =$

* Lists of structure factors, thermal parameters, bond lengths and angles involving H atoms, and bond angles at hydrogen-bonded atoms for both compounds, and Table 3, have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33516 (44 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic positional parameters in fractional coordinates* ($\times 10^4$, *for* H $\times 10^3$) *for disodium bis(glycylglycinato)nickelate*(II) *octahydrate*

Numbers in parentheses are estimated standard deviations in the units of the least significant digit of the preceding number.

| | *x* | *y* | *z* |
|---|---|---|---|
| Ni | 0 | 728 (1) | 2500 |
| Na | 2489 (0·6) | 2213 (2) | 2274 (1) |
| O(1) | 1683 (1) | 2369 (4) | 4134 (3) |
| O(2) | 112 (1) | −1838 (4) | 3665 (5) |
| O(3) | 764 (1) | −3894 (4) | 5045 (2) |
| O(4) | 2472 (1) | 4401 (5) | 3807 (2) |
| O(5) | 1868 (1) | 5033 (4) | 1093 (2) |
| O(6) | 3170 (1) | 4802 (5) | 2529 (3) |
| O(7) | 4232 (1) | 3145 (5) | 4021 (3) |
| N(1) | 252 (1) | 3023 (5) | 1704 (3) |
| N(2) | 837 (1) | 646 (4) | 3530 (2) |
| C(1) | 834 (1) | 3738 (6) | 2521 (3) |
| C(2) | 1142 (1) | 2135 (5) | 3472 (3) |
| C(3) | 1083 (1) | −988 (6) | 4402 (3) |
| C(4) | 616 (1) | −2336 (5) | 4364 (3) |
| H(1) | 27 (2) | 228 (6) | 113 (3) |
| H(2) | 12 (2) | 405 (8) | 159 (4) |
| H(3) | 107 (2) | 399 (6) | 208 (3) |
| H(4) | 85 (2) | 525 (8) | 301 (4) |
| H(5) | 134 (2) | −209 (5) | 429 (3) |
| H(6) | 131 (2) | −32 (7) | 519 (4) |
| H(7) | 217 (2) | 418 (8) | 387 (4) |
| H(8) | 270 (2) | 412 (8) | 433 (4) |
| H(9) | 148 (3) | 469 (9) | 73 (5) |
| H(10) | 190 (2) | 566 (7) | 70 (4) |
| H(11) | 317 (3) | 519 (9) | 200 (5) |
| H(12) | 346 (2) | 446 (7) | 288 (4) |
| H(13) | 453 (2) | 306 (7) | 393 (4) |
| H(14) | 429 (2) | 211 (9) | 434 (5) |

99·6 (1), $\beta = 89·5$ (1), $\gamma = 90·1$ (1)°, $V = 1066$ (4) Å$^3$, $D_m = 1·61$ (2) (by flotation in $CHCl_3/CHBr_3$), $D_x = 1·64$ g cm$^{-3}$, $Z = 2$ for FW 527·0, and $\mu$(Cu $K\alpha$) = 24·2 cm$^{-1}$. The unit-cell dimensions were fitted by least squares to values of sin $\theta$ for 49 high-angle reflections. The diffraction symmetry indicated that the space group was $P\bar{1}$ or $P1$, and the choice of the former was corroborated by the structure analysis.

### *X-ray data collection*

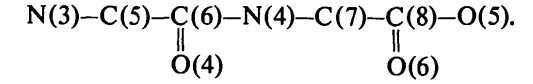
The data for this structure were recorded on the same diffractometer as was used for the previous compound, but with the instrument operated under computer control (Freeman *et al.*, 1970). The dimensions of the crystal were 0·07 × 0·24 × 0·10 mm. The reflection intensities were measured with the crystal rotating about the [010] direction. The control parameters for the scan-range calculations as defined in Freeman *et al.* (1970) were: $\Delta\lambda = 0·007$ Å, $X = 0·6$°, $\varphi_m = 1·0$°, $P = 0·001$, $\delta\mu = 0·05$°. The scan speed was set at 0·05° s$^{-1}$, and the counter aperture was 3°. The data were corrected for the usual effects, as described for the preceding structure. The absorption corrections were computed for a (2 × 6 × 4) grid parallel to **a**, **b** and **c** respectively. The transmission factors were 0·74–0·85. There were 3553 independent reflections; these included 682 reflections with $I < 2\sigma(I)$ which were omitted from all subsequent calculations.

### *Solution and refinement*

The structure was solved by means of standard Patterson and Fourier syntheses. The two glycylglycine residues in the complex anion are unrelated by crystallographic symmetry, unlike those in the octahydrate complex, which are related by a twofold axis. Two $Na^+$ ions were found to lie on special positions in space group $P\bar{1}$. A third $Na^+$ ion is in a general position.

The structure was refined using the same method as for the preceding analysis. However, plots of $||F_o| - s|F_c||$ against $|F_o|$ and $\sin^2\theta/\lambda^2$ revealed systematic trends which were represented better by weights $w = 1 - \exp[-20(\sin\theta/\lambda + 0·18)^2]$ than by the 'statistical' weights $w = 1/\sigma^2(F)$. The 12 H atoms which were bonded to C or N atoms were included in the calculated structure amplitudes. Their positions were calculated after each cycle of least squares. Their isotropic temperature factors were given fixed values of 7 Å$^2$. It was assumed that two H atoms lie at 1·05 Å from a C (or 0·95 Å from a N) atom in a plane which bisects the angle between the other two bonds formed by that atom, and that the angle between the two C—H or N—H bonds is 109·5°. After eight cycles of refinement the residual and weighted residual for the observed reflections converged to 0·073 and 0·092 respectively. In the final cycle in which it was varied no positional parameter shifted by more than 0·1 standard deviation and no thermal parameter by more than 0·5 standard deviation. An $(F_o - F_c)$ synthesis calculated using the final values of the parameters had no excursions of magnitude greater than 0·5 e Å$^{-3}$.

The final positional parameters are listed in Table 2.* The numbering of one peptide chain is the same as in $Na_2Ni(H_{-1}GG)_2.8H_2O$. The second peptide chain is labelled:




## Description of the structure

The complex anions in the two compounds are chemically identical. Each Ni atom is coordinated by two tridentate glycylglycinate residues. The metal is bound to each dipeptide at the N(amino), N(peptide) and O(carboxyl) atoms. The approximate planarity of each ligand confirms that the Ni-binding N(peptide)

* See deposition footnote.

Table 2. *Atomic positional parameters in fractional coordinates* ($\times 10^4$) *for disodium bis(glycylglycinato)-nickelate(II) nonahydrate, including the calculated positions of the hydrogen atoms*

Numbers in parentheses are estimated standard deviations in the units of the least significant digit of the preceding number.

| | *x* | *y* | *z* |
|---|---|---|---|
| Ni | 2372 (0·4) | 1608 (2) | 673 (1) |
| Na(1) | 5000 | 0 | 0 |
| Na(2) | 5000 | 0 | 5000 |
| Na(3) | 209 (1) | 2236 (5) | 3949 (2) |
| O(1) | 1448 (2) | 2790 (9) | −3206 (5) |
| O(2) | 1719 (2) | −990 (8) | 1247 (4) |
| O(3) | 831 (2) | −2884 (11) | 481 (7) |
| O(4) | 3324 (2) | 4756 (8) | 4505 (5) |
| O(5) | 3091 (2) | −1052 (7) | −53 (4) |
| O(6) | 4032 (2) | −2248 (8) | 607 (15) |
| O(7) | 4388 (3) | 3022 (9) | −764 (6) |
| O(8) | 4068 (3) | 1999 (9) | 6062 (5) |
| O(9) | 4475 (2) | −3526 (9) | 3421 (6) |
| O(10) | 4851 (2) | −2092 (9) | 7261 (6) |
| O(11) | 776 (2) | 5747 (9) | 5166 (6) |
| O(12) | 226 (3) | 3413 (13) | 1525 (6) |
| O(13) | 1177 (2) | −129 (9) | 4131 (5) |
| O(14) | 194 (2) | 1608 (8) | 6638 (5) |
| O(15) | 3519 (2) | 8173 (10) | 6923 (6) |
| N(1) | 2823 (2) | 3760 (10) | −752 (6) |
| N(2) | 1792 (2) | 1207 (10) | −1112 (6) |
| N(3) | 1896 (2) | 4315 (9) | 2233 (6) |
| N(4) | 2952 (2) | 2100 (9) | 2462 (5) |
| C(1) | 2408 (3) | 4144 (12) | −2008 (7) |
| C(2) | 1836 (3) | 2570 (10) | −2123 (6) |
| C(3) | 1253 (3) | −292 (11) | −1093 (7) |
| C(4) | 1263 (3) | −1506 (11) | 313 (7) |
| C(5) | 2327 (3) | 5423 (11) | 3411 (7) |
| C(6) | 2918 (2) | 3955 (10) | 3478 (6) |
| C(7) | 3511 (2) | 690 (12) | 2387 (7) |
| C(8) | 3554 (3) | −1003 (10) | 858 (6) |
| H(1) | 2261 | 5899 | −1807 |
| H(2) | 2659 | 3791 | −3051 |
| H(3) | 3197 | 3015 | −1178 |
| H(4) | 2926 | 5239 | −148 |
| H(5) | 1257 | −1568 | −2097 |
| H(6) | 845 | 724 | −1060 |
| H(7) | 2457 | 7073 | 3157 |
| H(8) | 2099 | 5634 | 4484 |
| H(9) | 1556 | 3648 | 2711 |
| H(10) | 1743 | 5467 | 1673 |
| H(11) | 3504 | −283 | 3296 |
| H(12) | 3906 | 1797 | 2494 |

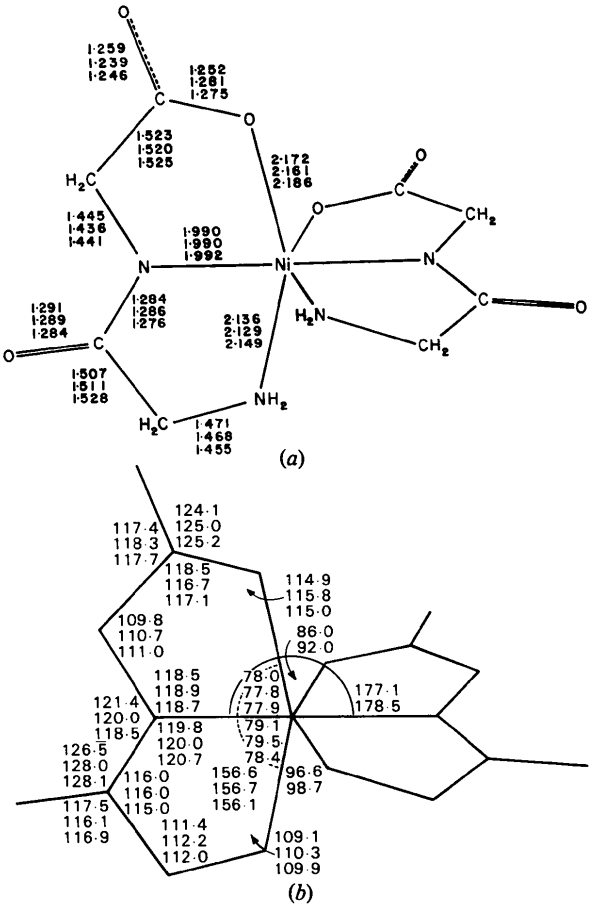



Fig. 2. (*a*) Bond lengths (Å) and (*b*) bond angles (°) of the bis(glycylglycinato)nickelate(II) anion. The values are taken (in descending order in each group of three values) from $Na_2Ni(H_{-1}GG)_2.8H_2O$, ligand 1 of $Na_2Ni(H_{-1}GG)_2.9H_2O$, and ligand 2 of $Na_2Ni(H_{-1}GG)_2.9H_2O$. Additional bond angles involving donor atoms of two *different* ligands are: $NH_2$–Ni–O(carboxyl) = 93·2, 88·1, 90·5°; $NH_2$–Ni–N(peptide) = 102·9, 99·5, 100·6°; N(peptide)–Ni–N(peptide) = 99·8, 103·1, 103·3°. Estimated standard deviations (*L* = light atom):

| | $Na_2Ni(H_{-1}GG)_2.8H_2O$ | $Na_2Ni(H_{-1}GG)_2.9H_2O$ |
|---|---|---|
| Ni–*L* | 0·003 Å | 0·005 Å |
| *L*–*L* | 0·005 | 0·008 |
| *L*–Ni–*L* | 0·15° | 0·2° |
| Ni–*L*–*L* | 0·2 | 0·4 |
| *L*–*L*–*L* | 0·3 | 0·5. |

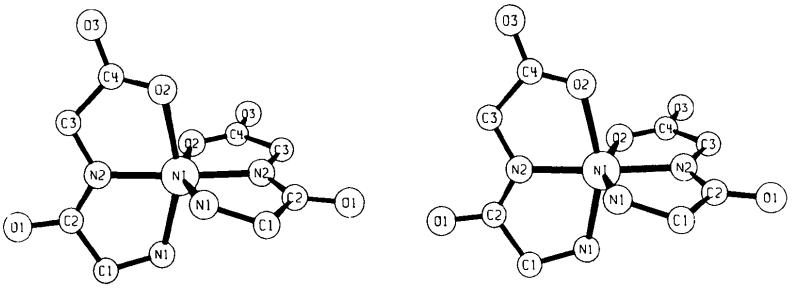


Fig. 1. A stereoscopic view of one bis(glycylglycinato)nickelate(II) anion in $Na_2Ni(Gly\text{-}H_{-1}Gly)_2.8H_2O$. Drawings were made with the program *ORTEP* (Johnson, 1965).

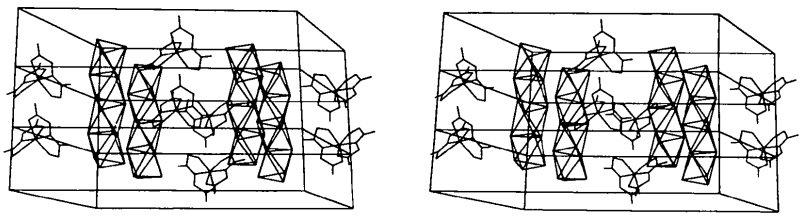


Fig. 3. A stereoscopic view of part of the contents of three unit cells of $Na_2Ni(Gly\text{-}H_{-1}Gly)_2.8H_2O$. The direction of **b** is upwards, **a** is left to right, and **c** is towards the observer. The $Na^+$–$O_6$ polyhedra are represented by lines drawn between the O atoms.

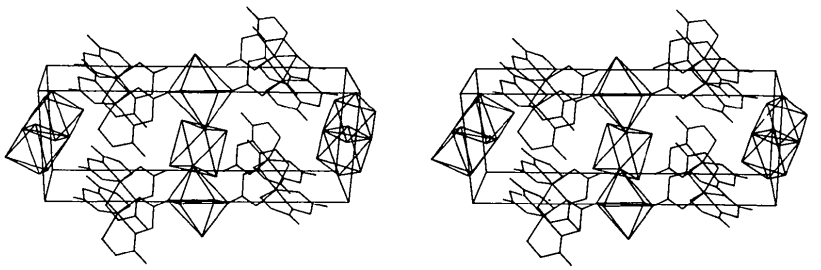


Fig. 4. A stereoscopic view of a unit cell of $Na_2Ni(Gly\text{-}H_{-1}Gly)_2.9H_2O$. The direction of **c** is upwards, **a** is left to right, and **b** is away from the observer.

atom is deprotonated. The coordination is the same as in $Cu(Gly\text{-}H_{-1}Gly).3H_2O$ (Strandberg, Lindqvist & Rosenstein, 1961), but since there are two glycylglycinates per metal atom the complex ions carry double negative charges. A stereoscopic view of one anion is shown in Fig. 1. The dimensions are given in Fig. 2.

The unit cells of both the octahydrate and the nonahydrate have negatively and positively charged regions. The negative regions contain the $Ni(Gly\text{-}H_{-1}Gly)_2^{2-}$ ions. The positive regions consist of $Na^+$ ions surrounded by octahedra consisting mostly of water molecules. Adjacent Na–O polyhedra form chains by sharing faces (in the octahydrate), edges and corners (in the nonahydrate). The chains and sheets of Na–O polyhedra are arranged differently in the two types of crystal (Figs. 3 and 4).

### *The ligand molecules*

The two structures contain a total of three crystallographically independent glycylglycinate residues: one in $Na_2Ni(H_{-1}GG)_2.8H_2O$ and two in $Na_2Ni(H_{-1}GG)_2.9H_2O$. There are no differences greater than three standard deviations between corresponding bond distances and angles in the three ligands (Fig. 2). The dimensions of the dipeptide residues are the same as those of the free ligand, except for a slight lengthening of the C′=O(peptide) and shortening of the N(peptide)–C′ bonds. These changes are characteristic of metal binding at N(peptide) atoms (Freeman, 1967).

### *Metal–ligand bonds*

The average Ni–N(amino) and Ni–O(carboxyl) distances in the present complexes are 2·14 and 2·17 Å respectively. Corresponding values taken from recent structure analyses are 2·08 (1) and 2·06 (1) Å in diaquabis(glycinato)nickel(II) (Freeman & Guss, 1968), 2·100 (5) and 2·012 (5) Å in diaquabis(L-serinato)nickel(II) (van der Helm & Hossain, 1969), and 2·103 (4) and 2·071 (3)–2·108 (3) Å in bis(glycinato)bis(imidazole)nickel(II) (Freeman & Guss, 1972). The significant lengthening of these bonds in the dipeptide complexes is probably caused by the presence of the central Ni–N(peptide) bonds which are relatively stronger (1·99 Å) than the Ni–O and Ni–N bonds to the remaining unidentate ligands in the amino-acid complexes (2·07–2·10 Å).

### *Peptide groups*

The peptide groups $C_\alpha$–CO–N in both structures are planar within the limits of precision. The Ni and $C'_\alpha$ atoms lie at distances of 0·16–0·42 and 0·00–0·07 Å from the peptide group planes, respectively. The configurations of the bonds at the N(peptide) atoms are approximately trigonal-planar. The deviations of individual atoms from the planes fitted to various groups of atoms are given in Table 3.*

* See deposition footnote.

### $Na^+$ *ions and hydrogen bonds in* $Na_2Ni(H_{-1}GG)_2.8H_2O$

Each $Na^+$ ion is at the centre of a distorted octahedron of O atoms belonging to three water molecules, O(4), O(5) and O(6), and their symmetry-related equivalents, O(4′), O(5′) and O(6′) (Table 4). Adjacent Na–O octahedra share faces to form $-Na^+-(H_2O)_3-Na^+-(H_2O)_3-$ chains which run in the [010] direction. The chains are packed to form sheets parallel to the (100) planes (Fig. 3).

The hydrogen-bonding scheme is shown in Table 5. The H atom positions are known from the structure analysis. Each of the water molecules O(4), O(5) and O(6) forms two hydrogen bonds and has contacts with two $Na^+$ ions. The water molecule O(7) forms three hydrogen bonds. The hydrogen bonds link the $-Na^+-(H_2O)_3-$ chains to the peptide complexes:

O(peptide)···H–O(4)–H···O(peptide)

O(peptide)···H–O(5)–H···O(carboxyl)

O(peptide)···H–O(6)–H···O(7)–H···O(carboxyl)
H
O(carboxyl)–Ni.

Two features of the hydrogen bonding are unusual. The O(peptide) atom O(1) makes contacts in the range 2·77 to 3·01 Å with four water molecules. These have all been included in Table 5, although the longest one or two are on the borderline between weak hydrogen bonds and non-bonded contacts. The N(amino) atom, on the other hand, forms no hydrogen bonds at all. The positions of the two H(amino) atoms were determined unequivocally, are consistent with an approximately tetrahedral bond configuration for the $-NH_2$ group, and are inconsistent with hydrogen bonding between the N(amino) atom and its nearest neighbours. Two contacts with the N(amino) atom, N(1)···O($2^{viii}$) = 3·13 Å and N(1)···O($3^{xii}$) = 3·21 Å, are thereby identified as non-bonded contacts. These are the only contacts shorter than 3·3 Å between adjacent anions.

Table 4. *Dimensions of the sodium ion–water polyhedra*

(*a*) Interatomic distances (Å) in $Na_2Ni(Gly\text{-}H_{-1}Gly)_2.8H_2O$

Atoms marked with a prime are at $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$.

| | Distance from Na | | Distance from Na |
|---|---|---|---|
| O(4) | 2·550 (4) | O(5′) | 2·428 (4) |
| O(4′) | 2·343 (4) | O(6) | 2·361 (4) |
| O(5) | 2·394 (5) | O(6′) | 2·487 (4) |

(*b*) Interatomic distances (Å) in $Na_2Ni(Gly\text{-}H_{-1}Gly)_2.9H_2O$

The superscript symbols are explained in Table 6.

| | Distance from Na(1) | | Distance from Na(3) |
|---|---|---|---|
| O(6) | 2·535 (6) | O(11) | 2·448 (6) |
| O(7) | 2·372 (6) | O($11^{iii}$) | 2·461 (6) |
| O($10^{i}$) | 2·528 (6) | O(12) | 2·343 (6) |
| | | O(13) | 2·500 (6) |
| | Distance from Na(2) | O(14) | 2·451 (6) |
| | | O($14^{ii}$) | 2·352 (7) |
| O(8) | 2·403 (5) | | |
| O(9) | 2·527 (6) | | |
| O(10) | 2·510 (6) | | |

### $Na^+$ *ions and hydrogen bonds in* $Na_2Ni(H_{-1}GG)_2.9H_2O$

There are three crystallographically independent types of $Na^+$ ion in this structure (Table 4). They belong to two independent chains of Na–O octahe-

Table 5. *Hydrogen bonds in* $Na_2Ni(Gly\text{-}H_{-1}Gly)_2.8H_2O$

A list of bond angles at hydrogen-bonded atoms has been deposited.

Symmetry code

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| None | $x$, | $y$, | $z$ | | | | | |
| (i) | $\frac{1}{2}-x$, | $-\frac{1}{2}+y$, | $\frac{1}{2}-z$ | (v) | $\frac{1}{2}-x$, | $\frac{1}{2}+y$, | $\frac{1}{2}-z$ | (ix) | $x$, | $1-y$, | $\frac{1}{2}+z$ |
| (ii) | $\frac{1}{2}-x$, | $\frac{1}{2}-y$, | $1-z$ | (vi) | $\frac{1}{2}+x$, | $\frac{1}{2}+y$, | $z$ | (x) | $x$, | $-y$, | $\frac{1}{2}+z$ |
| (iii) | $x$, | $1-y$, | $-\frac{1}{2}+z$ | (vii) | $\frac{1}{2}-x$, | $-\frac{1}{2}-y$, | $1-z$ | (xi) | $-\frac{1}{2}+x$, | $-\frac{1}{2}+y$, | $z$ |
| (iv) | $x$, | $-y$, | $-\frac{1}{2}+z$ | (viii) | $-x$, | $y$, | $\frac{1}{2}-z$ | (xii) | $-x$, | $1+y$, | $\frac{1}{2}-z$ |

Hydrogen-bond lengths (Å)

Estimated standard deviations: $d_{O-H} = 0.04$ Å, $d_{H\cdots O} = 0.04$ Å, and $d_{O\cdots O} = 0.005$ Å.

| O–H···O | Equivalent bond O···H–O | $d_{O-H}$ | $d_{H\cdots O}$ | $d_{O\cdots O}$ |
|---|---|---|---|---|
| O(4)–H(7)···O(1) | – | 0·89 | 1·95 | 2·769 |
| O(4)–H(8)···O($1^{ii}$) | O(1)···H($8^{ii}$)–O($4^{ii}$) | 0·69 | 2·12 | 2·798 |
| O(5)–H(10)···O($1^{iii}$) | O(1)···H($10^{ix}$)–O($5^{ix}$) | 0·72 | 2·28 | 2·968 |
| O(5)–H(9)···O($3^{iv}$) | O(3)···H($9^{x}$)–O($5^{x}$) | 0·94 | 1·77 | 2·707 |
| O(6)–H(11)···O($1^{v}$) | O(1)···H($11^{i}$)–O($6^{i}$) | 0·77 | 2·28 | 3·011 |
| O(6)–H(12)···O(7) | – | 0·71 | 2·05 | 2·759 |
| O(7)–H(13)···O($2^{vi}$) | O(2)···H($13^{xi}$)–O($7^{xi}$) | 0·91 | 1·84 | 2·743 |
| O(7)–H(14)···O($3^{vii}$) | O(3)···H($14^{vii}$)–O($7^{vii}$) | 0·75 | 2·20 | 2·932 |

dra: $-[Na^+(H_2O)_3(O_{carboxyl})]-(H_2O)-[Na^+(H_2O)_4]-(H_2O)-$ linking Na(1) and Na(2) octahedra parallel to the [001] direction, and $-[Na^+(H_2O)_2]-(H_2O)_2-[Na^+(H_2O)_2]-(H_2O)_2-$ linking Na(3) octahedra parallel to the [010] direction respectively. As in the octahydrate, the chains are packed into sheets which separate the layers of complex anions. The ions Na(1) and Na(2) lie on alternate centres of symmetry at $(\frac{1}{2},0,0)$ and $(\frac{1}{2},0,\frac{1}{2})$. The coordination octahedra of adjacent ions share corners occupied by water molecules O(10). All except one of the other octahedron corners are also occupied by water molecules. The exception is an O(carboxyl) atom O(6) which interacts with Na(1).

The ion Na(3) is in a general position. Its O octahedron shares two edges with neighbouring octahedra. The shared octahedron edges are skew, *i.e.* they are not parallel and do not have a common corner. They have their centres on the symmetry centres at $(0,0,\frac{1}{2})$ and $(0,\frac{1}{2},\frac{1}{2})$.

The coordinates of the H atoms in the nonahydrate were not determined directly during the structure analysis, but the hydrogen-bonding scheme can be deduced unequivocally (Table 6). In contrast to the bonding in the octahydrate, there are direct N(amino)–H···O(carboxyl) links between neighbouring complexes. Hydrogen bonds from the water molecules link each glycylglycinate ligand exclusively to one chain of Na–O octahedra. The peptide and carboxyl O atoms of ligand 1, O(1) to O(3), are hydrogen-bonded only to the water molecules O(11) to O(14) which are associated with Na(3). Ligand 2 [atoms O(4) to O(6)] accepts hydrogen bonds only from the water molecules O(7) to O(10) around Na(1) and Na(2), and from a free water molecule, O(15).

Table 6. *Hydrogen bonds in* $Na_2Ni(Gly\text{-}H_{-1}Gly)_2.9H_2O$

A list of bond angles at hydrogen-bonded atoms has been deposited.

Symmetry code

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| None | $x$, | $y$, | $z$ | (viii) | $x$, | $y$, | $1+z$ |
| (i) | $x$, | $y$, | $-1+z$ | (ix) | $-x$, | $-y$, | $-z$ |
| (ii) | $-x$, | $-y$, | $1-z$ | (x) | $x$, | $1+y$, | $1+z$ |
| (iii) | $-x$, | $1-y$, | $1-z$ | (xi) | $x$, | $-1+y$, | $-1+z$ |
| (iv) | $x$, | $1+y$, | $z$ | (xii) | $1-x$, | $-y$, | $1-z$ |
| (vi) | $x$, | $-1+y$, | $z$ | (xiii) | $1-x$, | $-y$, | $-z$ |
| (vii) | $1-x$, | $-1-y$, | $1-z$ | | | | |

Hydrogen-bond lengths (Å)

'H–' indicates a proton donor.

| | Equivalent bond | $d_{N\cdots O}$ or $d_{O\cdots O}$ |
|---|---|---|
| O(7)–H···O(6$^{iv}$) | O(6)···H–O(7$^{vi}$) | 2·893 (8) |
| O(7)–H···O(8$^{i}$) | O(8)···H–O(7$^{viii}$) | 2·841 (8) |
| O(8)–H···O(4) | – | 2·777 (7) |
| O(8)–H···O(15$^{vi}$) | O(15)···H–O(8$^{iv}$) | 2·712 (8) |
| O(9)–H···O(4$^{vi}$) | O(4)···H–O(9$^{iv}$) | 2·860 (7) |
| O(9)–H···O(6) | – | 2·866 (7) |
| O(10)–H···O(9$^{vii}$) | O(9)···H–O(10$^{vii}$) | 2·885 (8) |
| O(10)–H···O(15$^{vi}$) | O(15)···H–O(10$^{iv}$) | 2·865 (8) |
| O(11)–H···O(1$^{viii}$) | O(1)···H–O(11$^{i}$) | 2·809 (7) |
| O(11)–H···O(13$^{iv}$) | O(13)···H–O(11$^{vi}$) | 2·815 (8) |
| O(12)–H···O(3$^{iv}$) | O(3)···H–O(12$^{vi}$) | 2·774 (8) |
| O(12)–H···O(3$^{ix}$) | O(3)···H–O(12$^{ix}$) | 2·859 (8) |
| O(13)–H···O(1$^{viii}$) | O(1)···H–O(13$^{i}$) | 2·710 (7) |
| O(13)–H···O(2) | – | 2·746 (7) |
| O(14)–H···O(1$^{viii}$) | O(1)···H–O(14$^{i}$) | 2·756 (8) |
| O(15)–H···O(4) | – | 2·680 (7) |
| O(15)–H···O(5$^{x}$) | O(5)···H–O(15$^{xi}$) | 2·768 (7) |
| N(1)–H(2)···O(5$^{iv}$) | O(5)···H(2$^{vi}$)–N(1$^{vi}$) | 3·007 (9) |
| N(3)–H(8)···O(2$^{iv}$) | O(2)···H(8$^{vi}$)–N(3$^{vi}$) | 3·007 (8) |

## Chemical significance

### *General considerations*

The complexes formed by peptides with a number of transition-metal ions at low pH undergo additional proton dissociations when the pH is raised. At low pH the metal atoms are chelated *via* the terminal amino group and the O of the first peptide (= amide) group of the ligands. At higher pH, up to three protons are lost successively from the peptide groups. The deprotonations are accompanied by the formation of metal–N(peptide) bonds. Potentiometric-titration, spectroscopic and kinetic data for the deprotonation and complexation reactions are supported by crystal structures (many still available only as preliminary publications) in the cases of $Cu^{II}$, $Ni^{II}$, $Co^{III}$ and $Pt^{II}$ (Freeman, 1973).

In tri- and tetrapeptide (and amino-acid amide) complexes of $Ni^{II}$ the loss of peptide protons is accompanied by a change in colour from pale green or blue to yellow, and by a change from paramagnetic to diamagnetic properties. It may be inferred that the formation of the Ni–N(peptide) bonds leads to a transition from octahedral to square-planar coordination (Manyak, Murphy & Martell, 1955; Martin, Chamberlin & Edsall, 1960; Kim & Martell, 1967). This transition can be rationalized in simple ligand-field-theory terms: N(peptide) atoms are stronger-field donors compared with O(peptide) atoms, and the crystal field stabilization energy (CFSE) of square-planar $Ni^{II}$ is considerably larger than that of octahedral $Ni^{II}$ with respect to identical ligands. The CFSE is further enhanced by the shorter metal–ligand bond lengths in the square-planar compared with the octahedral complexes (Paniago & Margerum, 1972; Margerum & Dukes, 1973; Freeman, Guss & Sinclair, 1978).

### *Anomalous behaviour of* Ni–*dipeptide complexes*

The $Ni^{II}$ complexes of glycylglycine and other dipeptides are anomalous in relation to all other classes of Ni–peptide complexes. On the one hand, the Ni atoms are bonded to deprotonated N(peptide) atoms of the glycylglycinate residues. This is shown by the

coplanarity of the Ni atoms and the peptide groups. On the other hand, the solutions of Ni–dipeptide complexes remain blue even at high pH (Martin *et al.*, 1960; Mason, Chamberlain & Wilkins, 1971) and there is now no doubt that the $Ni(Gly\text{-}H_{-1}Gly)_2^{2-}$ anions remain octahedral. According to the arguments presented in the preceding section there should be a considerable gain in CFSE if $Ni(H_{-1}GG)_2^{2-}$ adopted a bis(bidentate) square-planar configuration with the Ni bonded to two N(amino) and two N(peptide) atoms, instead of the bis(tridentate) octahedral configuration which is actually found.

The retention of an octahedral configuration by the bis(dipeptide) complexes is particularly curious in view of the behaviour of the related bis(amino-acid amide) complexes. At high pH, the 1:2 Ni–glycinamide complex loses two protons to form the *yellow* complex $Ni(NH_2CH_2CONH)_2$ (Martin, Chamberlin & Edsall, 1960; Komorita, Hidaka & Shimura, 1968; Mason *et al.*, 1971). The analogous yellow complex bis(L-prolinamidato)nickel(II) dihydrate has been shown by crystal structure analysis to have square-planar N(amino)–N(peptide) coordination (Tsukihara, Katsube, Fujimori & Ishimura, 1972).

What causes two glycylglycinate ligands in $Ni(H_{-1}GG)_2^{2-}$ to remain tridentate and mutually perpendicular, while the ligand field of two N(amino) and two N(peptide) donors alone causes a change to square-planar coordination in the case of glycinamidate? Antecedent authors have largely by-passed this question. Unfortunately, there are no thermodynamic data available for the $Ni(GG)_2 \rightarrow Ni(H_{-1}GG)_2^{2-}$ deprotonation reaction. The only reported attempt to make the necessary calorimetric measurements was frustrated by the precipitation of $Ni(OH)_2$ (Lim & Nancollas, 1971). The contribution of the present work is to eliminate structural features (such as abnormal metal–ligand interactions, intramolecular hydrogen bonds) as causes of the unique behaviour of Ni–dipeptide complexes.

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