Crystal Structures of Four Nickel Complexes of Glycine and Glycine Peptides

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THE complexes formed by nickel(II) with amino-acids and peptides at low pH are blue or blue-green. As the pH is raised, the Ni^{II} complexes of the glycyl-peptides with three or more residues turn yellow, corresponding to a transition from paramagnetic to diamagnetic species and from octahedral to square-planar co-ordination.[1,2] The dissociation of protons from the peptide groups accompanies this transition.[1,3] In the case of glycylglycine, the colour does not change to yellow at high pH, but dissociation of the peptide protons at pH ~10 has been established from potentiometric titration data by Martin *et al.*[1] (though not in a similar study by Kim and Martell[3]). We now report the results of *X*-ray crystal-structure analyses of one Ni^{II}–amino-acid and of three Ni^{II}–peptide complexes prepared at high pH.

The structural information available in this area is limited to four reported crystal structure analyses[4–7] of bis-(α-aminoacidato)Ni^{II} complexes. Only for the histidine derivative have the results of a three-dimensional refinement been published.[6] In order to obtain accurate metal–ligand bond-lengths and angles from a simple structure for comparison with related but more complicated complexes, we first re-examined the structure of diaquobisglycinatonickel(II). This was determined in 1945[4] from three two-dimensional, incompletely resolved, projections. The structure is shown in Figure 1, and some results from the three-dimensional refinement are shown in the Table.

Solutions of the bisglycylglycinato complex of Ni^{II} at pH 10—12 yielded two types of crystals. These differed in colour, composition, and crystal symmetry. Structure analyses showed that both were disodium salts of the same bisglycylglycinato-nickelate(II) ion, one being an octahydrate

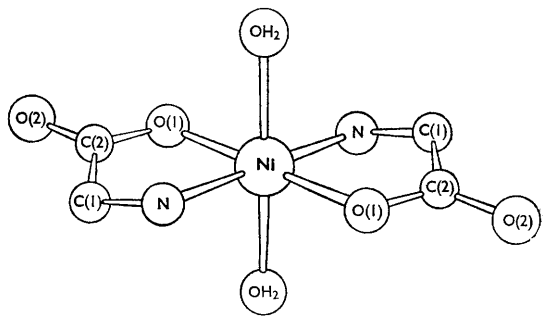

FIGURE 1. *Structure of diaquobisglycinatonickel*(II).

(monoclinic) and the other a nonahydrate (triclinic). In each structure, two glycylglycine molecules act as tridentate chelates through their N(amino), N(peptide), and O(carboxyl) atoms.

Summary of metal–ligand bond lengths and angles
(*E.s.d.'s*: *bond lengths*, ~0·01 Å; *angles*, ~0·4°)

Complex	$Ni(Gly)_2(H_2O)_2$	$Na_2Ni(Gly–Gly)_2,8H_2O$ (monoclinic)	$Na_2Ni(Gly–Gly)_2,9H_2O$ (triclinic)		$Na_2Ni(Gly–Gly–Gly–Gly),8H_2O$
Bond or angle					
Ni–N(1)(amino)	2·08 Å	2·14 Å	2·11 Å	2·15 Å	1·93 Å
Ni–N(2)(peptide)		1·99	2·01	2·02	1·84
Ni–N(3)(peptide)					1·83
Ni–N(4)(peptide)					1·87
Ni–O(carboxyl)	2·06	2·17	2·16	2·18	
Ni–O(water)	2·10				
N(amino)–Ni–N(peptide) *or* O(carboxyl)	81·1°	79·1°	79·9°	78·9°	85·8°
N(peptide)–Ni–N(peptide) *or* O(carboxyl)		78·0	77·7	77·7	84·5 86·8

In the monoclinic form the two ligands lie in roughly perpendicular planes with respect to each other, and are related by a two-fold axis. In the triclinic form, the ligands are crystallographically independent but their relationship is, to a first approximation, the same. The complex ion is shown in Figure 2. The individual peptide

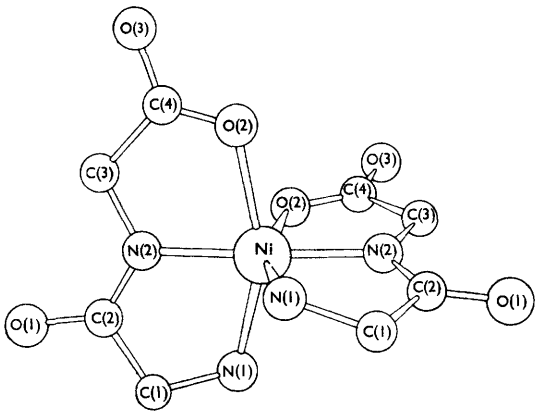

FIGURE 2. *Structure of the bisglycylglycinatonickelate*(II) *ion in both* $Na_2Ni(Gly–Gly)_2,8H_2O$ *and* $Na_2Ni(Gly–Gly)_2,9H_2O$.

O : C·N·C groups are approximately planar and the Ni atoms are coplanar with them. The N(peptide) atoms are therefore trigonal and must be de-protonated. Except for obvious dimensional differences, the $Ni(Gly–Gly)_2^{2-}$ ion has the same structure as the $Co(Gly–Gly)_2^-$ ion in ammonium bisglycyclglycinatocobaltate(III)–$2H_2O$.[8]

In all except two of many experiments, the preparation of a triglycylglycinato-complex of Ni^{II} from alkaline solution led to the isolation of crystals which were isomorphous with those of disodium triglycylglycinatocuprate(II)–$10H_2O$.[9] This confirmed the predictions[1–3] that the triglycylglycinatonickelate(II) ion contains square-planar Ni^{II}, and that the co-ordination is *via* the N(amino) and three de-protonated N(peptide) atoms of the ligand. No further work was done on this structure, although the isomorphism between the nickelate(II) and cuprate(II) complexes enabled the former to be used as a diluent for the latter in a recent solid-state e.s.r. study.[10]

On two exceptional occasions (when, however, the usual preparative procedure was followed), the triglycylglycinatonickelate(II) complex crystallised in a different form. All subsequent attempts to produce more of these crystals were unsuccessful and yielded the type which has already been mentioned. *X*-Ray data were therefore recorded with crystals from the exceptional batches. The structure analysis showed that the compound was a disodium salt octahydrate of the same triglycylglycinatonickelate(II) ion as found in the decahydrate discussed above. The differences between the two crystal structures (as in the case of the two bisglylglycinato-complexes) lay only in the arrangements of the Na^+ ions and water molecules. The complex ion is illustrated in Figure 3. The Ni atom lies 0·02 Å from a plane fitted to the four donor atoms. It is also coplanar with each of the peptide groups, again indicating that the three N(peptide) atoms are de-protonated. The requirement that the bond N(4)–C(9) must lie in or close to the plane of Ni, N(4), and C(8) implies that the carboxyl group can never be oriented for effective bonding in one of the vacant co-ordination positions of the Ni atom. The assignment of the i.r. band at 1590 $cm.^{-1}$ to a 'weak' CO_2^-–Ni interaction[3] is therefore questionable, at least in this complex.

The bond lengths and angles of the ligands in these four complexes do not differ significantly or systematically from those reported in similar Cu^{II} complexes.[11a] Details of these dimensions will be reported elsewhere. The lengths of, and the

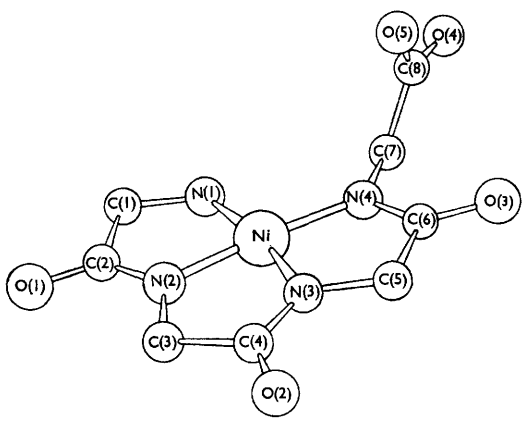

FIGURE 3. *Structure of the triglycylglycinatonickelate*(II) *ion in* $Na_2Ni(Gly–Gly–Gly–Gly),8H_2O$.

angles between, the metal–ligand bonds are listed in the Table. As in Cu^{II} complexes,[11b] the bonds from the metal to tetrahedral N(amino) atoms

are longer than those to trigonal N(peptide) atoms. Bonds in the square-planar Ni^{II} complex are, however, significantly shorter than corresponding bonds in the octahedral complexes. The mean contractions are 0·19 Å for Ni–N(amino) and 0·16 Å for Ni–N(peptide) bonds, respectively.

Crystal data: Diaquobisglycinatonickel(II) was monoclinic with $a = 7{\cdot}626(5)$, $b = 6{\cdot}596(5)$, $c = 9{\cdot}670(5)$ Å, $\beta = 116{\cdot}57(1)°$, $\mu = 34{\cdot}0$ cm.$^{-1}$; space group, $P2_1/c$; 967 reflexions (74 unobservably weak) were recorded photographically and estimated visually.

Disodium bisglycylglycinatonickelate(II)–8H_2O crystallised from a mixture of nickel(II) hydroxide with glycylglycine (0·5 M) and sodium hydroxide (0·5 M) on dropwise addition of ethanol after removal of the excess of nickel hydroxide. The square blue plates were monoclinic with $a = 27{\cdot}42(2)$, $b = 6{\cdot}19(1)$, $c = 13{\cdot}93(1)$ Å, $\beta = 121{\cdot}91(7)°$, $D_m = 1{\cdot}64$, $D_c = 1{\cdot}62$ g. cm.$^{-3}$, $Z = 4$ for $Na_2C_8H_{12}O_6N_4Ni,8H_2O$, $\mu = 24{\cdot}2$ cm.$^{-1}$; space group, $C2/c$; 1851 reflexions (226 unobservably weak) were recorded on an automated Supper equi-inclination diffractometer with Cu-K_α radiation.

Disodium bisglycylglycinatonickelate(II)–9H_2O crystallised as blue-green needles simultaneously with the preceding complex. From its appearance and method of preparation, we assume that this compound is identical with the reported decahydrate of Manyak *et al.*[12] The crystals were triclinic with $a = 21{\cdot}32(1)$, $b = 5{\cdot}77(1)$, $c = 8{\cdot}79(1)$ Å, $\alpha = 99{\cdot}68(5)°$, $\beta = 89{\cdot}49(4)°$, $\gamma = 90{\cdot}18(6)°$, $D_m = 1{\cdot}64$, $D_c = 1{\cdot}61$ g. cm.$^{-3}$, $Z = 2$ for $Na_2C_8H_{12}O_6N_4Ni,9H_2O$, $\mu = 24{\cdot}1$ cm.$^{-1}$; space group, $P\bar{1}$; the data consisted of 3552 reflexions (686 unobservably weak) recorded as for the preceding complex.

Disodium glycylglycylglycylglycinatonickelate-(II)–8 H_2O was prepared by the addition of peptide (0·1 g.) to water (1 ml.) in the presence of nickel-(II) hydroxide. Addition of sodium hydroxide (0·1 g.) and gentle warming gave a strongly alkaline yellow solution. After removal of the excess of nickel hydroxide, ethanol was slowly added dropwise until the solution just became cloudy. On standing, the complex crystallised in the form of yellow needles, triclinic with $a = 7{\cdot}733(9)$, $b = 9{\cdot}786(9)$, $c = 14{\cdot}061(10)$ Å, $\alpha = 70{\cdot}07(5)°$, $\beta = 75{\cdot}50(5)°$, $\gamma = 87{\cdot}92(5)°$, $D_m = 1{\cdot}66$, $D_c = 1{\cdot}68$ g. cm.$^{-3}$, $Z = 2$ for $Na_2C_8H_{10}O_5N_4Ni,8H_2O$; space group, $P\bar{1}$; the intensities of 3708 reflexions (543 below the observable threshold) were measured photometrically on integrated Weissenberg photographs.

Crystals of disodium glycylglycylglycylglycinatonickelate(II)–10H_2O were triclinic with $a = 7{\cdot}67$, $b = 10{\cdot}14$, $c = 14{\cdot}82$ Å, $\alpha = 93{\cdot}2°$, $\beta = 107{\cdot}5°$, $\gamma = 94{\cdot}2°$. They were isomorphous with Na_2Cu-(Gly–Gly–Gly–Gly),10H_2O for which $a = 7{\cdot}665$, $b = 10{\cdot}204$, $c = 14{\cdot}872$ Å, $\alpha = 93{\cdot}8°$, $\beta = 107{\cdot}65°$, $\gamma = 94{\cdot}3°$.

The structures were solved by three-dimensional Patterson and Fourier methods, and were refined by full-matrix least-squares. The residuals R were: $Ni(Gly)_2(H_2O)_2$, 0·092; $Na_2Ni(Gly–Gly)_2$,-8H_2O, 0·057 (including hydrogen atoms); Na_2Ni-$(Gly–Gly)_2$,9H_2O, 0·11 (incomplete); Na_2Ni(Gly–Gly–Gly–Gly),8H_2O, 0·092.

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