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Crystallographic Studies of Metal–Peptide Complexes. X. Disodium Triglycylglycinatonickelate(II) Octahydrate and Disodium Triglycylglycinatonickelate(II) Decahydrate

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The structures of two triglycylglycine complexes of Ni^{II}, disodium triglycylglycinatonickelate(II) octahydrate and disodium triglycylglycinatonickelate(II) decahydrate, have been determined from three-dimensional photographic and counter X-ray diffraction data respectively. The crystals of the octahydrate are triclinic with $a = 7{\cdot}73$ (1), $b = 9{\cdot}79$ (1), $c = 14{\cdot}06$ (1) Å, $\alpha = 70{\cdot}07$ (5), $\beta = 75{\cdot}50$ (5), $\gamma = 84{\cdot}92$ (5)°, $Z = 2$, and space group $P\bar{1}$. The crystals of the decahydrate are also triclinic with $a = 7{\cdot}74$ (1), $b = 10{\cdot}17$ (1), $c = 14{\cdot}48$ (2) Å, $\alpha = 92{\cdot}8$ (1), $\beta = 107{\cdot}2$ (1), $\gamma = 95{\cdot}4$ (1)°, $Z = 2$, space group $P\bar{1}$, and are isomorphous with a Cu^{II} complex whose structure was determined earlier [Freeman & Taylor (1965). *Acta Cryst.* **18**, 939–952]. The two hydrates contain the same Ni^{II}–tetrapeptide complex anion. The triglycylglycinate residue is coordinated to a Ni ion *via* the N(amino) and three N(peptide) atoms. The coordination is square-planar, and this is consistent with the yellow colour and diamagnetic behaviour of the complex. The positional and anisotropic thermal parameters for both complexes were refined by full-matrix least squares. The values of the final residuals R, the numbers of measured and unobservably weak reflections, and the estimated standard deviations of the positional parameters of the light atoms are 0·09, 3708, 543, 0·005 Å and 0·043, 3571, 385, and 0·003 Å respectively. The metal–ligand bonds [mean Ni–N(amino) = 1·924 Å, mean Ni–N(peptide) = 1·84 Å] are, on the average, 0·16 Å shorter than those in octahedral Ni^{II} complexes with similar ligands.

Introduction

The preceding paper (part IX; Freeman & Guss, 1978) described the structures of two types of crystals containing the bis(glycylglycinato)nickelate(II) anion. The coordination was found to be octahedral, the metal being bound to the ligands *via* the N(amino), N(peptide) and O(carboxyl) atoms. Solutions containing glycylglycine and Ni^{II} remain blue and paramagnetic even at high pH, indicating that the coordination remains octahedral.

Aqueous solutions of triglycylglycine and Ni^{II} at low pH are likewise blue and paramagnetic, but may be titrated with alkali to yield a yellow and diamagnetic complex species. The change (which is analogous to the 'biuret' reaction of peptides in the presence of Cu^{II} ions) is accompanied by the loss of three protons from each peptide molecule (Martin, Chamberlin & Edsall, 1960; Mathur & Martin, 1965; Kim & Martell, 1967). We have been able to isolate two types of crystal from the solution at high pH. Their structures are reported in the present paper. A preliminary account of the work has been published (Freeman, Guss & Sinclair, 1968).*

Experimental

The tetrapeptide (0·1 g) was added to water (1 ml) in the presence of freshly precipitated and thoroughly washed nickel(II) hydroxide. Addition of sodium hydroxide (0·1 g) and gentle warming produced a strongly alkaline yellow solution. Excess nickel(II) hydroxide was removed, and ethanol was added dropwise until the solution just became cloudy. The solution was allowed to stand. Both compounds crystallized as yellow needles. The octahydrate was prepared on only one occasion in 1965. All subsequent attempts, including many variations of the preceding method, yielded only the decahydrate.

The crystals of both complexes decomposed very rapidly in air. All crystals used for X-ray measurements were coated with a thin layer of Perspex (acrylic) dissolved in 1,2-dichloroethane. Crystals treated in this way showed no decomposition for periods of as long as one month. All diffraction measurements were made with Cu $K\alpha$ radiation.

$Na_2[Ni(H_{-3}GGGG)].8H_2O$

Crystal data

The complex crystallized with a triclinic unit cell having $a = 7{\cdot}73$ (1), $b = 9{\cdot}79$ (1), $c = 14{\cdot}06$ (1) Å, $\alpha = 70{\cdot}07$ (5), $\beta = 75{\cdot}50$ (5), $\gamma = 84{\cdot}92$ (5)°, $V = 968$ (3)

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* Abbreviations: HGGGG represents triglycylglycine in its zwitterion form $^{+}NH_3CH_2CO\text{–}(NHCH_2CO)_3\text{–}O^{-}$; and $H_{-3}GGGG^{4-}$ represents the deprotonated ligand in $Na_2[NH_2CH_2\text{-}CO\text{–}(N^{-}CH_2CO)_3\text{–}O^{-}].xH_2O$, where $x = 8$ or 10.

Å^3, $D_m = 1{\cdot}66$ (2) (by flotation in ethanol/1,2-dibromoethane),$D_x = 1{\cdot}68$ g cm^{-3}, $Z = 2$ for FW 491·0. The choice of $P\bar{1}$ for the space group was corroborated by the structure refinement. The cell dimensions were obtained from uncalibrated precession photographs [λ(Cu $K\alpha$) = 1·5418 Å] and correspond to the cell containing the three shortest non-coplanar vectors.

X-ray data

The intensity data for this structure analysis (hKl, $0 \leq K \leq 12$) were recorded photographically on multiple-film packs in an integrating Weissenberg camera, and were measured with a Nonius microdensitometer (Mark I). Three crystal specimens were used. Our inability to repeat the preparation of the crystals precluded the subsequent recording of counter data or even the collection of a set of correlation film data. Lorentz and polarization corrections were applied, but no corrections for absorption or extinction were made. The data were placed on a single scale by using a Wilson plot to calculate a scale factor for each reciprocal-lattice layer. There were 3705 independent reflections, including 543 which were classified as unobservably weak [$I < 2{\cdot}5\sigma(I)$] and omitted from the subsequent calculations. The layer scale factors were subsequently checked by treating them as variables in several isotropic least-squares refinement cycles. The 'refined' values differed by less than 5% from the 'Wilson plot' values, and the latter were retained for the final refinement calculations.

Solution and refinement

The structure was solved by standard Patterson and heavy-atom Fourier methods. Refinement was carried out by minimizing the function $\sum w(|F_o| - s|F_c|)^2$ using the full-matrix least-squares program *ORFLS* (Busing, Martin & Levy, 1962). The weights w were derived from subjective figures of merit assigned to the original observations. The atomic scattering factors used were those for Ni^{2+}, 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 values over the entire range of sin θ. The contributions of H atoms bonded to N and C atoms were included in the calculated structure amplitudes. Their positions were calculated on the assumption that C—H and N—H bond lengths were 1·05 and 0·95 Å, respectively, and their temperature factors were assumed to be equal to those of the atoms to which they were attached.

The final residual R ($= \sum||F_o| - s|F_c||/\sum |F_o|$) was 0·09. In the final cycle in which it was varied, no positional parameter changed by more than 0·3 standard deviation and no thermal parameter changed by more than one standard deviation. A final $(F_o - F_c)$ synthesis had no excursions of magnitude greater than 0·5 e Å^{-3}. The final positional parameters are listed in Table 1.*

Table 1. *Atomic positional parameters in fractional coordinates* (×10^4) *for disodium triglycylglycinatonickelate*(II) *octahydrate, 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	2880 (1)	8524 (1)	218 (1)
Na(1)	5911 (2)	4187 (2)	4017 (2)
Na(2)	998 (4)	2201 (3)	4460 (2)
O(1)	1808 (5)	9233 (4)	−2507 (3)
O(2)	1909 (5)	12710 (4)	−347 (3)
O(3)	3461 (5)	8558 (4)	2918 (3)
O(4)	879 (5)	5967 (4)	3179 (3)
O(5)	3011 (6)	4372 (5)	3647 (4)
O(6)	5500 (5)	6644 (4)	4156 (3)
O(7)	8591 (5)	3941 (5)	4666 (3)
O(8)	5959 (6)	1697 (5)	3993 (4)
O(9)	8324 (5)	5295 (5)	2303 (3)
O(10)	229 (6)	2651 (5)	2867 (3)
O(11)	1213 (5)	1924 (4)	6175 (3)
O(12)	2599 (9)	63 (7)	4314 (4)
O(13)	2783 (6)	3827 (5)	961 (4)
N(1)	3298 (6)	6844 (5)	−238 (3)
N(2)	2352 (5)	9489 (5)	−1051 (4)
N(3)	2502 (5)	10292 (4)	408 (3)
N(4)	3346 (5)	7823 (5)	1543 (3)
C(1)	2620 (9)	7137 (7)	−1181 (5)
C(2)	2225 (7)	8749 (6)	−1627 (4)
C(3)	1994 (6)	11037 (5)	−1279 (3)
C(4)	2138 (6)	11412 (6)	−343 (4)
C(5)	2716 (6)	10331 (6)	1370 (4)
C(6)	3194 (6)	8797 (6)	2012 (4)
C(7)	3853 (6)	6360 (5)	2095 (3)
C(8)	2474 (6)	5500 (6)	3052 (4)
H(1)	2682	6024	295
H(2)	4533	6636	−392
H(3)	3577	6812	−1732
H(4)	1434	6550	−983
H(5)	2953	11625	−1944
H(6)	717	11282	−1421
H(7)	3758	11057	1236
H(8)	1531	10690	1776
H(9)	4156	5777	1577
H(10)	5006	6455	2340

$Na_2Ni(H_{-3}GGGG).10H_2O$

Crystal data

The complex crystallized with a triclinic unit cell having $a = 7{\cdot}74$ (1), $b = 10{\cdot}17$ (1), $c = 14{\cdot}48$ (2) Å,

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* Lists of structure factors, thermal parameters, bond lengths and angles involving H atoms, and angles at atoms involved in hydrogen bonds and some Na$^+$—O interactions for both compounds, and Table 3, have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33518 (57 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

$\alpha = 92{\cdot}8$ (1), $\beta = 107{\cdot}2$ (1), $\gamma = 95{\cdot}4$ (1)°, $V = 1081$ (4) Å^3, $D_m = 1{\cdot}63$ (2) (by flotation in ethanol/1,2-dibromoethane), $D_x = 1{\cdot}62$ g cm^{-3}, $Z = 2$ for FW 527·1, and μ(Cu $K\alpha$) = 24·1 cm^{-1}. The cell dimensions were fitted to the θ values of high-angle reflections measured on an equi-inclination diffractometer [λ(Cu $K\alpha_1$) = 1·5404, λ(Cu $K\alpha_2$) = 1·5443 Å]. The crystals used for these measurements were rotated about vectors parallel to the three unit-cell edges. The cell dimensions of the isomorphous Cu complex, $Na_2Cu(H_{-3}GGGG).10H_2O$, are $a = 7{\cdot}665$ (6), $b = 10{\cdot}204$ (9), $c = 14{\cdot}872$ (10) Å, $\alpha = 93{\cdot}60$ (3), $\beta = 107{\cdot}65$ (5), $\gamma = 94{\cdot}30$ (5)° (Freeman & Taylor, 1965). The structure refinement corroborates the choice of space group as $P\bar{1}$.

X-ray data

The data were recorded using three Perspex-coated crystals mounted parallel to the [100], [010] and [001] directions respectively. Their dimensions were 0·28 × 0·10 × 0·16, 0·32 × 0·08 × 0·20, and 0·32 × 0·18 × 0·24 mm. The transmission factors later applied to the data recorded from the three crystals were in the ranges 0·73–0·79, 0·57–0·70 and 0·54–0·67 respectively. The intensity measurements were made with a computer-controlled Supper equi-inclination diffractometer (Freeman, Guss, Nockolds, Page & Webster, 1970). The scan-range and scan-speed parameters as defined in Freeman *et al.* (1970) were: $\Delta\lambda = 0{\cdot}007$ Å, $X = 0{\cdot}4°$, $\varphi_m = 1{\cdot}0°$, $P = 0{\cdot}001$, $\delta\mu = 0{\cdot}05°$, $\varphi'_{\max} = 0{\cdot}3333$, $\varphi'_{\min} = 0{\cdot}05°$ s^{-1}, and $R_e = 0{\cdot}05$. The counter aperture was varied between 3° 7′ and 3° 15′. The data were corrected for Lorentz, polarization and absorption effects (Coppens, Leiserowitz & Rabinovich, 1965), but not for extinction. After the application of these corrections, the data from the three crystal specimens were placed on a common scale by the method of Rae (1965). There were 385 unobservably weak reflections [$I < 2\sigma(I)$] among the 3571 observations. The unobservably weak reflections were omitted from the subsequent calculations. The weights of the observations were obtained by combining the known statistical errors with estimates of the systematic errors derived from multiply observed reflections (Freeman & Guss, 1972). The constants in the polynomial $V_s[F(hkl)] = l + m|F| + n|F|^2$ which represented the contributions of the systematic errors to the variances of F were $l = 18{\cdot}2$, $m = -15{\cdot}3 \times 10^{-2}$, and $n = 7 \times 10^{-4}$.

Refinement

The physical constants, program and procedures used for the refinement were the same as for the preceding compound. The atomic coordinates in $Na_2Cu(H_{-3}GGGG).10H_2O$ (Freeman & Taylor, 1965) were used as starting parameters. After three

Table 2. *Atomic positional parameters in fractional coordinates* ($\times 10^4$, *for* H $\times 10^3$) *for disodium triglycylglycinatonickelate*(II) *decahydrate*

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

	x	y	z
Ni	3084 (0·7)	6454 (0·4)	5289 (0·4)
Na(1)	5577 (2)	1468 (1)	8744 (1)
Na(2)	1829 (2)	6033 (1)	9903 (1)
O(1)	−520 (3)	6818 (2)	2753 (2)
O(2)	1676 (3)	2627 (2)	4640 (2)
O(3)	6381 (3)	5301 (2)	7683 (2)
O(4)	3868 (3)	7779 (2)	8042 (2)
O(5)	6242 (3)	9317 (2)	8406 (2)
O(6)	2858 (3)	1234 (2)	7499 (2)
O(7)	4962 (3)	3595 (2)	9290 (2)
O(8)	2598 (4)	8326 (3)	9619 (2)
O(9)	2560 (5)	1663 (3)	9744 (2)
O(10)	7820 (4)	2996 (3)	8372 (2)
O(11)	8647 (4)	6102 (3)	9491 (2)
O(12)	2372 (4)	5338 (2)	8456 (2)
O(13)	721 (4)	8749 (2)	6903 (2)
O(14)	9840 (4)	9813 (3)	8514 (2)
O(15)	3829 (4)	979 (2)	5759 (2)
N(1)	2983 (4)	8253 (3)	4937 (2)
N(2)	1365 (3)	6025 (2)	4109 (2)
N(3)	2960 (3)	4674 (2)	5396 (2)
N(4)	4835 (3)	6586 (2)	6513 (2)
C(1)	1424 (5)	8321 (3)	4064 (3)
C(2)	667 (4)	6953 (3)	3583 (2)
C(3)	829 (4)	4607 (3)	3839 (2)
C(4)	1881 (4)	3879 (3)	4676 (2)
C(5)	4129 (4)	4239 (3)	6275 (2)
C(6)	5211 (4)	5451 (3)	6889 (2)
C(7)	5904 (4)	7773 (3)	7069 (2)
C(8)	5264 (4)	8318 (3)	7897 (2)
H(1)	310 (5)	884 (4)	534 (3)
H(2)	406 (8)	852 (5)	476 (4)
H(3)	30 (5)	875 (4)	419 (3)
H(4)	161 (6)	895 (4)	365 (3)
H(5)	−53 (5)	446 (3)	376 (2)
H(6)	113 (4)	432 (3)	322 (2)
H(7)	339 (4)	372 (3)	664 (2)
H(8)	499 (5)	369 (3)	612 (3)
H(9)	720 (4)	763 (3)	735 (3)
H(10)	588 (6)	849 (5)	663 (3)
H(11)	208 (6)	183 (4)	748 (3)
H(12)	224 (4)	63 (3)	734 (2)
H(13)	530 (5)	387 (4)	889 (3)
H(14)	436 (6)	417 (4)	903 (3)
H(15)	304 (8)	830 (6)	921 (4)
H(16)	169 (5)	868 (3)	941 (3)
H(17)	295 (8)	130 (5)	1027 (4)
H(18)	174 (5)	122 (4)	935 (3)
H(19)	870 (6)	287 (4)	820 (3)
H(20)	718 (5)	377 (3)	802 (3)
H(21)	833 (6)	670 (4)	975 (3)
H(22)	818 (5)	603 (3)	898 (3)
H(23)	191 (7)	482 (5)	809 (4)
H(24)	285 (5)	595 (3)	815 (3)
H(25)	−15 (7)	825 (5)	635 (4)
H(26)	145 (7)	830 (5)	709 (4)
H(27)	881 (5)	964 (4)	846 (3)
H(28)	996 (6)	952 (5)	804 (3)
H(29)	323 (5)	153 (4)	532 (3)
H(30)	371 (5)	120 (4)	624 (3)

cycles of full-matrix least squares with isotropic thermal parameters the residual R converged to 0·11. H atom coordinates were derived from an $(F_o - F_c)$ synthesis. The decrease in R following the inclusion of the H atoms with fixed isotropic thermal parameters was found to be significant at the 95% confidence level (Hamilton, 1964). Continued refinement with anisotropic thermal parameters for all the non-hydrogen atoms and isotropic thermal parameters for the H atoms reduced the residual to 0·043. A final $(F_o - F_c)$ synthesis showed no excursions greater than 0·3 e Å^{-3}. The final positional parameters are listed in Table 2.*

Description of the structures

In the crystal structures of the two bis(glycylglycinato)nickelate(II) complexes described in the preceding paper, the differences between the complex anions were less significant than the differences in the molecular packing and the environments of the Na$^+$ ions. The same is true for the present two structures. The triglycylglycinatonickelate(II) anions in the octahydrate and decahydrate are almost identical. The most significant differences occur between the corresponding carboxyl C—O bond lengths in the two structures. The cause lies in differences between the Na$^+$-ion contacts and hydrogen bonds at the O(carboxyl) atoms. Except where otherwise stated, the numerical values quoted in the following discussion are those for $Na_2Ni(H_{-3}GGGG).10H_2O$, since its structure was determined with higher precision.

The $Ni(H_{-3}GGGG)^{2-}$ *anion*

A stereoscopic diagram of the $Ni(H_{-3}GGGG)$ anion is shown in Fig. 1, and the dimensions are given in Fig. 2. The peptide molecule is bonded to a Ni atom by the N(amino) and three N(peptide) atoms. The donor atoms are coplanar to within 0·02 Å (plane 1, Table 3).* The carboxyl group is not bound to the Ni atom. It makes an angle of 99·6° with the coordination plane (planes 1 and 5, Table 3).

The three peptide groups, C_α—C(=O)—N, are all planar. The deviations of the Ni atoms from the peptide group planes are 0·014, 0·035 and 0·062 Å respectively (Table 3). The result is that all three chelate rings lie very close to a common plane. The dihedral angles about the C—C bonds between the trigonal peptide atoms N(2) and N(3), and N(3) and N(4) are −0·2 and 1·4° respectively. The corresponding dihedral angle in

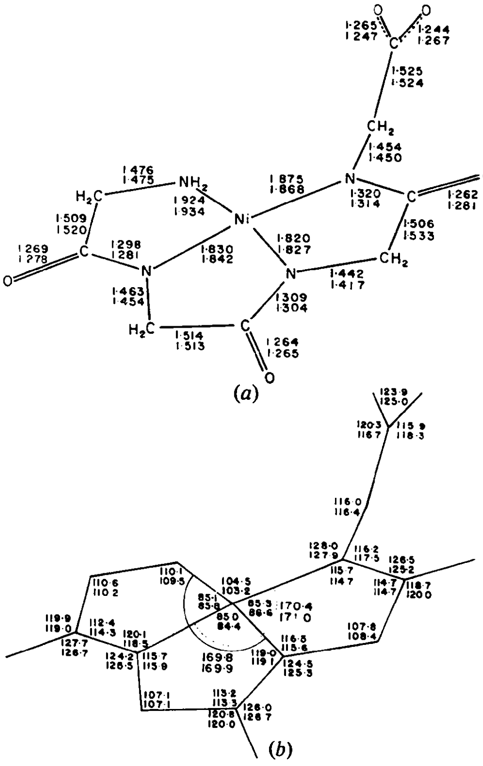

Fig. 2. (*a*) Bond lengths (Å) and (*b*) bond angles (°) in the Ni(Gly-H$_{-1}$Gly-H$_{-1}$Gly-H$_{-1}$Gly)$^{2-}$ anion. The two values of each dimension are taken from the structure analyses of $Na_2Ni(H_{-3}GGGG).10H_2O$ (upper) and $Na_2Ni(H_{-3}GGGG).8H_2O$ (lower) respectively. Estimated standard deviations (L = light atom):

	$Na_2Ni(H_{-3}GGGG).8H_2O$	$Na_2Ni(H_{-3}GGGG).10H_2O$
Ni—L	0·005 Å	0·004 Å
L—L	0·007	0·005
L—Ni—L	0·2°	0·2°
Ni—L—L	0·4	0·3
L—L—L	0·4	0·3.

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* See deposition footnote.

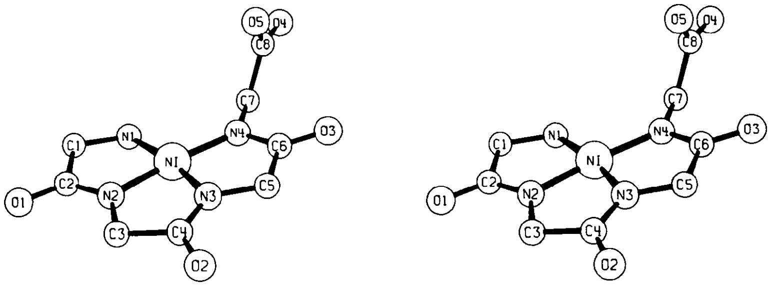

Fig. 1. A stereoscopic view (Johnson, 1965) of a triglycylglycinatonickelate(II) anion in the structure of $Na_2Ni(H_{-3}GGGG).10H_2O$.

the range which contains the tetrahedral amino atom N(1) is 9·3°. It is the non-planarity of this chelate ring which accounts for the slight tetrahedral distortion from a perfectly planar arrangement of the four donor atoms.

The metal–ligand bonds [Ni–N(amino) = 1·924 Å, Ni–N(peptide) = 1·830, 1·820, 1·875 Å] are significantly shorter than in the related Cu complex (2·028, 1·923, 1·912, 1·944 Å). The bond to N(4) is the longest of the three metal–N(peptide) bonds. This seems to be a general phenomenon in metal–peptide complexes (Freeman, 1967). The two central N(peptide) atoms of the tetrapeptide are subject to severe constraints because each belongs to two chelate rings. The strains in the ensemble of three fused chelate rings can probably be accommodated most easily by the donor atoms at the ends, *i.e.* the N(amino) atom and the third N(peptide) atom.

There are significant differences between the dimensions of the ligand molecule and those of free peptides. As in other complexes where metal–N(peptide) bonds occur, the C=O bonds in the peptide groups are lengthened (mean in complex = 1·275, mean in free peptides = 1·24 Å) and the OC–N bonds are shortened (mean in complex = 1·300, mean in free peptides = 1·325 Å). These changes are consistent with increased contributions from the resonance form $-\mathrm{N}^{+}{=}\mathrm{C}{-}\mathrm{O}^{-}$ (Freeman, 1967, 1973).

Crystal structure of $\mathrm{Na_2Ni(H_{-3}GGGG)}.8\mathrm{H_2O}$

The complex anions in this structure are stacked in columns parallel to the [100] direction. The columns are arranged along [010] to form layers. Between layers run infinite chains of $\mathrm{Na^{+}{-}O_6}$ octahedra (Fig. 3). The carboxyl atom O(5) of each $\mathrm{Ni(H_{-3}GGGG)^{2-}}$ anion is at the shared corner of two $\mathrm{Na^{+}{-}O_6}$ octahedra. The complex anions are thus anchored directly to the chains of cation octahedra.

All the other contacts involving the peptide ligands are hydrogen bonds. The twelve hydrogen bonds between each peptide molecule and the surrounding water molecules (Table 4) comprise: (i) two N(amino)–H···O(water) bonds from N(1); (ii) seven O(peptide)···H–O(water) bonds involving O(1), O(2) and O(3); and (iii) three O(carboxyl)···H–O(water) bonds which all involve O(4). Conversely, each water molecule is hydrogen-bonded to at least one N or O atom of a peptide. There are, in addition, four types of O(water)–H···O(water) hydrogen bonds.

Table 4. *Hydrogen bonds in* $\mathrm{Na_2Ni(H_{-3}GGGG)}.8\mathrm{H_2O}$

A list of angles at atoms involved in hydrogen bonds has been deposited. In Tables 4 and 5(*a*), superscripts denote atoms whose coordinates are related to those in Table 1 by the following code.

None	x,	y,	z	(vii)	$-x$,	$1-y$,	$-z$
(i)	$1-x$,	$1-y$,	$1-z$	(viii)	x,	$-1+y$,	$1+z$
(ii)	$-1+x$,	y,	z	(ix)	$-x$,	$1-y$,	$1-z$
(iii)	$1+x$,	y,	z	(x)	x,	$-1+y$,	z
(iv)	$1-x$,	$1-y$,	$-z$	(xi)	x,	$1+y$,	$-1+z$
(v)	$1-x$,	$-y$,	$1-z$	(xii)	x,	$1+y$,	z
(vi)	$1-x$,	$2-y$,	$-z$	(xiv)	$-x$,	$-y$,	$1-z$

Hydrogen-bond lengths (Å)

	Equivalent bond	
N(amino)···water		
N(1)–H···O(13)	–	2·863 (7)
N(1)–H···O(13$^{\mathrm{iv}}$)	O(13)···H–N(1$^{\mathrm{iv}}$)	3·035 (6)
O(peptide)···water		
O(1)···H–O(8$^{\mathrm{iv}}$)	O(8)–H···O(1$^{\mathrm{iv}}$)	2·718 (7)
O(1)···H–O(10$^{\mathrm{vii}}$)	O(10)–H···O(1$^{\mathrm{vii}}$)	2·771 (5)
O(1)···H–O(11$^{\mathrm{xi}}$)	O(11)–H···O(1$^{\mathrm{viii}}$)	2·732 (7)
O(2)···H–O(9$^{\mathrm{vi}}$)	O(9)–H···O(2$^{\mathrm{vi}}$)	2·817 (6)
O(2)···H–O(13$^{\mathrm{xii}}$)	O(13)–H···O(2$^{\mathrm{x}}$)	2·676 (6)
O(3)···H–O(6)	–	2·766 (5)
O(3)···H–O(12$^{\mathrm{xii}}$)	O(12)–H···O(3$^{\mathrm{x}}$)	2·758 (7)
O(carboxyl)···water		
O(4)···H–O(7$^{\mathrm{ii}}$)	O(7)–H···O(4$^{\mathrm{iii}}$)	2·716 (6)
O(4)···H–O(9$^{\mathrm{ii}}$)	O(9)–H···O(4$^{\mathrm{iii}}$)	2·803 (6)
O(4)···H–O(11$^{\mathrm{ix}}$)	O(11)–H···O(4$^{\mathrm{ix}}$)	2·766 (6)
Water···water		
O(6)–H···O(11$^{\mathrm{i}}$)	O(11)···H–O(6$^{\mathrm{i}}$)	2·870 (6)
O(8)···H···O(12$^{\mathrm{v}}$)	O(12)···H···O(8$^{\mathrm{v}}$)	2·841 (6)
O(9)···H–O(10$^{\mathrm{iii}}$)	O(10)–H···O(9$^{\mathrm{ii}}$)	2·829 (6)
O(10)···H–O(13)	–	2·838 (7)

The details of the hydrogen-bonding scheme and the $\mathrm{Na^{+}}$-ion contacts are shown in Tables 4 and 5 respectively. The H atoms were not located in the structure analysis. The assignment of the hydrogen-bond protons in Table 4 is unequivocal except in the bond O(8)···O(12). The octahedral arrangement about one of the $\mathrm{Na^{+}}$ ions is severely distorted by one very long contact, Na(2)···O(12$^{\mathrm{xiv}}$). There are no intercomplex contacts shorter than the sum of the van der Waals radii of the atoms concerned.

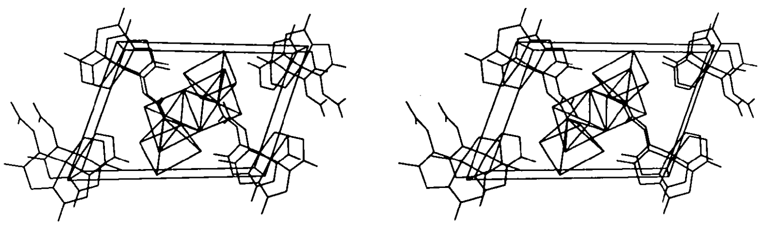

Fig. 3. A stereoscopic view of a unit cell of $\mathrm{Na_2Ni(H_{-3}GGGG)}.8\mathrm{H_2O}$ (**b** upwards, **c** left to right, and **a** away from the observer).

Table 5. *Dimensions of* Na$^+$–O *octahedra*

A list of angles involved in some Na$^+$–O interactions has been deposited.

(*a*) Interatomic distances in $Na_2Ni(H_{-3}GGGG).8H_2O$

Superscripts are defined in Table 4.

	Distance from Na(1)		Distance from Na(2)
O(5)	2·405 (6) Å	O(5)	2·506 (6) Å
O(6)	2·465 (5)	O(7^{ii})	2·440 (6)
O(6^{i})	2·405 (5)	O(10)	2·348 (5)
O(7)	2·428 (5)	O(11)	2·380 (5)
O(8)	2·445 (6)	O(12)	2·379 (6)
O(9)	2·606 (6)	O(12^{xiv})	3·421 (5)

(*b*) Interatomic distances in $Na_2Ni(H_{-3}GGGG).10H_2O$

Superscripts are defined in Table 6.

	Distance from Na(1)		Distance from Na(2)
O(5^{ii})	2·355 (4) Å	O(7)	2·395 (6) Å
O(6)	2·313 (6)	O(8^{ix})	2·436 (4)
O(7)	2·404 (5)	O(10)	2·567 (5)
O(8^{ix})	2·359 (6)	O(11)	2·417 (4)
O(9)	3·107 (6)	O(11^{xi})	2·365 (5)
O(10)	2·417 (5)	O(12^{ix})	2·347 (5)

Crystal structure of $Na_2Ni(H_{-3}GGGG).10H_2O$

The crystals of this complex are, as has already been mentioned, isomorphous with those of $Na_2Cu(H_{-3}GGGG).10H_2O$ (Freeman & Taylor, 1965). A stereoscopic diagram of the structure (Fig. 4) shows the way in which the carboxyl groups of the peptides link the metal–peptide complex ions to the chains of Na$^+$–O octahedra. The types and number of hydrogen bonds formed between the N(amino), O(peptide) and O(carboxyl) atoms of the peptide ligands and the surrounding water molecules (Table 6) are identical with those listed as categories (i) to (iii) for the octahydrate, with the addition of (iv) two O(carboxyl)···H–O(water) bonds involving O(5), the O(carboxyl) atom which lies at one corner of the octahedron around Na(1).

The ten water molecules all have approximately tetrahedral environments (Table 6). Four of these, O(9), O(13), O(14) and O(15), form four hydrogen bonds. Two, O(6) and O(12), bind a Na$^+$ ion and form three hydrogen bonds. The remaining four water molecules, O(7), O(8), O(10) and O(11), are at the shared corners of two Na$^+$-ion octahedra. Each makes two O···Na$^+$ contacts (Table 5) and forms two hydrogen bonds.

Chemical significance

The transition from blue to yellow Ni^{II} complexes at high pH is a general phenomenon among amino-acid amides, tri- and higher oligopeptides and peptide amides. The special case of Ni^{II}–dipeptide complexes has been discussed in the preceding paper (Freeman & Guss, 1978). In the general case, the colour change at pH 9–10 is accompanied by the dissociation of protons (Martin, Chamberlin & Edsall, 1960), and by a transition from the high-spin to the low-spin state of the Ni^{II} atom (Mathur & Martin, 1965; Kim & Martell, 1969). The present work confirms the correctness of the explanation originally given by Martin *et al.* (1960). As predicted, the yellow complex formed by triglycylglycine and Ni^{II} at high pH has a square-planar coordination geometry in which the Ni atom is bonded to the amino group and to the deprotonated N atoms of three peptide groups. It is shown that the peptide groups [–N$^-$–C(=O)–C$_\alpha$–] are planar, and that the Ni–N(peptide) bonds lie close to the peptide group planes.

The transition from octahedral (high-spin) to square-planar (low-spin) coordination in Ni^{II} complexes is accompanied by a reduction in the occupancy of the $d_{x^2-y^2}$ orbital. The reduced shielding in the directions of the remaining donor atoms results in a shortening of the Ni–ligand bonds. We are able to determine the extent

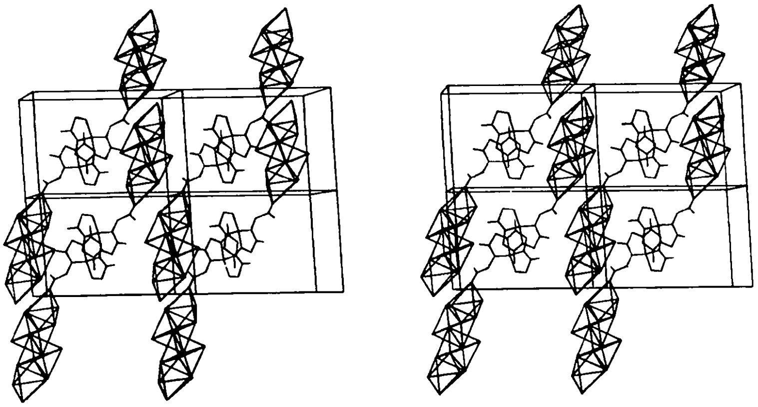

Fig. 4. A stereoscopic view of four unit cells of $Na_2Ni(H_{-3}GGGG).10H_2O$ (**b** upwards, **c** left to right, and **a** away from the observer).

Table 6. *Hydrogen bonds in* $Na_2Ni(H_{-3}GGGG).10H_2O$

A list of angles at atoms involved in hydrogen bonds has been deposited. In Tables 5(*b*) and 6, superscripts denote atoms whose coordinates are related to those in Table 2 by the following code.

None	x,	y,	z	(iv)	$-1+x$,	y,	z	(viii)	x,	$1+y$,	z
(i)	$1-x$,	$1-y$,	$1-z$	(v)	$-x$,	$1-y$,	$1-z$	(ix)	$1-x$,	$1-y$,	$2-z$
(ii)	x,	$-1+y$,	z	(vi)	$-1+x$,	$-1+y$,	z	(x)	$1+x$,	y,	z
(iii)	$1-x$,	$-y$,	$1-z$	(vii)	$1+x$,	$1+y$,	z	(xi)	$2-x$,	$1-y$,	$2-z$

Hydrogen-bond lengths (Å)

$(X\text{–H}\cdots Y)$ or $(Y\cdots\text{H–}X)$	Equivalent bond $(Y\cdots\text{H–}X)$ or $(X\text{–H}\cdots Y)$	d_{X-H}	$d_{H\cdots Y}$	$d_{X\cdots Y}$
N(amino)···water				
N(1)–H(1)···O(15^{i})	O(15)···H(1^{i})–N(1^{i})	0·79	2·21	2·899 (6)
N(1)–H(2)···O(15^{viii})	O(15)···H(1^{ii})–N(1^{ii})	0·97	2·02	2·983 (6)
O(peptide)···water				
O(1)···H(11^{v})–O(6^{v})	O(6)–H(11)···O(1^{v})	0·89	1·89	2·773 (6)
O(1)···H(19^{i})–O(10^{i})	O(10)–H(19)···O(1^{i})	0·81	2·26	3·005 (6)
O(1)···H(23^{v})–O(12^{v})	O(12)–H(23)···O(1^{v})	0·71	2·03	2·733 (7)
O(2)···H(25^{v})–O(13^{v})	O(13)–H(25)···O(2^{v})	0·96	1·71	2·672 (8)
O(2)···H(29)–O(15)	–	0·92	1·82	2·720 (7)
O(3)···H(20)–O(10)	–	0·81	1·77	2·791 (6)
O(3)···H(22)–O(11)	–	0·73	2·03	2·720 (7)
O(carboxyl)···water				
O(4)···H(15)–O(8)	–	0·77	2·04	2·793 (5)
O(4)···H(24)–O(12)	–	0·90	1·98	2·806 (5)
O(4)···H(26)–O(13)	–	0·75	2·10	2·803 (7)
O(5)···H(17^{ix})–O(9^{ix})	O(9)–H(17)···O(5^{ix})	0·81	2·01	2·802 (8)
O(5)···H(27)–O(14)	–	0·78	1·97	2·739 (5)
Water···water				
O(6)–H(12)···O(13^{ii})	O(13)···H(12^{viii})–O(6^{viii})	0·73	2·11	2·831 (7)
O(7)–H(14)···O(12)	–	0·81	2·04	2·839 (7)
O(8)–H(16)···O(14^{iv})	O(14)···H(16^{x})–O(8^{x})	0·80	2·11	2·867 (7)
O(9)···H(21^{ix})–O(11^{ix})	O(11)–H(21)···O(9^{ix})	0·79	2·05	2·835 (6)
O(9)–H(18)···O(14^{vi})	O(14)–H(18^{vii})–O(9^{vii})	0·81	2·01	2·802 (8)
O(13)···H(28^{iv})–O(14^{iv})	O(14)–H(28)···O(13^{x})	0·77	2·05	2·814 (6)

of this contraction because the same Ni–ligand bond types occur in the present square-planar complexes and in the octahedral complexes of the preceding paper.

	⟨*d*[Ni–N(amino)]⟩	⟨*d*[Ni–N(peptide)]⟩
Octahedral $Ni(H_{-1}GG)_2^{2-}$	2·14 Å	1·99 Å
Square planar $Ni(H_{-3}GGGG)^{2-}$	1·92	1·84

Independent determinations of the Ni–ligand bond lengths in a square-planar complex are available from the structure analysis of bis(L-prolinamidato)nickel(II) hydrate (Tsukihara, Katsube, Fujimori & Ishimura, 1972). The mean values *d*[Ni–N(amino)] = 1·924, *d*[Ni–N(peptide)] = 1·864 Å, from Tsukihara *et al.* are in excellent agreement with the present work. On the other hand, we have already noted (Freeman & Guss, 1978) that the Ni–N(amino) bonds in $[Ni(H_{-1}GG)_2]^{2-}$ are about 0·03 Å longer than similar bonds in octahedral Ni–amino-acid complexes. Accordingly we estimate the bond contraction between octahedral and square-planar Ni^{II} conservatively as 0·16 Å, the weighted mean obtained from the shortening of the Ni–N(amino) bond (0·18–0·21 Å) and three Ni–N(peptide) bonds (0·15–0·16 Å). A difference of 0·16 (3) Å was also found by Nyburg & Wood (1964) for the Ni–N bonds in the blue and yellow forms of bis(*meso*-stilbenediamine)nickel(II) dichloroacetate.

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References

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.

Coppens, P., Leiserowitz, L. & Rabinovich, D. (1965). *Acta Cryst.* **18**, 1035–1038.

Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104–109.

Freeman, H. C. (1967). *Adv. Protein Chem.* **22**, 257–424.

Freeman, H. C. (1973). *Inorganic Biochemistry*, Vol. 1, edited by G. L. Eichhorn, pp. 121–166. Amsterdam, New York: Elsevier.

Freeman, H. C. & Guss, J. M. (1972). *Acta Cryst.* B**28**, 2090–2096.

Freeman, H. C. & Guss, J. M. (1978). *Acta Cryst.* B**34**, 2451–2458.

Freeman, H. C., Guss, J. M., Nockolds, C. E., Page, R. & Webster, A. (1970). *Acta Cryst.* A**26**, 149–152.

Freeman, H. C., Guss, J. M. & Sinclair, R. L. (1968). *Chem. Commun.* pp. 485–487.

Freeman, H. C. & Taylor, M. R. (1965). *Acta Cryst.* **18**, 939–952.

Hamilton, W. C. (1964). *Statistics in Physical Science.* New York: Ronald Press.

International Tables for X-ray Crystallography (1962). Vol. III, p. 214. Birmingham: Kynoch Press.

Johnson, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

Kim, M. K. & Martell, A. E. (1967). *J. Am. Chem. Soc.* **89**, 5138–5144.

Kim, M. K. & Martell, A. E. (1969). *J. Am. Chem. Soc.* **91**, 872–879.

Martin, R. B., Chamberlin, M. & Edsall, J. T. (1960). *J. Am. Chem. Soc.* **82**, 495–498.

Mathur, R. & Martin, R. B. (1965). *J. Phys. Chem.* **69**, 668–671.

Nyburg, S. C. & Wood, J. S. (1964). *Inorg. Chem.* **3**, 468–476.

Rae, A. D. (1965). *Acta Cryst.* **19**, 683–684.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Tsukihara, T., Katsube, Y., Fujimori, K. & Ishimura, Y. (1972). *Bull. Chem. Soc. Jpn*, **45**, 1367–1371.

Acta Cryst. (1978). B**34**, 2466–2472

Decacarbonyl-μ-hydrido-μ-vinyl-*triangulo*-triosmium: A Combined X-ray and Neutron Diffraction Study

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$HOs_3(C_2H_3)(CO)_{10}$ is monoclinic with $a = 9{\cdot}914\,(3)$, $b = 14{\cdot}398\,(5)$, $c = 12{\cdot}416\,(4)$ Å, $\beta = 99{\cdot}77\,(5)°$, space group $P2_1/n$, $Z = 4$. The structure was solved by the heavy-atom method for the X-ray data, and the H atoms were located by a neutron difference synthesis. The X-ray scattering was dominated by the Os contribution, which enabled a single set of atomic positional and thermal parameters to be refined simultaneously by least squares on 1927 X-ray data (with $\sin\theta/\lambda > 0{\cdot}352$ Å^{-1}) and 1197 profile-fitted neutron data. The final R' values were 0·0317 (X-ray) and 0·0287 (neutron). The combined refinement was more precise, and freer from systematic errors, than individual refinements on full X-ray or neutron data alone. The vinyl group and hydride both bridge the $(OC)_3Os–Os(CO)_3$ edge of the $Os_3(CO)_{10}$ cluster; all the carbonyls are terminal. The vinyl group and the Os to which it is σ-bonded [C(41)–Os(3) 2·107 (3) Å] are coplanar to within 0·15 Å; the slight lengthening of the C–C double bond and distortions from planarity are consistent with a π interaction with Os(2) [C(41)–Os(2) 2·273 (3), C(42)–Os(2) 2·362 (3) Å]. The hydride bridges the same edge of the Os_3 triangle as the vinyl group, with Os(2)–H(1) 1·813 (4), Os(3)–H(1) 1·857 (4) Å and Os–H–Os 101·6 (2)°; the significantly shorter Os–H bond is made by the vinyl π-bonded Os atom.

Introduction

In single-crystal X-ray diffraction studies of structures containing both light and very heavy elements, the light-atom positions are determined relatively imprecisely, and it may prove impossible to find the H atoms. The light atoms can be found more precisely by neutron diffraction studies, but because neutron-beam