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The Crystal and Molecular Structure of [*N*,*N*′-Di(2-aminoethyl)malondiamidato]nickel(II) Trihydrate

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The crystal and molecular structure of the neutral complex [*N*,*N*′-di(2-aminoethyl)malondiamidato]nickel(II) trihydrate, $Ni(C_7H_{14}N_4O_2)\cdot 3H_2O$, isolated from aqueous solution at alkaline pH, has been determined from three-dimensional X-ray data collected with an automatic diffractometer. The complex crystallizes in the monoclinic space group $P2_1/c$, with four molecules in a unit cell of dimensions $a = 7.397$ (1) Å, $b = 9.053$ (1) Å, $c = 18.690$ (4) Å, and $\beta = 102.80$ (4)°; $d_{\mathrm{obsd}} = 1.65$ (2) g/cm^3 and $d_{\mathrm{calcd}} = 1.627$ g/cm^3. The structure, including hydrogen atoms, was refined by a least-squares method to a weighted R value of 0.042 for all 3324 reflections significantly different from background. The donor amine and amide nitrogen atoms are bonded to the metal in a trapezoidal array with distances of 1.921 and 1.869 (±0.002) Å, respectively. The four nitrogens of the ligand form a distorted square-planar structure with the nickel ion. Adjacent molecules in layers parallel to the *bc* plane are held together by hydrogen bonds to the waters of hydration. A charge density refinement has been carried out on the diffraction data yielding net atomic charges for the atoms in the compound. The results indicate a small residual positive charge of approximately +0.5 (2) electron on the nickel atom.

Introduction

Transition metal ions such as copper,[1,2] nickel,[3,4] and cobalt[5] are known to form complexes with peptides at high pH in which the peptide hydrogens are dissociated. There have also been several studies recently on model peptide-like ligands in which the amide hydrogens are labilized when the molecules are complexed by these same metals.[6-9]

In the case of nickel(II), the peptide complexes at alkaline pH are mainly yellow and diamagnetic and have square-planar coordination. It has been well established that in these deprotonated complexes the nickel ion is coordinated to the nitrogen of the peptide groups both in solution and in the solid state.[10] With the peptide-like ligands, the same coordination with nickel occurs in solution under the same conditions.[7,8]

In the course of our thermodynamic investigations of metal complex formation in solution, we have become interested in species formed in which there is proton labilization due to complex formation with certain metal ions.[11] The investigation of the structure of the nickel complex of *N*,*N*′-di(2-aminoethyl)malondiamide prepared at alkaline pH was undertaken as a part of a study designed to elucidate the factors which determine the bonding geometry of metal ions in biological systems. This compound was especially of interest because it offered an opportunity to compare the results with those of similar nickel glycine peptides and because the complex possesses two deprotonated peptide-like residues in the ligand portion of the complex. Further, we hope to make correlations to subsequent thermodynamic investigations of these model complexes in solution and use the results of this study to aid in the interpretation of thermodynamic parameters.

Experimental Section

The complex was prepared according to the procedure of Hill and Raspin.[7] It was twice recrystallized from water by slow evaporation of the solvent to yield hexagonal-shaped yellow needles of the trihydrate suitable for X-ray analysis.

Crystal Data.—A single crystal was mounted along the needle (*a*) axis. Precession photographs of zero and upper layers (*h*0*l*, *h*1*l*, *hk*0, and *hk*1) taken with Ni-filtered Cu Kα radiation indicated a monoclinic system. Systematic absences occurred in the *h*0*l* reflections (*h*0*l* absent for $l = 2n + 1$) and 0*k*0 reflection (0*k*0 absent for $k = 2n + 1$). These absences are consistent with the space group $P2_1/c$ which was confirmed by subsequent analysis.

The cell parameters were determined from a least-squares refinement of the diffractometer setting angles of 12 carefully centered reflections (Busing, *et al.*[12]). Using Zr-filtered Mo Kα radiation (λ 0.71069 Å), the lattice constants at room temperature (~25°) were found to be $a = 7.397$ (1) Å, $b = 9.053$ (1) Å, $c = 18.690$ (4) Å, and $\beta = 102.80$ (4)°.

The experimental density of the crystals was determined by the flotation method using a mixture of bromoform and chloroform. For four formula units in the cell, the calculated density is 1.627 g/cm^3, which agrees well with the observed density of 1.65 (2) g/cm^3.

Data Collection.—A second crystal of approximate dimensions $0.13 \times 0.17 \times 0.30$ mm^3 was used for data collection. The eight faces of the crystal were indexed by optical and X-ray means and its physical dimensions were measured under a microscope with a micrometer eyepiece for subsequent absorption corrections.

The intensities were measured on a Picker diffractometer at room temperature, using Zr-filtered Mo Kα radiation, a scintillation counter, and 3° takeoff angle. A total of 4576 reflections were measured by the moving-crystal, moving-counter technique using a $1.50° + 0.692 \tan\theta$ scan in 2θ at a scan rate of 1°/min ($2\theta_{\max} = 60°$, in addition a number of reflections with l negative were collected in the range $60° < 2\theta < 100°$). Background intensities were estimated by stationary counting for 10 sec at each end of the scan.

Three standard reflections were measured after every 30 reflections to monitor changes in tube intensity or crystal reflectivity. A scaling correction was applied to the data to account for variations attributed to changes in tube voltage. Such variations were limited to about 4% except during two periods in which a sudden discontinuous increase in intensity of 15% was observed. A visual examination of the crystal after the data were taken gave no indication of decomposition.

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The data were corrected for Lorentz and polarization effects and absorption ($\mu = 16.1\ \text{cm}^{-1}$) using the data processing and absorption correction program DATAP written by Coppens, *et al.*[13] In the absorption correction a grid having 216 sampling points (*i.e.*, 6 × 6 × 6) was used. The transmission factors varied from 0.83 to 0.76. The standard deviations on the observed intensities were estimated from the expression $\sigma^2(I - B) = (I + B)/10 + C^2(I - B)^2$ where I is the observed intensity, B is the summed background, and $C = 0.03$ and where the first term on the right-hand side of the equation is an evaluation of the statistical counting error and the second term is an evaluation of an error proportional to the strength of the signal.

By averaging symmetry-related reflections, 3794 independent reflections were obtained, and for 3324 of these $F_o^2 \geqslant 4\sigma(F_o^2)$.

Structure Determination and Refinement

The Ni–Ni and Ni–N vectors could be identified in a three-dimensional Patterson synthesis, calculated with a modification of A. Zalkin's Fourier program. A least-squares refinement on the scale factor, overall temperature factor, and nitrogen and nickel positions yielded agreement factors of 0.42 and 0.47 for $R\ (= (\Sigma|F_o - k|F_c||)/\Sigma|F_o|)$ and $R_w\ (= (\Sigma w|F_o - k|F_c||^2/\Sigma wF_o^2)^{1/2})$. The other nonhydrogen atoms of the ligand were found in a subsequent Fourier map which, however, failed to produce the positions of the oxygen atoms of the water molecules. These and the hydrogen atoms were located in a difference map obtained after a number of additional least-squares cycles of refinement.

In the final cycles all nonhydrogen atoms were included with an anisotropic thermal parameter, while anomalous dispersion for Ni^{2+} was allowed for ($\Delta f'$ and $\Delta f''$ were taken from ref 14) and an isotropic extinction parameter was included in the refinement. Reflections were considered unobserved when $F_o^2 \leqslant 4\sigma(F_o^2)$. In this case a term $F_c^2 - 4\sigma(F_o^2)$ was included in the least-squares summation whenever $F_c^2 < 4\sigma(F_o^2)$. The final agreement factors including 3324 symmetry-independent reflections are $R = 0.044$ and $R_w = 0.042$. The maximum shift in any parameters in the final cycle was less than $^1/_{10}$ of the corresponding standard deviation.

The atomic scattering factors used were as given by Cromer and Waber[15] (Ni^{2+}, C, N, O) and Steward, Davidson, and Simpson[16] (H).

The final observed structure factors (FO), standard deviations (SIG), calculated structure factors (FC), and the extinction transmission factor (EX) if <0.99 are listed in ref 17, while the final atomic coordinates and thermal parameters are given in Tables I and II, respectively.

Discussion

Description of the Structure.—The interatomic distances and bond angles are given in Figure 1 and Table III. Figure 2 gives a perspective drawing of the nickel complex structure.

The square-planar coordination for the complex is confirmed. The nickel atom is coordinated to the two amine nitrogens and the two amide nitrogens. The nickel and four nitrogens define a least-squares plane which in the monoclinic coordinate system has the equation $7.304x + 1.376y - 4.865z - 1.649 = 0$. The nickel atom is in the square plane (the deviation is -0.0006 ± 0.0003 Å), while the maximum deviation of any nitrogen atom from the plane is 0.052 ± 0.002 Å. The distances of the coordinating atoms from this plane are given in Table IV. There is some puckering of the nitrogen rings with two nonadjacent nitrogens being above and the other two nitrogens below the least-squares plane.

The distances of all the nonhydrogen atoms in the

TABLE I

FINAL POSITIONAL PARAMETERS AND THEIR STANDARD DEVIATIONS[a]

	x	y	z
Ni	2822.3 (0.4)	819.5 (0.3)	1080.5 (0.1)
N(1)	2654 (3)	2878 (2)	1302 (1)
N(2)	2034 (3)	1401 (2)	1014 (1)
N(3)	3113 (3)	−1174 (2)	872 (1)
N(4)	3564 (3)	246 (2)	2094 (1)
C(1)	1222 (4)	3576 (3)	713 (1)
C(2)	1495 (3)	2966 (2)	−10 (1)
C(3)	2106 (3)	662 (2)	−499 (1)
C(4)	2771 (3)	−915 (3)	−455 (1)
C(5)	3167 (3)	−1809 (2)	245 (1)
C(6)	3591 (4)	−2136 (3)	1526 (1)
C(7)	2992 (4)	−1322 (3)	2140 (1)
O(1)	1671 (3)	1210 (2)	−1137 (1)
O(2)	3559 (3)	−3167 (2)	185 (1)
O(3)	4206 (3)	−4617 (2)	−997 (1)
O(4)	1178 (3)	3860 (2)	−1854 (1)
O(5)	2263 (3)	4866 (3)	2569 (1)
H(1)	3735 (41)	3281 (31)	1258 (15)
H(2)	2501 (45)	3090 (35)	1700 (18)
H(3)	1386 (41)	4603 (33)	722 (16)
H(4)	−35 (43)	3270 (33)	779 (16)
H(5)	2529 (39)	3494 (33)	−177 (15)
H(6)	373 (41)	3059 (30)	−368 (16)
H(7)	4036 (49)	−961 (36)	−646 (18)
H(8)	1932 (42)	−1498 (34)	−816 (17)
H(9)	5013 (38)	−2339 (31)	1662 (14)
H(10)	2936 (42)	−3060 (34)	1449 (17)
H(11)	3575 (39)	−1766 (30)	2639 (15)
H(12)	1674 (42)	−1362 (33)	2069 (15)
H(13)	4762 (45)	255 (33)	2218 (16)
H(14)	2993 (55)	826 (41)	2379 (21)
H(15)	4788 (48)	−5315 (41)	−787 (18)
H(16)	3922 (49)	−4142 (37)	−704 (19)
H(17)	2019 (53)	4395 (40)	−1580 (20)
H(18)	1271 (51)	3077 (42)	−1640 (20)
H(19)	1448 (61)	5339 (50)	2430 (24)
H(20)	2023 (52)	4691 (41)	2940 (22)

[a] Standard deviations are given in parentheses. All parameters are times 10^4.

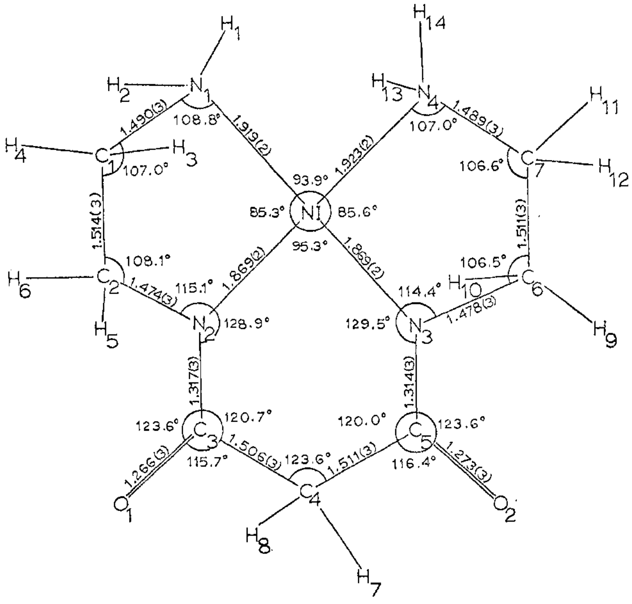

Figure 1.—Intramolecular bond lengths and bond angles in [*N*,*N*′-di(2-aminoethyl)malondiamidato]nickel(II) trihydrate.

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[17] A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number INORG-72-1371. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

TABLE II

FINAL THERMAL PARAMETERS AND THEIR STANDARD DEVIATIONS[a]

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	89.5 (0.5)	40.1 (0.3)	9.5 (0.1)	0.5 (0.3)	8.0 (0.1)	−1.3 (0.1)
N(1)	128 (4)	53 (2)	14 (1)	−4 (2)	12 (1)	−6 (1)
N(2)	100 (3)	42 (2)	11 (1)	9 (2)	7 (1)	2 (1)
N(3)	112 (3)	40 (2)	11 (1)	2 (2)	8 (1)	2 (1)
N(4)	124 (4)	66 (2)	11 (1)	1 (2)	6 (1)	−2 (1)
C(1)	123 (5)	49 (3)	20 (1)	17 (3)	11 (1)	−3 (1)
C(2)	119 (4)	46 (2)	16 (1)	9 (3)	7 (1)	3 (1)
C(3)	84 (3)	52 (2)	12 (1)	−3 (2)	6 (1)	1 (1)
C(4)	138 (4)	53 (2)	12 (1)	5 (3)	13 (1)	−2 (1)
C(5)	85 (4)	42 (2)	13 (1)	−1 (2)	7 (1)	−1 (1)
C(6)	158 (5)	51 (2)	13 (1)	8 (3)	7 (1)	5 (1)
C(7)	144 (5)	69 (3)	11 (1)	−8 (3)	11 (1)	2 (1)
O(1)	190 (4)	72 (2)	11 (1)	18 (2)	9 (1)	5 (1)
O(2)	175 (4)	50 (2)	17 (1)	24 (2)	14 (1)	−3 (1)
O(3)	157 (4)	68 (2)	16 (1)	2 (2)	12 (1)	−1 (1)
O(4)	171 (4)	86 (3)	19 (1)	−7 (3)	0 (1)	11 (1)
O(5)	155 (4)	136 (3)	19 (1)	24 (3)	22 (1)	11 (1)

	B, Å^2		B, Å^2		B, Å^2
H(1)	2.1 (6)	H(8)	2.7 (6)	H(15)	3.4 (7)
H(2)	3.1 (7)	H(9)	2.0 (5)	H(16)	3.2 (7)
H(3)	2.4 (6)	H(10)	2.9 (6)	H(17)	4.1 (8)
H(4)	2.6 (6)	H(11)	2.1 (5)	H(18)	4.1 (8)
H(5)	2.2 (6)	H(12)	2.4 (6)	H(19)	5.4 (1.1)
H(6)	2.2 (6)	H(13)	2.5 (6)	H(20)	3.8 (8)
H(7)	3.9 (7)	H(14)	4.8 (9)		

[a] Standard deviations are given in parentheses. All β_{ij} values are times 10^4. The β_{ij}'s are defined by the following expression for the temperature factors: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

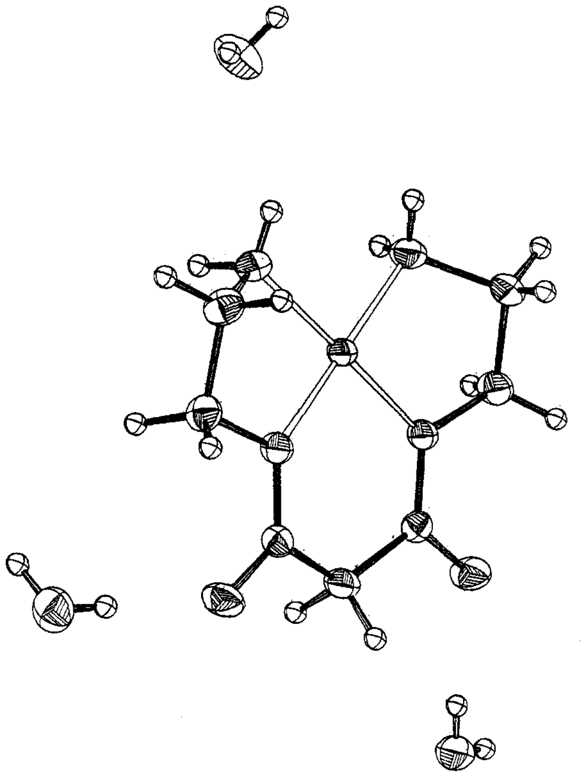

Figure 2.—A perspective drawing of the [*N*,*N*′-di(2-aminoethyl)malondiamidato]nickel (II) trihydrate asymmetric unit.

complex from a least-squares plane through the four nitrogens (equation: $7.309x + 1.340y - 4.835z - 1.659 = 0$) are given in Table V. All of the carbon atoms of the ethylenediamine side residues are on one side of the plane whereas the carbons of the malonate residue backbone are on the other side of the plane especially the methylene carbon C(4) which is displaced by 0.464 (2) Å.

Thus the nickel coordination plane is slightly distorted. Further evidence for distortion from square-planar coordination is provided by the fact that the Ni–N_{amine} distance (1.92 Å) is slightly greater than the Ni–N_{amide} distance (1.87 Å), while N–Ni–N bond angles show appreciable deviation from 90° of $\sim\pm5°$ (94.6_{av} as compared to 85.4_{av}). There is no significant metal–metal interaction with the closest Ni–Ni contact occurring at 5.34 Å for the symmetry pair x, y, z and $\bar{x}$, $\bar{y}$, $\bar{z}$.

Layers of molecules are parallel to the *bc* plane (Figure 3). The molecules in the layers are held together

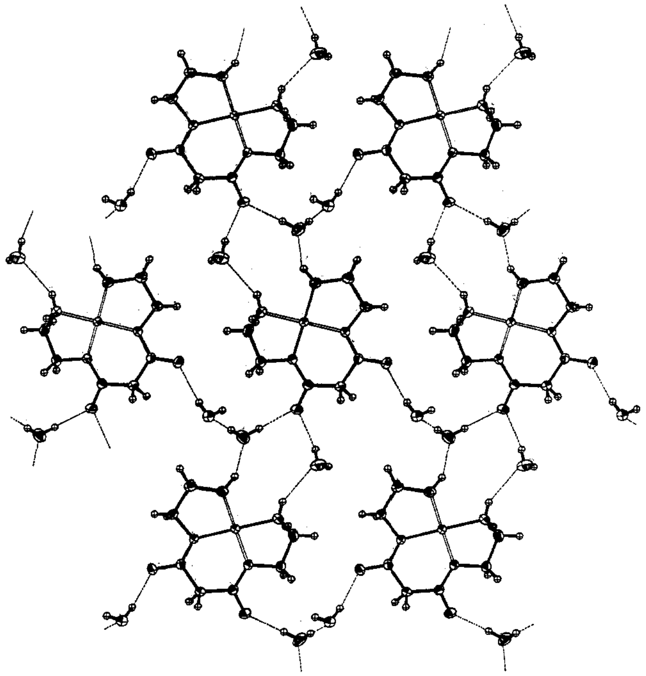

Figure 3.—The packing and hydrogen-bonding scheme of [*N*,*N*′-di(2-aminoethyl)malondiamidato]nickel(II) trihydrate as shown projected down the *b* axis.

TABLE III

BOND LENGTHS AND ANGLES IN THE STRUCTURE OF $Ni(C_7H_{14}N_4O_2) \cdot 3H_2O$

Intramolecular Bonds (Å)

Ni–N(1)	1.919 (2)	N(4)–H(13)	0.87 (3)
Ni–N(2)	1.869 (2)	N(4)–H(14)	0.92 (4)
Ni–N(3)	1.869 (2)	C(1)–H(3)	0.94 (3)
Ni–N(4)	1.923 (2)	C(1)–H(4)	1.00 (3)
N(1)–C(1)	1.490 (3)	C(2)–H(5)	1.01 (3)
N(2)–C(2)	1.474 (3)	C(2)–H(6)	0.95 (3)
N(2)–C(3)	1.317 (3)	C(4)–H(7)	1.07 (4)
N(3)–C(5)	1.314 (3)	C(4)–H(8)	0.97 (3)
N(3)–C(6)	1.478 (3)	C(6)–H(9)	1.04 (3)
N(4)–C(7)	1.489 (3)	C(6)–H(10)	0.96 (3)
C(1)–C(2)	1.514 (3)	C(7)–H(11)	1.02 (3)
C(3)–C(4)	1.506 (3)	C(7)–H(12)	0.96 (3)
C(4)–C(5)	1.511 (3)	O(3)–H(15)	0.82 (4)
C(6)–C(7)	1.511 (3)	O(3)–H(16)	0.76 (4)
C(3)–O(1)	1.266 (3)	O(4)–H(17)	0.86 (4)
C(5)–O(2)	1.273 (3)	O(4)–H(18)	0.81 (4)
N(1)–H(1)	0.90 (3)	O(5)–H(19)	0.74 (5)
N(1)–H(2)	0.80 (3)	O(5)–H(20)	0.77 (4)

Nonbonded Intramolecular Distances (Å)

N(1)–N(2)	2.566 (3)	N(2)–N(3)	2.763 (2)
N(3)–N(4)	2.577 (3)	N(1)–N(4)	2.807 (3)

Distances between H-Bonded Atoms (Å)

O(1)···H(18)	1.92 (4)	O(3)···H(17)	1.96 (4)
O(1)···H(20)	1.98 (4)	O(4)···H(14)	2.19 (4)
O(2)···H(16)	1.95 (4)	O(5)···H(2)	2.32 (3)
O(1)···H(18)–O(4)	2.733 (3)	O(3)···H(17)–O(4)	2.810 (3)
O(1)···H(20)–O(5)	2.732 (3)	N(1)–H(2)···O(5)	3.037 (3)
O(2)···H(16)–O(3)	2.701 (3)	N(4)–H(14)···O(4)	3.029 (3)

Interatomic Angles (Deg)

N(1)–Ni–N(2)	85.25 (8)	N(2)–C(2)–H(5)	107.4 (1.7)
N(2)–Ni–N(3)	95.32 (8)	N(2)–C(2)–H(6)	110.6 (1.7)
N(3)–Ni–N(4)	85.63 (8)	H(5)–C(2)–H(6)	110.2 (2.3)
N(4)–Ni–N(1)	93.87 (9)	C(3)–C(4)–H(7)	108.5 (1.8)
Ni–N(1)–C(1)	108.8 (1)	C(3)–C(4)–H(8)	109.2 (1.8)
Ni–N(2)–C(2)	115.1 (1)	C(5)–C(4)–H(7)	104.5 (1.8)
Ni–N(3)–C(6)	114.4 (1)	C(5)–C(4)–H(8)	106.4 (1.8)
Ni–N(4)–C(7)	107.0 (1)	H(7)–C(4)–H(8)	102.7 (2.5)
Ni–N(2)–C(3)	128.9 (2)	N(3)–C(6)–H(9)	110.5 (1.5)
Ni–N(3)–C(5)	129.5 (2)	N(3)–C(6)–H(10)	111.7 (1.9)
N(1)–C(1)–C(2)	107.0 (2)	C(7)–C(6)–H(9)	110.5 (1.5)
N(2)–C(2)–C(1)	108.1 (2)	C(7)–C(6)–H(10)	108.3 (1.9)
N(2)–C(3)–C(4)	120.7 (2)	H(9)–C(6)–H(10)	109.3 (2.4)
N(2)–C(3)–O(1)	123.6 (2)	C(6)–C(7)–H(11)	111.5 (1.6)
N(3)–C(5)–C(4)	120.0 (2)	C(6)–C(7)–H(12)	109.8 (1.7)
N(3)–C(5)–O(2)	123.6 (2)	N(4)–C(7)–H(11)	111.1 (1.6)
N(3)–C(6)–C(7)	106.5 (2)	N(4)–C(7)–H(12)	108.9 (1.8)
N(4)–C(7)–C(6)	106.6 (2)	H(11)–C(7)–H(12)	108.9 (2.3)
C(2)–N(2)–C(3)	115.4 (2)	C(7)–N(4)–H(13)	106.3 (2.0)
C(5)–N(3)–C(6)	115.5 (2)	C(7)–N(4)–H(14)	109.8 (2.3)
C(3)–C(4)–C(5)	123.6 (2)	Ni–N(4)–H(13)	108.3 (2.0)
C(4)–C(3)–O(1)	115.7 (2)	Ni–N(4)–H(14)	110.5 (2.3)
C(4)–C(5)–O(2)	116.4 (2)	H(13)–N(4)–H(14)	114.5 (3.1)
Ni–N(1)–H(1)	105.8 (1.8)	O(2)···H(16)–O(3)	168.3 (3.5)
Ni–N(1)–H(2)	117.5 (2.3)	H(15)–O(3)–H(16)	107.1 (3.4)
C(1)–N(1)–H(1)	105.2 (1.8)	O(1)···H(18)–O(4)	175.9 (3.8)
C(1)–N(1)–H(2)	111.3 (2.4)	H(17)–O(4)–H(18)	103.2 (3.3)
H(1)–N(1)–H(2)	107.5 (2.9)	N(1)–H(2)···O(5)	149.9 (3.0)
N(1)–C(1)–H(3)	109.8 (1.8)	H(19)–O(5)–H(20)	95.9 (4.0)
N(1)–C(1)–H(4)	108.5 (1.7)		
C(2)–C(1)–H(3)	109.7 (1.8)		
C(2)–C(1)–H(4)	108.7 (1.7)		
H(3)–C(1)–H(4)	113.1 (2.5)		
C(1)–C(2)–H(5)	111.3 (1.6)		
C(1)–C(2)–H(6)	109.2 (1.7)		

TABLE IV

LEAST-SQUARES PLANE OF THE NICKEL AND FOUR NITROGEN ATOMS—DISTANCES OF ATOMS IN THE COORDINATION SPHERE FROM THE LEAST-SQUARES PLANE

Atom	Distance, Å	Atom	Distance, Å
Ni	−0.0006 (3)	N(3)	0.039 (2)
N(1)	0.052 (2)	N(4)	−0.030 (2)
N(2)	−0.020 (2)		

TABLE V

LEAST-SQUARES PLANE OF THE BASIC COMPLEX MOLECULE—DISTANCES OF ALL NONHYDROGEN ATOMS FROM THE LEAST-SQUARES PLANE DEFINED BY THE FOUR NITROGENS

Atom	Distance, Å	Atom	Distance, Å
Ni	−0.0084 (3)	C(2)	−0.164 (3)
N(1)	0.037 (2)	C(3)	0.211 (2)
N(2)	−0.034 (2)	C(4)	0.464 (3)
N(3)	0.038 (2)	C(5)	0.295 (2)
N(4)	−0.033 (2)	C(6)	−0.058 (3)
C(1)	−0.631 (3)	C(7)	−0.683 (3)
O(1)	0.275 (3)	O(2)	0.429 (3)

by hydrogen bonds with the waters of hydration and van der Waals forces between the molecules. No hydrogen bonds exist between the layers. Two water molecules are hydrogen bonded to a carbonyl oxygen of one molecule and to amine nitrogens in an adjacent molecule. The third and last water molecule in the asymmetric unit is hydrogen bonded to a carbonyl oxygen and to another water molecule. Each complex molecule has a total of five hydrogen bonds associated with it. The intermolecular angles (Table III) associated with the hydrogen bonds appear to be reasonable: the hydrogen atoms are close to the lines connecting donor and acceptor pairs. The crystal structure is stabilized by this complex hydrogen-bonding network.

Comparison with Other Compounds.—The nickel-to-amide nitrogen distances are significantly shorter than the nickel-to-amine nitrogen distances but are in good agreement with nickel–amide nitrogen distances observed for other compounds having square coordination (Table VI), which average to 1.86 Å as compared to 1.869 Å in this study. The nickel–amine nitrogen bond is also in good agreement with those observed for other compounds having square-planar coordination, which average to 1.92 Å as compared to 1.921 Å in the present investigation.

The absence of any peaks in the difference Fourier maps for hydrogens bonded to the amide nitrogens as well as the trigonal configuration about these nitrogens supported by the bond angles confirms the dissociation of the amide protons on formation of the complex. To date no complexes have been analyzed in the solid state containing a protonated and coordinated amide nitrogen.

It is also interesting to note from Table VI that where there is double-bond character about the nitrogen in a square-planar complex with nickel(II), it results in shorter Ni–N bonds similar to the $Ni–N_{amide}$ bonds in this study. This is evident for the imines, oximes, and imide listed in this table which average to 1.85 Å.

Finally, in the study of three glycine peptide complexes with nickel by Freeman, *et al.*,[10] two of which are octahedral and the third of which is square planar, the $Ni–N_{peptide}$ bonds are all shorter than the $Ni–N_{amine}$ bonds, again in agreement with this investigation.

Charge Refinement.—The charge refinement on this compound with the ELS (extended L-shell) method has been described elsewhere.[18] The results which are

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[18] P. Coppens, D. Pautler, and J. F. Griffin, *J. Amer. Chem. Soc.*, **93**, 1051 (1971).

TABLE VI

COMPARISON OF AVERAGE BOND LENGTHS WITH THOSE OF RELATED COMPOUNDS

Complex[a]	Bond		Distance, Å	Ref
A. Square-Planar Complexes				
NiAMD	$Ni-N_{amide}$		1.869 2)	*b*
NiPCA	$Ni-N_{amide}$		1.87 (1)	*c*
Ni(Gly)$_4$	$Ni-N_{peptide}$		1.85 (1)	*d*
		Av	1.86	
NiAMD	$Ni-N_{amine}$		1.921 (2)	*b*
NiAO	$Ni-N_{amine}$		1.91 (1)	*e*
Ni(Gly)$_4$	$Ni-N_{amine}$		1.93 (1)	*d*
		Av	1.92	
NiAO	$Ni-N_{oxime}$		1.86 (1)	*e*
NiG	$Ni-N_{oxime}$		1.87 (1)	*f*
NiDMG	$Ni-N_{oxime}$		1.85 (2)	*g*
NiMEG	$Ni-N_{oxime}$		1.86 (2)	*h*
		Av	1.86	
NiHAD	$Ni-N_{imine}$		1.83 (2)	*i*
NiPDA	$Ni-N_{imine}$		1.83 (1)	*j*
		Av	1.83	
NiDHA	$Ni-N_{imide}$		1.832 (9)	*k*
B. Octahedral Complexes				
Ni(Gly-Gly)$_2$ (monoclinic)	$Ni-N_{peptide}$		1.99 (1)	*d*
Ni(Gly-Gly)$_2$ (triclinic)	$Ni-N_{peptide}$		2.02 (1)	*d*
		Av	2.01	
Ni(Gly-Gly)$_2$ (monoclinic)	$Ni-N_{amine}$		2.14 (1)	*d*
Ni(Gly-Gly)$_2$ (triclinic)	$Ni-N_{amine}$		2.13 (1)	*d*
		Av	2.14	

[a] NiAMD = *N,N'*-di(2-aminoethyl)malondiamidatonickel(II) trihydrate; NiPCA = bis(pyridine-2-carboxamido)nickel(II) dihydrate; Ni(Gly)$_4$ = disodium glycylglycylglycylglycinatonickelate(II) octahydrate; NiAO = bis(2-amino-2-methyl-3-butanone oximato)nickel(II) chloride monohydrate; NiG = bis(glyoximato)nickel(II); NiDMG = bis(dimethylglyoximato)-nickel(II); NiMEG = nickel methylethylglyoxime; NiHAD = hexamethyltetraazacyclotetradecatetraenenickel(II); NiPDA = bis(*o*-phenylenediamino)nickel; Ni(Gly-Gly)$_2$ (monoclinic) = disodium bis(glycylglycinato)nickel(II) octahydrate; and Ni(Gly-Gly)$_2$ (triclinic) = disodium bis(glycylglycinato)nickelate(II) nonahydrate. [b] This work. [c] S. C. Chang, D. Y. Park, and N. C. Li, *Inorg. Chem.*, **7**, 2144 (1968). [d] See ref 10. [e] E. O. Schlemper, *Inorg. Chem.*, **7**, 1130 (1968). [f] M. Calleri, G. Ferraris, and D. Viterbo, *Acta Crystallogr.*, **22**, 468 (1967); R. K. Murmann and E. O. Schlemper, *ibid.*, **23**, 667 (1967). [g] D. E. Williams, G. Wohlauer, and R. E. Rundle, *J. Amer. Chem. Soc.*, **81**, 755 (1959). [h] E. Frasson and C. Panattoni, *Acta Crystallogr.*, **13**, 893 (1960). [i] I. E. Maxwell and M. F. Baily, *Chem. Commun.*, 883 (1966). [j] G. S. Hall and R. H. Soderberg, *Inorg. Chem.*, **7**, 2300 (1968). [k] S. Kiryu, *Acta Crystallogr.*, **23**, 392 (1967).

given in Table VII indicate that the Ni atom is almost neutral: a small positive charge of 0.46 ± 0.17 electron is found. Reasonable agreement exists between the charges on chemically equivalent atoms in each half of the complex. Oxygen and nitrogen atoms are found to be negative, in agreement with their electronegativities. The carbon atoms are slightly negative except C(3) and C(5) which are bonded to the malonate residue oxygen atoms. Thus, the overall charge distribution appears reasonable. At present, no theoretical calculations are available for comparison with the experimental results.

TABLE VII

[*N,N'*-DI(2-AMINOETHYL)MALONDIAMIDATO]NICKEL(II) TRIHYDRATE ATOMIC CHARGES OBTAINED WITH HF BASIS SET[a] (EXTENDED L SHELL)

Ni	+0.46 (17)	H(3)	+0.03 (5)
N(1)	−0.24 (7)	H(4)	+0.08 (5)
N(2)	−0.30 (6)	H(5)	+0.06 (5)
N(3)	−0.32 (6)	H(6)	+0.05 (5)
N(4)	−0.11 (6)	H(7)	+0.13 (6)
C(1)	−0.10 (8)	H(8)	+0.09 (5)
C(2)	−0.12 (8)	H(9)	+0.06 (5)
C(3)	+0.14 (8)	H(10)	+0.01 (5)
C(4)	−0.26 (9)	H(11)	+0.08 (5)
C(5)	+0.18 (8)	H(12)	+0.10 (5)
C(6)	−0.09 (8)	H(13)	+0.15 (5)
C(7)	−0.09 (8)	H(14)	+0.19 (6)
O(1)	−0.31 (5)	H(15)	+0.17 (6)
O(2)	−0.43 (5)	H(16)	+0.13 (6)
O(3)	−0.22 (5)	H(17)	+0.18 (6)
O(4)	−0.26 (5)	H(18)	+0.15 (6)
O(5)	−0.19 (6)	H(19)	+0.19 (6)
H(1)	+0.11 (5)	H(20)	+0.19 (6)
H(2)	+0.11 (6)		
R, %	4.4	No. of observations	3323
R_w, %	4.0	No. of variables	48

[a] Only the positional and thermal parameters of the nickel atom were refined. Oxygen atoms, 3, 4, and 5 belong to water molecules.

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