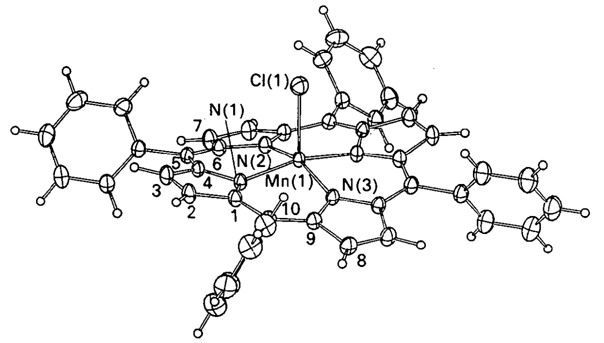

Fig. 1. *ORTEP* plot (Johnson, 1965) of the complex showing the atomic labels used (30% thermal ellipsoids). Atoms not otherwise designated are C atoms.

atoms. The porphinato ligand is deformed into a saddle conformation with pairs of opposing pyrrole rings disposed either up or down. This leads to the four N atoms being non-coplanar and to a distortion of the coordination geometry towards trigonal pyramidal. The bond lengths from the Mn atom to the two N atoms distorted further away from the chloro ligands are longer: 2.026 (2) and 2.033 (2) Å compared with 2.000 (2) Å. A similar result is seen in the structure of the acetone solvate (Tulinsky & Chen, 1977) though in that case it is of marginal significance. The average Mn—N bond lengths in the two structures are not significantly different. The Mn atom in the present structure lies further from the N_4 plane than it does in the acetone solvate: 0.32 compared with 0.27 Å; as a probable consequence of this, the Mn—Cl bond length is found to be significantly shorter: 2.345 (1) compared with 2.363 (2) Å. The porphinato group is also more deformed from planarity in the present structure, the largest deviation being 0.58 Å compared with 0.49 Å in the acetone solvate. All of this suggests a degree of plasticity in the coordination geometry.

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cis-[Diaquabis(1-aminocyclohexanecarboxylato)nickel(II)]–Water (1/1)

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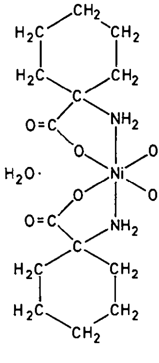
Abstract. (α-6-22)-Diaquabis[(1-amino-κN)cyclohexanecarboxylato-κO]nickel(II) hydrate, [Ni($C_7H_{12}NO_2$)$_2$(H_2O)$_2$].H_2O, $M_r = 397.0$, monoclinic, Cc, $a = 27.073$ (7), $b = 6.145$ (2), $c = 11.605$ (4) Å, $\beta = 107.24$ (3)°, $V = 1844$ (1) Å^3, $Z = 4$, $D_x = 1.43$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 1.09$ mm^{-1}, $F(000) = 848$, $T = 293$ (1) K, $R = 0.032$ for 1831 reflections. The single Ni atom is hexacoordinated by two bidentate ligands, through the amino N atoms and the carboxylate O atoms, and by O atoms of two water molecules. The N atoms are in *trans* positions and the water molecules are in *cis* positions. The third water molecule is not coordinated but participates in a hydrogen-bonding network. The nickel–ligand distances are 2.059 (4) for Ni—O(carboxyl), 2.095 (4) and 2.098 (4) for Ni—O(water), and 2.054 (7) and 2.082 (7) Å for Ni—N.

Introduction. The structure analysis of the title compound is a continuation of the investigation of the metal complexes of aromatic and heterocyclic amino acids (Boudreau & Haendler, 1992; Haendler, 1989).



The Cu complex with 1-aminocyclohexanecarboxylic acid exhibited both planar and bipyramidal (or its rectangular pyramidal distortion) structures in the two molecules of the asymmetric unit. It was of interest to study the corresponding Ni complex to determine the effect of the coexistence of the amino and the carboxyl groups on the same C atom. Increasing evidence of the importance of nickel as an essential trace element in biology indicates the significance of structures of complexes bearing even a minor relationship to the nickel metalloenzymes (Lancaster, 1988).

Experimental. Crystals were grown by slow evaporation of a mixture of aqueous nickel(II) acetate tetrahydrate and a 50% ethanol solution of 1-aminocyclohexanecarboxylic acid in a 1:2 ratio. Samples were often contaminated with a white product, probably $[R\mathrm{NH_3}]\mathrm{OAc}$, most of which could be removed with methanol. Calculated for $\mathrm{Ni(C_7H_{12}NO_2)_2.3H_2O}$: C 42.34, H 7.61, N 7.05%; found: C 42.38, H 7.74, N 6.86%. The crystal used was a light-blue rectangular parallelepiped, 0.19 × 0.35 × 1.00 mm. Nicolet four-circle diffractometer, graphite-monochromatized Mo $K\alpha$ radiation. 15 reflections ($2\theta > 20°$) for least-squares refinement of cell parameters at 293 (1) K. No absorption correction. Max. $(\sin\theta)/\lambda = 0.650$ Å^{-1}; h −34 to 32, k 0 to 7, l 0 to 14. Six check reflections, measured every 300 reflections, no indication of deterioration or misalignment. ω scan, scan range 0–90°, scan rate 2–4° min^{-1}, background/scan time ratio 0.50. 11 steps taken, 9 used in intensity calculations. 2θ values in range $3 \leq 2\theta \leq 55°$. Standard deviation in intensity computed from $\sigma^2(I) = (C_t + k^2B)$; C_t is total scan count, k is scan time/background time ratio, B is total background count. For counter weights $\sigma_F = \{[\sigma(F_o)]^2 + (0.03|F_o|)^2\}^{1/2}$. 2487 reflections measured, 2206 accepted, 2095 independent reflections, 264 unobserved with $I < 2.5\sigma(I)$. 1831 reflections, including 111 $h00$ and $hk0$ Friedel pairs with averaged intensities, were used for the structure determination (Stout & Jensen, 1989); $R_{\mathrm{int}} = 0.030$. The structure was solved by a combination of the VAX version of the *DIRDIF* system (Beurskens *et al.*, 1985) and the *NRCVAX* programs (Gabe, Lee & Le Page, 1985) and confirmed a suggestion made by Cynthia Day of Crystalytics Company during the collection of the data. Systematic extinctions implicated *Cc* and *C*2/*c* as possible space groups. Statistical tests favored *Cc* and refinement was begun on that basis. This assignment was supported by the ultimate chemically and structurally sensible results. A Patterson map indicated that the Ni atom lay close to a pseudo-special position ($y = 0$). Successive passes of *DIRDIF* destroyed the supersymmetry and located the remaining 23 non-H atoms. Isotropic least-squares refinement on F, using the block-diagonal approximation, converged at $R = 0.08$ for the 24 non-H atoms. Full-matrix refinement with anisotropic thermal parameters converged at $R = 0.047$. The positions of the 20 ring H atoms were calculated and the refinement of the 44 atoms continued, with the individual U values of the H atoms fixed; $R = 0.040$. The remaining ten H atoms were then located on a difference Fourier map or by superposition of a model on a scaled projection. The final full-matrix refinement, with all 54 atoms, 305 variables (only the H-atom U values were fixed), 1831 reflections, Friedel pairs averaged, no anomalous-dispersion corrections, converged at $R = 0.032$, $w = 1/\sigma^2(F_o)$, $wR = 0.033$. $(\Delta/\sigma)_{\max} = 0.05$, $(\Delta/\sigma)_{\mathrm{av}} = 0.017$ for non-H atoms; 0.29 and 0.12 for H atoms. $S = 1.33$. Final difference map showed max. and min. peaks of 0.32 and −0.33 e Å^{-3}. No systematic errors as functions of $\sin^2\theta$ or F_o; no significant correlations. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). *ORTEP*II (Johnson, 1976) was used for the thermal-ellipsoid plot.

Discussion. Final positional parameters of all atoms except the cyclohexane H atoms are given in Table 1* and principal bond distances and angles, including those for the hydrogen-bonding systems, are given in Table 2. A view of the *bc* plane (for one half of the *a* axis) is shown in projection in Fig. 1. The hydrogen-bonding system is indicated. The thermal-ellipsoid plot is shown in Fig. 2. Some H atoms have been omitted for clarity.

The Ni atom is hexacoordinated; the resulting octahedron is slightly distorted. There are two chelated 1-aminocyclohexanecarboxylate groups, each with an amino group and a carboxylate group bonded to the Ni atom. The amino groups are in axial positions on the cyclohexane rings; the carboxyl groups are in equatorial positions. The two N atoms of the chelated ligands are in the *trans* octahedral location. The bonding O atoms of the carboxyl groups thus have a *cis* orientation, as do the two coordinated water molecules. The third water molecule is not coordinated and occupies a position between two asymmetric units of the complex. The Ni—O distances for the carboxyl groups of the two ligands agree within the e.s.d.'s, 2.059 (4) and 2.059 (4) Å, as do those for the coordinated water molecules, 2.095 (4) and 2.098 (4) Å. There is greater

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, ring bond distances and angles, plane equations and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55485 (34 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD0088]

Table 1. *Final positional parameters and equivalent Debye–Waller factors* (Å^2)

$$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Ni	0.00000	0.98451 (9)	0.00000	1.696 (22)
O(11)	0.1029 (1)	0.7586 (7)	0.3091 (3)	2.90 (16)
O(12)	0.0310 (2)	0.8669 (6)	0.1725 (4)	2.41 (16)
O(21)	−0.0880 (2)	0.4535 (7)	−0.1404 (5)	4.53 (21)
O(22)	−0.0218 (2)	0.6765 (6)	−0.0654 (4)	2.44 (16)
O(10)	0.0159 (2)	1.2991 (7)	0.0709 (4)	3.51 (21)
O(20)	−0.0279 (2)	1.1183 (6)	−0.1736 (4)	2.43 (16)
O(30)	0.0485 (2)	0.3831 (7)	0.3069 (4)	3.35 (18)
N(1)	0.0757 (3)	0.9567 (11)	0.0006 (6)	2.26 (24)
N(2)	−0.0757 (3)	0.9760 (10)	0.0087 (7)	2.52 (25)
C(10)	0.0792 (2)	0.8339 (8)	0.2076 (4)	2.07 (18)
C(11)	0.1114 (2)	0.8796 (8)	0.1197 (4)	1.85 (17)
C(12)	0.1384 (2)	0.6689 (9)	0.1016 (5)	2.79 (22)
C(13)	0.1750 (3)	0.7054 (11)	0.0251 (7)	3.75 (29)
C(14)	0.2153 (3)	0.8796 (18)	0.0829 (8)	4.59 (40)
C(15)	0.1899 (3)	1.0914 (12)	0.1019 (6)	3.49 (27)
C(16)	0.1519 (2)	1.0542 (10)	0.1750 (6)	3.00 (24)
C(20)	−0.0688 (2)	0.6276 (8)	−0.0905 (5)	2.57 (19)
C(21)	−0.1061 (2)	0.7862 (8)	−0.0546 (4)	2.09 (18)
C(22)	−0.1465 (3)	0.8639 (12)	−0.1714 (6)	3.00 (25)
C(23)	−0.1907 (3)	0.9915 (16)	−0.1492 (8)	5.30 (38)
C(24)	−0.2164 (3)	0.8590 (24)	−0.0708 (10)	6.99 (64)
C(25)	−0.1770 (3)	0.7966 (19)	0.0458 (8)	6.21 (47)
C(26)	−0.1330 (3)	0.6658 (13)	0.0255 (6)	4.23 (30)
H(10*A*)	0.008 (2)	1.418 (8)	0.032 (4)	1.86
H(10*B*)	0.023 (2)	1.312 (11)	0.146 (6)	3.04
H(20*A*)	−0.045 (3)	1.245 (13)	−0.173 (7)	5.30
H(20*B*)	−0.005 (3)	1.123 (11)	−0.207 (6)	4.33
H(30*A*)	0.026 (3)	0.402 (12)	0.333 (6)	3.94
H(30*B*)	0.067 (2)	0.509 (12)	0.320 (6)	3.54

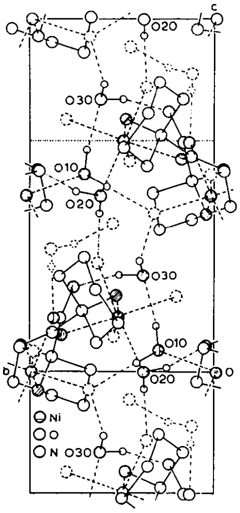

Fig. 1. View of the *bc* plane for half the *a* axis. The ligand bonds are indicated as solid lines, the coordination bonds by dashed lines and the hydrogen bonds by dash-dotted lines. Atoms outside the half cell are indicated by dashed circles.

Table 2. *Principal bond distances* (Å), *angles* (°) *and hydrogen-bond parameters* (Å, °)

Ni—O(12)	2.059 (4)	Ni—O(22)	2.059 (4)
Ni—O(10)	2.095 (4)	Ni—O(20)	2.098 (4)
Ni—N(1)	2.054 (7)	Ni—N(2)	2.082 (7)
O(11)—C(10)	1.251 (6)	O(21)—C(20)	1.254 (7)
O(12)—C(10)	1.263 (6)	O(22)—C(20)	1.255 (7)
N(1)—C(11)	1.509 (8)	N(2)—C(21)	1.490 (8)
C(10)—C(11)	1.551 (6)	C(20)—C(21)	1.547 (7)
C(11)—C(12)	1.532 (7)	C(21)—C(22)	1.544 (8)
C(11)—C(16)	1.532 (7)	C(21)—C(26)	1.531 (8)
O(12)—Ni—O(10)	88.0 (2)	O(22)—Ni—O(10)	174.8 (2)
O(12)—Ni—O(20)	176.4 (2)	O(22)—Ni—O(20)	91.4 (2)
O(12)—Ni—N(1)	81.3 (2)	O(22)—Ni—N(1)	95.8 (2)
O(12)—Ni—N(2)	93.9 (3)	O(22)—Ni—N(2)	79.4 (2)
O(10)—Ni—N(1)	89.2 (2)	O(20)—Ni—N(1)	96.3 (2)
O(10)—Ni—N(2)	95.4 (2)	O(20)—Ni—N(2)	88.8 (3)
Ni—O(12)—C(10)	117.0 (3)	Ni—O(22)—C(20)	117.8 (3)
Ni—N(1)—C(11)	113.4 (4)	Ni—N(2)—C(21)	113.8 (4)
O(12)—Ni—O(22)	91.5 (2)	O(10)—Ni—O(20)	89.4 (2)
N(1)—Ni—N(2)	173.2 (3)		
O(11)—C(10)—O(12)	123.8 (5)	O(21)—C(20)—O(22)	124.4 (5)
O(11)—C(10)—C(11)	117.0 (4)	O(21)—C(20)—C(21)	116.6 (5)
O(12)—C(10)—C(11)	119.2 (4)	O(22)—C(20)—C(21)	119.0 (4)
N(1)—C(11)—C(10)	109.1 (4)	N(2)—C(21)—C(20)	108.5 (4)
N(1)—C(11)—C(12)	110.0 (5)	N(2)—C(21)—C(22)	109.6 (5)
N(1)—C(11)—C(16)	110.4 (4)	N(2)—C(21)—C(26)	111.8 (5)
C(10)—C(11)—C(12)	108.7 (4)	C(20)—C(21)—C(22)	107.9 (4)
C(10)—C(11)—C(16)	108.9 (4)	C(20)—C(21)—C(26)	109.0 (5)

$H_2O\cdots O$	$O\cdots O$	O—H	$H\cdots O$	$O—H\cdots O$
$O(10)\cdots O(22^{i})$	2.823 (6)	0.85 (5)	1.98 (5)	171 (5)
$O(10)\cdots O(30^{i})$	2.667 (6)	0.84 (7)	1.84 (7)	168 (6)
$O(20)\cdots O(12^{ii})$	2.724 (6)	0.82 (7)	1.93 (7)	163 (7)
$O(20)\cdots O(21^{i})$	2.724 (6)	0.90 (8)	1.85 (8)	162 (7)
$O(30)\cdots O(11)$	2.734 (6)	0.91 (8)	1.84 (7)	166 (6)
$O(30)\cdots O(22^{iii})$	2.760 (6)	0.77 (7)	2.05 (7)	154 (7)

Symmetry code: (i) $x, 1+y, z$; (ii) $x, 2-y, z-\frac{1}{2}$; (iii) $x, 1-y, z+\frac{1}{2}$.

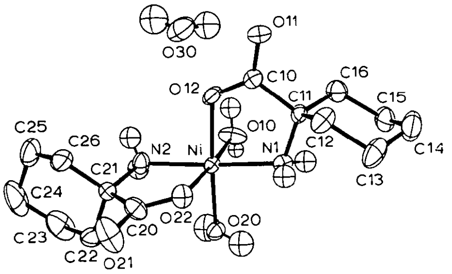

Fig. 2. Thermal-ellipsoid plot of the molecule.

variation in the Ni—N distances, 2.057 (7) and 2.082 (7) Å, and this difference is reflected in some of the chelate-ring distances and angles. Bidentate ligands permit some of freedom of motion, in contrast to more-rigid polydentate ligands. The closest approach of the non-bonded water to an Ni atom is 3.686 (4) Å. Bond distances reported for hydrated Ni complexes generally range from 2.02 to 2.11 Å for Ni—O and from 2.04 to 2.14 Å for Ni—N. A recent report on the hexaaquanickel bromate lists 2.061 (2) Å for the observed Ni—O distance and 2.065 Å for the corrected rigid bond (Blackburn, Gallucci & Gerkin, 1991).

There are six potential hydrogen-bonding situations, as indicated by distance and angle parameters. These are listed in Table 2. There is no indication of anything other than two-centre bonds. Each water molecule forms two hydrogen bonds; O(30) is the recipient of a third. The combination results in a linkage between asymmetric units in the *bc* plane. The bonding is illustrated in Fig. 1.

The Ni complex can be contrasted with the Cu complex (Haendler, 1989) in which two chelated molecules are in each of four asymmetric units. In one molecule, the N atoms are in a *cis* position with the Cu in a planar configuration. In the second molecule, the N atoms are in the *trans* position with the Cu atom intermediate between a distorted pentacoordinated trigonal bipyramid and a distorted rectangular pyramid. The metal–ligand distances are greater in the Ni complex than in the Cu complex and the O—*M*—N angle is slightly smaller.

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Structure of Sodium 6-Hydroxy-2-methyl-3-thioxo-2*H*-1,2,4-triazin-5(4*H*)-onate 1.25-Hydrate

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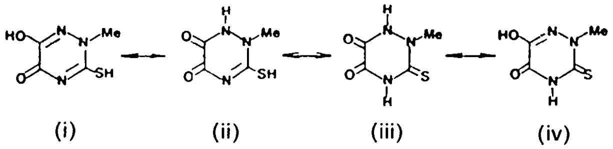
Abstract. $Na^+.C_4H_4N_3O_2S^-.1.25H_2O$, $M_r = 202.61$, monoclinic, $P2_1/c$, $a = 11.032\,(2)$, $b = 9.793\,(1)$, $c = 15.867\,(2)$ Å, $\beta = 103.53\,(1)°$, $V = 1666.7\,(7)$ Å^3, $Z = 8$, $D_m = 1.618\,(5)$, $D_x = 1.623$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.396$ mm^{-1}, $F(000) = 836$, $T = 293\,(2)$ K, final $R = 0.035$ and $wR = 0.042$ for 2465 observed reflections. There are two formula units in the asymmetric unit. The Na atoms are sixfold coordinated with two different arrangements of ligands. The two triazine units are equal within standard deviations. The structure can be regarded as being constituted of layers linked together by Na coordination polyhedra along the *yz* plane. One water molecule has a population of 0.5 linking layers with weak hydrogen bonds.

Introduction. The title compound was investigated in connection with studies on the synthesis of pharmaceutical compounds. It is an intermediate for the synthesis of ceftriaxone, which belongs to the third generation of cephalosporin antibiotics (Neu, Meropol & Fu, 1981). Infrared spectroscopy, mass spectrometry or proton magnetic resonance cannot permit complete identification of which of the four possible tautomeric forms, (i)–(iv) (Štefanič, Valenčič, Tišler, Kobal, Vitezič & Japelj, 1990), is present in this compound. Therefore we have confirmed the structure by X-ray investigation. The compound was isolated as a hydrated Na salt and the crystals for diffraction measurement were grown by slow evaporation of cold water–methanol solution.


(i) (ii) (iii) (iv)

Experimental. A prismatic crystal with approximate dimensions 0.18 × 0.25 × 0.65 mm was used for data

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