

***N,N'*-Bis(2-salicylideneaminoethyl)(ethylenediamine)nickel(II) Trihydrate**

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Abstract. $C_{20}H_{24}N_4O_2Ni \cdot 3H_2O$, monoclinic, $I2/a$, $a = 21.966$ (6), $b = 15.881$ (3), $c = 17.296$ (3) Å, $\beta = 134.8$ (1)°, $Z = 8$, $D_m = 1.45$, $D_c = 1.445$ g cm⁻³. The complex ligand is hexadentate, in the same conformation as, and with molecular geometry very similar to, that in the hexahydrate previously described [Cradwick, Cradwick, Dodson, Hall & Waters, *Acta Cryst.* (1972), B28, 45–49]. The two structures differ mainly in the pattern of hydrogen bonding between water molecules.

Introduction. Brown crystals were prepared as previously described for the tetrahydrate (Dodson & Hall, 1961). Data were collected on a Hilger & Watts automated four-circle diffractometer, with Zr-filtered Mo $K\alpha$ radiation, a θ - 2θ scan technique, a scan rate of 1° min⁻¹, and 20 s background counts at the extremity of each scan. A set of 2896 observed data was obtained.

Systematic absences were $hkl: h + k + l$ odd; $h0l: h$ or l odd. Space group $I2/a$ was assumed, and the structure solved without difficulty. The Ni atom position was determined from the Patterson function, and other non-hydrogen atoms from difference syntheses. Only three water molecules were apparent. Refinement was by full-matrix least squares, minimizing $\sum w(F_o - F_c)^2$, with weights based on the relationship $\sigma(I) = [\sigma^2(c) + (0.04I)^2]^{1/2}$, where $\sigma^2(c)$ is the variance from counting statistics. Structure factors were calculated with atomic scattering factors as listed in *International Tables for X-ray Crystallography* (1962). Anisotropic thermal parameters were assumed for Ni, isotropic for other atoms; R converged at 0.083. A difference synthesis confirmed that no other non-hydrogen atom was present, and revealed most of the H atoms of the complex ligand. Those that could not be so placed were included at calculated positions, and H positional coordinates

Table 1. Atom coordinates ($\times 10^4$, for H $\times 10^3$) and temperature factors ($\times 10$)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)		<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
Ni	1466 (1)	8089 (1)	2901 (1)	*	O(W1)	1399 (4)	1473 (4)	4971 (5)	59 (1)
N(1)	1443 (3)	7065 (4)	3577 (4)	31 (1)	O(W2)	394 (5)	1498 (5)	1661 (7)	90 (2)
N(2)	1322 (4)	7163 (4)	1879 (5)	36 (1)	O(W3)	1302 (5)	524 (5)	3540 (6)	85 (2)
N(3)	105 (4)	8269 (4)	1493 (5)	35 (1)	H(N1)	177 (5)	723 (5)	171 (6)	
N(4)	1550 (4)	9117 (4)	2299 (5)	36 (1)	H(N2)	-33 (5)	828 (5)	171 (6)	
O(1)	1511 (3)	8798 (3)	3933 (4)	33 (1)	H(2)	239 (5)	989 (5)	537 (6)	
O(2)	2780 (3)	8001 (3)	4037 (3)	34 (1)	H(3)	315 (5)	948 (5)	757 (6)	
C(1)	2009 (4)	8575 (4)	4950 (5)	29 (1)	H(4)	348 (4)	795 (5)	815 (6)	
C(2)	2387 (5)	9199 (5)	5760 (6)	39 (2)	H(5)	268 (4)	684 (5)	662 (6)	
C(3)	2902 (5)	8994 (5)	6844 (7)	47 (2)	H(7)	195 (5)	642 (5)	485 (6)	
C(4)	3082 (5)	8147 (6)	7195 (7)	52 (2)	H(8.1)	151 (5)	564 (5)	364 (6)	
C(5)	2721 (5)	7530 (5)	6411 (7)	47 (2)	H(8.2)	53 (5)	619 (5)	263 (6)	
C(6)	2200 (4)	7722 (4)	5301 (6)	32 (1)	H(9.1)	122 (5)	579 (5)	167 (6)	
C(7)	1870 (4)	7006 (5)	4582 (5)	35 (1)	H(9.2)	208 (5)	619 (5)	285 (6)	
C(8)	1164 (5)	6295 (5)	2934 (6)	40 (2)	H(10.1)	42 (4)	784 (5)	35 (6)	
C(9)	1482 (5)	6327 (5)	2373 (6)	42 (2)	H(10.2)	26 (4)	672 (5)	39 (6)	
C(10)	482 (5)	7282 (5)	756 (6)	43 (2)	H(11.1)	-41 (4)	705 (5)	88 (6)	
C(11)	-202 (5)	7592 (5)	706 (7)	44 (2)	H(11.2)	-74 (5)	789 (5)	-20 (6)	
C(12)	6 (6)	9131 (6)	1100 (7)	48 (2)	H(12.1)	-12 (5)	958 (5)	154 (6)	
C(13)	745 (5)	9378 (5)	1198 (7)	43 (2)	H(12.2)	-53 (5)	911 (5)	27 (6)	
C(14)	2184 (5)	9636 (5)	2860 (6)	40 (2)	H(13.1)	74 (5)	904 (5)	64 (6)	
C(15)	2998 (4)	9470 (5)	3958 (6)	36 (1)	H(13.2)	72 (5)	5 (5)	118 (6)	
C(16)	3595 (6)	151 (6)	4487 (7)	49 (2)	H(14)	212 (5)	35 (5)	239 (6)	
C(17)	4366 (6)	72 (6)	5527 (8)	60 (2)	H(16)	347 (5)	1071 (5)	404 (6)	
C(18)	4614 (6)	9341 (6)	6091 (8)	57 (2)	H(17)	469 (5)	67 (5)	567 (6)	
C(19)	4067 (5)	8630 (5)	5622 (7)	46 (2)	H(18)	508 (5)	908 (5)	701 (6)	
C(20)	3254 (5)	8686 (5)	4504 (6)	34 (1)	H(19)	411 (4)	802 (5)	605 (6)	

* The temperature factor for the Ni atom was $\exp[-(0.0010h^2 + 0.0016k^2 + 0.0019l^2 - 0.0008hk + 0.0016hl - 0.0010kl)]$.

Table 2. Bond lengths (Å) and bond angles (°) about the nickel atom

Ni—O(1)	2.056 (4)	C(5)—C(6)	1.404 (10)	C(12)—C(13)	1.556 (11)
Ni—O(2)	2.053 (4)	C(6)—C(1)	1.419 (9)	C(13)—N(4)	1.473 (9)
Ni—N(1)	2.026 (5)	C(6)—C(7)	1.447 (9)	N(4)—C(14)	1.280 (9)
Ni—N(2)	2.147 (5)	C(7)—N(1)	1.268 (8)	C(14)—C(15)	1.438 (10)
Ni—N(3)	2.162 (5)	N(1)—C(8)	1.463 (9)	C(15)—C(16)	1.463 (10)
Ni—N(4)	2.011 (5)	C(8)—C(9)	1.538 (10)	C(16)—C(17)	1.330 (12)
O(1)—C(1)	1.305 (8)	C(9)—N(2)	1.477 (9)	C(17)—C(18)	1.509 (13)
C(1)—C(2)	1.405 (9)	N(2)—C(10)	1.471 (9)	C(18)—C(19)	1.380 (12)
C(2)—C(3)	1.373 (11)	C(10)—C(11)	1.519 (10)	C(19)—C(20)	1.429 (10)
C(3)—C(4)	1.410 (12)	C(11)—N(3)	1.476 (9)	C(20)—C(15)	1.415 (9)
C(4)—C(5)	1.390 (12)	N(3)—C(12)	1.469 (9)	C(20)—O(2)	1.312 (8)
O(1)···O(W3)	2.781 (9)	O(W3)···O(W2)	2.811 (11)	O(W3)···O(W1)	2.794 (9)
O(2)···O(W1)	2.763 (7)	O(W1)···O(W2)	2.795 (10)		
O(1)—Ni—O(2)	91.8 (3)	O(2)—Ni—N(1)	89.1 (2)	N(1)—Ni—N(3)	100.3 (2)
O(1)—Ni—N(1)	86.8 (2)	O(2)—Ni—N(2)	91.9 (3)	N(1)—Ni—N(4)	177.2 (2)
O(1)—Ni—N(2)	168.9 (3)	O(2)—Ni—N(3)	168.7 (3)	N(2)—Ni—N(3)	83.1 (3)
O(1)—Ni—N(3)	95.0 (3)	O(2)—Ni—N(4)	88.3 (3)	N(2)—Ni—N(4)	98.3 (3)
O(1)—Ni—N(4)	92.2 (3)	N(1)—Ni—N(2)	82.9 (2)	N(3)—Ni—N(4)	82.5 (3)

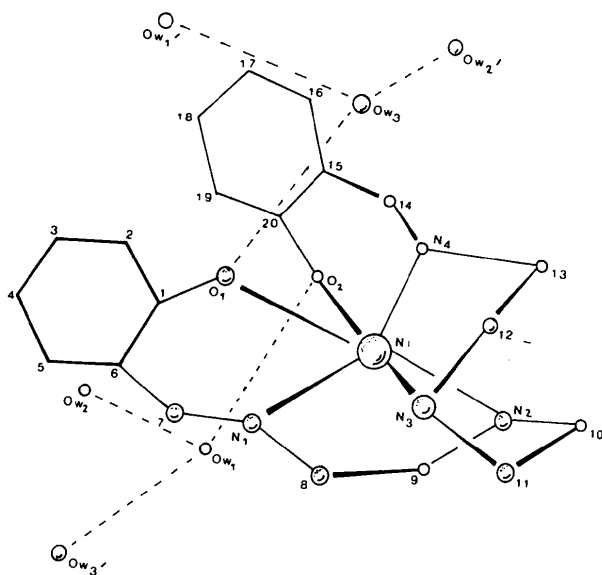


Fig. 1. The complex molecule (non-hydrogen atoms only) and related water molecules.

were refined, with a constant isotropic temperature factor of 6.0 \AA^2 . The final R was 0.072 ,* the reduction on inclusion of the H atoms being significant ($\alpha < 0.005$) by the Hamilton (1965) test. A final difference synthesis failed to reveal the H atoms attached to the water O atoms. Atom coordinates and temperature factors are listed in Table 1, H atoms being named according to the atom to which they are attached. Bond lengths and the angles about Ni are listed in Table 2. Bonds to

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32443 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. Mean planes and atom displacements from them (Å)

Equations of planes are of the form $Ax + By + Cz + D = 0$, where A, B, C are direction cosines with respect to a, b, c respectively, and x, y, z and D are in Å.

Plane 1: Ni, O(1), C(1), C(6), C(7), N(1)

$$-0.9240x - 0.0122y - 0.3823z - 0.9314 = 0$$

Ni	-0.289 (2)	O(1)	0.286 (8)	C(1)	-0.050 (10)
C(6)	-0.190 (10)	C(7)	0.020 (10)	N(1)	0.223 (8)

Plane 2: C(1), C(2), C(3), C(4), C(5), C(6)

$$-0.9888x - 0.0250y - 0.14702z + 0.3681 = 0$$

C(1)	0.010 (10)	C(2)	-0.004 (13)	C(3)	-0.002 (14)
C(4)	0.001 (14)	C(5)	0.005 (14)	C(6)	-0.011 (11)
C(7)	-0.004 (10)	N(1)	-0.110 (8)	Ni	-0.895 (2)
O(1)	0.039 (8)				

Plane 3: Ni, O(2), C(20), C(15), C(14), N(4)

$$0.7730x - 0.4003y - 0.4922z - 6.8871 = 0$$

Ni	-0.253 (2)	O(2)	0.278 (6)	C(20)	-0.075 (11)
C(15)	-0.164 (10)	C(14)	0.047 (11)	N(4)	0.168 (9)

Plane 4: C(15), C(16), C(17), C(18), C(19), C(20)

$$0.8909x - 0.3075y - 0.3342z - 4.6514 = 0$$

C(15)	-0.031 (11)	C(16)	0.012 (15)	C(17)	0.003 (15)
C(18)	0.001 (15)	C(19)	-0.020 (13)	C(20)	0.035 (12)
C(14)	-0.062 (12)	N(4)	-0.209 (10)	Ni	-0.773 (2)
O(2)	0.141 (7)				

H atoms range from 0.89 to 1.24 \AA , with standard deviations of $ca 0.08 \text{ \AA}$. Bond angles within the ligand are within error of expected values (see, e.g., Lingafelter & Braun, 1966). The complex molecule is shown in Fig. 1, together with the immediately related water molecules.

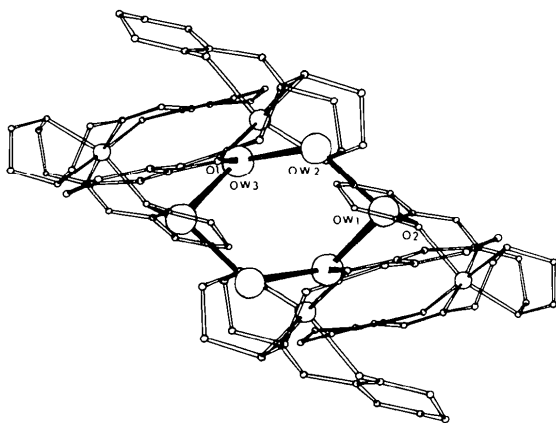


Fig. 2. The closed ring of water molecules, and related complex ligands. Hydrogen bonds are shown as bold lines.

Discussion. *N,N'*-bis(2-salicylideneaminoethyl)(ethylenediamine)nickel(II) was shown (Dodson & Hall, 1961) to crystallize both as a hexahydrate and as a lower hydrate (previously described as a tetrahydrate, but shown here to be a trihydrate). The crystal structure of the hexahydrate has been determined (Cradwick, Cradwick, Dodson, Hall & Waters, 1972), and the complex ligand shown to be hexadentate and to possess diad symmetry. In the present trihydrate, the complex ligand is again hexadentate and the molecular conformation is almost identical with that observed in the hexahydrate structure. In this structure the molecule is not constrained to diad symmetry, but the deviations from such symmetry are small (never greater than 0.13 Å), and only represent the influence of the lower environmental symmetry on the more deformable regions of the molecule, *viz* the salicylideneimine chelate rings, which are not uncommonly distorted from planarity (*e.g.* Baker, Clark, Hall & Waters, 1967). The deviations from coplanarity of these rings are shown in Table 3, where by contrast the phenyl groups are shown to be accurately planar. Almost all individual bond lengths and angles in the molecule are within error of those of the previous study, and consequently the features previously remarked upon are again observed. Thus, the Ni–N(amino) distances of 2.15–2.16 Å, which are normal, the Ni–N(imino) distances of 2.01–

2.03 Å and the Ni–O distances of 2.05–2.06 Å, which are longer than often observed for salicylideneimine chelates (Lingafelter & Braun, 1966), the N–Ni–N angles of 82–83°, which are normal for ethylenediamine chelates, and the N–Ni–O angles of 87–88°, which are low for salicylideneimine chelate bite angles, are confirmed as characteristic features of the molecule.

The crystal structure of the hexahydrate was of interest in that the water molecules form linear columns in which one water molecule in three forms a hydrogen bond to a phenolic O of the ligand, but otherwise the assembly of water molecules is a structural unit in its own right, independent of the complex molecule (Cradwick *et al.*, 1972). In the trihydrate herein described the water molecules form, not a continuous sequence, but closed hexagonal rings, as depicted in Fig. 2. Water molecule O(W2) forms hydrogen bonds only within this ring, but O(W1) and O(W3) are hydrogen bonded to oxygens O(2) and O(1) respectively, of different complex ligands. Each closed ring of water molecules is then hydrogen bonded to four different complex ligands, which form the connecting links between rings, as in Fig. 1. None of the water molecules achieves its full hydrogen-bonding potential, whereas in the more ice like assembly in the crystalline hexahydrate two of the three independent water molecules do form four hydrogen bonds. The average number of such bonds per water molecule is thus greater for the hexahydrate, $3\frac{2}{3}$ as against $2\frac{2}{3}$, and this may well be the basis for its preferential crystallization from aqueous solvents (Dodson & Hall, 1961).

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