

# The Crystal Structure of the Hexahydrate of Bis-salicylidene-triethylenetetramine Nickel (II)

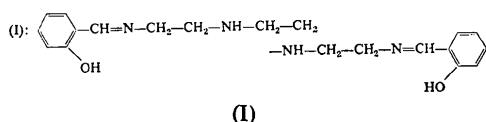
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The crystal structure of bis-salicylidene-triethylenetetramine nickel hexahydrate has been determined, using three-dimensional X-ray data. The crystals are tetragonal,  $a = 19.32$ ,  $c = 13.16$  Å, space group  $P4/ncc$ . The geometry about the nickel atom is octahedral, the ligand being hexadentate. The water molecules form columns by the sharing of faces between decahedral units, which are similar to the dodecahedra commonly observed in clathrate hydrates. Hydrogen bonds connect the water assemblies to the oxygen atoms of the nickel complex.

The complex formed between the Schiff's base bis-salicylidene-triethylenetetramine (I)



and nickel (II) has been shown (Dodson & Hall, 1961) to crystallize as both a hexahydrate and a tetrahydrate and in an anhydrous modification, all three being paramagnetic with moment  $3.0 \pm 0.1$  B.M. The hydrates retain their paramagnetism on dehydration. These results may be interpreted as indicating an octahedral complex in which the ligand is hexadentate, but the infrared spectra appeared, on analogy with reported spectra of similar compounds (Das Sarma & Bailar,

1955) to be typical of a tetradentate ligand. Moreover, the complex molecule in the hexahydrate was shown, on the basis of space group requirements, to possess  $C_2$  symmetry and this was interpreted as eliminating any reasonably strain-free hexadentate model.

This paper describes the crystal structure of the hexahydrate, and demonstrates that the latter interpretation was erroneous, and that in this molecule the ligand is indeed hexadentate.

## Experimental

Green acicular crystals, m.p.  $88^\circ$ , were prepared as previously described. The crystal data are:  $C_{20}H_{24}NiN_4O_2 \cdot 6H_2O$ ,  $M = 519$ , tetragonal,  $a = 19.32 \pm 0.02$ ,  $c = 13.16 \pm 0.02$  Å,  $U = 4912$  Å<sup>3</sup>,  $D_m$  (by flotation)  $= 1.38 \pm 0.01$ ,  $Z = 8$ ,  $D_c = 1.40$ . Systematic absences in  $hk0$  when  $h+k$  is odd, in  $0kl$  when  $l$  is odd, in  $hhl$  when  $l$  is odd; space group  $P4/ncc$ . Cu  $K\alpha$  radiation,  $\lambda = 1.5418$  Å,  $\mu = 15$  cm<sup>-1</sup>. Cell dimensions were determined by the method of Main & Woolfson (1963). Intensity data were measured visually from Weissenberg photographs for the layers  $h0l-h$ ,  $10$ ,  $l$  and  $hk0-hk7$ . The crystals used were respectively a square needle of edge 0.1 mm and a cube (cut from a similar needle) of side 0.1 mm. No absorption correction was made. The various layers were scaled by a least-squares procedure (Rae, 1965), and a data set of 1425 observed reflexions obtained.

The Patterson synthesis confirmed that the nickel atom lay on the diad axis at  $\bar{x}$ ,  $x$ ,  $\frac{1}{2}$  (with respect to the centre of inversion as origin), and a superposition map based on the Ni-Ni vectors revealed the light atoms. The structure so obtained was refined by least-squares, using unit weights and assuming isotropic thermal motion, to an  $R$  index of 0.13. The hydrogen atoms of the ligand were then included at their calculated positions, but were not refined. The refinement of the heavier atoms was continued assuming anisotropic thermal motion; the weights used hereafter were calculated as  $1/w = 1 + [(F-b)/a]^2$ , where  $a$  and  $b$  were chosen such that  $\langle w(\Delta F)^2 \rangle$  was invariant with  $|F|$ . At the conclusion

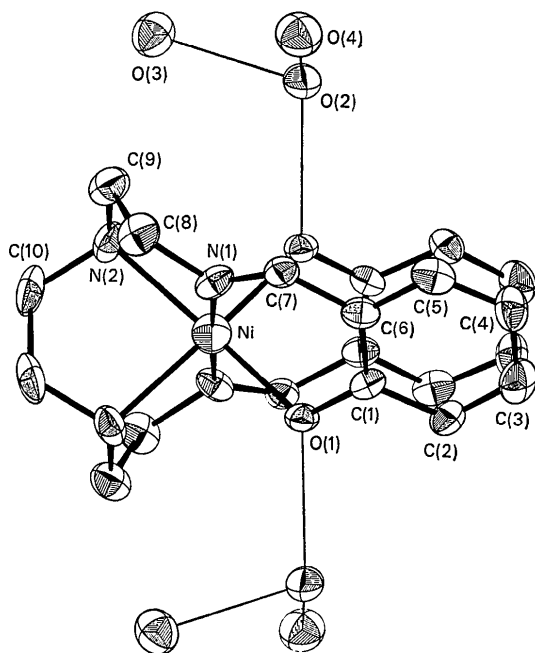


Fig. 1. The thermal ellipsoids and atom numbering scheme of the bis-salicylidene-triethylenetetramine nickel molecule.

of the least-squares refinement the  $R$  index was 0.101.

Atom coordinates are listed in Table 1, thermal parameters in Table 2, observed and calculated structure factors in Table 3, and bond lengths and angles in Table 4. The atom numbering system and the thermal ellipsoids are shown in Fig. 1 and the structure is shown in Fig. 2.

Table 1. *Atom coordinates* ( $\times 10^4$ ) (*origin at*  $\bar{1}$ )

Atom	$x/a$	$y/b$	$z/c$
Ni	5218 (1)	4782	2500
N(1)	5625 (3)	5224 (4)	1235 (5)
N(2)	6305 (4)	4682 (4)	2846 (5)
O(1)	4281 (3)	4893 (3)	1773 (4)
O(2)	6057 (3)	6697 (3)	3150 (5)
O(3)	7079 (3)	5991 (3)	4258 (5)
O(4)	6532 (3)	7140 (3)	1246 (5)
C(1)	4126 (4)	5506 (4)	1403 (6)
C(2)	3459 (4)	5768 (4)	1469 (7)
C(3)	3290 (5)	6423 (5)	1144 (7)
C(4)	3786 (5)	6847 (5)	692 (7)
C(5)	4441 (5)	6595 (4)	576 (6)
C(6)	4626 (4)	5926 (4)	894 (5)
C(7)	5338 (4)	5720 (4)	756 (6)
C(8)	6358 (4)	5077 (5)	1063 (7)
C(9)	6701 (4)	5081 (5)	2091 (7)
C(10)	6489 (5)	3940 (5)	2884 (9)
H(N2)	6388	4898	3552
H(C2)	3083	5466	1760
H(C3)	2804	6588	1227
H(C4)	3659	7328	464
H(C5)	4802	6907	257
H(C7)	5637	5985	224
H(C8, 1)	6575	5431	612
H(C8, 2)	6414	4601	751
H(C9, 1)	6738	5581	2319
H(C9, 2)	7179	4882	2020
H(C10, 1)	6404	3763	3602
H(C10, 2)	7002	3893	2734

## Discussion

The geometry about the nickel atom is essentially octahedral, with all six potential coordinating atoms of the bis-salicylidene-triethylenetetramine molecule bonded to the one metal atom; the ligand is thus hexadentate. The water molecules form continuous columns about the tetrad axes  $\frac{1}{4}, \frac{1}{4}, z$  and  $\frac{3}{4}, \frac{3}{4}, z$ . The unit of these columns is a decahedron, bounded by two square and eight

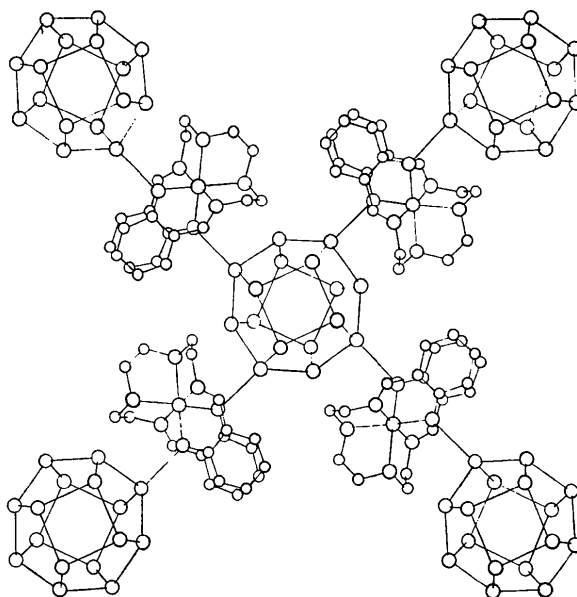


Fig. 2. Projection of half the unit cell on (001), origin at 4. The other half is generated by a  $c$  glide passing through the fourfold axes.

Table 2. *Thermal parameters* ( $\text{\AA}^2$ )

The values of  $U_{ij}$  for the anisotropic atoms are multiplied by  $10^3$ .

Anisotropic atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Ni	40.3 (1.3)	40.3	41.6 (0.9)	0.1 (0.8)	-1.5 (1.2)	-1.5
N(1)	23 (3)	44 (4)	23 (3)	-4 (3)	-1 (3)	-4 (3)
N(2)	27 (3)	45 (4)	34 (3)	9 (3)	-9 (3)	-9 (3)
O(1)	26 (3)	22 (3)	35 (3)	-6 (2)	-6 (2)	6 (2)
O(2)	32 (3)	31 (3)	64 (4)	-6 (2)	-7 (3)	1 (3)
O(3)	42 (4)	52 (4)	51 (4)	-1 (3)	-2 (3)	-4 (3)
O(4)	50 (4)	47 (4)	56 (4)	-7 (3)	-8 (3)	-2 (3)
C(1)	22 (4)	33 (4)	26 (4)	-5 (3)	0 (3)	0 (4)
C(2)	22 (4)	38 (5)	45 (5)	-2 (3)	5 (4)	-4 (4)
C(3)	40 (5)	49 (5)	33 (5)	9 (4)	-14 (4)	0 (4)
C(4)	42 (5)	32 (5)	43 (5)	10 (4)	-22 (4)	9 (4)
C(5)	46 (5)	35 (5)	26 (4)	-9 (4)	-1 (4)	4 (4)
C(6)	32 (4)	29 (4)	22 (3)	-7 (4)	-2 (3)	0 (3)
C(7)	29 (4)	28 (4)	32 (4)	-2 (3)	-11 (3)	-3 (3)
C(8)	36 (4)	49 (5)	30 (4)	-1 (4)	8 (4)	-5 (4)
C(9)	31 (5)	51 (5)	39 (5)	-2 (4)	-1 (4)	-11 (4)
C(10)	34 (5)	54 (6)	72 (7)	2 (4)	-16 (5)	0 (5)

Isotropic atom	$B$	Atom	$B$	Atom	$B$
H(N2)	2.8	H(C5)	2.9	H(C9, 1)	3.3
H(C2)	2.7	H(C7)	2.5	H(C9, 2)	3.3
H(C3)	3.1	H(C8, 1)	2.8	H(C10, 1)	4.2
H(C4)	3.0	H(C8, 2)	2.8	H(C10, 2)	4.2

pentagonal faces. The square face is common to adjacent decahedra in the column. The phenolic oxygen of the complex accepts a hydrogen bond from water molecule O(2) of the decahedron, and the two components of the structure are thus interrelated, as in Fig. 2.

Table 3. Observed and calculated structure factors (x 10)

Table with multiple columns for Miller indices (h, k, l) and structure factors (FO, FC). It includes observed values (FO) and calculated values (FC) for various reflections, with some cells containing error bars or specific values. The table is organized into groups based on the Miller indices.

Bond lengths in the nickel complex molecule appear to be normal. Thus within the ethylenediamine chelate, the Ni-N bond length of 2.16 Å to the amino nitrogen, and the N-Ni-N angles of 80.4 and 82.5° are similar to values recently reported (Cradwick & Hall, 1971). The dimensions of the salicylideneimine residue are characteristic for this ligand (Lingafelter & Braun, 1966). The Ni-N and Ni-O bonds, at 2.03 and 2.06 Å respectively, are longer than was observed in many such chelates (Lingafelter & Braun, 1966), but previous studies have mainly been on diamagnetic complexes; longer coordinating bonds are characteristic of octahedral paramagnetic nickel complexes (Stewart, Lingafelter & Breazeale, 1961). The O-Ni-N angle, 85.2°, is however much smaller than is commonly observed [e.g. 93.4° in bis-(*N*-methyl-salicylaldiminato)nickel, Fox & Lingafelter, 1967] and this would appear to evidence the strain involved in the formation of the hexadentate complex. The chelate ring is considerably

distorted from planarity, but the phenyl group remains planar, within error. The deviations from the least-squares plane through the chelate ring for Ni, N(1), C(7), C(6), C(1), O(1) are -0.332, 0.221, 0.0631, -0.231, -0.079, 0.358 Å respectively.

The decahedron which comprises the unit of the water structure is related to the pentagonal dodecahedron, the basic unit of the clathrate hydrates (Jeffrey & McMullan, 1967), in which the square basal faces are also pentagons. The tetrakaidecahedron in which the basal faces are hexagons is also known in the clathrate hydrates, but the present decahedron has not previously been reported as a unit of associated water molecules.

As presently reported the assembly is not strictly a polyhedron, as the pentagonal faces are not planar, the mean deviation from the mean plane being 0.16 Å. The volume of the polyhedron bound by the mean planes is 105 Å<sup>3</sup>. The oxygen-oxygen edges range from 2.78-2.82 Å, as in the clathrate hydrates. There are 16 ver-

Table 4. Bond lengths and angles

## (a) Chelate molecule

Ni—N(1)	2.029 (7) Å	O(1)—C(1)	1.32 (1) Å
Ni—N(2)	2.159 (7)	C(1)—C(2)	1.39 (1)
Ni—O(1)	2.058 (6)	C(2)—C(3)	1.38 (1)
N(1)—C(7)	1.27 (1)	C(3)—C(4)	1.39 (1)
N(1)—C(8)	1.46 (1)	C(4)—C(5)	1.37 (1)
C(8)—C(9)	1.51 (1)	C(5)—C(6)	1.40 (1)
C(9)—N(2)	1.47 (1)	C(6)—C(1)	1.43 (1)
N(2)—C(10)	1.48 (1)	C(6)—C(7)	1.44 (1)
C(10)—C(10')	1.55 (2)		
O(1)—Ni—O(1')	91.9°	C(1)—C(2)—C(3)	122.5°
O(1)—Ni—N(1)	85.2	C(2)—C(3)—C(4)	120.6
O(1)—Ni—N(1')	92.9	C(3)—C(4)—C(5)	118.4
O(1)—Ni—N(2)	164.4	C(4)—C(5)—C(6)	122.1
O(1)—Ni—N(2')	94.7	C(5)—C(6)—C(1)	119.4
N(1)—Ni—N(1')	177.4	C(5)—C(6)—C(7)	117.3
N(1)—Ni—N(2)	80.4	C(7)—N(1)—C(8)	119.4
N(1)—Ni—N(2')	101.6	Ni—N(1)—C(8)	114.9
N(2)—Ni—N(2')	82.5	N(1)—C(8)—C(9)	106.6
Ni—O(1)—C(1)	117.8	C(8)—C(9)—N(2)	112.1
O(1)—C(1)—C(6)	122.2	C(9)—N(2)—Ni	108.4
O(1)—C(1)—C(2)	121.1	C(9)—N(2)—C(10)	113.9
C(1)—C(6)—C(7)	123.0	Ni—N(2)—C(10)	109.2
C(7)—N(7)—Ni	123.6	N(2)—C(10)—C(10')	111.6
C(6)—C(7)—N(1)	124.1	Ni—O(1)—O(2)	122.7
C(6)—C(1)—C(2)	116.7	C(1)—O(1)—O(2)	118.6

The prime refers to atoms related by the symmetry operation:

$$\bar{y}, \bar{x}, \frac{1}{2} - z$$

## (b) Decahedron

O(1)—O(2)	2.64 (1) Å	O(2)—O(4)	2.80 (1) Å
O(2)—O(3)	2.81 (1)	O(3)—O(4''')	2.82 (1)
O(2)—O(3')	2.78 (1)	O(4)—O(4'')	2.83 (1)
O(1)—O(2)—O(3)	97.0°	O(2'')—O(3)—O(4''')	115.7°
O(1)—O(2)—O(3')	123.9	O(2)—O(4)—O(3*)	134.1
O(1)—O(2)—O(4)	118.8	O(2)—O(4)—O(4')	114.5
O(3)—O(2)—O(3')	100.0	O(2)—O(4)—O(4'')	99.8
O(3)—O(2)—O(4)	112.5	O(3*)—O(4)—O(4')	101.1
O(3')—O(2)—O(4)	103.0	O(3*)—O(4)—O(4'')	108.6
O(2)—O(3)—O(2'')	107.7	O(4')—O(4)—O(4'')	90
O(2)—O(3)—O(4''')	109.3		

The superscripts refer to the following symmetries:

$$\frac{1}{2} - y, x, z; \quad '' \quad y, \frac{1}{2} - x, z; \quad '''' \quad y, x, (\frac{1}{2} + z) - 1; \quad * \quad y, x, \frac{1}{2} + z.$$

tices and 24 edges to the decahedron, but as basal faces are shared there are 12 vertices and 20 edges per unit of the column. There are then four hydrogen atoms excess to each unit, one *per* three water molecules, and these form hydrogen bonds to the phenolic oxygen atoms of the nickel complex. The column of water molecules, infinite in one-dimension, represents an extremely compact assembly of water molecules provided that hydrogen acceptors of appropriate number and dimension are available, but it could not be extended to a three-dimensional structure in their absence. The structure is then in no sense a clathrate or potential clathrate, but is an interesting intermediate between these compounds and more conventional hydrates in which the arrangement of water molecules, *per se*, is less extensive.

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## The Crystal and Molecular Structure of 2-Dimethylaminoethyl Selenolbenzoate Hydrochloride

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The crystal structure of the local anesthetic 2-dimethylaminoethyl selenolbenzoate hydrochloride has been determined. The crystals are monoclinic,  $P2_1/c$  with  $a=12.287$  (3),  $b=6.945$  (1),  $c=15.523$  (3) Å and  $\beta=94.57$  (2)°. Least-squares refinement on 2411 observed reflections resulted in an  $R$  value of 0.051. The  $\overset{+}{N}-C-C-Se$  group adopts the *trans* conformation with a torsion angle about the C-C bond of 174.4°. The two Se-C bond distances are both 1.945 Å with estimated standard deviations of 0.005 Å. The C-Se-C angle is 96.4 (2)°. Cell constants for four related compounds are also given.

### Introduction

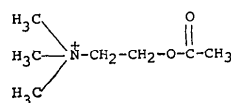
The conformations of biologically active molecules related to acetylcholine (I) have been extensively studied (Chothia, 1970; Chothia & Pauling, 1970; Shefter & Mautner, 1969). These molecules all incorporate the  $\overset{+}{N}-C-C-R_1$  group where  $R_1$  may be oxygen, sulfur or selenium. While these short chains are formally flexible, the  $\overset{+}{N}-C-C-O$  group usually adopts a *gauche* conformation (Pauling, 1968; Sundaralingam, 1968; Chothia & Pauling, 1970). Other studies show that the  $\overset{+}{N}-C-C-S$  and  $\overset{+}{N}-C-C-Se$  groups take up the *trans* conformation (Shefter & Mautner, 1969).

In this work five members of a series of local anesthetics related to the tertiary analog of benzoylcholine, 2-dimethylaminoethyl benzoate (II, with  $R_1=O$ ,  $R_2=O$ ) were investigated. These compounds are obtained by systematically replacing the ether oxygen in

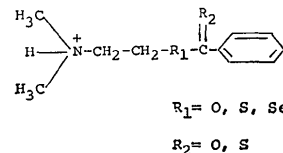
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the parent molecule (position  $R_1$ ) with sulfur or selenium and the carboxyl oxygen (position  $R_2$ ) with sulfur. Only the selenolester 2-dimethylaminoethyl selenolbenzoate hydrochloride ( $R_1=Se$ ,  $R_2=O$ ) was selected for complete structure determination.



(I)



(II)

$R_1 = O, S, Se$   
 $R_2 = O, S$

Crystals of the parent compound ( $R_1=O$ ,  $R_2=O$ ) proved highly deliquescent and were not investigated. The structure of the closely related 2-diethylaminoethyl *p*-aminobenzoate HCl (procaine HCl) was determined instead and a discussion of these results will appear subsequently (Dexter, 1972).