S	0,8829 (1)	0,2463 (2)	0,5514 (2)	0,0490 (6)
O	0,8181 (4)	0,1531 (7)	0,5176 (6)	0,071 (3)
N(1)	1,2132 (5)	−0,0715 (8)	0,7385 (6)	0,052 (3)
N(2)	1,1188 (4)	0,0829 (7)	0,6607 (5)	0,044 (2)
N(3)	1,0743 (4)	−0,1175 (7)	0,6754 (5)	0,044 (2)
N(4)	0,9554 (4)	0,0048 (8)	0,5890 (5)	0,052 (2)
N(5)	0,9428 (4)	−0,2033 (7)	0,6069 (5)	0,049 (2)
C(1)	1,1349 (5)	−0,0284 (9)	0,6900 (6)	0,045 (3)
C(2)	0,9899 (5)	−0,1012 (9)	0,6212 (6)	0,046 (3)
C(3)	0,8749 (6)	0,331 (1)	0,6409 (6)	0,072 (3)
C(4)	0,8594 (6)	0,361 (1)	0,4635 (7)	0,065 (3)
C(51)	0,8529 (6)	−0,192 (1)	0,5493 (8)	0,058 (4)
C(52)	0,9746 (6)	−0,329 (1)	0,6245 (7)	0,056 (3)

Tableau 2. Paramètres géométriques (Å, °)

Pt—Cl(1)	2,308 (3)	N(2)—C(1)	1,29 (1)
Pt—S	2,216 (3)	N(3)—C(1)	1,41 (1)
Pt—N(2)	2,003 (7)	N(3)—C(2)	1,39 (1)
Pt—N(4)	1,971 (9)	N(4)—C(2)	1,31 (1)
S—O	1,462 (8)	N(5)—C(2)	1,36 (1)
S—C(3)	1,78 (1)	N(5)—C(51)	1,47 (1)
S—C(4)	1,79 (1)	N(5)—C(52)	1,46 (1)
N(1)—C(1)	1,36 (1)		
Cl(1)—Pt—S	93,6 (1)	Pt—N(2)—C(1)	127,2 (7)
Cl(1)—Pt—N(2)	90,5 (2)	C(1)—N(3)—C(2)	124,9 (8)
Cl(1)—Pt—N(4)	178,5 (3)	Pt—N(4)—C(2)	128,6 (6)
S—Pt—N(2)	175,0 (3)	C(2)—N(5)—C(51)	117,8 (8)
S—Pt—N(4)	87,0 (2)	C(2)—N(5)—C(52)	125,1 (8)
N(2)—Pt—N(4)	88,9 (3)	C(51)—N(5)—C(52)	115,4 (8)
Pt—S—O	112,4 (3)	N(1)—C(1)—N(2)	122,8 (9)
Pt—S—C(3)	109,6 (3)	N(1)—C(1)—N(3)	113,0 (8)
Pt—S—C(4)	114,9 (4)	N(2)—C(1)—N(3)	124,3 (7)
O—S—C(3)	108,4 (6)	N(3)—C(2)—N(4)	123,8 (8)
O—S—C(4)	109,4 (5)	N(3)—C(2)—N(5)	115,5 (8)
C(3)—S—C(4)	101,4 (6)	N(4)—C(2)—N(5)	120,7 (7)

N(4)—Pt—N(2)—C(1)	−15,2 (8)
N(2)—Pt—N(4)—C(2)	10,4 (8)
Pt—N(2)—C(1)—N(1)	−169,9 (7)
Pt—N(2)—C(1)—N(3)	10 (1)
C(2)—N(3)—C(1)—N(1)	−174,1 (8)
C(2)—N(3)—C(1)—N(2)	6 (1)
C(1)—N(3)—C(2)—N(4)	−11 (1)
C(1)—N(3)—C(2)—N(5)	172,3 (8)
Pt—N(4)—C(2)—N(3)	0 (1)
Pt—N(4)—C(2)—N(5)	176,2 (6)
C(51)—N(5)—C(2)—N(3)	−179,5 (8)
C(51)—N(5)—C(2)—N(4)	4 (1)
C(52)—N(5)—C(2)—N(3)	−15 (1)
C(52)—N(5)—C(2)—N(4)	168,2 (9)

N(1)···Cl(2^i)	3,18 (1)	N(2)···Cl(2^i)	3,297 (8)
N(1)···Cl(2^{ii})	3,169 (9)	N(3)···Cl(2^{ii})	3,208 (8)
N(2)···Cl(1)	3,070 (8)	N(4)···O	2,75 (1)

Codes de symétrie: (i) $\frac{1}{2}+x, y-\frac{1}{2}, z$; (ii) $2-x, y-1, \frac{3}{2}-z$.

La structure a été résolue par la méthode de l'atome lourd et la Fig. 1 réalisée avec le programme *ORTEP*II (Johnson, 1976). Tous les programmes utilisés appartiennent au système *SDP* (B. A. Frenz & Associates, Inc., 1982): affinement des paramètres x, y, z, β_{ij} pour les atomes non hydrogène; les H n'ont été ni trouvés par différence Fourier, ni placés.

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Schiff Bases and Their Complexes with Metal Ions. I. 2-Hydroxy-*N-n*-propyl-1-naphthaldimine (1) and Bis(2-hydroxy-κO-*N-n*-propyl-1-naphthaldiminato-κN)nickel(II) (2)

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Abstract

(1) [systematic name: 1-(2-aza-1-penten-1-yl)-2-naphthol], $C_{14}H_{15}NO$, is a bidentate ligand used for the preparation of (2), $[Ni(C_{14}H_{14}NO)_2]$. It has an unexpectedly short C2—O [1.254(8) Å] bond length, and a H···N intramolecular close contact [2.403(7) Å]. In (2), the asymmetric unit comprises two half-complexes. The coordination of the Ni^{II} ions is square planar with bond angles between 88.0(1) and 92.0(1)°. The Ni—O distances are 1.826(2) and 1.913(2) Å and the Ni—N distances are 1.827(2) and 1.911(2) Å in the two complexes.

Comment

Schiff bases and their biologically active complexes have been studied during the last decade. Several complexes of salicylaldimine (Kessissoglou, Raptopoulou, Bakalbassis, Terzis & Mrozinski, 1992; Bhatia, Bindlish,

Saini & Jain, 1981; Calligaris, Nardin & Randaccio, 1972; Stewart & Lingafelter, 1959) and 2-hydroxy-1-naphthaldimine derivatives (Fernandez-G., Rosales, Toscano & Tapia, 1986; Fernandez-G., Rosales-Hoz, Rubio-Arroyo, Salcedo, Toscano & Vela, 1987; Cariati, Ganadu, Zoroddu, Mansani & Quidacciolu, 1985) have been characterized and used as models for biological systems (Chen & Martell, 1987; Pyrz, Roe, Stern & Que, 1985; Costamagna, Vargas, Latorre, Alvarado & Mena, 1992). Some of these complexes include nickel, which is found in biological systems such as jack-bean urease (Dixon, Gazzola, Watters, Blakeley & Zerner, 1975) and in some hydrogenases (Walsh & Orme-Johnson, 1987). The Schiff base complexes have also been used in catalytic reactions (Hamilton, Drago & Zombeck, 1987). The structures of N-n-propyl-2-hydroxy-1-naphthaldimine, (1), and bis(N-n-propyl-2-hydroxy-κO-1-naphthaldiminato-κN)nickel(II), (2), were determined to compare the geometrical features of the free ligand (1) and the Schiff base nickel complex (2), in order to understand the effects of the ligand on complexation.
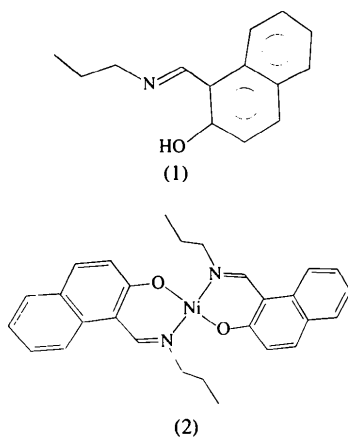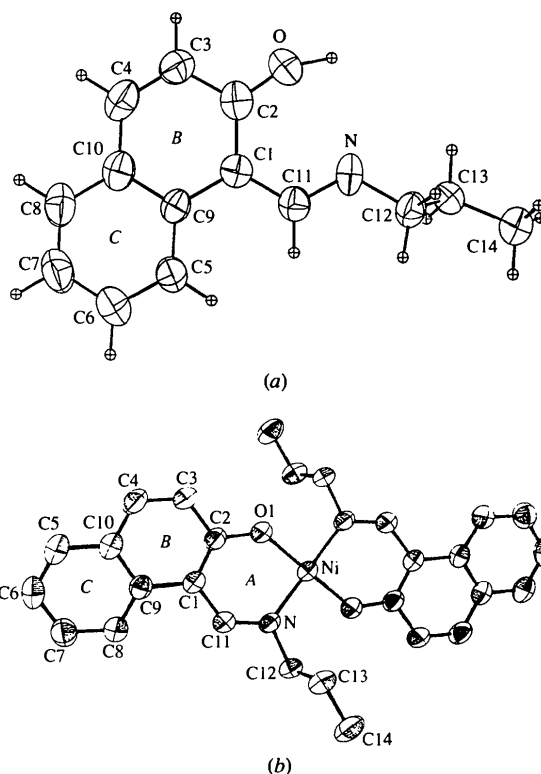

(1)

(2)

(a)

(b)

Fig. 1. SNOOPI (Davies, 1983) drawings of (a) (1) and (b) (2) with the atomic numbering schemes. The displacement ellipsoids are drawn at the 50% probability level.

Fig. 1 shows the molecule and complex with the atomic numbering. The existence of O—H···N intramolecular hydrogen bonding in Schiff base ligands has been confirmed by NMR spectroscopy (Khoo, 1988). In (1), O—H and H—C=N— protons are observed at δ = 14.40 and 8.65 p.p.m., respectively. As a result of hydrogen bonding the imine proton (H—C=N—) of (1) gives a doublet, but in metal complex (2) a singlet is produced. In the solid state an intramolecular close contact between the N atom and the H atom bonded to the O atom [H···N = 2.403 (7) Å] is observed. The magnetic susceptibility of (2) at 293 K is μ = 0, indicating that the complex has a square-planar structure.

The dihedral angles between the least-squares planes are B/C = 0.6 (3)° in (1) and A/B = 3.4 (2), A/C = 4.8 (2), B/C = 1.5 (2), A'/B' = 7.2 (2), A'/C' = 6.9 (2), B'/C' = 1.7 (2)° in (2) (Fig. 1). In Table 3, the

bond lengths of several nickel (II) complexes of naphthaldimine derivatives are compared with our values. The Ni—O and Ni—N distances [1.826 (2), 1.827 (2) and 1.913 (2), 1.911 (2) Å, respectively] agree with the values in these square-planar coordinated complexes. On the other hand, in cis-[N,N'-ethylenebis(1-imino-methyl-2-naphthalato)nickel(II)] (Freiburg, Reichert & Melchers, 1980), the Ni—O [1.847 (3)] and Ni—N [1.834 (3) Å] distances are significantly different from the present values because of the cis-coordination of O and N atoms. The coordination of the bidentate ligand (1) around the Ni atoms is square planar; the bond angles about the Ni atoms are between 88.0 (1) and 92.0 (1)°. The large bidentate ligand (1) is effective in forming square-planar coordination with the Ni^{II} ion and it plays a significant role in determining the geometry of (2).

Experimental

(1) was prepared from the reaction of 2-hydroxy-1-naphthaldehyde and n-propylamine according to the literature method (Prasad & Tandon, 1973) and crystallized from n-heptane. Suitable crystals of (2) were obtained from the reaction of (1) with nickel(II) acetate tetrahydrate in methanol, and recrystallized from n-heptane.

Compound (1)

Crystal data

$C_{14}H_{15}NO$
$M_r = 213.28$
Monoclinic
$P2_1/c$
$a = 10.167\,(5)$ Å
$b = 8.797\,(3)$ Å
$c = 13.155\,(7)$ Å
$\beta = 96.41\,(4)°$
$V = 1169.2\,(9)$ Å^3
$Z = 4$
$D_x = 1.212$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 10–15°$
$\mu = 0.56$ mm^{-1}
$T = 293$ K
Prismatic
$0.30 \times 0.30 \times 0.30$ mm
Yellow

Data collection

CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction:
  empirical (North, Phillips & Mathews, 1968)
  $T_{min} = 0.909$, $T_{max} = 1.00$
3390 measured reflections
1683 independent reflections

777 observed reflections
  $[F \geq 3\sigma(F)]$
$\theta_{max} = 75°$
$h = -1 \rightarrow 12$
$k = -1 \rightarrow 11$
$l = -16 \rightarrow 16$
3 standard reflections
  monitored every 150 reflections
  intensity decay: 1%

Refinement

Refinement on F
$R = 0.055$
$wR = 0.064$
581 reflections
145 parameters
H atoms positioned geometrically and not refined

Weighting scheme: see below
$(\Delta/\sigma)_{max} = 0.005$
$\Delta\rho_{max} = 0.26$ e Å^{-3}
$\Delta\rho_{min} = -0.35$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from International Tables for X-ray Crystallography (1974, Vol. IV)

Triclinic
$P\bar{1}$
$a = 10.655\,(5)$ Å
$b = 10.688\,(5)$ Å
$c = 12.575\,(5)$ Å
$\alpha = 119.27\,(3)°$
$\beta = 96.56\,(3)°$
$\gamma = 103.23\,(4)°$
$V = 1172.1\,(10)$ Å^3
$Z = 2$
$D_x = 1.374$ Mg m^{-3}

Cell parameters from 25 reflections
$\theta = 7–28°$
$\mu = 1.38$ mm^{-1}
$T = 293$ K
Prismatic
$0.80 \times 0.50 \times 0.50$ mm
Yellow

Data collection

CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction:
  empirical (North, Phillips & Mathews, 1968)
  $T_{min} = 0.599$, $T_{max} = 0.812$
5376 measured reflections
4565 independent reflections

3620 observed reflections
  $[F \geq 3\sigma(F)]$
$\theta_{max} = 75°$
$h = -1 \rightarrow 13$
$k = -13 \rightarrow 13$
$l = -15 \rightarrow 15$
3 standard reflections
  monitored every 150 reflections
  intensity decay: 1%

Refinement

Refinement on F
$R = 0.044$
$wR = 0.064$
3378 reflections
301 parameters
H atoms calculated geometrically and not refined

Weighting scheme: see below
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.72$ e Å^{-3}
$\Delta\rho_{min} = -1.38$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from International Tables for X-ray Crystallography (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (1)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O	0.3443 (5)	0.1376 (6)	0.6568 (4)	0.066 (2)
N	0.5743 (5)	0.0298 (7)	0.7150 (4)	0.053 (2)
C1	0.3857 (7)	-0.0185 (9)	0.8039 (5)	0.045 (3)
C2	0.3020 (7)	0.0675 (9)	0.7295 (6)	0.051 (4)
C3	0.1618 (7)	0.0720 (10)	0.7388 (6)	0.062 (3)
C4	0.1111 (7)	0.0040 (10)	0.8169 (6)	0.064 (4)
C5	0.4073 (7)	-0.1694 (9)	0.9673 (5)	0.051 (3)
C6	0.3500 (8)	-0.2369 (9)	1.0465 (5)	0.062 (4)
C7	0.2151 (9)	-0.2270 (10)	1.0519 (7)	0.069 (4)
C8	0.1379 (8)	-0.1500 (9)	0.9789 (6)	0.065 (4)
C9	0.3302 (6)	-0.0893 (9)	0.8898 (5)	0.042 (3)
C10	0.1918 (7)	-0.0803 (9)	0.8954 (6)	0.053 (3)
C11	0.5204 (7)	-0.0331 (8)	0.7908 (5)	0.048 (3)
C12	0.7126 (6)	-0.0006 (9)	0.6958 (5)	0.054 (3)
C13	0.7184 (7)	-0.0965 (9)	0.6014 (5)	0.055 (3)
C14	0.8581 (7)	-0.1100 (10)	0.5721 (6)	0.075 (4)

Compound (2)

Crystal data

$[Ni(C_{14}H_{14}NO)_2]$
$M_r = 483.25$

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ni	1/2	0	1/2	0.0396 (3)
O1	0.6652 (2)	0.1061 (2)	0.6120 (2)	0.0517 (9)
N	0.4222 (2)	-0.0222 (3)	0.6223 (2)	0.0424 (9)
C1	0.6188 (3)	0.1371 (3)	0.8038 (3)	0.095 (3)
C2	0.7041 (3)	0.1587 (3)	0.7327 (3)	0.095 (3)
C3	0.8438 (3)	0.2393 (4)	0.7927 (3)	0.086 (2)
C4	0.8954 (3)	0.2955 (3)	0.9172 (3)	0.077 (2)
C5	0.8678 (3)	0.3368 (4)	1.1227 (3)	0.060 (2)
C6	0.7896 (4)	0.3222 (4)	1.1965 (3)	0.065 (2)
C7	0.6520 (4)	0.2487 (4)	1.1443 (3)	0.083 (2)
C8	0.5943 (3)	0.1891 (4)	1.0182 (3)	0.057 (2)
C9	0.6727 (3)	0.2011 (3)	0.9386 (3)	0.063 (2)
C10	0.8124 (3)	0.2783 (3)	0.9929 (3)	0.080 (2)
C11	0.4828 (3)	0.0434 (3)	0.7416 (3)	0.074 (2)
C12	0.2830 (3)	-0.1254 (3)	0.5824 (3)	0.045 (2)
C13	0.2740 (3)	-0.2901 (4)	0.5074 (3)	0.056 (2)
C14	0.1308 (4)	-0.3974 (4)	0.4486 (4)	0.073 (2)
Ni'	1/2	1/2	1/2	0.0406 (3)
O1'	0.3948 (2)	0.3184 (2)	0.3593 (2)	0.0552 (10)
N'	0.5408 (2)	0.5861 (2)	0.4007 (2)	0.0413 (9)
C1'	0.3722 (3)	0.3849 (3)	0.2044 (3)	0.0425 (9)
C2'	0.3415 (3)	0.2852 (3)	0.2461 (3)	0.0455 (10)
C3'	0.2484 (3)	0.1349 (3)	0.1612 (3)	0.0553 (14)
C4'	0.1918 (3)	0.0877 (3)	0.0403 (3)	0.0568 (14)
C5'	0.1625 (3)	0.1333 (4)	-0.1342 (3)	0.0587 (17)
C6'	0.1899 (4)	0.2251 (4)	-0.1803 (3)	0.063 (2)

C7′	0.2744 (3)	0.3758 (4)	−0.0993 (3)	0.0623 (19)	C5—C10—C4	120.6 (3)	C5′—C10′—C4′	120.8 (3)

C7′	0.2744 (3)	0.3758 (4)	−0.0993 (3)	0.0623 (19)
C8′	0.3326 (3)	0.4303 (4)	0.0256 (3)	0.0549 (17)
C9′	0.3094 (3)	0.3367 (3)	0.0753 (3)	0.0436 (9)
C10′	0.2209 (3)	0.1854 (3)	−0.0067 (3)	0.0476 (13)
C11′	0.4769 (3)	0.5277 (3)	0.2839 (3)	0.0429 (9)
C12′	0.6512 (3)	0.7310 (3)	0.4564 (3)	0.0468 (13)
C13′	0.7866 (3)	0.7113 (4)	0.4726 (3)	0.0558 (17)
C14′	0.8973 (3)	0.8653 (4)	0.5454 (4)	0.0706 (17)

Table 3. *Selected geometric parameters* (Å, °) *for compounds* (1) *and* (2) *and related structures*

Compound (1)

C1—C2	1.439 (9)	C5—C9	1.404 (9)
C1—C9	1.458 (8)	C5—C6	1.383 (9)
C1—C11	1.404 (9)	C6—C7	1.380 (10)
C2—O	1.254 (8)	C7—C8	1.350 (10)
C2—C3	1.445 (9)	N—C11	1.313 (8)
C3—C4	1.340 (10)	N—C12	1.480 (8)
C4—C10	1.450 (10)	C12—C13	1.508 (9)
C8—C10	1.420 (10)	C13—C14	1.518 (9)
C9—C10	1.420 (9)		

C2—C1—C9	120.1 (6)	C7—C8—C10	121.4 (8)
C2—C1—C11	118.4 (7)	C1—C9—C5	122.9 (6)
C9—C1—C11	121.5 (7)	C1—C9—C10	119.2 (7)
C1—C2—O	123.4 (6)	C5—C9—C10	117.8 (7)
C1—C2—C3	118.1 (7)	C4—C10—C8	122.4 (7)
O—C2—C3	118.5 (8)	C4—C10—C9	118.5 (7)
C2—C3—C4	121.3 (8)	C8—C10—C9	119.1 (8)
C3—C4—C10	122.6 (7)	C1—C11—N	123.4 (7)
C6—C5—C9	121.0 (7)	C11—N—C12	122.5 (6)
C5—C6—C7	121.0 (8)	N—C12—C13	111.4 (6)
C6—C7—C8	119.8 (8)	C12—C13—C14	112.2 (6)

N—C12—C13—C14	171.9 (6)	C4—C3—C2—O	−177.6 (8)
C4—C10—C9—C5	179.0 (7)	C8—C10—C9—C1	179.7 (7)
C11—N—C12—C13	108.6 (7)	C12—N—C11—C1	−173.0 (7)
C2—C1—C9—C5	−177.3 (7)	C11—C1—C9—C5	3.3 (1.1)
C11—C1—C9—C10	−175.5 (7)	C9—C1—C11—N	−179.5 (7)

Compound (2)

Ni—N	1.913 (2)	Ni′—N′	1.911 (2)
Ni—O1	1.826 (2)	Ni′—O1′	1.827 (2)
O1—C2	1.306 (3)	O1′—C2′	1.305 (3)
C1—C2	1.403 (4)	C1′—C2′	1.392 (4)
C1—C9	1.461 (4)	C1′—C9′	1.458 (4)
C1—C11	1.422 (4)	C1′—C11′	1.428 (4)
C2—C3	1.430 (4)	C2′—C3′	1.431 (4)
C3—C4	1.359 (4)	C3′—C4′	1.353 (4)
C4—C10	1.418 (4)	C4′—C10′	1.424 (5)
C5—C6	1.355 (5)	C5′—C6′	1.356 (5)
C5—C10	1.419 (4)	C5′—C10′	1.417 (4)
C6—C7	1.395 (5)	C6′—C7′	1.399 (5)
C7—C8	1.381 (4)	C7′—C8′	1.381 (4)
C8—C9	1.409 (4)	C8′—C9′	1.406 (4)
C9—C10	1.419 (4)	C9′—C10′	1.417 (4)
N—C11	1.305 (3)	N′—C11′	1.300 (3)
N—C12	1.485 (3)	N′—C12′	1.477 (3)
C12—C13	1.505 (4)	C12′—C13′	1.510 (4)
C13—C14	1.516 (4)	C13′—C14′	1.524 (4)

N—Ni—O1	88.0 (1)	N′—Ni′—O1′	88.6 (1)
N—Ni—O1B	92.0 (1)	N′—Ni′—O1′B	91.5 (1)
C2—O1—Ni	131.0 (2)	C2′—O1′—Ni′	130.4 (2)
C12—N—Ni	119.8 (2)	C12′—N′—Ni′	120.1 (2)
C11—N—Ni	125.5 (2)	C11′—N′—Ni′	125.0 (2)
C11—N—C12	114.7 (2)	C11′—N′—C12′	114.9 (2)
C12—C13—C14	112.6 (3)	C12′—C13′—C14′	110.6 (3)
C13—C12—N	111.6 (2)	C13′—C12′—N′	112.0 (2)
C1—C11—N	127.1 (3)	C1′—C11′—N′	127.0 (3)
C2—C1—C11	119.4 (3)	C2′—C1′—C11′	119.4 (3)
C9—C1—C11	120.7 (3)	C9′—C1′—C11′	120.1 (3)
C9—C1—C2	119.7 (3)	C9′—C1′—C2′	120.2 (2)
C1—C2—O1	124.3 (2)	C1′—C2′—O1′	124.0 (2)
C3—C2—O1	116.3 (3)	C3′—C2′—O1′	116.4 (3)
C3—C2—C1	119.3 (3)	C3′—C2′—C1′	119.5 (3)
C4—C3—C2	121.3 (3)	C4′—C3′—C2′	120.9 (3)
C10—C4—C3	121.2 (3)	C10′—C4′—C3′	121.5 (3)
C9—C10—C4	119.8 (3)	C9′—C10′—C4′	119.5 (3)

C5—C10—C4	120.6 (3)	C5′—C10′—C4′	120.8 (3)
C5—C10—C9	119.6 (3)	C5′—C10′—C9′	119.7 (3)
C10—C9—C1	118.6 (3)	C10′—C9′—C1′	118.3 (3)
C8—C9—C1	123.8 (3)	C8′—C9′—C1′	124.1 (3)
C8—C9—C10	117.7 (3)	C8′—C9′—C10′	117.5 (3)
C7—C8—C9	121.0 (3)	C7′—C8′—C9′	121.3 (3)
C6—C7—C8	121.0 (3)	C6′—C7′—C8′	120.7 (3)
C5—C6—C7	119.5 (3)	C5′—C6′—C7′	119.3 (3)
C6—C5—C10	121.3 (3)	C6′—C5′—C10′	121.4 (3)

C14—C13—C12—N	−171.2 (4)	C14′—C13′—C12′—N′	172.8 (3)
C13—C12—N—Ni	73.0 (4)	C13′—C12′—N′—Ni′	−73.2 (4)
C12—N—Ni—O1	9.8 (3)	C12′—N′—Ni′—O1′	−13.5 (3)
C13—C12—N—C11	−105.0 (4)	C13′—C12′—N′—C11′	107.6 (4)
C4—C10—C9—C8	−179.0 (4)	C4′—C10′—C9′—C8′	−178.4 (4)

	(1)	(2a)	(2b)	(3)	(4)
C11—N	1.313 (8)	1.305 (4)	1.300 (3)	1.297 (4)	1.310 (6)
C2—O	1.254 (8)	1.306 (3)	1.305 (3)	1.305 (4)	1.301 (5)
Ni—N		1.913 (2)	1.911 (2)	1.912 (3)	1.904 (4)
Ni—O		1.826 (2)	1.827 (2)	1.832 (2)	1.827 (3)
C1—C2	1.439 (9)	1.403 (4)	1.392 (4)	1.397 (5)	1.400 (6)
C2—C3	1.445 (9)	1.430 (4)	1.431 (4)	1.434 (4)	1.425 (6)
C3—C4	1.340 (10)	1.359 (4)	1.353 (4)	1.358 (5)	1.349 (7)
C4—C10	1.450 (10)	1.418 (4)	1.424 (5)	1.421 (5)	1.416 (7)
C11—C1	1.404 (9)	1.422 (4)	1.428 (4)	1.429 (4)	1.424 (6)

Notes: (1), (2*a*), (2*b*) present work, (3) bis{*N*-[(1,3-dioxolan-2-yl)methyl]-2-hydroxy-1-naphthaldiminato}nickel(II) (Fernandez-G., Rosales-Hoz, Rubio-Arroyo, Salcedo, Toscano & Vela, 1987), (4) bis[*N*-(2,2-diethoxyethyl)-2-oxo-1-naphthylmethylideneaminato]-nickel(II) (Fernandez-G., Rosales, Toscano & Tapia, 1986).

Values of R_{int} have not been calculated since symmetry-related reflections were deleted before calculation. H atoms were positioned geometrically 1.0 Å from the corresponding atoms. Initially, a unit weighting scheme was used, but in the final stages of the refinement the weights were assigned using the Chebychev method as described by Carruthers & Watkin (1979) and incorporated into the *CRYSTALS* program package (Watkin, Carruthers & Betteridge, 1985).

The programs used were *CRYSTALS*, *SHELX90* (Sheldrick, 1990) and *SNOOPI* (Davies, 1983).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, angles involving H atoms and least-squares-planes data have been deposited with the IUCr (Reference: AB1153). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A New Schiff Base Complex: {N-[3-(2-Aminoethylamino)propyl]salicylideneaminato-O,N,N',N''}bromozinc(II)

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Abstract

[Zn(satnen)Br], where satnen = $H_2N(CH_2)_2NH(CH_2)_3$-$N{=}CHC_6H_4O^-$, is the first example of a complex containing a tetradentate Schiff base derived from 1,6-diamino-3-azahexane. The Zn atom is bonded to five atoms (Br, O and three N atoms) and its coordination polyhedron can be described either as a distorted trigonal bipyramid (the Br atom being situated in the equatorial plane) or as a distorted tetragonal pyramid (with the Br atom at the apex). The Zn—Br bond is unusually long [2.4812(7) Å]. The bonding distances within the phenyl ring vary between 1.34(2) and 1.42(1) Å. The longer distances involve those C atoms which are connected either to O or to the C(H)=N-fragment. There are two intermolecular N—H···X, X = Br, O, hydrogen bonds; the X = O bond is extremely weak.

Comment

There are two reasons for this study. Firstly, the cation environments in related Zn complexes, *i.e.* in [Zn(saden)H₂O]Br, (I) (Kratochvíl, Ondráček, Novotný & Haber, 1991) and [Zn(naden)Br], (II) (Ondráček, Kratochvíl & Haber, 1994) are highly distorted {saden = N-[2-(2-aminoethylamino)ethyl]-salicylideneaminato-O,N,N',N'' and naden = 1-[2-(2-aminoethylamino)ethylimino]methyl-2-naphtholato-O,N,N',N''}. The distortion is caused at least partly by the short N—N bite distances which manifest themselves by rather acute N—Zn—N' and N'—Zn—N'' angles (79–82°). The longer trimethylene chain between two of the N atoms in the present ligand should partly relieve this strain and so lead to more regular arrangement around the central atom. Secondly, from stability studies of complexes with multidentate ligands, it has been deduced that complexes with adjacent five- and six-membered chelate rings are more stable than those where pairs of either six- or five-membered rings are joined (Hancock, 1992). The present complex can form two isomers, (III) and (IV). From Hancock's conclusions, it can be predicted that (III) would be more stable than (IV). In the solid state the isomeric form proves, rather surprisingly, to be (IV) rather than (III). The structure is depicted in Fig. 1.

(I)   (II)   (III)   (IV)
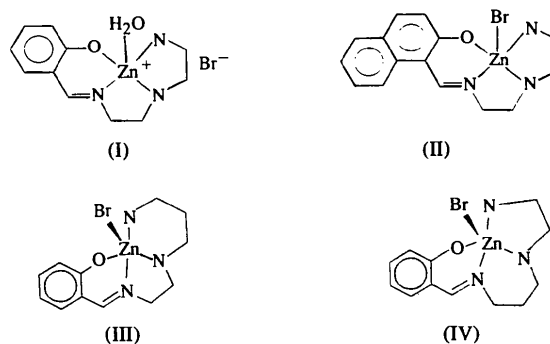
All the atoms of the pseudo-aromatic chelate and phenyl rings [O, N(3), C(6)–C(12)] lie approximately in a plane ($\chi^2 = 48.38$). The adjacent six-membered ring [Zn, N(2), C(3), C(4), C(5), N(3)] has a chair conformation. The atoms N(2), C(3), C(5) and N(3) are nearly coplanar ($\chi^2 = 1.11$). The conformation of the five-membered ring is between a half chair and a C(2) envelope: the deviations of C(1) and C(2) from the plane of Zn, N(1) and N(2) are 0.138(7) and −0.529(8) Å, respectively, and the value of the N(1)—C(1)—C(2)—N(2) torsion angle is 53.9(5)°.

When compared with the related naden and saden Zn complexes, the present structure is closer to a trigonal bipyramidal arrangement with N(1) and N(3) in axial positions. In contrast, both N(1) and N(3) are in equatorial positions in (II) (Ondráček, Kratochvíl & Haber, 1994) and (I) (Kratochvíl, Ondráček, Novotný &