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Classification and Distortion in Six-coordinate Bis(salicylaldiminato)nickel(II) Complexes: Crystal Structure of Bis[2-[[(2-hydroxyphenyl)methylene]amino]-1-phenyl-1,3-propanediolato]nickel(II).2H$_2$O

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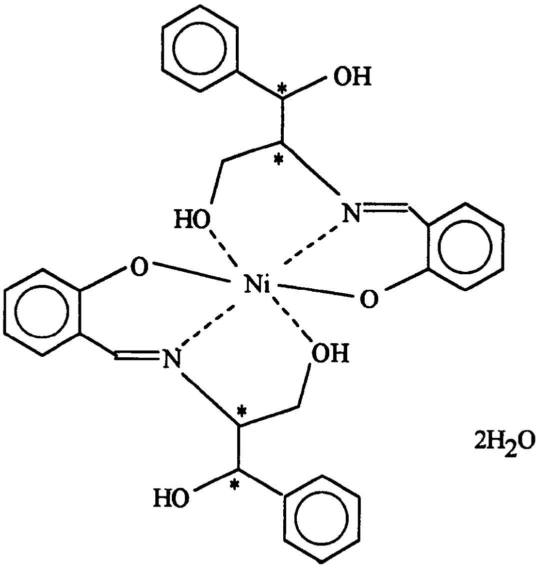
Abstract

The crystal structure of a Ni^{II} complex with a tridentate chiral ligand has been determined with a final R of 0.042. The crystals were hexagonal, space group $P6_1$ with $Z = 6$, $a = b = 18.498$ (2), $c = 16.328$ (2) Å. The complex shows local tetrahedral (skewed) coordination of the metal by two salicyladimine ligands with a tetrahedrality angle of 89.4 (2)° and the Ni shifted by 0.13 Å from the geometric center of the coordination octahedron, both values being the largest ones observed so far in similar Ni^{II} six-coordinate complexes. Also a new, simple classification of six-coordinate bis(salicylaldiminato) complexes, based on the relative positions of coordinating atoms, has been proposed.

1. Introduction

Asymmetric cyclopropane formation is catalyzed by homogeneous chiral metal complexes. The first such example was described in 1966 by Nazaki *et al.* (1966) and, since then, a large number of efficient metal catalysts with Schiff bases derived from *N*-substituted salicylaldimine derivatives have been developed. Reactivity and steric behavior of the complexes depend mainly on the coordination number of metal M, the conformational rigidity induced by M and, of course, the chemical and spatial nature of the substituent R_1 [Fig. 1, formula (1)]. The knowledge of the structure of these complexes is essential for understanding the mechanism of the catalytic reactions.

The most efficient catalysts in direct asymmetric cyclopropanation of diene precursors with diazoesters are copper complexes with Schiff bases derived from aromatic aldehydes and chiral amino alcohols. A chiral ligand, (+)-(1*S*,2*S*)-2-(2-hydroxybenzylidene)amine-1-phenyl-1,3-propanediol, has been successfully used as a ligand in a copper chelate in highly enantioselective Michael reactions (Desimoni *et al.*, 1990). This observation prompted us to study the structure of this and other metal complexes. We have attempted to crystallize copper, nickel, zinc, manganese, cobalt and iron chelates. Although beautifully colored crystals have been obtained from the appropriate solutions containing the ligand and the respective metal salt in a 2:1 molar ratio, powder diffraction spectra revealed their identity with the ligand crystal (Główka *et al.*, 1996), except for the Ni^{II} and Cu^{II} complexes. Unfortunately, the Cu^{II} complex could not be crystallized in a form suitable for X-ray single crystal diffraction studies and thus only the crystal structure of bis[2-[[(2-hydroxyphenyl)methylene]amino]-1-phenyl-1,3-propanediolato]nickel(II) [(2) in Fig. 1] has been determined. Its structure in solution has been proposed based upon spectroscopic data by Segla & Elias (1988). We hoped that this study might also throw some light on the structure of the copper complex.



(2)

2. Experimental

Data were collected on a KM4 four-circle diffractometer at room temperature. The structure was solved by direct methods and refined by full-matrix least-squares (Sheldrick, 1990). Absorption was neglected. Secondary extinction was corrected according to Larson (1967). The two hydrated ligands were refined alternatively (as blocks) with Ni cation incorporated into the the first block. H atoms attached to carbons were calculated geometrically and refined isotropically at fixed distances of 0.96 Å from C. Other H atoms were located from ΔF maps and refined freely with isotropic thermal parameters. One H atom from water molecule O(*w*1) could not be located.

Details of data collection and refinement are gathered in Table 1† and atomic coordinates in Table 2.

3. Results and discussion

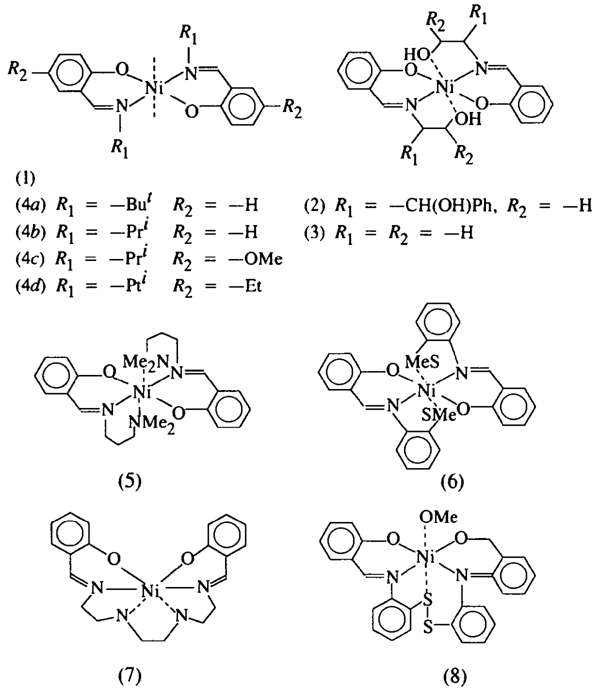
3.1. *Description of the structure*

All bond lengths and angles in the structure are similar to those observed in bis(salicylaldiminato)nickel(II) complexes (Table 3) and there is no need for a detailed discussion. An unusual feature of the structure is the distortion of the Ni coordination sphere.

The study showed that in the title compound the metal is six-coordinate (Fig. 2). The octahedron is formed by two phenolic O atoms in a *cis* position, two O atoms of the aliphatic hydroxy groups also in a *cis* position and two N atoms in a *trans* position. It is in accordance with the geometry postulated from solution structure (Segla & Elias, 1988) and with the crystal structure of a very similar complex, bis[*N*-(2-hydroxy-1-benzylidene)-2-hydroxyethylaminato]nickel(II) [Chumakov *et al.*, 1991; Fig. 1, (3)]. The two complexes have the same tridentate backbone of the chelate ligands and the same coordination spheres of Ni with N···Ni···N

Table 1. *Experimental details*

Crystal data	
Chemical formula	$C_{32}H_{32}N_2NiO_6.2H_2O$
Chemical formula weight	635.36
Cell setting	Hexagonal
Space group	$P6_1$
a (Å)	18.498 (2)
c (Å)	16.328 (2)
V (Å^3)	4839.05 (14)
Z	6
D_x (Mg m^{-3})	1.308
Radiation type	Cu *Kα*
Wavelength (Å)	1.54178
No. of reflections for cell parameters	34
θ range (°)	20–45
μ (mm^{-1})	1.19
Temperature (K)	293
Crystal form	Prisms
Crystal size (mm)	0.30 × 0.25 × 0.20
Scan width (°)	$\Delta\omega(\theta) = 1.1° + 0.38\text{tg}\theta$
Crystal color	Pale green
Data collection	
Diffractometer	KM4
Data collection method	ω–2θ scans
Absorption correction	None
No. of measured reflections	6772
No. of independent reflections	3380
No. of observed reflections	3666
Criterion for observed reflections	$F > 3\sigma(F)$
R_{int}	0.034
$\theta_{\max}$ (°)	80
Range of *h*, *k*, *l*	$0 \rightarrow h \rightarrow 21$ $-21 \rightarrow k \rightarrow 0$ $-19 \rightarrow l \rightarrow 0$
No. of standard reflections	2
Frequency of standard reflections	Every 100 reflections
Intensity decay (%)	2.5
Refinement	
Refinement on	*F*
R	0.042
wR	0.042
S	1.75
No. of reflections used in refinement	3723
H-atom treatment	Isotropic refinement with constraints
Weighting scheme	$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max}$	0.09
Data-to-parameters ratio	16.3 for block I and 16.6 for block II
$\Delta\rho_{\max}$ (e Å^{-3})	0.30
$\Delta\rho_{\min}$ (e Å^{-3})	−0.45
Extinction method	Larson (1967)
Extinction coefficient	0.004
Source of atomic scattering factors	*SHELXTL/PC* (Sheldrick, 1990)



(1)
(4*a*) R_1 = —Bu^t R_2 = —H
(4*b*) R_1 = —Pr^i R_2 = —H
(4*c*) R_1 = —Pr^i R_2 = —OMe
(4*d*) R_1 = —Pt^i R_2 = —Et
(2) R_1 = —CH(OH)Ph, R_2 = —H
(3) R_1 = R_2 = —H

Fig. 1. Structures of bis(salicylaldiminato)nickel(II) complexes.

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† Lists of atomic coordinates, anisotropic displacement parameters, complete geometry and structure factors have been deposited with the IUCr (Reference: KA0036). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^ia^j\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Ni(1)	0.2773 (1)	0.4401 (1)	1/2	0.041 (1)
O(*w*1)	0.4518 (4)	0.4864 (4)	0.6538 (4)	0.081 (3)
C(101)	0.3192 (3)	0.5498 (3)	0.6883 (3)	0.043 (2)
O(101)	0.4062 (2)	0.5953 (2)	0.7119 (2)	0.048 (2)
C(102)	0.3088 (3)	0.5816 (3)	0.6061 (3)	0.039 (2)
N(102)	0.3492 (2)	0.5572 (2)	0.5426 (3)	0.036 (2)
C(103)	0.2178 (3)	0.5458 (3)	0.5789 (3)	0.045 (3)
O(103)	0.1858 (2)	0.4610 (2)	0.5543 (2)	0.047 (2)
C(111)	0.2674 (3)	0.5554 (4)	0.7578 (3)	0.051 (3)
C(112)	0.2281 (4)	0.4897 (5)	0.8108 (4)	0.085 (4)
C(113)	0.1821 (6)	0.4945 (8)	0.8764 (6)	0.136 (8)
C(114)	0.1734 (6)	0.5610 (8)	0.8885 (7)	0.129 (8)
C(115)	0.2127 (4)	0.6277 (7)	0.8362 (6)	0.106 (5)
C(116)	0.2601 (4)	0.6248 (5)	0.7698 (4)	0.073 (4)
C(120)	0.4254 (3)	0.6065 (3)	0.5225 (3)	0.040 (2)
C(121)	0.4746 (3)	0.5878 (3)	0.4672 (3)	0.044 (3)
C(122)	0.4483 (3)	0.5081 (3)	0.4335 (3)	0.045 (3)
O(122)	0.3749 (2)	0.4435 (2)	0.4453 (2)	0.054 (2)
C(123)	0.5052 (4)	0.4997 (4)	0.3832 (3)	0.056 (3)
C(124)	0.5838 (4)	0.5644 (4)	0.3686 (4)	0.070 (4)
C(125)	0.6099 (4)	0.6430 (4)	0.4020 (4)	0.070 (4)
C(126)	0.5560 (3)	0.6538 (4)	0.4506 (3)	0.056 (3)
O(*w*2)	0.3557 (4)	0.2959 (4)	0.4760 (4)	0.080 (3)
C(201)	0.2334 (4)	0.3205 (4)	0.3178 (4)	0.056 (3)
O(201)	0.2370 (3)	0.2484 (3)	0.3400 (3)	0.080 (3)
N(202)	0.1924 (2)	0.3279 (3)	0.4572 (3)	0.041 (2)
C(202)	0.1679 (3)	0.3257 (3)	0.3722 (3)	0.043 (3)
O(203)	0.2401 (2)	0.4752 (2)	0.3825 (2)	0.048 (2)
C(203)	0.1630 (3)	0.4042 (3)	0.3570 (3)	0.049 (3)
C(211)	0.2141 (5)	0.3108 (4)	0.2277 (4)	0.066 (4)
C(212)	0.2761 (6)	0.3574 (5)	0.1734 (5)	0.094 (6)
C(213)	0.2633 (10)	0.3486 (9)	0.0882 (7)	0.149 (11)
C(214)	0.1855 (10)	0.2892 (9)	0.0611 (7)	0.152 (14)
C(215)	0.1230 (9)	0.2403 (8)	0.1141 (6)	0.128 (9)
C(216)	0.1376 (6)	0.2519 (6)	0.1983 (5)	0.099 (6)
C(220)	0.1547 (3)	0.2600 (3)	0.4989 (4)	0.048 (3)
C(221)	0.1725 (3)	0.2502 (3)	0.5828 (3)	0.050 (3)
C(222)	0.2420 (4)	0.3116 (4)	0.6274 (4)	0.053 (3)
O(222)	0.2946 (2)	0.3845 (2)	0.5980 (2)	0.059 (2)
C(223)	0.2543 (5)	0.2907 (5)	0.7069 (4)	0.082 (4)
C(224)	0.2009 (6)	0.2167 (6)	0.7401 (5)	0.117 (7)
C(225)	0.1304 (6)	0.1544 (5)	0.6986 (6)	0.117 (6)
C(226)	0.1191 (5)	0.1737 (4)	0.6193 (5)	0.083 (4)

and two O···Ni···O (phenolic and ethanolic) angles of 171.5 (2), 89.9 (2) and 85.3 (2)° in (2) and 169.7 (3), 94.4 (2) and 87.9 (1)° in (3), respectively.

In contrast, of the 40 known tetracoordinate bis(salicylaldiminato)nickel(II) complexes found in the Cambridge Structural Database (1995) all are square planar except four (Fig. 1). These four structures [(4*a*) Ashida *et al.*, 1976; (4*b*) Braun & Lingafelter, 1967; (4*c*) Fox *et al.*, 1964; (4*d*) Johnston & Horrocks, 1971)] can be considered to have local tetrahedral coordination with the tetrahedrality angle θ proposed by Holm & O'Connor (1971) ranging from 78.8 to 85.3° (Fig. 3).

In (2) the third chelating claw (C—C—OH), attached to the imino N atom, is probably too 'short' to enable coplanarity of the two salicylaldimine ligands with perpendicular orientations of the hydroxy groups. This proposition is supported both by the coplanarity of the two salicyladimine systems in the bis[*N*-(3-dimethylaminopropyl)salicyladiminato)nickel(II) complex [(5) Di Vaira & Orioli, 1967; Fig. 1] having a longer and unrestricted third claw $-CH_2-CH_2-CH_2-NMe_2$ and by the tetrahedral coordination of Ni^{II} by two salicylaldimines with a geometrically restricted third claw *R* [(6) Obodovskaya *et al.*, 1976; (7) Cumming *et al.*, 1977; in Fig. 1 and Table 3].

Another interesting feature of the title structure is the presence of two hydroxy groups in the substituent R_1. Both are two C atoms away from the imine N atom and both are capable of being a third claw. The two free

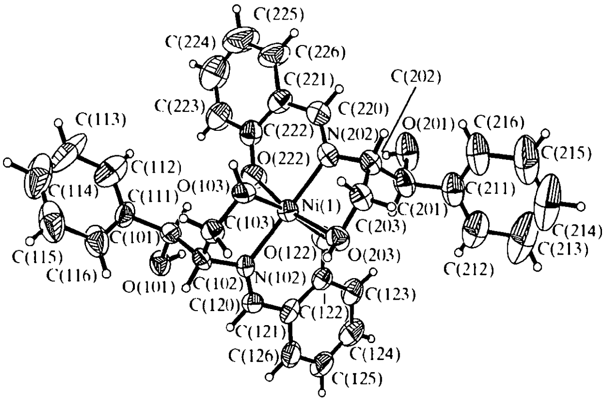

Fig. 2. General view and labeling of non-H atoms used in this study. Thermal ellipsoids were drawn at 50% probability. Water molecules are omitted for clarity.

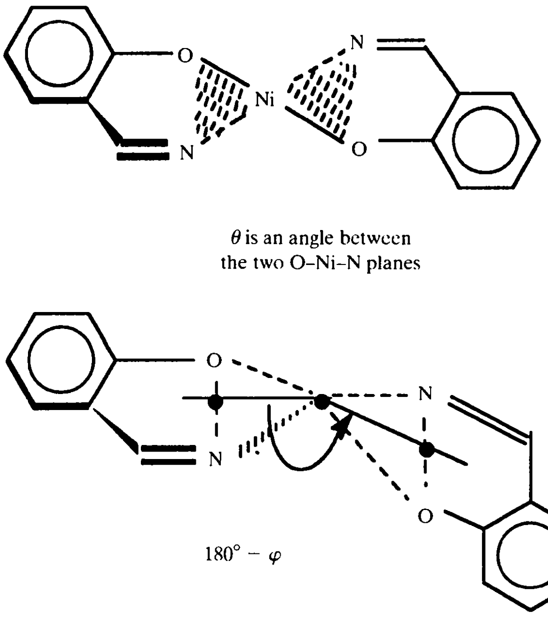

Fig. 3. Definitions of bending (φ) and tetrahedrality (θ) angles.

Table 3. *Geometric parameters describing* Ni^{II} *coordination in six-coordinate bis(salicylaldiminato) complexes*

Structures are also analogs of six-coordinate bis(salicylaldiminato)nickel(II) complexes with N atom(s) replacing isosteric aromatic or imine CH group(s) and/or S replacing O. The values have been taken from the Cambridge Structural Database (1995). h is the Ni deviation from the NONO plane. $\Delta x = |l_{x1} - l_{x2}|$, where l_x = Ni···X bond length (Å). ΔN and ΔO are calculated in an analogous way. $\Delta G = [(\Delta X)^2 + (\Delta N)^2 + (\Delta O)^2]^{0.5}$.

		Compound	Octahedron deformation parameters (° and Å)							Valency angles (°)			
No.	Type	REFCODE	θ	φ	h	Δx	ΔN	ΔO	ΔG	X···Ni···X	N···Ni···N	O···Ni···O	R
(*a*)	*A*(*ttt*)	ABOTNI	0.0	0.0	0.00	0.00	0.00	0.00	0.00	180.0	180.0	179.9	0.047
(*b*)		NIMAPS	0.6	0.6	0.01	0.03	0.01	0.02	0.04	179.6	179.7	179.1	0.076
(*c*)		LATNID	4.4	4.4	0.05	0.09	0.00	0.00	0.09	177.8	177.0	177.0	0.054
(*d*)		NICBPS	7.9	4.4	0.05	0.33	0.03	0.04	0.34	176.9	172.4	175.0	0.036
(*d*)		CSPYNI	8.9	4.8	0.06	0.37	0.01	0.03	0.37	176.2	171.2	176.7	0.046
(*e*)	*B*(*tcc*)	BIZWEM	1.2	8.1	0.02	0.00	0.00	0.00	0.00	178.0	99.4	90.1	0.039
(*f*)	*C*(*ctc*)	CURDIC	76.2	50.1	0.59	0.05	0.01	0.00	0.06	75.0	177.9	103.8	0.031
(*g*)		KONBOE	82.9	48.1	0.58	0.01	0.00	0.01	0.01	86.3	171.7	97.8	0.068
(*h*)		KIPCAN	83.1	66.7	0.83	0.02	0.00	0.05	0.06	96.9	172.9	82.9	0.044
(*i*)		TANSNI	84.7	52.4	0.62	0.00	0.01	0.00	0.01	88.2	174.5	95.4	0.088
(*j*)		YALBES	86.1	50.5	0.60	0.00	0.01	0.02	0.02	87.9	169.7	94.4	0.055
(*k*)		DAZNOH	86.8	53.1	0.64	0.00	0.06	0.05	0.08	88.8	174.0	93.6	0.129
(*l*)		NIMMBP	86.8	55.7	0.69	0.19	0.01	0.01	0.19	88.9	174.2	93.2	0.031
(*m*)		VALPNI10	87.3	49.5	0.61	0.04	0.01	0.01	0.05	84.4	171.1	94.0	0.170
(*g*)		KONBUK	87.6	60.3	0.71	0.04	0.00	0.03	0.04	86.8	177.5	92.5	0.031
(*n*)		SAENNJ	88.2	60.2	0.74	0.02	0.01	0.00	0.02	83.0	177.1	91.8	0.072
(*n*)		SATEAN	88.3	58.9	0.74	0.00	0.00	0.00	0.00	82.5	177.3	91.9	0.101
(*p*)		FACVEK	88.5	63.9	0.80	0.06	0.00	0.01	0.06	87.0	173.7	88.5	0.051
(*q*)		VAVHAB	88.6	58.7	0.72	0.01	0.01	0.01	0.01	93.1	179.2	88.7	0.047
(*q*)		VAVHAB	88.7	58.8	0.72	0.02	0.01	0.00	0.02	92.3	179.3	88.8	0.047
(*r*)		BUCMOB	88.9	58.3	0.72	0.02	0.03	0.19	0.20	96.8	176.5	90.7	0.063
(*s*)		(2)	89.4	53.4	0.64	0.13	0.02	0.02	0.14	85.3	171.5	89.9	0.042
(*c*)	*D*(*cct*)	LATNEZ	86.9	70.9	0.90	0.01	0.05	0.04	0.06	88.9	95.0	157.9	0.065
(*t*)		AZXBNI	88.6	71.5	0.92	0.05	0.03	0.06	0.09	91.8	93.6	157.3	0.038
(*p*)		FACVAG	89.8	56.8	0.71	0.00	0.00	0.00	0.00	90.7	90.6	177.5	0.069
(*u*)	*E*(*ccc*)	SIRCIF	88.8	52.3	0.64	0.42	0.01	0.00	0.42	90.8	100.4	94.8	0.034

(*a*) Johnston & Horrocks (1971); (*b*) Di Vaira & Orioli (1967); (*c*) Macchia *et al.* (1993); (*d*) Boge *et al.* (1977); (*e*) Goodwin *et al.* (1982); (*f*) Elias *et al.* (1985); (*g*) Choudhury *et al.* (1992); (*h*) Zimmer *et al.* (1991); (*i*) Obodovskaya *et al.* (1976); (*j*) Chumakov *et al.* (1991); (*k*) Rao *et al.* (1985); (*l*) Freyburg *et al.* (1979); (*m*) Capasso *et al.* (1974); (*n*) Cumming *et al.* (1977); (*o*) Cradwick *et al.* (1972); (*p*) Casellato *et al.* (1986); (*q*) Duran *et al.* (1989); (*r*) Levan *et al.* (1983); (*s*) this study; (*t*) Lalancette *et al.* (1976); (*u*) Manzur *et al.* (1989).

aliphatic hydroxy groups in this complex participate in hydrogen bonds as hydrogen donors (Tables 4 and 5). As potential hydrogen acceptors (lone-pair donors) are already used in the formation of the complex, two water molecules have been built into the crystal to play the role of H acceptors. However, the H atoms of these water molecules are not utilized as proton donors in any hydrogen bond, which might be the reason for the difficulties we have had in finding the second H atom of each water molecule and in refining the atoms found.

3.2. *Classification of six-coordinate bis(salicylaldiminato) complexes*

Table 3 lists selected structural parameters for all six-coordinated nickel(II) complexes with di- and tridentate (2-hydroxybenzylidene)amines and close analogs (see notes under Table 3) found in the Cambridge Structural Database (1995). It clearly shows that there are two distinct structure types: those which are coplanar (X···Ni···X angle ~180°) and those which are skewed (X···Ni···X angle ~90°), Fig. 4(*a*). The first group (types *A* and *B* in Fig. 5) consists of six structures with a small tetrahedrality angle θ (Holm & O'Connor, 1971), calculated as a twist of the two O—Ni—N planes (Fig. 3). The structures have either a bidentate ligand (X is an anion or a covalently bonded alkyl group) or a long chain connecting N and X.

The other group (types *C*, *D* and *E*, 19 examples) includes structures with θ angles over 75°; most having θ angles exceeding 85°. This group, with a planar bis(salicylaldiminato)nickel(II) moiety, has three coordination types (Table 3 and Fig. 5): with only N(imine) atoms in *trans* positions (15 structures), O(phenolic) atoms in *trans* positions (three structures) and with all three pairs of equivalent atoms in *cis* positions [one structure – (8); Macchia *et al.*, 1993]. It shows that a 'skew' coordination of Ni^{II} by two tridentate salicylaldimine ligands (types *C*, *D* and *E*) is quite common. The twisting of the two salicylaldimine systems results in bending (angle φ defined in Fig. 3). The two deformation parameters are correlated with a correlation parameter of 0.971. The geometry of a six-coordinate bis(salicylaldiminato)nickel(II) complex is usually described by the relative positions of equivalent atoms (*cis* or *trans*), Fig. 5, or by three valency angles,

Table 4. *Selected geometric parameters*

	Molecule 1	Molecule 2
Ni(1)—N(02)	2.016 (4)	2.001 (4)
Ni(1)—O(03)	2.110 (5)	2.241 (4)
Ni(1)—O(22)	1.988 (4)	2.012 (4)
C(01)—O(01)	1.446 (6)	1.415 (10)
C(01)—C(02)	1.517 (8)	1.545 (10)
C(02)—N(02)	1.475 (8)	1.455 (7)
C(02)—C(03)	1.535 (7)	1.521 (9)
N(02)—C(20)	1.280 (6)	1.285 (7)
C(03)—O(03)	1.429 (7)	1.435 (5)
C(20)—C(21)	1.442 (9)	1.443 (9)
C(21)—C(22)	1.413 (9)	1.419 (7)
C(22)—O(22)	1.298 (5)	1.298 (6)
N(02)—Ni(1)—O(03)	79.5 (2)	78.8 (2)
N(02)—Ni(1)—O(22)	91.1 (2)	89.4 (2)
O(03)—Ni(1)—O(22)	169.2 (2)	168.2 (1)
O(01)—C(01)—C(02)	109.3 (3)	108.6 (5)
O(01)—C(01)—C(11)	108.6 (4)	105.0 (6)
C(02)—C(01)—C(11)	115.2 (6)	115.0 (6)
C(01)—C(02)—N(02)	108.7 (5)	107.9 (4)
C(01)—C(02)—C(03)	114.5 (4)	112.9 (4)
N(02)—C(02)—C(03)	106.3 (4)	107.2 (4)
Ni(1)—N(02)—C(02)	114.0 (2)	115.7 (3)
Ni(1)—N(02)—C(20)	125.3 (4)	126.2 (4)
C(02)—N(02)—C(20)	120.6 (4)	117.9 (4)
C(02)—C(03)—O(03)	108.5 (5)	108.6 (5)
Ni(1)—O(03)—C(03)	112.9 (3)	107.0 (3)
N(02)—C(20)—C(21)	126.3 (5)	125.4 (5)
Ni(1)—O(22)—C(22)	127.7 (4)	126.7 (4)
N(102)—Ni(1)—N(202)		171.7 (2)
O(103)—Ni(1)—N(202)		93.0 (2)
O(122)—Ni(1)—N(202)		96.0 (2)
N(102)—Ni(1)—O(203)		96.8 (2)
O(103)—Ni(1)—O(203)		85.2 (2)
O(122)—Ni(1)—O(203)		90.7 (2)
N(102)—Ni(1)—O(222)		95.0 (2)
O(103)—Ni(1)—O(222)		96.1 (2)
O(122)—Ni(1)—O(222)		89.9 (2)
O(01)—C(01)—C(02)—C(03)	−173.0 (5)	176.4 (4)
O(01)—C(01)—C(02)—N(02)	68.4 (5)	58.0 (5)
C(01)—C(02)—C(03)—O(03)	−73.5 (6)	−66.2 (5)
N(02)—C(02)—C(03)—O(03)	46.5 (5)	52.5 (5)
C(03)—C(02)—C(01)—C(11)	−50.5 (6)	−66.3 (6)
C(02)—C(03)—O(03)—Ni(1)	−33.3 (5)	−41.1 (5)
N(02)—Ni(1)—O(03)—C(03)	9.4 (4)	16.6 (4)
O(03)—Ni(1)—N(02)—C(02)	18.2 (4)	12.9 (4)
O(03)—Ni(1)—N(02)—C(20)	−166.3 (5)	−162.6 (6)
O(22)—Ni(1)—N(02)—C(20)	8.4 (5)	18.1 (6)
Ni(1)—N(02)—C(20)—C(21)	−1.2 (9)	−6.5 (10)
N(02)—C(20)—C(21)—C(22)	−7.2 (10)	−9.0 (12)
C(20)—C(21)—C(22)—O(22)	3.5 (10)	3.2 (13)
C(21)—C(22)—O(22)—Ni(1)	8.0 (9)	17.2 (11)
N(02)—Ni(1)—O(22)—C(22)	−11.9 (5)	−23.6 (6)

N···Ni···N, O···Ni···O and X···Ni···X (Table 3), and deformation of the coordination (twist of the two salicylaldimine systems) by the tetrahedrality angle θ. The valency angles at Ni^{II} may deviate from 180 or 90° by as much as 15°. The θ angle is also useful for distinguishing planar and skewed (tetrahedral) orientations of the salicylaldimine systems. However, the use of θ, although very convenient, is not sensitive to another important feature – distortion of the coordination sphere of the complex. In four-coordinate square-planar bis(salicylaldiminato) complexes, deviation of the metal from the NONO plane (h) is sufficient to describe distortion. In six-coordinate complexes, however, especially when the two salicylaldimine systems are not coplanar, either O···Ni···O or N···Ni···N is ~90° (Table 3). In this case, the use of the same parameter, deviation h of the metal from the NONO 'plane' defined by perpendicularly oriented pairs of NO atoms, is meaningless because h is geometrically correlated with the tetrahedrality angle θ, having a correlation parameter of 0.998. Thus, we have tried to describe distortion of the coordination octahedron by differences between equivalent Ni···X(N,O) distances. The differences, absolute values ΔX, ΔN, ΔO and $\Delta G = [(\Delta X)^2 + (\Delta N)^2 + (\Delta O)^2]^{0.5}$ (Table 3), may be significant, even in

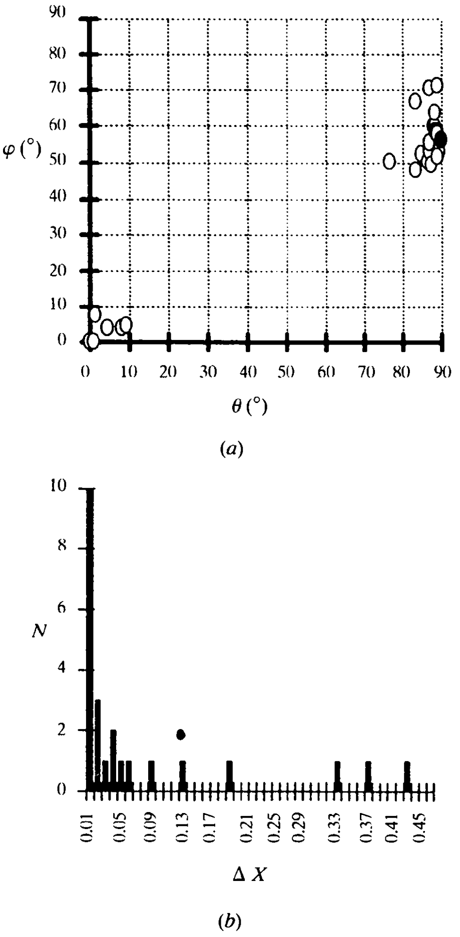

Fig. 4. Deformation statistics in the six-coordinate bis(salicylaldiminato)nickel(II) complex structures. Filled dots represent values obtained in this study. (*a*) Bending angle φ (°) *versus* tetrahedrality angle θ (°). Two clusters represent two distinct classes of structures, with planar ($\theta \simeq 0°$) and skewed coordination ($\theta \simeq 90°$) of Ni^{II} by two salicylaldimine molecules. (*b*) Population of length differentiations in the two Ni···X bonds (Å).

Table 5. *Hydrogen-bonding geometry (Å, °)*

X—H···Y	X—H (Å)	H···Y (Å)	X—H···Y (°)
O(101)—H(001)···O(w1)$^{\rm i}$	0.93 (9)	1.78 (9)	176 (3)
O(201)—H(002)···O(w2)$^{\rm i}$	0.75 (6)	2.19 (7)	167 (7)
O(103)—H(103)···O(w2)$^{\rm ii}$	0.83 (4)	1.80 (4)	162 (6)
O(203)—H(203)···O(101)$^{\rm iii}$	0.93 (6)	1.87 (6)	168 (4)

Symmetry codes: (i) x, y, z; (ii) $y, -x+1, z-\frac{1}{6}$; (iii) $-x+y, -x+1, z-\frac{1}{3}$.

chemically symmetrical complexes. Most important in bis(salicylaldiminato)nickel(II) complexes is ΔX (Fig. 4*b*). The values of ΔX over 0.2 Å refer to obvious cases, when the two 2X's are different atoms. As ΔN and ΔO in bis(salicylaldimine)nickel(II) complexes always refer to the same atoms in the chemical sense, their values rarely exceed 0.05 Å. ΔN = 0.06 Å for DAZNOH (Rao *et al.*, 1985) results rather from low accuracy, as R = 0.129. Another surprising result is that for BUCMOB (Levan *et al.*, 1983), ΔO = 0.19 Å. However, in this case the two O atoms are structurally different. The only inexplicable value ΔX = 0.131 (5) has been found in this study for two hydroxy groups (X) in *cis* positions (Fig. 2). It means that the Ni atom is distinctly shifted from the geometrical center of its coordination octahedron and one of the reasons for that may be the chirality of ligands causing asymmetry of the Ni surroundings.

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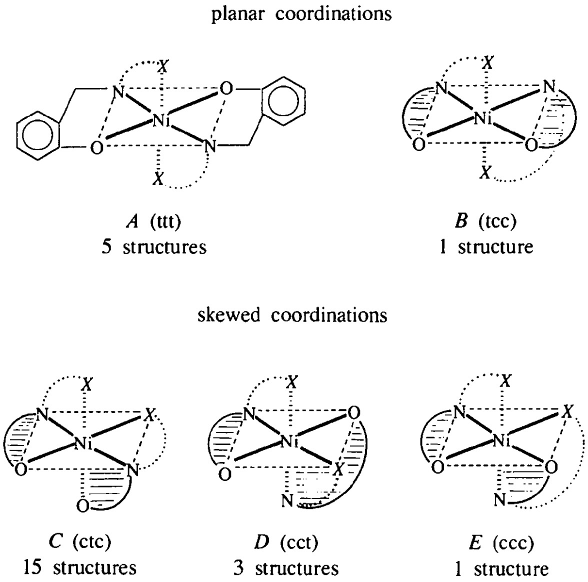

A (ttt)
5 structures

B (tcc)
1 structure

C (ctc)
15 structures

D (cct)
3 structures

E (ccc)
1 structure

Fig. 5. Structure types of six-coordinate bis(salicylaldiminato)nickel(II) complexes.

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