N-o-tolyl-2-hydroxy-1-naphthaldimine and its Ni^{II} complex. Conformational changes of free ligand by chelatation

Branko Kaitner,⁽¹⁾* Ernest Meštrović,⁽¹⁾ and Gordana Pavlović⁽¹⁾

Received December 11, 1996

The main scope of the paper deals with keto/amine-enol/imine tautomerism in the solid state of an N-aryl substituted naphthaldimine and conformational changes of this ligand after coordinating to the nickel atom. The N-o-tolyl-2-hydroxy-1-naphthaldimine (I) crystallizes in the orthorhombic space group $P 2_1 2_1 2_1$ with cell dimensions a = 7.8641(4), b = 12.712(1), c = 13.853(1) Å and corresponding bis-bidentate nickel complex (II) in the monoclinic space group $P 2_1/c$ and unit cell dimensions a = 7.436(3), b = 22.050(5), c = 8.643(4) Å, $\beta = 95.05(6)^{\circ}$. In the nonplanar molecule of (I) the presence of the enol tautomer is found. In (II) the metal atom has the characteristic square-planar coordination with Ni^{II} on crystallographically imposed inversion centers. Two naphthaldimine moieties are not coplanar showing stepped conformation with step height 1.034 Å.

KEY WORDS: *N*-aryl naphthaldimines; conformational changes; keto-enol tautomerism; stepped conformation; X-ray molecular and crystal structure.

Introduction

The function of a metal atom in metalloproteins is determined by the structural characteristics which include not only the metal environment, but depends on the structural arrangement in the second coordination sphere as well. Schiff base class of compounds and their metal complexes have been used for years as structural models for numerous biological systems.¹ By adequate designing of the ligand it is possible to investigate the factors modifying the metal coordination sphere and the electronic properties of the reaction center. Nickel in the form of the complex compound has been found in very low amount in jack-bean urease as well as in some hydrogenases.¹

The salicylaldimine type of Schiff bases as well as their metal complexes have been studied comprehensively (by x-ray, nmr, esr, UV, IR, and other techniques) more than any other kind of Schiff base derivatives.² In comparison to that, the structural data on the Schiff bases derived from various naphthaldimines and related complexes are quite rare.³⁻¹² The type of the substituent, either alkyl or aryl, on the azomethine nitrogen of naphthaldimines can affect remarkably the magnetic, dielectric, spectral, and other properties of free ligands and their transition metal complexes. Replacing the hydrogen atom from either an N-H...O or an O-H...N intramolecular hydrogen bond in the ligand by chelatation influences the stereochemistry of the chelate ring dramatically. The main structural feature distinguishing free and bonded ligand appears in (i) a large difference in so called O...N chelate ring 'bite' distance, (ii) changes in the complex metallacyclic chelate ring bond distances and angles associated with electron re-distribution or, to a certain extent, with delocalization of π electrons,⁸ and (iii) significantly different N-substituent spatial orientation. The coordination of the nickel atom in bis-bidentate complexes with N-substituted Schiff base ligands is square planar with N and O chelating atoms trans to each other. In four-coordinate Ni^{II} and Cu^{II} complexes which should be, at least at first sight, perfectly planar a

⁽¹⁾ Chemistry Department, Laboratory of General & Inorganic Chemistry, Faculty of Science, University of Zagreb, 10000 Zagreb, Ul. kralja Zvonimira 8, Croatia.

^{*} To whom correspondence should be addressed.

deviation from planarity is often found. Deviation from planarity manifests as a fold in a chelate ring along a line through the O and N donor atoms. The conformation of a *bis*-chelate complex molecule is said to be "stepped." The step distance is defined as the perpendicular separation between the chelate ring planes. The orthorhombic form of *bis*(*N*-methylsalicylideneiminato)nickel(II) is the only exception with ideal planar molecules.¹³ The factors influencing the step height could be the size and electron nature of N-substituent although the crystal packing forces should not been overlooked, as well.

We prepared and structurally characterized N-o-tolyl-2-hydroxy-1-naphthaldimine (Compound I) and bis(N-o-tolyl-2-hydroxy-1-naphthaldiminato)nickel(II) (Compound II) in order to establish the conformational and stereochemical dissimilarity of the ligand in (I) and (II).

Experimental

Syntheses

Compound (I) has been prepared by refluxing methanolic solutions of equimolar amounts of *o*-toluidine (1 mmol; 0.107 cm³) and 2-hydroxy-1-naphthaldehyde (1 mmol; 0.172 g). Single pale yellow crystals were obtained by evaporation from the acetone solution (20 mg/4 cm³), m.p. = 128°C, yield 75% (0.196 g).

Compound (II) was synthesized by refluxing methanolic solutions of Compound (I) (2 mmol; 0.522 g), and NiCl₂·6H₂O (1 mmol; 0.238 g) with 67% yield (0.388 g). The yellow green precipitate was separated from mother liquor, and recrystallized as olive green prisms by the liquid phase diffusion procedure from chloroform as solvent and *n*-hexane as precipitant in the ratio 1:5.

X-ray analysis

Crystal data and summary of intensity data collection and structure refinement are listed in Table 1. The intensities were corrected for Lorentz and polarization effects for both (I) and (II), while empirical absorption corrections using DIFABS¹⁴ had been applied in the case of (II) with min. and max. absorption corrections 0.719 and 1.571. The structure of (I) was solved applying the direct methods (MULTAN80 incorporated in NRCVAX) and (II) by the heavy-atom method revealing the nickel atom positional parameters. Scattering factors for neutral atomic species were taken from the International Tables for X-ray Crystallography.¹⁵ Refinement of both structures was performed by full-matrix least-squares procedure based on F. Hydrogen atoms bound to carbon atoms were placed at calculated positions after appropriate maxima had been noted in difference electron density Fourier maps $(C-H 0.95 \text{\AA})$ according to the stereochemical rules for sp² and sp³ hybridized carbon atoms. The appropriate orientation of the methyl groups in both structures had been checked by contour electron density map. At the final stage of refinement the location of the intramolecular hydrogen bond H atom in (I) was determined as a small diffuse electron density (0.22 $e/Å^3$). The enantiomer form of (I) was unequivocally established by refining the chirality n Rogers' parameter.¹⁶ Hydrogen atoms were included in structure factor calculations with $U_{iso}(H) = 1.2 U_{eq}(C)$, but not refined. Programs for structure solution, refinement and drawings: NRCVAX¹⁷ program package and ORTEP II.¹⁸

Results and discussion

The molecular structure perspective view of Compounds (I) and (II) in a general orientation are shown in Fig. 1. The atomic coordinates of non-hydrogen atoms are listed in Table 2.

Compound (I)

Proton transfer process (keto–enol tautomerism) responsible for the thermochromic and photochromic effects in Schiff base derivatives are in the most cases reversible and do not necessarily induce large structural changes within molecule, i.e., they can take place even at low temperatures. A feature of molecular geometry of Schiff bases having attached OH group in position 2 of the aryl aldehyde system in the solid state is the presence of either keto-amine or enol–imine tautomer form. Conversely to salicylaldimine derivatives for which mainly the enol tautomer was established in the solution and in the crystal, the molecular structure of various naphthaldimines determined so far, shows that the solid state is dominated by the keto-amine tautomer.^{3,4,19}

In the structure of *N-o*-tolyl-2-hydroxy-1-naphthaldimine (I) the enol-imine tautomer was detected

	Compound (I)	Compound (II)			
Crystal data					
Empirical formula	C ₁₈ H ₁₅ NO	$C_{36}H_{28}N_2NiO_2$			
Formula weight	261.32	579.34			
Color and Shape	Yellow; prism	Olive green; prism			
Crystal system and space group	Orthorhombic, $P2_12_12_1$	Monoclinic, $P2_1/c$			
Crystal dimentions,mm	$0.71 \times 0.52 \times 0.43$	$0.50 \times 0.31 \times 0.21$			
Unit cell dimensions					
<i>a</i> , Å	7.8641(4)	7.436(3)			
b, Å	12.712(1)	22.050(5)			
<i>c</i> , Å	13.853(1)	8.643(4)			
β,°		95.05(6)			
Cell volume, Å ³	1384.9(2)	1411.6(9)			
Formula, units per unit cell	4	2			
D_{cale} , g cm ⁻³	1.25	1.36			
Absorption coefficient, μ , mm ⁻¹	0.07	0.72			
Data collection (at 293 K)					
Diffractometer	Philips PW1100; STOE upgraded				
Graphite monochromated radiation, Å	$\lambda(\text{Mo }K\alpha) = 0.7107$				
Scan mode and 20 data collection range, °	ω; 4 to 54	ω/2θ; 4 to 54			
Range of h, k, l	0 to 10, 0 to 16, 0 to 17	-9 to 9, 0 to 28, 0 to 11			
Reflections measured	3487 including Friedel pairs	3171			
Independent reflections	$3019 (R_{int} = 0.037)$	$2805 (R_{int} = 0.0.31)$			
Observed reflections with $[I_{net} \ge 2\sigma (I_{net})]$	1775	1971			
Refinement					
F(000)	552	604			
No. of parameters varied	181	187			
Data to parameter ratio	9.8	10.5			
$(\Delta/\sigma)_{max}$	0.002	0.002			
$k \text{ in } w^{-1} = [\sigma^2 F_o + k F_o^2]$	0.0020	0.0015			
Final residuals: R; wR; GoF	0.037; 0.055; 1.06	0.032; 0.052; 1.16			
Chirality parameter, η	0.48(6.38)				
Largest ΔF peak and hole, e Å ⁻³	0.12; -0.12	0.24; -0.28			
Computer programs	NRCVAX, DIFA	BS, ORTEP II			

Table 1. Crystal data and summary of intensity data collection and structure refinement.

^a The unit cell dimensions were determined by fitting of 40 (I) and 20 (II) strong general reflections setting angles in the range $20 \le 2\theta \le 35^{\circ}$ and $22 \le 2\theta \le 29^{\circ}$, respectively.

from the molecular geometry considerations. The decision on the sort of the tautomer is based on the Car-O bond distance [1.320(3) Å]. The hydrogen atom in the *intra*molecular hydrogen bridge is represented with a quite diffuse ΔF peak located 1.198(2) Å and 1.377(2) Å apart from the O1 and N1, respectively.

The O1-C12 bond length 1.320(3) Å corresponds closely to the value of oxygen-to-carbon single bond 1.362 Å found in phenols, and N1-C1 1.291(3) Å differs negligibly from the double bond distance 1.279 Å in the Car-C=N-C system.²⁰ The well known D_{2h} quinoid arrangement of the bond distances within naphthalene fused rings is established according to the very short C13-C14 bond distance 1.346(5) Å.^{3,4} The chelate ring including a strong *intra*molecular hydrogen bridge with the "bite" distance N1...O1

2.503(3) Å and O1-H···N1 angle $153.0(1)^{\circ}$ is almost completely coplanar with the naphthalene moiety with corresponding dihedral angle $1.86(7)^{\circ}$.

The molecule (I) itself is not planar due to the twist of the phenyl ring of the azomethine nitrogen substituent (o-tolyl) out of the chelate plane [C1-N1-C21-C26 torsion angle $36.8(2)^{\circ}]$. The reasons for such a conformation of an N-aryl derivative are not completely clear because two almost planar N-aryl naphthaldimines published recently suggests the delocalization of π electrons.³ The twisting of the o-tolyl moiety is probably affected by the molecular environment in the crystalline state. The close contacts between discrete molecules in the solid state are in the range of normal van der Waals electrostatic interactions.²¹





Compound (II)

Fig. 1. Compound (I) and Compound (II) depicted by ORTEP II program showing the molecules in the general orientation with our crystallographic atom numbering scheme. The displacement ellipsoids are plotted with 30% (I) and 50% (II) probability level, respectively.

Compound (II)

The nickel atom in (II) is required to be at the centre of symmetry according to the unit cell content, with O and N donor atoms from bidentate ligands positioned *trans* to each other. The form of the metal atom coordination polyhedron is irregular square planar with corresponding geometrical parameters: Ni-O1 1.827(2) Å, Ni-N1 1.895(2) Å, O1-Ni-N1 91.85(8)°, and O1-Ni-N1¹ 88.15(8)° [(i): -x, -y, -z]. The molecule possesses a stepped conformation²² stated as the vertical distance between the best chelate planes amounting to 1.034 Å. As a result of

Table 2. Final positional parameters of nonhydrogen atoms $(\times 10^4)$ and equivalent isotropic thermal motion coefficients $(\mathring{A}^2)^a$

Atom	x	у	Z	B _{eq}
	-	Compound (I)		
01	8649(3)	3303(2)	7172(1)	6.80(9)
N1	7428(2)	4552(1)	8385(1)	4.78(8)
Cl	7395(3)	3801(2)	9013(1)	4.2(1)
C11	7954(3)	2758(2)	8777(1)	4.2(1)
C12	8600(3)	2565(2)	7842(2)	5.3(1)
C13	9251(4)	1555(3)	7609(2)	6.7(1)
C14	9202(4)	769(2)	8260(3)	6.8(1)
C15	8524(3)	902(2)	9201(2)	5.2(1)
C16	8473(4)	65(2)	9867(3)	6.7(1)
C17	7857(4)	201(2)	10766(3)	7.2(2)
C18	7236(3)	1185(2)	11043(2)	6.2(1)
C19	7259(3)	2015(2)	10417(2)	5.0(1)
C110	7902(3)	1910(1)	9474(2)	4.3(1)
C21	6995(3)	5605(2)	8608(1)	4.4(1)
C22	6189(3)	6201(2)	7890(2)	5.0(1)
C23	5788(3)	7239(2)	8099(2)	6.1(1)
C24	6172(4)	7681(2)	8978(2)	6.6(1)
C25	6982(4)	7100(2)	9674(2)	6.5(1)
C26	7412(3)	6061(2)	9490(2)	5.5(1)
C27	5760(4)	5715(2)	6930(2)	6.9(1)
		Compound (II)		
Ni	0	0	0	2.30(2)
01	-889(3)	752(1)	389(2)	2.9(1)
N1	-1411(3)	-366(1)	1466(2)	2.4(1)
C1	-2010(4)	-76(1)	2628(3)	2.6(1)
C11	-1930(3)	560(1)	2879(3)	2.4(1)
C12	-1477(4)	942(1)	1669(3)	2.5(1)
C13	-1678(4)	1583(1)	1811(3)	3.4(1)
C14	-2317(4)	1828(1)	3093(3)	3.5(1)
C15	-2792(4)	1461(1)	4355(3)	3.0(1)
C16	-3447(4)	1720(1)	5686(4)	3.8(1)
C17	-3828(5)	1376(2)	6920(4)	4.3(1)
C18	-3571(5)	749(1)	6866(3)	3.9(1)
C19	-2959(4)	478(1)	5581(3)	3.3(1)
C110	-2567(4)	823(1)	4277(3)	2.7(1)
C21	-1778(4)	-1009(1)	1382(3)	2.7(1)
C22	-2766(4)	-1248(1)	98(3)	3.0(1)
C23	-3063(5)	-1874(1)	65(4)	4.1(1)
C24	-2395(5)	-2241(1)	1249(4)	4.5(2)
C25	-1387(5)	-1996(1)	2517(4)	4.3(1)
C26	-1091(4)	-1378(1)	2593(3)	3.3(1)
C27	-3537(5)	-854(2)	-1220(4)	4.8(2)

^a B _{ea}	is the	mean	of	the	princip	al axes	of	thermal	ellipso	vid.
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proton substitution by the nickel atom, the N1··O1 'bite' distance enlarges significantly to 2.674(3) Å compared to that in the free ligand.

In the complex chelate ring there is a general tendency of shortening the O-C, and C-C, and lengthening of the N-C bond distance in comparison

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to the same bond values in Schiff base itself, suggesting the delocalization of electron density to a certain extent.⁸ The quinoidal bond lengths assembly as in non-coordinated naphthaldimine is pronounced in the complex, too.

The o-tolyl ring system is twisted out of the chelate plane by rotating around the N1-C21 single bond. The N-substituent out-of-plane twisting defined by the C1-N1-C21-C22 torsion angle in (I) [34.1(3)°] and (II) $[59.7(7)^{\circ}]$ differs remarkably (Fig. 2). This is the consequence of sterical hindrances caused by (i) approaching of two ligands rather closely to each other in complex and (ii) enlarging of bond angles inside the chelate ring. The former refers to the close intramolecular approach of one of the methyl hydrogen atoms to the oxygen atom of the adjacent ligand, and the later imposes spatial restrictions to the hydrogen atoms bonded to C1, C19, and C26 to be accomodated without problems. Due to those spatial demands the naphthaldimine ligand is not planar. The C=N imino moiety is significantly out of the naphthalene plane [chelate ring to naphthalene ring interplanar angle is $6.23(7)^{\circ}$]. It should be noted that in the analogous bis bidentate nickel(II) complexes with N- β -naphthyl-, N-phenyl-, and N-p-tolyl-2-hydroxy-1-naphthaldimine a similar trend in stereochemical behavior was observed.^{23,24}



Compound (II)

Fig. 2. Projection of Compound (I) and (II) with equally oriented naphthalene plane perpendicular to the plane of paper drawn by PLUTON 92. Different spatial orientation of o-tolyl substituent with respect to the n phthalene moiety is clearly visible.

An unusually short contact Ni to H from the methyl group 2.703(1) Å is less than the sum of van der Waals radii for nickel and hydrogen atom, but it should not therefore be considered the Ni coordination is of the 4 + 2 type.²¹ All interactions between neighboring molecules are electrostatic in nature and none is shorter than 3.5 Å.

Acknowledgment

The authors are grateful for funding from the Ministry of Science and Technology, Republic of Croatia.

Supplementary Material. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1003/5262 (for I) and CCDC-1003/5263 (for II). Copies of available material can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or email: deposit@ccdc.cam.ac.uk.)

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