

Available online at www.sciencedirect.com



Polyhedron 23 (2004) 1293-1302



# Complexes of zinc(II) halides with *N*-benzyl- and *N*-*p*-tolyl-2-oxo-1-naphthylideneamine – preparation and characterization

Zora Popović<sup>a,\*</sup>, Vibor Roje<sup>a</sup>, Gordana Pavlović<sup>b</sup>, Dubravka Matković-Čalogović<sup>a</sup>, Maša Rajić<sup>c</sup>, Ivan Leban<sup>d</sup>

<sup>a</sup> Faculty of Science, Laboratory of General and Inorganic Chemistry, Department of Chemistry, University of Zagreb, Ul. kralja Zvonimira 8, HR-10000 Zagreb, Croatia

<sup>b</sup> Faculty of Textile Technology, University of Zagreb, Pierottijeva 6, HR-10000 Zagreb, Croatia

<sup>c</sup> Laboratory for Thermal Analysis, Brodarski Institute – Marine Research and Special Technology, Av. V. Holjevca 20, HR-10000 Zagreb, Croatia

<sup>d</sup> Laboratory of Inorganic Chemistry, Faculty of Chemistry and Chemical Technology, University of Ljubljana, P.O. Box 537,

1001 Ljubljana, Slovenia

Received 22 July 2003; accepted 8 December 2003 Available online 9 April 2004

Dedicated to Professor Milan Sikirica on the occasion of his 70th birthday

#### Abstract

A series of novel complexes, dihalo-bis(*N*-benzyl-2-oxo-1-naphthylideneamine-*O*)zinc(II),  $ZnX_2(bznapH)_2$  (1–3), dihalo-bis(*N*-*p*-tolyl-2-oxo-1-naphthylideneamine-*O*)zinc(II),  $ZnX_2(tolnapH)_2$  (4–6), of the general formula  $[ZnX_2(LH)_2] X = Cl$ , Br, I, have been prepared. The crystal structures of four compounds (1–4) reveal four coordinated zinc centres by two halogen and two oxygen atoms from the Schiff-base in the form of distorted tetrahedra. Complex 4 crystallizes as the one-to-one solvate with ethanol.

The tetrahedral distortion is most pronounced in the structure of  $ZnI_2(bznapH)_2$  complex. X-ray structural data showed that the Schiff-base ligand in the naphthylideneamine tautomeric form is weakly bound to Zn atom in 1–4 (being in the range from 1.952(3) Å in 2 to 2.002(3) Å in 4). The molecular structures of 1–4 are governed by the type of halide and the corresponding Schiff-base. Although the structure comparison of  $ZnX_2(bznapH)_2$  vs.  $ZnX_2(tolnapH)_2$  leads to the conclusion that ligand spatial accomodation (non-planar bznapH with aliphatic interruption vs. aromatic tolnapH) is the dominating factor in the crystal structures. The crystal structures of 2–4 are dominated by van der Waals forces. There is a weak intermolecular hydrogen bond of the C–H···Cl type in 1 (3.710(5) Å joining molecules into endless chains. The UV–Vis and <sup>1</sup>H NMR spectra, obtained in ethanolic and acetone solution indicate that the complexes do not exist in the solutions.

© 2004 Elsevier Ltd. All rights reserved.

Keywords: Zinc complexes; Schiff-bases; Crystal structures; IR; UV and NMR spectroscopy; Thermal analysis

# 1. Introduction

In the context of our investigation of mercury(II) compounds with Schiff-bases [1], we undertook the investigation of the analogous zinc(II) compounds in order to make more complete the coordination chemistry of the group 12 metals. It is well known that zinc and

Schiff-bases play important roles in biological systems; zinc mainly as a part of metalloenzymes [2] and Schiff-bases as the intermediates in aminoacid metabolism [3,4].

This paper reports the synthesis, IR, NMR and UV characterization as well as thermal studies of a series of 1:2 complexes of zinc(II) halides with *N*-benzyl-, *N*-*p*-tolyl-2-oxo-1-naphthylideneamine. The crystal structures of the complexes **1**–**4** have been determined by crystal X-ray diffractometry.

<sup>\*</sup> Corresponding author. Tel.: +385-1-4606652; fax: +385-1-4611191. *E-mail address:* zpopovic@chem.pmf.hr (Z. Popović).



Schiff-bases derived from O-hydroxy aromatic aldehydes such as salicylaldehyde and 2-hydroxy-1-naphthaldehyde with the N,O-donor set react with the zinc ion to yield two different types of compounds, i.e. metal chelates and adducts of general formulas ZnL<sub>2</sub> and  $ZnX_2 \cdot 2LH$ , respectively, both containing a four-coordinated zinc metal centre [5]. The chelate zinc complexes of the  $ZnL_2$  type where L = salicylaldiminato ligand are well known, but according to the Cambridge Structural Database [6a,6b] there are only two zinc(II) complexes with the Schiff-bases derived from 2-hydroxy-1-naphthaldehyde that are structurally characterized. One of them (refcode: POGJAW) [7] contains a five-coordinated zinc atom (three nitrogen atoms, one oxygen atom and one bromine atom) and the other has a tetrahedrally coordinated zinc atom (refcode: SUQWOK) [8]. According to our best knowledge, there is only one more zinc(II) complex with a Schiff-base derived from 2-hydroxy-1-naphthaldehyde and that has only been characterized spectroscopically [9]. There is no structural characterization of zinc adducts with the naphthaldimine type of Schiff-bases.

The crystal structures of these non-coordinated ligands have not been determined up until now. The tautomeric equilibrium of the Schiff-bases derived from 2-hydroxy-1-naphthaldehyde and amines (1:1 molar ratio), in the solid state [10–12] as well as in solution [3], is usually shifted toward the keto-amine tautomeric form (Scheme 1). There are also examples of the structures of this Schiff-base type that in the solid state exist in the enol-imine tautomeric form [13].

## 2. Experimental

All reagents used were purchased from Aldrich, solvents from Kemika-Zagreb and were used without further purification. C, H and N analysis was provided by the Analytical Services Laboratory of the Ruđer Bošković Institute. The IR spectra of all mentioned compounds were recorded in a Perkin–Elmer Fourier Transform 1600 spectrometer in the range of 4000–450 cm<sup>-1</sup> as KBr discs. The UV–Vis spectra were recorded using a Varian Cary 300 operating in the range 190–900 nm. The <sup>1</sup>H NMR spectra were recorded in a Varian Gemini 300 spectrometer, at 20 °C. All chemical shifts,

in parts per million (ppm), are referred to TMS. Digital resolution was 0.32 Hz per point. The thermal measurements were performed using a simultaneous TGA– DTA analyser (TA Instruments, SDT Model 2960 coupled with MS). The samples were placed in small alumina sample pans. The TGA and DTA curves were obtained by placing the samples of about 2 mg in mass, in open sample pans, with a heating rate of 10 °C min<sup>-1</sup> and argon (purity above 99.996%) flowing at the rate of 50 ml min<sup>-1</sup>. The SDT was calibrated with indium.

## 2.1. Preparation of the ligands and basic analytical data

The Schiff-bases *N*-benzyl-2-oxo-1-naphthylideneamine (bznapH) [14] and *N*-*p*-tolyl-2-oxo-1-naphthylideneamine (tolnapH) were prepared by the conventional condensation method.

*[bznapH]*. Chemical analysis: found (required for C<sub>18</sub>H<sub>15</sub>NO) C, 82.73 (82.89); H, 6.18 (5.79); N, 5.66 (5.36). Melting point: 98.5 °C. Selected IR-max (KBr disc, cm<sup>-1</sup>): 1629vs (C=O), 1542s and 1209m-s (C-N). Selected UV–Vis absorptions (EtOH):  $\lambda_{max}/nm$  ( $\epsilon/dm^3$  mol<sup>-1</sup> cm<sup>-1</sup>) 231 (45370), 307 (10920) and 420 (11010). <sup>1</sup>H NMR peaks (d<sub>6</sub>-acetone): 14.98 (s, 1H, –OH), 9.36 (s, 1H, HC=N), 8.14-6.92 (m, 11H, Ar–H), 4.91 (s, 2H, –CH<sub>2</sub>–).

*[tolnapH]*. Chemical analysis: found (required for C<sub>18</sub>H<sub>15</sub>NO) C, 82.05 (82.89); H, 5.77 (5.79); N, 5.46 (5.36). Melting point: 131 °C. Selected IR-max (KBr disc, cm<sup>-1</sup>): 1619vs (C=O), 1543s and 1211m-s (C–N). Selected UV–Vis absorptions (EtOH):  $\lambda_{max}/nm$  ( $\epsilon/dm^3$  mol<sup>-1</sup> cm<sup>-1</sup>) 233 (47420), 318 (13810) and 440 (16370). <sup>1</sup>H NMR peaks (d<sub>6</sub>-acetone): 15.73 (s, 1H, –OH), 9.68 (s, 1H, *H*C=N), 8.44-7.06 (m, 10H, Ar–*H*), 2.36 (s, 3H, –CH<sub>3</sub>).

# 2.2. Preparation of the complexes and basic analytical data

#### 2.2.1. General procedure

Ethanolic solutions of the corresponding zinc(II) salts and the appropriate Schiff-base in a 1:2 molar ratio were refluxed for several hours. The reaction mixture was then left to stand for two days. The compounds were filtered off, washed with ethanol and dried in vacuo. After standing for a few days, the filtrates 1–4

Z. Popović et al. | Polyhedron 23 (2004) 1293-1302

raute r	Tal	ble	1
---------	-----	-----	---

General and crystal data and summary of intensity data collection and structure refinement for 1, 2, 3 and 4

Compound	1	<b>2</b> <sup>a</sup>	<b>3</b> <sup>b</sup>	4
Formula	$C_{36}H_{30}Cl_2N_2O_2Zn$	$C_{36}H_{30}Br_2N_2O_2Zn$	C <sub>18</sub> H <sub>15</sub> INOZn <sub>0.5</sub>	$C_{36}H_{30}Cl_2N_2O_2Zn \cdot EtOH$
$M_{ m r}$	658.91	747.81	420.90	698.93
Colour and habit	colourless, prism	yellow, plate	yellow, needle	yellow, plate
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	<i>Cc</i> (No. 9)	$P2_1/n$ (No. 14)	<i>P</i> 2/ <i>c</i> (No. 13)	<i>P</i> 1̄ (No. 2)
Crystal dimensions (mm)	$0.596 \times 0.498 \times 0.284$	$0.29 \times 0.28 \times 0.09$	$0.10 \times 0.05 \times 0.01$	$0.40 \times 0.20 \times 0.01$
Temperature (K)	293	200	200	293
Unit cell parameters				
a (Å)	13.4309(15)	12.6821(1)	12.1548(3)	10.089(5)
$b(\mathbf{A})$	19.7654(19)	38.3182(4)	8.6508(2)	11.571(3)
c (Å)	12.049(4)	13.1555(2)	17.7188(4)	16.318(5)
α (°)				108.758(19)
β (°)	93.33(2)	94.179(1)	92.452(2)	102.52(3)
γ (°)				92.76(2)
$V(\mathbf{A}^3)$	3193.2(12)	6375.99(13)	1861.40(8)	1746.5(12)
Z	4	8	4	2
$D_{\text{calc}} (\text{g cm}^{-3})$	1.371	1.558	1.502	1.329
$\mu (\mathrm{mm}^{-1})$	0.971	3.3	2.348	0.9
F(000)	1360	3008	824	
$\theta$ range for data collection (°)	3–30	3-55	4-54	2-27
h, k, l range	-18 to 18; 18 to 27; -11	-16 to $16$ ; $-46$ to $48$ ;	-15 to 15; -11 to 10; -22	-12 to 12; -14 to 13;
	to 16	-1/ to $1/$	to 22	0 to 20
Diffractometer	PW 1100 upgraded by	Nonius Kappa CCD	Nonius Kappa CCD	PW 1100 upgraded by
	Stoe	area-detector		Stoe
Soon tuno		diffractometer		
Number of measured	ω 6221	ω 16242	ω 6712	ω 7510
reflections	0521	10243	0/13	/519
Number of independent	6137 (0.031)	9606 (0.026)	3895 (0.024)	7519 (0.00)
reflections $(R_{\rm ex})$	0157 (0.051)	9000 (0.020)	5055 (0.024)	(0.00)
Number of refined	388 (two restraints)	792	199	421
parameters				
Number of observed	3532	6507	2571	1812
reflections $I \ge 2\sigma(I)$				
Range of transmission	0.6117; 0.7776			
factors minimum,	,			
maximum <sup>c</sup>				
Crystal face indices,	(100; -100) 0.298			
distances from centroid (mm)	(10-1; -101) 0.249			
	(010; 0-10) 0.142			
$R^{d} w R^{e} I \ge \sigma(I)$ ]	0.043; 0.124	0.046; 0.089	0.047; 0.151	0.048; 0.1396
R, wR (all data)	0.094; 0.106	0.088; 0.078	0.078; 0.128	0.099; 0.257
$g_1, g_2$ in $w^{\mathrm{f}}$	0.0844; 0	0.0227; 6.8592	0.0805; 1.2948	0.0624; 0
Goodness-of-fit on $F^2$ ,	0.91	1.08	1.002	0.705
$S^{ m g}$				
Maximum and minimum	0.44 and -0.28	-0.40 and 0.44	0.652 and -0.69	0.34 and -0.60
electron density (e $A^{-3}$ )				
Flack parameter	0.006(14)			
Maximum $\Delta/\sigma$	0.001	0.001	0.001	0.001
Extinction coefficent		0.00025(8)		

<sup>a</sup> The asymmetric unit contains two crystallographically independent molecules.

<sup>b</sup> The iodine atom lies on the twofold axis.

<sup>c</sup>Absorption correction type: numerical Gaussian for 1; only scaling for 2 and 3; not applied for 4.

Absorption correction type: numerical categories (1, 2)  ${}^{d}R = \sum ||F_o| - |F_c|| / \sum |F_o|.$   ${}^{e}wR = \left[\sum (F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2\right]^{1/2}.$   ${}^{f}w = 1/[\sigma^2(F_o^2) + [(g_1P)^2 + g_2P] \text{ where } P = (F_o^2 + 2F_c^2)/3.$  ${}^{g}S = \sum [w(F_o^2 - F_c^2)^2 / (N_{obs} - N_{param})]^{1/2}.$ 

yielded crystals of good quality for X-ray diffraction experiment.

 $[ZnCl_2(bznapH)_2]$  (1). Reaction time: 4 h. Colour: yellow-brownish Yield: 60%. Anal. Found (required for

 $C_{36}H_{30}Cl_2N_2O_2Zn$ ): C, 64.78 (65.62); H, 4.85 (4.59); N, 4.20 (4.25); Zn, 10.17 (9.92%). Selected IR-max (KBr disc, cm<sup>-1</sup>): 1634vs (C=O), 1548s (C=C) and 1212m-s (C-N).

 $[ZnBr_2(bznapH)_2]$  (2). Reaction time: 4 h. Colour: yellow. Yield: 76%. *Anal.* Found (required for C<sub>36</sub>H<sub>30</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>2</sub>Zn): C, 57.85 (57.82); H, 4.00 (4.04); N, 3.75 (3.75); Zn, 8.43 (8.74%). Selected IR-max (KBr discs, cm<sup>-1</sup>): 1633vs (C=O), 1548s (C=C) and 1211m-s (C–N).

 $[ZnI_2(bznapH)_2]$  (3). Reaction time: 6 h. Colour: yellow. Yield: 76%. *Anal.* Found (required for C<sub>36</sub>H<sub>30</sub>I<sub>2</sub>N<sub>2</sub>O<sub>2</sub>Zn): C, 51.27 (51.36); H, 3.78 (3.59); N, 3.39 (3.33); Zn, 7.97 (7.77%). Selected IR-max (KBr discs, cm<sup>-1</sup>): 1633vs (C=O), 1548s (C=C) and 1211m-s (C–N).

 $[ZnCl_2(tolnapH)_2]$  (4). Reaction time: 4 h. Colour: yellow. Yield: 90%. Anal. Found (required for C<sub>36</sub>H<sub>30</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>Zn): C, 65.31 (65.62); H, 4.75 (4.59); N, 4.17 (4.25); Zn, 9.60 (9.92%). Selected IR-max (KBr discs, cm<sup>-1</sup>): 1626vs (C=O), 1548s (C=C) and 1216m-s (C–N).

 $[ZnBr_2(tolnapH)_2]$  (5). Reaction time: 1 h. Colour: yellow. Yield: 89%. *Anal.* Found (required for C<sub>36</sub>H<sub>30</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>2</sub>Zn): C, 57.76 (57.82); H, 4.26 (4.04); N, 3.87 (3.75); Zn, 8.53 (8.74%). Selected IR-max (KBr discs, cm<sup>-1</sup>): 1626vs (C=O), 1548s (C=C) and 1217m-s (C–N).

 $[ZnI_2(tolnapH)_2]$  (6). Reaction time: 4 h. Colour: yellow. Yield: 86%. Anal. Found (required for C<sub>36</sub>H<sub>30</sub>I<sub>2</sub>N<sub>2</sub>O<sub>2</sub>Zn): C, 51.74 (51.36); H, 4.27 (3.59); N, 3.21 (3.33); Zn, 7.87 (7.77%). Selected IR-max (KBr discs, cm<sup>-1</sup>): 1622vs (C=O), 1547s (C=C) and 1216m-s (C–N).

# 2.3. X-ray single crystal analyses of the compounds 1, 2, 3 and 4

Relevant data on the summary of intensity data collection for the structures 1–4 are given in Table 1. Data collection for 1 and 4 were controlled by the STADI4 program [15]. Lattice constants were obtained by the least-squares refinement from the settings of 46 reflections  $(10^\circ \le \theta \le 16^\circ)$  for 1 and 21 reflections  $(8^\circ \le \theta \le 15^\circ)$  for 4. 7383 reflections with  $1^\circ \le \theta \le 28^\circ$  and 3409 reflections with  $1^\circ \le \theta \le 28^\circ$  were used for unit cell refinement for structures 2 and 3, respectively. Two sets of 311 frames and one of 167 frames were collected at the crystal-detector distance of 70 mm, 0.6° scans, 12 s per frame for structure 2 and two sets of 187 and 62 frames at the crystal-detector distance of 45 mm, 1.0° scans, 30 s per frame for structure 3.

Reference reflections were monitored periodically showing no significant intensity decay for all four structures. The data were corrected for Lorentz-polarization by the X-RED [16] program for 1 and 4 and by DENZO-SMN [17] for 2 and 3. The Gaussian absorption correction based on the crystal dimensions by the X-RED [16] program was performed for 1, but for 2 and **3** only scaling based on all symmetrically dependent reflections were applied.

The structures were solved by direct methods implemented in the SHELXS [18] program. The applied refinement procedure based on the  $F^2$  values against all reflections included the anisotropic model for all non-H atoms using the SHELXL [19] program. The hydrogen atoms were generated at ideal geometrical positions [Csp<sup>2</sup>–H 0.93, Csp<sup>3</sup>–H 0.97 Å, Csp<sup>3</sup>–H 0.96 Å for phenyl, methylene and methyl carbon atoms with  $U_{\rm iso}({\rm H}) = 1.2$  or 1.5  $U_{\rm eq}({\rm C})$ ] and refined applying the riding model. In the structure of compound 1 the hydrogen atoms belonging to the nitrogen atoms of the C=N group were found, but finally refined at idealized stereochemical positions (N-H 0.86 Å) by the riding model procedure. Structurally identical hydrogen atoms in 2 and 3 were found in the electron density difference Fourier maps and refined freely [N1–H1N 0.74(4) Å and N2-H2N 0.83(4) Å in 2 and N1-H1N 0.64(4) A in 3].

In the structure of compound 4, due to the poorer quality X-ray diffraction data (data-to-parameter ratio is less than 4.5), the positional disorder of the atoms C1, C2 and O3 of the ethanol molecule could not be refined, thus hydrogen atoms belonging to C1, C2 and O3 were not modelled. The hydrogen atom which belongs to the N2 atom is found in the electron density difference Fourier map and is refined freely, but the hydrogen atom which belongs to N1 atom could not be found and it was generated at an ideal position and refined by the riding model procedure (N-H 0.86 Å). The standard deviations of the molecular geometry of 4 are significantly larger than in 1, 2 and 3 making the comparison of its geometry to the other ones impossible. Only the main stereochemical features of the solid state structure of 4 could be obtained, but not the fine structural details. Graphical work has been performed by the program platon-98 [20].

# 3. Results and discussion

#### 3.1. General aspects

The reactions of zinc(II) halides with *N*-benzyl-2-oxo-1-naphthylideneamine and *N-p*-tolyl-2-oxo-1-naphthylideneamine in ethanolic solution, give complexes of the general formula  $[ZnX_2(HL)_2](X = Cl, Br, I)$  (Scheme 2). The isolated compounds are stable in air at room temperature, but do not exist in DMSO, DMF, pyridine, chloroform, acetone or ethanol solutions, i.e. they undergo decomposition, which is revealed by <sup>1</sup>H NMR and UV spectra. Compound **4** crystallizes as an ethanolic solvate, but its crystals, losing the ethanol, slowly decompose into the unsolvated compound at room temperature.

$$ZnX_2 + 2LH$$
  $\xrightarrow{EtOH}$   $ZnX_2 (LH)_2$ 

LH = N-benzyl-2-oxo-1-naphthylideneamine (bznapH) N-p-tolyl-2-oxo-1-naphthylideneamine (tolnapH)



 $ZnX_{2}(bznapH)_{2}$  [X = Cl (1), Br (2), I (3)] ZnX<sub>2</sub>(tolnapH)<sub>2</sub> [X = Cl (4), Br (5), I (6)]



#### 3.2. Spectroscopic studies

The IR spectra of the free Schiff-bases and compounds 1-6 are quite similar in the "finger print" region. The common feature of all these spectra is a very weak and broad stretching band in the  $3000-1800 \text{ cm}^{-1}$  region that can be assigned as the v(NH) stretching band. The very strong absorption band in the region of 1630-1610  $cm^{-1}$ , is due to the C=O stretching vibrations and indicates the presence of the keto-amine tautomeric form of the Schiff-base, both in the free ligand and in the complexes. Furthermore, the strong absorption bands in the region of  $1550-1540 \text{ cm}^{-1}$  that can be assigned to the C=C stretching accompanied with that in the region of 1220–1210 cm<sup>-1</sup> that suggests C=N stretching, confirm the existence of the keto-amine tautomeric form of the Schiff-base [21-23], suggesting metal-to-ligand coordination via the carbonyl oxygen atom.

The UV–Vis absorption spectra measured for the absolute ethanolic solution of the zinc complexes (1-6) suggest that they decompose when dissolved. Such a conclusion can be drawn because of the similarity of the spectra of the free ligands with those measured for the solution of the complexes. Moreover, that is quite consistent with the our previous results obtained for the mercury(II) halide adducts with the same ligand [1]. The spectra reveal a predominance of the keto-amine tautomeric form of both ligands [24,25].

We also measured the <sup>1</sup>H NMR spectra in acetone. The NMR measurements show that complexes 1-6 are not stable in acetone either. This conclusion was drawn from the fact that there are no significant changes in the <sup>1</sup>H NMR chemical shifts of the dissolved compounds in comparison with those of the free ligands. In the <sup>1</sup>H NMR spectrum of bznapH the signals of azomethine and hydroxyl protons appear at 9.36 and 14.98 ppm, while in tolnapH they appear at 9.68 and 15.73 ppm, respectively. The signals corresponding to Ar-H appear in the region 6.9–8.2 ppm and 7.0–8.5 ppm for bznapH and tolnapH, respectively. At 4.91 ppm the signal corresponding to the two methylene protons for bznapH have been observed and that at 2.36 ppm corresponds to the three methyl protons for tolnapH [8,26,27].

# 3.3. X-ray structural studies

The structural study of the four zinc complexes 1–4 was undertaken in order to establish the general mode of ligating of this type of Schiff-base, dependence of the zinc coordination sphere geometry on the type of zinc halide (chloride, bromide and iodide) and to compare results with the 1:1 mercury halide adducts of the same Schiff-base which have been previously structurally characterized by us [1].

In the  $ZnX_2 \cdot 2LH$  adducts or in the  $[ZnX_2(LH)_2]$ complexes zinc retains  $X^-$  ions in the coordination sphere and thus neutral LH Schiff-base completes the coordination sphere bonding monodentately by either oxygen or nitrogen ligating centre, but not with both donor atoms. Contrary to the ZnL<sub>2</sub> complexes where the Schiff-base is bound in an anionic form, the intramolecular hydrogen bond of the O–H···N or N–H···O type is preserved in the adducts or in the  $[ZnX_2(LH)_2]$ type of complexes. Usually, the type of intramolecular hydrogen bond found in the adduct or in the [ZnX<sub>2</sub>(LH)<sub>2</sub>] complexes and non-coordinated Schiffbase is different, thus leading to the change of the tautomeric form of the Schiff-base ligand upon complexation [5]. Adducts of the type  $ZnX_2 \cdot 2LH$  are only known for salicylaldimine Schiff-bases and according to the Cambridge Structural Database [6a,6b] there are three such adducts: N-isopropylsalicylaldimine with ZnI<sub>2</sub> (refcode: VATROX) [28], dichloro-bis(2-(o-tolyliminomethyl)phenolato-O)-zinc(II) (refcode: XAXVIB) [29] and bis(1-anilinomethylidene-2-oxo-1H,2H-naphthalene-chloro)-zinc (refcode: VIRVUN) [30]. The common feature of these three adducts is stronger Zn-X bonds (2.564(1)-2.587(1) A range for the Zn-I bond in VATROX, 2.2401(7) A for the Zn–Cl bond in XAXVIB and 2.203(7), 2.226(7), 2.201(7) and 2.217(8) A for the Zn–Cl bonds in VIRVUN) and weaker Zn–O bonds being in the range from 1.955 A (mean value) in VAT-ROX to 2.00(1) Å in VIRVUN. These Zn–O bond distances are longer than in the chelate ZnL<sub>2</sub> complexes (the average Zn–O bond distance value in the  $ZnL_2$ complexes with salicylaldimine Schiff bases is 1.926 Å). This elongation is the consequence of the Schiff-base ligation in the neutral form in the adducts and the participation of N,O-donor atoms in the intramolecular hydrogen bond formation. The length of the N–H $\cdot \cdot \cdot O$ intramolecular hydrogen bond varies from 2.499 Å in VIRVUN to 2.636 Å in VATROX.



Fig. 1. ORTEP drawing of  $ZnCl_2(bznapH)_2$  (1) with the atom numbering scheme. The thermal ellipsoids are at the 50% probability level.



Fig. 2. The crystal packing of  $ZnCl_2(bznapH)_2$  (1) showing the intermolecular C212–H21A···Cl1 hydrogen bonds by dashed lines that link molecules into endless chains parallel to the *y*-axis. The other hydrogen atoms are omitted for clarity.



Fig. 3. ORTEP drawing of  $ZnBr_2(bznapH)_2$  (2) with atom the numbering scheme. The thermal ellipsoids are at the 50% probability level. There are two crystallographically independent molecules within the asymmetric unit. Only one is shown for clarity.

The crystal structures of the two isostructural adducts, HgX<sub>2</sub>(bznapH) (X = Cl, Br) revealed dimers formed by bridging halogen atoms and generated a 2+2effective coordination sphere of the mercury atoms [1]. The dimers are joined only by the van der Waals contacts.



Fig. 4. ORTEP drawing of  $ZnI_2(bznapH)_2$  (3) with the atom numbering scheme. The thermal ellipsoids are at the 50% probability level. Symmetry code: (a): 1 - x, y, 3/2 - z.



Fig. 5. ORTEP drawing of  $ZnCl_2(tolnapH)_2\cdot EtOH$  (4) with the atom numbering scheme. The thermal ellipsoids are at the 50% probability level.

In the zinc complexes 1–4 the common feature is the distorted tetrahedral coordination sphere of the zinc atom formed by two halogen atoms [Zn1–Cl1 2.215(2) and Zn1–Cl2 2.229(2) Å in 1; Zn1–Br1 2.344(1), Zn1–Br2 2.356(1), Zn2–Br3 2.371(1) and Zn2–Br4 2.355(1) Å in 2 and Zn1–I1 2.564(1) Å in 3, Zn–Cl1 2.255 (2) and Zn–Cl2 2.204 (2) in 4] and two oxygen atoms from two neutral monodentate Schiff bases [Zn1–O1 1.968(4) and Zn1–O2 1.982(3) Å in 1, Zn1–O1 1.960(3), Zn1–O2 1.975(3), Zn2-O3 1.957(3) and Zn2–O4 1.952(3) Å in 2, Zn1–O1 1.968(4) Å in 3, Zn–O1 1.976(3) and Zn–O2 2.002(3) Å in 4] (Figs. 1, 3, 4 5). The Zn–O bond distance values are comparable with those found in zinc complexes with salicylaldimines (VATROX, XAXVIB, VIRVUN) and are longer than in the chelate complexes.

In the structures of complexes 1–4 the X1–Zn–X2 bond angles are the most deformed from ideal tetrahedral geometry. The degree of deformation is most pronounced in the iodo derivative [X1–Zn–X2 bond angles values are 118.81(7)° in **1**, 119.49(3)° in **2**, 123.49(4)° in **3** and 120.94(7)° in **4**].

The dihedral angles between planes of the naphthalene rings and phenyl rings of the *N*-substituents (Table 3) indicate non-planarity of the ligands in the 1–3 complexes, while in 4 the corresponding dihedral angles are remarkably smaller, but still the molecules are not planar [20.3(2)° and 22.2(3)° in 4 vs. the range from  $56.2(5)^{\circ}$  to  $81.7(2)^{\circ}$  for 1, 2 and 3]. The tendency of a stacking arrangement of planar tolnapH molecules is observed in the structure of HgCl<sub>2</sub>(tolnapH) [1] causing the needle-shaped crystal morphology.

In **2**, the rings 1 and 2 are oriented to each other by approx.  $70^{\circ}$ , while other rings (3–8) do not deviate significantly from planarity (Table 3).

The molecules are mutually connected only by van der Waals interactions, except in 1 where weak intermolecular hydrogen bonds of the C-H···Cl type link molecules into endless chains parallel to the y-axis.

Table 2

Relevant interatomic distances (A) a	nd angles (°) for th	e compounds 1, 2, 3 and 4	1
--------------------------------------	----------------------	---------------------------	---

	1	2	3	4	
Interatomic distances					
Zn1–X1 <sup>a</sup>	2.2149(15)	2.3435(7)	2.5639(6)	2.255(2)	
Zn1–X2 <sup>a</sup>	2.2292(18)	2.3558(8)		2.204(2)	
Zn2–X3 <sup>a</sup>		2.3708(8)			
Zn2–X4 <sup>a</sup>		2.3551(8)			
Zn1–O1	1.968(4)	1.960(3)	1.968(4)	1.976(4)	
Zn1–O2	1.982(3)	1.975(3)		2.002(3)	
Zn2–O3		1.957(3)			
Zn2–O4		1.952(3)			
O1–C12 <sup>b</sup>	1.283(6)	1.305(5)	1.298(6)	1.310(6)	
O2–C22	1.285(5)	1.298(5)		1.319(7)	
O3–C32		1.301(5)			
O4–C42		1.294(5)			
N1-C111 <sup>c</sup>	1.294(10)	1.298(6)	1.280(6)	1.307(8)	
N2-C211	1.299(5)	1.291(5)		1.327(7)	
N3-C311		1.300(6)			
N4-C411		1.302(6)			
Bond angles					
X1-Zn1-X2 <sup>ad</sup>	118.81(7)	119.49(3)	123.49(4)	120.94(7)	
X1–Zn1–O1	112.37(12)	116.03(9)	103.06(11)	99.22(13)	
X1–Zn1–O2 <sup>e</sup>	117.59(10)	100.65(8)	108.25(11)	98.34(10)	
X2–Zn1–O1 <sup>f</sup>	112.42(13)	109.31(9)	110.59(15)	116.32(11)	
X2–Zn1–O2	101.01(9)	114.53(10)		114.06(12)	
O1–Zn1–O2	90.93(14)	93.61(12)		105.18(15)	
Br3–Zn2–Br4		116.92(3)			
Br3–Zn2–O3		119.66(9)			
Br3–Zn2–O4		96.54(11)			
Br4–Zn2–O3		107.00(9)			
Br4–Zn2–O4		120.70(10)			
O3–Zn2–O4		94.37(14)			

 $^{a}$ X1 = Cl1 in 1, Br1 in 2 and I in 3;X2 = Cl2 in 1 and Br2 in 2; X3 = Br3 in 2; X4 = Br4 in 2.

<sup>b</sup>O1–C2 in 3.

<sup>c</sup>N1–C11 in **3**.

<sup>d</sup> I–Zn–I<sup>i</sup> in **3** (i = 1 – x, y, 3/2 - z).

<sup>e</sup> I–Zn–O1<sup>i</sup> in 3 (i = 1 - x, y, 3/2 - z).

<sup>f</sup>O1–Zn–O1<sup>i</sup> in **3** (i = 1 – x, y, 3/2 - z).

Table 3 Dihedral angles between planes defined by the naphtahlene and phenyl rings atoms in 1, 2, 3 and 4

Number of plane	Plane defined by atoms	Dihedral angle (°)
Compound 1		
1	C11-C110	1,2 56.2(5)
2	C113-C118	
3	C21-C210	3,4 62.0(5)
4	C213–C218	
Compound 2		
1	C11-C110	1,2 70.1(2)
2	C113-C118	
3	C21–C210	3,4 81.7(2)
4	C213-C218	
5	C31–C310	5,6 80.5(2)
6	C313–C318	
7	C41–C410	7,8 80.3(2)
8	C413–C418	
Compound 3		
1	C1-C10	1,2 70.5(4)
2	C13-C18	
Compound 4		
1	C11-C110	1,2 20.3(2)
2	C112-C116	
3	C21-C210	3,4 22.2(3)
4	C212–C216	

(Table 4, Fig. 2.) [31,32]. This hydrogen bond does not influence the Zn–Cl1 bond distance since it is comparable with the Zn–Cl2 bond distance (atom Cl2 does not participate in hydrogen bond formation) [Zn1–Cl1 2.215(2) and Zn1–Cl2 2.229(2) Å in 1].

The significant difference of the Zn–Cl1 and Zn–Cl2 bond distances in **4** (Table 2) can indicate the participation of the Cl1 atom in the O–H···Cl intermolecular hydrogen bond formation with the O3 atom of an ethanol molecule (Cl1···O3 distance is 3.266(7) Å).

Table 4									
Hydrogen	bond	geometry	(Å,	°)	in	1,	2	and	3

So, the conclusion is that the geometry of the zinc coordination sphere in the three complexes 1-3 is not affected by the crystal packing forces (i.e. intermolecular hydrogen bonds). Therefore, the bond distances and angles values within the coordination sphere are mutually comparable.

## 3.4. Description of the ligands

The bznapH and tolnapH Schiff-bases exist in the keto-amine tautomeric form in all four complexes (1–4) revealing the N–H···O resonance assisted intramolecular hydrogen bond (RAHB) [range for the N···O distance is 2.565(5)-2.599(5) Å] (Table 4). The same tautomeric form is found in the crystal structures of the analogous 1:1 adducts with mercury(II) halides [1].

The C=N bond distance values are in the range from 1.280(6) Å in 3 to 1.299(5) Å in 1. The C–O bond distance values (1.283(6)–1.301(5) Å) are shortened in relation to the Csp<sup>2</sup>–OH bond distance value in phenols (1.36 Å) [33]. These two bonds, C=N and Csp–O, are the most sensitive indicators of the proton location, on the oxygen or nitrogen site, i.e. on the type of the tautomer. In the mercury analogues the intramolecular hydrogen bond N–H···O is 2.58(1) Å in the chloro derivative and 2.59(1) Å in the bromo derivative.

The geometry of the ligands in the complexes 1-4 are comparable with the similar non-coordinated naphthaldimines in the keto-amine form, indicating the labile bounding of the ligands with the zinc centre.

# 3.5. Thermal analysis

The samples of the free ligands, bznapH and tolnapH, as well as the zinc complexes 1-6 were heated from room temperature up to 700 °C.

Hydrogen bond geometry (A	(1) in 1, 2 and 3				
$D - H \cdots A$	d(D-H)	$d(\mathbf{H} \cdot \cdot \cdot \mathbf{A})$	∠DHA	$d(\mathbf{D}\cdots\mathbf{A})$	
1					
N1–H1···O1	0.86	1.984	127	2.591(8)	
$N2-H2\cdots O2$	0.86	1.938	133	2.599(5)	
$C212\text{-}H21A\cdots Cl1^{i}$	0.97	2.800	157	3.710(5)	
2					
$N1-H1N\cdots O1$	0.74(4)	1.99(5)	137(5)	2.576(5)	
$N2-H2N\cdots O2$	0.83(4)	1.91(4)	135(4)	2.565(5)	
N3–H3N···O3	0.90(5)	1.89(4)	132(4)	2.589(5)	
$N4\!\!-\!\!H4N\!\cdots\!O4$	0.69(4)	2.05(5)	133(5)	2.574(6)	
3					
$N1-H1N\cdots O1$	0.64(4)	2.13(4)	128(5)	2.571(6)	
4					
N1–H1···O1	0.86	1.856	2.552(6)	137	
$N2-H2\cdots O2$	0.79(3)	1.95(3)	2.602(6)	141(4)	

Symmetry code (i): -1/2 + x, -1/2 - y, -1/2 + z.

1301

Table 5

Thermoanalytical data for bznapH and tolnapH and its Zn(II) complexes

Compound	Process Temperature (°C)		Accumulated	weight loss (%)
			Found	Calculated
BznapH	Melting (endo)	98.50		
	Degradation (endo)	150-400	88	100
	Residue	400	12	
TolnapH	Melting (endo)	139.22		
	Degradation (endo)	100-300	100	100
ZnCl <sub>2</sub> (bznapH) <sub>2</sub> (1)	Degradation of ligand (endo)	200–380	70.4	79.3
	Elimination of Cl (exo)	340-550	9.83	10.77
	Residue	550	19.77	9.93
$ZnBr_2(bznapH)_2$ (2)	Degradation of ligand (endo)	200-375	61.6	69.86
	Elimination of Br (exo)	330-600	20.37	21.64
	Residue	600	18.03	8.05
$ZnI_2(bznapH)_2$ (3)	Degradation of ligand (endo)	200-365	54.56	62.05
	Elimination of Br (exo)	325-650	29.43	30.17
	Residue	650	16.01	7.78
ZnCl <sub>2</sub> (tolnapH) <sub>2</sub> (4)	Melting (endo)	211.82		
	Degradation of ligand (endo)	200-310	31.54	39.65
	Degradation of ligand (endo)	310-365	31.35	39.65
	Elimination of Cl (exo)	365-500	9.21	10.77
	Residue	500	27.9	9.93
ZnBr <sub>2</sub> (tolnapH) <sub>2</sub> (5)	Degradation of ligand (endo)	200-300	26.32	34.93
	Degradation of ligand (endo)	300-370	27.76	34.93
	Elimination of Br (exo)	370-600	20.54	21.64
	Residue	600	25.38	8.75
$ZnI_2(tolnapH)_2$ (6)	Degradation of ligand (endo)	200-305	23.21	31.03
	Degradation of ligand (endo)	305–385	24.27	31.03
	Elimination of I (exo)	385–640	28.96	30.17
	Residue	640	23.56	7.78

The DTA curves of the complexes 1-3 were dominated by the typical endothermic minima, which correspond to the melting points (Table 5). Degradation of bznapH (ca. 88%) was observed in the range of 200–400 °C and was characterized by the endothermic peak in the DTA-curve. On heating the samples 1-3 up to 600 °C elimination of halogen occurred which was determined by an exothermic peak but still ca. 20% of the initial mass of the samples was left as a mixture of carbonated residue and zinc.

Thermal analysis of the complexes 4-6 showed that only the zinc chloride complex 4 melts, while 5 and 6 initially underwent degradation over two consecutive endothermic processes. Elimination of halogen was represented by the exothermic peak. As for 1–3, there was also ca. 25% of the initial mass left in the sample pan.

# 4. Supplementary material

Atomic coordinates and equivalent isotropic displacement parameters, calculated hydrogen atom parameters, anisotropic thermal parameters and bond lengths and angles have been deposited and allocated deposition numbers at the Cambridge Crystallographic Data Centre (CCDC Nos. 198366–198369 for structures **1**, **2**, **3** and **4**, respectively). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; email: deposit@ccdc.caom.ac.uk or www.ccdc.com.ac.uk). All structural factor tables are available from the authors upon request.

#### Acknowledgements

This research was supported by the Ministry of Science and Technology of the Republic of Croatia (Grant Nos. 0119633, 0119632 and 01920202). The crystallographic data for structures **2** and **3** were collected on the KappaCCD Nonius diffractometer in the Laboratory of Inorganic Chemistry, Faculty of Chemistry and Chemical Technology, University of Ljubljana, Slovenia. We acknowledge with thanks the financial contribution of the Ministry of Education, Science and Sport, Republic of Slovenia through grants X-2000 and PO-511-103,

which thus made the purchase of the apparatus possible. We thank the INA d.d. Zagreb, Division of Strategic Development, Research and Investment for allowing us to record the UV–Vis spectra on their instrument.

# References

- Z. Popović, V. Roje, G. Pavlović, D. Matković-Čalogović, M. Rajić, G. Giester, Inorg. Chim. Acta 332 (2001) 65.
- [2] R.H. Prince, Zinc and Cadmium, in: G. Wilkinson (Ed.), Comprehensive Coordination Chemistry, vol. 5, Pergamon Press, Oxford, 1987, p. 1001.
- [3] J. Costamagna, J. Vargas, R. Lattore, A. Alvarado, G. Mena, Coord. Chem. Rev. 119 (1992) 67.
- [4] W. Kaim, B. Schwederski, Bioinorganic Chemistry: Inorganic Elements in the Chemistry of Life, Wiley, Chichester, 1994.
- [5] A.D. Garniovskii, A.L. Nivorozhkin, V.I. Minkin, Coord. Chem. Rev. 126 (1993) 1.
- [6] (a) Cambridge Structural Database, V5.24, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, England, November, 2002
  - (b) F.H. Allen, Acta Crystallogr., Sect. B 58 (2002) 380.
- [7] J. Ondráček, B. Kratochvíl, V. Haber, Collect. Czech. Chem. Commun. 59 (1994) 1809.
- [8] T. Hökelek, Z. Kl, M. Iklan, M. Toy, J. Mol. Struct. 523 (2000) 61.
- [9] B.B. Mahapatra, M.K. Raval, A.K. Behera, A.K. Das, J. Indian, Chem. Soc. 72 (1995) 161.
- [10] M. Gavranić, B. Kaitner, E. Meštrović, J. Chem. Crystallogr. 26 (1996) 23.
- [11] B. Kaitner, G. Pavlović, Acta Crystallogr., Sect. C 52 (1996) 2573.
- [12] G.O. Dudek, J. Am. Chem. Soc. 85 (1963) 694.
- [13] B. Kaitner, E. Meštrović, G. Pavlović, J. Chem. Crystallogr. 28 (1998) 77.

- [14] G. Pavlović, Ph.D. Thesis, University of Zagreb, 1998 (abstract in English).
- [15] Stoe & Cie, STADI4, Diffractometer Control Program for Windows, Darmstadt, Germany, 1995.
- [16] Stoe & Cie, X-RED, Data Reduction Program for Windows, Darmstadt, Germany, 1995.
- [17] Z. Otwinowski, W. Minor, in: C.W. Carter Jr., R.M. Sweet (Eds.), Methods in Enzymology, Macromolecular Crystallography – Part A, vol. 276, Academic Press, London, 1997, p. 307.
- [18] G.M. Sheldrick, SHELXS-97: Program for the Solutions of Crystal Structures, University of Göttingen, Germany, 1997.
- [19] G.M. Sheldrick, SHELXL-97: Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.
- [20] A.L. Spek, Acta Crystallogr., Sect. A 46 (1990) 34.
- [21] S.R. Salman, N.A.I. Saleh, Spectrosc. Lett. 30 (1997) 1289.
- [22] J.W. Ledbetter Jr., J. Phys. Chem. 81 (1977) 54.
- [23] T. Yuzawa, H. Takahashi, H. Hamaguchi, Chem. Phys. Lett. 202 (1993) 221.
- [24] L. Antonov, W.M.F. Fabian, D. Nedeltcheva, F.S. Kamounah, J. Chem. Soc., Perkin Trans. 2 (2000) 1173.
- [25] P. Nagy, R. Herzfeld, Spectrosc. Lett. 31 (1998) 221.
- [26] J.-C. Zhuo, Magn. Res. Chem. 37 (1999) 259.
- [27] H. Ünver, Spectrosc. Lett. 34 (2001) 783.
- [28] F.A. Bottino, P. Finocchiaro, E. Libertini, G. Mattern, Z. Kristallogr. 187 (1989) 71.
- [29] D. Ülkü, C. Arc, M.N. Tahir, O. Atakol, Acta Crystallogr., Sect. C 56 (2000) 1298.
- [30] V.S. Sergienko, A.E. Mistryukov, V.V. Litvinov, M.I. Knyazhanskii, A.D. Garnovskii, M.A. Porai-Koshits, Koord. Khim. 16 (1990) 168.
- [31] R. Taylor, O. Kennard, J. Am. Chem. Soc. 104 (1982) 5063.
- [32] G.R. Desiraju, T. Steiner, The Weak Hydrogen Bond, IUCr, Oxford Science Publications, Oxford, 2001.
- [33] F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen, R. Taylor, J. Chem. Soc. Perkin Trans. II (1987) S1.