

# Molecular structure of *N,N'*-*o*-phenylene-bis(salicylideneaminato)zinc(II), Zn(saloph), according to gas-phase electron diffraction and quantum-chemical calculations

G.V. Girichev<sup>a,\*</sup>, N.I. Giricheva<sup>b,1</sup>, N.V. Tverdova<sup>a,2</sup>, E.D. Pelevina<sup>a,b,2</sup>, N.P. Kuzmina<sup>c,3</sup>, O.V. Kotova<sup>c,3</sup>

<sup>a</sup> Ivanovo State University of Chemistry and Technology, Department of Physics, Engels av 7, 153 000 Ivanovo, Russia

<sup>b</sup> Ivanovo State University, Department of Physical Chemistry, Ermak st. 39, 153 025 Ivanovo, Russia

<sup>c</sup> Lomonosov Moscow State University, Department of Chemistry, Leninskie gory, 119899 Moscow, Russia

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## ABSTRACT

The molecular structure of *N,N'*-*o*-phenylene-bis(salicylideneaminato)zinc(II) has been determined by synchronous gas-phase electron diffraction (GED) and mass spectrometric experiment at 626(5) K and by density functional theory calculations (B3LYP/Stuttgart ECP(Zn), TZV (O, N, C, H) with the addition of d-polarization functions; in case of N, O with the addition of p-diffuse functions; B3LYP/Stuttgart ECP(Zn), cc-pVTZ (O, N, C, H)). Both experimental and theoretical approaches yielded the structure of  $C_2$ -symmetry with a planar  $ZnN_2O_2$  coordination site. The overall ligand conformation is also planar with small distortion towards an umbrella-shape. The most important structure parameters are  $r_{h1}(Zn-N) = 2.072(12)$  Å;  $r_{h1}(Zn-O) = 1.926(7)$  Å;  $\angle NZnN = 77.4(1.4)^\circ$ ;  $\angle NZnO = 90.4(1.4)^\circ$ ;  $\angle OZnO = 101.9(2.5)^\circ$ . Structural features of tetra-coordinate zinc complexes are discussed.

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## 1. Introduction

Transition metal compounds containing Schiff base ligands were a subject of numerous investigations for many years due to their biological significance and applications in different fields such as catalysis, molecular architectures, magnetism, materials chemistry, etc. [1–7]. For example, luminescent transition metal compounds widely have been used as a sensors and a probers for a variety of chemical and biological substances; as emitters in organic light-emitting diodes (OLED). Among luminescent metal complexes, Schiff's base zinc complexes become popular due to their excellent fluorescent properties depending upon only the ligand caused by filled d-shell of  $Zn^{2+}$  ion. This peculiarity of zinc complexes opens possibility to create the new materials with desired functions by means of bringing different substituent to the frame of organic ligands. So far as unique chemical and physical properties of coordination compounds often are associated with the molecular structure it could be interestingly to examine influ-

ence of different Schiff base ligands on overall structure of the zinc complexes with the aim of development of stereochemical theories of coordination chemistry.

One of the trends of industry showing significant interest to these compounds is the chemical vapor deposition (MO CVD) technology. Particularly in CVD processes a new type of the sufficiently volatile heteronuclear compounds made from lanthanide chelate complexes and 3d metal complexes with Schiff bases are mainly used as molecular precursors for the production of films for various purposes [8–10]. Therefore, investigation of the structure and properties of these compounds in the gas-phase is very important for understanding various types of the chemical processes in MO CVD technologies.

The basic structural features and properties of metal bis-chelate complexes were summarized in review [11]. By now only the structure of several molecules among a great variety of Schiff base metal complexes have been determined by gas-phase electron diffraction. According to the references [12,13] the molecules *N,N'*-ethylene-bis(acetylacetonaminato)zinc(II), (Zn(acacen)) and *N,N'*-ethylene-bis(salicylideneaminato) zinc(II), (Zn(salen)) belong to  $C_2$ -symmetry, the coordination fragment  $ZnN_2O_2$  possesses the structure in between planar and tetrahedral with dihedral angle between  $OZnN$  planes belonging to different moieties metalocycles  $43^\circ$  and  $35^\circ$ , respectively. The authors [14] supposed that in case the metal ion  $M^{2+}$  possesses a spherical d-shell ( $d^0$ ,  $d^{10}$  and probably  $d^5$ ) the chelate ligands are perpendicular to each other

\* Corresponding author. Tel.: +7 4932 359874; fax: +7 4932 417995.

E-mail addresses: [girichev@isuct.ru](mailto:girichev@isuct.ru), [g.v.girichev@mail.ru](mailto:g.v.girichev@mail.ru) (G.V. Girichev), [tverdova@isuct.ru](mailto:tverdova@isuct.ru) (N.V. Tverdova), [kuzmina@inorg.chem.msu.ru](mailto:kuzmina@inorg.chem.msu.ru) (N.P. Kuzmina), [kotova@inorg.chem.msu.ru](mailto:kotova@inorg.chem.msu.ru) (O.V. Kotova).

<sup>1</sup> Tel.: +7 4932 373703.

<sup>2</sup> Tel.: +7 4932 359874; fax: +7 4932 417995.

<sup>3</sup> Tel.: +7 495 9393836.

due to electrostatic repulsion between the charge on atoms which belong to the different ligands (for example, the zinc bis-acetylacetonate  $\text{Zn}(\text{acac})_2$  has  $D_{2d}$ -symmetry [15,16]). The reason of observing distortion of a pseudo-tetrahedral structure towards a planar one in aforementioned zinc complexes is ethylene “bridge” connecting both moieties chelate fragments of ligand. According to Refs. [16–21] the structures of some copper and nickel bis-chelate complexes in gas-phases are square planar.

According to Ref. [22] this compound exists in two crystal modifications of different color (orange and yellow). In both crystalline modifications  $\text{Zn}(\text{saloph})$  is a dimer. The dimeric unit can be described as a distorted pentacoordinate square-pyramidal geometry formed around ion Zn by two atoms N and two atoms  $\text{O}_t$  of the saloph ligand as the basal plane and one bridging  $\text{O}_b$  atom of the adjacent ligand as the apical atom. The dimeric unit contains three different distances Zn–O, the shortest of these was found for the unbridged oxygen (Zn– $\text{O}_t$ ). The crystal structure of  $\text{Zn}(\text{salen})$  [23], like  $\text{Zn}(\text{saloph})$  complex, shows the dimeric complex with five-coordinated environment of zinc ion. More space-saving crystal packing is observed for the yellow phase of  $\text{Zn}(\text{saloph})$  whose unit cell contains eight dimeric molecules. The unit cell of orange species of  $\text{Zn}(\text{saloph})$  consists of four dimeric molecules only.

Recent X-ray investigation of  $\text{Zn}(\text{saloph})$  [24] states that the crystal consists of discrete molecules. The  $\text{Zn}^{2+}$  ion is four-coordinated by two N atoms and two O atoms of the ligand in a square-planar geometry.

This work is a part of study of Schiff base metal complexes and is devoted to deriving the molecular structure of *N,N*-*o*-phenylenebis(salicylideneaminato)zinc(II),  $\text{Zn}(\text{saloph})$  and to comparison of coordination center in some zinc compounds with organic ligands.

## 2. Computational methods

The molecule of  $\text{Zn}(\text{saloph})$  (see Fig. 1) was studied by DFT computations utilizing B3LYP hybrid method. The core electron shell (1s2s2p) of the zinc atom was described by the relativistic effective core potential (ECP) [25]. For the description of the zinc valence shell the (8s7p6d2f1g/6s5p3d2f1g) basis set [26] has been used. All other atoms were described by triple- $\zeta$  valence basis sets:

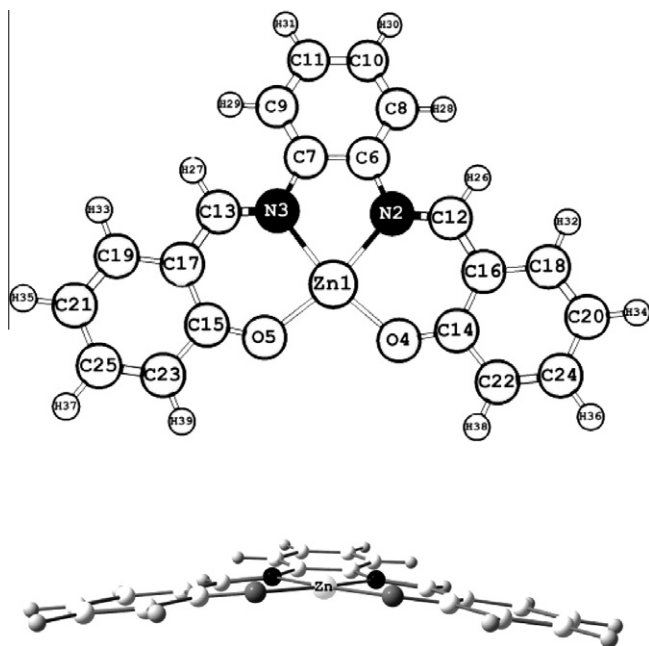


Fig. 1. The structure of molecule  $\text{Zn}(\text{saloph})$  with atomic numbering ( $C_s$ -symmetry).

(11s6p/5s3p) in case of C, N, O and (5s/3s) in case of H [27] (designated as TZV) with the addition of d-polarization functions:  $\zeta_d = 1.28(\text{O})$ ,  $\zeta_d = 0.98(\text{N})$ ,  $\zeta_d = 0.72(\text{C})$  [28],  $\zeta_d = 1.0(\text{H})$  [29]; in case of N, O, with the addition of p-diffuse functions:  $\zeta_p = 0.048(\text{N})$ ,  $\zeta_p = 0.059(\text{O})$  [30]. As a check of the quality of our calculations we optimized the  $\text{Zn}(\text{saloph})$  complex with a larger basis set (designated as cc-pVTZ) for atoms (C, O, N (22s7p2d1f/4s3p2d1f), H (7s2p1d/3s2p1d)) [31]. The ECP and basis set were obtained from the Extensible Computational Chemistry Environment Basis set Data base [32]. All DFT calculations on  $\text{Zn}(\text{saloph})$  were carried out using PC GAMESS 7.0 version [33] of GAMESS software package, running under Linux operating system.

Molecular structure of  $\text{Zn}(\text{saloph})$  was optimized and the force fields were calculated under  $C_{2v}$ -,  $C_2$ - and  $C_s$ -symmetry. The force field of  $C_s$ -model (B3LYP/Stuttgart ECP(Zn),TZV (O, N, C, H) with the addition of d-polarization functions; in case of N, O with the addition of p-diffuse functions) was transferred to the Shrink program [34] for calculation of vibrational corrections to the internuclear distances and the root-mean-square vibrational amplitudes at the temperature of the gas-phase electron diffraction experiment. Here the approach taking into account nonlinear effects (second approximation) have been used for calculating the set of corrections.

## 3. Experimental

The preparation of the  $\text{Zn}(\text{saloph})$  is described in Refs. [35,36]. The purity of compound was proved by elemental analysis for the metal, IR spectroscopy, and mass spectrometry.

The gas-phase electron diffraction patterns and the mass spectra were recorded simultaneously using the techniques described in Refs. [37,38]. The conditions of the GED/MS experiment are shown in Table 1.

The optical densities of exposed films (Kodak SO-163) were recorded for two nozzle-to-plate distances:  $L_1 = 598$  mm and  $L_2 = 338$  mm. Six electron diffraction patterns of the substance and two electron diffraction patterns of the  $\text{ZnO}$  crystal standard were obtained for each camera distance. The patterns of  $\text{ZnO}$  were recorded before and after the electron diffraction measurements for the substance to control the stability of the electron wavelength.

The gas-phase electron diffraction patterns were scanned on a computer controlled microphotometer [39] with a step of 0.1 mm along the diagonal of the plate. A  $10 \times 130$  mm<sup>2</sup> area was scanned; the number of equidistant scan lines was 33. The total intensity curves were obtained in the ranges  $s = 1.4$ – $15.9 \text{ \AA}^{-1}$  and  $s = 2.4$ – $27.0 \text{ \AA}^{-1}$ . The experimental and theoretical intensities  $sM(s)$  as well as the radial distribution curves  $f(r)$  are compared in Figs. 2 and 3, respectively.

## 4. Structural analysis

Preliminary the mass spectra of vapors were recorded over a wide temperature range in order to find the optimal conditions

Table 1

The conditions of combined gas-phase electron diffraction and mass spectrometric experiment.

Nozzle-to-plate distance (mm)	338	598
Electron beam current ( $\mu\text{A}$ )	1.64	0.84
Temperature of the effusion cell (K)	628(5)	623(5)
Accelerating voltage (kV)	77	81
Ionization voltage in mass spectrometer (V)	50	50
Residual gas pressure (torr)	$3 \times 10^{-6}$	$3 \times 10^{-6}$
Exposition time (s)	140	70

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