

# Synthesis, spectral studies and X-ray crystal structure of *N,N'*-(±)-*trans*-1,2-cyclohexylenebis(3-ethoxysalicylideneamine) H<sub>2</sub>(*t*-3-EtOsalchxn)

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## Abstract

The synthesis, spectra and X-ray crystal structure of *N,N'*-(±)-*trans*-1,2-cyclohexylenebis(3-ethoxysalicylideneamine) H<sub>2</sub>(*t*-3-EtOsalchxn), a salen-type ligand, are reported. The Schiff base was characterized by elemental analysis, m.p., IR, electronic spectra, <sup>1</sup>H and <sup>13</sup>C NMR spectra. The spectra are discussed and compared with those of *N,N'*-(±)-*trans*-1,2-cyclohexylenebis(salicylideneamine), H<sub>2</sub>(*t*-salchxn). The electronic and IR spectra were also resolved by deconvolution. The influence of the ethoxy group on the IR, electronic spectrum, <sup>1</sup>H and <sup>13</sup>C NMR spectra is discussed. Strong intramolecular forces are present as supported by the IR and <sup>1</sup>H NMR spectra and the X-ray crystal structure. An intermolecular hydrogen bond is observed and appears twice in a pair of molecules in the unit cell. © 2007 Elsevier B.V. All rights reserved.

**Keywords:** Intermolecular; Intramolecular; Hydrogen bonding; Schiff base; *t*-3-EtOsalchxn; Deconvolution

## 1. Introduction

Schiff bases are compounds containing the azomethine group,  $-\text{R,R}'\text{C}=\text{N}$ , prepared by the condensation reaction of a primary amine with active carbonyl group. Due to the versatility of their steric and electronic properties, which can be fine tuned by choosing the appropriate amine and the substituents on an aromatic ring of the carbonyl compound, transition metal complexes with Schiff base ligands have been widely studied [1–8]. Although many structures of transition metal complexes with Schiff base ligands have been determined, a relatively small number of free Schiff bases have been structurally characterized [9–14]. A

large number of Schiff base ligands, pertaining to the salicylidene family have been prepared. Due to the various synthetic procedures, numerous Schiff bases of various structure types have been synthesized. Probably the best known Schiff base ligand is *N,N'*-ethylenebis(salicylideneiminato) or H<sub>2</sub>salen, which is a bifunctional and tetradentate (ONNO) ligand. The more general term salen-type ligand is used in the literature to describe the class of [O, N, N, O] bis-Schiff base ligands. Generally, the salicylidene ligands are prepared in situ, rather than being isolated in the solid state, and then reacted with the metal ion to yield the desired complex. As a result, most of the crystallographic data reported for H<sub>2</sub>salen and salen-type are those of metal complexes rather than the free ligands themselves [14]. Knowing the structures of free Schiff

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base ligands could be important in view of comparison with the structure of Schiff base complexes.

Schiff bases are very useful in analytical chemistry as a selective chelating titrant for copper(II) [15], as a extraction reagent for the spectrophotometric determination of copper(II) [16], as a chromogenic reagent for determination of nickel in some natural food samples [17], in the spectrophotometric microdetermination of cobalt(II) [18], for ion-pair extraction of divalent metal cations [19] and as a complexing agent for on-line sorbent extraction/preconcentration and flow injection–flame atomic absorption spectrometry [20]. Another application of Schiff bases is the formation of films and/or polymers [21,22]. The films are utilized to protect copper against corrosion [23,24]. Schiff bases have been studied for their applications in non-linear optics [25,26]. An interesting Schiff base, *N,N'*-ethylenebis(pyridoxylideneiminato), derived from the condensation of pyridoxal, a Vitamin B<sub>6</sub> complex derivative, with ethylenediamine [27,28], has been studied as a useful model for assimilation of uranium by living beings [28].

Schiff bases have interesting photo-physical properties as thermochromism and photochromism providing potential applications as organic materials for reversible optical data storage. Since these photo-physical properties are governed by intramolecular proton transfer from the hydroxyl O atom to the imine N atom, several studies have focused on the nature of the hydrogen bonding in such material [14].

Tautomerism in Schiff bases with OH group in ortho position to the imino group both in solution and in solid state were investigated using spectroscopy and X-ray crystallography techniques [29]. Schiff bases with OH group in ortho position to the imino group are of interest mainly due to the existence of either O—H...N or O...H—N type of hydrogen bond and tautomerism between enol-imine and keto-amine form, Fig. 1. The Schiff bases derived from salicylaldehyde generally form the O—H...N type of hydrogen bonding, regardless of the nature of the *N*-substituent [30–34]. Compounds derived from 2-hydroxy-1-naphthaldehyde, both types of hydrogen bonds were found [35–37].

In these compounds, short hydrogen bonds between the OH group in *ortho* position to the imino group and the imine nitrogen are due to the stereochemistry. Whereas strong intramolecular hydrogen bonding is reported to

exist within the crystalline lattice of H<sub>2</sub>salen, governing a number of its properties [32], no crystallographic data have been reported thus far for H<sub>2</sub>(*t*-3-EtOsalchxn), C<sub>24</sub>H<sub>30</sub>N<sub>2</sub>O<sub>4</sub>.

In this paper, we investigate the structure of the title compound in order to reveal the presence of either the enol-imine or keto-amine forms related with hydrogen bonding by using NMR, UV–visible, IR and X-ray crystallographic techniques in the solution and solid states. For a better understanding of the spectra and the influence of the ethoxy group of the title compound, the NMR, UV–visible, IR spectra of *N,N'*-(±)-*trans*-1,2-cyclohexylenebis(salicylideneamine), H<sub>2</sub>(*t*-salchxn) are also studied. The electronic and IR spectra were also resolved by deconvolution.

## 2. Experimental section

### 2.1. Reagents and techniques

Methyl sulfoxide-*d*<sub>6</sub>, 99.9 atom% D, DMSO-*d*<sub>6</sub>; 3-ethoxysalicylaldehyde 97%, (±)-*trans*-1,2-diaminocyclohexane 99%, were purchased from Aldrich and were used as received. All other solvents and reagents were obtained commercially and were used without further purification. Analyses were made by Microanalytical laboratory of the Universidade Federal de São Carlos, São Carlos, São Paulo, Brazil. Carbon, nitrogen and hydrogen analysis were performed on an AE-1108 CNHS-O Fisons apparatus. Melting point was measured on the Meltemp II Laboratory Devices apparatus using a capillary tube. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of the compounds in CDCl<sub>3</sub> with tetramethylsilane, TMS, as an internal standard, were obtained using a Bruker ARX 400 MHz 9.4 T spectrometer. NMR spectra using the 2D-NMR techniques, HMBC and HSQC, were obtained in CDCl<sub>3</sub>.

IR spectra of the compound were recorded on a Bomem Michelson 102 FT IR spectrophotometer in KBr discs (1% by weight in KBr) and were recorded in the 250–4000 cm<sup>-1</sup>. The UV–visible spectra were measured using a Shimadzu UV-1650PC spectrometer. The electronic spectra of the acetonitrile solutions were obtained using 1.000 cm quartz cells, at room temperature, 23 ± 1 °C. The electronic spectra and IR spectra were resolved by deconvolution using the Voigt function, amplitude, Gaussian/

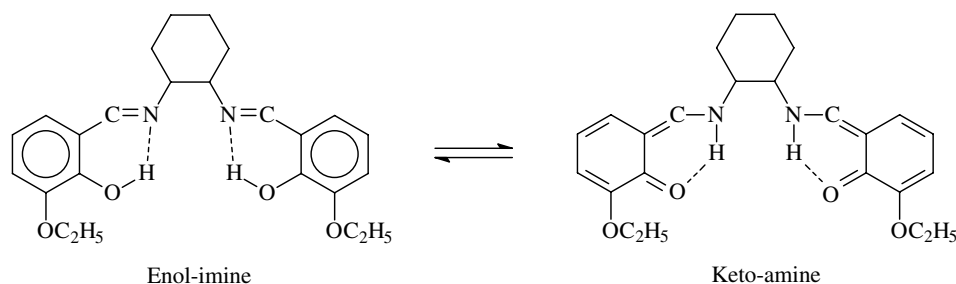


Fig. 1. Tautomerism between enol-imine and keto-amine form for H<sub>2</sub>(*t*-3-EtOsalchxn).

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