

Short Note

# *N,N'*-Bis(3-ethoxy-2-hydroxybenzylidene)-phenylene-1,3-diamine Methanol Solvate

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**Abstract:** A crystal structure and thermal characterization of a multisite Schiff base containing N<sub>2</sub>O<sub>2</sub>-inner and O<sub>4</sub>-outer coordination sites are reported. The title compound was characterized by X-ray structure analysis, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR and ATR-FTIR spectroscopy, TG/DSC and TG-FTIR techniques. The compound crystallizes as a methanol solvate in the triclinic system, space group *P* $\bar{1}$ . The stable at room temperature compound, during heating in the air, first loses a methanol molecule. At higher temperature, the sample decomposition is associated with a strong exothermic effect and the emission of large amounts of carbon dioxide, carbon monoxide and ammonia.

**Keywords:** multisite Schiff base; thermal stability; N<sub>2</sub>O<sub>4</sub> compartmental ligand; salen ligand

## 1. Introduction

Schiff bases are extensively studied, mainly due to their coordination abilities and diverse biological activities. In the case of salen-type Schiff bases, the nature and amount of substituents (Br, Cl, NO<sub>2</sub>, OCH<sub>3</sub>, and OC<sub>2</sub>H<sub>5</sub>) in the phenyl ring of the salicylaldehyde and the kind of diamines used (e.g., length of the aliphatic chain), influence the crystal structure and physicochemical properties of compounds. The electron-withdrawing group, e.g., NO<sub>2</sub>, makes the OH group of the salicylaldehyde more acidic, whereas the strong electron-donating group, e.g., OCH<sub>3</sub>, induces the opposite effect. Due to the possibility of using various functional groups, it is possible to create polidentate ligands with specific complex-forming properties. Nitrogen and oxygen atoms play a key role in it because they can coordinate different amounts and kinds of metal ions. Among them there are, e.g., 6,6'-dimethoxy-2,2'-[*m*-phenylene-bis(nitrilomethylidene)]diphenol [1], *N,N'*-bis(3-ethoxy-2-hydroxybenzylidene)-phenylene-1,3-diamine [2], and 6,6'-diethoxy-2,2'-[4,5-dimethyl-*o*-phenylene-bis(nitrilomethylidene)]-diphenol-ethanol-water [3]. They differ in the type of diamine used for their synthesis and the methoxy or ethoxy group substituent in the aromatic ring. These compounds are used in the synthesis of macrocyclic compounds having metal chelating sites as well as a guest binding site. They are useful for building cooperative functional host–guest systems [4–7]. One of the biggest advantages of them is that metalation of the salen moieties changes the phenol oxygen atoms into negatively charged phenoxo groups, with better coordination ability to another metal ion. Thermal analysis allows us to determine/assess the presence of solvent molecules (e.g., water, methanol) in the structure of compounds and to determine endothermic and/or exothermic effects related to desolvation, melting or decomposition processes.

As a continuation of the studies on salen-type Schiff bases, the hexadentate ligand (being capable of coordinating the metal ions through the donor nitrogen and oxygen atoms) was synthesized, and its structure and properties were investigated.



**Citation:** Osypiuk, D.; Bartyzel, A.; Cristóvão, B. *N,N'*-Bis(3-ethoxy-2-hydroxybenzylidene)-phenylene-1,3-diamine Methanol Solvate. *Molbank* **2023**, *2023*, M1688. <https://doi.org/10.3390/M1688>

Academic Editor: René T. Boéré

Received: 4 June 2023

Revised: 29 June 2023

Accepted: 3 July 2023

Published: 5 July 2023



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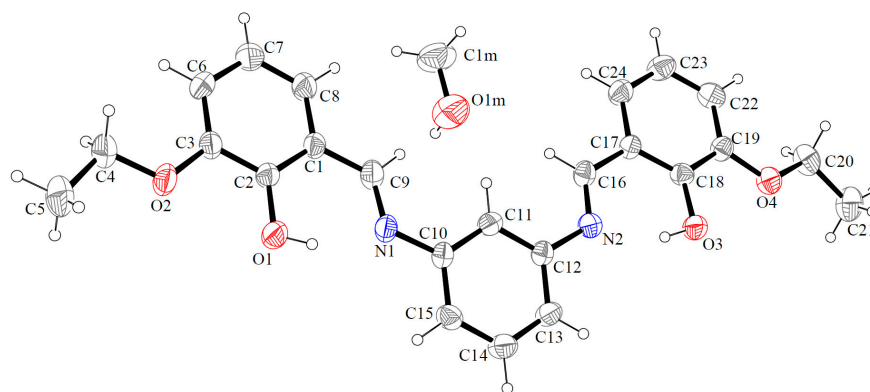
## 2. Results and Discussion

The methods of synthesis, the ratio of the used reagents, the pH of the solution, and the type of solvent significantly affect the structure of synthesized compounds. Two polymorphs can be differentiated by their morphology, which is very important, e.g., in drug design. The polymorphic compounds differ in their physicochemical properties, such as color, stability, solubility, crystal form, etc., which may be assigned to the different crystal packing arrangements. The different properties of the polymorphic compounds influence their potential applications [8–11]. The title compound,  $C_{24}H_{24}N_2O_4 \cdot MeOH$  ( $H_2Lphen$ ), is a methanol solvate that crystallizes in the triclinic space group  $P\bar{1}$ , whereas the earlier-reported analogous Schiff base synthesized by Ha (the solvent-free compound) crystallizes in another space group, orthorhombic  $P2_12_12_1$  [2]. The compound reported by Ha [2] was prepared in ethanol and recrystallized from a mixture of acetone, ether, and pentane at  $-85^\circ C$ . As a result, an orange-red solid was obtained. Crystals suitable for X-ray diffraction analysis were obtained from a toluene solution. In our synthesis, single-crystal growth at room temperature in a methanol solution led to the formation of light brown crystals, which is in agreement with Desiraju's claim that polymorphisms can be strongly solvent-dependent [11].

$H_2Lphen$  with two imino nitrogen atoms, two phenolic oxygen atoms, and two oxygen atoms of the ethoxyl group is an example of a polydentate ligand that can be potentially used for the synthesis of multinuclear complexes of interesting structures and physicochemical (luminescent, catalytic, magnetic, etc.) and biological properties.

### 2.1. Crystal and Molecular Structure

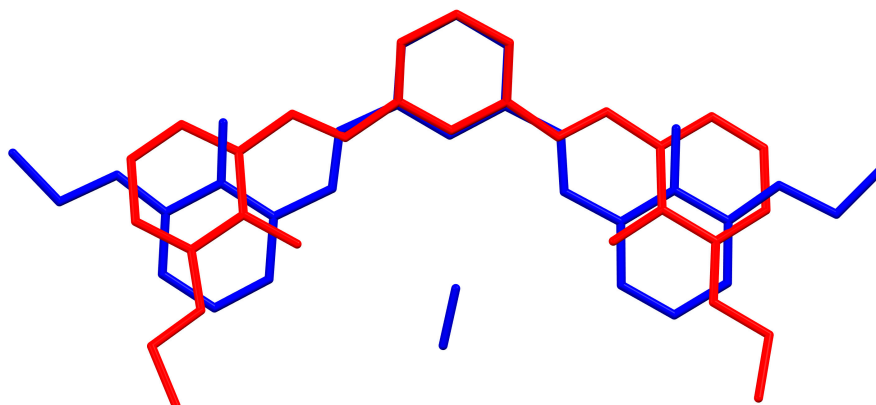
Crystallographic data of the Schiff base  $H_2Lphen$  are collected in Tables S1–S3 of the Supplementary Materials. The crystal structure, with the atomic numbering scheme, is shown in Figure 1. In the crystal structure of the compound, the N1–C9 and N2–C16 distances of 1.281(4) and 1.279(4) Å, respectively, are almost the same and match with the C=N double bond, indicating that the imino N atoms (N1, N2) are  $sp^2$ -hybridized.



**Figure 1.** Molecular structure with atom numbering scheme of the hexadentate Schiff base.

Three benzene rings are roughly parallel: the dihedral angles between the mean planes formed by central benzene ring C10/C11/C12/C13/C14/C15 and the lateral benzene rings C1/C2/C3/C6/C7/C8 and C17/C18/C19/C22/C23/C24, are  $8.4(2)^\circ$  and  $10.3(2)^\circ$ , respectively. The dihedral angle between the lateral benzene rings is  $4.7(2)^\circ$ . Whereas in the polymorphic crystal structure reported by Ha [2], the values of the dihedral angles between respective benzene rings (central and lateral) are greater and equal to  $28.0(1)^\circ$  and  $31.4(1)^\circ$ . This means that the structure of the solvent-free compound is not planar and the dihedral angle between the mean planes of the lateral benzene rings is equal to  $12.2(1)^\circ$  [2]. Moreover, in the present compound, rotation of the hydroxyethoxyphenyl units relative to the nitrogen atoms is observed compared to the previously described structure (Figure 2). The ethoxy substituents are also situated nearly parallel to their respective carrier benzene rings. Intramolecular hydrogen bonds  $O-H \cdots N$  exist between the imine nitrogen atoms

N1 and N2 and the neighbouring phenolic oxygen atoms O1 and O3, respectively, with  $d(\text{O}\cdots\text{N}) = 2.607(4)$  and  $2.611(5)$  Å, respectively and form six-membered rings S(6).

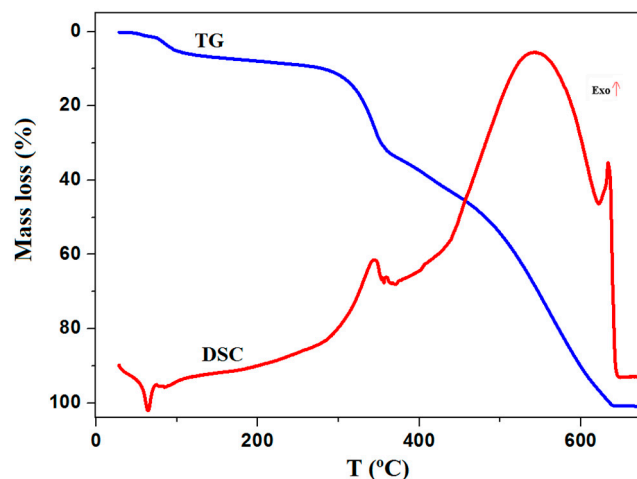


**Figure 2.** Comparison of the structures of the solvate (blue) and the solvent-free compound (red). Hydrogen atoms have been omitted for clarity.

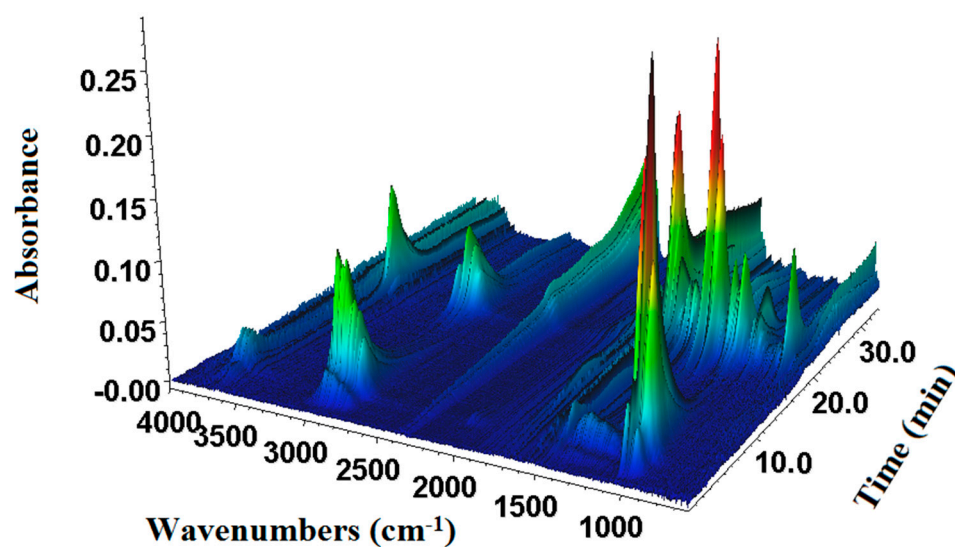
The observed C–O<sub>phenolic</sub> bond distances C2–O1 and C18–O3 1.351(4) and 1.357(4) Å, respectively, are consistent with the C–O single bonds, as well as the external C–OR bond distances: C3–O2 1.377(4) and C19–O4 1.376(4) Å. The methanol molecule is bound to the Schiff base by the hydrogen bond O1m–H1m $\cdots$ O2. In addition, the CH<sub>3</sub>OH molecule is involved in weak C16–H16 $\cdots$ O1m bonds as an acceptor, which leads to the formation of supramolecular dimeric units, as shown in Figure S1 (Supplementary information).

## 2.2. Thermal Properties

As shown in Figure 3, the title compound is stable up to  $\sim 55$  °C. As the temperature increases, the mass of the sample decreases slowly up to  $\sim 110$  °C. The first mass loss equal to 6.8% corresponds to the release of one methanol molecule (mass loss calculated at 7.3%). The desolvation process is accompanied by the small endothermic effect (with the maximum at  $\sim 64$  °C) seen on the DSC curves. The value of enthalpy is equal to 22.88 kJ/mol. In addition, the desolvation process is also confirmed via TG-FTIR analysis (Figures 4 and S2).



**Figure 3.** TG and DSC curves of thermal decomposition of the Schiff base in air.



**Figure 4.** FTIR spectra of gaseous products evolved during the decomposition of the title Schiff base.

In the FTIR spectrum of the gaseous product of the sample decomposition, the characteristic vibration bands associated with the presence of methanol molecules are observed at  $3368\text{ cm}^{-1}$ ,  $1307\text{ cm}^{-1}$  and  $1095\text{ cm}^{-1}$ , respectively. The solvent-free compound is stable up to  $\sim 260\text{ }^{\circ}\text{C}$ . After exceeding this temperature, the mass sample decreases, which points to a gradual decomposition process accompanied by an exothermic effect visible in the DSC curves. The composition of the intermediate solid decomposition products of the heated sample could not be determined. At higher temperature, carbon dioxide and carbon monoxide are mainly emitted. The bands characteristic of ammonia are also seen. The characteristic doublet bands at  $2240\text{--}2400\text{ cm}^{-1}$  and  $669\text{ cm}^{-1}$ , respectively, assigned to stretching and deformation vibrations of carbon dioxide molecules, are seen in the TG-FTIR spectrum (Figure 4), whereas the presence of carbon monoxide is confirmed by the specific bands at  $2060\text{--}2240\text{ cm}^{-1}$ . The bands at  $1800\text{--}1400\text{ cm}^{-1}$  and  $1200\text{--}800\text{ cm}^{-1}$  are characteristic of ammonia.

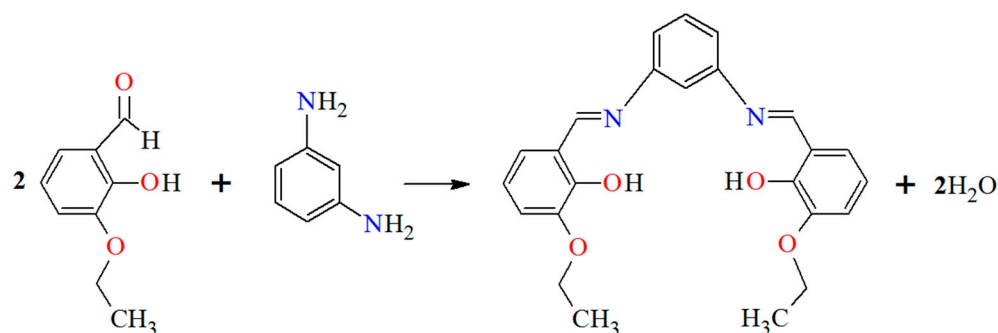
### 3. Materials and Methods

The reagent-grade chemicals, i.e., 2-hydroxy-3-ethoxybenzaldehyde, *m*-phenylenediamine and methanol, were purchased from commercial sources and used as received without further purification.

The contents of C, H and N were established on a CHN/CHNS EuroEA3000 analyser (EuroVector, Pavia, Italy). Nicolet 6700 spectrophotometer, accurate with the Smart iTR attachment (diamond crystal), was employed to record the ATR-FTIR spectrum over  $4000\text{--}525\text{ cm}^{-1}$  (Figure S3, Supplementary materials). NMR spectra were recorded with a Bruker Ascend ( $500/126\text{ MHz }^1\text{H}/^{13}\text{C}$ ) spectrometer at room temperature using  $\text{CDCl}_3$  as a solvent. Chemical shifts ( $\delta$ ) are reported in ppm, and spectra were calibrated using residual solvent peaks. Thermal analysis was carried out by the thermogravimetric (TG) and differential scanning calorimetry (DSC) methods using the SETSYS 16/18 analyser (Setaram, Cranbury, NJ, USA). The experiments were carried out under air flow in the temperature range of  $30\text{--}700\text{ }^{\circ}\text{C}$  at a heating rate of  $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ . The sample  $7.58\text{ mg}$  was heated in  $\text{Al}_2\text{O}_3$  crucibles. The TG-FTIR analysis was carried out using the TGA Q5000 analyser TA Instruments, New Castle, Delaware, USA, interfaced to the Nicolet 6700 FTIR spectrophotometer (Thermo Scientific, Waltham, MA, USA). The sample was put in an open platinum crucible and heated from ambient temperature to  $700\text{ }^{\circ}\text{C}$ . The analysis was carried out at a heating rate of  $20\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ . Gas analysis was performed by matching the spectra against those from the spectrum library Nicolet TGA Vapor Phase of the software Omnic together with the literature sources [12].

### 3.1. Synthesis

The Schiff base was obtained by refluxing a mixture of *m*-phenylenediamine (0.54 g, 5.00 mmol) and 2-hydroxy-3-ethoxybenzaldehyde (1.66 g, 10.00 mmol) in methanol (50 mL) for 1 h (Scheme 1). After cooling to room temperature, the brown crystalline product precipitated out, and the product was washed with cold methanol. Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of the filtrated solution. The  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$  spectra fully agree with the proposed structure (Figures S4 and S5, Supplementary materials). Yield 78%. Anal. (%) for  $\text{C}_{25}\text{H}_{28}\text{N}_2\text{O}_5$  (MW: 436.49). Calcd: C 68.73; H, 6.41; N, 6.41. Found: C, 68.60; H, 6.20; N, 6.10. ATR-FTIR ( $\text{cm}^{-1}$ ):  $\nu(\text{O-H})$  3535 w,  $\nu(\text{N-H})$  3058 w,  $\nu(\text{CH}_3)_{\text{as}}$  2977 w,  $\nu(\text{C=N})$  1612 vs,  $\nu(\text{C=C})$  1571 vs,  $\nu(\text{C=C})$  1457 vs,  $\nu(\text{C-H})$  1392 m,  $\sigma(\text{O-H})$  1370 m,  $\nu(\text{C-O})$  1244 vs,  $\nu(\text{C-C})$  1114 m,  $\sigma(\text{C-H})$  1078 m,  $\rho(\text{C-H})$  1013 m,  $\gamma(\text{O-H})$  832 m,  $\gamma(\text{C-H})$  733 vs.  $^1\text{H NMR}$  ( $\delta$ , ppm,  $\text{CDCl}_3$ ): 1.53 (t, 6H,  $-\text{CH}_3$ ), 3.51 (s, 3H,  $-\text{CH}_3(\text{methanol})$ ), 4.17–4.19 (q, 4H,  $-\text{CH}_2$ ), 6.89–6.92 (t, 2H, ArH), 7.02–7.07 (m, 4H, ArH), 7.21–7.23 (ddd, 2H, ArH), 7.29 (s, 1H, ArH), 7.47–7.50 (t, 1H, ArH), 8.70 (s, 2H,  $-\text{CH}$ ), 13.50 (s, 2H,  $-\text{OH}$ );  $^{13}\text{C NMR}$  ( $\delta$ , ppm,  $\text{CDCl}_3$ ): 14.91 ( $-\text{CH}_3$ ), 64.70 ( $-\text{CH}_2$ ), 113.56–130.38 ( $\text{C}_{\text{ar}}$ ), 147.75 ( $\text{C}_{\text{ar-N}}$ ), 149.45 ( $\text{C}_{\text{ar-OH}}$ ), 151.72 (C-OR), 163.35 (C=N).



**Scheme 1.** Scheme of *N,N'*-bis(3-ethoxy-2-hydroxybenzylidene)-phenylene-1,3-diamine synthesis.

### 3.2. X-ray Crystal Structure Determination

Measurement of single-crystal (collection, cell refinement and data reduction) was made on an Oxford Diffraction Xcalibur CCD diffractometer (MoK $\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$ ) using the CrysAlis program [13]. A multiscan absorption correction was applied. Crystal data, data collection and structure refinement details are reported in Table S1. The structure was solved by the direct method using the SHELXS-2018 and refined by the full-matrix least-squares on  $F^2$  using the SHELXL-2018 [14] (both programs are part of WinGX software [15]). All the non-hydrogen atoms were refined with anisotropic displacement parameters. The H-atoms attached to carbon were positioned geometrically and refined by applying the riding model. The O-bound H atoms were located on a difference Fourier map and refined freely or with O–H distances restrained to 0.82  $\text{\AA}$  using the DFIX command. Next, when hydroxyl hydrogen atoms with appropriate positions were determined, the DFIX commands were removed, and the hydrogen atoms were refined again using the AFIX 1 command with an appointed temperature factor data of  $-1.5000$ . The molecular graphics were prepared using the following programs: ORTEP3 [15] and Mercury [16]. The geometrical calculations were performed using the PLATON program [17].

## 4. Conclusions

The consistent results of X-ray, thermal and spectral analysis show that the title salen type Schiff base crystallized with one methanol molecule. The molecular structure of the compound is stabilized by intra- and intermolecular hydrogen bonds. Due to the large number of donor atoms, the title compound seems to be a good candidate for obtaining multinuclear complexes.

**Supplementary Materials:** Table S1: Crystal data and structure refinement for H<sub>2</sub>Lphen; Table S2: Selected geometric parameters for H<sub>2</sub>Lphen; Table S3: Hydrogen-bond geometry [ $\text{\AA}$ ,  $^\circ$ ] for H<sub>2</sub>Lphen; Figure S1: Hydrogen bonds viewed along the a-axis; Figure S2: Comparison of FTIR spectra of gaseous products of the Schiff base, decomposition in nitrogen and FTIR spectra of gaseous methanol; Figure S3: FTIR spectrum of H<sub>2</sub>Lphen; Figure S4: <sup>1</sup>H-NMR spectrum of H<sub>2</sub>Lphen; Figure S5: <sup>13</sup>C-NMR spectrum of H<sub>2</sub>Lphen.

**Author Contributions:** D.O.: Conceptualization, Methodology, Writing—original draft—Formal analysis, Investigation. A.B.: Conceptualization, Resources, Methodology, Writing—original draft—review and editing, Formal analysis, Investigation. B.C.: Conceptualization, Methodology, Investigation, Supervision, Writing—original draft—review and editing. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research received no external funding.

**Data Availability Statement:** The CIF files have been deposited in the Cambridge Crystallographic Data Center (CCDC). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif) (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

**Conflicts of Interest:** The author declares no conflict of interest.

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