



### مطالعه ی ساختار کریستالی لیگاند باز شیف دو تایی جدید شامل اتم های دهنده ی سخت

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#### چکیده فارسی

باز شیف دوتایی جدید شامل ۲-آمینو تیو فنل های سولفید غیر دهنده از واکنش ۵-متیل سالیسیل آلدهید با ۲-آمینوتیوفنل در محلول متانول با نسبت استوکیومتری ۱:۱ طراحی و سنتز شده است. لیگاند باز شیف به وسیله طیف سنجی های FT-IR، <sup>1</sup>H NMR، UV/Vis، آنالیز عنصری و هدایت شناسایی شده است. ساختار کریستالی لیگاند باز شیف به وسیله ی پراش پرتو X تک بلور تعیین شده است. لیگاند باز شیف در ساختار تری کلینیک متبلور می شود و دارای گروه فضایی *P-1* بوده و پارامترهای سلولی برای این لیگاند عبارتند از:  $a= 9.3158 (19)$ ,  $b= 11.937 (2)$ ,  $c= 12.794 (3)$  and  $V= 1230.3 (5) \text{ \AA}^3$ ,  $Z= 2$ ,  $F(000)= 508$  and  $\alpha= 78.02 (3) \text{ deg}$ ,  $\beta= 68.69 (3) \text{ deg}$ ,  $\gamma= 68.71 (3)$ .

واژه‌های کلیدی: باز شیف، سخت، سنتز، دهنده، ساختار کریستالی، ۲-آمینو تیو فنل

### Crystal Structure Studies of A New Double Schiff base Ligand Containing Hard Donor Atoms

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#### Abstract

A new double Schiff base ligand containing 2-aminothiophenol was designed and synthesized by the reaction of 5-methyl salicylic aldehyde with 2-aminothiophenol in 1:1 molar ratio in methanolic solution. The Schiff base ligand has been characterized by FT-IR, <sup>1</sup>H NMR, UV/Vis spectroscopies, elemental analysis and conductometry. The crystal structure of the Schiff base ligand has been determined by single crystal X-ray diffraction. This Schiff base ligand crystallizes in triclinic system with space group *P-1* and cell parameters containing:  $a= 9.3158 (19)$ ,  $b= 11.937 (2)$ ,  $c= 12.794 (3)$  and  $V= 1230.3 (5) \text{ \AA}^3$ ,  $Z= 2$ ,  $F(000)= 508$  and  $\alpha= 78.02 (3) \text{ deg}$ ,  $\beta= 68.69 (3) \text{ deg}$ ,  $\gamma= 68.71 (3)$ .

Keywords: Schiff base, Hard, Synthesis, Donor, Crystal structure, 2-aminothiophenol



### Introduction

Schiff bases are molecules that contain the azomethine group ( $-\text{CH}=\text{N}-$ ) in their structures which are generally synthesized by the condensation of primary amines and active carbonyl groups. They are one of the most important classes of ligands and have played an important role in the development of coordination chemistry as they readily form stable complexes with most transition metals (Sousa et al., 2003). Moreover, possessing particular biological activity gives them an important place in diverse fields of chemistry and biochemistry (Kaya et al., 2010). Tetradentate Schiff bases with a  $\text{N}_2\text{O}_2$  donor atom set are well known to coordinate with various metal ions. Transition metal complexes of Schiff bases are one of the most adaptable and thoroughly studied systems. These complexes have applications in clinical, analytical, industrial, catalysts and organic synthesis. The high stability potential of Schiff base complexes with different oxidation states extended the application of these compounds as excellent catalysts in organic redox and electrochemical reduction reactions (Canali et al., 1998).

### Results and discussion

In the crystalline form, double Schiff base ligand was formed and a disulfide compound obtained due to the chemical irreversibility of the oxidation of SH groups in two moles of Schiff base ligands and formation intermolecular disulfide S-S bonds after deprotonation (Shafaatian et al., 2015). The structure details of Schiff base ligand was determined by X-ray crystallography. The X-ray crystal structure of this ligand was shown in Fig. 1.

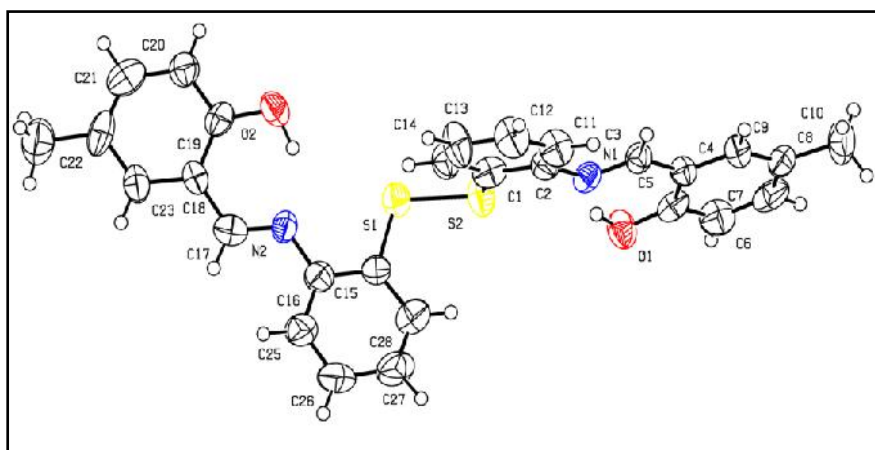


Fig. 1: X-ray structure of double Schiff base ligand

This Schiff base ligand crystallizes in triclinic system with space group  $P-1$  and cell parameters containing:  $a = 9.3158$  (19),  $b = 11.937$  (2),  $c = 12.794$  (3) and  $V = 1230.3$  (5)  $\text{Å}^3$ ,  $Z = 2$ ,  $F(000) = 508$  and  $\alpha = 78.02$  (3) deg,  $\beta = 68.69$  (3) deg,  $\gamma = 68.71$  (3). Details of crystal data, data collections, and structure refinement were summarized in Table 1.



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**Table 1:** Crystallographic and structure refinement data for Schiff base ligand.

Empirical formula	C <sub>28</sub> H <sub>24</sub> N <sub>2</sub> O <sub>2</sub> S <sub>2</sub>
Formula weight	484.61
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	triclinic
Space group	<i>P</i> -1
Crystal size (mm <sup>3</sup> )	0.37×0.22×0.21
<i>a</i> (Å)	9.3158(19)
<i>b</i> (Å)	11.937(2)
<i>c</i> (Å)	12.794(3)
$\alpha$ (°)	78.02(3)
$\beta$ (°)	68.69(3)
$\gamma$ (°)	68.71(3)
V [Å <sup>3</sup> ]	1230.3(5)
Z	2
Density <sub>calc</sub> (g cm <sup>-3</sup> )	1.308
Theta Min-Max [Deg]	2.6-26.4
F(000)	508
absorpt_coefficient_mu	0.245
Data collected	9290
Tot., Uniq. Data, R(int)	8485, 4694, 0.181
Parameters / restraints	247 / 0
Observed Data [I > 2.0 sigma(I)]	935
R, wR2, S <sup>a</sup>	0.0523, 0.1079, 0.62
_refine_ls_goodness_of_fit_ref	0.621
Min. and Max. Resd. Dens. [e/Å <sup>3</sup> ]	0.20, 0.16

$$^a w = 1/[\sigma^2(F_o^2) + (0.0000P)^2] \text{ where } P = (F_o^2 + 2F_c^2)/3$$

Selected bond lengths and angles for double Schiff base ligand were given in Tables 2 and 3. Structural parameters which have shown in these tables are in good agreement with previously reported for similar compounds (Shafaatian, B., et. al, 2014). For example the bond length of S-C, O-C, N-C and O-H in this Schiff base ligand lies in the range of 1.787 (8)-1.803 (8) Å, 1.355 (10)-1.363 (10) Å, 1.301 (10)-1.413 (9) Å and 0.8900-0.9600 Å, respectively.





**Table 2:** Selected bond distances (Å) for the Schiff base ligand.

S1 – S2	2.040 (3)	C17 – C18	1.447 (11)
S1 – C15	1.787 (8)	C18 – C19	1.403 (12)
S2 - C1	1.803 (8)	C18 – C23	1.417 (12)
O1 – C5	1.363 (10)	C19 – C20	1.377 (11)
O2 – C19	1.355 (10)	C20 – C21	1.388 (13)
N1 – C2	1.413(9)	C21 – C22	1.364 (15)
N1 – C3	1.301 (10)	C22 – C24	1.510(14)
O1 – H1	0.8900	C22 – C23	1.405 (12)
N2 – C17	1.278 (11)	C25 – C29	1.381 (13)
O2 – H13	0.9600	C26 – C27	1.430 (15)
N2 – C16	1.398 (10)	C27 – C28	1.370 (15)

## Experimental

### Synthesis of tetradentate Schiff base ligand

A solution of 2-hydroxy-5-methyl benzaldehyde (0.649 g, 5.18 mmol) in 7 mL of absolute ethanol at 60 °C was slowly added to a solution of 2-aminothiophenol (0.706 g, 5.18 mmol) in 7 mL of absolute ethanol at 60 °C and the mixture stirred for 8 hours in 80 °C under an inert atmosphere of argon. After removal of the solvent, the yellow precipitate was obtained and washed with n-hexane. Then, the product was dried in vacuo at room temperature. (yield: 72%), yellow, m.p: 175 °C, Anal. Calc. for [C<sub>28</sub>H<sub>24</sub>N<sub>2</sub>S<sub>2</sub>O<sub>2</sub>] (H<sub>2</sub>L): (M.W: 484.61), C, 69.13; H, 4.97; N, 5.76; S, 13.18%. Found: C, 68.94; H, 4.89; N, 6.06; S, 12.98%; IR (KBr,  $\nu$ /cm<sup>-1</sup>): 1613  $\nu$ (CN) (imine), 1156  $\nu$ (CO) (phenolic), 3436  $\nu$ (OH), 1441  $\nu$ (C=C) (aromatic), 753  $\nu$ (CS). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>): 12.66 (1H, s, –OH), 9.45 (1H, s, –OH) 8.62 (1H, s, CH=N), 7.00-7.71(phenylic hydrogen group), 2.37 (3H, s, –CH<sub>3</sub>).

### Crystal structure determination and refinement

Single-crystal X-ray diffraction data for double Schiff base ligand were collected at 293 K. The X-ray diffraction measurements were made on a Single Crystal X-Ray Diffractometer STOE IPDS-2T with graphite monochromated Mo-K $\alpha$  radiation. For the double Schiff base ligand, yellow needle shape crystal was chosen using a polarizing microscope and was mounted on a glass fiber which was used for data collection. Cell constants and orientation matrices for data collection were obtained by least-squares refinement of diffraction data from 4694 unique reflections. The structure was solved by direct methods using the SHELXS-97 program (Sheldrick, 1997) and refined by full-matrix least-squares techniques SHELXL-97 (Sheldrick, 1997) on F2. The subsequent difference Fourier maps were then refined on F2 by a full-matrix least squares procedure using anisotropic displacement parameters.



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The atomic factors were taken from the International Tables for X-ray Crystallography. All refinements were performed using the X-STEP32 crystallographic software package.

**Table 3:** Selected bond angles (deg) for the Schiff base ligand.

S2-S1-C15	104.8 (3)	C1-C14-C13	119.0 (7)
S1-S2-C1	104.3 (3)	S1-C15-C16	116.1 (6)
C2-N1-C3	121.3 (6)	C16-C15-C28	120.2 (8)
C5-O1-H1	109.00	S1-C15-C28	123.7 (7)
C16-N2-C17	124.6 (8)	N2-C16-C25	124.3 (8)
C19-O2-H13	106.00	N2-C16-C15	117.1 (8)
C2-C1-C14	120.9 (7)	C15-C16-C25	118.5 (7)
S2-C1-C14	123.9 (6)	N2-C17-C18	124.3 (8)
S2-C1-C2	115.2 (6)	C17-C18-C19	119.4 (8)

### Conclusion

A new double Schiff base ligand containing 2-aminothiophenol was synthesized and characterized by the spectroscopic techniques such as UV-Vis spectroscopy, FT-IR, <sup>1</sup>H NMR, elemental analysis, conductometry and X-ray crystallography. This ligand was coordinated to metal complexes through hard donor atoms such as oxygen and nitrogen. This Schiff base ligand crystallizes in triclinic system with space group *P-1*.

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