



بیست و سومین همایش بلورشناسی و کانی‌شناسی ایران



23rd Symposium of Crystallography & Mineralogy of Iran

۸ و ۷ بهمن ماه ۱۳۹۴ دانشگاه دامغان

مطالعه ی ساختار کریستالی لیگاند باز شیف چهار دندانه ی جدید با اتم های

N_2O_2 دهنده ی

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چکیده فارسی

لیگاند باز شیف جدید به وسیله ی واکنش تراکمی ۲-هیدروکسی-۱-نفتالدهید با ۲-آمینواتان تیول در محلول اتانول سنتز شده است. این محصول به وسیله طیف سنجی های FT-IR, 1H NMR, UV/Vis, آنالیز عنصری و هدایت شناسایی شد. علاوه بر این، ساختار کریستالی لیگاند باز شیف به وسیله ی پراش پرتو X تک بلور تعیین شده است. بر طبق ساختار کریستالی، لیگاند باز شیف شامل یک پیوند دی سولفیدی است. این لیگاند باز شیف در ساختار مونوکلینیک و با گروه فضایی $P2_1/c$ متبلور می شود و پارامترهای سلولی برای این لیگاند عبارتند از: $a = 20.970 (4)$, $b = 6.6964 (13)$, $c = 8.0557 (16)$ and $V = 1130.5 (4) \text{ \AA}^3$, $Z = 2$, $F(000) = 4$

واژه های کلیدی: باز شیف، چهار دندانه، سنتز، ساختار کریستالی

Crystal Structure Studies of A New Tetradentate Schiff Base Ligand with N_2O_2 Donor Atoms

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Abstract

The new Schiff base ligand was synthesized by the reaction condensation of 2-hydroxy-1-naphthaldehyde and 2-aminoethanethiole in an ethanolic solution. This product was characterized by FT-IR, UV/Vis, 1H NMR, fluorescence spectroscopy, elemental analysis and conductometry. Furthermore, the crystal structure of the Schiff base ligand was determined by single crystal X-ray diffraction. According to the crystal structure, the Schiff base ligand was contained disulfide bond. This Schiff base ligand crystallizes in monoclinic system with space group $P2_1/c$ and cell parameters containing: $a = 20.970 (4)$, $b = 6.6964 (13)$, $c = 8.0557 (16)$ and $V = 1130.5 (4) \text{ \AA}^3$, $Z = 2$, $F(000) = 4$.

Keywords: Schiff base, Tetradentate, Synthesis, Crystal structure



Introduction

Schiff base ligands have significant importance in chemistry, especially in the development of Schiff base complexes, because this ligands can form stable complexes with different metal ions (Johnson et al., 1996). Schiff base ligands act as good chelating agents for different metal ions. Coordination of such compounds with metal ions, often enhance their biological activities (Singh et al., 2009). Transition metal complexes with oxygen and nitrogen donor Schiff bases are of particular interest because of their ability to possess unusual configurations, be structurally labile and their sensitivity to molecular environments. Schiff base ligands have proven to be very effective in constructing supramolecular architectures such as coordination polymers, double helixes and triple helicates (Ziessel, 2001).

Results and discussion

The SH groups of two Schiff bases were oxidized to form double Schiff base ligand and disulfide Schiff base was formed during the formation of crystalline form in the air (Shafaatian et al., 2015). Intermolecular S-S bond in the Schiff base ligand was observed in crystalline structure and also its data was obtained by different spectroscopy methods. The structure of the double Schiff base ligand was determined by X-ray crystallography and was shown in Fig. 1.

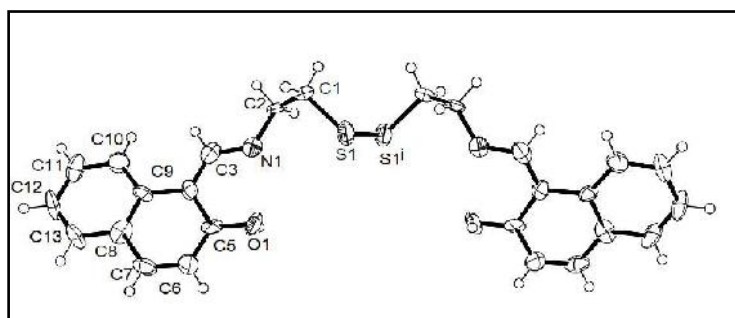


Fig. 1: X-ray structure of tetradentate Schiff base ligand

This Schiff base ligand crystallizes in a monoclinic system with space group $P2(1)/c$ with cell parameters: $a = 20.970$ (4), $b = 6.6964$ (13), $c = 8.0557$ (16) and $V = 1130.5$ (4) \AA^3 , $Z = 2$, $F(000) = 4$. All atoms of this group are located in a plane. Furthermore, X-ray crystallographic analysis showed that the structure of Schiff base ligand containing N_2O_2 donor atoms is planar. Details of crystal data, data collections, and structure refinement were summarized in Table 1.

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 bridging of disulfide is 2.033 (4) \AA , the N-C and C-C bond lengthd in double Schiff base ligand lies in the range of 1.331 (12)- 1.487 (11) \AA and 1.355 (15)- 1.491 (11) \AA , respectively.



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

Empirical formula	C ₂₆ H ₂₄ N ₂ O ₂ S ₂
Formula weight	460.59
Temperature (K)	293
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	<i>P</i> 2/ <i>c</i>
Crystal size (mm ³)	0.08×0.11×0.29
<i>a</i> (Å)	20.970(4)
<i>b</i> (Å)	6.6964(13)
<i>c</i> (Å)	8.0557(16)
α (°)	90
β (°)	92.02(3)
γ (°)	90
<i>V</i> [Å ³]	1130.5(4)
<i>Z</i>	2
Density _{calc} (g cm ⁻³)	1.353
Theta Min-Max [Deg]	3.6, 25.0
<i>F</i> (000)	484
absorpt_coefficient_mu	0.262
Data collected	9290
Tot., Uniq. Data, <i>R</i> (int)	0, 1939, 0.000
Parameters / restraints	247 / 0
Observed Data [<i>I</i> > 2.0 sigma(<i>I</i>)]	343
<i>R</i> , <i>wR</i> ₂ , <i>S</i> ^a	0.0590, 0.1188, 0.54
_refine_ls_goodness_of_fit_ref	0.537
Min. and Max. Resd. Dens. [e/Å ³]	-0.20, 0.25

^a $w = 1/(\sigma^2(F_o^2) + (0.0590 \times F_o^2)^2 + 0.1188 \times F_o^2 + 0.54)$ WHERE $P = (F_o^2 + 2FC^2)/3$



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

S1 –C1	1.821 (8)	C9 –C10	1.374 (13)
S1 –S1	2.033 (4)	C10 –C11	1.385 (13)
O1–C5	1.291 (12)	C11 –C12	1.399 (16)
N1 –C2	1.487 (11)	C1 –H11	1.351 (15)
N1 –C3	1.331 (12)	C1 –H12	0.9700
O1 –H1	0.9800	C1 –C12	0.9700
C1 –C2	1.491 (11)	C2 –H9	0.9700
C3 –C4	1.355 (15)	C2 –H10	0.9700
C4 –C5	1.457 (14)	C3 –H8	0.9300
C4 –C9	1.469 (12)	C6H7 –H7	0.9300
C5 –H6	1.424 (14)	C7 –H6	0.9300

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

C8-H13-H2	119.2	C1 -C14 -C13	119.0 (7)
C12-H13-H2	119.2	S1 -C15 -C16	116.1 (6)
C12-C13-C8	121.6 (10)	C16 -C15 -C28	120.2 (8)
C11-C12-H3	120.9	S1 -C15 -C28	123.7 (7)
C13-C12-H3	120.9	N2 -C16 -C25	124.3 (8)
C13-C12-C11	118.1 (8)	N2 -C16 -C15	117.1 (8)
C12-H11-H4	119.4	C15 -C16 -C25	118.5 (7)
C10-C11-H4	119.4	N2 -C17 -C18	124.3 (8)
C10-C11-C12	119.4	C17 -C18 -C19	119.4 (8)



Experimental

Synthesis of tetradentate Schiff base ligand

2-hydroxy-5-methylbenzaldehyde (0.532 g, 3.910 mmol) in MeOH (7 mL) was added dropwise to a solution of cysteamine (0.302 g, 3.910 mmol) in MeOH. The obtained yellow solution was stirred and heated on a water bath at 53 °C for 6 hours. The color of the solution turned to yellow. 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: 75%), Anal. Calc. for [C₂₆H₂₄N₂O₂S₂] (A): (M.W: 460.59), C, 67.80; H, 5.25; N, 6.08; S, 13.92%. Found: C, 67.47; H, 4.85; N, 6.28; S, 14.02%. IR (KBr, ν/cm^{-1}): 1634 $\nu(\text{CN})$ (imine), 1140 $\nu(\text{CO})$ (phenolic), 637 $\nu(\text{S-S})$, 1401-1542 $\nu(\text{C=C})$ (aromatic), 2900 $\nu(\text{CH})$, 818 $\nu(\text{CS})$. ¹H NMR (DMSO-d₆): 14.11 (1H, s, -OH), 9.15 (1H, s, CH=N), 6.74-8.08 (phenylic hydrogen group).

The suitable yellow single crystals of tetradentate Schiff base ligand containing N₂O₂ donor atoms were obtained by slow evaporation of Schiff base ligand in methanolic solution during ten days at room temperature.

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

Conclusion

A new Schiff base ligand containing N₂O₂ donor atoms was synthesized and characterized by the spectroscopic techniques such as UV-Vis spectroscopy, FT-IR, ¹H NMR, elemental analysis, conductometry and X-ray crystallography. This Schiff base ligand can coordinate as a tetradentate ligand through N₂O₂ donor atoms of phenolic and azomethine groups to metal ions. This Schiff base ligand crystallizes in monoclinic with space group P2/c and with cell parameters: a= 20.970 (4), b= 6.6964 (13), c= 8.0557(16) and V= 1130.5 (4) Å³, Z= 2, F(000)= 4. According to the crystal structure, the Schiff base ligand was contained disulfide bond.

Acknowledgement

I gratefully acknowledge the support of this work by Damghan University Research Council.

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