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تعیین ساختار تک بلور لیگاند باز شیف جدید شامل پیوند دی سولفید

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چکیده فارسی

باز شیف جدید شامل اتم های سولفید غیر دهنده به وسیله واکنش ۲-هیدروکسی-۴-متوکسی بنزآلدئید با سیستامین در محلول متانول با نسبت استوکیومتری ۱:۱ طراحی و سنتز شد. لیگاند باز شیف به وسیله طیف سنجی های FT-IR, ^{1}H NMR, UV/Vis و آنالیز عنصری و هدایت شناسایی شدند. ساختار کریستالی لیگاند باز شیف به وسیله ی پراش پرتو X تک بلور تعیین شده است. لیگاند باز شیف دارای ساختار مونوکلینیک و گروه فضایی *P21* بوده و پارامترهای سلولی برای این لیگاند عبارتند از:

a= 5.1012 (10), b= 10.827 (2), c= 18.616 (4) and V = 1019.1 (4) Ang^3, Z=2, F(000)= 444 and α= 90 deg, β= 97.61 (3) deg, γ= 90 deg.

واژه‌های کلیدی: باز شیف، دی سولفید، سنتز، لیگاند، ساختار کریستالی

Single Crystal X-Ray Determination of A New Sciff base Ligand Containing Disulfide Bond

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Abstract

A new Schiff base ligand containing non donor atoms of sulfide was designed and synthesized by the reaction of 2-hydroxy-4-methoxybenzaldehyde with cysteamine in 1:1 molar ratio in methanolic solution. The Schiff base ligand have been characterized by FT-IR, ^{1}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 monoclinic system with space group *P21* and cell parameters containing: a= 5.1012(10), b= 10.827(2), c= 18.616(4) and V= 1019.1(4) Ang^3, Z= 2, F(000)= 444 and α= 90 deg, β= 97.61(3) deg, γ= 90 deg.

Keywords: Schiff base, disulfide, Synthesis, Ligand, Crystal structure

Introduction

Schiff base ligands with sulfur and nitrogen donor atoms in their structures act as a good chelating agents for metal ions. Furthermore, the field of binucleating ligands and their metal

complexes has been receiving considerable attention in recent years. These ligands can coordinate two of the same, or different, metal ions at a suitable predetermined distance to bind and activate a small molecule between the metal centers (Mishra et al., 2005) Such systems of transition metal complexes may be of interest in relating structures to interesting magnetic behaviours in homo- and hetero-dimetallic complexes and may mimic aspects of two-metal biosites in various proteins and enzymes. Also, interesting studies have been devoted to the development of synthetic procedures, in order to prepare new multidentate ligands with the potential ability of forming bridged polynuclear species (Kruger et al., 1994).

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.

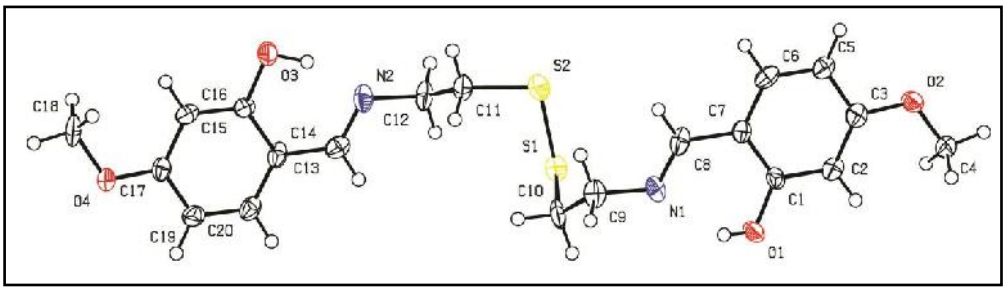

Fig. 1: X-ray structure of disulfide Schiff base ligand

This Schiff base ligand crystallizes in a monoclinic system with *P21* and cell parameters: a= 5.1012 (10), b= 10.827 (2). c= 18.616 (4) and V= 1019.1 (4) Ang^3, Z=2, F(000) = 444 and α= 90 deg, β= 97.61 (3) deg and γ= 90 deg. 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 S-C, O-C, N-C and O-H in this Schiff base ligan lies in the range of 1.804 (8)-1.818 (10) Å, 1.336(11)-1.410 (12) Å, 0.78-0.95 (10) Å and 1.243 (12)-1.459 (11) Å, respectively.

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

Empirical formula	C_{20} H_{24} N_2 O_4 S_2
Formula weight	420.55
Temperature (K)	120(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	*P21*
Crystal size (mm^3)	0.45 x 0.30 x 0.05 mm
a (Å)	5.1012(10)
b (Å)	10.827(2)
c (Å) α(°)	18.616(4) 90
β(°) γ(°)	97.61(3) 90
V [Ang**3]	1019.1(4)
Z	2
$Density_{calc}$ (g cm^{-1})	1.370
Theta Min-Max [Deg]	2.9, 25.0
F(000)	444
absorpt_coefficient_mu	0.290

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

S1 –C10	1.818 (10)	N1 –C8	1.243 (12)
S1 –S2	2.038 (4)	N1 –C9	1.459 (11)
S2-C11	1.804 (8)	N2 –C13	1.257 (13)
O1 –C1	1.336 (11)	N2 –C12	1.459 (10)
O1 –H1	0.78 (11)	C1 –C7	1.393(12)
O2 –C3	1.369(10)	C1 –C2	1.409(11)
O2 –C4	1.410 (12)	C2 –C3	1.352(13)
O3 –C15	1.356 (11)	C2 –H2	0.9500
O3 –H3	0.95 (10)	C3 –C5	1.409(13)
O4 –C17	1.350 (10)	C14 –C15	1.417(13)
O4 –C18	1.463 (12)	C15 –C16	1.387(12)

Experimental

Synthesis of tetradentate Schiff base ligand

To a solution of 2-hydroxy-4-methoxybenzaldehyde (0.067 g, 0.441 mmol) in MeOH (5 mL) was added to a solution of cysteamine (0.034 g, 0.441 mmol) in MeOH and the yellow solution was stirred and heated on a water bath at 54 °C for 10 h. Then, the solvent was evaporated, the oily yellow precipitate was washed with methanol and dried in vacuo at room temperature. The single crystal of Schiff base ligand was grown in methanol by slow evaporation of methanol at room temperature and its structure was determined by X-ra crystallography.

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-Kα 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.

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

C10-S1-S2	104.6(4)	O1 -C1 –C2	118.3 (8)
C11-S2-S1	105.1(3)	C7 -C1 –C2	119.8 (8)
C1-O1-H1	114(8)	C3 –C2 –C1	120.1 (8)
C3-O2-C4	116.4(7)	C3 –C2 -H2	119.9
C15-O3-H3	101(7)	C1 –C2 –H9	119.9
C17-O4-C18	116.8(7)	C2 –C3 –O2	124.7 (8)
C8-N1-C9	118.6(8)	C2 –C3 -C5	120.7 (8)
C13–N2-C2	117.7(9)	O2 –C3 –C5	114.6 (8)
O1-C1-C7	121.8(7)	C6 –C5 –H5	120.5

Conclusion

A new imine ligand containing disulfide bond with oxygen and nitrogen donor atoms was synthesized and characterized by the spectroscopic techniques such as UV–Vis spectroscopy, FT-IR, ^{1}H NMR, elemental analysis, conductometry and X-ray crystallography. This ligand can not coordinate coordinate through sulfur atoms. This Schiff base ligand crystallizes in monoclinic with space group *P21* and with cell parameters: a= 5.1012 (10), b= 10.827 (2), c= 18.616 (4) and V= 1019.1 (4) Ang^{3}, Z= 2, F(000)= 444 with α= 90 deg, β= 97.61 (3) deg and γ= 90 deg.

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References

Kruger P. E., B. Moubaraki B., Murray K. S., Tiekink E. R. T., 1994. Synthesis, structure, magnetism and electrochemistry of binuclear nickel(II) and copper(II) complexes of an unsymmetrical pentadentate Schiff-base ligand. *Chem. Soc., Dalton Trans*., 2129-2134.

Mishra A. K., Manav N., Kaushik N. K., 2005. Organotin(IV) complexes of thiohydrazones: synthesis, characterization and antifungal study. *Spectrochim. Acta A*, 61, 3097-3101.

Shafaatian B., Ozbakzaei Z., Notash B., Rezvani S. A., 2015. Synthesis, characterization, single crystal X-ray determination, fluorescence and electrochemical studies of new dinuclear nickel(II) and oxovanadium(IV) complexes containing double Schiff base ligands. *Spectrochim. Acta A*, 140, 248-255.

Shafaatian B., Soleymanpour A., Kholghioskouei N., Notash B., Rezvani S.A., 2014. Synthesis, crystal structure, fluorescence and electrochemical studies of a new tridentate Schiff base ligand and its nickel(II) and palladium(II) complexes. *Spectrochim. Acta A*, 128 363-369

Sheldrick G.M., SHELXS97, *A Program for Crystal Structure Solution*, University of Gottingen, Germany, 1997.

Sheldrick G.M., SHELXL97, *A Program for Crystal Structure Refinement*, University of Gottingen, Germany, 1997.