Synthesis, Photostudies, Biological Activity, Metal Complexes and Theoretical Study from New Schiff Bases Derived from 3-hydroxy Benzaldehyde and 1,3-Phenylene di amine

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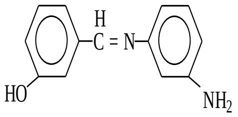
Abstract

Two new Schiff bases derived from 3-hydroxy benzaldehyde and 1,3-phenylene di amine have been prepared and identified by FTIR, UV. Spectroscopy and elemental analysis. The electronic spectra in ethanol, Benzene, dioxane, acetone and ethyl acetate were measured and interpreted. The metal complexes of these Schiff bases with divalent Cu, Co, Ni, Cd, trivalent Fe have been investigated by UV-visible spectrophotometry in neutral ethanolic solutions. One of these bases namly Bis-3-hydroxybenzaldene -N-N(1,3-phenylenediamine) ($C_{20}H_{16}N_2O_2$) was specific ligand to Co(II) as 1:1 propotion in addition to the biological activity and theoretical study using hyperchem program.

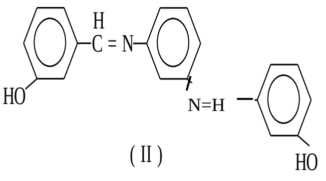
Introduction

It is well known that Schiff bases were specific ligands for many metal ions (1-3). Schiff bases derived from m-hydroxybenzaldehyde showed many applications for metal ion complexes (4-7). Reactive and functional Schiff bases polymers were synthesized and studied. Metal ion uptake behavior of these resins was investigated (8-10). Some Schiff bases formed metal complexes in addition to the biological activity (11-13). Schiff bases were investigated and studied in different spectrophotometry methods such as elemental analysis (CHN), FTIR, Uv-visiale and in different solvent (14,15). In this work the aromatic amine m-phenylene di amine has been not used for preparing Schiff base before with m-hydroxybenzaldehyde directly. Tow Schiff bases were synthesized and identified by elemental analysis FTIR, UV-spectrophotometry method. One of them was found to be specific ligand for Co (II) ion. Moreover the theoretical study of compound II and its metal complex, biological activity have been done.

Experimental



(I)



(II)

Compound (I) was prepared by direct fusion for m-hydroxybenzaldehyde then added to equal mole of melting m-phenyllenediamin. The mixture was heated gently (boiling must be avoided) for 15 mints. Ayellow solid mass formed, then dissolved in boiling ethanol the product recrystallized twice (ethanol+few drops of octane) Apale crystalline product formed after cooling m.p. (135-137) ^{0}C.

Compound (II) prepared by adding appropriate amounts of compound (I) with m-hydroxybenzaldehyde the mixture dissolved in ethanol after cooling acrystalline product was separated and recrystallized twice from ethanol m.p.(148-150) ^{0}C .

Melting point determined on (Gallenhamp) apparatus. The analysis of CHN was carried out by (Ero EA Elemental Analyser) in Al-mustansiria university. The FTIR and UV. Visible spectra were measured by (VARAN UV-visible) and (SHIMADZU FTIR-84005) spectrophotometer using a quartz cell of (1.0cm) pathlenght.

Results and Discussion

* Elemental analysis

Elemental analysis for compounds I and II was founded in addition to the calculated values as in Table (1).

Table (1)
Elemental analysis for comp. I and II.

Comp.	*Founded*			*Calculated*		
	%C	*%H*	*%N*	*%C*	*%H*	*%N*
I	72.165	5.191	11.225	73.584	5.663	13.207
II	74.625	4.367	8.885	75.949	6.329	8.860

* FTIR

FTIR was carried out as (KBr-disk) ν1653cm^{-1}=(C=N) and ν3200cm^{-1}=(N-H) for compound (I). while ν1587cm^{-1}=(C=N) in compound (II) and disappearance of ν_{N-H} and δ_{N-H} was very clear.

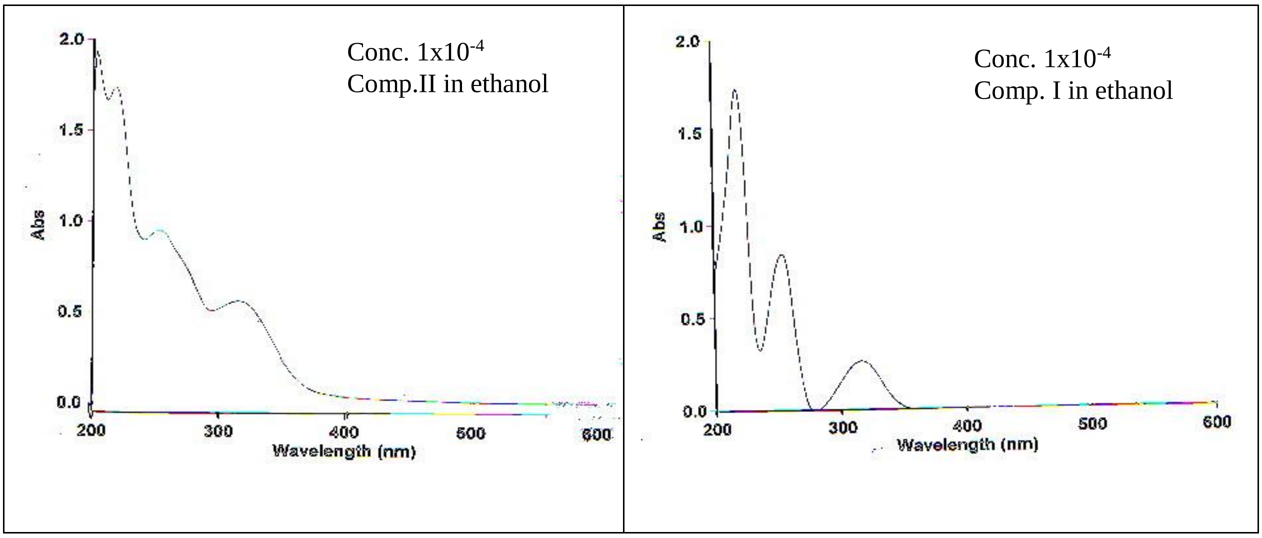
*Electronic spectra

Table (2) represents the UV-visible absorption bands for molecules I, II in ethanol, ethylacetate-dioxane, benzene and acetone.

Table (2)
Electronic spectra bands for comp. I and II in different solvents.

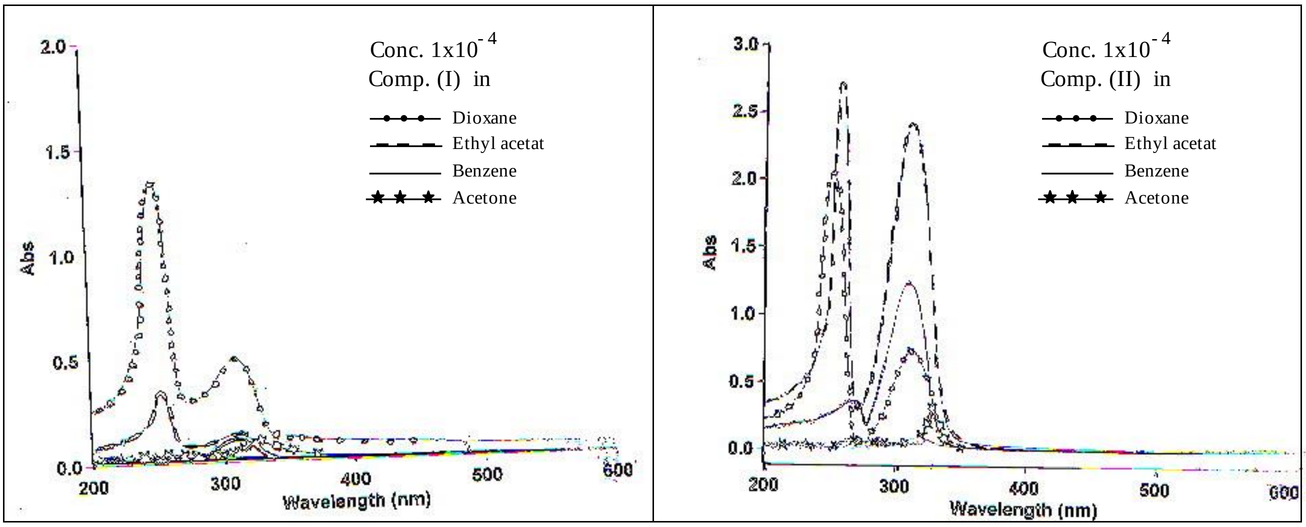
Solvent	*Comp. (I)* $\lambda_{max}(\varepsilon/m^2mol^{-1})$	*Comp. (II)* $\lambda_{max}(\varepsilon/m^2mol^{-1})$
Ethanol	316(560), 253(950), 218 (1730)203(1930)	316(490), 254(1500), 214 (2930)
Ethylacetate	310(560), 260(400)	310(2400), 297(2750)
Benzene	310(150)	305(1200), 297(44)
Dioxane	310(500), 260(1400)	309(570)
Acetone	330(110)	326(300)

The bands (203-205), (214-218), (250-260) nm in ethanol are comparable with absorption bands at 293, 243 and 204 nm of m-hydroxybenzaldehyde due to the local excitation of phenyl ring. These bands correspond to the three π→π* transition at 184, 203, 256 nm bands of benzene molecule (4). In the spectra of molecules I and II which contain a phenyl ring a fourth bands were observed. The band (316-330) nm was not observed in the spectrum of m-hydroxybenzaldehyde, this band attributed to n→π* transition which originates from phenyl rings and directed to azomethine group. The spectra of compounds I and II in different solvents polar and non polar as indicated in Figs.(1) and (2).



For comp. (II) For comp. (I)

Fig. (1) Electronic spectra in ethanol.



For comp. (I) For comp. (II)

Fig. (2) Electronic spectra in different solvent.

In Fig. (2) some bands are not observed because of the absorption of the solvent at (200-250)nm and the band (316-330)nm is observed in different solvents. The shift in the wave length (λ) was not very big or not founded in some bands because the transitions Л-Л*, n-Л* didn't effected by the solvent changing . But the difference in the absorbance of the bands return to the absorbance coefficients for the solvents were different.

***Stability in aqueous medium**

The Schiff bases (I) was decaied immediately in aqueous solution but (II) was stable for 24 hrs. The spectrum in Fig.(3) which indicate the stability of comp. II.

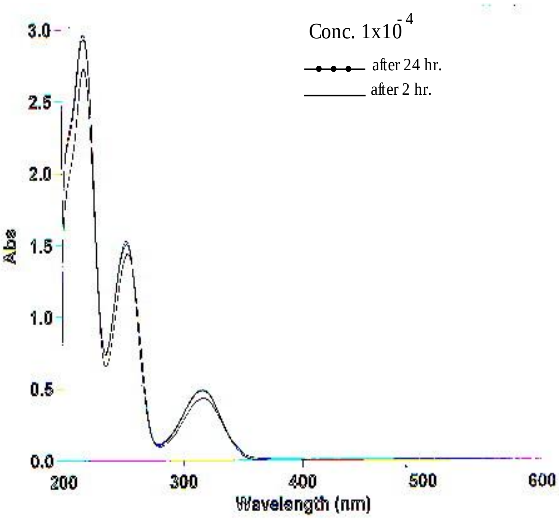


Fig. (3) The stability of comp. II in aqueous medium.

* Metal Complexes

The compound (I) didn't form complexes with any (Di) and (Trivalent) metals but II was founded a specific ligand for Co^{+2}. The molar ratio was (1:1) (metal: ligand) in neutral ethanolic solution. The complex has been investigated by the molar ratio method all measurement were carried out immediately after mixing. The concentrations of the metal and the Schiff bases were between (10^{-3}-5×10^{-4}) M. when the ratio $[Co^{+2}]/[I]$ less than one complex didn't formed but when the ratio was from (1-5) a pink complexes in ethanol was formed at λ_{max}=535 nm (ε =1000-500)m^2mol^{-1}. the ratio method is shown in Fig (4).

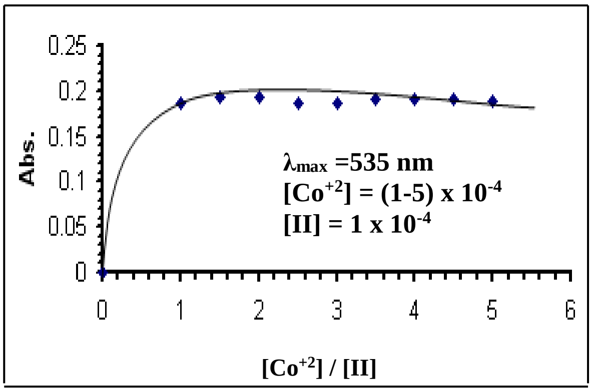


Fig. (4) Ratio method for complex of compound II with Co^{+2}.

* Theoretical study

The conformation of the Schiff base II obtained from molecular mechanistic calculation was fully re-optimized to estimate the binding energy, enthalpy of formation and total energy for compound II by using the PM^3 semi-empirical methodata value of Geometry optimization constant (0.01 Kcal mol^{-1}) as in Table (2).

Table (2)
Conformation energetic in (Kcal mol^{-1}) at 300 K^o for Schiff base (II) and its metal complex.

Comp.	*Total Energy*	*Binding Energy*	*Heat of formation*	*Electronic Energy*
II	-4504.41	----	----	----
Complex	-83321.48	-4016.72	750.663	-635262.3

Fig. (5): explain the electronic density of the compound II to investigate the reactive sites of the molecules. Also one can interpret the stereochemistry and rate of many reactions involving electrophiles and nucleophilies in terms of the properties of frontier orbitals (HOMO highest occupied molecular orbital) and (LUMO, lowest unoccupied molecular orbital). The LUMO of transition metal ions prefer to react with the HOMO 2(C=N) for Comp. II. and the Fig. (6) show the compound as balls and cylinders. So the most probable suggestion was to connect the Schiff bases II with the metal ion Co^{+2} by the azomethin groups.

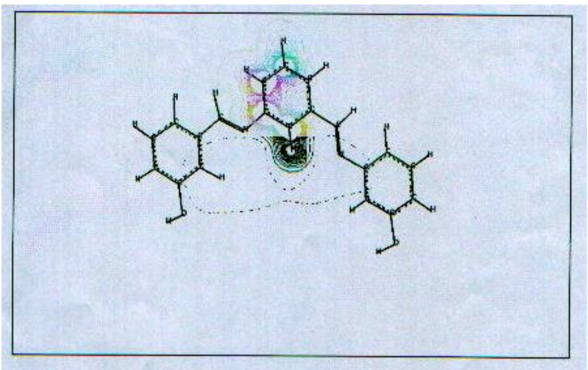


Fig.(5) Electronic density(HOMO and LUMO) for Schiff base II.

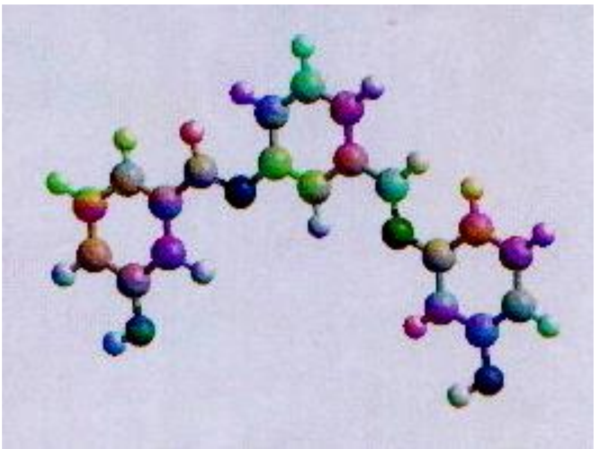


Fig. (6) Balls and cylinders.

*Biological activity

The antibacterial activity of compound II against arepresentive species of bacteria namely Esherichiacoli (E-coli), Salmonunella and Psendomonus in Table (3). The main anti bacterial activity of compound II, may be attributed to the interaction between groups of -OH, -C=N- in this compound and binding sites on the bacterial cell envelop. This show compound II may be metabolized to toxic product on degradation and thus affects the bacterial growth. But compound I didn't show any antibacterial activity, may be return to absence of two function groups -OH, C=N- in spite of founding a free -NH_2. The concentration was one in test.

Table (3)
The antibacterial results.

Comp.	*E-coli*	*Posed.*	*Sal.*
I	-	-	-
II	+ +	+ +	+ +

(0-3)mm = -
(6-9)mm = ±
(10-14)mm = +
(15-18)mm = ++

References

[1] A. A Saeed and A. Y. Khder "Characterization and Investigations of metal complexes of some new Schiff bases derived from 2,2-di-pyridyl ketone and diamines" Canadian Journal of applied spectroscopy Vol. (39), No. (6), 1994.

[2] Roy. Somnath, Mandal, Tarak Nath, Barik, Anil Kumar Gupta. "Synthesis, characterization and X-ray crystal structures of Co(III) and Mn(II) complexes pyrimidine derived Schiff base ligands" Journal Article 2008.

[3] Tagenine Jeewoth, Minu G. Bhowon and Henri Li Kam Wah. "Schiff base metal complexes from 2,3-diamin-pyridine" Journal Transition metal chemistry Volume 24, No. 4 /August 1994 .

[4] SAMAL S. DAS. R. R., ACHARYA S., MOHAPATRA P., DEY R. K. "A Comparative study on metal ion uptake behavior of chelating resins derived from the formaldehyde condensed phenolic Schiff bases of 4,4'-diaminodiphenylsulfone and hydroxybenzaldehydes" Journal polymer-plastics technology and engineering. ISS (0360-2559 CODEPPTEC-7) Vol. 41 n2, PP(224-246) 2002 .

[5] Rosa Moreno, Malgorzata Rosal and Albert Moyano. "Salicyaldehyde Schiff bases derived from 2-ferroceyl-2-amino alcohols. Part 1 "New chiral ligands for the titanium-catalyzed enantioselective cyanation of aldehydes" J. tetrahedron: Asymmetry Vol. 17, ISSU 7, 3 April, pages 1089-1103, 2006.

[6] Hai Feng SONG, Miao CHEN, Yong Min LIANG, Ling SHI, Guo Sheng HUANG "Synthesis and Characterization of Novet Mercapto- end Ferroceyl Derivatives with base linkage" Chinese chemical Lelters Vol. 15, No. 9, PP 1087, 2004.

[7] PELIN SOZEN, YURDANUR AKGUL, FUNDA DEMIRHAN, "Synthesis and spectroscopypic characterization of new Schiff bases Cu(tBu salpphen)]$_2$, [$MoCl_2$(salpphen)]$_2$ and Sn_2Cl_2(tBu salpphen).2HEt_3 Adduct. Turk J. Chem. Vol. (31) Pages 201-209 2007.

[8] Ayman M. Atta, N.O. Shaker and N. E. Maysour. "Influence of the molecular structure on the chemical resistivity and thermal stability of cured Schiff bases epoxy resins" J. Cat. Insit. location 4, 12, 2006.

[9] Zelliha Hayvali and Didem Yardimci "Synthesis and spectroscopic characterization of asymmetric Schiff bases derived from 4'- formylbenzo-15-crown-5 containing recognition sites for alkali and transition metal guest cations". Journal. Transition metal chemistry volume 33, Number 4, May, 2008.

[10] M. Saidul Islam, M. Akhter Farooque and M. A. K. Bodruddoza. "Antineoplastic Activity of 2-oxobenzylidien (3-oxo aniline) Cu(II) Ethylene diamine". Journal of Biological sciences Vol. 5, No. 3, PP. 335-337, 2002.

[11] Har Lal Singh and A. K. Varshney "Synthetic, structural and Biochemical studies of Organotin (IV) with Schiff bases Having Nitrogen and Sulphur Donor Ligand). J. Bioinorganic chemistry and application Vol. 2006, Article ID (3245), 7 pages, 2006.

[12] Wondrak, Georg T. "Reactivity-Based Drug Discovery Using Vitamin B_6 Derived pharmacopheres" Mini Reviews in medical chemistry, Vol. 8, Number (5), PP 519-528, May 2008.

[13] Casimir BLONSKI, Danielle DE MOISSA, Jacques PERIE and Jurgen SYGUSCH. "Inhibition of rabit muscle aldolase by phosphory ylated aromatic compounds" Biochem. J. 323(71-77), 1997.

[14] Marcin Ziolek, Jacek Kubicki, Andrze Macie Jewski, Ryszard Naskrecki, Anna Grabowska. "Enol-Keto tautomerism of aromatic photochromic Schiff base N, N-bis(salicylidene)-p-phenylenediamine: Ground state equilibrium and excited state deactivation studied by solvatochromic measurements on Ultrafast time scale. J. chem.. phys. (P, S, G, E, B) 12 451 81 6599708 124(12), Mar. 28, 2006.

[15] Abdullah M. Asiri and Khadija O. Badahdah. "Synthesis of some New Anil: Part 1. Reaction of 2-Hydroxybenzadehyde and 2- Hydroxynaphthldehyde with2-Aminopyridene and 2-Aminopyrzine". J. Molecules, volume 12(8), page 1796-1804, 2008.

[16] H. H. Jaffe and M. Orchin, "Theory and Application of Ultraviolet spectroscopy" John Wiley and sons, Inc., u th printing 1966.

الخلاصة

تم تحضير قاعدتي شف المشتقتين من 3-هيدروكسي بنزالديهايد و 1،3- فنيلين داي امين وشخصتا بالطرق الطيفية فوق البنفسجية وتحت الحمراء وتحليل العناصر الدقيق (كاربون، هيدروجين، نتروجين). قيست الاطياف الالكترونية في الايثانول، البنزين، الاسيتون والاثيل أسيتيت. كما تمت دراست معقدات المعدن (الثنائية والثلاثية التكافؤ) لهذه القواعد بواسطة الاطياف الالكترونية في المنطقة المرئية في محاليل الايثانول المتعادلة. المركب II ($C_{20}H_{16}N_2O_2$) الذي يدعى بثنائي -3-هيدروكسي بنزالديهايد-N،N-(1،3-فنيلين داي امين) ليكاند خاص لأيون الكوبلت الثنائي Co(II) كان بنسبة (1:1) عززت هذه الدراسة بواسطة الدراسة النظرية باستخدام برنامج الهايبركم.