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Synthesis and characterization of a New Schiff base ligand type N₂O₂ and their Cobalt (II), Nickel (II), Copper (II), and Zinc (II) complexes

Adil A Awad¹, Mohammed Mujbel Hasson¹, Alaa abbas fadhel², Bassam faron Alfarhani³

¹Department of Chemistry, College of Science, Al-Mustansirya University, Baghdad, Iraq.

²Al-furat al-awsat technical University Iraq.

³Department of Chemistry, College of Science, Al-Qadisiyah University, Qadisiyah, Iraq.

E-mail: adel80200999@yahoo.com

Abstract. New schiff base bis (salicylidene) tetramethylbenzidine (bstmb) was prepared via the condensation of salicylaldehyde with 3, 3', 5,5'-tetramethylbenzidine in an ethanol solution. Four complexes were prepared by reaction of schiff base with metal acetat where m(ii), [co, ni, cu, and zn]. The schiff base ligand and their complexes were characterized by using infrared, ¹h nmr spectroscopy, uv-visible spectra, solubility, melting point, (c.h.n) analysis, and molar conductance. The potentiometer analysis of the metal complexes revealed 1:1 (schiff base: metal particle) stoichiometry.

Keywords: schiff base ; metal complexes ; tetramethylbenzidine; azomethine group

Introduction

It is well known that Schiff base type ligands have been intensively used in the designing of wide range of stable coordination compounds ^[1]. Such coordinating behavior of Schiff bases offered opportunities for the following: i) enhancing the stability of either heterogeneous or homogeneous catalyst^[2-5], ii) tuning metal centered electronic factors and iii) inducing substrate chirality. Coordination metal complexes based on Schiff bases with nitrogen- sulfur or nitrogen-oxygen donors are interesting due to their ability to form mimic biologically significant metalloenzymes ^[6]. Furthermore, Schiff base metal complexes with nitrogen, sulfur and oxygen donors have been exhibited wide range of biological activities^[7-9]: antiviral, antifungal, antitumor, antibacterial, anti-inflammatory, bactericidal and fungicidal. Schiff base compound have been taken considerable attention by many researchers for many reasons like ease of preparation, stability, in addition to its wide applications in various fields. The general formula of these compound are (R₁R₂C=NR₃) which usually contains an imine or azomethine group (-C=N-)^[10]. Schiff base compounds could be gained through condensation reaction of the aromatic or aliphatic amine with carbonyl compound (aldehyde or ketone). Schiff base compound have plenty of application, it is used as dyes, rubber accelerators, liquid crystals in electronic display systems and reaction intermediates^[11]. Also Schiff base complexes have played important rule with therapeutic value for example Schiff base complexes of transition



metals have considerable importance as therapeutic value in medical field, for examples, Cobalt (III) Schiff base complexes were used as potential antiviral agents and anti-tubercular agent, while platinum Schiff base complexes have utilized as an anti-cancer agent^[12]. Recently copper Schiff base complexes were used as catalysts for radical cyclisation reactions losing the functional groups due to reductive nature of C-C bond formation through generation of organo-cobalt intermediate^[13]. In this work four of new Schiff base complexes of transition metal ;[Co(BSTMB)]₂, [Ni(BSTMB)]₂, [Cu(BSTMB)]₂.2H₂O, and [Zn(BSTMB)]₂ were prepared according to previous methods in literature.

Experimental

Instrumentation

Gallenkamp MF B600 010F melting point apparatus was used to measure the melting points of the prepared compounds. Elemental analyses (C.H.N.S) were recorded using an EA-034. While (Co, Ni, Cu and Zn) were obtained by the aid of a Shimadzu-670 A flame atomic absorption. FT-IR-8300 Shimadzu Spectrophotometer was used to carry out the Infrared spectra in the range of (4000-400) cm⁻¹. While, Bruker BM6 magnetic balance was used to measure the magnetic susceptibilities of the prepared compounds in the solid state. Molar conductivity of the prepared compounds was obtained at RT by using an Electrolytic Conductivity Measuring set Model MC-1-Mark V (platinum electrode (EDC 304) with cell constant (1cm⁻¹)). Electronic spectra of the samples (10⁻³ M in DMF) were recorded at RT using a UV-1650PC-Shimadzu Spectrophotometer. might have been recorded over DMSO-d₆ utilizing An Bruker 300MHz for tetramethylsilan (TMS) as an inward standard

B) Materials and Methods

All chemical were of highest purity and were used as received

Preparation of the Schiff Base (BSTMB)

In around bottom flask salicylaldehyde (2.442 ml, 0.02mol) was dissolved in hot ethanol. A solution of tetramethylbenzidine (0.01mol) was added in hot ethanol. the reaction mixture heated at reflux for 3-4h . After cooling to room temperature the solid yield was collected by filtration, the precipitate washed by using an ethanol, diethyl ether and purity of the ligand checked by TLC.^[2]

Preparation of the Complexes [(M(BSTMB))₂]

In around bottom flask Schiff Base (BSTMB)(0.01mol) was dissolved in hot ethanol, a hot ethanolic solution of M(CH₃COO)₂. n H₂O (0.01mol) was gradually added to the reaction . The mixture was stirred and treated by 25% aqueous ammonia to precipitate the product as a pale yellow precipitate. The crud product was isolated by filtration, and washed with ethanol and diethyl ether. The Crude product was recrystallized by using a hot ethanol^[14,15].

Results and discussion

Bis(salicyldene)tetra methyl benzidine (BSTMB), was prepared by the ethanol solution between salicylaldehyde and 3, 3', 5,5' tetramethylbenzidine in mole ratio of (2:1).The formation of Schiff base ligand was confirmed by using elemental analyses, FTIR,UV-Vis as well as ¹H NMR spectroscopy. Schiff base complexes[M((BSTMB))₂] were obtained by reaction of Schiff base(BSTMB) with variety of metal ion (M =Co²⁺, Ni²⁺, Cu²⁺ and Zn²⁺) in an ethanol in a 1:1 molar ratio . Rapid deposition was achieved in ambient conditions.

The color, elemental analysis melting points, and molar conductivity values as well as analysis spectroscopy of the prepared complexes, confirmed the neutral complexes with the formation (Table. 1,2 and 3).

The solubility of the prepared $[M((BSTMB)_2)]$ complexes in different solvents were tested, they are found slightly soluble in benzene and acetone, while an easily soluble in nitrobenzene, diethyl ether and dimethyl formamide, but they are insoluble in water and common organic solvents. The molar conductance measurement (Table. 4) of these complexes in $(1 \times 10^{-3}M)$ dimethylformamide solution are with in the range $(8.5-10.2) \text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$, suggesting their non-electrolytic nature ^[16].

The $^1\text{H NMR}$ spectra in (BSTMB) Figure (1) showed the following characteristics chemical shifts (DMSO- d_6) as a solvent) singlet peak at 12.8 that could be assigned to two protons of hydroxyl group. Also, the singlet peak for azomethine protons was appeared at 8.7. The multiple peaks between 7.7 for eight protons of the phenyl ring that is attached to the hydroxyl group appeared while the singlet signal at 7.0 suggesting the attribution of the four protons of the central rings of benzene. The spectrum was also showed a singlet at 2.3 that could be assigned to twelve protons of the methyl group. Note: In this spectrum, the peaks at 2.5 and 3.35 are for the solvent (DMSO- d_6) and dissolved water in (DMSO- d_6) respectively.

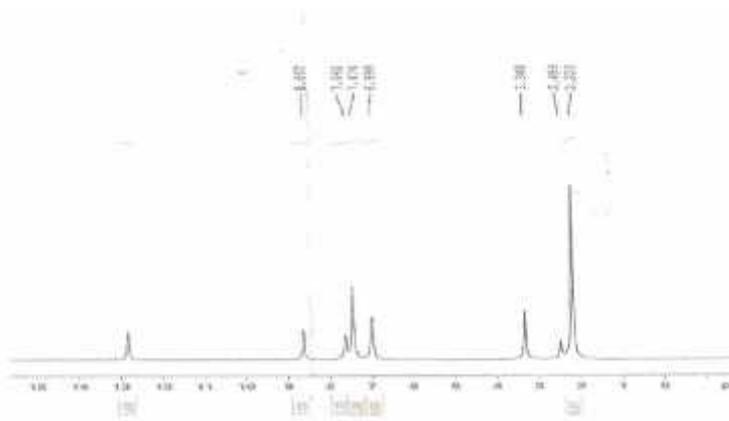


Figure (1) $^1\text{H NMR}$ spectra of (BSTMB)

FTIR spectrum for Schiff base (Table. 5) displays a band around 1600cm^{-1} which should be assigned to $\nu(\text{C}=\text{N})$ stretching vibration of azomethine group. Bands located at $(1500-1300) \text{cm}^{-1}$, $(1170-930) \text{cm}^{-1}$, $890-800 \text{cm}^{-1}$ were assigned to the $\nu(\text{C}-\text{H})$ bending vibration mode, $\nu(\text{C}-\text{N})$ stretching vibration, and $\nu(\text{C}-\text{C})$ stretching mode, respectively^[17-20]. But the bands in the ranges $(520-560) \text{cm}^{-1}$ and $(478-460) \text{cm}^{-1}$ were attributed to $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$ stretching vibrations respectively. Therefore, IR spectra indicate to the coordination of free Schiff base ligand with divalent metal through O, and N atoms.

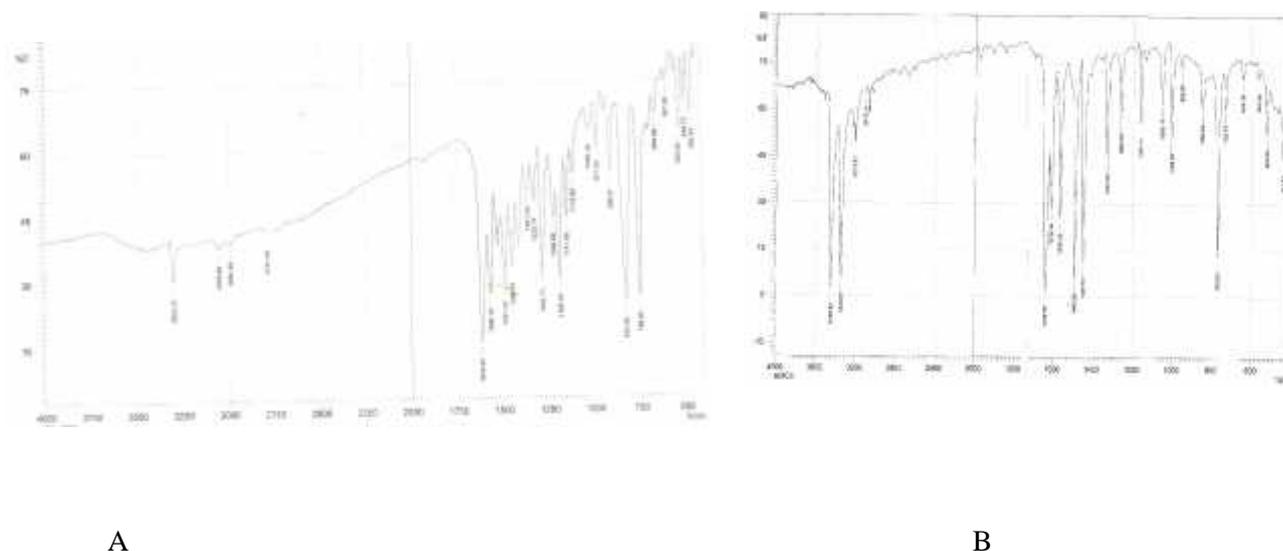


Figure.(2) FTIR Spectra of (A) (BSTMB), (B) $[Cu(BSTMB)]_2 \cdot 2H_2O$

Cu(II) has a d^9 electronic configuration with one unpaired electron. Generally, Cu(II) complexes^[21] are formed by either, using the d-orbitals (square planar or distorted-octahedral) or without using d-orbitals (tetrahedral). In all cases, the room temperature magnetic moment value of Cu(II) are observed in the range: 1.8 - 2.2 B.M.^[22]. In this context, the magnetic moment values of Cu(II) complexes with distorted octahedral geometry were found to be at the lower end of this range. In our case, the observed room temperature magnetic moment of Cu(II) complex is 1.92 B.M. This can give an indication for the formation of binuclear-type complex^[23,24] with square planar geometry at each copper center (two azomethyne nitrogen of tetramethylbenzidine moiety far apart, and the analytical data coupled with the magnetic moment, suggest that the complex is magnetically dilute). Similarly with Cu(II) complex, the Ni(II) complex shows a magnetic moment of 2.67 B.M. which proved the formation of bridged binuclear-type complex with tetrahedral geometry at each nickel center^[25]. The magnetic moment of Co(II) complex was found to be 4.71 B.M., which suggests that the complex is tetrahedral geometry. The Zn(II) complex is found to be diamagnetic as expected (Table. 2).

The UV-Visible spectrum of ligand in ethanol ($10^{-3}M$) shows distinct absorption at three bands: 46729, 36764 and 29325cm^{-1} . The first and second bands are assigned to the $\pi \rightarrow \pi^*$ transition of the aromatic system of the ligand molecule, but the third band is due to the $n \rightarrow \pi^*$ transition of the unshared electron of oxygen in the hydroxyl group. The Co(II) complexes show four bands at 15435, 16615, 17185 and 19015cm^{-1} assigned to the ${}^4A_2 \rightarrow {}^4T_1(p)$ transition for square-planar geometry. The Ni(II) complexes exhibit two bands at 16025 and 28653cm^{-1} assigned to the ${}^3T_1(F) \rightarrow {}^3T_1(P)$ and charge transfer (ct) transition respectively in square-planar geometry. The Cu(II) complexes show two bands at 16977 and 20833cm^{-1} due to the transition of ${}^2B_{1g} \rightarrow {}^2A_{1g}$, transition, and (ct) respectively, suggesting a square-planar structure complex^[26]. The result of this study was listed in (Table. 6).

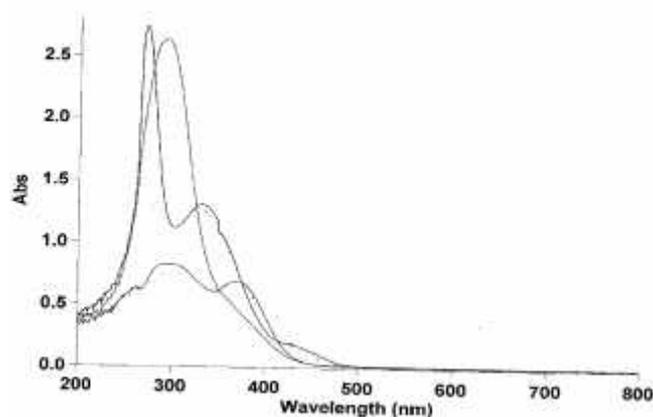


Figure.3 UV-Vis spectra of (1) BSTMB, (2) $[\text{Co}(\text{BSTMB})]_2$, (3) $[\text{Cu}(\text{BSTMB})]_2 \cdot 2\text{H}_2\text{O}$

Table 1: The Percentage Yield, Color and Decomposition Temperatures of the metal complexes

Compounds	Yield	Color	Decomposition Temperature($^{\circ}\text{C}$)
(BSTMB)	75	Orange	250d
$[\text{Co}(\text{BSTMB})]_2$	58	Greenish blue	325d
$[\text{Ni}(\text{BSTMB})]_2$	70	Reddish brown	340d
$[\text{Cu}(\text{BSTMB})]_2 \cdot 2\text{H}_2\text{O}$	65	Green	310d
$[\text{Zn}(\text{BSTMB})]_2$	65	Orangish yellow	335d

Where (BSTMB) is the Schiff base, d=decompose.

Table 2: The Conductivity Measurement of the Complexes in $1 \times 10^{-3}\text{M}$ DMF Solution and magnetic moment.

Compound	$\mu_{\text{eff}}(\text{b.m.})$	$M(\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1})$
$[\text{Co}(\text{BSTMB})]_2$	4.71	9.8
$[\text{Ni}(\text{BSTMB})]_2$	2.67	10.2
$[\text{Cu}(\text{BSTMB})]_2 \cdot 2\text{H}_2\text{O}$	1.92	8.5
$[\text{Zn}(\text{BSTMB})]_2$	Diamagnetic	9.5

Table 3: The C.H.N of the complexes Found (Calc) %

Compounds	C	H	N	M
(BSTMB)	79.83(80.35)	5.98(6.25)	6.01(6.25)	-----
$[\text{Co}(\text{BSTMB})]_2$	71.52(71.28)	4.98(5.14)	5.23(5.54)	11.47(11.68)
$[\text{Ni}(\text{BSTMB})]_2$	71.53(71.32)	5.02(5.15)	5.21(5.54)	11.23(11.63)
$[\text{Cu}(\text{BSTMB})]_2 \cdot 2\text{H}_2\text{O}$	68.01(68.24)	5.10(5.30)	5.21(5.30)	11.96(12.04)
$[\text{Zn}(\text{BSTMB})]_2$	70.12(70.39)	5.30(5.09)	5.67(5.47)	12.26(12.78)

Table 4: The Solubility test of the Complexes in H₂O and Some Common Organic Solvents

Solvent	[Co(BSTMB)] ₂	[Ni(BSTMB)] ₂	[Cu(BSTMB)] ₂ .2H ₂ O	[Zn(BSTMB)] ₂
Water	IS	IS	IS	IS
Methanol	IS	IS	IS	IS
ethanol	IS	IS	IS	IS
Dichloromethane	IS	IS	IS	IS
Nitrobenzene	S	S	S	S
Acetone	SS	SS	SS	SS
Diethyl ether	S	S	S	S
Diemethyl form amide	S	S	S	S
Benzene	SS	SS	SS	SS

Where S means soluble, SS slightly soluble and IS means insoluble

Table 5: The Infrared Spectral Data of the (BSTMB) and its Metal (II) Complex Compounds (cm⁻¹)

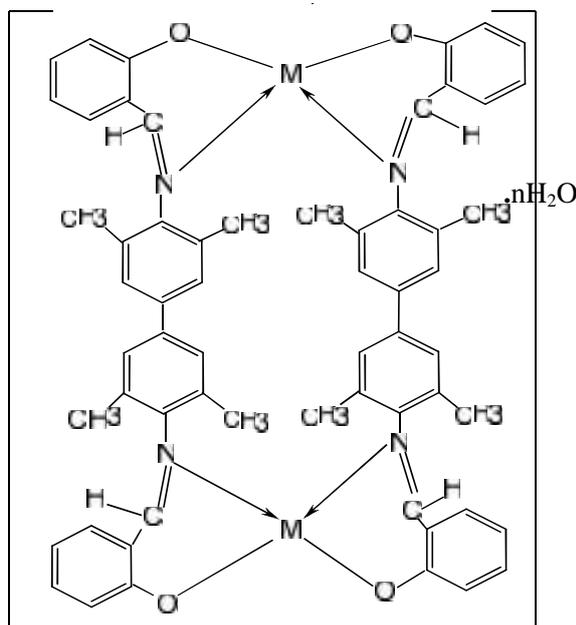
Compounds	(M-N)	(M-O)	(C-H)	(C-O)	(C-N)	(C=N)	(O-H)water
BSTMB	1568	1282	1188	1618	
[Co(BSTMB)] ₂	525	460	1380	1147	1175	1635	
[Ni(BSTMB)] ₂	530	471	1382	1200	1200	1650	
[Cu(BSTMB)] ₂ .2H ₂ O	530	441	1492	1329	1163	1639	3448br
[Zn(BSTMB)] ₂	550	478	1467	1274	1190	1614	

Table 6: the UV-Visible spectral data of the complexes and their assignment

Compound	Band max cm ⁻¹	Assignments
(BSTMB)	46729, 36764cm ⁻¹ 29325cm ⁻¹	*
[Co(BSTMB)] ₂	15435,16615,17185	n * ⁴ A ₂ ⁴ T ₁ (P)
[Ni(BSTMB)] ₂	16025, 28653 cm ⁻¹ ,CT	¹ A _{1g} ¹ A _{2g} , E _g
[Cu(BSTMB)] ₂ .2H ₂ O	16977 ,20833cm ⁻¹	² B _{1g} ² A _{1g} , ² B _{2g} and ² E _g

Conclusion

Based on the results obtained through infrared measurements, ultraviolet rays, and molar connectivity, we can propose the structural formula of the complexes



Scheme. 1: The general molecular structure of the Schiff base metal (II) complexes
Ni(II),Co(II)and Zn(II), n=0 when M=Cu(II) n=2

M=

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