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

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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 acetate 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\(^\text{[12]}\). 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\(^\text{[13]}\). In this work four of new Schiff base complexes of transition metal;\([\text{Co(BSTMB)}]_2\), \([\text{Ni(BSTMB)}]_2\), \([\text{Cu(BSTMB)}]_2\)\(_\text{2H}_2\text{O}\), and \([\text{Zn(BSTMB)}]_2\) 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 \((4000-400) \text{ cm}^{-1}\). 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 \((1\text{ cm}^{-1})\)). Electronic spectra of the samples \((10^{-3} \text{ M in DMF})\) were recorded at RT using a UV-1650PC-Shimadzu Spectrophotometer. might have been recorded over DMSO-d\(_6\) utilizing An Brucker 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 \((2.442 \text{ ml, 0.02mol})\) 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\(^\text{[2]}\).

**Preparation of the Complexes \([\text{M(BSTMB)}]_2\)**

In around bottom flask Schiff Base (BSTMB)\((0.01mol)\) was dissolved in hot ethanol, a hot ethanolic solution of \(\text{M(CH}_3\text{COO)}_2\). \(\text{n H}_2\text{O} \) \((0.01mol)\) 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\(^\text{[14,15]}\).

**Results and discussion**

Bis(salicyldene)tetramethyl 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 \(^1\text{H}\) NMR spectroscopy. Schiff base complexes\([\text{M(BSTMB)}]_2\) were obtained by reaction of Schiff base\((\text{BSTMB})\) with variety of metal ion \((\text{M =Co}^{2+},\text{Ni}^{2+},\text{Cu}^{2+}\text{and Zn}^{2+})\) 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 \([\text{M}((\text{BSTMB})_2)]\) complexes in different solvents were tested, they are found slightly soluble in benzene and acetone, while 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 \((1 \times 10^{-3})\) dimethylformamide solution are within the range \((8.5-10.2)\) ohm\(^{-1}\) cm\(^2\) mol\(^{-1}\), suggesting their non-electrolytic nature \(^{[16]}\).

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

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{NMR_spec}
\caption{\(^1\text{H} \text{NMR} \) spectra of (BSTMB)}
\end{figure}

\textbf{FTIR spectrum for Schiff base (Table. 5)} displays a band around 1600 cm\(^{-1}\) which should be assigned to \(v(\text{C==N})\) stretching vibration of azomethine group. Bands located at \((1500—1300)\) cm\(^{-1}\), \((1170—930)\) cm\(^{-1}\), \(890—800\) cm\(^{-1}\) were assigned to the \(v(\text{C—H})\) bending vibration mode, \(v(\text{C—N})\) stretching vibration, and \(v(\text{C—C})\) stretching mode, respectively\(^{[17-20]}\). But the bands in the ranges \((520—560)\) cm\(^{-1}\) and \((478—460)\) cm\(^{-1}\) were attributed to \(v(\text{M—O})\) and \(v(\text{M—N})\) stretching vibrations respectively. Therefore, IR spectra indicate to the coordination of free Schiff base ligand with divalent metal through O, and N atoms.
Cu(II) has a d⁹ electronic configuration with one unpaired electron. Generally, Cu(II) complexes 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. 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 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 complexes is magnetically dilute). Similarly with Cu(II) complex, the Ni(II) complex show a magnetic moment of 2.67 B.M which proved the formation of bridged binuclear-type complex with tetrahedral geometry at each nickel center. The magnetic moment of Co(II) complex was found to be 4.71 B.M., the suggest 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 (10⁻³M) show distinct absorption at three bands 46729 , 36764and 29325cm⁻¹ the first and second bands assigned to the π→π*transition of aromatic system of the ligand molecule but the third band due to n→π* transition of unshared of electron of oxygen in hydroxyl group. The Co(II) complexes show four bands at 15435,16615,17185 and 19015cm⁻¹ ⁴A₂→⁴T₁(p) transition for square-planar geometry. The Ni (II) complexes exhibit two bands at 16025and28653cm⁻¹ assigned to the ³T₁ (F) → ³T₁ (P) and charge transfer (c t) transition respectively in square-planer geometry. The Cu(II) complexes shows two bands at 16977 and20833cm⁻¹ due to the transition of ²B₁g→²A₁g, transition ,and (ct) respectively suggesting a square-planer structure complexes, the resuelt of this study was listed in (Table. 6)
Figure 3 UV-Vis spectra of (1) BSTMB, (2) [Co(BSTMB)]\textsubscript{2}, (3) [Cu(BSTMB)]\textsubscript{2}.2H\textsubscript{2}O

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

| Compounds          | % Yield | Color            | Decomposition Temperature(°C) |
|--------------------|---------|------------------|--------------------------------|
| (BSTMB)            | 75      | Orange           | 250d                           |
| [Co(BSTMB)]\textsubscript{2} | 58      | Greenish blue    | 325d                           |
| [Ni(BSTMB)]\textsubscript{2} | 70      | Reddish brown   | 340d                           |
| [Cu(BSTMB)]\textsubscript{2}.2H\textsubscript{2}O | 65      | Green            | 310d                           |
| [Zn(BSTMB)]\textsubscript{2} | 65      | Orangish yellow  | 335d                           |

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

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

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

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

| Compounds          | C     | H     | N     | M     |
|--------------------|-------|-------|-------|-------|
| (BSTMB)            | 79.83 (80.35) | 5.98 (6.25) | 6.01 (6.25) | ------ |
| [Co(BSTMB)]\textsubscript{2} | 71.52 (71.28) | 4.98 (5.14) | 5.23 (5.54) | 11.47 (11.68) |
| [Ni(BSTMB)]\textsubscript{2} | 71.53 (71.32) | 5.02 (5.15) | 5.21 (5.54) | 11.23 (11.63) |
| [Cu(BSTMB)]\textsubscript{2}.2H\textsubscript{2}O | 68.01 (68.24) | 5.10 (5.30) | 5.21 (5.30) | 11.96 (12.04) |
| [Zn(BSTMB)]\textsubscript{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)]₂·2H₂O | [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 formamide | 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       | ν (M-N) | ν (M-O) | ν (C-H) | ν (C-O) | ν (C-N) | ν (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)]₂·2H₂O |     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 | π→π*                         |
| [Co(BSTMB)]₂     | 15435,16615,17185 | ¹A₁g→¹T₁g(P)               |
| [Ni(BSTMB)]₂     | 16025, 28653 cm⁻¹,CT | ¹A₁g→¹A₂g, E<sub>g</sub> |
| [Cu(BSTMB)]₂·2H₂O | 16977,20833cm⁻¹   | ²B₁g→²A₁g, ²B₁g and ²E<sub>g</sub> |

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 

$\text{Ni(II),Co(II) and Zn(II), } n=0 \text{ when } M=\text{Cu(II)} \ n=2$

References

[1] You .Z.L., Zhu. H.L.. Anorg Z. (2004). Allg. Chem., 630, 2754.
[2] Balasubramanian. K.P., Parameswari. K. Chinnusamy. V. Prabhakaran. R. K. (2006). Spectrochim. Acta, Part A, 65, 678. Natarajan.
[3] Nakajima,K. Ando,Y. Mano, H. Kojima. M. (1998). Inorg. Chim. Acta, 274, 184.
[4] Clercq.B.D. Verpoort.F. (2002). Macromolecules, 35, 8943.
[5] Opstal,T. Verpoort. F. (2003). Angew. Chem. Int. Ed., 42, 2876.
[6] Clercq .B.D., Verpoort. F. (2002). Adv. Synth. Catal., 344, 639.
  a. Clercq .B.D., Lefebvre. F. Verpoort. F. (2003). Appl. Catal. A, 247, 345. 7-
[7] Patil .S.A., Naik V.H., Kulkarni A.D, Kulkarni .Badami.P.S. (2010). Spectrochim. Acta, Part A, 75, 347.
[8] Agarwal. R.K., Singh. L., Sharma. D.K. (2006). Bioinorg. Chem. Appl., 2006, 1
[9] Pramanik A.K., Jana. M.S., Mondal T.K. (2013). J. Coord. Chem., 66, 4067.
[10] Kalita ,M., Gogoi .P., Barman P., Sarma B. (2014). J. Coord. Chem., 67, 2445.
[11] Clerk, A. J., Filik, R. P., Thomas, G. H., and Wongtap, H. (1998). Generation and
[12] Cyclization of Homogeneous and Solid Supported Copper (II) Schiff Base Complexes, Journal American Chemical Society, 1: 216, 743.
[13] Clerk A. J., Duncalf R. P., Filik R. P., Thomas G. H., and Wongtap H. (1999),N- Alkyl-pyridylmethanimines as Tuneable Alternatives to Bipyridine Ligan in Copper Medicated Atom Transfer Radical Cyclization Reactions, Tetrahedron Letters,1: 3807-3812.
[14] Zacharias P. S. (1984). Binuclear Cobalt (II) Complexes of Tetradeutate Schiff Base Ligand, Indian Journal of Chemistry, 23A; 26-29.
[15] Angelici, R. J. (1971). Synthesis and Techniques in Inorganic Chemistry, W. B. Saunders Company, New York, 2nd Edition, 115-125.
[16] Geary, W. J. (1971). The Use of Conductivity Measurement in Organic Solvents for the Characterization of Coordination Compounds, Coordination Chemistry Review, 7: 82-110.
[17] Nakomato, K. (1963). Infrared Spectra of Inorganic and Coordination Compounds”, Willey, New York, pp. 234-241.
[18] Silverstein, S. M. and Bassler, G. C. (1967). Spectrophotometric Identification of Organic Compounds, Wiley, New York, pp. 12-23.
[19] Koji N. (1977). Infrared Absorption Spectroscopy, 2nd Edition, Holden-Day Inc, San Francisco, 20-49.
[20] Patel, K. S. and Agwara, M. O. (1990). Hexamethylenetetramine Complexes of Divalent Metal Nitrates, Nigerian Journal of Science, 24: 107.
[21] Xishi, T., Xian, H. Y., Qiang, C. and Minyu, T. (2003). Synthesis of Some Transition Metal Complexes of a Novel Schiff Base Ligand Derived from 2, 2’ – Bis(p-Methoxy Phenylamine) and Salicylic Aldehyde, Molecules, 8: 439-443.
[22] Patel K S& woods JAO, Synth React Inorg Met-org Chem,20(1990)909.
[23] Maurya R C, Verma R&Singh H, Synth React Inorg Met-org Chem,33(2003)1036.
[24] Choudhary H,Ghosh RA,Sarkar B N, Banerjee S P & Gosh B K,Indian J Ch,(2007)1393.
[25] Ganesh K S & Krishnan C N, Synth React Inorg Met-org Chem,24(1994)1789.
[26] Dutta R L& Syamal A, Elements magnetochemistry,2nd Edn, (Affiliated East-Wast Press Pvt Ltd, New Delhi)1993,pp.152,153.