



## SYNTHESIS AND CHARACTERIZATION OF TRANSITION METAL COMPLEXES OF PENTADENTATE SCHIFF BASE LIGAND

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### Abstract

Transition metal complexes of pentadentate Schiff base ligand possessing ONNNO donor sites have been synthesized and characterized by infrared, electronic and elemental analysis. Various characterizations suggested the formation of Mn(II) and Co(II) and Cu(II) complexes having square pyramidal structures or square planar structures.

**Keywords:** Schiff base, metal complexes, pentadentate



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### 1. Introduction

Metal ions play a vital role in the development and metabolic functioning of all living beings when present within their permissible limits. Their presence is required for various biochemical processes at the cellular level, such as oxygen transportation, electron transfer reactions [1-10], as cofactor in a varied class of enzymes [9,11-16,21], plant photosynthesis [17] and in insulin-like activities [18]. They also act as redox-active centres and/or Lewis acids to play an important role in the functioning of enzymes such as nitrogenase, haloperoxidase, carboxypeptidase, carbonic anhydrase [1,19-21] etc. Apart from biological importance, transition metals have widespread industrial applications in pharmaceuticals [22], medicinal chemistry [1,23], catalysis [24-28], metal plating, leather tanning, metal corrosion inhibition, wood preserving industries [29,30], fabrication of wires and batteries [31], and production of various alloys [26].

Schiff base complexes of transition metals have great role in the development of coordination chemistry. A number of complexes on diprotic Schiff base ligand containing ONO donor groups have also reported. Tridentate phenol substituted ONO donor Schiff base-derived ligands have been chosen for the present work as these act as workhorses for coordination chemists as one can prepare several different complexes from similar ligands

and the modification of the ligand is generally an easy task. The rapid development of these type of ligands resulted in an enhanced research activity in the field of coordination chemistry leading to very interesting results. These ligands can contain both hard and soft electron donors and we can find rigid and flexible parts in their structures. Schiff bases that contain aryl substituents are substantially more stable and more readily synthesized, while those which contain alkyl substituents are relatively unstable. Schiff bases of aliphatic aldehydes are relatively unstable and readily polymerizable, while those of aromatic aldehydes having effective conjugation are more stable. The stability of a complex depends mainly on the favourable Lewis acid-Lewis base interactions and chelate effects. Typically, hard Lewis acids, such as metal cations with high oxidation states, can easily form complexes with hard Lewis bases like hydroxyl-containing ligands and vice versa. Hence, phenol substituted Schiff base easily form complexes with transition metal ions. The present work deals in extension of the Schiff base ligand reported previously as a chromogenic sensor for iron species. Herein, synthesis and characterization of Mn(II), Co(II) and Cu(II) complexes of ONNNO receptor.

## **2. Experimental**

### **2.1. Materials**

All the reagents namely 2-hydroxy-4-methoxybenzophenone (Sigma-Aldrich), diethylenetriamine (Merck), manganese acetate tetrahydrate (Sigma-Aldrich), copper acetate monohydrate (Acros Organics), cobalt chloride hexahydrate (Loba Chemie), sodium methoxide (Spectrochem), diphenyltin(IV) oxide (Aldrich) were purchased and used as such. All the solvents were purchased commercially, dried before use and stored over molecular sieves. Synthesis of all compounds was performed under a dry nitrogen atmosphere using Schlenk technique.

### **2.2. Physical measurements**

Infrared spectra were routinely obtained on Bruker alpha Eco-ATR spectrometer. Mass spectral measurements (ESI source with capillary voltage 2500 V) were carried out on a VG Analytical (70-S) spectrometer. C, H, N elemental microanalyses were obtained on a FLASH-2000 organic elemental analyzer.

### **2.3. Synthesis of Schiff base with ONNNO donor system**

For the synthesis of Schiff base, a solution of diethylenetriamine (0.47 mL, 4.4 mmol) in 2-propanol was added to a solution of 2-hydroxy-4-methoxybenzophenone (2 g, 8.8 mmol) dissolved in 2-propanol (50 mL). The contents were refluxed for 6 hours and thereafter,

solvent was removed using rotary evaporator. It resulted in yellow oil, which became solid when kept in refrigerator for few days. The compound was recrystallized in methanol.

### **2.3.1. Characterization of Schiff base**

*(N,N'-bis((2-hydroxy-4-methoxyphenyl)(phenyl)methylene)diethyl-enetriamine)*

Yield: 86 %, M.p.: 98-100°C; FT-IR (cm<sup>-1</sup>): 1588 (C=N), 3060 (OH), 3305 (NH); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 1.457 (b, 1H, CNHC) 2.78 (t, 4H, CCH<sub>2</sub>NH, J = 0.018 Hz), 3.28 (t, 4H, CCH<sub>2</sub>N=C, J = 0.018 Hz), 3.70 (s, 6H, OCH<sub>3</sub>), 6.011 (d, 2H<sup>b</sup>, J = 0.030 Hz), 6.215 (s, 2H<sup>a</sup>), 6.51 (d, 2H<sup>c</sup>, J = 0.029 Hz) 7.14-7.39 (m, 5H, -Ph), 15.9 (s, 2H, Ar-OH). <sup>13</sup>C NMR (75.57 MHz, CDCl<sub>3</sub>): δ (ppm) 45.44 (CCH<sub>2</sub>N=C), 49.47 (NCH<sub>2</sub>C), 55.16 (OCH<sub>3</sub>), 101.74-132.92 (aromatic carbons), 164.12 (C<sup>e</sup>) 170.08 (C<sup>c</sup>), 174.19 (C=N), MS (% relative abundance of m/z assignment): 524 (100, M + H)<sup>+</sup>, 1069 (7.99, M + Na + H)<sup>+</sup>.

### **2.4. Synthesis of Schiff base complexes**

Solution of Schiff base (1.046 g, 2 mmol) in 20 mL methanol was added dropwise to triethylamine (0.407 g, 2 mmol) in 10 mL absolute ethanol. This mixture was then added to respective metal salts in 20 mL methanol at room temperature. The reaction mixture was refluxed for 2 h under nitrogen, filtered cold and the product washed several times with diethylether.

**Complex 1:** copper acetate monohydrate (0.402 g, 2 mmol,) Yield: 75 %. M.p.: >300 °C. FT-IR (cm<sup>-1</sup>): 591 (Mn-O), 423 (Mn-N), 1342 (C-O), 1605 (C=N), 2919, 2937 (C-H), 3308 b(O-H); MS (% relative abundance of m/z assignment): 524 (78) [L + H]<sup>+</sup>, 587 (100) [M + 2H]<sup>+</sup>, 610 (50.84) [M + Na + 2H]<sup>+</sup>, 632 (27.87) [M + 2Na + H]<sup>+</sup>; Elem. anal. calcd. C<sub>32</sub>H<sub>31</sub>CuN<sub>3</sub>O<sub>4</sub>: C, 63.25; H, 5.02; N, 6.98; requires C, 65.68; H, 5.34; N, 7.18

**Complex 2:** manganese acetate tetrahydrate (0.491 g, 2 mmol); Yield: 80 %. M.p.: >300 °C. FT-IR (cm<sup>-1</sup>): 571 (Mn-O), 438 (Mn-N), 1300 (C-O), 1608 (C=N), 2850, 2919 (C-H); MS (% relative abundance of m/z assignment): 574 (80.84) [M - 2 H]<sup>+</sup>, 601 (50.84) [M + Na + 2H]<sup>+</sup>; Elem. anal. calcd. C<sub>32</sub>H<sub>31</sub>MnN<sub>3</sub>O<sub>4</sub>: C, 64.62; H, 4.98; N, 6.75; requires C, 66.66; H, 5.42; N, 7.29;

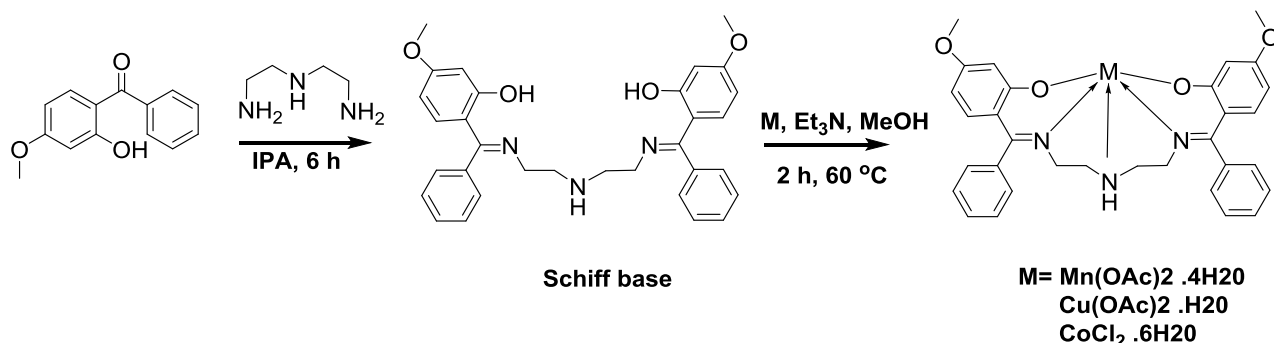
**Complex 3:** cobalt chloride hexahydrate (0.623g, 2 mmol); Yield: 75 %. M.p.: 248-250 °C. FT-IR (cm<sup>-1</sup>): 548, 648 (Mn-O), 462 (Mn-N), 1338 (C-O), 1614 (C=N); MS (% relative abundance of m/z assignment): 524 (100) [L + H]<sup>+</sup>, 582 (23.52) [M + 2H]<sup>+</sup>, Elem. anal. calcd. C<sub>32</sub>H<sub>31</sub>CoN<sub>3</sub>O<sub>4</sub>: C 65.11, H 5.20, N 6.52, O 10.18; requires C, 66.20; H, 5.38; N, 7.24; O, 11.02.

### 3. Results and discussion

#### 3.1. Synthesis and characterization of Schiff base and its Complexes

Herein, a Schiff base has been prepared by the condensation reaction of diethylenetriamine and 2-hydroxy-4-methoxybenzophenone and complexes by refluxing solution of ligand and respective metal salts in methanol (Scheme 1). The formation of Schiff base was confirmed by IR, NMR, mass spectrometry. Strong bands at 1588, 3060 and 3305  $\text{cm}^{-1}$  may be attributed to the stretching frequency for the azomethine ( $>\text{C}=\text{N}-$ ), OH and NH groups, respectively. A signal at 16.24 ppm in  $^1\text{H}$  NMR corroborated to the presence of hydrogen bonding between phenolic OH and azomethine N ( $\text{O}-\text{H}\dots\text{N}=\text{C}$ ).  $^{13}\text{C}$  NMR spectrum of **1** showed a peak at 174.19 due to  $\text{C}=\text{N}$  in addition to aromatic signals.

The IR spectra of Complexes demonstrated characteristic peaks for M-O and M-N in the respective regions at 518-648 and 423-462  $\text{cm}^{-1}$ . The (OH) vibrational band around 3060 of ligand disappears in the spectra of complexes. The shift of (NH) to lower wavenumbers in all complexes support chelation. The IR spectrum of complexes displayed shifting of azomethine ( $>\text{C}=\text{N}-$ ) stretching frequency to region 1554-1614 in comparison to the free ligand (1588  $\text{cm}^{-1}$ ) indicating the formation of M-N bond.



#### Scheme 1 General scheme for the synthesis of Schiff base complexes

Electronic spectra of Mn Complex in DMF, exhibit very weak bands at 460 nm, and for Co(II) complex at 372 and 415 nm and for Cu(II) complex at 439 nm. It is impossible to identify the type of transitions in square pyramid complexes. The spectra of the present complexes are different from those of octahedral and tetrahedral complexes. The magnetic moment of the Mn is 1.73 confirming the presence of one unpaired electron in a square-planar or square pyramid structure and Cu 1.76 confirming the +2 oxidation state of Cu(II) suggesting the square planar structure and 2.43 BM for Co(II) complex suggesting square pyramidal structure.

#### 4. Conclusions

Mn(II), Co(II) and Cu(II) complexes of pentadentate Schiff bases were prepared under nitrogen and characterized by IR, and elemental analysis. Various characterizations suggesting the formation of square pyramidal or square planar structures for the complexes.

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