

# Magnetic, Spectral and Structural Studies of First Row Transition Metal Complexes with Schiff-base Ligand Containing Donor Atoms

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**Abstract:** A series of first row transition metal binuclear complexes  $[(M)_2(L^{1-})_2(H_2O_4)] [M=Co(II), Ni(II), Cu(II) \text{ or } Zn(II)]$  with Schiff base ligand have been synthesized and characterized by elemental analysis, spectral studies, molar mass and molar conductance as well as magnetic moment and magnetic susceptibility measurement methods. On the basis of above physicochemical and spectrometric measurements it is proposed that the compounds act in a bi-dentate manner. Such complexes have varieties of useful pharmaceutical activities and many of them gained wide acceptance in clinical practices. The Schiff base and its resulting complexes have been tested for their antifungal activity against various organisms. Excepting Zn(II) all complexes are colored. Molar conductivity range supports non-electrolytic nature of the complexes. Electronic spectral bands and magnetic susceptibility study suggest an octahedral stereochemistry for the complexes.

**Keywords:** Stereochemistry, Binuclear Complexes, Magnetic Susceptibility, Molar Conductance.

## 1. Introduction

Schiff base ligands containing donor atoms have been of great importance in coordination chemistry as a chelating agent. In coordination chemistry, the functionally substituted Schiff bases [1] bearing additional donor sites represent the most important class of polydentate ligands capable of forming mono-, bi- and polynuclear complexes with transition metal ions. Schiff base metal complexes being the backbone of coordination chemistry find diversified applications [2-4] in several fields of our life. Polynuclear complexes are coordination compounds containing two or more metal atoms or ions, in a single coordination sphere. The two atoms may be held together through direct metal-metal bonds, through bridging ligands, or both. Polynuclear complexes [5] discussed in terms of their structures and magnetic properties, with a focus on self-assembly reactions lead to predictable cluster and grid structures. Magneto-structural studies and correlations will be highlighted with magnetic properties in addition to recent studies with high nuclearity grids and clusters [6,7]. Recently synthesis, magnetic, spectrometric and crystal structure studies of some of the one dimensional supramolecular chains of first row transition metals have been reported [8-10]. Zinc finger protein and zinc complexes with scorpionate ligands [11] have made an upsurge in the research activity of zinc.

The invention of Schiff base initiated by Hugo Schiff [1] in 1864 and propagated by D.H. Bush [12], N. F. Curtis [13] and many others has become the pioneer of the research area [14]. Consequently, in continuation of our earlier interest in the field of binuclear-complexes of first row transition metals with donor ligands derived by Schiff base condensation of 2-amminothiophenol with diketones is being communicated.

## 2. Experimental

### 2.1. Materials and methods:

All the reagents, metal chlorides along with sodium hydroxide and solvents such as diketones, 2-aminothiophenol, ethanol, benzil, DMSO, DMF were purchased commercially from Merck and Aldrich and used without any further purification. Chlorides of first row transition metals were also used as supplied. For the estimation of metals, the complexes were first decomposed to bring them in their proper ionic solution and then they were analyzed quantitatively. Cobalt was estimated from its ionic solution by oxidizing it with few drops of conc.  $\text{HNO}_3$  after repeated heating and cooling. Oxide of cobalt was converted into nitrate. On expelling  $\text{HNO}_3$  by heating, it was treated with excess of conc.  $\text{H}_2\text{SO}_4$  to convert it into sulphate. Finally it was heated between  $450\text{-}500^\circ\text{C}$  and weighed as  $\text{CoSO}_4$ .

Nickel was precipitated as bis-DMG nickel(II) in ammonical medium from the ionic solution of nickel chloride. The precipitate was heated at  $110\text{-}120^\circ\text{C}$  and weighed as nickel compound. Copper was estimated by repeated evaporation of the weighed amount of its complex with  $\text{HNO}_3$  and  $\text{HClO}_4$  in a Pyrex beaker until a clear solution was obtained. The solution was further boiled with  $\text{HCl}$  and the volume was reduced to 10-15ml. Now the resulting solution was diluted with water and Cu was determined iodometrically. On the other hand zinc was estimated by EDTA titration in an alkaline medium having pH 10.

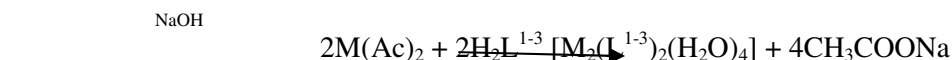
### 2.2. Synthesis of Ligands [ $\text{H}_2\text{L}^{1-3}$ ]:

A series of ligands  $\text{H}_2\text{L}^{1-3}$  have been prepared by condensation reaction. Ethanolic solution of diketones (0.01 mol.) was added with constant stirring to an ethanolic solution of 2-aminothiophenol (0.02 mol.) and refluxed for about 6 hours. The resulting solution was concentrated and allowed to undergo slow evaporation at low pressure when crystals separated. Crystals were filtered, washed with ethanol, dried in air and analyzed for carbon, hydrogen, nitrogen and sulphur.

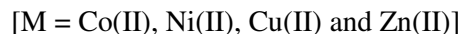
### 2.3. Synthesis of complexes [ $\text{M}_2(\text{L}^{1-3})_2(\text{H}_2\text{O})_4$ ]:

A general method used to synthesize the binuclear complexes of first row transition metals. An ethanolic chloride solution of cobalt, nickel, copper and zinc were added separately to the ethanolic solution of diketone-(2-aminothiophenol) in a molar ratio (2 : 2 = M : L) or (1 : 1 = M : L) followed by the addition of an aqueous solution of  $\text{NaOH}$  (0.02 mol.) to the resulting mixture. Now the mixture was refluxed separately for about 4 hours. The formed precipitates were collected by filtration, washed several times with ethanol and water and finally dried in oven at  $110^\circ\text{C}$ .

The synthetic reaction during the synthesis of metal complexes can be represented as



Reflux



Analytical results were found to be within one percent of deviation as compared to proposed formulation.

### 2.4. Physical Measurements:

Elemental analysis of C, H, N and S was carried out micro-analytically at CDRI Lucknow. The electronic absorption spectra of the complexes were recorded with Hitachi-300 spectrophotometer at CDRI Lucknow. Infrared spectra were also recorded at CDRI Lucknow on Perkin Elmer 577 spectrophotometer using KBr disc in the range of  $4000\text{-}400\text{ cm}^{-1}$ . Magnetic susceptibility of all the complexes were measured by Guoy's method using  $\text{Hg}[\text{Co}(\text{NCS})_4]$  as calibrant. Electrical conductivity of the solution of complexes was measured by conductivity meter Systronics model 300 at room temperature in DMF using N/10 and N/100 KCl solution. Pure DMF and conductivity water were used as solvent.

**Table-1: Colour, yield, decomposition temperature, analytical and molar conductance data of the complexes of diketone-(2-aminothiophenol)**

Compound	Colour	Yield (Gram)	Decomp. (0°)	Analytical Data (Cal./Found %)				Cal.(Found) %	$\Lambda_M$
				C	H	N	S		
[(Co) <sub>2</sub> (L <sup>1</sup> ) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]	Dark Brown	78	322	64/63.57	5.33/5.18	9.33/9.15	21.33/21.02	15.01(14.98)	8
[(Ni) <sub>2</sub> (L <sup>1</sup> ) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]	Yellow	76	341	64/63.57	5.33/5.18	9.33/9.15	21.33/21.02	15.03(15.00)	13
[(Cu) <sub>2</sub> (L <sup>1</sup> ) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]	Brown	73	319	64/63.57	5.33/5.18	9.33/9.15	21.33/21.02	15.97(15.84)	11
[(Zn) <sub>2</sub> (L <sup>1</sup> ) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]	Yellow	77	339	64/63.57	5.33/5.18	9.33/9.15	21.33/21.02	16.41(16.37)	17
[(Co) <sub>2</sub> (L <sup>2</sup> ) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]	Dark Brown	68	328	65/64.58	5.38/5.16	9.41/9.17	21.35/21.07	15.08(14.96)	9
[(Ni) <sub>2</sub> (L <sup>2</sup> ) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]	Yellow	72	356	65/64.55	5.37/5.16	9.43/9.14	21.36/21.04	15.04(15.01)	8
[(Cu) <sub>2</sub> (L <sup>2</sup> ) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]	Brown	74	321	65/64.53	5.36/5.15	9.42/9.15	21.32/21.05	15.95(15.82)	12
[(Zn) <sub>2</sub> (L <sup>2</sup> ) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]	Yellow	75	341	65/64.57	5.34/5.14	9.40/9.16	21.34/21.03	16.01(16.07)	14
[(Co) <sub>2</sub> (L <sup>3</sup> ) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]	Dark Brown	76	332	65/64.78	3.96/3.92	6.93/6.88	15.84/15.76	11.87(11.79)	8
[(Ni) <sub>2</sub> (L <sup>3</sup> ) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]	Yellow	70	342	65/64.88	3.96/3.92	6.93/6.88	15.84/15.76	11.88(11.78)	10
[(Cu) <sub>2</sub> (L <sup>3</sup> ) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]	Brown	71	328	65/64.84	3.96/3.92	6.93/6.88	15.84/15.76	12.66(12.59)	15
[(Zn) <sub>2</sub> (L <sup>3</sup> ) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]	Yellow	69	358	65/64.87	3.96/3.92	6.93/6.88	15.84/15.76	13.00(12.97)	16

**Table-2: Important IR spectral data of the complexes of diketone-(2-aminothiophenol) (cm<sup>-1</sup>)**

Compound	$\nu(\text{H}_2\text{O})$	$\nu(\text{C}=\text{N})$	Rocking $\nu(\text{H}_2\text{O})$	Wagging $\nu(\text{H}_2\text{O})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{S})$
[(Co) <sub>2</sub> (L <sup>1</sup> ) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]	3413	1591	874	758	376	498
[(Ni) <sub>2</sub> (L <sup>1</sup> ) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]	3412	1592	875	756	384	487
[(Cu) <sub>2</sub> (L <sup>1</sup> ) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]	3454	1586	847	764	374	490
[(Zn) <sub>2</sub> (L <sup>1</sup> ) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]	3415	1595	874	723	373	492
[(Co) <sub>2</sub> (L <sup>2</sup> ) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]	3412	1590	876	759	375	499
[(Ni) <sub>2</sub> (L <sup>2</sup> ) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]	3411	1591	876	756	383	489
[(Cu) <sub>2</sub> (L <sup>2</sup> ) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]	3454	1585	848	763	372	491
[(Zn) <sub>2</sub> (L <sup>2</sup> ) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]	3417	1595	876	722	373	492
[(Co) <sub>2</sub> (L <sup>3</sup> ) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]	3412	1595	891	755	377	496
[(Ni) <sub>2</sub> (L <sup>3</sup> ) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]	3416	1592	869	756	383	489
[(Cu) <sub>2</sub> (L <sup>3</sup> ) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]	3442	1591	879	763	375	491
[(Zn) <sub>2</sub> (L <sup>3</sup> ) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]	3455	1581	856	742	376	497

### 3. Results and Discussion

The complexes obtained from diketone-(2-aminothiophenol) were powders, stable in air at room temperature, insoluble in common organic solvents such as acetone, methanol and chloroform. Their decomposition temperature supports the binuclear structure of these complexes. Characterization has been done on the basis of elemental analysis, conductivity, magnetic and spectral study.

#### 3.1. Electrolytic conductivity:

Molar conductance of the complexes in DMSO was found in the range of (8-17) ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. This indicates complexes to be non-electrolytic [11] in nature supporting anions to act in a coordinated mode.

#### 3.2. Infrared spectra:

Spectral bands of the complexes when compared with that of the free ligand provide ample evidences for the mode of binding of the ligand to the metal ion. In the infrared spectrum of diketone-(2-

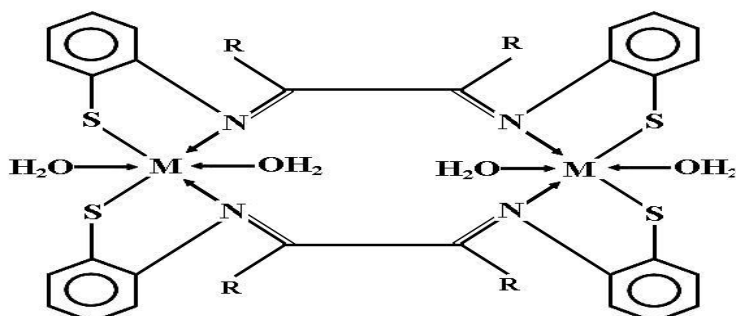
aminothiophenol) ligand, a sharp band observed at  $1595\text{ cm}^{-1}$  was assigned to the  $\nu(\text{C}=\text{N})$  mode of the azomethine group which was shifted to lower wave numbers in all the complexes, suggesting the coordination of the azomethinenitrogen to the metal ion centers [15]. This is further substantiated by the presence of the new band at  $372\text{-}384\text{ cm}^{-1}$  assignable to  $\nu(\text{M}-\text{N})$ .

The characteristic thiophenolic  $\nu(\text{S}-\text{H})$  mode was observed at  $2475\text{ cm}^{-1}$ . A band at  $1293\text{ cm}^{-1}$  due to  $\nu(\text{C}-\text{S})$  thiophenolic was also observed in the spectrum of ligand<sup>14</sup>. The disappearance of thiophenolic  $\nu(\text{S}-\text{H})$  bond in the complexes under study suggests the coordination by thiophenolic sulphur after deprotonation to the metal ion. This is further supported by the shifting of  $\nu(\text{C}-\text{S})$  thiophenolic to lower wave numbers in all the metal complexes [16]. The IR spectra [17] of the complexes also show a band in the  $3411\text{-}3455\text{ cm}^{-1}$  region, indicating the presence of coordinated water in these complexes. The presence of coordinated water was further confirmed by the appearance of a non-ligand band [18] in the  $847\text{-}891\text{ cm}^{-1}$  and  $722\text{-}764\text{ cm}^{-1}$  region, assignable to the rocking and wagging modes of water, respectively.

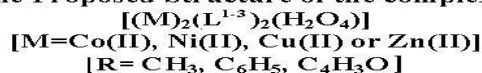
### 3.3. Magnetic moment and electronic spectra:

The electronic spectra of the free ligand diketone-(2-aminothiophenol) and its first row transition metal complexes were recorded in DMSO at room temperature. Electronic absorption spectral [19] data of the ligand shows the  $\pi \rightarrow \pi^*$  transitions related to benzene ring in the range  $43000\text{-}44000\text{ cm}^{-1}$  and imine  $n \rightarrow \pi^*$  transitions in the range  $30500\text{-}31000\text{ cm}^{-1}$ . The  $[(\text{M})_2(\text{L}^{1-3})_2(\text{H}_2\text{O})_4]$  complex exhibits one band in the range  $9850\text{-}10000$  and another band in the range of  $23800\text{-}23900\text{ cm}^{-1}$ . The bands are assigned to the transitions  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})(\nu_1)$  and  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})(\nu_3)$  respectively. The magnetic moment of the cobalt complex at room temperature was observed in the range of  $4.20\text{ - }4.60$  B.M. per metal atom. On the basis of the position of the bands and the magnetic moment value the geometry of  $[(\text{M})_2(\text{L}^{1-3})_2(\text{H}_2\text{O})_4]$  complex is presumably octahedral.

Similarly the magnetic moment of nickel complex was found in the range of  $3.75\text{ - }3.80$  B.M. corresponding to two unpaired electrons. Electronic spectra [20] of the aforesaid complex display three absorption bands in the range  $11250\text{ - }11570$ ,  $16200\text{ - }16350$ , and  $28115\text{ - }26240\text{ cm}^{-1}$ . These bands can be assigned to three spin allowed transitions  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$ ,  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$  and  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$  respectively. The position of these bands indicates that the complex has an octahedral geometry around Ni(II) ions. The electronic spectra of copper complex shows a single broad band in the region  $20000\text{ - }20300\text{ cm}^{-1}$  attributable to  ${}^2\text{T}_{2g} \rightarrow {}^2\text{E}_g$  transition indicative of distorted octahedral geometry around Cu(II) ions. A low energy band at  $10341\text{ cm}^{-1}$  and the magnetic moment [21] of  $1.78$  B.M. per Cu(II) ion support the octahedral geometry the copper complex. Zinc complex shows zero magnetic moment suggesting the diamagnetic nature of the complex. The electronic spectra of Zn(II) complex shows a single broad band in the region  $23000\text{-}25000\text{ cm}^{-1}$  attributable to charge transfer transition. The electronic spectroscopy does not permit the establishment of a clear cut stereochemistry for Zn(II) complex. But taking into consideration of similarity with light congeners, Zn(II) complex has been proposed to have octahedral geometry. Hence the proposed structure of transition metal complexes  $[(\text{M})_2(\text{L}^{1-3})_2(\text{H}_2\text{O})_4]$  having octahedral geometry is shown as :



The Proposed Structure of the complexes



#### 4. Conclusion

Present programme reveals that complexes of first row transition metals with diketone-(2-amminothiophenol) assume an octahedral geometry by virtue of their magnetic moment values but Zn(II) complex being diamagnetic in nature and having zero magnetic moment value is proposed to have octahedral geometry due to its similarity with light congeners.

**Acknowledgement:** The author is thankful to Principal Dr.Meena Prasad for providing laboratory and library facilities and also to the staffs of P.G. Department of Chemistry, Samastipur College, Samastipur for their cooperation.

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