



## Synthesis and Properties of Manganese, Cobalt, Nickel and Copper complexes of tetradentate N<sub>6</sub>-macrocyclic ligand

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### Abstract

The Schiff base technique was used to create the 12-membered tetradentate N<sub>6</sub>-macrocyclic complexes with Mn<sup>II</sup>, Co<sup>II</sup>, Ni<sup>II</sup>, and Cu<sup>II</sup>. The general composition of these complexes was discovered to be [M(L)X] (where M is Mn<sup>II</sup>, Co<sup>II</sup>, Ni<sup>II</sup>, and Cu<sup>II</sup>.; X is Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and L is Ligand). By using elemental analysis, conductance, magnetic susceptibility, IR spectra, electronic spectra, and NMR spectral analyses, the ligand and its transition metal complexes were identified. According to the spectral data, the geometry of metal sulphate and chloride complexes is tetrahedral for the former and octahedral for the latter.

**Keywords:** Macrocyclic, Tetradentate, Mn<sup>II</sup>, Co<sup>II</sup>, Ni<sup>II</sup> and Cu<sup>II</sup>.

### Introduction

Macrocyclic ligands are described as cyclic compounds that typically contain donor atoms spaced within organic frames, either aliphatic or aromatic units (1). Because of their biological actions, which include antitumor, antibacterial, antiviral, and antifungal effects, transition metal macrocyclic complexes have attracted a lot of attention. Their capacity to form tetradentate chelates with necessary heavy metal ions, bonding through sulphur and nitrogen, is what allows them to engage in such biological functions (2–6). Because they resemble natural systems like porphyrin and cobalamine, complexes of metal ions with macrocyclic ligands are important (7).

In this article, we describe the synthesis and characterization of ligand-containing Mn<sup>II</sup>, Co<sup>II</sup>, Ni<sup>II</sup>, and Cu<sup>II</sup> Complexes. The elemental analysis, molar conductance, magnetic susceptibility, IR, electronic, and NMR spectra studies have all been used to determine the complexes' potential geometry.

## Experimental

### Materials and methods

All of the compounds utilised to make the ligands were BDH quality, AR grade substances. The CHN-Rapid Analyzer was used to do the microelemental analysis. Using a dip-type platinized platinum electrode, conductivity was measured on a Toshniwals conductivity bridge. The Rast Camphor method was used to determine the molecular weights. Using a Guoy balance, the magnetic susceptibilities were tested. On an EM 300-30MHZ NMR spectrometer in DMSO, proton NMR spectra were captured. The materials' IR spectra (KBr) were captured using a shimadze FTIR-8400s Spectro-Photometer. On the Lamda 35 spectrometer, the electronic spectra for chloroform were captured.

### Synthesis of ligand

Following this procedure, a heated solution of L-glycine (0.02 mol) in methanol was added to a methanolic solution (50 ml) of trimethoprim (0.02 mol). After vigorous stirring, the mixture was refluxed over a water bath. Concentrated hydrochloric acid (1 ml) was then added, and the mixture continued to reflux for 6–8 hours. Then, it was concentrated to only half its original volume, and left alone for two days. The resulting light brown crystals were then dried at 600C after being washed in methanol and ether. Alcohol was used to recrystallize the crude product. The approach produced a 90–95 percent yield of the desired condensation product more easily.

{C<sub>32</sub>H<sub>38</sub>N<sub>10</sub>O<sub>6</sub>}, Yield: 95 %; color: pale brown . Anal. Calc. for C<sub>32</sub>H<sub>38</sub>N<sub>10</sub>O<sub>6</sub> (Mw:658); C,58.34; H,5.82; N,21.26. Found: C,58.64; H,5.90; N,21.12. IR (KBr,cm-1): 3503  $\gamma$ (NH<sub>2</sub>),3090 $\gamma$ (NH), 1640(C= N),1154 $\gamma$ as(C-C-N),1565,985(pyrimidine ring). <sup>1</sup>HNMR ( DMSO, ppm)  $\delta$ = 2.0(4H,s,-C-CH<sub>2</sub>-);  $\delta$ = 2.4(4H,t,free-NH<sub>2</sub>);  $\delta$ = 3.7(18H,s,-OCH<sub>3</sub>);  $\delta$ = 5.4 (2H,s,ring NH);  $\delta$ = 6.6 (4H,S,Pyrimidine-CH<sub>2</sub>-Ar);  $\delta$ = 7.8 (2H,d,pyrimidine -H);  $\delta$ = 8.3 (4H,d,Ar-H).

### Synthesis of the metal complexes

To a solution of the metal chloride(or) sulphate (0.01 mol) in methanol were added and refluxed for 5hrs. The resultant solution was cooled two days and the crystals which separated out were filtered washed with methanol-ether mixture (1:1) and dried in vacuum (8-10) over anhydrous CaCl<sub>2</sub>.

{Mn (L<sub>1</sub>)Cl<sub>2</sub>}: Yield: 86 %; color: pale pink. Anal. Calc. for [Mn(C<sub>32</sub>H<sub>38</sub>N<sub>10</sub>O<sub>6</sub>)Cl<sub>2</sub>]: C,48.32; H,4.75; N,17.82. Found: C,48.99; H,4.88; N,17.86. IR (KBr,cm-1): 3346  $\gamma$ (NH<sub>2</sub>),3050 $\gamma$ (NH), 1599(C= N),1115 $\gamma$ as(C-C-N),1506,958 (pyrimidine ring),542(M-N),318(M-Cl).  $\Lambda_m/\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$  (in CH<sub>3</sub>CN): 32.18.  $\mu_{\text{eff}}$  (300K): 5.83 B.M.

{Mn (L<sub>1</sub>)SO<sub>4</sub>}: Yield: 81 % ; color: cream white. Anal. Calc. for [Mn(C<sub>32</sub>H<sub>38</sub>N<sub>10</sub>O<sub>6</sub>)SO<sub>4</sub>] : C,47.38; H,4.80; N,17.20. Found: C,47.47; H,4.73; N,17.29. IR (KBr,cm<sup>-1</sup>): 3405  $\gamma$ (NH<sub>2</sub>), 3030 $\gamma$ (NH), 1589 (C= N),1129 $\gamma$ as(C-C-N),1570, 992 (pyrimidine ring), 511 (M-N), 907 (SO<sub>4</sub>).  $\Lambda_m/\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ (in CH<sub>3</sub>CN): 130.  $\mu_{\text{eff}}$  (300K): 5.48 B.M.

{Co (L<sub>1</sub>)Cl<sub>2</sub>}: Yield: 83 % ; color: dark pink , Anal. Calc. for [Co(C<sub>32</sub>H<sub>38</sub>N<sub>10</sub>O<sub>6</sub>)Cl<sub>2</sub>] : C, 48.26; H, 4.81; N,17.66. Found: C,48.80; H,4.86; N,17.80. IR (KBr,cm<sup>-1</sup>): 3405  $\gamma$ (NH<sub>2</sub>), 3008 $\gamma$ (NH), 1589 (C= N), 1129 $\gamma$ as(C-C-N), 1530, 958 (pyrimidine ring), 507 (M-N), 335 (M-Cl).  $\Lambda_m/\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ (in CH<sub>3</sub>CN): 20.00.  $\mu_{\text{eff}}$  (300K): 5.14 B.M.

{Co (L<sub>1</sub>)SO<sub>4</sub>}:Yield: 80 %; color: blue. Anal. Calc. for [Co(C<sub>32</sub>H<sub>38</sub>N<sub>10</sub>O<sub>6</sub>)SO<sub>4</sub>] : C,47.33; H,4.80; N,17.20. Found: C,47.23; H,4.71; N,17.21. IR (KBr,cm<sup>-1</sup>): 3404  $\gamma$ (NH<sub>2</sub>), 3167 $\gamma$ (NH), 1422 (C= N), 1129 $\gamma$ as(C-C-N), 1500, 909 (pyrimidine ring), 507 (M-N), 992 (SO<sub>4</sub>).  $\Lambda_m/\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ (in CH<sub>3</sub>CN): 95.00.  $\mu_{\text{eff}}$  (300K): 4.42 B.M.

{Ni (L<sub>1</sub>)Cl<sub>2</sub>}: Yield: 78 %; color: pale green , Anal. Calc. for [Ni(C<sub>32</sub>H<sub>38</sub>N<sub>10</sub>O<sub>6</sub>)Cl<sub>2</sub>] : C, 48.76; H, 4.86; N,17.77. Found: C,48.66; H,4.83; N,17.70. IR (KBr,cm<sup>-1</sup>): 3503  $\gamma$ (NH<sub>2</sub>), 3053  $\gamma$ (NH), 1590 (C= N), 1145  $\gamma$ as(C-C-N), 1558, 890 (pyrimidine ring), 530 (M-N), 320 (M-Cl).  $\Lambda_m/\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ (in CH<sub>3</sub>CN): 12.78.  $\mu_{\text{eff}}$  (300K): 3.10 B.M.

{Ni (L<sub>1</sub>) SO<sub>4</sub>}: Yield: 82 %; color: dark green. Anal. Calc. for [Ni(C<sub>32</sub>H<sub>38</sub>N<sub>10</sub>O<sub>6</sub>)SO<sub>4</sub>] : C,45.73; H,4.56; N,16.67. Found: C,45.70; H,4.60; N,16.62. IR (KBr,cm<sup>-1</sup>): 3505  $\gamma$ (NH<sub>2</sub>), 3023 $\gamma$ (NH), 1590 (C= N), 1152  $\gamma$ as(C-C-N), 1565, 885 (pyrimidine ring), 523 (M-N), 1060 (SO<sub>4</sub>).  $\Lambda_m/\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ (in CH<sub>3</sub>CN): 125.  $\mu_{\text{eff}}$  (300K): 3.72 B.M.

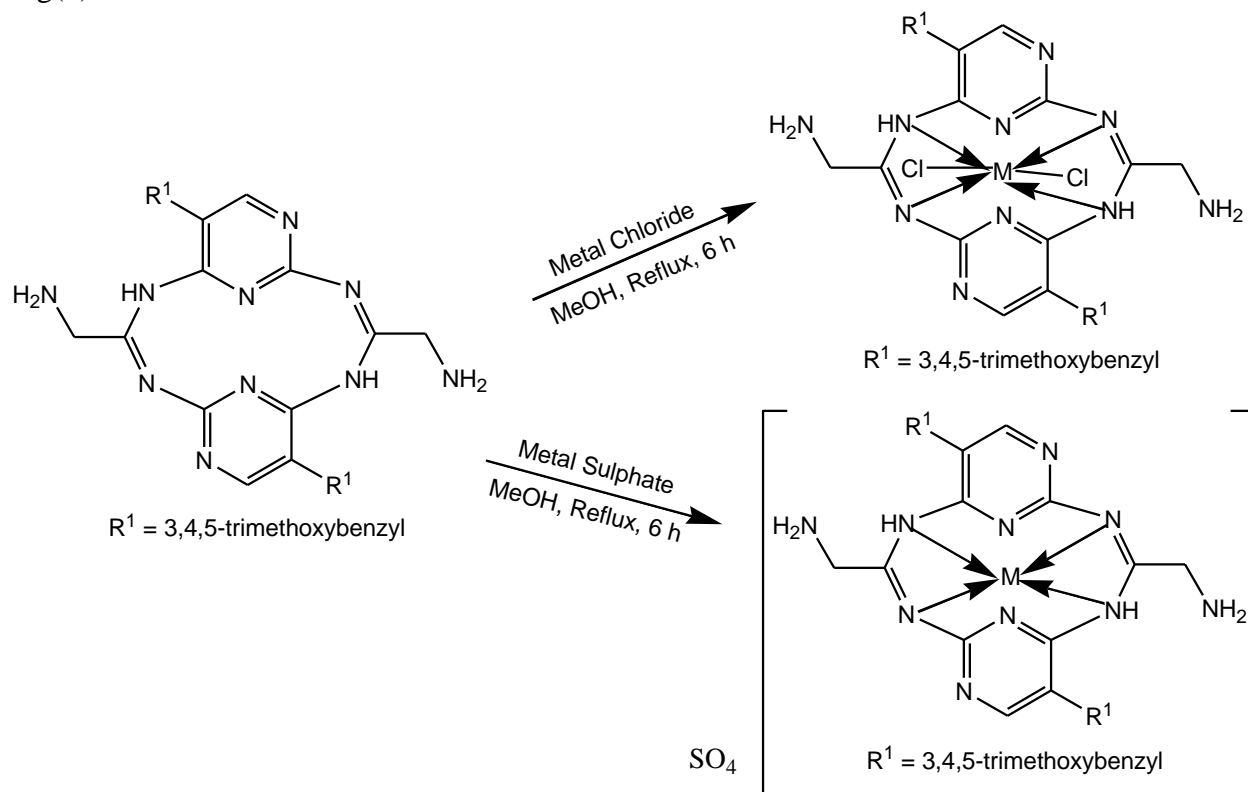
{Cu (L<sub>1</sub>)Cl<sub>2</sub>}: Yield: 88 %; color: green , Anal. Calc. for [Cu(C<sub>32</sub>H<sub>38</sub>N<sub>10</sub>O<sub>6</sub>)Cl<sub>2</sub>] : C, 48.42; H, 4.88; N,17.36. Found: C,48.46; H,4.83; N,17.60. IR (KBr,cm<sup>-1</sup>): 3364  $\gamma$ (NH<sub>2</sub>), 3040 $\gamma$ (NH), 1595 (C= N), 1154  $\gamma$ as(C-C-N), 1595, 959 (pyrimidine ring), 571 (M-N), 348 (M-Cl).  $\Lambda_m/\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ (in CH<sub>3</sub>CN): 40.19.  $\mu_{\text{eff}}$  (300K): 1.95 B.M.

{Cu (L<sub>1</sub>) SO<sub>4</sub>}: Yield: 80 %; color: red orange. Anal. Calc. for [Cu(C<sub>32</sub>H<sub>38</sub>N<sub>10</sub>O<sub>6</sub>)SO<sub>4</sub>] : C,46.80; H,4.59; N,17.10. Found: C,46.97; H,4.68; N,17.12. IR (KBr,cm<sup>-1</sup>): 3403  $\gamma$ (NH<sub>2</sub>), 3035 $\gamma$ (NH), 1589 (C= N), 1130 $\gamma$ as(C-C-N), 1528, 899 (pyrimidine ring), 524 (M-N), 1042 (SO<sub>4</sub>).  $\Lambda_m/\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ (in CH<sub>3</sub>CN): 120.  $\mu_{\text{eff}}$  (300K): 1.26 B.M.

## Results and discussion

The Schiff base macrocyclic complexes were prepared from C<sub>32</sub>H<sub>38</sub>N<sub>10</sub>O<sub>6</sub> in the presence of MX (where M= Mn<sup>II</sup>,Co<sup>II</sup>,Ni<sup>II</sup> and Cu<sup>II</sup> X=Cl<sup>-</sup>,SO<sub>4</sub><sup>2-</sup>) produced a new series of 12-membered

tetradentate macrocyclic metal complexes of the type  $M(L_1)Cl_2$  and  $M(L_1)SO_4$  as shown in Fig(1).



**Fig (1): Proposed structure of metal(II) chloride/sulphatamacrocyclic complexes of  $L_1$**

The resulting colored solids are non-hygroscopic metal derivatives that are stable at room temperature. The molecular weight analysis of these complexes confirms that they are monomeric. In comparison to DMF and DMSO, all of the complexes are only marginally soluble in methanol or ethanol. The complexes' analytical data and calculated values are in good agreement, supporting the suggested composition for each complex.

### Molar conductance

The molar conductance of these macrocyclic complexes of ( $L_1$ ) in acetonitrile were measured and the calculated molar conductance values.

The molar conductivities of the sulphate complexes ( $L_1$ ) in acetonitrile are in the range of 90-130  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$  which is characteristic of 1:1 electrolytes, indicating that the sulphate groups are ionic in nature. The conductivities of the metal chloride complexes are in the range of 20-48  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$  suggest that all of them non-electrolytes (11). The presence of chloride ions is evident only after decomposition of the complexes, probably due to their presence in the coordination sphere.

## IR spectra

The infrared spectra of the ligand are compared with those of the complexes to determine the bonding mode of the ligand to the metal in the complexes. The IR spectrum of the macrocyclic complexes of ligand indicate that the trimethoprim and L- glycine moieties are present. The asymmetric and symmetric stretching vibrations and deformation vibrations of the  $\text{NH}_2$  group of amino acid observe bands at  $3503$  and  $837\text{ cm}^{-1}$  respectively. This clearly shows that primary –  $\text{NH}_2$  group of amino acid do not take part in coordination (12). The free macrocyclic ligand exhibits bands at  $3090$  and  $1640\text{ cm}^{-1}$  which are assigned to N-H modes of the secondary amino group and C=N mode of the imine group respectively (13-15). In all the  $\text{Mn}^{\text{II}}$ ,  $\text{Co}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$  and  $\text{Cu}^{\text{II}}$  macrocyclic complexes secondary N-H and C=N frequency of the compound was decreases to the free ligands in range  $40\text{-}70\text{ cm}^{-1}$  and  $20\text{-}30\text{ cm}^{-1}$ . Thus, the ligand coordinates through secondary amine and imine nitrogens of the macrocyclic ring (16).

There are fairly strong IR spectral bands in the region  $3123$  to  $2965\text{ cm}^{-1}$  due to the C-H and C-N-C stretch of the pyrimidine ring, benzyl aromatic ring and methoxy groups also appear in the spectra of the complexes in the same region indicates that they do not take part in coordination.

The appearance of a new moderately intense band in the region  $543\text{-}506\text{ cm}^{-1}$  assignable to (M-N) further confirms the involvement of nitrogen in coordination (17). In the sulphate complexes a broad band of strong intensity is observed near  $1100\text{ cm}^{-1}$  which is characteristic of uncoordinated  $\text{SO}_4^{2-}$  ion and confirms its presence in the outer sphere of the complex ion (18). In addition to that the frequencies of sulphate appear at  $1100$  and  $625\text{ cm}^{-1}$  respectively without any splitting. It shows tetrahedral symmetry for the sulphate group (19). The frequencies found at  $970$  and  $1042\text{ cm}^{-1}$  which are assigned to aromatic in plane deformation and aromatic out-of-plane ring deformation respectively are not at all affected indicating that ring nitrogens (pyrimidine nitrogens) are no coordinated to the metal ion.

## Magnetic measurements and Electronic spectra

Manganese complex: The magnetic moment of the manganese(II) complex was found to be  $5.9$  B.M., which indicates a high spin ( $d^5$ ) system. The magnetic moment of manganese(II) chloride and sulphate complexes are  $5.83$  B.M and  $5.48$  B.M. So, this may suggest octahedral or tetrahedral coordination for the metal ion (20). The electronic spectra of the manganese(II) chloride complex exhibits to a very weak bands at  $10204\text{ cm}^{-1}$  which are assigned to  ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{G})$  transition. This observation reveal that the stereochemistry of this complex is consistent with six coordinate octahedral geometry. The electronic spectrum of manganese(II) sulphate complex exhibit bands do not show narrow d-d transitions are over shadowed by stronger charge transfer transitions (21,22).

Cobalt complex: The magnetic moment of the cobalt (II) sulphate is 4.42 B.M suggesting tetrahedral (23) and Cobalt(II) chloride register magnetic moment value of 5.14 B.M., which indicates the octahedral geometry (24). The electronic spectra of the Cobalt(II) chloride complex shows three bands at 10193, 11248 and 19763  $\text{cm}^{-1}$  which can be assigned to  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ ,  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$ , and  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$  transitions respectively, in an octahedral geometry (25-27). The electronic spectrum of the Cobalt(II) sulphate complex also found in the range  $18793\text{cm}^{-1}$  in the near infrared region is due to  ${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$  transition. These transitions are characteristic of cobalt(II) sulphate in a tetrahedral environment.

Nickel complex: The magnetic moment of the Nickel (II) sulphate is 3.72 B.M suggesting tetrahedral (28,29) and Nickel(II) chloride register magnetic moment value of 3.10 B.M., which indicates the octahedral geometry (30). The electronic spectra of the Nickel(II) chloride complex shows three bands at 9290, 15548 and 25000  $\text{cm}^{-1}$  which can be assigned to  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}(\text{F})$ ,  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ , and  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$  transitions respectively, in an octahedral geometry (31-33). The electronic spectrum of the Nickel(II) sulphate complex shows absorptions at  $8660\text{cm}^{-1}$  along the peaks at  $14286\text{--}14800\text{cm}^{-1}$  in the visible region which are assignable to  ${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{A}_2$  and  ${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_1(\text{P})$  transitions corresponding to tetrahedral geometry (34,35).

Copper complex: The magnetic moment of the copper (II) chloride complex at room temperature is found to be 1.95 B.M., corresponding to the presence of one unpaired electron which offers the possibility of octahedral geometry (24). The copper (II) sulphate complex exhibits magnetic moment value of 1.26 B.M., indicating one unpaired electron showing paramagnetic character with tetrahedral geometry (36). The electronic spectrum of the copper (II) chloride complex shows a broad band in the range  $12107\text{cm}^{-1}$  in the visible region is due to  ${}^2\text{E}_g - {}^2\text{T}_{2g}$  transition, which is in good agreement with a distorted octahedral geometry for copper (II) ion (37-39). The electronic spectrum of copper (II) sulphate complex shows two electronic absorption bands, a low energy and less intense one at  $10616\text{cm}^{-1}$  and a relatively high energy and less intense at  $14535\text{cm}^{-1}$ . Tetrahedral complexes of copper (II) are known (40) to have a band assigned to  $\text{dx}^2\text{-y}^2\text{-dyz}$  transition has been reported for certain copper (II) complexes with a pseudo tetrahedral geometry.

## NMR spectra

The proton magnetic resonance (41,42) spectra of the ligand  $\text{C}_{32}\text{H}_{38}\text{N}_{10}\text{O}_6$  are recorded in DMSO solvent using TMS as internal standard. The spectral data gives some important information to conclude the formation of ligand. The spectrum shows seven signals which are observed at seven different regions from the TMS. This indicates that there are seven different types of protons.  ${}^1\text{H}$ -NMR spectrum of the macrocyclic ligand displays peaks at  $\delta = 2.0$  (4H, s, -C-CH<sub>2</sub>-);  $\delta = 2.4$  (4H, t, free-NH<sub>2</sub>);  $\delta = 3.7$  (18H, s, -OCH<sub>3</sub>);  $\delta = 5.4$  (2H, s, ring NH);  $\delta = 6.6$  (4H, s, Pyrimidine-CH<sub>2</sub>-Ar);  $\delta = 7.8$  (2H, d, pyrimidine -H);  $\delta = 8.3$  (4H, d, Ar-H) and thus the  ${}^1\text{H}$ -

NMR spectrum confirms the presence of trimethoprim and L-glycine moieties in the macrocyclic condensed product. From the ratio of the intensities of the peak the number of protons can be calculated as 38.

## **Conclusion**

According to the electrical conductance values for the complexes in acetonitrile, the sulphate complexes are ionic in character and the chloride complexes are non-electrolytic. By comparing with the ligand, IR spectral analyses show the complexes' coordination site. The magnetic moments of the complexes show that they are all very paramagnetic in nature and have high spin. The octahedral and tetrahedral geometry of all the complexes is supported by magnetic and electronic spectrum analyses. For the complexes, <sup>1</sup>H-NMR spectral analyses were conducted to determine the mode of coordination suggested by the IR spectrum.

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## **Conflict of Interest**

I hereby declare that all the authors and corresponding authors do not have any conflict of interest.

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