



## Synthesis, Characterization Study of Schiff base Complexes derived from Ampicillin and 4-Hydroxy-3-methoxy benzaldehyde

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### ABSTRACT

Ampicillin is a derived form of penicillin which is semi synthetic  $\beta$ -lactum antibiotic used to treat bladder infections, pneumonia, respiratory infection. Schiff's bases are the most widely studied chelating ligands in coordination chemistry. Recently metal complexes of Schiff bases particularly derived from carbonyl compounds base on hetero-cyclic rings have been the centre of attraction in many areas. Present paper brief the synthesis of AHMBL and its transition metal (II) complexes and also the coordination/characterization studies such as magnetic susceptibility, molar conductance, Electronic spectra, Thermal study, FT-IR, H-NMR, XRD and SEM.

**Keywords:** Schiffbase, Ampicillin, 4-hydroxy, 3-methoxy benzaldehyde, Metal complexes.

### INTRODUCTION

Schiff bases are compounds that are derived by condensation reaction of primary amines with carbonyl groups (Abbas H Abdulasada *et al.*, 2018). Schiff base ligand are 'privileged ligands' and are able to stabilize different metals in various oxidation states. It are extensively studied due to synthetic flexibility, selectivity and sensitivity

towards variety of metal ions. It have application towards, degradation of organic compounds, radiopharmaceuticals and as corrosion inhibitors in especially acidic environments for various alloys and metals like steel, aluminium and copper. Complexes of transition and non-transition metals with Schiff base ligands are promising materials for opto electronic applications due to their outstanding photo and electroluminescent properties and the



case of synthesis that readily allows structural modification for optimization of material properties. Various transition and inner transition metals complexes with bi, tri- and tetradentate Schiff bases containing nitrogen and oxygen donor atoms play important role in biological systems and represent interesting models for metalloenzymes, which efficiently catalyze the reduction of dinitrogen and dioxygen (Mohammed Shakir, 2010). The Schiff base derivatives are infer in the field of optical chemistry and biochemistry. It have been utilized as synthons in the preparation of a number of industrial and biologically active compounds like formazans, 4-thiazolidinines, benzoxazines and so forth, via ring closure, cycloaddition and replacement reaction (Anu Kajal *et al.*, 2013), (Jarrahpur. A *et al.*, 2007).

### Literature review

The articles related to the present study were reviewed for more clearance of the study.

## MATERIALS AND METHODS

### Synthesis of Schiffbase ligand (AHMB)

The synthesis of ligand AHMB held as follows. To an ethanolic solution of Ampicillin (0.05 mol) in alkali medium and 4-hydroxy 3-methoxy benzaldehyde (0.05 mol) in 10 mL ethanolic solution was dropped with constant mixing and heated under reflux for 2 h on a heating mentle at 60°C (Isac Sobana Raj, *et al.*, 2015). Then, the reaction mixture was cooled by pouring it into cool water Fine shinning yellow precipitate of (AHMB) formed was filtered off, washed thoroughly with ethanol-water and stored in a vacuum decicator to dry.

### Synthesis of $[M(AHMB)_2(NO_3)_2]$ complexes

The Schiff base transition metal complexes were synthesized as per the following literature procedure (Issac Sobana Raj *et al.*, 2015). A 0.1 mol of ligand (AHMB) was dissolved in 10 mL of ethanol. To this a solution of 0.05 mol  $M(NO_3)_2 \cdot xH_2O$  (where M = Mn(II), Co(II), Ni(II), Cu(II) and

Zn(II) in 10 mL water, ratio of 2:1 was added drop by drop with constant stirring under relax for 10-12 h in a heating mantle at 60-70°C. The product was cooled by pouring it into cool water. A fine precipitate complexes formed was filtered off and dried.

## Findings and analysis

### Molar conductivity of complexes

Molar conductivity of the transition metal complexes synthesised were measured using a systronic conductivity bridge type 305. Ethanol was the solvent, the observed values in the range 47-63  $ohm^{-1}cm^2mol^{-1}$  are tabulated in the table given below.

**Table 1: Molar conductance of AHMBL ligand and their metal complexes**

S.No.	Denotion of compounds	Molar conductance ( $ohm^{-1} cm^2mol^{-1}$ )
1	AHMBL	-
2	Mn(AHMBL) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	52
3	Co(AHMBL) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	47
4	Ni(AHMBL) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	61
5	Cu(AHMBL) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	56
6	Zn(AHMBL) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	63

Molar conductivity values suggests that those are non-electrolytes

### FT-IR spectra

FT-IR spectroscopy technique was utilized for find the bonding nature of AHMBL and their transition metal complexes. The FT-IR spectrum of (AHMBL) and their metal complexes are shown in Fig. 1-6. The stretching representation was given in the Table 2.

The FT-IR range at 1666  $cm^{-1}$  Schiff base ligand indicates the presence of (C–N) group. In following metal complexes this value varies from 15 to 20  $cm^{-1}$  indicates a strong double bond character of the imine band and the azomethine nitrogen atom has coordination with transition metal ion. This is also confirmed by the intensity band around 462  $cm^{-1}$  assigned to (M–N) vibration.

**Table 2 : FT-IR data for ligand (AHMBL) and their transition metal complexes**

Ligand/Complexes	$V_{C-H}$	$V_{C=C}$	$V_{C=N}$	$V_{S=O}$	$V_{O-H}$ $V_{NO_2}$	$V_{H_2O}$	$V_{N-H}$	$V_{m-N}$	$V_{m-O}$
AHMBL	3062.96	1519.91	1666.50	1381	3332.99	3471	1519		
Mn(AHMBL) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	3093.82	1504.48	1650.79	1357	3341.44	3595	1504	462	586
Co(AHMBL) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	3032.96	1509.81	1648.50	1364	3345.12	3524	1509	455	596
Ni(AHMBL) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	3011.42	1491.71	1652.50	1329	3330.70	3499	1521	431	594
Cu(AHMBL) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	3071.21	1456.91	1653.50	1391	3325.24	3506	1532	462	598
Zn(AHMBL) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	3044.01	1479.12	1647.27	1346	3339.70	3571	1501	432	586

The broad band at  $3332\text{ cm}^{-1}$  of FT-IR shows the stretching frequency of hydroxyl compound. The band ranges from  $3340\text{ cm}^{-1}$ – $3325\text{ cm}^{-1}$  exhibit the non-coordination of  $-\text{H}_2\text{O}$  molecules in metal complexes to the central metal ion. This also proved by the  $\text{M}-\text{O}$  vibrational bands from  $598\text{ cm}^{-1}$ – $586\text{ cm}^{-1}$ .

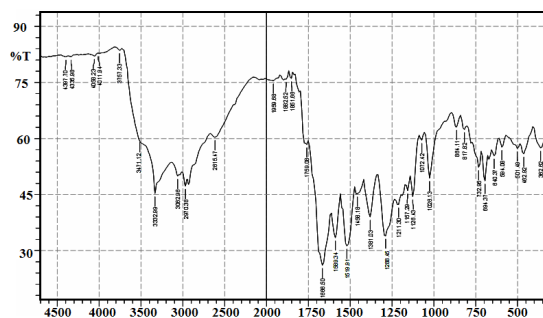


Fig. 1. FT-IR spectrum of the Schiff base ligand (AHMBL)

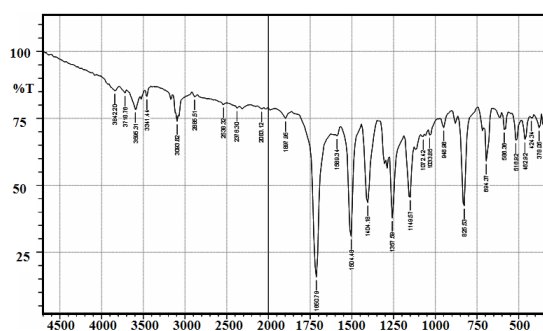


Fig. 2. FT-IR spectrum of the  $[\text{Mn}(\text{AHMBL})_2(\text{NO}_3)_2]$  complex

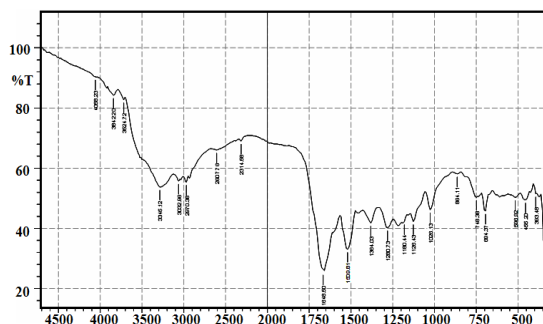


Fig. 3. FT-IR spectrum of the  $[\text{Co}(\text{AHMBL})_2(\text{NO}_3)_2]$  complex

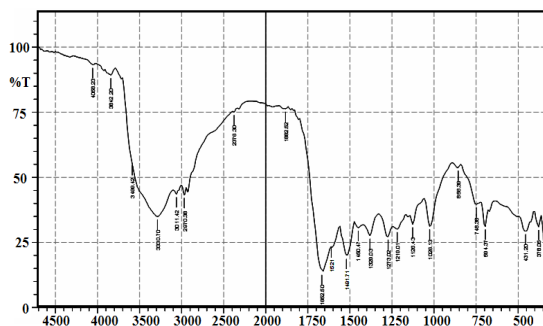


Fig. 4. FT-IR spectrum of the  $[\text{Ni}(\text{AHMBL})_2(\text{NO}_3)_2]$  complex

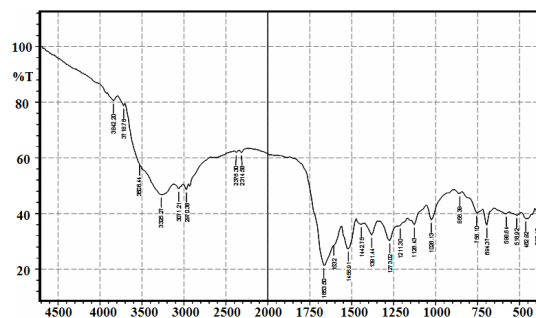


Fig. 5. FT-IR spectrum of the  $[\text{Cu}(\text{AHMBL})_2(\text{NO}_3)_2]$  complex

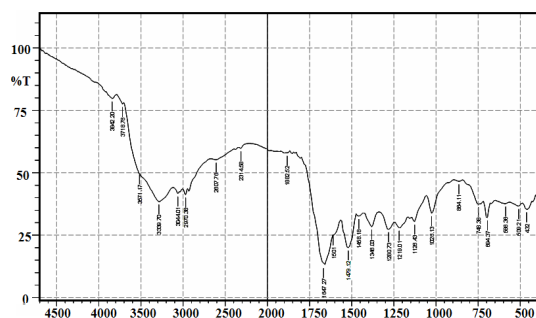


Fig. 6. FT-IR spectrum of the  $[\text{Zn}(\text{AHMBL})_2(\text{NO}_3)_2]$  complex

### Electronic spectra

To find information regarding the coordination geometry, electronic spectra of the synthesised complex were determined with DMF at normal temperature notices and compared with magnetic moment values and parameters. The observed data was given in Table 3. Low intensity absorption bands and low molar extinction belongs to d-d-electron transition.

The colour of synthesised ligand (AHMBL) is yellow and the metal complexes synthesised from the schiff base ligand (AHMBL) are different and also it differ from the corresponding metal ions, it seems the properties of the metal complexes are different from its corresponding metal ions.

The Schiff base ligand (AHMBL) showed two different absorption bands at 251 nm and 330 nm assigned  $(\pi-\pi^*)$  electronic transition and  $(n-\pi^*)$  electronic transition.

In the observation ligand has two absorption bands assigned to  $\pi-\pi^*$  and  $n-\pi^*$  transitions. The spectra of metal complexes also has the same transitions, but they shifted lower and higher frequencies confirming the coordination of ligand with transition metal ions.

**Table 3: Electronic spectral data of ligand (AHMBL) and their complexes**

Ligand/complexes	λ <sub>max</sub> (nm)	Electronic transition	Charge transfer	Geometry
AHMBL	251	π-π*		
	330	n-π*		
Mn(AHMBL) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	272, 314	π-π*	<sup>6</sup> A <sub>1g</sub> → <sup>4</sup> TAg	Octahedral
	414, 502	n-π*	<sup>6</sup> A <sub>1g</sub> → <sup>4</sup> E <sub>g</sub>	
Co(AHMBL) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	312, 347	π-π*	<sup>4</sup> T <sub>1g</sub> → <sup>4</sup> T <sub>2g</sub> (F)	Octahedral
	471, 556, 639	n-π*	<sup>4</sup> T <sub>1g</sub> → <sup>4</sup> A <sub>2g</sub> (F) <sup>4</sup> T <sub>1g</sub> → <sup>4</sup> T <sub>1g</sub> (P)	
Ni(AHMBL) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	269, 352	π-π*	<sup>3</sup> A <sub>2g</sub> (F) → <sup>3</sup> T <sub>2g</sub> (F)	Octahedral
	471, 584, 761	n-π*	<sup>3</sup> A <sub>2g</sub> (F) → <sup>3</sup> T <sub>1g</sub> (F) <sup>3</sup> A <sub>2g</sub> (F) → <sup>3</sup> T <sub>1g</sub> (P)	
Cu(AHMBL) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	287, 366	π-π*	<sup>2</sup> E <sub>g</sub> → <sup>2</sup> T <sub>2g</sub>	Octahedral
	771	n-π*		
Zn(AHMBL) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	264	π-π*	No d-d transition	Octahedral
	363	n-π*		

Metal complex [Mn(AHMBL)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>], showed four absorption bands. Two are of low wavelength shows the presence of (π-π\*) and (n-π\*) transition. The third and fourth are at low intensity and high wavelength region that is 414 nm and 502 nm are attributed to charge transfer which is (<sup>6</sup>A<sub>1g</sub> – <sup>4</sup>A<sub>1g</sub>, <sup>6</sup>A<sub>1g</sub> → <sup>4</sup>E<sub>g</sub>) electronic transitions assumed the complex is high spin octahedral geometry.

The metal complex [Co(AHMBL)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>], showed five absorption bands. Two bands are low wavelength which are in UV-region that is 312nm, 347nm shows (π-π\*), (n-π\*) transitions. The other are in visible region are 417nm, 556nm, 639nm can be assigned the charge transfer of <sup>4</sup>T<sub>1g</sub> → <sup>4</sup>T<sub>2g</sub>(F), <sup>4</sup>T<sub>1g</sub> → <sup>4</sup>A<sub>2g</sub>(F), <sup>4</sup>T<sub>1g</sub> → <sup>4</sup>T<sub>1g</sub>(P). This showed it is octahedral geometry.

The electronic spectrum of [Ni(AHMBL)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>] also showed five bands. Two were in UV-region and the other three in visible region appeared at 417nm, 584nm, 761nm) which showed the charge transfer <sup>3</sup>A<sub>2g</sub>(F) → <sup>3</sup>T<sub>2g</sub>(F), <sup>3</sup>A<sub>2g</sub>(F) → <sup>3</sup>T<sub>1g</sub>(F), <sup>3</sup>A<sub>2g</sub>(F) → <sup>3</sup>T<sub>1g</sub>(P) (d-d) electronic transition. These showed Ni(II) complex showed octahedral geometry.

The Cu(II) complex of synthesised ligand has three electronic spectrum, one with low intensity at 771nm to charge transfer <sup>2</sup>E<sub>g</sub> → <sup>2</sup>T<sub>2g</sub> electronic transition, suggested octahedral geometry.

Electronic spectrum of Zn(II) complex produced only two bands in UV region and there is no absorption in visible region because of completely filled d-orbitals. The geometry of Zn(II) complex is octahedral.

### Magnetic susceptibility measurements

The magnetic susceptibility value of metal complexes synthesised from Schiff base ligand (AHMBL) are given below

**Table 4: Magnetic susceptibility values of metal complexes**

Ligand/complexes	μ <sub>eff</sub> (BM) calculated	μ <sub>eff</sub> (BM) observed
Mn(AHMBL) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	5.41	5.33
Co(AHMBL) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	4.29	4.64
Ni(AHMBL) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	3.06	3.73
Cu(AHMBL) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	1.83	2.11
Zn(AHMBL) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	Diamagnetic	Diamagnetic

The magnetic moment of Mn(II), Co(II) and Ni(II) complexes of ligand shows high spin octahedral geometry. But Cu(II) complex shows low magnetic moment indicates low spin distorted octahedral geometry Zn(II) complex shows zero magnetic moment because of d10 system of electronic configuration.

### <sup>1</sup>H NMR spectra studies

<sup>1</sup>H NMR spectrum of synthesised ligand (AHMBL) and its Zn(II) metal complex were recorded in chloroform solution (CDCl<sub>3</sub>). Tetramethyl silane (TMS) calibrate the chemical shifts of each analyte proton which act as internal standard.

The Fig. 4.8 and 4.9 showed the recorded signals of <sup>1</sup>H NMR spectrum of ligand and metal complexes. In ligand a singlet at δ = 12.12ppm was attributed to hydrogen of Ar(OH) group. A signal at δ = 8.127 ppm showed azomethine proton (N = CH). A strong signal appeared between δ (3-4ppm, 2H) was due to excess phenyl amine group.

The Zn(II) complex was examined and compared with ligand showed Zn(II) complex was shifted downfield compared ligand.

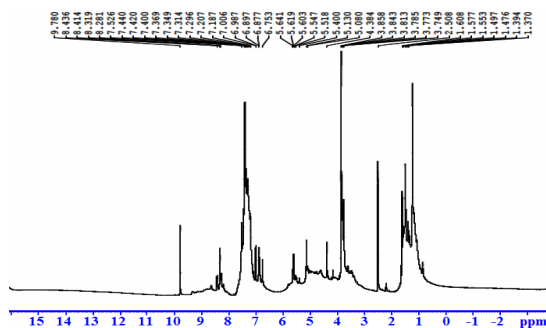


Fig. 7. <sup>1</sup>H NMR spectrum of Schiff base ligand (AHMBL)

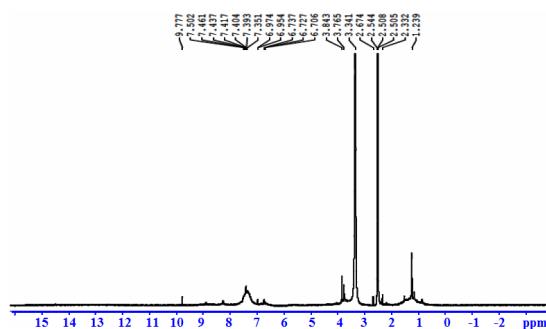


Fig. 8. <sup>1</sup>H NMR spectrum of [Zn(AHMBL)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>] complex

From the data, the structure of coordinated metal complex compounds prepared from ligand (AHMBL) is shown in Figure.

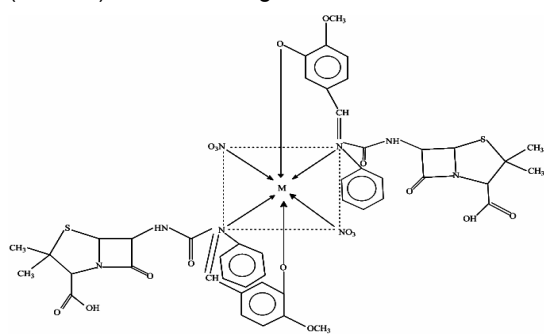


Fig. 9. Structure of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complex of schiff base ligand (AHMBL)

### XRD Analysis

X-ray diffraction gives information about crystallographic structure, chemical composition and physical properties of materials. Examined value of powder XRD for the ligand (AHMBL) and its metal complex [Cu(AHMBL)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>] data are listed in table 5 and 6. The graphical representation showed feeble peaks for ligand which explains the microcrystalline nature of the sample and also the strong peak

indicates the complex formation. Scherrer's equation is used to determine the size of crystals in the form of powder.

$$\tau = \frac{K\lambda}{\beta \cos\theta}$$

Where  $\tau$ -particle size,  $K = 0.9$  (shape factor),  $\lambda$  - X-ray wavelength,  $\beta$  - line broadening at half the maximum intensity,  $\theta$  - Bragg angle.

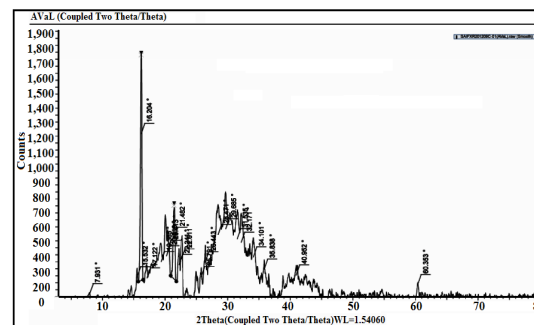


Fig. 10. Diffractogram of Schiff base ligand (AHMBL)

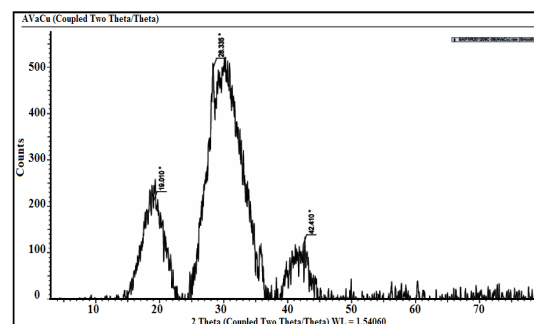


Fig. 11. Diffractogram of [Cu(AHMBL)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>] complex

### SEM Analysis

SEM (Scanning Electron Microscopy) investigate a wide range of materials for surface fractures, flaws, corrosion or contaminants. It gives magnified images of the sample's surface topography. The SEM images of ligand (AHMBL) and Ni(II) complex are shown in Figure 12 and 13.

The figure showed the ligand look like cheese structure and metal complex looks gravel like structure.

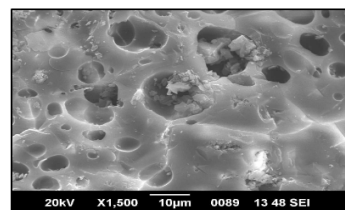


Fig. 12. SEM pattern of ligand (AHMBL)

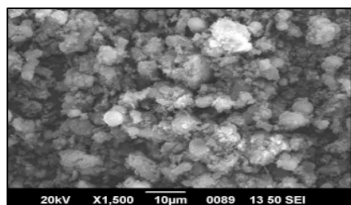


Fig. 13. SEM pattern of metal complex

### CONCLUSION

The Schiff base ligand AHMB synthesised from Ampicillin and 4-hydroxy, 3-methoxy benzaldehyde. And Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) metal complexes were derived from AHMBL. They were characterized by following physico-chemical methods. FTIR, UV-Vis, <sup>1</sup>HNMR spectroscopy, molar

conductivity, magnetic moment data. The XRD and SEM analysis support to find the size and morphology of ligand and metal complexes. They were also recommended to study their biological activity for the pharmacological appliances.

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### Conflict to interest

The authors declare that they have no conflict of interest.

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