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PREPARATION, CHARACTERIZATION AND ANTIMICROBIAL ACTIVITIES OF SOME TRANSITION METAL COMPLEXES WITH 4-HYDROXYPYRIDINE AND NITRITE ION

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ABSTRACT

By the irradiation of microwave, transition metal complexes of zinc, cadmium and mercury were prepared with the ligands 4–hydroxypyridine (4-HP) and Nitrite ion $(NO_2)^-$ .These complexes were studied for metal estimation, electrical conductance, CHN analysis, IR, electronic and NMR spectra. All the synthesized complexes were studied and screened for antibacterial and antifungal activities in detail.

KEYWORDS: **Microwave, 4-hydroxypyridine, Nitrite, Antibacterial, Antifungal**

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INTRODUCTION

Microwave assisted synthesis is a fast emerging field in synthesizing compounds. It reduces both the amount of solvent used in the synthesis and reaction time[1]. The reactions in MW field take place 10 to 100 times more rapidly than the reactions in the non MW fields. Moreover, higher or comparable yields are frequently reported[2]. That is why these complexes were synthesized using MW field. The applications and contributions of complexes prepared in this way have shown to establish equilibrium with the ecosystem[3]. The Zn(II), Cd(II) and Hg(II) complexes of 4–hydroxypyridine (4-HP) and NO_2^- ion have their impact on nature[4]. Thus, the study of these complexes by metal estimation, CHN analysis, electrical conductance, IR, electronic and NMR spectra gives its characteristic values. Further, they were screened for antibacterial and antifungal activities.

MATERIALS AND METHODS

AnalaR grade metal nitrate and metal chloride were purchased. The solvents used viz., DMSO, acetonitrite, methanol, ethanol were also of AnalaR grade and used as such. 4–hydroxypyridine was purchased from Alfa Aesar company.

INSTRUMENTAL ANALYSIS

Elemenator Vario ELIII was used for elemental analysis. A digital conductivity bridge (Equiptronics, EQ660) at 30°C in acetonitrile medium (10^{-3}M) was used to measure the electrical conductivity. Perkin Elmer Spectrum R X I (4000 – 400 cm^{-1}) was used for IR spectral study with KBr pellet technique. Varian Cary 5000 (175 – 800nm) was used to record the electronic spectra by diffused reflection method . Bruker AVIII (500 MHz FT NMR) with TMS as internal standard was used for ^1H and ^{13}C NMR spectral study. Using agar well diffusion method antibacterial and antifungal activities were screened.

SYNTHESIS OF THE COMPLEXES

Zinc nitrate, cadmium nitrate and mercury chloride in methanol medium lg each (3.33 mmol, 3.22 mmol, 3.64 mmol) and 0.63g, 0.61g, 0.69g, (6.63mmol, 6.42 mmol, 7.26 mmol) respectively with 4 – hydroxypyridine were irradiated in microoven for about 10 seconds. Then, sodium nitrite of 0.47g, 0.45g, 0.51g (6.70 mmol, 6.46 mmol, 7.30 mmol) was added and the mixture was irradiated for about 10 seconds in a micro oven. The complexes formed were filtered, washed with ethanol and dried. The metal estimation, CHN analysis and electrical conductance were done.

Table 1
Analytical data of the complexes

S. No.	Complexes	Colour	Yield %	C %	H %	N %	Metal %	Conductance (Ohm^{-1} cm^2 mol^{-1})
1.	$[Zn(4HP)_2(NO_2)_2]$	Colourless	55.2	34.53 (34.55)	2.87 (2.89)	16.09 (16.11)	18.79 (18.81)	70.80
2.	$[Cd(4HP)_2(NO_2)_2]$	Colourless	48.6	30.44 (30.46)	2.53 (2.55)	14.17 (14.19)	28.46 (28.48)	69.00
3.	$[Hg(4HP)_2(NO_2)_2]$	Colourless	54.7	24.85 (24.87)	2.06 (2.08)	11.58 (11.60)	41.52 (41.54)	86.50

Theoretical values are given in parenthesis.

RESULTS AND DISCUSSION

The percentage yield of Zn(II), Cd(II) and Hg(II) complexes was 55.2, 48.6 and 54.7 respectively. The low electrical conductance values indicate that the complexes were non electrolytes[5] , as shown in Table 1.

IR SPECTRA

The IR Spectra of the ligand 4-HP show absorption peaks at 3644 cm^{-1} for OH, 3060 cm^{-1} for C-H in aromatic ring, 1521 cm^{-1} for C=N and 1637cm^{-1} for C=C. These peaks shifted respectively in complexes confirming the ligands entry into the coordination sphere[6-8]. It was recorded that for zinc complex the OH peak shifted to 3440cm^{-1}, in C-H aromatic the peak shifted to 2926cm^{-1}, in C=N, the peak shifted to 1479cm^{-1}, and in C=C the peak moved to 1636cm^{-1} [9-11]. The values of NO_2 group band in Zn(II), Cd(II) and Hg(II) complexes have also shifted to 746 cm^{-1}, 889 cm^{-1} and 801 cm^{-1} respectively. The M–N values of 519 cm^{-1}, 529 cm^{-1} and 517 cm^{-1} further show the entry of ligands into the coordination sphere[12]. Table 2, Figure 1 and Figure 2.

Table 2
IR spectral data of the ligand and its complexes (cm^{-1})

S.No	Compound	–OH	C – H Aromatic ring	C = N	C – N	C = C	M – N	NO_2
1	4-HP	3644	3060	1521	1377	1637	-	-
2	$[Zn(4HP)_2(NO_2)_2]$	3440	2926	1479	1391	1636	519	746
3	$[Cd(4HP)_2(NO_2)_2]$	3430	2858	1443	1296	1660	529	889
4	$[Hg(4HP)_2(NO_2)_2]$	3441	2963	1394	1261	1626	517	801

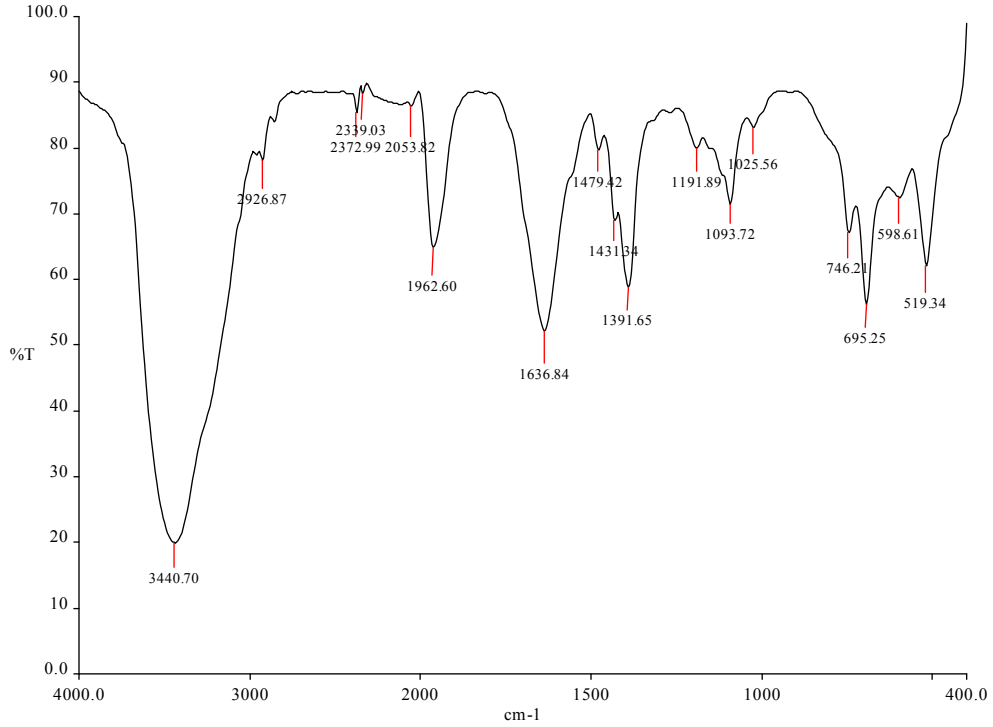

Figure 1
IR spectrum of zinc(II) complex.

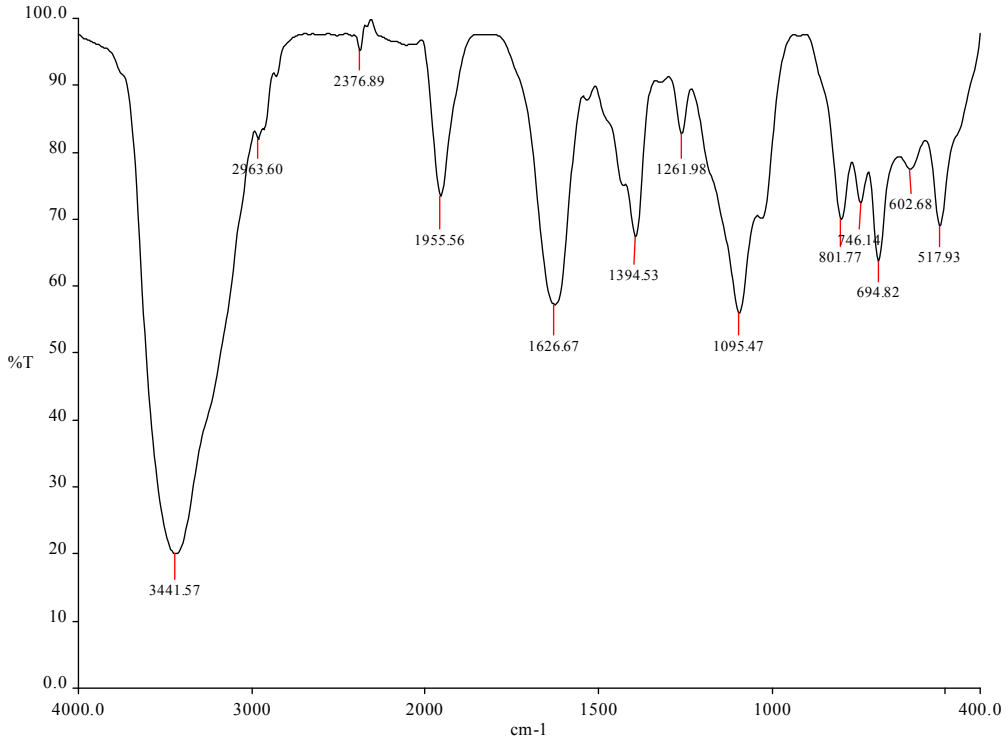

Figure 2
IR spectrum of mercury(II) complex.

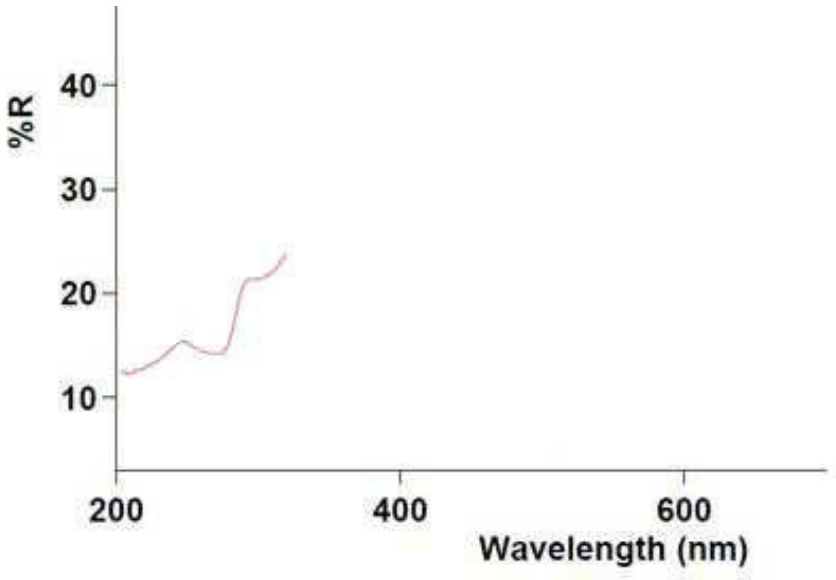

Figure 3
Electronic spectrum of zinc(II) complex.

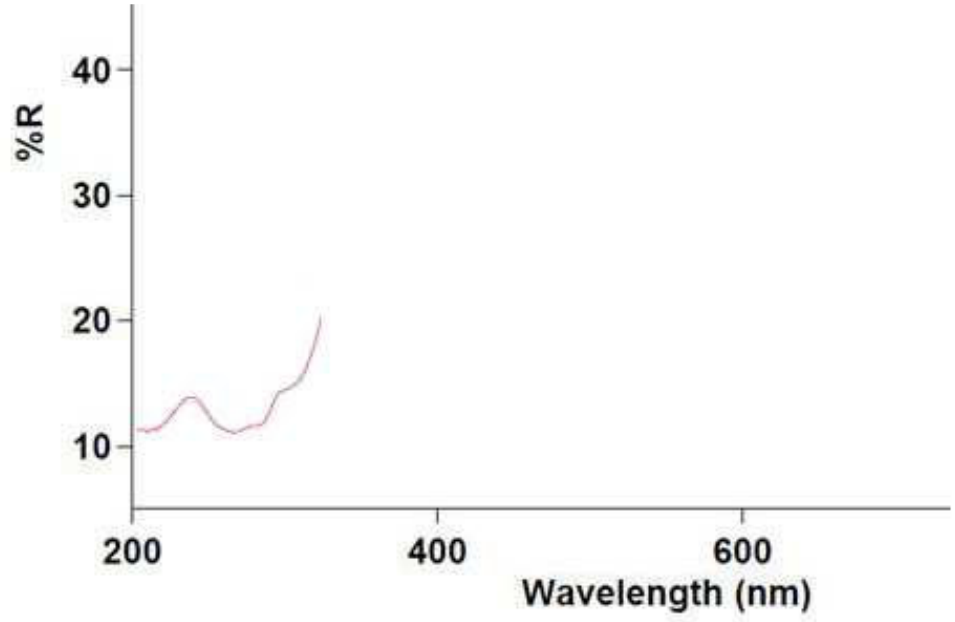

Figure 4
Electronic spectrum of cadmium(II) complex.

ELECTRONIC SPECTRA

The electronic spectra of Zn(II), Cd(II) and Hg(II) complexes gave λ max values at 310nm, 309nm and 312nm respectively. This suggests the coordination of ligand with the metal ions. The electronic spectra of d^{10} elements generally consist of ligand to metal / metal to ligand (LMCT/MLCT)[13-15]. The suggested structure for these four coordinated are pseudotetrahedral. Table 3, Figure 3 and Figure 4.

Table 3
Electronic spectral data of complexes

S.No	Complex	λ max (nm)	Assignment	Probable geometry
1	$[Zn(4\text{-}HP)_2(NO_2)_2]$	310	Charge Transfer	Square planar
2	$[Cd(4\text{-}HP)_2(NO_2)_2]$	309	Charge Transfer	pseudotetrahedral
3	$[Hg(4\text{-}HP)_2(NO_2)_2]$	312	Charge Transfer	pseudotetrahedral

^{1}H NMR SPECTRA

^{1}H NMR spectra for the ligand 4-HP and the complexes were recorded. For the ligand 4-HP, a peak at δ 6.22 – 6.24 shows aromatic H, δ 7.70 for phenolic hydrogen and δ 2.50 for H – C = N. A slight shift in these values for complexes confirms the coordination of the ligand with metal ion[16,17]. Table 4, Figure 5 and Figure 6.

Table 4
^{1}H NMR spectral data for the compounds in (δ) ppm

S.No	Compound	Phenolic – OH	Aromatic H	H – C = N
1	4-HP	7.70	6.22 – 6.24	2.50
2	$[Zn(4\text{-}HP)_2(NO_2)_2]$	7.96 – 7.98	6.56 – 6.57	2.50
3	$[Cd(4\text{-}HP)_2(NO_2)_2]$	7.66	6.13	2.50
4	$[Hg(4\text{-}HP)_2(NO_2)_2]$	7.70 – 7.71	6.20 – 6.21	2.50

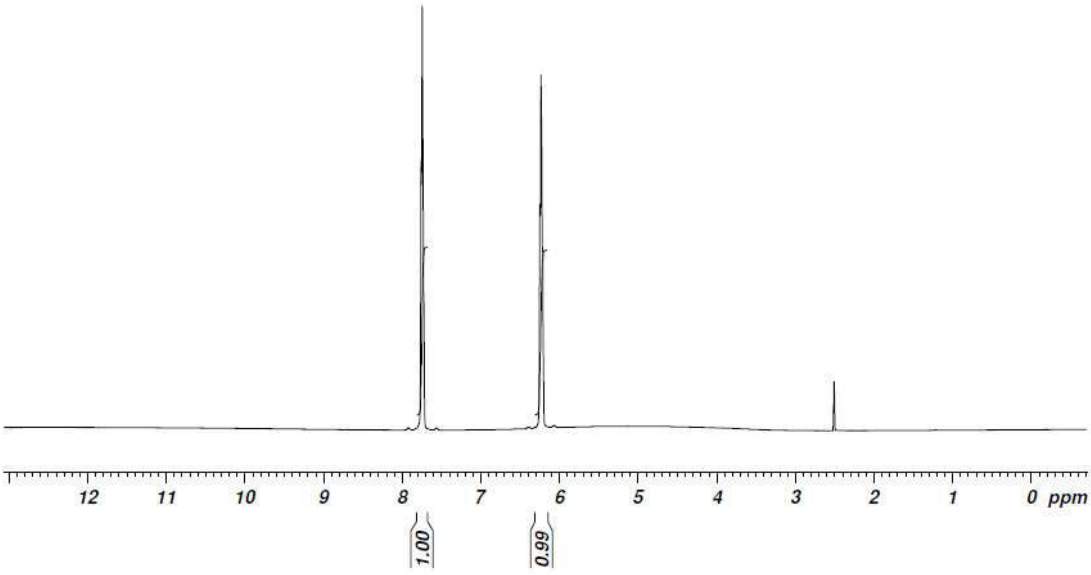

Figure 5
^{1}H NMR spectrum of 4-HP

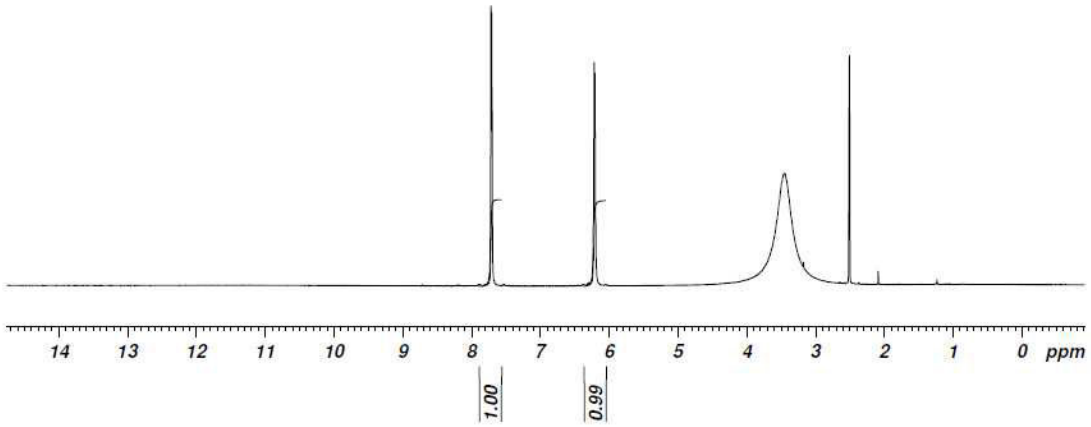

Figure 6
^{1}H NMR spectrum of mercury complex

^{13}C NMR SPECTRA

When compared with the ligand 4-HP, the ^{13}C NMR δ values undergo little shift in the complexes, confirming the complex formation [18]. Table 5, Figure 7 and Figure 8.

Table 5
^{13}C NMR spectral data for the compounds in ppm

S.No	Compound	Aromatic C	C = N	C – OH
1	4-HP	116.00 – 140.00	39.39 – 40.39	116.68
2	$[Zn(4\text{-}HP)_2(NO_2)_2]$	116.00 – 142.00	39.17 – 40.18	116.36
3	$[Cd(4\text{-}HP)_2(NO_2)_2]$	117.00 – 138.00	39.30 – 40.30	117.58
4	$[Hg(4\text{-}HP)_2(NO_2)_2]$	116.00 – 141.00	39.45 – 40.46	116.63

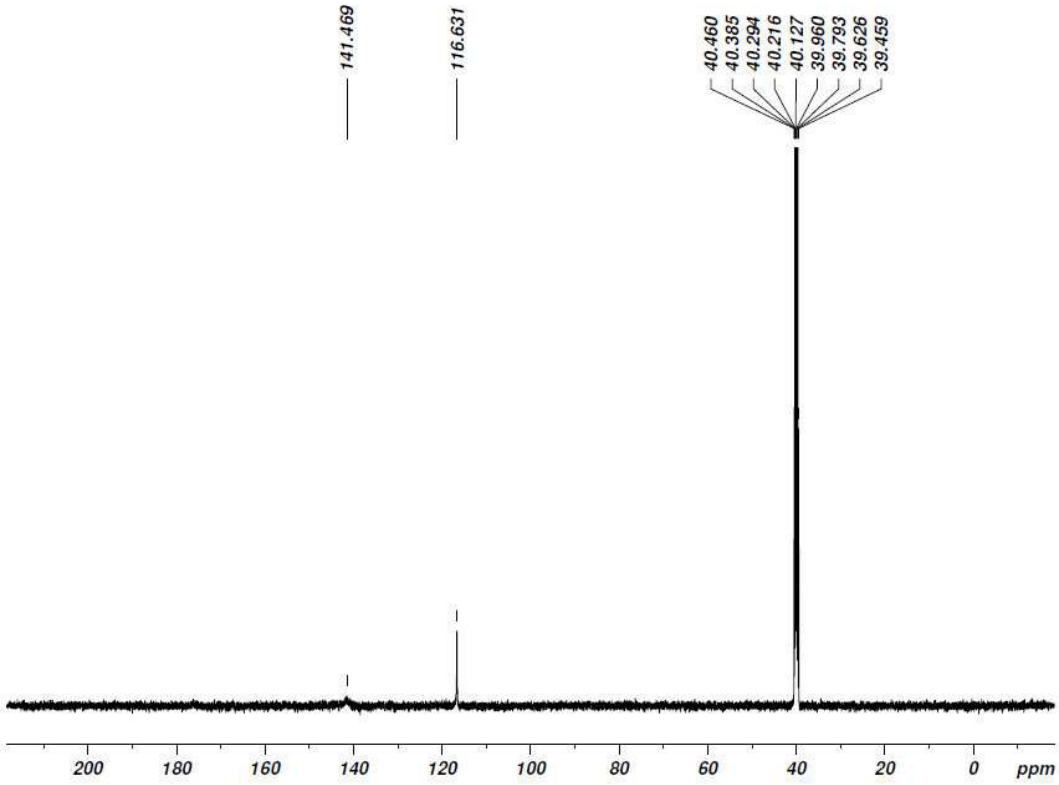

Figure 7
^{13}C NMR spectrum of mercury complex

ANTIMICROBIAL ACTIVITY

The ligand 4-HP is active against *Escherichia coli* and *Aspergillus flavus.* The mercury complex is highly active against *Klebseilla pnemoniae* and the two fungi *Aspergillus Niger* and *Aspergillus flavus* . Remaining complexes are moderately active against these two bacteria and fungi. This may be due to the absorption of zinc and cadmium by the microorganisms for their metabolic activity either induced or normal which were reported earlier[19–22]. Table 6.

Table 6
Antimicrobial Activities of ligand and complexes with standards (mm)

S.No	Compounds	*Escherichia coli*	*Klebseilla pnemoniae*	*Aspergilles Niger*	*Aspergillus Flavus*
1	4-HP	25	-	-	10
2	$[Zn(4\text{-}HP)_2(NO_2)_2]$	5	-	20	20
3	$[Cd(4\text{-}HP)_2(NO_2)_2]$	11	5	-	10
4	$[Hg(4HP)_2(NO_2)_2]$	14	20	40	28
5	Ampicillin	25	5	-	-
6	Fluconozole	-	-	25	20

CONCLUSION

The synthesized complexes are $[Zn\ (4\text{-}HP)_2\ (NO_2)_2]$, $[Cd\ (4\text{-}HP)_2\ (NO_2)_2]$ and $[Hg\ (4\text{-}HP)_2\ (NO_2)_2]$ The formation of these complexes were confirmed by analytical, IR, UV – visible, ^{1}H NMR, and ^{13}C NMR spectral data. The probable geometries for these complexes are square planar for zinc complex and pseudotetrahedral for cadmium and mercury complex. All the complexes were found to be potentially active towards *Escherichia coli, Klebseilla pnemoniae,*

Aspergillus Niger and *Aspergillus Flavus* with reference to the standard.

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Conflict of Interest

Conflict of declared none.

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