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Synthesis, Structural Studies and Antimicrobial Activities of Zinc (II), Cadmium (II) and Mercury (II) Complexes Containing 4 – Hydroxypyridine and Azide Ion as Ligands

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Abstract

Microwave irradiation was used to prepare Zn(II), Cd(II) and Hg(II) complexes with 4– hydroxypyridine (4-HP) and azide ion as ligands. The structures of these complexes were arrived on the basis of metal estimation, elemental analysis, conductivity measurement and spectral data. All the complexes and the ligand 4-HP were screened for their antimicrobial activities.

Keywords: 4 – hydroxypyridine, microwave, azide, antimicrobial.

Introduction

4–hydroxypyridine and its derivatives act as important ligands[1-4]. In recent years, a significant number of research work is being carried out with 4–hydroxypyridine as ligand[5]. They have wide range of applications in pharmaceutical and organic synthesis[6,7]. Many aromatic nucleophilic substitutions with 4–hydroxypyridine result in varied number of compounds[8]. Considering the various antimicrobial activities of heterocyclic compounds, 4–hydroxypyridine contemplates and contributes to the synthesis of many metal complexes with antimicrobial activities[9–11].

Material and Methods

Metal nitrates, sodium azide and solvents viz., DMSO, acetonitrile, methanol and ethanol used in the experiments were of AnalaR grade. They were used without further purification. 4–hydroxypyridine was purchased from Alfa Aesar company and used as such.

Instrumental Analyses: For the complexes prepared, the elemental analysis was carried out using Elementar Vario EL III CHNS analyzer. The electrical conductivity measurements were carried out in acetonitrile medium (10^{-3} M) using a digital conductivity bridge (Equiptronics, EQ660) at 30°C. The IR spectra were recorded using Perkin Elmer Spectrum R X I with the rage of 4000 – 400 cm^{-1} range based on KBr pellet technique. The UV- Visible spectra were recorded using Varian Cary 5000 ranging 200 – 800 nm by solid state diffused reflectance method. The ^{1}H NMR and ^{13}C NMR spectra were recorded in DMSO using Bruker AV III 500 MHz FT NMR Spectrometer. The antimicrobial studies of 4–hydroxypyridine and the complexes were done by using agar well diffusion method.

Synthesis of metal complexes: A mixture of metal (II) nitrate, chloride, viz., $Zn(NO_3)_2.6H_2O$, $Cd(NO_3)_2.4H_2O$ and $HgCl_2$ in methanol lg each, (3.33, 3.22 and 3.64 mmol respectively) with 4 – hydroxypyridine, 0.63g, 0.61g, 0.69g (6.63, 6.42, 7.26 mmol) was irradiated in a microwave oven for about 10 seconds. Then sodium azide weighing 0.43g, 0.42g, and 0.47g (6.62, 6.46, 7.23 mmol respectively) in about 20ml ethanol was added and the mixture was irradiated for about 10 seconds. The precipitated complexes were filtered, washed with ethanol, dried and kept in air tight containers. The complexes thus prepared were studied for their metal estimation, elemental analysis and electrical conductance data, to arrive at the formulae of the complexes. The electrical conductance values show that the nature of the complexes is non electrolyte[12] as show in table-1, figure-1.

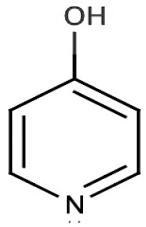

Figure-1
4 - hydroxypyridine

Results and Discussion

IR Spectra: The IR spectral data of 4–hydroxypyridine (4-HP) and metal complexes are given in Table-2. For 4-HP the band at 3640 cm^{-1} corresponds to phenolic (–OH) group which is slightly shifted in the complexes confirming the entry of 4-HP into the coordination sphere[13]. Azide ion in complexes show asymmetric stretching at 2089cm^{-1} and the symmetric stretching at 1350cm^{-1}. These frequency values shift to 10-15cm^{-1} of positive and negative shift, which confirms azide ion entry into the coordination sphere[13]. Further the IR spectra of the

complexes exhibit new bands 593 to 535 cm^{-1} attributed to M–N. The IR spectra of zinc and mercury complexes are shown in figure-2 and figure-3.

Electronic Spectral Studies: The metal ions in the zinc(II), cadmium(II) and mercury(II) complexes have d^{10} electronic configuration[14]. The electronic spectra of these three complexes show charge transfer transition at 302 nm, 310 nm and 311 nm respectively, table-3, figure-4 and figure-5.

^{1}H – NMR Spectra: The ^{1}H NMR spectrum of the ligand 4- HP was recorded in DMSO[15,16]. The H^{1}NMR spectroscopy was used for the confirmation of the bonding of ligand with the metal ions. The ^{1}H NMR spectrum of 4-HP in DMSO a multiplet at δ 6.22-6.24 due to aromatic proton, the values for phenolic proton are seen at δ 7.73-7.76 and for N=C-H the values at δ 2.5. In the complexes these values are shifted. As show in table-4, figure-6.

^{13}C – NMR Spectra: In the ligand 4-HP the δ value for the aromatic carbon appeared in 116 – 140 ppm which to 150 ppm, in the Cd(II) complex and the frequency of the value of C–OH 116.68 ppm has also shifted to 116.83 ppm.

In N=C the value of 39.39–40.39 ppm was shifted to 39.38–40.38 ppm[17,18]. This shows the entry of 4 - HP in the coordination sphere. Similar results arrived at for zinc and mercury complexes as shown in table-5, figure- 7.

Antimicrobial Activity: Antimicrobial studies were carried out by dissolving the ligand and complexes in DMSO[19,20]. Ampicillin and fluconozole were used as standards. The zones of inhibitions are shown in mm. The results indicate that the complexes have moderate antibacterial activity when compared to the ligand 4-HP and they have high antifungal activity table-6.

Table-1
Analytical data of the complexes

S. No	Complexes	Colour	Yield %	Percentage				Electrical conductance Ohm^{-1} cm^2 mol^{-1}
				C	H	N	Metal	
1.	$[Zn (4\text{-}HP)_2 (N_3)_2]$	Colourless	56.6	35.33 (35.36)	2.94 (2.96)	32.97 (32.99)	19.23 (19.25)	62.60
2.	$[Cd (4\text{-}HP)_2 (N_3)_2]$	Colourless	49.7	31.04 (31.06)	2.58 (2.60)	28.96 (28.98)	29.06 (29.07)	74.60
3.	$[Hg (4\text{-}HP)_2 (N_3)_2]$	Colourless	40.5	25.27 (25.29)	2.11 (2.12)	23.57 (23.59)	42.22 (42.24)	78.30

Theoretical values are given in parenthesis

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

S.No.	Ligand / Complex	γ(– OH)	γ(C – H)	γ(C = C)	γ(M – N)	γ(N_3)
1.	4-HP	3644	3060	1637	-	-
2.	$[Zn (4\text{-}HP)_2 (N_3)_2]$	3441	2926	1638	534	2101
3.	$[Cd (4\text{-}HP)_2 (N_3)_2]$	3441	2936	1625	557	2098
4.	$[Hg (4\text{-}HP)_2 (N_3)_2]$	3442	2932	1611	592	2079

Table-3
Electronic spectral data of the complexes (nm)

S.No.	Complex	λ Max (nm)	Assignment	Probable Geometry
1.	$[Zn (4\text{-}HP)_2 (N_3)_2]$	302	Charge Transfer	Square Planar
2.	$[Cd (4\text{-}HP)_2 (N_3)_2]$	310	Charge Transfer	Pseudodetrahedral
3.	$[Hg (4\text{-}HP)_2 (N_3)_2]$	311	Charge Transfer	Pseudodetrahedral

Table-4
^{1}H – NMR Spectral data of the ligand and cadmium complex (δ)

S.No.	Compound	Aromatic – H	Phenolic – OH	N = C – H	N – C – H
1.	4-HP	6.22 – 6.24	7.73 – 7.73	2.50	-
2.	$[Cd (4\text{-}HP)_2 (N_3)_2]$	6.31 – 6.36	7.83	3.44	3.16

Table-5
^{13}C – NMR spectral data of the ligand and cadmium complex (ppm)

S.No.	Compound	Aromatic carbons	C – OH	N = C	N – C
1.	4-HP	116.00 – 140.00	116.68	40.39	39.39
2.	$[Cd (4\text{-}HP)_2(N_3)_2]$	150.00	116.83	40.38	39.38

Table-6
Antimicrobial activities data (mm)

S.No.	Compound	*Escherichia coli*	*Bacillus subtilis*	*Aspergillus flavus*
1.	4-HP	25	10	10
2.	$[Zn (4\text{-}HP)_2 (N_3)_2]$	10	22	35
3.	$[Cd (4\text{-}HP)_2 (N_3)_2]$	10	-	40
4.	$[Hg (4\text{-}HP)_2 (N_3)_2]$	15	20	25
5.	Ampicillin	25	15	-
6.	Fluconozole	-	-	20

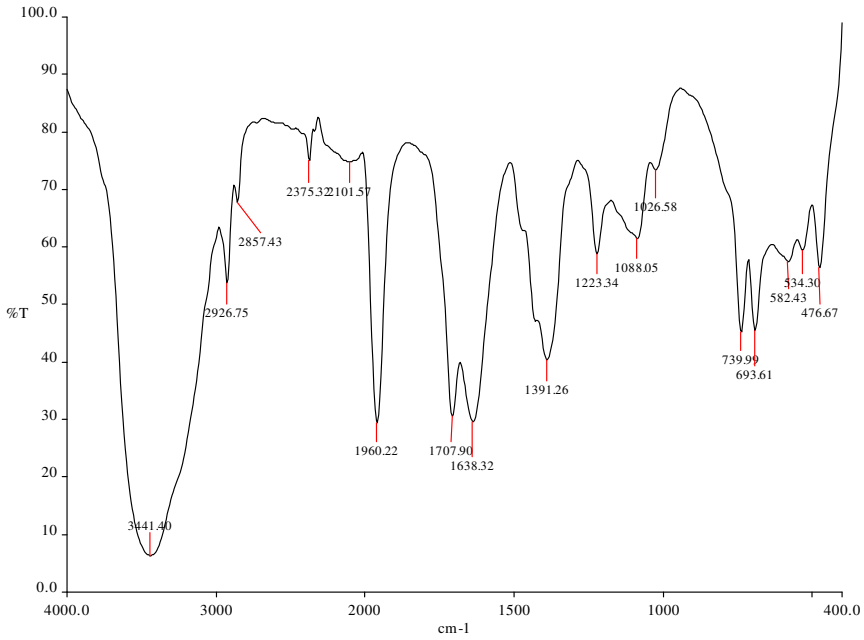

Figure-2
IR spectrum of zinc complex

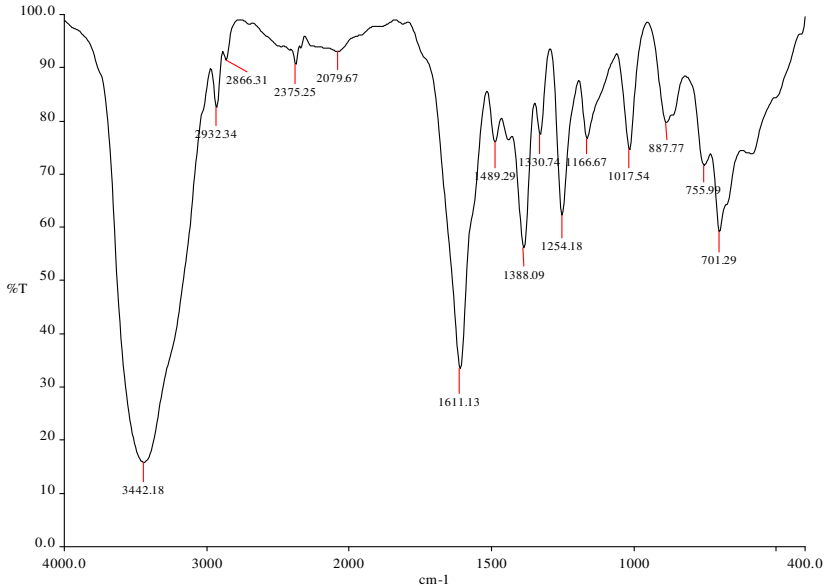

Figure-3
IR spectrum of mercury complex

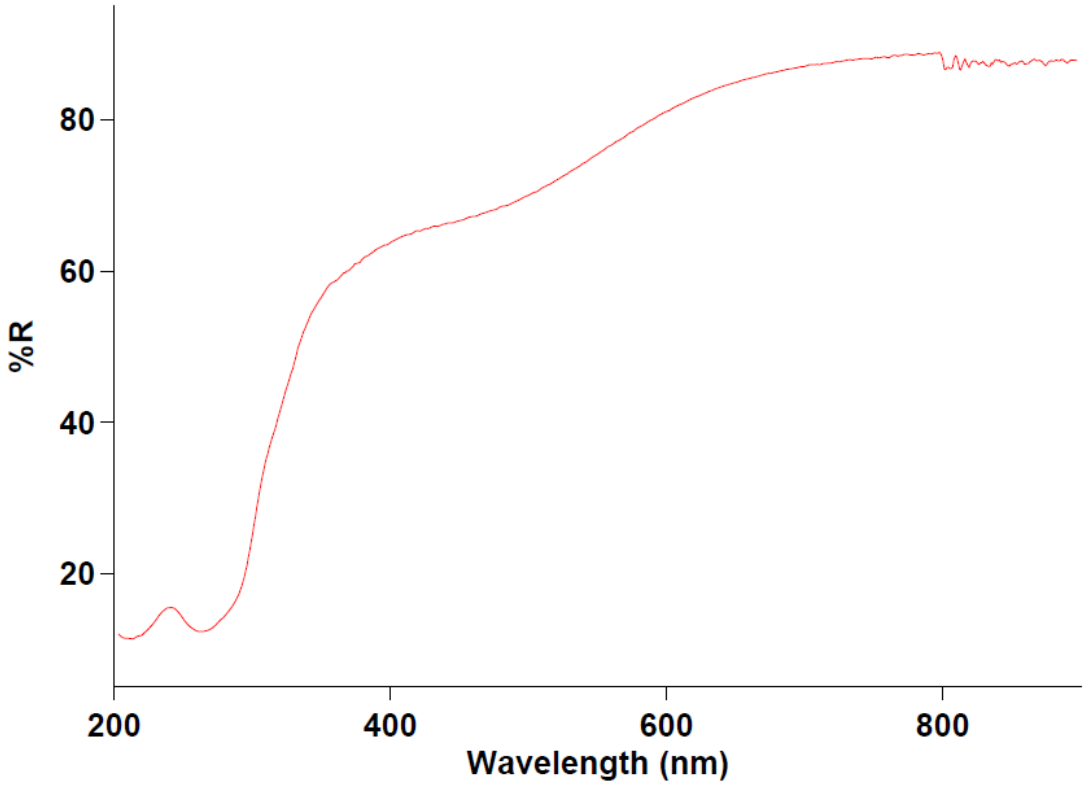

Figure-4
UV-Visible spectrum of cadmium complex

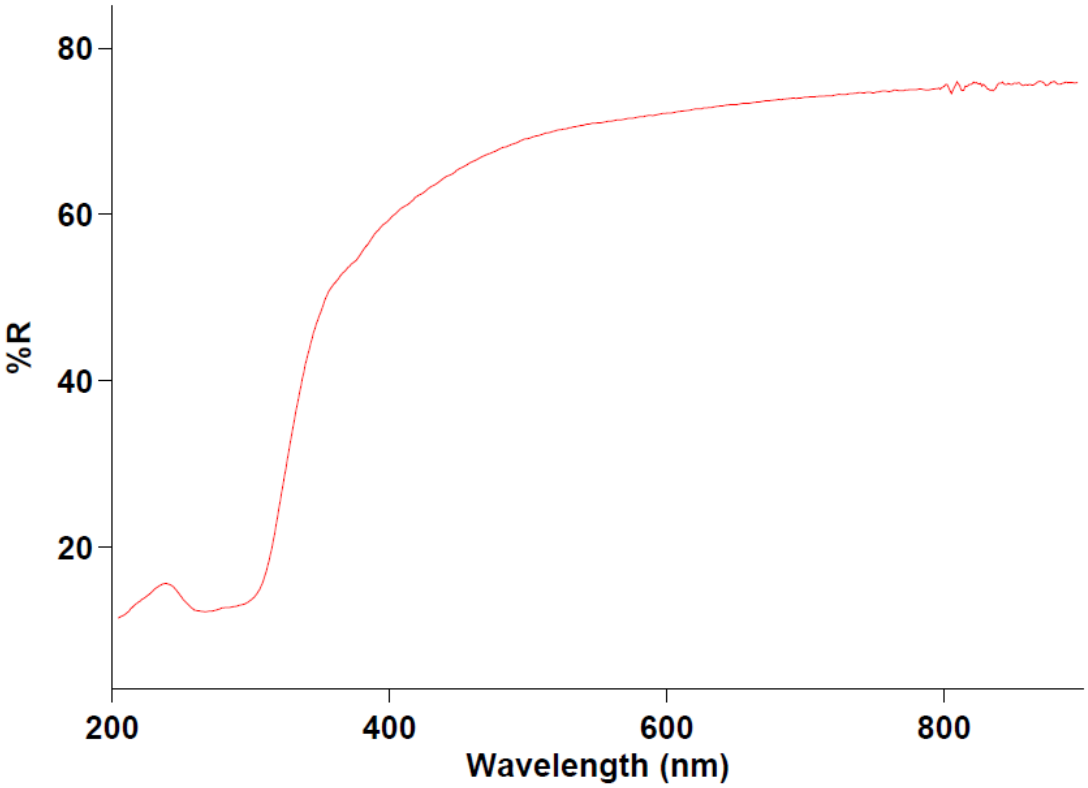

Figure-5
UV-Visible spectrum of mercury complex

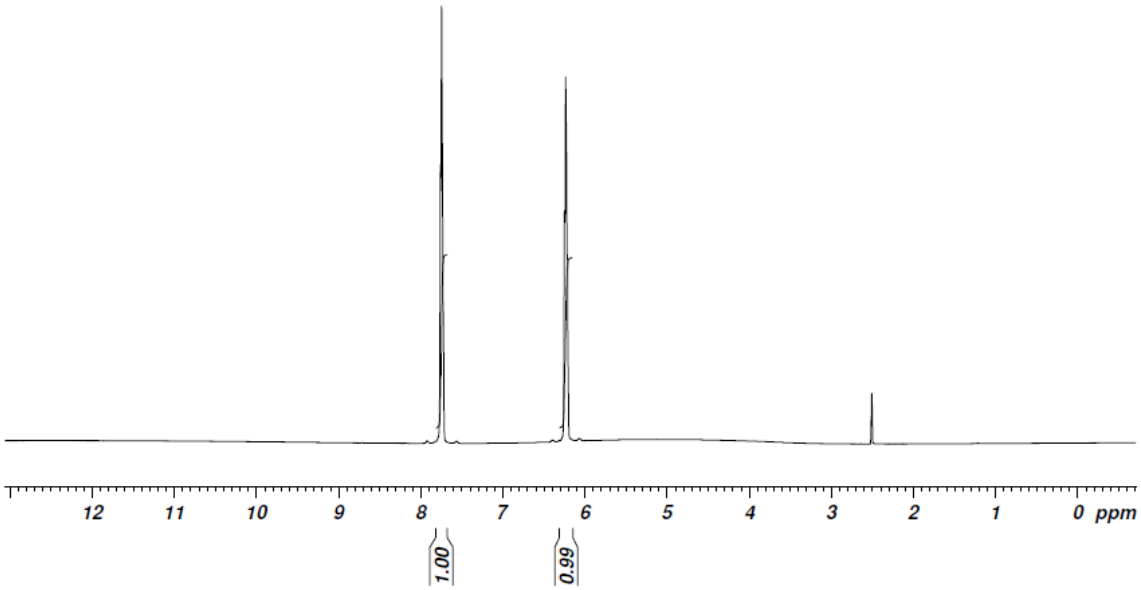

Figure-6
^{1}H NMR spectrum of 4-HP

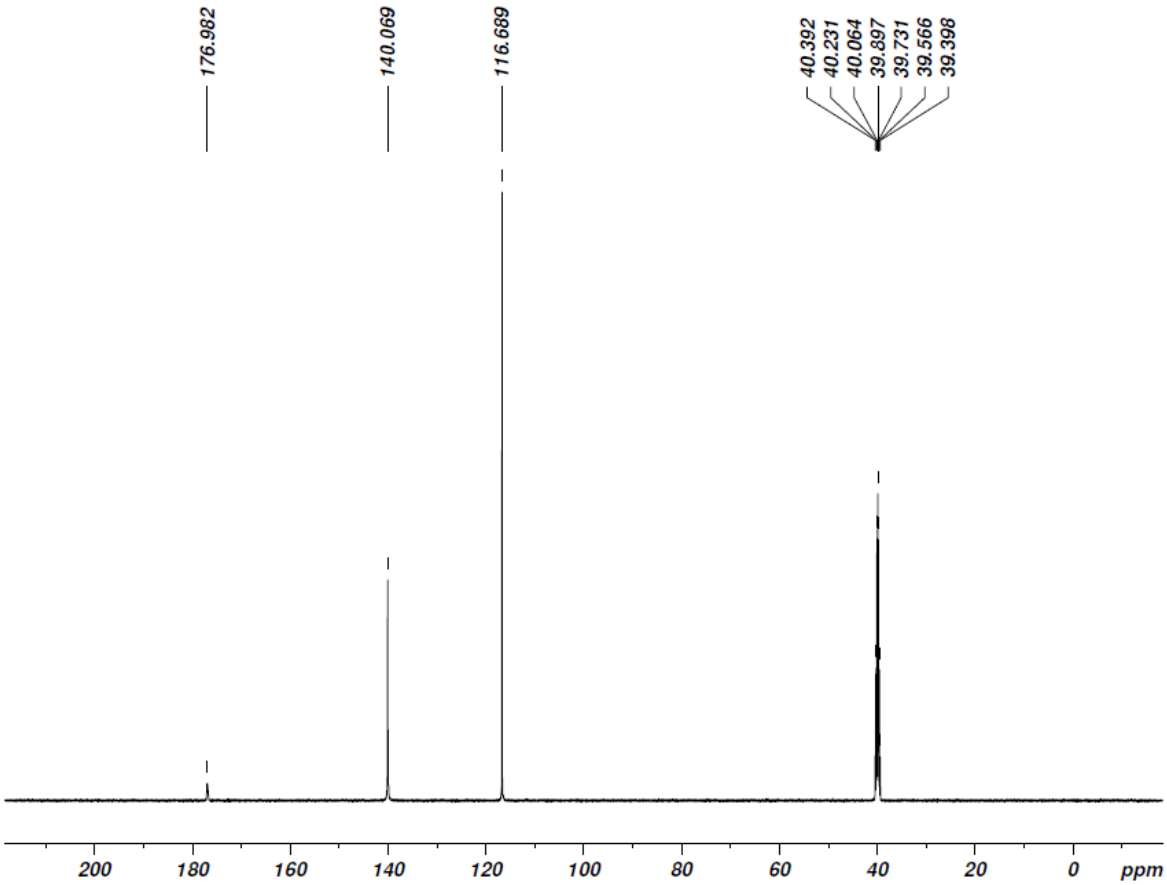

Figure-7
^{13}C NMR spectrum of 4-HP

Conclusion

Three complexes of Zn(II), Cd(II) and Hg(II) with 4–hydroxypyridine and azide ion as ligands were synthesized and their properties were characterized. From the results of metal estimation, elemental analysis, conductivity measurements, IR, UV–visible and NMR spectral data the formulae of the complexes are found to be $[Zn(4\text{-}HP)_2(N_3)_2]$, $[Cd(4\text{-}HP)_2(N_3)_2]$ and $[Hg(4\text{-}HP)_2(N_3)_2]$ and the structure of the complexes are square planar for zinc(II) complex and pseudotetrahedral for cadmium(II) and mercury(II) complexes. The antimicrobial study on these complexes show moderate activity against bacteria and high activity against fungus, when compared to the free ligand 4-HP.

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