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Spectroscopic, Thermal and Biological Studies of Zn(II), Cd(II) and Hg(II) Complexes Derived from 3-Aminopyridine and Nitrite Ion

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ABSTRACT. Microwave assisted syntheses of Zn(II), Cd(II) and Hg(II) complexes with 3-aminopyridine (3AP) and nitrite (NO_2^-) ions have been reported. The metal complexes were characterized by elemental analyses, molar conductance, IR, Far-IR, electronic, NMR (^1H, ^{13}C), thermal and electron impact mass spectral studies. The spectroscopic studies reveal the composition, the nature of nitrite ligand in the complexes, electronic transitions, chemical environments of C and H atoms thermal degradation of the complexes. On the basis of characterization data, distorted tetrahedral geometry is suggested for Zn(II), Cd(II) and Hg(II) complexes. The organic ligand (3AP) and their metal complexes were screened against gram negative pathogenic bacteria and fungi in vitro. The results are compared with our previous report *J. Korean Chem. Soc.* **2013**, *57*, 341 on 4-aminopyridine and nitrite ion complexes of the same metal ions.

Key words: 3-Aminopyridine, Nitro complex, Mixed ligand complexes, Biological activities

INTRODUCTION

Transition metal complexes have attracted attentions of inorganic, metallo-organic as well as bio-inorganic chemists because of their extensive applications in wide ranging areas from material to biological sciences,[1] for e.g., as vulcanization agents, protector for painting, catalysts, antioxidants and pharmaceuticals.[2] Several metal complexes are known to accelerate the drug action and also therapeutically important viz., platinum (anticancer), silver (antimicrobial), gold (antiarthritic), bismuth (antiulcer), antimony (antiprotozoal), vanadium (antidiabatic), iron (antimalarial) and chromium (antidiabetic), nickel, copper (antitumor), cadmium and mercury (antibacterial). Metal ions have the tendency to bind and interact with biological molecules like proteins and DNA. The efficacy of the various organic therapeutic agents can often be enhanced upon coordination with a suitable metal ion.[3] The pharmacological activity of metal complexes is highly dependent on the nature of the metal ions and the donor sequence of the ligands because different ligands exhibit different biological properties.[4] Metal complexes containing oxygen donor ligands as a primary ligand and heteroaromatic N-bases as an auxiliary ligand have been of special interest as they can display exceptionally high stability.[5] The heterocyclic compounds, containing N-donor ligand system like 3-aminopyridine (3AP), play a significant role in many biological systems, being a component of several vitamins and drugs.[6,7] Pyridine derivatives are widely applied in medicine as anticancer,[8] anti-hypertension and antifungal agents.[9]

Metal complexes of pyridine derivatives have also been successfully used as model systems for the design of new metallo-pharmaceutical compounds.[10] It has been found that metals like copper and zinc bound to ligand containing oxygen and nitrogen show enhanced property of antihypertensive drugs, antimalarial, antimicrobial, electron transfer or any type of oxygen transport reaction.[11–15] The number of metalloproteins which need zinc ions to stabilize their structure and to allow their function is increasing in the order: members of oxidoreductase < hydrolase – ligase < lyase family[16] and Cu/Zn superoxide dismutase[17] are among the several hundred zinc-proteins presents in our body.

The present study deals with the synthesis, spectral characterization (IR, Far-IR, electronic, NMR and mass), thermal (DSC/TGA) and microbial activities (antibacterial and antifungal) of mixed ligand metal complexes of Zn(II), Cd(II) and Hg(II) derived from 3AP and nitrite ions as a part of our ongoing research on the syntheses, characterizations and biological activity studies of aminopyridine based metal complexes in our lab.[18]

EXPERIMENTAL

All the chemicals used were of AR grade from Sigma – Aldrich Company and were used as received. Ethanol was distilled over calcium oxide before use. Microwave irradiations were used for the complex preparation from domestic microwave oven (model IFB-25 PG 1S) at 900W power for 10 seconds.

Synthesis of Zn(II), Cd(II) and Hg(II) Complexes (1, 2 and 3)

A warm ethanolic solution (20 ml) of zinc nitrate hexahydrate $Zn(NO_3)_2.6H_2O$ (0.29 g, 1 mmol)/cadmium nitrate tetrahydrate,$Cd(NO_3)_2.4H_2O$ (0.21g,1mmol/mercuric nitrate monohydrate, $Hg(NO_3)_2.H_2O$ (0.35 g, 1 mmol) were mixed together with warm ethanolic solution (20 ml) of 3AP (0.19 g, 2 mmol) with constant stirring. The resulting solution was then treated with an ethanolic suspensions of sodium nitrite (0.13g, 2 mmol) with continuous stirring. After keeping the mother liquor for few hours, the corresponding complexes **1**, **2** and **3** were separated out, which were filtered, washed with cold ethanol and dried in a vacuum desiccator over anhydrous calcium chloride.

$$M(NO_3)_2.XH_2O + 2(3AP) + 2NaNO_2 \rightarrow [M(3AP)_2(NO_2)_2] + 2NaNO_3 + XH_2O$$

Where, M = Zn(II), Cd(II) and Hg(II); 3AP = 3-aminopyridine

Physical Measurements

Elemental analyses (carbon, hydrogen and nitrogen) were analyzed using Elementar Vario EL III (Germany) model analyzer. The metal content was estimated by volumetric and Atomic Absorption Spectrometry. Molar conductance were measured in DMF on the Equiptronics, digital conductivity meter, (Model EQ-660), where the cell constant was calibrated with 0.1 M KCl solution and DMF was used as the solvent. The IR Spectra (4000 – 400 cm^{-1}) were taken at 27 ºC using Perkin Elmer spectrometer, model Spectrum X1 in KBr disc and Far-IR spectra were taken at 27 ºC using FT-IR Thermo Nicolet (model 6700) spectrometer in which polyethylene was used as calibrant. The electronic spectra were recorded by the diffused reflectance technique[19] on Varian Cary (model 5000) Spectrophotometer. The ^1H NMR and ^{13}C NMR spectra of the organic ligand and the complexes were recorded in d_6- DMSO on a BRUKER 500 MHz spectrometer at room temperature using TMS as an internal reference. The thermal measurements were performed using universal $V_{4.5A}$ Thermal Analyzer Instruments (SDTQ 600 $V_{20.5}$ Build 15). The DSC and TGA curves were obtained by placing the samples in small open platinum pans with a heating rate of 10 ºC/min and a nitrogen (purity above 99.99%) flow rate of 50 ml/min. All samples were heated from 0 ºC to 1000 ºC. Electron impact mass spectra were recorded on JOEL GC mate mass spectrometer.

Microbial Studies

Cultures of phytopathogenic (Gram-negative) bacteria such as *Raoultella planticola* (MTCC, 2272), *Shigella flexineri* (MTCC, 1457) and *Pseudomonas aeruginosa* (MTCC, 1688) and fungi such as *Aspergillus niger* (MTCC, 961) and *Candida albicans* (MTCC, 183) were procured from Microbial type culture collection and gene bank, Chandigarh, India and maintained on slants of Potato Dextrose Agar (PDA) and Nutrient Agar (NA) media.

Antibacterial Studies

The antibacterial and antifungal activities of the ligands (3AP and nitrite ions) and their complexes have been studied by well diffusion technique[20] and Agar plate technique[21] respectively. The antibacterial activities of the ligand (3AP) and its metal complexes against test bacteria *R. planticola*, *S. flexineri* and *P. aeruginosa* at different concentrations were checked by well diffusion technique. Twenty milliliters of sterilized nutrient agar (NA) media was poured in each pettri-dish. After solidification 0.1 ml of test bacteria spreads over the medium using a spreader. The test compounds in measured quantities were dissolved in DMF to get concentrations of 100, 75, 50 and 25 μgml^{-1}. Using sterile cork borer (6 mm in diameter), four holes were made in each dish, then tested compounds dissolved in DMF were poured into these holes. Finally, the dishes were incubated at 37 ºC for 24 h where clear or inhibition zones detected around each hole. DMF was used as a control and streptomycin used as a standard drug under the same conditions for each organism and by subtracting the diameter of inhibition zone resulting with DMF from that obtained in each case, the antibacterial activities can be calculated as a mean of three replicates.

Antifungal Studies

Aspergillus niger and *Candida albicans* fungi were used as the test organism for which the growth inhibition capacity of the free ligands ($NaNO_2$ and 3AP) and its complexes have been screened. According to the agar plate technique, the compounds were directly mixed to the DMF in different (400, 200, 100 μgml^{-1}) concentrations. The discs measuring

5 mm in diameter were prepared from Whatman No.1 filter paper sterilized by dry heat at 140 ºC for 1 h. The sterilized discs were soaked with the fungus and were placed on the medium with the help of the inoculum needle. The discs were inverted and kept in an incubator at 27 ºC for 72 h. The inhibation zones thus formed was measured (in mm) after 72 h. Chlorothalonil used as commercial fungicide and DMF served as control. The growth of fungus was measured by the recording the diameter of fungal colony.

RESULTS AND DISCUSSION

All the metal complexes are stable under room temperature. The complexes are soluble in DMF and DMSO. On the basis of elemental analyses, the complexes were found to have the composition as shown in *Table* 1. The molar conductivity values for the mixed ligand complexes in DMF solvent (1.0×10^{-3} M) were in the range (19.7–22.4) Ω^{-1} cm^2 mol^{-1} which assigned to be non-electrolytic nature.[22]

IR and Far-IR Spectra

The IR spectral frequency of the ligands and their metal complexes are given in *Fig.* 1. The IR spectral evidence concerning the aromatic character of the 3AP summarized.[23,24] The most typical IR frequency bands of 3AP in this study correspond to skeleton vibrations at 1586, 1486, 1439 cm^{-1} and out of plane frequencies at 800 and 706 cm^{-1}. 3AP has two nitrogen atoms, each having lone pair electrons to donate. It is well known that when amino nitrogen atom involved in coordination, a drastic red shift will be observed in NH_2 stretching vibrations ($\Delta = 150 - 200$ cm^{-1}).[25,26] Since red shift is not observed in NH_2 stretching vibrations, it is concluded that amino group nitrogen of 3AP does not involve coordination in all the complexes studied like in the case of 4-aminopyridine (4AP) in our previous work.[18]

The pyridine skeleton bands in complexes **1**, **2** and **3** appeared at 1378, 1380 and 1389 cm^{-1} respectively. The

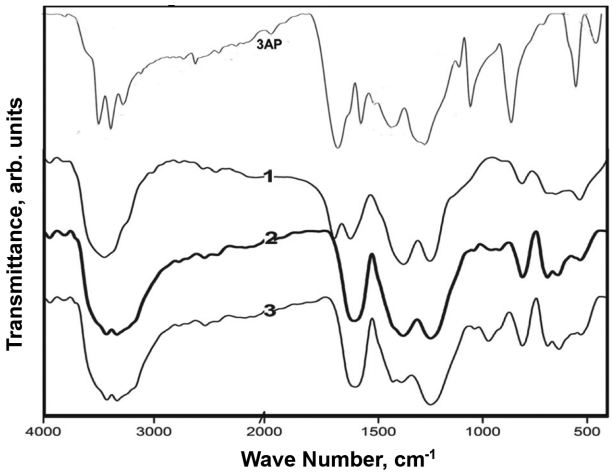

***Figure* 1.** IR Spectra of 3AP, **1**, **2** and **3**.

$\upsilon_a NH_2$ and $\upsilon_s NH_2$ bands for complex **1** appeared at 3448 cm^{-1} as broad; in complex **2** at 3428, 3334 cm^{-1} and in complex **3** at 3425 and 3332 cm^{-1}, respectively. The out of plane peak γC–H observed for complexes **1**, **2** and **3** at 811,809 and 810 cm^{-1}; The δNH_2 band for complexes **1**, **2** and **3** appeared at 1633, 1612 and 1609 cm^{-1}, respectively. The υ_a N=O, υ_s N–O and ν_b N–O bands of nitrite ion displayed its bands in complex **1** at 1378,1253 and 811 cm^{-1}; In complex **2** which were appeared at 1380, 1250 and 809 cm^{-1} and in complex **3**, the same group frequency of bands observed at 1389, 1250 and 810 cm^{-1}, respectively. The ring breathing mode of the complexes **1**, **2** and **3** are observed at 909, 920 and 972 cm^{-1}. This mode is known to be very sensitive to co-ordination of pyridine ring from endocyclic nitrogen lone pairs and increases in wave number on the co-ordination strength.[27,28] Thus, it is concluded that nitrogen of the pyridine ring is involved in the coordination of all the complexes studied.

The nitrite group has three fundamental modes at 1358, 1262 and 838 cm^{-1} which are all active with infrared region. Upon coordination, the band positions are shifted as com-

***Table* 1.** Elemental analyses and molar conductance of 3AP and the complexes

Complex	Molecular Weight (g/mol)	Colour	Yield %	Elemental content Found (Calcd.), %				Λm (Ω^{-1}cm^2 mol^{-1})
				M	C	H	N	
$C_5H_6N_2$ (3AP)	94.0	Pale brown	–	–	63.45 (63.83)	6.32 (6.83)	29.76 (29.78)	–
$[Zn(3AP)_2(NO_2)_2]$ $ZnC_{10}H_{12}N_6O_4$	345.4	Pale yellow	74	18.86 (18.92)	34.64 (34.76)	3.41 (3.47)	24.29 (24.32)	17.3
$[Cd(3AP)_2(NO_2)_2]$ $CdC_{10}H_{12}N_6O_4$	392.4	Dirty White	68	28.57 (28.64)	30.62 (30.58)	3.10 (3.05)	21.34 (21.40)	15.9
$[Hg(3AP)_2(NO_2)_2]$ $HgC_{10}H_{12}N_6O_4$	480.6	White	72	41.62 (41.73)	24.85 (24.96)	2.47 (2.49)	17.51 (17.47)	23.4

pared to the free nitrite ion frequencies. The shift exhibited by the asymmetric and symmetric stretching frequencies are used to indicate the mode of bonding of the nitrite group, whether it is coordinated through nitrogen atom (nitro) complex or through the oxygen atom (nitrito) complex.[29,30] In general, the wagging mode for nitro complexes appears approximately at 640 cm^{-1}. The waging mode is observed at 640±10 cm^{-1} for complexes **1**, **2** and **3** which confirms the complexes **1**, **2** and **3** are nitro in nature. It is interesting to note here that in our previous work, no wagging mode of NO_2 was observed due to the O-coordination to the metal ions, in which only the position of the amino group was different from the present study.[18] In the nitro complexes, ν_a NO_2 lies at higher and ν_s NO_2 at lower values than the free ion frequencies. The N–O bending band appears in the region between 850 and 750 cm^{-1}.[31] The absorption band, observed at 500–560 cm^{-1} can be attributed to ν(M–N).[32] The ν(M–N) stretching frequency is also expected in the range of 230-290 cm^{-1} in Far-IR spectra.[33]

Electronic Spectra

The electronic spectra of the complexes **1–3** are shown in *Fig.* 2; these complexes do not show any characteristic bands due to central metal ion like our previous study of 4AP complexes.[18] Compared with 4AP complexes, the π→π* transition of the pyridine ring and n→π* transition of the "–N=O" of the complex show increase in wave length.[35] These two transitions appear as two distinct peaks; this must be due to the position of the amino group and nature of the nitrite ligand, i.e., nitro. Note that $–NO_2$ group contains delocalized π bond on O–N–O σ bond and this might be the reason for the increase in wave length.

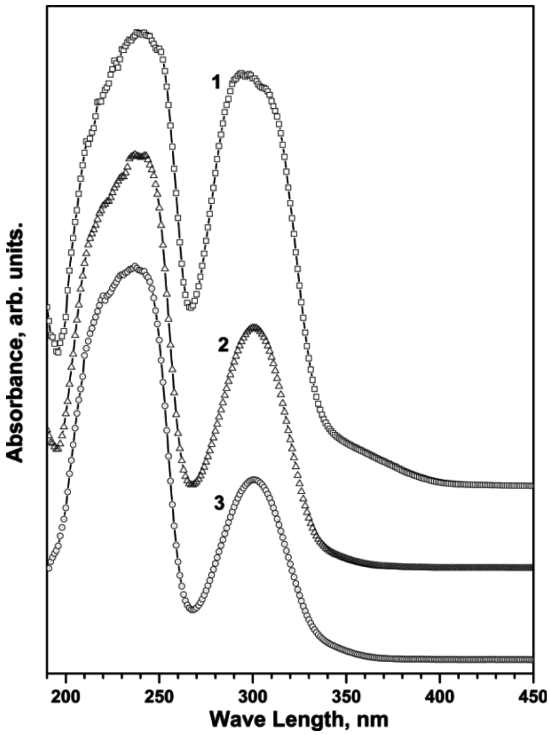

***Figure* 2.** Electronic spectra of the complexes **1**, **2** and **3**.

***Table* 2.** ^{1}H NMR chemical shifts (δ ppm^{-1})[a], complexation shifts (Δδ ppm^{-1})[b,c] and H–H coupling constants (J_{HH}/H_Z)[d] in the mixed ligand metal complexes

Compound		3AP	1	2	3
H-2	δ	8.00	7.86	7.88	7.88
	J_{HH}	(d)	7.85(d)	Broadened	7.87(d)
	Δδ		−0.14	−0.12	−0.12
H-4	δ	6.98	7.07	6.97	6.96
	J_{HH}	(q)	7.05(q)	6.95(d)	6.94(q)
	Δδ		0.09	−0.01	−0.02
H-5	δ	7.06	7.18	7.09	7.08
	J_{HH}	(q)	7.15(q)	7.06(q)	7.05(q)
	Δδ		0.12	0.03	0.02
H-6	δ	7.99	7.63	7.67	7.67
	J_{HH}	(d)	7.62 (d)	7.66(d)	7.66(d)
	Δδ		−0.36	−0.32	−0.32
H-(NH_2)	δ	5.59	5.59	5.42	5.40
	J_{HH}	(s)	(s)	(s)	(s)
	Δδ				

[a]Referred to TMS in DMSO solutions.
[b]Complexation shifts are defined as the difference of proton chemical shifts between the complex and parent molecule.
[c]Sign(+) denotes deshielding effect, while(−) denotes shielding effect.
[d]Digital resolution ± 0.30 Hz; (s) singlet, (d) doublet, (q) quartet.

***Table* 3**. ^{13}C NMR chemical shifts (δ ppm^{-1})[a] and complexation shifts (Δδ ppm^{-1})[b,c] in the mixed ligand metal complexes

Compound		3AP[d]	1	2	3
C-2	δ	139.8	136.4	137.1	137.1
	Δδ		−3.4	−2.7	−2.7
C-4	δ	123.6	125.1	124.5	124.5
	Δδ		1.5	0.9	0.9
C-5	δ	121.3	122.1	121.1	120.9
	Δδ		0.8	−0.2	−0.4
C-6	δ	137.3	135.6	136.5	136.5
	Δδ		−1.7	−0.8	−0.8
(C-3)NH_2	δ	142.5	146.3	145.7	145.7
	Δδ		3.8	3.2	3.2

[a]Referred to TMS in DMSO solutions.
[b]Complexation shift is defined as the difference of carbon chemical shifts in the complex and the parent molecule.
[c]sign(+) denotes deshielding effect, while(−) denotes shielding effect.
[d]Taken from reference 37.

Thus, the bands observed in all the complexes **1**, **2** and **3** are at the same region, indicating the retention of the aromatic character of 3AP. It has been reported that a metal is capable of forming d–p bands with ligands containing nitrogen as donor atoms.[36]

NMR Spectra

The ^1H and ^{13}C data for **1**, **2** and **3 c**omplexes with the literature values of the parent 3AP molecule are presented in *Table* 2 and *Table* 3. The ^1H and ^{13}C NMR data of free 3AP are cited from the literature.[37,38] The chemical shift for the pyridine proton signals of the 3AP belonging to C(2)H, C(4)H, C(5)H and C(6)H are at 8.00 (d), 6.98 (q), 7.06 (q) and 7.99 (d) ppm, respectively. In complex **1**, the ^1H NMR signals of C(2) H, C(4)H, C(5)H and C(6)H protons displayed at 7.85(d), 7.05(q), 7.15(q) and 7.62(d) ppm; In complex **2**, the same proton signals appeared at 7.88 (broadened), 6.95(d), 7.06(q) and 7.66(d) ppm and in complex **3**, the proton signals appeared at 7.87(d), 6.94(q), 7.05(q) and 7.66(d) ppm, respectively. The C(3)–NH_2 proton for 3AP displayed at 5.59(s) which is observed at 5.59(s) for **1**, 5.42(S) for **2** and 5.40(S) for **3** complexes, respectively. The ^1H spectra (*Fig.* 3) of **1**, **2** and **3** complexes confirm the retention of aromatic character by the ligand after coordination and only an insignificant downfield shift with a difference of 0.02–0.12 ppm for the peaks is established. The signals of the H-2 and H-6 protons are found to be shielded in all the complexes.

The ^{13}C NMR (*Fig*. 4) of 3AP displayed five signals for C-2, C-4, C-5, C-6 and (C-3) NH_2 at 139.8, 123.6, 121.3, 137.3 and 142.5 ppm. In complex **1**, signals for the same carbons observed at 136.4, 125.1, 122.1, 135.6 and 146.3 ppm; In complex **2**, signals observed at 137.1, 124.5,

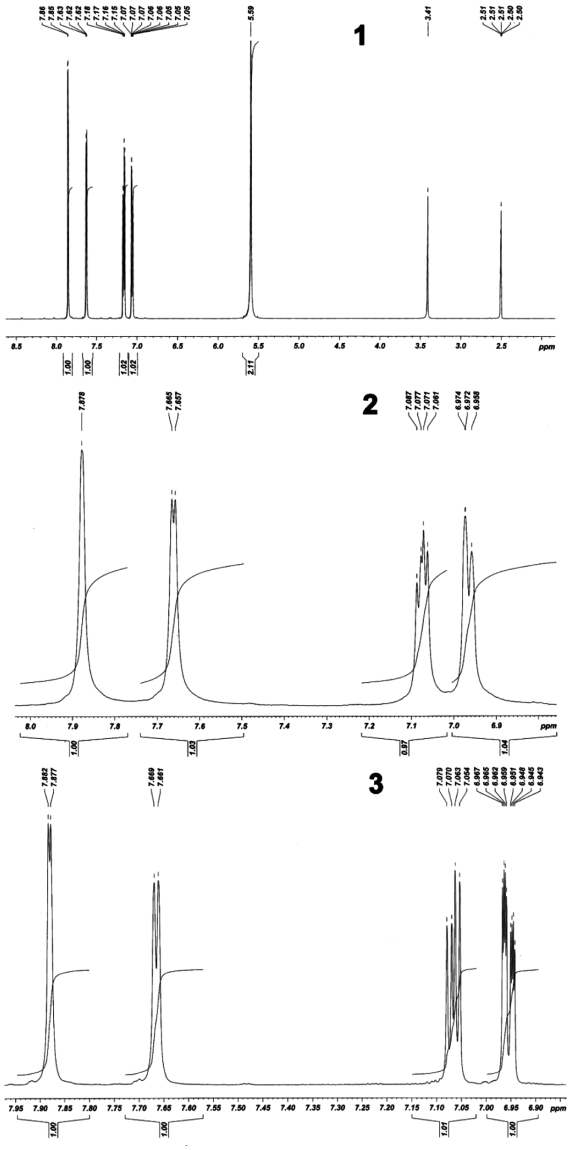

***Figure* 3.** ^1H NMR Spectra for **1**, **2** and **3**.

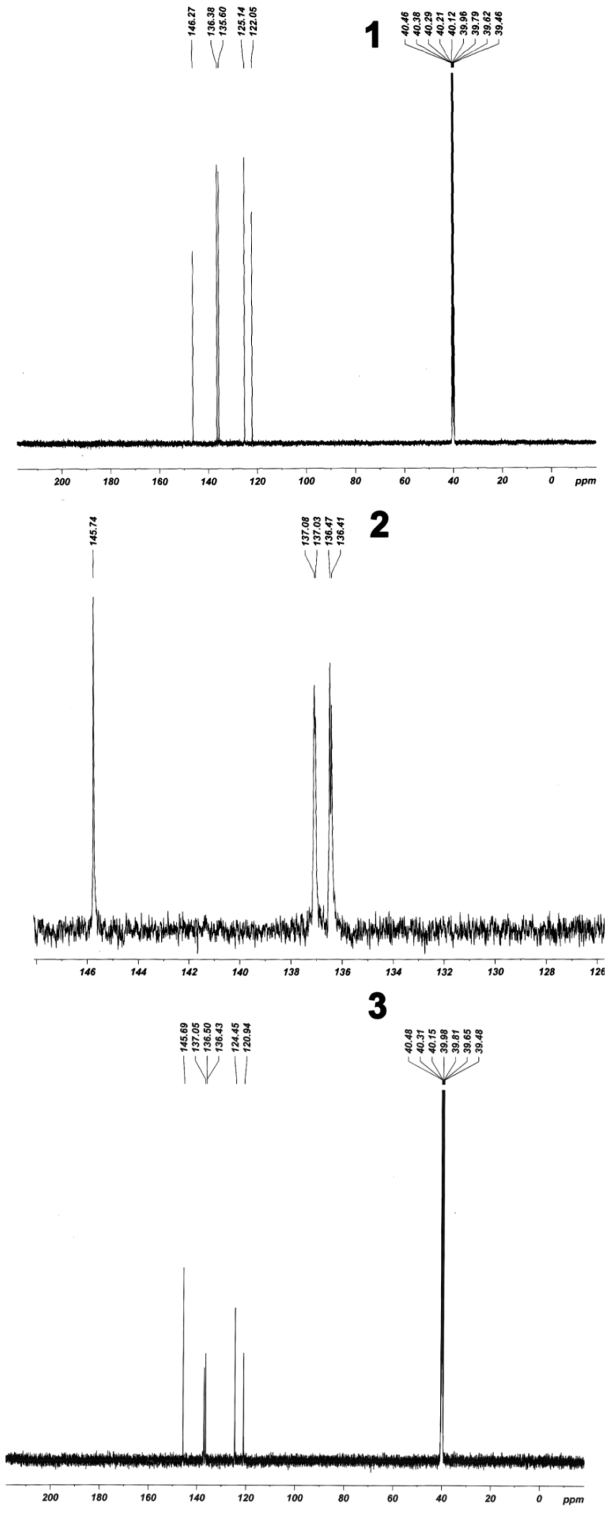

Figure **4.** ^{13}C NMR Spectra for **1**, **2** and **3**.

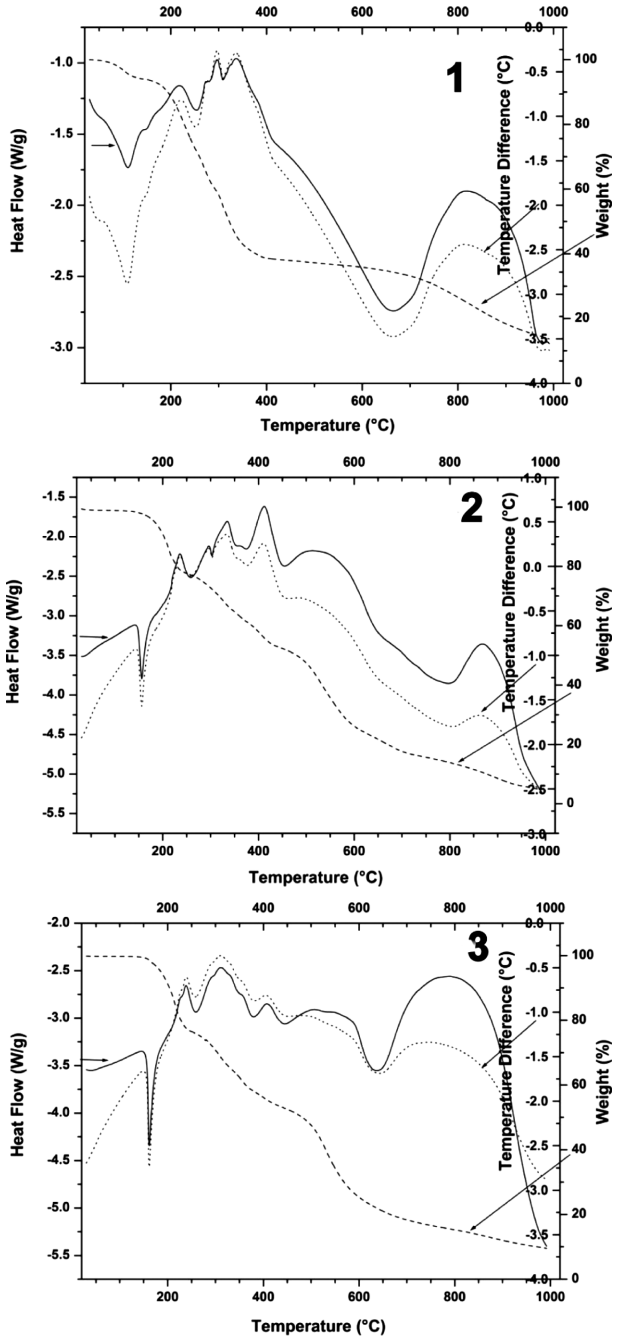

Figure **5.** DSC-TGA curves for the complexes **1, 2** and **3**.

121.1, 136.5 and 145.7 ppm and in complex **3** signals appeared at 137.1, 124.5, 120.9, 136.5 and 145.7 ppm, respectively. In the ^{13}C spectra of complexes **1**, **2** and **3** all the aromatic carbon atoms are shifted 0.24–3.42 ppm downfield relatively to the corresponding ligand molecule. The ^{13}C NMR spectra for C-2 is found to be more shielded. The insignificant chemical shift (d) and complexation shift (Dd) observed in both ^{1}H and ^{13}C NMR of **1**, **2** and **3** complexes. Therefore it could be concluded that the aromaticity of the pyridine ring is preserved upon complexation.

Thermal Studies

Thermogravimetric analyses DSC, TGA are used to get information about the thermal stability of the complexes and suggest a general scheme for thermal decomposition of the complexes. The DSC/ TGA curves of complexes **1**, **2** and **3** are given in *Fig*. 5.

The thermogram of complex **1** shows four decomposition steps within the temperature range from 0 to 900 °C. The first decomposition step within the temperature range of 0–120 °C corresponds to the loss of hydrated water molecule[39] of hydration with mass loss of 5.0% (calcd. 5.21%). The second decomposition step corresponds to loss of NO_2 and $C_5H_7N_2$ within the temperature range from 120–290 °C with the mass loss 35% (calcd. 40.53%). The third decomposition step starts from 290 and continuous up to 400 °C correspond to loss of NO and $C_5H_7N_2$ with the mass loss of 25% (calcd. 35–90%). The fourth step within the temperature range from 670–900 °C corresponds to the loss of metal oxide resides (ZnO) with mass loss of 21% (calcd. 23.56%). It is clear from these data that these mass losses are accompanied by endothermic peaks at 110, 254, 659 °C and exothermic peak at 308 °C. The overall weight-loss amounts to 86.26% (calcd. 86%). The exo and endo peak behavior is typical of the energy release and the energy absorption due to the structural rearrangement of a complex.[40]

The TGA curve of complex **2** shows four decomposition steps within the temperature range of 50–1000 °C. The first step corresponds to the loss of H_2O, NO_2 and NO with mass loss of 23% (calcd. 23.93%) in the temperature range from 50–260 °C accompanied by an endothermic peak at 156.07 °C. The second decomposition step from 260–440 °C accompanied by two exothermic peaks at 325 °C and 415 °C with the mass corresponds to $C_5H_7N_2$ with the mass loss of 24%. The third decomposition step starts at 440 °C and ends with 610 °C corresponds to the loss of $C_5H_7N_2$ with mass loss of 23%. The fourth step in the temperature range of 610–950 °C corresponds to the loss of metal oxide residues (CdO) with mass loss of 25.5% (calcd. 32.59%) accompanied by an exothermic peak at 875 °C. The overall weight loss amount to 94.14 (calcd. 95.5%).

The thermogram of complex **3** shows three decomposition stages within the temperature range of 50–1000 °C. The first step corresponds to the loss of H_2O, NO_2 and NO within the temperature range from 50–245 °C with the mass loss of 23% (calcd. 19.54%). The second step starts from 245–450 °C corresponds to the loss of $C_5H_7N_2$ with mass loss of 24% (calcd. 19.54%). The third decomposition step in the temperature range from 450–950 °C corresponds to the mass loss of $C_5H_7N_2$ along with metal oxide residues (HgO) with the mass loss of 43% (calcd. 45.04%). These steps are accompanied by two endothermic peaks at 161.62 and 641 °C. The overall weight loss amounts to 90.28% (calcd. 90%).

From the characterization studies, the suggested structure of the complexes is shown in *Fig*. 6.

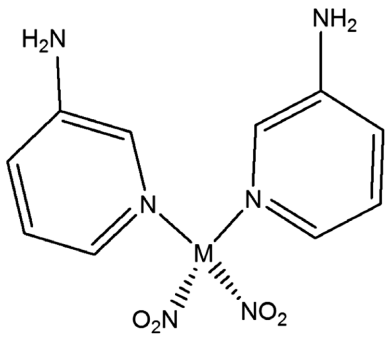

***Figure* 6.** Suggested structure of the complexes **1**, **2** and **3**, where M=Zn(II), Cd(II) and Hg(II).

Mass Spectra

The electron impact mass spectra provide a vital character for interpretation of the structures of the metal complexes; but the formations of new ions during fragmentations are completely different from the parent compound because of rearrangements and it complicates the mass analysis.[41] The complexes **1**, **2** and **3** showed molecular ion peaks at 345.2, 393.0 and 481.0 respectively. It proves the suggested structures of the metal complexes. Moreover, the key fragment ion peak at m/z = 92.0 for complex **1** is due to 3AP or aminopyridine. The other fragments of the complex **1** are difficult to be recognized. In complex **2**, the different mass fragments observed at m/z = 93, 111 and 206 are probably due to the formation of 3AP, pyridine oxide and cadmium nitrite fragments and it supports the suggested structure for complex **2**. The different fragments of complex **3** give the peaks at m/z = 92, 97, 111, 136, 298, 336 and 393.

Microbial Studies

Antibacterial studies

The antibacterial results (*Fig*. 7) show that the metal complexes **1**, **2** and **3** are more active than free ligand 3AP. *Fig*. 7a clearly reveals that no antibacterial activity for the free ligand $NaNO_2$. From the *Fig.* 7b, it is clear that the complex **2** shows excellent activity than the other complexes **1** and **3**. The antibacterial activity of the complexes shows the following order: **2** > **3** > **1** > 3AP. In general

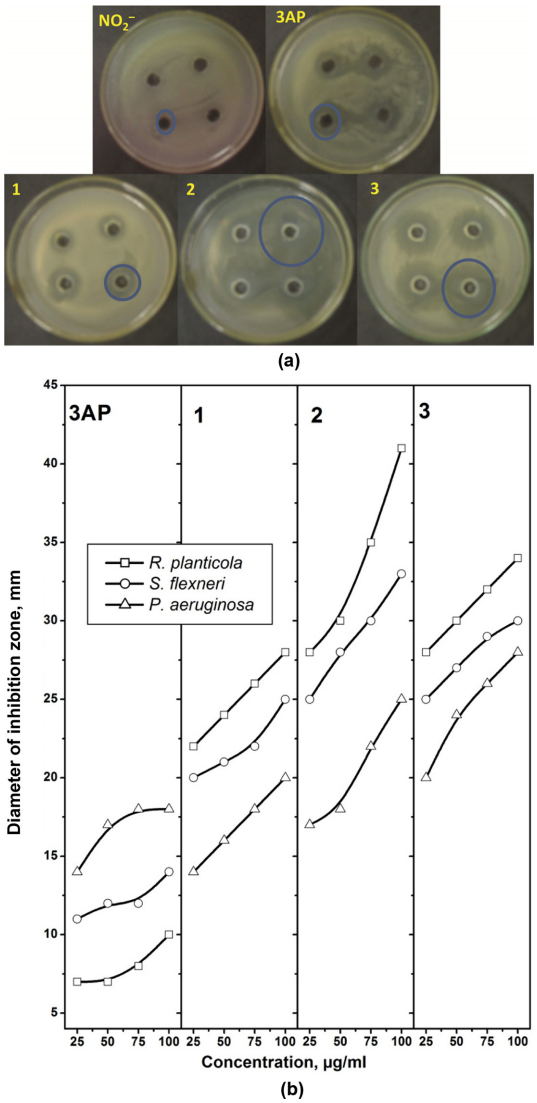

***Figure* 7.** (**a**) Agar plates of tested free ligands and complexes **1**, **2** and **3** against the bacterium, *P. aeruginosa* (**b**) Antibacterial activity of the ligand 3AP and complexes **1**, **2** and **3** against the bacteria, *R. planticola, S. flexineri* and *P. aeruginosa.*

complexes **2** and **3** show the better antibacterial activity than the free organic ligand.

It has also been observed that concentration plays a vital role in increasing the degree of inhibition. The inhibition capacity of complexes increases as their concentration increases. The antibacterial results were more or less similar to our earlier results of 4AP complexes.[18] It reveals that the position of the amino group in the pyridine ring does not play a role in deciding the antibacterial activity.

Antifungal activity

The antifungal activity of the free ligands (3AP and NO_2^-) and the complexes **1**, **2** and **3** are given in *Table* 4. Free ligands show poor/no activity against the tested fungi. From the table it is clear that the complexes **2** and **3** is highly active against the fungi *A.niger* and *C. albicans.* The complex **1** does not show good antifungal activity. The antifungal character of the complexes shows the following order: **2** > **3** > **1** > 3AP. The antifungal activity is also a concentration dependent. The activity increases with the increase of concentration of the complexes. The antibacterial and antifungal activity of the complexes and the ligands posses the same order of reactivity. Antifungal activity also shows similar trend of 4AP complexes.[18]

CONCLUSION

From the elemental analyses and molar conductance data, the probable formulae of the complexes arrived. 3AP acts as monodentate ligand through the nitrogen of the pyridine ring and nitro ligand coordinate the metal ion through the nitrogen atom. From the IR and Far-IR spectral data confirm that the **1**, **2** and **3** are nitro complexes. Electronic spectral data showed that complexes **1**, **2** and **3** possess two well resolved bands in the same region revealed

***Table* 4.** Antifungal activities of compounds and standard reagents

Compound	Fungus tested	Antifungal activity at concentration (μgml^{-1})		
		400	200	100
Ligand(NO_2^-)	*C.albicans*	*	*	*
	A.niger	*	*	*
Ligand(3AP)	*A.niger*	**	*	*
	C.albicans	**	*	*
Complex **1**	*A.niger*	***	**	**
	C.albicans	***	***	**
Complex **2**	*A.niger*	****	****	***
	C.albicans	****	****	****
Complex **3**	*A.niger*	****	***	***
	C.albicans	****	***	***

*- poor/no activity; **- moderate activity; ***- good activity; ****- excellent activity

the tetrahedral geometry. NMR (^{1}H, ^{13}C) and electron impact mass spectral studies indicate that the aromatic nature of the pyridine ring preserved upon complexation. The electron impact mass spectral studies and thermal studies also support the suggested structure of the complexes. The results of antibacterial, antifungal studies show that metal complexes possess noble antibacterial activity, antifungal activity with the following order: **2** > **3** > **1** which is similar with our previous results on 4AP complexes.[18] Concentration plays a vital role, when the concentration of the complexes increases the activity also increases. The metal complexes **2** and **3** may be used as antibacterial and antifungal agents with careful precautions.

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