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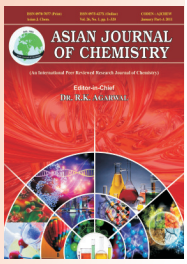

Synthesis, Characterization and Antimicrobial Screening of Some 4-Acylpyrazoloimines and Some 3*d* Transition Metal(II) Complexes

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Some 4-acylpyrazoloimines and their 3*d* transition metal(II) complexes have been synthesized. The ligands and their 3*d* transition metal complexes were characterized by elemental analysis, molar conductance, magnetic susceptibility measurements and spectroscopic methods. The ligands behaved as mono-anion ONO or ONS donor molecules. Microanalysis, electronic spectral and magnetic measurements showed the metal complexes as ML_2 type. All the synthesized compounds were screened for their *in vitro* antimicrobial activity against some gram positive and gram negative clinical bacterial strains. Antimicrobial activity test results showed that the metallic derivatives are more active against the bacterial strains than the imines.

Keywords: Synthesis, Pyrazoloimine, Spectroscopic methods, Antimicrobial activity, Complexes.

INTRODUCTION

For decades, considerable attention has been paid to heterocyclic β-diketones with pyrazolone nucleus and their derivatives, due to their interesting chemistry, pharmaceutical importance and high biological activity. Initially researches were restricted to oxygen donor ligands[1-5], however the search for pyrazolone derivatives with more sites for ligation in metal complexes has prompted other workers to synthesize imines[6-11]. The resultant compounds have several electron-rich donor centers, also they have some interesting behaviour due to their tendency to form the enol and keto form as a result of tautomeric effect[12,13]. An array of transition metal complexes with very interesting and often unusual structural and chemical properties have been reported[14-20]. Imines and their metal derivatives are well known for their interesting physico-chemical and pharmacological characteristics[21-30]. The use of hydrazones in biological systems as iron chelators[31-32] has further increased the interest in their study. In the present study, we present potential ONO and ONS donor pyrazoloimines and their Cu(II), Ni(II) and Co(II) complexes. The antimicrobial activity of the ligands and metal complexes is also reported.

EXPERIMENTAL

All the solvents are of analytical grade and were used without further purification. 1-Phenyl-3-methylpyrazol-5-one, isonicotinic acid hydrazide, thiosemicarbazide and benzoyl hydrazide were used as supplied by Fluka. 1-Phenyl-3-methyl-4-benzoyl-pyrazol-5-one, 1-phenyl-3-methyl-4-hexanoyl-pyrazol-5-one and 1-phenyl-3-methyl-4-butyryl-pyrazol-5-one were synthesized in accordance with reported literature procedures[1]. Elemental analyses of C, H and N were performed by using Carlo erba elemental analyzer EA 1108. Melting point was obtained with a Fisher John melting point apparatus. Magnetic moments were done on a magnetic susceptibility balance-Sherwood Scientific Cambridge, Model No. MK-I. The molar conductance of the complexes was measured using Innolab conductivity meter Level 1. The percentage of metal in the complexes were determined using an Agilent ICP-MS7500Ce. IR spectra were recorded on a Perkin Elmer Spectrum 100. ^{1}H and ^{13}C NMR spectra were obtained from a Bruker AV 500 MHz for ^{1}H and 125 MHz for ^{13}C using a 5 mm Quadra Nuclei Probe (QNP).

Synthesis of 4-acylpyrazoloimines: *N*'-[(Z)-(3-Methyl-5-oxo-1-phenyl-4,5-dihydro-1*H*-pyrazol-4-yl)hexylidene] pyridine-4-carbohydrazide(Hepim1),*N*'-[(Z)-(3-methyl-5-oxo-1-phenyl-4,5-dihydro-1*H*-pyrazol-4-yl)hexylidene] benzohydrazide(Hepim2),(2E)-2-[1-(3-methyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)(phenyl)methylidene] hydrazinecarbothioamide(Bepim) and (2E)-2-[1-(3-methyl-5-oxo-1-phenyl-4,5-dihydro-1*H*-pyrazol-4-yl)butylidene] hydrazinecarbothioamide (Bupim) were synthesized as follows:

A solution of 4-acyl-3-methyl-1-phenylpyrazol-5-one (0.01 mol) in 30 mL ethanol was mixed with a solution of appropriate -NH_2 functionalized molecule *e.g.*, isonicotinic acid hydrazide, thiosemicarbazide or benzoyl hydrazide (0.01 mol) in ethanol (20 mL). The mixture was refluxed for 2 h and cooled (Fig. 1). The precipitate formed was isolated by gravity filtration and recrystallized from ethanol.

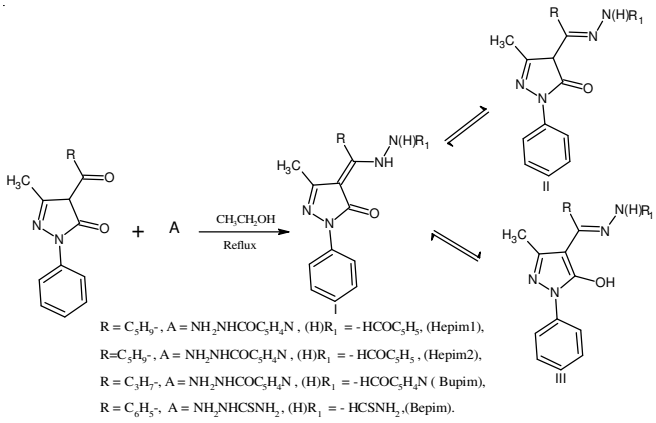


Fig. 1. Synthesis of 4-acylpyrazoloimines

Synthesis of metal complexes of 4-acylpyrazoloimines To an ethanolic solution (20 mL) of Hepim1, Hepim2, Bupim or Bepim (0.001 mol), ethanolic solution (10 mL) of the corresponding metal(II) chloride (0.001 mol) was added with constant stirring. The coloured mixture was then refluxed for 4 h. The resulting metal complex was filtered hot, washed with boiling mixture of 1:1 water/ethanol, dried under suction and kept in vacuum over $CaCl_2$.

Antimicrobial test: *Escherichia coli*, *Pseudonomas aeruginosa*, *Klebsiella pneumoniae*, *Staphylococcus aureus*, *Salmonella gallinarum* and *Bacillus subtilis* were isolated from clinical samples. The gram positive and gram negative bacteria were identified using bio-chemical methods[33]. Antimicrobial activity of the study compounds was studied by Agar well diffusion method[34]. Colonies of each test bacterium were suspended in sterile normal saline and adjusted to match 0.5 Mcfarland turbidity standard. Each bacterial suspension was used to spread onto the surface of sterile Mueller Hinton agar plates. The surface of the plates were allowed to dry and a sterile cork borer of 6 mm diameter was used to bore wells in the agar plates. 50 mL of dilute solution (20 mg/mL) of each synthesized compound was delivered into each well. The plates were allowed to stand for 0.5 h to aid diffusion and then incubated at 37 °C for 24 h. After incubation the zones of inhibition were measured and the mean recorded.

RESULTS AND DISCUSSION

All the metal complexes are coloured, soluble in polar solvents (dimethyl sulphoxide, dimethyl formamide and anhydrous ethanol) but insoluble in hydrocarbon solvents such as, hexane, pentane and tetrahydrofuran and carbon tetrachloride. Analytical and physical data of all the study compounds are shown in Table-1. The complexes are non-electrolytes in DMSO, as evident from the molar conductivity values which range[35-37] from 9-15 Ω^{-1} cm^2 mol^{-1}.

FT-infrared spectra: The infrared spectra of the pyrazoloimines and their metal complexes were recorded in the range of 4000-370 cm^{-1}. Some important vibrational bands in the IR spectral of the imines and their metal complexes are shown in Table-2. Two strong vibrational bands (cm^{-1}); 1612, 1600 (Hepim1), 1630, 1606 (Hepim2) and 1613, 1593 (Bupim) have been assigned to ν(C=O) of the hydrazide moiety and the pyrazolone ring, respectively[38-40]. The band observed at 1579 cm^{-1} was assigned to ν(C=O) of the pyrazolone ring in Bepim. ν(C=O) bands of the hydrazide moieties in (Hepim1), (Hepim2) and Bupim shifted to lower frequencies in the metal complexes, which is an indication that the oxygen atoms are involved in coordination[41-43]. Bands in the region of 1563-1599 cm^{-1} have been assigned to imino ν(C=N) in all the metal complexes. The bands in the region of 1420-1463 cm^{-1} in the metal complexes have been assigned to ν(C-O)[38,44]. The bands around 3300-3100 cm^{-1} have been assigned to ν(N-H). In the spectral of metal complexes low frequency bands in the range 451-408 cm^{-1} were assigned to ν(M-N), the bands in the range 555-506 cm^{-1} were assigned to ν(M-O)[45-48] while the bands in the region 696-690 cm^{-1} were assigned to ν(M-S). In the spectral of Bepim

TABLE 1
ANALYTICAL AND PHYSICAL DATA OF THE LIGANDS AND THEIR METAL COMPLEXES

Compound	Colour	m.f.	Yield (%)	Elemental analysis (%): Found (calcd.)				
				C	H	N	M	m.p. (°C)
Hepim1	Red	$C_{22}H_{25}N_5O_2$	75	67.72 (67.52)	6.53 (6.39)	18.24 (17.90)	–	235
CuHepim1	Dark green	$C_{44}H_{48}N_{10}O_4Cu$	60	62.10 (62.58)	5.32 (5.73)	15.98 (16.59)	7.10 (7.53)	260
CoHepim1	Brown	$C_{44}H_{48}N_{10}O_4Co$	68	62.42 (62.92)	5.12 (5.76)	16.12 (16.68)	6.89 (7.02)	278
NiHepim1	Reddish brown	$C_{44}H_{48}N_{10}O_4Ni$	65	62.22 (62.94)	5.97 (5.76)	16.22 (16.69)	6.23 (6.99)	288
Hepim2	Yellow	$C_{23}H_{26}N_4O_2$	75	70.75 (70.77)	6.90 (6.67)	14.60 (14.36)	–	201
CuHepim2	Dark green	$C_{46}H_{50}N_8O_4Cu$	65	65.26 (65.58)	5.75 (5.98)	13.59 (13.30)	7.80 (7.54)	255
NiHepim2	Green	$C_{46}H_{50}N_8O_4Ni$	67	65.71 (65.96)	6.31 (6.02)	13.34 (13.38)	6.88 (7.01)	235
CoHepim2	Yellow	$C_{46}H_{50}N_8O_4Co$	68	65.42 (65.94)	5.77 (6.02)	12.88 (13.30)	6.73 (7.03)	275
Bupim	Red	$C_{20}H_{21}N_5O_2$	75	67.99 (66.12)	5.56 (5.79)	19.12 (19.28)	–	250
CuBupim	Green	$C_{40}H_{40}N_{10}O_4Cu$	60	60.36 (60.94)	5.56 (5.11)	17.99 (17.77)	7.60 (8.06)	268
CoBupim	Reddish brown	$C_{40}H_{40}N_{10}O_4Co$	62	61.52 (61.30)	5.52 (5.15)	17.94 (17.88)	7.66 (7.52)	295
NiBupim	Brown	$C_{40}H_{40}N_{10}O_4Ni$	62	60.89 (61.31)	5.76 (5.15)	17.30 (17.88)	7.10 (7.49)	288
Bepim	Yellow	$C_{18}H_{17}N_5OS$	80	61.54 (61.53)	4.96 (4.56)	20.09 (19.94)	–	219
CuBepim	Dark brown	$C_{36}H_{32}N_{10}O_2S_2Cu$	66	56.44 (56.56)	4.97 (4.22)	18.58 (18.33)	8.70 (8.31)	229
CoBepim	Brown	$C_{36}H_{32}N_{10}O_2S_2Co$	67	56.39 (56.91)	4.07 (4.25)	18.64 (18.44)	7.13 (8.36)	315
NiBepim	Green	$C_{36}H_{32}N_{10}O_2S_2Ni$	68	57.20 56.92)	4.89 (4.25)	18.75 (18.45)	8.10 (8.37)	290

TABLE-2
RELEVANT IR ABSORPTION BANDS ASSIGNMENT FOR THE IMINES AND METAL COMPLEXES

Compound	νN-H	νC=O[a]	νC=O[b]	νC=N	νN-N	νC-O	νC=S	νM-O	νM-N	νM-S
Hepim1	3056	1612	1600	-	1025	-	-	-	-	-
CuHepim1	3057	1601	-	1591	1031	1451	-	506	415	-
NiHepim1	3385	1602	-	1564	1003	1420	-	509	408	-
CoHepim1	3373	1600	-	1563	1079	1450	-	510	451	-
Hepim2	3206	1630	1606	-	1026	-	-	-	-	-
CuHepim2	3317	1605	-	1592	1026	1453	-	506	415	-
NiHepim2	3171	1605	-	1594	1027	1440	-	509	451	-
CoHepim2	3284	1600	-	1563	1073	1463	-	539	409	-
Bupim	3056	1631	1593	-	1011	-	-	-	-	-
CuBupim	3089	1591	-	1580	1059	1446	-	506	417	-
NiBupim	3384	1594	-	1567	1060	1452	-	513	450	-
CoBupim	3120	1593	-	1574	1075	1445	-	509	450	-
Bepim	3340	-	1579	-	1025	-	836	-	-	-
CuBepim	3287	-		1599	1035	1437	857	515	417	691
NiBepim	3371	-		1598	1036	1458	865	555	420	696
CoBepim	3059	-		1592	1025	1455	854	507	409	690

[a]νC = O hydrazide moiety, [b]νC = O pyrazolone ring

and its metal complexes the bands in the region 836-865 cm^{-1} were assigned to ν(C=S), the shift to higher frequencies in the metal complexes 20-30 cm^{-1} suggest that there is coordination to the metals *via* (C=S). Generally the ligands exist in the keto-amine form (I) in the solid state, but they reacted in the enol-imine form (III) (Fig. 1) when coordinated to metal ions in solution. The tridentate ligands coordinated *via* pyrazolone ring enolic (C-O), azomethine (C=N), hydrazide side chain (C=O) or the thiosemicarbazide (C=S).

^{1}H and ^{13}C NMR spectra: Previous works on 4-acylpyrazol-5-one derivatives and imines[4,49-52] have been taken into consideration in the assignments of the proton signals of imines in the present study. ^{1}H NMR spectral data of the imines are listed in Table-3. The main features of interest observed in the ^{1}H NMR spectral include the signals of the 3-methyl substituents at δ ppm values upfield in the range δ 2.36-2.51 ppm. The 4-acyl protons in Hepim1 and Hepim2 which are basically made up of the terminal -CH_3 and the methylene protons. The signals of the methyl protons appeared as triplets, while the signals of the methylene protons appeared as either triplets or multiplets depending on the number of hydrogen atoms vicinal to the methylene hydrogens[53]. Relatively high frequency proton chemical shifts ranging from 6.85-10.23 ppm were assigned to phenyl hydrogens and -NH-.

^{13}C NMR spectra data: The chemical shift and carbon assignments are displayed in Tables 4 and 5. All assignments are based on literature[4,49]. Assignments were done based on the structures in Fig. 2. The signals downfield have been assigned to carbon atom depending on the extent of deshielding of the carbons, while the signals upfield have been assigned to

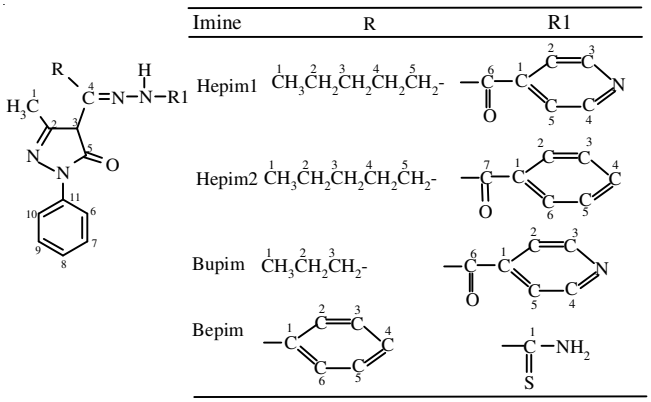


Fig. 2. ^{13}C NMR numbering schemes for 4-acylpyrazoloimines

TABLE-3
PROTON NMR SPECTRA DATA OF 4-ACYLPYRAZOLOIMINES IN $CDCl_3$ (CHEMICAL SHIFTS IN δ ppm RELATIVE TO TMS)

Imine	3-Methyl protons	4-Acyl protons		Phenyl protons
		Methyl	Methylene	
Hepim1	2.51 (s, 3H, -CH_3)	0.83 (t, 3H, -CH_2CH_3)	2.92 (t, 2H, N=C-CH_2 1.24 – 1.67 (m, 6H, (-CH_2-)$_3$	7.11 –8.79 (m, 9H, 2ph), NH
Hepim2	2.36 (s, 3H, -CH_3)	0.76 (t, 3H, -CH_2CH_3)	2.86(t, 2H, N=C-CH_2-1.07 – 1.81 (m, 6H, (-CH_2-)$_3$	7-24 –9.77 (m, 9H, 2ph), NH
Bupim	2.45 (s, 3H, -CH_3)	1.03 (t, 2H,N=C-CH_2-)	2.91 (t, 2H, N=C-CH_2-) 1.67 – 1.75 (m, 2H, (-CH_2-)	7.11 – 8.79 (m, 9H, 2ph), NH
Bepim	2.5 (s, 3H, -CH_3)	-	-	7.15 -10.33 (m, 10H, 2ph), NH

TABLE-4
^{13}C NMR CHEMICAL SHIFTS OF THE 4-ACYLPYRAZOLOIMINES (δ ppm RELATIVE TO TMS)

Imine	Carbon										
	1	2	3	4	5	6	7	8	9	10	11
Hepim1	14.14	150.82	100.01	151.20	165.68	119.84	129.22	124.39	129.22	119.84	147.30
Hepim2	13.90	132.51	119.93	132.59	138.43	120.48	127.48	125.07	127.48	120.48	129.07
Bupim	14.16	165.16	119.83	146.85	165.95	121.66	128.69	124.74	128.69	121.66	150.72
Bepim	15.67	148.03	130.31	147.50	164.60	118.64	126.44	120.99	126.44	118.64	143.94

TABLE-5
^{13}C NMR CHEMICAL SHIFTS OF R AND R1 SIDE CHAINS (δ ppm RELATIVE TO TMS)

Imine		Carbon						
		1	2	3	4	5	6	7
Hepim1	R	16.99	22.99	27.89	31.64	54.99	-	-
	R1	121.96	118.51	139.42	139.42	118.51	151.20	-
Hepim2	R	17.53	22.33	28.21	31.77	33.55	-	-
	R1	127.66	126.64	125.21	126.64	125.21	126.64	147.17
Bupim	R	16.36	22.07	29.75	-	-	-	-
	R1	118.58	117.69	146.85	146.85	117.69	169.24	-
Bepim	R	128.84	128.59	128.31	128.84	128.31	128.59	-
	R1	178.76	-	-	-	-	-	-

shielded carbons and also taking into consideration the relative shielding effect on the carbons. The highest frequency chemical shifts were either assigned to -CO in the 4-acylpyrazoloimines while the lowest frequency chemical shifts were assigned to -CH_3 of the 3-methyl, the -CH_3 and methylene of the 4-acyl moieties. The assignments of the phenyl carbons in rings were done on the basis that the nitrogen atom attached to the phenyl group shields the *ortho* carbon more strongly than the *para* carbon while the *meta* carbon is the least shielded[4,52].

Electronic spectra and magnetic measurements: The significant electronic absorption bands in the spectra of the ligands and their metal complexes recorded in DMSO solution are presented in Table-6. High frequency bands in the region 44,000-25,000 cm^{-1} have been assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions[54-56]. The Cu(II) complexes show bands in the region 11,000-12,000, 15,000-16,000 and 21,000-22,000 cm^{-1}, assignable to $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions, respectively[57-61]. The observed magnetic moments in the range 1.96-2.07 B.M. suggest octahedral geometry for the complexes[57]. The Cu(II) complexes are expectedly distorted because the Cu(II) octahedral ground state has an extra electron in the e_g set of *d*-orbitals that is strongly anti-bonding with ligands, which results in a symmetry lowering Jahn-Teller distortion of the metal environment[62]. All the Ni(II) complexes were found to be paramagnetic species with magnetic moments values in the range 2.90-2.98 BM, which are consistent with octahedral geometry. The ground state for Ni(II) with d^8 configuration in an octahedral field is ^3F, while the excited state with spin permitted transition is ^3P. The ^3P state which is not split is designated as $^3T_{1g}(P)$, while the ^3F state is split into three states $^3A_{2g}$, $^3T_{2g}$ and $^3T_{1g}(F)$, with $^3A_{2g}$ being the ground state. The Ni(II) complexes display bands in the region 10,000, 14,000-15,000 and 23,000-24,000 cm^{-1} that are assignable to $^3A_{2g} \rightarrow {}^3T_{2g}(F)$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transitions[63]. The three bands in the region 10,000-11,000 cm^{-1}, 15,000-18,000 and 19,000-23,000 cm^{-1} observed for Co(II) complexes have been assigned to $^4T_{1g}$ (F) $\rightarrow$ $^4T_{1g}(P)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}$ and $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ transitions respectively[57]. The magnetic moment values in the range 4.70-4.92 BM. and the observed electronic transitions indicate high spin octahedral geometry of the complexes.

Antimicrobial activity: All the synthesized compounds were tested *in vitro* for their antimicrobial activity against Gram negative bacterial strains *Escherichia coli* (EC), *Pseudonomas aeruginosa* (PA) , *Klebsiella pneumonia (*KP) and *Salmonella gallinarium* (SG), Gram positive bacterial strains *Staphylococcus aureus* (SA) and *Bacillus subtilis* (BS). The results of antimicrobial screening are shown in Table-7. The results showed that in general that metal complexes were more active than the imines, with the only exception in the case of Bepim against *Bacillus subtilis*. This observation is consistent with the proposition of the overtone's concept and chelation theory[64]. The overtone's concept of cell permeability stipulates that the lipid membrane that surrounds the cell favours the passage of

TABLE-6
ELECTRONIC SPECTRA, MAGNETIC MOMENTS AND CONDUCTIVITY DATA

Compound	Bands (cm^{-1}) (ε, L $mol^{-1}cm^{-1}$)	Assigned transition	μ_{eff} (BM)	λ_M ($\Omega^{-1}cm^2$ mol^{-1})
Hepim1	44,643(2240),28,249(1080),25,842(1080)	$n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, $\pi \rightarrow \pi^*$	-	-
Cu Hepim1	12,775(156),15,412(218), 22,522(134)	$^2B_{1g} \rightarrow {}^2B_{2g}$, $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{1g} \rightarrow {}^2E_g$	1.96	14.86
Ni Hepim1	10,232(184),14,566(212),24,523(304)	$^3A_{2g} \rightarrow {}^3T_{2g}(F)$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$, $^3A_{2g} \rightarrow {}^3T_{1g}(P)$	2.98	14.32
Co Hepim1	11,435(111),18,753(334),23,665(210)	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$, $T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	4.92	13.44
Hepim2	44,053(2870),38,610(3210),33,898(351)	$n \rightarrow \pi^*$, $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$	-	-
Cu Hepim2	11,312(233),16,112(328), 21,422(184)	$^2B_{1g} \rightarrow {}^2B_{2g}$, $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{1g} \rightarrow {}^2E_g$	2.09	10.32
Co Hepim2	10,264(164),18,425(124),23,241(253)	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$, $T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	4.89	12.56
Ni Hepim2	11,234(145),14,666(176),23,548(288)	$^3A_{2g} \rightarrow {}^3T_{2g}(F)$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$, $^3A_{2g} \rightarrow {}^3T_{1g}(P)$	2.90	9.30
Bupim	43,478(4420),38,910(4230),27,448(2880)	$n \rightarrow \pi^*$, $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$	-	-
CuBupim	12,556(234),15,643(134), 21,268(154),	$^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{1g} \rightarrow {}^2B_{2g}$ $^2B_{1g} \rightarrow {}^2E_g$	2.05	13.67
CoBupim	11,125(345),18,645(243), 23,866(213),	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$, $T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	4.85	10.32
NiBupim	11,431(132),14,354(158),23,924(330)	$^3A_{2g} \rightarrow {}^3T_{2g}(F)$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$, $^3A_{2g} \rightarrow {}^3T_{1g}(P)$	2.97	12.86
Bepim	44,248(3240),38,760(3800),28,653(1280)	$n \rightarrow \pi^*$, $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$	-	-
CuBepim	12,534(166),16,367(80),21,423(215)	$^2B_{1g} \rightarrow {}^2B_{2g}$, $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{1g} \rightarrow {}^2E_g$	2.07	11.78
CoBepim	10,214(226),15,456(72.1),19,724(71.6)	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$, $T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	4.70	12.57
NiBepim	10,212(213)15,722 (212), 23,364 (149)	$^3A_{2g} \rightarrow {}^3T_{2g}(F)$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$, $^3A_{2g} \rightarrow {}^3T_{1g}(P)$	2.90	8.80

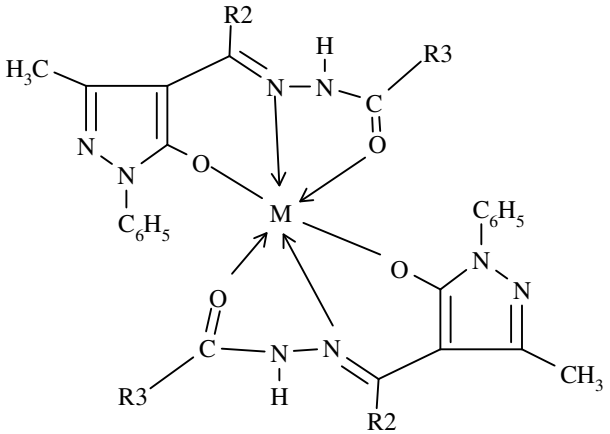
only lipid soluble materials, the implication of this is that lipophilicity is an important factor for antimicrobial activity. On chelation, the polarity of the metal ion is reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups[65,66]. This increases the delocalization of π-electrons over the whole chelate ring and enhances the penetration of the complexes into the lipid membranes and by so doing blocking the metal binding sites on the enzymes of the microorganisms, thus the compounds deactivate various cellular enzymes, which play vital role in the metabolic pathways of the organisms[67,68]. This is in agreement with documented facts that the ultimate action of antimicrobial agents is the denaturation of proteins of the cell, which as a result, impairs normal cellular processes[69].

TABLE-7
ANTIMICROBIAL DATA OF SYNTHESIZED COMPOUNDS (ZONE OF INHIBITION IN mm)

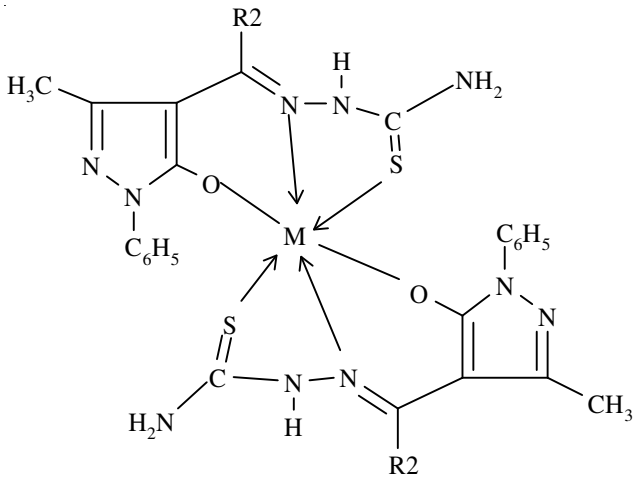
Compound	EC	PA	SG	KP	BS	SA
Hepim1	+	+	+	+	++	++
CuHepim1	++	++	++	++	++	+++
NiHepim1	++	++	++	++	++	++
CoHepim1	++	++	++	++	++	++
Hepim2	-	-	-	-	-	-
CuHepim2	++	++	++	++	++	++
NiHepim2	+++	++	+	+	++	++
CoHepim2	++	++	++	++	++	++
Bupim	+++	++	-	-	-	-
CuBupim	+++	+++	++	++	++	+
NiBupim	++++	+++	++	++	+	+
CoBupim	+++	++	+	+	+	+
Bepim	+	+	+	+	++	+
CuBepim	++	++	++	++	++	+
NiBepim	++	++	++	++	++	+
CoBepim	++	++	++	++	++	++

+ (inhibition zone < 10 mm), ++ (inhibition zone 10-13 mm), +++ (inhibition zone 14-20 mm), ++++ (inhibition zone > 20 mm)
EC = *Escherichia coli*, PA = *Pseudonomas aeruginosa*, SG = *Salmonella gallinarium*, KP = *Klebsiella pneumonia*, BS = *Bacillus subtilis*, SA = *Staphylococcus aureus*

On the basis of microanalytical data, magnetic moments, conductivity measurements and spectral analysis, the following structures have been proposed for the metal complexes.



R2=$CH_3(CH_2)_3CH_2$- , R3=C_5H_5N- (Hepim1), R2=$CH_3(CH_2)_3CH_2$- , R3=C_6H_5- (Hepim2)
R2=$CH_3CH_2CH_2$- , R3=C_5H_5N- (Bupim), M= Co(II), Cu(II), Ni(II)



R2= C_6H_5-(Bepim), M= Co(II), Cu(II), Ni(II).

Conclusion

Some pyrazoloimines and their metal(II) derivatives have been synthesized and characterized. The spectra data showed that the ligands exist in the solid state in the keto-amine form and coordinated in the keto-imine form as mono-anionic species. The analytical data show that the metal: Ligand ratio is 1:2 in all complexes studied. The electronic data and magnetic moments are in favour of octahedral geometry for all the complexes. The metal complexes showed better anti-microbial activity when compared with the ligands.

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