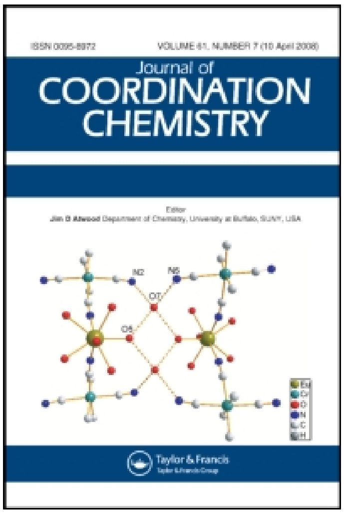

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Iron(III)5(2'-hydroxyphenyl)-3-(4-X-phenyl)pyrazolinates and their addition complexes with N, P donor ligands: synthesis, spectral and antimicrobial investigations

K. V. Sharma[a]; Vandana Sharma[b]; U. N. Tripathi[c]
[a] Department of Engg. Chemistry, Mahakal Institute of Technology, Ujjain 456664, (India) [b] School of Studies in Chemistry, Vikram University, Ujjain 456010, (India) [c] Department of Chemistry, D.D.U. Gorakhpur University, Gorakhpur 273001, (India)

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Iron(III)5(2′-hydroxyphenyl)-3-(4-X-phenyl)pyrazolinates and their addition complexes with N, P donor ligands: synthesis, spectral and antimicrobial investigations

K. V. SHARMA*†, VANDANA SHARMA‡ and U. N. TRIPATHI§

†Department of Engg. Chemistry, Mahakal Institute of Technology, Ujjain 456664 (India)
‡School of Studies in Chemistry, Vikram University, Ujjain 456010 (India)
§Department of Chemistry, D.D.U. Gorakhpur University, Gorakhpur 273001 (India)

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Iron(III)5(2′-hydroxyphenyl)-3-(4-X-phenyl)pyrazolinates of the type $(C_{15}H_{12}N_2OX)_3Fe$ [where X = –H, –Cl, $–CH_3$, $–OCH_3$] have been synthesized by reaction of anhydrous $FeCl_3$ with the sodium salts of pyrazoline in 1 : 3 molar ratio. Their addition complexes with N and P donor ligands [2,2′-bipyridine, 1,10-phenanthroline and triphenylphosphine] were prepared in 1:1 molar ratio. These newly synthesized derivatives have been characterized using elemental analysis (C, H, N and Fe), molecular weight measurement, magnetic moment data, FAB mass, ^{31}P NMR and Mössbauer spectral data. The complexes have been examined for crystalline/amorphous nature through XRD; all complexes are amorphous. Octahedral geometry around iron(III) confirms the presence of three bidentate pyrazoline ligands in iron(III)5(2′-hydroxyphenyl)-3-(4-X-phenyl)pyrazolinates. In addition complexes pyrazoline is monodentate. The bidentate and monodentate behavior of pyrazoline ligands was confirmed by IR spectral data. All the complexes were tested for their *in-vitro* antimicrobial activity. The metal complexes and their adducts exhibit better antibacterial and antifungal activity than the pyrazolines.

Keywords: Pyrazoline; 2,2′-Bipyridine; 1,10-Phenanthroline; Triphenylphosphine; Antimicrobial activity; Iron(III)pyrazolinates

1. Introduction

Preparation of heterocyclic compounds is a major challenge of modern heterocyclic chemistry; pyrazolines are an important class of heterocyclic compounds which are used in industry as dyes, antioxidants in lubricating oils [1] and in agriculture as catalysts for decarboxylation reactions and inhibitors in plant growth [2–4]. Due to their non-toxicity [5], they are also used as local anesthetics [6]. Organic derivatives of pyrazoline are used extensively in photography [7]. Reports are available for a large number of other hydroxylphenyl substituted heterocycles used as analgesic [8, 9], antitumor [10], antitussive [11], anti-inflammatory [12] and anticonvulsant agents [13, 14]. These are

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*Corresponding author. Email: sharmak_v@yahoo.co.in

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also applicable for cardiovascular activities [15] and antidepressant activities [16]. The metal complexes of 5(2′-hydroxyphenyl)-3-phenylpyrazoline with Ni(II), Co(II) and Cu(II) have been prepared in our laboratory by extraction method [17]. Similar types of ligands have been used to prepare complexes of cobalt, copper and nickel [18]. The synthesis, spectral and antimicrobial studies of diorganotin(IV)3(2′-hydroxyphenyl)-5-(4-substituted phenyl)pyrazolinates, triorganotin(IV)3(2′-hydroxyphenyl)-5-(4-substituted phenyl)pyrazolinates and chlorodiorganotin(IV)3(2′-hydroxyphenyl)-5-(4-substituted phenyl)pyrazolinates have been carried out in our laboratories [19–21]. In continuation of our work [22], we synthesized iron(III)5(2′-hydroxyphenyl)-3-(4-X-phenyl)pyrazoline complexes [X = –H, –Cl, $-CH_3$, $-OCH_3$] and their addition complexes with N and P donor ligands, i.e. 2,2′-bipyridine, 1,10-phenanthroline and triphenylphosphine. We have investigated spectral and antimicrobial activities of these complexes. Iron is the most important transition element involved in living systems, being vital to both plants and animals. Iron plays crucial roles in the transport and storage of oxygen and also in electron transport; with only a few possible exceptions in the bacterial world, there would be no life without iron.

2. Experimental

All chemicals were analytical grade quality. Solvents were rigorously dried and purified before use by standard procedure [23]. The ligand 5(2′-hydroxyphenyl)-3-(4-X-phenyl)pyrazoline was prepared by reported procedure [24].

2.1. *Synthesis of 5(2′-hydroxyphenyl)-3-(4-X-phenyl)pyrazolinates of iron*

The new iron(III)pyrazolinates were prepared by the following route:

$$FeCl_3 + 3(C_{15}H_{12}N_2OX)Na \xrightarrow[\text{Room Temp.}]{\text{Isopropanol}} (C_{15}H_{12}N_2OX)_3Fe + 3NaCl$$

$$[\text{where } X = -H,\ -Cl,\ -CH_3,\ -OCH_3]$$

Freshly cut sodium was taken in a flask containing isopropanol and refluxed (~1/2 h) till a clear solution of sodium isopropoxide was obtained. Solution of 5(2′-hydroxyphenyl)-3-(4-X-phenyl)pyrazoline [X = –H, –Cl, $-CH_3$, $-OCH_3$] in isopropanol was added and reaction was continued for 1 h when a constant yellow color was obtained. The reaction mixture was cooled to room temperature and alcoholic solution of anhydrous iron(III) chloride was added dropwise with constant stirring. The reaction mixture was further stirred for 20–24 h till the color of reaction mixture changed from yellow to reddish-black. Reaction mixture was filtered through alkoxy funnel under vacuum to separate the solid compound, which was washed with hot water to remove sodium chloride formed as byproduct and finally with alcohol. The solid so obtained was dried at 100°C. The data for synthesis of individual compounds are given in table 1.

Table 1. Synthetic, analytical and physical property data for 5(2′-hydroxyphenyl)-3-(4-X-phenyl)pyrazolinates of iron.

Reactants								Analysis, % found (Calcd)			
Anhydrous $FeCl_3$ *g* (mmol)	Sodium *g* (mmol)	Ligand *g* (mmol)	Molar ratio	Product (color)	Yield %	Melting point (°C)	Mol. wt. found (Calcd)	C	H	N	Fe
0.63 (3.91)	0.26 (11.73)	HPPP 2.79 (11.73)	1 : 3 : 3	$Fe(L_a)_3$ (Black)	80	200	767.65 (766.84)	70.67 (70.41)	5.90 (5.12)	10.79 (10.94)	7.20 (7.27)
0.55 (3.44)	0.23 (10.32)	HPCPP 2.81 (10.32)	1 : 3 : 3	$Fe(L_b)_3$ (Black)	87	240	869.32 (871.84)	61.95 (61.99)	4.14 (4.16)	9.64 (9.63)	6.40 (6.41)
0.60 (3.70)	0.25 (11.12)	HPMPP 2.80 (11.12)	1 : 3 : 3	$Fe(L_c)_3$ (Black)	88	234	807.62 (808.84)	71.25 (71.28)	5.62 (5.61)	10.36 (10.38)	6.91 (6.90)
0.56 (3.50)	0.24 (10.50)	HPMeoPP 2.81 (10.50)	1 : 3 : 3	$Fe(L_d)_3$ (Black)	86	215	854.32 (856.84)	67.28 (67.29)	5.27 (5.29)	9.81 (9.80)	6.50 (6.52)

HPPP, L_a = 5(2′-hydroxyphenyl)-3-phenylpyrazoline.
HPCPP, L_b = 5(2′-hydroxyphenyl)-3-(4-chlorophenyl)pyrazoline.
HPMPP, L_c = 5(2′-hydroxyphenyl)-3-(4-methylphenyl)pyrazoline.
HPMeoPP, L_d = 5(2′-hydroxyphenyl)-3-(4-methoxyphenyl)pyrazoline.

2.2. *Reactivity of 5(2′-hydroxyphenyl)-3-(4-X-phenyl)pyrazolinates of iron with N and P donor ligands*

A solution of N and P donor ligands (i.e. 2,2′-bipyridine, 1,10-phenanthroline and triphenylphosphine) in chloroform was added dropwise with constant stirring to weighed amounts of pyrazolinates of iron dissolved in dry chloroform during 24 h at room temperature until the color underwent a change. Reaction mixture was filtered through an alkoxy funnel under vacuum to separate the solid, which was washed with distilled water and finally with alcohol. The solid so obtained was dried at 100°C. The data for synthesis of individual compounds are given in tables 2, 3 and 4.

3. Physical measurements

IR spectra were recorded as KBr pellets on a Perkin-Elmer spectrum RXI spectrophotometer. Molecular weights were determined on a Knoauer Vapour pressure Osmometer in $CHCl_3$ at 45°C. Elemental analysis of iron was done by standard procedure. Carbon, hydrogen and nitrogen were estimated by an Elementor Vario ELIII Carlo1108 elemental analyzer. Magnetic moment studies were carried on a Gouy balance at room temperature. The FAB mass spectra were recorded on a JEOL SX 102/DA-6000 mass spectrometer. The ^{31}P NMR spectra were recorded in the solid state. The Mössbauer data were taken with ^{57}Co diffused into a Rh matrix. The experiment was performed at room temperature (about 300 K). The absorber was kept stationary and the source was moving with velocity ranging from 0 to $\pm 10\,mm\,s^{-1}$. All spectra were taken without an applied magnetic field and found to be quadrupole doublets. The isomer shift is positive in each case. The complexes were examined for crystalline/amorphous nature through XRD.

3.1. *Antimicrobial investigations*

Antimicrobial activity tests were performed by using article disc method [25, 26]. The 5 mm Whatmann 41 and 42 filter article discs were sterilized and immersed in test solution. Each test solution was prepared by dissolving 100 mg in 1 mL acetone. The saturated discs were taken out and held in the air for a few seconds to evaporate acetone and then transferred aseptically on seeded agar plate. One article disc soaked in acetone only was also placed on the agar as control.

To prepare agar plate nutrient, agar medium was used for bacteria and sabaraud dextrose agar for fungi. Active nutrient broth culture of bacteria and potato dextrose agar culture for fungi were used to seed the nutrient agar plate. To prepare seed plate 20 mL medium was poured in a sterile Petri dish and left to solidify. Thereafter with the help of a swab, bacteria from the growth culture or fungal spores taken in distilled water were spread on the agar plate. After 30 min article discs with compound were laid on the seeded plate. The bacterial plates were incubated at 36°C and fungal plates at 28°C. After 24 h inhibitions were observed and diameter measured.

The synthesized complexes have been subjected to *in vitro* antimicrobial activity testing with various plant and human pathogenic bacteria and fungi. A disc soaked in acetone alone was used as a control under the same conditions and no inhibition zone

Table 2. Synthetic, analytical and physical property data for adducts of 5(2′-hydroxyphenyl)-3-(4-X-phenyl)pyrazolinates of iron with 2,2′-bipyridine.

Reactants							Analysis, % found (Calcd)			
Complex *g* (mmol)	2,2′-Bipyridine $C_{10}H_8N_2$ *g* (mmol)	Molar ratio	Product (color)	Yield %	Melting point (°C)	Mol. wt. found (Calcd)	C	H	N	Fe
$Fe(L_a)_3$ 1.66 (2.16)	0.33 (2.16)	1 : 1	$Fe(L_a)_3$(bipy) (Reddish-brown)	86	>360	922.03 (923.03)	71.54 (71.57)	5.14 (5.13)	12.11 (12.14)	16.06 (16.05)
$Fe(L_b)_3$ 1.69 (1.94)	0.30 (1.94)	1 : 1	$Fe(L_b)_3$(bipy) (Reddish-brown)	81	>360	1025.98 (1028.03)	64.27 (64.26)	4.30 (4.31)	10.88 (10.89)	5.41 (5.43)
$Fe(L_c)_3$ 1.67 (2.07)	0.32 (2.07)	1 : 1	$Fe(L_c)_3$(bipy) (Reddish-black)	88	>360	966.13 (965.03)	72.16 (72.19)	5.58 (5.54)	11.61 (11.61)	5.78 (5.80)
$Fe(L_d)_3$ 1.69 (1.97)	0.30 (1.97)	1 : 1	$Fe(L_d)_3$(bipy) (Reddish-brown)	82	>360	1012.53 (1013.03)	56.90 (56.91)	5.26 (5.27)	11.07 (11.06)	5.54 (5.53)

$Fe(L_a)_3$ = 5(2′-hydroxyphenyl)-3-phenylpyrazolinate of iron.
$Fe(L_b)_3$ = 5(2′-hydroxyphenyl)-3-(4-chlorophenyl)pyrazolinate of iron.
$Fe(L_c)_3$ = 5(2′-hydroxyphenyl)-3-(4-methylphenyl)pyrazolinate of iron.
$Fe(L_d)_3$ = 5(2′-hydroxyphenyl)-3-(4-methoxyphenyl)pyrazolinate of iron.

Table 3. Synthetic, analytical and physical property data for adducts of 5(2′-hydroxyphenyl)-3-(4-X-phenyl)pyrazolinates of iron with 1,10-phenanthroline.

Reactants							Analysis, % found (Calcd)			
Complex *g* (mmol)	1,10-Phenanthroline $C_{12}H_8N_2$ *g* (mmol)	Molar ratio	Product (color)	Yield %	Melting point (°C)	Mol. wt. found (Calcd)	C	H	N	Fe
$Fe(L_a)_3$ 1.61 (2.11)	0.38 (2.11)	1 : 1	$Fe(L_a)_3$(phen) (Reddish-brown)	82	>360	948.63 (947.05)	72.28 (72.29)	4.98 (4.97)	11.81 (11.83)	5.93 (5.91)
$Fe(L_b)_3$ 1.65 (1.90)	0.34 (1.90)	1 : 1	$Fe(L_b)_3$(phen) (Reddish-brown)	84	>360	1050.53 (1052.05)	65.10 (65.07)	4.21 (4.22)	10.63 (10.65)	5.31 (5.32)
$Fe(L_c)_3$ 1.6356 (2.02)	0.36 (2.02)	1 : 1	$Fe(L_c)_3$(phen) (Reddish-brown)	87	>360	988.32 (989.05)	72.83 (72.86)	5.39 (5.40)	11.34 (11.33)	5.65 (5.66)
$Fe(L_d)_3$ 1.65 (1.92)	0.34 (1.92)	1 : 1	$Fe(L_d)_3$(phen) (Reddish-brown)	88	>360	1038.89 (1037.05)	69.49 (69.50)	5.13 (5.15)	10.82 (10.80)	5.41 (5.40)

$Fe(L_a)_3 = 5(2'$-hydroxyphenyl)-3-phenylpyrazolinate of iron.
$Fe(L_b)_3 = 5(2'$-hydroxyphenyl)-3-(4-chlorophenyl)pyrazolinate of iron.
$Fe(L_c)_3 = 5(2'$-hydroxyphenyl)-3-(4-methylphenyl)pyrazolinate of iron.
$Fe(L_d)_3 = 5(2'$-hydroxyphenyl)-3-(4-methoxyphenyl)pyrazolinate of iron.

Table 4. Synthetic, analytical and physical property data for adducts of 5(2′-hydroxyphenyl)-3-(4-X-phenyl)pyrazolinates of iron with triphenylphosphine.

Reactants							Analysis, % found (Calcd)			
Complex *g* (mmol)	Triphenylphosphine $C_{18}H_{15}P$ *g* (mmol)	Molar ratio	Product (color)	Yield %	Melting point (°C)	Mol. wt. found (Calcd)	C	H	N	Fe
$Fe(L_a)_3$ 1.49 (1.94)	0.50 (1.94)	1 : 1	$Fe(L_a)_3(PPh_3)$ (Reddish-black)	83	>360	1026.89 (1029.13)	73.56 (73.53)	5.28 (5.29)	8.15 (8.17)	5.45 (5.44)
$Fe(L_b)_3$ 1.53 (1.76)	0.46 (1.76)	1 : 1	$Fe(L_b)_3(PPh_3)$ (Reddish-black)	84	224	1135.04 (1134.13)	66.71 (66.72)	4.50 (4.53)	7.43 (7.41)	4.98 (4.94)
$Fe(L_c)_3$ 1.51 (1.86)	0.48 (1.86)	1 : 1	$Fe(L_c)_3(PPh_3)$ (Reddish-black)	82	>360	1070.89 (1071.13)	74.00 (74.01)	5.64 (5.65)	7.89 (7.85)	5.21 (5.23)
$Fe(L_d)_3$ 1.31 (1.78)	0.46 (1.78)	1 : 1	$Fe(L_d)_3(PPh_3)$ (Reddish-black)	89	170	1116.13 (1119.13)	70.82 (70.83)	5.41 (5.40)	7.53 (7.51)	4.98 (5.00)

$Fe(L_a)_3$ = 5(2′-hydroxyphenyl)-3-phenylpyrazolinate of iron.
$Fe(L_b)_3$ = 5(2′-hydroxyphenyl)-3-(4-chlorophenyl)pyrazolinate of iron.
$Fe(L_c)_3$ = 5(2′-hydroxyphenyl)-3-(4-methylphenyl)pyrazolinate of iron.
$Fe(L_d)_3$ = 5(2′-hydroxyphenyl)-3-(4-methoxyphenyl)pyrazolinate of iron.

was observed. Each distinct inhibition zone was measured as diameter in mm, both antibacterial and antifungal activity can be calculated as a mean of three replicates.

4. Results and discussion

The 5(2′-hydroxyphenyl)-3-(4-X-phenyl)pyrazolinates of iron and their adducts with N and P donor ligands (i.e. 2,2′-bipyridine, 1,10-phenanthroline and triphenylphosphine) are solids of reddish-brown to reddish-black color. They are non-hygroscopic and stable at room temperature. These iron(III) complexes are soluble in organic (chloroform, dichloromethane) and coordinating (pyridine, DMSO and THF) solvents on slight heating. These complexes are monomeric in dilute chloroform solution at 45°C. The elemental analysis (C, H, N, Fe) data are in accord with the stoichiometry proposed. The data are summarized in tables 1–4.

The magnetic moment values for pyrazolinates of iron(III) and their adduct complexes are compiled in table 6 with magnetic moment values between 5.48–5.91 BM. The value 5.92 is normally found for the hexacoordinate iron(III) complexes [27]. The magnetic moment values are consistent with octahedral geometry around iron.

4.1. *Infrared spectra*

The assignments of infrared spectral bands for iron(III)pyrazolinates and their addition complexes have been given in table 5. The band due to υ(OH) originally found in the

Table 5. IR spectral data for 5(2′-hydroxyphenyl)-3-(4-X-phenyl)pyrazolinates of iron and their adduct complexes with 2,2′-bipyridine, 1,10-phenanthroline and triphenylphosphine.

	Infra red (cm^{-1})			
Adducts	υ(N–H)	υ(C=N)	υ(M–N)	υ(M–O)
Fe(L$_a$)$_3$	3446	1654	421	597
Fe(L$_b$)$_3$	3424	1621	460	580
Fe(L$_c$)$_3$	3408	1614	480	568
Fe(L$_d$)$_3$	3415	1620	473	581
Fe(L$_a$)$_3$(bipy)	3420	1618	466	563
Fe(L$_b$)$_3$(bipy)	3423	1601	470	579
Fe(L$_c$)$_3$(bipy)	3415	1589	475	570
Fe(L$_d$)$_3$(bipy)	3418	1592	474	590
Fe(L$_a$)$_3$(phen)	3440	1598	426	604
Fe(L$_b$)$_3$(phen)	3417	1596	477	580
Fe(L$_c$)$_3$(phen)	3419	1599	479	566
Fe(L$_d$)$_3$(phen)	3424	1600	468	579
Fe(L$_a$)$_3$(PPh$_3$)	3444	1610	–	592
Fe(L$_b$)$_3$(PPh$_3$)	3421	1613	–	583
Fe(L$_c$)$_3$(PPh$_3$)	3416	1616	–	567
Fe(L$_d$)$_3$(PPh$_3$)	3425	1617	–	584

L$_a$ = 5(2′-hydroxyphenyl)-3-phenylpyrazoline.
L$_b$ = 5(2′-hydroxyphenyl)-3-(4-chlorophenyl)pyrazoline.
L$_c$ = 5(2′-hydroxyphenyl)-3-(4-methylphenyl)pyrazoline.
L$_d$ = 5(2′-hydroxyphenyl)-3-(4-methoxyphenyl)pyrazoline.
bipy = 2′,2′-bipyridine.
phen = 1,10-phenanthroline.
PPh$_3$ = triphenylphosphine.

region 3080–3050 cm^{-1} in the spectra of ligand is absent in spectra of complexes, indicating involvement of phenolic OH in bond formation via deprotonation. The band in the region 3446–3408 cm^{-1} assigned to υ(N–H) is at almost the same position with respect to spectra of free pyrazoline ligand suggesting non-involvement of N–H in bond formation. The υ(C=N) found at 1654–1614 cm^{-1} is shifted to higher wavenumber suggesting coordination through nitrogen of C=N [28], confirming the bidentate nature of ligand. The absorptions at 3444–3415 cm^{-1} and 1618–1589 cm^{-1} are assigned to υ(N–H) and υ(C=N), respectively, in almost the same position as the ligand, suggesting the non-involvement of N–H and C=N groups in bonding to the addition complexes with N and P donor ligands indicating monodentate pyrazoline. The new bands in the region 604–563 cm^{-1} and 480–421 cm^{-1} may be ascribed to υ(M–O) and υ(M–N) stretching vibrations, respectively, in pure and addition complexes with N donor ligands. In case of P donor ligand only one new band due to υ(M–O) is found in the region 592–567 cm^{-1}.

4.2. *^{31}P NMR spectra*

The ^{31}P NMR spectra of addition complexes of iron(III)pyrazolinates with triphenylphosphine in solid state have a broad single peak in the range δ 38.2–30.8 ppm. This indicates the coordinaton between Fe(III) and P atom of triphenylphosphine [29–32].

4.3. *Electronic spectra*

The electronic spectra of pyrazolinates of iron(III) and their addition complexes are tabulated in table 6. The band observed in the region 13851–13022 cm^{-1} may be assigned to $^6A_{1g} \rightarrow {}^4T_{1g}$ transition. The other bands in the region 48990–28220 cm^{-1} could be due to charge transfer transitions. The position of various bands are in good agreement with the data reported for iron(III) complexes [33]. The structure of iron(III)di-*iso*-propyl-dithiophosphate has been confirmed by X–ray crystallography [34]. In the addition complexes three pyrazoline ligands are bonded with phenolic oxygen, two coordination sites are satisfied with two nitrogen atoms of nitrogen donor bases, i.e. 2,2′-bipyridine and 1,10-phenanthroline and one is occupied by solvent. In PPh_3 complexes, three coordination sites are phenolic oxygen of pyrazoline ligands, one by triphenylphosphine and two by solvent.

4.4. *FAB mass spectra*

The FAB mass spectra of the complexes of 5(2′-hydroxyphenyl)-3-(4-X-phenyl)pyrazoline [substituted group, X = –methyl] and adduct complexes of iron(III)pyrazolinates with 2,2′-bipyridine [$Fe(L_a)_3$bipy], L_a = 5(2′-hydroxyphenyl)-3-phenylpyrazoline, gives information about the molecular weight of the complexes. The molecular ion peak (M^+) along with other characteristic peaks showing various fragmentations were observed. The mass spectra of $Fe(L_c)_3$, L_c = 5(2′-hydroxyphenyl)-3-(4-methylphenyl)pyrazoline, exhibiting molecular ion peak at $m/z = 809$, suggests the monomeric nature of the complex. Peaks are observed at 716, 623, 530, 439, 348, 257, 218, 179 and 140 m/z after

Table 6. Electronic spectral data and magnetic moment data for 5(2′-hydroxyphenyl)-3-(4-X-phenyl)pyrazolinates of iron and their adducts with 2,2′-bipyridine, 1,10-phenanthroline and triphenylphosphine.

	Electronic spectral bands		
Complexes	Assignment	Band (cm^{-1})	Magnetic moment (BM)
$Fe(L_a)_3$	$^6A_{1g} \longrightarrow {}^4T_{1g}$	13530	5.49
	Charge Transfer	30030, 46426	
$Fe(L_b)_3$	$^6A_{1g} \longrightarrow {}^4T_{1g}$	13813	5.90
	Charge Transfer	32400, 46428	
$Fe(L_c)_3$	$^6A_{1g} \longrightarrow {}^4T_{1g}$	13551	5.83
	Charge Transfer	30253, 46420	
$Fe(L_d)_3$	$^6A_{1g} \longrightarrow {}^4T_{1g}$	13022	5.79
	Charge Transfer	31400, 46248	
$Fe(L_a)_3$(bipy)	$^6A_{1g} \longrightarrow {}^4T_{1g}$	13145	5.48
	Charge Transfer	28240, 48990	
$Fe(L_b)_3$(bipy)	$^6A_{1g} \longrightarrow {}^4T_{1g}$	13851	5.91
	Charge Transfer	28680, 48739	
$Fe(L_c)_3$(bipy)	$^6A_{1g} \longrightarrow {}^4T_{1g}$	13560	5.69
	Charge Transfer	28692, 48452	
$Fe(L_d)_3$(bipy)	$^6A_{1g} \longrightarrow {}^4T_{1g}$	13070	5.68
	Charge Transfer	28246, 48580	
$Fe(L_a)_3$(phen)	$^6A_{1g} \longrightarrow {}^4T_{1g}$	13542	5.85
	Charge Transfer	28220, 48390	
$Fe(L_b)_3$(phen)	$^6A_{1g} \longrightarrow {}^4T_{1g}$	13817	5.76
	Charge Transfer	28640, 48252	
$Fe(L_c)_3$(phen)	$^6A_{1g} \longrightarrow {}^4T_{1g}$	13511	5.84
	Charge Transfer	28428, 48339	
$Fe(L_d)_3$(phen)	$^6A_{1g} \longrightarrow {}^4T_{1g}$	13030	5.57
	Charge Transfer	28780, 48384	
$Fe(L_a)_3(PPh_3)$	$^6A_{1g} \longrightarrow {}^4T_{1g}$	13533	5.72
	Charge Transfer	33580, 49490	
$Fe(L_b)_3(PPh_3)$	$^6A_{1g} \longrightarrow {}^4T_{1g}$	13845	5.89
	Charge Transfer	32280, 49547	
$Fe(L_c)_3(PPh_3)$	$^6A_{1g} \longrightarrow {}^4T_{1g}$	13527	5.54
	Charge Transfer	31490, 49380	
$Fe(L_d)_3(PPh_3)$	$^6A_{1g} \longrightarrow {}^4T_{1g}$	13118	5.77
	Charge Transfer	35310, 50779	

L_a = 5(2′-hydroxyphenyl)-3-phenylpyrazoline.
L_b = 5(2′-hydroxyphenyl)-3-(4-chlorophenyl)pyrazoline.
L_c = 5(2′-hydroxyphenyl)-3-(4-methylphenyl)pyrazoline.
L_d = 5(2′-hydroxyphenyl)-3-(4-methoxyphenyl)pyrazoline.
bipy = 2′,2′-bipyridine.
phen = 1,10-phenanthroline.
PPh_3 = triphenylphosphine.

successive removal of $-C_6H_5O^\bullet$, $-C_6H_5O^\bullet$, $-C_6H_5O^\bullet$, $-C_7H_7^\bullet$, $-C_7H_7^\bullet$, $-C_7H_7^\bullet$, $-C_3H_3^\bullet$, $-C_3H_3^\bullet$ and $-C_3H_3^\bullet$, respectively. In case of $[Fe(L_a)_3bipy]$, addition complex shows molecular peak at $m/z = 924$, again suggesting monomeric complex. Peaks observed at 822, 720, 643, 566, 489, 396, 303, 210,171, 132 and 93 m/z after successive removal of $-C_5H_4N^\bullet$, $-C_5H_4N^\bullet$, $C_5H_4N^\bullet$, $-C_6H_5^\bullet$, $-C_6H_5^\bullet$, $-C_6H_5^\bullet$, $-C_6H_5O^\bullet$, $-C_6H_5O^\bullet$, $-C_6H_5O^\bullet$, $-C_3H_3^\bullet$, $-C_3H_3^\bullet$ and $-C_3H_3^\bullet$.

4.5. *Mössbauer spectra*

The Mössbauer spectra of all the complexes were taken at room temperature (about 300 K). The Mössbauer parameters are summarized in table 8. The isomer shift is 1.79×10^{-8} eV to 1.61×10^{-8} eV for complexes. The magnitude of isomer shift is comparable to the reported data at room temperature for various Fe(III) and Fe(II) complexes having six-coordinate metal ion [35, 36]. The isomer shift is positive in each case. The Mössbauer effect provides a powerful probe to chemical state and the environment of iron atoms [37]. The difference in s-electron densities, quadrupole coupling constant (QCC) and electric field gradient are calculated, assuming the asymmetry parameter (η) to be zero. QCC gives information about coordination number of the complexes [38], as the coordination number increases, the metal ion tends to be spherically symmetric and quadrupole coupling constant decreases.

Quadrupole splitting at room temperature suggests electric field gradient at the metal ion due to the presence of ligand around the ion or may be due to distortion from octahedral geometry to an elongated octahedral geometry by the complex. Quadrupole splitting in complexes are higher (table 8), where ligands may provide asymmetric hexacoordination to metal and that electric field gradient is significant. Since magnetic splitting does not appear in these complexes, the states remain doubly degenerate showing the Kramer's degeneracy. Linewidths of the complexes are large in comparison to the natural linewidth (4.665×10^{-9} eV) of ^{57}Fe, due to Doppler broadening of an improper functioning of Mössbauer apparatus or saturation effects in the absorber or in the source. However, there are also a number of inherent physical processes causing line broadening.

4.6. *Microbial assay*

The antibacterial activity of the 5(2′-hydroxyphenyl)-3-(4-X-phenyl)pyrazolinates of iron and their adducts with N and P donor ligands were tested against bacterial species *Staphylococcus aureus*, *Staphylococcus typhi*, *Bacillus sublitis*, *Saccharomyces cerevisae*, *Candida albicans*, *Pencillium notatum*, *Aspergillus flavus*, *Mucor mucedo*, *Pseudomonas aerginosa*, *Klebsilla pneumoniae*, *Vibrio parahaemolyticus*, *Escherichia coli* (table 7).

The antimicrobial studies shows that the 5(2′-hydroxyphenyl)-3-(4-X-phenyl) pyrazolinates of iron(III) and their addition complexes with N, P donor ligand have greater activity towards all tested bacteria and fungi than free pyrazolines.

Nevertheless, it is difficult to make an exact structure and activity relationship between antimicrobial activity and the structure of these complexes. The complexation of the 5(2′-hydroxyphenyl)-3-(4-X-phenyl)pyrazolinates of iron(III) with N and P donor ligands results in increased activity.

5. Conclusions

A series of pyrazolinates of iron(III) and their adducts with N, P donor ligands are consistent with octahedral six co-ordinate [39–42] with three bidentate pyrazoline ligands in complexes of the type $(C_{15}H_{12}N_2OX)_3Fe$. However, in adducts pyrazoline ligand is monodentate, where one or two co-ordination sites in nitrogen and phosphorus adducts are satisfied by solvent. On the basis of XRD all complexes are amorphous.

Table 7. Antimicrobial activity of free pyrazoline ligands, 5(2′-hydroxyphenyl)3-(4-X-phenyl)pyrazolinates of iron and their adducts with N, P donor ligands.

	Fungi	Gram(+ve) bacteria		Gram(−ve) bacteria								
Compounds	*A. flavus*	*P. notatum*	*M. mucedo*	*B. subtilis*	*S. aureus*	*E. coli*	*S. typhi*	*K. pneumoniae*	*V. parahaemolyticus*	*P. aeruginosa*	*S. cerevisae*	*C. albicans*
L_a	10	10	–	09	08	–	–	–	–	–	–	–
L_b	10	–	–	08	07	–	–	–	–	–	–	–
L_c	07	–	–	07	07	–	–	–	–	–	–	–
L_d	07	–	–	07	06	–	–	–	–	–	–	–
$Fe(L_a)_3$	20	21	–	20	22	09	07	–	–	–	–	–
$Fe(L_b)_3$	22	08	–	21	21	08	06	–	–	–	–	–
$Fe(L_c)_3$	23	07	–	18	16	07	–	–	–	–	–	05
$Fe(L_d)_3$	23	08	–	19	18	09	08	–	–	–	–	03
$Fe(L_a)_3$(bipy)	21	09	–	22	22	07	–	–	–	–	–	06
$Fe(L_b)_3$(bipy)	22	07	–	20	19	08	07	–	–	–	–	04
$Fe(L_c)_3$(bipy)	16	06	–	21	17	11	06	–	–	–	–	–
$Fe(L_d)_3$(bipy)	15	08	–	19	15	08	08	–	–	–	–	03
$Fe(L_a)_3$(phen)	22	07	–	21	24	09	–	–	–	–	–	02
$Fe(L_b)_3$(phen)	21	06	–	20	21	07	06	–	–	–	–	–
$Fe(L_c)_3$(phen)	20	09	–	18	22	10	–	–	–	–	–	–
$Fe(L_d)_3$(phen)	21	08	–	17	19	07	–	–	–	–	–	03
$Fe(L_a)_3(PPh_3)$	22	10	–	23	20	06	07	–	–	–	–	02
$Fe(L_b)_3(PPh_3)$	23	08	–	21	17	09	–	–	–	–	–	–
$Fe(L_c)_3(PPh_3)$	24	07	–	10	15	10	08	–	–	–	–	04
$Fe(L_d)_3(PPh_3)$	23	06	–	11	16	08	07	–	–	–	–	–

(Diameter of inhibition zone measured in mm, article disc 5 mm, inhibition zone measured excluding article disc diameter, - = not active, amount of complexes taken 100 mg mL^{-1}). L_a = 5(2′-hydroxyphenyl)-3-phenylpyrazoline. L_b = 5(2′-hydroxyphenyl)-3-(4-chlorophenyl)pyrazoline. L_c = 5(2′-hydroxyphenyl)-3-(4-methylphenyl)pyrazoline. L_d = 5(2′-hydroxyphenyl)-3-(4-methoxyphenyl)pyrazoline. bipy = 2′,2′-bipyridine. phen = 1,10-phenanthroline. PPh_3 = triphenylphosphine.

Table 8. Mössbauer spectral data for 5(2′-hydroxyphenyl)-3-(4-X-phenyl)pyrazolinates of iron and their adducts with 2,2′-bipyridine, 1,10-phenanthroline and triphenylphosphine ($1\,\text{eV} = 2.080014 \times 10^{7}\,\text{mm s}^{-1}$).

Compounds	Linewidth $\times 10^{-8}$ eV	Area of the line $\times 10^{-8}$ eV	Isomer shift $\times 10^{-8}$ eV	Quadrupole splitting $\times 10^{-8}$ eV	Electric field gradient $\times 10^{-8}$ eV	Quadrupole coupling constant $\times 10^{-8}$ eV	Δs-electron density $\times 10^{-8}$ eV
$Fe(L_a)_3$	2.65 ± 0.07	0.18 ± 0.003	1.74 ± 0.05	3.21 ± 0.06	3.21 ± 0.06	0.53 ± 0.01	10.85 ± 0.30
$Fe(L_b)_3$	3.94 ± 0.55	0.17 ± 0.002	1.71 ± 0.02	3.10 ± 0.25	3.10 ± 0.25	0.35 ± 0.04	10.56 ± 0.21
$Fe(L_c)_3$	3.34 ± 0.07	0.85 ± 0.002	1.64 ± 0.03	3.49 ± 0.04	3.50 ± 0.04	0.58 ± 0.01	10.25 ± 0.15
$Fe(L_d)_3$	3.08 ± 0.02	0.83 ± 0.005	1.63 ± 0.02	3.34 ± 0.02	3.34 ± 0.02	0.56 ± 0.01	10.21 ± 0.10
$Fe(L_a)_3$(bipy)	2.76 ± 0.07	0.15 ± 0.003	1.79 ± 0.05	3.18 ± 0.06	3.18 ± 0.06	0.52 ± 0.01	10.81 ± 0.30
$Fe(L_b)_3$(bipy)	3.90 ± 0.57	0.18 ± 0.002	1.74 ± 0.03	3.12 ± 0.24	3.12 ± 0.24	0.38 ± 0.04	10.51 ± 0.21
$Fe(L_c)_3$(bipy)	3.36 ± 0.06	0.81 ± 0.002	1.66 ± 0.03	3.44 ± 0.04	3.44 ± 0.04	0.56 ± 0.01	10.25 ± 0.15
$Fe(L_d)_3$(bipy)	3.05 ± 0.03	0.80 ± 0.002	1.68 ± 0.02	3.36 ± 0.02	3.36 ± 0.02	0.57 ± 0.01	10.23 ± 0.10
$Fe(L_a)_3$(phen)	2.96 ± 0.06	0.17 ± 0.003	1.72 ± 0.05	3.24 ± 0.06	3.24 ± 0.06	0.54 ± 0.01	10.83 ± 0.30
$Fe(L_b)_3$(phen)	3.94 ± 0.55	0.19 ± 0.004	1.73 ± 0.02	3.13 ± 0.25	3.13 ± 0.25	0.31 ± 0.04	10.55 ± 0.21
$Fe(L_c)_3$(phen)	3.33 ± 0.06	0.87 ± 0.003	1.68 ± 0.03	3.50 ± 0.03	3.50 ± 0.03	0.59 ± 0.01	10.21 ± 0.15
$Fe(L_d)_3$(phen)	2.87 ± 0.06	0.83 ± 0.005	1.65 ± 0.02	3.36 ± 0.02	3.36 ± 0.02	0.57 ± 0.01	10.20 ± 0.10
$Fe(L_a)_3(PPh_3)$	3.94 ± 0.54	0.19 ± 0.003	1.71 ± 0.05	3.26 ± 0.06	3.26 ± 0.06	0.55 ± 0.01	10.79 ± 0.30
$Fe(L_b)_3(PPh_3)$	3.34 ± 0.07	0.18 ± 0.002	1.75 ± 0.02	3.10 ± 0.25	3.10 ± 0.25	0.36 ± 0.04	10.53 ± 0.21
$Fe(L_c)_3(PPh_3)$	3.08 ± 0.02	0.85 ± 0.002	1.64 ± 0.03	3.40 ± 0.05	3.40 ± 0.05	0.58 ± 0.01	10.26 ± 0.15
$Fe(L_d)_3(PPh_3)$	3.36 ± 0.06	0.83 ± 0.003	1.61 ± 0.02	3.31 ± 0.02	3.31 ± 0.02	0.57 ± 0.01	10.18 ± 0.10

L_a = 5(2′-hydroxyphenyl)-3-phenylpyrazoline. L_b = 5(2′-hydroxyphenyl)-3-(4-chlorophenyl)pyrazoline. L_c = 5(2′-hydroxyphenyl)-3-(4-methylphenyl)pyrazoline. L_d = 5(2′-hydroxyphenyl)-3-(4-methoxyphenyl)pyrazoline. bipy = 2′,2′-bipyridine. Phen = 1,10-phenanthroline. PPh_3 = triphenylphosphine.

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