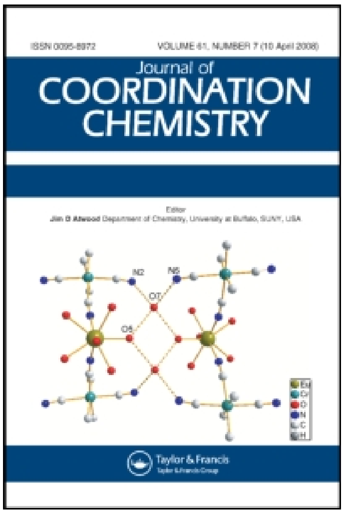

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Synthesis, spectral and biological investigations of 5(2'-hydroxyphenyl)-3-(4-substituted-phenyl) pyrazolinates of cobalt(II) and their addition complexes with N, P donor ligands

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Synthesis, spectral and biological investigations of 5(2′-hydroxyphenyl)-3-(4-substituted-phenyl) pyrazolinates of cobalt(II) and their addition complexes with N, P donor ligands

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5(2′-Hydroxyphenyl)-3-(4-substituted-phenyl)pyrazolinates of cobalt(II) of the type $(C_{15}H_{12}N_2OX)_2Co$ [here substituted group X is –H, –Cl, $-CH_3$ or $-OCH_3$] have been synthesized by reaction of anhydrous cobalt(II)chloride with the sodium salt of the pyrazolines in 1 : 2 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. The newly synthesized complexes were characterized by elemental analyses, molecular weight measurement, magnetic susceptibility, IR, electronic, ^{31}P NMR and FAB mass spectra. All complexes are amorphous as determined by XRD. Tetrahedral geometry around cobalt(II) has been suggested, confirming the presence of two pyrazoline bidentate ligands, cobalt(II)5-(2′-hydroxyphenyl)-3-(4-substituted-phenyl)pyrazolinates. Upon ligand addition, pyrazoline changes to monodentate. The bidentate and monodentate behavior of pyrazoline ligands was confirmed by IR spectral data. The metal complexes and their adducts exhibit good antibacterial and antifungal activity, better than the pyrazolines.

Keywords: Pyrazoline; 2,2′-Bipyridine; 1,10-Phenanthroline; Triphenylphosphine; Biological investigation; Cobalt(II)pyrazolinates

1. Introduction

Pyrazolines are an important class of heterocyclic compounds, used in industries as dyes, antioxidants in lubricating oils [1] and in agriculture as catalysts for decarboxylation reactions as well as inhibitors in plant growth [2–4]. Due to their non toxic properties [5] they are also used as local anesthetics [6]. Organic derivatives of pyrazoline are used extensively in photography [7]. A large number of other hydroxylphenyl substituted heterocycles have been used as analgesic [8, 9], antitumor [10], antitussive [11], anti-inflammatory [12] and anticonvulsant agents [13, 14]. These are also applicable for cardiovascular activities [15] and antidepressant

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activities [16]. Metal complexes of 5(2′-hydroxyphenyl)-3-phenylpyrazoline with Ni(II), Co(II) and Cu(II) have been prepared in our laboratory [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 [19–21]. In continuation of our work [22] on synthesis, spectral and antimicrobial investigations of iron(III)5(2′-hydroxyphenyl)-3-(4-*x*-phenyl)pyrazoline complexes and their addition complexes with N and P donor ligands [23], we synthesized cobalt(II)5(2′-hydroxyphenyl)-3-(4-substituted-phenyl)pyrazoline complexes [here substituted groups are –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. Cobalt is the most important transition element involved in living systems, vital to both plants and animals. Vitamin B_{12} is a related complex of cobalt, whose redox properties are apparently utilized in the biological synthesis of the ligands attached to iron in hemoglobin.

2. Experimental

All chemicals used were analytical grade quality. Solvents were used after rigorously drying and purifying before use by standard procedure [24]. The ligand 5(2′-hydroxyphenyl)-3-(4-substituted-phenyl)pyrazoline was prepared by reported procedure [25].

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

The new cobalt(II)pyrazolinates were prepared by the following route:

$$CoCl_2 + 2(C_{15}H_{12}N_2OX)Na \xrightarrow[\text{Room Temp.}]{\text{Isopropanol}} (C_{15}H_{12}N_2OX)_2Co + 2NaCl$$

$$X = -H, -Cl, -CH_3, -OCH_3$$

Freshly cut sodium was taken in a flask containing isopropanol and refluxed (~1/2 hour) till a clear solution of sodium isopropoxide was obtained. Solution of 5(2′-hydroxyphenyl)-3-(4-substituted-phenyl)pyrazoline in isopropanol was added and reaction continued for 1 h when a constant yellow color was obtained. The reaction mixture was cooled to room temperature and alcoholic solution of anhydrous cobalt(II)chloride was added dropwise with constant stirring. The reaction mixture was further stirred for 20–24 h, till the color underwent a change from yellow to dark brown. The reaction mixture was filtered under vacuum to separate the solid, which was washed with hot water to remove sodium chloride 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 data for 5(2′-hydroxyphenyl)-3-(-4-substituted-phenyl)pyrazolinates of cobalt.

	Reactants								Analysis, % Found (Calcd)			
S. No. (Compound No.)	Anhydrous $CoCl_2$ g (mmol)	Sodium g (mmol)	Ligand g (mmol)	Molar ratio	Product (Color)	Yield %	M.P. (°C)	Mol. Wt. Found (Calcd)	C	H	N	Co
1			HPPP	1 : 2 : 2	$Co(L_a)_2$ (Brown)	92	275					
	0.73	0.25	2.68					531.98	67.60	4.92	10.53	11.04
	(5.64)	(11.30)	(11.30)					(532.93)	(67.91)	(4.91)	(10.52)	(11.06)
2			HPCPP	1 : 2 : 2	$Co(L_b)_2$ (Brown)	96	>360					
	0.64	0.22	2.71					603.98	59.75	4.02	9.28	9.78
	(4.98)	(9.96)	(9.96)					(602.93)	(59.76)	(4.01)	(9.29)	(9.77)
3			HPMPP	1 : 2 : 2	$Co(L_c)_2$ (Brown)	93	>360					
	0.69	0.24	2.69					560.91	68.53	5.38	9.99	10.52
	(5.34)	(10.69)	(10.69)					(560.93)	(68.52)	(5.39)	(9.98)	(10.51)
4			HPMeoPP	1 : 2 : 2	$Co(L_d)_2$ (Brown)	98	>360					
	0.65	0.23	2.71					590.13	64.75	5.12	9.40	9.91
	(5.05)	(10.11)	(10.11)					(592.93)	(64.76)	(5.10)	(9.44)	(9.94)

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-substituted-phenyl)pyrazolinates of cobalt with N and P donor ligands*

A solution of 2,2′-bipyridine, 1,10-phenanthroline or triphenylphosphine in chloroform was added dropwise with constant stirring during 24 h at room temperature to weighed pyrazolinates of cobalt dissolved in dry chloroform till the color of the reaction mixture underwent a change. The reaction mixture was filtered 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 2–4.

2.3. *Physical measurements*

IR spectra were recorded as KBr pellets on a Perkin-Elmer spectrum RX1 spectrophotometer. Molecular weights were determined on a Knoauer vapour pressure osmometer in $CHCl_3$ at 45°C. Elemental analysis of cobalt was done by standard procedure. Carbon, hydrogen and nitrogen were estimated by Elementor Vario ELIII Carlo1108 elemental analyzer. Magnetic measurements were carried out on a Gouy balance at room temperature. Electronic spectra were recorded in chloroform solution on a Perkin-Elmer Lambda15 spectrophotometer. The FAB mass spectra were recorded on a JEOL SX 102/DA-6000 mass spectrometer. The ^{31}P NMR spectra were recorded in solid state on a Bruker Advance DRX-300 spectrometer at room temperature. The complexes were examined for crystalline/amorphous nature through XRD on a Philips compact X-ray diffraction analyzer model PW 1710.

2.4. *Biological investigation*

2.4.1. Antibacterial bioassay. All synthesized complexes were screened *in vitro* for their antibacterial activity against four Gram-negative (*E. coli*, *S. flexenari*, *P. aeruginosa*, and *S. typhi*) and two Gram-positive (*B. subtilis* and *S. aureus*) bacterial strains using the agar-well diffusion method [26]. Two to eight hours old bacterial inoculums containing approximately 10^4–10^6 colony forming units (CFU) mL^{-1} were used in these assays. The wells were dug in the media with the help of sterile metallic borers with centers at least 24 mm. Recommended concentration (100 µL) of the test sample (1 mg mL^{-1} in DMSO) were introduced in the respective wells. Other wells supplemented with DMSO and the reference antibacterial drug, imipenum, served as negative and positive controls, respectively. The plates were incubated immediately at 37°C for 20 h. Activity was determined by measuring the diameter of zones showing complete inhibition (mm). Growth inhibition was compared [27] with the standard drug. In order to clarify any participating role of DMSO in the biological screening, separate studies were carried out with only DMSO and they showed no activity against bacterial strains.

2.4.2. Antifungal activity. Antifungal activities of all compounds were studied against six fungal cultures, *T. longifusus*, *C. albicance*, *A. flavus*, *M. cains*, *A. niger*, and *C. glaberata*. Sabouraud dextrose agar was seeded with 10^5 (CFU)/mL fungal spore

Table 2. Synthetic, analytical and physical data for adduct compounds of 5(2′-hydroxyphenyl)-3-(4-substituted-phenyl)pyrazolinates of cobalt with 2,2′-bipyridine.

	Reactants							Analysis, % Found (Calcd)			
S. No. (Compound No.)	Complex g (mmol)	2,2′-Bipyridine $C_{10}H_8N_2$ g (mmol)	Molar ratio	Product (color)	Yield %	M.P. (°C)	Mol. Wt. Found (Calcd)	C	H	N	Co
5	$Co(L_a)_2$ 1.54 (2.90)	0.45 (2.90)	1 : 1	$Co(L_a)_2$(bipy) (Greenish-brown)	82	340	686.16 (689.12)	69.65 (69.66)	4.94 (4.97)	12.20 (12.19)	8.64 (8.55)
6	$Co(L_b)_2$ 1.58 (2.63)	0.41 (2.63)	1 : 1	$Co(L_b)_2$(bipy) (Greenish-brown)	88	>360	789.01 (759.12)	63.30 (63.29)	4.21 (4.25)	11.60 (11.07)	7.78 (7.76)
7	$Co(L_c)_2$ 1.56 (2.78)	0.43 (2.78)	1 : 1	$Co(L_c)_2$(bipy) (Greenish-brown)	85	344	715.89 (717.12)	70.31 (70.35)	5.32 (5.34)	11.71 (11.71)	8.25 (8.22)
8	$Co(L_d)_2$ 1.58 (2.66)	0.41 (2.66)	1 : 1	$Co(L_d)_2$(bipy) (Greenish-brown)	87	>360	748.7 (749.12)	67.31 (67.34)	5.10 (5.11)	11.23 (11.22)	7.89 (7.87)

Table 3. Synthetic, analytical and physical data for adduct compounds of 5(2′-hydroxyphenyl)-3-(4-substituted-phenyl)pyrazolinates of cobalt with 1,10-phenanthroline.

	Reactants							Analysis, % Found (Calcd)			
S. No. (Compound No.)	Complex g (mmol)	1,10-Phenanthroline $C_{12}H_8N_2$ g (mmol)	Molar ratio	Product (Color)	Yield %	M.P. (°C)	Mol. Wt. Found (Calcd)	C	H	N	Co
9	$Co(L_a)_2$ 1.49 (2.80)	0.50 (2.80)	1 : 1	$Co(L_a)_2$(phen) (Greenish-brown)	86	>360	711.54 (713.14)	70.66 (70.68)	4.80 (4.81)	11.79 (11.78)	8.24 (8.26)
10	$Co(L_b)_2$ 1.53 (2.55)	0.46 (2.55)	1 : 1	$Co(L_b)_2$(phen) (Greenish-brown)	83	>360	790.03 (783.14)	64.34 (64.36)	4.10 (4.12)	10.74 (10.73)	7.53 (7.52)
11	$Co(L_c)_2$ 1.51 (2.69)	0.48 (2.69)	1 : 1	$Co(L_c)_2$(phen) (Greenish-brown)	94	>360	743.08 (741.14)	71.26 (71.25)	5.15 (5.17)	11.32 (11.34)	7.91 (7.95)
12	$Co(L_d)_2$ 1.53 (2.58)	0.46 (2.58)	1 : 1	$Co(L_d)_2$(phen) (Greenish-brown)	88	>360	771.54 (773.14)	68.31 (68.30)	4.92 (4.95)	10.89 (10.87)	7.61 (7.62)

Table 4. Synthetic, analytical and physical data for adduct compounds of 5(2′-hydroxyphenyl)-3-(4-substituted-phenyl)pyrazolinates of cobalt with triphenylphosphine.

	Reactants							Analysis, % Found (Calcd)			
S. No. (Compound No.)	Complex g (mmol)	Triphenylphosphine $C_{18}H_{15}P$ g (mmol)	Molar ratio	Product (Color)	Yield %	M.P. (°C)	Mol. Wt. Found (Calcd)	C	H	N	Co
13	$Co(L_a)_2$ 1.34 (2.51)	0.65 (2.51)	1 : 1	$Co(L_a)_2(PPh_3)$ (Brown)	82	218	791.45 (795.22)	72.41 (72.44)	5.22 (5.20)	7.08 (7.05)	7.45 (7.41)
14	$Co(L_b)_2$ 1.39 (2.31)	0.60 (2.31)	1 : 1	$Co(L_b)_2(PPh_3)$ (Brown)	87	>360	860.08 (865.22)	62.40 (62.42)	4.51 (4.54)	6.44 (6.47)	6.82 (6.81)
15	$Co(L_c)_2$ 1.36 (2.42)	0.63 (2.42)	1 : 1	$Co(L_c)_2(PPh_3)$ (Brown)	86	>360	822.01 (823.22)	72.88 (72.89)	5.52 (5.51)	6.82 (6.81)	7.14 (7.16)
16	$Co(L_d)_2$ 1.38 (2.33)	0.61 (2.33)	1 : 1	$Co(L_d)_2(PPh_3)$ (Reddish-black)	80	>360	848.89 (855.22)	70.15 (70.16)	5.25 (5.30)	6.54 (6.55)	6.92 (6.90)

suspensions and transferred to petri plates. Discs soaked in 20 mL (10 µg mL^{-1} in DMSO) of all compounds were placed at different positions on the agar surface. The plates were incubated at 32°C for seven days. The results were recorded as zones of inhibition in mm and were compared with standard drugs Miconazole and Amphotericin B.

3. Results and discussion

The 5(2′-hydroxyphenyl)-3-(4-substituted-phenyl)pyrazolinates of cobalt and their adducts with 2,2′-bipyridine, 1,10-phenanthroline and triphenylphosphine are brown to greenish-brown solids, non-hygroscopic and stable at room temperature. These complexes are soluble in common organic (chloroform, dichloromethane) and coordinating (pyridine, DMSO and tetrahydrofuran) solvents on slight heating, and monomeric in dilute chloroform at 45°C. Elemental analysis (C, H, N, Co) data are in good accord with stoichiometry proposed. The data are summarized in tables 1–4.

3.1. *Magnetic susceptibility*

The observed magnetic moments of pyrazolinates of cobalt(II) and their adducts are given in table 5. The theory of magnetic susceptibility for cobalt(II) was given by Schlapp and Penney [28] and the best summary of results on the magnetic behavior of cobalt compounds is that of Figgis and Nyholm [29]. The observed magnetic moments for cobalt(II) complexes are diagnostic of the coordination geometry about the metal ion. Tetrahedral cobalt(II) complexes possess three unpaired electrons, but may be distinguished by the magnitude of deviation of μ_{eff} from the spin-only value.

Table 5. Electronic spectral data and magnetic moment data for 5(2′-hydroxyphenyl)-3-(4-substituted-phenyl)pyrazolinates of cobalt and their adduct complexes with 2,2′-bipyridine, 1,10-phenanthroline and triphenylphosphine.

S. No.	Electronic spectral bands: Assignment	Electronic spectral bands: Band (cm^{-1})	Magnetic moment (B.M.)
1	$^4A_2(F) \longrightarrow {}^4T_1(P)$	15100	3.93
2	$^4A_2(F) \longrightarrow {}^4T_1(P)$	16430	3.92
3	$^4A_2(F) \longrightarrow {}^4T_1(P)$	15250	3.97
4	$^4A_2(F) \longrightarrow {}^4T_1(P)$	16220	3.99
5	$^4A_2(F) \longrightarrow {}^4T_1(P)$	15310	4.12
6	$^4A_2(F) \longrightarrow {}^4T_1(P)$	16937	4.15
7	$^4A_2(F) \longrightarrow {}^4T_1(P)$	15490	4.24
8	$^4A_2(F) \longrightarrow {}^4T_1(P)$	16338	4.18
9	$^4A_2(F) \longrightarrow {}^4T_1(P)$	15214	4.30
10	$^4A_2(F) \longrightarrow {}^4T_1(P)$	15103	4.33
11	$^4A_2(F) \longrightarrow {}^4T_1(P)$	16430	4.27
12	$^4A_2(F) \longrightarrow {}^4T_1(P)$	15250	4.36
13	$^4A_2(F) \longrightarrow {}^4T_1(P)$	16220	4.29
14	$^4A_2(F) \longrightarrow {}^4T_1(P)$	15310	4.11
15	$^4A_2(F) \longrightarrow {}^4T_1(P)$	16936	4.32
16	$^4A_2(F) \longrightarrow {}^4T_1(P)$	15490	4.19

The magnetic moment of tetrahedral cobalt(II) complexes with an orbitally non-degenerate ground term is increased above the spin-only value via contributions from higher orbitally degenerate terms and occurs in the range 4.2–4.7 BM [30, 31]. The magnetic measurements on the complexes reported herein of 3.92–4.36 BM are consistent with three unpaired electrons in a tetrahedral configuration.

3.2. *Infrared spectra*

The assignments of infrared spectral bands for cobalt(II)pyrazolinates and their addition complexes are given in table 6. The υ(OH) in the region 3080–3050 cm^{-1} in spectra of the ligand is absent in spectra of complexes, indicating involvement of phenolic OH in bond formation via deprotonation. The band at 3420–3410 cm^{-1} assigned to υ(N–H) is found at almost the same position as free pyrazoline, suggesting non-involvement of N–H in bond formation. The υ(C=N) (1640–1601 cm^{-1}) shifts to higher wavenumber suggesting coordination through nitrogen [32], confirming bidentate ligand. In addition complexes, bands in the region 3436–3411 cm^{-1} and 1630–1585 cm^{-1} assigned to υ(N–H) and υ(C=N), respectively, are at the same position as ligand, suggesting non-involvement of N–H and C=N in bonding. This may indicate monodentate pyrazoline in addition complexes with N and P donor ligands. New bands in the region 412–374 cm^{-1} and 480–435 cm^{-1} are ascribed to υ(M–O) and υ(M–N) stretching vibrations, respectively. For PPh$_3$ complexes, only one new band for υ(M–O) is found in the region 410–390 cm^{-1}.

3.3. ^{31}*P NMR spectra*

The ^{31}P NMR spectra of addition complexes of cobalt(II)pyrazolinates with triphenylphosphine in solid state have a broad single peak in the range δ 36.3–31.2 ppm, indicating coordinaton between Co(II) and triphenylphosphine [33–36].

Table 6. IR spectral data for 5(2′-hydroxyphenyl)-3-(4-substituted-phenyl)pyrazolinates of cobalt and their adduct complexes with 2,2′-bipyridine, 1,10-phenanthroline and triphenylphosphine.

	Infrared (cm^{-1})			
S. No.	υ(N–H)	υ(C=N)	υ(M–N)	υ(M–O)
1	3419	1640	475	396
2	3415	1601	480	376
3	3420	1608	477	359
4	3410	1601	472	374
5	3418	1600	478	385
6	3417	1595	470	383
7	3412	1589	440	398
8	3436	1590	438	392
9	3424	1592	435	412
10	3416	1585	445	395
11	3421	1594	464	389
12	3415	1588	471	396
13	3428	1628	–	390
14	3411	1604	–	410
15	3414	1607	–	406
16	3430	1630	–	409

Table 7. Antibacterial bioassay data of free pyrazoline ligands, 5(2′-hydroxyphenyl)-3-(4-substituted-phenyl)pyrazolinates of cobalt and their adduct complexes with N and P donor ligands.

	Gram(−ve) bacteria				Gram(+ve) bacteria	
Compound	*E. coli*	*S. flexenari*	*P. aeruginosa*	*S. typhi*	*S. aureus*	*B. sublitisi*
L_a	00	00	00	00	08	09
L_b	00	00	00	00	07	08
L_c	00	00	00	00	07	07
L_d	00	00	00	00	06	07
$Co(L_a)_2$	10	06	14	15	18	17
$Co(L_b)_2$	11	08	13	16	20	18
$Co(L_c)_2$	11	10	14	14	21	15
$Co(L_d)_2$	16	07	11	15	19	19
$Co(L_a)_2$(bipy)	11	07	17	19	19	18
$Co(L_b)_2$(bipy)	12	09	15	18	21	18
$Co(L_c)_2$(bipy)	13	11	18	16	22	16
$Co(L_d)_2$(bipy)	17	08	13	16	20	20
$Co(L_a)_2$(phen)	12	08	16	18	20	19
$Co(L_b)_2$(phen)	13	09	17	17	22	19
$Co(L_c)_2$(phen)	13	12	16	15	20	17
$Co(L_d)_2$(phen)	18	08	14	16	19	21
$Co(L_a)_2(PPh_3)$	12	07	18	19	21	20
$Co(L_b)_2(PPh_3)$	17	09	16	17	21	20
$Co(L_c)_2(PPh_3)$	13	12	17	15	19	18
$Co(L_d)_2(PPh_3)$	17	09	14	16	20	19
Standard drug (Imipenem)	30	27	27	26	30	28

(Diameter of inhibition zone measured in mm, paper disc 5 mm, inhibition zone measured excluding paper disc diameter, amount of complexes taken 1 mg mL^{-1} of DMSO.)

3.4. *Electronic spectra*

The electronic spectral data of pyrazolinates of cobalt(II) and their addition complexes are listed in table 5. Only one strong band in the region 16937–15100 cm^{-1} assigned to the d–d transition $^4A_2(F) \longrightarrow {}^4T_1(P)$ suggests tetrahedral geometry for cobalt(II) complexes [37, 38] and their adducts. The tetrahedral geometry involves two bidentate pyrazoline ligands in pure complexes, and in addition complexes two monodentate pyrazolines are bonded with phenolic oxygen and the remaining two coordination sites are two nitrogens of 2, 2′-bipyridine or 1, 10-phenanthroline, or, in the case of PPh_3, one coordination site is satisfied by triphenylphosphine and one through a solvent molecule.

3.5. *FAB mass spectra*

The FAB mass spectra of the complexes gives the molecular ion peak (M^+) along with other fragmentations. The mass spectra of $Co(L_c)_2$ ($L_c = 5(2'$-hydroxyphenyl)-3-(4-methylphenyl)pyrazoline) exhibited a molecular ion peak at $m/z = 561$, suggesting monomeric nature of the complex. For $[Co(L_a)_2bipy]$, the molecular peak at $m/z = 689$ suggests a monomer.

3.6. *Biological activity*

The biological activity of 5(2′-hydroxyphenyl)-3-(4-substituted-phenyl)pyrazolinates of cobalt and their adducts were screened for antibacterial activity against *E. coli*,

Table 8. Antifungal bioassay data of free pyrazoline ligands, 5(2′-hydroxyphenyl)-3-(4-substituted-phenyl)pyrazolinates of cobalt and their adduct complexes.

Compound	Organism					
	T. longifusus	*C. albicans*	*A. flavus*	*M. canis*	*A. niger*	*C. glaberate*
L_a	00	00	10	00	06	00
L_b	00	00	10	00	07	00
L_c	00	00	07	00	05	00
L_d	00	00	07	00	05	00
$Co(L_a)_2$	11	07	20	01	09	05
$Co(L_b)_2$	05	09	21	02	08	00
$Co(L_c)_2$	12	10	18	01	06	00
$Co(L_d)_2$	10	04	19	04	06	00
$Co(L_a)_2(bipy)$	12	08	21	03	08	00
$Co(L_b)_2(bipy)$	07	10	22	04	07	07
$Co(L_c)_2(bipy)$	13	12	20	05	06	00
$Co(L_d)_2(bipy)$	12	06	20	01	06	00
$Co(L_a)_2(phen)$	14	08	22	02	09	00
$Co(L_b)_2(phen)$	06	11	21	02	08	00
$Co(L_c)_2(phen)$	14	12	19	03	07	05
$Co(L_d)_2(phen)$	11	06	22	01	06	00
$Co(L_a)_2(PPh_3)$	12	09	21	04	08	00
$Co(L_b)_2(PPh_3)$	07	10	22	01	08	00
$Co(L_c)_2(PPh_3)$	14	11	19	02	07	00
$Co(L_d)_2(PPh_3)$	11	08	19	01	06	00
Standard drug*	A	B	C	D	E	F

*A = Miconazole (70 μg mL^{-1}), B = Miconazole (110.8 μg mL^{-1}), C = Amphotericin B (20 μg mL^{-1}), D = Miconazole (98.4 μg mL^{-1}), E = Miconazole (73.24 μg mL^{-1}), F = Miconazole (110.8 μg mL^{-1}). (Diameter of inhibition zone measured in mm, paper disc 5 mm, inhibition zone measured excluding paper disc diameter, amount of complexes taken 200 μg mL^{-1}).

S. flexenari, *P. aeruginosa*, *S. typhi*, *B. subtilis* and *S. aureus* and for antifungal activity against *T. longifusus*, *C. albicance*, *A. flavus*, *M. cains*, *A. niger* and *C. glaberata*. The results are listed in tables 7 and 8.

5(2′-Hydroxyphenyl)-3-(4-substituted-phenyl)pyrazolinates of cobalt(II) and their addition complexes have higher activity than the free ligand, as anticipated from Overtone's concept and chelation theory [39]. Nevertheless, it is difficult to make an exact structure and activity relationship between antimicrobial activity and the structure of these complexes.

4. Conclusion

The present study describes a series of pyrazolinates of cobalt(II) and their adducts with donor ligands. Although it is quite difficult to comment on the molecular structure of these compounds without X-ray crystal structure analysis, a number of cobalt(II) structures have been described as tetrahedral [40–44]. The two pyrazoline ligands are bidentate in complexes of the type $(C_{15}H_{12}N_2OX)_2Co$ and monodentate in the addition complexes, and tetrahedral geometry around cobalt(II) is proposed. On the basis of XRD the complexes are amorphous. The biological investigations indicate that the 5(2′-hydroxyphenyl)-3-(4-substituted-phenyl)pyrazolinates of cobalt(II) and their addition complexes have greater activity towards all tested bacteria and fungi than free pyrazoline. Generally, it is suggested that the complexes deactivate various cellular enzymes, which play a vital role in various metabolic pathways of the micro organisms.

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References

[1] R.G. Mastin. *Chem. Abstr.*, **43**, 11782 (1949); *U.S.2*, **25A**, 16 (1961).
[2] J.R. Shah, N.R. Shah. *Indian J. Chem.*, **21A**, 312 (1982).
[3] J.R. Shah, S.K. Das, R.P. Patel. *J. Indian Chem. Soc.*, **50**, 228 (1973).
[4] J.R. Shah, N.R. Shah. *J. Inorg. Nucl. Chem.*, **43**, 1593 (1981).
[5] T.B. Crowford, H.B. Nisbet, D. Ritchie. *J. Pharm. Pharmacol.*, **4**, 294 (1952).
[6] F.N. Schultz, R.N. Hill. *J. Pharmacol.*, **64**, 324 (1940).
[7] Fujiphoto Film Ltd., Jpn. Kokai Tokyo Jp 81, 40, 825; *Chem. Abstr.*, **96**, 190611 (1982).
[8] J. Lee, J. Ziering, H. Heinemann. *J. Org. Chem.*, **12**, 885 (1947).
[9] F. Becic, D. Zavrsnic, L. Zulic, E. Becic. *Periodicum Biologorum*, **4**, 321 (2001), *Chem. Abstr.*, **137**, 379873 (2002).
[10] E. Bombardelli. *PCT*, *Int. Appl. WO*, **43**, 219 (1997); *Chem. Abstr.*, **128**, 34909 (1998).
[11] O.J. Braenden, N.B. Reddy, B. Habach. *Bull. World Health Org.*, **13**, 935 (1955).
[12] W.D. Soloman, T.K. Ravi, K. Annadwai. *Indian Drugs*, **36**, 466 (1999); *Chem. Abstr.*, **132**, 222481 (2000).
[13] A.H. Backet, A.F. Cosy. *Bull. Norcot.*, **9**, 37 (1957).
[14] K. Shrivastav, R. Chandra, A.K. Kumar. *Indian J. Chem.*, **41**, 2371 (2002); *Chem. Abstr.*, **138**, 271582 (2003).
[15] V. Malhotra, S. Pathak, R. Nath, D. Mukerjee, K. Shanker. *Indian J. Chem.*, **41**(B)6, 1310 (2002); *Chem. Abstr.*, **137**, 370021 (2002).
[16] E. Palaska, M. Aytemir, I.T. Uzbay, D. Erol. *Eur. J. Med. Chem.*, **36**, 539 (2001); *Chem. Abstr.*, **136**, 183749 (2002).
[17] N.S. Chattree, T.C. Sharma. *Asian J. Chem.*, **6**, 405 (1994).
[18] C. Natarajan, P. Tharmaraj. *Indian J. Chem.*, **30**, 722 (1991).
[19] U.N. Tripathi, G. Venubabu, M. Safi Ahmad, S.S. Rao Kolisetty, A.K. Shrivastava. *Appl. Organomet. Chem.*, **20**, 669 (2006).
[20] U.N. Tripathi, M. Safi Ahmad, G. Venubabu, P. Ramakrishna. *J. Coord. Chem.*, **60**, 1709 (2007).
[21] U.N. Tripathi, M. Safi Ahmad, G. Venubabu, P. Ramakrishna. *J. Coord. Chem.*, **60**, 1777 (2007).
[22] U.N. Tripathi, K.V. Sharma, A. Chaturvedi, T.C. Sharma. *Polish J. Chem.*, **77**, 109 (2003).
[23] K.V. Sharma, V. Sharma, U.N. Tripathi. *J. Coord. Chem.* (Accepted) (2008).
[24] A.I. Vogel. *Text Book of Quantitative Organic Analysis*, ELBS and Longman, London (1978).
[25] T.C. Sharma, V. Saxena, N.J. Reddy. *Acta Chim. (Budapest)*, **93**, 415 (1977).
[26] A. Rahman, M.I. Choudhary, W.J. Thomsen. *Bioassay Techniques for Drug Development*, Harwood Academic, Amsterdam, The Netherlands (2001).
[27] J.L. McLaughlin, C.J. Chang, D.L. Smith. *Stud. Nat. Prod. Chem.*, **9**, 383 (1991).
[28] R. Schlapp, W.G. Penney. *Phys. Rev.*, **42**, 666 (1932).
[29] B.N. Figgis, R.S. Nyholm. *J. Chem. Soc.*, 4190 (1958).
[30] M. Kato, H.B. Jonassen, J.C. Fanning. *Chem. Rev.*, **64**, 99 (1964).
[31] A. Earnshaw. *Introduction to Magnetochemistry*, Elsevier, Amsterdam (1968).
[32] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, John Wiley & Sons, Interscience, New York (1997).

[33] F.A. Cotton, G. Wilkinson. *Advanced Inorganic Chemistry: A Comprehensive Text*, John Wiley and Sons, Toronto (1980).
[34] J.F. Nixon, A. Pidcock. *Ann. Rep. NMR Spectrosc.*, **2**, 345 (1969).
[35] K.R. Dixon. *In Multinuclear NMR*, Plenum Press, New York (1987).
[36] K.W. Feindel, R.E. Wasylishen. *Can. J. Chem.*, **82**, 27 (2004).
[37] A.B.P. Lever. *Inorganic Electronic Spectroscopy*, Elsevier, New York (1968).
[38] U.N. Tripathi, M.S. Singh. *J. Ind. Chem. Soc.*, **76**, 360 (1999).
[39] B.G. Tweedy. *Phytopathology*, **55**, 910 (1964).
[40] A. Romerosa, C. Saraiba-Bello, M. Serrano-Ruiz, A. Caneschi, V. McKee, M. Peruzzini, L. Sorace, F. Zanobini. *Dalton Trans.*, 3233 (2003).
[41] J.R. Anacona, M. Azocar, O. Nusetti, C. Rodriguez-Barbarin. *Transition Met. Chem.*, **28**, 24 (2003).
[42] C. Bianchini, G. Mantovani, A. Meli, F. Migliacci. *Organometallics*, **22**, 2545 (2003).
[43] R.L. Paul, Z.R. Bell, J.C. Jeffery, J.A. McCleverty, M.D. Ward. *PANS*, **99**, 4883 (2002).
[44] P.R. Meehan, E.C. Alyea, R.P. Shakya, G. Ferguson. *Polyhedron*, **17**, 11 (1998).