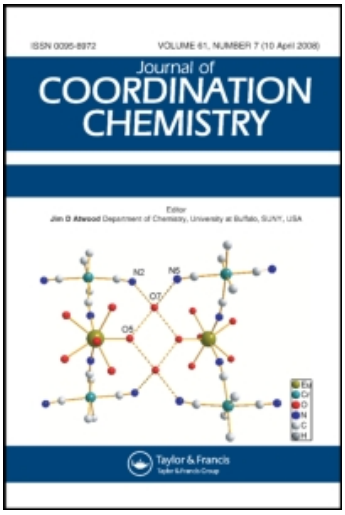

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Synthesis, spectroscopic, antimicrobial and anti-inflammatory studies of 5(2'-hydroxyphenyl)-3-(4-x-phenyl)pyrazolinates of copper(II) and their addition complexes with donor ligands

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Synthesis, spectroscopic, antimicrobial and anti-inflammatory studies of 5(2′-hydroxyphenyl)-3-(4-x-phenyl)pyrazolinates of copper(II) and their addition complexes with donor ligands

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Complexes of copper(II) with 5(2′-hydroxyphenyl)-3-(4-x-phenyl)pyrazolines, $(C_{15}H_{12}N_2OX)_2Cu$ [X = –H, –Cl, $–CH_3$, $–OCH_3$] have been synthesized with their addition complexes with 2,2′-bipyridine, 1,10-phenanthroline and triphenylphosphine. The complexes were characterized by elemental analyses, molecular weight measurement, magnetic, conductivity measurement, IR, electronic, ^{31}P NMR, ESR and FAB mass spectra. The complexes were examined for crystalline/amorphous nature through XRD. Square-planar geometry around copper(II) is suggested with two bidentate pyrazoline ligands. In the additional complexes pyrazoline is monodentate. The bidentate and monodentate behavior of pyrazoline ligands was confirmed by IR and ^{31}P NMR spectral data. All complexes were tested for *in vitro* antibacterial and antifungal activity and exhibit very good antibacterial and antifungal activity; coordination has a pronounced effect on the microbial activities. The brine shrimp bioassay was also carried out to study their *in vitro* cytotoxic properties. All complexes and adducts displayed potent cytotoxic activity against *Artemia salina*. Anti-inflammatory activity was also carried out by the carrageenan induced rat paw edema test. The complexes and adducts were found to have higher anti-inflammatory activity.

Keywords: Antimicrobial activity; Anti-inflammatory activity; Copper(II) pyrazolinates; Cytotoxicity; Pyrazoline; Triphenylphosphine; 1,10-Phenanthroline; 2,2′-Bipyridine

1. Introduction

The pyrazolines are an important class of poly-aza heteroaromatic compounds, presenting a variety of biological activity ranging from analgesic [1, 2], antitumor [3], antitussive [4], anti-inflammatory [5, 6], anticonvulsant [7], cardiovascular [8] and antidepressant [9] activities. Pyrazolines are well-known for their importance in industries as dyes, antioxidants in lubricating oils [10], photography [11], in agriculture as catalysts for decarboxylation reactions and as inhibitors in plant growth [12–14].

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Due to their non toxicity [15], they are also used as local anesthetics [16]. Coordination chemistry of pyrazoline has received attention for biological implications. 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 were used to prepare complexes of cobalt, copper and nickel [18]. The synthesis, spectral and antimicrobial studies of diorganotin (IV), triorganotin (IV) and chlorodiorganotin (IV)pyrazolinates were carried out in our laboratories [19–21]. As part of our continuing efforts [22] for synthesis, spectral and antimicrobial investigations of 5(2′-hydroxyphenyl)-3-(4-x-phenyl)pyrazoline complexes and their addition complexes with donor ligands [23], we have prepared a series of copper(II)5 (2′-hydroxyphenyl)-3-(4-x-phenyl)pyrazoline complexes. All complexes were screened for their *in vitro* biological and anti-inflammatory activity. A thorough search of the literature in relation to biological requirements and toxicity of Cu led to the following conclusions: copper is an essential mineral/nutrient in human and animal health [24–31]. Interruptions in Cu transport or excretion are the basis for many chronic and spontaneous human and animal diseases such as Alzheimer's, ''Mad Cow'' disease, and Sway back. Wilson and Menkes diseases in humans arise through faulty Cu homeostasis and both have been linked to the expression of Cu-dependent ATPase enzymes that regulate the flow of Cu into the system and out of cells copper proteins, e.g. hemocyanin, tyrosinase, cytochrome *c* oxidase and laccase play an important role in electron transfer during biochemical metabolism. Copper also plays numerous physiological roles in all organisms and is used in the treatment of a wide variety of metabolic disorders.

2. Experimental

2.1. *Materials*

Ethanol, isopropanol, chloroform, dimethylformamide (DMF), dimethylsulphoxide (DMSO) and pyridine were analytical grade. Cupric chloride(anhydrous), benzaldehyde, *p*-chlorobenzaldehyde, *p*-methylbenzaldehyde, *p*-methoxybenzaldehyde, *o*-hydroxyacetophenone, sodium hydroxide, hydrochloric acid, acetic acid, hydrazine hydrate, 2,2′-bipyridine, 1,10-phenanthroline and triphenylphosphine were used as received. Solvents were purified and dried by standard procedure [32]. The ligand 5(2′-hydroxyphenyl)-3-(4-x-phenyl)pyrazoline was prepared by reported procedure [33].

2.2. *Synthesis of 5(2′-hydroxyphenyl)-3-(4-x-phenyl)pyrazolinates of copper*

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

$$CuCl_2 + 2(C_{15}H_{12}N_2OX)Na \xrightarrow[\text{Room temp.}]{\text{Isopropanol}} (C_{15}H_{12}N_2OX)_2Cu + 2NaCl$$

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

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-x-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 copper(II) chloride was added dropwise with constant stirring. The reaction mixture was further stirred for 20–24 h till the color changed from yellow to dark brown. Reaction mixture was filtered under vacuum to separate the solid compound, which was washed with hot water to remove sodium chloride formed as by-product 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.

2.3. *Synthesis of addition complexes of 5(2′-hydroxyphenyl)-3-(4-x-phenyl) pyrazolinates of copper with 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 amounts of pyrazolinates of copper dissolved in dry chloroform till the color of reaction mixture changed. Reaction mixture was filtered under vacuum to separate the solid compound, 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.

2.4. *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 copper was done by standard procedure. Carbon, hydrogen and nitrogen were estimated by an Elementor Vario ELIII Carlo1108 elemental analyzer. Magnetic moment studies were carried out on a Gouy balance at room temperature. Electronic spectra were recorded in

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

	Reactants								Analysis, % Found (Calcd)			
S. No. (Compd. No.)	Anhydrous $CuCl_2$ g (mmole)	Sodium g (mmole)	Ligand g (mmole)	Molar Ratio	Product (Color)	Yield %	M.P. (°C)	Mol. Wt. Found (Calcd)	C	H	N	Cu
1			HPPP		$Cu(L_a)_2$							
	0.75	0.25	2.65	1:2:2	(Brown)	86	276	535.21	66.28	4.62	10.39	11.75
	(5.57)	(11.16)	(11.16)					(537.37)	(67.03)	(4.88)	(10.42)	(11.83)
2			HPCPP		$Cu(L_b)_2$							
	0.66	0.22	2.69	1:2:2	(Brown)	88	368	608.32	59.10	3.45	9.10	10.32
	(4.93)	(9.87)	(9.87)					(607.54)	(59.31)	(3.98)	(9.22)	(10.46)
3			HPMPP		$Cu(L_c)_2$							
	0.71	0.24	2.67	1:2:2	(Brown)	91	376	564.40	68.85	5.46	9.85	11.30
	(5.30)	(10.61)	(10.61)					(565.40)	(67.96)	(5.35)	(9.91)	(11.24)
4			HPMeoPP	1:2:2	$Cu(L_d)_2$							
	0.67	0.23	2.69		(Brown)	83	382	595.80	64.20	4.98	9.56	10.65
	(5.02)	(10.04)	(10.04)					(597.54)	(64.32)	(5.06)	(9.38)	(10.63)

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

S. No. (Compd. No.)	Reactants: Complex g (mmole)	Reactants: 2,2′-Bipyridine $C_{10}H_8N_2$	Molar Ratio	Product (Color)	Yield %	M.P. (°C)	Mol. Wt. Found (Calcd)	Analysis, % Found (Calcd): C	H	N	Cu
5	$Cu(L_a)_2$										
	1.54	0.45	1 : 1	$Cu(L_a)_2$(bipy)	87	385	692.45	70.00	4.65	11.98	9.21
	(2.88)	(2.88)		(Greenish-brown)			(693.73)	(69.25)	(4.94)	(12.11)	(9.16)
6	$Cu(L_b)_2$										
	1.59	0.40	1 : 1	$Cu(L_b)_2$(bipy)	88	240	761.87	62.85	4.30	10.68	8.65
	(2.61)	(2.61)		(Greenish-brown)			(763.73)	(62.91)	(4.22)	(11.00)	(8.32)
7	$Cu(L_c)_2$										
	1.56	0.43	1 : 1	$Cu(L_c)_2$(bipy)	84	381	720.62	68.14	5.24	11.28	8.75
	(2.77)	(2.77)		(Greenish-brown)			(721.73)	(69.90)	(5.31)	(11.64)	(8.80)
8	$Cu(L_d)_2$			$Cu(L_d)_2$(bipy)							
	1.58	0.41	1 : 1	(Greenish-brown)	80	360	753.10	66.71	5.00	11.60	8.29
	(2.65)	(2.65)					(753.73)	(66.93)	(5.08)	(11.15)	(8.43)

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

S. No. (Compd. No.)	Reactants: Complex g (mmole)	Reactants: 1,10-Phenanthroline $C_{12}H_8N_2$ g (mmole)	Molar Ratio	Product (Color)	Yield %	M.P. (°C)	Mol. Wt. Found (Calcd)	Analysis, % Found (Calcd): C	H	N	Cu
9	$Cu(L_a)_2$										
	1.49	0.50	1 : 1	$Cu(L_a)_2$(phen)	82	370	714.86	70.62	4.25	11.02	8.34
	(2.78)	(2.78)		(Light brown)			(717.75)	(70.28)	(4.77)	(11.71)	(8.85)
10	$Cu(L_b)_2$										
	1.54	0.45	1 : 1	$Cu(L_b)_2$(phen)	89	272	789.25	65.12	4.10	10.28	7.98
	(2.53)	(2.53)		(Light brown)			(787.75)	(64.03)	(4.09)	(10.67)	(8.06)
11	$Cu(L_c)_2$										
	1.51	0.48	1 : 1	$Cu(L_c)_2$(phen)	92	269	750.32	71.10	5.67	11.26	8.23
	(2.68)	(2.68)		(Light brown)			(745.75)	(70.86)	(5.14)	(11.27)	(8.52)
12	$Cu(L_d)_2$										
	1.53	0.46	1 : 1	$Cu(L_d)_2$(phen)	90	365	772.56	65.98	4.32	10.89	8.12
	(2.57)	(2.57)		(Light brown)			(777.75)	(67.95)	(4.92)	(10.80)	(8.17)

chloroform/pyridine on a Perkin-Elmer Lambda15 spectrophotometer. ESR spectra were obtained at room temperature. 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.

2.5. *Biological activity*

Antibacterial and antifungal activities were studied as previously reported [34, 35].

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

S. No. (Compd. No.)	Reactants: Complex g (mmole)	Reactants: Triphenyl phoshine $C_{18}H_{15}P$ g (mmole)	Molar Ratio	Product (Color)	Yield %	M.P. (°C)	Mol. Wt. Found (Calcd)	Analysis, % Found (Calcd): C	H	N	Cu
13	$Cu(L_a)_2$										
	1.34	0.65	1 : 1	$Cu(L_a)_2(PPh_3)$	87	380	798.56	72.35	5.12	7.09	7.95
	(2.50)	(2.50)		(Brown)			(799.83)	(72.08)	(5.16)	(7.00)	(7.94)
14	$Cu(L_b)_2$										
	1.39	0.60	1 : 1	$Cu(L_b)_2(PPh_3)$	90	376	867.14	66.54	4.38	9.26	7.32
	(2.29)	(2.29)		(Brown)			(869.83)	(66.28)	(4.52)	(6.44)	(7.30)
15	$Cu(L_c)_2$										
	1.36	0.63	1 : 1	$Cu(L_c)_2(PPh_3)$	80	389	825.65	72.01	5.64	6.74	7.60
	(2.41)	(2.41)		(Brown)			(827.83)	(72.55)	(5.48)	(6.76)	(7.67)
16	$Cu(L_d)_2$										
	1.38	0.61	1 : 1	$Cu(L_d)_2(PPh_3)$	92	378	858.23	69.57	5.19	6.57	7.42
	(2.32)	(2.32)		(Brown)			(859.83)	(69.85)	(5.27)	(6.51)	(7.39)

2.5.1. Cytotoxicity. Brine shrimp (*Artemia salina* leach) eggs were hatched in a shallow rectangular plastic dish (22×32 cm), filled with artificial seawater, prepared [36] with commercial salt mixture and double distilled water. An unequal partition was made in the plastic dish with the help of a perforated device. Approximately 50 mg of eggs were sprinkled into the large compartment, which was darkened while the matter compartment was opened to ordinary light. After two days, nauplii were collected by a pipette from the lighted side. A sample of the test compound was prepared by dissolving 20 mg of each compound in 2 mL of DMF. From this stock solution, 500, 50, 5 $\mu g\,mL^{-1}$ were transferred to 9 vials (three for each dilution were used for each test sample and LD_{50} is the mean of three values) and one vial was kept as control having 2 mL of DMF only. The solvent was allowed to evaporate overnight. After two days, when shrimp larvae were ready, 1 mL of seawater and 10 shrimps were added to each vial (30 shrimps/dilution) and the volume was adjusted with seawater to 5 mL per vial. After 24 h, the numbers of survivors were counted. Data were analyzed by Finney computer program to determine the LD_{50} values [37].

2.5.2. Anti-inflammatory activity. Anti-inflammatory studies were performed using a plethysmometer to measure carrageenan induced rat volume following the method of Winter *et al.* [38]. Adult male wister albino rats (90–125 g) were fasted for 18 h but with free access to water. Each treatment i.e. standard drug and Cu(II) complexes of 5(2′-hydroxyphenyl)-3(4-x-phenyl)pyrazoline was administered at a dose of 100 $mg\,kg^{-1}$ body weight orally in 0.2% CMC suspension. Half an hour following the treatment 0.1 mL of 1% solution of a carrageenan was injected in the right hind paw planter aponeurosis; the paw was measured immediately before giving carrageeran and again 3 h later by means of plethysmograph. Edema was measured in a pre-calibrated plethysmograph, the difference between the volumes of the paw measured before and

3 h after giving carrageenan. The percent inhibition of inflammation after 3 h was calculated by the method of Newbould [39] using the following formula:

$$\% \text{ Inhibition, } I = 100[1 - (a - x/b - y)]$$

where x = mean foot volume of rats before the administration of carrageenan injection in the test and standard group, a = mean foot volume of rats after the administration of carrageenan injection in the test and standard group, y = mean foot volume of rats before the administration of carrageenan injection in the control group and b = mean foot volume of rats after the administration of carrageenan injection in the control group.

3. Results and discussion

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

3.1. *Magnetic and conductivity measurements*

The room temperature magnetic susceptibility measurements of complexes are given in table 5. The observed μ_{eff} values between 1.79–1.97 B.M. correspond to the presence of one unpaired electron [40]. The value 1.73 B.M. is normally found for square-planar copper(II) [41, 42]. The magnetic moments of the Cu(II) complexes were in the expected range for square-planar complexes. The conductance values of the complexes are in the range 15.6–18.3 $\Omega^{-1}\,cm^2\,mol^{-1}$ (table 5), indicating non-electrolytes [43].

3.2. *Infrared spectra*

The most significant IR spectral bands with assignments for copper(II) pyrazolinates and their addition complexes are listed in table 6. The band due to υ(OH) originally found in the region 3080–3050 cm^{-1} in the spectra of ligands is absent in the spectra of complexes, indicating involvement of phenolic OH in bond formation. The band in the region 3446–3420 cm^{-1} assigned to υ(N–H) is almost unchanged, suggesting non-involvement of N–H in bond formation. The υ(C=N) group at 1653–1618 cm^{-1} is shifted to higher wavenumber suggesting coordination through nitrogen of C=N [44], confirming bidentate ligand. In addition complexes, the absorptions at 3445–3415 cm^{-1} and 1605–1584 cm^{-1} assigned to υ(N–H) and υ(C=N), respectively, are at almost the same position as for free ligand, suggesting non-involvement in bonding, indicating monodentate pyrazoline. New bands in the region 544–510 cm^{-1} and 435–410 cm^{-1}

Table 5. Electronic spectra, magnetic moment and conductivity data for 5(2′-hydroxyphenyl)-3-(4-x-phenyl)pyrazolinates of copper and adducts with 2,2′-bipyridine, 1,10-phenanthroline and triphenylphosphine.

S. No.	Electronic spectral bands		Magnetic moment (B.M.)	Λ_m ($\Omega^{-1}\,cm^2\,mol^{-1}$)
	Assignment	Band (cm^{-1})		
1	$^2B_{1g} \longrightarrow {}^2A_{1g}$	15800	1.95	15.8
	$^2B_{1g} \longrightarrow {}^2E_g$	21800		
2	$^2B_{1g} \longrightarrow {}^2A_{1g}$	16292	1.86	16.3
	$^2B_{1g} \longrightarrow {}^2E_g$	27537		
3	$^2B_{1g} \longrightarrow {}^2A_{1g}$	17593	1.97	17.5
	$^2B_{1g} \longrightarrow {}^2E_g$	26982		
4	$^2B_{1g} \longrightarrow {}^2A_{1g}$	16722	1.80	17.2
	$^2B_{1g} \longrightarrow {}^2E_g$	23333		
5	$^2B_{1g} \longrightarrow {}^2A_{1g}$	15770	1.94	15.6
	$^2B_{1g} \longrightarrow {}^2E_g$	20790		
6	$^2B_{1g} \longrightarrow {}^2A_{1g}$	16041	1.90	16.8
	$^2B_{1g} \longrightarrow {}^2E_g$	22981		
7	$^2B_{1g} \longrightarrow {}^2A_{1g}$	16142	1.79	17.6
	$^2B_{1g} \longrightarrow {}^2E_g$	23333		
8	$^2B_{1g} \longrightarrow {}^2A_{1g}$	16332	1.87	18.3
	$^2B_{1g} \longrightarrow {}^2E_g$	21718		
9	$^2B_{1g} \longrightarrow {}^2A_{1g}$	15746	1.88	16.6
	$^2B_{1g} \longrightarrow {}^2E_g$	21410		
10	$^2B_{1g} \longrightarrow {}^2A_{1g}$	16302	1.84	17.8
	$^2B_{1g} \longrightarrow {}^2E_g$	22637		
11	$^2B_{1g} \longrightarrow {}^2A_{1g}$	16817	1.98	15.9
	$^2B_{1g} \longrightarrow {}^2E_g$	22387		
12	$^2B_{1g} \longrightarrow {}^2A_{1g}$	16799	1.95	17.7
	$^2B_{1g} \longrightarrow {}^2E_g$	22714		
13	$^2B_{1g} \longrightarrow {}^2A_{1g}$	15480	1.89	18.2
	$^2B_{1g} \longrightarrow {}^2E_g$	21893		
14	$^2B_{1g} \longrightarrow {}^2A_{1g}$	16465	1.85	16.7
	$^2B_{1g} \longrightarrow {}^2E_g$	22110		
15	$^2B_{1g} \longrightarrow {}^2A_{1g}$	16734	1.98	16.1
	$^2B_{1g} \longrightarrow {}^2E_g$	21700		
16	$^2B_{1g} \longrightarrow {}^2A_{1g}$	16817	1.92	15.9
	$^2B_{1g} \longrightarrow {}^2E_g$	22145		

may be ascribed to υ(M–O) and υ(M–N) stretching vibrations; for PPh_3 only one new band due to υ(M–O) is found in the region 540–522 cm^{-1}.

3.3. *^{31}P NMR spectra*

The ^{31}P NMR spectra of addition complexes of copper(II) pyrazolinates with triphenylphosphine in solid state show a broad single resonance in the range δ 34.3–30.2 ppm, indicating coordinaton of triphenylphosphine [45–48].

3.4. *Electronic spectra*

Electronic spectral data of pyrazolinates of copper(II) are tabulated in table 5. Strong bands in the region 17593–15480 cm^{-1} and 27537–20790 cm^{-1} can be assigned

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

S. No.	Infrared (cm^{-1})			
	υ(N–H)	υ(C=N)	υ(M–N)	υ(M–O)
1	3446	1653	435	517
2	3420	1629	428	511
3	3444	1618	410	526
4	3430	1636	412	528
5	3445	1600	423	510
6	3441	1585	432	534
7	3440	1578	424	542
8	3435	1584	416	527
9	3418	1604	417	515
10	3424	1589	429	538
11	3415	1602	414	544
12	3421	1595	416	519
13	3418	1590	–	522
14	3429	1605	–	540
15	3418	1587	–	532
16	3439	1584	–	536

to $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions, respectively, for square-planar copper(II) [49–51]. The square-planar geometry around copper(II) is complete with two bidentate pyrazolines in pure complexes. For addition complexes, two monodentate pyrazolines and 2,2′-bipyridine or 1,10-phenanthroline complete the coordination; for PPh_3, one site is occupied by solvent.

3.5. *ESR spectra*

ESR spectra of copper(II) complexes have been measured at room temperature in polycrystalline solid state. In an octahedral crystal field, the ground state is ^2E_g for which ESR resonances are not readily observable. However, a large John-Tellor distortion lowers the symmetry bringing the ground state to a Kramer doublet, and spectra are thus readily observed at room temperature. The D_{4h} symmetry stabilizes the d_{z^2} orbital and leaves the unpaired electron either in $d_{x^2-y^2}$ or d_{xy} orbital for which g values are given by the following equations:

$$g_{||} = 2.0023 + 8\lambda/\Delta E\left(d_{x^2-y^2} - d_{xy}\right)$$
$$g_{\perp} = 2.0023 + 2\lambda/\Delta E\left(d_{x^2-y^2} - d_{xz}, d_{yz}\right)$$

In an axial symmetry, the g values are related by $G = (g_{\parallel} - 2/g_{\perp} - 2)$ which measures the exchange interaction between copper centers in polycrystalline solids [52–54]. If $G > 4$, exchange is negligible; values of $G < 4$ indicate considerable exchange in the solid. The g_{av} values have been calculated according to the reaction $g_{av} = (1/3)\ (g_{\parallel} + 2g_{\perp})$ and gave values in the range 2.1 ± 0.1, in agreement with an orbitally non-degenerate ground state. The g value obtained corresponds to molecular g values, characteristics of square-planar geometry around copper(II). In square-planar complexes the unpaired electron lies in the $d_{x^2-y^2}$ orbital giving $^2B_{1g}$ as the ground state with $g_{\parallel} > g_{\perp}$ while the

unpaired electron lies in the d_{z^2} orbital giving $^2A_{1g}$ as the ground state with $g_\perp > g_\parallel$. From the observed values, it is clear that $g_\parallel > g_\perp$, indicating that the structures are square planar [55, 56]. The ESR spectral data are given in table 7.

3.6. *FAB mass spectra*

The FAB mass spectrum of the complexes of 5(2′-hydroxyphenyl)-3-(4-methylphenyl) pyrazoline and $[Cu(L_a)_2bipy]$ give molecular ion peaks (M^+) along with other fragmentations. $Cu(L_c)_2$ exhibited a molecular ion peak at $m/z = 566$, suggesting monomer. For $[Cu(L_a)_2bipy]$, a molecular peak at $m/z = 694$ suggests a monomer.

3.7. *Biological activity*

The 5(2′-hydroxyphenyl)-3-(4-x-phenyl)pyrazolinates of copper and their adducts were screened for antibacterial activity against *E. coli*, *S. flexenari*, *P. aeruginosa*, *S. typhi*, *B. subtilis* and *S. aureus* and for antifungal activity against *T. longifusus*, *C. albicans*, *A. flavus*, *M. canis*, *F. soloni* and *C. glaberata*. The results are listed in tables 8 and 9.

5(2′-Hydroxyphenyl)-3-(4-x-phenyl)pyrazolinates of copper(II) and their addition complexes with donor ligands have higher activity than the free ligand, explained on the basis of Overtone's concept and chelation theory [57]. Complexes disturb the respiration process of the cell and thus block the synthesis of proteins which restricts further growth of organisms. In the present study, it can be clearly seen that different ligands provide variation in the observed biological activity.

3.8. *Cytotoxic bioassay*

All synthesized complexes were screened for their cytotoxicity (brine shrimp bioassay) using the protocol of Meyer *et al*. [58]. From data recorded in table 10, it is evident that

Table 7. ESR spectral data for 5(2′-hydroxyphenyl)-3-(4-x-phenyl)pyrazolinates of copper and adduct with 2,2′-bipyridine, 1,10-phenanthroline and triphenylphosphine.

S. No.	$H_\parallel$ (Gauss)	$H_\perp$ (Gauss)	$g_\parallel$	$g_\perp$	g_{av}	G
1	2630	3512	2.412	1.842	2.032	2.645
2	2700	3510	2.408	1.852	2.037	2.757
3	2625	3550	2.476	1.831	2.046	2.816
4	2700	3600	2.406	1.806	2.060	2.093
5	2712	3530	2.442	1.841	2.041	2.780
6	2658	3542	2.436	1.834	2.034	2.627
7	2703	3514	2.479	1.830	2.046	2.817
8	2700	3540	2.402	1.857	2.038	2.811
9	2687	3560	2.412	1.842	2.032	2.608
10	2746	3150	2.367	2.110	2.159	3.336
11	2684	3070	2.422	2.118	2.219	3.576
12	2653	3610	2.477	1.830	2.045	2.807
13	2677	3552	2.381	1.831	2.014	2.254
14	2715	3240	2.406	1.851	2.036	2.725
15	2846	3180	2.427	1.810	2.077	2.247
16	2834	3187	2.420	1.834	2.029	2.530

Table 8. Antibacterial bioassay data of free pyrazoline ligands, 5(2′-hydroxyphenyl)-3-(4-x-phenyl)pyrazolinates of copper and adducts with donor ligands.

	Gram(−ve) bacteria				Gram(+ve) bacteria	
Compound	*E. coli*	*S. flexenari*	*P. aeruginosa*	*S. typhi*	*S. aureus*	*B. subtilis*
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
$Cu(L_a)_2$	15	10	17	18	20	20
$Cu(L_b)_2$	16	11	16	19	22	21
$Cu(L_c)_2$	17	12	17	17	23	18
$Cu(L_d)_2$	19	09	12	18	21	22
$Cu(L_a)_2$(bipy)	18	12	25	20	23	22
$Cu(L_b)_2$(bipy)	17	15	23	22	22	21
$Cu(L_c)_2$(bipy)	19	12	21	19	21	22
$Cu(L_d)_2$(bipy)	21	11	16	20	23	23
$Cu(L_a)_2$(phen)	19	13	24	21	24	22
$Cu(L_b)_2$(phen)	17	12	20	23	23	21
$Cu(L_c)_2$(phen)	18	16	23	20	20	22
$Cu(L_d)_2$(phen)	21	12	17	21	22	23
$Cu(L_a)_2(PPh_3)$	17	10	25	19	23	21
$Cu(L_b)_2(PPh_3)$	18	12	21	20	20	20
$Cu(L_c)_2(PPh_3)$	19	13	22	18	23	21
$Cu(L_d)_2(PPh_3)$	21	10	14	21	21	22
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).

Table 9. Antifungal bioassay data of free pyrazoline ligands, 5(2′-hydroxyphenyl)-3-(4-x-phenyl)pyrazolinates of copper and their adducts.

	Organism					
Compound	*T. longifusus*	*C. albicans*	*A. flavus*	*M. canis*	*F. soloni*	*C. glaberata*
L_a	00	00	10	00	00	00
L_b	00	00	10	00	00	00
L_c	00	00	07	00	00	00
L_d	00	00	07	00	00	00
$Cu(L_a)_2$	15	09	23	01	00	05
$Cu(L_b)_2$	08	11	24	02	00	00
$Cu(L_c)_2$	17	12	21	01	00	00
$Cu(L_d)_2$	13	06	22	04	00	00
$Cu(L_a)_2$(bipy)	18	10	24	03	00	00
$Cu(L_b)_2$(bipy)	10	12	25	04	00	07
$Cu(L_c)_2$(bipy)	20	13	22	05	00	00
$Cu(L_d)_2$(bipy)	16	08	23	01	00	00
$Cu(L_a)_2$(phen)	18	12	25	02	00	00
$Cu(L_b)_2$(phen)	10	13	24	02	00	00
$Cu(L_c)_2$(phen)	19	15	21	03	00	05
$Cu(L_d)_2$(phen)	18	08	24	01	00	00
$Cu(L_a)_2(PPh_3)$	18	11	24	04	00	00
$Cu(L_b)_2(PPh_3)$	11	12	25	01	00	00
$Cu(L_c)_2(PPh_3)$	17	13	21	02	00	00
$Cu(L_d)_2(PPh_3)$	15	09	23	01	00	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}).

Table 10. Brine shrimp bioassay data of free pyrazoline ligands, 5(2′-hydroxyphenyl)-3-(4-x-phenyl)pyrazolinates of copper and adducts.

Compound	LD_{50} ($M\,mL^{-1}$)
L_a	1.112×10^{-3}
L_b	1.609×10^{-3}
L_c	1.750×10^{-3}
L_d	1.246×10^{-3}
$Cu(L_a)_2$	8.175×10^{-4}
$Cu(L_b)_2$	7.022×10^{-4}
$Cu(L_c)_2$	8.839×10^{-4}
$Cu(L_d)_2$	7.113×10^{-4}
$Cu(L_a)_2$(bipy)	8.849×10^{-4}
$Cu(L_b)_2$(bipy)	9.725×10^{-4}
$Cu(L_c)_2$(bipy)	8.884×10^{-4}
$Cu(L_d)_2$(bipy)	7.732×10^{-4}
$Cu(L_a)_2$(phen)	9.625×10^{-4}
$Cu(L_b)_2$(phen)	7.831×10^{-4}
$Cu(L_c)_2$(phen)	8.996×10^{-4}
$Cu(L_d)_2$(phen)	9.321×10^{-4}
$Cu(L_a)_2(PPh_3)$	8.456×10^{-4}
$Cu(L_b)_2(PPh_3)$	7.138×10^{-4}
$Cu(L_c)_2(PPh_3)$	8.934×10^{-4}
$Cu(L_d)_2(PPh_3)$	8.413×10^{-4}

Table 11. Anti-inflammatory activities of 5(2′-hydroxyphenyl)-3-(4-x-phenyl)pyrazolinates of copper and their adducts with donor ligands.

Compounds	No. of animals used	Dose ($mg\,kg^{-1}$) body wt.	Initial volume* 0.0 hours	Final volume* After 3 hours	Volume of edema*	% Inhibition
Control	8	100	0.575	1.105	0.530	–
Standard drug (Diclofenac)	8	100	0.540	0.905	0.365	31.13
$Cu(L_a)_2$	8	100	0.819	0.931	0.112	78.87
$Cu(L_b)_2$	8	100	0.821	0.950	0.129	75.56
$Cu(L_c)_2$	8	100	0.811	0.921	0.110	79.25
$Cu(L_d)_2$	8	100	0.826	0.950	0.124	76.60
$Cu(L_a)_2$(bipy)	8	100	0.809	0.911	0.102	80.75
$Cu(L_b)_2$(bipy)	8	100	0.817	0.935	0.118	77.74
$Cu(L_c)_2$(bipy)	8	100	0.805	0.912	0.107	79.81
$Cu(L_d)_2$(bipy)	8	100	0.815	0.938	0.123	76.79
$Cu(L_a)_2$(phen)	8	100	0.819	0.925	0.106	80.00
$Cu(L_b)_2$(phen)	8	100	0.826	0.935	0.109	79.43
$Cu(L_c)_2$(phen)	8	100	0.819	0.921	0.102	80.76
$Cu(L_d)_2$(phen)	8	100	0.831	0.950	0.119	77.55
$Cu(L_a)_2(PPh_3)$	8	100	0.809	0.915	0.106	80.00
$Cu(L_b)_2(PPh_3)$	8	100	0.815	0.938	0.123	76.79
$Cu(L_c)_2(PPh_3)$	8	100	0.805	0.912	0.107	79.81
$Cu(L_d)_2(PPh_3)$	8	100	0.817	0.935	0.118	77.74

*Average of four readings.

all complexes and adducts have potent cytotoxic activity as $LD_{50} = 7.022 \times 10^{-4}$ to 9.724×10^{-4} against *Artemia salina* while all ligands were almost inactive for this assay.

3.9. *Anti-inflammatory activity*

5(2′-Hydroxyphenyl)-3(4-x-phenyl)pyrazolinates of copper were tested for anti-inflammatory effects; differences were observed between the complexes and standard drug (table 11).

At equal doses 5(2′-hydroxyphenyl)-3(4-x-phenyl)pyrazolinates of Cu(II) were more effective than the standard drug, providing evidence for a unique metabolite Cu-dependent metabolic process for tissue maintenance. A metal compound may be responsible for anti-inflammatory activity of those agents, which have clinical use [59–63]. 5(2′-Hydroxyphenyl)-3(4-x-phenyl)pyrazolinates of copper, which have not been generally recognized as possible active metabolites, may be responsible for anti-inflammatory activity of clinically used anti-inflammatory agents.

4. Conclusion

On the basis of analytical and spectral data, a square-planar geometry [64–66] around copper(II) is proposed with two bidentate pyrazoline ligands in $(C_{15}H_{12}N_2OX)_2Cu$ while addition complexes have monodentate pyrazoline. On the basis of XRD, the complexes are amorphous. The antimicrobial studies show that 5(2′-hydroxyphenyl)-3-(4-x-phenyl)pyrazolinates of copper(II) have greater activity towards all tested bacteria, fungi and inflammation than free pyrazolines. The copper complexes deactivate various cellular enzymes which play a vital role in metabolic pathways of the micro organisms. The role of 5(2′-hydroxyphenyl)-3(4-x-phenyl)pyrazolinates of copper at cellular/enzymatic level is an area for further research.

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