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Complexation Behaviour of 5(2′-Hydroxyphenyl)-3-phenylpyrazoline with Some Metallic Moieties

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The development of a clean procedure for the preparation of heterocyclic compounds is a major challenge of modern heterocyclic chemistry in view of the environmental, practical and hence economic issue. Pyrazolines are an important class of heterocyclic compounds. They are used in industries as dyes, lubricating oils as antioxidants and in agriculture as catalysts for decarboxylation reaction as well as inhibitors for plant growth [1–3]. In day-to-day life organic derivatives of pyrazolines are also extensively used in photography [4]. The metal complexes of 5(2′-hydroxyphenyl)-3-phenylpyrazoline with Ni(II), Co(II), Cu(II) have been prepared in our laboratory by the extraction method [5]. Similar type of ligands have also been used to prepare complexes of cobalt, copper and nickel [6], but a detailed investigation is missing.

In continuation to our previous work on sulphur ligand derivatives of biologically important metals [7], it was thought worthwhile to report an improved method of the complexation of 5(2′-hydroxyphenyl)-3-phenylpyrazoline with some metallic moieties *viz.* Fe(III), Co(II), Ni(II), Cu(II) and Cd(II).

All the chemicals used were of analytical grade quality. Solvents were used after drying [8]. The ligand 5(2′-hydroxyphenyl)-3-phenylpyrazoline was prepared by reported procedure [9]. Freshly cut pieces of sodium were taken in a flask with excess of isopropanol and refluxed (~1/2 hour), till a clear solution of sodium isopropoxide was obtained. The benzene solution of 5(2′-hydroxyphenyl)-3-phenylpyrazoline was then added and the reaction mixture was further refluxed for 1 hour, whereby a constant yellow colour was obtained. The reaction mixture was cooled to room temperature and then an alcoholic solution of anhydrous metal chloride was added dropwise with constant stirring. The reaction mixture was further stirred for 15–20 hours, till the colour of reaction mixture underwent a change. 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.

Table 1. Synthetic, analytical and physical property data for the complexes.

S. No.	Reactants			Molar ratio	Product (colour)	Yield % (g)	M.P. (°C)	Mol. Wt. Found (Calcd.)
	Metal chloride g (mmole)	Sodium g (mmole)	Ligand[#] g (mmole)					
01.	$FeCl_3$ 0.4233 (2.6081)	0.1799 (7.8217)	1.8623 g (7.8247)	1:3:3	$(C_{15}H_{13}N_2O)_3Fe$ (black)	60 (1.2010)	200	757.66 (767.68)
02.	$CoCl_2$ 0.4894 (3.7666)	0.1733 (7.5347)	1.7932 g (7.5344)	1:2:2	$(C_{15}H_{13}N_2O)_2Co$ (dark brown)	57.9 (1.1580)	275	543.42 (533.49)
03.	$NiCl_2$ 0.4869 (3.5744)	0.1727 (7.5086)	1.7871 g (7.5098)	1:2:2	$(C_{15}H_{13}N_2O)_2Ni$ (light green)	83.75 (1.6750)	360*	523.30 (533.27)
04.	$CuCl_2$ 0.5004 (3.7204)	0.1711 (7.4391)	1.7711 g (7.4391)	1:2:2	$(C_{15}H_{13}N_2O)_2Cu$ (light brown)	85.7 (1.7154)	276	526.18 (538.10)
05.	$CdCl_2$ 0.6255 (3.7404)	0.1569 (6.8214)	1.6235 g (6.8214)	1:2:2	$(C_{15}H_{13}N_2O)_2Cd$ (brown)	55.62 (1.1104)	360*	572.92 (586.96)

[#] 5(2′-hydroxyphenyl)-3-phenylpyrazoline [$C_{15}H_{13}N_2OH$].

*The compound could not melt even up to 360°C.

Infrared spectra were recorded as KBr pellets on Perkin-Elmer 577 spectrophotometer. Molecular weights were determined on a Knoauer Vapour Pressure Osmometer in $CHCl_3$ at 45°C. Elemental analysis of iron, cobalt, nickel, copper and cadmium was done by standard procedure [10]. Carbon, hydrogen and nitrogen were estimated by Coleman CHN analyzer. Magnetic moment studies were carried out on a Gouy balance at room temperature. Electronic spectra were recorded in chloroform solution on Hitachi-U-2000 spectrophotometer.

Table 2. IR spectral data for complexes and ligand.

S No.	Compounds	Infra-red (cm^{-1})				
		ν(N–H)	ν(O–H)	ν(C=N)	ν(M–N)	ν(M–O)
01.	Ligand	3320	3080	1595	–	–
02.	$(C_{15}H_{13}N_2O)_3Fe$	3446	–	1654	421	697
03.	$(C_{15}H_{13}N_2O)_2Co$	3419	–	1640	425	696
04.	$(C_{15}H_{13}N_2O)_2Ni$	3446	–	1653	418	696
05.	$(C_{15}H_{13}N_2O)_2Cu$	3446	–	1653	435	697
06.	$(C_{15}H_{13}N_2O)_2Cd$	3445	–	1616	423	697

Ligand = $C_{15}H_{13}N_2OH$; [5-(2′-hydroxyphenyl)-3-phenylpyrazoline].

All the complexes are crystalline solids of green to black colour, non-hygroscopic and stable at room temperature. Iron(III), cobalt(II) and copper(II) complexes are soluble in common organic (benzene, chloroform, carbontetrachloride) and coordinating (pyridine, tetrahydrofuran and dimethylsulphoxide) solvents. Nickel(II) complex is soluble in chloroform, while cadmium(II) complex is soluble in pyridine, tetrahydrofuran and dimethylsulphoxide only. These complexes are monomeric in dilute chloroform solution at 45°C except Cd(II) complex, which is practically insoluble in common organic solvents and soluble in coordinating solvents suggesting polymerization in the compound. The elemental analysis (C, H, N, M; M = metal) data is in accordance with the stoichiometry proposed for respective complexes. The metal ligand ratio for iron(III) complex is 1:3 and 1:2 for cobalt(II), nickel(II), copper(II) and cadmium(II) complexes. The magnetic moment data for complexes are summarized in Table 3. These values are in good agreement with the spin only value calculated for respective number of unpaired electrons in monomeric compounds [11]. The nickel(II) and cadmium(II) complexes are diamagnetic in nature.

The IR spectra of these complexes exhibit bands in the region 3446–3419 cm^{-1}, which may be ascribed to ν(N–H) modes. The ν(C=N) vibrations have been recorded in the region 1654–1616 cm^{-1} [12], new bands (not present in pyrazoline ligand) in the region 435–418 and 697–696 cm^{-1} have been observed which may be due to ν(M–N) and ν(M–O) stretching vibrations. The appearance of these two new bands suggests that the 5(2′-hydroxyphenyl)-3-phenylpyrazoline behaves as monobasic bidentate ligand.

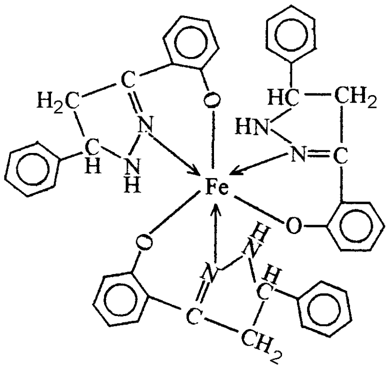
Table 3. Electronic spectral and magnetic moment data for complexes.

S No.	Complexes	Electronic spactral bands		Magnetic moment (B.M.) Found (Calcd.)
		assignment	bands (cm^{-1})	
01.	$(C_{15}H_{13}N_2O)_3Fe$	${}^6A_{1g} \rightarrow {}^4T_{1g}$ charge transfer	13530 30030, 46426	5.49 (5.92)
02.	$(C_{15}H_{13}N_2O)_2Co$	${}^6A_2\ (F) \rightarrow {}^4T_1\ (P)$	15100	3.59 (3.87)
03.	$(C_{15}H_{13}N_2O)_2Ni$	${}^1A_{1g} \rightarrow {}^1B_{2g}$ ${}^1A_{1g} \rightarrow {}^1B_{1g}$	25147 20225	–
04.	$(C_{15}H_{13}N_2O)_2Cu$	${}^2B_{1g} \rightarrow {}^2A_{1g}$ ${}^2B_{1g} \rightarrow {}^2E_g$	15800 21800	1.82 (1.73)

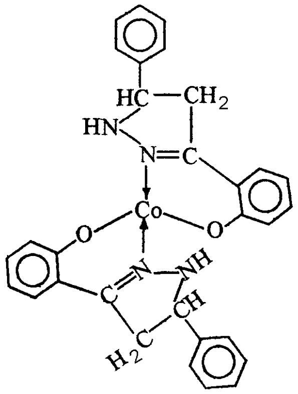
The electronic spectral data of complexes are summarized in Table 3. The iron(III) complex shows band at 13530 cm^{-1} assigned to ${}^6A_{1g} \rightarrow {}^4T_{1g}$ transition. The positions of various bands are in good agreement with the data reported for hexa-coordinated iron(III) complexes, which have also been confirmed by X-ray crystallography [13,14]. The six coordination number for iron(III) complex is possible only when the ligand behaves as bidented moiety because there number of ligand is three. The cobalt(II) complex has tetrahedral geometry with the only one d–d transition. Its spectrum exhibits major band at 15100 cm^{-1}, which could be assigned to ${}^4A_2(F) \rightarrow {}^4T_1(P)$ transition [15]. The four coordination number for cobalt(II) complex suggests tetrahedral geometry with the presence of two pyrazoline ligand. The spectrum of nickel(II) complex exhibits two bands at 25147 cm^{-1} and 20225 cm^{-1} assigned to ${}^1A_{1g} \rightarrow {}^1B_{2g}$ and ${}^1A_{1g} \rightarrow {}^1B_{1g}$ transition respectively, which are in good agreement with square planar geometry of the complex [16]. The two strong bands at 15800 cm^{-1} and 21800 cm^{-1} assigned to ${}^2B_{1g} \rightarrow {}^2A_{1g}$ and ${}^2B_{1g} \rightarrow {}^2E_g$ are in agreement with square planar geometry of copper(II) complex [7,17]. The square planar structure of nickel(II) and copper(II) complexes is possible only when the two pyrazoline ligand is attached with metal centre, which is proved by elemental analysis.

${}^1H$ NMR spectra of nickel(II) and cadmium(II) complexes were recorded at 300 MHz on a DRX 300 instrument in $CDCl_3$. The aromatic protons of nickel(II) complex were observed as a multiplet in the region 7.4–6.6 ppm. The integration ratio is in accordance with the presence of 9 protons. The peak due to hydroxyl proton (originally present at 11.15 ppm in ligand) is completely missing from the spectrum of the complex suggesting the bonding through hydroxyl oxygen atom. The unaffected appearance of a peak due to N–H at 5.08 ppm as a broad singlet could be assigned to N–H vibrations suggesting the non-involvement of N–H group in bond formation [18]. The skeletal protons of five membered ring are observed at 3.4 and 2.5 ppm as a broad singlet could be assigned to CH and CH_2 group respectively [19]. The overall broadening in the signals could possibly be due to the inherent magnetic moment in nickel(II) complex.

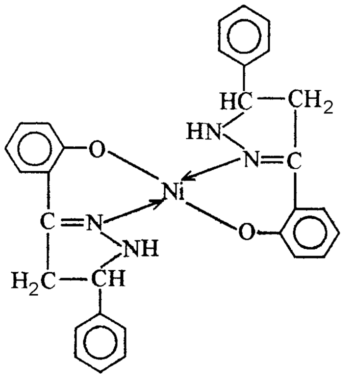
The aromatic protons of cadmium(II) complex are observed in the region of 7.7–6.9 ppm as a multiplet. The complete absence of the peak due to hydroxyl proton confirms the involvement of hydroxyl oxygen in bond formation. The unaffected appearance of a band due to N–H at 4.25 ppm as a singlet suggests the non-involvement



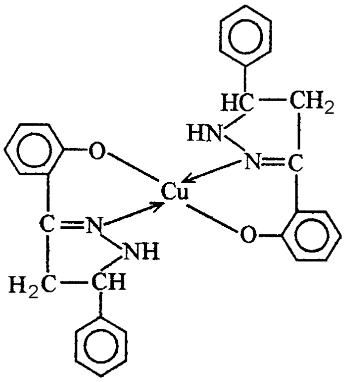
Iron(III) 5–(2'–hydroxyphenyl)–3–phenylpyrazoline



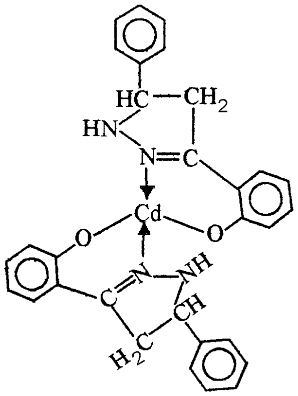
Cobalt(II) 5–(2'–hydroxyphenyl)–3–phenylpyrazoline



Nickel(II) 5–(2'–hydroxyphenyl)–3–phenylpyrazoline



Copper(II) 5–(2'–hydroxyphenyl)–3–phenylpyrazoline



Cadmium(II) 5–(2'–hydroxyphenyl)–3–phenylpyrazoline

of N–H group in bond formation. The skeletal proton of five membered rings shows sharp singlets at 3.1 and 2.5 ppm due to CH and CH_2 groups respectively [19].

^{13}C NMR spectra of nickel(II) and cadmium(II) complexes have been recorded in $CDCl_3$ and DMSO-d_6 on a DRX 300 instrument. The assignments have been made on the basis of available literature along with the spectrum of the ligand. The spectrum of nickel(II) complex shows the presence of all important signals with reference to ligand. The signal observed in the region 128–125 ppm as broad singlet could be assigned to aromatic carbon [19]. The signal found at 155 ppm in the spectrum of ligand, assigned to C–N, is shifted to downfield at 173 ppm in the spectrum of the compound showed the involvement of imino nitrogen in coordination [18]. All other signals were found at their respective positions as in ligand.

The signal observed in the spectrum of the cadmium(II) complex in the region 129–125 ppm as broad singlet may be assigned to aromatic carbon. The signal at 169 ppm due to imino carbon of C=N group is shifted downfield with reference to the spectrum of ligand suggesting the involvement of imino nitrogen in coordination. All other signals were found at their respective positions as in ligand. ^{13}C NMR along with ^{1}H NMR spectrum of the complexes indicates towards the bidentate nature of the ligand in these complexes. The tetrahedral structure of Cd(II) complex is indicated by the presence of two pyrazoline ligand with metal.

On the basis of above studies hexacoordinated octahedral for Fe(III), tetracoordinated square planar for Cu(II) and Ni(II), tetracoordinated tetrahedral for Co(II) and Cd(II) centres could tentatively be proposed.

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