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SYNTHESIS AND CHARACTERIZATION OF METAL CHELATES WITH 1, 5-DIARYL-3- (2-HYDROXYPHENYL) FORMAZANS

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ABSTRACT

Copper, cobalt and nickel chelates of 1, 5-diaryl-3- (2-hydroxyphenyl) formazans were synthesized and characterized by physical and spectroscopic methods. Their stability constants were also determined.

Key words : Formazans, Copper, Cobalt, Nickel

INTRODUCTION

Metal complexes of organic compounds have found increasing applications in diverse fields[1, 2]. Formazans and their metal chelates can be used together with disperse dyes in single step dyeing of cellulosic-polyester blends, for dyeing or printing of paper, leather and polyamide fibres[3].

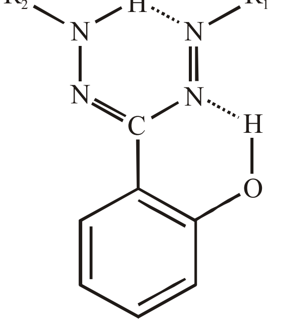

Fig. 1

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Compound	R_1	R_2
1a	C_6H_5	C_6H_5
1b	C_6H_5	$C_{10}H_7$
1c	C_6H_5	C_6H_4 (COOH)
1d	C_6H_5	C_3H_2NS

They are also used to detect the presence of trace elements in ores[4] and in the development of new type of oxidative and reductive chromogenic reagents in clinical analysis as an indicator of cell viability with less cytotoxicity[5, 6]. Some metal chelates of formazans can be used reliably to measure metabolic activity of cell cultures *in vitro* for the assessment of growth characteristics and in various biological researches[7]. Though several such applications have been reported for metal chelates of formazans, structural aspects of these chelates were not much discussed earlier. The present paper deals with the synthesis and characterization of the copper (II), nickel (II) and cobalt (II) complexes with the formazans

EXPERIMENTAL

Synthesis of 1, 5-diaryl-3- (2-hydroxyphenyl) formazans

The compounds were synthesized by the reaction of phenylhydrazone of salicylaldehyde with aryldiazonium salts.

Preparation of salicylaldehyde phenylhydrazone

A solution of salicylaldehyde (12 g, 0.1 mol) in 75% v/v ethanol-water mixture (250 mL) was mixed with an ethanolic solution (250 mL) of phenyl hydrazine (12.2 g, 0.1 mol) and refluxed on boiling water bath for about 3 h. The precipitate formed on cooling to room temperature was filtered, washed with water, recrystallised from ethanol (m. p. 144ºC reported. 142ºC).

Preparation of the formazan

The aryl diazonium salts of aniline, 1-aminonaphthalene, anthranilic acid and 2-aminothiazole were prepared as reported [13].

The diazonium salt solution (0.025 mol) was added slowly with stirring to an ice cooled aqueous methanolic solution of the salicylaldehyde phenylhydrazone (400 mL) containing sodium hydroxide (10.5 g) also. Stirring was continued for about 1 h. The precipitate formed was filtered, washed with water and extracted into ether. The ether extract was dried using anhydrous magnesium sulphate. On evaporation of ether, pure formazan was obtained.

Preparation of metal chelates

The 1, 5-diaryl-3- (2-hydroxyphenyl) formazans (0.025 mol) was extracted in to a boiling methanolic solution (150 mL) of metal (II) acetate (0.05 mol) and glacial acetic acid (1 mL). The precipitate was collected, washed with the boiling methanol and dried. It was recrystallised from methanol.

RESULTS AND DISCUSSION

The metal complexes (II) were prepared using the above formazans (**1a**, **1b**, **1c** and **1d**) and they were characterized by physical, analytical and spectral studies. Their stability constants were also determined.

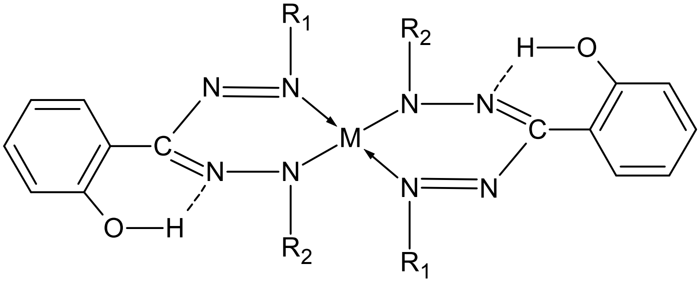

Fig. 2

Physical, analytical and spectral results are given in the following tables.

Table 1 : Physical, analytical and U. V. spectral data of metal complexes of 1, 5-diphenyl-3- (2-hydroxyphenyl) formazan (1a)

Metal	M. P. (^{0}C)	Elemental analysis found (calcd) in %				λmax (nm)
		C	H	N	metal	
Cu (II)	>300	66.54 (65.74)	4.54 (4.32)	15.84 (16.16)	8.95 (9.16)	296 261
Co (II)	>300	65.87 (66.18)	3.85 (4.06)	15.82 (16.25)	8.68 (8.53)	295 261

Metal	M. P. (^{0}C)	Elemental analysis found (calcd) in %				λmax (nm)
		C	H	N	metal	
Ni (II)	>300	69.45 (69.98)	4.34 (4.35)	16.87 (16.26)	8.532 (8.52)	804 306 262

Table 2 : Physical, analytical and U. V. spectral data of metal chelates of 1-phenyl-5-(1-naphthyl-3- (2-hydroxyphenyl)formazan (1b)

Metal	M. P. (^{0}C)	Elemental analysis found (calcd) in %				λmax (nm)
		C	H	N	Metal	
Cu (II)	>300	69.2 (69.56)	4.62 (4.28)	14.81 (14.2)	7.92 (8.01)	429 310
Co (II)	>300	69.25 (69.95)	3.95 (4.31)	14.50 (16.17)	8.2 (7.46)	429 310
Ni (II)	>300	68.92 (69.98)	3.85 (4.36)	14.54 (14.2)	8.23 (7.44)	433 309

Table 3.Physical, analytical and U. V. spectral data of metal chelates of 1-phenyl-5-(2- carboxy phenyl)-3- (2-hydroxyphenyl)formazan (1c)

Metal	M. P. (^{0}C)	Elemental analysis found (calcd) in %				λmax (nm)
		C	H	N	metal	
Cu (II)	>280	55.48 (56.79)	3.37 (3.31)	13.68 (13.25)	15.01 (15.03)	730, 470 310, 285
Co (II)	>280	56.84 (57.54)	3.39 (3.36)	14.2 (13.43)	15.5 (14.13)	455 310
Ni (II)	>280	55.3 (57.59)	3.54 (3.35)	13.68 (13.43)	15.5 (14.08)	630 315 204

Table 4 : Physical, analytical and U. V. spectral data of 1-phenyl-5-thiazolyl-3- (2-hydroxyphenyl)formazan (1d)

Metal	M. P. (^{0}C)	Elemental analysis found (calcd) in %				λmax (nm)
		C	H	N	Metal	
Cu (II)	>280	54.85	4.01	19.25	8.25	640
		(54.27)	(3.39)	(19.78)	(8.98)	360
Co (II)	>290	54.7	3.50	19.28	7.96	730, 310, 255
		(54.62)	(3.41)	(19.91)	(8.38)	
Ni (II)	>300	54.25	3.51	19.2	8.9	615
		(54.64)	(3.13)	(19.92)	(8.35)	310

All the complexes synthesized are crystalline solids soluble in common organic solvents. Elemental and analytical data of the compounds correspond to their formulation as structure given in Fig. 2. The intensity of the broad band of the free ligand in IR spectra of the complexes in the region 2400-3800 cm^{-1} has decreased considerably and confined to the region 2800-3200 cm^{-1}. This indicates the existence of internal hydrogen bonding.

N. M. R. spectra

In these types of ligands, in which two acidic protons are present, only one of them is replaced by metal ion during complex formation. The spectra clearly demonstrate that the phenolic proton is not eliminated and it is involved in intermolecular hydrogen bonding with one of the azo nitrogen as in the free ligand. This conclusion is based on the fact that the phenolic proton signal of the free ligand at ~δ 11 ppm was also observed in the spectra of the diamagnetic nickel (II) complexes with slight shift in the position. The integrated intensities of the aryl protons agree well with the formulation of the complex.

Potentiometric studies on the acidity and chelation of 1, 5-diaryl-3- (2-hydroxy phenyl) formazan

The proton-ligand and metal-ligand stability constants of Co^{II}, Ni^{II} and Cu^{II} complexes of 1, 5-diaryl-3- (2-hydroxy phenyl)formazan were determined in 50% v/v aqueous dioxan medium[8, 9].

The proton-ligand formation number $\bar{n}_A$ calculated by half-integral and mid-point methods from the pH *vs* $\bar{n}_A$ plots (Fig. 3). The mean values are presented in Table 5.

Table 5: The acid dissociation constants of 1, 5-diaryl-3- (2-hydroxy phenyl) formazan

Compounds	pK
1a	9.30
	7.52
1b	9.22
	7.48
1c	9.20
	7.50
	6.10
1d	9.24
	7.54

From the Table 5, it follows that pK phenolic proton dissociates prior to the NH function. The decreasing trend in pK values from **1a** through **1d** can be attributed to electron withdrawing effects of the aryl substituents.

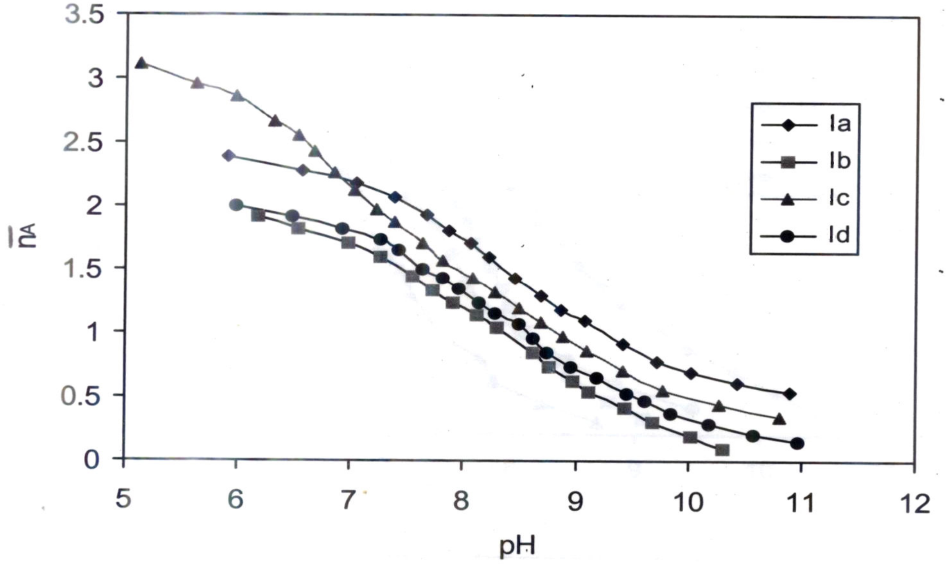

Fig. 3 : Proton-ligand formation curves for 1, 5-diaryl-3- (2-hydroxyphenyl) formazan

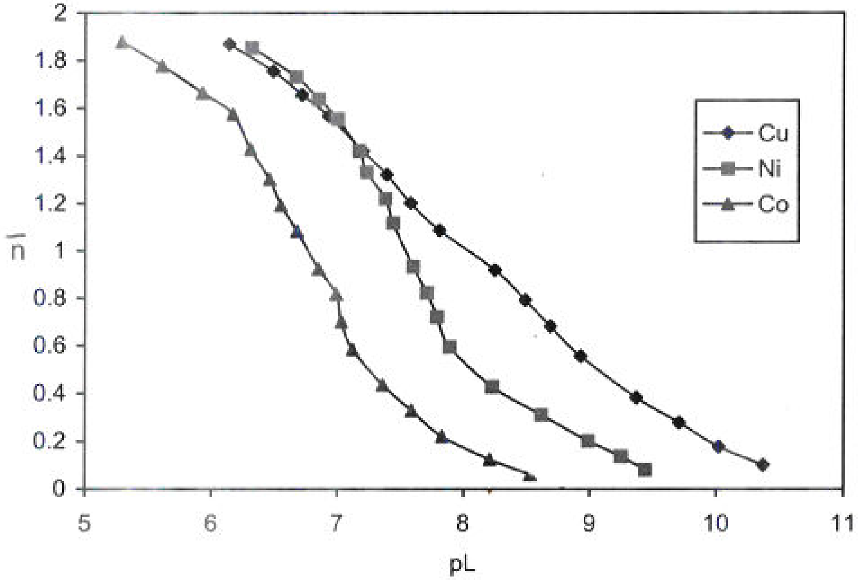

Fig. 4 : Metal-ligand formation curves for 1a

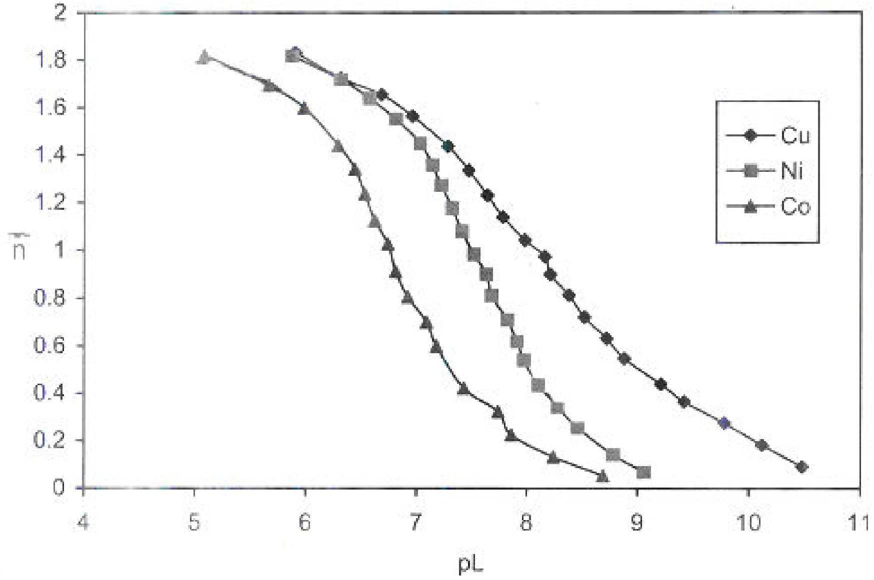

Fig. 5 : Metal-ligand formation curves for 1b

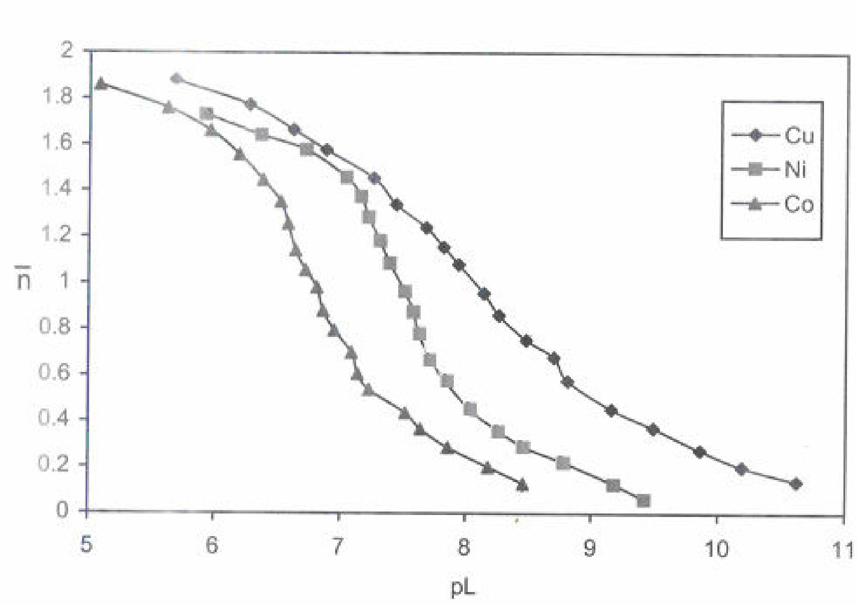

Fig 6 : Metal-ligand formation curves for 1c

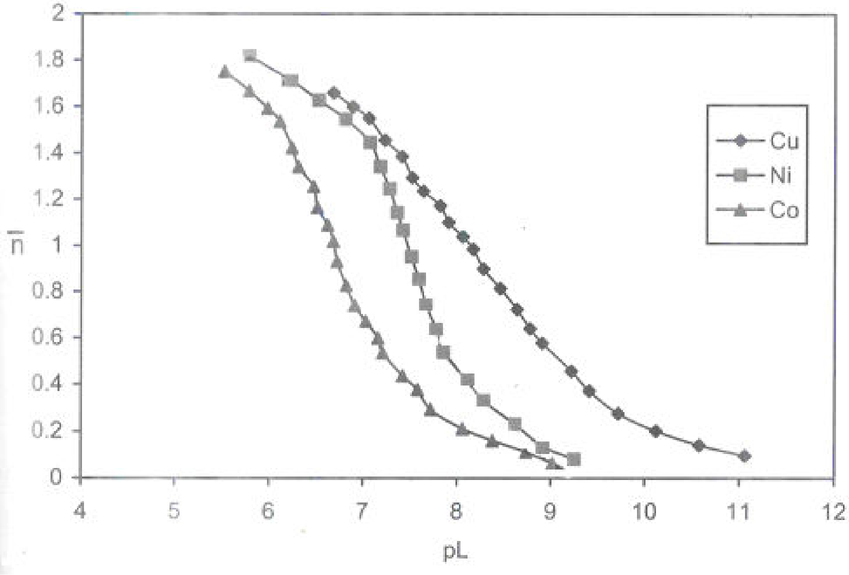

Fig. 7 : Metal-ligand formation curves for 1d

The stability constants for the cobalt (II), nickel (II) and copper (II) complexes agree with the Irving-William natural order of stability[10]. The log K_n values (Table 6) show an increasing trend when electron withdrawing groups are present in the ring. Since log K_1 > log K_2, it indicates a decrease in the bond strength with successive attachment of the ligand molecules. However, the observed differences between the two values suggest the essentially planar geometry of the chelates.

Table 6 : Metal-ligand stability constants of 1, 5-diaryl-3- (2-hydroxyphenyl) formazans

Metal (II) ions	Stability constants	Ligands			
		1a	1b	1c	1d
Cu^{2+}	log K_1	9.1	9.02	9	9.05
	log K_2	7.03	7.12	7.1	7.13
Ni^{2+}	log K_1	8.03	8	7.95	7.98
	log K_2	7.05	6.92	6.96	6.9
Co^{2+}	log K_1	7.21	7.3	7.35	7.28
	log K_2	6.27	6.18	6.28	6.14
Zn^{2+}	log K_1	7.74	7.81	7.88	7.92
	log K_2	6.82	6.48	6.61	6.56

The physical, analytical and spectral results of formazans (I) are listed in Tables 7 and 8.

Table 7 : Physical, analytical and U. V. spectral data of the 1, 5-diary l-3- (2-hydroxyphenyl) formazans

Compounds	M. P. (°C)	Elemental analysis found (calcd) %			λ_{max} (nm)
		C	H	N	
1a	110	73.54 (72.15)	5.65 (5.63)	18.01 (17.72)	381 262
1b	140	78.01 (76.66)	5.01 (4.91)	16.85 (15.30)	309 244
1c	135	65.41 (66.66)	4.01 (4.44)	16.41 (15.55)	380 310

Compounds	M. P. (°C)	Elemental analysis found (calcd) %			λ_{max} (nm)
		C	H	N	
1d	125	60.51 (59.44)	3.98 (4.02)	20.58 (21.67)	386 242

Table 8 : Characteristic ir stretching bands of 1, 5-diaryl-3- (2-ydroxyphenyl) formazans

Compounds				Probable assignments
1a	**1b**	**1c**	**1d**	
1454	1459	1454	1456	*v*N=N
1565	1602	1610	1612	*v*C=N

The U. V. spectra of all the compounds show broad absorption maxima at about 380 and 300 nm due to the various chromophoric groups present in the compounds. The IR spectra of the compounds display a broad brand extending in the range 2400- 3800 cm^{-1}. The observed breadth and intensity of the band indicates the involvement of the phenolic OH group also in hydrogen bonding in addition to the N-H……. N hydrogen bonded system of the formazan structure.

Presence of an OH group on the phenyl ring brought out marginal shift in the stretching frequency of C=C, N=N etc[11, 12]. However, the C=N frequency shifted considerably to lower value, presumably due to the involvement of its nitrogen in hydrogen bonding with the phenolic OH group (Table 8).

The ^1H NMR spectra unequivocally support the structure of the compounds. In the low field region, two well resolved one portion signals exist in all the spectra. The signal at about δ 15 ppm is due to the N-H….. N proton. The slightly broadened signal at δ ~ 11 ppm may be confidently assigned to the phenolic proton, which is involved in strong internal hydrogen bonding with the adjacent N atom of the formazan structure. The spectrum of 1c shows an additional ^1H signal in the low field at δ 15.5 ppm for the carboxylic proton signals as expected.

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