



**Study of Effect of Strong Resonance Stabilized Intramolecular Hydrogen Bonding in 1-(1-hydroxy-2-naphthyl)-3-(phenyl or substituted phenyl)-prop-2-en-1-ones And on Their Complexation with Some Transition Metals Through <sup>1</sup>H-NMR and Electronic Spectroscopic Investigations**

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**ABSTRACT**

*Some copper (II), nickel (II) and cobalt (II) complexes of naphthalene analogues of 2'-hydroxychalcones have been synthesized and characterized. The complexes have the general formula  $ML_2.XH_2O$  ( $X=2$  or  $0$ ) where  $L$  is the deprotonated ligand, the naphthyl chalcone and  $M$  is the divalent metal ion. In the present study, the effect of strong resonance stabilized intramolecular hydrogen bonding in naphthalene analogues of 2'-hydroxychalcones and on their complexation with transition metals such as copper(II), nickel(II) and cobalt(II) has been studied through their <sup>1</sup>H-NMR and electronic spectroscopic investigations.*

**Keywords:** <sup>1</sup>H-NMR spectra, electronic spectra, chalcones, complexes, absorption, intramolecular hydrogen bonding and chelates.

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**INTRODUCTION**

Chalcones and their derivatives are found to possess a wide spectrum biological activity and multiprotecting biochemical activity as reported[1-13]. Chalcones and their derivatives find varied applications as reported earlier[11-13]. Ortho-hydroxy chalcones have good chelating properties and were exploited as analytical reagents for estimation of different metal ions[14]. 2'-hydroxychalcones and their heterocyclic and naphthalene analogues are also reported to form coordination complexes[14-26]. Ruthenium complexes of 2'-hydroxychalcones[27-34], chalcone oximes[35] and chalcone semi carbazones[36,37] are synthesized and characterized by analytical and spectroscopic methods.

**MATERIALS AND METHODS**

**Materials:** All reagents and chemicals used were of AnalaR grade. All solvents used were of standard/spectroscopic grade.

**Synthesis:** The naphthalene analogues of 2'-hydrochalcones, 1-(1-hydroxy-2-naphthyl)-3-phenyl-prop-2-en-1-one(BenchaH), 1-(1-hydroxy-2-naphthyl)-3-(2-methoxyphenyl)-prop-2-en-1-one(o-AnichaH), 1-(1-

hydroxy-2-naphthyl)-3-(4-methoxyphenyl)-prop-2-en-1-one(p-AnichaH), 1-(1-hydroxy-2-naphthyl)-3-(3,4-methylenedioxy phenyl)-prop-2-en-1-one(PipchaH), 1-(1-hydroxy-2-naphthyl)-3-(3,4-dimethoxy phenyl)-prop-2-en-1-one (VerchaH) were prepared by the procedure as reported with their general structure by us[11-13]. The metal complexes of these naphthyl chalcones, BenchaH, o-AnichaH, p-AnichaH, PipchaH and VerchaH were prepared as per the procedure reported by us elsewhere [11-13].

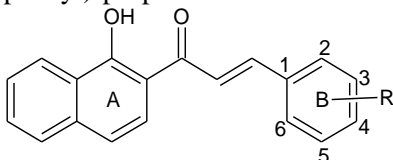
**Physical Measurements:** The proton magnetic resonance spectra were recorded on NMR-R-600, Hitachi (Japan) and Varian XL-100 NMR, Nuclear Magnetic Resonance Spectrometers using TMS as internal standard and  $\text{CDCl}_3$  as solvent. The ultraviolet and visible spectra were recorded on a Jasco, Model-870, (Japan) recording spectrophotometer using a quartz cell of 1 cm optical path. Methanol was used as a solvent blank. The diffuse reflectance spectra of solid metal complexes were taken on a UV-Visible, 260-Shimadzu (Japan) spectrophotometer fitted with a reflectance assembly, using pure barium sulphate as a reference.

## RESULTS AND DISCUSSION

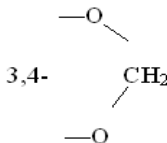
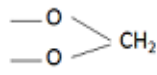
**NMR Spectra of Some Ligands:** Nuclear magnetic resonance spectra of the naphthylchalcones, 1-(1-hydroxy-2-naphthyl)-3-(4-methoxyphenyl)-prop-2-en-1-one [p-AnichaH] and 1-(1-hydroxy-2-naphthyl)-3-(3,4-methylene dioxy phenyl)-prop-2-en-1-one [PipchaH] are recorded in  $\text{CDCl}_3$  solution [Table-1].

The NMR spectrum of the naphthyl chalcone, p-AnichaH in  $\text{CDCl}_3$  solution reveals a sharp singlet at  $\delta$  3.85 which is due to the protons of a methoxy group [38] at  $\text{C}_4$ . Two signals which appear as doublets at  $\delta$  6.93 - 6.96 and  $\delta$  8.47 - 8.49 are due to the two alkenic or olefinic ( $=\text{CH}$ ) protons [39-41]. These naphthyl chalcones having unsymmetrically substituted double bonds contain non-equivalent olefinic hydrogens that are coupled to each other. Therefore, due to these, two non-equivalent alkenic protons, two signals appear as doublets and this is comparable [39,40,42] to the NMR spectrum of trans-cinnamic acid in which the two non-equivalent alkenic protons of it give two signals which appear as doublets at  $\delta$  6.5 and  $\delta$  7.8. The aromatic protons are observed as complex multiplets in the range of  $\delta$  7.25-7.97, but the naphthyl and phenyl protons could not be assigned separately [39-41]. M.M.H. Khalil et.al [39] in their study of reaction of 2'-hydroxy methoxylated chalcone with group 6 and 8 metal carbonyl complexes observed a singlet at  $\delta$  12.82ppm in the above said chalcone and it was attributed due to  $-\text{OH}$  forming intramolecular hydrogen bonding with carbonyl group by them. V.N.Patange and B.R. Arbad [41] observed the same signal as a singlet at  $\delta$  18.16ppm for the heterocyclic analogue of chalcones. S.B.Sirsat et.al [40] got the singlet due to phenolic  $-\text{OH}$  group in the range of  $\delta$  10.5-13.5ppm for some novel hetero-aryl chalcones. Therefore, the resonance signal which appears as a sharp singlet at  $\delta$  14.98 is attributed to the phenolic proton which is  $\text{D}_2\text{O}$  exchangeable and this is due to the phenolic  $-\text{OH}$  group forming intramolecular hydrogen bonding with the carbonyl group as stated above.

**Table-1:** NMR spectral data on some of the naphthylchalcones, 1-(1-hydroxy-2-naphthyl)-3-(phenyl or substituted phenyl)-prop-2-en-1-ones in  $\text{CDCl}_3$  solution



Sr.No.	Ligand	Substituent -R=	Observed Shift in $\delta$ (ppm)	Assignment
1	p-AnichaH	4 - $\text{OCH}_3$	3.85	$-\text{OCH}_3$
			6.93-6.96	$=\text{CH}$
			7.25-7.97	aromatic protons
			8.47-8.49	$=\text{CH}$
			14.98	$-\text{OH}$ (Phenolic) ( $\text{D}_2\text{O}$ exchangeable)

2	PipchaH		6.02 6.83-6.85 7.13-7.90 8.46-8.48 14.92	
				=CH aromatic protons =CH -OH(Phenolic) (D <sub>2</sub> O exchangeable)

The NMR spectrum of the naphthyl chalcone, PipchaH in CDCl<sub>3</sub> solution exhibits a sharp singlet at  $\delta$  6.02 which is due to the protons of the methylene dioxy group. Like p-AnichaH, in this naphthyl chalcone also, two signals which appear as doublets at  $\delta$  6.83 – 6.85 and  $\delta$  8.46 – 8.48 are due to the two non-equivalent alkenic or olefinic (=CH) protons[39-41] which are coupled to each other. The aromatic protons are observed as complex multiplets[39-41] in the range of  $\delta$  7.13 – 7.90. However, like p-AnichaH, here in this case also, the naphthyl and the phenyl protons could not be assigned separately. The signal which appears as a sharp singlet at  $\delta$  14.92 is due to the phenolic proton which is D<sub>2</sub>O exchangeable and this is due to intramolecular hydrogen bonding as suggested above[39].

The presence of the phenolic -OH group in these chalcones is again demonstrated by D<sub>2</sub>O exchange. As expected, the D<sub>2</sub>O exchange of this labile proton[42,43] results in the disappearance of the NMR signal for the phenolic -OH group. It has long been recognized[44,45] that protons involved in hydrogen bonding exhibit very marked deshielding. Such a proton comes into resonance at low field. The down field shift depends upon the strength of the hydrogen bonding. In the absence of hydrogen bonding, the shielding behavior of hydroxylic proton is comparable to that of the protons of a methyl group. However, when it participates in hydrogen bonding, very marked deshielding occurs. This deshielding is particularly marked when intramolecular hydrogen bonding may occur. In the case [44] of the -OH group on benzene, which is intramolecularly bonded with some other group in the ortho-position, the absorption for -OH proton may occur even at the negative tau value e.g. salicylic acid[44]; -0.6  $\tau$ (10.6  $\delta$ ), methylsalicylate[46]; -0.58 $\tau$ (10.58  $\delta$ ), o-hydroxy acetophenone[46]; -2.05 $\tau$ (12.05  $\delta$ ). Enols show strong intramolecular hydrogen bonding which is further stabilized by resonance. Due to this, a great deshielding effect is caused and absorption for such a proton occurs at the higher negative tau value e.g. In the case of acetylacetone, the hydroxylic proton of its enol form appears at a strikingly low field position of -5.18 $\tau$  (15.18 $\delta$ ). Even greater deshielding is observed for the chelated -OH protons of phenols such as salicylaldehyde[47](- 8.1  $\tau$  or 18.1  $\delta$ ). In the light of this discussion, it is reasonable to assume that the signals which appear as sharp singlets in the hydroxy naphthyl chalcones, p-AnichaH and PipchaH at  $\delta$ 14.98 (-4.98 $\tau$ ) and  $\delta$ 14.92 (-4.92 $\tau$ ) respectively due to phenolic protons are further indicative of strong resonance stabilized intramolecular hydrogen bonding in these naphthyl chalcones. Thus, NMR studies clearly indicate the chelated -OH protons of these naphthyl chalcones, and this is further supported by electronic spectral studies to be followed hereinafter. In the case of isomeric hydroxy naphthyl chalcones, Natarajan et.al [16] have reported a signal at  $\delta$ 12.7 (-2.7 $\tau$ ), characteristic of hydroxylic proton which is also suggestive of strong hydrogen bonding in these naphthyl chalcones.

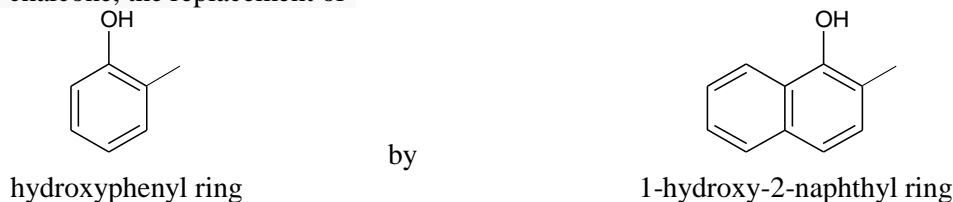
**Electronic Spectra of the Ligands:** The electronic spectra of chalcones have been studied at large by various groups of investigators[39,48-50,52,53,56-72]. Dhar and Singh[48] reported that the chalcone, the parent member of the series shows two main absorption bands in ethanolic solution: One at 310 nm( $\epsilon$ , 27,000) referred to as band I or K-band arising probably, due to the  $\pi$ - $\pi^*$  electronic transition of the whole molecule, while the other band at 226 nm ( $\epsilon$ , 10,500) referred to as Band II. In the present study(Table-2), the ligand BenchaH, the parent naphthalene analogue of 2'- hydroxychalcone, in methanolic solution) shows four main bands at 405 nm( $\epsilon$ , 4780), 324 nm ( $\epsilon$ , 14,576), 266 nm ( $\epsilon$ ,8605) and at 207 nm ( $\epsilon$ , 15,019).

**Table-2:** Electronic absorption spectral data of the ligands, 1-(1-hydroxy-2-naphthyl)-3-(phenyl or substituted phenyl)-prop-2-en-1-ones, in methanolic solution.

Ligand	Substituent -R =	Band I(K-band)		Band II		Other Bands			
		$\lambda_{\max}$ in nm ( $\nu$ in $\text{cm}^{-1}$ )	$\epsilon$	$\lambda_{\max}$ in nm ( $\nu$ in $\text{cm}^{-1}$ )	$\epsilon$	$\lambda_{\max}$ in nm ( $\nu$ in $\text{cm}^{-1}$ )	$\epsilon$	$\lambda_{\max}$ in nm ( $\nu$ in $\text{cm}^{-1}$ )	$\epsilon$
BenchaH	-H	405 (24691)	4780	324 (30864)	14576	266 (37594)	8605	207 (48309)	15019
Ortho-AnichaH	2-OCH <sub>3</sub>	410 <sup>(sh)</sup> (24390)	7525	362 (27624)	10332	267 (37453)	10081	208 (48077)	23486
Para-AnichaH	4-OCH <sub>3</sub>	408 <sup>(sh)</sup> (24510)	1761	361 (27701)	2926	262 (38168)	2503	205 (48780)	4271
PipchaH	3,4- -O-CH <sub>2</sub> -O-	407 <sup>(sh)</sup> (24570)	2139	374 (26738)	2660	271 (36900)	2790	212 (47170)	4485
VerchaH	3,4- (-OCH <sub>3</sub> ) <sub>2</sub>	407 <sup>(sh)</sup> (24570)	6896	374 (26738)	8018	264 (37879)	8812	210 (47619)	14251

Trakroo and Mukhedkar[49] observed that ethanolic solution of trans-2'-hydroxychalcone shows bands at 344 nm( $\epsilon$ , 1100) and 316 nm( $\epsilon$ , 2000). Dhar and Singh[50] observed that the ethanolic solution of the same 2'-hydroxychalcone shows bands at 362 nm( $\epsilon$ , 4560) which was described as the K-band, 332 nm( $\epsilon$ , 5810), 255 nm( $\epsilon$ , 6300), 218nm( $\epsilon$ , 18200) and at 207nm( $\epsilon$ , 19840).

Thus, the replacement of phenyl ring of the benzoyl moiety in the unsubstituted parent chalcone[48] ( $\lambda_{\max}$  310nm,  $\epsilon$ , 27000, solvent- Ethanol) by 1-hydroxy-2-naphthyl ring in the present unsubstituted hydroxy naphthylchalcone, BenchaH, produces a large bathochromic shift ( $\Delta\lambda$ , +95 nm) of K-band and this is accomplished by a considerable decreases in its intensity viz. approximately one sixth of original value which is in accordance with the reported observation[50]. This large bathochromic shift can be accounted for as the combination of extended conjugation, the substituent effect due to hydroxylic function as well as due to intramolecular hydrogen bonding[50]. The later effect is also responsible for causing a bathochromic shift as shown by Dannenberg[51] in the case of salicylic acid. But, from 2'-hydroxychalcone (in ethanolic solution) to BenchaH (in methanolic solution), here in after referred to as the reference chalcone, the replacement of-



-results in the possible bathochromic shift of band I or K-band from 362 nm( $\epsilon$ , 4560) to 405 nm( $\epsilon$ , 4780), band II from 255 nm( $\epsilon$ , 6300) to 324 nm( $\epsilon$ , 14,576), a band at 218nm( $\epsilon$ , 18,200) to 266 nm( $\epsilon$ , 8605) and this may be due to extended conjugation. However, the modified E band of the phenyl group[52] observed in 2'-hydroxychalcone at 207 nm ( $\epsilon$ , 19,840) has been observed in the present case at the same position i.e. 207 nm( $\epsilon$ , 15,019), but they differ in their  $\epsilon$  values. Dhar and Singh[50]observed some K-bands as a shoulder or inflection and the same is held true in the present case also. However, in the present study, it is

observed that K-band is more prominent in chloroform solution spectra as exemplified by the typical case of PipchaH.

In the present study, examination of the Table-2, for the naphthyl chalcone ligands, shows two main absorption bands, one in the range of 405-410 nm (referred to as Band I or K-Band) arising probably, due to  $\pi-\pi^*$  electronic transition of the whole molecule, while the other absorption band lies in the range of 324-374 nm (Band II). Jurd and Horowitz[53] concluded with a generalization that the intensity of Band II is usually weaker than the intensity of K-band. But Dhar and Singh[48,50] observed that in unsubstituted 2'-hydroxychalcone and some other substituted 2'-hydroxychalcones, the intensity of K-band is weaker than the intensity of Band II. In the present study, the intensity of K-Band in unsubstituted naphthyl chalcone BenchaH, which is an analogue to 2'-hydroxychalcone and all other substituted naphthyl chalcones is weaker than the intensity of Band II which is in agreement with the observations of above said investigators [48,50].

Substitution in the ring B of the naphthylchalcone molecule causes invariably a red shift of Band II. With respect to the reference chalcone, a maximum shift of 50 nm each was found in the case of the chalcones, PipchaH and VerchaH with 3,4 -O-CH<sub>2</sub>-O- and 3,4-(OCH<sub>3</sub>)<sub>2</sub> substituents respectively. However, a red shift of 38 nm and 37 nm was found in the case of chalcones o-AnichaH and p-AnichaH with 2-OCH<sub>3</sub> and 4-OCH<sub>3</sub> substituents respectively. Thus, it seems that disubstitution in the ring B causes more red shift of Band II than the red shift produced by monosubstitution in the same ring

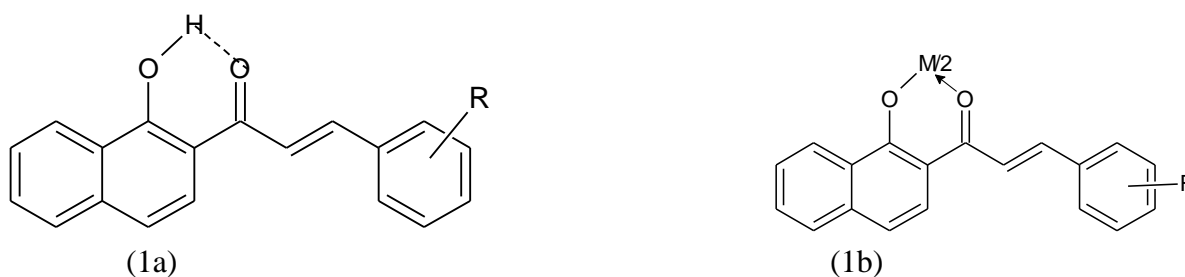
However, the shift of K-band, ( $\Delta\lambda$ ), has been found to be marginal which is in consonance with the results of earlier investigators[50]. A maximum shift of 5 nm was found to be in the chalcone o-AnichaH whereas others showed a small shift of 2-3 nm with respect to the reference chalcone. Thus, it seems that substitution in the ring B does not produce much difference in the  $\pi$ - electron system of the whole molecule.

The chalcones under present study are mostly red-orange in colour. According to the theories of colour and chemical constitution, for a substance to appear red-orange, it should absorb around 480-510 nm. Except the Band I or K (observed in the range of 405-410 nm) in the chalcones under consideration, all other absorption bands lie in the UV region. As discussed in detail earlier under NMR studies, in o-hydroxychalcones there exists a resonance stabilized intramolecular hydrogen bonding between the 2'-hydroxyl group and keto group[39,49,54]. It is argued that conjugated chelation is responsible for the shift to shorter wavelength[54]. In the ground state the structure of the carbonyl (>C=O) group contains an important contribution from the polar form  $>C^+ \quad O^-$  ( $>C^{\delta+} \text{-----} O^{\delta-}$ ). As this group is more polar in the ground state than the excited state, the non-bonding electrons in the ground state are stabilized (relative to the excited state) by hydrogen bonding, resulting in the shifting of absorption to shorter wavelength (higher energy)[46]. It is also known from studies on other chromophoric systems[46], that intramolecular hydrogen bonding increases photostability[55], possibly as a result of an increased rate of vibrational decay to the ground state, resulting in the absorption at shorter wavelength. Thus, the hydrogen bonding shifts[44] the electronic absorptions to shorter wavelength. This resonance stabilized intramolecular hydrogen bonding in the present naphthyl chalcones is further confirmed by NMR studies as discussed earlier.

**Electronic Spectra of the Metal Complexes:** All the electronic spectra of the complexes (Table-3) were compared with the electronic spectra of ligands. Electronic spectra (in methanolic solutions) of the metal chelates bear close resemblance to those of the ligands and they are almost virtually identical. Such type of results are already reported by various investigators[73,74]. It is therefore, concluded that no much structural alteration of the ligands occur during complexation[73].

Detailed study of the results of the spectral data of the metal complexes indicates that the K-band or Band I in the ligands in the range of 405-410 nm is also observed in the metal chelates in the range of 397-413 nm. Further Band II in the ligands in the range of 324-374 nm is also observed in the range of 323-377 nm. One more band which is observed in the range of 262-271 nm in ligands is observed in the range of 260-273 nm in the metal chelates. The modified E-band in the ligands in the range of 205-212 nm is observed in the range of 204-212 nm for the complexes. In general, from ligands to the complexes, the absorption maxima showed an erratic shift to lower or higher wavelength of about 10 nm in few cases, a marginal shift in most of the cases, while in few cases no shift in the wavelength was observed, This observation is similar to the one made by Saha, Bhatnagar and Banerji[75]. However the  $\epsilon$  values of the metal chelates and the ligands at those wavelengths are found to differ, indicating the presence of two ligand moieties in the metal chelates[74,76].

The  $\sigma$ - and  $\pi$ -electrons system of the naphthyl chalcone ligands whose coordination behavior is under investigation, were theoretically expected to undergo substantial change on coordination with the metal ion. But as cited above, it is evident that practically no much structural alteration of the ligands occurs during complexation. This could be explained on the basis of the facts as discussed earlier in NMR studies, that in o-hydroxychalcones, there exists an intramolecular hydrogen bonding between the 2'-hydroxy group and keto group. Such resonance stabilized hydrogen bonding also referred to as the conjugate chelation is responsible for the increased photostability[55]of the molecule. The chelation in the six-membered ring ketones as like the present ones have been found to be much stronger than in the five membered ring.



Where, M = Cu(II), Ni(II) & Co(II)

IR spectra of the metal chelates are compatible with the structure that would result if the chelated hydrogen of the ligand as shown in the structure (1a), is replaced by metal ion as in structure(1b), without much structural alteration of the ligand during complexation[73], suggesting that in general the  $\sigma$  – and  $\pi$ -electron system of the ligands did not undergo much considerable alteration on coordination to the metal ion. This accounts for the electronic spectra of the metal chelates bearing close resemblance to those of the ligands. Thus, the effect of perturbation due to the metal ion could not be examined by comparison of the electronic spectra of the ligands with those of their metal complexes. The intense ligand(charge transfer) band ( $\epsilon > 10^3$ ) in the ultraviolet region, which tails off into the blue end of the visible spectrum causes the substances to appear red or brown and presumably masks any low intensity ligand field band which might be present above  $20,000 \text{ cm}^{-1}$ [16,17,26]. So, it is not possible to make useful observations on the ligand field parameters from the solution spectra. Therefore, the solution spectra were not of much help as a wealth of information regarding the geometry and electronic structure of the metal complexes could not be obtained due to lack of d-d transition bands in these spectra.

However, the diffuse reflectance spectra recorded for the most of the solid complexes do show some of the d-d transitions, as discussed here in after.

**Table-3:** Electronic absorption spectral data on metal complexes of 1-(1-hydroxy-2-naphthyl)-3-(phenyl or substituted phenyl)-prop-2-en-1-ones in methanolic solution.

Sr.No.	Compound	$\lambda$ max in nm ( $\nu$ in $\text{cm}^{-1}$ )	$\epsilon$	Assignment (Transition)
1	Cu (Bencha) <sub>2</sub>	397 (25189)	3826	Band I or K-Band
		324 (30864)	10489	Band II
		271 (36900)	6364	Intra-ligand
		207 (48309)	11779	Intra-ligand
		*680 <sup>(sh)</sup> (14706)	-	$^2B_{1g} \longrightarrow ^2B_{2g}$
		*463 <sup>(br)</sup> (21598)	-	$^2B_{1g} \longrightarrow ^2E_g$
2	Ni (Bencha) <sub>2</sub>	413 (24213)	1998	Band I or K -Band
		326 (30675)	3665	Band II
		264 (37879)	6540	Intra-ligand
		209 (47847)	8139	Intra-ligand
		*740 <sup>(ln)</sup> (13514)	-	$^3A_{2g} \longrightarrow ^3T_{1g}(F)$
		*436.8 <sup>(br)</sup> (22894)	-	$^3A_{2g} \longrightarrow ^3T_{1g}(P)$
3	Co (Bencha) <sub>2</sub>	408 (24510)	3052	Band I or K -Band
		323 (30960)	16197	Band II
		262 (38168)	11464	Intra-ligand
		207 (48309)	21938	Intra-ligand
		*444 (22523)	-	$^4T_{1g}(F) \longrightarrow ^4T_{1g}(P)$
		*348 (28736)	-	Charge transfer

4	Cu (o-Anicha) <sub>2</sub>	*400 <sup>(sh)</sup> (25000)	7691	Band I or K -Band
		363 (27548)	9028	Band II
		265 (37736)	9299	Intra-ligand
		211 (47393)	21554	Intra-ligand
5	Ni (o-Anicha) <sub>2</sub> . 2 H <sub>2</sub> O	*400 <sup>(sh)</sup> (25000)	7373	Band I or K -Band
		353 (28329)	12839	Band II
		269 (37175)	11457	Intra-ligand
		207 (48309)	31281	Intra-ligand
		*740 <sup>(In)</sup> (13514)	-	<sup>3</sup> A <sub>2g</sub> → <sup>3</sup> T <sub>1g</sub> (F)
		*460 <sup>(br)</sup> (21739)	-	<sup>3</sup> A <sub>2g</sub> → <sup>3</sup> T <sub>1g</sub> (P)
6	Co (o-Anicha) <sub>2</sub> . 2 H <sub>2</sub> O	405 <sup>(sh)</sup> (24691)	6710	Band I or K -Band
		353 (28329)	8939	Band II
		265 (37736)	9135	Intra-ligand
		209 (47847)	31575	Intra-ligand
		*460 <sup>(br)</sup> (21739)	-	<sup>4</sup> T <sub>1g</sub> (F) → <sup>4</sup> T <sub>1g</sub> (P)
		*330 (30303)	-	Charge Transfer
7	Cu (p-Anicha) <sub>2</sub>	405 <sup>(sh)</sup> (24691)	1970	Band I or K -Band
		358 (27933)	3482	Band II
		267 (37453)	2540	Intra-ligand
		204 (49020)	5077	Intra-ligand
		*685 <sup>(sh)</sup> (14599)	-	<sup>2</sup> B <sub>1g</sub> → <sup>2</sup> B <sub>2g</sub>
		*460 <sup>(br)</sup> (21739)	-	<sup>2</sup> B <sub>1g</sub> → <sup>2</sup> E <sub>g</sub>



8	Ni (p-Anicha) <sub>2</sub> . 2 H <sub>2</sub> O	405	15191	Band I or K -Band
		(24691)		
		348	28790	Band II
		(28736)		
		264	20458	Intra-ligand
		(37879)		
9	Co (p-Anicha) <sub>2</sub> . 2 H <sub>2</sub> O	206	39168	Intra-ligand
		(48544)		
		*760 <sup>(In)</sup>	-	<sup>3</sup> A <sub>2g</sub> → <sup>3</sup> T <sub>1g</sub> (F)
		(13158)		
		*470 <sup>(br)</sup>	-	<sup>3</sup> A <sub>2g</sub> → <sup>3</sup> T <sub>1g</sub> (P)
		(21277)		
10	Cu (Pipcha) <sub>2</sub>	400 <sup>(sh)</sup>	12864	Band I or K -Band
		(25000)		
		354	19776	Band II
		(28249)		
		260	34051	Intra-ligand
		(38462)		
11	Ni (Pipcha) <sub>2</sub> . 2 H <sub>2</sub> O	205	37521	Intra-ligand
		(48780)		
		*470 <sup>(br)</sup>	-	<sup>4</sup> T <sub>1g</sub> (F) → <sup>4</sup> T <sub>1g</sub> (P)
		(21277)		
		*408 <sup>(sh)</sup>	1546	Band I or K -Band
		(24510)		
10	Cu (Pipcha) <sub>2</sub>	370	1955	Band II
		(27027)		
		267	2458	Intra-ligand
		(37453)		
		208	3889	Intra-ligand
		(48077)		
10	Cu (Pipcha) <sub>2</sub>	*680 <sup>(sh)</sup>	-	<sup>2</sup> B <sub>1g</sub> → <sup>2</sup> B <sub>2g</sub>
		(14706)		
		*482 <sup>(br)</sup>	-	<sup>2</sup> B <sub>1g</sub> → <sup>2</sup> E <sub>g</sub>
		(20747)		
		419	-	Charge transfer
		(23866)		
11	Ni (Pipcha) <sub>2</sub> . 2 H <sub>2</sub> O	405 <sup>(sh)</sup>	9577	Band I or K -Band
		(24691)		
		366	14217	Band II
		(27322)		
		272	15723	Intra-ligand
		(36765)		
11	Ni (Pipcha) <sub>2</sub> . 2 H <sub>2</sub> O	208	27578	Intra-ligand
		(48077)		

		*744 <sup>(In)</sup> (13441)	-	${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$
		*431.2 <sup>(br)</sup> (23191)	-	${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$
12	Co (Pipcha) <sub>2</sub> . 2H <sub>2</sub> O	405 <sup>(sh)</sup> (24691) 370 (27027)	7421  9967	Band I or K -Band  Band II
		262 (38168) 207 (48309) *497 <sup>(br)</sup> (20121)	15519  23702  -	Intra-ligand  Intra-ligand  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
13	Cu(Vercha) <sub>2</sub>	400 <sup>(sh)</sup> (25000) 377 (26525) 267 (37453) 205 (48780)	3790  4042  6131  8785	Band I or K - Band  Band II  Intra-ligand  Intra-ligand

\*-Diffuse Reflectance Spectra, Sh- Shoulder, Br- Broad, In- Inflection.

### Diffuse Reflectance Spectra of solid Complexes

**Copper(II) Complexes:** They mostly show a broad unsymmetrical band[77] and therefore their centered absorption maxima are reported in all cases.

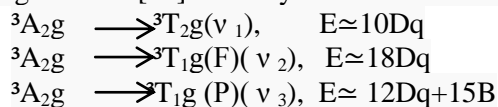
The broad unsymmetrical bands with the absorption maxima centered at about 21,000 cm<sup>-1</sup> and a distinct shoulder at about 14,650 cm<sup>-1</sup> may be assigned[14,15,23,78] to the spin allowed transitions  ${}^2B_{1g} \rightarrow {}^2E_g$  and  ${}^2B_{1g} \rightarrow {}^2B_{2g}$  respectively which are characteristic of square- planar geometry[14,15,23,78].

The absorption bands are unsymmetrical, seeming to encompass several overlapping transitions. The broadness of the band may be due to Jahn-Teller distortion. Duff et. al [79] suggested that the absorption bands in the region are due to tetragonally distorted octahedral environment around Cu<sup>2+</sup> ion. However, the studies[80] on electronic spectra of Cu(II) complexes indicate that the three transitions  ${}^2B_{1g} \rightarrow {}^2A_{2g}$ ,  ${}^2B_{1g} \rightarrow {}^2B_{2g}$  and  ${}^2B_{1g} \rightarrow {}^2E_g$  are close in energy and often give rise to a single broad absorption envelope.

**Nickel(II) Complexes:**

The nickel (II) complexes show a poorly defined deflection in the range of 13150-13525  $\text{cm}^{-1}$  and a broad band in the range of 21200 - 23200 $\text{cm}^{-1}$  which are respectively assigned to  ${}^3\text{A}_{2g} \longrightarrow {}^3\text{T}_{1g}(\text{F})(\nu_2)$  and  ${}^3\text{A}_{2g} \longrightarrow {}^3\text{T}_{1g}(\text{P})(\nu_3)$  crystal field transitions in an octahedral field[16,81].

Since the lowest energy transitions  ${}^3\text{A}_{2g} \longrightarrow {}^3\text{T}_{2g}(\nu_1)$  is not observed, the various ligand field splitting energy ( $\Delta$  or 10Dq), Racah inter-electronic repulsion parameter (B), covalent factor ( $\beta$ ),  $\beta^0$  could not be calculated. However, an attempt has been made to calculate these parameters approximately by using the following relations[82] and they are summarized in Table-4.

**Table 4.**

Complex	10Dq	B	$\beta$	$\beta^0$	$\nu_2/\nu_1$
Ni(Bencha) <sub>2</sub>	7508 $\text{cm}^{-1}$	926 $\text{cm}^{-1}$	0.877	12.3%	1.79
Ni(Pipcha) <sub>2</sub> .2H <sub>2</sub> O	7467 $\text{cm}^{-1}$	948 $\text{cm}^{-1}$	0.898	10.2%	1.80

The approximately calculated ratio  $\nu_2/\nu_1 = 1.79$  or 1.80 is well within the range 1.6-1.82 which is considered as an identification of octahedral geometry in the Ni (II) complexes[82]. The observed values of 10Dq and B are very close to the reported values[81] for the octahedral Ni (II) complexes of 2',4'-dihydroxy-5'-(4-methoxy) cinnamoyl-4-methoxychalcone.

**Cobalt(II) Complexes:** Considering the positions and intensity of the bands in the range of 28736 $\text{cm}^{-1}$  to 30303 $\text{cm}^{-1}$ , they could be assigned[16,26] to a charge transfer transition.

Broad bands with their absorption maxima centred in the range of 20100-22525 $\text{cm}^{-1}$  are attributed to the transition  $\nu_3$  i.e.  ${}^4\text{T}_{1g}(\text{F}) \longrightarrow {}^4\text{T}_{1g}(\text{P})$ , characteristic of octahedral geometry[15,73,83-85] the transitions  $\nu_1$  and  $\nu_2$  are not observed. The broad and irregular nature of these bands may be due to the encompassment of several overlapping transitions. Thus, the electronic spectra of Co (II) complexes gave no much information as the weak spin-forbidden d-d transitions were fully covered by the tail of broad and strong charge transfer band[86] around 29,000 $\text{cm}^{-1}$  as stated above.

The earlier researchers[26], Natarajan and Tharmaraj, in their studies on Co (II), Ni (II), Cu (II) complexes of 1-hydroxy-2-naphthyl(4-X-Styryl) Ketones i.e. 1-(1-hydroxy-2-naphthyl)-3-(phenyl or 4-substituted phenyl)-2-propen-1-ones, could not obtain the complete electronic absorption spectra either in mull, silicone grease or in solution, Furthermore, they could not obtain any transitions from the reflectance spectra. It seems that no attempt was made by them to compare the electronic spectra of the ligands with those of metal complexes. However, in the present study, as discussed earlier, the author has obtained a good wealth of information by comparing the solution spectra of the ligands with those of the metal complexes. Moreover, quite a good number of transitions have been obtained from the solid reflectance spectra of the metal complexes under present consideration and this has helped in determining and confirming the geometry of the metal complexes. However, by adjusting the solution concentrations, these researchers[26], could observe only with the help of the derivative graph, a few bands for the complexes of only one ligand, 1-hydroxy-2-naphthyl styryl ketone (which is represented as BenchaH in the present study). All the Cu(II) chelates are anhydrous monomers of trans-square-planar configuration, while the diaquo Ni(II) and Co(II) chelates have high spin trans-octahedral configuration.

The anhydrous Ni(Bencha)<sub>2</sub> and Co(Bencha)<sub>2</sub> complexes (serial numbers: 2 and 3, Table-3) are polymers [16,26,87], possibly a trimer[16,26,87] and a tetramer[87] respectively with a high spin trans-octahedral

configurations which are comparable to the reported[87] configurations for Ni(II) and Co(II) complexes of acetylacetonate with the same type of donor(chromophoric) system as the present one.

### APPLICATIONS

A broad spectrum biological activity and multiprotecting biochemical activity is possessed by chalcones and their relative compounds. Ortho-hydroxy chalcones are exploited as analytical reagents for estimation of different metal ions as they have good chelating properties. They have variety of commercial and industrial applications such as artificial sweeteners, fluorescent whitening agents, stabilizers against heat and light, in color photography, scintillators, organic brightening additives and polymerization catalysts, to name a few. Some of the metal complexes of chalcones and their related compounds have antimicrobial activity.

<sup>1</sup>H-NMR spectroscopy is the most powerful tool to detect the intramolecular hydrogen bonding. Electronic spectra are useful in establishing the geometry of complexes and also to detect and confirm the intramolecular hydrogen bonding with its effect in altering the spectral properties in the ligands as well as on their complexation with metal ions.

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