

Infrared Spectroscopic Investigations 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

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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 $ML_2 \cdot XH_2O$ ($X=2$ or 0) where, L is the deprotonated ligand, the naphthyl chalcone and M is the divalent metal ion. The present paper deals with the effect of strong resonance stabilized intramolecular hydrogen bonding on the IR spectral properties of the naphthalene analogues of 2'-hydroxychalcones as mentioned above and also on their complexation with transition metals such as Cu(II), Ni(II) and Co(II). The conjugated chelation alters considerably the IR spectral properties of these compounds and plays a prominent role in coordination chemistry. IR spectroscopy is the most sensitive and direct method for the study of hydrogen bonding.

Keywords: Chalcones, Metal complexes, Intramolecular hydrogen bonding, Conjugated chelation

Introduction

The chemistry of chalcones and related compounds has been recognized as a significant field of study. Due to synthetic importance and varied biological activities of chalcones, an increasing amount of interest has been taken in their synthesis and various studies. The enone function in the chalcone due to the keto-ethylenic group confers biological activity to these compounds. These α , β -unsaturated ketones known as chalcones and also their derivatives are found to possess a wide spectrum biological and multiprotecting biochemical activities as well as number of commercial and industrial applications as reported¹⁻¹³ with references there in. Literature survey shows many patents describing the usefulness of chalcones and their derivatives. Chalcones and their derivatives find varied applications as reported earlier¹¹⁻¹³. Ortho-hydroxychalcones have good chelating properties and were exploited

as analytical reagents for estimation of different metal ions¹⁴. 2'-hydroxychalcones and their heterocyclic and naphthalene analogues are also reported to form coordination complexes¹⁴⁻²⁶. Ruthenium complexes of 2'-hydroxychalcones²⁷⁻³⁴, chalcone oximes³⁵ and chalcone semicarbazones^{36,37} are synthesized and characterized by analytical and spectroscopic methods. The synthesis and biological study of some new chalcones and pyrazole derivatives are also reported³⁸. Synthesis and antimicrobial activities of Co(II), Ni(II) and Cu(II) complexes of some 2'-hydroxychalcones are also reported³⁹. Synthesis and *in vitro* antiplaque activity of chalcone, flavonol and flavonol derivatives are also carried out⁴⁰. The quantitative structure-activity relationships of mosquito larvicidal activities of a series of chalcones and some derivatives are also reported⁴¹. Some researchers^{16,23,26,39,42-44} have carried out thermal studies of chalcones as a part of their various studies.

M A Rahman⁴⁵ in his review with the references there in, has highlighted the latest synthesised chalcones and their derivatives possessing a wide range of pharmacological activities, such as antimalarial, anticancer, antiprotozoal (antileishmanial and antitrypanosomal), antiinflammatory, antibacterial, antifilarial, antifungal, antimicrobial, mosquito larvicidal⁴¹, anticonvulsant and antioxidant activities. They also show⁴⁵ inhibition of the enzymes, especially mammalian alpha-amylase, cyclooxygenase (COX) and monoamine oxidase (MAO) and antimitotic activity too. Because of this, chalcones and their derivatives have once again attracted the increasing focus of the scientists for exploring newer and newer potent pharmacological activities in them.

This year, we have reported⁴⁶ the presence and the effect of resonance stabilized intramolecular hydrogen bonding resulting into conjugate chelation in these naphthyl chalcones under present consideration and on their complexation with transition metals, Cu(II), Ni(II) and Co(II) through their electronic and ¹H NMR spectroscopic investigations. The conjugate chelation considerably alters the spectroscopic properties of the compounds and plays a very prominent role in the coordination chemistry particularly in changing the spectroscopic properties. ¹H 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. Spectroscopic studies including the IR spectroscopic studies are very useful tools for the above said investigations.

Recently, we have investigated⁴⁷ the indepth thermal studies of the same metal complexes as under present study, through their TGA and DTA analysis. The thermal studies supports an octahedral configuration as established from their electronic spectra for all the diaquo Ni(II) and Co(II) complexes of the ligands *o*-AnichaH, *p*-AnichaH and PipchaH with two water molecules providing fifth and sixth coordination sites

As reported in the literature⁴⁸, I have investigated in detail the physico-analytical and magnetic susceptibility measurement study of the same metal complexes as under present study. The magnetic susceptibility measurements of these transition metal complexes have been carried out at room temperature by Faraday method. The magnetic moments of some copper complexes under present study are also determined from their ESR spectra recorded under different experimental conditions. The proposed structures, square planar, octahedral and oligomeric, wherever applicable, of metal complexes under present study are represented and explained in detail. This encouraged me to carry out the present work in which an attempt has been made to study and confirm the effect of intramolecular hydrogen bonding as mentioned above

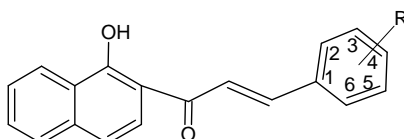
in the coordination chemistry of the compounds under consideration through their explorative IR spectroscopic investigations which further confirms the observations and results as reported^{46,48}.

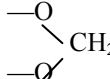
Experimental

All reagents and chemicals used were of Analar grade. All solvents used were of standard and spectroscopic grade. The IR spectra of metal complexes and the constituent ligands were recorded in KBr pellets on a Nicolet, USA, FT-IR Spectrophotometer in the range 4000-400 cm^{-1} .

Synthesis of naphthalene analogues of 2'-hydroxychalcones (Ligands)

The naphthalene analogues of 2'-hydroxychalcones, 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 reported¹¹⁻¹³ with their general structure as shown below:



S. No.	Ligand No.	Ligand designated as	-R
1	L-1	BenchaH	-H
2	L-2	<i>o</i> -AnichaH	2-OCH ₃
3	L-3	<i>p</i> -AnichaH	4-OCH ₃
4	L-4	PipchaH	3,4- 
5	L-5	VerchaH	3,4-(-OCH ₃) ₂

Synthesis of metal complexes of naphthyl chalcones

The metal complexes of these naphthyl chalcones, BenchaH, *o*-AnichaH, *p*-AnichaH, PipchaH and VerchaH were prepared as per the procedure reported in our earlier work¹¹⁻¹³.

Results and Discussion

The FT-IR spectra of all ligands and their metal complexes have been recorded in KBr discs in the region 4000-400 cm^{-1} . Some of the structurally important FT-IR bands observed in the constituent ligands and their metal complexes with their assignments are summarized in Tables 1 and 2.

IR spectra of the ligands

The spectra are quite complex due to the presence of a large number of bands with varying intensities. Hence, assignment of all the bands without ambiguity is not possible. However, an attempt has been made to identify and assign some of the structurally important bands on the basis of the reported infrared spectra of some chalcones^{15-17,23,26,49-56}. Some of these like νCH (Aromatic), $\nu\text{C}=\text{O}$, $\nu\text{Ph}-\text{C}=\text{C}$, $\text{Ph}-\text{C}-\text{C}$ (in plane), δOH (Phenol) and $\nu\text{C}-\text{O}$ (Phenol) are in good agreement with the reported values^{16,17,26,55}.

Table 1. Some important IR Bands in the ligands, 1-(1-hydroxy-2-naphthyl)-3-(phenyl or substituted phenyl)prop-2-en-1-ones and their assignments

S. No.	Compound	νCH (Aromatic) cm^{-1}	$\nu\text{C}=\text{O}$ cm^{-1}	$\nu\text{Ph-C}=\text{C}$ cm^{-1}	Ph-C-C (in plane) cm^{-1}	δOH (phenol) cm^{-1}	$\nu\text{C-O}$ (phenol) cm^{-1}
1	BenchaH	3050	1628 (1625)*	1574 (1572)*	1467	1351	1281
2	<i>o</i> -AnichaH	3060	1632	1579	1470	1357	1283
3	<i>p</i> -AnichaH	~3050	1632 (1620)*	1566 (1550)*	1470	1357	1289
4	PipchaH	3050	1629	1576	1488	1340	1308
5	VerchaH	~3040	1638	1573	1470	1340	1308

* Literature values²⁶**Table 2.** Some important IR bands in the metal complexes of 1-(1-hydroxy-2-naphthyl)-3-(phenyl or substituted phenyl) prop-2-en-1-ones and their assignments

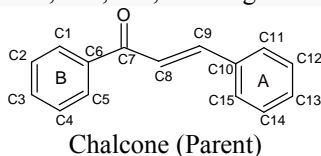
S. No	Compound	νCH (Aromatic) cm^{-1}	$\nu\text{C}=\text{O}$ cm^{-1}	$\nu\text{Ph-C}=\text{C}$ cm^{-1}	Ph-C-C (in plane) cm^{-1}	$\nu\text{C-O}$ (phenol) cm^{-1}	$\nu\text{M-O}$ cm^{-1}
1	Cu(Bencha) ₂	~3065	1610 (1610)*	1557 (1550)*	1479	1320	614 (612)*
2	Ni(Bencha) ₂	3060	1615 (1605)*	1562 (1565)*	1464	1317	574 (573)*
3	Co(Bencha) ₂	3080	1610 (1612)*	1568 (1562)*	1489	1300	575 (577)*
4	Cu (<i>o</i> -Anicha) ₂	3060	1610	1553	1468	1314	607
5	Ni (<i>o</i> -Anicha) ₂ .2H ₂ O	3060	1620	1567	1489	1313	596
6	Co (<i>o</i> -Anicha) ₂ .2H ₂ O	3050	1614	1561	1485	1310	590
7	Cu (<i>p</i> -Anicha) ₂	3050	1603 (1590)*	1550 (1540)*	1478	1320	593 (590)*
8	Ni (<i>p</i> -Anicha) ₂ .2H ₂ O	3060	1607 (1595)*	1557 (1555)*	1485	1314	576 (570)*
9	Co (<i>p</i> -Anicha) ₂ .2H ₂ O	~3060	1604 (1600)*	1561 (1555)*	1460	1309	572 (568)*
10	Cu (Pipcha) ₂	3060	1604	1555	1472	1320	616
11	Ni (Pipcha) ₂ .2H ₂ O	3060	1608	1563	1488	1316	617
12	Cu (Pipcha) ₂ .2H ₂ O	3050	1608	1568	1489	1315	618
13	Cu (Vercha) ₂	~3045	1613	1553	1472	1319	620

* Literature values²⁶

The broad bands in the 3060-3040 cm^{-1} region for all the ligands have been ascribed to $\nu\text{CH(Aromatic)}$ vibrations⁵⁵ and they are not substituent dependent. Chalcones and their naphthalene analogues like the ones under present considerations are α , β unsaturated ketones containing two aromatic rings which are interconnected by highly electrophilic three carbons, -CH = CH - C = O system that assumes linear or nearly planar structure. The chalcones possess conjugated double bonds and a completely delocalized π electron system on both the rings.

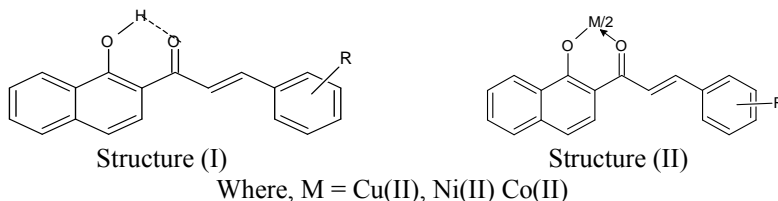
As reported⁴⁵ in the review, the chalcones have crystal structure. The molecule forms a zigzag chain by C - H--- π (arene) hydrogen bonds along the c axis. There also exists

intermolecular hydrogen bonding interactions involving C11 acting as H-bond donor, via H11, to O in the adjacent molecules at –X, 1-Y, 1-Z, resulting in a three dimensional network.



But in the presence of strong resonance stabilized intramolecular hydrogen bonding in the present chalcones, the possibility of this type of intermolecular hydrogen bonding may be ruled out.

As reported earlier⁴⁶, NMR studies clearly indicate that in *o*-hydroxychalcones, there exists an intramolecular hydrogen bonding between the 2'-hydroxy group and keto group. The keto-ethylenic group or enone function is in conjugation with phenyl or substituted phenyl group on one side and hydroxy naphthyl group on the other side. Such resonance stabilized hydrogen bonding also referred to as the conjugate chelation is responsible for the increased photostability 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. This hydrogen bond is the strongest as the hydrogen bonded structure is stabilized by the resonance.



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 (I), is replaced by metal ion as in structure (II), without much structural alteration of the ligand during complexation, suggesting that in general the σ – and π -electron system of the ligands did not undergo much considerable alteration on coordination to the metal ion. This accounts for the spectra of the metal chelates bearing close resemblances to those of the ligands. This is further confirmed by the fact that in the present study as indicated later, the IR spectra of the complexes suggest that carbonyl group is perturbed only slightly by coordination to the metal⁴³.

As reported earlier⁴⁸, the ligands in the present study can form β -ketoenolate anion like β -diketones such as acetylacetonate, due to tautomerisation and ionization. As stated earlier⁴⁸, the presence of bulky substituents on the β -diketonates sterically impedes oligomerisation. But, due to the dispersal of negative charge on the two oxygen atoms and also on the carbon atoms of the ring of the anion of BenchaH *i.e.* Bencha⁻, very large number of resonance structures are possible leading a very high resonance stabilization of this β -ketoenolate anion under consideration and perhaps this may be even far more than the resonance stabilization in acetylacetonate ion. This very high resonance stabilization may outweigh steric hindrance effect, if any, and makes the anion highly stable and this makes the proposed trimeric and tetrameric structures(X) and (XI) respectively highly stable.

The chelating ligands such as acetylacetonate enjoy resonance stabilization as a result of forming six membered rings having some aromatic character which stabilizes the chelate ring making it even more stable and this holds true even for the ligands with chelate ring

under present consideration as explained subsequently. Chelate effect in conjunction with ability of the ligands to act as π – acceptors as well as σ – donors further enhances the stability. Ligand-metal π bonding further enhances delocalization of electrons as compared to that of the free ligand, producing some resonance stabilization.

Chelate ligands form more stable complexes than analogous monodentate ligands. Unsaturated ligands with a system of double and single bonds form very stable metal complexes containing six membered rings which include the metal ion also. This is because in such complexes the electron density is delocalized and spread over the ring which is thus stabilized by resonance. Such complexes containing chelating ligands with delocalized electronic structures are stabilized by electronic effect in addition to favourable entropy change during the chelation process.

Steric factor plays a significant roll in chelation. This arises due to the presence of a bulky group either attached to or near to a donor atom to cause mutual repulsion between the ligands thereby weakening the metal-ligand bond and this leads to lesser stability which is not so in present ligands. The chelate rings obey more or less the same type of steric requirements with respect to conformations as do organic rings. Unlike organic ring system, maximum stability in chelate rings usually arises from five membered rings because the metal atom is larger than a carbon atom and the bond angles at the metal (L- M -L) will be 90° in square planar and octahedral complexes in contrast to an optimum angle of 109.5° for tetrahedral carbon. But for ligands like the present naphthyl chalcones under present consideration and acetylacetonates which exhibit resonance effects, six membered rings are highly stable.

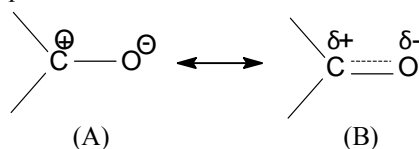
Hydrogen bonding occurs between a proton donor group, X-H (hydroxyl, amine or amide groups) and a proton acceptor, y (oxygen, nitrogen and halogen atoms). Hydrogen bonds are the strongest when the hydrogen bonded structure is stabilized by resonance. Hydrogen bonding alters the force constant of both donor and acceptor groups. The frequencies of the stretching and bending vibrations are altered. The X-H stretching band moves to lower frequencies usually with increased intensity and band broadening. The stretching frequency of the acceptor group like $>C=O$ is also reduced, but it is to a lesser extent than that for X-H, the proton donor group. Depending on the strength of the bond, the shift in the $C=O$ stretching frequency may vary from 15 to 50 cm^{-1} and above, while the shift in the X-H stretching frequency may vary from 100 to over 500 cm^{-1} . Intramolecular hydrogen bonding decreases the carbonyl frequency to a greater extent than the intermolecular hydrogen bonding. But on the other hand, the X-H bending vibration generally shows a small shift to higher frequency on hydrogen bond formation. The strength of the hydrogen bond is measured in terms of the difference in frequency between free OH and hydrogen bonded OH absorptions. The strength of the hydrogen bond is also determined by the molecular geometry and the nature of the proton donor and acceptor groups. The O-H stretching vibration of alcohols and phenols (like the present hydroxy naphthyl chalcones) are sensitive to hydrogen bonding.

In *o*-hydroxyacetophenone, strong intramolecular hydrogen bonding occurs and the absorption due to hydrogen bonded O-H appears at 3077 cm^{-1} as a broad and weak band. On the other hand, its structural isomer, *p*-hydroxyacetophenone shows a sharp peak at 3600 cm^{-1} in dilute CCl_4 due to free hydroxy group.

The resonance effect is observed in adjacent group containing π electrons. For example, the $C = O$ stretching vibrations in a ketone and the $C = C$ stretching mode in ethene derivatives are usually near 1725 and 1650 cm^{-1} respectively. However in conjugated system

$>C=C-C=O$, their frequencies are shifted to lower frequencies (higher wavelength) to 1693 and 1641 cm^{-1} respectively for $C=O$ and $C=C$. The conjugation of $C=O$ group with a $C=C$ group results in delocalization of π electrons of both the unsaturated groups. Because of this there is an increase in double bond character of the $C-C$ linkage connecting two doubly bonded groups and a decrease in the double bond character of both the $C=O$ and $C=C$ groups. This is as a result of the fact that the π electrons of the conjugated groups tend to delocalize over the entire molecule. The magnitude of the effect depends on the type of conjugation and on the specific compounds. For example, the conjugation of a $C=O$ group with an alkene or phenyl group causes absorption in the 1665-1685 cm^{-1} region as in acetophenone where the frequency appears at 1685 to 1687 cm^{-1} .

Thus in infrared spectroscopy⁵²⁻⁵⁴, conjugation of ethylenic double bonds, or a carbonyl group and double bonds causes a shift from normal position to a longer wavelength. The unconjugated carbonyl group in acetone shows a band at 1718 cm^{-1} , while conjugation with one phenyl group, as in acetophenone as stated above lowers the frequency to 1685-1687 cm^{-1} and conjugation with two phenyl groups, as in benzophenone further lowers the frequency to 1655 cm^{-1} . Whether this shift due to mesomerism or to an actual lengthening of the bonds is not known. It is indicated that whenever, there is an increased opportunity for the contribution of the ionic resonance structure A, to the carbonyl group, B, a shift to higher wavelength or lower frequencies is observed.

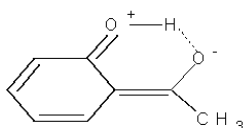


As expected from the participation of A, the shifted band also has greater intensity.

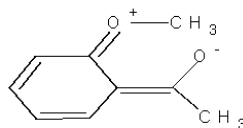
Unsubstituted parent chalcone *i.e.* benzylidene acetophenone with structure shown earlier, shows a carbonyl band at 1659 cm^{-1} , which is due to the conjugation with phenyl groups and an aliphatic double bond. Introduction of a hydroxyl group in 2' or 2- position is expected to shift the carbonyl band to higher wavelength or lower frequency^{52,54}. Accordingly, both the 2'-hydroxychalcone and 2-hydroxychalcone shows^{52,54} the carbonyl band at 1639 cm^{-1} . But, 2'-acetoxychalcone exhibits its carbonyl band⁵² at around 1663 cm^{-1} . Therefore, as expected acetylation was found to cause the absorption band to return to the original position. All these observations are explained as follows. It must be recalled that acetophenone the carbonyl band is observed at 1685 to 1687 cm^{-1} . But, when a hydroxyl group is introduced at ortho-position to the keto group in acetophenone, the carbonyl frequency is shifted from 1685-1687 cm^{-1} to 1635 cm^{-1} , this effect of hydroxyl group, ortho to keto group in *o*-hydroxyacetophenone was first noted by Gordy⁵⁷ who attributed it to hydrogen bonding between the hydroxyl group and keto group. Rasmussen *et al.*⁵⁸ reinterpreted this shift as due to a conjugate-chelate system and also suggested that such a system is necessary for the occurrence of extreme shifts. Careful examination of the spectrum of *o*-hydroxyacetophenone indicates the absence of any band characteristic of free hydroxyl group. Similar behaviour was previously noted in the *o*-hydroxyanthraquinones⁵⁹ and it was attributed to intramolecular hydrogen bonding. However, in 2-acetoxyacetophenone, the acylated product of *o*-hydroxyacetophenone, the carbonyl band is shifted back to higher frequency.

All these three facts seem to indicate further that conjugate chelation is responsible for the shift to the shorter frequency. However, *o*-methoxyacetophenone, where clearly

neither hydrogen bonding nor conjugated chelation is possible, shows a band at 1649 cm^{-1} . It seems likely therefore that this shift to longer wavelength or lower frequencies is due to participation of the resonance forms such as (III) in hydroxy derivative and (IV) in the case of the methoxyl derivative.



Structure (III)



Structure (IV)

The increased stabilization in structure (I), due to the chelate ring plus presumably the greater ability of the hydroxyl group to donate electrons to the ring is responsible for the absorption in the high wavelength or the lower frequency in (III) than (IV). The tendency of the acetoxy group to donate electrons is very meager and this accounts for the acetoxy derivative not markedly differing from unsubstituted acetophenone.

It is a general observation that a chelated hydroxyl group⁵⁸ does not show any absorption at 3600 cm^{-1} ; the band shifts to lower frequency regions and generally broad, probably due to the close vibrational levels⁶⁰. Hydrogen bonding in enols and chelates is particularly strong. Literature survey reveals that very broad band may appear in regions as low as 2500 cm^{-1} in chelated compounds. Hydrogen bonding usually seems to broaden the band sometimes so broad as to be overlooked and shift if to lower frequencies. The stronger the hydrogen bonding, the greater is the lowering of the fundamental O -- H vibration frequency. Hydrogen bonding involves the lengthening of the original –O-H bond which therefore gets weakened *i.e.* its force constant is reduced and therefore the stretching frequency is reduced. As stated earlier, the hydrogen bonding is also indicated by marked increase in the intensity of the absorption, longest shifts are observed, when the hydrogen bonding involves –O-H groups and the least when it involves –N-H group. There are also reports about broadening and large shifting of hydroxyl bands to the extent of disappearance. This is illustrated by the example of 1, 4-dihydroxy-anthraquinone and 2, 2'-dihydroxyazobenzene in which the hydroxyl absorption is so much shifted and broadened that when these compounds are examined under normal conditions, no band is detectable. It has also been observed that –O-H absorptions are shifted to such an extent as stated earlier, that they overlap and obscure the absorption due to –C-H regions and this makes the measurement almost impossible. Accordingly, it is observed⁵² that 2'-hydroxychalcone does not show the characteristic hydroxyl band.

As discussed earlier, it must be restated that intramolecular hydrogen bonding between carbonyl and hydroxyl groups shows lowering in carbonyl frequency^{53,61}. The values obtained by the earlier researchers²⁶ for some of the bands observed in the ligands BenchaH and p-AnichaH and their complexes are also given in Tables 1 and 2. As stated earlier, in 2'-hydroxychalcone, the carbonyl bands occurs at 1639 cm^{-1} . Natarjan *et al.*¹⁶ reported $\nu\text{C=O}$ band at 1622 cm^{-1} in 1-(2-hydroxy-1-naphthyl)-3-phenyl-2-propen-1-one. Natarjan and Tharmaraj²⁶ reported $\nu\text{C=O}$ at 1625 cm^{-1} in 1-(1-hydroxy-2-naphthyl)-3-phenyl-2-propen-1-one and this band in the same compound is observed in the present study at 1628 cm^{-1} . Thus, from 2'-hydroxychalcone (the parent hydroxylchalcone) to the corresponding isomeric naphthalene analogues *i.e.* the parent isomeric hydroxynaphthyl chalcones, the replacement of the hydroxy phenyl ring by the hydroxyl naphthyl ring further shifts the carbonyl band from 1639 to 1628 - 1622 cm^{-1} and this further lowering in frequency may attributed to the extended conjugation^{52,53}.

In the light of above discussion, it is clear that the intense bands observed in the range of 1638-1628 cm^{-1} , in the FTIR spectra of the ligands, the hydroxy naphthyl chalcones, whose metal complexes are under present study, is attributed to $\nu\text{C}=\text{O}$. In the present ligands, the frequency $\nu\text{C}=\text{O}$ is found to be the substituent dependent and follows the order:



In all the ligands, the $\nu\text{C}=\text{C}$ could not be identified because of its possible merger^{17,62} with $\nu\text{C}=\text{O}$.

The medium to high intensity bands appearing in the 1579-1566 cm^{-1} region for all the ligands are assigned to the $\nu\text{Ph-C}=\text{C}$ vibrations^{15,17,23,26,49,55,56}. The bands appearing in the 1488-1467 cm^{-1} region in all the ligands are ascribed to the Ph-C-C (in plane) vibrations¹⁷.

The strong absorption bands were observed for the δOH (phenol) vibrations^{23,49,55} in the range 1357-1340 cm^{-1} region for all the ligands. The intense bands in the 1308-1281 cm^{-1} region for all the ligands have been attributed to the $\nu\text{C-O}$ (phenol) vibrations^{16,23,55,56}.

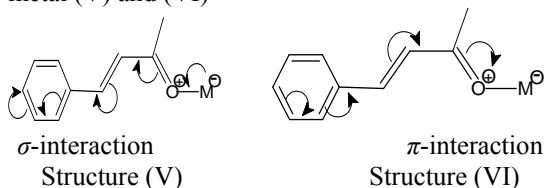
IR spectra of the metal complexes

The infrared spectra of transition metal complexes are quite complex as they in general contain numerous bands of varying intensities. Hence, it is not possible to assign all the bands. However, some structurally important bands have been identified to draw inferences about the nature of bonding in these complexes.

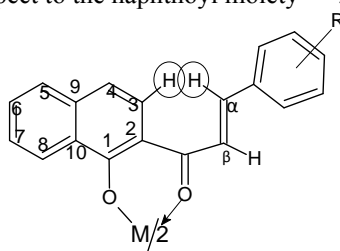
The $\nu\text{C}=\text{O}$ bands in the FT-IR spectra of the metal complexes occur in the 1620-1603 cm^{-1} region. As stated earlier, this band occurs in the ligands in the 1638-1628 cm^{-1} region. Thus, this band is shifted to lower frequencies^{15-17,23,26,49,50,56} in metal complexes as compared to ligands. The shift towards lower frequencies is due to the coordination of the $>\text{C}=\text{O}$ group to the metal ion through oxygen resulting in decrease of bond order of carbon to oxygen linkage^{15,23,49,56}. With respect to the ligands, $\nu\text{C}=\text{O}$ of the metal complexes is lowered in general by 12 cm^{-1} [in the case of $\text{Ni}(\text{o-Anicha})_2 \cdot 2\text{H}_2\text{O}$] to 29 cm^{-1} [in the case of $\text{Cu}(\text{p-Anicha})_2$] indicating that coordination occurred via oxygen atom of the carbonyl oxygen group⁴³. And this decrease observed in these complexes is comparatively much smaller than that observed ($\Delta\nu = 55\text{-}40 \text{ cm}^{-1}$) in the case of other metal complexes of chalcones and their heterocyclic analogues¹⁵. Stronger intramolecular hydrogen bonding in the ligands lead to a smaller decrease¹⁶ in the $\nu\text{C}=\text{O}$ frequency. The magnitude of decrease in $\nu\text{C}=\text{O}$ in these complexes would suggest both σ and π interaction of $\text{C}=\text{O}$ with the metal and this is explained in detail later. The intramolecular hydrogen bonding in the ligands under present study has been further confirmed from the electronic spectra and ^1H NMR spectra of the ligands and the electronic spectra of metal complexes as reported⁴⁶.

As stated earlier, in relation to the ligands, $\nu\text{C}=\text{O}$ of the metal complexes under consideration is lowered by 12-29 cm^{-1} , whereas the decrease observed in the case of 2' - hydroxychalcones complexes¹⁷ is 1-7 cm^{-1} and this is explained as follows.

The magnitude of decrease in $\nu\text{C}=\text{O}$ in these complexes would suggest both σ - and π -interactions with the metal (V) and (VI)



Due to the extended conjugation, a much lower $\nu_{\text{C=O}}$ value in the metal complexes of 2'-hydroxychalcones than in *o*-hydroxyarylcarbonyl complexes and *o*-hydroxycrotonophenone complexes⁶³ is expected but indeed a relatively higher value is observed¹⁷. The π^* orbital of the isolated C=O group in *o*-hydroxyarylcarbonyl complexes is localized more on carbon than on oxygen while, in chalcone complexes, the π^* orbital of the conjugated system including the phenyl group will be found delocalized over the other carbon nuclei also⁶⁴. As a result, $d_{\pi}\text{-}p_{\pi}$ back-bonding involving these orbitals would cause a very small change in C=O bond order in the chalcone complexes and this is reflected in the very small decrease in $\nu_{\text{C=O}}$ on coordination. The greater ligand field strength of *o*-hydroxycrotonophenone is due to a strong $d_{\pi}\text{-}\pi^*_3$ interaction which arises from the low energy of the π^*_3 orbital (compared with π^* of isolated C=O) of the conjugated system whereas in 2'-hydroxychalcones¹⁷, a further extension of conjugation is found to increase the ligand field strength. But, in the metal complexes under present study, the mesomeric interaction of the phenyl group with the metal is decreased due to the lack of the planarity of the naphthoyl moiety in the molecule. For effective delocalization of electron in a conjugated system, the molecule must be planar (or nearly so). Molecular model²³ (VII) shows that C₃-hydrogen of the naphthalene and α -hydrogen of the styryl group are very close to each other, within the sum of their van der Waals radii, thus causing greater steric repulsion. This forces the styryl moiety of the complex out of plane with respect to the naphthoyl moiety^{16,26}.



Structure (VII)

A comparative study of the electronic transmission effect of chalcone and β -naphthyl analogue of chalcone⁶⁵ has shown that there is deviation from planarity in the latter, inhibiting conjugative interaction. Many ligands with more than one donor atom have geometries such that they can form more than one coordinate covalent bond to the same metal ion. Such ligands are known as potential chelating ligands which of course must be non linear and must form bond with reasonable angle(somewhere near 90° or 109.5°) at the metal atom. By analogy with 2'-hydroxychalcones¹⁷, the ligands under present study are expected to be strong field ligand. But these ligands behave as weak field ligand because the energy of the of the π^*_3 orbital of the conjugated system is not lowered sufficiently to cause strong $d_{\pi}\text{-}\pi^*_3$ interaction due to the inhibition of the extensive conjugation arising from steric repulsion²⁶ as discussed above.

The $\nu_{\text{CH(Aromatic)}}$ bands⁵⁵ appearing in the 3060-3040 cm^{-1} region in the ligands are observed in the region 3080-3045 cm^{-1} region in the complexes.

The phenylalkene, $\nu_{\text{Ph-C=C}}$ vibrations observed in the 1579-1566 cm^{-1} region in the ligands is shifted to lower frequencies^{16,26,49} (by 5-26 cm^{-1}) in the metal complexes in which it is found in the 1568-1550 cm^{-1} region. The phenylalkene vibration is found to be metal sensitive and for the same phenyl substituent, it varies as $\text{Co} > \text{Ni} > \text{Cu}$; this indicates relatively greater delocalization of electrons from highly populated d-orbitals of copper. This observed order is in total agreement with the order reported for metal complexes of other chalcones^{17,26}.

The Ph-C-C (in plane) vibration¹⁷ bands appearing in the ligands in the 1488-1467 cm⁻¹ region are found to be at the 1489-1460 cm⁻¹ in the complexes. From ligands to complexes, there are changes in these phenyl vibrations and roughly these vibrations may reflect the participation of the phenyl ring in mesomeric interaction with the metal.

The strong absorption bands observed for the δ OH (phenol) vibration^{15,23,49,55} in the range 1357-1340 cm⁻¹ region for all the ligands, were not observed in the complexes indicating the deprotonation of phenolic -OH of the ligand^{15,49}.

The intense bands in the 1308-1281 cm⁻¹ region for all the ligands, attributed to the ν C-O (Phenol) vibrations^{16,23,55,56} were observed in the 1320-1300 cm⁻¹ region in the metal complexes. Thus, from the ligands to metal complexes, this band shifted positively (7-39 cm⁻¹) upon coordination, a result which suggests that both carbonyl oxygen and phenolic oxygen are involved in coordination to the metal^{16,23}.

M-O stretching vibration

As expected, the IR spectra of the metal complexes show M-O stretching vibration as discussed below. Strong bands in the complexes in the region around 620-572 cm⁻¹ are attributed to ν M-O vibrations and suggest bonding between metal ligand oxygen atoms^{15-17,26,49}.

These bands are metal as well as phenyl substituent sensitive. For the same phenyl substituent, it follows the crystal field stabilization energy order, namely Co < Ni < Cu, which indicates that it is determined by ligand field. This order is in accordance with Irving – Williams order of stabilities^{16,26}. However, this order is equalized in the case of complexes of the ligand PipchaH and this deviation may be probably due to the presence of the additional heterocyclic ring in this ligand as compared to other ligands. But, as regards the effect of ligand substitution on ν M-O, no regular sequence could be observed. It seems that electronic effects of the substituent are propagated to the chelate ring and that the resonance capacities of the substituents are important in determining ν M-O.

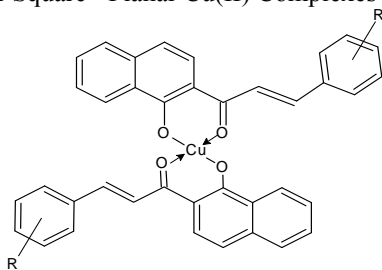
The ν Cu-O bands are observed in the 620-593 cm⁻¹ region, the ν Ni-O bands in the 617-514 cm⁻¹ region, whereas the ν Co-O bands are in the 618-572 cm⁻¹ region. The small change in ν M-O (and ν C=O) with change in the metal ions in the chalcone complexes can be attributed to the delocalization effects operating strongly in the conjugated system which minimize any vibration caused by changing the metal. This 'buffering action' is analogous to that of acetylacetonate complexes⁶⁶.

As shown earlier, the mesomeric interaction of the phenyl group with metal ion in chalcone complexes can be represented by structures (V) and (VI). The effect of mesomeric electron release by the phenyl group is to increase the negative charge on the oxygen atom and cause a general strengthening of the M-O bonds. Superimposed on this effect, there would be an increased tendency towards π -bonding in the M-O linkages. It can be seen that these effects would strengthen the M-O and C-C bonds more than the C=O bonds of the chelate ring⁶⁷. This would also lead to significant shifts in the phenyl vibrations. So, it is concluded that π -delocalization assumes great importance in deciding the nature of bonding, structure and stability of carbonyl complexes.

Structures of metal complexes

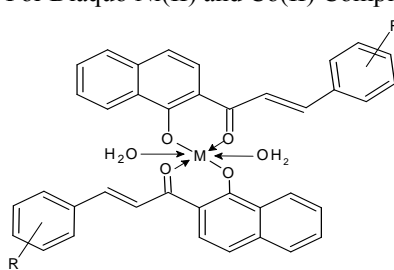
On the basis of magnetic, physical and analytical data, spectral and thermal properties⁴⁶⁻⁴⁸, it is found that all the copper(II) chelates are anhydrous monomers of trans-square-planar configuration, while the diaquo nickel(II) and cobalt(II) chelates have a high spin trans-octahedral configuration¹³ and may be represented by the structures (VIII) and (IX) respectively as shown below, which are already reported⁴⁸.

For Square - Planar Cu(II) Complexes



Structure (VIII)

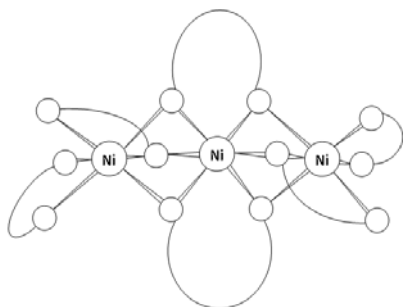
For Diaquo Ni(II) and Co(II) Complexes



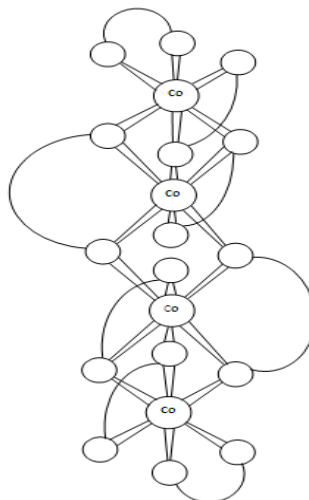
Structure (IX)

M = Ni(II) and Co(II)

The anhydrous Ni(Bencha)₂ and Co(Bencha)₂ complexes are polymers^{16,26,68}, possibly a trimer^{16,26,48,68} and a tetramer^{48,68} respectively with a high-spin trans-octahedral configuration which are comparable to the reported⁶⁸ configurations for Ni(II) and Co(II) complexes of acetylacetonate with the same type of donor system as the present one. As a result of the sharing⁶⁸ of some oxygen atoms, each metal atom achieves octahedral coordination. These two complexes may be represented by schematic structures (X) and (XI) respectively which are same as the structures reported^{68,69} for Ni(II) and Co(II) complexes of acetylacetonate. These structures (X) and (XI) are explained in detail in the earlier report⁴⁸.



Structure(X)



Structure(XI)

Schematic representation of trimeric structure of bis(Bencha) nickel(II). The unlabeled circles represent O(oxygen) atoms and the curved lines connecting them in pairs represent the remaining portions of the anion of the BenchaH rings

Schematic representation of tetrameric structure of bis(Bencha) cobalt(II). The unlabeled circles represent O(oxygen) atoms and the curved lines connecting them in pairs represent the remaining portions of the anion of the BenchaH rings

Conclusion

The strong resonance stabilized intramolecular hydrogen bonding and also conjugated chelation considerably alters the IR spectroscopic properties of the compound and plays a

very significant role in the coordination chemistry. IR spectroscopy as discussed is a very useful tool not only to detect the intramolecular hydrogen bonding but also its effects in the molecule and also the effects of conjugated chelation. It is also very useful in determining the geometries of the metal complexes. For the study of hydrogen bonding IR spectroscopy is the most sensitive and direct method.

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