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Effect of Extensive Conjugation of Coordinated C=O on the Nature of Bonding and Stereochemistry in Co(II), Ni(II) and Cu(II) 2′-Hydroxy-4-X-chalcone Complexes : Hammett Correlation and an Evidence for Metal-Ligand π-Bonding

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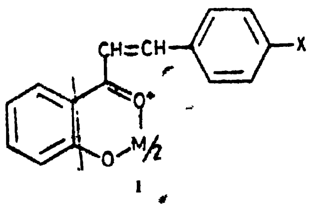
Cu(II), Ni(II) and Co(II) *bis*-chelates of the type ML_2, where L=2′-hydroxy-4-X-chalcone (X=CH_3, CH_3O, Cl, Br), have been prepared and investigated. All of them are monomeric, low-spin and square-planar. The plot of ν(C=O) and ν(PhC=C) of the ligands against the Hammett σ-constants is a straight line. On the other hand, plots of ν(C=O), ν(PhC=C) and ν(M−O) of the complexes of a metal against the σ-parameters yield two straight lines ; the points for the electron-releasing substituents and the unsubstituted complex lie on one straight line and those for the electron-withdrawing substituents and the unsubstituted complex on the other. This indicates the presence of both σ and π-interaction between metal and ligand. The electron-releasing substituents favour σ-interaction while the electron-withdrawing substituents π-interaction and the unsubstituted complexes are more stable than the substituted ones. The stability of the complexes, on the basis of ν(M−O), follows the order H > CH_3 > CH_3O > Br > Cl ; the M−L σ-bond being more important than the M−L π bond. For a given substituent, the order of stability of the complexes is Cu > Ni < Co as expected from crystal field theory.

METAL ions like Co(II), Ni(II), etc. are forced by the highly conjugated porphyrin and other related systems to assume low-spin configurations. Introduction of substituents on the porphyrin nucleus also affects further coordination of the metal with additional ligands as in hemoproteins[1]. Hence it may be of importance to know the behaviour of the metal ions when they are coordinated to simple conjugated organic molecular systems. In order to investigate this aspect, we isolated and studied metal(II) complexes of some α,β-unsaturated *o*-hydroxyarylcarbonyl compounds[2,3] and their Schiff bases[4]. Simple conjugation of C=O with C=C in *o*-hydroxycrotonophenone complexes[2] is found to enhance the ligand field strength while extensive conjugation in 2′-hydroxy-5′-X-chalcone complexes[3] forces nickel(II) and cobalt(II) to achieve a low-spin configuration. This has been ascribed to extensive $d\pi-\pi_3^*$ interaction.

Further, the substituents in the 5′ position in these complexes affect the nature of the metal-carbonyl interaction indirectly. Actually, ν(M−O) is found to be substituent sensitive though ν(C=O) is little affected. One would expect the introduction of substituents in the 4-position of 2′-hydroxychalcone to affect the electronic properties of C=O significantly due to the presence of CH=CH group which can effectively transmit[5] the electronic effects of the substituents. Thus the substituent effect on the metal-carbonyl interaction will be ostensible in the case of 2′-hydroxy-4-X-chalcone complexes. The preparation and the results of our investigation on Co(II), Ni(II) and Cu(II) complexes of some 2′-hydroxy-4-X-chalcones (**1**) are described in this paper.



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M=Cu(II), Ni(II), Co(II)
X=H, CH_3, OCH_3, Cl, Br

Experimental

Benzaldehydes used were reagent grade chemicals. 4-Bromobenzaldehyde was prepared by the Sandmayer reaction[6a]. The metal salts were of analytical reagent grade. Element analyses were performed by the Central Drug Research Institute, Lucknow, India. The metal content of the complexes were estimated by EDTA titrations after decomposing the complexes with a mixture of conc. HNO_3 and H_2O_2, and by thermogravimetric analysis. Thermogravimetric analysis was performed on a Stanton recording thermobalance on *ca*

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100 mg sample in air with a linear heating rate of 5° min^{-1}. Thermal decomposition studies were also carried out on a Perkin-Elmer differential scanning calorimeter.

The magnetic susceptibility measurements were carried out at 302-304 K and at 8000 G in a Gouy balance, $HgCo(SCN)_4$ being used as calibrant. Diamagnetic corrections were made by using Pascal's constants. IR spectra (4000-200 cm^{-1}) were obtained in Nujol between sodium chloride plates and in KBr phase on a Perkin-Elmer 577 spectrophotometer. IR spectra (300-650 cm^{-1}) were also obtained in Nujol on a Beckman IR 12 spectrophotometer. Electronic spectral measurements were made on chloroform solutions and on Nujol mulls adhered to filter paper in a Carl-Zeiss DMR 21 spectrophotometer. Molar conductivities were obtained on approximately 1×10^{-3} *M* dimethylformamide solutions in a conductivity meter.

Synthesis of ligands: 2-Hydroxyacetophenone was prepared by the Frie's method[6b]. 2'-Hydroxy-4-methylchalcone, 2'-hydroxy-4-methoxychalcone, 4-chloro-2'-hydroxychalcone and 4-bromo-2'-hydroxychalcone were prepared by condensing the 2-hydroxyacetophenone with the corresponding benzaldehyde in the presence of 50% sodium hydroxide solution[7].

Synthesis of complexes: The *bis*-chelates of cobalt(II), nickel(II) and copper(II) with 2'-hydroxy-4-X-chalcones were obtained by using the methods employed for the preparation of *bis*(2'-hydroxychalconato)metal(II) complexes.

Results and Discussion

All the complexes are obtained as amorphous compounds. All the nickel complexes are yellow while those of copper and cobalt show some shade of brown, indicating the presence of very rich charge-transfer or ligand transitions in organic solvents like chloroform, benzene, etc. Methoxy and chloro substituents decrease the solubility of the complexes in chloroform. DSC studies and the weight loss experiments revealed the absence of water of coordination in all the chelates. On the basis of these results and element analysis (Table 1), all the *bis*-chelates have been assigned the general formula ML_2. This is supported by conductivity measurements in DMF and molecular weight measurements in diphenyl.

Magnetic properties: The magnetic moments of all the copper(II) complexes are close to the spin-only value of 1.73 B.M. (Table 1). This reveals the presence of one unpaired electron in copper(II) with a ${}^2B_{1g}$ ground state, in a square planar environment. The diamagnetic nature of the nickel(II) complexes and the magnetic moments of cobalt(II) complexes (~3.0 B.M.) suggest a low-spin square planar geometry for them. Mixing of the higher ligand field term, ${}^2A_{2g}$ into ${}^2A_{1g}$ ground term by spin-orbit coupling raises the moment of cobalt complexes considerably above the spin-only value of 1.73 B.M.[8].

Ligand field spectra: The spectra of all the copper(II) complexes display (Table 2) in the solid

TABLE 1—ANALYTICAL DATA AND MAGNETIC MOMENTS OF *bis*(2'-HYDROXY-4-X-CHALCONATO)METAL(II) COMPLEXES

X	Colour	Formula	Analysis %, Found/(Required) M	C	H	μ_{eff} B.M.
CH_3	brown	CuL_2	11.51 (11.80)	69.82 (71.30)	4.53 (4.60)	1.79
CH_3O	brown	CuL_2	11.33 (11.16)	68.20 (67.42)	4.63 (4.57)	1.75
Cl	brown	CuL_2	11.21 (11.00)	61.87 (62.20)	3.92 (3.80)	1.82
Br	brown	CuL_2	9.15 (9.52)	54.47 (53.95)	3.29 (3.00)	1.80
CH_3	yellow	NiL_2	11.03 (11.00)	72.38 (72.10)	4.85 (4.90)	dia[A]
CH_3O	yellow brown	NiL_2	10.71 (10.40)	69.10 (68.00)	4.41 (4.60)	dia[A]
Cl	yellow brown	NiL_2	10.70 (10.20)	61.98 (62.80)	3.92 (3.80)	dia[A]
Br	yellow	NiL_2	9.01 (8.86)	54.91 (54.34)	3.21 (3.02)	dia[A]
CH_3	deep brown	CoL_2	11.52 (11.10)	72.32 (72.10)	4.87 (4.90)	2.90
CH_3O	pink brown	CoL_2	10.51 (10.43)	68.35 (67.99)	4.72 (4.60)	2.85
Cl	pink brown	CoL_2	10.03 (10.20)	64.54 (62.70)	3.86 (3.80)	3.01
Br	pink brown	CoL_2	8.94 (8.89)	55.20 (54.33)	3.17 (3.02)	3.00

[A] Diamagnetic

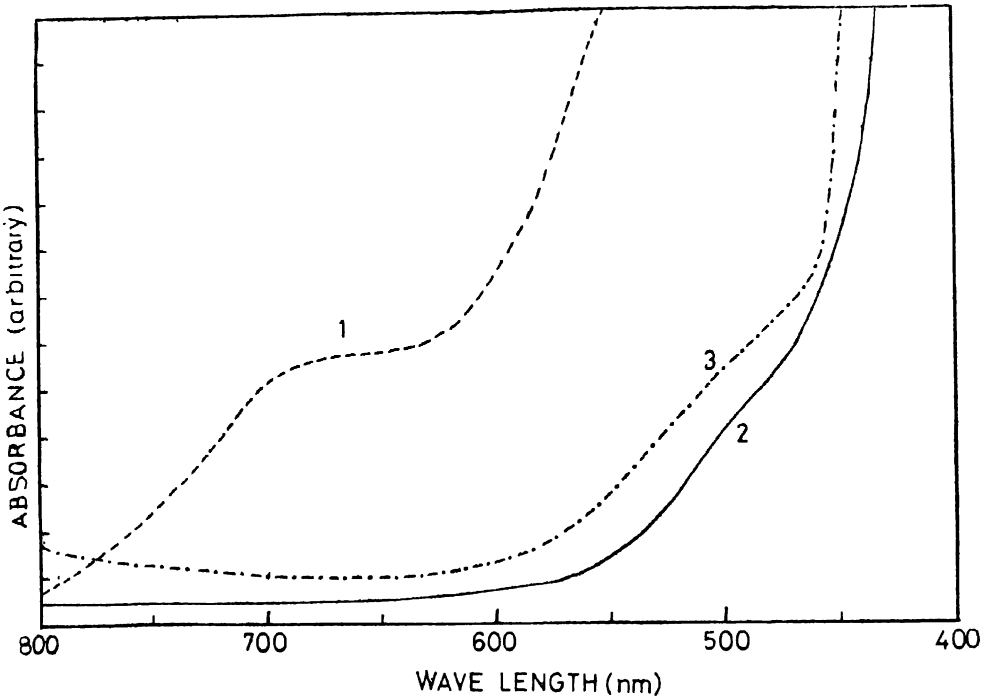


Fig. 1. Ligand field spectra of 2′-hydroxy-4-methylchalcone complexes in Nujol. 1. CuL_2 ; 2. NiL_2 ; 3. CoL_2.

TABLE 2—ELECTRONIC SPECTRAL DATA OF COPPER(II) 2′-HYDROXY-4-X-CHALCONE COMPLEXES; ν_{max} IN cm^{-1} AND ϵ IN PARENTHESIS

Complex	X	Nujol	Chloroform
CuL_2	CH_3	15500	15390 (24)
CuL_2	CH_3O	15500	15410 (51)
CuL_2	Cl	15500	15410 (86)
CuL_2	Br	15500	15410 (38)

state (Fig. 1) and in chloroform solution, a broad shoulder around 15500 cm^{-1} on the intense ligand band. This suggests that the metal ion is in an essentially square planar geometry and the ligand field band arises due to a combination of the transitions[9], ${}^2B_{1g}\rightarrow{}^2A_{1g}$, ${}^2B_{1g}\rightarrow{}^2B_{2g}$ and ${}^2B_{1g}\rightarrow{}^2E_g$. The similarity of the spectra in the solid state and in chloroform solution indicates that the solid complexes dissolve in chloroform without any structural change. The absorption bands of the chloro and methoxy compounds are highly intense. This may be because of the electron-releasing polar effect of the methoxy group which enhances the electron density on metal. In the case of chloro substituted complex, this is due to the electron withdrawing effect of this substituent, which enhances π-bonding (cf. discussion on ir spectra) and mixes[10] the metal and ligand orbitals thereby removing the centre of symmetry of the square complex.

All the nickel(II) complexes in Nujol (Fig. 1) show invariably a shoulder around 20000 cm^{-1} on the intense ligand band and no other absorption below this. This is characteristic of a *trans*-square planar environment for nickel and the observed feature is due to ${}^1A_{1g}\rightarrow{}^1A_{2g}$ (ν_2) transition[11a]. It was difficult to discern this band in chloroform solution.

All the cobalt complexes in Nujol (Fig. 1) exhibit a broad band around 8400 cm^{-1} and a shoulder near 19800 cm^{-1} on the high intensity ligand band. This is consistent with a *trans*-square environment for low-spin cobalt(II). The low frequency band may be assigned tentatively to a transition from the lower filled orbitals (${}^2A_{1g}$, e^4_g b^2_{2g} a^1_{1g}) to the a_{1g} ($d_z{}^2$) orbital and the other transition from these orbitals to the empty b_{1g} ($d_{x^2-y^2}$) σ-antibonding orbital[11b].

Infrared spectra : The assignment of the infrared bands observed in the present complexes is similar to that in metal(II) 2′-hydroxy-5′-X-chalcone complexes[8]. Thus, the intense band in the 1622-1640 cm^{-1} region (Table 3) is assigned to ν(C=O) [+ν(C=C)] and the other intense band in the 1550–1575 cm^{-1} to ν(PhC=C). The metal sensitive band below 600 cm^{-1} is assigned tentatively to coupled ν(M–O). The assignment of these bands is supported by their sensitivity to metal and phenyl substitution. No complex displays a band characteristic of coordinated water around 3300 cm^{-1}.

Effect of coordination and metal ion substitution : In metal complexes, the observed lowering of ν(C=O) and ν(PhC=C) of the ligands shows the involvement of the conjugated C=O group in σ and π-interaction with metal. The order of magnitude

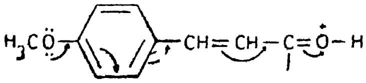
TABLE 3—INFRARED VIBRATIONAL FREQUENCIES (CM^{-1}) OF 2'-HYDROXY-4-X-CHALCONES AND THEIR METAL(II) COMPLEXES

X	Hammett	M	$\nu(C=O)$	$\nu(PhC=C)$	$\nu(M-O)$
CH_3	−0.17	H^A	1638	1562	—
CH_3O	−0.27	H^A	1635	1554	—
Cl	0.23	H^A	1644	1567	—
Br	0.23	H^A	1643	1556	—
CH_3	−0.17	Cu	1627	1546	585
CH_3O	−0.27	Cu	1622	1543	582
Cl	0.23	Cu	1626	1546	573
Br	0.23	Cu	1630	1550	575
CH_3	−0.17	Ni	1632	1562	574
CH_3O	−0.27	Ni	1630	1556	570
Cl	0.23	Ni	1633	1557	567
Br	0.23	Ni	1634	1564	568
CH_3	−0.17	Co	1630	1560	576
CH_3O	−0.27	Co	1626	1554	572
Cl	0.23	Co	1631	1556	569
Br	0.23	Co	1634	1564	571

^{A}Ligands

of interaction of C=O with metal, as shown by these frequencies, is Co> Ni <Cu. This is consistent with the order of stability of the complexes expected on the basis of crystal field theory[8,12]. $\nu(M-O)$ also shows the same order. The small change in $\nu(M-O)$ and $\nu(C=O)$ with change in metal is due to the delocalisation effects operating strongly in the conjugated systems[8,13].

Effect of phenyl substitution : Introduction of substituents into the 4-position of 2'-hydroxychalcone and its metal complexes is expected to affect $\nu(C=O)$, $\nu(M-O)$ and other vibrations if the conjugated system is effective in transmitting the electronic effects of the substituents to the carbonyl oxygen atom. The Hammett equation relating the infrared frequencies to the substituent constants is $\nu=\nu_0+\rho\sigma$ where ν_0 is the statistical quantity corresponding to the frequency for the parent member of the series[14]. This has been shown to be applicable for $\nu(C=O)$ of the substituted acetophenone and other compounds. $\nu(C=O)$ and $\nu(PhC=C)$ values of the ligands and complexes are plotted against Hammett σ-parameters. A straight line is obtained for the ligands ; the electron releasing substituents decrease $\nu(C=O)$ and $\nu(PhC=C)$ (**2**) while the electron withdrawing substituents tend to increase these frequencies (**3**). On the other hand, two different



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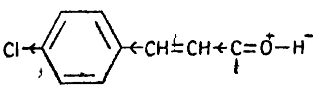

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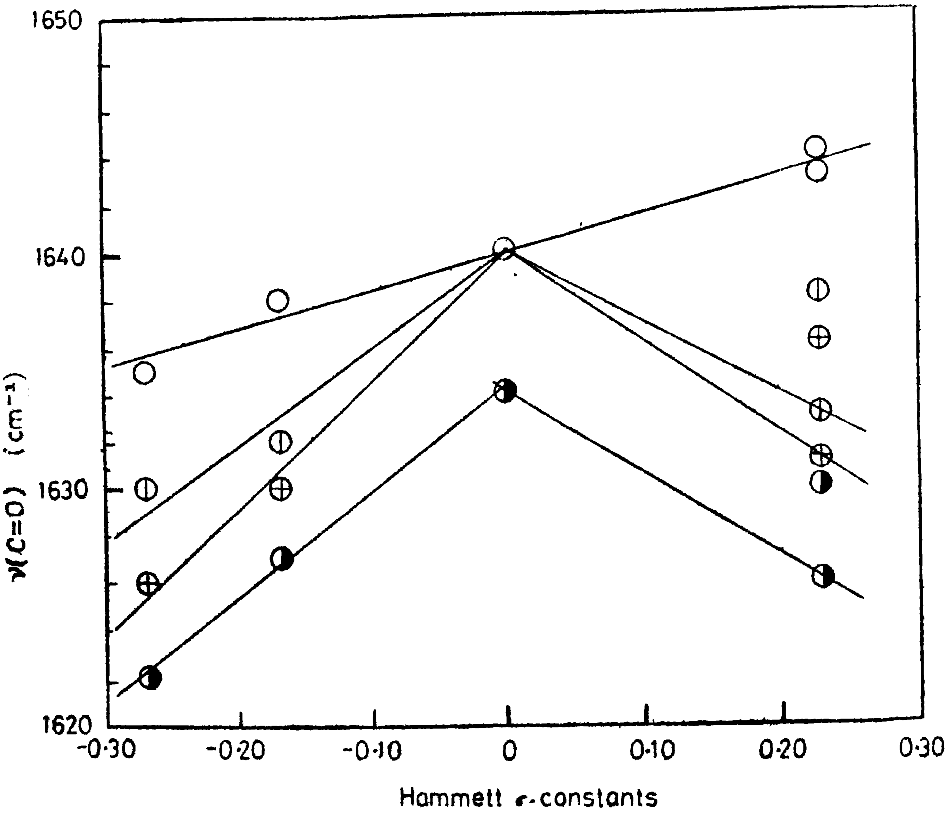
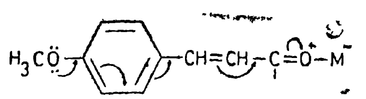


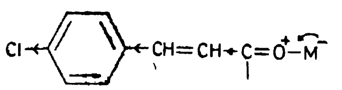
Fig. 2. Hammett plot for $\nu(C=O)$ of 2'-hydroxy-4-X-chalcones and their metal(II) complexes.
○ — ligand ; ⦶ — nickel ; ⊕ — cobalt ; ◑ — copper.

straight lines are obtained for the complexes (Fig. 2). Points for the electron donor substituents lie on one of these lines ($\rho=25{\cdot}79$) and points for the electron acceptor substituents lie on the other ($\rho=-26$ to -74). The correlation coefficients (Table 4) are very close to unity in almost all the cases showing a surprisingly good correlation of the frequencies with σ-values.

The occurrence of two branches of Hammett line is probably due to two different mechanisms involved in the interaction of the metal with C−O group. The positive slope of ν(C=O) and ν(PhC=C) for CH_3, CH_3O and H substituents indicates the reduction in bond order of C=O. This implies that σ-interaction (4) is facilitated by the electron releasing effect of these substituents. On the other hand, the negative slopes for Cl, Br and H substituents show reduction in bond order of C=O. This shows that π interaction (5) is encouraged by the electron withdrawing polar effect of the substituents.



4. σ-interaction.



5. π-interaction.

In other words, the electron sink property of the phenyl is decreased or increased by the electron donating or withdrawing substituents, respectively.

Thus the 4-substituents increase either σ or π-interaction. It then must follow that the 4-substituted chalcone complexes be more stable than the unsubstituted 2′-hydroxychalcone complexes. But it should be noted that the p-methoxy substituent, while facilitating σ-interaction, decreases π-interaction as inferred from decreased C=O bond order. On the other hand the 4-chloro substituent discourages σ-interaction while favouring π-interaction. Then the order of over-all interaction and hence the stability of the 4-substituted metal complexes should not follow from ν(C=O) or ν(PhC=C) but from ν(M−O) only as the latter is determined by crystal field effects[8].

The effect of substituents on ν(M−O) is summarised in Fig. 3. It is seen that both electron withdrawing and electron donating substituents decrease

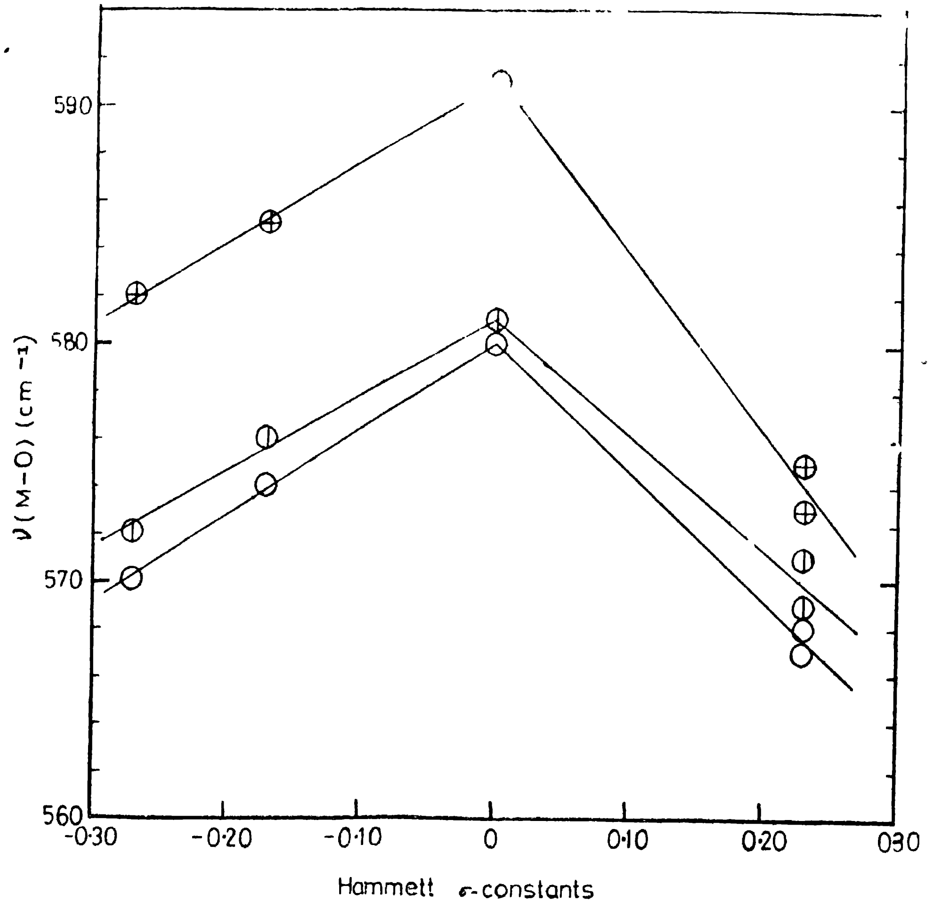


Fig. 3. Hammett plot for ν(M−O) of *bis*(2′-hydroxy-4-X-chalconato) metal(II) complexes. ⊕ — copper; ○ — nickel; ⦶ — cobalt.

TABLE 4 – RESULTS OF CORRELATION ANALYSIS OF INFRARED FREQUENCIES AND HAMMETT SUBSTITUENT CONSTANTS

M	Substituents	IR vibration	Reaction constant ρ	Correlation coefficient r
H[A]	CH_3O, CH_3, H Br, Cl, H	ν(C=O)	15.9	0.9857
H[A]	CH_3O, CH_3, H Br, Cl, H	ν(Ph−C=C)	66.1	0.9670
Cu	CH_3O, CH_3, H	ν(C=O)	44.1	0.9986
Cu	Br, Cl, H	ν(C=O)	26.1	0.8660
Cu	CH_3O, CH_3, H	ν(Ph−C=C)	25.7	0.9978
Cu	Br, Cl, H	ν(Ph−C=C)	8.7	0.5000
Cu	CH_3O, CH_3, H	ν(M−O)	33.5	0.9991
Cu	Br, Cl, H	ν(M−O)	73.9	0.9948
Ni	CH_3O, CH_3, H	ν(C=O)	36.2	0.9890
Ni	Br, Cl, H	ν(C=O)	28.3	0.9912
Ni	CH_3O, CH_3, H	ν(Ph−C=C)	71.0	0.9962
Ni	Br, Cl, H	ν(Ph−C=C)	63.0	0.9226
Ni	CH_3O, CH_3, H	ν(M−O)	36.9	0.9994
Ni	Br, Cl, H	ν(M−O)	54.3	0.9976
Co	CH_3O, CH_3, H	ν(C=O)	52·6	0.9956
Co	Br, Cl, H	ν(C=O)	32.5	0.9449
Co	CH_3O, CH_3, H	ν(Ph−C=C)	78.9	0.9956
Co	Br, Cl, H	ν(Ph−C=C)	65.2	0.9078
Co	CH_3O, CH_3, H	ν(M−O)	32.9	0.9964
Co	Br, Cl, H	ν(M−O)	47.8	0.9878

[A] Ligand

ν(M−O) and hence metal-carbonyl interaction in comparison with the parent 2′-hydroxychalcone complexes. It then follows that the 4-substituted chalcone complexes are less stable than the unsubstituted ones. It is interesting to note that copper(II) 2′-hydroxy-4-methoxychalcone complex as shown by the formation constants is less stable than the copper(II) 2′-hydroxychalcone complex[15]. Further, the order of stability on the basis of ν(M−O) is H>CH_3>CH_3O>Br>Cl. This shows that σ-bonding in 4-methoxy complexes is more important than the π-bonding in 4-chloro complexes in determining the stability.

In this connection it may be mentioned that a plot of equilibrium constant for the displacement of 1-dodecane coordinated to platinum(II) by substituted styrenes against σ-constants furnished a concave plot[16]. Both the electron releasing and electron withdrawing substituents increase the stability of the complex relative to styrene complexes by strengthening σ and π-bonds respectively of olefinic linkage with metal.

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