

## Effect of Extensive Conjugation of Coordinated Imine on Nature of Bonding & Structure of Cu(II), Ni(II) & Co(II) Complexes of 2'-Hydroxychalconeimine†

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Bis(2'-hydroxychalconato)copper(II) reacts with *p*-monoamines and ethylenediamine to form schiff base complexes of the type  $ML_2$  where L is N-R-2'-hydroxychalconeimine ( $R = H, CH_3, Et, n\text{-Pr}, n\text{-Bu}, CH_2-$ ). The Cu(II) complexes are also obtained from the preformed schiff bases by amine-exchange and template reactions and by reaction *in situ*. Extensive conjugation of  $C=O$  in the chalcone complex facilitates the attack of the amines. On the other hand, extensive conjugation of  $C=N$  in the imine complex ( $R = H$ ) does not facilitate the amine exchange. The structure and nature of bonding in the complexes have been established with the help of elemental analyses, thermal studies, magnetic measurements and ligand field and infrared spectra. All the Cu(II) bis-chelates are monomeric and possess *trans*-square planar structure. The corresponding nickel complexes possess associated pseudooctahedral structure and cobalt complexes tetrahedral configuration. All the ethylenediamine derivatives exhibit *cis*-square planar geometry. The tendency of these complexes to form pyridine adducts is affected by the nature of R group. IR studies reveal that conjugation is damped in the chalconeimines resulting in a relatively weak ligand field strength. Only  $\nu_{Cu-O}$  and  $\nu_{Cu-N}$  are affected by the R substituent;  $\nu_{C=N}$  and  $\nu_{Ph-C=C}$  remain almost constant.

Though extensive work has been done on the salicylaldehyde complexes with transition metal ions to bring out the effect of nitrogen substituent, R, on the nature of bonding and structure, the effect of extensive conjugation of coordinated  $C=N$  has not received any attention. Such a study is expected to throw light on the possibility of using the tetradentate schiff base complexes as models for the biometallic chelates like hemin and vitamin  $B_{12}$  (ref. 1) and metal-protein interaction<sup>2</sup>. It is the extensive conjugation in the porphyrins which imparts unique properties to them; thus introduction of substituents in their nucleus modifies the ligand field strength<sup>3</sup>.

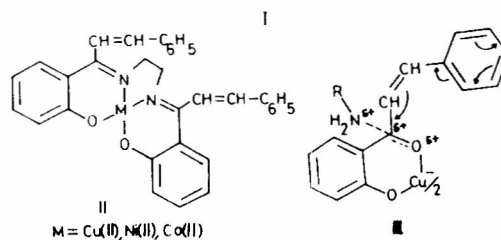
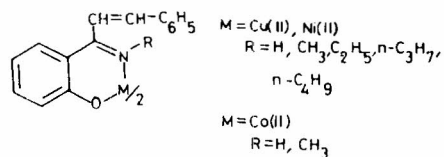
In continuation of our work on 2'-hydroxychalcone-metal(II) complexes<sup>4</sup>, it was thought worthwhile to investigate the effects of extensive conjugation on the structure of 2'-hydroxychalconeimine complexes. In the present paper are reported the preparation and the results of our investigation on Cu(II), Ni(II) and Co(II) complexes (I and II) of 2'-hydroxychalconeimines.

### Materials and Methods

Metal salts used were of AR grade. 2'-Hydroxychalcone and bis(2'-hydroxychalconato)-metal(II) complexes were prepared as reported already<sup>4</sup>. The schiff base complexes were prepared employing different methods used for obtaining Cu(II)<sup>5,6</sup>, Ni(II)<sup>7</sup> and Co(II)<sup>8</sup> salicylaldehyde complexes.

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**Synthesis of metal complexes: From the preformed chalcone complexes**—Bis(2'-hydroxychalconato)copper(II) was suspended in methanol and stirred with a slight excess of the *p*-monoamine or an equivalent amount of ethylenediamine. The precipitate that separated out was filtered and washed with small amounts of methanol. The same procedure was employed for obtaining the nickel imine complex ( $R = H$ ). The other nickel complexes were prepared by mixing a slight excess of the alkylamine with the chalcone complex in chloroform, concentrating the solution to a small volume and adding *n*-hexane to this. The cobalt complexes were prepared by heating to reflux the chalcone complex with required amount of the amines in methanol in an atmosphere of nitrogen. All the complexes were recrystallised from chloroform-*n*-hexane.

**From the preformed schiff bases**—2'-Hydroxychalcone in ethanol was heated to reflux with a slight

excess of the amines or equivalent amount of ethylenediamine and this solution was then added to an aqueous solution of Cu(II) acetate. The products were filtered, washed with aq. ethanol and recrystallised from *n*-hexane-chloroform.

*By template reaction*—To the cuprammonium complex obtained by mixing an aqueous solution of cupric chloride and excess of concentrated ammonia was added an ethanolic solution of 2'-hydroxychalcone with stirring. The reaction mixture was worked-up, as in the previous case, to obtain the complex.

*By imine exchange*—Bis(2'-hydroxychalconeiminato)copper(II) was heated to reflux with excess of methylamine for 12 hr or with equivalent amount of ethylenediamine for 3 hr. The products were obtained by usual work-up as in the previous case.

Analyses and physical measurements on the schiff base complexes were carried out as reported earlier for the chalcone complexes<sup>4</sup>.

### Results and Discussion

The Cu(II) chalconeimine complexes are dark-green or brown crystalline solids and the Ni(II) and Co(II) complexes yellow to brown powders. They are insoluble in water but soluble in common organic solvents such as chloroform, benzene, etc. TGA, DSC and mass loss experiments reveal that all of them are anhydrous species. The results of elemental analyses (Table 1) and thermal studies are consistent with the general formula  $ML_2$  for all the complexes. Conductivity measurements in DMF solution indicate that the complexes are non-ionic and this supports the assigned formula. The molecular weights of the Cu(II) complexes determined cryoscopically in diphenyl (71°) correspond to their monomeric nature.

The Cu(II) chalcone complex when treated with the amine gives the imine complex in the cold itself. The perturbation of C=O by coordination to copper facilitates the attack of the amines on the carbonyl carbon<sup>9</sup>. Further, the transition state (III) is stabilised by extensive conjugation. Such a stabilisation is not possible in the formation of salicylaldehyde complexes from salicylaldehyde complexes and hence they are formed only when refluxed with amines. However, the exchange of one coordinated amine by another of high basicity is not facile. This is because of the less effective conjugation of C=N with C=C, which does not stabilise the transition state (similar to III). Template synthesis and reaction *in situ* also afford chalconeimine complexes which are identical with those obtained from the preformed schiff bases and preformed chalcone complex.

*Magnetic moments*—The magnetic moments of all the Cu(II) complexes fall in the range 1.84–2.33 B.M.

Table 1—Analytical and Magnetic Moment Data and Colour of the Metal(II) Complexes ( $ML_2$ )<sup>a</sup>

R	Colour	Found (calc) %				$\mu_{\text{eff}}$ (B.M.)
		M	C	H	N	
H	Green	12.40 (12.52)	70.72 (70.93)	4.90 (4.73)	5.61 (5.52)	2.25
CH <sub>3</sub>	Greenish brown	11.95 (11.87)	72.12 (71.70)	5.41 (5.23)	5.21 (5.23)	1.94
C <sub>2</sub> H <sub>5</sub>	Brown	11.62 (11.28)	73.01 (72.40)	5.46 (5.68)	5.05 (4.97)	1.97
<i>n</i> -C <sub>3</sub> H <sub>7</sub>	Do	11.23 (10.74)	73.41 (73.03)	6.28 (6.09)	4.82 (4.73)	2.12
<i>n</i> -C <sub>4</sub> H <sub>9</sub>	Dark brown	10.07 (10.26)	72.98 (73.60)	6.72 (6.46)	4.47 (4.52)	2.33
CH <sub>2</sub> –	Do	12.10 (11.91)	72.09 (71.97)	4.98 (4.87)	5.25 (5.25)	2.21
H	Yellow	11.75 (11.68)	71.32 (71.61)	4.85 (4.77)	5.56 (5.57)	2.68
CH <sub>3</sub>	Light brown	11.29 (11.06)	72.67 (72.36)	5.41 (5.28)	5.30 (5.28)	2.50
C <sub>2</sub> H <sub>5</sub>	Brown	10.74 (10.51)	73.25 (73.03)	5.91 (5.73)	5.02 (5.01)	2.97
<i>n</i> -Pr	Do	10.25 (10.01)	73.21 (73.63)	6.06 (6.14)	4.73 (4.77)	2.88
<i>n</i> -Bu	Do	9.31 (9.55)	73.69 (74.18)	6.83 (6.51)	4.59 (4.56)	2.72
CH <sub>2</sub> –	Dark brown	11.51 (11.10)	72.91 (72.63)	5.07 (4.92)	5.23 (5.30)	Dia- mag.
H	Brown	11.60 (11.71)	70.23 (71.58)	4.95 (4.77)	5.51 (5.57)	4.32
CH <sub>3</sub>	Do	11.52 (11.10)	73.51 (72.32)	5.49 (5.27)	5.35 (5.27)	4.55
CH <sub>2</sub> –	Do	11.54 (11.14)	73.57 (72.60)	5.23 (4.90)	5.41 (5.29)	2.40

<sup>a</sup>Compounds obtained from copper(II) chalcone complex. Compounds obtained through other routes also analysed satisfactorily.

(Table 1), showing the presence of one-unpaired electron in Cu(II) in a distorted planar geometry.

The Ni(II) bis-chelates possess moments in the range 2.50–2.97 B.M. (Table 1); this suggests that Ni(II) is present in an octahedral and not in a tetrahedral or pseudo-tetrahedral environment<sup>10</sup>. This is in contrast to that in Ni(II) N-R-salicylaldehyde complexes<sup>9</sup> most of which are diamagnetic in the solid state but paramagnetic in non-coordinating solvents due to intermolecular association. Similar associated structures are suggested for the chalconeimine complexes even in the solid state. However, the molecular weights determined in molten diphenyl (71°) represent only a slight degree of association ( $\bar{n}=1.3$ ). This may be because association is prevented at high temperatures and actually an equilibrium between the polymer and the monomer may exist. In the case of N-methylchalconeimine complex in chloroform, Beer's law is not obeyed at 16000 cm<sup>-1</sup> where octahedral Ni(II) absorbs. This supports associated structure.

Thus it is clear that the chalconeimines are relatively weak field ligands.

The diamagnetism of N, N'-ethylene-bis(2'-hydroxychalconeiminato)nickel (II) and the  $\mu_{\text{eff}}$  (2.4 B.M.) of a similar Co(II) complex are suggestive of square planar structure<sup>4</sup> for them. The bis-chelates of Co(II) display moments of the order of 4.4 B.M.; this is consistent with a  $^4A_2$  ground state<sup>11</sup> of Co(II) in a tetrahedral environment as in salicylaldehyde complexes. Attempts to isolate the complexes with higher N-alkyl groups were not fruitful. Molecular models indicate severe steric strain in them.

**Ligand field spectra**—The electronic spectra of bis-chelates of copper in the solid state and in chloroform solution are almost identical, indicating that solid complexes do not undergo structural changes on dissolution. The spectra exhibit a single broad shoulder around  $16000\text{ cm}^{-1}$  due to a combination of  $^2B_{1g} \rightarrow ^2A_{1g}$ ,  $^2B_{1g} \rightarrow ^2B_{2g}$  and  $^2B_{1g} \rightarrow ^2E_g$  transitions occurring in Cu(II) in  $D_{2h}$  symmetry<sup>12</sup>. For the *n*-Pr and *n*-Bu complexes, this band is of higher intensity, showing much distortion from planarity of the chelate ring. This distortion arises due to the steric interaction between the R group and the 3'-H and the phenolic oxygen on the other ligand moiety<sup>9</sup>.

In the tetradentate complex formed from ethylenediamine the ligand field feature is shifted to  $17500\text{ cm}^{-1}$ , indicating formation of stronger Cu-ligand bonds. The tetradentate nature of the ligand is responsible for the high ligand field strength. Further, the considerably high intensity of the band for this complex with *cis*-planar  $\text{CuO}_2\text{N}_2$  coordination structure ( $C_{2v}$ ) is presumed to reveal the purely electronic contribution to the transition moment in as much as the transitions are now electronically allowed<sup>13</sup>.

Amongst the bis-chelates, only the imine complex shows appreciable shift of the main feature to high frequency ( $17800\text{ cm}^{-1}$ ) with enhanced intensity in pyridine solution; this is indicative of adduct formation. In the N-alkyl derivatives, the band is shifted slightly to lower frequencies but with enhanced intensities. Further, the intensity decreases with increase in chain length of the alkyl group. This reveals that the bulky alkyl groups hinder the approach of the base to the metal. The weak adduct formation of the bridged complex, as inferred from its band with lower frequency and increased intensity in pyridine solution, is because of the strong ligand field produced in the equatorial plane.

All the Ni(II) bis-chelates display a less intense band around  $8500\text{ cm}^{-1}$  in the solid state and around  $8850\text{ cm}^{-1}$  in chloroform. On account of the tailing of the intense ligand (CT) band into the visible region, no other band is discernible. The observed band is

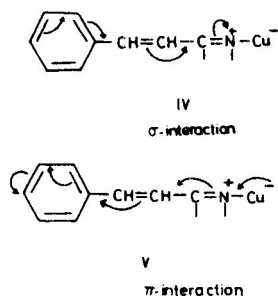
assigned tentatively to  $^3B_{3g} \rightarrow ^3B_{2g}$  transition in axially perturbed Ni(II) situated in a *trans*-planar structure in accordance with Maki's model for such weak-field systems<sup>14</sup>. The shift of this band to high frequency with increased intensity in pyridine reveals adduct formation. This band in pyridine around  $9400\text{ cm}^{-1}$  and the shoulder around  $15400\text{ cm}^{-1}$  are interpreted as  $\nu_1$  and  $\nu_2$  transitions respectively in Ni(II) in an octahedral environment. The shoulder around  $13300\text{ cm}^{-1}$  may originate from spin-forbidden transition. The bridged Ni(II) complex shows a well-defined shoulder around  $18600\text{ cm}^{-1}$ . This is characteristic of low-spin Ni(II) in a *trans*-square planar environment<sup>4</sup>, the band being due to  $^1A_{1g} \rightarrow ^1A_{2g}$  ( $\nu_2$ ) transition. The spectrum of the complex in pyridine indicates that adduct formation is resisted due to the stabilisation of  $\uparrow A_{1g}$  ground state by the tetradentate ligand.

The intensity of the low energy band in pyridine and chloroform decreases as chain length of R group increases. This reveals that adduct formation and association respectively are sensitive to the R group as in Cu(II) complexes.

The cobalt complexes with R=H, CH<sub>3</sub> display in nujol a band around  $8000$  and shoulders around  $14500$  and  $18700\text{ cm}^{-1}$ . The low energy band may be interpreted as  $\nu_2$  transition in Co(II) with a tetrahedral configuration<sup>15</sup>. The shoulders may be considered as a doublet of  $\nu_3$  transition. The tetradentate Co(II) complex in nujol exhibits a broad band around  $8500$  and a broad shoulder near  $22000\text{ cm}^{-1}$  on the high intensity ligand absorption. This is consistent with a square environment<sup>4</sup> for Co(II).

The infrared spectra ( $\nu_{\text{max}}$  in  $\text{cm}^{-1}$  throughout the discussion) of the complexes obtained by different routes were superimposable indicating that one and the same product has been obtained in the different methods of preparation.

On reacting the chalcone complex with amines, the intense  $\nu(\text{C}=\text{O})$  in the  $1632\text{--}1647$  range disappears and  $\nu(\text{C}=\text{C})$  which merges with it makes its appearance as a less intense band around  $1620$ . The  $\nu(\text{C}=\text{N})$  in the complexes appears around  $1600$ . The assignment of both  $\nu(\text{C}=\text{C})$  and  $\nu(\text{C}=\text{N})$  is supported by their sensitivity to metal and R group. The intense doublet in the range  $1300\text{--}1350$  is assigned to  $\nu(\text{C}=\text{O})$  (phenolic). The intense  $\nu(\text{Ph}-\text{C}=\text{C})$  observed in the  $1550\text{--}1575$  range in the chalcone complex<sup>4</sup> is shifted to  $1575\text{--}1583$  region in the imine complexes. Since  $\nu(\text{Ph}-\text{C}=\text{C})$  decreases with increasing  $\sigma$ - and  $\pi$ -interactions of  $\text{C}=\text{O}$  with metal in the chalcone complexes, it follows that  $\sigma$ - and  $\pi$ -interactions (see structures IV and V) in the imine complexes are not effective. This explains why  $\nu(\text{C}=\text{N})$  occurs in the same region as in salicylaldehyde complexes<sup>10</sup>. Thus, it is obvious that  $\text{Ph}-\text{C}=\text{C}-\text{C}=\text{N}$  is not as well conjugated a system



as Ph.C=C-C=O. On account of this,  $d_{\pi}-\pi^*$  interaction in the imine complexes is not effective and the electronegative phenyl group decreases the basicity of nitrogen by inductive effects. These confer a weak ligand field strength to the bidentate imines. Thus the low-spin square-planar Ni(II) and Co(II) chalcone complexes react with amines to provide high-spin associated octahedral and tetrahedral chalconeimine complexes respectively.

Compared with Ni(II) and Co(II) complexes, in Cu(II) complexes  $\nu(\text{C}=\text{N})$ ,  $\nu(\text{C}=\text{C})$  and  $\nu(\text{Ph}-\text{C}=\text{C})$  occur at lower wave-numbers due to their  $d^9$ -configuration<sup>16</sup>. Based on these frequencies, the order of stabilities of the complexes for a given alkyl substituent is: Co ~ Ni < Cu; this is in accordance with the Irving-Williams order of stability.

*Effect of alkyl substitution*—Though the variation in R does not affect  $\nu(\text{C}=\text{N})$  etc. much,  $\nu(\text{Cu}-\text{O})$  and  $\nu(\text{Cu}-\text{N})$  are sensitive to R. Thus  $\nu(\text{Cu}-\text{N})$  increases ( $\Delta\nu 15 \text{ cm}^{-1}$ ) and  $\nu(\text{Cu}-\text{O})$  decreases ( $\Delta\nu 22 \text{ cm}^{-1}$ ) on passing from imine to N-methyl complex. The electron density on nitrogen is increased by the methyl group and is not effectively delocalised into the poorly conjugated system; hence, the insensitivity of  $\nu(\text{C}=\text{N})$  to variation in R. The increased electron density, on the other hand, strengthens the Cu-N  $\sigma$ -bond. Consequent upon this Cu-O  $\sigma$ -bond is weakened.

For the other N-alkyl complexes,  $\nu(\text{Cu}-\text{O})$  and  $\nu(\text{Cu}-\text{N})$  remain constant but the former occurs at slightly higher wavenumbers and the latter at slightly lower wavenumbers as compared to the N-CH<sub>3</sub> compound. This is consistent with the less basic nature of the alkylamines in comparison with methylamine.

In the bridged complex, both  $\nu(\text{Cu}-\text{O})$  and  $\Delta(\text{Cu}-\text{N})$  assume values higher than those of the bis-chelates. This is due to the higher ligand field strength of the tetradenate ligand as evidenced from spectral data.

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