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Unsaturated Polycarbonyl Compounds and their Metal Complexes

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A new series of unsaturated polycarbonyl compounds in which the keto group attached to olefinic linkage has been synthesized by the reaction of acetoacetanilide and aromatic aldehydes under specified conditions. The existence of these compounds predominantly in the intramolecularly hydrogen bonded enol form has been well demonstrated from their IR, ^{1}H NMR and mass spectral data. Details on the formation of their complexes with Ni(II), Cu(II), and Zn(II) and their nature of bonding are discussed on the basis of analytical, IR, ^{1}H NMR and mass spectral data.

Keywords: Polycarbonyl compounds, Metal complexes, IR spectra, ^{1}H NMR spectra and mass spectra

INTRODUCTION

Curcuminoids, a group of structurally related 1,3-dicarbonyl compounds in which the keto groups are directly linked to olefinic carbons, constitute the major physiologically active principle of the traditional Indian medicinal plant turmeric (*Curcuma longa,* Linn, *Zingiberacea* family) and several other related species of wide pharmacological interest [1,2]. These natural curcuminoids, their synthetic analogues and their metal complexes are known to exhibit anticancer [1-5], antioxidant [4,6] and anti-inflammatory [7] activities. The alkenyl linkage appears to be a major factor in determining their biological properties. Therefore, synthesis and characterization of unsaturated dicarbonyl compounds possessing extended conjugation are of considerable importance. Even though literature is extensive on the synthesis, structural characterization and applications of metal complexes of β-ketoanilides in which the carbonyl groups are directly attached to alkyl/aryl functions [8-10], reports are scanty on unsaturated polycarbonyl compounds derived from β-ketoanilides. The present communication reports the synthesis and characterization of a new series of polycarbonyl compounds, in which the keto function is directly bonded to a -CH=CH- group, and their typical metal complexes.

EXPERIMENTAL

Carbon, hydrogen, and nitrogen percentages were determined by micro analyses (Heraeus Elemental analyzer) and metal contents by AAS (Perkin Elmer 2380). The electronic spectra of the compounds were recorded in methanol solution (10^{-4} M) on a 1601 Shimadzu UV-Vis spectrophotometer, IR spectra (KBr discs) on a 8101 Shimadzu FTIR spectrophotometer, ^{1}H NMR spectra ($CDCl_3$ or DMSO-d_6) on a Varian 300 NMR spectrometer, ESR spectra (X-band) at 77 K on a Varian E 112 ESR spectrometer and mass spectra on a Jeol/SX-102 mass spectrometer (FAB using Argon and *meta*-nitrobenzyl alcohol as the matrix). Molar conductance of the complexes was determined in DMF at 28 ± 1 °C using solutions of about 10^{-3} M concentration. Magnetic susceptibilities were determined at room temperature on a Guoy type magnetic balance.

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Synthesis of Unsaturated β-Ketoanilides and Diketoanilides

The aldehydes used for the preparation include *m*-hydroxybenzaldehyde, *m*-methoxybenzaldehyde, and *m*-chlorobenzaldehyde. A mixture of acetoacetanilide (1.77 g, 0.01 mol) and boric oxide (0.35 g, 0.005 mol) in dry ethyl acetate was stirred on a magnetic stirrer for about 1 h. To this, a solution of aromatic aldehyde (0.01 mol) and tri(sec-butyl)borate (4.6 g, 0.02 mol) dissolved in dry ethyl acetate (~15 ml) was added and stirred for ~5 h with the slow addition of *n*-butylamine (0.5 ml in 5 ml dry ethyl acetate) and the reaction mixture was kept overnight. Hot HCl (0.4 M, 7.5 ml, ~70 ºC) was added and again stirred for ~l h. The mixture was extracted repeatedly with ethyl acetate and the combined extracts were evaporated to dryness on a water bath to get a pasty mass. To this 10 ml of 2 M HCl was added and kept for ~24 h. The solution was stirred well and the precipitate formed was filtered. The TLC of the products revealed the presence of two compounds and were quantitatively separated by column chromatography as outlined below.

The crude product was dissolved in minimum quantity of dry ethyl acetate and placed over a column (2 × 100 cm) densely packed with silica gel (mesh 60-120) and eluted with 3:5 v/v chloroform-acetone mixture at a uniform flow rate of 2 ml min^{-1}. As the elution proceeds, two bands were developed in the column, a pale yellow lower band and an orange red upper band. The lower region on evaporation gave the pure unsaturated β-ketoanilide **1**. The upper region was collected as 10 ml aliquots in separate tubes and in each case the purity was established by TLC. The combined eluates on evaporation gave the pure unsaturated diketoanilide **2**.

Synthesis of Metal Complexes of Unsaturated β-Ketoanilide

To a refluxing solution of the β-ketoanilide in ethanol (0.002 mol, 20 ml) was added an aqueous solution of the metal(II) acetate (0.001 mol, 15 ml) drop by drop with stirring. The pH of the solution was adjusted around 6 using sodium acetate and refluxing was continued for ~4 h. The solution was concentrated to half the volume and then cooled in ice. The precipitated complex was filtered, washed several times with water, then with ethanol, recrystallized from hot methanol and dried in vacuum.

Synthesis of Metal Complexes of Unsaturated Diketoanilide

To a refluxing solution of the compound in methanol (0.001 mol, 20 ml) was added an ethanolic solution of metal(II) acetate (0.001 mol, 15 ml) drop by drop with stirring. The pH of the solution was adjusted around 6 using sodium acetate and refluxing was continued for ~3 h. The solution was concentrated to half the volume. The precipitated complex was filtered, washed several times with water, recrystallized from hot ethanol and dried in vacuum.

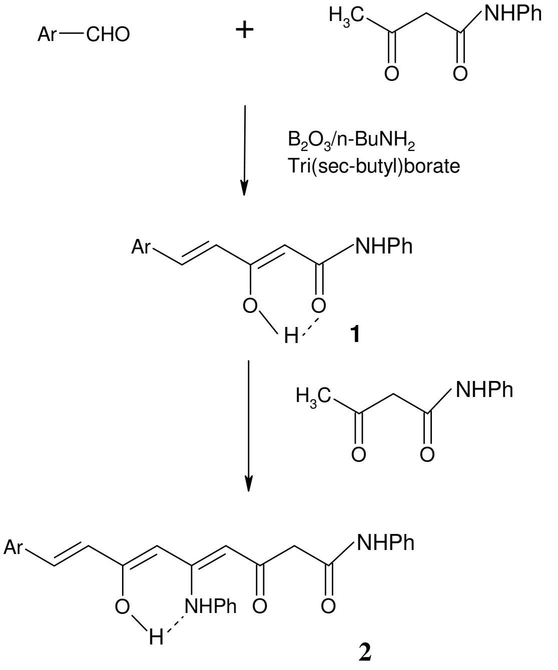
RESULTS AND DISCUSSION

A well established synthetic route to 'unsaturated' β-dicarbonyl compounds is based on the synthesis of curcuminoids [11] using the reaction of aromatic aldehydes and β-dicarbonyl compounds containing at least one acetyl group in presence of boric oxide, tri(sec-butyl)borate and n-butylamine. The use of boric oxide and tri(sec-butyl)borate is to prevent Knoevenagel type condensation and facilitate Claisen type condensation by the formation of a boron complex of the diketone. However, in the present study, when acetoacetanilide was employed as the dicarbonyl compound two products **1** and **2** (Scheme 1) were formed probably due to the electronic effects of the amide carbonyl.

Characterization of Unsaturated β-Ketoanilides and their Metal Complexes

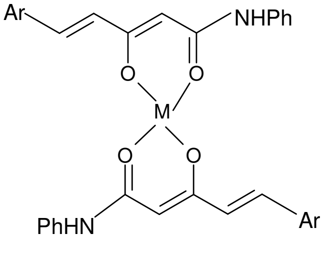
The elemental analytical data of the unsaturated β-ketoanilides synthesized from various aromatic aldehydes are given in Table 1. They formed stable complexes with Ni(II), Cu(II), and Zn(II) ions. The analytical data (Table 1) together with non-electrolytic nature in DMF (specific conductance < 10 Ω^{-1} cm^{-1}; 10^{-3} M solution) suggest [ML_2] stoichiometry for the complexes. The Ni(II) and Zn(II) chelates are diamagnetic while Cu(II) complexes showed normal paramagnetic moment. The observed electronic, IR, ^{1}H NMR and mass spectra of the complexes are fully consistent with the structure **3**.

Infrared spectra. Acetoacetanilide exists predominantly in the keto form with very small percentage of the enol content [9]. Thus its IR spectrum is characterized by the presence of two strong bands at ~1720 cm^{-1} and ~1667 cm^{-1} due to acetyl



Unsaturated β-ketoanilides (1)	Unsaturated diketoanilidies (2)	Ar-
HL^1	L^a	3-Hydroxyphenyl
HL^2	L^b	3-Methoxyphenyl
HL^3	L^c	3-Chlorophenyl

Scheme 1



M = Ni(II), Cu(II), Zn(II)

3

and the amide carbonyls respectively. The spectra of all the unsaturated β-ketoanilides show two intense bands at ~1670 cm^{-1} and ~1640 cm^{-1} (Table 2) assignable to the stretching of the amide carbonyl and to partially enolized cinnamoyl carbonyl function, respectively [12]. The broad band in the region 2800-3500 cm^{-1} suggests the existence of the compounds predominantly in the enolic form [13]. The spectra of all the compounds showed a prominent band at ~970 cm^{-1} typical of *trans* -CH=CH- group.

Spectra of all the complexes in the 1600-1800 cm^{-1} region showed an intense and slightly broadened band at ~1630 cm^{-1} (Table 3). In acetoacetanilide complexes both the acetyl and amide carbonyls show appreciable decrease in frequencies up on complexation [9]. Therefore, by considering the position and broadened nature it can be presumed that the partially enolised cinnamoyl and amide carbonyl stretching frequencies of metal complex absorbs almost in identical values and coalesce and appear as a broad band. Thus, the band at ~1630 cm^{-1} is due to metal bonded dicarbonyl functions. The broad band in the region 2800-3500 cm^{-1} cleared up in the spectra of metal complexes indicating the replacement of enolic proton by the metal cation during complexation. That the carbonyl groups are involved in bonding with the metal ion as in structure **3** is further supported by the appearance of two medium intensity bands at ~420 cm^{-1} and ~470 cm^{-1} assignable to $\nu_{M\text{-}O}$ [12].

^{1}H NMR spectra. The ^{1}H NMR spectra of the unsaturated β-ketoanilides show two one proton signals at ~9.50 ppm (broad) and at ~12.50 ppm (Table 4) assignable to the NH and enol protons [14,15] of structure **1**, respectively. The olefinic proton signals appeared at ~8.30 ppm. The aryl proton signals are observed in the range 6.85-7.55 ppm as a complex multiplet.

The most characteristic feature of the ^{1}H NMR spectra of diamagnetic Ni(II) and Zn(II) complexes is the absence of the low field enol proton signal of the ligands. The NH proton signal remained almost unaffected, which strongly supports that only the enol proton has been replaced by the metal ion and the amide nitrogen is excluded from coordination. The methine proton signal shifted appreciably to low fields compared to the shift in the olefinic protons. This may be due to the aromatic character that might have been imparted to the C_3O_2M ring system of the chelates by the highly conjugated groups attached to the dicarbonyl moiety. The integrated intensities of various signals agree well with the [ML_2] stoichiometry of the complexes. That the phenolic OH group

Table 1. Physical and Analytical Data of Unsaturated β-Ketoanilides and their Metal Complexes

Compound/ Empirical formula	M.P. (°C)	Yield (%)	Elemental analysis: Found (Calcd.)%			
			C	H	N	M
HL^1 ($C_{17}H_{15}NO_3$)	76	65	72.35 (72.60)	5.50 (5.34)	5.02 (4.98)	-
HL^2 ($C_{18}H_{17}NO_3$)	84	68	72.88 (73.22)	5.46 (5.76)	4.70 (4.75)	-
HL^3 ($C_{17}H_{14}ClNO_2$)	112	72	67.44 (68.00)	4.52 (4.67)	4.62 (4.67)	-
[NiL$^1_2$] ($C_{34}H_{28}N_2NiO_6$)	216	70	61.22 (60.32)	4.77 (4.86)	4.50 (4.54)	10.02 (9.52)
[NiL$^2_2$] ($C_{36}H_{32}N_2NiO_6$)	198	70	66.44 (66.80)	4.74 (4.95)	4.22 (4.33)	9.31 (9.07)
[NiL$^3_2$] ($C_{34}H_{26}Cl_2N_2NiO_4$)	186	72	61.98 (62.22)	4.11 (3.97)	4.65 (4.27)	9.14 (8.95)
[CuL$^1_2$] ($C_{34}H_{28}CuN_2O_6$)	204	62	60.81 (59.85)	4.74 (4.83)	4.58 (4.50)	10.11 (10.22)
[CuL$^2_2$] ($C_{36}H_{32}CuN_2O_6$)	188	68	65.12 (66.30)	4.70 (4.91)	4.31 (4.30)	9.98 (9.75)
[CuL$^3_2$] ($C_{34}H_{26}CuCl_2N_2O_4$)	176	70	62.34 (61.77)	4.12 (3.94)	4.26 (4.23)	9.54 (9.62)
[ZnL$^1_2$] ($C_{34}H_{28}N_2O_6Zn$)	156	76	60.54 (59.67)	4.84 (4.81)	4.39 (4.49)	10.46 (10.49)
[ZnL$^2_2$] ($C_{36}H_{32}N_2O_6Zn$)	164	72	66.84 (66.12)	5.04 (4.90)	4.34 (4.29)	9.88 (10.01)
[ZnL$^3_2$] ($C_{34}H_{26}Cl_2N_2O_4Zn$)	178	70	61.22 (61.60)	3.84 (3.93)	3.76 (3.62)	9.54 (9.87)

L = Deprotonated ligand.

Table 2. Characteristic IR Stretching Frequencies (cm^{-1}) of Unsaturated β-Ketoanilides

Compound	(C=O) amide	(C=O) chelated	(C=C) phenyl/ (C=C) alkenyl/ amide II	amide III	CH=CH *trans*	amide V	amide IV	amide VI
HL^1	1672 s	1638 s	1580 m,1546 m 1528 m,1525 m	1242 m	967 m	690 m	656 m	610 m
HL^2	1668 s	1640 s	1590 m,1542 m 1530 m,1518 m	1234 m	970 m	693 m	658 m	608 m
HL^3	1678 s	1640 s	1598 m,1573 m 1546 m,1510 m	1238 m	970 m	695 m	660 m	614 m

Table 3. Characteristic IR Stretching Frequencies (cm^{-1}) of Cu(II) Complexes of Unsaturated β-Ketoanilides

Complex	(C=O)	(C=C) aryl	(C=C) alkenyl	(C-C-C) chelate ring	(CH=CH) *trans*	M-O
[CuL$^1_2$]	1632 s	1556 m 1586 m	1540 m	1520 m	968 m	418 m 472 m
[CuL$^2_2$]	1626 s	1560 m 1582 m	1546 m	1522 m	970 m	416 m 474 m
[CuL$^3_2$]	1624 s	1560 m 1584 m	1550 m	1526 m	971 m	418 m 470 m

L = Deprotonated ligand

Table 4. ^{1}H NMR Spectral Data of Unsaturated β-Ketoanilides and their Ni(II) and Zn(II) Complexes

Compound	Enolic OH	NH	Methine	CH=CH	Phenyl substituent
HL^1	12.57 (singlet)	9.21 (singlet)	5.99 (singlet)	8.20 (doublet) 8.02 (doublet)	10.05 (singlet)
HL^2	12.34 (singlet)	9.57 (singlet)	5.87 (singlet)	8.30 (doublet) 8.06 (doublet)	3.83 (singlet)
HL^3	12.46 (singlet)	9.17 (singlet)	5.89 (singlet)	8.30 (doublet) 8.12 (doublet)	-
[NiL$^1_2$]	-	9.23 (singlet)	6.58 (singlet)	8.22 (doublet) 8.04 (doublet)	10.05 (singlet)
[NiL$^2_2$]	-	9.54 (singlet)	6.34 (singlet)	8.32 (doublet) 8.12 (doublet)	3.82 (singlet)
[NiL$^3_2$]	-	9.14 (singlet)	6.34 (singlet)	8.36 (doublet) 8.20 (doublet)	-
[ZnL$^1_2$]	-	9.20 (singlet)	6.50 (singlet)	8.24 (doublet) 8.08 (doublet)	10.04 (singlet)
[ZnL$^2_2$]	-	9.59 (singlet)	6.28 (singlet)	8.36 (doublet) 8.16 (doublet)	3.83 (singlet)
[ZnL$^3_2$]	-	9.15 (singlet)	6.36 (singlet)	8.38 (doublet) 8.20 (doublet)	-

L = Deprotonated ligand

Table 5. Mass Spectral Data of Unsaturated β-Ketoanilides and their Cu(II) Complexes

Compound	Mass spectral data (m/z)
HL^1	281, 204, 189, 162, 161, 147, 134, 120, 119
HL^2	295, 218, 203, 186, 175, 162, 161, 134, 133, 120, 109
HL^3	300, 223, 208, 193, 186, 165, 162, 151, 134, 123, 120
$[CuL^1_2]$	625, 623, 548, 546, 533, 531, 490, 488, 471, 469, 441, 439, 387, 385, 346, 281, 203, 201, 189, 162, 120
$[CuL^2_2]$	653, 651, 576, 574, 561, 559, 533, 531, 499, 497, 469, 467, 413, 411, 295, 186, 175, 162, 134, 120, 109
$[CuL^3_2]$	662, 660, 585, 583, 570, 568, 542, 540, 508, 506, 478, 476, 422, 420, 300, 223, 186, 165, 162, 134, 120

L = Deprotonated ligand.

Table 6. ESR Parameters of Cu(II) Complexes of Unsaturated β-Ketoanilides in DMF at 77 K

Cu(II) complexes of	g_{II}	$g_{\perp}$	$A_{II} \times 10^{-4}$ (cm^{-1})	$A_{\perp} \times 10^{-4}$ (cm^{-1})
HL^1	2.268	2.050	154	45.4
HL^2	2.260	2.056	160	44.2

of HL^1 is not involved in bonding with the metal ion is clearly indicated [16] in the spectra of its Ni(II) and Zn(II) complexes (Table 4).

Mass spectra. Mass spectra of all the unsaturated β-ketoanilides showed intense molecular ion peak, $P^+/(P + 1)^+$ thereby confirming the formulation of the compounds [17]. Peaks due to $(Ar\text{-}CH\text{=}CH\text{-}CO)^+$, $(p\text{-}C_6H_5)^+$, $(p\text{-}C_6H_5NH)^+$, $(p\text{-}C_6H_5NHCO)^+$, $(p\text{-}ArC_2H_2)^+$, etc. are characteristic of all the spectra (Table 5). The FAB mass spectra of the Cu(II) complexes showed molecular ion peaks corresponding to $[CuL_2]$ stoichiometry of the complexes. Peaks correspond to CuL^+, L^+, fragments of L^+ are also present in the spectra. The spectra of all the chelates contain a number of fragments containing copper in the 3:1 natural abundance of ^{63}Cu and ^{65}Cu isotopes (Table 5).

ESR spectra. The ESR spectra of the copper(II) complexes of HL^1 and HL^2 were recorded at 77 K in DMF solution. The observed g and A values (Table 6) are comparable to that reported for copper acetoacetanilide [18]. This suggests the presence of appreciable delocalization in the chelate ring.

Electronic spectra. The UV spectra of the unsaturated β-ketoanilides show two broad bands with maxima at ~380 nm and ~260 nm due to the various $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. In complexes these absorption maxima shifted appreciably to low wave numbers. The Cu(II) complexes showed a broad visible band, λ_{max} at ~15,000 cm^{-1}. This, together with the measured μ_{eff} values (~1.72 BM) suggests the square-planar geometry [19]. In agreement with this, spectra recorded in pyridine revealed a broad band centered at ~11,000 cm^{-1} which indicates the formation of octahedral pyridine adducts. The observed diamagnetism and broad

Table 7. Antimicrobial Activity (Diameter Inhibition Zone in mm) of Unsaturated β-Ketoanilides and their Metal Complexes

Compound	*Aspergillus niger*	*Aspergillus parasiticus*	*Rhizopus oryzae*
Nystatin	10	10	10
HL^1	22	18	14
HL^2	20	16	12
HL^3	21	16	10
$[NiL^1_2]$	18	14	10
$[NiL^2_2]$	16	15	10
$[NiL^3_2]$	17	12	10
$[CuL^1_2]$	20	16	10
$[CuL^2_2]$	16	14	10
$[CuL^3_2]$	16	13	10
$[ZnL^1_2]$	14	12	10
$[ZnL^2_2]$	12	12	11
$[ZnL^3_2]$	12	11	10

L = Deprotonated ligand.

medium-intensity band at ~17,600 cm^{-1} in the spectra of the Ni(II) chelates suggest their square-planar geometry. In conformity, the spectra of the chelates in pyridine solution (10^{-3} M) showed three bands corresponding to configurational change to octahedral due to the association of pyridine. The three well-separated absorption bands at λ_{max} ~8,145, ~13,340 and ~24,455 cm^{-1} correspond to the transitions; $^3A_{2g} \rightarrow {}^3T_{2g}$; $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ respectively.

Biological studies. Unsaturated β-dicarbonyl compounds such as curcuminoids are known to possess antifungal and antimicrobeal activities in addition to their numerous biological significance [1-7,20]. Since the unsaturated β-ketoanilides are structurally related to curcuminoids, the antifungal activity of these compounds and their typical metal complexes were also studied by disk diffusion technique [21] using agar nutrient as the medium. A 1000 ppm solution of Nystatin in DMSO was used as the standard. Stock solutions (10^{-3} M) were prepared by dissolving the compounds in DMSO solution. A well was made on the agar medium inoculated with the microorganism and was filled with the test solution using a micropipette. The plate was incubated at 35 ºC for 24 h. During this period the test solution diffused and growth of the inoculated microorganism was affected. The antifungal activity was measured by noting the diameter of the inhibition zone around each well.

The three different fungal strains used include *Aspergillus niger, Aspergillus parasiticus*, and *Rhizopus oryzae*. The results reveal that the compounds possess significant activity against all the tested organisms, and the free ligands exhibited more activity than their metal complexes. HL^1, which possess an -OH group in the aromatic ring, show maximum activity (Table 7).

Characterization of Unsaturated Diketoanilides and their Metal Complexes

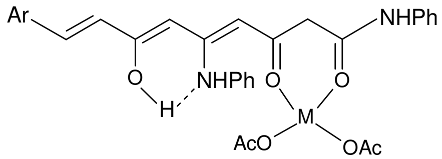
On column chromatographic separation, about 30% of the unsaturated diketoanilide was obtained. The compounds are stable, show sharp melting points and are soluble in common organic solvents. Elemental analysis (Table 8), IR, ^1H NMR and mass spectral data of the compounds are in agreement

Table 8. Physical and Analytical Data of Unsaturated Diketoanilides and their Metal Complexes

Compound/ Empirical formula	M.P. (°C)	Yield (%)	Elemental analysis: Found (Calcd.)%			
			C	H	N	M
L^a	122	35	73.49	5.40	6.31	-
$(C_{27}H_{24}N_2O_4)$			(73.64)	(5.45)	(6.36)	
L^b	114	32	73.88	5.98	6.32	-
$(C_{28}H_{26}N_2O_4)$			(74.01)	(5.73)	(6.17)	
L^c	98	28	71.45	4.87	6.12	-
$(C_{27}H_{23}ClN_2O_3)$			(70.59)	(5.01)	(6.10)	
$[NiL^a(OAc)_2]$	190	68	60.30	4.84	4.60	9.54
$(C_{31}H_{30}N_2NiO_8)$			(60.32)	(4.86)	(4.54)	(9.52)
$[NiL^b(OAc)_2]$	212	70	60.52	5.14	4.44	9.64
$(C_{32}H_{32}N_2NiO_9)$			(60.98)	(4.92)	(4.45)	(9.32)
$[NiL^c(OAc)_2]$	232	75	54.58	4.43	4.24	8.76
$(C_{31}H_{29}ClN_2NiO_8)$			(55.55)	(4.18)	(4.18)	(8.77)
$[CuL^a(OAc)_2]$	198	70	59.74	4.80	4.54	10.24
$(C_{31}H_{30}CuN_2O_8)$			(59.85)	(4.83)	(4.50)	(10.22)
$[CuL^b(OAc)_2]$	166	66	60.14	4.74	4.76	9.87
$(C_{32}H_{32}CuN_2O_9)$			(60.52)	(4.89)	(4.41)	(10.01)
$[CuL^c(OAc)_2]$	178	65	56.43	4.34	4.22	9.53
$(C_{31}H_{29}ClCuN_2O_8)$			(55.15)	(4.15)	(4.15)	(9.42)
$[ZnL^a(OAc)_2]$	156	68	59.54	4.92	4.41	10.44
$(C_{31}H_{30}N_2O_8Zn)$			(59.67)	(4.81)	(4.49)	(10.49)
$[ZnL^b(OAc)_2]$	168	74	60.78	4.88	4.76	10.24
$(C_{32}H_{32}N_2O_9Zn)$			(60.34)	(4.87)	(4.40)	(10.27)
$[ZnL^c(OAc)_2]$	196	65	55.68	4.78	4.23	9.76
$(C_{31}H_{29}ClN_2O_8Zn)$			(55.00)	(4.14)	(4.14)	(9.67)

-OAc = Acetate

with structure **2**. These compounds formed well defined and crystalline complexes with acetate salts of Cu(II), Ni(II), and Zn(II) ions. The observed C, H, N and metal percentages suggest $[ML(OAc)_2]$ stoichiometry for the complexes (Table 8). All metal complexes are non-electrolytes in DMF (specific conductance < 10 Ω^{-1} cm^{-1}; 10^{-3} M solution). The Ni(II) and Zn(II) chelates are diamagnetic while Cu(II) complexes showed normal paramagnetic moment. The observed IR, ^1H NMR and mass spectra of the complexes are fully consistent with the structure **4**.



M = Ni(II), Cu(II), Zn(II)

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Infrared spectra. The spectra of all the unsaturated diketoanilides show three strong bands at ~1720 cm^{-1}, ~1660 cm^{-1} and ~1620 cm^{-1} assignable to the stretching of the amide carbonyl (amide I), alkenyl carbonyl and the partially enolized

Table 9. IR and Mass Spectral Data of Unsaturated Diketoanilides

Compound	IR bands (cm^{-1})			Mass spectral data (m/z)
	ν (C=O) amide I	ν (C=O) olefinic	ν (C=O) cinnamoyl	
L^a	1722 s	1660 s	1618 s	440, 363, 348, 347, 323, 320, 306, 293, 286, 279, 278, 256, 162, 161, 147, 134, 120, 119
L^b	1718 s	1662 s	1617 s	454, 377, 362, 334, 300, 292, 270, 162, 134, 120
L^c	1720 s	1658 s	1619 s	459, 382, 305, 367, 275, 339, 325, 297, 120, 134, 162

Table 10. Characteristic IR Stretching Bands and Mass Spectral Data of the Cu(II) Complexes of Unsaturated Diketoanilides

Complex	IR (cm^{-1})					Mass spectral data (m/z)
	(C=O) cinnamoyl	(C=O) metal chelated	(C=C) phenyl/ (C=C) alkenyl/ amide II	amides III, IV, V &VI	(M-O)	
$[CuL^a(OAc)_2]$	1621 s	1632 s	1592 m,1545 m, 1498 m,1530 m	1248 m, 656 m, 693 m, 617 m	418 m 468 m	623, 621, 564, 562, 529, 531, 505, 503, 440, 439, 437, 363, 320, 278,162, 161, 134, 120
$[CuL^b(OAc)_2]$	1619 s	1636 s	1545 m,1516 m, 1490 m,1514 m	1238 m, 654 m, 691 m, 604 m	422 m 470 m	637, 635, 578, 576, 519, 517, 545, 543, 454, 377, 362, 334, 300, 292, 270, 134, 120
$[CuL^c(OAc)_2]$	1619 s	1641 s	1580 m,1541 m, 1498 m,1518 m	1234 m, 656 m, 690 m, 618 m	426 m 482 m	642, 640, 583, 581, 522, 524, 548, 550, 172, 235, 237, 294, 296, 353, 355, 459, 305, 120

cinnamoyl carbonyl functions of structure **2**, respectively (Table 9). Spectra of the compounds in the region below 1600 cm^{-1} show several medium intensity bands due to various C=C and C-N stretching vibrations and to N-H, N-C=O bending, etc. IR spectra of all the compounds showed a prominent band at ~970 cm^{-1} typical of *trans* -CH=CH- absorption. The broad band in the region 2800-3500 cm^{-1} suggests the existence of the compounds predominantly in the intramolecular hydrogen bonded enolic form [13]. This broad band remained almost unaffected in the IR spectra of the complexes, indicating that the enolic OH is not replaced during complex formation. The band at ~1720 cm^{-1} of the free ligand disappeared in the spectra of all complexes and instead a comparatively broad and intense band appeared at ~1640 cm^{-1} (Table 10). The partially enolised cinnamoyl carbonyl stretching of the free ligand at ~1620 cm^{-1} remained unaltered in the spectra of all

Table 11. ^{1}H NMR Spectral Data of Unsaturated Diketoanilides and their Ni(II) and Zn(II) Complexes

Compound	Enolic OH	NH	Methine	Methylene	CH=CH	Acetate	Phenyl substituent
L^a	13.18 (singlet)	10.10 (singlet) 9.88 (singlet)	5.97 (singlet)	3.58 (singlet)	8.26 (doublet) 8.08 (doublet)	-	10.05 (singlet)
L^b	12.50 (singlet)	9.99 (singlet) 9.78 (singlet)	5.89 (singlet)	3.50 (singlet)	8.30 (doublet) 8.02 (doublet)	-	3.84 (singlet)
L^c	12.14 (singlet)	9. 98 (singlet) 9. 81 (singlet)	6.01 (singlet)	3.59 (singlet)	8.34 (doublet) 8.16 (doublet)	-	-
$[NiL^a(OAc)_2]$	13.16 (singlet)	10.04 (singlet) 9.86 (singlet)	5.96 (singlet)	4.18 (singlet)	8.30 (doublet) 8.10 (doublet)	2.56 (singlet)	10.05 (singlet)
$[NiL^b(OAc)_2]$	12.48 (singlet)	9.96 (singlet) 9.76 (singlet)	5.87 (singlet)	4.20 (singlet)	8.32 (doublet) 8.08 (doublet)	2.54 (singlet)	3.85 (singlet)
$[NiL^c(OAc)_2]$	12.12 (singlet)	9.96 (singlet) 9.81 (singlet)	6.03 (singlet)	4.14 (singlet)	8.36 (doublet) 8.18 (doublet)	2.58 (singlet)	-
$[ZnL^a(OAc)_2]$	13.18 (singlet)	10.08 (singlet) 9.84 (singlet)	5.99 (singlet)	4.12 (singlet)	8.32 (doublet) 8.12 (doublet)	2.54 (singlet)	10.04 (singlet)
$[ZnL^b(OAc)_2]$	12.52 (singlet)	9.95 (singlet) 9.76 (singlet)	5.85 (singlet)	4.16 (singlet)	8.34 (doublet) 8.04 (doublet)	2.56 (singlet)	3.84 (singlet)
$[ZnL^c(OAc)_2]$	12.14 (singlet)	9.94 (singlet) 9.84 (singlet)	6.01 (singlet)	4.16 (singlet)	8.38 (doublet) 8.20 (doublet)	2.54 (singlet)	-

the chelates. These indicate that the amide and alkenyl carbonyl groups are involved in coordination with the metal ion. Monodentate acetate usually shows two bands at ~1620 cm^{-1} and ~1310 cm^{-1} due to antisymmetric and symmetric stretching, respectively [12]. Since carbonyl absorption of the compounds also appeared in this region, the band at ~1620 cm^{-1} could not be located. However, a medium intensity band observed at ~1320 cm^{-1} suggests the monodentate coordination of the acetate groups. That the carbonyl groups are involved in bonding with the metal as in structure **4** is further supported by the appearance of two medium intensity bands in the region 420-480 cm^{-1} assignable to ν_{M-O} vibrations [12]. Thus, the IR spectra of complexes support the neutral bidentate coordination of the unsaturated diketoanilides.

^{1}H NMR spectra. The ^{1}H NMR spectra of the compounds displayed a one-proton singlet at ~13 ppm due to the intramolecularly hydrogen bonded enolic proton [14,15]. Two one-proton signals at ~10.00 ppm and ~9.80 ppm indicate the different electronic environment of the two NH protons (Table 11). The methine proton of structure **2** appeared at ~6.00 ppm and the aromatic protons in the range 7.00-8.00 ppm. The enolic and NH proton signals of the free ligand remained almost unaffected in the ^{1}H NMR spectra of the diamagnetic Ni(II) and Zn(II) complexes indicating the non-involvement of these protons in complexation. Unlike in the spectra of the ligands, the complexes show a signal at ~2.50 ppm due to methyl protons of acetate groups. That the phenolic OH group of L^a is not involved in bonding with the metal ion is clearly indicated [16] in the spectra of their complexes where the phenolic signal remains unaltered (Table 11).

Table 12. ESR parameters of Cu(II) complexes of unsaturated diketoanilides in DMF at 77 K

Cu(II) complexes of	$g_{\|}$	$g_{\perp}$	$A_{\|} \times 10^{-4}$ (cm^{-1})	$A_{\perp} \times 10^{-4}$ (cm^{-1})
L^a	2.268	2.051	156	45.5
L^b	2.262	2.058	161	44.1

Mass spectra. Mass spectra of all the unsaturated diketoanilides showed intense molecular ion peak, $P^+/(P + 1)^+$ thereby confirming the formulation of the compounds [17]. Peaks due to $[\text{Ar-CH=CH-C=O}]^+$, $[\text{Ar-CH=CH(C=O)-CH}_2]^+$ and $[p\text{-C}_6\text{H}_5\text{NHCO}]^+$ confirm the condensation of the γ-methyl group of acetoacetanilide with aromatic aldehyde (Table 9). The FAB mass spectra of the Cu(II) complexes show intense molecular ion peak due to $[\text{CuL(OAc)}_2]$. Peaks due to the removal of one or both acetate groups, $[\text{CuL}]^+$ and L^+ are characteristic of all the spectra. The spectra of all the chelates contain a number of fragments containing copper in the 3:1 natural abundance of ^{63}Cu and ^{65}Cu isotopes (Table 10).

ESR spectra. The ESR spectra of the copper(II) complexes of L^a and L^b were recorded at 77 K in DMF solution. The observed g and A values (Table 12) are comparable to that reported for copper acetoacetanilide [18]. This suggests the presence of appreciable delocalization in the chelate ring.

Electronic spectra. The UV spectra of the diketoanilides show two broad bands with maxima at ~370 nm and ~265 nm due to the various $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. The absorption maxima of the metal chelates bear close resemblance with the free ligands which indicates that no structural alteration of the ligand has occurred during complexation. However, the values shifted slightly to longer wavelength in the spectra of the metal complexes indicating the involvement of the carbonyl group in metal complexation. In the copper(II) complexes the presence of a broad visible band at ~15,000 cm^{-1} and the measured μ_{eff} values (1.75-1.81 B.M.) support the square-planar structure [19]. The observed diamagnetism and broad medium-intensity band at ~17,800 cm^{-1} in the visible spectra of the nickel(II) chelates undoubtedly suggest their square planar geometry. In conformity, visible spectra of the chelates in pyridine solution (10^{-3} M) showed three bands corresponding to a configurational change from square planar to octahedral due to the association of pyridine. The three well-separated absorption bands at $\lambda_{\max}$ ~8,230, ~13,560 and ~24,350 cm^{-1} correspond to the transitions $^3A_{2g} \rightarrow {}^3T_{2g}$; $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ respectively.

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