Metal complexes of unsaturated polycarbonyl compounds derived from benzoyl acetone and aromatic aldehydes

Muhammed Basheer Ummathur [a,*], Anjali Krishnan [a], Mathew Paul Ukken [b]

[a] Department of Chemistry, Unity Women's College, Manjeri, Kerala-676122, India
[b] Department of Chemistry, Christ College, Irinjalakuda, Kerala-680125, India

Abstract

Condensation of aromatic aldehydes with benzoyl acetone under specified conditions yielded two series of polycarbonyl compounds in which the keto group is attached to olefinic linkage. Spectral and analytical data revealed the formation of an unsaturated triketone from pyridine-3-carbaldehyde and unsaturated diketone from furfural, salicylaldehyde and 2-hydroxynaphthaldehyde. Analytical, IR, ^{1}H NMR and mass spectral data suggest neutral bidentate coordination for the unsaturated triketone with Ni(II), Cu(II) and Zn(II) ions. In the [ML$_2$] complexes of the unsaturated diketones, the intramolecularly hydrogen bonded enol proton is replaced by the metal ion.

1. Introduction

Extensive literature is available on the synthesis, structural characterization and applications of metal complexes of β-diketones, in which the carbonyl groups are directly attached to alkyl/aryl functions [1]. However reports are scanty on β-diketones in which the keto group attached to olefinic linkage. In recent years a number of β-dicarbonyl compounds in which the carbonyl function(s) bonded to olefinic linkage(s) have gained considerable importance [2-4] mainly because of the fact that such compounds are structurally related to the active chemical constituents of several traditional medicinal plants. For instance, curcuminoids, the active chemical components present in the Indian medicinal plant turmeric (*Curcuma longa,* Linn, *Zingiberacea* family) contain three β-dicarbonyl compounds in which the diketo function is directly linked to –CH=CH– groups [5]. Such 'unsaturated' β-dicarbonyl compounds and their metal complexes possess interesting biochemical properties such as antitumour, antioxidant, antifungal and antimicrobial activities [2-4,6]. In continuation of our studies on unsaturated polycarbonyl compounds and their metal complexes [2,3,7] we here report the synthesis and characterization of two series of polycarbonyl compounds in which the keto function is directly bonded to a -CH=CH- group. Typical metal complexes of these compounds were also synthesized and characterized.

---

* Corresponding author. Tel.: +91 9446885154, fax: +91 4832767142.
 E-mail address: mbummathur@rediffmail.com (M.B. Ummathur)

2. Experimental

Carbon, hydrogen and nitrogen percentages were determined by microanalyses (Heraeus Elemental analyzer) and metal contents of complexes by AAS (Perkin Elmer 2380). The electronic spectra of the compounds in methanol (10^{-4} mol L^{-1}) were recorded on a 1601 Shimadzu UV-Vis. spectrophotometer, IR spectra (KBr discs) on an 8101 Shimadzu FTIR spectrophotometer, ^{1}H NMR spectra (CDCl$_3$ or DMSO-d$_6$) on a Varian 300 NMR 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 ($\sim 10^{-3}$ mol L^{-1}) at 28±1 °C. Magnetic susceptibilities were determined at room temperature on a Guoy type magnetic balance.

2.1. Synthesis of unsaturated carbonyl compounds (HL^1, HL^2, HL^3 and L^a)

The unsaturated carbonyl compounds were synthesized by the reaction of aromatic aldehydes with benzoyl acetone in presence of boric oxide and tri(*sec*-butyl)borate using *n*-butylamine as the condensing agent. The aldehydes used for the condensation reaction were furfural, salicylaldehyde, 2-hydroxynaphthalene-1-carbaldehyde and pyridine-3-carbaldehyde. A typical procedure for the synthesis is given below.

Benzoyl acetone (0.01 mol) and boric oxide (0.005 mol) were mixed and made into a paste with dry ethyl acetate and stirred for ~1 h at room temperature. To this, a solution of aromatic aldehyde (0.01 mol) and tri(*sec*-butyl)borate (0.02 mol) dissolved in dry ethyl acetate (~15 mL) was added and stirred for ~3 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 (~70 °C) HCl (0.4 M, 7.5 mL) was added and again stirred for ~1 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 mol L^{-1} HCl was added and stirred for ~1 h. The precipitate formed was filtered, washed with water, ethanol and dried in vacuum. The compounds were recrystallized from hot benzene to get chromatographically (TLC) pure material.

2.2. Synthesis of Cu(II), Ni(II) and Zn(II) complexes

To a refluxing solution of the compound in ethanol (0.002 mol, 20 mL) an aqueous solution of the metal(II) acetate (0.001 mol, 15 mL) was added and the reaction mixture was refluxed for ~2 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.

2.3. Determination of antimicrobeal activity

The four different fungal strains used were *Aspergillus niger, Aspergillus parasiticus, Rhizopus oryzae* and *Candida albicans*. The organism selected for antibacterial study was *Staphylococcus aureus*. The cup-plate technique was employed for antifungal activity and disk diffusion technique [8, 9] for antibacterial activity. Nutrient agar media was used for maintaining pure fungal/bacterial culture and to lawn the fungus/bacteria for detecting the antimicrobial activity. It was prepared by dissolving peptone (1 g), meat extract (0.5 g), NaCl (0.5 g) and agar (2.5 g) in distilled water (100 mL) and adjusting the pH of the medium to 7.2-7.4 using 10 % NaOH. Subaraud's agar media was used for maintaining pure culture of all four fungi. It was prepared by dissolving peptone (1g), D-glucose (4 g) and agar (2.5 g) in distilled water (100 mL) and adjusting the pH of the medium about 5.6-6.0 using 10% HCl. Nutrient broth was used for preparing broth culture of the test fungus/bacteria and its composition was the same as that of nutrient agar, excluding agar. Normal saline was used as a suspension of

fungal/bacterial spores for lawning. It was prepared by dissolving NaCl (0.95 g) in distilled water (100 mL). Solutions of the test compounds were prepared in DMSO and for sterilizing, all the media used were autoclaved at 121 °C for 20 min.

The fungi *Aspergillus niger*, *Aspergillus paraciticus* and *Rhizopus oryzae* species, suspension of spores were prepared in normal saline. For this each fungus were grown on subaraud's glucose agar till they get sporulated. These spores were scrapped off and suspended in about 3.5 mL of normal saline. In the case of *Candida albicans* the suspension was made by using the cells collected from the slope of the subaraud's agar.

To prepare the mat growth of fungi on petriplates, this spore suspension was poured on the surface of the plates. Plates were allowed to dry in an incubator at 37 °C for 1h. Using an agar punch, wells (10 mm) were made on these plates. In each well 75 μls (2000 ppm, 10^{-3} mol L^{-1}) of the compounds in DMSO were added along with DMSO and standard nystatin in separate wells and the mixture was incubated at 30 °C for 36 h. During this period, the test solution was 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 (mm).

In the case of antibacterial activity a uniform lawn of bacteria *Staphylococcus* (gm +ve) was spread evenly in petriplates as in the case for fungus. Discs impregnated with the compound in DMSO were placed and the antibacterial activity measured from the diameter of the zone of inhibition (mm).

3. Results and discussion

Unsaturated β-diketones such as naturally occurring curcuminoids are generally synthesized by Claisen type condensation of aromatic aldehydes with β-diketones containing at least one acetyl group. The reaction is usually carried out in presence of boric oxide and tri(*sec*-butyl)borate in order to prevent the more facile Knoevenagal type condensation [5]. Condensation of aromatic aldehydes with acetyl acetone leads to the formation of both mono and bis condensation products [2,3]. In the case of benzoyl acetone only the monocondensation product, unsaturated diketone, is obtained by Claisen reaction as in Scheme 1.
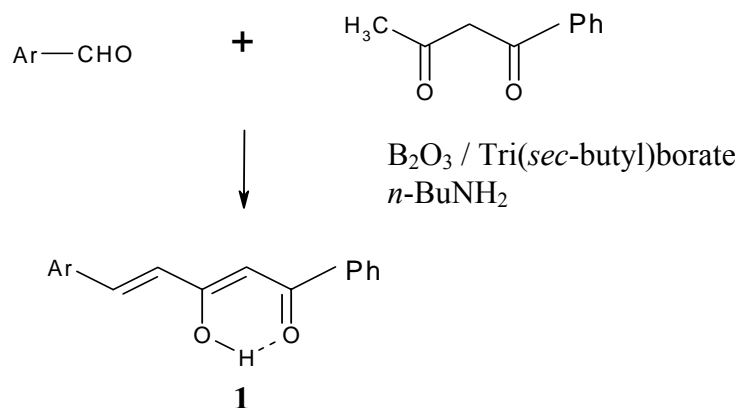
Compound	Ar-
HL^1	2-Furyl
HL^2	2-Hydroxyphenyl
HL^3	2-Hydroxy-1-naphthyl

Scheme 1

However condensation of pyridine-3-carbaldehyde with benzoyl acetone yielded an unsaturated triketone by both Claisen and Knoevenagal condensations as in Scheme 2. These data of the compounds are discussed separately.

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

2
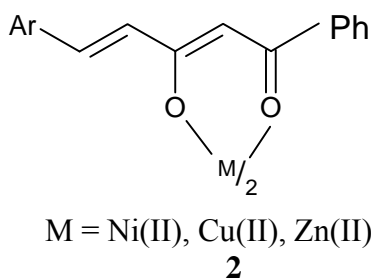
Table 1

Physical and analytical data of the unsaturated carbonyl compounds and their metal complexes.

Compound/ Empirical formula	Yield %	M.P. ^{0}C	Elemental Analysis: Found (Calculated)%			
			C	H	N	M
HL^1 C$_{15}$H$_{12}$O$_3$	54	103	74.94 (75.00)	5.04 (5.00)	-	-
HL^2 C$_{17}$H$_{14}$O$_3$	65	112	76.60 (76.69)	5.28 (5.26)	-	-
HL^3 C$_{21}$H$_{16}$O$_3$	60	140	79.64 (79.75)	5.08 (5.06)	-	-
L^a C$_{26}$H$_{21}$NO$_3$	65	112	78.84 (78.99)	5.32 (5.32)	3.56 (3.54)	-
[NiL$^1_2$] C$_{30}$H$_{22}$NiO$_6$	60	160	67.17 (67.08)	4.16 (4.10)	-	10.96 (10.94)
[NiL$^2_2$] C$_{34}$H$_{26}$NiO$_6$	65	130	69.25 (69.30)	4.44 (4.42)	-	10.06 (9.97)
[NiL$^3_2$] C$_{42}$H$_{30}$NiO$_6$	60	120	73.04 (73.18)	4.34 (4.36)	-	8.41 (8.52)
[NiL^a(OAc)$_2$] C$_{30}$H$_{27}$NNiO$_7$	65	130	62.88 (62.97)	4.74 (4.72)	2.46 (2.45)	10.28 (10.27)
[CuL$^1_2$] C$_{30}$H$_{22}$CuO$_6$	60	150	66.34 (66.48)	4.02 (4.06)	-	11.70 (11.73)
[CuL$^2_2$] C$_{34}$H$_{26}$CuO$_6$	55	145	68.55 (68.74)	4.33 (4.38)	-	10.60 (10.71)
[CuL$^3_2$] C$_{42}$H$_{30}$CuO$_6$	70	218	72.50 (72.67)	4.30 (4.33)	-	9.22 (9.16)
[CuL^a(OAc)$_2$] C$_{30}$H$_{27}$CuNO$_7$	60	160	62.38 (62.44)	4.66 (4.68)	2.46 (2.43)	11.14 (11.02)
[ZnL$^1_2$] C$_{30}$H$_{22}$O$_6$Zn	70	148	66.38 (66.25)	3.99 (4.05)	-	11.94 (12.03)
[ZnL$^2_2$] C$_{34}$H$_{26}$O$_6$Zn	60	130	68.38 (68.53)	4.36 (4.37)	-	11.14 (10.98)
[ZnL$^3_2$] C$_{42}$H$_{30}$O$_6$Zn	65	150	72.38 (72.48)	4.36 (4.31)	-	9.44 (9.40)
[ZnL^a(OAc)$_2$] C$_{30}$H$_{27}$NO$_7$Zn	70	140	62.36 (62.24)	4.62 (4.67)	2.39 (2.42)	11.44 (11.30)

-OAc - Acetate

3.1. Characterization of unsaturated diketones (HL[1]-HL[3]) and their metal complexes

Analytical, IR, ^{1}H NMR and mass spectral data (Table 1) of the reaction products of benzoyl acetone with aromatic aldehydes (furfural, salicylaldehyde and 2-hydroxynaphthaldehyde) suggest that the condensation has occurred in the 1:1 ratio as in structure 1. The analytical data (Table 1) together with non-electrolytic nature in DMF (specific conductance $<10\Omega^{-1}cm^{-1}$; 10^{-3} mol L^{-1} solution) suggest [ML$_2$] stoichiometry of 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 2 of the complexes.
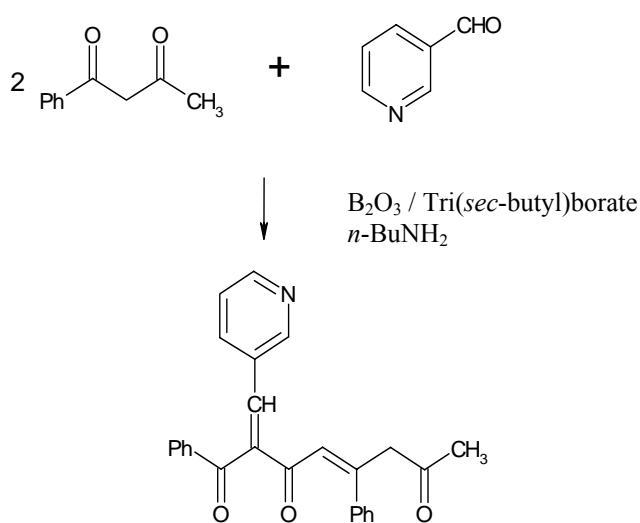
Scheme 2

3.2. Infrared spectra

The spectra of all the unsaturated β-diketones show two intense bands at ~1635 and ~1615 cm^{-1} indicating the existence of the compounds predominantly in the intramoleculearly hydrogen bonded enolic form and enolised towards the cinnamoyl functions [3,10]. This is inferred from the fact that no free benzoyl carbonyl band (~1660 cm^{-1}) or cinnamoyl carbonyl band (~1645 cm^{-1}) are observed in the double bond region of the spectra. The broad band in the region 2500-3500 cm^{-1} also suggests the existence of the compounds predominantly in the enolic form. The spectra of all the compounds showed a prominent band at ~970 cm^{-1} typical of *trans* –CH=CH– group [10].

In the IR spectra of all the complexes the bands at ~ 1645 and 1615 cm^{-1} of the ligands disappeared and two new bands appeared at ~1600 and 1580 cm^{-1} due to metal chelated carbonyl groups [2, 11]. The broad band in the region 2500-3500 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 2 is further supported by the appearance of two medium intensity bands at ~420 cm^{-1} and ~470 cm^{-1} assignable to ν_{M-O} [11] (Table 2).

Table 2
Characteristic IR stretching bands (cm^{-1}) of the unsaturated diketones and their metal complexes.

Compound	C=O benzoyl	C=O cinnamoyl	CH=CH *trans*	M–O
HL^1	1636	1616	970	-
[NiL$^1_2$]	1608	1580	960	469, 428
[CuL$^1_2$]	1610	1582	962	457, 418
[ZnL$^1_2$]	1602	1584	966	460, 424
HL^2	1638	1612	965	-
[NiL$^2_2$]	1604	1576	960	476, 418
[CuL$^2_2$]	1598	1570	972	474, 428
[ZnL$^3_2$]	1600	1574	970	470, 420
HL^3	1635	1614	974	-
[NiL$^3_2$]	1604	1575	973	454, 416
[CuL$^3_2$]	1608	1572	972	468, 418
[ZnL$^2_2$]	1606	1576	968	464, 422

3.3. ^{1}H NMR spectra

The ^{1}H NMR spectra of the unsaturated diketones displayed a one proton signal at ~δ 16 ppm due to the intramolecularly hydrogen bonded enolic proton [12, 13]. The spectra of HL^2 and HL^3 displayed signals at δ13.83 and 13.76 ppm due to the phenolic OH groups. The *trans* orientation of the –CH=CH– group is evident from their observed *J* values (~16 Hz). Integrated intensities of all the protons agree well with the structure 1 of the compounds.

In the ^{1}H NMR spectra of the diamagnetic Ni(II) and Zn(II) complexes the low field signal due to the enol proton of the ligands is absent indicating its replacement by the metal ion during complexation. The methine proton signal shifted appreciably to low field compared to the shift in the olefinic protons. This may be due to the aromatic character that might have been imparted to the C$_3$O$_2$M 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 as in structure 2. That the phenolic OH group of HL^2 and HL^3 are not involved in bonding with the metal ion is clearly indicated [14] in the spectra of their Ni(II) and Zn(II) complexes where the phenolic signal remains unaltered. The assignments of various proton signals observed are assembled in Table 3.

Table 3
^{1}H NMR spectral data (δ, ppm) of the unsaturated diketones and their Ni(II) and Zn(II) complexes.

Compound	Enolic OH	Methine	CH=CH	Aryl	Phenyl substituent
HL^1	16.22	5.98	8.24, 8.06	7.25-7.89	-
[NiL$^1_2$]	-	6.58	8.26, 8.12	7.22-7.82	-
[ZnL$^1_2$]	-	6.54	8.24, 8.06	7.26-7.90	-
HL^2	16.30	5.94	8.34, 8.06	7.26-7.82	13.83
[NiL$^2_2$]	-	6.52	8.38, 8.10	7.20-7.92	13.81
[ZnL$^2_2$]	-	6.48	8.34, 8.09	7.26-7.82	13.83
HL^3	16.08	5.82	8.33, 8.13	7.26-7.86	13.76
[NiL$^3_2$]	-	6.46	8.36, 8.16	7.30-7.96	13.74
[ZnL$^3_2$]	-	6.52	8.37, 8.15	7.28-7.82	13.75

3.4. Mass spectra

Mass spectra of all the unsaturated β-diketones showed intense molecular ion peak, thereby confirming the formulation of the compounds [15]. Peaks due to (Ar-CH=CH-CO)$^+$, (P – C$_6$H$_5$)$^+$, (P - C$_6$H$_5$CO)$^+$, (P - ArC$_2$H$_2$)$^+$, etc. are characteristic of all the spectra. The FAB mass spectra of the Cu(II) complexes showed molecular ion peaks corresponding to [CuL$_2$] stoichiometry. Peaks correspond to [CuL]$^+$, L$^+$ and 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 4).

Table 4
Mass spectral data of unsaturated carbonyl compounds and their Cu(II) complexes.

| Compound	Mass spectral data (m/z)
HL^1	240, 163, 147, 135, 121, 119, 105, 93
HL^2	266, 189, 161, 147, 119, 105
HL^3	316, 239, 211, 197, 169, 147, 119, 105
L^a	395, 380, 352, 338, 318, 290, 236, 208, 187
[CuL$^1_2$]	543, 541, 466, 464, 450, 448, 438, 436, 422, 420, 389, 387, 357, 355, 333, 331, 301, 299, 240, 163, 147,135, 121, 119
[CuL$^2_2$]	595, 593, 518, 516, 490, 488, 476, 474, 448, 446, 441, 439, 385, 357, 355, 301, 299, 283, 266, 189, 161, 147,119
[CuL$^3_2$]	695, 693, 618, 616, 590, 588, 541, 539, 526, 524, 498, 496, 485, 483, 357, 355, 316, 301, 299, 239, 211, 169, 147, 119
[CuL^a(OAc)$_2$]	578, 576, 519, 517, 460, 458, 395, 380, 352, 338, 318, 290, 208, 236, 187

3.5. Electronic spectra

The UV spectra of the unsaturated β-diketones show two broad bands with maxima at ~380 nm and ~270 nm due to the various n→π* and π→π* transitions. In complexes these absorption maxima shifted appreciably to low wave numbers. The Cu(II) complexes showed a broad visible band, λ_{max} at ~14,750 cm^{-1}. This, together with the measured μ_{eff} values (~1.74 BM) suggests the square-planar geometry [16]. In agreement with this, spectra recorded in pyridine, a broad band centered at ~11,000 cm^{-1} was observed which indicates the formation of octahedral pyridine adducts. The observed diamagnetism and broad medium-intensity band at ~17,800 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} mol L^{-1}) showed three bands corresponding to configurational change to octahedral due to the association of pyridine. The three well-separated absorption bands at λ_{max} ~8,000, ~13,500 and ~24,000 cm^{-1} correspond to the transitions; ^{3}A$_{2g}$ →^{3}T$_{2g}$; ^{3}A$_{2g}$ →^{3}T$_{1g}$(F) and ^{3}A$_{2g}$ →^{3}T$_{1g}$(P) respectively.

3.6. Characterization of unsaturated triketone (L^a) and its metal complexes

The compound is stable, show sharp melting point and is soluble in common organic solvents. Elemental analysis (Table 1), IR, ^{1}H NMR, and mass spectral data of the compound

are in agreement with structure 3. The compound 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 $[ML^a(OAc)_2]$ stoichiometry of the complexes (Table 1). 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 the Cu(II) complex showed a normal paramagnetic moment (1.76 BM). The observed IR, ^{1}H NMR and mass spectra of the complexes are fully consistent with the structure 4.

M = Ni(II), Cu(II), Zn(II)   **4**
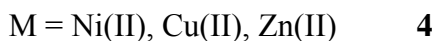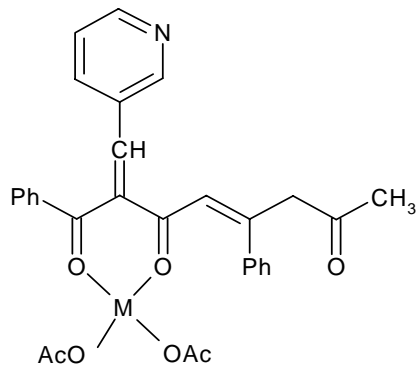
3.7. Infrared spectra

The spectrum of the unsaturated triketone show three strong bands at 1710 cm^{-1}, 1660 cm^{-1} and 1650 cm^{-1} assignable respectively to the stretching of the acetyl carbonyl, alkenyl carbonyl and the benzoyl carbonyl [2,10] functions of structure 3. Unlike in the spectra of the unsaturated diketones, the compound do not show broad band in the region 2500-3500 cm^{-1} suggesting the existence of the compound predominantly in the triketo form. The bands at 1660 and 1650 cm^{-1} of the free ligand disappeared in the spectra of all the complexes and instead a comparatively broad and intense band appeared at ~1630 cm^{-1}. The free acetyl carbonyl stretching of the free ligand at 1710 cm^{-1} remained unaltered in the spectra of all the chelates. These indicate that the benzoyl and alkenyl carbonyl groups are involved in coordination with the metal ion and acetyl carbonyl is excluded from coordination [2,11]. Monodentate acetate usually show two bands at ~1620 cm^{-1} and ~1310 cm^{-1} due to antisymmetric and symmetric stretching respectively. 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} suggest the monodentate coordination of the acetate groups [11]. 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 [11]. Thus IR spectra of the complexes support the neutral bidentate coordination of the unsaturated triketone. Important bands that appeared in the spectra are given in Table 5.

Table 5
Characteristic IR stretching bands (cm^{-1}) of the unsaturated triketone and its metal complexes.

Compound	C=O acetyl	C=O olefinic	C=O cinnamoyl	M–O
L^a	1710	1660	1650	-
$[NiL^a_2]$	1708		1630	420, 480
$[CuL^a_2]$	1710		1626	423, 476
$[ZnL^a_2]$	1713		1622	428, 472

3.8. ^{1}H NMR spectra

The ^{1}H NMR spectrum of the unsaturated triketone do not displayed any band above δ 10 ppm indicating the existence of the compound predominantly in the triketo form [12, 13]. The compound displayed a signal at δ 2.21 ppm assignable to methyl protons of acetyl group. The methylene proton signal is appeared at δ 3.58 ppm. The signals at δ 5.96 and 6.12 ppm are due to methine protons. The phenyl and pyridyl protons appeared as a complex multiplet in the range δ 7.43 to 7.90 ppm. Integrated intensities of all the protons agree well with the structure 3 of the compound. In the ^{1}H NMR spectra of the diamagnetic Ni(II) and Zn(II) complexes two new signals appeared at ~δ 2.40 and 2.60 ppm due to methyl protons of acetate groups. Integrated intensities of all other signals do not show much variation from the ligand spectrum and agree well with the formulation of the complexes as in structure 4. The assignments of various proton signals observed are assembled in Table 6.

Table 6
^{1}H NMR spectral data (δ, ppm) of the unsaturated triketone and its Ni(II) and Zn(II) complexes.

Compound	CH_3CO	Methine	CH_2	Aryl/ Pyridyl	CH_3COO
L[a]	2.21	5.96, 6.12	3.58	7.43-7.90	-
[NiL[a](OAc)$_2$]	2.19	5.98, 6.14	3.60	7.23-7.80	2.40, 2.62
[ZnL[a](OAc)$_2$]	2.22	6.02, 6.17	3.62	7.36-7.88	2.38, 2.60

3.9. Mass spectra

The formation of the compound is well confirmed from the presence of an intense P^+ peak at m/z 395 in its mass spectrum. Peaks due to $(P - C_6H_5)^+$, $(P - C_6H_5CO)^+$, $(P - CH_3CO)^+$, etc. are characteristic of the spectrum. That the compound contains an acetyl group is clearly indicated with the appearance of an intense $(P - 43)^+$ peak. The FAB mass spectrum of the Cu(II) complex show intense molecular ion peak due to [CuL[a](OAc)$_2$]. Peaks due to the removal of one or both acetate groups, [CuL]$^+$ and L$^+$ are characteristic of the spectrum. The spectrum of the chelate contain a number of fragments containing copper in the 3:1 natural abundance of ^{63}Cu and ^{65}Cu isotopes (Table 4).

3.10. Electronic Spectra

The UV spectrum of the unsaturated triketone showed two broad bands with maxima at 380 nm and 260 nm due to the various n→π* and π→π* transitions. The absorption maxima of the metal chelates bear close resemblance with the free ligand 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 [17] indicating the involvement of the carbonyl group in metal complexation. In the Cu(II) complex the presence of a broad visible band at 15,000 cm^{-1} and the measured μ_{eff} value (1.75 B.M.) support the square-planar structure [16]. The observed diamagnetism and broad medium-intensity band at 17,800 cm^{-1} in the visible spectrum of the Ni(II) chelate undoubtedly suggest its square planar geometry. In conformity, the visible spectrum of the chelate in pyridine solution (10^{-3} M) showed three bands corresponding to configurational change from square planar to octahedral due to the association of pyridine. The three well-separated absorption bands at λ_{max} 8,240, 13,550 and 24,360 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.

3.1. Antimicrobial studies

Various biological activities exhibited by unsaturated β-diketones such as curcuminoids have been the subject of numerous physiological and clinical studies [2-4,7]. In the present study the antifungal and antibacterial activities of the unsaturated carbonyl compounds and their metal complexes were carried out.

Table 7
Antimicrobial activity (diameter inhibition zone in mm) of the unsaturated diketones and their metal complexes.

Compound	*Aspergillus niger*	*Aspergillus parasiticus*	*Rhizopus oryzae*	*Candida albicans*
DMSO	10	10	10	10
Nystatin	12	12	11	12
HL^1	14	13	14	13
HL^2	18	16	18	15
HL^3	20	26	25	20
$[NiL^1_2]$	12	12	11	11
$[NiL^2_2]$	14	14	12	12
$[NiL^3_2]$	16	21	12	20
$[CuL^1_2]$	16	14	14	15
$[CuL^2_2]$	26	14	14	15
$[CuL^3_2]$	29	18	18	20
$[ZnL^1_2]$	14	11	10	10
$[ZnL^2_2]$	14	12	14	13
$[ZnL^3_2]$	14	13	14	14

The data (Table 7) revealed that unsaturated diketones possess antifungal activity comparable to that of the drug Nystatin. Among the compounds, HL^2 and HL^3, which contain an OH group in the *ortho* position of the aryl ring were found to be highly active against all the four fungal strains studied, as in curcuminoids [2]. In many cases metal complexation increased the activity of the unsaturated diketones. Among the chelates, Cu(II) complexes are found to be highly active. The studies of the antibacterial activity of the unsaturated diketones and their metal complexes revealed that none of them showed significant activity against *Styphylococcus aureus*. The unsaturated triketone and its metal complexes did not show significant activity against all of the tested microbes.

4. Conclusion

The reaction between benzoyl acetone and aromatic aldehydes under specified conditions yielded two types of unsaturated carbonyl compounds. Spectral and analytical data revealed the formation of an unsaturated triketone from pyridine-3-carbaldehyde and unsaturated diketone from furfural, salicylaldehyde and 2-hydroxynaphthaldehyde. The existence of the unsaturated diketones in the intramolecularly hydrogen bonded enol form has been well demonstrated from their analytical and spectral data. Analytical, physical and spectral data of their [ML$_2$] complexes with Ni(II), Cu(II), and Zn(II) showed the monobasic bidentate coordination in which the intramolecularly hydrogen bonded enolic proton is replaced by metal cation.

The antifungal studies reveal that the compounds possess significant activity against all the tested organisms. The compounds containing an OH group in the *ortho* position of the aryl ring were found to be highly active and in many cases metal complexation increased the activity. The analytical and spectral data revealed the existence of unsaturated triketone in the triketo form. Its Ni(II), Cu(II), and Zn(II) complexes showed [M(L)(OAc)$_2$] stoichiometry with neutral bidentate coordination using the diketo moiety and acetate groups of the metal salt, while the acetyl carbonyl group is excluded from coordination.

References

[1] R.C. Mehrotra, R. Bohra, D.P. Gaur, Metal β-diketonates and Allied Derivatives, Academic Press, New York, 1978.

[2] V.D. John, K. Krishnankutty, Appl. Organometal. Chem. 20 (2006) 477-482, Transition Met. Chem. 30 (2005) 229-233, Synth. React. Inorg. Met.- Org. Chem. 33 (2003) 343-358, V.D. John, G. Kuttan, K. Krishnankutty, J. Exp. Clin. Cancer Res. 21 (2002) 219-224.

[3] K. Krishnankutty, P. Venugopalan, Synth. React. Inorg. Met- Org. Chem. 28 (1998) 1313-1325, J. Indian Chem. Soc. 74 (1997) 562-564.

[4] S.M. Khopde, K.I Priyadarsini, P. Venketesan, M.N.A. Rao, Biophys. Chem. 80 (1999) 85-91, R.J. Anto, K.N.D. Babu, K.N. Rajasekharan, R. Kuttan, Cancer Lett. 94 (1995) 74-84.

[5] H.J.J. Pabon, Rec. Trav. Chim. 83 (1964) 237-240.

[6] V.S. Govindarajan, CRC Critical Reviews in Food Science and Nutrition 199 (1961) 12-30.

[7] K. Krishnankutty, M.B. Ummathur, Russian J. Coord. Chem. 34 (2008) 502-510, Polish J. Chem. 82 (2008) 963-971, Chinese J. Chem. 26 (2008) 453-458, J. Indian Chem. Soc. 83 (2006) 639-644, J. Indian Chem. Soc. 83 (2006) 663-667, J. Indian Chem. Soc. 83 (2006) 883-887.

[8] C.H. Collins, P.M. Lyne, Microbial Methods, Butterworths, London, 1970.

[9] L. M. Prescott, J.P. Harley, D.A. Klein, Microbiology, WCB, Pubuque (USA) 1990.

[10] L.J. Bellamy, The Infrared Spectra of Complex Molecules, Chapman and Hall, London, 1980.

[11] N. Nakamoto, Infrared Spectra and Raman Spectra of Inorganic and Coordination Compounds, John Wiley & Sons, New York, 1997.

[12] R.L. Lintvedt, H. F. Holtzdaw Jr., J. Am. Chem. Soc. 88 (1966) 2713-2716.

[13] P.J. Roughley, D.A. Whiting, J. Chem. Soc. Perkin Trans. I (1973) 2379-2388.

[14] D.C. Nonhebel, Tetrahedron 24 (1968) 1869-1874.

[15] C.G. Macdonald, J.S. Shannon, Aust. J. Chem. 19(1966) 1545-1551.

[16] K.C. Joshi, V.N. Pathak, Coord. Chem. Rev. 22 (1977) 37-122.

[17] J.P. Fackler, Jr. F.A. Cotton, D.W. Barnum, Inorg. Chem. 2 (1963) 102-106.