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Unsaturated *β*-ketoesters and their Ni(II), Cu(II) and Zn(II) complexes

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Abstract: A new series of *β*-ketoesters in which the keto group is attached to the olefinic linkage were synthesized by the reaction of methyl acetoacetate and aromatic aldehydes under specified conditions. The existence of these compounds predominantly in the intramolecularly hydrogen bonded enol form was well demonstrated from their IR, ^{1}H-NMR and mass spectral data. Details on the formation of their [ML$_2$] complexes with Ni(II), Cu(II) and Zn(II) and the nature of the bonding are discussed on the basis of analytical and spectral data.

Keywords: unsaturated *β*-ketoesters; metal complexes; IR; ^{1}H-NMR; mass spectra.

INTRODUCTION

Numerous reports exist on the synthesis, characterization and applications of metal complexes of *β*-ketoesters in which the keto group is attached to alkyl/aryl functions.[1] However, no systematic investigation has appeared on *β*-ketoesters in which the keto group is linked to an olefinic linkage. In recent years such "unsaturated" *β*-dicarbonyl compounds and their metal complexes have gained considerable importance[2–12] mainly because of the observation that the active constituents of several medicinal plants contain such compounds. A typical example is curcuminoids, the active chemical constituents of turmeric (*Curcuma longa*, Linn., Zingiberaceae family), a traditional Indian medicinal plant.[5,6] These natural curcuminoids were reported to possess anticancer,[7] antitumor,[8] anti-oxidant,[8,9] anti-inflammatory,[10] antiviral and immunomodulatory activities.[11] Synthetic curcuminoids are reported to be more potent anticarcinogenic and antimutagenic[12] agents. Therefore, investigations on such unsaturated carbonyl systems and their metal complexes have tremendous importance. In continuation of our studies on unsaturated polycarbonyl compounds and their metal com-

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plexes,[2,3,13,14] the synthesis and characterization of a new series of "unsaturated" *β*-ketoesters and their typical metal complexes are reported herein.

EXPERIMENTAL

Methods and instruments

Carbon, hydrogen and nitrogen percentages were determined by microanalyses (Heraeus Elemental analyzer) and the metal contents of the complexes by AAS (Perkin Elmer 2380). The electronic spectra of the compounds in methanol (10^{-4} mol/L) 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 *m*-nitrobenzyl alcohol as the matrix). The molar conductance of the complexes was determined in DMF ($\approx 10^{-3}$ mol/L) at 28±1 °C. Magnetic susceptibilities were determined at room temperature on a Gouy-type magnetic balance.

Synthesis of the unsaturated β*-ketoesters* HL^1–HL^6

The aldehydes used for the preparation of unsaturated *β*-ketoesters were: benzaldehyde, naphthalene-1-carbaldehyde, 4-hydroxybenzaldehyde, vanillin, 4-(dimethylamino)benzaldehyde and 2-hydroxynaphthalene-1-carbaldehyde. A typical procedure for the synthesis is given below.

Methyl acetoacetate (1.16 g, 0.010 mol) and boric oxide (0.35 g, 0.0050 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 (0.010 mol) and tri(*sec*-butyl) borate (4.6 g, 0.020 mol), dissolved in dry ethyl acetate (≈ 15 mL), was added and stirred for ≈ 5 h with the slow addition of *n*-butylamine (0.50 mL in 5.0 mL dry ethyl acetate) and the reaction mixture was kept overnight. HCl (0.40 M, 7.5 mL) was added and the mixture again stirred for ≈ 1 h. Subsequently, the mixture was extracted repeatedly with ethyl acetate and the combined extracts were evaporated to dryness on a water bath. The obtained pasty mass was stirred with methanol (15 mL) for ≈ 2 h and was then kept in an ice bath under constant stirring for ≈ 3 h. The precipitated compound was filtered and recrystallized from hot benzene thus producing the chromatographically (TLC, silica gel as adsorbent) pure compound.

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

To a refluxing solution of the unsaturated *β*-ketoester in ethanol (0.0020 mol, 20 mL), an ethanolic solution of metal(II) acetate (0.0010 mol, 15 mL) was added dropwise under stirring. The pH of the solution was adjusted to around 6 using sodium acetate and the refluxing was continued for ≈ 3 h. The solution was then concentrated to half its volume and cooled to room temperature. The precipitated complex was filtered, washed with water, then with methanol, and finally recrystallized from hot ethanol.

RESULTS AND DISCUSSION

A well-established synthetic route to "unsaturated" *β*-dicarbonyl compounds is based on the synthesis of curcuminoids[5] using the reaction of aromatic aldehydes and acetylacetone 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 the Knoevenagel-type condensation and facilitate the Claisen-type condensation by the formation of a boron complex of the diketone. This reaction usually yields a mixture of both the mono and bis-condensation products. In the present study, when methyl acetoacetate was employed, only the monocondensation product was formed.

The compounds were stable, showed sharp melting points and were soluble in common organic solvents. The formulas and elemental analytical data of the unsaturated β-ketoesters synthesized from various aromatic aldehydes are given in Tables I and II. The analytical data (Table III) together with their non-electrolytic nature in DMF (the specific conductance of a 10^{-3} mol/L solution was $< 10\ \Omega^{-1}\ \mathrm{cm}^{-1}$) suggest [$ML_2$] stoichiometry of the complexes. The Ni(II) and Zn(II) chelates were diamagnetic, while the Cu(II) complexes showed a normal paramagnetic moment. The observed electronic, IR, ^{1}H-NMR and mass spectra were fully consistent with the presentation of unsaturated β-ketoesters (Scheme 1) and of the complexes (Scheme 2).

TABLE I. Abbreviations of the prepared β-ketoesters and Ar constituent

Compound	Ar-
HL^1	Phenyl
HL^2	1-Naphthyl
HL^3	4-Hydroxyphenyl
HL^4	3-Hydroxy-4-methoxyphenyl
HL^5	4-(Dimethylamino)phenyl
HL^6	2-Hydroxy-1-naphthyl

IR spectra

Methyl acetoacetate exists predominantly in the keto form with a very small percentage of the enol form[15] and exhibits the most characteristic bands in the region 1600–1800 cm^{-1}, due to the ester carbonyl at ≈ 1750 cm^{-1}, the acetyl carbonyl at ≈ 1720 cm^{-1} and the β-hydroxy-α,β-unsaturated ester carbonyl of the enol form at ≈1650 cm^{-1}. The spectra of all the unsaturated β-ketoesters showed three strong bands at ≈ 1740 cm^{-1}, ≈ 1670 cm^{-1} and ≈ 1640 cm^{-1}, assignable to the stretching of the ester carbonyl, the β-hydroxy-α,β-unsaturated ester carbonyl of the enol form and the cinnamoyl carbonyl function[16] (Table IV). The spectra of all the compounds showed a prominent band at ≈ 970 cm^{-1} typical of the *trans*--CH=CH– group.[17] The broad band in the region 2800–3500 cm^{-1} suggests the existence of the compounds predominantly in the intramolecularly hydrogen bonded enolic form.[17]

The spectra of all the complexes showed an intense and slightly broadened band at ≈ 1630 cm^{-1} in the 1600–1800 cm^{-1} region (Table V). In the metal chelates of methyl acetoacetate both the acetyl and ester carbonyls show an appreciable decrease in frequencies upon complexation.[15] Therefore, by considering its position and shape it can be presumed that this band originates from a metal bonded dicarbonyl function. The broad band in the region 2800–3500 cm^{-1} was absent in the spectra of the metal complexes, indicating the replacement of the eno-

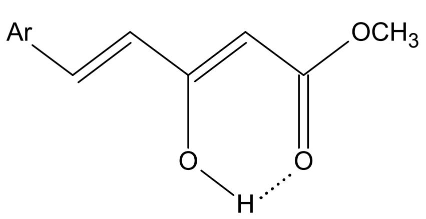
TABLE II. Analytical, ^{1}H-NMR and mass spectral data of the prepared unsaturated β-ketoesters

Compound	M.p. °C	Yield %	Elemental Analysis Found (Calculated), %			^{1}H-NMR (δ/ppm)					Mass spectral data *m*/*z*
			C	H	N	Enolic OH	Ester OCH_3	Methine	CH_2	Aryl substituent	
HL[1] $C_{12}H_{12}O_3$	54	72	70.49 (70.59)	5.89 (5.88)	–	12.168	3.128	6.768	3.684	–	204, 189, 173, 145, 131, 127, 103, 101
HL[2] $C_{16}H_{14}O_3$	68	70	75.64 (75.59)	5.46 (5.51)	–	12.354	3.098	6.876	3.634	–	254, 239, 223, 195, 181, 153, 127, 101
HL[3] $C_{12}H_{12}O_4$	86	74	65.50 (65.45)	5.44 (5.45)	–	12.358	3.142	6.548	3.634	10.046 (OH)	221, 205, 189, 161, 147, 127, 119, 101
HL[4] $C_{13}H_{14}O_5$	64	70	62.48 (62.40)	5.64 (5.60)	–	13.123	3.292	6.895	3.684	10.154 (OH) 3.918 (OCH_3)	247, 232, 216, 188, 174, 146, 127, 120, 101
HL[5] $C_{14}H_{17}NO_3$	57	68	68.12 (68.01)	6.80 (6.88)	5.65 (5.67)	13.258	3.162	6.542	3.568	2.938 ($N(CH_3)_2$)	251, 235, 219, 191, 177, 149, 127, 123, 101
HL[6] $C_{16}H_{14}O_4$	60	72	71.18 (71.11)	5.14 (5.19)	–	13.160	3.122	6.938	3.546	10.798 (OH)	270, 255, 239, 211, 197, 169, 143, 127, 101

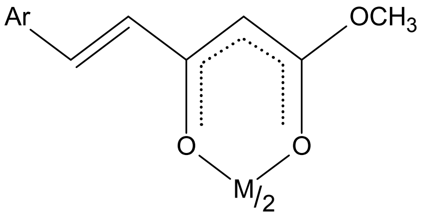
TABLE III. Physical and analytical data of the isolated Cu(II), Ni(II) and Zn(II) complexes (L – deprotonated ligand (abbreviated as in Table I))

Complex	M.p. °C	Yield %	Elemental Analysis Found (Calculated), %			
			C	H	N	M
$[\mathrm{NiL}^1{}_2]$ $C_{24}H_{22}NiO_6$	210	72	62.09 (61.97)	4.72 (4.73)	–	12.64 (12.63)
$[\mathrm{NiL}^2{}_2]$ $C_{32}H_{26}NiO_6$	202	68	67.98 (68.00)	4.62 (4.60)	–	10.44 (10.40)
$[\mathrm{NiL}^3{}_2]$ $C_{24}H_{22}NiO_8$	236	70	58.04 (57.98)	4.42 (4.43)	–	11.78 (11.82)
$[\mathrm{NiL}^4{}_2]$ $C_{26}H_{26}NiO_{10}$	226	70	55.98 (56.04)	4.69 (4.67)	–	10.56 (10.55)
$[\mathrm{NiL}^5{}_2]$ $C_{28}H_{32}N_2NiO_6$	198	76	61.13 (61.01)	5.82 (5.81)	5.11 (5.08)	10.62 (10.66)
$[\mathrm{NiL}^6{}_2]$ $C_{32}H_{26}NiO_8$	260	68	64.33 (64.35)	4.40 (4.36)	–	9.86 (9.84)
$[\mathrm{CuL}^1{}_2]$ $C_{24}H_{22}CuO_6$	196	74	61.38 (61.34)	4.64 (4.69)	–	13.49 (13.53)
$[\mathrm{CuL}^2{}_2]$ $C_{32}H_{26}CuO_6$	214	70	67.38 (67.42)	4.59 (4.57)	–	11.01 (11.16)
$[\mathrm{CuL}^3{}_2]$ $C_{24}H_{22}CuO_8$	208	72	57.48 (57.42)	4.36 (4.39)	–	12.74 (12.67)
$[\mathrm{CuL}^4{}_2]$ $C_{26}H_{26}CuO_{10}$	176	68	55.52 (55.56)	4.59 (4.63)	–	11.33 (11.32)
$[\mathrm{CuL}^5{}_2]$ $C_{28}H_{32}CuN_2O_6$	192	70	60.42 (60.48)	5.69 (5.76)	4.99 (5.04)	11.42 (11.44)
$[\mathrm{CuL}^6{}_2]$ $C_{32}H_{26}CuO_8$	256	74	63.88 (63.84)	4.30 (4.32)	–	10.60 (10.56)
$[\mathrm{ZnL}^1{}_2]$ $C_{24}H_{22}O_6Zn$	192	70	61.11 (61.10)	4.70 (4.67)	–	13.84 (13.87)
$[\mathrm{ZnL}^2{}_2]$ $C_{32}H_{26}O_6Zn$	188	68	67.24 (67.21)	4.58 (4.55)	–	11.38 (11.44)
$[\mathrm{ZnL}^3{}_2]$ $C_{24}H_{22}O_8Zn$	208	68	57.25 (57.21)	4.34 (4.37)	–	13.02 (12.99)
$[\mathrm{ZnL}^4{}_2]$ $C_{26}H_{26}O_{10}Zn$	186	74	55.43 (55.38)	4.60 (4.62)	–	11.52 (11.60)
$[\mathrm{ZnL}^5{}_2]$ $C_{28}H_{32}N_2O_6Zn$	206	72	60.24 (60.28)	5.68 (5.74)	5.01 (5.02)	11.74 (11.73)
$[\mathrm{ZnL}^6{}_2]$ $C_{32}H_{26}O_8Zn$	252	70	63.68 (63.64)	4.34 (4.31)	–	10.80 (10.84)

lic proton by a metal cation during complexation. The involvement of the carbonyl groups in coordination, as shown in Scheme 2, is further supported by the appearance of two medium intensity bands at ≈ 420 cm^{-1} and ≈ 470 cm^{-1} assignable to $\nu_{M–O}$.[16]



Scheme 1. Presentation of the prepared unsaturated *β*-ketoesters (abbreviations are given in Table I).



Scheme 2. Simplified presentation of the structure of the metal complexes with unsaturated *β*-ketoesters. Abbreviations as in Table I.

TABLE IV. Characteristic IR stretching bands (cm^{-1}) of the unsaturated *β*-ketoesters (HL$^{1-6}$ as in Table I)

HL^1	HL^2	HL^3	HL^4	HL^5	HL^6	Probable assignments
1742	1738	1740	1730	1736	1720	(C=O) Ester
1660	1658	1689	1668	1666	1665	(C=O) Olefinic
1624	1620	1643	1635	1630	1635	(C=O) Cinnamoyl
1591	1590	1597	1580	1582	1577	(C=C) Phenyl/alkenyl
1562	1542	1573	1545	1546	1568	
1546	1536	1546	1528	1528	1520	
1528	1518	1512	1525	1520	1496	
967	969	970	986	970	966	CH=CH *trans*
–	–	3056	3070	–	3066	Phenolic OH

TABLE V. Characteristic IR stretching frequencies (cm^{-1}) and mass spectral data of the prepared Cu(II) complexes

Complex/ Empirical formula	IR bands (cm^{-1})				Mass spectral data (*m*/*z*)
	(C=O) Ester	(C=O) Cinnamoyl	(C=C) Aryl/alkenyl	M–O	
$[\mathrm{CuL}^1_2]$ $C_{24}H_{22}CuO_6$	1625 *s*	1595 *s*	1556 *s* 1580 *s* 1542 *m*	428 *m* 470 *m*	469, 451, 440, 438, 409, 407, 368, 366, 337, 335, 317, 315, 265, 263, 204, 201, 189, 173, 127
$[\mathrm{CuL}^2_2]$ $C_{32}H_{26}CuO_6$	1626 *s*	1593 *s*	1562 *s* 1580 *s* 1544 *m*	416 *m* 474 *m*	571, 569, 540, 538, 509, 507, 418, 416, 387, 385, 317, 315, 265, 263, 254, 239, 203, 201, 195, 181
$[\mathrm{CuL}^3_2]$ $C_{24}H_{22}CuO_8$	1630 *s*	1590 *s*	1560 *s* 1584 *s* 1550 *m*	420 *m* 470 *m*	503, 501, 472, 470, 441, 439, 384, 382, 353, 351, 317, 315, 265, 263, 221, 205, 203, 201, 147, 119
$[\mathrm{CuL}^4_2]$ $C_{26}H_{26}CuO_{10}$	1630 *s*	1585 *s*	1567 *s* 1577 *s* 1546 *m*	416 *m* 487 *m*	563, 561, 532, 530, 501, 499, 414, 412, 383, 381, 317, 315, 265, 263, 251, 219, 203, 201, 191, 127, 101
$[\mathrm{CuL}^5_2]$ $C_{28}H_{32}CuN_2O_6$	1622 *s*	1599 *s*	1561 *s* 1581 *s* 1545 *m*	416 *m* 485 *m*	557, 555, 526, 524, 495, 493, 411, 409, 380, 378, 317, 315, 265, 263, 247, 232, 203, 201, 174, 120, 101
$[\mathrm{CuL}^6_2]$ $C_{32}H_{26}CuO_8$	1635 *s*	1590 *s*	1560 *s* 1570 *s* 1546 *m*	425 *m* 476 *m*	603, 601, 572, 570, 541, 539, 434, 432, 403, 401, 317, 315, 270, 265, 263, 255, 239, 203, 201, 127, 101

^{1}H-NMR spectra

The ^{1}H-NMR spectra of the unsaturated β-ketoesters displayed a one proton singlet at $\delta \approx 13$ ppm due to the intramolecularly hydrogen bonded enolic proton.[18] The olefinic and methylene proton signals appeared at $\delta \approx 6–7$ ppm and $\delta \approx 3–4$ ppm. The aryl proton signals were observed in the δ range 7–7.8 ppm as a complex multiplet. The position and integrated intensities of all the signals (Table II) agree well with the proposed structure of the compounds (Scheme 1).

In the ^{1}H-NMR spectra of the diamagnetic Ni(II) and Zn(II) complexes, the low field enol proton signal of the ligands was absent indicating its replacement by the metal ion during complexation. The OCH_3 proton signal remained almost unaffected. The methylene proton signal was shifted appreciably to low field compared to the shift of 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 the various signals conform to $[ML_2]$ stoichiometry of the complexes. The aryl substituents were not involved in bonding with the metal ion, which is clearly indicated[2] in the spectra of their Ni(II) and Zn(II) complexes in which the signals remain unaltered.

Mass spectra

Mass spectra of all the unsaturated β-ketoesters showed an intense molecular ion peak, $P^+/(P + 1)^+$, thereby confirming the formulation of the compounds.[19] Peaks due to $(Ar–CH=CH–CO)^+$, $(P – OCH_3)^+$, $(P – COOCH_3)^+$, $(P – ArC_2H_2)^+$, *etc*. are characteristic for all the spectra (Table II). The FAB mass spectra of the Cu(II) complexes showed molecular ion peaks corresponding to $[CuL_2]$ stoichiometry of the complexes. Peaks corresponding to $[CuL]^+$, L^+ and fragments of L^+ were also present in the spectra (Table V). The spectra of all the chelates have a number of fragments containing copper in the 3:1 natural abundance of ^{63}Cu and ^{65}Cu isotopes.

Electronic spectra

The UV spectra of the unsaturated β-ketoesters showed two broad bands with maxima at ≈ 390 nm and ≈ 260 nm due to the various $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. In the complexes, these absorption maxima were shifted appreciably to lower wave numbers. The Cu(II) complexes showed a broad visible band, λ_{max} at ≈ 15,000 cm^{-1}. This, together with the calculated μ_{eff} values (≈ 1.74 μ_B) suggests square-planar geometry.[20] A broad band centered at ≈ 11000 cm^{-1} observed in spectra recorded in pyridine indicated the formation of octahedral pyridine adducts. The diamagnetism and the broad 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}

mol/L) showed three bands corresponding to a configurational change to octahedral due to the association of pyridine. The three well-separated absorption bands at λ_{max} around 8,145, 13,345 and 24,450 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.

CONCLUSIONS

Six new unsaturated β-ketoesters in which the keto group was attached to an olefinic linkage were synthesized by the reaction of methyl acetoacetate and aromatic aldehydes. Analytical, IR, ^{1}H-NMR and mass spectral data revealed a 1:1 product in which the methyl group of the ester had undergone a Claisen condensation with the aromatic aldehyde. The existence of these unsaturated β-ketoesters in the intramolecularly hydrogen bonded enol form was well demonstrated from their analytical and spectral data. Analytical, physical and spectral data of the [ML$_2$] complexes of Ni(II), Cu(II) and Zn(II) showed monobasic bidentate coordination in which the intramolecularly hydrogen-bonded enolic proton had been replaced by a metal cation.

ИЗВОД

НЕЗАСИЋЕНИ β-КЕТОЕСТРИ И ЊИХОВИ Ni(II), Cu(II) И Zn(II) КОМПЛЕКСИ

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Реакцијом метил-ацетоацетата и ароматичних алдехида под наведеним условима добијена је нова серија β-кетоестара у којима је кето група припојена олефинској вези. Из њихових IR, ^{1}H-NMR и масених спектралних података показано је постојање ових једињења претежно у енолном облику са интрамолекулском водоничном везом. Детаљи о грађењу њихових [ML$_2$] комплекса са Ni(II), Cu(II) и Zn(II) и природи веза су дискутовани на основу аналитичких и спектралних података.

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