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Synthesis and characterization of two unsaturated tetraketones and their metal complexes

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ABTRACT

The reaction between terephthalaldehyde and acetylacetone under specified conditions yielded two types of unsaturated tetraketones in which the keto-groups are attached to olefinic linkages. The existence of one of the compound (H_2L) in the intramolecularly hydrogen-bonded enol form and other (L) in the keto-form have been well demonstrated from their IR, ^{1}H NMR and mass spectral data. Dibasic tetradentate coordination of H_2L in its $[M_2L_2]$ complexes and neutral bidentate coordination of L in its $[ML(OAc)_2]$ complexes [M = Ni(II) and Cu(II)] have been established on the basis of analytical and spectral data.

KEYWORDS

Unsaturated tetraketones;
Metal complexes;
IR spectra;
^{1}H NMR spectra;
Mass spectra.

INTRODUCTION

Extensive literature is available on the synthesis, characterization and applications of coordination compounds of polyketones containing alkyl/aryl groups directly linked to the carbonyl functions[1-3]. Reports also appeared on the synthesis, characterization and applications of biologically important diketones that contain olefinic linkages attached to the diketo function as in curcuminoids[4-6]. However reports are scanty on unsaturated polyketones and their metal complexes. In continuation of our studies on unsaturated β-diketones and their metal complexes[5-8], we here report the synthesis and characterization of two unsaturated tetraketones (H_2L and L) obtained by the condensation between acetylacetone and terephthalaldehyde. Typical Ni(II) and Cu(II) complexes of these compounds were also synthesized and characterized.

EXPERIMENTAL

Materials and methods

Carbon and hydrogen contents were determined by microanalyses (Heraeus Elemental analyzer) and metal contents of complexes by AAS (Perkin Elmer 2380). The UV spectra of the compounds in methanol (10^{-6} M) were recorded on a JASCO V-550 UV-Visible spectrophotometer, IR spectra (KBr discs) on a JASCO FT/IR 4100 instrument, ^{1}H NMR spectra ($CDCl_3$ or DMSO-d_6) on a JE02 JMS 60011 NMR spectrometer and mass spectra on a JEOL-JMS 600H, FAB mass spectrometer. Molar conductance of the complexes was determined in DMF (~10^{-3} mol/L) at 28±1^{0}C. Magnetic susceptibilities were determined at room temperature on a Guoy type magnetic balance at room temperature (28±1^{0}C) using $Hg[Co(NCS)_4]$ as standard.

Synthesis of unsaturated tetraketones, β,β'-Bis(1,3-butanedione)-1,4-divinylidinobenzene (H_2L) and β,β,β',β'-(Tetraacetyl)-1,4-divinylidinobenzene (L)

Acetylacetone (0.5 ml, 0.01 mol) was mixed with boric oxide (0.7 g, 0.01 mol) in dry ethylacetate (5 ml) and stirred on a magnetic stirrer for ~1 h. To the mixture a solution of terephthalaldehyde (0.67 g, 0.01 mol) and tri(*sec*-butyl)borate (5.3 ml, 0.01 mol) dissolved in dry ethylacetate (~10 ml) was added. The mixture was cooled to ~0°C and stirred for 10 minutes. To this *n*-butylamine (0.2 ml in 5 ml dry ethylacetate) was added slowly during half an hour and stirred for ~4 h. The reaction mixture was kept overnight. To the yellow orange solution obtained, a cold solution (~5 °C) of HCl (0.4 M, 7.5 ml) was added and the mixture was again stirred for ~l h in an ice bath. The mixture was extracted repeatedly with ethylacetate and the combined extracts were evaporated to dryness on a water bath to get a pasty mass. This pasty mass is stirred well with HCl (2 M, 10 ml) for half an hour. The precipitate formed was filtered off, washed with water and then with ethanol and dried in vacuum. The TLC of the products revealed the presence of two compounds, which were quantitatively separated by column chromatography as outlined below.

The crude product was dissolved in a minimum quantity of acetone and a little amount of silica were added and dried. It was then placed over a column (2 x 100 cm) densely packed with silica gel (mesh 60–120) using 1 : 1 v/v chloroform-toluene mixture. It was then eluted with the same solvent system at a uniform flow rate of 2 ml/min. As the elution proceeds, two bands were developed in the column: a lower yellow band and an upper orange band. The lower 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 unsaturated tetraketone, H_2L (Figure 1). It was washed with ethanol and then with benzene, dried in vacuum and recrystallised from ethanol.

After the complete elution of the first compound the second band was eluted using a 5 : 1 v/v mixture of chloroform and toluene. The eluates were collected in aliquots of 10 ml in separate tubes and checked by TLC. The combined extracts on removing the solvent in vacuum yielded the unsaturated tetraketone, L (Figure 2). It was washed with ethanol, dried in vacuum and recrystallised from ethanol.

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

To a solution of the tetraketone (2.98g, 0.01 mol) in ethylacetate (50 ml) a solution of the metal(II) acetate (0.01 mol) in minimum amount of water was added drop by drop with stirring. The pH of the solution was adjusted around 7 using sodium acetate. The mixed solution was refluxed for ~4 h. The solution was concentrated to half the volume and cooled to room temperature. The precipitated complex was filtered off and washed several times with ethylacetate, acetone and then with water. The solid product was recrystallized from hot ethanol and dried in vacuum.

Determination of magnetic susceptibility

A thin cylindrical glass tube, filled with the sample is vertically suspended from the beam of a balance in draught free enclosure in such a way that its lower end lies between the poles of an electromagnet. The weight of the sample is determined with the field off and with the field on. Corrections for diamagnetism of the constituents were made using Pascal's constants[9]. The effective magnetic moments were calculated using the formula $\mu_{eff} = 2.83x[\chi_{M.}T]^{1/2}x9.274x10^{-24}$ Am^2 where χ_M is the corrected molar susceptibility and T is the room temperature.

RESULTS AND DISCUSSION

Claisen-Schmidt 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 yielded 'unsaturated' *β*-dicarbonyl compounds. The use of boric oxide and tri(*sec*-butyl)borate is to prevent Knoevenagel condensation by the formation of a boron complex of the diketone[10]. If the protection of the active methylene group is not efficient under the reaction condition, Knoevenagel condensation may also occur. In the present study two products (H_2L and L) were obtained by Claisen-Schmidt and Knoevenagel condensations respectively.

The elemental analytical data of H_2L and L (TABLE

1) suggests that the condensation between acetylacetone and terephthalaldehyde has occurred in the 2:1 ratio as in Figures 1 and 2. The compounds formed stable complexes with Ni(II) and Cu(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 $[M_2L_2]$ and $[ML(OAc)_2]$ stoichiometry for the complexes of H_2L and L respectively. The Ni(II) chelates are diamagnetic, while Cu(II) complexes showed the normal paramagnetic moment. The observed UV, IR, ^{1}H NMR and mass spectral data of the complexes are fully consistent with the Figures 3 and 4.

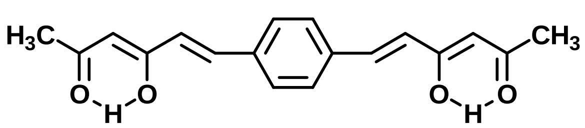


Figure 1 : Structure of H_2L

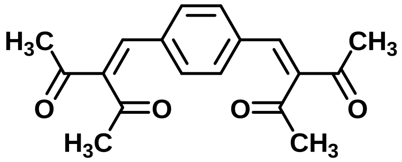
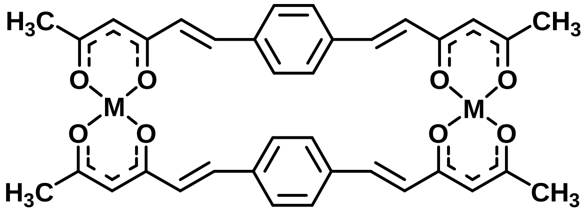
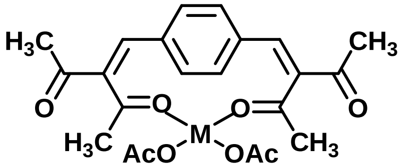


Figure 2 : Structure of L



M = Ni(II) and Cu(II)

Figure 3 : Structure of the metal complexes of H_2L



M = Ni(II) and Cu(II)

Figure 4 : Structure of the metal complexes of L

Infrared spectra

The spectrum of H_2L shows two intense bands at 1636 and 1615 cm^{-1} assignable respectively to the intramolecularly hydrogen bonded acetyl and cinnamoyl carbonyl stretching vibrations. The observed position and intensity of these bands indicate that the compound exist entirely in the enolic form and enolised towards the cinnamoyl function[6,11] as in Figure 1. This is inferred from the fact that no free acetyl carbonyl band (~1720 cm^{-1}) or cinnamoyl carbonyl band (~1645 cm^{-1}) are observed in the double bond region of the spectrum. The broad band in the region 2500-3500 cm^{-1} also suggests the existence of the compound predominantly in the enolic form. The spectrum of the compound showed a prominent band at 970 cm^{-1} typical of *trans*–CH=CH– group[5,12].

TABLE 1 : Physical and analytical data of unsaturated tetraketones and their metal complexes

Compound / Molecular formula	Yield %	m.p. ^{0}C	μ_{eff} Am^2	Elemental Analysis: Found (Calculated)% C	H	M
H_2L $C_{18}H_{18}O_4$	50	145	-	72.40 (72.48)	6.02 (6.04)	-
$[Ni_2L_2]$ $C_{36}H_{32}Ni_2O_8$	55	>300	-	60.96 (60.89)	4.50 (4.51)	16.62 (16.55)
$[Cu_2L_2]$ $C_{36}H_{32}Cu_2O_8$	65	>300	16.2×10^{-24}	59.94 (60.08)	4.42 (4.45)	17.62 (17.67)
L $C_{18}H_{18}O_4$	30	160	-	72.52 (72.48)	6.06 (6.04)	-
$[Ni(L)(OAc)_2]$ $C_{22}H_{24}NiO_8$	50	>300	-	55.54 (55.61)	5.04 (5.06)	12.41 (12.37)
$[Cu(L)(OAc)_2]$ $C_{22}H_{24}CuO_8$	65	>300	16.5×10^{-24}	55.14 (55.05)	5.03 (5.00)	13.28 (13.25)

The spectrum of L shows an intense band at 1694 cm^{-1} assignable to the stretching of the conjugated free acetyl carbonyl groups of Figure 2 and no other band is observed in the 1650-1750 cm^{-1} region indicating the existence of all the four carbonyl groups in identical environments[11]. The compound does not show broad band in the region 2500-3500 cm^{-1} suggesting its existence predominantly in the tetraketo form.

In the IR spectra of the complexes of H_2L the bands at 1636 and 1615 cm^{-1} of the ligand disappeared and two new bands appeared at ~1600 and 1580 cm^{-1} due to metal chelated carbonyl groups[12]. The broad band in the region 2500-3500 cm^{-1} cleared up in the spectra of metal complexes indicating the replacement of enolic protons by the metal cations during complexation[5] as in Figure 3.

The spectra of the metal complexes of L displayed two strong bands at ~1695 and ~1625 cm^{-1} assignable respectively to the free acetyl and metal coordinated acetyl carbonyl stretching vibrations[12]. Monodentate acetate usually shows two bands at ~1620 cm^{-1} and ~1310 cm^{-1} due to antisymmetric and symmetric stretching respectively. Since carbonyl absorption of the complexes 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[7,12]. Thus IR spectra of the complexes support the neutral bidentate coordination of L as in Figure 4.

That the carbonyl groups are involved in bonding with the metal as in Figures 3 and 4 is further supported by the appearance of two medium intensity bands in the region at 420-480 cm^{-1} assignable to $\nu_{M\text{-}O}$ vibrations[8,12]. Important bands that appeared in the spectra are given in TABLE 2.

TABLE 2 : Characteristic IR stretching bands (cm^{-1}) of the unsaturated tetraketones and their metal complexes

Compound	C=O acetyl	C=O cinnamoyl	CH=CH *trans*	M–O
H_2L	1636 s	1615 s	970 m	-
$[Ni_2L_2]$	1600 s	1580 s	968 m	480 m, 420 m
$[Cu_2L_2]$	1602 s	1584 s	966 m	478 m, 422 m
L	1694 s	-	-	-
$[Ni(L)(OAc)_2]$	1695 s, 1625 s	-	-	470 m, 430 m
$[Cu(L)(OAc)_2]$	1697 s, 1628 s	-	-	478 m, 428 m

^1H NMR spectra

The ^1H NMR spectrum of H_2L displayed a signal at δ 16.40 ppm due to the intramolecularly hydrogen bonded enolic protons[5,6]. The methine proton signals are observed at δ 5.80 ppm. Integrated intensities of all the protons agree well with the Figure 1 of the compound.

The ^1H NMR spectrum of L does not displayed any band above δ 10 ppm indicating its existence predominantly in the tetraketo form[13]. The spectrum of the compound is characterized by the presence of a twelve-proton singlet at δ 2.50 ppm due to the resonance of methyl protons indicating the presence of all the four methyl groups in the same environment as in Figure 2.

In the ^1H NMR spectrum of the diamagnetic Ni(II) complex of H_2L the low field signal due to the enol protons of the ligand is absent indicating their replacement by the metal ions during complexation[6,13]. The methine proton signal shifted appreciably to low field compared to the shift in the olefinic protons due to the aromatic character imparted to the C_3O_2M ring systems by the highly conjugated groups attached to the dicarbonyl moiety. The alkenyl proton signals with a *J* value of ~16 Hz suggest the *trans* nature of the alkene double bond, as it is in the free ligand[6]. The aryl proton signals are observed in the range δ 7.04-7.90 ppm as a complex multiplet. The integrated intensities of various signals agree well with the $[M_2L_2]$ stoichiometry of the complexes as in Figure 3.

In the ^1H NMR spectrum of the diamagnetic Ni(II) complex of L two new six-proton singlets appeared at δ 2.70 and 2.80 ppm due to methyl protons of metal chelated acetyl and acetate groups in addition to the six-proton singlet at δ 2.5 ppm of the methyl protons of free acetyl groups as in Figure 4. The aryl proton signals are observed in the range δ 7.20-7.80 ppm as a complex multiplet. The assignments of various proton signals observed are assembled in TABLE 3.

TABLE 3 : ^1H NMR spectral data (δ, ppm) of the unsaturated tetraketones and their Ni(II) complexes

Compound	Enolic OH	Methyl	Methine	CH=CH	Aryl
H_2L	16.40 (2H)	2.41(6H)	5.80(2H)	8.26(2H), 8.08(2H)	7.04-7.97 (4H)
$[Ni_2L_2]$	-	2.50(12H)	6.46(4H)	8.36(4H), 8.20(4H)	7.12-7.80 (8H)
L	-	2.50(12H)	5.70(2H)	-	7.20-7.80 (4H)
$[Ni(L)(OAc)_2]$	-	2.53(6H) 2.70 (6H) 2.80(6H)	5.76(2H)	-	7.22-7.90 (4H)

Mass spectra

Mass spectrum of H_2L shows intense molecular ion peak at m/z 298, thereby confirming the formulation of the compound[14]. Peaks due to $(CH_3COCH_2CO)^+$ and $(P - CH_3COCH_2CO)^+$ excludes the possibility of Knoevenagel condensation and confirms the Claisen-Schmidt reaction at the γ-methyl group of acetylacetone. Peaks due to successive removal of two acetyl groups are also characteristic of the spectrum.

The formation of L is well confirmed from the presence of an intense P^+ peak at m/z 298 in its mass spectrum. Peaks due to the successive removal of four acetyl groups and the absence of peaks due to $(P - CH_3COCH_2CO)^+$ and $(CH_3COCH_2CO)^+$ clearly support the knoevenagel condensation at the active methylene group of acetylacetone.

The FAB mass spectra of the Cu(II) complexes of H_2L and L show intense molecular ion peaks corresponding to $[Cu_2L_2]$ and $[CuL(OAc)_2]$ stoichiometry. Peaks correspond to $[Cu_2L]^+$, L^+ and fragments of L^+ are also present in the spectra. The spectrum of $[CuL(OAc)_2]$ show peaks due to the removal of one or both acetate groups. The spectra of the chelates contain a number of fragments containing copper in the 3:1 natural abundance of ^{63}Cu and ^{65}Cu isotopes[7] (TABLE 4).

TABLE 4 : Mass spectral data of the unsaturated tetraketones and their Cu(II) complexes

Compound	Mass spectral data (m/z)
H_2L	298, 255, 241, 213, 212, 198, 184, 170, 156, 128
L	298, 255, 212, 169, 126
$[Cu_2L_2]$	722, 718, 424, 422, 361, 359, 298, 255, 212, 198, 184, 170, 128
$[Cu(L)(OAc)_2]$	481, 479, 422, 420, 363, 361, 438, 436, 395, 393, 298, 255, 126

UV spectra

The UV spectra of H_2L and L shows two broad bands with maxima at ~380 and ~270 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 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 indicating the involvement of the carbonyl groups in metal complexation[15].

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