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Synthesis and characterization of two conjugated β-diketones and their metal complexes

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ABSTRACT

Two conjugated β -diketones (HL) have been synthesized by the reaction of benzoylacetone with aromatic aldehydes (cinnamaldehyde and naphthalene-2-carbaldehyde) under specified conditions. Analytical and spectral data indicate that the compounds exist in the intramolecularly hydrogen bonded keto-enol tautomeric form. Monobasic bidentate coordination of the compounds in their [FeL₃] and [ML₂] complexes [M = VO(II), Co(II), Ni(II) and Cu(II)] has been established by analytical and spectral data. The Ni(II) chelates are diamagnetic while all other complexes show normal paramagnetic moment.

Keywords: Conjugated β -diketones; Metal complexes; spectral data.

INTRODUCTION

The various biological activities of curcuminoids, a group of naturally occurring unsaturated β -diketones, have been attributed to the highly conjugated dicarbonyl functions as well as the nature and position of the substituents on the aryl rings [1-4]. The biochemical activities of the metal complexes are also dependant on these structural factors apart from the nature of the metal ion [5-13]. In order to reveal the structural influence, it is necessary to synthesize related compounds having restricted structural variations. As a part of our investigation on compounds structurally related to curcuminoids [14-18], we here report the synthesis and characterization of two new conjugated β -diketones obtained by condensing benzoylacetone with cinnamaldehyde and naphthalene-2-carbaldehyde. VO²⁺, Fe³⁺, Co²⁺, Ni²⁺ and Cu²⁺ complexes of these ligand systems are also synthesized and characterized.

MATERIALS AND METHODS

Carbon and hydrogen 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) were recorded on a 1601 Shimadzu UV-Vis. spectrophotometer, IR spectra (KBr discs) on an 8101 Shimadzu FTIR spectrophotometer, ¹H NMR spectra (CDCl₃ or DMSO-d₆) 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 (~ 10^{-3} mol/L) at 28±1^oC. Magnetic susceptibilities were determined at room temperature on a Guoy type magnetic balance.

Synthesis of conjugated β -diketones (HL¹ and HL²)

The conjugated β -diketones were prepared by the condensation of aromatic aldehydes (cinnamaldehyde and naphthalene-2-carbaldehyde) with benzoylacetone-boric oxide complex in ethylacetate medium in the presence of tri(*sec*-butyl)borate and *n*-butyl amine by the methods reported earlier [17,18].

Synthesis of metal complexes

To a refluxing solution of the compound in ethanol (0.02 mol, 20 mL) an aqueous solution of the metal salt (0.01 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 to room temperature. The precipitated complex was filtered, washed several times with water, recrystallized from hot methanol and dried in vacuum. The metal salts used were acetates of Cu(II), Ni(II) and Co(II); VOSO₄ and hydrated FeCl₃.

RESULTS AND DISCUSSION

Analytical (Table 1) and spectral data of the conjugated β -diketones suggest that the condensation between aromatic aldehydes and benzoylacetone has occurred in the 1:1 ratio as in figure 1. The observed elemental analytical data (Table 1) suggest [ML₂] stoichiometry of the complexes except for Fe(III) which have [FeL₃] stoichiometry. All the complexes behave as non-electrolytes (specific conductance <15 Ω^{-1} cm⁻¹; 10⁻³ M solution in DMF) and do not contain the anion of the metal salt used for their preparation. The Ni(II) complexes are diamagnetic while all others show normal paramagnetic moment. The observed spectral data of the complexes are compatible with the structure that would result when the chelated enol proton of the ligand is replaced by metal ion as in figure 2.



 $Ar = Styryl (HL^{1}) and 2-Naphthyl (HL^{2})$

Figure 1. Structure of the conjugated β -diketones



M = VO(II), Co(II), Ni(II) and Cu(II); n = 2, Fe(III); n = 3

Infrared spectra

The spectra of conjugated β -diketones show two intense bands at ~1630 and ~1615 cm⁻¹ assignable respectively to the intramolecularly hydrogen bonded benzoyl and α,β -unsaturated carbonyl stretching vibrations. This is inferred from the fact that no free benzoyl carbonyl band (~1660 cm⁻¹) or free α,β -unsaturated carbonyl band (~1645 cm⁻¹) are observed in the double bond region of the spectra. The observed position and intensity of these bands indicate that the compounds exist entirely in the enolic form and enolised towards the unsaturated carbonyl function [18,19] as in figure 1. The broad band in the region 2500-3500 cm⁻¹ also suggests the existence of the compounds in the intramolecularly hydrogen bonded enolic form. The spectra of the compounds showed a prominent band at ~970 cm⁻¹ typical of *trans* –CH=CH– group [9,19].

In the IR spectra of all the complexes the bands at ~ 1630 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 [12,20] as in figure 2. 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. The Co(II) complexes showed bands at ~3400 cm⁻¹ indicating the presence of coordinated water molecules [20]. That the carbonyl groups are involved in bonding with the metal ion is further supported by the appearance of two medium intensity bands at ~420 and ~480 cm⁻¹ assignable to v_{M-O} [20]. Important bands that appeared in the spectra are given in Table 2.

Figure 2. Structure of the metal complexes of conjugated β -diketones

	Yield (%)	M.P. (⁰ C)	µ _{eff} (BM)	Elemental Analysis:			UV	
Compound/				Found (Calculated)%			0	v
Molecular formula				С	Н	М	λ_{max} (nm)	log ε
HL^1	(0)	78	-	82.70	5.80		258	4.06
$C_{19}H_{16}O_2$	00			(82.61)	(5.80)	-	365	4.13
HL^2	70	70	-	83.92	5.30		269	4.11
$C_{21}H_{16}O_2$	70			(84.00)	(5.33)	-	370	4.78
$[VO(L^1)_2]$	55	210	1.69	74.04	4.85	8.22	290	4.36
$C_{38}H_{30}O_5V$	55	210		(73.91)	(4.86)	(8.26)	396	4.53
$[VO(L^2)_2]$	65	109	1.66	75.61	4.54	7.75	292	4.21
$C_{42}H_{30}O_5V$	05	190		(75.80)	(4.51)	(7.66)	394	3.98
$[\operatorname{Fe}(\operatorname{L}^{1})_{3}]$	60	129	5.89	77.50	5.13	6.32	288	4.34
$C_{57}H_{45}FeO_6$	00	156		(77.65)	(5.11)	(6.34)	390	4.22
$[\operatorname{Fe}(\mathrm{L}^2)_2]$	55	120	5.83	79.28	4.72	5.76	292	4.61
$C_{63}H_{45}FeO_6$	55			(79.34)	(4.72)	(5.86)	388	3.96
$[Co(L^1)_2(H_2O)_2]$	60	110	4.77	72.66	5.07	9.32	284	4.66
$C_{38}H_{32}CoO_5$	00			(72.74)	(5.10)	(9.40)	392	4.23
$[Co(L^2)_2(H_2O)_2]$	50	130	4.82	74.58	4.72	8.70	280	4.56
$C_{42}H_{32}CoO_5$	50			(74.67)	(4.74)	(8.73)	385	4.22
$[Ni(L^1)_2]$	70	>300	-	75.14	4.92	9.62	284	4.56
$C_{38}H_{30}NiO_4$	70			(74.91)	(4.93)	(9.64)	390	4.43
$[Ni(L^2)_2]$	65	120	-	76.61	4.55	8.85	280	4.70
$C_{42}H_{30}NiO_4$	05			(76.75)	(4.57)	(8.94)	388	4.33
$[Cu(L^1)_2]$	70	198	1.80	74.36	4.87	10.32	289	4.21
$C_{38}H_{30}CuO_4$				(74.32)	(4.89)	(10.36)	398	4.28
$[Cu(L^2)_2]$	65	65 242	1.79	76.28	4.52	9.70	281	4.21
$C_{42}H_{30}CuO_4$				(76.19)	(4.53)	(9.60)	389	3.86

Table:- 1 Physical, analytical and UV spectral data of the conjugated β-diketones and their metal complexes

Table 2:- Characteristic IR stretching bands (cm⁻¹) of the conjugated β -diketones and their metal complexes

Compound	C=O benzoyl	C=O α,β-unsaturated	CH=CH trans	M–O
HL^1	1628 s	1619 s	971 m	-
$[VO(L^1)_2]$	1606 s	1576 s	990 m	490 m, 430 m
$[\operatorname{Fe}(\mathrm{L}^{1})_{3}]$	1610 s	1575 s	995 m	472 m, 410 m
$[Co(L^1)_2(H_2O)_2]$	1604 s	1578 s	996 m	486 m, 422 m
$[Ni(L^1)_2]$	1602 s	1575 s	951 m	474 m, 424 m
$[Cu(L^1)_2]$	1607 s	1576 s	994 m	460 m, 418 m
HL^2	1629 s	1610 s	972 m	-
$[VO(L^2)_2]$	1609 s	1576 s	970 m	490 m, 425 m
$[Fe(L^2)_3]$	1605 s	1576 s	966 m	470 m, 420 m
$[Co(L^2)_2(H_2O)_2]$	1610 s	1580 s	967 m	478 m, 432 m
$[Ni(L^2)_2]$	1600 s	1579 s	970 m	469 m, 428 m
$[Cu(L^2)_2]$	1608 s	1577 s	966 m	481 m, 420 m

s = strong, m = medium

¹H NMR spectra

The ¹H NMR spectra of the conjugated β -diketones displayed a one proton signal at δ 16 ppm due to the intramolecularly hydrogen bonded enolic proton [21,22]. The methine proton signal appeared at δ 6 ppm. The alkenyl signals with their observed *J* values (\sim 16 Hz) suggest *trans* configuration about the olefinic function in the compounds. Integrated intensities of all the protons agree well with the figure 1 of the compounds.

In the ¹H NMR spectra of the diamagnetic Ni(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 due to the aromatic character imparted to the C_3O_2Ni ring system by the highly conjugated groups attached to the dicarbonyl moiety [15]. The integrated intensities of various signals agree well with the [NiL₂] stoichiometry of the complexes as in figure 2. The aryl proton signals are observed in the range δ 6.92-8.00 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 conjugated β -diketones and their Ni(II) complexes

Compound	Enolic OH	Methine	CH=CH	Aryl
HL^1	16.08	5.96	7.98-8.10	6.92-7.95
$[Ni(L^1)_2]$	-	6.50	8.24, 8.14	7.22-7.82
HL ²	16.20	5.92	8.57, 8.28	7.26-8.00
$[Ni(L^2)_2]$	-	6.48	8.32, 8.12	7.22-7.90

Mass spectra

Mass spectra of the conjugated β -diketones showed intense molecular ion peaks in conformity with their formulation [23]. Peaks due to (Ar-CH=CH-CO)⁺, (P - C₆H₅)⁺, (P - C₆H₅CO)⁺, (P - ArC₂H₂)⁺, etc. are characteristic of all the spectra. The FAB mass spectra of the Cu(II) complexes showed molecular ion peaks corresponding to [CuL₂] stoichiometry. Peaks correspond to [CuL]⁺, L⁺ and fragments of L⁺ are also present in the spectra [24]. The spectra of all the chelates contain a number of fragments containing copper in the 3:1 natural abundance of ⁶³Cu and ⁶⁵Cu isotopes. Important fragments appeared in the spectra are given in Table 4.

Compound	Mass spectral data (m/z)
HL^1	276, 199, 171, 157, 129, 119, 105
HL^2	300, 223, 195, 181, 153, 127, 119, 105
$[Cu(L^1)_2]$	615, 613, 510, 508, 486, 484, 405, 403, 383, 381, 276, 199, 129, 119
$[Cu(L^2)_2]$	663, 661, 558, 556, 510, 508, 453, 451, 357, 355, 300, 195, 181, 105

Table 4.	Mass spectral	data of the	conjugated	R -diketones a	nd their (Cu(II)	complexes
Table 4	Mass spectral	uata of the	conjugateu	p-unkeromes and	iu men	$Cu(\Pi)$	complexes

UV spectra

The UV spectra of the conjugated β -diketones show two broad bands with maxima at ~370 and ~270 nm due to 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 [25] indicating the involvement of the carbonyl groups in metal complexation (Table 1).

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