

Metal Complex of Some Conjugated 1,3-Diketones

MATHEW PAUL and K. KRISHNANKUTTY*

Department of Chemistry, Calicut University, Calicut-673 635, India

Four new conjugated 1,3-diketones and their Cu(II), Ni(II) and Co(II) chelates of ML_2 composition have been synthesized and characterised. The electronic, ir, 1H nmr and mass spectral data of the compounds are discussed.

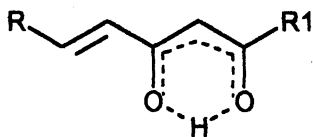
Key Words: Metal, Complexes, Conjugated 1,3-Diketones.

INTRODUCTION

In continuation of our studies¹ on metal complexes of 1,3-diketones in which the carbonyl groups are directly linked to olefinic function², we here report the synthesis and characterisation of four new conjugated 1,3-diketones **1a–1d** and their Cu(II), Ni(II) and Co(II) complexes.

EXPERIMENTAL

Preparation of the 1,3-diketones: The conjugated 1,3-diketones were prepared by the condensation of cinnamaldehyde/naphthaldehyde with acetylacetone/benzoylacetone, as detailed below.



1

	R	R ₁
a	C ₆ H ₅ CH=CH	CH ₃
b	2-naphthyl	CH ₃
c	C ₆ H ₅ CH=CH	C ₆ H ₅
d	2-naphthyl	C ₆ H ₅

Synthesis of 1a and 1b (6-aryl-5-hexene-2,4-diones)

To a mixture of acetylacetone (0.075 mol) and boric oxide (0.055 mol) in dry ethyl acetate (50 mL) also containing tri(sec-butyl)borate (0.1 mol) kept at ca. 0°C, a solution of the aldehyde, cinnamaldehyde/naphthaldehyde (0.025 mol) in dry ethyl acetate (15 mL) and n-butylamine (0.5 mL) was added dropwise for 90 min with constant stirring. The stirring was continued for an additional period of ca. 2 h and the solution was set aside overnight. The reaction mixture was stirred

for *ca.* 1 h with hot (*ca.* 50°C) hydrochloric acid (0.04 M, 20 mL) and extracted repeatedly with ethyl acetate. The combined extracts were concentrated in vacuum and subjected to column chromatography (silica gel, mesh 60–120). The yellow band developed in the lower region was recovered by successive elution with 5 : 1 v/v mixture of chloroform-acetone and the combined eluates evaporated to get pure substance. All the compounds isolated were recrystallised from hot benzene.

Synthesis of 1c and 1d (5-aryl-1-phenyl-4-pentene-1,3-diones)

Benzoylacetone (0.005 mol) mixed with boric oxide (0.005 mol) and 5 mL dry ethyl acetate was stirred well for *ca.* 1 h. The stirring was further continued for *ca.* 1 h with the slow addition of a solution of cinnamaldehyde/naphthaldehyde (0.005 mL) in dry 5 mL ethyl acetate followed by tri(*sec*-butyl) borate (0.01 mL) and 0.05 mL of *n*-butylamine. After stirring for an additional period of *ca.* 3 h, the solution was set aside overnight. Hot (*ca.* 60°C) hydrochloric acid (0.4 M, 7.5 mL) was then added to the reaction mixture and again stirred for *ca.* 1 h before extraction with ethyl acetate. The washed extracts were combined, concentrated and the residual paste obtained was stirred with hydrochloric acid (2 M, 10 mL). The separated solid product was collected, washed with water (5 mL) then with ethanol (5 mL) and dried under reduced pressure. The compounds were recrystallised from hot benzene to get t.l.c. (silica gel) pure material.

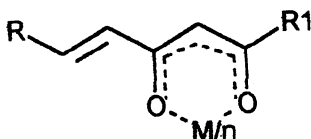
Preparation of metal complexes: The Cu(II), Ni(II) and Co(II) complexes of the compounds were prepared by the following general method. To a refluxing solution of the diketone (0.002 mol) in methanol (15 mL), an aqueous solution of metal(II) acetate (0.001 mol, 10 mL) was added and the reaction mixture was refluxed for *ca.* 3 h. The precipitated product on cooling to room temperature was filtered, washed with water, then with ethanol and dried in vacuum.

Carbon and hydrogen percentages reported are by microanalysis and the metal percentage by using a Perkin-Elmer 2380/AAS. Electronic spectra were recorded in methanol solution (10^{-4} M) on a UV-1601 Shimadzu recording spectrophotometer, IR spectrum (KBr pellets) on a Shimadzu 8101A FTIR spectrophotometer, ^1H NMR on a Jeol 400 NMR spectrometer and mass spectra on a Jeol/sx-102 (FAB) mass spectrometer.

RESULTS AND DISCUSSION

All the diketones are crystalline in nature with sharp melting points. Analytical and physical data of the compounds are presented in Table-1.

These diketones formed stable complexes of Cu^{2+} , Ni^{2+} and Co^{2+} with sharp melting points. Elemental analysis data (Table-2) of all the complexes suggest they are of ML_2 stoichiometry. All the complexes behave as non-electrolytes (specific conductance $< 15 \Omega^{-1} \text{cm}^{-1}$ in DMF) and do not contain the anion of the metal salt used for their preparation. Electronic, IR, NMR and mass 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 structure 2.



$M = \text{Cu}^{2+}, \text{Ni}^{2+}, \text{Co}^{2+}$ for $n = 2$

Structure-2

	<u>R</u>	<u>R₁</u>
a	$\text{C}_6\text{H}_5\text{CH}=\text{CH}$	CH_3
b	2-naphthyl	CH_3
c	$\text{C}_6\text{H}_5\text{CH}=\text{CH}$	C_6H_5
d	2-naphthyl	C_6H_5

TABLE-1
ANALYTICAL AND PHYSICAL DATA OF CONJUGATED 1,3-DIKETONES

Compound	Yield (%)	m.p. (°C)	Elemental Analysis		λ_{max} (nm)
			Calculated	(Found)	
			C	H	
1a $\text{C}_{14}\text{H}_{14}\text{O}_2$	70	82	78.51 (78.13)	6.54 (6.51)	388.4 284
1b $\text{C}_{16}\text{H}_{14}\text{O}_2$	50	68	80.67 (80.33)	5.88 (5.85)	392 290
1c $\text{C}_{19}\text{H}_{16}\text{O}_2$	70	78	82.61 (82.31)	5.80 (5.76)	415 289
1d $\text{C}_{21}\text{H}_{16}\text{O}_2$	50	104	84.00 (83.72)	5.33 (5.31)	411 281

Characterisation of conjugated 1,3-diketones

The UV spectra of the compounds in 95% ethanol (10^{-3} M) show two bands with λ_{max} at ca. 400 and 290 nm. The band at ca. 400 nm assignable to the $n \rightarrow \pi^*$ transition of the carbonyl chromophore and the band at ca. 290 nm to the conjugated $\text{C}=\text{C} \pi \rightarrow \pi^*$ transition. Compared to acetylacetone and benzoylacetone these absorption bands showed a shift to low energy region due to higher conjugation. In the metal complexes the former band showed a bathochromic shift indicating the involvement of the dicarbonyl function in complexation.

That the compounds exist in the intramolecularly hydrogen bonded enol form as in structure 1 is clearly indicated in their IR spectra. Thus no band assignable to the stretching of free acetyl carbonyl of **1a** and **1b** and benzoyl carbonyl of **1c** and **1d** is present in the spectra. The IR spectra of **1a** and **1b** show an intense band at ca. 1690 cm^{-1} and that of **1c** and **1d** at ca. 1640 cm^{-1} assignable respectively to the chelated acetyl and benzoyl carbonyl stretch^{3, 5}. Another strong band appearing at ca. 1630 cm^{-1} in the spectra of all the compounds can safely

be assigned to the stretching of cinnamoyl/naphthyl carbonyl function. The four prominent bands observed in the region 1600–1550 cm^{-1} are presumably due to various $\nu(\text{C}=\text{C})$ vibrations. The intense and broad band in the region 3500–2300 cm^{-1} indicates strong intramolecular hydrogen bonding as in structure 1. A medium intensity band appearing at *ca.* 990 cm^{-1} in the spectra of the compounds can be assigned to the *trans* —CH=CH— absorption. The important IR absorptions and their probable assignments are given in Table-3.

TABLE- 2
ANALYTICAL AND PHYSICAL DATA OF METAL CHELATES
OF CONJUGATED 1,3-DIKETONES

Metal-Chelates	Yield (%)	m.p. ($^{\circ}\text{C}$)	Elemental Analysis Calculated (Found)			λ_{max} (nm)
			C	H	M	
1a ($\text{C}_{14}\text{H}_{14}\text{O}_2$) ₂ Cu	70	> 300	68.64	5.31	12.98	459
			(68.57)	(5.30)	(12.97)	290
1b ($\text{C}_{16}\text{H}_{14}\text{O}_2$) ₂ Cu	60	> 300	71.44	4.84	11.82	382
			(71.38)	(4.83)	(11.81)	291
1c ($\text{C}_{19}\text{H}_{16}\text{O}_2$) ₂ Cu	70	198	74.32	4.89	10.36	408.5
			(74.27)	(4.85)	(10.34)	
1d ($\text{C}_{21}\text{H}_{16}\text{O}_2$) ₂ Cu	55	242	76.19	4.54	9.61	388.5
			(72.24)	(4.03)	(9.60)	281
1a ($\text{C}_{14}\text{H}_{13}\text{O}_2$) ₂ Ni	70	> 320	69.32	5.36	12.11	366
			(69.13)	(5.34)	(12.08)	278
1b ($\text{C}_{16}\text{H}_{13}\text{O}_2$) ₂ Ni	55	> 320	72.09	4.88	11.82	365
			(71.90)	(4.86)	(10.99)	295
1c ($\text{C}_{19}\text{H}_{15}\text{O}_2$) ₂ Ni	70	330	74.92	4.93	9.64	333.5
			(74.90)	(4.90)	(9.63)	
1d ($\text{C}_{21}\text{H}_{15}\text{O}_2$) ₂ Ni	50	120	76.75	4.57	8.94	385
			(72.37)	(4.50)	(8.93)	311.9
1a ($\text{C}_{14}\text{H}_{13}\text{O}_2$) ₂ Co(H_2O) ₂	60	120	69.29	5.36	5.36	422
			(69.28)	(5.35)	(5.30)	289
1b ($\text{C}_{16}\text{H}_{13}\text{O}_2$) ₂ Co(H_2O) ₂	50	> 320	72.05	4.87	11.06	398
			(71.90)	(4.86)	(11.03)	298
1c ($\text{C}_{19}\text{H}_{15}\text{O}_2$) ₂ Co(H_2O) ₂	65	110	74.89	4.93	9.68	416
			(74.87)	(4.92)	(9.67)	289
1d ($\text{C}_{21}\text{H}_{15}\text{O}_2$) ₂ Co(H_2O) ₂	50	130	76.92	4.57	8.97	384.5
			(72.08)	(4.50)	(8.94)	280

In the spectra of metal complexes, bands in the region 1690–1630 cm^{-1} almost disappeared, but instead two new bands appeared at *ca.* 1610 and 1585 cm^{-1} of appreciable intensity assignable to the metal chelated carbonyl groups. The replacement of enolic proton by metal ion is also evident from the absence of the broad free ligand band in the region 3500–2500 cm^{-1} in the spectra of complexes⁴. Further evidence for complex formation is from the appearance of two medium

intensity bands in the region $500\text{--}400\text{ cm}^{-1}$ due to $\nu(\text{M—O})$ vibrations. The IR spectra of Cu(II) chelates are given in Table-4, as other complexes have similar spectra.

TABLE-3
CHARACTERISTICS OF IR DATA (cm^{-1}) OF CONJUGATED 1,3-DIKETONES

Compounds				Probable assignments
1a	1b	1c	1d	
1689	1690	—	—	$\nu(\text{C=O})$ acetyl
—	—	1640	1638	$\nu(\text{C=O})$ benzoyl
1630	1625	1628	1629	$\nu(\text{C—O})$ cinnamoyl/naphthyl
1610	1577	1589	1590	
1579	1512	1510	1517	$\nu(\text{C—C})$ phenyl/alkenyl
1492	1450	1452	1461	
1425	1425	1440	1440	$\nu_{\text{asym}}(\text{C—C—C})$ chelate ring
1392	1384	1380	1388	$\nu_{\text{sym}}(\text{C—C—C})$ chelate ring
1149	1134	1141	1168	$\beta(\text{C—H})$ chelate ring
1070	1045	1072	1080	
985	970	991	972	$\nu(\text{CH—CH—})$ <i>trans</i>
756	775	752	773	$\nu(\text{C—H})$ chelate ring

TABLE-4
CHARACTERISTICS OF IR DATA (cm^{-1}) OF CONJUGATED 1, 3-DIKETONES

Copper(II) chelate of				Probable assignments
1a	1b	1c	1d	
1615	1620	1630	1629	$\nu(\text{C=O})$ metal chelated acetyl/benzoyl
1585	1590	1586	1588	$\nu(\text{C=O})$ metal chelated cinnamoyl
1530	1561	1520	1524	$\nu(\text{C—C})$ phenyl/alkenyl
1515	1540	1485	1486	
1465	1515	1448	1458	
1415	1440	1395	1428	$\nu_{\text{asym}}(\text{C—C—C})$ chelate ring
1403	1404	1360	1406	$\nu_{\text{sym}}(\text{C—C—C})$ chelate ring
1136	1165	1139	1167	$\beta(\text{C—H})$ chelate ring
1060	1025	1073	1044	
994	970	994	960	$\nu(\text{CH=CH—})$ <i>trans</i>
755	776	751	767	$\nu(\text{C—H})$ chelate ring
485	490	503	482	$\nu(\text{M—O})$ chelate ring
460		475	450	

The ^1H nmr spectra of all the conjugated 1,3-diketones displayed a one proton signal *ca.* δ 15.85 ppm due to strong intramolecularly hydrogen bonded enol form. Other signals appeared are in the range δ 6.056–6.587 (methine protons),

δ 2.415–2.503 (methyl proton in **1a** and **1b**), 7.519–8.662 (alkenyl protons), 6.883–8.418 (aryl protons). The trans orientation of the alkenyl groups of the compounds are evident from their observed J values. The characteristic chemical shift of various protons are summarised in Table 5.

The most characteristic feature of the ^1H NMR spectra of the diamagnetic nickel(II) chelates is the absence of proton signal at δ 15.85 ppm. This strongly suggests the replacement of the enolic proton by the metal ions as in structure **2**. The integrated intensities of the aryl and alkenyl signals are in agreement with the 1 : 2 metal ligand stoichiometry of the complexes.

TABLE- 5
CHARACTERISTIC ^1H NMR SPECTRAL DATA OF CONJUGATED 1,3-DIKETONES

Compounds of				Probable assignments chemical shift (δ ppm)
1a	1b	1c	1d	
15.84	15.85	16.08	15.88	enolic
7.51 (1H)	8.66 (1H)	7.95 (1H)	8.57 (1H)	alkenyl
7.50 (1H)	8.46 (1H)	7.95 (1H)	8.51 (1H)	
7.49–6.88 (5H)	8.41–7.11 (7H)	7.93–6.92 (10H)	8.28–7.47 (12H)	aryl
6.05 (1H)	6.58 (1H)	6.27 (1H)	6.40 (1H)	methine
2.41 (3H)	2.50 (3H)	—	—	methyl

Mass spectra of all the compounds showed an intense molecular ion peaks $\text{P}^+/\text{P} + 1^+$. The cleavage of CH_3COCH_2 fragment from the molecular ion explains the origin of intense $(\text{P}-57)^+$ peak, a characteristic feature of **1a** and **1b**, while other prominent peaks appearing in the spectra are $(\text{P}-\text{COCH}_3)^+$, $(\text{P}-\text{CH}_3\text{COCH}_2-\text{CO})^+$, $(\text{P}-\text{Ph}-\text{CO})^+$, Ph^+ , $(\text{P}-\text{CH}_2-\text{CO}-\text{Ph})^+$ and elimination of $\text{CH}_2=\text{C}=\text{O}$ from $(\text{P}-\text{PhCO})^+$ are most prominent. The FAB mass spectra of the Cu(II) chelates show prominent peaks due to $[\text{CuL}_2]^+$ which justifies the formulation of the chelates. The base peak in all the case is due to ligand and peaks due to $(\text{CuL})^+$, L^+ and fragments of L^+ are sometimes more intense than the molecular ion peak. Another striking feature of all the spectra of complexes is the presence of a large number of fragments containing copper. They are easily identified because of the 2 : 1 natural abundance of ^{63}Cu and ^{65}Cu .

REFERENCES

1. P. Venugopalan and K. Krishnankutty, *J. Indian Chem. Soc.*, **75**, 98 (1988); *Asian J. Chem.*, **10**, 453 (1998); *Synth. React. Inorg. Met.-Org. Chem.*, **28**, 1313 (1988).
2. P. Claesin, P. Tuchinda and V. Rentrakul, *J. Indian Chem. Soc.*, **71**, 509 (1994).
3. L.J. Bellamy, *The Infrared Spectra of Complex Molecules*, Academic, London, Vol. 2 (1980); L.J. Bellamy, G.S. Spicer and J.D.H. Stickland, *J. Chem. Soc.*, 4653 (1953).
4. K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, 4th Edn., Wiley, New York (1976).
5. James U. Lowe (Jr.) and Lloyd N. Ferguson, *J. Org. Chem.*, **30**, 3001 (1965).