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Synthesis and Characterisation of Co(II), Ni(II) and Cu(II) Complexes of Some 6-Aryl-5-hexene-2,4-diones

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A series of 6-aryl-5-hexene-2,4-diones and their Co(II), Ni(II) and Cu(II) complexes of ML_2 stoichiometry have been synthesized and characterised. The electronic, ir, ^1H NMR, mass spectral and thermogravimetric data are discussed.

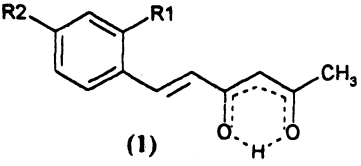
Key Words: Synthesis, Characterization, Co, Ni, Cu complexes, 6-Aryl-5-hexene-2,4-diones.

INTRODUCTION

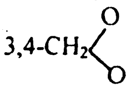
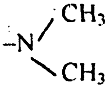
In continuation of our studies[1] on 1,3–diketones in which the carbonyl groups are directly linked to olefinic (—CH═CH—) groups and their metal complexes, we report here the synthesis and characterisation of four new 6-aryl-5-hexene-2,4–diones (**1a–1d**)) and their Co(II), Ni(II) and Cu(II) complexes. Such unsaturated 1,3-dicarbonyl moieties are the basic structural units present in the active chemical components of several traditional Indian medicinal plants[2] such as *Curcuma longa* (turmeric).

EXPERIMENTAL

The 1,3-diketones (**1a–1d**)) were synthesized by the condensation of substituted aromatic aldehydes [*o*-tolualdehyde, *p*-ethoxybenzaldehyde, pipernal and *p*-(N,N-dimethylamino)benzaldehyde] with acetylacetone as reported earlier[1, 3] for related compounds. A typical procedure is given below.



(1)

	R1	R2
1a	CH_3	H
1b	H	CH_3-CH_2-O
1c	H	
1d	H	

Acetylacetone (0.075 mol) mixed with boric oxide (0.055 mol) was suspended in dry ethylacetate (50 mL) containing tri(sec-butyl)borate (0.1 mol). To this mixture kept at *ca.* 0°C, a solution of aromatic aldehyde (0.025 mol) in dry ethyl acetate (15 mL) and *n*-butylamine (0.5 mL) were 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 recation mixture was then stirred for *ca.* 1 h with hot *ca.* (50°C) hydrochloric acid (0.4 M, 20 mL) and extracted repeatedly with ethyl acetate. The combined extracts was concentrated in vacuum and purified by 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 on evaporation yielded the 6-aryl-5-hexene-2,4-diones. The compounds were recrystallised from hot benzene to get chromatographically (TLC) pure material.

Preparation of metal complexes: Copper(II), nickel(II) and cobalt(II) complexes 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, and cooled to room temperature. The precipitated complex 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 atomic absorption spectrophotometer. Electronic spectra were recorded in methanol solution (10^{-4} M) on a UV-1601 Schimadzu recording spectrophotometer, IR spectra (KBr pellets) on a Schimadzu 81101A FTIR spectrophotometer, ^{1}H NMR on a Jeol 400 NMR spectrometer, mass spectra on a Jeol/Sx-102 (FAB) mass spectrometer and the thermal analysis were carried out using a TGAV5.1A Dupont 2100 system, in an atmosphere of nitrogen at a constant heating rate of 10°C min^{-1} and a 5 mg of sample size was employed for each study.

RESULTS AND DISCUSSION

The 6-aryl-5-hexene-2,4-diones formed are crystalline in nature with sharp melting points. The yield, melting points and the observed carbon, hydrogen percentages of the compounds are presented in Table-1.

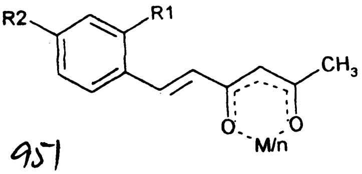
TABLE-1
ANALYTICAL AND PHYSICAL DATA OF 6-ARYL-5-HEXANE-2,4-DIONES

Compound	Yield (%)	m.p. (°C)	Elemental Analysis% Calculated (found)		λ_{max} (nm)
			C	H	
1a,$C_{13}H_{14}O_2$	50	82	77.22	6.90	409
			(76.84)	(6.89)	312
1b,$C_{14}H_{16}O_3$	65	75	72.41	6.89	415
			(72.10)	(6.86)	335
1c,$C_{13}H_{12}O_4$	50	122	67.24	5.17	401
			(66.95)	(5.15)	310
1d,$C_{14}H_{17}NO_2$	70	60	72.72	7.35	410.5
			(72.59)	(7.30)	328

These compounds formed stable metal complexes with Cu^{2+}, Ni^{2+} and Co^{2+}. Elemental analysis data of all the complexes (Table-2) corresponds to ML_2

TABLE-2
ANALYTICAL AND PHYSICAL DATA OF METAL CHELATES OF THE 6-ARYL-5-HEXENE-2,4-DIONES

Metal Chelates	Yield (%)	m.p. (°C)	Elemental Analysis(%) Calculated (found)			λ_{max} (nm)
			C	H	M	
1a, $(C_{13}H_{13}O_2)_2Cu$	70	234	67.01 (66.95)	5.58 (5.57)	13.65 (13.63)	409 314
1b, $(C_{14}H_{15}O_3)_2Cu$	65	230	63.94 (63.81)	5.71 (5.70)	12.09 (12.07)	443 333
1c, $(C_{13}H_{11}O_4)_2Cu$	70	232	59.37 (59.31)	4.18 (4.17)	12.09 (12.07)	391 285
1d, $(C_{14}H_{16}NO_2)_2Cu$	70	228	64.18 (64.12)	6.11 (6.10)	12.13 (11.88)	416 288
1a,$(C_{13}H_{13}O_2)_2Ni$	75	> 300	67.73 (67.53)	5.64 (5.62)	12.74 (12.70)	409 289
1b, $(C_{14}H_{15}O_3)_2Ni$	70	136	64.53 (64.36)	5.76 (5.74)	11.27 (11.24)	416 330
1c, $(C_{13}H_{11}O_4)_2Ni$	75	> 300	59.92 (59.77)	4.22 (4.21)	11.27 (11.24)	397 286
1d, $(C_{14}H_{16}NO_2)_2Ni$	75	184	64.78 (64.61)	6.16 (6.15)	11.30 (11.28)	409 288
1a, $(C_{13}H_{13}O_2)_2Co(H_2O)_2$	75	160	67.69 (67.56)	5.60 (5.40)	12.78 (12.72)	400 299
1b, $(C_{14}H_{15}O_3)_2Co(H_2O)_2$	60	110	64.50 (64.36)	5.76 (5.74)	11.31 (11.28)	416 315
1c, $(C_{13}H_{11}O_4)_2Co(H_2O)_2$	70	130	59.99 (55.37)	4.22 (4.45)	11.31 (11.29)	402 277
1d, $(C_{14}H_{16}NO_2)_2Co(H_2O)_2$	75	150	64.75 (64.03)	6.17 (6.05)	11.36 (11.35)	415 289



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M = Cu^{2+}, Ni^{2+}, Co^{2+}

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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. The diketones and their metal complexes were characterised on the basis of their electronic, IR, NMR and mass spectral data.

The UV spectra of the compounds in 95% ethanol (10^{-3} M) showed two broad bands at *ca.* 415 and 300 nm respectively due to carbonyl and olefinic functions. In the meal complexes the former bond showed a bathochromic shift (5–16 nm) indicating the involvement of the dicarbonyl function in complexation.

The IR spectra of the diketones show two prominent band at *ca.* 1665 and 1630 cm^{-1} assignable respectively to the chelated acetyl and cinnamoyl ν(C=O) vibrations[1,4]. The observed position and intensity of these bands indicate that the compounds exists entirely in the enol form and are enolised towards the cinnamoyl function. The intense and broad band observed in the region 3500–2100 cm^{-1} is undoubtedly due to the presence of strong intramolecular hydrogen bonding in these compounds[4], which is also evident from the lowering of acetyl carbonyl stretching frequency. At least four prominent bands are observed in the region 1590–1400 cm^{-1} presumably due to the various ν(C=C) vibrations. A medium intensity band at *ca.* 931 cm^{-1} is possibly arising from the *trans* —CH=CH— double bond absorption. Important infrared bands and their assignments are given in Table-3.

TABLE-3

CHARACTERISTIC IR DATA (cm^{-1}) OF 6-ARYL-5-HEXANE-2,4-DIONES

Compounds				Probable assignments
1a	1b	1c	1d	
1665	1665	1600	1666	ν(C=O) (chelated acetyl)
1615	1625	1630	1620	ν(C=O) (chelated cinnamonyl)
1589	1600	1596	1600	ν(C=C) (phenyl)/(alkenyl)
1550	1560	1560	1541	
1510	1510	1510	1510	
1480	1475	1492	1485	ν_{asym}(C—C—C) (chelate ring)
1430	1450	1442	1436	ν_{sym}(C—C—C)(chelate ring)
1100 1039	1170 1114 1043	1161 1103 1035	1163 1062	β(C—H) (chelate ring)
930	921	931	939	ν(—CH=CH—) (*trans*)
727	725	730	725	ν(C—H) (chelate ring)

In complexes the broad free band in the region 3500–2500 cm^{-1} is cleared up which indicate that the chelated proton is replaced by metal ion during complexation. The region above 2000 cm^{-1} in complexes show several medium and weak intensity bands due to various aliphatic and aromatic C—H stretching vibrations. The most characteristic feature of the spectra of the metal complexes is the absence of any strong bands in the region 1800–1600 cm^{-1} due to free or hydrogen bonded carbonyl function. However two new bands appeared in the spectra of all the complexes in the region 1630–1580 cm^{-1} in addition to the various ν(C=C) vibrations are assignable to metal chelated carbonyl stretching[5]. Further evidence for complex formation is from the appearance of two medium inensity bands in the region 500–400 cm^{-1} due to ν(M—O) vibrations. Thus their data strongly supports the structure **2** of the complexes. Since all the metal complexes have very similar spectral bands only the characteristic ir bands of the copper(II) complexes are tabulated in Table-4.

TABLE-4

CHARACTERISTIC IR DATA (cm^{-1}) OF COPPER (II) CHELATES OF 6–ARYL–5–HEXENE–2,4–DIONES

Copper(II) chelates of				Probable assignments
1a	**1b**	**1c**	**1d**	
1624	1640	1631	1628	ν(C=O) (metal coordinated acetyl)
1590	1614	1602	1607	ν(C=O) (metal coordinated cinnamonyl)
1575	1580	1585	1590	ν(C—C) (phenyl)/(alkenyl)
1560	1540	1560	1560	
1518	1512	1523	1507	
1480	1470	1490	1480	ν_{asym}(C—C—C) (chelate ring)
1460	1450	1445	1450	ν_{sym}(C—C—C) (chelate ring)
1103 1040	1170 1120 1043	1180 1103 1029	1157 1026	β(C—H) (chelate ring)
971	960	968	951	ν(—CH=CH—) (*trans*)
732	720	720	737	ν(C—H) (chelate ring)
519 490	493 418	476 418 408	476 447 416	ν(Cu—O) (chelate ring)

The ^1H NMR spectra of the all 6-aryl hexanoids show a one proton signal in the downfield region at δ 15.85 ppm assignable to intramolecularly hydrogen bonded enolic proton. The methine proton signal is observed at δ 6.0028 to 6.477 ppm which is considerably shifted to low field compared with methine proton of acetylacetone, may be due to the extended delocalisation of the molecule. The observed signals and their assignments are given in Table-5. The integrated intensities of all the signals agree with the formulation as in structure **1**.

The most characteristic feature of the ^1H NMR spectra of the diamagnetic nickel(II) chelates is the absence of the proton signals at δ 15.85 ppm. This strongly suggests the replacement of enolic proton by the metal ions in the complexes. The methine signal is shifted towards the downfield of the spectra indicating the decreased electron density around the central carbon atom of the pseudo aromatic metal chelate ring system. The integrated intensities of the various signals are in agreement with the 1 : 2 metal ligand stoichiometry of the chelates.

TABLE-5

^{1}H NMR SPECTRAL DATA OF 6-ARYL-5-HEXENE-2,4-DIONES

Chemical shift (ppm)				Assign-ments
1a	**1b**	**1c**	**1d**	
115.848	15.863	15.856	15.857	enolic
8.076 (1H) 7.905 (1H)	7.638 (1H) 7.598 (1H)	7.612 (1H) 7.473 (1H)	7.574 (1H) 7.535 (1H)	alkenyl
7.879–6.972 (4H)	7.511–7.254 (4H)	7.695–7.267 (3H)	6.653–7.453 (4H)	aryl
6.414 (1H)	6.477 (1H)	6.002 (1H)	6.288 (1H)	methine
2.474 (3H) 2.175 (3H)	4.048 (2H) 2.453 (3H) 1.435 (3H)	3.795 (2H) 2.155 (3H)	3.077 (3H) 3.003 (3H) 2.125 (3H)	methyl

Mass Spectra: All the diketones showed intense molecular ion $P^+/(P + 1)^+$ peaks in confirmity with their formulation. The cleavage of the acetyl fragment from the molecular ion explains the origin of the intense $(P - 43)^+$ peak, a characteristic feature of all the spectra. Other prominent peaks appeared in the spectra are due to $(P—CH_3COCH_2)^+$, $(P—CH_3COCH_2CO)^+$, $ArCH^+$, Ar^+. The FAB mass spectra of the copper(II) chelates show prominent peaks due to $[CuL_2]^+$ which justifies the formulation of the chelates as in structure **2**. The base peak in all the case is due to the ligand and ligand fragments. Another striking feature of all the spectra 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 isotopes.

Thermogravimetric Analysis: Thermogravimetric analysis of **1c** and its Cu(II), Ni(II) and Co(II) complexes were also studied. The thermograms of the Cu(II) and Co(II) complexes show a two stage decomposition pattern while for Ni(II) it is a single stage decomposition. In all the cases the decomposition pattern agree with their formulation since the mass-loss from TG and theoretically expected are in good agreement (Table-6).

TABLE-6

Compound/Complexes (Molecular mass)	Temp. ranges in TG (K)	Mass loss (%)	
		Experimental	Theoretical
1c=HL, $C_{13}H_{12}O_4$ (232)	373–353 563–1013	51.00 49.00	52.59 47.41
$Cu(L)_2$ (525.54)	373–623 633–913	46.40 32.00	45.50 42.41
$Ni(L)_2$ (520.69)	373–943	88.16	85.66
$Co(L)_2(H_2O)_2$ (520.93)	304–553 554–739	16.01 64.89	16.12 68.48

Kinetic parameters such as apparent activation energy (E), pre exponential factor (A) and entropy of activation (ΔS) for each stage were evaluated based on three non-mechanistic equations[8–10], also, computed the correlation coefficient (r) using the weighted least-square method (LSM) for the equation suggested by Coast-Redfern, Horowitz-Metzger and MacCallum-Tanner and their results are given in Table-7. The order of each stage of the decomposition reaction of the compound and their complexes was determined.[11]

TABLE-7
KINETIC PARAMETERS FOR THE DECOMPOSITION OF 1c AND ITS METAL COMPLEXES

Compound	Equations	E kcal mol^{-1}	log A s^{-1}	ΔS kcal deg^{-1} mol^{-1}	Correlation coefficient (r)
1c = $C_{13}H_{12}O_4$	CR	11.32	2.38	–48.68	0.996
1st stage	MT	9.13	4.46	–39.14	0.994
	HM	11.13	2.20	–49.49	0.990
2nd stage	CR	17.04	1.68	–52.74	0.988
	MT	18.41	4.84	–38.27	0.992
	HM	17.56	1.85	–51.95	0.988
$(C_{13}H_{11}O_4)_2Cu$	CR	27.81	8.38	–21.47	0.970
1st stage	MT	32.64	13.38	1.42	0.960
	HM	36.57	11.93	–5.24	0.970
2nd stage	CR	21.98	3.68	–43.48	0.987
	MT	23.03	6.71	–29.61	0.991
	HM	22.27	3.72	–43.26	0.981
$(C_{13}H_{11}O_4)_2Ni$	CR	15.30	2.04	–50.85	0.968
Single stage	MT	16.19	5.08	–36.95	0.977
	HM	17.07	2.64	–48.09	0.971
$(C_{13}H_{11}O_4)_2Co(H_2O)_2$	CR	3.00	0.26	–67.51	0.984
1st Stage	MT	4.23	2.56	–47.78	0.990
	HM	6.30	0.12	–58.97	0.994
$(C_{13}H_{11}O_4)_2Co$	CR	51.26	14.55	6.47	0.994
2nd stage	MT	52.18	17.56	20.26	0.995
	HM	54.90	16.75	11.96	0.995

CR = Coats-Redfern; MT = MacCallum-Tanner; HM = Horowitz–Metzger.

From the data it can be concluded that the values of thermodynamic parameter are comparable and indicates a common reaction mode. The activation energies are low in 1st stage when compared with the 2nd stage transition and also it shows that the rate of reaction is fast during the first stage. For decomposition kinetics it has been observed that greater the thermal stability of the complex larger the activation energy for decomposition. The lowest values of activation energies are for cobalt complexes where the first stage decomposition is utilised to remove the coordinated water. The negative ΔS values indicates a more ordered activated structure and that the reactions are slower than normal.

REFERENCES

1. P. Venugopalan and K. Krishnankutty, *J. Indian Chem Soc.*, **75**, 98 (1998); *Asian J.Chem*,, **10**, 453 (1998); *Synth. React. Inorg. Met.-Org.Chem.*, 1313 (1998).
2. V.S. Govindarajan, CRC Critical Reviews in Food Science and Nutrition, **12**, 199 (1980); P.Cleason, P. Tuchinda and V.Rentrakul, *J. Indian Chem.* Soc., **71**, 509 (1994).
3. P.J. Roughley and D.A. Whiting, *J. Chem. Soc., Perkin Trans.*, **1**, 2379 (1973).
4. L.J. Bellamy, The Infrared Spectra of Complex Molecules, Academic, London, Vol. 2 (1980); L.J. Bellamy, G.S. Spicer and J.D.H. Strickland, *J. Chem. Soc.*, 4653 (1953).
5. K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, 4th Edn., Wiley, New York, (1976).
6. D.C. Nonhebel, *Tetrahedron*, **24**, 1869 (1968).
7. W.W. Wendlandt, Thermal Methods of Analysis, 2nd Edn., Elsevier, Amsterdam (1963).
8. A.W. Coats and J.P. Redfern, *Nature (London)*, **201**, 68 (1964).
9. H.H. Horowitz and G. Metzger, *Anal. Chem.*, **163**, 35 (1464).
10. J.R. MacCallum and J. Tanner, *Eur. Polym. J.*, 6, 1033 (1970).
11. P.M. Madhusudanan, P.N.K. Nambissan and C.G.R. Nair, *Thermochim. Acta*, **9**, 149 (1974).

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