



CONJUGATED TETRACARBONYL LIGANDS AND THEIR METAL COMPLEXES

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ABSTRACT

The Claisen-Schmidt condensation between β -dicarbonyl compounds (benzoylacetone and acetoacetanilide) and terephthalaldehyde under specified conditions yielded a new series of conjugated tetracarbonyl compounds. Their existence in the intramolecularly hydrogen-bonded enol form (H_2L) is confirmed from their IR, ¹H NMR and mass spectral data. Dibasic tetradentate coordination of the compounds in their $[Co_2(L)_2(H_2O)_4]$, $[Ni_2(L)_2]$ and $[Cu_2(L)_2]$ complexes is established based on analytical and spectral data.

Keywords: Conjugated tetracarbonyl compounds, Metal complexes, IR spectra, ¹H NMR spectra, Mass spectra.

1. INTRODUCTION

Design and synthesis of polydentate and macrocyclic ligand systems have become a fascinating area of modern coordination chemistry mainly because of the increasing academic, industrial and biological interest exhibited by metal complexes of these types of compounds [1]. Literature reveals that metal complexes of organic compounds containing carbonyl functions have proliferated much during recent years. This trend is evident from the numerous reports of ligand systems based on β -dicarbonyl and related polycarbonyl compounds [2]. They exist predominantly in the highly conjugated enol tautomer and are known to form diverse types of metal complexes [3, 4]. Many of these complexes show interesting structures and unique spectral and magnetic properties that are of interest in bioinorganic studies [5, 6]. In continuation of our studies on conjugated polycarbonyl compounds and their metal complexes [7, 8], we hereby report the synthesis and characterization of two conjugated polycarbonyl compounds (H_2L) obtained by the condensation between terephthalaldehyde and β -dicarbonyl compounds (benzoylacetone and acetoacetanilide). Typical Co(II), Ni(II) and Cu(II) complexes of these compounds were also synthesized and characterized.

2. MATERIAL AND METHODS

Carbon, hydrogen and nitrogen 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, ¹H 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 ($\sim 10^{-3}$ mol/L) at $28 \pm 1^\circ C$. Magnetic susceptibilities were determined at room temperature on a Guoy type magnetic balance at room temperature ($28 \pm 1^\circ C$) using $Hg[Co(NCS)_4]$ as standard.

2.1. Synthesis of conjugated tetracarbonyl compound from benzoylacetone, (H_2L)¹

A mixture of benzoylacetone (1.62 g, 0.01 mol), boric oxide (0.7g, 0.01 mol) and 5 mL dry ethyl acetate were stirred for ~ 1 h. To this mixture, a solution of terephthalaldehyde (0.67 g, 0.005 mol) in 5 mL dry ethyl acetate was added slowly followed by 2.3 mL (0.01 mol) of tri(*sec*-butyl) borate drop by drop. The mixture was warmed to about $60^\circ C$ for ~ 10 minutes. *n*-butylamine (0.2 mL) was added drop by drop and then stirred for ~ 4 h, and kept overnight. The mixture was stirred for ~ 1 h after adding a hot solution of 0.4 M HCl (10 mL). The product was extracted using ethyl acetate several times and the combined extracts were

evaporated to a pasty mass. Stirred well with 2 M HCl (10 mL) for half an hour, washed with water, then with ethanol and dried in vacuum. TLC of the material indicated the presence of impurities and therefore subjected to column chromatography as given below.

The benzene solution of the product was placed over a column (2×50 cm) densely packed with silica gel (mesh 60-120) and eluted with 1:8 v/v acetone-petroleum ether mixture at a uniform flow rate of about 2 mL per minute. As the elution proceeded, two bands were developed in the column; a yellow lower band and a red orange upper band. The eluates of the lower band on evaporation yielded golden yellow crystals with sharp melting point. The upper orange band was collected by eluting with 1:2 v/v acetone-petroleum ether mixture and on evaporation yielded orange crystals. Though the compound was identified as a Knoevenagel condensation product, no further studies were carried out because of its very low yield.

2.2. Synthesis of conjugated tetracarboxyl compound from acetoacetanilide, (H₂L²)

Acetoacetanilide (1.77 g, 0.01 mol) and boric oxide (0.7g, 0.01 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 terephthalaldehyde (0.67 g, 0.005 mol) and tri (*sec*-butyl) borate (0.02 mol) dissolved in dry ethyl acetate were added, and stirred for ~5h with the slow addition of *n*-butylamine (0.5 mL). The mixture was kept overnight. To this, hot HCl (0.4 M, 7.5 mL) was added and again stirred for ~1h. It was then extracted with ethyl acetate and dried to yield a pasty mass. To this, 10mL of 2 M HCl was added and kept for ~24h. The solution was stirred well and the precipitate formed was filtered and dried. The purity was checked by TLC and revealed the presence of two compounds and they were separated by column chromatography as outlined below.

The crude product was dissolved in minimum quantity of dry ethyl acetate and placed over a column densely packed with silica gel (mesh 60-120) and eluted with 5:1 chloroform-acetone mixture at a uniform flow rate of 2 mL per minute. As the elution proceeded, two bands were developed in the column, a lower yellow band and an upper orange band. The lower portion was collected as 10 mL aliquots in separate tubes and combined eluates on evaporation yielded solid yellow product which on recrystallization from hot benzene gave golden yellow crystals with sharp melting point.

The orange band was discarded because of its impure nature.

2.3. Synthesis of Co(II), Ni(II) and Cu(II) complexes

A solution of the conjugated tetracarboxyl compound (0.005 mol) in 30 mL ethyl acetate-methanol (1:1 v/v) mixture was refluxed on a boiling water bath for half an hour. To this, a solution of metal(II) acetate (0.005 mol) in 20 mL methanol was added drop by drop and again refluxed for ~6h. The solution was then concentrated to half the volume, cooled to room temperature and the precipitated complex was filtered. It was then washed several times with ethyl acetate, methanol followed by water and recrystallized from hot ethanol to get the pure compound.

3. RESULTS AND DISCUSSION

The observed elemental percentages (Table 1) suggest that one equivalent of terephthalaldehyde has condensed with two equivalents of β -dicarbonyl compounds. The observed analytical and spectral data are in conformity with Fig.1 of the compounds. The compounds formed stable complexes with Co(II), Ni(II) and Cu(II) ions. The analytical data (Table 1) together with non-electrolytic nature in DMF (specific conductance $<10 \Omega^{-1} \text{ cm}^{-1}$; 10^{-3} M solution) suggest [Co₂(L)₂(H₂O)₄], [Ni₂(L)₂] and [Cu₂(L)₂] stoichiometry for the complexes. The Ni(II) chelates are diamagnetic, while Co(II) and Cu(II) complexes showed normal paramagnetic moment. The observed spectral data of the complexes are fully consistent with Fig. 2.

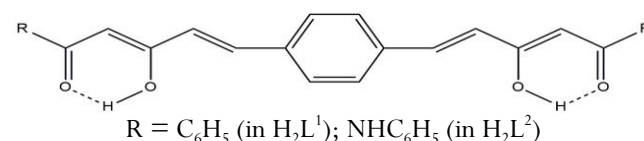
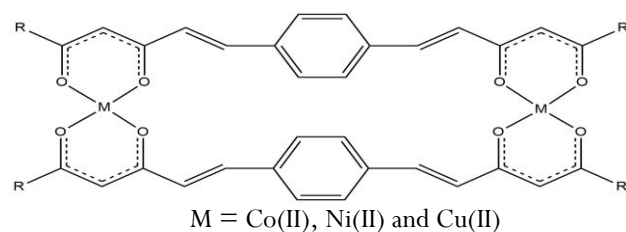


Fig. 1: Structure of the conjugated tetracarboxyl compounds (H₂L)



Co(II) complexes contain two coordinated water molecules on each Co(II)

Fig. 2: Structure of the metal complexes of conjugated tetracarboxyl compounds

Table 1: Physical and analytical data of the conjugated tetracarbonyl compounds and their metal complexes

Compound/ Molecular formula	M.P. °C	μ_{eff} BM	Elemental Analysis: Found (Calculated)%			
			C	H	N	M
H_2L^1 $\text{C}_{28}\text{H}_{22}\text{O}_4$	230	-	79.48 (79.62)	5.19 (5.21)	-	-
$[\text{Co}_2(\text{L}^1)_2(\text{H}_2\text{O})_4]$ $\text{C}_{56}\text{H}_{48}\text{Co}_2\text{O}_{12}$	>300	4.80	65.15 (65.25)	4.65 (4.66)	-	11.33 (11.44)
$[\text{Ni}_2(\text{L}^1)_2]$ $\text{C}_{56}\text{H}_{40}\text{Ni}_2\text{O}_8$	>300	-	70.00 (70.19)	4.19 (4.18)	-	12.22 (12.26)
$[\text{Cu}_2(\text{L}^1)_2]$ $\text{C}_{56}\text{H}_{40}\text{Cu}_2\text{O}_8$	>300	1.75	74.26 (74.37)	4.43 (4.43)	-	13.10 (13.14)
H_2L^2 $\text{C}_{28}\text{H}_{24}\text{N}_2\text{O}_4$	240	-	74.30 (74.34)	5.30 (5.31)	6.14 (6.19)	-
$[\text{Co}_2(\text{L}^2)_2(\text{H}_2\text{O})_4]$ $\text{C}_{56}\text{H}_{52}\text{N}_4\text{Co}_2\text{O}_{12}$	>300	4.79	61.52 (61.66)	4.77 (4.77)	5.13 (5.14)	10.77 (10.81)
$[\text{Ni}_2(\text{L}^2)_2]$ $\text{C}_{56}\text{H}_{44}\text{N}_4\text{Ni}_2\text{O}_8$	>300	-	65.91 (66.05)	4.30 (4.32)	5.52 (5.50)	11.48 (11.54)
$[\text{Cu}_2(\text{L}^2)_2]$ $\text{C}_{56}\text{H}_{44}\text{N}_4\text{Cu}_2\text{O}_8$	>300	1.76	65.30 (65.43)	4.28 (4.28)	5.44 (5.45)	12.32 (12.37)

3.1. Infrared spectra

The IR spectrum of H_2L^1 in the 1600-1700 cm^{-1} region 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 [8-10]. Absence of free benzoyl carbonyl band ($\sim 1660 \text{ cm}^{-1}$) and free α, β -unsaturated carbonyl band ($\sim 1645 \text{ cm}^{-1}$) in the double bond region of the spectrum confirm the existence of the compound entirely in the enolic form and enolisation towards the unsaturated carbonyl function as in Fig. 1.

Acetoacetanilide exist predominantly in the keto form with very small percentage of enol content. Therefore the most characteristic bands in the IR spectrum of acetoacetanilide are due to the amide carbonyl and acetyl carbonyl at 1667 and 1720 cm^{-1} respectively [8, 11]. The spectrum of H_2L^2 shows only two prominent bands at 1663 and 1654 cm^{-1} in the 1650-1800 cm^{-1} region. These bands cannot be assigned to a free cinnamoyl carbonyl stretching because such conjugated carbonyl groups usually absorb below 1650 cm^{-1} . Therefore the band at 1663 cm^{-1} is due to the amide carbonyl stretching and the band at 1654 cm^{-1} is due to partially enolised cinnamoyl carbonyl function as in Fig. 1.

The spectra of H_2L^1 and H_2L^2 showed a prominent band at $\sim 970 \text{ cm}^{-1}$ typical of *trans* -CH=CH- group [10]. The band observed at $\sim 1600 \text{ cm}^{-1}$ in the spectra is due to $\nu_{\text{C}=\text{C}}$ stretching vibrations. The presence of broad band in the 2800-3500 cm^{-1} region of the spectra also

support the intramolecularly hydrogen bonded enolic form of the compounds as in Fig. 1.

In the IR spectra of the metal complexes of H_2L^1 and H_2L^2 , the carbonyl bands of the free ligands disappeared. Two new bands appeared in the IR spectra of the metal complexes of H_2L^1 at ~ 1610 and $\sim 1580 \text{ cm}^{-1}$ due to metal chelated carbonyl groups [10]. Two new bands appeared in the IR spectra of the metal complexes of H_2L^2 at ~ 1630 and $\sim 1610 \text{ cm}^{-1}$ due to metal chelated carbonyl groups [12]. Further, the broad band due to intramolecularly hydrogen bonded dicarbonyl function in the region 2800-3500 cm^{-1} disappeared in the spectra of all the metal complexes indicating the replacement of enolic protons by the metal cation during complexation as in Fig. 2. The Co(II) complexes showed bands at $\sim 3400 \text{ cm}^{-1}$ indicating the presence of coordinated water molecules [12, 13]. 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 $\sim 480 \text{ cm}^{-1}$ assignable to $\nu_{\text{M}-\text{O}}$. Important bands that appeared in the spectra are given in Table 2.

3.2. ^1H NMR spectra

The ^1H NMR spectra of H_2L^1 and H_2L^2 displayed a two proton signal at $\sim \delta$ 16 ppm due to the intramolecularly hydrogen bonded enolic protons [9]. The methine proton signals appeared at $\sim \delta$ 6 ppm. The alkenyl signals with their observed *J* values ($\sim 16 \text{ Hz}$) suggest

trans configuration about the olefinic function in the compounds [10, 11]. Aryl protons appear as a complex multiplet in the range δ 7.00-8.00 ppm. The absence of methyl proton signals in the spectra clearly suggests the condensation of methyl groups of benzoyl acetone and acetoacetanilide with terephthalaldehyde. The ^1H NMR spectrum of H_2L^2 shows a two proton signal at δ 13.12 ppm due to NH protons of the anilide group [11]. The position and integrated intensities of all the protons agree well with the Fig. 1 of the compounds.

In the ^1H NMR spectra of the diamagnetic Ni(II) complexes of H_2L^1 and H_2L^2 , the downfield signal near \sim 16 ppm due to intramolecularly hydrogen bonded enol protons disappeared confirming the metal complexation as in Fig. 2. The methine proton signal shifted appreciably to low field while the olefinic and aryl protons are slightly shifted to downfield due to the metal complexation of the dicarbonyl moiety. The position of NH proton signal of H_2L^2 is only marginally

altered in the spectrum of its Ni(II) complex indicating their non-involvement in coordination [9-11]. The assignments of various proton signals observed are assembled in Table 3.

3.3. Mass spectra

The FAB mass spectra of H_2L^1 and H_2L^2 show moderately intense molecular ion peaks in agreement with Fig 1. Several intense peaks are observed in the spectra due to successive removal of different fragments from the molecular ion [14].

The FAB mass spectra of the Cu(II) complexes of H_2L^1 and H_2L^2 showed molecular ion peaks corresponding to $[\text{Cu}_2\text{L}_2]$ stoichiometry as in Fig. 2. Peaks due to L^+ and fragments of L^+ are also present in the spectra. The spectra of all the chelates contain a number of fragments containing copper in the 3:1 natural abundance of ^{63}Cu and ^{65}Cu isotopes [9, 10]. Important fragments appeared in the spectra are given in Table 4.

Table 2: Characteristic IR stretching bands (cm^{-1}) of the conjugated tetracarbonyl compounds and their metal complexes

Compound	C=O	C=O cinnamoyl	CH=CH <i>trans</i>	M-O
H_2L^1	1630 s	1615 s	970 m	-
$[\text{Co}_2(\text{L}^1)_2(\text{H}_2\text{O})_4]$	1610 s	1580 s	972 m	420 m, 480 m
$[\text{Ni}_2(\text{L}^1)_2]$	1612 s	1578 s	968 m	422 m, 470 m
$[\text{Cu}_2(\text{L}^1)_2]$	1608 s	1582 s	972 m	414 m, 482 m
H_2L^2	1663 s	1654 s	970 m	-
$[\text{Co}_2(\text{L}^2)_2(\text{H}_2\text{O})_4]$	1630 s	1610 s	974 m	420 m, 486 m
$[\text{Ni}_2(\text{L}^2)_2]$	1625 s	1608 s	972 m	410 m, 470 m
$[\text{Cu}_2(\text{L}^2)_2]$	1628 s	1610 s	968 m	425 m, 482 m

Table 3: ^1H NMR spectral data (δ , ppm) of the conjugated tetracarbonyl compounds and their Ni(II) complexes

Compound	Enolic OH	NH	Methine	CH=CH	Aryl
H_2L^1	16.40 (2H)	-	5.80 (2H)	8.26 (2H), 8.08 (2H)	7.02-7.99
$[\text{Ni}_2(\text{L}^1)_2]$	-	-	6.56 (4H)	8.34 (4H), 8.18 (4H)	7.12-7.80
H_2L^2	16.08 (2H)	13.12 (2H)	5.90 (2H)	8.28 (2H), 8.10 (2H)	7.10-7.92
$[\text{Ni}_2(\text{L}^2)_2]$	-	13.04 (2H)	6.52 (4H)	8.32 (4H), 8.16 (4H)	7.22-7.90

Table 4: Mass spectral data of the conjugated tetracarbonyl compounds and their Cu(II) complexes

Compound	Mass spectral data (m/z)
H_2L^1	422, 317, 275, 249, 212, 173, 147, 128, 105
$[\text{Cu}_2(\text{L}^1)_2]$	969, 967, 892, 890, 815, 813, 738, 736, 661, 659, 549, 547, 422, 317, 275, 173, 147, 128, 105
H_2L^2	452, 332, 290, 264, 212, 188, 162, 128, 120
$[\text{Cu}_2(\text{L}^2)_2]$	1029, 1027, 937, 935, 845, 843, 753, 751, 661, 659, 577, 579, 452, 332, 290, 212, 188, 128, 120

3.4. Electronic spectra

The UV spectra of H_2L^1 and H_2L^2 show two broad bands with maxima at \sim 380 and \sim 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].

The Cu(II) complexes showed a broad visible band, λ_{\max} at $\sim 14,800 \text{ cm}^{-1}$. This, together with the measured μ_{eff} values ($\sim 1.75 \text{ BM}$), suggest their square-planar geometry. The observed diamagnetism and broad medium-intensity band at $\sim 17,650 \text{ cm}^{-1}$ in the spectra of the Ni(II) chelates suggest their square-planar geometry. The spectra of the Co(II) chelates showed three bands at $\lambda_{\max} \sim 9,500$, $\sim 12,000$ and $\sim 20,000 \text{ cm}^{-1}$ corresponding to the transitions ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}$; ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$; ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$, respectively. The transition to ${}^4A_{2g}$ is very weak and appears as a shoulder. This, together with the measured μ_{eff} values ($\sim 4.80 \text{ BM}$), suggest their octahedral geometry with two coordinated water molecules [13, 16].

4. CONCLUSION

A new series of conjugated tetracarbonyl compounds, where two dicarbonyl functions are attached to the 1, 4-positions of the phenyl ring, were synthesized by the Claisen-Schmidt condensation between terephthalaldehyde and two different β -dicarbonyl compounds; benzoylacetone and acetoacetanilide. Spectral data unequivocally confirmed the enol tautomeric form of these tetracarbonyl compounds. The observed analytical and spectral data suggested that the conjugated tetracarbonyl compounds functioned as dibasic tetradentate ligands in their Cu(II), Ni(II) and Co(II) complexes. The Ni(II) and Cu(II) chelates are square planar while Co(II) complexes are in octahedral environment with two coordinated water molecules on each Co(II).

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Conflicts of Interest

The authors declare no conflict of interest.

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