

## Cd (II), Hg (II) AND Pb (II) COMPLEXES OF SOME SYNTHETIC CURCUMINOID ANALOGUES

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### ABSTRACT

Cd (II), Hg (II) and Pb (II) complexes of 1,7-diarylheptanoids and 1,5-diarylpentanoids (Ar = phenyl and styryl) with [ML<sub>2</sub>] stoichiometry have been prepared and characterized on the basis of their analytical, spectral, magnetic and conductance data. In all the complexes, ligands behave as monobasic bidentate in which the intramolecularly hydrogen bonded enolic proton is replaced by the metal ion.

**Key words:** Synthetic curcuminoids, 1,7-Diarylheptanoids, 1,5-Diarylpentanoids, Metal complexes, Spectral data.

### INTRODUCTION

The harmful effects of heavy metals in humans can be minimized or prevented by chemically modifying the biochemically active forms of the metal ion<sup>1,2</sup>. Thus, by the administration of chelating agents, these metals can be removed from the body as insoluble metal chelates<sup>3-5</sup>. Even though literature is extensive on the metal-chelating properties of curcumin in the selective removal of heavy metals<sup>6-8</sup>, the structural characterization of these metal chelates received scanty attention. In continuation of our studies on the structure and coordination behavior of synthetic curcuminoid analogues<sup>9-17</sup>, here we have reported the synthesis and structural characterization of some heavy metal ion complexes of synthetic curcuminoids.

### EXPERIMENTAL

#### 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<sup>-4</sup> mol/L) were recorded on a 1601 Shimadzu UV-Vis. spectrophotometer, IR spectra (KBr discs) on an 8101 Shimadzu FTIR spectrophotometer, <sup>1</sup>H NMR spectra (CDCl<sub>3</sub> or DMSO-d<sub>6</sub>) 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 ( $\sim 10^{-3}$  mol/L) at  $28 \pm 1^\circ\text{C}$ . Magnetic susceptibilities were determined at room temperature on a Guoy type magnetic balance.

### Synthesis of 1,7-diarylheptanoids (HL<sup>1</sup>, HL<sup>2</sup>) and 1,5-diarylpentanoids (HL<sup>a</sup>, HL<sup>b</sup>)

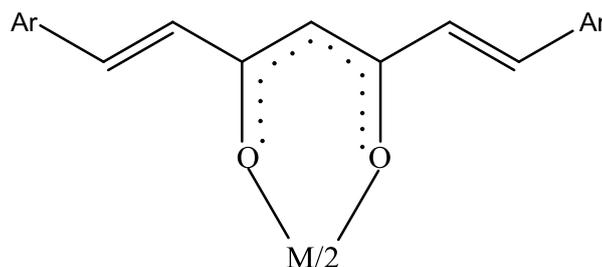
The compounds were prepared by the condensation of aromatic aldehydes (benzaldehyde and cinnamaldehyde) with acetylacetone/benzoylacetone-boric oxide complex in ethylacetate medium in the presence of tri (*sec*-butyl) borate and *n*-butyl amine by the methods reported earlier<sup>14,16-18</sup>.

### Synthesis of metal complexes

To a refluxing solution of the compound in methanol (0.02 mol, 20 mL) a methanolic solution of the metal (II) acetate (0.01 mol, 15 mL) was added and the reaction mixture was refluxed for  $\sim 2$  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.

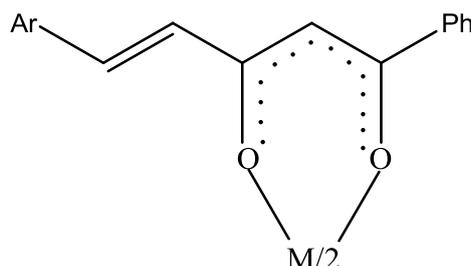
## RESULTS AND DISCUSSION

The observed elemental analytical data (Table 1) suggest  $[\text{ML}_2]$  stoichiometry of the complexes. All the complexes behave as non-electrolytes (specific conductance  $< 10 \Omega^{-1} \text{cm}^{-1}$ ;  $10^{-3}$  M solution in DMF). Magnetic measurements indicate that all the complexes are diamagnetic in nature, as expected. The spectral data of the complexes of 1,7-diarylheptanoids are in conformity with Fig. 1 and of 1,5-diarylpentanoids with Fig. 2.



M = Cd (II), Hg (II) and Pb (II); Ar = Phenyl (HL<sup>1</sup>) and styryl (HL<sup>2</sup>)

**Fig. 1: Structure of the metal complexes of 1,7-diarylheptanoids**



M = Cd (II), Hg (II) and Pb (II); Ar = Phenyl (HL<sup>a</sup>) and styryl (HL<sup>b</sup>)

**Fig. 2: Structure of the metal complexes of 1,5-diarylpentanoids**

**Table 1: Physical and analytical data of the metal complexes**

Compound/ molecular formula	Colour	Yield (%)	M.P. (°C)	Elemental analysis: found (Calculated)%		
				C	H	M
[Cd(L <sup>1</sup> ) <sub>2</sub> ] C <sub>38</sub> H <sub>30</sub> CdO <sub>4</sub>	Dark brown	45	278	68.70 (68.84)	4.50 (4.53)	17.12 (16.97)
[Cd(L <sup>2</sup> ) <sub>2</sub> ] C <sub>46</sub> H <sub>38</sub> CdO <sub>4</sub>	Red	48	160	71.92 (72.02)	5.00 (4.96)	14.75 (14.67)
[Cd(L <sup>a</sup> ) <sub>2</sub> ] C <sub>34</sub> H <sub>26</sub> CdO <sub>4</sub>	Reddish brown	53	145	66.54 (66.73)	4.25 (4.27)	18.32 (18.48)
[Cd(L <sup>b</sup> ) <sub>2</sub> ] C <sub>38</sub> H <sub>30</sub> CdO <sub>4</sub>	Red	58	194	68.68 (68.84)	4.54 (4.53)	16.85 (16.97)
[Hg(L <sup>1</sup> ) <sub>2</sub> ] C <sub>38</sub> H <sub>30</sub> HgO <sub>4</sub>	Yellowish red	73	>300	60.60 (60.75)	4.03 (4.00)	26.52 (26.72)
[Hg(L <sup>2</sup> ) <sub>2</sub> ] C <sub>46</sub> H <sub>38</sub> HgO <sub>4</sub>	Yellow	76	250	64.48 (64.60)	4.42 (4.45)	23.66 (23.47)
[Hg(L <sup>a</sup> ) <sub>2</sub> ] C <sub>34</sub> H <sub>26</sub> HgO <sub>4</sub>	Coffee brown	70	123	58.08 (58.28)	3.75 (3.73)	28.70 (28.80)
[Hg(L <sup>b</sup> ) <sub>2</sub> ] C <sub>38</sub> H <sub>30</sub> O <sub>4</sub> Hg	Black	78	154	60.58 (60.75)	4.02 (4.00)	26.70 (26.72)
[Pb(L <sup>1</sup> ) <sub>2</sub> ] C <sub>38</sub> H <sub>30</sub> O <sub>4</sub> Pb	Coffee brown	50	226	60.14 (60.22)	3.92 (3.96)	27.22 (27.36)
[Pb(L <sup>2</sup> ) <sub>2</sub> ] C <sub>46</sub> H <sub>38</sub> O <sub>4</sub> Pb	Brown	52	>300	64.21 (64.10)	4.45 (4.41)	23.85 (24.06)
[Pb(L <sup>a</sup> ) <sub>2</sub> ] C <sub>34</sub> H <sub>26</sub> O <sub>4</sub> Pb	Dark brown	68	254	57.76 (57.74)	3.67 (3.70)	29.32 (29.47)
[Pb(L <sup>b</sup> ) <sub>2</sub> ] C <sub>38</sub> H <sub>30</sub> O <sub>4</sub> Pb	Yellowish brown	73	267	60.28 (60.22)	3.99 (3.96)	27.19 (27.36)

### Infrared spectra

The IR spectra of the 1,7-diarylheptanoids show a strong band at  $\sim 1625\text{ cm}^{-1}$  due to the stretching of the chelated carbonyl functions<sup>14,16,19</sup>. The spectra of 1,5-diarylpentanoids show two intense bands at  $\sim 1630$  and  $\sim 1615\text{ cm}^{-1}$  assignable to the intramolecularly hydrogen bonded benzoyl and  $\alpha,\beta$ -unsaturated carbonyl stretching vibrations<sup>17,19</sup>. The broad band in the region  $2500\text{-}3500\text{ cm}^{-1}$  suggests the existence of the compounds in the intramolecularly hydrogen bonded enolic form<sup>9,19</sup>.

In the IR spectra of the metal complexes of 1,7-diarylheptanoids, the band at  $\sim 1625\text{ cm}^{-1}$  of the ligand disappeared and a strong band assignable to the stretching of the coordinated carbonyl moiety<sup>14,20</sup> appeared at  $\sim 1580\text{ cm}^{-1}$  as in Fig. 1. The bands at  $\sim 1630$  and  $\sim 1615\text{ cm}^{-1}$  of the 1,5-diarylpentanoids disappeared and two new bands appeared at  $\sim 1600$  and  $\sim 1580\text{ cm}^{-1}$  due to metal chelated carbonyl groups<sup>17,20</sup> as in Fig. 2.

The broad band in the region 2800-3500  $\text{cm}^{-1}$  cleared up in the spectra indicating the replacement of enolic proton by the metal cation during complexation<sup>20</sup>. The prominent band at  $\sim 975 \text{ cm}^{-1}$  is typical of a *trans* -CH=CH- group which remained unaltered in the spectra of metal complexes<sup>14</sup>. That the carbonyl groups are involved in bonding with the metal ion is further supported by the appearance of two medium intensity bands at  $\sim 420$  and  $\sim 480 \text{ cm}^{-1}$  assignable to  $\nu_{\text{M-O}}$ <sup>20</sup>. Important bands that appeared in the spectra are given in Table 2.

**Table 2: Characteristic IR stretching bands ( $\text{cm}^{-1}$ ) of the metal complexes**

Compound	C=O benzoyl	C=O $\alpha,\beta$ -unsaturated	CH=CH <i>trans</i>	M-O
[Cd(L <sup>1</sup> ) <sub>2</sub> ]	-	1580 s	976 m	470 m, 418 m
[Hg(L <sup>1</sup> ) <sub>2</sub> ]	-	1582 s	980 m	480 m, 420 m
[Pb(L <sup>1</sup> ) <sub>2</sub> ]	-	1572 s	975 m	472 m, 414 m
[Cd(L <sup>2</sup> ) <sub>2</sub> ]	-	1580 s	976 m	482 m, 422 m
[Hg(L <sup>2</sup> ) <sub>2</sub> ]	-	1578 s	961 m	478 m, 424 m
[Pb(L <sup>2</sup> ) <sub>2</sub> ]	-	1586 s	984 m	460 m, 416 m
[Cd(L <sup>a</sup> ) <sub>2</sub> ]	1608 s	1578 s	972 m	460 m, 418 m
[Hg(L <sup>a</sup> ) <sub>2</sub> ]	1610 s	1576 s	974 m	490 m, 420 m
[Pb(L <sup>a</sup> ) <sub>2</sub> ]	1606 s	1578 s	966 m	480 m, 422 m
[Cd(L <sup>b</sup> ) <sub>2</sub> ]	1600 s	1580 s	968 m	478 m, 422 m
[Hg(L <sup>b</sup> ) <sub>2</sub> ]	1602 s	1576 s	970 m	479 m, 420 m
[Pb(L <sup>b</sup> ) <sub>2</sub> ]	1604 s	1570 s	972 m	486 m, 424 m

s = strong, m = medium

### <sup>1</sup>H NMR spectra

The <sup>1</sup>H NMR spectra of the 1,7-diarylheptanoids and 1,5-diarylpentanoids displayed a one proton signal at  $\sim \delta$  16 ppm due to the intramolecularly hydrogen bonded enolic proton and a one proton signal at  $\sim \delta$  6 ppm due to methine proton<sup>14,17</sup>. The alkenyl signals with their observed *J* values ( $\sim 16$  Hz) suggest *trans* configuration about the olefinic function in the compounds. In the <sup>1</sup>H NMR spectra of the diamagnetic Pb(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 due to the aromatic character imparted to the C<sub>3</sub>O<sub>2</sub>M ring system by the highly conjugated groups attached to the dicarbonyl moiety<sup>21,22</sup>. The integrated intensities of various signals agree well with the [ML<sub>2</sub>] stoichiometry of the complexes as in Figures 1 and 2. The assignments of various proton signals observed are assembled in Table 3.

**Table 3: <sup>1</sup>H NMR spectral data ( $\delta$ , ppm) of the Pb(II) complexes**

Compound	Methine	CH = CH	Aryl
[Pb(L <sup>1</sup> ) <sub>2</sub> ]	6.34	8.10, 8.26	7.12-7.96
[Pb(L <sup>a</sup> ) <sub>2</sub> ]	6.42	8.27, 8.38	7.20-8.00

## Mass spectra

The  $[ML_2]$  stoichiometry of the complexes is clearly evident from the presence of prominent peak due to  $[ML_2]^+$  parent ion in the FAB mass spectra. Other important peaks are due to the elimination of Ar, ArCH=CH, ArCO, PhCO *etc* from the molecular ion or subsequent fragments<sup>9,23</sup>. Important fragments appeared in the spectra are given in Table 4.

**Table 4: Mass spectral data of the metal complexes**

Compound	Mass spectral data (m/z)
$[Cd(L^1)_2]$	663, 586, 560, 532, 509, 457, 432, 355, 276, 270, 199, 173, 131, 103
$[Pb(L^2)_2]$	862, 759, 705, 656, 553, 548, 450, 391, 234, 157, 129, 103
$[Hg(L^a)_2]$	697, 620, 594, 592, 566, 543, 487, 466, 435, 389, 382, 304, 277, 173, 105

## UV spectra

The UV spectra of the 1,7-diarylheptanoids and 1,5-diarylpentanoids 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<sup>9,24</sup> indicating the involvement of the carbonyl groups in metal complexation.

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