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La(III) complexes of some 1,7-diaryl-1,6-heptadiene-3,5-diones

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ABSTRACT

La(III) complexes with the formula $[LaL_2Cl(H_2O)_2]$ of five 1,7-diarylheptanoids (HL) derived from acetylacetone and aromatic aldehydes (2-hydroxynaphthaldehyde, 4-methoxybenzaldehyde, 4-hydroxybenzaldehyde, 4-dimethylaminobenzaldehyde and 4-hydroxy-3-methoxybenzaldehyde) have been synthesized. Analytical, IR, ^{1}H NMR and mass spectral data indicate the monobasic bidentate coordination in which the intramolecularly hydrogen bonded enol proton is replaced by La(III) ion.

KEYWORDS

1,7-Diarylheptanoids;
La(III) complexes;
IR spectra;
^{1}H NMR spectra;
Mass spectra.

INTRODUCTION

The chemistry of lanthanide β-diketonates has assumed considerable importance because of their practical use as potential laser materials[1]. The application of certain lanthanide chelates called shift reagents for NMR spectral elucidation has become an extremely useful analytical technique[2]. Many of the reported studies on lanthanide β-diketonates are based on synthetic β-diketones in which the diketo function is directly linked to alkyl/aryl groups[3-5]. No report appeared on lanthanide complexes of β-diketones in which the diketo group is linked to alkenyl function. Such unsaturated β-diketones have gained considerable importance in recent years[6-8] because these structural types constitute the major biologically active compounds present in several traditional Indian medicinal plants like curcuminoids[9], (1,7-diaryl-1,6-heptadiene-3,5-diones), the active chemical constituent of the herbaceous Indian medicinal plant turmeric (*Curcuma longa*, Linn, *Zingiberacea* family). In continuation of our studies on such unsaturated β-diketones and their metal complexes[6,7,10], we here report the synthesis and characterization of La(III) complexes of five unsaturated β-diketones (HL^1-HL^5) obtained by the condensation between acetylacetone and aromatic aldehydes; 2-hydroxynaphthaldehyde, 4-methoxybenzaldehyde, 4-hydroxybenzaldehyde, 4-dimethylaminobenzaldehyde and 4-hydroxy-3-methoxybenzaldehyde.

EXPERIMENTAL

Materials and methods

Carbon, hydrogen and nitrogen percentages were determined by microanalyses (Heraeus Elemental analyzer) and metal contents by igniting to ~1000°C and weighing as La_2O_3. The IR spectra (KBr discs) were recorded on a 8101 Shimadzu FTIR spectrophotometer, ^{1}H NMR spectra in $CDCl_3$ or DMSO-d_6 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 at 28±1^{0}C using solution of about 10^{-3} M concentration.

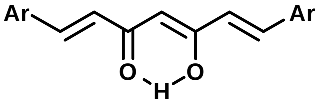
Synthesis of La(III) complexes of 1,7-diarylheptanoids, $[LaL_2Cl(H_2O)_2]$

The 1,7-diarylheptanoids were synthesized by the condensation between acetylacetone and aromatic aldehydes in presence of boric oxide and tri(*sec*-butyl)borate using *n*-butylamine as the condensing agent[6,7].

A solution of $LaCl_3$ (0.01 mol, 25 mL 1:3 v/v aqueous methanol) was added slowly with stirring to a methanolic solution of the 1,7-diarylheptanoid (0.02 mol, 25 mL). The pH of the reaction mixture was carefully maintained at 7.56 in order to prevent the precipitation of $La(OH)_3$. The mixture was stirred for ~12 h and concentrated to half the original volume. The precipitated complex on cooling to room temperature was filtered, washed with ethanol and recrystallized from hot methanol to get chromatographically (TLC) pure compound.

RESULTS AND DISCUSSION

All the 1,7-diarylheptanoids (Figure 1) formed stable and well defined complexes with $LaCl_3$. They show sharp melting points and are soluble in common organic solvents like methanol, chloroform, DMF and DMSO. The analytical data (TABLE 1) together with non-electrolytic nature in DMF (specific conductance $<10^{-1}$cm^{-1}; 10^{-3} M solution) suggest 1:2 metal-ligand stoichiometry. Magnetic measurements indicate that all the complexes are diamagnetic in nature, as expected. The observed IR, ^{1}H NMR and mass spectral data of the complexes are in conformity with the formula $[LaL_2Cl(H_2O)_2]$ as in Figure 2.



Ar = 2-Hydroxynaphthyl (HL^1); 2-Methoxyphenyl (HL^2); 4-Hydroxyphenyl (HL^3); 4-Dimethylaminophenyl (HL^4); 4-Hydroxy-3-methoxyphenyl (HL^5)

Figure 1 : Structure of 1,7-diarylheptanoids

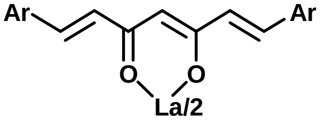


Figure 2 : Tentative mode of coordination of the La(III) ion with 1,7-diarylheptanoids

TABLE 1 : Physical and analytical data of the La(III) complexes

Complex/ Empirical formula	Yield %	m.p. ^{0}C	Elemental Analysis: Found (Calculated)%			
			C	H	N	La
$[La(L^1)_2Cl(H_2O)_2]$ $C_{54}H_{42}ClLaO_{10}$	60	207	63.40 (63.26)	4.08 (4.10)	-	13.65 (13.56)
$[La(L^2)_2Cl(H_2O)_2]$ $C_{42}H_{42}ClLaO_{10}$	65	216	57.12 (57.25)	4.73 (4.77)	-	15.65 (15.78)
$[La(L^3)_2Cl(H_2O)_2]$ $C_{38}H_{34}ClLaO_{10}$	70	203	55.20 (55.31)	4.12 (4.12)	-	16.74 (16.85)
$[La(L^4)_2Cl(H_2O)_2]$ $C_{46}H_{54}N_4ClLaO_6$	65	198	59.28 (59.20)	5.66 (5.79)	3.08 (3.00)	14.75 (14.90)
$[La(L^5)_2Cl(H_2O)_2]$ $C_{42}H_{42}ClLaO_{14}$	75	218	53.46 (53.37)	4.42 (4.45)	-	14.75 (14.71)

Infrared spectra

The IR spectra of the 1,7-diarylheptanoids are characterized by the presence of a strong band at ~1625 cm^{-1} and a broad band in the range 2800-3500 cm^{-1} due to respectively, the stretching of the chelated carbonyl and the intramolecularly hydrogen bonded enol functions. The absence of any band assignable to a normal α,β-unsaturated carbonyl group in the region 1640-1740 cm^{-1} of the spectra indicates that these compounds exist entirely in the enolic form[6,7] as in Figure 1.

In the IR spectra of the La(III) complexes the band at ~1625 cm^{-1} due to the stretching of the chelated carbonyl is absent and, instead, a strong band assignable to the stretching of the coordinated carbonyl moiety appeared at ~1580 cm^{-1} indicating the replacement of enol proton by metal ion during complexation[6,11]. The intensity and breadth of the band in the 2800-3500 cm^{-1} region increased appreciably indicating the presence of different types of O-H vibrations in the complexes. Considering the fact that the enol proton is replaced by metal ion, this broadness is due to coordinated water molecules. This fact is further supported from the appearance of two or more weak but prominent bands in the 1630-1660 cm^{-1} region of the spectra assignable to H-O-H bending[11,12]. From the observed breadth and intensity, these bands cannot be assigned to the carbonyl functions. That the carbonyl groups are involved in metal chelate formation is further evident from the appearance of two medium intensity bands in the region 418-480 cm^{-1} due to ν(La-O) vibrations[11]. In the far IR region, spectra of the complexes displayed medium intensity band at ~350 cm^{-1} due to ν(La-Cl) vibrations indicating the coordination through chloride ion. The prominent band at ~975 cm^{-1} is typical of a *trans* –CH=CH- group which remained unaltered in the spectra of metal complexes[6]. Thus the IR spectra strongly support the coordination through dicarbonyl moiety of 1,7-diarylheptanoid, water molecules and chloride ion. Important bands that appeared in the spectra are given in TABLE 2.

TABLE 2 : Characteristic IR stretching bands (cm^{-1}) of La(III) complexes

Complex	Chelated (C=O)	H-O-H bending	(CH=CH) *trans*	(La–O)	(M-Cl)
$[La(L^1)_2Cl(H_2O)_2]$	1582 s	1628 w 1658 w	975 m	418 m 468 m	354 m
$[La(L^2)_2Cl(H_2O)_2]$	1576 s	1625 w 1650 w	970 m	420 m 478 m	358 m
$[La(L^3)_2Cl(H_2O)_2]$	1578 s	1622 w 1656 w	972 m	422 m 456 m	350 m
$[La(L^4)_2Cl(H_2O)_2]$	1585 s	1629 w 1657 w	968 m	426 m 470 m	360 m
$[La(L^5)_2Cl(H_2O)_2]$	1580 s	1628 w 1660 w	970 m	421 m 480 m	356 m

^{1}H NMR spectra

The ^{1}H NMR spectra of the 1,7-diarylheptanoids displayed a characteristic downfield singlet at ~δ 16 ppm due to the intramolecularly hydrogen bonded enolic proton[6,7] as in Figure 1. The methine proton signal is invariably located at ~ 5.90 ppm and olefinic protons at ~δ 7.50 ppm.

In the ^{1}H NMR spectra of the diamagnetic La(III) complexes the low field signal at ~δ 16 ppm due to the intramolecularly hydrogen bonded enolic proton is absent indicating its replacement by the metal ion during complexation[10]. The methine proton signal shifted appreciably to low field compared to the shift in the olefinic protons. This may be due to the aromatic character that might have been imparted to the C_3O_2M ring system of the chelates by the highly conjugated groups attached to the dicarbonyl moiety. The alkenyl proton signals with a *J* value of ~16 Hz suggest the *trans* nature of the alkene double bond, as it is in the free ligands[6]. Aryl protons appear in the range δ 6.50-7.30 ppm as a complex multiplet. That the aryl substituents are not involved in bonding with the metal ion is clearly indicated[13] in the spectra of their La(III) complexes where the signals remain unaltered. The integrated intensities of various signals agree well with the structure of the complexes as in Figure 2. The assignments of various proton signals observed are assembled in TABLE 3.

TABLE 3 : ^{1}H NMR spectral data (δ, ppm) of La(III) complexes

Complex	Methine	CH=CH *trans*	Aryl	Aryl substituent
$[La(L^1)_2Cl(H_2O)_2]$	6.62 s	7.63 d, 7.78 d	6.64-7.27 m	10.46 s
$[La(L^2)_2Cl(H_2O)_2]$	6.59 s	7.58 d, 7.69 d	6.66-7.18 m	3.89 s
$[La(L^3)_2Cl(H_2O)_2]$	6.66 s	7.64 d, 7.76 d	6.50-7.25 m	10.48 s
$[La(L^4)_2Cl(H_2O)_2]$	6.48 s	7.62 d, 7.76 d	6.55-7.30 m	2.93 s
$[La(L^5)_2Cl(H_2O)_2]$	6.54 s	7.68 d, 7.82 d	6.76-7.20 m	10.16 s, 3.92 s

s = singlet, d = doublet, m = multiplet

Mass spectra

In addition to intense molecular ion peaks $P^+/(P+1)^+$, peaks due to elimination of O, OH, H_2O, $C_3HO_2^+$, $[ArCHCHCO]^+$ and $[ArCHCHCOCH_2]^+$ species from the molecular ion are the most common feature of the mass spectra of 1,7-diarylheptanoids[6,7]. The FAB mass spectra of the La(III) complexes showed molecular ion peaks corresponding to $[LaL_2Cl(H_2O)_2]$ stoichiometry. Peaks correspond to $[LaL_2Cl]^+$, $[LaL_2]^+$, $[LaL]^+$, $[P-H_2O]^+$, L^+ and fragments of L^+ are also present in the spectra. The spectra of all the chelates contain a number of fragments containing chlorine in the 2:1 natural abundance of ^{35}Cl and ^{37}Cl isotopes (TABLE 4).

TABLE 4 : Mass spectral data of La(III) complexes

Complex	Mass spectral data (m/z)
$[La(L^1)_2Cl(H_2O)_2]$	1026, 1024, 1008, 1006, 990, 988, 953, 829, 827, 815, 813, 632, 630, 546, 407, 211, 197
$[La(L^2)_2Cl(H_2O)_2]$	882, 880, 864, 862, 846, 845, 809, 721, 719, 705, 560, 558, 474, 335, 175, 161
$[La(L^3)_2Cl(H_2O)_2]$	826, 824, 808, 806, 790, 789, 753, 679, 677, 665, 663, 540, 538, 446, 307, 147, 161
$[La(L^4)_2Cl(H_2O)_2]$	934, 932, 916, 914, 898, 897, 861, 760, 758, 746, 744, 586, 584, 500, 361, 188, 174
$[La(L^5)_2Cl(H_2O)_2]$	946, 944, 928, 926, 910, 908, 875, 873, 872, 769, 767, 755, 753, 592, 590, 506, 367, 191, 177

Electronic spectra

The UV spectra of the 1,7-diarylheptanoids exhibited two absorption maxima in the range 385-450 and ~260 nm assignable respectively to the various n→π* and π→π* transitions of the highly conjugated molecule[6,7]. 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 (~10 nm) indicating the involvement of the carbonyl group in metal complexation[14].

CONCLUSIONS

La(III) complexes of five 1,7-diarylheptanoids (HL) derived from acetylacetone and aromatic aldehydes (2-hydroxynaphthaldehyde, 4-methoxybenzaldehyde, 4-hydroxybenzaldehyde, 4-dimethylaminobenzaldehyde and 4-hydroxy-3-methoxybenzaldehyde) have been synthesized. Analytical, IR, ^{1}H NMR and mass spectral data indicate the monobasic bidentate coordination in which the intramolecularly hydrogen bonded enol proton is replaced by the La(III) ion. The structure of the complexes correspond to $[LaL_2Cl(H_2O)_2]$ stoichiometry with the coordination through dicarbonyl moiety of 1,7-diarylheptanoid, water molecules and chloride ion.

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