

# Mixed Ligand Complexes of Some Trivalent Lanthanide Ions with Unsaturated 1,3-Diketones

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**Abstract**— 16 mixed ligand complexes of trivalent lanthanide ions [Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Dy(III), Er(III) and Yb(III)] with unsaturated 1,3-diketones (HL) derived from acetylacetone and aromatic aldehydes [benzaldehyde, cinnamaldehyde, furfural, salicylaldehyde, 2-chlorobenzaldehyde, 2-hydroxy-1-naphthaldehyde, 4-(N,N-dimethyl)aminobenzaldehyde, vanillin and 3,4-dimethoxybenzaldehyde] have been synthesised and characterised by various analytical and spectral techniques. Gd(III) complexes of HL derived from benzaldehyde and furfural, and Yb(III) complex derived from cinnamaldehyde are in agreement with  $[ML_3(H_2O)_2]$  stoichiometry. All other complexes conform to  $[ML_2(NO_3)(H_2O)_2]$  stoichiometry with bidentate nitrate coordination.

**Keywords**— Unsaturated 1,3-diketones; Ln(III) complexes; Enol proton; Monobasic bidentate; Spectral data.

## I. INTRODUCTION

In continuation of our investigations on unsaturated 1,3-diketones and their lanthanide complexes [1]-[3], we here report the synthesis and spectral characterization of complexes of Ln(III) ions; Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Dy(III), Er(III) and Yb(III), with unsaturated 1,3-diketones (HL<sup>1</sup>-HL<sup>9</sup>). The unsaturated 1,3-diketones were prepared by the condensation between acetylacetone and aromatic aldehydes; benzaldehyde, cinnamaldehyde, furfural, salicylaldehyde, 2-chlorobenzaldehyde, 2-hydroxy-1-naphthaldehyde, 4-(N,N-dimethyl)aminobenzaldehyde, vanillin and 3,4-dimethoxybenzaldehyde.

## II. EXPERIMENTAL

### A. Materials and Methods

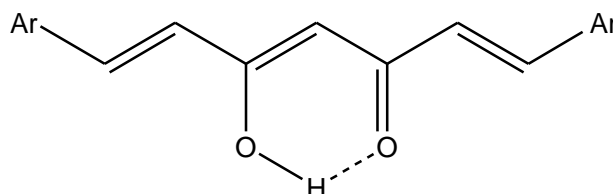
Carbon, hydrogen and nitrogen percentages were determined by microanalyses (Heraeus Elemental analyzer) and metal contents by igniting the complexes to  $\sim 1000^\circ\text{C}$  and weighing as  $\text{Ln}_2\text{O}_3$ . Electronic spectra of the complexes in methanol ( $10^{-4}$  mol/L) were recorded on a 1601 Shimadzu UV-Vis. spectrophotometer, IR spectra (KBr discs) on an 8101 Shimadzu FTIR spectrophotometer 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  $28 \pm 1^\circ\text{C}$  using solution of about  $10^{-3}$  M concentration. Magnetic susceptibilities were determined using a Guoy type magnetic balance at room temperature ( $28 \pm 1^\circ\text{C}$ ) with  $\text{Hg}[\text{Co}(\text{NCS})_4]$  as the standard. All the chemicals and solvents were of reagent grade (Merck, Fluka and Sigma-Aldrich) and were used without further purification.

### B. Synthesis of Lanthanide Complexes of Unsaturated 1,3-Diketones

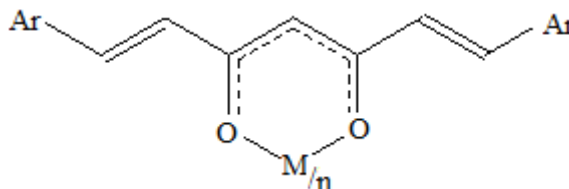
The unsaturated 1,3-diketones (Fig. 1) were synthesized by the Claisen-Schmidt condensation between aromatic aldehydes and acetylacetone by the methods reported earlier [4]-[9]. The Ln(III) complexes were also prepared by our earlier reported methods [1]-[3].

## III. RESULTS AND DISCUSSION

All the synthesised metal complexes are stable with finite melting points. They are soluble in majority of the common organic solvents. The non-ionic nature of all these complexes are confirmed by their non-electrolytic nature in DMF (specific conductance  $< 10\Omega^{-1}\text{cm}^{-1}$ ;  $10^{-3}$  M solution). Magnetic moment values obtained suggest weak ligand field with the expected number of unpaired electrons. Gd(III) complexes of HL derived from benzaldehyde and furfural, and Yb(III) complex derived from cinnamaldehyde are in agreement with  $[ML_3(H_2O)_2]$  stoichiometry. The results of all other complexes are in agreement with  $[ML_2(NO_3)(H_2O)_2]$  stoichiometry with the nitrate ion as a chelating bidentate ligand (TABLE I). Analytical and spectral data strongly support the monobasic bidentate coordination of the unsaturated 1,3-diketones in all metal complexes as in Fig. 2.



**Fig. 1.** Structure of the unsaturated 1,3-diketones: Ar = Phenyl (HL<sup>1</sup>); Styryl (HL<sup>2</sup>); 2-Furyl (HL<sup>3</sup>); 2-Hydroxyphenyl (HL<sup>4</sup>); 2-Chlorophenyl (HL<sup>5</sup>); 2-Hydroxy-1-naphthyl (HL<sup>6</sup>); 4-(N,N-dimethyl)aminophenyl (HL<sup>7</sup>); 4-Hydroxy-3-methoxyphenyl (HL<sup>8</sup>) and 3,4-dimethoxyphenyl (HL<sup>9</sup>).



**Fig. 2.** Tentative mode of coordination of the lanthanide ions with unsaturated 1,3-diketones; M = Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Dy(III), Er(III) and Yb(III); The proposed structure also contains two coordinated water molecules; n =3 is proposed for [Gd(L<sup>1</sup>)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>], [Gd(L<sup>3</sup>)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>] and [Yb(L<sup>2</sup>)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>]; n =2 and one bidentate nitrate ion coordination is proposed for all other [M(L)<sub>2</sub>(NO<sub>3</sub>)(H<sub>2</sub>O)<sub>2</sub>] complexes.

TABLE I  
PHYSICAL, ANALYTICAL, UV AND IR SPECTRAL DATA OF THE Ln(III) COMPLEXES OF UNSATURATED 1,3-DIKETONES

Complex/ Empirical Formula	M.P. °C	$\mu_{\text{eff}}$ BM	Elemental Analysis: Found (Calculated)%				UV $\lambda_{\text{max}}$	IR stretching bands (cm <sup>-1</sup> )			
			C	H	N	M		Chelated (C=O)	H-O-H bending	(M-O)	Chelated (NO <sub>3</sub> <sup>-</sup> )
[Pr(L <sup>7</sup> ) <sub>2</sub> (NO <sub>3</sub> )(H <sub>2</sub> O) <sub>2</sub> ]/ C <sub>46</sub> H <sub>54</sub> N <sub>5</sub> PrO <sub>9</sub>	208	2.86	58.02 (57.44)	5.66 (5.62)	7.36 (7.28)	14.90 (14.67)	388, 265	1582	1628	408, 417	1302, 1026,1472
[Pr(L <sup>9</sup> ) <sub>2</sub> (NO <sub>3</sub> )(H <sub>2</sub> O) <sub>2</sub> ]/ C <sub>46</sub> H <sub>50</sub> NPrO <sub>21</sub>	256	2.98	50.98 (50.50)	4.52 (4.57)	1.26 (1.28)	12.89 (12.90)	374, 267	1581	1621	408, 420	1294, 1032,1475
[Nd(L <sup>7</sup> ) <sub>2</sub> (NO <sub>3</sub> )(H <sub>2</sub> O) <sub>2</sub> ]/ C <sub>46</sub> H <sub>54</sub> N <sub>5</sub> NdO <sub>9</sub>	207	3.80	57.02 (57.26)	5.62 (5.60)	7.28 (7.26)	14.98 (14.94)	386, 268	1584	1630	406, 418	1300, 1023,1477
[Nd(L <sup>9</sup> ) <sub>2</sub> (NO <sub>3</sub> )(H <sub>2</sub> O) <sub>2</sub> ]/ C <sub>46</sub> H <sub>50</sub> NNdO <sub>21</sub>	248	3.82	50.02 (50.36)	4.62 (4.56)	1.25 (1.28)	12.92 (13.14)	388, 270	1584	1628	410, 421	1292, 1035,1477
[Sm(L <sup>7</sup> ) <sub>2</sub> (NO <sub>3</sub> )(H <sub>2</sub> O) <sub>2</sub> ]/ C <sub>46</sub> H <sub>54</sub> N <sub>5</sub> SmO <sub>9</sub>	224	6.04	56.88 (56.91)	5.58 (5.57)	7.34 (7.22)	15.11 (15.46)	380, 262	1584	1621	409, 420	1296, 1025,1479
[Eu(L <sup>4</sup> ) <sub>2</sub> (NO <sub>3</sub> )(H <sub>2</sub> O) <sub>2</sub> ]/ C <sub>38</sub> H <sub>34</sub> NEuO <sub>15</sub>	186	6.75	51.02 (50.89)	4.02 (3.79)	1.58 (1.56)	16.94 (16.96)	388, 266	1586	1628	406, 416	1292, 1028,1475
[Gd(L <sup>1</sup> ) <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub> ]/ C <sub>57</sub> H <sub>49</sub> GdO <sub>8</sub>	274	7.82	67.92 (67.19)	4.77 (4.81)	-	15.94 (15.42)	378, 260	1590	1639	411, 417	-
[Gd(L <sup>3</sup> ) <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub> ]/ C <sub>45</sub> H <sub>37</sub> GdO <sub>14</sub>	268	7.88	56.93 (56.37)	4.18 (3.86)	-	16.97 (16.39)	376, 260	1588	1632	409, 420	-
[Gd(L <sup>2</sup> ) <sub>2</sub> (NO <sub>3</sub> )(H <sub>2</sub> O) <sub>2</sub> ]/ C <sub>38</sub> H <sub>30</sub> NCl <sub>4</sub> GdO <sub>9</sub>	153	7.86	48.02 (48.36)	3.12 (3.18)	1.48 (1.48)	16.76 (16.65)	379, 268	1583	1627	409, 419	1296, 1025,1475
[Gd(L <sup>8</sup> ) <sub>2</sub> (NO <sub>3</sub> )(H <sub>2</sub> O) <sub>2</sub> ]/ C <sub>42</sub> H <sub>42</sub> NGdO <sub>17</sub>	234	7.88	51.02 (50.96)	4.12 (4.25)	1.40 (1.42)	15.98 (15.87)	378, 266	1589	1630	407, 418	1288, 1027,1470
[Dy(L <sup>6</sup> ) <sub>2</sub> (NO <sub>3</sub> )(H <sub>2</sub> O) <sub>2</sub> ]/ C <sub>54</sub> H <sub>42</sub> NDyO <sub>13</sub>	222	5.60	60.02 (60.28)	4.00 (3.91)	1.29 (1.30)	14.98 (15.16)	386, 274	1587	1627	403, 417	1290, 1024,1480
[Er(L <sup>4</sup> ) <sub>2</sub> (NO <sub>3</sub> )(H <sub>2</sub> O) <sub>2</sub> ]/ C <sub>38</sub> H <sub>34</sub> NErO <sub>15</sub>	186	3.98	50.02 (50.05)	3.82 (3.73)	1.54 (1.54)	18.98 (18.33)	390, 269	1588	1630	404, 416	1294, 1025,1470
[Er(L <sup>3</sup> ) <sub>2</sub> (NO <sub>3</sub> )(H <sub>2</sub> O) <sub>2</sub> ]/ C <sub>38</sub> H <sub>30</sub> NCl <sub>4</sub> ErO <sub>9</sub>	184	3.80	48.02 (47.85)	3.12 (3.15)	1.48 (1.47)	17.66 (17.52)	376, 270	1581	1628	408, 417	1290, 1027,1478
[Er(L <sup>7</sup> ) <sub>2</sub> (NO <sub>3</sub> )(H <sub>2</sub> O) <sub>2</sub> ]/ C <sub>46</sub> H <sub>54</sub> N <sub>5</sub> ErO <sub>9</sub>	209	3.78	55.63 (55.93)	5.44 (5.47)	6.94 (7.09)	17.09 (16.92)	382, 260	1583	1625	407, 420	1290, 1022,1485
[Er(L <sup>9</sup> ) <sub>2</sub> (NO <sub>3</sub> )(H <sub>2</sub> O) <sub>2</sub> ]/ C <sub>46</sub> H <sub>50</sub> NErO <sub>21</sub>	254	3.97	49.16 (49.33)	4.50 (4.47)	1.22 (1.25)	15.06 (14.92)	379, 266	1581	1626	408, 419	1295, 1023,1472
[Yb(L <sup>2</sup> ) <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub> ]/ C <sub>69</sub> H <sub>61</sub> YbO <sub>8</sub>	224	1.78	69.88 (69.58)	5.11 (5.13)	-	14.63 (14.54)	392, 268	1581	1630	407, 419	-

#### A. Infrared Spectra

The IR spectra of all the unsaturated 1,3-diketones are characterised by the presence of a strong band at ~1625 cm<sup>-1</sup> and a broad band in the range 2800-3500 cm<sup>-1</sup> due to the stretching of the chelated carbonyl and the intramolecularly hydrogen bonded enol functions respectively. 1640-1740 cm<sup>-1</sup> region of the

spectra does not contain any band assignable to a normal  $\alpha,\beta$ -unsaturated carbonyl group confirming the existence of the compounds in the enol tautomeric form [5]-[9] as in Fig. 1.

In the IR spectra of all the metal complexes the band at  $\sim 1625\text{ cm}^{-1}$  due to the stretching of the chelated carbonyl is absent and a new strong band appeared at  $\sim 1580\text{ cm}^{-1}$  assignable to the stretching of the metal coordinated carbonyl group. The replacement of enol proton by metal ion during complex formation is clearly evident from these observations. The broad band observed in the free ligands showed appreciable variations in the spectra of the metal complexes. The breadth of this band increased appreciably and the intensity is also fairly high. The presence of O-H vibrations in the complexes due to coordinated water molecules can be inferred from these changes in the spectra. The presence of coordinated water molecules is again confirmed by the appearance of weak but prominent bands in the  $1630\text{-}1660\text{ cm}^{-1}$  region of the spectra assignable to H-O-H bending vibrations [10]. The observed breadth and intensity of these bands clearly rule out the possibility of carbonyl vibrations at these regions. The appearance of medium intensity bands in the  $400\text{-}420\text{ cm}^{-1}$  region of the spectra, due to  $\nu(\text{M-O})$  vibrations also underlines the participation of carbonyl groups in metal chelate formation [1]-[3], [10].

The spectra of all the metal complexes except  $[\text{Gd}(\text{L}^1)_3(\text{H}_2\text{O})_2]$ ,  $[\text{Gd}(\text{L}^3)_3(\text{H}_2\text{O})_2]$  and  $[\text{Yb}(\text{L}^2)_3(\text{H}_2\text{O})_2]$  showed two medium intensity bands at  $\sim 1300$  and  $1020\text{ cm}^{-1}$  assignable to the asymmetric and symmetric stretching of nitrate group respectively. The bidentate coordination of nitrate ion is evident from their separation of  $\sim 180\text{ cm}^{-1}$  and the presence of an additional band at  $\sim 1470\text{ cm}^{-1}$  [11]. Important bands that appeared in the spectra are given in TABLE I.

#### B. Mass Spectra

The FAB mass spectra of the typical metal complexes;  $[\text{Er}(\text{L}^4)_2(\text{NO}_3)(\text{H}_2\text{O})_2]$ ,  $[\text{Gd}(\text{L}^8)_2(\text{NO}_3)(\text{H}_2\text{O})_2]$  and  $[\text{Gd}(\text{L}^1)_3(\text{H}_2\text{O})_2]$  showed molecular ion peaks in accordance with their formulation. Peaks due to the successive removal of ligand fragments are characteristic of all the spectra (TABLE II).

TABLE II  
MASS SPECTRAL DATA OF SOME TYPICAL Ln(III) COMPLEXES OF UNSATURATED 1,3-DIKETONES

Complex	Mass Spectral Data (m/z)
$[\text{Er}(\text{L}^4)_2(\text{NO}_3)(\text{H}_2\text{O})_2]$	911, 893, 875, 813, 751, 604, 586, 568, 536, 474, 307, 297, 160, 147
$[\text{Gd}(\text{L}^8)_2(\text{NO}_3)(\text{H}_2\text{O})_2]$	989, 971, 953, 891, 829, 622, 604, 586, 524, 462, 367, 255, 190, 177
$[\text{Gd}(\text{L}^1)_3(\text{H}_2\text{O})_2]$	1018, 1000, 982, 887, 756, 743, 625, 494, 468, 275, 193, 144, 131

#### C. Electronic Spectra

Two absorption maxima of the free ligands, observed at  $\sim 385$  and  $\sim 260\text{ nm}$  due to various  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transitions [5]-[9], are shifted slightly to longer wavelength ( $\sim 10\text{ nm}$ ) in the UV spectra of all the metal complexes indicating the involvement of carbonyl groups in metal complexation [1]-[3]. The electronic spectra of all the complexes showed several weak absorption bands due to various f-f transitions. As the recorded spectra are not quantitative, specific assignment of the transitions are not carried out.

#### IV. CONCLUSIONS

13 mixed ligand complexes of trivalent lanthanide ions [Pr(III), Nd(III), Sm(III), Eu(III), Er(III) and Yb(III)] with the formula  $[\text{ML}_2(\text{NO}_3)(\text{H}_2\text{O})_2]$  and 3 mixed ligand complexes of trivalent lanthanide ions [Gd(III) and Dy(III)] with the formula  $[\text{ML}_3(\text{H}_2\text{O})_2]$  have been prepared by the reaction between  $\text{Ln}(\text{NO}_3)_3$  and unsaturated 1,3-diketones (HL). The proposed structural formulae of the complexes are confirmed by various analytical and spectral techniques. The existence of nitrate ion as a chelating bidentate ligand in the  $[\text{ML}_2(\text{NO}_3)(\text{H}_2\text{O})_2]$  complexes is strongly supported by the methods used for structural characterisation.

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