

# Pr(III), Nd(III), Eu(III), Er(III) and Yb(III) Complexes of Some 1,7-Diaryl-1,6-heptadiene-3,5- diones

Malini Parakkulangara Thrithody<sup>#1</sup>, Muhammed Basheer Ummathur<sup>\*2</sup>

<sup>#</sup>PG Department of Chemistry, Zamorin's Guruvayurappan College, Calicut, Kerala-673014, India

<sup>\*</sup>PG Department of Chemistry, KAHM Unity Women's College, Manjeri, Kerala-676122, India

<sup>1</sup>ptmalini@gmail.com

<sup>2</sup>mbummathur@gmail.com

**Abstract**— Pr(III), Nd(III), Eu(III), Er(III) and Yb(III) complexes of four 1,7-diarylheptanoids (HL) derived from acetylacetone and aromatic aldehydes (2-hydroxynaphthaldehyde, 4-methoxybenzaldehyde, 4-hydroxybenzaldehyde and 4-hydroxy-3-methoxybenzaldehyde) have been synthesized. Analytical and spectral data strongly support  $[ML_2(NO_3)(H_2O)_2]$  stoichiometry for the metal complexes. In all the metal complexes the 1,7-diarylheptanoids behave as monobasic bidentate in which the intra-molecularly hydrogen bonded enol proton is replaced by the metal cation. IR spectral data clearly revealed the bidentate coordination of nitrate ion in all these mixed ligand complexes.

**Keywords**— 1,7-Diarylheptanoids; Metal complexes; IR spectra, Mass spectra and Electronic spectra.

## I. INTRODUCTION

Extensive literature is available on various aspects of lanthanide complexes of several  $\beta$ -diketones [1]-[3]. These complexes include neutral, anionic and mixed ligand systems having different stoichiometry. The importance of metal complexes of naturally occurring unsaturated  $\beta$ -diketones such as curcuminoids (1,7-diaryl-1,6-heptadiene-3,5-diones) are also well documented in modern coordination chemistry [4]-[6]. But reports are scanty on lanthanide complexes of these types of unsaturated  $\beta$ -diketones [7]. In continuation of our research work on such unsaturated  $\beta$ -diketones and their metal complexes [7]-[10], we here report the synthesis and spectral characterization of the metal complexes of five trivalent lanthanide cations; Pr(III), Nd(III), Eu(III), Er(III) and Yb(III) with four unsaturated  $\beta$ -diketones (HL<sup>1</sup>-HL<sup>4</sup>). These unsaturated  $\beta$ -diketones were synthesized by the Claisen-Schmidt condensation between acetylacetone and aromatic aldehydes; 2-hydroxynaphthaldehyde, 4-methoxybenzaldehyde, 4-hydroxybenzaldehyde and 4-hydroxy-3-methoxybenzaldehyde.

## 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 metal oxides,  $M_2O_3$ . The IR spectra (KBr discs) were recorded 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 at room temperature on a Guoy type magnetic balance at room temperature ( $28 \pm 1^\circ\text{C}$ ) using  $Hg[Co(NCS)_4]$  as standard. All the chemicals and solvents were of reagent grade (Merck, Fluka and Sigma-Aldrich) and were used without further purification.

### B. Synthesis of Pr(III), Nd(III), Eu(III), Er(III) and Yb(III) Complexes of 1,7-Diarylheptanoids

The 1,7-diarylheptanoids were synthesized by the condensation between aromatic aldehydes and acetylacetone in presence of tri(*sec*-butyl)borate and boric oxide using *n*-butylamine as the condensing agent by the methods reported earlier [11]-[15].

The lanthanide metal oxides ( $M_2O_3$ ) were dissolved in nitric acid. The solution was evaporated to a small volume, diluted with water and evaporated nearly to dryness to get the corresponding metal nitrates,  $M(NO_3)_3$ . A solution of metal nitrate (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 (0.03 mol, 25 mL). The pH of the reaction mixture was carefully maintained [Pr(III), Nd(III), Eu(III) = 6.6, Er(III) = 6.3 and Yb(III) = 6.1] in order to prevent the precipitation of metal hydroxides. The mixture was stirred for  $\sim 12$  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.

### III. RESULTS AND DISCUSSION

Stable and well defined metal complexes are formed by all 1,7-diarylheptanoids (Fig. 1) with  $M(NO_3)_3$ . The metal complexes show sharp melting points and are soluble in common organic solvents like methanol, chloroform, DMF and DMSO. The analytical data (TABLE I) together with non-electrolytic nature in DMF (specific conductance  $<10\Omega^{-1}cm^{-1}$ ;  $10^{-3}$  M solution) suggest their 1:2 metal-1,7-diarylheptanoid stoichiometry. Magnetic measurements showed that all the complexes are paramagnetic with normal paramagnetic moments. The observed IR and mass spectral data of the complexes are in agreement with Fig. 2.

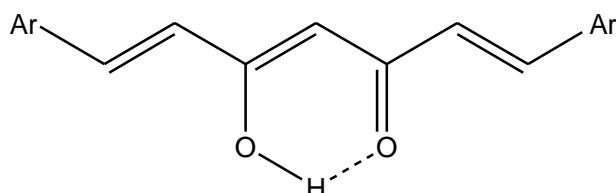


Fig. 1. Structure of 1,7-diarylheptanoids; Ar = 2-Hydroxynaphthyl (HL<sup>1</sup>); 4-Methoxyphenyl (HL<sup>2</sup>); 4-Hydroxyphenyl (HL<sup>3</sup>); 4-Hydroxy-3-methoxyphenyl (HL<sup>4</sup>)

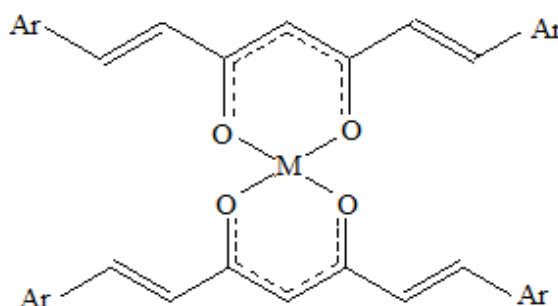


Fig 2. Tentative mode of coordination of the M(III) ion with 1,7-diarylheptanoids; M = Pr(III), Nd(III), Eu(III), Er(III) and Yb(III); The proposed structure also contains one bidentate nitrate ion and two coordinated water molecules

TABLE I  
PHYSICAL AND ANALYTICAL DATA OF THE METAL COMPLEXES OF 1,7-DIARYLHEPTANOIDS

Complex/ Empirical Formula	M.P. °C	$\mu_{\text{eff}}$ BM	Elemental Analysis: Found (Calculated)%			
			C	H	N	M
[Pr(L <sup>1</sup> ) <sub>2</sub> (NO <sub>3</sub> )(H <sub>2</sub> O) <sub>2</sub> ]/ C <sub>54</sub> H <sub>42</sub> NPrO <sub>13</sub>	158	3.26	62.11 (61.54)	4.07 (3.99)	1.43 (1.32)	13.52 (13.38)
[Pr(L <sup>2</sup> ) <sub>2</sub> (NO <sub>3</sub> )(H <sub>2</sub> O) <sub>2</sub> ]/ C <sub>42</sub> H <sub>42</sub> NPrO <sub>13</sub>	168	3.30	56.28 (55.45)	4.71 (4.62)	1.71 (1.54)	15.83 (15.50)
[Pr(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>34</sub> NPrO <sub>13</sub>	198	3.26	54.00 (53.46)	4.12 (3.99)	1.80 (1.64)	16.71 (16.52)
[Pr(L <sup>4</sup> ) <sub>2</sub> (NO <sub>3</sub> )(H <sub>2</sub> O) <sub>2</sub> ]/ C <sub>42</sub> H <sub>42</sub> NPrO <sub>17</sub>	214	3.28	52.08 (51.80)	4.69 (4.32)	1.57 (1.44)	14.73 (14.48)
[Nd(L <sup>1</sup> ) <sub>2</sub> (NO <sub>3</sub> )(H <sub>2</sub> O) <sub>2</sub> ]/ C <sub>54</sub> H <sub>42</sub> NNdO <sub>13</sub>	153	3.20	61.52 (61.34)	4.04 (3.97)	1.49 (1.33)	14.06 (13.65)
[Nd(L <sup>2</sup> ) <sub>2</sub> (NO <sub>3</sub> )(H <sub>2</sub> O) <sub>2</sub> ]/ C <sub>42</sub> H <sub>42</sub> NNdO <sub>13</sub>	204	3.26	55.68 (55.24)	4.71 (4.60)	1.62 (1.53)	16.08 (15.81)
[Nd(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>34</sub> NNdO <sub>13</sub>	196	3.28	53.92 (53.26)	4.02 (3.97)	1.71 (1.64)	17.05 (16.85)
[Nd(L <sup>4</sup> ) <sub>2</sub> (NO <sub>3</sub> )(H <sub>2</sub> O) <sub>2</sub> ]/ C <sub>42</sub> H <sub>42</sub> NNdO <sub>17</sub>	200	3.22	52.34 (51.62)	4.54 (4.30)	1.51 (1.43)	14.99 (14.78)
[Eu(L <sup>1</sup> ) <sub>2</sub> (NO <sub>3</sub> )(H <sub>2</sub> O) <sub>2</sub> ]/ C <sub>54</sub> H <sub>42</sub> NEuO <sub>13</sub>	194	3.75	61.13 (60.90)	4.12 (3.95)	1.52 (1.32)	14.53 (14.28)
[Eu(L <sup>2</sup> ) <sub>2</sub> (NO <sub>3</sub> )(H <sub>2</sub> O) <sub>2</sub> ]/ C <sub>42</sub> H <sub>42</sub> NEuO <sub>13</sub>	183	3.80	54.99 (54.78)	4.79 (4.57)	1.71 (1.58)	16.83 (16.51)
[Eu(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>34</sub> NEuO <sub>13</sub>	198	3.78	52.96 (52.78)	4.12 (3.93)	1.83 (1.62)	17.62 (17.34)
[Eu(L <sup>4</sup> ) <sub>2</sub> (NO <sub>3</sub> )(H <sub>2</sub> O) <sub>2</sub> ]/ C <sub>42</sub> H <sub>42</sub> NEuO <sub>17</sub>	240	3.78	51.53 (51.22)	4.62 (4.27)	1.61 (1.43)	15.71 (15.28)
[Er(L <sup>1</sup> ) <sub>2</sub> (NO <sub>3</sub> )(H <sub>2</sub> O) <sub>2</sub> ]/ C <sub>54</sub> H <sub>42</sub> NErO <sub>13</sub>	197	9.18	60.67 (60.04)	4.07 (3.89)	1.36 (1.30)	15.94 (15.50)
[Er(L <sup>2</sup> ) <sub>2</sub> (NO <sub>3</sub> )(H <sub>2</sub> O) <sub>2</sub> ]/ C <sub>42</sub> H <sub>42</sub> NErO <sub>13</sub>	203	9.24	54.12 (53.88)	4.82 (4.49)	1.71 (1.50)	18.14 (17.88)
[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>34</sub> NErO <sub>13</sub>	212	9.22	52.21 (51.86)	4.11 (3.87)	1.68 (1.59)	19.64 (19.02)
[Er(L <sup>4</sup> ) <sub>2</sub> (NO <sub>3</sub> )(H <sub>2</sub> O) <sub>2</sub> ]/ C <sub>42</sub> H <sub>42</sub> NErO <sub>17</sub>	226	9.20	50.92 (50.44)	4.70 (4.20)	1.51 (1.40)	17.11 (16.74)
[Yb(L <sup>1</sup> ) <sub>2</sub> (NO <sub>3</sub> )(H <sub>2</sub> O) <sub>2</sub> ]/ C <sub>54</sub> H <sub>42</sub> NYbO <sub>13</sub>	182	4.25	59.99 (59.72)	3.98 (3.97)	1.52 (1.29)	16.13 (15.95)
[Yb(L <sup>2</sup> ) <sub>2</sub> (NO <sub>3</sub> )(H <sub>2</sub> O) <sub>2</sub> ]/ C <sub>42</sub> H <sub>42</sub> NYbO <sub>13</sub>	174	4.20	53.92 (53.55)	4.63 (4.46)	1.62 (1.49)	18.52 (18.39)
[Yb(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>34</sub> NErO <sub>13</sub>	201	4.18	51.79 (51.52)	3.99 (3.84)	1.79 (1.58)	19.83 (19.55)
[Yb(L <sup>4</sup> ) <sub>2</sub> (NO <sub>3</sub> )(H <sub>2</sub> O) <sub>2</sub> ]/ C <sub>42</sub> H <sub>42</sub> NPrO <sub>17</sub>	242	4.22	50.43 (50.15)	4.32 (4.18)	1.52 (1.39)	17.48 (17.22)

#### A. Infrared Spectra

A strong band at  $\sim 1625\text{ cm}^{-1}$  and a broad band in the range  $2800\text{--}3500\text{ cm}^{-1}$  are observed in the IR spectra of all 1,7-diarylheptanoids due to the stretching of the chelated carbonyl and the intra-molecularly hydrogen bonded enol functions respectively.  $1640\text{--}1740\text{ cm}^{-1}$  region of the spectra does not contain any

band assignable to a normal  $\alpha,\beta$ -unsaturated carbonyl group confirming the existence of the compounds entirely in the enol tautomeric form as in Fig. 1 [10]-[14].

The band at  $\sim 1625\text{ cm}^{-1}$  due to the stretching of the chelated carbonyl is absent in the IR spectra of all the metal complexes. Instead, a strong band assignable to the stretching of the coordinated carbonyl moiety appeared at  $\sim 1580\text{ cm}^{-1}$ . These observations strongly support the replacement of enol proton by metal ion during complex formation [16], [17]. The intensity and breadth of the band in the  $2800\text{-}3500\text{ cm}^{-1}$  region increased appreciably indicating the presence of different types of O-H vibrations in the complexes due to coordinated water molecules. The appearance of two or more weak but prominent bands in the  $1630\text{-}1660\text{ cm}^{-1}$  region of the spectra assignable to H-O-H bending also support the presence of coordinated water molecules in these complexes [17]. From the observed breadth and intensity, these bands cannot be assigned to the carbonyl functions. The participation of carbonyl groups in metal chelate formation is further confirmed from the appearance of two medium intensity bands in the  $400\text{-}480\text{ cm}^{-1}$  region due to  $\nu(\text{M-O})$  vibrations [17].

The spectra of all the complexes showed two medium intensity bands at  $\sim 1300\text{ cm}^{-1}$  and  $1020\text{ cm}^{-1}$  assignable respectively to the asymmetric and symmetric stretching of nitrate group [16]. The separation between these two bands is found to be  $\sim 180\text{ cm}^{-1}$  indicating that the nitrate group is bonded as a chelating bidentate ligand. The bidentate coordination of nitrate ion is also evident from the presence of a band at  $\sim 1470\text{ cm}^{-1}$  in the spectrum of all the complexes [16].

The prominent band observed at  $\sim 975\text{ cm}^{-1}$  is typical of a *trans*  $-\text{CH}=\text{CH}-$  group which remained unaltered in the spectra of metal complexes [11]-[14]. Thus the IR spectra strongly support the coordination through dicarbonyl moiety of 1,7-diarylheptanoid, water molecules and nitrate ion. Important bands that appeared in the spectra are given in TABLE II.

TABLE II  
CHARACTERISTIC IR STRETCHING BANDS ( $\text{CM}^{-1}$ ) OF THE METAL COMPLEXES OF 1,7-DIARYLHEPTANOIDS

Complex	Chelated (C=O)	H-O-H Bending	(M-O)	(M-N)
$[\text{Pr}(\text{L}^1)_2(\text{NO}_3)(\text{H}_2\text{O})_2]$	1587	1624	419, 457	1300, 1020
$[\text{Pr}(\text{L}^2)_2(\text{NO}_3)(\text{H}_2\text{O})_2]$	1583	1627	409, 417	1308, 1016
$[\text{Pr}(\text{L}^3)_2(\text{NO}_3)(\text{H}_2\text{O})_2]$	1586	1621	410, 418	1290, 1022
$[\text{Pr}(\text{L}^4)_2(\text{NO}_3)(\text{H}_2\text{O})_2]$	1576	1623	409, 419	1300, 1008
$[\text{Nd}(\text{L}^1)_2(\text{NO}_3)(\text{H}_2\text{O})_2]$	1586	1633	411, 420	1312, 1010
$[\text{Nd}(\text{L}^2)_2(\text{NO}_3)(\text{H}_2\text{O})_2]$	1583	1628	409, 417	1302, 1020
$[\text{Nd}(\text{L}^3)_2(\text{NO}_3)(\text{H}_2\text{O})_2]$	1584	1631	408, 417	1300, 1015
$[\text{Nd}(\text{L}^4)_2(\text{NO}_3)(\text{H}_2\text{O})_2]$	1581	1627	407, 416	1309, 1020
$[\text{Eu}(\text{L}^1)_2(\text{NO}_3)(\text{H}_2\text{O})_2]$	1584	1629	409, 417	1310, 1018
$[\text{Eu}(\text{L}^2)_2(\text{NO}_3)(\text{H}_2\text{O})_2]$	1579	1631	407, 437	1303, 1018
$[\text{Eu}(\text{L}^3)_2(\text{NO}_3)(\text{H}_2\text{O})_2]$	1581	1630	405, 444	1300, 1015
$[\text{Eu}(\text{L}^4)_2(\text{NO}_3)(\text{H}_2\text{O})_2]$	1583	1629	406, 446	1307, 1018
$[\text{Er}(\text{L}^1)_2(\text{NO}_3)(\text{H}_2\text{O})_2]$	1586	1627	409, 417	1310, 1018
$[\text{Er}(\text{L}^2)_2(\text{NO}_3)(\text{H}_2\text{O})_2]$	1576	1623	407, 437	1300, 1018
$[\text{Er}(\text{L}^3)_2(\text{NO}_3)(\text{H}_2\text{O})_2]$	1586	1626	405, 444	1290, 1012
$[\text{Er}(\text{L}^4)_2(\text{NO}_3)(\text{H}_2\text{O})_2]$	1589	1624	406, 446	1309, 1010
$[\text{Yb}(\text{L}^1)_2(\text{NO}_3)(\text{H}_2\text{O})_2]$	1587	1631	403, 417	1310, 1010
$[\text{Yb}(\text{L}^2)_2(\text{NO}_3)(\text{H}_2\text{O})_2]$	1583	1628	405, 426	1300, 1012
$[\text{Yb}(\text{L}^3)_2(\text{NO}_3)(\text{H}_2\text{O})_2]$	1580	1626	415, 480	1292, 1012
$[\text{Yb}(\text{L}^4)_2(\text{NO}_3)(\text{H}_2\text{O})_2]$	1583	1629	426, 476	1301, 1009

### B. Mass Spectra

The FAB mass spectra of the typical metal complexes of 1,7-diarylheptanoids showed molecular ion peaks corresponding to  $[\text{ML}_2(\text{NO}_3)(\text{H}_2\text{O})_2]$  stoichiometry. All the spectra showed peaks corresponding to  $[\text{ML}_2(\text{NO}_3)]^+$  and  $[\text{ML}_2]^+$  in the expected isotopic abundance of the metals. Other prominent peaks are due to ligand fragments [11]-[15]. The important mass spectral fragments are assembled in TABLE III.

TABLE III  
MASS SPECTRAL DATA OF SOME TYPICAL METAL COMPLEXES OF 1,7-DIARYLHEPTANOIDS

Complex	Mass Spectral Data (m/z)
$[\text{Pr}(\text{L}^1)_2(\text{NO}_3)(\text{H}_2\text{O})_2]$	1053, 1035, 1017, 955, 407, 270, 244, 216, 203, 175, 149, 143
$[\text{Nd}(\text{L}^2)_2(\text{NO}_3)(\text{H}_2\text{O})_2]$	912, 894, 876, 814, 335, 320, 228, 202, 174, 133
$[\text{Eu}(\text{L}^3)_2(\text{NO}_3)(\text{H}_2\text{O})_2]$	864, 846, 828, 766, 307, 226, 200, 172, 131
$[\text{Er}(\text{L}^4)_2(\text{NO}_3)(\text{H}_2\text{O})_2]$	727, 709, 691, 629, 367, 256, 230, 202, 163

### C. Electronic Spectra

The UV spectra of the 1,7-diarylheptanoids exhibited two absorption maxima in the range ~385 and ~260 nm assignable respectively to the various  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transitions of the highly conjugated molecule [7]. In the spectra of all the complexes these bands are slightly shifted to longer wavelength (~10 nm) indicating the involvement of the carbonyl groups in metal complexation [7], [10].

The electronic spectra of all the complexes showed several weak absorption bands in the low energy region. Even though these bands are not prominent, they indicated the complex formation and probable involvement of the f orbitals of the lanthanide ions. The origin of these weak transitions can be associated with the various f-f transitions possible in these complexes. Since the recorded spectra are not quantitative, specific assignment of the transitions are not possible and therefore no attempt is made in this regard. However the available data clearly justified complexation of the 1,7-diarylheptanoids with the lanthanide ions.

## IV. CONCLUSIONS

Mixed ligand complexes of lanthanides; Pr(III), Nd(III), Eu(III), Er(III) and Yb(III) with four 1,7-diarylheptanoids (HL) derived from acetylacetone and aromatic aldehydes (2-hydroxynaphthaldehyde, 4-methoxybenzaldehyde, 4-hydroxybenzaldehyde and 4-hydroxy-3-methoxybenzaldehyde) have been synthesized. Analytical, IR and mass spectral data indicate the monobasic bidentate coordination in which the intra-molecularly hydrogen bonded enol proton is replaced by the metal cation. The proposed structure of the complexes correspond to  $[ML_2(NO_3)(H_2O)_2]$  stoichiometry with the coordination through dicarbonyl moiety of 1,7-diarylheptanoid, water molecules and nitrate ion in a bidentate mode.

## ACKNOWLEDGMENT

The authors are thankful to University Grants Commission, New Delhi, India for providing financial assistance. Thanks are due to RSIC, CDRI, Lucknow; IIT, Mumbai; RSIC, IIT, Chennai and Department of Chemistry, University of Kerala for providing analytical and spectral facilities.

## REFERENCES

- [1] M. Milanova, J. Zaharieva, I. Manolov, M. Getzova, and D. Todorovsky, "Synthesis, thermal behaviour, optical and pharmacological properties and immobilization", *J. Rare Earths*, vol. 28, pp. 66-74, 2020.
- [2] M. Ismail, S. J. Lyle, and J. E Newbery, "Preparation and properties of lanthanide complexes of some  $\beta$ -diketones", *J. Inorg. Nucl. Chem.*, vol. 31, pp. 1715-1724, 1969.
- [3] W. H. Hegazy, and I. H. Al-Motawaa, "Lanthanide complexes of substituted  $\beta$ -diketone hydrazone derivatives: synthesis, characterization, and biological activities", *Bioinorg. Chem. Appl.*, doi:10.1155/2011/531946, pp. 1-10, 2011.
- [4] S. Wanninger, V. Lorenz, A. Subhan, and F. T. Edelmann, "Metal complexes of curcumin – synthetic strategies, structures and medicinal applications", *Chem. Soc. Rev.*, vol. 44, pp. 4986-5002, 2015.
- [5] A. Shakeri, Y. Panahi, T. P. Johnston, and A. Sahebkar, "Biological properties of metal complexes of curcumin", *BioFactors*, vol. 45, pp. 304-317, 2019.
- [6] M. Pröh, U. S. Schuber, W. Weigan, and M. Gottschaldt, "Metal complexes of curcumin and curcumin derivatives for molecular imaging and anticancer therapy", *Coord. Chem. Rev.*, vol. 307, pp. 32-41, 2016.
- [7] K. Krishnankutty, P. T. Malini, and M. B. Ummathur, "La(III) complexes of some 1,7-diaryl-1,6-heptadiene-3,5-diones", *Inorg. Chem. An Indian J.*, vol. 6(2), pp. 99-103, 2011.
- [8] R. Pallikkavil, M. B. Ummathur, and K. Krishnankutty, "Synthesis, characterization and antioxidant studies of Cd(II), Hg(II) and Pb(II) complexes of some synthetic curcuminoids", *Res. J. Chem. Sci.*, vol. 5(6), pp. 40-45, 2015.
- [9] R. Pallikkavil, M. B. Ummathur, S. Sreedharan, and K. Krishnankutty, "Synthesis, characterization and antimicrobial studies of Cd(II), Hg(II), Pb(II), Sn(II) and Ca(II) complexes of curcumin", *Main Group Met. Chem.*, vol. 36(3-4), pp. 123-127, 2013.
- [10] V. D. John, M. B. Ummathur, and K. Krishnankutty, "Synthesis, characterization and antitumour studies of some synthetic curcuminoid analogues and their aluminium complexes", *J. Coord. Chem.*, vol. 66(9), pp. 1508-1518, 2013.
- [11] V.D. John, and K. Krishnankutty, "Antitumour activity of synthetic curcuminoid analogues (1,7-diaryl-1,6-heptadiene-3,5-diones) and their copper complexes", *Appl. Organometal. Chem.*, vol. 20(8), pp. 477-482, 2006.
- [12] V.D. John, and K. Krishnankutty, "Synthesis, characterization and antitumour activities of some synthetic curcuminoid analogues and their copper complexes", *Transition Met. Chem.*, vol. 30, pp. 229-233, 2005.
- [13] K. Krishnankutty, and V.D. John, "Synthesis, Characterization, and Antitumour Studies of Metal Chelates of Some Synthetic Curcuminoids", *Synth. React. Inorg. Met.-Org. Chem.*, vol. 33, pp. 343-358, 2003.
- [14] V.D. John, G. Kuttan, K. Krishnankutty, "Anti-tumour studies of metal chelates of synthetic curcuminoids", *J. Exp. Clin. Cancer Res.*, vol. 21(2), pp. 219-224, 2002.
- [15] K. Krishnankutty, and P. Venugopalan, "Metal Chelates of Curcuminoids", *Synth. React. Inorg. Met.-Org. Chem.*, vol. 28, pp. 1313-1325, 1998.
- [16] N. Nakamoto, *Infrared Spectra and Raman Spectra of Inorganic and Coordination Compounds*, John Wiley & Sons, New York, 1997.
- [17] L.J. Bellamy, *The Infrared Spectra of Complex Molecules*, Chapman and Hall, London, 1980.