

Synthesis and Structural Characterisation of Tb(IV) Complexes of Curcuminoids

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Abstract— Tb(IV) complexes with the formula $[\text{TbL}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$ of three curcuminoids (HL) derived from acetylacetone and aromatic aldehydes (benzaldehyde, 2-hydroxy-1-naphthaldehyde and vanillin) have been synthesized and characterised by analytical and spectral methods. The results revealed the monobasic bidentate coordination of curcuminoids in which their intramolecularly hydrogen bonded enol proton is replaced by Tb(IV) ion.

Keywords— Curcuminoids; Tb(IV) complexes; Enol proton; IR spectra and Mass spectra.

I. INTRODUCTION

The complexes of Tb(III) ion with various 1,3-dicarbonyl compounds are well documented in the literature in view of their structural variations and applications in diverse fields [1]-[5]. Even though reports on Tb(IV) complexes with various ligands appeared recently [6], [7], reports are scanty on its complexes with 1,3-dicarbonyl compounds. No report exists in the general literature on Tb(IV) complexes of unsaturated 1,3-dicarbonyl compounds like curcuminoids. In continuation of our studies on such medicinally important 1,3-dicarbonyl compounds and their lanthanide complexes [8], [9], we here report the synthesis and structural characterisation of three Tb(IV) complexes of curcuminoids.

II. EXPERIMENTAL

A. Materials and Methods

Carbon, hydrogen and nitrogen contents were determined by microanalyses (Heraeus Elemental analyzer) and terbium content of complexes by igniting to $\sim 1000^\circ\text{C}$ and weighing as its oxide. UV spectra of the compounds 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 ($\sim 10^{-3}$ mol/L) at $28 \pm 1^\circ\text{C}$. A Guoy type magnetic balance at room temperature ($28 \pm 1^\circ\text{C}$) using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as standard was used for determining magnetic susceptibilities. All the chemicals and solvents used were of reagent grade (Merck, Fluka and Sigma-Aldrich).

B. Synthesis of Tb(IV) Complexes of Curcuminoids

The curcuminoids were synthesized by the condensation between acetylacetone and aromatic aldehydes (benzaldehyde, 2-hydroxy-1-naphthaldehyde and vanillin) by the methods reported earlier [10], [11].

A solution of $\text{Tb}(\text{NO}_3)_4$ (0.01 mol, 25 mL 1:3 v/v aqueous methanol) was added slowly with stirring to a methanolic solution of the curcuminoid (0.04 mol, 25 mL). The pH of the reaction mixture was carefully maintained at 7.04 in order to prevent the precipitation of terbium hydroxide. 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.

III. RESULTS AND DISCUSSION

All the curcuminoids (HL, Fig. 1) formed stable complexes with Tb(IV) ion. The complexes are soluble in common organic solvents. $[\text{TbL}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$ stoichiometry is proposed for the complexes from their analytical data (TABLE I) and their non-electrolytic nature in DMF solvent (specific conductance $< 10\Omega^{-1}\text{cm}^{-1}$; 10^{-3} M solution). The observed magnetic moments of the complexes are in accordance with seven unpaired electrons corresponding to the +4 oxidation state of Tb(IV) ion in a weak

ligand field. From the observed IR and mass spectral data Fig.2 can be proposed as the structure for the complexes.

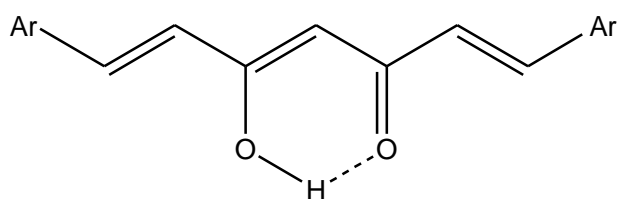


Fig. 1. Structure of curcuminoids; Ar = Phenyl (HL¹); 2-Hydroxy-1-naphthyl (HL²); 4-Hydroxy-3-methoxyphenyl (HL³)

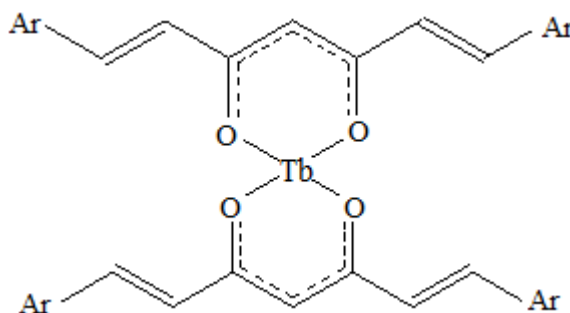


Fig 2. Tentative mode of coordination of the Tb(IV) ion with curcuminoids; The proposed structure also contains two bidentate nitrate ions and two coordinated water molecules

TABLE I
PHYSICAL, ANALYTICAL, UV AND IR SPECTRAL DATA OF THE Tb(IV) COMPLEXES OF CURCUMINOIDS

Complex/ Empirical Formula	M.P. °C	μ_{eff} BM	Elemental Analysis: Found (Calculated)%				UV λ_{max}	IR stretching bands (cm ⁻¹)			
			C	H	N	Tb		Chelated (C=O)	H-O-H bending	(M-O)	Chelated (NO ₃ ⁻)
[Tb(L ¹) ₂ (NO ₃) ₂ (H ₂ O) ₂] C ₃₈ H ₃₄ N ₂ TbO ₁₂	214	7.90	52.11 (52.47)	4.07 (3.91)	3.23 (3.22)	18.52 (18.30)	378, 262	1586	1629	407, 420	1290, 1025,1475
[Tb(L ²) ₂ (NO ₃) ₂ (H ₂ O) ₂] C ₅₄ H ₄₂ N ₂ TbO ₁₆	171	7.88	56.88 (57.19)	3.71 (3.71)	2.42 (2.47)	13.83 (14.03)	382, 264	1587	1630	407, 417	1296, 1030,1472
[Tb(L ³) ₂ (NO ₃) ₂ (H ₂ O) ₂] C ₄₂ H ₄₂ N ₂ TbO ₂₀	234	7.86	48.02 (47.86)	4.12 (3.99)	2.68 (2.66)	14.98 (15.10)	376, 260	1584	1628	409, 419	1292, 1020,1470

A. Infrared Spectra

The existence of curcuminoids entirely in the enolic form is evident from the presence of a strong band at ~1625 cm⁻¹ due to the stretching of the chelated carbonyl and a broad band in the range 2800-3500 cm⁻¹ due to the intramolecularly hydrogen bonded enol functions [10], [11]. The enol tautomeric form of the compounds as in Fig. 1 is further supported by the absence of any band in the 1640-1740 cm⁻¹ region of the spectra assignable to a normal α,β -unsaturated carbonyl group.

In the IR spectra of the Tb(IV) complexes the band at ~1625 cm⁻¹ due to the stretching of the chelated carbonyl disappeared and 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 [8], [9] [12]. 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 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 [9], [12]. From the observed breadth and intensity, these bands cannot be assigned to the carbonyl functions. The involvement of carbonyl groups in metal chelate formation is further supported from the presence of two medium intensity bands in the 400-430 cm⁻¹ region due to ν (Tb-O) vibrations [12]. The prominent band observed at ~975 cm⁻¹ due to *trans*-CH=CH- group remained unaltered in the spectra of metal complexes [10], [11].

Two medium intensity bands observed at ~1300 and 1020 cm⁻¹ due to the asymmetric and symmetric stretching of nitrate group and their separation of ~180 cm⁻¹ indicate its coordination as a chelating bidentate ligand. The bidentate coordination of nitrate ion is further confirmed from the presence of a band at ~1470 cm⁻¹ in the spectra of all the complexes [12], [13]. Hence the IR spectral data clearly support the

complexation through the carbonyl oxygens of curcumin, water molecules and nitrate ion. Important bands appeared in the IR spectra are assembled in TABLE I.

B. Mass Spectra

The FAB mass spectra of the Tb(IV) complexes showed molecular ion peaks corresponding to $[\text{Tb}(\text{L})_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$ stoichiometry. Peaks due to successive removal of water and nitrate groups, L^+ and fragments of L^+ are also present in the spectra. The important mass spectral fragments are assembled in TABLE II.

TABLE II
MASS SPECTRAL DATA OF Tb(IV) COMPLEXES OF CURCUMINOIDS

Complex	Mass Spectral Data (m/z)
$[\text{Tb}(\text{L}^1)_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$	869, 851, 833, 771, 709, 594, 576, 558, 496, 434, 275, 198, 144, 121
$[\text{Tb}(\text{L}^2)_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$	1133, 1115, 1097, 1035, 973, 726, 708, 646, 407, 264, 143
$[\text{Tb}(\text{L}^3)_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$	1053, 1035, 1017, 955, 893, 686, 668, 650, 367, 244, 123

C. UV Spectra

The UV spectra of the curcuminoids exhibited two absorption maxima at ~ 380 and ~ 260 nm corresponding to the various $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of Fig. 1 [10], [11]. The values shifted slightly to longer wavelength (~ 10 nm) in the spectra of the metal complexes indicating the involvement of the carbonyl groups in metal complexation [8], [9].

IV. CONCLUSIONS

Tb(IV) complexes of three curcuminoids (HL) derived from acetylacetone and aromatic aldehydes (benzaldehyde, 2-hydroxynaphthaldehyde and vanillin) have been synthesized. Analytical, IR and mass spectral data indicate the monobasic bidentate coordination of curcuminoids in which the intramolecularly hydrogen bonded enol proton is replaced by the Tb(IV) ion with the formation of a stable six-membered metal chelate ring. The proposed structure of these mixed ligand non-ionic complexes correspond to $[\text{TbL}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$ stoichiometry with the bidentate coordination of curcuminoids, bidentate coordination of nitrate ions and two coordinated water molecules.

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REFERENCES

- [1] M. Das and S. E. Livingstone, "Mass spectral studies of lanthanide chelates. I. Samarium, europium, gadolinium and terbium chelates of thenoyltrifluoroacetone", *Austr. J. Chem.*, vol. 28(7), pp 1513–1516, 1975.
- [2] K. P. Zhuravlev, V. A. Kudryashova, and V. I. Tsaryuk, "Luminescence and energy transfer processes in europium and terbium complexes with 2-substituted cycloalkanones and 1,10-phenanthroline derivatives" *J. Photochem. Photobiol. A: Chem.*, vol. 314(1), pp 14–21, 2016. <https://doi.org/10.1016/j.jphotochem.2015.08.001>
- [3] I. Hemmila, "Time-resolved fluorometric determination of terbium in aqueous solution" *Anal. Chem.*, vol. 57(8), pp. 1676–1681, 1985. <https://doi.org/10.1021/ac00285a037>
- [4] I. V. Taydakov, R. I. Avetisov, and N. P. Datskevich, "Tris(1,5-dimethyl-1H-pyrazol-4-yl)-4,4,4-trifluorobutane-1,3-dionato(dimethanol)terbium(III): synthesis, crystal structure, and luminescent properties", *Russ. J. Coord. Chem.*, vol. 45, pp. 883–888, 2019. <https://doi.org/10.1134/S1070328419120078>
- [5] N. Filipescu, W. F. Sager, and F. A. Serafin, "Substituent Effects on Intramolecular Energy Transfer. II. Fluorescence spectra of europium and terbium β -diketone chelates", *J. Phys. Chem.*, vol. 68(11), pp. 3324–3346, 1964. <https://doi.org/10.1021/j100793a039>
- [6] C. T. Palumbo, I. Zivkovic, R. Scopelliti, and M. Mazzanti, "Molecular complex of Tb in the +4 oxidation state", *J. Am. Chem. Soc.*, vol. 141(25), pp. 9827–9831, 2019. <https://doi.org/10.1021/jacs.9b05337>
- [7] A. R. Willauer, C. T. Palumbo, R. Scopelliti, I. Zivkovic, I. Douair, L. Maron, and M. Mazzanti, "Stabilization of the oxidation state +IV in siloxide-supported terbium compounds", *Angewandte Chemie*, vol. 132(9), pp. 3577–3581, 2020 <https://doi.org/10.1002/ange.201914733>
- [8] 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, pp. 99–103, 2011.
- [9] P. T. Malini, and M. B. Ummathur, "Pr(III), Nd(III), Eu(III), Er(III) and Yb(III) complexes of some 1,7-diaryl-1,6-heptadiene-3,5-diones", *J. Appl. Sci. Comput.*, vol. 9, pp. 72–75, 2020. DOI:16.10089.JASC.2020.V719.453459.150801220
- [10] P. Venugopalan, and K. Krishnankutty, "Metal chelates of curcuminoids" *Synth. React. Inorg. Met- Org. Chem.*, vol. 28, pp. 1313–1325, 1998.
- [11] V.D. John, G. Kuttan, and K. Krishnankutty, "Antitumour studies of metal chelates of synthetic curcuminoids" *J. Exp. Clin. Cancer Res.*, vol. 21, pp. 219–224, 2002.
- [12] N. Nakamoto, *Infrared Spectra and Raman Spectra of Inorganic and Coordination Compounds*, John Wiley & Sons, New York, 1997.
- [13] G. R. A. Wyllie, O. Q. Munro, C. E. Schulz, and W. R. Scheidt, "Structural and physical characterization of (nitrate)iron(III) porphyrinates $[\text{Fe}(\text{por})(\text{NO}_3)]$ — variable coordination of nitrate", *Polyhedron*, vol. 26(16), 4664–4672, 2007. doi: 10.1016/j.poly.2007.03.048