

Lanthanide & Actinide Complexes of Embelin

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Lanthanide and actinide complexes of embelin (2,5-dihydroxy-3-undecyl-2,5-cyclohexadiene-1, 4-dione) have been prepared and characterised on the basis of thermal, spectral and magnetic studies. Embelin acts as a tetradentate ligand coordinating through its carbonyl and phenolic oxygens.

We have earlier reported the preparation and characterisation of complexes of embelin with some transition metals¹. In the present study, complexes of embelin with some lanthanides and actinides have been synthesised and characterised on the basis of elemental analysis, spectral, thermal and magnetic studies.

Acetates of La, Pr, Nd, Sm, Gd, Dy and Y were prepared from the respective oxides (99.99% pure) obtained from M/s Indian Rare Earths Limited, Udyogamandal, Kerala. Thorium nitrate (99.9% pure, IRE, Bombay) and uranyl nitrate (BDH, AR) were used for the preparation of the corresponding complexes. Pure natural embelin was prepared by the method of Fieser and Chamberlin^{1,2}.

For the preparation of the complexes, aqueous ethanolic solutions of the lanthanide acetates (acidified with a few drops of acetic acid) and an ethanolic solution of the ligand in 2:3 molar ratio (with the ligand in a slight excess) were mixed together and refluxed on a water-bath for 20-30 min. Th(IV) and U(VI) complexes were prepared by mixing together thorium nitrate and the ligand in 1:2 molar ratio and uranyl nitrate and the ligand in 1:1 molar ratio. The complexes, which precipitated out, were repeatedly washed with aqueous ethanol to remove any excess ligand. They were then dried *in vacuo* over P₄O₁₀. The complexes were analysed for the metals by the conventional methods^{3,4}. Elemental analyses (C and H) were carried out at the Microanalytical Laboratory of NCL, Pune and at the Modular Laboratories, BARC, Bombay.

IR spectra were recorded as KBr pellets on a Perkin Elmer 397 IR spectrophotometer. Simultaneous TG, DTG and DTA were carried out on a derivatograph (Mom OD-102 model). Magnetic susceptibilities were measured at room temperature (27 ± 1°C) by

the Gouy method⁵ using Hg[Co(NCS)₄] as the calibrant. As the complexes were found to be insoluble in most of the common organic solvents, conductance measurements could not be carried out. These complexes were insoluble in camphor and biphenyl and, hence, molecular weight determinations too (by Rast's method) could not be carried out. The electronic spectra were recorded in the solid state by the mull technique following a procedure recommended by Venanzi⁶ using a Hitachi - 200-20 model spectrophotometer.

Analytical data of the complexes (Table 1) suggest the compositions M₂L₃.4H₂O for the lanthanide complexes, and ThL₂.2H₂O and UO₂L.2H₂O for the actinide complexes. The insolubility of the complexes in most of the common organic solvents probably indicates a polymeric nature. All the complexes showed a tendency to absorb moisture and hence the experimentally determined values of the metal content (Table 1) are slightly lower than the theoretically expected values. On drying these chelates at 50°C *in vacuo* for 16 hr, mass loss corresponding to four water molecules for the lanthanides and two water molecules for the actinides was observed. Hence, water molecules in these chelates may be regarded as lattice-held⁷.

The important IR frequencies of the lanthanide and actinide complexes are presented in Table 1. The O-H stretching frequency is observed as a strong band at 3300 cm⁻¹ for embelin. The disappearance of this band indicates that the phenolic hydrogens are lost on chelation. The broad, medium intense peak occurring between 3300 and 3400 cm⁻¹ in the spectra of lanthanide and actinide complexes may be attributed to the O-H stretching frequency of the water molecules. The O-H bending frequency of water molecules is overlapped by the bands due to the ligand. The carbonyl stretching frequency, observed as a strong peak at 1610 cm⁻¹ in the ligand, is shifted to 1500-1520 cm⁻¹ in the spectra of all the complexes. The IR spectra of the octahedral complexes of embelin with some transition metals are characterised¹ by the carbonyl stretching frequency at 1520 cm⁻¹. Thus, embelin acts as a tetradentate ligand coordinating through its carbonyl and phenolic oxygens.

The magnetic data of the complexes are presented in Table 1. La(III), Y(III), Th(IV) and U(VI) complexes are diamagnetic, as expected. The measured magnetic moments of the complexes agree well with the theoretical values calculated from the Van Vleck formula⁸.

Table 1—Analytical, Magnetic, Spectral and Thermal Data of the Lanthanide and Actinide Complexes of Embelin

Complex	Elemental analysis*			μ_{eff} (B.M.)	IR bands		Thermal data*		
	% metal	% C	% H		$\nu\text{O-H}$ (cm^{-1})	$\nu\text{C=O}$ (cm^{-1})	pd ^t **	% mass loss [†]	% mass loss ^{††}
[La ₂ (em) ₃].4H ₂ O	20.2 (22.7)	51.1 (49.9)	6.8 (6.5)	—	3400	1520	240	6.0 (5.8)	71.0 (73.4)
[Pr ₂ (em) ₃].4H ₂ O	20.9 (22.9)	51.8 (49.7)	6.8 (6.5)	3.8 (3.62) [†]	3400	1520	240	6.0 (5.9)	76.0 (73.2)
[Nd ₂ (em) ₃].4H ₂ O	21.4 (23.3)	48.9 (49.5)	6.2 (6.5)	3.8 (3.68) [†]	3360	1500	240	6.0 (5.8)	76.0 (72.8)
[Sm ₂ (em) ₃].4H ₂ O	24.4 (24.1)	50.2 (49.0)	6.3 (6.4)	1.96 (1.55- 1.65) [†]	3400	1510	250	7.0 (5.8)	71.0 (72.0)
[Gd ₂ (em) ₃].4H ₂ O	24.1 (24.9)	47.8 (48.5)	6.3 (6.3)	7.94 (7.94) [†]	3380	1505	240	6.0 (5.7)	71.0 (71.3)
[Dy ₂ (em) ₃].4H ₂ O	23.6 (25.5)	48.2 (48.1)	6.3 (6.3)	10.74 (10.6) [†]	3380	1515	250	7.0 (5.6)	73.0 (70.7)
[Y ₂ (em) ₃].4H ₂ O	15.0 (15.8)	53.5 (54.4)	7.3 (7.1)	—	3380	1495	250	7.0 (6.4)	81.0 (79.9)
[Th(em) ₂].2H ₂ O	26.1 (27.2)	49.6 (47.9)	5.9 (6.1)	—	3400	1510	260	4.0 (4.2)	70.0 (69.0)
[UO ₂ (em)].2H ₂ O	38.2 (39.8)	35.2 (34.1)	5.3 (4.7)	—	3400	1500	220	6.0 (6.0)	55.0 (53.1)

em = C₁₇H₂₄O₄; *theoretical values in brackets; **procedural decomposition temperature; †calculated using the Van Vleck values; ‡after dehydration; ††after decomposition

Electronic spectra of the complexes were recorded in the solid state by the mull technique⁶ in the range 200-800 nm. Ligand absorptions and charge-transfer transitions complicate the assignments of the observed bands in the UV and the visible regions. The electronic spectrum of the ligand shows absorption maxima at 17800, 28570 and 33330 cm^{-1} . All the complexes show absorption maxima at 15600, 25000 and 28000 cm^{-1} . Most of the absorption bands due to *f-f* transitions of lanthanide ions in the UV and the visible regions were obscured in the present complexes by the very strong ligand absorptions in this region.

Thermal behaviour

Thermal studies of the metal complexes were carried out under static air conditions. Thermoanalytical data obtained from TG, DTG and DTA are presented in Table 1. The complexes exhibit dehydration and decomposition stages. A broad endothermic peak extending between 50°C and 200°C was observed indicating the loss of water molecules. All the lanthanide and actinide complexes are hygroscopic and, hence, the mass loss corresponding to the dehydration step is slightly higher than the theoretical value. In the case of transition metal complexes dehydration started only after 120°C¹. However, about 90% of the mass loss corresponding to dehydration of the lanthanide and actinide complexes of embelin was observed between

50°C and 100°C in the TG curves and only < 10% was observed between 100°C and 180°C. Vacuum drying at ~ 50°C was observed to yield completely dehydrated lanthanide and actinide complexes indicating that the water present was water of crystallization⁹.

The decomposition stage extends over a broad range and is mainly exothermic in nature with a small endothermic peak at 350-380°C for all the complexes. Ligand decomposition is characterised by endothermic peaks at 230, 280, 320 and 460°C and the main exothermic decomposition starts only at 470°C. The overall effect is, however, endothermic. In the complexes, DTG peaks are paralleled by endothermic and exothermic DTA peaks. Exothermicity of the decomposition of the present complexes could be attributed to the concomitant oxidation reactions of the ligand. The decomposition stage of the complexes consists of exothermic peaks in the ranges 220°-320° and 400°-480°C and an endothermic peak between 320° and 380°C. Independent pyrolysis carried out for all the complexes gave the final mass loss comparable to the values obtained from the thermograms. Final residues of the pyrolysis of all the complexes (upto ~ 800°C) were subjected to chemical analysis^{3,4} and were found to have metal contents corresponding to the compositions of Ln₂O₃, U₃O₈ and ThO₂. All the complexes underwent complete decomposition at ~ 800°C giving the respective stable oxides.

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