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Complexes of Embelin with Cr(III) and Fe(III)

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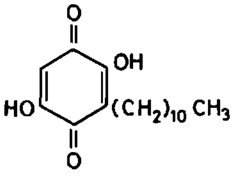
Embelin (2,5-dihydroxy-3-undecyl-2,5-cyclohexadiene-1,4-dione) isolated from the berries of the Indian shrub, *Embelia ribes*, is of great medicinal importance, because of its anthelmintic, analgesic and antifertility properties [1–3]. In view of its relevance in biological systems, attempts have been made to synthesize and characterize metal complexes of embelin [4, 5]. We are reporting here the complexes of embelin with Fe(III) and Cr(III). They have been synthesised and characterised by elemental analysis, vibrational and electronic spectra as well as by thermal and magnetic studies.



Embelin

Experimental

Pure natural embelin was prepared by the method of Fieser and Chamberlin [1]. Aqueous ethanolic solutions of the corresponding metal acetates and ethanolic solutions of the ligand in 2:3 molar ratio (with the ligand in slight excess) were mixed together and refluxed on a water bath for 20–30 min. The metal complexes precipitated out and were washed repeatedly with aqueous ethanol to remove adhering impurities. The complexes were dried under vacuum over P_4O_{10}.

The complexes were decomposed with a mixture of HCl and HNO_3 and the metal content estimated by atomic absorption spectrophotometery (IL-751 model AAS). Elemental analysis of the complexes were carried out at the micro-analytical laboratory of NCL, Pune. IR spectra (400–4000 cm^{-1}) were recorded as KBr pellets on a Perkin-Elmer 397 IR spectrophotometer. Simultaneous TG, DTG and DTA of the samples were carried out on a Derivatograph (Mom – OD-102 model). Magnetic susceptibilities were measured by the Gouy method using mercury tetrathiocyanato cobaltate(II) as the calibrant [6]. As the complexes were found to be insoluble in most of the common organic solvents, conductance measurements and molecular weight determinations could not be carried out. The electronic spectra of the complexes in the range 200–2000 nm were recorded in the solid state by a mull technique recommended by Venanzi [7] using a Hitachi-UV–Vis near infrared spectrophotometer.

Results and Discussion

Analytical data of the complexes (Table I) suggest an M_2L_3 composition for the Fe(III) and Cr(III) complexes. The insolubility of the complexes in most of the common organic solvents indicates a polymeric nature. A similar polymeric nature has also been reported for the divalent metal complexes [4].

TABLE I. Analytical Data of the Cr(III) and Fe(III) Complexes of Embelin

Complex	Colour	Elemental analysis: found (calculated)			μ_{eff} (BM)	Electronic spectra (cm^{-1})	Important IR bands ν(C=O) (cm^{-1})
		Metal (%)	C (%)	H (%)			
$Cr_2(Em)_3$	dull black	10.21 (10.61)	62.62 (62.44)	7.48 (7.35)	3.68	8330 15000 28570 33330	1510
$Fe_2(Em)_3$	dull black	11.12 (11.33)	62.81 (61.94)	7.92 (7.3)	5.8	14290 16390 18690 24100 28550 33330	1490

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TABLE II. Thermo-Analytical Data of the Cr(III) and Fe(III) Complexes of Embelin

Complex[a]	PDT[b] from TG	Peak temperature		Decomposition temperature range		Mass loss after decomposition (%): found (calculated)	
		DTG	DTA	DTG	DTA	from TG	from independent pyrolysis
$Cr_2(Em)_3$	220	320	340 *exo*	220–360	220–360 *exo*	85	84.86
		400	390 *endo*	360–420	360–420 *endo*	(84.49)	(84.49)
		440	440 *exo*	420–700	420–850 *exo*		
$Fe_2(Em)_3$	230	280	260 *exo*	230–300	230–330 *exo*	84.4	84.1
		400	430 *endo*	340–460	360–450 *endo*	(83.81)	(83.81)
		500	500 *exo*	450–700	450–850 *exo*		

[a] Em = $C_{17}H_{24}O_4^{=}$. [b] Procedural decomposition temperature.

IR Spectra

The important IR frequencies of the Fe(III) and Cr(III) complexes are presented in Table I. The O–H stretching frequency is observed as a strong band at 3300 cm^{-1} for embelin. The disappearance of this band in the complexes indicates the loss of phenolic hydrogens on chelation. The absence of the broad medium intense peak occurring between 3300 and 3400 cm^{-1} indicates the absence of water molecules which had been observed for some divalent transition metal complexes of embelin [4]. The carbonyl stretching frequency observed as a strong peak at 1610 cm^{-1} is found shifted to 1510 cm^{-1} and 1490 cm^{-1} for the Cr(III) and Fe(III) complexes respectively. Thus embelin acts as a tetradentate ligand coordinating through its carbonyl and phenolic oxygens.

Electronic Spectra and Magnetic Properties

The electronic spectral bands observed for the iron(III) complex at 14 290 cm^{-1} and 16 390 cm^{-1} (Table I) may be attributed to the $^6A_1 \rightarrow {}^4T_1(G)$ and to the $^6A_1 \rightarrow {}^4E(G)$, $^6A_1 \rightarrow {}^4A_1(G)$ doublet respectively. The band at 18 690 cm^{-1} may be due to the $^6A_1 \rightarrow {}^4E$ transition while the remaining one at 24 100 cm^{-1} may be due to the $^6A_1 \rightarrow {}^4F$ transition. These bands are in conformity with a tetrahedral coordination for the iron(III) complex [8].

Iron(III) complexes generally have magnetic moments between 5.1 and 6.0 BM and irrespective of their stereochemistry [8]. The iron(III) embelin complex has a room temperature magnetic moment of 5.8 BM which is comparable with values reported for other tetrahedral iron(III) complexes [8, 9].

For the Cr(III) complexes, the observed electronic spectral bands at 8330 cm^{-1} and 15 000 cm^{-1} could be assigned to the $^4T_1(F) \rightarrow {}^4A_2$ and $^4T_1(F) \rightarrow {}^4T_1(P)$ transitions. These values compare well with bands for other tetrahedrally coordinated Cr(III) compounds such as tungstochromic acid [10] and hence a tetrahedrally coordinated structure is proposed for the Cr(III) embelin complex especially in view of steric hindrance caused by the bulky embelin molecules [11].

The observed μ_{eff} value of 3.68 BM, though close to the spin-only value for a d^3 ion, is comparable to lower than expected magnetic moments reported for other four-coordinated chromium(III) complexes [11].

Thermal Studies

Thermal studies of the complexes were carried out under static air conditions. Thermoanalytical data obtained from TG, DTG and DTA curves and independent pyrolysis are presented in Table II. The absence of a dominant endotherm upto 220 ℃ indicates the absence of coordinated water molecules. The decomposition is mainly exothermic with an endothermic shift at around 360 ℃. Ligand decomposition is mainly endothermic in nature. Exothermicity of the decomposition of the complexes may be attributed to the concomitant oxidation reactions of the ligand, Independent pyrolysis carried out on the complexes gave final mass loss values comparable to those obtained from the thermograms. Final residues of pyrolysis of the complexes (upto ~900 ℃) were subjected to chemical analysis [12] and were found to correspond to Fe_2O_3 and Cr_2O_3 respectively. The complexes undergo complete decomposition at ~900 ℃ giving the respective stable oxides.

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