Inorganica Chimica Acta, 117 (1986) 187–189

Nature and Composition of La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Dy(III) and Ho(III) Complexes of Embelin

M. L. DHAR* and ONKAR SINGH

Department of Chemistry, Jammu University, Jammu-180001, India

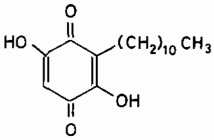
(Received January 21, 1986)

Abstract

The isolation and characterization of nine polymeric complexes of the general formula $[M(L)_{1.5}S_2]_n$ (where M is the metal ion, L the ligand and S the solvent, C_2H_5OH) of La(III) and Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III), Dy(III), Ho(III) with the biologically active compound embelin using elemental and thermal analysis, infrared and electronic spectral studies is reported.

Introduction

The benzoquinone derivative embelin (2,5-dihydroxy-3-undecyl-*p*-benzoquinone) possesses anthelmintic, analgesic and antifertility activities [1–6]. It has also been used as an analytical reagent [7–9]. Embelin gives intense colour reactions with a large number of metal ions including lanthanides on paper chromatograms. The present work constitutes a part of the systematic study of the composition and nature of these metal complexes.



Experimental

Preparation of Embelin [10]

Embelin was isolated from embelia ribe seeds. The seeds were dried and cleaned, powdered and subjected to extraction by petroleum ether in a soxhlet assembly. It separated from the petroleum extract. It was crystallized from hot acetic acid and recrystallized as orange yellow plates from an ether–benzene mixture; melting point (m.p.) 142 °C (literature 142–143 °C).

Preparation of Solid Complexes

The metal complexes in all cases were prepared by mixing the metal ion and ligand in stoichiometric proportions (determined from solution studies) in ethanol. The complex was precipitated from the concentrated solution by controlled addition of distilled water. It was dried under vacuum over anhydrous $CaCl_2$. All the reagents used were of analytical grade.

Physical Measurements

Estimation of C and H was carried out by combustion method using a micro analyser. Metal (M) content was estimated by ignition of the complexes to their respective oxides and by the usual analytical procedures. The IR spectra of embelin and the complexes were recorded in the region of 4000–200 cm^{-1} using KBr pellets. Electronic absorption spectra of the complexes were recorded as diffuse reflectance spectra on VSU2P (Carl Zeiss) spectrophotometer from 50000 to 10000 cm^{-1}. Thermal analysis of a representative complex of Sm(III) was carried out by obtaining simultaneous DTA and TGA thermoanalytical curves on Paulik–Paulik Erdey MOM derivatograph (Hungary).

Results and Discussion

The elemental analysis results for C, H and metal (M) given in Table I are in close agreement with those calculated for the following composition: $[La(C_{17}H_{24}O_4)_{1.5}(C_2H_5OH)_2]_n$, $[Ce(C_{17}H_{24}O_4)_{1.5}(C_2H_5OH)_2]_n$, $[Pr(C_{17}H_{24}O_4)_{1.5}(C_2H_5OH)_2]_n$, $[Nd(C_{17}H_{24}O_4)_{1.5}(C_2H_5OH)_2]_n$, $[Sm(C_{17}H_{24}O_4)_{1.5}(C_2H_5OH)_2]_n$, $[Gd(C_{17}H_{24}O_4)_{1.5}(C_2H_5OH)_2]_n$, $[Tb(C_{17}H_{24}O_4)_{1.5}(C_2H_5OH)_2]_n$, $[Dy(C_{17}H_{24}O_4)_{1.5}(C_2H_5OH)_2]_n$ and $[Ho(C_{17}H_{24}O_4)_{1.5}(C_2H_5OH)_2]_n$ of the complexes.

The compositions are further supported by IR spectral studies of the ligand and the complexes. The infrared spectrum of the ligand recorded in the region 4000–200 cm^{-1} has three strong bands at 3322, 1610 and 1190 cm^{-1} assigned to ν(O–H), ν(C=O) and ν(O–C) stretching vibrations (Table II).

---

*Author to whom correspondence should be addressed.

0020-1693/86/$3.50

TABLE I. Elemental Analysis (%) of the Complexes

Complex	Colour	Calculated			Found		
		C	H	M	C	H	M
$[La(C_{17}H_{24}O_4)_{1.5}(C_2H_5OH)_2]_n$	black	52.92	7.17	20.67	52.51	7.19	20.49
$[Ce(C_{17}H_{24}O_4)_{1.5}(C_2H_5OH)_2]_n$	black	52.82	7.16	20.90	52.69	7.10	20.29
$[Pr(C_{17}H_{24}O_4)_{1.5}(C_2H_5OH)_2]_n$	balck	52.76	7.15	21.00	52.57	7.40	22.40
$[Nd(C_{17}H_{24}O_4)_{1.5}(C_2H_5OH)_2]_n$	black	52.50	7.11	21.39	52.39	7.39	21.30
$[Sm(C_{17}H_{24}O_4)_{1.5}(C_2H_5OH)_2]_n$	black	52.03	7.05	22.09	52.41	7.17	22.21
$[Gd(C_{17}H_{24}O_4)_{1.5}(C_2H_5OH)_2]_n$	black	51.50	6.98	22.88	51.28	6.89	22.49
$[Tb(C_{17}H_{24}O_4)_{1.5}(C_2H_5OH)_2]_n$	black	51.38	6.96	23.06	51.19	6.48	23.21
$[Dy(C_{17}H_{24}O_4)_{1.5}(C_2H_5OH)_2]_n$	black	51.11	6.93	23.46	51.69	6.43	23.36
$[Ho(C_{17}H_{24}O_4)_{1.5}(C_2H_5OH)_2]_n$	black	50.94	6.90	23.73	50.59	6.45	23.35

TABLE II. Principal Bands (cm^{-1}) of Infrared Spectral Data of Complexes

Complex	ν(C=O)	ν(O–C)	ν(M–O) or ν(M–O + C–C)	
$C_{17}H_{26}O_4$ (ligand)[a]	1610	1190		
$[La(C_{17}H_{24}O_4)_{1.5}(C_2H_5OH)_2]_n$	1530	1200	1480	450
$[Ce(C_{17}H_{24}O_4)_{1.5}(C_2H_5OH)_2]_n$	1520	1222	1490	440
$[Pr(C_{17}H_{24}O_4)_{1.5}(C_2H_5OH)_2]_n$	1530	1220	1490	445
$[Nd(C_{17}H_{24}O_4)_{1.5}(C_2H_5OH)_2]_n$	1540	1210	1460	460
$[Sm(C_{17}H_{24}O_4)_{1.5}(C_2H_5OH)_2]_n$	1530	1230	1500	455
$[Gd(C_{17}H_{24}O_4)_{1.5}(C_2H_5OH)_2]_n$	1540	1218	1480	445
$[Tb(C_{17}H_{24}O_4)_{1.5}(C_2H_5OH)_2]_n$	1530	1215	1470	440
$[Dy(C_{17}H_{24}O_4)_{1.5}(C_2H_5OH)_2]_n$	1520	1220	1480	452
$[Ho(C_{17}H_{24}O_4)_{1.5}(C_2H_5OH)_2]_n$	1530	1220	1480	450

[a] $C_{17}H_{26}O_4$ = embelin (2,5-dihydroxy-3-undecyl-*p*-benzoquinone).

TABLE III. Principal Electronic Spectral Bands (cm^{-1}) of Complexes

Complex	Electronic absorption bands (cm^{-1})	Assignments
$[La(C_{17}H_{24}O_4)_{1.5}(C_2H_5OH)_2]_n$	28571	intra ligand charge transfer
$[Ce(C_{17}H_{24}O_4)_{1.5}(C_2H_5OH)_2]_n$	42586	$^2D_{5/2} \leftarrow {}^2F_{5/2}$
	34915	$^2D_{3/2} \leftarrow$
$[Pr(C_{17}H_{24}O_4)_{1.5}(C_2H_5OH_2]_n$	16230	$^1D_2 \leftarrow {}^3H_4$
$[Nd(C_{17}H_{24}O_4)_{1.5}(C_2H_5OH)_2]_n$	26881	$^2P_{1/2} \leftarrow {}^4I_{9/4}$
	17241	$^4F_{9/2} \leftarrow {}^4I_{9/2}$
	15337	$^4G_{5/2} \leftarrow$
	13661	$^4G_{7/2} \leftarrow$
	12658	$^4G_{9/2} \leftarrow$
$[Sm(C_{17}H_{24}O_4)_{1.5}(C_2H_5OH)_2]_n$	25510	$^6P_{3/2} \leftarrow {}^6H_{5/2}$
	20202	$^4I_{3/2} \leftarrow$
$[Gd(C_{17}H_{24}O_4)_{1.5}(C_2H_5OH)_2]_n$	26315	$^6P_{7/2} \leftarrow {}^8S_{7/2}$
$[Tb(C_{17}H_{24}O_4)_{1.5}(C_2H_5OH)_2]_n$	26795	$^5D_3 \leftarrow {}^7F_6$
$[Dy(C_{17}H_{24}O_4)_{1.5}(C_2H_5OH)_2]_n$	25000	$^4I_{13/2} \leftarrow {}^6H_{5/2}$
	16660	$^6H_{3/2} \leftarrow$
	12254	$^6F_{5/2} \leftarrow$
$[Ho(C_{17}H_{24}O_4)_{1.5}(C_2H_5OH)_2]_n$	23809	$^5G_6 \leftarrow {}^4I_8$
	21459	$^4G_4 \leftarrow$
	16025	$^5F_5 \leftarrow$

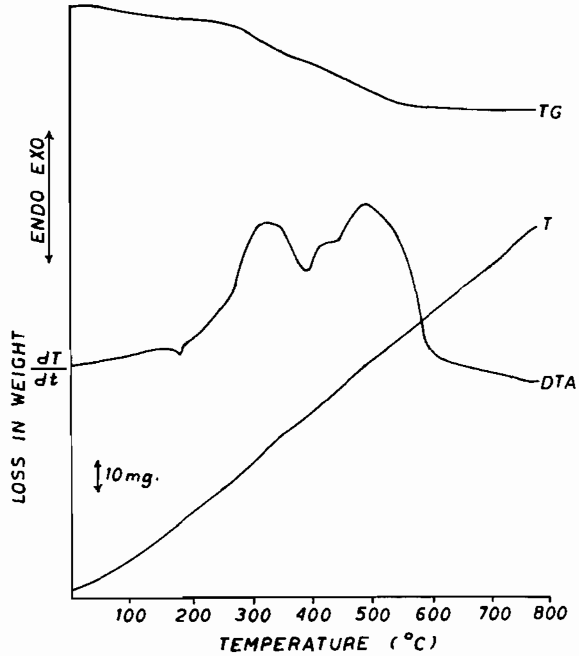


Fig. 1. Simultaneous DTA-TG curves of $[Sm(C_{17}H_{24}O_4)_{1.5}(C_2H_5OH)_2]_n$.

The spectra of the complexes recorded in the same region show significant shifts in these bands because of changes in force constants due to coordination to metal ions. The ν(O–H) band due to intramolecular hydrogen bonded hydroxyl in the ligand spectrum appears at 3322 cm^{-1}. This band disappears in all the complexes due to coordination of the ligand to the metal ion through the oxygen of the hydroxyl and abstraction of proton. The ν(C=O) and ν(O–C) frequency bands in the ligand spectrum also get shifted to lower values showing coordination to metal ion through oxygen of the carbonyl function. In addition to above changes, new bands appear in the region 460–440 cm^{-1} as a result of the ν(M–O) or ν(M–O + C–C) stretching modes. The presence of coordinated ethanol molecules is shown by the appearance of bands in the region 1500–1460 cm^{-1}.

The electronic spectral data of lanthanide complexes with probable assignments [11–17] given in Table III suggest square antiprism geometry for these complexes [18, 19]. The other bands in these complexes are assigned as charge transfer bands of the types metal-to-ligand and ligand-to-metal, electron transfers and electronic transitions within the ligand activated by the presence of ligand fields.

Figure 1 shows the simultaneous DTA and TG curves of the Sm(III) complex recorded with 40 mg of the sample, sensitivity 200 mg, at the heating rate of 10 °C per minute. The DTA curve reveals that the compound remains unchanged up to 170 °C beyond which it undergoes decomposition with one endothermic peak at 180 °C assigned to the loss of the two coordinated ethanol molecules and two exothermic peaks (one broad at 310 °C and one sharp at 485 °C) assigned to the loss of hydrocarbon side chain of the ligand. One endothermic peak at 385 °C and with a shoulder at 440 °C indicates some interchanges in the complex. The first arrest in TGA curve corresponding to DTA peaks of the complex shows a weight loss of 13.0% (calc. loss 13.5%). After the complete decomposition, the loss in weight shown by the TG curves is 75% (calc. 74.37%) corresponding to the formation of Sm_2O_3.

From the above discussion of results it is concluded that embelin coordinates to the metal ions through its two coordinating sites provided by the carbonyl and their adjacent hydroxyls. This results in the formation of polymeric complexes. The coordinated ethanol molecules make up the required coordination number. The complexes are represented as: $[M(L)_{1.5}S_2]_n$ where M = La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III), Dy(III) and Ho(III); $L = C_{17}H_{24}O_4{}^{2-}$; $S = C_2H_5OH$.

References

1 O. P. Gupta, K. K. Anand, M. Ali, A. J. Chatak Ray and C. K. Atal, *Indian J. Exp. Biol., 14,* 356 (1976).
2 M. Krishnaswami and K. K. Purushathaman, *Indian J. Exp. Biol., 18,* 638 (1980).
3 M. Krishnaswami and K. K. Purushothaman, *Indian J. Exp. Biol., 18,* 1359 (1980).
4 S. Chauhan, S. Agrawal, R. Mathur and R. K. Gupta, *Experientia, 35(a),* 1183 (1979).
5 W. J. Dunn and W. Svante, *J. Med. Chem., 23,* 595 (1980).
6 C. Seshadri, D. Suganthan and K. Santhakumari, *Indian J. Exp. Biol., 17,* 1389 (1979).
7 Ch. Bheemasankara Rao and V. Venkateswarlu, *Z. Anal. Chem., 185,* 216 (1962).
8 Ch. Bheemasankara Rao and V. Venkateswarlu, *Z. Anal. Chem., 192,* 183 (1963).
9 Ch. Bheemasankara and V. Venkateswarlu, *Z. Anal. Chem., 178,* 227 (1961).
10 Ch. Bheemasankara and V. Venkateswarlu, *Indian J. Pharm., 24,* 262 (1962).
11 D. G. Karraker, *Inorg. Chem., 7,* 473 (1968); *6,* 1863 (1967).
12 M. Mareizok, H. A. Plettinger and W. H. Zachariasen, *Acta Crystallogr., 14,* 237 (1961).
13 L. J. Rayon, *Inorg. Chem., 8,* 2053 (1969).
14 L. J. Rayon and C. K. Jφrgenson, *J. Phys. Chem., 70,* 2845 (1966).
15 B. R. Judd, *Phys. Rev., 127,* 750 (1962).
16 R. C. Vickery, *J. Chem. Soc.,* 421 (1952).
17 R. D. Fischer and H. Fischer, *J. Org. Chem., 27,* 273 (1965).
18 J. A. Cunningham, D. E. Sands and W. F. Wagner, *Inorg. Chem., 6,* 499 (1967).
19 T. Phillips II, D. E. Sands and W. F. Wagner, *Inorg. Chem., 7,* 2295 (1963).