Thermochimica Acta, 204 (1992) 321–327
Elsevier Science Publishers B.V., Amsterdam

Thermal dissociation of metal–plant-auxin chelates

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(Received 7 June 1991)

Abstract

Tris(indole-3-butyrato)M(III), tris(indole-3-propionato)M(III)$\cdot X H_2O$, where $X = 0$ (M = Eu) and $X = 3/4$ (M = Gd), and triaquatris(1-naphthaleneacetato)M(III)$\cdot X H_2O$, where $X = 1$ (M = Eu) and $X = 1/4$ (M = Gd), have been synthesized, and justified compositionally and structurally with respect to the oxidation number and the coordination number of the metal ions. Furthermore, the solid state reactions identified can be considered to be slow processes that follow first-order kinetics.

INTRODUCTION

The mode of action of plant auxins has been a controversial subject [1–4]. Sawhney and co-workers in their earlier studies [5–10], reported on the non-ionic character of metal–plant-auxin chelates satisfying metal ligancy and oxidation number. We present here some of the thermal and kinetic conclusions on Eu(III) and Gd(III) plant-auxin (IBA, IPA, NAA) chelates.

EXPERIMENTAL

All the chemicals used were of analytical grade.

Reagents

The plant auxins studied were IBA, IPA and NAA; and the metal salts used were $Eu(NO_3)_3 \cdot 6H_2O$ and $Gd(NO_3)_3 \cdot 5H_2O$.

Apparatus

The samples (see Table 1 for sample size) were pyrolysed in air on a Stanton–Redcroft thermal analyser STA 781 at a heating rate of 10°C min^{-1}.

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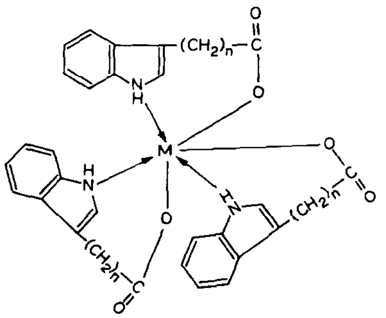
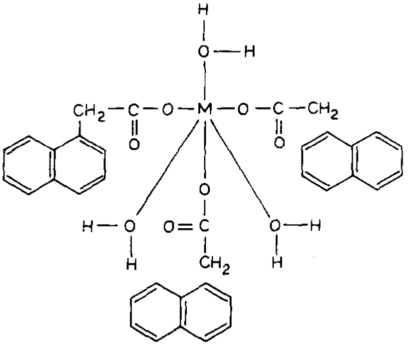


Scheme 1. M = Eu, Gd; $n = 2$, M = Eu/Gd for IPA complex; $n = 3$, M = Eu/Gd for IPA complex.



Scheme 2. $x = 1$, M = Eu; $x = 1/4$, M = Gd.

Chelate isolation

The aqueous metal solution was added slowly, and with constant stirring, to a warm aqueous solution of the sodium salt of the plant auxin. The precipitate thus obtained was filtered, washed with water and dried at 40–60°C.

Chemical analysis conformed to the structures shown in Schemes 1 and 2.

RESULTS AND DISCUSSION

Plant auxins (IBA, IPA, NAA) chelate tripositive, 6-coordinate metal ions (Eu(III) and Gd(III)) forming products with compositions $\mathrm{Eu \cdot R_3}$ (**I**), $\mathrm{Eu \cdot R'_3}$ (**II**) and $\mathrm{[Eu \cdot R''_3 \cdot 3H_2O]H_2O}$ (**III**) and $\mathrm{Gd \cdot R_3 \cdot (5/2)H_2O}$ (**IV**), $\mathrm{Gd \cdot R'_3 \cdot (3/4)H_2O}$ (**V**) and $\mathrm{[Gd \cdot R''_3 \cdot 3H_2O](1/4)H_2O}$ (**VI**). Products **I** and **II** are hydrated, whereas **III–VI** have coordinated lattice or both types of water molecules. Their thermal stability ranges from 60 to 100°C. **III**, **IV**, **V** and **VI** lost lattice water molecules in the temperature ranges H_2O

TABLE 1

Thermal results on metal–plant-auxin chelates

Chelate [a]	Sample size (mg)	T_i (pdt) [b] (°C)	T_f (°C)	$T_f - T_i$ (°C)	Sigmoids (TG) or dips (DTG) (instability limits)
$Eu \cdot R_3$	117	62	390	328	2 (62–190°C; 235–390°C)
$Eu \cdot R'_3$	108	100	535	435	2 (100–195°C; 270–535°C)
$[Eu \cdot R''_3 \cdot 3H_2O]H_2O$	72	75	475	400	4 (75–100°C; 150–195°C; 250–350°C; 400–475°C)
$Gd \cdot R_3 \cdot (5/2)H_2O$	95	90	615	525	3 (90–125°C; 165–320°C; 365–615°C)
$Gd \cdot R' \cdot (3/4)H_2O$	120	70	650	580	3 (70–105°C; 150–420°C; 470–650°C)
$[Gd \cdot R'' \cdot 3H_2O](1/4)H_2O$	100	85	600	515	4 (85–115°C; 135–200°C; 240–445°C; 480–600°C)

[a] R, R′ and R″ are anions of IBA, IPA and NAA respectively.

[b] pdt, procedural decomposition temperature.

(75–100°C), (5/2)H_2O (90–125°C), (3/4)H_2O (70–105°C) and (1/4)H_2O (85–115°C) respectively, resulting in the complex-species $Eu \cdot R''_3 \cdot 3H_2O$ (**VII**), $Gd \cdot R_3$ (**VIII**), $Gd \cdot R'_3$ (**IX**) and $Gd \cdot R''_3 \cdot 3H_2O$ (**X**). **VII** and **X** lost three coordinated water molecules in the ranges 150–195°C and 135–200°C, respectively, leaving anhydrous chelates of composition $Eu \cdot R''_3$ (**XI**) and $Gd \cdot R''$ (**XII**). The anhydrous species **I**, **II**, **VIII**, **IX**, **XI** and **XII** began to lose organic matter at 62°C, 100°C, 165°C, 150°C, 250°C and 240°C, respectively and on reaching plateaux starting at 190°C, 195°C, 320°C, 420°C, 350°C and 445°C, lost organic matter corresponding to (11/8)R, (5/8)R′, (15/14)R″, (3/2)R, (3/2)R′ and (19/8)R″ respectively, yielding new intermediates of compositions Eu · (13/8)R, Eu · (19/8)R′, Eu · (27/14)R″, Gd · (3/2)R, Gd · (3/2)R and Gd · (15/8)R″, which on further increase in temperature changed to Eu_2O_3 or Gd_2O_3.

TABLE 2

Pyrolysis data on metal–plant-auxin chelates [a]

Stable phase and temp. range (°C)	Loss	Loss (%)		Eu_2O_3 (%)	
	(Temp. range)	Found	Calc.	Found	Calc.
Eu–IBA chelate					
$Eu\cdot R_3$ (up to 62°C)	–	–	–	–	–
$Eu\cdot(13/8)R$ (190–235°C)	$(11/8)R$ (62–190°C)	35.90	36.92	–	–
Eu_2O_3 (390°C onwards)	$(13/8)R$ (235–390°C)	75.21	76.87	24.79	23.13
Eu–IPA chelate					
$Eu\cdot R'_3$ (up to 100°C)	–	–	–	–	–
$Eu\cdot(19/8)R'$ (195–270°C)	$(5/8)R'$ (100–195°C)	17.59	16.55	–	–
Eu_2O_3 (535°C onwards)	$Eu\cdot(19/8)R'$ (270–535°C)	76.85	75.22	23.15	24.48
Eu–NAA chelate					
$[Eu\cdot R''_3\cdot 3H_2O]H_2O$ (up to 75°C)	–	–	–	–	–
$Eu\cdot R''_3\cdot 3H_2O$ (100–150°C)	H_2O (75–100°C)	2.78	2.26	–	–
$Eu\cdot R''_3$ (195–250°C)	$3H_2O$ (150–195°C)	11.11	11.25	–	–
$Eu\cdot(27/14)R''$ (350–400°C)	$(15/14)R''$ (250–350°C)	36.11	36.13	–	–
Eu_2O_3 (475°C onwards)	$(27/14)R''$ (400–475°C)	77.78	81.00	22.22	22.00
Gd–IBA chelate					
$Gd\cdot R_3\cdot(5/2)H_2O$ (up to 90°C)	–	–	–	–	–
$Gd\cdot R_3$ (125–165°C)	$(5/2)H_2O$ (90–125°C)	5.26	5.54	–	–
$Gd\cdot(3/2)R$ (320–365°C)	$(3/2)R$ (165–320°C)	43.60	43.00	–	–
Gd_2O_3 (615°C onwards)	$(3/2)R$ (365–615°C)	73.60	80.00	26.30	22.00
Gd–IPA chelate					
$Gd\cdot R'_3\cdot(3/4)H_2O$ (up to 70°C)	–	–	–	–	–
$Gd\cdot R'_3$ (105–150°C)	$(3/4)H_2O$ (70–105°C)	1.67	1.83	–	–
$Gd\cdot(3/2)R'$ (420–470°C)	$(3/2)R'$ (150–420°C)	40.00	40.20	–	–
Gd_2O_3 (650°C onwards)	$(3/2)R'$ (470–650°C)	76.67	78.71	23.33	24.54

TABLE 2 (continued)

Stable phase and temp. range (°C)	Loss (Temp. range)	Loss (%)		Eu_2O_3 (%)	
		Found	Calc.	Found	Calc.
Gd–NAA chelate					
$[Gd \cdot R''_3 \cdot 3H_2O](1/4)H_2O$ (up to 85°C)	–	–	–	–	–
$Gd \cdot R'' \cdot 3H_2O$ (115–135°C)	$(1/4)H_2O$ (85–115°C)	3.00	2.84	–	–
$Gd \cdot R''_3$ (200–240°C)	$3H_2O$ (135–200°C)	9.00	9.66	–	–
$Gd \cdot (15/8)R''$ (445–480°C)	$(19/8)R''$ (240–445°C)	65.00	65.63	–	–
Gd_2O_3 (600°C onwards)	$(15/8)R''$ (480–600°C)	77.00	77.13	23.00	22.87

[a] R, anion of IBA; R′, anion of IPA; R″, anion of NAA.

Table 1 contains the thermal data; the stability limits of the various forms of the chelates, together with the analytical data, are given in Table 2.

The overall solid state reaction, which resembles a reaction of the type A(s) → B(s) + C(g), the kinetics of which could be studied thermally by the Freeman and Carroll method, follows first-order kinetics which can be demonstrated, following the Dave and Chopra method (eqns. (1) and (2) [11] and the Coats and Redfern method [12] (see eqn. (3)):

$$k = \frac{(A/m_0)^{n-1}(\mathrm{d}x/\mathrm{d}t)}{(A-a)^n} \tag{1}$$

where A is the total area under the DTG curve, m_0 is the mole fraction of the reactant, a is the area at time t under the DTG curve, $\mathrm{d}x/\mathrm{d}t$ the deviation from base line of the DTG curve and n the order of the reaction. If $n = 1$, eqn. (1) reduces to

$$k = \frac{(\mathrm{d}x/\mathrm{d}t)}{(A-a)} \tag{2}$$

$$\log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \log\frac{AR}{aE}\left(1-\frac{2RT}{E}\right) + \frac{E}{213RT} \tag{3}$$

In eqn. (3), α is the fraction of the sample decomposed at time t, a the heating rate, A the pre-exponential factor, E the activation energy, R the gas constant and n the order of reaction.

Table 3 gives the kinetic data for the different solid state reactions; with low values of Z, the reactions could be said to be slow processes.

TABLE 3

Kinetic data on metal–plant-auxin chelates

Reaction [a]	n		E (kJ mol^{-1})		Z^* [d]
	DC [b]	CR [c]	DC	CR	DC
Eu – IBA chelate					
$Eu \cdot R_3 \rightarrow Eu \cdot (13/8)R + (11/8)R$	1	1	17	27	0.0398
$Eu \cdot (13/8)R \rightarrow Eu_2O_3 + dp$	1	1	30	120	0.0398
Eu – IPA chelate					
$Eu \cdot R'_3 \rightarrow Eu \cdot (19/8)R' + (5/8)R'$	1	1	23	50	0.7943
$Eu \cdot (19/8)R' \rightarrow Eu_2O_3 + dp$ [e]	1	1	23	48	0.0398
Eu – NAA chelate					
$[Eu \cdot R''_3 \cdot 3H_2O]H_2O \rightarrow Eu \cdot R''_3 \cdot 3H_2O + H_2O$	1	1	142	–	0.2512
$Eu \cdot R''_3 \cdot 3H_2O \rightarrow Eu \cdot R''_3 + 3H_2O$	1	1	104	108	0.3162
$Eu \cdot R''_3 \rightarrow Eu \cdot (27/14)R'' + (15/14)R''$	1	1	38	59	0.0794
$Eu \cdot (27/14)R'' \rightarrow Eu_2O_2 + dp$	1	1	24	174	0.1995
Gd – IBA chelate					
$Gd \cdot R_3 \cdot (5/2)H_2O \rightarrow Gd \cdot R_3 + (5/2)H_2O$	1	1	160	79	−0.2
$Gd \cdot R_3 \rightarrow Gd \cdot (3/2)R + (3/2)R$	1	1	75	46	0.3981
$Gd \cdot (3/2)R \rightarrow Gd_2O_3 + dp$	1	1	104	106	0.6309
Gd – IPA chelate					
$Gd \cdot R'_3 \cdot (3/4)H_2O \rightarrow Gd \cdot R' + (3/4)H_2O$	1	1	128	96	−1.6
$Gd \cdot R'_3 \rightarrow Gd \cdot (3/2)R' + (3/2)R'$	1	1	56	49	0.0501
$Gd \cdot (3/2)R' \rightarrow Gd_2O_3 + dp$	1	1	181	106	0.0630
Gd – NAA chelate					
$[Gd \cdot R''_3 \cdot 3H_2O](1/4)H_2O \rightarrow Gd \cdot R''_3 \cdot 3H_2O + (1/4)H_2O$	1	1	106	–	0.7943
$Gd \cdot R''_3 \cdot 3H_2O \rightarrow Gd \cdot R''_3 + 3H_2O$	1	1	34	46	0.6309
$Gd \cdot R''_3 \rightarrow Gd \cdot (5/8)R'' + (19/8)R''$	1	1	39	45	0.0630
$Gd \cdot (5/8)R'' \rightarrow Gd_2O_3 + dp$	1	1	80	160	0.0501

[a] R, anion of IBA, R′, anion of IPA and R″ = anion of NAA.

[b] DC, Dave and Chopra method.

[c] CR, Coats and Redfern method.

[d] Z^*, collision number per unit volume and unit time.

[e] dp, decomposition product.

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