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Thermal and spectral studies of some rare earth chelates of chlorojuglone antibacterials

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Abstract

The metal chelates of juglone, 3-chlorojuglone and 2,3-dichlorojuglone with trivalent lanthanum, cerium and praseodymium have been synthesised. The thermal, spectral and magnetic properties of these chelates were investigated to study the effect of substitution on the chelating ability of the ligand.

INTRODUCTION

Juglones (hydroxynaphthoquinones) are well known antibacterial agents [1]. It has been observed that the presence of a hydroxyl group at either the ortho or para position to one of the carbonyl groups and the chloro group in the quinonoid ring, favours their antibacterial character [2–4]. A literature survey has revealed that no detailed work has been reported on the rare earth chelates of juglones and their derivatives, except for the metal chelates of lawsone (2-hydroxy-1,4-naphthoquinone) [5] and plumbagin (2-methyl-5-hydroxy-1,4-naphthoquinone) [6–8]. It therefore seemed desirable to synthesise and study the thermal, spectral and magnetic properties of some trivalent rare earth chelates of juglone (5-hydroxy-1,4-naphthoquinone) (**I**), 3-chlorojuglone (**II**) and 2,3-dichlorojuglone (**III**) (see Scheme 1), and to compare the results to see the effect of substitution.

EXPERIMENTAL

Syntheses

All the chemicals used in the preparation of the ligands and metal chelates were A.R. grade. Juglone (5-hydroxy-1,4-naphthoquinone) was

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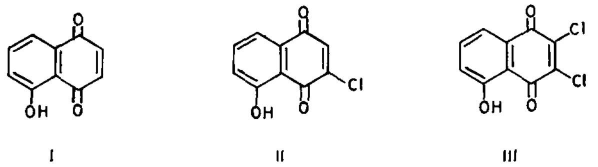

Scheme 1.

synthesised from 1,5-dihydroxynaphthalene (Fluka A.G.) according to procedures published by Bernthsen and Semper [9] and Jesaitisand and Krantz [10]. 3-Chlorojuglone was prepared by chlorination of juglone as reported by Thomson [11,12]. 2,3-Dichlorojuglone was prepared by chlorination of juglone in hot glacial acetic acid solution following the method suggested by Wheeler et al. [13]. The chelates of lanthanum(III), cerium(III) and praseodymium(III) with juglone, 3-chlorojuglone and 2,3-dichlorojuglone were synthesised by employing procedures similar to those for the rare earth chelates reported earlier [5].

Instrumentation

Elemental analyses of ligands and metal chelates were performed in the microanalytical laboratory of Poona University using a HOSLI-C,H- microanalysis instrument. Lanthanides were estimated by known methods [5,14].

A laboratory-built thermobalance, consisting of a chainomatic balance of 0.1 mg accuracy, a silica tube furnace pyrometer (Electroflow, England) of 10 ° C accuracy to 1000 ° C, a temperature controller (type 8 D-IP, automatic electric) and a chromel–alumel thermocouple in the vicinity of the sample, was employed in the experiment. A constant heating rate of 3 ° C min^{-1} and 50–70 mg sample weights of 200 mesh particle size were used for the thermal measurements. All measurements were carried out in static air atmosphere between room temperature and 600 ° C in a hard Corning-glass cup. The performance of the instrument was checked with reference to the TG of $CaC_2O_4 \cdot H_2O$ and $CuSO_4 \cdot 5H_2O$. The temperatures were corrected for thermocouple non-linearity and for procedural decomposition temperatures.

The IR spectra of the ligands and their metal chelates were recorded in nujol mulls on a Perkin–Elmer Model 337 spectrophotometer.

Magnetic susceptibilities were measured at room temperature by the Faraday method [15]. Diamagnetic corrections [16] for the ligands were applied and the values of the effective magnetic moments were calculated.

RESULTS AND DISCUSSION

All the metal chelates were of various shades of violet and red. The elemental analyses indicated the composition of these chelates to be

TABLE 1

Analytical, thermal and magnetic moment data on lanthanide chelates of juglones

Chelate [a]	Colour	Yield (%)	Magnetic moment μ_{eff} (BM)	Decomp. temp. (°C)	Elemental analyses (calc.)	
					C (%)	H (%)
Juglone chelates						
$[LaL_3(H_2O)_2]$	Deep violet	78	Diamagnetic	312	52.04 (51 88)	2.81 (2.74)
$[CeL_3]$	Brownish violet	67	2.69	280	54.17 (54.62)	2.30 (2.27)
$[PrL_3(H_2O)_2]$	Dark violet	92	3.74	312	51 65 (51.73)	2.63 (2.73)
3-Chlorojuglone chelates						
$[LaL_3(H_2O)_2]$	Reddish violet	85	Diamagnetic	318	45.47 (45.15)	2.12 (2.01)
$[CeL_3(H_2O)_2]$	Brownish red	83	2.68	285	44.81 (45.08)	2.07 (2.00)
$[PrL_3(H_2O)]$	Brownish red	70	3.66	314	46.21 (46.06)	1.81 (1.79)
2,3-Dichlorojuglone chelates						
$[LaL_3(H_2O)_2]$	Reddish violet	78	Diamagnetic	322	40.62 (39.95)	1.51 (1.45)
$[CeL_3(H_2O)]$	Violet–brown	75	2.53	285	40.12 (40.72)	1.31 (1.24)
$[PrL_3(H_2O)_2]$	Dark violet	72	3 27	318	40.08 (39.86)	1 49 (1.43)

[a] L = ligand, i.e juglone, 3-chlorojuglone or 2,3-dichlorojuglone

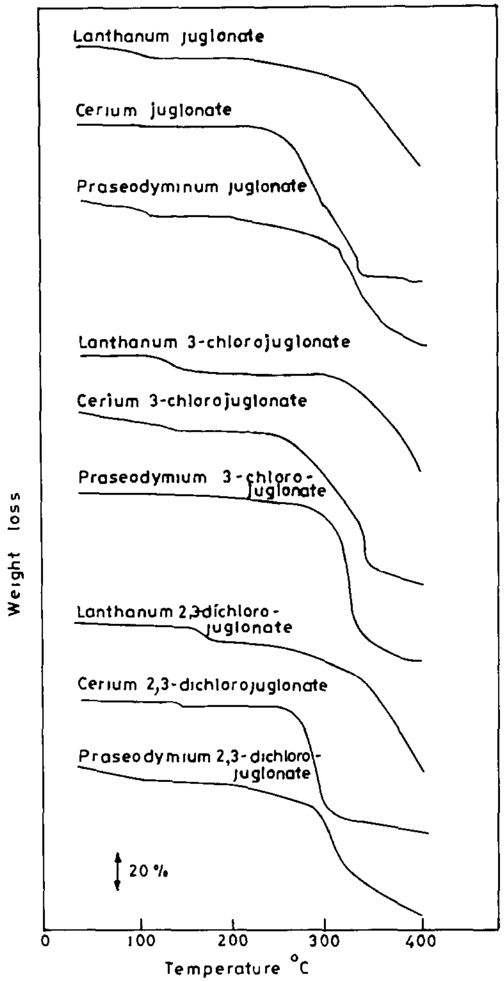

Fig. 1 Thermograms of rare earth chelates.

$[ML_3(H_2O)_n]$ (where M stands for trivalent lanthanide ion, L for ligand and $n = 0$, 1 or 2), see Table 1.

Thermal studies

The TG curves (Fig. 1) for all the metal chelates, except that of Ce(III) juglonate, showed weight losses within the range 70–250 °C, corresponding to the loss of coordinated water molecules. The weight losses above 250 °C are due to the decomposition of the chelates. The TG curves showed a continuous weight loss within the temperature range 250–700 °C, with formation of metal oxide as final product; cerium(III) juglonate was found to be anhydrous. The thermal as well as the elemental analyses of the remaining chelates indicated the presence of two coordinated water molecules in all the chelates except praseodymium(III) 3-chlorojuglonate and cerium(III) 2,3-dichlorojuglonate in which only one coordinated water molecule was observed. The weight-loss curve for the anhydrous compound (cerium(III) juglonate) shows a one-step decomposition while those for the other chelates display two steps. Since the thermal analysis was carried out in air atmosphere, the final decomposition product was the metal oxide. The thermal stability sequence for these chelates can be given as lanthanum chelates > praseodymium chlelates > cerium chelates. Comparison of the thermal stabilities shows that the chelates of 2,3-dichlorojuglone are thermally more stable than those of 3-chlorojuglone and juglone. This is consistant with our previous report [17].

Infrared studies

The IR spectra of all the chelates show a broad band of medium intensity in the region 3100–3500 cm^{-1}, indicative of (O–H) stretching mode due to presence of coordinated water, as was indicated by the thermogravimetric data. Cerium(III) juglonate does not show any absorption in the region 3100–3500 cm^{-1} which, together with thermal analysis data, indicates clearly the anhydrous nature of this chelate. The bands in the region 1650–1670 and 1620–1630 cm^{-1} are due to free carbonyl and chelated carbonyl, respectively. The (C–O) stretching frequency occurring in the ligands as a strong band in the region 1195–1225 cm^{-1}, is shifted towards higher frequencies in all juglonates and 2,3-dichlorojuglonates, but is shifted slightly towards a lower frequency region in the case of the 3-chlorojuglonates. The (C–Cl) stretching frequency appearing in the ligands at around 785 cm^{-1} does not show any notable shift towards higher frequencies after chelation. The (M–O) stretching frequencies are seen in the 530–595 cm^{-1} region for all the chelates.

Magnetic properties

The magnetic moments of these chelates, after applying the diamagnetic correction for the ligand, are close to the theoretical values calculated using the appropriate equations of Van Vleck and Frank [18] (Table 1). Slightly lower values of magnetic moments in the case of some of the chelates may be due to crystal field effects [19]. The lanthanum chelates of all three ligands were diamagnetic while the remaining chelates were paramagnetic. It was observed that the values of the magnetic moments of these chelates were lowered following halo-substitution on the ligand molecule.

CONCLUSIONS

The results obtained by TGA, IR and magnetic measurements indicate the possibility of a much higher coordination number in lanthanide chelates of juglone and chlorojuglones which is consistent with the reports by Moeller et al. [20]. In all the chelates, except cerium(III) juglonate, water acts as an additional ligand.

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