

ANTIPYRINE COMPLEXES OF RARE EARTH PERCHLORATES

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ABSTRACT

Rare earth perchlorate-antipyrine (ap) complexes of the formula $\text{Ln}(\text{ClO}_4)_3 \cdot 6 \text{ ap}$ have been prepared and characterised. Infrared and electronic spectra showed the co-ordination through carbonyl oxygen. Conductivity and molecular weight data indicated a co-ordination number of six for these complexes.

INTRODUCTION

ANTIPYRINE complexes of rare earth perchlorates and iodides have been used in the separation of these elements.¹⁻³ The fluorescence spectra of terbium hexa-antipyrine triiodide and perchlorate,^{4, 5} the electron spin resonance spectra of gadolinium hexa-antipyrine triiodide,⁶ and the X-ray studies of terbium hexa-antipyrine triiodide,⁷ have also been reported. However, none of these studies reveals whether the co-ordination is through oxygen of the carbonyl or through nitrogen. Consequently the antipyrine complexes of rare earth perchlorates have been prepared and their structure investigated from cryoscopic conductivity, infrared and electronic spectral studies.

EXPERIMENTAL

Materials.—Lanthanum oxides 99.9% purity were obtained from Lindsay Co., U.S.A. Cerium hydroxide was prepared from Ce (III) nitrate solution by aqueous ammonia. Antipyrine E. Merck was used. Acetonitrile, Dimethylformamide (DMF) and nitrobenzene were purified by standard methods.⁸

Preparation of hydrated perchlorates.—A slight excess of lanthanum oxide [Ce (III) hydroxide] was treated with hot, dilute perchloric acid solution. The resulting solution was filtered and evaporated to dryness on a water-bath. The product was used directly for the preparation of the complexes,

Preparation of the complexes.—To about 1 g. of the hydrated perchlorate in water was added 10 ml. of 2 M. antipyrine solution in water. After standing, the precipitate formed was filtered off, washed several times with water. The compounds were dried *in vacuo* over CaCl_2 .

The complexes are non-hygroscopic, insoluble in non-polar solvents and soluble in polar solvents. The colour of the complexes are closely similar in shade and intensity to the colours of the simple salts of the corresponding lanthanons. These complexes are very stable and decompose around 290°C .

Analyses.—The metal content of the complexes was estimated by the oxalate-oxide method. Perchlorate was converted into chloride by fusing the complex (~ 0.1 g.) with sodium nitrite at 500° in a nickel crucible⁹ and the chloride was estimated by Volhard's method. Antipyrine was estimated by Kolthoff's method.¹⁰ Analytical results agreed to the formulae $\text{Ln}(\text{ClO}_4)_3 \cdot 6\text{ap}$ (where $\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Gd}, \text{or Y}$) within 0.1%.

Infrared spectra.—The infrared spectra of all the complexes and antipyrine in KBr pellets were taken in Perkin Elmer Model 421 recording spectrophotometer. The spectra of antipyrine and cerium complex are reproduced in Fig. 1.

Electronic absorption spectra.—The electronic absorption spectra of the complexes and antipyrine dissolved in pure acetonitrile were taken with Hilger Uvispek spectrophotometer, model H 700, employing 1 cm. matched quartz cells.

Conductivity measurements.—The molar conductance of the complexes in conductivity water, DMF and nitrobenzene solutions were determined in Siemen's conductivity bridge using an immersion cell (LTA type) (cell constant 0.665) at 25°C . The concentrations of the solutions used are 0.001 M in DMF and water and 0.0005 M in nitrobenzene.

Cryoscopic measurements.—Molecular weights were determined with Backmann's freezing point method in water.

RESULTS AND DISCUSSION

The molar conductance of the complexes in DMF, nitrobenzene and water are 221 ± 4 , 80 ± 2 and 349 ± 7 $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$ respectively, and are in good agreement with those reported for 1:3 electrolytes in DMF ($200\text{--}260$ $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$),¹¹ in nitrobenzene (~ 80 $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$)¹² and in water (~ 360 $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$).¹³ The molecular weight of the complexes in water 154 ± 10 compared with the theoretical molecular weight

~ 1580 , shows complete dissociation. The molecular weight in nitrobenzene could not be determined on account of limited solubility.

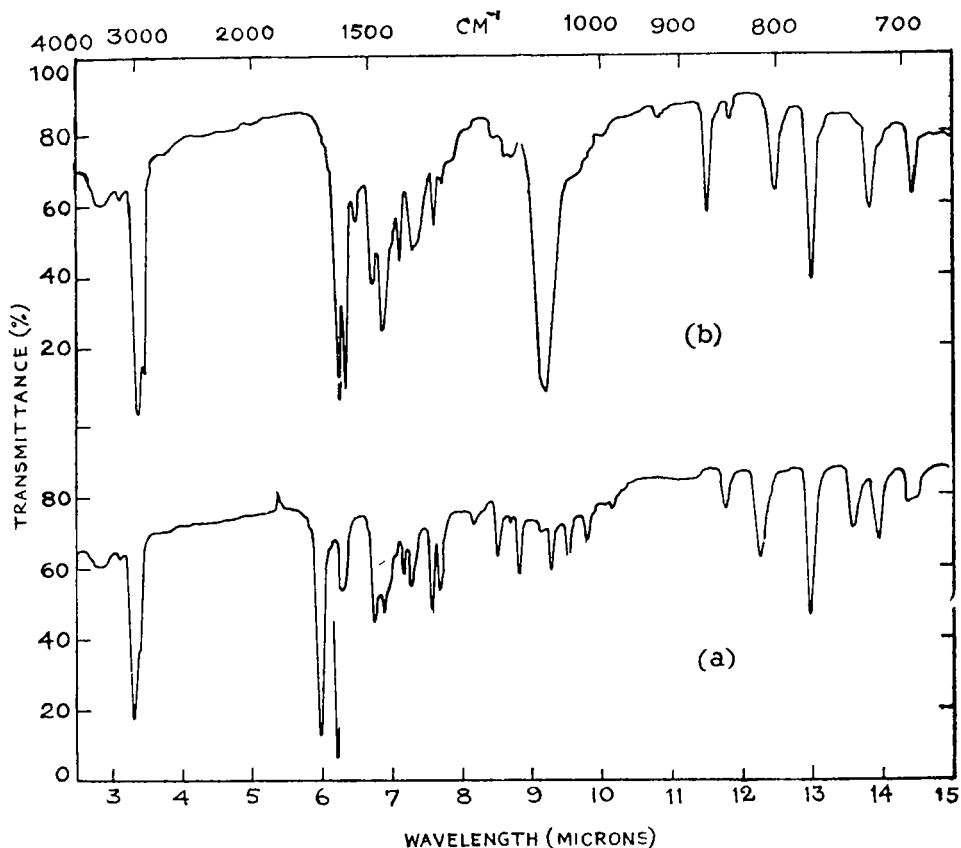
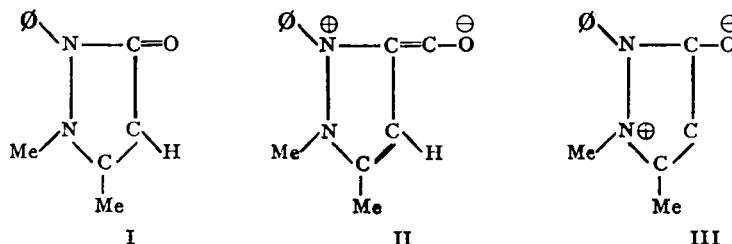


FIG. 1. Infrared spectra of (a) Antipyrine, (b) Cerium complex.

The infrared spectra of the various solid complexes are similar, showing thereby that these ions having same electronic charge and almost same size should have the same accepting capacity. Most of the bands are assigned by considering the monosubstituted benzene¹⁴ and the five membered pyrazolone ring systems.¹⁵ In general, in the complexes, the free antipyrine bands are greatly enhanced in intensity and the weak shoulders are resolved as medium intense bands.

The very strong band at 1658 cm^{-1} in the spectra of antipyrine is assigned to the carbonyl frequency.¹⁶ The infrared spectra of the complexes show a considerable shift ($\sim 58 \text{ cm}^{-1}$) of the carbonyl absorption to a lower frequency. The lowering of absorption frequency of the carbonyl group indicates a

decrease in the stretching force constant and hence co-ordination through oxygen. This is also expected from the resonance structures of antipyrine (I-III), which make the carbonyl oxygen a strong donor.^{17, 18}



Similar arguments have been advanced for co-ordination through oxygen in ligands containing X-O group, where X = C, N, P, As or S.¹⁹ Absence of bands around 1658 cm^{-1} indicate the absence of free antipyrine molecules.

The C—H out of plane deformation at 913 cm^{-1} in free antipyrine is shifted to 870 cm^{-1} in the complexes.

In all the complexes, the strong band around 1085 cm^{-1} is due to the asymmetric vibration of the perchlorate ion (ν_3). This indicates the non-co-ordination of the perchlorate group to the metal ion. The weak band around 925 cm^{-1} assigned to the ν_1 of the perchlorate ion, is present even in ionic perchlorates²⁰ as well as in rare earth perchlorates.²¹

It is expected that the shift in the carbonyl frequency in the antipyrine complexes is a measure of the strength of the metal-oxygen bond and therefore the stability of the complexes. The observed shifts of $\sim 58 \text{ cm}^{-1}$ in the present case are less than those observed for trivalent metal complexes²² ($\sim 65 \text{ cm}^{-1}$) as compared with free antipyrine, showing thereby that the rare earth complexes are less stable than trivalent transition metal complexes.

Antipyrine has three intense ultraviolet absorption bands in alcohol, 223 ($\log \epsilon = 3.91$), 247 ($\log \epsilon = 3.97$), and 273 $\text{m}\mu$ ($\log \epsilon = 3.98$) and the

absorption appears to arise from the systems¹⁷ $\text{Ph}-\overset{\curvearrowright}{\text{N}}-\overset{\curvearrowright}{\text{C}}=\overset{\curvearrowright}{\text{O}}$ and $\text{Me}-\overset{\curvearrowright}{\text{N}}-\overset{\curvearrowright}{\text{C}}\text{Me}=\overset{\curvearrowright}{\text{CH}}-\overset{\curvearrowright}{\text{C}}=\overset{\curvearrowright}{\text{O}}$. In acetonitrile, it gives two bands at 243 ($\log \epsilon$

$= 3.97$) and 278 $\text{m}\mu$ ($\log \epsilon = 3.95$). The 243 $\text{m}\mu$ band, in the case of complexes, undergoes a blue shift to 230 $\text{m}\mu$ ($\log \epsilon = 4.78$) while the 278 $\text{m}\mu$ ($\log \epsilon = 4.45$) remains unaltered. The lone pairs are better donors than

bound π -electrons, the oxygen lone pair in this case would take part in bonding. This will result in a substantial positive charge on the oxygen atom, since the antipyrine rare earth complexes are fairly strong complexes and should have substantial dative charge transfer contribution to the ground state. Such a positive charge on the oxygen could produce a sufficient stabilization of the nitrogen lone pair-carbonyl π -electrons to explain the observed blue shift.

These complexes are six co-ordinated and can be represented as $[\text{Ln}(\text{ap})_6] [\text{ClO}_4]_3$.

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