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M. Radhakrishnan [a] & P. K. Radhakrishnan [a]
[a] School of Chemical Sciences , Mahatma Gandhi University , Kottayam, 686 560, Kerala, India

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# SYNTHESIS, SPECTRAL AND THERMAL STUDIES ON BROMIDE COMPLEXES OF La(III), Nd(III), Gd(III), Ho(III) AND Er(III) WITH 4-N-(2'-HYDROXY-1'-NAPHTHYLIDENE)AMINOANTIPYRINE

**M. Radhakrishnan and P. K. Radhakrishnan***
**School of Chemical Sciences, Mahatma Gandhi University,**
**Kottayam-686 560, Kerala, India**

## ABSTRACT

Five complexes of the bromides of La, Nd, Gd, Ho and Er with 4-N-(2'-hydroxy-1'-naphthylidene)aminoantipyrine (HNAAP) of the general composition $[Ln(HNAAP)_2Br_2]Br$ where Ln=La, Nd, Gd, Ho and Er have been synthesised and characterised. Electronic and infrared spectra of the complexes indicate the weak covalent character of the metal-ligand bond and the neutral tridentate behaviour of the ligand. Thermogravimetric studies of the complexes in nitrogen atmosphere indicate that these complexes are stable upto about 240° C and undergo decomposition in two stages forming the respective metal bromides as the final products. The kinetic parameters for the first decomposition stage were calculated using the Coats-Redfern equation. The rate controlling process for the first stage obeys the Ginstling-Brounshtein model which represents three-dimensional

diffusion with spherical symmetry. There is no regular variation in the values of the kinetic parameters of the decomposition of the complexes as with other common physical constants.

## INTRODUCTION

As a continuation of our work on Schiff base complexes of lanthanides[1-8], we report here the spectral and thermal studies of a series of complexes of the bromides of La, Nd, Gd, Ho and Er with 4-N-(2'-hydroxy-1'-naphthylidene)aminoantipyrine. The Schiff base being an anitpyrine derivative possessing antibacterial and antiinflamatory properties, the complexes would be expected to be of physiological importance[9]. The structure of the Schiff base is given in Figure 1.

## RESULTS AND DISCUSSION

The reaction between HNAAP and metal bromides may be shown by the following representative equation,

$$2\text{HNAAP} + \text{MBr}_3 . 6\text{H}_2\text{O} \longrightarrow [\text{M(HNAAP)}_2\text{Br}_2]\text{Br} + 6\text{H}_2\text{O}$$

All the complexes are slightly hygroscopic, brown coloured solids which are soluble in DMF, acetone, methanol, ethanol, acetonitrile and nitrobenzene but insoluble in benzene and chloroform.

The elemental analysis data (Table I) suggest that the complexes have the general formula $\text{Ln(HNAAP)}_2\ \text{Br}_3$ where Ln=La, Nd, Gd, Ho and

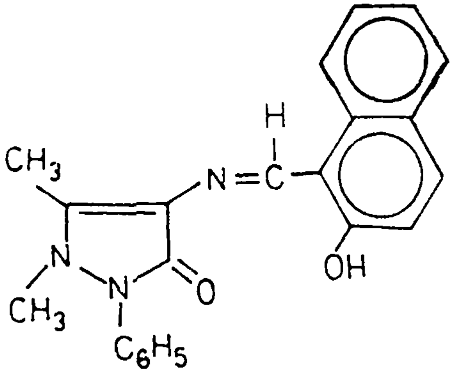

Fig. 1. 4-N-(2'-Hydroxy-1'-naphthylidene)aminoantipyrine

Er. The molar conductance values of the complexes in acetonitrile and nitrobenzene show 1:1 electrolytic behaviour[10].

## Infrared Spectra

The important IR frequencies of the free ligand and those of the complexes are given in Table II. The IR spectrum of the Schiff base HNAAP shows a broad, medium intensity band around 3440 $cm^{-1}$ attributed to the stretching vibration of the phenolic OH group. This band is shifted to about 3340 $cm^{-1}$ in the complexes. Also, the medium intensity band observed at 1305 $cm^{-1}$ for the ligand, which is due to the phenolic C-O antistretching vibration, is shifted about 1320$cm^{-1}$ in the complexes. These suggest the coordination of the phenolic oxygen to the metal ion[11-13]. The spectrum of HNAAP shows a very strong band at 1635 $cm^{-1}$ assigned to the carbonyl stretching vibration. This band is shifted to about 1615 $cm^{-1}$ in

## Table I

### Analytical[a] and Molar Conductance[b] Data of Lanthanide Bromide Complexes of HNAAP

| No | Complex | Formula weight | Yield, % | M.P.,°C | Analysis | | | | | Molar conductance | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Ln% | Br% | C % | H % | N % | Nitrobenzene | Acetonitrile |
| 1. | $[La(HNAAP)_2Br_2]Br$ | 1093.41 | 90 | 205 | 12.94<br>(12.70) | 21.60<br>(21.92) | 48.77<br>(48.28) | 3.52<br>(3.47) | 7.74<br>(7.68) | 32.4 | 137.7 |
| 2. | $[Nd(HNAAP)_2Br_2]Br$ | 1098.74 | 91 | 201 | 13.45<br>(13.12) | 22.00<br>(21.81) | 48.92<br>(48.05) | 3.49<br>(3.45) | 7.61<br>(7.64) | 30.4 | 132.4 |
| 3. | $[Gd(HNAAP)_2Br_2]Br$ | 1111.75 | 91 | 209 | 14.05<br>(14.14) | 21.96<br>(21.56) | 48.06<br>(47.49) | 3.38<br>(3.41) | 7.65<br>(7.55) | 32.4 | 129.5 |
| 4. | $[Ho(HNAAP)_2Br_2]Br$ | 1119.43 | 90 | 202 | 14.61<br>(14.73) | 21.27<br>(21.41) | 48.10<br>(47.16) | 3.45<br>(3.39) | 7.56<br>(7.50) | 29.9 | 125.4 |
| 5. | $[Er(HNAAP)_2Br_2]Br$ | 1121.76 | 92 | 203 | 14.97<br>(14.91) | 21.78<br>(21.37) | 47.91<br>(47.06) | 3.44<br>(3.38) | 7.60<br>(7.48) | 28.3 | 130.5 |

[a] Calculated values in parenthesis

[b] $10^{-3}$ M solution used; $ohm^{-1}\ cm^2\ mole^{-1}$

[c] Empirical formulae; $C_{44}H_{38}N_6O_4Br_3M$.

Table II

Important IR Absorptions ($cm^{-1}$) of HNAAP and Lanthanide Bromide Complex of HNAAP

| Sl. No | Complex | ν(O-H) | ν(C=O) | ν(C=N) | ν(C-O) | ν(M-Br) |
|---|---|---|---|---|---|---|
| 1. | HNAAP | 3440 w | 1635 s | 1585 s | 1305 w | - |
| 2. | $[La(HNAAP)_2Br_2]Br$ | 3340 s | 1615 s | 1570 w | 1320 s | 293 s |
| 3. | $[Nd(HNAAP)_2Br_2]Br$ | 3340 s | 1615 s | 1570 w | 1320 s | 293 s |
| 4. | $[Gd(HNAAP)_2Br_2]Br$ | 3340 s | 1615 s | 1570 w | 1320 s | 293 s |
| 5. | $[Ho(HNAAP)_2Br_2]Br$ | 3340 s | 1615 s | 1570 w | 1320 s | 293 s |
| 6. | $[Er(HNAAP)_2Br_2]Br$ | 3340 s | 1615 s | 1570 w | 1320 s | 293 s |

s= Strong ; w = Weak

the complexes showing that the carbonyl oxygen is coordinated to the metal ion[1]. A very strong band at 1585 $cm^{-1}$ attributed to the hydrogen bonded C=N stretching vibration is shifted to about 1570 $cm^{-1}$ indicating the coordination of the azomethine nitrogen[2]. The complexes show a strong band at 293 $cm^{-1}$ which is not present in the spectrum of the ligand. This band may be assigned to the metal-bromide stretching vibration[14]. These results are in agreement with the conductance data that show that two of the bromide ions are coordinated to the metal ion.

## Electronic Spectra

The electronic spectrum of the ligand in acetonitrile shows absorption maxima at 25.25 kK which may be assigned to n → π* transitions. The above band is slightly red-shifted to about 25.83 kK in the complexes. The spectra of the complexes of Nd, Ho and Er show some f-f transitions, the tentative assignments of which are given in Table III. The Sinha covalency parameter ($\delta$), the inter-electronic repulsion parameter '$\beta$', the bonding parameter ($b^{1/2}$) and the covalency angular overlap parameter ($\eta$) have been calculated from the electronic spectra. The $\beta$ values are found to be less than unity and the $b^{1/2}$ and $\eta$ values are positive suggesting covalency in the metal-ligand bond. The $\delta$ values being less than 1.5 indicate a weak covalent character of the metal-ligand bond in the present complexes[15, 16].

## Thermal Behaviour

Thermogravimetric analysis of the five complexes of La, Nd, Gd, Ho and Er was carried out in nitrogen atmosphere. The thermograms

**Table III**
**Electronic Spectral Data of the Nd and Er Bromide Complexes of HNAAP**

| Complex | Band (kK) | Tentative assignment | Covalency parameters calculated |
|---|---|---|---|
| Nd | 12.44 | $^4I_{9/2} \longrightarrow {}^4F_{7/2}$ | $\beta = 0.9973$<br>$\delta = 0.2657$<br>$b^{1/2} = 0.0257$<br>$\eta = 0.0013$ |
| Ho | 23.25<br>18.36 | $^5I_8 \longrightarrow {}^5G_5$<br>$^5I_8 \longrightarrow {}^5F_4$ | $\beta = 0.9973$<br>$\delta = 0.0262$<br>$b^{1/2} = 0.0267$<br>$\eta = 0.0013$ |
| Er | 19.04 | $^4I_{15/2} \longrightarrow {}^4S_{3/2}$ | $\beta = 0.9927$<br>$\delta = 0.7353$<br>$b_{1/2} = 0.0427$<br>$\eta = 0.0036$ |

are presented in Figures 3 to 7. The TG curves show that the complexes are stable upto about 240° C and then undergo decomposition in two stages. The first decomposition stage occurs in the region 240° C - 480° C corresponding to a DTG peak at about 325° C. The second stage decomposition starts at about 480° C. This stage cannot be well characterised because the mass loss corresponds to less than one ligand molecule. Also, anhydrous metal bromides partially formed start to sublime at about 780° C. Hence a steady mass loss is observed.

The correlation coefficients 'r' were calculated using the nine mechanism-based equations for the first stage decomposition of the five complexes. The form of g ($\alpha$) which gave the highest value for the correlation coefficient was chosen as the one representing the mechanism of that particular decomposition reaction[17]. In the present work, the best fit for the correlation coefficient was obtained with the equation shown below.

$$g(\alpha) = (1\text{-}2/3\alpha) - (1\text{-}\alpha)^{2/3}.$$

Thus, the mechanism followed by the five bromide complexes is a three-dimensional diffusion with spherical symmetry[18]. This represents the Ginstling-Brounshtein model[18]. All five complexes show similar thermal behaviour probably because of their similar structure. This is evident from their similar values of activation energy.

The kinetic parameters, especially E and S, are helpful in assigning the strength of the bonding in these complexes. The activation energy at the major decomposition stage, <u>viz</u>., the first stage is in the range 115-150 J $mol^{-1}$. This low value indicates that the ligands are loosely bound to the central lanthanide ion. The values of E do not show a definite trend. The E values of La and Gd are more or less the same. This may be attributed to their spherical electronic configuration (4 $f^{\circ}$ and $f^{7}$, respectively). The entropy of activation does not show a definite trend. However, the values are negative for the five complexes. The negative values indicate that the activated complex has a more ordered structure than the reactants and that the reactions are slower than normal[19-23]. The values of E, A and S are given in Table IV. The proposed structure for the complexes is shown in Fig. 2.

## EXPERIMENTAL

### Materials

The bromides of La, Nd, Gd, Ho, Er were prepared by dissolving the respective oxides (99.99% pure) in 48% hydrobromic acid and crystallising out the salt by evaporating the solution on a steam bath. The ligand was prepared from 4-aminoantipyrine and 2-hydroxy naphthaldehyde by the method reported earlier[24].

### Preparation of the Complexes

Three mmol (1.072 g) of the ligand was dissolved in the minimum amount of acetone and refluxed on a water bath. One mmol of the metal salt dissolved in about 10 mL methanol was added drop by drop to the ligand solution kept under reflux. The resulting solution was refluxed for about 3 hours, cooled to room temperature, filtered and concentrated by evaporation by placing over a water bath. The brown viscous mass obtained was washed repeatedly with hot benzene to remove the excess ligand. Finally the complex was dried *in vacuo* over $P_2O_5$.

The complexes were analysed for the metal and bromide[25] content by the conventional methods. Conductivities of the complexes in acetonitrile and nitrobenzene ($10^{-3}$ M solutions) were measured at room

### Table IV
### Kinetic Parameters for the Thermal Decomposition of Lanthanide Bromide Complexes of HNAAP

| No. | Complex | Stage | E(Jmol$^{-1}$) | A(S$^{-1}$) | S(J mol$^{-1}$) |
|---|---|---|---|---|---|
| 1. | $[La(HNAAP)_2Br_2]Br$ | 1 | 146.5 | 932.7 | -193.8 |
| 2. | $[Nd(HNAAP)_2Br_2]Br$ | 1 | 115.0 | 37.28 | -220.4 |
| 3. | $[Gd(HNAAP)_2Br_2]Br$ | 1 | 144.2 | 714.2 | -196.1 |
| 4. | $[Ho(HNAAP)_2Br_2]Br$ | 1 | 126.9 | 57.4 | -217.8 |
| 5. | $[Er(HNAAP)_2Br_2]Br$ | 1 | 136.0 | 257.2 | -205.1 |

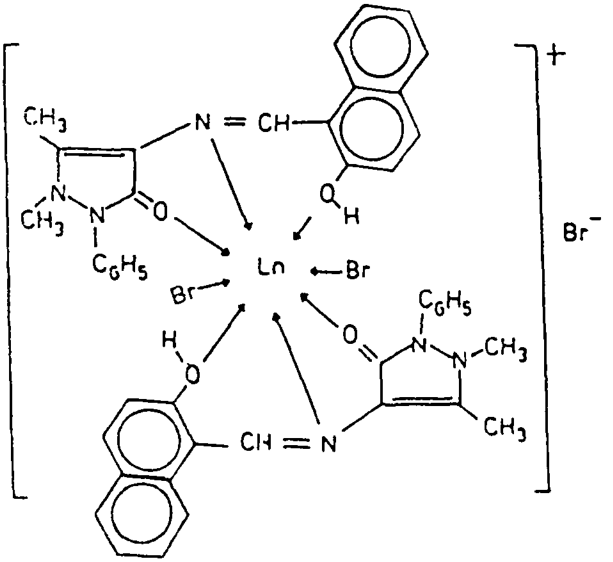

Fig. 2. The Tentative Structure of the Complexes

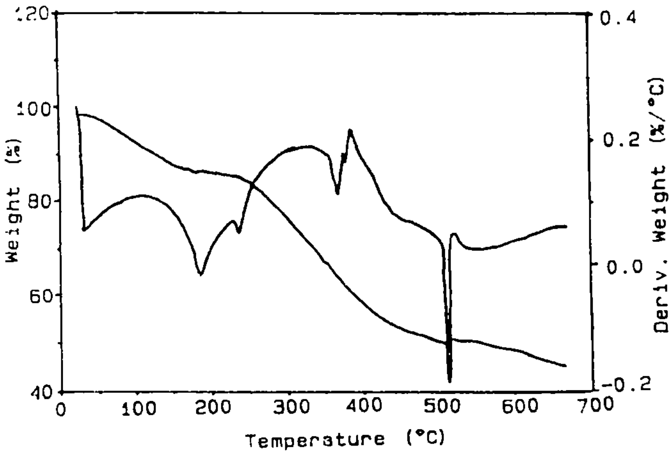

Fig. 3. TG Diagram of $[La(HNAAP)_2Br_2]Br$

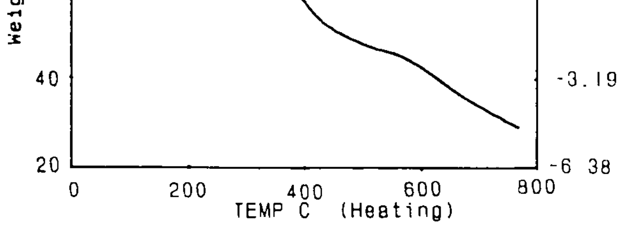

Fig. 4. TG Diagram of $[Nd(HNAAP)_2Br_2]Br$

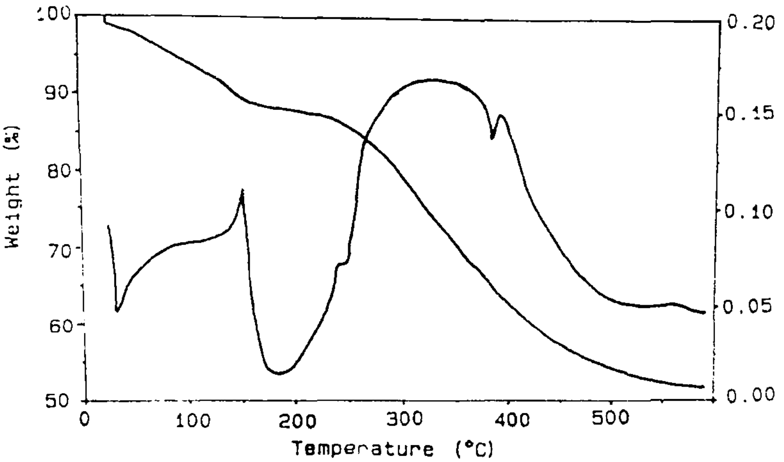

Fig. 5.TG Diagram of [Gd(HNAAP)$_2$Br$_2$]Br

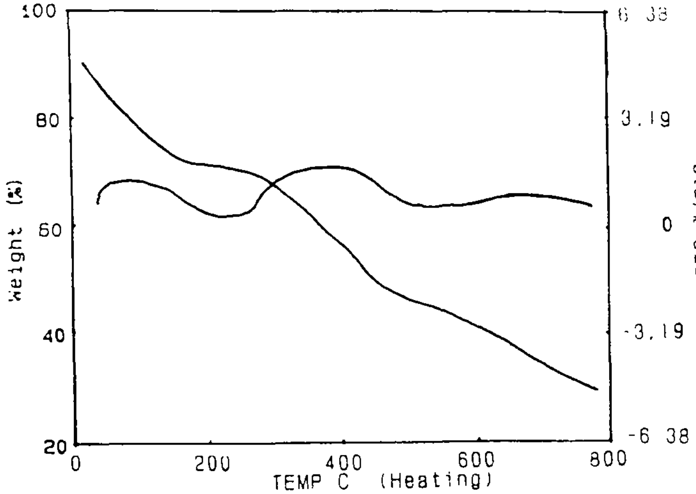

Fig. 6. TG Diagram of [Ho(HNAAP)$_2$Br$_2$]Br

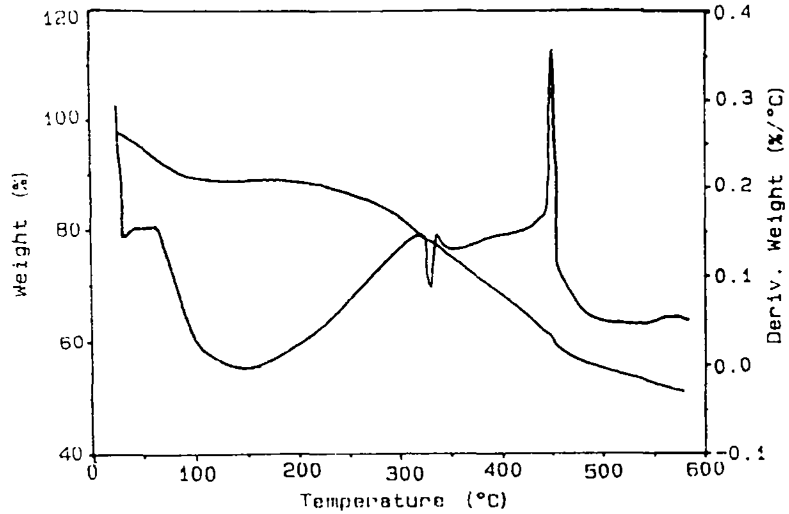

Fig. 7. TG Diagram of $[Er(HNAAP)_2Br_2]Br$

temperature using a Toshniwal conductivity bridge with a dip-type cell and platinum electrode (cell constant = 0.9588 cm$^{-1}$). The far-infrared spectra in the range 50-500 cm$^{-1}$ were recorded on a Brucker IFS 66 V FT-IR spectrometer in the range 4000-400 cm$^{-1}$ on a Shimadzu - IR-470 spectrophotometer. Electronic spectra of the ligand and the complexes in acetonitrile were recorded in the range 200-1100 nm on a Shimadzu -UV-160- A spectrophotometer. Thermogravimetric analyses of the La, Gd and Er complexes were carried out in nitrogen atmosphere on a Shimadzu-DT-40 thermal analyzer and that of Nd and Ho were carried out on a Seiko Instruments Inc. analyzer.

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## REFERENCES

1. P. K. Radhakrishnan, P. Indrasenan and C. G. R. Nair, Polyhdron, 3, 67 (1984).
2. P. K. Radhakrishnan, J. Ind. Chem. Soc., 61, 838 (1984).
3. P. K. Radhakrishnan, Inorg. Chim. Acta, 110, 211 (1985).
4. P. K. Radhakrishnan, Polyhedron, 5, 995 (1986).
5. M. K. M. Nair and P. K. Radhakrishnan, Polyhedron, 12, 1227 (1993).
6. M. K. M. Nair and P. K. Radhakrishnan, Proc. Indian Acad.Sci. (Chem.Sci.), 107 , 19 (1995).
7. M. K. M. Nair and P. K. Radhakrishnan, Synth. React. Inorg. Met.-Org. Chem., 25, 1077 (1995).
8. M. Joseph, M. K. M. Nair and P. K. Radhakrishnan, Synth. React. Inorg. Met.-Org. Chem., 25, 1331 (1995).
9. L. Singh, G. Mohan, R. K. Parashai, S. P. Tripathi and R. C. Sharma, Curr. Sci., 55, 846 (1986).
10. W. J. Geary, Coord. Chem. Rev., 7, 81 (1971).
11. S. Gopinathan, M. P. Degaonka, A. M. Hundekar and C. Gopinathan, Ind. J. Chem, 32A, 262 (1993).

12. J. E. Kovacic, Spectrochim. Acta, 23A, 183 (1967).

13. C. S. Marvel, S. A. Asepey and A. Dudley, J. Am. Chem. Soc., 78, 4904 (1956).

14. K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds", Wiley, New York (1986).

15. S. P. Sinha, Spectrochim. Acta, 22, 57 (1966).

16. D. G. Karakker, Inorg. Chem., 10, 1863 (1967).

17. T. Gangadevi, M. Subba Rao and T. R. Narayanankutty, Indian J. Chem., 19A, 303 (1980).

18. V. Satava, Thermochim. Acta, 2, 423 (1971).

19. T. Moeller, "International Reviews of Science, Inorg. Chem. Series", 1, VII, K. W. Bagnal (Ed), 2, 282 (1972).

20. A. A. Frost and R. G. Pearson, "Kinetics and Mechanism", Wiley, New York (1961).

21. S. Mathew, C. G. R. Nair and K. N. Ninan, Thermochim. Acta, 144, 33 (1989).

22. K. K. Aravindakshan and K. Muraleedharan, Thermochim. Acta, 155, 247 (1989).

23. T. Gangadevi, K. Muraleedharan and M. P. Kannan, Thermochim. Acta, 191, 105 (1991).

24. T. Radhakrishnan, P. T. Joseph and C. P. Prabhakaran, J. Inorg. Nucl. Chem., 38, 2217 (1976).

25. M. R. G. Nair, M. J. Kurian and C. P. Prabhakaran, Talenta, 28, 395 (1981).

26. A. I. Vogal, "A Text Book of Quantitative Inorganic Analysis", ELBS, London (1961).

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Referee I: G. R. Choppin
Referee II: K. Moedritzer