

## Synthesis and physicochemical studies of the chloride and bromide complexes of yttrium and lanthanides with 4-N-(4'-antipyryl-methylidene)aminoantipyrine

M K MURALEEDHARAN NAIR and  
P K RADHAKRISHNAN\*

School of Chemical Sciences, Mahatma Gandhi University, Kottayam 686 560, India

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**Abstract.** Twenty new complexes of chlorides and bromides of yttrium and lanthanides with the Schiff base 4-N-(4'-antipyrylmethylidene)aminoantipyrine (AA) have been prepared and characterised. They have the general formula,  $[\text{Ln}(\text{AA})_2\text{Cl}_3]$  and  $[\text{Ln}(\text{AA})_2\text{Br}_2]\text{Br}$  where Ln = Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho and Er. Molar conductance studies indicate slight dissociation for the chloride complexes and 1:1 electrolytic behaviour for the bromide complexes. The magnetic moments of all the complexes agree well with Van Vleck values. The infrared spectra reveal that AA functions as a terdentate ligand in all these complexes coordinating through the oxygens of both the carbonyl groups and the azomethine nitrogen. Electronic spectra of Nd, Ho and Er for the chloride complexes and that of Pr, Nd, Ho and Er for the bromide complexes show weak covalency in the metal–ligand bond.

**Keywords.** Rare earth metal–Schiff base complexes; aminoantipyrine.

### 1. Introduction

In earlier communications, we have reported the synthesis and characterisation of the complexes of the Schiff base 4-N-(4'-antipyrylmethylidene)aminoantipyrine (AA) (figure 1) with the nitrates (Muraleedharan Nair and Radhakrishnan 1993) and perchlorates (Muraleedharan Nair and Radhakrishnan 1995) of yttrium and lanthanides. In the present communication, we report our studies of the preparation and characterisation of the complexes of AA with the chlorides and bromides of yttrium and lanthanides.

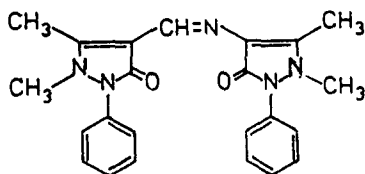
### 2. Experimental

#### 2.1 Reagents

The chlorides/bromides of Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho and Er were prepared by dissolving the respective oxides (99.99% pure) in 60% hydrochloric/hydrobromic acid and crystallising out the salt by evaporating the solution on a steam bath. The Schiff base AA was prepared by condensing a 1:1 mixture of 4-aminoantipyrine and 4-antipyrine carboxaldehyde in ethanolic medium.

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\*For correspondence



**Figure 1.** Structure of the Schiff base, 4-N-(4'-antipyrylmethylidene)aminoantipyrine (AA).

## 2.2 Preparation of the complexes

The chloride complexes were prepared by mixing ethanolic solutions of the metal chloride (1 mmol) in 15 ml and the ligand (2.5 mmol) in 50 ml and refluxing the mixture on a water-bath for about 5 h. The resulting solution was cooled, filtered and concentrated. The yellow solid obtained was washed several times with hot chloroform to remove the excess ligand. Finally the complexes were recrystallised from methanol and dried under vacuum over phosphorus(V)oxide. The bromide complexes were prepared by the same method as the chloride complexes except that the reaction time was about 3 h instead of 5 h.

## 2.3 Physical methods and analyses

All these complexes were analysed for the metal content by the method (Nair *et al* 1981) of 'peaceful pyrolysis' and for the chloride and bromide contents by Volhard's method (Vogel 1978). Conductivities of the complexes in nitrobenzene, DMF and methanol ( $10^{-3}$  M solution) were measured at room temperature using a Toshniwal conductivity bridge with a dip-type cell and a platinum electrode (cell constant =  $0.9588 \text{ cm}^{-1}$ ). The infrared spectra of the ligand and the complexes were recorded in the range  $4000\text{--}400 \text{ cm}^{-1}$  on a Shimadzu-IR-470 spectrophotometer and in the range  $600\text{--}200 \text{ cm}^{-1}$  on a Perkin-Elmer 983 IR spectrophotometer. Electronic spectra of the ligand and the complexes in the solid state (by grinding the dry solid with nujol and pasting it on a filter paper) were recorded in the range  $200\text{--}1100 \text{ nm}$  on a Shimadzu-UV-160A spectrophotometer. Magnetic moments were measured at room temperature using a Gouy balance with mercury(II)tetra-thiocyanatocobaltate(II) as calibrant. Proton NMR spectral studies were done on an NMR-GSX-400 instrument using  $\text{DMSO-}d_6$  as solvent.

## 3. Results and discussion

Analytical data (table 1) of the present complexes indicate that these complexes have the general formula  $\text{Ln}(\text{AA})_2\text{Cl}_3$  and  $\text{Ln}(\text{AA})_2\text{Br}_3$ , where  $\text{Ln} = \text{Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho}$  and  $\text{Er}$ . All these complexes are pale-yellow solids, which are soluble in acetonitrile, DMF, ethanol, methanol and nitrobenzene and insoluble in acetone, benzene, carbon tetrachloride, chloroform and ethyl acetate.

### 3.1 Electrical conductance

Molar conductance values (table 1) in nitrobenzene and acetonitrile suggest slight dissociation for chloride complexes and 1:1 electrolytic behaviour for bromide complexes (Geary 1971). Slightly higher values of conductivity were observed in DMF and methanol

**Table 1.** Analytical<sup>a</sup>, molar conductance<sup>b</sup> and magnetic moment data of rare earth chloride/bromide complexes of AA.

Compound	Ln (%)	Cl/Br (%)	Molar conductance				$\mu_{\text{eff}}$ (BM)
			C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	CH <sub>3</sub> CN	MeOH	DMF	
<i>Chloride complexes</i>							
[Y(AA) <sub>2</sub> Cl <sub>3</sub> ]	8.91 (8.92)	10.69 (10.66)	11.99	56.47	189.1	98.09	—
[La(AA) <sub>2</sub> Cl <sub>3</sub> ]	13.37 (13.26)	10.03 (10.16)	12.70	58.91	198.8	129.05	—
[Pr(AA) <sub>2</sub> Cl <sub>3</sub> ]	13.33 (13.43)	10.11 (10.14)	10.11	51.23	187.6	118.11	3.55
[Nd(AA) <sub>2</sub> Cl <sub>3</sub> ]	13.71 (13.70)	10.13 (10.10)	10.79	47.78	181.2	120.90	3.61
[Sm(AA) <sub>2</sub> Cl <sub>3</sub> ]	14.26 (14.21)	10.13 (10.05)	9.63	49.27	196.2	122.20	1.84
[Eu(AA) <sub>2</sub> Cl <sub>3</sub> ]	14.22 (14.33)	10.02 (10.03)	12.45	56.21	187.1	117.81	3.39
[Gd(AA) <sub>2</sub> Cl <sub>3</sub> ]	14.69 (14.76)	9.90 (9.98)	6.27	51.33	172.7	99.71	8.10
[Dy(AA) <sub>2</sub> Cl <sub>3</sub> ]	15.27 (15.18)	9.78 (9.93)	11.39	52.25	191.1	105.69	10.76
[Ho(AA) <sub>2</sub> Cl <sub>3</sub> ]	15.28 (15.37)	9.88 (9.91)	5.27	48.62	189.9	111.72	10.62
[Er(AA) <sub>2</sub> Cl <sub>3</sub> ]	15.48 (15.55)	9.92 (9.89)	6.71	49.79	195.1	119.17	9.55
<i>Bromide complexes</i>							
[Y(AA) <sub>2</sub> Br <sub>2</sub> ]Br	07.67 (07.86)	21.12 (21.20)	25.50	—	149.7	98.5	—
[La(AA) <sub>2</sub> Br <sub>2</sub> ]Br	11.75 (11.77)	20.47 (20.30)	28.81	—	151.7	113.2	—
[Pr(AA) <sub>2</sub> Br <sub>2</sub> ]Br	11.99 (11.92)	20.16 (20.29)	31.27	—	148.5	108.2	3.54
[Nd(AA) <sub>2</sub> Br <sub>2</sub> ]Br	12.11 (12.16)	20.24 (20.21)	24.75	—	161.7	120.7	3.69
[Sm(AA) <sub>2</sub> Br <sub>2</sub> ]Br	12.62 (12.61)	20.24 (20.11)	26.22	—	142.7	105.9	1.84
[Eu(AA) <sub>2</sub> Br <sub>2</sub> ]Br	12.78 (12.73)	20.20 (20.08)	31.71	—	149.5	107.8	3.44
[Gd(AA) <sub>2</sub> Br <sub>2</sub> ]Br	13.07 (13.12)	19.90 (19.99)	26.35	—	135.5	111.1	8.32
[Dy(AA) <sub>2</sub> Br <sub>2</sub> ]Br	13.50 (13.49)	19.93 (19.91)	27.19	—	140.9	99.8	10.37
[Ho(AA) <sub>2</sub> Br <sub>2</sub> ]Br	13.56 (13.67)	19.80 (19.87)	31.75	—	146.7	103.2	10.52
[Er(AA) <sub>2</sub> Br <sub>2</sub> ]Br	13.79 (13.84)	19.76 (19.83)	29.15	—	151.9	117.5	9.69

<sup>a</sup>Calculated values in parenthesis; <sup>b</sup>10<sup>-3</sup> M solutions used, ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>

which may be due to the partial displacement of coordinated chloride/bromide ion by the solvent molecule (Geary 1971). Thus, the chloride and bromide complexes may be formulated as  $[\text{Ln}(\text{AA})_2\text{Cl}_3]$  and  $[\text{Ln}(\text{AA})_2\text{Br}_2]\text{Br}$  respectively, where Ln = Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho and Er.

### 3.2 Infrared spectra

Infrared spectral data of the ligand show strong bands at 1658 and 1596  $\text{cm}^{-1}$  due to  $\nu(\text{C}=\text{O})$  and  $\nu(\text{C}=\text{N})$  stretching vibrations respectively. In the spectra of these complexes the corresponding bands are shifted to about 1625 and 1586  $\text{cm}^{-1}$  respectively, suggesting the coordination of both the carbonyl oxygens and the azomethine nitrogen (Radhakrishnan 1986). The  $\nu(\text{M}-\text{O})$  and  $\nu(\text{M}-\text{N})$  stretching vibrations are observed at about 540 and 470  $\text{cm}^{-1}$  respectively in the chloride complexes and 550 and 470  $\text{cm}^{-1}$  respectively in the bromide complexes (Agarwal and Tandon 1979). The Ln-Cl and Ln-Br stretching vibrations are observed in the regions 280–270 and 230–220  $\text{cm}^{-1}$  respectively which are not present in the spectrum of the ligand (Nakamoto 1986). This result is in conformity with the conductivity data and the inference that all the chloride ions and two of the bromide ions are coordinated to the metal ion in these complexes.

### 3.3 Proton NMR spectra

The proton NMR spectrum of the Schiff base shows the azomethine proton resonance at 8.35 $\delta$ . This band is red-shifted to 8.42 $\delta$ , 8.45 $\delta$ , 8.5 $\delta$  and 8.5 $\delta$  in complexes of yttrium chloride, yttrium bromide, lanthanum chloride and lanthanum bromide respectively. These results suggest the coordination of the azomethine nitrogen (Jagannathan and Soundararajan 1981) in the present complexes.

### 3.4 Electronic spectra

The electronic spectrum of the ligand in acetonitrile and in the solid state has absorption maxima at 28.74 and 40.49 kK which may be attributed to the  $n \rightarrow \pi^*$  and

**Table 2a.** Electronic spectral data of Nd, Ho and Er chloride complexes of AA.

Complex	Band (kK)	Tentative assignments	Covalency parameters calculated
Nd	17.159	$^4I_{9/2} \rightarrow ^4G_{5/2}, ^2G_{7/2}$	$\beta = 0.9939$
	13.423	$^4I_{9/2} \rightarrow ^4F_{7/2}$	$b^{1/2} = 0.0391$
	12.520	$^4I_{9/2} \rightarrow ^4G_{5/2}$	$\delta = 0.6137$ $\eta = 0.0032$
Ho	22.19	$^5I_8 \rightarrow ^5G_5$	$\beta = 0.9979$
	18.58	$^5I_8 \rightarrow ^5S_2, ^5G_4$	$b^{1/2} = 0.0229$
	15.52	$^5I_8 \rightarrow ^5F_5$	$\delta = 0.2105$ $\eta = 0.0011$
Er	19.21	$^4I_{15/2} \rightarrow ^2H_{11/2}$	$\beta = 0.9973$
	18.43	$^4I_{15/2} \rightarrow ^5S_{3/2}$	$b^{1/2} = 0.0259$
	15.29	$^4I_{15/2} \rightarrow ^4F_{9/2}$	$\delta = 0.2707$ $\eta = 0.0013$

**Table 2b.** Electronic spectral data of Pr, Nd, Ho and Er bromide complexes of AA.

Complex	Band (kK)	Tentative assignments	Covalency parameters calculated
Pr	16.88	${}^3H_4 \rightarrow {}^1D_2$	$\beta = 0.9970$
	20.64	${}^3H_4 \rightarrow {}^3P_0$	$\delta = 0.3009$
	21.25	${}^3H_4 \rightarrow {}^3P_1$	$b^{1/2} = 0.0274$
	22.42	${}^3H_4 \rightarrow {}^3P_2$	$\eta = 0.0013$
Nd	11.47	${}^4I_{9/2} \rightarrow {}^4F_{3/2}$	$\beta = 0.9967$ $\delta = 0.3311$ $b^{1/2} = 0.0287$ $\eta = 0.0017$
	12.49	${}^4I_{9/2} \rightarrow {}^4F_{5/2}$	
	13.44	${}^4I_{9/2} \rightarrow {}^4F_{7/2}$	
	14.64	${}^4I_{9/2} \rightarrow {}^4F_{9/2}$	
	17.23	${}^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$	
	19.10	${}^4I_{9/2} \rightarrow {}^4G_{7/2}$	
	19.53	${}^4I_{9/2} \rightarrow {}^2G_{9/2}$	
Ho	15.52	${}^5I_8 \rightarrow {}^5F_5$	$\beta = 0.9970$
	18.55	${}^5I_8 \rightarrow {}^5S_2, {}^5S_4$	$\delta = 0.3009$
	22.17	${}^5I_8 \rightarrow {}^5G_5$	$b^{1/2} = 0.0274$ $\eta = 0.0013$
Er	15.33	${}^4I_{15/2} \rightarrow {}^2F_{9/2}$	$\beta = 0.9980$
	18.45	${}^4I_{15/2} \rightarrow {}^5S_{3/2}$	$\delta = 0.2004$
	19.18	${}^4I_{15/2} \rightarrow {}^2H_{11/2}$	$b^{1/2} = 0.0224$ $\eta = 0.0013$

$\pi \rightarrow \pi^*$  transitions respectively. The above bands are shifted to 28.91–29.44 and 42–45.15 kK respectively in the chloride complexes and to 29.24–29.55 and 40.98–42.15 kK respectively in the bromide complexes. The electronic spectra of the complexes of the chlorides of Nd, Ho and Er and the bromides of Pr, Nd, Ho and Er show some  $f-f$  transitions, the tentative assignments of which are given in table 2. The energies at which the various  $f-f$  bands appear in the complexes are lower compared to those of the corresponding aquo-ions (Sinha and Schmidtke 1965). This red-shift has been attributed to nephelauxetic effect (Sinha and Schmidtke 1965), the extent of which may be used as a measure of the metal–ligand covalent bonding. The Sinha covalency parameter ( $\delta$ ), the interelectronic repulsion parameter ( $\beta$ ), the bonding parameter ( $b^{1/2}$ ) and covalency angular overlap parameter ( $\eta$ ) have been calculated (Sinha 1966) from the spectra of all the above mentioned complexes. The values of ' $\beta$ ' are found to be less than unity while  $b^{1/2}$  and ' $\eta$ ' values are positive suggesting covalency in the metal–ligand bonding. However, ' $\delta$ ' values of the complexes are below 1.5 which indicate weak covalent bonding in the present complexes (Karraker 1967).

### 3.5 Magnetic properties

The magnetic data (table 1) indicate that the magnetic moments of the present complexes show a little deviation from Van Vleck values (Van Vleck and Frank 1929) which suggest that the  $4f$  electrons play only a small role in bonding.

#### 4. Conclusion

From the analytical and spectral data, it is concluded that the present Schiff base, AA, acts as a tridentate ligand coordinating through both the carbonyl oxygens and through the nitrogen of the azomethine group. In the chloride complexes, all the three chloride ions are involved in coordination giving a coordination number of nine to the metal ion. In the bromide complexes, only two of the three bromide ions are coordinated assigning a coordination number of eight to the metal ion. Being an antipyrine derivative, the present ligand may exhibit some antibacterial and anti-inflammatory properties. The corresponding metal complexes would be expected to exhibit the physiological properties with enhanced intensity.

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