

## Yttrium and lanthanide nitrate complexes of $N,N^1$ -bis(4-antipyrylmethylidene)ethylenediamine

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**Abstract.** Complexes of yttrium and lanthanide nitrates with a Schiff base,  $N,N^1$ -bis(4-antipyrylmethylidene)ethylenediamine (BAME) having the general formula  $[Ln(BAME)_2(NO_3)](NO_3)_2$ , where  $Ln = Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho$  and  $Er$  have been synthesised and characterised by elemental analyses, molar conductance in non-aqueous solvents, electronic, infrared and proton NMR spectra. BAME acts as a neutral bidentate ligand coordinating through both azomethine nitrogen atoms. One of the nitrate groups is coordinated in a bidentate manner. A coordination number of six may be assigned to the metal ion in these complexes. The covalency parameters evaluated from the solid state electronic spectra suggest weak covalent character of the metal-ligand bond.

**Keywords.** Schiff base; lanthanides; yttrium; complexes;  $N,N^1$ -bis(4-antipyrylmethylidene)ethylenediamine.

### 1. Introduction

In continuation of our earlier investigations on the nitrate complexes of yttrium and lanthanides with antipyryne derivatives<sup>1–6</sup>, we report here the synthesis and characterisation of a new series containing ten complexes of yttrium and lanthanide nitrates with the Schiff base,  $N,N^1$ -bis(4-antipyrylmethylidene)ethylenediamine (BAME) (figure 1). The ligand being an antipyryne derivative, the present complexes would be expected to be of physiological importance and may possess both antibacterial and antiinflammatory properties<sup>7,8</sup>.

### 2. Experimental

#### 2.1 Preparation of the metal salts

The metal nitrates were prepared by dissolving the respective oxides (99.99%) in 60% nitric acid and then crystallising the salt by evaporating the solution on a steam bath.

#### 2.2 Preparation of the Schiff base

The Schiff base was prepared by the condensation of ethylenediamine with 4-antipyryne carboxaldehyde in ethyl acetate medium. The Schiff base formed was light yellow in colour with melting point 185°C (yield, 80%). The purity was checked by TLC, infrared

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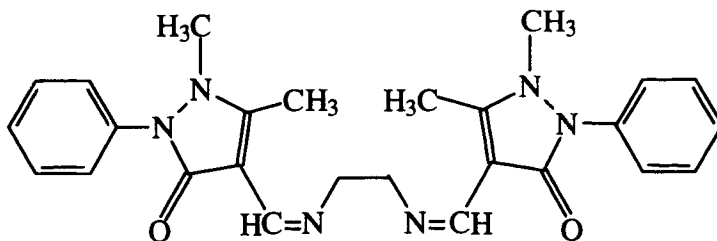


Figure 1.  $N,N^1$ -Bis(4-antipyrylmethylidene)ethylenediamine

spectrum and elemental analyses (found: C, 68.0%; H, 6.09% and N 18.29%; calculated for C, H and N: 68.39%, 6.18% and 18.41%; formula weight: 456.54).

### 2.3 Preparation of the complexes

One mmol (0.4 g) of the metal nitrate was dissolved in 10 ml of acetonitrile and it was added to a boiling solution of the ligand, obtained by dissolving 2.2 mmol (1.0 g) of BAME in 30 ml of acetonitrile taken in a 100 ml round bottom flask, kept on a boiling water bath. The resulting solution was refluxed further for about six hours, cooled, filtered and the filtrate was concentrated. The viscous mass so obtained was then washed several times with hot benzene to remove the excess ligand. The solid complex separated was recrystallised by stirring vigorously a saturated solution of the complex in acetonitrile with a few drops of benzene. It was filtered and dried under vacuum over phosphorus (V) oxide.

### 2.4 Measurements

All the complexes were analysed for the metal content by the method reported earlier<sup>9</sup>. Molar conductances in nitrobenzene, acetonitrile and DMF ( $10^{-3}$  M solutions) were measured at room temperature using a Toshniwal conductivity bridge with a dip-type cell of platinum electrodes (cell constant: 0.1098). The infrared spectra of the ligand and the complexes were recorded in the range  $4000-400\text{ cm}^{-1}$  on a Shimadzu IR 470 spectrophotometer and in the range  $400-100$  on a Bruker IFS 66v FT-IR spectrophotometer. Electronic spectra were recorded in  $\text{CH}_3\text{CN}$  ( $10^{-4}$  M solutions) and in the solid state (using a paste with Nujol) on a Shimadzu UV 160A spectrophotometer in the range 200–900 nm. The C, H and N analyses were carried out using a Heraeus CHNO rapid analyser. The  $^1\text{H}$  NMR spectra were recorded using  $\text{DMSO-d}_6$  as the solvent on a JEOL GSX 400 instrument.

## 3. Results and discussion

All the complexes are yellowish, non-hygroscopic solids. They are soluble in acetone, acetonitrile, DMF, DMSO, ethanol, methanol and nitrobenzene but insoluble in benzene, carbon tetrachloride, chloroform and toluene.

The analytical data (table 1) of the complexes indicate that all ten complexes have the general formula  $\text{Ln}(\text{BAME})_2(\text{NO}_3)_3$ , where  $\text{Ln} = \text{Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho}$  and Er.

**Table 1.** Analytical data of yttrium and lanthanide nitrate complexes of BAME

Complex	%Metal	%Carbon	%Hydrogen	%Nitrogen
[Y(BAME) <sub>2</sub> (NO <sub>3</sub> )](NO <sub>3</sub> ) <sub>2</sub>	7.43 (7.48)	52.36 (52.57)	4.71 (4.75)	17.58 (17.69)
[La(BAME) <sub>2</sub> (NO <sub>3</sub> )](NO <sub>3</sub> ) <sub>2</sub>	11.19 (11.22)	50.61 (50.44)	4.59 (4.56)	16.90 (16.97)
[Pr(BAME) <sub>2</sub> (NO <sub>3</sub> )](NO <sub>3</sub> ) <sub>2</sub>	11.39 (11.36)	50.29 (50.36)	4.51 (4.55)	16.89 (16.95)
[Nd(BAME) <sub>2</sub> (NO <sub>3</sub> )](NO <sub>3</sub> ) <sub>2</sub>	11.64 (11.60)	50.33 (50.23)	4.50 (4.54)	16.94 (16.90)
[Sm(BAME) <sub>2</sub> (NO <sub>3</sub> )](NO <sub>3</sub> ) <sub>2</sub>	12.02 (12.03)	49.86 (49.98)	4.55 (4.52)	16.91 (16.82)
[Eu(BAME) <sub>2</sub> (NO <sub>3</sub> )](NO <sub>3</sub> ) <sub>2</sub>	12.22 (12.15)	49.78 (49.92)	4.54 (4.51)	16.70 (16.80)
[Gd(BAME) <sub>2</sub> (NO <sub>3</sub> )](NO <sub>3</sub> ) <sub>2</sub>	12.49 (12.52)	49.51 (49.71)	4.46 (4.49)	16.83 (16.73)
[Dy(BAME) <sub>2</sub> (NO <sub>3</sub> )](NO <sub>3</sub> ) <sub>2</sub>	12.80 (12.88)	49.72 (49.50)	4.45 (4.47)	16.60 (16.66)
[Ho(BAME) <sub>2</sub> (NO <sub>3</sub> )](NO <sub>3</sub> ) <sub>2</sub>	13.11 (13.05)	49.69 (49.41)	4.50 (4.46)	16.51 (16.62)
[Er(BAME) <sub>2</sub> (NO <sub>3</sub> )](NO <sub>3</sub> ) <sub>2</sub>	13.29 (13.21)	49.08 (49.32)	4.49 (4.46)	16.68 (16.59)

Calculated values in parentheses

**Table 2.** Molar conductance data of yttrium and lanthanide nitrate complexes of BAME

Complexes	Molar conductance <sup>a</sup>		
	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	CH <sub>3</sub> CN	DMF
[Y(BAME) <sub>2</sub> (NO <sub>3</sub> )](NO <sub>3</sub> ) <sub>2</sub>	49.86	254.84	166.20
[La(BAME) <sub>2</sub> (NO <sub>3</sub> )](NO <sub>3</sub> ) <sub>2</sub>	44.32	268.14	161.77
[Pr(BAME) <sub>2</sub> (NO <sub>3</sub> )](NO <sub>3</sub> ) <sub>2</sub>	50.97	255.95	155.12
[Nd(BAME) <sub>2</sub> (NO <sub>3</sub> )](NO <sub>3</sub> ) <sub>2</sub>	52.63	260.38	168.12
[Sm(BAME) <sub>2</sub> (NO <sub>3</sub> )](NO <sub>3</sub> ) <sub>2</sub>	47.64	252.62	169.52
[Eu(BAME) <sub>2</sub> (NO <sub>3</sub> )](NO <sub>3</sub> ) <sub>2</sub>	58.17	254.84	156.23
[Gd(BAME) <sub>2</sub> (NO <sub>3</sub> )](NO <sub>3</sub> ) <sub>2</sub>	52.63	260.38	154.01
[Dy(BAME) <sub>2</sub> (NO <sub>3</sub> )](NO <sub>3</sub> ) <sub>2</sub>	55.40	265.92	157.34
[Ho(BAME) <sub>2</sub> (NO <sub>3</sub> )](NO <sub>3</sub> ) <sub>2</sub>	47.09	249.30	152.90
[Er(BAME) <sub>2</sub> (NO <sub>3</sub> )](NO <sub>3</sub> ) <sub>2</sub>	49.86	260.38	160.66

<sup>a</sup>10<sup>-3</sup> M solutions were used; in ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>

### 3.1 Electrical conductance

The observed molar conductance values of the complexes (table 2) in nitrobenzene, acetonitrile and DMF are in agreement with the values corresponding to 1:2 electrolytes<sup>10</sup>. Thus, the nitrate complexes of BAME may be represented as [Ln(BAME)<sub>2</sub>(NO<sub>3</sub>)](NO<sub>3</sub>)<sub>2</sub>, where Ln = Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho and Er.

### 3.2 Infrared spectra

The important infrared frequencies of the free ligand BAME and that of the complexes are given in table 3. The bands observed at 1648 and 1594  $\text{cm}^{-1}$  in the spectrum of the free ligand are attributed to the stretching vibrations of the ring carbonyl and azomethine group, respectively. The band at 1594  $\text{cm}^{-1}$  is found to be shifted in the spectra of the complexes and appears at 1604  $\text{cm}^{-1}$ , indicating that both of the azomethine nitrogen atoms are coordinated to the metal ion<sup>11</sup>. Another broad band observed around 380  $\text{cm}^{-1}$  due to  $\nu_{\text{Ln}-\text{N}}$  supports the coordination of azomethine nitrogen in these complexes<sup>12</sup>. But the band at 1648  $\text{cm}^{-1}$  remains practically unaltered at 1649  $\text{cm}^{-1}$  suggesting that the carbonyl oxygens are not coordinated to the metal ion in these complexes<sup>13</sup>. Besides, the complexes show characteristic vibrational frequencies of both ionic and coordinated nitrate groups. A very strong band observed around 1384  $\text{cm}^{-1}$  indicates the presence of ionic nitrate group<sup>5</sup> and it is due to the  $\nu_3$  vibration of the nitrate group of  $D_{3h}$  symmetry. This is supported by another band of medium intensity observed around 820  $\text{cm}^{-1}$  due to the  $\nu_2$  vibration of the ionic nitrate<sup>14,15</sup>. The presence of coordinated nitrate group is indicated by the bands observed around 1438 and 1250  $\text{cm}^{-1}$  due to the  $\nu_4$  and  $\nu_1$  vibrations respectively of the nitrate group of  $C_{2v}$  symmetry<sup>15</sup>. A medium band observed around 1054  $\text{cm}^{-1}$  due to the  $\nu_2$  vibration of the nitrate group ( $C_{2v}$ ) stands as additional evidence for the presence of coordinated nitrate ion. The difference in wave numbers between the two highest frequency bands ( $\nu_4 - \nu_1$ ) of the  $C_{2v}$  nitrate is about 192  $\text{cm}^{-1}$ , which indicates that the coordinated nitrate ion is bidentate,<sup>1,16</sup>. Besides, the weak band observed at around 464  $\text{cm}^{-1}$  due to Ln-O stretching vibration<sup>17</sup> provides an additional evidence for the coordination of nitrate oxygen in these complexes because the carbonyl oxygen atoms of the ligand BAME are not coordinated to the metal ion. These results, which are in conformity with the conductance data, indicate that one of the nitrate ions is coordinated in a bidentate fashion while the other two nitrates remain as counter ions.

### 3.3 Proton NMR spectra

The  $^1\text{H}$  NMR spectrum of BAME, shows the resonance signal corresponding to the azomethine proton at  $\delta$  8.21 ppm as a singlet with respect to TMS. The other signals corresponding to the phenyl, =N-CH<sub>2</sub>-, -N-CH<sub>3</sub> and =C-CH<sub>3</sub> are obtained in the regions  $\delta$  7.46–7.29 ppm (multiplet),  $\delta$  3.60 ppm (singlet),  $\delta$  3.29 ppm (singlet) and  $\delta$  2.53 ppm (singlet) respectively in the spectrum of the free ligand. But, in the nitrate complexes of Y and La, the azomethine proton signal is observed at  $\delta$  7.85 and 7.80 ppm respectively, indicating that both the azomethine nitrogens are coordinated<sup>18</sup> to the metal ion. The other signals are found in the regions  $\delta$  7.56–7.14 ppm as a multiplet,  $\delta$  3.54 ppm as a singlet,  $\delta$  3.34 ppm as a singlet and  $\delta$  2.50 ppm as a singlet with respect to TMS corresponding to the phenyl, =N-CH<sub>2</sub>-, -N-CH<sub>3</sub> and =C-CH<sub>3</sub> groups in the spectrum of the complexes.

### 3.4 Electronic spectra

The electronic spectrum of BAME shows two maxima at 24.81 kK and 40.00 kK corresponding to  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transitions. But, in the spectra of the complexes the  $n \rightarrow \pi^*$  band is found to be red-shifted and appears in the region 24.75–24.15 kK, while

Table 3. Important infrared spectral bands ( $\text{cm}^{-1}$ ) of BAME and its yttrium and lanthanide nitrate complexes

Compound	NO <sub>3</sub> (coordinated)							NO <sub>3</sub> (ionic)		
	$\nu_{\text{C-O}}$	$\nu_{\text{C-N}}$	$\nu_{\text{Ln-O}}$	$\nu_{\text{Ln-N}}$	$\nu_4$	$\nu_1$	$\nu_2$	$\nu_3$	$\nu_3$	$\nu_2$
BAME	1648 vs	1594 s	—	—	—	—	—	—	—	—
[Y(BAME) <sub>2</sub> (NO <sub>3</sub> )](NO <sub>3</sub> ) <sub>2</sub>	1650 vs	1605 s	464 w	380 b	1436 s	1250 s	1054 m	1384 vs	—	820 m
[La(BAME) <sub>2</sub> (NO <sub>3</sub> )](NO <sub>3</sub> ) <sub>2</sub>	1649 vs	1604 s	465 w	381 b	1438 s	1252 s	1054 m	1386 vs	—	821 m
[Pr(BAME) <sub>2</sub> (NO <sub>3</sub> )](NO <sub>3</sub> ) <sub>2</sub>	1650 vs	1604 s	465 w	380 b	1436 s	1250 s	1054 m	1386 vs	—	820 m
[Nd(BAME) <sub>2</sub> (NO <sub>3</sub> )](NO <sub>3</sub> ) <sub>2</sub>	1648 vs	1605 s	464 w	381 b	1438 s	1248 s	1052 m	1386 vs	—	822 m
[Sm(BAME) <sub>2</sub> (NO <sub>3</sub> )](NO <sub>3</sub> ) <sub>2</sub>	1648 vs	1605 s	464 w	381 b	1438 s	1250 s	1054 m	1385 vs	—	820 m
[Eu(BAME) <sub>2</sub> (NO <sub>3</sub> )](NO <sub>3</sub> ) <sub>2</sub>	1650 vs	1604 s	464 w	380 b	1436 s	1250 s	1054 m	1384 vs	—	821 m
[Gd(BAME) <sub>2</sub> (NO <sub>3</sub> )](NO <sub>3</sub> ) <sub>2</sub>	1648 vs	1604 s	465 w	380 b	1436 s	1248 s	1054 m	1384 vs	—	821 m
[Dy(BAME) <sub>2</sub> (NO <sub>3</sub> )](NO <sub>3</sub> ) <sub>2</sub>	1648 vs	1605 s	464 w	381 b	1436 s	1250 s	1053 m	1386 vs	—	822 m
[Ho(BAME) <sub>2</sub> (NO <sub>3</sub> )](NO <sub>3</sub> ) <sub>2</sub>	1649 vs	1605 s	464 w	380 b	1438 s	1250 s	1054 m	1384 vs	—	822 m
[Er(BAME) <sub>2</sub> (NO <sub>3</sub> )](NO <sub>3</sub> ) <sub>2</sub>	1648 vs	1605 s	464 w	380 b	1438 s	1250 s	1054 m	1384 vs	—	820 m

vs-very strong, s-strong, m-medium, w-weak, b-broad

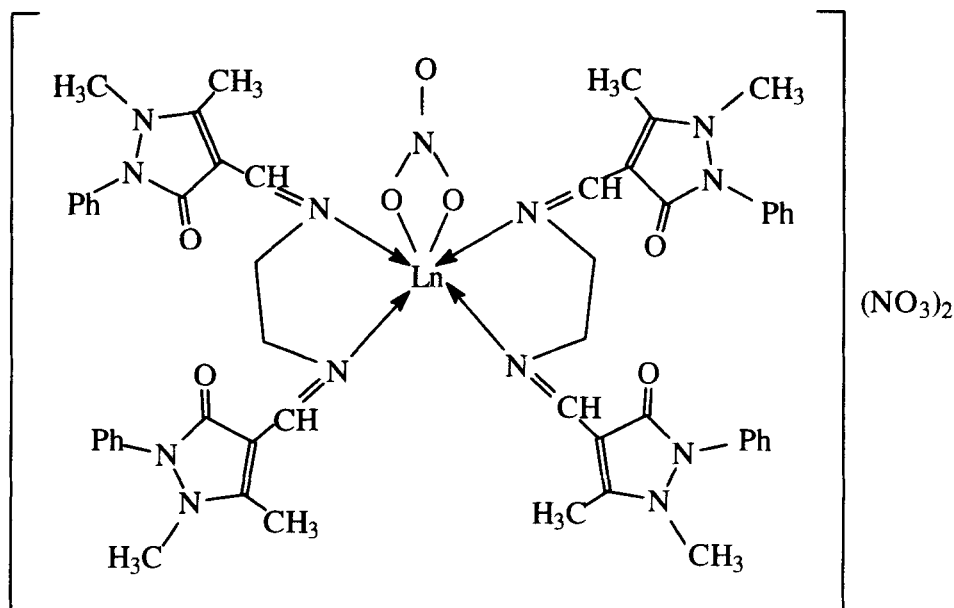
**Table 4.** f-f transitions of the nitrate complexes of Pr, Nd, Sm, Ho, and Er with BAME

Compound	Abs. Max. (kK)	Tentative assignments	Covalency parameters calculated
Pr	16.83	$^3H_4 \rightarrow ^1D_2$	$\beta = 0.9955$
	20.57	$^3H_4 \rightarrow ^3P_0$	$\delta = 0.4520$ $b^{1/2} = 0.0335$ $\eta = 0.0022$
Nd	11.41	$^4I_{9/2} \rightarrow ^4F_{3/2}$	$\beta = 0.9910$
	12.42	$^4I_{9/2} \rightarrow ^4F_{5/2}$	$\delta = 0.9082$
	13.42	$^4I_{9/2} \rightarrow ^4F_{7/2}$	$b^{1/2} = 0.0474$
	17.15	$^4I_{9/2} \rightarrow ^4G_{5/2}, ^2G_{7/2}$	$\eta = 0.0045$
Sm	22.62	$^6H_{5/2} \rightarrow ^4G_{9/2}$	$\beta = 0.9965$
			$\delta = 0.3512$ $b^{1/2} = 0.0295$ $\eta = 0.0017$
Ho	15.43	$^5I_8 \rightarrow ^5F_5$	$\beta = 0.9970$
	22.07	$^5I_8 \rightarrow ^5G_6$	$\delta = 0.3009$ $b^{1/2} = 0.0274$ $\eta = 0.0015$
Er	12.39	$^4I_{15/2} \rightarrow ^4I_{9/2}$	$\beta = 0.9983$
	15.24	$^4I_{15/2} \rightarrow ^4F_{9/2}$	$\delta = 0.1702$
	19.08	$^4I_{15/2} \rightarrow ^2H_{11/2}$	$b^{1/2} = 0.0206$ $\eta = 0.0008$

the  $\pi \rightarrow \pi^*$  is observed as blue-shifted to the region 42.01–40.65 kK. The f-f bands are observed only in the complexes of Pr, Nd, Sm, Ho and Er and are found to be slightly red-shifted with respect to the corresponding aquo ions. The values of covalency parameters  $\beta$ ,  $\delta$ ,  $b^{1/2}$  and  $\eta$  are calculated<sup>19,20</sup> (table 4). The values of  $\beta$  are less than unity and that of  $\eta$  and  $b^{1/2}$  are positive, suggesting some covalent character of the metal-ligand bond, but it is weak as indicated by the values of  $\delta$ , which are less than 1.5. Further, the hypersensitive bands observed in the complexes of Nd, Ho and Er have close resemblance to that of the six-coordinated complexes reported earlier<sup>21</sup>. Hence, a coordination number of six is assigned to the metal ion in these complexes. Since Nd, Ho and Er nitrate complexes of BAME are isomorphous with the remaining nitrate complexes of BAME, the same coordination number may be assigned to the other metal ions also in these complexes. Besides, the electronic spectra of the nitrate complexes, both in solid and solution states have identical nature and hence, it may be inferred that these complexes maintain the same structure in both of these media. The tentative structure of the complexes is given in figure 2.

#### 4. Conclusion

BAME acts as a neutral bidentate ligand coordinating through both the azomethine nitrogen atoms in these complexes. One of the nitrate groups is coordinated to the metal ion in a bidentate manner. Hence, a coordination number of six may be assigned to the metal ion in these complexes.



where, Ln = Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho or Er; Ph =  $-C_6H_5$

Figure 2. Tentative structure of the complexes.

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