

Synthesis and physicochemical studies of yttrium and lanthanide nitrate complexes of 1,2-(diimino-4'-antipyrynyl)ethane

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Abstract. Yttrium and lanthanide nitrate complexes of the Schiff base, 1,2-(diimino-4'-antipyrynyl)ethane (GA), of the type $[Ln(GA)_2(NO_3)_3]$ (where Ln = Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho or Er) have been synthesised and characterised by elemental analyses, electrical conductance, magnetic susceptibility, infrared, proton NMR and electronic spectra, and thermogravimetric studies. Infrared and proton NMR spectra of these complexes show that GA acts as a neutral tetradentate ligand and that all the three nitrate groups are coordinated monodentately. The electronic spectra of the Pr, Nd, Ho and Er complexes suggest reasonable covalency in the metal-ligand bond. The magnetic moments of these complexes are in agreement with the van Vleck values. All these complexes are thermally stable up to about 200°C. A coordination number of eleven may be assigned to the metal ions in these complexes.

Keywords. Schiff base; lanthanides; yttrium; complexes; 1,2-(diimino-4'-antipyrynyl)ethane.

1. Introduction

It is becoming increasingly evident that the coordination chemistry of yttrium and lanthanides is of application to a wide variety of chemical and applied problems. Also, Schiff bases and their complexes of the tripositive yttrium and lanthanide ions are known to possess physiological and pharmacological properties (Gao and Rhodes 1990; Wang *et al* 1990). In continuation of our previous work (Radhakrishnan *et al* 1984; Radhakrishnan 1986; Muraleedharan Nair and Radhakrishnan 1993) on Schiff base complexes of yttrium and lanthanide nitrates, we now report the preparation and characterisation of the complexes of yttrium and lanthanide nitrates with a tetradentate Schiff base, 1,2-(diimino-4'-antipyrynyl)ethane (GA) (figure 1). The resulting complexes are expected to be of structural, physiological and technological importance.

2. Experimental

2.1 Preparation of the metal salts and the ligand

The nitrates of Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho and Er were prepared from the respective oxides (99.99% pure) and 60% nitric acid as reported earlier (Radhakrishnan *et al* 1984). The Schiff base was prepared by the condensation of glyoxal and 4-aminoantipyryne in

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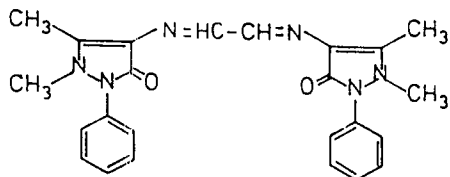


Figure 1. Structure of 1,2-(diimino-4'-antipyrinyl)ethane.

ethanolic medium (yield: 90%; m.p.: 264°C). Its purity was tested by elemental analysis (calcd. for $C_{24}H_{24}N_6O_2$: C 67.29%, H 5.61% and N 19.63%; Found C 67.11%, H 5.57% and N 19.51%), TLC and infrared spectroscopy.

2.2 Preparation of the complexes

The metal nitrate (1 mmol) in acetone (10 ml) was added to a boiling suspension of the Schiff base (2.2 mmol) in acetone (50 ml). This mixture was refluxed over a water bath for 3 h. The brown complex precipitated was filtered and washed with hot ethyl acetate to remove excess ligand. Finally, the complexes were recrystallised from methanol and dried *in vacuo* over P_4O_{10} .

2.3 Measurements

These complexes were analysed for metal content by the conventional method (Nair *et al* 1981) and C, H, N contents on a HERAEUS rapid analyser. The molar conductance was measured using a Toshniwal conductivity bridge with dip-type conductance cell and platinum electrode (cell constant = 0.9588 cm^{-1}). The magnetic susceptibilities were measured at room temperature by the Gouy method using mercury(II) tetrathiocyanatocobaltate(II) as calibrant. The infrared spectra of the ligand and the complexes were recorded in $4000\text{--}400 \text{ cm}^{-1}$ range on a Shimadzu-IR-470 spectrophotometer using the KBr disc technique. The solid state electronic spectra (as a paste with Nujol mull) were recorded in the region $200\text{--}1100 \text{ nm}$ on a Shimadzu-UV-160A spectrophotometer. The proton NMR spectral studies in $\text{DMSO-}d_6$ were carried out on NMR-GSX-400 instrument. Thermogravimetric studies were carried out under a nitrogen atmosphere using a Shimadzu-DT-40 thermal analyser (sample: 10 mg; heating rate: $10^\circ\text{C}/\text{min}$).

3. Results and discussion

All the complexes are non-hygroscopic, brown-coloured solids. They are soluble in acetonitrile, DMF, DMSO and methanol, and insoluble in acetone, nitrobenzene and toluene. The analytical data (table 1) show that all the complexes can be represented by the general formula $\text{Ln}(\text{GA})_2(\text{NO}_3)_3$, where $\text{Ln} = \text{Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho}$ or Er.

3.1 Electrical conductance

The molar conductivities (table 1) of 10^{-3} M solutions of the complexes in DMF and nitrobenzene suggest their non-electrolytic nature (Geary 1971). Thus, the complexes may be formulated as $[\text{Ln}(\text{GA})_2(\text{NO}_3)_3]$, where $\text{Ln} = \text{Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho}$ or Er.

Table 1. Analytical^a, molar conductance^b and magnetic moment data of the rare earth nitrate complexes of GA.

Complex	Analysis (%)				Molar conductance		μ_{eff} (BM)
	Ln	C	H	N	C ₆ H ₅ NO ₂	DMF	
[Y(GA) ₂ (NO ₃) ₃]	7.8 (7.9)	50.1 (50.1)	4.2 (4.2)	18.5 (18.6)	7.2	20.1	—
[La(GA) ₂ (NO ₃) ₃]	11.9 (11.8)	48.0 (48.8)	4.0 (4.1)	17.7 (17.8)	5.2	22.3	—
[Pr(GA) ₂ (NO ₃) ₃]	11.9 (11.9)	48.6 (48.7)	4.0 (4.1)	17.8 (17.8)	9.1	14.7	3.42
[Nd(GA) ₂ (NO ₃) ₃]	12.2 (12.2)	48.5 (48.6)	4.0 (4.1)	17.7 (17.7)	7.3	15.2	3.61
[Sm(GA) ₂ (NO ₃) ₃]	12.6 (12.6)	48.1 (48.3)	4.0 (4.0)	17.6 (17.6)	11.5	17.9	1.89
[Eu(GA) ₂ (NO ₃) ₃]	12.7 (12.7)	48.3 (48.2)	3.9 (4.0)	17.5 (17.6)	6.3	22.7	3.39
[Gd(GA) ₂ (NO ₃) ₃]	13.1 (13.1)	47.9 (48.0)	4.0 (4.0)	17.6 (17.5)	9.3	22.1	8.17
[Dy(GA) ₂ (NO ₃) ₃]	13.4 (13.5)	47.7 (47.7)	3.9 (4.0)	17.4 (17.4)	7.0	31.7	10.55
[Ho(GA) ₂ (NO ₃) ₃]	13.6 (13.7)	47.7 (47.7)	3.9 (4.0)	17.4 (17.4)	8.3	28.9	10.61
[Er(GA) ₂ (NO ₃) ₃]	13.8 (13.8)	47.5 (47.6)	4.0 (4.0)	17.4 (17.4)	7.7	17.2	9.69

^aCalculated values in parentheses; ^b10⁻³ M solutions used, ohm⁻¹ mol⁻¹ cm²

3.2 Infrared and proton NMR spectra

The infrared spectral data (table 2) of the Schiff base GA show a very strong band at 1650 cm⁻¹ which may be attributed to the C=O stretching vibration. On complexation this band is shifted to the region 1620 cm⁻¹, showing that both the carbonyl oxygens are involved in coordination (Radhakrishnan *et al* 1984). Also the band at 1576 cm⁻¹ assignable to the azomethine stretching of GA is shifted to the region 1586–1588 cm⁻¹, thereby indicating coordination by both the azomethine nitrogen atoms (Liu Guofa *et al* 1990). The infrared spectra of the complexes also show two medium bands at about 1424 and 1310 cm⁻¹, which are assigned to ν_4 and ν_1 stretching vibrations of coordinated nitrate groups. Since $\nu_4-\nu_1$ is about 110 cm⁻¹, the nitrate coordination is monodentate in nature (Nakamoto 1986). Thus, a coordination number of eleven may be assigned to the metal ion in these complexes. The Ln–O and Ln–N stretching vibrations are observed at about 562 and 472 cm⁻¹ respectively in the spectra of the complexes (Agarwal and Tandon 1979).

Proton NMR spectra show the –CH=N-proton resonance at 8.35 δ in the pure ligand, at 8.55 δ in the yttrium complex, and at 8.6 δ in the lanthanum complex, with respect to TMS, suggesting coordination by the azomethine nitrogen (Jagannathan and Soundararajan 1981). The different band assignments are given in table 3.

Table 2. Important infrared absorptions (cm^{-1}) of GA and rare earth metal nitrate complexes with GA.

Compound	$\nu(\text{C=O})$	$\nu(\text{C=N})$	$\nu_4(\text{NO}_3)$	$\nu_1(\text{NO}_3)$	$\nu(\text{Ln-O})$	$\nu(\text{Ln-N})$
GA	1650s	1576s	—	—	—	—
[Y(GA) ₂ (NO ₃) ₃]	1620s	1588s	1424m	1312m	560w	472w
[La(GA) ₂ (NO ₃) ₃]	1620s	1586s	1420m	1312m	560w	470w
[Pr(GA) ₂ (NO ₃) ₃]	1620s	1588s	1424m	1312m	562w	470w
[Nd(GA) ₂ (NO ₃) ₃]	1620s	1586s	1424m	1312m	560w	472w
[Sm(GA) ₂ (NO ₃) ₃]	1620s	1588s	1424m	1310m	560w	472w
[Eu(GA) ₂ (NO ₃) ₃]	1620s	1586s	1422m	1312m	560w	470w
[Gd(GA) ₂ (NO ₃) ₃]	1620s	1586s	1422m	1312m	562w	472w
[Dy(GA) ₂ (NO ₃) ₃]	1620s	1588s	1424m	1312m	560w	472w
[Ho(GA) ₂ (NO ₃) ₃]	1620s	1588s	1422m	1312m	562w	472w
[Er(GA) ₂ (NO ₃) ₃]	1620s	1588s	1424m	1312m	560w	472w

s strong; m medium; w weak

Table 3. Important proton NMR bands (ppm) of GA and complexes of the nitrates of yttrium and lanthanum (in DMSO-*d*₆).

GA	[Y(GA) ₂ (NO ₃) ₃]	[La(GA) ₂ (NO ₃) ₃]	Assignment
2.2 sh, s	2.2 sh, s	2.21 sh, s	=C-CH ₃
2.4 br, s	2.4 br, s	2.4 br, s	-N-CH ₃
3.1 sh, s	3.1 br, s	3.1 br, s	-N-CH ₃
7.1 br, m	7.1 br, m	7.1 br, m	-C ₆ H ₅
7.7 br, m	7.7 br, m	7.7 br, m	-C ₆ H ₅
8.35 sh, s	8.55 sh, s	8.60 sh, s	-CH=N-

sh sharp; br broad; s singlet; m multiplet

3.3 Electronic spectra

The electronic spectra of the ligand in the solid state show the $n \rightarrow \pi^*$ transition at 382 nm and the $\pi \rightarrow \pi^*$ transition at 255 nm. In the spectra of the complexes the $n \rightarrow \pi^*$ bands are absent and the $\pi \rightarrow \pi^*$ bands appear at 242–244 nm. The $f-f$ bands are observed in the complexes of Pr, Nd, Ho and Er and their tentative assignments are given in table 4 along with the calculated covalency parameters (Sinha 1966; Karakker 1967). The interelectronic repulsion parameter (β) is less than unity and the value of covalency angular overlap parameter ($b^{1/2}$) and bonding parameter (η) are positive, indicating covalency in the metal–ligand bond. Since the Sinha covalency parameter (δ) is less than 1.5 in these complexes, there is only weak covalent character in the metal–ligand bond of these complexes.

3.4 Magnetic moment data

The room temperature magnetic moments (table 1) suggest that all complexes are paramagnetic except those of the yttrium and lanthanum as expected. The measured magnetic moments agree well with van Vleck values (van Vleck and Frank 1929) suggesting the nonparticipation of $4f$ electrons in bonding.

Table 4. Electronic spectral data of rare earth metal nitrate complexes of GA.

Complex	λ_{\max} (nm)	Tentative assignment	Covalency parameters ^a
Pr	593	$^3H_4 \rightarrow ^1D_2$	$\beta = 0.9961$
	485	$^3H_4 \rightarrow ^3P_0$	$\delta = 0.3916$
	470	$^3H_4 \rightarrow ^3P_1$	$b^{1/2} = 0.0312$
	448	$^3H_4 \rightarrow ^3P_2$	$\eta = 0.0020$
Nd	873	$^4I_{9/2} \rightarrow ^4F_{3/2}$	$\beta = 0.9936$
	746	$^4I_{9/2} \rightarrow ^4F_{7/2}$	$\delta = 0.6441$
	687	$^4I_{9/2} \rightarrow ^4F_{9/2}$	$b^{1/2} = 0.0400$
	581	$^4I_{9/2} \rightarrow ^4G_{5/2}, ^2G_{7/2}$	$\eta = 0.0032$
	526	$^4I_{9/2} \rightarrow ^4G_{7/2}$	
	514	$^4I_{9/2} \rightarrow ^4G_{9/2}$	
Ho	539	$^5I_8 \rightarrow ^5S_2, ^5F_4$	$\beta = 0.9960$
	452	$^5I_8 \rightarrow ^5S_5$	$\delta = 0.4016$
			$b^{1/2} = 0.0316$
			$\eta = 0.0020$
Er	655	$^4I_{15/2} \rightarrow ^4F_{9/2}$	$\beta = 0.9950$
	544	$^4I_{15/2} \rightarrow ^4S_{3/2}$	$\delta = 0.5025$
	522	$^4I_{15/2} \rightarrow ^2H_{11/2}$	$b^{1/2} = 0.0353$
			$\eta = 0.0025$

^aCalculated values

3.5 Thermogravimetric data

Thermogravimetric analyses of these complexes suggest that they are highly stable up to about 200°C, as there is no mass loss, indicating the absence of any small molecules of water or solvents. All complexes show the same type of decomposition pattern at high temperatures. They decompose in two stages, in the temperature ranges 200–450 and 450–650°C. The first stage, corresponding to a mass loss of 40%, may be due to the loss of one ligand and the decomposition of the nitrate groups. The second stage, amounting to a mass loss of about 36.1%, may be assigned to the loss of the second ligand species along the complete conversion of the nitrate to the stable anhydrous lanthanum oxide. The decomposition is complete at about 700°C, yielding the respective rare earth oxide as the final product. Similar decomposition patterns for all the ten complexes suggest similar structures.

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References

- Agarwal S K and Tandon J P 1979 *Monatsh. Chem.* **110** 401
 Gao X M and Rhodes J 1990 *J. Immunol.* **144** 2883
 Geary W J 1971 *Coord. Chem. Rev.* **7** 81

- Jagannathan R and Soundararajan S 1981 *Inorg. Nucl. Chem. Lett.* **17** 65
Karraker D G 1967 *Inorg. Chem.* **6** 1863
Liu Guofa, Na Chongwu, Li Bin and Mao Kunyuan 1990 *Polyhedron* **9** 2019
Muraleedharan Nair M K and Radhakrishnan P K 1993 *Polyhedron* **12** 1227
Nair M R G, Kurian M J and Prabhakaran C P 1981 *Talanta* **28** 395
Nakamoto K 1986 *Infrared and Raman spectra of inorganic and coordination compounds*
(New York: Wiley) p 251
Radhakrishnan P K, Indrasenan P and Nair C G R 1984 *Polyhedron* **3** 67
Radhakrishnan P K 1986 *Inorg. Chim. Acta* **110** 211
Sinha S P 1966 *Spectrochim. Acta* **22** 57
van Vleck J H and Frank N 1929 *Phys. Rev.* **34** 1499
Wang P H, Keck E J, Lien E J and Lai M C C 1990 *J. Med. Chem.* **33** 608