

Complexes of lanthanide nitrates with N,N-diethylantipyrine-4-carboxamide

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Abstract. New complexes of lanthanide nitrates with N,N-diethylantipyrine-4-carboxamide (DEAP), with the general formulae $[\text{Ln}_2(\text{DEAP})_3][\text{NO}_3]_6$ (where Ln = La, Pr, Nd, Sm, Tb, Ho, Er, Yb and Y) have been isolated and characterized by chemical analysis and various physical methods such as electrolytic conductance, IR and ^{13}C NMR spectral data. Electrolytic conductance values and infrared spectral studies indicate that the nitrate groups are coordinated. Infrared and ^{13}C NMR spectral analysis show that the ligand DEAP is coordinated to the tripositive metal ion through the diethylcarboxamide carbonyl and antipyrine carbonyl oxygens in a bidentate fashion.

Keywords. Lanthanide nitrate complexes; N,N-diethylantipyrine-4-carboxamide; electrolytic conductance; infrared; ^{13}C NMR.

1. Introduction

Antipyrine and its derivatives such as 4-aminoantipyrine and 4-dimethylaminoantipyrine are known to form stable complexes with a variety of lanthanide salts (Koppikar *et al* 1978). A literature survey on antipyrine reveals that the 4-position of antipyrine is amenable to a variety of organic reactions such as the Friedel-Craft's acylation, Mannich reaction and Vilsmeier formylation, and therefore it should be possible to introduce a suitable functional group at 4-position of the antipyrine ring and make it a potential new multidentate ligand for metal ions. In this communication we report the preparation and characterization of lanthanide nitrate complexes with DEAP.

2. Experimental

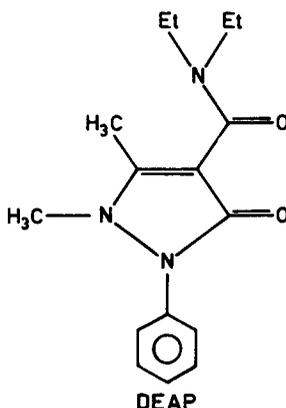
2.1 Materials

Antipyrine used was an E Merck product. Lanthanide oxides (99.9% pure) were obtained from the Indian Rare-Earths Limited, Kerala State, India. All solvents were purified by standard methods.

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2.2 Preparation of the ligand (DEAP)

DEAP was prepared from antipyrine via the formation of 4-formylantipyrine (Ledurt *et al* 1961), which in turn was first oxidized to antipyrine-4-carboxylic acid by potassium permanganate, and the acid then converted to the amide (Takahashi and Kanemaksu 1958) through the formation of acid chloride. ^1H NMR: CDCl_3 , 1.18 δ (*t*, CH_3 of N-ethyl group); 2.37 δ and 3.17 δ (*s*, CH_3 's of the antipyrine group); 3.50 δ (*q*, CH_2 of N-ethyl group); 7.35 δ (*m*, phenyl group of antipyrine).



2.3 Preparation of lanthanide nitrates

Hydrated lanthanide nitrates were prepared by dissolving the corresponding oxides in 50% nitric acid and evaporating the solution on a steam bath.

2.4 Preparation of lanthanide nitrate complexes

Hydrated lanthanide nitrate (1 mM) dissolved in hot ethylacetate (5 ml) was treated with the ligand (4 mM) also taken in ethyl acetate (10 ml). The solution was stirred for 5 minutes, when a sticky solid separated. The ethyl acetate was decanted off, the residual solid washed thrice with hot ethyl acetate (15 ml) to remove the unreacted ligand (if any) and the solid finally dried at the pump (≈ 3 mm/Hg) at 60°C for about 45 minutes to obtain the complex.

2.5 Analyses

The metal and anion contents were estimated as reported previously (Rajasekar and Soundararajan 1979). The ligand was analysed spectrophotometrically by the calibration curve method at 265 nm in aqueous solution.

2.6 Physical measurements

Conductance, infrared, and ^{13}C NMR for the complexes were obtained by methods reported earlier (Rajasekar and Soundararajan 1979).

3. Results and discussion

The analytical data presented in table 1 reveal that the complexes have the general composition $[\text{Ln}_2(\text{DEAP})_3][\text{NO}_3]_6$, where Ln = La, Pr, Nd, Sm, Tb, Ho, Er, Yb and Y. The complexes are stable, although they were stored over Phosphorus(V) oxide *in vacuo* to prevent any possible absorption of water.

Molar conductance values in CH_3CN indicate that all the nitrate groups are non-ionic (Geary 1971).

The principal IR bands relevant to the immediate discussion regarding the nature of coordination of the ligand to the tripositive metal ions are presented in table 2. The antipyrine carbonyl stretching frequency appearing at 1690 cm^{-1} in the ligand is lowered by about 55 cm^{-1} in the complexes, while the diethylcarboxamide carbonyl stretching frequency appearing at 1630 cm^{-1} is lowered by about 30 cm^{-1} upon complexation. The shift in these carbonyl stretching frequencies to lower fields, due to the drainage of electron density from the C=O bond, amply demonstrates the participation of the antipyrine carbonyl and diethylcarboxamide oxygens in the bonding to the metal ions. The $\Delta\nu_{\text{CO}}$ (where $\Delta\nu_{\text{CO}} = \nu_{\text{CO}(\text{ligand})} - \nu_{\text{CO}(\text{complex})}$) for the antipyrine carbonyl in the present complexes is of the same order as those for antipyrine complexes (58 cm^{-1}) of lanthanide perchlorates (Krishnamurthy and Soundararajan 1967). Therefore, the present value of $\Delta\nu_{\text{CO}}$ is much greater than those in 4-aminoantipyrine complexes (30 cm^{-1}) (Chacko *et al* 1975). The strength of antipyrine carbonyl to metal bond, follows the sequence



Nitrate groups are capable of bonding to a metal ion in a unidentate or bidentate fashion. Coordination involving either mode lowers the symmetry of the ionic nitrate from D_{3h} to C_{2v} . The two situations cannot, in general, be unambiguously distinguished on the basis of the IR data alone. In the absence of Raman data, the combination bands which generally appear in the region 1700–1800 region have been used for structural assignments of the nitrate groups (Curtis and Curtis 1965). The observation of two weak bands in the above said region and the absence of a strong band at $\approx 1350\text{ cm}^{-1}$ in all the complexes studied, rules out the possibility of

Table 1. Analytical and molar conductance data for DEAP complexes.

Complexes	% Found			% Calculated			$\Lambda_{\text{M}}^{\circ}$ (in CH_3CN)
	Metal	Ligand	Anion	Metal	Ligand	Anion	
$[\text{La}_2(\text{DEAP})_3][\text{NO}_3]_6$	18.51	57.03	24.69	18.40	56.98	24.61	15
$[\text{Pr}_2(\text{DEAP})_3][\text{NO}_3]_6$	18.47	56.83	24.55	18.61	56.83	24.55	12
$[\text{Nd}_2(\text{DEAP})_3][\text{NO}_3]_6$	18.52	56.74	24.39	18.54	56.60	24.45	16
$[\text{Sm}_2(\text{DEAP})_3][\text{NO}_3]_6$	19.49	56.21	24.26	19.60	56.13	24.26	14
$[\text{Tb}_2(\text{DEAP})_3][\text{NO}_3]_6$	20.47	55.51	24.12	20.50	55.51	23.98	11
$[\text{Ho}_2(\text{DEAP})_3][\text{NO}_3]_6$	21.11	55.18	23.76	21.11	55.08	23.80	8
$[\text{Er}_2(\text{DEAP})_3][\text{NO}_3]_6$	21.38	55.01	23.69	21.31	54.95	23.74	14
$[\text{Yb}_2(\text{DEAP})_3][\text{NO}_3]_6$	21.99	54.61	23.57	21.91	54.53	23.56	10
$[\text{Y}_2(\text{DEAP})_3][\text{NO}_3]_6$	12.60	61.03	26.28	12.60	61.03	26.37	10

* Molar conductance in $\text{Ohms}^{-1}\text{ cm}^2\text{ mol}^{-1}$

Table 2. The principal absorption bands in the IR spectra of DEAP and its lanthanide nitrate complexes (in cm^{-1}).

DEAP	La	Pr	Nd	Sm	Tb	Ho	Er	Yb	Y	Assignment
	1776 vw	1775 vw	1775 w	1780 w	1785 w	1775 w	1782 vw	1785 vw	1785 w	$\nu_2(\text{A}_1) + \nu_5(\text{A}_1)$
	1745 w	1745 m	1745 m	1740 w	1750 w	1745 m	1740 w	1752 vw	1745 w	$\nu_2(\text{A}_1) + \nu_6(\text{B}_2)$ nitrate
1690 s	1635 s	1635 vs	1635 vs	1635 vs	1635 s	1630 s	1635 s	1630 s	1635 s	C=O (antipyrine)
1625 s	1600 s	1600 vs	1600 s	1600 s	1600 m	1600 m	1600 m	1600 m	1600 m	C=O (carboxamide)
	1470 s, br	1466 vs, br	1472 vs, br	1485 vs, br	1470 vs, br	1475 vs, br	1475 br	1485 br	1485 br	$\nu_1(\text{A}_1)$ nitrate
	1300 vs, br	1285 s	1315 s, br	1312 s, br	1315 s, br	1315 s	1310 s, br	1305 s, br	1305 s, br	$\nu_4(\text{B}_2)$ nitrate
	1040 vs	1045 m	1045 m	1040 vs	1038 vs	1040 s	1038 vs	1040 vs	1038 s	$\nu_2(\text{A}_1)$ nitrate
	825 s	822 m	825 m	825 s	820 s	822 s	820 s	822 s	822 s	$\nu_3(\text{B}_1)$ nitrate
	805 m	796 m	790 m	796 m	796 s	796 w	798 m	796 m	798 m	
	750 vs	755 s	755 s	750 s	755 vs	750 s	760 vs	755 vs	755 s	$\nu_5(\text{A}_1)$ nitrate
	702 s	702 s	702 s	702 s	$\nu_6(\text{B}_2)$ nitrate					

s - strong; vs - very strong; m - medium; br - broad; w - weak.

Table 3. ^{13}C NMR data (All values are in δ with respect to TMS).

Nucleus	DEAP	La^{3+} complex	Y^{3+} complex
Antipyrine CO	164.24	167.20	166.90
Carboxamide CO	162.54	164.00	163.28
N-CH ₂	35.00	33.98	33.92
N-CH ₃	13.30	13.24	13.27

an ionic nitrate group in these complexes. The data further suggest that only one type of coordinated nitrate group is present in these complexes. The separation of the combination bands observed in the present complexes is in the range $33\text{--}40\text{ cm}^{-1}$, indicating a bidentate mode of coordination of the nitrate group in all these complexes. This is in accordance with the observation of Haque *et al* (1971) that bidentate nitrate is preferred in the complexes of *f*-block transition metals. This can be attributed to the favourable metalnitrate interaction for a given degree of nitrate-nitrate repulsion.

Additional evidence regarding the coordinating nature of the ligand with the lanthanide ions is obtainable from a study of ^{13}C NMR spectrum of the ligand and its diamagnetic La^{3+} and Y^{3+} complexes (table 3). The resonances of the carbonyl carbons, namely, the diethylcarboxamide carbonyl carbon and antipyrine carbonyl carbon appear at $162.54\ \delta$ and $164.24\ \delta$, respectively, in the ligand DEAP. The former shows a downfield shift of about $1.46\ \delta$ in La^{3+} and $0.74\ \delta$ in Y^{3+} complexes respectively, while the latter exhibits a downfield shift of about $2.96\ \delta$ in La^{3+} complex and $2.66\ \delta$ in Y^{3+} complex. The downfield shift of the two complexes respectively, while the latter exhibits a downfield shift of about $2.957\ \delta$ in La^{3+} complex and $2.675\ \delta$ in Y^{3+} complex. The downfield shift of the two resonances can be attributed to the deshielding of the carbonyl oxygens, because of bonding of the carbonyl oxygens to the lanthanide ions and a concomitant reduction in the $\text{C}=\text{O}$ π -bond order. The coordination of the two carbonyl oxygens is further supported by the upfield shifts observed in the carbons of the N-CH₂ (closer to the diethylcarboxamide moiety) and N-CH₃ (far away from the carbonyl group) groups.

With the available data presented here, a nine coordinate geometry can tentatively be assigned for all the complexes of DEAP.

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