

SYNTHESIS AND SPECTROSCOPIC INVESTIGATIONS OF COMPLEXES OF LANTHANIDE NITRATES WITH N-(4-METHYL-2-PYRIDYL)-ACETAMIDE

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ABSTRACT

New complexes of lanthanide nitrates with N-(4-methyl-2-pyridyl)-acetamide (4-me-aapH) of the general formulae $[\text{Ln}(4\text{-me-aapH})_2][\text{NO}_3]_3$ (where Ln = La–Yb and Y) have been synthesised and characterised by chemical analysis, molar conductivity and physical methods such as infrared, ^{13}C NMR and electronic spectra in the visible region. Molar conductance and infrared data point to the presence of coordinated nitrate groups. Infrared and ^{13}C NMR data have been interpreted in terms of the coordination of the ligand to the metal ion through the oxygen of the secondary amide and nitrogen of the heterocyclic ring, in a bidentate fashion. Coordination number of ten seems probable for the complexes.

INTRODUCTION

RESULTS AND DISCUSSION

A SURVEY of literature shows that a large number of oxygen donor ligands have been used for complexing with a number of lanthanide salts¹. It is only recently that complexes in which aromatic nitrogen and even aliphatic nitrogen serve as donor atoms² have been prepared. The presence of oxygen and nitrogen, both as donor atoms, in a neutral ligand has received little attention so far. In this communication we wish to report the synthesis of and spectroscopic investigations on complexes of lanthanide nitrates with 4-Me-aapH, in which both the oxygen and nitrogen are situated so favourably as to function as a potential bidentate ligand.

Analytical results of the compounds conform to the general formulae $[\text{Ln}(4\text{-Me-aapH})_2][\text{NO}_3]_3$ (where Ln = La–Yb and Y). All the complexes were soluble in methanol, acetone, acetonitrile and dimethylformamide, but insoluble in chloroform and benzene. The results of analysis agreed with the calculated values within the limits of experimental errors.

EXPERIMENTAL

Materials

4-Me-aapH was prepared from 2-amino-4-methylpyridine as reported in the literature⁴. All solvents were purified by standard methods.

Hydrated lanthanide nitrates were prepared by dissolving the corresponding oxide (99.9% pure) in 50% nitric acid and evaporating the solution on a water-bath.

Preparation of the Complexes

Hydrated lanthanide nitrate (1 mM) dissolved in hot methanol (10 mM) was added dropwise with stirring to the ligand (3 mM) also taken in methanol (5 ml). The solvent was evaporated on a steam-bath. The sticky solid obtained was washed thrice with hot chloroform (5 ml) and finally dried in vacuum (*ca.* 3 mm/Hg) at 60° C for about 45 minutes. The metal and anion contents were estimated as reported previously⁵. The physical methods of measurement have been reported earlier⁶.

Molar conductance values in acetonitrile indicate that the nitrate groups are all non-ionic⁷.

The principal infrared bands and their assignments are shown in Table I. From a comparison of the spectra of the ligand and its complexes, the nature of coordination of the ligand to the metal ion can very well be understood. The amide I band appearing at 1675 cm^{-1} in the ligand is lowered by 30 cm^{-1} on complexation. On the other hand, the amide IV and amide VI bands exhibit shifts in the opposite direction, thereby proving that oxygen of the secondary amide group is coordinated to the metal^{8,9}. This is further supported by the shifts to higher frequencies of the amide II and amide III bands.

$\nu_{\text{C}=\text{C}}$ and $\nu_{\text{C}=\text{N}}$ stretching modes of the complexes are shifted to higher frequencies compared to the ligand, indicating that the double bond character of C=C and C=N bond increases as a consequence of coordination by nitrogen¹⁰. Ring in-plane deformations also shift to higher frequencies, as a consequence of the coordination of the heterocyclic nitrogen to the metal^{8,10}.

Nitrate groups are capable of coordinating to the metal ion in a unidentate or bidentate fashion. The two situations, in the absence of Raman data, cannot, in general, be unambiguously distinguished on the basis of infrared data alone. The combination bands of the nitrate group which generally appear at 1700

TABLE I
IR spectral data for 4-Me-aapH and its complexes

Ligand	La	Pr	Nd	Tb	Ho	Er	Yb	Y	Assignment
	1775vw	1775vw	1775vw	1778vw	1775vw	1770vw	1765vw	1775vw	$\nu_2(A_1) + \nu_5(A_1)$
1675vs	1740vw	1740vw	1740vw	1740vw	1735vw	1740vw	1740vw	1738vw	$\nu_2(A_1) + \nu_6(B_2)$ nitrate
1675vs	1660m	1655s	1655s	1640s	1650s	1642s	1655s	1645s	amide I
1618vs	1630vs	1630s	1630vs	1622s	1630vs	1628vs	1638vs	1595sh	$\nu_{C=C}, \nu_{C=N}$ stretching
1575vs	1586sh	1590sh	1586sh	1590sh	1590sh	1590sh	1595sh		amide II
1550s	1570m	1570s	1560s	1560s	1575s	1566m	1578s		
1470s	1475vs, b	1475vs, b	1475vs, b	1472vs, b	1475vs, b	1472v, b	1475s, b	1475vs, b	$\nu_1(A_1) +$ ligand
1305vs } 1285 } 1270 }	1300s, b	1300s, b	1300s, b	1298s, b	1300s, b	1300, b	1300s, b	1298s, b	amide III + $\nu_4(B_2) +$ ligand
1170vs	1175m	1175m	1175m	1175m	1175m	1175m	1175m	1175m	ring CH
1120	1130m	1130m	1130m	1135m	1132m	1130m	1132m	1130m	deformations
1040s	1040vs	1040vs	1040vs	1035vs	1038vs	1038vs	1038vs	1032vs	$\nu_2(A_1) +$ ligand
975s	990s	990s	990m	990m	990s	990m	985vs	985vs	CH ₃ rocking
830vs	828vs	830m	830m	830m	832m	835m	830s	832vs	$\nu_3(B_1) +$ ligand
		820s	820s	820s	820vs	820vs	820s	820vs	
750m	750s	750vs	750s	750	750s	750s	755s	750vs	$\nu_5(A_1) +$ CH out-of- plane bending
728s	730s	730s	730s	730s	730vs	730vs	730s	730vs	
680s	687w, sh	687w, sh	687w, sh	687w, sh	687w, sh	687w, sh	687w, sh	687w, sh	amide IV
617vs	620s	620vs	620s	620s	620s	620m	620vs	620s	ring deformations
555vs	562s, b	562vs	562vs	565m, b	565s, b	562m, b	562s, b	562s	amide VI
417m	426w	426w	426w	426w	425m	425m	425w	427s	ring out-of-plane deformations

Abbreviations : vs = very strong; s = strong; m = medium; w = weak; b = broad; sh = shoulder.

1800 region have been used for structural assignments for the nitrate groups^{11,12}. In the present complexes, the presence of two weak bands in the above said region appears to suggest that the nitrate groups are coordinated to the metal ions in a bidentate fashion. It has been shown that *f*-block transition metals prefer bidentate coordination of the nitrate groups, to monodentate or ionic coordination which is attributed to the favourable metal-nitrate interaction for a given degree of nitrate-nitrate repulsion¹³. All the other bands of the nitrate group (bidentate) have been assigned on the basis of the available literature^{11-12,14-17}. The positions of these bands agree well with those reported in literature.

The nature of bonding of the amide group is also shown by the ¹³C NMR spectra. The resonance for the carbonyl carbon which appears at 169.699 δ in the ligand is shifted to lower field to 172.644 δ and 172.706 δ in the case of La³⁺ and Y³⁺ complexes

respectively. This lower field shift is indicative of the deshielding of the carbonyl carbon due to the reduction in the π -bond order of C=O bond, as a consequence of the coordination of the amide oxygen to the metal ion.

The deshielding of C₃, C₄ and C₅ resonances and the shielding of C₂ and C₆ resonances of the heterocyclic ring, are similar to those observed in the study of the effect of protonation, on the ¹³C chemical shifts of pyridine¹⁸. The shielding of C₂ and C₆ resonances can be taken as evidences of coordination of the ring nitrogen to Ln³⁺ ions. Moreover, factors such as changes in π -bond order on complexation or protonation and changes in the average excitation energy to the paramagnetic term of the ¹³C shielding parameters contribute to the upfield shifts of the C₂ and C₆ resonances of the ring.

The electronic spectral assignments of Nd³⁺, Ho³⁺ and Er³⁺ complexes along with their J level values are

shown in Table II. Sinha's¹⁹ covalency parameter δ has been calculated from the expression,

$$\delta = [(1 - \beta) / \beta] \times 100,$$

where δ is the average value of $\nu_{\text{complex}} / \nu_{\text{aquo}}$. The positive value of δ is suggestive of a certain amount of covalency in the metal-ligand bond.

TABLE II

Electronic spectral data of Nd, Ho and Er complexes

Nd ³⁺		Ho ³⁺		Er ³⁺	
J level	Energy (KK)	J level	Energy (KK)	J level	Energy (KK)
⁴ G _{9/2}	19.46	⁵ G ₅	24.04	⁴ F _{7/2}	20.53
⁴ G _{7/2}	18.94	⁵ F ₃	21.98	⁴ H _{11/2}	19.04
⁴ G _{5/2}	17.09	⁴ S ₂ , ⁵ F ₄	18.62		
$\beta = 0.9869$		$\beta = 0.0263$		$\beta = 0.9934$	
$\delta = 1.327$		$\delta = 0.3900$		$\delta = 0.6643$	

The shapes and positions of the bands are similar both in the solid state and in solution. This indicates a similarity in the coordination around the metal ions in both the states. In the present complexes the bands were not well split to allow a comparison to be made with the reported hypersensitive shapes of some β -diketonates of known coordination number²⁰.

With the available data presented here, a tentative coordination number of ten is assigned to the complexes of 4-Me-aapH.

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