

## STUDIES OF SUBSTITUTED AMIDO DERIVATIVES OF LANTHANIDES

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**ABSTRACT.** The synthesis of lanthanide amido derivatives of the type  $\text{Ln}(\text{CH}_3\text{CONR})_3$  (I),  $(i\text{-OPr})\text{Ln}(\text{C}_6\text{H}_5\text{CONC}_6\text{H}_5)_2$  (II), where  $\text{Ln} = \text{La, Pr, Nd}$ ;  $\text{R} = \text{C}_6\text{H}_5$ ,  $p\text{-NO}_2\text{C}_6\text{H}_4$ ,  $p\text{-BrC}_6\text{H}_4$ , are described. The physical properties, elemental analyses and IR spectra indicate deprotonation of the secondary amide. Anion coordination is proposed as chelating bidentate ligands.

## INTRODUCTION

The presence of amido group as a repeating unit in biologically important polypeptides and proteins [1] has developed great interest. The coordination of amides to metal is through oxygen in most cases [2-4] except in few cases where coordination of amide to metal is through nitrogen atom [5,6]. In addition to coordination a proton may be lost from the amide  $\text{NH}_2$  or  $\text{NH}$  group resulting in the formation of an amide derivative involving O-C-N-M bonding as shown in silver [7], platinum [8,9], mercury [10] and aluminium [11] complexes. In the present work preparation of amido derivatives is described by the reaction of lanthanide isopropoxides with N-phenylbenzamide, N-*p*-bromophenylacetamide and N-*p*-nitrophenylacetamide involving deprotonation of the amide group (-CONH-).

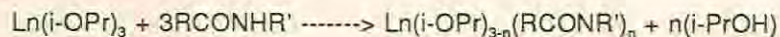
## EXPERIMENTAL

The substituted amides like N-phenylbenzamide, N-phenylacetamide, N-*p*-bromophenylacetamide and N-*p*-nitrophenylacetamide were further purified by recrystallisation from ethanol. Lanthanum, praseodymium and neodymium isopropoxides were prepared [12,13] under anhydrous conditions by refluxing a mixture of lanthanide isopropoxide and amide, in anhydrous benzene, with molar ratio of 1:1, 1:2, 1:3 and 1:4. The molar ratio of 1:4 gave the desired complexes. In case of N-phenyl-, N-*p*-bromophenyl- and N-*p*-nitrophenyl acetamides insoluble solids obtained, were washed with 1:1 mixture of benzene and ethanol and dried under reduced pressure ( $10^{-2}$  torr/4 hr). N-phenyl benzamide gave a benzene soluble amido derivative which was isolated by concentrating the filtrate, and removing the excess benzene under vacuum.

Lanthanides in the product were determined as  $\text{Ln}_2\text{O}_3$  [14]. Nitrogen was determined by Kjeldahl method and isopropanol in the azeotrope determined by oxidimetric method [15]. Bromine was estimated by Volhard's method [14]. The results of the elemental analysis show good agreement with the expected values.

## DISCUSSION

When lanthanide isopropoxide was mixed in 1:3 molar ratio with substituted acetamides separately and refluxed in benzene for 6 hr, isopropanol was liberated according to the following reaction:



where Ln = La, Pr, Nd; n = 3 when RCONHR' = CH<sub>3</sub>CONHC<sub>6</sub>H<sub>5</sub>, CH<sub>3</sub>CONH-*p*-C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>, CH<sub>3</sub>CONH-*p*-C<sub>6</sub>H<sub>4</sub>Br; n = 2 when RCONHR' = C<sub>6</sub>H<sub>5</sub>CONHC<sub>6</sub>H<sub>5</sub>.

Table 1. IR spectral frequencies of lanthanide complexes (cm<sup>-1</sup>)

Complex/Free Ligand	<sup>ν</sup> H	<sup>ν</sup> C=O Amide-I	<sup>ν</sup> N-H Amide-II	<sup>ν</sup> C-N Amide-III	<sup>ν</sup> CO l-OPr	<sup>ν</sup> M-O/M-N
1. C <sub>6</sub> H <sub>5</sub> CONHC <sub>6</sub> H <sub>5</sub>	3318, s	1660, s	1528, s	1258, s	--	--
2. La(C <sub>6</sub> H <sub>5</sub> CONC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (l-OPr)	--	1652, s	1530, w	1262, s	1025, s 1100, m	642, m 612, m 506, m
3. Pr(C <sub>6</sub> H <sub>5</sub> CONC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (l-OPr)	--	1650, s	1522, w	1260, s	1022, s 1070, s	650, w 610, w 510, w 398, w
4. Nd(C <sub>6</sub> H <sub>5</sub> CONC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (l-OPr)	--	1650, s	1530, sh	1265, s	1030, m 1078, m	650, w 618, m 512, w 405, w
5. CH <sub>3</sub> CONH <i>p</i> -C <sub>6</sub> H <sub>4</sub> Br	3200, m	1672, s	1585, s	1278, s	1168, m	--
6. La(CH <sub>3</sub> CON <i>p</i> -C <sub>6</sub> H <sub>4</sub> Br) <sub>3</sub>	--	1665, s	1580, sh	1265, s	--	625, w 665, w 402, w
7. Pr(CH <sub>3</sub> CON <i>p</i> -C <sub>6</sub> H <sub>4</sub> Br) <sub>3</sub>	--	1670, s	1580, w	1272, s	--	655, w 568, w 508, w
8. Nd(CH <sub>3</sub> CON <i>p</i> -C <sub>6</sub> H <sub>4</sub> Br) <sub>3</sub>	--	1668, s	1580, w	1272, s	--	622, w 502, w 400, s
9. CH <sub>3</sub> CONH <i>p</i> -C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>	3280, m	1688, s	1585, s	1278, s	--	--
10. La(CH <sub>3</sub> CON <i>p</i> -C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> ) <sub>3</sub>	--	1678, s	1570, w	1265, s	--	630, w 530, w
11. Pr(CH <sub>3</sub> CONH <i>p</i> -C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> ) <sub>3</sub>	--	1680, s	1572, w	1272, s	--	630, w 580, w 535, w 445, w
12. Nd(CH <sub>3</sub> CONH <i>p</i> -C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> ) <sub>3</sub>	--	1680, s	1572, sh	1272, s	--	632, w 538, w 445, w 378, w
13. CH <sub>3</sub> CONHC <sub>6</sub> H <sub>5</sub>	3290, s	1678, s	1562, s	1263, s	--	--
14. La(CH <sub>3</sub> CONHC <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	--	1660, s	1555, w	1258, s	--	660, w 608, w
15. Pr(CH <sub>3</sub> CONHC <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	--	1660, s	1550, w	1260, s	--	650, w 610, w 550, w 408, w
16. Nd(CH <sub>3</sub> CONHC <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	--	1655, s	1555, w	1255, w	--	666, w 610, w 538, w 405, w

s= strong, w=weak, m=medium, sh=shoulder



The reactions are quite facile and the products obtained were in quantitative yields. It has also been observed that the reactions of *p*-substituted *N*-phenyl acetamides were relatively faster compared to that of *N*-phenylacetamide. This may be due to the substituent in *p*-position which increases the basic character of *N* in the NH group and facilitate deprotonation of NH group of the anilides. All these complexes are solid and coloured, except those of *N-p*-nitrophenylacetamide complexes which are yellow. These complexes are insoluble in organic solvents except those of *N*-phenylbenzamide derivatives, which are soluble in benzene. Polymeric configuration of the complexes may contribute to their insolubility. The solids are susceptible to moisture, but quite stable in dry air. Most derivatives were stable up to 300 °C, except those of *N*-phenylbenzamido and *N-p*-nitrophenyl acetamide which show characteristic melting points.

The IR spectra of many secondary amides have been studied in solid and solution phases [16-18]. An intense band observed at 3270 cm<sup>-1</sup>, in solid state of free amides, is due to N-H vibrations. The  $\nu_{\text{N-H}}$  vibrations in the lanthanide amido complexes have disappeared suggesting deprotonation of amide [8-10]. The  $\nu_{\text{C=O}}$  vibrations in anilides appear at 1680 cm<sup>-1</sup> [16]. But in the lanthanide amido complexes these occur at lower frequency by 5-10 cm<sup>-1</sup> compared to the corresponding vibrations in the free amides [8-10]. The decrease in the carbonyl frequency in these derivatives, on replacement of hydrogen atom by the heavy metal atom may indicate the involvement of carbonyl oxygen in coordination to the metal atom. The strong absorption at 1560-1530 cm<sup>-1</sup> (amide II band) and at 1270 cm<sup>-1</sup> (amide III band) appear in spectra of free anilides. The band is due to ( $\delta_{\text{NH}} + \nu_{\text{CN}}$ ) vibrations but in complexes in this region, a very weak band is observed which suggests the absence of NH group in molecules.

The region under 700 cm<sup>-1</sup> is the region of various M-X (X = O, N etc.) vibrations. Lanthanide amido derivatives show 3 to 4 bands in this region which might be due to (M-O/M-O + M-N) stretching vibrations [19-21]. Some of these metal ligands modes produce weak bands which are difficult to distinguish from ligand vibrations [22].

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### REFERENCES

1. Zabicky, J. *The Chemistry of Anilides*, Interscience: London; 1970.
2. Paul, R.C. *New Pathways in Inorganic Chemistry*, Ebsworth, E.A.V.; Maddock, A.G. and Sharpe, A.G. eds, Cambridge University Press: Cambridge; 1968.
3. Ojima, H. *Inorganic Chemistry: Coordination Behaviour of the Amide Group*, Kagaku No Rvoiki; 1972, 26, p. 246.
4. Homer, R.B. and Johnson, C.D. *The Chemistry of Amides*, Interscience: London; 1970; p 187.
5. Rao, C.A.; Mahapatra, B.K.; Guru, G. *J. Ind. Chem. Soc.* 1976, 53, 1240.
6. Farona, M.F.; Ayers, W.T.; Ramsey, B.G.; Grasselli, O.J.G. *Inorg. Chim. Acta.*, 1969, 3, 503.
7. Chernyaev, I.I.; Nazarova, L.A. *Neorg. Khim. Akad. Nauk. SSSR*, 1951, 26, 101.
8. Brown, D.B.; Burbank, R.D.; Robin, M.B. *J. Am. Chem. Soc.* 1969, 91, 2895.
9. Brown, D.B.; Burhank, R.D.; Robin, M.B. *J. Am. Chem. Soc.*, 1968, 90, 5621.
10. Brown, D.B.; Robin, M.B. *Inorg. Chim. Acta.*, 1969, 3, 644.
11. Matrofanova, E.V.; Stepovik, D.P. *Zh. Obshch. Khim.* 1969, 36, 1488.
12. Misra, S.N.; Misra, T.N.; Kapoor, R.N.; Mehrotra, R.C. *Chem. Ind.*, 1963, 120.

13. Misra, S.N.; Misra, T.N.; Mehrotra, R.C. *Aust. J. Chem.*, **1968**, 21, 797.
14. Vogel, A.I. *Textbook of Quantitative Inorganic Analysis*, Longman: London; 1985; p 432.
15. Bradley, D.C.; Abad-El-Halim, F.M.; Wardlaw, W. *J. Chem. Soc.*, **1950**, 3450.
16. Richards, R.F.; Thompson, H.W. *J. Chem. Soc.*, **1947**, 1248.
17. Belamy, L.J. *The Infrared Spectra of Complex Molecules*, Methuen: London; 1958; pp 209-220.
18. Rao, C.N.R. *Chemical Applications of Infrared Spectroscopy*, Academic Press: New York; 1963.
19. Sinha, S.P. *Complexes of Rare Earths*, Pergamon: Oxford; 1966.
20. Febraro, J.R.; Basile, L.J.; Kovocil, D.L. *Inorg. Chem.*, **1966** 5, 391.
21. Forsberg, J.H. *Coordination Chemistry Review*, **1973**, 10, 195.
22. Katon, J.E.; Fearirhellar, Jr.W.R.; Pustingu, J.V. *J. Anal. Chem.*, **1964**, 36, 2126.