

2, 4-LUTIDINE-1-OXIDE COMPLEXES OF LANTHANIDE NITRATES AND CHLORIDES

N. S. NAVANEETHAM AND S. SOUNDARARAJAN*

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560 012

ABSTRACT

2, 4-Lutidine-1-oxide (2, 4-LutO) complexes of lanthanide nitrates of the formulae $\text{Ln}(\text{NO}_3)_3(2, 4\text{-LutO})_4$ where $\text{Ln} = \text{La}$ and Pr , $\text{Nd}_2(\text{NO}_3)_6(2, 4\text{-LutO})_7$ and $\text{Ln}(\text{NO}_3)_3(2, 4\text{-LutO})_3$ where $\text{Ln} = \text{Tb}$, Dy and Yb and $\text{LnCl}_3(2, 4\text{-LutO})_5$ where $\text{Ln} = \text{La}$, Pr , Nd , Tb , Dy and Yb , have been prepared and characterised by chemical analysis, IR, NMR, and conductance data. IR data indicate both mono and bidentate nitrate groups in the complexes of La and Pr-nitrates and only bidentate nitrate groups in the other lanthanide nitrate complexes. Proton NMR data along with the IR data show that the ligand coordinates to the metal through the oxygen. Conductance data of the complexes in acetonitrile suggest that all the anions are coordinated to the metal.

1. INTRODUCTION

2-METHYL pyridine-1-oxide (2-PicO) and 2,6-dimethyl pyridine-1-oxide (2,6-LutO) complexes of lanthanide nitrates have the same metal to ligand ratio, indicating that the steric effect due to the methyl groups at 2, and 2 : 6 positions of the pyridine-1-oxide, respectively is the same^{1,2}. However, the steric effect is less in the 2-PicO complexes compared to 2,6-LutO complexes of the lanthanide chlorides^{3,4}. In this paper we report the complexes of 2,4-dimethylpyridine-1-oxide (2,4-LutO) with lanthanide nitrates and chlorides. The complexes have been characterised by analytical, IR, NMR and conductance data and the results have been compared with those of the corresponding complexes of 2-PicO and 2, 6-LutO.

2. EXPERIMENTAL

2.1. Materials

2, 4-Lutidine was obtained from Aldrich Chemical Co., U.S.A. Lanthanide oxides 99.9% pure, were obtained from Indian Rare Earths Ltd., Kerala State. All other chemicals used were of reagent grade. Solvents were purified by standard methods.

2.2. Preparation of the ligand 2, 4-LutO

The ligand prepared according to the method given by Ochiai⁵, by the N-oxidation of 2, 4-Lutidine, was purified by distillation under reduced pressure (110°/1 mm Hg).

2.3. Preparation of the hydrated lanthanide salts

The hydrated lanthanide nitrates were prepared by dissolving the corresponding oxides in dilute nitric acid and evaporating the solution on a steam bath. Hydrated lanthanide chlorides were prepared similarly, using hydrochloric acid.

2.4. (a) Preparation of the lanthanide nitrate complexes

Hydrated lanthanide nitrate (0.6 mM) was mixed with excess ligand (3.6 mM) followed by the addition of acetone (2-3 ml) and heated on a steam bath with stirring, to get a clear solution. On heating the

solution, with stirring, on the steam bath, a solid was formed, which was stirred with benzene (10 ml), filtered, washed with benzene dried and preserved over phosphorus (V) oxide in a vacuum desiccator.

(b) Preparation of lanthanide chloride complexes

0.6 mM of the hydrated lanthanide chloride was mixed with 3.6 mM of the ligand and heated on the steam bath, with stirring. The salt dissolved first and on continuous heating and stirring, a solid complex formed which was stirred with about 10 ml of benzene, filtered, washed with benzene, dried and preserved over phosphorus (V) oxide in a vacuum desiccator.

2.5. Analyses

The metal content of the complexes was estimated by EDTA titrations using xylenol orange as the indicator⁶. The nitrate and the chloride were estimated by the nitron-nitrate method⁷ and Volhard's method respectively. The ligand 2,4-LutO was estimated spectrophotometrically at 254 nm, using the calibration curve method. The analytical data are presented in Table I.

2.6. Physical Methods

The IR spectra of the complexes of lanthanide nitrates in nujol mulls, of the lanthanide chloride complexes in KBr pellets and of the ligand (neat) were recorded on a Carl-Zeiss-UR-10 Infrared spectrophotometer. The principal IR bands and their tentative assignments are given in Table II.

Proton NMR spectra of the complexes and the ligand were recorded on a Varian T-60 instrument using CDCl_3 as the solvent and TMS as the internal standard (Table III).

Conductance measurements in acetonitrile were carried out in a Sieman's conductivity bridge using an immersion cell (type LTA), calibrated with standard KCl solution. The concentrations of the solutions used were of the order of 0.001 M (Table I).

3. RESULTS AND DISCUSSION

Both the nitrate and the chloride complexes are hygroscopic and are soluble in chloroform and aceto-

* To whom all correspondence should be directed.

TABLE I
Analytical and Molar Conductance Data

Complexes	% Metal		% Ligand		% Anion		Molar Conductance in acetonitrile at 23° C ohms ⁻¹ cm ² g mole ⁻¹
	Found	Calculated	Found	Calculated	Found	Calculated	
La (NO ₃) ₃ (LutO) ₄	17.08	17.01	62.43	60.37	22.74	22.77	57.55
Pr (NO ₃) ₃ (LutO) ₄	17.36	17.20	59.78	60.08	22.69	22.72	85.65
Nd ₂ (NO ₃) ₆ (LutO) ₇	18.65	18.97	55.62	56.68	24.62	24.44	54.93
Tb (NO ₃) ₃ (LutO) ₃	22.17	22.23	52.37	51.69	26.08	25.72	67.12
Dy (NO ₃) ₃ (LutO) ₃	22.46	22.51	52.04	51.42	38.15
Yb (NO ₃) ₃ (LutO) ₃	23.57	23.76	51.06	50.69	39.64
LaCl ₃ (LutO) ₅	16.09	16.15	70.08	71.47	12.24	12.38	34.98
PrCl ₃ (LutO) ₅	16.56	16.33	69.52	71.31	12.13	12.35	49.06
NdCl ₃ (LutO) ₅	16.88	16.66	70.81	71.04	12.08	12.30	81.2
TbCl ₃ (LutO) ₅	18.28	18.05	72.33	69.85	11.9	12.1	52.62
DyCl ₃ (LutO) ₅	18.67	18.4	72.14	69.56	11.96	12.05	35.14
YbCl ₃ (LutO) ₅	19.34	19.34	69.12	68.77	11.59	11.91	26.47

TABLE II
I.R. Spectra of 2, 4-LutO complexes of lanthanide nitrates in nujol mull

2, 4-LutO*	La	Pr	Nd	Tb	Dy	Yb	Assignment
1245 vs	1240 vs	1240 vs	1235 vs	1235 vs	1235 vs	1230 vs	N-O stretching
830 s	830 s	832 s	830 s	830 s	830 s	830 s	N-O bending
800 s	810 s	810 s	810 s	810 s	810 s	810 s	C-H out-of-plane
	1758 vw } 1780 vw }	1758 vw } 1785 vw }	1770 vw	1780 vw	1780 vw	1785 vw	$\nu_2(A_1) + \nu_5(B_2)$ Nitrate
	1740 vw	1745 vw	1745 vw	1745 w	1742 vw	1748 w	$\nu_2(A_1) + \nu_6(B_2)$ Nitrate
1045 m	1050 s	1050 s	1035 s	1035 s	1038 s	1040 s	$\nu_2(A_1)$ Nitrate + Ligand
	1345 s	1345 s	1315 s	1315 s br	1315 s br	1325 s br	$\nu_4(B_2)$ Nitrate
	825 s	825 s	820 s	820 s	820 s	820 s	$\nu_3(B_1)$ Nitrate
740 s	740 m	740 m	745 m	745 s	745 s	745 s	$\nu_5(A_1)$ Nitrate + Ligand
	715 vw	710 vw	708 vw	710 vw	710 w	710 w	$\nu_5(B_2)$ Nitrate

I.R. Spectra of 2, 4-LutO complexes of lanthanide chlorides in KBr pellets

1245 vs	1235 vs	1235 vs	1235 vs	1230 s	1230 s	1235 s	N-O stretching
830 s	830 w	830 w	830 w	835 br	830 w	830 w	N-O bending
800 s	808 s	808 s	808 s	800 m	810 s	810 s	C-H-out-of-plane
1485 vs	1480 s	1480 s	1480 s } 1490 s }	1490 s	1490 s br	1480 s } 1495 s }	Ring breathing

* Ligand = neat.

vs = very strong, s = strong, w = weak, vw = very weak, m = medium, br = broad.

TABLE III
 Proton NMR Spectral Data

Compound	(6-H)	(3, 5-H)	2-CH ₃	4-CH ₃
2, 4-LutO	1.94	3.04	7.57	7.72
La (NO ₃) ₃ (LutO) ₄	1.75	3.02	7.49	7.69
Pr (NO ₃) ₃ (LutO) ₄	-6.13	0.8 (3-H) } 1.14 (5-H) }	5.1	6.5
Nd ₂ (NO ₃) ₆ (LutO) ₇	-3.56	1.24 (3-H) } 1.64 (5-H) }	6.04	6.74
Yb (NO ₃) ₃ (LutO) ₃	1.63	4.55 (3-H) } 4.98 (5-H) }	8.03	8.62
LaCl ₃ (LutO) ₅	1.20	2.85	7.35	7.65
PrCl ₃ (LutO) ₆	0.34	-0.18 (3-H) } 1.85 (5-H) }	5.42	6.17
NdCl ₃ (LutO) ₆	0.0	1.67 (3-H) } 2.3 (5-H) }	6.87 (2 and 4 CH ₃)	
YbCl ₃ (LutO) ₅	6.65	5.084	8.85 (2 and 4 CH ₃)	

Spectra of 2, 4-LutO and its complexes were obtained in CDCl₃.

TMS was used as the internal reference. Chemical shifts are given in τ .

nitrile. They are insoluble in benzene and carbon tetrachloride. The colours of the complexes resemble those of the parent salts but appear to be less intense.

Analytical data show that the complexes of lanthanide nitrates have the formulae Ln (NO₃)₃ (2, 4-LutO)₄ where Ln = La and Pr, Nd₂ (NO₃)₆ (2, 4-LutO)₇, and Ln (NO₃)₃ (2, 4-LutO)₃ where Ln = Tb, Dy and Yb. The corresponding complexes of lanthanide chlorides have the formula LnCl₃ (2, 4-LutO)₅ where Ln = La, Pr, Nd, Tb, Dy and Yb. The ligand to metal ratio in the heavier lanthanide nitrate complexes is the same as in the corresponding complexes of 2-PicO and 2, 6-LutO^{1,2}.

Molar conductance data in acetonitrile indicate that all the complexes behave as nonelectrolytes in this solvent⁸, suggesting thereby that all the anions are coordinated to the metal.

The IR spectra of the complexes of the lanthanide nitrates show that the N-O stretching vibration of the ligand occurring at 1245 cm⁻¹ is shifted to 1240 cm⁻¹ in the La and Pr-complexes and to 1230-35 cm⁻¹ in the complexes of Nd, Tb, Dy and Yb. The shift to lower frequencies indicates the coordination of the ligand through the oxygen of N-O group. The $\Delta\nu_{N-O}$ (5-15 cm⁻¹) in these complexes being less than that observed for the corresponding 2-PicO (20-35 cm⁻¹) and 2,6-LutO (21-30 cm⁻¹) complexes with lanthanide nitrates^{1,2}, suggests a weaker metal-ligand bond. The shift of the C-H out of plane vibration

of the ligand at 800 cm⁻¹ to 810 cm⁻¹ in all the complexes is indicative of the drainage of electron density from the pyridine ring to the metal ion. The nature of binding of the nitrate groups to the metal can be predicted by examining the combination bands in the 1700-1800 cm⁻¹ region of the IR spectrum⁹⁻¹³. There are three combination bands in the spectra of the complexes of La (1740, 1758 and 1780 cm⁻¹) and Pr (1745, 1758 and 1785 cm⁻¹) nitrates, showing thereby the presence of both mono and bidentate nitrate groups¹⁴. The spectra of the complexes of Nd, Tb, Dy and Yb nitrates containing only two combination bands with a separation of 28-38 cm⁻¹ which lies in the range (29-54 cm⁻¹) reported for bidentate nitrate groups^{11,13} reveals bidentate bonding of the nitrate groups in these complexes.

The IR spectra of lanthanide chloride complexes resemble closely. The $\Delta\nu_{N-O}$ (10-15 cm⁻¹) which is less than that found in the corresponding complexes^{5,4} of 2-PicO (1723 cm⁻¹) and 2, 6-LutO (18-23 cm⁻¹) points to a weaker metal-ligand bond. However the $\Delta\nu_{N-O}$ value for the chloride complexes being more than that for the corresponding nitrate complexes of 2, 4-LutO, suggests a stronger metal-ligand bond in the chloride complexes. This may be attributed to a better donor property of the nitrate group compared to that of the chloride. The C-H out-of-plane vibration of the ligand shifts to a higher wave number by 10 cm⁻¹ as in the case of the nitrate complexes.

The proton NMR spectra of the diamagnetic complexes are sharp and well resolved. The doublet occurring at 1.94τ in the free ligand corresponds to the 6-H signal, while that at 3.04τ is due to the 3-H and 5-H and those at 7.57τ and 7.72τ to 2-methyl and 4-methyl proton signals respectively. A significant shift of the aromatic proton signals of the ligand arises from a deshielding of the protons due to the drainage of the electron density from the ligand to the metal, on coordination. The down field shift of the 6-H signal of the ligand in the lanthanum nitrate complex is less than that in the complex of lanthanum chloride. This may be due to a greater metal ion-oxygen interaction, in agreement with the IR data, in the chloride complex, and a weaker metal ion-oxygen interaction and/or an interaction of 6-H with the coordinated nitrate groups^{15,16} in the nitrate complex. The isotropic shifts for the Pr, Nd and Yb, complexes show that both contact and pseudocontact interactions are operative as is generally observed for paramagnetic lanthanide complexes^{17,18}. The 2 and 4-methyl proton signals of the ligand merge in the NMR spectrum of Nd(III) and Yb(III) chloride complexes. Tb(III) and Dy(III) nitrate and chloride complexes show very much broadened signals whose positions could not be measured accurately. The 3-H and 5-H signal of the ligand splits into two in the case of Yb(III) nitrate, Pr(III) and Nd(III) (both nitrate and chloride) complexes. In the cases of Pr(III), Nd(III) and Yb(III) complexes, for which the position of the signals could be measured, the assignments of 3-H and 5-H have been made as per the data given for 2-PicO complexes of lanthanide iodides¹⁹. The broadening of the 5-H signal compared to that of 3-H in Pr(III) complexes is indicative of the proximity of the 5-H of the ligand to the metal ion. The broadening of the 6-H signal in all the paramagnetic complexes is due to the relaxation effects.

4. BONDING AND COORDINATION NUMBER

The proton NMR data along with the IR data for the complexes of lanthanide nitrates and chlorides indicate the coordination of the ligand through the oxygen of the N-O group and a weaker metal-ligand bond in the complexes of lanthanide nitrates compared to that in the chloride complexes.

The non-electrolytic behaviour of the La and Pr nitrate complexes in acetonitrile, in conjunction with the IR data for the nitrate groups suggest a coordination number of 8 or 9 for the lanthanide ions according to whether one or two nitrate groups are bidentate. In the Nd(III) nitrate complex the formula being $\text{Nd}_2(\text{NO}_3)_6(2,4\text{-LutO})_7$, the IR data indicating only bidentate nitrate groups and in view of the non-electrolytic behaviour of the complex in acetonitrile, a tentative coordination number of 10 has been assigned,

involving an oxygen bridging of 2,4-LutO ligand. For the other complexes the conductivity data along with the IR data suggest a coordination number of 9 in consonance with that found in the 2-picO and 2, 6-LutO complexes of lanthanide nitrates^{1,2}.

The IR data of the lanthanide chloride complexes along with the non-electrolytic behaviour of the complexes in acetonitrile, suggest a coordination number of 8 for the lanthanide ions in these complexes, which is in line with that found for the corresponding complexes of 2-PicO⁴.

ACKNOWLEDGEMENTS

One of the authors (N. S. N.) thanks the University Grants Commission (U.G.C.) for a fellowship under Faculty improvement programme.

1. Ramakrishnan, L. and Soundararajan, S., *Monatsh. Chem.*, 1976, 107, 1095.
2. —, *Ph.D. Thesis*, Indian Institute of Science, 1977.
3. Sivapullaiyah, P. V., *Ph.D. Thesis*, Indian Institute of Science, 1976.
4. — and Soundararajan, S., *Curr. Sci. (India)*, 1976, 45, 711.
5. Ochiai, E., *J. Org. Chem.*, 1953, 18, 548.
6. Kolthoff, I. M. and Elwing, P. J., *Treatise on Analytical Chemistry*, Part II, New York, Interscience, 1963, 8, 57.
7. Vogel, A. I., *A Text Book of Quantitative Inorganic Analysis*, 3rd edition, The English Language Book Society and Longmans, London, 1962, p. 583.
8. Geary, W. J., *Coord. Chem. Rev.*, 1971, 7, 81.
9. Curtis, N. F. and Curtis, Y. M., *Inorg. Chem.*, 1965, 4, 804.
10. Addison, C. C., Logan, N., Wallwork, S. C. and Garner, C. D., *Quart. Rev. Chem. Soc.*, 1971, 25, 289.
11. Lever, A. B. P., Montovani, E. and Ramaswamy, B. S., *Canad. J. Chem.*, 1971, 49, 1957.
12. Foster, R. J. and Hendriker, D. G., *Inorg. Chim. Acta*, 1972, 6, 371.
13. Ferraro, J. R., Cristallini, C. and Fox, I., *J. Inorg. Nucl. Chem.*, 1967, 29, 139.
14. Strallo, D. K., Drage, R. S. and Donoghue, J. T., *Inorg. Chem.*, 1962, 1, 848.
15. Hart, F. A., Newbery, J. E. and Shaw, D., *J. Inorg. Nucl. Chem.*, 1970, 32, 3585.
16. Miller, J. D. and Frince, R. H., *J. Chem. Soc.*, 1965, p. 3185.
17. Lesis, W. B., Jackson, J. A., Lemons, J. F. and Tauke, H., *J. Chem. Phys.*, 1962, 36, 694.
18. Sanjets, J. K. M., Hanson, S. W. and Williams, E. H., *J. Am. Chem. Soc.*, 1972, 94, 5325.
19. Ramakrishnan, L. and Soundararajan, S., *Proc. Indian Acad. Sci.*, 1977, 86 A (1), 59.