

THE SYNTHESIS AND PROPERTIES OF 2-*m*-TOLYLAMINO-4-*m*-TOLYIMINO-2-PENTENE COMPLEXES OF THE TRIPOSITIVE LANTHANIDE IONS

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ABSTRACT

The reaction of 2-*m*-tolylamino-4-*m*-tolylimino-2-pentene (TTP) with a lanthanide (III) nitrates in anhydrous acetonitrile yields solid compounds of the types $[\text{Ln}(\text{TTP})_4](\text{NO}_3)_3$; $[\text{Ln}(\text{TTP})_4\text{NO}_3](\text{NO}_3)_2$; and $[\text{Ln}(\text{TTP})_3(\text{NO}_3)_2](\text{NO}_3)$; where $\text{Ln}^{3+} = \text{La, Pr, Nd, Sm, Er, and Yb}$ and $\text{TTP} = 2\text{-}m\text{-tolylamino-4-}m\text{-tolylimino-2-pentene}$. Nitrate ion coordination in several of the complexes is established by infrared data. The decrease in metal ion radius across the lanthanide series does not affect the number of ligand molecules coordinated to the Ln^{3+} ion, but the coordination by nitrate is affected. The result is a variation of total coordination number of the cation.

INTRODUCTION

LANTHANIDE (III) nitrate chelates, with 2-phenylamino-4-phenylimino-2-pentene, 2-benzylamino-4-benzylimino-2-ene, etc., were recently synthesised and characterised¹⁻². In this communication, the isolation and characterisation of lanthanide nitrate chelates with 2-*m*-tolylamino-4-*m*-tolylimino-2-pentene (TTP) are described.

EXPERIMENTAL SECTION

Reagents

The anhydrous lanthanide (III) nitrates were prepared from lanthanide oxides³. Reagent grade acetonitrile was dried by distillation with phosphorus pentoxide. TTP was prepared by the procedure reported elsewhere⁴.

Synthesis of the complexes.—A solution of TTP in acetonitrile (12 mM for tetrakis, and 6 mM for

tris chelates) was added slowly to a well stirred lanthanide nitrate solution (2 mM) in acetonitrile employing a dry box. The precipitate thus formed was refluxed for 8 hr for completion of the reaction.

Analysis.—Carbon, hydrogen, and nitrogen were estimated by micro methods. Metal estimations were carried out by standard procedures⁵. A complete list of lanthanide chelates and their analytical data are given in Table I. The infrared spectra were recorded on a Perkin-Elmer infracord spectrophotometer model 521 in KBr pellets.

RESULTS AND DISCUSSION

Infrared Spectra.—The infrared spectra of EEE chelates of the lanthanide (III) nitrate in the regions of nitrate absorption are given in Table II. Assignments of the nitrate ion absorption are

TABLE I
Compounds prepared and the analytical data

Compounds prepared*	Colour	% Metal		% C		% H		% N	
		Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
$[\text{La}(\text{TTP})_4\text{NO}_3](\text{NO}_3)_2$	White	9.64	9.85	63.28	63.36	6.38	6.30	10.69	10.56
$[\text{Pr}(\text{TTP})_4\text{NO}_3](\text{NO}_3)_2$	Green	9.77	9.99	63.20	63.10	6.37	6.32	10.68	10.60
$[\text{Nd}(\text{TTP})_4\text{NO}_3](\text{NO}_3)_2$	Violet	9.97	10.15	63.05	62.88	6.36	6.46	10.64	10.58
$[\text{Sm}(\text{TTP})_4\text{NO}_3](\text{NO}_3)_2$	White	10.33	10.48	62.81	62.86	6.33	6.39	10.60	10.40
$[\text{Er}(\text{TTP})_4](\text{NO}_3)_3$	Pink	11.37	11.48	62.09	62.25	6.25	6.29	10.48	10.46
$[\text{Yb}(\text{TTP})_4](\text{NO}_3)_3$	White	11.73	11.99	61.84	61.74	6.23	6.32	10.44	10.30
$[\text{La}(\text{TTP})_3(\text{NO}_3)_2](\text{NO}_3)$	White	11.96	12.16	58.87	58.78	5.93	6.16	10.84	10.78
$[\text{Pr}(\text{TTP})_3(\text{NO}_3)_2](\text{NO}_3)$	Green	12.12	13.08	58.76	58.80	5.92	6.04	10.82	10.83
$[\text{Nd}(\text{TTP})_3(\text{NO}_3)_2](\text{NO}_3)$	Violet	12.34	12.45	58.62	58.60	5.91	5.89	10.80	10.70
$[\text{Sm}(\text{TTP})_3(\text{NO}_3)_2](\text{NO}_3)$	White	12.78	12.94	58.32	58.40	5.88	5.80	10.74	10.70
$[\text{Er}(\text{TTP})_2(\text{NO}_3)_3](\text{NO}_3)$	Pink	14.04	15.01	57.49	57.32	5.79	5.80	10.57	10.60
$[\text{Yb}(\text{TTP})_2(\text{NO}_3)_3](\text{NO}_3)$	White	14.46	15.10	57.22	57.18	5.77	5.76	10.54	10.46

* Designation of coordination sphere dictated by i.r. spectral data.

TABLE II

I.R. Data for '3' representative complexes indicating the nature of the nitrate groups (in cm^{-1})*

Complex	ν_1	ν_2	ν_3	$\nu_1 + \nu_2$	$\nu_1 = \nu_3$	$2\nu_1$	Nature of the Nitrate group
$[\text{La}(\text{TTP})_3\text{NO}_3]$	820 (m)	1360 (s)	700 (w)	1750 (vw)	2382 (vw)	2055 (vw)	Ionic
$(\text{NO}_3)_2$	796 (m)	1350 (s)	768 (w)	1710 (vw)	2270 (vw)		Monodentate
		1490 (s)	726 (w)	1725 (vw)	2415 (vw)	2050 (vw)	
$[\text{La}(\text{TTP})_4](\text{NO}_3)_2$	832 (m)	1355 (s)	706 (w)	1750 (vw)	2416 (vw)	2045 (vw)	Ionic
$[\text{La}(\text{TTP})_3(\text{NO}_3)_2]$	828 (m)	1365 (s)	704 (w)	1748 (vw)	2375 (vw)	2060	Ionic
$(\text{NO}_3)_2$	809 (m)	1250 (s)	690 (vw)	1723 (vw)	2290 (vw)	2070	Bidentate
		1495 (s)	746 (m)	1758 (vw)	2545 (vw)		

* Assignments based on ref. no. (7).

based upon two possible symmetry types, D_{3h} (free nitrate) and C_{2v} coordinated nitrate⁶⁻⁸.

All the tris chelates show absorptions characteristic of both the ionic and bidentate nitrate groups, and hence the complexes have been formulated as $[\text{Ln}(\text{TTP})_3(\text{NO}_3)_2](\text{NO}_3)$ on the basis of steric grounds. The infrared spectra of these chelates show a greater weakening of ν_3 , greater splitting of ν_3 and ν_4 and large shift of ν_2 to lower frequency.

The lighter tetrakis chelates La^{3+} to Sm^{3+} have absorption characteristic of both ionic and monodentate nitrate groups and hence the chelates have been formulated as $[\text{Ln}(\text{L})_4\text{NO}_3](\text{NO}_3)_2$ on the basis of steric grounds. The infrared spectra of the nitrate ions are similar for the chelates, the main differences from bidentate chelates being the considerable weakening of ν_3 , splitting of ν_3 and ν_4 and a small shift of ν_2 to lower frequency.

The complexes $\text{Ln}(\text{TT})_4](\text{NO}_3)_3$, ($\text{Ln} = \text{Er}$ and Yb) with eight amine donor groups show bands corresponding only to ionic nitrate groups. It is apparent that as the radius of the lanthanide ion decreased, the single coordinated nitrate group in the tetrakis chelates is forced out from the coordination sphere due to steric crowding of the amine ligand molecules.

The tetrakis chelates of heavier lanthanides show strong absorption at 3240 cm^{-1} , which is shifted by 50 cm^{-1} towards the higher frequency when a nitrate group is introduced into the coordination sphere (La^{3+} to Sm^{3+}). A slight splitting of this band is also observed. The effect of coordination is clearly demonstrated for tris chelates (bands observed at $\sim 3298 \text{ cm}^{-1}$) in which three well resolved bands are observed. In each case how-

ever, the stretching frequencies of coordinated NH groups is less than the free ligand value (3328 cm^{-1}). This may be attributed to the combined effects of coordination to a positive metal ion⁹ and hydrogen bonding between the anion present and the NH proton¹⁰. The large number of amino bands observed upon nitrate coordination may be attributed to non-equivalent sets of amino groups. The increase in frequency of one set may result from repulsions between the nitrogen end of the NH dipole and the coordinated nitrate ion or poorer hydrogen bonding of the amino protons with the coordinated nitrate ion.

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