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The Template Synthesis and Characterization of Hexaaza 18-Membered Macrocyclic Complexes of Cerium(III), Praseodymium(III) and Neodymium-(III) Nitrates*

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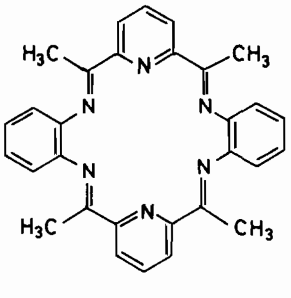

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We have previously described the preparation and characterization of heavier trivalent lanthanide (Tb to Lu) complexes containing 14-membered quadridentate macrocyclic ligands [1]. The lighter lanthanide ions (La to Gd) have been found to be ineffective as templates for the synthesis of this macrocycle. The important factor which must be taken into account in the planning of the synthesis of macrocyclic compounds with the aid of metal ion is the ratio of cation diameter to ligand cavity size. The cavity of 14-membered macrocycle is too small to enclose the lighter lanthanides. It was therefore interesting to investigate the template action of these ions in the synthesis of macrocyclic ligands with greater ring size. We found that the lanthanum ion may act as a template for the synthesis of 18-membered hexaaza sexidentate macrocyclic compounds [2, 3]. The formation of the lanthanide complexes of some macrocyclic Schiff bases has recently been reported [4, 5].

This paper reports the preparation and characterization of Ce(III), Pr(III) and Nd(III) macrocyclic complexes derived from 2,6-diacetylpyridine and *o*-phenylenediamine.

The complexes of 2,7,13,18-tetramethyl-4,5:15,16-dibenzo-3,6,14,17,23,24-hexaazatricyclo[17.3.1 1.^{8,12}]tetrakoza-1(23),2,4,6,8,10,12(24),13,15,17,19,21-dodecaene ligand (**L**) have been prepared by adding *o*-phenylenediamine (2 mmol) in methanol (15 ml) (purified by column chromatography on alumina using chloroform as eluent and recrystallized from benzene and chloroform) to the mixture of appropriate hydrated lanthanides (1 mmol) in methanol (15 ml) and 2,6-diacetylpyridine (2 mmol) in methanol (15 ml). The reaction mixture was heated under reflux with stirring for 4 h. After cooling and partial evaporation of solvent the resulting microcrystalline precipitates were filtered off, washed with ether and dried in a dessicator over P_2O_5.

The complexes appear to be air stable products, moderately soluble in CH_3CN and DMSO.

The isolated complexes are formulated as $[LnL(NO_3)_3]\cdot 2H_2O$, where Ln = Ce, Pr and Nd on the basis of spectral data and thermal analysis. Elemental analysis figures are consistent with the above formula (Table I).

The infrared spectra of the complexes (Table II) taken in the region 4000–200 cm^{-1} are all very similar to one another and provide some information regarding the bonding in the complexes. The most diagnostic absorption band is C=N stretching mode observed at *ca.* 1600 cm^{-1}. The infrared spectra of all complexes are devoid of uncondensed functional groups ($-NH_2$, C=O) stretching modes of starting materials. It therefore may be concluded that cyclization has occurred to give the desired macrocyclic compounds. The profile of the pyridine ring vibrations observed in the 1600–1400 cm^{-1} region is characteristic of coordinated pyridine [6]. There is also a strong band at 1000 cm^{-1}

TABLE I. Yields and Analytical Data for the Complexes.

Complex	Yield (%)	Calculated			Found		
		%C	%H	%N	%C	%H	%N
$[CeL(NO_3)_3]\cdot 2H_2O$	68	43.27	3.63	15.14	43.38	3.71	15.04
$[PrL(NO_3)_3]\cdot 2H_2O$	70	43.27	3.63	15.13	43.31	3.66	15.08
$[NdL(NO_3)_3]\cdot 2H_2O$	67	43.06	3.61	15.06	42.89	3.57	15.02

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TABLE II. Infrared (cm^{-1}) and Electronic (nm) Spectral Data for the Complexes.

Complex	$\nu_{C=N}$	ν_{py}	ν_{Ln-N}	$\nu_{NO_3^-}$	ν_{O-H}	λ
$[CeL(NO_3)_3]\cdot 2H_2O$	1610	1590, 1570, 1460, 1000	300	1465, 1288, 1040, 820, 740	3400	225, 240 280, 355
$[PrL(NO_3)_3]\cdot 2H_2O$	1608	1595, 1568, 1455, 1000	290	1465, 1295, 1040, 823, 745	3400	228, 238, 275, 357
$[NdL(NO_3)_3]\cdot 2H_2O$	1610	1590, 1570, 1455, 1000	290	1470, 1290, 820, 743	3380	225, 235, 277, 358

typical for metal bonding at the pyridine nitrogen atom [7]. All infrared spectra show medium bands at 290–300 cm^{-1}. It seems reasonable tentatively to assign these absorptions to metal–nitrogen stretching vibration [7, 8].

The broad diffuse band of medium intensity in the 3450–3350 cm^{-1} region is observed in the infrared spectrum for all complexes indicating the symmetric and antisymmetric O–H stretching modes for lattice water. The absorption characteristic of coordinated water does not appear in the infrared spectrum of these complexes. The thermogravimetric analysis confirms this observation indicating the loss of two molecules of water at 40–70 °C for all the complexes.

Information about the bonding mode of the nitrate ions and thus about the tentative coordination number of lanthanides in these complexes may also be obtained from the infrared spectra. The free nitrate ion has relatively high symmetry (D_{3h}) and its infrared spectrum consists of three absorptions bands at *ca.* 1390, 830 and 720 cm^{-1}. When a nitrate ion becomes coordinated in monodentate, bidentate or bridging fashion its effective symmetry is reduced to only C_{2v}. This causes the degeneracies to split and all modes to be infrared active. Hence, it is easy to distinguish between ionic and coordinated nitrate groups [9].

The infrared spectrum of all complexes (Table II) demonstrates the presence of coordinated nitrates. The band characteristic of ionic nitrate at 1390 cm^{-1} does not appear. The two new bands associated with the asymmetric stretch appear near 1470 and 1290 cm^{-1}. The separation ($\Delta\nu$) of the nitrate stretching fundamentals has been used as a criterion to distinguish between degree of covalency of the nitrate coordination [10]. $\Delta\nu$ increases as the coordination of the nitrate groups increases from monodentate to bidentate and/or bridging. The magnitude of this separation (177, 170 and 180 cm^{-1} for Ce(III), Pr(III) and Nd(III) complexes, respectively) is indicative of a strong interaction of the oxygen atoms of the nitrates with the lanthanide ions and typical of bidentate bonding. The mode at *ca.* 1040 cm^{-1}, normally forbidden in the infrared spectrum for ionic nitrates, becomes alowed and gives evidence for chelating bidentate behaviour of the nitrate groups in all three complexes.

The electronic spectra of solutions of the complexes in acetonitrile taken in the range 220–700 nm exhibit absorption bands attributable to the coordinated macrocycle and may be assigned to the $\pi \rightarrow \pi^*$ transitions of the ligand [3, 11].

The mass spectra of the complexes provide strong evidence for the presence of macrocyclic compounds showing the highest fragment at m/z 470 corresponding to the molecular weight of the uncoordinated macrocycle. The elemental compositions of the most abundant ion and other principal fragmentation ions and proposed fragmentation pathways are similar as reported previously [3].

The cerium(III), praseodymium(III) and neodymium(III) ions have been therefore found to be effective templates for the synthesis of a conjugated 18-membered hexaaza macrocyclic ligand. References to the known structures of related 18-membered macrocyclic complexes and examination of molecular model of this macrocycle reveals that its cavity would have a diameter of not less than 5.4 Å [4, 12]. Thus these lanthanide ions with the twelve coordinate ionic diameter 2.50–2.54 Å [13] are sufficiently large to be effectively bounded to all six nitrogen donor atoms of this macrocycle.

On the basis of the spectral and analytical data along with molecular model analysis it seems reasonable to assign a tentative coordination number of twelve for the lanthanide ions in the studied complexes. The metal ion is presumably coordinated to the six nitrogen atoms of the macrocyclic ligand and to six oxygen atoms of bidentate nitrate groups. Such a high coordination number is especially observed for lanthanide nitrates of oxygen and nitrogen donor macrocyclic complexes [14]. The nitrate ions, contrary to, for example, perchlorates, are known to be very good complexing agents towards the lanthanides. Thus the complexation of the lanthanides by macrocycles depends not only on the size and rigidity of the internal cavity of the ligand but also on the complexing properties of the anions involved in the coordination.

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