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Preparation and Characterization of Lanthanum(III) Complex of the Hexadentate Macrocyclic Ligand 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

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Although transition metal complexes of the macrocyclic ligands have been known for several years the coordination of the rare earth elements by synthetic polyaza macrocycles has been little studied [1–3].

In previous papers we have described the results of our investigations concerning the possibility of using the rare earth elements as templates in the synthesis of the nitrogen donor macrocycles. We have reported the preparation and characterization of trivalent Sc, Tb, Dy, Ho, Er, Tm, Yb and Lu complexes containing 14-membered quadridentate hexaaza macrocyclic ligand [4, 5]. The lighter lanthanides (La to Gd) have been found to be ineffective as templates for the synthesis of this macrocycle under similar conditions. Instead, the ring-opened complexes have been formed [5]. It was therefore interesting to investigate the template action of lighter lanthanides in the synthesis of macrocyclic ligands with greater ring size. We have recently reported the preparation and characterization of 18-membered hexaaza macrocyclic complex of lanthanum(III) perchlorate formed in the reaction of 2,6-diacetylpyridine and ethylenediamine using a metal ion as a template for the ring closure [6].

The synthesis of the title ligand (L) in the absence of metal ion and also in the presence of Cu(II) ion under which conditions the macrocycle was isolated as the binuclear complex, has been reported [7]. Attempts to prepare a Ba(II) complex of this macrocycle have so far proved unsuccessful [8].

The template condensation of 2,6-diacetylpyridine with *o*-phenylenediamine in the presence of lanthanum(III) nitrate is the subject of this paper.

The lanthanum(III) complex of L has been prepared as its nitrate salt 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 $La(NO_3)_3 \cdot 6H_2O$ (obtained from La_2O_3) (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 hours. The yellow solution turned light brown. The resulting yellow-brown microcrystalline precipitate was filtered off, washed with ether and dried in a dessicator over P_2O_5. A mineral acid is not necesary for the cyclization to occur. However, in the presence of several drops of dilute nitric acid the complex is formed more rapidly and the reaction is complete after 2 hours.

The formulation of this complex as $[La(C_{30}H_{26}N_6)(H_2O)_2](NO_3)_3$ follows from spectral data (i.r., u.v.–vis., n.m.r. and m.s.) and thermal analysis. Elemental analysis figures are consistent with the above formula. The complex appears to be an air stable solid, moderately soluble in CH_3CN and DMSO.

The infrared spectrum of the complex in KBr pellets taken in the region 4000–300 cm^{-1} confirms the formation of the macrocyclic compound by the absence of the bands characteristic of carbonyl and amine groups in the starting materials and the appearance of a strong absorption band at 1609 cm^{-1} attributable to the coordinated $>$C=N stretching mode [4, 9]. The spectrum contains medium to strong bands at 1590, 1572, 1460 and 1415 cm^{-1} as expected for high energy pyridine vibrations. The low energy pyridine bands are observed at 620 and 420 cm^{-1} suggesting the coordination of pyridine nitrogen [4–6, 10].

The nitrate ion vibrations observed in the infrared spectrum of the complex at 1360 and 840 cm^{-1} are consistent with the presence of the noncoordinated nitrate groups [11]. However, the presence of coordinating nitrate groups cannot be completely ruled out since the combination regions which are commonly used to establish the coordination mode of these anions are obscured by vibrations arising from the ligand.

The νOH absorption band appears in the infrared spectrum of the complex at 3330 cm^{-1}. In addition, weak bands are detectable at 855 and 555 cm^{-1} as expected for rocking or wagging modes of water molecules coordinated to the metal [4–6, 12, 13]. The thermogravimetric analysis confirms this observation indicating the loss of two water molecules at 105–150 °C.

The electronic spectrum of solutions of the complex in acetonitrile taken in the range 220–700 nm exhibits absorption bands at 225, 245, 278 and 358 nm. Absorption in this region is attributable to the coordinated macrocycle and may be assigned to the $\pi \rightarrow \pi^*$ transitions of the ligand [9, 14].

The nuclear magnetic resonance spectrum of the complex obtained in CD_3CN solution with TMS as internal standard shows the pyridine ring protons at δ 8.2–8.6, the benzene ring protons at δ 6.9–7.4 and the methyl protons at δ 2.6 ppm. Integrated

TABLE I. Mass Spectrum of the Ligand (L).[a]

m/z	41	43	44	51	65	77	78	80	91	92	104
% rel. int.	17	16	18	10	29	24	18	24	18	24	18
m/z	108	118	133	147	158	169	194	195	196	207	220
% rel. int.	47	24	47	12	12	10	24	24	18	5	35
m/z	221	228	234	235	236	247	260	276	311	322	337
% rel. int.	18	12	29	41	29	5	6	29	40	10	13
m/z	352	363	455	456	469	470[L]$^+$					
% rel. int.	47	6	94	29	11	100					

[a] All peaks greater than 5% of the base peak (100%) are recorded.

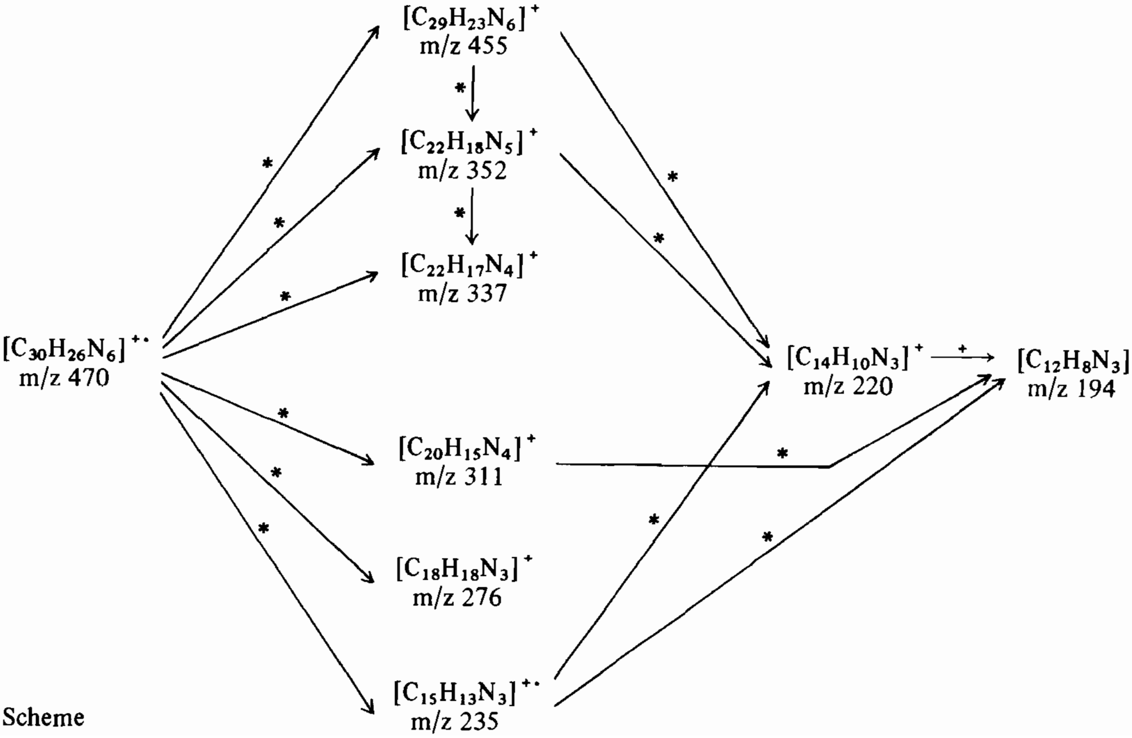
TABLE II. Elemental Composition of the Principal Ions in the Mass Spectrum of the Ligand.

Measured mass	Calculated mass	Composition
470.22178	470.22174	$C_{30}H_{26}N_6$
455.19849	455.19828	$C_{29}H_{23}N_6$
352.15631	352.15611	$C_{22}H_{18}N_5$
337.14536	337.14522	$C_{22}H_{17}N_4$
311.11714	311.12958	$C_{20}H_{15}N_4$
276.14945	276.14997	$C_{18}H_{18}N_3$
235.11078	235.11087	$C_{15}H_{13}N_3$
220.08732	220.08741	$C_{14}H_{10}N_3$
194.07302	194.07177	$C_{12}H_8N_3$

intensities of the above signals are in the ratio 3:4:6, respectively, consistent with the proposed formulation of the complex.

Further evidence for the formation of the macrocycle comes from the mass spectrum of the complex. The highest m/z fragment observed at m/z 470 corresponds to the molecular weight of the uncoordinated macrocycle. The occurrence of a strong peak corresponding to the free macrocycle instead of the parent ion peak of the macrocyclic complex is quite common for the other related macrocycles and has been reported in the mass spectra of these compounds [14–17]. The 75 eV mass spectrum of the ligand L is listed in Table I. The elemental compositions of the most abundant ion $[L]^{+\bullet}$ at m/z 470 and other principal fragmentation ions at m/z 455, 352, 311, 276, 235, 220 and 194 were determined by high resolution measurements and are compiled in Table II.

On the basis of the accurate mass determination and with the benefit of the metastable transition, the fragmentation pathways for this macrocyclic ligand are proposed as outlined in the Scheme.

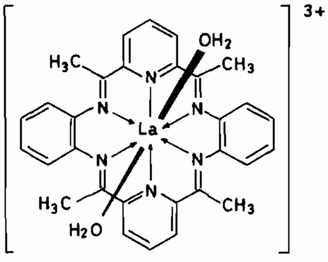


Scheme

The presence of an asterisk (*) in the Scheme indicates that metastable peaks are observed for the fragmentation in question.

These data provide evidence for the presence of the macrocycle in the complex. The lanthanum ion has been therefore found to be an effective template for the synthesis of a conjugated, 18-membered hexaaza macrocyclic ligand. The result can be rationalized in terms of metal ion radius and the dimension of the macrocycle cavity. Reference to the known structures of related 18-membered macrocyclic complexes shows that the macrocycle cavity would have a diameter of not less than 5.4 Å [8, 15, 18]. Thus the lanthanum ion with the octacoordinate ionic diameter of 2.32 Å [19] is sufficiently large to be effectively bonded to all six nitrogen atoms of the planar 18-membered macrocycle.

On the basis of the spectral and analytical data along with the molecular model analysis and on the assumption that this conjugated macrocycle maintains a near planar configuration it seems reasonable to propose a hexagonal bipyramidal structure (I) for the complex of formula $[La(L)(H_2O)_2]^{3+}$ similar to those reported recently for related macrocyclic compounds [8, 15]. It seems therefore likely that the metal ion is coordinated to the six nitrogen atoms lying in the equatorial plane and to two molecules of water in axial positions. The tentative coordination number of eight can be assigned for the lanthanum ion in this complex. However, the available evidence is not sufficient to preclude the nitrate groups coordination. The concept of noncoordinating anion inferred mainly from infrared spectroscopy may be frequently misleading in lanthanide complexes. It is proved that differing degrees of coordination produce varying effects on the vibration spctrum. 'Semi-coordination', a term used to define this delicate balance between coordinated and noncoordinated anion [20] seems to play an important role in the stabilization of a particular geometry around a lanthanide ion.



(I)

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