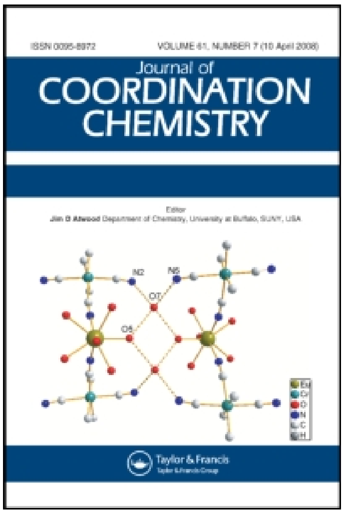

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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Qiu-Yun Chen[a]; Qin-Hui Luo[a]; Yu-Hua Mei[a]; Yong-Jiang Liu[a]; Zhong-Yuan Zhou[b]
[a] State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing, P.R. China [b] Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu, P.R. China

To cite this Article Chen, Qiu-Yun , Luo, Qin-Hui , Mei, Yu-Hua , Liu, Yong-Jiang and Zhou, Zhong-Yuan(2000) 'Synthesis, Characterization and Crystal Structure of an Unsymmetric Samarium(III) Cryptate', Journal of Coordination Chemistry, 51: 2, 125 — 134

To link to this Article: DOI: 10.1080/00958970008055124

URL: http://dx.doi.org/10.1080/00958970008055124

J. Coord. Chem., 2000, Vol. 51, pp. 125–134
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SYNTHESIS, CHARACTERIZATION AND CRYSTAL STRUCTURE OF AN UNSYMMETRIC SAMARIUM(III) CRYPTATE

QIU-YUN CHEN[a], QIN-HUI LUO[a,*], YU-HUA MEI[a],
YONG-JIANG LIU[a] and ZHONG-YUAN ZHOU[b]

[a]*State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, P.R. China;* [b]*Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu 610015, P.R. China*

(Received 23 June 1999; In final form 1 October 1999)

The complex $[Sm(H_3L)(NO_3)(H_2O)](NO_3)_2 \cdot H_2O$ was synthesized by the (2+3) condensation of tris(2-aminoethyl)amine with 2,6-diformyl-4-chlorophenol in the presence of Sm^{3+}. Its crystal structure has been determined. In the complex the coordination number of Sm^{3+} is nine. A water molecule is encapsulated in the cryptate as a guest, confirmed by electrospray mass spectrometry, thermal analysis and the X-ray crystal structure.

Keywords: Samarium(III); cryptate; crystal structure; macrocyclic ligand

INTRODUCTION

Recently the design and synthesis of macrocyclic ligands and their lanthanide complexes have aroused people's increasing interest owing to their importances in basic and applied chemistry.[1–3] For example, lanthanide complexes with encapsulating ligands have been extensively studied as supramolecular devices.[4] Lanthanide complexes of macrocyclic ligands have potential applications in biological systems and medical diagnostics, such as luminescence labels, fluorescent probes and NMR image-constrast agents.[5–8] In addition, they can also be used as catalysts for RNA cleavage,[9] NMR shift reagents *etc.*[10]

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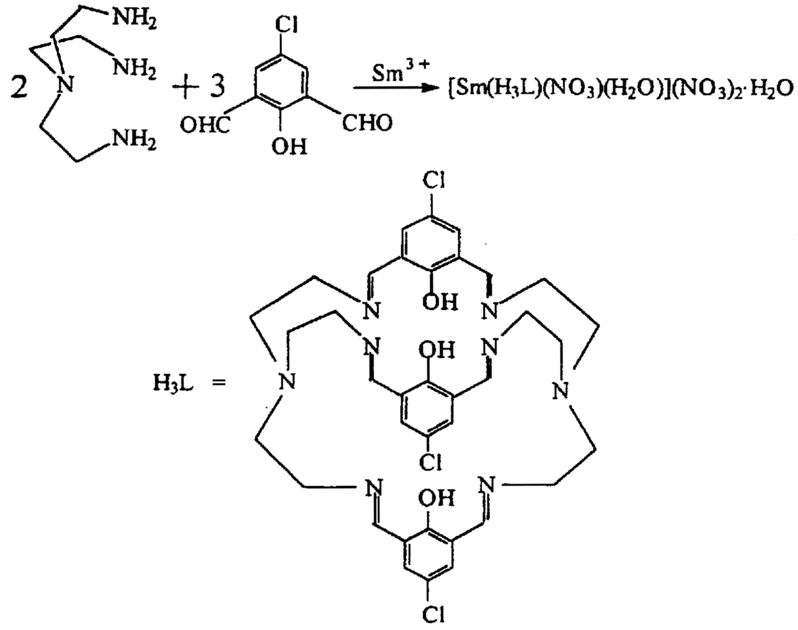
[*] Corresponding author.



SCHEME 1 The synthesis of the cryptate $[Sm(H_3L)(NO_3)(H_2O)](NO_3)_2 \cdot H_2O$.

Mononuclear and dinuclear lanthanide complexes with two-dimensional macrocyclic ligands have been extensively studied.[1] However, only a few lanthanide complexes with three-dimensional macrocyclic ligands have been reported.[11–13] The crystal structure of a samarium complex with a three-dimensional ligand has not been reported. Herein, we report the samarium complex $[Sm(H_3L)(NO_3)(H_2O)](NO_3)_2 \cdot H_2O$ synthesized by (2 + 3) Schiff-base condensation of tris(2-aminoethyl)amine (tren) with 2,6-diformyl-4-chloro-phenol (dfp) in the presence of Sm^{3+} (Scheme 1). The samarium complex has also been characterized by several physical methods. The crystal structure shows that the coordination number of Sm^{3+} is nine, and a water molecule acts as a guest encapsulated in the macrocycle being demonstrated by ES-MS and thermoanalysis. The results were compared with other analogous lanthanide complexes.

EXPERIMENTAL

All materials and solvents were of reagent grade and were used as received. Hydrated samarium nitrate was prepared by dissolving Sm_2O_3 (99.99%) in excess nitric acid; 2,6-diformyl-4-chloro-phenol and tren were prepared by literature methods.[14,15]

Physical Measurements

Elemental analysis was performed on a Perkin-Elmer 240c analytical instrument. Electrical conductivity in DMF solution containing $\sim 10^{-4}\,\mathrm{mol\,dm^{-3}}$ complex was measured using a BSD-A conductometer (Jiangsu, China). The IR spectrum was measured as a KBr disc using a Nicolet 5 DX FT-IR spectrophotometer. Thermoanalysis was performed on a SDT 2960 TA thermoanalyser under an argon atmosphere with a heating rate of $10^\circ\mathrm{C\,min^{-1}}$. The electrospray mass spectrum (ES-MS) was determined on a Finnigan LCQ mass spectrograph; the concentration of the sample was about $1.0\,\mu\mathrm{mol\,dm^{-3}}$. The diluted solution was electrosprayed at a flow rate of $5 \times 10^{-6}\,\mathrm{dm^{-3}\,min^{-1}}$ with a needle voltage of +4.5 kV. The mobile phase was an aqueous solution of methanol (v/v, 1 : 1). The sample was run in the positive-ion mode.

Preparation of $[Sm(H_3L)(NO_3)(H_2O)](NO_3)\cdot H_2O$

A methanol solution ($20\,\mathrm{cm^3}$) containing tren (0.117 g, 0.80 mmol) was added dropwise to a stirred methanol solution ($40\,\mathrm{cm^3}$) containing dfp (0.221 g, 1.2 mmol) and $Sm(NO_3)_3\cdot 6H_2O$ (0.797 g, 0.44 mmol). The reaction mixture was refluxed for 4 h, and then allowed to cool to room temperature. The yellow product $[Sm(H_3L)(NO_3)(H_2O)](NO_3)_2\cdot H_2O$ was filtered off, washed with diethyl ether and dried in a vacuum desiccator, yield, 0.28 g (62.5%). *Anal.* Calc. for $C_{36}H_{43}Cl_3N_{11}O_{14}Sm$ (%): C, 38.90; H, 3.87; N, 13.86. Found: C, 39.30; H, 4.01; N, 13.45; IR ($\mathrm{cm^{-1}}$): 3300s [ν(OH)]; 1650s [ν(C=N)]; 1640s [ν(C=N)]; 1541s [ν(C–O)]; 1470s [ν(N=O)]; 1384s [$\nu(NO_3)$]; 1296s [$\nu_{asym}(NO_2)$ and 1051s [$\nu_{sym}(NO_2)$]; Λm (DMF, 298 K): $110\,\mathrm{s\,cm^2\,mol^{-1}}$. Yellowish crystals of $[Sm(H_3L)(NO_3)(H_2O)](NO_3)_2\cdot H_2O$ suitable for X-ray structure determination were obtained by slow evaporation of the above filtrate at room temperature over one month.

Crystal Structure Determination

A yellow prismatic crystal with dimensions 0.20 × 0.16 × 0.14 mm was mounted on a glass fibre and used for the structure determination. Crystallographic data for the cryptate $[Sm(H_3L)(NO_3)(H_2O)](NO_3)_2\cdot H_2O$ are summarized in Table I. Diffraction data were collected using Siemens P4

TABLE I Crystal data and structure refinement for $[Sm(H_3L)(NO_3)(H_2O)](NO_3)_2 \cdot H_2O$

Empirical formula	$C_{36}H_{43}Cl_3N_{11}O_{14}Sm$
Formula weight	1110.51
Temperature	294(2) K
Crystal system	Orthorhombic
Space group	*Pbca*
Unit cell dimensions	$a = 16.979(3)$ Å, $\alpha = 90°$
	$b = 20.658(4)$ Å, $\beta = 90°$
	$c = 24.721(5)$ Å, $\gamma = 90°$
Volume, Z	8671(3) $Å^3$, 8
Density (calculated)	1.701 $Mg\,m^{-3}$
Absorption coefficient	1.619 mm^{-1}
$F(000)$	4488
Crystal dimensions	$0.2 \times 0.16 \times 0.14$
Limiting indices	$0 \leq h \leq 19, 0 \leq k \leq 23, 0 \leq l \leq 29$
Radiation (Å)	MoKα (0.71073 Å)
Scan mode	ω
2θ range (deg)	4.28–50.02
Reflections collected	5323
Independent reflections	5196 ($R_{int} = 0.0000$)
Goodness-of fit on F^2	0.909
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0666$, $wR_2 = 0.1612$
R indices (all data)	$R_1 = 0.1631$, $wR_2 = 0.2094$
Largest diff. peak and hole	0.922 and −0.629 eÅ

$w = 1/\sigma^2(F^2) + (0.10000P)^2 + 0.000P$; $P = (F_o^2 + 2F_c^2)/3$.

diffractometer with graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å) using the ω scan mode and corrected for absorption by semi-empirical methods. Some 5323 reflections (5196 unique) were collected in range $2.14° \leq \theta \leq 25.01°$. The structure was solved by SHELXTL-86[16] direct methods using the programs contained in the XSCANS package. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed at calculated position and refined as riding atoms with individual isotropic displacement parameters. Full-matrix least-squares refinement was on F^2 using SHELXTL 93[17] with all independent data. The final cycle gave $R = 0.067$ and $R_w = 0.161$ based on 5196 reflections $[I > 2\sigma(I)]$ (max/min residual electron density 0.922 and −0.629 $eÅ^{-3}$). All calculations were performed using the programs contained in SHELXTL package. Final atomic coordinate and selected bond distances and angles are given in Tables II and III, respectively. Full lists of crystallographic data are available from the authors upon request.

RESULTS AND DISCUSSION

The value of molar conductivity (110 $s\,cm^2 mol^{-1}$) of the complex in DMF is located in the range between that of 1 : 1 electrolytes and that of 1 : 2

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$). $U(eq)$ is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	*x/a*	*y/b*	*z/c*	*U(eq)*
Sm(1)	2015(1)	5905(1)	9332(1)	51(1)
Cl(1)	764(1)	2476(1)	8967(1)	84(1)
Cl(2)	578(1)	8225(1)	7071(1)	101(1)
Cl(3)	6273(1)	6362(1)	10 522(1)	90(1)
O(1)	2432(1)	4955(1)	8865(1)	56(1)
O(2)	2283(1)	6617(1)	8632(1)	61(1)
O(3)	3427(1)	5839(1)	9277(1)	62(1)
O(4)	783(1)	5230(1)	9281(1)	59(1)
O(5)	1069(1)	5652(1)	8508(1)	72(1)
O(6)	110(1)	4958(1)	8567(1)	95(1)
N(9)	648(1)	5281(1)	8757(1)	64(1)
N(1)	2355(1)	4870(1)	7786(1)	67(1)
N(2)	2152(1)	4967(1)	9992(1)	57(1)
N(3)	1263(1)	6108(1)	10 285(1)	63(1)
N(4)	889(1)	6721(1)	9296(1)	66(1)
N(5)	3473(1)	6637(1)	7949(1)	65(1)
N(6)	3986(1)	5334(1)	7573(1)	79(1)
N(7)	4253(1)	4956(1)	8717(1)	60(1)
N(8)	2674(1)	6707(1)	9970(1)	49(1)
C(1)	2093(1)	4397(1)	8881(1)	57(1)
C(2)	1858(1)	4033(1)	8396(1)	63(1)
C(3)	1466(1)	3444(1)	8450(1)	70(1)
C(4)	1321(1)	3193(1)	8918(1)	64(1)
C(5)	1541(1)	3498(1)	9387(1)	53(1)
C(6)	1915(1)	4098(1)	9383(1)	59(1)
C(7)	2029(1)	4371(1)	9929(1)	54(1)
C(8)	2131(1)	5204(1)	10 575(1)	79(1)
C(9)	1329(1)	5522(1)	10 635(1)	66(1)
C(10)	439(1)	6206(1)	10 155(1)	69(1)
C(11)	317(1)	6791(1)	9772(1)	75(1)
C(12)	697(1)	7063(1)	8898(1)	59(1)
C(13)	1101(1)	7197(1)	8395(1)	58(1)
C(14)	737(1)	7588(1)	8029(1)	65(1)
C(15)	1097(2)	7767(1)	7532(1)	68(1)
C(16)	1843(1)	7580(1)	7442(1)	70(1)
C(17)	2232(1)	7185(1)	7818(1)	60(1)
C(18)	1878(1)	6997(1)	8298(1)	51(1)
C(19)	3049(2)	7001(1)	7675(1)	79(1)
C(20)	4263(1)	6457(1)	7774(1)	77(1)
C(21)	4245(2)	5933(1)	7334(1)	91(1)
C(22)	4611(1)	4911(1)	7764(1)	79(1)
C(23)	4372(1)	4507(1)	8256(1)	72(1)
C(24)	4820(1)	5152(1)	9005(1)	64(1)
C(25)	4778(1)	5621(1)	9447(1)	65(1)
C(26)	5453(1)	5747(1)	9736(1)	53(1)
C(27)	5407(1)	6166(1)	10 149(1)	63(1)
C(28)	4715(1)	6470(1)	10 277(1)	54(1)
C(29)	4033(1)	6383(1)	9986(1)	53(1)
C(30)	4071(1)	5932(1)	9563(1)	60(1)
C(31)	3369(1)	6747(1)	10 174(1)	66(1)
C(32)	2061(1)	7121(1)	10 237(1)	73(1)
C(33)	1605(1)	6680(1)	10 587(1)	70(1)

TABLE II (*Continued*)

Atom	*x/a*	*y/b*	*z/c*	*U(eq)*
C(34)	3474(1)	4977(1)	7195(1)	78(1)
C(35)	2583(2)	5090(2)	7250(1)	98(1)
C(36)	2025(1)	4326(1)	7874(1)	58(1)
N(10)	1399(1)	3536(1)	6617(1)	46(1)
O(7)	2131(1)	3493(2)	6671(1)	93(1)
O(8)	1199(2)	3953(1)	6265(1)	128(2)
O(9)	1025(2)	3014(1)	6549(2)	189(2)
N(11)	3229(1)	1363(1)	6318(2)	338(3)
O(10)	3755(2)	980(2)	6465(2)	180(2)
O(11)	2518(2)	1331(3)	6487(2)	229(3)
O(12)	3456(3)	1891(1)	6117(2)	391(6)
O(1W)	3062(2)	5582(2)	8375(1)	229(2)
O(2W)	1525(1)	1809(1)	6041(2)	237(2)

TABLE III Selected bond distances (Å) and angles (°) for $[Sm(H_3L)(NO_3)(H_2O)]^{2+}$

Sm(1)–O(1)	2.3856(14)	Sm(1)–N(2)	2.544(2)
Sm(1)–O(2)	2.3162(14)	Sm(1)–N(4)	2.551(2)
Sm(1)–O(3)	2.4069(3)	Sm(1)–N(8)	2.545(2)
Sm(1)–O(4)	2.523(3)	Sm(1)–N(3)	2.712(2)
Sm(1)–O(5)	2.648(2)	O(2)–C(18)	1.331(2)
O(1)–C(1)	1.289(3)	O(4)–N(9)	1.322(4)
O(3)–C(30)	1.315(2)	O(5)–N(9)	1.214(2)
N(10)–O(7)	1.253(3)	O(6)–N(9)	1.225(2)
N(10)–O(8)	1.271(4)	N(11)–O(10)	1.247(4)
N(10)–O(9)	1.261(4)	N(11)–O(11)	1.279(4)
		N(11)–O(12)	1.258(4)
O(2)–Sm(1)–O(1)	95.83(5)	O(2)–Sm(1)–O(3)	78.39(5)
O(1)–Sm(1)–O(3)	68.26(5)	O(2)–Sm(1)–O(4)	118.47(4)
O(1)–Sm(1)–O(4)	76.49(5)	O(3)–Sm(1)–O(4)	142.54(5)
O(2)–Sm(1)–N(8)	89.94(5)	O(1)–Sm(1)–N(8)	134.85(5)
O(3)–Sm(1)–N(8)	68.56(5)	O(4)–Sm(1)–N(8)	139.18(4)
O(2)–Sm(1)–N(2)	160.92(5)	O(1)–Sm(1)–N(2)	69.93(5)
O(3)–Sm(1)–N(2)	84.37(5)	O(4)–Sm(1)–N(2)	71.70(5)
N(8)–Sm(1)–N(2)	93.36(5)	O(2)–Sm(1)–N(4)	72.58(5)
O(1)–Sm(1)–N(4)	138.48(5)	O(3)–Sm(1)–N(4)	141.55(5)
O(4)–Sm(1)–N(4)	75.00(5)	N(8)–Sm(1)–N(4)	85.51(5)
N(2)–Sm(1)–N(4)	126.50(5)	O(2)–Sm(1)–O(5)	70.68(5)
O(1)–Sm(1)–O(5)	69.15(5)	O(3)–Sm(1)–O(5)	123.37(4)
O(4)–Sm(1)–O(5)	49.24(4)	N(8)–Sm(1)–O(5)	150.72(5)
N(2)–Sm(1)–O(5)	113.45(5)	N(4)–Sm(1)–O(5)	69.40(5)
O(2)–Sm(1)–N(3)	130.05(5)	O(1)–Sm(1)–N(3)	133.46(5)
O(3)–Sm(1)–N(3)	121.87(5)	O(4)–Sm(1)–N(3)	74.78(5)
N(8)–Sm(1)–N(3)	64.47(5)	N(2)–Sm(1)–N(3)	66.67(5)
N(4)–Sm(1)–N(3)	64.89(5)	O(5)–Sm(1)–N(3)	114.37(5)

electrolytes in this solvent.[18] Owing to the large volume of the complex, its conductivity value is slightly lower than that of simple complexes of 1 : 2 electrolytes in DMF. The IR spectrum of the complex shows two bands at 1650 and 1640 cm^{-1} attributable to ν(C=N). The presence of the double peak was caused by the unsymmetrical coordination of samarium(III) ion to imino nitrogen atoms. Bands at 1470 and 1296 cm^{-1} are due to ν(N=O) and $\nu_{asym}(NO_2)$, respectively, of the coordinated nitrate. The $\nu_{sym}(NO_2)$ vibration at 1051 cm^{-1} is characteristic of a bidentate nitrate group.[19,20] The very intense band at 1385 cm^{-1} is characteristic of ionic nitrate.[21] The IR spectrum shows that there are both coordinated and ionic nitrates in the complex. The abovementioned experimental results are in agreement with the predicted chemical formula. In the cryptate, the three phenolic protons have not been lost, being different to complexes[11] reported by Nelson and others. This difference is possibly caused by the different synthesis methods, different lanthanide ions, the different duration of heating and the pH of the solution. Nelson *et al.* used NaOH to adjust the solution pH and used Na^+ as a template, resulting in the loss of the phenolic protons.

In the thermogram of the complex, there are three weight losses from room temperature to 400°C. The complex lost 3.0% of its weight at 50–130°C corresponding to two water molecules (calc. 3.24%). The second process was at 250–320°C, during which 11.4% of the total weight was lost, corresponding to two uncoordinated nitrate ions (calc. 11.17%). Finally, a weight loss of 5.61% at 321–365°C occurred, due to the coordinated nitrate ion (calc. 5.58%). The exact temperatures at which loss of water in outer-sphere of complex and of the encapsulated water could not be determined, because their endothermic peaks in the DTA curve overlapped with each other. This indicated the encapsulated water is linked to the macrocycle by weak interaction. This is in agreement with the crystal structure of the cryptate (Figure 1).

Electrospray mass spectra of the cryptate in methanol display several peaks which can be assigned to new species formed by encapsulating different number of solvent molecules (H_2O or MeOH) or protons. For example, the peaks at *m/z* 552.5 and 515.5 are due to the formation of the cryptate cation encapsulating water molecules and methanol. In addition, the coordinated nitrate anion and chlorine atoms on the benzene rings can also be lost under the ES-MS conditions. The mass spectrum is dominated by a peak at *m/z* 235.5 due to $[Sm(H_3L)(MeOH)(H_3O)],^{4+}$ indicating that three phenolic protons and a water molecule still remain in the complex. This is in agreement with the results of thermoanalysis and crystal structure. No peaks due to the fragmentation of the cryptand were observed. This shows that the macrocycle is rather stable in methanol solution. The fragmentation pattern is shown in Scheme 2.

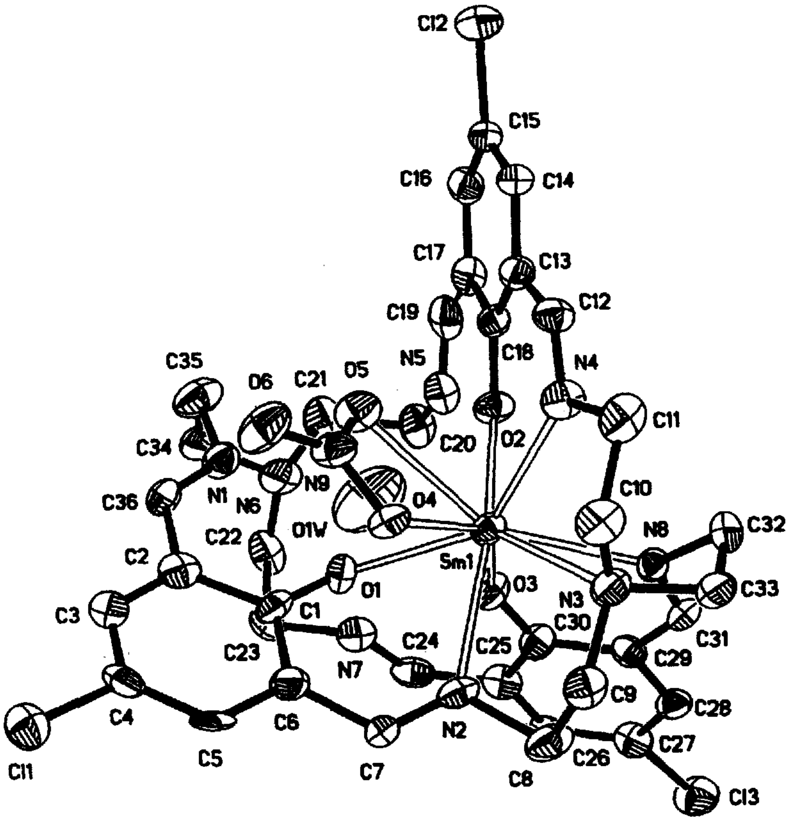
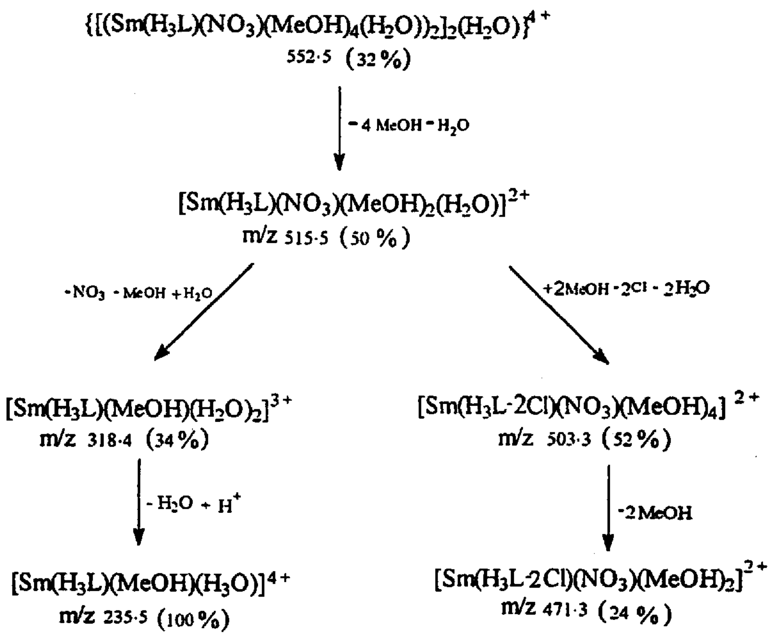


FIGURE 1 Crystal structure of the $[Sm(H_3L)(NO_3)(H_2O)]^{2+}$ ion.

Crystal Structure

The crystal structure of the complex cation $[Sm(H_3L)(NO_3)(H_2O)]^{2+}$ is shown in Figure 1. Selected bond distances and angles are shown in Table III. In the complex Sm(III) is placed asymmetrically at one end of the cavity and is nine-coordinated by three imino nitrogen atoms (N(2), N(4) and N(7)), three phenolic oxygen atoms (O(1), O(2) and O(3)), one of the bridgehead nitrogen atoms N(3), and two oxygens of the bidentate nitrate (O(4), O(5)), forming a distorted coordination polyhedron. Distances between two oxygens of the bidentate nitrate and Sm(III) are 2.523 and 2.648 Å, and Sm–N (imino) distances are in the range 2.544–2.551 Å, shorter than Nd–N (imino) and larger than Ln–N (imino) (Ln = Dy, Gd, Tb)[11,12] in analogous cryptates. The distance between Sm(1) and the bridgehead



SCHEME 2 Electrospray-induced fragmentation pattern of $[Sm(H_3L)(NO_3)(H_2O)]^{2+}$ (relative abundance given in parentheses).

nitrogen atom N(3) is 2.712 Å, showing the weak interaction of Sm(III) with the amine nitrogen, in contrast to the strong interaction of Sm(III) with the imino nitrogen and phenolic oxygen. The distance between the two bridgehead nitrogens N(3) and N(6) is 8.298 Å, shorter than in analogous cryptates Dy(III)(8.361 Å)[12] and Nd(III)(8.381 Å),[13] and showing that the cryptand (H_3L) can contract or expand the cavity in order to meet requirements of geometric configuration. The Sm(1)···O(1w) distance is 3.035 Å, much larger than that of Gd(1)–O(1w) (2.426 Å)[11] in $[GdL'(H_2O)(NO_3)]^{2+}$ (L′ represents a cryptand similar to H_3L, synthesized by the (2 + 3) condensation of tren with 2,6-diformyl-4-tert-butyl-phenol). This shows that there is no coordination between Sm(III) and the water molecule included in the cavity (Figure 1).

People have disputed the position of phenolic protons in complexes of macrocycles containing phenol groups, a problem made difficult if the phenolic protons transfer to N of the imino groups.[12] In the samarium cryptate, the Sm–O (phenoxy) distances are in the range 2.316–2.406 Å and the average distance is 2.369 Å, larger than Ln–O (phenoxy) (Ln = Dy(III), Tb(III) and Gd(III))[11,12] in its analogues. This implies that the phenolic protons are still attached to the phenolic oxygens which coordinated to Sm, and the interactions between the phenolic protons and coordinated phenolic oxygen atoms weaken and lengthen the Sm–O bond distances. This is in agreement with a previous report.[12]

Acknowledgements

The project was supported by the National Natural Science Foundation of China.

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