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Synthesis and crystal structural characterization of an unsymmetric neodymium(III) cryptate

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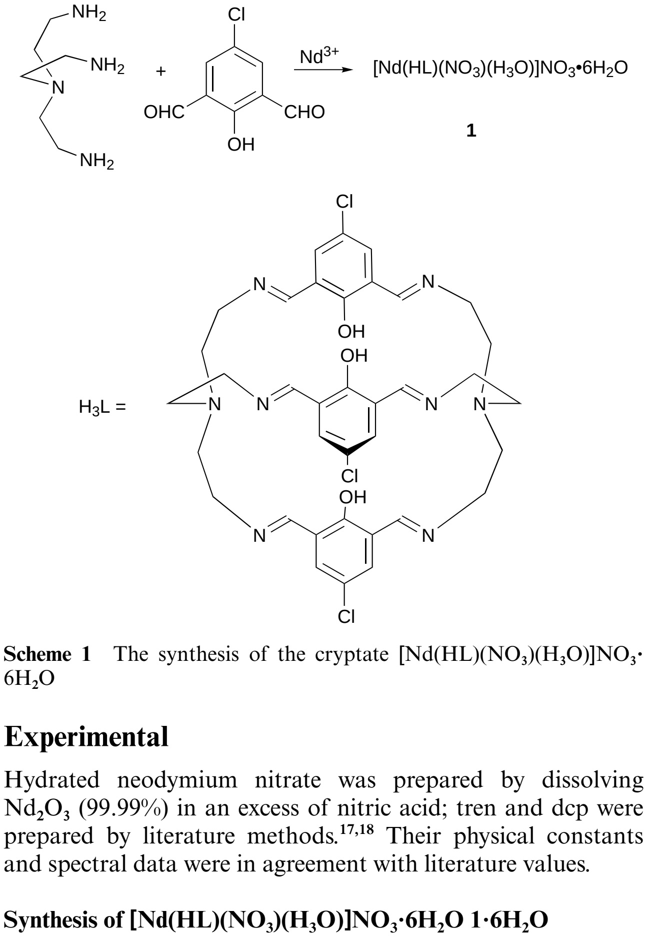
The complex $[Nd(HL)(NO_3)(H_3O)]NO_3{\cdot}6H_2O$ was synthesized by the 2 + 3 condensation of tris(2-aminoethyl)amine (tren) with 2,6-diformyl-4-chlorophenol in the presence of Nd^{3+} as the template. The complex has been characterized by elemental analysis, molar conductivity and IR spectroscopy. The crystal structure of the complex $[Nd(HL)(NO_3)(H_3O)]NO_3{\cdot}2MeOH$ has been determined. The co-ordination number of neodymium(III) is nine and its co-ordination geometry is monocapped square antiprismatic. One oxonium ion acts as a guest molecule encapsulated in the cryptate. The existence of the oxomium ion was confirmed by electrospray mass spectrometry, thermal analysis, X-ray crystal structure determination and ^1H NMR spectroscopy.

The design and synthesis of macrocyclic ligands and their lanthanide complexes are a fascinating area of research, owing to their importance in basic and applied chemistry.[1–3] The ability of macrocyclic ligands to recognize lanthanide(III) ions makes them valuable for the development of applications such as selected separation of metals and supramolecular devices.[4,5] Lanthanide complexes of macrocyclic ligands are important as fluorescent probes in biological systems, as luminescence labels and as medical diagnostics.[6–9] In addition, they can also be used as catalysts for RNA cleavage and NMR shift reagents.[10,11]

Many lanthanide(III) complexes are able to exhibit fluorescence in the solid state, but their fluorescence efficiency in aqueous solution is substantially lowered, owing to the co-ordination of water molecules to the lanthanide atoms.[12] Therefore it is important to protect the metal as efficiently as possible from co-ordination of water molecules when preparing lanthanide complexes with strong fluorescence properties in aqueous solution.

The cryptand ligands possess spherical cavities and special recognition sites toward metal ions and small molecules. They are able to shield the metal ions from interaction with water molecules. The lanthanide cryptates derived from tris(2-aminoethyl)amine (tren) and 2,6-diformyl-4-methylphenol (dfp) have been reported previously by Nelson and co-workers[13] and Fenton and co-workers.[14] They have reported the crystal structures of lanthanide (Gd^{III}, Tb^{III}, Eu^{III} and Dy^{III}) complexes of phenolate-bridged macrobicyclic ligands. The structures of the complexes depend on reaction conditions.

Herein we report on the synthesis of a novel neodymium(III) cryptate $[Nd(HL)(NO_3)(H_3O)]NO_3{\cdot}6H_2O$ **1**$\cdot 6H_2O$ derived from the 2 + 3 Schiff-base condensation of tren with 2,6-diformyl-4-chlorophenol (dcp) in the presence of Nd^{3+} (Scheme 1). The crystal structure shows that the co-ordination number of Nd^{3+} is nine and its co-ordination geometry is monocapped square antiprismatic. It is interesting to note that an oxonium ion acts as a guest encapsulated in the host macrocycle by hydrogen bonds. The existence of the oxonium ion in the inner sphere of the complex was confirmed by electrospray mass spectrometry, thermal analysis, an X-ray structure determination and ^1H NMR spectroscopy. Only a few structures of oxonium ions encapsulated in crown ethers have been reported,[15,16] but to our knowledge, lanthanide cryptates which act as host molecules to encapsulate guest oxonium ions have not been reported up to now.



Scheme 1 The synthesis of the cryptate $[Nd(HL)(NO_3)(H_3O)]NO_3{\cdot}6H_2O$

Experimental

Hydrated neodymium nitrate was prepared by dissolving Nd_2O_3 (99.99%) in an excess of nitric acid; tren and dcp were prepared by literature methods.[17,18] Their physical constants and spectral data were in agreement with literature values.

Synthesis of $[Nd(HL)(NO_3)(H_3O)]NO_3{\cdot}6H_2O$ 1$\cdot 6H_2O$

A reagent grade methanol solution (7.0 cm^3) containing tren (0.102 g, 0.70 mmol) was added dropwise to a stirred solution of dcp (0.109 g, 0.63 mmol) and $Nd(NO_3)_3{\cdot}6H_2O$ (0.154 g, 0.35 mmol) in methanol (12 cm^3). After refluxing for 3–4 h, the cotton-like precipitate was filtered off while the mixture was hot and acetonitrile (10 cm^3) was added to the filtrate. Concentration of the solution resulted in the yellowish product $[Nd(HL)(NO_3)(H_3O)]NO_3{\cdot}6H_2O$ which was filtered off, washed with methanol followed by diethyl ether and then dried in a vacuum desiccator. Yield 0.15 g (58%) (Found: C, 38.26; H, 4.09; N, 11.63. $C_{36}H_{52}Cl_3N_{10}NdO_{16}$ requires C, 38.22; H, 4.63; N, 12.38%); ν_{max}/cm^{-1} 3416w [ν(OH)], 1650s [ν(C=N)], 1541s [ν(C–O)], 1470s [ν(N=O)], 1384s [$\nu(NO_3^-)$], 1296s [$\nu_{asym}(NO_2)$] and 1051s [$\nu_{sym}(NO_2)$]; λ_{max}/nm (MeOH) 394 (ε 12 000 dm^3 mol^{-1} cm^{-1}), 225 (52 000); Λ_m (DMF, 298 K) 75 S cm^2 mol^{-1}.

Physical measurements

The electrical conductivity of a solution of compound **1**·6H_2O in DMF at 25 ± 0.1 °C was measured using a BSD-A conductometer (Jiangsu, China). The IR spectrum was measured as a KBr disc using a Nicolet 5DX FT-IR spectrophotometer. Thermoanalyses of the complexes were performed on a SDT 2960C TA thermoanalyser under an argon atmosphere with a rate of 10 °C min^{-1}. Proton NMR spectroscopy was performed in $(CD_3)_2SO$ on a Bruker AM-500 spectrometer ($SiMe_4$ used as the internal reference). The electrospray mass spectrum (ES–MS) was determined on a Finnigan LCQ mass spectrograph, the concentration of the sample was about 1.0 mmol dm^{-3}. The diluted solution was electrosprayed at a flow rate of 5×10^{-6} 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.

Crystallography

A yellowish prismatic crystal of $[Nd(HL)(NO_3)(H_3O)]NO_3$·2MeOH **1**·2MeOH suitable for X-ray diffraction was isolated from a MeCN–MeOH solution of **1**·6H_2O by diffusion of diethyl ether over 1 week.

Crystal data. $C_{38}H_{48}Cl_3N_{10}NdO_{12}$, $M = 1087.45$, orthorhombic, $a = 17.139(4)$, $b = 20.840(4)$, $c = 24.965(5)$ Å, $U = 8916.8(32)$ Å^3, $T = 293(2)$ K, space group *Pbca*, graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å), $Z = 8$, $D_c = 1.620$ g cm^{-3}, $F(000) = 4424$, μ(Mo-Kα) = 1.416 mm^{-1}.

Crystal structure determination. A yellow crystal with dimensions 0.35 × 0.32 × 0.26 mm was mounted on a glass fiber and used for structure determination. The intensities were collected on a Siemens P4 diffractometer using the ω–2θ scan mode with a variable scan speed of 5.5–50.0° min^{-1} (in ω). 9316 Reflections (7840 unique) were collected in the range $1.95 < \theta < 25°$. The data were corrected for Lorentz and polarization effects during data reduction using XSCANS.[19]

All computations were carried out on a 586 personal computer using the SHELXTL PC program package.[20] The structure was solved by the heavy atom method and refined on F^2 by the full-matrix least-squares method using SHELXTL version 5.0.[20] All the non-hydrogen atoms were refined anistropically. The C atoms of the methanol molecules [site occupancy factor (s.o.f.) for C(37) and C(37′) fixed at 0.5, s.o.f. = 0.5 for C(38) and C(38′)] and the ionic nitrate [s.o.f. = 0.7 for O(7), O(8) and O(9), s.o.f. = 0.3 for O(7′), O(8′) and O(9′)] were found to be disordered. The H atoms of the oxonium ion were found from a Fourier-difference map and refined with fixed U_{iso}. All the hydrogen atoms were placed in calculated positions and assigned fixed isotropic thermal parameters at 1.2 times the equivalent isotropic *U* of the atoms to which they are attached (1.5 times for the O–H and methyl groups) and allowed to ride on their respective parent atoms. The contributions of these hydrogen atoms were included in the structure-factor calculations. The weighting scheme was $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $3P = (2F_c^2 + F_o^2)$ and *a* and *b* are constants adjusted by the program. The final $R'(F^2)$ was 0.1370, with conventional $R(F)$ 0.0768 (*R* factor defined in ref. 20), goodness of fit = 0.945. The maximum and minimum peaks corresponded to +0.765 and −0.735 e Å^{-3} respectively. Selected bond distances and angles are listed in Table 1.

CCDC reference number 186/900.

Table 1 Selected bond distances (Å) and angles (°) for $[Nd(HL)(NO_3)(H_3O)]^+$

Nd(1)–O(1)	2.329(2)	Nd(1)–O(3)	2.421(2)
Nd(1)–O(2)	2.431(2)	Nd(1)–N(7)	2.543(2)
Nd(1)–N(5)	2.567(2)	Nd(1)–O(5)	2.578(2)
Nd(1)–N(2)	2.585(2)	Nd(1)–O(4)	2.653(2)
Nd(1)–N(1)	2.747(2)	O(1)–C(9)	1.254(3)
O(2)–C(21)	1.304(3)	O(3)–C(33)	1.275(3)
O(4)–N(9)	1.292(3)	O(5)–N(9)	1.293(3)
O(6)–N(9)	1.208(4)	N(2)–C(3)	1.254(4)
N(3)–C(10)	1.272(4)	N(5)–C(15)	1.258(4)
N(6)–C(22)	1.275(4)	N(7)–C(27)	1.255(4)
N(8)–C(34)	1.250(4)	N(10)–O(9)	1.254(3)
N(10)–O(9′)	1.256(3)	N(10)–O(8)	1.264(3)
N(10)–O(7′)	1.273(3)	N(10)–O(8′)	1.276(3)
O(1)–Nd(1)–O(3)	97.76(6)	O(1)–Nd(1)–O(2)	78.87(6)
O(3)–Nd(1)–O(2)	69.26(6)	O(1)–Nd(1)–N(7)	163.51(7)
O(3)–Nd(1)–N(7)	70.33(7)	O(2)–Nd(1)–N(7)	86.06(7)
O(1)–Nd(1)–N(5)	89.05(7)	O(3)–Nd(1)–N(5)	134.55(7)
O(2)–Nd(1)–N(5)	68.16(7)	N(7)–Nd(1)–N(5)	91.56(7)
O(1)–Nd(1)–O(5)	117.64(6)	O(3)–Nd(1)–O(5)	74.51(6)
O(2)–Nd(1)–O(5)	142.03(6)	N(7)–Nd(1)–O(5)	71.19(7)
N(5)–Nd(1)–O(5)	139.77(7)	O(1)–Nd(1)–N(2)	71.25(7)
O(3)–Nd(1)–N(2)	139.80(7)	O(2)–Nd(1)–N(2)	139.89(7)
N(7)–Nd(1)–N(2)	125.23(8)	N(5)–Nd(1)–N(2)	84.91(7)
O(5)–Nd(1)–N(2)	77.09(7)	O(1)–Nd(1)–O(4)	70.94(7)
O(3)–Nd(1)–O(4)	69.56(7)	O(2)–Nd(1)–O(4)	124.01(7)
N(7)–Nd(1)–O(4)	113.27(7)	N(5)–Nd(1)–O(4)	151.92(7)
O(5)–Nd(1)–O(4)	47.98(7)	N(2)–Nd(1)–O(4)	70.32(7)
O(1)–Nd(1)–N(1)	129.54(7)	O(3)–Nd(1)–N((1)	131.95(7)
O(2)–Nd(1)–N(1)	121.66(7)	N(7)–Nd(1)–N(1)	64.66(8)
N(5)–Nd(1)–N(1)	63.85(7)	O(5)–Nd(1)–N(1)	75.93(7)
N(2)–Nd(1)–N(1)	64.99(7)	O(4)–Nd(1)–N(1)	113.94(7)
C(9)–O(1)–Nd(1)	138.8(2)	C(21)–O(2)–Nd(1)	141.4(2)
C(33)–O(3)–Nd(1)	129.7(2)	N(9)–O(4)–Nd(1)	98.7(2)
N(9)–O(5)–Nd(1)	102.4(2)	C(1)–N(1)–Nd(1)	106.0(2)
C(25)–N(1)–Nd(1)	109.8(2)	C(13)–N(1)–Nd(1)	111.0(2)
C(3)–N(2)–Nd(1)	126.7(2)	C(2)–N(2)–Nd(1)	119.1(2)
C(15)–N(5)–Nd(1)	135.5(2)	C(14)–N(5)–Nd(1)	111.1(2)
C(27)–N(7)–Nd(1)	126.6(2)	C(26)–N(7)–Nd(1)	113.5(2)

See http://www.rsc.org/suppdata/dt/1998/1377/ for crystallographic files in .cif format.

Results and Discussion

Characteristics of the cryptate

The value of the solution molar conductivity indicates that complex **1**·6H_2O is a 1 : 1 electrolyte.[21] The results of the molar conductivity and elemental analysis showed that one of the phenolic protons of the cryptand was lost during co-ordination, which is in agreement with that of the X-ray structural determination. The two strong peaks at 394 and 225 nm in the electronic spectrum are designated to the transition of the benzene rings and C=N groups respectively. In the IR spectrum the bands at 1470 and 1296 cm^{-1} are due to ν(N=O) (ν_1) and $\nu_{asym}(NO_2)$ (ν_5) respectively of the co-ordinated nitrate. The $\nu_{sym}(NO_2)$ vibration (ν_2) at 1051 cm^{-1} is characteristic of a bidentate nitrate group. The separation of the ν_1 and ν_5 modes has been used as a criterion to distinguish between mono- and bi-dentate chelating nitrates.[22,23] The observed magnitude of separation (174 cm^{-1}) indicates bidentate co-ordination of the nitrate ion in this instance. The strong sharp band at 1384 cm^{-1} is characteristic of ionic nitrate.[24] The IR spectrum shows that there are both co-ordinated and ionic nitrates in the complex.

Thermogravimetric analyses

Thermogravimetric analyses show that the number of exocyclic solvent molecules varies with experimental conditions because of their instability. After $[Nd(HL)(NO_3)(H_3O)]NO_3$·2MeOH **1**·2MeOH was vacuum-dried over $CaCl_2$ for 3 d, the oxonium

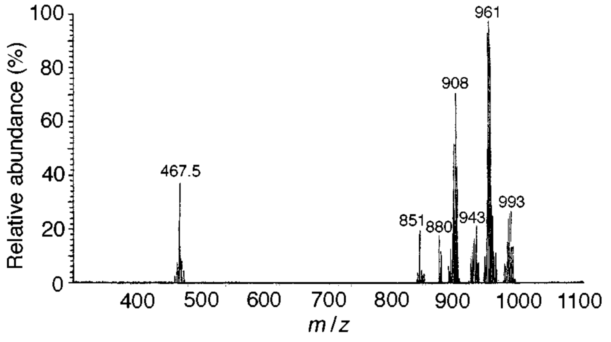


Fig. 1 The ES mass spectrum of $[Nd(HL)(NO_3)(H_3O)]^+$ in methanol

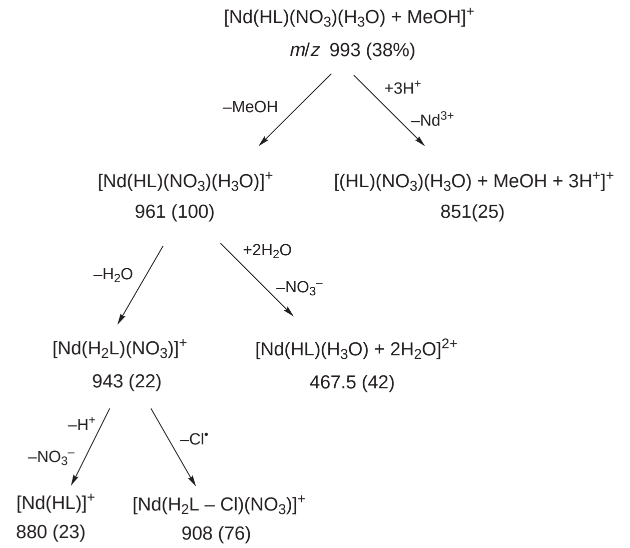
ion in the cavity was still intact, while all the methanol molecules were lost, then $[Nd(HL)(NO_3)(H_3O)]NO_3$ **1** was formed. When **1**·2MeOH was air dried, $[Nd(HL)(NO_3)(H_3O)]NO_3$·MeOH **1**·MeOH containing one methanol molecule in the outer sphere of the complex was obtained. In the thermogram of complex **1**·MeOH there are three weight loss processes from room temperature to 500 °C. The complex began to lose 4.74% of its weight at about 60–110 °C corresponding to one water molecule and one methanol molecule (calc. 4.62%). However, the exact temperature at which loss of water and methanol occurred could not be determined because their endothermic peaks in the DTA curve overlapped with each other. The second process was from 210 to 290 °C, 11.38% of the total weight was lost which corresponded to loss of two nitrate ions (*i.e.* a co-ordinated and an outer sphere nitrate, calc. 11.75%). Finally, a weight loss of 10.09% at 291–340 °C due to loss of the three chlorine atoms on the benzene rings (calc. 10.00%) occurred. Under the same conditions complex **1** lost only one water molecule at about 110 °C (found, 1.76%; calc. 1.86%) in the first step and the remaining weight loss processes are the same as those of complex **1**·MeOH. The temperature at which water is lost in these systems is lower than that of co-ordinated water and higher than that of lattice water. This is in agreement with the crystal structure of the cryptate [Fig. 2(a)] in which the oxonium ion is linked to the macrocycle only by hydrogen bonds.

Electrospray mass spectrum

The relatively new technique of electrospray mass spectrometry (ES–MS) allows pre-existing ions in solution to be transferred very gently into the gas phase with minimal fragmentation.[25] Fig. 1 show the positive-ion ES mass spectrum of a solution of the cryptate in methanol. Several peak clusters are observed due to seven and two abundant isotopes for neodymium and chlorine atoms respectively. The peak clusters of the cryptate have a complex isotopic distribution which provides a basis for determining the atomic composition of the ion. In Fig. 1 most of the peaks originate from the most abundant mass in the isotopic mass distributions. The mass spectrum is dominated by the peak at *m*/*z* 961 which is due to $[Nd(HL)(NO_3)(H_3O)]^+$ indicating that the oxonium ion is still encapsulated in the macrocycle. The other main peaks can be assigned to new species formed by solvation or protonation of the complex cation, loss of the nitrate ligand or the phenolic proton. The peak at *m*/*z* 908 is due to the formation of the new cryptate $[Nd(H_2L - Cl)(NO_3)]^+$, a chlorine free radical is lost from the benzene ring when the new cryptate forms. The peak at *m*/*z* 467.5 is assigned to $[Nd(HL)(H_3O) + 2H_2O]^{2+}$. No peaks due to the fragmentation of the cryptand were observed. It shows that the macrocycle is rather stable in methanol solution. The fragmentation pattern is shown in Scheme 2.

Crystal structure

The structure of the complex cation $[Nd(HL)(NO_3)(H_3O)]^+$ is shown in Fig. 2(a). In the complex Nd^{III} is placed asymmetrically at one end of the cavity and is nine-co-ordinated; by three imino nitrogen atoms [N(2), N(5) and N(7)], three phenolic oxygens O(1), O(2), O(3), one of the bridgehead nitrogen atoms N(1) and two oxygens of the bidentate nitrate O(4), O(5). The co-ordination polyhedron can best be described as a mono-capped square antiprism [Fig. 2(b)] in which the co-ordinated bridgehead nitrogen N(1) is the cap and the four oxygen atoms O(1), O(2), O(3), O(4) form the basal plane. The distance between Nd^{III} and the basal plane is 1.086(5) Å. The upper plane consists of N(2), N(5), N(7) and O(5). The distance between the upper plane and Nd^{III} is 1.368(5) Å. The biplanar angle between the two planes is 7.5(4)°. The co-ordination distances are 2.578 and 2.653 Å respectively for two oxygens of the bidentate nitrate to Nd^{III}, in the range 2.330–2.432 Å for the phenolic oxygens, 2.542–2.585 Å for the imino nitrogens and the distance of Nd(1)–N(1) is 2.747 Å, implying weak interaction between the Nd^{III} and bridgehead nitrogen atom. The distance between the two bridgehead nitrogens N(1)···N(4) is 8.381(5) Å, being very close to that reported for $[Dy(H_3L^1)(NO_3)]^{2+}$ (8.361 Å) (H_3L^1 represents a cryptand similar to H_3L synthesized by the 2 + 3 condensation of tren with dfp).[14]



Scheme 2 Electrospray-induced fragment pattern of $[Nd(HL)(NO_3)(H_3O)]^+$ (relative abundance given in parentheses)

Table 2 Bond distances (Å) and bond angles (°) of hydrogen bonds in $[Nd(HL)(NO_3)(H_3O)]^+$

Donor···acceptor	Angles	O···N	OH···N
O(1w)–H(1wA)···N(6)	175.3(4)	2.447(5)	1.599(5)
O(1w)–H(1wB)···N(8)	174.1(4)	2.498(5)	1.651(5)
O(1w)–H(1wC)···N(3)	175.4(4)	2.526(5)	1.678(5)

At one end of the cavity, an oxonium ion is encapsulated in the host macrocycle. The Nd(1)···O (oxonium) distance is 3.023(5) Å, which implies that there is no interaction between the two atoms. The oxonium ion is linked with three non-co-ordinated imino nitrogen atoms N(3), N(6), N(8) by hydrogen bonds. The bond distances and angles of hydrogen bonds are listed in Table 2. The angle Nd(1)–O (oxonium)–N(4) is 173.1(4)° because this arrangement can give the minimum repulsion.

Nelson and co-workers[13] have confirmed that the protons transfer from the phenolic oxygens to non-co-ordinated imino nitrogens in their diamagnetic lanthanide cryptates using NMR spectroscopy. However, in our cryptate proton transfer is not the case. One of the three phenolic protons is lost during co-ordination, the other two phenolic protons remain in the

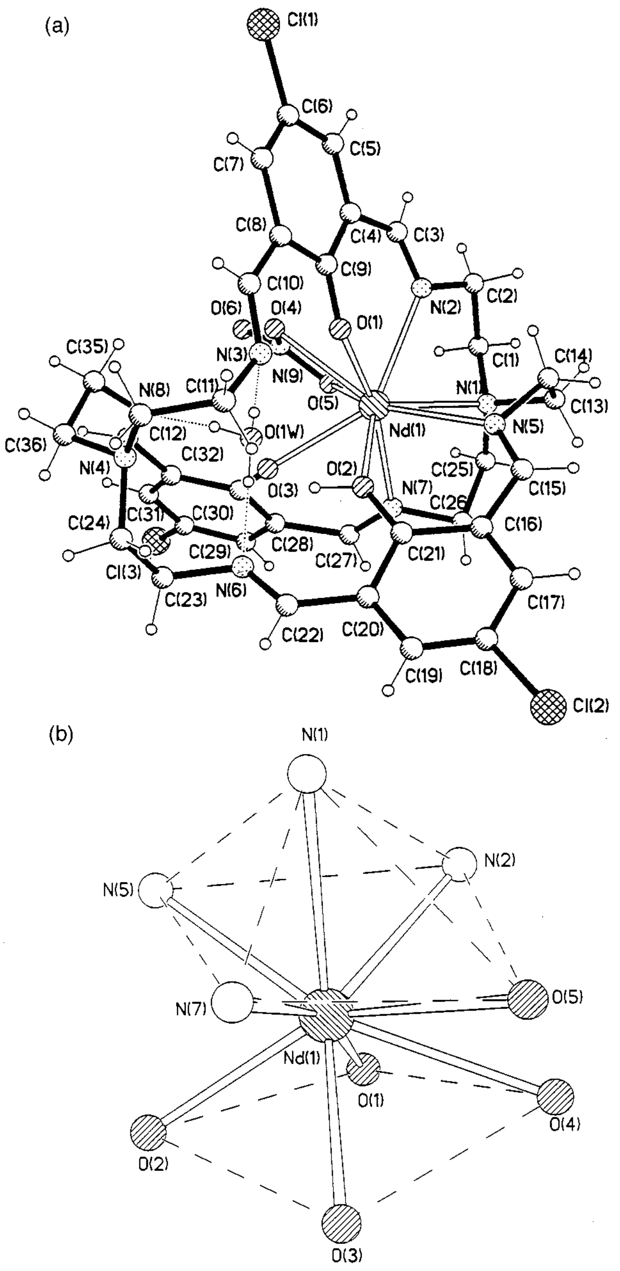


Fig. 2 (a) Crystal structure of the $[Nd(HL)(NO_3)(H_3O)]^+$ complex ion; (b) monocapped square antiprismatic co-ordination in the complex cation

cryptate. As a result of the interaction between the phenolic proton and the attached phenolic oxygen atom, the distance of the phenolic C–O bond and the bond angle of Nd–O–C are different from those of phenoxy groups. The bond distance of C(21)–O(2) is 1.304 Å, which is longer than the other two phenolic C–O bonds. The angle of C(21)–O(2)–Nd(1) is 141.4°, which is also larger than the other two corresponding angles. Therefore we suggest that a proton is attached to the O(2) atom. Such a behavior is also observed in the case of the lanthanide(III) complexes of 2 + 2 macrocycles obtained by condensation of dcp with diethylenetriamine.[26,27] Although the Nd^{III} ion in our complex is paramagnetic, the ^1H NMR spectrum shows a broad signal characteristic of the oxonium ion in the range δ 10–11, which is in agreement with that of analogous oxonium complexes.[28,29] The other proton has been located on the water molecule from the Fourier-difference map. In the inner sphere of lanthanide macrocyclic complexes, the water molecule usually co-ordinates to the central lanthanide ion, thus decreasing its luminescence efficiency. However, in our complex the oxonium ion is not co-ordinated to the central metal ion and this kind of structure is rarely reported.

Acknowledgements

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