Structure and Properties of Some Lanthanoid(III) Perchlorates with the Cryptand 4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane

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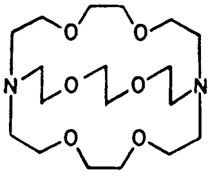
Some complexes of lanthanoid(III) perchlorates with the title ligand (L) have been prepared in methyl cyanide. Three series have been obtained with formulae (*i*) Ln[ClO$_4$]$_3$·L·MeCN (Ln = Pr, Nd, or Eu), (*ii*) Ln[ClO$_4$]$_3$·L·H$_2$O·0.5MeCN (Ln = La, Ce, Sm, Eu, Dy, or Ho), and (*iii*) Ln[ClO$_4$]$_3$·L·MeCONH$_2$ (Ln = Er or Yb). The crystal and molecular structure of the Eu[ClO$_4$]$_3$·L·MeCN complex has been determined from *X*-ray diffractometric data. Crystals are orthorhombic, space group $P2_12_12_1$, with a = 33.567(4), b = 10.646(2), c = 8.821(2) Å, and Z = 4. The structure has been refined by least-squares techniques to R 0.072 for 1 037 reflections. The europium(III) ion is ten-co-ordinated to the eight donor atoms of L and to two oxygen atoms of a [ClO$_4$]$^-$ ion. The co-ordination polyhedron can be described as a bicapped square antiprism. The i.r. and electronic spectra of the cryptates are discussed. The complexes of Sm, Eu, and Yb exhibit electron-transfer transitions in agreement with the optical electronegativity value of 3.0 for the cryptand.

As an extension of our previous studies on the synthesis, structure, and electronic properties of lanthanoid complexes, we are now interested in a systematic investigation of co-ordination compounds of these metal ions with macrocyclic ligands of the crown ether and cryptand types. These ligands form remarkably stable complexes with some cations of class A metals, such as the alkali and alkaline-earth metals,[1] but few studies have been made with lanthanoids.[2] Our aim is to isolate lanthanoid complexes in the oxidation states of II, III and IV, which are also kinetically and thermodynamically stable in water and/or organic solvents. In this respect, macrocyclic ligands of suitable cavity size and screening ability seem promising.

When this research was in progress a preliminary report by Gansow *et al.*[3] appeared on the preparation and solution behaviour of some cryptates of La, Pr, Eu, Gd, and Yb with the title ligand (hereafter called L) and two similar cryptands. More recently, Hart *et al.*[4] have described the reactions of lanthanum and praseodymium nitrates with (L) as well as the crystal structure of the compound [La(NO$_3$)$_2$L]$_3$[La(NO$_3$)$_6$]·2MeOH.


L

The present paper reports the synthesis and characterization of the complexes of some lanthanoid(III) perchlorates with the cryptand L. Under our conditions three series of complexes were isolated: (*i*) Ln[ClO$_4$]$_3$·L·MeCN (Ln = Pr, Nd, or Eu); (*ii*) Ln[ClO$_4$]$_3$·L·H$_2$O·0.5MeCN (Ln = La, Ce, Sm, Eu, Dy, or Ho); and (*iii*) Ln[ClO$_4$]$_3$·L·MeCONH$_2$ (Ln = Er or Yb). The crystal structure of the complex [Eu(ClO$_4$)L]-[ClO$_4$]$_2$·MeCN has been determined by *X*-ray analysis. A partial account of this work has already been published.[5]

EXPERIMENTAL

The presence of water in the reaction mixtures of lanthanoid perchlorates and the cryptand L in MeCN favours separation of gelatinous basic precipitates. Therefore anhydrous lanthanoid perchlorates were used (Ln = La, Ce, Pr, Nd, Sm, or Eu) which were obtained by slowly heating the hydrated salts to 200 °C at 0.1 mmHg.[6,†] With the heavier lanthanoids (Ln = Dy, Ho, Er, or Yb), where such a procedure fails,[6] the MeCN solutions of the hydrated perchlorates were heated under reflux for 20 h through a Soxhlet extractor packed with molecular sieves.[2f] This procedure, however, produced some acetamide, which forms adducts with the erbium and ytterbium cryptates.

Preparation of the Complexes.—A solution of the lanthanoid perchlorate (1 mmol) in anhydrous MeCN (10 cm^3) was added to cryptand L (1.10 mmol). After a few minutes, crystals of cryptate separated, which were filtered off, washed with a mixture of methyl cyanide and diethyl ether, and dried *in vacuo* at room temperature. Recrystallization was carried out by dissolving the complexes in methyl cyanide and reprecipitating them with diethyl ether. With the cerium(III) complex all the operations were performed under pure nitrogen and with deoxygenated solvents. Table 1 reports analytical data, colours, and molar conductances of the complexes. The presence of acetamide, methyl cyanide, and water was confirmed by i.r. spectra.

Spectral Measurements.—Electronic spectra both in solution and by reflectance were recorded with a Cary 17 spectrophotometer. The i.r. spectra were recorded as Nujol mulls on a Perkin-Elmer model 283 spectrophotometer.

X-Ray Crystallography.—*Crystal data.* $C_{20}H_{39}Cl_3EuN_3O_{18}$, M = 867.88, Orthorhombic, space group $P2_12_12_1$, a = 33.567(4), b = 10.646(2), c = 8.821(2) Å, U = 3 152.2 Å^3, Z = 4, D_c = 1.84 g cm^{-3}, $F(000)$ = 1 752, λ(Mo-K_α) = μ(Mo-K_α) = 23.2 cm^{-1}.

Data collection. The yellow crystals of [Eu(ClO$_4$)L]-[ClO$_4$]$_2$·MeCN are parallelipipeds. Because of the sensitivity of this complex to air, the crystal under examination (*ca.* 0.65 × 0.35 × 0.10 mm) was sealed in a glass capillary. Cell parameters were determined by least-squares refinement of 20 reflections centred on a four-circle Philips PW 1 100 automatic diffractometer at *ca.* 22 °C using Mo-K_α radiation. The intensity data were collected, on the same

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[†] Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

TABLE 1

Analytical and physical data for $Ln[ClO_4]_3 \cdot L$ complexes

Complex	Colour	Analysis (%) [a] C	H	N	Λ [b] $S\,cm^2\,mol^{-1}$
$La[ClO_4]_3 \cdot L \cdot H_2O \cdot 0.5MeCN$	White	26.9 (26.8)	4.9 (4.7)	4.3 (4.1)	345
$Ce[ClO_4]_3 \cdot L \cdot H_2O \cdot 0.5MeCN$	White	26.4 (26.7)	4.7 (4.7)	4.1 (4.1)	342
$Pr[ClO_4]_3 \cdot L \cdot MeCN$	Pale green	27.9 (28.0)	4.7 (4.6)	5.0 (4.9)	336
$Nd[ClO_4]_3 \cdot L \cdot MeCN$	Pale lilac	27.8 (27.9)	4.6 (4.6)	5.0 (4.9)	355
$Sm[ClO_4]_3 \cdot L \cdot H_2O \cdot 0.5MeCN$	White	26.0 (26.4)	4.8 (4.6)	4.2 (4.1)	
$Eu[ClO_4]_3 \cdot L \cdot MeCN$	Yellow	27.6 (27.7)	4.4 (4.5)	4.7 (4.8)	336
$Eu[ClO_4]_3 \cdot L \cdot H_2O \cdot 0.5MeCN$	Yellow	26.5 (26.4)	4.5 (4.6)	4.1 (4.0)	342
$Dy[ClO_4]_3 \cdot L \cdot H_2O \cdot 0.5MeCN$	White	25.6 (26.0)	4.7 (4.5)	3.9 (4.0)	327
$Ho[ClO_4]_3 \cdot L \cdot H_2O \cdot 0.5MeCN$	Pale pink	26.1 (26.0)	4.7 (4.5)	4.3 (4.0)	335
$Er[ClO_4]_3 \cdot L \cdot MeCONH_2$	Pale pink	26.4 (26.5)	4.6 (4.6)	4.7 (4.6)	358
$Yb[ClO_4]_3 \cdot L \cdot MeCONH_2$	White	26.5 (26.5)	4.6 (4.6)	4.7 (4.6)	348

[a] Calculated values are given in parentheses. [b] For *ca.* 10^{-3} mol dm^{-3} solutions in methyl cyanide at 25 °C. Under the same conditions, values of 159 S cm^2 mol^{-1} for $[NBu_4][ClO_4]$ and 293 S cm^2 mol^{-1} for $[NEt_4]_2[CoBr_4]$ have been obtained.

diffractometer, in the range $6 \leqslant 2\theta \leqslant 40^\circ$ using graphite-monochromatized Mo-K_α radiation and the θ—ω scan technique: scans of 0.7° in ω were recorded across the peaks in 10 s intervals (background counted for 5 s on each side of the peak). Three standard reflections were measured every 100 min during the data collection. The intensities of these reflections slowly and continuously decreased to *ca.* 70% of their initial value at the end of data collection. The intensities of all the reflections were therefore rescaled on the basis of the standard reflections. Standard deviations and intensities were calculated as described elsewhere,[7] using a value of the instability factor k of 0.03. The 1 037 reflections having $I \geqslant 3\sigma(I)$ were considered observed and used in the structure analysis. An absorption correction was applied by a numerical method: transmission factors varied between 0.53 and 0.78. The intensities were also corrected for Lorentz and polarization effects. Atomic scattering factors for Eu, Cl, O, N, and C atoms were taken from ref. 8, those for H from ref. 9 (all for the neutral state). Corrections for anomalous dispersion effects for Eu and Cl were applied in the refinement stage:[10] application of the $\Delta f''$ corrections allowed a determination of the absolute structure.

TABLE 2

Atomic parameters ($\times 10^4$) for $[Eu(ClO_4)L][ClO_4]_2 \cdot MeCN$

Atom	X	Y	Z
Eu	1 087(1)	1 413(2)	978(3)
Cl(1)	494(4)	1 477(15)	4 022(20)
Cl(2)	4 202(5)	4 086(14)	1 340(14)
Cl(3)	2 716(4)	2 950(13)	6 193(20)
O(1)	888(11)	2 066(31)	3 854(48)
O(2)	404(12)	853(38)	2 379(50)
O(3)	490(14)	324(43)	4 922(47)
O(4)	215(13)	2 478(42)	4 445(47)
O(5)	4 446(12)	4 133(34)	2 622(45)
O(6)	3 898(15)	3 112(39)	1 414(50)
O(7)	4 480(16)	3 712(60)	111(54)
O(8)	3 978(17)	5 195(43)	1 147(65)
O(9)	3 076(13)	2 937(34)	7 038(45)
O(10)	2 406(13)	3 553(54)	7 012(50)
O(11)	2 775(12)	3 820(40)	4 950(43)
O(12)	2 583(11)	1 717(45)	5 793(57)
N(1)	1 308(13)	3 802(44)	1 579(47)
N(2)	866(11)	−911(32)	362(38)
C(1)	1 749(15)	3 783(54)	2 281(57)
C(2)	1 768(13)	2 815(45)	3 203(51)
O(13)	1 724(9)	1 635(35)	2 437(37)
C(3)	1 927(15)	490(46)	2 957(56)
C(4)	1 577(16)	−278(50)	3 848(82)
O(14)	1 252(9)	−353(29)	2 716(34)
C(5)	1 006(13)	−1 441(52)	2 890(46)
C(6)	709(14)	−1 614(50)	1 710(54)
C(7)	1 421(20)	4 445(62)	38(76)
C(8)	1 601(13)	3 739(49)	−1 187(62)
O(15)	1 383(8)	2 597(26)	−1 202(39)
C(9)	1 613(17)	1 904(51)	−2 200(67)
C(10)	1 815(16)	812(51)	−1 643(60)
O(16)	1 554(9)	198(27)	−644(35)
C(11)	1 449(15)	−1 043(44)	−1 321(57)
C(12)	1 202(13)	−1 733(40)	−283(44)
C(13)	973(18)	4 401(54)	2 356(68)
C(14)	619(18)	4 300(55)	1 608(62)
O(17)	597(8)	3 196(25)	767(39)
C(15)	316(17)	3 125(47)	−248(61)
C(16)	393(16)	2 388(52)	−1 628(60)
O(18)	602(9)	1 166(30)	−1 059(46)
C(17)	322(16)	68(51)	−1 142(79)
C(18)	544(15)	−932(47)	−841(76)
C(20)	2 933(13)	3 869(39)	800(58)
C(21)	2 789(16)	2 571(51)	960(78)
N(3)	2 711(12)	1 591(50)	953(64)

Structure determination and refinement. The positions of the europium and chlorine atoms were obtained from a three-dimensional Patterson synthesis. Successive three-dimensional Fourier syntheses showed the positions of all the non-hydrogen atoms. Refinement was performed with the full-matrix least-squares program of Busing and Levy, as adapted by Stewart.[11] The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$. Anisotropic temperature factors were used for Eu and Cl atoms, isotropic temperature factors for the other atoms. The hydrogen atoms of the cryptand L were introduced in calculated positions (C–H 0.95 Å) with temperature factors $B_H = 1 + B_{C(attached)}$. These atoms were not refined. At this point the absolute configuration of the complex was determined by mixed cycles on the two possible configurations, which gave R values of 0.072 and 0.075, respectively. The final R' factor $\{[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$ was 0.075. Final atomic parameters with their standard deviations are given in Table 2. A final ΔF Fourier synthesis did not show remarkable features. The observed and calculated structure factors and thermal parameters are available as Supplementary Publication No. SUP 22458 (10 pp.).*

RESULTS AND DISCUSSION

Description of the Structure.—The structure of $[Eu(ClO_4)L][ClO_4]_2 \cdot MeCN$ consists of $[Eu(ClO_4)L]^{2+}$ cations, $[ClO_4]^-$ anions, and interposed MeCN solvent molecules. The europium atom is ten-co-ordinate, being linked to the eight donor atoms of the cryptand molecule and to two oxygen atoms of a $[ClO_4]^-$ group. The co-ordination polyhedron can be described in terms of a distorted square-bicapped antiprism having the two nitrogen

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

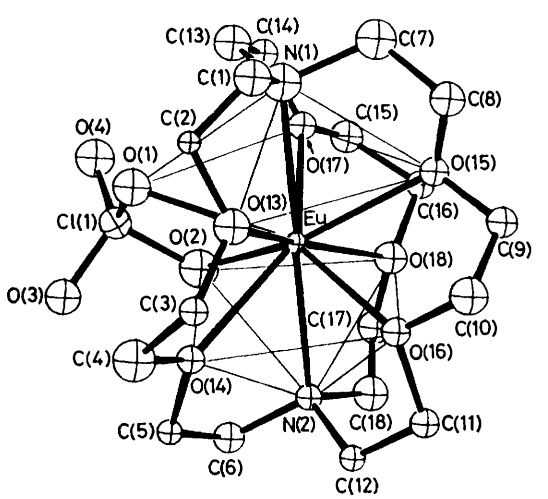

FIGURE 1 Perspective view of the $[\mathrm{Eu(ClO_4)L}]^{2+}$ cation

atoms in axial positions and the eight oxygen atoms at the vertices of the two squares (Figure 1). Figure 2 shows a stereoscopic view of the cell. Selected bond distances and angles are given in Table 3. The deviations from the idealized geometry, which are mainly due to the geometrical requirements of the oxygen atoms of the $[\mathrm{ClO_4}]^-$ anion, are rather small: N(1)–Eu–N(2) 179.4(14)°; the two square planes, whose least-squares equations are $10.50X + 9.81Y + 2.03Z = 3.83$ and $10.87X + 9.77Y + 2.04Z = 1.66$, respectively, form with the N(1)–Eu–N(2) least-squares line angles of 87.16 and 87.57°, respectively. The displacements of these atoms from the least-squares plane are all <0.1 Å. The angles between the diagonals of the two squares are in the range 33—56°, in good agreement with this antiprismatic geometry.

The Eu–N [2.70(5) and 2.64(3) Å], Eu–O(perchlorate) [2.71(4) and 2.67(4)], and Eu–O(ether) distances [2.44(4)—2.52(3), mean 2.49 Å] are much shorter than the corresponding distances found in the 12-co-ordinate lanthanum complex $[\mathrm{La(NO_3)_2L}]_3[\mathrm{La(NO_3)_6}]\cdot2\mathrm{MeOH}$.[4] Such differences can be ascribed to the different ionic radii of the metals which depend on the co-ordination number.[12] In both structures the M–N are much longer than the M–O(ether) distances. This result, which has also been found in other complexes of L with alkali and alkaline-earth metal ions,[13] is probably due to the smaller electron density on the nitrogen atoms compared to the oxygen atoms.

The Eu–O(ether) distances can also be compared with the Eu–O distances found in nine-co-ordinate $[\mathrm{Eu(O_2CCH_2OH)_3}]$ in which the average Eu–O(carboxyl) distance is 2.45 Å and the average Eu–O(alcohol) is 2.62 Å;[14] this difference may also be caused by the different electric charges on these two types of oxygen atom. In the present complex, the Eu–O(perchlorate) distance (mean 2.69 Å) is 0.20 Å longer than the mean Eu–O(ether) distance. This is indicative of the weak co-ordination by the perchlorate anion. In contrast, with the $[\mathrm{La(NO_3)_2L}]^+$ species, the La–O(nitrate) and La–O(ether) distances are approximately equal.[4]

TABLE 3

Interatomic distances (Å), angles (°), and their respective standard deviations

(a) Selected bond lengths

Eu–N(1)	2.70(5)	Cl(1)–O(4)	1.47(5)
Eu–N(2)	2.64(3)	Cl(2)–O(5)	1.40(4)
Eu–O(1)	2.71(4)	Cl(2)–O(6)	1.46(5)
Eu–O(2)	2.67(4)	Cl(2)–O(7)	1.49(5)
Eu–O(13)	2.51(3)	Cl(2)–O(8)	1.41(5)
Eu–O(14)	2.49(3)	Cl(3)–O(9)	1.42(5)
Eu–O(15)	2.50(3)	Cl(3)–O(10)	1.42(5)
Eu–O(16)	2.49(3)	Cl(3)–O(11)	1.45(4)
Eu–O(17)	2.52(3)	Cl(3)–O(12)	1.43(5)
Eu–O(18)	2.44(4)	C–O (av.)	1.44
Cl(1)–O(1)	1.47(4)	N–C (av.)	1.53
Cl(1)–O(2)	1.62(5)	C–C (av.)	1.45
Cl(1)–O(3)	1.46(5)		

(b) Selected bond angles

N(1)–Eu–N(2)	179.4(1.4)	O(2)–Eu–O(15)	143.9(1.1)
N(1)–Eu–O(1)	69.1(1.1)	O(2)–Eu–O(16)	133.7(1.1)
N(1)–Eu–O(13)	64.9(1.2)	O(2)–Eu–O(17)	69.0(1.1)
N(1)–Eu–O(15)	64.4(1.1)	O(2)–Eu–O(18)	75.1(1.2)
N(1)–Eu–O(17)	59.0(1.1)	O(13)–Eu–O(14)	64.2(1.1)
N(2)–Eu–O(2)	69.2(1.2)	O(13)–Eu–O(15)	90.5(1.0)
N(2)–Eu–O(14)	58.7(1.0)	O(13)–Eu–O(16)	78.8(1.0)
N(2)–Eu–O(16)	64.6(1.0)	O(13)–Eu–O(17)	121.6(1.1)
N(2)–Eu–O(18)	63.9(1.1)	O(13)–Eu–O(18)	163.3(1.1)
N(1)–Eu–O(2)	110.8(1.3)	O(14)–Eu–O(15)	139.9(1.0)
N(1)–Eu–O(14)	121.9(1.1)	O(14)–Eu–O(16)	79.7(1.0)
N(1)–Eu–O(16)	115.4(1.1)	O(14)–Eu–O(17)	139.5(1.0)
N(1)–Eu–O(18)	115.5(1.2)	O(14)–Eu–O(18)	121.4(1.0)
N(2)–Eu–O(1)	111.3(1.0)	O(15)–Eu–O(16)	64.5(0.9)
N(2)–Eu–O(13)	115.6(1.2)	O(15)–Eu–O(17)	79.8(1.0)
N(2)–Eu–O(15)	115.2(1.0)	O(15)–Eu–O(18)	75.8(1.1)
N(2)–Eu–O(17)	120.6(1.0)	O(16)–Eu–O(17)	139.6(1.0)
O(1)–Eu–O(2)	54.1(1.2)	O(16)–Eu–O(18)	86.6(1.1)
O(1)–Eu–O(13)	72.9(1.1)	O(17)–Eu–O(18)	65.9(1.0)
O(1)–Eu–O(14)	70.9(1.0)	O(1)–Cl(1)–O(2)	104.6(2.4)
O(1)–Eu–O(15)	133.4(1.0)	O(1)–Cl(1)–O(3)	114.9(2.5)
O(1)–Eu–O(16)	145.7(1.0)	O(1)–Cl(1)–O(4)	106.9(2.4)
O(1)–Eu–O(17)	73.5(1.1)	O(2)–Cl(1)–O(3)	98.0(2.4)
O(1)–Eu–O(18)	123.5(1.1)	O(2)–Cl(1)–O(4)	113.9(2.4)
O(2)–Eu–O(13)	121.0(1.2)	O(3)–Cl(1)–O(4)	117.8(2.7)
O(2)–Eu–O(14)	74.8(1.1)		

It is noteworthy that the cryptand L is sufficiently flexible to allow additional ligands to approach the tervalent metal ion, thus increasing its co-ordination number. On the other hand, conductivity data (Table 1)

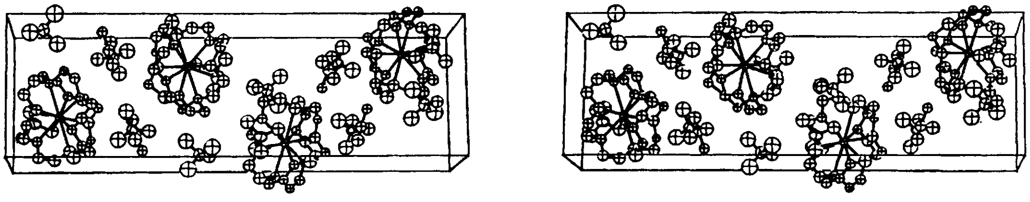

FIGURE 2 Stereoscopic view of $[\mathrm{Eu(ClO_4)L}][\mathrm{ClO_4}]_2\cdot\mathrm{MeCN}$. The *b* axis is vertical, the *a* axis horizontal, and the *c* axis points into the paper

show that all the complexes behave as 3 : 1 electrolytes in 10^{-3} mol dm^{-3} MeCN solutions, irrespective of their stoicheiometry. In complexes of series (*i*), ionization of the bound perchlorate anion is presumably favoured by solvent co-ordination.

Infrared Spectra.—With the present complexes only the ν_4 vibration (in T_d symmetry) is diagnostic of co-ordination of the perchlorate group since the ν_3 vibration strongly interferes with the ligand absorptions. The i.r. spectra of all complexes of series (*i*) show splittings of the ν_4 vibrations of the perchlorate anion with two bands at 620 and 645 cm^{-1}. This is consistent with the determined structure of the europium complex, having both free (620 cm^{-1}) and co-ordinated (645 cm^{-1}) [15] perchlorate. The same structure can thus be suggested for all complexes of series (*i*). On the other hand, for complexes of series (*ii*) and (*iii*), no splitting of the ν_4 vibration is observed. It is suggested, therefore, that only ionic perchlorate is present.

Finally, the complexes of series (*iii*) exhibit broad bands at 3 200—3 400 cm^{-1} and sharp bands at 1 665 and 1 590 cm^{-1} which are attributed to NH stretching, amide I and amide II bands, respectively, of acetamide.[16] In chloroform solution, acetamide exhibits the amide I and amide II bands at 1 680 and 1 600 cm^{-1}, respectively. Red shifts of these two bands have been considered to be diagnostic of amide co-ordination to a Lewis acid through the oxygen atom. In the present case, however, the observed red shifts of 10—15 cm^{-1} are too small to draw any definite conclusion about the co-ordination of acetamide to the lanthanoid ion.

Electronic Spectra.—The *f–f* bands of these cryptates in MeCN solution show only small changes with respect to those of the corresponding anhydrous perchlorates in the same solvent. In addition, the cryptates of samarium, europium, and ytterbium exhibit very broad absorption bands with maxima at 41 300, 32 100 (32 500 in the solid), and 38 100 cm^{-1}, respectively. These transitions can be safely attributed to electron transfer from the highest-energy molecular orbitals of the ligands to 4*f* orbitals.[17,18] Using the frequency values of these band maxima and the values for the uncorrected optical electronegativities of 1.6(Sm), 1.9(Eu), and 1.8(Yb),[17] one obtains a value of 3.0 for the optical electronegativity of the ligand moiety. In particular, such electron transitions probably involve chiefly the tertiary amine nitrogens, rather than ether oxygens, since solutions of the corresponding anhydrous perchlorates in ether solvents, such as dioxan or tetrahydrofuran, do not exhibit electron-transfer bands in these spectral regions. Moreover, a methyl cyanide solution of the europium perchlorate complex formed with the crown ether 1,4,7,10,13,16-hexaoxacyclo-octadecane has an electron-transfer band at 40 000 cm^{-1}.[19] The value of 3.0 for the optical electronegativity of cryptand L compares favourably with those attributed to ammonia and primary amines, *i.e.* 3.3 and 3.2, respectively.[17]

Finally, in MeCN solution the cerium(III) cryptate exhibits four sharp bands at 36 400 (560), 39 500 (730), 42 300 (390), and 44 700 cm^{-1} (ε 390 dm^3 mol^{-1} cm^{-1}); at >47 000 cm^{-1} MeCN is opaque. These bands can be safely assigned as four of the five 4*f*–5*d* transitions which are expected with cerium(III) chromophores of low symmetry.

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