DALTON

Synthesis and spectroscopy of unsymmetric mononuclear lanthanide cryptates. Structure of two europium(III) cryptates co-existing in the same crystal $[EuL(OH_2)]\cdot[Eu(HL)(NCS)]\cdot9H_2O\cdot2MeCN\cdot EtCN\cdot EtOH$ (H_3L = a phenol-bridged N_8O_3 Schiff-base cryptand)

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Lanthanide cryptates of a phenol-bridged N_8O_3 Schiff-base cryptand (H_3L) have been synthesized by transmetallation with the sodium cryptate $[Na(H_2L)]$, where the cryptand was obtained by a basic template condensation of tris(2-aminoethyl)amine and 2,6-diformyl-4-methoxyphenol. The structure of $[EuL(OH_2)]\cdot[Eu(HL)(NCS)]\cdot9H_2O\cdot2MeCN\cdot EtCN\cdot EtOH$ showed the coexistence in the same crystal of two kinds of unsymmetric eight-co-ordinate europium(III) cryptates with different second ligands. The Eu–NCS linkage in $[Eu(HL)(NCS)]$ is linear [Eu–N≡C–S 175(2), N≡C–S 179(2)° and Eu–N 2.42(1) Å].

The design and synthesis of lanthanide complexes of macrocyclic ligands have been attracted much current attention.[1] These compounds have been studied as supramolecular devices,[2–4] as fluorescent probes and luminescent labels in biological systems and medical diagnostics,[5–7] as efficient catalysts for cleavage of RNA,[8] as contrast-enhancing agents in magnetic resonance imaging,[9,10] as NMR shift and relaxation reagents,[11–12] and as effective chelators in the separation and purification of lanthanides.[13,14] The lanthanide complexes of two-dimensional phenolate-bridged macrocyclic ligands have been extensively studied and reviewed.[1] Drew *et al.*[15] reported the crystal structure of lanthanide (Y^{3+}, Tb^{3+} and Gd^{3+}) complexes of three-dimensional phenolate-bridged macrobicyclic ligands (cryptands). However, to our knowledge, only two phenolate-bridged N_8O_3 Schiff-base cryptands have been synthesized, by a (2 + 3) condensation of tris(2-aminoethyl)amine with 2,6-diformyl-4-Y-phenol (Y = Me or Bu^t) with a neutral sodium template.[15–20]

Herein we present a deprotonated analogue (H_2L^-) formed by a (2 + 3) condensation of tris(2-aminoethyl)amine with 2,6-diformyl-4-methoxyphenol under basic conditions. By transmetallation with the sodium cryptate, the lanthanide complexes of the cryptand in three protonated forms [$H_3L(C_{39}H_{48}N_8O_6)$, HL^{2-} and L^{3-}] were synthesized and characterized by spectroscopic studies (one- and two-dimensional NMR, IR and electronic), as well as by the crystal structure analysis of two independent eight-co-ordinate europium(III) cryptates coexisting in the same crystal. The lanthanide cryptates possess an unsymmetric mononuclear eight-co-ordinate structure in which the cryptand provides one site for the metal ion, another for protons or is empty. Such cryptands could be used to form d–f heterobinuclear cryptates with metal ions in close proximity, and thus enable metal–metal interactions and their potential applications.

Experimental

General

Lanthanide perchlorate and isothiocyanate salts were prepared from the corresponding oxides and chloride (99.9%, China), respectively. 2,6-Diformyl-4-methoxyphenol was prepared by the procedure described by Taniguchi.[21] Tris(2-aminoethyl)amine (tren) was prepared by a modified method, for which the starting materials tris(2-chloroethyl)amine hydrochloride and sodium diformylamide were prepared according to Kimura *et al.*[22] and Han and Hu,[23] respectively. All solvents were commercial products, used without further purification. Spectroscopic measurements were carried out with Varian Unity 500 MHz [NMR, $(CD_3)_2SO$, $SiMe_4$ as internal standard], MAT 8230 (FAB mass), Perkin-Elmer 577 (IR, KBr disc), Shimadzu UV-3000 (electronic) and Shimadzu RF-540 (luminescence) instruments. Elemental analysis was performed by the analytic division of the State Key Laboratory of Structure Chemistry in our institute.

Syntheses

$[Na(H_2L)]$ 1. An anhydrous methanol solution (50 cm^3) of tren (0.146 g, 1 mmol) was added dropwise to a suspension of NaOH (0.060 g, 1.5 mmol) and 2,6-diformyl-4-methoxyphenol (0.270 g, 1.5 mmol) in anhydrous methanol (50 cm^3) at room temperature over 1 h. The resulting orange precipitate of compound **1** was filtered off, washed with methanol and chloroform and dried over $CaCl_2$. Yield 71% (Found: C, 62.65; H, 6.65; N, 15.2. $C_{39}H_{47}N_8NaO_6$ requires C, 62.7; H, 6.35; N, 15.0%). λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) (MeCN) 258 (14 900) and 370 (10 000). IR: 3543, 3411w (NH), 3244, 3012, 2995, 2939, 2906, 2842, 2810, 1643vs (CN), 1597, 1460vs, 1431, 1317, 1300, 1259, 1217, 1192, 1155s, 1051, 960, 815 and 754 cm^{-1}. *m/z* 748 (*M* + 2H) and 726 (*M* + 3H − Na).

$[Na(H_3L)]ClO_4$ 2. A mixture of an excess of anhydrous $NaClO_4$ (0.8 g) and 2,6-diformyl-4-methoxyphenol (0.270 g, 1.5 mmol) in anhydrous methanol (50 cm^3) was added dropwise to an anhydrous methanol solution (50 cm^3) of tren (0.146 g, 1 mmol). After stirring for 2 h, the resulting red precipitate **2** was filtered off, washed with methanol and chloroform and dried over $CaCl_2$. Yield 74% (Found: C, 55.3; H, 5.70; N, 13.25. $C_{39}H_{48}ClN_8NaO_{10}$ requires C, 55.3; H, 5.65; N, 13.25%). λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) (MeCN) 278 (13 100), 365 (9300) and 480 (9100). IR: 3502w (NH), 2941, 2902, 2837, 1645vs (CN), 1537, 1458, 1384, 1300, 1089s (ClO_4^-), 796 and 626 cm^{-1}.

$[La(H_3L)(dmf)][ClO_4]_3\cdot H_2O$ 3. A solution of compound **1** (0.149 g, 0.2 mmol) or **2** (0.169 g, 0.2 mmol) in acetonitrile (20 cm^3) was added to a stirred solution of lanthanum perchlorate

(0.22 g, *ca.* 0.4 mmol) in ethanol (20 cm^3) and heated to reflux for 0.5 h. The reaction was cooled to room temperature, a yellow powder was filtered off and recrystallized from dimethylformamide (dmf). Slow diffusion of diethyl ether into the solution over 1 week resulted in yellow needle crystals. Yield 83% based on H_3L (Found: C, 40.0; H, 4.60; N, 10.4. $C_{42}H_{57}Cl_3LaN_9O_{19}$ requires C, 40.25; H, 4.55; N, 10.05%). λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 250 (15 780), 280 (12 650) and 435 (8000). IR: 3404w (NH), 3076, 2937, 2860, 2841, 1652vs (CN), 1604, 1548s, 1479s, 1352, 1292, 1219, 1089s (ClO_4^-), 842, 804s, 667 and 624 cm^{-1}.

$[EuL(OH_2)]\cdot[Eu(HL)(NCS)]\cdot 9H_2O\cdot 2MeCN\cdot EtCN\cdot EtOH$ 4. A mixture of compound **1** (0.149 g, 0.2 mmol) or **2** (0.169 g, 0.2 mmol) in acetonitrile (20 cm^3) and europium isothiocyanate (0.174 g, 0.4 mmol) in ethanol (20 cm^3) was stirred and heated to reflux for 0.5 h. The reaction solution was filtered. The yellow filtrate was allowed to evaporate at room temperature over 2 months, whereupon orange cubic crystals of compound **4** suitable for X-ray analysis were obtained. The EtCN crystalline solvent came from an impurity in acetonitrile (cp. grade). Yield 61% (based on H_3L) (Found: C, 48.4; H, 5.90; N, 13.15. $C_{88}H_{128}Eu_2N_{20}O_{23}S$ requires C, 48.7; H, 5.95; N, 12.9%). λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 285 (39 600) and 438 (31 900). IR: 3406w (H_2O), 3066, 2898, 2858, 2839, 2054vs (NCS), 1652vs (CN), 1637s, 1604, 1548s, 1477s, 1350s, 1294s, 1215, 1041 and 806 cm^{-1}.

Crystallography

Crystal data. $C_{88}H_{128}Eu_2N_{20}O_{23}S$, **4**, $M = 2170.11$, triclinic, space group $P\bar{1}$, $a = 16.267(11)$, $b = 16.802(22)$, $c = 20.111(17)$ Å, $\alpha = 109.93(10)$, $\beta = 103.25(10)$, $\gamma = 95.31(9)°$, $U = 4941.4$ Å^3. Cell data were based upon the setting angles of 25 reflections with $14 < \theta < 15°$. $\lambda = 0.710\,73$ Å, $Z = 4$, $D_c = 1.46$ g cm^{-3}, $F(000) = 2244$. Orange cubic crystals, hygroscopic. Crystal dimensions $0.30 \times 0.25 \times 0.25$ mm, μ(Mo-Kα) = 13.6 cm^{-1}.

Data collection and processing. Crystals were encapsulated in gel. Enraf-Nonius CAD 4 diffractometer, ω–2θ mode with ω-scan width = $0.5 + 0.350 \tan \theta$, Mo-Kα radiation. 14 305 Reflections measured at 293 K ($2 \leqslant 2\theta \leqslant 46.0°$; $0 \leqslant h \leqslant 17$, $-18 \leqslant k \leqslant 18$, $-22 \leqslant l \leqslant 22$), 13 728 unique of which 10 628 had $I > 3.00\sigma(I)$. $R_{int} = 0.016$ after absorption correction (maximum and minimum transmission factors = 0.999 and 0.854). Lorentz-polarization, an anisotropic decay and an empirical absorption correction were applied, using the program DIFABS.[24]

Structure analysis and refinement. The structure was solved using the Patterson heavy-atom method which revealed the positions of the Eu atoms. The remaining atoms were located in subsequent Fourier-difference synthesis. Hydrogen atoms of the cryptands were located in calculations but were not refined. The final cycle of full-matrix least-squares refinement (*F*) was based on 10 628 reflections [$I > 3.00\sigma(I)$] and 1068 variable parameters and converged with *R* and *R′* values of 0.069 and 0.083, respectively. The weighting scheme was $w = [\sigma^2(F_o^2) + (0.010F_o)^2 + 1.0]^{-1}$. Goodness of fit = 1.74. The maximum and minimum peaks on the final Fourier-difference map corresponded to 2.72 (a ghost in the solvent region) and −0.09 e Å^{-3}. All non-hydrogen atoms of the crystalline solvents were revealed by the Fourier-difference synthesis. A EtCN molecule was found in the crystal and came from impure acetonitrile. No SCN^- anion was found that isothiocyanate bound to the Eu atom in the cryptate. Some solvent molecules had high thermal motion and were possibly disordered, although we were unable to refine a satisfactory model. All calculations were performed on a COMPAQ computer using the MoLEN PC program.[25]

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/193.

Results and Discussion

Synthesis and spectroscopic properties

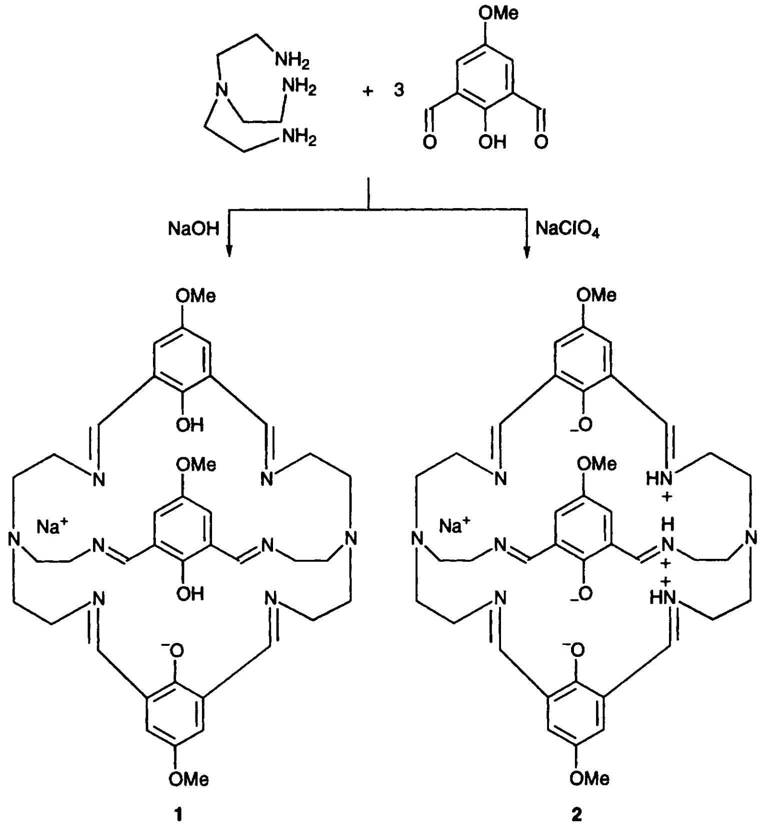
The sodium cryptates were synthesized by different sodium templating reactions as shown in Scheme 1. Cryptates **1** and **2** were obtained under basic and neutral conditions, respectively. The basic template synthesis gave the deprotonated cryptand H_2L^- in high yield and purity. The FAB mass spectrum of **1** had only two important peaks at *m*/*z* 748 and 726, corresponding to a mononuclear sodium cryptate and a metal-free cryptand, respectively. Only monometal products formed under basic or neutral conditions, with 1 or 3 equivalents of the template ions. However, similar sodium template synthesis resulted in binuclear sodium complexes of phenolate-bridged Schiff-base (2 + 2) macrocycles.[26] This shows that the cavity size selectivity plays an important role in the (2 + 3) condensation process.

The IR spectra of all cryptates **1**–**4** show no bands characteristic of aldehydes and primary amine groups. However, all possess a very strong band in the range 1642–1652 cm^{-1}, assigned to the imino stretching mode, supporting the Schiff-base formation. The NMR spectra also show no peaks assigned to CHO and NH_2 groups, again confirming the formation of the (2 + 3) macrobicycle.

There is some difference in spectroscopic features between compounds **1** and **2** as shown in Table 1. Cryptate **2** possesses a similar ^1H NMR pattern to those of unsymmetric mononuclear cryptates reported by Nelson and co-workers,[16] consisting of two pairs of imine and aromatic resonances. It shows two different sites in the cryptand, one occupied by a sodium ion, another by three protons transferred from the phenol to the imine groups, resulting in a broad peak at δ 14.22 assigned to three $C{=}NH^+$ groups. However, the spectrum of **1** at room temperature shows no splitting of imine and aromatic resonances. The singlet peaks at δ 8.45, 6.95 and 13.79 are much better resolved, and are assigned to six imine CH, six aromatic CH and 2 H transferred from two phenol groups, respectively. The unsplit broad spectrum is indicative of a fast proton transfer or conformational exchange in solution. The IR spectrum of **1** also shows a broad band at 3411 cm^{-1} with two shoulder bands at 3543 and 3244 cm^{-1} assigned to NH stretching, whereas that of **2** only has a broad band at 3502 cm^{-1} in this region.

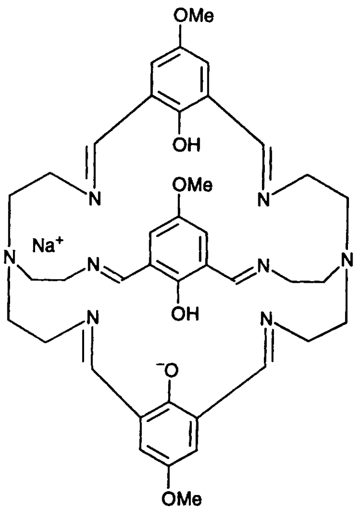
In solution, compounds **1** and **2** display two and three bands in their electronic spectra, respectively. These are attributed to π–π* transitions. Compound **1** possesses only two bands in the UV region, close to the corresponding absorption of **2**. However, **2** has another strong band (λ = 480 nm, ε = 9100 dm^3 mol^{-1} cm^{-1}).

Owing to low solubility, sodium cryptates **1** and **2** are not suitable for further NMR experiments. However, the lanthanide cryptate **3** exhibits good solubility and kinetic stability, and is suitable for the ^{13}C and two-dimensional NMR studies. The ^1H NMR spectrum shows that **3** possesses the same resonance pattern as described by Drew *et al.*[15] for scandium(III) and yttrium(III) analogues, consisting of two pairs of distinguishable imine CH and aromatic CH resonances. There is a clearly resolved ^1H–^1H coupling of 15 Hz at δ 8.81, 8.78, which can only be explained on the basis of *trans* coupling to a proton on the imino nitrogen ($HC{=}NH^+$) in accord with a similar unsymmetric lead(II) mononuclear cryptate.[16] The correlation spectroscopy (COSY) experiment also shows the

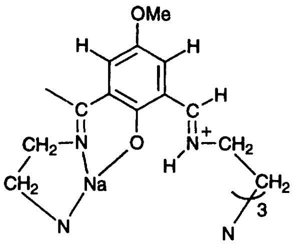


Scheme 1

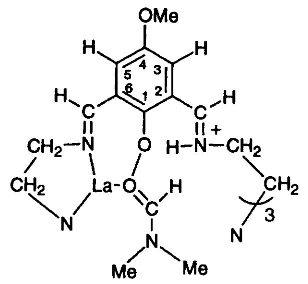
Table 1 NMR data for the cryptates



1



2



3

Cryptate	NH^+	$HC{=}N^+$	HC=N	Ph	OCH_3	$=N^+CH_2$	$=NCH_2$	$>NCH_2$	HC=O (dmf)	NMe (dmf)
1	13.79 (s)		8.46 (br)	6.95 (br)	3.67		3.59, 3.55	2.81br		
2	14.22	8.32 (br)	8.25	7.15 6.92	3.76	3.66	3.25	2.90, 2.68		
3	12.53 (br)	8.81, 8.78	8.35	7.60 7.24	3.75	3.39	3.31	2.74br	7.96	2.89, 2.96
(^{13}C)		169.5	166.1	166.7 (C^1) 125.8 (C^2) 134.0 (C^3) 147.9 (C^4) 121.2 (C^5) 115.7 (C^6)	56.0	58.6	59.3	59.5	162.3	30.7 35.7

At 500 MHz, room temperature, solvent $(CD_3)_2SO$, $SiMe_4$ as internal standard.

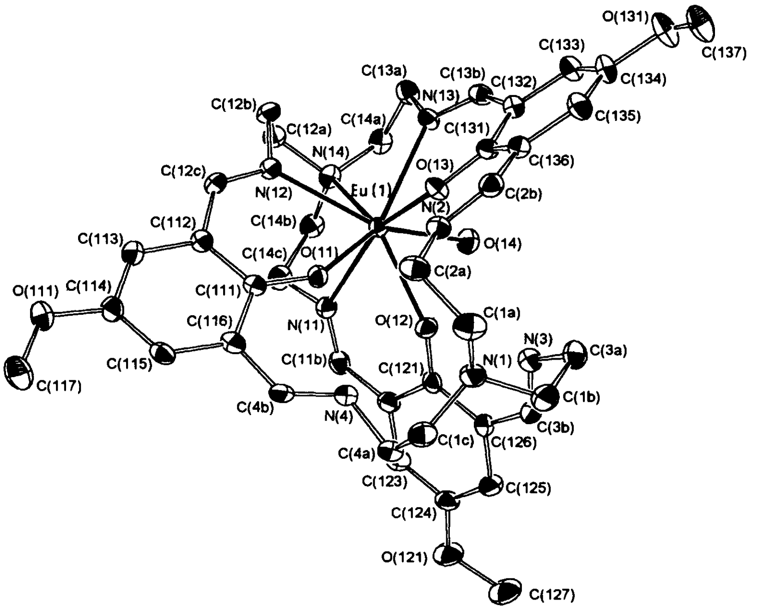


Fig. 1 Structure of cryptate [EuL(OH$_2$)]

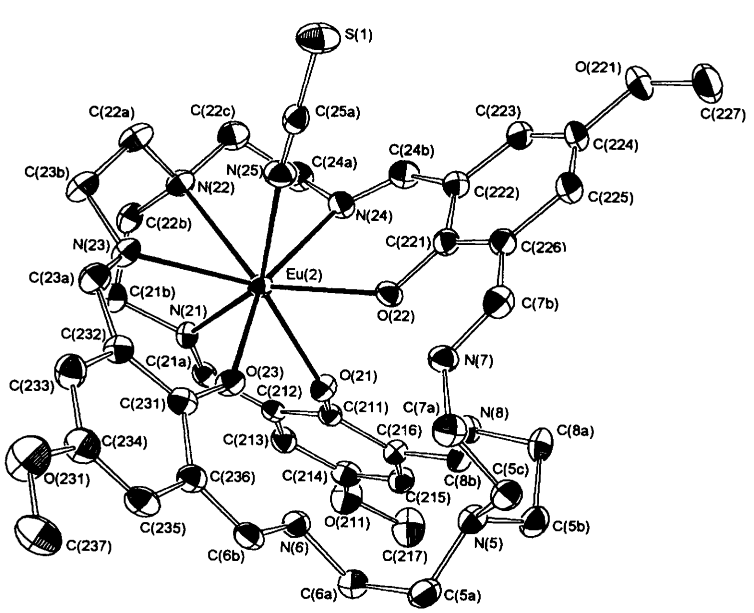


Fig. 2 Structure of cryptate [Eu(HL)(NCS)]

imine resonances at δ 8.81, 8.87 coupling to NH$^+$ at δ 12.53, together with a weak coupling to one CH$_2$ resonance at δ 3.31. The ^{13}C NMR and ^{13}C–H COSY suggest two kinds of imino C at δ 169.5 and 166.1, respectively. All experiments reveal that there is an unsymmetric proton-transfer process from phenol to imino nitrogen upon lanthanum(III) co-ordination, resulting in formation of HC=NH$^+$ groups (NH$^+$ at δ 12.53, HC=N$^+$ at δ 8.81 and 8.87). The CH resonance of the protonated imine shows a larger downfield shift than that of the neutral co-ordinated imine at δ 8.35.

A comparison with the NMR spectra shows that cryptate **2** has the same protonated form (H$_3$L) as that of **3**. However, the corresponding resonances of **3** are much better resolved than those of **2**, indicating that the lanthanide cryptate possesses less conformational mobility than the sodiun cryptate which presents broad overlapped peaks at corresponding chemical shifts. This is attributed to the higher co-ordination numbers and higher charge of lanthanide ions together with stronger metal–ligand bonding. The co-ordination between metal and dmf in **3** may also reduce the conformational mobility of the cryptand.

It is worthwhile mentioning that the proton transfer upon co-ordination of lanthanide in solution is very sophisticated. When lanthanium(III) perchlorate reacted with sodium cryptate **1** (which contains H$_2$L$^-$) in dmf, cryptate **3** which contains H$_3$L was obtained; however, when europium(III) isothiocyanate reacted with **1** or **2** (containing H$_3$L) in MeCN–EtOH, complex **4** containing both HL^{2-} and L^{3-} was obtained and characterized by crystal-structure analysis. Whether protonated or deprotonated cryptand (H$_3$L, H$_2$L$^-$, H$_2$L^{2-} or L^{3-}) was present, only monometal cryptates were formed. The N$_8$O$_3$ phenolate-bridged Schiff-base cryptand exhibits high mononuclear size selectivity towards lanthanide(III) or sodium(I) ions as described above. The luminescence spectra of **2** and **4** were analysed at 20 °C in ethanol. A weak ligand luminescence was observed (cryptate **2**, λ_{em} = 550, λ_{ex} = 360; cryptate **4**, λ_{em} = 525, λ_{ex} = 300 nm), but no lanthanide emission.

Table 2 Selected bond distances (Å) and angles (°) for $[EuL(OH_2)]\cdot[Eu(HL)(SCN)]\cdot 9H_2O\cdot 2MeCN\cdot EtCN\cdot EtOH$

Cryptate $[EuL(OH_2)]$		Cryptate $[Eu(HL)(NCS)]$	
Eu(1)–O(11)	2.357(8)	Eu(2)–O(21)	2.350(8)
Eu(1)–O(12)	2.353(8)	Eu(2)–O(22)	2.349(9)
Eu(1)–O(13)	2.257(8)	Eu(2)–O(23)	2.264(8)
Eu(1)–O(14)	2.437(8)	Eu(2)–N(21)	2.53(2)
Eu(1)–N(11)	2.502(9)	Eu(2)–N(22)	2.662(8)
Eu(1)–N(12)	2.534(9)	Eu(2)–N(23)	2.58(2)
Eu(1)–N(13)	2.59(1)	Eu(2)–N(24)	2.50(2)
Eu(1)–N(14)	2.69(1)	Eu(2)–N(25)	2.42(1)
N(2)–C(2b)	1.29(2)	N(6)–C(6b)	1.30(2)
N(3)–C(3b)	1.29(1)	N(7)–C(7b)	1.30(2)
N(4)–C(4b)	1.30(2)	N(8)–C(8b)	1.30(2)
N(11)–C(11b)	1.25(1)	N(21)–C(21a)	1.26(2)
N(12)–C(12b)	1.28(2)	N(23)–C(23a)	1.29(2)
N(13)–C(13b)	1.27(2)	N(24)–C(24b)	1.26(2)
		S–C(25a)	1.63(2)
		N(25)–C(25a)	1.15(2)
O(11)–Eu(1)–O(12)	71.0(3)	O(21)–Eu(2)–O(22)	70.3(3)
O(11)–Eu(1)–O(13)	79.4(3)	O(21)–Eu(2)–O(23)	78.5(3)
O(11)–Eu(1)–O(14)	143.8(3)	O(21)–Eu(2)–N(21)	69.4(3)
O(11)–Eu(1)–N(11)	86.3(4)	O(21)–Eu(2)–N(22)	126.3(4)
O(11)–Eu(1)–N(12)	69.9(4)	O(21)–Eu(2)–N(23)	139.9(3)
O(11)–Eu(1)–N(13)	139.5(2)	O(21)–Eu(2)–N(24)	86.8(4)
O(11)–Eu(1)–N(14)	126.7(4)	O(21)–Eu(2)–N(25)	142.8(3)
O(12)–Eu(1)–O(13)	85.4(3)	O(22)–Eu(2)–O(23)	85.9(3)
O(12)–Eu(1)–O(14)	72.8(4)	O(22)–Eu(2)–N(21)	137.9(4)
O(12)–Eu(1)–N(11)	72.8(3)	O(22)–Eu(2)–N(22)	135.5(3)
O(12)–Eu(1)–N(12)	138.8(4)	O(22)–Eu(2)–N(23)	131.8(3)
O(12)–Eu(1)–N(13)	131.8(3)	O(22)–Eu(2)–N(24)	73.0(3)
O(12)–Eu(1)–N(14)	134.5(2)	O(22)–Eu(2)–N(25)	72.7(3)
O(13)–Eu(1)–O(14)	97.9(3)	O(23)–Eu(2)–N(21)	97.3(4)
O(13)–Eu(1)–N(11)	156.9(3)	O(23)–Eu(2)–N(22)	134.5(3)
O(13)–Eu(1)–N(12)	99.7(3)	O(23)–Eu(2)–N(23)	71.7(3)
O(13)–Eu(1)–N(13)	71.6(4)	O(23)–Eu(2)–N(24)	157.5(3)
O(13)–Eu(1)–N(14)	135.0(3)	O(23)–Eu(2)–N(25)	102.1(3)
O(14)–Eu(1)–N(11)	83.1(3)	N(21)–Eu(2)–N(22)	66.0(3)
O(14)–Eu(1)–N(12)	144.8(3)	N(21)–Eu(2)–N(23)	88.1(3)
O(14)–Eu(1)–N(13)	69.4(3)	N(21)–Eu(2)–N(24)	93.3(3)
O(14)–Eu(1)–N(14)	80.4(3)	N(21)–Eu(2)–N(25)	145.2(3)
N(11)–Eu(1)–N(12)	92.2(3)	N(22)–Eu(2)–N(23)	66.0(4)
N(11)–Eu(1)–N(13)	129.1(3)	N(22)–Eu(2)–N(24)	68.0(3)
N(11)–Eu(1)–N(14)	68.0(3)	N(22)–Eu(2)–N(25)	79.9(3)
N(12)–Eu(1)–N(13)	87.6(3)	N(23)–Eu(2)–N(24)	128.6(3)
N(12)–Eu(1)–N(14)	65.6(3)	N(23)–Eu(2)–N(25)	71.3(5)
N(13)–Eu(1)–N(14)	65.8(3)	N(24)–Eu(2)–N(25)	79.5(4)
		Eu(2)–N(25)–C(25a)	175(2)
		S–C(25a)–N(25)	179(2)

Crystal structure of $[EuL(OH_2)]\cdot[Eu(HL)(NCS)]\cdot 9H_2O\cdot 2MeCN\cdot EtCN\cdot EtOH$ 4

The X-ray determination revealed the coexistence in the same crystal of two independent cryptates, together with 13 solvent molecules. Since there is no dissociated anion in the crystal, the protonated forms of the cryptand ligands can be defined according to the requirement for electrovalence equilibrium for the two independent cryptates. In the same crystal, one cryptate has deprotonated cryptand L^{3-} and H_2O, another has deprotonated cryptand HL^{2-} and NCS^-. Their structures are presented in Figs. 1 and 2, respectively. Relevant bond distances and angles are given in Table 2.

In both cryptates the Eu atoms have similar eight-co-ordination and the same intracryptand donors $N_4(O^-)_3$, resulting in two similar distorted dodecahedrons. The cryptand presents two different sites, one functioning as host for one Eu^{3+} ion and the other empty (in L^{3-}) or as host for a proton (in HL^{2-}). This unsymmetric monometal co-ordination is somewhat similar to those of other reported monometal cryptates.[15–18] The empty site has a cavity size of about 5 Å, capable of encapsulating another metal ion to form a heterodinuclear cryptate. Unlike some transition-metal ions,[16,18–20] such as Cd^{2+}, Mn^{2+}, Cu^{2+}, Co^{2+} or Fe^{2+}, giving corresponding dinuclear cryptates, only mononuclear lanthanide cryptates were formed with the present phenolate-bridged N_8O_3 Schiff-base cryptand in the presence of an excess of lanthanide ions. It has not yet been possible to add a second lanthanide ion to this cryptand to give f–f homo- or hetero-dinuclear cryptates. This is probably due to the high co-ordination numbers and large radii of lanthanides.

The Eu–O and Eu–N distances in the cryptand are in the range reported by Drew *et al.*,[15] indicating that the same intracryptand $N_4(O^-)_3$ donor set results in the same co-ordination geometry whether as a protonated or deprotonated cryptand (H_3L, H_2L^-, HL^{2-} or L^{3-}). The average Eu–O distance is 2.32 Å [ranging from 2.257(8) to 2.357(8) Å], slightly longer than that of a two-dimensional phenol-based Schiff-base macrocyclic europium(III) complex (2.28 Å), while the average distance Eu–N (imine) distance is 2.54 Å, approximately equal to that of the latter.[27] In contrast, the lanthanide complexes of tren and phenol-based Schiff-base tripodal ligands (*i.e.* open cryptands or hemicryptands) with the same $N_4(O^-)_3$ donor set are highly unstable and very sensitive to moisture. Hitherto no crystal structure has been reported which is comparable with the europium(III) cryptates in **4**, although a series of corresponding complexes have been synthesized under anhydrous conditions.[28]

By comparison with the europium(III) cryptate of the polyoxygen donor cryptand 222(4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane)[29] the Eu–O (phen-1) distance is significantly about 0.2 Å shorter than Eu–O (ether) [2.44(4)–2.52(3) Å], showing a stronger metal–ligand bonding in the phenolate-bridged cryptand than in the polyether cryptand; the Eu–N (bridgehead) distances of **4** are 2.69(1) and 2.662(8) Å, respectively, almost equal to those of the europium(III) complex of 222 cryptand [2.70(5) and 2.64(3) Å].

As shown in Table 2, the cryptates in compound **4** have highly similar structures. The small differences may arise mainly from the co-ordination of the second ligands, which provide an O donor in $[EuL(OH_2)]$ and a N donor in $[Eu(HL)(NCS)]$, respectively. The Eu atom of $[EuL(OH_2)]$ has an eight-co-ordinate environment with a N_4O_4 donor set, being isostructural to the lanthanide cryptates described by Drew *et al.*,[15] while the Eu atom of $[Eu(HL)(NCS)]$ is eight-co-ordinated by a N_5O_3 donor set. In $[EuL(OH_2)]$ the Eu–O (H_2O) is 2.437(8) Å, apparently, longer than that of Eu–O (intracryptand). This indicates that the bonding between Eu and O of water is weaker than that between Eu and O^- of phenolate.

In cryptate $[Eu(HL)(NCS)]$ the Eu–N (isothiocyanate) distance is 2.42(1) Å, in the range of values for one of the reported triisothiocyanate macrocyclic europium(III) complexes[30] having Eu(1)–NCS 2.475(8)–2.527(8) Å and Eu(2)–NCS 2.411(9)–2.439(5) Å. The N(25)–C(25a) and S–C(25a) distances are 1.15(2) and 1.63(2) Å, respectively, and the bond angles Eu(2)–N(25)–C(25a) and S–C(25a)–N(25) are 175(2) and 179(2)°, respectively. This indicates that the Eu–NCS and NCS groups are nearly linear. There are two main bonding forms for a co-ordinated isothiocyanate ligand.[31] One is a linear resonance form M–N≡C–S (M–N–C 180°, Pauling bond lengths N≡C 1.15 and C–S 1.81 Å); another is a bent resonance form M–N=C=S (M–N–C 120°, Pauling bond lengths N=C 1.29 and C=S 1.61 Å). The Eu–NCS linkage in this cryptate is in the linear form Eu–N≡C–S, although the C–S bond length is shorter by *ca.* 0.2 Å than expected for such a form.[31] The other isothiocyanate lanthanide(III) complex reported[32] $[NBu_4]_3[Er(NCS)_6]$ is a similar case, in which the Er–N–C–S groups are nearly linear [Er–N–C 174(2)°, Er–N 2.34(2), S–C 1.61(3) Å].

Acknowledgements

We thank the State Key Laboratories of Structural Chemistry and Coordination Chemistry of China and the Chinese Postdoctoral Science Foundation for support.

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Received 13*th March* 1996; *Paper* 6/01787H