Complex Formation between 1,1′-(1,4,10,13-Tetraoxa-7,16-diazacyclooctadecane-7,16-dicarbonyl)ferrocene and Yttrium Perchlorate†

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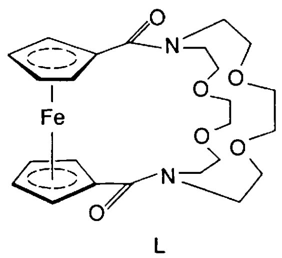
Multinuclear NMR and X-ray crystallography have revealed that the complex formed between yttrium perchlorate, 1,1′-(1,4,10,13-tetraoxa-7,16-diazacyclooctadecane-7,16-dicarbonyl)ferrocene (L) and water has a 1:2:1 stoichiometry (Y^{3+}:cryptand:H_2O) and confirmed that in complexes of this kind the amide carbonyl groups act as ligands and adopt the *cis* configuration within the cryptate.

In recent years we have reported on the synthesis, structure and cation-binding properties of a range of cryptands containing metallocene units.[1–10] The structures of several of these molecules have been determined by X-ray crystallography and in every case reported so far the amide carbonyl groups have been shown to be *trans* within the crystalline cryptand.[6,8,11,12] Multinuclear NMR studies have shown that the same *trans* configuration of the carbonyl groups exists in solution at ambient[2] but also that at elevated temperature the rotation of the carbonyl groups becomes fast on the NMR time-scale.[3] Further multinuclear NMR experiments suggested very strongly that on complexation with di- or tri-valent cations the carbonyl groups were involved as co-ordinating ligands and that in such complexes the carbonyl functions adopted a *cis* configuration.[10] This paper reports multinuclear NMR data (^{13}C and ^{89}Y) on complex formation between the cryptand 1,1′-(1,4,10,13-tetraoxa-7,16-diazacyclooctadecane-7,16-dicarbonyl)ferrocene (L) and $Y(ClO_4)_3 \cdot 6H_2O$ in acetonitrile–dichloromethane solution. The complex $[YL_2(H_2O)][ClO_4]_3$ was subsequently isolated and a determination of its structure by X-ray crystallography confirmed the predictions of the NMR experiments, thus enhancing our understanding of the complexes formed by cryptands containing metallocene units and amide carbonyl functions.



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Experimental

Yttrium-89 and ^{13}C *NMR Spectroscopy.*—A solution of $Y(ClO_4)_3 \cdot 6H_2O$ (1.251 g, 2.53 × 10^{-3} mol) in CH_3CN–CD_3CN (2.5 cm^3) was placed in a 10 mm o.d. NMR tube and the ^{89}Y NMR spectrum was observed at 12.222 MHz, 5.9 T (Bruker WM250). No decoupling was used,[13] relaxation delays were typically 12 s and the number of scans was in the range 400–1500. Aliquots of dimethylformamide (dmf) (0.25 cm^3, 3.23 × 10^{-3} mol) were added successively and the ^{89}Y NMR shift was recorded after the addition of each aliquot using the initial signal as reference (Table 1). A plot of $\delta(^{89}Y)$ *vs.* the molar ratio of dmf:Y^{3+} is shown in Fig. 1. The ^1H and ^{13}C NMR spectra were recorded in 5 mm tubes on a Bruker WX 360 spectrometer.

Table 1 Yttrium-89 δ values in CH_3CN relative to $Y(ClO_4)_3 \cdot 6H_2O$ in the presence of increasing molar quantities of dmf

Molar ratio $Y(ClO_4)_3 \cdot 6H_2O$:dmf	$\delta(^{89}Y)$
1:1.3	−0.3
1:2.6	−3.8
1:3.8	−6.7
1:5.1	−10.0
1:6.4	−12.3
1:7.7	−13.4
1:9.0	−15.0
1:10.2	−15.0
1:11.5	−15.5

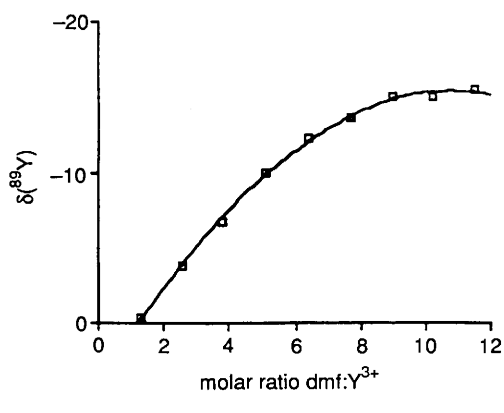

Fig. 1 Plot of $\delta(^{89}Y)$ of $Y(ClO_4)_3 \cdot 6H_2O$ in CH_3CN–CD_3CN at 12.222 MHz (5.9 T) against molar ratio of dmf:Y^{3+}

Preparative Details.—The cryptand L was prepared as described previously[1] and purified by dissolution in CH_3CN

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 2 Carbon-13 and ^{89}Y NMR data for the complex $[YL_2(H_2O)][ClO_4]_3$ in CD_3CN-CH_3CN

$\delta(^{89}Y)^a$	$\delta(^{13}C)^b$	Assignment	$\delta(^{13}C)^c$
−6.0	173.7	C=O	173.9
	78.6	*ipso*-C	78.9
	77.7	FeC	77.7
	74.0	OCH_2	74.2
	72.4	FeC	72.7
	72.2	FeC	72.2
	70.7	FeC	70.9
	70.5	OCH_2	70.7
	70.2	OCH_2	70.5
	67.1	OCH_2	67.4
	52.6	NCH_2	52.5
	52.0	NCH_2	51.8

[a] Values are referenced to $Y(ClO_4)_3{\cdot}6H_2O$ at 0 ppm. The reference tube (5 mm) was located using spacers inside a 10 mm tube containing the complex. [b] $Y^{3+}:L = 1:1$. [c] $Y^{3+}:L = 1:2$.

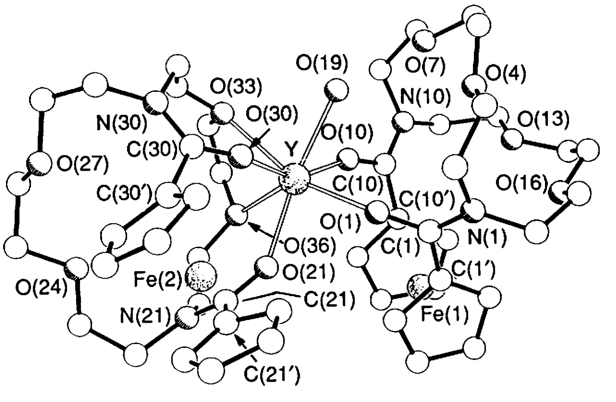

Fig. 2 The molecular structure of $[YL_2(H_2O)]^{3+}$

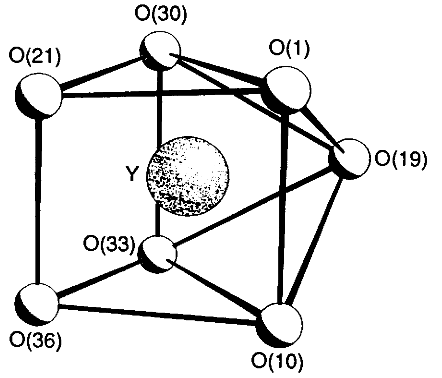

Fig. 3 The capped prismatic co-ordination geometry about yttrium. The O ⋯ O distances are in the range 2.64 Å for O(33) ⋯ O(36) to 3.43 Å for O(1) ⋯ O(30)

Table 3 Selected bond lengths (Å) and angles (°) for $[YL_2(H_2O)][ClO_4]_3$ with estimated standard deviations (e.s.d.s) in parentheses

Y–O(1)	2.207(4)	Y–O(10)	2.213(4)
Y–O(19)	2.334(6)	Y–O(21)	2.218(5)
Y–O(30)	2.216(4)	Y–O(33)	2.470(6)
Y–O(36)	2.461(6)	O(1)–C(1)	1.253(7)
C(1)–N(1)	1.313(10)	N(10)–C(10)	1.321(9)
C(10)–O(10)	1.272(7)	O(21)–C(21)	1.264(8)
C(21)–N(21)	1.311(11)	N(30)–C(30)	1.298(9)
C(30)–O(30)	1.235(7)		
O(1)–Y–O(10)	83.4(2)	O(1)–Y–O(19)	81.7(2)
O(10)–Y–O(19)	77.4(2)	O(1)–Y–O(21)	80.1(2)
O(10)–Y–O(21)	124.5(2)	O(19)–Y–O(21)	149.2(2)
O(1)–Y–O(30)	102.0(2)	O(10)–Y–O(30)	154.5(2)
O(19)–Y–O(30)	78.7(2)	O(21)–Y–O(30)	81.0(2)
O(1)–Y–O(33)	160.3(2)	O(10)–Y–O(33)	89.2(2)
O(19)–Y–O(33)	78.8(2)	O(21)–Y–O(33)	118.9(2)
O(30)–Y–O(33)	77.3(2)	O(1)–Y–O(36)	131.3(2)
O(10)–Y–O(36)	80.2(2)	O(19)–Y–O(36)	137.0(2)
O(21)–Y–O(36)	72.6(2)	O(30)–Y–O(36)	112.2(2)
O(33)–Y–O(36)	64.6(2)	C(1′)–C(1)–O(1)	116.4(6)
C(1′)–C(1)–N(1)	122.0(5)	O(1)–C(1)–N(1)	121.3(6)
C(10′)–C(10)–N(10)	122.5(5)	C(10′)–C(10)–O(10)	117.8(6)
N(10)–C(10)–O(10)	119.3(6)	C(21′)–C(21)–O(21)	117.6(7)
C(21′)–C(21)–N(21)	124.5(7)	O(21)–C(21)–N(21)	117.9(6)
C(30′)–C(30)–N(30)	118.4(5)	C(30′)–C(30)–O(30)	120.0(6)
N(30)–C(30)–O(30)	121.2(7)		

(in which the dimeric species is insoluble) followed by chromatography through neutral alumina. The cryptate was prepared by adding solid L (0.9 g, 1.8×10^{-3} mol) to a solution of $Y(ClO_4)_3{\cdot}6H_2O$ (0.9 g, 1.8×10^{-3} mol, prepared from yttrium carbonate, Aldrich) in CH_3CN-CD_3CN (8:1, 4 cm^3). The solution changed from an orange colour to a deep wine red, the bathochromic shift being consistent with the formation of a complex.[7] The ^1H NMR spectrum is very similar to that observed earlier[4] for complex formation with divalent cations and the ^{89}Y and ^{13}C NMR data are shown in Table 2. This table also contains the ^{13}C NMR data for a complex formed in solution from a 2:1 molar ratio of L to yttrium perchlorate. Crystals were grown from the 1:1 molar ratio NMR solution by prolonged standing (*ca.* 2 weeks) in the NMR tube at ambient temperature and after separation and drying under high vacuum gave a satisfactory elemental analysis (Found: C, 39.9; H, 4.40; N, 3.90. $C_{48}H_{66}Cl_3Fe_2N_4O_{25}Y$ requires C, 41.1; H, 4.75; N, 4.00%) for a molecular composition $[YL_2(H_2O)][ClO_4]_3$. The crystals are stable to air and can be handled without difficulty. A sample of this crystalline material was redissolved in CD_3CN and gave an *identical* ^{13}C NMR spectrum to that of the original cryptate solution (Table 2). There was not sufficient crystalline material, however, to obtain an ^{89}Y NMR spectrum.

Crystal-structure Determination of $[YL_2(H_2O)][ClO_4]_3$.—*Crystal data.* $C_{48}H_{66}Cl_3Fe_2N_4O_{25}Y$, $M = 1406.0$, triclinic, space group $P\bar{1}$, $a = 10.769(5)$, $b = 15.247(5)$, $c = 18.184(6)$ Å, $\alpha = 93.17(3)$, $\beta = 90.91(3)$, $\gamma = 106.57(3)°$, $U = 2865$ Å^3, $Z = 2$, $D_c = 1.63$ g cm^{-3}, $\mu = 74$ cm^{-1}, $F(000) = 1448$.

Data were measured on a Nicolet R3m diffractometer with Cu-Kα radiation ($\lambda = 1.541\ 78$ Å, graphite monochromator) using ω scans. 7184 Independent reflections were measured ($2\theta < 110°$) and of these 5733 had $|F_o| > 3\sigma(|F_o|)$ and were considered to be observed. The data were corrected for Lorentz and polarisation factors; an empirical absorption correction (ellipsoidal) based on 310 azimuthal measurements was applied; maximum and minimum transmission factors 0.177 and 0.074. The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. A ΔF map revealed the presence of disorder in one of the cyclopentadienyl rings. Two orientations of equal weight were identified and these were refined anisotropically subject to a C–C distance constraint. There is also disorder in two of the three perchlorate ions with occupancies of 0.6 and 0.4 in one case and 0.7 and 0.3 in the other. In both the major-occupancy oxygen atoms were refined anisotropically and the minor-occupancy atoms isotropically. The positions of the hydrogen atoms of the aqua ligand were also located from a ΔF map and these were refined isotropically subject to an O–H distance constraint. The positions of the remaining hydrogens were idealised, C–H 0.96 Å, assigned isotropic thermal parameters, $U(H) = 1.2U_{eq}(C)$ and allowed to ride on their parent carbon atoms. Refinement was by block-cascade full-matrix least squares to R 0.059, R' 0.063 [$w^{-1} = \sigma^2(F) + 0.001\ 40F^2$]. Selected bond lengths and angles are given in Table 3, atomic coordinates in Table 4.

Table 4 Atomic coordinates (× 10^4) for $[YL_2(H_2O)][ClO_4]_3$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Y	−44(1)	3140(1)	2277(1)	C(26″)	−4692	581	2846
Fe(1)	3265(1)	4946(1)	3708(1)	C(27″)	−5493	757	3416
C(1′)	1463(6)	5053(4)	3982(3)	C(28″)	−5297	1718	3499
C(2′)	2478(7)	5835(5)	4279(4)	C(29″)	−4376	2138	2980
C(3′)	3279(7)	5498(5)	4752(3)	O(21)	−110(5)	2392(3)	3294(3)
C(4′)	2799(7)	4535(5)	4737(4)	C(21)	539(6)	1655(5)	3613(4)
C(5′)	1693(7)	4252(5)	4262(4)	N(21)	86(6)	1035(4)	3536(3)
C(6′)	4483(7)	5723(5)	2985(4)	C(23)	−540(9)	−630(6)	3235(6)
C(7′)	5180(7)	5381(6)	3504(4)	O(24)	−1348(7)	−483(4)	2663(5)
C(8′)	4757(7)	4425(6)	3457(4)	C(25)	−1893(11)	−1318(7)	2229(9)
C(9′)	3781(7)	4136(5)	2898(4)	C(26)	−2383(10)	−1081(7)	1546(8)
C(10′)	3604(6)	4934(5)	2595(3)	O(27)	−3377(6)	−651(4)	1635(4)
O(1)	−109(4)	4234(3)	3109(2)	C(28)	−3925(9)	−408(6)	996(5)
C(1)	283(6)	4958(4)	3513(3)	C(29)	−4358(7)	409(5)	1173(4)
N(1)	−390(5)	5552(4)	3570(3)	N(30)	−3266(6)	1223(4)	1395(3)
C(2)	−1680(7)	5295(5)	3223(4)	C(30)	−3026(6)	1611(5)	2056(4)
C(3)	−1923(8)	5899(7)	2657(5)	O(30)	−2098(5)	2299(4)	2191(3)
O(4)	934(6)	5991(5)	2141(3)	C(31)	−2466(9)	1690(8)	812(5)
C(5)	−1235(10)	6277(6)	1461(5)	C(32)	−1223(9)	1629(8)	732(6)
C(6)	−21(10)	6454(6)	1007(5)	O(33)	−172(5)	2287(5)	1069(3)
O(7)	421(5)	5688(4)	971(3)	C(34)	958(11)	2055(12)	881(6)
C(8)	1512(8)	5798(6)	513(4)	C(35)	1834(9)	2117(8)	1397(5)
C(9)	2239(8)	5148(6)	688(4)	O(36)	1464(5)	2200(3)	2138(3)
N(10)	3030(5)	5363(4)	1387(3)	C(37)	1540(12)	1423(9)	2510(7)
C(10)	2720(6)	4849(4)	1955(3)	C(38)	1328(9)	1286(9)	3200(7)
O(10)	1686(4)	4184(3)	1916(2)	Cl(1)	−8046(2)	−663(1)	1190(1)
C(11)	4261(7)	6101(5)	1352(4)	O(101)	−9372(4)	−1124(5)	1171(4)
C(12)	4143(8)	7052(5)	1574(4)	O(102)	−7802(7)	59(3)	713(3)
O(13)	3297(5)	7018(3)	2145(3)	O(103)	−7620(7)	−321(4)	1914(2)
C(14)	3465(8)	7853(5)	2553(5)	O(104)	−7356(6)	−1287(4)	954(3)
C(15)	2222(8)	7898(5)	2868(4)	Cl(2)	5424(2)	3491(2)	1011(1)
O(16)	1766(5)	7223(3)	3368(3)	O(201)	5206(9)	3011(6)	1654(4)
C(17)	588(7)	7250(5)	3663(4)	O(202)	4551(6)	4003(5)	931(5)
C(18)	−48(7)	6392(4)	4049(4)	O(203)	6709(4)	4021(6)	969(6)
O(19)	−947(5)	4008(3)	1528(3)	O(204)	5162(10)	2815(6)	396(4)
Fe(2)	−3570(1)	1313(1)	3767(1)	O(221)	4793(10)	2616(5)	1257(7)
C(21′)	−1682(7)	1568(5)	4073(4)	O(223)	6380(10)	3953(8)	1566(6)
C(22′)	−2471(10)	855(8)	4473(7)	O(224)	6053(11)	3397(9)	356(4)
C(23′)	−3380(10)	1170(10)	4833(6)	Cl(3)	6954(2)	7920(1)	4638(1)
C(24′)	−3185(8)	2061(8)	4716(4)	O(301)	6166(6)	7322(4)	5116(4)
C(25′)	−2134(8)	2321(6)	4244(4)	O(302)	7742(8)	8704(4)	5027(4)
C(30′)	−3855(7)	1099(6)	2724(4)	O(303)	7677(8)	7462(5)	4215(5)
C(26′)	−3965	226	2997	O(304)	6116(8)	8218(7)	4151(5)
C(27′)	−4961	51	3518	O(322)	6828(12)	8807(4)	4757(8)
C(28′)	−5467	816	3567	O(323)	8267(5)	7953(9)	4795(8)
C(29′)	−4821(12)	1452(10)	3094(8)	O(324)	6637(13)	7595(9)	3901(3)
C(30″)	−4002(7)	1435(5)	2577(4)				

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

X-Ray analysis of a single crystal from the NMR solution reveals the formation of a 1:2 complex (Fig. 2) with the yttrium co-ordinated to the two ferrocenyl (amide carbonyl) oxygen atoms and two adjacent ether oxygen atoms of one macrocycle, and to the two ferrocenyl (amide carbonyl) oxygen atoms of the other. The seventh co-ordination site is occupied by an aqua ligand. The geometry at yttrium is mono-capped trigonal prismatic (Fig. 3) with the Y–O distances in the range 2.207(4)–2.470(6) Å. This appears to be the first reported example of this geometry involving seven-co-ordinate yttrium.[14] The shortest distances are to the four carbonyl oxygen atoms, each at *ca.* 2.2 Å. In both cryptand units, the amide carbonyl functions of each ferrocene unit adopt *cis* geometries which confirms the conclusions reached from the NMR data on complexes formed between L and divalent metal cations.[10] However, in the process of binding to the yttrium centre, each amide function is rotated out of the plane of its associated cyclopentadiene ring. The out-of-plane rotations differ, with those associated with N(1) and N(10) inclined by *ca.* 37 and 42° and those associated with N(21) and N(30) by *ca.* 10 and 60° respectively. The amide groups show only small departures from planarity with the mean torsional twists about their central C–N bonds in the range 5–12°. The aqua ligand forms an intramolecular hydrogen bond to O(7) at 2.82 Å, and an intermolecular hydrogen bond to one of the perchlorate anions.

The ^{89}Y NMR data in Table 1 are displayed as a titration curve in Fig. 1. This reveals that, as expected, amide ligands cause an upfield shift of the ^{89}Y signal[13,15] and that the maximum co-ordination number of amide carbonyl groups with the Y^{3+} cation is in the region of seven to nine. In fact, between 1 and 6 mol of dmf added, the chemical shift for ^{89}Y moves upfield by *ca.* 3 ppm per carbonyl group. The addition of the first aliquot (equivalent to 1.3 mol) of dmf, however, gives rise to only a small upfield shift (−0.3 ppm) in the ^{89}Y signal. The yttrium perchlorate used for the experiment was shown (by ^1H NMR spectroscopy) to be the hexahydrate and subsequent additions of 1, 2 and 3 more equivalents of water to the acetonitrile solution caused *downfield* shifts in the Y^{3+} NMR spectrum of, on average, 4 ppm per mol of water added. Thus the upfield shift of -3 ppm is due to displacement of water molecules (*ca.* -4 ppm per mol of H_2O), combined with co-ordination to an equivalent mol of dmf (*ca.* $+1$ ppm), resulting in an overall displacement of approximately -3 ppm per amide carbonyl ligand. On addition of the first mol of dmf however, little, if any, water is displaced and hence the $\delta(^{89}Y)$ value remains approximately the same.

A sample of the solid material used for the crystal structure was then dissolved in CD_3CN and the resultant ^{13}C NMR data are shown in Table 2. Clearly there is only one species in solution which gives rise to twelve carbon signals composed of two NCH_2 signals, four OCH_2 signals, four ferrocene CH, one ferrocene quaternary carbon and one carbonyl carbon. If one assumes that the ^{13}C NMR spectrum is that of the 1:2 complex, there must be rapid exchange, on the NMR time-scale, of the Y^{3+} cation between the ethyleneoxy bridges of the host cryptand molecules. The alternative explanation of a 1:1 complex in solution would necessitate a rapid exchange on the NMR time-scale between the 1:1 cryptate and the extra molecule of cryptand released from the crystal stoichiometry [equation (1)].

$$[YL_AL_B(H_2O)]^{3+} \rightleftharpoons [YL_A(H_2O)]^{3+} + L_B \rightleftharpoons L_A + [YL_B(H_2O)]^{3+} \quad (1)$$

When a 1:1 molar ratio mixture of L and $Y(ClO_4)_3\cdot 6H_2O$ was prepared at a much higher concentration (*ca.* 0.45 mol dm^3) in CH_3CN–CD_3CN however, precisely the same ^{13}C NMR spectrum was observed as that obtained from dissolution of the crystals. If a 1:1 complex was dominant in this solution, it is obvious that the spectrum would not match that of the dissolved crystals since as discussed above the latter would reflect an averaged spectrum of the 1:1 complex and free L. Thus the ^{13}C NMR spectrum is best explained by a 1:2 complex and this conclusion is reinforced by the solution spectrum at a 2:1 molar ratio of L to Y^{3+} (Table 2) and by the ^{89}Y NMR data. The 1:1 molar mixture in solution gave an ^{89}Y NMR signal at δ -6 relative to $Y(ClO_4)_3\cdot 6H_2O$. Assuming a 2:1 ($L:Y^{3+}$) stoichiometry for the complex, the observation of only one ^{89}Y signal means that there must be rapid exchange of complexed and free Y^{3+} on the NMR time-scale. This is consistent with the observation of a total of twelve ^{13}C signals for the complex. Furthermore an approximate calculation based on equation (2) predicts a resultant ^{89}Y δ value of -5.5,

$$\begin{array}{lccc} & 2Y(ClO_4)_3\cdot 6H_2O + 2L \rightleftharpoons & & \\ \delta(^{89}Y) & 0 & & \\ & [YL_2(H_2O)]^{3+} + & [Y(H_2O)_7]^{3+} + 4H_2O & (2) \\ & -15 & +4 & \end{array}$$

compared with the experimental value of -6.0. The calculated value arises from the average of rapid exchange between free yttrium heptahydrate (at δ $+4$) and the complexed monohydrate (at δ -15), the latter being calculated on the basis of the replacement of five water ligands by four amide carbonyl ligands and an ethyleneoxy ligand. The second ethyleneoxy ligand then serves to fill the co-ordination shell of yttrium to seven in line with the crystal structure. Thus the ^{89}Y and ^{13}C NMR spectra are consistent with a complex involving 2 mol of the cryptand per mol of Y^{3+} as required by the X-ray analysis. In conclusion the interaction of yttrium perchlorate with the cryptand forms a crystalline 1:2 complex with two pairs of amide carbonyl carbons, each in *cis* configurations, co-ordinated to the Y^{3+} cation as predicted by earlier NMR results with divalent cations.

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