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The complexation of Y^{3+} by 1,1′-(1,4,10-trioxa-7,13-diazacyclopentadecane-7,13-diyldicarbonyl)ferrocene

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Abstract

Multinuclear (^{1}H, ^{13}C and ^{89}Y) NMR has been used to study complex formation in solution between the ferrocene-containing cryptand 1,1′(1,4,10-trioxa-7,13-diazacyclopentadecane-7,13-diyldicarbonyl)ferrocene (**1**) and yttrium perchlorate (**2**). The results show that in acetonitrile as solvent, two complexes (**3a** and **3b**) can be formed, with stoichiometries of 1:1 and 2:1 (ligand: Y^{3+}) respectively, both of which involve coordination of the cation by a *cis* configuration of the amide carbonyl groups resulting in a plane of symmetry in each complex that is not present in the host cryptand. Exchange between the complexes, and between the complexes and free yttrium, is slow on the NMR time scale, and the yttrium complexes show an unusual two-bond coupling between ^{89}Y and the carbon atoms of the amide carbonyl groups.

1. Introduction

Cryptands incorporating metallocene units yield ionophores within which metal–metal interaction is possible. Thus ferrocene-containing cryptands have been shown to have useful electrochemical and chromogenic properties [1,2] and hence may be important as molecular sensors [3] or catalysts, possibly photoactivated, in redox or polymerisation processes [4]. The ferrocene-containing cryptand 1,1′-(1,4,10-trioxa-7,13-diazacyclopentadecane-7,13-diyldicarbonyl)ferrocene (**1**) is three-fold non-symmetric in its bridging unit and therefore offers an excellent probe for the structure of cryptates formed by this cryptand in solution. Crystallographic studies have revealed the structure of **1** in the solid state to involve a *trans* configuration of the carbonyl groups [5] and detailed ^{1}H and ^{13}C NMR studies have confirmed this configuration in solution [5]. On complexation with divalent cations (Be^{2+}, Mg^{2+}, Ca^{2+} and Ba^{2+}) however, the NMR evidence indicates that the resultant 1:1 cryptates involve *cis*-coordination by the amide carbonyls with the metal cation probably on the short side of the macrocyclic ring [6]. This conclusion is reached by the observation of a reduction in ^{13}C resonance signals from 22 to 11 on complexation consistent with the introduction of a plane of symmetry into the cryptand unit of the cryptate. So far, however, there is no X-ray data available on cryptates derived from **1** but a cryptate formed between the symmetrical cryptand (**4**) and yttrium perchlorate gave stable crystals with a 2:1 stoichiometry (ligand: Y^{3+}) in which both sets of amide carbonyl oxygens were coordinated *cis* to the Y^{3+} ion providing a coordination sphere of seven within a capped trigonal biprism [7]. The three extra ligands comprised two from oxygen atoms in one arm of one of the macrocyclic ligands and one (at the cap) from a mole of water. The paper also reported some yttrium NMR data that confirmed coordination of the yttrium by the amide carbonyl groups in solution, and revealed, by the observation of only one averaged ^{89}Y signal, rapid exchange between complexed and uncomplexed yttrium on the NMR time scale. It therefore seemed appropriate to study the solution state NMR of the complexation of Y^{3+} by **1** and the results of this investigation are reported below.

2. Experimental details

The cryptand (**1**) was synthesized, isolated, and purified (by condensation of 1,1′-bis(chlorocarbonyl)ferrocene with 1,4,10-trioxa-7,13-diazacyclopentadecane) as described previously [6]. Yttrium perchlorate (**2**) was

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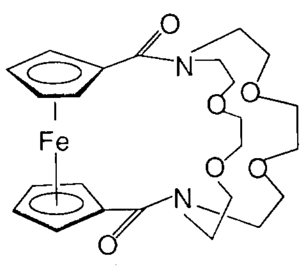

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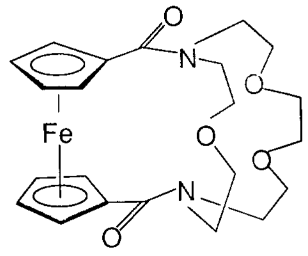


(1)

prepared by treating yttrium carbonate (Aldrich) with six moles of perchloric acid followed by evaporation of the resultant aqueous solution and drying of the residue at 100°C and 0.02 mm for several hours. The resultant yttrium perchlorate contained 4.7 moles of H_2O per mole of $Y(ClO_4)_3$ as assessed by ^1H NMR in CD_3CN relative to a known quantity of benzene.

The ^1H and ^{13}C NMR experiments were carried out as follows. A solution of **1** (0.025 g, 5.48×10^{-5} mole) in CD_3CN (1 ml) was treated successively with aliquots (2.74×10^{-5} mole) of a solution of (**2**) in CD_3CN. The solution changed from an orange colour to a deep wine red indicative of complex formation [7] and the ^1H and ^{13}C NMR spectra were recorded in 5 mm tubes on a Bruker AM 360 MHz instrument operating at 90.56 MHz for ^{13}C NMR spectra. The ^{89}Y NMR data were obtained on a Bruker WM 250 at 12.2 MHz using a 10 mm o.d. NMR tube and a more highly concentrated (0.45 M) solution at a molar ratio of 1:1 in **1** and **2**. No decoupling was used [8], relaxation delays were typically 16 s and the number of scans was approximately 3000.

TABLE 1. The ^{13}C NMR data (ppm) of complexes of **1** with $Y(ClO_4)_3$ and $Ca(ClO_4)_2$ in CD_3CN

Carbon Atom in (1)/ M^{n+}	$\partial^{13}C$				
	2(1):Y^{3+}	(1):Y^{3+}	(1):Be^{2+} [a]	(1):Ca^{2+} [a]	(1):Ba^{2+} [a]
8/12	50.1	50.1	50.9	49.6	49.0
6/14	54.2	53.9	54.4	53.7	52.9
5/15	69.1	68.9	67.3	70.6	71.4
2/3	71.1	70.9	70.3	71.9	72.0
9/11	72.9	73.2	71.2	73.7	72.6
1/1′	77.6	77.2	76.9	78.9	78.8
2/2′	71.1	70.8	71.2	77.5	76.7
3/3′	73.7	73.3	73.9	72.2	71.4
4/4′	73.1	72.9	73.9	72.9	72.2
5/5′	77.7	77.6	78.2	70.8	70.3
> C=O	173.1 (d) [b]	172.5 (d) [b]	174.0	173.1	171.4

[a] from ref. 6; [b] $^2J_Y = 3.0(\pm 0.2$ Hz).

3. Results and discussions

The ^{13}C NMR spectra of the 2:1 and 1:1 (ligand: M^{n+}) complexes formed between **1** and **2** in CD_3CN are shown in Table 1. These complexes were formed by adding half mole aliquots of **2** to **1** and taking spectra after each addition. At a 2:1 ratio (ligand: Y^{3+}) the complex was mainly (90%) that of 2:1 stoichiometry but on reaching a mole ratio of 1:2 the mixture was almost entirely that of the 1:1 complex. At intermediate mole ratios (*i.e.* 1:1) a mixture of the complexes of 2:1 and 1:1 stoichiometry was observed with the latter predominating and accounting for 65% of complexed **1**. However, with a 1:1 mole mixture at higher concentration (0.45 M as used for the ^{89}Y NMR data, *vide infra*) the 2:1 complex with the lower field carbonyl carbon was more in evidence and accounted for 70% of complexed **1**. The two ^{13}C spectra are very similar, which shows that the coordination in both complexes is almost identical with a plane of symmetry through each molecule of the host consistent with *cis* configurations of the amide carbonyl ligands. Furthermore, the ^1H spectra of the 1:1 complexes between **1** and either Y^{3+} or Ca^{2+} were almost identical (Table 2) demon-

TABLE 2. ^1H δ-values (ppm) for the 1:1 complexes of **1** with Ca^{2+} and Y^{3+} in CD_3CN

1:Ca^{2+}		Assignment	(1):Y^{3+}	
∂^1H	Integ		∂^1H	Integ
5.12	2	2/2′	5.18	2
5.08	2	5/5′	5.09	2
4.65	2	8B/12B	4.61	2
4.57	2	3/3′	4.58	2
4.55	2	4/4′	4.54	2
4.42	2	6B/14B	4.46	2
4.02	2	9B/11B	4.00	2
3.90	2	5B/15B	3.67–3.88 (m)	8
3.82	2	5A/15A		
3.78	2	2A/3A, 2B/3B		
3.58	2	9A/11A	3.55	2
3.13	2	6A/14A	3.16	2
2.93	2	8A/12A	2.97	2

strating a remarkable similarity between the structures of the two complexes. For the complex of 1:1 stoichiometry (excess Y^{3+}), the NMR assignments were confirmed by a combination of a COSY spectrum (Fig. 1) and a ^{13}C–^{1}H heteronuclear correlation spectrum (Fig. 2) as used for the complexes of **1** with alkaline earth cations [6]. The complexes of **1** with Be^{2+}, Ca^{2+}, Ba^{2+} and Y^{3+} showed almost identical ^{13}C–^{1}H correlation spectra in the NCH_2 region with the high field carbon (*cis* to the carbonyl group) associated with the most widely spread AB protons on C_8 and C_{12} resonating at about 3.0 and 4.7 ppm (Fig. 2).

It has been argued that this pattern of NCH_2 signals is associated with complexation of the cation on the short side of the macrocyclic ring and it seems reasonable to assume that this occurs for all the complexes of **1** studied so far. This conclusion is reinforced by the observation that all the proton spectra for the 1:1 complexes with Be^{2+}, Ca^{2+}, Ba^{2+} and Y^{3+} are remarkably similar especially in the region of the cyclopentadiene protons (Table 3). There is however one slight anomaly. For the complexes of **1** with Be^{2+} and Y^{3+}, the ^{13}C–^{1}H correlation spectra shows that the lowest field cpd carbon (C5′, *-trans* to the carbonyl group) is associated with the second lowest field proton, whereas the lowest field proton (H2′, *cis* to the carbonyl group) is associated with the highest field carbon. In the 1:1 complexes of **1** with Ca^{2+} and Ba^{2+}, however, the reverse is true, i.e. the lowest field proton correlates with the lowest field carbon. This leads to the suspicion that the original ^{1}H assignments for the Ca^{2+} and Ba^{2+} complexes of **1** [6] may have been in error, so the H2′ should have been labelled H5′, H5′ labelled H2′, H3′ labelled H4′, and H4′ labelled H3′.

The formation of alkaline earth complexes are characterised by coordination numbers of 4 (Be^{2+}) to 6 or higher (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}) [8,9] and the rare earth cations are known to have coordination numbers of 7, 8 or 9. Thus, it is reasonable to expect 2:1 (ligand:cation) complexes especially for high charge density cations such as Y^{3+} and this has already been found for complexes of **4** with $Y(ClO_4)_3$ [7]. Variable temperature ^{1}H and ^{13}C NMR studies also support the concept of a mixture of 2:1 and 1:1 stoichiometry. At

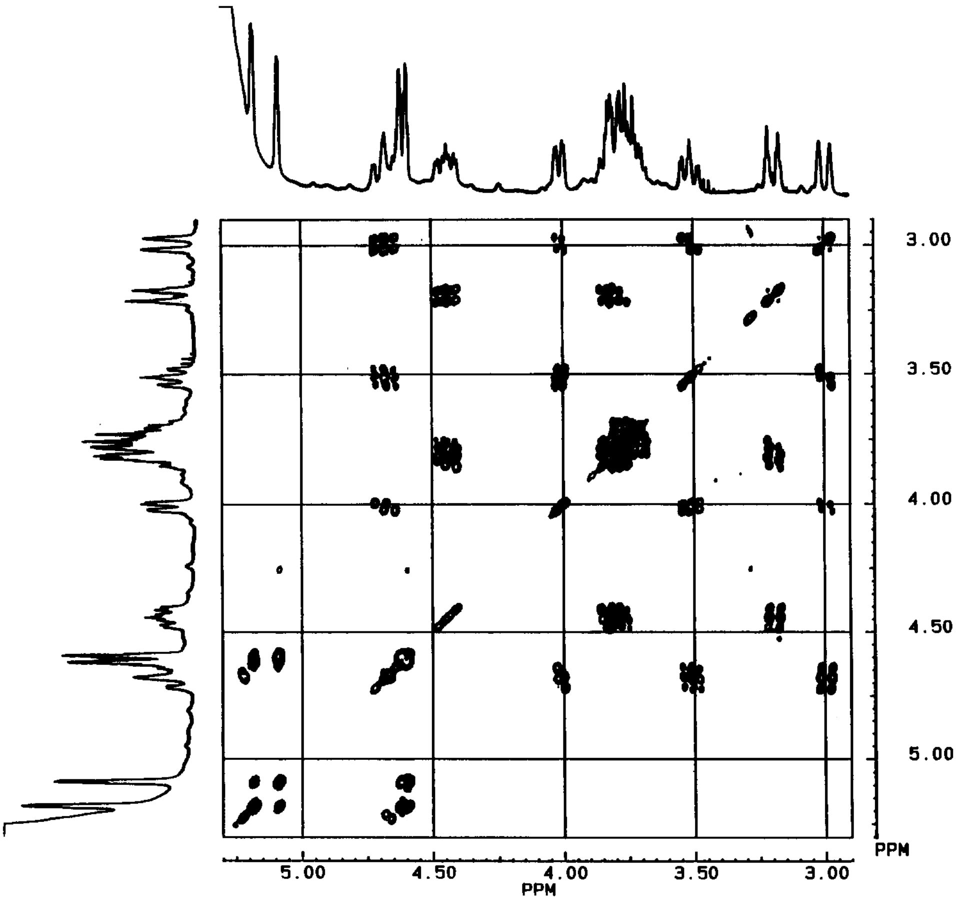
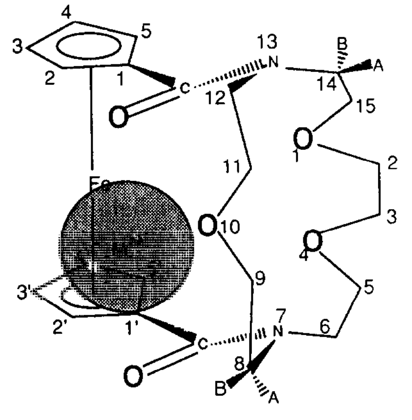


Fig. 1. The COSY NMR spectrum of the 1:1 complex of **1** with $Y(ClO_4)_3$ in CD_3CN.



1 :M^{n+}

TABLE 3. Cyclopentadiene ^{1}H δ-values (ppm) for the 1:1 complexes of **1** with Be^{2+}, Ca^{2+}, Ba^{2+} and Y^{3+}.

	∂^1H			
	(**1**):Y^{3+}	(**1**):Be^{2+} [a]	(**1**):Ca^{2+} [a]	(**1**):Ba^{2+} [a]
$H_{2/2'}$	5.18	5.38	5.12	5.06
$H_{3/3'}$	4.58	4.68	4.57	4.51
$H_{4/4'}$	4.54	4.63	4.55	4.47
$H_{5/5'}$	5.09	4.95	5.08	4.88

[a] from ref. 6.

lower temperature, the proportion of 2:1 complex increased slightly as found earlier for complexes of **4** with Mg^{2+} [10] and these reversible changes appear to be consistent with a more exothermic process associated with a 2:1 stoichiometry. Conversely, at temperatures > 30°C (up to 70°C) the proportion of the higher field carbonyl carbon increased slightly, indicative of the equilibrium shifting towards the 1:1 complex. The effects, however, were not nearly so dramatic as observed with **4** [10].

Since ^{89}Y is NMR active ($I = 1/2$) there was an opportunity to study the effects of complexation on the chemical shift of the guest. The yttrium perchlorate used for these experiments was shown to contain 4.7 H_2O and this compound in CD_3CN was used as the yttrium standard. We have shown previously, that addi-

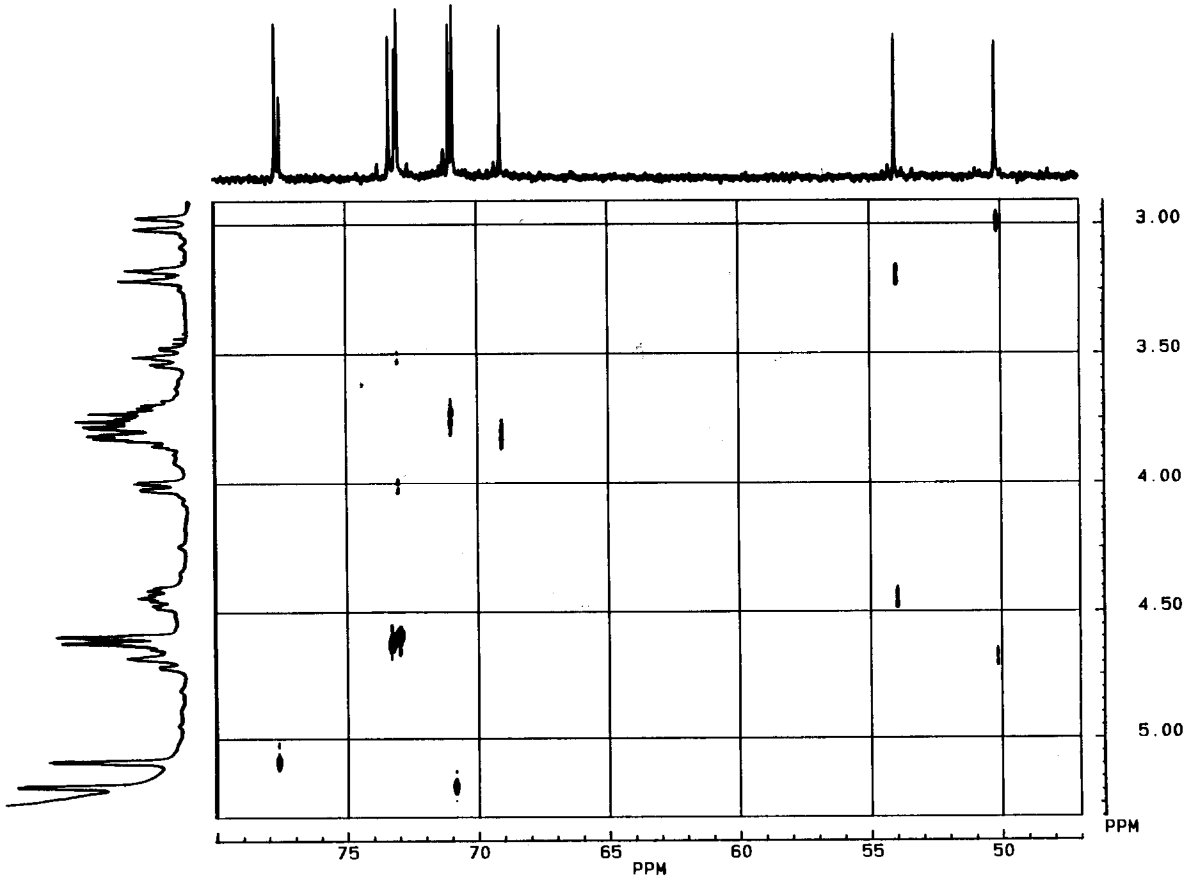


Fig. 2. The ^{1}H–^{13}C heteronuclear correlation spectrum of the 1:1 complex of **1** with $Y(ClO_4)_3$ in CD_3CN.

tion of water caused a downfield shift of the ^{89}Y signal by about 4 ppm mol^{-1} of added H_2O and that replacement of a water molecule by amide carbonyl ligands produces an upfield shift of about -3 ppm per carbonyl group [7]. When the yttrium spectrum of a 1:1 molar mixture of (1) and $Y(ClO_4)4.7H_2O$ was recorded, two signals were observed at $+11.6$ ppm (33%) and -6.7 ppm (67%) relative to $Y(ClO_4)_3 4.7H_2O$ as the standard. The low field peak corresponds to $Y(ClO_4)_3 7.6H_2O$ (calculated δ ^{89}Y, $+11.6$ ppm) and we know from the ^1H and ^{13}C spectrum of the *same* solution that complexes of 1:1 and 2:1 (ligand: Y^{3+}) stoichiometry exist in solution in a molar ratio of 30:35. Thus the two yttrium signals associated with 1:1 and 2:1 complex formation must appear at approximately the same chemical shift (-6.7 ppm) which probably explains why the signal is broad ($w_{1/2}$ *ca.* 1 ppm) relative to hydrated ^{89}Y. The area under the signal at -6.7 ppm is equivalent to 67% of the available yttrium which corresponds quite closely to a mixture of 35 mol% of the 2:1 complex plus 30 mol% of the 1:1 complex leaving 35 mol% of yttrium free. The coincidence of the two ^{89}Y signals may be explained if it is assumed that the formation of the 1:1 complex involves displacement of two moles of H_2O by amide groups (shift of *ca.* -6 ppm) whereas the formation of the 2:1 complex merely involves extra coordination to the yttrium or possible replacement of acetonitrile molecules from the solvent sheath with little, if any, change in the ^{89}Y nmr shift. When a 1:1 mole mixture of **1** and **2** was prepared by adding **1** slowly to a solution of **2** in CD_3CN, the ^1H and ^{13}C NMR spectra showed a mixture of 1:1 complex and 2:1 complex in a ratio of 85:15. Clearly, therefore the two complexes once formed, do not equilibrate rapidly, thus reinforcing the contention that the ^{89}Y signal at -6.7 ppm is comprised of two coincident chemical shifts. Thus the ^{89}Y NMR is consistent with the data acquired for the ^{13}C spectra showing a mixture of 1:1 and 2:1 stoichiometry for the complexes. Finally, the tight binding associated with these complexes is emphasised by the observation of two-bond coupling between the yttrium nuclei and the carbonyl carbon in *both* complexes. The value of $^2J_Y = 3.0$ (± 0.2) Hz is small but to the best of our knowledge is the first reported example of two-bond $^{89}Y-^{13}C$ coupling. It contrasts with the lack of coupling observed for the 2:1 complex of **4** with **2** which must therefore be a looser association of amide ligands and the guest cation.

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