

Cryptates from cryptands containing a ferrocene unit

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Abstract

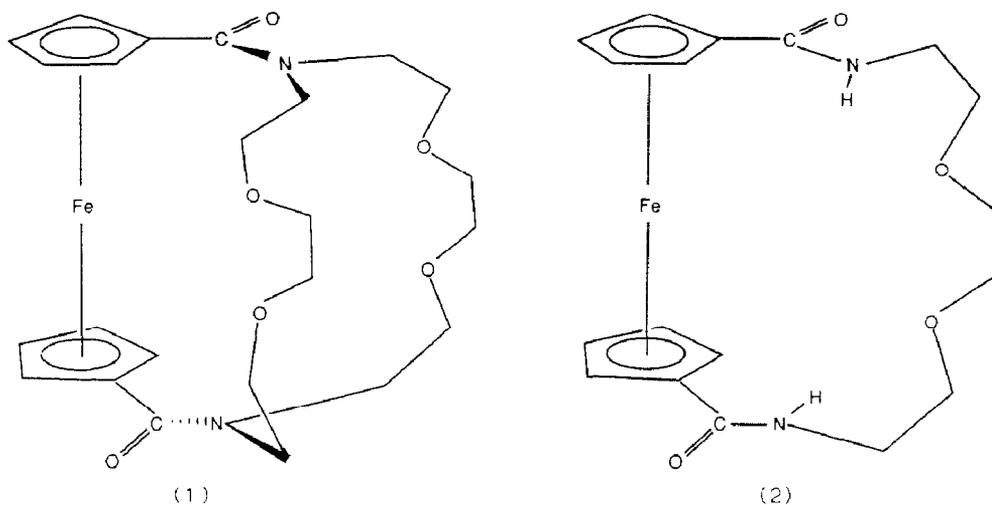
The interaction of 1,1'-(1,4,10,13-tetraoxa-7,16-diazacyclo-octadecane-7,16-diylidicarbonyl)ferrocene (**1**) with a range of divalent cations has been examined by ¹³C NMR spectroscopy, which reveals the formation of 1/1 and 2/1 (host/guest) complexes in a ratio dependent upon the conditions. Several 1/1 cryptates have been isolated and characterised by microanalysis, IR and multinuclear NMR spectroscopy and the IR data for solutions of the complexes confirm the conclusions reached by ¹³C NMR.

Introduction

During recent years we have studied the synthesis [1], structure [2] and dynamic behaviour [3] of a number of cryptands (e.g. **1**) and macrocycles (e.g. **2**) containing metallocene units, and our assignment of the *trans*-configuration of the carbonyl groups in **1** by multinuclear NMR has been confirmed by recent X-ray studies [4,5]. We became aware through UV/vis, spectroscopic studies [6] and cyclic voltammetry experiments [7] that these compounds complex with a variety of divalent and trivalent metal cations, and we now report the isolation of some of these cryptates and the formation of both 1/1 and 2/1 (host/guest) complexes in solution as evidenced by IR and ¹³C NMR spectroscopic data. The position of equilibrium between the 1/1 and 2/1 complexes in solution depends upon the concentration and temperature, and evidence is presented to show that the amide carbonyl groups are involved in the coordination to the metal cations.

Results and discussion

The complexation of the cryptand **1** with a range of dications (Be²⁺, Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺, Mn²⁺ and Zn²⁺) and trications (Eu³⁺, Tb³⁺ and Dy³⁺) as perchlorates or tetrafluoroborates in methylene chloride/acetonitrile (CH₂Cl₂/CH₃CN) mixtures is accompanied by bathochromic shifts of the *d-d* transition at



ca. 465 nm associated with the ferrocene unit [8] and a concomitant increase in the intensity of this absorption band. In cases where the resultant cryptates were isolated, they analysed (see Experimental section) for 1/1 (host/guest) complexes. When these complexes were redissolved in 50/50 $\text{CHCl}_3/\text{CH}_3\text{CN}$ or when the complexes were prepared in the same solvent mixture by mixing solutions of **1** and the metal cation, the ^{13}C NMR spectra revealed the presence of two species in solution, neither of which corresponded to the spectrum of the cryptand **1***. Furthermore, the proportions of the two compounds were dependent upon concentration and temperature. A typical example of the ^{13}C NMR spectra is found for the cryptate formed between **1** and $\text{Mg}(\text{ClO}_4)_2$ in 50/50 $\text{CDCl}_3/\text{CD}_3\text{CN}$ (Fig. 1), and this may be taken as an illustration of the behaviour of the whole range of complexes. Figure 2 reveals the changes in the NCH_2 signals of the cryptate with temperature. Considerable changes also occur in the signals of the carbonyl carbons and *ipso* carbons ($\text{C}(1)$) and these data are summarised in Table 1 for two concentrations of the cryptate and compared with the same signals for the uncomplexed free cryptand. The signals for OCH_2 and ferrocene carbons also undergo changes which permit a complete assignment of the signals from the two cryptates by a combination of variable temperature ^{13}C NMR and DEPT spectra (Table 2). It can be seen from the data that higher temperature and lower concentration favour the component which shows the largest downfield shift of the carbonyl carbon. This component is the 1/1 complex and the remaining ^{13}C NMR data are ascribed to a 2/1 (host/guest) complex, in which, we suggest, the charge on the metal cation is dispersed by coordination with four amide carbonyl groups (rather than two for the 1/1 complex) which results in a smaller downfield shift of the amide carbonyl ^{13}C signals. Furthermore, there is clearly no coalescence between the signals of the two cryptates (Fig. 2) but, instead, the proportion of each as reflected by peak intensity, changes with temperature. This demonstrates that there is an equilibrium between

* Large changes are also observed in the ^1H NMR spectra of the cryptates relative to the host cryptand, but the complexity of these changes necessitates discussion in a subsequent publication.

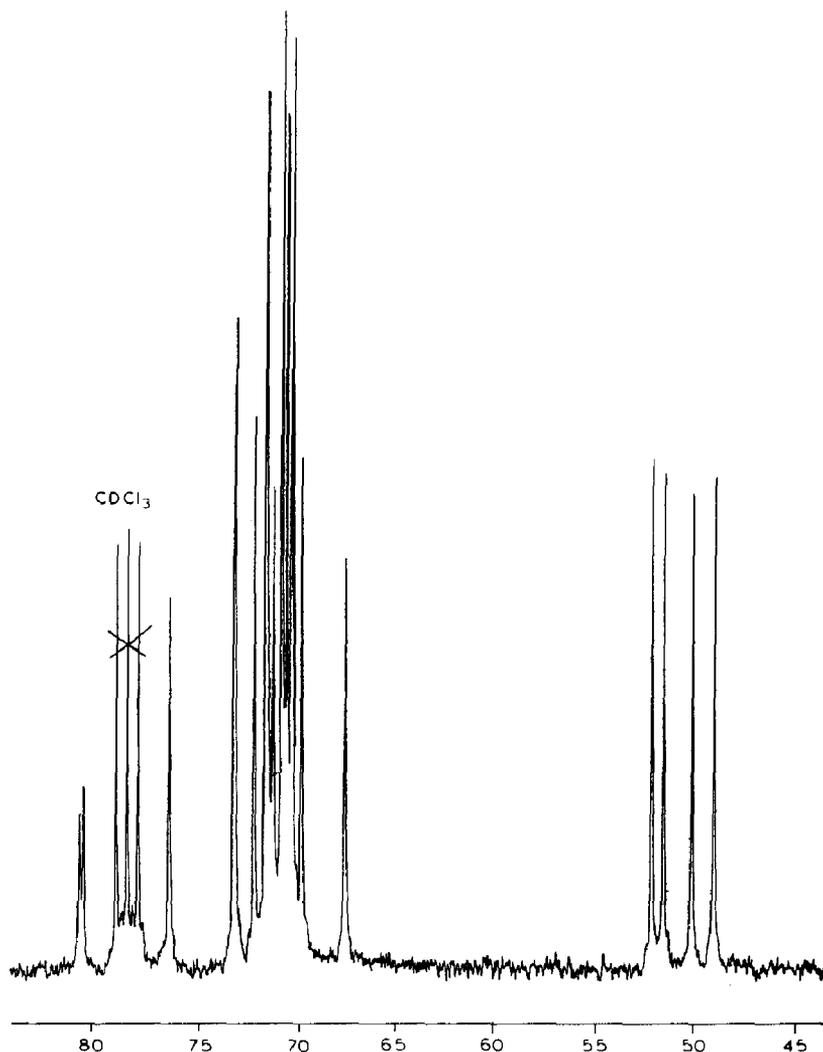


Fig. 1. The ^{13}C NMR spectrum of the complex formed between **1** and $\text{Mg}(\text{ClO}_4)_2$ in $\text{CDCl}_3/\text{CD}_3\text{CN}$ (1/1, at ca. 0.1 M) at 30°C ; FeC , OCH_2 , and NCH_2 signals only. Carbonyl carbon signals appear at 175.0 and 171.5 ppm.

the two cryptates which shifts slowly on the NMR time scale but sufficiently quickly on the experimental time scale for the changes to be observed*. It is reasonable to expect higher concentrations and lower temperatures to favour the 2/1 complex since coordination with four carbonyl oxygens would be favoured by higher concentration, and is likely to be more exothermic than coordination with two.

* We have also carried out model studies of complex formation by $(\text{Me}_2\text{NCO}((\text{C}_5\text{H}_4))_2\text{Fe}$ using UV spectroscopy (at $\leq 10^{-3}\text{ M}$ in the host) and found 2/1 (host/guest) stoichiometry, which reveals that the amide carbonyl groups are sufficient for complex formation. A parallel UV study of complex formation between **1** and M^{2+} , again at $\leq 10^{-3}\text{ M}$ in **1**, revealed as expected at such dilution, 1/1 stoichiometry. With **2** however, the stoichiometry was 2/1 (host/guest) at UV concentrations. These and a range of results including equilibrium constants determined by the UV technique, will be reported in a subsequent paper.

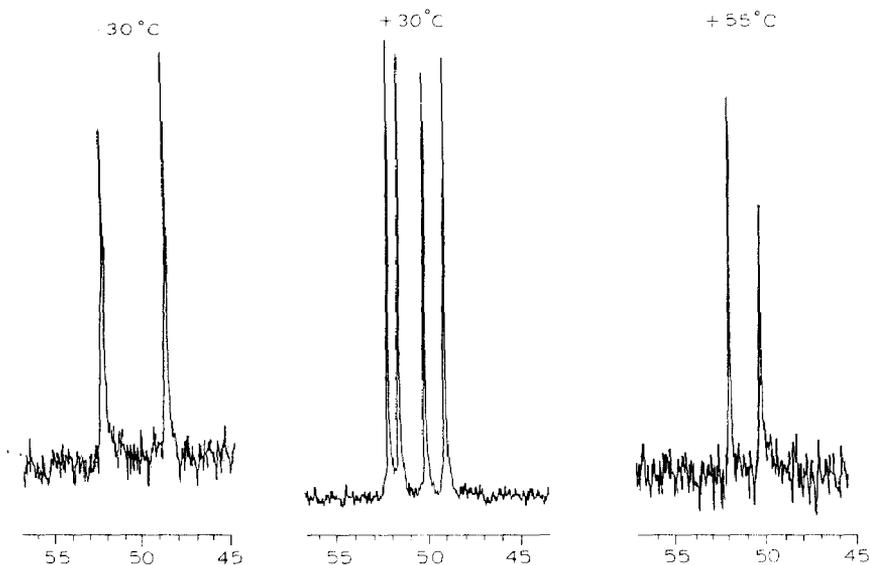


Fig. 2. The NCH_2 region of the ^{13}C NMR spectrum of the complex between **1** and Mg^{2+} in $\text{CDCl}_3/\text{CD}_3\text{CN}$ at -30 , 30 , and 55°C .

Table 1

Selected $\delta(^{13}\text{C})$ values for **1** and $\text{1/Mg}(\text{ClO}_4)_2$ in $\text{CD}_3\text{CN}/\text{CDCl}_3$ over a range of temperature and concentration

(a) **1** in $\text{CD}_3\text{CN}/\text{CDCl}_3$ at ambient temperature ^a

$\delta(^{13}\text{C})$ (ppm)	Assignment ^b
49.8 } 51.8 }	NCH_2
79.9	<i>ipso</i> -C
170.7	C=O

(b) $\text{1/Mg}(\text{ClO}_4)_2$ at 0.05 M

δ (-35°C)	δ (-5°C)	δ (35°C)	Assignment
48.9(1) ^d	49.5(3)	50.2(> 95) }	NCH_2
50.8(1)	51.3(3)	51.9(> 95) }	(1/1 cryptate)
48.0(3)	48.6(1)	- (< 5) }	NCH_2
52.1(3)	52.3(1)	- (< 5) }	(2/1 cryptate)
-	80.4	81.4	<i>ipso</i> -C(1/1)
79.6	-	-	<i>ipso</i> -C(2/1)
-	174.0	175.0	C=O(1/1)
171.2	171.5	-	C=O(2/1)

(c) $\text{1/Mg}(\text{ClO}_4)_2$ at 0.15 M

δ (-30°C)	δ (0°C)	δ (55°C)	Assignment
- (< 5) ^d	50.1(2)	50.5(3) }	NCH_2
- (< 5)	51.6(2)	51.8(3) }	(1/1)
48.4(> 95)	49.2(3)	49.6(1) }	NCH_2
52.0(> 95)	52.1(3)	52.2(1) }	(2/1)
-	80.6	80.9	<i>ipso</i> -C(1/1)
80.5	80.5	80.6	<i>ipso</i> -C(2/1)

^a The spectrum does not change over a temperature range from -30 to $+50^\circ\text{C}$. ^b See ref. 2. ^c For DEPT spectra: see ref 10. ^d Figures in brackets are the proportions of 1/1 vs. 2/1 complexes as reflected by ^{13}C peak intensities.

Table 2

^{13}C NMR spectra of complexes formed between **1** and a variety of metal cations (M^{2+}) in $\text{CD}_3\text{CN}/\text{CDCl}_3$ at ca. 0.1 M in **1**^a

C=O	<i>ipso</i> -C	FeC	OCH ₂	NCH ₂
<i>Be</i> ²⁺ 1/1 complex at -30°C				
173.8	77.1	78.6	70.4	52.04
		73.8	70.2	51.99
		72.9	69.3	
		72.8	66.7	
<i>Be</i> ²⁺ 2/1 complex at -30°C				
172.5	80.1	72.2	<i>b</i>	52.4
		70.9	<i>b</i>	48.3
		70.0 (2 signals)	<i>b</i>	
C=O	<i>ipso</i> -C	FeC	OCH ₂	NCH ₂
<i>Mg</i> ²⁺ 1/1 complex				
175.0	81.4	75.7	71.9	51.9
		72.9	70.9	50.1
		72.2	70.5	
		70.9	67.1	
<i>Mg</i> ²⁺ 2/1 complex				
171.5	80.4	73.3	71.5	52.1
		73.1	70.6	48.8
		72.1	70.3	
		70.9	69.7	
C=O	<i>ipso</i> -C	FeC	OCH ₂	NCH ₂
<i>Ca</i> ²⁺ 1/1 complex				
174.2	80.5	75.2	72.6	51.7
		71.9	70.6	49.7
		71.7	68.3	
		70.5	67.3	
<i>Ca</i> ²⁺ 2/1 complex				
173.1	<i>b</i>	73.9	71.4	51.7
		73.1	69.5	48.7
		<i>b</i>	<i>b</i>	
		<i>b</i>	<i>b</i>	
C=O	<i>ipso</i> -C	FeC	OCH	NCH ₂
<i>Sr</i> ²⁺ 1/1 complex				
173.8	81.4	75.1	72.7	51.7
		72.2	70.9	49.6
		71.8	68.8	
		70.6	67.8	
C=O	<i>ipso</i> -C	FeC	OCH ₂	NCH ₂
<i>Ba</i> ²⁺ 1/1 complex				
172.9	81.0	75.2	71.6	51.3
		71.5	70.9	49.3
		71.4	68.2	
		70.3	68.0	
<i>Ba</i> ²⁺ 2/1 complex				
172.4	80.9	74.1	70.5	51.6
		72.8	69.5	48.6
		71.7	68.7	
		70.1	<i>b</i>	

(continued)

Table 2 (continued)

C=O	<i>ipso-C</i>	FeC	OCH ₂	NCH ₂
<i>Zn²⁺ 1/1 complex</i>				
175.1	80.9	75.3	72.2	53.0
		73.8	70.4	52.8
		72.9	70.3	
		72.0	67.5	
<i>Zn²⁺ 2/1 complex</i>				
171.3	80.2(br)	73.2	71.0	52.1
		72.8	70.6	48.8
		72.2	70.2	
		^b	69.2	

^a At ambient unless indicated otherwise. ^b Not observable, either due to overlap or low intensity.

Similar changes were observed for the complexes formed by **1** with Be²⁺, Ca²⁺, Sr²⁺, Ba²⁺, and Zn²⁺ (Table 2) although in some cases signal overlap precluded a complete assignment of the OCH₂ and FeC signals. In one case (Sr²⁺) only one complex (presumably 1/1 by comparison with the complexes of Mg²⁺ and Ca²⁺) was observed, probably because of a fortuitous combination of concentration and temperature. With Be²⁺, the 2/1 complex was only observable at -30 °C, which explains why the two sets of spectral data are reported at this temperature. Further evidence for the involvement of the amide carbonyls in the first coordination sphere of the cryptates is provided by IR data in the solid state and in solution (Table 3). The shift in $\nu(\text{C=O, str.})$ to lower wavenumbers on complexation indicates an increase in the bond length of the amide carbonyl consistent with the expected higher degree of polarisation on complexation with the metal cation. Furthermore, in some cases in solution, two new carbonyl absorptions are observed that may be assigned to 1/1 (low frequency) and 2/1 (host/guest, higher frequency) complexes. This interpretation is confirmed by the variable temperature solution IR spectra of the Mg²⁺ and Zn²⁺ complexes (Table 4) which reveal that when the temperature is raised the proportion of 1/1 complex (with the lower carbonyl frequency) increases relative to the 2/1 complex (at higher frequency). Thus the ¹³C and IR data complement each other and suggest that the principal coordinating functional group

Table 3

Infrared stretching frequencies (cm⁻¹) of 1/M²⁺ cryptates

M(X) ₂	ν (cm ⁻¹)	
	KBr disc	Solution (CD ₃ CN)/CDCl ₃
-	1615	1620
Mg(ClO ₄) ₂	1561	1605,1562
Ca(ClO ₄) ₂	1559	1605,1569
Sr(ClO ₄) ₂	1599	"
Ba(ClO ₄) ₂	1600	"
Zn(BF ₄) ₂	1569	1610,1576

" Not recorded.

Table 4

Infrared absorption frequencies (cm^{-1}) for cryptates in $\text{CH}_3\text{CN}/\text{CDCl}_3$ at various temperatures ^a

Metal salt		-30 °C	0 °C	20 °C
$\text{Mg}(\text{ClO}_4)_2$	(2/1)	1610(1)	1610(2)	1610(1)
	(1/1)	1560(1)	1560(3)	1561(2)
$\text{Zn}(\text{BF}_4)_2$	(2/1)	1600(1)	1600(1)	1600(1)
	(1/1)	1560(1)	1560(2)	1560(5)

^a Figures in brackets represent approximate ratios of 1/1 and 2/1 complexes.

contributing to formation of the complexes is the amide carbonyl, a group known to complex strongly with a range of dications [9].

Experimental

¹³C NMR spectra were recorded on either a Bruker AM360 operating at 90.55 MHz or a Bruker WM 250 operating at 62.9 MHz using a DEPT programme [10] to give CH signals as positive (+) and the OCH_2 and NCH_2 carbons as negative signals (-) relative to TMS. Infrared spectra were recorded on a Perkin Elmer 983G spectrometer as either KBr discs or solutions in 50/50 $\text{CD}_3\text{CN}/\text{CDCl}_3$. Microanalyses were performed at the Microanalytical Laboratory at University College, London. Compound **1** was prepared as described previously [1]. The alkaline earth perchlorates were purchased from Aldrich or Alfa Chemical Companies and were dried at 120 °C and 0.01 mmHg for 3 h before use. The zinc tetrafluoroborate was prepared as described by Underhill and Hathaway [11] as a complex with acetonitrile, and the acetonitrile content was estimated by ¹H NMR.

The general procedure for the preparation of the 1/1 cryptates from **1** and MX_2 was as follows, all operations being carried out in a dry box under nitrogen.

The cryptand **1** (200 mg, 0.4 mmol) was dissolved in dry CH_2Cl_2 (2 ml) and a solution of the metal perchlorate or tetrafluoroborate (0.4 mmol) in dry CH_3CN (1 ml) was added dropwise during 5 min. The solution was stirred for 30 min, then dry diethyl ether was added dropwise to precipitate the complex. The dark orange

Table 5

Microanalytical data

Complex	(Found (calcd.) (%))		
	C	H	N
1 / $\text{Mg}(\text{ClO}_4)_2$	39.37	4.73	4.43
	(39.83)	(4.47)	(3.87)
1 / $\text{Ca}(\text{ClO}_4)_2$	39.94	4.33	3.86
	(38.98)	(4.37)	(3.79)
1 / $\text{Sr}(\text{ClO}_4)_2$	37.79	4.81	3.53
	(36.63)	(4.11)	(3.56)
1 / $\text{Ba}(\text{ClO}_4)_2$	33.87	3.53	3.13
	(34.45)	(3.86)	(3.35)
1 / $\text{Zn}(\text{BF}_4)_2$	41.34	4.87	4.57
	(41.09)	(4.61)	(3.99)

powder was filtered off and recrystallised from acetonitrile/ether several times to give orange powders of the 1/1 complexes in yields of 50–80%. The analytical results are shown in Table 5.

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