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THE SYNTHESIS AND STRUCTURE OF NOVEL FERROCENE BIS-CROWN ETHERS

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Summary

The synthesis of novel ferrocene bis-crown ethers is reported. Variable temperature ^{13}C NMR studies on these compounds reveal a common intramolecular dynamic process involving rotation about the N–CO bond.

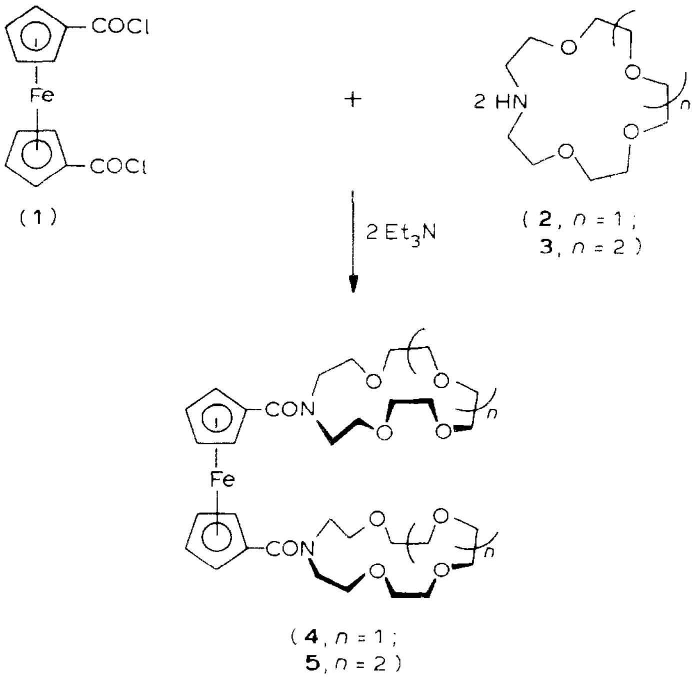
Several groups of workers have recently reported the syntheses of macrocyclic compounds containing the ferrocene unit as an integral part of the macrocyclic skeleton [1–6]. These multidentate ligands incorporate a crown ether framework designed to bind guest metal cations in close proximity to the iron metallocene atom. Hence these compounds can facilitate the study of metallocene metal atom-guest metal cation interactions at short interatomic distances using electrochemical and spectroscopic techniques.

The condensation of 1,1′-bis(chlorocarbonyl)ferrocene (**1**) [7] with the aza-crown ethers **2** and **3** [8] in the presence of triethylamine gave after column chromatography (alumina, 99% CH_2Cl_2, 1% MeOH) the respective ferrocene bis-crown ethers **4** (85% yield, m.p. 69–70°C orange crystals) and **5** (80% yield, m.p. 65–66°C orange crystals) (see Scheme 1). Both new bis-crown ethers gave satisfactory elemental analyses, ^1H NMR and molecular weights by mass spectrometry.

The ^{13}C NMR of **4** and **5** were recorded at various temperatures and the details of the spectra are reported in Tables 1 and 2.

At $-20°C$ the ^{13}C NMR reveals two absorptions for the respective N-CH_2 carbons of **4** and **5**. On warming these individual signals begin to broaden and at temperatures of 46.3°C for **4** and 46°C for **5** coalescence is observed (Fig. 1). Also the respective eight and ten OCH_2 carbon absorptions of **4** and **5** collapse to give simplified broadened peaks.

These observations suggest that at the coalescence temperatures and above the aza-crown ether rings of **4** and **5** are no longer fixed relative to the respective carbonyl groups and rotation about the amide N–CO bond is fast on the NMR timescale (Fig. 2).



(1)

(2, n = 1;
3, n = 2)

(4, n = 1;
5, n = 2)

The $\Delta G^{\ddagger}$ values for this intramolecular dynamic process common to both **4** and **5** were calculated using initially the Gutowsky equation [9]:

$k = \pi \Delta \nu / \sqrt{2}$

where $\Delta \nu$ is the frequency separation of resolved signals at the temperature at which

TABLE 1

VARIABLE TEMPERATURE ^{13}C NMR DATA FOR **4** FROM BROAD BAND DECOUPLED AND DEPT SPECTRA [4] (solvent CDCl$_3$; ref. TMS)

Assignment	δ (−20°C)	δ (20°C)	δ (55°C)
N–C	49.62	49.84	49.6 br
N–C	50.32	50.78	
O–C	68.21		
	69.21	69.14	
	69.36	70.09	
	69.46	70.20	
	69.50	70.67	69.9 br
	69.61	71.59	70.8 br
	70.00	71.92	71.4 br
	71.10		71.6 br
Ferrocene–C	71.32 [a]		
	71.45 [a]		
Ferrocene–C(*ipso*)	78.21	79.30	79.37
C=O	169.27	169.35	169.42

[a] Integrates for two carbons.

TABLE 2

VARIABLE TEMPERATURE ^{13}C NMR DATA FOR **5** FROM BROAD BAND DECOUPLED AND DEPT SPECTRA [4] (solvent $CDCl_3$; ref. TMS)

Assignment	δ (−20°C)	δ (20°C)	δ (55°C)
N–C	47.22	47.53	48.3 br
N–C	49.20	49.43	
O–C	69.08		
	69.62		
	69.87	69.46	
	70.11	69.90	
	70.18	70.37	69.9 br
	70.26 [a]	70.52	70.6 br
	70.31 [a]	70.66	70.7 br
	70.42	71.66	70.9 br
		71.80	
Ferrocene–C	71.64 [a]		71.58
	71.70 [a]		71.88
Ferrocene–C (*ipso*)	79.26	79.83	79.41
C=O	169.71	169.81	169.86

[a] Integrates for two carbons.

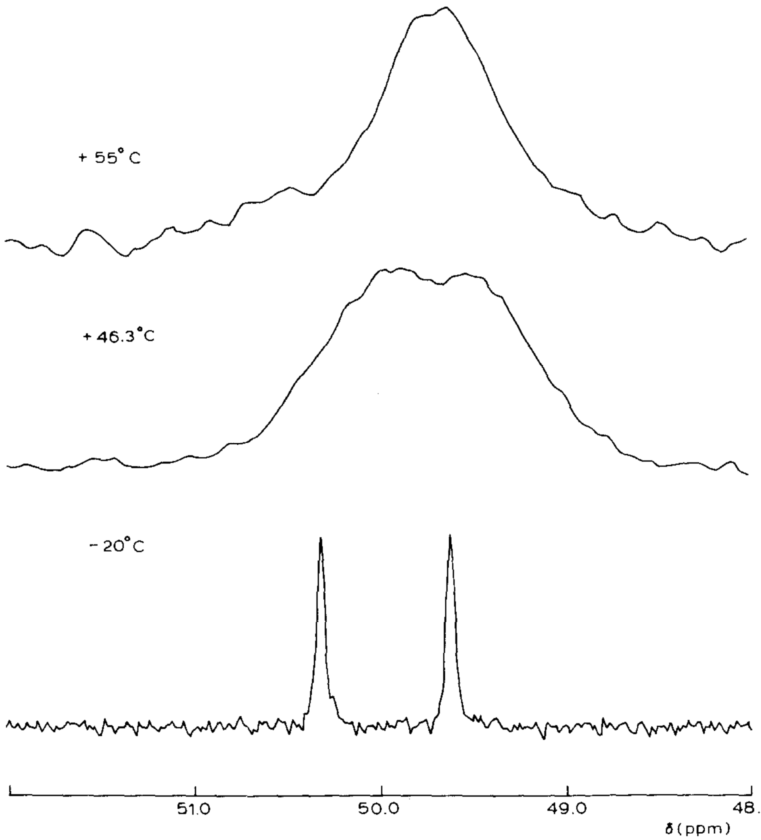


Fig. 1. Expanded variable temperature broad band decoupled ^{13}C NMR spectra of the N–C region of **4** at 100 MHz in $CDCl_3$.

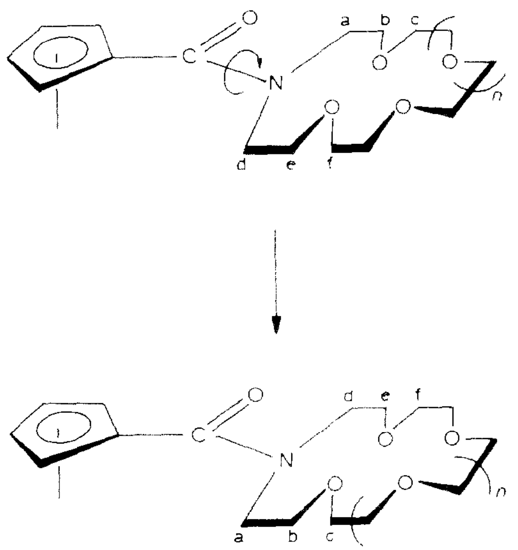


Fig. 2. Rotation about the N-CO bond in **4** ($n = 1$) and **5** ($n = 2$).

the amide bond rotation was stopped on the NMR timescale. The energy barriers $\Delta G^{\ddagger}$ were then obtained from the equation [10]:

$$\Delta G^{\ddagger} = 2.303\ RT_c(10.319 - \log_{10}k + \log_{10}T_c)$$

where R 8.314 J $\mathrm{mol^{-1}}$ $\mathrm{deg^{-1}}$ and T_c is the respective coalescence temperatures. $\Delta G^{\ddagger}$ values for rotation about the amide bond in **4** is 65 kJ $\mathrm{mol^{-1}}$ and **5** is 62 kJ $\mathrm{mol^{-1}}$. These results are in good agreement with the barriers to rotation about conventional amide linkages [11]. The coordination chemistries of these ferrocene bis-crown ethers are currently under investigation.

Experimental

^{1}H NMR spectra were recorded at 400 MHz and ^{13}C NMR spectra at 67.8 and 100 MHz using TMS as internal standard.

1,1′-Bis(chlorocarbonyl)ferrocene, aza-15-crown-5 and aza-18-crown-6 were prepared according to literature methods [7,8]. Toluene was dried by distillation from sodium.

*1,1′-Bis(1,4,7,10-tetraoxa-13-azacyclopentadecane-13-carbonyl)ferrocene (**4**)*

A solution of 1,1′-bis(chlorocarbonyl)ferrocene (0.71 g, 2.28 mmol) in dry toluene (70 ml) was added dropwise over 30 min to a stirred solution of aza-15-crown (1.0 g, 4.56 mmol) in toluene (100 ml) containing triethylamine (0.46 g, 4.56 mmol). When addition was complete stirring was continued for 1 h and the solution filtered. After removal of solvents the crude product was chromatographed on a column of alumina using methylene chloride/1% methanol. An orange band was collected and after solvents were removed recrystallisation from diethyl ether/hexane gave **4** (1.31 g, 85%) as orange crystals, m.p. 69–70°C. Anal. Found: C, 56.9; H, 7.4; N, 4.4. $C_{32}H_{48}N_2O_{10}$ calcd.: C, 56.8; H, 7.1; N, 4.2%. m/z 676.

^{1}H NMR ($CDCl_3$): δ 3.46–3.63 (m, 40H), 4.21 (t, *J* 1.7 Hz, 4H) and 4.54 (t, *J* 1.7 Hz, 4H).

1,1′-Bis(1,4,7,10,13-pentaoxa-16-azacyclo-octadecane-16-carbonyl)ferrocene (5)

The procedure for the preparation of **5** followed that described for **4**. A solution of 1,1′-bis(chlorocarbonyl)ferrocene (0.295 g, 0.95 mmol) in dry toluene (50 ml) was added dropwise over 30 min to a stirred solution of aza-18-crown-6 (0.5 g, 1.9 mmol) in toluene (70 ml) containing triethylamine (0.19 g, 1.9 mmol). When addition was complete stirring was continued for 1 h and the solution filtered. Removal of solvents gave the crude product which was chromatographed on an alumina column using methylene chloride/1% methanol. Recrystallisation from diethyl ether/hexane gave **5** (0.58 g, 80%) as orange crystals, m.p. 65–66°C. Anal. Found: C, 56.7; H, 7.0; N, 3.4. $C_{36}H_{56}N_2O_{12}$ calcd.: C, 56.4; H, 7.3; N, 3.7%. *m/z* 764.

^{1}H NMR ($CDCl_3$): δ 3.60–3.77 (m, 48H), 4.33 (t, *J* 2 Hz, 4H) and 4.65 (t, *J* 2 Hz, 4H).

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