Synthesis and Coordinating Properties of a Ferrocenophane containing a Pyridine Unit

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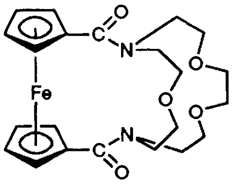
The cryptand **3**, containing both a ferrocene unit and a 2,6-disubstituted pyridine unit, forms complexes with di- and tri-valent cations; the X-ray crystal structure of a 2 : 1 (host : guest) complex with Ca^{2+} shows that the metal cations are coordinated by a *cis*-configuration of the carbonyl groups on the short (pyridyl) side of the macrocyclic ring, which confirms the interpretation of the ^1H and ^{13}C NMR data of the complexes in solution.

In recent years we have reported on the synthesis, structure and cation-binding properties of a variety 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 groups have been shown to be *trans* in the solid compound.[6,8,11,12] Multinuclear NMR experiments using an unsymmetrical host cryptand **1** showed that, on complexation with di- and tri-valent cations, the carbonyl groups were involved as coordinating ligands and adopted a *cis* configuration in such complexes.[10] This conclusion was confirmed by the X-ray crystallographic analysis of the 2 : 1 (host : guest) complex of the symmetrical cryptand **2** with an yttrium cation.[13] We now report the first synthesis of an unsymmetrical cryptand **3**, containing both a pyridine ring and a ferrocene unit, and describe a study of its complex formation with a variety of di- and tri-valent cations.

The cryptand **3** was synthesised by the route outlined in Scheme 1 and isolated by column chromatography on alumina using dichloromethane/1–2% methanol as eluant.† The ^1H and ^{13}C NMR spectra, which were assigned by a combination of COSY and $^1H/^{13}C$ heteronuclear correlation spectra,‡ are entirely consistent with structure **3** and demonstrate, once again, that the cryptand has the carbonyl groups orientated *trans* to each other. Thus the ^{13}C NMR spectrum shows a total of twenty-seven signals due to the non-equivalence of all the carbon atoms of **3**. The spectrum is analogous to that observed for **1**, a cryptand that has also been shown to retain the *trans* configuration of the carbonyl groups in the solid state.[6]

The pyridyl cryptand **3** formed complexes in CD_3CN with a series of cationic guests (Na^+, Ca^{2+}, Ba^{2+} or Y^{3+}) as detected by bathochromic shifts in the UV-VIS spectra and by $^1H/^{13}C$ NMR spectroscopy; for example, the addition of a molar equivalent of the Y^{3+} cation as $Y(ClO_4)_3$, to a 0.05 mol dm^{-3} solution of **3** in CD_3CN resulted in the formation of unequal (3 : 1, by integration) amounts of two complexed species as illustrated in the ^1H NMR spectra of Fig. 1. The two doublets and one triplet seen in the pyridine region of uncomplexed **3** were replaced by a doublet and a triplet (integral ratio 2 : 1) for each complex species. At ambient temperature the upfield doublet and triplet accounted for 75% of complexed **3** but on heating to 340 K this decreased to 64% whilst the intensity of the most downfield doublet–triplet pair showed a proportionate increase. The most likely explanation is that the upfield signals represent a complex of 2 : 1 (host : guest) stoichiometry and the downfield signals are due to a complex of 1 : 1 stoichiometry with the complexes present in an initial molar ratio of 1.5 : 1.0. The ^{13}C NMR spectra of the complexes supported the conclusions reached from the ^1H NMR data in that two sets of signals were observed, each consisting of 14 peaks.§ Clearly an element of symmetry exists in both complexes as indicated by the observation of one carbonyl carbon and three pyridyl carbons for each complex instead of the two carbonyl and five pyridyl carbons of the parent cryptand. These data are analogous to those found for complexation of **1**[10] and may again be explained by rotation of the amide carbonyls to a *cis*-configuration in order to coordinate the cations, thus introducing a plane of symmetry into both complexes. The only remaining question, therefore,



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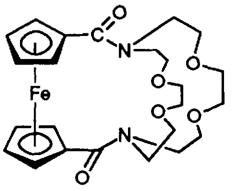

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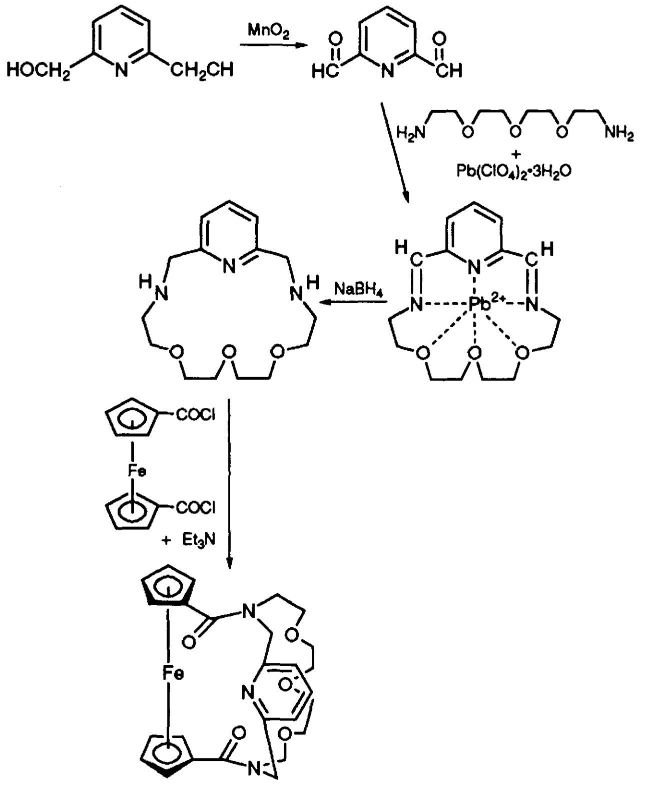

3

Scheme 1

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† FABMS (glycerol matrix) 625 (M^+ + glycerol). Satisfactory elemental analyses were found for C, H and N.

‡ *Selected spectroscopic data* for **3**: ^{13}C NMR ($CDCl_3$) δ 79.25, 77.64 (ferrocenyl *ipso*-C); 76.32, 74.70, 74.67, 74.19, 71.66, 71.22, 70.53, 69.98 (ferrocenyl CH); 55.32, 51.82, 50.76, 49.08 (NCH_2); 72.39, 71.91, 71.72, 70.36, 70.19, 68.20 (OCH_2); 157.48, 156.12 (pyridine *ipso*-C); 136.94, 120.30, 120.26 (pyridine CH); 171.44, 170.92 (C=O).

§ *Selected spectroscopic data* for the complexes of **3** with Ca^{2+}: 1 : 1 (host : guest) complex ^{13}C NMR (CD_3CN) δ 79.1 (ferrocenyl *ipso*-C); 77.4, 73.1, 72.8, 70.2 (ferrocenyl C*H*); 53.7, 52.7 (NCH_2); 72.6, 71.1, 70.6 (OCH_2); 158.1 (pyridine *ipso*-C); 139.4, 122.0 (pyridine CH); 172.8 (C=O). 2 : 1 (host : guest) complex ^{13}C NMR (CD_3CN) δ 78.7 (ferrocenyl *ipso*-C); 78.5, 73.7, 71.8, 69.8 (ferrocenyl CH); 55.9, 54.5 (NCH_2); 72.7, 71.9, 70.8 (OCH_2); 154.9 (pyridine *ipso*-C); 139.4, 121.8 (pyridine CH); 173.5 (C=O).

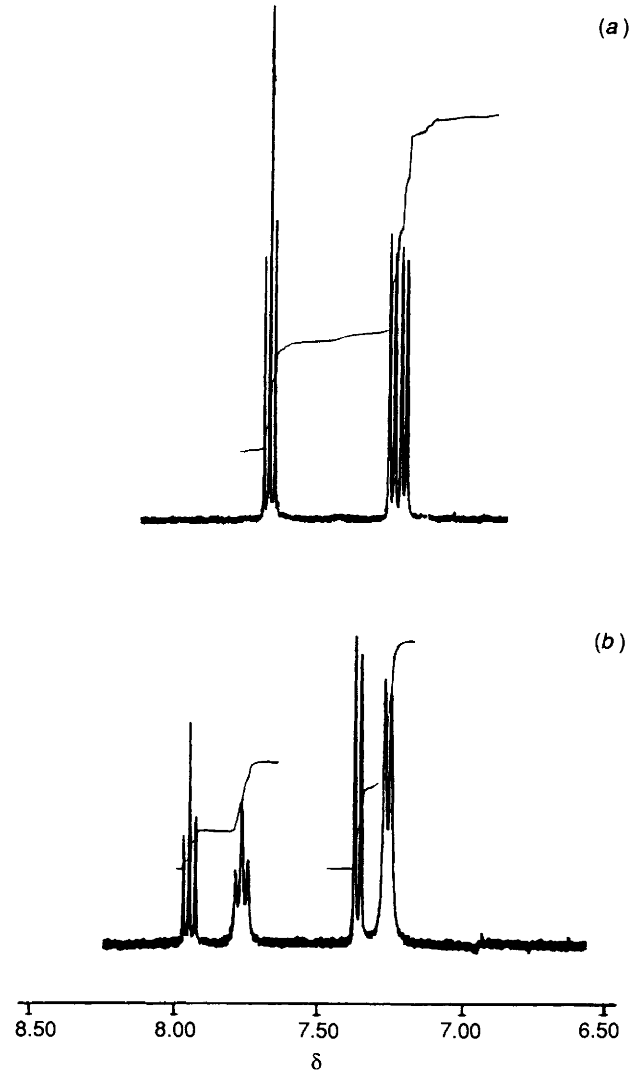

Fig. 1 The pyridine region of the ^1H NMR spectrum of (*a*) **3** and (*b*) the reaction of **3** with $Y(ClO_4)_3$ in CD_3CN

is whether the cations are coordinated on the 'short' pyridine side of the host cryptand or on the 'long' trioxyethylene bridge.

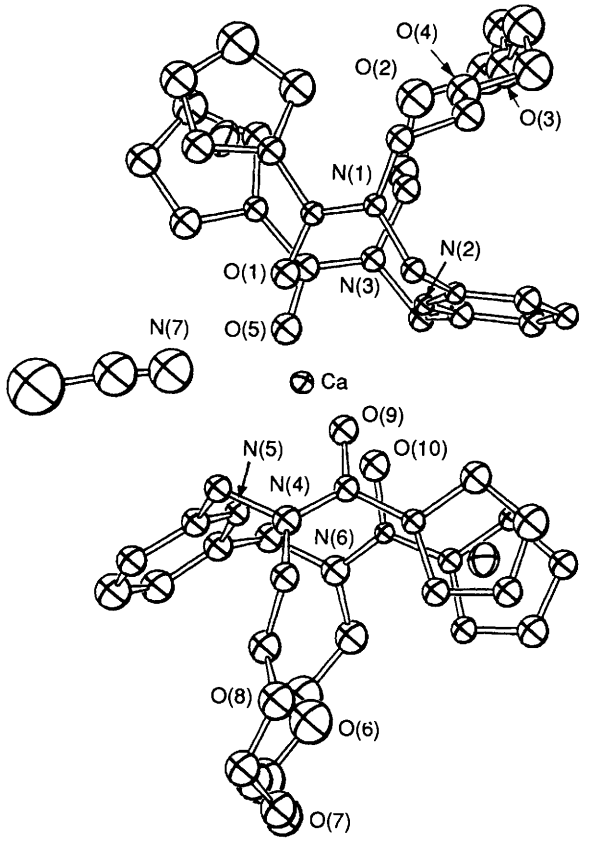

Fig. 2 X-Ray crystal structure of the 2 : 1 (host : guest) complex of **3** with Ca^{2+}, showing the numbering scheme for the ligand [C(1)–C(27)] (perchlorate counter ions omitted)

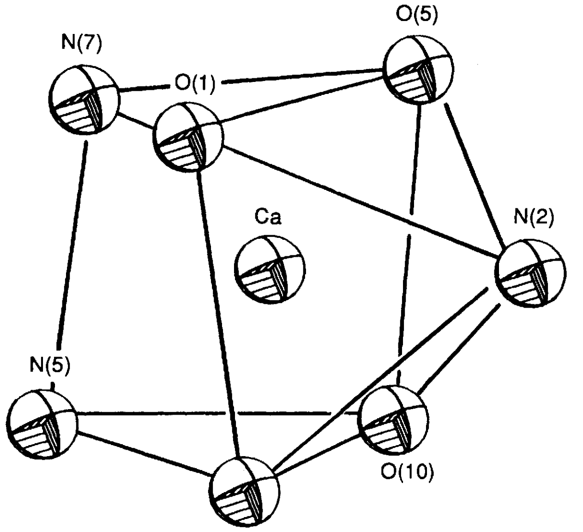

Fig. 3 The coordination geometry around Ca^{2+} in the 2 : 1 (host : guest) complex with **3**; bond lengths to Ca (Å) O(1), 2.290(13); O(5), 2.309(13); O(9), 2.299(14); O(10), 2.277(14); N(2), 2.795(14); N(5), 2.751(15); N(7), 2.517(24)

X-Ray analysis of a single crystal of the 2 : 1 (host : guest) complex of **3** with Ca^{2+}, derived from slow evaporation of a CD_3CN solution, resolved the question by showing that the calcium was complexed on the short (pyridine) side of the macrocycle (Fig. 2).¶ The calcium ion is seven-coordinate, bound within a capped trigonal prism (Fig. 3) involving two pairs of *cis*-amide carbonyl ligands, two pyridine nitrogen atoms (one of which, N-2, comprises the cap) and a third nitrogen (N-7), which belongs to a mole of solvent acetonitrile. The four oxygen atoms of the carbonyl groups are disposed in a square planar configuration about the Ca^{2+}, with Ca–O distances of *ca.* 2.30 Å. The calcium bonds to the pyridine nitrogens (N-2 and N-5) are larger at 2.751(15) and 2.795(14) Å, but are still close to the sum of the effective ionic radius of seven-coordinate Ca^{2+} (1.20 Å)[14a] and the van der Waals radius of N (1.55 Å).[14b] The more flexible Ca–N-7 (solvent) bond length is 2.517(24) Å. The calcium ion lies 0.42 Å out of the plane of the four carbonyl oxygen atoms with N-2 on the opposite side of the plane at a distance of 2.36 Å. The

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¶ *Crystal data* for $C_{56}H_{62}D_3CaCl_2Fe_2N_7O_{18}$, $M = 1349.86$, triclinic, space group $P\bar{1}$, $Z = 2$, $a = 13.692(6)$, $b = 15.234(8)$, $c = 15.636(6)$ Å, $\alpha = 113.44(4)$, $\beta = 95.61(4)$, $\gamma = 97.58(4)°$, $U = 2926$ Å^3, $D_c = 1.53$ g cm^{-3}, $\mu = 62.6$ cm^{-1}, $F(000) = 1400$, Cu-Kα radiation ($\lambda = 1.5418$ Å), $5 < 2\theta < 70°$; 2535 reflections of which 1806 had $I_{net} > 2.5\sigma(I_{net})$, $R = 0.066$, $R_w = 0.071$. The structure was solved by direct methods and Fourier difference synthesis using the NRCVAX programme package.[22] Refinement was carried out by full-matrix least-squares analysis with anisotropic temperature factors for Fe, Ca, Cl and the perchlorate oxygen atoms and isotropic temperature factors for C, N, and ligand oxygen atoms. The hydrogen atoms were included as fixed contributions in calculated positions. Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

carbonyl bond lengths and the distances between the carbonyl oxygens and the calcium cation are similar to those found[13] for the 2 : 1 (host : guest) complex between **2** and Y^{3+}. In all four cases, the amide nitrogen, carbonyl group and adjacent ferrocenyl carbon atom are planar to within 0.02 Å and are rotated out of the plane of their respective cyclopentadiene rings to a greater or lesser extent. The groups associated with N-4 and N-6 are rotated by *ca.* 27 and 21°, respectively, and those associated with N-1 and N-3 by *ca.* 5 and 38°, respectively. These rotations probably explain why the carbonyl groups are orientated *cis* to the pyridine bridge. The carbonyl groups bend in towards the cation to achieve the maximum possible interaction and the whole amide unit must tilt in order to retain its planarity. Consequently, the NCH_2 carbons *trans* to the carbonyls must move away from each other and, hence, the oxyether bridge associated with these carbon atoms unfolds, enabling the pyridine nitrogen to interact with the cation.

The crystal structure of a mixed donor macroyclic complex of calcium, in which the macrocycle contains a pyridine ring, has been reported.[15] The structure was eight-coordinate with a Ca–N(pyr) bond length of 2.64 Å, somewhat shorter than those observed here. A few other macrocyclic complex crystal structures have also been reported in which alkaline[16,17] or alkaline earth[18] cations are complexed by pyridyl or bipyridyl nitrogen atoms. In this system, the structural restraints in the ligand framework of **3** bring about configurational and conformational changes upon cation binding, which apparently enable pyridine coordination to be favoured over oxygen coordination. The cryptand **3**, therefore, serves as a useful model of naturally occurring allosteric systems,[19–21] in which binding at one site triggers a conformational change in the molecule allowing specific binding to occur at a remote site.

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References

1 A. P. Bell, P. J. Hammond and C. D. Hall, *J. Chem. Soc., Perkin Trans.* 1, 1983, 707.
2 P. D. Beer, P. J. Hammond, C. Dudman and C. D. Hall, *J. Organomet. Chem.*, 1984, **263**, C37.
3 P. J. Hammond, P. D. Beer, C. Dudman, I. P. Danks and C. D. Hall, *J. Organomet. Chem.*, 1986, **306**, 367.
4 C. D. Hall, I. P. Danks, M. Lubienski and N. W. Sharpe, *J. Organomet. Chem.*, 1990, **384**, 139.
5 C. D. Hall and N. W. Sharpe, *Organometallics*, 1990, **9**, 952.
6 C. D. Hall, I. P. Danks, S. C. Nyburg, A. W. Parkins and N. W. Sharpe, *Organometallics*, 1990, **9**, 1602.
7 C. D. Hall, I. P. Danks and N. W. Sharpe, *J. Organomet. Chem.*, 1990, **390**, 227.
8 C. D. Hall, A. W. Parkins, S. C. Nyburg and N. W. Sharpe, *J. Organomet. Chem.*, 1991, **407**, 107.
9 C. D. Hall and N. W. Sharpe, *J. Organomet. Chem.*, 1991, **405**, 365.
10 C. D. Hall, J. H. R. Tucker and N. W. Sharpe, *Organometallics*, 1991, **10**, 1727.
11 P. D. Beer, C. D. Bush and T. A. Hamor, *J. Organomet. Chem.*, 1988, **339**, 133.
12 M. C. Grossel, M. R. Goldspink, J. A. Jriljac and S. C. Weston, *Organometallics*, 1991, **10**, 851.
13 C. D. Hall, J. H. R. Tucker, A. Sheridan, S. Y. F. Chu and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 1992, 3133.
14 (*a*) R. D. Shannon, *Acta Crystallogr., Sect. A*, 1976, **32**, 751; (*b*) J. E. Huheey, *Inorg. Chem.*, 3rd ed. Harper and Row, London, 1983, p. 184.
15 O. A. Raevski, V. V. Tkachev. L. O. Atovmyan, V. E. Zubareva, I. I. Bugak and D. G. Batyr, *Koord. Khim.*, 1988, **14**, 1697; D. E. Fenton, D. H. Cook, I. W. Nowell and P. E. Walker, *J. Chem. Soc., Chem. Comm.*, 1978, 279.
16 L. Echegoyen, A. DeCian, J. Fischer and J.-M. Lehn, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 838.
17 V. McKee, M. R. J. Dorrity, J. F. Malone, D. Marrs and J. Nelson, *J. Chem. Soc., Chem. Comm.*, 1992, 383.
18 N. A. Bailey, D. E. Fenton, P. C. Hellier, P. D. Hempstead, V. Cassellato and P. A. Vigato, *J. Chem. Soc., Dalton Trans.*, 1992, 2809.
19 J. Rebek Jr., T. Costello, L. Marshall, R. Wattley, R. C. Goodwood and K. Onan, *J. Am. Chem. Soc.*, 1985, **107**, 7481.
20 P. D. Beer and A. S. Rothin, *J. Chem. Soc., Chem. Comm.*, 1988, 52.
21 Y. Kokube, Y. Sumida, M. Hayashi and H. Ogoshi, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1496.
22 E. J. Gabe, Y. Le Page, P. F. Charland, F. C. Lee and P. S. White, *J. Appl. Crystallogr.*, 1989, **22**, 384.