Journal of Organometallic Chemistry, 352 (1988) C13–C16
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

Metallocene-bridged cryptands

I. X-Ray structural study of 1,1″; 1′,1‴-bis(1,4,10,13-tetraoxa-7,16-diazacyclooctadecane-7,16-diyldicarbonyl)bisferrocene

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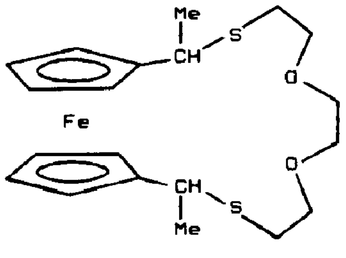
(Received April 11th, 1988)

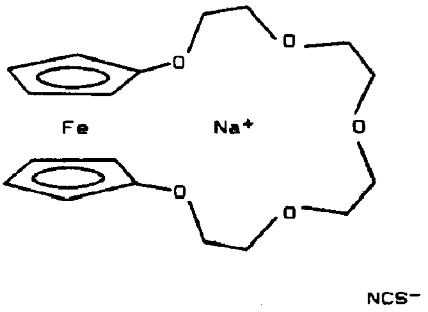
Abstract

An X-ray diffraction study of the title compound has revealed a centrosymmetric molecule with a large cryptand cavity (radius ca. 1.65 Å), in agreement with ion-extraction experiments.

The capacity of crown ethers and cryptands [1] to bind metal ions selectively offers exciting possibilities for the construction of ion-specific detectors and related devices [2]. A key problem lies in constructing a ligand in which there is detectable electronic interaction brought about by metal-ion binding. One approach has been to incorporate dye moieties into the crown/cryptand skeleton [3]; another is to bridge the cryptand with a metallocene unit such as ferrocene [4–7]. A number of polyoxa- and polythia-ferrocenophanes have been reported [4,5], and the crystal structures of a polyoxathiaferrocenophane (**1**) [5], and a thiocyanate complex (**2**) [6] have been described.



(**1**)



(**2**)

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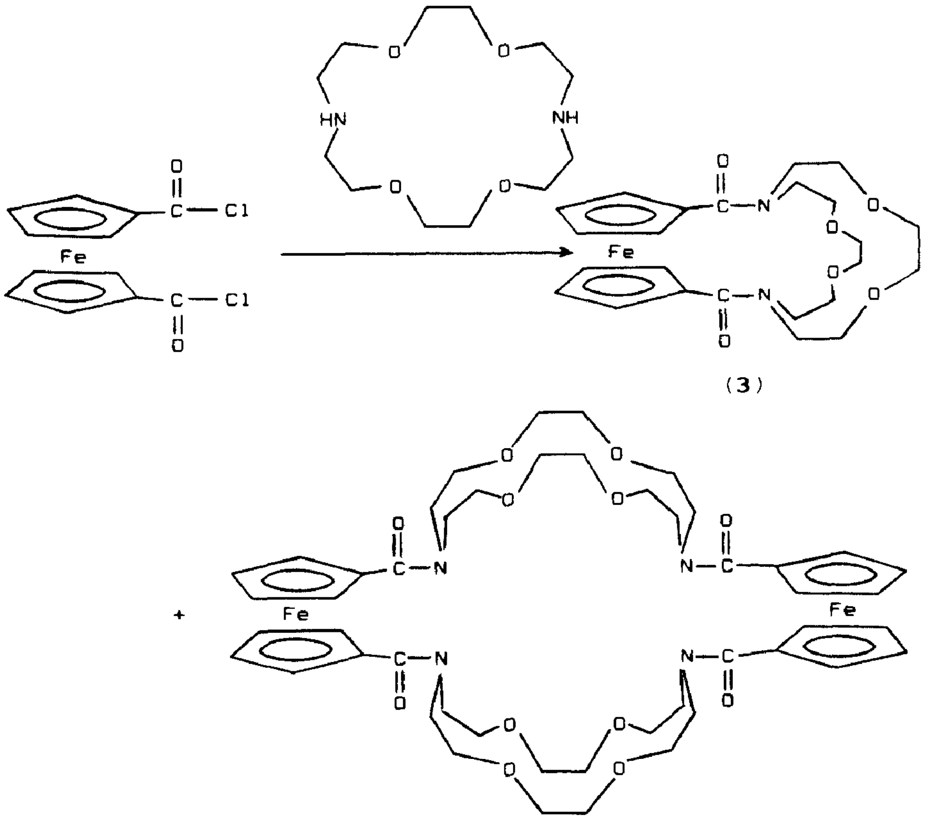
Reaction of 1,1′-bis(chlorocarbonyl)ferrocene with diaza-[18]-crown-6 gives 1,1′-(1,4,10,13-diazacyclooctadecane-7,16-diyldicarbonyl)bisferrocene (**3**) and the cryptand dimer **4**, the title compound [7]. A crystal structure of the monomer **3** as its dihydrate has just been reported [8]. We now report an X-ray structural study of the dimer, the results of which provide further insight into its previously reported dynamic NMR behaviour [7,9]; we also comment on its ion-binding properties.



(**3**)

(**4**)

The X-ray structure of **4** shown in Fig. 1 * reveals that the cyclopentadienyl rings of each of the ferrocene units are staggered and tilted slightly towards the centre of the cryptand cavity (mean tilt angle 2.5°). Small deviations from planarity have previously been observed in the macrocyclic ferrocenophane crown ether (**1**) (tilt angle 2.3°) [5] and the thiocyanate complex **2** (tilt angle 3.3°) [6]. In the former case the cyclopentadienyl rings were eclipsed but in the latter they are staggered.

The internal diameter of the cavity of **4** is estimated to be ca. 3.3 Å using Chem-X [10]. Whilst the molecular conformation of the cryptand is probably a poor

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* Crystal data for **4**: $Fe_2C_{49}H_{64}N_4O_{12}$, $M = 1000.73$, triclinic, space group $P\bar{1}$, a 11.709(5), b 13.310(2), c 15.527(8) Å, α 94.29(3), β 96.73(4), γ 101.00(3)°, U 2347.2 Å^3, $Z = 2$, D_c 1.419 g cm^{-3}. The structure was solved by Patterson and difference techniques, and refined [11] using 2830 unique data $I > 3\sigma(I)$, measured on an Enraf–Nonius CAD-4F diffractometer with Mo-K_α radiation μ 6.83 cm^{-1}. The final R value is 0.090. Atomic coordinates, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

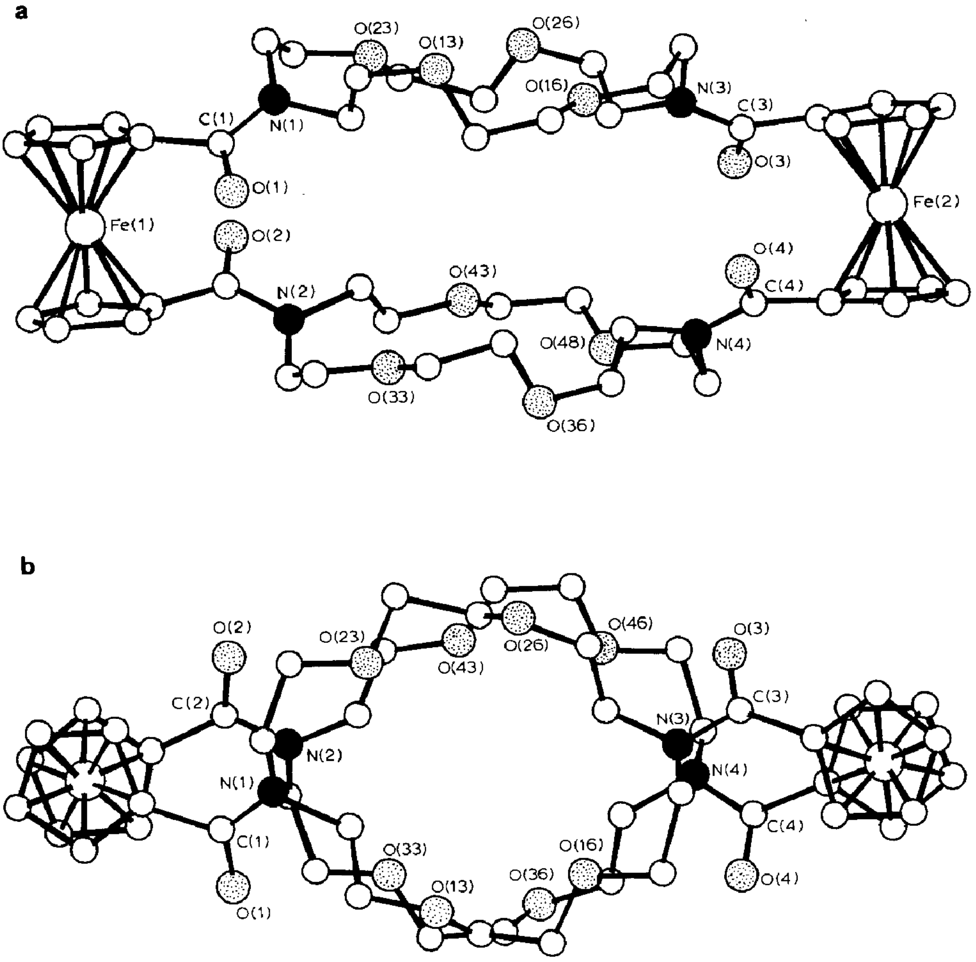

Fig. 1. Two views of the molecular structure of **4** with selected atoms labelled. Selected distances: Fe–C (average) 2.03 Å, Fe(1)–Fe(2) 14.57 Å, O(13)–O(26) 5.52 Å, O(16)–O(23) 5.46 Å, O(33)–O(46) 5.64 Å, O(36)–O(43) 5.12 Å, O(13)–O(46) 7.99 Å, O(16)–O(43) 6.34 Å, O(23)–O(36) 7.78 Å, O(26)–O(33) 7.38 Å.

representation of that to be expected for a cryptate (the oxygen bridges are lying external to the cavity for example, Fig. 1), extraction experiments do suggest a maximum complexing efficiency for Rb^+ ($> Cs^+ > K^+ > Na^+$) consistent with such a cavity size. The average cavity size for the individual crown ether rings suggests a maximum ion-binding diameter of ca. 2.6 Å but no evidence for binding of Li^+ or Na^+ has been found.

A particularly noteworthy feature of the dynamic NMR data for **4** is that two different dynamic processes are observed and it has been suggested that the barrier for rotation about the amide C(O)–N bond has a higher activation energy ($\Delta G^\ddagger$ 67 kJ mol^{-1}) than that for rotation about the ferrocene–carbonyl bond ($\Delta G^\ddagger$ 50 kJ mol^{-1}) [7]. Consistent with this view, the amide units are approximately planar in **4** but each carbonyl group is tilted well away from the plane of the ferrocenyl cyclopentadienyl rings (by ca. 35°). Each carbonyl is disposed *trans* relative to its neighbours, as previously proposed [7].

The solid-state structure of **4** emphasises the rigidity of the ferrocene spacer and that there is little likelihood of direct interaction of the iron atoms with a bound metal ion. We are, however, currently exploring the possibility of electron transfer processes between the ferrocene units and reducible metal ions bound in the cavity.

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