

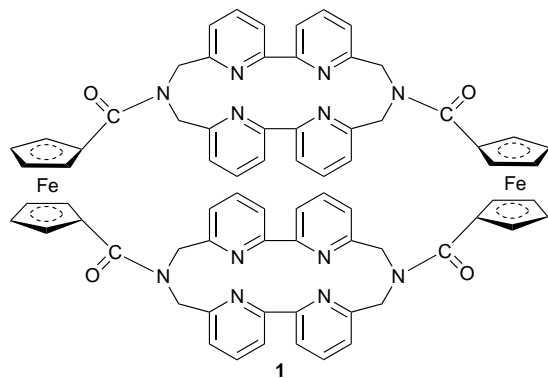
Sodium springs another surprise

C. Dennis Hall,* Thi-Kim-Uyen Truong, James H. R. Tucker† and Jonathan W. Steed

Department of Chemistry, King's College London, Strand, London, UK WC2R 2LS

The X-ray crystallographic structures of the novel redox-active cryptand **1** and its homobinuclear complex with sodium perchlorate are reported and discussed.

The synthesis, structure, electrochemistry and complex formation of cryptands containing metallocene units have attracted considerable attention in recent years.¹ A common synthetic procedure to the compounds involves the condensation of 1,1'-ferrocene bis-acid chloride with diazamacrocycles which generally produces a mixture of monomeric and dimeric cryptands containing amide functions.² All the available solution NMR data and X-ray crystallographic data show that the amide functions are disposed *trans* to each other.^{3–5} Complex formation with a range of mono-, di- and tri-valent cations then involves rotation of the amide carbonyl groups to *cis* orientations which allows their coordination to the guest cation usually in conjunction with other oxygen atoms of the polyether chains or heterocyclic units within the macrocyclic structure.^{6,7} Recent work has involved the synthesis of analogous cryptands incorporating nitrogen ligands in the form of phenanthroline units which also have the carbonyl groups within the host cryptand disposed *trans* to each other.^{8,9} These cryptands were designed with the objective of complexing lanthanide cations in order to create redox-active luminescent cryptates and the work reported here represents an extension of this concept to the synthesis of the dimeric cryptand **1** containing four 2,2'-bipyridyl units.



Cryptand **1**‡ was synthesised in the usual way from ferrocene bis-acid chloride and the appropriate diamine, prepared by a modification§ of the literature procedure.¹⁰ No trace of the monomeric species was found but a trimeric amide was separated and characterised.¶ The ¹³C NMR of **1** in CDCl₃ showed a total of 16 signals consisting of four ferrocene C–H carbons, one carbonyl carbon, two CH₂N signals, six CH bipyridyl signals and three quaternary bipyridyl signals. The *ipso*-ferrocene carbons and one of the quaternary bipyridyl carbons were not observed but the spectrum is consistent with a structure in which the carbonyl groups on each ferrocene unit are either *cis* or *trans* to each other. The ¹H NMR data were also consistent with this conclusion. The definitive evidence, however, is provided by the X-ray crystal structure of the cryptand (Fig. 1).|| It is immediately obvious that the carbonyl groups, located on the periphery of the cryptand, are mutually

trans to each other with two of the bipyridyl units on the outside of the cryptand virtually orthogonal to the two corresponding bipyridyl units filling the cavity. Thus π – π stacking interactions are minimal and the crystal adopts a configuration which appears to minimise the dipole moment and maximise close packing.

Downfield shifts of most of the ¹H NMR signals of **1** were indicative of complex formation with Na⁺ but at NMR concentrations (*ca.* 5×10^{-2} M) complexes with other cations (*e.g.* Ca²⁺ or Eu³⁺) precipitated thus making it difficult to achieve a complete NMR analysis of the latter cryptates which is still in hand. The sodium complex was sufficiently soluble, however, to achieve a full analysis (by 2D NMR) and in summary, twice as many ¹³C signals were observed in the complex as in the parent compound, a result which is entirely consistent with the crystal structure reported below. The binuclear sodium perchlorate complex of **1** crystallised from CH₂Cl₂–MeCN solution and the resultant single crystal was found to contain four molecules of solvent acetonitrile per molecule of the complex. Far more interestingly however, X-ray crystallography revealed the two sodium cations each bound in a centrosymmetrical structure by the four bipyridyl nitrogen atoms of one macrocyclic ring and one carbonyl oxygen of the other macrocyclic system in an approximate square pyramidal configuration (Fig. 2). Each uncomplexed amide function remained *trans* to its partner but was not involved in binding the cation. The sodium–nitrogen bond distances varied from 2.373(7) to 2.579(7) Å and the Na–O distance was unusually short at 2.191(6) Å. The N–Na–N bond angles in the square pyramid varied from 67.7(2) to 84.8(2)° and the O–Na–N bond angles from 105.2(2) to 136.0(2)°. The configuration achieved in the crystal enabled all the amide groups to remain planar and in the plane of the cyclopentadienyl rings in each case. This

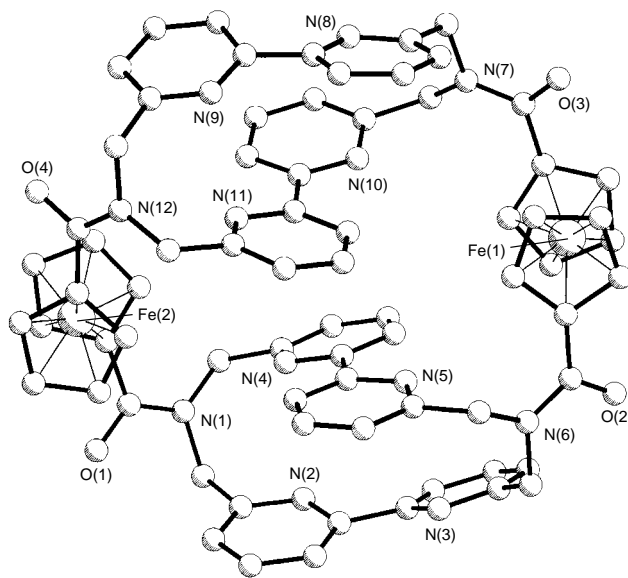


Fig. 1 X-Ray crystallographic structure of ligand **1** showing all four amide carbonyl bonds *trans* relative to each other

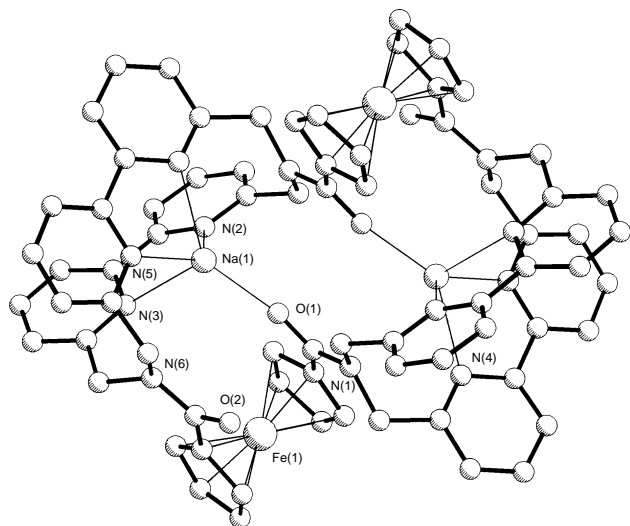


Fig. 2 X-Ray crystallographic structure of the homo-binuclear complex of **1** with sodium perchlorate (counter-ions not included)

leaves a distance of 5.57 Å between the complexed sodium cations, a feature which should enable a suitable anion (*e.g.* cyanate) or dianion (*e.g.* oxalate) to be accommodated within the cleft of the cryptate. This aspect of the complexation will be the subject of future work. The perchlorate counter ions are a considerable distance from the sodium cations with the nearest Na...Cl distance of ClO₄ at 7.88 Å and the nearest Na...O distance of ClO₄ at 6.66 Å. This confirms that the sodium cations are fully encapsulated by the cryptand which should therefore be effective as a redox-active phase transfer host. Finally, the highly unusual feature of sodium a 'hard' cation, complexed by four pyridyl nitrogens and an amide carbonyl oxygen in a five-coordinate square pyramidal configuration should be addressed. Preorganized rather than predisposed oligopyridine ligands are known to form helical complexes with sodium cations,^{11,12} and macrocycles or cryptands containing phenanthroline¹³ or bipyridyl¹⁴ units are also known to complex sodium albeit in the latter case as a cryptatium species. There are very few examples, however, of sodium complexed by four nitrogen and one oxygen donor atoms and none in which the configuration of the complex is a square pyramid. Nelson and coworkers have characterised a mononuclear cryptate with a distorted trigonal bipyramidal configuration about the sodium composed of four nitrogen donors and a water molecule situated in an equatorial position.¹⁵ The Na–N bond length varies from 2.520 to 2.636 Å and the Na–O distance is 2.241 Å significantly longer than that observed in the cryptate from **1**. It seems that sodium is indeed capable of more than one surprise.¹¹

We thank King's College London for a Junior Research Studentship (to T.-K.-U. T.) and for financial support in purchasing X-ray equipment. Thanks are also due to Jane Hawkes and Jon Cobb (KCL/ULIRS) for NMR data and Dr K. Welham (School of Pharmacy/ULIRS) for mass spectra.

Footnotes and References

* E-mail: c.d.hall@kcl.ac.uk

† Present address: Dept. of Chemistry, The University of Exeter, Stocker Road, Exeter, UK, EX4 4QD.

‡ All new compounds were characterised by accurate mass spectrometry and multinuclear NMR spectroscopy.

§ We are indebted to Dr. Anders Døssing (Copenhagen) for the generous gift of 6,6'-dimethyl-2,2'-bipyridine and a disclosure of their procedure to 6,6'-dibromomethyl derivatives.

¶ Details to be reported in the full paper.

|| *Crystal data* for **1**. C₇₄H₆₀Cl₄Fe₂N₁₂O₄, *M* = 1434.84, monoclinic, space group *P*2₁/*n*, *a* = 14.450(1), *b* = 28.621(1), *c* = 16.181(1) Å,

β = 103.05(1), *U* = 6517.51(6) Å³, *Z* = 4, *D*_c = 1.462 Mg m⁻³, *μ* = 0.67 mm⁻¹, *T* = 293(2) K, 9856 unique reflections.

Refinement converged with *wR*₂ = 0.2278, which corresponds to a conventional *R*-factor of 0.081 for data with *I* > 2σ(*I*).

Crystal data for the Na complex of **1**. C₇₂H₅₆Fe₂N₁₂O₄·2Na·ClO₄·4CH₃CN, *M* = 1674.08, monoclinic, space group *P*2₁/*c*, *a* = 9.3880(2), *b* = 29.2720(8), *c* = 13.2400(4) Å, *β* = 97.895(1), *U* = 3603.9(2) Å³, *Z* = 2, *D*_c = 1.543 Mg m⁻³, *μ* = 0.57 mm⁻¹, *T* = 293(2) K, 3604 unique reflections.

Experimental: orange prismatic crystals (0.4 × 0.1 × 0.1 mm) were prepared by slow evaporation of an MeCN–CH₂Cl₂ solution of the compound (as the triflate salt) in the presence of excess NBu₄ClO₄ and mounted on a thin glass fibre using a fast setting epoxy resin. A total of 360 oscillation frames of 45 s exposure time with 0.5° rotation in *φ* were recorded using a Nonius Kappa CCD diffractometer, with a detector to crystal distance of 35 mm. The crystal was indexed from the first ten frames using the DENZO package¹⁶ and positional data were refined along with diffractometer constants to give the final unit cell parameters. Integration and scaling of the whole data set resulted in a total of 3604 unique data which were corrected for Lorentz and polarisation effects and were used in subsequent refinement. The structure was solved using the direct methods option of SHELXS-86¹⁷ and developed *via* alternating least squares cycles and difference Fourier synthesis (SHELXL-93).¹⁸ All non-hydrogen atoms were modelled anisotropically except those of the two disordered molecules of acetonitrile and the oxygen atoms of the disordered perchlorate. Hydrogen atoms are assigned an isotropic thermal parameter 1.2 times that of the parent atom and allowed to ride. Hydrogen atoms were not included for the acetonitrile solvent molecules within the lattice as a consequence of their severely disordered nature. This disorder was eventually modelled in terms of a total of twelve different atom positions with refined occupancies ranging from 1.0 to 0.25. Even this model proved chemically unsatisfactory but since the solvent exhibits no significant interactions with the complex it was accepted as giving the best fit to the diffraction data. The disorder of the perchlorate anion was successfully modelled in terms of rotation about the Cl(1)–O(40) axis resulting in a total of nine different positions for the three oxygen atoms. Refinement converged with *wR*₂ = 0.2533, which corresponds to a conventional *R*-factor of 0.077 for data with *I* > 2σ(*I*). CCDC 182/619.

- P. D. Beer, *Adv. Inorg. Chem.*, 1992, **39**, 79; D. Dietrich, P. Viout and J.-M. Lehn, *Macrocyclic Chemistry*, VCH, Weinheim, 1993, ch. 3; J.-M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, 1995, ch. 8.
- A. P. Bell, P. J. Hammond and C. D. Hall, *J. Chem. Soc., Perkin Trans. 1*, 1983, 707.
- P. D. Beer, J. Elliot, P. J. Hammond, C. Dudman and C. D. Hall, *J. Organomet. Chem.*, 1984, **263**, C37.
- P. D. Beer, C. D. Bush and J. A. Hamor, *J. Organomet. Chem.*, 1988, **339**, 133.
- C. D. Hall, I. P. Danks, S. C. Nyburg, A. W. Parkins and N. W. Sharpe, *Organometallics*, 1990, **9**, 1602; C. D. Hall, A. W. Parkins, S. C. Nyburg and N. W. Sharpe, *J. Organomet. Chem.*, 1991, **407**, 107.
- C. D. Hall, J. H. R. Tucker and N. W. Sharpe, *Organometallics*, 1991, **10**, 1727.
- C. D. Hall, J. H. R. Tucker, A. Sheridan, S. Y. F. Chu and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 1992, 3133; C. D. Hall, J. H. R. Tucker, S. Y. F. Chu, A. W. Parkins and S. C. Nyburg, *J. Chem. Soc., Chem. Commun.*, 1993, 1505.
- C. D. Hall and T.-K.-U. Truong, *J. Organomet. Chem.*, 1996, **519**, 185.
- C. D. Hall, T.-K.-U. Truong and S. C. Nyburg, *J. Organomet. Chem.*, 1997, in press.
- J.-C. Rodriguez-Ubis, B. Alpha, D. Plancherel and J.-M. Lehn, *Helv. Chim. Acta*, 1984, **67**, 2264.
- E. C. Constable, *Nature*, 1994, **367**, 415.
- T. W. Bell and H. Jouselin, *Nature*, 1994, **367**, 441.
- J. K. Judice, S. J. Keipert and D. J. Cram, *J. Chem. Soc., Chem. Commun.*, 1993, 1323.
- L. Echegoyen, A. DeCian, J. Fischer and J.-M. Lehn, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 838.
- V. McKee, M. R. J. Dorrity, J. F. Malone, D. Marrs and J. Nelson, *J. Chem. Soc., Chem. Commun.*, 1992, 383.
- Z. Otwinowski and W. Minor, *Methods Enzymol.*, 1996, **276**, ed. C. W. Carter and R. M. Sweet.
- G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
- G. M. Sheldrick, SHELXL-93, University of Göttingen, 1993.

Received in Cambridge, UK, 11th July 1997; 7/04975G