Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Tetrabutylammonium *meso*-octamethylcalix[4]pyrrole fluoride dichloromethane solvate

Salvatore Camiolo,[a] Simon J. Coles,[a]* Philip A. Gale,[a] Michael B. Hursthouse[a] and Jonathan L. Sessler[b]

[a]Department of Chemistry, University of Southampton, Southampton SO17 1BJ, England, and [b]Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712-1167, USA

Correspondence e-mail: s.j.coles@soton.ac.uk

Received 29 June 2001
Accepted 31 July 2001
Online 10 August 2001

The title compound, $C_{16}H_{36}N^{+}\cdot C_{28}H_{36}N_4\cdot F^{-}\cdot CH_2Cl_2$, is a calix[4]pyrrole macrocycle acting as a fluoride receptor by means of hydrogen bonding. Geometric comparisons with the previously published non-isostructural chloride-bound analogue are presented.

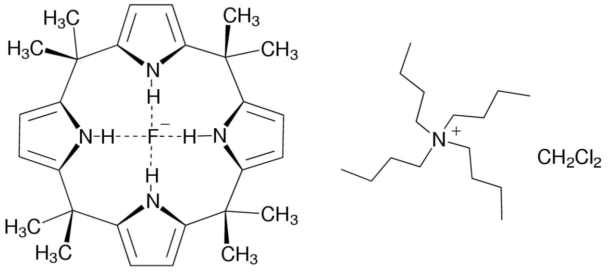
Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.006 Å
Disorder in solvent or counterion
R factor = 0.074
wR factor = 0.216
Data-to-parameter ratio = 9.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The anion complexation properties of the calix[4]pyrrole family of macrocycles (Sessler & Gale, 2000) has been an area of continuing interest since the first paper describing anion complexation in these systems was published in 1996 (Gale *et al.*, 1996). In this paper, we present the crystal structure of the fluoride complex, (I), of *meso*-octamethylcalix[4]pyrrole, a macrocycle regarded as the ‘parent’ of this class of receptor due to its original synthesis by Baeyer in 1886 from acetone and pyrrole (Baeyer, 1886). This structure is of particular interest as calix[4]pyrroles are selective receptors for fluoride.



(I)

The structure of the title compound, (I), is *meso*-octamethyl-substituted calix[4]pyrrole coordinated to a fluoride anion, the charge of which is balanced by a tetrabutylammonium (TBA) cation, crystallizing with a dichloromethane (DCM) solvent [Fig. 1 (top) shows the disordered TBA in its major component, whilst Fig. 1 (bottom) depicts the minor conformation]. For clarity, Fig. 2 depicts solely the macrocycle–anion complex. The crystal structure of the TBA chloride complex of (I) was published in 1996 (Gale *et al.*, 1996) (CSD refcode TEQKIJ; Allen & Kennard, 1993), but is not isostructural, as one might expect, with the structure reported herein. The structure of (I) therefore allows a comparison of the effects of chloride and fluoride binding to the parent macrocycle.

The macrocycle adopts a cone conformation in order to allow all four NH protons to hydrogen bond to the fluoride anion (Fig. 2). The average N···F separation is 2.767 (7) Å

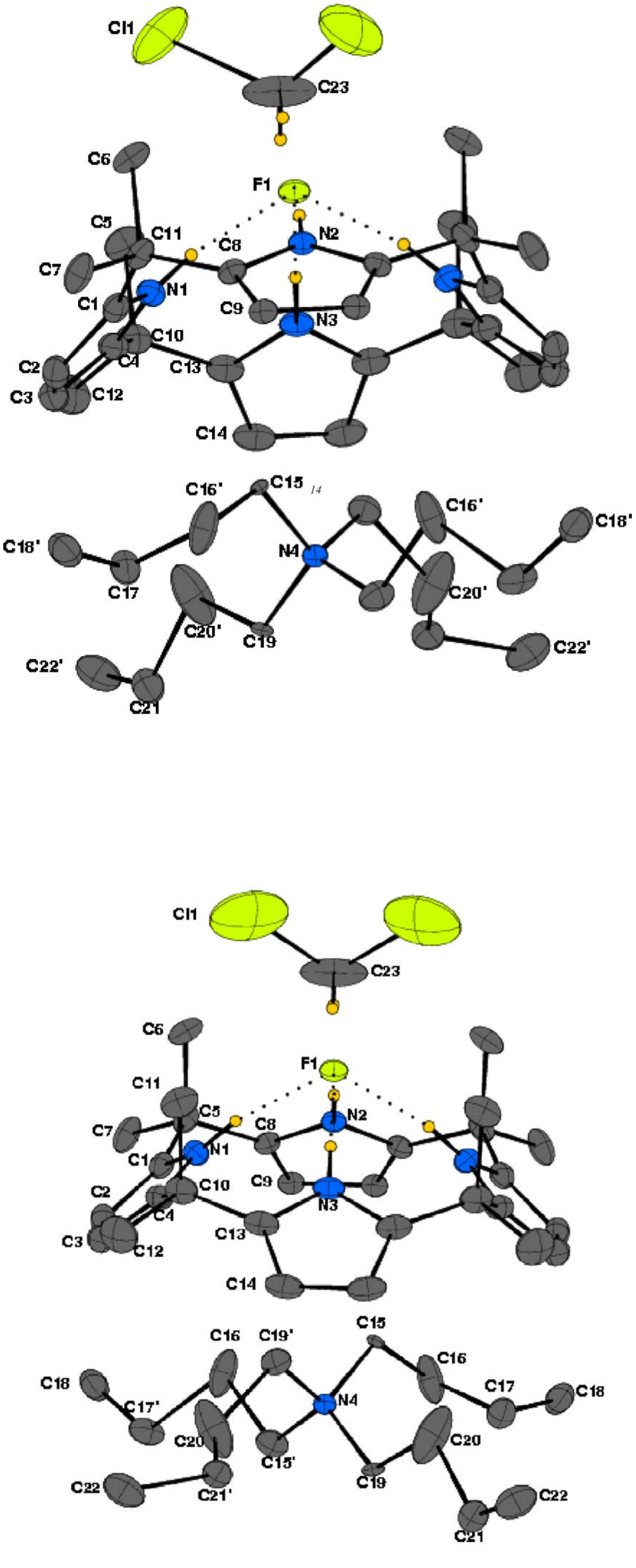


Figure 1
View of (I) (50% probability displacement ellipsoids), showing the disordered TBA in the major component (top) and the minor component (bottom).

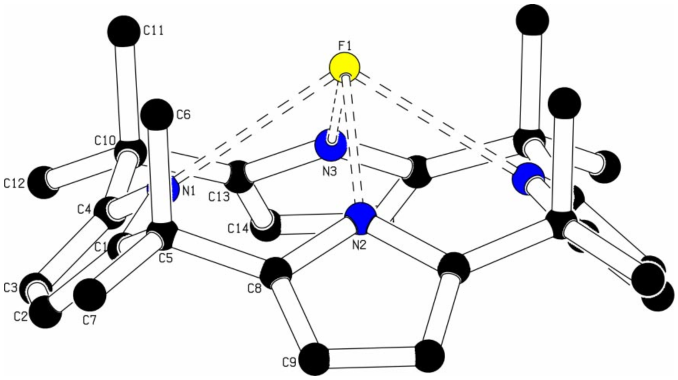


Figure 2
The *meso*-octamethylcalix[4]pyrrole complex with fluoride.

[3.303 (5) Å] and the average H···F interaction distance is 1.905 (7) Å [2.404 (6) Å], values in square brackets indicating the equivalent value for the chloride complex. The N···N cross-ring separations are N1···N1^{i} = 4.688 (3) Å [4.723 (4) Å] and N2···N3 = 4.688 (3) Å [4.682 (5) Å] [symmetry code: (i) $-x + 1$, y, z], whilst the cavity formed by the *meso*-C atoms is an average of 5.043 Å in length [5.07 Å] and 7.132 Å diagonally [7.169 Å]. These geometric parameters demonstrate a slight contraction of the fluoride-bound macrocycle with respect to that of the chloride complex. The *meso*-C atoms deviate from planarity with an average r.m.s. deviation from the plane of −0.2162 Å [−0.202 Å]. The dihedral angles formed between this plane and the pyrrole rings are 41.57 (5), 44.25 (5) and 40.03 (6)° [45.28 (6), 45.56 (7), 46.18 (5) and 41.05 (6)°] for the N1, N2 and N3 rings, respectively. The average dihedral angle between these planes is smaller for the fluoride *versus* the chloride complex, reflecting the smaller radius of F$^-$ and hence the need for the pyrrole rings to be less angled with respect to the macrocycle. An average angle of 109.47 (3)° on both unique *meso*-C atoms (C5 and C10) indicates ideal tetrahedral geometry and hence absence of any strain imposed on the macrocycle due to coordination to the anion.

Experimental

Compound (I) was synthesized according to literature methods (Gale *et al.*, 1996). Crystals of the tetrabutylammonium fluoride complex of (I) were obtained by slow evaporation of a dichloromethane solution of (I) in the presence of excess tetrabutylammonium fluoride.

Crystal data

$C_{16}H_{36}N^+\cdot C_{28}H_{36}N_4\cdot F^-\cdot CH_2Cl_2$
$M_r = 764.91$
Orthorhombic, $Pmn2_1$
$a = 19.846$ (4) Å
$b = 10.653$ (2) Å
$c = 10.469$ (2) Å
$V = 2213.3$ (8) Å^3
$Z = 2$
$D_x = 1.148$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 45620 reflections
$\theta = 2.9$–27.5°
$\mu = 0.19$ mm^{-1}
$T = 100$ (2) K
Block, colourless
0.18 × 0.16 × 0.16 mm

Acta Cryst. (2001). E**57**, o816–o818 Salvatore Camiolo *et al.* • $C_{16}H_{36}N^+\cdot C_{28}H_{36}N_4\cdot F^-\cdot CH_2Cl_2$ **o817**

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans to fill Ewald sphere
Absorption correction: multi-scan (*SORTAV*; Blessing, 1997)
$T_{\min} = 0.967$, $T_{\max} = 0.971$
5325 measured reflections
2739 independent reflections
2396 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.020$
$\theta_{\max} = 27.5°$
$h = -25 \rightarrow 25$
$k = -13 \rightarrow 0$
$l = 0 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.074$
$wR(F^2) = 0.216$
$S = 1.09$
2739 reflections
291 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1422P)^2 + 0.5073P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.054$
$\Delta\rho_{\max} = 0.69$ e Å^{-3}
$\Delta\rho_{\min} = -0.73$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.023 (10)
Absolute structure: Flack (1983)
Flack parameter = 0.0 (3)

Disorder was found to be present in the TBA cation. The butyl arms of the TBA exhibit conformational disorder in the 1 and 3 positions with the major component 60% occupied.

Cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1990) and *CAMERON* (Watkin *et al.*, 1993).

The authors thank EPSRC for funding of crystallographic facilities and for a project studentship (SC). PAG thanks the Royal Society for a University Research Fellowship.

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 1, 31–37.
Baeyer, A. (1886). *Ber. Dtsch Chem. Ges.* **19**, 2184–2196.
Blessing, R. H. (1997). *J. Appl. Cryst.* **30**, 421–429.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Gale, P. A., Sessler, J. L., Král, V. & Lynch, V. (1996). *J. Am. Chem. Soc.* **118**, 5140–5141.
Hooft, R. (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods Enzymol.* **276**, 307–326.
Sessler, J. L. & Gale, P. A. (2000). *The Porphyrin Handbook*, Vol. 6, edited by K. M. Kadish, K. M. Smith & R. Guilard, pp. 257–278. Burlington, MA, and San Diego, CA: Academic Press.
Sheldrick, G. M. (1997). *SHELXL*97 and *SHELXS*97. University of Göttingen, Germany.
Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.
Watkin, D. M., Pearce, L. & Prout, C. K. (1993). *CAMERON*. Chemical Crystallography Laboratory, University of Oxford, England.

o818 Salvatore Camiolo *et al.* • $C_{16}H_{36}N^+ \cdot C_{28}H_{36}N_4 \cdot F^- \cdot CH_2Cl_2$ *Acta Cryst.* (2001). E**57**, o816–o818