Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

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Gareth W. Bates[a]; Philip A. Gale[a]; Mark E. Light[a]
[a] School of Chemistry, University of Southampton, Southampton, SO17 1BJ, UK

To cite this Article Bates, Gareth W. , Gale, Philip A. and Light, Mark E.(2008) 'Interactions of Organic Halide and Nitrate Salts with *meso*-Octamethylcalix[4]pyrrole', Supramolecular Chemistry, 20: 1, 23 — 28
To link to this Article: DOI: 10.1080/10610270601089378
URL: http://dx.doi.org/10.1080/10610270601089378

Supramolecular Chemistry, January–March 2008 Vol. 20 (1–2), pp. 23–28

Interactions of Organic Halide and Nitrate Salts with *meso*-Octamethylcalix[4]pyrrole

GARETH W. BATES, PHILIP A. GALE* and MARK E. LIGHT

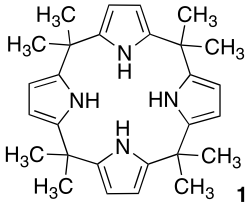
School of Chemistry, University of Southampton, Southampton, SO17 1BJ, UK

(Received 19 September 2006; Accepted 27 October 2006)

Proton NMR titrations have been performed with *meso*-octamethylcalix[4]pyrrole and a variety of organic chloride and bromide salts in dichloromethane-d_2. The results show apparently increasing chloride stability constants within each set of anion salts (tetrabutylammonium <imidazolium<pyridinium). Addition of 1-ethyl-3-methylimidaolium (EMIM) nitrate to dichloromethane-d_2 solutions of calix[4]pyrrole caused significantly larger downfield shifts of the pyrrole NH protons of calix[4]-pyrrole than addition of equimolar quantities of tetrabutylammonium nitrate. The first crystal structure of a nitrate complex of a calix[4]pyrrole is also presented.

Keywords: Anion receptors; Pyrrole; Crystallography

The discovery that *meso*-octamethylcalix[4]pyrrole [1] (**1**) functions as an anion receptor [2] has led on to the synthesis of a variety of calix[4]pyrrole derivatives [3–6], expanded calixpyrroles [7–11], strapped calixpyrroles [12,13] and N-confused calixpyrroles [14,15] which show varying degrees of anion affinity. Our discovery with the Sessler and Moyer groups that calixpyrrole can function as an ion-pair receptor in the solid-state with large charge diffuse cations such as caesium or imidazolium sitting in the anion-induced calixpyrrole cup [16] has shed light on some anomalies in the measurement of the anion stability constants with the parent macrocycle with a redetermination of the chloride affinity of the macrocycle in a variety of solvents and with a range of tetraalkylammonium and tetralkylphosphonium salts showing very significant counter cation and solvent effects [17]. We have also recently shown that N-confused calix[4]pyrrole can include 1,3-dialkylimidazolium cations in its anion-induced cup shape cavity [18] and have extended the solid-state studies on the parent macrocycle to show that N-ethylpyridinium cations can also be included in the cup [19]. In this short paper we report the results of ^{1}H NMR titrations in dichloromethane-d$_2$ solution. The results show that changing the nature of the cation has a dramatic effect on the observed stability constant of the macrocycle with chloride and bromide.



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Compound **1** was synthesised as reported previously [2]. Proton NMR titrations were conducted in dichloromethane-d_2 and stability constants obtained using the EQNMR computer program [20]. The apparent chloride and bromide stability constants are shown in Tables I and II respectively. Titrations were performed with 1-ethyl-3-methylimidazolium (EMIM) chloride and bromide, 1-butyl-3-methylimidazolium (BMIM) chloride and bromide and *N*-ethylpyridinium (EtPy) chloride and bromide. The results are compared to literature values for tetrabutylammonium (TBA) chloride and bromide stability constants obtained under similar conditions. The results show that in both cases the stability constants increase for a given anion in the order tetrabutylammonium < 1-ethyl-3-methylimidazolium < 1-butyl-3-methylimidazolium < N-ethylpyridinium (Tables I and II). This is illustrated in Fig. 1 that shows the NMR titration curves for the four salts

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*Corresponding author. E-mail: philip.gale@soton.ac.uk

ISSN 1061-0278 print/ISSN 1029-0478 online
DOI: 10.1080/10610270601089378

TABLE I Titration data of calix[4]pyrrole with various organic chloride salts.[a]

Organic Salt	Association Constant K_a (M^{-1})
TBACl	430[b]
EMIMCl	2240
BMIMCl	5960
EtPyCl	$>10^4$

[a] Titrations conducted at 300K in dichloromethane-d_2. Errors estimated to be <15%. [b] data from ref 8 (conducted at 295K)

TABLE II Titration data of calix[4]pyrrole with various organic bromide salts.[a]

Organic Salt	Association Constant K_a (M^{-1})
TBABr	10
EMIMBr	200
BMIMBr	280
EtPyBr	1180

[a] Titrations conducted at 300K in dichloromethane-d_2. Errors estimated to be <15%.

of bromide. We have previously shown that both imidazolium and pyridinium cations bind to the anion-induced calix[4]pyrrole cup in the solid state in chloride and bromide complexes of **1**. These results illustrate that moving from alkylammonium to aromatic positively charged cations such as imidazolium or pyridinium in solution under the conditions of this experiment results in an increase in the observed stability constants for chloride and bromide. However, when these studies were repeated in DMSO-d_6/0.5% water solution, no significant changes in the anion affinity of the receptor were observed between different salts of the same anion with a stability constant of approximately 1000 M^{-1} observed with chloride and only a weak interaction with bromide at 300 K.

Evidence for the inclusion of the aromatic cations in the calix[4]pyrrole cup in the presence of a coordinating anion in dichloromethane solution is shown in Fig. 2. Tetrafluoroborate is a relative 'innocent' i.e. non-coordinating anion and the spectrum of this salt shows the protons resonances of the hydrogens in the 4- and 5-positions of the imidazolium ring at approximately 7.3 ppm (Fig. 2c) (in the case of the EMIM Cl salt these proton resonances are observed at a similar chemical shift of 7.4 ppm (Fig. 2d)). We would expect a higher degree of ion-pairing in dichloromethane-d_2 solution in the chloride salt than the tetrafluoroborate salt and this may be reflected in the approximately 2 ppm downfield shift of this resonance when going from the BF_4^- to Cl^- salt solution. In the presence of calix[4]pyrrole (spectrum of free ligand shown in Fig. 2a) and one equivalent of EMIM Cl (Fig. 2b) it is interesting to note that the resonances for the hydrogens in the 4- and 5-positions of the imidazolium ring shift upfield by approximately 0.9 ppm and 1.2 ppm whilst the resonance of the hydrogen in the 2-position shifts upfield by approximately 3.2 ppm relative to the EMIM Cl salt alone. We believe this evidence is consistent with inclusion of the imidazolium cation in the anion-induced cavity of the calix[4]pyrrole in solution resulting in shielding of the imidazolium protons and a reduction in imidazolium-chloride ion-pairing. Similar results were observed with the BMIMCl (see [16]) and EtPyCl salts in dichloromethane-d_2 solution. Interestingly, when the same spectra were recorded in DMSO-d_6/0.5% water solution, much less significant shifts were observed, evidence that leads us to suggest that cation inclusion does not occur in this solvent mixture (Fig. 3).

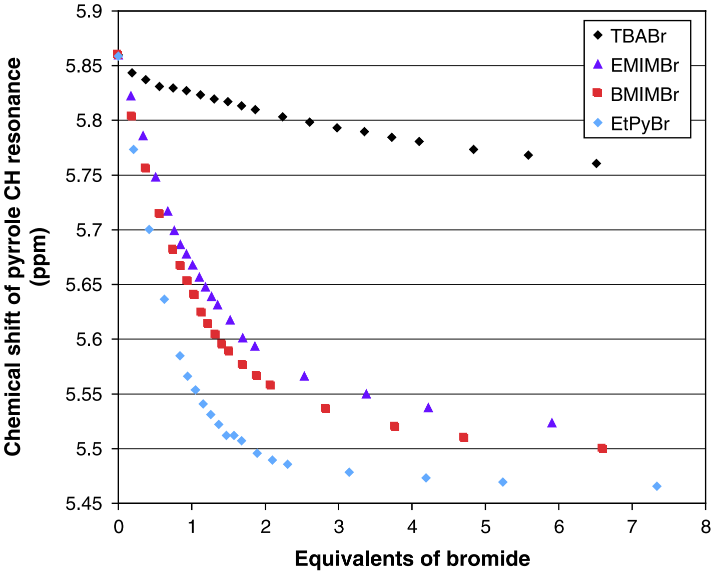

FIGURE 1 Proton NMR titration curves for the addition of tetrabutylammonium, 1-ethyl-3-methylimidazolium, 1-butyl-3-methylimidazolium and N-ethylpyridinium bromide salts in dichloromethane-d_2 following the pyrrole β-CH proton.

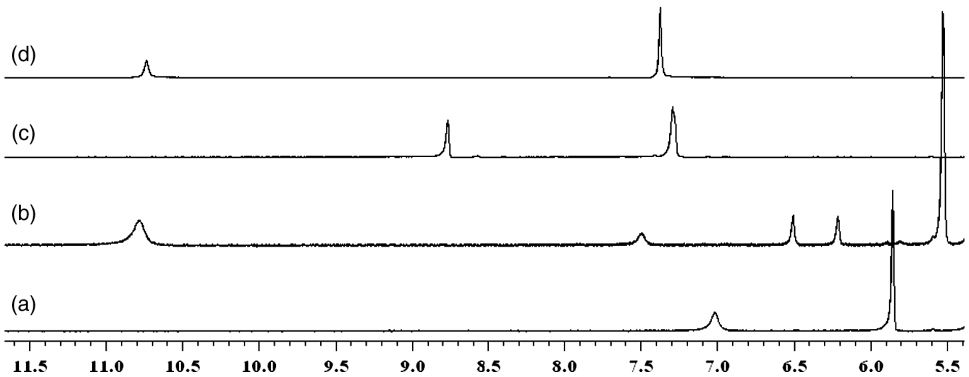

FIGURE 2 Stack plot of the ^{1}H NMR spectra in dichloromethane-d_2 of: a) *meso*-octamethylcalix[4]pyrrole; b) *meso*-octamethylcalix[4]pyrrole +1equiv. 1-ethyl-3-methylimidazolium chloride; c) 1-ethyl-3-methylimidazolium tetrafluoroborate d) 1-ethyl-3-methylimidazolium chloride. Chemical shift shown in ppm.

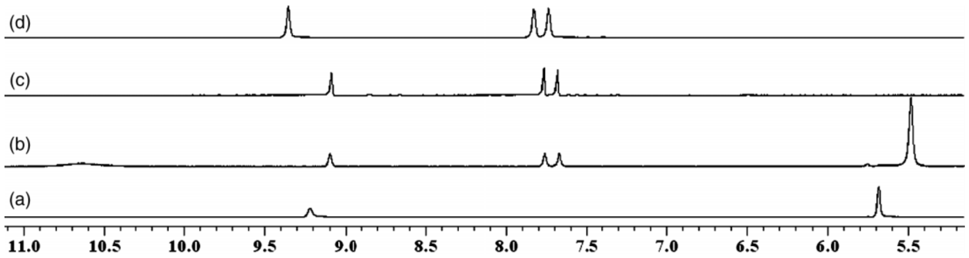

FIGURE 3 Stack plot of the ^{1}H NMR spectra in DMSO-d$_6$/0.5% water: a) *meso*-octamethylcalix[4]pyrrole; b) *meso*-octamethylcalix[4]pyrrole +1equiv. 1-ethyl-3-methylimidazolium chloride; c) 1-ethyl-3-methylimidazolium tetrafluoroborate d) 1-ethyl-3-methylimidazolium chloride. Chemical shift shown in ppm.

Crystals of the EMIM Cl complex of **1** were obtained by slow evaporation of a dichloromethane solution of the macrocycle (see Crystal Data). The structure shows the imidazolium cation in the calixpyrrole cup (Fig. 4), as was observed previously, and sheet formation in the *ab* plane *via* imidazolium CH···anion hydrogen bonds (Fig. 5). The distance from the carbon atoms in the 4- and 5-positions of the

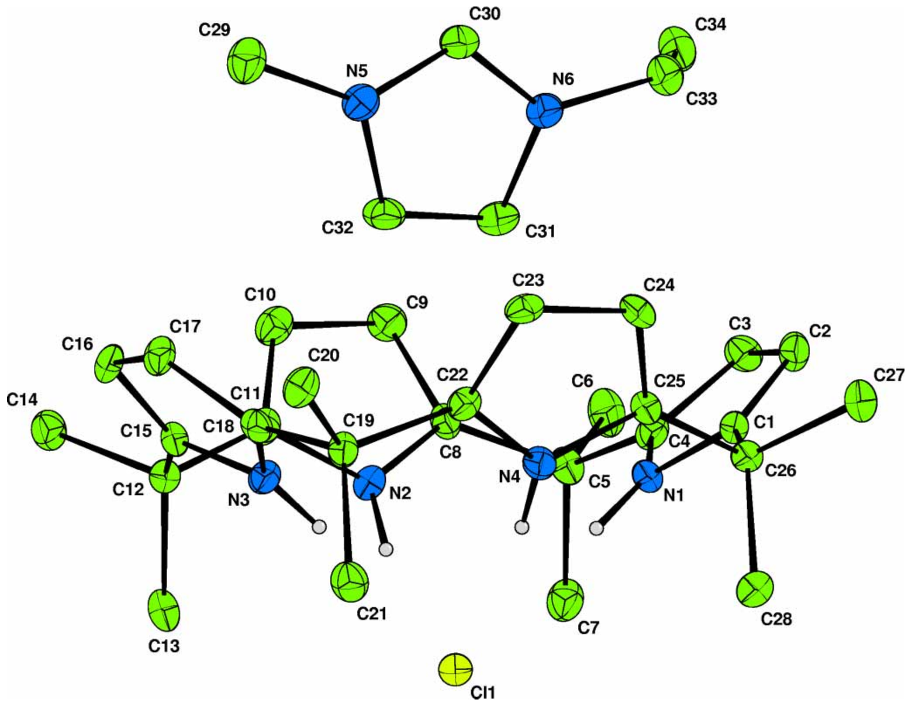

FIGURE 4 The X-ray crystal structure of the EMIM Cl complex of **1**. Thermal ellipsoids are drawn at the 35% probability level. CH hydrogen atoms have been omitted for clarity.

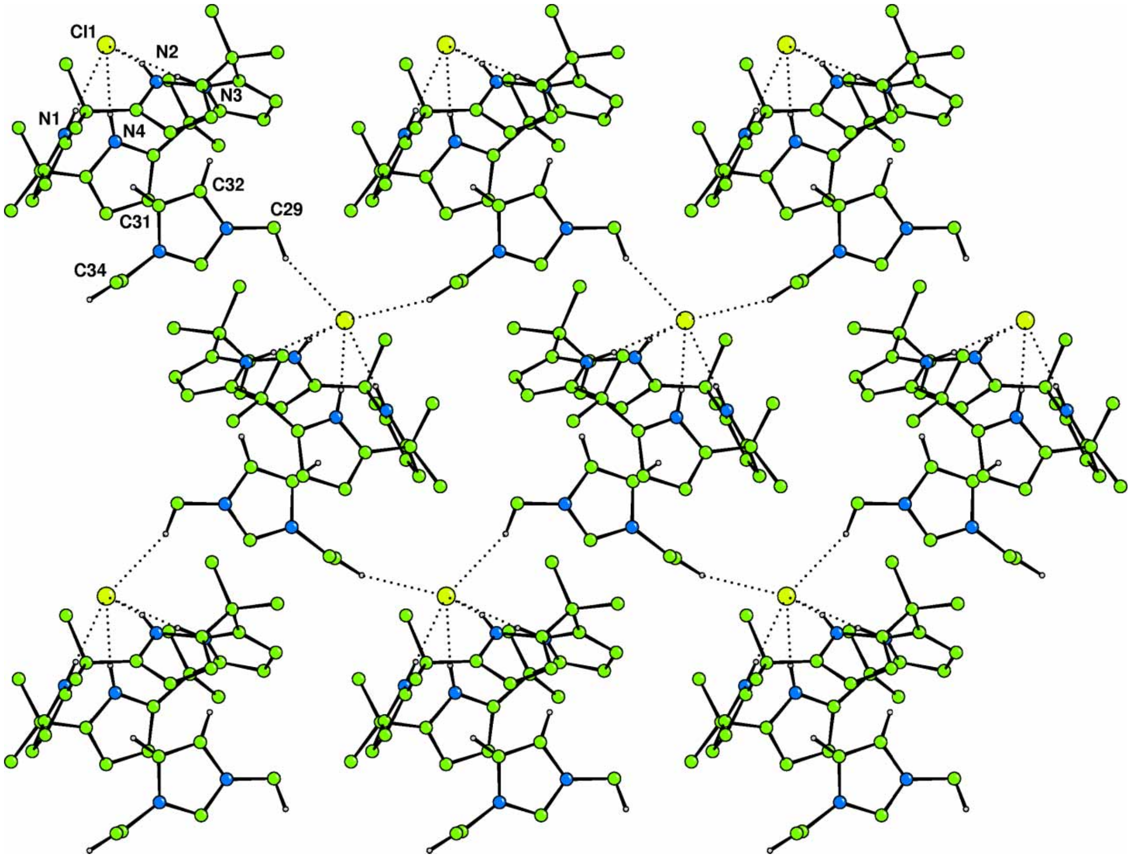

FIGURE 5 Hydrogen-bonded network in the *ab* plane of the EMIM Cl – **1** complex.

imidazolium rings to the centroid of the adjacent pyrrole ring were found to be C32···cent (3.346 Å) and C31···cent (3.513 Å). Other hydrogen bonding distances are shown in Table III.

NMR titration experiments were also conducted with tetrabutylammonium nitrate and 1-ethyl-3-methylimidazolium nitrate in dichloromethane-d_2. The addition of the tetrabutylammonium salt caused only a small continuous shift in the proton resonances in the macrocycle. The data obtained with the EMIM NO_3 titration could not be fitted adequately to a simple binding model (possibly due to a more complex equilibrium in solution involving the formation of higher order complexes in solution with nitrate (c.f. the X-ray crystal structure of the $CsCO_3$ complex of **1** in [16]) and the involvement of the imidazolium cation in the equilibrium in a non-innocent capacity). However it is interesting to note that significant downfield shifts of the NH resonances were observed upon addition of the imidazolium salt. For example upon addition of one equivalent of nitrate salt, the NH resonances would shift downfield by 0.1 ppm in the case of the tetrabutylammonium salt and by 0.8 ppm in the case of the imidazolium salt (under the same conditions the shift with chloride increases from 2.0 ppm with the tetrabutylammonium salt to 3.7 ppm with EMIM Cl and from 0.3 ppm with TBA Br to 1.9 ppm with EMIM Br). Crystals of the dichloromethane solvate of the EMIM NO_3 complex of **1** were obtained by slow evaporation of a dichloromethane solution of the macrocycle in the presence of excess EMIM salt (see Crystal Data). The structure (Fig. 6) shows a single oxygen atom in the nitrate anion (O3) bound to all four of the pyrrole NH groups in the macrocycle (N···O 2.990(12)–3.053(12)Å). The imidazolium cation once again occupies the calixpyrrole cup and is within hydrogen bonding distance of a nitrate ion in an adjacent complex (Fig. 7) with C32···O1 3.388(12)Å and C32···O2 3.398(12)Å (Table IV).

TABLE III Hydrogen bonding interactions [Å and °] in the EMIM Cl – **1** complex.

D—H···*A*	*d*(*D*—H)	*d*(H···*A*)	*d*(*D*···*A*)	⟨(*D*H*A*)
N1—H1···Cl1	0.88	2.41	3.293(6)	179.5
N2—H2A···Cl1	0.88	2.50	3.306(5)	153.2
N3—H3A···Cl1	0.88	2.35	3.231(4)	176.2
N4—H4···Cl1	0.88	2.44	3.300(6)	165.3
C34—H34B···Cl1	0.98	2.81	3.617(5)	140.5
C29—H29A···Cl1	0.98	2.85	3.702(6)	145.9

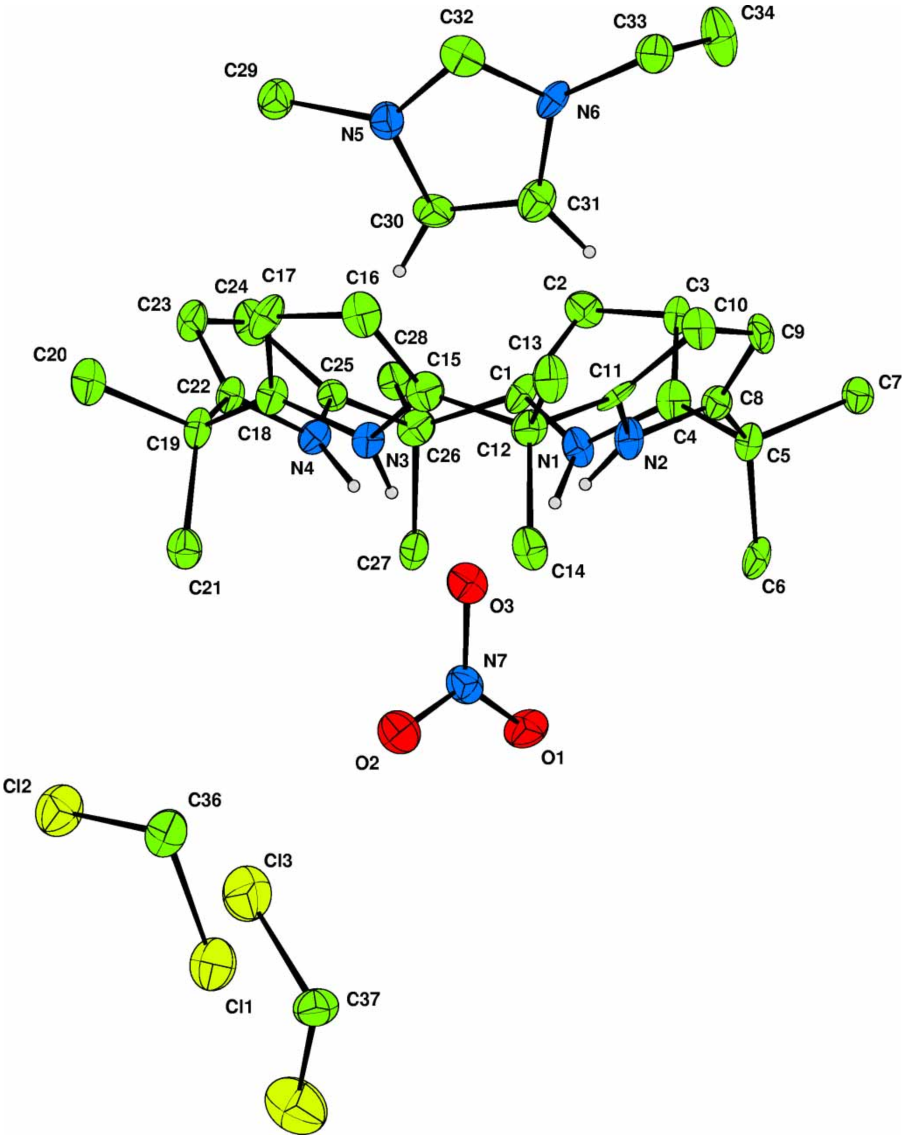

FIGURE 6 The X-ray crystal structure of the EMIM NO_3 complex of **1** (dichloromethane solvate). Thermal ellipsoids drawn at the 30% probability level.

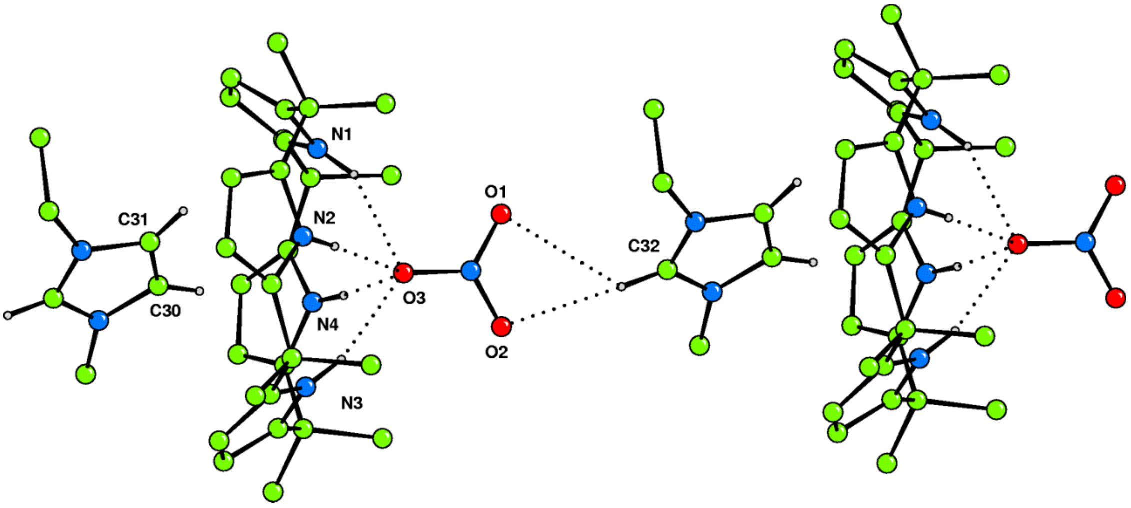

FIGURE 7 Hydrogen bonding in the EMIM NO_3 complex of **1**.

TABLE IV Hydrogen bonds [Å and °].

D—H···*A*	*d*(*D*—H)	*d*(H···*A*)	*d*(*D*···*A*)	⟨(*D*H*A*)
N4—H4···O3	0.88	2.12	2.990(12)	169.9
N1—H1···O3	0.88	2.19	3.004(12)	153.4
N2—H2···O3	0.88	2.18	3.053(12)	173.4
N3—H3···O3	0.88	2.10	2.956(12)	163.7
C32—H32···O1	0.95	2.72	3.388(12)	128.06
C32—H32···O2	0.95	2.45	3.398(12)	176.59

Symmetry transformations used to generate equivalent atoms:
(i) −x,y,−z + 1/2

Previous studies have shown that changing the length of alkyl chain in the counter cation (tetraalkylammonium or tetraalkylphosphonium) has a dramatic effect on the stability constants of chloride with **1** [17]. Here we have shown that imidazolium and pyridinium chloride and bromide salts appear to be bound more strongly by **1** in dichloromethane-d_2 than tetrabutylammonium salts. This is dramatically illustrated in the case of bromide in that the apparent stability constant is two orders of magnitude higher with N-ethylpyridinium than tetrabutylammonium bromide. Similarly, although a stability constant could not be obtained, addition of EMIM nitrate to **1** causes a significantly more pronounced downfield shift of the pyrrole NH protons than addition of tetrabutylammonium nitrate. This evidence, together with shielding of the imidazolium CH protons observed upon addition of calix[4]pyrrole to a solution of the EMIM Cl salt further supports the hypothesis [16] that large charge diffuse cations such as imidazolium and pyridinium are included in the anion-induced calix[4]pyrrole cavity in dichloromethane-d_2 solution (but not in DMSO-d_6/0.5% water).

CRYSTAL DATA FOR EMIM CL AND EMIM NO_3

Crystal data for EMIM Cl: **1** CCDC 621598 $C_{34}H_{47}N_6Cl$, Mr = 575.23, T = 120(2) K, monoclinic, space group $P2_1/c$, $a = 10.587(7)$, $b = 16.49(4)$, $c = 18.55(2)$Å, $\beta = 105.87(9)°$, $V = 3116(8)$Å^3, $\rho_{calc} = 1.226$ g cm^{-3}, $\mu = 0.156$ mm^{-1}, Z = 4, reflections collected: 25395, independent reflections: 5482 ($R_{int} = 0.1335$), final R indices [$I > 2\sigma I$]: $R1 = 0.0747$, $wR2 = 0.1320$, R indices (all data): $R1 = 0.1494$. $wR2 = 0.1561$.

Crystal data for EMIM NO_3: **1** CCDC 621599 (The crystals were poor quality and produced a reduced quality refinement) $C_{35.5}H_{50}N_7Cl_3O_3$, Mr = 729.17, T = 120(2) K, monoclinic, space group $C2/c$, $a = 43.504(9)$, $b = 14.730(7)$, $c = 11.894(2)$Å, $\beta = 101.66(3)°$, $V = 7465(3)$Å^3, $\rho_{calc} = 1.298$ g cm^{-3}, $\mu = 0.29$ mm^{-1}, Z = 8, reflections collected: 21083, independent reflections: 6274 ($R_{int} = 0.1755$), final R indices [$I > 2\sigma I$]: $R1 = 0.1650$, $wR2 = 0.3889$, R indices (all data): $R1 = 0.2849$. $wR2 = 0.4468$.

Acknowledgements

We would like to thank the EPSRC and Crystal Faraday for a studentship (GWB) and the EPSRC together with Professor Mike Hursthouse for access to the crystallographic facilities at the University of Southampton.

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