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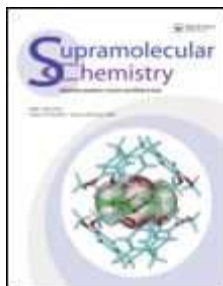
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Interactions of organic halide and nitrate salts with *meso*-octamethylcalix[4]pyrrole

Gareth W. Bates, Philip A. Gale* and Mark E. Light

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

philip.gale@soton.ac.uk

Abstract

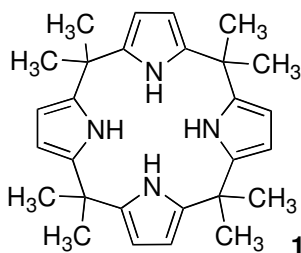
Proton NMR titrations have been performed with *meso*-octacalix[4]pyrrole and a variety of organic chloride and bromide salts in dichloromethane-*d*₂. The results show apparently increasing chloride stability constants within each set of anion salts (tetrabutylammonium < imidazolium < pyridinium). Addition of 1-ethyl-3-methylimidazolium (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]pyrrole¹ (**1**) functions as an anion receptor² has led on to the synthesis of a variety of calix[4]pyrrole derivatives,³ expanded calixpyrroles,⁴ strapped calixpyrroles⁵ and *N*-confused calixpyrroles⁶ 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 cup⁷ 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.⁸ We have also recently shown that *N*-confused

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4 calix[4]pyrrole can include 1,3-dialkylimidazolium cations in its anion-induced cup
5 shape cavity⁹ and have extended the solid-state studies on the parent macrocycle to
6 show that N-ethylpyridinium cations can also be included in the cup.¹⁰ In this short
7 paper we report the results of ¹H NMR titrations in dichloromethane-d₂ solution. The
8 results show that changing the nature of the cation has a dramatic effect on the
9 observed stability constant of the macrocycle with chloride and bromide.
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27 Compound **1** was synthesised as reported previously.² Proton NMR titrations were
28 conducted in dichloromethane-*d*₂ and stability constants obtained using the EQNMR
29 computer program.¹¹ The apparent chloride and bromide stability constants are shown
30 in Tables 1 and 2 respectively. Titrations were performed with 1-ethyl-3-
31 methylimidazolium (EMIM) chloride and bromide, 1-butyl-3-methylimidazolium
32 (BMIM) chloride and bromide and *N*-ethylpyridinium (EtPy) chloride and bromide.
33 The results are compared to literature values for tetrabutylammonium (TBA) chloride
34 and bromide stability constants obtained under similar conditions. The results show
35 that in both cases the stability constants increase for a given anion in the order
36 tetrabutylammonium < 1-ethyl-3-methylimidazolium < 1-butyl-3-methylimidazolium
37 < *N*-ethylpyridinium (Tables 1 and 2). This is illustrated in Figure 1 that shows the
38 NMR titration curves for the four salts of bromide. We have previously shown that
39 both imidazolium and pyridinium cations bind to the anion-induced calix[4]pyrrole
40 cup in the solid state in chloride and bromide complexes of **1**. These results illustrate
41 that moving from alkylammonium to aromatic positively charged cations such as
42 imidazolium or pyridinium in solution under the conditions of this experiment results
43 in an increase in the observed stability constants for chloride and bromide. However,
44 when these studies were repeated in DMSO-*d*₆/0.5% water solution, no significant
45 changes in the anion affinity of the receptor were observed between different salts of
46 the same anion with a stability constant of approximately 1000M⁻¹ observed with
47 chloride and only a weak interaction with bromide at 300K.
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Table 1: 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	$> 10^4$

^aTitration conducted at 300K in dichloromethane- d_2 . Errors estimated to be $< 15\%$. ^b data from ref 8 (conducted at 295K)

Table 2: 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

^aTitration conducted at 300K in dichloromethane- d_2 . Errors estimated to be $< 15\%$.

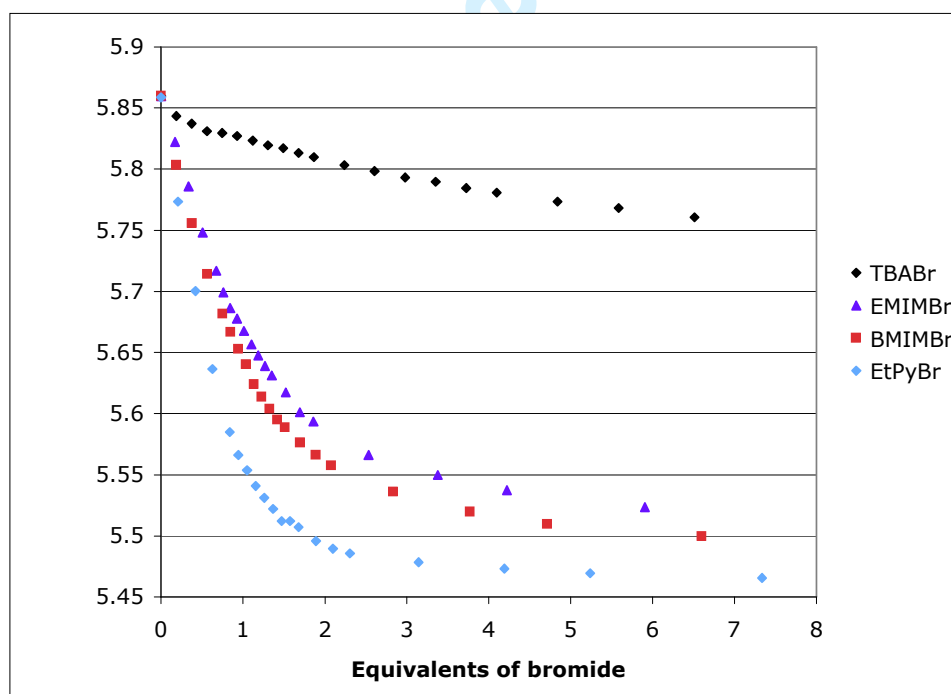


Figure 1 Proton NMR titration curves for the addition of tetrabutylammonium, 1-ethyl-3-methylimidazolium, 1-butyl-3-methylimidazolium and N-ethylpyridinium bromide salts in dichloromethane- d_2 following the pyrrole β -CH proton

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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 Figure 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 (Figure 2c) (in the case of the EMIM Cl salt these proton resonances are observed at a similar chemical shift of 7.4 ppm (Figure 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 Figure 2a) and one equivalent of EMIM Cl (Figure 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 and 1.2ppm whilst the resonance of the hydrogen in the 2-position shifts upfield by approximately 3.2ppm 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 reference 7) 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 (Figure 3).

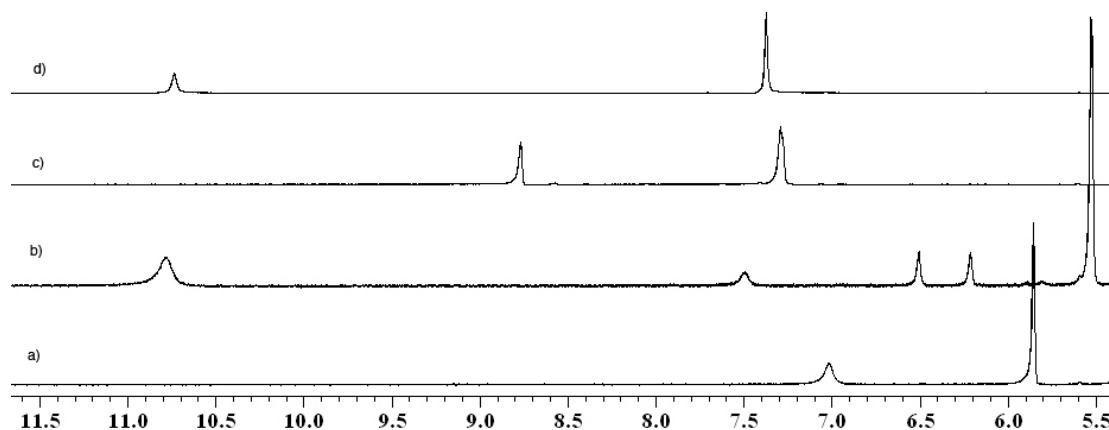


Figure 2: Stack plot of the ^1H NMR spectra in dichloromethane- d_2 of : a) *meso*-octamethylcalix[4]pyrrole; b) *meso*-octamethylcalix[4]pyrrole + 1equiv. 1-ethyl-3-methylimidazolium chloride; c) 1-ethyl-3-methylimidazolium tetrafluoroborate d) 1-ethyl-3-methylimidazolium chloride.

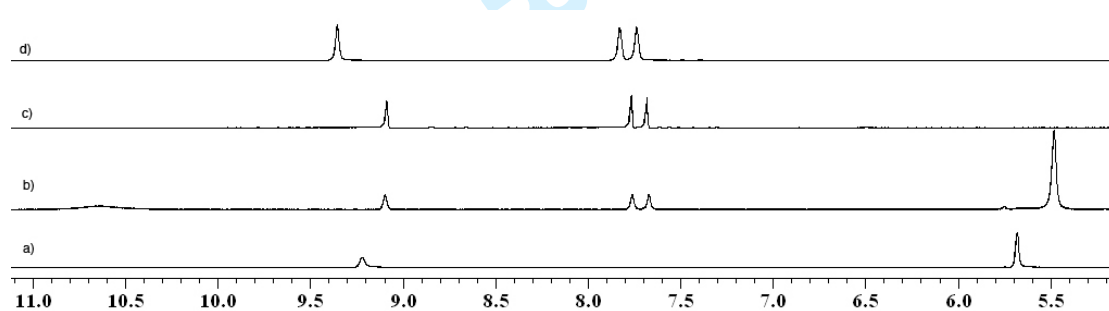


Figure 3 Stack plot of the ^1H NMR spectra in DMSO- d_6 /0.5% water a) *meso*-octamethylcalix[4]pyrrole b) *meso*-octamethylcalix[4]pyrrole + 1equiv. 1-ethyl-3-methylimidazolium chloride c) 1-ethyl-3-methylimidazolium tetrafluoroborate d) 1-ethyl-3-methylimidazolium chloride.

Crystals of the EMIM Cl complex of **1** were obtained by slow evaporation of a dichloromethane solution of the macrocycle. \ddagger The structure shows the imidazolium cation in the calixpyrrole cup (Figure 4), as was observed previously, and sheet formation in the *ab* plane *via* imidazolium $\text{CH}^+\cdots$ anion hydrogen bonds (Figure 5). The distance from the carbon atoms in the 4- and 5-positions of the imidazolium rings to the centroid of the adjacent pyrrole ring were found to be C32 \cdots cent (3.346Å) and C31 \cdots cent (3.513Å). Other hydrogen bonding distances are shown in Table 3.

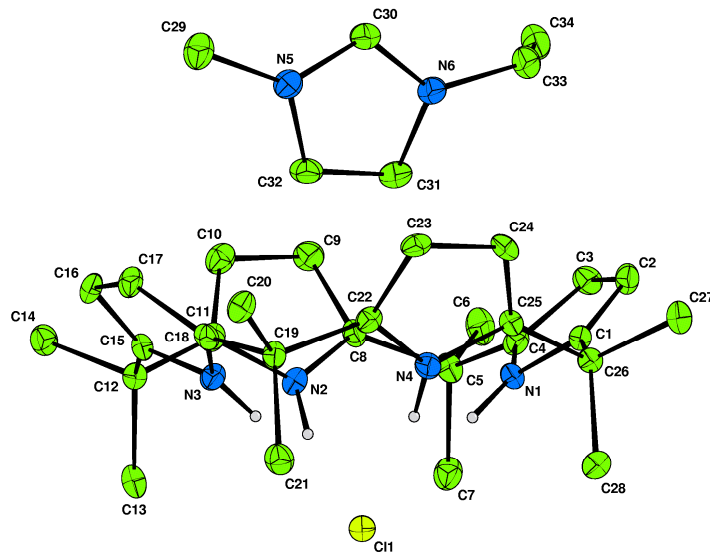


Figure 4 The X-ray crystal structure of the EMIM Cl complex of **1**. Thermal ellipsoids are drawn at the 35% probability level. CH hydrogen atoms have been omitted for clarity.

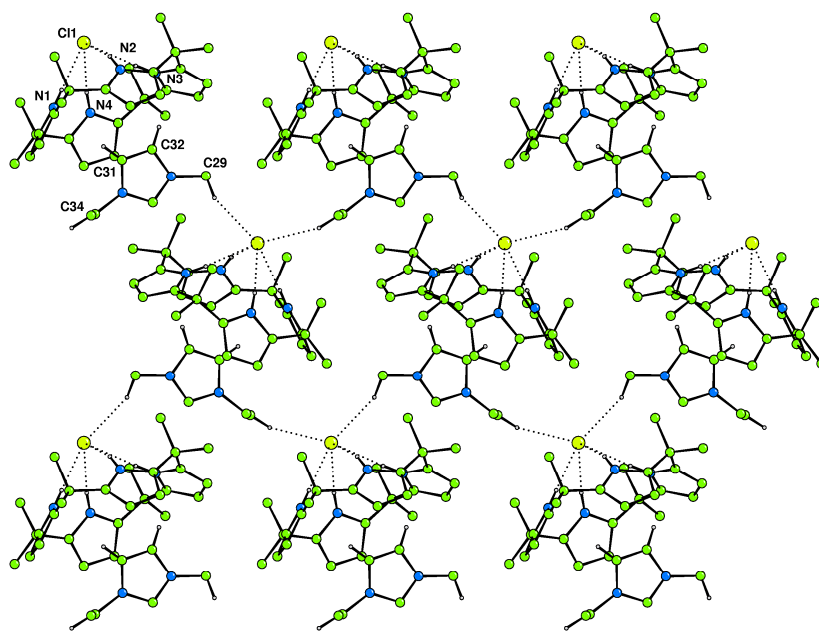


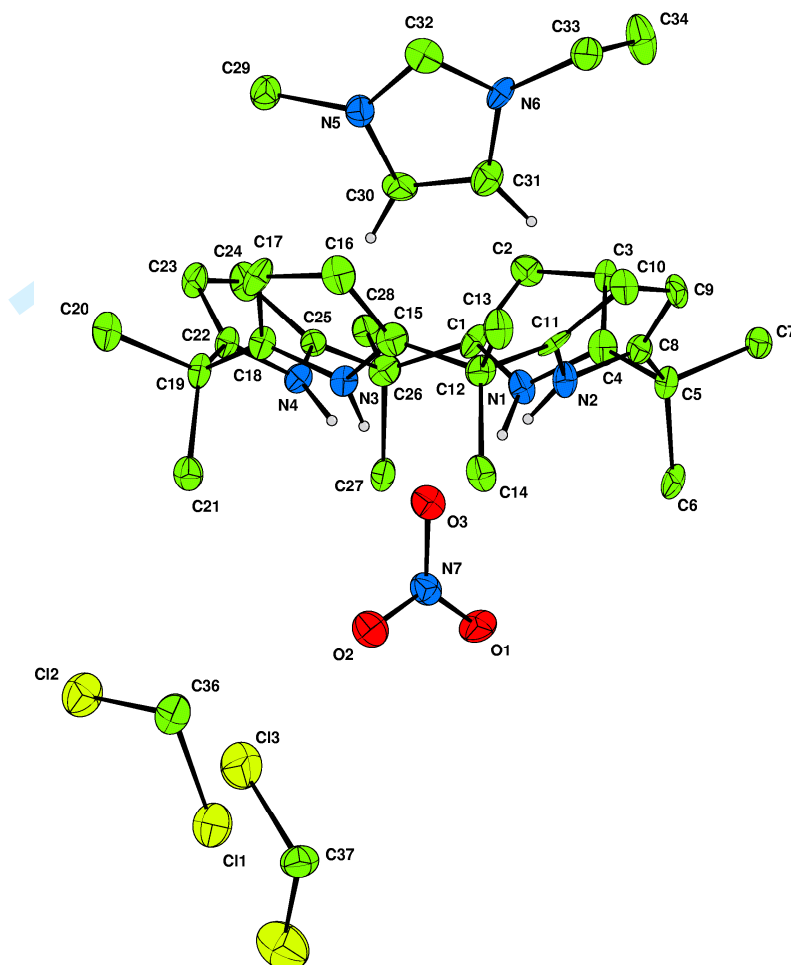
Figure 5 Hydrogen-bonded network in the *ab* plane of the EMIM Cl – **1** complex.

Table 3 Hydrogen bonding interactions [\AA and $^\circ$] in the EMIM Cl – **1** complex.

$D-H\cdots A$	$d(D-H)$	$d(H\cdots A)$	$d(D\cdots A)$	$\angle(DHA)$
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

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 reference 7) 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. § The structure (Figure 6) shows a single oxygen atom in the nitrate anion (O3) bound to all four of the pyrrole NH groups in the macrocycle ($\text{N}\cdots\text{O}$ 2.990(12)–3.053(12) \AA). The imidazolium cation once again occupies the calixpyrrole cup and is

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4 within hydrogen bonding distance of a nitrate ion in an adjacent complex (Figure 7)
5 with $C32 \cdots O1$ 3.388(12)Å and $C32 \cdots O2$ 3.398(12)Å (Table 4).
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40 Figure 6 The X-ray crystal structure of the EMIM NO₃ complex of **1**
41 (dichloromethane solvate). Thermal ellipsoids drawn at the 30% probability level.
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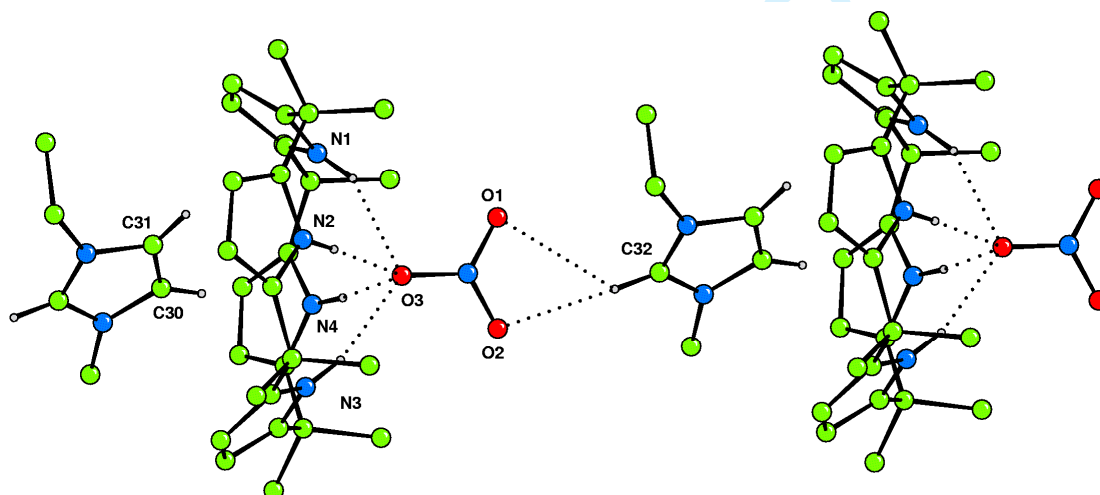


Figure 7 Hydrogen bonding in the EMIM NO₃ complex of **1**.

Table 4 Hydrogen bonds [\AA and $^\circ$].

$D-H\cdots A$	$d(D-H)$	$d(H\cdots A)$	$d(D\cdots A)$	$\angle(DHA)$
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**.⁸ 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 hypothesis⁷ 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)**.

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.

References and Footnotes

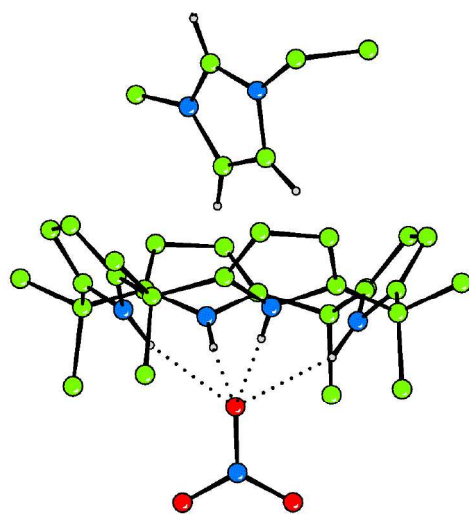
‡ Crystal data for EMIM Cl - **1** CCDC 621598 C₃₄H₄₇N₆Cl, Mr = 575.23, T = 120(2) K, monoclinic, space group *P2₁/c*, *a* = 10.587(7), *b* = 16.49(4), *c* = 18.55(2) Å, β = 105.87(9)°, *V* = 3116(8) Å³, ρ_{calc} = 1.226 g cm⁻³, μ = 0.156 mm⁻¹, *Z* = 4, reflections collected: 25395, independent reflections: 5482 (*R*_{int} = 0.1335), final *R* indices [*I* > 2σ*I*]: *R*1 = 0.0747, *wR*2 = 0.1320, *R* indices (all data): *R*1 = 0.1494. *wR*2 = 0.1561.

§ Crystal data for EMIM NO₃ - **1** CCDC 621599 (The crystals were poor quality and produced a reduced quality refinement) C_{35.5}H₅₀N₇Cl₃O₃, 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, β = 101.66(3)°, *V* = 7465(3) Å³, ρ_{calc} = 1.298 g cm⁻³, μ = 0.29 mm⁻¹, *Z* = 8, reflections collected: 21083, independent reflections: 6274 (*R*_{int} = 0.1755), final *R* indices [*I* > 2σ*I*]: *R*1 = 0.1650, *wR*2 = 0.3889, *R* indices (all data): *R*1 = 0.2849. *wR*2 = 0.4468.

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30 Graphical abstract

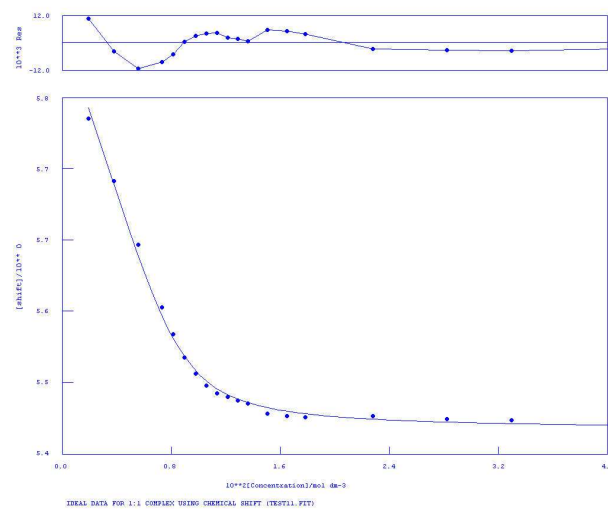
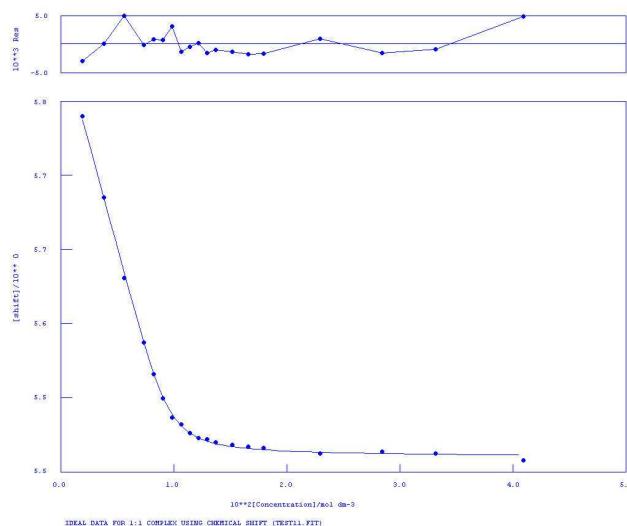


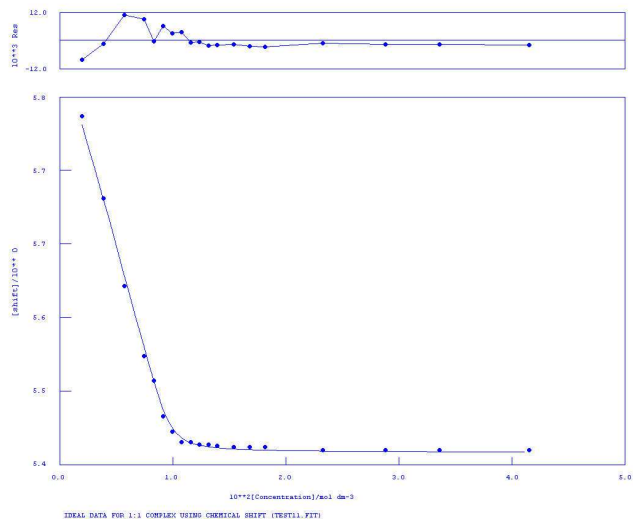
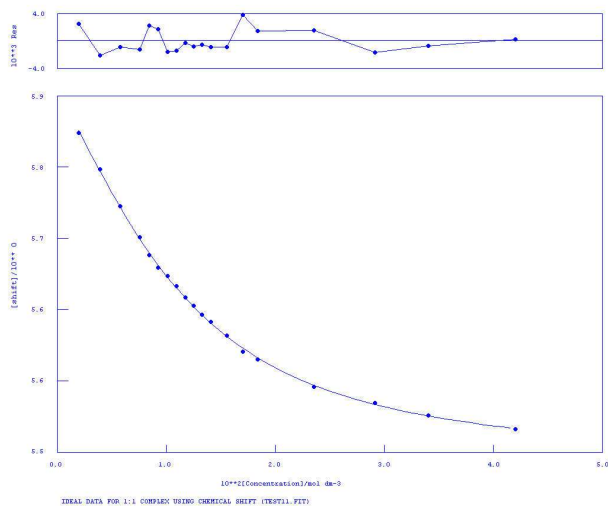
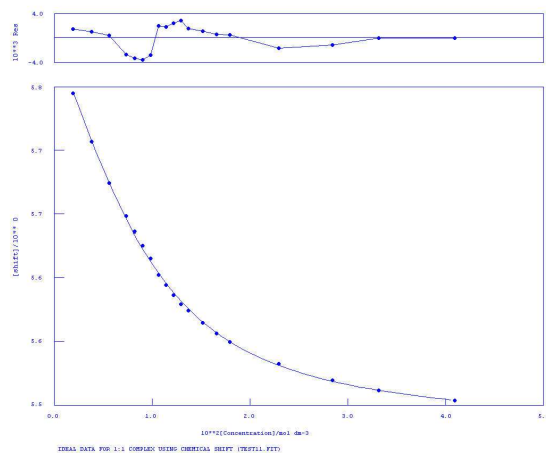
Interactions of organic halide salts with *meso*-octamethylcalix[4]pyrrole

Gareth W. Bates, Philip A. Gale* and Mark E. Light

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

Supplementary Information

Figure S1 EMIM Cl NMR titration in CD₂Cl₂Figure S2 BMIM Cl NMR titration in CD₂Cl₂

Figure S3 EtPy Cl NMR titration in CD_2Cl_2 Figure S4 EMIM Cl NMR titration in CD_2Cl_2 Figure S5 BMIM Br NMR titration in CD_2Cl_2

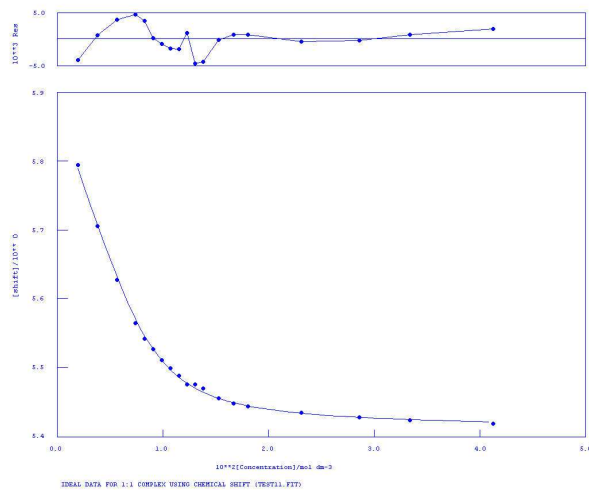


Figure S6 EtPy Br NMR titration in CD_2Cl_2

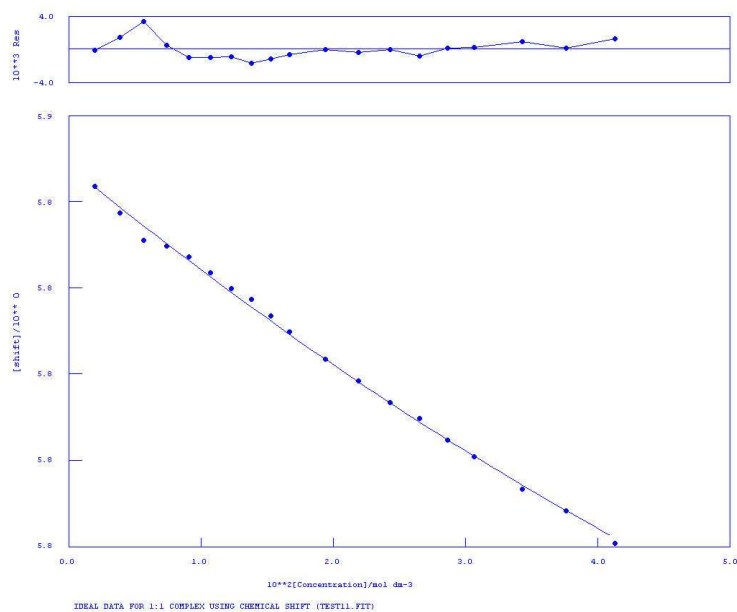
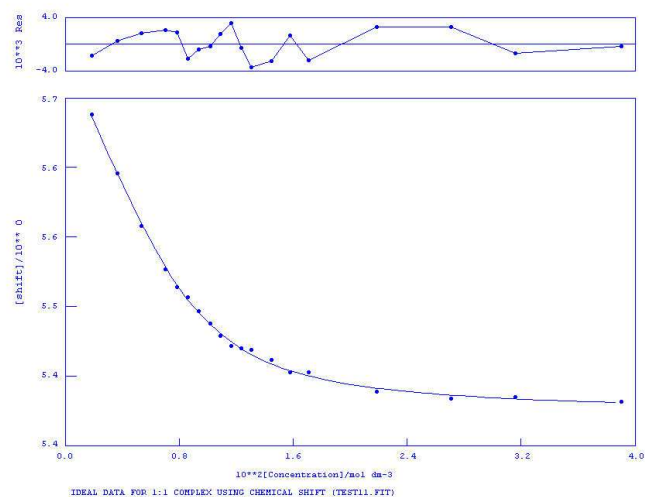
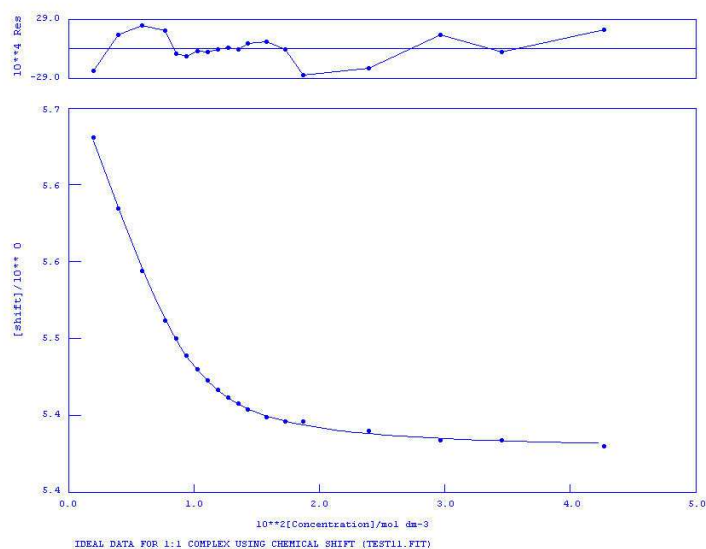
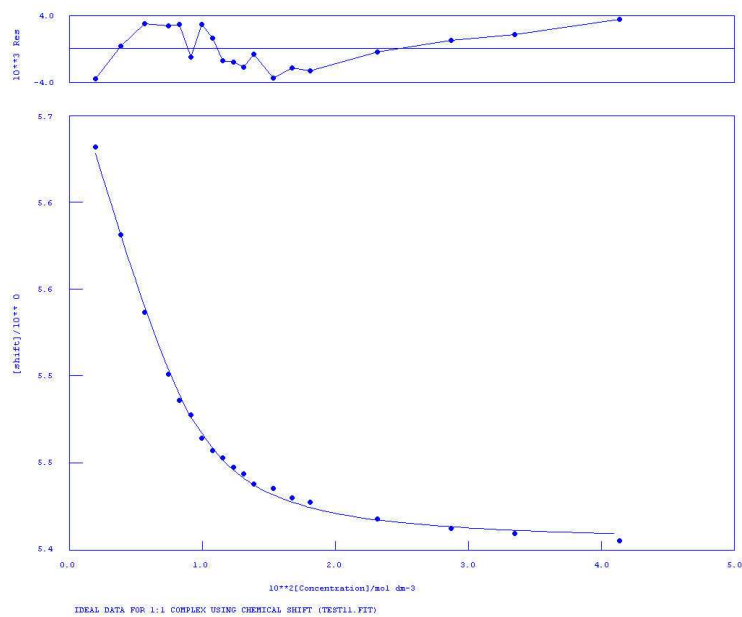
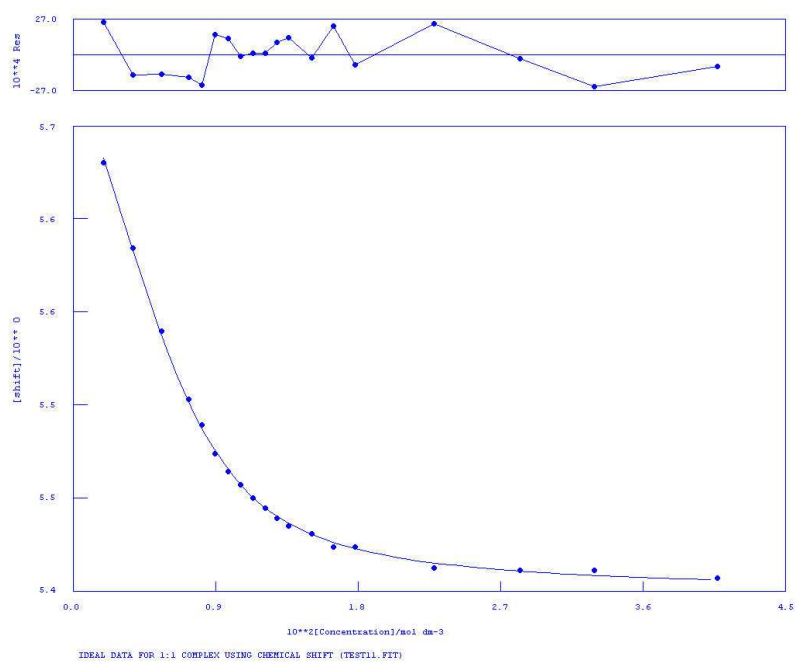
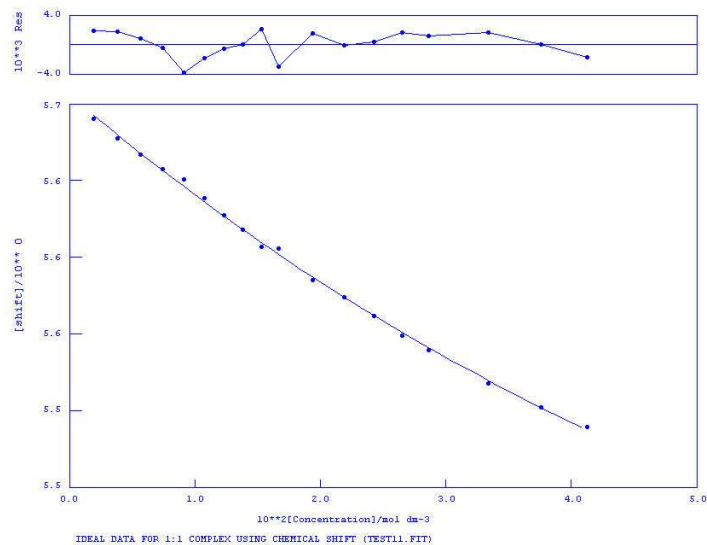
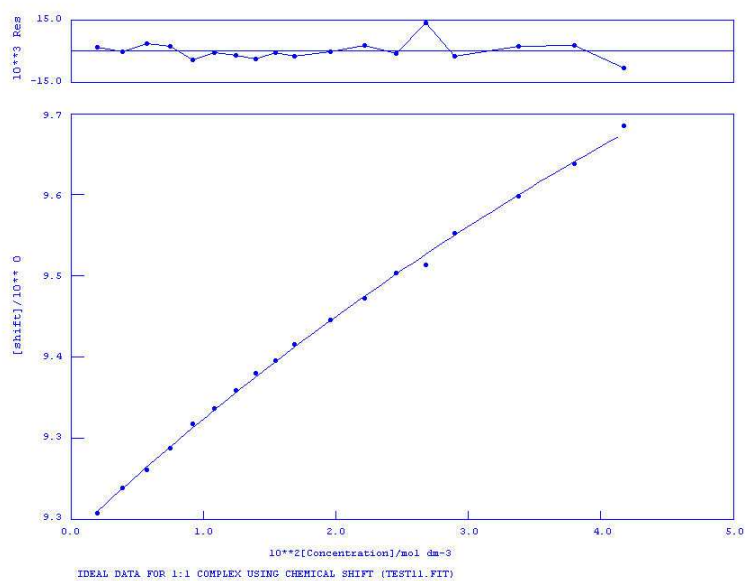


Figure S7 TBA Br titration in CD_2Cl_2

Figure S8 BMIMCl in DMSO-d₆/0.5% waterFigure S9 EMIMCl in DMSO-d₆/0.5% water

Figure S10 EtPyCl in DMSO-d₆/0.5% waterFigure S11 TBA Cl in DMSO-d₆/0.5% water

Figure S12 BMIMBr in DMSO-d₆/0.5% waterFigure S13 EMIMBr in DMSO-d₆/0.5% water

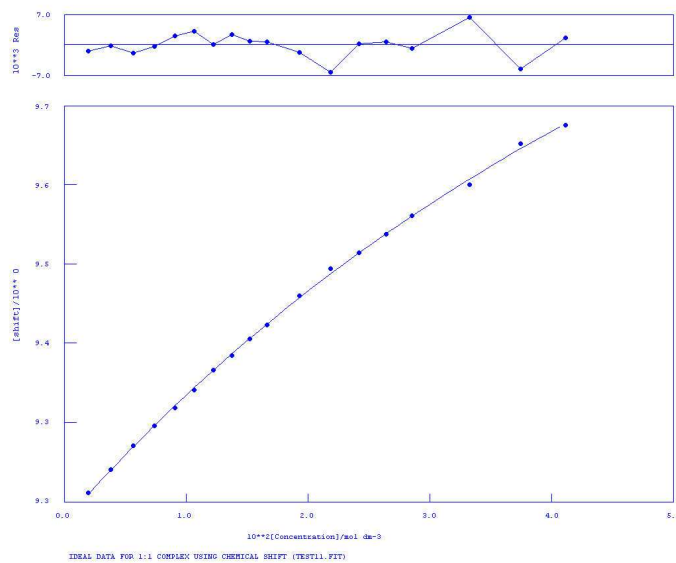


Figure S13 EtPyBr in DMSO-d₆/0.5% water

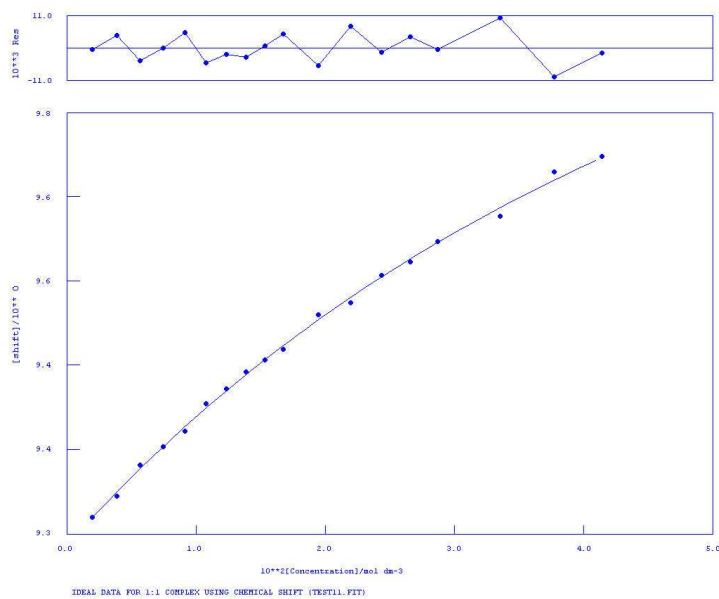


Figure S14 TBABr in DMSO-d₆/0.5% water

Table 1: 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	$> 10^4$

^aTitration conducted at 300K in dichloromethane- d_2 . Errors estimated to be $< 15\%$. ^b data from ref 8 (conducted at 295K)

Table 2: 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

^aTitration conducted at 300K in dichloromethane- d_2 . Errors estimated to be < 15%.

Table 3 Hydrogen bonding interactions [\AA and $^\circ$] in the EMIM Cl – **1** complex.

<i>D</i> –H... <i>A</i>	<i>d</i> (<i>D</i> –H)	<i>d</i> (H... <i>A</i>)	<i>d</i> (<i>D</i> ... <i>A</i>)	\angle (<i>DHA</i>)
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

Table 4 Hydrogen bonds [\AA and $^\circ$] in the EMIM NO_3 complex of **1**.

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

Symmetry transformations used to generate equivalent atoms:

(i) $-x, y, -z+1/2$