Intermediate-spin iron(III) octaethyltetraazaporphyrinates with weakly co-ordinating anions: synthesis, characterization and crystal structure †

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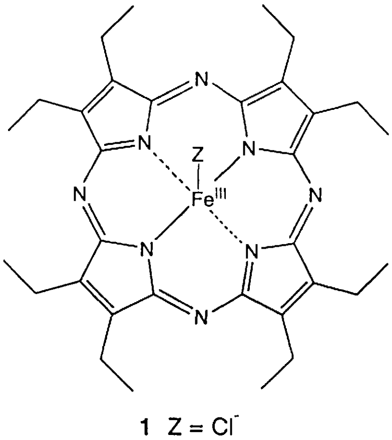
The metathesis reaction of AgZ (Z = ClO_4^-, PF_6^-, SbF_6^- or $CF_3CO_2^-$) with chloroiron(III) 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetraazaporphyrinate chloride, Fe(oetap)Cl, in tetrahydrofuran or toluene gave the Fe(oetap)Z derivatives in approximately 70% yield. The complexes are air-stable solids but decompose in solution to $[Fe(oetap)]_2O$ (Z = ClO_4^- or $CF_3CO_2^-$) or Fe(oetap)F (Z = PF_6^- or SbF_6^-). They have been characterized by variable-temperature magnetic susceptibility measurements and Mössbauer, UV/VIS, IR and ESR spectroscopies. In addition, Fe(oetap)ClO_4 has been structurally characterized by single-crystal X-ray diffraction. All of the complexes are intermediate-spin ($S = \frac{3}{2}$) based on their magnetic properties and Mössbauer and ESR spectra.

The close relationship between metal spin state and metalloporphyrin structure has been investigated extensively.[1] Due to their importance in natural systems, iron porphyrins and related complexes have received particular attention.

Recently, an iron porphyrin analogue, chloroiron(III) 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetraazaporphyrinate, Fe(oetap)Cl **1**, was characterized as intermediate spin ($S = \frac{3}{2}$).[2] This is in sharp contrast to the high-spin ($S = \frac{5}{2}$) ground state observed for the related iron(III) porphyrinate halides.[3] The unusual $S = \frac{3}{2}$ spin state is favoured in d^5 compounds of axial symmetry when structural or electronic factors destabilize the $d_{x^2-y^2}$ orbital to the point where it is unoccupied. Such is believed to be the case for the iron in Fe(oetap)Cl where the small metal-binding 'hole' and the small displacement of the iron atom from the azaporphyrin plane combine to raise the $d_{x^2-y^2}$ orbital energy. Similar destabilization of the $d_{x^2-y^2}$ orbital in five-co-ordinate iron(III) porphyrinates is not observed unless a weakly co-ordinating anion (ClO_4^-, PF_6^-, SbF_6^-, BF_4^- or $B_{11}CH_{12}^-$) is present.[4] Weaker axial ligands result in shorter distances between the iron atom and the porphyrin core which increases the energy of the $d_{x^2-y^2}$ orbital. In these cases, the destabilization of the $d_{x^2-y^2}$ orbital is not enough to prevent its partial occupancy resulting in observation of the Maltempo admixed spin state, which contains contributions from both the intermediate- and high-spin states.[5]

Although the magnetic properties and EPR spectrum of complex **1** supported the $S = \frac{3}{2}$ assignment, the crystal structure showed iron displacement from the macrocycle plane outside the range reported by Scheidt and Reed [1c] for complexes with some intermediate-spin character. In order to distinguish between a simple $S = \frac{3}{2}$ and an admixed, $S = \frac{3}{2}, \frac{5}{2}$, state, the compounds Fe(oetap)Z **2**–**5**, where Z = ClO_4^-, PF_6^-, SbF_6^- or $CF_3CO_2^-$, respectively, were prepared. By analogy to the porphyrin case, weakly co-ordinating anions will stabilize the $S = \frac{3}{2}$ ground state. Comparison of the spectroscopic and magnetic properties of these complexes with those of the chloro complex will confirm or refute the assignment of **1** as a simple $S = \frac{3}{2}$ complex. This and the more general problem of characterizing compounds of unusual spin states has prompted the present investigation of these Fe(oetap)Z derivatives.



1 Z = Cl^-
2 Z = ClO_4^-
3 Z = PF_6^-
4 Z = SbF_6^-
5 Z = $CF_3CO_2^-$

In addition, it may be possible to induce some low-spin ($S = \frac{1}{2}$) character in these complexes. Although complexes of this type generally contain strong-field axial ligands,[6] a low-spin, five-co-ordinate iron(III) porphyrinate bearing a weak axial ligand, the hydrogensulfido ion, has been reported.[7]

Results and Discussion

The compounds were easily synthesized by treating 1 equivalent of AgZ (Z = ClO_4^-, PF_6^-, SbF_6^- or $CF_3CO_2^-$) with Fe(oetap)Cl in dry solvent. Crystallization of the products occurred directly from the reaction medium on concentration or addition of heptane. The presence of the anion, Z, was verified by elemental analysis and infrared spectroscopy. Visible spectra of Fe(oetap)Cl **1**, and the four derivatives, Fe(oetap)Z **2**–**5** (Z = ClO_4^-, PF_6^-, SbF_6^- or $CF_3CO_2^-$),

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† *Non-SI units employed:* $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}, G = 10^{-4} T.

were recorded in toluene, tetrahydrofuran and dichloromethane (Table 1). All complexes exhibit five main bands in the visible region. The spectrum of the trifluoroacetate complex is very similar to that of the chloride derivative and neither spectrum exhibits a strong dependence on solvent. The spectra of the perchlorate, hexafluorophosphate and hexafluoroantimonate complexes are very similar in all three solvents, showing more solvent dependence than either the chloride or trifluoroacetate derivatives. In general, the spectra of the complexes containing the weaker co-ordinating anions show red shifts in the three highest-wavelength bands. In methylene chloride the highest-wavelength band is split into two.

The magnetic susceptibilities of complexes **2**–**5** were measured between 80 and 295 K and analysed in terms of the Curie–Weiss law (Table 1). The room-temperature magnetic moments are in the range of 3.44–4.06 μ_B. A room-temperature magnetic moment of 3.89 μ_B was reported for **1**.[2] These compare to the expected spin-only value for $S = \frac{3}{2}$ of 3.87 μ_B and strongly suggest simple $S = \frac{3}{2}$ spin states for all five complexes.[8] The related complex, Fe(oep)ClO_4 (oep = 2,3,7,8,12,13,17,18-octaethylporphyrinate), which is believed to be an admixed $S = \frac{3}{2}, \frac{5}{2}$ system, has a room-temperature moment of 4.8 μ_B.[4a,b,h] The θ values in Table 1 suggest that there is antiferromagnetic exchange in complexes with axial ligands containing fluorine atoms. The exchange could be a fluorine-mediated interaction or a lattice effect, as was observed for Fe(tpp)($B_{11}CH_{12}$) (tpp = 5,10,15,20-tetraphenylporphyrinate).[4m] Evidence against the latter is the fact that Fe(oetap)ClO_4 crystallizes as 'face-to-face' dimers (see below) and yet shows a small θ value.

The Mössbauer spectra of complexes **2**–**5** were recorded on microcrystalline samples at room temperature (Table 1). All but the hexafluoroantimonate complex resulted in observation of a single doublet with large quadrupole splitting, ΔE_Q. Our failure to observe a spectrum for Fe(oetap)SbF_6 is attributed to the presence of the antimony atom and equipment limitations. While Mössbauer spectra for Fe(tpp)SbF_6 have been reported, these were collected at 77 K or lower, beyond the temperature range of our apparatus.[4g,m] The observed ΔE_Q of 3.36–4.38 mm s^{-1} for **2**–**5** are larger than the 2.98 mm s^{-1} observed for **1**.[2] These splittings compare to the reported values of 3.16 and 3.14 mm s^{-1} for Fe(oep)ClO_4.[4b,h] Although less definitive than the susceptibility data, such large ΔE_Q values are characteristic of intermediate-spin complexes of this type. Smaller quadrupole splittings have been reported for both low-spin ($\Delta E_Q \approx 1.6$–2.3 mm s^{-1}) and high-spin ($\Delta E_Q \approx 0.5$–1.3 mm s^{-1}) iron(III) porphyrinates.[9] The unusually large ΔE_Q of Fe(oetap)ClO_4 may reflect an extremely asymmetric environment for iron in this complex.

The ESR spectra were recorded for complexes **2**–**5** at 8 K as dilute ($\approx 1 \times 10^{-3}$ mol dm^{-3}) solutions in toluene. All four spectra were nearly identical (Table 1). As was the case for Fe(oetap)Cl, very broad spectra (linewidths at half height $\approx$500 G) consistent with axially symmetric complexes were obtained.[2] Values of $g_\perp$, which are known to depend on spin state in complexes of this type,[10] were measured between 3.55 and 4.05 consistent with the $S = \frac{3}{2}$ spin-state assignment in these complexes. A $g_\perp$ of 3.98 was reported for **1**.[2] These are significantly less than the $g_\perp$ of 4.75 reported for Fe(tpp)ClO_4, an $S = \frac{3}{2}, \frac{5}{2}$ mixed-spin-system.[4d] In the ESR spectra of some Fe(oetap)ClO_4 and Fe(oetap)PF_6 samples, a minor signal was observed at $g_\perp \approx 6.0$. Since this signal was small (< 10% of integrated intensity) and was not present in all samples, it was assumed to be a trace impurity.

Single crystals of complex **2** suitable for X-ray diffraction were grown by vapour diffusion of hexanes into a toluene–tetrahydrofuran (thf) solution of the tetraazaporphyrin over the course of several weeks. The ORTEP[11] diagram, with the atomic numbering scheme, is shown in Fig. 1.

The eight ethyl groups of Fe(oetap)ClO_4 are directed towards the same side of the porphyrin plane, the side that is occupied by the axial perchlorate ligand. This configuration of the peripheral ethyl groups and perchlorate ligand leaves one side of the macrocycle unobstructed and the unit-cell diagram shows Fe(oetap)ClO_4 crystallizes as slightly offset 'face-to-face' pairs. The closest iron–iron distance is 4.09 Å while the separation between mean macrocycle planes is 3.7 Å. Dimerization of macrocycles has been observed in a number of molecules of this type and is due to π–π interactions.[4f,m,12] The tetraazaporphyrin core shows neither significant 'doming' nor 'ruffling' distortions.

Selected average bond lengths of complex **2** are compared to those of related complexes, Fe(oetap)Cl,[2] Fe(oetap)ClO_4[4f] and Fe(oep)Cl,[13] in Table 2. The close relationship between the displacement of iron from the porphyrin plane and the occupancy of the $d_{x^2-y^2}$ orbital. (*i.e.* iron spin state) has been noted by Scheidt and Reed[1c] in complexes of this type. Large displacements of iron from the macrocycle plane (0.39–0.62 Å) are observed for high-spin ($S = \frac{5}{2}$) complexes in which the antibonding $d_{x^2-y^2}$ orbital is occupied. Presumably repulsive interactions between the electron in the iron $d_{x^2-y^2}$ orbital and electrons on the pyrrolic nitrogens prevent the iron atom from

Table 1 Characterization data for complexes **1**–**5**

	1	**2**	**3**	**4**	**5**
UV/VIS (nm) (thf)	315, 366, 431, 554, 670	328, 382, 485, 565, 696	326, 381, 487, 566 (sh), 693	326, 374, 487, 568 (sh), 618, 695	310 (sh), 372, 444, 560, 676
(CH_2Cl_2)	315, 369, 444, 564, 680	310, 372, 502, 561, 683, 713 (sh)	305, 372, 505, 560 (sh), 715	313, 372, 506, 558 (sh), 722	308, 372, 446, 570, 689
(C_6H_5Me)	318, 364, 436, 555, 672	312, 375, 497, 582, 711	312, 372, 505, 558 (sh), 687	322, 372, 509, 588 (sh), 722	310 (sh), 371, 445, 566, 684
Magnetic susceptibility (80–295 K)					
$\mu_{eff}/(\mu_B)$	3.89	3.87	3.44–3.94	3.55–3.79	3.80–4.06
C	1.92	1.86	2.07	1.83	2.13
Θ/K	0.21	0.89	−32.9	−12.9	−14.0
Mössbauer					
Isomer shift/mm s^{-1}	0.28(1)	0.35(1)	0.30(1)	—	0.23(1)
ΔE_Q/mm s^{-1}	2.98(1)	4.38(2)	4.02(1)	—	3.36(3)
ESR (8 K)					
$g_\perp$	3.98	3.98	4.05	4.07	3.55
$g_\parallel$	1.99	1.99	2.04	2.01	2.01

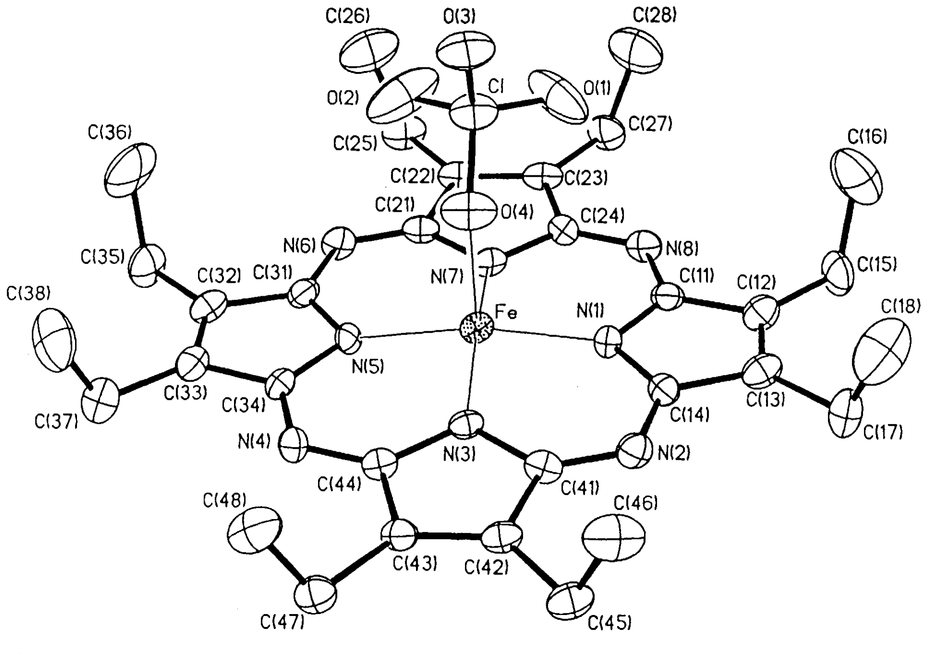

Fig. 1 Thermal ellipsoid plot (30% probability) of complex **2**. Solvent and hydrogen atoms omitted for clarity

Table 2 Selected average bond distances (Å) for complex **2** and related iron(III) porphyrinates and tetraazaporphyrinates

Distance/Å	Fe(oetap)ClO$_4$ *	Fe(oetap)Cl^2	Fe(oep)ClO$_4$^{4f}	Fe(oep)Cl^{13}
Fe–N$_p$	1.913(7)	1.929(7)	1.994(10)	2.063(4)
Fe–axial ligand	2.091(9)	2.278(2)	2.067(9)	2.231(2)
N$_p$–C$_t$	1.895(8)	1.897(3)	1.977(10)	2.010(4)
Displacement of Fe from N$_p$ plane	0.263(3)	0.352(3)	0.26(1)	0.463(9)

* The standard deviations given are the larger of the individual standard deviations or the standard deviation of the mean.

dropping into the macrocycle plane. For iron(III) porphyrinates in which the $d_{x^2-y^2}$ orbital is unoccupied ($S = \frac{1}{2}$ or $\frac{3}{2}$) or partially occupied (admixed $S = \frac{3}{2}, \frac{5}{2}$) smaller displacements of iron from the macrocycle plane (*ca.* 0.00–0.30 Å) are observed.

As can be seen from Table 2, the displacement of iron from the macrocycle plane is smallest in complex **2** and Fe(oep)-ClO$_4$, suggesting their spin states are closest to pure $S = \frac{3}{2}$. Iron displacement from the azaporphyrin plane in **1** is significantly larger, in fact outside the range defined by Scheidt and Reed for admixed-spin complexes. However, it is not as large as in Fe(oep)Cl, a complex known to be high spin. Comparison of the Fe atom displacements in **1** and **2** is complicated by the large difference in axial ligand strengths. The chloride ligand of **1** draws the iron out of the azaporphyrin to a greater extent than does the perchlorate ligand of **2**. Thus when using metal displacement from the macrocycle plane to evaluate spin states the strength of the axial ligands must be considered.

Comparison of the structure of complex **2** and that of perchloratoiron(III) octaethylporphyrinate reveals the sensitivity of spin state to structure in these complexes.[14] Note that the displacements of the iron atoms from the mean macrocycle planes in **2** and Fe(oep)ClO$_4$ are identical, yet the former is an admixed $S = \frac{3}{2}, \frac{5}{2}$ system while the latter is a pure $S = \frac{3}{2}$ system. This spin-state difference is not due to a difference in the strength of interaction with the perchlorate axial ligand because the azaporphyrin complex has a longer iron–perchlorate distance. The difference in spin states must be due to the size of the metal-binding 'hole' (the average distance between the macrocycle centre and pyrrolic nitrogen atoms, N$_p$–C$_t$) which is just over 0.08 Å larger in the porphyrin complex than in **2**. This again points out the problem of assigning spin state based only on metal displacement from the macrocycle plane.

Conclusion

Comparison of the magnetic and spectroscopic properties of complexes Fe(oetap)Z (Z = Cl$^-$, ClO$_4$$^-$, PF$_6$$^-$, SbF$_6$$^-$ or CF$_3$CO$_2$$^-$) shows little difference, confirming the original intermediate-spin state assignment of **1**. Of the parameters used to distinguish a simple $S = \frac{3}{2}$ complex from an admixed ($S = \frac{5}{2}, \frac{3}{2}$) complex, temperature-dependent magnetic susceptibility and ESR *g* values are the most definitive. Mössbauer quadrupole splittings, while able to distinguish between low-, intermediate- and high-spin complexes, showed no difference between $S = \frac{3}{2}$ and $S = \frac{5}{2}, \frac{3}{2}$ admixed-spin complexes. Displacements of iron from the macrocycle plane in complexes of this type are dependent on both the spin state and axial ligand strength and thus are of limited utility in the absence of a common axial ligand. No evidence for any low-spin ($S = \frac{1}{2}$) character in **2**–**5** was observed.

Experimental

General considerations

The free-base octaethyltetraazaporphyrin and its iron(III) chloride complex were prepared as described in the literature.[2,15] Silver salts were obtained commercially and used without further purification. All solvents were reagent grade and distilled in a dry-box from sodium–benzophenone. Manipulations involving air- or water-sensitive compounds were done inside a Braun MB150 or Vacuum Atmospheres inert-atmosphere glove-box maintained at < 1 ppm oxygen and water. Samples were submitted to MHW Laboratories, Phoenix, AZ, for elemental analysis.

Visible spectra were obtained on a computer-controlled Perkin-Elmer Lambda 4 UV/VIS spectrometer using software obtained from Softways, IR spectra on a Perkin-Elmer model

Table 3 Crystallographic data for complex **2**

Formula	$C_{35.2}H_{44}ClFeN_8O_4$
M	692.0
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	10.398(4)
b/Å	14.307(9)
c/Å	14.303(6)
α/°	78.73(4)
β/°	69.52(4)
γ/°	69.37(4)
U/Å^3	1859(2)
Z	2
Crystal dimensions/mm	0.24 × 0.26 × 0.26
Crystal colour	Black
D_c/g cm^{3}	1.309
T/K	296
F(000)	772.69
Diffractometer	Siemens P4
Monochromator	Graphite
Radiation (λ/Å)	Mo-Kα (0.710 73)
2θ Scan range/°	4.0–44.0
Data collected (h,k,l)	±10, ±14, +15
Reflections collected	4691
Independent reflections	4472
Observed reflections $[F_o \geq 4\sigma(F_o)]$	2902
Standards (variation in %)	3 per 197 (< 1)
R	0.0806
R'	0.1015
$\Delta\sigma_{max}$	0.000
Δ_ρ/e Å^{-3}	0.89
N_o/N_v	6.9
Goodness of fit	1.32

1750 FT IR instrument using IDRIS software and ESR spectra on 0.001 mol dm^{-3} solutions in toluene at 8 K on a Brüker ECS 106 spectrometer with an Oxford Instruments cryostat. Experimental details for measuring the Mössbauer spectra and the magnetic susceptibilities have been reported previously.[2] The raw susceptibility data were corrected for the susceptibility of the holder and the diamagnetism of the ligand atoms by Pascal's constants[16] and converted into molar susceptibilities from which the magnetic moments were calculated as $\mu = 2.828\ (\chi_m T)^{\frac{1}{2}}$. The experimental data were analysed by a non-linear least-squares fitting program GRAFIT, as described previously.[17]

Preparation of Fe(oetap)Z 2–5 (Z = ClO_4^-, PF_6^-, SbF_6^- or $CF_3CO_2^-$)

CAUTION: Perchlorate salts of metal complexes with organic ligands are potentially explosive.[18]

The procedure, given below for Fe(oetap)ClO$_4$, was identical for all of the compounds except that toluene was used as the solvent for the preparation of Fe(oetap)(CF$_3$CO$_2$). The complex Fe(oetap)Cl (0.250 g, 0.399 mmol) was dissolved in tetrahydrofuran (30 cm^3) and silver perchlorate (0.100 g, 0.44 mmol) was added as a solid. The red solution was refluxed for 10 min and filtered through Celite to remove the silver chloride precipitate. Addition of heptane (15 cm^3) and cooling resulted in the precipitation of a dark green solid, Fe(oetap)ClO$_4$·thf (0.238 g, 78%). The colour of the solid is purple-red when the particle size is smaller.

Perchloratoiron(III) octaethyltetraazaporphyrinate 2. IR (Nujol): 1136, 896, 878 and 615 cm^{-1}. UV/VIS (log ε) (toluene): 312 (4.51), 375 (4.34), 497 (4.25), 582 (3.99) and 711 nm (3.83) (Found: C, 56.20; H, 6.80; N, 14.95. Calc. for $C_{32}H_{40}ClFeN_8O_4{\cdot}C_4H_8O$: C, 56.60; H, 6.35; N, 14.65%).

Hexafluorophosphatoiron(III) octaethyltetraazaporphyrinate 3. IR (Nujol): 840 and 558 cm^{-1}. UV/VIS (log ε) (toluene): 312 (4.63), 372 (4.46), 505 (4.17), 558 (4.22) and 687 nm (4.19) (Found: C, 53.20; H, 5.80; N, 14.05. Calc. for $C_{32}H_{40}F_6FeN_8P{\cdot}C_4H_8O$: C, 53.40; H, 6.00; N, 13.85%).

Hexafluoroantimonatoiron(III) octaethyltetraazaporphyrinate, 4. IR (Nujol): 658 cm^{-1}. UV/VIS (log ε) (toluene): 322 (4.70), 372 (4.53), 509 (4.62), 588 (4.14) and 722 nm (4.05) (Found: 47.70; H, 5.30; N, 12.30. Calc. for $C_{32}H_{40}F_6FeN_8Sb{\cdot}C_4H_8O$: C, 48.00; H, 5.40; N, 12.35%).

Trifluoroacetatoiron(III) octaethyltetraazaporphyrinate 5. IR (Nujol): 1699, 1397, 1185, 1156 and 1141 cm^{-1}. UV/VIS (log ε) (toluene): 310 (4.49), 371 (4.28), 445 (4.06), 566 (4.03) and 686 nm (4.09) (Found: C, 59.45; H, 5.85; N, 14.25. Calc. for $C_{34}H_{40}F_3FeO_2{\cdot}0.5C_6H_5CH_3$: C, 59.90; H, 5.90; N, 14.90%).

X-Ray crystallography

Single crystals of complex **2** were grown by vapour diffusion of hexanes into a toluene–thf solution. A suitable crystal was mounted with epoxy cement on a glass fibre. Crystal, data collection, and refinement parameters are reported in Table 3. Unit-cell parameters were obtained by the least-squares fit of 24 reflections (20 ≤ 2θ ≤ 25°). Although the primitive triclinic unit cell readily transforms to *C*- or *I*-centred monoclinic cells, an exhaustive investigation proved all chemically plausible solutions in possible monoclinic space groups to be computationally unstable. The structure was solved by direct methods, completed by subsequent Fourier-difference syntheses and refined by full-matrix least-squares procedures. A weighting scheme of the form $w^{-1} = \sigma^2(F) + 0.0040F^2$ was used. Absorption corrections were ignored because of the small absorption coefficient (μ = 5.24 cm^{-1}). Attempts to model five peaks in the difference map, not associated with the compound ion pair, as chemically reasonable solvent molecules were less than satisfactory. These apparent solvent molecule atoms were assigned carbon identities with refinable partial occupancies and included in all calculated parameters. All non-hydrogen, non-solvent atoms were refined with anisotropic displacement coefficients. All solvent atoms were refined isotropically while hydrogen atoms were treated as idealized contributions. All software and sources of the scattering factors are contained in the SHELXTL PLUS program library.[19]

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

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