Hydrogen-bond Acceptor Abilities of Tetrachlorometalate(II) Complexes in Ionic Liquids†

Peter B. Hitchcock,[a] **Kenneth R. Seddon***,[b] **and Thomas Welton**[c]
[a] *School of Chemistry and Molecular Sciences, University of Sussex, Falmer, Brighton BN1 9QJ, UK*
[b] *School of Chemistry, David Keir Building, The Queen's University of Belfast, Belfast BT9 5AG, UK*
[c] *Department of Chemistry, University of Exeter, Stocker Road, Exeter EX4 4QD, UK*

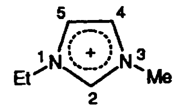
The novel salts $[emim]_2[CoCl_4]$ and $[emim]_2[NiCl_4]$ (emim = 1-ethyl-3-methylimidazolium cation) have been prepared for use as crystallographic models in an extended X-ray absorption fine structure (EXAFS) study in ambient-temperature ionic liquids. The salts have been characterized both spectroscopically and crystallographically. The crystals are isomorphous, and contain two distinct anions with differing interactions within the extended hydrogen-bonded structures. The implications of these results for the structure of ambient-temperature ionic liquids are discussed.

The role and nature of cation–anion interactions in ambient-temperature ionic liquids are the subject of much current interest. Although the controversy over the existence of hydrogen bonding in ionic liquids [1–3] is now essentially resolved, some workers still doubt its existence.[4] In *N,N'*-dialkylimidazolium systems, the combination of the crystal structures of 1-ethyl-3-methylimidazolium iodide ([emim]I)[5] and chloride ([emim]Cl),[6] the IR spectra[2] of the [emim]Cl–$AlCl_3$ ionic liquids, NMR solution studies of [emim]X (X = Cl, Br or I) salts in conventional molecular solvents,[3] and MNDO semi-empirical calculations[7] has demonstrated unambiguously the importance of hydrogen-bonded interactions between all of the ring protons (H^2, H^4 and H^5) of the cation and halide anions. In contrast, for the uranium salts $[emim]_2[UCl_6]$ and $[emim]_2[UO_2Cl_4]$,[8] and the ruthenium salt $[emim]_3[Ru_2Br_9]$,[9] the absence of such interactions has been noted. We present here the crystal structures of $[emim]_2[MCl_4]$ (M = Co or Ni), which clearly demonstrate the involvement of all three ring protons in hydrogen bonds with the tetrachlorometalate(II) anion, as well as IR data which support this view. In addition to the intrinsic interest in the salts themselves, these structures were used as the crystalline models for a recent extended X-ray absorption fine structure (EXAFS) study of the structure of chlorometalate(II) solutes in ambient-temperature ionic liquids.[10]

Experimental

Starting Materials and Solvents.—The preparation of [emim]Cl has been described elsewhere.[11] Anhydrous cobalt(II) chloride and nickel(II) chloride were prepared from the hydrates (FSA) by treatment with sulfinyl chloride (BDH).[12] Ethanenitrile (Aldrich) and nitromethane (Aldrich) were dried by distillation *in vacuo* from phosphorus(V) oxide.

Preparation of 1-*Ethyl*-3-*methylimidazolium Tetrachlorocobaltate*(II).—The compound [emim]Cl (3.95 g, 27 mmol) was dissolved in dry ethanenitrile (15 cm^3) and anhydrous cobalt(II) chloride (1.96 g, 15 mmol) was added. The mixture was heated under reflux, under dry dinitrogen, for 2 h. The resulting hot solution was filtered under dry dinitrogen and the volume of the filtrate reduced by a half by continuous evacuation. The solution was cooled, at −13 °C, overnight and the resulting crystals were isolated by Schlenk filtration. The blue crystals were dried *in vacuo* for 48 h. Yield 2.95 g (46.4%), m.p. 100–102 °C, μ_{eff} 4.6 ± 0.1 μ_B (lit.,[13] 4.50–4.72 μ_B) (Found: C, 34.05; H, 5.35; Cl, 33.00; N, 13.15. $C_{12}H_{22}Cl_4CoN_4$ requires C, 34.05; H, 5.25; Cl, 33.50; N, 13.25%).



$[emim]^+$

Preparation of 1-*Ethyl*-3-*methylimidazolium Tetrachloronickelate*(II).—The compound [emim]Cl (4.12 g, 28 mmol) was dissolved in dry ethanenitrile (15 cm^3) and anhydrous nickel(II) chloride (2.01 g, 16 mmol) was added. The mixture was treated as above and the resulting blue crystals were isolated by Schlenk filtration and dried *in vacuo* for 48 h. Yield 2.93 g (44.7%), m.p. 92–93 °C, μ_{eff} 3.6 ± 0.2 μ_B (lit.,[14] 3.87 μ_B) (Found: C, 34.00; H, 4.90; N, 13.10. $C_{12}H_{22}Cl_4N_4Ni$ requires C, 34.10; H, 5.25; N, 13.25%).

General Techniques.—Magnetic susceptibilities of the salts were measured using a Johnson Mathey magnetic susceptibility balance. Diamagnetic corrections were calculated using Pascals constants.[15] Electronic absorption spectra were recorded using a Varian Cary 2300 spectrophotometer for solutions of the chlorometalate salts in ethanenitrile using 1 cm path length cells in the region 220–2100 nm (45 455–4762 cm^{-1}). The IR spectra of $[emim]_2[MCl_4]$ (M = Co or Ni) in the region 4000–2000 cm^{-1} were recorded as hexachlorobutadiene mulls on CsI plates, whilst the spectra of the salts in the region 2000–200 cm^{-1} were recorded as Nujol mulls on CsI plates. All IR spectra were recorded using a Perkin Elmer 598 infrared spectrophotometer controlled by a Perkin Elmer 3600 Data Station.

Crystal-structure Determinations.—Crystals of $[emim]_2[CoCl_4]$ and $[emim]_2[NiCl_4]$ were prepared by recrystallization from solutions in dry nitromethane. The crystals were isolated by Schlenk filtration and dried in a stream of dry dinitrogen. Crystals were selected and mounted in Lindemann capillary tubes for structural analysis. Data for both crystals were collected on an Enraf-Nonius CAD4 diffractometer with a maximum scan time of 1 min. There was no crystal decay in either case. The structure of $[emim]_2[CoCl_4]$ was solved by a

---

† Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Non-SI unit employed: $\mu_B \approx 9.274\,02 \times 10^{-24}\ JT^{-1}$.

Table 1 Experimental conditions, data collection and refinements for $[emim]_2[MCl_4]$ (M = Co or Ni)

Formula	$C_{12}H_{22}Cl_4CoN_4$	$C_{12}H_{22}Cl_4N_4Ni$
M_r	423.08	422.84
Crystal size/mm	2.0 × 0.4 × 0.4	0.3 × 0.3 × 0.3
Crystal system	Tetragonal	Tetragonal
Space group	$I4_1/a$	$I4_1/a$
$a = b$/nm	1.4128(3)	1.4112(6)
c/nm	1.9491(1)	1.9436(16)
U/nm^3	3.8904	3.8711
Z	8	8
F(000)	1736	1744
D_c/g cm^{-3}	1.45	1.47
λ (Mo-Kα)/nm	0.071 069	0.071 069
hkl intensities	$+h+k+l$	$+h+k+l$
Scan mode	θ–2θ	θ–2θ
Scan width, Δθ/°	0.8 + 0.35 tan(θ)	0.8 + 0.35 tan(θ)
θ limits/°	2–25	2–25
Total unique collected reflections	1930	1913
μ/cm^{-1}	14.3	15.6
Max. absorption correction	1.37	None
Min. absorption correction	0.73	None
No. of reflections $I > \sigma(I)$ in the least-squares refinement	1304	1060
Final R[a]	0.057	0.051
Final R'[b]	0.074	0.066

[a] $R = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$. [b] $R' = \{\Sigma w(|F_o| - |F_c|)^2\}/\Sigma w|F_o|^2$.

Table 2 Infrared data for $[emim]_2[MCl_4]$ (M = Co or Ni) in the region 4000–400 cm^{-1}

$[CoCl_4]^{2-}$	$[NiCl_4]^{2-}$	Cl^- *	Assignment
3145m	3145m	3137m	Aromatic C–H str.
3105s	3104s	—	Aromatic C–H str.
3083s	3081s	3078s	Aromatic C–H ··· X str.
2993m	2982w	3000m	Aliphatic C–H str.
2957m	2954w	—	Aliphatic C–H str.
1572s	1572s	1572s	Ring str. (sym.)
—	—	1421m	Me C–H str. (sym.)
1342m	1342m	1339w	Me C–H bend (sym.)
1328w	—	—	Ring str. (sym.)
1260w	1259w	1252w	Ring C–H bend (sym.)
1173s	1173s	1172s	Ring str. (sym.)
1103w	—	1111m	Ring C–H in-plane bend
1087w	1088w	1096w	Ring C–H in-plane bend
1023w	—	1030w	Combination
857m	858m	850m	C–H in-plane bend
787m	786m	775m	
721w	721w	723m	C–H in-plane bend
634w	634w	644m	Ring bend (asym.)
623m	623m	619m	Ring bend (asym.)

* Data for [emim]Cl for comparison from ref. 2.

Table 3 Electronic spectral data for $[emim]_2[CoCl_4]$ in MeCN

Transition	ν_{max}/cm^{-1}	ε/dm^3 mol^{-1} cm^{-1}
$^4A_2 \longrightarrow {}^4T_1$ (P)	16 230	shoulder
	15 800	254
	15 610	shoulder
	14 960	360
	14 380	414
$^4A_2 \longrightarrow {}^4T_1$ (F)	6 100	46
	5 510	45
	5 210	43
	4 880	40

Table 4 Electronic spectral data for $[emim]_2[NiCl_4]$ in MeCN

Transition	ν_{max}/cm^{-1}	ε/dm^3 mol^{-1} cm^{-1}
$^3T_1 \longrightarrow {}^3T_1$ (P)	15 200	222
	14 200	228
$^3T_1 \longrightarrow {}'T_2$ (D)	11 600	7
$^3T_1 \longrightarrow {}^3A_2$	7 500	26

combination of MULTAN[16] (Co and Cl atoms) and difference maps (C and N atoms). For $[emim]_2[NiCl_4]$, the coordinates from the structure of the $[CoCl_4]^{2-}$ salt were used as the starting values. For both structures, refinement was by full-matrix least squares with $w = \sigma^{-2}(F)$ and with anisotropic thermal parameters for the non-hydrogen atoms. For $[emim]_2[CoCl_4]$, the hydrogen atoms bonded to the imidazolium ring, which were identifiable on the difference map, were included at fixed idealized geometry with B_{iso} of $1.3B_{eq}$ for the carbon atoms to which they were bonded. For $[emim]_2[NiCl_4]$, the ring hydrogen atoms were located on the difference map and refined isotropically. Other details of the methods used are summarized in Table 1.

Results and Discussion

Infrared Spectra.—The IR data for the chlorometalate salts, in the region 4000–400 cm^{-1}, are presented in Table 2. Comparison is made with the spectrum of [emim]Cl.[2]

The IR spectra of the salts in the region 4000–2000 cm^{-1} are dominated by both aromatic and aliphatic C–H stretching. The presence of a strong broad peak in the region 3100–3000 cm^{-1} has been used to infer the formation of hydrogen bonds in ionic liquids.[2] This peak is present in the spectra of $[emim]_2[MCl_4]$ (M = Co or Ni), for which hydrogen bonds are clearly demonstrated in their crystal structures. The region 2000–400 cm^{-1} shows internal vibrations of the imidazolium ring and is used as the 'fingerprint' region for the presence of the planar imidazolium ring.

The spectra in the region 400–200 cm^{-1} are dominated by the metal–chlorine vibrations of $[CoCl_4]^{2-}$ [294, 287(sh) cm^{-1}] and $[NiCl_4]^{2-}$ [291(sh), 284 cm^{-1}]. These results compare well with the spectra of $[NEt_4]_2[MCl_4]$ (M = Co or Ni),[14] and are characteristic of slightly distorted T_d symmetry.

Electronic Absorption Spectra.—The electronic spectral data for $[emim]_2[CoCl_4]$ are presented in Table 3. The spectrum exhibits a strong band at *ca.* 15 040 cm^{-1} containing a shoulder and three well defined peaks, giving rise to the intense blue colour of the salt, and a weaker band at *ca.* 5420 cm^{-1}. This agrees well with the spectrum of $[NBu_4]_2[CoCl_4]$ in CH_2Cl_2.[13] The Orgel diagram[17] for a d^7 (ground term ^4F) ion in a tetrahedral field predicts three bands: ν_1, $^4A_2 \longrightarrow {}^4T_2$; ν_2, $^4A_2 \longrightarrow {}^4T_1$ (F); and ν_3, $^4A_2 \longrightarrow {}^4T_1$ (P). Of these, ν_2 and ν_3 are observed in this spectrum; the band ν_1 lies outside the range of the spectrum recorded here.

The electronic spectral data for $[emim]_2[NiCl_4]$ are presented in Table 4. The spectrum reveals a strong band at *ca.* 14 700 cm^{-1}, consisting of two well resolved components, a much weaker absorption at 11 600 cm^{-1} and a third band at *ca.* 7490 cm^{-1}. The spectrum is in good agreement with that of $[PMePh_3]_2[NiCl_4]$ in ethanenitrile.[18] The Orgel diagram[17] for a d^8 (ground term ^3F) ion in a tetrahedral ligand field predicts three bands: ν_1, $^3T_1 \longrightarrow {}^3T_2$; ν_2, $^3T_1 \longrightarrow {}^3A_2$; ν_3, $^3T_1 \longrightarrow {}^3T_1$ (P). Of these ν_3 and ν_2 are observed in the spectral region reported here. The weak band at 11 600 cm^{-1} can be attributed to a spin-forbidden transition to an upper state arising from the ^1D state of the free ion ($^3T_1 \longrightarrow {}^1T_2$).[17]

Crystal Structures of $[emim]_2[MCl_4]$ (M = Co *or* Ni).—The crystals of $[emim]_2[MCl_4]$ (M = Co or Ni) are isomorphous, and the data are presented in Tables 5–9. The individual atoms are given two labels: those derived from the systematic ring-numbering nomenclature of the compounds, and crystallo-

Table 5 Fractional atomic coordinates ($\times 10^4$, except H $\times 10^3$) for $[emim]_2[CoCl_4]$ with estimated standard deviations in parentheses

Atom		*x*	*y*	*z*
Co(1)		0	5000	2500
Co(2)		5000	5000	0
Cl(1)		1306.8(9)	4897.3(9)	3178.1(6)
Cl(2)		4230.9(8)	3907.4(9)	651.1(6)
N(1)	N^3	2886(3)	6906(3)	1009(2)
N(2)	N^1	3266(3)	8036(3)	326(2)
C(1)	C^2	3601(4)	7313(4)	670(2)
C(2)	C^4	2058(4)	7401(4)	878(3)
C(3)	C^5	2315(4)	8111(4)	450(3)
C(4)	NCH_3	2960(5)	6075(5)	1458(3)
C(5)	CH_2CH_3	3816(6)	8751(7)	−96(4)
C(6)	CH_2CH_3	4734(7)	8527(8)	−242(6)
H(1)	H^2	424	711	68
H(2)	H^4	144	727	105
H(3)	H^5	191	858	27

Table 6 Intramolecular distances (nm) and angles (°) for $[emim]_2$-$[CoCl_4]$ with estimated standard deviations in parentheses

Co(1)–Cl(1)	0.2275(1)	Co(2)–Cl(2)	0.2275(1)
N(1)–C(1)	0.1337(7)	N(1)–C(2)	0.1386(7)
N(1)–C(4)	0.1468(8)	N(2)–C(1)	0.1310(7)
N(2)–C(3)	0.1370(7)	N(2)–C(5)	0.1517(10)
C(2)–C(3)	0.1355(8)	C(5)–C(6)	0.1364(13)

Cl(1)–Co(1)–Cl(1)	108.97(5)	Cl(1)–Co(1)–Cl(1)	109.72(4)
Cl(2)–Co(2)–Cl(2)	112.18(4)	Cl(2)–Co(2)–Cl(2)	108.13(4)
C(1)–N(1)–C(2)	109.3(4)	C(1)–N(1)–C(4)	125.7(5)
C(2)–N(1)–C(4)	124.9(5)	C(1)–N(2)–C(3)	108.9(5)
C(1)–N(2)–C(5)	127.7(5)	C(3)–N(2)–C(5)	123.2(5)
N(1)–C(1)–N(2)	108.3(4)	N(2)–C(5)–C(6)	116.5(8)

Table 7 H ··· Cl contacts < 0.295 nm for $[emim]_2[MCl_4]$

	M = Co	M = Ni
H(1) ··· Cl(2)	0.259	0.256(7)
H(2) ··· Cl(1)	0.277	0.284(6)
H(3) ··· Cl(1)	0.275	0.263(6)

Table 8 Fractional atomic coordinates ($\times 10^4$) for $[emim]_2[NiCl_4]$ with estimated standard deviations in parentheses

Atom		*x*	*y*	*z*
Ni(1)		0	5000	2500
Ni(2)		5000	5000	0
Cl(1)		1294(1)	4899(1)	3176(1)
Cl(2)		4232(1)	3906(1)	633(1)
N(1)	N^3	2876(4)	6896(4)	1019(3)
N(2)	N^1	3263(4)	8048(4)	337(3)
C(1)	C^2	3598(4)	7320(4)	670(4)
C(2)	C^4	2074(4)	7406(5)	879(4)
C(3)	C^5	2312(5)	8122(5)	451(4)
C(4)	NCH_3	2953(6)	6060(5)	1467(5)
C(5)	CH_2CH_3	3813(7)	8753(9)	−83(5)
C(6)	CH_2CH_3	4723(8)	8550(9)	−214(8)
H(1)	H^2	4210(51)	7011(50)	719(45)
H(2)	H^4	1497(38)	7242(39)	1031(30)
H(3)	H^5	1918(41)	8662(41)	232(34)

graphic labels in the form X(*n*) [*e.g.* H^2 is equivalent to H(1)]. The parallel labels are defined in Tables 5 and 8.

Short H ··· Cl contacts are presented in Table 7. In a survey of neutron diffraction data, Taylor and Kennard[19] have demonstrated, using the values of 0.12 and 0.175 nm for the van der Waals radii of hydrogen and chlorine atoms respectively, that a contact shorter than 0.295 nm reliably indicates the presence of a C–H ··· Cl hydrogen bond. The local structure around a single cation is shown in Fig. 1. The shortest contacts [H(1) ··· Cl(2); H^2 ··· Cl] of 0.259 nm for the $[CoCl_4]^{2-}$ salt and 0.256(7) nm for the $[NiCl_4]^{2-}$ salt indicate that a strong, discrete hydrogen bond is formed between the H^2 proton of the imidazolium ring and a chlorine atom of the anion. In addition, the contacts H(2) ··· Cl(1) (H^4 ··· Cl) and H(3) ··· Cl(1) (H^5 ··· Cl) (0.263–0.284 nm) show that there are significant hydrogen-bonding interactions between the anions and the H^4 and H^5 protons of the imidazolium rings.

Table 9 Intramolecular distances (nm) and angles (°) of $[emim]_2$-$[NiCl_4]$ with estimated standard deviations in parentheses

Ni(1)–Cl(1)	0.2254(2)	Ni(2)–Cl(2)	0.2253(2)
N(1)–C(1)	0.1364(8)	N(1)–C(2)	0.1369(9)
N(1)–C(4)	0.1470(10)	N(2)–C(1)	0.1303(9)
N(2)–C(3)	0.1365(9)	N(2)–C(5)	0.1503(13)
C(1)–H(1)	0.097(7)	C(2)–C(3)	0.1350(10)
C(2)–H(2)	0.090(5)	C(3)–H(3)	0.104(6)
C(5)–C(6)	0.134(2)		

Cl(1)–Ni(1)–Cl(1)	108.66(7)	Cl(1)–Ni(1)–Cl(1)	109.88(6)
Cl(2)–Ni(2)–Cl(2)	113.73(6)	Cl(2)–Ni(2)–Cl(2)	107.38(6)
N(2)–C(5)–C(6)	117.0(10)	N(1)–C(1)–N(2)	108.8(5)
C(1)–N(1)–C(2)	106.7(5)	C(1)–N(1)–C(4)	126.3(6)
C(2)–N(1)–C(4)	127.0(6)	C(1)–N(2)–C(3)	109.7(6)
C(1)–N(2)–C(5)	127.2(6)	C(3)–N(2)–C(5)	123.1(6)
N(1)–C(1)–H(1)	115.0(50)	N(2)–C(1)–H(1)	136.0(50)
N(1)–C(2)–C(3)	108.1(6)	N(1)–C(2)–H(2)	123.0(40)
C(3)–C(2)–H(2)	128.0(40)	N(2)–C(3)–C(2)	106.7(6)
N(2)–C(3)–H(3)	121.0(30)	C(2)–C(3)–H(3)	132.0(30)

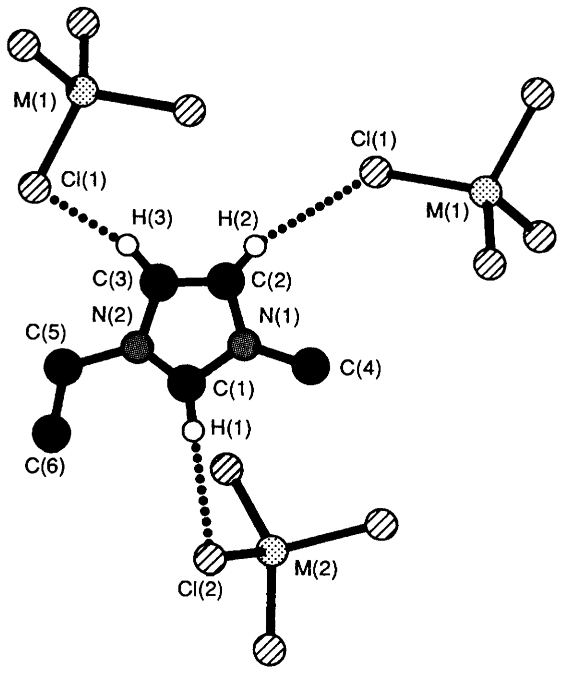


Fig. 1 Local structure around a single cation in $[emim]_2[MCl_4]$ (M = Co or Ni)

In each of the structures, two crystallographically distinct anions are found, which hydrogen bond with *either* H^2 protons (Fig. 2) *or* H^4 and H^5 (Fig. 3) protons of the imidazolium ring, but not both. Nevertheless, *all* of the chlorine atoms of the anion are involved in a complex three-dimensional hydrogen-bonding network. It is interesting to note that a hydrogen-bonded ring structure, reminiscent of that in 1-ethyl-2,3-dimethylimidazolium chloride,[20] is found (Fig. 4).

It can be seen (Tables 6 and 9) that the $[MCl_4]^{2-}$ (M = Co or Ni) anion is approximately tetrahedral with mean Co–Cl and Ni–Cl bond lengths of 0.2275(1) and 0.2254(2) nm respectively.

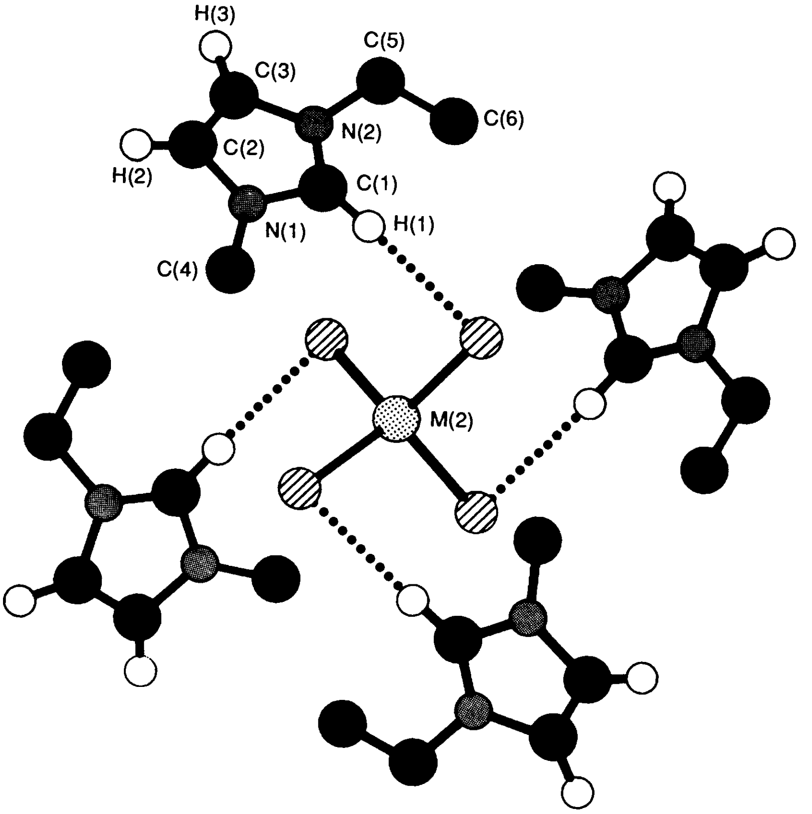


Fig. 2 Local structure around a single anion [M(2)] in $[emim]_2[MCl_4]$ (M = Co or Ni)

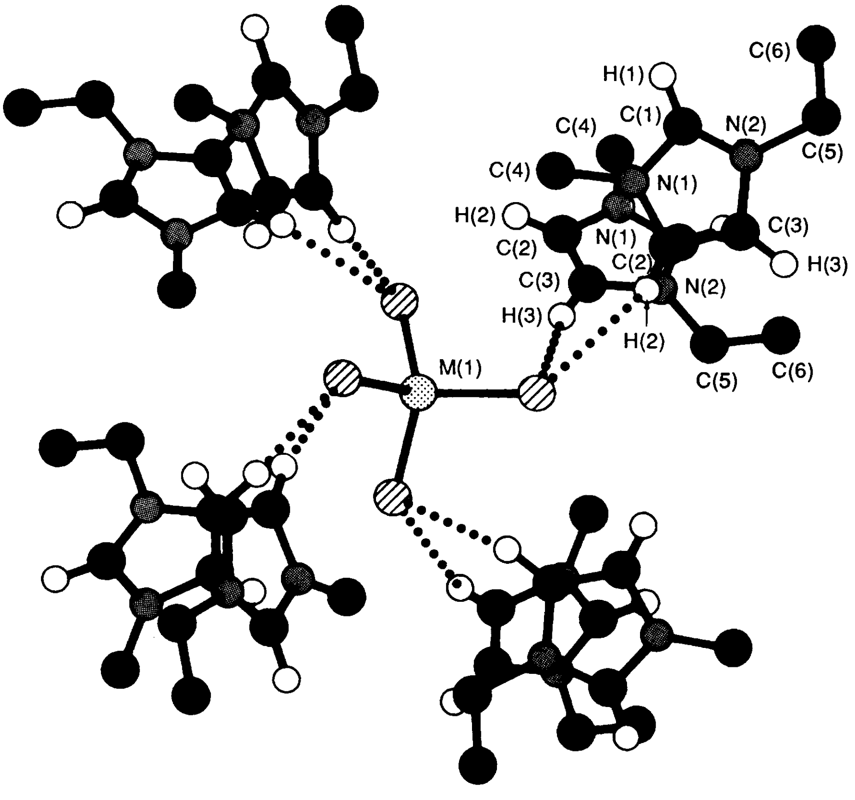


Fig. 3 Local structure around a single anion [M(1)] in $[emim]_2[MCl_4]$ (M = Co or Ni)

A survey of 14 crystal structures[21] containing the $[CoCl_4]^{2-}$ ion reveals that when it is claimed that the chlorine atom is hydrogen bonded to a cation, the mean Co–Cl bond length is 0.2284(25) nm and that when no such interaction is claimed, the mean Co–Cl bond length is 0.2253(22) nm. Unfortunately, with the data sets currently available, these differences cannot be considered as statistically significant. Similarly, the paucity of crystallographic data in the literature for salts of the $[NiCl_4]^{2-}$ ion[22] precludes a similar analysis for the $[emim]_2[NiCl_4]$ salt. However, the M–Cl bond lengths in our salts are significantly

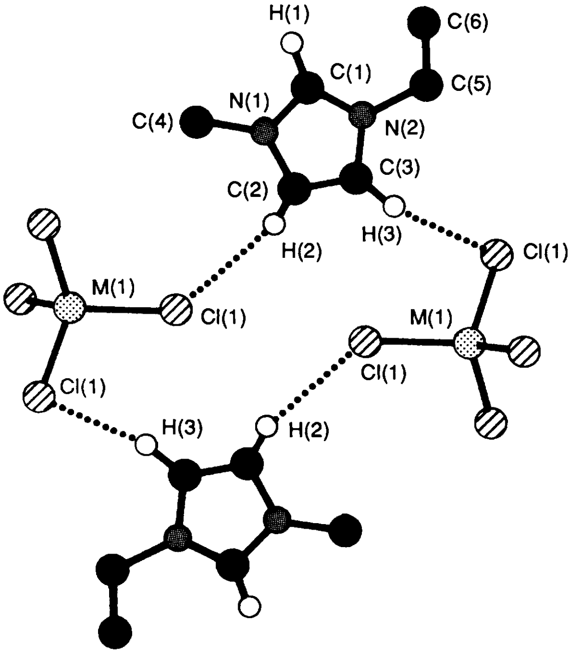


Fig. 4 Hydrogen-bonded ring structure in [emim]$_2$[MCl$_4$] (M = Co or Ni)

longer than the mean bond lengths in the corresponding tetramethylammonium salts, of 0.2254(14) and 0.2234(8) nm,[21a] for which no hydrogen bonding is either claimed or expected.

Conclusion

The structures presented here clearly demonstrate that the 1-ethyl-3-methylimidazolium cation forms discrete hydrogen bonds with the $[MCl_4]^{2-}$ ions (M = Co or Ni). The strongest interaction (*i.e.* the shortest C–H ··· Cl bond length) occurs at the H^2 proton of the imidazolium ring; weaker, yet still significant, hydrogen bonds are formed at the H^4 and H^5 protons of the ring. This observation, together with that of crystallographically distinct anions, bound to either the H^2 or the H^4 and H^5 protons of the imidazolium ring, demonstrates that the salts cannot be described as a simple collection of ion pairs. All ring protons and all chlorine atoms of the anions are involved in an extended three-dimensional hydrogen-bonded network.

From data now available,[5,6,8,9] it can be seen for the simple halide salts [emim]X (X = Cl or I) and the complex salts [emim]$_2$[MCl$_4$] that hydrogen bonding makes an important contribution to the structure of the salt, whilst for the salts [emim]$_2$[UCl$_6$] and [emim]$_2$[UO$_2$Cl$_4$], there is no hydrogen bonding present. Clearly the nature of the potential hydrogen-bond acceptor site is important in determining whether hydrogen bonds will form. Combining this information with unpublished IR data on a number of transition-metal halide salts[23] has allowed this observation to be rationalized. If the charge density (ρ) of each halide atom within the complex ion is approximated to the square of the overall charge of the ion, z, divided by the number of halide atoms in the complex, x, as in equation (1), then if $\rho \geqslant 1$, hydrogen bonds will form; if $\rho < 1$ hydrogen bonds will not form. This rule leads to the prediction that hydrogen bonding is not likely in salts with a singly charged tetrahedral anion, such as $[AlCl_4]^-$.

$$\rho = \frac{z^2}{x} \qquad (1)$$

The implications of these results are that hydrogen-bonding interactions are important in determining the structure of the [emim]Cl–AlCl$_3$ ionic liquids, in compositions with an excess of [emim]Cl, but are unlikely in compositions containing an excess of aluminium(III) chloride.

Acknowledgements

We are indebted to the BP Venture Research Unit for their generous funding, and to the SERC for a postgraduate award (to T. W.).

References

1 A. A. Fannin, jun., L. A. King, J. A. Levisky and J. S. Wilkes, *J. Phys. Chem.*, 1984, **88**, 2609.
2 S. Tait and R. A. Osteryoung, *Inorg. Chem.*, 1984, **23**, 4352.
3 A. G. Avent, P. A. Chaloner, M. P. Day, K. R. Seddon and T. Welton, in *Proceedings of the Seventh International Symposium on Molten Salts*, The Electrochemical Society, Pennington, NJ, 1990, p. 98.
4 D. M. MacArthur, G. A. Nazari and R. Aroca, in *Proceedings of the Seventh International Symposium on Molten Salts*, The Electrochemical Society, Pennington, NJ, 1990, p. 134.
5 A. K. Abdul-Sada, A. M. Greenway, P. B. Hitchcock, T. J. Mohammed, K. R. Seddon and J. A. Zora, *J. Chem. Soc., Chem. Commun.*, 1986, 1753.
6 C. J. Dymek, jun., D. A. Grossie, A. V. Fratini and W. W. Adams, *J. Mol. Struct.*, 1989, **213**, 25.
7 C. J. Dymek, jun. and J. J. P. Stewart, *Inorg. Chem.*, 1989, **28**, 1427.
8 P. B. Hitchcock, T. J. Mohammed, K. R. Seddon, J. A. Zora, C. L. Hussey and E. H. Ward, *Inorg. Chim. Acta*, 1986, **113**, L25.
9 D. Appleby, P. B. Hitchcock, K. R. Seddon, J. E. Turp, J. A. Zora, C. L. Hussey, J. R. Sanders and T. A. Ryan, *J. Chem. Soc., Dalton Trans.*, 1990, 1879.
10 A. J. Dent, K. R. Seddon and T. Welton, *J. Chem. Soc., Chem. Commun.*, 1990, 315.
11 A. K. Abdul-Sada, A. M. Greenway, K. R. Seddon and T. Welton, *Org. Mass Spectrom.*, in the press.
12 A. R. Pray, *Inorg. Synth.*, 1957, **5**, 153.
13 F. A. Cotton, D. M. L. Goodgame and M. Goodgame, *J. Am. Chem. Soc.*, 1961, **83**, 4690.
14 D. M. Adams, J. Chatt, J. M. Davidson and J. Gerratt, *J. Chem. Soc.*, 1963, 2189.
15 Landolt-Bornstein, *Zallenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik und Technik*, 6th edn. (Old Series), Springer Verlag, Berlin, 1967, vol. 2, part 10.
16 G. Germain, P. Main and M. M. Woolfson, *Acta Crystallogr., Sect. A*, 1971, **27**, 368.
17 L. E. Orgel, *J. Chem. Phys.*, 1955, **23**, 1004.
18 D. M. L. Goodgame, M. Goodgame and F. A. Cotton, *J. Am. Chem. Soc.*, 1961, **83**, 4161.
19 R. Taylor and O. Kennard, *J. Am. Chem. Soc.*, 1982, **104**, 5063.
20 A. K. Abdul-Sada, S. Al Juaid, A. M. Greenway, P. B. Hitchcock, M. J. Howells, K. R. Seddon and T. Welton, *Struct. Chem.*, 1990, **1**, 391.
21 (*a*) J. R. Wiesner, R. C. Srivastava, C. H. L. Kennard, M. DiVaira and E. C. Lingafelter, *Acta Crystallogr.*, 1967, **23**, 565; (*b*) W. J. Vermin, G. C. Verschoor and D. J. W. Ijdo, *Acta Crystallogr., Sect. B*, 1976, **32**, 3325; (*c*) C. J. J. van Loon and D. Visser, *Acta. Crystallogr., Sect. B*, 1977, **33**, 188; (*d*) M. A. Porai-Koshits, *Sov. Phys.-Crystallogr. (Engl. Transl.)*, 1956, **1**, 224; (*e*) A. L. Macdonald and J. Trotter, *Can. J. Chem.*, 1974, **52**, 734; (*f*) C. K. Prout and P. Murray-Rust, *J. Chem. Soc., A*, 1969, 1520; (*g*) U. Geiser, R. D. Willet and R. M. Gaura, *Acta. Crystallogr., Sect. C*, 1984, **40**, 1346; (*h*) G. Bombieri, E. Forsellini, A. Del Pra and M. L. Tobe, *Inorg. Chim. Acta*, 1980, **40**, 71; (*i*) L. Antolini, G. Marcotrigiano, L. Menabue and G. C. Pellacani, *Inorg. Chem.*, 1979, **18**, 2652; (*j*) A. C. Bonamartini, M. Nardelli and C. Palmieri, *Acta Crystallogr., Sect. B*, 1972, **28**, 1207; (*k*) H. W. Smith and W. J. Stratton, *Inorg. Chem.*, 1977, **16**, 1640; (*l*) I. Søtofte and K. Nielsen, *Acta Chem. Scand., Ser. A*, 1981, **35**, 739; (*m*) J. Trotter and S. H. Witlow, *J. Chem. Soc. A*, 1970, 460.
22 P. Pauling, *Inorg. Chem.*, 1966, **5**, 1498; G. D. Stucky, J. B. Folkers and T. J. Kistenmacher, *Acta Crystallogr.*, 1967, **23**, 1064; W. J. Vermin, G. C. Verschoor and D. J. Ijdo, *Acta Crystallogr., Sect. B*, 1976, **32**, 3325.
23 K. R. Seddon and T. Welton, unpublished work.

Received 6th *April* 1993; *Paper* 3/01963B