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1,3-Di(alkoxy)imidazolium-based Ionic Liquids: Improved Synthesis and Crystal Structures

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A new and convenient synthetic pathway to 1,3-di(alkoxy)imidazolium bis(trifluoromethylsulfonyl)amides and novel 1,3-di(alkoxy)imidazolium tetrachloroferrates was developed. As an intermediate isolation step of the respective hexafluorophosphates was required in previously reported preparations, they suffered from low overall yields and additional expense. The use of FeCl₃/HCl resulted in substantially improved yields and allows one-pot preparations with good scalability. Results of single-crystal X-ray structure determination of the new tetrachloroferrate salts are discussed.

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Ionic liquids (IL) are defined as salts melting below 100°C. Over the past decades, their development has been fast-paced and offers unexpected opportunities in numerous fields ranging from electrochemistry to biology.^[1] Their recognition as academic curiosities has shifted meanwhile to rank them as indispensable technical tools for process design and engineering. The large number of organic cations and anions that can be combined to form different IL is one of the most important conceptual features of these compounds, allowing a wide range of tailorable physicochemical properties (conductivity, density, viscosity, polarity, solubility).^[2] In particular, the highly versatile imidazole parent structure gives access to an exceptional variability of substitution patterns with extreme synthetic ease, thus even impacting the related chemical realm of nitrogen heterocyclic (NHC) carbenes.^[3] Regarding anions, special chemical and theoretical interest has emerged in hydrophobic IL, mainly based on the bis(trifluoromethylsulfonyl)amide ('triflimide') anion.^[4] Owing to their low residual water content, their hydrolytic and chemical stability and low viscosity, all these classes of IL are valuable sorption media for greenhouse gases,^[5,6] electrolytes,^[7] agents for NHC-mediated transition metal catalysis,^[8] and sacrificial substances in radiation-induced fragmentations.^[9]

Despite growing ecological and toxicological concerns,^[10–12] IL may, under strict measures of eco-containment, even be considered environmentally friendly. This predicate is attributable to their mostly non-volatile nature,^[13,14] and qualifies them as greener alternatives to traditional volatile organic solvents.^[15] In general, the concept of deliberate chemical

fates.^[17] Furthermore, the presence of ester functions, especially with long alkyl side chains, renders the IL more easily (but only partially) biodegradable. Unfortunately, the (quaternized) imidazolium core was reported to be resistant to biological and abiotic degradation.^[17,18] Principally, a partial biodegradation of imidazolium salts by alteration or removal of a side chain functionality does not justify the presumption of overall reduced toxicity.^[19] A successful tool for effective cation degradability is the attachment of side chains by weakly bonded links, offering intentional chemical scission. This can be conveniently realized by the incorporation of N-O single bonds, as already described for alkoxypyridinium, alkoxymorpholinium,^[19] 1-alkyl-3-alkoxyimidazolium,^[20] and di(alkoxy)imidazolium^[21–23] moieties, which bear the fundamental advantage of cationic core degradability by complete removal of the entire side chains.^[24,25] On fragmentation (e.g. by stepwise hydrogenation),^[22] such 1,3-di(alkoxy)imidazolium-based IL are convert-ible to the parent structure of imidazole,^[26,27] which has been identified as a non-toxic natural compound, abundant in edible lentils.^[28] Another mode of (partial) core degradation was recently demonstrated by mild alkaline hydrolysis.^[29,30] In such degradation steps, the essential triflimide anion can be recycled unchanged.

IL degradation is still in its infancy. Comparative toxicity

and biodegradability studies of IL based on 1-alkyl-3-

methylimidazolium cations with or without different oxygenated

functional groups^[2,16] (hydroxyl, ester, and ether) revealed

that the presence of oxygen groups on the imidazolium cation

reduces the toxicity of the respective triflimides or octyl sul-



Scheme 1. Improved synthesis of 1,3-di(alkoxy)imidazolium triflimides.

Besides physical property profiles and safety requirements, good accessibility in terms of preparative efficiency and affordability are relevant for both laboratory and larger scales. As a consequence, aqueous reaction media are frequently used, especially when alkyl sulfates are used for alkylation^[31] as is the case with the synthesis of 1,3-di(alkoxy)imidazolium salts. After the starting compound 1-hydroxyimidazole-3-oxide is prepared by well-proved literature procedures,^[26,32,33] alkylation is carried out using dialkyl sulfates to give the respective 1,3-di(alkyloxy) imidazolium alkyl sulfate intermediates, which are difficult to isolate. A change of the alkylation medium would not really be practicable, because hydroxyimidazole N-oxides are only readily soluble in water. Hitherto, the cation prepared had to be isolated by precipitation as a hexafluorophosphate from the aqueous reaction mixtures (yield of this step 73 %). Ion metathesis using lithium triflimide and extraction with dichloromethane yielded the hydrophobic triflimides (yield for this step 78 %, resulting in an overall yield of 57 %).^[24] In order to skip the elaborate and expensive intermediate hexafluorophosphate-based isolation step, convenient procedures to 1,3-di(alkyloxy)imidazolium triflimides were considered. For instance, the direct ion metathesis of 1,3-di(alkyl)imidazolium alkyl sulfates using lithium triflimide yields up to 81 %.^[34] Unfortunately, this method is not suitable for similar 1,3-di(alkoxy)imidazolium alkyl sulfates (yield $\sim 40\%$), because too much of the residual alkyl sulfate is soluble in the triflimide-containing organic phase. Therefore, the respective direct metathesis to analytically pure triflimides would require the use of considerably more than stoichiometric equivalents of lithium triflimide and this consequently renders the approach economically and ecologically unacceptable.

Based on the experience that even on the combination of aqueous solutions of 1,3-di(alkyl)imidazolium chlorides with aqueous solutions of ferric chloride,^[35] the resulting paramagnetic tetrachloroferrates form binary phase systems, we were curious if this low affinity for H₂O or, preferably, H₂O/HCl could be exploited for workup purposes from aqueous dialkyl sulfate-based alkylation mixtures, as the new tetrachloroferrates are interesting IL in their own right.^[36]

The replacement of expensive ammonium hexafluorophosphate by ferric chloride/hydrochloric acid^[24] resulted in a costeffective, improved synthesis via tetrachloroferrates (**1a**, **1b**, pathway A, Scheme 1) and chlorides (**2a**, **2b**, pathway B, Scheme 1). Fortunately, the entire reaction sequence from the starting 1-hydroxyimidazolium-3-oxide to 1,3-di(alkoxy) imidazolium triflimides (**3a**, **3b**) can be conducted in a onepot synthesis, as the desired triflimide product can be extracted in a final step with dichloromethane, resulting in 74% overall yield. Although methyl sulfates are known for their tendency to migrate partially into the organic phase, none was detectable in the resulting products. Products from pathway A show a fairly low iron content of <3 ppm and a lower chloride content ($0.04 \text{ mg Cl g}^{-1}$ IL) than their analogues from pathway B (2.3 mg Cl g^{-1} IL).

Consequently, two affordable methods led to the same target product. Pathway A, using FeCl₃/HCl, allows the isolation of the two solid intermediates 1,3-dimethoxyimidazolium tetrachloroferrate (1a) and 1,3-diethoxyimidazolium tetrachloroferrate (1b). Single crystals suitable for X-ray measurements of 1a were directly harvested from the mother liquor. Single-crystal X-ray diffraction analysis of the salts revealed interesting information about interionic interactions and conformations of the ions involved. Crystal data and structure refinement details are summarized in Table 1. The respective distances and angles are given in Table 2. The asymmetric unit of 1a contains two independent ion pairs. The tetrachloroferrate(III) ions deviate only slightly from ideal tetrahedral geometry. One cation adopts a syn and the other an anti conformation with respect to the imidazole plane. The methoxy groups are twisted out of the imidazole plane by 88° in the svn and by 90° and 77° in the anti conformers. Interplanar angles are calculated from the leastsquares plane N1-C1-N2-C2-C3 and the pertinent N-O-C planes. Hydrogen atoms of the imidazolium ring and of the methoxy groups are engaged in short contacts with the chlorine atoms of the anions, as shown in Fig. 1a. In a previous report on 1,3-di(alkoxy)imidazolium salts,^[24] two distinct conformations, syn and anti, of the alkoxy groups with respect to the imidazolium ring plane were described only for two polymorphs of a hexafluorophosphate. In the crystal structure of 1b, the imidazolium cation displays several short C-H···Cl contacts to four surrounding tetrachloroferrate(III) anions (Fig. 1b). The ethoxy groups are arranged in anti conformation, rotated out of the ring plane by 89° and 65° respectively.

It was not possible to isolate the intermediate chlorides (2a, 2b) of pathway B. Nevertheless, this did not affect the

Compound	1a	1b	3b,A
CCDC no.	903893	903894	903895
Chemical formula	C ₅ H ₉ N ₂ O ₂ ·Cl ₄ Fe	$C_7H_{13}N_2O_2 \cdot Cl_4Fe$	$C_7H_{13}N_2O_2 \cdot C_2F_6NO_4S_2$
M_r	326.79	354.84	437.34
Crystal size [mm ³]	0.40 imes 0.25 imes 0.22	0.30 imes 0.20 imes 0.12	0.31 imes 0.18 imes 0.15
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1/c$	$P2_1/n$
a [Å]	7.1156(2)	8.3306(3)	12.1565(4)
b [Å]	14.3223(3)	13.4364(4)	11.5005(3)
<i>c</i> [Å]	12.6720(5)	13.3154(4)	12.8449(4)
β [°]	91.846(2)	91.805(3)	98.905(2)
$V[Å^3]$	1290.76(7)	1489.70(8)	1774.15(9)
Ζ	4	4	4
$D_x [g \mathrm{cm}^{-3}]$	1.68	1.58	1.64
$\mu [{\rm mm}^{-1}]$	1.97	1.72	0.39
<i>F</i> (000) [e]	652	716	888
Diffractometer	Nonius Kappa CCD	Oxford Gemini Ultra	Nonius Kappa CCD
Data collection method	ϕ and ω scans	ω scans	ϕ and ω scans
Temperature [K]	233	173	233
θ_{\max} [°]	27.5	25.4	25.0
h, k, l range	$-9 \le h \le 8$	$-10 \le h \le 7$	$-14 \le h \le 14$
	$-18 \le k \le 18$	$-14 \le k \le 16$	$-13 \le k \le 13$
	$-15 \le l \le 16$	$-14 \le l \le 16$	$-15 \le l \le 13$
Measured reflections	8847	8754	9407
Independent reflections (R_{int})	5626 (0.039)	2714 (0.027)	3121 (0.022)
Observed reflections $[I \ge 2\sigma(I)]$	5230	2324	2605
Restraints/parameters	1/254	0/147	0/235
$R_1/wR_2 \left[I \ge 2\sigma(I)\right]$	0.038/0.098	0.025/0.057	0.036/0.093
R_1/wR_2 (all data)	0.042/0.101	0.032/0.061	0.045/0.099
Goodness-of-fit	1.04	1.03	1.05
$\Delta \rho_{\text{max/min}} [\text{e} \text{\AA}^{-3}]$	0.75/-0.33	0.45/-0.40	0.27/-0.33

Table 1. Crystal data and structure refinement de

Table 2. Hydrogen bond parameters in the crystal structures of 1a, 1b, and 3b,A

Interaction	H…A [Å]	D…A [Å]	DH…A [°]	Symmetry operation A
1a				
$C3-H\cdots Cl3$	2.802(1)	3.725(5)	167.6(3)	<i>x</i> , <i>y</i> , <i>z</i>
C9–H····Cl2	2.883(1)	3.663(5)	138.2(4)	<i>x</i> , <i>y</i> , <i>z</i>
$C1-H\cdots Cl2$	2.801(1)	3.567(4)	139.5(3)	1-x, 1/2+y, 2-z
C4–H····Cl6	2.828(1)	3.686(6)	147.8(3)	-1+x, y, z
$C6-H\cdots C18$	2.733(1)	3.575(5)	149.5(3)	x, y, 1+z
$C10-H\cdots Cl7$	2.820(1)	3.780(1)	171.2(6)	2-x, 1/2+y, 2-z
1b				
$C3-H\cdots Cl3$	2.7540(6)	3.410(2)	126.8(1)	<i>x</i> , <i>y</i> , <i>z</i>
C4–H····Cl3	2.8315(6)	3.664(3)	142.2(1)	-1 + x, y, z
C2-H····Cl1	2.8788(6)	3.778(2)	158.2(1)	1-x, -1/2+y, 1.5-z
$C1-H\cdots Cl4$	2.7360(6)	3.621(3)	155.2(1)	-1+x, $1/2-y$, $1/2+z$
3b,A				
$C2-H\cdots N3$	2.491(2)	3.296(3)	143.7(1)	<i>x</i> , <i>y</i> , <i>z</i>
С3–Н…О5	2.487(2)	3.357(3)	154.0(1)	1 - x, 1 - y, -z
$C1-H\cdots O4$	2.247(2)	3.137(3)	157.5(1)	-1/2 + x, $1/2 - y$, $1/2 + z$
$C1-H\cdots O6$	2.505(2)	3.156(3)	126.5(1)	-1/2 + x, $1/2 - y$, $1/2 + z$

yield of the target triflimides. As the FeCl₄-based IL are valuable isolable intermediates for further ion metathesis, pathway A may be more favourable for such purposes.

During the elaboration of these new methods, it surprisingly turned out that one of our target IL, 1,3-diethoxyimidazolium triflimide (**3b**), which was reported to be a liquid at room temperature, was actually a subcooled melt, which now solidified at room temperature (melting point \sim 31°C). Single crystals of **3b**,**A** and **3b**,**B** were grown from dichloromethane at room temperature. In the crystal structure of **3b**,**A**, the imidazolium ring protons are involved in quite short contacts with the N and O atoms of three triflimide anions (Fig. 1c). The ethoxy groups are rotated out of the ring plane by 78° and 89°, adopting an *anti* conformation. The triflimide anion adopts the *trans* conformation with a C8–S1...S2–C9 torsion angle of 177°. When we had seed crystals of **3b**,**A** at hand, it was even possible to crystallize the formerly liquid 1,3-diethoxyimidazolium triflimide prepared by the previous protocol (via the hexafluorophosphate



Fig. 1. Interionic hydrogen bonds in the crystal structures of (a) 1a; (b) 1b; and (c) 3b,A.

intermediate). This is also true of liquid samples purchased from commercial sources (Sigma–Aldrich). Further data (electrochemical window, dynamic viscosity, specific conductivity, thermal stability) of the liquid triflimides are given elsewhere.^[24]

In conclusion, there are various needs for hydrophobic, coredegradable 1,3-di(alkyloxy)imidazolium triflimides in the fields of IL research and catalysis. By the development of the synthesis described herein, these ILs are now more easily accessible in bulk. Usually, when new compounds are introduced, their application potential is not completely exploited, and also the experimental procedures for their preparation are not fully optimized. Therefore, this resumption and development of the synthesis of these special classes of compounds may contribute to the generation of further interest in the wider community and propagate their application.^[37]

Experimental

Crystal data were recorded using an Oxford Diffraction Gemini-R Ultra diffractometer and a Nonius Kappa Charges Coupled Device diffractometer (radiation type for all structures: $Mo_{K\alpha}$). Crystallographic data reported in this manuscript have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-903893, CCDC-903894, CCDC-903895. Copies of the data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

General Procedure for the Preparation of 1,3-Di(alkoxy) imidazolium Tetrachloroferrates (**1a**, **1b**) and Bis(trifluoromethylsulfonyl)amides (**3a**, **3b**)

A mixture of the respective dialkyl sulfate (2 equiv.) and 1-hydroxyimidazole 3-oxide (1 equiv.) was stirred at room temperature for 1.5 h. Then NaHCO₃ (1 equiv.) was added and stirring was continued overnight. After the addition of H_2O and more stirring, two pathways were pursued.

In pathway A, HCl (37 wt-% aqueous solution, 1 equiv.) and FeCl₃ (1 equiv.) were added in succession to the clear solution, which resulted in an additional FeCl₄ phase. This magnetic phase could be separated by the addition of a few millilitres of dichloromethane in a separatory funnel. After removal of the solvent, several analyses were conducted on these intermediate tetrachloroferrate salts (**1a**, **1b**).

In pathway B, the addition of HCl only (37%, 1 equiv.) resulted in a clear solution.

Lithium triflimide (1 equiv.) was added directly to the respective aqueous solutions from both pathways in order to obtain the hydrophobic 1,3-di(alkoxy)imidazolium triflimides by ion metathesis. Stirring at room temperature overnight and extraction with dichloromethane yielded the products **3a** and **3b**.

Supplementary Material

Further details about experimental procedures and analytical data, including differential scanning calorimetry and thermogravimetry, are available on the Journal's website.

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