Cu(I)/(II) based catalytic ionic liquids, their metallo-laminate solid state structures and catalytic activities in oxidative methanol carbonylation†

Marion Stricker,[a] Thomas Linder,[b] Benjamin Oelkers[a] and Jörg Sundermeyer*[a]

Received 8th March 2010, Accepted 19th May 2010
DOI: 10.1039/c003948a

Three types of copper-containing catalytic ionic liquids (CILs) have been synthesised and fully characterised by spectroscopy, elemental, thermal and, in most cases, XRD analyses. Whereas *type I* ILs comprise copper exclusively in the cation (*e.g.* $[Cu(Im^{12})_4][PF_6]$, Im^{12} = 1-dodecylimidazole), *type II* ionic liquids contain Cu(I) in both the cation and the anion (*e.g.* $[Cu(Im^{12})_2][CuBr_2]$) and *type III* ILs incorporate copper solely in form of halocuprate(I)/(II) anions (*e.g.* $[DMIM][CuBr_2]$, DMIM = 1-dodecyl-3-methylimidazolium). A limitation concerning the preparation of a series of *type II* ionic liquids has been observed by the formation of the neutral compound $[Cu(Im^{12})I]_6$ instead of the expected IL $[Cu(Im^{12})_2][CuI_2]$. The novel ILs reveal a metallo-laminate structure in the crystalline state. The salts have a liquidus range of up to 300 °C before decomposition takes place. Their catalytic properties in the synthesis of dimethyl carbonate from MeOH, CO and O_2 have been studied.

Introduction

Ionic liquids with chlorometallate ions have been known for about 60 years, and in the course of this period they have been applied in several catalytic reactions. Catalytic ionic liquids (CILs) are a subgroup of task-specific ionic liquids containing a catalytically active cation or anion or both. The first ILs containing chloroaluminate ions were developed by *Hurley* and *Rice* in 1948.[1,2] Ionic liquids based on acidic chloroaluminates have been used both as solvents and catalytic species for reactions usually catalysed by the *Lewis* acid $AlCl_3$, *e.g.* for catalytic *Friedel-Crafts* alkylation[3] or stoichiometric *Friedel-Crafts* acylation.[4,5] An example of the fact that complex anions can generally be obtained by reaction of *Lewis* acidic transition metal halides with organic halide salts is a *Friedel-Crafts* acylation process, patented by *Seddon et al.*,[6] involving an acidic chloroferrate ionic liquid catalyst.[7] Making use of the *Lewis* acid CuCl, *Chauvin et al.* reported on the application of the ionic liquid $[BMIM][CuCl_2]$ as solvent in a biphasic system within the rhodium catalysed hydrogenation of 1-pentene.[8] An interesting example of a redox-active copper(II)-based CIL is $[BMIM]_4[Cu_4(\mu^4\text{-}O)Cl_{10}]$ used in the aerobic oxidation of 2,3,5-trimethyl phenol yielding the corresponding quinone.[9] In 2005 the group of *Iwasawa* synthesised metal ion containing IL catalysts by reaction of 1-methyl-3-(trimethoxysilylpropyl)imidazolium chloride and surface silanol groups of silica, followed by the addition of MCl_2 (M = Mn, Fe, Co, Ni, Cu, Pd). However, only the immobilised Cu(II) catalyst containing $[CuCl_4]^{2-}$ ions was very active in the *Kharasch* reaction of styrene with CCl_4.[10] Ionic liquids comprising a tetrachlorocuprate anion, *e.g.* $[DMIM]_2[CuCl_4]$, have also been used as antimicrobial agents.[11] From a mixture of the chlorocuprate(II) containing ionic liquid $[DPYR]_2[CuCl_4]$ (DPYR = 1-dodecylpyridinium) and 6-*O*-palmitoyl ascorbic acid (1 : 1 ratio) CuCl nanoplatelets were obtained.[12] Thus, copper containing ILs are also of interest from the materials chemist's point of view.

Because of the large variety of partly unexpected structural motifs of halocuprates(I)/(II) this field of research is still attracting a lot of interest. In 1976 *Smith* reviewed structural and physical properties of chlorocuprates(II) $A_xCu_yCl_z$, where A is a discrete cation.[13] Ten years later a review dealing with the stacking of planar, bibridged copper(II) halide oligomers was published.[14] Beyond the structural aspect, only a few attempts to design cuprate(II)-based ionic liquids for their use in further transformations were made.[15] Similar to Cu(II), a rich structural diversity in halocuprate(I) complexes is known and has been studied in order to ascertain whether the structural features of complexes can be understood with respect to the reaction parameters used in the synthesis from solution.[16,17,18,19] These studies revealed that both the variable coordination of d^{10} Cu(I) and the tendency of the cuprate(I) species to form polynuclear structures is strongly influenced by the size, the concentration and polarisability of the cations.[20] The relevance of the cation size on the nature of iodocuprates(I) was first recognised by *Hartl* and *Mahdjour-Hassan-Abadi*.[21] Structural motifs and trends in metal coordination numbers in halocuprates(I) and -argentates(I) have been reviewed by *Jagner* and *Helgesson*.[16]

Recently, we studied the influence of the type and amount of added *N*-donor ligand, the anion and the oxidation state on the copper catalysed oxidative carbonylation of methanol to dimethyl carbonate (DMC). We found that 1-methylimidazole (Im^1) has a pronounced effect on the activity and selectivity of

---

[a] *Fachbereich Chemie, Philipps-Universität Marburg, 35032 Marburg, Germany. E-mail: jsu@staff.uni-marburg.de; Fax: +49 642 1282 5711; Tel: +49 642 1282 5693*
[b] *Department of Chemistry, University of Calgary, 2500, University Drive NW, Calgary AB, Canada T2N 1N4.*
E-mail: thomas.linder@ucalgary.ca; Tel: +1 40 3220 6543

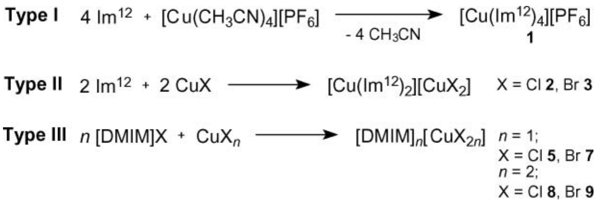
† CCDC reference numbers 769702–769706. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c003948a

neutral catalysts of the type $[(Im^1)_mCuX_n]$ ($m = 2$–4, $n = 1, 2$; X = Cl, Br, I).[22] The aim of the present study is to provide a set of well-defined copper(I)/(II) containing ILs which may serve as fairly lipophilic, redox-active, non-volatile catalysts in a sustainable DMC synthesis. DMC shows great promise for green chemistry concepts: it can be used as a substitute for toxic phosgene or toxic dimethylsulfate in the production of polycarbonates, isocyanates and urethanes.[23] Furthermore, it can be utilised as a non-toxic methylating agent or as a solvent for lithium electrolytes in battery technology.[23]

Results and discussion

Synthesis and characterisation

The neutral *N*-donor ligand 1-dodecylimidazole (Im^{12}) was prepared according to a slightly modified literature method.[47] The *type I* ionic liquid tetrakis(1-dodecylimidazole)copper(I) hexafluorophosphate was prepared at room temperature applying four equivalents of the *N*-donor ligand and one equivalent of $[Cu(CH_3CN)_4][PF_6]$ (Scheme 1).



Scheme 1 Syntheses of *type I*, *type II* and *type III* ILs.

Crystallisation gave analytically pure $[Cu(Im^{12})_4][PF_6]$ (**1**) (mp 27.0 °C). It is interesting to note, that the main peak in ESI-MS (positive mode) corresponds with the cation $[Cu(Im^{12})_2]^+$ indicating that this linear 14 valence electron (VE) species has a pronounced stability.

This kind of 14 VE cation was also discovered in *type II* ILs: treatment of CuCl and CuBr (or $CuBr{\cdot}SMe_2$), respectively, with an equimolar amount of 1-dodecylimidazole in CH_3CN as mediator at ambient temperature quantitatively leads to a ligand induced dissociation of the relevant coordination polymer into colourless crystalline bis(1-dodecylimidazole)cupronium dihalogenocuprate ILs, namely $[Cu(Im^{12})_2][CuX_2]$ (X = Cl **2**,[24] Br **3**) (Scheme 1). **2** and **3** reveal melting points at 73.0 °C and 66.0 °C, respectively. Whereas these ionic liquids have comparably high melting points, we found that some of the analogous compounds $[Cu(Im^n)_2][CuX_2]$ ($n = 2, 4, 6, 8$; X = Cl, Br) are even RTILs. Their synthesis, characterisation and applications tested at the moment will be reported in a forthcoming contribution. Provided that the synthesis is done strictly under inert gas, this is one of the simplest processes for the synthesis of a pure IL as we do not face any problems with respect to impurities by other ions. Interestingly, under identical conditions CuI does not dissociate into a salt. Instead, the crystalline, neutral hexameric compound $[Cu(Im^{12})I]_6$ (**4**) was isolated from highly concentrated CH_3CN solution. Even at a higher molar ratio of Im^{12} : CuI = 2 : 1, no well-characterised ionic species such as $[Cu(Im^{12})_2]I$ or polynuclear iodocuprates(I) were obtained. It was pointed out by *Andersson* and *Jagner* that miscellaneous efforts using large cations to prepare a crystalline mononuclear diiodocuprate(I) anion $[CuI_2]^-$ failed. Instead, polynuclear iodocuprates(I) revealing anions such as $[Cu_2I_4]^{2-}$, $[Cu_5I_7]^{2-}$, $[Cu_3I_4]^-$ or $[Cu_2I_3]^-$ were obtained.[20] As the melting point (76.7 °C) of the neutral hexamer **4** is very close to that of the ionic chloro and bromo species **2** and **3**, we believe that the sum of *van der Waals* forces between the anti-colinear packed alkyl chains tends to have a stronger impact on the melting point than anion-cation interactions.

Type III ILs contain 1-alkyl-3-methylimidazolium cations with long carbon chains in order to lower their solubility in water, the by-product of the DMC synthesis. *Type III* ILs $[DMIM]_n[CuX_{2n}]$ ($n = 1$, X = Cl **5**, Br **7**; $n = 2$, X = Cl **8**, Br **9**) were obtained by conversion of [DMIM]X (X = Cl, Br)[25] and the required amount of the corresponding Cu(I)/(II) halide CuX_n ($n = 1, 2$; X = Cl, Br) using very small amounts of CH_3CN as mediator (Scheme 1). Interestingly, single crystals grown from a supercooled liquid sample of **5** (mp −16.2 °C) contained two different cuprate(I) species in the unit cell, the expected dichlorocuprate anion $[CuCl_2]^-$ and the trichlorocuprate anion $[CuCl_3]^{2-}$. Consequently, we synthesised this compound (**6**) purposely for reasons of further characterisation (mp 26.2 °C). IL **7** (mp 26.7 °C) also crystallises in an unexpected way, namely as its tetramer $[DMIM]_4[Cu_4Br_8]$. *Type III* ILs $[DMIM]_2[CuX_4]$ (X = Cl **8**, Br **9**), both revealing their melting point at 27.3 °C, were obtained similarly to **5** and **7** (Scheme 1). Though the tetrachlorocuprate(II) **8** has already been mentioned in literature as an antibacterial agent,[11] its synthesis and characterisation is described herein for the first time, to the best of our knowledge.

All the ionic liquids **1–3** and **5–9** are stable at ambient temperature and at their melting points under inert gas atmosphere. Crystal structure analysis, ^1H and ^{13}C NMR spectroscopy, ESI mass spectrometry, elemental analysis, thermogravimetric analysis and differential scanning calorimetry were applied to identify and characterise the compounds. In general, in the case of compounds **1–4** the chemical shifts of the aromatic protons and those of the NCH_2 group are shifted downfield with respect to the free 1-dodecylimidazole upon complexation. Similarly, a downfield shift of the methylene carbon atom directly bonded to the imidazole is observed in the ^{13}C NMR spectra, except for the hexameric compound **4**, for which this signal could not be detected. It can be assumed that the positive charge at the copper(I) ion exerts influence on the imidazole ring. In all cases the aromatic signals are not observed in the ^{13}C NMR spectra which is in agreement with the fact that the signals of the corresponding protons are very broad at room temperature. By means of VT ^1H NMR measurements we observe baseline separated signals for the neighbouring protons 4 and 5 of the imidazole ring and a sharp signal for the aromatic proton in 2-position at 233 K. In case of *type I* and *type II* ionic liquids the counter anions seem to have no influence on the chemical shifts as the NMR data of the Cu(I) complexes **1–4** differ only marginally.

For the 1-dodecyl-3-methylimidazolium halocuprate(I) ILs **5–7** we assume the existence of some cation-anion interactions even in solution, *i.e.* hydrogen bonds between the anion and the proton in 2-position of the imidazolium ring. The corresponding shifts for δ_H and δ_C differ significantly from the relevant starting materials [DMIM]X (X = Cl, Br). Deduced from increasing deshielding of the C-2 and H-2 signals the order of the hydrogen bond strength is as follows: $[CuBr_2]^- \approx [CuCl_2]^- <$ $[CuCl_2]^-/[CuCl_3]^{2-} \approx Br^- < Cl^-$. In the case of the paramagnetic tetrahalocuprate-based compounds **8** and **9** the ^1H NMR spectra expectedly show broadened signals. The C-2 signals of both compounds are shifted upfield by several ppm compared to the corresponding signals of the respective starting material.

Crystal structures of $[Cu(Im^{12})_4][PF_6]$ (**1**), $[Cu(Im^{12})_2][CuBr_2]$ (**3**), $[Cu(Im^{12})I]_6$ (**4**), $[DMIM][CuCl_2]\cdot[DMIM]_2[CuCl_3]$ (**6**) and $[DMIM]_4[Cu_4Br_8]$ (**7**) were determined by single crystal XRD analyses. Colourless prismatic crystals of **1** were obtained from MeOH solution at room temperature. In the case of the cupronium dihalogenocuprate(I) **3** colourless crystal plates suitable for X-ray structural analysis were grown from CH_3CN–Et_2O at −20 °C. Colourless prismatic crystals of **4** were obtained from CH_3CN at room temperature. For **6** and the *type III* IL **7**, colourless crystal plates were grown from the melt of **5** at room temperature and from CH_3CN–EtOAc at 4 °C, respectively. Details of the crystal data of all compounds are given in the Experimental section. All but one copper(I) containing compounds crystallise in the triclinic space group $P\bar{1}$ with $Z = 2$. The hexameric compound **4** crystallises in the very same space group, but with $Z = 1$.

The molecular structure of $[Cu(Im^{12})_4][PF_6]$ (**1**) with the partial atomic numbering scheme is depicted in Fig. 1. The copper ion in complex **1** reveals the most common coordination of Cu(I) which is the tetrahedral one. The four chemically equivalent, but crystallographically different, 1-dodecylimidazole ligands are connected to the copper(I) ion *via* the *N*-donor atoms. It is worth having a look at the steric arrangement of the alkyl moieties, at which two assumptions have to be made: 1. The imidazole rings can be considered as planar and 2. the *N*-atom is sp^2 hybridised and thus trigonal planar coordinated. The alkyl chains of all four ligands show significant deviations from the almost ideal ring planes as the corresponding dihedral angles, *e.g.* C101-N102-C104-C105 for ligand 1, are as follows: 82.4° (ligand 1) 54.6° (ligand 2), 84.4° (ligand 3) and 79.4° (ligand 4). Ligand 1 reveals an additional characteristic as the torsion angle N102-C104-C105-C106 determined at 60.5° means that the hydrogen atoms of C105 and C106 adopt approximately a *gauche* conformation. The reason for the observed geometry is that the *van der Waals* forces between the alkyl chains seem to have the strongest impact on the lattice structure so that an anti-colinear zig-zag arrangement of the alkyl moieties is aimed for “at all costs”. Consequently, a laminar lattice structure is formed revealing a Cu(I)-Cu(I) layer-to-layer distance of 21.0 Å.

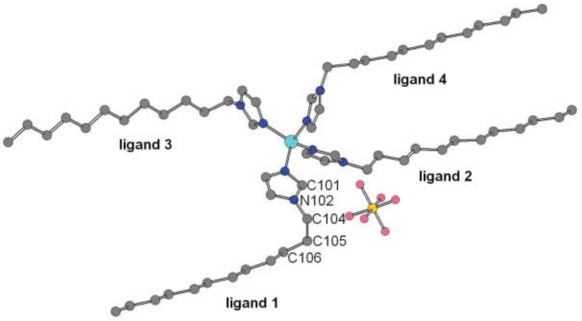


Fig. 1 Molecular structure of the *type I* IL $[Cu(Im^{12})_4][PF_6]$ (**1**).

No cation-anion contacts are observed as the shortest distance between copper and a fluorine atom of PF_6^- is found to be 4.8 Å.

Fig. 2 shows the molecular structure of **3** with the partial atomic numbering scheme. At this point it should be mentioned that the molecular structures of the two *type II* ILs $[Cu(Im^{12})_2][CuCl_2]$[24] and $[Cu(Im^{12})_2][CuBr_2]$ (**3**) show only marginal differences, as expected. The Cu(I) complex **3** has two Cu(I) ions with nearly linear coordination each.

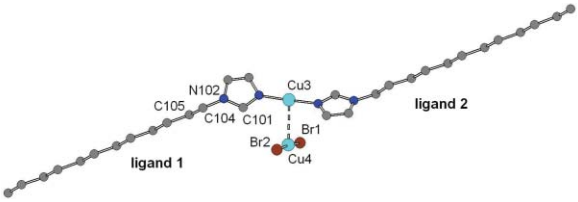


Fig. 2 Molecular structure of the *type II* IL $[Cu(Im^{12})_2][CuBr_2]$ (**3**).

There are only a few examples of structurally characterised compounds revealing Cu(I) ions with two *N*-donors in their coordination sphere,[26] whereas anions such as $[CuCl_2]^-$ are known very well.[27] The steric arrangement of the cationic and anionic species of **3** is as follows: the coordination axes N–Cu–N and Br–Cu–Br are twisted with respect to each other, namely at 82.6°. The torsion angles differ significantly from 90°, contrary to the compound $[CuL^1][CuCl_2]$ (L^1 = octamethyl-5,5′-di(2-pyridyl)ferrocene)[28] showing near orthogonality for the corresponding coordination axes: N1-Cu1-Cu2-Cl1 = 85.5°, N2-Cu1-Cu2-Cl2 = 89.4°.[26] Within the molecular cation of **3** the two imidazole planes are twisted with respect to each other at an angle of 24.1°. As expected for this linear molecular structure the alkyl chains show only marginal deviation from the imidazole ring plane. Thus, the dihedral angles, *e.g.* C101-N102-C104-C105 for ligand 1, are only 64.1° (ligand 1) and 49.4° (ligand 2). As a consequence, the lattice structure of **3** (Fig. 3) is simpler than in the case of **1**. It has to be pointed out that the Cu–Cu distance within the molecular structure of IL **3** is quite short, namely 2.79 Å, compared to that in metallic copper (d(Cu–Cu) = 2.56 Å). This value is similar to that reported for $[CuL^1][CuCl_2]$ (d(Cu1-Cu2) = 2.81 Å).[28] The short Cu–Cu distance and the perpendicular orientation of the N–Cu–N and Br–Cu–Br axes is a consequence of cation-anion electrostatic attraction and steric repulsion. Expectedly, the lattice structure of **3** (Fig. 3) also reveals a metallo-laminate structure with the alkyl chains arranged antiparallel due to *van-der-Waals* interactions.

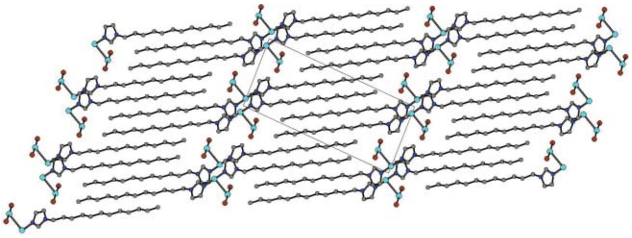


Fig. 3 Lattice structure of **3**, view along the *a*-axis.

The nitrogen coordinated Cu(I) ions of the organic-inorganic hybrid material are separated from each other by a laminar organic layer with a thickness of 20.7 Å. It is obvious that the copper(I) ions of the corresponding dibromocuprate(I) anions show the very same distance.

Even though the neutral hexameric compound $[Cu(Im^{12})I]_6$ (**4**) does not fit in the context of ionic liquids, its hexameric formula unit will be discussed very shortly. The partial atomic numbering scheme is depicted in Fig. 4.

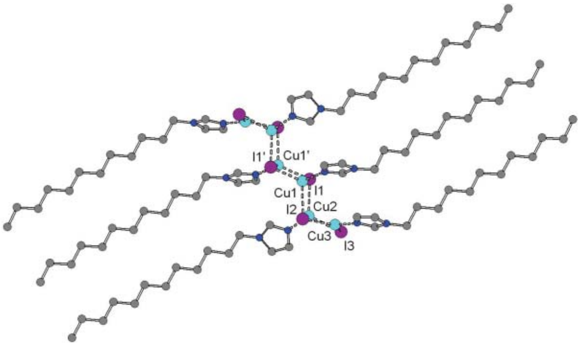


Fig. 4 Structural motif of the neutral compound $[Cu(Im^{12})I]_6$ (**4**).

There is a crystallographic centre of inversion at the centre of the Cu1 ··· Cu1′ axis. While Cu1 and Cu2 reveal the coordination number 4, Cu3 shows only the coordination number 3. As a consequence, the bent ladder structure consisting of Cu_2I_2 rings is terminated. To the best of our knowledge **4** is only the second example of an inversion-symmetric hexameric oligomer $[Cu(L)I]_6$. The first example was published by *Cariati et al.* in 2005,[29] who applied 4-(dimethylamino)pyridine as *N*-donor ligand L. The characteristics of their compound agree very well with our findings. Both the hexameric oligomer **4** and that of *Cariati et al.* exhibit covalent character as the average value of the Cu–I distances is 2.65 Å in each case and therefore nearly the same as in the cubic zinc blende structure $[CuI]_n$ (2.63 Å).[30]

After many attempts to grow crystals of $[DMIM][CuCl_2]$ (**5**) from solution we finally obtained crystals directly from the liquid after several months. However, we were surprised by the result of the crystal structure analysis as not only a dichlorocuprate, but also a trichlorocuprate anion was found. A view of the lattice structure of the mixed chlorocuprate(I) $[DMIM][CuCl_2]\cdot[DMIM]_2[CuCl_3]$ (**6**) is given in Fig. 5.

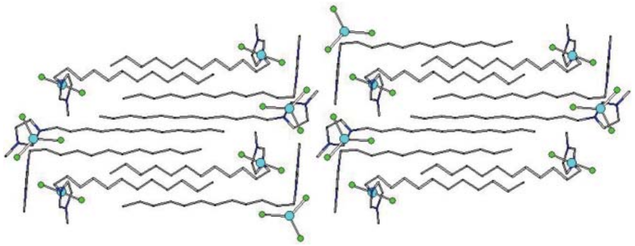


Fig. 5 Molecular packing in the crystal of $[DMIM][CuCl_2]\cdot[DMIM]_2[CuCl_3]$ (**6**), view along the *b*-axis. Turquoise: Cu, green: Cl, dark blue: nitrogen, grey: carbon.

To the best of our knowledge, there exists no further example of a single-crystal structure comprising monomeric $[CuCl_2]^-$ and trigonal planar $[CuCl_3]^-$ ions. However, *Köhn et al*. reported on a compound revealing dimeric $([CuCl_2]^-)_2$ and trigonal planar $[CuCl_3]^-$ ions in the crystalline state.[31] Having a look at the lattice structure of **6** it becomes obvious again that it is dominated by the sum of *van der Waals* forces. Thus, the alkyl chains are in an anti-colinear arrangement which is only reached by the partial bending of the alkyl moieties as already observed for the lattice structure of **1**. In this case the relevant dihedral angles between the alkyl chains and the corresponding imidazole ring planes are 82.7°, 57.7° and 64.6° so that a significant bending is found for all three crystallographically different imidazolium cations. There exist no Cu–Cu contacts. The layer-to-layer distance is the largest of all examples presented herein, namely 25.3 Å.

To the best of our knowledge $[DMIM]_4[Cu_4Br_8]$, the tetramer of IL **7**, is only the second example of a bromocuprate(I) with a tetrameric structure in the crystalline state. The first example, $[hdp]_4[Cu_4Br_8]$ (hdp = 1-hexadecylpyridinium), was reported by *Lang et al*.[32] Another anion of the type $[Cu_4X_8]^{4-}$ containing two four-coordinated and two three-coordinated copper(I) atoms, but iodide instead of bromide, was published by *Hartl*.[33] In contrast to the compound discussed by *Lang et al.*,[32] the crystal structure of **7** shows two independent tetrameric species $[Cu_4Br_8]^{4-}$ in the unit cell. For reasons of distinguishing the two chemically equivalent, but crystallographically different, anions they are labelled **A** and **B** (Fig. 6).

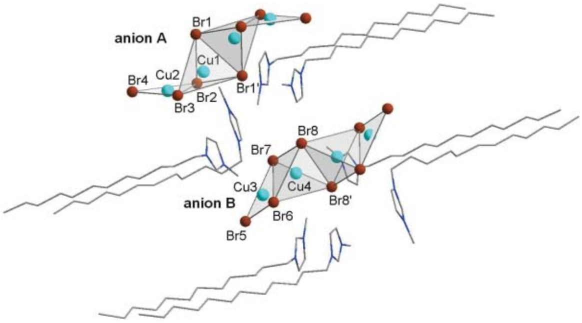


Fig. 6 Molecular packing in the crystal of the *type III* IL **7**.

The two independent tetranuclear, centrosymmetrical anions **A** and **B** incorporate two slightly distorted tetrahedra $[CuBr_4]$ connected by the edges. Additionally, each tetrahedron shares one edge with an almost ideal trigonal planar $[CuBr_3]$ group, in which the Br–Cu–Br angles are in the range of 115.6° to 124.3°. On the contrary, $[hdp]_4[Cu_4Br_8]$ reveals a significant distortion of the trigonal planar geometry, as the corresponding values are between 109.5° and 129.0°. Interestingly, the Cu–Cu distances within the tetrameric anions range from 2.67 Å to 3.05 Å, in part even shorter than in the case of the cupronium-cuprate **3**. The layer-to-layer distance of this organic-inorganic hybrid material is 24.6 Å.

Thermal analysis methods - TGA and DSC

As the copper-containing ionic liquids presented herein have been tested as catalysts in the synthesis of dimethyl carbonate and are currently applied in gas absorption experiments, it is mandatory to know the operating range of these compounds. The melting points were determined *via* DSC, the decomposition points (defined at 5% weight loss) by means of TGA. All sample preparations were done in a glovebox, all measurements were taken under nitrogen atmosphere. Provided that the long-term thermal stability does not differ too much from that value defined *via* dynamic TGA the operating range of the ILs can be assumed as presented in Fig. 7.

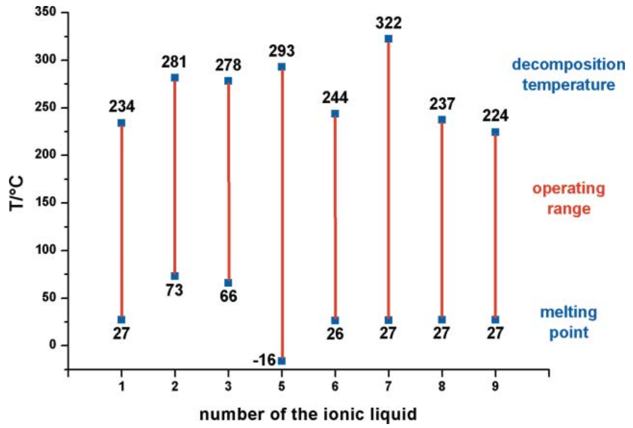


Fig. 7 Operating range of the novel ILs [Cu(Im^{12})$_4$][PF$_6$] (**1**), [Cu(Im^{12})$_2$][CuCl$_2$] (**2**), [Cu(Im^{12})$_2$][CuBr$_2$] (**3**), [DMIM][CuCl$_2$] (**5**), [DMIM][CuCl$_2$]·[DMIM]$_2$[CuCl$_3$] (**6**), [DMIM][CuBr$_2$] (**7**), [DMIM]$_2$[CuCl$_4$] (**8**), [DMIM]$_2$[CuBr$_4$] (**9**).

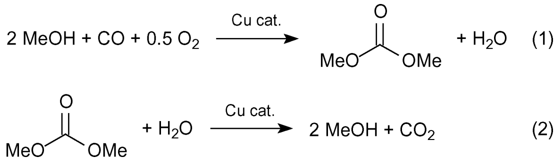
Among the ionic liquids **1–3**, comprising the neutral ligand Im^{12}, the melting point of the hexafluorophosphate based compound (**1**) is about 40 K lower than those of the dihalogenocuprate based ILs (**2**, **3**). This might be due to two different reasons: firstly, the less ordered lattice structure of **1** and secondly, the comparatively weaker interaction of the PF_6^- anion of **1** with the cation. The dihalogenocuprate anions interact weakly with the cupronium cations, which can be proven by the above-mentioned comparatively short Cu–Cu distances.

Comparing the melting points of ILs with [Cu(Im^{12})$_2$]$^+$ and [DMIM]$^+$, respectively, the melting points reveal the following dependence on the anion: [CuCl$_2$]$^-$ > [CuBr$_2$]$^-$ for the cupronium based ILs and the other way round, *i.e.* [CuBr$_2$]$^-$ > [CuCl$_2$]$^-$, for the imidazolium based ones. The first observation is in accordance with the general finding that, in most cases, an increasing size of the anionic species with an identical charge, *i.e.* a good distribution of charge, leads to a decrease in the melting point.[34] The second result might be the consequence of the tetrameric nature of the bromocuprate(I) anion in **7**.

As the oxidative carbonylation of MeOH to DMC is performed at 120 °C, it is a mandatory assumption for the choice of a potential catalyst that its decomposition only begins well above the reaction temperature. By means of Fig. 7 it can be established that this condition is fulfilled by all novel ILs presented herein. However, it should be taken into account that high decomposition temperatures do not imply long-term thermal stability at or below these temperatures.[35]

Copper-containing ILs in the oxidative carbonylation of methanol

Associated with the ENICHEM process, an important industrial catalytic procedure for the production of dimethyl carbonate (DMC),[36] there exists an intrinsic problem which has to be resolved (Scheme 2): the very same copper species which is performing the redox reaction (1) yielding one equivalent DMC and one equivalent of the by-product water may also serve as a *Lewis* acid in the undesired hydrolysis of DMC - or intermediates in the catalytic cycle - to MeOH and CO_2 (2).



Scheme 2 Oxidative carbonylation of MeOH to DMC (ENICHEM).

Besides this selectivity problem there can be found several problems in the patent literature: poor conversions (30% per batch),[37] low selectivities,[38] reactor corrosion[39,40] or the problem of separating suspended catalyst salts.[41] In order to avoid those disadvantages BAYER applied an inorganic molten salt mixture, *i.e.* an eutectic mixture of CuCl and KCl.[42,43] As already mentioned we recently found that the *Lewis* acidity of Cu(II) chloride can be "buffered", while redox activity and dioxygen uptake is promoted by 1-alkylimidazole ligands at copper, at which a higher selectivity is obtained.[22] Thus, we ideally combined the molten salt approach of BAYER and our own results to design and test new copper-containing catalytic ionic liquids (CIL). In order to check if the herein presented copper-containing ILs are generally able to catalyse the synthesis of DMC, we started using 5 mol% Cu with respect to MeOH. Thus, differences in selectivity and conversion are displayed in a better way than by using the CIL as solvent. For the purpose of comparison we also tested two *in situ* mixtures, namely [CuCl + 4 Im^{12}] and [CuCl + 4 Im^1], most probably yielding the ILs [Cu(Im^n)$_4$]Cl (n = 1, 12) analogous to **1**. The results obtained by applying *method A* (Experimental section), except those of the catalytic runs with the ILs **5**, **7**, **8** and **9** (prepared *in situ*), are listed in Table 1. The reason for omitting the catalytic activities of **5**, **7**, **8** and **9** is that these very corrosive 1,3-dialkylimidazolium based ILs reveal unreproducible mass balances, presumably due to side reactions.

The best catalysts are the dihalogenocuprates **2** and **3**, in which the bromide containing one gives slightly better results for both conversion and selectivity. In accordance with our previous studies on neutral copper 1-alkylimidazole complexes as catalysts[22] we find that the presence of chloride or bromide is essential for the catalyst performance. The PF_6^- salt **1** shows much lower values for conversion and selectivity. Furthermore, 1-alkylimidazole ligands at copper tend to promote the O_2 uptake and to inhibit steel corrosion.[22]

In further experiments we studied the catalytic performance of the best catalyst presented herein, [Cu(Im^{12})$_2$][CuBr$_2$] (**3**), at different catalyst concentrations (0.5–5 mol% Cu with respect

Table 1 Catalyst activities in synthesis of DMC[a]

Catalyst	Conversion/%	Selectivity/%
[Cu(Im^{12})$_4$][PF$_6$] (**1**)	31	58
[Cu(Im^{12})$_2$][CuCl$_2$] (**2**)	60	83
[Cu(Im^{12})$_2$][CuBr$_2$] (**3**)	62	89
[CuCl + 4 Im^{12}]	48	78
[CuCl + 4 Im^1]	45	73

[a] Reaction conditions: 5 mol% Cu (total) with respect to MeOH (30 mmol), 3 bar O_2, 50 bar CO, 4 h, 120 °C.

Table 2 Variation of catalyst concentration[a]

Catalyst/mol%	0.5	1.0	2.0	5.0
Conversion/%	32	37	40	44
Selectivity/%	88	79	85	88

[a] Reaction conditions: catalyst **3** (x mol% Cu with respect to MeOH), 150 mmol MeOH, 5 bar O_2, 35 bar CO, 4 h, 120 °C.

to MeOH) and in a long-term experiment. For this purpose, we upscaled the reaction according to *method B* (Experimental section). The results are given in Table 2.

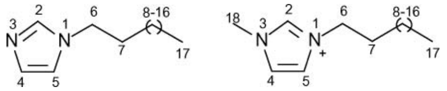
As expected, the conversion increases with an increasing molar concentration of copper. In a batch reaction - as performed in our case - the conversion is limited by the amount of O_2 initially fed to the CO/O_2 mixture. The selectivity can be considered as nearly constant. In order to check the long-term stability of catalyst **3** we did five successive runs using the very same catalyst load (5 mol% Cu with respect to MeOH) each and applying *method B* (Experimental section). Thus, the CIL **3** was treated at temperatures from 120 °C to 180 °C over a period of 24 h. The conversions and selectivities were identical within the accuracy of measurement.

Moreover, we tried to figure out the reasons for the above-mentioned problems concerning the application of 1,3-dialkylimidazolium halocuprates(I/II). Thus, two compounds were generated *in situ* under the conditions of *method B* applying 1 mol% Cu with respect to MeOH: 1. [EMMIM][$CuCl_2$] (EMMIM = 1-ethyl-2,3-dimethylimidazolium), not containing an acidic proton in the 2-position of the imidazolium ring, and 2. [DPYR][$CuCl_2$], as a non-imidazolium based compound. Although the acidic proton in 2-position is absent in [EMMIM][$CuCl_2$], this compound is as corrosive to V4A steel as all the herein presented and tested 1,3-dialkylimidazolium based ILs. Consequently, the corrosion is not simply induced by deprotonation in 2-position in the presence of O_2 and subsequent formation of HCl or HBr. Furthermore, we found that [EMMIM][$CuCl_2$] yields reproducible values for conversion (31%) and selectivity (79%), which means that the poor mass balances are not an intrinsic problem concerning imidazolium based ILs. [DPYR][$CuCl_2$] causes no corrosion and leads to reproducible results for conversion (29%) and selectivity (88%).

Experimental

All operations were carried out under argon using vacuum line and standard *Schlenk* techniques. Solvents were used after drying and purification according to generally used methods under inert atmosphere.[44] After pre-desiccation and distillation the solvents were stored in absorption columns over Al_2O_3/molecular sieve 3 Å/R3-11G-catalyst (BASF AG). The following compounds were synthesised according to literature: CuCl,[45] CuBr[45] and [$Cu(CH_3CN)_4$][PF_6].[46] The synthesis of 1-dodecylimidazole (Im^{12}) was performed by modification of the procedure of *Kucharski et al.*,[47] the syntheses of the 1-dodecyl-3-methylimidazolium halides ([DMIM]X, X = Cl, Br) analogous to *Dupont et al.*[25] CO (3.5) and O_2 (4.8) were obtained from MESSER GRIESHEIM.

Melting points were measured by differential scanning calorimetry *via* a DSC 821^e calorimeter (Fa. METTLER TOLEDO) with a heating rate of 10 °C min^{-1}. Thermogravimetric analysis (TGA) was performed using a TGA/SDTA 851^e apparatus (Fa. METTLER TOLEDO) between 25 and 800 °C; the heating rate was 10 °C min^{-1}. ESI mass spectra were recorded on a FINNIGAN TSQ 700 spectrometer. If the peaks are assigned, the observed isotopic pattern is consistent with the simulated natural isotopic distribution. ^1H and ^{13}C NMR spectra were acquired on a BRUKER AC 300 spectrometer. Chemical shifts δ are reported in ppm relative to tetramethylsilane (TMS). The atom numbering is according to Scheme 3. Coupling constants $^nJ_{xy}$ are given in Hz, but only quoted if reasonable, *i.e.* if the corresponding ones can be determined.



Scheme 3 Atomic numbering scheme of Im^{12} and [DMIM]$^+$.

IR spectra were recorded on a BRUKER ALPHA ATR-FT-IR spectrometer when the remark (substance) is given and on a NICOLET 510 M FT-IR spectrometer using KBr single crystal plates when (Nujol) is noted. Elemental analyses were carried out on a HERAEUS CHN rapid analyser. For sonication a BANDELIN (Model Sonorex Super RK 103 H, ultrasonic frequency 35 kHz) was used at room temperature. X-ray data collections were performed at 100 K or 193 K *via* area-detector diffractometers (IPDS I, IPDS II, STOE) using graphite-monochromatised Mo-K_α-radiation (λ = 71.073 pm). For the purpose of structure solution the programmes SHELXS-86, SHELXS-97, SHELXL-97 (*Sheldrick*[48]), SIR92, SIR97 (*Giacovazzo et al.*[49,50]), STOE IPDS software (STOE[51]) were applied. The molecular structure diagrams were produced using Diamond 3.1.[52]

All catalytic experiments were carried out in a 100 mL V4A stainless steel autoclave with a glass insert and a Teflon®-coated magnetic stirring bar. The autoclave was sealed with an EPDM O-ring and equipped with a 100 bar manometer as well as with a Pt-100-thermoelement in the aluminium heating block for the purpose of temperature control (±1 °C). All organic catalysis products were analysed by quantitative gas chromatography *via* a HRGC 5300 (CARLO ERBA INSTRUMENTS) equipped with a deactivated fused silica guard column (5 m × 0.53 mm, Fa. J & W SCIENTIFIC) and a Rtx™-200 analytical column (30 m × 0.53 mm × 0.50 µm, Fa. RESTEK); *method A*: split injector (1 : 20); FID temperature 200 °C, isothermal at 100 °C, toluene as internal standard (IS), methyl propyl ketone as diluting solvent; *method B*: split injector (1 : 20); FID temperature 200 °C, temperature profile: 90 °C (1 min) → 250 °C (45 °C min^{-1}, 12 min), toluene as IS, cyclohexanone as diluting solvent.

Catalysis

The values for conversion and selectivity given in the tables are based on the average of at least two experiments that have been reproduced within the accuracy of measurement.

Experimental procedure with isolated catalyst

Method A: The glass insert filled with the copper complex (5 mol% Cu with respect to MeOH) and methanol (961 mg, 30 mmol) was placed into the autoclave, followed by sonication for ten minutes to homogenise the reaction mixture. The autoclave was filled at room temperature with 3 bar O_2 and additional 50 bar CO. After disconnecting from the gas supply the autoclave was put into a preheated (150 °C) aluminium heating block. Within 5 min the autoclave reached the reaction temperature of 120 °C at which its content was stirred for 4 h. When starting depressurisation the temperature of the aluminium heating block was raised to 180 °C and the autoclave was depressurised over a period of 10 min *via* two liquid nitrogen traps connected consecutively. Finally, all volatiles were collected at 180 °C and 10^{-2} mbar in the very same traps. To the condensate toluene (500 µL) as IS was added. After diluting the condensate with 10 mL methyl propyl ketone the homogeneous mixture was analysed by quantitative gas chromatography. Identification and quantification of the products was achieved by comparison of retention times and calibrated integrals with an authentic sample.

Method B: A fivefold amount was used with respect to MeOH (4.81 g, 150 mmol) and 5 bar O_2 and 35 bar CO were applied. After having followed *method A* in all other details the condensate was treated as follows: toluene (369 mg, 4 mmol) as IS was added to the condensate. After diluting 50 µL of this mixture with cyclohexanone (950 µL) the homogeneous mixture was analysed by quantitative gas chromatography. Identification and quantification of the products was achieved by external calibration with internal standard.

Experimental procedure with catalyst prepared *in situ*

The anhydrous copper salt (5 mol% Cu with respect to MeOH) and Im^{12} or [DMIM]X (X = Cl, Br; molar quantities dependent on the desired ILs) as well as MeOH (961 mg, 30 mmol) were placed into the autoclave and the procedure described above was followed.

Preparation of the complexes

$[Cu(Im^{12})_4][PF_6]$ (1). To a *Schlenk* flask charged with $[Cu(CH_3CN)_4][PF_6]$ (186 mg, 0.50 mmol) 1-dodecylimidazole (Im^{12}) (473 mg, 2.00 mmol) was added. The reaction vessel was placed in an ultrasonic bath at ambient temperature for *ca.* 10 min. The CH_3CN released from the Cu(I) salt was removed *in vacuo* and the colourless viscous residue was dried by freeze-drying to give $[Cu(Im^{12})_4][PF_6]$ (**1**) (574 mg, 99%) as a colourless solid (Found: C, 62.15; H, 9.74; N, 10.13. $C_{60}H_{112}CuF_6N_8P$ requires C, 62.44; H, 9.78; N, 9.71%); mp 27.0 °C (from MeOH), decomp. 234.0 °C; δ_H(300.1 MHz; CD_3CN) 0.88 (3 H, t, CH_3), 1.26 (18 H, br s, CH_2(8–16)), 1.68–1.84 (2 H, m, CH_2(7)), 3.98 (2 H, t, CH_2(6)), 6.75–7.40 (2 H, m, CH(4,5)) and 7.67 (1 H, br s, CH(2)); δ_C(75.5 MHz; CD_3CN) 14.4 (CH_3), 23.4, 27.1, 29.7, 30.1, 30.2, 30.3, 30.4, 31.5, 32.7 (CH_2(7–16)) and 48.1 (CH_2(6)); *m/z* (ESI; CH_3CN) 237.2325 ($[C_{15}H_{28}N_2+H]^+$, 47%. $C_{15}H_{29}N_2$ requires 237.2325), 340 (56) and 535.3793 ($[C_{30}H_{56}CuN_4]^+$, 100. $C_{30}H_{56}CuN_4$ requires 535.3796); *m/z* (negative ESI; CH_3CN) 144.9645 ($[PF_6]^-$, 100%. F_6P requires 144.9647) and 313 ($[2\ PF_6 + Na]^-$, 43). IR (substance) ν_{max}/cm^{-1} = 3138w, 2922vs, 2852vs, 1684w, 1516s, 1465s, 1403, 1376, 1284, 1236s, 1108s, 1088s, 1032, 836vs, 732s, 661s, 627 and 557s. Single crystals of **1** were obtained from MeOH at room temperature, mounted in inert oil and transferred to the cold N_2 stream of the diffractometer.

$[Cu(Im^{12})_2][CuCl_2]$ (2). To a *Schlenk* flask filled with CuCl (1.21 g, 12.22 mmol) a solution of Im^{12} (3.06 g, 12.95 mmol) in CH_3CN (5 mL) was added. It was placed in an ultrasonic bath at ambient temperature for about 30 min. The solvent was removed *in vacuo* and the precipitate was washed with ether and dried under vacuum to give $[Cu(Im^{12})_2][CuCl_2]$ (**2**) (4.06 g, 99%) as a fine crystalline colourless solid (Found: C, 53.87; H, 8.58; N, 8.45. $C_{30}H_{56}Cl_2Cu_2N_4$ requires: C, 53.72; H, 8.41; N, 8.35%); mp 73.0 °C (from CH_3CN), decomp. 281.4 °C; δ_H(300.1 MHz; CD_3CN) 0.88 (3 H, t, CH_3), 1.26 (18 H, br s, CH_2(8–16)), 1.69–1.85 (2 H, m, CH_2(7)), 4.01 (2 H, t, CH_2(6)) and 7.11–8.68 (3 H, m, Im-H); δ_C(75.5 MHz; CD_3CN) 14.4 (CH_3), 23.4, 27.0, 29.7, 30.0, 30.1, 30.2, 30.3, 30.8, 31.2, 32.6 (CH_2(7–16)) and 48.9 (CH_2(6)); *m/z* (ESI; CH_3CN) 237 ($[C_{15}H_{28}N_2 + H]^+$, 83%), 340 (80) and 535.3793 ($[C_{30}H_{56}CuN_4]^+$, 100. $C_{30}H_{56}CuN_4$ requires 535.3796); *m/z* (negative ESI; CH_3CN) 132.8681 ($[CuCl_2]^-$, 33%. Cl_2Cu requires 132.8679), 179 (100), 223 (74), 233 (23), 277 (22), and 323 (19). IR (substance) ν_{max}/cm^{-1} = 3122, 3051w, 2949, 2916vs, 2847s, 1690w, 1610w, 1533, 1520, 1466, 1442, 1399w, 1375, 1357, 1288, 1255w, 1240, 1110s, 1053, 1039, 1026, 1006w, 962, 890w, 845, 833, 757vs, 730, 721, 654s, 630, 506w, 444w and 428w.

$[Cu(Im^{12})_2][CuBr_2]$ (3). Applying the very same procedure as in the case of **2**, but involving $CuBr{\cdot}SMe_2$ or CuBr instead of CuCl, $[Cu(Im^{12})_2][CuBr_2]$ (**3**) was obtained in quantitative yield as a colourless solid (Found: C, 47.44; H, 7.53; N, 7.32. $C_{30}H_{56}Br_2Cu_2N_4$ requires C, 47.43; H, 7.43; N, 7.38%); mp 66.0 °C (from CH_3CN), decomp. 278.3 °C; δ_H(300.1 MHz; CD_3CN) 0.88 (3 H, t, CH_3), 1.26 (18 H, br s, CH_2(8–16)), 1.76 (2 H, quintet, ^3J 7.1, CH_2(7)), 3.99 (2 H, t, ^3J 7.2, CH_2(6)), 6.78–7.48 (2 H, m, CH(4–5)) and 7.67–8.11 (1 H, m, CH(2)); δ_C(75.5 MHz; CD_3CN) 14.4 (CH_3), 23.4, 27.0, 29.7, 30.0, 30.1, 30.2, 30.3, 30.9, 31.3, 32.6 (CH_2(7–16)) and 48.8 (CH_2(6)); *m/z* (ESI; CH_3CN) 237 ($[C_{15}H_{28}N_2 + H]^+$, 45%), 340 (24) and 535.3786 ($[C_{30}H_{56}CuN_4]^+$, 100. $C_{30}H_{56}CuN_4$ requires 535.3796); *m/z* (negative ESI; CH_3CN) 222.7651 ($[CuBr_2]^-$, 25%. Br_2Cu requires 222.7648), 264 (57) and 313 (88). IR (substance) ν_{max}/cm^{-1} = 3122, 3112, 3049w, 2949, 2916vs, 2847s, 1685w, 1608w, 1533, 1520, 1465, 1442, 1397w, 1376w, 1341w, 1288, 1255w, 1239, 1110, 1100, 1053w, 1039w, 1026w, 960w, 889w, 843, 832, 755s, 728, 722, 654s, 630, 505w, 444w and 427w. Single crystals of **3** were obtained from CH_3N–Et_2O at −20 °C, mounted in inert oil and transferred to the cold N_2 stream of the diffractometer.

$[Cu(Im^{12})I]_6$ (4). To a *Schlenk* flask charged with CuI (952 mg, 5.00 mmol) a solution of Im^{12} (1.27 g, 5.35 mmol) in CH_3CN (50 mL) was added. After stirring at room temperature for 2 h the solvent was removed under vacuum. The colourless precipitate was washed with ether and dried *in vacuo* to give $[Cu(Im^{12})]_6$ (**4**) (691 mg, 32%) as a colourless solid (Found: C, 41.95; H, 6.93; N, 6.62. $C_{90}H_{168}Cu_6I_6N_{12}$ requires C, 42.21; H, 6.61; N, 6.56%); mp 76.7 °C (from CH_3CN), decomp. 253.5 °C; δ_H(300.1 MHz; CD_3CN) 0.88 (3 H, t, CH_3), 1.27 (18 H, br s, CH_2(8–16)), 1.68–1.86 (2 H, m, CH_2(7)), 4.01 (2 H, t, CH_2(6)) and 7.17–9.41 (3 H, m, Im-H); δ_C(75.5 MHz; CD_3CN) 14.4

(CH_3) and 23.4, 27.1, 29.7, 30.0, 30.1, 30.2, 30.3, 31.3, 32.7 (CH_2(7–16)); *m/z* (ESI; CH_3CN) 237 ($[C_{15}H_{28}N_2 + H]^+$, 25%), 340 (12) and 535 ($[C_{30}H_{56}CuN_4]^+$, 100). IR (Nujol) ν_{max}/cm^{-1} = 3129w, 3111, 1601w, 1524, 1516, 1285, 1235, 1109 s, 1037, 1024, 937, 827, 814, 745, 731, 654, 627 and 619. Applying a CuI : Im[12] ratio of 1 : 2 instead of 1 : 1 yielded the very same result. Single crystals of **4** were grown by means of recrystallisation from CH_3CN at room temperature, mounted in inert oil and transferred to the cold N_2 stream of the diffractometer.

[DMIM][CuCl$_2$] (5). To a *Schlenk* flask filled with CuCl (200 mg, 2.02 mmol) a solution of 1-dodecyl-3-methylimidazolium chloride ([DMIM]Cl) (580 mg, 2.02 mmol) in CH_3CN (5 mL) was added. The reaction vessel was placed in an ultrasonic bath at ambient temperature for about 10 min. The solvent was removed in *vacuo* and the light-yellow highly viscous residue was dried by freeze-drying to give [DMIM][CuCl$_2$] (**5**) (780 mg, quantitative yield) (Found: C, 49.64; H, 7.83; N, 7.32. $C_{16}H_{31}Cl_2CuN_2$ requires C, 49.80; H, 8.10; N, 7.26%); mp −16.2 °C (from CH_3CN), decomp. 293.0 °C; δ_H(300.1 MHz; CD_3CN) 0.80–0.92 (3 H, m, CH_2CH_3), 1.26 (18 H, br s, CH_2(8–16)), 1.72–1.88 (2 H, m, CH_2(7)), 3.78–3.86 (3 H, m, CH_3), 4.06–4.17 (2 H, m, CH_2(6)), 7.30–7.42 (2 H, m, CH(4–5)) and 8.45–8.52 (1 H, m, CH(2)); δ_C(75.5 MHz; CD_3CN) 14.3 (CH_3(17)), 23.3, 26.6, 29.5, 30.0, 30.2, 30.3, 30.6, 32.6 (CH_2(7–16)), 36.9 (CH_3(18)), 50.5 (CH_2(6)), 123.2 (CH(5)), 124.6 (CH(4)) and 136.8 (CH(2)); *m/z* (ESI; CH_3CN) 251.2479 ($[C_{16}H_{31}N_2]^+$, 100%. $C_{16}H_{31}N_2$ requires 251.2482); *m/z* (negative ESI; CH_3CN) 132.8680 ($[CuCl_2]^-$, 90%. Cl_2Cu requires 132.8679), 170 (20), 233 (5) $[Cu_2Cl_3]^-$ and 321 (10). IR (substance) ν_{max}/cm^{-1} = 3140w, 3100, 2921vs, 2852s, 1569, 1464, 1377w, 1338w, 1165s, 1090w, 1022w, 836, 743, 650, 620s and 404. Single crystals grown from the melt at ambient temperature after several months, mounted in inert oil and transferred to the cold N_2 stream of the diffractometer turned out to be [DMIM][CuCl$_2$]·[DMIM]$_2$[CuCl$_3$] (**6**).

[DMIM][CuCl$_2$]·[DMIM]$_2$[CuCl$_3$] (6). The selective synthesis of **6** was carried out as follows: to a *Schlenk* flask filled with CuCl (200 mg, 2.02 mmol) a solution of [DMIM]Cl (869 mg, 3.03 mmol) in CH_3CN (5 mL) was added. The reaction vessel was placed in an ultrasonic bath at ambient temperature for about 10 min. The solvent was removed *in vacuo* and the greyish residue was dried by freeze-drying to give [DMIM][CuCl$_2$]·[DMIM]$_2$[CuCl$_3$] (**6**) (1069 mg, quantitative yield) (Found: C, 53.86; H, 8.65; N, 8.24. $C_{48}H_{93}Cl_5Cu_2N_6$ requires C, 54.46; H, 8.85; N, 7.94%); mp 26.2 °C (from CH_3CN), decomp. 243.7 °C; δ_H(300.1 MHz; CD_3CN) 0.87 (3 H, t, CH_2CH_3), 1.26 (18 H, br s, CH_2(8–16)), 1.82 (2 H, quintet, ^3J 7.0, CH_2(7)), 3.85 (3 H, s, CH_3), 4.15 (2 H, t, ^3J 7.4, CH_2(6)), 7.37–7.40 (1 H, m, CH(5)), 7.40–7.43 (1 H, m, CH(4)) and 8.91 (1 H, s, CH(2)); δ_C(75.5 MHz; CD_3CN) 14.4 (CH_3(17)), 23.4, 26.7, 29.6, 30.0, 30.1, 30.2, 30.3, 30.6, 32.6 (CH_2(7–16)), 36.9 (CH_3(18)), 50.5 (CH_2(6)), 123.2 (CH(5)), 124.5 (CH(4)) and 137.3 (CH(2)); *m/z* (ESI; CH_3CN) 251.2480 ($[C_{16}H_{31}N_2]^+$, 100%. $C_{16}H_{31}N_2$ requires 251.2482); IR (substance) ν_{max}/cm^{-1} = 3138w, 3086, 2950, 2920vs, 2850s, 1639w, 1568, 1464, 1378, 1336, 1288w, 1221w, 1163vs, 1104w, 1020w, 880w, 829, 819s, 763, 723, 652, 642, 618vs, 601 and 411s.

[DMIM][CuBr$_2$] (7). Exerting the very same procedure as in the case of **5**, but using the relevant bromide, [DMIM][CuBr$_2$] (**7**) was obtained in quantitative yield in form of a nearly colourless solid (Found: C, 40.31; H, 6.69; N, 5.86. $C_{16}H_{31}Br_2CuN_2$ requires C, 40.48; H, 6.58; N, 5.90%); mp 26.7 °C (from CH_3CN), decomp. 322.3 °C; δ_H(300.1 MHz; CD_3CN) 0.87 (3 H, t, CH_2CH_3), 1.27 (18 H, br s, CH_2(8–16)), 1.82 (2 H, quintet, ^3J 7.2, CH_2(7)), 3.83 (3 H, s, CH_3), 4.13 (2 H, t, ^3J 7.2, CH_2(6)), 7.35 (1 H, t, ^4J 1.8, CH(5)), 7.38 (1 H, t, ^4J 1.8, CH(4)) and 8.50 (1 H, s, CH(2)); δ_C(75.5 MHz; CD_3CN) 14.4 (CH_3(17)), 23.3, 26.6, 29.6, 30.0, 30.2, 30.3, 30.6, 32.6 (CH_2(7–16)), 37.0 (CH_3(18)), 50.5 (CH_2(6)), 123.2 (CH(5)), 124.6 (CH(4)) and 136.8 (CH(2)); *m/z* (ESI; CH_3CN) 251.2480 ($[C_{16}H_{31}N_2]^+$, 100%. $C_{16}H_{31}N_2$ requires 251.2482); *m/z* (negative ESI; CH_3CN) 222.7651 ($[CuBr_2]^-$, 23%. $CuBr_2$ requires 220.7648), 264 (35) and 314 (23). IR (substance) ν_{max}/cm^{-1} = 3139w, 3099, 3062, 2915vs, 2849vs, 1619w, 1570, 1466, 1429, 1377, 1337, 1284w, 1165vs, 1088w, 1019w, 842, 754, 721, 657, 623, 615 and 412w. Single crystals of **7** were grown from CH_3CN–EtOAc at 4 °C, mounted in inert oil and transferred to the cold gas stream of the diffractometer.

[DMIM]$_2$[CuCl$_4$] (8). To a *Schlenk* flask charged with a melt of anhydrous $CuCl_2$ (67 mg, 0.50 mmol) and [DMIM]Cl (287 mg, 1.00 mmol) CH_3CN (20 mL) were added for reasons of homogenisation. The reaction vessel was placed in an ultrasonic bath at room temperature for about 10 min. The solvent was removed *in vacuo* and the yellow highly viscous residue was dried by freeze-drying to give [DMIM]$_2$[CuCl$_4$] (**8**) as solid (354 mg, quantitative yield) (Found: C, 53.91; H, 8.74; N, 7.65. $C_{32}H_{62}Cl_4CuN_4$ requires C, 54.27; H, 8.82; N, 7.91%); mp 27.3 °C (from CH_3CN), decomp. 237.2 °C; δ_H(300.1 MHz; CD_3CN) 0.80–0.94 (3 H, m, CH_2CH_3), 1.18–1.59 (18 H, m, CH_2(8–16)), 2.09 (2 H, br, CH_2(7)), 4.12 (3 H, br, CH_3), 4.32 (2 H, br, CH_2(6)), 7.41 (2 H, br, CH(4–5)) and 9.33 (1 H, br, CH(2)); δ_C(75.5 MHz; CD_3CN) 13.9 (CH_3(17)), 22.8, 27.9, 29.6, 29.8, 29.9, 30.0, 30.1, 30.2, 32.1 (CH_2(7–16)), 41.7 (CH_3(18)), 54.0 (CH_2(6)), 123.3 (CH(5)), 125.0 (CH(4)) and 130.5 (CH(2)); *m/z* (ESI; CH_3CN) 251.2480 ($[C_{16}H_{31}N_2]^+$, 100%. $C_{16}H_{31}N_2$ requires 251.2482); IR (substance) ν_{max}/cm^{-1} = 3143w, 3100, 2916vs, 2849vs, 1633w, 1571, 1558, 1468, 1431, 1375w, 1340w, 1287w, 1166vs, 1094w, 1022w, 859, 838, 765, 720, 662, 653, 619vs and 412w.

[DMIM]$_2$[CuBr$_4$] (9). Applying the very same procedure as in case of **8** [DMIM]$_2$[CuBr$_4$] (**9**) was obtained in quantitative yield as dark purple solid. (Found: C, 43.81; H, 7.00; N, 6.49. $C_{32}H_{62}Cl_4CuN_4$ requires C, 43.38; H, 7.05; N, 6.32%); mp 27.3 °C (from CH_3CN), decomp. 224.2 °C; δ_H(300.1 MHz; CD_3CN) 0.88 (3 H, t, CH_2CH_3), 1.20–1.62 (18 H, m, CH_2(8–16)), 2.12 (2 H, br, CH_2(7)), 4.17 (3 H, br, CH_3), 4.41 (2 H, br, CH_2(6)), 7.50 (2 H, br, CH(4–5)) and 9.52 (1 H, br, CH(2)); δ_C(75.5 MHz; CD_3CN) 13.8 (CH_3(17)), 22.7, 27.9, 29.4, 29.8, 29.9, 30.0, 30.1, 32.0 (CH_2(7–16)), 41.3 (CH_3(18)), 53.2 (CH_2(6)), 123.5 (CH(5)), 125.2 (CH(4)) and 133.2 (CH(2)); *m/z* (ESI; CH_3CN) 251.2480 ($[C_{16}H_{31}N_2]^+$, 100%. $C_{16}H_{31}N_2$ requires 251.2482); IR (substance) ν_{max}/cm^{-1} = 3133w, 3095, 3056, 2953, 2919vs, 2851vs, 1717w, 1569, 1466, 1428, 1376, 1335w, 1162vs, 1089w, 1020w, 860, 842, 746s, 720, 660, 649 and 621s.

Crystal structure determination

[Cu(Im^{12})$_4$][PF$_6$] (1). $C_{60}H_{112}CuF_6N_8P$, M = 1154.09, triclinic, a = 11.7007(14), b = 13.6056(16), c = 21.043(3) Å, U = 3278.2(7) Å^3, T = 173(2) K, space group $P\bar{1}$ Z = 2, 44190 reflections collected, 12685 independent (R_{int} = 0.1488) which were used in all calculations. The final wR_2 was 0.1142 (all data).

[Cu(Im^{12})$_2$][CuBr$_2$] (3). $C_{30}H_{56}Br_2Cu_2N_4$, M = 759.69, triclinic, a = 9.002(3), b = 9.454(3), c = 20.757(6) Å, U = 1728.4(9) Å^3, T = 193(2) K, space group $P\bar{1}$ Z = 2, 21313 reflections collected, 21313 independent (R_{int} = 0.0000) which were used in all calculations. The final wR_2 was 0.2386 (all data).

[Cu(Im^{12})I]$_6$ (4). $C_{45}H_{84}Cu_3I_3N_6$, M = 1280.50, triclinic, a = 9.755(5), b = 13.580(5), c = 20.657(5) Å, U = 2590.3(6) Å^3, T = 193(2) K, space group $P\bar{1}$ Z = 1, 25669 reflections collected, 9463 independent (R_{int} = 0.0350) which were used in all calculations. The final wR_2 was 0.0787 (all data).

[DMIM][CuCl$_2$]·[DMIM]$_2$[CuCl$_3$] (6). $C_{48}H_{93}Cl_5Cu_2N_6$, M = 1058.16, triclinic, a = 8.8041(4), b = 12.5714(5), c = 25.2820(11) Å, U = 2791.1(2) Å^3, T = 100(2) K, space group $P\bar{1}$ Z = 2, 43338 reflections collected, 11820 independent (R_{int} = 0.0997) which were used in all calculations. The final wR_2 was 0.0914 (all data).

[DMIM]$_4$[Cu$_4$Br$_8$] (7). $C_{64}H_{124}Br_8Cu_4N_8$, M = 1899.15, triclinic, a = 10.3068(13), b = 16.172(2), c = 25.595(4) Å, U = 4093.0(10) Å^3, T = 193(2) K, space group $P\bar{1}$ Z = 2, 40859 reflections collected, 14954 independent (R_{int} = 0.2262) which were used in all calculations. The final wR_2 was 0.1803 (all data).

Conclusions

We synthesised and fully characterised a number of ionic liquids containing copper in the anion or the cation or both. Some of them are RTILs and some turned out to be promising catalysts for the oxidative carbonylation of methanol to dimethyl carbonate. Of particular interest are the unique cupronium cuprate ionic liquids [Cu(Im^{12})$_2$][CuX$_2$] (X = Cl, Br) forming crystalline laminate structures at ambient temperature. However, some of the homologous cupronium cuprates with shorter *N*-alkyl chains are room temperature ionic liquids. This finding opens up new perspectives, namely the use of these catalysts as an IL film on solid supports (SILP concept). This will be the focus of further collaborative studies.

Acknowledgements

We gratefully acknowledge financial support by the DFG priority program SPP 1191 (Su 127/9-2) and stimulating discussions within this community of referees and research partners.

References

1 F. H. Hurley, *US Pat.*, 2 446 331, 1948; F. H. Hurley, *Chem. Abstr.*, 1949, **43**, P7645b.
2 F. H. Hurley and T. P. Wier Jr., *J. Electrochem. Soc.*, 1951, **98**, 207–212.
3 J. A. Boon, J. A. Levisky, J. L. Pflug and J. S. Wilkes, *J. Org. Chem.*, 1986, **51**, 480–483.
4 M. J. Earle, K. R. Seddon, C. J. Adams and G. Roberts, *Chem. Commun.*, 1998, 2097–2098.
5 A. Stark, B. L. MacLean and R. D. Singer, *J. Chem. Soc., Dalton Trans.*, 1999, 63–66.
6 P. N. Davey, C. P. Newman, K. R. Seddon and M. J. Earle, *WO Pat.*, 9 919 288, 1999.
7 P. Wasserscheid and P. Schulz, in *Ionic Liquids in Synthesis*, ed. P. Wasserscheid and T. Welton, WILEY-VCH, Weinheim, 2nd ed., 2008, vol. 2, p. 383.
8 Y. Chauvin, L. Mußmann and H. Olivier, *Angew. Chem.*, 1995, **107**, 2941–2943, (*Angew. Chem., Int. Ed. Engl.*, 1996, **34**, 2698–2700).
9 H. Sun, K. Harms and J. Sundermeyer, *J. Am. Chem. Soc.*, 2004, **126**, 9550–9551.
10 T. Sasaki, C. Zhong, M. Tada and Y. Iwasawa, *Chem. Commun.*, 2005, 2506–2508.
11 M. Earle, K. Seddon, M. Gilea, G. Boberly, B. Gilmore and M. McLaughlin, *WO Pat.*, 125 222, 2009.
12 A. Taubert, *Angew. Chem.*, 2004, **116**, 5494–5496, (*Angew. Chem., Int. Ed.*, 2004, **43**, 5380–5382).
13 D. W. Smith, *Coord. Chem. Rev.*, 1976, **21**, 93–158.
14 U. Geiser, R. D. Willett, M. Lindbeck and K. Emerson, *J. Am. Chem. Soc.*, 1986, **108**, 1173–1179.
15 H. Sun, K. Harms and J. Sundermeyer, *Z. Kristallogr.*, 2005, **220**, 42–44, and references cited therein.
16 S. Jagner and G. Helgesson, *Adv. Inorg. Chem.*, 1991, **37**, 1–45.
17 S. Andersson, M. Håkansson and S. Jagner, *Inorg. Chim. Acta*, 1993, **209**, 195–199.
18 C. Hasselgren, G. Stenhagen, L. Öhrström and S. Jagner, *Inorg. Chim. Acta*, 1999, **292**, 266–271.
19 C. H. Arnby, S. Jagner and I. Dance, *CrystEngComm*, 2004, **6**, 257–275.
20 S. Andersson and S. Jagner, *Acta Chem. Scand., Ser. A*, 1986, **40a**, 52–57, and references cited therein.
21 H. Hartl and F. Mahdjour-Hassan-Abadi, *Angew. Chem.*, 1981, **93**, 804–805, (*Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 772–773).
22 V. Raab, M. Merz and J. Sundermeyer, *J. Mol. Catal. A: Chem.*, 2001, **175**, 51–63.
23 For a review see: D. Delledone, F. Rivetti and U. Romano, *Appl. Catal., A*, 2001, **221**, 241–251.
24 X. Li, M. Merz, J. Kipke, K. Harms and J. Sundermeyer, presented in part, *i.e.* crystal structure of [Cu(Im^{12})$_2$][CuCl$_2$], at the 35th International Conference on Coordination Chemistry (35-ICCC), 2002, Heidelberg.
25 J. Dupont, C. S. Consorti, P. A. Z. Suarez and R. F. de Souza, *Org. Synth.*, 2002, **79**, 236–240.
26 U. Siemeling, U. Vorfeld, B. Neumann and H.-G. Stammler, *Chem. Commun.*, 1997, 1723–1724, and references cited therein.
27 B. J. Hathaway, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, R. Gillard and J. A. McCleverty, Pergamon, Oxford, 1st ed., 1987, vol. 5, pp. 534–774.
28 B. Neumann, U. Siemeling, H.-G. Stammler, U. Vorfeld, J. G. P. Delis, P. W. N. M. van Leeuwen, K. Vrieze, J. Fraanje, K. Goubitz, F. F. de Biani and P. Zanello, *J. Chem. Soc., Dalton Trans.*, 1997, 4705–4711.
29 E. Cariati, D. Roberto, R. Ugo, P. C. Ford, S. Galli and A. Sironi, *Inorg. Chem.*, 2005, **44**, 4077–4085.
30 D. A. Keen and S. Hull, *J. Phys.: Condens. Matter*, 1995, **7**, 5793–5804.
31 R. D. Köhn, G. Seifert, Z. Pan, M. F. Mahon and G. Kociok-Köhn, *Angew. Chem.*, 2003, **115**, 818–820, (*Angew. Chem., Int. Ed.*, 2003, **42**, 793–796).
32 J. Lang, H. Zhu, X. Xin and M. Chen, *Chem. J. Chin. Univ.*, **13**, 18.
33 H. Hartl, *Angew. Chem.*, 1987, **99**, 925–927, (*Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 927–928).
34 P. Wasserscheid and W. Keim, *Angew. Chem.*, 2000, **112**, 3926–3945, (*Angew. Chem., Int. Ed.*, 2000, **39**, 3772–3789).
35 M. Kosmulski, J. Gustafsson and J. B. Rosenholm, *Thermochim. Acta*, 2004, **412**, 47.
36 A. Klausener and J.-D. Jentsch, in *Applied Homogeneous Catalysis with Organometallic Compounds*, ed. B. Cornils and W. A. Herrmann, WILEY-VCH, Weinheim, 1st ed., 1996, vol. 1, p. 175.
37 U. Romano, R. Tesei, G. Cipriani, L. Micucci, *US Pat.*, 4 218 391, 1980.
38 B. K. Nefedov, N. S. Sergeeva and Y. T. Eidus, *Izv. Akad. Nauk SSSR Ser. Khim.*, 1973, **4**, 804–806.

39 T. Yamamoto, K. Imaizumi and Y. Maeda, *Corrosion*, 1989, **45**, 506–509.

40 D. M. Fenton and P. J. Steinwand, *J. Org. Chem.*, 1974, **39**, 701–704.

41 E. Perrotti, G. Cipriani, *DE Pat.*, 2 110 194, 1976.

42 Z. Kricsfalussy, H. Waldmann and H.-J. Traenckner, *EP Pat.*, 0 636 601, 1995.

43 Z. Kricsfalussy, H. Waldmann and H.-J. Traenckner, *Ind. Eng. Chem. Res.*, 1998, **37**, 865–866.

44 W. L. F. Armarego and D. D. Perrin, *Purification of Laboratory Chemicals*, Elsevier, Burlington, 4th ed., 1996.

45 R. N. Keller and H. D. Wycoff, *Inorg. Synth.*, 1946, **2**, 1–4.

46 G. J. Kubas, *Inorg. Synth.*, 1979, **19**, 90–92.

47 S. Kucharski, R. Janik, M. Bryjak, M. Bieńkowski, A. Chyla and J. Sworakowski, *Pol. J. Chem*, 1995, **69**, 447–460.

48 G. M. Sheldrick, *SHELXS-86, SHELXS-97, Programmes for Crystal Structure Solution*, 1986, 1997, Universität Göttingen, Germany; G. M. Sheldrick, *SHELXL-97, Program for refinement of crystal structures*, University of Göttingen, Germany, 1997.

49 A. Altomare, G. L. Cascarano, C. Giacovazzo and A. Guagliardi, *J. Appl. Crystallogr.*, 1993, **26**, 343–350.

50 A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Crystallogr.*, 1999, **32**, 115–119.

51 *STOE IPDS Software*, 1996, Stoe & Cie GmbH, Darmstadt, Germany.

52 K. Brandenburg, *Diamond 3.1, Crystal Impact GbR*, 2005, Bonn, Germany.