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Carboxyl-Functionalized Task-Specific Ionic Liquids for Solubilizing Metal Oxides

Peter Nockemann,*,† Ben Thijs,† Tatjana N. Parac-Vogt,† Kristof Van Hecke,† Luc Van Meervelt,† Bernard Tinant,‡ Ingo Hartenbach,§ Thomas Schleid,§ Vu Thi Ngan,† Minh Tho Nguyen,† and Koen Binnemans†

Department of Chemistry, Katholieke Universiteit Leuven, Celestijnenlaan 200F, bus 2404, B-3001 Leuven, Belgium, Unité CSTR, Université Catholique de Louvain, 1 Place Louis Pasteur, 1348 Louvain-la-Neuve, Belgium, and Institut für Anorganische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart, Germany

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Imidazolium, pyridinium, pyrrolidinium, piperidinium, morpholinium, and quaternary ammonium bis(trifluoromethylsulfonyl)imide salts were functionalized with a carboxyl group. These ionic liquids are useful for the selective dissolution of metal oxides and hydroxides. Although these hydrophobic ionic liquids are immiscible with water at room temperature, several of them form a single phase with water at elevated temperatures. Phase separation occurs upon cooling. This thermomorphic behavior has been investigated by ^{1}H NMR, and it was found that it can be attributed to the temperature-dependent hydration and hydrogen-bond formation of the ionic liquid components. The crystal structures of four ionic liquids and five metal complexes have been determined.

Introduction

Ionic liquids are often considered as “supersolvents” for many classes of organic and inorganic compounds.[1−5] Several remarkable reports on the superior solvent properties of ionic liquids have been published. For instance, cellulose dissolves in 1,3-dialkylimidazolium chloride ionic liquids and can be regenerated from such an ionic liquid solution by the simple addition of water.[6] Also remarkable is the ability of chloroaluminate ionic liquids to dissolve kerogen, i.e., the solid bituminous materials found in oil shales and which are very difficult to dissolve in conventional organic solvents.[7] Although some ionic liquids can dissolve sulfidic ore metals,[8] the inorganic chemist working with ionic liquids is facing the problem that the solubility of ionic inorganic compounds in ionic liquids is often very low.[9,10] This is a consequence of the fact that most of the ionic liquids described in the literature contain weakly coordinating anions like tetrafluoroborate,[11,12] hexafluorophosphate,[13,14] or bis(trifluoromethylsulfonyl)imide.[15] These ionic liquids with fluorinated anions have lower melting points and viscosities than ionic liquids with coordinating anions like chloride or carboxylate ions, but their solvating abilities are very poor.[16] The presently used “second-generation” ionic liquids are much less moisture-sensitive than the so-called “first-generation” haloaluminate ionic liquids,[4,17,18] but they are inferior

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* To whom correspondence should be addressed. E-mail: Peter.Nockemann@chem.kuleuven.be.

† Katholieke Universiteit Leuven.

‡ Université Catholique de Louvain.

§ Universität Stuttgart.

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solvents for inorganic salts. The low solubility of metal salts is a serious drawback for possible applications of ionic liquids that require high concentrations of dissolved metal salts, e.g., the electrodeposition of metals[19,20] or solvents for the synthesis of nanoparticles.[21,22] Unfortunately, quantitative data on the solubility of metal salts in ionic liquids are still very scarce. The mechanism of the solubilization of metal ions in ionic liquids is an issue that needs to be further investigated because it has recently been reported that the coordination environments of the solvates in ionic liquids might be quite unique.[23,24] The solubility of metal salts in ionic liquids can be increased by mixing the ionic liquid with coordinating additives with a low vapor pressure. An example is the addition of poly(ethylene glycol)s to ionic liquids.[25] Other examples are the "deep eutectic solvents" developed by Abbott and co-workers, like a mixture of choline chloride and urea[26,27] or a mixture of choline chloride and carboxylic acids.[28] Furthermore, metal-containing ionic liquids that incorporate the metal ion as a cation or anion exhibit a high miscibility with other ionic liquids.[29−32] Still another approach to increase the solubility of metal salts in ionic liquids is to use ionic liquids with appending coordinating groups. These are the so-called *task-specific ionic liquids*. They were first introduced by Davis and co-workers[33,34] and are actively being explored by other researchers.[35−42] As a rule, these task-specific ionic liquids are not used as single-component ionic liquids, but they are mixed with more conventional ionic liquids. The rationale for using mixtures rather than pure task-specific ionic liquids is that the task-specific ionic liquids often have a higher melting point and a higher viscosity than conventional ionic liquids. Moreover, the conventional ionic liquids are, in general, much cheaper than the task-specific ionic liquids.

Recently, we have reported on the task-specific ionic liquid betainium bis(trifluoromethylsulfonyl)imide, [Hbet][Tf_2N].[43] This ionic liquid, bearing a carboxyl group, has a selective solubilizing ability for metal oxides. Soluble metal oxides are the trivalent rare earths uranium(VI) oxide, zinc(II) oxide, cadmium(II) oxide, mercury(II) oxide, nickel(II) oxide, copper(II) oxide, palladium(II) oxide, lead(II) oxide, and silver(I) oxide. Insoluble or very poorly soluble are oxides of iron, cobalt, aluminum, and silicon. Also, metal hydroxides can be solubilized in this ionic liquid. The metals can be stripped from [Hbet][Tf_2N] by treatment of the ionic liquid with an acidic aqueous solution. After transfer of the metal ions to the aqueous phase, the ionic liquid can be recycled for reuse. Betainium bis(trifluoromethylsulfonyl)imide forms one phase with water at high temperatures, whereas phase separation occurs below 55.5 °C (temperature-switch behavior). The mixtures of the ionic liquid with water also show a pH-dependent phase behavior: two phases are formed at low pH, whereas one phase is present under neutral or alkaline conditions.

In this paper, several novel structural derivatives of betainium bis(trifluoromethylsulfonyl)imide (Figure 1) are described. All of these variants bear a carboxyl group attached to a positively charged nitrogen atom. Cationic cores that were considered are the imidazolium, pyridinium, pyrrolidinium, piperidinium, and morpholinium heterocycles. In addition, analogues of betainium bis(trifluoromethylsulfonyl)imide by replacement of one of the methyl groups of the betainium cation by a longer alkyl chain were synthesized. The rationale for synthesizing these derivatives was to explore the influence of the cation on the properties of these task-specific ionic liquids. A change of the cation not only influences the physical properties like the melting point, viscosity, and hydrophobicity but also the acidity of the carboxyl group and hence the selectivity of the metal oxide dissolution process.

Experimental Section

General Techniques. Elemental analyses (carbon, hydrogen, and nitrogen) were performed using a CE Instruments EA-1110 elemental analyzer. Fourier transform infrared (FTIR) spectra were recorded on a Bruker IFS-66 spectrometer. The samples were measured using the KBr pellet method or as a thin film between

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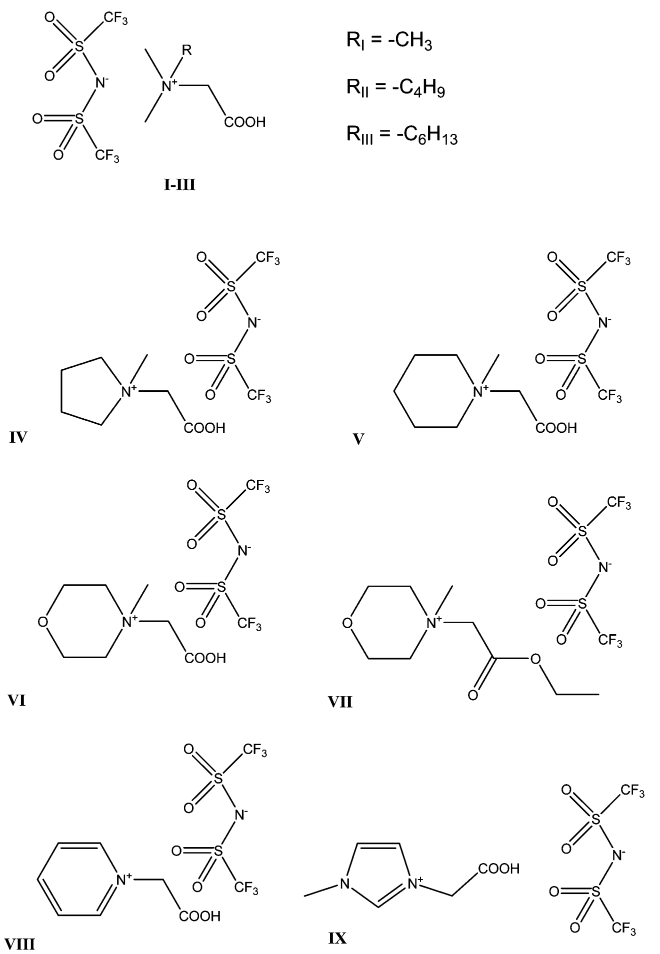

Figure 1. Structures of the ionic liquids. **I**: betainium bis(trifluoromethylsulfonyl)imide, [HBet][Tf_2N] (R = CH_3). **II**: *N*-butyl-*N*-dimethylbetainium bis(trifluoromethylsulfonyl)imide, [C_4HBet][Tf_2N] (R = C_4H_9). **III**: *N*-hexyl-*N*-dimethylbetainium bis(trifluoromethylsulfonyl)imide, [C_6HBet][Tf_2N] (R = C_6H_{13}). **IV**: *N*-carboxymethyl-*N*-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, [HbetmPyr][Tf_2N]. **V**: *N*-carboxymethyl-*N*-methylpiperidinium bis(trifluoromethylsulfonyl)imide, [HbetmPip][Tf_2N]. **VI**: *N*-carboxymethyl-*N*-methylmorpholinium bis(trifluoromethylsulfonyl)imide, [HbetmMor][Tf_2N]. **VII**: *N*-carboxymethyl-*N*-methylmorpholinium ethyl ester bis(trifluoromethylsulfonyl)imide, [EtHbetmMor][Tf_2N]. **VIII**: *N*-carboxymethylpyridinium bis(trifluoromethylsulfonyl)imide, [HbetPy][Tf_2N]. **IX**: 1-carboxymethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [HbetmIm][Tf_2N].

KBr windows. ^{1}H NMR spectra were recorded on a Bruker Avance 300 spectrometer (operating at 300 MHz for ^{1}H NMR). The water content of the ionic liquids was determined by a coulometric Karl Fischer titrator (Mettler Toledo coulometric Karl Fischer titrator model DL39). The viscosity of the ionic liquids was measured at room temperature by the falling-ball method (Gilmont Instruments). Differential scanning calorimetry (DSC) measurements were carried out on a Mettler-Toledo DSC822e module (scan rate of 10 °C/min under a helium flow). High-temperature dissolution experiments of the metal oxides were performed in a poly(tetrafluoroethylene) (PTFE)-lined acid digestion bomb (No. 4744, 45 mL, Parr Instrument Co.). Lithium bis(trifluoromethylsulfonyl)imide was purchased from IoLiTec. All other chemicals were obtained from Acros Organics or from Aldrich-Sigma.

Crystallography. X-ray intensity data for [HbetPy][Tf_2N], [HbetmPyr][Tf_2N], [HbetmIm][Tf_2N], [EtbetmMor][Tf_2N], and [Cu_2(betmMor)$_4$][Tf_2N]$_4$ were collected on a SMART 6000 diffractometer equipped with a CCD detector using Cu Kα radiation (λ = 1.541 78 Å). The images were interpreted and integrated with the program *SAINT* from Bruker.[44] The intensity data sets for the single crystals of [Cu_2(mbetIm)$_4$(H_2O)$_2$][Tf_2N]$_4$(H_2O) and [Eu_2(betmMor)$_6$(H_2O)$_4$][Tf_2N]$_6$ were collected on a Nonius Kappa CCD diffractometer using graphite-monochromatized Mo Kα radiation (λ = 0.710 69 Å). [Cu_2(betmPyr)$_4$(H_2O)$_2$][Tf_2N]$_4$ and [Cd(betPy)$_2$(H_2O)$_2$][Tf_2N]$_2$ were measured on a Rigaku diffractometer equipped with a RU200 rotating anode and a MAR345 image plate using graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å). All nine structures were solved by direct methods and refined by full-matrix least squares on F^2 using the *SHELXTL* program package.[45] Non-hydrogen atoms were anisotropically refined and the hydrogen atoms in the riding mode with isotropic temperature factors fixed at 1.2U(eq) of the parent atoms (1.5 times for methyl groups). CCDC 698586−698594 contain the supplementary crystallographic data for this paper and can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax +44-1223-336033; or deposit@ccdc.cam.ac.uk). The crystallographic data of the complexes are summarized in Tables 1 and 2.

Computational Methods. Density functional theory (DFT) calculations were performed by making use of the *Gaussian03* package.[46] The DFT B3LYP was used for all calculations. The large basis set 6-311++G(d,p), a triplet-split valence basis set with additional diffuse sp functions, and one d function on heavy atoms and diffuse s functions and one p function on hydrogen atoms were used for single-point calculations. The optimizations were carried out using the DGauss valence double-ζ basis set, called DGDZVP2.

Synthesis. The synthesis of the ionic liquids and the metal complexes is described in the Supporting Information.

Results

Synthesis and Characterization. Different structural variants of the previously described task-specific ionic liquid [Hbet][Tf_2N] were synthesized. All of these variants are bearing a carboxyl group attached to the positively charged nitrogen atom of the cation. A first modification was the replacement of a methyl group of the betainium cation by a longer alkyl chain (a butyl or hexyl chain). By the addition of a longer alkyl chain to the nitrogen atom, it can be expected that the polarity of the ionic liquid decreases and thereby the solubility properties change (higher solubility in nonpolar solvents). On the other hand, alkyl chains are electron-donating groups, and their presence decreases the acidity of the carboxyl group. The betainium compounds with a butyl or hexyl chain were prepared by the reaction of the corresponding bromoalkane with the ethyl ester of glycine betaine under solventless conditions. The hydrobromide salt was recrystallized from methanol and dissolved in water. An aqueous solution of lithium bis(trifluoromethylsulfonyl)imide was added, and the hydrophobic ionic liquid phase separated from the water phase after the metathesis reaction. The synthesis of the ionic liquids with heterocyclic cations was partially based on literature procedures. For the *N*-carboxymethyl-

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Table 1. Summary of the Crystallographic Data of the Ionic Liquids

	[HbetPy][Tf_2N]	[HbetmPyr][Tf_2N]	[HbetmIm][Tf_2N]	[EtbetmMor][Tf_2N]
formula	$C_9H_8F_6N_2O_6S_2$	$C_9H_{14}F_6N_2O_6S_2$	$C_8H_9F_6N_3O_6S_2$	$C_{11}H_{18}F_6N_2O_7S_2$
MW	418.31	424.36	421.32	468.41
dimens (mm^3)	0.3 × 0.3 × 0.15	0.3 × 0.2 × 0.1	0.5 × 0.4 × 0.1	0.4 × 0.2 × 0.2
cryst syst	triclinic	monoclinic	triclinic	monoclinic
space group	$P1$ (No. 1)	$P2_1/c$ (No. 14:b1)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14:b1)
a (Å)	8.0812(3)	15.6959(16)	9.3990(7)	13.0236(8)
b (Å)	8.1092(3)	7.0808(8)	10.4524(7)	8.5641(7)
c (Å)	13.7815(5)	15.3090(13)	17.0877(13)	17.3436(12)
α (deg)	77.576(2)	90.000	96.992(4)	90.000
β (deg)	76.722(2)	108.721(4)	92.566(5)	110.307(3)
γ (deg)	62.6590(10)	90.000	108.232(4)	90.000
V (Å^3)	774.49(5)	1611.4(3)	1576.5(2)	1814.2(2)
Z	2	4	4	4
D_{calcd} (g/cm^3)	1.794	1.749	1.775	1.715
temp (K)	100	100	100	100
limiting indices	$-9 \leq h \leq 9$	$-18 \leq h \leq 19$	$-11 \leq h \leq 11$	$-13 \leq h \leq 15$
	$-9 \leq k \leq 9$	$-8 \leq k \leq 8$	$-12 \leq k \leq 12$	$-9 \leq k \leq 10$
	$-16 \leq l \leq 16$	$-18 \leq l \leq 18$	$-19 \leq l \leq 20$	$-21 \leq l \leq 20$
$\mu_{Cu\ K\alpha}$ (mm^{-1})	4.109	3.951	4.059	3.617
abs corrn	multiscan	multiscan	multiscan	multiscan
F(000)	420	864	848	960
no. of measd reflns	13 228	15 225	18 380	16 567
no. of unique reflns	4947	3106	5947	3414
no. of obsd reflns [$I_0 < 2\sigma(I_0)$]	4869	2689	5030	2720
no. of param refined	454	236	459	255
GOF on F^2	1.029	1.079	1.029	1.043
R1	0.0447	0.0374	0.0500	0.0420
wR2	0.1093	0.0962	0.1377	0.0981
R1 (all data)	0.0453	0.0435	0.0615	0.0569
wR2 (all data)	0.1099	0.0999	0.1643	0.1067

Table 2. Summary of the Crystallographic Data of the Metal Complexes

	[Cu_2(betmMor)$_4$]-[Tf_2N]$_4$	[Cu_2(betmPyr)$_4$(H_2O)$_2$]-[Tf_2N]$_4$	[Cu_2(betmIm)$_4$(H_2O)$_2$]-[Tf_2N]$_4$	[Cd(betPy)$_2$(H_2O)$_2$]-[Tf_2N]$_2$	[Eu_2(betmMor)$_6$(H_2O)$_4$]-[Tf_2N]$_6$
formula	$C_{36}H_{52}Cu_2F_{24}N_8O_{28}S_8$	$C_{36}H_{56}Cu_2F_{24}N_8O_{26}S_8$	$C_{32}H_{40}Cu_2F_{24}N_{12}O_{28}S_8$	$C_{18}H_{14}Cd\ F_{12}N_4O_{14}S_4$	$C_{54}H_{78}Eu_2F_{36}N_{12}O_{48}S_{12}$
MW	1884.52	1856.55	1880.34	979.02	3036.04
dimens (mm^3)	0.4 × 0.3 × 0.2	0.4 × 0.2 × 0.18	0.4 × 0.2 × 0.1	0.18 × 0.15 × 0.1	0.6× 0.6 × 0.1
cryst syst	monoclinic	triclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14:b2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14:b2)	$P2_1/n$ (No. 14:b2)
a (Å)	14.8237(5)	10.363(2)	8.2389(5)	7.8760(16)	16.050(3)
b (Å)	15.5544(5)	11.112(2)	14.2055(9)	26.280(5)	14.729(3)
c (Å)	14.8893(5)	16.118(3)	14.649(1)	16.588(3)	22.604(5)
α (deg)	90.00	75.95(3)	81.659(4)	90.00	90.00
β (deg)	92.131(2)	78.11(3)	74.037(5)	103.20(3)	94.873(3)
γ (deg)	90.00	89.73(3)	75.644(4)	90.00	90.00
V (Å^3)	3430.7(2)	1759.9(7)	1591.6(2)	3342.7(12)	5324.3(19)
Z	2	1	1	4	2
D_{calcd} (g/cm^3)	1.824	1.752	1.962	1.945	1.894
temp (K)	100	120	100	120	100
limiting indices	$-18 \leq h \leq 18$	$-12 \leq h \leq 12$	$-9 \leq h \leq 10$	$-8 \leq h \leq 8$	$-19 \leq h \leq 19$
	$0 \leq k \leq 18$	$-13 \leq k \leq 13$	$-17 \leq k \leq 17$	$-30 \leq k \leq 30$	$-17 \leq k \leq 17$
	$0 \leq l \leq 18$	$-20 \leq l \leq 20$	$0 \leq l \leq 18$	$-19 \leq l \leq 19$	$-27 \leq l \leq 27$
$\mu_{Cu\ K\alpha}$ (mm^{-1})	4.420	0.983	1.093	1.038	1.556
abs corrn	multiscan	none	refdelf	none	multiscan
F(000)	1900	938	942	1928	3024
no. of measd reflns	31 503	37 400	6234	25 172	70 910
no. of unique reflns	6480	6923	5071	5111	13 135
no. of obsd reflns [$I_0 < 2\sigma(I_0)$]	5584	6343	6234	4424	10 937
no. of param refined	480	478	492	580	865
GOF on F^2	1.033	1.058	1.140	1.100	1.065
R1	0.0488	0.0572	0.0662	0.0456	0.0600
wR2	0.1260	0.1592	0.1717	0.1183	0.1707
R1 (all data)	0.0572	0.0605	0.0845	0.0546	0.0739
wR2 (all data)	0.1332	0.1629	0.1840	0.1256	0.1839

functionalized morpholinium, pyrrolidinium, piperidinium, and imidazolium compounds, a method earlier reported by Dega-Szafran and Przybylak was used.[47] The cations were prepared by quaternizing the heterocycle with the ester of chloroacetic acid. After quaternization, the ester was converted into the corresponding acid, and the chloride anion was exchanged for a bis(trifluoromethylsulfonyl)imide anion by a metathesis reaction. These hydrophobic bis(trifluoromethylsulfonyl)imide ionic liquids separated from the water phase. For the synthesis of the *N*-carboxymethylpyridinium bis(trifluoromethylsulfonyl)imide, a metathesis reaction was used to exchange the chloride anions for a bis(trifluoromethylsulfonyl)imide anion, starting from the commercially available *N*-carboxymethylpyridinium hydrochloride.

[C_6Hbet][Tf_2N] was obtained as a highly viscous liquid at room temperature, but it cannot be excluded that it is a supercooled liquid that would crystallize upon standing for a prolonged time. All of the other compounds were also obtained first as viscous liquids, but all crystallized. However, their melting points are rather low, and the crystalline compounds were found to be hygroscopic. When the ionic liquids are arranged according to increasing melting point, one finds *N*-carboxymethyl-*N*-pyridinium bis(trifluoromethylsulfonyl)imide (mp = 32 °C), *N*-carboxymethyl-*N*-methylpiperidinium bis(trifluoromethylsulfonyl)imide (mp = 32 °C), *N*-carboxymethyl-*N*-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (mp = 39 °C), 1-carboxymethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (40 °C), *N*-carboxymethyl-*N*-methylmorpholinium bis(trifluoromethylsulfonyl)imide (mp = 55 °C), and betainium bis(trifluoromethylsulfonyl)imide (mp = 55 °C). These melting point values correspond to the onset temperature as measured by DSC. Replacement of the carboxyl group by an ester group reduces the melting point: the melting point of the ester [EtbetmMor][Tf_2N] is 46 °C, whereas that of the corresponding carboxylic acid [HbetmMor][Tf_2N] is 55 °C.

The molten task-specific ionic liquids with the COOH functional group are highly viscous liquids. To make these ionic liquids easier to handle, they can be mixed (diluted) with other ionic liquids. For instance, the ionic liquid 1-carboxymethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide was found to be miscible in all mass proportions with the ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, and these mixtures have a lower viscosity than the task-specific ionic liquid itself.

Solid-State Structures of Ionic Liquids. Single crystals suitable for X-ray diffraction study were obtained for [HbetPy][Tf_2N], [HbetmPyr][Tf_2N], [HbetmIm][Tf_2N], and [EtbetmMor][Tf_2N]. The ionic liquids crystallized spontaneously after the liquids were cooled to room temperature and left to stand for about 3 days.

The crystal structure of [HbetPy][Tf_2N] consists of protonated *N*-carboxymethylpyridinium cations and bis(trifluoromethylsulfonyl)imide anions (Figure 2). In contrast to the crystal structure of [Hbet][Tf_2N],[43] no direct O−(H)···O hydrogen bonds between the anions and the carboxylic function could be observed. Instead, two *N*-carboxymethylpyridinium cations are forming dimers that are connected by strong hydrogen bonds [O−(H)···O distance of 1.79−1.80 Å or O···O distance of 2.63−2.64 Å]. The molecular structure of such a cation−cation pair of [HbetPy][Tf_2N] is shown in Figure 2a. The O−H···O angles of the hydrogen bonds are 175.1 and 179.7°. The O−C−O angles of the carboxyl groups in [HbetPy][Tf_2N] are 127.0 and 126.7°. Besides the strong hydrogen bonding between the cations, several short C−H···O and C−H···F contacts between [Tf_2N]$^-$ anions and the cations can be observed, ranging from 2.52 to 2.96 Å and from 2.47 to 2.91 Å, respectively.

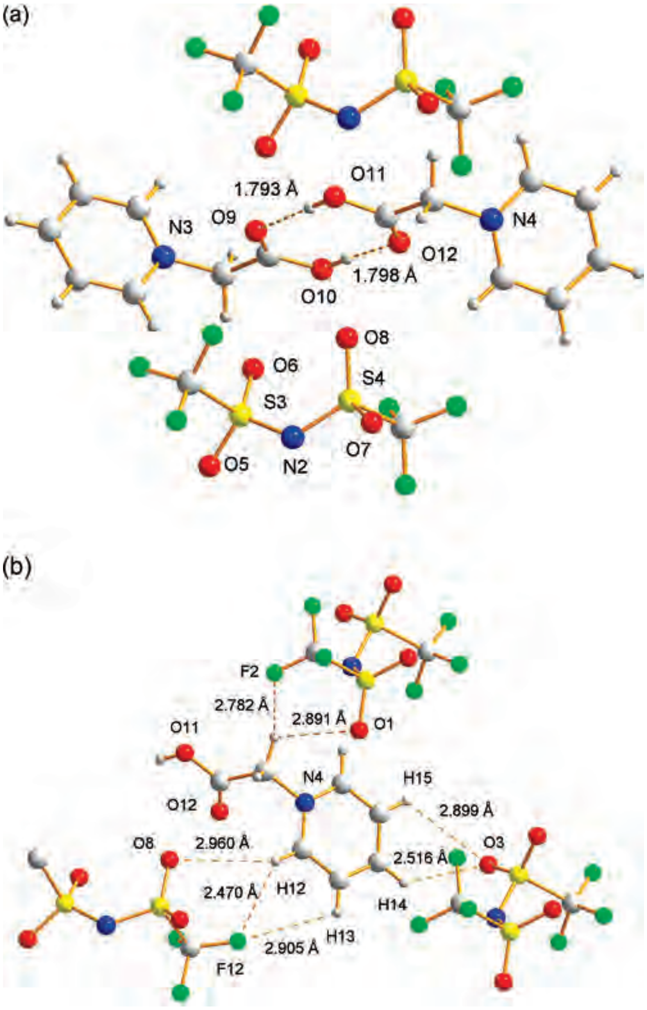

Figure 2. (a) Molecular structure of *N*-carboxymethyl-*N*-pyridinium bis(trifluoromethylsulfonyl)imide, [HbetPy][Tf_2N]. (b) Hydrogen-bonding interactions of the cation with the surrounding bis(trifluoromethylsulfonyl)imide anions.

The crystal structure of *N*-carboxymethyl-*N*-methylpyrrolidinium bis(trifluoromethyl-sulfonyl)imide, [HbetmPyr][Tf_2N], consists of protonated *N*-carboxymethyl-*N*-methylpyrrolidinium cations and [Tf_2N]$^-$ anions (Figure 3). Similarly to the crystal structure of [HbetPy][Tf_2N], the cations form pairs that are connected by strong hydrogen bonds [O−(H)···O distance of 1.86 Å or O···O distance of 2.67 Å). The O−H···O angle of the hydrogen bond is almost linear with 178.4°. The O−C−O angle of the carboxyl group in [HbetmPyr][Tf_2N] is 125.6°. Several short C−H···O and C−H···F contacts between [Tf_2N]$^-$ anions and the cations can be observed, ranging from 2.48 to 2.92 Å and from 2.64 to 2.90 Å, respectively. The carboxymethyl group is in the equatorial position with respect to the pyrrolidinium ring, whereas the methyl group is in the axial position.

A similar arrangement of anions and cations was also found in the crystal structure of *N*-carboxymethyl-*N*-methylimidazolium bis(trifluoromethylsulfonyl)imide, [HbetmIm][Tf_2N] (Figure 4). The cations form pairs that are connected by strong hydrogen bonds with an O−(H)···O distance of

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(47) Dega-Szafran, Z.; Przybylak, R. *J. Mol. Struct.* **1997**, *437*, 107–121.

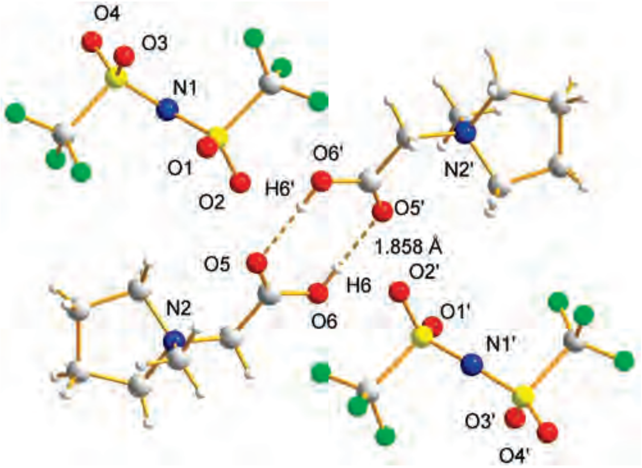

Figure 3. Molecular structure of *N*-carboxymethyl-*N*-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, [HbetmPyr][Tf_2N].

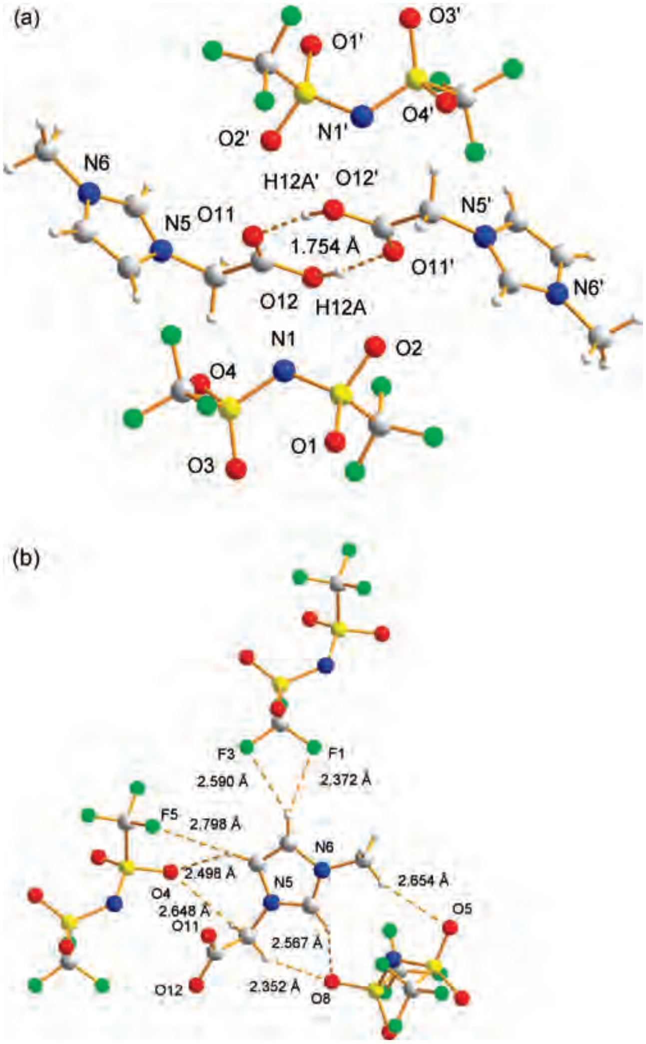

Figure 4. (a) Molecular structure of 1-carboxymethyl-3-imidazolium bis(trifluoromethylsulfonyl)imide, [HbetmIm][Tf_2N]. (b) Hydrogen-bonding interactions of the cation with the surrounding bis(trifluoromethylsulfonyl)imide anions.

1.75−1.89 Å and an O···O-distance of 2.62−2.65 Å, respectively. The O−H···O angles of the hydrogen bonds are 165.4 and 171.0°. The O−C−O angle of the carboxyl groups in [HbetmIm][Tf_2N] are both 126.3°. Several short C−H···O and C−H···F contacts between [Tf_2N]$^-$ anions and the acidic hydrogen atoms of the cation can be observed, ranging from 2.35 to 2.65 Å and from 2.37 to 2.80 Å, respectively. These "second-order" interactions are shorter compared to the interactions in the crystal structures of [HbetPy][Tf_2N] and [HbetmPyr][Tf_2N]. The short contacts in the surroundings of the *N*-carboxymethyl-*N*-methylimidazolium cation are shown in Figure 4b.

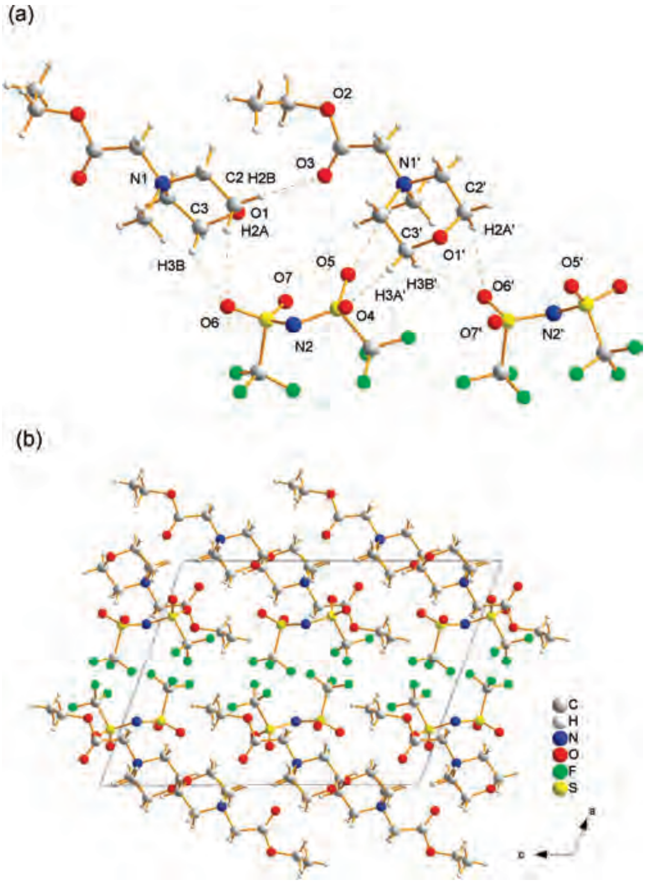

Figure 5. (a) Molecular structure of *N*-carboxymethyl-*N*-methylmorpholinium ethyl ester bis(trifluoromethylsulfonyl)imide, [EtHbetmMor][Tf_2N]. (b) Packing of the molecules in the crystal structure of *N*-carboxymethyl-*N*-methylmorpholinium ethyl ester bis(trifluoromethylsulfonyl)imide, [EtHbetmMor][Tf_2N].

The crystal structure of *N*-carboxymethyl-*N*-methylmorpholinium ethyl ester bis(trifluoromethylsulfonyl)imide, [EtbetmMor][Tf_2N], could also be determined (Figure 5). The structure of this compound allows one to obtain more information on the interactions of the ions in the solid state in the absence of a strong hydrogen-bond donor like the carboxyl function. As expected, no strong hydrogen bonding could be observed. Despite the absence of "classical" hydrogen bonding, short C−H···O and C−H···F contacts are present. Oxygen atoms of the bis(trifluoromethylsulfonyl)imide anion are directed toward the hydrogen atoms in the 2 and 3 positions of the morpholinium ring within distances ranging from O−H = 2.47 to 2.70 Å. The carbonyl oxygen atom of the ester group is also directed toward neighboring hydrogen atoms of the morpholinium ring in the 2 position within a distance of 2.61−2.65 Å. The oxygen of the morpholinium ring interacts weakly with the hydrogen on the 2 and 3 positions of a neighboring ring (2.44−2.65

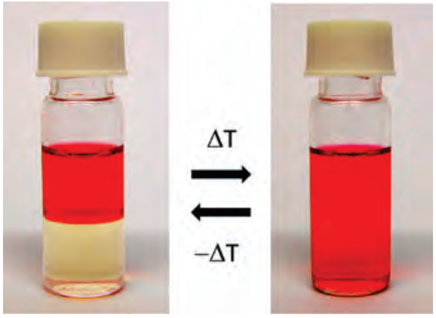

Figure 6. Illustration of the temperature-dependent phase behavior of a binary ionic liquid/water mixture. The red color (methyl red, dissolved in the aqueous layer) was added to accentuate the phase boundaries.

Å, respectively). The short contacts around a *N*-carboxymethyl-*N*-methylmorpholinium ethyl ester cation are also visible in Figure 5a. The morpholine ring has a chair conformation with the carboxymethyl group in the equatorial postion and the methyl group in the axial position. In the packing of the crystal structure, the cations are arranged into layers parallel to the (100) plane and alternate with layers of the bis(trifluoromethylsulfonyl)imide anions (Figure 5b).

Thermomorphic Behavior. The ionic liquid [Hbet][Tf_2N] displays a thermomorphic "phase-switching" behavior at 55 °C.[43] Above this critical temperature, a two-phase water/ionic liquid mixture turns into a one-phase system (Figure 6). Upon cooling below 55 °C, the one-phase mixture separates again into two immiscible phases. For the temperature-dependent miscibility studies, a 1:1 ratio (mass/mass) of the ionic liquid and water was considered.

In [C_4Hbet][Tf_2N] and [C_6Hbet][Tf_2N], one methyl group on the nitrogen atom of the betainium cation is replaced by butyl and hexyl chains, respectively. This alkyl chain makes the resulting ionic liquids more hydrophobic than [Hbet][Tf_2N], and they influence the thermomorphic behavior of these ionic liquids: by heating of a two-phase system of [C_4Hbet][Tf_2N]/H_2O or [C_6Hbet][Tf_2N]/H_2O, the two phases remain immiscible, even at elevated temperatures. The nonpolar alkyl chains hinder the hydration of the ions and prevent the formation of a one-phase system with water upon heating.

[HbetmPyr][Tf_2N] does not form one phase with water, even at elevated temperatures. The same behavior was observed for [Hbetmpip][Tf_2N]. [HbetmMor][Tf_2N] shows a tendency to dissolve in a water phase at elevated temperatures. The critical temperature is 52 °C. The phase transition of the temperature-dependent miscibility was not defined as sharp as it was in the case for [Hbet][Tf_2N]: instead of a distinct transition to a homogeneous phase, a clouding was observed at the transition temperature, which slowly clarified after about 5 min. Replacement of the carboxyl function of [HbetmMor][Tf_2N] by an ester group prevents the thermomorphic behavior: a two-phase region was observed at all temperatures. [Hbetmim][Tf_2N] switches from a two-phase ionic liquid/water system to an one-phase system at 64 °C. [HbetPy][Tf_2N] exhibits thermomorphic behavior at temperatures of around 55 °C.

Nuclear magnetic resonance (NMR) studies have been performed in order to gain additional insight into the nature of the temperature-dependent miscibility of ionic liquids with water. ^{1}H NMR spectra of the pure ionic liquid [HBet][Tf_2N] recorded at 25 and 70 °C showed resonances at 3.95 and 4.84 ppm, which could be unambiguously assigned to three equivalent CH_3 groups and a NCH_2 group, respectively. In addition, at both temperatures a sharp resonance at 10.58 ppm was observed, indicating involvement of a carboxylic proton in a strong hydrogen bonding (Figure 7). This is in good agreement with the solid-state structure of [HBet][Tf_2N] in which hydrogen bonds between carboxylic protons of the betainium cations and the nitrogen atom of the bis(trifluoromethylsulfonyl)imide anion have been observed.[43] ^{1}H NMR spectra of [HBet][Tf_2N] recorded in the presence of an equal volume of water at room temperature were identical with the spectrum of this compound recorded in the absence of water. However, when the sample of [HBet][Tf_2N] containing water was heated to 70 °C, at which point a one-phase system was formed, the resonance at 10.58 ppm disappeared, indicating the absence of hydrogen bonding between the anion and the cation of [HBet][Tf_2N] upon miscibility of water. In Figure 8, the phase diagram of the binary mixture of [HbetmMor][Tf_2N] and water is shown; the line indicates the phase transition temperature at different compositions.

An analogous behavior was observed for [HbetmMor]-[Tf_2N], in which ^{1}H NMR spectra indicated the loss of hydrogen bonding upon formation of a one-phase system with water. Interestingly, the hydrogen bonding detected in the ^{1}H NMR spectra of [HbetmPip][Tf_2N], which does not exhibit temperature-dependent miscibility with water, remained unaffected upon the addition of water and heating of the sample up to 100 °C. These results indicate that the formation of one phase with water above the critical temperature results in the breakage of hydrogen bonding that exists in a pure ionic liquid. It is likely that, upon formation of a one-phase system, hydrogen bonds between the ionic liquid components and water are formed. However, these are difficult to assess, most likely because of the fast exchange of carboxylate protons on the NMR time scale. So, it can be concluded that the thermomorphic behavior can be explained by the total solvation of the anion and cation of the ionic liquid by water molecules. The hydrogen bonds between the betainium cation and the bis(trifluoromethylsulfonyl)imide anion or between two betainium cations, respectively, break, and each ion will be surrounded by a hydration shell of water molecules.

Theoretical Results. The interaction energies between cations and anions have been calculated by DFT methods based on the crystal structures obtained for [HbetPyr][Tf_2N], [HbetPy][Tf_2N], and [HbetmIm][Tf_2N]. In order to estimate the contributions of the different interactions in the crystal structures, pairs of two cations and their neighboring anions were virtually separated into neutral halves. The highest calculated total interaction energies [obtained by single-point B3LYP/6-311++G(d,p) calculations] were found for [HbetPy][Tf_2N] (168.0 kcal/mol) and [HbetmIm][Tf_2N] (160.7 kcal/mol) (see Table 3). The calculated total interaction energy for [HbetPyr][Tf_2N] is lower (140.6 kcal/mol),

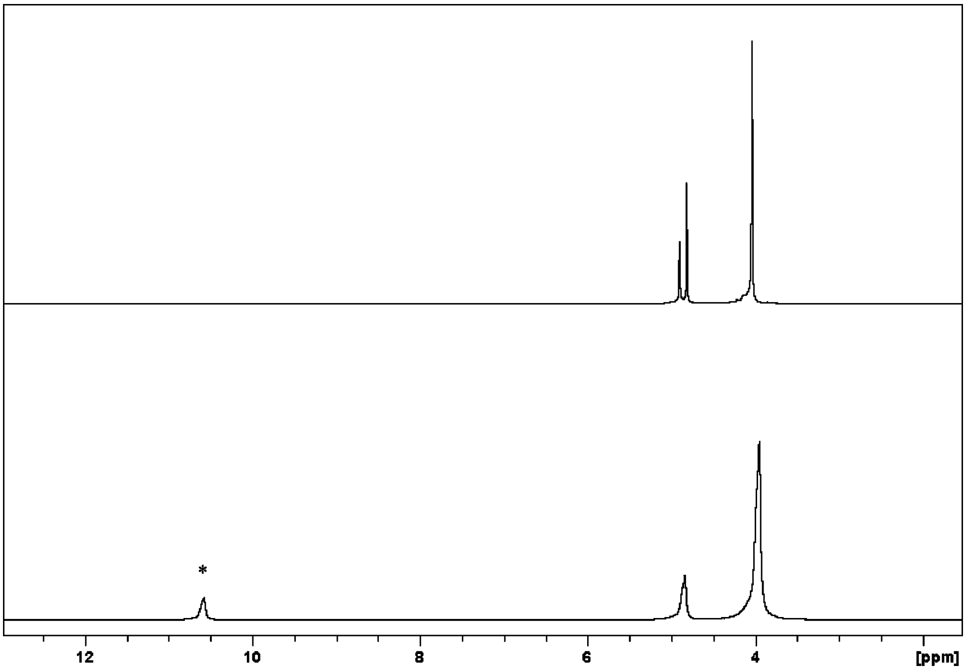

Figure 7. ^{1}H NMR spectrum of neat [Hbet][Tf$_2$N] (lower spectrum) at 70 °C and the ^{1}H NMR spectrum of [Hbet][Tf$_2$N] dissolved in H_2O at 70 °C (upper spectrum). The proton resonance at 10.58 ppm (marked with an asterisk) in the neat sample disappears in the single-phase solution at 70 °C.

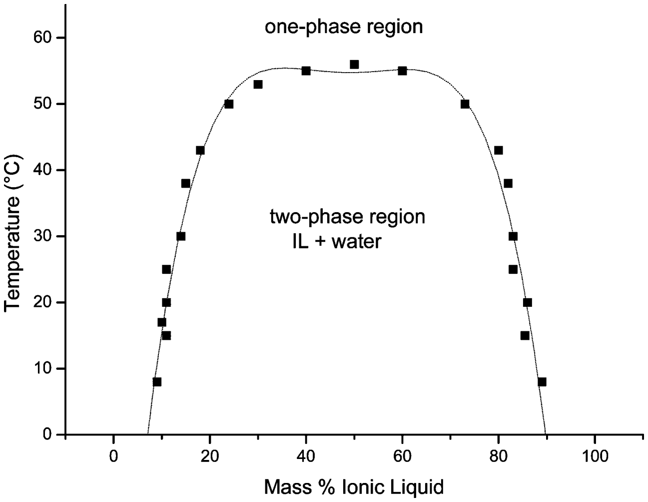

Figure 8. Phase diagram of the binary mixture of *N*-carboxymethyl-*N*-methylmorpholinium bis(trifluoromethylsulfonyl)imide, [HbetmMor][Tf$_2$N], and water.

Table 3. Interaction energies (kcal/mol) for [HbetPyr][Tf$_2$N], [HbetPy][Tf$_2$N], and [HbetmIm][Tf$_2$N][a]

ionic liquid	average cation−anion interaction energy	interaction energy between two neutral halves	total interaction energy
[HbetPyr][Tf$_2$N]	−57.8	−25.0	−140.6
[HbetPy][Tf$_2$N]	−63.1	−41.8	−168.0
[HbetmIm][Tf$_2$N]	−72.4	−15.9	−160.7

[a] These values are obtained by single-point B3LYP/6-311++G(d,p) calculations from the crystal structures.

which can be explained by the weaker average cation−anion interaction energy (57.8 kcal/mol compared to 63.1 kcal/mol for [HbetPy][Tf$_2$N] and 72.4 kcal/mol for [HbetmIm]-[Tf$_2$N]). Contrary to the nonaromatic pyrrolidinium-based cation [HbetPyr]$^+$, the aromatic pyridinium- and imidazolium-based cations [HbetPy]$^+$ and [HbetmIm]$^+$ contain acidic ring hydrogen atoms that are able to form hydrogen bonds to the anions. This is also demonstrated by optimizations of the structures of each one cation and one bis(trifluoromethylsulfonyl)imide anion in the gas phase. The calculations were performed at the B3LYP/DGDZVP2 level for [HbetPyr][Tf$_2$N] and [HbetmIm][Tf$_2$N] (see Figure 9) and show that for the [HbetmIm]$^+$ cation the hydrogen bonding of the anion with the acidic ring hydrogen atom is preferred over the interaction with the carboxyl group. In the optimized structure for [HbetPyr][Tf$_2$N], an interaction with the carboxyl function is found.

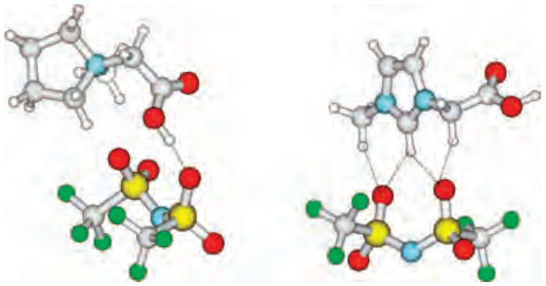

Figure 9. Optimized structures in the gas phase for [HbetPyr][Tf$_2$N] (left) and [HbetmIm][Tf$_2$N] (right). The calculations were performed at the B3LYP/DGDZVP2 level.

Solubilization of Metal Oxides. An interesting property of all of these ionic liquids functionalized with a carboxyl group is their solubilizing power toward metal oxides and metal hydroxides. A range of metal oxides and hydroxides dissolves in these ionic liquids. In a typical experiment, the ionic liquid (1 g) was mixed with a stoichiometric amount of the metal oxide or hydroxide (or a slight excess of the metal oxide or hydroxide) and 5 mL of water. A stoichiometric amount of metal oxide M_xO_y is present if for every mole of M_xO_y the amount of ionic liquid equals x times the oxidation state of the metal. For instance, 6 mol of ionic liquid has to be added to 1 mol of M_2O_3. If the amount of M_2O_3 exceeds the stoichiometric amount, the excess of metal oxide will remain undissolved. The mixture was stirred under reflux for 12 h. After filtration, water was evaporated under vacuum. The following oxides were found to be soluble in the ionic liquids: Sc_2O_3, Y_2O_3, La_2O_3, Pr_6O_{11}, Nd_2O_3, Sm_2O_3, Eu_2O_3, Gd_2O_3, Tb_4O_7, Dy_2O_3, Ho_2O_3, Er_2O_3, Tm_2O_3, Yb_2O_3, Lu_2O_3, UO_3, PbO, ZnO, CdO, HgO, CuO, Ag_2O, NiO, and PdO. The following hydroxides were found to be soluble in the ionic liquids: $Pb(OH)_2$, $Zn(OH)_2$, $Cd(OH)_2$, $Cu(OH)_2$, $Ni(OH)_2$, $Fe(OH)_2$, $Fe(OH)_3$, $Co(OH)_2$, $Cr(OH)_3$, $Mn(OH)_2$, LiOH, NaOH, KOH, RbOH, CsOH, $Mg(OH)_2$, $Ca(OH)_2$, $Sr(OH)_2$, and $Ba(OH)_2$. Some of the corresponding metal complexes were characterized by means of element analysis and single-crystal X-ray diffraction (see the next section). As discussed in our previous paper, the presence of water facilitates the dissolution process.[43] This is probably due to the fact that the water molecule aids in the deprotonation of the carboxyl group. The solubility of the metal oxides or hydroxides in the task-specific ionic liquids is high because the ionic liquid allows dissolution of stoichiometric amounts of the oxide or hydroxide. Co_3O_4, CoO, Co_2O_3, Cr_2O_3, FeO, and Fe_2O_3 were found to be insoluble in the ionic liquids under the experimental conditions used to dissolve the other oxides. However, these oxides could be solubilized in the ionic liquids (including in [Hbet][Tf_2N]) by using a digestion bomb and higher temperatures. In a typical experiment, the ionic liquid (1 g) was mixed with a stoichiometric amount of the metal oxide and 5 mL of water. The mixture was treated by heating of the oxide/ionic liquid/water mixture in an oven at 140 °C for 24 h in a PTFE-lined acid digestion bomb. After filtration, water was evaporated under vacuum.

Crystal Structures of Metal Complexes. The crystal structures of five metal complexes have been determined by single-crystal X-ray diffraction: the copper(II) complexes of [HbetmMor][Tf_2N], [HbetmPyr][Tf_2N], and [HbetmIm][Tf_2N], the europium(III) complex of [HbetmMor][Tf_2N], and the cadmium(II) complex of [HbetPy][Tf_2N]. Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of aqueous solutions of these metal complexes at room temperature.

The crystal structure of the [Cu_2(betmMor)$_4$][Tf_2N]$_4$ complex consists of four μ_2-bridging *N*-carboxymethyl-*N*-methylmorpholinium cations and four bis(trifluoromethylsulfonyl)imide anions (Figure 10). The two copper(II) ions exhibit a distorted square-pyramidal coordination sphere. No coordinated water molecules could be observed. The copper−copper distance is quite short (2.63 Å), and the two metal centers are bridged by four μ_2 *N*-carboxymethyl-*N*-methylmorpholinium cations [*d*(Cu−O) = 1.96−1.97 Å]. Two coordinating bis(trifluoromethylsulfonyl)imide anions complete the coordination sphere [*d*(Cu1−O5) = 2.18 Å].

The crystal structure obtained after dissolution of Eu_2O_3 in [HbetmMor][Tf_2N] results in the dimeric complex [Eu_2(betmMor)$_6$(H_2O)$_4$][Tf_2N]$_6$ that consists of [Eu_2(betmMor)$_8$(H_2O)$_4$]$^{6+}$ cations and the bis(trifluorosulfonyl)imide anions [Tf_2N]$^-$ (Figure 11). The two europium(III) ions in this centrosymmetric complex are linked by two μ_2-bridging and two chelating-bridging carboxylate groups of the zwitterionic *N*-carboxymethyl-*N*-methylmorpholinium ligands. Each europium(III) ion is further surrounded by one additional chelating ligand and two coordinating water molecules. The noncoordinating [Tf_2N]$^-$ anions form hydrogen bonds to these water molecules with O−O distances ranging from 2.71 to 2.80 Å.

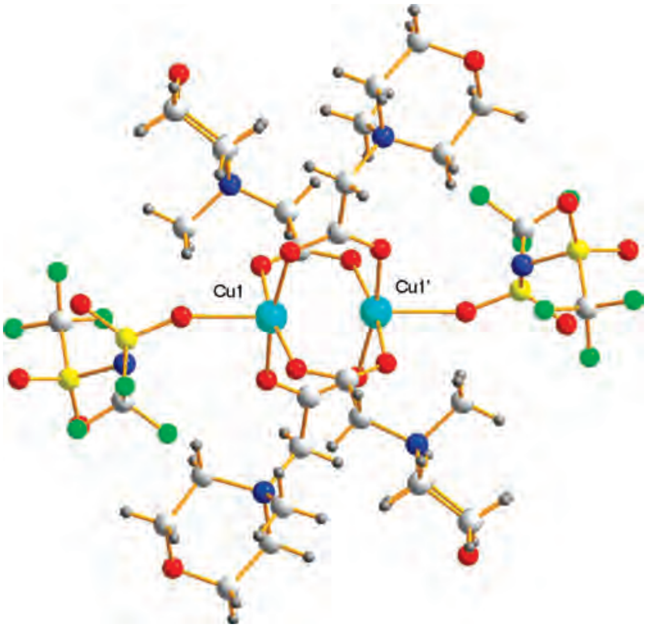

Figure 10. Molecular structure of [Cu_2(betmMor)$_4$][Tf_2N]$_4$. The two noncoordinating bis(trifluoromethylsulfony)imide anions are omitted for clarity.

The crystal structure of the dimeric [Cu_2(betmPyr)$_4$(H_2O)$_2$][Tf_2N]$_4$ complex consists of four μ_2-bridging *N*-carboxymethyl-*N*-methylpyrrolidinium cations, two coordinating water molecules, and four bis(trifluoromethylsulfonyl)imide anions (Figure 12). Both copper(II) ions exhibit a distorted square-pyramidal coordination sphere. The copper(II)−copper(II) distance is 2.69 Å. In analogy to the [Cu_2(betmPyr)$_4$(H_2O)$_2$][Tf_2N]$_4$ complex, there are slightly different bond lengths found for the copper(II)−oxygen bond of the carboxylate groups [*d*(Cu−O) = 1.96−1.98 Å]. Each copper(II) ion is coordinated to a water molecule [*d*(Cu−O) = 2.13 Å]. Four bis(trifluoromethylsulfonyl)imide anions are connected via the oxygen atoms by weak hydrogen bonds to the two coordinated water molecules [*d*(O−H···O) = 2.85−2.98 Å].

The structure of [Cu_2(betmIm)$_4$(H_2O)$_2$][Tf_2N]$_4$(H_2O) exhibits the same dimeric core of the complex consisting of four μ_2-bridging *N*-carboxymethyl-*N*-methylimidazolium cations and two coordinating water molecules. In contrast to the structure with the *N*-carboxymethyl-*N*-methylpyrrolidinium cations, the four bis(trifluoromethylsulfonyl)imide anions prefer hydrogen bonding with the acidic protons of imidazolium cations rather than with the coordinated water molecules (Figures 13 and 14). These hydrogen bonds range from 2.36 to 2.70 Å. Both copper(II) ions exhibit a distorted square-pyramidal coordination sphere. The copper(II)−copper(II) distance is 2.65 Å. Each copper(II) ion is coordinated to a water molecule [*d*(Cu−O) = 2.13 Å], which form hydrogen bonds to the oxygen atoms of a neighboring *N*-carboxymethyl-*N*-methylimidazolium ligand. This hydro-

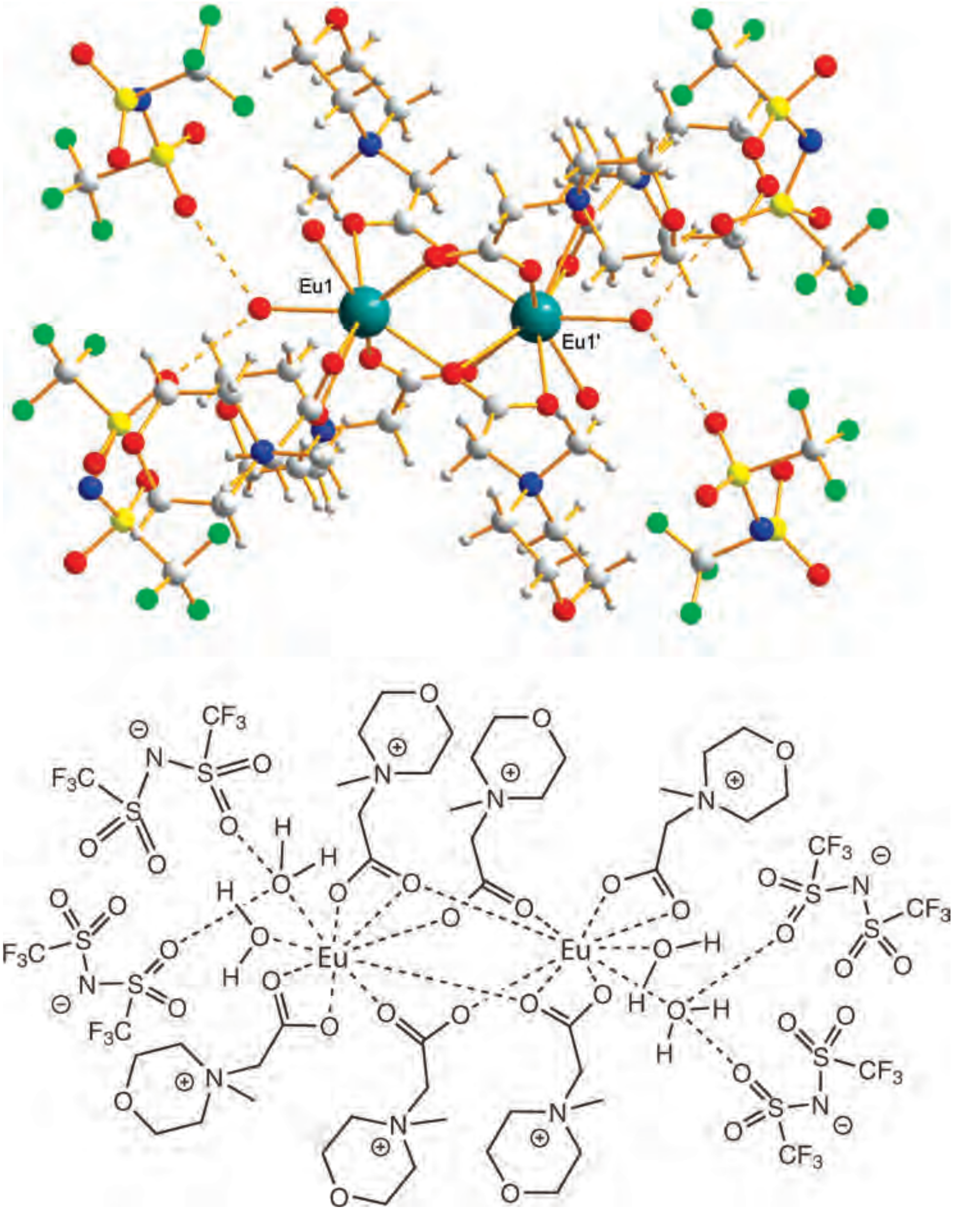

Figure 11. (a) Molecular structure of $[Eu_2(betmMor)_6(H_2O)_2][Tf_2N]_6$. The two noncoordinating bis(trifluoromethylsulfony)imide anions are omitted for clarity. (b) Schematic presentation of the structure of $[Eu_2(betmMor)_6(H_2O)_2][Tf_2N]_6$.

gen bonding arranges the dimers to strands along the [100] direction.

The crystal structure of the cadmium(II) *N*-carboxymethylpyridinium bis(trifluoromethylsulfonyl)imide complex, $[Cd(betPy)_2(H_2O)_2][Tf_2N]_2$, consists of infinite rows of $[Cd(betPy)]^+$ units along the *a* axis surrounded by two noncoordinating bis(trifluoromethylsulfonyl)imide anion as counterions. The average cadmium−cadmium distance is 4.00 Å. In Figure 13, the linkage of the μ_2-bridging carboxylate groups of the *N*-carboxymethylpyridinium ligands coordinating to two cadmium(II) ions is shown, with typical Cd−O distances of 2.44−2.48 Å. Two water molecules are coordinated to each cadmium(II) ion, with an average bond length (Cd−O) of 2.33 Å.

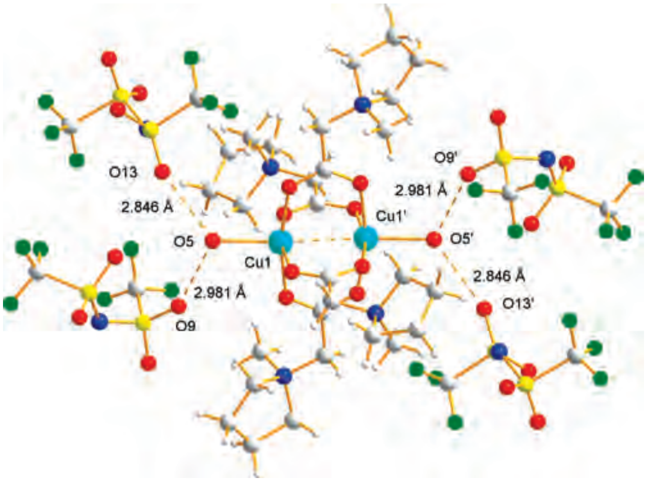

Figure 12. Molecular structure of $[Cu_2(betmPyr)_4(H_2O)_2][Tf_2N]_4$. Two bis(trifluoromethylsulfony)imide anions are omitted for clarity.

Discussion

Betainium salts of the type that we describe in this paper have been investigated in the past by several research groups

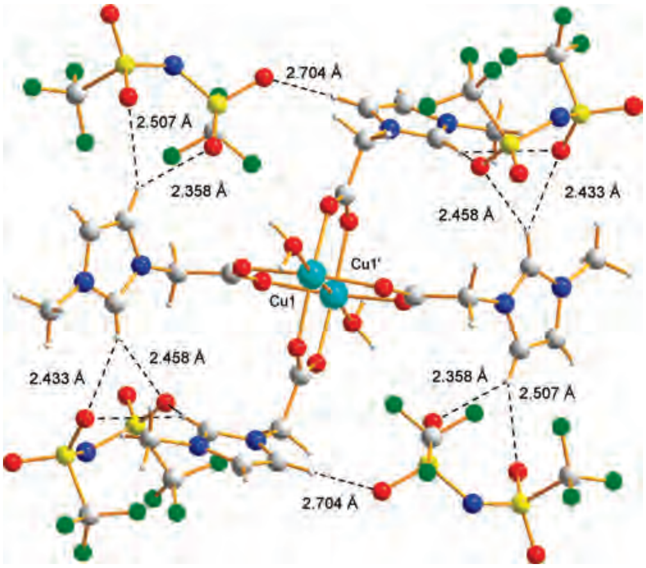

Figure 13. Molecular structure of [Cu$_2$(betmIm)$_4$(H$_2$O)$_2$][Tf$_2$N]$_4$(H$_2$O).

and mainly by Dega-Szafran, Szafran, and coworkers.[48−52] These authors have studied the zwitterionic form of the complexes and salts of mineral acids. None of these salts are ionic liquids. It is only by the use of the bis(trifluoromethylsulfonyl)imide anion that salts with a sufficiently low melting point can be obtained. These low melting points can be attributed to the conformational disorder of bis(trifluoromethylsulfonyl)imide anions and to the limited involvement of these anions in hydrogen-bond formation. The temperature-dependent miscibility of the bis(trifluoromethylsulfonyl)imide ionic liquids is a fascinating phenomenon.[43] Köddermann and co-workers investigated by DFT calculations and IR spectroscopy mixtures of different ionic liquids with water and showed that hydrogen bonding can play an important role for the phase behavior of these ionic liquids.[53] Different types of conformers were found for [C$_2$mim][Tf$_2$N]. There exists a double-donor conformer in which the water molecules form two hydrogen bonds to one [Tf$_2$N]$^-$ group. In another conformer is a single-donor conformer in which the water molecules form a strong hydrogen bond to the anion. Therefore, the most probable explanation of the thermomorphic behavior observed for the [Hbet][Tf$_2$N]/water system (and for mixtures of similar ionic liquids with water) is the loss of the cation−anion hydrogen bonding upon heating. At high temperatures, the cation and anion are fully solvated by water molecules. We found evidence for this process by ^{1}H NMR spectroscopy. An analogous behavior for [C$_4$mim][BF$_4$] has already been described by Dullius et al. (1998).[54] Here, the temperature-dependent miscibility could only be observed upon cooling of the system to 5 °C. Therefore, it is feasible to assume that the hydrogen bonds between anion and cation are relatively weak in [C$_4$mim][BF$_4$] and do only exist at low temperature. At higher temperatures, the solvation of the ions is favored. Rebelo et al. performed a detailed thermodynamic study of the [C$_4$mim][BF$_4$]/water system. These authors performed a case study to model other ionic liquid/water systems.[55] The most detailed studies on the temperature-dependent miscibility of ionic liquids with organic solvents have focused on alcohols as solvents.[56,57] The temperature-dependent phase behavior of mixtures of these ionic liquids could be applied for chemical separations. There is currently a strong interest in the thermomorphic behavior of ionic liquids and organic solvents (or water) because of its importance for product separation.[58] It should also be mentioned that binary mixtures of different ionic liquids have been reported to be mutually immiscible.[59]

The solubility for metal oxides is comparable for all ionic liquids that we investigated; the oxides of the trivalent lanthanide ions, uranium(VI) lead(II), zinc(II), cadmium(II), mercury(II), copper(II), silver(II), nickel(II), palladium(II), and manganese(II), are good to reasonably soluble in these ionic liquids. This similar solubilizing ability is also reflected by the proton acceptor properties of betaine (pK_a = 1.73), pyridine betaine (pK_a = 1.99), and *N*-methylmorpholine betaine (pK_a = 2.04), which are in a comparable range.[60,62] To aid in the solubilization process, the addition of water is necessary. Although the oxides Co$_3$O$_4$, CoO, Co$_2$O$_3$, Cr$_2$O$_3$, FeO, and Fe$_2$O$_3$ are not soluble in the ionic liquids under normal conditions, solubilizing could be achieved in a Teflon-lined digestion bomb at 160 °C. This means that virtually all of the metal oxides can be solubilizing in these types of ionic liquids thanks to the presence of the carboxyl function.

Some other carboxyl-functionalized ionic liquids have been described earlier in the literature. Li and co-workers published on a *N*-carboxyalkylpyridinium-functionalized ionic liquid with [BF$_4$]$^-$, [PF$_6$]$^-$, and [CF$_3$SO$_3$]$^-$ anions.[61] The authors determined the physical and chemical properties, but they did not comment on the complex-forming abilities of these types of ionic liquids. Szafran and co-workers func-

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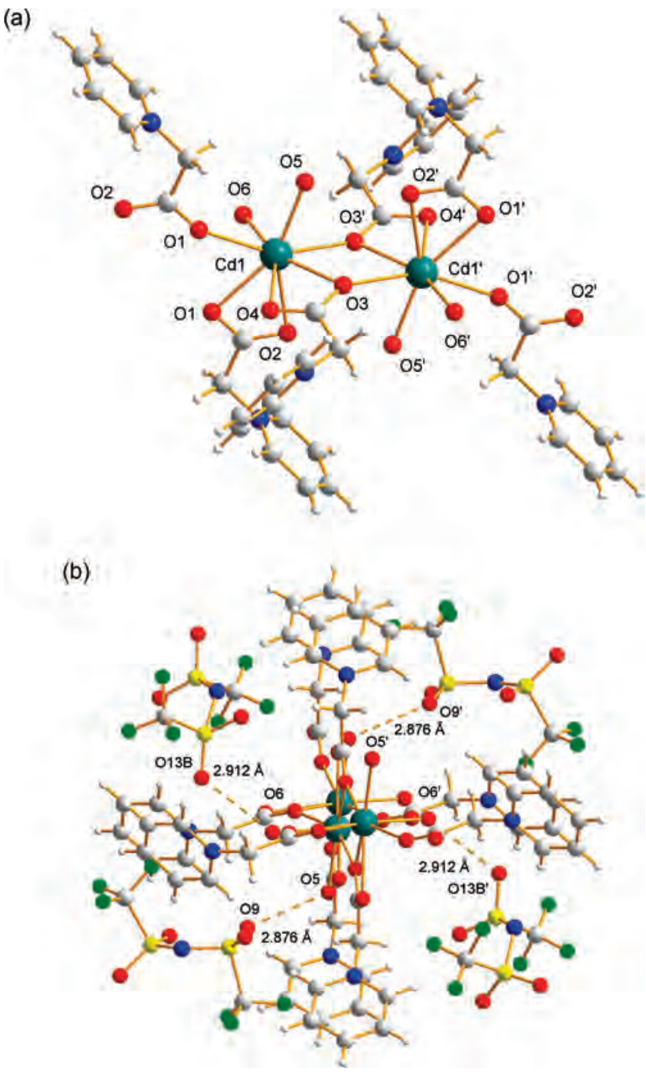

Figure 14. (a) Part of the polymeric crystal structure of $[Cd(betPy)_2(H_2O)_2][Tf_2N]_2$. (b) Polymeric chain in the structure viewed along the [100] direction.

tionalized the piperidinium cation with a carboxylic group, but these compounds are not ionic liquids.[62−65] The authors found for chloride salts that were investigated that the acidic hydrogen atom links two molecules of the carboxylated *N*-methylpiperidinium into a centrosymmetric cation through a very short O−H···O hydrogen bond. The position of the hydrogen-bonded proton is controlled by the halide ions. Imidazolium ionic liquids bearing a carboxylic group in combination with $[BF_4]^-$, $[PF_6]^-$, and $[CF_3SO_3]^-$ anions have been synthesized for use as an extractant, a catalyst, and a solvent for chemical reactions.[66,67] Bartsch and Dzyuba described the *N*-carboxymethyl-*N*-methylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquid as a solvent for Diels−Alder reactions.[68] These authors reported that this ionic liquid is a highly viscous liquid at room temperature. However, we found that the compound after removal from a refrigerator (−25 °C), where it was kept for several weeks, crystallized when it was allowed to warm up to room temperature. A melting point of 40 °C was found, although the melting point was difficult to determine because of the hygroscopicity of the ionic liquid. Differences in the melting points can be due to the fact that ionic liquids are often obtained as supercooled liquids that crystallize only in the presence of seed crystals. On the other hand, water or halide impurities might also cause different melting points because the presence of these impurities is known to strongly affect the physical properties of ionic liquids.[69]

The crystal structural data of the ionic liquids and their metal complexes complement the data available in the literature on similar systems (which are not ionic liquids). Dega-Szafran et al. published the crystal structure of bis(pyridiniumbetainium) perchlorate.[70] Only one hydrogen bond between to the *N*-carboxymethylpyridinium cation and the zwitterionic derivative could be observed, with a bond length of 2.45 Å. The perchlorate anions were not involved in the hydrogen bonding. The same authors found a hydrogen bond [$d(O\cdots Cl^-)$ = 2.92 Å] with the chloride anion for the *N*-carboxymethylpyridinium hydrochloride.[39] Dega-Szafran et al. also reported on the crystal structure of *N*-morpholine betaine complexes with phosphate and picric acid.[71,72]

Recently, we reported on a range of crystal structures obtained after dissolution of metal oxides and hydroxides in the ionic liquid betainium bistriflimide.[73] It was shown that the zwitterionic nature of the betaine ligand and the weakly coordinating ability of the bistriflimide anion facilitate the incorporation of metal ions into oligonuclear and polynuclear metal complexes. Song and co-workers report on a monomeric neodymium(III) structure with the zwitterionic *N*-carboxymethylpyridinium ligands $[Nd(betPy)_4(H_2O)_4](ClO_4)_3$.[74] Perchlorate anions were used as counterions. The coordination sphere of the neodymium(III) ion is an eight-coordinated distorted dodecahedral polyhedron. Mak and co-workers report on dimeric copper(II) structures, $[Cu_2(betPy)_4(H_2O)_2](NO_3)_4\cdot 2H_2O$ with *N*-carboxymethylmethylpyridinium ligands.[75] To the best of our knowledge, no metal complexes with the *N*-morpholine betaine or the *N*-pyrrolidine betaine ligand have been reported so far.

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Conclusions

This work illustrates that the principle of using a task-specific ionic liquid with a carboxyl functional group for solubilizing metal oxides is not only applicable to the betainium bis(trifluoromethylsulfonyl)imide ionic liquid that we described previously[43] but to similar ionic liquids as well. However, the temperature-dependent miscibility with water, including the formation of one phase above the critical temperature, is not always as pronounced as it is in the archetype [Hbet][Tf_2N] ionic liquid. The best performance of temperature-dependent miscibility was observed for the *N*-carboxymethyl-*N*-methylimidazolium bis(trifluoromethylsulfonyl)imide and for the *N*-carboxymethylpyridinium bis(trifluoromethylsulfonyl)imide ionic liquids. The presence of the carboxylic group gives to this class of ionic liquids a good solubilizing ability for metal oxides and metal hydroxides. Further research will be directed toward the development of new types of task-specific ionic liquids with coordinating groups that show a high specificity for a given metal ion.

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Supporting Information Available: Synthetic procedure and analytical data for the ionic liquids and metal complexes, solubility of the ionic liquids in organic solvents, and a CIF file of the crystal structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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