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Low-Melting Salts Based on a Glycolated Cobalt Bis(dicarbollide) Anion

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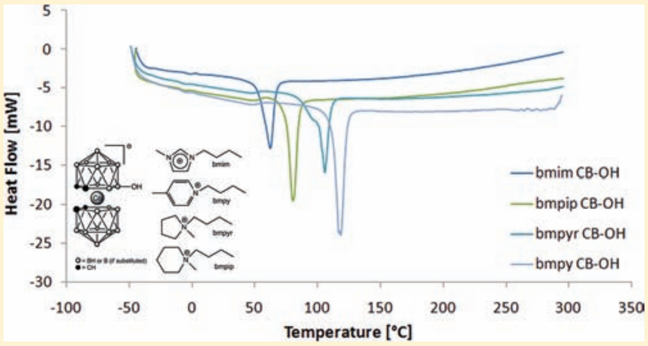
Ⓢ *Supporting Information*

ABSTRACT: A new series of low-melting quaternary ammonium salts based on a glycolated cobalt bis(dicarbollide) anion structure have been synthesized and characterized, and their spectroscopic and physicochemical properties have been studied. The lowest melting point was obtained for 1-butyl-3-methylimidazolium (~50 °C) followed by 1-butyl-1-methylpiperidinium (~80 °C), 1-butyl-1-methylpyrrolidinium (~95 °C), and 1-butyl-4-methylpyridinium salts (~115 °C). The salts were thermally stable up to 180 °C [decomposition of an oligo(ethylene glycol) chain] and contained variable amounts of water. The flexible oligo(ethylene glycol) chains contributed to the waxy state of salts. The solubility of the salts was determined for 76 solvents that are commonly used in organic chemistry. Generally, the solubility increased with the dipole moment and relative polarity of the solvent. Salts exhibited good solubility in ketones and esters; moderate solubility was observed in alcohols, aromates, and chlorinated solvents, and poor solubility was obtained in ethers. The salts were practically insoluble in higher hydrocarbons and water. Salts are dissolved in the form of ion pairs or separated ions, depending on the nature of the solvent.



INTRODUCTION

Ionic liquids (ILs) are nonvolatile, nonflammable, and thermally stable low-melting salts that are frequently composed of organic cations and polyatomic inorganic or organic anions. ILs are defined as salts with melting points below 100 °C, commonly even below room temperature (RTILs), and whose melted composition consists of discrete anions and cations. Their low melting temperatures are due to delocalization of a charge on voluminous ions. The most widely used cations are imidazolium, pyridinium, pyrrolidinium, piperidinium, ammonium, or phosphonium derivatives bearing at least one alkyl chain. The range of anions found in ILs is wide, including the important family of weakly coordinating hydrophobic species, such as halide anions, nitrate, perchlorate, tetrafluoroborate, hexafluorophosphate, tosylate, acetate, triflate [(trifluoromethyl)sulfonate], and bis[(trifluoromethyl)sulfonyl]imide. The large number of possible cation−anion combinations allows the design of tailor-made ILs for a desired task. The rapid emergence of ILs as alternative solvents has also promoted a rapidly growing number of applications, such as those for separations and catalysis, energetic materials, lubricants, electrolytes, and additives in paints, plastics, and cleaning agents.[1−5] Thus, they are useful in liquid−liquid extraction (LLE),[6] liquid-phase microextraction (LPME),[7] and solid-phase microextraction (SPME).[8] ILs possess many favorable properties, such as nonvolatility, nonflammability, good solubility of many compounds, high viscosity, and high polarity. These attributes make them unique stationary phases in gas chromatography.[9] The miscibility of ILs with acetonitrile facilitates their use for adjustment of the analyte mobility and separation in nonaqueous capillary electrophoresis (CE).[10] With the same principle as that shown for CE, imidazolium cations can interact with silanol groups on the alkylsilica surface in a liquid chromatography (LC) column and compete with the polar group in the analytes for the silanol groups.[11] ILs were used as the sensing materials in quartz crystal microbalance sensors for the detection of organic vapors.[12] ILs can produce many more homogeneous sample solutions, and they possess greater vacuum stability than most solid matrixes. For these reasons, the use of ILs as matrixes for matrix-assisted laser desorption/ionization coupled with mass spectrometry (MALDI-MS) could enhance reproducibility and sensitivity.[13] Compared to traditional electrolyte solutions, ILs offer a broader range of electrochemical potentials and favorable optical properties for in situ vis/near-IR and Raman spectroelectrochemistry of nanocarbon species (single-walled carbon nanotubes and fullerene peapods).[14] Moreover, they can act as templates and precursors to inorganic materials as well as solvents, but their utilization in inorganic synthesis

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processes has only recently been explored.[15−17] Recently, biologically active ions and building blocks of active pharmaceutical ingredients have been used to make new pharmaceutically active ILs.[18]

Boron clusters (boranes, carboranes, and metallacarboranes) and their derivatives were discovered more than 5 decades ago. These artificial compounds display very specific properties, such as high chemical inertness, three-dimensional aromaticity, rigid skeleton structure, a high degree of lipophilicity, and a delocalized negative charge (if any).[19−22] They are able to form dihydrogen bonds between a partially negatively charged hydrogen that is bound to an electropositive boron atom (hydrogen atoms in the B−H group have hydride-like character) and a partially positively charged hydrogen located on common organic molecules (OH, NH, and SH).[22,23] Despite their chemical stability, boron cluster anions can be functionalized to obtain several derivatives with different types and degrees of substitution.[24−27] Currently, scientists have been primarily interested in the use of boron cluster anions for pharmaceutical applications.[28−35] The most important technical application of boron clusters is their utilization as selective extraction agents for lanthanide and actinide cations from nuclear waste solutions.[35−41] Boron clusters can be utilized in the preparation of light-emitting materials (fluorophores),[42−46] in catalysis[35,47,48] or in the construction of ion-selective-electrode membranes,[49−51] as special polymers,[52,53] or in material chemistry.[35,54−57]

The first low-melting salts containing a boron cluster as the anion were synthesized a few years ago. These studies yielded a variety of new of boron-containing salts, including imidazolium salts with [*closo*-$CB_{11}H_{12}$]$^-$ derivatives,[58] ILs of stannaboranes ([1-(*R*)-*closo*-$SnB_{11}H_{11}$]$^-$),[59] 1-pentylpyridinium salt of [*closo*-$CB_{11}H_{12}$]$^-$,[60] salts of [*nido*-$C_2B_9H_{12}$]$^-$ and [*closo*-$CB_{11}H_{12}$]$^-$,[61] salts of [*closo*-$B_{12}H_{11}NR_3$]$^-$ anions (R = alkyl) with a wide range of cations (even Li^+ or H^+),[62] and salts of [*closo*-1,2-$C_2B_{10}H_{11}$]$^-$.[63] A recent study combined either imidazolium or phosphonium cations with four boron cluster anions, ([*commo*-3,3′-Co(1,2-$C_2B_9H_{11}$)$_2$]$^-$, [*nido*-$C_2B_9H_{12}$]$^-$, and two perhalogenated dianions [*closo*-$B_{12}Cl_{12}$]$^{2-}$ and [*closo*-$B_{10}Cl_{10}$]$^{2-}$).[64] The latest study combines [*nido*-$C_2B_9H_{12}$]$^-$ with diether-functionalized ammonium cations.[65]

In this paper, we describe the preparation of a set of low-melting salts based on the combination of 1-butyl-3-methylimidazolium, 1-butyl-4-methylpyridinium, 1-butyl-1-methylpyrrolidinium, and 1-butyl-1-methylpiperidinium cations (abbreviated as [bmim]$^+$, [bmpy]$^+$, [bmpyr]$^+$, and [bmpip]$^+$, respectively) with various anionic derivatives of the cobalt bis(dicarbollide) moiety. In contrast to classic ILs, these new salts display unusual properties because of the presence of the cobalt bis(dicarbollide) moiety, such as atypical H−H interactions, and, thus, they have great potential especially in the field of separation methods (CG, LC, CE, LLE, LPME, SPME, and MALDI).

It should be noted that based on IUPAC nomenclature the correct name should be 3,3′-*commo*-cobaltabis(undecahydro-1,2-dicarba-*closo*-dodecaborane) (1−)ate.[66] In the literature, alternative names are also used, such as bis(1,2-dicarbollido)-cobalt(III) (1−)ate, cobalta(III) bis(1,2-dicarbollide), cobalt(III) bis(1,2-dicarbollide), cobalt dicarbollide, cobalt bis(dicarbollide), and COSAN. The term cobalt bis(dicarbollide) seems the most widely used in the recent literature and will be used within this article.[67]

Anionic derivatives based on the placement of a cobalt bis(dicarbollide) moiety at position 8: hydrogen (abbreviated in this paper as [CB]$^-$), hydroxyl group ([CB-OH]$^-$), or oligo(ethylene glycol) chain with 2, 4, 6, 8, or 10 ethylene glycol units ([CB-2EG]$^-$, [CB-4EG]$^-$, [CB-6EG], [CB-8EG]$^-$, and [CB-10EG]$^-$, respectively) are shown on Figure 1.

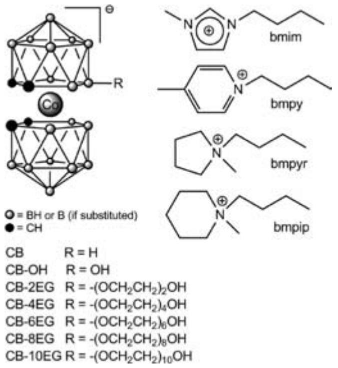

Figure 1. Schematic structures of quaternary ammonium cations and cobalt bis(dicarbollide) based anions. The abbreviations used in this work are also shown.

Compounds have been characterized by NMR, Fourier transform infrared, elemental analysis, powder X-ray diffraction, differential scanning calorimetry, and thermogravimetric analysis. In addition to these characterizations, other important properties such as the decomposition temperature have been studied, and the solubility of all newly synthesized compounds in 76 commonly used organic solvents has been explored for these compounds.

■ EXPERIMENTAL SECTION

General Comments and Chemicals. NMR spectra were recorded on a Varian Mercury Plus 300 MHz (FT, ^1H at 300 MHz, ^{13}C at 75 MHz, ^{19}F at 282 MHz) instrument using tetramethylsilane and C_6F_6 as the external standards (solution of standards in capillary). Chemical shifts are quoted in ppm (δ-scale; s, singlet; bs, broad singlet; d, doublet; t, triplet; m, multiplet). Solvents: $CDCl_3$ and deuterated dimethyl sulfoxide (DMSO-d_6).

The IR spectra were collected using an Avatar 320 FT-IR spectrometer (Thermo Nicolet), and samples were prepared using the KBr pellet method. Spectra were measured in the range of 4000−400 cm^{-1}, and 64 scans were accumulated per spectrum at 1 cm^{-1} resolution. For data analysis, the spectral data were processed using *OMNIC 7.1* software (Thermo Nicolet).

Thermogravimetric analysis (TGA) was performed using thermobalance TG-750 (Stanton-Redcroft, Great Britain). Samples were heated in an argon atmosphere from room temperature to 150 °C at a heating rate of 10 °C/min. TGA was used for the determination of the water content of prepared salts. Samples contain nonstoichiometric amounts of water, if any. The thermal stability was measured using TG-750 and Setsys Evolution (Setaram, France), where the samples were heated from room temperature to 900 °C under various atmospheres (air, nitrogen, and argon).

Differential scanning calorimetry (DSC) measurements were performed using a DSC 131 calorimeter (Setaram, France) from −50 to 200 °C in an argon atmosphere. The DSC data were collected upon the first melting of samples. Selected samples have been measured by repetitive heating and cooling, but because of slow crystallization (some samples need days or weeks to crystallize), a significant amount of information was lost after the first cycle. Curve fitting of the experimental data was performed using nonlinear optimization (Marquardt method) implemented in the software *Calisto* (Setaram).

Elemental analysis (C, H, and N) was performed using an Elementar Vario El III and Perkin-Elmer 2400 by heating samples up to 1200 °C in an oxygen atmosphere.

Powder X-ray diffraction (PXRD) data were collected at room temperature with an X'Pert Pro $\theta{-}\theta$ powder diffractometer with parafocusing Bragg−Brentano geometry using Cu Kα radiation (λ = 1.5418 Å; U = 40 kV; I = 30 mA).

The chemicals used were as follows: cesium cobalt bis(dicarbollide) ($[Cs]^+[CB]^-$) and 8-dioxane-3-cobalt bis(dicarbollide) (Katchem Ltd., Czech Republic); sodium hydride (60% suspension in oil), diethylene glycol, tetraethylene glycol, hexaethylene glycol, octaethylene glycol, 1-butyl-3-methylimidazolium hexafluorophosphate ($[bmim]^+[PF_6]^-$), 1-butyl-4-methylpyridinium hexafluorophosphate ($[bmpy]^+[PF_6]^-$), 1-butyl-1-methylpyrrolidinium hexafluorophosphate ($[bmpyr]^+[PF_6]^-$), and 1-butyl-1-methylpiperidinium ($[bmpip]^+[PF_6]^-$) hexafluorophosphate (all Sigma-Aldrich); silica gel (60−100 mm, Merck). All solvents were purchased from Penta (Czech Rep.) and Sigma-Aldrich and dried according to standard procedures. All reactions requiring anhydrous conditions were performed using anhydrous solvents and in an inert atmosphere.

Sodium Cobalt Bis(dicarbollide) ($[Na]^+[CB]^-$). The cesium salt of cobalt bis(dicarbollide) ($[Cs]^+[CB]^-$) was converted to sodium salts using the extraction procedure. The general procedure used has been previously described.[68] The aqueous solution of the cesium salt was acidified by sulfuric acid (50%). It was then extracted three times with diethyl ether. The organic layer was shaken with an aqueous solution of sodium carbonate and re-extracted five times with water. The solvent was evaporated under reduced pressure and high temperature (60 °C), and the solid residue was dried under vacuum at 100 °C. The sodium salts of cobalt bis(dicarbollide) ($[Na]^+[CB]^-$) were obtained at a nearly quantitative yield.

$[Na]^+[8\text{-}(OH)\text{-}(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})\text{-}3,3'\text{-}Co]^-$ ($[Na]^+[CB\text{-}OH]^-$). The compound was prepared using a modified procedure described in the literature.[69] Cesium cobalt bis(1,2-dicarbollide) (4 g, 8.8 mmol) was suspended in 60% sulfuric acid and heated for 4.5 h at 120 °C. After cooling, the reaction mixture was diluted with water (250 mL) and extracted with diethyl ether (3 × 200 mL). The organic phase was carefully neutralized/extracted with a saturated solution of $NaHCO_3$ (200 mL), dried over anhydrous Na_2SO_4, and evaporated. The crude product was purified by column chromatography on silica (eluent: 2:1 dichloromethane/acetonitrile), subsequently dried under vacuum for 6 h at 100 °C, and yielded 2.69 g (84%) of $[Na]^+[CB\text{-}OH]^-$.

$[Na]^+[8\text{-}(C_4H_9O_3)\text{-}(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})\text{-}3,3'\text{-}Co]^-$ ($[Na]^+[CB\text{-}2EG]^-$). The compound was prepared using a modified procedure described in the literature.[70] A solution of sodium hydroxide (1.2 g, 40 mmol) in water (50 mL) was added to a stirred solution of 8-dioxane-3-cobalt bis(dicarbollide) (4 mmol) in 1,2-dimethoxyethane (50 mL), and this reaction mixture was stirred at 75 °C for 45 min [thin-layer chromatography (TLC) monitoring; CH_2Cl_2]. The reaction mixture was cooled, diluted with brine (250 mL), and extracted with ethyl acetate (4 × 100 mL). The mixed organic phase was subsequently extracted with water (100 mL) and brine (100 mL), dried over anhydrous Na_2SO_4, filtered, and dried under vacuum for 6 h at 100 °C to give pure $[Na]^+[CB\text{-}2EG]^-$ (1.71 g, 95%).

General Procedure for the Preparation of Glycolated Cobalt Bis(Dicarbollide) Derivatives. The compound was prepared using a modified procedure described in the literature.[71−73] A stirred suspension of sodium hydride (5 mmol) in 1,2-dimethoxyethane (40 mL) was added to a solution of the corresponding ethylene glycol (4.5 mmol) in 1,2-dimethoxyethane (40 mL) at room temperature, and the mixture was subsequently stirred at 70 °C in an inert atmosphere for 10 min. Then, 8-dioxane-3-cobalt bis(dicarbollide) (4 mmol) in 1,2-dimethoxyethane (40 mL) was added, and the reaction mixture was stirred at 70 °C for an additional 30 min (TLC monitoring; CH_2Cl_2). After evaporation of volatile compounds, the crude product was purified by column chromatography on silica [gradient from CH_2Cl_2 to 1:1 (v/v) CH_2Cl_2−MeCN]. The product was dried under vacuum for 6 h at 100 °C.

$[Na]^+[8\text{-}(C_8H_{17}O_5)\text{-}(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})\text{-}3,3'\text{-}Co]^-$ ($[Na]^+[CB\text{-}4EG]^-$): 1.69 g (79%)
$[Na]^+[8\text{-}(C_{12}H_{25}O_7)\text{-}(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})\text{-}3,3'\text{-}Co]^-$ ($[Na]^+[CB\text{-}6EG]^-$): 2.22 g (88%)
$[Na]^+[8\text{-}(C_{16}H_{33}O_9)\text{-}(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})\text{-}3,3'\text{-}Co]^-$ ($[Na]^+[CB\text{-}8EG]^-$): 2.03 g (71%)
$[Na]^+[8\text{-}(C_{20}H_{41}O_{11})\text{-}(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})\text{-}3,3'\text{-}Co]^-$ ($[Na]^+[CB\text{-}10EG]^-$): 1.85 g (58%)

Water Content of Cobalt Bis(dicarbollide) Derivatives. The water content of all cobalt bis(dicarbollide) derivatives was analyzed using TGA. The samples contained nonstoichiometric amounts of water, if any. The water content of $[Cs]^+[CB]^-$ was below 0.05%, but the sodium analogue $[Na]^+[CB]^-$ contained 13.6%. The water content of sodium salts generally decreases with the increasing length of oligo(ethylene glycol) chain, namely, $[Na]^+[CB]^-$ ~ 13.6%, $[Na]^+[CB\text{-}OH]^-$ ~ 10.3%, $[Na]^+[CB\text{-}2EG]^-$ ~ 5.2%, $[Na]^+[CB\text{-}4EG]^-$ ~ 0.82%, $[Na]^+[CB\text{-}6EG]^-$ ~ 0.96%, $[Na]^+[CB\text{-}8EG]^-$ ~ 0.67%, and $[Na]^+[CB\text{-}10EG]^-$ ~ 0.39% w/w.

General Procedure for the Preparation of Glycolated Cobalt Bis(Dicarbollide) Ammonium Salts. These salts were prepared by mixing solutions of the appropriate precursors in dichloromethane with approximately 2% excess of a cationic precursor ($[bmim]^+[PF_6]^-$, $[bmpy]^+[PF_6]^-$, $[bmpyr]^+[PF_6]^-$, and $[bmpip]^+[PF_6]^-$). Inorganic salt ($[Na]^+[PF_6]^-$ or $[Cs]^+[PF_6]^-$) and an excess of a cationic precursor have been removed by repeated extraction of the mixture between dichloromethane and water. Inorganic salts and cationic precursors are much more soluble in water than new ILs; thus, this separation is very effective. After each extraction step, the purity was evaluated (the presence of $[PF_6]^-$ anion in product) by ^{19}F NMR, which is an advantage of $[PF_6]^-$-based precursors compared with slightly cheaper chlorides. Elongation of the chain led to glycol-like characteristics in the products. For this reason, all of the salts that were prepared were originally waxy, and only $[CB]^-$- and $[CB\text{-}OH]^-$-based salts solidified with aging. The products were allowed to dry under reduced pressure and further dried under vacuum for 6 h at 100 °C. If necessary, water residues were removed using azeotropic evaporation with anhydrous ethanol, and then the salts were dried under vacuum. The purity was checked by ^{19}F NMR and confirmed by elemental analysis.

Water Content of Prepared Salts. All prepared salts were immediately completely anhydrous after drying (checked by TGA and confirmed by elemental analysis). Because the hydration of salts is an important property, salts were left in open air for 3 days. The water content of all salts was again analyzed using TGA. The samples contained nonstoichiometric amounts of water, if any. The products in the solid state ($[CB]^-$- and $[CB\text{-}OH]^-$-based salts) often contained negligible amounts of water in contrast to the salts in the waxy state, which tended to absorb more water. Salts based on $[CB\text{-}4EG]^-$ contained the most moisture, with approximately two stoichiometric water molecules. The data from TGA were in agreement with the data from elemental analyses.

Characterization. The yields of synthesis, elemental analysis of both hydrated and anhydrous forms of salts, and ^1H NMR, IR, and PXRD data for salts in the solid state at room temperature are provided in the Supporting Information.

Solubility of Salts in Various Solvents. The solubility of salts in 76 commonly used solvents in organic chemistry has been determined by the simple dissolution of small amounts of salt in appropriate amounts of solvent. This was performed for three concentrations of the compound−solvent system: 0.1 mg of salt was dissolved (completely or partially) in 1 mL of solvent (~0.1 g/L), 1 mg in 1 mL (~1 g/L), and 1 mg in 0.1 mL (~10 g/L). On the basis of the solubility of the salts, they were assigned to one of four groups: <0.1 g/L (insoluble), 0.1−1 g/L (poorly soluble), 1−10 g/L (soluble), and >10 g/L (well soluble).

■ RESULTS AND DISCUSSION

A total of 28 salts with low melting temperatures that were based on the cobalt bis(dicarbollide) anion in combination with 1-butyl-3-methylimidazolium, 1-butyl-4-methylpyridinium,

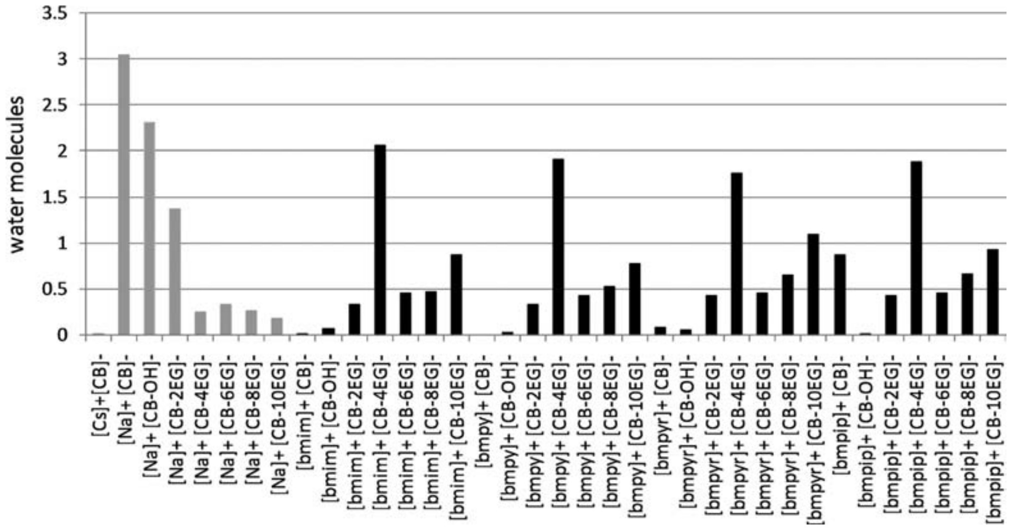

Figure 2. Stoichiometric amounts of water of precursors (gray) and prepared low-melting salts (black).

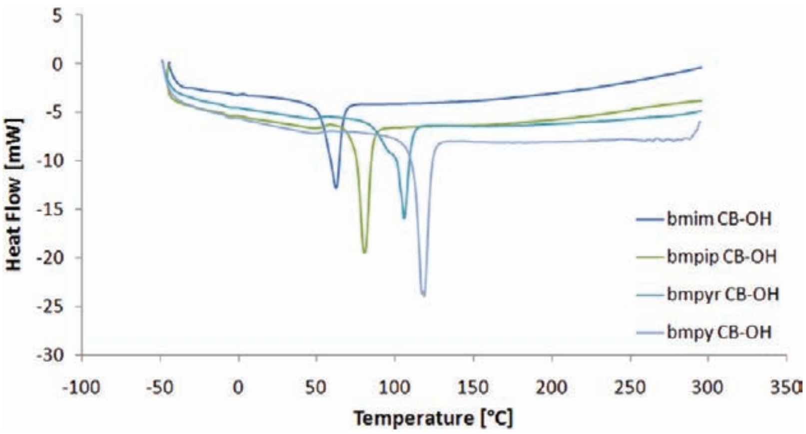

Figure 3. DSC curves of [CB-OH]$^-$-based salts.

1-butyl-1-methylpyrrolidinium, and 1-butyl-1-methylpiperidinium cations, have been prepared and characterized. All but one were prepared for the first time in this study. The salt based on [bmim]$^+$[CB]$^-$ has been previously described by Nieuwenhuyzen et al.,[64] but a different preparation method was used here. The structures and abbreviations for the salts are provided in Figure 1.

The salts were prepared by conventional metathetic reactions (described in the Experimental Section). Products based on [CB]$^-$ and [CB-OH]$^-$, after drying and leaving in the air, contained negligible amounts of water (mostly up to 0.2% by weight; see Figure 2). An increasing chain length of oligo(ethylene glycol) caused an increase in the water content for all salts, but [CB-4EG]$^-$-based salts stand out of the trend and demonstrate substantially higher water content than all other salts (determined by TGA). Generally, precursor ILs themselves tend to be hydrophobic (mainly because of the hydrophobic character of the [PF$_6$]$^-$ anion) and also slightly hygroscopic (depending mainly on the nature of the anion and the length of the aliphatic chain of the cation).[1,74−78] Cobalt bis(dicarbollide) based precursors also tended to contain water (see Figure 2; for exact values, see the Experimental Section), but the trends in the water content for these precursors [decreasing with prolongation of the oligo(ethylene glycol) chain] differed from the trends observed for the prepared salts.

It has been demonstrated by solid-state NMR that sodium cations in [Na]$^+$[CB]$^-$ are somehow separated from cobalt bis(dicarbollide) anions, forming channels that are filled with highly mobile water molecules.[79] Oligo(ethylene glycol) chains can bind sodium cations through oxygen atoms (similar to binding of cations by crown ethers), and thus relatively hydrophobic ethylene groups are directed to the surface of the ion pair. It is expected that the sodium cation is close to the central cobalt atom,[53] which causes an increase in the hydrophobicity, a rapid decrease in the aqueous solubility, and a decrease in the hygroscopicity by an increase in the length of the chain.

Conversely, the chain length influences the properties of salt products in the opposite way. An increasing hygroscopicity of products occurs with prolongation of the chain, which is most likely caused by interactions between free water molecules and chains in the product. They can also form channels filled with mobile water molecules. The [CB-4EG]$^-$-based salts stand out from the trend and display substantially higher water content than other salts (approximately two stoichiometric water molecules).

The thermal stability of the salts has been determined using TGA and PXRD. Selected samples have been heated up to 900 °C using various conditions (two apparatuses; air, nitrogen, and argon atmospheres). It has been observed that (oligo)ethylene

Table 1. DSC Analysis of 28 Low-Melting Salts[a]

	T_g [°C]				T_m [°C]
$[bmim]^+[CB]^-$		−4.2			55.5
$[bmim]^+[CB\text{-}OH]^-$		−4.8			53.4
$[bmim]^+[CB\text{-}2EG]^-$		−10.3			48.1 (47.5, 56.2)
$[bmim]^+[CB\text{-}4EG]^-$					49.3 (40.3, 49.7, 64.8)
$[bmim]^+[CB\text{-}6EG]^-$	−29.6				52.1 (33.4, 53.0)
$[bmim]^+[CB\text{-}8EG]^-$	−26.4				48.7 (48.4, 49.2)
$[bmim]^+[CB\text{-}10EG]^-$	−31.0				49.5 (33.5, 51.2, 68.3)
$[bmpyr]^+[CB]^-$		−4.8	53.5		90.2, 117.1
$[bmpyr]^+[CB\text{-}OH]^-$		−9.1	51.4		99.7 (83.9, 101.3)
$[bmpyr]^+[CB\text{-}2EG]^-$		−9.5	51.1		
$[bmpyr]^+[CB\text{-}4EG]^-$		−8.7	52.5		
$[bmpyr]^+[CB\text{-}6EG]^-$	−37.5	−4.5	52.5		99
$[bmpyr]^+[CB\text{-}8EG]^-$	−34.7	−9.5	51.5		
$[bmpyr]^+[CB\text{-}10EG]^-$	−37.3	−8.4	52.6		
$[bmpip]^+[CB]^-$		−4.0	55.3		87.3 (81.8, 88.6)
$[bmpip]^+[CB\text{-}OH]^-$		−9.3	54.5		75.1
$[bmpip]^+[CB\text{-}2EG]^-$		−9.0	54.5		
$[bmpip]^+[CB\text{-}4EG]^-$		−3.1	58.1		
$[bmpip]^+[CB\text{-}6EG]^-$	−38.9	−7.8	53.2		
$[bmpip]^+[CB\text{-}8EG]^-$	−34.3	−7.8	53.7		
$[bmpip]^+[CB\text{-}10EG]^-$	−36.3	−3.4	50.7	57.0	
$[bmpy]^+[CB]^-$		−8.5	53.4		118.5
$[bmpy]^+[CB\text{-}OH]^-$		−8.3	54.6		112.3
$[bmpy]^+[CB\text{-}2EG]^-$		−7.9	53.7		
$[bmpy]^+[CB\text{-}4EG]^-$		−4.1	52.7		
$[bmpy]^+[CB\text{-}6EG]^-$	−30.3	−8.5	49.1		
$[bmpy]^+[CB\text{-}8EG]^-$	−25.9	−8.0	50.8		
$[bmpy]^+[CB\text{-}10EG]^-$	−30.5	−7.5	52.9		

[a] Glass transition (T_g) and melting point (T_m) temperatures evaluated by deconvolution of the merged peaks are in brackets.

glycol chains tend to decompose at approximately 180 °C and that the cations tend to decompose from 300 to 420 °C, depending on stabilization by the counterions. The cobalt bis(dicarbollide) cages start to oxidize (if oxygen was presented) at approximately 700 °C to form B_2O_3 and cobalt-based microparticles. Oxidation has been observed by heat flow and an increase in the weight. The products look like black balls of wire and have been analyzed by PXRD and elemental analysis.

Melting points and glass transition temperatures have been analyzed using DSC (Figure 3). The temperatures are shown in Table 1. The first observed glass transition appeared at −38.9 to −25.9 °C. It was observed only for salts based on $[CB\text{-}6EG]^-$, $[CB\text{-}8EG]^-$, and $[CB\text{-}10EG]^-$ anions. Generally, bmpyr and bmpip salts have lower glass transition temperatures (−38.9 to −34.3 °C) than $[bmim]^+$ and $[bmpy]^+$ salts (−31.0 to −25.9 °C). There is not any clear trend in temperatures as a function of the chain length; however, $[CB\text{-}8EG]^-$-based salts seem to have slightly higher temperatures than $[CB\text{-}6EG]^-$- and $[CB\text{-}10EG]^-$-based salts. The second glass transition temperature region was between −10.3 and −3.1 °C without any clear trend in temperatures among the salts. The third temperature region between 49.1 and 58.1 °C was detected for all salts except $[bmim]^+$-based salts. For $[bmim]^+$-based salts, the melting point was observed in this region. The $[bmim]^+$-based salts tend to form various polymorphs and display multiple melting points. These melting temperatures are relatively similar, and thus the table shows an average temperature (onset) and temperatures evaluated by deconvolution of the merged peaks (values in parentheses). It should be noted that the intensity of the peak corresponding to the melting point increases with aging of the samples due to slow crystallization. In contrast with data from the literature,[64] we have observed melting points of $[bmim]^+[CB]^-$, but this may be due to the measurement of an older sample. The lowest melting points obtained were for $[bmim]^+$-based salts (~50 °C), followed by $[bmpip]^+$-based salts (~80 °C), $[bmpyr]^+$-based salts (~95 °C), and $[bmpy]^+$-based salts (~115 °C). The chain length influenced the melting points only up to 10 °C; thus, its effect is significantly smaller than the effect of the cation.

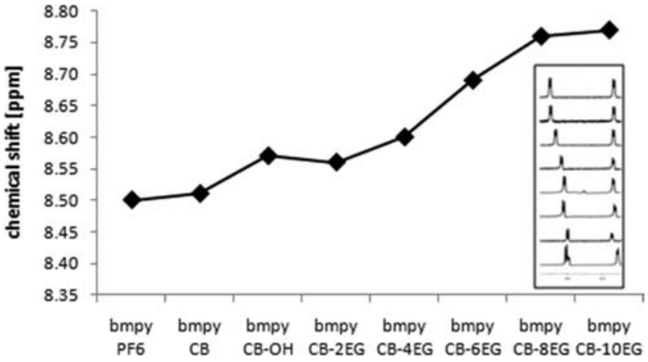

Figure 4. Dependence of the chemical shift of the aromatic signal of $[bmim]^+$ as a function of the counterion (^1H NMR in $CDCl_3$) with a cut of spectra (inset).

NMR spectra for all samples have been measured in deuterated chloroform and DMSO. In agreement with

Table 2. Solubility of Low-Melting Salts in 76 Solvents and the Physical Properties of the Solvents

	Dipole moment μ [D]	Relative polarity E_T^N	log P_{ow} @ 25°C	Solubility in water [g/100 g] @ 25°C	Solubility of water in [g/100 g] @ 25°C	bmim							bmpyr							bmpip							bmpy						
						CB	CB-OH	CB-2EG	CB-4EG	CB-6EG	CB-8EG	CB-10EG	CB	CB-OH	CB-2EG	CB-4EG	CB-6EG	CB-8EG	CB-10EG	CB	CB-OH	CB-2EG	CB-4EG	CB-6EG	CB-8EG	CB-10EG	CB	CB-OH	CB-2EG	CB-4EG	CB-6EG	CB-8EG	CB-10EG
1,1,1-Trichloroethane	1.7	17	2.36	0.13	0.034	░	░	■	■	■	■	■	░	░	■	■	■	■	■	░	░	■	■	■	■	■	░	░	■	■	■	■	■
1,2-Dichloroethane	1.83	32.7	1.63	0.81	0.15	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
1,2-Dimethoxyethane	1.71	23.1	-0.21	∞	∞	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
2-Methoxyethanol	2.04	66.7	-0.6	∞	∞	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
2-Methyl propan-2-ol	1.66	38.9	0.36	∞	∞	□	□	░	░	░	░	░	□	□	□	░	░	░	░	□	□	□	□	□	□	□	□	□	□	□	□	□	□
2-Methyl tetrahydrofuran	1.38	17.9	1.25	15.6	4.9	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
2-Methylpropan-1-ol	1.79	55.2	0.75	8.5	15	░	░	■	■	■	■	■	░	░	■	■	■	■	■	░	░	■	■	■	■	■	░	░	■	■	■	■	■
4-Methylpentan-2-one	2.7	26.9	1.31	1.8	1.8	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Acetic acid	1.68	64.8	-0.24	∞	∞	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Acetone	2.69	35.5	-0.24	∞	∞	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Acetonitrile	3.92	46	-0.34	∞	∞	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Acetylacetone	2.78	57.1	2.14	19.2	5	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Benzene	0	11.1	2.13	0.18	0.063	░	░	░	■	■	■	■	░	░	░	■	■	░	░	░	░	■	■	■	■	░	░	░	■	■	■	■	░
Benzonitrile	4.18	33.3	1.56	0.2	0.87	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Bis(2-methoxyethyl) ether	1.97	24.4	-0.54	∞	∞	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Butan-1-ol	1.75	60.2	0.75	7.3	20.4	░	░	■	■	■	■	■	░	░	■	■	■	■	■	░	░	■	■	■	■	■	░	░	■	■	■	■	■
Butan-2-ol	1.79	50.6	0.71	19.8	65.1	░	░	■	■	■	■	■	░	░	■	■	■	■	■	░	░	■	■	■	■	■	░	░	■	■	■	■	■
Butanone	2.76	32.7	0.29	26	12	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Butyl acetate	1.84	24.1	1.82	0.68	1.3	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Carbon tetrachloride	0	5.2	2.64	0.077	0.008	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Cyclohexane	0	0.6	3.44	0.0055	0.01	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□
Diethyl carbonate	0.9	18.5	1.21	1.82	0.93	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Diethyl ether	1.15	11.7	0.89	6.9	1.3	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░
Dichloromethane	1.14	30.9	1.15	1.3	0.2	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Diisopropyl ether	1.22	10.5	2.03	1.2	0.62	□	□	░	░	░	░	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	░	░	░	░
Dimethyl acetamide	3.72	40.1	-0.77	∞	∞	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Dimethyl carbonate	0.87	23.2	0.23	14	2.6	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Dimethyl formamide	3.82	40.4	-1.01	∞	∞	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Dimethyl sulfoxide	4.06	44.4	-1.35	∞	∞	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Di-n-butyl ether	1.17	7.1	3.21	0.03	0.2	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□
Dioxan	0.45	16.4	-0.42	∞	∞	■	■	░	■	■	■	■	■	■	░	░	░	░	░	░	░	░	░	░	░	░	■	■	░	■	■	■	■
Ethanol	1.66	65.4	-0.32	∞	∞	■	■	■	■	■	■	■	░	■	■	■	■	■	■	■	■	■	■	■	■	■	░	░	■	■	■	■	■
Ethyl acetate	1.78	22.8	0.73	7.7	3.3	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Ethyl acetoacetate	2.93	57.7	1.23	13.4	3.8	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Ethyl formate	1.94	31.5	0.27	13	11.1	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Ethylene glycol	2.31	79	-2.27	∞	∞	░	░	░	░	░	░	░	░	░	░	░	░	░	░	□	□	░	░	░	░	░	□	░	░	░	░	░	░
Formic acid	1.82	72.8	-0.54	∞	∞	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Glycerol	4.21	81.2	-2.56	∞	∞	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□
Hexamethylphosphoramide	5.54	31.5	0.28	∞	∞	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Hexan-2-one	3.08	29	1.38	1.6	1.6	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Hexane	0.09	0.9	3.9	0.00095	0.011	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□
Chloroform	1.15	25.9	1.94	0.82	0.072	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Isobutyl acetate	1.86	22.8	1.78	0.66	1.1	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Isopropyl acetate	1.87	20.5	1.22	3	1.9	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Methanol	2.87	76.2	-0.74	∞	∞	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Methyl acetate	1.68	25.3	0.18	24.5	8.2	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Methyl isopropyl ketone	2.77	31.5	0.84	6.4	2.3	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Methyl *tert*-butyl ether	1.36	14.8	1.2	4.3	1.4	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░

Solubility	□	░	▓	■
	< 0.1 g/L	0.1-1 g/L	1-10 g/L	> 10 g/L

Table 2. continued

	Dipole moment μ [D]	Relative polarity E_T^N	log P_{ow} @ 25°C	Solubility in water [g/100 g] @ 25°C	Solublity of water in [g/100 g] @ 25°C	bmim							bmpyr							bmpip							bmpy						
						CB	CB-OH	CB-2EG	CB-4EG	CB-6EG	CB-8EG	CB-10EG	CB	CB-OH	CB-2EG	CB-4EG	CB-6EG	CB-8EG	CB-10EG	CB	CB-OH	CB-2EG	CB-4EG	CB-6EG	CB-8EG	CB-10EG	CB	CB-OH	CB-2EG	CB-4EG	CB-6EG	CB-8EG	CB-10EG
Methyl *tert*-butyl ketone	2.75	25.6	1.2	2	2.4	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Nitrobenzene	4.22	32.4	1.85	0.19	0.24	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Nitroethane	3.6	39.8	0.18	4.8	1	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Nitromethane	3.56	48.1	-0.33	11	2	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
N-Methyl formamide	3.86	72.2	-0.97	∞	∞	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
N-Methyl pyrrolidine-2-one	4.09	36	-0.54	∞	∞	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
n-Octane	0	1.2	5.18	0.00006	0.008	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□
n-Octanol	1.76	53.7	---	0.032	3.8	□	□	□	░	░	░	░	□	□	□	□	░	░	░	□	□	□	□	□	□	░	□	□	□	□	□	□	□
o-Dichlorobenzene	2.5	22.5	3.28	0.016	0.3	░	░	■	■	■	■	■	░	░	■	■	■	■	■	░	░	■	■	■	■	■	░	░	■	■	■	■	■
o-Tolunitrile	3.77	33.9	2.21	0.018	0.072	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
o-Xylene	0.45	7.1	3.12	0.02	0.05	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░
Pentan-2-one	2.7	32.1	0.91	6.3	2.9	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Pentan-3-one	2.82	26.5	0.82	3.5	2.4	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Pentane	0	0.9	3.39	0.038	0.012	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□
Petroleum ether	0.09	0.9	3.7	0.004	0.012	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□
Propan-1-ol	3.09	61.7	0.25	∞	∞	░	░	■	■	■	■	■	░	░	■	■	■	■	■	░	░	■	■	■	■	■	░	░	■	■	■	■	■
Propan-2-ol	1.66	54.6	0.13	∞	∞	░	░	■	■	■	■	■	░	░	■	■	■	■	■	░	░	■	■	■	■	■	░	░	■	■	■	■	■
Propanoic acid	1.68	61.1	0.32	∞	∞	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Propyl acetate	1.78	21	1.24	2.3	2.6	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Pyridine	2.37	30.2	0.65	∞	∞	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Sulfolane	4.81	41	-0.77	∞	∞	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Tetrahydrofuran	1.75	20.7	0.46	∞	∞	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Toluene	0.31	9.9	2.69	0.052	0.033	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░
Triethylamine	0.66	4.3	1.36	5.8	3.8	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□
Trifluoroacetic acid	2.28	100	-2.1	∞	∞	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Trifluoromethyl benzene	2.6	24.1	3.01	0.014	0.021	░	░	■	■	■	■	■	░	░	■	■	■	■	■	░	░	■	■	■	■	■	░	░	■	■	■	■	■
Tri-n-butylamine	0.78	4.3	1.52	0.0041	0.12	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□	□
Water	1.85	100	---	∞	∞	□	□	□	□	□	░	░	□	□	□	□	░	░	░	□	□	□	□	□	□	░	□	□	□	□	□	□	░

Solubility	□	░	▒	■
	< 0.1 g/L	0.1-1 g/L	1-10 g/L	> 10 g/L

expectations, the samples in chloroform tended to form ion pairs; thus, the spectra of the cationic moieties are significantly different in the presence of various anionic moieties (clearly visible in aromatic regions of [bmim]$^+$ and [bmpy]$^+$ spectra; for exact chemical shifts, see the Supporting Information). In the case of [bmpy]$^+$ salts, these effects seem to be stronger with increasing length of the oligo(ethylene glycol) chain (Figure 4). On the other hand, the spectra for samples dissolved in DMSO display only negligible differences in comparison to the superposed spectra of the precursors. Therefore, it seems that samples dissolved in DMSO are presented only in the form of separated ions or mainly in the form of separated ions when both forms are present (i.e., ion pairs and separated ions).

The IR spectra for all samples were measured using the KBr pellet method; the values and figures are in the Supporting Information. Generally, peaks belonging to cations tended to become wider with increasing length of the oligo(ethylene glycol) chain. This finding correlates with crystalline salts becoming waxy with increasing length of the chain.

The solubility of all 28 salts was determined in 76 different solvents. The properties of the solvents and solubility of salts are summarized in Table 2. For simplicity, the solubility is visualized by gray scale; the darker gray shade means that the salt demonstrated the higher solubility in the specified solvent. Table 2 summarizes the basic properties of the solvents: dipole moment,[80] relative polarity,[81,82] log P_{ow},[80,83] solubility of the solvent in water and solubility of water in the solvent.[80,82] Dipole moments of molecules are due to the nonuniform distribution of charges on various atoms, and generally, polar compounds (compounds with permanent dipole moment) prefer to dissolve in polar solvents. Relative polarity is a normalized empirical parameter of solvent polarity. It is derived from the UV/vis charge-transfer absorption at long-wavelengths for the negatively charged solvatochromic pyridinium N-phenolate betaine dyes (Dimroth and Reichardt), where Me_4Si = 0 and water =100 at 25 °C. The values for relative polarity are normalized by measurements of solvent shifts in the absorption spectra and were obtained from a literature.[81] The octanol−water partition coefficient (P_{ow}) is defined as the ratio of the equilibrium concentrations of a dissolved compound in a two-phase system consisting of octanol and water ($P_{ow} = c_o/c_w$). The P_{ow} is widely used as a hydrophobicity descriptor.[84]

Generally, the solubility of cobalt bis(dicarbollide) salts increases with the dipole moment and relative polarity of the solvents. The prepared salts were very soluble in ketones and esters, moderately soluble in alcohols, aromates, and chlorinated solvents, and not very soluble in ethers. The salts were practically insoluble in higher hydrocarbons and water.

■ CONCLUSIONS

In this study, we synthesized low-melting salts based on 1-butyl-3-methylimidazolium ([bmim]$^+$), 1-butyl-1-methylpiperidinium ([bmpip]$^+$), 1-butyl-1-methylpyrrolidinium ([bmpyr]$^+$), and 1-butyl-4-methylpyridinium salts ([bmpy]$^+$) in combination with cobalt bis(dicarbollide) and hydroxylated and glycolated cobalt bis(dicarbollide) anions. The lowest melting points obtained were for salts based on [bmim]$^+$ (~50 °C), followed by [bmpip]$^+$ (~80 °C), [bmpyr]$^+$ (~95 °C), and [bmpy]$^+$ (~115 °C). When the chain length was varied, the melting points exhibited relatively little change (up to 10 °C). The salts were thermally stable up to 180 °C [decomposition of oligo(ethylene glycol) chain], but the cations tended to decompose at temperatures from 300 to 420 °C, depending on the cation and on stabilization by the counterion. The cobalt bis(dicarbollide) cages started to oxidize (if oxygen was presented) near 700 °C to form B_2O_3 and cobalt-based microparticles. The salts contained variable amounts of water, depending on the length of the oligo(ethylene glycol) chain. The water content was relatively independent of the cation. The presence of oligo(ethylene glycol) caused a waxy property in the salts, and only salts with unsubstituted and hydroxylated cobalt bis(dicarbollide) solidified with aging. The solubility of the salts increased with the dipole moment and relative polarity of the solvents (based on a set of 76 of the most commonly used solvents in organic chemistry), and the salts were dissolved in the form of ion pairs or separated ions depending on the nature of the solvent. The salts demonstrated good solubility in ketones and esters, moderate solubility in alcohols, aromates, and chlorinated solvents, and poor solubility in ethers and were practically insoluble in higher hydrocarbons and water.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Schematic structures of quaternary ammonium cations and cobalt bis(dicarbollide) based anions, characterization of prepared salts, water content of precursors and prepared low-melting salts, PXRD patterns of salts and their precursors, DSC curves of the prepared salts, dependence of the chemical shift in the aromatic signal of bmpy as a function of the counterion, and IR spectra of prepared salts measured using the KBr pellet method. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Wasserscheid, P.; Welton, T. *Ionic Liquids in Synthesis*, 2nd ed.; Wiley-VCH Verlag GmbH & Co.: Weinheim, Germany, 2008.

(2) Brennecke, J. F.; Rogers, R. D.; Seddon, K. R. *ACS Symp. Ser.* **2007**, *975*, 1−408.

(3) Li, Z.; Jia, Z.; Luan, Y.; Mu, T. *Curr. Opin. Solid State Mater. Sci.* **2008**, *12*, 1−8.

(4) Ma, Z.; Yu, J. H.; Dai, S. *Adv. Mater.* **2010**, *22*, 261−285.

(5) Kokorin, A. In *Ionic Liquids: Applications and Perspectives* Kokorin, A., Ed.; InTech: Rijeka, Croatia, 2011; p 674.

(6) Wei, G. T.; Yang, Z. S.; Chen, C. J. *Anal. Chim. Acta* **2003**, *488*, 183−192.

(7) Liu, J.; Jiang, G. B.; Chi, Y. G.; Cai, Y. Q.; Zhou, Q. X.; Hu, J. T. *Anal. Chem.* **2003**, *75*, 5870−5876.

(8) Liu, J. F.; Li, N.; Jiang, G. B.; Li, J. M.; Jonsson, J. A.; Wen, M. J. *J. Chromatogr. A* **2005**, *1066*, 27−32.

(9) Armstrong, D. W.; He, L. F.; Liu, Y. S. *Anal. Chem.* **1999**, *71*, 3873−3876.

(10) Vaher, M.; Koel, M.; Kaljurand, M. *Chromatographia* **2001**, *53*, S302−S306.

(11) He, L. J.; Zhang, W. Z.; Zhao, L.; Liu, X.; Jiang, S. X. *J. Chromatogr. A* **2003**, *1007*, 39−45.

(12) Liang, C. D.; Yuan, C. Y.; Warmack, R. J.; Barnes, C. E.; Dai, S. *Anal. Chem.* **2002**, *74*, 2172−2176.

(13) Armstrong, D. W.; Zhang, L. K.; He, L. F.; Gross, M. L. *Anal. Chem.* **2001**, *73*, 3679−3686.

(14) Kavan, L.; Dunsch, L. *ChemPhysChem* **2003**, *4*, 944−950.

(15) Bartůněk, V.; Rak, J.; Král, V.; Smrčková, O. *J. Fluorine Chem.* **2011**, *132*, 298−301.

(16) Vollmer, C.; Janiak, C. *Coord. Chem. Rev.* **2011**, *255*, 2039−2057.

(17) Bartůněk, V.; Jakeš, V.; Král, V.; Rak, J. *J. Fluorine Chem.* **2012**, *135*, 358−361.

(18) Hough, W. L.; Smiglak, M.; Rodriguez, H.; Swatloski, R. P.; Spear, S. K.; Daly, D. T.; Pernak, J.; Grisel, J. E.; Carliss, R. D.; Soutullo, M. D.; Davis, J. H.; Rogers, R. D. *New J. Chem.* **2007**, *31*, 1429−1436.

(19) King, R. B. *Chem. Rev.* **2001**, *101*, 1119−1152.

(20) Chen, Z. F.; King, R. B. *Chem. Rev.* **2005**, *105*, 3613−3642.

(21) Sivaev, I. B.; Bregadze, V. I. *Eur. J. Inorg. Chem.* **2009**, 1433−1450.

(22) Lesnikowski, Z. J. *Collect. Czech. Chem. Commun.* **2007**, *72*, 1646−1558.

(23) Fanfrlík, J.; Lepšík, M.; Horinek, D.; Havlas, Z.; Hobza, P. *ChemPhysChem* **2006**, *7*, 1100−1105.

(24) Sivaev, I. B.; Bregadze, V. I. *Collect. Czech. Chem. Commun.* **1999**, *64*, 783−805.

(25) Grimes, R. N. *Carboranes*, 2nd ed.; Academic Press (an imprint of Elsevier): Amsterdam, The Netherlands, 2011.

(26) Barbera, G.; Vaca, A.; Teixidor, F.; Sillanpaa, R.; Kivekas, R.; Vinas, C. *Inorg. Chem.* **2008**, *47*, 7309−7316.

(27) Li, T. J.; Jalisatgi, S. S.; Bayer, M. J.; Maderna, A.; Khan, S. I.; Hawthorne, M. F. *J. Am. Chem. Soc.* **2005**, *127*, 17832−17841.

(28) Valliant, J. F.; Guenther, K. J.; King, A. S.; Morel, P.; Schaffer, P.; Sogbein, O. O.; Stephenson, K. A. *Coord. Chem. Rev.* **2002**, *232*, 173−230.

(29) Cígler, P.; Kožíšek, M.; Řezáčová, P.; Brynda, J.; Otwinowski, Z.; Pokorná, J.; Plešek, J.; Grüner, B.; Dolečková-Marešová, L.; Máša, M.; Sedláček, J.; Bodem, J.; Krausslich, H. G.; Král, V.; Konvalinka, J. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 15394−15399.

(30) Rak, J.; Kaplánek, R.; Král, V. *Bioorg. Med. Chem. Lett.* **2010**, *20*, 1045−1048.

(31) Rak, J.; Jakubek, M.; Kaplánek, R.; Matějíček, P.; Král, V. *Eur. J. Med. Chem.* **2011**, *46*, 1140−1146.

(32) Issa, F.; Kassiou, M.; Rendina, L. M. *Chem. Rev.* **2011**, *111*, 5701−5722.

(33) Scholz, M.; Hey-Hawkins, E. *Chem. Rev.* **2011**, *111*, 7035−7062.

(34) Pokorná, J.; Cígler, P.; Kožíšek, M.; Řezáčová, P.; Brynda, J.; Plešek, J.; Grüner, B.; Sedláček, J.; Bodem, J.; Kraeusslich, H. G.; Král, V.; Konvalinka, J. *Antiviral Ther.* **2006**, *11*, S29−S29.

(35) Plešek, J. *Chem. Rev.* **1992**, *92*, 269−278.

(36) Vinas, C.; Gomez, S.; Bertran, J.; Teixidor, F.; Dozol, J. F.; Rouquette, H. *Chem. Commun.* **1998**, 191−192.

(37) Vinas, C.; Gomez, S.; Bertran, J.; Teixidor, F.; Dozol, J. F.; Rouquette, H. *Inorg. Chem.* **1998**, *37*, 3640−3643.

(38) Grüner, B.; Plešek, J.; Báča, J.; Císařová, I.; Dozol, J. F.; Rouquette, H.; Vinas, C.; Selucký, P.; Rais, J. *New J. Chem.* **2002**, *26*, 1519−1527.

(39) Selucký, P.; Rais, J.; Lučaníková, M.; Grüner, B.; Kvíčalová, M.; Fejfarová, K.; Císařová, I. *Radiochim. Acta* **2008**, *96*, 273−284.

(40) Grüner, B.; Kvíčalová, M.; Plešek, J.; Šícha, V.; Císařová, I.; Lučaníková, M.; Selucký, P. *J. Organomet. Chem.* **2009**, *694*, 1678−1689.

(41) Grüner, B.; Kvíčalová, M.; Selucký, P.; Lučaníková, M. *J. Organomet. Chem.* **2010**, *695*, 1261−1264.

(42) Kokado, K.; Tokoro, Y.; Chujo, Y. *Macromolecules* **2009**, *42*, 9238−9242.

(43) Kokado, K.; Tokoro, Y.; Chujo, Y. *Macromolecules* **2009**, *42*, 2925−2930.

(44) Peterson, J. J.; Simon, Y. C.; Coughlin, E. B.; Carter, K. R. *Chem. Commun.* **2009**, 4950−4952.

(45) Dash, B. P.; Satapathy, R.; Gaillard, E. R.; Norton, K. M.; Maguire, J. A.; Chug, N.; Hosmane, N. S. *Inorg. Chem.* **2011**, *50*, 5485−5493.

(46) Nicoud, J. F.; Bolze, F.; Sun, X. H.; Hayek, A.; Baldeck, P. *Inorg. Chem.* **2011**, *50*, 4272−4278.

(47) Douvris, C.; Ozerov, O. V. *Science* **2008**, *321*, 1188−1190.

(48) El-Zaria, M. E.; Arii, H.; Nakamura, H. *Inorg. Chem.* **2011**, *50*, 4149−4160.

(49) Stoica, A. I.; Vinas, C.; Teixidor, F. *Chem. Commun.* **2008**, 6492−6494.

(50) Stoica, A. I.; Vinas, C.; Teixidor, F. *Chem. Commun.* **2009**, 4988−4990.

(51) Masalles, C.; Teixidor, F.; Borros, S.; Vinas, C. *J. Organomet. Chem.* **2002**, *657*, 239−246.

(52) Masalles, C.; Borros, S.; Vinas, C.; Teixidor, F. *Adv. Mater.* **2000**, *12*, 1199−1202.

(53) Llop, J.; Masalles, C.; Vinas, C.; Teixidor, F.; Sillanpaa, R.; Kivekas, R. *Dalton Trans.* **2003**, 556−561.

(54) Farras, P.; Teixidor, F.; Kivekas, R.; Sillanpaa, R.; Vinas, C.; Grüner, B.; Císařová, I. *Inorg. Chem.* **2008**, *47*, 9497−9508.

(55) Farras, P.; Cioran, A. M.; Šícha, V.; Teixidor, F.; Štíbr, B.; Grüner, B.; Vinas, C. *Inorg. Chem.* **2009**, *48*, 8210−8219.

(56) Nunez, R.; Juarez-Perez, E. J.; Teixidor, F.; Santillan, R.; Farfan, N.; Abreu, A.; Yepez, R.; Vinas, C. *Inorg. Chem.* **2010**, *49*, 9993−10000.

(57) Grüner, B.; Mikulášek, L.; Báča, J.; Císařová, I.; Böhmer, V.; Danila, C.; Reinoso-Garcia, M. M.; Verboom, W.; Reinhoudt, D. N.; Casnati, A.; Ungaro, R. *Eur. J. Org. Chem.* **2005**, 2022−2039.

(58) Larsen, A. S.; Holbrey, J. D.; Tham, F. S.; Reed, C. A. *J. Am. Chem. Soc.* **2000**, *122*, 7264−7272.

(59) Ronig, B.; Pantenburg, I.; Wesemann, L. *Eur. J. Inorg. Chem.* **2002**, *2*, 319−322.

(60) Zhu, Y. H.; Ching, C. B.; Carpenter, K.; Xu, R.; Selvaratnam, S.; Hosmane, N. S.; Maguire, J. A. *Appl. Organomet. Chem.* **2003**, *17*, 346−350.

(61) Dymon, J.; Wibby, R.; Kleingardner, J.; Tanski, J. M.; Guzei, I. A.; Holbrey, J. D.; Larsen, A. S. *Dalton Trans.* **2008**, *22*, 2999−3006.

(62) Justus, E.; Rischka, M.; Wishart, J. F.; Werner, K.; Gabel, D. *Chem.—Eur. J.* **2008**, *14*, 1918−1923.

(63) Matsumi, N.; Miyamoto, M.; Aoi, K. *J. Organomet. Chem.* **2009**, *694*, 1612−1616.

(64) Nieuwenhuyzen, M.; Seddon, K. R.; Teixidor, F.; Puga, A. V.; Vinas, C. *Inorg. Chem.* **2009**, *48*, 889−901.

(65) Liu, S. M.; Chen, Z. J.; Zhang, Q. H.; Zhang, S. G.; Li, Z. P.; Shi, F.; Ma, X. Y.; Deng, Y. Q. *Eur. J. Inorg. Chem.* **2011**, *12*, 1910−1920.

(66) Adams, R. M. *Pure Appl. Chem.* **1972**, *30*, 683−710.

(67) Rais, J.; Grüner, B. Extraction with Metal Bis(dicarbollide) Anions. In *Ion Exchange and Solvent Extraction*; Marcus, Y., SenGupta, A. K., Marinski, J. A., Eds.; Marcel Dekker, Inc.: New York, 2004; pp 243−334.

(68) Plešek, J.; Baše, K.; Mareš, F.; Hanousek, F.; Štíbr, B.; Heřmánek, S. *Collect. Czech. Chem. Commun.* **1984**, *49*, 2776−2789.

(69) Plešek, J.; Grüner, B.; Báča, J.; Fusek, J.; Císařová, I. *J. Organomet. Chem.* **2002**, *649*, 181−190.

(70) Sivaev, I. B.; Starikova, Z. A.; Sjoberg, S.; Bregadze, V. I. *J. Organomet. Chem.* **2002**, *649*, 1−8.

(71) Teixidor, F.; Pedrajas, J.; Rojo, I.; Vinas, C.; Kivekas, R.; Sillanpaa, R.; Sivaev, I.; Bregadze, V.; Sjoberg, S. *Organometallics* **2003**, *22*, 3414−3423.

(72) Grüner, B.; Plešek, J.; Báča, J.; Dozol, J. F.; Lamare, V.; Císařová, I.; Bělohradský, M.; Čáslavský, J. *New J. Chem.* **2002**, *26*, 867−875.

(73) Semioshkin, A. A.; Sivaev, I. B.; Bregadze, V. I. *Dalton Trans.* **2008**, 977−992.

(74) Freire, M. G.; Neves, C. M. S. S.; Carvalho, P. J.; Gardas, R. L.; Fernandes, A. M.; Marrucho, I. M.; Santos, L. M. N. B. F.; Coutinho, J. A. P. *J. Phys. Chem. B* **2007**, *111*, 13082−13089.

(75) Jin, H.; O'Hare, B.; Dong, J.; Arzhantsev, S.; Baker, G. A.; Wishart, J. F.; Benesi, A. J.; Maroncelli, M. *J. Phys. Chem. B* **2008**, *112*, 81−92.

(76) Kolbeck, C.; Lehmann, J.; Lovelock, K. R. J.; Cremer, T.; Paape, N.; Wasserscheid, P.; Froba, A. P.; Maier, F.; Steinruck, H. P. *J. Phys. Chem. B* **2010**, *114*, 17025−17036.

(77) Rak, J.; Ondo, D.; Tkadlecová, M.; Dohnal, V. *Z. Phys. Chem.* **2010**, *224*, 893−906.

(78) Ondo, D.; Tkadlecová, M.; Dohnal, V.; Rak, J.; Kvíčala, J.; Lehmann, J. K.; Heintz, A.; Ignatiev, N. *J. Phys. Chem. B* **2011**, *115*, 10285−10297.

(79) Matějíček, P.; Brus, J.; Jigounov, A.; Pleštil, J.; Uchman, M.; Procházka, K.; Gradzielski, M. *Macromolecules* **2011**, *44*, 3847−3855.

(80) Marcus, Y. *The Properties of Solvents*; Wiley Series in Solutions Chemistry; John Wiley & Sons Ltd.: Chichester, U.K., 1988.

(81) Reichardt, C. *Chem. Rev.* **1994**, *94*, 2319−2358.

(82) Smallwood, I. M. *Handbook of organic solvent properties*; John Wley & Sons Inc.: New York, 1996.

(83) http://logkow.cisti.nrc.ca/logkow/index.jsp.

(84) Zhao, Y. H.; Abraham, M. H. *J. Org. Chem.* **2005**, *70*, 2633−2640.