Ionic Liquids

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Low-Viscosity Paramagnetic Ionic Liquids with Doubly Charged $[Co(NCS)_4]^{2-}$ Ions**

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For about ten years, the focus of a considerable number of scientific publications has been on ionic liquids (ILs), which are composed of ions and have melting points below 100 °C.[1] An essential reason for the interest in this substance class are some unusual and often very useful materials characteristics. There are for example large electrochemical windows, hardly measurable vapor pressures at ambient temperature, large fluid ranges, and outstanding solubility characteristics.[2] In contrast to conventional solvents, ILs have the advantage that properties can be varied by a large number of various combinations of possible cations and anions. To minimize Coulomb interactions and to reach low melting points, the usage of bulky 1,3-disubstituted imidazolium, pyridinium, or tertiary ammonium or phosphonium cations is very common. Extensive research activities are presently focused on the question of how specific physical chemical properties of ILs are correlated with electronic and steric effects (composition–structure–property relations).[3]

Metal-ion-containing ILs are a very interesting subclass of Ils: not only because of the above-mentioned properties, but also they may have interesting magnetic or catalytic properties.[4] Investigations on (BMIm)$[FeCl_4]$ (BMIm = 1-butyl-3-methylimidazolium) were sensational: it was shown that droplets can be affected by magnets.[5] Therefore, ILs with paramagnetic transition metal cations have been discussed as suitable candidates for magnetic and magnetorheological fluids.[6] Apart from a few examples (mostly based on rare-earth-metal ions),[7] investigations of transition-metal-based ILs have been limited to 3d elements (M) in monoanionic halogenido complexes of the type $[MX_4]^-$ (X = halide, usually X = Cl).[4–6,8] In terms of potential applications, almost all of these substances have undesired properties, such as high viscosity, insolubility in water, or hydrolytic instability.

Herein we present a new class of ionic liquids that contain doubly negatively charged tetraisothiocyanatocobaltate(II) anions and that have the appearance of blue ink.[9] Despite the fact that doubly charged anions are present, surprisingly some of these compounds have glass-transition temperatures that lie far below room temperature and have low viscosities. Furthermore, these ILs are distinguished by useful features, such as good stabilities towards water and oxygen and also good solubility in many solvents. The four compounds $A_x[Co(NCS)_4]$ with A = EMIm (1-ethyl-3-methylimidazolium) and $x = 2$ (**1**), A = BMIm (1-butyl-3-methylimidazolium) and $x = 2$ (**2**), A = EMDIm (3,3′-(ethane-1,2-diyl)bis(1-methylimidazolium) and $x = 1$ (**3**), and A = PPN (bis(triphenylphosphine)iminium) and $x = 2$ (**4**) were investigated in more detail. These ILs were characterized by single-crystal X-ray diffraction, elemental analyses, IR and UV/Vis spectroscopy, temperature-dependent thermal analyses (differential scanning calorimetry), susceptibility measurements, and also temperature-dependent measurements of viscosities, densities, surface tensions, electric conductivities, and enthalpies of vaporization.

The new ILs **1**–**4** can be obtained in excellent yields (80–98 %) by two different reaction pathways, an aqueous and an anhydrous one. The optimized synthetic procedures are depicted in Scheme 1. The halides of 1,3-dialkylimidazolium mono- or dications and PPN cations were reacted with $CoCl_2$ and KSCN or with anhydrous $K_2[Co(NCS)_4]$ in aqueous or anhydrous solutions in metathesis reactions. The dark blue liquids[10] **1** and **2** ("ionic inks") and solids **3** and **4**, respectively, are obtained in high purity by repeated extraction or recrystallization processes followed by vacuum-drying procedures. All the reaction steps were optimized with respect to purity and optimization of reaction times.

The good solubility of the title compounds in polar and in non-polar solvents is remarkable. Compound **1** is soluble in H_2O, CH_3CN, DMF, DMSO, acetone, dichloromethane, and nitromethane, and insoluble in diethyl ether and hexane. In general, the solubility depends on the length of the alkyl chains of the imidazolium cation. The solubility behavior of the title substances differs significantly from already known magnetic ILs, which contain tetrahalogenidometalate anions and show low solubility in polar solvents, especially in H_2O. Furthermore, some of the latter substances are unstable in the presence of water and hydrolyze easily. Aqueous solutions of

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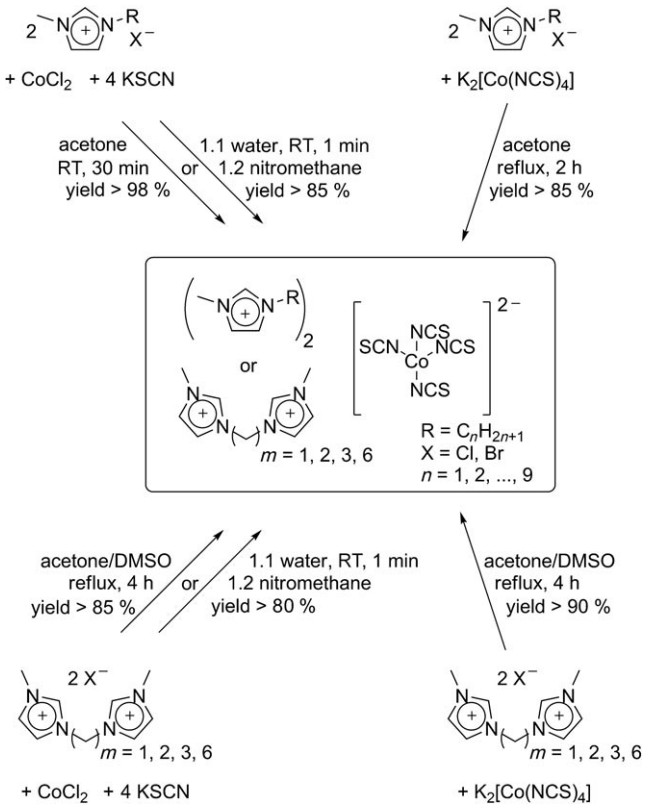

Scheme 1. General reaction scheme for the synthesis of ILs with $[Co(NCS)_4]^{2-}$ ions and bulky imidazolium-based cations.

1 are stable with respect to hydrolytic decomposition reactions over a period of weeks.

Single-crystal X-ray structures could be established for compounds **3** and **4**.[11] Suitable single crystals were grown from saturated solutions, either by slow evaporation of the solvent from acetone solutions or by slow diffusion of acetone into DMSO solutions. The structures are built up of tetrahedrally coordinated cobalt(II) ions (N atoms of the four isothiocyanato ligands) and isolated cations (**3**, Figure 1; **4**, Figure 2). The tetrahedrally coordinated cobalt(II) ions with strong ligands such as N-bonded NCS^- ions are responsible for the deep blue color ("cobalt blue").

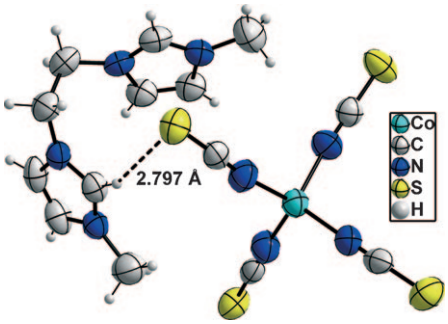

Figure 1. View of the crystal structure of **3**, with the dashed line marking the S···H hydrogen bond (ellipsoids set at 50% probability).

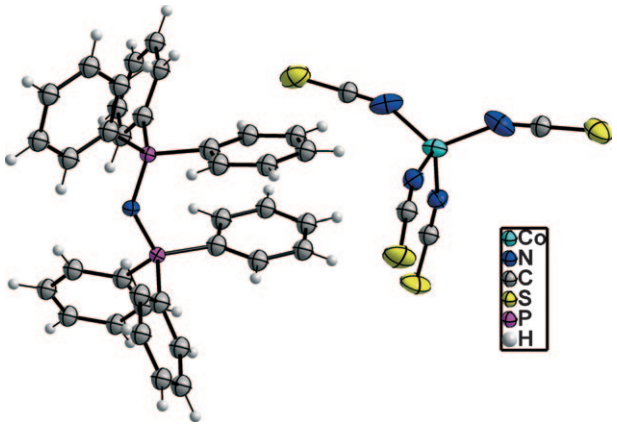

Figure 2. View of the crystal structure of **4** (only one of the two symmetry-equivalent cations is shown; ellipsoids set at 50% probability).

Compound **3** crystallizes in the non-centrosymmetric orthorhombic space group $Pna2_1$, and **4** in $P2_12_12$. Distances between atoms of the cations and the anions lie within the expected ranges. N-Co-N angles within the anions differ significantly from ideal tetrahedral geometry and range from 106.4(1)° to 111.8(1) (**3**), and 105.17(6)° to 118.9(1) (**4**). These values are in accordance with comparable angles found in, for example, $Hg[Co(NCS)_4]$ (105.6°–117.4°).[13] The ideal linear bonding of the NCS^- ligands to the cobalt ion is also absent. The average Co-N-C angle is 173.3° in **3** and 156.4° in **4** (Figure 2). The latter can be compared well with 156.7° found in $Na_2[Co(NCS)_4]\cdot 8H_2O$.[14] The sulfur atom of one thiocyanate group and the most acidic hydrogen atom of the imidazolium dication in **3** show a weak hydrogen contact (C–H···S 2.797(1) Å; Figure 1). These kinds of hydrogen contacts can also be found in other thiocyanate-based complexes, and they play an important role for the physicochemical properties of ionic liquids.[3,7,8,15]

The thermal properties of compounds **1**–**4** were analyzed by means of dynamic differential scanning calorimetry (DSC). For compounds **1** and **2**, no melting points were detected, but glass-transition temperatures of −62 °C (**1**) and −61 °C (**2**). Compound **3** has a melting point of 183 °C, and compound **4** 152 °C. The title substances show no detectable thermal decompositions below 250 °C under inert-gas conditions.

Magnetic susceptibility measurements for a sample of compound **2** were carried out by using a LOT-Oriel PPMS and a Faraday balance in the temperature range 2–333 K. Compound **2** is paramagnetic with an effective magnetic moment of $\mu_{eff} = 4.40\ \mu_B$. This value is typical for high-spin cobalt(II) systems ($S = 3/2$; spin-only value $\mu_{eff} = 3.87\ \mu_B$). The Curie–Weiss temperature θ is −0.9 K, indicating very weak antiferromagnetic interactions. This is in accordance with the large distances between the cobalt-based anions (for example, 8.57 Å in **3**). The absence of cooperative magnetic effects is observed in all ILs known to date that are based on transition-metal or rare-earth-metal complex anions.[5,7]

The density of **1** was measured in the temperature range of 15–50 °C in steps of 5 K using a vibrating-tube densiom-

eter.[16] The linear temperature dependence is given by Equation (1):

$$\rho(T) = 1.49957 - 7.234 \times 10^{-4}\, T \quad (1)$$

where $\rho(T)$ is in units of $g\,cm^{-3}$ and T in K; the estimated error is $\pm 5 \times 10^{-5}\ g\,cm^{-3}$.

The density at 25 °C is 1.28385(5) $g\,cm^{-3}$. From the temperature dependence of the density, the thermal expansion coefficient in the investigated temperature range is calculated to be $\alpha = 5.66 \times 10^{-4}\ K^{-1}$.

Values of the kinematic viscosity $\nu(T)$, the dynamic viscosity $\eta(T)$, and ion conductivity $\kappa(T)$ of **1** were also measured in the temperature range of 15 to 50 °C. The viscosities $\nu(T)$ were determined using an Ubbelohde viscometer, and the values of the ion conductivities $\kappa(T)$ by means of an conductivity meter. The temperature dependence of both properties is given by Vogel–Fulcher–Tammann equations [Eq. (2)]:[17]

$$\eta(T) = \eta_0 \exp\left(\frac{B}{T - T_0}\right) \text{ or } \kappa(T) = \kappa_0 \exp\left(\frac{B}{T - T_0}\right) \quad (2)$$

The fit parameters of the viscosity are $\eta_0 = 0.07(5)$ mPa s, $B = 968(181)$ K, $T_0 = 172(12)$ K and for the ion conductivity $\kappa_0 = 73(15)\ S\,m^{-1}$, $B = -469(43)$ K and $T_0 = 208(5)$ K. At 25 °C, the dynamic viscosity is 145.4 mPa s for **1**. This value is very low in comparison with other Ils that contain transition-metal-based complex anions, such as trihexyldecylphosphonium tetraisothiocyanatocobaltate(II) (2435 mPa s, 20 °C).[9]

Physicochemical properties can only be compared reasonably if the amount of impurities, especially moisture, is known.[18] For this reason, vacuum dried **1** with water contents of between 0.02 and 0.08 wt % can be assigned to the low-viscosity region of ILs (for comparison, (EMIm)NTf_2 (Ntf_2 = bis(trifluoromethylsulfonyl)imide): $\eta = 32.6$ MPa s at 25 °C). In contrast, the viscosity of ILs with tetrahalogenidometalate anions is in the range of that of honey or resin-like compounds.

The ion conductivity of **1** is 0.400 $S\,m^{-1}$ at 25 °C. This value is in the range of other ILs, for example (EMIm)[BF_4] (1.55 $S\,m^{-1}$) and (BMIm)[BF_4] (0.35 $S\,m^{-1}$).[19] In contrast, ILs with tetrahalometalate anions show significantly lower ion conductivities; for example, $(BMIm)_2[CoCl_4]$, $9.35 \times 10^{-3}\ S\,m^{-1}$.[20] This shows the special properties of the compounds studied herein. Obviously there are weaker intermolecular interactions between the ions of these compounds, which lead to lower viscosities and higher ion conductivities.

Surface-tension measurements were carried out on compound **1** in the temperature range 15 to 45 °C by means of the pendant drop method. The surface tension $\sigma(T)$ is linearly dependent on the temperature following Equation (3):

$$\sigma(T) = 85.02 - 9.94 \times 10^{-2}\, T \quad (2)$$

where the units of $\sigma(T)$ are in $mN\,m^{-1}$ and T in K, and the expected uncertainty is $\pm 2.5 \times 10^{-2}\ mN\,m^{-1}$.

The value at 25 °C (55.37 $mN\,m^{-1}$) is lower than that for other conventional liquids, such as water (71.8 $mN\,m^{-1}$), but greater than for other ILs.[21]

The molar enthalpy of vaporization $\Delta_{vap}H$ of **1** was determined by isothermal thermogravimetrical measurements. Even though the vapor pressure is a crucial property of liquids with respect to possible technical applications, to date only a few values of the enthalpy of vaporization of ILs are known owing to the very low vapor pressure and the challenges that therefore arise in determining these values.[22] The enthalpy of vaporization of **1** is $\Delta_{vap}H = 150.3(8)\ kJ\,mol^{-1}$ at 25 °C. Surprisingly, this value is in the same range as those of other monocationic–monoanionic ILs. In contrast however, this value is quite low in comparison with (BMIm)[$FeCl_4$] ($\Delta_{vap}H = 170(1)\ kJ\,mol^{-1}$) or other dicationic ILs.[21] This result is in accordance with the low viscosity of compound **1**, indicating weak intermolecular interactions. To correlate physicochemical properties, which basically depend on structures and energies of interactions (such as viscosity, self-diffusion coefficient, molar mass), good correlations are known for conventional solvents.[23] The predicted value of $\Delta_{vap}H$ for compound **1** differs significantly by a factor of two from the measured value however, which clearly shows the difference between conventional solvents and transition-metal-based ILs.

The salts $(EMIm)_2[Co(NCS)_4]$ (**1**) and $(BMIm)_2[Co(NCS)_4]$ (**2**), which are liquids down to temperatures of −62 °C, and the EMDIm- and PPN-based substances **3** and **4**, which are solids at room temperature, are strongly paramagnetic substances. These compounds are stable to hydrolysis, in contrast to other known paramagnetic RTILs, which contain tetrahalogenidometalate anions. Compounds **1** and **2** are distinguished by low viscosities, even though doubly charged anions are present. This behavior can be rationalized with the aid of Pearson's HSAB concept. The soft pseudohalide anions have weaker directed interactions with the hard hydrogen atoms of the imidazolium cations than the halogen groups. This leads to the much lower values of viscosity and enthalpy of vaporization and the high ion conductivities. The observed combination of chemical and physical properties of Ils that contain imidazolium cations and $[Co(NCS)_4]^{2-}$ anions should lead to interesting possible applications of Ils.

Experimental Section

Details for all the experimental investigations are given in the Supporting Information. All samples for the measurements of physicochemical properties were dried by heating at 120 °C for at least 3 h and applying a diffusion pump vacuum. With Karl–Fischer titrations, the moisture content was determined to be between 0.08 and 0.02 mass %.

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[11] Crystal structure analyses: X-ray diffraction data were collected using a Bruker-Nonius APEX-X8-CCD diffractometer with MoKα radiation ($\lambda = 0.71073$ Å, graphite-monochromated). The structures were solved using the SHELXS-97 program (direct methods) and refined using SHELXL-97 (full-matrix least-squares refinements on F^2 data).[12] All H atoms were fixed on idealized positions and refined using riding models. **3**: dark blue crystals, orthorhombic, $Pna2_1$ (No. 33), $a = 14.2029(6)$, $b = 15.9356(6)$, $c = 9.6485(4)$ Å, $V = 2183.8(2)$ Å^3, $Z = 4$, $R1 = 0.0472$ ($I > 2\sigma(I)$), $wR2 = 0.0997$ (all data), 8146 symmetry-independent data, 244 parameters, 1 restraint. **4**: dark blue crystals, orthorhombic, $P2_12_12$ (No. 18), $a = 12.5943(5)$, $b = 25.3785(9)$, $c = 10.7521(4)$ Å, $V = 3436.6(2)$ Å^3, $Z = 2$, $R1 = 0.0311$ ($I > 2\sigma(I)$), $wR2 = 0.0798$ (all data), 13071 symmetry-independent data, 411 parameters. CCDC 743435 (**3**) and CCDC 743433 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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