



Crystallisation of inorganic salts containing 18-crown-6 from ionic liquids

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Dedicated to Prof. Paul Pregosin on the occasion of his 65th birthday in recognition of his many seminal contributions to chemistry, including ionic liquids.

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ABSTRACT

Reaction of the zwitterionic imidazolium salt $[(\text{CH}_2\text{COOH})(\text{CH}_2\text{COO})\text{im}]$ with K_2CO_3 or BaO in the presence of 18-crown-6 affords the salts $[(\text{CH}_2\text{COO})_2\text{im}][\text{K}(18\text{-crown-6})]$ and $[(\text{CH}_2\text{COO})_2\text{im}]_2[\text{Ba}(18\text{-crown-6})]$, respectively. Recrystallisation of these crown complexes from the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide, $[\text{emim}][\text{Tf}_2\text{N}]$, at a water interface, results in the formation of new salts in which the original anion is replaced by Tf_2N^- . Single crystal X-ray diffraction has been performed on two of the salts. Notably, the potassium structure containing 18-crown-6 and Tf_2N^- forms a linear chain coordination polymer that can be regarded as metal organic frameworks (MOFs). Moreover, this study provides insights into the separation of group I and II metal ions using crown ethers in combination with ionic liquids.

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1. Introduction

Ionic liquids (ILs) are non-volatile solvents that have been extensively studied in synthesis and catalysis [1–4]. Many ILs are non-coordinating or weakly coordinating which endows them with potentially interesting properties for the synthesis of inorganic (metal containing) compounds and materials [5] such as transition metal complexes [6,7] and coordination polymers [8]. For example, in a coordination polymer isolated from the reaction of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and 1,3-bis(4-pyridyl)propane in 1-butyl-3-methylimidazolium tetrafluoroborate, $[\text{bmim}][\text{BF}_4]$, the cations and anions of the IL do not interact directly with the Cu-centres, although the tetrafluoroborate anions are maintained in the macrostructure in order to balance the charge.

More recently it has been found ILs comprising the Tf_2N^- anion may coordinate to metals via the O, N and S atoms in various chelating bonding-modes [9–11]. Indeed, the coordinating ability of ILs has led to many interesting applications [12]. Imidazolium-based ILs can be used as solvents for the separation of radioactive materials such as UO_2^{2+} [13]. Europium-based ILs and dysprosium-based ILs can be used as soft luminescent materials [14,15].

It has also been shown that ILs can be used to separate group I and II metals in combination with crown ethers [16–18]. The mechanism of the separation process is believed to involve co-crystallisation of the imidazolium-based salts with 18-crown-6 containing metal ions [19], and the driving force for the inclusion of neutral 18-crown-6 ether into the packing of the imidazolium salts appears to be due to non-covalent interactions such as hydrogen bonding, π -stacking and electrostatic interactions [20]. It is worth noting that functionalized ILs in which an 18-crown-6 moiety is covalently linked to an imidazolium cation have also been reported [21] and many functionalized ILs contain groups that can potentially coordinate to metal centres have been reported [22,23].

As far as we are aware, solid-state structures of the group I or II metal ions isolated from ILs in the presence of crown ethers, have not been reported. Previously we prepared an imidazolium based acid (HA, Fig. 1) [24]. Deprotonation of the acid affords a zwitterionic acid A, which can be further de-protonated leading to A^- , and proved to be a versatile group for the formation of metal organic frameworks with various topologies [25–27] including structures based on group I and II metal ions [28].

Accordingly, we hypothesised that these zwitterions may facilitate the crystallisation of group I and II 18-crown-6 complexes from ILs and in this paper we describe how crystals suitable for single crystal X-ray diffraction analysis were obtained using this strategy.

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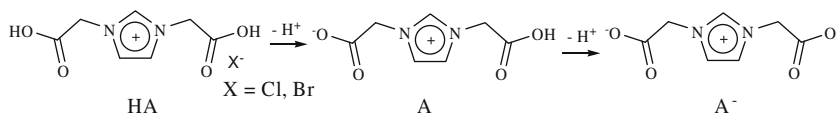


Fig. 1. Carboxylic imidazolium salt HA and zwitterions A and A⁻.

2. Results and discussion

Reaction of the zwitterionic acid A with potassium carbonate or barium oxide in the presence of 18-crown-6 affords **1** and **2**, respectively, as shown in Scheme 1. Both **1** and **2** are soluble in water and insoluble in organic solvents of low polarity. The slight excess of 18-crown-6 used in the synthesis is easily removed by washing with diethyl ether. It is worth noting that reaction of the zwitterionic acid A with SrCO₃ in the presence of 18-crown-6 does not lead to the formation of the corresponding complex incorporating the 18-crown-6 ligand. Washing the reaction mixture with diethyl ether completely removes the 18-crown-6 moiety, leaving a product in a form of Sr[A]₂, and reflective of the poor fit of the strontium dication into the macrocycle.

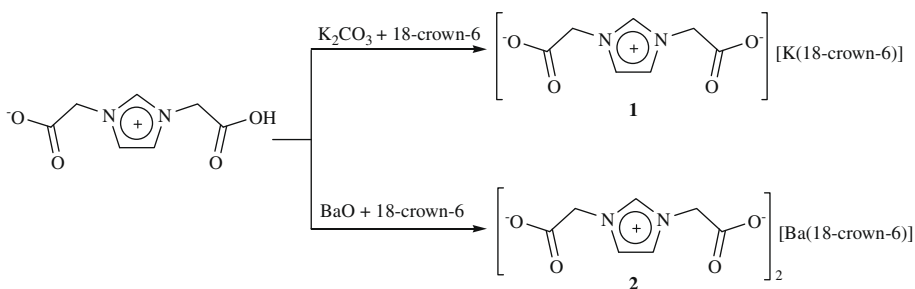
The spectroscopic features of complexes **1** and **2** are quite similar. The ¹H NMR spectra of **1** and **2** exhibit a singlet resonance at 3.50 ppm corresponding to the CH₂ units in the crown. The CH₂ group in the imidazolium system displays a singlet at 4.81 ppm. Electrospray ionisation mass spectra of **1** and **2** in H₂O display peaks that are readily attributed to [K(18-crown-6)]⁺ and [Ba(18-crown-6)][A]⁺ (*m/z* = 303 for **1** and *m/z* = 585 for **2**), in positive mode at a concentration of 1.0 ppm. In negative ion mode a peak at *m/z* = 183 corresponding to A⁻ is observed in both **1** and **2**.

It has been reported that ILs can be used to separate group I and II metals in combination with 18-crown-6 [16–19]. In order to elucidate solid-state structures of the group I or II complexes isolated from ILs in the presence of crown ethers, we attempted to crystallize both **1** and **2** in the commonly used IL 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide, [emim][Tf₂N]. Addition of an aqueous solution of **1** to [emim][Tf₂N] results in a biphasic system. Over a period of 2 days plate-like crystals of **3** gradually

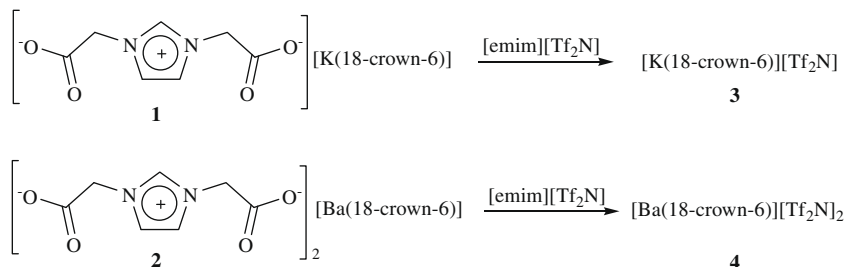
form at the IL-water interface (see Scheme 2). To the best of our knowledge growth of single crystals with the assistance of ILs is rare [8,11]. Similarly, treatment of **2** with [emim][Tf₂N] affords **4**, but the quality of the obtained crystals was not sufficient for X-ray diffraction analysis.

Both **3** and **4** are considerably less soluble in water than **1** and **2**, presumably due to the presence of the hydrophobic Tf₂N anion, and enabling the facile separation of the potassium and barium ions from the aqueous phase. In the ¹H NMR spectra of **3** and **4** the signals representing the hydrogen atoms of the imidazolium moiety are replaced by those of the Tf₂N anion. Mass spectra of **3** reveal peaks corresponding to [K(18-crown-6)]⁺ (*m/z* = 303) and cation–anion aggregates such as [[K(18-crown-6)]₂(Tf₂N)]⁺ (*m/z* = 886). In the case of **4** the mass spectrum is dominated by a peak at *m/z* = 682 corresponding to [Ba(18-crown-6)][Tf₂N]⁺. Aggregates similar to those observed for **3** and **4** are not uncommon in electrospray ionisation mass spectra of ILs [29,30].

Single crystals of **2** and **3** were analysed by X-ray diffraction. Both **2** and **3** crystallise in triclinic systems and the crystallographic data are listed in Table 1 (see Section 3). The asymmetric unit in **2** consists of two zwitterionic anions, one Ba²⁺ and seven water molecules (Fig. 2). The barium ion is disordered over two sites (A and B) having occupancy factors of 0.837(1) and 0.163(1), respectively. The coordination around each metal emanates from the 18-crown-6 ether [Ba–O distances ranging from 2.881(3) to 3.006(3) Å for site A], two water molecules [Ba–O_{water} varying from 2.724(3) to 2.801(3) Å for site A] and two bridging imidazolium anions (one belonging to the asymmetric unit; Ba–O = 2.849(3) Å, and the other obtained by symmetry, Ba–O = 2.794(4) Å). The C–O distances in the crown moiety are between 1.413(5) and 1.441(5) Å. The overall structure is completed



Scheme 1. Synthesis of complexes **1** and **2**.



Scheme 2. Synthesis of complexes **3** and **4**.

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