Mixed halide/oxoanion-templated frameworks

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A tetrahedral tetra-amidinium compound **1⁴⁺** was crystallised in the presence of a range of anions (Cl^- , Br^- , NO_3^- , oxalate²⁻) giving a range of interesting solid state structures assembled through amidinium...anion hydrogen bonding interactions. Mixing the chloride or bromide salts of **1⁴⁺**, i.e. **1-4Cl** or **1-4Br**, and inorganic oxalate salts in water gave crystals of ordered three-dimensional network structures containing both oxalate and halide anions. These interesting "mixed anion" frameworks exhibit high thermal stability to heat and hydrolysis but are not significantly porous. Importantly, these materials are significantly more robust than the analogous terephthalate-containing framework materials.

Introduction

The development of anions as templates for self-assembled supramolecular structures is still in its infancy, presumably due in part to the difficulties of selectively interacting with anions.¹ Recently however, a range of anion-templated constructs have been reported including the anion-templated syntheses of interlocked structures,² cages³ and stimuli-responsive pseudorotaxanes.⁴

While anion-directed self-assembly is underexplored, there has been considerable success in engineering hydrogen-bonded constructs, in particular hydrogen-bonded framework materials. Notable results in this area include Ward's guanidinium sulfonate frameworks⁵ and Wuest's neutral hydrogen bonded materials.⁶ More recently, Frišićić has demonstrated that imidazolium cations and sulfate anions form frameworks that are analogous to transition metal *imidazolate* materials.⁷

Inspired by this work, we recently reported⁸ the anion-templated synthesis of 3D framework materials taking advantage of the favourable hydrogen bonding interactions between a tetratopic tetra-amidinium receptor **1⁴⁺** and terephthalate (TP) anions (Scheme 1).⁹ Remarkably, these frameworks form *in water* in minutes and only the terephthalate anion results in the formation of a robust framework, while a range of other anions (halides, nitrate, sulfate, isophthalate) do not give framework materials. The initially-formed tetragonal phase (*tet*-[**1-2TP**]_n) contains large, connected pores, and readily converts to an orthorhombic phase containing non-connected pores upon heating. Given that *tet*-[**1-2TP**]_n loses crystallinity upon drying (and hence does not show gas adsorption), we were interested to see if other salts of **1⁴⁺** could be used to form more stable materials, in particular if the smaller dicarboxylate anion oxalate could be used to prepare a more compact, and potentially more robust framework.

In the present work, we investigate the solid state structures of the chloride, bromide, nitrate and oxalate (**ox**) salts of **1⁴⁺**. While we were unable to synthesise the targeted material [**1-2ox**]_n, we instead isolated and characterised the novel mixed anion frameworks, [**1-ox-2Cl**]_n and [**1-ox-2Br**]_n.

Scheme 1. Previously-reported synthesis of anion-templated 3D frameworks in water.⁸

Results and discussion

Synthesis and structures of **1-4Cl**, **1-4Br** and **1-4NO₃**

The synthesis of **1-4Cl**, **1-4Br** and **1-4NO₃** has previously been reported.⁸ Briefly, tetraphenylmethane is selectively tetra-brominated to give tetrakis(4-bromophenyl)methane (**2**), the bromo- groups are converted to nitrile groups to give tetrakis(4-cyanophenyl)methane (**3**), and this is then converted to **1⁴⁺** using LiHMDS (Scheme 2). We have found that the previously-reported method for converting **2** to **3** using copper(I) cyanide in refluxing DMF¹⁰ is problematic both in terms of the potential dangers of working with ionic cyanide salts and the difficulties of removing and rendering safe the excess cyanide and other copper salts used during the reaction. Instead, we have found Weissman's procedure¹¹ to be advantageous: this uses potassium ferrocyanide(II) as a (relatively) non-toxic cyanide source, and requires only a simple aqueous work-up. Using this procedure, we obtained **3** in good yield (89%). Treatment of **3** with LiHMDS followed by ethanolic HCl gives **1-4Cl**. Anion exchange reactions then give **1-4Br** and **1-4NO₃**.⁸

Scheme 2. Conversion of **2** to **3** using Weissman's palladium-catalysed reaction.¹¹

We were able to obtain single crystals of **1·4Cl**, **1·4Br** and **1·4NO₃** suitable for SCXRD studies by vapour diffusion techniques. The structure of **1·4Cl** is shown in Figure 1, and adopts a channel like structure with some of the chloride anions filling these channels. Despite their high positive charge, the tetra-amidinium cations are relatively close-packed, presumably to maximise favourable hydrogen bonding interactions with the chloride anions. These hydrogen bonds are quite short and involve both the “forward” and “sideways” facing amidinium protons [N...Cl distances: 3.187(7)–3.375(8) Å, H...Cl distances: 2.44–2.55 Å, 81–85% of the sum of the van der Waals radii of hydrogen and chlorine¹²].

Figure 1. Views of the solid state structure of **1·4Cl** (some hydrogen atoms omitted for clarity, PLATON-SQUEEZE¹³ used).

The overall structure of **1·4Br** is relatively similar to that of **1·4Cl**. Again the tetra-amidinium cations pack relatively closely together forming channels, which are filled with bromide anions (Figure 2). The structure is assembled through N–H...Br hydrogen bonds, with these bonds approximately the same length as those in **1·4Cl**, when accounting for the increased size of bromide compared to chloride [N...Br distances: 3.284(2)–3.469(2) Å, H...Br distances: 2.47–2.70 Å, 81–88% of the sum of the van der Waals radii of hydrogen and bromide¹²].

Figure 2. Views of the solid state structure of **1·4Br** (some hydrogen atoms omitted for clarity, PLATON-SQUEEZE¹³ used).

Surprisingly, the structure of **1·4NO₃** (Figure 3) is similar to the halide salts of **1⁴⁺**, despite containing a polyatomic rather than monoatomic anion. Channels are formed from “pillars” of close-packed tetra-amidinium cations, with nitrate anions and solvent molecules filling these channels.

Amidinium...nitrate hydrogen bonds vary more in length than in the halide anion-containing structures, with some contacts quite short [N...O distances: 2.827(12)–3.122(12) Å, H...O distances: 1.93–2.38 Å, 71–88% of the sum of the van der Waals radii of hydrogen and oxygen¹²].

Figure 3. Views of the solid state structure of **1·4NO₃** (solvent molecules and some hydrogen atoms omitted for clarity).

While the structures of **1·4Cl**, **1·4Br**, **1·4NO₃** appear to be somewhat ordered network structures, it should be noted that these are not “genuine” framework materials. The crystals dissolve readily in polar organic solvents to give sharp ¹H NMR spectra, consistent with these solvents disrupting the hydrogen bonding interactions that hold the solid state networks together.

Synthesis and structures of mixed anion frameworks

We next attempted to prepare frameworks of the form [**1·2ox**]_n by mixing aqueous solutions of **1·4Cl** and **Na₂·ox**, in a manner analogous to that used to prepare [**1·2TP**]_n frameworks.⁸ Mixing aqueous solutions of **1·4Cl** and **Na₂·ox** gave a clear, colourless solution, which upon standing for a few hours gave large block-like crystals. However, SCXRD studies revealed that these were not the targeted product [**1·2ox**]_n but rather a mixed framework, [**1·ox·2Cl**]_n (Figure 4).

The structure crystallises in the tetragonal space group P4/n, with a quarter of the tetra-amidinium receptor, a quarter of an oxalate anion and two chloride anions (on special positions) within the asymmetric unit cell. The “forward”-facing amidinium hydrogen atoms form hydrogen bonds to an oxalate anion, which is disordered about the four-fold rotation axis [Figures 4b and 4c, N...O = 2.778(5), 2.789(5) Å; H...O = 1.93, 1.93 Å; 71% of the sum of the van der Waals radii of hydrogen and oxygen¹²]. The “sideways”-facing amidinium hydrogen atoms form hydrogen bonds to chloride anions [Figure 4b, N...Cl = 3.283(4), 3.370(4) Å; H...Cl = 2.45, 2.55 Å; 81 and 85 % of the sum of the van der Waals radii of hydrogen and chlorine¹²] resulting in a structure that is quite densely-packed. Small (62 Å³) voids are located about the special positions – these appear to contain water molecules, but it was not possible to sensibly model these solvents and so PLATON-SQUEEZE¹³ was used to include this electron density in the refinement.

Figure 4. Views of the solid state structure of $[1\text{-ox-}2\text{Cl}]_n$ (some hydrogen atoms omitted for clarity, two positions of disordered oxalate anion displayed in pink and blue).

We also attempted this synthesis starting from lithium oxalate or tetrabutylammonium oxalate, but in both cases this returned the same product. Using a large excess of sodium oxalate also gave the same mixed anion framework. Mixing **1-4Br** and **Na₂ox** gave the bromide-containing mixed framework $[1\text{-ox-}2\text{Br}]_n$, while no crystals were obtained when starting from **1-4NO₃**. The bromide-containing mixed anion framework $[1\text{-ox-}2\text{Br}]_n$ (Figure 5) is isostructural with $[1\text{-ox-}2\text{Cl}]_n$ with the same disorder of the oxalate anion and very similar hydrogen bonding arrangements.

Figure 5. View of the solid state structure of $[1\text{-ox-}2\text{Br}]_n$ (some hydrogen atoms omitted for clarity).

Both of the mixed anion frameworks form reproducibly and were prepared “in bulk” in good yields by simply mixing aqueous solutions of **1-4Cl** or **1-4Br** and sodium oxalate (93 and 61% for $[1\text{-ox-}2\text{Cl}]_n$ and $[1\text{-ox-}2\text{Br}]_n$, respectively).¹⁴ These materials were characterised by ¹H NMR spectroscopy of the acid-digested framework (without acid, the frameworks are insoluble in all tested solvents), IR spectroscopy, thermogravimetric analysis (TGA) and powder X-ray diffraction (PXRD) experiments. We also conducted gas adsorption measurements on $[1\text{-ox-}2\text{Cl}]_n$, which revealed that this material does not absorb N₂ gas.

Stability testing of $[1\text{-ox-}2\text{Cl}]_n$ and $[1\text{-ox-}2\text{Br}]_n$

PXRD experiments: PXRD studies revealed that both $[1\text{-ox-}2\text{Cl}]_n$ and $[1\text{-ox-}2\text{Br}]_n$ retain good crystallinity on drying, and that the structure of the bulk material is consistent with that observed by SCXRD experiments. We investigated the stability of $[1\text{-ox-}2\text{Cl}]_n$ by boiling a sample of this material in water for two hours. No change in the PXRD pattern of the material was observed upon boiling (Figure 6), suggesting that the frameworks are stable with respect to hydrolysis. This is in contrast to $[1\text{-}2\text{TP}]_n$, which converts from a tetragonal to orthorhombic phase upon boiling in water.⁸

Figure 6. PXRD pattern of $[1\text{-ox-}2\text{Cl}]_n$ before and after boiling in water for two hours. The pattern calculated from the SCXRD structure is provided for comparison.

TGA experiments: TGA traces were recorded for both of the mixed halide/oxalate frameworks. These suggest the presence of a small amount of included solvent (consistent with conclusions drawn from SCXRD experiments), which is removed upon initial heating. The materials then remain stable until approximately 280 °C – surprisingly high considering these supramolecular materials are held together by relatively weak hydrogen bonding interactions. Figure 7 shows the TGA traces from 30 to 350 °C for $[1\text{-ox-}2\text{Cl}]_n$ and $[1\text{-ox-}2\text{Br}]_n$, as well as both phases of the terephthalate-based framework $[1\text{-}2\text{TP}]_n$ (full decomposition traces for $[1\text{-ox-}2\text{Cl}]_n$ and $[1\text{-ox-}2\text{Br}]_n$ are provided in the ESI). It is noticeable that the mixed halide/oxalate frameworks show significantly higher thermal stability than the analogous terephthalate-containing materials,⁸ in which thermal decomposition begins at approximately 230 °C.

Figure 7. TGA traces of $[1\text{-ox-2Cl}]_n$ and $[1\text{-ox-2Br}]_n$ and comparison with TGA traces of tetragonal and orthorhombic phases of $[1\text{-2TP}]_n$.⁸

Conclusions

Several salts of the tetra-amidinium receptor **14+** were structurally characterised; in all cases the structures are assembled through relatively short N–H...anion hydrogen bonds. The halide salts **1-4Cl** and **1-4Br** react with sodium oxalate in water to give crystalline framework materials. Surprisingly, these are not the targeted $[1\text{-2ox}]_n$ networks, but rather the new mixed-anion containing frameworks $[1\text{-ox-2Cl}]_n$ and $[1\text{-ox-2Br}]_n$. These materials are relatively tightly-packed, and show noticeably higher thermal stability than the related framework $[1\text{-2TP}]_n$. We are continuing to investigate these types of hydrogen bonded anion-containing materials, with the aim of combining an open, porous structure and the high stability observed herein.

Experimental

Synthesis and characterisation

General remarks: Solvents and reagents were bought from commercial suppliers and used as received. Tetrakis(4-bromophenyl)methane was prepared by bromination of tetraphenylmethane as previously described.¹⁰ While tetraphenylmethane is commercially-available, for cost reasons it was prepared in two steps from triphenylmethyl chloride as previously described.¹⁵ **1-4Cl**, **1-4Br** and **1-4NO₃** were prepared from **3** as previously described.⁸ Details of instrumentation are given in the ESI.

Tetrakis(4-cyanophenyl)methane (3): To a Schlenk flask was added de-oxygenated DMAc (25 mL), followed by tetrakis(4-bromophenyl)methane **2** (1.0 g, 1.6 mmol), potassium ferrocyanide(II) trihydrate (1.4 g, 3.2 mmol) and sodium carbonate (0.68 g, 6.4 mmol). The mixture was again de-oxygenated with bubbling nitrogen, and palladium(II) acetate (29 mg, 8 mol%, 2 mol% per bromo group) was added. The reaction was then heated to 130 °C overnight under a nitrogen atmosphere. The resulting dark brown suspension was cooled to room temperature, and then diluted with dichloromethane (50 mL). The solution was filtered, and the filtrate taken to dryness under reduced pressure. The resulting brown oil was dissolved in dichloromethane (2 mL) and pet. spirits added until no more

precipitation was observed (~ 70 mL). The cream-coloured powder was isolated by filtration, washed with pet. spirits and air dried to give **3**. Yield: 0.59 g (1.4 mmol, 89%).

*Spectral data were consistent with those previously-reported.*¹⁶

¹H NMR (CDCl₃): 7.64 (d, *J* = 8.5 Hz), 7.27 (d, *J* = 8.5 Hz) ppm.

¹³C NMR (CDCl₃): 148.7, 132.5, 131.2, 118.0, 111.8, 65.8 ppm.

[1-ox-2Cl]_n: A solution of sodium oxalate (5.5 mg, 0.040 mmol) in water (3 mL) was added to a solution of **1-4Cl** (13 mg, 0.020 mmol) in water (2 mL). The clear colourless solution was left to stand for three days, after which the resulting very pale yellow crystals were isolated by filtration, washed with water and air dried. Yield: 13 mg (0.19 mmol, 93%)^{14†}.

¹H NMR [d₆-DMSO containing a drop conc. DCl(aq)]: 9.60* (br. s), 9.34* (br. s), 7.95 (d, *J* = 8.4 Hz, 8H), 7.55 (d, *J* = 8.4 Hz, 8H) ppm. IR (*inter alia*): 1694, 1609, 1567, 1532, 1482 (strong) cm⁻¹ (C=O, C=N and C=C stretches).

*These peaks integrate to a value lower than the expected 8H, presumably due to H/D exchange.

†Mmol and % yield corrected to account for ~6.5% water, as indicated by TGA.

[1-ox-2Cl]_n was also characterised by SCXRD, PXRD and TGA (see ESI).

[1-ox-2Br]_n: A solution of sodium oxalate (6.7 mg, 0.050 mmol) in water (2 mL) was added to a solution of **1-4Br** (20 mg, 0.025 mmol) in water (2 mL). The clear colourless solution was left to stand for three days, after which the resulting very pale yellow crystals were isolated by filtration, washed with water and air dried. Yield: 12 mg (0.015 mmol, 61%)^{14†}.

¹H NMR [d₆-DMSO containing a drop conc. DCl(aq)]: 9.53* (br. s), 9.27* (br. s), 7.93 (d, *J* = 8.3 Hz, 8H), 7.56 (d, *J* = 8.3 Hz, 8H) ppm. IR (*inter alia*): 1694, 1608, 1567, 1531, 1483 (strong) cm⁻¹ (C=O, C=N and C=C stretches).

*These peaks integrate to a value lower than the expected 8H, presumably due to H/D exchange.

†Mmol and % yield corrected to account for ~6.5% water, as indicated by TGA.

[1-ox-2Br]_n was also characterised by SCXRD, PXRD and TGA (see ESI).

X-ray crystallography

Single crystal data were collected using mirror-monochromated Cu Kα radiation at 150 K on an Agilent Supernova diffractometer. Raw frame data (including data reduction, interframe scaling, unit cell refinement and absorption corrections) were processed using CrysAlis PRO.¹⁷ Structures were solved with SUPERFLIP¹⁸ and refined using full-matrix least-squares on *F*² within the CRYSTALS suite.¹⁹ All non-hydrogen atoms were refined with anisotropic displacement parameters. C–H hydrogen atoms were generally visible in the Fourier difference map, and were initially refined with restraints on bond lengths and angles, after which the positions were used as the basis for a riding model.²⁰ O–H and N–H hydrogen atoms were generally visible in the Fourier difference map, and

their positions were refined with restraints on bond lengths and angles. Selected crystallographic data are summarized in Table S1, and full crystallographic data are provided in CIF format as Supporting Information (CCDC Numbers: 1531015–1531019).

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