Electronic Supplementary Material (ESI) for CrystEngComm.

Mixed halide/oxoanion-templated frameworks

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Details of instrumentation

NMR spectra were collected on Varian Gemini, Bruker Avance 400 spectrometers and are referenced to the residual solvent signal.[S1] Infrared spectra were recorded on a Perkin-Elmer Spectrum Two FT-IR Spectrometer fitted with an ATR Two Single Reflection Diamond. Thermogravimetric analyses were recorded on a TA Instruments Q500 analyser.

Details of instruments used to record PXRD and SCXRD data are given in the respective sections of the Supporting Information.

NMR spectra

NMR spectra of 3

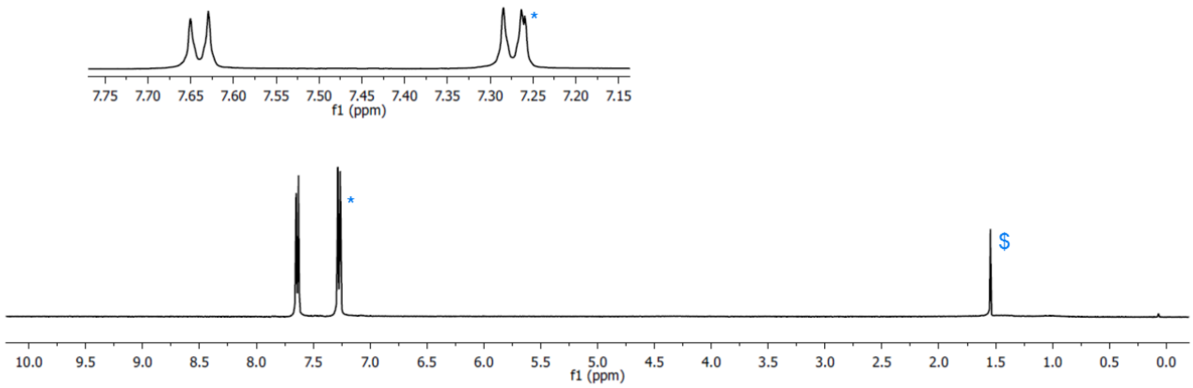

Figure S1. ^{1}H NMR spectrum of **3** (400 MHz, 298 K, CDCl$_3$, peak marked * corresponds to residual solvent signal, peak marked $ corresponds to water).

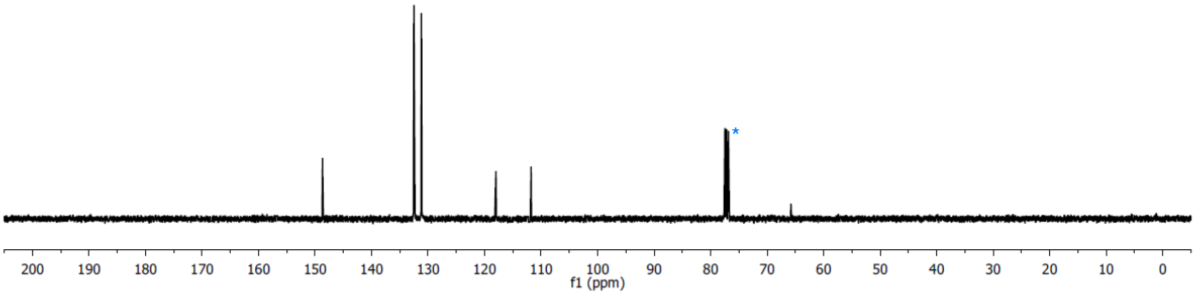

Figure S2. ^{13}C NMR spectrum of **3** (101 MHz, 298 K, CDCl$_3$, peak marked * corresponds to residual solvent signal).

^{1}H NMR spectrum of [1·ox·2Cl]$_{n}$

NB: Even upon addition of DCl$_{(aq)}$, a clear solution was not obtained. A ^{1}H NMR spectrum was recorded of the resulting suspension (Figure S3).

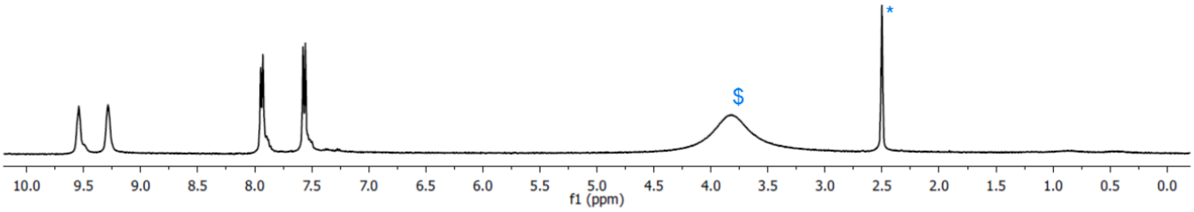

Figure S3. ^{1}H NMR spectrum of [**1**·**ox**·**2Cl**]$_{n}$ (400 MHz, 298 K, d$_{6}$-DMSO containing a drop DCl$_{(aq)}$, peak marked * corresponds to residual solvent signal, peak marked $ corresponds to water).

^{1}H NMR spectrum of [1·ox·2Br]$_{n}$

NB: Even upon addition of DCl$_{(aq)}$, a clear solution was not obtained. A ^{1}H NMR spectrum was recorded of the resulting suspension (Figure S4).

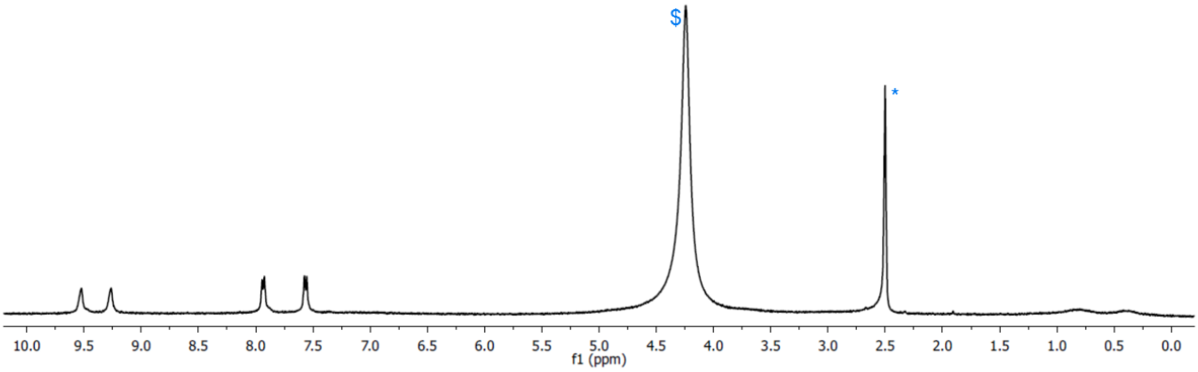

Figure S4. ^{1}H NMR spectrum of [**1**·**ox**·**2Br**]$_{n}$ (400 MHz, 298 K, d$_{6}$-DMSO containing a drop DCl$_{(aq)}$, peak marked * corresponds to residual solvent signal, peak marked $ corresponds to water).

Thermogravimetric analysis (TGA)

Both frameworks lose approximately 6.5 wt.% upon initial heating, which we attribute to the loss of water associated with the material (Figure S5). This would correspond to approximately 2.4 water molecules per [**1·ox·2Cl**] and 2.7 water molecules per [**1·ox·2Br**] unit. Continued heating results in further weight loss, which seems to occur in several distinct steps. It is not immediately apparent what part(s) of the framework result in these steps.

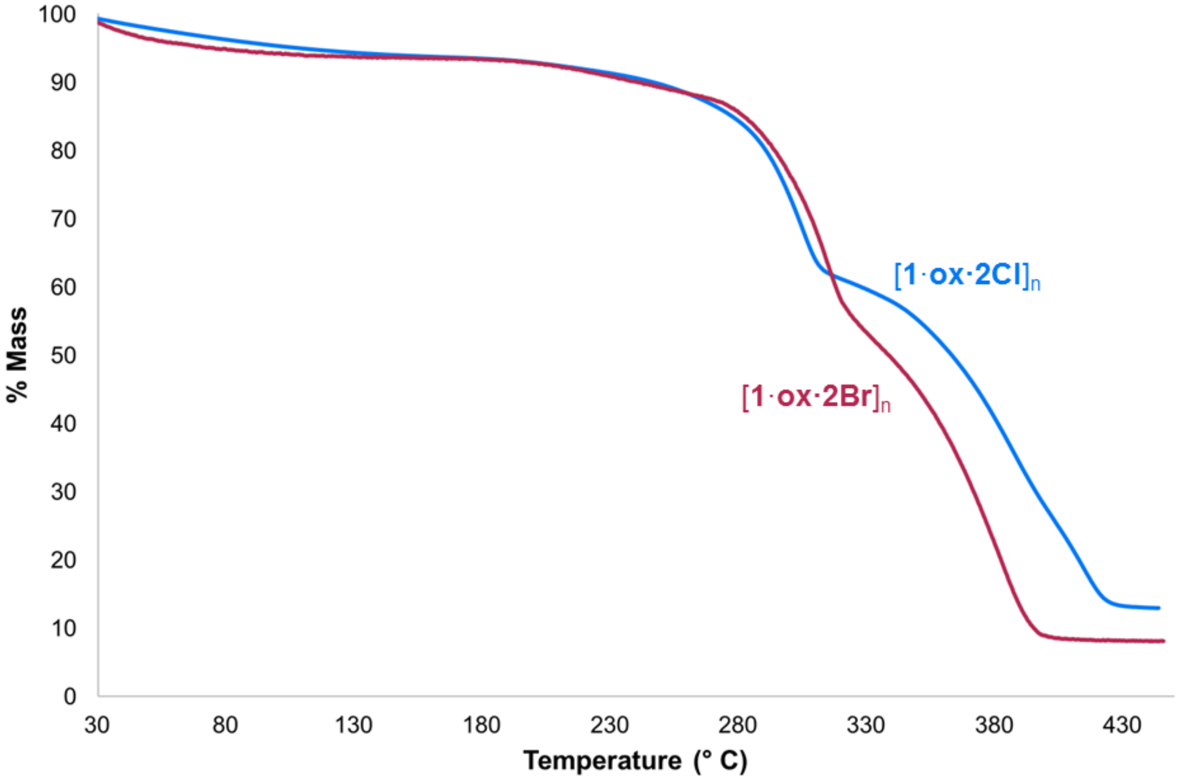

Figure S5. TGA traces of mixed anion frameworks (recorded at 10 °C/min under N_2).

Elemental analysis (EA)

EA data were recorded at London Metropolitan University.

In both cases, the EA suggests that the frameworks contain or are associated with some residual water. This is to be expected given their highly-charged nature, and the presence of water indicated by TGA. The amounts of water do not match perfectly between TGA and EA, but this is perhaps not surprising given that TGA data were recorded on freshly air-dried samples, while EA data were recorded on thoroughly vacuum-dried samples that were then shipped from Australia to the U.K.

In the case of [**1·ox·2Br**]$_n$, a good match is observed between calculated and observed values assuming two water molecules per framework unit (Table S1). In the case of [**1·ox·2Cl**]$_n$, the match is not as good, which may imply the presence of a trace of inorganic impurity.

Table S1. Elemental analysis data and calculated values.

	C	H	N
[1·ox·2Cl]$_n$			
observed values, run 1	50.61	4.33	14.42
observed values, run 2	50.69	4.37	14.49
observed values, average	*50.65*	*4.35*	*14.46*
*calc. for [**1**·ox·2Cl]·4H$_2$O*	*51.46*	*5.57*	*15.49*
[1·ox·2Br]$_n$			
observed values, run 1	48.48	4.35	13.98
observed values, run 2	48.56	4.35	14.06
observed values, average	*48.52*	*4.35*	*14.02*
*calc. for [**1**·ox·2Br]·2H$_2$O*	*47.95*	*4.67*	*14.43*

Powder X-ray diffraction (PXRD)

General comments on PXRD

PXRD data were recorded at room temperature on a PANalytical Empyrean diffractometer using Cu Kα radiation and a PIXcel detector.

PXRD traces were recorded at 293 K; patterns calculated from SCXRD data are also provided, although it should be noted that SCXRD data were recorded at 150 K.

PXRD of [1·ox·2Cl]$_n$

The observed PXRD trace of [**1·ox·2Cl**]$_n$ (Figure S6) shows relatively good agreement with that calculated from the SCXRD data. While peaks are observed in the calculated positions, peak intensities differ somewhat.

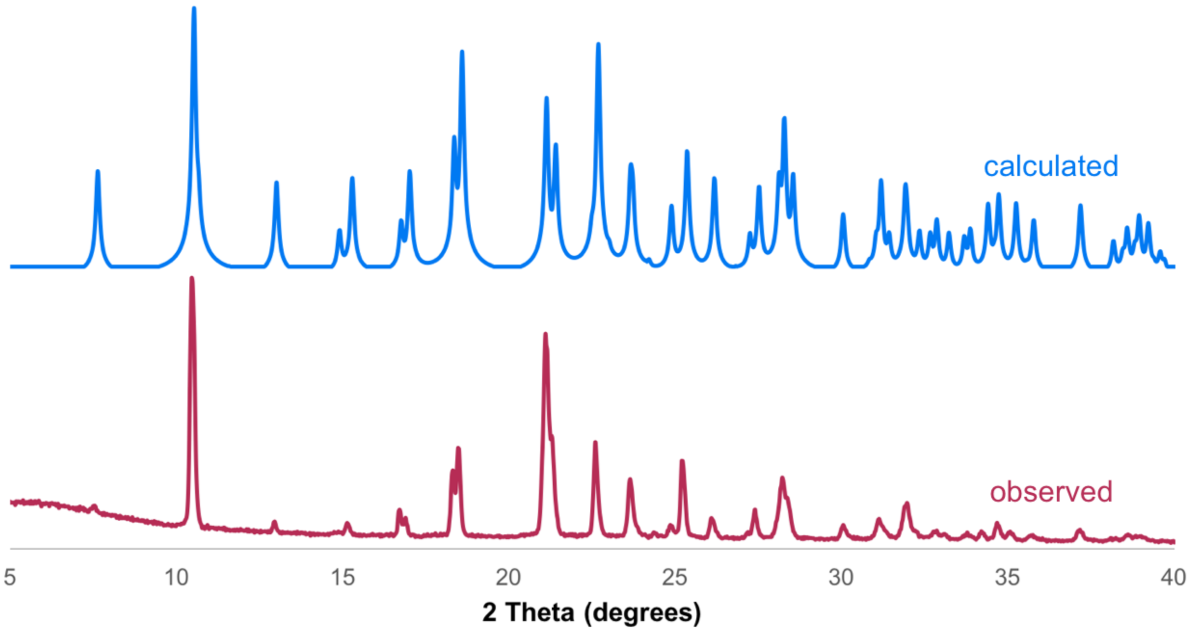

Figure S6. PXRD trace of [**1·ox·2Cl**]$_n$, and comparison with pattern calculated from SCXRD data.

PXRD of [1·ox·2Br]$_n$

The observed PXRD trace of [**1·ox·2Cl**]$_n$ (Figure S7) shows moderately good agreement with that calculated from the SCXRD data. While peaks are generally observed in the calculated positions, peak intensities differ significantly.

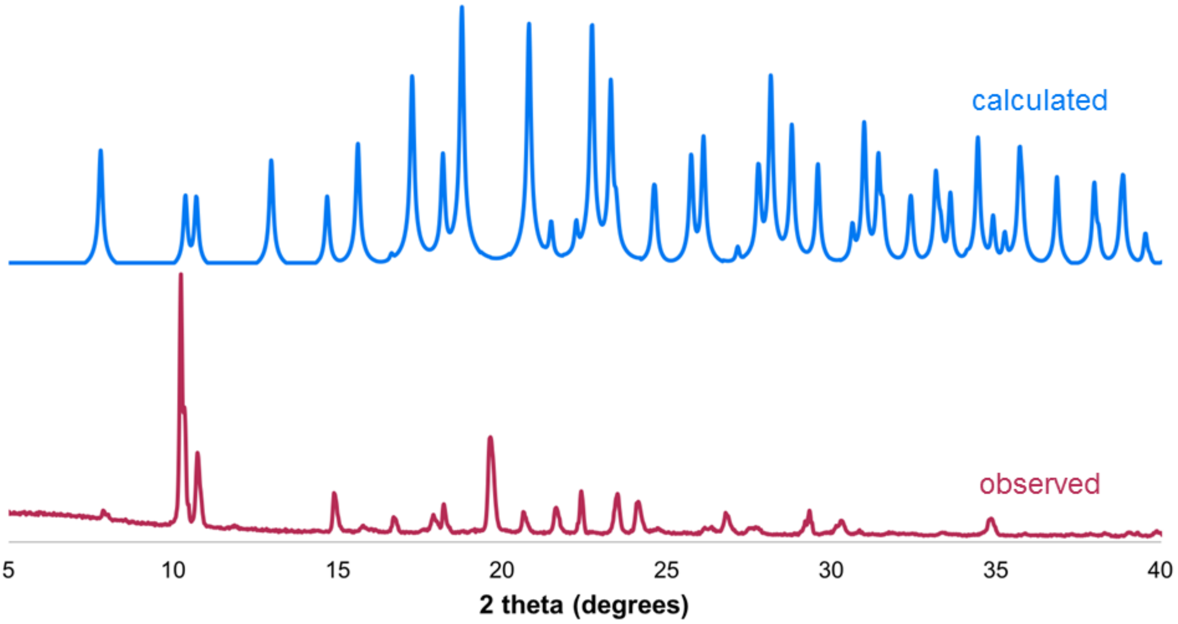

Figure S7. PXRD trace of [**1·ox·2Br**]$_n$, and comparison with pattern calculated from SCXRD data.

Single crystal X-ray diffraction (SCXRD)

General comments on SCXRD

Data were collected using mirror-monochromated Cu Kα radiation on an Agilent SuperNova diffractometer. Crystals were cooled to 150 K using a Cryostream N2 open-flow cooling device[S2] in all cases. Raw frame data (including data reduction, interframe scaling, unit cell refinement and absorption corrections) were processed using CrysAlisPro.[S3]

Structures were solved with SIR92[S4] or SUPERFLIP[S5] and refined using full-matrix least-squares on F^2 within the CRYSTALS suite.[S6] 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.[S7] O–H and N–H hydrogen atoms were generally visible in the Fourier difference map and were refined with restraints on bond lengths and angles.

Full crystallographic data in CIF format are provided as Supporting Information (CCDC Numbers: 1531015–1531019). Selected data are summarised in Table S2 and individual structures are discussed in more detail below.

Structure of 1·4Cl

Crystals of **1·4Cl** were obtained by diffusing acetone vapour into an aqueous solution of the compound. The compound crystallises in the tetragonal space group *P4/ncc*, with one quarter of a molecule of $\mathbf{1}^{4+}$ in the asymmetric unit cell as well as three chloride anions on special positions. A region of diffuse electron density is present, which may be due to solvent molecules disordered over special positions. This could not be modelled sensibly and so PLATON-SQUEEZE[S8] was used to include this electron density in the refinement. A small amount of residual electron density is located close to the chloride anions. It was not necessary to use any crystallographic restraints except for those on N–H bond lengths and angles.

Structure of 1·4Br

Crystals of **1·4Br** were obtained by diffusing diethyl ether vapour into a solution of the compound in ethanol/water. The compound crystallises in the monoclinic space group *P2/n*, with one half of a molecule of $\mathbf{1}^{4+}$ in the asymmetric unit cell as well as three bromide anions, two of which are on special positions. A region of diffuse electron density is present, which appears to be due to ethanol and water solvent molecules. This could not be modelled sensibly and so PLATON-SQUEEZE[S8] was used to include this electron density in the refinement. It was not necessary to use any crystallographic restraints except for those on N–H bond lengths and angles.

Structure of 1·4NO$_3$

Crystals of **1·4NO$_3$** were obtained by diffusing diethyl ether vapour into a solution of the compound in methanol. The compound crystallises in the triclinic space group *P-1*, with two molecules of **1**$^{4+}$, eight nitrate anions, three methanol molecules and one water molecule in the asymmetric unit cell. Several crystals were screened, but all gave “split-looking” diffraction patterns; after investigating several crystals, the most “single-looking” one was selected and a dataset collected, although diffraction data are only of moderate quality. A twin law was found using the ROTAX[S9] programme and the occupancies of the two components refined. Due to the relatively low quality of the data, it was necessary to apply restraints to some bond lengths and to the thermal and vibrational ellipsoid parameters of some atoms. It was not possible to sensibly refine the O–H hydrogen atom positions for the water and methanol solvent molecules, so there were inserted at idealised hydrogen bonding positions and used as the basis for a riding model.

Structure of [1·ox·2Cl]$_n$

Crystals were grown by mixing aqueous solutions of **1·4Cl** and sodium oxalate, and leaving the mixture to stand for a few hours. The compound crystallises in the tetragonal space group *P4/n*. The asymmetric unit cell contains one quarter of a molecule of **1**$^{4+}$, two chloride anions on special positions, and one quarter of an oxalate anion located about a special position. A small amount of residual electron density remains, which is located close to a four-fold rotation axis; this could not be sensibly modelled and so PLATON-SQUEEZE[S8] was used to include the electron density in the refinement. Apart from restraints on N–H bond lengths and angles, it was not necessary to include any crystallographic restraints in the refinement.

Structure of [1·ox·2Br]$_n$

Crystals were grown by mixing aqueous solutions of **1·4Br** and sodium oxalate, and leaving the mixture to stand for a few hours. The compound crystallises in the tetragonal space group *P4/n*. The asymmetric unit cell contains one quarter of a molecule of **1**$^{4+}$, two bromide anions on special positions, and one quarter of an oxalate anion located about a special position. A small amount of residual electron density remains, which is located close to a four-fold rotation axis; this could not be sensibly modelled and so PLATON-SQUEEZE[S8] was used to include the electron density in the refinement. Apart from restraints on N–H bond lengths and angles, it was not necessary to include any crystallographic restraints in the refinement.

Table S2. Selected crystallographic data.

Compound	**1·4Cl**[a]	**1·4Br**[a]	**1·4**$\mathbf{NO_3}$	**[1·ox·2Cl]**$_\mathbf{n}$[a]	**[1·ox·2Br]**$_\mathbf{n}$[a]
Formula	$C_{29}H_{32}N_8$, 4(Cl)	$C_{29}H_{32}N_8$, 4(Br)	2($C_{29}H_{28}N_8$), 8(NO_3), 3(CH_4O), H_2O	$C_{29}H_{32}N_8$, C_2O_4, 2(Cl)	$C_{29}H_{32}N_8$, C_2O_4, 2(Br)
Formula weight	634.44	812.24	1595.44	651.55	740.45
a (Å)	11.7352(2)	13.3818(3)	11.6729(15)	11.86816(16)	12.07173(18)
b (Å)	11.7352(2)	7.12090(10)	11.8954(9)	11.86816(16)	12.07173(18)
c (Å)	25.3812(13)	21.9744(4)	26.963(2)	11.6198(2)	11.3545(3)
α (º)	90	90	101.982(7)	90	90
β (º)	90	95.8782(19)	91.167(8)	90	90
γ (º)	90	90	90.664(8)	90	90
Unit cell volume ($Å^3$)	3495.39(18)	2082.94(4)	3661.1(3)	1636.69(3)	1654.66(4)
Crystal system	tetragonal	monoclinic	triclinic	tetragonal	tetragonal
Space group	*P4/ncc*	*P2/n*	$P\bar{1}$	*P4/n*	*P4/n*
Z	4	2	2	2	2
Reflections (all)	16382	23995	22057	14714	15992
Reflections (unique)	1781	4221	12917	1466	1673
R_{int}	0.038	0.040	0.041	0.028	0.033
R_1 [$I > 2\sigma(I)$]	0.144	0.039	0.139	0.071	0.074
$wR_2(F^2)$ (all data)	0.242	0.101	0.347	0.194	0.188

[a] PLATON-SQUEEZE[S8] used.

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