Zeolite-like nitride–chlorides with a predicted topology†

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We describe the synthesis and structures of the first tantalum-containing nitride–chlorides, $Ba_3Ta_3N_6Cl$ and $Ba_{15}Ta_{15}N_{33}Cl_4$, and the structurally related $Ba_3Si_3N_5OCl$, and their relationship with a theoretical silaceous framework.

Since the discovery of the ion-exchange properties of zeolites, inorganic frameworks have been a burgeoning interdisciplinary research area, due to their unique chemical and physical properties, such as cation exchange and catalysis, and distinctive structural features.[1] Where frameworks are built up from tetrahedral units, they often crystallise in known zeolite types or closely analogous structures, hosting atoms or molecules inside cages or tunnels formed by the framework.[2,3] Most inorganic frameworks are based upon oxygen-containing polyhedra, *e.g.* MO_4 tetrahedra, but there is a growing list of examples of condensed framework structures based upon non-oxide anions and mixed-anion systems. Examples of nitride frameworks include $Ca_3Ga_2N_4$, containing two interpenetrating networks formed from corner-sharing GaN_4^{9-} tetrahedra,[4] $Ba_2Nd_7Si_{11}N_{23}$, which is the first nitridosilicate with a zeolitic Si–N network,[5] and HP_4N_7[6] which contains PN_4^{7-} tetrahedra. Examples of mixed-anion frameworks include $Zn_7[P_{12}N_{24}]Cl_2$[7] and $Ln_4[Si_4O_{3+x}N_{7-x}]Cl_{1-x}O_x$ with Ln = Ce, Pr, Nd and $x \approx 0.2$, which is the only family of compounds to show a zeolite-like framework containing the oxide, nitride and chloride ions.[8,9] Organic–inorganic hybrid open frameworks show a few examples of zeolite-related compounds containing an electropositive metal (alkali, alkaline-earth metal, or lanthanide) and a transition metal, but, to date, we are not aware of any purely inorganic framework showing this feature.[10] Framework structures based on tetrahedrally coordinated tantalum have not been reported, although several examples of tantalum nitride compounds containing TaN_4^{7-} tetrahedra are known, *e.g.* Li_4TaN_3[11] and Sr_2TaN_3,[12] but these contain chains of tetrahedra rather than extended 3-D frameworks.

Here we report the preparation and structural characterisation of the first two tantalum containing nitride–chlorides, $Ba_3Ta_3N_6Cl$ (**1**) and $Ba_{15}Ta_{15}N_{33}Cl_4$ (**2**), which are also the first multinary nitride–chlorides to show a zeolite-like framework. This is not found in a naturally occurring framework, but has been predicted as a possible low energy structure for SiO_2 from theoretical calculations.[13] We therefore prepared the analogous silicate compound and obtained $Ba_3Si_3N_5OCl$ (**3**), which shows a 3-D framework based on $Si(O/N)_4$ tetrahedra and is isostructural with $Ba_3Ta_3N_6Cl$.

The preparation of multinary nitride–chloride compounds is experimentally difficult. In fact, only four such nitride–chlorides are known to date: $Ba_{25}Nb_5N_{19}Cl_{18}$,[14] $Ba_5(MoN_4)O_{0.75}Cl_{2.5}$,[14] $Ba_4[WN_4]Cl_2$[15] and $LiBa_4[Mo_2N_7]\cdot BaCl_2$.[16] Single crystals of $Ba_3Ta_3N_6Cl$, $Ba_{15}Ta_{15}N_{33}Cl_4$ and $Ba_3Si_3N_5OCl$ were prepared using a technique originally employed for nitrides[17] and subsequently adapted to more complicated systems.‡ The synthesis is based on the observation that single crystals of ternary nitride–chlorides containing alkali or alkaline-earth metals and transition metals can be grown on foils of transition metal by reaction of the foil with molten alkali or alkaline-earth metal nitrides and chlorides. This is a productive route to new mixed-anion compounds but tends to yield small single crystals within an amorphous matrix and chemical analysis of products is therefore unreliable.

Crystals of $Ba_3Ta_3N_6Cl$ and $Ba_{15}Ta_{15}N_{33}Cl_4$ were found in the same batch. A scanning electron microscopy (SEM) photograph (Fig. 1) shows that the crystals are hexagonal shaped plates of the order of microns in their longest dimension. Crystal size rendered structural determination using a conventional laboratory X-ray source impossible. Crystals were examined using synchrotron radiation at Station 16.2SMX of the Daresbury SRS, UK. Crystal selection proved very laborious and a large number of possible samples were examined before suitable single crystals were found. Data collection and structure solution were routine, but structural refinement was complicated by the presence of nitrogen bound to tantalum, owing to their vastly different scattering lengths. However, structural studies give definitive information about the frameworks: if Fourier difference maps are calculated with the nitride absent from the final model, peaks are found at the nitride positions. Disordered guest species (Ba, Cl) can be located in a similar manner. Crystal structure analysis[18,19] showed both **1** and **2**

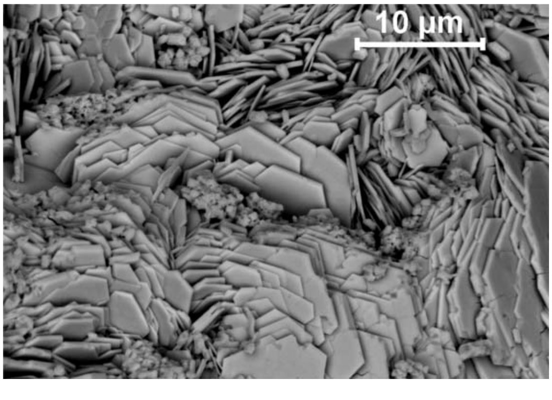

Fig. 1 SEM photograph of $Ba_3Ta_3N_6Cl$ and $Ba_{15}Ta_{15}N_{33}Cl_4$ crystals.

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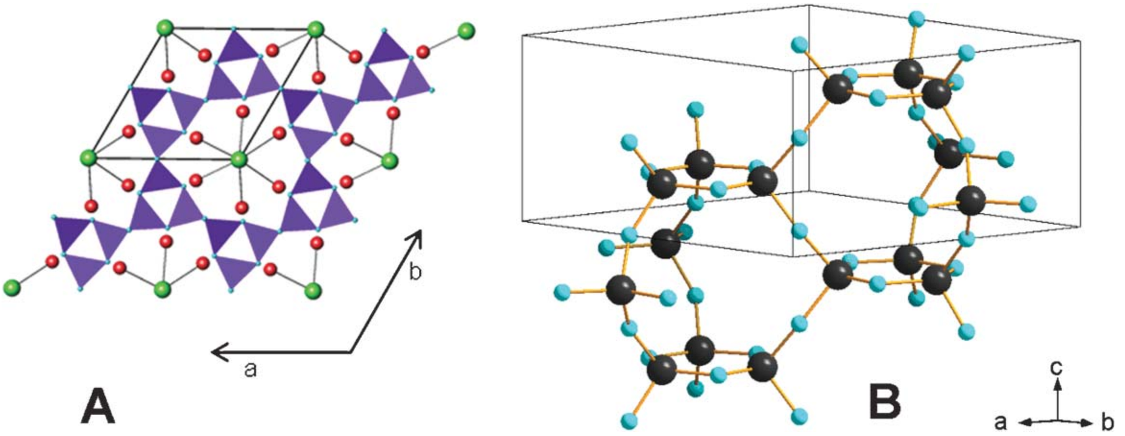

Fig. 2 **A**: Framework common to **1**, **2**, and **3** viewed down *c*. **B**: highlights the fourfold connectivity of the framework. Colour scheme: N cyan, Ta or Si grey, Ba red, Cl green.

crystallise in $P\bar{6}2c$ with topologically equivalent frameworks formed from TaN_4 tetrahedra (Fig. 2A). It initially appeared from the diffraction images that **1** and **2** had the same unit cell, but careful inspection showed extra reflections. **2** is related to **1** by a fivefold expansion of the unit cell along *c* but this preserves the framework topology. Tetrahedra assemble into triangular clusters (3-rings) in the *ab* plane by corner sharing. The two remaining vertices of each tetrahedron each link to another triangular cluster displaced along *c* (Fig. 2B). Assembly of these clusters produces 12-rings in the *ab* plane and 6-rings parallel to [100] and [110].

Microcrystal diffraction[20] revealed that the framework prepared with silicon, $Ba_3Si_3N_5OCl$, (**3**), is isostructural with **1** and displays the same number and orientation of guest species. It was not possible using X-ray diffraction to determine whether any ordering of the O/N was present and the oxygen is statistically disordered over the framework in the model employed. The framework structure common to $Ba_3Ta_3N_6Cl$, $Ba_{15}Ta_{15}N_{33}Cl_4$, and $Ba_3Si_3N_5OCl$ is shown in Fig. 2.

In **1**, **2** and **3** Ba^{2+} cations and chloride anions occupy the channels centred along [001]; the chloride anions are located at centre and are coordinated by six Ba^{2+} cations. In **1** and **3** the single chloride anion resides on the 4*e* position (0, 0, *z*), and is half occupied. The fivefold expansion along *c* in **2** conserves the framework topology and differences arise only in the number and position of the extra-framework species. There are three chloride positions in **2**, each (0, 0, *z*), two of which are fully occupied while the third is disordered over two symmetry equivalent sites 1.63(6) Å apart. The changes in chloride content and positions are accompanied by small changes in the positions adopted by the barium cations; this ordering gives rise to the fivefold expansion in **2**. Final difference Fourier maps for **2** suggested the presence of some further nitrogen within the structure. Additional nitride, not involved in framework formation, was added to the model in octahedral holes formed from three Ta and three Ba ions, subject to the constraint that the Ta oxidation state could not exceed +5. The formula for **2** is best written $Ba_{15}Ta_{15}N_{30}Cl_4[N_3]$, where the distinction between framework and interstitial nitrogen is clear.

Charge balancing constraints in **1** imply that the formal oxidation station for tantalum is +4.333, suggesting the presence of a small amount of Ta^{3+} which was not crystallographically resolved. In **1** the Ta–N distances are 1.96(4) and 1.962(5) Å. These are in good agreement with other Ta/N phases where the tantalum oxidation state is +5 such as Li_4TaN_3,[11] Sr_2TaN_3,[12] Ba_2TaN_3.[21]

All three compounds show frameworks with patterns of cavities defined by corner-linked tetrahedra: TaN_4 in **1** and **2**, $Si(O/N)_4$ in **3**. As is common in mixed-anion compounds, such as $Ba_{25}Nb_5N_{19}Cl_{18}$, $Ba_5(MoN_4)O_{0.75}Cl_{2.5}$[14] and $Ba_4[WN_4]Cl_2$,[15] the most electronegative anion only bonds to the most electropositive cation.

Interestingly, the Si/N/O and Ta/N frameworks observed in **1**, **2** and **3** cannot be related to a naturally occurring one, but adopt one predicted for SiO_2.[13] Foster *et al.* enumerated a number of possible frameworks for the empirical formula SiO_2 and then optimised these structures using the lattice energy minimisation program GULP.[22] In this way, a total of 23 unknown but chemically feasible frameworks were identified. The present example is related to one such hypothetical zeolite (no. 89 from Foster *et al.*) which is a relatively low density SiO_2 polymorph with a relatively high accessible volume. The observed framework within **1**, **2**, and **3** can be generated from the hypothetical example in $P6_3/mmc$ with $a = b = 9.0685$ and $c = 5.189$ Å by reducing the symmetry to the subgroup $P\bar{6}2c$. Topologically the frameworks are identical (Fig. 3) but the reduction in symmetry is a consequence of rotation and distortion of the tetrahedra within the framework. In $P6_3/mmc$ the silicon occupies a 6*h* Wyckoff site (mm2) and in $P\bar{6}2c$ it also occupies the 6*h* (m..) site but this has lower symmetry. In **2** (fivefold expansion) there are three symmetry independent Ta sites: one 6*h* (m..) and two 12*i* (1) sites.

In conclusion, we have prepared $Ba_3Ta_3N_6Cl$ and $Ba_{15}Ta_{15}N_{33}Cl_4$, which are not only the first multinary nitride–chlorides to contain tantalum, but also the first multinary nitride–chlorides to

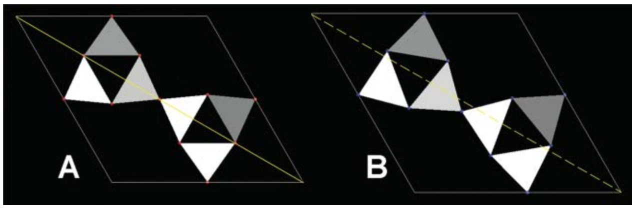

Fig. 3 Theoretical (A) and experimental (B) structures. Solid yellow line represents a mirror plane. Dashed line indicates an absent mirror plane.

exhibit a zeolite-related framework. These are topologically identical to a framework predicted for SiO_2 by lattice energy minimisation. The discovery of these new framework materials augurs well for the future synthesis of a wide variety of complex mixed-anion solids.

Notes and references

‡ The synthesis of **1** and **2** was carried out in an inert atmosphere. A 1 : 1 mixture of polycrystalline $BaCl_2$ and Ba_2N was placed in a hand made tantalum crucible under flowing nitrogen. The mixture was heated for 36 h at 1273 K then cooled to room temperature. Single crystals were found to have grown on the walls of the tantalum crucible. An analogous procedure employing a 1 : 1 : 1 mixture of polycrystalline $BaCl_2$, Ba_2N and SiO_2 within a niobium crucible was used to synthesise **3**.

Single crystal X-ray diffraction data were collected on Station 16.2SMX of the UK Synchrotron Radiation Source, Daresbury, λ = 0.7848 Å. Crystals were covered in perfluoropolyether oil and mounted on the end of a two-stage glass fibre and cooled to 150 K in a nitrogen gas cryostream. Data were collected using a Bruker D8 diffractometer fitted with an APEXII CCD area detector. Semi-empirical corrections were applied to model absorption and incident beam decay. Structures were solved using direct methods and refined using least squares refinement against all unique F^2 values. Further details of the crystal structure investigations may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: (+49) 7247-808-666; E-mail: crysdata(at)-fiz-karlsruhe.de, http://www.fiz.karlsruhe.de/request_for_deposited_data.html) on quoting the appropriate CSD number: 418216, 418217, 418218, for **1**, **2**, and **3** respectively.

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19 Crystal data for **2**, $Ba_{15}Ta_{15}N_{30}Cl_4N_3$: M = 10770.97, hexagonal, $a = b$ = 10.1545(3) and c = 29.9170(18) Å, V = 2671.6(2) Å^3, T = 150 K, space group $P\bar{6}2c$ (no. 190), weak extra reflections suggested a fivefold expansion from **1**, Z = 1, μ = 41.63 mm^{-1}, size 30 × 15 × 15 μm. 16 811 reflections, 2480 unique which were used in all calculations, R_{int} = 0.1003. $R(F^2)$ = 0.0474.

20 Crystal data for **3**, $Ba_3Si_3N_5OCl$: M = 1235.58, hexagonal, $a = b$ = 9.5604(13) and c = 5.5520(15) Å, V = 439.47(15) Å^3, space group $P\bar{6}2c$ (no. 190), Z = 1, μ = 13.97 mm^{-1}, size 40 × 10 × 10 μm. 1267 reflections, 403 unique which were used in all calculations, R_{int} = 0.0499. $R(F^2)$ = 0.0504.

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