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Novel ternary N-containing mixed-anion compounds with ionic and covalent features†

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Two novel N-containing ternary mixed-anion compounds, $Ba_{25}Nb_5N_{19}Cl_{18}$ and $Ba_5(MoN_4)O_{0.75}Cl_{2.5}$ have been prepared and structurally characterised: their unique structure is due to the presence of both ionic and covalent bonds.

Ternary mixed-anion compounds can be defined as compounds containing two cations of a different nature, normally an alkali or an alkaline earth metal or a lanthanide, and a transition metal, and two or more anions (general formula $A_aM_mX_xY_y$ where A = alkali or an alkaline earth metal or a lanthanide, M = transition metal and X, Y = anions). The chemistry of ternary mixed-anion compounds has received attention in the past few years since the discovery of superconductivity in oxide–halide ternary compounds, such as $Sr_2CuO_2F_{2+\delta}$.[1] Nevertheless, the chemistry of other ternary mixed-anion compounds, such as nitride–chlorides, is largely unexplored due to the difficulty in preparing these materials. However, research into these ternary mixed-anion compounds is of considerable interest, as anions of a different nature in the same structural context may lead to a deeper understanding of the role of anions other than oxygen in inorganic compounds. For example, different anions in a compound may occupy different crystallographic sites depending on parameters such as electronegativity, size, and charge. Ultimately such research may lead to the synthesis of materials of an unusual and potentially useful kind.

Herein, we report the synthesis and structural characterisation of the first niobium nitride–chloride $Ba_{25}Nb_5N_{19}Cl_{18}$ and the first molybdenum nitride–oxide–chloride, $Ba_5(MoN_4)O_{0.75}Cl_{2.5}$, in the form of single crystals.

Our synthetic route is based on the concept that the growth of single crystals of ternary compounds containing transition metals can be achieved on the surface of a transition metal thin foil. This synthetic route constitutes an expansion of the synthetic route previously used to prepare ternary nitrides containing alkaline earth metals and transition metals (general formula $A_aM_mN_n$) in Nottingham. Single crystals of Ba_3MoN_4 were grown on the surface of a Mo thin foil by reaction with molten Ba_2N.[2] $Ba_{25}Nb_5N_{19}Cl_{18}$ **1** was prepared by reaction of Ba_2N and $BaCl_2$ with Nb metal. $Ba_5(MoN_4)O_{0.75}Cl_{2.5}$ **2** was prepared by reaction of Ba_2N, $BaCl_2$ and BaO with Mo metal. To prepare $Ba_{25}Nb_5N_{19}Cl_{18}$ **1** and $Ba_5(MoN_4)O_{0.75}Cl_{2.5}$ **2**, the Ba starting reagents were placed in a crucible made out of Nb or Mo metal foil, respectively. The crucible was placed inside a stainless steel container, which was placed into a silica tube. All manipulations have to be carried out in a nitrogen filled glove box as both reagents and products are air/moisture sensitive. The silica tubes were heated at 1000 °C for 50 h to allow the melting of the Ba reagents and the reaction with the transition metal foil. The reactions were then slow-cooled to room temperature at 1 °C/hour to allow the growth of good size single crystals. Flowing nitrogen was allowed to pass through the silica tubes during the reactions. Single crystals of $Ba_{25}Nb_5N_{19}Cl_{18}$ **1** and $Ba_5(MoN_4)O_{0.75}Cl_{2.5}$ **2** were found to have grown on the walls of the transition metal crucibles. A suitable crystal, separated from the batch, was used for the X-ray crystallographic studies in each case. The structure of $Ba_{25}Nb_5N_{19}Cl_{18}$ **1** is illustrated in Fig. 1 and crystallographic details are given below.[3] Nb^{5+} is tetrahedrally coordinated by nitrogen and forms isolated monomeric (Nb1–Nb3) and corner-linked dimeric Nb–N tetrahedral units (Nb4 and Nb5). The presence of dimeric Nb–N units is suggested by crystallographic data, which show that N44 is bonded to both Nb4 and Nb5. This constitutes an unusual situation for Nb, which tends to form edge-sharing polyhedra in ternary and quaternary nitrides and oxynitrides such as Li_7NbN_4,[4] $Li_3Ba_2NbN_4$[5] and $Li_{16}(NbN_4)_2O$.[6] The only example of monomeric $(NbN_4)^{7-}$ units is found in the more complex compound $Ba_9(NbN_4)_2N(N_3)$, which contains nitride and azide ions.[7] The presence of both monomeric $(NbN_4)^{7-}$ and dimeric $(Nb_2N_7)^{11-}$ isolated tetrahedral units in the same structural context constitutes a peculiar feature of $Ba_{25}Nb_5N_{19}Cl_{18}$ **1** (see Fig. 1). Nb^{5+} cations form almost regular tetrahedra with N^{3-} anions, whereas Ba cations form heavily distorted polyhedra with both N and Cl anions in this compound.

Moreover, to our knowledge, $Ba_{25}Nb_5N_{19}Cl_{18}$ **1** is the first ternary nitride–chloride including a group V transition metal element. There are very few examples of ternary nitride–chlorides in the literature and all reported to date contain transition metals belonging to group VI.

The structure of $Ba_5(MoN_4)O_{0.75}Cl_{2.5}$ **2** is illustrated in Fig. 2 and crystallographic details are given below.[3] To our knowledge, $Ba_5(MoN_4)O_{0.75}Cl_{2.5}$ **2** (Fig. 2) is the first N-

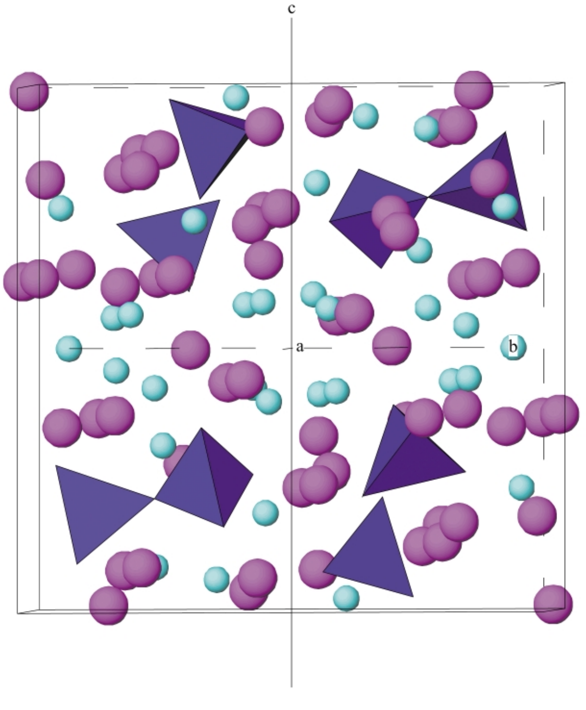

Fig. 1 Structure of $Ba_{25}Nb_5N_{19}Cl_{18}$ **1** showing the presence of both monomeric $(NbN_4)^{7-}$ and dimeric $(Nb_2N_7)^{11-}$ isolated tetrahedral units. The purple spheres represent the Ba ions, the blue spheres represent the Cl ions

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† Dedicated to the late Marten Barker.

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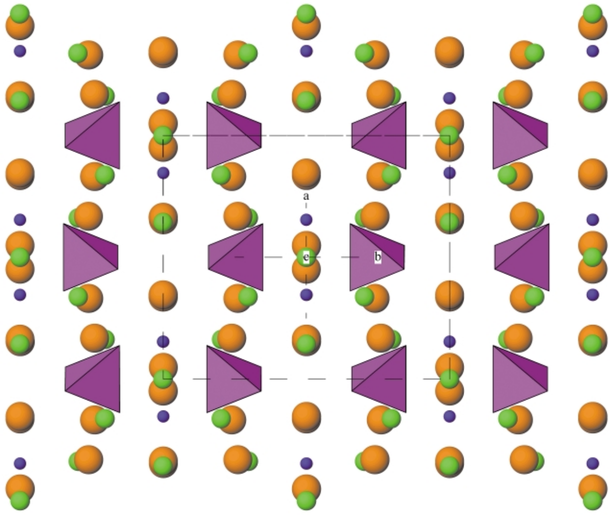

Fig. 2 Structure of $Ba_5(MoN_4)O_{0.75}Cl_{2.5}$ **2** showing $(MoN_4)^{6-}$ tetrahedral isolated units. The orange spheres represent the Ba ions, the green spheres represent the Cl ions and the blue spheres represent the O ions

containing ternary mixed-anion phase including three different anions in the same chemical formula. In $Ba_5(MoN_4)O_{0.75}Cl_{2.5}$ **2**, Mo is four-coordinated by nitrogen and forms isolated Mo–N tetrahedral units which are typical of ternary molybdenum nitrides.[8] As with the Nb^{5+}, the Mo^{6+} cations form almost regular tetrahedra with N^{3-} anions,[3] whereas the Ba cations form heavily distorted polyhedra with N, Cl and O anions.

Interestingly, the crystallographic data indicate that in $Ba_{25}Nb_5N_{19}Cl_{18}$ **1**, Nb is only coordinated by N whereas Ba is coordinated by both N^{3-} and Cl^-. In $Ba_5(MoN_4)O_{0.75}Cl_{2.5}$ **2**, Mo is only coordinated by N whereas Ba is coordinated by all three anions present in the compound. We propose that the reason for this is that Cl^- and O^{2-} are more electronegative than N^{3-} and therefore tend to bond only to the most electropositive cation available, *i.e.* the barium.

We estimated the nature of the bonds involved in $Ba_{25}Nb_5N_{19}Cl_{18}$ **1** and $Ba_5(MoN_4)O_{0.75}Cl_{2.5}$ **2** using the difference in electronegativity (Δ) of the elements involved. The results of our calculations are summarised in Table 1. We observed that in $Ba_{25}Nb_5N_{19}Cl_{18}$ **1** and $Ba_5(MoN_4)O_{0.75}Cl_{2.5}$ **2** all the bonds involving transition metals can be considered covalent ($\Delta < 1.7$) and all the bonds involving Ba can be considered ionic ($\Delta > 1.7$). This suggests that ternary mixed anion compounds can be seen as formed by covalent and ionic areas. There are only very few ternary nitride–chlorides published in the open literature: $LiBa_4[Mo_2N_7]\cdot BaCl_2$[9] and $Ba_4[WN_4]Cl_2$.[10] As with our mixed-anion compounds, $LiBa_4[Mo_2N_7]\cdot BaCl_2$ and $Ba_4[WN_4]Cl_2$ can be seen as formed by covalent and ionic areas, as shown by the values of Δ listed in Table 1. Crystallographic data reported by Gudat *et al.*[8,9] indicate that Mo and W are only coordinated by N whereas Ba (Li) is coordinated by both N^{3-} and Cl^-. In all the ternary mixed-anion compounds mentioned above N^{3-} is the only anion which bonds to both transition metals and Ba and therefore the Ba–N bond can be considered the linking trade between the covalent and ionic areas.

Table 1 Differences in electronegativity (Δ) for cation–anion bonds in $Ba_{25}Nb_5N_{19}Cl_{18}$ **1**, $Ba_5(MoN_4)O_{0.75}Cl_{2.5}$ **2**, $LiBa_4[Mo_2N_7]\cdot BaCl_2$[8] and $Ba_4[WN_4]Cl_2$[9]

Bond	Δ
W–N	0.68
Mo–N	0.88
Nb–N	1.44
Ba–N	2.15
Ba–Cl	2.27
Ba–O	2.55

In summary, we herein report the synthesis and structural characterisation of the first niobium nitride–chloride $Ba_{25}Nb_5N_{19}Cl_{18}$ **1** and the first molybdenum nitride–oxide–chloride, $Ba_5(MoN_4)O_{0.75}Cl_{2.5}$ **2**. We characterised the structures of $Ba_{25}Nb_5N_{19}Cl_{18}$ **1** and $Ba_5(MoN_4)O_{0.75}Cl_{2.5}$ **2** using single crystal X-ray diffraction data. These compounds show unique structures together with the presence of both covalent and ionic bonds in the same structural context. This latter feature is particularly prevalent in mixed-anion compounds containing anions with very different polarisabilities, *e.g.* N^{3-}, Cl^- and O^{2-}. We conclude that, in general, ternary mixed-anion compounds can be seen as formed by ionic and covalent areas, linked together by the less electronegative anion.

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Notes and references

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3 For both compounds, data were collected on a Bruker SMART1000 CCD area detector diffractometer. The crystals were cooled to and maintained at 150 K using an Oxford Cryosystems nitrogen gas flow cryostat. *Crystal data* for **1**: $Ba_{25}Cl_{18}N_{19}Nb_5$, M = 4802.34, triclinic, space group $P\bar{1}$ (no. 2), a = 12.5942(13), b = 13.5297(14), c = 20.635(2) Å, α = 89.813(2), β = 89.590(2), γ = 87.684(2)°, U = 3513.1(6)Å^3 , T = 150 K, Z = 2, μ(Mo-Kα) = 15.23 mm^{-1}, 29386 reflections measured, 15547 unique (R_{int} = 0.041) which were used for all calculations. The final $wR(F^2)$ was 0.1227 and $R1$ was 0.0494 for 11728 observed data. *Crystal data* for **2**: $Ba_5Cl_{2.50}MoN_4O_{0.75}$, M = 939.30, monoclinic, space group $C2/m$ (no. 12), a = 10.8277(14), b = 11.8401(15), c = 10.3631(14) Å, β = 111.960(3)°, U = 1232.2(3) Å^3, T = 150 K, Z = 4, μ(Mo-Kα) = 17.22 mm^{-1}, 2399 reflections measured, 1374 unique (R_{int} = 0.026) 1369 reflections were used in all calculations. The final $wR(F^2)$ was 0.115 for these data and $R1$ was 0.0413 for 1199 observed data. The above formula gave a more satisfactory refinement against the X-ray data than the initial model with partially occupied Cl sites and fully occupied O, which gave the stoichiometric formula $Ba_5MoN_4Cl_2O$. However, it resulted in unacceptably large atomic displacement parameters for the oxygen atom and residual electron density in the region of the Cl. CCDC reference numbers 183479 and 183480. See http://www.rsc.org/suppdata/cc/b2/b203382h/ for crystallographic data in CIF or other electronic format.

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