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# New families of mixed alkaline-earth nitridomolybdates and nitridotungstates, $(Ba,Sr)_3[MN_4]$ (M = Mo, W) †

**Charles F. Baker, Marten G. Barker, Alexander J. Blake, Claire Wilson and Duncan H. Gregory** *

*School of Chemistry, University of Nottingham, University Park, Nottingham, UK NG7 2RD.*
*E-mail: Duncan.Gregory@Nottingham.ac.uk*

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Two new families of nitrides containing molybdenum(VI) and tungsten(VI) were synthesised by the reaction of barium and strontium nitride with either molybdenum or tungsten foils at high temperature in sealed stainless steel crucibles. The reactions yielded single crystalline products determined by X-ray diffraction to form orthorhombic structures in the space group *Pbca* (no. 61). The compounds are isostructural with the "low temperature" polymorph of $Ba_3MoN_4$ and form solid solutions within the limits investigated. The structures contain isolated $[Mo(W)N_4]^{6-}$ tetrahedra and alkaline-earth cations distributed across three crystallographic sites dependent on cationic radius. The title compounds are the first examples of mixed strontium–barium transition metal nitrides.

## Introduction

In recent years the study of ternary and higher nitrides has become more extensive.[1] Interest in the chemistry of the Group 5 and 6 ternary nitrides has grown significantly, largely due to striking comparisons with oxosilicates.[2] The tetrahedral $[SiO_4]^{4-}$ unit in silicate chemistry is structurally analogous to the $[MN_4]^{n-}$ (M = Nb, Ta, $n = 7$; M = Mo, W, $n = 6$) units found in Group 5 and 6 nitride chemistry. In silicate chemistry, the permutations of linking and arranging $SiO_4$ units are immense.[3] A currently much smaller range of comparable structures is found in the chemistry of the nitridometalates(V and VI). Despite this, examples already exist of isolated units (monometalates), dimers (dimetalates), chains (monopolymetalates), sheets (phyllometalates) and three-dimensional networks (tectometalates). Compounds containing electropositive Group 1 and 2 elements, A–M–N (A = alkali or alkaline-earth metal, M = Group 6 metal) form examples within all these structural classes.

Among the earliest examples of these nitridometalates are the $Li_6MN_4$ compounds (M = Cr, Mo, W) with *anti* $CaF_2$-type structures containing lithium, transition metals and defects ordered across tetrahedral sites.[4] The alkaline-earth–Group 6 metal nitrides also tend to adopt mononitridometalate structures. Of these, $Ba_3Mo(W)N_4$ forms two polymorphs: a low-temperature orthorhombic[5] and a high-temperature trigonal form.[6] By contrast, $Sr_3MoN_4$[7,8] has been reported only as a monoclinic structure while Group 2 metal–chromium nitrides form nitridometallates(III) $A_3CrN_3$ (A = Ca, Sr, Ba), containing trigonal-planar $[CrN_3]^{6-}$ anions.[9] Mixing alkali and alkaline-earth metals leads to more condensed structures such as $LiBa_4[M_2N_7]$ (M = Mo, W) and $LiBa_4[Mo_2N_7]\cdot BaCl_2$.[10] Both structural groups comprise Group 1 and 2 cations surrounding $[M_2N_7]^{9-}$ dimeric anions. In the nitride chloride the tetrahedra adopt a so-called "eclipsed" conformation in the $Mo_2N_7$ dimer, whereas in $LiBa_4[M_2N_7]$ (M = Mo, W), the tetrahedra are "staggered" across the M–N–M linkage. These units are structurally analogous to the $[Si_2O_7]^{6-}$ dimers in thortveitite ($Sc_2Si_2O_7$)-like compounds.[11]

Further condensation is largely restricted to alkali metal containing compounds. In these nitrides the role of the cationic component is crucial with structure changing dramatically as the identity and composition of the alkali metal(s) is modified. In $Na_3Mo(W)N_3$, $^1_\infty[Mo(W)N_2N_{2/2}]^{3-}$ anionic chains adopt hexagonal rod packing[12] which switches to a tetragonal packing conformation (as in the silicate $Ba[SiO_2OH]_2\cdot 2H_2O$)[13] as sodium is partially replaced by the heavier alkali metals, *e.g.* $Na_2KWN_3$ and $Na_{11}Rb[WN_3]_4$.[14] In $Na_5A[WN_3]_2$ (A = Rb, Cs) however, the chains lie in one plane with Rb(Cs) cations linking the chains into layers interspersed with sodium.[15] Mixed alkali metal compounds with a significantly lower proportion of sodium condense further to form 2D and 3D structures. $Na_2K_{13}W_7N_{19}$ consists of layers of corner sharing W–N tetrahedra.[16] Further condensation, such as that shown by $Cs_5Na[W_4N_{10}]$, results in a three-dimensional network where each tungsten atom is bonded to one terminal nitrogen and three bridging nitrogens.[17]

The consequences of mixing alkaline-earth metals in nitrido-molybdates and -tungstates are far less-studied. Only two mixed Group 2 metal compounds, $Ca_2SrWN_4$ and $Ba_2CaWN_4$ have been previously reported.[18,19] Whereas $Ca_2SrWN_4$ crystallises in the orthorhombic structure (space group *Pbca*) found at lower temperature for $Ba_3MoN_4$ and $Ba_3WN_4$, the mixed barium–calcium compound, $Ba_2CaWN_4$ is observed to adopt an alternative orthorhombic structure in space group *Fddd* with a far larger unit cell. The packing of the isolated $[MN_4]$ tetrahedra change as a result from hexagonal to cubic close packed.

Although the number of known nitrides containing both strontium and barium is small—only a handful have been previously reported[20,21]—the apparent tolerance of this class of materials to accommodate similarly charged cations of varying size, with silicates as an analogous precedent, suggests many other mixed Group 2 nitridometalates(VI) should exist. As part of our studies of such nitrides, in this paper we report the synthesis and structural characterisation of two new families of mixed alkaline-earth nitrides. These investigations describe two solid solutions of compounds with cation arrangements depending on the relative composition and sizes of the constituent alkaline-earth metals.

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† Dedicated to Dr Marten G. Barker in memoriam.

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**Table 1** Reactant ratios for (A,A′)$_3$MN$_4$ nitrides

| Compound | Ratio of Ba$_2$N : Sr$_2$N/g | Ba : Sr ratio | M | Nominal composition |
|---|---|---|---|---|
| **1** | 0.82 : 0.18 | 3 : 1 | Mo | Ba$_{2.25}$Sr$_{0.75}$MoN$_4$ |
| **2** | 0.61 : 0.40 | 1 : 1 | Mo | Ba$_{1.5}$Sr$_{1.5}$MoN$_4$ |
| **3** | 0.33 : 0.66 | 1 : 3 | Mo | Ba$_{0.75}$Sr$_{2.25}$MoN$_4$ |
| **4** | 0.82 : 0.18 | 3 : 1 | W | Ba$_{2.25}$Sr$_{0.75}$WN$_4$ |
| **5** | 1.00 : 0.66 | 1 : 1 | W | Ba$_{1.5}$Sr$_{1.5}$WN$_4$ |
| **6** | 0.33 : 0.66 | 1 : 3 | W | Ba$_{0.75}$Sr$_{2.25}$WN$_4$ |

## Experimental

### Starting materials

All manipulations were carried out using nitrogen- or argon-filled glove boxes (*ca.* 5 ppm O$_2$, <5 ppm water). The alkaline-earth nitrides (Sr$_2$N and Ba$_2$N) were prepared by the reaction of the metals with nitrogen gas at 700 K in liquid sodium for 16 h.[22] Strontium pieces (*ca.* 5 g, Aldrich 99%) and barium cut from a rod (*ca.* 5 g, Alfa 99+%) were cleaned of surface oxide and placed in stainless steel crucibles. Liquid sodium (*ca.* 20 cm$^3$) was added and the crucibles were placed into separate reaction vessels with cold fingers. The reaction vessels were removed from the box, attached to a vacuum/gas line, evacuated and refilled with nitrogen (*ca.* 2 atm). The vessels were heated to 700 K for 16 h under a positive pressure of N$_2$ then cooled. The excess sodium was removed by vacuum distillation at 750 K for 24 h. This method produces nitrides with negligible amounts of alkaline-earth oxide or hydroxide. The product powders were purple/black crystalline Sr$_2$N and black poorly crystalline Ba$_2$N. The products were identified using powder X-ray diffraction (PXD) using a Philips XPERT $\theta$–$2\theta$ diffractometer (Cu-K$\alpha$ radiation) with reference to the ICDD (JCPDS) database.

Molybdenum foil (Goodfellow, 99.9%, 0.127 mm) and tungsten foil (Goodfellow, 99%, 0.127 mm) were used as supplied.

### Ternary nitride synthesis

Single crystals of the six compounds were grown by the reactions of Sr$_2$N and Ba$_2$N with Mo and W foils. All manipulations were carried out in an argon-filled glove box. Sr$_2$N and Ba$_2$N (*ca.* 1–2 g) in desired ratios were ground together and the mixtures were placed in Mo or W foil tubes (Table 1). Since other similar preparations had resulted in reaction between the binary alkaline-earth nitrides and metal foils,[23] no attempt was made to add molybdenum or tungsten powder as starting materials. The A$_2$N mixtures were not made into pellets in order to maximise contact with the surrounding Mo or W tubes. The filled tubes were placed in stainless steel crucibles, which were sealed under argon using an arc welder. The crucibles were placed in a tube furnace and heated to 1400 K. The temperature was held for 5 d then slow cooled over 2 d (20 K h$^{-1}$). A constant stream of argon was passed over the crucibles to reduce aerial oxidation. Upon removal from the furnace, the crucibles were mechanically cleaned to remove any oxide coating and cut open in a nitrogen-filled glove box.

The metal foils were coated with red–brown irregular crystals. Typically, nothing remained of the binary nitride, though traces of the alkaline-earth metal itself were observed at the bottom of crucibles. Crystals were removed by gently bending or scraping the foil. Crystals suitable for single crystal X-ray diffraction were selected by spreading on a microscope slide and viewing under an optical microscope. Selected crystals were placed in a drop of moisture-free RS3000 perfluoropolyether oil (Riedel de Hahn) on a small glass slide.

### Structure determination

Selected crystals (typical dimensions 0.2 × 0.1 × 0.05 mm) were attached to a dual-stage glass fibre using RS3000 oil before mounting on the diffractometer. The crystals were frozen into place using a stream of cold nitrogen gas at 150 K. All data sets were collected on a Bruker SMART 1000 CCD with graphite monochromated Mo-K$\alpha_1$ radiation. The unit cells of all compounds were indexed in the orthorhombic space group *Pbca* with cell parameters in the range $a$ = 10.503–10.70, $b$ = 9.733–10.13, $c$ = 11.672–12.04 Å using *ca.* 800 (Mo) or *ca.* 900 (W) reflections in each case for $3 \leq 2\theta \leq 29°$. Structure solution by direct methods using SIR97[24] showed that all of the compounds were isostructural to the previously known compounds orthorhombic Ba$_3$[MN$_4$] (M = Mo, W)[5] and Ca$_2$Sr[WN$_4$].[18] The structures were refined on $F^2$ for all reflections using SHELXL-97,[25] through WinGX.[26] Refinements proceeded smoothly with temperature factors for all metal atoms in each compound refined anisotropically. Nitrogen temperature factors were also refined anisotropically with restraints applied as appropriate. The fractional occupancies of the three alkaline-earth metal positions were refined constraining the total occupancy to 1 on each site. *R*-factors and difference peaks for **1** were slightly higher than in the other compounds. Given the position of the maximum and minimum (0.92 and 0.68 Å from A1 (Ba) respectively) these are not structurally significant and combined with the geometric precision of the solution suggest relatively poor crystal quality. Final crystallographic parameters for all of the compounds are shown in Table 2.

CCDC reference numbers 188975–188980.

See http://www.rsc.org/suppdata/dt/b2/b206427h/ for crystallographic data in CIF or other electronic format.

## Results and discussion

All of the compounds prepared crystallise in the orthorhombic space group *Pbca* (no. 61) and are isostructural with the low temperature (LT) form of Ba$_3$MN$_4$ (M = W, Mo) and Ca$_2$SrWN$_4$.[5,18] Atomic parameters for the compounds (**1**–**6**) including refined A site occupancy factors are shown in Table 3. Full descriptions of this structure type can be found in ref. 5 but essentially the structure consists of isolated MN$_4$ tetrahedra which align in rows parallel to the *a*-axis and in two different (..abab..) layers parallel to the *b* and *c* directions (Fig. 1a). The

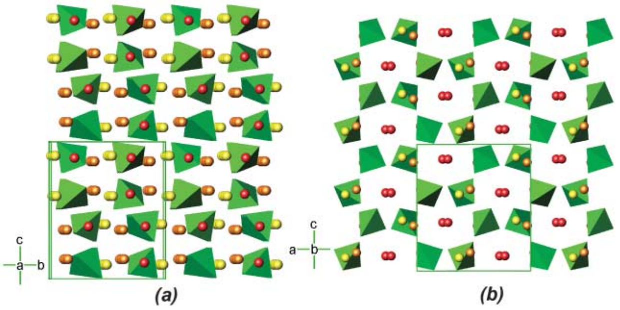

**Fig. 1** Structure of (Ba,Sr)$_3$MN$_4$ (M = Mo, W): (a) as a [100] projection, illustrating layers of isolated [MoN$_4$]$^{6-}$ tetrahedra stacked along the [010] direction. Between and within these are situated the alkaline-earth cations, (b) as a [010] projection illustrating hexagonal "channels" of isolated [MoN$_4$]$^{6-}$ tetrahedra within which are located A1 cations. A1 (red spheres), A2 (orange spheres) and A3 (yellow spheres).

**Table 2** Crystallographic data for $(Ba,Sr)_3MN_4$ nitrides

| Compound | **1** | **2** | **3** | **4** | **5** | **6** |
|---|---|---|---|---|---|---|
| Formula | $Ba_{2.11}Sr_{0.89}MoN_4$ | $Ba_{1.74}Sr_{1.26}MoN_4$ | $Ba_{0.81}Sr_{2.19}MoN_4$ | $Ba_{2.27}Sr_{0.73}WN_4$ | $Ba_{1.38}Sr_{1.62}WN_4$ | $Ba_{0.73}Sr_{2.27}WN_4$ |
| Formula weight | 519.93 | 501.29 | 454.93 | 615.18 | 571.15 | 539.17 |
| Temperature/K | 150(2) | 150(2) | 150(2) | 150(2) | 150(2) | 150(2) |
| Wavelength (Mo-Kα)/Å | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | Orthorhombic | Orthorhombic | Orthorhombic | Orthorhombic | Orthorhombic | Orthorhombic |
| Space group | *Pbca* | *Pbca* | *Pbca* | *Pbca* | *Pbca* | *Pbca* |
| $a$/Å | 10.662(5) | 10.588(5) | 10.503(2) | 10.702(5) | 10.5850(10) | 10.506(3) |
| $b$/Å | 10.095(5) | 9.979(5) | 9.733(2) | 10.132(5) | 9.8730(9) | 9.750(3) |
| $c$/Å | 12.002(5) | 11.935(5) | 11.672(2) | 12.036(5) | 11.8530(11) | 11.682(3) |
| $U$/Å$^3$ | 1291.8(10) | 1261.0(10) | 1193.2(4) | 1305.1(10) | 1238.7(2) | 1196.6(6) |
| $Z$ | 8 | 8 | 8 | 8 | 8 | 8 |
| $\mu$/mm$^{-1}$ | 21.783 | 23.159 | 26.696 | 36.933 | 40.929 | 43.909 |
| Reflections collected/unique ($R_{int}$) | 7654/1802<br>(0.044) | 11327/1786<br>(0.044) | 7323/1679<br>(0.059) | 6277/1813<br>(0.047) | 11202/1775<br>(0.042) | 6323/1676<br>(0.077) |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1{}^a = 0.0700$<br>$wR_2{}^b = 0.1726$ | $R_1 = 0.0201$<br>$wR_2 = 0.0403$ | $R_1 = 0.0340$<br>$wR_2 = 0.0776$ | $R_1 = 0.0284$<br>$wR_2 = 0.0500$ | $R_1 = 0.0255$<br>$wR_2 = 0.0700$ | $R_1 = 0.0388$<br>$wR_2 = 0.0866$ |
| $R$ indices (all data) | $R_1 = 0.0738$<br>$wR_2 = 0.1761$ | $R_1 = 0.0285$<br>$wR_2 = 0.0419$ | $R_1 = 0.0454$<br>$wR_2 = 0.0801$ | $R_1 = 0.0432$<br>$wR_2 = 0.0522$ | $R_1 = 0.0305$<br>$wR_2 = 0.0717$ | $R_1 = 0.0628$<br>$wR_2 = 0.0940$ |

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(|F_o{}^2| - |F_c{}^2|)^2/\Sigma w(F_o{}^2)^2]^{1/2}$.

alkaline-earth metal atoms fill octahedral holes within the structure. The A1 position lies between tetrahedra in the same row (or layer), whereas the A2 and A3 positions lie between the rows (layers). Alternatively, the A1 cations can be considered to sit within "hexagonal channels" bounded by unconnected $[MN_4]^{6-}$ anions running down the *b*-axis. A2 and A3 cations lie at the periphery of these channels (Fig. 1b). In fact, A1 cations are connected to three of the $MN_4$ tetrahedra within each hexagon in a trigonal planar arrangement while the A2 and A3 cations are surrounded by four $MN_4$ units in a tetrahedral fashion.

Throughout the two families, the larger of the two alkaline-earth metal cations occupies the A1 site. In the barium-rich nitrides (**1**,**2**,**4**) and also **5** the A1 site is exclusively occupied by Ba. As the Sr/Ba ratio tends to ≥2 (as in strontium-rich **3** and **6**), additional Sr is forced on to the A1 site to share with Ba (*e.g.* **6** has an approximately 1/3 : 2/3 mix of Sr : Ba on the A1 site). Conversely, the A3 site is preferentially filled by the smaller alkaline-earth metal and is occupied solely by Sr (**2**,**3**,**5**,**6**) except in the compounds with the highest Ba content (**1**,**4**). By contrast, the A2 site is shared between both alkaline-earth elements in all of the compounds and is populated in preference to the larger (smaller) A1 site (A3 site) by the smaller (larger) metal as the composition changes. This is by no means unexpected, since in orthorhombic $Ba_3Mo(W)N_4$,[5] the average Ba–N bond lengths are 3.06 (3.09), 2.87 (2.90) and 2.82 (2.81 Å) respectively, A1 ≥ A2 ≥ A3. Furthermore, in $Ca_2SrWN_4$,[18] where Ca/Sr = 2, the metal ordering is complete with the Sr cation exclusively occupying the A1 site and the Ca cations located only in the A2 and A3 positions.

Bond lengths in the nitridometalates are collected in Table 4. Considering first the transition metal coordination environment, the $MN_4$ tetrahedral unit is essentially structurally invariant irrespective of the Sr : Ba ratio or whether W replaces Mo at the centre of the tetrahedron. These Mo(W)–N tetrahedra are typical of 0D nitrido-molybdates and -tungstates of this type. Individual M–N bond lengths vary from 1.850(6) Å in **3** to 1.883(7) Å in **5**, but the mean distance is effectively constant at 1.87 Å. This is in excellent agreement with previous analyses of transition metal–nitrogen distances in the nitridometalates(VI) of molybdenum and tungsten where this mean distance is unchanging regardless of the identity of the constituent cations, tetrahedral connectivity or overall structural dimensionality.[2] Hence it is unsurprising that the bond lengths are within similar ranges to those found in LT–$Ba_3MoN_4$[5] [1.848(10)–1.885(10) Å; $\bar{d}$(Mo–N) = 1.87 Å] and $Ca_2SrWN_4$[18] [1.853(18)–1.896(19) Å; $\bar{d}$(W–N) = 1.87 Å]. Bond valence calculations, using parameters proposed by Brese and O'Keeffe,[27] performed for the tetrahedral M sites for **1**–**6** yield Group 6 metal valences greater than the expected (VI) (from 6.2 in **1** and **2** to 6.7 in **6**). This is not uncommon in ternary nitrides of the heavier Group 6 metals and indicates the presence of significant π-bonding between metal and nitrogen. The π contribution becomes more important in the tetrahedral units of Group 5 and 6 with higher dimensionality structures. In these compounds terminal M–N bonds are typically shorter than bridging bonds by about 0.1 Å and as the connectivity increases the bridging bonds become relatively longer (*ca.* 1.9–1.95 Å).[2] However, in structures with isolated $MN_4$ tetrahedra, such as the title compounds, the four tetrahedral bonds are approximately the same length.

The three A sites can be viewed as octahedral holes, but the octahedral coordination of the A1, A2 and A3 cations is extremely distorted (Fig. 2). In fact, the A1–N octahedron contains two bonds of 3.1 Å or greater which might be considered more accurately as interactions while the A3–N2 bond varies between 3.3–3 Å as Ba is replaced by Sr. The mean bond lengths of the three A sites are commensurate with first the refined populations and the expected order A1 ≥ A2 ≥ A3 and second a decrease in A–N bond length as $Ba^{2+}$ is progressively replaced by smaller $Sr^{2+}$. There is only a negligible change in mean A–N bond lengths as W replaces Mo (allowing for slight

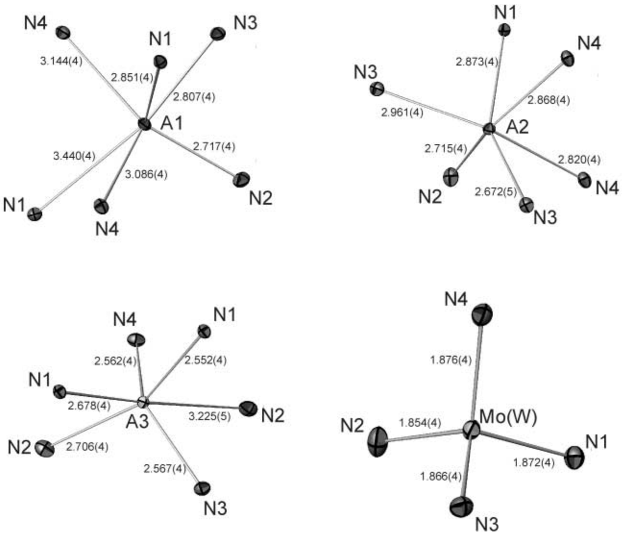

**Fig. 2** Metal coordination environments in $A_3Mo(W)N_4$ nitrides. Bond lengths (in Å) shown are for compound **2**.

**Table 3** Final atomic parameters for (Ba,Sr)$_3$MN$_4$ nitrides

| Compound | **1** | **2** | **3** | **4** | **5** | **6** |
|---|---|---|---|---|---|---|
| Formula | Ba$_{2.11}$Sr$_{0.89}$MoN$_4$ | Ba$_{1.74}$Sr$_{1.26}$MoN$_4$ | Ba$_{0.81}$Sr$_{2.19}$MoN$_4$ | Ba$_{2.27}$Sr$_{0.73}$WN$_4$ | Ba$_{1.38}$Sr$_{1.62}$WN$_4$ | Ba$_{0.73}$Sr$_{2.27}$WN$_4$ |
| A(1), *8c* | | | | | | |
| *x* | 0.7267(1) | 0.7282(1) | 0.7261(1) | 0.7263(1) | 0.7283(1) | 0.7254(1) |
| *y* | −0.3065(1) | −0.3088(1) | −0.3116(1) | −0.3071(1) | −0.3124(1) | −0.3128(1) |
| *z* | −0.1161(1) | −0.1162(1) | −0.1176(1) | −0.1161(1) | −0.1171(1) | −0.1175(1) |
| $U_{eq}$ | 0.011(1) | 0.012(1) | 0.011(1) | 0.010(1) | 0.009(1) | 0.014(1) |
| SOF | 1.0 Ba | 1.0 Ba | 0.725(7) Ba<br>0.275(7) Sr | 1.0 Ba | 1.0 Ba | 0.68(1) Ba<br>0.32(1) Sr |
| A(2), *8c* | | | | | | |
| *x* | 0.4715(1) | 0.4713(1) | 0.4702(1) | 0.4712(1) | 0.4702(1) | 0.4701(1) |
| *y* | −0.6267(1) | −0.6272(1) | −0.6294(1) | −0.6272(1) | −0.6286(1) | −0.6303(1) |
| *z* | −0.1460(1) | −0.1458(1) | −0.1433(1) | −0.1462(1) | −0.1451(1) | −0.1438(1) |
| $U_{eq}$ | 0.008(1) | 0.011(1) | 0.008(1) | 0.08(1) | 0.008(1) | 0.011(1) |
| SOF | 0.90(1) Ba<br>0.10(1) Sr | 0.738(4) Ba<br>0.262(4) Sr | 0.087(7) Ba<br>0.913(7) Sr | 0.946(7) Ba<br>0.054(7) Sr | 0.378(8) Ba<br>0.622(8) Sr | 0.05(1) Ba<br>0.95(1) Sr |
| A(3), *8c* | | | | | | |
| *x* | 0.3747(1) | 0.3755(1) | 0.3741(1) | 0.3754(1) | 0.3755(1) | 0.3749(1) |
| *y* | 0.0315(1) | 0.0318(1) | 0.0299(1) | 0.0319(1) | 0.0318(1) | 0.0300(2) |
| *z* | −0.1053(1) | −0.1047(1) | −0.1034(1) | −0.1053(1) | −0.1037(1) | −0.1031(1) |
| $U_{eq}$ | 0.006(1) | 0.009(1) | 0.007(1) | 0.007(1) | 0.007(1) | 0.011(1) |
| SOF | 0.22(1) Ba<br>0.78(1) Sr | 1.0 Sr | 1.0 Sr | 0.319(7) Ba<br>0.681(7) Sr | 1.0 Sr | 1.0 Sr |
| Mo, W *8c* | | | | | | |
| *x* | 0.4030(1) | 0.4030(1) | 0.4011(1) | 0.4032(1) | 0.4018(1) | 0.4006(1) |
| *y* | −0.2983(1) | −0.2984(1) | −0.3044(1) | −0.2990(1) | −0.3015(1) | −0.3053(1) |
| *z* | −0.1150(1) | −0.1150(1) | −0.1125(1) | −0.1150(1) | −0.1135(1) | −0.1125(1) |
| $U_{eq}$ | 0.008(1) | 0.010(1) | 0.006(1) | 0.008(1) | 0.006(1) | 0.009(1) |
| N(1), *8c* | | | | | | |
| *x* | 0.5049(10) | 0.5060(4) | 0.5048(6) | 0.5052(8) | 0.5060(6) | 0.5064(10) |
| *y* | −0.1827(9) | −0.1816(4) | −0.1854(6) | −0.1835(8) | −0.1827(7) | −0.1879(12) |
| *z* | −0.0327(8) | −0.0331(3) | −0.0315(5) | −0.0339(6) | −0.0320(6) | −0.0321(9) |
| $U_{eq}$ | 0.010(2) | 0.012(1) | 0.007(1) | 0.012(2) | 0.011(1) | 0.012(2) |
| N(2), *8c* | | | | | | |
| *x* | 0.2744(9) | 0.2729(4) | 0.2637(6) | 0.2725(7) | 0.2686(6) | 0.2629(11) |
| *y* | −0.2010(9) | −0.2002(4) | −0.2088(7) | −0.2035(8) | −0.2037(7) | −0.2091(13) |
| *z* | −0.1793(9) | −0.1788(3) | −0.1718(6) | −0.1811(7) | −0.1745(5) | −0.1728(9) |
| $U_{eq}$ | 0.014(2) | 0.017(1) | 0.013(2) | 0.015(2) | 0.011(1) | 0.018(3) |
| N(3), *8c* | | | | | | |
| *x* | 0.5051(11) | 0.5027(4) | 0.4978(6) | 0.5032(7) | 0.4996(6) | 0.4990(10) |
| *y* | −0.3777(9) | −0.3789(4) | −0.3858(6) | −0.3798(8) | −0.3834(7) | −0.3867(12) |
| *z* | −0.2218(8) | −0.2249(3) | −0.2273(6) | −0.2227(6) | −0.2273(6) | −0.2272(9) |
| $U_{eq}$ | 0.012(2) | 0.014(1) | 0.010(1) | 0.011(2) | 0.012(1) | 0.012(2) |
| N(4), *8c* | | | | | | |
| *x* | 0.3423(10) | 0.3415(4) | 0.3440(6) | 0.3399(7) | −0.3429(6) | 0.3441(10) |
| *y* | −0.4265(9) | −0.4286(4) | −0.4369(6) | −0.4271(8) | −0.4328(7) | −0.4370(13) |
| *z* | −0.0166(8) | −0.0156(3) | −0.0090(6) | −0.0169(6) | −0.0120(5) | −0.0077(9) |
| $U_{eq}$ | 0.012(2) | 0.014(1) | 0.011(1) | 0.011(2) | 0.008(1) | 0.015(2) |

variations in A stoichiometry) consistent with the idea of a "rigid" [MN$_4$]$^{6-}$ building block. Octahedral coordination is favoured in ternary barium or strontium Group 6 nitrides although both higher and lower coordination numbers are known. For example, trigonal (HT)-Ba$_3$WN$_4$ has barium coordination numbers varying from 6–7,[6] monoclinic Sr$_3$MN$_4$ (M = Mo, W) has 5, 6 and 7 coordinate Sr$^{2+}$ ions[7,8] and Sr$_4$[MoN$_4$]O contains Sr in two 7 coordinate sites and eight 6 coordinate sites.[23] In A$_3$Cr$^{III}$N$_3$, where the transition metal coordination is reduced from 4 to 3, the alkaline-earth metals occupy 5 coordinate positions.[9] Bond valence calculations weighted for the refined cation distributions give results for the A sites varying from 1.4 for the A1 site (0.68 Ba : 0.32 Sr) in **6** to 2.4 for the A3 site (0.22 Ba : 0.78 Sr) in **1**. Overall, however, the average valences are slightly less than 2 (1.8–1.9), which is typical of Group 2 metals in ternary nitrides.[28]

Overall, the Sr/Ba compounds show a continuous solid solution from LT-Ba$_3$M(W)N$_4$ to (Ba$_{1-x}$Sr$_x$)$_3$MN$_4$; $x \approx 0.75$ (Fig. 3). Sr$_3$MoN$_4$ and Sr$_3$WN$_4$ ($x$ = 1) crystallising with monoclinic structures have been reported but *orthorhombic* compounds with these compositions have not yet been prepared.[7,8] Within the limits investigated, lattice parameters, cell volume and A–N bond lengths all vary linearly with $x$, obeying Vegard's law and consistent with the stepwise replacement of Ba with smaller Sr. It remains to be seen where the extent of the solid solution is located before a phase change is induced, or indeed if isostructural orthorhombic forms of Sr$_3$Mo(W)N$_4$ exist. The existence of this structure type for both Ca/Sr and Ba/Sr compounds suggests an inherent tolerance to large variations in cation size.

The compounds prepared are the first examples of mixed Sr/Ba transition metal nitrides. The germanium-containing compounds (Ba$_{1-x}$Sr$_x$)$_3$Ge$_2$N$_2$ and (Ba$_{1-x}$Sr$_x$)$_5$Ge$_2$N$_6$ are the only other examples of Ba/Sr ternary or higher nitrides, although the former are perhaps more accurately nitride germanides.[20] In the former compounds the alkaline-earth

**Table 4** Selected bond lengths and mean distances (in Å) in $(Ba,Sr)_3MN_4$ nitrides

| Compound | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Formula | $Ba_{2.11}Sr_{0.89}MoN_4$ | $Ba_{1.74}Sr_{1.26}MoN_4$ | $Ba_{0.81}Sr_{2.19}MoN_4$ | $Ba_{2.27}Sr_{0.73}WN_4$ | $Ba_{1.38}Sr_{1.62}WN_4$ | $Ba_{0.73}Sr_{2.27}WN_4$ |
| A(1)–N(1) | 2.856(10) | 2.851(4) | 2.814(6) | 2.854(8) | 2.863(7) | 2.787(11) |
| A(1)–N(1) | 3.464(11) | 3.440(4) | 3.404(7) | 3.490(8) | 3.430(7) | 3.420(11) |
| A(1)–N(2) | 2.724(10) | 2.717(4) | 2.686(7) | 2.701(8) | 2.727(6) | 2.680(11) |
| A(1)–N(3) | 2.777(11) | 2.807(4) | 2.814(6) | 2.809(8) | 2.839(7) | 2.796(10) |
| A(1)–N(4) | 3.099(9) | 3.086(4) | 2.953(6) | 3.110(8) | 3.040(6) | 2.936(12) |
| A(1)–N(4) | 3.216(10) | 3.144(4) | 3.092(7) | 3.212(8) | 3.110(6) | 3.102(12) |
| $\bar{d}$[A(1)–N] | 3.02(1) | 3.01(1) | 2.96(1) | 3.03(1) | 3.00(1) | 2.96(1) |
| A(2)–N(1) | 2.891(10) | 2.873(4) | 2.735(6) | 2.901(8) | 2.818(7) | 2.725(11) |
| A(2)–N(2) | 2.756(10) | 2.715(4) | 2.597(6) | 2.752(8) | 2.658(6) | 2.588(11) |
| A(2)–N(3) | 2.698(10) | 2.672(4) | 2.582(6) | 2.693(8) | 2.627(7) | 2.584(11) |
| A(2)–N(3) | 3.000(10) | 2.961(4) | 2.936(6) | 3.019(8) | 2.953(7) | 2.938(11) |
| A(2)–N(4) | 2.835(10) | 2.820(4) | 2.718(7) | 2.871(8) | 2.783(6) | 2.714(10) |
| A(2)–N(4) | 2.897(9) | 2.868(4) | 2.779(6) | 2.916(8) | 2.836(6) | 2.798(11) |
| $\bar{d}$[A(2)–N] | 2.85(1) | 2.82(1) | 2.72(1) | 2.86(1) | 2.78(1) | 2.72(1) |
| A(3)–N(1) | 2.592(9) | 2.552(4) | 2.527(6) | 2.606(8) | 2.526(7) | 2.534(11) |
| A(3)–N(1) | 2.714(9) | 2.678(4) | 2.642(6) | 2.726(8) | 2.667(7) | 2.667(12) |
| A(3)–N(2) | 2.728(10) | 2.706(4) | 2.716(6) | 2.781(8) | 2.717(7) | 2.736(12) |
| A(3)–N(2) | 3.257(10) | 3.225(5) | 3.032(7) | 3.245(9) | 3.141(7) | 3.038(12) |
| A(3)–N(3) | 2.605(11) | 2.567(4) | 2.527(7) | 2.603(8) | 2.542(7) | 2.519(11) |
| A(3)–N(4) | 2.582(11) | 2.562(4) | 2.562(6) | 2.572(8) | 2.578(6) | 2.577(10) |
| $\bar{d}$[A(3)–N] | 2.75(1) | 2.72(1) | 2.67(1) | 2.76(1) | 2.70(1) | 2.67(1) |
| M–N(1) | 1.876(9) | 1.872(4) | 1.850(6) | 1.874(8) | 1.878(6) | 1.851(11) |
| M–N(2) | 1.855(10) | 1.854(4) | 1.850(6) | 1.878(8) | 1.855(6) | 1.864(12) |
| M–N(3) | 1.863(11) | 1.866(4) | 1.859(6) | 1.870(8) | 1.883(7) | 1.869(11) |
| M–N(4) | 1.868(9) | 1.876(4) | 1.866(6) | 1.881(8) | 1.875(6) | 1.871(11) |
| $\bar{d}$(M–N) | 1.86(1) | 1.87(1) | 1.86(1) | 1.88(1) | 1.87(1) | 1.87(1) |

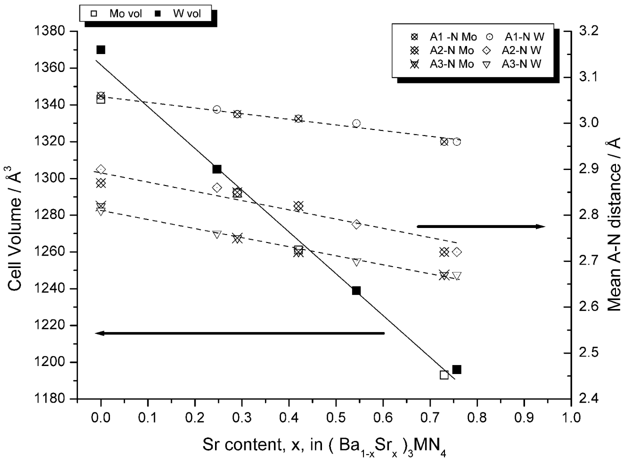

**Fig. 3** Plot of cell volume (solid markers) and mean A–N distances (open markers) against Sr content, $x$, in $(Ba_{1-x}Sr_x)_3MN_4$ for M = Mo (crossed) and W (dotted). Values for $x = 0$ compounds are taken from ref. 5. Trend lines serve only as guides to the eye.

metals are 2, 3 or 5 coordinate to N and complete their coordination spheres with Ge atoms. In similarity to the title compounds, of the three available A sites, the smallest is largely occupied by Sr and the largest site populated by Ba only. The limited examples of other mixed alkaline-earth nitrides containing Group 6 elements exhibit structures in which the A positions are completely ordered, as in $Ca_2SrWN_4$ and $Ba_2CaWN_4$.[18,19] Interestingly, however, the pseudo-binary sub-nitride $(Ba,Sr)_2N$ exhibits complete cation disorder whereas in $Ca_{4-x}Sr_x[CN_2]N_2$ there is a partial cation ordering with Ca and Sr sharing three of the four available sites and Ca exclusively occupying the remaining position.[21,29] These observations may be as much synthesis as structure (and composition) dependent and are likely only to be clarified as the database of available compounds increases.

In summary, two new families of mixed alkaline-earth nitridometalates(VI) have been synthesised for the first time. The structures of these compounds, as solved by single crystal X-ray diffraction are isotypic with LT-$Ba_3Mo(W)N_4$ and exhibit continuous solid solutions within the studied limits. The ordered cation distribution evolves with the alkaline-earth metal composition. These are the first examples of mixed Ba/Sr transition metal nitrides.

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