

Synthesis and structure of new mixed alkaline-earth nitridomolybdates and nitridotungstates, $(\text{Ba,Ca})_3[\text{MN}_4]$ ($\text{M} = \text{Mo}, \text{W}$)[†]

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Received 12th November 2002, Accepted 29th January 2003

First published as an Advance Article on the web 10th February 2003

New molybdenum(vi) and tungsten(vi) nitrides were synthesised by the reaction of barium nitride and calcium 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 (LT) form of $\text{Ba}_3\text{Mo(W)N}_4$. The structures contain isolated $[\text{Mo(W)N}_4]^{6-}$ tetrahedra and partially disordered alkaline earth cations whose distribution across three crystallographic sites is dependent on cationic radius.

Introduction

Recently, studies of ternary and higher nitrides have become more extensive.¹ Interest in the chemistry of the group 5 and 6 ternary nitrides has grown significantly, largely due to analogies with oxosilicates.² The tetrahedral $[\text{SiO}_4]^{4-}$ unit in silicate chemistry is isotopic with the $[\text{MN}_4]^{n-}$ ($\text{M} = \text{Nb}, \text{Ta}, n = 7; \text{M} = \text{Mo}, \text{W}, n = 6$) 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 exists in the chemistry of the nitridometalates(v and vi). Despite this, isolated units (monometalates), dimers (dimetalates), chains (monopolymetalates), sheets (phyllometalates) and three-dimensional networks (tectometalates) are already found in this group of compounds. Compounds containing electropositive group 1 and 2 elements, A-M-N ($\text{A} = \text{alkali or alkaline earth metal}, \text{M} = \text{group VI metal}$) form examples within all these structural classes.

Mononitridometalates are the most common of these compounds with the *anti*- CaF_2 -type Li_6MN_4 nitrides ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) among the earliest examples.⁴ Alkaline earth metals also form mononitridometalates with Mo and W. Of these, $\text{Ba}_3\text{Mo(W)N}_4$ forms two polymorphs: a low-temperature orthorhombic⁵ and a high-temperature trigonal form⁶ whereas Sr_3MoN_4 ^{7,8} has been reported only as a monoclinic structure. Mixing s-block metals can lead to more condensed structures such as $\text{LiBa}_4[\text{M}_2\text{N}_7]$ ($\text{M} = \text{Mo}, \text{W}$) and $\text{LiBa}_4[\text{Mo}_2\text{N}_7]\cdot\text{BaCl}_2$ ⁹ which both contain $[\text{M}_2\text{N}_7]^{9-}$ dimeric anions. In the 1D structures of $\text{Na}_3\text{Mo(W)N}_3$, $[\text{Mo(W)N}_2\text{N}_{2/2}]^{3-}$ anionic chains adopt hexagonal rod packing¹⁰ transforming to a tetragonal packing conformation (as in the silicate $\text{Ba}[\text{SiO}_2\text{OH}]_2\cdot 2\text{H}_2\text{O}$)¹¹ as sodium is partially replaced by the heavier alkali metals, e.g. Na_2KW_3 and $\text{Na}_{11}\text{Rb}[\text{WN}_3]_4$.¹² Mixed alkali metal compounds with much lower ratios of sodium condense further to form 2D and 3D structures. For example, $\text{Na}_2\text{K}_{13}\text{W}_7\text{N}_{19}$ consists of layers of corner sharing W–N tetrahedra.¹³ Further condensation, such as that shown by $\text{Cs}_5\text{Na}[\text{W}_4\text{N}_{10}]$, results in a three-dimensional network where each tungsten atom is bonded to one terminal nitrogen and three bridging nitrogens.¹⁴

The results of mixing alkaline earth metals in nitridomolybdates and -tungstates are far less-studied. Until recently only two mixed group 2 metal compounds, Ca_2SrWN_4 and Ba_2CaWN_4 had been reported.^{15,16} Ca_2SrWN_4 is isostructural

with the previously designated low temperature (LT) forms of Ba_3MoN_4 and Ba_3WN_4 .⁵ We have since discovered that mixed barium–strontium nitridometalates $(\text{Ba,Sr})_3\text{Mo(W)N}_4$ exist over a broad range of alkaline earth metal compositions and also crystallise with the orthorhombic (*Pbca*) $\text{Ba}_3\text{Mo(W)N}_4$ structure [for $0 \leq x \leq 0.75$ in $(\text{Ba}_{1-x}\text{Sr}_x)_3\text{Mo(W)N}_4$].¹⁷ By contrast, the one reported mixed barium–calcium compound, Ba_2CaWN_4 adopts an alternative structure in the orthorhombic space group *Fddd* with a far larger unit cell and the arrangement of the isolated $[\text{MN}_4]$ tetrahedra changes from hexagonal close packed (HCP) to cubic close packed (CCP).¹⁶

The number of nitrides containing both calcium and barium is very small.^{16,18–20} Despite the size contrast between the two cations and the subsequent reluctance to share crystallographic sites, our previous observations in the Ba–Sr–Mo(W)–N systems suggested that other mixed nitridometalates(vi) should exist. Here we report the synthesis and structural characterisation of three new barium–calcium nitrides. The flexibility of the cation sublattice permits partial disorder with an overall cation arrangement determined by the relative composition and sizes of the constituent alkaline earth metals. All three Ba–Ca compounds form orthorhombic structures based on HCP rather than CCP arrays of $[\text{MN}_4]^{6-}$ tetrahedral anions.

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 subnitrides (Ca_2N and Ba_2N) were prepared by the reaction of the metals with nitrogen gas at 700 K in liquid sodium for 16 h.^{21,22} A calcium ingot (*ca.* 5 g, Alfa 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 cm³) 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 1050 K (Ca_2N) or 750 K (Ba_2N) for 24 h. This method produces nitrides with negligible amounts of alkaline earth oxide or hydroxide. The product powders were green/black, crystalline Ca_2N and black poorly crystalline Ba_2N . The

[†] Dedicated to Dr Marten G. Barker *in memoriam*.

Table 1 Crystallographic data for (Ba,Ca)₃MN₄ nitrides

Compound	1	2	3
Formula	Ba _{2.23} Ca _{0.77} MoN ₄	Ba _{1.52} Ca _{1.48} MoN ₄	Ba _{1.44} Ca _{1.56} WN ₄
Formula weight	444.87	420.06	499.94
Temperature/K	150(2)	150(2)	150(2)
Wavelength, λ(Mo-Kα)/Å	0.71073	0.71073	0.71073
Crystal system, space group	Orthorhombic, <i>Pbca</i>	Orthorhombic, <i>Pbca</i>	Orthorhombic, <i>Pbca</i>
Unit cell dimensions/Å			
<i>a</i>	10.441(2)	10.2710(5)	10.3049(12)
<i>b</i>	9.967(2)	9.5946(5)	9.5822(12)
<i>c</i>	11.938(3)	11.7207(6)	11.7405(14)
Unit cell volume, <i>U</i> /Å ³	1242.3(5)	1155.03(10)	1159.3(2)
<i>Z</i> , Calculated density, ρ/g cm ⁻³	8, 5.227	8, 4.831	8, 5.729
Absorption coefficient, μ/mm ⁻¹	16.466	13.613	30.754
Reflections collected/unique (<i>R</i> _{int})	7236/1730 (0.069)	8166/1638 (0.072)	4876/1564 (0.047)
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ ^a = 0.0370, <i>wR</i> ₂ ^b = 0.0850	<i>R</i> ₁ = 0.0262, <i>wR</i> ₂ = 0.0658	<i>R</i> ₁ = 0.0357, <i>wR</i> ₂ = 0.0788
<i>R</i> Indices (all data)	<i>R</i> ₁ = 0.0529, <i>wR</i> ₂ = 0.0881	<i>R</i> ₁ = 0.0296, <i>wR</i> ₂ = 0.0672	<i>R</i> ₁ = 0.0485, <i>wR</i> ₂ = 0.0822
Largest diff. peak and hole/e Å ⁻³	1.93, -2.33	1.74, -1.22	3.19, -3.20

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

products were identified using powder X-ray diffraction (PXD) using a Philips X'PERT θ - 2θ diffractometer (Cu-K α 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 were grown by the reactions of Ca₂N and Ba₂N with Mo and W foils. All manipulations were carried out in an argon-filled glove box. Ba₂N and Ca₂N (*ca.* 1–2 g) were ground together in 3 : 1 (Mo) and 1 : 1 (Mo, W) ratios and the mixtures were placed in Mo or W foil tubes. Hence the nominal composition of products was expected to be Ba_{2.25}Ca_{0.75}MoN₄ (**1**), Ba_{1.5}Ca_{1.5}MoN₄ (**2**) and Ba_{1.5}Ca_{1.5}WN₄ (**3**). Since other similar preparations had resulted in reaction between the binary alkaline earth nitrides and metal foils,^{17,23} no attempt was made to add molybdenum or tungsten powder as starting materials. The A₂N 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 minimise 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, platy crystals. Typically, nothing remained of the binary nitride, although traces of alkaline earth metals 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 them on a microscope slide and viewing under an optical microscope. Selected crystals were placed in a drop of moisture-free RS3000 perfluoropolyether oil on a small glass slide.

Structure determination

Selected crystals (typical dimensions 0.1 mm × 0.1 mm × 0.05 mm) were attached to a dual-stage glass fibre using RS3000 oil before mounting on the diffractometer and flash freezing under a nitrogen gas flow at 150 K. All data sets were collected on a Bruker SMART 1000 CCD area detector diffractometer with graphite-monochromated Mo-K α radiation. All compounds crystallised in the orthorhombic space group *Pbca* and the cell dimensions were refined using reflections for $6 \leq 2\theta \leq 57^\circ$. Structure solution by direct methods using SIR97²⁴ showed that all of the compounds were isostructural

to the previously known compounds orthorhombic Ba₃[MN₄] (M = Mo, W)⁵ and Ca₂Sr[WN₄].¹⁵ The structures were refined on *F*² using SHELXL-97,²⁵ through WinGX.²⁶ Refinements proceeded smoothly with displacement parameters for all metal atoms in each compound refined anisotropically. Nitrogen displacement parameters 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 unity on each site. Maximum peaks of residual electron density for the three compounds were located within 1 Å of the heaviest atom (Ba, Ba and W in **1**, **2** and **3**, respectively) and are not structurally significant. Final crystallographic parameters for all of the compounds are shown in Table 1.

CCDC reference numbers 197516–197518.

See <http://www.rsc.org/suppdata/dt/b2/b211138a/> 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 LT-Ba₃MN₄ (M = W, Mo) and Ca₂SrWN₄.^{5,15} Atomic parameters for the compounds (**1**–**3**) including refined A site occupancy factors are shown in Table 2. The structure consists of isolated MN₄ tetrahedra which align in rows parallel to the *a*-axis and in two different (. . .ABAB. . .) layers parallel to the *b* and *c* directions. The 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 [MN₄]⁶⁻ anions running down the *b*-axis. A2 and A3 cations lie at the periphery of these channels (Fig. 1(a)). In fact, A1 cations are connected to three of the MN₄ tetrahedra within each hexagon in a trigonal planar arrangement while the A2 and A3 cations are surrounded by four MN₄ units in a tetrahedral fashion. If the structure is viewed in terms of N-centred polyhedra, the anion sublattice has a remarkably two-dimensional basis reminiscent of the group 2 subnitrides (Fig. 1(b)).^{22,27} Layers of edge-sharing N1-(A,M) and N4-(A,M) polyhedra (five- and six-coordinate, respectively) stack perpendicular to the *c*-direction in an . . .ABABA. . . repeat pattern. N2 and N3 are located between these slabs, forming a second set of edge-sharing polyhedral layers (. . .A'B'A'B'A' . . .). The two sets of layers are connected along the [001] direction through the polyhedral edges to complete the 3D structure.

As in the (Ba,Sr)₃MN₄ families,¹⁷ the larger of the two alkaline earth metal cations in the (Ba,Ca)₃MN₄ nitrides

Table 2 Final atomic parameters for (Ba,Ca)₃MN₄ nitrides

Compound	1	2	3
Formula	Ba _{2.23} Ca _{0.77} MoN ₄	Ba _{1.52} Ca _{1.48} MoN ₄	Ba _{1.44} Ca _{1.56} WN ₄
A(1), <i>8c</i>			
<i>x</i>	0.7341(1)	0.7370(1)	0.7370(1)
<i>y</i>	-0.3089(1)	-0.3178(1)	-0.3193(1)
<i>z</i>	0.1160(1)	0.1180(1)	0.1184(1)
<i>U</i> _{eq}	0.014(1)	0.013(1)	0.012(1)
SOF	1.0 Ba	1.0 Ba	1.0 Ba
A(2), <i>8c</i>			
<i>x</i>	0.4675(1)	0.4680(1)	0.4676(1)
<i>y</i>	-0.6228(1)	-0.6259(1)	-0.6269(1)
<i>z</i>	0.1453(1)	0.1462(1)	0.1462(1)
<i>U</i> _{eq}	0.013(1)	0.013(1)	0.012(1)
SOF	1.0 Ba	0.523(2) Ba, 0.477(2) Ca	0.436(4) Ba, 0.565(4) Ca
A(3), <i>8c</i>			
<i>x</i>	0.3770(1)	0.3790(1)	0.3789(2)
<i>y</i>	0.0333(1)	0.0330(1)	0.0332(2)
<i>z</i>	0.1052(1)	0.1029(1)	0.1027(2)
<i>U</i> _{eq}	0.013(1)	0.011(1)	0.010(1)
SOF	0.227(4) Ba, 0.773(4) Ca	1.0 Ca	1.0 Ca
Mo, W <i>8c</i>			
<i>x</i>	0.4050(1)	0.4036(1)	0.4034(1)
<i>y</i>	-0.2891(1)	-0.2945(1)	-0.2961(1)
<i>z</i>	0.1192(1)	0.1161(1)	0.1154(1)
<i>U</i> _{eq}	0.012(1)	0.012(1)	0.010(1)
N(1), <i>8c</i>			
<i>x</i>	0.5065(8)	0.5093(4)	0.5095(8)
<i>y</i>	-0.1756(9)	-0.1775(4)	-0.1776(8)
<i>z</i>	0.0322(7)	0.0308(3)	0.0293(7)
<i>U</i> _{eq}	0.018(2)	0.014(1)	0.009(2)
N(2), <i>8c</i>			
<i>x</i>	0.2848(8)	0.2728(5)	0.2702(10)
<i>y</i>	-0.1801(10)	-0.1884(5)	-0.1899(9)
<i>z</i>	0.1901(7)	0.1781(4)	0.1766(9)
<i>U</i> _{eq}	0.024(2)	0.028(1)	0.022(2)
N(3), <i>8c</i>			
<i>x</i>	0.5078(7)	0.5010(4)	0.4996(9)
<i>y</i>	-0.3739(9)	-0.3800(5)	-0.3820(10)
<i>z</i>	0.2255(7)	0.2307(3)	0.2305(9)
<i>U</i> _{eq}	0.015(2)	0.021(1)	0.020(2)
N(4), <i>8c</i>			
<i>x</i>	0.3334(8)	0.3379(4)	0.3379(8)
<i>y</i>	-0.4207(9)	-0.4288(4)	-0.4318(9)
<i>z</i>	0.0254(7)	0.0167(3)	0.0153(8)
<i>U</i> _{eq}	0.019(2)	0.016(1)	0.014(2)

occupies the A1 site. In all three compounds the A1 site is exclusively occupied by Ba. Conversely, the A3 site is preferentially filled by the smaller alkaline earth metal and is occupied solely by Ca except in the compound with the highest Ba content (**1**). 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 not only correlates well with the trends seen in the equivalent Ba–Sr compounds,¹⁷ but is also consistent with Ba₃Mo(W)N₄ where the average Ba–N bond lengths are 3.06 Å (3.09 Å), 2.87 Å (2.90 Å) and 2.82 Å (2.81 Å), respectively, A1 ≥ A2 ≥ A3.⁵ In Ca₂SrWN₄ metal ordering is complete with Sr exclusively occupying the A1 site and Ca located only in the A2 and A3 positions.¹⁵

Bond lengths in the nitridometalates are collected in Table 3. The MN₄ tetrahedral unit is essentially structurally invariant irrespective of the Ca : Ba ratio or whether W or Mo lies at the centre of the tetrahedron. The Mo(W)–N tetrahedra are typical

of 0D nitrido-molybdates and -tungstates of this type. Individual M–N bond lengths vary from 1.835(5) Å in **2** to 1.880(9) Å in **1**, but the mean distance is effectively constant. This is consistent 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-Ba₃MoN₄ [1.848(10)–1.885(10) Å; $\bar{d}(\text{Mo–N}) = 1.87 \text{ \AA}$],⁵ Ca₂SrWN₄ [1.853(18)–1.896(19) Å; $\bar{d}(\text{W–N}) = 1.87 \text{ \AA}$]¹⁵ and (Ba,Sr)₃MN₄ [1.850(6)–1.883(7) Å; $\bar{d}(\text{M–N}) = 1.87 \text{ \AA}$].¹⁷ Bond valence calculations, using parameters proposed by Brese and O’Keeffe,²⁸ performed for the tetrahedral M sites for 1–3 yield group 6 metal valences greater than the expected (vi) (Table 4). This is normal in ternary nitrides of the heavier group 6 metals, indicating a significant π -contribution to bonding between metal and nitrogen. In nitridometalates(vi) with higher

Table 3 Selected bond lengths and mean distances (in Å) in (Ba,Ca)₃MN₄ nitrides

Compound	1	2	3
Formula	Ba _{2.23} Ca _{0.77} MoN ₄	Ba _{1.52} Ca _{1.48} MoN ₄	Ba _{1.44} Ca _{1.56} WN ₄
A(1)–N(1)	2.901(8)	2.885(4)	2.904(9)
A(1)–N(1) ⁱⁱ	3.353(8)	3.297(4)	3.301(9)
A(1)–N(2) ⁱ	2.699(9)	2.718(5)	2.729(10)
A(1)–N(3)	2.778(8)	2.823(4)	2.842(10)
A(1)–N(3) ⁱ	3.487(8)	3.295(4)	3.291(10)
A(1)–N(4) ⁱⁱ	3.027(9)	2.999(4)	2.957(9)
A(1)–N(4) ⁱⁱⁱ	3.257(9)	3.028(4)	3.055(9)
\bar{d} (A(1)–N)	3.07(1)	3.01(1)	3.01(1)
A(2)–N(1) ⁱⁱⁱ	2.933(9)	2.814(4)	2.795(8)
A(2)–N(2) ^{iv}	2.749(9)	2.573(5)	2.549(10)
A(2)–N(3)	2.693(9)	2.581(5)	2.568(10)
A(2)–N(3) ^v	2.951(9)	2.851(5)	2.861(10)
A(2)–N(4)	2.840(9)	2.769(4)	2.764(9)
A(2)–N(4) ⁱⁱⁱ	2.943(8)	2.810(4)	2.815(9)
\bar{d} (A(2)–N)	2.85(1)	2.73(1)	2.73(1)
A(3)–N(1) ^{vii}	2.486(9)	2.386(4)	2.374(9)
A(3)–N(1)	2.631(9)	2.566(4)	2.576(9)
A(3)–N(2)	2.545(9)	2.545(4)	2.565(10)
A(3)–N(2) ^{vi}	3.470(10)	3.218(5)	3.186(10)
A(3)–N(3) ^{viii}	2.527(8)	2.454(4)	2.462(10)
A(3)–N(4) ^{vi}	2.438(8)	2.473(4)	2.482(9)
\bar{d} (A(3)–N)	2.68(1)	2.61(1)	2.61(1)
M–N(1)	1.866(9)	1.855(4)	1.873(8)
M–N(2)	1.863(9)	1.835(5)	1.853(10)
M–N(3)	1.864(8)	1.865(4)	1.867(10)
M–N(4)	1.880(9)	1.864(4)	1.878(9)
\bar{d} (M–N)	1.87(1)	1.85(1)	1.87(1)

ⁱ $x + 1/2, y, -z + 1/2$. ⁱⁱ $x + 1/2, -y - 1/2, -z$. ⁱⁱⁱ $-x + 1, -y - 1, -z$. ^{iv} $-x + 1/2, y - 1/2, z$. ^v $-x + 1, y - 1/2, -z + 1/2$. ^{vi} $-x + 1/2, y + 1/2, z$. ^{vii} $-x + 1, -y, -z$. ^{viii} $-x + 1, y + 1/2, -z + 1/2$.

Table 4 Results of bond valence calculations for metal sites in 1–3

Compound	1	2	3
Site valences:			
A1	1.8	1.9	1.9
A2	2.2	2.0	2.0
A3	2.2	2.1	2.0
M	6.4	6.6	6.7

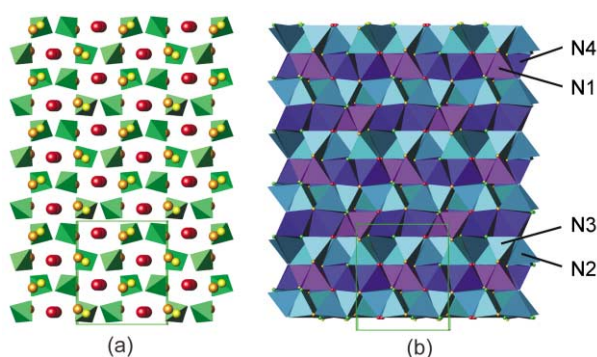


Fig. 1 Structure of (Ba,Sr)₃MN₄ (M = Mo, W) as a [010] projection illustrating: (a) hexagonal "channels" of isolated [MoN₄]₆ tetrahedra within which are located A1 cations (red spheres), A2 (orange spheres) and A3 (yellow spheres) (b) edge-sharing N-centred polyhedra; layers of edge-sharing N1–(A,M) and N4–(A,M) polyhedra stack in layers perpendicular to the *c*-direction (. . .ABABA. . .). N2 and N3 are located between these layers.

dimensional structures, 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 MN₄ tetrahedra, such as the title compounds, the four bonds are often approximately the same length.

The three A sites can be viewed as octahedral holes, but as in the (Ba,Sr)₃MN₄ mononitridometalates the octahedral coordination of the A1, A2 and A3 cations is extremely distorted (Fig. 2). In fact, the A1 (Ba)–N environment could be regarded as seven-coordinate but two bonds are consistently of *ca.* 3.2 Å or greater (three bonds in 1). Similarly, the A3–N2 bond length is much larger than the other nitrogen distances within the first coordination sphere and so the A3 site could be viewed as five-coordinate. Thus within a *ca.* 3.2 Å limit the A1, A2 and A3 cations are five-, six- and five-coordinate to N, respectively. Conversely the N sites (N1–N4) are five-, four-, five- and six-coordinate. The mean bond lengths of the three A sites are commensurate with first the refined populations and

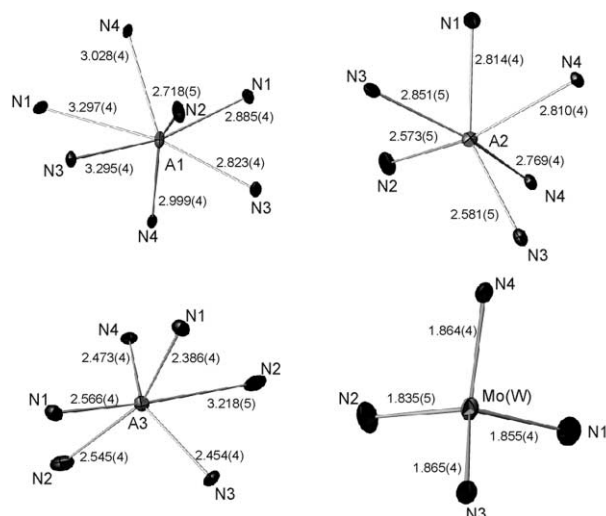


Fig. 2 Metal coordination environments in A₃MN₄ nitrides. Bond lengths (in Å) shown are for compound 2. Interactions beyond 3.2 Å are also shown.

the expected order $A1 \geq A2 \geq A3$ and second a decrease in A–N bond length as Ba^{2+} is replaced by smaller Ca^{2+} (comparing **1** to **2** and **3**). There is no change in mean A–N bond lengths as W replaces Mo from **2** to **3** (given slight variations in A stoichiometry). This is again consistent with the idea of a “rigid” $[MN_4]^{6-}$ building block. The alkaline earth coordination environments are unexceptional for nitrides of this type. For example, trigonal HT- Ba_3WN_4 has barium coordination numbers varying from six to seven,⁶ monoclinic Sr_3MN_4 (M = Mo, W) has five-, six- and seven-coordinate Sr^{2+} ions,^{7,8} and $Sr_4[MoN_4]O$ contains Sr in two seven-coordinate sites and eight six-coordinate sites.²³ Bond valence calculations weighted for the refined cation distributions and including the longer interactions listed in Table 3, give results for the A sites all close to the expected value (Table 4).

Aside from previously reported Ba_2CaWN_4 ,¹⁶ the compounds prepared are the only examples of mixed Ba–Ca transition metal nitrides. The subnitrides $Na_nBa_{14}CaN_6$ ($n = 7, 8, 14, 17, 21, 22$) are the only other reported examples of mixed Ba–Ca nitrides of any kind.^{18–20} Here, the alkaline earth metals occupy discrete sites within the $Ba_{14}CaN_6$ cluster common to this family. In fact, when Sr is introduced in the subnitrides, it always partially substitutes on the Ca site and the Ba–Ca(Sr) distribution always remains ordered. Hence **1–3** present the first evidence for Ca : Ba disorder in nitrides. The slowly growing number of other mixed alkaline earth nitrides containing group 6 elements suggests an evolution of structure with composition. The A positions are completely ordered in stoichiometric compositions such as Ca_2SrWN_4 but inevitably partial A site disorder is invoked in non-stoichiometric compounds in the phase space between the end members and 1 : 2 and 2 : 1 (A : A') A_3MN_4 compositions.^{15,17} The existence of **1–3** suggests a solid solution of LT- A_3MN_4 compounds should exist in the Ba–Ca–W(Mo)–N systems just as in the Ba–Sr–W(Mo)–N systems.¹⁷

Of particular note in the context of structure vs. composition vs. A site distribution, of course, is that **1–3** adopt LT- Ba_3MN_4 structures as opposed to the *Fddd* orthorhombic structure so far unique to Ba_2CaWN_4 .¹⁶ Although this latter compound has not been reported with the LT- Ba_3MN_4 structure, **1** is compositionally very close to being its molybdenum analogue. Furthermore **2** and **3** suggest that as the Ba : Ca ratio is decreased the LT- Ba_3MN_4 structure is retained (as in the Ba–Sr–W(Mo)–N systems). From this limited evidence, the *Fddd* structure would appear to be another polymorph within the (Ba,Ca)₃–WN₄ system. Ba_2CaWN_4 was synthesised at a lower temperature (1223 K) than **1–3**.¹⁶ It remains to be seen, therefore, whether the HT (trigonal) structure is attainable in mixed A_3MN_4 nitrides at higher temperatures and also whether the *Fddd* structure exists at lower temperatures within the phase diagrams of all A–A'–M–N systems. Given the evidence supporting a lower temperature polymorph, it is suggested that the potential (A,A')₃M^{VI}N₄ polymorphs be redesignated α - (*Fddd*), β - (LT- Ba_3MN_4) and γ - (HT- Ba_3MN_4), respectively.

In summary, new mixed alkaline earth nitridometalates(vi) have been synthesised for the first time. The structures of these compounds, as solved from single crystal X-ray diffraction data, are isotopic with LT- $Ba_3Mo(W)N_4$, unlike previously reported Ba_2CaWN_4 .¹⁶ The group 2 cations exhibit partial disorder unprecedented in nitrides; a distribution which evolves with the alkaline earth metal composition.

Acknowledgements

D. H. G. would like to thank the EPSRC for the award of an Advanced Research Fellowship, for associated funding and for the award of a diffractometer.

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