Cr(v)–Cr(v) dimers in Ae₄[Cr₂N₆] (Ae = Ca and Sr)

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Single crystals of the isostructural compounds $Ae_4[Cr_2N_6]$ (Ae = Ca and Sr) were synthesised in a mixed sodium–gallium melt at 900 °C. The reactions were performed in sealed niobium tubes with NaN_3 as the nitrogen source. The compounds crystallise in the triclinic space group $P\bar{1}$ (No. 2) with similar lattice parameters. The structure contains $[Cr_2N_6]^{8-}$, isolated anionic units of edge-sharing tetrahedra that permit chromium–chromium bonding.

Introduction

In the last fifteen years there have been many reports describing the synthesis of new ternary nitrides containing an alkaline earth (Ae) and a first row transition (M) element.[1] The structures of compounds containing the earlier transition elements, groups 5 to 8, can be described in terms of nitridometallate anions based upon isolated or condensed metal centred MN_n^{z-} units, often trigonal planar[2–10] or tetrahedral.[11,12] This is in contrast to compounds containing the later transition elements cobalt, nickel and copper whose structures often have a higher transition metal to nitrogen ratio and exhibit –M–N–M– chains that can be linear or bent.[13–20] Some of these latter compounds have structures that include examples of bent anionic units with nitrogen bridged M–M distances on the order of their elemental distances. A direct, non-nitrogen bridged M–M bond in nitrides is uncommon, but two examples are known:[21,22] $Li_6Ca_2[Mn_2N_6]$[21] and $Ca_6[Cr_2N_6]H$[22] contain the ethane-like anions $[Mn_2N_6]^{10-}$ and $[Cr_2N_6]^{11-}$ respectively.

In contrast, $Li_4Sr_2[Cr_2N_6]$,[23] contains chromium(v) centred nitrogen tetrahedra condensed into edge sharing pairs. This brings the chromium centres into close proximity to one another, their separation being 249.7 pm. This is comparable to 252 pm, the chromium–chromium separation in the element. This compound is diamagnetic at room temperature with a large estimated Cr(v)–Cr(v) exchange energy, J (*i.e.* $J/k_b \geq$ 2000 K). These facts suggest that the electrons from each d^1 chromium atom are involved in a two-centre two-electron chromium–chromium bond. Both $Ca_6[Cr_2N_6]H$[22] and Li_4Sr_2-$[Cr_2N_6]$[23] presented a departure from the previously known alkaline earth chromium nitride phases. These all contained isolated nitridochromate anions either in the form of trigonal planar units $(Ae_3CrN_3,$ Ae = Ca, Sr, Ba)[2,10] or tetrahedra, $Ba_5[CrN_4]N$.[12]

This paper reports the synthesis and structural characterisation of $Ae_4[Cr_2N_6]$ (Ae = Ca or Sr), a pair of compounds that contain the same $[Cr_2N_6]^{8-}$ dimeric unit that is found in Li_4-$Sr_2[Cr_2N_6]$. The growth of these new compounds also extends the technique of using sodium as a reaction medium for the synthesis of ternary nitrides by adding gallium to the melt. Gallium has been used in the synthesis of the ternary nitrides $Ln_3T_2N_6$ (Ln = La, Ce, Pr; T= Ta, Nb)[24] where its success is presumably mainly due to the fact that many transition metals have some solubility in liquid gallium at high temperatures. This is in contrast to sodium, in which all early transition metals have negligible solubility.[25] However, as sodium is thought to help to activate nitrogen[26] it seems plausible that both elements could be needed to grow a variety of early transition metal nitrides. Exemplifying this concept is the recent report that single crystals of CrN could be grown from a mixed sodium–gallium melt, but not from a melt containing either of these elements alone.[27]

Experimental

Single crystals of the title compounds were synthesised in an identical manner. Due to the air instability of both the reagents and products, all manipulations were carried out in an argon filled glove box. Na, Ga, Ae, Cr and NaN_3 were placed into a niobium tube such that the atomic ratios of Na : Ga : Ae : Cr : N_2 were approximately 6 : 4 : 1 : 1 : 1.25. The corresponding masses are Na (Aldrich, A.C.S reagent grade) 200 mg, Ga (99.99%) 0.469 mg, Ca/Sr (both filed from rod) 67/149 mg, Cr (99%) 87 mg and NaN_3 (99.9%) 90 mg. The niobium container was sealed under *ca.* 1 atm of argon in a Centorr Associates arc furnace and then itself sealed under vacuum in a fused silica tube in order to be protected from subsequent oxidation during heating. These starting materials were heated to 900 °C in 15 h, remained at temperature for 36 h at which point the furnace was shut off and allowed to cool naturally. If it is assumed that no nitrogen reacted, a nitrogen pressure of *ca.* 36 atm at the reaction temperature would have been produced by the decomposition of NaN_3. If only the known binary nitrides formed, either approximately 15 (Sr_2N and CrN) or 12 atm (Ca_3N_2 and CrN) of nitrogen would have remained in the niobium tube. If all the alkaline earth present in the tubes formed $Ae_4[Cr_2N_6]$ and the remaining chromium formed CrN then a residual nitrogen pressure of *ca.* 7 atm would have remained at the reaction temperature. Unreacted sodium was removed by sublimation from the products by heating the niobium tube to ~300 °C under a pressure of *ca.* 10^{-6} atm for 8 h. No elemental gallium remained in either tube.

Both the calcium and strontium reactions were repeated in an identical manner but without gallium. The products of both reactions were the known alkaline earth nitride, Ca_3N_2 or Sr_2N, and chromium metal. In another series of experiments 6 mg of lithium (Alfa, 99.999%) was added to the list of reagents in the approximate molar ratio of Cr : Li 2 : 1. This did not change the nature of the reaction products formed from the strontium containing tube *i.e.* no evidence of $Li_4Sr_2[Cr_2N_6]$ was found. Another phase was, however, formed in the calcium containing tube. Clear, transparent plates of $LiCaGaN_2$ were observed. The structure of this new phase will be reported shortly.

Attempts were made to produce a phase pure sample of $Ca_4[Cr_2N_6]$ for property measurements through various means. Sealed tube experiments were carried out with a variety of calcium to chromium ratios but in all cases orange crystals of CaGaN could be seen by eye. A pressed pellet of CrN (251 mg) and Ca_3N_2 (389 mg, both made from the respective element's reaction with ammonia) with a Ca : Cr : N ratio of approximately 2 : 1 : 2.4 was placed into a niobium tube. The extra nitrogen required to further oxidise the chromium was supplied with the addition of sodium azide (80 mg). This quantity of sodium azide provides a nitrogen pressure of approximately 30 atm at the reaction temperature of 900 °C and

Table 1 Crystal data and structure refinement for $Ca_4[Cr_2N_6]$ and $Sr_4[Cr_2N_6]$ [a]

Empirical formula	Ca_2CrN_3	Sr_2CrN_3
Formula weight (M)	174.19	269.27
Temperature	173(2) K	173(2) K
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/pm	555.65(6)	571.83(18)
b/pm	572.02(5)	595.36(19)
c/pm	632.82(6)	665.9(2)
α/degree	72.619(2)	72.718(8)
β/degree	68.012(2)	68.022(8)
γ/degree	63.969(2)	64.436(7)
Volume	0.16539(3) nm³	0.18713(10) nm³
Z	2	2
Density (calculated)	3.498 Mg m⁻³	4.779 Mg m⁻³
Absorption coefficient (μ)	6.311 mm⁻¹	31.035 mm⁻¹
Reflections collected	2454	2350
Independent reflections	1244 [R_{int} = 0.0259]	1172 [$R(int)$ = 0.0271]
Goodness-of-fit on F^2	1.095	1.066
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0316$, $wR2 = 0.0853$	$R1 = 0.0348$, $wR2 = 0.0850$
R indices (all data)	$R1 = 0.0343$, $wR2 = 0.0868$	$R1 = 0.0407$, $wR2 = 0.0872$

[a] $R1 = \Sigma||F_o| - F_c||/\Sigma|F_o|$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_o^2)^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [(F_o^2) + 2F_c^2] \div 3$.

changes the Cr : N ratio to 1 : 3.5. This niobium container was then sealed under vacuum in a fused silica tube and heated for 100 h. The sodium was removed as before, the pellet re-formed and the procedure repeated with heating times of 300 and 100 h. In both these cases a nitrogen atmosphere was supplied by the decomposition of sodium azide (45 and 65 mg respectively). This whole procedure was also carried out with sodium azide present only in the initial heating *i.e.* the second and third heatings were carried out in the argon atmosphere supplied by the arc furnace. The former technique yielded a homogeneous vine-green powder and the latter a much darker brown–green powder. The powder X-ray diffraction patterns of both samples were characterised by broad, low intensity peaks. Neither pattern could be successfully indexed as many peaks coalesced into broad humps but it could be seen that the peak positions in each sample were different. Therefore, no property measurements were carried out.

Single crystals of both title compounds were selected for X-ray and electron microprobe analysis. X-ray data were collected with Mo-Kα radiation on a Bruker SMART CCD equipped with a graphite monochromator. The Bruker software package SAINT[28] was used to integrate both sets of data, an empirical absorption correction[29] was applied and the files for SHELX[30] prepared by XPREP.[31] The structures were solved by direct methods. Initially only the alkaline earth and the chromium atoms were located, the nitrogen sites were subsequently found from the Fourier difference map. Powder X-ray diffraction was performed on a Scintag 2000 theta–theta diffractometer with Cu-Kα radiation. Due to the facile nature of the reaction of all these products with air, the powder diffraction samples were prepared in an argon filled glove-box and covered with Mylar film.

The elemental composition of the crystals was elucidated by electron microprobe analysis using a JEOL 8900 Electron Microprobe. In order to prevent decomposition or oxygen contamination of the samples, they were transferred from an argon filled glove box to the microprobe in a specially designed portable antechamber that avoids any air exposure while transferring the sample to the microprobe.[32]

Results and discussion

Ca₄[Cr₂N₆]

After the removal of the unreacted sodium, the reaction vessel was taken into an argon filled glove box. In the base of the tube was a mass of shiny orange and silver crystals that were identified as a mixture of $Ca_4[Cr_2N_6]$, CaGaN, Cr_2GaN and

$Na_{22}Ga_{39}$.[33] These phases were identified in powder X-ray diffraction patterns and/or their single crystal derived unit cells. However, indexing of the peaks from the new phase based on powder diffraction alone is difficult, due to significant overlapping of peaks from the many phases present. Some of these crystals were placed into polybutene oil for optical inspection and single crystal selection. In addition to needle-like silver crystals of $Na_{22}Ga_{39}$ and shiny orange plate-like crystals of CaGaN, some shiny dark green crystals were also observed. Several of these green crystals were loaded onto the goniometer head so that a stream of cold nitrogen froze the oil and held the crystals stationary and protected from the air. A suitable trigonal prismatic crystal was found (0.2 × 0.03 × 0.03 mm³) and, following data collection, the crystal structure was obtained in the space group $P\bar{1}$ (No. 2). The program ADDSYM[34] was used in order to check for higher symmetry but none was found. The crystallographic results are summarized in Table 1.

The atomic coordinates found were standardised with STRUCTURE TIDY[35] and are shown in Table 2. The anisotropic displacement factors are also tabulated and presented in Table 3. In support of the elemental composition obtained by crystallography, semi-quantitative electron microprobe spectroscopy of the sample showed only the presence of calcium and chromium in approximately the correct ratio of Ca/Cr = 2.25 ± 0.04. This ratio is an average of eight readings taken from the flat faces of two intergrown crystals. As is typical for microprobe analysis, when the crystal faces cannot be polished and when standards containing a known ratio of calcium and chromium are not used, the data cannot be corrected to obtain the ideal Ca/Cr ratio of 2. No sodium, gallium or niobium peaks were observed. In addition, wavelength dispersive analysis revealed the presence of nitrogen; no signal was found for oxygen.

Sr₄[Cr₂N₆]

A procedure very close to that explained above was followed in the analysis of the strontium containing sample. As in the previous case, the phases present were identified in powder X-ray diffraction patterns and/or by their single crystal derived unit cells. Again, the number of phases present makes it difficult to index the peaks from the new phase. Following the removal of the unreacted sodium and transportation into the glove box a mass of mainly silver crystals of $Na_{22}Ga_{39}$ and $SrGa_4$ was observed in the base of the tube. However, on one side of some silvery–grey polycrystalline masses were shiny green crystals. The colour of these was a little darker than that of the $Ca_4[Cr_2N_6]$. Semi-quantitative electron microprobe spectro-

Table 2 Atomic positions and equivalent isotropic displacement parameters ($pm^2 \times 10^{-1}$) for $Ca_4[Cr_2N_6]$ and $Sr_4[Cr_2N_6]$. Those for $Sr_4[Cr_2N_6]$ are listed second in italics

Atom	Wyckoff position	x	y	z	U_{eq}
Ca1	2i	0.1548(1)	0.4507(1)	0.1962(1)	6(1)
Sr1	*2i*	*0.1569(1)*	*0.4456(1)*	*0.1951(1)*	*3(1)*
Ca2	2i	0.5880(1)	0.1844(1)	0.6760(1)	5(1)
Sr2	*2i*	*0.5840(1)*	*0.1842(1)*	*0.6708(1)*	*2(1)*
Cr	2i	0.8530(1)	0.0599(1)	0.1902(1)	4(1)
Cr	*2i*	*0.8599(2)*	*0.0582(1)*	*0.1837(1)*	*1(1)*
N1	2i	0.0949(5)	0.1718(4)	0.5725(4)	7(1)
N1	*2i*	*0.1003(8)*	*0.1631(7)*	*0.5878(6)*	*3(1)*
N2	2i	0.1901(5)	0.1040(4)	0.0074(4)	6(1)
N2	*2i*	*0.1910(8)*	*0.0867(8)*	*0.0076(6)*	*3(1)*
N3	2i	0.6059(5)	0.3681(4)	0.2467(4)	7(1)
N3	*2i*	*0.6290(9)*	*0.3568(8)*	*0.2391(7)*	*5(1)*

Table 3 Anisotropic displacement parameters ($pm^2 \times 10^{-1}$) for $Ca_4[Cr_2N_6]$ (first line in each column) and $Sr_4[Cr_2N_6]$ (listed in italics where appropriate). The anisotropic displacement factor exponent takes the form: $2\pi[h^2a^{*2}U_{11} + 2hka^*b^*U_{12} + \ldots]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ca1	9(1)	5(1)	5(1)	0(1)	−3(1)	−2(1)
Sr1	*5(1)*	*1(1)*	*4(1)*	*0(1)*	*−3(1)*	*−2(1)*
Ca2	6(1)	5(1)	5(1)	−1(1)	−1(1)	−2(1)
Sr2	*2(1)*	*2(1)*	*4(1)*	*0(1)*	*−2(1)*	*−1(1)*
Cr	5(1)	3(1)	3(1)	0(1)	−1(1)	−2(1)
N1	8(1)	6(1)	5(1)	1(1)	−3(1)	−3(1)
N2	6(1)	7(1)	5(1)	−2(1)	−1(1)	−4(1)
N3	8(1)	5(1)	7(1)	−2(1)	−2(1)	0(1)

scopy of the green crystals found strontium and chromium in the ratio of Sr/Cr = 1.69 ± 0.05. This ratio is an average of twelve readings taken from the flat faces of two separate crystals. In none of these measurements was a sodium, gallium or niobium signal observed. Wavelength dispersive analysis again revealed the presence of nitrogen with no signal found for oxygen.

A sample of the tube contents was also placed into polybutene oil for single crystal selection. Several of the green crystals were loaded onto the goniometer head, where a stream of cold nitrogen froze the oil and held the crystals stationary and protected from the air. The unit cells found were of triclinic symmetry with cell parameters virtually identical to each other and similar to that of the calcium compound except that the cell volume had increased by ~13.5%. Data were collected from a distorted crystal of approximately octahedral shape ($0.18 \times 0.18 \times 0.1$ mm³). As expected, the structure was subsequently solved in the space group $P\bar{1}$ (No. 2) and the crystallographic results are summarized in Table 1. The atomic coordinates found were standardised with STRUCTURE TIDY[35] and are shown in Table 2, along with those of $Ca_4[Cr_2N_6]$. It can be seen that these compounds are isotypic. The displacement factors are also tabulated and presented in Table 3, along with those of $Ca_4[Cr_2N_6]$. Only the strontium atoms could be anisotropically refined in $Sr_4[Cr_2N_6]$. It was not possible to anisotropically refine the other elements in this compound without non-positive definite thermal parameters being generated for some or all of the elements. This is likely due to an absorption correction error; SADABS cannot model the crystal shape (distorted octahedron) sufficiently well with only the three dimensions that it requires as input. This problem is compounded by strontium's high absorption of Mo-Kα radiation. The calculated value of the absorption coefficient of $Sr_4[Cr_2N_6]$ is 31.035 mm⁻¹, approximately five times that of $Ca_4[Cr_2N_6]$. The large number of faces (12) of the crystal precluded a satisfactory face-indexed absorption correction and, unfortunately, a more regular crystal could not be found.

In both sets of reaction products there was no evidence for the formation of the previously discovered chromium nitrides,

Ae_3CrN_3 ($Ae = Ca^{2}$ and Sr^{10}). It appears that, under these conditions, the title compounds are the more stable species.

CCDC reference numbers 204378 and 204379.

See http://www.rsc.org/suppdata/dt/b3/b302015k/ for crystallographic data in CIF or other electronic format.

Structure description

Within the family of Ae–M–N there are two compounds that adopt the same stoichiometry as $Ae_4[Cr_2N_6]$, namely Sr_2VN_3 and Ba_2VN_3.[11] These compounds are not isostructural with each other nor with the title compounds. A similarity that they do share with the title compounds is that they are based upon MN_4 tetrahedra. However, in the nitridovanadates these units corner share to form infinite one-dimensional chains. Chromium(v) has been previously reported in the compounds $Ba_5[CrN_4]N$[12] and in $Li_4Sr_2[Cr_2N_6]$.[23] Both of these compounds are based upon CrN_4 tetrahedra but in the former compound they are isolated and in latter they condense into dimers of edge sharing tetrahedra, $[Cr_2N_6]^{8-}$. This is the same anionic feature that is observed in the isostructural title compounds. These dimers reside in a sea of cations, and eclipse each other along the three crystallographic axes, as shown in Fig. 1.
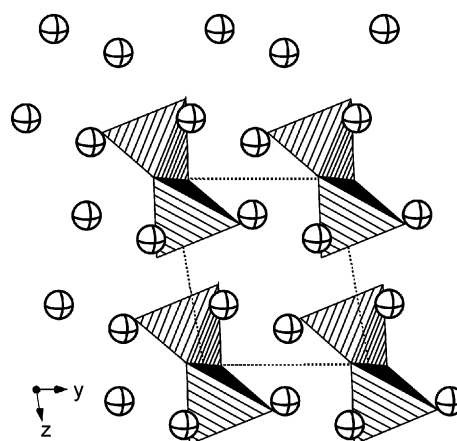

Fig. 1 The crystal structure of $Ae_4[Cr_2N_6]$ showing the edge-sharing pairs of CrN_4 tetrahedra. They are situated in rows parallel to the unit cell axes in amongst the alkaline earth cations (crossed circles). The unit cell edges in the b–c plane are shown by a dotted box.

The Cr_2N_6 unit is shown in Fig. 2 along with the chromium–chromium bond length found in both title compounds; that corresponding to $Sr_4[Cr_2N_6]$ is in brackets. As can be seen, this distance (245 *vs.* 248 pm) does not vary significantly with the identity of the alkaline earth. A chromium–chromium distance of 249 pm is observed in $Li_4Sr_2[Cr_2N_6]$, again not significantly different. All of these distances are comparable to 252 pm, the chromium–chromium separation in the element. Chromium–nitrogen bond lengths in the compounds are also almost

Table 4 The calculated bond valence sums for the atoms in $Ca_4[Cr_2N_6]$, Ca_3CrN_3, $Sr_4[Cr_2N_6]$, Sr_3CrN_3 and $Ba_5[CrN_4]N$. Only Ae–nitrogen and chromium–nitrogen interactions are used to calculate the total valence sums

	$Ca_4[Cr_2N_6]$	Ca_3CrN_3	$Sr_4[Cr_2N_6]$	Sr_3CrN_3	$Ba_5[CrN_4]N$
Ae	2.049, 2.185	1.758, 1.719	1.712, 1.929	1.286	2.038, 1.804, 2.166, 1.970
Cr	4.641	3.473	4.643	4.172	5.176
N	2.969, 3.087, 2.819	3.131, 2.769	2.762, 2.922, 2.599	2.677	2.814, 3.374, 2.816

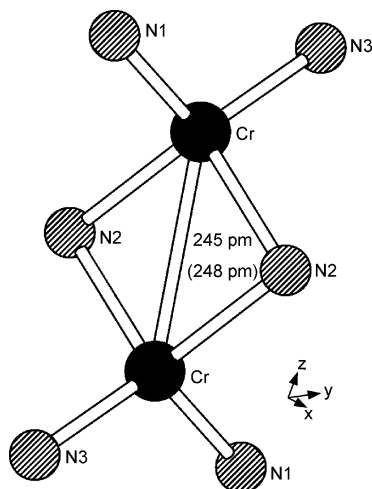**Fig. 2** The local coordination of the Cr(v) ions. The chromium–chromium bond distance is shown, the first number refers to that found in $Ca_4[Cr_2N_6]$, the number in brackets to that found in $Sr_4[Cr_2N_6]$. In both compounds the chromium–nitrogen distances all lie in the range of 170 to 190 pm.

identical ranging from 170 to 190 pm compared to 170 to 189 pm found in $Li_4Sr_2[Cr_2N_6]$.

As is found in the vast majority of nitride compounds, the nitrogen atoms are all six-coordinate, as shown in Fig. 3. These distorted octahedra can be separated into two types, one in which the nitrogen is bonded to two chromium atoms *i.e.* it is a bridging nitrogen in the chromium dimer, and a second in which the central nitrogen atom bonds only to one chromium. Both these types have four bonds to calcium (strontium) in the range 251 to 271 pm (264 to 292 pm) but the non-bridging nitrogen has an extra calcium (strontium) neighbour at 308 pm (307 pm). The nitrogen atoms then complete their hexaco-ordination by forming bond(s) to chromium. The bridging nitrogen–chromium distances are 188 pm and 191 pm (187 and 190 pm), longer than the non-bridging nitrogen chromium distances of 170 or 174 pm (171 or 174 pm). Both the Ae atoms are seven-fold coordinate to nitrogen at distances that range from 242 to 320 pm or 269 pm to 318 pm for $Ca_4[Cr_2N_6]$ and $Sr_4[Cr_2N_6]$ respectively.
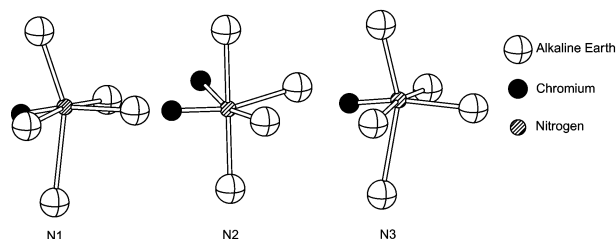

Fig. 3 The coordination environment of the three nitrogen atoms. In the case of N1 and N3, the long N–Ae bond is that pointing downwards.

The bond valence sums for each the elements were calculated for the title compounds with the program EUTAX.[36] Internal values of the required R_{ij} were used. $R_{CaN} = 214$ and $R_{SrN} = 223$ pm are as listed in ref. 36 and $R_{CrCr} = 232$ pm can be derived from ref. 37. The results obtained are detailed in Table 4, where

they are compared to the values calculated for the known calcium and strontium compounds, Ae_3CrN_3 with Ae = Ca[2] and Sr.[10] Also included are the results from another chromium(v) compound, $Ba_5[CrN_4]N$[12] ($R_{BaN} = 247$ pm). The bond valence sums for the calcium and nitrogen atoms in $Ca_4[Cr_2N_6]$ and Ca_3CrN_3 are close to the expected values of 2 and 3. The bond valence sum of strontium is as expected in the title compound but is significantly higher than that found in Sr_3CrN_3. The lower than expected value found in Sr_3CrN_3 is similar to the strontium bond valence sum in Sr_2N[38] and has been attributed to an "over-stretching" of the Ae–N sub-lattice.[10] Interestingly, the bond valence sums reported here for calcium in Ca_3CrN_3 are smaller than 2, in contrast to the previously reported values of 2.16 and 2.20.[10] We assume that different values of R_{ij} were used in the previous calculations. The chromium–nitrogen inter-actions lead to bond valence sums for chromium in $Ae_4[Cr_2N_6]$ that are a little lower than the formal oxidation state. However, they are definitely larger than those of the Cr(III) found in Ca_3CrN_3 and Sr_3CrN_3. They are also slightly lower than the value found for Cr(v) in $Ba_5[CrN_4]N$. This difference is due to the pairing of the tetrahedra. When this occurs the average Cr–N bond length increases from 175.5 pm in $Ba_5[CrN_4]N$ to 180.5 pm ($Ca_4[Cr_2N_6]$) or 184.2 pm ($Sr_4[Cr_2N_6]$). The sixth chromium electron appears to form a bond to the neighbouring chromium centre, a thought partially justified by a calculated Cr–Cr bond valence of 0.71 ($Ca_4[Cr_2N_6]$) or 0.65 ($Sr_4[Cr_2N_6]$) and the short Cr–Cr distance of ~245 pm. It is also interesting to examine the individual chromium–nitrogen distances. The internal R_{ij} for a chromium–nitrogen bond in EUTAX is 185 pm. The bridging chromium–nitrogen distances are 170 to 190 pm, suggesting some bond orders are greater than one. The terminal nitrogen–chromium distances of 170 to 174 pm have bond orders near 1.4, while the bridging nitrogen atoms have bond orders near 1.0. Furthermore, all the chromium–nitrogen bond lengths are shorter than the reported *molecular* chromium–nitrogen single bond length of 200 pm[10] but longer than 157 pm, the Cr–N triple bond length.[10]

As the present case illustrates, the use of molten alloys of Na to prepare ternary or more complex nitrides, especially those containing transition elements or rare earths, is likely to be much more productive than using pure Na. This is likely due to the low solubility of transition elements in liquid Na.[25] Indeed, the nitrides that have been prepared as small X-ray sized single crystals from Na melts are primarily those of main group elements: Si, Ge, Al, Ga, In, Zn, and Cu. Cu may be considered as a main group element here, since its oxidation state is +1. It is interesting that even a Na : Ga ratio of 3 : 2 appears to impart enough solubility to Cr to form novel nitrides. It is likely that this method can be extended to other Na alloying elements, such as Sn, In and Zn for example.

However, the use of such alloys may not always result in the preparation of nitrides. There are two concerns: thermo-dynamic and kinetic. The thermodynamics is complicated by the possibility of forming many different intermetallic compounds from the melt, as we saw in the present examples. Since the free energy of nitride formation is small,[39] at least compared to, for example, oxides, and since some intermetallic compounds have reasonably large free energies of formation, it may be that in a given system the intermetallics are more stable than the nitrides. In that case no nitrides will form. For example, in other studies we have found that in reactions containing Na, Ca

and In with Ca/In ≈ 0.1 (as well as NaN_3) as the nitrogen source, only $CaIn_2$ is formed. Apparently, at the reaction temperature $CaIn_2$ (melting point 835 °C[25]) is more thermodynamically stable than Ca_3N_2. At higher Ca : In ratios (near 1 : 1) Ca_2InN[40] is found. We conclude that the alloy composition plays an important role in the relative stability of intermetallic phases and nitrides.

Kinetic factors are also important. In the present case, the title compounds are not obtained when gallium is left out of the melt and chromium does not react with the nitrogen to any measurable extent. This result must be kinetic, since the free energy of formation is sufficient to form CrN and there is excess nitrogen in the reaction mixture. Perhaps a thin coating of CrN on the chromium is sufficient to impede any further reaction. This coating should not form if the chromium is soluble in the melt. It may also be that particular alloy melts could form a "skin" of insoluble nitride at the melt surface that prevents further reaction of the N_2 gas with the melt. This is precisely what happens in the case of the reaction of gallium with NH_3 to produce GaN. The surface of gallium becomes coated with a thin layer of GaN effectively stopping the reaction.[41] It is interesting to note, that in that specific case, the addition of 5% bismuth to the gallium prevents the formation of the passivation layer of GaN and the reaction proceeds readily to completion.[41] In any case, one must be aware of the potential role of kinetics in obtaining or preventing the formation of desired phases.

Nonetheless, the use of alloy melts, especially melts of Na with later main group elements, appears to be a productive synthetic strategy for the synthesis of novel nitrides.

Conclusions

Two isostructural compounds that double the number of known ternary chromium(v) nitrides have been synthesised from a mixed sodium gallium melt. The main feature of the adopted triclinic structure is the reappearance of the $[Cr_2N_6]^{8-}$ unit, previously seen in the compound $Li_4Sr_2[Cr_2N_6]$.[23]

Acknowledgements

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