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Two New Structurally Related Strontium Gallium Nitrides: Sr_4GaN_3O and $Sr_4GaN_3(CN_2)$

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The strontium gallium oxynitride Sr_4GaN_3O and nitride–carbodiimide $Sr_4GaN_3(CN_2)$ are reported, synthesized as single crystals from molten sodium at 900 °C. Red Sr_4GaN_3O crystallizes in space group *Pbca* (No. 61) with $a = 7.4002(1)$ Å, $b = 24.3378(5)$ Å, $c = 7.4038(1)$ Å, and $Z = 8$, as determined from single-crystal X-ray diffraction measurements at 150 K. The structure may be viewed as consisting of slabs $[Sr_4GaN_3]^{2+}$ containing double layers of isolated $[GaN_3]^{6-}$ triangular anions arranged in a "herringbone" fashion, and these slabs are separated by O^{2-} anions. Brown $Sr_4GaN_3(CN_2)$ has a closely related structure in which the oxide anions in the Sr_4GaN_3O structure are replaced by almost linear carbodiimide $[CN_2]^{2-}$ anions [$Sr_4GaN_3(CN_2)$: space group $P2_1/c$ (No. 14), $a = 13.4778(2)$ Å, $b = 7.4140(1)$ Å, $c = 7.4440(1)$ Å, $\beta = 98.233(1)°$, and $Z = 4$].

Introduction

The investigation of novel nitrides is a growth area of solid-state chemistry in the search for new materials and properties. The different charges and chemical requirements of the anions of oxygen and nitrogen mean that nitrides often exhibit structural features completely different from those encountered in oxides. Examples include the first-row transition-metal and main-group-metal compounds containing $[MN_3]^{n-}$ triangular anions, for example, Ca_6MN_5 (M = Mn, Fe, Ga),[1,2] Sr_6GaN_5,[3] Ca_3MN_3 (M = V,[4] Cr,[5] Mn[6]), and AE_3MN_3 (AE = Sr, Ba; M = Cr,[7] Mn,[8] Fe,[9] Ga[3]). These compounds show that Ga^{3+} may often be substituted for trivalent transition-metal cations. Gallium also commonly occurs in tetrahedral coordination by nitrogen. However, the compounds $AE_3Ga_2N_4$ (AE = Sr,[10] Ba[11]) contain edge-shared GaN_4 tetrahedra and $Ca_3Ga_2N_4$[10] and $Sr_3Ga_3N_5$[10] contain both edge- and vertex-shared tetrahedra, and these frameworks contrast with the vertex-sharing only of GaO_4 tetrahedra in gallates. Many of these gallium nitrides have been synthesized by dissolving the metals in liquid sodium under several atmospheres of nitrogen gas, and this technique has indeed been applied to the growth of nitrides of the late transition and other main-group metals and in the synthesis of gallium nitride single crystals.[12] Gallium itself has been employed by DiSalvo and co-workers as a flux for the growth of crystals of transition-metal nitrides.[13−15] Here we describe the synthesis of two new structurally related strontium gallium nitrides containing $[GaN_3]^{6-}$ anions, which were discovered while attempting to introduce early transition metals into solution in alkaline earth−sodium−gallium melts and synthesize crystals of ternary and higher nitrides containing first-row metals.

Experimental Section

Synthesis. Most of the reactants and products used in this work are air-sensitive, so all manipulations of solids were carried out in

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a Glove Box Technology argon-filled recirculating drybox with a combined O_2 and H_2O content of less than 5 ppm. For synthesis of the title compounds, the reagents used were strontium pieces (99%, Aldrich), gallium pieces (99.9999%, Alfa Aesar), sodium azide (99%, Aldrich), sodium (99+%, BDH), and graphite (99.9995%, Alfa Aesar). Strontium and gallium, and in some instances graphite, were placed along with sodium azide and sodium in a tantalum tube (9-mm outer diameter, 0.5-mm wall thickness, 120-mm long, and closed at one end), which was welded closed under 1 atm of purified argon and then sealed inside an evacuated silica ampule. The amount of NaN_3 used was limited so as to restrict the maximum possible pressure in the tantalum tube to 35 atm. The reported crystal of Sr_4GaN_3O was obtained from a reaction in which NaN_3 (78 mg), Sr (70 mg), Ga (55 mg), and Na (200 mg) were placed inside the tube. The reported crystal of $Sr_4GaN_3(CN_2)$ was obtained from a reaction in which NaN_3 (78 mg), Sr (70 mg), Ga (28 mg), C (5 mg), and Na (200 mg) were placed in the tube. These two tubes were heated to 900 °C at 2 °C min^{-1}, and this temperature was maintained for 48 h, after which the tubes were cooled at 0.1 °C min^{-1} to 400 °C and then removed from the furnace. Earlier reactions that also yielded crystals of the title products had used soak temperatures of between 800 and 900 °C and soak times of between 2 and 4 days. Reactions similar to those described above, but in which vanadium (99.5%, Aldrich), iron (99.5%, Alfa Aesar), and manganese (99+%, Aldrich) powders were also included in quantities equimolar with gallium, were also investigated. In each case, the excess sodium present at the end of the reaction was removed by sublimation under a dynamic vacuum of 10^{-2} mbar at 350 °C. Single crystals were extracted by dispersing the product in paratone oil. Additional reactions made use of SrO obtained by decomposition of $SrCO_3$ (99.994%, Alfa Aesar) in an alumina crucible under a dynamic vacuum at 950 °C and Sr_2N obtained by the reaction at 900 °C between Sr and a flow of N_2 gas, which had been cleaned by passage over a titanium wire held at 800 °C. Powders were assessed for phase purity using powder X-ray diffraction measurements carried out on a Philips PW1050/81 diffractometer operating in a Bragg−Brentano geometry.

Chemical Analysis. Energy-dispersive analysis of X-rays (EDX) was carried out on single crystals using a JEOL JSM-840A scanning electron microscope equipped with an Oxford Instruments ISIS300 EDX system. It was not possible to obtain a quantitative analysis for carbon, nitrogen, or oxygen using this instrument.

Single-Crystal X-ray Diffraction. Crystals protected under paratone oil were mounted in a nylon loop and immobilized in the frozen oil at 150 K using an Oxford Instruments cooling system. Data were collected using an Enraf Nonius FR590 κCCD machine using Mo Kα radiation ($\lambda = 0.710$ 71 Å) achieved using a graphite monochromator. Data were analyzed with the DENZO-SMN programs.[16] Analytical absorption corrections[17] were applied through the PLATON[18] interface. Initial structural models were determined by direct methods using SHELXS-97[19] implemented within the Win-GX suite,[20] and the structure refinements were completed using SHELXL-97.[19] A search for additional symmetry was checked by ADDSYM.[21] Atomic coordinates were standardized with STRUCTURE TIDY.[22]

Table 1. Results of Single-Crystal X-ray Refinements at 150 K for Sr_4GaN_3O and $Sr_4GaN_3(CN_2)$

formula	Sr_4GaN_3O	$Sr_4GaN_3(CN_2)$
radiation	Mo Kα, $\lambda = 0.710$ 73 Å	
instrument	Enraf Nonius FR590 κCCD	
Physical form	red plate	brown plate
T/K	150(1)	150(1)
cryst syst	orthorhombic	monoclinic
space group	*Pbca*	$P2_1/c$
fw	478.23	502.26
a/Å	7.4002(1)	13.4778(2)
b/Å	24.3378(5)	7.4140(1)
c/Å	7.4038(1)	7.4440(1)
β/deg		98.233(1)
V/Å^3	1333.46(4)	736.17(2)
Z	8	4
ρ_{calc}/Mg m^{-3}	4.764(2)	4.532(2)
no. of variables	83	101
GOF on F^2	1.094	1.158
R1	0.0388	0.0284
wR2	0.0868	0.0675

Results

A large proportion of the products of these reactions were identified by single-crystal diffraction measurements as yellow $Sr_3Ga_2N_4$.[10] Additional red crystals found in the carbon- and transition-metal-free reactions at 900 °C and constituting about 5% of the bulk product had a Sr/Ga ratio of 79(1):21(1) (i.e., 4:1), as determined by EDX analysis, and single-crystal X-ray diffraction measurements produced an orthorhombic cell with $a = 7.4002(1)$ Å, $b = 24.3378(5)$ Å, and $c = 7.4038(1)$ Å and systematic absences consistent with the space group *Pbca*. Structure solution using direct methods suggested the stoichiometry Sr_4GaX_4, where X is a first-row anion. The red transparent nature of the crystals suggests that only closed-shell species are present, consistent with either a nitride deficiency or an oxynitride: Sr_4GaN_3O. Analysis of the single-crystal diffraction data suggested that all four of the crystallographic anion sites were fully occupied. The oxide ions are presumed to arise from contamination of the surface of the strontium or sodium introduced into the reaction. Attempts to increase the yield of the minority Sr_4GaN_3O phase by intentionally allowing sodium to tarnish before being placed in the reaction vessel were unsuccessful; the yield of the red crystals remained approximately constant in the reactions (constituting about 5% of the bulk by visual inspection) and an additional white powder was produced, which was not identified. The refinement results for Sr_4GaN_3O are given in Table 1, and the list of atomic coordinates is presented in Table 2.

In a reaction in which both gallium and iron powder were included in the reaction mixture, some brown platelike crystals were identified as a minority phase (1−2% of the bulk sample), which had a Sr/Ga ratio of 80(2):20(2) (i.e., 4:1), with negligible iron present, as determined by EDX analysis. The unit cell was determined to be monoclinic with $a = 13.4778(2)$ Å, $b = 7.4140(1)$ Å, $c = 7.4440(1)$ Å, and $\beta = 98.233(1)°$, and systematic absences were consistent with the space group $P2_1/c$. Structure solution using direct methods revealed that the structure was closely related to that of Sr_4GaN_3O but with one of the anion sites replaced

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Table 2. Atomic Parameters for Sr_4GaN_3O Obtained from Single-Crystal X-ray Diffraction Data at 150 K

atom[a]	*x*	*y*	*z*	$100U_{iso,eq}$/Å^2
Sr1	0.0374(1)	0.0624(1)	0.1567(1)	1.0(1)
Sr2	0.2066(1)	0.1481(1)	0.4819(1)	1.0(1)
Sr3	0.3605(1)	0.4306(1)	0.3308(1)	1.0(1)
Sr4	0.4597(1)	0.2570(1)	0.2402(1)	1.0(1)
Ga	0.2082(1)	0.1728(1)	0.0098(1)	0.8(1)
O	0.245(1)	0.0281(3)	0.4931(7)	2.0(2)
N1	0.0607(8)	0.3693(3)	0.3481(7)	1.2(1)
N2	0.2072(7)	0.2499(2)	0.0037(6)	0.8(2)
N3	0.3643(8)	0.1289(3)	0.1532(7)	1.1(1)

[a] All atoms are located on general 8*c* positions.

Table 3. Refined Atomic Parameters for $Sr_4GaN_3(CN_2)$ Obtained from Single-Crystal X-ray Diffraction Data at 150 K

atom[a]	*x*	*y*	*z*	$100U_{iso,eq}$/Å^2
Sr1	0.01262(4)	0.74779(6)	0.49349(6)	0.85(1)
Sr2	0.18090(3)	0.48000(6)	0.28495(6)	0.74(1)
Sr3	0.35367(3)	0.32174(6)	0.01481(6)	0.67(1)
Sr4	0.66776(3)	0.34483(6)	0.33270(6)	0.61(1)
Ga	0.14525(4)	0.01349(7)	0.29058(7)	0.57(1)
N1	0.7749(3)	0.3576(6)	0.0424(6)	1.01(9)
N2	0.0042(3)	0.0039(6)	0.2568(6)	0.60(8)
N3	0.2183(3)	0.1553(6)	0.1411(6)	0.95(9)
N4	0.6210(3)	0.0032(6)	0.1424(6)	0.82(9)
N5	0.4764(3)	0.1056(7)	0.2803(6)	1.15(9)
C	0.5462(4)	0.0526(7)	0.2051(7)	0.70(9)

[a] All atoms are located on general 4*e* positions.

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) for Sr_4GaN_3O

Sr1−N3	2.499(6)	Sr3−N1	2.481(6)
Sr1−O1	2.571(7)	Sr3−N1	2.674(6)
Sr1−N1	2.832(6)	Sr3−O1	2.775(6)
Sr1−N3	2.913(6)	Sr3−N3	2.791(6)
Sr1−O1	2.988(7)	Sr3−O1	2.826(6)
Sr1−O1	3.042(6)	Sr3−O1	3.286(7)
Sr2−N2	2.485(6)	Sr4−N2	2.567(5)
Sr2−N3	2.740(6)	Sr4−N2	2.576(5)
Sr2−N3	2.761(6)	Sr4−N2	2.641(5)
Sr2−O1	2.931(7)	Sr4−N2	2.708(5)
Sr2−N1	2.940(6)	Sr4−N1	2.910(6)
Sr2−N1	2.947(6)	Sr4−N3	3.260(6)
Ga−N2	1.880(6)	N2−Ga−N3	125.4(2)
Ga−N3	1.899(6)	N2−Ga−N1	121.2(2)
Ga−N1	1.921(6)	N3−Ga−N1	113.2(3)

by a carbodiimide anion $[CN_2]^{2-}$, as described in detail below. Carbon presumably occurs adventitiously in the strontium or, perhaps more likely, the iron (which was used as-received) in the reaction. Crystals of this phase constituting 5−10% of the bulk product were subsequently obtained in the absence of any added iron but with the introduction of some graphite powder, as described in the Experimental Section; the refinement results for a crystal of $Sr_4GaN_3(CN_2)$ derived from this carbon-containing reaction are given in Table 1, with the list of atomic coordinates given in Table 3. Selected bond lengths and angles for both Sr_4GaN_3O and $Sr_4GaN_3(CN_2)$ are listed in Tables 4 and 5.

Table 5. Selected Bond Lengths (Å) and Bond Angles (deg) for $Sr_4GaN_3(CN_2)$

Sr1−N2	2.581(4)	Sr3−N3	2.496(4)
Sr1−N2	2.583(4)	Sr3−N5	2.627(4)
Sr1−N2	2.649(4)	Sr3−N4	2.721(4)
Sr1−N2	2.720(4)	Sr3−N4	2.862(4)
Sr1−N1	3.026(5)	Sr3−N5	2.877(5)
Sr1−N3	3.204(5)	Sr3−N1	2.937(5)
Sr2−N2	2.476(4)	Sr3−N3	3.105(5)
Sr2−N4	2.653(4)	Sr3−N5	3.317(5)
Sr2−N3	2.711(4)	Sr4−N1	2.476(4)
Sr2−N3	2.812(4)	Sr4−N4	2.720(4)
Sr2−N1	2.856(5)	Sr4−N3	2.759(4)
Sr2−N1	3.102(5)	Sr4−N1	2.767(5)
Ga−N2	1.883(4)	Sr4−N5	2.784(5)
Ga−N3	1.904(4)	Sr4−N4	2.927(4)
Ga−N1	1.912(4)	Sr4−N5	3.108(5)
N2−Ga−N3	122.7(2)	C−N4	1.227(7)
N2−Ga−N1	121.8(2)	C−N5	1.226(7)
N3−Ga−N1	115.1(2)	N5−C−N4	174.8(6)

Further investigations of the reactions in which first-row transition metals were introduced into the melt have yielded some new compounds, indicating that the strategy of using Na/Ga melts helps to introduce first-row early transition metals into the melt. Bailey and DiSalvo[15] have reported $AE_4Cr_2N_6$ (AE = Ca, Sr) synthesized from such a melt, and Yamane and co-workers have reported that the inclusion of first-row transition-metal additives in Na/Ga melts influences the crystal growth of wurtzite-type gallium nitride with some incorporation of manganese into the crystals.[23] Nitrides containing second-row early metals such as molybdenum have been synthesized using Na/Ga melts by DiSalvo and co-workers.[24] In our investigations, iron appears not to be incorporated as described above; however, the inclusion of vanadium powder in the reaction mixture did yield black crystals of a compound with an apparent cubic lattice parameter of 3.95 Å and containing V and Ga in a 3:1 ratio according to the results of EDX studies, and tentatively identified as the anti-perovskite $GaNV_3$, analogous to $ZnNFe_3$ and $InNFe_3$.[25] Upon close inspection of the single-crystal diffraction pattern, this compound appears to be an anti-perovskite subtly distorted from cubic symmetry and has not yet been characterized fully. The inclusion of manganese powder in reactions containing graphite powder has yielded crystals of a new, and apparently gallium-free, strontium manganese nitride carbodiimide of approximate composition $Sr_3MnX_3(CN_2)_{0.3}$ (where X is a first-row anion) containing triangular MnX_3 anions, although we have thus far been unable to characterize this compound satisfactorily on account of crystallographic disorder of the carbodiimide units.

Discussion

Comparison of the Structures of Sr_4GaN_3O and $Sr_4GaN_3(CN_2)$. The structures of the two compounds are shown in Figure 1. Both contain slabs that may be formulated as $[Sr_4GaN_3]^{2+}$. These contain isolated triangular $[GaN_3]^{6-}$ anions with mean Ga−N bond distances of 1.900 Å (standard deviation of 0.020 Å) for Sr_4GaN_3O and 1.905 Å (standard deviation of 0.009 Å) for $Sr_4GaN_3(CN_2)$, which are consistent with the distances of 1.938(7) and 1.895(10) Å determined for the equilateral triangular units observed in Sr_3GaN_3 and Sr_6GaN_5, respectively.[3] The GaN_3 triangular units observed here are planar within experimental uncertainty. These triangular units are arranged in a herringbone fashion when

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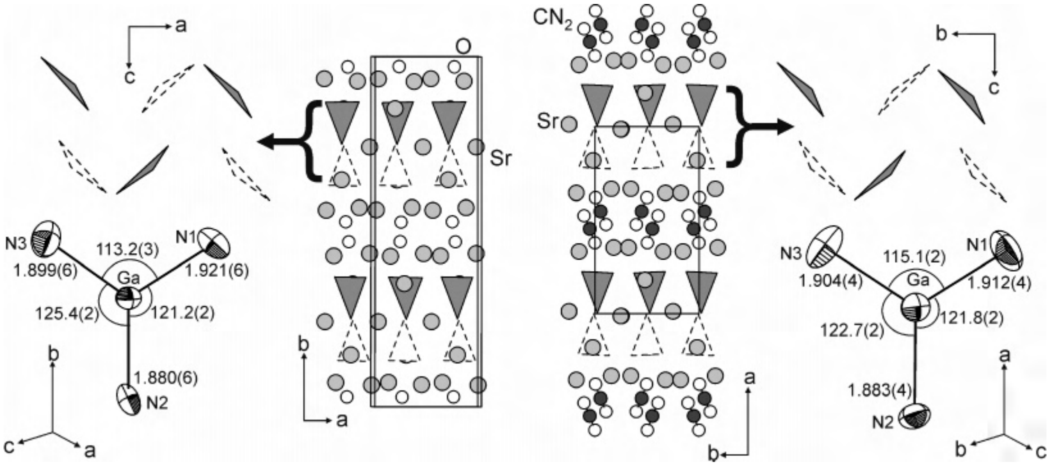

Figure 1. Crystal structures of Sr_4GaN_3O (left) and $Sr_4GaN_3(CN_2)$ (right) obtained from refinement against single-crystal X-ray diffraction data collected at 150 K. The upper details show the similar relative arrangements of the isolated $[GaN_3]^{6-}$ anions in the $[Sr_4GaN_3]^{2+}$ slabs of two structures: the dashed triangles indicate the lower layer of GaN_3 units, which point up, and the solid triangles indicate the upper layer of GaN_3 units, which point down. The lower details show the bond lengths (in Å), bond angles (in degrees), and displacement ellipsoids (99% level) for the triangular $[GaN_3]^{6-}$ anions in the two compounds.

Table 6. Results of Madelung Potential Calculations for $Sr_4GaN_3O^a$

	Madelung potential/V			
site	O on site O	O on site N1	O on site N2	O on site N3
Sr1	−18.76	−24.06	−27.81	−22.44
Sr2	−18.96	−16.68	−15.57	−16.22
Sr3	−19.02	−21.74	−27.11	−23.54
Sr4	−18.37	−12.93	−4.88	−13.40
Ga	−35.01	−29.44	−26.67	−29.36
O	17.36	18.05	13.65	18.19
N1	29.58	24.79	30.38	30.16
N2	31.38	36.58	36.04	36.43
N3	29.63	30.07	30.14	24.70
energy per formula unit/kJ mol^{-1}	−27100	−26186	−25344	−26195

[a] An explanation of the table appears in the text. Calculations were carried out using the EUTAX package.[26]

viewed perpendicular to the slabs, and within the slabs, one can define two layers of GaN_3 triangles, which point in opposite directions as shown in Figure 1. These slabs are separated by either oxide (in Sr_4GaN_3O) or carbodiimide (in $Sr_4GaN_3(CN_2)$) ions, which are coordinated solely by strontium ions. With the constraint that the metals are fully oxidized and the anion sites are fully occupied (see above), we apportion the oxide and nitride anions between the four anion sites in Sr_4GaN_3O on the following basis: the similarity of the two structures suggests the formal substitution of the divalent oxide ion in Sr_4GaN_3O by the divalent carbodiimide ion in $Sr_4GaN_3(CN_2)$, the GaX_3 triangles are very similar to those observed previously in nitrides,[3] and the ion designated as oxide in Sr_4GaN_3O is coordinated only by the highly electropositive and oxophilic strontium. Furthermore, Madelung potential calculations (Table 6) carried out using the EUTAX program[26] supported the location of oxygen on the anion site exclusively coordinated by strontium rather than on any of the other anion sites: four calculations were carried out, with O^{2-} placed on each anion site in turn and with N^{3-} occupying the other sites. The sets of potentials with O on one of sites N1, N2, or N3 are inconsistent with the expectation[27] that the potential ϕ_i in volts at any ion site i will scale with the charge on the ion q_i according to $\phi_i = -\alpha q_i$, where α takes a value of 9−12 depending on the inverse of the ionic radius. Furthermore, according to the calculations, location of O on the site solely coordinated by Sr yielded the lowest energy per formula unit by 3.4% over the nearest alternative (Table 6).

Attempts to synthesize a single-phase powder sample of Sr_4GaN_3O using reactions between stoichiometric quantities of Sr_2N, SrO, and GaN under flowing nitrogen gas at 900 °C were unsuccessful, with the X-ray powder diffractograms of the resulting multiphase products giving no match with the calculated pattern of Sr_4GaN_3O. Also, we were not able to synthesize larger single crystals, so we have been unable to employ neutron diffraction techniques to address experimentally the question of O/N order versus disorder in this compound. The coordination environments for the anions in both compounds are shown in Figure 2. In both compounds, one of the nitride anions (N2) is in almost octahedral (NSr_5Ga) coordination, and the other two nitride ions (N1 and N3), which complete the Ga coordination sphere, are best described as 7-coordinate, with Sr−N distances of up to 3.26 Å in Sr_4GaN_3O and 3.208 Å in $Sr_4GaN_3(CN_2)$ included in the coordination sphere. The oxide ion in Sr_4GaN_3O is also 7-coordinate, and one can identify eight Sr^{2+} cations, which coordinate the $[CN_2]^{2-}$ anion in $Sr_4GaN_3(CN_2)$.

The displacement ellipsoid for the oxide ion Sr_4GaN_3O is larger than that for the other ions, reflecting the fact that the site is larger than is ideal for this ion. The bond valence sum calculated by EUTAX[26] for oxide located at the center of this site is 1.0, compared with mean values of 1.4 for the Sr ions, 2.4 for the nitride ions, and 2.5 for the Ga ions. The ion identified as carbodiimide in $Sr_4GaN_3(CN_2)$ has been observed previously in the syntheses carried out using molten sodium as a growth medium for nitrides. Indeed, in the reactions carried out as part of this work in which additional carbon was added to the reaction mixture, a large proportion

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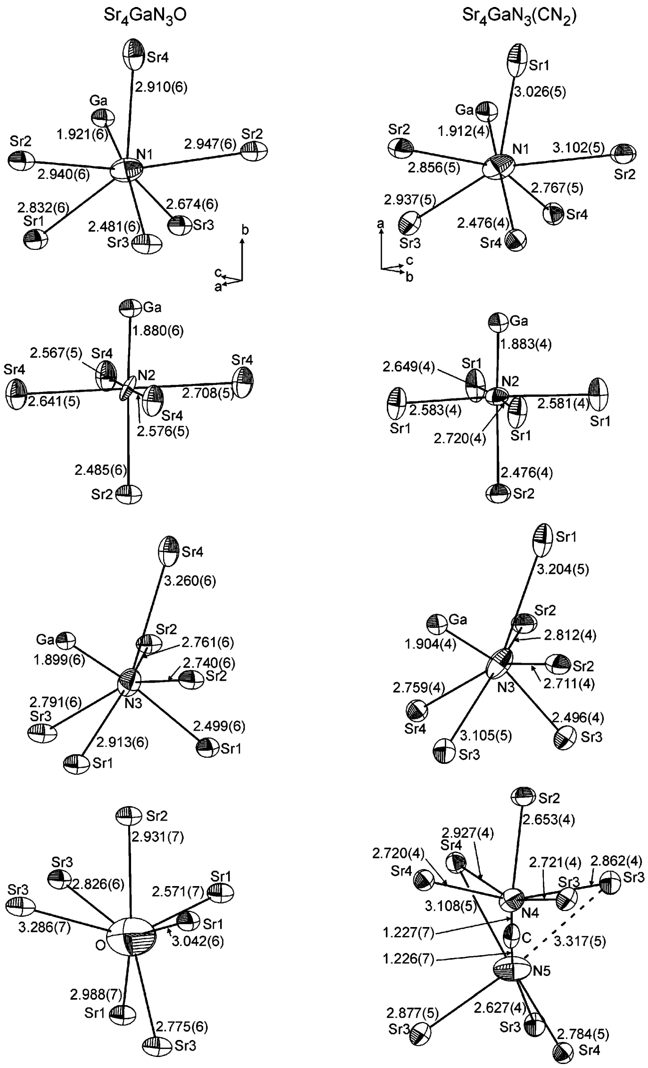

Figure 2. Anion coordination environments in Sr_4GaN_3O (left) and $Sr_4GaN_3(CN_2)$ (right). 99% displacement ellipsoids are shown.

of the product consisted of crystals of the binary carbodiimide $Sr(CN_2)$[28] as well as $Sr_4GaN_3(CN_2)$. Although azide is present in the reaction mixture, the reactions are carried out at temperatures far in excess of that at which sodium azide decomposes to the elements. The carbodiimide ion in $Sr_4GaN_3(CN_2)$ is very symmetrical, with bond lengths of 1.226(7) and 1.227(7) Å, which compare closely with those in other carbodiimides[29] including $Sr(CN_2)$ (C−N distances of 1.228 and 1.222 Å)[28] and the recently reported $Mn(CN_2)$ (identical C−N distances of 1.227 Å).[30] The azide ion has shorter N−N distances (1.17 Å in the two forms of NaN_3).[31] The correct assignment of the almost linear anion (N−C−N angle of 173.6°) in $Ba_9(NbN_4)_2O(CN_2)$ as a carbodiimide is discussed in ref 32. The $[CN_2]^{2-}$ anion in $Sr_4GaN_3(CN_2)$ is also not quite linear: the bond angle is 174.8(6)°, presumably as a consequence of packing effects in the crystal. The displacement ellipsoid of the carbon atom in the $[CN_2]^{2-}$ anion in $Sr_4GaN_3(CN_2)$ is slightly elongated along the direction of the C−N bonds, as is also found in $Ba_9(NbN_4)_2O(CN_2)$.[32] It is possible that this indicates a slight asymmetry in the carbodiimide anion, which is disordered in the crystal. A survey of carbodiimides and cyanamides carried out by Dronskowski[33] and co-workers[34] and backed up by density functional theory calculations concludes that the energy cost associated with a small shift of the C atom away from the center of the anion is small and, furthermore, that deviations of the bond angle by 5° from linearity [as observed in $Sr_4GaN_3(CN_2)$] are even less significant. The two compounds reported here represent, to the best of our knowledge, the second example of a pair of compounds that have similar structures except for the replacement of oxide by carbodiimide or cyanamide. Meyer and co-workers[35] recently reported the synthesis and structure of the compound $LaCl(CN_2)$ with a structure related to the PbFCl-type structure of LaOCl. We attempted to synthesize a third compound analogous to Sr_4GaN_3O and $Sr_4GaN_3(CN_2)$ containing the imide ion $[NH]^{2-}$ in place of oxide or carbodiimide by the reaction of a stoichiometric mixture of strontium and gallium metals with flowing ammonia (99.98%, BOC) at 800 °C (two treatments of 6 h with intermediate regrinding). However, the only identifiable crystalline product in the X-ray powder diffraction pattern was α-SrNH.[36,37]

Conclusions

Two compounds containing very similar slabs $[Sr_4GaN_3]^{2+}$, containing triangular $[GaN_3]^{6-}$ units, have been identified, and these may be "pillared" by either oxide or carbodiimide anions. These robust slabs suggest the possible synthesis of other structurally related intergrowth compounds. Preliminary results suggest that when both gallium and sodium are present in the melt, early transition metals may be incorporated into the nitride products.

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Supporting Information Available: X-ray crystallographic data for Sr_4GaN_3O and $Sr_4GaN_3(CN_2)$ (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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