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Sr_4N_3: A Hitherto Missing Member in the Nitrogen Pressure Reaction Series $Sr_2N \rightarrow Sr_4N_3 \rightarrow SrN \rightarrow SrN_2$**

Yurii Prots, Gudrun Auffermann, Michael Tovar, and Rüdiger Kniep*

In the course of our investigations on the formation and existence of diazenides of strontium,[1] we developed an analytical method for quantitative nitrogen speciation.[2] By means of this technique (carrier-gas hot extraction with a controlled temperature program), we could confirm the results of the structure determinations on SrN ($\widehat{=}(Sr^{2+})_4[N^{3-}]_2[N_2^{2-}]$) and $Sr[N_2]$ ($\widehat{=}(Sr^{2+})[N_2^{2-}]$). The system was calibrated by using, for example, Sr_2N[3] (the starting material of the high-pressure synthesis of diazenides).[1] In the course of our studies, it turned out that Sr_2N, synthesized at ambient pressure, often contains significant portions of diazenide which were not clearly visible by X-ray or spectroscopic investigations.[4] In principle, these experimental results would be consistent with a homogeneity range of Sr_2N towards SrN according to (partial) formation of mixed crystals $Sr_{2-x}N$ (complete miscibility in the limits $0 \leq x \leq 1$), although previous studies[1] had provided "no indication for homogeneity ranges" of the nitride diazenides. In fact, we now find that at lower N_2 reaction pressure (already above 1 bar), Sr_2N reacts to the hitherto "overlooked" nitride–diazenide Sr_4N_3.

Sr_4N_3, a dark gray powder with metallic luster, was synthesized in autoclaves[5] by the reaction of Sr_2N with molecular nitrogen (9 bar) at 650 °C for 6 h.[6] No impurities were detected by X-ray and neutron diffraction investigations[7] at ambient pressure nor by chemical analysis.[9] The contents of oxygen, hydrogen, and carbon were below the limits of detection. At constant reaction temperature (650 °C) and time (6 h), the diffraction pattern of Sr_4N_3 was observed up to a reaction pressure of 100 bar amongst the characteristic reflections of SrN. The lattice parameters of Sr_4N_3 and SrN, determined at ambient pressure, remained unchanged within the standard deviations.

The crystal structure of the air- and moisture-sensitive microcrystalline powder of Sr_4N_3 was solved by a combination of X-ray and neutron diffraction.[7] The observed and calculated neutron diffraction diagram, as well as the difference profile, are given in Figure 1. The crystal structure of Sr_4N_3 is depicted in Figure 2 (center) showing the close relation to the starting material Sr_2N (left) and the next higher "pressure stage" SrN (right). The evident structural relation makes it reasonable to suppose the reaction paths during the formation of Sr_4N_3 via an intercalation step.[10] Thus, these structural chemical facts can easily be described when starting with the subnitride Sr_2N[3] as the host structure ($CdCl_2$ type). In the first step of the N_2-pressure induced intercalation which occurs already at about 1 bar (p_{N_2}), one half of the octahedral holes ($\square^{(o)}$) between two adjacent layers $^2_\infty(Sr_{6/3}N)$ along [001] in the host structure, are occupied by N_2. Thus, packages of

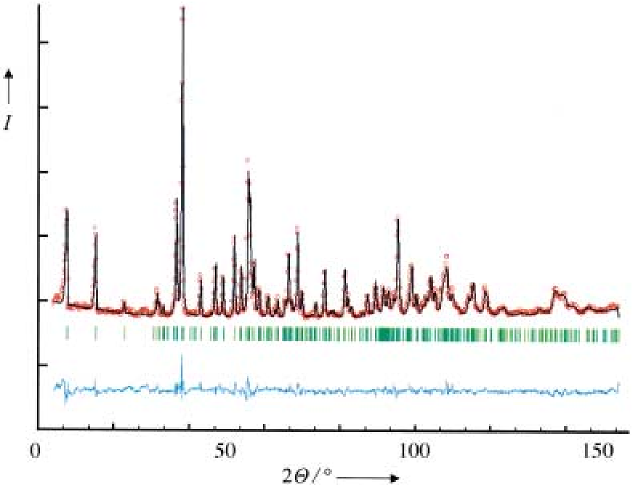

Figure 1. Neutron diffraction diagram of $Sr_4N_3 \widehat{=} Sr_8[N]_4[N_2]$ (powder diffractometer E9, HMI Berlin) at 298 K: Observed (red dots), calculated (black solid line), and difference profiles (blue line). The green ticks mark the positions of the Bragg reflections of the monoclinic C-centered cell.[7]

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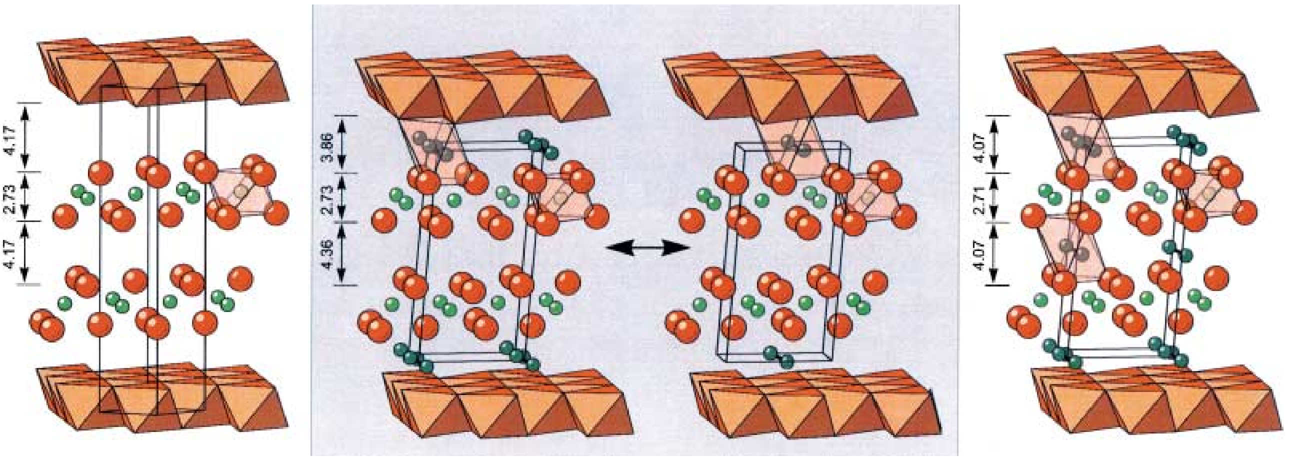

Figure 2. Crystal structures of $Sr_2N \hat{=} (Sr^{+1.5})_2[N^{3-}]$ (left), $Sr_4N_3 \hat{=} (Sr^{+1.5})_4(Sr^{2+})_4[N^{3-}]_4[N_2{}^{2-}]$ (center) and $SrN \hat{=} (Sr^{2+})_4[N^{3-}]_2[N_2{}^{2-}]$ (right). The top and bottom boundaries of the figures are represented by layers of $Sr_{6/3}N$ octahedra centered by $[N^{3-}]$ (polyhedral representation). Ball-and-stick representation between the polyhedral layers: $Sr^{+1.5/2+}$: red; $[N^{3-}]$: light green; $[N_2{}^{2-}]$: dark green. Transparent octahedra allow a better orientation. On the assumption of ordered N_2 occupation, the two limiting primitive structures of Sr_4N_3 are emphasized by the gray background; in fact, a C-centered cell with half-occupation of the octahedral holes is found (see text and [7]). The numbers (in Å) correspond to the *d* values of neighboring Sr layers. Although the thicknesses of the layers of the unoccupied octahedral layers in Sr_4N_3 (4.36 Å) are significantly larger than those in Sr_2N (4.17 Å), the interatomic distances Sr–Sr between the Sr layers are in a comparable order of magnitude (Sr_2N: 4.73; Sr_4N_3: 4.73, 4.78, and 4.83 Å).

layers $\{(Sr_{6/3}N)\square^{(o)}_{0.5}[N_2]^{(o)}_{0.5}(Sr_{6/3}N)\}$ are formed leading to the composition Sr_4N_3. These packages contain the diazenide ion $N_2{}^{2-}$ (N=N bond length: 1.22 Å), and the closely coordinating strontium ions are oxidized from oxidation state +1.5 (host: $(Sr^{+1.5})_2\,[N^{3-}]$) to +2. This results in layered packages with the ionic formula **1**:

$$\ldots\square^{(o)}_{0.5}\,\square^{(o)}_{0.5}\{(Sr^{+1.5}_{3/3}N^{3-}Sr^{2+}_{3/3})\square^{(o)}_{0.5}[N_2{}^{2-}]\square^{(o)}_{0.5}(Sr^{2+}_{3/3}N^{3-}Sr^{+1.5}_{3/3})\}\square^{(o)}_{0.5}\,\square^{(o)}_{0.5}\ldots \qquad \mathbf{1}$$

The strontium ions at the boundaries of the packages are in the low-valent oxidation state +1.5 and form together with the adjacent $Sr^{+1.5}$ layers the (metallic) subregions with unoccupied octahedral holes.

In the first intercalation step (formation of Sr_4N_3), the diazenide dumbbells can, in principle, occupy two octahedral holes within the layers (Figure 2 (center); see also ionic formula **1**). Evidently, the spatial separation of the diazenide layers ($c = 13.76$ Å) makes an alternative occupation of the octahedral holes possible although, within every layer, the same kind of octahedral holes are always occupied. In fact, the diffraction pattern indicates a C-centered space group, thus leading to a half-occupation of all the octahedral holes by the N_2 species.[7] The octahedral holes between neighboring $Sr^{+1.5}$ layers remain empty.

X-ray investigations showed that, already at a N_2 reaction pressure of 10 bar ($T = 650\,°C$) the second intercalation stage (SrN;[1] Figure 2, right) can be identified besides Sr_4N_3. For the formation of this state, additionally, one half of the empty octahedral holes between the $Sr^{+1.5}$ double layers are occupied in an ordered manner: $\{Sr^{+1.5}_4Sr^{2+}_4[N^{3-}]_4[N_2{}^{2-}]\} + N_2 \rightarrow \{Sr^{2+}_8[N^{3-}]_4[N_2{}^{2-}]\}[N_2{}^{2-}]$. The stepwise oxidation of strontium is now finished. At higher N_2 reaction pressure (above 500 bar), besides SrN, the tetragonal diazenide $Sr[N_2]$[1] is formed (close structural relationship to the monoclinic $Ba[N_2]$),[11] which is obtained as a single-phase product above 5000 bar (p_{N_2}).

It has already been reported[1] that SrN and $Sr[N_2]$ thermally decompose (300–400 °C) at ambient pressure under argon to give Sr_2N (release of molecular nitrogen). Sr_4N_3 reacts in the same way. Interestingly, in this connection, the analytically ascertained contents of diazenides in Sr_2N[2] are obviously caused by "impurities" of Sr_4N_3. Analytically pure Sr_2N, prepared from the elements at ambient pressure, will certainly be obtained only after additional treatment (650 °C) in vacuum (10^{-6} bar). This finding would be consistent, on the basis of the close structural relations, with a deintercalation process, although our investigations on the preservation of topochemical host–guest relations for intercalation and deintercalation in the system Sr–N, are not yet finished.[10]

Sr_4N_3 belongs to the class of subcompounds with metallic character, a property which, for example, for the binary subnitride Ba_3N[12] is described with the following formula: $[Ba^{2+}]_3[N^{3-}] \cdot 3\,e^-$. Applying this to the strontium–subnitride–diazenide results in the formula $(Sr^{2+})_8[N^{3-}]_4[N_2{}^{2-}] \cdot 2\,e^-$, which does not reflect the peculiarity of the crystal chemistry of strontium (**1** and Figure 2, center). Therefore, we prefer, for the elucidation of the obviously mixed-valent Sr compound, the formula $(Sr^{+1.5})_4(Sr^{2+})_4[N^{3-}]_4[N_2{}^{2-}]$. This formula is not only consistent with the crystal structure, it also makes it readily apparent which of the Sr species, in the course of the reduction process of molecular nitrogen, are oxidized to Sr^{2+} during the formation of the second intercalation stage (SrN; see Figure 2 right). To answer the question of the real existence of "low-valent" strontium, additional experimental and theoretical studies are necessary.

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[6] Sr_4N_3 was synthesized by heating Sr_2N (prepared at 1120 K from the elements) in a molybdenum boat under a N_2 atmosphere (Messer Griesheim, given purity 99.999%, purified by oxisorb-catridges, Messer Griesheim) for 6 h at 920 K in an autoclave.[5] An initial pressure of 8 bar (corresponding to a reaction pressure of 9 bar) led to nearly single-phase Sr_4N_3. The course of the reaction was steadily controlled by a pressure gauge.

[7] Neutron diffraction experiments were carried out on the powder diffractometer E9 at the reactor BER II of the HMI Berlin. Sr_4N_3 was placed under argon into a cylindrical vanadium container (diameter 8 mm, length 47 mm, wall thickness 0.15 mm) and was closed with a cap containing an indium seal. Crystal structure data derived from neutron diffraction experiments with the wavelength $\lambda = 1.7965$ Å in the range $2° < 2\theta < 158°$ at 298 K and 2 K: monoclinic, space group $C2/m$, $Z = 2$; 298 K: $a = 6.7070(4)$, $b = 3.8280(2)$, $c = 13.7625(8)$ Å, $\beta = 96.519(5)°$, $V = 351.05(3)$ Å^3; Sr1 in (4*i*): $x = 0.413(1)$, $z = 0.1413(4)$; Sr2 in (4*i*): $x = 0.127(1)$, $z = 0.3406(3)$; N1 in (4*i*): $x = 0.775(1)$, $z = 0.2515(4)$; N2 in (4*i*): $x = 0.083(1)$, $z = 0.0217(6)$, occupancy factor = 0.5; $R_{profile} = 0.055$, $R_{Bragg} = 0.053$, number of observed reflections: 272. 2 K: $a = 6.6886(3)$, $b = 3.8173(2)$, $c = 13.7382(6)$ Å, $\beta = 96.447(3)°$, $V = 348.55(3)$ Å^3; Sr1 in (4*i*): $x = 0.4133(7)$, $z = 0.1412(3)$; Sr2 in (4*i*): x = 0.1290(7), $z = 0.3413(3)$; N1 in (4*i*): $x = 0.7748(6)$, $z = 0.2483(3)$; N2 in (4*i*): $x = 0.0850(8)$, $z = 0.0234(4)$, occupancy factor = 0.5; $R_{profile} = 0.066$, $R_{Bragg} = 0.047$, number of observed reflections: 261. The refinements were carried out using the program Fullprof.[8] Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-412394 and CSD-412395.

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[9] The nonmetallic components N, O, H, C were quantitatively determined by the carrier-gas hot extraction or combustion technique (TC 436 DR/5, RH 404 and C200CHLH (LECO)): Sr_4N_3 (N_{exp} 10.86(8), N_{calcd} 10.71 wt%). Si_3N_4 was used as a calibration standard. Impurities of O, H, and C were not detected (limits of detection: C < 0.1; H < 0.005; O < 0.05 wt%). Using a temperature ramping from 500–1500 K, it was not only possible to determine the nitrogen content[2] in $Sr_4N_3 \mathrel{\hat{=}} (Sr^{+1.5})_4(Sr^{2+})_4[N^{3-}]_4\ [N_2^{2-}]$ but also to quantify the two different nitrogen species in the molar ratio of 2:1.

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Ones, Thiones, and *N*-Oxides: An Exercise in Imidazole Chemistry**

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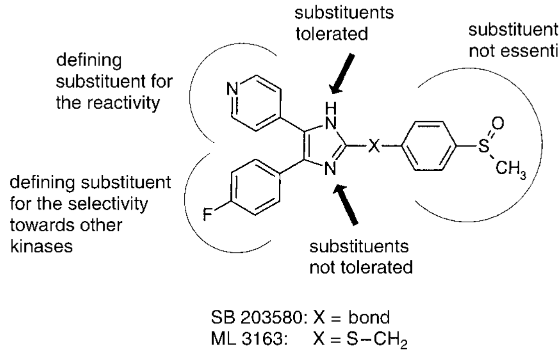
Dedicated to Prof. Dr. Wolfgang Wiegrebe on the occasion of his 70th birthday

The inhibition of the proinflammatory cytokines interleukin 1β (IL-1β) and tumor-necrosis factor α (TNF-α) has been recognized as a rewarding target for the development of tailor-made anti-inflammatory drugs.[1] Among the most promising small-molecular anticytokine agents are inhibitors of p38 MAP kinase, a serine/threonine-specific kinase involved in the biosynthesis and release of cytokines from immunocells.[2a] Like other potent inhibitors of p38 MAP kinase, our lead compound ML 3163 was derived from 5-(pyridin-4-yl)imidazole (SB 203580; Scheme 1), which binds to the ATP-binding site of the p38 kinase,[2b] and has demonstrated efficacy in various models.[2c] In the development of pharmaceuticals, in addition to bioactivity, the issues of bioavailability and toxicity must be addressed. For example, further development of SB 203580 itself has been obstructed by its liver toxicity, which is caused by interaction with cytochrome P450 (P450).[2d] Therefore, it is of general interest to the medicinal chemist to have a straightforward synthetic methodology which provides access to a large number of bioactive candidate molecules.



Scheme 1. Structural requirements for inhibition of p38 MAP kinase.

Herein we describe such a versatile synthetic strategy for the ready preparation of numerous structurally diverse

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