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SrN and SrN_2: Diazenides by Synthesis under High N_2-Pressure**

Gudrun Auffermann, Yurii Prots, and Rüdiger Kniep*

In the binary system Sr – N, only the existence of Sr_2N is certain.[1] This compound crystallizes in the $CdCl_2$ structure (layers of octahedra, Figure 1 left). Reports on a binary phase with the stoichiometry "SrN"[2] were corrected afterwards as these solids also contained hydrogen or carbon.[1, 3]

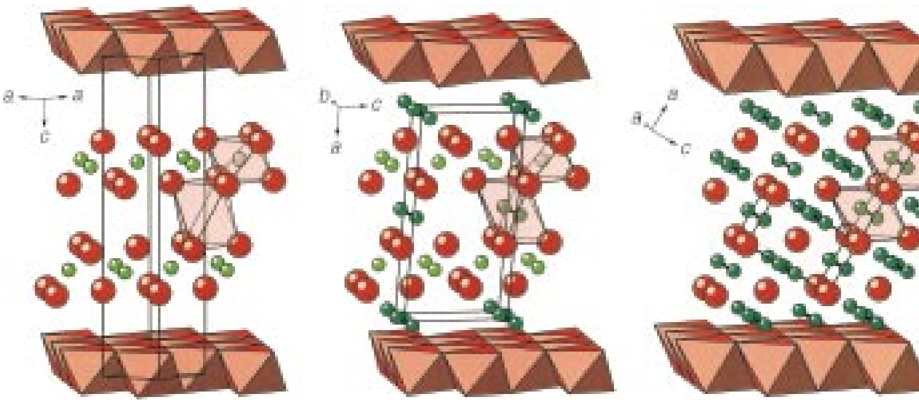

Figure 1. Crystal structures of Sr_2N (left), $SrN \mathrel{\hat{=}} (Sr^{2+})_4[N^{3-}]_2[N_2^{2-}]$ (center), and $SrN_2 \mathrel{\hat{=}} Sr^{2+}[N_2^{2-}]$ (right). The top and bottom boundaries of the figures are represented by layers of $Sr_{6/3}$ octahedra (polyhedral representation), occupied by $[N^{3-}]$ (Sr_2N, SrN) or $[N_2^{2-}]$ (SrN_2), respectively. Ball-and-stick representations between the polyhedral layers: Sr^{2+}, red; $[N^{3-}]$, light green; $[N_2^{2-}]$, dark green. The transparent octahedra contribute to a better visualization.

Recently, we carried out high-pressure experiments for the preparation of strontium – nitrogen compounds using our modified high-pressure equipment, which was originally constructed by Bronger and Auffermann[4] for the syntheses of extremely air- and moisture-sensitive metal hydrides and hydridometalates.

Using Sr_2N (blue-black powder with metallic luster) as the starting material (reaction temperature 920 K, reaction time 72 h), we obtained single-phase SrN (black-gray powder) under an N_2 pressure of 400 bar and single-phase SrN_2 (brown powder) under an N_2 pressure of 5500 bar.[5] No impurities of the phases were detected by X-ray and neutron diffraction investigations at ambient pressure[6] nor by chemical analysis.[12] The contents of carbon, hydrogen, and oxygen were below the detection limits.

The crystal structures of SrN and SrN_2 were solved by a combination of X-ray and neutron diffraction experiments on air- and moisture-sensitive microcrystalline powders.[6] The neutron diffraction diagrams (observed, calculated, and difference profile) are given in Figure 2. The crystal structures

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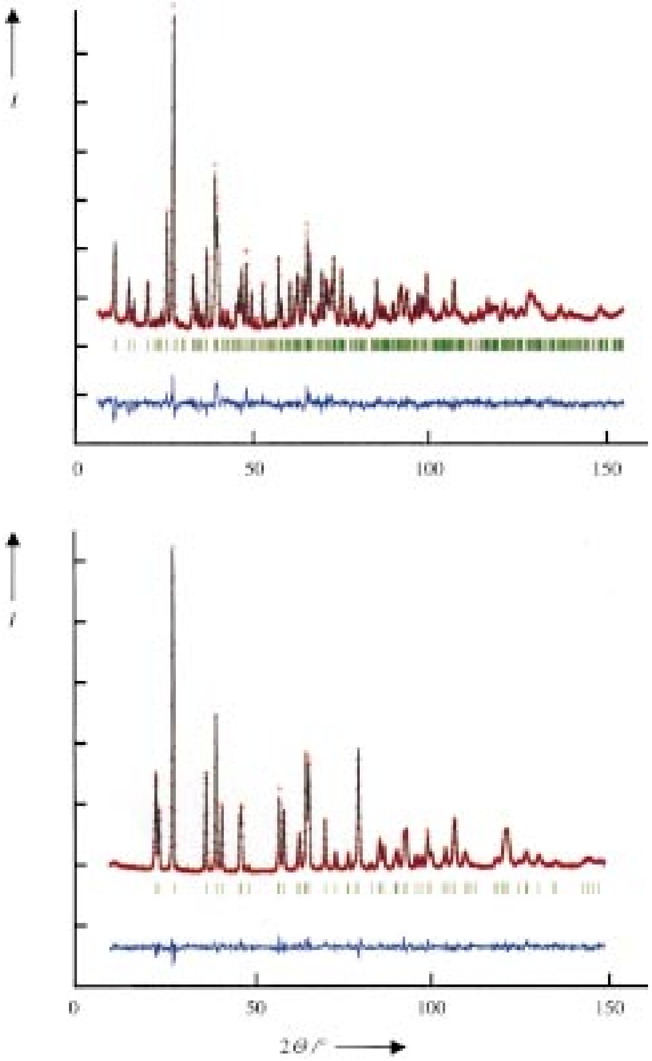

Figure 2. Neutron diffraction diagrams (298 K) of SrN (top) and SrN_2 (bottom).[6] The observed (red dots), calculated (black solid lines), and difference profiles (blue) are shown. The green ticks mark the positions of the Bragg reflections.

(Figure 1; center and right) can be topologically deduced from Sr_2N ($\rho_{\text{X-ray}} = 3.5\,\text{g}\,\text{cm}^{-3}$): at medium pressure (formation of SrN; $\rho_{\text{X-ray}} = 3.8\,\text{g}\,\text{cm}^{-3}$), one half of the free octahedral holes between the Sr_2N layers are occupied by diazenide ions in an ordered manner; consequently, the Sr_2N layers shift their positions relative to each other (monoclinic unit cell). The high-pressure conditions lead to a tetragonal phase (SrN_2; $\rho_{\text{X-ray}} = 4.2\,\text{g}\,\text{cm}^{-3}$; isotypic relation to the analogous modifications of the alkaline earth acetylides EA[C_2][13]) in which all octahedral holes of the nearly close-packed Sr matrix are occupied by [N_2^{2-}] ions.

Molecular nitrogen oxidizes strontium (oxidation state "+1.5" in Sr_2N) already at comparatively low nitrogen pressure (400 bar) to Sr^{2+} and is itself reduced to the level of the diazenide [N_2^{2-}]. De facto SrN is a nitride–diazenide $(Sr^{2+})_4[N^{3-}]_2[N_2^{2-}]$. Whether this step will lead to a better understanding of the effect of the catalyst in the Haber–Bosch process has still to be resolved.

Certainly, the formation of SrN_2 from Sr_2N proceeds via SrN as intermediate because, at a pressure below 5500 bar, mixtures of SrN and SrN_2 were obtained. No indication for homogenity ranges of the compounds was observed.[6, 12] Only use of an elevated pressure of 5500 bar gives the pure diazenide (SrN_2) as a single-phase product. From these results, one can conclude that a comproportionation reaction ($2[N^{3-}] + 2\,N_2 \rightarrow 3[N_2^{2-}]$) is of crucial importance in the formation of $Sr^{2+}[N_2^{2-}]$ from SrN ($\widehat{=} (Sr^{2+})_4[N^{3-}]_2[N_2^{2-}]$).

Thermal decomposition of SrN and SrN_2 takes place (argon; ambient pressure; Netzsch TG/DTA STA409; heating rate 5 K min^{-1}) in the temperature range from 573–673 K and 618–673 K, respectively. These processes are associated with the release of molecular nitrogen and the formation of Sr_2N. The reactions ($(Sr^{2+})_4[N^{3-}]_2[N_2^{2-}] \rightarrow Sr_2N + 1.5\,N_2$), which correspond to internal redox reactions, are in accordance with the oxidation state "$Sr^{+1.5}$" in the final product, Sr_2N.

In the crystal structures of SrN and SrN_2, the N–N distances in the diazenide units ($\bar{N}{=}\bar{N}^{2-}$) are 1.225(5) and 1.224(2) Å, respectively. These values are in good agreement with the N–N bond length of 1.236(3) Å observed in the diazenide-bridged complex $[MoCp^*Me_3](\mu\text{-}N_2)[WCp'Me_3]$ ($Cp^* = C_5Me_5$; $Cp' = C_5H_4Me$)[14] and, as expected, are significantly shorter than the N–N bond length in the protonated diazene ($[\mu\text{-}N_2H_2\{Fe(\text{“}N_HS_4\text{”})\}_2]$; N–N: 1.300(7) Å).[15]

The main focus of this contribution lies in the preparative and chemical aspects. Detailed descriptions of the crystal structures, as well as the magnetic susceptibility measurements (the investigations show a weak temperature-independent paramagnetism for all three compounds), will be given in a future paper.[11] Up to now, Raman spectra of the diazenides could not be recorded owing to the low thermal stability at ambient pressure. Our investigations on the system Ba–N also show the formation of diazenides under elevated nitrogen pressure.[16]

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[6] Neutron diffraction experiments were carried out on the high-resolution powder diffractometer E9 at the reactor BER II of the Hahn-Meitner-Institut, Berlin.[7] The samples were placed under argon into cylindrical vanadium containers (diameter: 8 mm (SrN) and 6 mm (SrN_2), length: 51 mm, wall thickness: 0.15 mm) and closed with a cap containing an indium seal. Two experiments were carried

out for both compounds with the wavelengths $\lambda = 1.7965(1)$ and $\lambda = 1.3066(1)$ Å in the range $2° < 2\theta < 158°$. Crystal structure data for $\mathrm{SrN_2}$ at 298 K derived from neutron diffraction experiments: tetragonal, space group *I*4/*mmm* (no. 139), $a = 3.8136(3)$, $c = 6.2855(4)$ Å, $V = 91.4(1)$ Å^3, $Z = 2$; Sr in (2a); N in (4e), $z = 0.4026(2)$; $R_{\text{profile}} = 0.0422$, $R_{\text{Bragg}} = 0.0358$; number of observed reflections: 61. Crystal structure data for SrN at 298 K from neutron diffraction experiments: monoclinic, space group *C*2/*m* (12), $a = 13.472(1)$, $b = 3.8121(3)$, $c = 6.7284(5)$ Å, $\beta = 94.720(1)°$, $V = 344.4(1)$ Å^3, $Z = 8$, Sr1 in (4i) $x = 0.1541(3)$, $z = 0.3926(7)$; Sr2 in (4i) x = 0.3561(4), $z = 0.0922(6)$; N1 in (4i) $x = 0.2442(3)$, $z = 0.7487(6)$; N2 in (4i) $x = 0.0223(3)$, $z = 0.0830(6)$; $R_{\text{profile}} = 0.0527$, $R_{\text{Bragg}} = 0.0663$; number of observed reflections: 690. The refinements have been carried out using the programs WinPLOTR[8] and FULLPROF.[9] The following scattering lengths were used: Sr 7.02 fm; N 9.36 fm.[10] 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-411555, and CSD-411556.

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[12] The nonmetallic components (N, O, H, C) were quantitatively determined by carrier-gas-hot-extraction or combustion techniques (TC 436 DR/5, RH 404 and C-200 CHLH (LECO)): SrN [N exp. 13.9(2) wt%, calcd 13.84 wt%]; $\mathrm{SrN_2}$ [N exp. 24.5(2) wt%, calcd 24.23 wt%]. Impurities of O, H, and C were not detected [detection limits: C < 0.1 wt%, H < 0.005 wt%, O < 0.05 wt%]. In $(\mathrm{Sr^{2+}})_4[\mathrm{N^{3-}}]_2[\mathrm{N_2^{2-}}]$, the existence of two different nitrogen species with the molar ratio 1:1 became obvious by temperature ramping (700–800 K) during the determination of the nitrogen content. As expected, only one maximum was observed for $\mathrm{Sr^{2+}}[\mathrm{N_2^{2-}}]$ and $(\mathrm{Sr}^{\text{“}1.5+\text{”}})_2[\mathrm{N^{3-}}]$ indicating the evidence of only one nitrogen species in each case.

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Dendron-Controlled Nucleation and Growth of Gold Nanoparticles**

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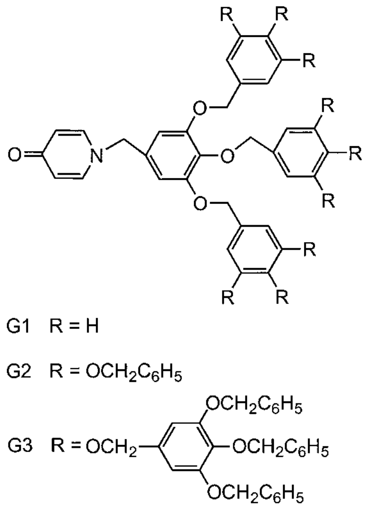
Nanoclusters of metals and semiconductors—which exhibit unusual size-dependent electronic, magnetic, optical, and catalytic properties due to the onset of “quantum effects”—are being heralded as the next generation of building blocks for designing modern materials.[1] However, these particles are metastable and cannot be isolated or manipulated without appropriate stabilization by organic capping ligands.[2] Various functionalized organic arrays including protein cages,[3] polymer matrices,[4] and surfactant vesicles[5] have been used previously to form nanoparticles by encapsulation. A more recent development is the use of polyamidoamine (PAMAM) dendrimers[6]—a class of highly branched, monodisperse, and globular synthetic polymers—to passivate nanoclusters of zero-valent metals,[7] metal oxides,[8] and metal sulfides.[8, 9] However, a simple relationship between particle size and dendrimer generation was not established.[10]

In contrast to classical dendrimers such as the PAMAM species, a dendron is a segment of dendrimer that possesses a focal point onto which the branching units of a dendritic architecture are attached.[11] If the focal moiety is capable of metal complexation, the specific metal–dendron interactions can be utilized to control reactions at this site.[12] We envision that such reactivity control in a confined and localized area may be used for the controlled growth and stabilization of nanoparticles. Such a concept is validated here with the production of gold nanocrystals using dendrons G1–G3 with a focal 4-pyridone functionality[13] as capping agents.



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