Na_3N—An Original Synthetic Route for a Long Sought After Binary Nitride

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Binary compounds and the binary phase diagrams of metals and nonmetals have been investigated thoroughly since the infancy of modern chemistry, metallography, and materials science. Still, in the last couple of years, a number of new binary compounds were reported, these new phases being mainly compounds of nitrogen. A common feature of these binary nitrides is that all were prepared using new or so far seldom used synthetic techniques. For example, the compound FeN was introduced into the iron–nitrogen phase diagram only few years ago. FeN was prepared by reactive sputtering of iron in an Ar/N_2 atmosphere.[1] Sn_3N_4 forms from SnI_4 with KNH_2 in liquid ammonia, followed by careful annealing at 300 °C.[2] The pressure-homologues rule connects the spinel with the recently reported high-pressure phases γ-Si_3N_4[3] and γ-Ge_3N_4,[4] produced by high-pressure high-temperature syntheses in laser-heated diamond anvil cells or multi-anvil arrangements. Binary nitrides of phosphorus have been known since the 19th Century,[5] but only in the middle of the 1990s were α- and β-P_3N_5 prepared (from a molecular precusor) in crystalline form and structurally characterized.[6] A high-pressure phase γ-P_3N_5 was prepared from a high-pressure high-temperature synthesis in a multi-anvil arrangement.[7] The diazenides (or pernitrides) $SrN{=}Sr_4[N]_2[N_2]$, $Sr[N_2]$,[8] and $Ba[N_2]$[9] were obtained for the first time under high nitrogen-gas-pressures of 400 bar to 5500 bar, while the barium compound apparently also can be prepared under low pressure by careful decomposition of barium azide. The diazenides can be considered as analogues of the peroxides and thus, together with the long-known azide ions, link the series to the polynitrogen compounds and ions, such as N_4[10] and N_5^+ (which was stabilized with the anion of a super acid, $N_5^+AsF_6^-$).[11]

From the alkali-metal nitrides only Li_3N was well characterized. Even at room temperature, Li_3N slowly forms from the elements and was studied intensively as a result of its potential application as a fast lithium ionic conductor.[12] The crystal structure of α-Li_3N was described as early as 1935:[13] it consists of parallel infinite chains $^1_\infty[\mathrm{LiN}_{2/2}{}^{2-}]$, arranged in a hexagonal-rod packing motif. These chains are connected by further lithium atoms, which leads to a hexagonal-bipyramidal coordination of the nitrogen atoms (Figure 1 a). This arrangement results in a low space filling and thus, it is not surprising, that two high-pressure polymorphs were described to date.[14]

The previous reports on the binary nitrides of the heavier alkali metals, on the other hand, seem doubtful. First hints of the formation of K_3N from the thermal decomposition of KNH_2 date back to the classical work on the isolation of alkali metals by Davy as well as Gay-Lussac and Thénard, performed at the beginning of the 19th Century.[15] Zehnder reported the formation of compounds from sodium and nitrogen after the activation of the elements by electric discharge, however, he suspected that the product obtained was sodium azide rather than sodium nitride.[16] In the following decades of the beginning 20th Century a lengthy dispute started, as to whether the obtained moisture-sensitive products contain a binary nitride. Most of the experimentalists tried to activate the nitrogen with electric discharges, but also reactions in the presence of iron as a catalyst, the decomposition of the azides, or the reaction of alkali-metal amalgams with nitrogen were investigated.[17] Typically, the argument for a successful formation of the nitride was the reaction of aqueous solutions of the reaction products with Neßlers reagent, but the possibility of a reduction of azide ions by hydrogen (from excess alkali metal and water) to ammonia could not be completely excluded. In summary, the reports of the successful preparation of binary nitrides of the heavier alkali metals Na, K, and Cs by any of these ways could never be reproduced without any doubt.

In this issue of *Angewandte Chemie* Fischer and Jansen finally report the successful preparation of Na_3N by an original synthetic route:[18] within a vacuum chamber the elements were transferred to the gas phase in an atomic state. The components were simultaneously deposited on a cooled substrate. In this way an optimal mixing of the components in the solid state was obtained. On heating to room temperature, apparently crystalline Na_3N formed, which is extremely moisture sensitive. The derived crystal structure of the anti-ReO_3 type has a surprisingly low space filling (Figure 1 b). The seemingly unusual linear coordination of sodium by nitrogen can be found analogously in the crystal structure of α-Li_3N, in which one third of the lithium atoms are linearly coordinated by nitrogen atoms. The decreasing coordination number of nitrogen from eight in α-Li_3N to six in Na_3N in the anti-ReO_3 type is reasonable, since sodium has a larger radius than lithium.

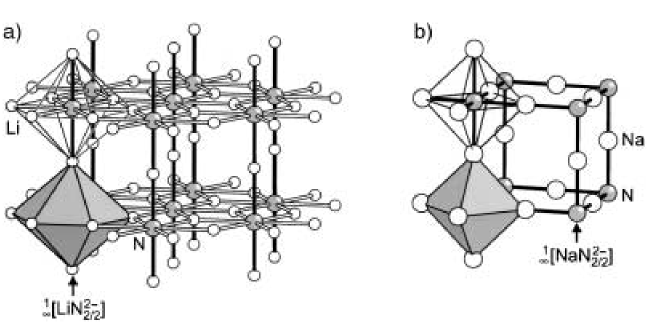

Figure 1. Sections of the crystal structures of a) α-Li_3N with parallel, one-dimensional infinite chains $^1_\infty[\mathrm{LiN}_{2/2}{}^{2-}]$ and nitrogen atoms in hexagonal-bipyramidal coordination and b) Na_3N (anti-ReO_3 structure type) with nitrogen atoms in octahedral coordination and one-dimensional infinite chains $^1_\infty[\mathrm{NaN}_{2/2}{}^{2-}]$ in all three directions.

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Jansen and co-workers have been involved in the prediction of the crystal structures of the binary alkali-metal nitrides for some time.[19] Interestingly, in the course of these studies the anti-ReO$_3$ type for the nitrides of Na, K, Rb, and Cs was not considered. From that fact it can be taken, that this structure type was not to be expected for Na$_3$N. Taking the synthetic conditions into account, one has to assume metastability for the obtained form of Na$_3$N. Since Na$_3$N was prepared only as a film on a sapphire substrate and since it is extremely moisture sensitive, no physical properties were determined so far. Surely, interesting results are to be expected.

With the synthetic technique presented by Fischer and Jansen it might be feasible to prepare the binary nitrides of K, Rb, and Cs, too. With the development of new synthetic routes further new (especially metastable) compounds of nitrogen might be expected in the near future. Such new compounds will inevitably have surprising structural chemistry and physical properties and, thus, provide new impulses in solid-state chemistry.

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Oligomerization of p53 upon Cooperative DNA Binding: Towards a Structural Understanding of p53 Function

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P53 is one of the most important gene products involved in cancer suppression, and has concomitantly been an interesting target for oncology research.[1] Despite its high pharmaceutical relevance, one of the basic biological principles of p53, its activation from a latent state to an active DNA-binding state, is still unclear. A recent paper now sheds light on some of the structural features associated with p53 activation and DNA binding.[2] The p53 protein is present in nonstressed cells in a latent form and at very low concentration. However, under different stress conditions—such as DNA damage, oncogene activation, hypoxia, or ribonucleotide depletion—it accumulates in the cell and is activated.[3] The activation of the p53 protein leads either to arrest of the cell cycle or to apoptosis.[4] The outcome of p53 activation, which is cell-type and/or stress dependent, prevents the damaged cells from dividing: p53 is a tumour-suppressor gene. Several lines of evidence show that the deletion or the mutation of the p53 gene favors development of cancer: mice homozygotes with inactivated p53 allele are highly sensitive to tumors,[5] p53 is mutated in about 50 % of the human cancers,[6] and p53 germline mutations are associated with the Li – Fraumeni syndrome.[7]

Although part of the p53 activity is mediated by protein – protein interactions, much of it is linked to its ability to bind to DNA and to regulate the transcription of several genes. P53 is a transcription factor and, like other transcription factors, contains several domains: a transactivation and proline-rich domain (residues 1 – 43 and 61 – 94, respectively) at the N-terminus; a DNA-binding domain in the middle of the protein (residues 110 – 286); and a tetramerization domain (residues 326 – 355) and a regulatory region (residues 363 – 393) at the C-terminus of the protein. While no structure of full-length p53 is known, structures have been determined for the individual domains by X-ray structure analysis or NMR spectroscopy (Figure 1). In particular, the determination of

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