

# A New Route to Metal Azides\*\*

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 80th birthday

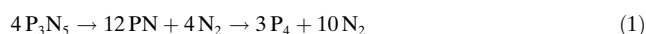
**Abstract:** Beside several other applications, metal azides can be used for the synthesis of nitridophosphates and binary nitrides. Herein we present a novel synthetic access to azides: Several metals, such as main-group, transition metals, and rare-earth metals, react with silver azide in liquid ammonia as a solvent giving the corresponding metal azides. In this work  $Mn(N_3)_2$ ,  $Sn(N_3)_2$ , and  $Eu(N_3)_2$ , as well as their ammonia complexes were synthesized for the first time through low-temperature methods. Also a simpler access to  $Zn(N_3)_2$  was possible. At room temperature and the respective vapor pressure of  $NH_3$ , it became possible to grow single crystals of the dinuclear holmium azide  $[Ho_2(\mu-NH_2)_3-(NH_3)_{10}](N_3)_3 \cdot 1.25 NH_3$ . We are confident that this new route could lead to novel metal azides as well as nitrides of the main-group, the transition, and the rare-earth metals upon careful decomposition.

The synthetic approach to hydrazoic acid and simple metal azides (e.g.  $NaN_3$ ) deriving from  $HN_3$  were discovered during the pioneering work of Theodor Curtius at the end of the 19th century.<sup>[1]</sup> However, it was only in the mid-1960s that chemists began to look at  $HN_3$  and its derivative compounds in more detail. Presumably, the severely explosive decomposition of most metal azides, especially the more covalent ones, and of  $HN_3$  itself, may have discouraged any further investigation.<sup>[1]</sup>

More recently, azides have moved into research targeting high-energy density materials (HEDM), thus exhibiting an expanding field of applications and a promising potential for chemical syntheses. As pseudohalides the structural–chemical properties comparison of azides, carbodiimides, cyanides,

cyanates, and thiocyanates is an interesting field. Especially as most of the crystal structures of transition-metal cyanides, carbodiimides, cyanates, and thiocyanates are hitherto unknown, whereas substantial progress has been made in the field of transition-metal azides. Thus,  $Mo(N_3)_6$ ,  $W(N_3)_6$ ,<sup>[2]</sup> and  $Ti(N_3)_4$ <sup>[3]</sup> were synthesized and structurally characterized as well as some new high-explosive main-group azides (e.g.  $As(N_3)_5$ ,  $Sb(N_3)_3$ ,<sup>[4]</sup>  $Bi(N_3)_3$ ,<sup>[5]</sup>  $(P_3N)(N_3)_3$ ,<sup>[6]</sup> or  $Te(N_3)_4$ ).<sup>[7]</sup> Other transition-metal azides, such as  $Nb(N_3)_5$  or  $Ta(N_3)_5$ , are difficult to synthesize and a full characterization has been hampered by their highly explosive character.<sup>[8]</sup> Another modern application of azides employs the high synthetic potential of these compounds in organic syntheses,<sup>[9]</sup> for example, the Curtius reaction or click cycloadditions.<sup>[10]</sup>

During the last few years, we have successfully utilized metal azides for the synthesis of novel nitridophosphates<sup>[11–13]</sup> and binary nitrides.<sup>[14]</sup> High  $N_2$  partial pressures, resulting in situ from thermolysis reactions of azides, have been used frequently in our synthetic approaches to synthesize metal-containing nitridophosphates starting from the respective metal azide and  $P_3N_5$ . Thereby phosphorus nitride  $P_3N_5$  (thermal decomposition  $>850^\circ C$  at normal pressure) is prevented from dissociating into the elements [Eq. (1)] at



the high reaction temperatures of above  $1000^\circ C$  that are indispensable for the crystallization of the targeted metal nitridophosphates.<sup>[11,12]</sup>

To expand this “azide route” to a more generalized synthetic approach, it was necessary to make pure azides of a wider choice of metals available. Interestingly, many of these potential compounds have never been synthesized in quantities larger than a few milligrams. Especially, many azides with oxophilic and hydrophilic cations are to date completely unknown.

Herein we describe the synthesis of the ammonia complexes and the pure, solvent-free, binary metal azides  $Mn(N_3)_2$ ,<sup>[15]</sup>  $Sn(N_3)_2$ ,  $Eu(N_3)_2$ , and  $Zn(N_3)_2$  utilizing a new synthetic approach: Electropositive metals (M) undergo a stoichiometric redox reaction with silver azide<sup>[16–18]</sup> while being dissolved in liquid and absolutely water-free ammonia [Eq. (2)].



According to our experience this redox reaction cannot be carried out in aqueous solutions or suspensions, because under such conditions the azide ions would be reduced to  $NH_3$

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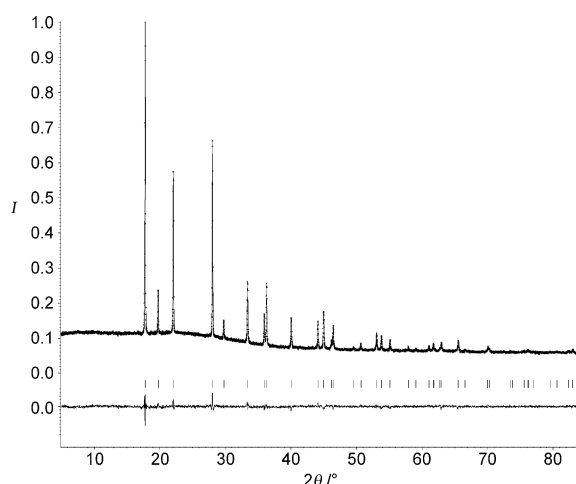
[\*\*] We thank Dipl.-Chem. Florian Pucher, Ludwig-Maximilians-Universität München, and B.Sc. Georg Monsch, Technische Universität München, for their preparative work. Generous financial support by the Fonds der Chemischen Industrie (FCI) and the Deutsche Forschungsgemeinschaft (DFG), project SCHN 377/11-1, is gratefully acknowledged. F.K. thanks the DFG for a Heisenberg fellowship.

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and stable aqua or oxo complexes of the respective metals would be formed.

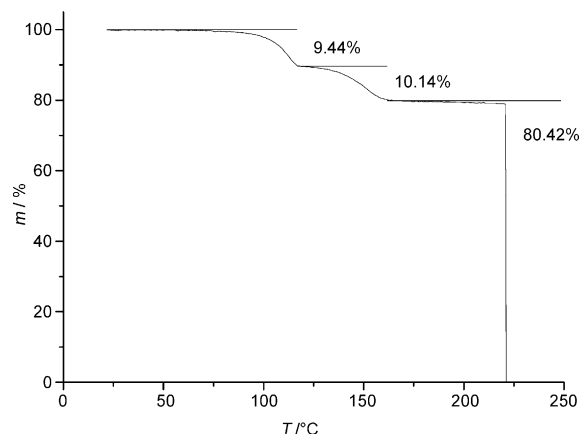
The redox reactions of silver azide and metals ( $M = \text{Mn}, \text{Sn}, \text{Zn}, \text{Eu}$ ) require a reaction time between 9 and 10 days at  $-40^\circ\text{C}$ . The reaction rates at  $-40^\circ\text{C}$  are slow though the redox potentials of Ag and the respective metal  $M$  differ significantly. In this case the reaction mixtures were intensively stirred using a magnetic stirrer when all  $\text{AgN}_3$  is dissolved (after approximately one day). As long as there is a residue of  $\text{AgN}_3$  the vessel only should be shaken very gently to prevent silver azide grains to be ground at the glass wall of the vessel. Crust formation occurring at the fluid level and consisting of silver azide at the beginning of the reaction and the respective metal azide at the end of the reaction have to be carefully scraped off the glass every day with a Teflon spatula. The scraping has to be performed with extreme care to prevent the highly hazardous, friction and shock sensitive azides (especially silver azide and tin azide) detonating. The elemental silver, which is generated by the redox reaction [Eq. (2)], has to be separated from the azide solution by filtration at  $-40^\circ\text{C}$ . After evaporation of  $\text{NH}_3$ , the raw metal azide products were obtained. Chemical analyses, X-ray powder diffraction, and FTIR-spectroscopy showed that  $\text{Sn}(\text{N}_3)_2$  and  $\text{Eu}(\text{N}_3)_2$  were obtained as amorphous and undefined complexes (in terms of their  $\text{NH}_3$  content), whereas well-crystallized and phase-pure  $\text{Mn}(\text{N}_3)_2(\text{NH}_3)_2$  and  $\text{Zn}(\text{N}_3)_2(\text{NH}_3)_2$ <sup>[19–21]</sup> were obtained as powders in the first reaction step. The crystal structure of  $\text{Zn}(\text{N}_3)_2(\text{NH}_3)_2$ , already described,<sup>[19]</sup> was verified for the bulk material by a Rietveld refinement. Through powder X-ray diffraction (Figure 1), the crystal structure of  $\text{Mn}(\text{N}_3)_2(\text{NH}_3)_2$  was obtained.  $\text{Mn}(\text{N}_3)_2(\text{NH}_3)_2$  crystallizes in the tetragonal space group  $I4/m$  and is isotypic to  $\text{Mg}(\text{N}_3)_2(\text{NH}_3)_2$ .<sup>[22]</sup>

Finally, the powders of the metal azide ammonia complexes ( $M = \text{Mn}, \text{Sn}, \text{Zn}, \text{Eu}$ ) were treated in high vacuum ( $2 \times 10^{-6}$  mbar) for several days at temperatures between 40 and  $110^\circ\text{C}$  to liberate  $\text{NH}_3$ . During these procedures explosions



**Figure 1.** Observed (crosses) and calculated (gray line) X-ray powder diffraction pattern of  $\text{Mn}(\text{N}_3)_2(\text{NH}_3)_2$ . Positions of Bragg reflections (vertical lines), difference profile for the Rietveld refinement (black line).

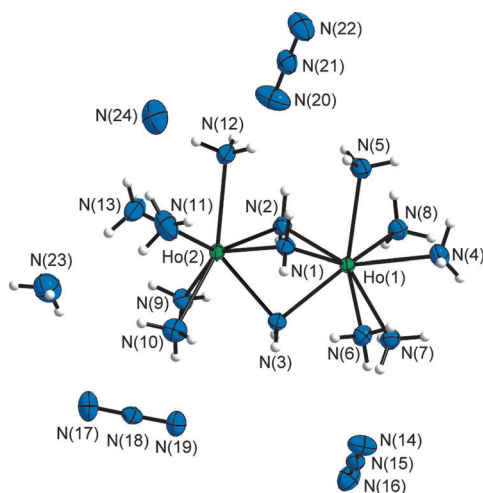
can easily be avoided by limiting the heating rate to below  $1^\circ\text{Cmin}^{-1}$ . The compounds  $\text{Mn}(\text{N}_3)_2$ ,  $\text{Sn}(\text{N}_3)_2$ , and  $\text{Zn}(\text{N}_3)_2$  were obtained as colorless powders, which readily undergo severe explosions.  $\text{Eu}(\text{N}_3)_2$  was obtained as an explosive and deep yellow powder. To our knowledge binary  $\text{Sn}(\text{N}_3)_2$  and  $\text{Eu}(\text{N}_3)_2$  have never been described in the literature.  $\text{Mn}(\text{N}_3)_2$ ,  $\text{Sn}(\text{N}_3)_2$ ,  $\text{Eu}(\text{N}_3)_2$ , and  $\text{Zn}(\text{N}_3)_2$  were unequivocally identified as solvent-free azides by FTIR-spectroscopy. Thermogravimetric analysis of  $\text{Mn}(\text{N}_3)_2(\text{NH}_3)_2$  shows decomposition in three steps (Figure 2). The first two steps marking the



**Figure 2.** Thermogravimetric analysis of  $\text{Mn}(\text{N}_3)_2(\text{NH}_3)_2$ . All percentages are in relation to the initial mass of  $\text{Mn}(\text{N}_3)_2(\text{NH}_3)_2$ .

elimination of ammonia molecules, whereas the last step can be unequivocally identified as exothermic decomposition of binary  $\text{Mn}(\text{N}_3)_2$ . The chemical formulae of the binary azides were calculated from the results of elemental analyses.

Considering that no single crystals of the ammonia complexes, but only microcrystalline or amorphous powders were obtained after several days of reaction time by the low-temperature method, the reaction was carried out in a glass ampule at room temperature and the respective vapor pressure of 8.5 bar. By choosing these conditions, the reactions proceeded to completion within several hours. The above mentioned azides were then isolated as described above. This method successfully yielded single crystals in the case of holmium after an additional storage of only four days at room temperature. The colorless crystals grew on the precipitated elemental silver. These were identified by single-crystal X-ray diffraction (details can be found in the Supporting Information) as dinuclear ammine complexes of holmium azide:  $[\text{Ho}_2(\mu\text{-NH}_2)_3(\text{NH}_3)_{10}(\text{N}_3)_3] \cdot 1.25\text{NH}_3$ . The asymmetric unit of tris- $\mu$ -amido decaammine diholmium(III) triazide ammonia (1/1.25) is shown in Figure 3. Two holmium atoms are bridged by three amide ligands. Five ammine ligands at each metal atom complete the coordination sphere. The  $\text{Ho-NH}_2$  distances are in the range 2.361(2) and 2.441(2) Å and are, of course, shorter than the  $\text{Ho-NH}_3$  distances which are between 2.543(2) and 2.606(2) Å. Three azide ions are found as counterions with N–N bond lengths around 1.17 Å. Two ammonia molecules of crystallization are present, whereof one of them is partially occupied (25 %).



**Figure 3.** View of the asymmetric unit of  $[\text{Ho}_2(\mu\text{-NH}_2)_3\text{-(NH}_3\text{)}_{10}](\text{N}_3)_3 \cdot 1.25\text{NH}_3$ . Thermal ellipsoids are set at 70% probability at 123 K, hydrogen atoms isotropic with arbitrary radii.<sup>[27]</sup>

In summary, the above described two methods afford the preparation of metal azides of the main-group, the transition metals, and the rare-earth metals. For the first time,  $\text{Sn}(\text{N}_3)_2$ , and  $\text{Eu}(\text{N}_3)_2$ , as well as their ammine complexes and the  $\text{NH}_3$  complexes of Mn and Ho azide, were synthesized and made available for subsequent investigations and syntheses.  $\text{Zn}(\text{N}_3)_2$  was obtained with our method in higher purity (free of solvent) and in a simpler way avoiding the use of  $\text{HN}_3$ .<sup>[23,24]</sup> In addition, a dinuclear ammine complex of holmium azide was synthesized and characterized by the determination of its single-crystal structure. We predict that this approach can be expanded to a number of further electropositive metals; currently, this new route is under investigation with further transition and rare-earth metals as well as some actinoids. The methods proposed herein expand on the currently available routes for the synthesis of azides from fluorides and trimethylsilyl azide.<sup>[25,26]</sup>

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