

Metal Azides

Binary Zinc Azides

Axel Schulz^[a, b] and Alexander Villinger^{*[a]}

Abstract: Pure, solvent-free $Zn(N_3)_2$ was prepared by reaction of diethyl zinc and hydrazoic acid in aprotic solvents. The single-crystal structure determination, along with the comprehensive characterization of α -Zn(N₃)₂ and two metastable polymorphs, could be achieved for the first time.

Introduction

Zinc azide, $Zn(N_3)_2$, has been known for more than 100 years, and its existence never been doubted.^[1,2] However, a closer look into the literature reveals that zinc azide has scarcely been characterized, and dependent on the method of preparation, only inconclusive or even contradictory analytical data can be found, while structural information is completely missing.^[3] First attempts to prepare $Zn(N_3)_2$ by aqueous methods were carried out by Curtius and Rissom in 1898.^[1] However, the reactions of elemental zinc with aqueous hydrazoic acid HN₃, or treatment of barium azide with zinc sulfate in water, always resulted in the precipitation of basic zinc azides $Zn(OH)_{2-x}(N_3)_x$ (x=0.9-1.0), which indicates that $Zn(N_3)_2$ is easily hydrolyzed in solution (Scheme 1).^[1,4c]

$$Zn \xrightarrow[(2-x)]{2 + N_{3(aq)}}_{H_{2}O} Zn(N_{3})_{2(aq)} \xrightarrow[H_{2}O]{BaSO_{4}} ZnSO_{4}$$

$$(2-x) H_{2}O \bigvee (-(2-x) H_{N_{3}})_{2(aq)} Zn(OH)_{2-x}(N_{3})_{x} x = 0.9 - 1.0$$

Scheme 1. Synthesis of aqueous $Zn(N_3)_2$ and hydrolysis to $Zn(OH)_{2-x}(N_3)_x$.

The formation of such non-stoichiometric zinc hydroxide azides was later confirmed by several groups, and it proved difficult to obtain the pure parent compound $Zn(OH)N_3$ (x=1), since x can take all values between 0.67 and 1.0, depending on the reaction conditions and sample preparation.^[4,5] Nevertheless, in 1957, Feitknecht and Zschaler could demonstrate on

[a]	Prof. Dr. A. Schulz, Dr. A. Villinger
	Institut für Chemie, Universität Rostock
	Albert-Einstein-Strasse 3a, 18059 Rostock (Germany)
	E-mail: alexander.villinger@uni-rostock.de
[b]	Prof. Dr. A. Schulz
	Abteilung Materialdesign
	Leibniz-Institut für Katalyse e.V. an der Universität Rostock
	Albert-Einstein-Strasse 29a, 18059 Rostock (Germany)
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Since these data disagree in large parts with the known, previously reported values, all previous syntheses of $Zn(N_3)_2$, and for comparison $Zn(N_3)_2$.2.5 H₂O and $Zn(OH)N_3$ were reinvestigated, indicating that some of the earlier work has to be revised.

the basis of powder X-ray data that a specific $Zn(OH)N_3$ phase, which obeys this exact constitution, can be prepared.^[5]

The first successful isolation of hydrated zinc azide with the putative formula $Zn(N_3)_2 \cdot 2H_2O$, obtained from the reaction of basic zinc carbonate $Zn_5(CO_3)_2(OH)_6$ and excess hydrazoic acid in water, was reported by Sood and Yoganarasimhan in 1971 (Scheme 2).^[6] Already in 1975, the composition was corrected to $Zn(N_3)_2 \cdot 3H_2O$ on the basis of powder X-ray diffraction data by Krischner and Winkler.^[7] Finally, more than 20 years later, a single-crystal structure determination by Krischner and Mautner revealed that the correct formula corresponds to $Zn(N_3)_2 \cdot 2.5 H_2O$.^[8]

$$\begin{aligned} & Zn_{5}(OH)_{6}(CO_{3})_{2} \xrightarrow{4P_{2}O} 5 Zn(N_{3})_{2} \cdot 2.5 H_{2}O \\ & Zn(NO_{3})_{2} \xrightarrow{2 KN_{3}} Zn(N_{3})_{2} \cdot 2 NH_{3} \xrightarrow{2 AgN_{3}} Zn \\ & Zn(NO_{3})_{2} \xrightarrow{2 KN_{3}} Zn(N_{3})_{2} \cdot 2 NH_{3} \xrightarrow{4P_{2}O_{10}} Zn(N_{3})_{2} \cdot 2.5 H_{2}O \\ & Zn(N_{3})_{2} \cdot 2 NH_{3} \xrightarrow{4P_{2}O_{10}} Zn(N_{3})_{2} \xrightarrow{4P_{2}O_{10}} Zn(N_{3})_{2} \cdot 2.5 H_{2}O \\ & Zn(OH)N_{3} \xrightarrow{HN_{3}} Zn(N_{3})_{2} \xrightarrow{4P_{2}O_{10}} Zn(N_{3})_{2} \xrightarrow{4P_{2}O_{10}} Zn(N_{3})_{2} \xrightarrow{4P_{2}O_{10}} Zn(N_{3})_{2} \cdot 2.5 H_{2}O \\ & Zn(OH)N_{3} \xrightarrow{HN_{3}} Zn(N_{3})_{2} \xrightarrow{4P_{2}O_{10}} Zn(N_{3})_{2} \xrightarrow{4P_{2}O_{10}} ZnCO_{3} \end{aligned}$$

Scheme 2. Preparation of $Zn(N_3)_2 \cdot 2.5 H_2O$, $Zn(N_3)_2 \cdot 2 NH_3$, and $Zn(N_3)_2$.

The analogous ammonia compound $Zn(N_3)_2 \cdot 2 NH_3$ has been known since 1907,^[9a] and is conveniently prepared by the reaction of potassium azide and zinc nitrate in liquid ammonia, as shown by Agrell and Vannerberg.^[9c] In 1971, they were able to determine the single-crystal structure, which displays a molecular assembly of tetrahedrally coordinated zinc centers in the solid state.^[9b,c] Only recently, Schnick, Kraus, and co-workers presented a new synthesis for $Zn(N_3)_2 \cdot 2 NH_3$, starting from elemental zinc and silver azide in liquid ammonia (Scheme 2).^[2] Furthermore, it could be demonstrated that thermal treatment in vacuo for several days resulted in the release of ammonia, yielding zinc azide with an approximate purity of 95 %,^[2, 10] as deduced from elemental analysis and IR spectroscopy. However, no further analytical data was supplied. Likewise, the dehy-

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dration of zinc azide hydrate with P_4O_{10} was described by Yoganarasimhan et al. (Scheme 2), and beside a correct elemental composition, DTA data (DTA = differential thermal analysis), IR spectra, and powder diffraction data were reported.^[11] In contrast, Winkler and Krischner found that zinc azide obtained by dehydration still contained a considerable amount of hydroxide and water, which was further supported by the published IR data.^[12]

As early as 1917, the synthesis of binary $Zn(N_3)_2$ was achieved by Wöhler and Martin in the reaction of freshly prepared zinc carbonate or basic zinc azide with dry, ethereal hydrazoic acid (Scheme 2).^[13] Zinc azide prepared by this procedure was found to contain only negligible amounts of hydroxide groups or residual water, and was very sensitive to friction and shock, as was later confirmed by Winkler and Krischner.^[12] Moreover, the latter were able to record powder X-ray diffraction data, which, however, differed considerably from the earlier data published by Yoganarasimhan and Jain (see above).^[11a,12]

Results and Discussion

Synthesis of Zn(N₃)₂

As already mentioned by Richter, it appears that pure zinc azide has never been isolated, because all methods of preparation involved water or nucleophilic solvents at some stage.^[14] To exclude hydrolysis during the synthesis, we decided to prepare binary zinc azide by means of an alkyl/azide exchange reaction in diethyl zinc (Scheme 3).^[15]

$$ZnEt_{2} \xrightarrow[-2 \text{ EHH}]{2 \text{ HN}_{3}} Zn(N_{3})_{2} \xrightarrow[-2 \text{ EHH}]{2 \text{ HN}_{3}} Zn(N_{3})_{2}$$

Scheme 3. Preparation of solvent-free Zn(N₃)₂.

In a first attempt, an excess of hydrazoic acid HN₃, generated by reaction of stearic acid and sodium azide in the melt, was condensed onto a frozen solution of commercially available diethyl zinc in n-hexane in vacuo. Upon warming to ambient temperature the vigorous formation of a voluminous precipitate was instantly observed, which was easily separated from the solvent by decantation followed by drying at 70 °C in vacuo. Colorless Zn(N₃)₂ prepared this way, was found to be highly amorphous; however, subsequent thermal treatment in fluorobenzene at 120°C for 12 h under endogenous pressure in a sealed glass ampoule yielded a microcrystalline material, which was well suitable for powder X-ray diffraction (Supporting Information, Figure S1).^[15] Finally, we found that $Zn(N_3)_2$ is more conveniently prepared by simple addition of ZnEt₂ in *n*hexane to a stirred solution of dry ethereal hydrazoic acid (1 M) at 0° C (Scheme 3). The reaction also proceeded within a few seconds, and after workup, pure, microcrystalline zinc azide (yields: 90-95%) is obtained, which proved to be identical to the material obtained before, as deduced from the powder diffraction data. The latter could be indexed in accord with the monoclinic space group $P2_1/n$, which differs however from the published data of Yoganarasimhan and Jain, as well as Winkler and Krischner, both providing orthorhombic, yet different lattice parameters.^[15,11a,12] This discrepancy provoked us to re-examine the previously reported syntheses of $Zn(N_3)_2$.

Therefore, we intended the direct syntheses of $Zn(N_3)_2$ ·2.5 H₂O and $Zn(N_3)_2$ ·2.NH₃ starting from $Zn(N_3)_2$ in the corresponding solvent (Scheme 3).^[15] While the NH₃ diadduct could easily be prepared by dissolution of neat $Zn(N_3)_2$ in liquid ammonia at -40 °C, followed by slow evaporation of solvent, the preparation of the analogous hydrate compound proofed somewhat more elaborate. If a saturated solution of zinc azide in aqueous concentrated hydrazoic acid (5 m) was allowed to cool slowly from 60 °C to ambient temperature, surprisingly, the deposition of large colorless needlelike crystals of $Zn(N_3)_2$, suited for single crystal X-ray structure determination, instead of the expected $Zn(N_3)_2$ ·2.5 H₂O was observed (Figure 1). However, the envisaged zinc azide hydrate, was also



Figure 1. Left: Perspective view of the one-dimensional chains of α -Zn(N₃)₂ in the crystal (view along [001]). Right: (top) ORTEP of the coordination sphere of α -Zn(N₃)₂ in the crystal. Ellipsoids set at 50% probability at 173 K (symmetry codes: (i) x+1, y, z; (ii) -x+1, -y, -z+1). Right (bottom): Perspective view of the unit cell of α -Zn(N₃)₂ (view along [100]).

accessible in good yields as colorless needle-like crystals by the same procedure, if diluted hydrazoic acid (2-3 m) was applied (Scheme 3). In accordance with previous reports, we observed that aqueous solutions of $Zn(N_3)_{27}$, which were not acidified with HN₃, readily precipitated highly amorphous basic zinc azide with the approximate composition $Zn(OH)_{2-x}(N_3)_x$ (x = 0.8–0.9) upon evaporation of solvent.^[15] Besides β -Zn(OH)N₃, which could be obtained by very slow evaporation of an aqueous solution of $Zn(N_3)_2$ for several days, we found that thermal treatment of amorphous basic zinc azides at 120°C for five days in a PTFE coated steel autoclave resulted in the formation of microcrystalline α -Zn(OH)N₃, which was well-suited for powder X-ray diffraction. In accord with the findings by Feitknecht and Zschaler, the data could be indexed and studied by means of a Rietveld refinement in the trigonal space group $R\bar{3}m$ (see below).^[15] However, a structure solution of α -Zn(OH)N₃ by charge-flipping and successive difference Fourier syntheses in the alternative polar space group R3m, suggests the presence of ordered N₃/OH layers in the structure, in analogy to β -Zn(OH)N₃ which could be refined in space group $P6_3mc$, in accord with the previous reports (Figure 4).^[5,15] In contrast, the N₃/OH positions in the structure of α -Zn(OH)N₃



were necessarily statistically disordered in the centrosymmetric space group $R\bar{3}m$ (Supporting Information, Table S6).^[5,15]

In agreement with the previous findings, both Zn(N₃)₂·2NH₃ and Zn(N₃)₂·2.5 H₂O released the vast bulk of solvent upon thermal treatment in vacuo at 60-130 °C, and 60-100 °C, respectively.^[2, 11, 12] Astonishingly, the material obtained this way, just as the product from simple dehydration of $Zn(N_3)_2 \cdot 2.5 H_2O$ with P₄O₁₀ for several days, were almost identical according to vibrational spectroscopy (IR/Raman).^[15] However, owing to its amorphous nature, zinc azide prepared by these procedures was not suited for powder X-ray diffraction and always contained traces of hydroxide impurities, or displayed residual N-H vibrations, respectively, as deduced from the IR spectra (Supporting Information, Figures S21, S22). Nevertheless, repeated slow heating to about 200°C resulted in the formation of roughly pure, microcrystalline $Zn(N_3)_2$, which, according to vibrational spectroscopy and powder diffraction, proved identical to our previously observed modification of $Zn(N_3)_{2}$, which will be denoted as α -Zn(N₃)₂ in the following.^[15] In contrast, we found that upon singular heating, amorphous zinc azide, obtained from dehydration of $Zn(N_3)_2$ ·2.5 H₂O, smoothly converts into crystalline material at about 136 °C, which differs considerably from α -Zn(N₃)₂, as further supported by DSC measurements, as well as high-temperature powder X-ray diffraction experiments (Supporting Information, Figures S9, S15). The powder X-ray data could be indexed in agreement with a trigonal unit cell (a = 5.99364(8), b = 19.0427(3) Å), which was later confirmed by a single crystal structure determination in space group P3₂21 (see below), displaying a metastable polymorph, denoted as β -Zn(N₃)₂ hereafter (Figure 2). It is interesting to note that β -zinc azide was also obtained if any of the Zn(N₃)₂ modifications was carefully heated to approximately 350°C in a sealed tube, leading to a turbid, off-white melt, which gently evolved gaseous nitrogen at that point, followed by expeditious cooling to ambient temperature, resulting in a pale brownish, but polycrystalline substance.^[15]

In a next series of experiments, we reinvestigated the preparation of Zn(N₃)₂ starting from dry ethereal hydrazoic acid HN₃ and $ZnCO_3$ or $Zn(OH)N_3$ as invented by Wöhler and Martin (Scheme 3), as well as after-treatment of amorphous zinc azide, obtained from dehydration of Zn(N₃)₂·2.5H₂O with ethereal HN₃ as described by Winkler and Krischner, respectively (see above).^[13,12] The conversion of zinc hydroxide azide or amorphous zinc azide proceeded quantitatively within three days at ambient temperature. During the course of the reaction, the supernatant was removed each day by decantation and replaced by fresh ethereal hydrazoic acid.^[15] In contrast, the reaction of dry ZnCO₃ was found to be rather slow, and still not complete even after one week, in accord with previous findings.^[13] However, the colorless, microcrystalline materials obtained could unequivocally be identified as phase pure α -Zn(N₃)₂ by means of powder X-ray diffraction, and surprisingly, traces of hydroxide or water were completely absent in the vibrational spectra (IR/Raman). Moreover, we were able to identify a further labile polymorph, denoted as γ -Zn(N₃)₂, which is initially formed as intermediate during the course of the reactions of ZnCO₃ or Zn(OH)N₃ in Et₂O, as deduced from the





Figure 2. Left: Perspective view of the unit cells of β -Zn(N₃)₂ (top, view along [010], symmetry codes: (i) *y*-1, *x*, *-z*; (iv) *x*-*y*+1, *-y*+2, *-z*+1/3) and γ -Zn(N₃)₂ (bottom, view along [110], symmetry codes: (i) *-x*+1/2, *y*+1/2, *-z*+1; (iv) *-x*, *y*, *-z*). Right: ORTEPs of the coordination spheres of β -Zn(N₃)₂ (top) and γ -Zn(N₃)₂ (middle) in the crystal. Ellipsoids set at 50% probability at 173 K (β -Zn(N₃)₂) and 60% probability at 123 K (γ -Zn(N₃)₂). Right (bottom): Top view of the two dimensional layer of γ -Zn(N₃)₂ in the crystal.

powder X-ray pattern of the dried reaction residue obtained after one day (Figure 2; Supporting Information, Figure S6).^[15]

Small crystals of γ -Zn(N₃)₂ suitable for X-ray structure determination and Raman spectroscopy could finally be grown on the surface of a thin layer of neat Zn(OH)N₃, which was in contact to dry, gaseous HN₃ from ethereal solution. Thereby, only tiny amounts of γ -Zn(N₃)₂, which crystallizes in the monoclinic space group C2, could be manually separated under the microscope after 12 h, while longer reaction times or physical stress led inherently to the complete transformation into polycrystalline α -Zn(N₃)₂, comparable to β -Zn(N₃)₂.^[15]

Since all reactions in ethereal hydrazoic acid yielded exclusively α -Zn(N₃)₂ as final product, it is quite reasonable to conclude that the powder X-ray data of Winkler and Krischner were erroneously indexed, which is further supported by the similar lattice parameter and the tripled *a* axis (compare α -Zn(N₃)₂: *P*2₁/*n*, *a*=3.4587(3), *b*=16.3546(15), *c*=6.9548(6) Å, β =95.444(5)°; vs. *Pcmn*, *a*=10.98(2), *b*=6.92(2), *c*=16.33(2) Å).^[15,12] This finally left the question as to why the analytical data (DSC, IR), as well as the reported powder X-ray data of Yoganarasimhan and Jain, indexed in an orthorhombic lattice (*a*=7.35, *b*=4.37, *c*=15.23 Å) were also inconsistent with our findings. However, a comparison of the published reflection data with the powder pattern of the basic zinc azides revealed that the reflections match considerably the X-ray pattern of β -Zn(OH)N₃ (Supporting Information, Figure S14), which



is further supported by the spectroscopic data (see below).^[11,15] Moreover, we found that the precipitation of zinc azide from strongly acidic aqueous solutions by addition of excess acetone yielded again only basic zinc azide after drying, instead of the expected pure azide, as reported by Yoganarasimhan and Sood.^[16]

Spectroscopic data

Pure α - and β -Zn(N₃)₂ were found to be very sensitive to friction and shock, and both azides violently explode with a bright blue flash of light on fast heating or ignition. Nevertheless, on slow heating rates (<20°/min), both compounds smoothly decomposed exothermally under release of N₂, thereby melting between 335–338 (α -Zn(N₃)₂) and 327–330 °C (β -Zn(N₃)₂), respectively, in contrast to the reported decomposition point of 289 °C obtained by Wöhler and Martin.^[17]

The slow thermal treatment of zinc azide up to 400 °C under argon in a sealed glass tube yielded a black residue, which could be identified as zinc nitride Zn₃N₂ by means of powder X-ray diffraction (Supporting Information, Figure S5), whereas heating in moist air resulted in hydrolysis yielding pure zinc oxide ZnO and HN₃. Thereby, only traces of basic zinc azides, as previously assumed in literature,^[4d,f,5] could be observed in the X-ray powder pattern during decomposition, which displayed mainly a mixture of ZnO and $Zn(N_3)_2$ (Supporting Information, Figure S8).^[15] In contrast, both α - and β -Zn(OH)N₃ were almost insensitive to friction and shock, and found to be reasonably stable in air for several months, albeit slow decomposition under release of hydrazoic acid was noticed. However, upon slow heating under argon, both modifications gently decomposed endothermally under release of HN₃ in the range 217–219 (α -Zn(OH)N₃) and 219–221 °C (β -Zn(OH)N₃), yielding pure ZnO, while fast heating resulted in an explosion.^[15]

As illustrated in Figure 3, all considered azides can easily be distinguished by means of vibrational spectroscopy. The ATR-IR and Raman spectra of α -, β -, and γ -zinc azide feature the presence of azido ligands, as indicated by the antisymmetric stretching mode ($v_{as}(N_3)$; 2187–2028 cm⁻¹, Table 1), the symmetric stretching mode ($v_s(N_3)$; 1427–1248 cm⁻¹), and the deformation mode of the N₃-unit ($\gamma/\delta(N_3)$; 629–579 cm⁻¹). The existence of more than one azido ligand results in in-phase (i.p.) and out-of-phase (o.p) coupling of vibrational modes (Table 1 and Figure 3). Moreover, combination modes of antisymmetric and symmetric vibrations $v_{as} + v_s(N_3)$ can be found in the IR spectra between 3465–3348 cm⁻¹, while the out-of-phase N-Zn-N stretching mode ($v_{o.p.}$ (N-Zn-N)) in the range 711– 683 cm⁻¹, as well as the in-phase vibrational mode ($v_{i,p}$ (N-Zn-N)) between 413–328 cm⁻¹ can be identified in the IR and Raman spectra, respectively (cf. $\nu_{i,p.}/\nu_{o.p.}$ (N-Cd-N) in Cd(N₃)₂: $329-248 \text{ cm}^{-1};$ $v_{i.p.}/v_{o.p}$ (N-Hg-N) in α -Hg(N₃)₂: 434-349 $\text{cm}^{-1}\text{)}.^{[15,18]}$ In contrast, for amorphous $\text{Zn}(N_3)_2$ obtained by desolvation of Zn(N₃)₂·2.5 H₂O or Zn(N₃)₂·2 NH₃, respectively, only broad vibrations are observed, which however cover the same range as found for the crystalline phases (Figure 3). It should be noted that these amorphous samples always display residual O-H/N-H vibrations in the IR spectra (see above),



Figure 3. Antisymmetric and symmetric stretching modes (Raman spectra) of the N₃ units (v_{as} N₃ and v_s N₃). Zn(N₃)₂* denotes amorphous zinc azide from dehydration of Zn(N₃)₂:2.5 H₂O.

Table 1. Selected crystallographic and structural data from single crystal analyses, melting points, and IR and Raman data. ^[a]				
	α -Zn(N ₃) ₂	β -Zn(N ₃) ₂	γ -Zn(N ₃) ₂	
Space	P2 ₁ /n	P3 ₂ 21 ^[1]	C2 ^[j]	
group				
$ ho_{calc.}^{[b]}$	2.559	2.536	2.518	
Zn–N ^[c]	1.986 cs ^[e,f]	2.002 ^[f]	2.005 ^[f]	
	2.037 es ^[e]	1.981 µ _{2(1,3)} ^[f]	1.992 µ _{2(1,3)}	
$N_{\alpha} - N_{\beta}^{[c]}$	1.228 cs	1.227	1.232	
	1.215 es	1.165 μ _{2(1,3)}	1.168 µ _{2(1,3)}	
$N_{\beta} - N_{\gamma}^{[c]}$	1.129 cs	1.135	1.138	
	1.138 es	1.165 μ _{2(1,3)}	1.168 µ _{2(1,3)}	
Zn…Zn ^[c,d]	3.083 cs	3.576	3.573	
	3.459 es	5.745 µ _{2(1,3)}	5.5142 µ _{2(1,3)}	
N-Zn-N ^[c]	81.58-121.12	95.68-123.86	101.00-	
			118.33	
$N_{\alpha}-N_{\beta}-N_{\gamma}^{[c]}$	179.05 cs	179.90	179.28	
	179.45 es	174.74 µ _{2(1,3)}	174.70 µ _{2(1,3)}	
M.p. ^[g]	335–338	327-330	_ ^[h]	
$\text{IR } \nu_{as}(\text{N}_3)$	2141, 2120	2164, 2134, 2115, 2091, 2028	_[h]	
Raman $\nu_{as}(N_3)$	2187, 2170, 2140, 2120	2135, 2116, 2105	2121	

[a] See Figure 1 and Figure 2 and the Supporting Information for details. Units: distances [Å], angles [°], m.p. [°C], wavenumbers [cm⁻¹], density (ρ_{calc}) [g cm⁻³]. [b] Calculated from single crystal data. [c] If there are more than one structurally comparable azido ligands, the average value is given. [d] closest Zn--Zn distances. [e] Refers to the bridging mode of the azido ligands with respect to corner-sharing or edge-sharing position within the ZnN₄ coordination polyhedra (see Figure 1 and Figure 2). [f] If not otherwise stated, the values correspond to the $\mu_{2(1,1)}$ -bridging azide units, while $\mu_{2(1,3)}$ denotes the 1,3-bridging mode of the N₃ units. [g] M.p. = T_{dec} . [h] Not isolated. [i] Flack parameter for β -Zn(N₃)₂: 0.06(3). [j] γ -Zn(N₃)₂ was refined as inversion twin (batch scale factor (BASF): 0.31(2)).

which in contrast, are completely absent in pure, crystalline zinc azides.^[15] On the other hand, the IR-spectra of basic zinc azides show a broad O-H stretching mode at 3564 for α -, and at considerably lower wave number of 3527 cm⁻¹ for β -



Zn(OH)N₃, indicating a stronger H bond for the latter (see below).^[15] Interestingly, in α -Zn(OH)N₃, the out-of-phase N-Zn-O stretching mode (v_{o,p}.(N-Zn-O)) at 659 cm⁻¹, as well as the inphase vibrational mode (v_{i,p}.(N-Zn-O)) between 452 and 423 cm⁻¹ in the IR and Raman spectra, respectively, are shifted to lower frequency, indicating a weaker Zn-O and Zn-N bond as compared to β -Zn(OH)N₃ (v_{o,p}.(N-Zn-O): 732, v_{i,p}.(N-Zn-O): 455 cm⁻¹). Accordingly, the antisymmetric stretching mode (v_{as}(N₃)) of the azide units in the Raman spectrum of α -Zn(OH)N₃ is found at 2091, but slightly shifted to higher frequency for the β -phase at 2102 cm⁻¹, in agreement with a higher degree of ionic bonding in the former (Figure 3 and Figure 4).^[15]

The 14 N NMR spectrum of zinc azide run in $[D_6]DMSO$ at 300 K shows two well-resolved resonances, a medium-sharp signal at $\delta = -136~(\Delta \nu_{1/2} = 32~\text{Hz})$ for the N_β atoms, and a remarkably broadened $N_{\alpha/\gamma}$ -resonance at $-283~\text{ppm}~(\Delta \nu_{1/2} = 290~\text{Hz}).^{[15]}$ The absence of a separate N_α resonance and the observation of only one set of azide signals, indicate strong quadrupole relaxation effects and a rapid ligand exchange on the NMR timescale,^{[19]} in accord with previously reported binary azides (for example, $-137~(\Delta \nu_{1/2} = 71~\text{Hz})$ and $-260~\text{ppm}~(\Delta \nu_{1/2} = 632~\text{Hz})$ for $Bi(N_3)_3).^{[20]}$ Interestingly, these resonances lie in a similar range as found for the analogous cadmium azide Cd(N_3)_2 (-133~(200) and -282~ppm~(1100~Hz)), while the $N_{\alpha/\gamma}$ resonance is considerably shifted to higher field, as compared to mercury azide Hg(N_3)_2 (-133~(65) and -261~ppm~(690~Hz)).



Figure 4. Top: Perspective view of the unit cells of α -Zn(OH)N₃ (right, view along [110]) and β -Zn(OH)N₃ (left, view along [110]). Bottom: Ball-and-stick drawings of the coordination spheres of the azide units in α -Zn(OH)N₃ (right) and β -Zn(OH)N₃ (left) in the crystal.

X-ray crystallography

In the single-crystal X-ray structures of α -, β -, and γ -zinc azide, the zinc atoms are in a tetrahedral coordination sphere (Figure 1 and Figure 2).^[15] While the ZnN₄ tetrahedra within all structures are further connected in a corner-sharing manner by bridging azide units with Zn-Zn distances in the range 3.459-3.576 Å, in α -Zn(N₃)₂ an additional edge-sharing interaction is observed, leading to a comparable shorter Zn---Zn distance of 3.083 Å. Besides this μ_2 -bridging interaction, which involves only one terminal N atom of the azide unit (denoted as $\mu_{2(1,1)}$, cf. Table 1), in β - and γ -zinc azide further linkages by 1,3-bridging azide groups including both terminal N atoms of the N₃ units (denoted as $\mu_{2(1,3)}$, cf. Table 1) are found. This 1,3-bridging results in large Zn…Zn distances of 5.745 in $\beta\text{-Zn}(N_3)_2$ and 5.514 Å in γ -Zn(N₃)₂. In α -Zn(N₃)₂, the edge-sharing interactions lead to the formation of double-tetrahedra, which are further assembled by corner-sharing azide units, resulting in one-dimensional, double-stranded chains along [100] (Figure 1). In contrast, the solid-state structures of β - and γ -Zn(N₃)₂ are composed of two-dimensional layers, which obey the ZnN₄ coordination tetrahedra in a corner-sharing, kagome-like lattice arrangement, comparable to the constitution of ${}^{2}_{\infty}$ [SiO₄]²⁻ networks in sheet silicates (Figure 2). These layers are further connected by $\mu_{2(1,3)}$ -bridging azide units, leading to a stacking along [001] in both modifications. However, while the network structure within the layers of β - and γ -phase are almost identical, both differ with respect to the stacking sequence. Thereby, in β -Zn(N₃)₂ each layer is rotated to the adjacent layers by 120° within staple direction, resulting in an alignment of every fourth layer, giving a sequence of a-b-c, whereas the layers in γ -Zn(N₃)₂ are not rotated with respect to the following layer, leading to an alignment of every third layer in an a-b-stacking sequence (Figure 2).

As illustrated in Table 1, the Zn-N and N-N distances vary only little dependent on the coordination mode of the azide units. However, in α -Zn(N₃)₂ slightly longer Zn–N bonds are found for the bridging azides in edge-sharing position with an average bond length of 2.037 Å, in comparison to the Zn-N distance to the corner-sharing N₃ units with 1.986 Å. These values lie slightly above the sum of the covalent radii for a zinc-nitrogen single bond ($\Sigma r_{cov}(Zn-N)$ 1.89 Å), but within the sum of the ion radii ($\Sigma r_{ion}(Zn-N)$ 2.06 Å) for a tetrahedral coordination sphere.^[21,22] For comparison, considerably elongated Zn-N distances between 2.109-2.137 Å are found for the octahedral coordinated zinc centers in Zn(N₃)₂·2.5H₂O (cf. $\Sigma r_{ion}(Zn-N) = 2.20$ Å).^[15,22] Interestingly, in β - and γ -zinc azide, the Zn–N distances to the $\mu_{2(1,3)}$ -bridging azides are comparably shorter (β -Zn(N₃)₂ 1.981, γ -Zn(N₃)₂ 1.992 Å) than the corresponding distances to the $\mu_{2(1,1)}\mbox{-bridging}\ N_3$ units with average bond distances of 2.002 for β -Zn(N₃)₂ and 2.005 Å for γ -Zn(N₃)₂, respectively. The $\mu_{2(1,1)}$ -bridging azide units adopt a typical trans-bent structure with short average $N_{\alpha}\!\!-\!\!N_{\beta}$ and $N_{\beta}\!\!-\!\!N_{\gamma}$ distances in the range 1.215–1.232 and 1.129–1.138 Å, and $N_{\alpha} N_{\rm B}\!\!-\!\!N_{\nu}$ angles, which however deviate only slightly from linearity (179.1–179.9°). While the $\mu_{2(1,1)}$ -bridging azide units always exhibit N_{α} -N_b bond lengths, which are longer than the N_{β} -N_y

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bonds, two equal distances of 1.165 (β -Zn(N₃)₂) and 1.168 Å (γ -Zn(N₃)₂) are found in the $\mu_{2(1,3)}$ -bridging azido ligands. Furthermore a strong bending with N_{α}-N_{β}-N_{γ} angles of 174.74 for β -Zn(N₃)₂ and 174.70° for γ -Zn(N₃)₂, respectively, is observed.

The structures of α - and β -Zn(OH)N₃ could be solved and refined on the basis of the powder X-ray data (see above).^[15] However, since the quality of the Rietveld refinements do not allow for a detailed discussion of structural parameters, we want to focus only on the basic structural features (Figure 4).^[15] In contrast to binary zinc azides, both modifications of basic zinc azide display the zinc atoms in an octahedral coordination sphere, which is composed of three hydroxide groups and three azide units. Thereby, each zinc atom is connected to six adjacent zinc atoms by μ_3 -bridging hydroxide and $\mu_{3(1,1,1)}$ -bridging azido ligands, leading to the formation of a layer composed of edge-sharing ZnO₃N₃ coordination polyhedra. As shown in Figure 4, the OH and N₃ units are each bound on opposite faces of the zinc planes, building an identical sheet structure in α - as well as β -Zn(OH)N₃. Contrarily, both modifications differ with regard to the bridging mode of OH and N₃units between adjacent layers. While the azide units in α -Zn(OH)N₃ are further connected to three neighboring OH groups, only one linear O-H···N_{azide} interaction is found for the azide units in β -Zn(OH)N₃, resulting in a slightly larger separation of the layers in the latter, in agreement with a higher density for α -Zn(OH)N₃ (Figure 4).^[15]

Conclusion

To summarize, a comprehensive study was carried out on the synthesis of pure α -Zn(N₃)₂, along with the isolation of two labile polymorphs, β - and γ -Zn(N₃)₂. While all binary zinc azides could be structurally characterized for the first time, the crystallographic and analytical data indicate that α -Zn(N₃)₂ was most likely first prepared by Wöhler and Martin as early as 1917. Contrarily, we could demonstrate that several later reports of pure Zn(N₃)₂ are doubtful or even wrong.

Experimental Section

Caution! Covalent azides are potentially hazardous and can decompose explosively under various conditions! Especially dry, crystalline $Zn(N_3)_2$ is extremely sensitive to shock and friction and can explode violently upon the slightest provocation. Appropriate safety precautions (safety shields, face shields, leather gloves, protective clothing) should be taken.

α -Zn(N₃)₂

Procedure 1: A Schlenk flask containing a mixture of sodium azide (NaN₃; neat, 0.228 g, 3.5 mmol) and stearic acid ($C_{17}H_{35}CO_2H$; neat, 0.996 g, 3.5 mmol) was connected to a second flask containing a frozen (and degassed) solution of diethyl zinc (ZnEt₂; 0.124 g, 1.0 mmol) in *n*-hexane (5 mL). The whole apparatus was evacuated in vacuo. The sodium azide/stearic acid mixture was heated to 70 °C and the semi-solid mixture was further heated to 130 °C within three hours while the hydrazoic acid HN₃ was continuously condensed on the frozen ZnEt₂ solution. The colourless mixture was warmed to ambient temperature, resulting in a colourless sus-

pension. The supernatant was separated from the precipitate by centrifugation and decantation. The residue was dried in vacuo, which gave almost amorphous α -Zn(N₃)₂ as colourless solid (yield 90–95%). Microcrystalline α -Zn(N₃)₂ was obtained by heating a suspension of amorphous Zn(N₃)₂ in degassed fluorobenzene under endogenous pressure at 120 °C for 12 h in a sealed glass tube. After cooling to ambient temperature over a period of one hour, the tube was opened in air, the suspension was quickly transferred to a Schlenk tube, and the supernatant was removed by syringe. Drying in vacuo at 70 °C gave microcrystalline α -Zn(N₃)₂ suitable for powder X-ray diffraction.

Procedure 2: To a stirred solution of ethereal hydrazoic acid HN₃ (1 м, 4.0 mmol, 4.0 mL), a solution of diethyl zinc ZnEt₂ (1 м in *n*-hexane, 1.5 mmol, 1.5 mL) was added dropwise at 0 °C over a period of one minute. The resulting colourless suspension was stirred for one hour at ambient temperature. The supernatant was separated from the precipitate by centrifugation and decantation. The residue was dried in vacuo which gave α-Zn(N₃)₂ as colourless solid (yield 90–95%).

Procedure 3: Neat basic zinc azide $(Zn(OH)_{(2-x)}(N_3)_{xr} x=0.8-1.0; 0.124 g, 1.0 mmol)$ was suspended in an ethereal solution of hydrazoic acid (HN₃; 1 м, 3.0 mmol, 3.0 mL) at ambient temperature. After stirring for one day, the supernatant was separated from the precipitate by centrifugation and decantation, and the residue was re-suspended in an ethereal solution of HN₃ (1 м, 3.0 mmol, 3.0 mL) and stirred at ambient temperature. This procedure was repeated two times. After removal of supernatant, the residue was dried in vacuo which gave α-Zn(N₃)₂ as colourless solid (yield 90–95%).

Procedure 4 (large crystals of α -Zn(N₃)₂): Neat Zn(N₃)₂ (any phase, 0.299 g, 2.0 mmol) was suspended in an aqueous solution of HN₃ (5 м, about 0.1 mL) at ambient temperature. The stirred suspension was heated to 60-70 °C and aqueous HN₃ (5 m, about 0.3 mL) was added dropwise, until a colourless solution was obtained. Slow cooling to ambient temperature (and further cooling to 5° C) resulted in the deposition of colourless needle-like crystals. Removal of supernatant by syringe, and drying in vacuo at 70 $^\circ\text{C}$ gave $\alpha\text{-}$ $Zn(N_3)_2$ as colourless crystals (yield 30–40%). The same procedure could be applied using basic zinc azide $(Zn(OH)_{(2-x)}(N_3)_{x'}) \times = 0.8-$ 1.0). M.p. 335–338 $^{\circ}\text{C};$ ^{14}N NMR (300 K, [D_6]DMSO, 36.14 MHz): $\delta\!=\!$ -136 (N_{β}, $\Delta \nu_{1/2}$ =62 Hz), -283 ppm (N_{ν}, $\Delta \nu_{1/2}$ =290 Hz); IR (ATR, 32 scans): $\tilde{v} =$ 3465 (w), 3403 (w), 3367 (w), 2658 (w), 2598 (w), 2540 (w), 2141 (s), 2120 (s), 1417 (w), 1368 (m), 1304 (m), 1277 (s), 1174 (w), 1154 (w), 675 (m), 587 (m), 579 \mbox{cm}^{-1} (m); Raman (785 nm, 10 mW, 25 °C, 10 acc., 30 sec.): $\tilde{\nu} = 2187$ (0.1), 2170 (1.3), 2140 (0.3), 2120 (0.2), 1375 (0.5), 1317 (0.7), 1289 (0.7), 1277 (1.0), 1180 (0.3), 1159 (0.3), 683 (0.5), 588 (0.5), 580 (0.5), 402 (0.6), 328 (0.8), 286 (1.3), 201 (1.4), 138 (5.5), 121 (8.6), 108 (7.5), 91 (10), 73 cm⁻¹ (6.6); elemental analysis calcd (%) for N₆Zn: N 56.24, Zn 43.76; found Zn 42.5.

β -Zn(N₃)₂

Polycrystalline β -Zn(N₃)₂: Neat amorphous Zn(N₃)₂ (from dehydrated Zn(N₃)₂:2.5 H₂O, about 0.01 g) was sealed in a small glass tube under argon at ambient pressure. The sample was slowly heated up to 150 °C (heating rate 20 °C min⁻¹) and then cooled to ambient temperature (cooling rate 30 °C min⁻¹), which gave β -Zn(N₃)₂ as polycrystalline, colourless solid (quantitative yield).

Crystalline β -Zn(N₃)₂ (suitable for X-ray): Neat amorphous Zn(N₃)₂ (from dehydrated Zn(N₃)₂·2.5 H₂O, about 0.001 g) was sealed in a small glass tube under argon at ambient pressure. The sample was slowly heated up to 345 °C (heating rate 20 °C min⁻¹), resulting

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in a turbid melt, which slowly started to evolve nitrogen. The sample was then cooled to ambient temperature (cooling rate $30 \,^{\circ}\text{Cmin}^{-1}$), which gave β -Zn(N₃)₂ as crystalline, pale brownish froth (quantitative yield). M.p. 327 $-330 \,^{\circ}\text{C}$; IR (ATR, 32 scans): $\tilde{\nu} = 3360 \,^{\circ}\text{(w)}$, 3348 (w, sh), 2535 (w), 2493 (w), 2164 (m), 2134 (m), 2115 (s), 2091 (s), 2028 (m), 1409 (w), 1269 (m), 1248 (s), 1166 (m), 699 (m), 617 (w), 599 (w), 585 cm⁻¹ (m); Raman (785 nm, 21 mW, 25 $^{\circ}\text{C}$, 12 acc., 20 sec.): $\tilde{\nu} = 2135 \,^{\circ}(0.4)$, 2116 (1.3), 2105 (0.2), 1427 (1.3), 1276 (1.8), 1250 (1.3), 1165 (0.2), 701 (0.2), 616 (0.3), 585 (0.3), 395 (0.4), 361 (0.5), 224 (2.6), 179 (4.3), 128 (10), 103 (9.3), 80 (9.5), 69 cm⁻¹ (8.4).

γ -Zn(N₃)₂

An aqueous solution of $Zn(N_3)_2$ (2 mL) was concentrated by rotary evaporation (200-20 mbar, 70 °C), resulting in the deposition of basic zinc hydroxy azide $(Zn(OH)_{(2-x)}(N_3)_{x'} x = 0.8-1.0)$ as thin layer on the glass surface. The residual supernatant and precipitate were removed by syringe and the coated glass surface was washed with water (dest., 0.5 mL) and shortly dried by rotary evaporation (200-20 mbar, 70°C). An ethereal solution of hydrazoic acid (1 м, 0.1 mL) was added and the reaction flask was stored at ambient temperature. Over a period of 12 h, the growth of small, needle-like crystals on the coated glass surface was observed, while longer reaction times always resulted in the complete transformation into crystalline α -Zn(N₃)₂. Some specimen of γ -Zn(N₃)₂ crystals were manually separated with a PTFE spatula for analytical purposes. Raman (785 nm, 2 mW, 25 °C, 10 acc., 20 sec.): $\tilde{v} = 2121$ (1.6), 1419 (1.0), 1277 (1.3), 1251 (4.0), 1164 (0.2), 711 (0.1), 630 (0.5), 583 (0.3), 413 (0.7), 250 (1.7), 222 (5.7), 189 (4.6), 180 (3.4), 153 (4.6), 136 (10), 97 $(4.6), 80 \text{ cm}^{-1} (5.5).$

Amorphous Zn(N₃)₂ (Dehydration of Zn(N₃)₂·2.5 H₂O)

Procedure 1: Neat, dry crystals of $Zn(N_3)_2 \cdot 2.5 H_2O$ (0.074 g, 0.50 mmol) were stored in a desiccator over P_4O_{10} (5 mbar) at ambient temperature. After two days, the turbid crystals were carefully ground by means of a PTFE spatula. Further storage in a desiccator over P_4O_{10} (5 mbar) at ambient temperature for two days gave amorphous $Zn(N_3)_2$ as colourless solid (yield: 90–95%).

Procedure 2: Neat, dry crystals of Zn(N₃)₂·2.5 H₂O (0.055 g, 0.29 mmol) were placed in a Schlenk flask and heated at 60 °C for two hours in vacuo. The residue was carefully ground by means of a PTFE spatula and then heated between 70–80 °C for three hours in vacuo, which gave amorphous Zn(N₃)₂ as colourless solid (yield: 90–95%). M.p. 136 °C (transition to crystalline β-Zn(N₃)₂). IR (ATR, 32 scans): $\tilde{\nu}$ =3564* (w), 3358 (w), 2659 (w), 2513 (w), 2089 (s), 1614* (w), 1394 (w), 1342 (w), 1249 (s), 1162 (m), 971* (w), 692 (m), 630* (w), 581 cm⁻¹ (m); Vibrations marked with an asterisk (*) are most probably caused by residual O–H impurities; Raman (785 nm, 50 mW, 25° C, 10 acc., 20 sec.): $\tilde{\nu}$ =2157 (0.1), 2120 (0.2), 1420 (0.4), 1278 (0.6), 1167 (0.1), 703 (0.1), 631 (0.1), 585 (0.1), 358 (0.3), 248 (1.3), 74 cm⁻¹ (10); elemental analysis calcd (%) for N₆Zn: N 56.24, Zn 43.76; found Zn 43.1.

Amorphous $Zn(N_3)_2$ (desolvation of $Zn(N_3)_2 \cdot 2 NH_3$)

Neat, dry Zn(N₃)₂·2NH₃ (0.045 g, 0.25 mmol) were placed in a Schlenk flask and heated stepwise from ambient temperature up to 130 °C within 30 h in vacuo, which gave amorphous Zn(N₃)₂ as colourless solid (yield: 90–95%). IR (ATR, 32 scans): $\tilde{\nu} = 3501^*$ (w), 3352 (w), 3273 (w), 2656 (w), 2539 (w), 2090 (s), 1609 (w), 1385* (w), 1263 (s), 1168 (m), 966* (w), 688 (m), 581 cm⁻¹ (m); Raman

(785 nm, 21 mW, 25 °C, 10 acc., 20 sec.): $\tilde{\nu}$ =2162 (0.2), 2118 (0.2), 1416 (0.6), 1290 (0.8), 694 (0.6), 581 (0.6), 370 (0.9), 296* (1.2), 253 (1.2), 62 cm⁻¹ (10). Vibrations marked with an asterisk (*) are most probably caused by residual N–H impurities.

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