

**Zn<sub>7</sub>[P<sub>12</sub>N<sub>24</sub>]Cl<sub>2</sub>—A Sodalite with a Phosphorus–Nitrogen Framework\*\***

By *Wolfgang Schnick\** and *Jan Lücke*

*Dedicated to Professor Karl-Heinz Büchel  
on the occasion of his 60th birthday*

Zeolites have increasingly found application as catalysts, molecular sieves, adsorbents, or ion exchangers in recent

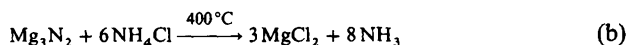
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[\*] Dr. W. Schnick, Dipl.-Chem. J. Lücke  
Institut für Anorganische Chemie der Universität  
Gerhard-Domagk-Strasse 1, D-W-5300 Bonn 1 (FRG)

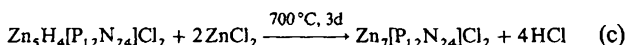
[\*\*] This work was supported by the Minister für Wissenschaft und Forschung des Landes Nordrhein-Westfalen, the Deutsche Forschungsgemeinschaft, and the Fonds der Chemischen Industrie.

years. The useful properties of these aluminosilicates are based particularly on the characteristic topology of the tetrahedral skeletal structures, which have the general composition  $\text{TO}_2$  ( $T = \text{Al}, \text{Si}$ ).<sup>[11]</sup> Instead of aluminum and silicon, many other elements such as B, P, Fe, Cr, Sb, As, Ga, Ge, Ti, Zr, and Hf can be incorporated as central atoms of the tetrahedrons in the zeolite lattice.<sup>[11, 21]</sup> These modifications succeed in tailoring the catalytic properties of zeolites for certain reactions.<sup>[21]</sup> However, hardly any proven facts on the exchange of elements of the anionic part of the lattice are known. Yet the replacement of oxygen by other electronegative elements such as nitrogen should be a promising method of modifying the properties and potential applications of this class of substances.

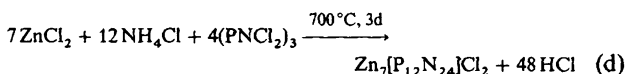
Recently we prepared pure, crystalline  $\text{HPN}_2$  through the ammonolysis of  $\text{P}_3\text{N}_5$  in thick-walled quartz ampules under pressure [Eq. (a)]. The required  $\text{NH}_3$  was formed in situ in another compartment of the apparatus by treatment of  $\text{Mg}_3\text{N}_2$  with  $\text{NH}_4\text{Cl}$  [Eq. (b)].<sup>[13]</sup>



The structural investigation<sup>[13]</sup> shows a  $[\text{PN}_2]^-$  skeleton isosteric with  $\beta$ -cristobalite, as has been found in  $\text{LiPN}_2$ .<sup>[41]</sup> Since these phosphorus(v) nitrides have structural similarities with silicates, the possibility of constructing zeolite-like P-N structures occurred to us. In fact, we succeeded in replacing  $\text{Mg}_3\text{N}_2$  by  $\text{Zn}_3\text{N}_2$  in the  $\text{HPN}_2$  preparation and we obtained a new compound with composition  $\text{Zn}_5\text{H}_4[\text{P}_{12}\text{N}_{24}]\text{Cl}_2$  in quantitative yield<sup>[51]</sup>. Analogously to  $\text{HPN}_2$ , a phosphorus(v) nitride had formed with molar ratio P:N = 1:2, while zinc from  $\text{ZnCl}_2$ , which is volatile under the given conditions, was incorporated into the solid while it forms. A complete exchange of the hydrogen atoms in the product was achieved afterwards through treatment with  $\text{ZnCl}_2$  accompanied by evolution of  $\text{HCl}$  [Eq. (c)].



Surprisingly however, the title compound  $\text{Zn}_7[\text{P}_{12}\text{N}_{24}]\text{Cl}_2$  can also be prepared by reaction of the inexpensive starting materials  $\text{NH}_4\text{Cl}$ ,  $\text{ZnCl}_2$ , and  $(\text{PNCl}_2)_3$  [Eq. (d)].



In all preparations  $\text{Zn}_7[\text{P}_{12}\text{N}_{24}]\text{Cl}_2$  forms as a fine crystalline and colorless powder insoluble in water and acid. Only in a special autoclave system<sup>[61]</sup> does  $\text{Zn}_7[\text{P}_{12}\text{N}_{24}]\text{Cl}_2$  decompose in dilute sulfuric acid ( $190^\circ\text{C}$ , 10 bar, 2 d; the phosphorus(v) nitride hydrolyses to ammonium hydrogen phosphate).

The powder diagram of the title compound indicates a cubic structure; the similarity to the powder diagram of sodalite  $\text{Na}_8[\text{Al}_6\text{Si}_6\text{O}_{24}]\text{Cl}_2$  is evident.<sup>[71]</sup> The Rietveld refinement of the crystal structure of  $\text{Zn}_7[\text{P}_{12}\text{N}_{24}]\text{Cl}_2$  on the basis of the powder diffraction data<sup>[81]</sup> confirmed the suspected

analogy.<sup>[91]</sup> It shows that phosphorus and nitrogen form a sodalite-like framework of corner-sharing  $\text{PN}_4$  tetrahedrons (Fig. 1). The P-N distance of 163.6(7) pm is comparable with that in  $\text{LiPN}_2$  (164.5(7) pm).<sup>[41]</sup> Also the experimentally determined P-N-P bond angle ( $125.8(4)^\circ$ ) agrees with the corresponding angle in  $\text{LiPN}_2$  ( $123.6(8)^\circ$ ).<sup>[41]</sup> This result is in

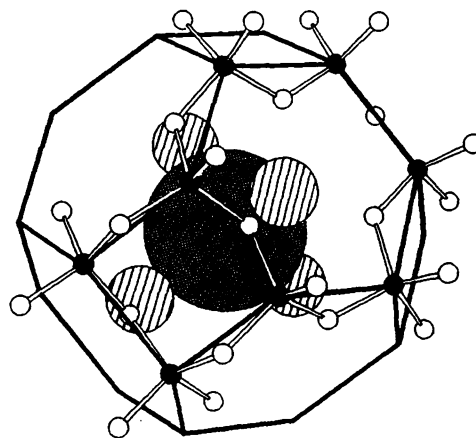


Fig. 1. Section of the crystal structure of  $\text{Zn}_7[\text{P}_{12}\text{N}_{24}]\text{Cl}_2$ . The  $[\text{P}_{12}\text{N}_{24}]$  framework of the sodalite type is constructed from  $[\text{P}_4\text{N}_4]$  and  $[\text{P}_6\text{N}_6]$  rings (P-N 163.6(7) pm). In the center of each  $\beta$  cage is a  $\text{Cl}^-$  ion, surrounded by tetrahedrally arranged  $\text{Zn}^{2+}$  ions (Zn-Cl 259.6(2) pm). The  $\text{Zn}^{2+}$  ions are coordinated in a distorted tetrahedral manner by one  $\text{Cl}^-$  ion and three N atoms (Zn-N 196.0(8) pm). Size of Zn and Cl correspond to the respective ionic radii. P: black, N: white, Cl: gray, Zn: striped.

accord with the topological similarity between the P-N part of the structure in  $\text{LiPN}_2$  (analogous to  $\beta$ -cristobalite) and the P-N structure found here: in both cases the network skeletons include  $\text{PN}_4$  tetrahedrons linked through all four apexes by corner-sharing. However, whereas three-dimensionally bonded  $[\text{P}_6\text{N}_6]$  rings occur exclusively in the  $\beta$ -cristobalite variant ( $\text{LiPN}_2$ ), in the sodalite framework  $[\text{P}_4\text{N}_4]$  rings are also found. The two types of rings together form capped octahedrons ( $\beta$  cages), which are typical building units of the sodalite type structure (Fig. 1). Situated at the center of each  $\beta$  cage is a  $\text{Cl}^-$  ion, in a tetrahedral environment of  $\text{Zn}^{2+}$  ions. Every metal cation has, besides the Zn-Cl contact (259.6(2) pm), three contacts to nitrogen atoms of the P-N framework (Z-N 196.0(8) pm) forming a distorted tetrahedron. In each case the contact distances correspond to the sum of the ionic radii.<sup>[101]</sup> Comparison of the composition of  $\text{Zn}_7[\text{P}_{12}\text{N}_{24}]\text{Cl}_2$ <sup>[51]</sup> with that of  $\text{Na}_8[\text{Si}_6\text{Al}_6\text{O}_{24}]\text{Cl}_2$  reveals a statistical occupation of the Zn positions (occupancy factor 7/8). However, a part of the  $\text{Zn}^{2+}$  ions may be replaced by two protons each. The P-N sodalite described here has a phase width of  $\text{Zn}_{(7-x)}\text{H}_{2x}[\text{P}_{12}\text{N}_{24}]\text{Cl}_2$  ( $0 \leq x \leq 2$ ). A continuous increase in the lattice constant is observed with increasing zinc content. Other metals such as Co, Ni, and Yb were also built into the P-N sodalite in place of zinc, as described by Equation (d).

Received: July 11, 1991 [Z4789 IE]  
Publication delayed at the authors' request  
German version: *Angew. Chem.* 1992, 104, 208

CAS Registry numbers:

$\text{P}_3\text{N}_5$ , 12136-91-3;  $\text{NH}_4\text{Cl}$ , 12125-02-9;  $\text{Zn}_3\text{N}_2$ , 128579-03-3;  $\text{Zn}_5\text{H}_4[\text{P}_{12}\text{N}_{24}]\text{Cl}_2$ , 136952-78-8;  $\text{ZnCl}_2$ , 7646-85-7;  $\text{Zn}_7[\text{P}_{12}\text{N}_{24}]\text{Cl}_2$ , 136952-79-9;  $(\text{PNCl}_2)_3$ , 940-71-6.

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- [4] W. Schnick, J. Lücke, *Z. Anorg. Allg. Chem.* **1990**, *588*, 19.
- [5] For the elemental analyses the products were hydrolyzed. Zinc was then determined complexometrically with EDTA, phosphorus photometrically as molybdovanadatophosphate, nitrogen photometrically as indophenol, and chloride argentometrically. In a parallel study the composition in the solid was checked by energy and wavelength dispersive X-ray microanalysis (EDX: Zn, P, Cl; WDX: absence of O). The presence of hydrogen (as N-H groups) was ascertained by IR spectroscopy.
- [6] Cf. O. Buresch, H. G. von Schnering, *Fresenius Z. Anal. Chem.* **1984**, *319*, 418.
- [7] I. Hassan, H. D. Grundy, *Acta Crystallogr. Sect. B* **1984**, *40*, 6.
- [8]  $Zn_7[P_{12}N_{24}]Cl_2$ :  $I\bar{4}3m$ ,  $a = 824.21(1)$  pm,  $Z = 1$ , Stoe-Stadi-P transmission powder diffractometer,  $Cu_{K\alpha 1}$  radiation, germanium monochromator, linear position-sensitive counter (Stoe Mini-PSD), Lindemann capillary, 5451 data points, measurement range  $10^\circ \leq 2\theta \leq 119^\circ$ , duration of measurement 12 h, 57 observed reflections, 3 refined site parameters, 4 temperature parameters. Rietveld refinement:  $R_{wp} = 0.0848$ ,  $R_1 = 0.076$ , GOF = 4.0. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-W-7514 Eggenstein-Leopoldshafen 2 (FRG) on quoting the depository number CSD-55611, the names of the authors, and the journal citation.
- [9] The P atoms in  $Zn_7[P_{12}N_{24}]Cl_2$  occupy positions identical to those of Al and Si in  $Na_8[Al_6Si_6O_{24}]Cl_2$ . The structure of the P-N sodalite described in the space group  $I\bar{4}3m$ , a Klassengleich supergroup ( $k2$ ) of  $P\bar{4}3n$ , which is the space group of Na sodalite.  $Zn_7[P_{12}N_{24}]Cl_2$  thus crystallizes in a defect variant of the  $Ca_8[Al_6Si_6O_{24}]O_2$  type; cf. V. I. Ponomarev, D. M. Kheiker, N. V. Belov, *Kristallografiya* **1970**, *15*, 918.
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