Phosphorus Oxonitridosodalites: Synthesis Using a Molecular Precursor and Structural Investigation by X-Ray and Neutron Powder Diffraction and ^{31}P MAS NMR Spectroscopy

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In memory of Jean Rouxel

Abstract: The oxonitridophosphates $M_{8-m}H_m[P_{12}N_{18}O_6]Cl_2$ (M = Cu, Li) with a sodalite-like $[P_{12}N_{18}O_6]^{6-}$ framework of corner-sharing PN_3O tetrahedra have been synthesized by the reaction of the respective metal chlorides with $(NH_2)_2P(O)NP(NH_2)_3 \cdot NH_4Cl$. In this precursor the desired molar ratio, P:O = 2:1, of the $[P_{12}N_{18}O_6]^{6-}$ framework structure has been preorganized on a molecular level. Analogous oxonitridosodalites have also been obtained from the metal salts MX (M = Cu, Li; X = Cl, Br, I) or Li_2S, the P/O and P/N components $OP(NH_2)_3$ and $SP(NH_2)_3$ or HPN_2, and NH_4X or MX as halogen sources. The crystal structures of the phosphorus oxonitridosodalites $Cu_{4.8}H_{3.2}[P_{12}N_{18}O_6]Cl_2$ (**1**), $Li_{5.5}H_{2.5}[P_{12}N_{18}O_6]Cl_2$ (**2**), $Li_{6.2}H_{1.8}[P_{12}N_{18}O_6]Br_2$ (**3**), and $Li_{5.8}H_{2.2}[P_{12}N_{18}O_6]I_2$ (**4**) have been investigated by using neutron and X-ray powder diffraction as well as ^{31}P MAS NMR spectroscopy. Rietveld refinements have been performed in the space group $I\bar{4}3m$ ($Z = 1$, $a = 820.25(1)$ to $830.81(2)$ pm for X = Cl to I). No experimental evidence for a crystallographic ordering of the N/O atoms and for other than PN_3O tetrahedra in the sodalite frameworks has been obtained.

Keywords: neutron diffraction • NMR spectroscopy • oxonitridophosphate • sodalite • solid-state structures

Introduction

During a systematic investigation of phosphorus nitrides[1] we have recently synthesized the nitridosodalite $Zn_7[P_{12}N_{24}]Cl_2$.[2] Unlike the well-known oxosodalites, in which frameworks of corner-sharing TO_4 tetrahedra (T = Si, Al, B, etc.) occur, these nitridosodalites contain corner-sharing PN_4 units. Substitutions of Zn^{2+} and Cl^- have yielded the nitridosodalites $M_{6+(n/2)-m}H_{2m}[P_{12}N_{24}]X_n$ ($0 \leq m \leq 4$, $n \leq 2$), M = Zn^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}; X = Cl^-, Br^-, I^-),[3, 4] ($M_8[P_{12}N_{24}]Y_2$ (M = Zn^{2+}, Co^{2+}, Cd^{2+}; Y = O^{2-}, S^{2-}, Se^{2-}, Te^{2-}),[5] and $M_6[P_{12}N_{24}]$ (M = Zn^{2+}).[6]

In all these nitridosodalites only divalent metal ions occur. However, for ion-exchange reactions analogous compounds containing monovalent metal ions instead of divalent ones would be desirable. Therefore we focused our attempts on the syntheses of isotypic oxonitridophosphate sodalites, where a partial substitution of the bridging atoms N^{3-} by O^{2-} would cause a charge reduction of the framework from $[P_{12}N_{24}]^{12-}$ to $[P_{12}N_{18}O_6]^{6-}$. As a consequence a complete substitution of the divalent metal ions by monovalent ones should be possible.

The concept of adjusting the framework charge as a function of the charge on the inner cage ions has recently been applied to the hydrothermal syntheses of cobalt-substituted aluminum phosphate sodalites.[7] However, a controlled partial substitution of the O-bridging atoms in framework structures of connected TO_4 tetrahedra (T = Al, Si, P, etc.) by nitrogen has never been achieved: this concept would significantly extend the structural variabilities of common oxidic zeolites.

With $(NH_2)_2P(O)NP(NH_2)_3$[8] we have now developed a molecular precursor compound, which allows precise control of the desired $[P_{12}N_{18}O_6]^{6-}$ framework stoichiometry during the formation of oxonitridosodalites. The precursor concept has been used widely for the syntheses of amorphous ceramics[9] and also in chemical vapor deposition (CVD). Recently, we used molecular precursor compounds for the synthesis of polymeric nonmetal nitrides, which show structural similarities to oxidic phosphates and silicates. These nitridophosphates and nitridosilicates are built up of connected PN_4 and/or SiN_4 tetrahedra. Thus we obtained crystalline single-phase $SiPN_3$,[10] α-P_3N_5,[11] and HP_4N_7,[12] starting from $Cl_3SiNPCl_3$, $P(NH_2)_4I$, and $(NH_2)_2P(S)NP$-

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$(NH_2)_3$, respectively. In these precursor compounds specific structural elements of the desired products are preorganized on a molecular level.

Results and Discussion

The precursor compound $(NH_2)_2P(O)NP(NH_2)_3$ is useful specifically for the controlled synthesis of $[P_{12}N_{18}O_6]^{6-}$ frameworks of the desired oxonitridosodalites. The molecular compound exhibits the required molar ratio, P:O = 2:1, and it already contains phosphorus atoms which are linked by a nitrogen bridge and which are tetrahedrally coordinated by N and O, respectively. Furthermore, $(NH_2)_2P(O)NP(NH_2)_3$ is easily transformed into oxygen-substituted polyphosphazenes during thermal condensation.[8]

Accordingly the reaction of LiCl with $(NH_2)_2P(O)NP(NH_2)_3$ yields the phosphorus oxonitridosodalite $Li_{5.5}H_{2.5}[P_{12}N_{18}O_6]Cl_2$ (**2**) directly [Eq. (1)].

$$6\,(NH_2)_2(O)P{-}N{=}P(NH_2)_3\cdot NH_4Cl + (8-m)\,MCl \longrightarrow M_{8-m}H_m[P_{12}N_{18}O_6]Cl_2 + (12+m)\,NH_3 + (12-m)\,NH_4Cl \tag{1}$$

During the synthesis of the molecular precursor the adduct $(NH_2)_2P(O)NP(NH_2)_3\cdot NH_4Cl$ is obtained primarily. The separation of NH_4Cl is complicated and the reaction product is normally obtained in low yield.[8] Other starting materials have therefore been tested. The reaction of the metal halides MX (CuCl, CuBr, LiCl, LiBr, LiI) with equimolar mixtures of HPN_2 and $OP(NH_2)_3$ yielded analogous P–O–N sodalites [Eq. (2)].

$$6\,OP(NH_2)_3 + 6\,HPN_2 + (8-m)\,MX \longrightarrow M_{8-m}H_m[P_{12}N_{18}O_6]X_2 + (6+m)\,NH_3 + (6-m)\,NH_4X \tag{2}$$

Abstract in German: *Die Oxonitridophosphate* $M_{8-m}H_m[P_{12}N_{18}O_6]Cl_2$ *(M = Cu, Li) wurden durch Reaktion des jeweiligen Metallchlorids mit* $(NH_2)_2P(O)NP(NH_2)_3\cdot NH_4Cl$ *erhalten. In diesem Precursor ist das molare Verhältnis P:O = 2:1 des* $[P_{12}N_{18}O_6]^{6-}$*-Gerüstes auf molekularer Ebene vororganisiert. Die Oxonitridophosphate bestehen aus einem sodalithanalogen* $[P_{12}N_{18}O_6]^{6-}$*-Gerüst aus eckenverknüpften* PN_3O*-Tetraedern. Analoge Oxonitridosodalithe wurden außerdem durch Reaktion der Metallsalze MX (M = Cu, Li; X = Cl, Br, I) oder* Li_2S*, den P/O- und P/N-Komponenten* $OP(NH_2)_3$ *und* $SP(NH_2)_3$ *oder* HPN_2 *und* NH_4X *oder MX als Halogenidquellen erhalten. Die Kristallstrukturen der Phosphor-oxonitridosodalithe* $Cu_{4,8}H_{3,2}[P_{12}N_{18}O_6]Cl_2$ *(**1**),* $Li_{5,5}H_{2,5}[P_{12}N_{18}O_6]Cl_2$ *(**2**),* $Li_{6,2}H_{1,8}[P_{12}N_{18}O_6]Br_2$ *(**3**), und* $Li_{5,8}H_{2,2}[P_{12}N_{18}O_6]I_2$ *(**4**) wurden durch Neutronen- und Röntgenbeugung an Pulvern sowie mittels* ^{31}P*-MAS-NMR-Spektroskopie untersucht. Die Rietveld-Verfeinerungen wurden in der Raumgruppe* $I\bar{4}3m$ *(Z = 1, a = 820.25(1)–830.81(2) pm für X = Cl–I) durchgeführt. Die experimentellen Ergebnisse deuten darauf hin, daß die sodalithanalogen Gerüste ausschließlich aus* PN_3O*-Tetraedern, ohne weitere Ausordnung der N/O-Atome, aufgebaut sind.*

The P–O–N sodalites obtained by this procedure often contain significant amounts of Cl^- which are affected by the used HPN_2. This starting material has been synthesized by ammonolysis of $(PNCl_2)_3$, so it often contains chloride. Therefore the reaction with metal bromides or iodides yielded P–O–N sodalites with mixed halide anions such as $Cu_5H_3[P_{12}N_{18}O_6]Cl_{0.1}Br_{1.9}$, $Li_{5.4}H_{2.6}[P_{12}N_{18}O_6]Cl_{0.1}Br_{1.9}$, or $Li_{5.7}H_{2.3}[P_{12}N_{18}O_6]Cl_{0.2}I_{1.8}$; however, compound **1** has also been synthesized by this procedure.

Contamination of the reaction products by Cl^- is avoided when HPN_2 is replaced by $SP(NH_2)_3$. This molecular precursor is easily transformed into polymeric phosphorus imide nitrides $H_{3x}P_3N_{5+x}$ by thermal condensation.[13] Thus the reaction of the metal halides MZ (LiCl, LiBr, LiI, CuCl, CuBr) with equimolar mixtures of $SP(NH_2)_3$ and $OP(NH_2)_3$ yielded $Li_{5.8}H_{2.2}[P_{12}N_{18}O_6]I_2$ (**4**) [Eq. (3)].

$$6\,OP(NH_2)_3 + 6\,SP(NH_2)_3 + (8-m)\,MX \longrightarrow M_{8-m}H_m[P_{12}N_{18}O_6]X_2 + m\,NH_3 + (6-m)\,NH_4X + 6\,(NH_4)_2S \tag{3}$$

Unlike the formation of oxygen-free nitridophosphate sodalites, where S^{2-} might be incorporated to form $Zn_8[P_{12}N_{24}]S_2$,[5] in P–O–N sodalites synthesized by using $SP(NH_2)_3$ no sulfur has been incorporated either into the framework or within the sodalite cages.

Lithium-containing P–O–N sodalites can also be obtained by the reaction of Li_2S with $OP(NH_2)_3$, $SP(NH_2)_3$, and NH_4X (X = Cl, Br, I) [Eq. (4)]. A specific advantage of this procedure is that the use of anhydrous lithium halides can be circumvented. By this method $Li_{6.2}H_{1.8}[P_{12}N_{18}O_6]Br_2$ (**3**) has been obtained.

$$6\,OP(NH_2)_3 + 6\,SP(NH_2)_3 + 2\,NH_4X + (4-m/2)\,Li_2S \longrightarrow Li_{8-m}H_m[P_{12}N_{18}O_6]X_2 + (10-m/2)\,H_2S + 20\,NH_3 \tag{4}$$

Since the P–O–N sodalites **1**–**4** have been obtained only as microcrystalline powders (crystal size 1–3 μm), powder diffraction experiments have been performed.

The powder diagrams of the P–O–N sodalites **1**–**4** (Figures 1 and 2) have been indexed unequivocally with the programs ITO[14] and TREOR-90.[15] Their similarity to the powder diagrams of P–N sodalites is evident.[2–6] The body-centered cubic cell has also been confirmed by synchrotron diffraction data (**1**, **2**) and neutron diffraction experiments (**2**). The cubic lattice constants (820.13(1) to 830.81(2) pm, (Table 1) compare well with those of P–N sodalites.[2–6] Since Li^+ and Cu^+ have almost the same ionic radii (Cu^+(CN 4), 74 pm; Li^+(CN 4) 73 pm)[16, 17] the P–O–N sodalites **1** and **2** have similar lattice constants, that of **2** being slightly increased because the compound has a higher metal content. The increase in size of the anions $Cl^- < Br^- < I^-$ causes an analogous increase in the lattice constants in the sequence **2** < **3** < **4**. In contrast, a partial replacement of the framework nitrogen by oxygen has only a minor effect on the lattice.

Rietveld refinements have been performed with the program GSAS[18] using the structure of $Zn_7[P_{12}N_{24}]Cl_2$[2] as a starting model. The results of the refinement are shown in Figures 1 (compound **1**, X-ray and neutron data) and 2 (compounds **2**, **3**, and **4**, X-ray data).

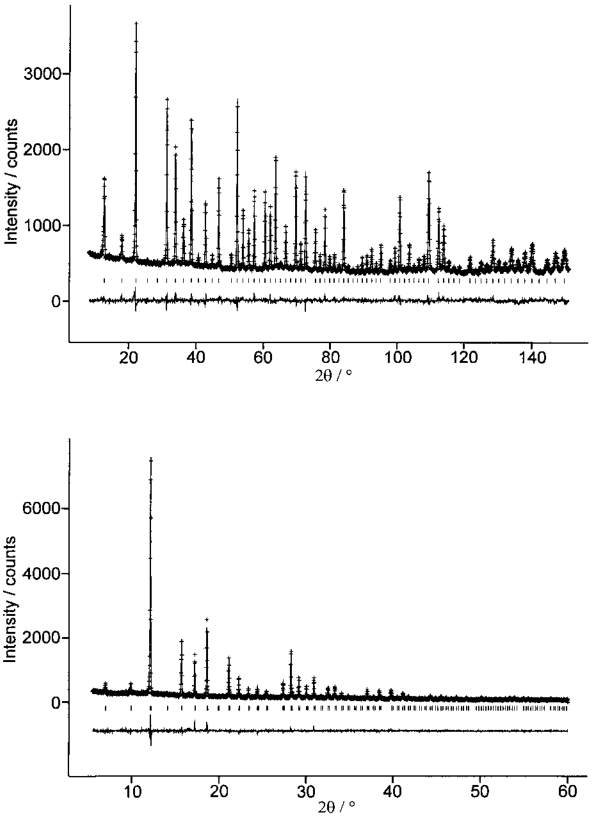

Figure 1. Powder diffraction patterns and difference profiles of the Rietveld refinements for **1**. Allowed peak positions are marked by vertical lines; crosses indicate observed and lines show calculated results. The neutron powder diffraction pattern (above) was obtained with the D2B high-resolution diffractometer of the Institute Laue Langevin (ILL) in Grenoble (France) ($\lambda = 127.63$ pm), whereas the X-ray powder diffraction pattern was recorded on a D5000 diffractometer (Siemens) using $Mo_{K\alpha}$ radiation (70.93 pm).

Table 1. Details of the crystal structure refinements by the Rietveld method of **1**–**4**.

Compound	Neutron diffraction **1**	X-ray diffraction **1**	X-ray diffraction **2**	X-ray diffraction **3**	X-ray diffraction **4**
M_r [g mol^{-1}]	1098.98	1098.98	831.41	924.46	1016.08
crystal system	cubic	cubic	cubic	cubic	cubic
space group	$I\bar{4}3m$	$I\bar{4}3m$	$I\bar{4}3m$	$I\bar{4}3m$	$I\bar{4}3m$
a [pm]	820.13(1)	820.25(1)	820.54(2)	824.58(3)	830.81(2)
V	551.62(1)	551.88(4)	552.44(3)	560.65(5)	573.46(4)
Z	1	1	1	1	1
T [K]	293(2)	293(2)	293(2)	293(2)	293(2)
λ [pm]	127.63	70.926	70.926	70.926	70.926
profile range (2Θ)	8–151	5.5–60	5.0–61	5.0–60	6.0–60
no. data points	2860	2725	2800	2750	2700
observed reflections	129	108	111	108	110
no. pos. parameters	14	8	8	8	8
no. profile parameters	11	9	9	9	9
no. background parameters	4	4	4	4	4
R_p	0.0251	0.0704	0.0851	0.0490	0.0928
wR_p	0.0333	0.0932	0.1144	0.0641	0.1294
R_F	0.0461	0.1271	0.1325	0.2410	0.1187

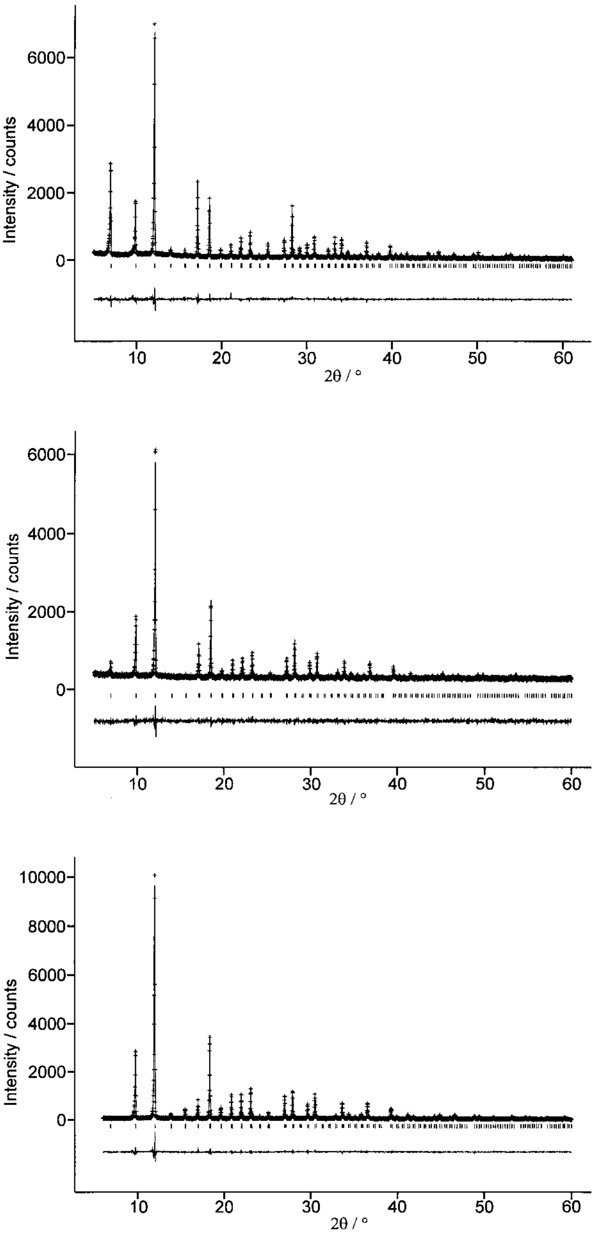

Figure 2. X-ray powder diffraction patterns and difference profiles of the Rietveld refinements of **2** (top), **3** (middle), and **4** (bottom). Allowed peak positions are marked by vertical lines; crosses indicate observed and lines show calculated results. The diffraction patterns were recorded on a D5000 diffractometer (Siemens) using $Mo_{K\alpha}$ radiation (70.93 pm).

On the basis of the neutron diffraction data, the fractional occupancy factors for N and O in compound **1** have been refined. A differentiation of both bridging atoms in the P–O–N sodalites is possible in principle because nitrogen and oxygen show a significant difference in their neutron scattering power ($b(\mathrm{N}) = 9.36 \times 10^{-15}$ m, $b(\mathrm{O}) = 5.803 \times 10^{-15}$ m).[19] The bridging atoms are located on the same Wyckoff position xxz (24g) with fractional site occupancy factors of 0.77(1) and 0.23(1) for N and O, respectively. Rietveld refinements have also been carried out in potential subgroups of cubic, rhombohedral, tetragonal, or orthorhombic symmetry in order to rule out a possible crystallographic ordering of the N/O atoms. In accordance with the neutron diffraction data and as has been proven by chemical analyses of compound **4**, the molar ratio N:O = 3:1 has been fixed for the Rietveld refinement of the X-ray powder diffraction data (**1**–**4**). Details of the final refinement are listed in Table 1.

Selected interatomic distances and angles as well as atomic coordinates and isotropic temperature factors are summarized in Tables 2 and 3.

Table 2. Selected interatomic distances [pm] and angles [°] of **1**–**4**.

Compound	Neutron diffraction **1**	X-ray diffraction **1**	X-ray diffraction **2**	X-ray diffraction **3**	X-ray diffraction **4**
P–(N,O)	160.6(4)	161.2(3)	161.4(2)	161.6(3)	161.6(3)
M–(N,O)	219.5(2)	217.2(6)	232.9(2)	202(2)	200(1)
M–X	215.6(4)	217.3(4)	232.9(2)	258(4)	278(3)
(N,O)-P-(N,O)	107.7(1)	108.0(2)	106.9(2)	107.5(2)	107.6(2)
	113.0(1)	112.4(2)	114.7(3)	113.5(4)	113.3(4)
P-(N,O)-P	129.0(1)	128.3(3)	128.0(3)	128.9(4)	130.7(4)

Table 3. Results of the structure refinements for **1**–**4**.

Compound	Neutron diffraction **1**	X-ray diffraction **1**	X-ray diffraction **2**	X-ray diffraction **3**	X-ray diffraction **4**
M in (8c) *x x x*					
x	0.1518(2)	0.1529(3)	0.164(2)	0.181(3)	0.193(2)
fractional occupancy factor	0.573(3)	0.590(5)	0.69(6)	0.78(4)	0.73(6)
B_{eq} [Å^2]	0.039(1)	0.036(1)	0.07(1)	0.01(1)	0.01(1)
P in (12d) ¼ ½ 0					
B_{eq} [Å^2]	0.0068(4)	0.0008(5)	0.0135(4)	0.011(1)	0.0094(6)
N/O in (24g) *x x y*					
x	0.1418(1)	0.1407(4)	0.1439(3)	0.1425(4)	0.1430(5)
y	0.4191(1)	0.4175(6)	0.4184(5)	0.4190(7)	0.4230(6)
fractional occupancy factor N	0.77(1)	0.75	0.75	0.75	0.75
fractional occupancy factor O	0.23(1)	0.25	0.25	0.25	0.25
B_{eq} [Å^2]	0.0097(1)	0.008(2)	0.013(1)	0.008(2)	0.006(1)
X in (2a) 0 0 0					
B_{eq} [Å^2]	0.064(2)	0.065(3)	0.037(1)	0.040(1)	0.0344(6)

According to the crystallographic results, and as confirmed by chemical analyses of compound **4**, the P–O–N sodalites contain a $[P_{12}N_{18}O_6]^{6-}$ framework structure of corner-sharing PN_3O tetrahedra (Figure 3). Complex arrangements XM_{4-n} (X = Cl, Br, I; M = Li, Cu; $0.9 < n < 1.6$) are localized within the *β*-cages. An isoelectronic $[Si_6Al_6O_{24}]^{6-}$ framework occurs in the oxosodalite $Na_8[Si_6Al_6O_{24}]Cl_2$. The aluminosilicate is formally derived from SiO_2 because of a partial substitution of the tetrahedral centers (Si) by aluminum. An analogous charge reduction is obtained in the P–O–N sodalites, which are formally derived from HPN_2 by partial substitution of the bridging atoms (N) by oxygen.

The distances P–(O,N) (160.6(4)–161.6(3) pm) vary between the values found in PON[20] (158.2(1)–159.2(1) pm) and the P–N distance in $Zn_7[P_{12}N_{24}]Cl_2$ (163.6(7) pm).[2] The bond angles P-(N,O)-P (128.0(3)–130.7(4)°) are similar to with the corresponding values in PON (131.59(0)°, 132.89(0)°)[20] and $Zn_7[P_{12}N_{24}]Cl_2$ (125.8(4)°)[2]. The X$^-$ ions at the center of the *β*-cages (Figure 3) are coordinated by monovalent metal ions (distances: Cu–Cl, 215.6(4) (neutron) and 217.3(4) pm (X-ray); Li–Cl, 232.9(2) pm; Li–Br, 258(4) pm; LiI, 278(3) pm). The metal ions exhibit three contacts with N/O atoms of the $P_6(N,O)_6$ rings, in addition to the contacts with the halide ions, thus forming distorted tetrahedra (distances: Cu–(O,N), 219.5(2) (neutron) and 217.2(6) pm (X-ray); Li–(O,N), 232.9(2), 202(2), and 200(1) pm). Approximately 0.25–0.4 of the metal ions per formula unit are replaced by hydrogen atoms. Crystallographic localization of these atoms in compounds **1**–**4** was not possible. However, the presence of the H atoms covalently bound to nitrogen atoms of the $[P_{12}N_{18}O_6]^{6-}$ framework has been confirmed unequivocally by IR spectroscopy (Figure 4).

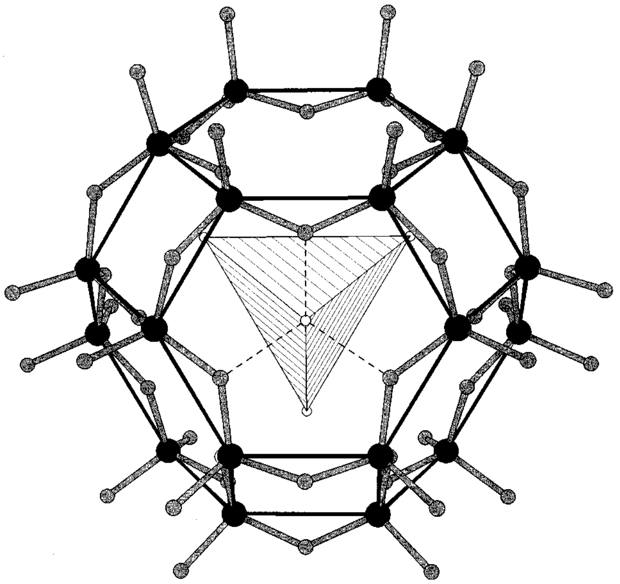

Figure 3. Section of the crystal structure of the P–O–N sodalites $M_{8-x}H_x[P_{12}N_{18}O_6]X_2$ (M = Cu, Li; X = Cl, Br, I). The zeolite-like *β*-cage is shown (P: black; N/O: gray; XM_4 tetrahedra M: small white circles).

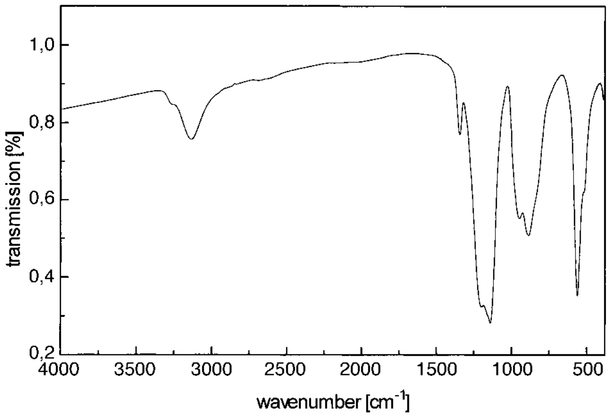

Figure 4. FTIR spectrum of **4**.

The IR spectra of compounds **1**–**4** are very similar. The IR absorptions observed at 3150 and 1345 cm^{-1} are typical for imido groups in the P–N sodalites $Zn_{7-m}H_{2m}[P_{12}N_{24}]Cl_2$.[3] According to the values for oxygen-free P–N sodalites, three groups of bands occur around 1150, 900, and 540 cm^{-1}, belonging to ν_{as}(P-(O,N)-P), ν_s(P-(O,N)-P), and δ(P-(O,N)-

P). A decrease in the local symmetry of the framework due to the partial substitution of N by O leads to a splitting of the IR bands.

Whereas the M – Cl distances are relatively short for **1** and **2** (sum of the ionic radii: Cu/Cl, 241 pm; Li/Cl, 240 pm)[16, 17] the distances M – N are found to be considerably shorter than the corresponding sums of the ionic radii (Cu/N, 206 pm; Cu/O, 198 pm; Li/N, 205 pm; Li/O, 197 pm).[16, 17] This might be attributable to a local distortion of the structure, with the metal ions M being moved from their ideal positions. The reason for this distortion might be that the eightfold position xxx (8c) is only fractionally occupied by 0.6 – 0.75 of the M atoms; the remaining 0.25 – 0.4 of the atoms are hydrogen. Similar indications of a disorder within the β-cages have been observed in the P – N sodalites $Zn_{7-m}H_{2m}[P_{12}N_{24}]Cl_2$.[3] In contrast, the distances M – X (X = Br, I) and M – (N,O) for **3** and **4** are close to the sum of the ionic radii (Li/Br, 255 pm; Li/I, 279 pm; Li/N, 205 pm; Li/O, 197 pm).[16, 17]

To obtain information about the chemical environment of the ^{31}P nuclei in the P – O – N sodalites, ^{31}P MAS NMR spectra of **4** have been recorded (Figure 5). A corresponding investigation of **1** was difficult, because this compound was always contaminated with small amounts of paramagnetic Cu metal which had been formed by the reduction of Cu^+ by NH_3. The ^{31}P MAS NMR spectrum of **4** exhibits one isotropic signal at $\delta = -8.7$. Despite the broadening of the signal (FWHM = 8 ppm) no splitting, and thus no evidence for other than PN_3O tetrahedra in the P – O – N-sodalite **4**, have been obtained. The chemical shift in nitridophosphates and oxonitridophosphates normally decreases with increasing degree of condensation (HP_4N_7, $\delta = -26$;[21] $Zn_8[P_{12}N_{24}]O_2$, $\delta = 3.6$;[22] $Zn_6[P_{12}N_{24}]$, $\delta = 2.0$;[22] $LiPN_2$, $\delta = 0.0$;[10, 22] Li_7PN_4, $\delta = 49.2/54.6$[23]) and decreasing formal charge per $P(N,O)_4$ tetrahedron (PON, $\delta = -0.9/-10.5$[20]). In less condensed nitrogen-substituted phosphate glasses, chemical shifts of $\delta = -10$ and $\delta = 0$ have been attributed to PO_3N and PO_2N_2 tetrahedra.[24] A similar relationship between the ^{29}Si chemical shift and the nitrogen content of condensed SiO_xN_{4-x} tetrahedra ($1 < x < 4$) has been observed in oxonitridosilicates.[25]

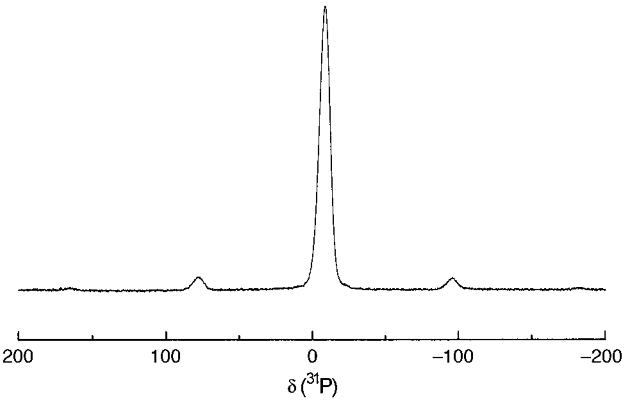

Figure 5. ^{31}P MAS NMR spectrum of **4** (observation frequency, 161.98 MHz; MAS frequency, 14 kHz).

Conclusions

A partial substitution of the bridging nitrogen atoms by oxygen in nitridosodalites has been accomplished with the synthesis of the oxonitridosodalites $M_{8-m}H_m[P_{12}N_{18}O_6]Z_2$ (M = Cu, Li; Z = Cl, Br, I). These compounds represent a link between oxophosphates and nitridophosphates. Thus the substitution of oxygen by nitrogen, and vice versa, allows a modification of phosphates which is comparable with the substitution of Si by Al yielding aluminosilicates. Several nitridosilicates have been obtained analogously, thus extending the structural possibilities of conventional oxosilicates;[26] furthermore, oxonitridosilicates have been investigated as well as oxonitridoaluminosilicates.[27]

Experimental Section

General techniques: All reactions involving solvents were performed under an Ar atmosphere using standard Schlenk techniques. CH_2Cl_2 was refluxed with P_4O_{10} and distilled before use. Solution ^{14}N NMR spectra were recorded at 18.070 MHz on a Bruker ARX250 spectrometer; neat CH_3NO_2 was used as an external reference. Solution ^{31}P NMR spectra were recorded at 101.254 MHz on the same spectrometer and they were referenced to 85 % H_3PO_4 as an external standard. Solid-state ^{31}P MAS NMR spectra were recorded at 161.98 MHz on a Bruker DSX 400 and were referenced to 85 % H_3PO_4 as an external standard. Infrared spectra were obtained on a Bruker IFS66v FTIR spectrometer (KBr pellets). X-ray microanalyses were performed by using a JEOL JSM-6400 scanning electron microscope equipped with an energy-dispersive spectrometer (germanium detector, Voyager 2100; Noran Instruments).

Starting materials: Phosphorus nitride imide (HPN_2) was synthesized from hexachlorocyclotriphosphazene ($PNCl_2)_3$) by multistage reaction under flowing ammonia (NH_3, 99.8 %; Linde) in a silica glass tube.[5] Phosphorothionic triamide ($SP(NH_2)_3$) and phosphoric triamide ($OP(NH_2)_3$) were obtained by reaction at − 78 °C of liquid NH_3 with previously distilled $SPCl_3$ (98 %; Fluka) and $OPCl_3$ (98 %; Fluka), respectively.[28, 13] LiCl was synthesized from LiH (98 %; Alfa) by reaction (500 °C, 6 h) with gaseous HCl which had been dried by passing it once over P_4O_{10} and twice through concentrated H_2SO_4. CuCl and CuBr were obtained according to the literature by reaction of $Cu(OAc)_2 \cdot H_2O$ with acetyl chloride and acetyl bromide, respectively, in a mixture of acetic acid containing more than 50 % (v/v) of acetic anhydride [Eqs. (5) and (6)].[29]

$$Cu(OAc)_2 \cdot H_2O + 2\,AcCl \longrightarrow CuCl_2 + (Ac)_2O + 2\,AcOH \tag{5}$$

$$2\,CuCl_2 \xrightarrow{\Delta T/(Ac)_2O} 2\,CuCl + Cl_2 \tag{6}$$

LiBr (puriss.; Fluka), LiI (purum; Fluka), and Li_2S (99 %; Alfa) were dried under vacuum ($p < 10^{-5}$ mbar, $T = 700\,^{\circ}C/24$ h, heating rate $1\,^{\circ}C\,min^{-1}$). The purity of the starting compounds was checked by powder X-ray diffraction and IR spectroscopy. Whereas in CuCl and Li_2S no water was detected, LiCl, LiBr and LiI still contained small amounts. All compounds were stored and handled in a glove-box under Ar.

$(NH_2)_2(O)P{-}N{=}P(NH_2)_3 \cdot NH_4Cl$: The adduct was synthesized [Eq. (7)] by reaction at − 78 °C of liquid ammonia with pentachlorooxodiphosphazene,

$$Cl_2(O)P{-}N{=}PCl_3 + 10\,NH_3 \longrightarrow (NH_2)_2(O)P{-}N{=}P(NH_2)_3 \cdot NH_4Cl + 4\,NH_4Cl \tag{7}$$

$Cl_2(O)P{-}N{=}PCl_3$,[30] which can be readily synthesized by reaction of PCl_5 with $(NH_4)_2SO_4$ [Eq. (8)]. The by-product $[Cl_3P{-}N{=}PCl_3]^+[PCl_6]^-$ can be converted into $Cl_2(O)P{-}N{=}PCl_3$, by reaction with SO_2 [Eq. (9)]. NH_4Cl formed during the ammonolysis of $Cl_2(O)P{-}N{=}PCl_3$ was removed by reaction with $(C_2H_5)_2NH$ followed by extraction of $(C_2H_5)_2NH_2Cl$ with CH_2Cl_2 [Eq. (10)].

$$4\,PCl_5 + (NH_4)_2SO_4 \longrightarrow 2\,Cl_2(O)P{-}N{=}PCl_3 + SO_2 + 8\,HCl + Cl_2 \qquad (8)$$

$$[Cl_3P{-}N{=}PCl_3]^+\,[PCl_6]^- + 2\,SO_2 \longrightarrow Cl_2(O)P{-}N{=}PCl_3 + 2\,SOCl_2 + OPCl_3 \qquad (9)$$

$$NH_4Cl + (C_2H_5)_2NH \longrightarrow NH_3\uparrow + (C_2H_5)_2NH_2Cl \qquad (10)$$

$Cl_2(O)P{-}N{=}PCl_3$: PCl_5 (93.5 g, 0.45 mol) and $(NH_4)_2SO_4$ (13.2 g, 0.1 mol) were added to $C_2H_2Cl_4$ (200 mL) and the mixture was refluxed for 1 h. The gaseous by-products were removed under vacuum (600–800 mbar). The mixture was allowed to cool to room temperature (RT) and SO_2 was bubbled through the solution for 20 min. After filtration followed by the evaporation of $C_2H_2Cl_4$ under vacuum, a yellowish oil was obtained which crystallized slowly at RT. The product was further purified by microdistillation ($p < 10^{-3}$ mbar, $T_{oil} = 90\,°C$). For this procedure the temperature should be kept as low as possible to avoid polycondensation. ^{31}P NMR (C_6D_6): $\delta_1 = -1.4$ (d), $\delta_2 = -11.4$ (d), $^2J_{PP} = 19$ Hz.

$(NH_2)_2(O)P{-}N{=}P(NH_2)_3 \cdot NH_4Cl$: In a three-necked bottle CH_2Cl_2 (300 mL, p.a.; Merck) was saturated with dried NH_3 (3.8; Linde) at $-78\,°C$ under a purified Ar atmosphere. A precooled solution of pentachlorooxodiphosphazene (6.7 g, 25 mmol) in CH_2Cl_2 (50 mL) was added dropwise with stirring. Subsequently the suspension was allowed to warm under an NH_3 atmosphere to room temperature. The product was isolated by filtration, $(C_2H_5)_2NH$ (20 mL, 0.192 mol) in CH_2Cl_2 (90 mL) was added, and the mixture was refluxed for 24 h. The $(C_2H_5)_2NH_2Cl$ formed was removed by extraction with hot CH_2Cl_2. Yield: 5.3 g, 23.5 mmol, 94 % of $(NH_2)_2(O)P{-}N{=}P(NH_2)_3 \cdot NH_4Cl$; ^{31}P NMR (D_2O): $\delta_1 = 18.4$ (d), $\delta_2 = 14.2$ (d), $^2J_{PP} = 30$ Hz; ^{14}N NMR (D_2O): $\delta(NH_4Cl) = -362$ (s, sharp), $\delta(H_{10}N_6OP_2) = -335$ (very broad); $(NH_2)_2(O)P{-}N{=}P(NH_2)_3 \cdot NH_4Cl$ (225.56): calcd. P 27.5, N 43.5, Cl 15.7; found: P 28.9, N 45.1, Cl 15.3.

$Cu_{4.8}H_{3.2}[P_{12}N_{18}O_6]Cl_2$ (1): Large amounts (typical yield 900 mg) of **1** for neutron diffraction experiments were obtained by the reaction of CuCl with HPN_2 and $OP(NH_2)_3$. In the first step CuCl (0.4703 g, 4.75 mmol), HPN_2 (0.342 g, 5.7 mmol), and $OP(NH_2)_3$ (0.5415 g, 5.7 mmol) were transferred under argon into the lower end of a silica glass ampoule (wall thickness 1 mm, internal diameter (i.d.) 18 mm, length 30 cm) and the opening was connected to a bubble counter filled with paraffin. The lower end of the ampoule was heated to 350 °C and kept there for 12 h. Ammonia which was formed during the reaction was released through the bubble counter. The mixture was allowed to cool to RT, ground to a fine powder in a glove-box, transferred into a silica glass ampoule (wall thickness 2 mm, i.d. 11 mm, length 100 mm), and sealed. In the second step the reaction mixture was heated to 700 °C ($1\,°C\,min^{-1}$) kept there for 48 h and then cooled to RT ($1\,°C\,min^{-1}$). During the synthesis the NH_4Cl which was formed sublimed to the upper end of the ampoule. $Cu_{4.8}H_{3.2}[P_{12}N_{18}O_6]Cl_2$ is stable to all solvents, acids, and alkalis at RT. Decomposition was accomplished in a microwave system (mls 2000; Mls GmbH) in a mixture of concentrated H_2SO_4 and 30 % H_2O_2 using Teflon vessels. $Cu_{4.8}H_{3.2}[P_{12}M_{18}O_6]Cl_2$ (1098.98): calcd.: P 33.8, N 22.9, Cu 27.8; found: P 31.5, N 23.2, Cu 25.7.

$Li_{5.5}H_{2.5}[P_{12}N_{18}O_6]Cl_2$ (2): LiCl (14.3 mg, 0.333 mmol) and $(NH_2)_2P(O)NP(NH_2)_3 \cdot NH_4Cl$ (90.2 mg, 0.4 mmol) were mixed thoroughly and transferred to a silica glass ampoule (wall thickness 2 mm, i.d. 11 mm, length 100 mm), which was then sealed. In the first step the mixture was heated to 200 °C ($1\,°C\,min^{-1}$) and kept there for 24 h, then it was heated to 700 °C ($1\,°C\,min^{-1}$) kept there for 48 h and finally cooled to RT ($1\,°C\,min^{-1}$). During the synthesis NH_4Cl formed sublimed to the upper end of the ampoule. The NH_3 evolved created pressures of up to 25 bar in the closed ampoule. $Li_{5.5}H_{2.5}[P_{12}N_{18}O_6]Cl_2$ is stable to all solvents, acids, and alkalis at RT. Decomposition was accomplished in a microwave system (mls 2000; Fa. Mls GmbH) in a mixture of concentrated H_2SO_4 and 30 % H_2O_2 using Teflon vessels. $Li_{5.5}H_{2.5}[P_{12}N_{18}O_6]Cl_2$ (831.41): calcd.: P 44.7, N 30.3, Li 4.6; found: P 41.7, N 31.9, Li 4.3;

$Li_{6.2}H_{1.8}[P_{12}N_{18}O_6]Br_2$ (3): Li_2S (12.9 mg, 0.281 mmol), $SP(NH_2)_3$ (49.4 mg, 0.444 mmol), $OP(NH_2)_3$ (42.2 mg, 0.444 mmol), and NH_4Br (55.1 mg, 0.563 mmol) were mixed thoroughly, transferred into a silica glass ampoule (wall thickness 2 mm, i.d. 11 mm, length 100 mm), and sealed. In the first step the mixture was heated to 200 °C ($1\,°C\,min^{-1}$) and kept there for 24 h, then heated to 700 °C ($1\,°C\,min^{-1}$) and kept there for 48 h, and finally cooled to RT ($1\,°C\,min^{-1}$). Excess NH_4Br, Li_2S, and the LiBr formed partially sublimed to the upper end of the ampoule during the reaction. Further impurities were dissolved in water. $Li_{6.2}H_{1.8}[P_{12}N_{18}O_6]Br_2$ is stable to all solvents, acids, and alkalis at RT. Decomposition of $Li_{6.2}H_{1.8}[P_{12}N_{18}O_6]Br_2$ was accomplished in a microwave system (mls 2000; Mls GmbH) in a mixture of concentrated H_2SO_4 and 30 % H_2O_2 using Teflon vessels. $Li_{6.2}H_{1.8}[P_{12}N_{18}O_6]Br_2$ (924.46): calcd.: P 40.2, N 27.3, Li 4.65; found P 38.2, N 27.7, Li 4.4.

$Li_{5.8}H_{2.2}[P_{12}N_{18}O_6]I_2$ (4): LiI (101.9 mg, 0.76 mmol), $SP(NH_2)_3$ (63.4 mg, 0.571 mmol), and $OP(NH_2)_3$ (54.3 mg, 0.571 mmol) were mixed thoroughly, transferred into a silica glass ampoule (wall thickness 2 mm, i.d. 11 mm, length 100 mm), and sealed. In the first step the mixture was heated to 200 °C ($1\,°C\,min^{-1}$) and kept there for 24 h, then heated to 700 °C ($1\,°C\,min^{-1}$) and kept there for 48 h, and finally cooled to RT ($1\,°C\,min^{-1}$). During the synthesis the NH_4I that was formed sublimed to the upper end of the ampoule. Excess LiI was dissolved in water. $Li_{5.8}H_{2.2}[P_{12}N_{18}O_6]I_2$ is stable to all solvents, acids, and alkalis at RT. Decomposition was accomplished in a microwave system (mls 2000; Fa. Mls GmbH) in a mixture of concentrated H_2SO_4 and 30 % H_2O_2 using Teflon vessels. $Li_{5.8}H_{2.2}[P_{12}N_{18}O_6]I_2$ (1016.08): calcd.: P 36.6, N 24.8, Li 4.0, H 0.2, O 9.4, I 25.0; found P 35.3, N 26.5, Li 4.4, H 0.5, O 9.2, I 24.5.

Crystal structure analysis: The X-ray diffraction patterns were obtained by using a Siemens D5000 automatic powder diffractometer in Debye–Scherrer geometry (glass capillaries, diameter 0.3 mm) with $Mo_{K\alpha}$ radiation (quartz monochromator) and a scintillation detector. High-resolution synchrotron powder diffraction data were collected at the X7A beamline of the National Synchrotron Light Source (NSLS), Brookhaven (USA), in order to rule out a splitting of the reflections due to possible symmetry reduction of the cubic lattice.

The neutron diffraction investigations of $Cu_{4.8}H_{3.2}[P_{12}N_{18}O_6]Cl_2$ (**1**) were performed with the high-resolution D2B powder diffractometer of the Institute Laue Langevin (ILL) in Grenoble (France). The sample (about 2 g) was enclosed in a vanadium can (diameter 8 mm, length 60 mm). A wavelength of 127.63 pm was selected by using a Ge (337) monochromator crystal.

Further details of the crystal structure investigations can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-408393 ($Cu_{4.8}H_{3.2}[P_{12}M_{18}O_6]Cl_2$, neutron diffraction), CSD-408394 ($Cu_{4.8}H_{3.2}[P_{12}M_{18}O_6]Cl_2$, X-ray diffraction), CSD-408395 ($Li_{5.5}H_{2.5}[P_{12}N_{18}O_6]Cl_2$), CSD-408396 ($Li_{6.2}H_{1.8}[P_{12}N_{18}O_6]Br_2$), and CSD-408397 ($Li_{5.8}H_{2.2}[P_{12}N_{18}O_6]I_2$).

Acknowledgments: Financial support by the Fonds der Chemischen Industrie, the Deutsche Forschungsgemeinschaft (Schwerpunktprogramm Nitridobrücken and Gottfried-Wilhelm-Leibniz-Programm), the Bundesministerium für Bildung, Wissenschaft, Forschung und Technologie (BMBF) in the Verbundprojekt Erforschung kondensierter Materie (Projekt 03-SC4BAY), and the ILL Grenoble is gratefully acknowledged. The authors also thank Dr. E. Suard and Dr. T. Hansen (ILL Grenoble) for their help during the neutron diffraction measurements, Dr. D. E. Cox and Dr. Q. Zhu (NSLS Brookhaven) for help during the synchrotron measurements, and Dr. J. Senker (University of Bayreuth) for the ^{31}P MAS NMR spectra.

Received: March 4, 1998 [F 1025]

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