



Nitridophosphates

CdP₂N₄ and MnP₂N₄ – Ternary Transition-Metal Nitridophosphates

Florian J. Pucher,^[a] Friedrich W. Karau,^[a] Jörn Schmedt auf der Günne,^[b] and Wolfgang Schnick^{*[a]}

Abstract: The ternary transition-metal nitridophosphates CdP_2N_4 and MnP_2N_4 have been synthesized under high-pressure high-temperature conditions (5–8 GPa, 1000–1300 °C) by using the multianvil technique. Cd and Mn azides can be used as the starting materials, however, with respect to safety considerations, it is much more advantageous to start from metal powders and phosphorus nitride imide, HPN_2 . Both nitridophosphates crystallize in a structure closely related to the mega calsilite structure type. As a result of the known issues concerning superstructures with this type of structure, TEM investigations were performed on CdP_2N_4 , which revealed that the megacalsilite superstructure is not equally pronounced in all

crystallites. By adding NH₄Cl as mineralizer, single crystals were obtained that exhibit unequally pronounced superstructure reflections. Consequently, an averaged structural model was used and refined by the Rietveld method [*P*6₃22, *a* = 16.7197(3), *c* = 7.6428(2) Å, *V* = 1850.3(2) Å³, *R*_p = 0.0671, *wR*_p = 0.0869 for CdP₂N₄ and *P*6₃22, *a* = 16.5543(2), *c* = 7.5058(2) Å, *V* = 1781.3(1) Å³, *R*_p = 0.0526, *wR*_p = 0.0697 for MnP₂N₄]. The ³¹P NMR spectra exhibit four signal groups at (6.4, 4.8), 0.8, and -9.7 ppm with pronounced shoulders belonging to the same phase in an approximate area ratio of 4.8:1.1:2.0, thereby proving at least eight P sites.

Introduction

Nitridophosphates represent a class of materials with high potential for various applications.^[1] Binary P₃N₅, which was first described in 1862, although its structure was only elucidated in 1997^[2–4] finds application as a gate insulator material in electronic devices and has been used for the production of incandescent lamps.^[5-7] Ternary nitridophosphates have been identified as Li⁺ ion conductors (LiPN₂, Li₇PN₄),^[8,9] possible gas storage materials $[P_4N_4(NH)_4NH_3]$,^[10,11] and hard materials (e.g., γ - $\mathsf{P}_3\mathsf{N}_5$ and $\mathsf{BeP}_2\mathsf{N}_4).^{[12-15]}$ Recent work shows that $\mathsf{Eu}^{2+}\text{-doped}$ nitridophosphates like MP_2N_4 :Eu²⁺ (M = Ca, Sr, Ba) and $Ba_3P_5N_{10}X:Eu^{2+}$ (X = Cl, I, Br) are promising luminescent materials that may find application as phosphors in (pc)LEDs.[16-18] One reason for this remarkable variety in materials properties is their structural similarity to silicates.^[1] The element combination P/N has the same number of valence electrons as the combination Si/O. Similarly to silicates, an anionic three-dimensional network of edge-sharing PN4 tetrahedra can be formed. However, N can guite easily connect not only two, but even three or four tetrahedron centers.[1,3,4,19-31]

 [a] Department of Chemistry, Chair in Inorganic Solid-State Chemistry, University of Munich (LMU), Butenandtstr. 5–13 (D), 81377 München, Germany E-mail: wolfgang.schnick@uni-muenchen.de http://www.cup.uni-muenchen.de/ac/schnick

[b] Department of Chemistry and Biology, University of Siegen, Adolf-Reichwein-Str. 2, 57076 Siegen, Germany

ORCID(s) from the author(s) for this article is/are available on the WWW under http://dx.doi.org/10.1002/ejic.201600042.

In nitridophosphates, P typically occurs in networks of more or less condensed PN₄ tetrahedra. But higher coordination numbers of P with respect to N can occur as well. Besides tetrahedra, square-pyramidal PN₅ structures have also been found in the high-pressure polymorphs γ -P₃N₅ and trigonal-bipyramids in γ -P₄N₆(NH) leading to a higher bond density and thus greater hardness.^[12,13,32] BeP₂N₄, which has recently been described, is another example with high hardness, and an even denser and harder high-pressure polymorph has been predicted.^[14,15] Transition-metal nitridophosphates are more difficult to synthesize because the corresponding phosphides are rather stable and their formation has to be avoided by carefully choosing appropriate synthesis conditions and starting materials. Besides $Zn_6P_{12}N_{24}$, which later was proved to be the quaternary compound $Zn_8P_{12}N_{24}O_2$,^[33,34] and Mn_2PN_3 , which crystallizes in a wurtzite-like structure,^[35] only main-group-element-containing ternary nitridophosphates have been described.^[36-48] With respect to the intriguing properties that can be expected (e.g., color, magnetism, electronic properties), access to transition-metal nitridophosphates remains a challenge.

Usually, ternary nitridophosphates are synthesized from the corresponding nitrides or azides and P_3N_5 .^[36-48] Azides are advantageous, especially in combination with high-pressure high-temperature synthesis.^[43,44] However, synthesis temperatures of around 1000 °C are necessary and P_3N_5 as well as most nitridophosphates undergo thermal decomposition with evolution of N_2 above 850 °C. By following the principle of Le Chatelier, an increased N_2 pressure stabilizes both the starting material P_3N_5 as well as the formed nitridophosphate. For most transition metals, the corresponding azides are highly explosive and have

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to be handled with particular care.^[49] Additionally, for most transition metals only subnitrides are stable and therefore an additional nitrogen source would be required when synthesizing ternary nitridophosphates. The use of halides and chalcogenides leads to quaternary compounds, and several (oxo)-nitride sodalites, for example, $M_{[6+(y/2)-x]}H_{2x}[P_{12}N_{24}]Z_y$ (M = Fe, Co, Ni, Mn; Z = Cl, Br, I; $0 \le x \le 4$; $y \le 2$) and $M_{8-m}H_m[P_{12}N_{18}O_6]X_2$ (M = Cu, Li; X = Cl, Br, I) have been synthesized in this way.^[50,51]

In this work we report on the synthesis of CdP_2N_4 and MnP_2N_4 . Although CdP_2N_4 may be prepared from the highly explosive azide,^[52] it is much more feasible to start from Cd powder and phosphorus nitride imide HPN₂. Metal powder and HPN₂ has been successfully used for the preparation of Mn_2PN_3 , however, under different synthesis conditions.^[35] Analogously to Si(NH)₂ in the synthesis of nitridosilicates, HPN₂ can be regarded as a polymeric acid in which the metal is dissolved.^[34,53] This safer preparation method was then successfully applied to the synthesis of MnP_2N_4 .

Results and Discussion

CdP₂N₄ can either be synthesized at 5–8 GPa and 1000–1300 °C from the metal azide and P₃N₅ according to Equation (1) or from Cd powder and HPN₂ according to Equation (2). The latter method can also be applied for the synthesis of MnP₂N₄. Crystallinity can be improved by adding small amounts of NH₄Cl.^[54]

$$3 \text{ Cd}(N_3)_2 + 2 \text{ P}_3 \text{N}_5 \rightarrow 3 \text{ CdP}_2 \text{N}_4 + 8 \text{ N}_2$$
(1)

$$M + 2 \text{ HPN}_2 \rightarrow MP_2N_4 + H_2 (M = \text{Cd}, \text{Mn})$$
(2)

In the case of MnP_2N_4 , the crude product contains considerable amounts of Mn phosphides, which can be dissolved by treating the product with dilute HCl.

Both compounds exhibit powder X-ray diffractograms that are very similar to the corresponding patterns of megacalsilitetype SrP₂N₄ and CaP₂N₄ and give similar lattice parameters upon indexing the reflections. Structure elucidation of the latter compounds from powder samples was difficult, because the megacalsilite superstructure is realized by the ordering effects of the N atoms.^[42] This results in very weak reflections corresponding to the superstructure. Owing to the larger diffraction contrast between Cd and N compared with Ca or Sr and N as in CaP₂N₄ and SrP₂N₄, it is even more difficult to visualize these structural details solely from PXRD data. Therefore, electron diffraction experiments were carried out on CdP₂N₄ samples. Three different types of crystallites were identified (Figure 1). Type 1 exhibits an analogous superstructure to that of SrP₂N₄ (megacalsilite type). However, as observed by X-ray diffraction, due to the larger difference in the number of electrons in Cd²⁺ compared with Sr²⁺ and the fact that the superstructure is mainly caused by the displacement of the N atoms, the superstructure reflections are considerably weaker in CdP₂N₄ crystallites. Type 2 crystals show diffuse scattering and an incommensurate superstructure occurs in type 3 crystallites. The diffuse intensities of the type 2 crystallites are oriented towards the reflections of the basic structure and are not always easy to distinguish from the megacalsilite superstructure.





Figure 1. Electron diffraction images of three different types of CdP_2N_4 crystallites, prepared from $Cd(N_3)_2$ and P_3N_5 , viewed along the [111] direction (superstructure cell). Type 1: SrP_2N_4 -like. Type 2: Diffuse intensities. Type 3: Incommensurate reflection intensities.

Examining the type 3 crystallites, the incommensurate reflections are closer to the main reflections of the basic structure than the corresponding reflections of the commensurate megacalsilite structure.

Several crystallites of CdP_2N_4 were examined and it was concluded that powder samples of CdP_2N_4 consist of several different phases that are distinguished by a more or less predominant superstructure. To allow the N atoms to order, temperature-programmed powder X-ray diffraction investigations were conducted. Although CdP_2N_4 is stable up to the remarkably high thermal decomposition temperature of 1050 °C, the incommensurate reflections move towards their regular Bragg positions (Figure 2). This point is reached at 400 °C and is stable up to 650 °C. At higher temperatures, these reflections disappear completely. Diffuse intensities could not be seen in this case, because they result solely in a broadening of the reflections. This broadening correlates to nearly 100 % of the background.



Figure 2. Section of the powder X-ray diffractogram of CdP₂N₄, prepared from Cd(N₃)₂ and P₃N₅. With increasing temperature, the incommensurate reflections move towards their regular Bragg positions. The (621) reflection occurs as a satellite of the (413) reflection at 20 °C and is at its regular Bragg position at 500 °C.

In spite of these findings, the annealing of CdP_2N_4 samples at higher temperatures did not lead to single-phase samples at room temperature. Consequently, a structure model to be refined from room-temperature powder X-ray diffraction data by the Rietveld method has to be an averaged model taking all the different types of crystallites into account (Figure 3). The megacalsilite superstructure can be derived from a highly symmetric basic structure (space group $P6_322$) by gradually reducing the symmetry. After a *klassengleiche* transition the unit cell of the superstructure is determined. In the following *translationengleiche* transition, two-fold axes are removed from the *ab* plane leading to space group $P6_3$.^[42,45] The first step of this symmetry reduction starting from the basic structure towards the full megacalsilite superstructure proved to be the best





model for CdP_2N_4 . In the basic structural model the P–N–P angles along the *c* axis exhibit values of 180°. By reducing the symmetry, the values for this angle can be refined to a more realistic value. However, the N atoms cannot order as freely as in the megacalsilite structure type (space group $P6_3$) because there is still a two-fold axis in the *ab* plane left.



Figure 3. Crystal structure of MnP_2N_4 and CdP_2N_4 , viewed along the *c* (left) and *b* (right) axes.

The ³¹P NMR spectra exhibit four signal groups belonging to a single crystalline phase with pronounced shoulders (Figure 4). The peak areas of these groups obtained by deconvolution of a quantitative 1D MAS NMR spectrum (not shown) have a ratio of approximately 4.8:1.1:2.0 for the peaks at (6.4, 4.8), 0.8 and -9.7 ppm, respectively, which reveals that the symmetry must be as low as in the megacalsilite structure so that eight P atoms occupy crystallographic sites with equal multiplicity. However, the PXRD data were not sufficient to prove this assumption sufficiently. In situ NMR experiments at higher temperature showed a slight reversible shift of the resonances but no fundamental change, which evidences the stability of the structure and indicates the absence of phase transitions.



Figure 4. ³¹P NMR double-quantum (DQ) single-quantum (SQ) correlation spectrum of CdP₂N₄, prepared from Cd(N₃)₂ and P₃N₅, recorded at room temperature. The diagonal line marks the position of the isochronous DQ spin pairs. DQ coherences were excited with the INADEQUATE sequence (symmetric protocol, 3 ms DQ excitation time). The spectrum proves that the observed peak groups at 6.4, 4.8, 0.8 and –9.7 ppm all belong to a single crystalline phase.

Recently, we succeeded in growing single crystals of a highly condensed nitridophosphate, namely β -HPN₂, by adding NH₄Cl as mineralizer.^[54] Under the reaction conditions, NH₄Cl decomposes into NH₃ and HCl, which probably protonates reversibly the growing nitridophosphate network. This cleaving and re-



Figure 5. Rietveld refinement of MnP₂N₄ (top) and CdP₂N₄ (bottom). Observed (crosses), calculated (line), and difference (gray line). Allowed Bragg reflection positions are marked with vertical lines.

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building of bonds seems to support crystallization.^[1] This method can also be applied to CdP_2N_4 and MnP_2N_4 . However, as can be seen from the electron diffraction experiments, the megacalsilite superstructure is not equally pronounced in different crystals. This fact also applies to larger crystals, which can be investigated by single-crystal X-ray diffraction experiments. Consequently, even when utilizing the NH₄Cl method, the bulk compounds are best investigated by Rietveld refinement of powder samples leading to an averaged superstructure.

Rietveld refinement of bulk samples of CdP₂N₄ and MnP₂N₄ consequently only allows the determination of averaged structural data (Figures 3 and 5). Owing to the high diffraction contrast between the metal ions and the N atoms, the latter are not easily located accurately and tend to be closer to the metal ions than the sum of the ionic radii. To circumvent this problem, the P–N distances can be restrained, because this type of bond typically has a rather narrow range of between 1.5 and 1.7 Å.^[45] Table 1 shows the results of the Rietveld refinement of CdP₂N₄ and MnP₂N₄.

Table 1. Crystallographic data for ${\rm CdP_2N_4}$ and ${\rm MnP_2N_{4,}}$ and details of the Rietveld refinement.

	CdP_2N_4	MnP_2N_4
Molar mass [g mol ⁻¹]	230.39	172.92
Crystal system	hexagonal	
Space group		<i>P</i> 6 ₃ 22 (no. 182)
Cell parameters		
a [Å]	16.7197(3)	16.5543(2)
b [Å]	16.7197(3)	16.5543(2)
c [Å]	7.6428(2)	7.5058(2)
Cell volume [Å ³]	V = 1850.3(2)	V = 1781.3(1)
Formula units per cell		24
ϱ_{calcd} [g cm ⁻³]	4.9623(2)	3.6168(1)
Diffractometer	Stoe StadiP	
Temperature [K]		298
Radiation, λ [Å]		Mo- <i>K</i> _{α1} , 0.70930
Detector		lin. PSD, $\Delta 2 \theta = 5^{\circ}$
Diffraction range [°]	$6 < 2\theta < 75$	$5 < 2\theta < 60$
Step width [°] (internal	0.3 (0.01)	
step width [°])		
Data points	6900	5400
Obsd. reflections	1964	1095
Background function	shifted Chebyshev	
Profile function	fundamental parameter	
Refined parameters	75	70
GoF	1.110	1.359
Final R indices		
R _p	0.06707	0.05261
wRp	0.07780	0.06979

Conclusions

 CdP_2N_4 and MnP_2N_4 have successfully been synthesized under high-pressure high-temperature conditions. CdP_2N_4 is accessible from the corresponding azide and P_3N_5 or from Cd powder and HPN₂. The latter method is evidently safer because $Cd(N_3)_2$ is highly hazardous and tends to deflagrate violently when exposed to thermal or mechanical shock. MnP_2N_4 was subsequently synthesized from Mn powder and HPN₂. Because in this case no additional N₂ pressure from the decomposition of the azide is available, partial dissociation of the product is observed and besides MnP₂N₄ there is also a reasonable amount of phosphides in the crude product. To obtain a phase-pure sample, the crude product can be treated with diluted mineral acids, a procedure in which the corresponding phosphides dissolve, but the nitridophosphate is left intact. Both compounds CdP₂N₄ and MnP₂N₄ are isotypic to SrP₂N₄, however, the megacalsilite superstructure is less pronounced. Electron diffraction analysis of CdP_2N_4 samples proved the presence of three different types of crystallites in the bulk material, which can be distinguished by differences in their diffraction intensities related to their superstructure. Temperature-programmed powder X-ray diffraction experiments showed that above 400 °C ordering effects can be observed and above 650 °C only the megacalsilite superstructure is stable. The ³¹P NMR spectroscopic data is in agreement with at least eight different P sites, which is also in accord with the megacalsilite superstructure. However, the powder Xray diffraction data recorded at room temperature only allow for Rietveld refinement in a higher symmetric space group (P6₃22) with only five distinguishable P sites. The main difference compared with the megacalsilite superstructure (space group $P6_3$) is the presence of a two-fold axis in the *ab* plane leading to higher ordering of the N atoms. The latter are far more difficult to locate compared with, for example, in SrP₂N₄ due to the considerably larger diffraction contrast between Cd and N. By applying the corresponding restraints to the Rietveld refinement of the bulk powder samples, the average structure, including a partial superstructure, could be refined. Although a superstructure in space group P63 was confirmed for SrP2N4, only a higher symmetric averaged structure could successfully be refined for CdP₂N₄. However, NMR measurements support the presence of at least eight different P sites, analogously to the structure proven for SrP₂N₄. Electron diffraction experiments showed that the superstructure is not equally pronounced in several crystallites, which was confirmed by singlecrystal X-ray diffraction experiments on larger crystals of CdP₂N₄ and MnP₂N₄. Consequently, the structural properties of bulk samples are best described by means of Rietveld refinement, whereas each single crystallite reveals different details of the real structure.

Experimental Section

Synthesis of the Starting Materials: P_3N_5 and HPN_2 were synthesized from (PNCl₂)₃ in a flow of dried NH₃ (Messer Griesheim, 3.8) according to literature procedures.^[55] Portions of around 8 g of (PNCl₂)₃ (ABCR, 98 %) were placed in an alumina boat that had previously been dried in vacuo (5×10^{-4} mbar) at 950 °C. The starting material was then heated to 100 °C at a rate of 0.8 °C/min in a light flow of NH₃ that had been dried by flowing through a column of KOH. The temperature was kept at 100 °C for 10 h. After cooling to room temperature, NH₃ was expelled with a flow of argon and the sample ground to a powder in a mortar. It was then placed in the crucible again and the procedure repeated at 130, 190, and 300 °C. In the last step, the sample was heated to 600 °C in vacuo to remove NH₄Cl and produce amorphous HPN₂. For P₃N₅, instead of 600 °C, a temperature of only 450 °C was applied, followed by a final step of 950 °C for 2 h in a flow of NH₃.

 $Cd(N_3)_2$ was synthesized from $CdCO_3$ (Merck, puriss.) and an aqueous solution of HN_3 according to a literature procedure. $^{[56]}$ Special





caution was necessary when handling even dilute solutions of HN_3 because the vapors are highly poisonous. Pure HN_3 , which is highly explosive and may detonate violently upon friction or thermal shock, may condensate onto cool surfaces, and is therefore important to avoid. A solution of about 24 % can be obtained by careful distillation. This solution was slowly added in excess (ca. 100 mL) to solid CdCO₃ (6 g, 34.8 mmol) and stirred for 3 d. The crystalline product was isolated and washed with cold water followed by ethanol and finally diethyl ether. After drying over P_4O_{10} in an evacuated desiccator the purity of the product was confirmed by powder X-ray diffraction.

Extreme caution is necessary when handling $Cd(N_3)_2$. It detonates vigorously upon friction or thermal shock. For safety reasons only amounts of up to a maximum of 90 mg were used. Spatulas of horn were used instead of metal ones. Mixing with other starting materials is preferably performed by using a micro ball mill after careful premixing in an agate mortar to avoid high friction.

High-Pressure Syntheses: High-pressure syntheses were carried out by using a modified Walker-type multianvil set-up.^[57] The starting materials were thoroughly and in the case of $Cd(N_3)_2$ very carefully mixed by using a micro ball mill three times for 3 min. A micro ball mill causes less friction than the usual agate mortar and pestle and is thus more suitable for handling highly sensitive compounds like transition-metal azides. The reaction mixture was then placed in a crucible of hexagonal BN (Hebosint S100, Henze, Germany), which was closed with a lid of the same material. The crucible was set in a graphite tube (SGL carbon, Germany) that serves as resistance heating. To minimize a thermal gradient, this tube was placed in a larger tube of the same material with two plates of porous MgO (Technoker, Germany) used to center the inner tube. This arrangement was placed in a tube of zirconia (Cesima Ceramics, Germany) as thermal insulator. Electrical contact was achieved through two small plates of Mo. The tube was then placed in an octahedron of Cr-doped MgO (5 % Cr₂O₃, Ceramic Substrates, United Kingdom) as pressure medium with an edge length of 18 mm. Cubes of WC (6 % Co, Hawedia, Germany) with truncated edges (11 mm truncated edge length) were used as anvils in a Walker-type multianvil apparatus. To prevent the pressure medium from flowing out through the gaps between the cubes, gaskets of pyrophyllite were used. These were supported by sheets of Bristol cardboard (269 g/ m², Bähr, Germany). Isolation of the cubes was realized by applying PTFE foil (Vitaflon, Germany). The assembled anvils form a larger cube that was held together by plates of glass-fiber-enhanced resin plates, to which small strips of copper were applied for electrical contact. This set-up was placed in a Walker-type multianvil apparatus. After reaching the desired synthesis pressure at a rate of 1 bar/ min of hydraulic oil pressure, the electrical heating was turned on. Following the temperature program the pressure was slowly reduced (1/3 bar/min). After the experiment, the sample was recovered by cracking the pressure medium open and removing carefully all other materials.

X-ray Diffraction: X-ray diffraction experiments were carried out with a Stoe StadiP diffractometer with Debye–Scherrer geometry, a PSD detector, and Mo- $K_{\alpha 1}$ radiation. For temperature-programed measurements, an electrical resistance furnace was employed. Rietveld refinement was carried out by using the GSAS/EXPGUI and the TOPAS Version 4.1 program packages.^[58–60]

Single-crystal X-ray diffraction was carried out with Bruker d8 venture and Nonius–Kappa CCD diffractometers using Mo- K_{α} radiation ($\lambda = 0.71073$ Å) and a graphite monochromator. Single-crystal structure solution was achieved by direct methods with the software package WinGX, which was also used for refinement using SHELX97.^[61]

Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the deposition numbers CSD-428137 (MnP₂N₄) and CSD-428140 (CdP₂N₄).

Electron Diffraction: Electron diffraction experiments were carried out with a Philips CM 30 transmission electron microscope with a super twin lens and LaB_6 cathode in SAD mode.

NMR Spectroscopy: NMR spectra were recorded with a 500 MHz (11.4 T) Bruker DSX 500 Avance FT NMR spectrometer. Zirconia rotors with diameters of 2.5 and 4 mm were used in combination with Bruker double-resonance probe heads at rotation frequencies of up to 25 kHz. The ³¹P chemical shifts are given relative to 85 % phosphoric acid ($\delta = 0$ ppm). High-temperature NMR experiments were performed with a LASER-heated Bruker 7 mm MAS NMR probe head at a spinning frequency of 3800–4000 Hz with a Tecmag Apollo console in a magnetic field of 4.7 T.

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