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Monoammonium Trimetaphosphimate $(NH_4)H_2(PO_2NH)_3$

Daniel Günther [1], Carsten Paulmann [2] and Oliver Oeckler [1,*]

[1] Institute for Mineralogy, Crystallography and Materials Science, Leipzig University, Scharnhorststr. 20, 04275 Leipzig, Germany
[2] Department of Earth System Sciences, University of Hamburg, Grindelallee 48, 20146 Hamburg, Germany
* Correspondence: oliver.oeckler@gmx.de

Abstract: Trimetaphosphimates show a rich structural variability in both cation coordination and anion arrangement. They are precursors for crystalline, as well as amorphous oxonitridophosphates. The ammonium trimetaphosphimate $(NH_4)H_2(PO_2NH)_3$ is formed during the decomposition of the corresponding acid in solution. The monoclinic crystal structure of the monoammonium salt was elucidated by single crystal X-ray diffraction using synchrotron radiation. The trimetaphosphimate monoanions exhibit a twist conformation and form crankshaft-like stacks along [100], which have so far only been observed in $(NH_4)_3(PO_2NH)_3{\cdot}H_2O$ and $Ag_3(PO_2NH)_3$. $(NH_4)H_2(PO_2NH)_3$ decomposes at 170 °C, forming a poorly crystalline phase. Therefore, it is a model system and possible precursor for the synthesis of oxonitridophosphates.

Keywords: trimetaphosphimate; single-crystal structure determination; thermal decomposition; hydrogen bonding; packing of rings

1. Introduction

Trimetaphosphimic acid was first mentioned by Stokes in 1895 [1]. Over the years, many of its salts have been synthesized, but only in 1965 Olthof et al. published the first crystal structure of a trimetaphosphimate in their report on $Na_3(PO_2NH)_3{\cdot}4H_2O$ [2]. To date, many more crystal structures with phosphimate rings have been described. A complete list of crystal structure determinations of trimetahosphimates is given in Table 1. Detailed investigation of these structures revealed a range of structural similarities between different salts. However, only a few compounds exhibit the same structure type, e.g., some salts with transition metal cations Co^{2+} and Zn^{2+} [3]. Most compounds are characterized by one molecule per asymmetric unit. The different cations often exhibit typical coordination known from other compounds, for instance, an octahedral environment for Na^+ ions or tetrahedral coordination of Ag^+ ions. Some unusual coordination numbers, like 9 for potassium [4,5] or 7 for earth alkaline ions [6,7], have also been observed. Depending on solvent water content, cation coordination polyhedra are built up from both the trimetaphosphimate anion and/or water molecules in different ratios. The trimetaphosphimate anions form different arrangements when packed in solid-state structures. In chain structures, anions lie side by side along one direction, whereas they lie on top of each other when they form stacks in structures that can be described as rod packings. In layered structures, chains or stacks are closely interconnected by hydrogen bonds and form anion packings that extend in two dimensions. In addition, network structures have been described occasionally [6,8]. Anions closely interconnected via hydrogen bonds can form pairs, which were found in several salts [9–11]. Likewise, complex anions that consist of transition metal centers coordinated by trimetaphosphimate anions can form rigid entities in mixed cationic salts [8,12–15].

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Table 1. A list of all crystal structure determinations of trimetaphosphimates.

Sum Formula	Space Group	Lattice Parameters	Cation Coordination	Anion Arrangement
$(H_3O)H_2(PO_2NH)_3 \cdot H_2O$ [16]	$P2_1/c$	a = 7.022(1) Å b = 14.008(1) Å c = 9.353(2) Å β = 93.34(2)°	irregular coordination of $H_3O^+/H_5O_2^+$ connected via hydrogen bonds	hexagonal pattern of anion stacks along [001]
$(H_3O)H_2(PO_2NH)_3 \cdot H_2O$ [17]	$P2_1/c$	a = 7.0289(3) Å b = 14.1700(7) Å c = 11.3378(6) Å β = 124.225°	irregular coordination of $H_3O^+/H_5O_2^+$ connected via hydrogen bonds	rectangular pattern of anion stacks along [001]
$(NH_4)H_2(PO_2NH)_3 \cdot CH_3OH$ [18]	$Pbca$	a = 15.025(3) Å b = 7.264(1) Å c = 19.252(1) Å	distorted tetrahedral coordination of NH_4^+ ions by O atoms from anions via hydrogen bonds	distorted hexagonal pattern of double chains along [010], solvent between the chains
$(NH_4)_3(PO_2NH)_3 \cdot H_2O$ [18]	$P2_1$	a = 6.5712(6) Å b = 12.9917(6) Å c = 6.9237(3) Å β = 102.133(6)°	irregular coordination of NH_4^+ ion (H atom positions not determined)	crankshaft-like anion stacks along [010]
$Na_3(PO_2NH)_3 \cdot H_2O$ [9]	$C2$	a = 9.8797(7) Å b = 12.2119(8) Å c = 7.6464(6) Å β = 104.394(6)°	distorted NaO_6 octahedra with all O atoms from anions or O atoms of 4 anions and 2 water molecules	hexagonal pattern of anion pairs stacked along [001]
$Na_3(PO_2NH)_3 \cdot H_2O$:Rh [6]	$C2/m$	a = 9.976(2) Å b = 12.105(3) Å c = 7.641(2) Å β = 104.95(3)°	disordered distorted NaO_6 octahedra with O atoms only from 4 anions and 2 water molecules	hexagonal pattern of anion pairs stacked along [001]
$Na_3(PO_2NH)_3 \cdot 4H_2O$ [2]	$P2_1/n$	a = 16.976(9) Å b = 7.834(3) Å c = 8.918(6) Å β = 97.08(7)°	distorted NaO_6 octahedra with O atoms from 5 anions and 1 water or from 3 anions and 3 water molecules	rectangular pattern of anion stacks along [010]
$Ag_3(PO_2NH)_3$ [4]	$P2_1/c$	a = 11.666(1) Å b = 7.864(1) Å c = 9.978(1) Å β = 106.91(1)°	distorted AgO_4 or AgO_3N tetrahedra	crankshaft-like anion stacks along [001]
$K_3(PO_2NH)_3$ [4,5]	$R\bar{3}$	a = 12.714(2) Å c = 10.179(2) Å	ninefold K coordination	hexagonal pattern of anion stacks along [001]
$Rb_3(PO_2NH)_3$ [5]	$R\bar{3}$	a = 12.9971(5) Å c = 10.5485(5) Å	ninefold Rb coordination	hexagonal pattern of anion stacks along [001]
$[C(NH_2)_3]_3(PO_2NH)_3 \cdot H_2O$ [10]	$Pbca$	a = 15.656(2) Å b = 10.6831(6) Å c = 20.918(2) Å	irregular coordination of $C(NH_2)_3^+$ involving 6 hydrogen bonds	layers of anion pairs in (001) plane
$Zn_3[(PO_2NH)_3] \cdot 14H_2O$ [3]	$P\bar{1}$	a = 7.443(5) Å b = 9.613(6) Å c = 9.834(5) Å α = 102.60(4)° β = 90.31(4)° γ = 99.92(4)°	distorted ZnO_6 octahedra, O atoms from 3 anions and 3 water or from 2 anions and 4 water molecules	distorted hexagonal pattern of anion stacks along [100], solvent between the chains
$Co_3[(PO_2NH)_3] \cdot 14H_2O$ [3]	$p\bar{1}$	a = 7.4605(1) Å b = 9.5706(2) Å c = 9.8851(2) Å α = 102.162(1)° β = 90.044(1)° γ = 99.258(1)°	distorted CoO_6 octahedra, O atoms from 3 anions and 3 water or from 2 anions and 4 water molecules	distorted hexagonal pattern of anion stacks along [100], solvent between the chains
$Cr(PO_2NH)_3 \cdot 7H_2O$ [19]	$P2_1/n$	a = 9.461(2) Å b = 10.760(2) Å c = 12.954(3) Å β = 92.68(3)°	distorted $Cr(H_2O)_6$ octahedra	anion stacks along [100] separated by solvent water
$Ce(PO_2NH)_3 \cdot 5H_2O$ [6,20]	$P2_12_12$	a = 7.3040(15) Å b = 9.1675(18) Å c = 9.5663(19) Å	CeO_8 quadratic antiprism, O atoms from 6 anions and 2 water molecules	layers of anions in (001) plane
$Pr(PO_2NH)_3 \cdot 5H_2O$ [6]	$P2_12_12$	a = 7.307(1) Å b = 9.159(1) Å c = 9.585(2) Å	PrO_8 quadratic antiprism, O atoms from 6 anions and 2 water molecules	layers of anions in (001) plane
$NaBa(PO_2NH)_3$ [7]	$C2/m$	a = 10.845(2) Å b = 10.250(2) Å c = 7.962(2) Å β = 115.18(3)°	distorted NaO_6 octahedra, Ba: 8 + 2 coordination	staggered arrangement of chains along [010]

Table 1. *Cont.*

Sum Formula	Space Group	Lattice Parameters	Cation Coordination	Anion Arrangement
$KSr(PO_2NH)_3 \cdot 4H_2O$ [7]	$P2_1/n$	a = 10.872(2) Å b = 10.496(2) Å c = 11.912(2) Å β = 111.98(3)°	Sr: sevenfold coordination by O atoms from 5 anions and 2 water molecules, K: nine-fold coordination by 4 O and 2 N anion atoms and 3 water molecules	layers parallel (100) of anion pairs stacked along [010]
$NH_4Sr(PO_2NH)_3 \cdot 4H_2O$ [7]	$P2_1/n$	a = 10.884(2) Å b = 10.485(2) Å c = 11.969(2) Å β = 111.43(3)°	Sr: sevenfold coordination by O atoms from 5 anions and 2 water molecules, NH_4^+: nine-fold coordination by O/N (H atom positions not determined)	layers parallel (100) of anion pairs stacked along [010]
$K_{1.3}(NH_4)_{1.7}Pr[(PO_2NH)_3]_2 \cdot 8H_2O$ [21]	$Pna2_1$	a = 25.623(8) Å b = 10.577(3) Å c = 8.632(2) Å	distorted PrO_8 quadratic antiprism, all O atoms from anions; K coordinated by 4 O atoms of anions and 3 water molecules	staggered stacks along [010] forming layer parallel (100) and additional anions in between
$Na_2K(PO_2NH)_3 \cdot 2H_2O$ [11]	$P\bar{1}$	a = 7.948(2) Å b = 8.034(2) Å c = 8.515(2) Å α = 75.84(3)° β = 83.54(3)° γ = 77.37(3)°	NaO_6 octahedra with O atoms from 3 anions and 3 water molecules, K: tenfold coordination by 5 O and 2 N atoms from anions and 3 H_2O	anion pairs stacked along [1$\bar{1}$0]
$Na_2Tl(PO_2NH)_3 \cdot 2H_2O$ [11]	$P\bar{1}$	a = 7.991(2) Å b = 7.993(2) Å c = 8.646(2) Å α = 76.83(3)° β = 83.81(3)° γ = 77.57(3)°	NaO_6 octahedra with O atoms from 3 anions and 3 water molecules, Tl: tenfold coordination by 5 O and 2 N atoms from anions and 3 H_2O	anion pairs stacked along [1$\bar{1}$0]
$Na_4\{Co[(PO_2NH)_3]_2\} \cdot 12H_2O$ high temperature-phase [12,13]	$C2/c$	a = 8.889(1) Å b = 19.018(2) Å c = 17.112(2) Å β = 104.59(1)°	disordered NaO_6 octahedra with O atoms from 2 anions and 4 water molecules, CoO_6 tetrahedra with O atoms of anions	layers of complex $\{Co[(PO_2NH)_3]_2\}^{4-}$ ·ions in (010) plane
$Na_4\{Co[(PO_2NH)_3]_2\} \cdot 12H_2O$ low temperature-phase [12,13]	$P2_1/n$	a = 8.887(2) Å b = 19.001(4) Å c = 17.072(3) Å β = 104.59(3)°	ordered NaO_6 octahedra, O atoms: 2 anions + 4 crystal water; CoO_6 tetrahedra with O atoms of anions	layers of complex $\{Co[(PO_2NH)_3]_2\}^{4-}$ ·ions in (010) plane
$Na_4\{Ni[(PO_2NH)_3]_2\} \cdot 12H_2O$ high temperature-phase [12,13]	$C2/c$	a = 8.944(1) Å b = 18.906(1) Å c = 17.236(1) Å β = 104.49(1)°	disordered NaO_6 octahedra with O atoms from 2 anions and 4 water molecules, NiO_6 tetrahedra with O atoms of anions	layers of complex $\{Ni[(PO_2NH)_3]_2\}^{4-}$ ·ions in (010) plane
$Na_4\{Ni[(PO_2NH)_3]_2\} \cdot 12H_2O$ low temperature-phase [12,13]	$P2_1/n$	a = 8.903(1) Å b = 18.902(2) Å c = 17.133(2) Å β = 104.62(1)°	ordered NaO_6 octahedra, O atoms: 2 anions + 4 crystal water; NiO_6 tetrahedra with O atoms of anions	layers of complex $\{Ni[(PO_2NH)_3]_2\}^{4-}$ ·ions in (010) plane
$Na_4\{Zn[(PO_2NH)_3]_2\} \cdot 12H_2O$ [13,14]	$C2/c$	a = 8.883(1) Å b = 18.994(2) Å c = 17.126(2) Å β = 104.54(1)°	disordered NaO_6 octahedra with O atoms from 2 anions and 4 water molecules, ZnO_6 tetrahedra with O atoms of anions	layers of complex $\{Zn[(PO_2NH)_3]_2\}^{4-}$ · ions in (010) plane
$NaZn[(PO_2NH)_3]_2\} \cdot 7H_2O$ [13]	$P\bar{1}$	a = 10.209(3) Å b = 9.256(2) Å c = 9.539(2) Å α = 116.02(4)° β = 97.7(3)° γ = 103.16(3)°	ZnO_6 octahedra with O atoms from 4 anions and 2 water or from 2 anions and 4 water molecules; (Na coordination not given in literature)	chains of comple $X[Zn(PO_2NH)_3(H_2O)_3]^-$ ions along [010]
$NaCo[(PO_2NH)_3]_2\} \cdot 7H_2O$ [13]	$P\bar{1}$	a = 10.207(3) Å b = 9.253(2) Å c = 9.530(2) Å α = 116.00(5)° β = 97.61(3)° γ = 103.17(5)°	CoO_6 octahedra with O atoms from 4 anions and 2 water or from 2 anions and 4 water molecules; (Na coordination not given in literature)	chains of comple $X[Co(PO_2NH)_3(H_2O)_3]^-$ ions along [010]
$Na_4\{Cu[(PO_2NH)_3]_2\} \cdot 10H_2O$ [13]	$P\bar{1}$	a = 9.1251(6) Å b = 9.3214(6) Å c = 9.6610(6) Å α = 94.840(5)° β = 108.652(6)° γ = 118.588(6)°	distorted CuO_6 bipyramids with O atoms from 4 anions and 2 water molecules; Na: distorted octahedra with O atoms from 2 anions and 4 water or trigonal bipyramidal coordination with O atoms from 2 anions and 3 water molecules	chains of complex $\{Cu[(PO_2NH)_3]_2\}^{4-}$ ions along [010]

Table 1. *Cont.*

Sum Formula	Space Group	Lattice Parameters	Cation Coordination	Anion Arrangement
$Na_4\{Hf(\mu\text{-}O)(\mu_4\text{-}OH)_6[(PO_2NH)_3]_4\}\cdot 18H_2O$ [15]	$Pa\bar{3}$	a = 22.678(3) Å	HfO_4 tetrahedra with O atoms from anions; NaO_6 octahedra with O atoms from 3 anions and 3 water or sevenfold coordination with O atoms from 2 anions and 5 water molecules	complex $\{Hf(\mu\text{-}O)(\mu_4\text{-}OH)_6[(PO_2NH)_3]_4\}^{4-}$ ions forming a 3D network
$Na_4\{Hf(\mu\text{-}O)(\mu_4\text{-}OH)_6[(PO_2NH)_3]_4\}\cdot 21H_2O$ [8]	$R\bar{3}$	a = 14.350(2) Å c = 50.348(10) Å	HfO_4 tetrahedra with O atoms from anions; NaO_6 octahedra with O atoms from 3 anions and 3 water or from 2 anions and 4 water molecules	bilayers of complex $\{Hf(\mu\text{-}O)(\mu_4\text{-}OH)_6[(PO_2NH)_3]_4\}^{4-}$ ions in (001) plane
$Na_4\{Zr(\mu\text{-}O)(\mu_4\text{-}OH)_6[(PO_2NH)_3]_4\}\cdot 18H_2O$ [8]	$Pa\bar{3}$	a = 22.693(3) Å	ZrO_4 tetrahedra with O atoms from anions; NaO_6 octahedra with O atoms from 3 anions and 3 water or sevenfold coordination with O atoms from 2 anions and 5 water molecules	complex $\{Zr(\mu\text{-}O)(\mu_4\text{-}OH)_6[(PO_2NH)_3]_4\}^{4-}$ ions forming a 3D network
$Na_4\{Zr(\mu\text{-}O)(\mu_4\text{-}OH)_6[(PO_2NH)_3]_4\}\cdot 21H_2O$ [8]	$R\bar{3}$	a = 14.303(2) Å c = 50.284(10) Å	ZrO_4 tetrahedra with O atoms from anions; NaO_6 octahedra with O atoms from 3 anions and 3 water or from 2 anions and 4 water molecules	bilayers of complex $\{Zr(\mu\text{-}O)(\mu_4\text{-}OH)_6[(PO_2NH)_3]_4\}^{4-}$ ions in (001) plane
$NaCa(PO_2NH)_3\cdot 8H_2O$ [8]	$P2_1/c$	a = 7.8138(16) Å b = 6.8026(14) Å c = 29.693(6) Å β = 92.18(3)°	Ca: seven-fold coordination to 5 anions and 2 water molecules; $Na(H_2O)_6$ octahedra	bilayers parallel (001) of anion stacks along [010]
$NaCa(PO_2NH)_3\cdot 4H_2O$ [6]	$R\bar{3}$	a = 17.863(3) Å c = 20.548(4) Å	Ca: seven-fold coordination to 6 anions and 1 water molecule; NaO_6 octahedra with all O atoms from anions	anions interconnected by Ca^{2+} and H bonds form zeolite-like framework
$NaCa(PO_2NH)_3$ [6]	$P2_13$	a = 9.34023(10) Å	distorted CaO_6 and NaO_6 octahedra	cubic arrangement of anions that form no stacks
$K_6\{Cu_3[(PO_2NH)_3]_4\}\cdot 6H_2O$ [6]	$P\bar{1}$	a = 8.498(2) Å b = 9.552(2) Å c = 13.222(3) Å α = 86.72(3)° β = 75.09(3)° γ = 70.95(3)°	Cu^{2+}: square-pyramidal and octahedral coordination with all O atoms from anions; K: seven- or tenfold coordination by O/N from anions and water molecules	alternating stacks of $\{Cu[(PO_2NH)_3]_2\}^{4-}$ and $\{Cu_2[(PO_2NH)_3]_2\cdot 2H_2O\}^{4-}$ complex ions along [10$\bar{1}$]
$Na_3\{Al[(PO_2NH)_3]_2\}\cdot 12H_2O$ [6]	$P\bar{1}$	a = 8.6824(15) Å b = 8.7399(16) Å c = 9.1973(14) Å α = 82.131(12)° β = 86.692(9)° γ = 87.505(12)°	AlO_6 octahedra with all O atoms from anions; NaO_6 octahedra with O atoms from 1 anion and 5 water molecules	honeycomb-like arrangement of chains of $\{Al[(PO_2NH)_3]_2\}^{3-}$ ions along [111]
$Na_3\{Fe[(PO_2NH)_3]_2\}\cdot 12H_2O$ [6]	$P\bar{1}$	a = 8.7584(4) Å b = 8.7283(3) Å c = 9.2182(4) Å α = 82.286(3)° β = 86.240(4)° γ = 88.365(3)°	FeO_6 octahedra with all O atoms from anions; NaO_6 octahedra with O atoms from 1 anion and 5 water molecules	honeycomb-like arrangement of chains of $\{Al[(PO_2NH)_3]_2\}^{3-}$ ions along [111]
$Na_3\{Ga[(PO_2NH)_3]_2\}\cdot 12H_2O$ [22]	$P\bar{1}$	a = 8.729(5) Å b = 9.902(5) Å c = 8.716(5) Å α = 97.84(2)° β = 87.88(2)° γ = 93.45(2)°	GaO_6 octahedra with all O atoms from anions; NaO_6 octahedra with O atoms from 1 anion and 5 water or from 6 water molecules	hexagonal pattern of chains of complex $\{Ga[(PO_2NH)_3]_2\}^{3-}$ ions along [111]

For some further trimetaphosphimates not mentioned in Table 1, only the chemical composition has been reported. In addition to the listed mixed Na/Ca salts, two compounds, $Ca_3[(PO_2NH)_3]\cdot xH_2O$ and $NaCa(PO_2NH)_3\cdot xH_2O$, with unknown solvent water content have been obtained [6]. Furthermore, several copper salts containing benzidine, nitrate anions and/or solvent water have been synthesized [23], as well as a range of mixed cationic compounds such as $Cd_3[(PO_2NH)_3]_2\cdot 11H_2O$, $NaCd(PO_2NH)_3\cdot 4H_2O$, $Hg_3(OH)_2(PO_2NH)_3\cdot 3H_2O$, $NaHg_2(PO_2NH)_3\cdot 4H_2O$, $Na_{1.5}Hg(OH)_{0.5}(PO_2NH)_3\cdot 2.5H_2O$ [13], $NaFe(PO_2NH)_3\cdot 8H_2O$, and $K_4Fe(PO_2NH)_3\cdot 5H_2O$ [24].

Herein, we report the new monoammonium trimetaphosphimate, $(NH_4)H_2(PO_2NH)_3$, with an unusual crankshaft-like stack of monoanions that involves an asymmetric unit with two formula units.

2. Materials and Methods

2.1. Synthesis

The synthesis is initially aimed at trimetaphosphimic acid, which is described in literature [16]. The starting material, $K_3(PO_2NH)_3$, was prepared as described by Stock et al. [4]. An amount of 4.921 g of $K_3(PO_2NH)_3$ was then dissolved in 15 mL water and cooled to ~0 °C using an ice bath. A total of 5 mL of $HClO_4$ (60%) was added dropwise to this solution while continuously stirring it. $KClO_4$ forms immediately and was removed by filtration after about 1 h. The filtrate was directly passed into 150 mL of acetone, where a white precipitate formed. After 18 h, the solid phase was removed by filtration; its powder X-ray diffraction (PXRD) pattern confirmed that it was pure trimetaphosphimic acid. The filtrate was then left to stand for a week. Again, crystals grew slowly. They were isolated by filtration and washed with acetone. A total of 0.625 g of transparent crystals of the title compound were obtained.

2.2. Single-Crystal Structure Analysis

Single crystal X-ray diffraction (SCXRD), using synchrotron radiation with a wavelength of 0.5000 Å, was carried out on a Huber kappa diffractometer at beamline P24 (DESY; Hamburg, Germany) equipped with a Pilatus CdTe 1M detector (Dectris, Switzerland). The crystal was selected using polarized light and glued on a glass fiber. Indexing and integration were done using the program Crysalis [25]. Scaling and semiempirical absorption correction were carried out using SADABS [26]. Structure solution and refinement were done with the SHELX program package (version 2017-1) [27,28]. Diamond was used for graphical visualization of the structure [29].

2.3. Powder Diffraction

PXRD measurements were carried out on a SmartLab diffractometer equipped with a Hypix-3000 detector (Rigaku, Japan). Cross beam optics with a multilayer mirror were used for monochromation and focusing of the beam (Cu-$K_{\alpha 1}$ radiation). A HTK 1200N reaction chamber from Anton Paar was used for heating. A small amount of the powdered compound was filled in a 0.3 mm capillary, which was sealed under an Ar atmosphere. Temperature-dependent measurements ranged between 30 °C and 900 °C with increments of 10 K.

3. Results and Discussion

3.1. Synthesis and Characterization

The synthesis, originally just aiming at trimetaphosphimic acid, shows that the latter at least partially hydrolyzes, forming ammonium ions. After removing trimetaphosphimic acid, a second crystallization step afforded the new compound $(NH_4)H_2(PO_2NH)_3$. Comparison of a measured and a calculated PXRD pattern based on SCXRD (Figure S1, S refers to figures and tables in the Supporting Information) shows that both reflection position and intensity agree very well. A few weak reflections could neither be assigned to $(NH_4)H_2(PO_2NH)_3$, nor any other known compound; they indicate a small proportion of an additional side product. As trimetaphosphimate monoanions are rather unusual, the additional phase might contain anions that are deprotonated to a higher extent. Also note that the direct reaction of ammonia and trimetaphosphimic acid typically affords $(NH_4)_3(PO_2NH)_3 \cdot H_2O$ [18].

It is known that trimetaphosphimic acid is not stable in water. Its complete reaction with water creates ammonia and phosphoric acid; however, partial hydrolysis may also occur. This ammonia then forms the monoammonium salt $(NH_4)H_2(PO_2NH)_3$, with remaining trimetaphosphimic acid as described by the following equations:

$$H_3(PO_2NH)_3 + 6H_2O \rightarrow 3\ NH_3 + 3H_3PO_4$$

$$NH_3 + H_3(PO_2NH)_3 \rightarrow (NH_4)H_2(PO_2NH)_3$$

3.2. Crystal Structure

Crystal structure analysis showed that $(NH_4)H_2(PO_2NH)_3$ (Figure 1) crystallizes in the monoclinic space group $P2_1/c$. Crystal data and refinement results are listed in Table 2, atom coordinates, Wyckoff positions, and anisotropic displacement parameters are given in Tables S1 and S2. The ammonium ions can clearly be distinguished from solvent water molecules, which had initially been assumed. Difference Fourier syntheses clearly revealed 4 significant electron density maxima and changing the presumed O site to an N site decreased the $R_{1(obs)}$ value significantly from 0.0327 to 0.0291. All further H atoms in the structure could also be located as significant residual densities. Free refinement of their atomic parameters is possible but leads to bond lengths with rather large standard deviations, whose absolute values appear somehow unreasonable although they are normal within ~4 standard deviations. Soft distance restraints were therefore used to keep O-H and N-H distances in the range of 0.85(2) Å and 0.89(2) Å, respectively. All H atoms exhibit reasonable acceptors for H bonds (Table S3). Donor–acceptor distances, H-atom–acceptor distances, and donor–H-atom-acceptor angles are in perfect agreement with moderately strong H bonds [30]. The complete scheme of H bonding is shown in Figure 1 with respect to one asymmetric unit.

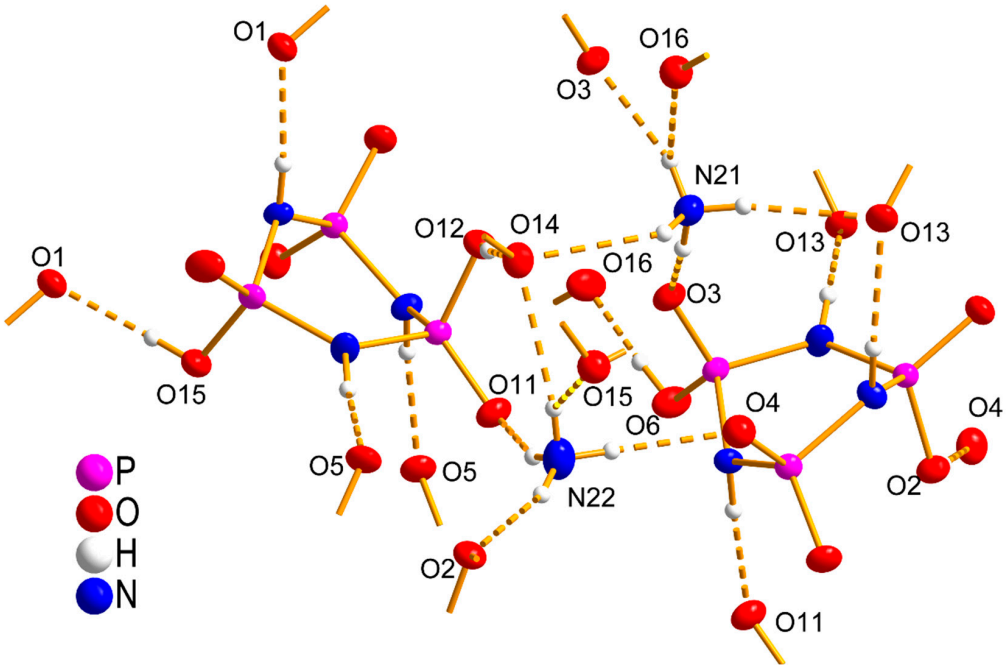

Figure 1. Asymmetric unit of $(NH_4)H_2(PO_2NH)_3$ with all H bonds and their acceptors.

Table 2. Results of the SCXRD refinement.

Sum Formula	**$(NH_4)H_2(PO_2NH)_3$**
Formula weight	254.02
Temperature (°C)	25
Crystal system	monoclinic
Space group	$P2_1/c$ (no. 14)
Lattice parameters (Å, °)	a = 10.2511(5) b = 14.0170(9) c = 11.9423(7) β = 101.633(3)
V (Å^3)	1680.74(17)
ρ_{calc} ($\frac{g}{cm^3}$)	2.008
Z	8
F(000)	1040

Table 2. *Cont.*

Sum Formula	**$(NH_4)H_2(PO_2NH)_3$**
Wave length (Å)	0.500
No. of reflections (unique)	31,031 (4152)
R_{int}	0.0758
R_σ	0.0388
μ (mm^{-1})	0.271
Absorption correction	semiempirical [26]
No. of parameters	290
Weighting scheme	$[\sigma^2(F_o^2) + (0.0482\ P)^2 + 0.4430\ P]^{-1}$ $P = \frac{Max(F_o^2)+2\cdot F_c^2}{3}$
$R1/wR2$ [I > 2σ (I)]	0.0291/0.0831
$R1/wR2$ (all reflections)	0.0302/0.0844
GooF	1.073
min./max. electron residue ($\frac{e}{3}$)	−0.53/0.47

The structure is built up from $[H_2(PO_2NH)_3]^-$ anions and NH_4^+ cations. In contrast to most trimetaphosphimates, the asymmetric unit contains two molecules. The unit cell content is shown in Figure S2. The anions build crankshaft-like stacks that extend along [100] (Figure 2). Such stacks of alternating trimetaphosphimate rings have so far only been described for $(NH_4)_3(PO_2NH)_3{\cdot}H_2O$ and $Ag_3(PO_2NH)_3$ [4,18]. The degree of deprotonation is thus not the decisive factor of the crankshaft-like sequence. The packing of these stacks corresponds to a rectangular pattern, which has so far only been found in $Na_3(PO_2NH)_3{\cdot}4H_2O$ and $(H_3O)H_2(PO_2NH)_3{\cdot}H_2O$ [2,17]. Both symmetry-independent NH_4^+ ions form three normal hydrogen bonds and an additional bifurcated one. A similar H bonding scheme is present for the cations in $(NH_4)_3(PO_2NH)_3{\cdot}H_2O$ [18] and Ag atoms in $Ag_3(PO_2NH)_3$ feature a comparable coordination by O atoms [4].

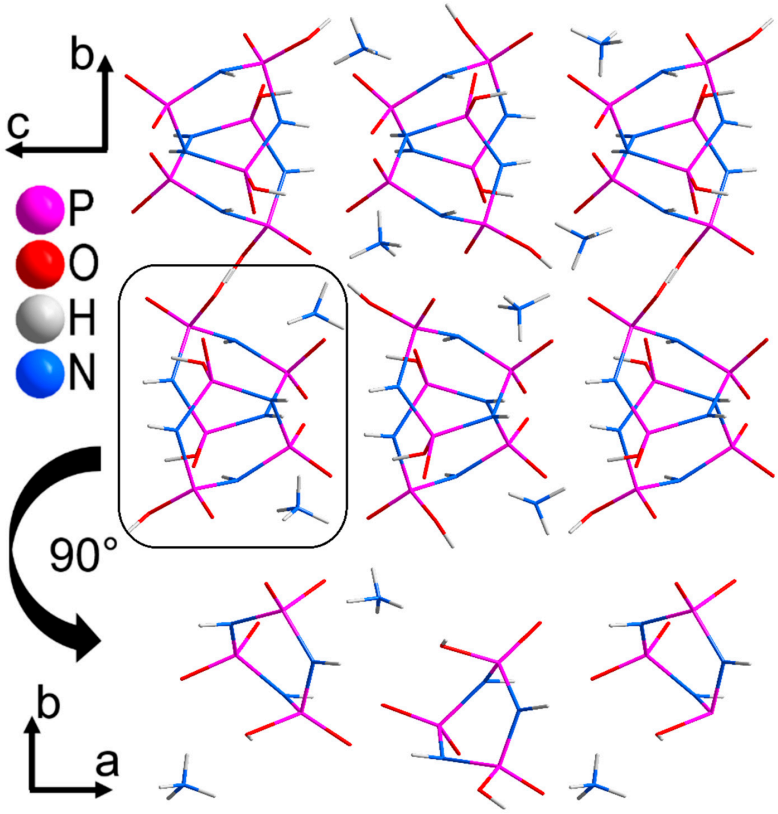

Figure 2. Crystal structure of $(NH_4)H_2(PO_2NH)_3$ with crankshaft-like stacks of the $[H_2(PO_2NH)_3]^-$ anions.

Puckering parameters [31] and analysis of the torsion angle sequence [32,33] were used in order to classify the conformation of the trimetaphosphimate rings. The sequence of torsion angles (Table S4 and Figure 3) can be described as x,x,−y,x,x,−y, which is characteristic for the twist conformation. The puckering parameters (Table S4) of $\theta \approx 90°$ and $\varphi \approx 2 \cdot 60° + 30°$ are in good agreement with the expected values of $\theta = 90°$ and $\varphi = 2 \cdot n° + 30°$ ($n \in N$) for twist conformations. One anion of the asymmetric unit is a bit closer to the ideal twist conformation.

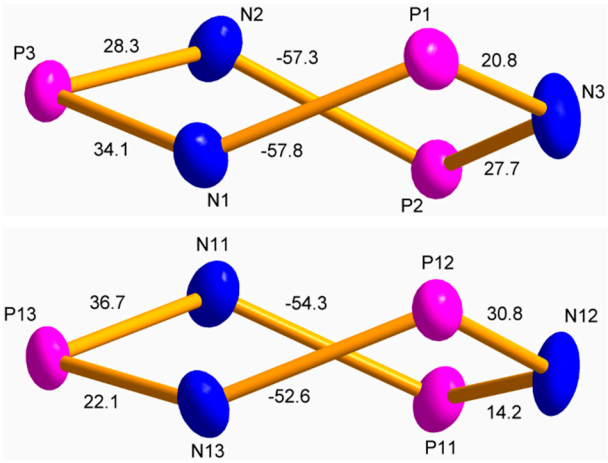

Figure 3. Side views of both P_3N_3 rings with torsion angles (in °) highlighting the twist conformation.

3.3. Thermal Behavior

Temperature-dependent PXRD (Figure S3) reveals decomposition of $(NH_4)H_2(PO_2NH)_3$ at 170 °C into a poorly crystalline phase. This phase further decomposes into an amorphous compound at 290 °C. Above 550 °C, a new crystalline phase begins to form. Its reflection pattern could not be assigned to any compound known in literature. This means that the ammonium salt can be viewed as a precursor for further compounds.

4. Conclusions

Besides trimetaphosphimic acid, which in fact crystallizes as an oxonium salt, and $(NH_4)H_2(PO_2NH)_3 \cdot CH_3OH$, the new compound $(NH_4)H_2(PO_2NH)_3$ is the only trimetaphosphimate containing monoanions. The fact that the anions cannot coordinate directly to metal cations may impede further deprotonation. The ammonium salts differ in the types and arrangement of stacks; the title compound contains crankshaft-like stacks in a rectangular pattern, whereas the known monoammonium salt, which contains methanol solvent molecules, forms a distorted hexagonal pattern of double chains. Compared to all known structures, rectangular patterns and crankshaft-like stacks are rarely observed for trimetaphosphimates.

The synthesis of the title compound corroborates the decomposition of trimetaphosphimic acid under formation of NH_3 as this is the only way to provide ammonium ions. $(NH_4)H_2(PO_2NH)_3$ decomposes to a sequence of amorphous and crystalline compounds upon heating. Therefore, it might be a possible precursor for oxonitridophosphates, especially if reactions are carried out close to the decomposition temperature.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/cryst13010111/s1. Figure S1: Comparison of measured and calculates PXRD patterns; Table S1: Atom coordinates and Wyckoff positions from single-crystal data; Table S2: Anisotropic displacement parameters; Table S3: Hydrogen bonding in $(NH_4)H_2(PO_2NH)_3$; distances between donors, H atoms and acceptors; Figure S2: Unit cell content of $(NH_4)H_2(PO_2NH)_3$; Table S4: torsion angles and puckering parameters of P_3N_3 rings; Figure S3: temperature-dependent PXRD of $(NH_4)H_2(PO_2NH)_3$.

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Data Availability Statement: CCDC 2191198 contains supplementary crystallographic data. These can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or by e-mail: deposit@ccdc.cam.ac.uk.

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