

Crystal Structure, Vibrational Spectrum and Thermal Behavior of the Ammonium Hexathiodiphosphate Dihydrate, $(\text{NH}_4)_4\text{P}_2\text{S}_6 \cdot 2\text{H}_2\text{O}$

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Single crystals of $(\text{NH}_4)_4\text{P}_2\text{S}_6 \cdot 2\text{H}_2\text{O}$ could be obtained and the crystal structure determined (monoclinic, $P2_1/c$ with $a = 6.931(1)$, $b = 12.730(2)$, $c = 17.446(2)$ Å, $\beta = 96.87(1)^\circ$, $V = 1528.2(4)$ Å³, $Z = 4$). The NH_4^+ and $[\text{P}_2\text{S}_6]^{4-}$ ions and the water molecules are involved in an extended hydrogen-bonding network. The FT-Raman and FT-IR spectra have been recorded and the observed vibrational frequencies assigned to tetrahedral NH_4^+ and $[\text{P}_2\text{S}_6]^{4-}$ (D_{3d}) ions as well as to H_2O molecules. The thermogravimetric analysis has shown that $(\text{NH}_4)_4\text{P}_2\text{S}_6 \cdot 2\text{H}_2\text{O}$ starts to decompose at around 60 °C (up to 170 °C), but no distinct intermediates could be observed.

Key words: Hexathiodiphosphate(IV), Hexathiodiphosphate, Crystal Structure, Raman, IR

Introduction

Based on a certain stability of the $[\text{P}_2\text{S}_6]^{4-}$ ion in cold aqueous solutions [1–7], very recently, the alkali thiophosphate hydrates $\text{K}_4\text{P}_2\text{S}_6 \cdot 4\text{H}_2\text{O}$, $\text{Rb}_4\text{P}_2\text{S}_6 \cdot 6\text{H}_2\text{O}$ and $\text{Cs}_4\text{P}_2\text{S}_6 \cdot 6\text{H}_2\text{O}$ could be obtained and structurally characterized [8] beside the long known $\text{Na}_4\text{P}_2\text{S}_6 \cdot 6\text{H}_2\text{O}$ [1–5, 9]. Several anhydrous hexathiodiphosphates have also been synthesized and investigated, *e. g.* $\text{Li}_4\text{P}_2\text{S}_6$ [10], some alkaline earth compounds, $M^{\text{II}}_2\text{P}_2\text{S}_6$ [11–13] as well as $(\text{NH}_4)_4\text{P}_2\text{S}_6$ [3, 4] and others. Despite these considerable efforts, structural information on thiodiphosphate hydrates are scarce. The ammonium compound $(\text{NH}_4)_4\text{P}_2\text{S}_6 \cdot 2\text{H}_2\text{O}$, as a system with an extended hydrogen-bonding network, is presented here. Due to its good solubility the title compound might be a syn-

Table 1. Crystallographic data and structure refinement parameters for $(\text{NH}_4)_4\text{P}_2\text{S}_6 \cdot 2\text{H}_2\text{O}$.

| | |
|---|--|
| Empirical formula | $\text{H}_{20}\text{N}_4\text{O}_2\text{P}_2\text{S}_6$ |
| Formula weight, g mol^{-1} | 362.50 |
| Crystal system/space group | monoclinic/ $P2_1/c$ (no. 14) |
| a , Å | 6.931(1) |
| b , Å | 12.730(2) |
| c , Å | 17.446(2) |
| β , deg | 96.87(1) |
| V , Å ³ | 1528.2(4) |
| Z | 4 |
| D_{calc} , g cm^{-3} | 1.58 |
| $\mu(\text{MoK}\alpha)$, mm^{-1} | 2.1 |
| $F(000)$, e | 760 |
| T , K | 223(2) |
| λ (MoK α radiation), Å | 0.71073 |
| $2\theta_{\text{max}}$, deg | 50.68 |
| Index range | $-8 \leq h \leq 8$, $-15 \leq k \leq 15$, $-21 \leq l \leq 21$ |
| Unique reflections | 2799 |
| Refined parameters | 207 |
| Goodness-of-fit on F^2 | 1.157 |
| $R_1 [I \geq 2\sigma(I)]/R_1$ (all data) | 0.0418/0.0644 |
| $wR_2 [I \geq 2\sigma(I)]/wR_2$ (all data) | 0.0659/0.0710 |
| $\Delta\rho_{\text{max/min}}$, e Å^{-3} | 0.453/–362 |

thon for the preparation of metal thiophosphates by soft chemistry reactions in aqueous solutions.

Experimental Section

Synthesis and characterization

$(\text{NH}_4)_4\text{P}_2\text{S}_6$ was prepared according to Falius and Krause [3] by adding NH_4NO_3 to an aqueous solution of $\text{Na}_4\text{P}_2\text{S}_6 \cdot 6\text{H}_2\text{O}$. The white squamous $(\text{NH}_4)_4\text{P}_2\text{S}_6$ crystals were filtered off and washed with ethanol. Single crystals of $(\text{NH}_4)_4\text{P}_2\text{S}_6 \cdot 2\text{H}_2\text{O}$ were obtained by recrystallization from ethanol/water (1 : 3) solutions at 5 °C after a few days.

The FT-Raman spectrum was recorded with a Raman module FRA 106 (Nd:YAG laser, 1064 nm, > 200 mW) attached to a Bruker IFS 66v interferometer. The FT-IR/FIR spectra were obtained from PE pellets (*ca.* 80–500 cm^{-1}) and KBr pellets, respectively, with the FT-IR interferometer.

The thermogravimetric (TG) analysis of the title compound was performed in an atmosphere of flowing argon (50 mL min^{-1}) at a heating rate of 5 K min^{-1} using a 951 thermogravimetric analyzer/TA Instruments.

X-Ray structure analysis

A suitable single crystal (colorless, crystal size: $0.25 \times 0.20 \times 0.20$ mm^3) was selected under a polarization micro-

Table 2. Selected interatomic distances (Å) and angles (deg) in the structure of $(\text{NH}_4)_4\text{P}_2\text{S}_6 \cdot 2\text{H}_2\text{O}$.

| | | | |
|----------|-----------|----------|-----------|
| P1–S1 | 2.021(1) | P2–S4 | 2.031(1) |
| P1–S2 | 2.027(1) | P2–S5 | 2.023(1) |
| P1–S3 | 2.019(1) | P2–S6 | 2.019(1) |
| P1–P2 | 2.263(1) | | |
| S1–P1–S2 | 112.58(5) | S4–P2–S5 | 112.54(5) |
| S1–P1–S3 | 112.37(5) | S4–P2–S6 | 112.91(5) |
| S2–P1–S3 | 112.28(5) | S5–P2–S6 | 111.37(5) |
| S1–P1–P2 | 105.35(4) | S4–P2–P1 | 105.94(4) |
| S2–P1–P2 | 106.40(4) | S5–P2–P1 | 106.70(4) |
| S3–P1–P2 | 107.28(4) | S6–P2–P1 | 106.86(4) |

scope and mounted in a glass capillary. Intensity data were collected on a Stoe IPDS II diffractometer using graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å). The structure was solved by Direct Methods and refined using least-squares methods on F^2 (SHELXS/L-97 [14]) with anisotropic displacement parameters for the non-H atoms. All H atom positions were detected in difference Fourier syntheses. Structure representations: DIAMOND [15] and POV-Ray [16]. Table 1 summarizes the crystal and other data pertinent to the structure determination. Selected interatomic distances and bond angles are listed in Table 2. Hydrogen bond details are given in Table 3.

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition number CSD-417640.

Results and Discussion

The crystal structure of $(\text{NH}_4)_4\text{P}_2\text{S}_6 \cdot 2\text{H}_2\text{O}$ is comprised of discrete $[\text{P}_2\text{S}_6]^{4-}$ anions, tetrahedral NH_4^+ cations and water molecules involved in an extended hydrogen-bonding network. The ethane-like $[\text{P}_2\text{S}_6]^{4-}$ anion is in a staggered conformation and integrated *via* $\text{S}-\text{NH}_4^+-\text{S}$ and $\text{S}-\text{H}_2\text{O}-\text{S}$ bridges into the three-dimensional network.

The P–P distance amounts to 2.263 Å and the P–S bond lengths range from 2.019 to 2.031 Å, similar to those reported for $\text{Na}_4\text{P}_2\text{S}_6 \cdot 6\text{H}_2\text{O}$ [9] and $\text{Li}_4\text{P}_2\text{S}_6$ [10]. The $[\text{P}_2\text{S}_6]^{4-}$ units are surrounded by ten NH_4^+ cations and four water molecules connected *via* hydrogen bonds, with $\text{N}\cdots\text{S}$ distances from 3.309 to 3.680 Å and $\text{O}\cdots\text{S}$ distances from 3.174 to 3.382 Å (Fig. 1).

The structure contains four crystallographically different NH_4^+ cations (Fig. 2). These ammonium ions exhibit slight deviations from the ideal tetrahedral sym-

Table 3. Selected hydrogen bond lengths (Å) and angles (deg) in $(\text{NH}_4)_4\text{P}_2\text{S}_6 \cdot 2\text{H}_2\text{O}$.

| | | | |
|---------|-------|-------------|-------|
| N4...O1 | 2.845 | N4–H43...O1 | 164.1 |
| N3...O2 | 2.884 | N3–H33...O2 | 164.4 |
| N4...O2 | 2.894 | N4–H44...O2 | 165.8 |
| N3...O1 | 3.007 | N3–H34...O1 | 176.7 |
| O1...S1 | 3.174 | O1–H1A...S1 | 154.2 |
| O2...S2 | 3.320 | O2–H2B...S2 | 174.1 |
| O1...S4 | 3.328 | O1–H1B...S4 | 165.1 |
| O2...S5 | 3.382 | O2–H2A...S5 | 155.9 |
| N3...S5 | 3.309 | N3–H31...S5 | 157.9 |
| N2...S1 | 3.336 | N2–H21...S1 | 167.2 |
| N1...S5 | 3.364 | N1–H11...S5 | 167.8 |
| N2...S4 | 3.415 | N2–H22...S4 | 173.1 |
| N3...S2 | 3.427 | N3–H32...S2 | 164.3 |
| N2...S3 | 3.436 | N2–H24...S3 | 162.6 |
| N1...S2 | 3.443 | N1–H13...S2 | 156.8 |
| N1...S6 | 3.456 | N1–H12...S6 | 148.8 |
| N1...S6 | 3.494 | N1–H14...S6 | 178.1 |
| N4...S4 | 3.497 | N4–H42...S4 | 175.0 |
| N4...S3 | 3.516 | N4–H41...S3 | 147.9 |
| N2...S4 | 3.680 | N2–H23...S4 | 140.2 |

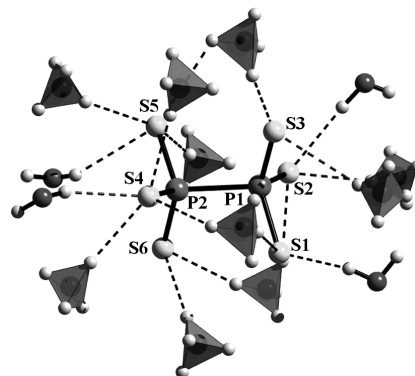


Fig. 1. The $[\text{P}_2\text{S}_6]^{4-}$ anion in $(\text{NH}_4)_4\text{P}_2\text{S}_6 \cdot 2\text{H}_2\text{O}$ with its full coordination environment (dotted lines represent hydrogen bonds).

metry with H–N–H bond angles between 106.3 and 113.1° for N1, 103.0 and 119.7° for N2, 105.0 and 115.2° for N3, and 105.4 to 113.3° for N4. N1 is connected *via* hydrogen bonds to three $[\text{P}_2\text{S}_6]^{4-}$ anions, one of which is bifurcated (Fig. 2). Its intermolecular $\text{N}\cdots\text{S}$ distances range from 3.364 to 3.494 Å, and $\text{N}-\text{H}\cdots\text{S}$ angles from 148.8 to 178.1°. Likewise, N2 is coordinated *via* hydrogen bonds to three $[\text{P}_2\text{S}_6]^{4-}$ anions (Fig. 2), with $\text{N}\cdots\text{S}$ distances ranging from 3.336 to 3.680 Å, and $\text{N}-\text{H}\cdots\text{S}$ angles from 140.2 to 173.1°. N3 and N4 are each coordinated to two $[\text{P}_2\text{S}_6]^{4-}$ anions (monodentate) and to two water molecules (Fig. 2). Therein the $\text{N}\cdots\text{S}$ distances range from 3.309 to 3.516 Å, the $\text{N}\cdots\text{O}$ distances from 2.845 to 3.007 Å, the $\text{N}-\text{H}\cdots\text{S}$ angles from 147.9 to 175.0°

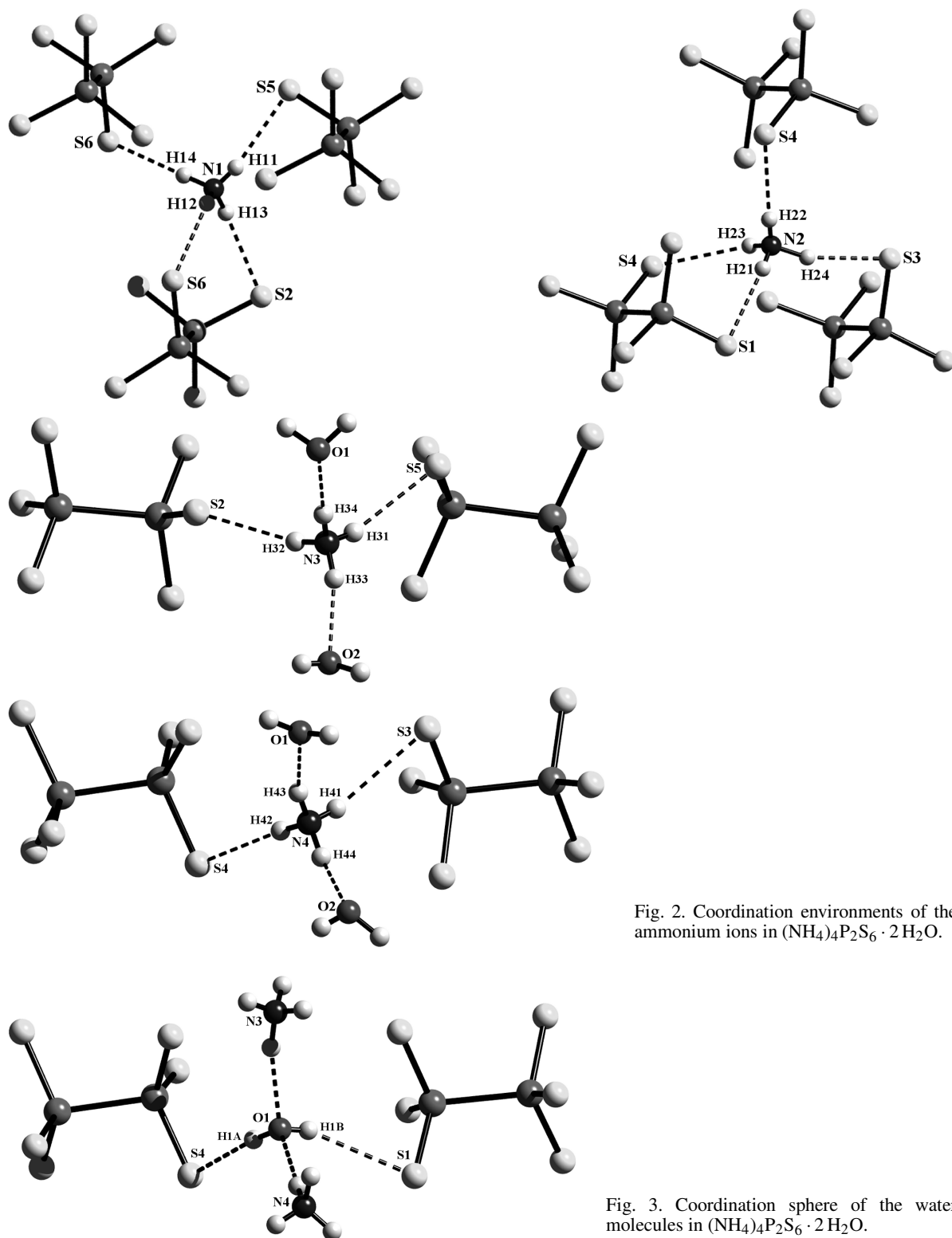


Fig. 2. Coordination environments of the ammonium ions in $(\text{NH}_4)_4\text{P}_2\text{S}_6 \cdot 2\text{H}_2\text{O}$.

Fig. 3. Coordination sphere of the water molecules in $(\text{NH}_4)_4\text{P}_2\text{S}_6 \cdot 2\text{H}_2\text{O}$.

| [P ₂ S ₆] ⁴⁻ in (NH ₄) ₄ P ₂ S ₆ · 2 H ₂ O | | K ₄ P ₂ S ₆ · 4 H ₂ O | | Na ₄ P ₂ S ₆ · 6 H ₂ O | | Assignment |
|--|------------------------|---|--------------------------------------|--|-----------------------------|---|
| Raman | IR | Raman [8] | IR [8] | Raman [9] | IR [9] | <i>D</i> _{3d} |
| 80 vvw | | 75 vvw | | | 87 w | Lattice vibrations |
| 125 vw | 104, 112 vw | 120 vw | 123 vw 135 w 143 vw 168 w-m | 101vw | 137 vw 150 vw 169 vvw | (<i>v</i> ₁₂ / E _u)? <i>v</i> ₉ / E _g (<i>resp.</i> A _g + B _g in C _{2h}) |
| | 155 vbr ^b | 153 m ^c 170 w ^c 188 m | | 162 vw | | <i>v</i> ₃ / A _{1g} <i>v</i> ₁₁ / E _u <i>v</i> ₈ / E _g (<i>resp.</i> A _g + B _g in C _{2h}) |
| 170 vw,sh 200 m | 239 s | 253 s ^c 268 sh ^c | 233 w-m | 263 s | 240 m-s | <i>v</i> ₆ / A _{2u} |
| 260 s | 299 w | | 283 vs | | 296 vs 299 sh | <i>v</i> ₂ / A _{1g} |
| 376 vs | | 377 vvs | | 376 vvs | (380 vw) 438 sh | <i>v</i> ₅ / A _{2u} Librat. H ₂ O |
| | 446 s | | 433 m 486 vw | | 443 s 480 w-m | <i>v</i> ₁ / A _{1g} <i>v</i> ₇ / E _g <i>v</i> ₁₀ / E _u |
| 550 s 580 w,sh | | 558 s 588 m | | 556 s 579 m | | |
| | 575 s | | 576 vs 599 sh | | 582 vs 592 sh | |
| | 635 vw,sh ^d | | | | 606 sh ^e | [Comb. ?] |

Table 4. Vibrational frequencies (cm⁻¹) of the [P₂S₆]⁴⁻ unit in crystalline (NH₄)₄-P₂S₆ · 2 H₂O with their estimated intensities and proposed assignments^a.

^a Estimated intensities: s: strong, m: medium, w: weak, v: very, sh: shoulder, br: broad; ^b very broad (questionable) absorption with maximum at 155 cm⁻¹; ^c assigned in [12] in C_{2h} according to E_g (*D*_{3d}) = A_g + B_g (in C_{2h}) in comparison to Sr₂P₂S₆; ^d combination (260 + 376 cm⁻¹)?; ^e combination/overtone (2 × 303 cm⁻¹)?.

| NH ₄ ⁺ in (NH ₄) ₄ P ₂ S ₆ · 2 H ₂ O | | NH ₄ ⁺ [17] | | Assignment |
|--|-------------------------------------|-----------------------------------|---------------------|---|
| Raman | IR | Raman | IR | <i>T</i> _d [16] |
| 1395 w-m 1411 w-m 1627 w 1686 w | 1365 vw,sh 1395 vs 1632 m | 1406 m | 1407 s | <i>v</i> ₄ / F ₂ |
| | 2756 w,br 2902 w,br 3071 w,br | | 2775 vvw 2924 vw | H–O–H bending <i>v</i> ₂ / E Comb.: 1365 + 1396 Comb.: 1365 + 1632 |
| 3220 vw,br | | 3160 w-m | 3270 vw | <i>v</i> ₁ / A <i>v</i> ₃ / F ₂ (+ H–O–H stretching) |

Table 5. Vibrational frequencies (cm⁻¹) of the NH₄⁺ and H₂O units in crystalline (NH₄)₄P₂S₆ · 2 H₂O with estimated intensities and with their proposed assignments^a.

^a Estimated intensities: s: strong, m: medium, w: weak, v: very, sh: shoulder, br: broad.

and the N–H···O angles from 164.1 to 176.7° (Table 3).

(NH₄)₄P₂S₆ · 2 H₂O contains two crystallographically different water molecules coordinated tetrahedrally by hydrogen bonds to two [P₂S₆]⁴⁻ anions and two NH₄⁺ cations (Fig. 3). The S···O distances are between 3.174 and 3.382 Å and the O–H···S angles between 154.2 and 174.1°. These values agree very well with those reported for Na₃[PO₂S₂] · 11 H₂O and Na₃[POS₃] · 11 H₂O [17].

Vibrational spectroscopy

The vibrational frequencies of crystalline (NH₄)₄P₂S₆ · 2 H₂O are summarized in Tables 4 and 5, along with their estimated intensities and proposed assign-

ments. The bands of the NH₄⁺ ions, H₂O molecules and [P₂S₆]⁴⁻ units can be clearly distinguished. H₂O and NH₄⁺ stretching vibrations are found above 3000 cm⁻¹ and the corresponding bending vibrations are detected around 1630 and 1400 cm⁻¹ (Table 5). The vibrational modes of NH₄⁺ are best assigned in comparison to those of other ammonium compounds [18, 19]. Below 650 cm⁻¹ the characteristic [P₂S₆]⁴⁻ stretching and bending modes can be recognized and the lattice vibrations are below *ca.* 150 cm⁻¹. The relevant spectral data of the [P₂S₆]⁴⁻ unit were compared to those published previously for K₄P₂S₆ · 4 H₂O [8] and Na₄P₂S₆ · 6 H₂O [9].

Dependent on the counterion or substituent, the [P₂S₆]⁴⁻ group can exist in different point groups (*D*_{3d}, *D*_{3h} and C_{2h} [12, 20]). The Raman and IR/FIR

spectra of the $[\text{P}_2\text{S}_6]^{4-}$ unit of the title compound are best interpreted and assigned with the point group D_{3d} . The vibrational analysis [5, 12, 20] results in

$$\Gamma_{\text{vib}}(D_{3d}/[\text{P}_2\text{S}_6]^{4-}) = 3 A_{1g}(\text{R}) + 3 E_g(\text{R}) \\ + A_{1u}(\text{i. a.}) + 2 A_{2u}(\text{IR}) + 3 E_u(\text{IR}),$$

with R = Raman, IR = infrared and i. a. = inactive. Further details are given in Table 4.

Thermal behavior

The thermal behavior of $(\text{NH}_4)_4\text{P}_2\text{S}_6 \cdot 2\text{H}_2\text{O}$ was investigated from r.t. up to 400 °C. The decomposition reactions start at around 60 °C and pro-

ceed to ca. 170 °C with a mass loss of more than 40 wt.-%. No distinct intermediate step/stage was observed.

In summary, the crystalline ammonium hexathiohypodiphosphate dihydrate, $(\text{NH}_4)_4\text{P}_2\text{S}_6 \cdot 2\text{H}_2\text{O}$, exhibits remarkable similarities with the recently investigated alkali salt hydrates, in particular $\text{K}_4\text{P}_2\text{S}_6 \cdot 4\text{H}_2\text{O}$ and $\text{Rb}_4\text{P}_2\text{S}_6 \cdot 6\text{H}_2\text{O}$ [8]. The crystal structure is dominated by distinct $[\text{P}_2\text{S}_6]^{4-}$ and NH_4^+ ions, which together with the water molecules are involved in an extended network with N–H...S, O–H...S and N–H...O hydrogen bonds. The relevant part of the vibrational spectrum is best interpreted by $[\text{P}_2\text{S}_6]^{4-}$ units of D_{3d} symmetry.

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