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Synthesis, crystal structures and properties of the trimetaphosphimates $NaBa(PO_2NH)_3$, $KSr(PO_2NH)_3\cdot 4H_2O$, and $NH_4Sr(PO_2NH)_3\cdot 4H_2O$

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Abstract

The three double salts sodium barium tri-μ-imidocyclotriphosphate, $NaBa(PO_2NH)_3$ (**1**), potassium strontium tri-μ-imidocyclotriphosphate tetrahydrate, $KSr(PO_2NH)_3\cdot 4H_2O$ (**2**), and ammonium strontium tri-μ-imidocyclotriphosphate tetrahydrate, $NH_4Sr(PO_2NH)_3\cdot 4H_2O$ (**3**), were synthesized by combining equimolar aqueous solutions of $Na_3(PO_2NH)_3\cdot 4H_2O$, $K_3(PO_2NH)_3$, or $(NH_4)_3(PO_2NH)_3\cdot H_2O$, respectively, with the corresponding alkaline earth nitrate. In case of compound **1**, suitable single crystals for X-ray crystal structure determination were solely obtained using gel crystallization in gelatine gels. The structures of **2** and **3** were found to be isotypic. All crystal structures were solved by single-crystal X-ray methods (**1**: $C2/m$, $a = 1084.5(2)$, $b = 1025.0(2)$, $c = 796.2(2)$ pm, $\beta = 115.18(3)^\circ$, $Z = 4$, $R_1 = 0.023$; **2**: $P2_1/n$, $a = 1087.2(2)$, $b = 1049.6(2)$, $c = 1191.2(2)$ pm, $\beta = 111.98(3)^\circ$, $Z = 4$, $R_1 = 0.025$; **3**: $P2_1/n$, $a = 1088.4(2)$, $b = 1048.5(2)$, $c = 1196.9(2)$ pm, $\beta = 111.43(3)^\circ$, $Z = 4$, $R_1 = 0.025$). In both structure types, the P_3N_3 rings of the trimetaphosphimate ions exhibit a chair conformation. In the crystal, the trimetaphosphimate ions act as mono and bidentate ligands of the alkali ions, and additionally as tridentate ones in case of the alkaline earth ions. Besides the oxygen atoms, the nitrogen atoms of the $(PO_2NH)_3{}^{3-}$ rings contribute to the coordination of the cations as well. In **2** and **3**, crystal water molecules complete the coordination of the metal ions. Extended hydrogen bonding reinforces the three-dimensional interconnection of the ions and the crystal water molecules in the structures of all three compounds.

Keywords: Trimetaphosphimate; Crystal structure; Hydrogen bonding; Vibrational spectroscopy

1. Introduction

During our systematic investigation of trimetaphosphimates (tri-μ-imidocyclotriphosphates) [1], we have primarily focused our interest on alkali metal and monovalent nonmetal trimetaphosphimates as well as transition metal trimetaphosphimates and reported about their syntheses, crystal structures and properties [2,3]. Usually, these compounds were obtained by two different approaches: The transition metal and nonmetal trimetaphosphimates have been obtained by the reaction of an aqueous solution of $Na_3(PO_2NH)_3\cdot 4H_2O$ [4] or $H_3(PO_2NH)_3\cdot 2H_2O$ [5] with the respective nitrate, halide or with the suitable base. The alkali trimetaphosphimates have been synthesized by the reaction of $(PNCl_2)_3$ with the respective acetate in a mixture of water and dioxane.

In the compounds with monovalent cations the trimetaphosphimate ions arrange in pairs, double layers, or build up a three-dimensional network [2a–d,g]. In the structures of transition metal trimetaphosphimates the $(PO_2NH)_3{}^{3-}$ ions either act as mono, bi, or tridentate ligands coordinating the transition metal ions (M), or do not take part in any coordination [3c]. Thus, barring the last case, infinite double chains with alternating metal and $(PO_2NH)_3{}^{3-}$ ions [2f], isolated ionic complexes $\{M[(PO_2NH)_3]_2\}^{x-}$ [3a,b], or complex anions $\{M_4(\mu_4\text{-O})(\mu\text{-OH})_6[(PO_2NH)_3]_4\}^{4-}$ [2e] are formed. These structural elements are interconnected in the crystal

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by N–H···O and O–H···O hydrogen bonds and, whenever present, by coordination to alkali cations and by integration of crystal water molecules forming a three-dimensional network.

Surprisingly, no alkaline earth metal containing trimetaphosphimate has been structurally characterized as yet. The existence and the synthesis of such compounds already have been mentioned in the literature [6,7]. In some cases, also spectroscopic or thermoanalytic investigations have been carried out [8–10]. However, the crystal structures of these compounds have not been elucidated as yet. In addition, their properties have been characterized only insufficiently.

In this contribution we describe the synthesis of the double salts $NaBa(PO_2NH)_3$ (**1**), $KSr(PO_2NH)_3 \cdot 4H_2O$ (**2**), and $NH_4Sr(PO_2NH)_3 \cdot 4H_2O$ (**3**), and their crystal structures and properties.

2. Experimental

2.1. Synthesis

$NaBa(PO_2NH)_3$ (**1**), $KSr(PO_2NH)_3 \cdot 4H_2O$ (**2**), and $NH_4Sr(PO_2NH)_3 \cdot 4H_2O$ (**3**) were synthesized by combining 0.05 M aqueous solutions of $Na_3(PO_2NH)_3 \cdot 4H_2O$ ([4]; 75.0 mg, 0.2 mmol in 4 ml of H_2O), $K_3(PO_2NH)_3$ ([2c]; 54.6 mg, 0.2 mmol in 4 ml of H_2O), or $(NH_4)_3(PO_2NH)_3 \cdot H_2O$ ([2a]; 61.2 mg, 0.2 mmol in 4 ml of H_2O), respectively, and $Ba(NO_3)_2$ (Merck, p. a.; 52.3 mg, 0.2 mmol in 4 ml of H_2O), resp. $Sr(NO_3)_2$ (Merck, p. a.; 42.3 mg, 0.2 mmol in 4 ml of H_2O). In case of **2** and **3**, transparent colorless crystals of the corresponding double salts were formed after a few days at room temperature. The precipitates were filtered and washed with small amounts of cold water and ethanol. The products are stable in air and slightly water-soluble.

In case of compound **1**, combining the two solutions of the reactants immediately led to the precipitation of the product which, however, was less crystalline. Highly microcrystalline products and suitable single crystals for X-ray crystal structure determination were obtained by crystallization in gelatine gels in U-tubes. For this purpose, gelatine (0.270 g, culinary gelatine, Ewald-Gelatine GmbH) was left to soak for 5 min in 15 ml H_2O. Subsequently, the mixture was heated until the gelatine had been completely dissolved. The solution was filled into an U-tube and left to gel in a refrigerator at 5 °C for 24 hours. Aqueous solutions of $BaCl_2 \cdot 2H_2O$ (244 mg, 1.0 mmol in 10 ml of H_2O; 1 eq) and $Na_3(PO_2NH)_3 \cdot 4H_2O$ (562 mg, 1.5 mmol in 10 ml of H_2O; 1.5 eq) were prepared and filled into the respective arms of the U-tube. The U-tube was closed with laboratory film (parafilm "M", American National Can Company). After four weeks a small number of transparent colorless single crystals besides many large poly-crystalline spheres of **1** (Fig. 1) and spherolitic grown fibres of an unknown phase have been isolated. Crystalline products of **1** are stable in air and hardly water-soluble.

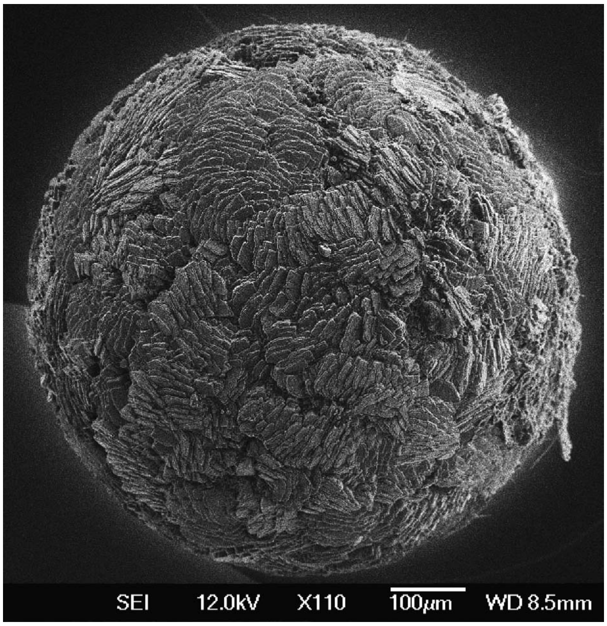

Fig. 1. REM picture of a poly-crystalline sphere of **1**.

Characterization was carried out by infrared spectroscopy, TG measurements, single-crystal and powder X-ray diffraction. The composition of the compounds was confirmed by EDX investigations.

2.2. Characterization

2.2.1. EDX investigations

Energy dispersive X-ray analyses of **1**, **2**, and **3** (as well as the REM picture of **1** mentioned above) were performed on a JSM 6500F scanning electron microscope (Jeol). All elements contained in the three compounds could be unequivocally detected and their compositions have been determined semi-quantitatively. Within the accuracy of the measurements, the resultant molar ratios of the elements in the compounds agree well with the theoretical values from the empirical formulas.

2.2.2. Infrared spectroscopy

FT-IR spectra of **1**, **2**, and **3** were recorded in transmission geometry in the range of 4000–450 cm^{-1} with an IR spectrometer IFS 66v/S (Bruker) using the KBr pellet technique. For a better comparison among each other all three spectra are presented in one figure (Fig. 2). The observed bands and their assignments are listed in Table 1. The assignments have been carried out from comparison of the observed spectra with previously published data [11].

2.2.3. Thermal behavior

TG measurements were performed under nitrogen flow in a DTA-TG thermoanalytical balance TGA 92-2400 (Se-