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Synthesis in the Melt and Characterization of Condensed Binary Phosphates $BaNH_4(PO_3)_3$, $BiNH_4P_4O_{12}$, and $Ti(NH_4)_2P_4O_{13}$

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Barium–ammonium polyphosphate ($BaNH_4(PO_3)_3$), bismuth–ammonium cyclotetraphosphate ($BiNH_4P_4O_{12}$), and titanium–ammonium tetraphosphate ($Ti(NH_4)_2P_4O_{13}$) have been synthesized in the melt of ammonium polyphosphate (NH_4PO_3). The prepared phosphates were characterized by chemical analysis, thin layer chromatography, and X-ray diffraction of powders. $BiNH_4P_4O_{12}$ was found to crystallize in the cubic system, space group $I43d$ with the unit-cell parameter $a = 15.105(2)$ Å. Thermal decomposition behavior of the phosphates was studied by thermogravimetry and crystalline products of degradation were identified.

INTRODUCTION

Ammonium polyphosphate (APP, NH_4PO_3) is a basic component of many fire retardant formulations which produce shielding intumescent char on the surface of burning polymer causing its extinction (1). Recently it was shown (2–4) that inorganic fillers (oxides, hydroxides, carbonates, silicates, etc.) might increase the fire retardant action of APP, because condensed ammonium–metal phosphates are formed upon heating APP combined with the inorganic filler (5, 6), thus improving the thermal insulating properties of the intumescent char. This practical aspect encouraged our systematic studies in the systems APP/metal or inorganic oxides or hydroxides or salts and resulted in developing a new advantageous method of synthesis of ammonium–metal condensed phosphates (7). This paper describes the synthesis, characterization, and thermal decomposition behavior of condensed phosphates $BaNH_4(PO_3)_3$, $BiNH_4P_4O_{12}$, and $Ti(NH_4)_2P_4O_{13}$.

EXPERIMENTAL

Materials

Ammonium polyphosphate, NH_4PO_3 (Exolit 422, Hoechst), barium nitrate, $Ba(NO_3)_2$, bismuth hydroxide, $Bi(OH)_3$, and methatitanic acid, $TiO_2 \cdot nH_2O$ (all reagent grade, Khimreaktiv), were used as received.

Synthesis

NH_4PO_3 combined with one of the above compounds was isothermally heated at 200–400°C in air. The progress of the reaction was monitored by X-ray diffraction and optical microscopy studies of periodic samples.

X-Ray Diffraction

X-ray diffraction of the virgin compounds and the crystalline products of thermal decomposition was carried out by the X-ray diffractometer (HZG-4A, Carl Zeiss, Jena) using Ni filtered CuK_α radiation (powdered samples, Si standard, scanning rate 0.5 grad/min).

Chemical Analysis

The phosphate anions were identified by thin layer chromatography (TLC, powder cellulose FND) using method of Prodan *et al.* (8). Colorimetric measurements of the yellow phosphorus–vanadium–molybdenum complex was used for phosphorus analysis (9). Standard procedures (described elsewhere (10)) were used for chemical analysis of barium by precipitation, of bismuth by complexonometry, of titanium by colorimetry, and of ammonia by the Keldal method.

Thermal Analysis

Thermogravimetry was carried out in ceramic pans, using the Mettler TA-3000 thermoanalyzer at a heating rate of 10°C/min under a nitrogen flow of 100 cm^3/min.

RESULTS AND DISCUSSION

Synthesis and Characterization

$NH_4PO_3/Ba(NO_3)_2$ system. The interaction between NH_4PO_3 and $Ba(NO_3)_2$ with molar ratios NH_4PO_3:

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TABLE 1
Results of Chemical Analysis of Binary Condensed Phosphates

$BaNH_4(PO_3)_3$			$BiNH_4P_4O_{12}$			$Ti(NH_4)_2P_4O_{13}$		
	found, %	calc., %		found, %	calc., %		found, %	calc., %
Ba	35.2	35.0	Bi	38.6	38.5	Ti	11.7	11.5
NH_3	4.2	4.3	NH_3	3.1	3.2	NH_3	8.1	8.2
P	23.8	23.7	P	22.6	22.8	P	29.6	29.8

$Ba(NO_3)_2 = (2 \div 10):1$ was studied at 300°C. Only one crystalline compound was found in the products independently on the ratio. The reaction in the system NH_4PO_3/$Ba(NO_3)_2$ is observed at an even lower temperature, 240–250°C. However, maximum yield was obtained at 300–320°C. The crystalline product was separated from the unreacted mixture at room temperature by washing in a water/acetone mixture (1 : 1), in which the crystalline phase is only slightly soluble. It is not recommended to use pure water because of extensive dissolution of the crystals.

TLC shows that the anion is a long chain polyphosphate. The results of the chemical analysis seen in Table 1 prove that the newly synthesized product is $BaNH_4(PO_3)_3$. X-ray powder diffraction data for $BaNH_4(PO_3)_3$ are listed in Table 2.

TABLE 2
X-Ray Powder Data for $BaNH_4(PO_3)_3$

d, Å	*I*, %	*d*, Å	*I*, %	*d*, Å	*I*, %
9.77	26	2.862	25	1.906	10
7.26	24	2.827	7	1.878	2
6.73	10	2.792	21	1.862	4
6.55	13	2.697	30	1.824	11
6.04	35	2.605	15	1.818	5
5.57	20	2.569	18	1.792	4
5.43	15	2.443	15	1.776	3
4.94	13	2.374	10	1.756	3
4.45	5	2.364	8	1.737	10
4.35	7	2.306	5	1.727	7
4.31	5	2.298	9	1.717	2
4.24	5	2.250	3	1.706	3
4.15	3	2.218	13	1.696	5
3.888	29	2.208	21	1.688	5
3.717	17	2.186	7	1.682	3
3.652	37	2.159	10	1.659	3
3.519	40	2.153	13	1.613	4
3.461	100	2.117	27	1.598	10
3.375	93	2.085	5	1.573	2
3.350	40	2.074	3	1.566	7
3.273	17	2.033	11	1.549	4
3.250	24	1.986	11	1.532	5
3.219	27	1.975	7	1.516	3
3.077	20	1.933	3	1.499	5
3.036	20	1.917	5	1.487	7

In contrast to many bivalent metals, Ba does not give crystalline binary condensed phosphates by heating with $(NH_4)_2HPO_4$ (11, 12). It seems that $BaNH_4(PO_3)_3$ is the first binary condensed NH_4^+/Ba^{2+} phosphate synthesized from the melt.

$NH_4PO_3/Bi(OH)_3$ system. Two binary NH_4^+/Bi^{3+} condensed phosphates, hydrotriphosphate $BiNH_4HP_3O_{10}$ and polyphosphate $BiNH_4(PO_3)_4$, prepared by reaction between Bi_2O_3 and excess of $(NH_4)_2HPO_4$ are reported in the literature (13). However, knowing that the chemistry of bismuth phosphates is similar to that of rare earth metal phosphates (14), one might expect other binary NH_4^+/Bi^{3+} condensed phosphates to occur. In fact, new crystals with morphology similar to that of $CeNH_4P_4O_{12}$ (15) were found after isothermal heating of the mixture $NH_4PO_3 : Bi(OH)_3 = (4 \div 6):1$ at 300°C for 10–12 h. The crystals are only slightly poorly soluble in water, therefore they were separated from the unreacted mixture by washing water.

Cyclotetraphosphate anion was detected by TLC in the newly synthesized compound. Table 1 shows the results of the chemical analysis and the calculated content of Bi, P, and NH_3 in $BiNH_4P_4O_{12}$. A good agreement is in favor of the crystallization of bismuth–ammonium cyclotetraphosphate.

The observed X-ray powder diffraction pattern of $BiNH_4P_4O_{12}$ is similar to that of binary condensed phosphates $M^{III}M^{I}P_4O_{12}$ type, where M^{III} is rare earth metal and M^{I} is an alkali metal or NH_4^+, known in the literature (14, 16) as the $NdCsP_4O_{12}$ crystalline type. Using the data for this crystalline type (16), the parameters of the unit cell of $BiNH_4P_4O_{12}$ were estimated: the cubic system, space group $I\bar{4}3d$, $a = 15.105(2)$ Å. Good agreement is observed between experimental and calculated X-ray diffraction data (Table 3).

To prepare $BiNH_4P_4O_{12}$ the experimental conditions must be maintained very carefully since $BiNH_4HP_3O_{10}$ is obtained with very high yield (70–80%) at isothermal heating of the mixture $NH_4PO_3/Bi(OH)_3$ at lower temperature (250–260°C). $BiNH_4(PO_3)_4$ is crystallized instead of $BiNH_4P_4O_{12}$ at longer isothermal heating (≥24 h) of the mixture at higher temperature (300–320°C).

$NH_4PO_3/TiO_2 \cdot nH_2O$ system. The interaction of

TABLE 3
X-Ray Powder Data for $BiNH_4P_4O_{12}$ (cubic)

$d_{observed}$, Å	I, %	$h\ k\ l$	$d_{calculated}$, Å	$d_{observed}$, Å	I, %	$h\ k\ l$	$d_{calculated}$, Å
6.184	100	2 1 1	6.167	1.984	4	7 3 0	1.983
5.355	13	2 2 0	5.341	1.919	7	6 5 1	1.918
4.782	6	3 1 0	4.777	1.890	5	8 0 0	1.888
4.041	35	3 2 1	4.037	1.806	11	6 5 3	1.805
3.380	28	4 2 0	3.378	1.781	4	6 6 0	1.780
3.222	35	3 3 2	3.220	1.757	17	7 4 3	1.756
3.083	14	4 2 2	3.083	1.732	3	6 6 2	1.733
2.964	80	4 3 1	2.962	1.710	7	7 5 2	1.710
2.759	16	5 2 1	2.758	1.648	11	8 4 2	1.648
2.593	4	4 3 3	2.591	1.629	12	6 5 5	1.629
2.451	24	5 3 2	2.450	1.592	7	7 5 4	1.592
2.387	5	6 2 0	2.388	1.558	6	7 6 3	1.558
2.332	18	5 4 1	2.331	1.541	4	8 4 4	1.542
2.227	7	6 3 1	2.227	1.495	4	7 7 2	1.496
2.181	8	4 4 4	2.180	1.466	8	9 4 3	1.467
2.134	5	5 4 3	2.136	1.440	7	7 6 5	1.440
2.096	6	6 4 0	2.095	1.402	6	8 6 4	1.402
2.056	38	5 5 2	2.056	1.390	5	9 6 1	1.391
2.018	11	6 4 2	2.019	1.304	6	7 7 6	1.305

$TiO_2 \cdot nH_2O$ with an excess of NH_4PO_3 at any temperature (200–400°C) leads to crystals with the morphology of thin plates. The crystals are poorly soluble in water and in phosphoric acid, which allows the unreacted residue to be easily removed. TLC shows that the new compound contains tetraphosphate anion. Results of the chemical analysis are in good agreement with calculated content of Ti, P, and NH_3 in $Ti(NH_4)_2P_4O_{13}$ (Table 1).

In the literature (17, 18) syntheses of $Si(NH_4)_2P_4O_{13}$ and $Ge(NH_4)_2P_4O_{13}$ from $(NH_4)_2HPO_4$ and SiO_2 and GeO_2, respectively, were reported. X-ray characterization showed that both Si and Ge binary phosphates are isostructural and both are with space group $P\bar{1}$. The X-ray powder diffraction pattern of $Ti(NH_4)_2P_4O_{13}$, shown in Table 4 is similar to that of Si and Ge binary phosphates, which seems to confirm that $Ti(NH_4)_2P_4O_{13}$ is also isostructural to them. However, our attempts to index X-ray diffraction peaks with indices of the crystalline cell of $Ti(NH_4)_2P_4O_{13}$ using data for $Si(NH_4)_2P_4O_{13}$ or $Ge(NH_4)_2P_4O_{13}$ do not give good results, probably due to a large distortion of the crystalline cell upon substitution of Si or Ge for Ti.

Thermal Decomposition

As seen from thermogravimetry (Fig. 1, curves a and a′), $BaNH_4(PO_3)_3$ is stable up to 340°C, above which a small weight loss (≈5%) is observed. X-ray diffraction analysis showed that $BaNH_4(PO_3)_3$ partially decomposes to $Ba(PO_3)_2$ (19). As chemical analysis showed, NH_4^+ is present in the solid residue of thermal decomposition up to 600°C. Amorphous glass is formed at 900°C.

$BiNH_4P_4O_{12}$ and $Ti(NH_4)_2P_4O_{13}$ decompose in three steps (Fig. 1, curves b, b′ and c, c′, respectively). Both bismuth tetraphosphate, $Bi_2P_4O_{13}$, and polyphosphate, $Bi(PO_3)_3$ (20, 21), are detected in the solid residue of thermal decomposition after the first step of weight loss (maximum rate at 322°C, curve b′). With increasing temperature above the second step of weight loss (377°C), the content of $Bi_2P_4O_{13}$ decreases, whereas the $Bi(PO_3)_3$ content increases. $BiNH_4P_4O_{12}$ decomposes according to the following scheme.

TABLE 4
X-Ray Powder Data for $Ti(NH_4)P_4O_{13}$

d, Å	I, %	d, Å	I, %	d, Å	I, %
7.43	100	3.321	16	2.444	2
6.65	2	3.218	11	2.381	1
5.13	9	3.140	12	2.334	5
4.51	4	3.108	2	2.297	2
4.36	3	3.035	3	2.215	3
4.15	1	2.973	1	2.179	1
4.01	1	2.928	5	2.130	1
3.950	3	2.827	3	2.731	1
3.864	3	2.753	1	2.065	2
3.711	1	2.692	1	2.038	2
3.682	1	2.677	1	1.945	1
3.620	3	2.658	3	1.926	1
3.597	2	2.600	1	1.867	1
3.537	1	2.529	1	1.811	1
3.365	5	2.482	2	1.727	1
3.335	5				

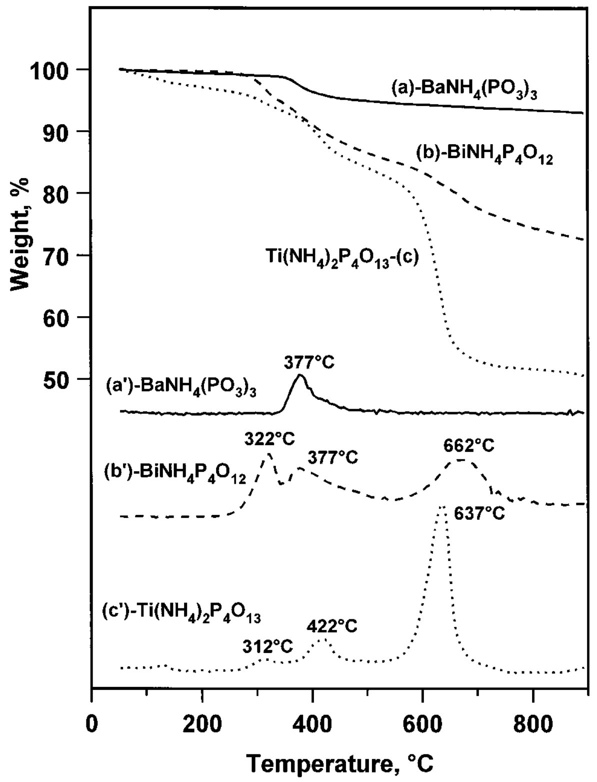

FIG. 1. Thermogravimetry (a, b, c) and derivative (a′, b′, c′) of (a, a′) $BaNH_4(PO_3)_3$, (b, b′) $BiNH_4P_4O_{12}$, and (c, c′) $Ti(NH_4)_2P_4O_{13}$. Heating rate, 10°C/min; nitrogen flow, 100 cm^3/min.

$$BiNH_4P_4O_{12} \xrightarrow[-H_2O]{-NH_3} Bi_2P_4O_{13} + \begin{matrix}\text{polyphosphoric}\\ \text{acids}\end{matrix} \rightarrow Bi(PO_3)_3 + \begin{matrix}\text{polyphosphoric}\\ \text{acids}\end{matrix} \qquad [1]$$

The excess of polyphosphoric acids evaporates in the third step of weight loss at 550–730°C. Amorphous glass is detected at 900°C.

Apart from loosing absorbed humidity at 50–200°C the onset of weight loss of $Ti(NH_4)_2P_4O_{13}$ corresponding to thermal decomposition is observed at 280°C (curves c and c′). After two steps of weight loss (maximum rate at 312°C and 422°C) where elimination of ammonia and water is observed, only TiP_2O_7 (22) is left as a crystalline product as detected by X-ray diffraction in solid residue. The third step of weight loss at 570–670°C is due to evaporation of polyphosphoric acids. No amorphous glass was found at 900°C, only crystalline TiP_2O_7.

It seems that binary condensed NH_4^+/Ba^{2+} and NH_4^+/Bi^{3+} phosphates give amorphous glasses at higher temperature because corresponding polyphosphates, $Ba(PO_3)_2$ and $Bi(PO_3)_3$, are soluble in polyphosphoric acids and create strong adducts with them. On the other hand, TiP_2O_7 is not soluble in these acids and therefore complete evaporation of polyphosphoric acids occurs at thermal decomposition of $Ti(NH_4)_2P_4O_{13}$.

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REFERENCES

1. H. L. Vandersall, *J. Fire Flamm.* **2,** 97 (1971).
2. G. F. Levchik, A. F. Selevich, S. V. Levchik, and A. I. Lesnikovich (to Byelorussian University, Minsk), Byelorussian Patient 76A, 1994.
3. S. V. Levchik, G. F. Levchik, G. Camino, and L. Costa, *J. Fire Sci.* **13,** 43 (1995).
4. S. V. Levchik, G. F. Levchik, G. Camino, L. Costa, and A. I. Lesnikovich, *Fire Mater.,* to be published.
5. G. F. Levchik, A. F. Selevich, S. V. Levchik, and A. I. Lesnikovich, *Thermochim. Acta.* **239,** 41 (1994).
6. G. F. Levchik, S. V. Levchik, P. D. Sachok, A. F. Selevich, A. S. Lyakhov, and A. I. Lesnikovich, *Thermochim Acta.* **257,** 117 (1995).
7. A. F. Selevich, G. F. Levchik, A. I. Lesnikovich, and S. V. Levchik (to Byelorussian University, Minsk), Byelorussian Patent 260A, 1994.
8. E. A. Prodan, I. L. Shashkova, and T. N. Galkova, *Zh. Anal. Khim.* **33,** 2304 (1978).
9. A. K. Babko and A. T. Pilipenko, "Photometric Analysis. The Methods of Nonmetals Identification," p. 83 Khimiya, Moscow, 1974. [in Russian]
10. G. Sharlo, "Methods of Analytical Chemistry Quantitative Analysis of Inorganic Substances." Khimia, Leningrad, 1966. [in Russian]
11. Z. A. Konstant and A. P. Dindune, "Phosphates of Bivalent Metals." Zinatne, Riga, 1987. [in Russian]
12. A. M. Smolegovskii, "The History of Crystallochemistry of Phosphates." Nauka, Moscow, 1986. [in Russian]
13. M. T. Averbuch-Pouchot and M. Baqieu-Beucher, *Z. Anorg. Allg. Chem.* **552,** 171 (1987).
14. B. N. Litvin and B. A. Masloboev, "Phosphates of Rare Earth Metals." Nauka, Leningrad, 1989. [in Russian]
15. M. Rzaigui and N. K. Ariguib, *J. Solid State Chem.* **49,** 391 (1983).
16. K. K. Palkina, S. I. Maksimova and L. G. Chibiskova, *Dokl. Akad. Nauk. SSSR* **257,** 357 (1981).
17. N. N. Chudinova, *Izv. Akad. Nauk. SSSR, Neorg. Mater* **15,** 833 (1979).
18. M. T. Averbuch-Pouchot and A. Durif, *J. Solid State Chem.* **18,** 391 (1976).
19. J. C. Grenier, C. Martin, and A. Durif, *Bull. Soc. Fr. Miner. Cristallogr.* **90,** 24 (1967).
20. L. A. Tezikova, N. N. Chudinova, P. M. Fedorov, and A. V. Lavrov, *Izv. Akad. Nauk. SSSR Neorg. Mater.* **10,** 2057 (1974).
21. N. N. Chudinova, *Izc. Akad. Nauk. SSSR, Neorg. Mater.* **15,** 833 (1979).
22. G. R. Levi and G. Peyronel, *Z. Kristallogr.* **92,** 190 (1935).