Crystal structures and physicochemical properties of mixed salts of ammonium nitrate and sulfate

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Mixed salts $(NH_4)_2SO_4 \cdot 2NH_4NO_3$ (**1**) and $(NH_4)_2SO_4 \cdot 3NH_4NO_3$ (**2**) were synthesized and studied by X-ray diffraction analysis. The unit cell parameters of these salts were determined and their crystal structures were solved. The thermal stability of the salts was studied by differential scanning calorimetry and thermogravimetric analysis. The temperatures and enthalpies of incongruent melting of compounds **1** and **2** were determined. The enthalpies of formation from the constituent salts were estimated.

Key words: mixed salts, ammonium nitrate, X-ray diffraction analysis, differential scanning calorimetry, temperature and enthalpy of incongruent melting.

Ammonium nitrate is a highly efficient nitrogen fertilizer containing 35 wt.% of bound nitrogen. However, this compound cannot be used in the pure form because of hygroscopicity and low resistance to detonation, resulting in certain transportation and storage problems, as well as problems of the incorporation of the fertilizer into the soil. The caking and explosivity of ammonium nitrate can be reduced by producing the fertilizer in granulated form or as paraffin-wax-coated crystals with stabilizing additives.[1] Ammonium sulfate is often used as such an additive. It is known[2,3] that ammonium sulfate and nitrate form mixed salts $(NH_4)_2SO_4 \cdot 2NH_4NO_3$ (**1**) and $(NH_4)_2SO_4 \cdot 3NH_4NO_3$ (**2**). However, information about their crystal structures reported in the literature is based exclusively on X-ray powder diffraction data[3,4] and the results of investigation of the crystal morphology.[5] To the best of our knowledge, single-crystal X-ray diffraction data for these salts are lacking.

The phase diagrams of the NH_4NO_3—$(NH_4)_2SO_4$ system proposed by different authors are also substantially different.[2,6—8] All researchers agree that compounds **1** and **2** undergo incongruent decomposition, but different ranges of thermal stability of these phases were reported. For example, Janecke *et al.*[2] suggested that the compound with an ammonium sulfate to nitrate ratio of 1 : 2 decomposes at 310 °C (583 K), whereas the upper stability limit of both stoichiometric phases was reported to be no higher than 180 °C (453 K) in another study.[8] It was hypothesized[7] that at 181 °C (454 K), the melt exists in equilibrium with solid ammonium sulfate, and $(NH_4)_2SO_4 \cdot 3NH_4NO_3$ decomposes at 162 °C (435 K) to give $(NH_4)_2SO_4$ and a NH_4NO_3-based solid solution. According to the results of the latest investigation[9] by thermogravimetric analysis (TGA), the upper stability limit of the 1 : 2 phase is 220 °C (493 K). These data need to be confirmed. The thermodynamic properties of the mixed salts have not been previously investigated.

The aim of the present study was to isolate single crystals of mixed salts **1** and **2**, refine their structures, determine the upper temperature range of the phase stability, and estimate their thermodynamic properties. We used single-crystal X-ray diffraction, X-ray powder diffraction, differential scanning calorimetry (DSC), and TGA.

Experimental

Single crystals of the mixed salts were obtained from ammonium nitrate and sulfate according to procedures described previously.[3] The starting ammonium nitrate (special purity grade) and ammonium sulfate (special purity grade) were purchased from the Limited Liability Company IREA 2000 (Russia) and were prepurified by recrystallization from water. The resulting salts were dried in a drying oven for 2 days at 45 °C and a residual gas pressure of $\sim 5 \cdot 10^{-8}$ Pa. The purified reagents were characterized by DSC and X-ray powder diffraction. The absence of impurities was verified by matching the X-ray diffraction patterns of the ammonium nitrate and sulfate to the patterns stored in the ICDD PDF2 database (cards 47—864 and 40—621, respectively) and by the coincidence of the temperatures and heats of phase transitions for NH_4NO_3 with the literature data.[10,11]

The salt $(NH_4)_2SO_4 \cdot 2NH_4NO_3$ (**1**) was prepared as follows. Ammonium sulfate (3.775 g) and ammonium nitrate (11.45 g) were placed (the molar ratio of $(NH_4)_2SO_4$ to NH_4NO_3 was 1 : 5) in a 50-mL beaker containing water (10 mL). The water—salt mixture was stirred at 20 °C for 1 h until the precipitate completely dissolved. The beaker with the solution was half-

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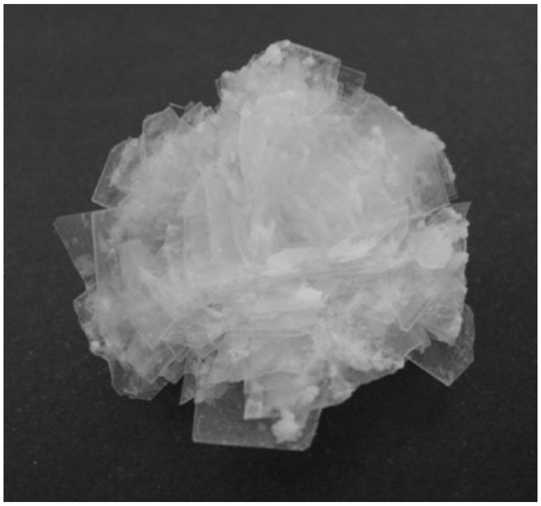
covered with parafilm and stored at ~20 °C for 5 days until a crystalline precipitate formed. The solution was removed by decantation. After the decantation, the crystals were separated into plates. This made it possible to decrease the content of impurities cocrystallized with $(NH_4)_2SO_4 \cdot 2NH_4NO_3$. When this procedure was not followed, the removal of moisture was accompanied by the formation of a white finely crystalline deposit containing ammonium nitrate on the crystal surface, as well as the formation of crystal druses, from which it was impossible to isolate single crystals of **1**. The plates were dried on a filter paper overnight. A photograph of the crystals is shown in Fig. 1, *a*.

The salt of the composition $(NH_4)_2SO_4 \cdot 3NH_4NO_3$ (**2**) was prepared from a mixture of ammonium sulfate (4.25 g), ammonium nitrate (28.1 g), and water (18 mL) (the molar ratio of $(NH_4)_2SO_4$ to NH_4NO_3 was 1 : 11). The water—salt mixture was heated to 50 °C and stirred for 20 min until the precipitate completely dissolved. The solution was slowly cooled and then kept at ~20 °C for 21 days until small transparent needle-like crystals formed on the bottom of the beaker. The solution was carefully removed by decantation, and the crystals that remained on the bottom were dried on a filter paper. Large crystals were separated under a microscope from smaller ammonium nitrate crystals. Crystals of the salt $(NH_4)_2SO_4 \cdot 3NH_4NO_3$ are shown in Fig. 1, *b*.

a



b

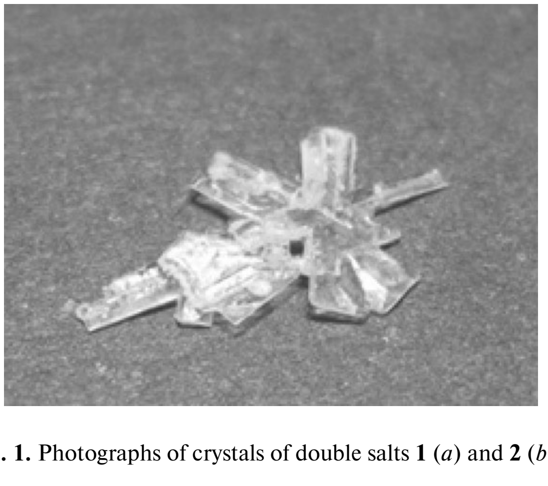


Fig. 1. Photographs of crystals of double salts **1** (*a*) and **2** (*b*).

To obtain samples of **1** and **2** in amounts sufficient for a calorimetric study, we slightly modified the procedures described in the publication.[3] To decrease the amount of the ammonium nitrate impurity, the crystals were taken from the solution immediately after the precipitation. Then the crystal surface was additionally purified by a wetted filter paper. This made it possible to substantially decrease the amount of the impurity phase compared to that obtained according to the conventional procedure for the synthesis of mixed salts. It was shown that the additional purification of the crystal surface enabled the preparation of higher-quality samples with a lower content of ammonium nitrate, whereas an increase in the evaporation rate of the solvent or the duration of the storage of crystals in the mother liquor affects the amount of the co-precipitated impurity to a lesser extent. This conclusion was based on the analysis of the peak area ratio in the DSC curve at 126 °C (399 K) corresponding to the phase transition with the maximum enthalpy of the solid-state transformation:

$$(NH_4NO_3)_{\text{tetr}} \rightleftharpoons (NH_4NO_3)_{\text{cub}},$$

where $(NH_4NO_3)_{\text{tetr}}$ and $(NH_4NO_3)_{\text{cub}}$ are the tetragonal and cubic phases, respectively.

Structural and thermoanalytical studies. Single crystals of **1** and **2** suitable for structural investigations were taken from the reaction mixture and mounted on an Enraf Nonius Cad-4 automated diffractometer (graphite monochromator, λ(Mo-Kα) = = 0.71073 Å, ~20 °C, $\omega/2\theta$-scan mode). The X-ray data collection and refinement statistics are given in Table 1. The monoclinic unit cell parameters of phases **1** and **2** were refined based on 24 well-centered reflections in the θ-angle range of 14.0—16.5 and 16.3—17.6°, respectively. The absorption correction was applied based on azimuthal scans of at least five reflections having the χ angle of ~90°. The structures were deposited with the Cambridge Structural Database (CSD-423626 (**1**) and CSD-423627 (**2**); Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: +(49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de)).

The X-ray powder diffraction analysis of polycrystalline samples was carried out on an IMAGE FOIL G670 Guinier camera (Huber) (Cu-Kα_1 radiation, λ = 1.54056 Å, a bent germanium single crystal as the monochromator, transmission geometry) at 25 °C in the 2θ-angle range of 10—70° using an Image Plate detector system. The samples were ground in an agate mortar and applied onto an X-ray amorphous dacron film using an X-ray amorphous glue. The X-ray powder diffraction data were compared with the X-ray patterns for the individual compounds stored in the ICDD PDF2 database (salt **1**, 42-0968; salt **2**, 42-0967).

The thermoanalytical experiments were carried out on a NETZSCH DSC 204 F1 instrument in a flow of dry artificial air (20 mL min^{-1}) or argon (50 mL min^{-1}) at a heating rate of 5 K min^{-1} in the temperature range of 0—400 °C. The measurements were performed in standard aluminum containers (V = 56 mm^3, d = 6 mm) with a tight-fitting lid with a hole. The measuring system was cooled with liquid nitrogen. The calibration of the instrument was performed based on the phase transition parameters of reference materials (C_6H_{12}, Hg, KNO_3, In, Sn, Bi, and CsCl; 99.99% purity). The systematic error of the calibration estimated based on the reference material (In) was 0.2 °C for the temperature and 5% for the heat.

Table 1. X-ray data collection and refinement statistics for the crystal structures of $(NH_4)_2SO_4 \cdot 2NH_4NO_3$ (**1**) and $(NH_4)_2SO_4 \cdot 3NH_4NO_3$ (**2**)

Parameter	**1**	**2**
Molecular formula	$H_{16}N_6O_{10}S$	$H_{20}N_8O_{13}S$
Molecular weight	292.25	362.22
Space group	$P2_1/c$	$P2_1$
a/Å	10.315(2)	9.969(2)
b/Å	11.399(2)	5.939(1)
c/Å	10.239(2)	12.430(3)
β/deg	105.99(3)	92.80(3)
V/Å^3	1157.3(4)	735.1(3)
Z	4	2
d_{calc}/g cm^{-3}	1.677	1.637
μ/mm^{-1}	0.337	0.304
θ-Scanning range, deg	2.05—30.00	2.05—34.96
Number of measured reflections	3571	3614
Number of independent reflections/number of parameters in refinement	3380/155	3469/201
R_{int}	0.0911	0.0428
R_1 ($I \geq 2(I)$)	0.0631	0.0848
wR_2 (based on all reflections)	0.1941	0.2612
Goodness-of-fit on F^2	1.017	1.119
Residual electron density /e Å^{-3}, ρ_{max}/ρ_{min}	0.609/–0.436	0.932/–0.735

The thermogravimetric analysis was performed on a NETZSCH TG 209 F1 instrument equipped with an alundum holder with a protection screen and a P-type temperature sensor. The experimental conditions were identical to those described above. Standard open alundum containers (V = 85 mm^3, d = 6.7 mm) were used. The temperature calibration was performed based on the melting points of reference materials (Ag, Al, Bi, In, and Sn; 99.99% purity). The accuracy of the weight measurements was within 0.5% (based on the reference material $CaC_2O_4 \cdot H_2O$). The samples were weighed on a SARTORIUS RESEARCH R 160P analytical balance with an accuracy of $1 \cdot 10^{-2}$ mg. The weights of the samples were 5—6 mg. The experimental data were processed with the use of the NETZSCH Proteus Thermal Analysis software. The phase transition temperature was determined from T_{onset} corresponding to the point of intersection of the tangents to the portions of the DSC curve with the minimum and maximum values of the derivative (before the peak extremum). The temperature, at which the decomposition begins to occur at a noticeable rate, was evaluated in a similar way. The heat effect of the process was determined from the DSC peak area (ISO 11357-1 standard).

Results and Discussion

Structural analysis. The crystal structures of two mixed-anion compounds were determined by single-crystal X-ray diffraction. The systematic absences of reflections for the crystal structure of salt **1** unambiguously determined the space group $P2_1/c$, whereas two space groups, $P2_1$ and $P2_1/m$, are possible for the crystal structure of salt **2**. The latter crystal structure was solved in the non-centrosymmetric space group $P2_1$. The subsequent analysis of the atomic positions showed that the the centrosymmetric space group is incorrect. The structures were solved by direct methods (SHELXS-97),[12] which located the atoms of the sulfate and nitrate groups. The nitrogen atoms of the ammonium groups were found by alternating the least-squares refinement and calculations of difference Fourier maps. The hydrogen atoms of the ammonium cation were not located. The final anisotropic refinement (SHELXL-97)[12] converged to R = 0.0848 (**1**) and 0.0631 (**2**) and showed that electron density peaks, which can be assigned to non-hydrogen atoms, are absent.

The unit cell parameters for compounds **1** and **2** determined by single-crystal X-ray diffraction are compared with the literature data in Table 2, which provides indirect evidence that these data can be used for the quantitative X-ray powder diffraction analysis.

According to the X-ray diffraction data, the crystal structures of compounds **1** and **2** consist of NO_3^- and SO_4^{2-} anions and NH_4^+ cations arranged in an ordered fashion and alternating in the corresponding stoichiometric ratios (Fig. 2). The nitrate anions are planar triangles with the N—O distances varying from 1.16 to 1.29 Å. It should be noted that the nitrate anion in the structure of $(NH_4)_4(NO_3)_2SO_4$ is more distorted than that in the structure of $(NH_4)_2SO_4 \cdot 3NH_4NO_3$. In both structures, the sulfate anions are almost regular tetrahedra; d(S—O) = = 1.46—1.48 Å. The analysis of the arrangement of the atoms in the structure of **2** confirmed the space group $P2_1$.

Table 2. Unit cell parameters of mixed salts of ammonium nitrate and sulfate **1** and **2** obtained previously and in the present study

Parameter	$(NH_4)_2SO_4 \cdot 2NH_4NO_3$ (**1**)			$(NH_4)_2SO_4 \cdot 3NH_4NO_3$ (**2**)		
	This study	[ICDD 44-799]*	See Ref. 4	This study	[ICDD 44-801]*	See Ref. 4
a/Å	10.315(1)	10.400	10.37	9.969(2)	9.940	9.98
b/Å	11.399(1)	11.400	11.46	5.939(1)	5.950	5.96
c/Å	10.239(1)	10.310	10.31	12.430(2)	12.390	12.48
β/deg	105.59	105.48	104.15	92.48	92.42	93.7

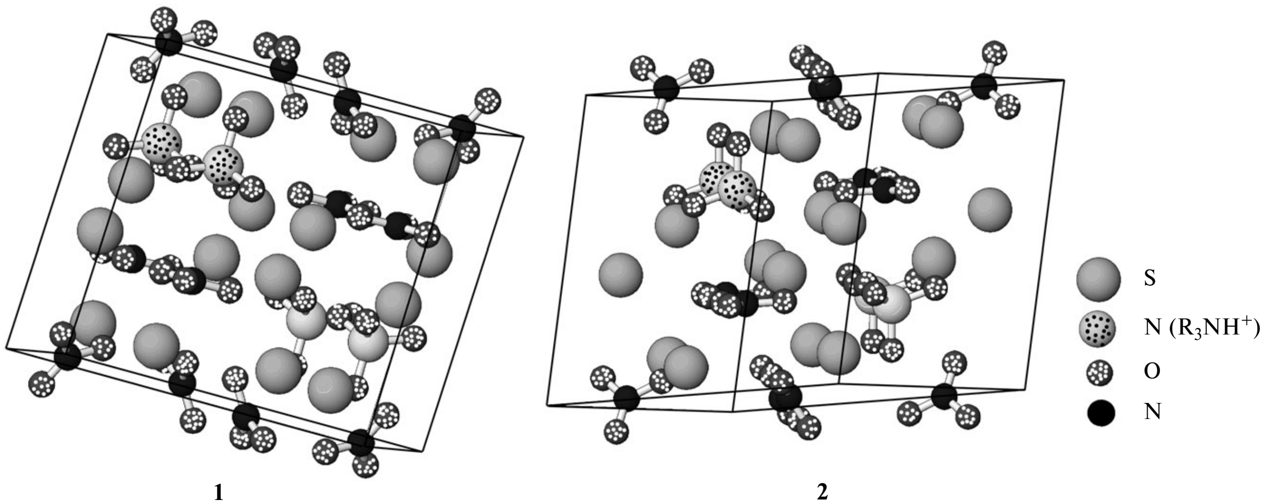
Thus, the arrangement of most of the atoms (all ammonium nitrogen atoms, the sulfate anion, and two nitrate anions) are consistent with the presence of a center of inversion and a mirror plane characteristic of the space group $P2_1/m$, whereas the position of the third nitrate anion (N(3), O(11), O(12), and O(13) atoms) is unambiguously indicative of the absence of the above-mentioned symmetry elements and defines the acentric space group $P2_1$. Since we failed to determine the positions of the hydrogen atoms, the orientation of the NH_4^+ cations remains unknown. However, the mutual arrangement of two types of anions and ammonium cations brings up a question of the role of hydrogen bonds in both crystal structures. Thus, the shortest distance between the nitrogen atom of the ammonium cation and the oxygen atom of the nitrate or sulfate anion is not smaller than 2.86 Å in **2** and 2.84 Å in **1**. This value is ~0.2 Å larger than the interatomic distance characteristic of N—H...O hydrogen bonds in inorganic compounds but corresponds to the length of the hydrogen bond between the R_3NH^+-type organic ammonium cations and the sulfate anion. Nevertheless, taking into account the rather high *R* factors, we did not calculate the positions of the hydrogen atoms considering the possible presence of hydrogen bonds.

Based on the experimental data, we calculated theoretical X-ray diffraction patterns for the mixed salts, which were used for the subsequent identification of compounds and the quantitative phase analysis of real fertilizers containing ammonium nitrate and sulfate.

The single-crystal X-ray diffraction data were used for performing the quantitative X-ray powder diffraction analysis of mixtures simulating the compositions of real fertilizers consisting of ammonium nitrate and sulfate. The X-ray powder diffraction data related to the molecular composition of the mixture are consistent, within 0.5 wt.%, with the results of the analysis for the ammonium, nitrate, and sulfate content. Taking into account that the discrepancy in the determination of the composition of the samples from the chemical analysis data obtained by different analytical methods varies from 0.2 to 2 wt.%, it can be concluded that the results of our structural studies can be used for the subsequent phase analysis of real fertilizers containing ammonium nitrate and sulfate.

Thermoanalytical investigations of samples of mixed salts **1** and **2** were performed in the temperature range of 30—220 °C under an artificial air or argon atmosphere. It was shown that the gas atmosphere has no significant effect on the results of investigation of the thermal decomposition of the mixed salts. To verify the reproducibility of the results, the measurements were carried out for samples synthesized under different conditions. In addition, we examined the reproducibility of the peak positions in the DSC curves of the same sample in several series of measurements. Figure 3 illustrates the DSC and TGA curves for mixed salt **1**. The plots additionally contain lines corresponding to the individual salts NH_4NO_3 and $(NH_4)_2SO_4$.

According to the results of the measurements, compound **1** is stable up to the temperature of 177.4±1.1 °C (450.4±1.1 K) (the peak maximum at ~185 °C (458 K)) and it does not undergo phase transitions up to the decomposition (see Fig. 3). The weight loss of the sample is observed at temperatures above 180 °C. The enthalpy of the peritectic decomposition is 33.3±1.9 kJ mol^{-1}. The X-ray powder diffraction analysis of the mixture, which was obtained by slowly cooling a sample preheated at a temperature above the decomposition temperature of compound **1**, showed that this mixture consists mainly of $(NH_4)_2SO_4 \cdot 3NH_4NO_3$ and ammonium sulfate. The X-ray diffraction patterns of the samples after the DSC analysis not always show reflections characteristic of $(NH_4)_2SO_4$. It should be noted that at small angles, the background line is rather uneven, which is indicative of



1 **2**

Fig. 2. General view of the crystal structures of **1** and **2**.

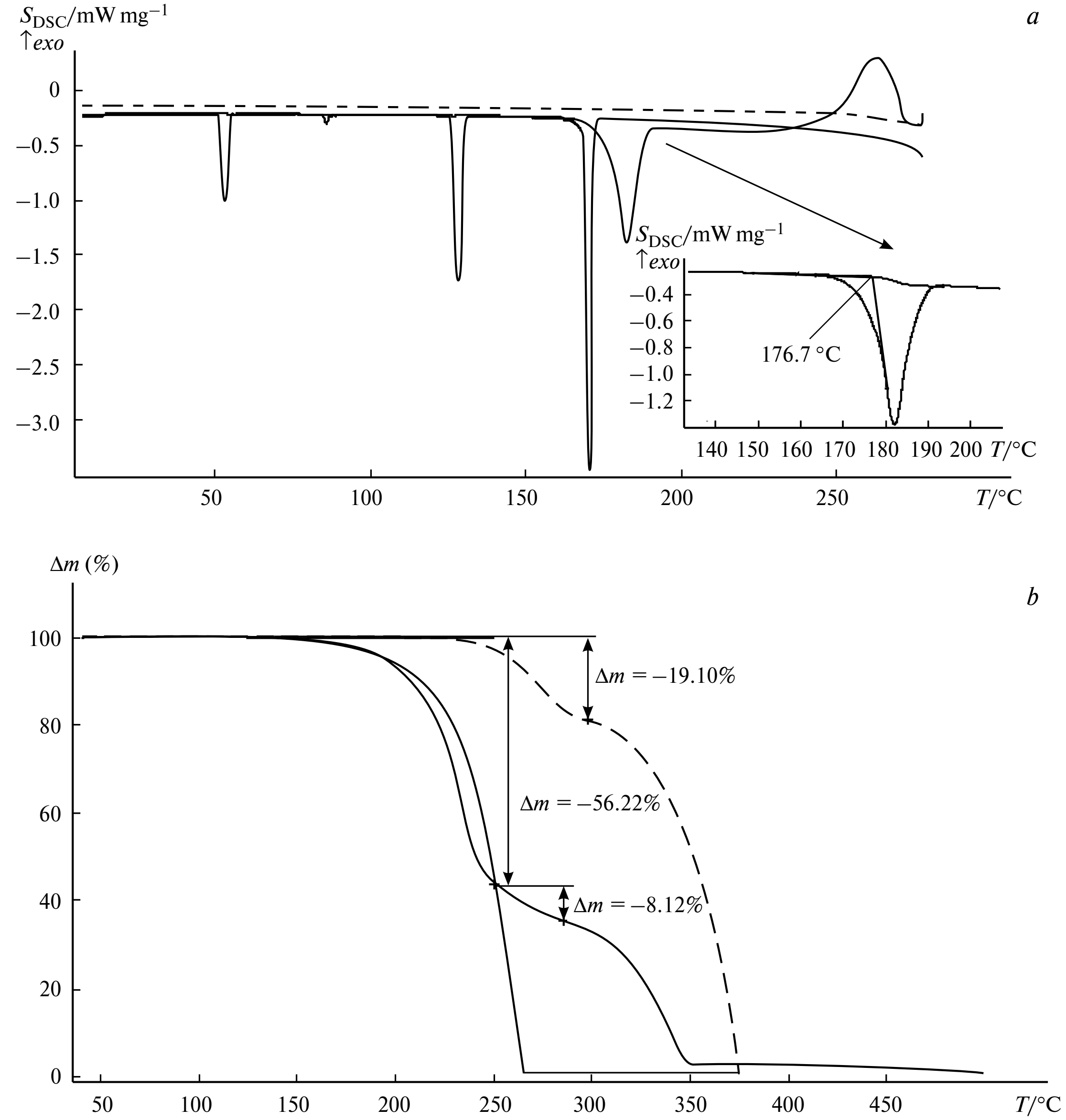


Fig. 3. DSC curve (*a*) and the weight loss curves (*b*) for single-crystal compound **1**, NH_4NO_3, and $(NH_4)_2SO_4$. Here and in Fig. 4, S_{DSC} is the detected signal. The thin line corresponds to ammonium nitrate; the dashed line, to ammonium sulfate; the thick line, to a single crystal of **1**. The inset shows the peritectic melting peak of the single crystal of **1**. The surface area bounded by the DSC curve and the base line is 102.1 J g^{-1}.

the presence of an amorphous phase. Based on the above results, we concluded that mixed salt **1** undergoes incongruent melting to form, upon the subsequent cooling, a mixture of $(NH_4)_2SO_4 \cdot 3NH_4NO_3$ and ammonium sulfate in the crystalline or X-ray amorphous state.

The thermal analysis of samples of the salt $(NH_4)_2SO_4 \cdot 3NH_4NO_3$ testifies that the selection of single crystals did not allow us to completely get rid of ammonium nitrate impurities. The minimum NH_4NO_3 content in the sample was 1.5 wt.% (as evaluated from the peak area at 126 °C (399 K)). Hence, the corresponding corrections were applied to the heat effect of decomposition of salt **2** calculated from the experimental data. As in the case of phase **1**, compound **2** does not undergo transformations and does not lose weight up to the peritectic decomposition temperature 176.4±0.4 °C (449.4±0.4 K). The enthalpy of incongruent melting of compound **2** is 43.6±2.3 kJ mol^{-1}. The X-ray powder diffraction analysis of the mixture, which was obtained by slowly cooling the sample preheated at a temperature above the decomposition temperature of compound **2** showed that the mixture contains $(NH_4)_2SO_4 \cdot 3NH_4NO_3$, ammonium nitrate and sulfate.

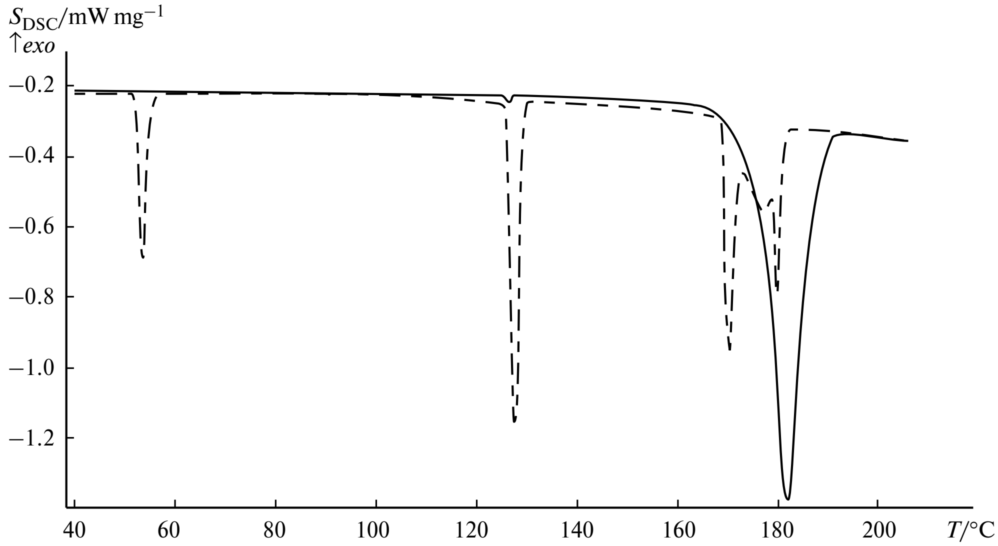


Fig. 4. DSC curves for a 2 : 1 mechanical mixture of ammonium nitrate and sulfate (dashed line) and a single crystal of **1** (solid line). The measurement rate is 5 K min^{-1}, under a dry argon atmosphere, the flow rate is 50 mL min^{-1}.

Estimation of the enthalpies of formation of mixed salts 1 and 2. To estimate $\Delta_f H$ for the mixed salts, we performed additional experiments on the decomposition of the individual compounds and mechanical mixtures of $(NH_4)_2SO_4$ and NH_4NO_3 of the same composition. Since at temperatures above the peritectic decomposition temperature, the DSC curves of the mixtures are identical to those of the individual compounds (see, for example, the thermogram of compound **1**, Fig. 4), it was suggested that the enthalpy of formation of the phases $(NH_4)_2SO_4 \cdot 2NH_4NO_3$ and $(NH_4)_2SO_4 \cdot 3NH_4NO_3$ can be estimated with the use of the thermochemical cycle given below (n = 2 or 3).

$$[(NH_4)_2SO_4 + n\ NH_4NO_3]_{298\ K} \longrightarrow$$
$$\longrightarrow [(NH_4)_2SO_4 + n\ NH_4NO_3]_{463\ K} \xrightarrow{463\ K}$$
$$\longrightarrow \text{Melt} + x\,(NH_4)_2SO_4 + Q_{p,1} \qquad (1)$$

$$[(NH_4)_2SO_4 \cdot nNH_4NO_3]_{298\ K} \longrightarrow$$
$$\longrightarrow [(NH_4)_2SO_4 \cdot nNH_4NO_3]_{463\ K} \xrightarrow{463\ K}$$
$$\longrightarrow \text{Melt} + x\,(NH_4)_2SO_4 + Q_{p,2} \qquad (2)$$

Melt is a melt.

Table 3. Enthalpies of formation ($\Delta_f H$) of mixed salts **1** and **2** at 298 K

Salt	$Q_{p,1}$	$Q_{p,2}$	$-\Delta_f H$/kJ mol^{-1}
	J g^{-1}		
1	73.05	114.04	12.0
2	96.92	117.07	7.5

The enthalpies of formation of compounds **1** and **2** at 25 °C (298 K) are equal to the differences between the total isobaric heat effects observed upon heating of the mixture ($Q_{p,1}$, Table 3) and the individual compounds to 190 °C (463 K) ($Q_{p,2}$, see Table 3), calculated from the DSC curves. This is a rather rough estimate; however, in the absence of high-accuracy calorimetric data, it can be used in calculations of the equilibria with the participation of mixed salts of ammonium sulfate and nitrate. The estimated enthalpies of formation of the mixed salts composed of ammonium sulfate and nitrate are given in Table 3.

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