Crystallographic Properties of the Ammonium Nitrate-Sulfates $3NH_4NO_3$-$(NH_4)_2SO_4$ and $2NH_4NO_3.(NH_4)_2SO_4$

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Morphological, optical, x-ray diffraction, and unit-cell properties are described for the ammonium nitrate-sulfates $3NH_4NO_3.(NH_4)_2SO_4$ and $2NH_4NO_3.(NH_4)_2SO_4$. Both salts are monoclinic. For the 3 : 1 salt, a = 12.39, b = 5.95, c = 9.94 A., and β = 92° 42′. For the 2 : 1 salt, a = 10.40, b = 11.40, c = 10.31 A., and β = 105° 48′. Evidence was not found for other distinct species intermediate between the 3:1 and 2:1 compositions, nor for solid solutions.

As a fast-growing fertilizer technology adds variety and complexity to its products, more and more importance attaches to phase identifications in the characterization of fertilizer materials. Interest in the development of ammonium nitrate–ammonium sulfate compositions as fertilizer materials prompted a study of the crystallographic properties of the double salts $3NH_4NO_3.(NH_4)_2SO_4$ and $2NH_4NO_3.(NH_4)_2SO_4$. Their properties have been described only in part, and inconsistencies mar the reports on the 2:1 salt.

Goniometric axial ratios, incomplete optical data, and powder x-ray data for the 3:1 salt were reported by Sokolov (*3*); his report also included powder x-ray data for a material he called the 2:1 salt. Optical data and unit-cell constants were reported by Janecke, Eissner, and Brill (*2*) for an orthorhombic species having hemimorphic symmetry and considered to be the 2:1 salt. Unit-cell constants for a 2:1 salt were reported also by Bragg (*1*), although he treated the symmetry as triclinic.

Each of the double salts characterized here was prepared in homogeneous species by two methods. Chemical composition, optical properties, and powder x-ray patterns were determined on those preparations that comprised coarse, clear crystals of euhedral form. Weissenberg single-crystal studies were made on selected crystals of each species.

Methods of Preparation

The 3:1 salt was prepared by slowly cooling a solution saturated at the boiling point with ammonium nitrate and ammonium sulfate, premixed in 6 to 1 mole ratio (method I). The 2:1 salt was made similarly, the solution being made strongly basic with ammonium hydroxide (method II). Both double salts were made (method III) from solution compositions derived from Sokolov's (*3*) study of equilibrium in the system ammonium nitrate–ammonium sulfate–water at 25° C. (3:1 salt, 19.04 moles of ammonium nitrate and 2.933 moles of ammonium sulfate per 100 moles of water; 2:1 salt, 14.99 moles of ammonium nitrate and 4.545 moles of ammonium sulfate per 100 moles of water).

Crystals of the 2:1 salt that were suitable for optical and x-ray studies were also obtained from other sources. When solutions containing ammonium nitrate and ammonium sulfate in mole ratios of 3.5 to 4.0 were evaporated slowly at room temperature over a period of several days, well formed plate crystals of the 2:1 salt appeared initially, although the preparations eventually became contaminated by crystals of ammonium sulfate. The 2:1 salt was found in mixed fertilizers containing ammonium nitrate and ammonium sulfate and as a product of the granulation of ammonium nitrate in the presence of dilute sulfuric acid and ammonia gas.

The chemical compositions of selected preparations of each salt and the types of examinations made on each preparation are shown in Table I.

Experimental Results

3:1 Salt. The 3:1 salt forms colorless monoclinic crystals, holohedral class $2/m$. The crystals usually are thin (010) plates elongated along c, common forms being {100}, {001}, and {101}. The habit may vary, however, to rod crystals having equally developed (100) and (010) and to blade crystals flattened on (100), elongated along b, and terminated by an (hki) set of vicinal character.

The crystals are biaxial (−), $2V$ = 42.5° (calcd. = 44.5°), with n_x = 1.489, n_y = 1.535, n_z = 1.543. The OAP is normal to (010), $b = n_z$, and $n_y \wedge c$ on (010) = 14° in acute β, β = 92.5°. No dispersion was detected. The specific gravity calculated from refractive indices and composition is 1.65.

Powder x-ray diffraction data for the 3:1 salt are shown in Table II. Rotation and Weissenberg photographs show that the unit cell is monoclinic with a = 12.39, b = 5.95, c = 9.94 A., and β = 92° 42′. The only systematic absence of reflections is ($0k0$) with k odd. The most probable space group is C^2_{2h}–$P2_1/m$ or C_2^2–$P2_1$. With 2[$3NH_4NO_3.(NH_4)_2SO_4$] per unit cell, the calculated specific gravity, 1.68, agrees well with the value calculated from refractive indices. With the holohedral symmetry indicated by the morphology, the y parameters of the two sulfur atoms, at least two ammonium-nitrogen atoms and at least two nitrate-nitrogen atoms are fixed at $^1/_4$.

2:1 Salt. The 2:1 double salt forms colorless monoclinic plates and tablets, holohedral class $2/m$. Crystals commonly are tabular on (001) with a tendency to elongate along a. The most prominent forms, aside from {001}, are the sets {110}, {011}, and sometimes {100}. Contact twinning is common, with (320) as the composition plane.

The crystals are biaxial (−), $2V$ = 60° (calcd. = 59.3°), with n_x = 1.471, n_y = 1.531, n_z = 1.552. The OAP is (010), $n_z \wedge a$ on (010) = 7° in obtuse β. β = 106°. No dispersion was detected. The specific gravity calculated from refractive indices and composition is 1.64.

The powder x-ray diffraction data for the 2:1 salt are shown in Table II. Rotation and Weissenberg photographs show that the unit cell is monoclinic

Table I. Characterization of Products

Salt	Method of Preparation	Chemical Analysis, % NH_4	NO_3	SO_4	Empirical Composition	Type of Examination[a]
3:1	I	24.2	45.6	28.9	2.45 $NH_4NO_3.(NH_4)_2SO_4$	O, P
	I	24.2	47.0	28.2	2.57 $NH_4NO_3.(NH_4)_2SO_4$	O, P
	III	24.1	49.6	25.8	2.98 $NH_4NO_3.(NH_4)_2SO_4$	O, P, W
	Theoretical	24.2	50.0	25.8		
2:1	II	24.6	40.4	33.7	1.87 $NH_4NO_3.(NH_4)_2SO_4$	O, P
	II	24.5	42.8	32.2	2.05 $NH_4NO_3.(NH_4)_2SO_4$	O, P
	III	24.4	41.2	33.3	1.91 $NH_4NO_3.(NH_4)_2SO_4$	O, P, W
	Theoretical	24.7	42.4	32.9		

[a] O, optical; P, powder x-ray; W, Weissenberg.

Table II. Powder Diffraction Data for 3:1 and 2:1 Salts[a]

d, A.	I	d, A.	I	d, A.	I
3 $NH_4NO_3.(NH_4)_2SO_4$					
12.3	vw	3.11	w	1.87	vw
7.73	w	2.98	m	1.84	vw
5.37	m	2.89[b]	s	1.77	vw
5.06	m	2.77[b]	w	1.68	vw
4.76[b]	s	2.68[b]	w	1.65	vw
4.54	m	2.49[b]	m	1.62	vw
4.14	vw	2.38	vw	1.58	vw
3.99	w	2.34[b]	m	1.46	vw
3.80	vw	2.27	w	1.44	vw
3.63	vw	2.19[b]	ms	1.42	vw
3.38	vw	2.09[b]	m	1.38	vw
3.25	s	1.99	vw	1.36	vw
3.17[b]	vs	1.93	vw		
2 $NH_4NO_3.(NH_4)_2SO_4$					
10.1	w	3.26	vs	2.12	m
7.52	w	3.17	s	2.03	w
6.70	w	2.92	s	1.93	w
5.45	w	2.84	ms	1.63	w
5.22	vw	2.65	vw	1.46	w
4.95	s	2.58	w	1.38	w
4.68	s	2.47	m	1.36	w
4.17	vw	2.40	m		
3.87	m	2.23	mw		

[a] Cu $K\alpha$ radiation; camera diameter, 14.32 cm. Intensities estimated visually: vs very strong; s strong; ms medium strong; m medium; mw medium weak; w weak; vw very weak.

[b] Correspond to interplanar spacings calculated from data of Sokolov (*3*) for the 3:1 salt.

with a = 10.40, b = 11.40, c = 10.31 A., and β = 105° 48′. The only systematic absences of reflections are $(h0l)$ when l is odd, and $(0k0)$ when k is odd. The most probable space group is C^5_{2h}–$P2_1/c$. With 4[$2NH_4NO_3$.$(NH_4)_2SO_4$] per unit cell, the calculated specific gravity, 1.64, is identical with the value derived from refractive indices. All the atoms are in general positions.

Discussion

The differences in sources and the departures from stoichiometric composition were without significant effect on the x-ray diffraction patterns of the respective salts. The same applied to the optical properties, with the exception that the value of n_z for 3:1-type products increased somewhat with decrease of the ratio below its nominal value.

The diffraction data listed by Sokolov (*3*) for the 3:1 salt agree well with the present measurements, but his listing lacks even some of the stronger characteristic reflections. The crystals he selected for optical goniometric study gave axial ratios and an interaxial angle which (with appropriate doubling of his value for a and c) agree well with the respective values derived from x-ray measurements:

	X-Ray	Goniometric
$a:b:c$	$2.0824:1:1.6706$	2.0818:1:1.6686
β	92° 42′	92° 42′

On the other hand, his partial report of optical data for the 3:1 salt appears to encompass properties of both salts. His optical examinations may have been made on a preparation contaminated with the 2:1 salt. Although the two salts differ morphologically, they might not be distinguished in a superficial examination of a mixture.

Literature on the 2:1 salt is in disagreement as to crystal system, optical properties, and diffraction data. Earlier reports unfortunatcly have not always specified precise chemical compositions.

The powder diffraction data given by Sokolov (*3*) are in much closer agreement with his reference x-ray data for ammonium sulfate than with the diffraction results reported here for the 2:1 salt. He did not report the optical properties.

The orthorhombic phase that Janecke, Eissner, and Brill (*2*) considered to be the 2:1 salt yielded optical data and unit-cell constants that cannot be reconciled with the results presented here. Their measured value of $2E$ (108.5°) corresponds to a value of $2V$ (64.2°) that is inconsistent with the value 76.9° which we computed from the refractive indices reported by them. Similar refractive indices were reported by Thomas and Hallimond (*4*), but they also reported essentially the same indices for the 3:1 salt. Unit-cell constants from Janecke yield a specific gravity of 1.76, whereas constants from Bragg (*1*) and from the present work yield significantly lower values —1.65 and 1.64, respectively. Bragg's thought of triclinic symmetry conflicts with the present finding of the higher monoclinic symmetry.

No evidence of polymorphism was found, nor any evidence of the existence of other distinct species intermediate in composition between the 3:1 and 2:1 salts.

Literature Cited

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