

Crystal Structure of $(\text{NH}_4)_4\text{H}_2(\text{SeO}_4)_3$ and $(\text{ND}_4)_4\text{D}_2(\text{SeO}_4)_3$ below 180 K

A. Pawłowski* and A. Haznar†,¹

*Institute of Molecular Physics, Polish Academy of Science, ul. M. Smoluchowskiego 17, 60-179 Poznań, Poland; and †Institute of Low Temperature and Structure Research, Polish Academy of Science, P.O. Box 1410, 50-950 Wrocław 2, Poland

Received January 16, 2001; in revised form April 11, 2001; accepted April 20, 2001; published online June 11, 2001

The structure of $(\text{NH}_4)_4\text{H}_2(\text{SeO}_4)_3$ and $(\text{ND}_4)_4\text{D}_2(\text{SeO}_4)_3$ superionic crystals below 180 K determined by X-ray single-crystal analysis is presented. The compounds have the following crystal data: $(\text{NH}_4)_4\text{H}_2(\text{SeO}_4)_3$ ($T = 140$ K), triclinic, space group $P-1$, $a = 7.647(2)$ Å, $b = 10.342(2)$ Å, $c = 10.558(2)$ Å, $\alpha = 114.41(3)^\circ$, $\beta = 93.22(3)^\circ$, $\gamma = 107.47(3)^\circ$, $V = 709.4(3)$ Å³, $Z = 2$, $R = 0.0358$; $(\text{ND}_4)_4\text{D}_2(\text{SeO}_4)_3$ ($T = 135$ K), triclinic, space group $P-1$, $a = 7.660(2)$ Å, $b = 10.345(2)$ Å, $c = 10.552(2)$ Å, $\alpha = 114.40(3)^\circ$, $\beta = 93.27(3)^\circ$, $\gamma = 107.50(3)^\circ$, $V = 710.3(3)$ Å³, $Z = 2$, $R_1 = 0.0325$. The two “acid” protons are involved in short hydrogen bonds of length ~ 2.5 Å linking three SeO_4 tetrahedra into a trimer. The dihydrogen triselenate anions are linked with the ammonium cations by weak H bonds (2.8–3.1 Å). No drastic changes in bond lengths within SeO_4 tetrahedra were observed between room temperature and ~ 140 K. The tendency to the N–H(D) ... O bond network contraction can be related to slowing the ammonium ions’s rotation. The mutual reorientation of SeO_4 tetrahedra in trimers evidenced by torsion angle changes is negligible in the studied temperature range. The obtained results are compared with those previously reported and the reasons are given that at low temperatures both crystals preserve room temperature, nonpolar $P-1$ space group. © 2001 Academic Press

Key Words: $(\text{NH}_4)_4\text{H}_2(\text{SeO}_4)_3$; $(\text{ND}_4)_4\text{D}_2(\text{SeO}_4)_3$; X-ray diffraction; crystal structure; phase transition.

INTRODUCTION

Tetraammonium dihydrogen triselenate, $(\text{NH}_4)_4\text{H}_2(\text{SeO}_4)_3$, belongs to the large group of hydrogen selenates with fast proton conductivity in the high-conductivity superionic phase. The crystal undergoes a superionic phase transition at $T_S = 378$ K. The transition is accompanied by an increase in the conductivity by 3 orders of magnitude. Above T_S the conductivity is isotropic with very low activation energy (1–3). The high-temperature phase is characterized by a fast reorientational dynamics of the H-bonded selenate tetrahedra (4) which results in dynamical disorder-

ing of the H bond network, leading to an increase in the number of structurally equivalent positions for protons. The fast structure diffusion of protons proceeds via the Grotthuss mechanism, in two steps: (i) proton transfer in the H bond between two adjacent SeO_4 tetrahedra, and (ii) subsequent reorganization of the proton environment, resulting in proton transport to a H bond with the next SeO_4 group. Thus, the structure of the hydrogen bond network and its evolution with temperature plays a crucial role in understanding fast proton transport mechanism. Our preliminary impedance spectroscopy measurements on $(\text{ND}_4)_4\text{D}_2(\text{SeO}_4)_3$ have shown that it is also a superionic conductor (with deuterons as a charge carriers) and that T_S does not change on deuteration.

At room temperature $(\text{NH}_4)_4\text{H}_2(\text{SeO}_4)_3$ is triclinic with space group $P-1$ and its unit cell contains two chemical units (5–7). The dihydrogen triselenate anions are linked by weak H bonds with the ammonium cations. The two “acid” protons are involved in short hydrogen bonds linking three SeO_4 tetrahedra into a trimer (Fig. 1). The $\text{Se}(1)\text{O}_4^{2-}$ ion is placed in the center of the trimer and its two oxygens O(11) and O(13) play the role of proton acceptors in the hydrogen bonds with two outlying HSeO_4^- anions. The trimers are aligned along the [021] crystallographic direction. The room-temperature structure of $(\text{ND}_4)_4\text{D}_2(\text{SeO}_4)_3$ is very close to that of the protonated crystal (7).

Recently a small peak was reported at ~ 182 K on the differential scanning calorimetry curve of $(\text{NH}_4)_4\text{H}_2(\text{SeO}_4)_3$ (8). On the basis of this observation as well as the results of a structural X-ray study at 141 K, the authors ascribed the polar $P1$ space group to the crystal below 182 K. They suggest also that the low-temperature phase is ferroelectric. However, the crystal structure at low temperature is very close to those obtained at room temperature and the conclusion about the $P1$ space group issues in fact from the DSC peak and from weak changes observed in the EPR study (8, 9).

Our previous X-ray studies of the crystal lattice parameters’ variations versus temperature do not show any phase transition but only some changes in their slope around 180 K. These results suggest that $(\text{NH}_4)_4\text{H}_2(\text{SeO}_4)_3$

¹ To whom correspondence should be addressed. Fax: (0 48 71) 3441 029. E-mail: haznar@int.pan.wroc.pl.

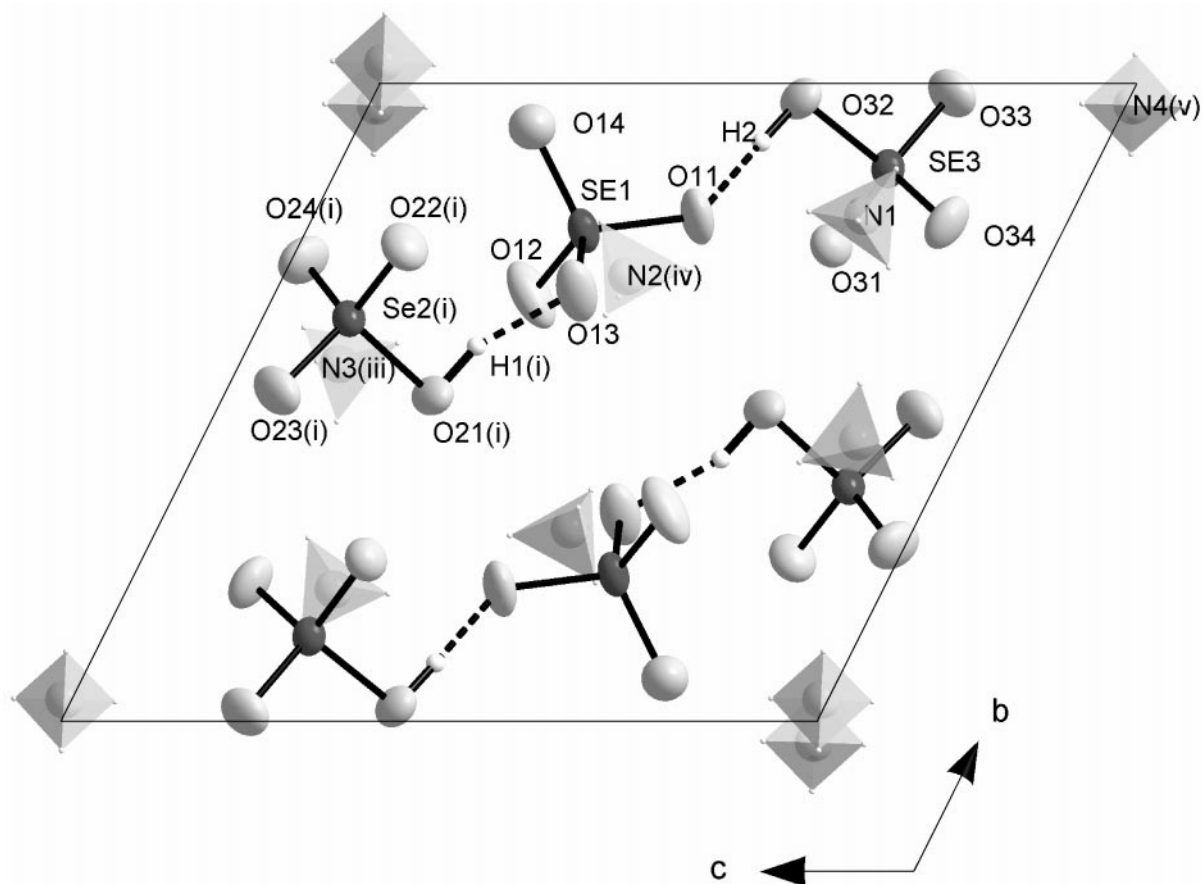


FIG. 1. Unit cell of the $(\text{NH}_4)_4\text{H}_2(\text{SeO}_4)_3$ and $(\text{ND}_4)_4\text{D}_2(\text{SeO}_4)_3$ crystals projected on the (100) plane (symmetry codes listed in Table 3).

at 135 K still has the $P-1$ space group (10). Therefore, we decided to re-examine the structure of $(\text{NH}_4)_4\text{H}_2(\text{SeO}_4)_3$ and its deuterated analogue both at room temperature and at low temperature. In this paper we present the complete set of low-temperature structure parameters for both crystals. The low-temperature structure of the deuterated crystal has not been reported yet. The obtained results are compared with those previously reported (7, 9) and, in the discussion, the reasons are given that at low temperatures both crystals still preserve the same nonpolar $P-1$ space group as at room temperature.

EXPERIMENTAL

Crystal Growth

The single crystals of $(\text{NH}_4)_4\text{H}_2(\text{SeO}_4)_3$ were grown at room temperature by slow evaporation from an aqueous solution of $(\text{NH}_4)_2\text{SeO}_4$ and H_2SeO_4 at a molar ratio of 1.4:1. The deuterated compound was obtained by fivefold recrystallization from D_2O . Because the compound is incongruently soluble, the mother solution was evaporated to dryness in subsequent recrystallizations in order to preserve

the proportions in solution. The obtained crystals were colorless and transparent.

Determination of Crystal Structure

The crystals of $(\text{ND}_4)_4\text{D}_2(\text{SeO}_4)_3$ and $(\text{NH}_4)_4\text{H}_2(\text{SeO}_4)_3$ were mounted on a KUMA Diffraction single-crystal diffractometer equipped with a two-dimensional area CCD detector. The samples were selected under a polarizing microscope and examined by a CCD detector. The $\text{MoK}\alpha$ graphite-monochromated radiation and the ω scan with $\Delta\omega = 0.75^\circ$ for one image were used for data collection. The 1060 images for six different runs covered approximately 95% of the Ewald sphere. The crystal data and experimental details are given in Table 1. The initial lattice parameters were calculated using about 165 reflections obtained from 30 images for 10 runs with different orientations in reciprocal space and then the lattice parameters were refined for all collected reflections. The temperature measurements in the 120–320 K range were performed using the CPC511 Oxford Cryosystem Cooler with cold nitrogen gas stream. The

TABLE 1
Details of Single-Crystal X-ray Data Collection
and Structure Refinement

Crystal Data		
Empirical formula	(NH ₄) ₄ H ₂ (SeO ₄) ₃	(ND ₄) ₄ D ₂ (SeO ₄) ₃
Formula weight	503.06	521.06
Temperature (K)	140(5)	135(5)
Crystal size (mm)	0.27 × 0.23 × 0.22	0.24 × 0.23 × 0.21
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1
Unit cell dimensions		
<i>a</i> (Å)	7.647(2)	7.660(2)
<i>b</i> (Å)	10.342(2)	10.345(2)
<i>c</i> (Å)	10.558(2)	10.552(2)
α (deg)	114.41(3)	114.40(3)
β (deg)	93.22(3)	93.27(3)
γ (deg)	107.47(3)	107.50(3)
Volume (Å ³)	709.4(3)	710.3(3)
<i>Z</i>	2	2
Calculated density (Mg/m ³)	2.355	2.436
Absorption coefficient μ (mm ⁻¹)	7.840	7.831
Data Collection		
Radiation, wavelength (Å)	MoK α , 0.71073	MoK α , 0.71073
Theta range for data collection (deg)	4.67 to 28.27	4.63 to 28.27
Limiting indices	-10 ≤ <i>h</i> ≤ 7, -13 ≤ <i>k</i> ≤ 13, -14 ≤ <i>l</i> ≤ 14	-10 ≤ <i>h</i> ≤ 8, -13 ≤ <i>k</i> ≤ 13, -13 ≤ <i>l</i> ≤ 14
Reflections collected/unique	8281/3324	5979/3323
<i>R</i> _{int}	0.0322	0.0377
Completeness to $\theta = 28.27$ (%)	94.5	94.4
<i>F</i> (000)	488	488
<i>E</i> ² - 1	0.973	0.978
Refinement		
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Corrections		
Lorentz polarization		
Absorption	For sphere	For sphere
Extinction coefficient	0.0072(4)	0.0025(2)
Data/restraints/parameters	3324/42/249	3323/42/249
Goodness-of-fit on <i>F</i> ²	1.128	1.111
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0358, <i>wR</i> ₂ = 0.0711	<i>R</i> ₁ = 0.0325, <i>wR</i> ₂ = 0.0732
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0483, <i>wR</i> ₂ = 0.0736	<i>R</i> ₁ = 0.0394, <i>wR</i> ₂ = 0.0751
Max. and Min. residual (e/Å ³)	1.605 and -0.812	1.422 and -0.902

The structure was solved by a direct method and subsequent difference Fourier syntheses with the SHELXTL_PLUS program system (G. M. Sheldrick, SHELXL, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1993). The structure refinement was done using SHELXL97 (G. M. Sheldrick, SHELXL, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997). Anisotropic thermal displacement parameters were used for all nonhydrogen atoms. The H atoms were located from the difference Fourier maps and the NH₄⁺ ions were constrained to perfect tetrahedra by DFIX instruction.

RESULTS AND DISCUSSION

The structural research in the wide temperature range presented in this paper confirms the previous structural study results that (NH₄)₄H₂(SeO₄)₃ and its deuterated analogue crystallize in centrosymmetric *P*-1 triclinic space group (5–7).

As was mentioned above, the low-temperature structural study results for (NH₄)₄H₂(SeO₄)₃ gave a crystal structure very close to that obtained at room temperature (9). It was admitted that the *P*-1 space group could have been ascribed to the low-temperature crystal structure; however, because of the anomaly at 182 K (8), the space group was assumed to be acentric *P*1. The transition at 182 K was evidenced by DSC and EPR measurements and related to the subtle changes within SeO₄ tetrahedra (8, 9); however, Baran *et al.* (11) did not detect by DSC any energetic effect below room temperature. The results reported in (8, 9), in our opinion, do not evidence unequivocally the structural phase transition with a *P*-1 → *P*1 symmetry change in the crystal at low temperatures.

There are known many examples of isostructural phase transitions in a solid state, i.e., transitions which occur without a change of the space group. Such a transformation takes place, for instance, in Cs₃H₃(SO₄)₄, where the SO₄ groups lose their stability above 360 K, which leads to the anomalies in the temperature dependencies of the frequency shift and of spectral width of the Brillouin components and to the appearance of new modes in the Raman spectra (12). Nevertheless, in the transition the space group of the crystal remains unchanged and the local symmetry above *T*_C is realized dynamically.

It is hard to judge when a structure should be described as exactly centrosymmetric (*P*-1) rather than only approximately so (*P*1) in the absence of conclusive noncrystallographic evidence. The centrosymmetric (*P*-1) description is preferred when (i) the original (*P*1) description leads to some unacceptable bond lengths which are improved when the coordinates are symmetrized, and (ii) the deviations from centrosymmetry are relatively small—deviations of the two-atom centers from the global center are less than 0.1 Å

temperature was stabilized to an accuracy of ± 0.5 K. The (ND₄)₄D₂(SeO₄)₃ crystal was measured at 255 K and 135 K, and the (NH₄)₄H₂(SeO₄)₃ crystal was measured at room temperature and at 140 K.

TABLE 2

Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic U_{eq} (Se, O, and N) and Isotropic U_{iso} (H and D) Displacement Parameters ($\text{\AA}^2 \times 10^3$) for (a) $(\text{NH}_4)_4\text{H}_2(\text{SeO}_4)_3$ at 140 K and (b) $(\text{ND}_4)_4\text{D}_2(\text{SeO}_4)_3$ at 135 K

Atom	x	y	z	$U_{\text{eq}}/U_{\text{iso}}^a$
(a) $(\text{NH}_4)_4\text{H}_2(\text{SeO}_4)_3$				
Se(1)	3490(1)	7692(1)	6328(1)	16(1)
O(11)	2976(4)	7903(3)	4909(3)	23(1)
O(12)	1590(4)	6691(3)	6609(3)	30(1)
O(13)	4901(4)	6719(3)	6001(3)	27(1)
O(14)	4466(4)	9354(3)	7703(3)	26(1)
Se(2)	3361(1)	3652(1)	1130(1)	15(1)
O(21)	4828(4)	4891(3)	2750(3)	23(1)
O(22)	1637(4)	2469(3)	1383(3)	21(1)
O(23)	2678(4)	4752(3)	653(3)	26(1)
O(24)	4588(4)	2776(3)	143(3)	26(1)
Se(3)	467(1)	8677(1)	2708(1)	15(1)
O(31)	-1255(3)	7443(3)	2931(3)	18(1)
O(32)	1971(4)	9784(3)	4332(3)	20(1)
O(33)	-193(4)	9863(3)	2367(3)	25(1)
O(34)	1589(4)	7828(3)	1583(3)	23(1)
N(1)	5191(4)	7909(3)	2743(3)	17(1)
N(2)	-1533(5)	7055(4)	5455(4)	28(1)
N(3)	1267(5)	5590(3)	-1346(3)	24(1)
N(4)	-2257(4)	372(4)	120(3)	21(1)
H(1)	4840(80)	4260(60)	3020(60)	62(19)
H(2)	2200(70)	9150(50)	4610(50)	44(15)
H(11)	6300(20)	7900(30)	2870(30)	43(15)
H(12)	4750(40)	7960(30)	3490(20)	46(15)
H(13)	5220(40)	8710(20)	2660(30)	25(12)
H(14)	4510(30)	7100(20)	2010(20)	30(13)
H(21)	-1500(40)	7080(30)	4656(17)	26(12)
H(22)	-1110(30)	6370(20)	5450(30)	60(20)
H(23)	-2670(20)	6820(30)	5570(30)	50(16)
H(24)	-870(40)	7910(20)	6140(20)	54(17)
H(31)	1300(30)	5910(20)	-1973(18)	0(8)
H(32)	2240(30)	6130(30)	-680(20)	70(20)
H(33)	280(30)	5640(30)	-1000(30)	80(20)
H(34)	1180(40)	4661(17)	-1730(30)	8(9)
H(41)	-2780(30)	530(20)	-460(20)	12(10)
H(42)	-1210(20)	1070(20)	520(30)	34(13)
H(43)	-2110(40)	-440(20)	-260(30)	90(20)
H(44)	-2860(40)	420(40)	770(20)	70(20)
(b) $(\text{ND}_4)_4\text{D}_2(\text{SeO}_4)_3$				
Se(1)	3491(1)	7695(1)	6329(1)	15(1)
O(11)	2984(3)	7907(2)	4910(2)	22(1)
O(12)	1582(3)	6690(2)	6608(2)	30(1)
O(13)	4900(3)	6724(2)	6008(2)	26(1)
O(14)	4465(3)	9358(2)	7711(2)	26(1)
Se(2)	3359(1)	3652(1)	1129(1)	14(1)
O(21)	4829(3)	4898(2)	2751(2)	21(1)
O(22)	1634(3)	2470(2)	1384(2)	21(1)
O(23)	2676(3)	4759(2)	656(2)	25(1)
O(24)	4580(3)	2776(2)	142(2)	24(1)
Se(3)	465(1)	8676(1)	2705(1)	14(1)
O(31)	-1251(2)	7442(2)	2924(2)	18(1)
O(32)	1982(2)	9799(2)	4332(2)	19(1)
O(33)	-197(3)	9858(2)	2363(2)	24(1)
O(34)	1579(2)	7827(2)	1585(2)	22(1)
N(1)	5192(3)	7911(2)	2746(2)	15(1)

TABLE 2—Continued

Atom	x	y	z	$U_{\text{eq}}/U_{\text{iso}}^a$
N(2)	-1526(3)	7062(3)	5461(2)	26(1)
N(3)	1276(3)	5593(2)	-1345(2)	22(1)
N(4)	-2255(3)	370(2)	107(2)	18(1)
D(1)	4930(40)	4410(30)	3100(30)	23(9)
D(2)	2170(60)	9270(40)	4560(40)	48(12)
D(11)	6279(12)	7899(16)	2867(17)	25(9)
D(12)	4760(20)	8002(17)	3492(10)	37(10)
D(13)	5250(20)	8714(10)	2664(15)	19(8)
D(14)	4490(20)	7146(14)	2036(13)	16(7)
D(21)	-1450(20)	7102(15)	4680(10)	34(10)
D(22)	-1104(17)	6412(11)	5509(19)	54(13)
D(23)	-2663(13)	6839(19)	5550(18)	32(9)
D(24)	-900(20)	7937(13)	6149(15)	39(10)
D(31)	1300(20)	5931(12)	-1959(10)	19(8)
D(32)	2250(16)	6135(19)	-681(14)	65(14)
D(33)	291(14)	5627(19)	-992(16)	41(11)
D(34)	1210(20)	4666(11)	-1744(19)	51(12)
D(41)	-2812(18)	521(13)	-482(12)	15(7)
D(42)	-1198(15)	1070(15)	500(17)	30(9)
D(43)	-2110(20)	-465(11)	-292(19)	52(12)
D(44)	-2874(19)	370(20)	741(12)	54(12)

^a U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

(13). In the structure of $(\text{NH}_4)_4\text{H}_2(\text{SeO}_4)_3$ at low temperatures described in the $P1$ space group (9), the bond lengths are quite reasonable but the deformation of Se(1) and Se(4) tetrahedra seems to be too strong since the strength of the two hydrogen bonds in the trimer does not change and no new H bonds appear. Besides, the deviation from centrosymmetry is very small, as are differences between lengths of equivalent bonds.

A recent study has shown (10) that the lattice parameters of both crystals exhibit continuous temperature variation. No drastic changes appeared in the vicinity of 180 K and only a change in the slope of the curves in a broad range below room temperature was observed. Also, dielectric studies revealed the broad, cusplike permittivity maximum which can be related to a glasslike transition, owing to a freezing of NH_4^+ rotational motions (10).

Taking the above considerations into account, we have redetermined the low-temperature structure for both compounds. The results implied that below 180 K the crystals do not change their symmetry. In both cases $|E^2 - 1|$ indicates a centrosymmetric space group (Table 1). The final discrepancy factors in the case of fitting to the acentric $P1$ space group do not decrease though the number of refined parameters is doubled and the elements of correlation matrix of the atoms positional parameters exceed 0.8.

Details of the structure refinement at 140 K and 135 K for $(\text{NH}_4)_4\text{H}_2(\text{SeO}_4)_3$ and $(\text{ND}_4)_4\text{D}_2(\text{SeO}_4)_3$, respectively, are given in Table 1, atomic coordinates and equivalent isotropic displacement parameters for nonhydrogen atoms and

TABLE 3
Selected Geometric Parameters (Å, °)

SeO ₄ tetrahedra	
(a) (NH ₄) ₄ H ₂ (SeO ₄) ₃ 140 K	(b) (ND ₄) ₄ D ₂ (SeO ₄) ₃ 135 K
Se(1)–O(11)	1.644(3)
Se(1)–O(12)	1.634(3)
Se(1)–O(13)	1.644(3)
Se(1)–O(14)	1.632(3)
Se(2)–O(21)	1.713(3)
Se(2)–O(22)	1.627(3)
Se(2)–O(23)	1.620(3)
Se(2)–O(24)	1.621(3)
Se(3)–O(31)	1.641(2)
Se(3)–O(32)	1.715(3)
Se(3)–O(33)	1.614(3)
Se(3)–O(34)	1.619(3)
O(14)–Se(1)–O(12)	110.5(1)
O(14)–Se(1)–O(13)	111.4(1)
O(12)–Se(1)–O(13)	107.4(1)
O(14)–Se(1)–O(11)	109.8(1)
O(12)–Se(1)–O(11)	109.8(1)
O(13)–Se(1)–O(11)	107.8(1)
O(23)–Se(2)–O(24)	116.2(1)
O(23)–Se(2)–O(22)	112.0(1)
O(24)–Se(2)–O(22)	110.9(1)
O(23)–Se(2)–O(21)	103.0(1)
O(24)–Se(2)–O(21)	106.3(1)
O(22)–Se(2)–O(21)	107.5(1)
O(33)–Se(3)–O(34)	114.3(1)
O(33)–Se(3)–O(31)	112.7(1)
O(34)–Se(3)–O(31)	110.9(1)
O(33)–Se(3)–O(32)	104.0(1)
O(34)–Se(3)–O(32)	108.2(1)
O(31)–Se(3)–O(32)	105.9(1)
Se(1)–O(11)	1.642(2)
Se(1)–O(12)	1.641(2)
Se(1)–O(13)	1.643(2)
Se(1)–O(14)	1.636(2)
Se(2)–O(21)	1.715(2)
Se(2)–O(22)	1.629(2)
Se(2)–O(23)	1.625(2)
Se(2)–O(24)	1.619(2)
Se(3)–O(31)	1.637(2)
Se(3)–O(32)	1.720(2)
Se(3)–O(33)	1.612(2)
Se(3)–O(34)	1.614(2)
O(14)–Se(1)–O(12)	110.4(1)
O(14)–Se(1)–O(11)	109.9(1)
O(12)–Se(1)–O(11)	109.8(1)
O(14)–Se(1)–O(13)	111.3(1)
O(12)–Se(1)–O(13)	107.4(1)
O(11)–Se(1)–O(13)	107.9(1)
O(24)–Se(2)–O(23)	116.4(1)
O(24)–Se(2)–O(22)	110.9(1)
O(23)–Se(2)–O(22)	111.9(1)
O(24)–Se(2)–O(21)	106.4(1)
O(23)–Se(2)–O(21)	102.73(9)
O(22)–Se(2)–O(21)	107.6(1)
O(33)–Se(3)–O(34)	114.4(1)
O(33)–Se(3)–O(31)	112.7(1)
O(34)–Se(3)–O(31)	110.7(1)
O(33)–Se(3)–O(32)	103.76(9)
O(34)–Se(3)–O(32)	108.15(9)
O(31)–Se(3)–O(32)	106.5(1)

D–H...A	Hydrogen Bonds			
	d(D–H)	d(H...A)	d(D...A)	<(DHA)
(a) (NH ₄) ₄ H ₂ (SeO ₄) ₃				
295 K				
O(21 ⁱ)–H(1 ⁱ)...O(13)	0.69(4)	1.87(5)	2.553(5)	177(4)
O(32)–H(2)...O(11)	0.70(4)	1.86(4)	2.562(5)	172(4)
N(4)–H(43)...O(22 ⁱⁱ)	0.756(14)	2.287(16)	3.014(5)	162(3)
140 K				
O(21 ⁱ)–H(1 ⁱ)...O(13)	0.81(5)	1.76(5)	2.559(4)	166(6)
O(32)–H(2)...O(11)	0.87(5)	1.71(5)	2.563(4)	168(5)
N(4)–H(43)...O(22 ⁱⁱ)	0.82(2)	2.09(2)	2.906(4)	174(3)
(b) (ND ₄) ₄ D ₂ (SeO ₄) ₃				
255 K				
O(21 ⁱ)–H(1 ⁱ)...O(13)	0.61(3)	1.96(3)	2.568(3)	172(3)
O(32)–H(2)...O(11)	0.67(4)	1.91(4)	2.575(3)	170(4)
N(4)–H(43)...O(22 ⁱⁱ)	0.86(1)	2.12(1)	2.982(3)	177(2)
135 K				
O(21 ⁱ)–H(1 ⁱ)...O(13)	0.76(3)	1.80(3)	2.562(3)	177(4)
O(32)–H(2)...O(11)	0.73(4)	1.85(4)	2.574(3)	169(5)
N(4)–H(43)...O(22 ⁱⁱ)	0.84(1)	2.07(1)	2.906(3)	175(2)

TABLE 3—Continued

Torsion Angles in Trimer			
(a) (NH ₄) ₄ H ₂ (SeO ₄) ₃ 295 K	(b) (ND ₄) ₄ D ₂ (SeO ₄) ₃ 255 K		
Se(1)–O(13)–O(21 ⁱ)–Se(2 ⁱ)	–83.6(1)	Se(1)–O(13)–O(21 ⁱ)–Se(2 ⁱ)	–82.9(1)
Se(3)–O(32)–O(11)–Se(1)	–141.6(2)	Se(3)–O(32)–O(11)–Se(1)	–142.8(2)
140 K			
135 K			
Se(1)–O(13)–O(21 ⁱ)–Se(2 ⁱ)	–81.0(1)	Se(1)–O(13)–O(21 ⁱ)–Se(2 ⁱ)	–81.3(1)
Se(3)–O(32)–O(11)–Se(1)	–144.7(1)	Se(3)–O(32)–O(11)–Se(1)	–144.3(1)

Symmetry codes: (i) 1 – x, 1 – y, 1 – z; (ii) – x, – y, – z; (iii) x, y, 1 + z; (iv) 1 + x, y, z; (v) – x, 1 – y, – z.

isotropic displacement parameters for hydrogen atoms are presented in Table 2, and selected bond lengths and angles are given in Table 3.

The differences between charge-density functions of the donor and acceptor oxygen atoms at a hydrogen bond manifest themselves in the structural dimensions of the donor and acceptor groups (14, 15)—in this case, the SeO₄ tetrahedra. The lengths of bonds Se(2)–O(21) and Se(3)–O(32), where O(21) and O(32) are donor oxygen atoms O_d involved in the short O...O hydrogen bonds, are both at low and high temperature considerably greater than all the remaining Se–O distances (Table 3). In other words, Se(2)O₄ and Se(3)O₄ tetrahedra are clearly distorted whereas Se(1)O₄ remains close to regular. At low temperature Se–O_d bonds lengthen in both crystals. Nevertheless, none of the Se–O bonds undergoes any drastic changes in the studied temperature range. The observed isotopic effect is in agreement with the previous structural study results (7).

The crystals structure refinement at room temperature shows that SeO₄ tetrahedra in (NH₄)₄H₂(SeO₄)₃ are smaller than those in the deuterated analogue (10), in contrast to results presented in (7). The difference decreases considerably with temperature, down to ~140 K. The mutual reorientation of SeO₄ groups evidenced by torsion angles (Table 3) is negligible in both crystals in the range between room temperature and ~140 K.

Besides the short O...O hydrogen bonds, there is also in the crystals a N–H...O bond network. The lengths of these considerably weaker H bonds are between 2.8 Å and 3.1 Å. Upon lowering the temperature a tendency to the network contraction is observed and the most evident is N(4)–H(43)...O(22ⁱⁱ) bond shortening (Table 3). At low temperature, stronger N...O interactions can be related to restraint of NH₄ ion's rotation as was discussed in (10).

CONCLUSIONS

Our structural study results do not confirm that at low temperature the (NH₄)₄H₂(SeO₄)₃ crystal and its deuterated analogue change their symmetry from

centrosymmetric $P-1$ space group to the acentric $P1$ one. Raman study, dielectric measurements (10), and our latest DSC study (16) also do not evidence a phase transition at about 180 K in the $(\text{NH}_4)_4\text{H}_2(\text{SeO}_4)_3$ crystal. The observed structural changes—shortening of N–H(D)...O bonds, slowing down of NH_4^+ rotation and of SeO_4 groups vibrations, as well as changes of torsion angles between the selenate tetrahedra—are not drastic and can be realized also in the $P-1$ centrosymmetric space group. Thus, we do not find any crystallographic nor noncrystallographic evidence indicating disappearance of a center of symmetry below 180 K so one should describe the structures of both crystals in the space group with the higher symmetry.

The DSC measurements and full Raman and dielectric studies of deuterated crystals are in progress.

ACKNOWLEDGMENTS

This work was supported by Grant 2P03B 024 16 from the Committee of Scientific Research in Poland.

REFERENCES

1. L. Szczesniak, B. Hilczer, and A. Pawłowski, *Phase Transit.* **51**, 209 (1994).
2. Cz. Pawlaczyk, F. E. Salman, A. Pawłowski, Z. Czapla, and A. Pietraszko, *Phase Transit.* **8**, 9 (1986).
3. Cz. Pawlaczyk and A. Pawłowski, *Phys. Stat. Sol. (a)* **113**, 447 (1989).
4. M. Połomska, *J. Mol. Struct.* **404**, 181 (1997).
5. A. Kruglik and M. A. Simonov, *Kristallografiya* **22**, 1082 (1977).
6. B. Hilczer, M. Połomska, and A. Pawłowski, *Solid State Ionics* **125**, 163 (1999).
7. T. Fukami and R. H. Chen, *Phys. Stat. Sol. (b)* **214**, 219 (1999).
8. T. Fukami and R. H. Chen, *Solid State Commun.* **112**, 213 (1999).
9. T. Fukami, N. Higa, and R. H. Chen, *Acta Phys. Pol. A* **97**, 663 (2000).
10. A. Pawłowski, B. Hilczer, M. Połomska, and A. Haznar, *Solid State Ionics*, accepted.
11. J. Baran, M. K. Marchewka, M. Drozd, and Z. Czapla, *Polish J. Chem.* **72(2)**, 355 (1998).
12. S. G. Lushnikov, V. H. Schmidt, L. A. Shuvalov, and V. V. Dolbinina, *Solid State Commun.* **113**, 639 (2000).
13. R. E. Marsh, *Acta Crystallogr. B* **55**, 931 (1999).
14. A. Katrusiak, *Phys. Rev. B* **48**, 2992 (1993).
15. A. Katrusiak, *Phys. Rev. B* **51**, 589 (1995).
16. L. Szczesniak and A. Pawłowski, to be published.