CRYSTALLOGRAPHY

The crystal structure of a new natural tetramethylammonium aluminosilicate $[N(CH_3)_4][Si_2(Si_{0.5}Al_{0.5})O_6]_2$

E. V. Sokolova, V. B. Rybakov, and L. A. Pautov

M. V. Lomonosov Moscow State University; Mineralogical Museum, Il'men' State Reserve

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In a study of specimens from the collection of S. Tsaregorodtsev, kept in the Mineralogical Museum of the Il'men' State Reserve, attention was drawn to a mineral from the metamorphic rocks of the Northern Urals (Man'-Khambo region), which was recorded as sodalite. The physical properties of this mineral and minerals of the sodalite group differ sharply, however. When the mineral is heated, it acquires a tarry-black color, and liberates a gas with the sharp odor of ammonia and hexamethylenetetramine. Microprobe analysis (Camebax Micro-Beam instrument, analyst K. I. Ignatenko, Institute of Geochemistry and Analytical Chemistry of the USSR Academy of Sciences) showed that only two elements are present: SiO_2 66.7, Al_2O_3 12.2 mass %, i.e., Si:Al = 5:1, in contrast to the ratio 1:1 in sodalite. The x-ray diffraction pattern of the mineral is closest to that of synthetic ammonium sodalite.[1] The unusual properties of the mineral: its optical properties (the refractive indices, weak anisotropy), the black color of the heating products, the chemical composition not characteristic of sodalite, the absence of typical absorption bands corresponding to the ammonium group in the IR spectrum, and its insolubility in acids, including hydrofluoric acid, stimulated its further study.

The x-ray diffraction study was carried out using a transparent pale-yellowish single crystal with linear dimensions 0.175 × 0.15 × 0.10 mm. The parameters of the orthorhombic unit cell of the mineral, found from 24 reflections in the range $15° \leq \theta \leq 16°$ on a CAD-4 diffractometer ($MoK\alpha$ radiation, graphite monochromator), are: $a = 8.984(3)$, $b = 8.937(2)$, $c = 8.927(2)$ Å, $V = 716.8(5)$ Å^3. The basic experimental material consisted of the intensities of 516 independent nonzero ($I \geq 2\sigma I$) reflections, obtained on the same diffractometer by $\theta/2\theta$ scanning of the profiles of the diffraction reflections (max $\sin\theta/\lambda = 0.703$ Å^{-1}). The recalculation of the intensities to $|F_{hkl}|$ and all the other calculations were carried out using the SDP set of programs. The absorption of radiation in the specimen was ignored because of the low value of $\mu r_{\max} = 0.12$. Analysis of the systematic absences in the set of intensities obtained showed unambiguously that an I translation was present. The similarity of all three unit cell parameters of the mineral to one another and also to the parameter $a = 8.87$ Å of the cubic cell of sodalite $Na_8Al_6O_{24}Cl_2$ (space group $P\bar{4}3n$), whose structure was determined by Pauling[2] in 1930 and later refined,[3] suggested that these minerals are structurally related. Initially, the structure was determined using the holohedral space group *Immm* by successive approximations of the three-dimensional electron density syntheses with intermediate refinement by the method of least squares (MLS); the calculation was started using two independent Si atoms and one Al atom with coordinates corresponding to the positions of the atoms of these kinds in the sodalite structure. The MLS refinement of the positional and thermal parameters of the Si, Al, and O atoms which form the tetrahedral environment of the cations, gave the low value $B_j = 0.8$ Å^2 for the Al atom compared with B_{ij} for the Si atoms, and suggested that this position is occupied by Si and Al atoms simultaneously. The subsequent refinement of the thermal corrections for the atoms using a mixed atomic scattering curve with the composition $(Si_{0.5}Al_{0.5})$ for the atom in the position x 0 1/2, where $x \approx 0.25$, led to equalization of their values. According to the microprobe analysis data, the ratio found is Si:Al = 5:1. The N atom is located at the $2a(000)$ site. A difference electron density synthesis at identical distances of about 1.5 Å from the N atom revealed 12 maxima forming a set of six tetrahedra around the N atom. These maxima were identified with C atoms. The slight scatter in the values of B_{ij} for the atoms of a given kind and the interatomic distances both in the cation tetrahedra and between the N and C atoms, howev-

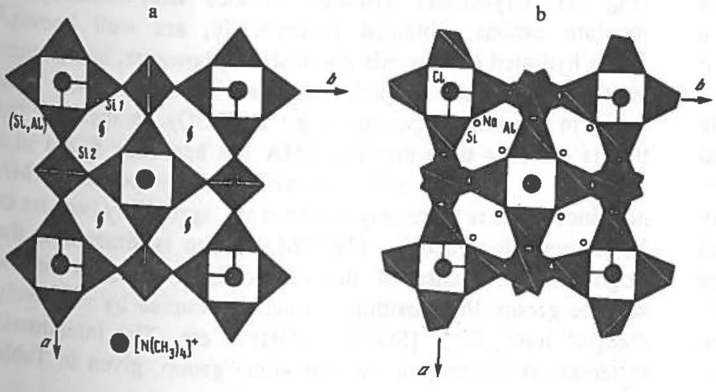

FIG. 1. The xy projection of the structures: TMA aluminosilicate (a) and sodalite (b).

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TABLE I. Coordinates and Isotropic Temperature Corrections for the Basis Atoms in the Structure of the New Natural Tetramethylammonium Aluminosilicate

Atom	*x*	*y*	*z*	B^{eq}, Å^2
Si1	0,000	0,2511 (2)	0,500	1,08 (2)
Si2	0,500	0,000	0,2491 (2)	1,05 (2)
($Si_{0,5}Al_{0,5}$)	0,2502 (1)	0,000	0,500	1,09 (2)
O1	−0,1463 (4)	0,1499 (5)	0,497 (3)	3,45 (9)
O2	0,1456 (4)	0,499 (2)	0,1491 (6)	3,8 (1)
O3	0,007 (2)	0,3540 (6)	0,3531 (6)	3,9 (1)
N	0,000	0,000	0,000	1,8 (1)
C1*	0,384 (3)	0,373 (3)	0,501 (1)	3,8 (5)
C2*	0,381 (3)	0,507 (1)	0,374 (3)	4,8 (5)
C3*	0,001 (1)	0,117 (4)	0,121 (4)	4,9 (6)

*The C atoms occupy their positions statistically to the extent of 1/3.

TABLE II. Interatomic Distances (Å) in the Structure of the New Natural Tetramethylammonium Aluminosilicate

Si1-tetrahedron		Si2-tetrahedron		($Si_{0.5}Al_{0.5}$)-tetrahedron	
Si1−O1	1,596(4) × 2	Si2−O2	1,593(4) × 2	($Si_{0,5}Al_{0,5}$)−O1	1,633(4) × 2
Si1−O3	1,603(5) × 2	Si2−O3	1,593(5) × 2	−O2	1,627(5) × 2
$(Si1-O)_{av}$	1,600	$(Si2-O)_{av}$	1,593	$[(Si_{0,5}Al_{0,5})-O]_{av}$	1,630
$(O-O)_{av}$	2,629	$(O-O)_{av}$	2,617	$(O-O)_{av}$	2,656
		$[N(CH_3)_4]^+$ group			
		N–C1	1,54(2)		
		N–C2	1,55(3)		
		N–C3	1,51(3)		
		$(N-C)_{cp}$	1,53		
		$(C-C)_{cp}$	2,49		

er, made it necessary to lower the symmetry and to continue the refinement of the structure using the hemisymmorphic space group *I*222. The coordinates and thermal corrections of the atoms were refined by the MLS in the full-matrix anisotropic (isotropic for the C atoms) approximation with allowance for absorption using the program DIFABS, included in the SDP set, as far as $R_{1hkl} = 0.047$, $R_{whkl} = 0.048$. Under the condition that each of the three independent carbon atoms occupies its own eightfold position statistically to the extent of 1/3, one of six possible sites of the tetrahedra is realized. The tetrahedral arrangement of the carbon atoms around the central N atom suggested that the structure contains the tetramethylammonium (TMA) ion $[N(CH_3)_4]^+$. This is confirmed indirectly by the previously described physical properties of the mineral. The structural formula of the TMA aluminosilicate TMA $[N(CH_3)_4][Si_2(Si_{0.5}Al_{0.5})O_6]_2$, space group *I*222, $Z = 2$, $d_{calc} = 2.01$, $d_{exp} = 2.02 \pm 0.01$ g· cm^{-3}, corresponds to the coordinates of the atoms of the structure and the interatomic distances given in Tables I[1)] and II.

The projection of the structure of TMA aluminosilicate along the *c* axis is shown in Fig. 1a. The two types of silicon tetrahedra and the mixed silicon−aluminum tetrahedron form a three-dimensional framework with the composition $[Si_2(Si_{0.5}\cdot Al_{0.5})O_6]^{0.5-}$. An Si−Al−O-framework with a similar structure is formed in the structure of sodalite (Fig. 1b), where the ratio Si:Al = 1:1, in contrast to the ratio 5:1 in the mineral being studied. In the structure being considered the arrangement of the cation tetrahedra relative to one another is slightly different from that in the sodalite structure, while the common structural pattern is preserved. The distribution of the cations of different kinds in the tetrahedral positions of the framework destroys its apparent cubic symmetry. The distances between the O atoms in the tetrahedra vary in the range 2.562-2.674 Å. The $(Si_{0.5}Al_{0.5})-O$ distances are slightly greater than the Si_1, Si_2-O distances (Table II).

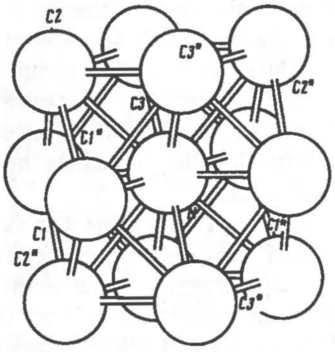

FIG. 2. General view of the $[N(CH_3)_4]^+$ group. The C atoms multiplied by the symmetry elements are marked with asterisks.

As counter-ions to the charged Si−Al−O-framework there are two $[N(CH_3)_4]^+$ groups per unit cell of the mineral (Fig. 2). Crystalline hydrated silicates with tetraalkylammonium cations, obtained synthetically, are well known.[4] These hydrated compounds are unstable, however, and decompose rapidly in air. Organic fragments have previously been found in natural compounds, e.g., $C_6(COO)_6$ in mellite,[5] but this is the first time that the TMA ion has been found in a mineral. In contrast with the synthetic compounds, TMA aluminosilicate is extremely stable in air, apparently because of its framework structure. The TMA group is situated at the origin of coordinates of the unit cell; in minerals of the sodalite group, this position is usually occupied by negatively charged ions: Cl$^-$, $[SO_4]^{2-}$, $(OH)^-$, etc. The interatomic distances in the tetramethylammonium group, given in Table

II, are in good agreement with published data for synthetic compounds. The statistical arrangement of the carbon atoms gives two tetrahedra in the unit cell of the mineral. The values of the distances from the C atoms of the TMA group to the O atoms (C1−O1 = 2.92(3), C2−O2 = 2.92(3), C3−O3 = 2.96(4) Å) indicate that the structure may contain a system of hydrogen bonds between the tetramethylammonium ion and the oxygen atoms.

The structural data obtained make it possible to distinguish the aluminum−silicon−oxygen framework as the basic element of the structure. The chemical and physical properties of the mineral differ from those of classical silicates, in which the cations are metal ions. In TMa aluminosilicate the interaction between the framework and the polyatomic cation is weakened and apparently involves a system of hydrogen bonds.

1)The values of the anisotropic thermal corrections for the atoms of the structure can be obtained from the authors of the present paper.

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[1] *ASTM* 14-17.

[2] L. Pauling, *Z. Krist.* **74,** 213 (1930).

[3] J. Von Lõns and H. Schulz, *Acta Cryst.* **23,** 434 (1967).

[4] Yu. F. Shepelev, "The crystal chemistry of silicates with complex cations and structural aspects of physicochemical processes in zeolites," *Author's Abstract of Doctoral Thesis* [in Russian], Leningrad (190).

[5] C. Giacovazzo, S. Menchetti, and F. Scordari, *Acta Cryst.* **B29,** 26 (1973).

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