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# LETTERS TO THE EDITOR

## The Synthesis and Structure of $(NH_4)_3(C_4H_9)_2NH_2SiMo_{12}O_{40} \cdot 2H_2O$

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A novel crystal, $(NH_4)_3(C_4H_9)_2NH_2SiMo_{12}O_{40} \cdot 2H_2O$, was synthesized by the sol–gel hydrothermal method. Single crystal X-ray diffraction shows that it is a novel compound with a framework structure. It crystallizes in the space group *Pnma* (orthorhombic), with $a = 13.712(7)$, $b = 15.384(7)$, $c = 20.230(5)$ Å, $V = 4269.8$ Å$^3$, $Z = 4$. The final discrepancy factor was $R = 0.041$, $R_w = 0.050$. The crystal consists of the heteropolyanion $SiMo_{12}O_{40}^{4-}$, $NH_4^+$, $(C_4H_9)_2NH_2^+$, and $H_2O$ molecules. The heteropolyanion $SiMo_{12}O_{40}^{4-}$ is an independent unit, assumed to have the Keggin structure. $SiMo_{12}O_{40}^{4-}$ forms a net in three dimensions conforming to the symmetry of the crystal; the cations $NH_4^+$ and $(C_4H_9)_2NH_2^+$ and the neutral $H_2O$ molecules are situated in the open spaces of the net structure. The structure is held together by $SiMo_{12}O_{40}^{4-}$, $NH_4^+$, $(C_4H_9)_2NH_2^+$, and $H_2O$ by electrostatic forces and hydrogen bonding. The Mo–O distance varies between 1.6 and 2.4 Å. 

### Introduction

The sol–gel method has been of interest as a novel synthetic technique (*1, 2*). It has many unique features when used in the synthesis of inorganic materials (*3, 4*). In an effort to identify new materials with interesting properties, we have recently employed the sol–gel hydrothermal synthesis techniques to produce oxide lattices containing both octahedral and tetrahedral sites. We report here the first example of a sol–gel hydrothermal synthesis product based on the ternary group (Si–Mo), which involves a new framework compound, $(NH_4)_3(C_4H_9)_2NH_2SiMo_{12}O_{40} \cdot 2H_2O$, made up of the heteropolyanion $SiMo_{12}O_{40}^{4-}$, the cations $NH_4^+$ and $(C_4H_9)_2NH_2^+$, and neutral $H_2O$ molecules.

### Synthesis

The mixture(I) of $(C_2H_5)_4SiO_4$ (229.99 ml), $H_2O$ (1639.7 ml), and $NH_3$ $H_2O$ (743.8 ml) was stirred for 6 hr in order to hydrolyze $(C_2H_5)_4SiO_4$ in the alkali medium. Then ammonium dimolybdate (176.55 g) was added

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TABLE I

ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS

| Atom | X | Y | Z | $U_{eq}$ |
|---|---|---|---|---|
| Mo(1) | 0.6052(1) | 0.3646(1) | 0.3396(9) | 1.27(3) |
| Mo(2) | 0.9333(1) | 0.3639(1) | 0.4500(9) | 1.39(3) |
| Mo(3) | 0.7074(1) | 0.4826(1) | 0.4795(1) | 1.49(3) |
| Mo(4) | 0.8369(2) | 0.250 | 0.3226(1) | 1.17(5) |
| Mo(5) | 0.5730(1) | 0.1295(1) | 0.5890(9) | 1.67(3) |
| Mo(6) | 0.8147(1) | 0.3686(1) | 0.6111(9) | 1.64(3) |
| Mo(7) | 0.4618(2) | 0.250 | 0.4425(1) | 1.47(5) |
| Si(1) | 0.7136(6) | 0.250 | 0.4754(4) | 1.1 (1) |
| O (11) | 0.4786(9) | 0.3382(9) | 0.3775(7) | 1.3 (3) |
| O (12) | 0.735 (1) | 0.3363(9) | 0.3202(7) | 1.5 (3) |
| O (13) | 0.574 (1) | 0.250 | 0.2855(9) | 1.1 (4) |
| O (14) | 0.574 (1) | 0.431 (1) | 0.2782(7) | 2.1 (3) |
| O (15) | 0.6391(9) | 0.4417(9) | 0.4069(7) | 1.6 (3) |
| O (21) | 0.829 (1) | 0.4422(9) | 0.4430(8) | 1.8 (3) |
| O (22) | 1.000 | 0.250 | 0.458 (1) | 1.7 (4) |
| O (23) | 0.9253(9) | 0.1621(9) | 0.3570(7) | 1.3 (3) |
| O (24) | 0.9071(9) | 0.3543(9) | 0.5427(6) | 1.3 (3) |
| O (25) | 1.301 (1) | 0.4287(9) | 0.4490(8) | 1.9 (3) |
| O (31) | 0.715 (1) | 0.5884(9) | 0.4638(8) | 2.0 (3) |
| O (41) | 0.875 (1) | 0.250 | 0.245 (1) | 1.8 (4) |
| O (51) | 0.687 (1) | 0.1118(9) | 0.6425(6) | 1.4 (3) |
| O (52) | 0.6031(9) | 0.4763(9) | 0.5405(7) | 1.7 (3) |
| O (53) | 0.572 (1) | 0.250 | 0.608 (1) | 2.0 (4) |
| O (54) | 0.495 (1) | 0.162 (1) | 0.5091(7) | 2.0 (3) |
| O (55) | 0.487 (1) | 0.090 (1) | 0.6394(8) | 2.6 (4) |
| O (62) | 0.794 (1) | 0.4917(9) | 0.5668(7) | 1.6 (3) |
| O (63) | 0.881 (1) | 0.409 (1) | 0.6719(9) | 3.0 (4) |
| O (64) | 0.815 (1) | 0.250 | 0.631 (1) | 1.2 (4) |
| O (71) | 0.342 (2) | 0.250 | 0.445 (1) | 2.7 (5) |
| O (10) | 0.628 (2) | 0.250 | 0.418 (1) | 2.1 (5) |
| O (20) | 0.705 (1) | 0.3373(8) | 0.5208(7) | 1.3 (3) |
| O (30) | 0.822 (1) | 0.250 | 0.438 (1) | 1.6 (4) |
| O (1) | 0.659 (2) | 0.250 | 0.160 (1) | 2.9 (5) |
| O (2) | 0.330 (2) | 0.750 | 0.039 (1) | 5.5 (8) |
| O (3) | 0.665 (4) | 0.750 | 0.315 (3) | 12 (2) |
| N | 0.292 (2) | 0.401 (1) | 0.333 (1) | 3.4 (5) |
| N (1) | 0.370 (5) | 0.750 | 0.227 (2) | 10 (2) |
| C (1) | 0.326 (4) | 0.682 (3) | 0.194 (2) | 15 (2) |
| C (2) | 0.395 (3) | 0.626 (4) | 0.152 (3) | 14 (2) |
| C (3) | 0.397 (3) | 0.530 (4) | 0.179 (2) | 15 (2) |
| C (4) | 0.319 (3) | 0.497 (2) | 0.216 (2) | 8 (1) |

into the mixture(I) to produce the mixture(II). When stirred, the sol–gelization was achieved in the mixture(II). After stirring 40 min diethylaminoethanol (186.77 ml) and dibutylamine (12.9 ml) were added. The product, called mixture(III), was stirred 3 hr, and HCl (0.1 *N*) was then added. The mixture(III) changed to yellowish; the pH value of the mixture(III) was approximately 3. The mixture(III) was contained in a stainless steel autoclave lined with polytetrafluoroethylene under autogenous pressure at 80°C for 2 days, and at 150°C for 7 days. The crystalline product was filtered, washed with distilled water, and dried at ambient temperature. Excellent single crystal suitable for structural analysis by X-ray diffraction could be readily selected.

## Determination of the Structure

A brown and transparent crystal was mounted in an Enraf–Nonius CAD 4 computer automatized four-circle diffractometer. The lattice constants at 296 K were measured with Mo$K\alpha$ ($\lambda$ = 0.71069 Å, graphite monochromator) on the basis of $\alpha_1$ automatically centered reflections: indexing was based on an orthorhombic system, with $a$ = 13.712(7), $b$ = 15.384(7), $c$ = 20.230(5) Å, $V$ = 4269.8 Å$^3$. Intensities were collected by means of the $2\theta$ scan technique in the range of $4° \leq 2\theta \leq 50°$. A total of 3862 reflec-

TABLE II

BOND DISTANCES (IN Å)

| | | | |
|---|---|---|---|
| Mo(1)–O(11) | 1.941(4) | Mo(5)–O(52) | 1.945(5) |
| Mo(1)–O(12) | 1.870(4) | Mo(5)–O(53) | 1.894(2) |
| Mo(1)–O(13) | 2.119(3) | Mo(5)–O(54) | 2.001(5) |
| Mo(1)–O(14) | 1.660(5) | Mo(5)–O(55) | 1.667(5) |
| Mo(1)–O(15) | 1.864(5) | Mo(5)–O(20) | 2.329(5) |
| Mo(1)–O(10) | 2.398(5) | Mo(6)–O(24) | 1.889(4) |
| Mo(2)–O(21) | 1.880(5) | Mo(6)–O(51) | 1.890(4) |
| Mo(2)–O(22) | 1.984(1) | Mo(6)–O(62) | 2.114(5) |
| Mo(2)–O(23) | 1.927(4) | Mo(6)–O(63) | 1.651(5) |
| Mo(2)–O(24) | 1.914(4) | Mo(6)–O(64) | 1.866(2) |
| Mo(2)–O(25) | 1.664(4) | Mo(6)–O(20) | 2.417(4) |
| Mo(2)–O(30) | 2.339(4) | Mo(7)–O(11) | 1.903(5) |
| Mo(3)–O(15) | 1.853(5) | Mo(7)–O(54) | 1.961(5) |
| Mo(3)–O(21) | 1.921(5) | Mo(7)–O(71) | 1.649(7) |
| Mo(3)–O(31) | 1.662(4) | Mo(7)–O(10) | 2.333(7) |
| Mo(3)–O(52) | 1.891(4) | Si(1)–O(10) | 1.643(4) |
| Mo(3)–O(62) | 2.131(4) | Si(1)–O(20) | 1.631(4) |
| Mo(3)–O(20) | 2.387(4) | Si(1)–O(30) | 1.665(7) |
| Mo(4)–O(12) | 1.931(4) | N(1)–C(1) | 1.39(2) |
| Mo(4)–O(23) | 1.944(4) | C(1)–C(2) | 1.54(2) |
| Mo(4)–O(41) | 1.656(8) | C(2)–C(3) | 1.58(2) |
| Mo(4)–O(30) | 2.344(7) | C(3)–C(4) | 1.39(4) |
| Mo(5)–O(51) | 1.919(4) | | |

TABLE III

BOND ANGLE (in degrees)

| | | | |
|---|---|---|---|
| O(11)–Mo(1)–O(12) | 152.1(2) | O(11)–Mo(1)–O(13) | 81.3(2) |
| O(11)–Mo(1)–O(14) | 101.2(2) | O(11)–Mo(1)–O(15) | 93.9(2) |
| O(11)–Mo(1)–O(10) | 72.6(2) | O(12)–Mo(1)–O(13) | 83.8(2) |
| O(12)–Mo(1)–O(14) | 103.2(2) | O(12)–Mo(1)–O(15) | 93.7(2) |
| O(12)–Mo(1)–O(10) | 81.0(2) | O(13)–Mo(1)–O(14) | 94.0(2) |
| O(13)–Mo(1)–O(15) | 163.2(2) | O(13)–Mo(1)–O(10) | 76.1(2) |
| O(14)–Mo(1)–O(15) | 102.8(2) | O(14)–Mo(1)–O(10) | 168.8(2) |
| O(15)–Mo(1)–O(10) | 87.1(2) | O(21)–Mo(2)–O(22) | 157.6(1) |
| O(21)–Mo(2)–O(23) | 90.9(2) | O(21)–Mo(2)–O(24) | 88.9(2) |
| O(21)–Mo(2)–O(25) | 103.2(2) | O(21)–Mo(2)–O(30) | 88.4(2) |
| O(22)–Mo(2)–O(23) | 85.5(2) | O(22)–Mo(2)–O(24) | 86.5(2) |
| O(22)–Mo(2)–O(25) | 99.3(2) | O(22)–Mo(2)–O(30) | 69.4(1) |
| O(23)–Mo(2)–O(24) | 158.3(2) | O(23)–Mo(2)–O(25) | 99.1(2) |
| O(23)–Mo(2)–O(30) | 72.9(2) | O(24)–Mo(2)–O(25) | 102.0(2) |
| O(24)–Mo(2)–O(30) | 85.4(2) | O(25)–Mo(2)–O(30) | 166.2(2) |
| O(15)–Mo(3)–O(21) | 91.3(2) | O(15)–Mo(3)–O(31) | 102.4(2) |
| O(15)–Mo(3)–O(52) | 96.8(2) | O(15)–Mo(3)–O(62) | 163.9(2) |
| O(15)–Mo(3)–O(20) | 97.2(2) | O(21)–Mo(3)–O(31) | 100.7(2) |
| O(21)–Mo(3)–O(52) | 152.6(2) | O(21)–Mo(3)–O(62) | 81.9(2) |
| O(21)–Mo(3)–O(20) | 81.1(2) | O(31)–Mo(3)–O(52) | 103.0(2) |
| O(31)–Mo(3)–O(62) | 93.3(2) | O(31)–Mo(3)–O(20) | 170.1(2) |
| O(52)–Mo(3)–O(62) | 83.3(2) | O(52)–MO(3)–O(20) | 73.2(2) |
| O(62)–Mo(3)–O(20) | 77.3(2) | O(12)–Mo(4)–O(12) | 86.9(3) |
| O(12)–Mo(4)–O(23) | 160.0(2) | O(12)–Mo(4)–O(23) | 160.0(2) |
| O(12)–Mo(4)–O(41) | 101.9(2) | O(12)–Mo(4)–O(30) | 87.8(2) |
| O(12)–Mo(4)–O(23) | 89.0(2) | O(12)–Mo(4)–O(30) | 87.8(2) |
| O(23)–Mo(4)–O(23) | 88.1(3) | O(23)–Mo(4)–O(41) | 98.1(2) |
| O(23)–Mo(4)–O(30) | 72.5(2) | O(41)–Mo(4)–O(30) | 166.5(3) |
| O(51)–Mo(5)–O(52) | 89.6(2) | O(51)–Mo(5)–O(53) | 91.8(3) |
| O(51)–Mo(5)–O(54) | 157.7(2) | O(51)–Mo(5)–O(55) | 100.1(2) |
| O(51)–Mo(5)–O(20) | 74.6(2) | O(52)–Mo(5)–O(53) | 157.5(2) |
| O(52)–Mo(5)–O(54) | 85.2(2) | O(52)–Mo(5)–O(55) | 98.9(2) |
| O(52)–Mo(5)–O(20) | 73.7(2) | O(53)–Mo(5)–O(54) | 85.0(3) |
| O(53)–Mo(5)–O(55) | 102.9(3) | O(53)–Mo(5)–O(20) | 85.0(2) |
| O(54)–Mo(5)–O(55) | 102.1(2) | O(54)–Mo(5)–O(20) | 83.1(2) |
| O(55)–Mo(5)–O(20) | 170.8(2) | O(24)–Mo(6)–O(51) | 152.6(2) |
| O(24)–Mo(6)–O(62) | 83.4(2) | O(24)–Mo(6)–O(63) | 102.7(2) |
| O(24)–Mo(6)–O(64) | 92.3(2) | O(24)–Mo(6)–O(20) | 80.9(2) |
| O(51)–Mo(6)–O(62) | 82.8(2) | O(51)–Mo(6)–O(63) | 101.6(2) |
| O(51)–Mo(6)–O(64) | 95.0(2) | O(51)–Mo(6)–O(20) | 73.0(2) |
| O(62)–Mo(6)–O(63) | 93.1(2) | O(62)–Mo(6)–O(64) | 164.8(2) |
| O(62)–Mo(6)–O(20) | 76.9(2) | O(63)–Mo(6)–O(64) | 102.1(3) |
| O(63)–Mo(6)–O(20) | 169.0(2) | O(64)–Mo(6)–O(20) | 83.0(2) |
| O(11)–Mo(7)–O(11) | 90.9(3) | O(11)–Mo(7)–O(54) | 159.5(2) |
| O(11)–Mo(7)–O(54) | 87.5(2) | O(11)–Mo(7)–O(71) | 98.1(2) |
| O(11)–Mo(7)–O(10) | 74.8(2) | O(11)–Mo(7)–O(54) | 87.5(2) |
| O(11)–Mo(7)–O(54) | 159.5(2) | O(11)–Mo(7)–O(71) | 98.1(2) |
| O(54)–Mo(7)–O(54) | 86.9(3) | O(54)–Mo(7)–O(71) | 102.3(2) |
| O(54)–Mo(7)–O(10) | 85.1(2) | O(71)–Mo(7)–O(10) | 169.7(3) |
| O(10)–Si(1)–O(20) | 110.0(2) | O(10)–Si(1)–O(30) | 108.4(2) |
| O(20)–Si(1)–O(20) | 110.8(2) | O(20)–Si(1)–O(30) | 108.8(2) |
| Mo(1)–O(11)–Mo(7) | 122.0(2) | Mo(1)–O(12)–Mo(4) | 147.5(2) |
| Mo(1)–O(13)–Mo(1) | 112.5(3) | Mo(1)–O(15)–Mo(3) | 157.1(3) |
| Mo(2)–O(21)–Mo(3) | 147.0(3) | Mo(2)–O(22)–Mo(2) | 124.2(7) |
| Mo(2)–O(23)–Mo(4) | 122.0(2) | Mo(2)–O(24)–Mo(6) | 146.5(2) |
| Mo(5)–O(51)–Mo(6) | 122.8(2) | Mo(3)–O(52)–Mo(5) | 122.2(2) |
| Mo(5)–O(53)–Mo(5) | 156.4(4) | Mo(5)–O(54)–Mo(7) | 148.5(3) |
| Mo(3)–O(62)–Mo(6) | 111.6(2) | Mo(6)–O(64)–Mo(6) | 155.6(4) |
| Mo(1)–O(10)–Mo(1) | 94.6(2) | Mo(1)–O(10)–Mo(7) | 90.6(2) |
| Mo(1)–O(10)–Si(1) | 124.1(2) | Mo(7)–O(10)–Si(1) | 123.4(4) |
| Mo(3)–O(20)–Mo(5) | 90.8(2) | Mo(3)–O(20)–Mo(6) | 93.9(1) |
| Mo(3)–O(20)–Si(1) | 124.9(3) | Mo(5)–O(20)–Mo(6) | 89.6(2) |
| Mo(5)–O(20)–Si(1) | 124.9(2) | Mo(6)–O(20)–Si(1) | 122.9(2) |
| Mo(2)–O(30)–Mo(2) | 97.1(2) | Mo(2)–O(30)–Mo(4) | 92.6(2) |
| Mo(2)–O(30)–Si(1) | 122.4(2) | Mo(4)–O(30)–Si(1) | 122.1(4) |

TABLE III—*Continued*

| | | | |
|---|---|---|---|
| C(1)–N(1)–C(1) | 98.2(2) | N(1)–C(1)–C(2) | 115.0(2) |
| C(1)–C(2)–C(3) | 124.1(2) | C(1)–C(2)–C(3) | 110.2(2) |
| C(2)–C(3)–C(4) | 121.0(2) | | |

tions were measured, of which 3409 with $|F| > 4.0\ \sigma\ |F|$ were considered unique and used for structure refinements. The data were reduced by applying *LP*, *K* (overall scale), and *B* (overall isotropic temperature) factors. We determined the absolute intensities and found that the space group is *Pnma*.

The positions of the atoms in an asymmetric unit were determined by Patterson and Fourier methods. Cascade matrix block-diagonal least-squares refinements of position coordinates and anisotropic thermal parameters of all nonhydrogen atoms yielded the final values $R = 0.041$ and $R_w = 0.050$, respectively.

## Description of the Structure and Discussion

The nonhydrogen atomic coordinates and equivalent thermal parameters $U_{eq}$, interatomic distances, and angles are listed in Tables I, II, and III, respectively.

The crystal structure consists of the heteropolyanion $SiMo_{12}O_{40}^{4-}$, of the cations $NH_4^+$ and $(C_4H_9)_2NH_2^+$, and of neutral $H_2O$ molecules. The heteropolyanion $SiMo_{12}O_{40}^{4-}$ is an independent unit, assumed to have a Keggin structure (*5*). Based on the symmetry of the space group, $SiMo_{12}O_{40}^{4-}$ forms a three-dimensional framework and $NH_4^+$, $(C_4H_9)_2NH_2^+$, and $H_2O$ are positioned in the interstices of the framework structure.

The perspective drawing of the $SiMo_{12}O_{40}^{4-}$ structure is shown in Fig. 1. $SiMo_{12}O_{40}^{4-}$ contains a symmetry plane of the crystallographic structure. Si, Mo(4), and Mo(7) are in this plane. The $SiO_4$ tetrahedron is at the center of the anion. In this anion, three $MoO_6$ octahedrons are

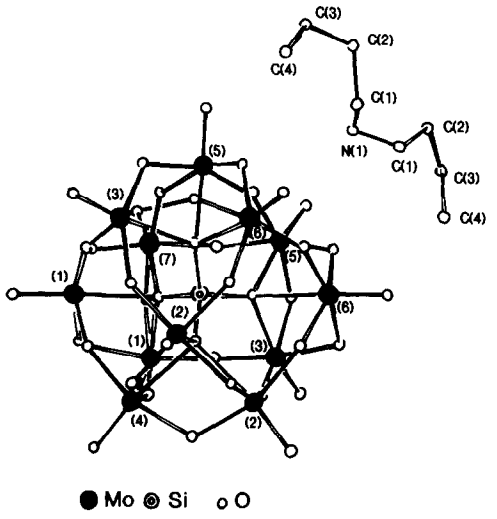


FIG. 1. Perspective drawing of the $SiMo_{12}O_{40}^{4-}$ structure.

linked together by sharing edges to form an $Mo_3O_{11}$ unit. The O atoms common to these three octahedra are also coordinated to the central Si atom. The four $Mo_3O_{11}$ groups are connected to each other by sharing corners. The Mo–Mo distance within the $Mo_3O_{11}$ group is 3.49–3.523 Å, and the distance between Mo atoms of different $Mo_3O_{11}$ units is longer than 3.6 Å. In ordered Keggin structures, the corresponding values are of the order of 3.4 and 3.7 Å, respectively (*6*). The Mo–Si distance is also very similar to the Mo–Mo distances of different $Mo_3O_{11}$ units (3.55 Å).

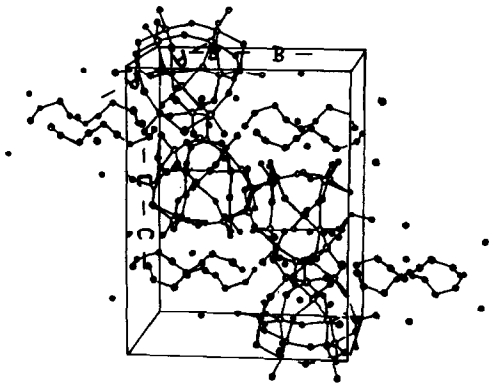


FIG. 2. The structure of the unit cell.

The Mo–O distances vary widely (from 1.6–2.4 Å). The shortest Mo–O distance is roughly 1.645–1.667 Å for the terminal oxygen atom. The longest Mo–O distance is nearly 2.4 Å for those oxygen atoms connected to either the Mo or the Si atom. The structure of tetrahedronal $SiO_4$ is normal (*7*). The Si–O distance is in the range 1.631–1.665 Å, and the O–Si–O angle differs by about 1° from that of the ideal tetrahedron.

The perspective drawing of the unit cell structure is shown in Fig. 2. Besides containing four heteropolyanions in the unit cell, there are four protonated dibutylamine cations $(C_4H_9)_2NH_2^+$, twelve $NH_4^+$ units, and eight $H_2O$ molecules. The structures of these cations or molecules are all normal. The protonated dibutylamines are located on the symmetry plane within the unit cell and are located in the interstices of the framework structure. The distances between the protonated dibutylamine and other atoms are not short of the normal van der Waals distance. The $NH_4^+$ in the structure is different from $(C_4H_9)_2NH_2^+$; these form hydrogen bonds with neighboring oxygen atoms. For example, the hydrogen atoms of $N(3)H_4^+$ form hydrogen bonds with O(1) (oxygen atom of water molecules), O(11), O(25), and O(62); the distance of the hydrogen bonds remains between 2.852 and 3.032 Å. As a result, the $NH_4^+$ cation of the structure is stable during heating.

## References


1. J. LIVAGE, M. HENRY, AND C. SANCHEZ, *Prog. Solid State Chem.* **18,** 259 (1988).
2. H. DISLICH, *Angew. Chem. Int. Ed. Engl.* **10,** 363 (1971).
3. B. J. J. ZELINSKI AND D. R. UHLMANN, *J. Phys. Chem. Solids* **45,** 1069 (1984).
4. G. W. SCHERER, *J. Non-Cryst. Solids* **87,** 199 (1986).
5. J. F. KEGGIN, *Proc. R. Soc. London Ser. A* **144,** 75 (1934).
6. R. STRANDBERG, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **33,** 3090 (1977).
7. A. F. WALLS, "Structural Inorganic Chemistry," 5th ed., Clarendon Press, London (1987).