CRYSTAL STRUCTURES AND MINERAL CHEMISTRY OF DOUBLE–SALT HYDRATES: II. THE CRYSTAL STRUCTURE OF MENDOZITE, $NaAl(SO_4)_2 \cdot 11H_2O$

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ABSTRACT

Mendozite [$NaAl(SO_4)_2 \cdot 11H_2O$] crystallizes in space group $C\ 2/c$ with $a = 21.75 \pm .03$, $b = 9.11 \pm 0.1$, $c = 8.30 \pm .01$ Å, $\beta = 92°28' \pm 5'$ and $Z = 4$. The structure was solved by a combination of the Patterson, Fourier, and symbolic addition methods. The final R–factor is 6.8% with individual anisotropic temperature factors. The principal structural units are: (1) corner–sharing, infinite $Na(O, H_2O)_6$ octahedral chains with two wing–like SO_4 tetrahedra attached to each octahedron, having the composition $[Na(H_2O)_3(SO_4)_2]^{3-}$, (2) independent $[Al(H_2O)_6]^{3+}$ octahedra, and (3) isolated water molecules, not bonded to any cations. The average $Na(O,Ow)$, $Al–Ow$, and $S–O$ distances are 2.408, 1.878, and 1.473 Å respectively.

The three known hydrates in the system $NaAl(SO_4)_2 \cdot nH_2O$ are soda alum ($n = 12$), mendozite ($n = 11$), and tamarugite ($n = 6$). The fact that soda alum dehydrates directly to tamarugite without giving rise to the intermediate mendozite phase is interpreted structurally as the consequence of the equal strengths of the $Na–Ow$ bonds in the alum structure. Thus the six water ligands of soda alum are lost simultaneously to form tamarugite. The mendozite $\rightarrow$ tamarugite transformation entails (1) the loss of structural water, and (2) the stripping away of coordination water around Na.

INTRODUCTION

In Paper I of this series (Robinson and Fang, 1969), we reported the crystal structure of tamarugite, the hexahydrate of sodium aluminum sulphate. This paper is concerned with the structure of mendozite, the undecahydrate. Early determination of this interesting structure, whose water content lies between that of soda alum and tamarugite, was rendered difficult because (1) it is rarely found in nature since it easily decomposes in air to tamarugite, (2) very little information on its synthesis was available before our note (Nordstrom, Robinson and Fang, 1969), and (3) the water content of the mineral was never unambiguously determined, due to lack of suitable single crystals.

The dehydration of soda alum proceeds directly to tamarugite, bypassing the intermediate hydrate, mendozite. Thus it was essential to determine the structure of this intermediate hydrate, so that the dehydration mechanism in the system $NaAl(SO_4)_2 \cdot nH_2O$ could be interpreted.

Experimental

A synthetically grown, nearly equant crystal of mendozite [NaAl(SO$_4$)$_2$·11H$_2$O], with mean dimension 0.25 mm., was selected for unit–cell parameter measurements and intensity collection. The following values were obtained: $a = 21.75 \pm .03$, $b = 9.11 \pm .01$, $c = 8.30 \pm .01$ Å, $\beta = 92°28' \pm 5'$ and $Z = 4$. The X-ray density of 1.781(5) g/cm^3 is in good agreement with the measured density of 1.765 g/cm^3 reported by Surganov (Palache *et al.*, 1951). Extinctions of the type $l \neq 2n$ for $h0l$ and $h + k \neq 2n$ for hkl indicated the space group of $C\ 2/c$ or Cc.

Three-dimensional intensity data were collected with an automated Buerger diffractometer (Weissenberg geometry) using Ni–filtered CuKα radiation. The reader is referred to Paper I of this series for detailed procedures. Toward the end of data collection, a tiny area in the central portion of the crystal became translucent. However, the bulk of the crystal remained transparent, and careful monitoring of the intensities of standard reflections gave no indication of change. Of the 1,554 spectra measured, 1,294 reflections were retained as "observed."

Determination and Refinement of the Structure

This seemingly simple structure defied every attempt at solution for a period of several years. Although there were many times when the work on this mineral was put aside, it was a record length of time in our experience.

Initially, we tried the symbolic addition procedure which has given us many rapid solutions of other structures. The normalized structure factor statistics (Table 1) indicated the centrosymmetric space group $C\ 2/c$. Despite numerous attempts in which everything conceivable was tried, including the use of the K–curve (Karle and Hauptman, 1953), the structure remained unsolved. Reminded that no single method was fool–proof, we tried other methods. It was hoped that the structure might be derived from that of soda alum by trial and error, but our attempts proved fruitless. The time–tested Patterson technique, coupled with the Fourier method, was then employed. Consequently we were able to unequivocally locate the position of the S atom and, in addition, to extract evidence of another "heavy" atom at either $4c$ or $4d$. However, we were able to no other atoms in subsequent Fourier maps.

Upon re-examination of the intensity distribution, it became obvious that the structure was far from "random" in that the reflections with *eeo* and *ooe* parities were very weak. This also strongly suggested the possibility of heavy atoms being located at equipoints $4c$ and/or $4d$. Structure factors were then calculated with S at $8f$, Al at $4c$ and Na at $4d$. Successive Fourier maps again failed to reveal additional atoms.

At this point the work on mendozite was set aside and the structures of other minerals, such as aenigmatite, kainite, and eudidymite, all of which contained elements of pseudo–symmetry, were solved by the symbolic addition procedure. The SORTE program of Bednowitz (1970) which permits manual intervention during the sign prediction procedure was used. Our expertise in the use of this versatile program was thus greatly increased, as was our confidence in our ability to solve any centrosymmetric structure by means of this method. Thus, we again tackled the mendozite structure.

The sign prediction process was manually initiated with the 30 largest E values. The list of known signs and symbols was then extended by use of SORTE. However, several passes through the computer were required, with considerable

TABLE 1. EXPERIMENTAL AND THEORETICAL VALUES OF
NORMALIZED STRUCTURE FACTORS

	EXP.	CENTRO.	NON-CENTRO.
$<|E|>$	.803	0.798	0.886
$<E^2-1>$	.973	0.968	0.736
$|E| \geq 3.0$	.00%	0.3%	0.01%
$|E| \geq 2.0$	5.1	5.0%	1.8%
$|E| \geq 1.0$	31.3	32.0%	37.0%

manual intervention between passes, in order to insure that sign prediction was proceeding normally. It is difficult to explain just what sort of manual intervention is required between passes since the action taken varies from pass to pass and from structure to structure. Suffice it to say that the manipulation of this program, when elements of pseudo–symmetry are present, is something of an art which can be learned only through experience. The resulting E–map, with 200 hkl's, revealed all atoms except $Ow(6)$, which was subsequently found by the difference Fourier method.

The least–squares calculations were performed with RFINE (Finger, 1969). The R–factor with all atoms included was 36.6 percent and decreased to 17.9 percent in four cycles, varying only the positional parameters. A difference map made at this time showed only background ripples. Another four cycles followed in which all positional and thermal parameters were varied, resulting in an R–factor of 10.4 percent. The last stage of the refinement included anisotropic temperature factors and an extinction correction parameter of $s = .6034 \times 10^{-4}$, where s is in the expression $F^2_{corr} = F^2_{unc}/(1 - sF^2_{unc})$. The final R–factor was 6.8 percent for 1269 reflections.

Table 2 lists the atomic coordinates and isotropic equivalent temperature factors. The observed and calculated structure factors appear in Table 6 which is on deposit.[1]

DESCRIPTION OF THE STRUCTURE

A polyhedral drawing of the structure of mendozite is shown in Figure 1. The dominant structural features are: (1) corner–sharing, infinite $Na(O,H_2O)_6$ octahedral chains with two wing–like sulphate tetrahedra attached to each octahedron, the chain composition being $[Na(H_2O)_3(SO_4)_2]_n^{3-}$, (2) isolated $[Al(H_2O)_6]^{3+}$ octahedra, which balance the charge of the Na chains, and (3) isolated water molecules not bonded directly to the cations. The three units are connected via hydrogen bonds. The good {100} cleavage and the indistinct {010}

cleavage break only hydrogen bonds whereas the {001} cleavage, also reported as indistinct, necessitates the breakage of the continuous Na chains and should therefore occur less frequently.

Selected interatomic distances and angles are given in Table 3. The SO_4 group exhibits the usual tetrahedral distances and angles. However, contrary to several other sulphates whose structures we have investigated, there is no lengthening of the S–O distance when an oxygen is also linked to another cation (the S–O(2) distance is not lengthened, although O(2) is also bonded to Na. The most probable explanation is that Na, unlike Fe^{3+}–containing minerals in which the lengthening is observed, possesses only a single charge and is thus unable to appreciably alter the covalent character of the S–O bond.

Coordination octahedra around Na atoms share corners through Ow(4) which is located at a special position on the 2–fold symmetry axis. The distortion of the Na octahedron is manifest in the interatomic angles which range from 79.4° to 100.6°. The $Al(H_2O)_6$ octahedron is regular with angles ranging from 89.0° to 91.0° and a mean cation–anion distance of 1.878 Å, almost identical to the values reported for soda alum and tamarugite. The Ow(6), which bonds to no cation, has six neighbouring O and H_2O within a 3.5 Å radius.

Although no attempt was made to locate hydrogen atoms, a possible hydrogen bonding scheme can be conjectured if the eleven protons can reasonably be assumed to lie somewhere between the partners of the 11 oxygen donor–acceptor pairs. Thus, if the sulphate oxygens

TABLE 2. POSITIONAL AND THERMAL PARAMETERS FOR MENDOZITE[a]

Atom	Equipoint	x	y	z	$B(Å^2)$[b]
Na	4a	0	0	0	2.05(6)
Al	4c	1/4	1/4	0	1.00(4)
S	8f	.1314(1)	.2532(1)	.5295(1)	1.22(4)
O(1)	8f	.1461(2)	.3955(3)	.6107(4)	1.82(7)
O(2)	8f	.0747(2)	.1926(4)	.5903(5)	2.56(8)
O(3)	8f	.1840(2)	.1544(4)	.5654(5)	2.49(8)
O(4)	8f	.1248(2)	.2758(4)	.3548(5)	2.40(8)
Ow(1)	8f	.2306(2)	.3024(4)	.2100(4)	1.87(7)
Ow(2)	8f	.1832(2)	.1231(3)	.9857(5)	1.86(7)
Ow(3)	8f	.1979(2)	.4037(3)	.9193(4)	1.58(6)
Ow(4)	4e	0	.1231(6)	1/4	2.99(12)
Ow(5)	8f	.0683(2)	.1864(4)	.9161(5)	2.25(7)
Ow(6)	8f	.0358(2)	.4291(4)	.1101(6)	3.68(10)

a Estimated standard deviations in parentheses.
b Anisotropic temperature factors converted to isotropic equivalents by use of the relation: $B = 4/3 (\Sigma_i \Sigma_j g_{ij} \beta_{ij})$ with the g_{ij}'s from the real space metric tensor.
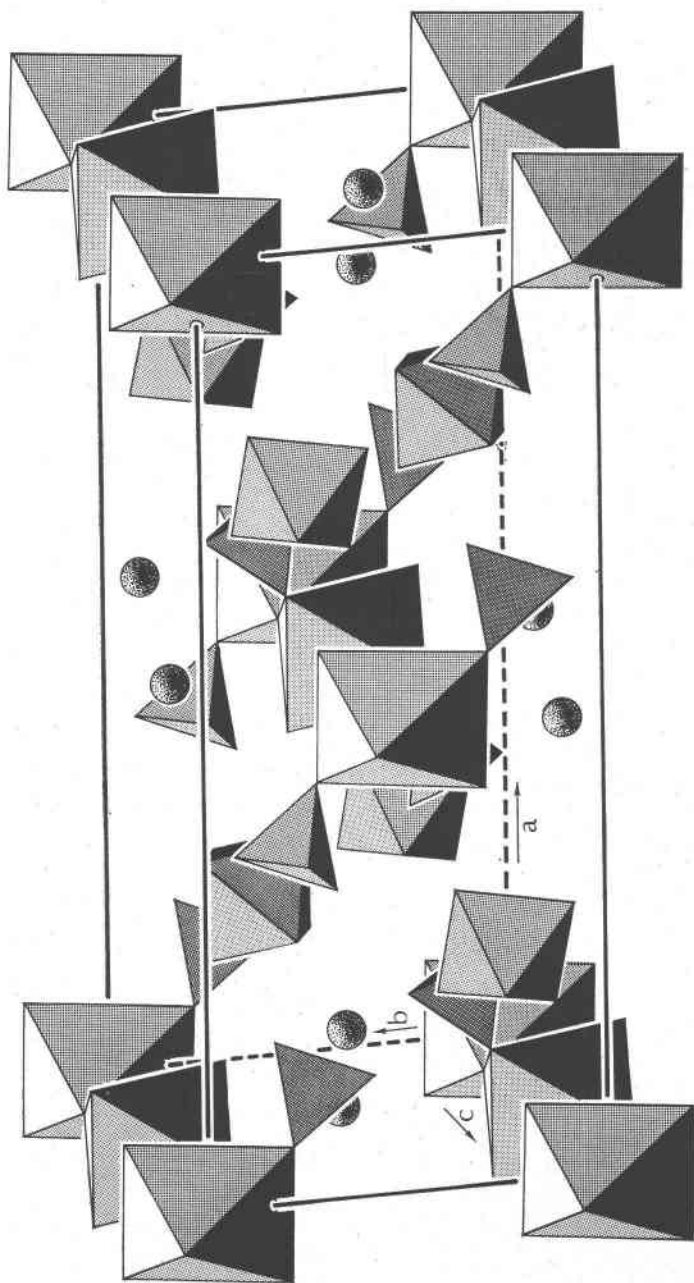
Fig. 1. A polyhedral representation of the mendozite structure. The Na(O,H₂O)₆ octahedral chains are parallel to the c-axis. Unshared smaller octahedra represent Al(H₂O)₆ groups, while the spheres depict isolated water molecules.

TABLE 3. INTERATOMIC DISTANCES(Å) AND ANGLES
(DEGREES) FOR MENDOZITE[a]

Tetrahedral coordination around S					
S-O(1)	1.489(3)	O(1)-O(2)	2.414(5)	O(1)-S-O(2)	109.8(2)
-O(2)	1.461(4)	O(1)-O(3)	2.381(4)	O(1)-S-O(3)	106.9(2)
-O(3)	1.475(4)	O(1)-O(4)	2.414(5)	O(1)-S-O(4)	109.6(2)
-O(4)	1.466(4)	O(2)-O(3)	2.420(5)	O(2)-S-O(3)	111.0(2)
		O(2)-O(4)	2.400(5)	O(2)-S-O(4)	110.2(2)
		O(3)-O(4)	2.397(5)	O(3)-S-O(4)	109.2(2)
Mean	1.473		2.404		109.4

Octahedral coordination around Na and Al					
Na Octahedron			**Al Octahedron**		
Na-O(2)	2.485(3) [2]		Al-Ow(1)	1.873(3) [2]	
-Ow(4)	2.358(2) [2]		-Ow(2)	1.857(3) [2]	
-Ow(5)	2.380(3) [2]		-Ow(3)	1.904(3) [2]	
Mean	2.408		Mean	1.878	
O(2)-Ow(4)	3.259(4) [2]		Ow(1)-Ow(2)	2.651(5) [2]	
-Ow(5)	3.110(5) [2]		-Ow(3)	2.651(5) [2]	
O(2')-Ow(4')	3.585(5) [2]		Ow(1')-Ow(2')	2.623(5) [2]	
-Ow(5')	2.713(5) [2]		-Ow(3')	2.690(5) [2]	
Ow(4)-Ow(5)	3.252(4) [2]		Ow(2)-Ow(3)	2.637(4) [2]	
-Ow(5')	3.447(5) [2]		-Ow(3')	2.683(5) [2]	
Mean	3.228		Mean	2.656	
O(2)-Na-Ow(4)	84.5(1) [2]		Ow(1)-Al-Ow(2)	90.6(2) [2]	
-Ow(4')	95.5(1) [2]		-Ow(2')	89.4(2) [2]	
-Ow(5)	79.4(1) [2]		-Ow(3)	90.8(2) [2]	
-Ow(5')	100.6(1) [2]		-Ow(3')	89.2(2) [2]	
Ow(4)-Na-Ow(5)	86.7(1) [2]		Ow(2)-Al-Ow(3)	89.0(1) [2]	
-Ow(5')	93.3(1) [2]		-Ow(3')	91.0(1) [2]	
Mean	90.0		Mean	90.0	

[a]Estimated standard deviations in parentheses. Multiplicity of
bonds and angles in brackets.

are regarded as proton acceptors, a hydrogen bond system based
on donor–acceptor geometry can be deduced. Table 4 shows possible
hydrogen bonding distances and angles thus derived and Table 5 lists
the electrostatic valences which would result from such a hydrogen
bonding configuration. Only three O or Ow atoms are not charge
balanced, all three being bonded to Na atoms. Thus, in order to
conform to Pauling's second rule, different electrostatic bond strengths,
depending on the Na(O,Ow) distances, should be assumed around Na.

COMPARISON OF THE THREE HYDRATION STATES OF $NaAl(SO_4)_2$

Comparison of the structures of the three hydrates, having the general
formula, $NaAl(SO_4)_2 \cdot nH_2O$, is of interest. In the structure of soda alum
($12H_2O$), both the Na and Al are surrounded by six water molecules,
resulting in three independent structural units of $[Na(H_2O)_6]^{1+}$,
$[Al(H_2O)_6]^{3+}$, and $2[SO_4]^{2-}$, connected only by hydrogen bonds (Cromer

TABLE 4. POSSIBLE HYDROGEN BONDING DISTANCES AND ANGLES

Atoms			Angles	Distances	
A	B	C	ABC	AB	BC
O(3)-	Ow(1)-	O(4)	107.2	2.604	2.653
O(3)-	Ow(2)-	Ow(5)	105.5	2.612	2.604
O(1)-	Ow(3)-	O(1')	113.6	2.754	2.701
O(4)-	Ow(4)-	O(4')	127.4	3.139	3.139
O(2)-	Ow(5)-	O(2')	94.4	2.713	3.110
O(1)-	Ow(6)-	Ow(6')	101.1	2.882	2.681

et al., 1967). In mendozite (11H$_2$O), however, there are insufficient water molecules to form independent octahedra around both Na and Al. As a result, the Na octahedra share corners while the Al octahedra remain insular. It is interesting to note that sufficient water is available to form the corner-sharing Na chain. Yet, in each Na octahedron, two of the six ligands are oxygens, thus leaving the excess water to form independent water molecules. In tamarugite (6H$_2$O), the water content is just sufficient to preserve the independent Al(H$_2$O)$_6$ octahedron, thus forcing Na to bond only to the sulphate oxygens in forming zig-zag chains composed of alternating irregular Na polyhedra and S tetrahedra.

Upon dehydration, soda alum transforms directly to tamarugite, bypassing mendozite. This can be attributed to the very regular octahedral coordination of Ow around Na in soda alum, leading to equal Na–Ow bond strengths. Thus, there is no structural or electrostatic reason for soda alum to lose only one of the water molecules surrounding the Na to allow dehydration to mendozite. The dehydration mechanism which transforms soda alum to tamarugite can be described as a movement of the Na atoms, stripped of their water ligands, into a position which allows bonding with the oxygens of the sulphate groups. Concurrently, the sulphate groups and the independent Al(H$_2$O)$_6$ octahedra reorient themselves to accommodate the Na atoms.

TABLE 5. BALANCE OF ELECTROSTATIC VALENCES

	Na	Al	S	H(d)	H(a)	TOTAL
O(1)			3/2		2 x 1/4	2
O(2)	1/6		3/2		2 x 1/4	2 + 1/6
O(3)			3/2		2 x 1/4	2
O(4)			3/2		2 x 1/4	2
Ow(1)		1/2		2 x 3/4		2
Ow(2)		1/2		2 x 3/4		2
Ow(3)		1/2		2 x 3/4		2
Ow(4)	2 x 1/6			2 x 3/4		2 - 1/6
Ow(5)	1/6			2 x 3/4	1/4	2 - 1/12
Ow(6)				2 x 3/4	2 x 1/4	2

Mendozite also dehydrates directly to tamarugite by losing (1) all water molecules bonded to Na, and (2) the water molecule, Ow(6), which is not linked to any cation. In the course of these structural transformations, the coordination polyhedron of Al remains essentially unchanged in its dimensions, as expected. However, gross changes in distances, angles and coordination number of the Na polyhedra have taken place.

Another interesting aspect of dehydration in light of this structural imformation is the possibility that a new phase in the $NaAl(SO_4)_2 \cdot nH_2O$ system with $n = 9$ might exist. The structural formula for mendozite can be written as $[Na(SO_4)_2(H_2O)_3]_n^{3-}[Al(H_2O)_6]^{3+}[2H_2O]^0$. Comparing this with that of tamarugite, $[Na(SO_4)_2]_n^{3-}[Al(H_2O)_6]^{3+}$, it is apparent that an intermediate phase with a formula $[Na(SO_4)_2(H_2O)_3]_n^{3-}[Al(H_2O)_6]^{3+}$ might exist, because it would be reasonable to suspect the water molecules of mendozite, not bonded to any cation, could be driven off before the water molecules bonded to the Na, thus giving rise to a 9–hydrate. This intermediate phase, though structurally possible, may be thermodynamically unstable, or metastable at best.

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