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Crystal structures of cetineite and its synthetic Na analogue $Na_{3.6}(Sb_2O_3)_3(SbS_3)(OH)_{0.6} \cdot 2.4H_2O$

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ABSTRACT

The mineral cetineite, $(K,Na)_{3+x}(Sb_2O_3)_3(SbS_3)(OH)_x \cdot (2.8 - x)H_2O$ with $x \simeq 0.5$, is hexagonal, $P6_3$, $a = 14.2513(3)$, $c = 5.5900(1)$ Å, and Z = 2; the synthetic Na analogue is also hexagonal, $P6_3$, $a = 14.152(3)$, $c = 5.5758(7)$ Å, and Z = 2. The structure of cetineite has been refined to $R = 0.032$ for 859 observed reflections and that of the synthetic Na analogue to $R = 0.048$ for 1434 observed reflections. The main structural feature of cetineite is an infinite tunnel parallel to the 6_3 axis, formed by the linkage of SbO_3 pyramids. $Na(H_2O)_6$ octahedra are statistically located within the tunnel, with "zeolitic" character. K atoms are on the interior of the tunnel wall and connect the S atoms of external SbS_3 pyramids to form a three-dimensional framework. The structure of the synthetic Na analogue is the same as that of cetineite, except for the positions of water molecules and for the occupancies of alkali atoms. The splitting of the Sb atom of the SbS_3 pyramid into two sites related by a pseudo–mirror plane is observed in both structures.

INTRODUCTION

The new species cetineite was described by Sabelli and Vezzalini (1987). The mineral, found in the Cetine mine (Tuscany, Italy), is the third naturally occurring oxide-sulfide species after kermesite, Sb_2S_2O, and sarabauite, $CaSb_{10}O_{10}S_6$. Its chemical composition is $(K,Na)_{3+x}(Sb_2O_3)_3(SbS_3)(OH)_x \cdot (2.8 - x)H_2O$ with $x \simeq 0.5$. This formula has been derived from both microprobe analyses (Sabelli and Vezzalini, 1987) and the present structure refinement.

To date, four synthetic compounds chemically and structurally related to cetineite have been reported: $K_3SbS_3 \cdot 3Sb_2O_3$ [= $K_3(Sb_2O_3)_3(SbS_3)$, Graf and Schäfer, 1975], $Na_3Sb_7O_9S_3$ [= $Na_3(Sb_2O_3)_3(SbS_3)$, Nakai et al., 1982a], $Na_3Sb_7O_9Se_3$ [= $Na_3(Sb_2O_3)_3(SbSe_3)$, Nakai et al., 1982b], and $Na_3SbSe_3 \cdot 3Sb_2O_3 \cdot 0.5Sb(OH)_3$ [= $Na_3(Sb_2O_3)_3(SbSe_3) \cdot 0.5Sb(OH)_3$, Kluger and Pertlik, 1985]. All these compounds crystallize in the hexagonal space group $P6_3$ with Z = 2. Graf and Schäfer (1975) first synthesized $K_3SbS_3 \cdot 3Sb_2O_3$ in an alkaline aqueous solution of K_2S and Sb_2S_3 and reported its crystal structure. The main structural features of the compound are (1) a large infinite tunnel around the 6_3 axis, formed by interconnected SbO_3 pyramids, and (2) an isolated SbS_3 pyramid. The SbO_3 tunnels and the SbS_3 pyramids are connected by the K atoms located on the internal wall of the tunnel (Graf and Schäfer, 1975).

During investigation of the (Na,K)-Sb-(S,O) system by Nakai et al. (1982a), a new compound—$Na_3Sb_7O_9S_3$—was found among the synthetic products, which include $NaSbS_2$, $Na_6Sb_4S_9$, $KSbS_2$, $K_2Sb_4S_7H_2O$, and three additional new synthetic compounds $Na_2Sb_4O_6S$, KSb_3S_5, and KSb_5S_8. Crystallochemical considerations of these artificial alkali sulfosalts by two of us (Nakai and Katsura) disclosed the unusual structural feature of the model reported for $K_3SbS_3 \cdot 3Sb_2O_3$ by Graf and Schäfer (1975): i.e., the K atoms located on the internal wall of the SbO_3 tunnel are coordinated by anions only from one side. Nakai and Katsura assumed that something was missing inside the tunnel because the K–anion bond is ionic and such a one-sided coordination by anions is unfavorable for K. Therefore the structure analysis of $Na_3Sb_7O_9S_3$ was made by Nakai and Katsura and revealed the following model: (1) Na is located at the center of the tunnel (on the 6_3 axis) surrounded by water molecules and (2) the Sb atom of the SbS_3 pyramid splits between two crystallographic sites. In order to confirm this model, the structure analysis of the Se analogue, $Na_3SbSe_3 \cdot 3Sb_2O_3$, was made by Nakai et al. (1982b). The result basically confirmed the model; however, the presence of a large electron density, as large as that of Se, at the center of the tunnel was observed in a difference Fourier map. Because of the conflicting results for the two structures, these data were left unpublished. Later on, the residual eletron density in the Se compound was clarified to be Sb by structure refinement, which supports the results of Kluger and Pertlik's (1985) structure analysis (see later).

At about the same time, the oxide-sulfide cetineite was discovered in Italy, and its crystal-structure determina-

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tion was undertaken by C. Sabelli, following Graf and Schäfer's model. Oxide-sulfide minerals are very rare in nature. Therefore for a better knowledge of this mineral group and for the structural classification of cetineite, it is important to investigate the crystal structure of this mineral and of the synthetic phase $Na_3Sb_7O_9S_3$, which can be considered the Na analogue of cetineite. The two refinements, performed independently by Sabelli and by Nakai and Katsura, are reported in the present paper.

During the preparation of this paper, the structure analysis of $Na_3SbSe_3 \cdot 3Sb_2O_3 \cdot 0.5Sb(OH)_3$ was independently carried out by Kluger and Pertlik (1985), who found the tunnels to be occupied by $Sb(OH)_3$ pyramids at the center and by Na atoms on the internal wall.

EXPERIMENTAL DETAILS

Crystallographic data and experimental conditions for intensity data measurements are summarized in Table 1. A thin prismatic crystal of cetineite, orange-red in color and with dimensions of 0.03 × 0.03 × 0.2 mm, was used by Sabelli for the intensity-data collection on a PW1100 four-circle diffractometer (Centro di Cristallografia Strutturale del CNR, Pavia, Italy). The cell dimensions were calculated by least-squares refinement of 33 reflections. On the other hand, a hexagonal prismatic crystal of the synthetic Na analogue of cetineite, reddish-yellow in color and with dimensions of 0.1 × 0.1 × 0.05 mm, was used by Nakai and Katsura for the data collection. The synthesis conditions have been reported elsewhere (Nakai et al., 1982a). The intensity data were collected on a Rigaku AFC-5 four-circle diffractometer (X-ray generator: Rotaflex RU200; operating conditions: 50 kV, 180 mA). The intensity measurement was repeated with the variable-background counting technique up to four times for each reflection, until $\sigma(F_o)/F_o$ was less than 0.05. The lattice parameters were determined by least-squares refinement of the 2θ values of 24 reflections.

Intensities were corrected for Lorentz polarization effects. The data for cetineite were also corrected for absorption ($\mu = 104.2$ cm^{-1}) using the semiempirical method by North et al. (1968). The systematic extinctions were consistent with the space groups $P6_3$ and $P6_3/m$; the structure refinements indicated that $P6_3$ is the correct one for both crystals.[1]

Scattering factors for neutral atoms (Sabelli) and anomalous dispersion coefficients (Sabelli, Nakai, and Katsura) were taken from *International Tables for X-ray Crystallography* (1974). Nakai and Katsura used the scattering factors for neutral atoms given by Cromer and Mann (1968).

Computations for cetineite were carried out on the Honeywell DPS-7 computer of the Computer Centre of Florence University, using a local version of ORFLS (Busing et al., 1962) and BONDLA (XRAY System, 1972). Computations for the synthetic Na analogue were performed on the FACOM M-382 computer of Science Information Processing Center of Tsukuba University, using RFINE2 and BADTEA (Finger, 1969).

TABLE 1. Crystal and experimental data

	Cetineite	Synthetic Na analogue
Crystal system	hexagonal	hexagonal
Space group	$P6_3$	$P6_3$
Z	2	2
Cell parameters		
a (Å)	14.2513(3)	14.152(3)
c (Å)	5.5900(1)	5.5758(7)
V (Å^3)	983.22	967.10
D_{calc} (g/cm^3)*	4.223	4.219
Crystal size (mm)	0.03 × 0.03 × 0.2	0.1 × 0.1 × 0.05
Monochromator	graphite	graphite
Radiation	Mo$K\alpha$	Mo$K\alpha$
λ	0.7107	0.70926
2θ range (°)	60	90
Scanning method	ω	$2\theta/\omega$
Scanning speed (°/min)	1.5	4
Standard reflections and max. intensity fluctuation	400, 040, 004 0.073(esd)	431, 002, 221 2.7(%)
Collected reflections (symmetry independent)	1157	2859
Observed reflections (criterion)	859(2.5σ)	1434(3σ)
R (R_w)	0.032	0.048(0.048)

* Based on cetineite $(K_{2.4}Na_{0.6})_{\Sigma 3.0}(Sb_2O_3)_3(SbS_3) \cdot 2.8H_2O$—formula weight = 1250.5; Na analogue $Na_{3.6}(Sb_2O_3)_3(SbS_3)(OH)_{0.6} \cdot 2.4H_2O$—formula weight = 1228.64.

STRUCTURE REFINEMENTS

Cetineite

The structural model by Graf and Schäfer (1975) on the synthetic $K_3SbS_3 \cdot 3Sb_2O_3$ was used as the starting point of the refinement by Sabelli. Two important differences between the starting model and the present structure were soon evident: (a) the presence of electron density inside the SbO_3 tunnel (which appears empty in the Graf and Schäfer structure) and (b) the splitting along the 3-fold axis of the Sb site, which therefore assumes a statistical distribution (about 50% Sb-site refined occupancy) above and below a quasi–mirror plane.

The electron-density maps revealed two maxima inside the SbO_3 tunnel. The first maximum of 9 e/Å^3, at the center of the channel ($2a$ position), was attributed to an Na atom; the second one of about six units, located in a $6c$ position, was attributed to water oxygen (Ow). Because of the 6_3 symmetry operator, this second site is repeated six times in an octahedral disposition around the Na atom. During the refinement, these two sites displayed partial occupancies, which converged to 0.58 for Na and to 0.94 for Ow. The site occupancy of the K atom, which lies in a general position near to the wall of the tunnel, remained close to 0.8 throughout the refinement.

Several cycles of isotropic and anisotropic full-matrix refinements resulted in a conventional R index of 0.032 for the observed reflections ($R = 0.049$ for all the data). A weight $w = 1/\sigma^2(F_o)$ was given to the observed reflections (zero weight to the "unobserved" ones). A final difference Fourier map showed the largest residual peak inside the channel to be 3 e/Å^3. This residual electron density could be attributable to an alternative site for the Ow atom. Moreover, there are other minor positive sites inside the tunnel. In one of these, an H atom could be located, forming an H bridge toward the O(1) atom, which is 2.642(8) Å distant from Ow. However, Ow-O(1) is an edge of the K polyhedron, and thus the question arises

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[1] At the beginning of the refinement the centric hypothesis in the space group $P6_3/m$ was tested, but further refinement steps showed poor convergence.

TABLE 2. Fractional atomic coordinates and thermal parameters

Atom	x	y	z	Occ.	B_{eq}	β_{11}	β_{22}	β_{33}
Cetineite								
Sb(1)A	⅓	⅔	0.8736*	0.5	1.62	349(42)	349	492(203)
Sb(1)B	⅓	⅔	0.6262(5)	0.5	1.71	216(35)	216	2003(268)
Sb(2)	0.16515(4)	0.44827(4)	0.2507(16)	1.0	1.65	255(4)	280(4)	1490(19)
Sb(3)	0.38670(4)	0.40287(4)	0.2518(17)	1.0	1.33	243(3)	220(3)	1043(19)
K	0.1814(2)	0.2814(2)	0.7471(29)	0.80(2)	3.13	485(20)	882(27)	1802(125)
S	0.3620(2)	0.5293(2)	0.7187(40)	1.0	4.37	349(17)	257(16)	7740(630)
Na	0	0	0.4904(44)	0.58(2)	1.36	181(31)	181	1509(441)
O(1)	0.2275(4)	0.3513(4)	0.2334(23)	1.0	1.62	227(37)	293(39)	1650(617)
O(2)	0.0646(18)	0.3541(21)	0.5020(30)	1.0	1.47	279(46)	340(64)	314(226)
O(3)	0.0595(20)	0.3589(23)	−0.0002(41)	1.0	2.92	491(161)	338(131)	3122(824)
Ow	0.0920(9)	0.1401(6)	0.2230(27)	0.94(3)	7.68	1421(98)	739(75)	3514(985)
Synthetic Na analogue of cetineite								
Sb(1)A	⅓	⅔	0.8736*	0.5	1.08	194(13)	194	722(108)
Sb(1)B	⅓	⅔	0.6263(8)	0.5	3.20	592(29)	592	2007(229)
Sb(2)	0.16383(5)	0.44662(5)	0.2475(10)	1.0	2.02	298(3)	345(4)	1935(21)
Sb(3)	0.38448(5)	0.40157(5)	0.2471(10)	1.0	1.65	319(3)	301(3)	1274(15)
Na(1)	0.1921(5)	0.3000(4)	0.7602(42)	1.01(2)	4.05	614(40)	561(40)	3666(298)
S	0.3575(3)	0.5267(3)	0.6967(12)	1.0	3.21	468(19)	346(17)	4055(275)
Na(2)	0	0	0.5149(77)	0.61(2)	1.68	291(42)	291	1243(641)
O(1)	0.2252(6)	0.3495(5)	0.2479(48)	1.0	2.57	340(42)	396(44)	2937(303)
O(2)	0.0606(16)	0.3522(16)	0.4958(35)	1.0	2.64	649(139)	407(116)	1062(376)
O(3)	0.0630(14)	0.3537(19)	0.9907(42)	1.0	3.26	250(90)	738(170)	3037(717)
Ow(1)	0.1301(17)	0.1148(19)	0.2756(95)	0.52	4.33	624(137)	1010(177)	1862(1461)
Ow(2)	0.1353(18)	0.1052(17)	0.7127(56)	0.48	3.44	726(155)	484(125)	1635(1223)

Note: Equivalent isotropic B (Å^2) calculated from anisotropic temperature factors (× 10^5) in the form $\exp -(\beta_{11}h^2 + \cdots + 2\beta_{12}hk + \cdots)$.
* Invariant, fixes the origin.

about its reliability for a hydrogen bond. On the basis of the above reasoning and considering also the "zeolitic" behavior of the atoms lying inside the tunnel, the positioning of H atoms was not attempted.

The chemical composition of cetineite derived from the present structural analysis is $(K_{2.4}Na_{0.6})_{\Sigma 3.0}(Sb_2O_3)_3(SbS_3)\cdot 2.8H_2O$. The formula directly determined by the electron-microprobe analyses is $(K_{1.78}Na_{1.57})_{\Sigma 3.35}(Sb_2O_3)_{3.03}(SbS_3)_{0.94}(OH)_{0.53}\cdot 2.64H_2O$ (Sabelli and Vezzalini, 1987). In order to verify the alkali content of the mineral, the K atomic position was refined both to K (80%) against vacancy and to K (50%) against Na (50%) without detecting any change in the R index or in the thermal behavior. Accordingly, the alkali content in cetineite could be $(K_{1.50}Na_{2.05})_{\Sigma 3.55}$ instead of $(K_{2.4}Na_{0.6})_{\Sigma 3.0}$, with a consequent introduction of (OH) in the structural formula. Since the alkali content coming from the microprobe analyses falls between the results of the two refinements and since it is difficult to establish if the Ow site is occupied by H_2O only or by (OH) too, the simplified formula $(K,Na)_{3+x}(Sb_2O_3)_3(SbS_3)(OH)_x\cdot(2.8 - x)H_2O$ with $x \simeq 0.5$ is preferred. This formula has been confirmed by the structure refinement of the synthetic Na analogue of cetineite as reported below.

Final atomic parameters are given in Table 2. Bond lengths and angles are presented in Table 3. Observed and calculated structure factors are listed in Table 4.[2]

Synthetic Na analogue of cetineite

The refinement was carried out by Nakai and Katsura following a similar procedure as for cetineite. Significant differences between the two structures were detected in the position of water molecules around the Na atom in the center of the SbO_3 tunnel and in the occupancies of the two alkali sites.

A difference Fourier map revealed two probable water oxygen positions, Ow(1) and Ow(2), around the 6_3 axis. The refinement gave lowest temperature factors and R index for the following occupancy model: 0.52 for Ow(1) and 0.48 for Ow(2). The refinement of the water position as in cetineite was also tried, but the calculation ended with a larger temperature factor (B = 8.6 Å^2), with 0.94 occupancy for Ow. Therefore the model given for cetineite was considered to be unsuitable for the synethetic Na analogue.

A full-matrix least-squares refinement with anisotropic temperature factors, isotropic for Ow(1) and Ow(2), was first carried out on the basis of the chemical formula $Na_3(Sb_2O_3)_3(SbS_3)\cdot 3.0H_2O$, with occupancies of $7/9$ (after Sabelli) for Na(1) and $2/3$ [$= 3(1 - 7/9)$] for Na(2). This yielded $R = 0.051$ ($R_w = 0.057$, weight = 1). On the contrary the refinement based on the chemical formula $Na_{3+x}(Sb_2O_3)_3(SbS_3)(OH)_x\cdot(3 - x)H_2O$ with variable occupancies for Na(1) and Na(2) ($x = 0.6$) reduced the R value to 0.048 ($R_w = 0.049$). Subsequently, anisotropic temperature factors were introduced for the water oxygen atoms. However the full anisotropic refinement based on the former model ($x = 0$) was unsuccessful because the temperature factors of the two Ow atoms became negative. On the other hand, the refinement based on the lat-

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[2] A copy of Table 4 may be ordered as Document AM-88-369 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Suite 414, Washington, D.C. 2006, U.S.A. Please remit $5.00 in advance for the microfiche.

TABLE 2—*Continued*

β_{12}	β_{13}	β_{23}
174	—	—
108	—	—
152(3)	93(45)	27(48)
133(3)	38(40)	166(37)
488(20)	54(164)	−302(178)
182(14)	348(112)	−174(100)
90	—	—
174(33)	288(218)	111(210)
123(42)	286(91)	161(96)
230(123)	−128(298)	195(276)
−138(71)	1246(397)	876(332)
97	—	—
296	—	—
186(3)	164(26)	11(33)
200(3)	7(28)	−7(29)
228(31)	139(238)	216(236)
243(16)	214(51)	−12(46)
146	—	—
228(37)	−477(240)	120(280)
231(103)	250(190)	97(172)
238(103)	−414(197)	137(259)
301(136)	−204(400)	−359(489)
174(117)	311(310)	215(280)

ter model ($x \neq 0$) converged successfully to the final R index of 0.048 ($R_w = 0.048$), with $x = 0.61(2)$. A difference Fourier synthesis for this final model revealed a maximum residual electron density of 2 e/Å^3 near the Sb(2) site, whereas the maximum residual inside the channel was 1 e/Å^3. Consequently the chemical formula $Na_{3+x}(Sb_2O_3)_3(SbS_3)(OH)_x \cdot (3 - x)H_2O$ with $x = 0.6$ has been proposed for the synthetic Na analogue of cetineite. This phase is a Na end member of cetineite.

Final atomic parameters and selected bond lengths and angles are compared with those for cetineite in Tables 2 and 3, respectively. Observed and calculated structure factors are listed in Table 4 (see footnote 2).

DESCRIPTION AND DISCUSSION OF STRUCTURES

Figure 1 shows the crystal structure of cetineite indicating Na(Ow)$_6$ octahedra and K atoms inside the SbO_3 tunnels and the SbS_3 pyramid outside them. The structure of the synthetic Na analogue is the same as that of cetineite, except for the site occupancies of the two alkali atoms and for the positions of water oxygen atoms.

The two independent SbO_3 pyramids are connected to each other to form an infinite tunnel around the 6_3 axis. With reference to this "hard" part of the structure, cetineite and the synthetic Na analogue are similar to $K_3SbS_3 \cdot 3Sb_2O_3$ (Graf and Schäfer, 1975) and $Na_3SbSe_3 \cdot 3Sb_2O_3 \cdot 0.5Sb(OH)_3$ (Kluger and Pertlik, 1985). There are only small differences in the Sb–O distances: the mean values of 1.979 Å for cetineite and 1.972 Å for the synthetic Na analogue are slightly shorter than those for the above two structures, 1.983 and 1.982 Å, respectively. The contents of the tunnels, on the other hand, are quite different among the four structures. Cetineite shows an Na(Ow)$_6$ octahedron in the center and K atoms on the interior wall of

TABLE 3. Selected interatomic distances (Å) and angles (°)

	Cetineite		Na analogue	
	Raw	Uncor.*	Raw	Uncor.*
Sb(1)A–S 3×	2.356(9)	2.395	2.385(5)	2.411
Sb(1)B–S 3×	2.251(6)	2.293	2.207(5)	2.246
S–S 3×	3.79(1)	3.83	3.761(8)	3.787
Sb(2)–O(1)	1.984(7)	2.007	1.959(10)	1.993
Sb(2)–O(2)	1.976(19)	2.000	1.970(18)	2.004
Sb(2)–O(3)	1.985(23)	2.012	1.985(21)	2.019
O(1)–O(2)	2.78(3)	2.80	2.73(3)	2.75
O(1)–O(3)	2.78(3)	2.80	2.73(3)	2.77
O(2)–O(3)	2.81(3)	2.83	2.82(3)	2.84
Sb(3)–O(1)	2.008(6)	2.027	1.991(8)	2.019
Sb(3)–O(2,C)	2.006(15)	2.025	1.971(24)	2.001
Sb(3)–O(3,B)	1.916(19)	1.947	1.952(26)	1.990
O(1)–O(2,C)	2.70(3)	2.72	2.71(2)	2.73
O(1)–O(3,B)	2.77(3)	2.79	2.71(2)	2.75
O(2,C)–O(3,B)	2.79(3)	2.81	2.76(3)	2.79
K,Na(1)–S	3.168(3)	3.199	2.897(6)	2.932
K,Na(1)–O(1)	3.00(2)	3.02	2.92(3)	2.95
K,Na(1)–O(1,A)	2.86(2)	2.88	2.79(3)	2.81
K,Na(1)–O(2)	2.73(3)	2.75	2.75(3)	2.78
K,Na(1)–O(2,B)	2.80(3)	2.82	2.67(2)	2.70
K,Na(1)–O(3,A)	2.86(4)	2.88	2.64(3)	2.67
K,Na(1)–O(3,B)	2.78(3)	2.81	2.79(2)	2.83

	Cetineite		Na analogue	
	Raw	Uncor.*	Raw	Uncor.*
K–Ow(A)	3.19(2)	3.25		
K–Ow(B)	3.08(1)	3.10		
K–Ow(D)	3.03(1)	3.06		
Na(1)–Ow(1)			3.56(5)	3.59
Na(1)–Ow(1,A)			3.69(5)	3.72
Na(1)–Ow(1,D)			2.46(3)	2.50
Na(1)–Ow(2)			2.47(2)	2.51
Na(1)–Ow(2,A)			3.83(4)	3.85
Na(1)–Ow(2,D)			3.42(3)	3.45
Na–Ow 3×	2.31(2)	2.37		
Na–Ow(B) 3×	2.19(2)	2.24		
Na(2)–Ow(1) 3×			2.20(4)	2.23
Na(2)–Ow(1,B) 3×			2.27(5)	2.31
Na(2)–Ow(2) 3×			2.06(4)	2.09
Na(2)–Ow(2,C) 3×			2.42(4)	2.45
S–Sb(1)A–S 3×	107.3(4)		104.1(2)	
S–Sb(1)B–S 3×	114.9(3)		116.9(1)	
O(1)–Sb(2)–O(2)	89(1)		87.8(10)	
O(1)–Sb(2)–O(3)	89(1)		87.7(11)	
O(2)–Sb(2)–O(3)	90(1)		90.8(8)	
O(1)–Sb(3)–O(2,C)	85(1)		86.4(8)	
O(1)–Sb(3)–O(3,B)	90(1)		86.8(8)	
O(2,C)–Sb(3)–O(3,B)	90(1)		89.4(10)	

Note: The equivalent positions (referred to Table 2) are designated by the letter in parentheses and are (A) = $x, y, 1 + z$; (B) = $y, y - x, ½ + z$; (C) = $y, y - x, - ½ + z$; (D) = $x - y, x, ½ + z$.

* The uncorrelated (uncor.) motion corrections of interatomic distances were made against the raw data.

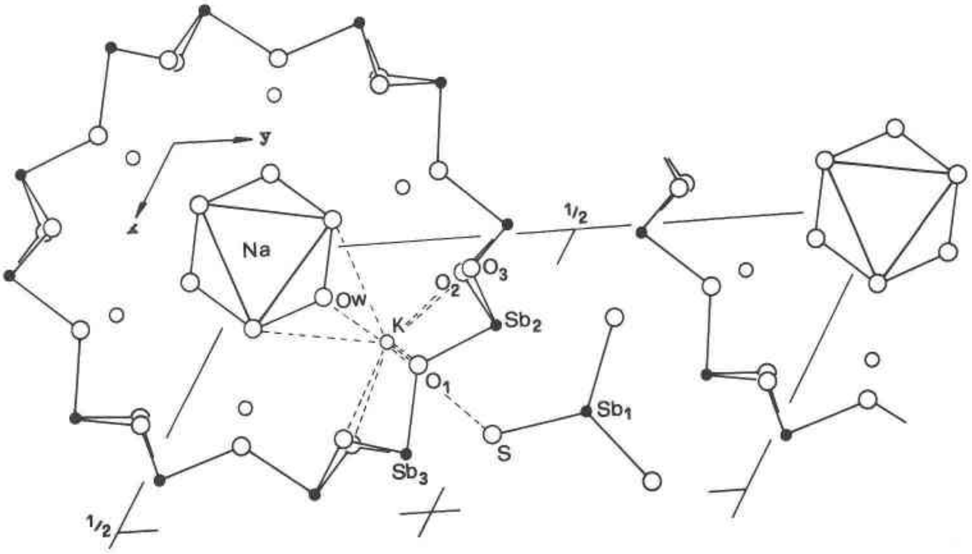

Fig. 1. The structure of cetineite viewed along the *c* axis.

the tunnel; the synthetic Na analogue has Na(2) $[Ow(1)_6Ow(2)_6]$ polyhedra in the center and Na(1) atoms on the wall; Graf and Schäfer's compound has only K atoms on the wall; and Kluger and Pertlik's compound contains an $Sb(OH)_3$ pyramid in the center and Na atoms on the wall. It appears that the empty channel in Graf and Schäfer's structure and the consequent one-sided coordination of the K atom are unfavorable for K owing to the ionic character of K–anion bonds.

In the Na octahedron of cetineite there are two different Na–Ow distances: 2.31(2) and 2.19(2) Å. These values, especially the second one, are relatively short if compared with the usual octahedral Na–O bond distances, i.e., 2.25–2.78 Å (*International Tables for X-ray Crystallography,* 1968). The shortening can be ascribed in part to the large apparent thermal anisotropy of the water oxygens. The uncorrelated motion corrections were calculated, and the corrected bond distances are given in Table 3. It must be considered here that the partial occupancies of atoms involved and the possibility of resonance of Ow would be also responsible for the short Na–Ow distances. The Ow–Na–Ow angles are 82.5(8), 88.2(9), 94.5(4)° between adjacent oxygens, and 176(1)° between opposite oxygens. The Na octahedra are joined to each other to form an apparent face-sharing chain along the 6_3 axis (Fig. 2). Since the occupancy of the Na site is partial, the Na–Ow chain is not really continuous. These structural features of the Na–Ow octahedra may indicate the instability of this portion of the structure.

In the channel of the synthetic Na analogue, Na(2) coordinates 6 Ow(1) and 6 Ow(2). The water molecule is statistically distributed between the two Ow sites with roughly half occupancy, so the resulting average coordination for Na(2) is octahedral. As in cetineite there are two different Na–Ow distances for each water molecule: Na(2)–Ow(1) = 2.27(5) and 2.20(4), and Na(2)–Ow(2) = 2.42(4) and 2.06(3) Å, indicating a large distortion from the ideal octahedral coordination. As discussed in later paragraphs, it is assumed that this distortion, as well as the one in cetineite, is due to structural rather than crystallochemical requirements related with the site splitting of the Sb(1) atom.

As depicted in Figure 2, ten atoms surround the K atom in cetineite (twice 0(1), 0(2), 0(3); three times Ow; and once S). The six K–O bonds range from 2.73(3) to 3.00(2) Å, with a mean value of 2.84 Å. The corresponding K–O mean value reported by Graf and Schäfer for their synthetic compound is a little longer: 2.87 Å. In the synthetic Na analogue of cetineite, the alkali atom is Na instead of K, with a mean Na–O distance of 2.76 Å, which agrees well with the corresponding value of 2.75 Å reported for $Na_3SbSe_3 \cdot 3Sb_2O_3 \cdot 0.5Sb(OH)_3$ (Kluger and Pertlik, 1985). In cetineite, on the side opposite to the oxygen atoms, there are three water molecules with K–Ow distances of 3.03(1), 3.08(1), and 3.19(2) Å. A fourth water molecule is located at 3.42(4) Å, a value apparently too long for a bond distance. The K–Ow bonds, weaker than the K–O bonds, represent the only linkage between the Na chain and the tunnel. Together with the asymmetry in Na-Ow octahedron and the partial occupancies of the involved atoms, the weakness of the K–Ow bonds account for the "zeolitic" character of the Na octahedron within the tunnel. Because of this character, Na in cetineite can be replaced by Sb in Kluger and Pertlik's compound. In the synthetic Na analogue, Na(1) has only two water oxygens at 2.46(3) an 2.47(2) Å. The next water oxygens are too far to be included in Na(1) coordination (Table 3). A similar coordination is present in Kluger and Perlik's compound, in which the Na–Ow distance is 2.41 Å.

Another important difference between cetineite and the Graf and Schäfer compound $K_3SbS_3 \cdot 3Sb_2O_3$ is represented by the behavior of the SbS_3 pyramid. In the structure of $K_3SbS_3 \cdot 3Sb_2O_3$, there is a unique SbS_3 pyramid, like the $SbSe_3$ pyramid in the Kluger and Pertlik compound. However, in cetineite as well as in the synthetic Na analogue, the Sb(1) atom is statistically distributed between two sites, Sb(1)A and Sb(1)B, both with an occupancy very close to 0.5. The Sb(1)A-Sb(1)B separation is 1.383(4) Å for cetineite and 1.379(7) Å for the Na analogue. As seen in Figure 2, these two positions (as well as those of all other atoms) are related by a quasi-mirror plane at $z = 1/4$ and $3/4$. The Sb(1)A–S bond distance of 2.356(8) Å in cetineite compares well with the value of 2.36(1) Å in $K_3SbS_3 \cdot 3Sb_2O_3$, whereas the Sb(1)B–S distance shows a shorter value of 2.251(5) Å. The corresponding Sb–S distances in the synthetic Na analogue are 2.385(5) and 2.207(5) Å, respectively. There is a peculiar similarity in the distorted forms of the two trigonal "bipyramids" Sb(1)A–3S–Sb(1)B and Na–3Ow–Na (Fig. 2). These phenomena could be attributed to domain structures or short-range ordering.

The strong anisotropy of S (parallel to the 3 axis) observed in Graf and Schäfer's compound is also observed in cetineite and in the synthetic Na analogue. Similar large thermal motion and anisotropy of S and Se atoms were observed in $Na_3SbSe_3 \cdot 3Sb_2O_3 \cdot 0.5Sb(OH)_3$ (Kluger and Pertlik, 1985) and also in sarabauite $CaSb_{10}O_{10}S_6$ (Nakai et al. 1978), in gerstleyite $Na_2(Sb,As)_8S_{13} \cdot 2H_2O$ (Nakai and Appleman, 1981), and in $Na_2Sb_4O_6S$ (Nakai et al., 1982a). This anisotropy of the chalcogen atom has been previously ascribed to its short bond distance to the Sb atom, because of the unusually low coordination number of S or Se: one in sarabauite, gerstleyite, $Na_2Sb_4O_6S$, and two in $Na_2SbSe_3 \cdot 3Sb_2O_3 \cdot 0.5Sb(OH)_3$. An additional reason for the strong anisotropy in the [001] direction may be found in the structures of cetineite and the Na analogue: on the basis of the observed site splitting of the Sb(1) atom, a tendency to a site splitting of the S atom in the same direction is also probable. If the splitting were small, without resolution of the two S sites, only a stretching of the thermal ellipsoid would be observed.

STRUCTURAL CLASSIFICATION AND COMPARISON WITH RELATED MINERALS

The presence of SbS_3 anionic groups in the structures of cetineite and its synthetic Na analogue allow them to be classified as sulfosalts of the Va_2 type with $\psi = 1.71$ (Nowacki, 1969). The parameter ψ is calculated as p/n, where p is the number of S and oxygen atoms and n the number of semimetal atoms in the chemical formula.

The structure of cetineite is apparently related to those of sarabauite and gerstleyite. In the structure of sarabauite, SbO_3 pyramids form four-membered Sb_4O_8 rings, which are connected by four-membered $Sb_4S_6O_2$ rings and two-membered Sb_2O_4 rings to form a two-dimensional network. The role of the Ca atom is to connect these networks into a three-dimensional structure. In the structure of gerstleyite, the SbS_3 pyramids share corners to form a complex chain parallel to [100]. Na–S bonds cross-link the chains into a slab structure parallel to (010). In comparison, in cetineite and its Na analogue, the role of the alkali atom is to connect the one-dimensional Sb–O tunnels with the isolated SbS_3 pyramids to form a three-dimensional structure. This behavior of the alkali atoms in sulfosalt structures has been pointed out in the classification of sulfosalt by Nakai et al. (1982a).

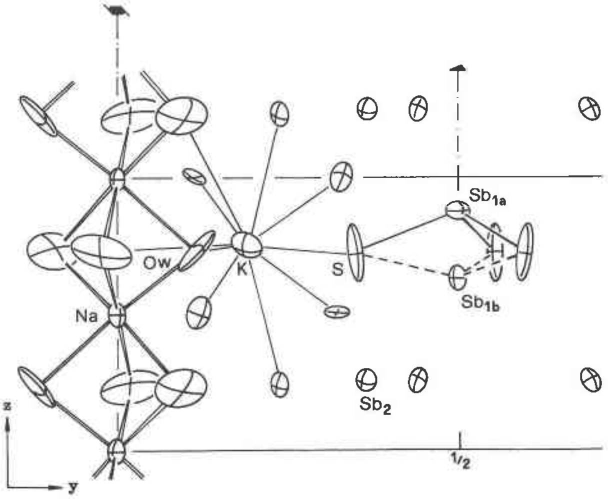

Fig. 2. A projection of the structure of cetineite showing the thermal behavior of the atoms (ellipsoids represent a 50% probability level). The Na–Ow chain along the 6_3 axis, the KO_6Ow_3S polyhedron, the split $Sb(1)S_3$ pyramid on the 3 axis, and isolated symmetry-repeated Sb(2) atoms are depicted.

Another common feature in the structures of gerstleyite, cetineite, and its Na analogue is that the water molecules are bound only to the alkali atoms.

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