

$P_2O_7^{4-}$ is found in eclipsed conformation; P—O distances range from 1.482 (6) to 1.617 (7) Å with P—O_{terminal} distances averaging 1.517 (6) Å and P—O_{bridging} distances longer [average 1.611 (6) Å]. The P—O—P angle is 122.1 (4)°. These distances are comparable to the values seen for other similar groups. BaCuP₂O₇ thus belongs to the family of dichromate structures in which P₂O₇ shows an eclipsed conformation and P₂O₇⁴⁻ ions appear in groups of two with bridging O atoms directed towards each other.

Ba²⁺ ions show ninefold coordination with Ba—O distances between 2.702 (6) and 3.001 (5) Å [average 2.840 (6) Å]. These distances are similar to those observed for Ba in BaCoP₂O₇ (2.70–2.97 Å). In α -Sr₂P₂O₇ (Hagman, Jansson & Magnéli, 1968), isostructural with α -Ba₂P₂O₇ (Morris, McMurdie, Evans, Paretzkin, DeGroot, Hubbard & Carmel, 1979), Sr²⁺ shows ninefold coordination. Thus the structures of BaCuP₂O₇ and BaCoP₂O₇ are isostructural. Both display dimers of $MP_2O_7^{2-}$ in which pairs of metal atoms are bridged by two O atoms. The solid-state structure of BaCuP₂O₇, thus, does not lead to a complete interpretation of its low-temperature magnetic behavior.

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CsSbO(SiO₃)₂: A New {uB, 1_∞¹}[¹²SiO₃] Chain Silicate

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Abstract. CsSbO(SiO₃)₂, $M_r = 422.82$, orthorhombic, $Pna2_1$, $a = 21.024$ (2), $b = 13.602$ (2), $c = 7.1287$ (7) Å, $V = 2038.6$ (7) Å³, $Z = 12$, $D_x = 4.131$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 9.66$ mm⁻¹, $F(000) = 2280$, $T = 293$ K, $R = 0.044$, $wR = 0.047$ for 2576 independent reflections. The structure consists of chains of corner-sharing SbO₆ octahedra, running parallel to the c axis and cross-linked to chains of corner-sharing SiO₄ tetrahedra running parallel to the a axis. This covalent framework delimits tunnels which extend through the structure parallel to the a axis and wherein Cs

atoms are situated. The overall silicate anion topology is {uB, 1_∞¹}[¹²SiO₃].

Introduction. As part of a search for layered or skeleton structures with covalent networks built up from MO₆ octahedra (M : high valent cation) and XO₄ tetrahedra ($X = \text{P, Si, Ge}$) the first alkali antimony(V) silicates KSbOSiO₄ (Crosnier, Guyomard, Verbaere & Piffard, 1990) and NaSbOSiO₄ (Pagnoux, Guyomard, Verbaere, Piffard & Tournoux, 1991), which are both isomorphous derivatives of KTiOPO₄, have recently been characterized. This paper reports the crystal structure determination of a monopolysilicate isolated during the

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Table 1. Atomic coordinates and thermal parameters

$$B_{\text{eq}} = (4/3) \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	$B_{\text{iso}}/B_{\text{eq}} (\text{\AA}^2)$
Cs(1)	0.00744 (8)	0.3533 (2)	0.7714 (2)	3.03 (3)
Cs(2)	0.16345 (8)	0.1349 (1)	0.7856 (3)	2.87 (3)
Cs(3)	0.3309 (1)	0.3400 (1)	0.7743 (3)	3.37 (3)
Sb(1)	-0.00042 (7)	-0.00428 (8)	0	0.243 (9)
Sb(2)	0.16903 (5)	0.51708 (7)	0.5333 (2)	0.30 (1)
Sb(3)	0.33328 (6)	0.01297 (6)	0.5340 (2)	0.26 (1)
Si(1)	0.0719 (2)	0.3812 (3)	0.2761 (7)	0.29 (5)
Si(2)	0.0843 (2)	0.1528 (3)	0.2453 (6)	0.37 (5)
Si(3)	0.2305 (2)	0.1391 (3)	0.2992 (7)	0.47 (5)
Si(4)	0.2508 (2)	0.3616 (3)	0.2998 (7)	0.31 (5)
Si(5)	0.4014 (2)	0.3725 (3)	0.2487 (6)	0.28 (5)
Si(6)	0.4267 (2)	0.1498 (3)	0.2776 (7)	0.27 (5)
O(1)	0.4887 (6)	0.4453 (8)	0.756 (2)	0.7 (2)
O(2)	0.1626 (5)	0.4560 (7)	0.783 (2)	0.5 (1)
O(3)	0.1732 (5)	0.5737 (7)	0.284 (2)	0.5 (1)
O(4)	0.4497 (5)	0.6235 (8)	0.942 (2)	0.4 (1)
O(5)	0.4187 (6)	0.4377 (8)	0.069 (2)	0.6 (2)
O(6)	0.4203 (6)	0.4269 (9)	0.442 (2)	0.8 (2)
O(7)	0.0503 (6)	0.1122 (9)	0.057 (2)	0.9 (2)
O(8)	0.2743 (6)	0.1230 (9)	0.117 (2)	0.9 (2)
O(9)	0.2447 (6)	0.4356 (9)	0.477 (2)	0.9 (2)
O(10)	0.0939 (7)	0.597 (1)	0.586 (2)	1.1 (2)
O(11)	0.1135 (6)	0.4069 (8)	0.460 (2)	0.5 (2)
O(12)	0.2499 (6)	0.5709 (8)	-0.023 (2)	0.5 (1)
O(13)	0.2098 (6)	0.3931 (9)	0.119 (2)	0.7 (2)
O(14)	0.1207 (6)	0.6330 (9)	0.955 (2)	0.5 (2)
O(15)	0.0840 (6)	0.4539 (8)	0.100 (2)	0.4 (1)
O(16)	0.0856 (6)	0.2696 (9)	0.216 (2)	0.8 (2)
O(17)	0.1588 (4)	0.1173 (6)	0.247 (1)	0.0 (1)
O(18)	0.2320 (6)	0.2527 (9)	0.367 (2)	0.6 (2)
O(19)	0.3232 (5)	0.3581 (7)	0.245 (1)	0.3 (1)
O(20)	0.4338 (6)	0.2664 (9)	0.238 (2)	1.0 (2)
O(21)	0.9960 (6)	0.3920 (9)	0.340 (2)	0.7 (2)

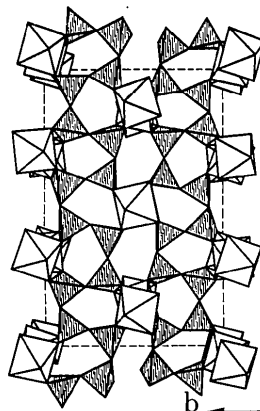
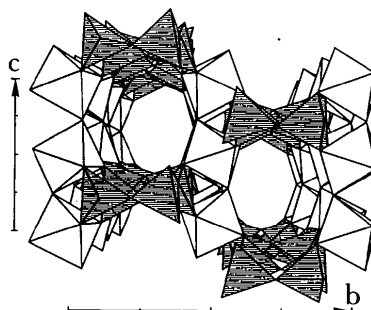
course of our investigations on the Cs₂O–Sb₂O₅–SiO₂ system: CsSbO(SiO₃)₂.

Experimental. *Synthesis.* Single crystals of CsSbO(SiO₃)₂ were grown from mixtures of CsNO₃, Sb₂O₃ and SiO₂. The chemicals were weighed out in a 2:1:2 molar ratio, *i.e.* with a 100% excess in Cs and Sb, and the mixture was heated in a platinum crucible at 673 K for 2 h to decompose CsNO₃ before calcining at 1573 K for 10 h in air.

Structure determination. The title compound was characterized and its structure determined by single-crystal X-ray diffraction, using an Enraf–Nonius CAD-4 diffractometer and Mo K α radiation ($\lambda = 0.71069 \text{ \AA}$). Unit-cell constants were refined by a least-squares procedure from powder data collected with an Inel curved multi-detector [0.2 mm capillary, $\lambda(\text{Cu K}\alpha_1) = 1.54059 \text{ \AA}$, silicon as standard].* Data collection was performed on a small colorless crystal $0.1 \times 0.1 \times 0.1 \text{ mm}$, $0.049 < \sin\theta/\lambda < 0.807 \text{ \AA}^{-1}$, with $0 \leq h \leq 33$, $-21 \leq k \leq 21$, $0 \leq l \leq 11$, scan mode θ – 2θ with $\Delta\theta = (1.0 + 0.35\tan\theta)^\circ$ and $(1.5 + \tan\theta) \text{ mm}$ counter slit. The scan speed was $5.49^\circ \text{ min}^{-1}$ for reflections with $\sigma(I)/I < 0.03$ or adjusted in a time limited to 90 s, down to

$1.03^\circ \text{ min}^{-1}$ for other reflections. Three check reflections were monitored every 3600 s and showed no evidence of decay. 9710 reflections were measured, of which 4483 were observed at $I > 3\sigma(I)$. They were corrected for Lorentz and polarization effects and, on account of the crystal shape, a spherical absorption correction was applied (min. and max. transmission coefficients: 0.418, 0.435). Among the 4483 reflections with $I > 3\sigma(I)$, 669 were unique. The remainder were averaged with $R_{\text{int}} = 0.036$ thus leading to a total of 2576 reflections which were used for structure solution and refinement. The systematic absences were consistent with the space groups $Pnam$ and $Pna2_1$ and structure determination was first conducted in the centrosymmetric space group. The heavy-atom positions were inferred from the Patterson map, the remaining atoms being located from successive electron density difference syntheses. No model could be refined successfully in the centrosymmetric space group, so $Pna2_1$ was chosen. The z coordinate of Sb(1) was held fixed to define the origin along the polar c axis.

The SDP software package (B. A. Frenz & Associates, Inc., 1982) was used for all calculations performed on a VAX 3900 computer. A full-matrix least-squares refinement was carried out minimizing the quantity $\sum w(F_o - F_c)^2$ and employing modified unit weights [$w = 1.0$ for $F_o < 0.8F_o \text{ max.}$ and $w =$

Fig. 1. [001] view of the [SbO(SiO₃)₂]⁻ covalent framework.Fig. 2. [100] view of the [SbO(SiO₃)₂]⁻ covalent framework.

* Lists of X-ray powder diffraction data, structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54404 (29 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Selected bond distances (Å) and bond angles (°) with e.s.d.'s

Sb(1)O ₆ octahedron						
Sb(1)	O(1)	O(1)	O(4)	O(5)	O(6)	O(7)
O(1)	<u>1.96 (2)</u>	3.89 (1)	2.88 (2)	2.68 (2)	2.67 (2)	2.80 (2)
O(1)	<u>175.9 (4)</u>	<u>1.93 (2)</u>	2.75 (3)	2.84 (2)	2.91 (2)	2.63 (2)
O(4)	88.6 (5)	<u>95.1 (5)</u>	<u>1.98 (1)</u>	2.76 (2)	2.82 (2)	3.93 (2)
O(5)	92.1 (6)	86.2 (6)	<u>88.4 (5)</u>	<u>1.99 (1)</u>	3.96 (2)	2.85 (2)
O(6)	85.6 (6)	96.2 (6)	91.1 (6)	<u>177.6 (6)</u>	<u>1.97 (1)</u>	2.72 (2)
O(7)	91.2 (6)	85.2 (6)	179.0 (6)	92.6 (6)	<u>87.9 (6)</u>	<u>1.95 (1)</u>
Sb(2)O ₆ octahedron						
Sb(2)	O(2)	O(3)	O(8)	O(9)	O(10)	O(11)
O(2)	<u>1.97 (2)</u>	3.91 (2)	2.88 (2)	2.80 (2)	2.79 (2)	2.61 (2)
O(3)	<u>177.9 (5)</u>	<u>1.94 (2)</u>	2.70 (2)	2.77 (2)	2.74 (2)	2.88 (2)
O(8)	94.3 (6)	<u>87.8 (6)</u>	<u>1.96 (1)</u>	2.77 (2)	2.80 (2)	3.93 (2)
O(9)	90.2 (6)	90.0 (6)	<u>89.2 (6)</u>	<u>1.98 (1)</u>	3.94 (2)	2.79 (2)
O(10)	90.4 (6)	89.4 (6)	91.2 (6)	<u>179.3 (7)</u>	<u>1.96 (1)</u>	2.77 (2)
O(11)	83.0 (5)	94.9 (5)	177.1 (6)	89.8 (6)	<u>89.8 (6)</u>	<u>1.97 (1)</u>
Sb(3)O ₆ octahedron						
Sb(3)	O(2)	O(3)	O(12)	O(13)	O(14)	O(15)
O(2)	<u>1.95 (2)</u>	3.91 (2)	2.78 (2)	2.73 (2)	2.84 (2)	2.80 (2)
O(3)	<u>178.0 (6)</u>	<u>1.97 (2)</u>	2.72 (2)	2.83 (2)	2.72 (2)	2.81 (2)
O(12)	90.5 (6)	<u>87.7 (5)</u>	<u>1.96 (1)</u>	2.75 (2)	2.85 (2)	3.93 (2)
O(13)	88.4 (5)	92.2 (5)	<u>89.2 (5)</u>	<u>1.96 (1)</u>	3.94 (2)	2.77 (2)
O(14)	92.5 (5)	87.0 (5)	92.6 (5)	<u>177.9 (6)</u>	<u>1.98 (1)</u>	2.76 (2)
O(15)	90.9 (5)	91.0 (5)	178.2 (6)	89.7 (5)	<u>88.4 (5)</u>	<u>1.97 (1)</u>
Si(1)O ₄ tetrahedron						
Si(1)	O(11)	O(15)	O(16)	O(21)		
O(11)	<u>1.62 (1)</u>	2.72 (2)	2.62 (2)	2.62 (2)		
O(15)	114.4 (7)	<u>1.62 (1)</u>	2.64 (2)	2.66 (2)		
O(16)	109.0 (7)	<u>110.0 (7)</u>	<u>1.60 (1)</u>	2.66 (2)		
O(21)	106.2 (7)	107.9 (7)	109.2 (7)	<u>1.67 (1)</u>		
Si(2)O ₄ tetrahedron						
Si(2)	O(4)	O(7)	O(16)	O(17)		
O(4)	<u>1.62 (1)</u>	2.75 (2)	2.66 (2)	2.67 (2)		
O(7)	115.9 (7)	<u>1.62 (2)</u>	2.53 (2)	2.65 (2)		
O(16)	111.3 (7)	<u>103.8 (7)</u>	<u>1.60 (1)</u>	2.59 (2)		
O(17)	110.0 (7)	109.2 (7)	<u>106.1 (6)</u>	<u>1.64 (1)</u>		
Si(3)O ₄ tetrahedron						
Si(3)	O(8)	O(12)	O(17)	O(18)		
O(8)	<u>1.61 (2)</u>	2.71 (2)	2.60 (2)	2.66 (2)		
O(12)	114.0 (7)	<u>1.62 (1)</u>	2.60 (2)	2.62 (2)		
O(17)	109.3 (7)	<u>108.6 (7)</u>	<u>1.58 (1)</u>	2.55 (2)		
O(18)	111.2 (7)	107.9 (7)	<u>105.6 (6)</u>	<u>1.62 (1)</u>		
Si(4)O ₄ tetrahedron						
Si(4)	O(9)	O(13)	O(18)	O(19)		
O(9)	<u>1.62 (2)</u>	2.72 (2)	2.62 (2)	2.60 (2)		
O(13)	114.6 (8)	<u>1.61 (2)</u>	2.65 (2)	2.65 (2)		
O(18)	108.7 (8)	<u>110.7 (7)</u>	<u>1.61 (1)</u>	2.60 (2)		
O(19)	106.3 (7)	109.7 (7)	<u>106.5 (7)</u>	<u>1.63 (1)</u>		
Si(5)O ₄ tetrahedron						
Si(5)	O(5)	O(6)	O(19)	O(20)		
O(5)	<u>1.60 (2)</u>	2.66 (2)	2.55 (2)	2.64 (2)		
O(6)	111.8 (7)	<u>1.61 (2)</u>	2.60 (2)	2.64 (2)		
O(19)	106.4 (7)	<u>108.3 (7)</u>	<u>1.59 (1)</u>	2.58 (2)		
O(20)	111.5 (8)	110.5 (8)	<u>108.1 (7)</u>	<u>1.60 (1)</u>		
Si(6)O ₄ tetrahedron						
Si(6)	O(10)	O(14)	O(20)	O(21)		
O(10)	<u>1.60 (2)</u>	2.73 (2)	2.61 (2)	2.62 (2)		
O(14)	115.8 (8)	<u>1.62 (1)</u>	2.64 (2)	2.61 (2)		
O(20)	108.1 (8)	<u>109.3 (7)</u>	<u>1.62 (1)</u>	2.62 (2)		
O(21)	108.6 (8)	106.8 (7)	<u>107.9 (7)</u>	<u>1.63 (1)</u>		
Cs—O distances						
O(21)	O(15)	O(10)	O(11)	O(15)	O(21)	
Cs(1)	3.13 (1)	3.15 (1)	3.16 (2)	3.23 (1)	3.48 (1)	3.50 (1)
O(12)	O(7)	O(17)	O(8)	O(4)		
Cs(2)	2.99 (1)	3.08 (1)	3.30 (1)	3.32 (2)	3.42 (1)	
O(9)	O(5)	O(6)	O(19)			
Cs(3)	3.08 (2)	3.10 (1)	3.25 (1)	3.37 (1)		

($0.8F_o \max./F_o$)² for $F_o \geq 0.8F_o \max.$]. Refinements were made by varying 163 structural parameters including anisotropic Cs and Sb temperature factors, an overall scale factor and an extinction parameter, g , which refined to $1.00 (8) \times 10^{-8}$. Results of the refinement for observed F 's are: $R = 0.044$ and $wR = 0.047$, $(\Delta/\sigma)_{\max} = 0.01$. Neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The final electron density synthesis showed only random fluctuations about the heavy atoms ($\Delta\rho = 2.9, -3.3 \text{ e } \text{Å}^{-3}$) and none of the peaks could be refined as additional atoms. Table 1* presents the final atomic coordinates and thermal parameters.

Discussion. The $[\text{SbO}(\text{SiO}_3)_2]^-$ three-dimensional framework is characterized by chains of corner-sharing SbO_6 octahedra cross-linked with chains of corner-sharing SiO_4 tetrahedra (Figs. 1 and 2). The chains of SbO_6 octahedra run parallel to the c axis. There are two types of chains. In the first, chains are built up from $\text{Sb}(1)\text{O}_6$ octahedra only and they are located at $x = y = 0$ and $x = y = \frac{1}{2}$, whereas in the second there are chains of alternate $\text{Sb}(2)\text{O}_6$ and $\text{Sb}(3)\text{O}_6$ octahedra, located at $x = \pm \frac{1}{3}$, $y = 0$ and $x = \pm \frac{1}{6}$, $y = \frac{1}{2}$. The corrugated chains of SiO_4 tetrahedra run parallel to the a axis. They run along axes located at $y = z = \pm \frac{1}{4}$. The periodicity of these chains corresponds to 12 SiO_4 tetrahedra, *i.e.* twice the number of independent positions of Si atoms. The topology of the silicate anion (Fig. 1) may be described as 'unbranched' following the terminology of Liebau (1985) and written as $\{uB, 1_{\infty}^1\}^{12}[\text{SiO}_3]$ (Liebau, 1985). The covalent framework delimits large tunnels running parallel to the a axis (Fig. 2) and wherein Cs atoms are situated.

Selected bond distances and angles are given in Table 2. It can be seen from this table that all of the coordination polyhedra are consistent with previous knowledge of Cs, Sb^{V} and silicate structural chemistry.

Owing to its structure $\text{CsSbO}(\text{SiO}_3)_2$ is a good candidate for ion-exchange reactions with smaller alkali ions. Preliminary experiments are promising and should lead to high alkali-ion mobility.

* See deposition footnote.

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