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A New Antimony(III) Molybdate with a Layer Structure: $KSbMo_2O_8$

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The crystal structure of $KSbMo_2O_8$ was determined from single-crystal X-ray diffraction data. It crystallizes in the triclinic space group $P\bar{1}$ with $a = 5.015(2)$, $b = 7.4216(6)$, $c = 10.304(1)$ Å; $\alpha = 90.45(1)$, $\beta = 100.29(2)$, $\gamma = 107.79(1)°$; $V = 358.5$ Å^3, $Z = 2$, $R = 0.028$, $R_w = 0.038$ for 1590 unique reflections with $I > 2.5\ \sigma(I)$. The structure contains layers of antimony molybdate with the potassium cations between the layers. Each layer is built up from strongly distorted MoO_6, MoO_5, and SbO_6 polyhedra and consists of two types of chains parallel to the a-axis. Sb_2O_{10} dimers, formed by two edge-sharing SbO_6 polyhedra, are connected by MoO_5 groups to form chains. The other type of chains is constructed from skew edge-shared MoO_6 octahedra, which are linked through Sb_2O_{10} dimers such that layers in the (010) plane are formed. Each K^+ cation is coordinated by nine oxygen atoms in a geometry of tricapped trigonal prism. © 1990 Academic Press, Inc.

Introduction

As a part of search for new mixed frameworks built up from corner-sharing octahedra and tetrahedra, we recently reported a new vanadium(III) molybdate, $CsV(MoO_4)_2$ (*1*). Structural study using single-crystal X-ray diffraction method revealed that $CsV(MoO_4)_2$ consisted of layers of corner-sharing $V(III)O_6$ octahedra and $Mo(VI)O_6$ tetrahedra with the Cs^+ cations located between the layers. The structure of $CsV(MoO_4)_2$ has the highest possible symmetry of the layers and belongs to the first structural type of the $AM(XO_4)_2$-layered phases according to the classification by Oyetola *et al.* (*2*). In the other structural types the layers are distorted due to a rotation of the XO_4 tetrahedra around an axis either parallel or perpendicular to the layers.

Since the lone-pair of electrons of Sb(III) often leads to very distorted coordination polyhedron, we undertook a synthetic and structural study on the molybdates of antimony. The present paper expands on our early work and describes the synthesis and crystal structure of $KSbMo_2O_8$, a compound whose composition appears similar to that of $CsV(MoO_4)_2$ but whose structure, though layer-like, is markedly different. The differences in structure may be correlated with the stereochemically active lone-pair of Sb(III).

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Experimental

Synthesis

Sb_2O_3 (99.9%), K_2MoO_4 (99.9%), and MoO_3 (99.9%) were obtained from Cerac Inc. Because K_2MoO_4 is hygroscopic, loading of the reactants was carried out in a glovebox which was flushed with nitrogen. Air-stable, yellow crystals of $KSbMo_2O_8$ were obtained by heating a pressed pellet of Sb_2O_3, K_2MoO_4, and MoO_3 (mole ratio 1 : 1 : 3) in a sealed silica ampoule at 490°C for 8 hr followed by slow cooling. The bulk product was checked for purity by means of powder X-ray diffraction by using a Rigaku powder diffractometer with filtered copper radiation. The diffraction pattern corresponded well with that calculated from the single-crystal data.

Single-Crystal X-Ray Structure Determination

A yellow crystal having the dimensions 0.44 × 0.05 × 0.06 mm was selected for indexing and intensity data collection on an Enraf–Nonius CAD4 diffractometer at room temperature. The orientation matrix and unit cell parameters were determined by least-squares fit of 25 peak maxima with $17 < 2\theta < 37°$. The intensity data were corrected for absorption, Lorentz, and polariztion effects. Corrections for absorption effects were based on ψ scans of a few suitable reflections with χ values close to 90° (*3*). Based on statistical analysis of intensity distribution and successful solution and refinement of the structure, the space group was determined to be $P\bar{1}$. The structure was solved by direct methods using SHELXTL-Plus programs (*4*) and refined by full-matrix least-squares refinement based on F values. The multiplicities of the K, Sb, and Mo atoms were allowed to refine but did not deviate significantly from full occupancy. Therefore, the metal atom sites were considered fully occupied in the final cycles of least-squares refinement.

TABLE I

CRYSTAL DATA, INTENSITY MEASUREMENT, AND REFINEMENT PARAMETERS FOR $KSbMo_2O_8$

Crystal data	
Space group	$P\bar{1}$
a	5.015(2) Å
b	7.4216(6) Å
c	10.304(1) Å
α	90.45(1)°
β	100.29(2)°
γ	107.79(1)°
V	358.5 Å^3
Z	2
D_x	4.453 g/cm^3
Linear absorption coefficient	77.2 cm^{-1}
Intensity measurement	
λ (Mo$K\alpha$)	0.70930 Å
2θ range	4.0 to 55.0°
Scan type	θ–2θ
Scan speed	5.5°/min
Scan width	0.65° + 0.35° tan θ
Standard reflections	$\bar{1}31$, $13\bar{5}$, $14\bar{2}$ (measured every 1 hr. no decay)
No. of unique reflections measured	1843
Structure solution and refinement	
No. of reflections included	1590 ($I > 2.5\ \sigma(I)$)
No. of parameters refined	110
R(F)	0.028
R_w(F)	0.038
Goodness-of-fit	2.10
Largest difference peak	1.87 e/Å^3
Largest difference hole	−2.90 e/Å^3

Crystal data, intensity measurement, and structure refinement parameters are collected in Table I. Table II contains the final atomic coordinates and thermal parameters. Selected bond distances and angles are given in Table III. Tables of observed and calculated structure factor amplitudes are available on request from the authors.

Description of the Structure and Discussion

A view of the structure along [100] is shown in Fig. 1. It has a layer structure with the potassium cations between the layers. Linkages between the adjacent layers

TABLE II

ATOMIC COORDINATES AND THERMAL PARAMETERS FOR $KSbMo_2O_8$

Atom	x	y	z	B(iso) (Å^2)[a]
K	0.40273(22)	0.03602(15)	0.31144(9)	1.64(4)
Sb	0.05281(6)	0.47011(4)	0.19223(3)	0.969(15)
Mo(1)	0.21191(7)	0.36463(5)	0.54004(3)	0.684(16)
Mo(2)	0.35783(8)	0.24446(5)	0.92693(4)	0.905(17)
O(1)	0.3589(6)	0.7079(4)	0.1738(3)	0.96(11)
O(2)	0.3740(6)	0.4695(5)	0.3862(3)	1.09(12)
O(3)	0.2655(7)	0.1493(5)	0.5387(3)	1.30(12)
O(4)	0.1351(7)	0.3793(5)	0.7127(3)	1.27(12)
O(5)	0.1980(7)	0.4275(5)	0.9662(3)	1.09(12)
O(6)	0.5079(7)	0.8100(5)	0.9192(3)	1.61(14)
O(7)	0.8950(7)	0.9582(5)	0.1449(3)	1.65(13)
O(8)	0.1336(6)	0.6741(5)	0.5524(3)	1.24(12)

Table of anisotropic thermal parameters (Å^2 × 100)[b]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
K	2.41(5)	2.05(5)	1.71(5)	0.84(4)	0.01(4)	−0.08(4)
Sb	1.00(2)	1.14(2)	1.73(2)	0.49(1)	0.42(1)	0.20(1)
Mo(1)	0.67(2)	1.00(2)	1.00(2)	0.35(1)	0.20(1)	0.18(1)
Mo(2)	0.95(2)	1.30(2)	1.41(2)	0.56(2)	0.42(1)	0.24(1)
O(1)	0.95(14)	1.30(14)	1.43(14)	0.47(12)	0.16(11)	0.02(11)
O(2)	1.13(14)	1.94(16)	1.03(13)	0.52(12)	0.01(11)	0.04(12)
O(3)	1.71(15)	1.59(15)	1.88(15)	0.92(13)	0.28(12)	0.24(12)
O(4)	2.10(17)	2.24(16)	1.29(14)	1.44(14)	1.00(12)	0.50(12)
O(5)	1.32(14)	1.92(16)	1.22(14)	1.05(13)	0.08(11)	−0.01(12)
O(6)	1.63(16)	2.46(18)	2.20(16)	0.78(14)	0.55(13)	0.79(14)
O(7)	1.43(16)	1.68(16)	2.95(17)	0.36(13)	0.05(14)	0.21(14)
O(8)	0.80(14)	1.84(16)	2.01(15)	0.46(12)	−0.03(12)	−0.05(12)

[a] B(iso) is the mean of the principal axes of the thermal ellipsoid.

[b] Anisotropic temperature factors are of the form Temperature = $\exp[-2\pi^2(h^2U_{11}a^{*2} + \ldots + 2hkU_{12}a^*b^* + \ldots)]$.

are made via O–K–O bonds. Each layer is built up from Sb(III)–O and Mo(VI)–O polyhedra (see Fig. 2). Before describing how the polyhedra are connected in the layer, one needs to know the coordination number (CN) of each cation in $KSbMo_2O_8$. The CN can be determined by the maximum cation–anion distance, L_{max}, that will still be considered a bond according to Donnay and Allmann (5). In the meantime one must also check the agreement with the valence sum rule by using the bond valence–bond length relationship. In the case of Mo(VI), Donnay and Allmann give 2.70 Å for L_{max}. Accordingly, Mo(1) is coordinated by six oxygen atoms at distances ranging from 1.700(3) to 2.451(3) Å. The Mo(1)–O bond distances can be divided into three different groups: two short distances at 1.700(3) and 1.759(3) Å, three medium ones at 1.895(3), 1.968(3), and 2.065(3) Å, and a very long one at 2.451(3) Å. The longest and shortest Mo(1)–O bonds are *trans* to each other (see Fig. 3). The shortest bond involves the oxygen atom, O(3), which is bonded to one Mo(1) and two K atoms. The sum of the bond valences for Mo(1)–O bonds using the formula derived by All-

TABLE III

BOND DISTANCES (Å) AND ANGLES (°) FOR $KSbMo_2O_8$

	Bond distances		
K–O(1)*c*	2.738(3)	K–O(2)	3.354(3)
K–O(3)	2.750(3)	K–O(3)*a*	2.750(3)
K–O(4)*e*	3.395(3)	K–O(6)*d*	2.695(3)
K–O(7)*c*	3.414(3)	K–O(7)*g*	2.699(3)
K–O(8)*d*	2.781(3)	Sb–O(1)	1.990(3)
Sb–O(2)	2.333(3)	Sb–O(4)*k*	2.013(3)
Sb–O(5)*f*	2.606(3)	Sb–O(5)*k*	2.167(3)
Sb–O(6)*k*	2.961(3)	Mo(1)–O(2)	1.968(3)
Mo(1)–O(2)*d*	2.065(3)	Mo(1)–O(3)	1.700(3)
Mo(1)–O(4)	1.895(3)	Mo(1)–O(8)	2.451(3)
Mo(1)–O(8)*k*	1.759(3)	Mo(2)–O(1)*d*	1.856(3)
Mo(2)–O(4)	2.638(3)	Mo(2)–O(5)	1.850(3)
Mo(2)–O(6)*o*	1.711(3)	Mo(2)–O(7)*d*	1.703(3)
	Bond angles		
O(1)–Sb–O(2)	81.4(1)	O(1)–Sb–O(4)*k*	89.8(1)
O(1)–Sb–O(5)*f*	73.7(1)	O(1)–Sb–O(5)*k*	83.7(1)
O(1)–Sb–O(6)*k*	148.6(1)	O(2)–Sb–O(4)*k*	91.0(1)
O(2)–Sb–O(5)*f*	118.6(1)	O(2)–Sb–O(5)*k*	160.4(1)
O(2)–Sb–O(6)*k*	129.8(1)	O(4)*k*–Sb–O(5)*f*	142.4(1)
O(4)*k*–Sb–O(5)*k*	76.2(1)	O(4)*k*–Sb–O(6)*k*	91.1(1)
O(5)*f*–Sb–O(5)*k*	68.7(1)	O(5)*f*–Sb–O(6)*k*	86.9(1)
O(5)*k*–Sb–O(6)*k*	66.3(1)	O(2)–Mo(1)–O(2)*d*	73.8(1)
O(2)–Mo(1)–O(3)	100.5(1)	O(2)–Mo(1)–O(4)	154.3(1)
O(2)–Mo(1)–O(8)	81.8(1)	O(2)–Mo(1)–O(8)*k*	89.8(1)
O(2)*d*–Mo(1)–O(3)	98.7(1)	O(2)*d*–Mo(1)–O(4)	88.0(1)
O(2)*d*–Mo(1)–O(8)	81.0(1)	O(2)*d*–Mo(1)–O(8)*k*	153.2(1)
O(3)–Mo(1)–O(4)	100.1(1)	O(3)–Mo(1)–O(8)	177.5(1)
O(3)–Mo(1)–O(8)*k*	105.2(1)	O(4)–Mo(1)–O(8)	77.4(1)
O(4)–Mo(1)–O(8)*k*	99.4(1)	O(8)–Mo(1)–O(8)*k*	75.6(1)
O(1)*d*–Mo(2)–O(4)	76.9(1)	O(1)*d*–Mo(2)–O(5)	122.1(1)
O(1)*d*–Mo(2)–O(6)*o*	108.6(1)	O(1)*d*–Mo(2)–O(7)*d*	105.3(1)
O(4)–Mo(2)–O(5)	67.7(1)	O(4)–Mo(2)–O(6)*o*	169.6(1)
O(4)–Mo(2)–O(7)*d*	80.4(1)	O(5)–Mo(2)–O(6)*o*	102.1(2)
O(5)–Mo(2)–O(7)*d*	111.8(1)	O(6)*o*–Mo(2)–O(7)*d*	106.0(2)

Note. Symmetry codes: (*a*) $1 - x, -y, 1 - z$; (*c*) $x, -1 + y, z$; (*d*) $1 - x, 1 - y, 1 - z$; (*e*) $-x, -y, 1 - z$; (*f*) $x, y, -1 + z$; (*g*) $-1 + x, -1 + y, z$; (*k*) $-x, 1 - y, 1 - z$; (*o*) $1 - x, 1 - y, 2 - z$.

mann (*6*) is 5.99, which is in excellent agreement with the formal oxidation state +6 for Mo(1). The $Mo(1)O_6$ polyhedron is strongly distorted and the octahedral distortion can be estimated by using the equation $\Delta = (1/6)\ \Sigma((R_i - \bar{R})/\bar{R})^2$, where R_i = an individual bond length and $\bar{R}$ = average bond length (*7*). The calculation result ($\Delta \times 10^4 = 156$) shows that the distortion is close to that in MoO_3 ($\Delta \times 10^4 = 151$). According to Shannon (*7*), the deviation of R_i from $\bar{R}$, for which a value of 1.920 Å has been calculated from a great number of structures, is proportional to Δ through an empirical coefficient, 3.73. We calculate $\bar{R}$ = 1.978 Å, very near the average observed value, 1.973 Å. Mo(2) is bonded to five O atoms at distances ranging from 1.703(3) to 2.638(3)

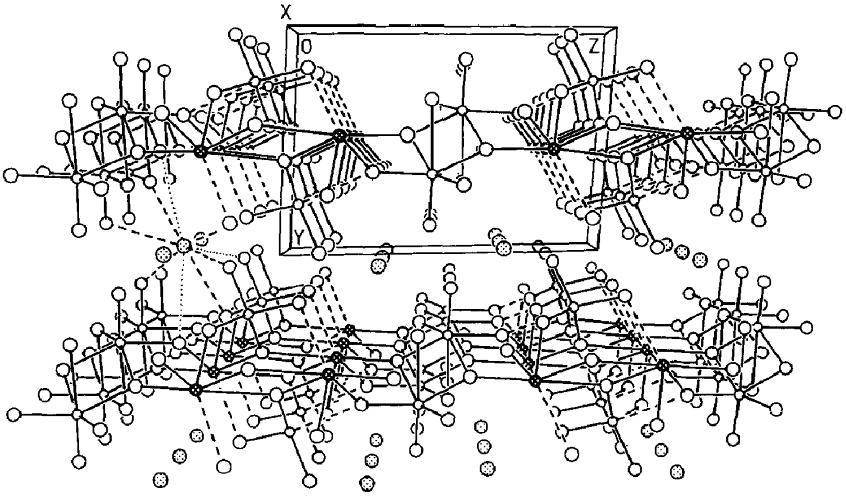

FIG. 1. A view of the structure of $KSbMo_2O_8$ along the *a*-axis. The K, Sb, Mo, and O atoms are represented by dotted, cross-hatched, and small and large open circles, respectively. The longest Sb–O and Mo(2)–O bonds are represented by dashed lines. The three longer K–O bonds are represented by dotted lines.

Å forming a drastically distorted polyhedron (see Fig. 4). The five Mo(2)–O bonds can also be divided into three groups: two short distances at 1.703(3) and 1.711(3) Å, two medium ones at 1.850(3) and 1.856(3) Å, and a very long one at 2.638(3) Å. The

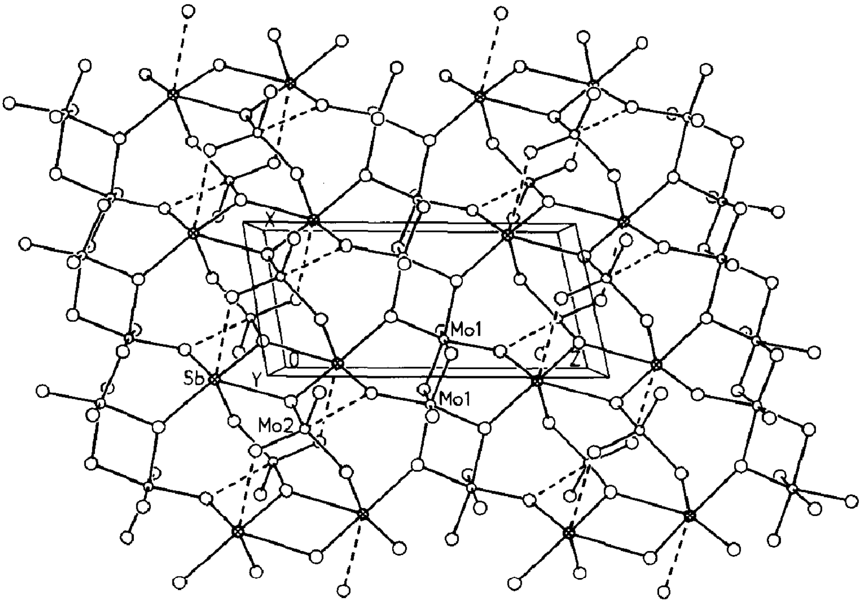

FIG. 2. A view of a layer in $KSbMo_2O_8$. The longest Sb–O and Mo(2)–O bonds are represented by dashed lines.

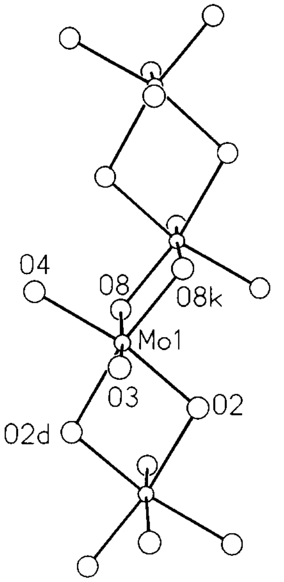

FIG. 3. A section of an infinite chain formed by Mo(1)O_6 octahedra sharing skew edges.

very large gap between the fifth bond (2.638(3) Å) and the fourth bond 1.856(3) Å) suggests that one may, as an approximation, consider the coordination of Mo(2) as four instead of five. However, the sum of the bond valences in this case is only 5.89 instead of 6.00 for five neighbors. The longest bond involves the oxygen atom, O(4), which is simultaneously bonded to Mo(1), Mo(2), Sb, and K atoms. The shortest bond involves the oxygen atom, O(7), which is bonded to one Mo(2) and two K atoms. According to the L_{max} (2.65 Å) for Sb(III)–O by Donnay and Allmann, the Sb atom in $KSbMo_2O_8$ is bonded to five oxygen atoms at distances ranging from 1.990(3) to 2.606(3) Å, forming a rather distorted square pyramid. It is noted that O(6) is situated at 2.961(3) Å from the Sb(III) ion in a position *trans* to the short axial bond, Sb–O(1) (see Fig. 4). The structure of the Sb–O polyhedron reflects the influence of the lone-pair of electrons on Sb(III). Bond valence sum of the five Sb–O bonds using the formula derived by Brown and Wu (*8*) is only 2.84 instead of 2.98 for six neighbors. According to the L_{max} for K–O (3.35 Å) the K^+ ion can be considered as being coordinated by six oxygen atoms with the K–O distances ranging from 2.695(3) to 2.781(3) Å in a geometry of distorted trigonal prism. Bond valence sum of the six K–O bonds using the formula by Allmann (*6*) is 0.93. Each K^+ cation is surrounded by three more oxygen atoms capping the three rectangular faces of a trigonal prism at 3.354(3)–3.414(3) Å (see Fig. 5). Bond valence sum of the nine K–O bonds is 1.05. Each K–O polyhedron shares four oxygen atoms, two O(3) and two O(7), with three adjacent K–O polyhedra. It is somewhat controversial as to how one should determine a CN in the case of Sb–O or K–O polyhedron. In the following we count an appropriate CN mainly on the basis of bond valence–bond length relationship. We conclude that each layer in $KSbMo_2O_8$ is built up from strongly distorted Mo(1)O_6, Mo(2)O_5, and SbO_6 polyhedra, and the K^+ cation is coordinated by nine oxygen atoms in a geometry of tricapped trigonal prism.

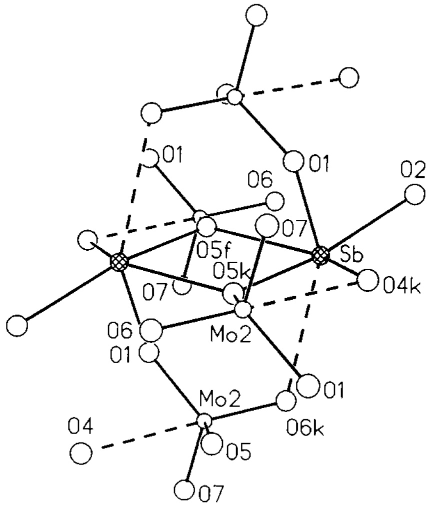

FIG. 4. A Sb_2O_{10} dimer with four surrounding Mo(2)O_5 polyhedra. The Sb–O(6) and Mo(2)–O(4) bonds are represented by dashed lines.

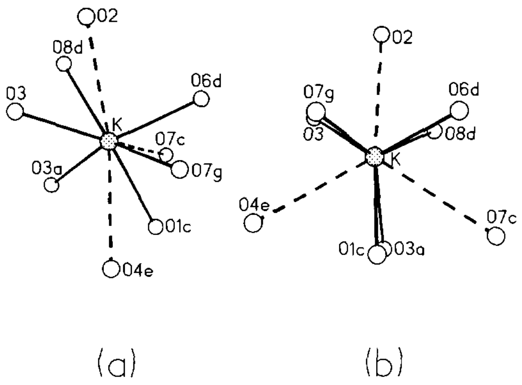

FIG. 5. The coordination of oxygen atoms around a K atom (a) in a direction nearly parallel to the *a*-axis and (b) showing the geometry of tricapped trigonal prism. The three longer K–O bonds are represented by dashed lines.

The Mo(1)O_6 octahedra share skew edges to form infinite chains parallel to the *a*-axis. Short (1.759(3) Å) and long (2.451(3) Å) Mo(1)–O bonds are involved in the unsymmetrical bridges between two Mo(1)O_6 octahedra. Two SbO_6 polyhedra share an edge to form a dimer with the two stereochemically active lone-pairs pointing in opposite directions. The bridges between two SbO_6 polyhedra are also unsymmetrical. Each Sb_2O_{10} dimer links two adjacent infinite chains by sharing four oxygen atoms with six Mo(1) atoms. Each Mo(2)O_5 group is bonded to a Sb(III) cation as a bidentate ligand and forms a bridge between two Sb(III) cations in an adjacent Sb_2O_{10} dimer with the fifth corner of the Mo(2)O_5 group, O(7), being coordinated only to K^+. Sb_2O_{10} dimers are connected by Mo(2)O_5 groups to form infinite chains running parallel to the *a*-axis. Chains of Mo(1)O_6 are connected through Sb_2O_{10} dimers such that layers of antimony molybdate in the *ac*-plane are formed. Adjacent layers are linked via O–K–O bonds.

To our knowledge, prior to this work no alkali metal antimony(III) molybdates were reported. Blasse and de Pauw reported two Sb(V) molybdates, $MSbMoO_6$ (M = Li, Na) (*9*), which adopt a structure of the columbite type. The compound $KSbMo_2O_8$ crystallizes in a new type of structure not previously encountered. This structural study also shows the great adaptability of Mo(VI)–O polyhedra in mixed frameworks. The synthesis from elements in place of K or Sb is under way and could generate novel frameworks.

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