

- Allmann, R. (1977). *Neues Jahrb. Mineral. Monatsh.* **3**, 136–144.
 Blessing, R. H. (1987). *Crystallogr. Rev.* **1**, 3–58.
 Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.
 Dowty, E. (1995). *ATOMS for Windows*. Version 3.1. Shape Software, 521 Hidden Valley Road, Kingsport, TN 37663, USA.
 Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
 Fischer, R. & Kuzel, H.-J. (1982). *Cem. Concr. Res.* **12**, 517–526.
 Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
 Johnson, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
 Sheldrick, G. M. (1997a). *SHELXS97. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
 Sheldrick, G. M. (1997b). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
 Tersis, A., Filippakis, S., Kuzel, H.-J. & Burzlaff, H. (1987). *Z. Kristallogr.* **181**, 29–34.

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V₂MnTeO₇

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Abstract

The title compound, divanadium manganese tellurite, V₂MnTeO₇, was obtained by hydrothermal methods. The structure of this compound is made up of slabs, running parallel to the *xy* plane, that contain TeO₃₊₁ units and MnO₆ octahedra, along with distorted VO₅ square pyramids and VO₆ octahedra. Examination of the metal environments and bond-valence-sum calculations show that this compound is an Mn^{II}/V^{IV}/Te^{IV} compound.

Comment

Recently, we have become interested in tellurium(IV) oxides due to their complex structures, as well as their potential as glass-forming materials (Stanworth, 1952). In our studies, we have explored the chemistry of first row transition metal tellurites, including the M₂Te₃O₈ series (Feger *et al.*, 1998), the mineral rodalquilarite, H₃Fe₂(TeO₃)₄Cl (Dusausoy & Protas, 1969; Feger & Kolis, 1998c), and two chloride compounds, Ba₂Cu₄Te₄O₁₁Cl₄ and BaCu₂Te₂O₆Cl₂ (Feger & Kolis, 1998b). With these results, and with the discovery of Na₃Mn₄Te₂O₁₂ (Feger & Kolis, 1998a), a Te^{VI} compound, we have decided to explore the chemistry of manganese tellurites further. We have previously isolated the known mineral spiroffite, Mn₂Te₃O₈, and recently we have attempted to add other unique building

blocks, such as vanadates, to influence the structure. This has led to the synthesis and characterization of the new compound, V₂MnTeO₇, the first transition metal vanadate–tellurite.

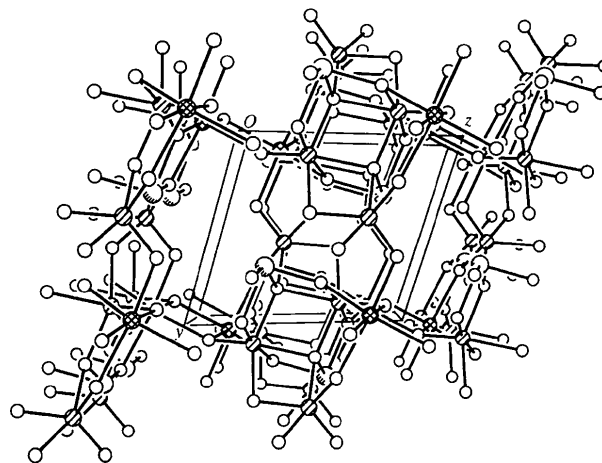


Fig. 1. Unit-cell view of V₂MnTeO₇ shown down the *x* axis. The striped spheres are V atoms, the cross-hatched spheres are Mn, the large shaded spheres are Te atoms, and the small open spheres are O atoms.

The structure of V₂MnTeO₇ is best viewed in terms of slabs running parallel to the *xy* plane (Fig. 1). These slabs are interconnected through Mn–O interactions, and can be further broken down into metal layers. Each slab consists of two of these layers containing the metal atoms, connected through O atoms. The metal coordination environments (Fig. 2) are typical, with the Mn atom in an octahedral environment, and the two V atoms in distorted octahedral and distorted square-pyramidal geometries. These V environments are both highly similar to those in the VTeO₄ phases, with the distorted octahedron of V1 nearly identical to

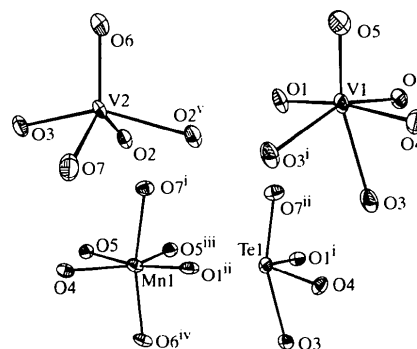


Fig. 2. Displacement ellipsoid plots of the four crystallographically distinct metal environments in V₂MnTeO₇, shown at the 70% probability level. Symmetry codes are as in Table 1.

that in α -VTeO₄ (Meunier *et al.*, 1972), and the V2 environment very similar to that in β -VTeO₄ (Meunier *et al.*, 1973). In addition, the V atoms both have typical vanadyl interactions with an O atom [V1—O5 = 1.668 (4) and V2—O6 = 1.641 (5) Å]. The Te atom sits within a TeO₃₊₁ fragment, which is also seen in several compounds, including Te₆O₁₁Cl₂ (Abriel, 1981) and CuTe₂O₅ (Hanke *et al.*, 1973).

In assigning oxidation states for the metal atoms, the O atoms were assumed to be -2 and the Te atoms were assumed to be tetravalent, due to the presence of a stereochemical lone pair in the TeO₃₊₁ environment. Using these assignments, there are ten positive charges which must be distributed over the remaining V and Mn atoms. The oxidation states of the remaining atoms were calculated through the use of bond-valence sums (Brown & Altermatt, 1985). This resulted in assignments of +2 for the Mn atom, and +4 for both crystallographically distinct V atoms. Calculations using other potential assignments resulted in either significantly overbonded or underbonded O atoms.

Experimental

Crystals of V₂MnTeO₇ were prepared from the hydrothermal reaction of V₂O₅ (79 mg, Strem, 99%), Mn₂O₃ (69 mg, Strem, 99%), and TeO₂ (69 mg, Strem, 99+%). The starting reagents were sealed in fused-silica tubing (1.6 ml sealed volume) with 0.7 ml 1 M aqueous NH₄Cl solution. The reaction tube was placed in a high-pressure autoclave, which was then pressurized with Ar gas to 17 000 kPa. The autoclave was then placed in a furnace and heated at 648 K. After the autoclave was removed from the furnace, the reaction products were filtered and washed with water and acetone. The title compound was obtained as air-stable red-brown blades in approximately 30% yield. Qualitative EDAX confirmed the presence of V, Mn, Te, and O, and the absence of impurities heavier than F.

Crystal data

V₂MnTeO₇
 $M_r = 396.42$
 Triclinic
 $P\bar{1}$
 $a = 6.712 (2) \text{ \AA}$
 $b = 6.892 (2) \text{ \AA}$
 $c = 7.855 (2) \text{ \AA}$
 $\alpha = 94.27 (2)^\circ$
 $\beta = 114.47 (2)^\circ$
 $\gamma = 114.79 (2)^\circ$
 $V = 286.4 (1) \text{ \AA}^3$
 $Z = 2$
 $D_x = 4.596 \text{ Mg m}^{-3}$
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.7107 \text{ \AA}$
 Cell parameters from 24 reflections
 $\theta = 9.6\text{--}16.7^\circ$
 $\mu = 10.34 \text{ mm}^{-1}$
 $T = 295.2 \text{ K}$
 Blade
 $0.31 \times 0.03 \times 0.02 \text{ mm}$
 Red-brown

Data collection

Rigaku AFC-7R diffractometer
 1154 reflections with $F > 2\sigma(F)$

ω - 2θ scans
 Absorption correction:
 empirical *via* ψ scans
 (North *et al.*, 1968)
 $T_{\min} = 0.04, T_{\max} = 0.81$
 1409 measured reflections
 1315 independent reflections

$R_{\text{int}} = 0.027$
 $\theta_{\max} = 27.54^\circ$
 $h = -7 \rightarrow 8$
 $k = -8 \rightarrow 8$
 $l = -7 \rightarrow 10$
 3 standard reflections
 every 100 reflections
 intensity decay: -0.19%

Refinement

Refinement on F
 $R = 0.028$
 $wR = 0.035$
 $S = 1.14$
 1154 reflections
 100 parameters
 $w = 1/[\sigma^2(F) + 0.0005F^2]$

$(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 1.53 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -1.22 \text{ e \AA}^{-3}$
 Extinction correction: none
 Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. Selected bond lengths (Å)

Te1—O1 ⁱ	1.916 (4)	V1—O2	1.950 (3)
Te1—O3	2.341 (6)	V1—O3	2.104 (4)
Te1—O4	1.866 (4)	V1—O3 ⁱ	1.964 (4)
Te1—O7 ⁱⁱ	1.940 (6)	V1—O4	2.095 (6)
Mn1—O1 ⁱⁱⁱ	2.147 (6)	V1—O5	1.668 (4)
Mn1—O4	2.118 (3)	V2—O2	1.931 (4)
Mn1—O5	2.326 (6)	V2—O2 ⁱ	1.963 (5)
Mn1—O5 ⁱⁱⁱ	2.101 (4)	V2—O3	1.959 (4)
Mn1—O6 ^{iv}	2.139 (5)	V2—O6	1.641 (5)
Mn1—O7 ^v	2.222 (5)	V2—O7	1.925 (5)
V1—O1	1.946 (6)		

Symmetry codes: (i) $-x, -y, 1-z$; (ii) $x-1, y, z$; (iii) $-1-x, -y, -z$; (iv) $-x, 1-y, 1-z$; (v) $1-x, 1-y, 1-z$.

The Te, Mn, and V atoms were located by direct methods, and the O atoms were located from progressive Fourier difference maps. After a reasonable model was reached, all atomic displacement parameters were refined anisotropically. The maximum and minimum residual density peaks were located 0.82 and 0.76 Å, respectively, from Te1.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1993). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXTL-Plus* (Sheldrick, 1990). Molecular graphics: *SHELXTL-Plus*.

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Supplementary data for this paper are available from the IUCR electronic archives (Reference: BR1206). Services for accessing these data are described at the back of the journal.

References

- Abriel, W. (1981). *Z. Naturforsch. Teil B*, **36**, 405–409.
 Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* **B41**, 244–247.
 Dusauroy, Y. & Protas, J. (1969). *Acta Cryst.* **B25**, 1551–1558.
 Feger, C. R. & Kolis, J. W. (1998a). *Acta Cryst.* **C54**, 1055–1057.
 Feger, C. R. & Kolis, J. W. (1998b). *Inorg. Chem.* Submitted.
 Feger, C. R. & Kolis, J. W. (1998c). *J. Solid State Chem.* Submitted.

- Feger, C. R., Schimek, G. L. & Kolis, J. W. (1998). *J. Solid State Chem.* Submitted.
- Hanke, K., Kupcik, V. & Lindqvist, O. (1973). *Acta Cryst.* **B29**, 963–970.
- Meunier, G., Darriet, J. & Galy, J. (1972). *J. Solid State Chem.* **5**, 314–320.
- Meunier, G., Darriet, J. & Galy, J. (1973). *J. Solid State Chem.* **6**, 67–73.
- Molecular Structure Corporation (1992). *MSC/AFC Diffractometer Control Software*. Version 4.3.0. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Molecular Structure Corporation (1993). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.6b. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Sheldrick, G. M. (1985). *SHELXS86. Crystallographic Computing 3*, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford University Press.
- Sheldrick, G. M. (1990). *SHELXTL-Plus*. Version 4.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Stanworth, J. E. (1952). *Nature*, **169**, 581–582.

minated by four O atoms in a Ψ -trigonal bipyramidal geometry. The Sb—O distances of 1.95 (1) (2 \times) and 2.17 (1) Å (2 \times) (Fig. 1) are in the range known for other Sb—O compounds [1.90 Å in Na₃SbO₃ (Stöver & Hoppe, 1980); 1.98 Å in cubic Sb₂O₃ (Svensson, 1974); 1.98 Å in orthorhombic Sb₂O₃ (Svensson, 1975)]. The two short Sb—O bonds in the equatorial position of the Ψ -trigonal bipyramid include an angle of 103.4 (3)°, whereas the O(equatorial)—Sb1—O(axial) angles deviate only slightly from 90°. The O—Sb—O angle involving the two axial ligands [161.0 (3)°] is appreciably smaller than 180°, in accordance with the Gillespie–Nyholm concept.

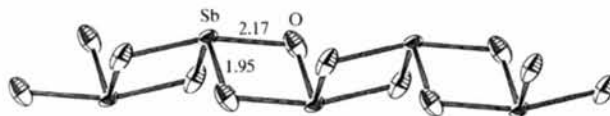


Fig. 1. View of the ∞ [SbO_{2/2}O'_{2/2}] chains (50% probability ellipsoids). Sb—O distances are given in Å.

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Caesium Dioxoantimonate(III), CsSbO₂

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Abstract

CsSbO₂ crystallizes in the monoclinic space group *C2/c*, is isotypic with NaBiO₂ and CsBiO₂, and contains infinite ∞ [SbO_{2/2}O'_{2/2}] chains running parallel to [001].

Comment

In the Cs—Sb—O system, the oxoantimonates(V) Cs₃SbO₄ (Duquenoy, 1974) and CsSbO₃ (Josien & Duquenoy, 1980) are known from X-ray powder investigations, but no structural parameters based on single-crystal data have been published until now. Whereas the complete series of alkali metal oxobismuthates(III) is known, the caesium oxoantimonate(III) CsSbO₂, which can be synthesized by reaction of Sb₂O₃ with elemental caesium, is the first Sb^{III} compound in the corresponding ternary Sb system to be characterized by single-crystal methods. It crystallizes in the monoclinic system with space group *C2/c* and is isotypic with the bismuthates(III) NaBiO₂ (Schwedde & Hoppe, 1972) and CsBiO₂ (Zoche & Jansen, 1997). In accordance with the lone pair of Sb^{III}, the Sb atoms are coor-

The SbO₄ Ψ -trigonal bipyramids are connected *via* common edges to form infinite ∞ [SbO_{2/2}O'_{2/2}] chains running parallel to the [001] direction. The chains form a hexagonal closed-rod packing.

Each Cs atom is coordinated by six O1 atoms in a distorted trigonal prismatic arrangement, with Cs—O distances ranging from 2.98 (1) to 3.38 (1) Å (Fig. 2). Their coordination polyhedra are connected *via* common edges to form chains running parallel to [101]; the

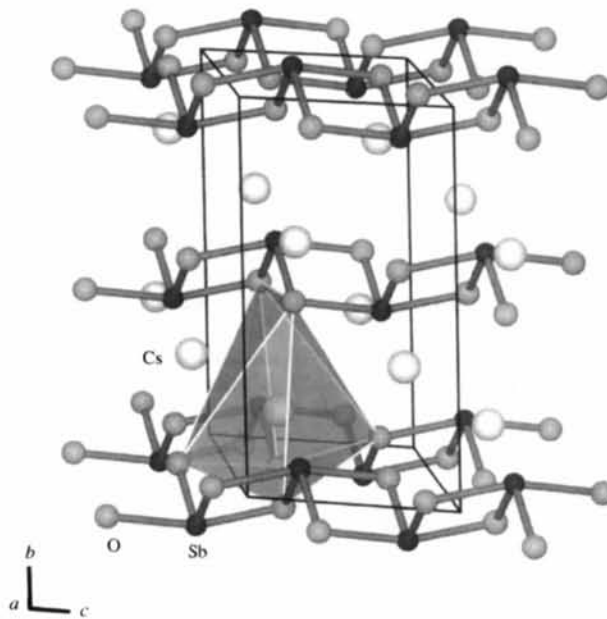


Fig. 2. The crystal structure of CsSbO₂ showing the caesium coordination polyhedron.