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The Thiotellurites $A_2Mn(TeS_3)_2$ (A = Cs, Rb): New Layered Solids Based on the Pyramidal TeS_3^{2-} Building Unit

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Introduction

A new trend in solid-state synthesis is to use milder synthetic conditions for the preparation of new materials with unusual structures and properties.[1] The recent application of molten polychalcogenide fluxes for both reagents and reaction media at intermediate temperatures ($200 < T < 500$ °C) proved to be a successful synthetic approach in such direction.[2–7] In our continued studies with mixed-polychalcogenide fluxes, we noticed the emergence of the TeS_3^{2-} fragment as a new and promising ligand with high multidenticity and bonding flexibility (like a polychalcogenide) as well as excellent thermal stability (more stable than polychalcogenide ligands).[7,8] For example, we recently discovered a new series of solids of the type $AMTeS_3$ (A = K, Rb, Cs; M = Cu, Ag), which feature TeS_3^{2-} in several bonding modes. Surprisingly, the coordination chemistry of this ligand in either soluble or solid-state compounds was unknown.[9–11] Since sulfur-rich $A_2S_xTe_y$ fluxes can reliably deliver a TeS_3^{2-} unit for coordination, we explored the reactivity of metals in such molten salts in order to obtain what would be termed thiotellurite compounds. Here we report two new compounds $Cs_2Mn(TeS_3)_2$ (**1**) and $Rb_2Mn(TeS_3)_2$ (**2**), which feature a new layered structure type based on TeS_3^{2-}.

Experimental Section

Chemicals in this work were used as obtained from commercial sources. Alkaline metal chalcogenides Rb_2S and Cs_2S were prepared in liquid ammonium from alkaline metals and chalcogen elements according to modified literature procedures.[3b,c,12] All manipulations were carried out in a glovebox under a nitrogen atmosphere.

Table 1. Crystallographic Data for $Cs_2Mn(TeS_3)_2$

formula	$Cs_2MnTe_2S_6$	space group	$P\bar{3}c1$ (No. 165)
fw	768.35	λ, Å	0.710 69
a, Å	6.974(2)	ρ_{calc}, g/cm^3	3.79
c, Å	15.896(3)	μ, cm^{-1}	113.3
V, Å^3	669.5(3)	R^a	0.026
Z	2	$R_w{}^b$	0.041

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Table 2. Positional Parameters and Equivalent Isotropic Thermal Parameters[a] for $Cs_2Mn(TeS_3)_2$ with Estimated Standard Deviations in Parentheses

atom	*x*	*y*	*z*	*B*(eq), Å^2
Cs	$^1/_3$	$^2/_3$	0.20311(6)	1.76(3)
Te	$^2/_3$	$^1/_3$	0.03892(6)	0.95(3)
Mn	0	0	0	0.96(8)
S	0.3257(5)	0.2055(4)	0.1077(2)	1.7(1)

[a] $B(\text{eq}) = {}^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Quantitative microprobe analysis was obtained with a JEOL JSM-35C scanning electron microscope (SEM) equipped with a Tracor northern energy dispersive spectroscopy (EDS) detector. UV/visible/near-IR diffuse reflectance spectra were measured at room temperature on a Shimadzu UV-3101PC double-beam, double-monochromator spectrophotometer. $BaSO_4$ powder was used as reference (100% diffuse reflectance). Spectra were processed as described elsewhere.[3b,c,7,8] Magnetic measurements were performed on a MPMS Quantum Design SQUID magnetometer.

Synthesis. $Cs_2Mn(TeS_3)_2$ (1). Amounts of 0.014 g (0.25 mmol) of Mn, 0.149 g (0.50 mmol) of Cs_2S, 0.064 g (2.0 mmol) of S, and 0.064 g (0.50 mmol) of Te were mixed and loaded into a Pyrex tube. The tube was evacuated to 10^{-4} Torr and sealed with a gas flame. It was then heated up to 270 °C in 12 h in a computer-controlled furnace and kept at constant temperature for an additional 4 days. Then, it was slowly cooled to 50 °C at a rate of 2 °C/h. Dark red crystals were obtained as a homogeneous product after isolation in DMF with a yield of 65% based on Mn. The crystals are relatively stable in moist air. An average composition of $Cs_{1.7}Mn_{1.0}Te_{2.1}S_{6.0}$ was found from EDS/SEM analysis of a large number of single crystals.

$Rb_2Mn(TeS_3)_2$ (2). Amounts of 0.014 g (0.25 mmol) of Mn, 0.102 g (0.50 mmol) of Rb_2S, 0.064 g (2.0 mmol) of S, and 0.064 g (0.50 mmol) of Te were used as described above. The reaction was held at 260 °C for 4 days. A red crystalline material was obtained in 80% yield. The compound reacts slowly with moist air, and the surface of the crystals gradually turns from red to black. An average composition of $Rb_{2.0}Mn_{1.0}Te_{2.2}S_{6.0}$ was found from EDS/SEM analysis.

X-ray Structure Determinations. Both compounds were examined by X-ray powder diffraction for the purpose of identification and phase purity. XRD data were recorded on a calibrated (with FeOCl as internal standard) Philips XRG-3000 computer-controlled powder diffractometer with Ni-filtered Cu Kα radiation operating at 35 kV and 35 mA. The powder diffraction patterns clearly show that the two compounds are isomorphous. The observed pattern of $Cs_2Mn(TeS_3)_2$ matches well with the calculated one based on the parameters obtained from the single-crystal structure analysis.[13a]

Single-crystal data for $Cs_2Mn(TeS_3)_2$ were collected on a Rigaku AFC6S diffractometer at 20 °C to a $2\theta_{max}$ of 50° using graphite-monochromated Mo Kα radiation. A total of 932 reflections were collected, with 510 of them independent and 269 observed with $F_o^2 > 3\sigma(F_o^2)$. The crystal showed no significant intensity decay upon monitoring three check reflections periodically throughout data collection. Systematic absences and intensity statistics identified the space group as $P\bar{3}c1$ (No. 165). The structure was solved by direct methods from SHELXS-86[13b] and refined with the TEXSAN[13c] package of crystallographic programs. An empirical absorption correction based on a ψ scan was applied to the data, followed by a DIFABS[13d] correction to the

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[†] A. P. Sloan Foundation Fellow, 1991–1993, and Camille and Henry Dreyfus Teacher Scholar, 1993–1995.

(1) Stein, A.; Keller, S. W.; Mallouk, T. E. *Science* **1993**, *259*, 1558–1564.
(2) Kanatzidis, M. G. *Chem. Mater.* **1990**, *2*, 353–363.
(3) (a) Kanatzidis, M. G.; Park, Y. *J. Am. Chem. Soc.* **1989**, *111*, 3767–3769. (b) Liao, J.-H.; Varotsis, C.; Kanatzidis, M. G. *Inorg. Chem.* **1993**, *32*, 2453–2462. (c) McCarthy, T. J.; Ngeyi, S.-P.; Liao, J.-H.; DeGroot, D. C.; Hogan, T.; Kannewurf, C. R.; Kanatzidis, M. G. *Chem. Mater.* **1993**, *5*, 331–340.
(4) (a) Dhingra, S.; Kanatzidis, M. G. *Science* **1992**, *258*, 1769–1772. (b) Park, Y.; Kanatzidis, M. G. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 914–915.
(5) (a) Park, Y.; DeGroot, D. C.; Schindler, J.; Kannewurf, C. R.; Kanatzidis, M. G. *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1325. (b) Park, Y.; Kanatzidis, M. G. *Chem. Mater.* **1991**, *3*, 781. (c) Zhang, X.; Park, Y.; Kanatzidis, M. G. Manuscript in preparation.
(6) (a) Sunshine, S. A.; Kang, D.; Ibers, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 6202–6204. (b) Kang, D.; Ibers, J. A. *Inorg. Chem.* **1988**, *27*, 549–551. (c) Keane, P. M.; Ibers, J. A. *Inorg. Chem.* **1991**, *30*, 1327–1329. (d) Keane, P. M.; Lu, Y.-J.; Ibers, J. A. *Acc. Chem. Res.* **1991**, *24*, 223–229.
(7) McCarthy, T.; Zhang, X.; Kanatzidis, M. G. *Inorg. Chem.* **1993**, *32*, 2944–2948.
(8) Zhang, X.; Kanatzidis, M. G. *J. Am. Chem. Soc.*, in press.
(9) Jumas, J.-C.; Bibes, M.; Maurin, M.; Philippot, E. *Acta. Crystallogr.* **1976**, *32B*, 444–448.
(10) Dittmar, G.; Schäfer, H. *Z. Anorg. Allg. Chem.* **1978**, *439*, 212–218.
(11) Gerl, H.; Eisenmann, B.; Roth, P.; Schäfer, H. *Z. Anorg. Allg. Chem.* **1974**, *407*, 135–143.
(12) (a) Klemm, W; Sodomann, H.; Langmesser, P. *Z. Anorg. Allg. Chemie*, **1939**, *241*, 281–304. (b) Feher, F. In *Handbuch der Praparativen Anorganischen Chemie*; Brauer, G., Ed.; Ferdinand Enke: Stuttgart, Germany, 1954; pp 280–281.
(13) (a) CERIUS Version 3.2, Molecular Simulations, 1993. (b) Sheldrick, G. M. In *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C., Goddard, R., Eds.; Oxford University Press: Oxford, U.K., 1985; pp 175–189. (c) TEXSAN-TEXRAY Structure Analysis Package, Molecular Structure Corp., 1985. (d) Walker, N.; Stuart, D. *Acta. Crystallogr.* **1983**, *A39*, 158–166.

0020-1669/94/1333-1238$04.50/0

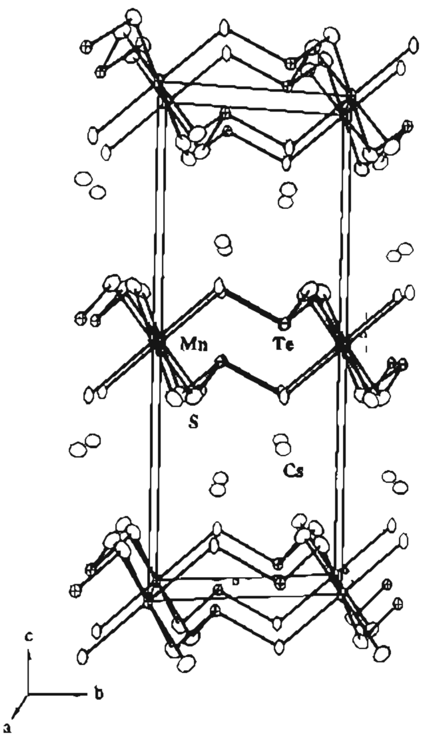
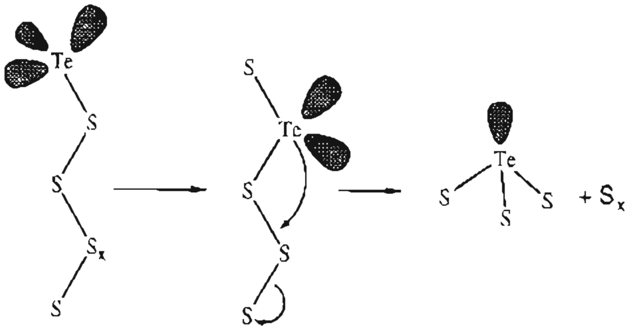


Figure 1. Unit cell of $Cs_2Mn(TeS_3)_2$ viewed down the *a*-axis. Cs^+ cations are between the layers.

Scheme 1



isotropically refined data. All atoms were eventually refined anisotropically. No extincion correction was applied. The crystallographic data and information of refinement are listed in Table 1. Atomic parameters with their estimated standard deviations are given in Table 2. Only cell parameters were determined for $Rb_2Mn(TeS_3)_2$ at −100 °C: $a = 6.910(2)$ Å, $c = 15.246(4)$ Å, $V = 630.4(4)$ Å^3.

Results and Discussion

Both compounds were synthesized from the reactions of Mn powder with A_2S_5Te in a 1:2 molar ratio. This proportion of Mn to flux is essential to avoid MnS_2 impurity. The temperature window, within which compounds **1** and **2** can be prepared in the flux, is relatively narrow, as they start to decompose to MnS_2 above 300 °C. The molten alkali metal polysulfide/telluride A_2TeS_n fluxes form readily from the fusion of alkali metal sulfide, elemental tellurium, and sulfur. Unlike a single polychalcogenide flux, such S-rich mixed fluxes favor the formation of pyramidal TeS_3^{2-} via the internal redox chemistry as illustrated in Scheme 1. The electron transfer between Te and S–S bonds is due to the large electronegativity difference between S and Te. The use of hetero-polychacogenide molten salts for chemical synthesis is an interesting departure from the more common homo-polychalcogenides and promises to afford new solids based on new building blocks. For example, solid-state metal thiotellurites represent an entirely new class of solids, akin to the mineral sulfo salts, accessible in this fashion.

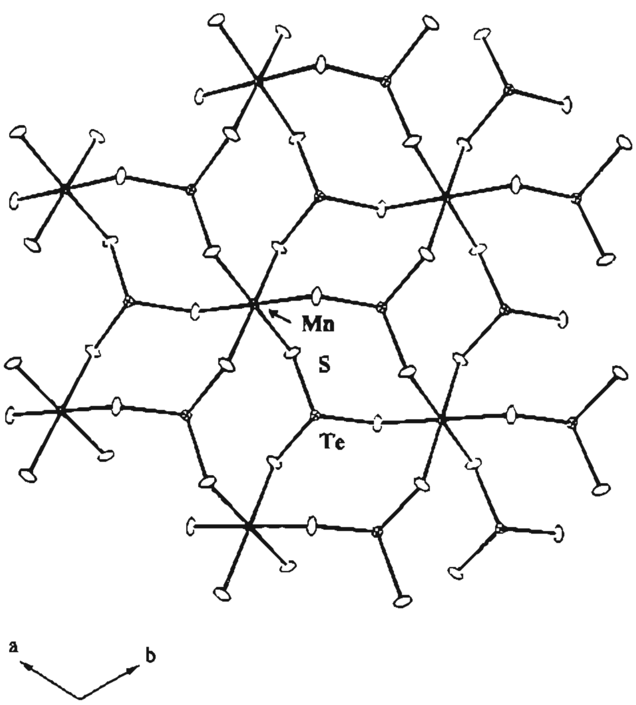


Figure 2. Structure and labeling scheme of one $[Mn(TeS_3)_2]_n^{2n-}$ layer viewed down the *c* axis.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for $Cs_2Mn(TeS_3)_2$ with Estimated Standard Deviations in Parentheses

Mn–S	2.624(3)	S–Mn–S	82.06(8)
Te–S	2.351(3)	S–Mn–S′	97.94(8)
Cs–S	3.532(3)	S–Mn–S′′′	180.0
Cs–S′	3.657(3)	S–Te–S	100.1(1)
Cs–Te	3.847(2)	Cs–Te–S	117.71(7)
		Mn–S–Te	109.8(1)

The structure of $Cs_2Mn(TeS_3)_2$ is shown in Figure 1. The anionic $[Mn(TeS_3)_2]_n^{2n-}$ layers are relatively flat and lie perpendicular to the *c* axis. They are separated by a bilayer of Cs^+ cations. Figure 2 shows the structure of one layer composed of octahedrally coordinated Mn^{2+} centers and TeS_3^{2-} pyramids. The MnS_6 octahedra share all the corners with neighboring TeS_3^{2-} pyramids and vice versa. The Mn atoms sit on centers with $\bar{3}$ symmetry and are located at the center of the layer. The shortest Mn···Mn distance is 6.974(2) Å. All Mn–S distances are equivalent at 2.624(3) Å, which is typical for six-coordinated Mn–S compounds. The S–Mn–S angles indicate a distorted coordination sphere of Mn from an ideal octahedron toward an elongated trigonal antiprism. This distortion can be attributed to the ionic interaction between the Cs^+ ions and S atoms which are located at the boundaries of the layers. Each Cs^+ cation is surrounded by six S atoms and one Te atom within a radius of 3.9 Å. In TeS_3^{2-}, the Te–S distance of 2.351(3) Å and S–Te–S angle of 100.1(1)° are similar to what has been observed in all previously known TeS_3^{2-} compounds and suggest a quite rigid unit.[7-11] This ligand bridges three Mn^{2+} ions, a bonding mode which had been previously seen only in $CsCuTeS_3$.[8] On the basis of a formal charge of +4 for Te, there is one lone pair of electrons presumably occupying the tip of the pyramid. Unlike those in other TeS_3^{2-} compounds, the Cs–Te distance of 3.847(2) Å in this structure falls in the range 3.7–4.2 Å for typical Cs–Te ionic distances.[5c,14] The selected bond distances and angles are listed in Table 3.

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(14) (a) Prins, C.; Cordfunke, E. H. P. *J. Less-Common Met.* **1984**, *104*, L1–L3. (b) Böttcher, V. P.; Kretschmann, U. *Z. Anorg. Allg. Chem.* **1982**, *491*, 39–46. (c) Böttcher, V. P.; Kretschmann, U. *Z. Anorg. Allg. Chem.* **1985**, *523*, 145–152.

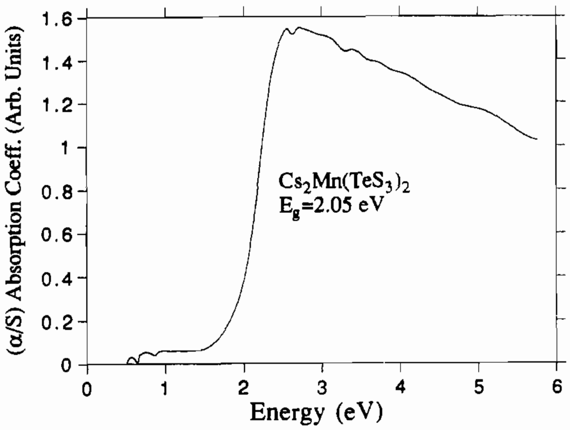

Figure 3. Optical absorption spectrum of $Cs_2Mn(TeS_3)_2$.

If we simplify the TeS_3^{2-} group as one hypothetical atom L, the $[MnL_2]_n^{2n-}$ layer is related to that of CdI_2.[15] It is noteworthy that the structure of $MnSO_3{\cdot}3H_2O$,[16] which contains one-dimensional ribbons resembling a piece cut out of a $[Mn(TeS_3)_2]_n^{2n-}$ layer. Of course TeS_3^{2-} and SO_3^{2-} are isoelectronic.

Both $Cs_2Mn(TeS_3)_2$ and $Rb_2Mn(TeS_3)_2$ are found to be wide-band-gap semiconductors from the study of their optical absorption spectra which are obtained from solid-state UV/vis/near-IR diffuse reflectance measurements. Figure 3 shows the spectrum of $Cs_2Mn(TeS_3)_2$, which reveals a band-gap of 2.05 eV. The band-gap was estimated from extrapolation of the absorption edge on the energy axis in an $(\alpha/s)^2$ vs E plot. Electronic excitation across the gap is expected to be S-to-Mn charge-transfer in character.

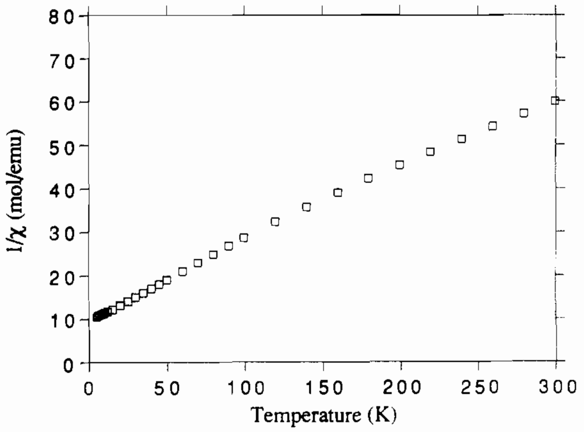

Figure 4. Variable-temperature magnetic susceptibility data, plotted as $1/\chi$ vs T, for polycrystalline $Cs_2Mn(TeS_3)_2$. The applied field was 2000 G. The magnetic moment varies linearly with the applied field up to 20 000 G.

$Cs_2Mn(TeS_3)_2$ is paramagnetic, nearly obeying the Curie–Weiss law over the temperature range 5–300 K. Figure 4 shows the reciprocal of molar susceptibility plotted vs temperature. The Θ value (Weiss temperature) is found to be −54.4 deg, suggesting weak antiferromagnetic interactions. The estimated μ_{eff} value of 6.6 μ_B from the magnetic data is slightly higher than the ideal 5.9 calculated for high-spin Mn^{2+} ions.

In conclusion, two new layered quaternary manganese thiotellurites have been prepared from a S-rich mixed molten polysulfide/telluride flux. The stabilization of this ligand in the flux, its expected high affinity for metal ions, and its high multidenticity indicate a great potential for new solid-state chemistry of a newly emerging class of compounds, the transition metal thiotellurites.

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Supplementary Material Available: Tables giving crystal data and details of the structure determination, atom coordinates, anisotropic thermal parameters of all atoms, and calculated and observed X-ray powder diffraction patterns for $Cs_2Mn(TeS_3)_2$ (3 pages). Ordering information is given on any current masthead page.

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(15) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon Press: Oxford, U.K., 1984; pp 258–260.

(16) Gmelin, L. *Handbuch der Anorganischen Chemie*; Springer-Verlag: Berlin, 1976; System Number 56, Part C6, pp 77–78.

Additions and Corrections

1993, Volume 32

Joydip Chakravarty, Somnath Dutta, Swapan Kumar Chandra, Partha Basu, and Animesh Chakravorty*: Chemistry of Variable-Valence VO^{z+} (z = 2, 3) Complexes: Synthesis, Structure, and Metal Redox of New $V^{V}O(ONO)(ON)$ and $V^{IV}O(ONO)(NN)$ Families.

Page 4252. In the caption to Figure 5a, two compounds are misidentified. The correct compounds are as follows: (ii) VO(azc)(bpy); (iii) VO(amp)(hq).