

Table I. Crystal Data for  $\text{SnMo}_6\text{S}_{8-x}$ 

nominal $x$	$a$ , Å	$c$ , Å	$c/a$	impurity
0	9.174 (1)	11.367 (3)	1.2391 (5)	$\text{Mo}_2\text{S}_3$
0.5	9.175 (4)	11.395 (3)	1.2419 (9)	Mo
1.0	9.180 (13)	11.395 (11)	1.241 (3)	Mo
1.5	9.175 (3)	11.395 (3)	1.2420 (7)	Mo + unidentifiable phase
2.0	9.176 (2)	11.397 (4)	1.2420 (7)	Mo + unidentifiable phase

Table II. Superconductivity Data for  $\text{SnMo}_6\text{S}_{8-x}$ 

nominal $x$	$c/a$	$T_c$ , K	$\Delta T_c$ , K
0	1.2391	11.25	1.32
0.5	1.2419	13.56	1.51
1.0	1.2423	13.48	1.49
1.5	1.2420	13.32	1.64
2.0	1.2420	14.46	1.18

the  $\bar{3}$  axis which is the body diagonal of the ternary element cube.

Though the materials are rhombohedral (the rhombohedral angle rarely deviates more than a degree from  $90^\circ$ ), they may also be indexed hexagonally. In Figure 1, the hexagonal  $c$  unit vector goes from the origin at atom 0 to atom 1 and coincides with the  $\bar{3}$  axis. The two  $a$  unit vectors are perpendicular to  $c$  along the face diagonals of adjacent unit cells, from the origin to atom 2 and atom 3.

Sergent and co-workers<sup>8</sup> found that the transition temperatures of different  $\text{PbMo}_6\text{S}_8$  samples approached a similar value as the annealing time at  $1100^\circ\text{C}$  was increased. The  $\text{SnMo}_6\text{S}_{8-x}$  samples discussed here were quenched after a single heat treatment without annealing in hopes of freezing samples far off stoichiometry. The products were visually inhomogeneous. All but  $\text{SnMo}_6\text{S}_8$  contained massive silver-white crystals, as well as the gray-black powders characteristic of the Chevrel phases. Debye-Scherrer X-ray photographs demonstrated that the silver-white crystals were molybdenum. Evidently the reaction conditions cause the fine Mo powder to form macroscopic crystals.

The fine gray-black powders were separated from the excess molybdenum and analyzed via X-ray diffraction. In each case, in addition to the desired phase, one or more impurity phases were detected. Table I lists the observed hexagonal lattice parameters as well as the impurities observed.

It is quite apparent that the listed stoichiometries are only nominal and the Chevrel phase composition is quite different. The  $a$  parameter is constant within experimental error. The  $c$  parameter increases as the nominal composition changes from  $\text{SnMo}_6\text{S}_8$  to  $\text{SnMo}_6\text{S}_{7.5}$ , and then it remains constant. The increase in  $c$  suggests that vacancies are introduced in the special-position sulfur sites on the  $\bar{3}$  axis. The fact that  $a$  remains constant suggests that there is no change in the occupancy of the general-position sulfur sites off the  $\bar{3}$  axis.

The observed superconducting critical temperatures and the associated ranges are listed with the corresponding  $c/a$  ratios in Table II. It is gratifying to note that the transition temperature is pushed up 2-3 K when the phase is driven off stoichiometry. The value found for the last sample (14.46 K) is the highest  $T_c$  for a tin molybdenum sulfide yet reported.

The fact that the lattice parameters and transition temperatures are unchanged beyond  $\text{SnMo}_6\text{S}_{7.5}$ , and the presence of substantial quantities of unreacted molybdenum in the products, suggests that a phase boundary has been reached.

The width of the transition in these materials is a source of concern. The width is generally 20 times broader than the transition in niobium metal measured on the apparatus described above ( $\Delta T_c = 0.060$  K for Nb). The presence of the impurity phases suggests that the problem may arise from inhomogeneity in the Chevrel phase. The lattice parameters presented here, on the other hand, are among the most precise data published for powder ternary molybdenum chalcogenides. Furthermore, the  $\text{PbMo}_6(\text{S}_{1-x}\text{Se}_x)_8$  series, which we have also studied, show no contamination, yet the samples still exhibit broad transitions.

### Summary

The series of materials  $\text{SnMo}_6\text{S}_{8-x}$  has been synthesized from the elements and investigated by X-ray diffraction and superconducting critical temperature. The crystal data suggest that the special-position chalcogen sites on the  $\bar{3}$  axis are chemically different from the other chalcogen sites. On going off stoichiometry, sulfur vacancies appear to be introduced on the special-position sites. The  $c/a$  ratio increases, and the superconducting critical temperature rises along with it. The phase boundary for  $\text{SnMo}_6\text{S}_{8-x}$  appears to be at  $\text{SnMo}_6\text{S}_{7.5}$ .

Registry No.  $\text{SnMo}_6\text{S}_8$ , 39432-50-3.

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### Crystal Data for Mixed-Anion Molybdenum Dichalcogenides

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The layered dichalcogenides<sup>1</sup>  $\text{MoS}_2$  and  $\text{MoSe}_2$  are of special interest as lubricants,<sup>2</sup> catalysts, and catalyst supports for hydrodesulfurization reactions,<sup>3</sup> precursors of intercalation superconductors,<sup>4</sup> and possible electrodes for photoelectrolysis.<sup>5</sup> In the pure, stoichiometric state they are moderate-gap semiconductors (1.75 eV for  $\text{MoS}_2$  and 1.4 eV for  $\text{MoSe}_2$ ),<sup>5</sup> presumably because the characteristic trigonal splitting of the d orbitals leads to filled d subbands. As part of a larger study on how small changes in chemical parameters affect superconductivity, we have had occasion to prepare the full solid solution series  $\text{MoS}_{2-x}\text{Se}_x$  ( $0 < x < 2$ ). The end compounds form both 2H and 3R polytypes. In each case, molybdenum atoms occupy trigonal-prismatic sites within the layers. In addition, in the system  $\text{MoS}_{2-x}\text{Se}_x$ , a continuous series of solid solutions can be prepared, all having the same 2H two-layer hexagonal structure (space group  $P6_3/mmc$ ). We report in this communication the evolution of lattice parameters of the mixed-anion system.

### Experimental Section

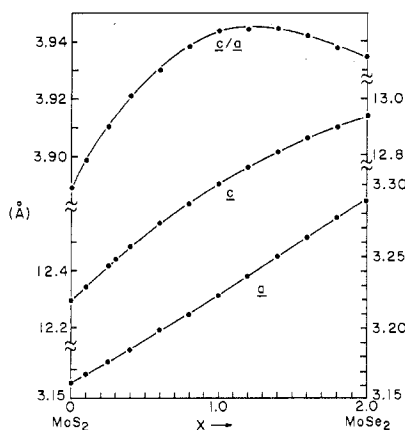
**Preparation of Samples.** A series of samples  $\text{MoS}_{2-x}\text{Se}_x$ , where  $x$  varied from 0 to 2, was prepared by direct reaction of stoichiometric

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Table I.  $\text{MoS}_{2-x}\text{Se}_x$  Crystal Data

compn	$a$ , Å	$c$ , Å	$c/a$	unit-cell vol, Å <sup>3</sup>
$\text{MoS}_2$	$3.1616 \pm 0.0005$	$12.2938 \pm 0.0052$	$3.885 \pm 0.0025$	106.42
$\text{MoS}_2^6$	3.1604	12.295	3.8819	
$\text{MoS}_{1.9}\text{Se}_{0.1}$	$3.1664 \pm 0.0003$	$12.3437 \pm 0.0015$	$3.8983 \pm 0.0008$	107.18
$\text{MoS}_{1.75}\text{Se}_{0.25}$	$3.1753 \pm 0.0002$	$12.4161 \pm 0.0018$	$3.9102 \pm 0.0008$	108.41
$\text{MoS}_{1.7}\text{Se}_{0.3}$	$3.1785 \pm 0.0003$	$12.4384 \pm 0.0010$	$3.9133 \pm 0.0007$	
$\text{MoS}_{1.6}\text{Se}_{0.4}$	$3.1837 \pm 0.0004$	$12.4831 \pm 0.0012$	$3.9209 \pm 0.0009$	109.58
$\text{MoS}_{1.4}\text{Se}_{0.6}$	$3.1972 \pm 0.0003$	$12.5640 \pm 0.0016$	$3.9297 \pm 0.0009$	111.22
$\text{MoS}_{1.2}\text{Se}_{0.8}$	$3.2080 \pm 0.0004$	$12.6328 \pm 0.0016$	$3.9379 \pm 0.0010$	112.59
$\text{MoS}_{1.0}\text{Se}_{1.0}$	$3.2219 \pm 0.0004$	$12.7053 \pm 0.0011$	$3.9434 \pm 0.0008$	114.22
$\text{MoS}_{0.8}\text{Se}_{1.2}$	$3.2354 \pm 0.0006$	$12.7607 \pm 0.0021$	$3.9441 \pm 0.0014$	115.68
$\text{MoS}_{0.6}\text{Se}_{1.4}$	$3.2462 \pm 0.0005$	$12.8154 \pm 0.0019$	$3.9442 \pm 0.0012$	116.95
$\text{MoS}_{0.4}\text{Se}_{1.6}$	$3.2627 \pm 0.0006$	$12.8612 \pm 0.0024$	$3.9419 \pm 0.0014$	118.57
$\text{MoS}_{0.2}\text{Se}_{1.8}$	$3.2766 \pm 0.0008$	$12.9013 \pm 0.0019$	$3.9374 \pm 0.0015$	119.95
$\text{MoSe}_2$	$3.2886 \pm 0.0012$	$12.9393 \pm 0.0084$	$3.9346 \pm 0.0040$	121.19
$\text{MoSe}_2^{14}$	$3.288 \pm 0.001$	$12.931 \pm 0.004$	$3.9328 \pm 0.0024$	

Figure 1. Variation of unit-cell parameters  $a$ ,  $c$ , and  $c/a$  with composition in the system  $\text{MoS}_{2-x}\text{Se}_x$ .

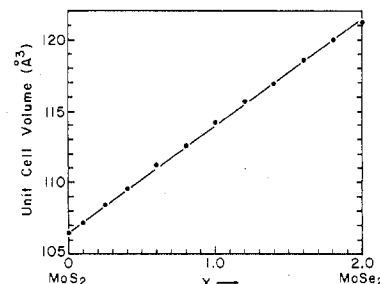
quantities of the elements in sealed, evacuated ( $<10^{-4}$  torr) silica tubes. Starting materials were 99.9% Mo powder (Alfa Inorganics), 99.9999% S (Atomergic Chemetals Co.), and 99.9% Se (Ventron Div., Alfa Products). Sample tubes were placed inside Kanthal coils and stacked in a box furnace. The temperature was raised to 900 °C over a period of 5 days. After 1 week at that temperature, samples were cooled to room temperature and shaken. Samples were then returned to the furnace for a second week at 900 °C. Wildervanck and Jellinek<sup>6</sup> had reported that prolonged heating at temperatures of at least 900 °C was necessary to produce a pure product. At the end of the second heating, samples were uniform, free-flowing powders.

**X-ray Investigation.** Powder X-ray patterns were made of each sample by using a Debye-Scherrer camera, diameter 114.6 mm, with nickel-filtered copper  $K\alpha$  radiation. Samples were not ground as this tends to destroy good layer-to-layer registry, leading to broadening of back reflection lines, but rather they were sieved through a no. 100 series mesh (0.149-mm opening) to facilitate capillary loading.

All lines on the diffraction patterns were read to 0.03 cm. Distances and angles were determined by the Straumanis method<sup>7</sup> which corrects for film shrinkage and errors in the camera radius. Lattice parameters were then determined by the method of Cohen's least squares for hexagonal systems<sup>8</sup> by using indexed, well-determined back reflection lines with  $\theta > 60^\circ$ .

## Results

Table I presents the results obtained for this system. All samples show a 2H structure. In all cases, all lines can be indexed on the basis of this structure. Spectra for  $\text{MoS}_2$  and  $\text{MoSe}_2$  agree very well with those reported for these compounds in the JCPDS powder files.

Figure 2. Variation of unit-cell volume with composition in the system  $\text{MoS}_{2-x}\text{Se}_x$ .

The dependence of  $a$ ,  $c$ , and  $c/a$  on  $x$  can be represented as follows:  $a$  (Å) =  $0.00371x^2 + 0.05691x + 3.1601$ ;  $c$  (Å) =  $-0.0865x^2 + 0.4924x + 12.297$ ;  $c/a$  =  $-0.0312x^2 + 0.0829x + 3.8907$ . As can be seen from Figure 1, the  $a$  parameter is nearly linear with  $x$ , the  $c$  parameter is parabolic, and the  $c/a$  ratio shows a clear maximum at  $x = 1.3$ , corresponding to  $\text{MoS}_{0.7}\text{Se}_{1.3}$ . Figure 2 shows the evolution of unit cell volume; it is essentially linear with  $x$ .

## Discussion

A study similar to this has been carried out<sup>9</sup> on the system  $\text{WS}_{2-x}\text{Se}_x$  materials which are isostructural with the molybdenum sulfoselenides. The variation of lattice parameters with  $x$  is nearly the same as seen in this study with allowances made for differences in the radii of molybdenum and tungsten. Indeed, the peak in  $c/a$  vs.  $x$  also occurs at  $x = 1.3$  in the tungsten series. Examination of other mixed-anion systems with layered structures (where materials are isostructural through the series), including  $\text{SnS}_{2-x}\text{Se}_x$ ,<sup>10</sup>  $\text{HfS}_{2-x}\text{Se}_x$ , and  $\text{TiS}_{2-x}\text{Se}_x$ ,<sup>12</sup> reveals that all have nonlinear variations in the  $c$  parameters vs.  $x$  leading to a peak in  $c/a$ .

There is general agreement that the nature of the bonding in molybdenum dichalcogenides is primarily covalent.<sup>13</sup> If a hard-sphere model applies, the unit-cell volume of  $\text{MoS}_{2-x}\text{Se}_x$  can be expressed as  $V = 2[V_{\text{Mo}} + (2-x)V_{\text{S}} + xV_{\text{Se}}]$ , implying a linear variation of unit-cell volume on composition. However, the observed value of  $dV/dx$ ,  $7.39 \text{ Å}^3$ , is almost twice as great as the value that would be predicted,  $4.53 \text{ Å}^3$ , by using standard covalent radii,  $1.17 \text{ Å}$  for  $\text{Se}^0$  and  $1.02 \text{ Å}$  for  $\text{S}^0$ , to calculate the atomic volumes. Clearly, the  $c$  axis is expanding faster than expected on a hard-sphere model. In going from

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MoS<sub>2</sub> to MoSe<sub>2</sub> the X-Mo-X sandwich thickness<sup>1</sup> changes hardly at all, viz., from 3.19 to 3.23 Å. However, the van der Waals gap between sandwiches increases significantly, i.e., from 2.96 for MoS<sub>2</sub> to 3.22 Å for MoSe<sub>2</sub>. Apparently, lone-pair repulsion across the van der Waals gap is greater between selenium atoms than between sulfur atoms, thus making the gap in MoSe<sub>2</sub> relatively wider. In the mixed solid solutions MoS<sub>2-x</sub>Se<sub>x</sub> it is believed that the first substitution of Se for S rapidly widens the gap but that subsequent replacement of more Se for S has less effect—hence, the peak in *c/a* vs. *x*. What remains a puzzle is how the peak in *c/a* affects the energy band structure. It is a curious fact that in the series 2H-MoS<sub>2-x</sub>Se<sub>x</sub> the end members are fine, dull-grey powders, whereas the middle members form sparkling, silver-grey microcrystallites. Unfortunately, it has so far been impossible to grow big enough crystals of the middle members to determine their electrical properties.

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**Registry No.** MoS<sub>2</sub>, 1317-33-5; MoSe<sub>2</sub>, 12058-18-3.

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**A New Route to Selenocarbonyl-Transition-Metal Complexes: Preparation of the (5,10,15,20-Tetraphenylporphinato)iron(II)-Selenocarbonyl Complex, Fe(TPP)(CSe), from the Carbenic Fe(TPP)(C(Cl)SeCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>) Complex**

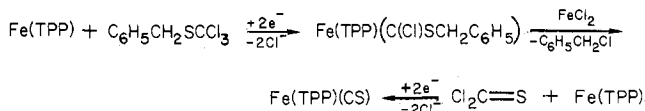
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The preparation of thiocarbonyl-iron(II) porphyrin complexes upon reduction of thiophosgene (Cl<sub>2</sub>CS) by iron(II) porphyrin in the presence of a reducing agent in excess has been reported.<sup>1,2</sup> More recently we have found a new indirect method<sup>3</sup> to prepare the same thiocarbonyl complexes by decomposition of the iron(II) porphyrin-carbene complexes obtained by reduction of benzyl trichloromethyl thioether (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>SCCl<sub>3</sub>) (Scheme I).

Whereas numerous examples of carbonyl- and thiocarbonyl-transition-metal complexes have been synthesized by different ways,<sup>4</sup> selenocarbonyl-metal complexes are still rare, and only few methods are available for their synthesis, probably because neither carbon monoselenide (CSe) nor selenophosgene (Cl<sub>2</sub>CSe) is stable.<sup>4</sup> Moreover very few carbene-transition-metal complexes with a selenium atom

**Scheme I**



directly bound to the carbenic carbon have been reported, and they have been prepared by indirect methods.<sup>5</sup>

This prompted us to try to prepare selenocarbonyl complexes by reduction of the readily available benzyl trichloromethyl selenoether (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>SeCCl<sub>3</sub>) by an iron(II) porphyrin, by analogy to Scheme I. This paper reports the isolation and characterization of the Fe(TPP)(C(Cl)SeCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sup>6</sup> and Fe(TPP)(CSe) complexes and compares their properties with those of the corresponding Fe(TPP)-carbonyl,<sup>7</sup> thiocarbonyl,<sup>1</sup> and -carbene<sup>8</sup> complexes.

Benzyl trichloromethyl selenoether is easily prepared by reaction between benzyl selenocyanate (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>SeCN) and chloroform in the presence of sodium hydroxide and a phase-transfer agent.<sup>9</sup> C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>SeCCl<sub>3</sub> (2 mmol) is added to a stirred benzene solution of Fe(TPP) (1 mmol) in the presence of an aqueous solution of sodium dithionite, as a reducing agent in excess, under argon. After 2-h reaction, washing with deaerated water, evaporation of solvents, and crystallization from benzene-pentane, a purple complex **I** is obtained (80% yield). All of its characteristics are in good agreement with the carbene-complex structure Fe(TPP)(C(Cl)SeCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>): elemental analysis (C, H, N, Cl);<sup>10</sup> electronic spectrum λ(C<sub>6</sub>H<sub>6</sub>) 411 nm (ε 2.2 × 10<sup>5</sup>), 521 (18 × 10<sup>3</sup>), and 548 (sh) similar to those of previously reported Fe(TPP)(carbene) complexes;<sup>8</sup> <sup>1</sup>H NMR δ (CDCl<sub>3</sub>, Me<sub>4</sub>Si, ppm) 8.70 (s, 8 H), 8.08 (m, 8 H), and 7.71 (m, 12 H) for the protons of the porphyrin ring and 6.88 (m, 3 H), 6.01 (m, 2 H), and 2.91 (s, 2 H) for the protons of the benzyl group; <sup>13</sup>C NMR δ (CDCl<sub>3</sub>, Me<sub>4</sub>Si, ppm) 144.8, 140.6, 132.2, 126.0, 125.3, 125.1, and 120.3 for the carbons of the porphyrin ring and two sharp, weak peaks at 38.1 and 265.1 corresponding respectively to the methylene and carbene carbons.<sup>11</sup> Complex **I** is a low-spin iron(II) complex as indicated by the positions and shapes of its <sup>1</sup>H NMR and <sup>13</sup>C NMR signals which are also indicative of an axial symmetry. Furthermore the pres-

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- This method of preparation is similar to that used for the analogous sulfur compounds: Makosza, M.; Fedoryński, M. *Synthesis*, **1974**, 274. C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>SeCCl<sub>3</sub>: bp 88 °C (12 mmHg); <sup>1</sup>H NMR δ (CDCl<sub>3</sub>, Me<sub>4</sub>Si, ppm) 7.45 (5 H), 4.65 (2 H); <sup>13</sup>C NMR δ (CDCl<sub>3</sub>, Me<sub>4</sub>Si, ppm) 134.0, 129.4, 128.7, 127.6, 77.7, 37.7; mass spectrum (70 eV, 140 °C) *m/e* 288 (for <sup>80</sup>Se and <sup>35</sup>Cl); elemental analysis (C, H, Cl). C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>SeCN is prepared from benzyl chloride and potassium selenocyanide in acetone: mp 78 °C; <sup>1</sup>H NMR δ (CDCl<sub>3</sub>, Me<sub>4</sub>Si, ppm) 7.50 (5 H), 4.18 (2 H); <sup>13</sup>C NMR δ (CDCl<sub>3</sub>, Me<sub>4</sub>Si, ppm) 135.3, 128.6, 128.3, 101.7, 32.9; mass spectrum (70 eV, 30 °C) *m/e* 197-195 with the good isotopic ratio for one selenium atom; elemental analysis (C, H, N).
- Actually the crystals were found to retain 1 mol of water, in agreement with <sup>1</sup>H NMR determination, even after 10 h under 10<sup>-2</sup> mmHg. Anal. Calcd for Fe(TPP)(C(Cl)SeCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)(H<sub>2</sub>O): C, 69.08; H, 4.12; N, 6.19; Cl, 3.92. Found: C, 69.32; H, 4.12; N, 6.12; Cl, 4.20.
- It is not possible to assign the phenyl carbon signals of the carbene ligand since they are superimposed with those of the porphyrin ring.