

Relationship between Superconductivity, Magnetic Susceptibility, and Crystal Structure in the Pseudobinary System $\text{PbMo}_6\text{S}_8\text{-PbMo}_6\text{Se}_8$ ¹

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Lead-molybdenum chalcogenides of the type $\text{PbMo}_6(\text{S}_{1-x}\text{Se}_x)_8$ have been synthesized from the elements across the entire solid-solution range from PbMo_6S_8 to PbMo_6Se_8 . Magnetic susceptibilities were measured by the Faraday method from 4.2 to 300 K. Superconducting critical temperatures were determined by an ac/mutual-inductance technique. All the susceptibilities show curious temperature dependences. With decreasing temperature the molar susceptibility of PbMo_6S_8 rises almost linearly from a value of 502×10^{-6} at room temperature to a maximum of 635×10^{-6} at about 35 K, after which it drops rather steeply to the superconducting state at 13.29 K. With PbMo_6Se_8 the susceptibility drops from 352×10^{-6} at room temperature to a minimum of 250×10^{-6} at about 30 K, after which it rises steeply to 300×10^{-6} just before going diamagnetic at the critical temperature of 3.89 K. Intermediate compositions generally (but not always) show both a minimum and a maximum. Extraction of the temperature-dependent parts leaves a zero-temperature susceptibility which correlates directly with the superconducting critical temperature. A previously noted linear relation between T_c and the crystallographic hexagonal c/a ratio is confirmed except for replacement of the last two sulfur atoms by selenium. Arguments are given for believing that selenium-for-sulfur substitution first occurs on general-position chalcogen sites and then on special-position sites on the $\bar{3}$ axis. Evidence is presented for proximity to the Fermi level of a van Hove singularity in the density of states.

Introduction

The ternary molybdenum chalcogenides,² often called Chevrel phases, can be formulated $\text{M}_x\text{Mo}_6\text{X}_8$, where M represents a vacancy, a rare earth element, or any of several metals such as Sn, Pb, Cu, etc., and X is S, Se, or Te. They are of special interest because they have curious structures³ and unusual combinations of properties (high superconducting critical temperatures,⁴ extraordinarily high critical magnetic fields,⁵ and apparent coexistence of superconductivity and magnetic ordering⁶).

Recently Delk and Sienko⁷ have shown that, when the Chevrel phases are grouped according to formal charge of the ternary element M, the superconductivity data can be represented by linear relations between T_c and the hexagonal c/a ratio. The Chevrel phases are generally rhombohedral, but they may be indexed hexagonally. As shown in Figure 1 the hexagonal c unit vector goes from the origin of the rhombohedral unit cell at atom 0 to atom 1 and coincides with the $\bar{3}$ axis. The two hexagonal a unit vectors are perpendicular to c along the face diagonals of adjacent unit cells, from the origin to atom 2 and atom 3. The rhombohedral angle α_R , which is the vertex angle of the ternary element cube measured at the origin, rarely deviates more than a degree from 90° . As a result, the ternary atoms form a nearly cubic array. Each

of the cubes contains an Mo_6X_8 cluster (cube of X atoms with face-centered Mo atoms) such that the cube of X atoms and the cube of ternary element M atoms share a common threefold axis. The Mo_6X_8 unit is rotated from cubic disposition relative to the ternary element lattice by about $15\text{-}20^\circ$. As a consequence of this rotation, the chalcogens in one unit cell come close to molybdenum atoms in an adjacent unit cell.

In all the ternary molybdenum chalcogenides, two of the chalcogens are of special interest by virtue of their position on the $\bar{3}$ axis. They are crystallographically distinct from the other six chalcogens and therefore are in a chemically unique environment. Vacancies in these two sites, as when $\text{SnMo}_6\text{S}_{8-x}$ is driven off stoichiometry,⁸ appear to raise the c/a ratio and increase the superconducting critical temperature. In this investigation we look at systematic replacement in PbMo_6S_8 of sulfur by selenium to fine-tune structural parameters and thereby identify critical influences that fix the magnitude of T_c .

Experimental Section

Sample Preparation. The compounds described here were prepared from ultrapure elements: Pb (99.9999% from Atomergic Chemetals Corp.), Mo (99.95% from United Mineral and Chemical Corp.), S (99.9999% from Atomergic Chemetals Corp.), and Se (99.9999% from Atomergic Chemetals Corp.). The Mo powder was reduced prior to use at 1000°C under a flow of hydrogen and stored in a vacuum desiccator until needed.

Appropriate amounts of the elements to form the series $\text{PbMo}_6(\text{S}_{1-x}\text{Se}_x)_8$ ($x = 0\text{-}1.0$ in 0.1 steps) were placed in degassed silica tubes, degassed at $\sim 10^{-6}$ torr, and sealed. The tubes were heated together in a box furnace, the temperature of which was raised to 1000°C over the course of 7 days. After 24 h at 1000°C the samples were air quenched and shaken vigorously. They were immediately reheated to 1200°C , kept there for 24 h, and finally air quenched. After being thoroughly ground under a helium atmosphere and resealed in degassed, evacuated silica ampules, the samples were annealed at 1150°C for 36 h and then at 1200°C for 8 h and air quenched. The resulting materials were fine, homogeneous, gray-black powders.

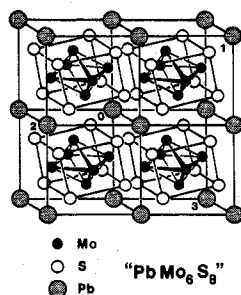
Powder X-ray Diffraction. X-ray diffraction photographs were made by using a 114.6-mm diameter Debye-Scherrer camera with nickel-filtered $\text{Cu K}\alpha$ radiation. Lines were indexed with the aid of a Fortran program that calculated the positions and intensities of possible reflections from available single-crystal data. A least-squares fit, with correction for absorption and camera radius error, was performed by using all lines with $\theta(hkl) > 30^\circ$ which could be indexed

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Table I. Crystal Data for $\text{PbMo}_6(\text{S}_{1-x}\text{Se}_x)_8$

x	$a_H, \text{\AA}$	$c_H, \text{\AA}$	$a_R, \text{\AA}$	$\alpha_R, \text{\AA}$	c/a	$\text{vol}_R, \text{\AA}^3$
0.0	9.197 (3)	11.497 (4)	6.548 (2)	89.21 (2)	1.2500 (8)	280.7 (3)
0.1	9.245 (1)	11.521 (6)	6.576 (2)	89.34 (1)	1.2461 (9)	284.3 (2)
0.2	9.292 (4)	11.550 (2)	6.603 (2)	89.43 (2)	1.2430 (8)	287.9 (3)
0.3	9.335 (4)	11.581 (4)	6.629 (3)	89.50 (2)	1.241 (1)	291.3 (4)
0.4	9.376 (4)	11.613 (1)	6.655 (2)	89.57 (2)	1.2386 (6)	294.7 (3)
0.5	9.410 (1)	11.654 (3)	6.679 (1)	89.57 (1)	1.2385 (5)	297.9 (2)
0.6	9.444 (3)	11.702 (5)	6.704 (2)	89.55 (2)	1.2391 (9)	301.3 (3)
0.7	9.474 (2)	11.748 (3)	6.727 (2)	89.52 (1)	1.2400 (6)	304.4 (2)
0.8	9.498 (2)	11.807 (3)	6.750 (1)	89.43 (1)	1.2431 (5)	307.4 (2)
0.9	9.516 (3)	11.884 (2)	6.773 (2)	89.25 (1)	1.2488 (5)	310.7 (2)
1.0	9.529 (2)	11.970 (4)	6.796 (2)	89.02 (1)	1.2562 (7)	313.7 (2)

Figure 1. Idealized structure of Chevrel phase PbMo_6S_8 .

unambiguously (typically 25–65 lines). This procedure yields lattice parameters with errors of less than one part per thousand.

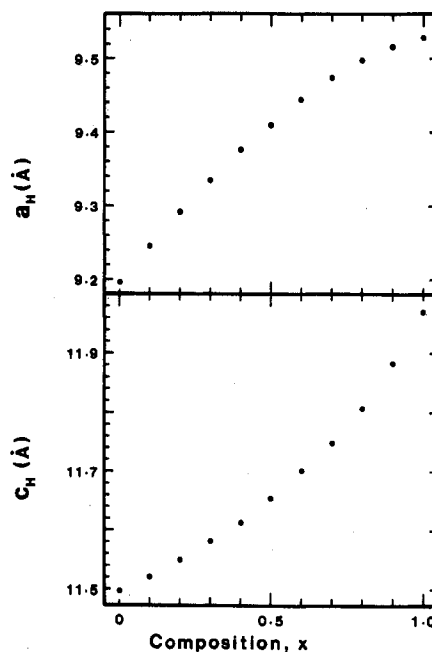
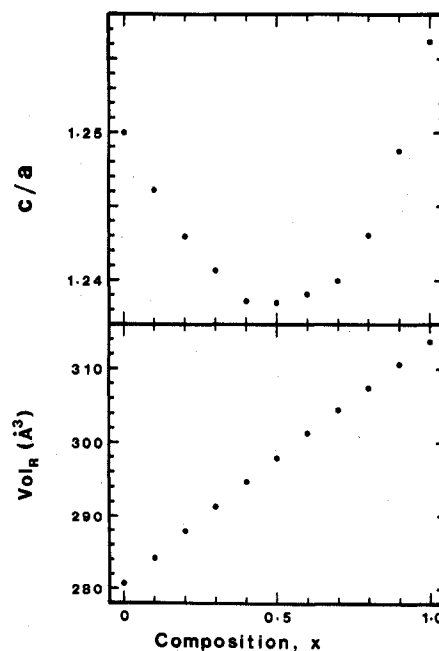
Superconducting Transition Determination. The transition to the superconducting state was monitored by using an ac mutual-inductance apparatus which has been described elsewhere.⁹ The onset of superconductivity is signaled by an abrupt increase in magnetic shielding when the sample becomes perfectly diamagnetic. Temperature was measured by using a calibrated CryoCal germanium thermometer, which was checked against the boiling point of helium and the transition temperatures of lead and niobium. The T_c value was taken as the temperature at which the inductively measured transition was half complete. The width of the transition is the temperature difference between the points where the transition is 10% and 90% complete.

Magnetic Susceptibility Measurement. Magnetic susceptibilities were measured from T_c to room temperature by the Faraday technique with a previously described apparatus.¹⁰ The temperature was measured with a germanium resistance thermometer (from CryoCal) in the range 1.5–100 K and with a copper/constantan thermocouple in the range 100–300 K. Temperature control was achieved with an Oxford Instruments DTC2 digital temperature controller using a gold plus 0.07% iron/chromel P thermocouple. Forces were measured with a Cahn RG electrobalance. The field gradient was calibrated by using $\text{HgCo}(\text{SCN})_4$ as a standard. Samples were held in a Spectrosil quartz bucket. The reported susceptibilities were field independent and have been corrected for the susceptibility of the bucket.

Results and Discussion

All lines in the X-ray diffraction photographs could be indexed to the appropriate rhombohedral lead–molybdenum chalcogenide, indicating the bulk samples were single phase. In some sample ampoules small crystals grew opposite the bulk sample. Gandolfi diffraction patterns of these could not be indexed to any combination of lead, molybdenum, and chalcogen published in the ASTM powder diffraction file. The impurity was always less than 0.1% of the bulk sample weight.

Rhombohedral and hexagonal lattice parameters are listed in Table I. The hexagonal parameters are shown as functions of composition in Figure 2. Both c and a show deviations from Vegard's law. Unit cell volume, however, varies linearly with composition. c/a is not a monotonic function of composition. Figure 3 shows the c/a ratio and the unit cell volume as functions of composition.

Figure 2. Hexagonal lattice parameters of $\text{PbMo}_6(\text{S}_{1-x}\text{Se}_x)_8$ as a function of the composition x .Figure 3. Rhombohedral unit cell volume and hexagonal c/a ratio of $\text{PbMo}_6(\text{S}_{1-x}\text{Se}_x)_8$ as a function of composition.

(9) W. Fisher, Ph.D. Thesis, Cornell University, 1978.

(10) J. Young, Ph.D. Thesis, Cornell University, 1971; L. Schneemeyer, Ph.D. Thesis, Cornell University, 1978.

The Vegard's law behavior of the unit cell volume and single-crystal data for PbMo_6S_8 and PbMo_6Se_8 ³ are consistent

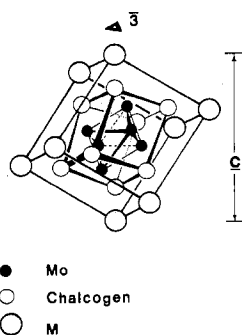


Figure 4. Hexagonal c parameter in relation to the rhombohedral unit cell.

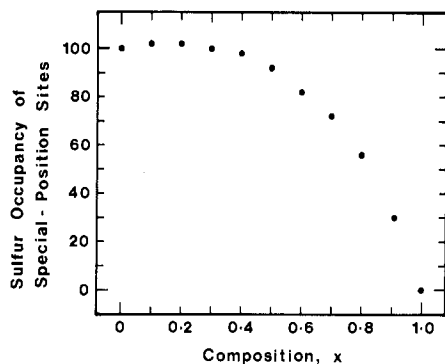


Figure 5. Apparent sulfur occupancy of special-position sites in $\text{PbMo}_6(\text{S}_{1-x}\text{Se}_x)_8$ as a function of composition.

with a hard-sphere model of the chalcogen ions. The dependence of the c parameter on composition can be calculated from such a model. Figure 4 shows that the c parameter can be decomposed into the sum of the length of the body diagonal of the chalcogen cube and twice the lead to special-position chalcogen separation. If the chalcogen cube is ideal (nearly the case, from single-crystal data), then eq 1 can be written,

$$c = 2(3^{1/2})r(\text{X}^{2-}) + 2[r(\text{Pb}^{2+}) + r(\text{X}^{2-})] \quad (1)$$

where $r(\text{X}^{2-})$ is the average radius of a chalcogen ion in the structure at a particular composition and $r(\text{Pb}^{2+})$ is the radius of the lead ion ($1.067 \pm 0.007 \text{ \AA}$ for PbMo_6S_8 and PbMo_6Se_8). For a random array of chalcogens, the c parameter should thus be a linear function of composition. The deviations observed here suggest that the chalcogens order with respect to the special-position sites just as vacancies do.^{3,8} The percent sulfur content of the special-position sites may be calculated by using the model and the following simplifying approximation. We treat the chalcogen cube as ideal and attribute deviations in c from linearity to deviations in the chalcogen-lead separation due to the difference between the actual average chalcogen radius on the special-position site and the average chalcogen radius expected from the actual composition. Figure 5 summarizes the results of this calculation. The crystal data strongly suggest that selenium atoms preferentially occupy the general-position sites. It appears that the selenium atoms are major occupants of the special positions only when $x > 0.8$. We return to this point when the magnetic and superconductivity data are discussed.

The superconducting transition temperatures are listed in Table II. The previously reported linear dependence of T_c on c/a is confirmed in Figure 6 with the exception of the selenium-most-rich compounds. These are the only two samples in which selenium is the dominant occupant of the special-position sites.

In order to probe the observed dependence of T_c on structure, we collected magnetic susceptibility data from T_c up to room temperature. The behavior observed is quite peculiar.

Table II. Superconducting Transition Temperatures for $\text{PbMo}_6(\text{S}_{1-x}\text{Se}_x)_8$

x	T_c , K	ΔT_c , K	c/a
0	13.29	2.55	1.2500
0.1	8.95	0.94	1.2461
0.2	6.26	0.94	1.2430
0.3	4.58	0.36	1.2407
0.4	3.41	0.99	1.2386
0.5	3.52	0.84	1.2385
0.6	3.62	0.81	1.2391
0.7	5.08	0.56	1.2400
0.8	6.09	0.48	1.2431
0.9	5.55	0.62	1.2488
1.0	3.89	0.93	1.2562

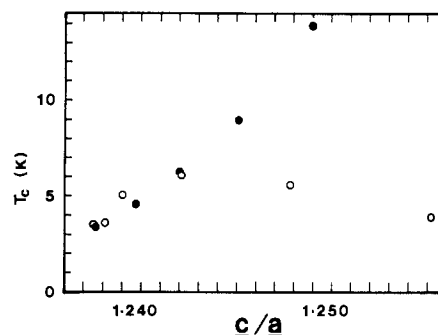


Figure 6. T_c as a function of c/a in the series $\text{PbMo}_6(\text{S}_{1-x}\text{Se}_x)_8$.

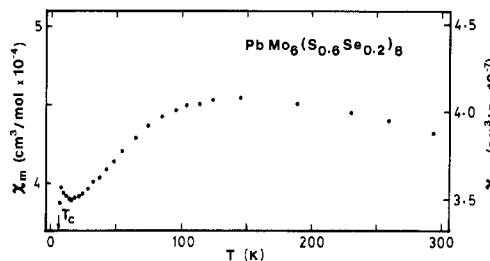


Figure 7. Susceptibility of $\text{PbMo}_6(\text{S}_{0.8}\text{Se}_{0.2})_8$ as a function of temperature.

All the samples, except the nonsubstituted sulfide, show a Curie-like tail at the lowest temperatures. As the temperature increases, the susceptibility does too. The susceptibility finally levels off or maximizes and decreases. Figure 7 shows the susceptibility of a representative sample. The low-temperature data ($\lesssim 40$ – 100 K) can be fitted to eq 2. The Curie constants

$$\chi_m(\text{obsd}) = C_m/T + B_m T + \chi_m(0 \text{ K}) \quad (2)$$

($\approx 3 \times 10^{-4} \text{ cm}^3 \text{ K mol}^{-1}$) are indicative of a small amount (a few parts per million) of a paramagnetic impurity. Figure 8 shows the susceptibilities corrected for the Curie tail.

The observed temperature dependences are not characteristic of metallic systems. In the absence of evidence for low-temperature crystallographic phase changes,^{3,11} it is necessary to consider the electronic structure of these materials. Pauli paramagnetism is usually temperature independent. However, in the presence of sharp structure in the density of states, the Pauli term can exhibit a temperature dependence. This fact has been used, for example, to explain the temperature behavior of the susceptibility of palladium¹² and of A15 compounds.¹³ The temperature dependence of the susceptibility of palladium is very similar to the behavior of the susceptibility of PbMo_6S_8 . The structure in the density of states is a van Hove singularity in the form of a saddle point.

(11) R. N. Shelton, Ph.D. Thesis, University California at San Diego, 1975.

(12) J. E. Van Dam and O. K. Andersen, *Solid State Commun.*, **14**, 645 (1974).

(13) A. M. Clogston and V. Jaccarino, *Phys. Rev.*, **121**, 1357 (1961).

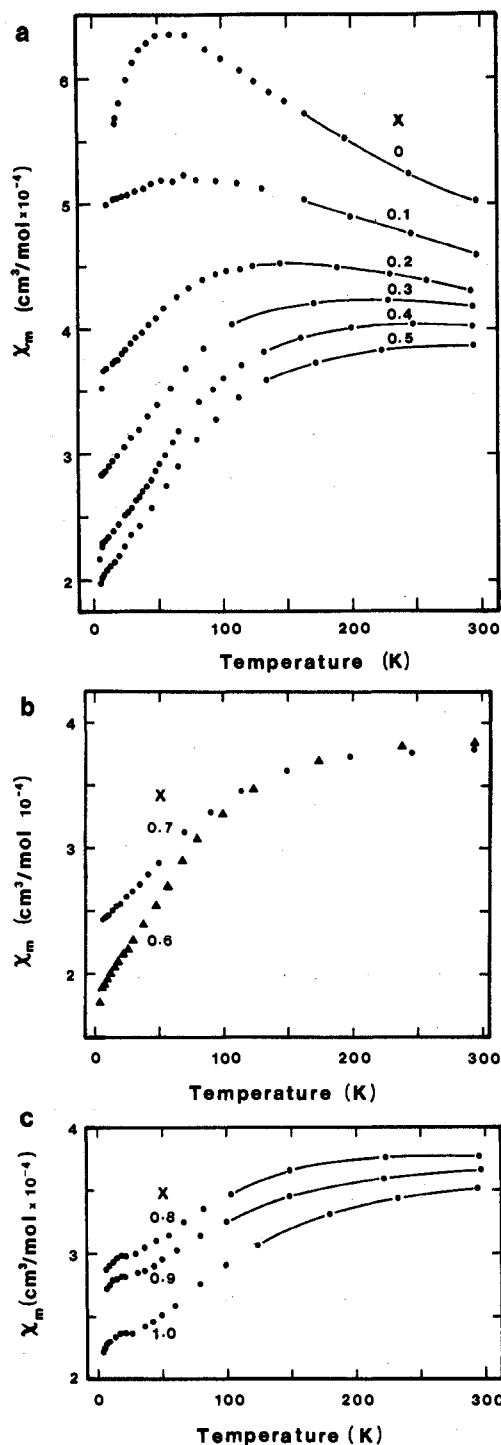


Figure 8. Susceptibility of $\text{PbMo}_6(\text{S}_{1-x}\text{Se}_x)_8$ vs. temperature: (a) $x = 0-0.5$; (b) $x = 0.6-0.7$; (c) $x = 0.8-1.0$.

Andersen, Klose, and Nohl performed band-structure calculations for several of these compounds.¹⁴ Sensitive pressure dependence of T_c in PbMo_6S_8 ¹¹ led them to place the Fermi level near a pronounced peak (and a van Hove singularity) in the density of states. Figure 9 shows the density of states they calculated. It is possible the van Hove singularity is responsible for the temperature dependence, but more detailed calculations are needed to verify this. We note that if the structure in the density of states is responsible, it is in a range of kT_{max} of the Fermi level where T_{max} is the temperature of

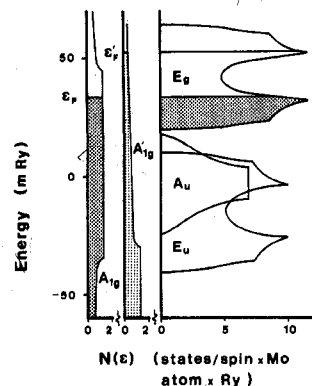


Figure 9. Density of states calculated for PbMo_6S_8 . Fermi level is at ϵ_F . A_{1g} band and ϵ_F Fermi level are also consistent with calculation as in ref 14.

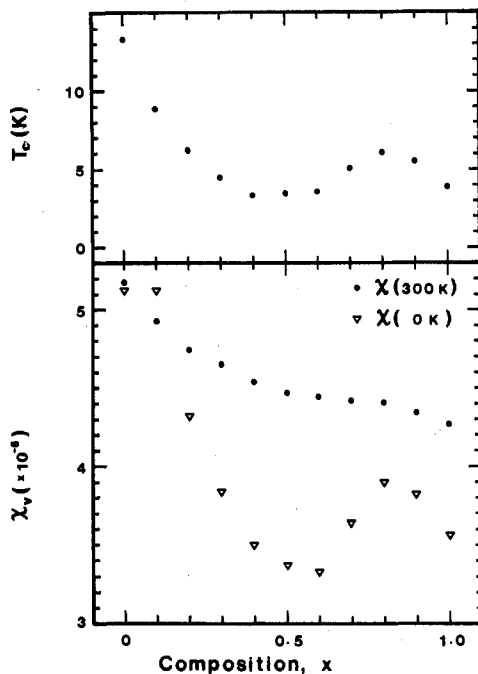


Figure 10. Room-temperature and 0 K volume susceptibilities corrected for core diamagnetism and T_c as functions of composition.

Table III. Susceptibilities at 300 and 0 K of $\text{PbMo}_6(\text{S}_{1-x}\text{Se}_x)_8$

x	χ_m^{300} , 10^{-4} cm^3/mol	χ_m^0 , 10^{-4} cm^3/mol	$\chi_m(\text{core})$, 10^{-4} cm^3/mol	$10^{-6} \times$ χ_v^{300}	$10^{-6} \times$ χ_v^0
0	5.02	4.94	-3.74	5.18	5.14
0.1	4.61	4.96	-3.82	4.92	5.13
0.2	4.32	3.59	-3.90	4.74	4.32
0.3	4.19	2.76	-3.98	4.66	3.84
0.4	4.00	2.16	-4.06	4.54	3.50
0.5	3.88	1.92	-4.14	4.47	3.38
0.6	3.85	1.81	-4.22	4.45	3.33
0.7	3.80	2.37	-4.30	4.42	3.64
0.8	3.78	2.85	-4.38	4.40	3.90
0.9	3.67	2.69	-4.46	4.34	3.82
1.0	3.52	2.21	-4.54	4.27	3.57

the susceptibility maximum or break.¹⁵ This is of the order of 1 mRy, a very tiny energy separation.

The three selenium-most-rich compounds all exhibit an anomaly at $\sim 25-30$ K, whose origin is not understood.

(14) O. K. Andersen, W. Klose, and N. Nohl, *Phys. Rev. [Sect.] B*, **17**, 1209 (1978).

(15) It is quite possible at temperatures above 300 K all samples would exhibit a decreasing susceptibility with increasing temperature, making them qualitatively the same.

The 300 and 0 K volume susceptibilities as corrected for core diamagnetism are shown in Table III. Figure 10 shows the values plotted as functions of composition together with corresponding values of T_c . It is remarkable that both $\chi_v(0\text{ K})$ and T_c exhibit the same composition dependence.

Pauli susceptibility, in general, is intimately related to the band structure of a compound. In the presence of complicated structure in the band, the 0 K Pauli volume susceptibility would be proportional to the density states at the Fermi level $N(\epsilon_F)$. Figure 10 indicates that T_c in these compounds depends strongly on $N(\epsilon_F)$, as would be in qualitative agreement with the simple BCS theory prediction (eq 3).

$$T_c \approx \langle \omega \rangle \exp[-1/(N(\epsilon_F)V)]$$

The fact that T_c and $N(\epsilon_F)$ are similarly dependent on c/a is puzzling. No immediate connection between c/a and $N(\epsilon_F)$

is apparent. Overlap between unit cells should depend on a_H alone, as is evident from $\text{SnMo}_6\text{S}_{8-x}$.⁸ More detailed band-structure calculations are needed to elucidate the relationship of T_c , c/a , and the susceptibility.

By way of summary, we have presented evidence for ordering of chalcogens in $\text{PbMo}_6(\text{S}_{1-x}\text{Se}_x)_8$ with respect to general- and special-position sites. The superconducting transition temperatures were found to be a linear function of c/a until selenium atoms substantially occupy the special-position sites. The 0 K volume susceptibility exhibits the same composition dependence as T_c , suggesting variations in T_c reflect changes in the density of states at the Fermi level. The manner in which c/a and $N(\epsilon_F)$ are connected is unclear; it needs to be investigated in more detail.

Registry No. PbMo_6S_8 , 39432-49-0; PbMo_6Se_8 , 62462-65-1.

Contribution from the Institute of Inorganic and Analytical Chemistry and the Institute of Crystallography, University of Lausanne, CH-1005 Lausanne, Switzerland

Study of $\text{PtX}_2(\text{PR}_3)_2$ in the Presence of PR_3 in CH_2Cl_2 Solution and the Cis-Trans Isomerization Reaction As Studied by ^{31}P NMR. Crystal Structure of $[\text{PtCl}(\text{PMe}_3)_3]\text{Cl}$

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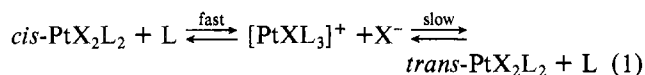
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The identity of the species present in dichloromethane solutions of PtX_2L_2 and L (L = PMe_3 , PEt_3 , *p-n*-Bu₃, $\text{P}(\text{tol})_3$ where *tol* = *p*-tolyl; Pt:L ratios from 1:0.05 to 1:5) are *cis*- and *trans*- PtX_2L_2 , $[\text{PtXL}_3]^+$ (X = Cl, Br), and $[\text{PtXL}_4]^+$ (X = Cl, Br, I; L = PMe_3). The only species with three coordinated phosphines which is five-coordinate in solution is $\text{PtI}_2(\text{PMe}_3)_3$, whose IR and NMR parameters are consistent with a square-pyramidal geometry having one phosphine in the apical position. All other "tris" complexes $[\text{PtXL}_3]^+$ are four-coordinate in solution as shown by UV and ^{31}P NMR spectroscopy, and this geometry is also found in the solid state ($[\text{PtCl}(\text{PMe}_3)_3]\text{Cl}$ X-ray crystal structure). The complexes $[\text{PtX}(\text{PMe}_3)_4]^+$ have a square-pyramidal geometry with X in the apical position. In the case of L = PMe_3 , ^{31}P NMR studies show that intermolecular phosphine exchange occurs between $[\text{PtClL}_3]^+$, $[\text{PtClL}_4]^+$, PtI_2L_3 , and free L, whose activation parameters, estimated from line-shape analysis, are reported. Contrary to previous reports, chloride ion is found to displace one phosphine from $[\text{PtClL}_3]^+$ ion, giving the *cis*- PtCl_2L_2 isomer in a fast step prior to *cis*-*trans* equilibration. The results indicate that the *cis*-*trans* isomerization of PtX_2L_2 catalyzed by L proceeds by rapid displacement of X⁻ by L followed by slow displacement of L by X⁻ and not by pseudorotation of a five-coordinate intermediate. A similar mechanism was established for the isomerization of the alkyl complex $\text{PtCl}(\text{CH}_2\text{CN})(\text{PPh}_3)_2$.

Introduction

Since the original proposal by Basolo and Pearson² of the double displacement mechanism for the phosphine-catalyzed *cis*-*trans* isomerization of tetragonal-planar platinum(II) complexes, many studies³⁻¹⁸ with conflicting results and in-

terpretations^{3-6,15} have appeared in the literature. The following mechanisms have been proposed to date: (a) a double displacement mechanism (eq 1) which implies phosphine ex-



change and an ionic intermediate from which X⁻ is able to displace L (This mechanism is in agreement with the stereospecific nature of all substitution reactions of platinum(II) complexes observed so far.), (b) a pseudorotation mechanism

- (1) (a) Institut de Chimie Minérale et Analytique. (b) Based, in part, on the Ph.D. thesis of R.F., Université de Lausanne. (c) Institut de Cristallographie.
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- (3) Haake, P.; Pfeiffer, R. M. *J. Am. Chem. Soc.* **1970**, *92*, 4996.
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