Crystals of the title compound were grown by evaporation of a chloroform solution under dry, deoxygenated N_2 (some decomposition occurred). The crystals were stable to air and extinguished well under a polarizing microscope. However, the crystals were somewhat shock sensitive. Attempts to grind crystals to spheres or even to separate clumps of crystals often resulted in poor light extinction properties and opaqueness. Several crystals with good optical characteristics were examined by X-rays and found to be composed predominantly of one crystal. For the crystal selected, ω, 2θ, and ω–2θ scans of several reflections and their Friedel mates gave satisfactory results for four octants. The data were collected in two of these (hkl and $\bar{h}kl$). The data from the other four octants showed scattering from at least two nearly aligned crystals. Although several troublesome crystallographic features exist, refinement has proceeded[11] to $R = 0.061$, $R_w = 0.068$, GOF = 0.63, for 2956 reflections with $I/\sigma(I) \geq 3.0$. The structure of the complex is presented in Figure 1.

Although alternations in S–S bond lengths are observed[2] in other compounds (of Mo and W) containing four-membered MS_4 rings, none appears here. In fact, the PtS_4 ring is asymmetrically puckered with S(2) substantially out of the plane of the remaining MS_3 atoms. The Pt–S and Pt–P bonds are comparable to those found[19] in $(Ph_3P)_2Pt(SH)_2$, but the Pt–S distances are rather longer than the Pt–S distances, 2.240 (7) and 2.260 (6) Å, in sulfur-rich $Pt(S_2CC_6H_4\text{-}i\text{-}Pr)(S_3CC_6H_4\text{-}i\text{-}Pr)$. The PtS_3C ring (1) in this latter compound is planar.[20]

1
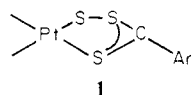
The puckering of the PtS_4 ring in $(Ph_3P)_2PtS_4$ compared with other MX_4 rings containing catenated sulfur is consistent with the presence of an excess of π-orbital electrons over requirements for delocalization and pseudoaromaticity. The high oxidation state of Mo(IV) and W(IV) in the MoS_4 and WS_4 ring systems presumably contributes to sulfur-to-metal π back-bonding in these compounds and a shortening of the S(2)–S(3) bond relative to the other S–S bonds. In the RS_4R compounds[18] the internal S(2)–S(3) distance is rather long and comparable with S–S distances in S_4^{2-} (Table I). In the

PtS_3C ring 1, the ligand has only six π electrons, suggesting a pseudoaromaticity. The geometry of the platinum coordination sphere in the title compound is that of a tetrahedrally distorted square plane. The tetrahedral distortion, defined by the angle between the PtP(1)–P(2) and PtS(1)–S(4) planes, is 10.9°.

Although phosphines remove a single sulfur atom from the PtS_3C ring, Ph_3P does not readily react with the PtS_4 ring. Electrophiles such as activated acetylene do appear to react with the PtS_4 ring. Further work on the reactivity of this compound and structure/reactivity relationships with other catenated metal–sulfur ring systems continues.

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The $(Mo_3Se_3^-)_\infty$ Chain

Sir:

In the course of their continuing work on ternary molybdenum chalcogenides, Potel, Chevrel, Sergent, and co-workers have recently synthesized some striking compounds of the stoichiometry $M_2Mo_6X_6$ (X = S, Se, Te; M = Na, K, In, Tl if X = Se; M = K, Rb, Cs if X = S; and M = In, Tl if X = Te).[1,2] $Tl_2Mo_6Se_6$, the best characterized of these compounds, has the structure **1**.

The structure can be considered as consisting of $(Mo_6Se_6^{2-})_\infty$ chains separated by columns of Tl^+ ions. $Tl_2Mo_6Se_6$ was reported to be superconducting at 3.5 K and showed a strong anisotropy in the upper critical field responsible for quenching the superconductivity. Also, the normal resistivity perpendicular to the chain axis was found to be several hundred times that parallel to the chain. Given the remarkable anisotropy in both the structure and properties of this material, the one-dimensional band structure of $(Mo_6Se_6^{2-})_\infty$ should provide much insight into the electronic structural properties of all these materials. The quintessential feature of the compounds is their *metallic* appearance. Nevertheless, we will suggest that some of these compounds could undergo a "Peierls distortion" leading to a semiconducting ground state. Conclusions similar to ours regarding these materials have been reached by Andersen, Kelly, and co-workers.[1d]

To make the argument which leads to this conclusion, we need to present the band structure for the $(Mo_6Se_6^{2-})_\infty$ chain.

(10) Schmidt, Max; Hoffman, Gerhard G. *Z. Anorg. Allg. Chem.* **1979**, *452*, 112–22. The stoichiometry in the original report by Kreutzer[5] is incorrect. The reported stoichiometry results in the intermediate product $(NH_4)_2Pt(S_5)_2$. In a later paper[6] concerning the degradation of the S_5 rings in $(NH_4)_2Pt(S_5)_x$ ($x = 2, 3$) by thiophiles, the correct stoichiometry is implied.

(11) Data were collected on a Syntex $P2_1$ diffractometer using the collection mode described previously.[12,13] No correction was made for absorption. Systematic absences implicated the space groups $P2_1/n$. With anisotropic temperature factors for Pt, S, P, and Cl, $R = 0.126$, including anomalous dispersion[14] for Pt. Three scale groups were used with scattering from two nearly aligned crystals assumed. Although R converged[15] to 7.5%, 71 reflections[16] had $R > 35\%$. These were deleted from the data. Phenyl H atoms were included at idealized positions 0.95 Å from the C atoms. The final difference Fourier has its largest peak, $\sim 1.0 \ e/Å^3$, at the Pt position.

(12) Stein, J.; Fackler, J. P.; McClune, G. J.; Fee, J. A.; Chan, L. T. *Inorg. Chem.* **1979**, *18*, 3511–9.

(13) Chen, W. H.; Fackler, J. P. *Inorg. Chem.* **1978**, *17*, 22–6.

(14) "International Tables for X-Ray Crystallography," 2nd ed.; Kynoch Press: Birmingham, England, 1965.

(15) $R = [\sum ||F_o| - |F_c||/\sum |F_o|]$; $R_w = [\sum w_i ||F_o| - |F_c||^2/\sum w_i |F_o|]^{1/2}$; GOF ("goodness of fit") $= [\sum w_i |F_o - F_c|^2/(N_o - N_v)]^{1/2}$; $w_i = 1/\sigma(F_o)^2$.

(16) These reflections have F_o/F_c fairly constant, consistent with the presence of a small, third, crystal. Rather than adding another scale factor to treat them, we omitted them from the data.

(17) Abrahams, S. C.; Bernstein, J. L. *Acta Crystallogr., Sect. B* **1969**, *B25*, 2365–70.

(18) Rucci, John S., Jr.; Bernal, Ivan. *J. Chem. Soc., Chem. Commun.* **1969**, 1453–4.

(19) Briant, Clive E.; Hughes, Glyn R.; Minshall, Peter C.; Mingos, D.; Michael P. *J. Organomet. Chem.* **1980**, *202*, C18–20.

(20) Chan, L.-T.; Koknat, F.; Fackler, J. P., Jr., submitted for publication.

(1) (a) Potel, M.; Chevrel, R.; Sergent, M. *Acta Crystallogr., Sect. B* **1980**, *B36*, 1545–1548. (b) Potel, M.; Chevrel, R.; Sergent, M.; Armici, J. C.; Decroux, M.; Fischer, Ø. *J. Solid State Chem.* **1980**, *35*, 286–290. (c) For a recent review on the structural and physical properties of superconducting ternary compounds see: Foner, S., Schwartz, B. B., Eds. "Superconductor Materials Science: Metallurgy, Fabrication and Applications"; Plenum Press: New York, 1981; Chapter 10. (d) For recent theoretical work see: Nohl, H.; Klose, W.; Andersen, O. K.; Kelly, P. J. In "Superconductivity in Ternary Compounds"; Fischer, Ø, Maple, M. B., Eds.; Springer-Verlag: New York, 1982; Chapter 6. See also: LeBeuze, A.; Lissillour, R.; Chermette, H.; Potel, M.; Chevrel, R.; Sergent, M., submitted for publication in *Solid State Commun.*

(2) A single compound had been previously synthesized with the formula $Tl_2Fe_6Te_6$, which is isostructural with the Mo compounds: Klepp, K.; Boller, M. *Monatsh. Chem.* **1979**, *110*, 677–684.
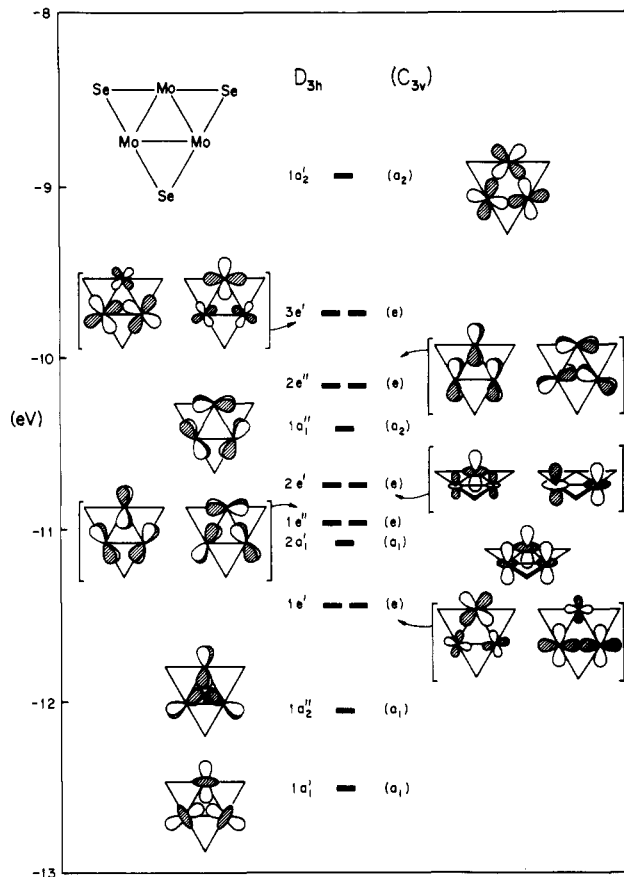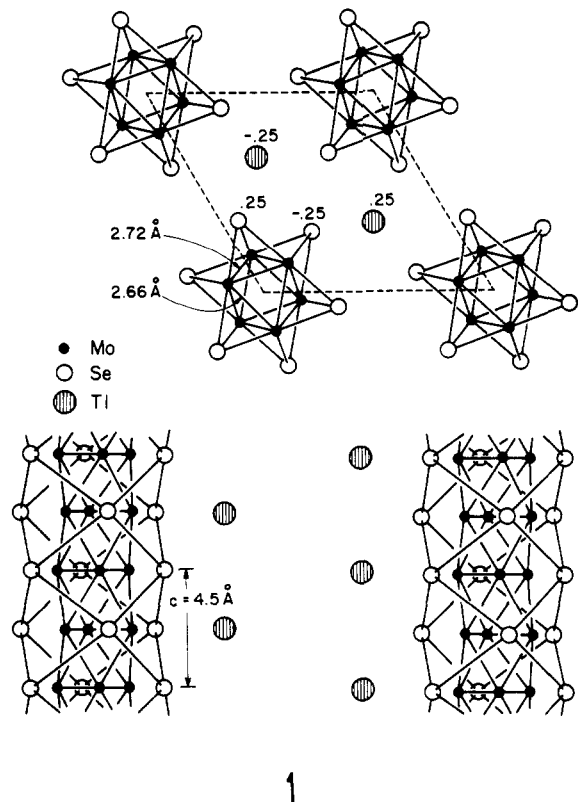
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The crystal orbitals comprising these bands are in turn most easily understood in terms of the orbitals of the Mo_3Se_3 fragment. The chains consist of staggered stacks of such units. As shown in Figure 1, the Mo d orbitals in Mo_3Se_3 give rise to a block of 15 orbitals with a width of approximately 3.6 eV. The orbitals are labeled according to the D_{3h} symmetry applicable for the fragment and (in parentheses) according to C_{3v} symmetry, which is appropriate for classifying the bands—C_{3v} symmetry is "preserved" for all wavevectors in the one-dimensional Brillouin zone.[3] We will not give here a detailed exposition of these orbitals; their ordering can be generally understood in terms of Mo–Mo bonding (or antibonding) and Mo–Se antibonding interactions.[4]

Turning to a consideration of the band structure of the $(Mo_6Se_6{}^{2-})_\infty$ chain, we shall sketch how the bands shown in Figure 2 derive from the fragment orbitals. There are two chemically equivalent fragments per translational subunit of the chain. As a result, all of the bands have the "folded" appearance[5] characteristic of a chain with a screw axis (a 6_3 axis in this case). For discussion purposes we will consider *both* branches of each band as part of one band. Qualitatively, the following things happen when we stack the fragments into a chain: (1) The $1a_1'$ and $1e'$ orbitals remain relatively "pure" upon forming the chain since these orbitals are not directed out of the plane of the fragment and hence overlap poorly with neighboring fragment orbitals. (2) The $1a_2''$ orbital of a given fragment is strongly directed toward the Se atoms of fragments just above and below and is expected to be pushed up (recall that the chain is a *staggered* stack of Mo_3Se_3 units). Actually, the $1a_2''$ and $2a_1'$ orbitals mix strongly in parts of the zone—the net effect being to push one band up high in energy while one
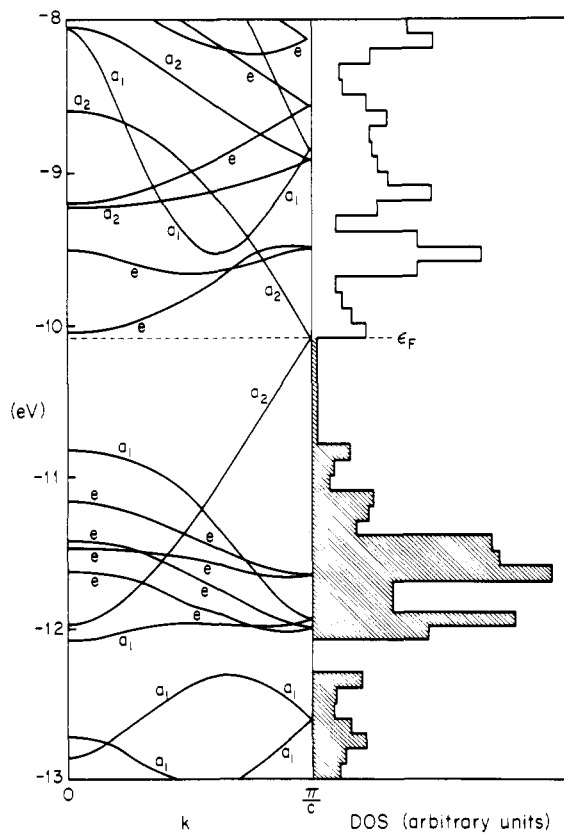
Figure 1. Orbitals for the Mo_3Se_3 fragment.

Figure 2. Bands for the $(Mo_6Se_6{}^{2-})_\infty$ chain. At right is the density of states (DOS). The lined levels are occupied. The Fermi level is marked by ϵ_F.

(3) The site symmetry relevant for the observed structures is C_{3h} for the fragment and C_3 for the band orbitals; however, the effect of geometry idealization is small and can be safely neglected.

(4) See, for example, the discussion for bridged M_2L_{10} complexes by: Shaik, S.; Hoffmann, R.; Fisel, C. R.; Summerville, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 4555–4572.

(5) The "unfolding" of such bands is natural in the extended-zone scheme: Ashcroft, N. W.; Mermin, N. D. "Solid State Physics"; Holt, Rinehart and Winston: New York, 1976.

band remains low. (3) A more complicated but similar situation obtains for the remaining four e type orbitals: two of

the resultant e bands lie high in energy; one is pushed low and one ends up just above the Fermi energy. Using the C_{3v} symmetry notation, we have up to now two low-lying a_1 bands and two low-lying e bands, which can accommodate 12 electrons per Mo_3Se_3 unit. Recall that the screw axis folds back each band, so that per Mo_6Se_6 repeat unit there are four low-lying a_1 bands and four e bands. These bands are responsible for most of the structure seen in the density of states[6] (DOS) below the Fermi level (see the right-hand side of Figure 2). Especially notable in the DOS is the clear separation between Mo–Mo bonding and antibonding levels for the chain.

Since we are considering a stack of $Mo_3Se_3^-$ units, we have a total of 13 metal electrons to account for and therefore one electron to put into the heretofore unconsidered but crucial a_2 band. The band to which we are referring is the comparatively wide band (3.4 eV) that rises from near the bottom of the bonding bands well up into the antibonding block. This band arises almost purely from the $1a_1''$ orbital of Mo_3Se_3; its (folded) cosine-like form and the many crossings with other bands are result of the unique rotational symmetry of the $1a_1''$ orbital.[7] The width of the a_2 band is a reflection of the excellent overlap between a_1'' orbitals on adjacent fragments, illustrated in **2**. Note that in the absence of the a_2 band and
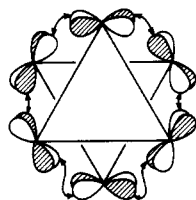
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its electron, a sizable 0.77-eV gap would appear—leading to semiconducting behavior.

Were the picture we have outlined here taken at face value, then the presence of the half-filled a_2 band should provide a

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(6) Kertész, M.; Hughbanks, T. *Phys. Rev. B: Condens. Matter* **1981**, *24*, 6870–6879.
(7) Actually, were it not for an avoided crossing with the upper a_2 band, this band would be about 4 eV in width.

driving force for a Peierls distortion (which in this case would be manifested in alternatively long and short spaces between the Mo_3Se_3 units in the chain). The effect of the distortion on the a_2 band will be to stabilize filled levels at the zone edge and destabilize unfilled levels so as to open up a band gap by splitting the two branches of the band. Of course this implies a semiconducting ground state, not superconducting.

There are reasons *not* to accept this picture at face value. First, our calculations[8] cannot be trusted to yield relative band energies so accurate as to decide whether the Fermi level lies above or below the e-band edge at the bottom of the antibonding block. Changes in parameters or in the method of calculation may affect this ordering. We think that it is likely that in $Tl_2Mo_6Se_6$ the Fermi level lies above this band edge—which would make the density of states fairly large at the Fermi energy and would be in accordance with simple expectations regarding the observed superconductivity. Furthermore, these crystals are, of course, three-dimensional and we may not be able to safely ignore the cations. How the Tl ions affect the picture we have presented is not clear, and they may subtly perturb the one-dimensional results. In any case, if the cations are K^+ as in $K_2Mo_6Se_6$, such an issue does not arise since electropositive potassium clearly will not appreciably contribute to levels near the Fermi level. Hence, we expect $K_2Mo_6Se_6$ may very well exhibit a pairing distortion and as a result be semiconducting.[9] We look forward to investigations into the structural and physical properties of these compounds.

Registry No. ($Mo_3Se_3^-$), 82638-61-7.

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(8) The calculations are of the extended Hückel type. Mo 4d, 5s, and 5p as well as Se 4s and 4p orbitals were included.
(9) Measurements on powder specimens of $K_2Mo_6Se_6$ indicate semiconducting behavior: Chevrel, R., private communication.

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Additions and Corrections

Geneviève Chottard,* Pierrette Battioni, Jean-Paul Battioni, Marc Lange, and Daniel Mansuy*: Resonance Raman Spectra of Iron Tetraphenylporphyrin Complexes: Characterization of Structure and Bonding Sensitive Bands.

Page 1720. Table II, footnote *a*: read superscript references 24 and 25 instead of references 20 and 21.—Geneviève Chottard

B. Corain,* C. Crotti, A. Del Pra, F. Filira, and G. Zanotti: Metal-Promoted Reactivity of Cyanogen toward Compounds Containing Active Hydrogen Atoms on Carbon. 2. Synthesis of a Fully Functionalized Substituted Pyrimidine from Cyanogen and Acetylacetone Catalyzed by Acetylacetonate Complexes of Transition Metals.

Page 2047. Table III should read as follows:

λ, nm	ϵ, M^{-1} cm^{-1}
270	16 900
287	17 900
344	12 400

—B. Corain

Anthony W. Addison,* Philip J. Burke, and Kim Henrick*: Crystal and Molecular Structure of Dipolar Spin-Coupled Dimers of an Irregularly Pentacoordinate Copper(II) Complex, [Cu(5-MeIin)(DBM)].

Page 61. In the last paragraph, third line from the bottom, the value 0.0613 cm^{-1} should be 0.0163 cm^{-1}.—Anthony W. Addison