most often to the 313-nm band,[12] and the presently assigned $^1A_{2g} \leftarrow {}^1A_{1g}$ d–d band of *trans*-Mo(CO)$_4$[P(*n*-Bu)$_3$]$_2$ is at 300 nm. Using the W–P MO model, one also predicts that the second d–d daughter state of $^1T_{1g}$, or $^1E_g[e_g{}^3(\sim 4d_{xz}, d_{yz})a_{1g}{}^1(\sim 4d_{z^2}); {}^1T_{1g}]$, is under band I and/or II, or $^1E_g < {}^1A_{2g}$, since its transition energy equals $^1T_{1g}[M(CO)_6] + {}^1/_2\delta(10Dq)$. The quantity $\delta(10Dq)$ is the difference $10Dq'[P(n\text{-Bu})_3] - 10Dq^\circ(CO)$, for which the magnitude of $10Dq^\circ$ and the inequality $10Dq' < 10Dq^\circ$ are known but $10Dq'$ is not known quantitatively.

The red-most weak optical shoulder near ~415 nm and its net positive MCD ellipticity are attributed to a spin-forbidden transition, $^3\Gamma \leftarrow {}^1A_{1g}$, which either is the partner, $^3E_u(a_{2u}{}^1e_g{}^3)$, of band I ($^1E_u(a_{2u}{}^1e_g{}^3)$), or is of "$^3T_{1g}$" ($t_{eg}{}^5e_g{}^1$) origin ($^3E_g[e_g{}^3(\sim 4d_{xz}, d_{yz})a_{1g}{}^1(\sim 4d_{z^2}); {}^3T_{1g}]$), the partner of $^1E_g(T_{1g})$.

In summary, MO origins, MO fates, excited-state symmetries, and excitation polarization assignments were made. Bands I and II are π^* CO ← ~4d^6 Mo MTLCT transitions to respectively excited states $^1E_u[a_{2u}{}^1(\pi^*\ CO)e_g{}^3(\sim 4d_{xz}, d_{xz}\ Mo)]$ and $^1A_{2u}[e_u{}^1(\sim \pi^*\ CO > 5p\ Mo)e_g{}^3(\sim 4d_{xz}, d_{yz}\ Mo)]$. Band C is a d–d transition involving the excited state $^1A_{2g}$-$[b_{2g}{}^1(\sim 4d_{x^2-y^2}); {}^1T_{1g}]$, and the d–d transition to $^1E_g[e_g{}^3(\sim 4d_{xz}, d_{yz})a_{1g}{}^1(\sim 4d_{z^2}); {}^1T_{1g}]$ is at lower energy than $^1A_{2g}$ by $^1/_2\delta$-$(10Dq)$ (under band I and/or II).

This excitation information is also photochemically interesting, and especially so since the two lowest energy long-lived spin-forbidden triplets are expected to be the d–d state ^3E_g-$[e_g{}^3(\sim 4d_{xz}, d_{yz})a_{1g}{}^1(\sim 4d_{z^2}); {}^3T_{1g}]$ and the MTLCT state $^3E_u[a_{2u}{}^1(\pi^*\ CO)e_g{}^3(\sim 4d_{xz}, d_{yz}\ Mo)]$ as a consequence of the above excitation findings. In state ^3E_g the molecule will be preferentially *z* axis (P–Mo–P) labilized. It is suggested that a wavelength-dependent quantitative photochemistry study (labeled ligand exchange or substitution) be undertaken in order to locate ^1E_g, and preferentially ^3E_g, more accurately. The photosubstitution study[13] of a similar complex, *trans*-Mo(CO)$_4$(PPh$_3$)$_2$, was carried out already at two wavelengths (366 and 313 nm) and gave results compatible with the present findings. For example, quantum yields for PPh$_3$ loss followed by CO entry are 0.30 and 0.20 at 366 and 313 nm, respectively, and *both* CO (QY = 0.30) *and* PPh$_3$ (QY = 0.33) photosubstitutions take place with irradiation at 366 nm (band I). Molecular series studies are under way.

Registry No. *trans*-Mo(CO)$_4$[P(*n*-Bu)$_3$]$_2$, 17652-79-8.

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X-ray Crystal and Molecular Structure of a Platinum(II) Complex Containing a PtS$_4$ Ring, [(C$_6$H$_5$)$_3$P]$_2$PtS$_4$·CHCl$_3$

Sir:

We report here the first crystal and molecular structure of a compound containing a PtS$_4$ ring although compounds containing PtS$_5$ rings have been known for nearly 100 years.[1] The only MS$_4$ rings that have known structures are for M = Mo and W (Table I).[2] Our interest in the reactivity of transition-metal complexes containing catenated sulfur[3] prompted this investigation. The title compound was originally prepared by Chatt and Mingos[4] from tetrakis(triphenylphosphine)platinum(0) and elemental sulfur. The sample used in the current study was prepared by the method of Kreutzer et al.[5] according to eq 1.[6-10]

$$(NH_4)_2Pt(S_5)_3 + 12(C_6H_5)_3P \rightarrow (NH_4)_2S + [(C_6H_5)_3P]_2PtS_4 + 10(C_6H_5)_3PS \quad (1)$$

Table I. Bond Lengths for S–S Bonds in Compounds with S$_4$ Structural Units (in Å)[a]

	S(1)–S(2)	S(2)–S(3)	S(3)–S(4)
(Ph$_3$P)$_2$PtS$_4$	2.024 (8)	2.022 (10)	2.081 (10)
[AsPh$_4$][Mo$_2$S$_{10}$](a)[b]	2.019 (5)	1.970 (6)	2.115 (5)
[AsPh$_4$]$_2$[Mo$_2$S$_{10}$](b)[b]	2.096 (16)	1.936 (19)	2.169 (14)
(Et$_4$N)$_2$MoS$_9$[c]	2.107 (1)	2.012 (1)	2.166 (1)
(η^5-C$_5$H$_5$)$_2$MoS$_4$[d]	2.081 (8)	2.018 (9)	2.085 (7)
(η^5-C$_5$H$_5$)$_2$WS$_4$[e]	2.105 (7)	2.016 (8)	2.116 (9)
BaS$_4$·H$_2$O(a)[f]	2.069 (4)	2.063 (4)	2.069 (4)
BaS$_4$·H$_2$O(b)[f]	2.079 (3)	2.062 (4)	2.079 (3)
[C$_6$H$_2$(OEt)$_2$S$_4$]$_2$(a)[g]	2.028 (5)	2.068 (5)	2.027 (5)
[C$_6$H$_2$(OEt)$_2$S$_4$]$_2$(b)[g]	2.034 (5)	2.067 (5)	2.024 (5)

[a] Abbreviations: Ph, C$_6$H$_5$; Et, C$_2$H$_5$. [b] Reference 2a. The S$_4$ ring is disordered with (a) the major component and (b) the minor one. [c] Reference 2d. [d] Reference 2b. [e] Reference 2c. [f] Reference 17. There were two independent S$_4$ chains (a and b). [g] Reference 18. The molecule has two S$_4$ units (a and b).

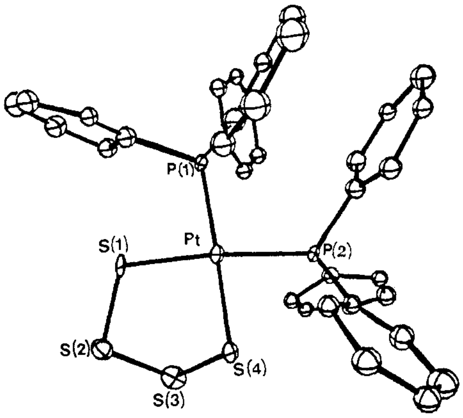

Figure 1. ORTEP diagram of (Ph$_3$P)$_2$PtS$_4$ (50% probability thermal ellipsoids). Important bond lengths (Å) and angles (deg): Pt–S(1), 2.360 (6); Pt–S(4), 2.366 (5); S(1)–S(2), 2.024 (8); S(2)–S(3), 2.022 (10); S(3)–S(4), 2.081 (10); Pt–P(1), 3.300 (5); Pt–P(2), 2.283 (5); P–C(av), 1.85 (2); C–C(av), 1.41 (3); S(1)–Pt–S(4), 92.0 (3); P(1)–Pt–P(2), 99.3 (2); S(1)–Pt–P(1), 82.6 (3); S(4)–Pt–P(2), 87.2 (3). The atom S(2) is 0.966 (7) Å removed from the least-squares P$_2$PtS$_4$ plane with no other atom more than 0.17 Å from this plane.

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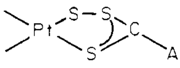
Crystals of the title compound were grown by evaporation of a chloroform solution under dry, deoxygenated N_2 (some decomposition occurred). The crystals were stable to air and extinguished well under a polarizing microscope. However, the crystals were somewhat shock sensitive. Attempts to grind crystals 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 $\omega-2\theta$ 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.

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE-8013141) and the National Institutes of Health (Grant GM-19050).

Registry No. $(Ph_3P)_2PtS_4\cdot CHCl_3$, 37662-43-4; $(NH_4)_2Pt(S_5)_3$, 23311-46-8.

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(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, ~1.0 e/Å^3, at the Pt position.

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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.

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