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# Platinum Thiotungsten Compounds.
# Crystal and Molecular Structure of Bis(triethylphosphine)platinum Tetrathiotungsten

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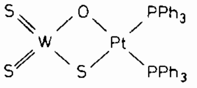
*Reaction of $(Ph_3P)_2PtCl_2$ with $Ph_3P$ and $(Ph_3PCH_3)_2WO_2S_2$ produced $(Ph_3P)_2PtWS_4$ and $(Ph_3P)_2PtWOS_3$. $[(C_2H_5)_3P]_2PtWS_4$ was similarly synthesized from $[(C_2H_5)_3P]_2PtCl_2$ and its structure determined by X-ray diffraction (R = 0.026). Crystal data: $P2_1/n$, a = 9.081, b = 14.516, c = 16.819 Å, β = 82.33°, Z = 4. The molecule consists of an approximately tetrahedral $WS_4$ unit bridged on one edge by $[(C_2H_5)_3P]_2Pt$.*

## Introduction

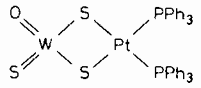
We have previously reported that the deoxygenation of the dithiatungstate ion, $WO_2S_2^{2-}$, with tertiary phosphines in the presence of Group Ib metal ions affords tetrathiatungstate derivatives. Examples include net-like compounds such as $(Ph_2PCH_3)_2Au_2WS_4$ [1] and novel cage compounds such as $(Ph_2PCH_3)_4Ag_4W_2S_8$ [2]. This paper describes an extension of this synthetic method to include a divalent transition metal, platinum, and the X-ray characterization of $[(C_2H_5)_3P]_2PtWS_4$ in which the $WS_4$ group is a bidentate ligand.

## Synthetic Chemistry

Reduction of $(Ph_3PCH_3)_2WO_2S_2$ with $Ph_3P$ in the presence of $(Ph_3P)_2PtCl_2$ gave $(Ph_3P)_2PtWS_4$, *1*, in low yield. Unlike the group Ib metal systems in which trithiatungstate clusters such as $[(p\text{-tolyl})_3P]_4Cu_4W_2O_2S_6$ [3] are minor by-products, $(Ph_3P)_2PtWOS_3$, *2*, was the major product of this reaction. No data are available which prove that *2* is the precursor of *1*. However, when $Ph_3P$ was omitted from the reaction, the yield of *1* was hardly affected but that of *2* decreased by about a factor of ten. Crystals of *2* suitable for X-ray diffraction studies have not been obtained but spectroscopic techniques suffice to discriminate between possible structures. We assume, on the basis of our previous structural studies [1, 3], that *2* contains a tetrahedral $WOS_3$ unit with an edge bridging platinum. The compound is monomeric in dimethylformamide and aggregated structures need not be considered. It then remains to be decided whether both bridging atoms are sulfur *2B* or if one oxygen and one sulfur are incorporated into the bridge *2A*.



2 A



2 B

The $\{^1H\}^{31}P$ NMR spectrum of *2* consists of a single resonance at −13.7 ppm (*i.e.* downfield of $H_3PO_4$) with $J\,^{31}P\text{–}^{195}Pt$ 3560 cps. This requires that the phosphorus nuclei be equivalent and is evidence for structure *2B*. Vibrational spectra are also consistent with *2B*. Strong bands in the infrared spectrum at 930, 910, 895, 500, 490, and 450 $cm^{-1}$ and in the Raman spectrum at 1034, 1011, and 512 $cm^{-1}$ were observed. The 512 $cm^{-1}$ Raman band, tentatively associated with the terminal W=S group, is at slightly higher frequency than in $WS_4$ or $WOS_3$ complexes of the coinage metals which contain doubly or singly bridging sulfurs [2, 3]. Coupling between W=O and W=S vibrations may occur and it is possible that pure modes are not observed. Consistent with our results, Müller and Heinsen [4] have interpreted the vibrational spectra of $[M(WOS_3)_2]^{2-}$ (M = Co, Ni, Zn) to indicate only sulfur coordination to the central metal atom M.

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TABLE I. Summary of Experimental Conditions.

| | |
|---|---|
| Molecular Formula | $C_{12}H_{30}P_2PtS_4W$ |
| Lattice Constants | $a = 9.081(1)$ Å<br>$b = 14.516(4)$<br>$c = 16.819(3)$<br>$\beta = 82.33(1)°$<br>$Z = 4$ |
| Density | $D_m = 2.24(2)$ g cm$^{-3}$<br>$D_x = 2.193$ g cm$^{-3}$ |
| Measurement Temperature | 22(1) °C |
| Radiation | MoK$\alpha$ ($\lambda = 0.71069$ Å) |
| Monochromator | Graphite, bisecting mode |
| Systematic Absences | $0k0$ absent for $k = 2n + 1$<br>$h0l$ absent for $h + l = 2n + 1$ |
| Space Group | $P2_1/n$ |
| General Equivalent Positions | x, y, z; –x, –y, –z<br>½ + x, ½ – y, ½ + z;<br>½ – x, ½ + y, ½ – z |
| Absorption Correction Method | Gaussian quadrature |
| Maximum Absorption Correction | 2.01 |
| Minimum Absorption Correction | 1.70 |
| Diffractometer | Four circle diffractometer, bisecting mode |
| Number of Unique Reflections | 3207 total (2424 observed, 783 unobserved) |
| $2\theta$ limits | 5–50° |
| Agreement Among Equivalent Reflections | R = 0.030, average deviation = $0.75\sigma$ |
| Derivation of Integrated Intensity | Integrated step scan |
| Unobserved Reflection Criterion | Reflections for which $I < 3\sigma(I)$ were classified unobserved |
| Criterion for $\sigma(I)$ | $\sigma(I)^2$ = Total counts + $2.18 \times 10^{-4}$ (total counts)$^2$ |
| Criterion for $\sigma(F)$ | $\sigma(F) = [F^2 + \sigma(I)/Lp]^{1/2} - F$ |

We assume that *1* contains a tetrahedral $WS_4$ core with an edge bridging $(Ph_3P)_2Pt$ group. This follows from the structure of the $(C_2H_5)_3P$ analogue (*vide infra*).

Reduction of $(Ph_3PCH_3)_2WO_2S_2$ in the presence of *cis*-$[(C_2H_5)_3P]_2PtCl_2$ produced monomeric $[(C_2H_5)_3P]_2PtWS_4$, 3. Its infrared spectrum exhibited two strong bands at 498 and 489 cm$^{-1}$, indicative of a $W(=S)_2$ group. The corresponding Raman bands occurred at 506 and 496 cm$^{-1}$; a much weaker band at 455 cm$^{-1}$ is probably associated with the sulfurs bridging platinum and tungsten. To further define the structure of these ternary metal sulfides, the structure of *3* was determined by X-ray methods.

## Experimental

### *(Ph$_3$P)$_2$PtWS$_4$ (1) and (Ph$_3$P)$_2$PtWOS$_3$ (2)*

A mixture of 1.58 g (2 mmol) $(Ph_3P)_2PtCl_2$, 0.54 g (2 mmol) $Ph_3P$, 1.66 g (2 mmol) $(Ph_3PCH_3)_2WO_2S_2$, and 100 ml $CH_2Cl_2$ was refluxed and stirred under nitrogen for five days. The reaction mixture was filtered to obtain 0.73 g *2*; the filtrate was evaporated to *ca.* 4 ml and an additional 0.5 g of the product was collected on a filter. The total yield was 1.23 g. The remaining $CH_2Cl_2$ solution was chromatographed on a 12″ × 1″ silica gel column. Dichloromethane eluted *1* as a yellow band. Slow evaporation of an acetone–dichloromethane solution yielded 0.15 g of bright yellow flakes. *Anal.*: Calcd. for *1*: C, 41.90; H, 2.91; P, 6.01; Pt, 18.91; S, 12.42; W, 17.85, mol. wt. 1031. Found: C, 42.14; H, 2.78; P, 6.32; Pt, 18.54; S, 12.91; W, 17.83, mol. wt. ($CHCl_3$) 1014. IR (Nujol): Strong bands at 505, 495, 455 [not coincident with bands in $(Ph_3P)_2PtCl_2$]. Raman spectrum (5145 Å excitation): 515, 509 cm$^{-1}$. Electronic spectrum (1,2-$C_2H_4Cl_2$): 390 nm (log$\epsilon$ 3.51). $\{^1H\}^{31}P$ NMR ($CH_2Cl_2$): –17.3 ppm (relative to external 85% $H_3PO_4$).

$(Ph_3P)_2PtWOS_3$ was purified by recrystallization from dimethylformamide. *Anal.* Calcd. for $C_{36}H_{30}OP_2PtS_3W$: C, 42.56; H, 2.96; Pt, 19.21; S, 9.45; W, 18.13; mol. wt. 1015. Found: C, 42.51; H, 3.26; Pt, 19.14; S, 9.53; W, 18.02; mol. wt. (dimethylformamide) 1046. IR (Nujol): Strong bands at 930, 910, 895, 500, 490 and 450 cm$^{-1}$. Raman spectrum: 1034, 1011, 512, 468 cm$^{-1}$. Electronic spectrum

TABLE II. Summary of Solution of Structure.

| | |
|---|---|
| Programs Used | XRAY 76. J. M. Stewart, The XRAY SYSTEM, Technical Report (1976) TR446, Computer Science Center, University of Maryland. |
| Atomic Scattering Factors | H: R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, *42*, 3175 (1965)<br>Others: D. T. Cromer, and J. B. Mann, *Acta Cryst.*, *A24*, 321 (1968) |
| Anomalous Scattering | Values for $\Delta f'$ and $\Delta f''$ from 'International Tables for X-ray Crystallography', Vol. IV, K. Lonsdale, ed., Kynoch Press, Birmingham, England (1962) |
| Solution | Direct methods for heavy atoms. Difference Fourier for light atoms |
| Extinction | No correction |
| Weighting Scheme | $w = 1/\sigma$ (F) for observed reflections<br>$w = 0$ for unobserved reflections |
| Refinement | Full matrix least squares. Refinement based on minimization of $\Sigma w/(F_{obs}^2 - F_{calc}^2)^2$ |
| R Value | $R = (\Sigma \vert \Delta F \vert)/\Sigma F_{obs}$ |

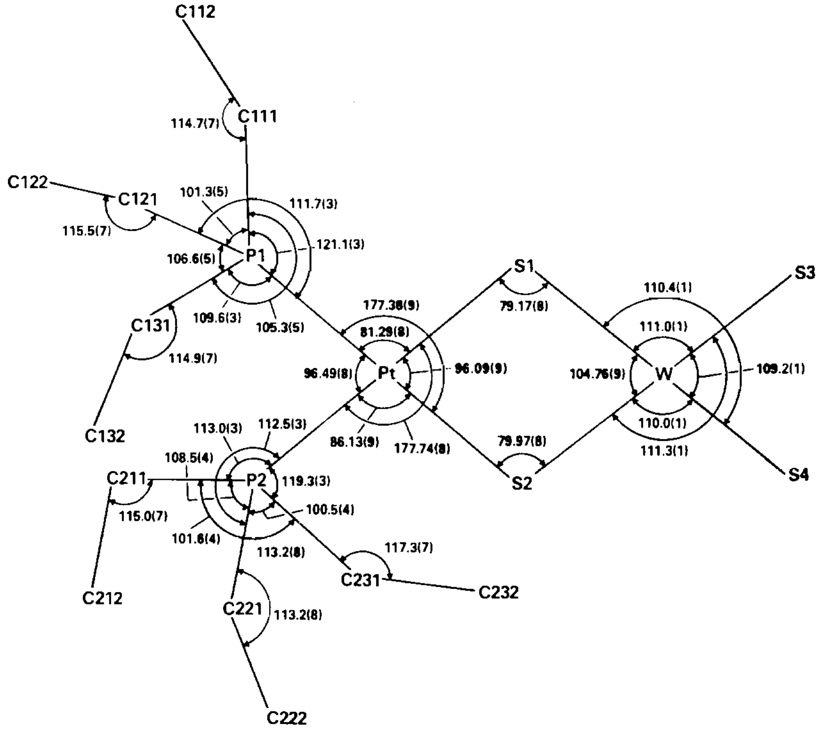


Fig. 1. Bond angles.

(DMF): 334(sh), 394(3.59) nm. $\{^1H\}^{31}P$ NMR (DMF): −13.7 ppm. $J^{31}P$–$^{195}Pt$ 3560 Hz.

### $[(C_2H_5)_3P]_2PtWS_4$ (3)

A solution of 0.4 g (1 mmol) *cis*-$(PEt_3)_2PtCl_2$ [5], 0.83 g (1 mmol) $(Ph_3PCH_3)_2WO_2S_2$ and 50 ml dichloromethane was stirred for seven days at room temperature. The reaction mixture was filtered, evaporated to a small volume, and chromatographed on a 12″ X 1″ Florisil column. Dichloromethane eluted a yellow band. Ethanol was added to the eluate and the solution concentrated on a rotary evaporator to give yellow needles. Yields ranged from 0.07 to 0.10 g. *Anal.* Calcd for $C_{12}H_{30}P_2PtS_4W$: C, 19.38; H, 4.04; P, 8.32; Pt, 26.24; S, 17.23; W, 24.76; mol. wt. 743. Found: C, 19.39; H, 4.20; P, 8.60; Pt, 27.40; S, 16.85; W, 25.29; mol. wt. ($CHCl_3$), 799. The compound decomposed without melting on heating. IR (KBr): 2955(m), 2920(w), 2860(w), 1540(w), 1500(w), 1460(w), 1250(br, w), 1037(s), 760(s), 730(w), 720(w), 498(s), 489(s), 452(m), 435(m) cm$^{-1}$. Raman (solid sample, 5145 Å excitation): 506(vs), 496(vs), 461(w), 317(w), 185(m), 113(w) cm$^{-1}$. $^1H$ NMR ($CDCl_3$): complex multiplets at

TABLE III. List of Atomic Parameters.[a]

| Atom | X | Y | Z | U11 (or U) | U22 | U33 | U12 | U13 | U23 |
|---|---|---|---|---|---|---|---|---|---|
| Pt | .21388(4) | .32126(3) | .78720(2) | .0200(2) | .0461(2) | .0210(2) | .0029(2) | –.0026(1) | .0040(2) |
| W | .34564(4) | .26405(3) | .93003(2) | .0329(2) | .0579(3) | .0245(2) | .0041(2) | –.0085(2) | .0045(2) |
| P1 | .3180(2) | .3215(2) | .6541(1) | .030(1) | .053(2) | .024(1) | .009(1) | .000(1) | .006(1) |
| P2 | –.0139(2) | .3772(2) | .7664(1) | .023(1) | .044(2) | .034(1) | .003(1) | –.004(1) | .006(1) |
| S1 | .4549(3) | .2645(2) | .8035(1) | .030(1) | .093(2) | .034(1) | .020(1) | –.002(1) | .013(1) |
| S2 | .1181(3) | .3182(3) | .9241(1) | .041(1) | .135(3) | .025(1) | .027(2) | .003(1) | .016(2) |
| S3 | .3388(4) | .1275(2) | .9794(2) | .086(2) | .070(2) | .054(2) | –.007(2) | –.020(2) | .020(2) |
| S4 | .4616(4) | .3528(2) | 1.0018(2) | .087(2) | .083(2) | .067(2) | .000(2) | –.042(2) | –.010(2) |
| C111 | .207(1) | .3509(7) | .5739(5) | .054(6) | .074(8) | .026(5) | .013(6) | –.004(5) | .003(5) |
| C112 | .296(1) | .3620(9) | .4913(5) | .081(8) | .12(1) | .022(5) | .024(8) | –.010(6) | .014(6) |
| C121 | .389(1) | .2078(8) | .6218(5) | .058(7) | .075(8) | .030(5) | .033(6) | –.003(5) | .000(5) |
| C122 | .277(1) | .1289(8) | .6366(8) | .083(9) | .052(8) | .10(1) | .011(7) | –.040(8) | .003(7) |
| C131 | .476(1) | .3993(8) | .6406(5) | .025(5) | .099(9) | .043(6) | –.006(6) | –.005(4) | .028(6) |
| C132 | .438(1) | .5009(8) | .6625(7) | .075(8) | .059(8) | .094(9) | –.019(7) | .011(7) | –.003(7) |
| C211 | –.004(1) | .4916(7) | .7202(5) | .034(5) | .051(6) | .037(5) | .002(5) | –.007(4) | –.001(5) |
| C212 | –.140(1) | .5190(7) | .6804(7) | .062(7) | .046(7) | .078(8) | .015(6) | –.038(6) | .008(6) |
| C221 | –.111(1) | .3004(7) | .7056(6) | .037(5) | .057(7) | .049(6) | –.008(5) | –.018(5) | .008(5) |
| C222 | –.130(1) | .2043(7) | .7396(7) | .069(8) | .044(7) | .087(9) | –.024(6) | –.018(7) | .003(6) |
| C231 | –.159(1) | .3946(7) | .8533(6) | .026(5) | .077(8) | .048(6) | .010(5) | .001(4) | .021(6) |
| C232 | –.144(1) | .4794(8) | .9058(6) | .084(8) | .073(8) | .055(7) | .006(7) | .016(6) | –.031(6) |
| H1111 | .13(1) | .300(6) | .571(5) | .07(3) | | | | | |
| H1112 | .15(1) | .411(6) | .589(5) | .07(3) | | | | | |
| H1211 | .43(1) | .210(6) | .562(5) | .07(3) | | | | | |
| H1212 | .48(1) | .192(6) | .652(5) | .07(3) | | | | | |
| H1311 | .55(1) | .376(7) | .675(5) | .07(3) | | | | | |
| H1312 | .52(1) | .395(6) | .581(5) | .07(3) | | | | | |
| H2111 | .01(1) | .540(6) | .764(5) | .07(3) | | | | | |
| H2112 | .09(1) | .495(6) | .678(5) | .07(3) | | | | | |
| H2211 | –.21(1) | .328(6) | .700(5) | .07(3) | | | | | |
| H2212 | –.05(1) | .298(6) | .648(5) | .07(3) | | | | | |
| H2311 | –.26(1) | .397(6) | .831(5) | .07(3) | | | | | |
| H2312 | –.16(1) | .336(6) | .888(5) | .07(3) | | | | | |

[a] The temperature factor has the form of exp (–T) where T = 8*(pi**2)*u)(sin(theta)/lambda)**2 for isotropic atoms, T = 2*(pi**2)*sumij(h(i)*h(j)*u(i, j)*astar(i)*astar(j)), for anisotropic atoms. Astar(i) are reciprocal axial lengths and h(i) are Miller indices. The e.s.d. of the last significant digit is given in parentheses.

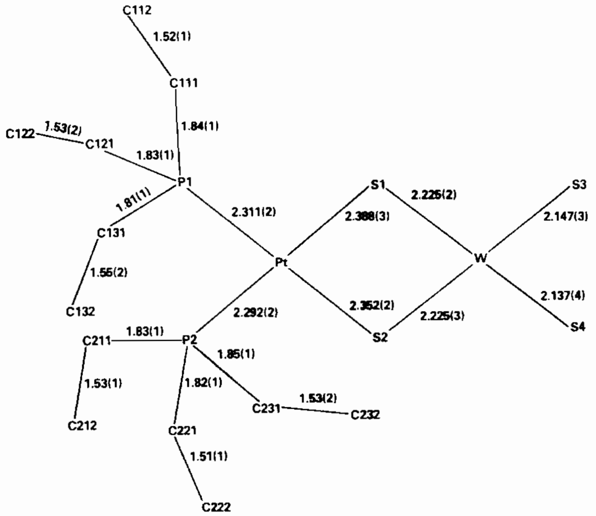


Fig. 1B. Bond distances.

–2.30, –1.25 ppm. $\{^1H\}^{31}P$ NMR ($CH_2Cl_2$): singlet at 13.9 ppm, $J^{31}P–^{195}Pt$ 3270 Hz. Electronic spectrum (1,2-$C_2H_4Cl_2$): $\lambda_{max}$ at 393 (3.60) 290 (4.18) nm.

The crystals used for X-ray diffraction work were grown by slow evaporation of a dichloromethane–toluene solution. The X-ray crystallographic experimental conditions are summarized in Tables I and II. A table of observed and calculated structure factors is available as supplementary material.

## Description of the Structure

$[(C_2H_5)_3P]_2PtWS_4$ consists of an approximately tetrahedral $WS_4$ unit with an edge bridging $[(C_2H_5)_3P]_2Pt$ moiety. Angles and interatomic distances are given in Fig. 1; an ORTEP drawing is shown in Fig. 2 [6]. The unsymmetrical nature of this bridging

TABLE IV. Platinum Sulfur Distances.

| *Compound* | *d(Pt–S)* Å | *Reference* |
|---|---|---|
| $[(Ph_3P)_2Pt(S_2F)][HF_2]$ | 2.322, 2.340 | a |
| $\{[(C_3H_7)_3P]Pt(SC_2H_5)Cl\}_2$ | 2.267–2.378 | b |
| $Pt_2S(CO)(Ph_3P)_3$ | 2.22 | c |
| $[Pt\{SP(C_2H_5)_2\}P(OPh)_3]_2$ | 2.377 | d |
| $PtBr_2(1,4\text{-}C_2H_4OS)_2$ | 2.281 | e |
| $Pt[S_2CN(i\text{-}C_4H_9)_2]_2[PhP(CH_3)_2]_2$ | 2.335, | f |
| $Pt(S_2CO)(Ph_3P)_2$ | 2.347, 2.326 | f |
| $(Ph_4As)[Pt(S_2COC_2H_5)_3]$ | 2.31 avg. | g |
| $Pt[S_2CN(C_2H_5)_2]_2$ | 2.30 | h |
| $PtS_2$ | 2.34 | i |
| $(NH_4)_2Pt(S_5)_3\cdot 2H_2O$ | 2.390 avg. | j |
| $[(C_3H_7)_3PPtClSCN]_2$ | 2.327 (*trans* to Cl)<br>2408 (*trans* to P) | k |
| $Pt_2Br_4[S(C_2H_5)_2]_2$ | 2.21 avg. | l |
| $[(C_2H_5)_3P]_2PtWS_4$ | 2.37 avg. | m |

[a] J. A. Evans, M. J. Hacker, R. W. D. Kemmitt, D. R. Russell, and J. Stocks, *Chem. Commun.*, 72 (1972). [b] M. C. Hall, J. A. J. Jarvis, B. T. Kilbourn, and P. G. Owston, *J. Chem. Soc. Dalton Trans.*, 1544 (1972). [c] A. C. Skapski and P. G. H. Troughton, *J. Chem. Soc. A*, 2772 (1969). [d] K. P. Wagner, R. W. Hess, P. M. Treichel, and J. C. Calabrese, *Inorg. Chem.*, *14*, 1121 (1975). [e] J. C. Barnes, G. Hunter, and M. W. Lown, *J. Chem. Soc. Dalton Trans.*, 458 (1977). [f] I. J. B. Lin, H. W. Chen, and J. P. Fackler, Jr., *Inorg. Chem.*, *17*, 394 (1978). [g] M. C. Cornock, R. O. Gould, C. L. Jones, J. D. Owen, D. F. Steele, and T. A. Stephenson, *J. Chem. Soc. Dalton Trans.*, 496 (1977). [h] A. Z. Amanov, G. A. Kukina and M. A. Porai-Koshits, *J. Struct. Chem. (Engl. Trans.)*, *8*, 149 (1967). [i] S. Furuseth, K. Selte, and A. Kjekshus, *Acta Chem. Scand.*, *19*, 257 (1965). [j] P. E. Jones and L. Katz, *Acta Cryst.*, *B25*, 745 (1969); (k) U. A. Gregory, J. A. J. Jarvis, B. T. Kilbourn, and P. G. Owston, *J. Chem. Soc. A*, 2770 (1970). [l] D. L. Sales, J. Stokes and P. Woodward, *J. Chem. Soc. A*, 1852 (1968). [m] This work.

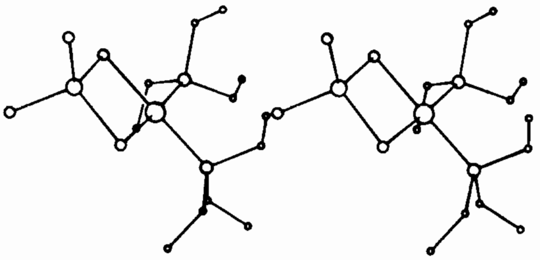


Fig. 2. Stereoview of bis(triethylphosphine)platinum tetrathiotungsten.

results in distortion of the tetrahedral angles about tungsten. Thus, <S(1)–W–S(2) is 104.8(1)° and <S(3)–W–S(4) is 109.2(1)°. The two independent tungsten–terminal sulfur distances, d(W–S(3)) and d(W–S(4)) are 2.147(3) and 2.137(4) Å respectively. These distances are consistent with formal W–S double bonds, examples of which are tabulated in Ref. 3. The bridging sulfur atoms form longer bonds to tungsten and d(W–S(1)) and d(W–S(2)) are 2.225(2) and 2.225(3) Å respectively. These longer distances presumably correspond to tungsten–sulfur single bonds and are quite close to those found in other ternary metal sulfur clusters. The mean W–S separation for doubly bridging sulfur in the net compound $(Ph_2PCH_3)_2Au_2WS_4$ is 2.22 Å [1]. In contrast, the mean d(W–S) for triply bridging sulfur in $[(C_7H_7)_3P]_4Cu_4W_2O_2S_6$ is 2.37 Å [3].

The coordination geometry about platinum is essentially square planar. The maximum deviation of any atom from the least squares plane calculated through P(1), P(2), S(1), and S(2) is 0.065 Å. The dihedral angle between this plane and that defined by W,S(3) and S(4) is 89.58°. The mean Pt–S separation is 2.37 Å, in reasonable agreement with other literature values, Table IV, which range from 2.22 to 2.41 Å. The mean d(Pt–P) is 2.30 Å, also within the range observed for other triethylphosphine platinum compounds. When compared with d(Pt–P) of 2.315 Å in $[(C_2H_5)_3P]_2PtBr_2$ [7] the *trans* effect of the bridging sulfurs is not striking.

## Discussion

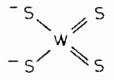
The structure of *3* consists of a tetrahedral $WS_4$ core acting as a bidentate ligand toward a *cis*-$[(C_2H_5)_3P]_2Pt$ moiety. Unlike $(Ph_4P)_2[Ni(MoS_4)_2]$, the

TABLE V. Metal–Metal Distances in Sulfur Bridged Complexes.

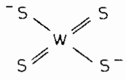
| *Predicted d(M–M)*[a] | | *Obsd.* | *(Compound)* | *Obsd. – Predicted* | *<MSM'* |
|---|---|---|---|---|---|
| Au–W | 2.813 | 2.84 | $[(Ph_2PMe)Au]_2WS_4$ | +0.03 | 75.2° |
| Au–Mo | 2.805 | 2.81 | $[Ph_2PMe)Au]_2MoS_4$ | +0.005 | 74.7° |
| Cu–W | 2.649 | 2.78 | $[(p\text{-}CH_3C_6H_4)_3P]_4Cu_4W_2O_2S_6$ | +0.13 | 74.8° |
| Ag–W | 2.816 | 3.00 | $(Ph_2PMe)_4Ag_4W_2S_8$ | +0.18 | 77.0° |
| Pt–W | 2.74 | 2.94 | $(Et_3P)_2PtWS_4$ | +0.20 | 79.6° |
| Ni–Mo | 2.61 | 2.80 | $[Ni(MoS_4)_2]^{2-}$ | +0.19 | 77.8° |

[a] From sums of atomic radii.

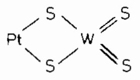
only other material in which this mode of bonding to a tetrathiametallate has been established by X-ray studies [8], the sulfur bridges between the two metals are unsymmetrical and are 0.15 Å closer to tungsten than to platinum. These data, taken with the unexceptional d(Pt–P), suggest that in *3*, bonding to the $WS_4$ unit which occurs through two of the sulfurs, involves only a minimal perturbation of the remainder of the tetrathiatungstate core. In the infrared spectra of *1*, *3*, and $[Ni(WS_4)_2]^{2-}$, on which a normal coordinate analysis has been carried out [9] the terminal W=S stretching bands are shifted to higher energy by about 45 $cm^{-1}$ relative to the triply degenerate W–S stretching mode at 455 $cm^{-1}$ in free $WS_4^{2-}$ [10]. This can be accounted for by noting that various resonance structures for $WS_4^{2-}$ such as *4a* and *4b* average formal tungsten–sulfur single and double bonds. This does not occur in the edge bridged complex *4c* in which the tungsten–sulfur bond order is seen to be greater. In agreement with this view of



4a



4b



4c

localized bonding in *3*, the low energy transition in the electronic spectrum, which is presumably due to a ligand → metal charge transfer process [10], is only slightly shifted from its value in $WS_4^{2-}$.

Earlier, it was postulated, on the basis of acute angles at the bridging sulfur atoms in $(Ph_2PCH_3)_2$-$Au_2WS_4$, that the Au–W separation of 2.84 Å may result from an attractive metal–metal interaction [1]. It could be argued, however, that the geometry found in this gold–tungsten sulfide could as well result from constraints imposed by a rigid system. Results obtained with *3* reveal that the geometry of Pt–S–W–S rhombus is not as constrained as might be thought: the interior angles at the bridging sulfurs have opened to 79.57° (avg.) and the metal–tungsten separation has increased to 2.947. This distance is 0.20 Å longer than that calculated from the sums of the atomic radii. The available X-ray data for ternary metal sulfides derived from molybdenum and tungsten thiametallates are summarized in Table V. They suggest that the MSM' units are somewhat flexible and if M–M' separations are ≤0.2 Å in excess of the sums of atomic radii, an attractive metal–metal interaction, sufficient to contract the M–S–M' bridging angles may exist.

Pidcock and co-workers have established empirical correlations between $^1J(Pt–P)$ and d(Pt–P) in a series of platinum(II) complexes [11, 12]. In *3*, d(Pt–P) avg. is 2.30 Å, one of the longer distance among the compounds considered in Ref. 11. The $^{195}Pt–^{31}P$ coupling constant, 3270 cps, appears to be too large to conform to these correlations. No unique explanation is obvious but graphical relationships may work best in groups of closely related compounds.

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