does not depend on *r*. The enzymatic digestion of Pt(1,3-dach)-DNA also indicates similar results, and the difference in the relative ratio of the two Pt(1,3-dach)[d(GpG)] compounds becomes much greater (1.0:0.26). Stereoselectivity observed in the experiment with the DNA presumably arises from a steric hindrance, being caused by the axially standing cyclohexane ring. Such steric hindrance may impede an approach toward DNA. This may be the reason for its weaker antitumor activity and toxicity.

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Synthesis of the Octathiotritungstate Anion, $W_3S_8^{2-}$. First Example of Square-Planar Coordination about a Tungsten Atom

Sir:

In recent years the WS_4^{2-} anion has been extensively used as a versatile bidentate ligand and for the syntheses of a variety of soluble binary or ternary metal sulfides.[1] In all these complexes derived from WS_4^{2-} the coordination geometries about the W atoms are either tetrahedral or square pyramidal.[2-8] Here we report the synthesis and structure of $[PPN]_2[W_3S_8]$ (PPN = bis(triphenylphosphoranylidene)ammonium). The central W atom in the $W_3S_8^{2-}$ ion is at the center of a square plane of S atoms; to our knowledge this is the first example in the coordination chemistry of W where square-planar geometry is observed.

The reactions of WS_4^{2-} with acids are known to lead to a mixture of thiotungstate anions,[3,8] although there are no previous reports of the $W_3S_8^{2-}$ ion. We have prepared it as $[PPN]_2[W_3S_8]$ by the reaction of $[NH_4]_2[WS_4]$ with H_2SO_4 according to the stoichiometry shown in (1), followed by addition of [PPN]Cl in

$$3WS_4^{2-} + 4H^+ \rightarrow W_3S_{9-x}^{2-} + 2H_2S + (1 + x)S\downarrow \qquad x = 0 \text{ or } 1 \tag{1}$$

methanolic solution. Although by following the stoichiometry shown in (1) we minimized the formation of $W_4S_{12}^{2-}$, it appears from the IR spectral data[9] that anions such as $W_3S_8O^{2-}$ and $W_3S_9^{2-}$ are also formed. Attempts to precipitate one of these thiotungstate anions selectively with the use of different tetraalkylammonium salts or separation of the anions by chromatographic techniques have not been successful. However, fractional crystallization by the slow diffusion of hexane into a dichloromethane solution of the crude product gives orange needle-like crystals of $[PPN]_2[W_3S_8]$ suitable for characterization by X-ray[10] and other physical methods.[9,11]

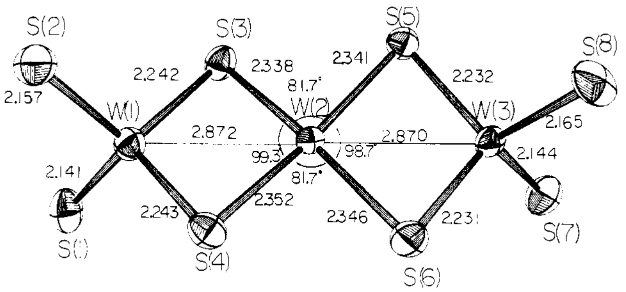

Figure 1. Structure of the $W_3S_8^{2-}$ ion. The labeling scheme and some bond distances and bond angles are shown. The estimated standard deviations in the W-W and W-S bond distances and the S-W-S bond angles are 0.001 Å, 0.004 Å, and 0.1°, respectively.

Table I. Comparisons of Thiotungstate Anions

anion	mean W-W, Å	formal oxidn states	no. of d electrons per W-W bond
$[W_4S_{12}]^{2-\,a}$	3.027	+6, +5, +5, +6	$^2/_3$
$[W_3S_8O]^{2-\,b}$	2.961	+6, +4, +6	1
$[W_3S_9]^{2-\,c}$	2.965	+6, +4, +6	1
$[W_2S_4(S_2C_2H_4)_2]^{2-\,d}$	2.862 (1)[f]	+5, +5	2
$[W_3S_8]^{2-\,e}$	2.871 (1)	+6, +2, +6[g]	2

[a] Reference 3. [b] Reference 2. [c] Reference 7. [d] Reference 5. [e] This work. [f] Estimated standard deviation of the mean is given only in those cases where equivalent distances were averaged. [g] An alternative assignment is +5, +4, +5, but this seems less likely because the terminal tungsten atoms have nearly perfect tetrahedral environments characteristic of the +6 state. With either assignment the number of d electrons per bond remains the same.

The structure of the $W_3S_8^{2-}$ ion is shown in Figure 1. The ion has pseudo-D_{2h} symmetry with tetrahedral coordination around the terminal W atoms. The central W atom has square-planar coordination of S atoms with a very slight tetrahedral distortion: deviations from the best weighted least-squares plane are W(2) = -0.0032 (6), S(3) = -0.179 (4), S(4) = 0.188 (4), S(5) = 0.167 (4), S(6) = -0.210 (4) Å.

Three different types of W-S bonds, four around the central W atom, four terminal ones, and four bonds involving terminal W and bridging S atoms, with average values 2.344 (3), 2.152 (6), and 2.237 (3) Å, respectively, are observed. The last two values are very close to the corresponding distances in the WS_4^{2-} anion and in bis(tetrathiotungstato) complexes.[1,12-15]

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(9) $[PPN]_2[W_3S_8]$ has IR bands at 495, 490, and 440 cm^{-1}. Bands (cm^{-1}) in related compounds as described by the authors are as follows: for $W_3S_8O^{2-}$,[2] 970 (W-O), 495 ($W-S_{term}$), 465 and 453 (W-S-W); for $W_3S_9^{2-}$,[8] 525 ($W-S_{apex}$), 490 and 485 ($W-S_{term}$), 465 and 435 (W-S-W); for $W_4S_{12}^{2-}$,[3] 525 ($W-S_{apex}$), 495 and 485 ($W-S_{term}$), 448 and 350 (W-S-W). From the relative intensities of the characteristic IR bands, less than 20% of the crude product is $[PPN]_2[W_3S_8]$ while more than 50% is $[PPN]_2[W_3S_9]$.
(10) Crystal data for $[PPN]_2[W_3S_8]$, $C_{72}H_{60}N_2P_4S_8W_3$: triclinic, C_i^1-$P\bar{1}$, $Z = 2$ in a cell of dimensions $a = 11.548$ (2) Å, $b = 15.175$ (5) Å, $c = 22.181$ (5) Å, $\alpha = 104.90$ (2)°, $\beta = 90.80$ (2)°, $\gamma = 110.31$ (2)°, and $V = 3500$ Å^3 at -150 °C. A total of 13 088 intensities were measured out to $2\theta(\text{Mo } K\alpha_1) = 40°$ to yield 6512 unique reflections after correction for absorption and averaging. Refinement was by full-matrix least-squares methods on F^2 with all unique data used. All non-hydrogen atoms were refined anisotropically. The positions of the H atoms were idealized and their contributions to F_o^2 included. The final cycle of refinement of 802 variables and 6512 observations converged to $R(F^2) = 0.064$. The conventional R index, $R(F)$, for the 4060 reflections having $F_o^2 > 3\sigma(F_o^2)$ is 0.037. A list of positional parameters is provided in Table II (supplementary material).
(11) Magnetic susceptibility measurements over the range 5-290 K indicate that $[PPN]_2[W_3S_8]$ is diamagnetic. The ^1H NMR spectrum of the material from -60 to +5 ppm shows no resonances that can be ascribed to possible W-H bonds, nor are there any characteristic IR bands for W-H stretching modes in the region 2200-1600 cm^{-1}. The cyclic voltammogram of $[PPN]_2[W_3S_8]$ (2.0 mM in acetonitrile) shows no reversible or quasi-reversible oxidation or reduction peaks between +2.0 and -2.0 V.
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The W-W distances, assigned formal oxidation states of the W atoms, and the number of d electrons available per W-W interaction are shown in Table I for $W_3S_8^{2-}$ and related ions. There is a trend of decreasing W-W bond distance with increase in the number of d electrons available per W-W bond. This trend is consistent with the results of a recent ab initio calculation carried out on $Mo_3S_9^{2-}$, where donation of electron density from the central Mo atom to the terminal ones is suggested.[16]

Acknowledgment. This research was supported by the National Science Foundation (Grant CHE 83-08076). S.B. acknowledges with gratitude leave from Alchemie Research Centre, Thane 400601, India.

Supplementary Material Available: Table II, a list of positional parameters (1 page). Ordering information is given on any current masthead page.

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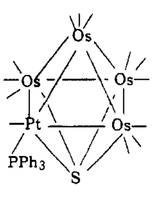
Synthesis of Square-Pyramidal Platinum-Osmium Clusters by Metal-Metal Exchange. Isolation and Structural Characterization of a Hexanuclear Intermediate

Sir:

The discovery that some metal alloys have catalytic properties far superior to those of their individual components has been a significant advance to the area of heterogeneous catalysis[1] and has also been a major stimulus for the study of heteronuclear (mixed-metal) cluster compounds.[2] Systematic routes for the synthesis of heteronuclear metal cluster compounds are now beginning to emerge. The metal-metal exchange reaction, e.g. (1),

$$M_nL_x + M'L'_y \rightarrow M_{n-1}M'L_{x-a}L'_{y-b} + ML_aL_b \qquad (1)$$

has been prominent among these, but this reaction is complicated mechanistically both by ligand exchange processes and by the sequence of metal-addition and -elimination steps that are frequently unobserved.[3,4] In this report we describe the synthesis of the square-pyramidal heteronuclear cluster $PtOs_4(CO)_{13}(PPh_3)(\mu_4\text{-}S)$ (**1**) from the reaction of the square pyramidal ho-



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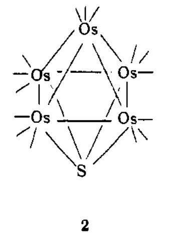

2

monuclear cluster $Os_5(CO)_{15}(\mu_4\text{-}S)$ (**2**) with $Pt(PPh_3)_2C_2H_4$. From this reaction we have also isolated the hexanuclear adduct $PtOs_5(CO)_{15}(PPh_3)_2(\mu_4\text{-}S)$ (**3**) and have shown that it is a precursor to **1**.

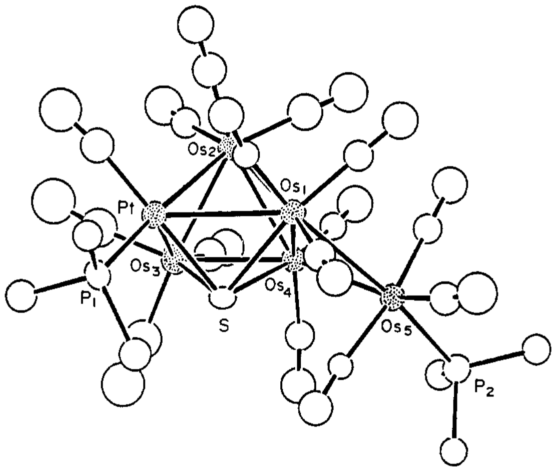

Figure 1. ORTEP diagram of $PtOs_5(CO)_{15}(PPh_3)_2(\mu_4\text{-}S)$ (**3**) showing 50% probability thermal motion ellipsoids. For clarity only carbon atoms directly attached to the phenyl rings have been included.

$Os_5(CO)_{15}(\mu_4\text{-}S)^5$ (**2**) (30 mg, 21 μmol) was mixed with $Pt(PPh_3)_2C_2H_4$ (15.5 mg, 21 μmol) in THF solvent at 0 °C and stirred for 0.5 h. After the mixture was warmed to 25 °C and stirred for an additional 2 h, the solvent was removed and the dark brown residue was separated on silica TLC plates with CH_2Cl_2/hexane, 35/65 v/v, solvent. Six bands were separated. In order of elution these were unreacted **2** (10%), brown **1** (6%), orange-red $Os_5(CO)_{14}PPh_3(\mu_4\text{-}S)$ (**4**)[6] (9%), green-brown **5**, brown **6**, and purple **3** (7%).[7] Compounds 5 and 6 are still under investigation. Compounds **1** and **3** have been characterized by IR and ^{31}P NMR spectroscopies,[7] elemental analyses,[8] and single-crystal X-ray diffraction analyses.[9] Compound **1** was found to be a structural analogue of **2** in which a $Pt(PPh_3)CO$ moiety was exchanged for one of the $Os(CO)_3$ units of the square base.[10,11]

Compound **3** is a hexanuclear species and its molecular structure is shown in the ORTEP diagram in Figure 1.[9,12] The cluster of

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(6) The identity of **4** was confirmed by an independent synthesis from the reaction of **2** with PPh_3. Anal. Calcd: C, 23.47; H, 0.92. Found: C, 23.60; H, 0.96.

(7) IR spectra were obtained on a Nicolet 5DXB FT-IR spectrometer in CH_2Cl_2 solvent. (CO) positions (cm^{-1}) are as follows: for **1**, 2087.4 (w), 2051.5 (s), 2019.7 (m), 1997.1 (w), 1972.9 (w); for **3**, 2064.5 (m), 2048.1 (s), 2035.9 (s), 2028.8 (s), 2017.1 (m), 1994.1 (m), 1971.9 (m), 1901.4 (w); for **4**, 2090.7 (s), 2055.8 (s), 2044.9 (s), 2028.9 (s), 2011.8 (s), 1996.4 (m), 1979.0 (m), 1977.0 (w), 1951.4 (w); for **5**, 2093.0 (w), 2086.6 (w), 2061.5 (s), 2050.9 (s), 2028.8 (s), 2021.8 (s), 2001.7 (w), 1792.7 (w); for **6**, 2076.3 (s), 2043.3 (s), 2029.4 (s), 2015.0 (s), 1986.1 (m), 1963.1 (m), 1903.9 (w), 1784.4 (w). ^{31}P NMR spectra in CD_2Cl_2 (δ vs. H_3PO_4): for **1**, 43.86 (t, J_{Pt-P} = 2601 Hz); for **3** 26.23 (t, J_{Pt-P} = 2442 Hz), 5.31 (s); for **4**, 35.34 (s).

(8) Elemental analyses were performed by MicAnal, Tucson, AZ. Anal. Cacld for **1**: C, 23.06; H, 0.93. Found: C, 22.95; H, 0.77. Calcd for **3**: C, 28.85; H, 1.41. Found: C, 29.12; H, 1.23. Calcd for **4**: C, 23.47; H, 0.92. Found: C, 23.6; H, 0.96.

(9) Intensity data were collected on an Enraf-Nonius CAD4 diffractometer by the Molecular Structure Corp., College Station, TX. Structure solutions and refinements were performed on a Digital Equipment Corp. VAX 11/782 computer by using the Enraf-Nonius program library SDP-Plus at the University of South Carolina. Diffraction data were corrected for the effects of absorption.

(10) Crystals of **1** were grown by slow evaporation of solvent from solutions in a CH_3OH/CH_2Cl_2 solvent mixture. The crystals belong to the triclinic space group $P\bar{1}$, No. 2, with a = 13.116 (4) Å, b = 9.655 (3) Å, c = 14.669 (4) Å, α = 89.68 (3)°, β = 104.79 (2)°, γ = 89.11 (3)°, Z = 2, and ρ_{calcd} = 2.99 g/cm³. The structure was solved by a combination of Patterson and difference Fourier techniques and was refined by using 4505 reflections ($F^2 \geq 3.0\sigma(F^2)$) to the final residuals R = 0.044 and R_w = 0.052.

(11) Selected interatomic distances (Å) for **1** are Pt-Os(1) = 2.900 (1), Pt-Os(3) = 2.875 (1), Pt-Os(4) = 2.749 (1), Os(1)-Os(2) = 2.799 (1), Os(1)-Os(4) = 2.802 (1), Os(2)-Os(3) = 2.770 (1), Os(2)-Os(4) = 2.911 (1), Os(3)-Os(4) = 2.862 (1), Pt-S = 2.326 (3), Os(1)-S = 2.477 (3), Os(2)-S = 2.445 (4), and Os(3)-S = 2.499 (4).

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