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Tetramethyldiplatinum(III) (Pt–Pt) Complexes with 2-Hydroxypyridinato Bridging Ligands. 3. Compounds with Diethyl Sulfide as the Axial Ligand

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Three compounds of the type $[Pt_2(CH_3)_4(xhp)_2Et_2S]$ have been prepared and structurally characterized: **1**, xhp = 2-hydroxypyridinate ion, hp^-; **2**, xhp = 2-hydroxy-6-fluoropyridinate ion, fhp^-; **3**, xhp = 2-hydroxy-6-methylpyridinate ion, mhp^-. All are obtained by treating $[Pt_2(CH_3)_4(Et_2S)_2]$ with the appropriate Ag(xhp) reagent. In each case there are a Pt–Pt bond, 2.561 (1)–2.571 (1) Å, spanned by a head-to-head pair of xhp^- ligands, two methyl groups on each platinum atom, and a diethyl sulfide ligand bonded to the platinum atom to which the hydroxypyridine oxygen atoms are also bonded. Possible reasons for the consistent adoption of this stoichiometry and structure regardless of the 6-substituent on the xhp ligand are discussed. Crystallographic data are as follows. **1**: $P\bar{1}$, $a = 5.544$ (3) Å, $b = 16.127$ (6) Å, $c = 9.412$ (6) Å, $\alpha = 79.02$ (4)°, $\beta = 108.12$ (4)°, $\gamma = 93.70$ (3)°, $V = 1210.0$ (1) Å^3, $Z = 2$. **2**: $P\bar{1}$, $a = 9.672$ (3) Å, $b = 16.397$ (6) Å, $c = 8.394$ (2) Å, $\alpha = 85.95$ (3)°, $\beta = 107.18$ (2)°, $\gamma = 99.30$ (3)°, $V = 1254.6$ (7) Å^3, $Z = 2$. **3**: *Pbca*, $a = 10.594$ (4) Å, $b = 32.459$ (8) Å, $c = 13.753$ (5) Å, $V = 4729$ (1) Å^3, $Z = 8$.

Introduction

In two other publications[1,2] from this laboratory, we have described the preparation, properties, and structures of compounds of the type $[Pt_2(CH_3)_4(xhp)_2L_n]$, where xhp is an abbreviation for the 2-hydroxypyridinate anion (X = H) or a 6-substituted derivative with X = F, Cl, Br, or CH_3, represented respectively by hp, fhp, chp, bhp, and mhp. As explained previously, our work took as its point of departure the previous studies by Vrieze and co-workers,[3,4] who, in 1976 and 1977, prepared a series of Pt(III) complexes by the oxidation of a binuclear Pt(II) compound with Ag(I), Tl(III), or Hg(II) salts of carboxylic acids (eq 1–3[3] (R

$$[Pt_2R_4(R'_2S)_2] + 2Ag(O_2CR'') \rightarrow [Pt_2R_4(O_2CR'')_2(R'_2S)_2] + 2Ag \quad (1)$$

$$[Pt_2R_4(R'_2S)_2] + Tl(O_2CR'')_3 \rightarrow [Pt_2R_4(O_2CR'')_2(R'_2S)_2] + Tl(O_2CR'') \quad (2)$$

$$[Pt_2R_4(R'_2S)_2] + Hg(O_2CR'')_2 \rightarrow [Pt_2R_4(O_2CR'')_2(R'_2S)_2] + Hg \quad (3)$$

= methyl, phenyl, *p*-tolyl; R′ = ethyl, *n*-propyl; R″ = CH_3, CF_3, *i*-Pr)). One of these complexes was subsequently characterized by X-ray crystallography.[5] We extended this work by showing that Ag(I) salts of 2-hydroxypyridinate anions could also be used to oxidize the binuclear Pt(II) precursors (eq 4, where xhp = hp^-,

$$[Pt_2(CH_3)_4((C_2H_5)_2S)_2] + 2Ag(xhp) \rightarrow [Pt_2(CH_3)_4(xhp)_2((C_2H_5)_2S)] + 2Ag \quad (4)$$

fhp^-, chp^-, bhp^-, or mhp^-). In both Vrieze's and our studies, it was shown that the axially coordinated diethyl sulfide molecules were easily displaced by pyridine or picoline molecules.

In addition to our work on the pyridine adducts of the $[Pt_2(CH_3)_4(xhp)_4]$ complexes, we have isolated and characterized three of the Et_2S adducts that are the immediate products of reaction 4. In each case they are monoadducts and we were interested in seeing whether the xhp ligands adopted a head-to-head (HH) or a head-to-tail (HT) arrangement.

Experimental Section

The silver salts Ag(hp), Ag(fhp), and Ag(mhp) were prepared as previously described,[1] and $[Pt_2(CH_3)_4((C_2H_5)_2S)_2]$ was made by the method of Vrieze and co-workers.[3,4]

Preparation of $[Pt_2(CH_3)_4(hp)_2((C_2H_5)_2S)]$ (1). A suspension of $[Pt_2(CH_3)_4((C_2H_5)_2S)_2]$ (2.0 g, 3.2 mmol) and Ag(hp) (1.28 g, 6.4 mmol) in 50 mL of dry benzene was stirred at room temperature for 48 h. During this time the color of the reaction mixture changed from white to blue-green and eventually appeared almost black. The mixture was filtered through Celite to remove colloidal Ag, and the solvent was removed under vacuum. The oily red-orange residue was then dissolved in toluene and subsequently purified by chromatography on a silica gel column (Mallinkrodt, Silicar, Grade 62, 60–200 mesh) prepared with a 1:1 (v/v) mixture of chloroform/toluene. Concentration of the eluate by slow evaporation in air yielded large red crystals of composition $[Pt_2(CH_3)_4(hp)_2((C_2H_5)_2S)]\cdot 0.5C_7H_8$. Yield: 1.95 g, 81%.

Preparation of $[Pt_2(CH_3)_4(fhp)_2((C_2H_5)_2S)]$ (2). A suspension of $[Pt_2(CH_3)_4((C_2H_5)_2S)_2]$ (1.5 g, 2.4 mmol) and Ag(fhp) (1.05 g, 4.8 mmol) in 50 mL of dry benzene was stirred at room temperature for 48 h. The suspension, which was initially white, gradually changed to green and eventually appeared black. The colloidal Ag was removed by vacuum filtration through Celite, and the solvent was removed under vacuum, leaving an oily, orange-red residue. The residue was dissolved in chloroform (ca. 50 mL) and purified by chromatography on a silica gel column prepared as described above. Large red crystals of composition $[Pt_2(CH_3)_4(fhp)_2((C_2H_5)_2S)]\cdot 0.5C_7H_8$ were obtained by refrigeration of a concentrated sample of the eluate at −10 °C for several days. Yield: 1.91 g, 74%.

Preparation of $[Pt_2(CH_3)_4(mhp)_2((C_2H_5)_2S)]$ (3). A suspension of $[Pt_2(CH_3)_4((C_2H_5)_2S)_2]$ (2.5 g, 4.0 mmol) and Ag(mhp) (1.78 g, 8.0 mmol) in 50 mL of dry benzene was stirred at room temperature for 72 h. The colloidal Ag was removed by vacuum filtration through Celite. The red-orange solution was subsequently evaporated by dryness under vacuum, leaving a red microcrystalline solid. The solid was then dissolved in chloroform and purified by chromatography on a silica gel column prepared as described above. Beautiful red crystals of composition $[Pt_2(CH_3)_4(mhp)_2((C_2H_5)_2S)]$ were obtained after refrigerating a concentrated sample of the eluate at 0 °C for several days. Yield: 2.65 g, 89%.

X-ray Crystallography. Experimental and computational methods used were those routinely employed in this laboratory.[6] For all three compounds crystallographic and procedural information is summarized in Table I. Some additional details are as follows. For **1**, the original absorption correction (by the ψ-scan method) was determined to be inadequate and an additional empirical absorption correction (DIFABS) was applied.[7] An additional correction for crystal decay was also supplied, as the monitoring of three intensity standards over the course of the data collection showed the crystal to be slowly losing solvent. The molecule resides on a general position in the unit cell, and the platinum atom positions were obtained from the direct-methods program MULTAN 11/82. Alternating least-squares cycles and difference Fourier maps revealed the remaining non-hydrogen atoms. No attempts were made to

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Table I. Crystallographic Data and Parameters for $[Pt_2(CH_3)_4(xhp)_2((C_2H_5)_2S)]$ (x = H, F, CH_3)

formula	$[Pt_2(CH_3)_4(hp)_2((C_2H_5)_2S)]\cdot 0.5C_7H_8$	$[Pt_2(CH_3)_4(fhp)_2((C_2H_5)_2S)]\cdot 0.5C_7H_8$	$[Pt_2(CH_3)_4(mhp)_2((C_2H_5)_2)S)]$
fw	774.76	810.74	756.74
space group	$P\bar{1}$	$P\bar{1}$	*Pbca*
syst abs	none	none	$0kl$, $k = 2n + 1$; $h0l$, $1 = 2n + 1$; $hk0$, $h = 2n + 1$
a, Å	8.544 (3)	9.672 (3)	10.594 (4)
b, Å	16.127 (6)	16.397 (6)	32.459 (8)
c, Å	9.412 (6)	8.394 (2)	13.753 (5)
α, deg	79.02 (4)	85.95 (3)	90.0
β, deg	108.12 (4)	107.18 (2)	90.0
γ, deg	93.70 (3)	99.30 (3)	90.0
V, Å^3	1210.0 (1)	1254.6 (7)	4729 (1)
Z	2	2	8
D_{calc}, g/cm^3	2.126	2.146	2.125
cryst size, mm	0.4 × 0.3 × 0.2	0.35 × 0.4 × 0.2	0.4 × 0.4 × 0.3
μ(Mo Kα), cm^{-1}	122.492	118.336	125.318
data colln instrum	P3F	P3F	CAD4
radiation (monochromated in incident beam)	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)
orientation reflcns: no.; range (2θ), deg	20; 5.02–21.76	25; 20.03–25.87	25; 21.44–29.12
temp, °C	25	25	25
scan method	θ–2θ	θ–2θ	θ–2θ
data colln range (2θ), deg	4.0–45.0	4.0–45.0	4.0–45.0
no. of unique data	3436	4725	3519
wt. no. of data with $F_o^2 > 3\sigma(Fo^2)$	2341	2614	2150
no. of params refined	253	259	244
transmissn factors: max; min	99.93%; 40.09%	99.99%; 52.78%	99.93%; 26.00%
R^a	0.048	0.058	0.046
$R_w{}^b$	0.062	0.083	0.059
quality-of-fit indicator^c	1.370	1.858	1.684
largest shift/esd for final cycle	0.25	0.36	0.24
largest peak, e/Å^3	1.639	1.417	1.224

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1\sigma^2(|F_o|)$. ^{c}Quality of fit $= [\sum w(|F_o| - |F_c|)^2/(N_{obs} - N_{params})]^{1/2}$.

locate the hydrogen atom positions. In addition to the dinuclear Pt(II) molecule, the structure contains a molecule of toluene as solvent of crystallization that is located around the inversion center at the origin. The toluene molecule shows 2-fold disorder, and C(21), the toluene methyl group carbon atom, was refined with half-occupancy. The nitrogen atom N(1), from one of the 2-hydroxypyridine bridging ligands, could not be refined successfully with anisotropic thermal parameters and thus was refined isotropically. All other atoms were refined with anisotropic thermal parameters. The largest peak in the final difference map was located near one of the platinum atoms.

For **2**, the absorption correction was again supplemented by the DIFABS[7] treatment. No decay correction was required. The platinum atom positions were obtained from the Patterson function. Alternating least-squares cycles and difference Fourier maps revealed the remaining non-hydrogen atoms as well as a molecule of toluene as solvent of crystallization. The toluene molecule resides around an inversion center at ($^1/_2$, 0, $^1/_2$) and shows 2-fold disorder. The toluene methyl group carbon atom, C(22), was therefore refined with an occupancy of 0.5. With the exception of the toluene carbon atoms, all atoms were refined with anisotropic thermal parameters.

For **3**, the platinum atom positions were obtained from the Patterson function. Alternating least-squares cycles and difference Fourier maps revealed the remaining non-hydrogen atoms. No attempt was made to locate and refine the hydrogen atom positions. Full-matrix least-squares refinement converged with anisotropic thermal parameters for all atoms. The largest peak in the final difference map was located near one of the platinum atoms.

Results and Discussion

The positional parameters for the three compounds are listed in Tables II–IV, and drawings of the molecules are presented in Figure 1. Important bond distances and angles for all three complexes are presented in Table V.

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for $[Pt_2(CH_3)_4(hp)_2((C_2H_5)_2S)]\cdot 0.5C_7H_8$

atom	x	y	z	B,^{a} Å^2
Pt(1)	0.52013 (8)	0.27150 (4)	0.47131 (7)	2.23 (2)
Pt(2)	0.31488 (7)	0.34042 (4)	0.21943 (7)	1.84 (1)
S(1)	0.1314 (5)	0.3942 (3)	−0.0108 (5)	2.5 (1)
O(1)	0.433 (1)	0.2664 (7)	0.118 (1)	3.1 (3)
O(2)	0.166 (1)	0.2296 (7)	0.263 (1)	2.7 (3)
N(1)	0.525 (2)	0.1767 (8)	0.346 (1)	1.7 (2)*
N(2)	0.303 (2)	0.2156 (8)	0.521 (1)	2.2 (3)
C(1)	0.491 (2)	0.192 (1)	0.189 (2)	2.7 (4)
C(2)	0.531 (2)	0.133 (1)	0.113 (2)	3.7 (5)
C(3)	0.598 (2)	0.059 (1)	0.191 (2)	3.6 (5)
C(4)	0.627 (2)	0.037 (1)	0.353 (2)	3.5 (5)
C(5)	0.587 (2)	0.099 (1)	0.420 (2)	2.5 (4)
C(6)	0.171 (2)	0.199 (1)	0.402 (2)	2.1 (4)
C(7)	0.039 (2)	0.149 (1)	0.430 (2)	2.9 (4)
C(8)	0.047 (2)	0.121 (1)	0.582 (2)	3.9 (5)
C(9)	0.179 (2)	0.143 (1)	0.698 (2)	3.7 (5)
C(10)	0.305 (2)	0.190 (1)	0.664 (2)	3.4 (4)
C(11)	0.226 (2)	0.383 (1)	−0.156 (2)	3.1 (4)
C(12)	0.130 (3)	0.432 (2)	−0.310 (2)	4.9 (6)
C(13)	−0.036 (3)	0.320 (2)	−0.051 (2)	4.6 (6)
C(14)	−0.159 (3)	0.334 (2)	0.038 (3)	5.9 (7)
C(15)	0.538 (2)	0.358 (1)	0.606 (2)	3.9 (5)
C(16)	0.736 (2)	0.312 (1)	0.442 (2)	4.4 (5)
C(17)	0.197 (2)	0.410 (1)	0.313 (2)	3.1 (4)
C(18)	0.460 (2)	0.444 (1)	0.187 (2)	3.8 (5)
C(19)	0.124 (4)	0.020 (2)	0.123 (3)	9.7 (8)
C(20)	0.001 (5)	0.074 (2)	0.054 (3)	9 (1)
C(21)	0.133 (4)	−0.060 (2)	0.078 (3)	8.6 (8)
C(22)	0.246 (7)	−0.111 (3)	0.141 (5)	6 (1)

^{a}Starred value indicates atom was refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$.

The molecular structures are all very similar and consist of binuclear Pt(III) molecules that have Pt–Pt single-bond distances ranging from 2.561 (1) to 2.571 (1) Å. The Pt_2 units are bridged in each case by two xhp$^-$ ligands that have an HH arrangement so that both 6-substituents are located on one end of the Pt–Pt vector. The other axial position is occupied in each case by a molecule of diethyl sulfide. The diethyl sulfide molecules are oriented so that the sulfur lone pair is directed between two cis methyl groups. In all three compounds the other axial site is unoccupied. In addition to the two bridging ligands and axial diethyl sulfide molecule, each compound has two cis methyl groups bonded to each platinum atom.

The Pt–Pt bond distances range from 2.561 (1) to 2.571 (1) Å for the three compounds. The Pt–S distances range from 2.285 (4) Å for the fhp$^-$-bridged compound to 2.303 (4) Å for the

Table III. Positional and Thermal Parameters and Their Estimated Standard Deviations for $[Pt_2(CH_3)_4(fhp)_2((C_2H_5)_2S)]\cdot 0.5C_7H_8$

atom	*x*	*y*	*z*	*B*,[a] Å^2
Pt(1)	0.28423 (7)	0.34391 (5)	0.18797 (9)	2.59 (2)
Pt(2)	0.04305 (7)	0.27966 (5)	−0.01753 (9)	2.96 (2)
S(1)	0.5069 (5)	0.3894 (4)	0.3696 (7)	3.6 (1)
F(1)	−0.240 (1)	0.207 (1)	0.067 (2)	6.3 (4)
F(2)	−0.046 (1)	0.1002 (8)	−0.113 (2)	5.1 (3)
O(1)	0.239 (1)	0.2371 (9)	0.342 (2)	3.6 (3)
O(2)	0.383 (1)	0.2655 (9)	0.071 (2)	3.5 (3)
N(1)	−0.002 (2)	0.224 (1)	0.203 (2)	2.9 (3)
N(2)	0.167 (1)	0.182 (1)	−0.022 (2)	2.5 (3)
C(1)	0.109 (2)	0.207 (1)	0.337 (2)	3.7 (5)
C(2)	0.079 (2)	0.155 (2)	0.468 (3)	5.2 (6)
C(3)	−0.063 (2)	0.123 (2)	0.468 (3)	4.6 (6)
C(4)	−0.177 (2)	0.143 (2)	0.330 (3)	5.4 (6)
C(5)	−0.136 (2)	0.191 (2)	0.205 (3)	4.8 (6)
C(6)	0.315 (2)	0.199 (1)	0.009 (2)	3.1 (5)
C(7)	0.392 (2)	0.138 (1)	−0.026 (3)	4.3 (5)
C(8)	0.315 (2)	0.064 (1)	−0.091 (3)	4.4 (5)
C(9)	0.161 (2)	0.045 (1)	−0.121 (3)	3.7 (5)
C(10)	0.097 (2)	0.108 (1)	−0.083 (2)	3.4 (5)
C(11)	0.547 (2)	0.317 (2)	0.542 (3)	5.7 (7)
C(12)	0.469 (3)	0.335 (3)	0.667 (3)	8 (1)
C(13)	0.650 (2)	0.374 (2)	0.275 (3)	5.1 (6)
C(14)	0.797 (3)	0.417 (2)	0.373 (4)	7.6 (8)
C(15)	0.196 (2)	0.415 (2)	0.310 (3)	4.9 (5)
C(16)	0.323 (2)	0.446 (2)	0.040 (3)	4.5 (6)
C(17)	−0.082 (2)	0.368 (2)	−0.029 (3)	5.5 (6)
C(18)	0.081 (2)	0.324 (1)	−0.235 (3)	4.1 (5)
C(19)	0.368 (4)	0.015 (3)	0.358 (5)	9 (1)*
C(20)	0.434 (4)	−0.056 (2)	0.386 (5)	8.6 (9)*
C(21)	0.570 (3)	−0.063 (2)	0.533 (4)	7.8 (8)*
C(22)	0.376 (5)	−0.114 (3)	0.285 (6)	

[a] Starred values indicate atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta_{11} \dotplus b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table IV. Positional and Thermal Parameters and Their Estimated Standard Deviations for $[Pt_2(CH_3)_4(mhp)_2((C_2H_5)_2S)]$

atom	*x*	*y*	*z*	*B*,[a] Å^2
Pt(1)	0.70283 (6)	0.36862 (2)	0.00456 (5)	2.89 (1)
Pt(2)	0.47526 (6)	0.38435 (2)	0.05518 (4)	2.67 (1)
S(1)	0.2677 (5)	0.4011 (2)	0.0853 (3)	4.1 (1)
O(1)	0.496 (1)	0.4359 (4)	−0.0382 (8)	3.8 (3)
O(2)	0.430 (1)	0.3490 (4)	−0.0703 (8)	3.8 (3)
N(1)	0.670 (1)	0.4081 (4)	−0.1160 (9)	2.7 (3)
N(2)	0.626 (1)	0.3166 (4)	−0.0715 (8)	2.5 (3)
C(1)	0.574 (1)	0.4360 (5)	−0.113 (1)	3.1 (4)
C(2)	0.558 (2)	0.4669 (5)	−0.186 (1)	3.8 (4)
C(3)	0.642 (2)	0.4673 (6)	−0.264 (1)	4.1 (4)
C(4)	0.739 (2)	0.4404 (5)	−0.268 (1)	3.6 (4)
C(5)	0.749 (2)	0.4090 (5)	−0.195 (1)	3.1 (4)
C(6)	0.852 (2)	0.3784 (6)	−0.192 (1)	4.4 (5)
C(7)	0.503 (2)	0.3194 (5)	−0.099 (1)	3.7 (4)
C(8)	0.441 (2)	0.2884 (6)	−0.159 (1)	4.8 (5)
C(9)	0.522 (3)	0.2563 (6)	−0.191 (1)	6.4 (6)
C(10)	0.651 (2)	0.2543 (7)	−0.164 (1)	6.1 (6)
C(11)	0.698 (2)	0.2852 (6)	−0.101 (1)	4.6 (5)
C(12)	0.831 (2)	0.2816 (7)	−0.067 (2)	5.5 (5)
C(13)	0.256 (2)	0.4557 (6)	0.059 (1)	4.4 (5)
C(14)	0.176 (2)	0.3811 (6)	−0.019 (2)	5.1 (5)
C(15)	0.136 (2)	0.4748 (7)	0.091 (2)	6.3 (6)
C(16)	0.153 (2)	0.3355 (9)	−0.000 (2)	8.5 (8)
C(21)	0.789 (2)	0.4176 (6)	0.067 (2)	4.4 (5)
C(22)	0.519 (2)	0.4187 (6)	0.178 (1)	4.2 (4)
C(23)	0.750 (2)	0.3320 (7)	0.122 (1)	4.7 (5)
C(24)	0.449 (2)	0.3346 (7)	0.143 (1)	5.2 (5)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

mhp$^-$-bridged compound. A plot of the Pt–Pt bond distances versus the Pt–S bond distances (supplementary material) shows an inverse linear correlation between the Pt–S axial bond distance and the metal–metal bond distance. The monopyridine-substituted analogues[2] do not show this type of correlation. The lack of any crystallographic symmetry for the compounds permits several large discrepancies to exist between some of the intramolecular bond distances and angles in the complexes (e.g., the two Pt–Pt–C angles for the methyl groups trans to oxygen atoms in **3** are 95.9 (6) and 87.4 (6)°).

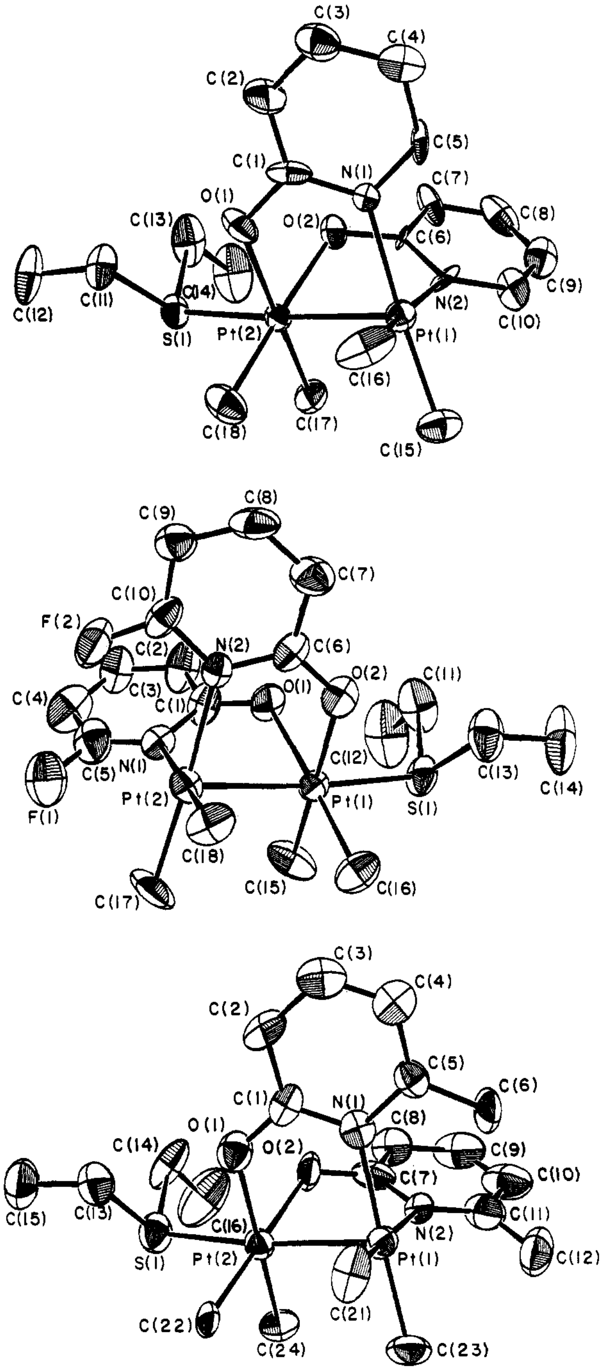

Figure 1. ORTEP drawings of the three $[Pt_2(CH_3)_4(xhp)_2Et_2S]$ molecules, with atoms represented by their thermal displacement ellipsoids drawn at the 40% probability level: top, compound **1** (hp); center, compound **2** (fhp); bottom, compound **3** (mhp).

All three compounds were prepared by essentially the same method. The reactions proceed smoothly, but it should be noted that although the reaction mixtures can be heated to increase the rate of the reaction, a decrease in the product yield was observed in all cases. Several unsuccessful attempts were made to obtain crystalline bis(diethyl sulfide)diplatinum(III) complexes from the original reaction filtrates and by adding additional diethyl sulfide to crystals of the mono(diethyl sulfide)diplatinum(III) products. These attempts yielded orange-red oils in all cases. Although crystalline compounds were not obtained from numerous attempts

Table V. Selected Bond Distances and Bond Angles for $[Pt_2(CH_3)_4(xhp)_2((C_2H_5)_2S)]$ (x = H, F, CH_3)[a]

Distances (Å)

compd	x	Pt–Pt	Pt–C	Pt–N	Pt–O	Pt–S
1	H	2.568 (1)	2.02 [1]	2.13 [3]	2.15 [3]	2.292 (4)
2	F	2.571 (1)	2.04 [1]	2.15 [2]	2.165 [7]	2.285 (4)
3	CH_3	2.561 (1)	2.05 [1]	2.14 [1]	2.124 [6]	2.303 (4)

Angles (deg)

	compd		
	1	**2**	**3**
Pt–Pt–S	176.4 (1)	174.5 (1)	174.3 (1)
Pt–Pt–N	83.5 [8]	83.5 [3]	86.2 [1]
Pt–Pt–O	84.1 [13]	83.8 [11]	83.8 [4]
Pt–Pt–C[b]	102.2 [7]	99.8 [10]	98.1 [8]
Pt–Pt–C[c]	95.4 [6]	96.8 [8]	97.0 [5]
C–Pt–Pt–C	29 [2]	27 [1]	24 [2]
O–Pt–Pt–N	25 [2]	23 [2]	21 [2]

[a] Estimated standard deviations shown in least significant digits are shown in parentheses. Values in brackets are average deviations from the mean value. [b] Trans to N. [c] Trans to O.

to prepare bis(diethyl sulfide)diplatinum(III) complexes, the presence or absence of these species in the orange-red oils was not determined. NMR studies are currently under way in an attempt to determine whether or not symmetric species are present.[8] The oils obtained from these reactions can be used to obtain the previously described pyridine-substituted complexes, or they can be chromatographed on silica gel columns to obtain good yields (75–90%) of compounds **1–3**. The compounds are soluble in a variety of organic solvents such as benzene, toluene, tetrahydrofuran, acetone, chloroform, and methylene chloride. Furthermore, the compounds are stable in the solid state and in solution for extended periods of time.

A comparison of compounds **1–3** with their mono(pyridine)-substituted analogues[1,2] shows many similarities and some significant differences. The Pt–Pt bond distances in compounds **1–3** are longer than those of their pyridine-substituted analogues by 0.015 Å. These bond length differences can be attributed to the presence of the diethyl sulfide axial ligand. In accordance with the established ordering of ligands as to trans influence and trans effect,[9] it might be expected that the diethyl sulfide molecule would exert a greater trans influence than an axial pyridine molecule and thus weaken the Pt–Pt bond. Another difference between compounds **1–3** and their pyridine-substituted analogues lies in the Pt–Pt–L_{ax} bond angles, which are more linear for compounds **1–3** by about 6°. Most of the other bond distances and angles in compounds **1–3** are similar to those in the pyridine-substituted complexes.

Although compounds **1–3** are structurally very similar to their pyridine-substituted analogues, they are different in that they do not rearrange to a symmetric form when excess diethyl sulfide is added. ^1H NMR studies with up to a 10-fold excess of ligand showed no indication of an HH = HT process. In fact, they seem to resist further substitution by diethyl sulfide at the vacant axial coordination site much in the same way as do the carboxylate-bridged Pt(III) complexes when PPh_3 or $P(OMe)_3$ is used as the axial donor ligand. Compounds **1–3** can be contrasted with the carboxylate-bridged Pt(III) complexes with axial diethyl sulfide molecules, for which both symmetric and asymmetric forms can be isolated. Since none of the carboxylate complexes with diethyl sulfide as the axial donor ligand(s) have been characterized by X-ray crystallography, no quantitative structural comparisons with compounds **1–3** can be made.

In our previous studies of the pyridine complexes, we have proposed steric arguments to explain the chief stoichiometric (i.e., one py or two) and structural (i.e., HH vs HT arrangements of xhp ligands) considerations, and there is no doubt that steric factors play a major role in the Et_2S adducts. With the mhp compound and the large Et_2S ligand, there seems no doubt that steric factors alone dictate the HH monoadduct as the only feasible product. With the hp and fhp compounds, however, the question becomes less clear-cut. With pyridine it was shown that diadducts of the HT isomer are accessible, and in fact preferred, in the presence of excess pyridine.

One possible explanation of the present results for the hp and fhp complexes is that the Et_2S ligand is that much more bulky than pyridine that the diadducts of the HT isomers are sterically inaccessible. While this might be plausible for the fhp case, it is less convincing for the hp case. In view of the observation by Vrieze that for the carboxylates, $[Pt_2(CH_3)_4(O_2CR)_2]$, ligands such as PPh_3 and $P(OMe)_3$ appear to favor the formation of monoadducts for electronic (i.e., trans influence) reasons, it also seems possible that for Et_2S there may be such an electronic effect. The electronic effect might even be the primary one, with the adoption of an HH arrangement of the hp and fhp ligands being simply a matter of making the best steric adaptation to an electronically driven situation. An unambiguous distinction here would appear to be elusive.

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Supplementary Material Available: Tables of bond lengths, bond angles, torsion angles, and anisotropic thermal parameters and a graph of Pt–Pt vs Pt–S distances (15 pages); lists of observed and calculated structure factors (37 pages). Ordering information is given on any current masthead page.

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(8) Abbott, E. H., Montana State University, private communication.

(9) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; p 1299.