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Abstract: The title complex was synthesized and its structure determined by three-dimensional x-ray crystallography using counter methods. Crystal data for bis[ethylenediamine(barbiturato)palladium(II)]-4-water, Pd<sub>2</sub>O<sub>10</sub>N<sub>8</sub>C<sub>12</sub>H<sub>28</sub>, space group  $P\overline{I}$ , Z = 1, a = 7.977 (1) Å, b = 8.777 (2) Å, c = 9.155 (2) Å,  $\alpha = 105.29$  (3)°,  $\beta = 99.36$  (2)°,  $\gamma 118.62$  (1)°, V = 510 Å<sup>3</sup>; 1504 reflections were collected by counter methods and the data refined to a conventional R value of 2.7%. The complex consists of dimeric molecules, the two halves of which are related by the crystallographically imposed inversion center. The palladium atoms are bonded to two adjacent ethylenediamine nitrogens, to a deprotonated ring nitrogen of the barbiturate ligand, and to the deprotonated tetrahedral ring carbon atom of another barbiturate ligand. The water molecules included in the lattice show close approaches to ligand oxygen and amine nitrogen atoms which, together with the observed hydrogen atom positions, indicate hydrogen bonding links to form an infinitely polymeric hydrogen-bonded network. The ligand environment about the metal is slightly distorted square planar. The barbiturate ligand is also approximately planar, the main deviation from planarity being due to the tetrahedral carbon atom which is coordinated to the metal atom.

# Introduction

As part of a program to investigate antitumor complexes of Pt(II), we undertook a study of the requirements for forming platinum blues.<sup>1</sup> Among the ligands forming blue complexes is barbituric acid. In order to establish more conveniently the interactions with some ligands we have employed Pd(II) instead of Pt(II). Except for the blues, both metal ions form similar diamagnetic tetragonal complexes with nitrogen heterocycles<sup>2</sup> with an advantage to Pd(II) because it reacts several powers of ten times more rapidly. In this paper we report the crystal structure of a dimeric complex of dianionic barbituric acid in which Pd(II) forms bonds to both a deprotonated amide nitrogen and a deprotonated tetrahedral carbon.

#### **Experimental Section**

Small, very thin, yellow plates of the subject complex crystallized from a solution originally containing enPd(H<sub>2</sub>O)<sub>2</sub>SO<sub>4</sub>, barbituric acid, and hydroxide ion in a 1:2:2 molar ratio. Every crystal of the sample was examined and the best chosen for the x-ray study. Crystal data for bis[ethylenediamine(barbiturato)palladium]-4-water, Pd<sub>2</sub>O<sub>10</sub>N<sub>8</sub>C<sub>12</sub>H<sub>28</sub>; mol wt 633, pale yellow crystal, space group  $P\overline{I}$ , Z = 1, a = 7.977 (1) Å, b = 8.777 (2) Å, c = 9.155 (2) Å,  $\alpha = 105.29$ (3)°,  $\beta = 99.36$  (2)°,  $\gamma = 118.62$  (1)°, V = 510 Å<sup>3</sup>, R = 2.7%, 1504 reflections,  $\rho$  calcd = 2.01 g cm<sup>-3</sup>,  $\rho$  obsd = 2.06 g cm<sup>-3</sup>,  $\mu$ (Mo K $\alpha$ ) = 18.0 cm<sup>-1</sup>; crystal dimensions (distances in mm of faces from centroid) (10\overline{I}) 0.12; (\overline{101}) 0.12; (001) 0.195; (00\overline{I}) 0.195; (1\overline{10}) 0.0075; (\overline{110}) 0.0075.

The Enraf-Nonius program SEARCH was used to obtain 15 accurately centered reflections which were then used in the program INDEX to obtain approximate cell dimensions and an orientation matrix for data collection. Refined cell dimensions and their estimated standard deviations were obtained from least-squares refinement of 28 accurately centered reflections. The mosaicity of the crystal was examined by the  $\omega$ -scan technique and judged to be satisfactory.

Collection and Reduction of the Data. Diffraction data were collected at 292 K on an Enraf-Nonius four-circle CAD-4 diffractometer controlled by a PDP8/M computer, using Mo K $\alpha$  radiation from a highly oriented graphite crystal monochromator. The  $\theta$ -2 $\theta$  scan technique was used to record the intensities for all nonequivalent reflections for which 1° < 2 $\theta$  < 48°. Scan widths (SW) were calculated from the formula SW =  $A + B \tan \theta$  where A is estimated from the mosaicity of the crystal and B allows for the increase in width of the peak due to  $K\alpha_1$ - $K\alpha_2$  splitting. The values of A and B were 0.60 and 0.30°, respectively. The calculated scan angle is extended at each side by 25% for background determination (BG1 and BG2). The net count is then calculated as NC = TOT - 2(BG1 + BG2) where TOT is the integrated peak intensity. Reflection data were considered insignificant if intensities registered less than 10 counts above background on

a rapid prescan, such reflections being automatically rejected by the computer.

The intensities of four standard reflections, monitored at 100 reflection intervals, showed no greater fluctuations during the data collections than those expected from Poisson statistics. The raw intensity data were corrected for Lorentz-polarization effects (including the polarization effect of the crystal monochromator) and then for absorption. Of the 1595 independent intensities recorded, 1504 had  $F_o^2 > 3\sigma(F_o^2)$ , where  $\sigma(F_o^2)$  was estimated from counting statistics.<sup>3</sup> These data were used in the final refinement of the structural parameters.

Determination and Refinement of the Structure. The positions of the metal atoms and of the four ligand donor atoms were obtained from a three-dimensional Patterson synthesis. The positions of the remaining nonhydrogen atoms were then determined from a Fourier difference synthesis.

Full-matrix least-squares refinement was based on F, and the function minimized was  $\Sigma w(|F_o| - |F_c|)^2$ . The weights w were then taken as  $[2F_o/\sigma(F_o^2)]^2$ , where  $|F_o|$  and  $|F_c|$  are the observed and calculated structure factor amplitudes. The atomic scattering factors for nonhydrogen atoms were taken from Cromer and Waber,<sup>4</sup> and those for hydrogen from Stewart et al.<sup>5</sup> The effects of anomalous dispersion for all nonhydrogen atoms were included in  $F_c$  using the values of Cromer and Ibers<sup>6</sup> for  $\Delta f'$  and  $\Delta f''$ . Agreement factors are defined as  $R = \Sigma ||F_o| - |F_c||/\Sigma ||F_o||$  and  $R_w = (\Sigma w(|F_o| - |F_c|)^2/\sigma w ||F_o|^2)^{1/2}$ . The principal programs used have been described.

This isotropic thermal parameters indicated a palladium-carbon bond and one uncoordinated barbiturate nitrogen atom. Interchange of the coordinated (tetrahedral) carbon and the uncoordinated nitrogen atoms leaves the connectivity of the barbiturate atoms correct, but worsens the refinement and leads to unreasonable temperature factors and improbable bond angles. Anisotropic temperature factors were introduced for the nonhydrogen atoms. After refinement, the positions of the hydrogen atoms were determined from Fourier syntheses, and these were included for three cycles of full-matrix leastsquares refinement and subsequently held fixed. The observation of the expected hydrogen atom position, attached to the tetrahedral barbiturate donor atom, confirms the characterization of the ligand atom as carbon. The model converged with R = 2.7,  $R_w = 3.8\%$ . The parameter shifts at convergence were less than one-tenth of their estimated standard deviations. The error in an observation of unit weight was 2.1. The structure factor calculation with all observed and unobserved reflections included (no refinement) gave R = 2.9%; on this basis it was decided that careful measurement of reflections rejected automatically by the computer during data collection would not significantly improve the results. A final Fourier difference synthesis was featureless. Tables of the observed structure factors are available.8

## **Results and Discussion**

The final positional and thermal parameters are given in



Figure 1. Stereoview of [Pd(en)barb]<sub>2</sub>.



Figure 2. Molecular packing in  $[Pd(en)barb]_2 \cdot (H_2O)_4$ .

Atom	X	Y	Z	$\beta_{11}$	$\beta_{22}$	β <sub>33</sub>	$\beta_{12}$	β <sub>13</sub>	β <sub>23</sub>
Pd	0.04713 (4)	-0.12996 (3)	0.20886 (3)	0.00838 (5)	0.00667 (4)	0.00418 (3)	0.00595 (6)	0.00159 (7)	0.00284 (6)
O2B	-0.1697 (4)	-0.4498 (3)	-0.1203(3)	0.0171 (5)	0.0079 (3)	0.0068 (4)	0.0134 (6)	-0.0008(7)	0.0021 (6)
O4B	-0.4965 (4)	-0.2910(3)	-0.4365(3)	0.0125 (5)	0.0098 (4)	0.0052 (3)	0.0088 (6)	-0.0047(7)	0.0014 (6)
O6B	-0.2025(4)	0.0503 (3)	0.1218 (3)	0.0176 (5)	0.0105 (4)	0.0045 (3)	0.0160 (6)	0.0066 (7)	0.0037 (6)
01	-0.2697 (5)	0.3214 (4)	0.0784 (4)	0.0222 (6)	0.0106 (4)	0.0152 (5)	0.0152 (8)	0.0116 (9)	0.0098 (7)
O2	-0.5410 (4)	-0.8206(4)	-0.2627(4)	0.0199 (6)	0.0155 (5)	0.0089 (4)	0.0172 (7)	0.0109 (8)	0.0091 (7)
NI	0.2397 (5)	-0.1083(4)	0.4004 (4)	0.0119 (6)	0.0110 (5)	0.0056 (4)	0.0104 (7)	0.0029 (8)	0.0048 (7)
N2	-0.1743 (5)	-0.3104(4)	0.2798 (4)	0.0125 (6)	0.0096 (4)	0.0084 (4)	0.0117(7)	0.0057 (8)	0.0069 (7)
N1B	-0.1629 (4)	-0.1846 (4)	0.0054 (4)	0.0109 (5)	0.0070 (4)	0.0041 (3)	0.0074 (7)	0.0025 (7)	0.0040 (6)
N3B	-0.3368 (4)	-0.3679(4).	-0.2729(4)	0.0121 (6)	0.0055 (4)	0.0035 (4)	0.0063 (7)	-0.0016 (8)	-0.0024(7)
C1	0.1219 (6)	-0.2612(5)	0.4557 (5)	0.0174 (8)	0.0128 (6)	0.0079 (5)	0.0160 (9)	0.0049 (11)	0.0102 (8)
C2	-0.0772 (6)	-0.2825(6)	0.4457 (5)	0.0181 (8)	0.0140 (6)	0.0080 (5)	0.0153 (10)	0.0086 (11)	0.0108 (9)
C6B	-0.2237 (5)	-0.0650 (4)	-0.0045 (4)	0.0071 (6)	0.0060 (5)	0.0050 (4)	0.0034 (8)	0.0032 (8)	0.0034 (7)
C2B	-0.2181 (5)	-0.3384 (5)	-0.1273 (4)	0.0073 (6)	0.0060 (5)	0.0045 (4)	0.0026 (8)	0.0015 (9)	0.0015 (8)
C4B	-0.3870 (5)	-0.2464(4)	-0.3007(4)	0.0064 (6)	0.0074 (5)	0.0048 (4)	0.0033 (8)	0.0022 (8)	0.0053 (7)
C5B	-0.3002 (5)	-0.0705 (4)	-0.1640 (4)	0.0081 (5)	0.0084 (5)	0.0057 (4)	0.0101 (7)	0.0025 (8)	0.0039(7)
HN11	0.302 (5)	-0.006 (4)	0.469 (4)	3.0 (7)					
HN12	0.332 (7)	-0.090 (6)	0.356 (6)	4.6 (13)					
HN21	-0.208 (5)	-0.403 (5)	0.230 (4)	2.0 (8)					
HN22	-0.253 (7)	-0.281 (6)	0.284 (6)	3.3 (11)					
H11	0.101 (6)	-0.372 (5)	0.397 (5)	2.3 (10)					
H12	0.188 (6)	-0.216 (5)	0.566 (5)	2.5 (10)					
H21	-0.044 (7)	-0.163 (6)	0.518 (6)	3.6 (12)					
H22	-0.168 (8)	-0.394 (7)	0.485 (7)	5.6 (16)					
HO11	-0.236 (7)	0.259 (6)	0.115 (6)	4.3 (13)					
HO12	-0.190 (5)	0.370 (4)	0.069 (4)	1.7 (8)					
HO21	-0.581 (5)	-0.855 (5)	-0.231 (4)	1.5 (8)					
HO22	-0.416 (9)	-0.717 (8)	-0.211 (8)	7.4 (19)					
H3B	-0.365 (5)	-0.449 (4)	-0.338 (4)	1.5 (7)					
H5B	-0.352 (3)	-0.037 (3)	-0.167 (3)	1.6 (4)					

<sup>a</sup> The form of the anisotropic thermal parameter is  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl]$ .

Table II. Bond Lengths (Å) for [Pd(en)barb]<sub>2</sub>·(H<sub>2</sub>O)<sub>4</sub>

Pd-N(1)	2.035 (2)	N(3B)-C(2B)	1.383 (4)
Pd-N(2)	2.070 (3)	N(3B)-C(4B)	1.371 (4)
Pd-N(1B)	2.062 (2)	C(4B)-C(5B)	1.451 (4)
Pd-C(5B)	2.142 (3)	C(5B)-C(6B)	1.467 (4)
O(2B)-C(2B)	1.223 (3)		
O(4B)-C(4B)	1.235 (3)	(O-H)	0.71
O(6B)-C(6B)	1.243 (3)	⟨N-H⟩	0.77
N(1)-C(1)	1.498 (4)	⟨C-H⟩	0.90
N(2)-C(2)	1.485 (4)		
C(1)-C(2)	1.492 (4)		
N(1B)-C(2B)	1.372 (4)		
N(1B)-C(6B)	1.367 (4)		

Table III. Bond Angles (deg) for [Pd(en)barb]<sub>2</sub>·(H<sub>2</sub>O)<sub>4</sub>

83.3 (1)	N(1B)-C(2B)- O(2B)	122.6 (2)
173.48 (9)	N(1B)-C(2B)-C(2B)-C(2B)	117.6 (2)
90.4 (1)	O(2B)-C(2B)-	119.8 (2)
92.99 (9)	N(3B) C(2B)-N(3B)-	125.7 (2)
172.2 (1)	C(4B)	110.2 (2)
1/3.2(1)	O(4B) - C(4B) - O(4B)	119.2 (2)
93.5 (1)	N(3B)-C(4B)-C(5B)	115.4 (2)
109.2 (2)	O(4B) - C(4B) - C(4B) - C(5B)	125.3 (2)
108.5 (2)	C(4B)-C(5B)-C(5B)-C(6B)	116.7 (2)
108.2 (2)	Pd-C(5B)-C(6B)	107.7 (2)
107.7 (2)	Pd-C(5B)-C(4B)	103.9 (2)
114.7 (2)	N(1B) - C(6B) - O(6B)	119.0 (2)
123.1 (2)	$N(1B)-C(\dot{6}B)-C(\dot{6}B)$	118.3 (2)
121.6 (2)	O(6B)-C(6B)- C(5B)	122.5 (2)
	<ul> <li>83.3 (1)</li> <li>173.48 (9)</li> <li>90.4 (1)</li> <li>92.99 (9)</li> <li>173.2 (1)</li> <li>93.5 (1)</li> <li>109.2 (2)</li> <li>108.5 (2)</li> <li>108.5 (2)</li> <li>108.2 (2)</li> <li>107.7 (2)</li> <li>114.7 (2)</li> <li>123.1 (2)</li> <li>121.6 (2)</li> </ul>	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

Table IV. Closest Intermolecular Contacts (Å)

Table I. Tables II and III contain the bond lengths and angles. The digits in parentheses in the tables are the estimated standard deviations in the least significant figures quoted and were derived from the inverse matrix in the course of least-squares refinement calculations. Figure 1 is the stereoscopic pair view of  $[Pd(en)barb]_2$ ·4H<sub>2</sub>O, while Figure 2 shows the molecular packing in the unit cell.

The complex consists of dimeric molecules, the two halves of which are related by the crystallographically imposed inversion center. The palladium atoms are bonded to two adjacent ethylenediamine nitrogens, and to a deprotonated ring nitrogen of the barbiturate ligand, and the deprotonated tetrahedral ring carbon of another barbiturate ligand. The water molecules included in the lattice show close approaches to ligand oxygen and amine nitrogen atoms which, together with the observed hydrogen atom position, indicate hydrogen bonding links to form an infinitely polymeric hydrogen bonded network, Table IV. The hydrogen on amide nitrogen N3B forms a relatively weak (2.94 Å) H bond to O4B in another dimer. The ligand environment about the metal atom is slightly distorted square planar (Table V), with the palladium atom 0.03 Å above the plane. The barbiturate ligand is also approximately planar, the main deviation from planarity being due to the tetrahedral carbon atom which is coordinated to the metal atom. The angle between the coordination plane and the barbituric acid plane is 79.6°. The structure bears some similarity to the dimer found for  $\beta$ -diketonate complexes of hexacoordinate trimethyl Pt(IV).9

With two amide nitrogens, the hydrogens of both of which should be capable of substitution by an appropriate metal ion, it might be surprising that the dianionic barbiturate molecules in the dimer are linked through only one (instead of two) nitrogen and one tetrahedral carbon to Pd(II) bond. Barbituric acid, however, is quite acidic with  $pK_a = 4.0$  and this ionization, usually attributed to deprotonation at C5, gives rise to the potentially aromatic barbiturate ion. A crystal structure of the salt ammonium barbiturate shows deprotonation at C5 and near planarity of the barbiturate ring.<sup>10</sup>

A. Nonhydrogen Contacts									
	Atom 1		Atom 2	Distance			Symmetry		
	O4B	3	C1	3.197		x - 1	y	z - 1	
	O4E	3	O4B	3.515		1 - x	1 - y	1 - z	
	B. Hydrogen Contacts								
A	tom l	H atom	Atom 2	Da	d <sup>b</sup>		Symmetry		
	01	HO11	O6B	2.786	1.98	x	y	x	
	01	HO12	O2B	2.972	2.53	x	y + 1	z	
	O2	HO21	O6B	2.861	2.35	-1 - x	-1 - y	- <i>z</i>	
	O2	HO22	O2B	2.887	2.02	x	у	z	
	NI	HN11	O2	2.976	2.28	1 + x	i+y	1 + z	
	N1	HN11	O4B	2.979	2.45	1 - x	1 - y	1 - z	
	N1	HN12	O2	3.125	2.34	x	y - 1	z	
	N2	HN21	<b>O</b> 1	2.910	2.21	x	y - 1	z	
	N2	HN22	O2	2.997	2.22	-1 - x	-1 - y	-z	
	N3B	H3B	O4B	2.940	2.25	-1 - x	-1 - y	-1 - z	

<sup>a</sup> Atom 1 to atom 2. <sup>b</sup> H atom to atom 2.

Table V. Coefficients of Least-Squares Planes AX + BY + CZ = D for  $[Pd(en)barb]_2 \cdot (H_2O)_4$ 

Plane	Atoms	A	В	C	D	Distances, Å
1	N(1), N(2), N(1B), C(5B')	0.594	-0.580	-0.558	0.440	N(1), 0.07; N(2), -0.06; N(1B), 0.06; C(5B'), -0.06; Pd, -0.03
II	N(1B), C(2B), N(3B), C(4B), C(5B), C(6B)	0.771	0.620	-0.146	-1.340	N(1B), 0.03; C(2B), 0.06; N(3B), 0.05; C(4B), -0.05; C(5B), 0.13; C(6B), -0.12
	Interplanar angle, deg	79	9.6		_	

Complexation of Pd(II) at C5B in the dimer shortens the C5B-C4B and C5B-C6B bonds by about 0.03 Å and lengthens the C4B-O4B and C6B-O6B bonds by about 0.03 Å compared with free barbituric acid.<sup>11</sup> The C4B-C6B angle is about 2° greater than in uncomplexed ligand. Other ring bond lengths including those to complexed N1B are less affected. The greatest bond angle change is at C2B-N1B-C6B, which is about 4° less and more nearly trigonal in the complex than in the free ligand.

The geometry of the barbiturate complex happens to be convenient for dimer formation. However, the existence of coordination sites at the two ends of the barbiturate ligand makes polymeric linkages seem even more likely in general, and this appears a possible mechanism for forming the polymeric linkages in the platinum blues. Distances between Pd and the two nitrogens of diaminoethane are unequal with the bond between Pd-N(1) being 0.035 Å shorter than that between Pd-N(2). This difference may reflect a greater trans effect of a tetrahedral carbon compared to a trigonal nitrogen.

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Supplementary Material Available: Tables of the observed structure factors (7 pages). Ordering information is given on any current masthead page.

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# Some Chemistry of Fluorinated Octahedral Sulfur Compounds

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Abstract: Reactive nucleophiles such as C<sub>6</sub>F<sub>5</sub>SLi and CF<sub>3</sub>SLi readily attack cis-SF<sub>4</sub>(OCF<sub>3</sub>)<sub>2</sub>, SF<sub>5</sub>Cl, CF<sub>3</sub>SF<sub>4</sub>Cl, and cis- $CF_3SF_4CF_3$  to form  $(R_F)_2S_3$  and  $(R_F)_2S_2$  ( $R_F = C_6F_5$ ,  $CF_3$ ) plus  $CF_2O$ ,  $R_FSCl$ ,  $CF_3Cl$ , and  $CF_4$ , respectively. With  $C_6F_5Li$ , cis-SF4(OCF3)2 yields (C6F5)2SF2, (C6F5)2SO, C6F6, and CF2O; SF5Cl gives (C6F5)2SO and C6F6; CF3SF4Cl forms  $(C_6F_5)_2S$ ,  $C_6F_6$ , and  $CF_3CI$ ; and cis-CF<sub>3</sub>SF<sub>4</sub>CF<sub>3</sub> produces CF<sub>3</sub>SF<sub>2</sub>CF<sub>3</sub> and  $C_6F_6$ . With LiN= $C(CF_3)_2$ , cis-SF<sub>4</sub>X<sub>2</sub> (X =  $OCF_3$ ,  $OSO_2F$ ) gives  $SF_3X = NCF(CF_3)_2$ ; cts- $CF_3SF_4CF_3$  forms  $(CF_3)_2SF_2 = NCF(CF_3)_2$  and  $(CF_3)_2SF_2 = NC(CF_3)_2$ . N=C(CF<sub>3</sub>)<sub>2</sub>; and  $F_4CF_2SF_4CF_2$  yields (CF<sub>3</sub>)<sub>2</sub>CFN=SF<sub>2</sub>(CF<sub>2</sub>)<sub>2</sub>SF<sub>2</sub>=NCF(CF<sub>3</sub>)<sub>2</sub>. In reactions with alcohols, ROH (R =  $(CF_3)_2(CH_3)C$ ,  $CH_3(CH_2)_8CH_2$ ,  $(CH_3)_3C$ ,  $C_6H_5CH_2CH_2$ ),  $cis-SF_4(OCF_3)_2$  produces the respective olefins  $(CF_3)_2$ -C==CH<sub>2</sub>, CH<sub>3</sub>(CH<sub>2</sub>)<sub>7</sub>CH==CH<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>C==CH<sub>2</sub>, and C<sub>6</sub>H<sub>5</sub>CH==CH<sub>2</sub>.

There is active research interest in the utilization of trigonal bipyramidal or octahedral sulfur compounds for investigating the stereochemistry about the sulfur atom. Earlier we reported the successful syntheses of a variety of stable new penta- and tetracoordinated sulfur(VI) compounds by stepwise defluorination reactions of  $SF_5X$  (X = Cl, Br) and  $CF_3SF_4Cl$ with the reactive nucleophile  $LiN=C(CF_3)_2$ .<sup>1</sup>

However, with the exception of sulfonium salts,<sup>2-5</sup> few compounds are available as suitable model compounds of trigonal bipyramidal<sup>6-8</sup> or octahedral sulfur. The behavior of trigonal bipyramidal sulfur with halogen ligands is evident from the literature,<sup>9-13</sup> although utilization of these compounds for such stereochemical studies has been rare. In fact,  $(C_6H_5)_2S(OC(CF_3)_2C_6H_5)_2$ , which was prepared by Martin and co-workers,<sup>14-19</sup> is the only example of a useful model trigonal bipyramidal sulfur compound leading to sulfilimines, epoxides, and olefins.

It is interesting to compare the behavior of octahedral sulfur compounds with that of compounds with trigonal bipyramidal sulfur. This work describes the stereochemical results which suggest that the octahedral sulfur compounds such as cis- $SF_4(OCF_3)_2$ , *cis*- $SF_4(OSO_2F)_2$ , *cis*- $CF_3SF_4CF_3$ ,  $SF_5Cl$ ,

SF<sub>5</sub>Br, and CF<sub>3</sub>SF<sub>4</sub>Cl are useful reagents with unusual properties for synthetic utility.

## **Results and Discussion**

The sulfurane,  $(C_6F_5)_4S$ , which is the first example of a compound with four carbon atoms bonded to sulfur, was synthesized by Sheppard et al.<sup>20,21</sup> by the replacement of the sulfur-fluorine atoms of  $C_6F_5SF_3$  in reaction with  $C_6F_5Li$  at -78 °C. This interesting compound is stable only to 0 °C.

We find that pentafluorothiophenyllithium readily attacks cis-SF<sub>4</sub>(OCF<sub>3</sub>)<sub>2</sub> or SF<sub>5</sub>Br at -78 °C to form bis(pentafluorophenyl)trisulfane and bis(pentafluorophenyl)disulfane. However, in its reaction with SF<sub>5</sub>Cl, in addition to the di- and trisulfanes,  $C_6F_5SCl$  is also produced.

O F OL

$$cis-SF_{4}(OCF_{3})_{2} \xrightarrow{C_{6}F_{5}SL_{1}} (C_{6}F_{5})_{2}S_{3} + (C_{6}F_{5})_{2}S_{2} + COF_{2}$$

$$SF_{5}Br \xrightarrow{C_{6}F_{5}SL_{1}} (C_{6}F_{5})_{2}S_{3} + (C_{6}F_{5})_{2}S_{2} + [Br_{2}]$$

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