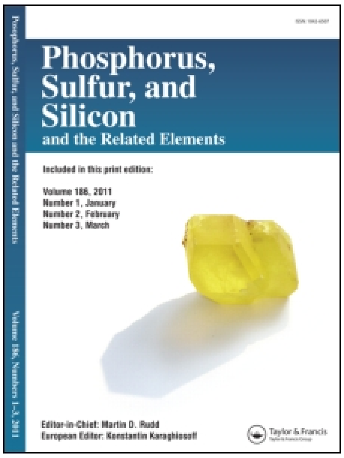

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# Structure of Antimony *tris*-(O,O-Diethyl Phosphorodithioate), a Passivation Agent for Contaminant Metals in the Catalytic Cracking of Crude Petroleum

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# SHORT COMMUNICATION
# Structure of Antimony *tris*-(O,O-Diethyl Phosphorodithioate), a Passivation Agent for Contaminant Metals in the Catalytic Cracking of Crude Petroleum

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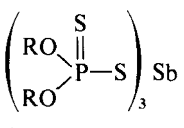
The coordination polyhedron of the antimony atom in antimony *tris*-(O,O-diethyl phosphorodithioate) is a distorted capped octahedron with a stereochemically active lone pair in the capping position and approximately on a molecular pseudo triad axis which passes through the antimony atom.

Reports have been published[1] [3] that the addition of relatively small amounts of "Phil-Ad CA" to the crude feed entering a catalytic cracking unit results in passivation of contaminant metals (mainly nickel, vanadium and iron). The presence of these contaminant metals on the cracking catalyst brings about an increase in hydrogen and coke yields and a decrease in gasoline yield. The major benefits which have been realized by use of "Phil-Ad CA" are: (1) an increase in product value as a result of an improved distribution of cracked products; (2) an increase in fluid catalytic cracking capacity inasmuch as less coke and light gases are formed; and (3) an ability to use oil feeds having higher contaminant metal concentrations. The refinery benefits at one cat cracker unit were reported[1] to amount to $18,000 per day.

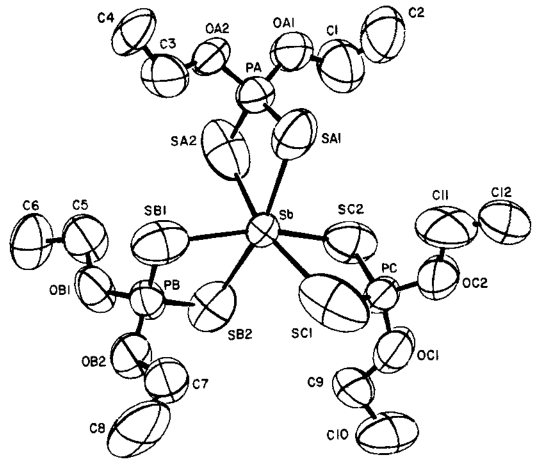
Since "Phil-Ad CA" is mainly a solution in liquid hydrocarbons of antimony (III) O,O-*bis*(*n*-propyl) phosphorodithioate (**1**), and since almost nothing is known about the fundamental chemistry of such compounds, we have initiated a program designed to remedy this situation. As an obvious starting point for new research, we have determined the structure of the ethyl analog, **2**, by single crystal X-ray diffraction analysis. The reason for the use of **2** in the structure determination rather than **1** is that **2** is a solid of melting point 56°C., while **1** is a liquid even at 0°C.[5]



**1** R = *n*-propyl
**2** R = ethyl

Crystals of **2** are monoclinic, space group $P2_1 - C_2^2$ (No. 4),[6] with $a = 8.624(2)$Å, $b = 9.707(4)$Å, $c = 17.521(6)$Å, $\beta = 92.83(2)°$, $Z = 2$, $D_{calc} = 1.536$ g/cm$^3$ and $D_{obs}$[7] $= 1.534$ g/cm$^3$. A total of 2751 independent reflections ($\pm h$, $+k$, $+1$) was examined, out to a maximum $2\theta_{MoK\bar{\alpha}} = 50°$, using an Enraf–Nonius CAD4 automated diffractometer, the $\theta$–$2\theta$ scan mode, and graphite monochromated MoK$\bar{\alpha}$ radiation. Initial coordinates for the Sb atom were obtained from a Patterson synthesis, and those for the remaining independent non-hydrogen atoms were determined by standard Fourier difference techniques. Anisotropic full-matrix least-squares refinement[8] of the structural parameters for these 28 non-hydrogen atoms and a scale factor has led to a convention residual $R = \Sigma\|Fo| - |Fc\|/\Sigma|Fo|$ of 0.080 and a weighted residual $R_w = \{\Sigma w(|Fo| - |Fc|)^2/\Sigma w|Fo|^2\}^{1/2}$ of 0.096 for the 1751 reflections having $I \geq 2\sigma_I$.

As illustrated in the accompanying Figure, the coordination polyhedron of the Sb atom can be described as a distorted capped octahedron[9] with



ORTEP plot of $Sb[S_2P(OEt)_2]_3$ viewed along the pseudo triad axis, with the lone pair directed toward the viewer. Thermal ellipsoids are at the 50% probability level.

a stereochemically active lone pair in the capping position and approximately on a molecular pseudo triad axis which passes through the Sb atom. The three bidentate ligands occupy uncapped face (uf)—capped face (cf) edges of the coordination polyhedron with an average bite of 3.215(12,16,24)Å.[10] The three remaining cf–uf edges have an average length of 3.966(14,95,142)Å. The stereochemical activity of the lone pair is reflected in an enlargement of the capped face relative to the uncapped face and in larger Sb—$S_{cf}$ bond lengths relative to the Sb—$S_{uf}$ bond lengths. The following average values are observed: $S_{cf}$ – $S_{cf}$, 4.361(16,137,205)Å; $S_{uf}$ – $S_{uf}$, 3.808(13,33,50)Å; Sb – $S_{cf}$, 2.827(12,29,44)Å, and Sb – $S_{uf}$, 2.601(10,19,29)Å. Concomitant with the above, interligand S—Sb—S angles involving long Sb—S bonds are greater than those involving the shorter bonds, the former averaging 100.9(2,35,53)° and the latter averaging 94.1(2,14,21)°. Interligand S—Sb—S angles average 72.5(2,8,12)°, in accordance with the ligand bite. The dihedral angle between the planes of the capped and uncapped faces is 3.2°, while the Sb atom lies between these planes at distances of 1.28Å from the former and 1.39Å from the latter.

Previous structural studies of 7 coordinated species having 3 identical bidentate ligands and a stereochemically active lone pair[11] include $[Sb(C_2O_4)_3]^{\equiv}$[12] and $Sb(S_2CNEt_2)_3$,[13] both having a pentagonal bipyramidal coordination polyhedron with a lone pair in an axial position; and

TABLE I

Atomic coordinates in crystalline $Sb[S_2P(OEt)_2]_3$.[a]

| Atom[b] Type | Fractional Coordinates 10⁴X | 10⁴Y | 10⁴Z |
|---|---|---|---|
| Sb | 7355(2) | 7500[c] | 7513(1) |
| SA1 | 4982(10) | 7834(9) | 6393(5) |
| SA2 | 6880(8) | 5105(12) | 6906(4) |
| SB1 | 5537(9) | 6738(10) | 8747(5) |
| SB2 | 9267(8) | 6628(9) | 8625(5) |
| SC1 | 8101(11) | 10354(16) | 7732(5) |
| SC2 | 9632(9) | 8123(8) | 6664(4) |
| PA | 5178(6) | 5829(7) | 6211(3) |
| PB | 7524(8) | 6252(7) | 9289(3) |
| PC | 9726(6) | 10045(7) | 7038(3) |
| OA1 | 5397(19) | 5513(20) | 5363(8) |
| OA2 | 3645(17) | 5052(17) | 6310(8) |
| OB1 | 7575(26) | 4714(16) | 9583(8) |
| OB2 | 7757(27) | 7007(14) | 10066(10) |
| OC1 | 11364(20) | 10385(20) | 7396(11) |
| OC2 | 9645(22) | 11043(26) | 6367(11) |
| C1 | 6710(34) | 5998(49) | 4974(18) |
| C2 | 6336(33) | 6581(42) | 4299(20) |
| C3 | 2772(30) | 5078(42) | 7025(12) |
| C4 | 1385(28) | 4383(29) | 6932(14) |
| C5 | 7300(40) | 3497(28) | 9084(15) |
| C6 | 7302(36) | 2275(25) | 9562(17) |
| C7 | 7712(42) | 8466(27) | 10082(16) |
| C8 | 7754(51) | 8902(43) | 10897(25) |
| C9 | 12024(32) | 9786(32) | 8093(13) |
| C10 | 13638(31) | 10419(38) | 8178(18) |
| C11 | 8258(32) | 11124(46) | 5871(19) |
| C12 | 8592(31) | 12129(40) | 5286(16) |

[a] Numbers in parentheses are estimated standard deviations.

[b] Atoms labeled to agree with Figure.

[c] Fixed.

TABLE II

Bond lengths in angstroms for $Sb[S_2P(OEt)_2]_3$.[a]

| Type[b] | Bond length | Type | Bond length |
|---|---|---|---|
| Sb—SA1 | 2.785(11) | PA—SA1 | 1.984(12) |
| Sb—SA2 | 2.590(13) | PA—SA2 | 1.992(10) |
| Sb—SB1 | 2.838(12) | PB—SB1 | 1.979(11) |
| Sb—SB2 | 2.629(10) | PB—SB2 | 1.983(11) |
| Sb—SC1 | 2.856(18) | PC—SC1 | 1.927(11) |
| Sb—SC2 | 2.583(9) | PC—SC2 | 1.976(11) |
| PA—OA1 | 1.52(2) | OB2—C7 | 1.40(3) |
| PA—OA2 | 1.53(2) | OC1—C9 | 1.44(3) |
| PB—OB1 | 1.58(2) | OC2—C11 | 1.43(3) |
| PB—OB2 | 1.55(2) | C1—C2 | 1.32(4) |
| PC—OC1 | 1.55(2) | C3—C4 | 1.38(4) |
| PC—OC2 | 1.53(2) | C5—C6 | 1.47(4) |
| OA1—C1 | 1.42(3) | C7—C8 | 1.49(5) |
| OA2—C3 | 1.48(3) | C9—C10 | 1.50(4) |
| OB1—C5 | 1.48(3) | C11—C12 | 1.46(5) |

[a,b] See Table I.

## TABLE III

Bond angles in degrees for $Sb[S_2P(OEt)_2]_3$.[a]

| Type[b] | Bond angle | Type | Bond angle |
|---|---|---|---|
| SA1—Sb—SA2 | 73.6(2) | OA1—PA—OA2 | 99.1(9) |
| SA1—Sb—SB1 | 98.8(2) | SB1—PB—SB2 | 109.9(5) |
| SA1—Sb—SB2 | 166.5(2) | SB1—PB—OB1 | 113.1(9) |
| SA1—Sb—SC1 | 97.7(3) | SB1—PB—OB2 | 112.4(10) |
| SA1—Sb—SC2 | 96.9(2) | SB2—PB—OB1 | 110.9(9) |
| SA2—Sb—SB1 | 89.8(3) | SB2—PB—OB2 | 111.1(9) |
| SA2—Sb—SB2 | 95.5(3) | OB1—PB—OB2 | 99.1(9) |
| SA2—Sb—SC1 | 163.0(2) | SC1—PC—SC2 | 109.7(6) |
| SA2—Sb—SC2 | 94.8(2) | SC1—PC—OC1 | 112.8(9) |
| SB1—Sb—SB2 | 72.6(2) | SC1—PC—OC2 | 112.4(11) |
| SB1—Sb—SC1 | 106.2(2) | SC2—PC—OC1 | 110.9(9) |
| SB1—Sb—SC2 | 164.3(2) | SC2—PC—OC2 | 110.2(10) |
| SB2—Sb—SC1 | 94.8(3) | OC1—PC—OC2 | 100.6(9) |
| SB2—Sb—SC2 | 92.0(2) | PA—OA1—C1 | 122 (2) |
| SC1—Sb—SC2 | 71.3(2) | OA1—C1—C2 | 114 (3) |
| Sb—SA1—PA | 86.2(4) | PA—OA2—C3 | 124 (1) |
| Sb—SA2—PA | 91.8(4) | OA2—C3—C4 | 111 (2) |
| Sb—SB1—PB | 86.0(3) | PB—OB1—C5 | 124 (1) |
| Sb—SB2—PB | 91.6(3) | OB1—C5—C6 | 108 (2) |
| Sb—SC1—PC | 86.0(5) | PB—OB2—C7 | 119 (2) |
| Sb—SC2—PC | 92.9(3) | OB2—C7—C8 | 108 (3) |
| SA1—PA—SA2 | 108.4(5) | PC—OC1—C9 | 125 (2) |
| SA1—PA—OA1 | 111.6(9) | OC1—C9—C10 | 104 (2) |
| SA1—PA—OA2 | 112.5(8) | PC—OC2—C11 | 120 (2) |
| SA2—PA—OA1 | 113.5(8) | OC2—C11—C12 | 106 (3) |
| SA2—PA—OA2 | 111.7(8) | | |

[a,b] See Table I.

## TABLE IV

Thermal parameters in crystalline $Sb[S_2P(OEt)_2]_3$.[a]

| | Anisotropic parameters[c] | | | | | |
|---|---|---|---|---|---|---|
| Atom[b] type | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
| Sb | 0.106(1) | 0.134(1) | 0.085(1) | −0.056(1) | −0.009(1) | 0.021(1) |
| SA1 | 0.177(7) | 0.107(6) | 0.183(7) | −0.028(6) | 0.025(5) | −0.005(6) |
| SA2 | 0.122(5) | 0.239(11) | 0.144(6) | 0.065(7) | 0.025(4) | 0.060(7) |
| SB1 | 0.133(5) | 0.138(7) | 0.199(8) | 0.016(5) | −0.032(5) | −0.025(6) |
| SB2 | 0.128(5) | 0.124(6) | 0.181(7) | −0.003(5) | 0.003(5) | −0.015(6) |
| SC1 | 0.165(7) | 0.363(20) | 0.139(6) | 0.091(11) | 0.026(6) | −0.054(10) |
| SC2 | 0.167(6) | 0.122(6) | 0.134(5) | 0.019(5) | −0.013(5) | −0.038(5) |
| PA | 0.087(4) | 0.106(5) | 0.091(4) | −0.011(3) | 0.001(3) | −0.004(3) |
| PB | 0.138(5) | 0.082(4) | 0.081(3) | −0.003(4) | 0.005(3) | 0.006(3) |
| PC | 0.088(3) | 0.084(4) | 0.106(4) | −0.015(3) | −0.002(3) | 0.006(3) |
| OA1 | 0.139(13) | 0.173(18) | 0.101(11) | −0.062(13) | 0.027(9) | −0.026(11) |
| OA2 | 0.125(11) | 0.115(12) | 0.111(10) | −0.055(10) | 0.017(8) | −0.014(10) |
| OB1 | 0.292(25) | 0.073(11) | 0.088(10) | −0.003(13) | −0.001(12) | 0.002(9) |
| OB2 | 0.259(20) | 0.052(9) | 0.112(12) | −0.020(11) | 0.003(12) | −0.012(8) |
| OC1 | 0.136(14) | 0.141(17) | 0.181(18) | −0.054(13) | −0.036(13) | 0.052(15) |
| OC2 | 0.151(14) | 0.211(24) | 0.178(16) | −0.082(16) | −0.069(13) | 0.091(17) |
| C1 | 0.149(25) | 0.245(46) | 0.146(26) | −0.021(29) | 0.013(21) | 0.034(31) |
| C2 | 0.130(23) | 0.207(37) | 0.189(31) | −0.029(24) | 0.023(22) | 0.048(30) |
| C3 | 0.128(19) | 0.242(39) | 0.092(16) | −0.046(25) | 0.041(15) | −0.032(22) |
| C4 | 0.125(21) | 0.143(27) | 0.156(25) | −0.060(20) | 0.067(20) | −0.041(21) |
| C5 | 0.251(35) | 0.088(21) | 0.120(21) | 0.001(23) | 0.001(21) | −0.010(17) |
| C6 | 0.200(27) | 0.073(19) | 0.176(27) | 0.011(18) | 0.047(22) | 0.003(18) |
| C7 | 0.231(30) | 0.094(20) | 0.115(20) | −0.020(21) | 0.015(20) | −0.019(17) |
| C8 | 0.311(52) | 0.171(36) | 0.265(45) | −0.107(37) | 0.103(40) | −0.133(35) |
| C9 | 0.184(27) | 0.132(24) | 0.107(18) | −0.023(22) | −0.047(18) | 0.034(19) |
| C10 | 0.135(23) | 0.162(31) | 0.214(34) | 0.016(24) | −0.076(23) | −0.020(28) |
| C11 | 0.127(23) | 0.237(46) | 0.191(32) | 0.003(28) | −0.086(23) | 0.007(34) |
| C12 | 0.154(25) | 0.215(46) | 0.140(23) | −0.013(27) | −0.047(19) | 0.025(27) |

[a,b] See footnotes to Table I.

[c] Anisotropic thermal parameters are of the form $\exp\{-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl)\}$.

$Sb(S_2COEt)_3$[14] having a distorted capped octahedral geometry with the lone pair in the capping position. The stereochemical activity of the lone pair in the xanthate is greater than that observed in the present study.[15] Another compound having the capped octahedral geometry and in which the stereochemical activity of the lone pair is essentially identical to that found in the present study is $Bi[(i - PrO)_2PS_2]_3$.[15] The additional close similarity of the Sb(III) and Bi(III) *tris*-diethyldithiocarbamates[13] reinforces the concept[16] that the III states of the two elements have similar characteristics.

Although compound **2** is chiral,[8] this is not apparent from its NMR spectrum taken in $CDCl_3$ solution. This consists of a triplet at $\delta 1.38$ ($J = 7$Hz) and two overlapping quartets at $\delta 4.18$ and 4.32. The overlapping quartets arise because the methylene hydrogens of the ethyl groups are also split by phosphorus and not because they are diastereotopic.[17]

As part of an ongoing investigation of the fundamental chemistry of compounds related to **1**, the active component of "Phil-Ad CA", we have found that **2** apparently undergoes a rapid redox reaction with anhydrous ferric chloride in acetonitrile solution, but the details of the reaction remain to be uncovered. It is known that the unshared pair of electrons of Sb(III) in its compounds coordinates readily with Fe(III) in its compounds.[18–21] However, it is not presently known whether or not this relates to the phenomenon of passivation of contaminant metals, such as iron, in the catalytic cracking of crude petroleum.

## EXPERIMENTAL

To 150 ml of absolute ethanol, maintained under an argon atmosphere, was added 66.6 g (0.3 mol) of phosphorus pentasulfide, and the mixture was maintained at 50°C with stirring until evolution of hydrogen sulfide abated and a homogeneous solution resulted (about 30 min.). To this solution was added 51.3 g (0.225 mol) of finely ground antimony trichloride, and the initially dark green mixture was stirred for about 10 min. until a homogeneous yellow solution resulted. The solution was concentrated at atmospheric pressure until a thick oil remained. This was extracted with many portions of Skelly F solvent (total about 1 *l*). Concentration of the Skelly F solution almost to dryness caused a yellow precipitate to form, and this was collected and recrystallized from Skelly F solvent. There was obtained 38.0 g (28%) of antimony *tris*-(O,O-diethyl phosphorodithioate) (**2**), m.p. 55.8–56.2°C; reported,[4] m.p. 56°C.

## ACKNOWLEDGEMENT

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