

The Crystal Structure of Tris-(*O,O'*-dimethyldithiophosphato)cobalt(III), $\text{CO}[(\text{CH}_3\text{O})_2\text{PS}_2]_3$

BY J. F. MCCONNELL AND A. SCHWARTZ

School of Physics, University of New South Wales, Box 1 Post Office, Kensington 2033, Australia

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Tris-(*O,O'*-dimethyldithiophosphato)cobalt(III) crystallizes in the monoclinic space group $C2/c$ with four molecules in the unit cell, $a = 13.895$, $b = 11.084$, $c = 13.020$ Å, $\beta = 98.81^\circ$. The structure was solved from diffractometer data by means of three-dimensional Patterson and Fourier syntheses and refined by full-matrix least-squares to an R of 0.069. The molecule has a twofold axis through the Co atom and one P atom, and the six S donor atoms form a distorted octahedron. The S-P, P-O, O-C bonds average 1.983, 1.574 and 1.440 Å, respectively, and agree very well with those found in similar compounds. The Co-S bonds average 2.322 Å, in agreement with other work.

Introduction

Metal complexes of dialkyldithiophosphates were first reported by Malatesta & Pizzotti (1945). Their intense colours and ready solubility in most organic solvents have attracted the interest of many coordination chemists. The two alkyl groups prevent the complexes from polymerizing and the P-S bond appears to have little double-bond character. Consequently, the internal electronic transitions of the ligand occur at high energy in the ultraviolet region, and the ligand field bands of the central transition metal ion are readily observed. Accordingly these complexes are very suitable for the study of octahedral $M(\text{III})\text{S}_6$ and square-planar $M(\text{II})\text{S}_4$ chromophores (Jørgensen, 1963).

A number of studies of the analytical applications of dialkyldithiophosphates have been made, especially in regard to their use in the extraction of metal ions from aqueous solution into organic solvents. Recently it was reported that the complexes $M(\text{dtp})_2$ ($M = \text{Ni}, \text{Pd}, \text{Pt}$; $\text{dtp} = \text{diethylthiophosphate ion}$) show considerable anticancer activity in the Walker carcinoma 256 (intramuscular) test in mice, while the nickel complex $\text{Ni}[(\text{ClCH}_2\text{CH}_2\text{O})_2\text{PS}_2]_2$ has significant larvicidal activity against *Tineola bisselliella* and could be a potential moth proofing agent for wool (Livingstone & Mihkelson, 1970).

Structures of various dialkyldithiophosphate complexes have been determined. For example, in the complex $\text{Ni}[(\text{MeO})_2\text{PS}_2]_2$, the nickel atom is at the centre of an almost square plane with the smaller S-Ni-S angle equal to 88.3° (Gilinskaya & Porai-Koshits, 1959; Kastalsky & McConnell, 1969). Trans-adduct formation with unidentate ligands distorts the chelate rings but does not affect the coplanarity (Ooi & Fernando, 1967). A bidentate nitrogen ligand forms a *cis* adduct by displacing one of the sulphur atoms in the plane of the chelate rings into an apical position; the resulting adduct has a distorted octahedral geometry with the S-Ni-S angle close to 80° (Livingstone & Mihkelson, 1970; Ooi, Carter & Fernando, 1968).

In the present work, the sulphur atoms form a distorted octahedron, in which the smallest S-Co-S angles are about 84° .

Experimental

The compound is soluble in water and most organic solvents, and crystallizes readily into deep purple bipyramids. Crystals suitable for X-ray studies were obtained by slow cooling of an acetone solution.

Crystal and molecular data

Tris-(*O,O'*-dimethyldithiophosphato)cobalt(III), $[(\text{CH}_3\text{O})_2\text{S}_2\text{P}_2]_3\text{Co}(\text{III})$.

Molecular weight 530.45 ($C = 12$).

Monoclinic, space group $C2/c$ with $Z = 4$.

Cell parameters at 20°C

$a = 13.895$ (7), $b = 11.084$ (6), $c = 13.020$ (7) Å
 $\beta = 97.81$ (5)°, $V = 1986$ (3) Å³.

Density: measured at $20^\circ\text{C} = 1.70$ g.cm⁻³ (flotation),
 calculated = 1.77 g.cm⁻³ for $Z = 4$.

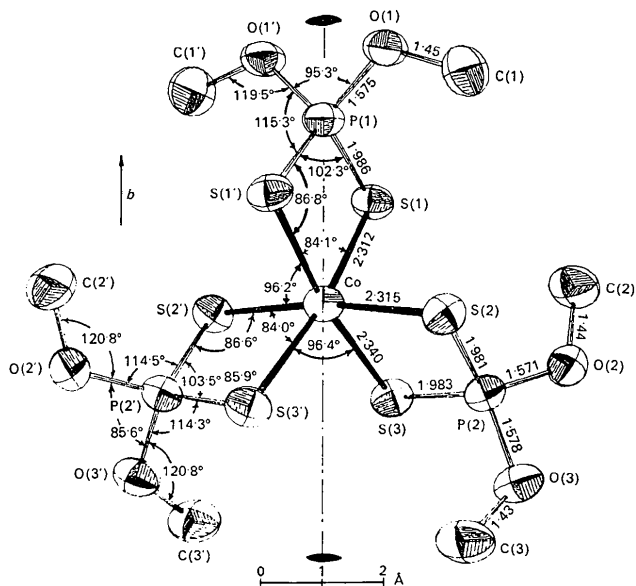


Fig. 1. Perspective view of the whole molecule, showing bond lengths (Å) and bond angles (°). Ellipsoids represent 50% probability.

Linear absorption coefficient for Cu $K\alpha$ radiation $\mu = 149\text{cm}^{-1}$.

Systematic absences: $hkl: h+k=2n+1$

$$h0l: \begin{cases} h=2n+1 \\ l=2n+1 \end{cases}$$

$$0k0: k=2n+1$$

The absences determine the space group as either Cc or $C2/c$. A Wilson plot indicated the centrosymmetric space group $C2/c$, which was subsequently confirmed by the structure determination.

The cell dimensions were obtained from photographs and refined by calculation from high-angle reflexions measured on a Siemens single-crystal diffractometer.

The integrated intensities were recorded with Nifiltered Cu $K\alpha$ radiation by the five-value method (Hoppe, 1965) using a θ - 2θ scan up to 70° with a scanning

range varying from 1.0° at low 2θ values to 2.8° at high 2θ . The scanning speed, although automatically controlled by the instrument, was set to an upper time limit of 0.6 sec per step of 0.1° .

The intensities were corrected for Lorentz and polarization factors and for absorption (Coppens, Leiserowitz & Rabinovich, 1965).

The crystal used had many faces, namely (100), $(\bar{1}00)$, (001), (00 $\bar{1}$), (110), $(\bar{1}\bar{1}0)$, $(\bar{1}10)$, (111), $(\bar{1}\bar{1}\bar{1})$, $(\bar{1}\bar{1}1)$, averaging 0.02 cm across opposite faces. The separation of parallel faces was measured accurately for the purpose of absorption correction. A reflexion was considered to be unobserved when the net count was less than 3σ above background, where $\sigma = (\text{total count for this reflexion})^{1/2}$. Such a reflexion was given an intensity value of 3σ .

Scattering factors were taken from *International*

Table 1. Fractional coordinates and thermal parameters ($\times 10^4$) with *e.s.d.*'s in parentheses

The B_{ij} 's are the coefficients in the expression: $T = \exp [-(B_{11}h^2 + \beta_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + B_{23}kl)]$.

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	0 (0)	1636 (2)	2500 (0)	46 (1)	54 (2)	40 (1)	0 (0)	14 (1)	0 (0)
S(1)	887 (2)	3186 (2)	1899 (2)	50 (1)	57 (2)	53 (2)	-7 (1)	18 (1)	4 (1)
S(2)	916 (2)	1491 (2)	4119 (2)	52 (1)	68 (2)	38 (1)	8 (1)	9 (1)	6 (1)
S(3)	1113 (2)	2297 (2)	2022 (2)	55 (1)	66 (2)	43 (1)	9 (1)	15 (1)	7 (1)
P(1)	0 (0)	4309 (3)	2500 (0)	55 (2)	47 (3)	47 (2)	0 (0)	5 (2)	0 (0)
P(2)	1758 (2)	357 (2)	3473 (2)	45 (1)	57 (2)	48 (2)	7 (1)	11 (1)	2 (1)
O(1)	514 (6)	5267 (6)	3284 (6)	74 (5)	53 (6)	56 (5)	0 (4)	-12 (4)	-3 (4)
O(2)	2859 (5)	728 (6)	3593 (6)	46 (4)	76 (7)	67 (5)	4 (4)	4 (3)	6 (5)
O(3)	1932 (6)	-891 (6)	4052 (6)	62 (5)	65 (6)	70 (5)	11 (4)	18 (4)	15 (6)
C(1)	1162 (11)	4860 (12)	4189 (10)	91 (10)	105 (12)	67 (8)	2 (9)	-29 (8)	-19 (8)
C(2)	3149 (9)	1891 (11)	3240 (11)	56 (7)	87 (11)	106 (11)	-14 (7)	26 (7)	8 (9)
C(3)	1128 (10)	-1629 (11)	4247 (11)	78 (9)	78 (10)	92 (10)	9 (8)	33 (8)	18 (8)

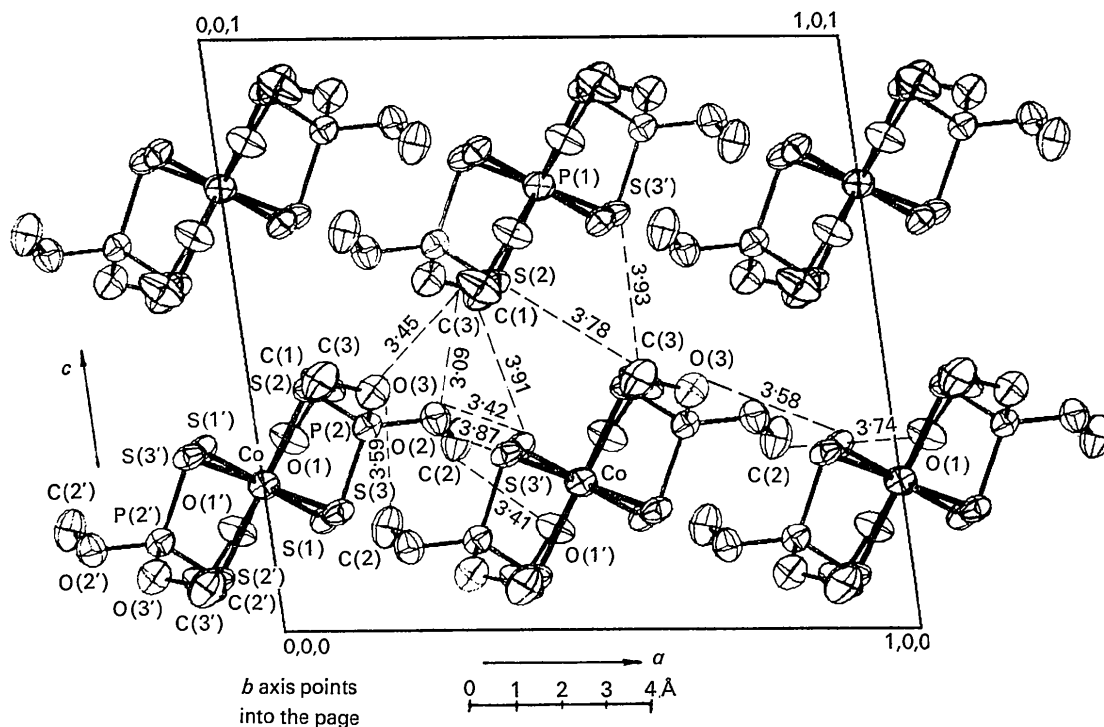


Fig. 2. The (010) projection of the unit cell, showing the smallest intermolecular contacts. Ellipsoids represent 50% probability.

TRIS-(O,O'-DIMETHYLDITHIOPHOSPHATO)COBALT(III)

Table 2. Observed and calculated structure factors (10 × absolute)

Reflexions marked \$ were not included in the refinement.
 Reflexions marked U were unobserved.

h	k	l	F _o	F _c	Phase
0	0	0	1000	1000	0
1	0	0	100	100	0
2	0	0	100	100	0
3	0	0	100	100	0
4	0	0	100	100	0
5	0	0	100	100	0
6	0	0	100	100	0
7	0	0	100	100	0
8	0	0	100	100	0
9	0	0	100	100	0
10	0	0	100	100	0
11	0	0	100	100	0
12	0	0	100	100	0
13	0	0	100	100	0
14	0	0	100	100	0
15	0	0	100	100	0
16	0	0	100	100	0
17	0	0	100	100	0
18	0	0	100	100	0
19	0	0	100	100	0
20	0	0	100	100	0
21	0	0	100	100	0
22	0	0	100	100	0
23	0	0	100	100	0
24	0	0	100	100	0
25	0	0	100	100	0
26	0	0	100	100	0
27	0	0	100	100	0
28	0	0	100	100	0
29	0	0	100	100	0
30	0	0	100	100	0
31	0	0	100	100	0
32	0	0	100	100	0
33	0	0	100	100	0
34	0	0	100	100	0
35	0	0	100	100	0
36	0	0	100	100	0
37	0	0	100	100	0
38	0	0	100	100	0
39	0	0	100	100	0
40	0	0	100	100	0
41	0	0	100	100	0
42	0	0	100	100	0
43	0	0	100	100	0
44	0	0	100	100	0
45	0	0	100	100	0
46	0	0	100	100	0
47	0	0	100	100	0
48	0	0	100	100	0
49	0	0	100	100	0
50	0	0	100	100	0
51	0	0	100	100	0
52	0	0	100	100	0
53	0	0	100	100	0
54	0	0	100	100	0
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56	0	0	100	100	0
57	0	0	100	100	0
58	0	0	100	100	0
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61	0	0	100	100	0
62	0	0	100	100	0
63	0	0	100	100	0
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65	0	0	100	100	0
66	0	0	100	100	0
67	0	0	100	100	0
68	0	0	100	100	0
69	0	0	100	100	0
70	0	0	100	100	0
71	0	0	100	100	0
72	0	0	100	100	0
73	0	0	100	100	0
74	0	0	100	100	0
75	0	0	100	100	0
76	0	0	100	100	0
77	0	0	100	100	0
78	0	0	100	100	0
79	0	0	100	100	0
80	0	0	100	100	0
81	0	0	100	100	0
82	0	0	100	100	0
83	0	0	100	100	0
84	0	0	100	100	0
85	0	0	100	100	0
86	0	0	100	100	0
87	0	0	100	100	0
88	0	0	100	100	0
89	0	0	100	100	0
90	0	0	100	100	0
91	0	0	100	100	0
92	0	0	100	100	0
93	0	0	100	100	0
94	0	0	100	100	0
95	0	0	100	100	0
96	0	0	100	100	0
97	0	0	100	100	0
98	0	0	100	100	0
99	0	0	100	100	0
100	0	0	100	100	0

Tables for X-ray Crystallography (1962) and corrected for anomalous dispersion from cobalt (Cromer, 1965).

1884 reflexions were measured of which 304 were unobserved (marked *U* in Table 2). Six strong reflexions denoted by \$ in Table 2, were eliminated from the refinement because they were obviously affected by extinction.

Structure determination

Space group *C2/c* has eight equivalent general positions. With four molecules per unit cell, therefore, the

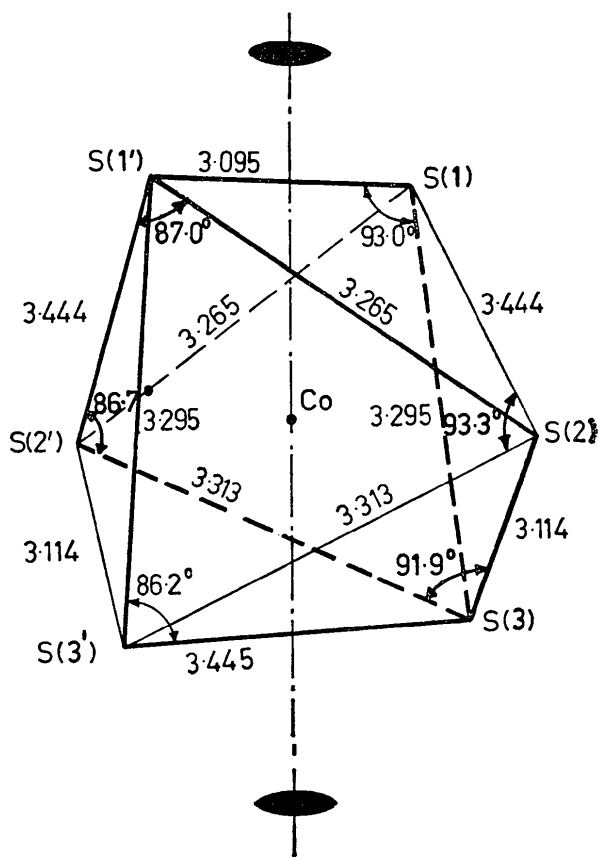


Fig. 3. Perspective view of the distorted octahedron formed by the sulphur atoms, showing interatomic distances and angles.

molecule must possess a twofold axis of symmetry, coinciding with a diad axis in the unit cell, with the Co and one P atom on this axis. These two atoms have therefore the special positions $(0, y, 0.25)$. An unsharpened Patterson map gave the *y* ordinates from the Harker line, as well as some probable S positions. Difference synthesis located all Co, S and P positions in the asymmetric unit (Co, 3S, 2P). This gave an *R* value of 0.453 excluding unobserved reflexions, and 0.474 using all reflexions. A least-squares cycle at this stage reduced *R* to 0.382(0.394). Another difference synthesis located all O and C atoms.

Refinement

Refinement was carried out on an IBM 360/50 computer for all non-hydrogen atoms using the least squares program *ORFLS* (Busing, Martin & Levy, 1962) which minimizes the function $\sum w(|F_o| - |F_c|)^2$. The weights *w* were taken as $1/\sigma^2$, where the e.s.d. σ was obtained from counting statistics. Applying individual isotropic temperature factors, *R* fell to 0.112 (0.146) in a few cycles and was reduced to 0.074 (0.094) after three cycles using anisotropic temperature factor.

In an attempt to locate the hydrogen atoms, a difference synthesis was carried out after a cycle of refinement using only reflexions for which $\sin \theta/\lambda > 0.3$. The purpose of this restriction was to eliminate errors in positional and thermal parameters produced by the non-inclusion of the hydrogen atoms. Data for the full range of θ were then employed in a difference synthesis. The methyl hydrogens were not indicated very clearly in the background, which was quite 'noisy', probably due to the fact that the dispersion correction applied is only approximate. As the hydrogen positions were of little interest, no further attempt to locate them was made.

Refinement of the non-hydrogen atoms (using all data) terminated at $R = 0.069(0.094)$. The figure of merit for 'goodness of fit' namely $[(\sum w\Delta^2/m-s)^{1/2}]$ was 0.619, where *m* and *s* are the number of observations and the number of variables respectively. The maximum coordinate shift in the last cycle was less than 0.1σ .

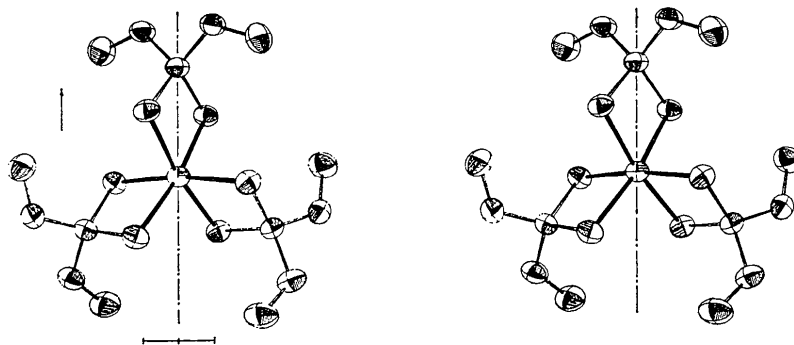


Fig. 4. Stereoscopic view of the molecule, approximately along the *c* axis. Ellipsoids represent 50% probability.

Table 1 gives the final positional and thermal parameters and Table 2 shows the observed and calculated structure factors on 10 times absolute scale.

A ΔQ synthesis using the final coordinates revealed a few small positive peaks (maximum 0.85 e. \AA^{-1} near the Co atom). They are probably due to the neglected H atoms and to dispersion errors.

Discussion of the structure

An *ORTEP* (Johnson, 1965) plot of the molecule is given in Fig. 1, on which are shown bond distances and angles. This is a perspective view of the molecule looking approximately along the *c* axis, with the *b* axis vertical, which shows the molecule at maximum resolution. The packing in the unit cell is shown in Fig. 2, which is a projection down the *b* axis. Co and P(1) atoms are superimposed in the Figure and the C(1), C(3) and S(2) atoms overlap considerably. The shortest intermolecular distances are indicated by dotted lines. A stereoscopic pair of projections of the molecule is shown in Fig. 4 viewed approximately along the *c* axis.

Bond lengths and angles were calculated using the program *ORFFE* (Busing, Martin & Levy, 1964), and are listed in Table 3, with their e.s.d.'s in parentheses.

Table 3. Bond lengths and angles with their e.s.d.'s in parentheses

Co—S(1)	2.312 (3) Å	S(1)—Co—S(2)	96.2°(1)
Co—S(2)	2.315 (2)	S(2)—Co—S(3)	84.0 (1)
Co—S(3)	2.340 (3)	Co—S(1)—P(1)	86.8 (1)
P(1)—S(1)	1.986 (3)	Co—S(2)—P(2)	86.6 (1)
P(2)—S(2)	1.981 (4)	Co—S(3)—P(2)	85.9 (1)
P(2)—S(3)	1.983 (4)	S(1)—Co—S(1')	84.1 (1)
P(1)—O(1)	1.575 (7)	S(3)—Co—S(3')	96.4 (1)
P(2)—O(2)	1.571 (7)	S(1)—P(1)—O(1)	115.3 (3)
P(2)—O(3)	1.578 (7)	S(2)—P(2)—O(2)	114.5 (4)
O(1)—C(1)	1.45 (1)	S(3)—P(2)—O(3)	114.3 (4)
O(2)—C(2)	1.44 (1)	O(1)—P(1)—O(1')	95.3 (4)
O(3)—C(3)	1.43 (1)	O(2)—P(2)—O(3)	85.6 (4)
		P(1)—O(1)—C(1)	119.5 (7)
		P(2)—O(2)—C(2)	120.8 (7)
		P(2)—O(3)—C(3)	120.8 (7)
		S(1)—P(1)—S(1')	102.3 (2)
		S(3)—P(2)—S(2)	103.5 (1)

The whole molecule, when viewed approximately along the *c* axis, has near trigonal symmetry, the six S atoms forming a distorted octahedron about the Co atom. This can be clearly seen in Fig. 3 where the S—S distances and relevant angles of the octahedron are shown. The bond lengths P—S (1.981 to 1.986 Å), P—O (1.571 to 1.578 Å) and O—C (1.43 to 1.45 Å) agree within the limits of error with those found in the Ni complexes (Kastalsky & McConnell, 1969). The Co—S bond lengths are slightly larger than the sum of the covalent radii 1.22 \AA (Co) and 1.04 \AA (S) given by Pauling (1960). Co—S(1) and Co—S(2) are obviously equal within the limits of error. In order to test whether Co—S(3) is significantly larger, the statistical test of Fischer—Behrens (Hamilton, 1964) was applied. The weighted mean

(weights = $1/\sigma^2$) of the first two bonds is $\bar{X}_1 = 2.314 \text{ \AA}$ with a variance $\sigma_1^2 = 13 \times 10^{-6} \text{ \AA}^2$. It was assumed that these two bonds belong to a population with a normal density function $N(\bar{X}_1, \sigma_1^2)$, and that the Co—S(3) bond belongs to a population $N(\bar{X}_2, \sigma_2^2)$ with $\bar{X}_2 = 2.340 \text{ \AA}$ and $\sigma_2^2 = 9 \times 10^{-6} \text{ \AA}^2$. The analysis gave a Behrens statistic $u = 6.6$, with a degree of freedom 2. From the *t*-distribution table, the probability $P(|u| > 6.6)$ was found to be 0.02 which is less than 0.05. Hence it is concluded that there is a significant difference at the 5% confidence level between the Co—S(3) bonds and the other two. This difference stems probably from the fact that P(1) is constrained in the crystal to be on a diad axis, so that the ligands have different environments. The weighted mean of all three Co—S bonds is 2.322 \AA with a variance of $22 \times 10^{-6} \text{ \AA}^2$.

In each ligand, the plane containing P, O and C lies approximately at right angles to the Co—S—P—S plane, the angles between the planes (least-squares fitted where appropriate) being 88.4 , 87.3 and 87.1° . There is, however, some distortion of the bonds about P from the tetrahedral values, as can be seen from Fig. 1.

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