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THE STRUCTURE OF BIS(O,O'-DIMETHYL DITHIOPHOSPHATO)-(TRIPHENYLPHOSPHINE)COBALT(II)

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The crystal and molecular structure of the title complex has been determined by X-ray diffraction. It is a distorted trigonal-bipyramidal complex: each dithiophosphato ligand spanns an oblique edge of the coordination polyhedron, and triphenylphosphine occupies the fifth coordination site with unusually long Co-P bond length of 2.551 Å.

We have already reported that bis(O,O'-diethyl dithiophosphato)cobalt(II) ($Co[S_2P(OEt)_2]_2$) forms 1:1 or 1:2 adducts with triphenylphosphine or some nitrogen bases, and that they should be trigonal-bipyramidal or octahedral.$^{1)}$ As $Co[S_2P(OEt)_2]_2$ is in a tetrahedral form,$^{2)}$ the deformation of the original complex cannot be avoided when some ligands bond to the complex to form the adducts. To establish the structure of the 1:1 adduct, we have attempted to determine the crystal structure of the complex, $Co[S_2P(OMe)_2](PPh_3)$, which gave crystals better than its ethyl derivative. Although some metal dithiophosphato complexes give different forms depending on the kinds of alkyl groups in their ligands, in the case of $Co[S_2P(OR)_2]_2(PPh_3)$, where R = Me and Et, they seem to be in the same form, because their colors, their visible spectra of solutions, and ν_{P-S} and ν_{Co-S} bands in IR spectra of them are almost the same, respectively.

The complex was prepared by the reaction of cobalt(II) chloride with sodium O,O'-dimethyl dithiophosphate and triphenylphosphine in water, and extracted with benzene. Green crystals were obtained by the evaporation of the solvent. They were recrystallized from benzene-hexane mixed solvent in the atmosphere of N_2.

The crystals are monoclinic with the space group $P2_1/n$, $a = 26.712(4)$, $b = 9.495(1)$, $c = 11.180(5)$ Å, $\beta = 95.43(3)°$ (MoK_α, $\lambda = 0.7107$ Å), and $Z = 4$.

The structure was solved by the heavy atom method and refined to give an R-value of 0.062 for the 4466 reflections collected on a Rigaku automated four circle diffractometer. A perspective drawing of the complex is shown in Fig. 1. Selected bond lengths and angles are shown in Fig. 2 and in Table 1, respectively.

The complex exhibits distorted trigonal-bipyramidal geometry. Each dithiophosphato ligand chelates to the cobalt atom axially and equatorially. The phosphorus atom of the triphenylphosphine lies in the equatorial plane. Co atom deviates by 0.1 Å towards S(4) from the S(1)-S(3)-P(3) plane. Though the bond lengths of the equatorial Co-S are in accordance with the sum (2.36Å) of the Pauling radii of Co(II) and S, the axial Co-S distances are longer than the equatorial ones by 0.245-0.33Å. Corresponding to the lengthening of the axial Co-S bond, P(1)-S(2) and P(2)-S(4) are shorter than P(1)-S(1) and P(2)-S(3) by 0.07 and 0.04 Å, respectively. The cobalt(II) complexes of this type are not common. The similar geometry has been reported only for the structure of $Co(S_2PPh_2)$(quinoline),$^{3)}$ where the Co-N(quinoline) bond length is normal. On the other hand, Co-P(3) of the present adduct (2.551Å), the longest in the known cobalt triphenylphosphine complexes, is out of the ordinary,$^{4)}$ and the bond angle of S(4)-Co-P(3) is much larger than 90°. Such distortion may alleviate the repulsion of sulfur atoms and phenyl groups (S(3)---H(22) = 2.95, S(2)---H(22) = 3.11, S(4)---H(6) = 3.24, and S(4)---C(6) = 3.78 Å). The unusual Co-P(3) bond length is compatible with the low value of the adduct formation constant in benzene.$^{5)}$

Table 1. Bond Angles (Deg.)

S(1)- Co -S(3)	123.75 (6)
S(2)- Co -P(3)	118.36 (6)
S(3)- Co -P(3)	117.40 (5)
S(1)- Co -S(2)	82.05 (6)
S(3)- Co -S(4)	81.55 (5)
S(2)- Co -P(3)	89.28 (5)
S(4)- Co -P(3)	102.31 (5)

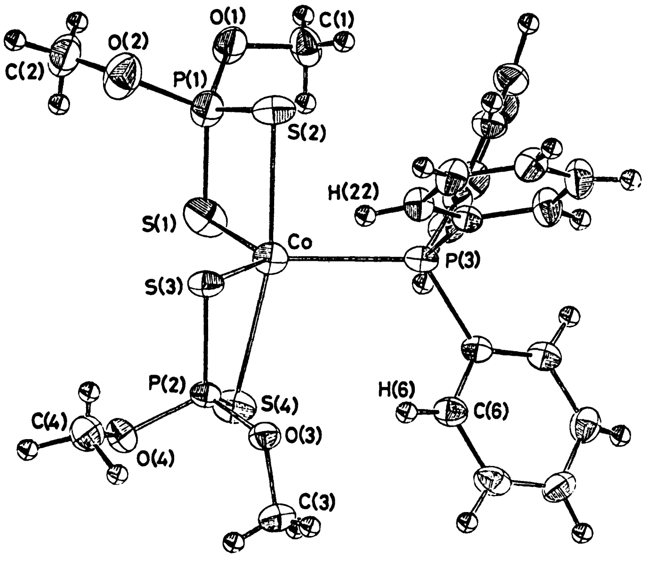

Fig. 1. Perspective Drawing of the Complex

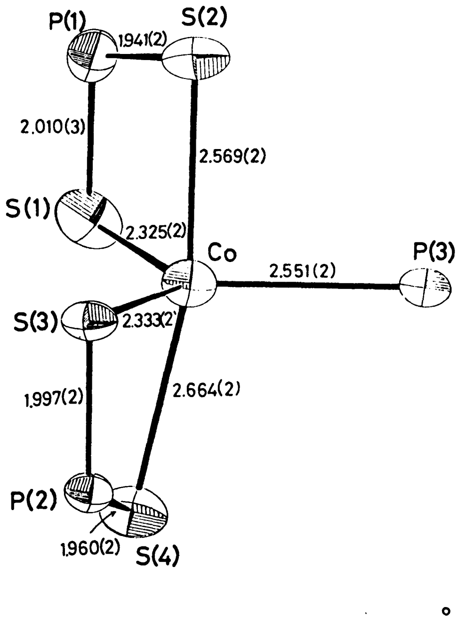

Fig. 2. Selected Bond Lengths (Å)

References and Notes

1) Y.Yamada, M.Shimoi, and A.Ouchi, Chem. Lett., 1978, 867.

2) C.K.Jørgensen, Acta Chem. Scand. 16, 2017 (1962).

3) A.C.Villa, C.Guastini, P.Porta, and A.A.G.Tomlinson, J. Chem. Soc. Dalton Trans., 1978, 956.

4) $Co[N(SiMe_3)_2]_2(PPh_3)$ is the complex with the longest Co-P bond length reported so far (2.479 Å); D.C.Bradley, M.B.Hursthouse, R.J.Smallwood, and A.J.Welch, J. Chem. Soc. Chem. Comm., 1972, 872.

5) Log K = 1.9 at 25°C, where $K = [CoL_2(PPh_3)]/\{[CoL_2][PPh_3]\}$ ($L = S_2P(OMe)_2$) The detail will be published elsewhere.

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