

$a = 12.346(3) \text{ \AA}$   
 $b = 20.167(7) \text{ \AA}$   
 $c = 11.269(3) \text{ \AA}$   
 $\alpha = 97.49(2)^\circ$   
 $\beta = 101.12(2)^\circ$   
 $\gamma = 106.44(2)^\circ$   
 $V = 2589.1(13) \text{ \AA}^3$   
 $Z = 2$   
 $D_x = 1.758 \text{ Mg m}^{-3}$   
 $D_m$  not measured

$\mu = 5.871 \text{ mm}^{-1}$   
 $T = 293(2) \text{ K}$   
 Block  
 $0.50 \times 0.20 \times 0.15 \text{ mm}$   
 Pale yellow

#### Data collection

Rigaku AFC-6S diffractometer  
 $\omega$ - $2\theta$  scans  
 Absorption correction:  
 $\psi$  scan (Coppens *et al.*, 1965)  
 $T_{\min} = 0.247$ ,  $T_{\max} = 0.415$   
 9529 measured reflections  
 9114 independent reflections

4557 reflections with  
 $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.0253$   
 $\theta_{\max} = 25^\circ$   
 $h = 0 \rightarrow 14$   
 $k = -23 \rightarrow 22$   
 $l = -13 \rightarrow 13$   
 3 standard reflections  
 every 150 reflections  
 intensity decay: 1%

#### Refinement

Refinement on  $F^2$   
 $R(F) = 0.043$   
 $wR(F^2) = 0.108$   
 $S = 0.957$   
 9114 reflections  
 535 parameters  
 H atoms constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0401P)^2 + 0.2158P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.475 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.484 \text{ e \AA}^{-3}$   
 Extinction correction: none  
 Scattering factors from  
*International Tables for Crystallography* (Vol. C)

Table 1. Selected bond lengths ( $\text{\AA}$ )

Se1—C11	1.923(7)	Se5—C51	1.920(9)
Se1—Cu2	2.3844(14)	Se5—Cu4	2.3848(14)
Se1—Cu1	2.3875(14)	Se5—Cu3	2.4283(14)
Se2—C21	1.922(8)	Se6—C61	1.940(8)
Se2—Cu1	2.3708(15)	Se6—Cu3	2.3812(15)
Se2—Cu4	2.4005(14)	Se6—Cu1	2.3995(15)
Se3—C31	1.936(8)	Cu1—Cu4	2.7086(15)
Se3—Cu4	2.3927(14)	Cu1—Cu2	2.7320(15)
Se3—Cu2	2.4337(15)	Cu1—Cu3	2.8116(16)
Se4—C41	1.918(8)	Cu2—Cu3	2.7210(15)
Se4—Cu3	2.3741(14)	Cu2—Cu4	2.7663(15)
Se4—Cu2	2.4263(14)	Cu3—Cu4	2.7884(17)

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1994). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1997). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a). Program(s) used to refine structure: *SHELXS97* (Sheldrick, 1997b). Molecular graphics: *XP* (Siemens, 1990). Software used to prepare material for publication: *SHELXL97*.

This work was supported by the National Natural Science Foundation of China (subject No. 29733080).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1255). Services for accessing these data are described at the back of the journal.

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*Acta Cryst.* (1999). **C55**, 1800–1802

### Bis(pyrimidine-2-thiolato-*N,S*)bis(trimethyl phosphite-*P*)cobalt(III) hexafluorophosphate

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(Received 10 March 1999; accepted 9 July 1999)

#### Abstract

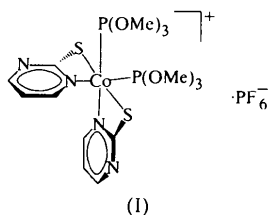
The title complex,  $[Co(C_4H_3N_2S)_2\{P(OCH_3)_3\}_2]PF_6$ , with mixed N-heterocyclic thiolate and trimethyl phosphite ligands, was synthesized and characterized by X-ray crystallography and spectroscopic measurements. The  $Co^{III}$  ion is six-coordinated and has a slightly distorted octahedral geometry, being coordinated to two pairs of N and S atoms of two monoanionic bidentate pyrimidine-2-thiolate ligands and the P atom of each of two monodentate trimethyl phosphite ligands,

with three pairs of essentially equal bonds distances [Co—N 1.968 (6) and 1.976 (5) Å, Co—P 2.174 (2) and 2.177 (2) Å, and Co—S 2.279 (2) and 2.282 (2) Å].

### Comment

Cobalt complexes with mixed phosphine and thiolate ligands have been the subject of many recent studies because of their intriguing structural variations, electron-transfer properties and possible catalytic applications (Marko *et al.*, 1985; Balch, 1971). With a combination of suitable tertiary phosphines and thiolates, various mono-, bi-, tri-, tetra- and octanuclear cobalt complexes have been reported (Kang *et al.*, 1996; Chen *et al.*, 1998). In these complexes, Co atoms can afford different valences and also exhibit various geometries. For instance, in the mononuclear complexes, the valence of the Co atoms can be +1, +2 or +3, with four- (Wei *et al.*, 1991), five- (Bianchini *et al.*, 1982) or six-coordination (Kita *et al.*, 1992) in square-planar, tetrahedral, trigonal-bipyramidal, square-pyramidal or octahedral geometry, depending on the number of donor atoms of the phosphine and thiolate ligands. Up to now, the majority of the thiolate ligands used in structural studies have been homocyclic and only a few heterocyclic ligands have been used.

The title compound, (I), consists of a  $[\text{Co}(\text{pymt})_2\text{-}\{\text{P}(\text{OCH}_3)_3\}_2]^+$  cation (pymt is pyrimidine-2-thiolate) and a  $\text{PF}_6^-$  anion. The cation contains a distorted octahedral  $\text{Co}^{\text{III}}$  ion which is chelated by two bidentate pymt ligands through their S and N atoms, and further coordinated to the P atoms of two trimethyl phosphite ligands.



The Co—N and Co—S bond distances show no remarkable features and fall into the normal range of bond distances found in related mononuclear cobalt complexes with mixed phosphine and thiolate ligands. However, the Co—P distances are slightly shorter than those of related complexes. A similar example can be found in the complex  $[\text{Co}(\text{bdt})_2\{\text{P}^n\text{Bu}_3\}]^-$  (bdt is *o*-benzenedithiolate; Kang *et al.*, 1991), in which the Co—P bond distance is 2.124 (2) Å, but the central Co atom is five-coordinated.

The C—S bond distances of (I) are shorter than the normal covalent distance (1.81 Å) of a single bond, suggesting that the thione form is the predominant coordination mode of the pymt ligand.

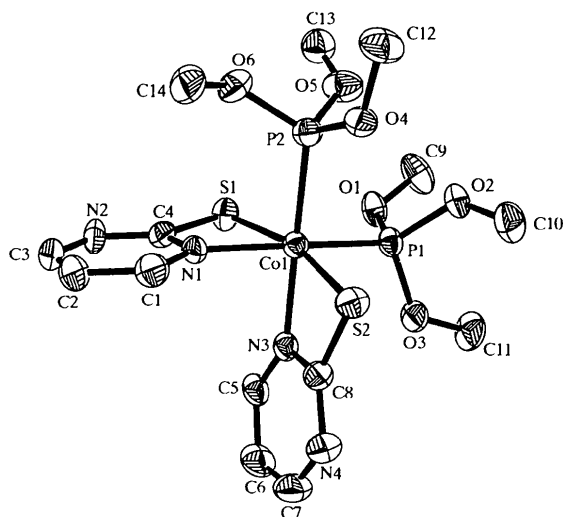


Fig. 1. The molecular structure of the  $[\text{Co}(\text{pymt})_2\{\text{P}(\text{OCH}_3)_3\}_2]^+$  cation with displacement ellipsoids at the 30% probability level.

### Experimental

To an absolute MeOH solution (30 ml) containing  $\text{CoCl}_2$  (1.0 mmol, 0.13 g) and NaOMe (2.0 mmol, 0.11 g) was added *via* syringes  $\text{P}(\text{OCH}_3)_3$  (0.60 ml, 4.0 mmol) followed by Hpymt (0.12 g, 1.0 mmol) with stirring. The solution turned deep red after 10 min. The reaction mixture was stirred for a further 30 min before filtration.  $\text{KPF}_6$  (1.0 mmol, 0.19 g) was added to the filtrate and the resulting solution allowed to stand at 277 K for several days to produce well shaped dark-red crystals (yield 60%). Analysis calculated for  $\text{C}_{14}\text{H}_{24}\text{CoF}_6\text{N}_4\text{O}_6\text{P}_3\text{S}_2$ : C 24.94, H 3.59, N 8.31%; found: C 24.74, H 3.65, N 8.27%; IR (KBr,  $\text{cm}^{-1}$ ): 3427 (w), 3131 (w), 3008 (w), 2959 (m), 2852 (w), 1564 (s), 1548 (m), 1466 (w), 1433 (m), 1376 (s), 1261 (m), 1179 (m), 1039 (s), 1015 (s), 842 (s), 801 (m), 752 (m), 725 (m), 662 (w), 555 (s), 490 (w), 465 (w).

### Crystal data

$[\text{Co}(\text{C}_4\text{H}_3\text{N}_2\text{S})_2(\text{C}_3\text{H}_9\text{O}_3\text{P})_2]\text{-PF}_6$

$M_r = 674.33$

Monoclinic

$P2_1/n$

$a = 15.194(3) \text{ \AA}$

$b = 11.059(2) \text{ \AA}$

$c = 16.262(3) \text{ \AA}$

$\beta = 102.19(3)^\circ$

$V = 2670.9(9) \text{ \AA}^3$

$Z = 4$

$D_x = 1.677 \text{ Mg m}^{-3}$

$D_m$  not measured

Mo  $K\alpha$  radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 7\text{--}15^\circ$

$\mu = 1.058 \text{ mm}^{-1}$

$T = 293(2) \text{ K}$

Block

$0.4 \times 0.3 \times 0.2 \text{ mm}$

Black

### Data collection

Siemens P3 diffractometer  
 $\omega$  scans

$R_{\text{int}} = 0.059$

$\theta_{\text{max}} = 25.05^\circ$

Absorption correction:  $h = -18 \rightarrow 17$   
 empirical  $\psi$  scan (North  $k = 0 \rightarrow 13$   
*et al.*, 1968)  $l = 0 \rightarrow 19$   
 $T_{\min} = 0.667$ ,  $T_{\max} = 0.809$  2 standard reflections  
 8406 measured reflections every 120 reflections  
 4721 independent reflections intensity decay: 1.5%  
 2936 reflections with  
 $I > 2\sigma(I)$

#### Refinement

Refinement on  $F^2$   $(\Delta/\sigma)_{\max} < 0.001$   
 $R[F^2 > 2\sigma(F^2)] = 0.067$   $\Delta\rho_{\max} = 0.41 \text{ e } \text{Å}^{-3}$   
 $wR(F^2) = 0.164$   $\Delta\rho_{\min} = -0.34 \text{ e } \text{Å}^{-3}$   
 $S = 1.079$  Extinction correction: none  
 4721 reflections Scattering factors from  
 324 parameters *International Tables for*  
 H atoms constrained *Crystallography* (Vol. C)  
 $w = 1/[\sigma^2(F_o^2) + (0.0324P)^2$   
 $+ 10.0714P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

The methyl C13 atom is disordered over two positions and was refined isotropically with half occupancy. No H atoms were included for this group. The major residual features in the final difference map lie close to the Co<sup>III</sup> atom.

Data collection: XSCANS (Siemens, 1994). Cell refinement: XSCANS. Data reduction: SHELXTL (Sheldrick, 1995). Program(s) used to solve structure: SHELXS97 (Sheldrick, 1997a). Program(s) used to refine structure: SHELXL97 (Sheldrick, 1997b). Molecular graphics: SHELXTL. Software used to prepare material for publication: SHELXTL.

This work has been supported by the State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, NNSF of China, by the NSF of Guangdong Province, and by the Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1474). Services for accessing these data are described at the back of the journal.

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*Acta Cryst.* (1999). **C55**, 1802–1804

### Bis[2-(1,3-benzothiazol-2-yl)phenolato-O,N]chlorooxorhenium(V)-dichloromethane (1/1.5)

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(Received 12 April 1999; accepted 22 July 1999)

#### Abstract

The X-ray structure of the title compound, [Re-(C<sub>13</sub>H<sub>8</sub>NOS)<sub>2</sub>ClO]·1.5CH<sub>2</sub>Cl<sub>2</sub>, shows distorted octahedral coordination geometry around rhenium. Bond lengths and angles are typical of related rhenium and technetium complexes. The average Re—N and Re—O distances are 2.140 (4) and 1.977 (4) Å, respectively. The Re=O and Re—Cl distances are 1.679 (4) and 2.365 (1) Å, respectively.

#### Comment

Current research in radiopharmacology involves the exploitation of the coordination chemistry of technetium as well as its congener, rhenium, to develop new radiotracers (Clarke & Podbielsky, 1987; Jurrisson *et al.*, 1993). The labelled compounds of the radioisotopes of rhenium (<sup>186</sup>Re/<sup>188</sup>Re) have been suggested as radiopharmaceuticals for therapy because of their energetic  $\beta$  particles and accompanying  $\gamma$  rays which are suitable for imaging (Dilworth & Parrotl, 1998). Despite the large number of rhenium complexes discovered thus far, studies of