

Structure of [1,2-Bis(dimethylphosphino)ethane]bis(*O*-ethyl dithiocarbonato-*S,S'*)cobalt(III) Tetraphenylborate, [Co(C₃H₅OS₂)₂(C₆H₁₆P₂)]₂[B(C₆H₅)₄]

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Abstract. $M_r = 770.7$, orthorhombic, $Pbnb$, $a = 14.641$ (3), $b = 21.666$ (6), $c = 12.417$ (3) Å, $V = 3939$ (2) Å³, $Z = 4$, $D_x = 1.30$, D_m (ethyl ether/bromofrom) = 1.31 (2) Mg m⁻³, λ (Mo $K\alpha$) = 0.70926 Å, μ (Mo $K\alpha$) = 0.747 mm⁻¹, $F(000) = 1616$, $T = 295$ (2) K, $R = 0.044$ for 1951 observed reflections. The central Co atom lies on a crystallographic twofold axis and is octahedrally coordinated by two P and four S atoms. The P atoms exert a *trans* influence on the Co–S bond distance; the Co–S distance with the S atom *trans* with respect to the P atom is 2.290 (2) Å, which is significantly longer than that of 2.255 (1) Å for the S atom in the *cis* position.

Introduction. Some new cobalt(III) complexes having alkylphosphine ligands were synthesized to investigate their spectral properties and molecular structures (Atoh, Kashiwabara, Ito, Fujita & Ito, 1981; Kinoshita, Kashiwabara, Fujita, Matsumoto & Ooi, 1981; Ohba, Saito, Ohishi, Kashiwabara & Fujita, 1983). As part of these investigations, the crystal structure of the title compound which contains *dmpe*, (CH₃)₂PCH₂CH₂P(CH₃)₂, has been determined.

Experimental. Crystals were obtained from an acetone–ethanol(1:1) solution and kindly supplied by Professor J. Fujita, Nagoya University, in the form of orange-red plates, grown perpendicular to **b**; preliminary determination of lattice parameters and the space group ($Pbnb$ from systematic absences: $0kl$, $k \neq 2n$; $hk0$, $k \neq 2n$; $h0l$, $h + l \neq 2n$) made with a Weissenberg camera; $Pbnb$ is derived from $Pccn$ by permutation of the standard abc to the $\bar{a}cb$ orientation, general equivalent positions $\pm[x, y, z; \frac{1}{2} - x, y, \frac{1}{2} - z; \frac{1}{2} + x, \frac{1}{2} - y, -z; -x, \frac{1}{2} - y, \frac{1}{2} + z]$; the cell edges were labelled so that $c < a < b$ to ensure a unique setting for determinative purposes (*International Tables for X-ray Crystallography*, 1959); approximate dimensions of crystal 0.5 × 0.45 × 0.15 mm, Rigaku automated four-circle diffractometer AFC-5, graphite monochromator, cell parameters refined by least-squares

methods on the basis of 21 2θ values, Mo $K\alpha$ radiation ($30 < 2\theta < 41^\circ$, $\lambda = 0.70926$ Å); intensity measurement performed to $2\theta = 55^\circ$ (the $+h, +k, +l$ set), θ – 2θ scan technique, scan speed 2° min⁻¹ (θ); the mean ratio of structure factors of the five standard reflections was $0.98 < \sum(|F_o|/|F_o|_{\text{initial}})/5 \leq 1.00$; the extinction rule was confirmed by 501 reflections giving 11 weak exceptions with $3\sigma(|F_o|) < |F_o|$, which were neglected; 4499 reflections measured, 196 weak reflections classified as unobserved [$|F_o| \leq 3\sigma(|F_o|)$], 2351 zero reflections, 1952 observed unique reflections used for the structure determination; corrections for Lorentz–polarization, but not for absorption; the Co and B atoms are required to lie on the twofold axis because of the space-group symmetry with $Z = 4$; the position of Co was deduced from a Patterson map, but an attempt to solve the structure by the heavy-atom method failed; direct methods with *MULTAN78* (Main, Hull, Lesinger, Germain, Declercq & Woolfson, 1978) gave the structure; starting with the positions of CoPS₂ and BC₆ the other non-H atoms were determined from electron-density maps and refined by block-diagonal least squares with anisotropic thermal parameters using the *UNICS III* computation program system (Sakurai & Kobayashi, 1979); 8 of the 23 H atoms were found from difference density maps, the others calculated; thermal parameters of H atoms fixed at 7 Å²; $\sum w||F_o| - |F_c||^2$ minimized, $w^{-1} = \sigma^2(|F_o|) + (0.015|F_o|)^2$; reflection 200 omitted because of secondary-extinction effect ($F_o^2/F_c^2 = 0.61$); final $R = 0.044$, $wR = 0.052$, $S = 2.0$ for 1951 observed reflections;* the maximum shift on the final cycle of refinement was 5.5σ for the y coordinate of the methyl H atom H(C6)3; no peaks higher than 0.3 e Å⁻³ were

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, bond lengths and bond angles in BPh₄ and a projection of the crystal structure along **c** have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38529 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters* ($\times 10^4$; for Co $\times 10^5$) and *equivalent isotropic thermal parameters* (Hamilton, 1959)

$$B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
Co	25000	15485 (2)	25000	3.3
B	2500	-12 (4)	7500	3.4
S(1)	2363 (1)	1674 (1)	4295 (1)	4.4
S(2)	3592 (1)	2269 (1)	2902 (1)	5.1
P	1476 (1)	808 (1)	2341 (1)	4.0
O	3666 (3)	2449 (2)	4980 (3)	5.7
C(1)	3245 (4)	2163 (2)	4178 (4)	4.3
C(2)	3321 (4)	2342 (3)	6078 (4)	5.9
C(3)	3831 (5)	2780 (3)	6801 (5)	7.9
C(4)	2076 (4)	78 (2)	2162 (5)	5.8
C(5)	675 (4)	851 (3)	1235 (5)	7.6
C(6)	751 (4)	717 (3)	3516 (5)	6.0
C(7)	2548 (4)	-468 (2)	8561 (4)	3.8
C(8)	3250 (4)	-469 (3)	9317 (4)	4.8
C(9)	3231 (5)	-877 (3)	10210 (4)	6.9
C(10)	2528 (5)	-1274 (3)	10358 (5)	7.2
C(11)	1833 (4)	-1302 (3)	9616 (5)	6.2
C(12)	1856 (4)	-905 (2)	8731 (5)	4.8
C(13)	3397 (3)	443 (2)	7437 (4)	3.6
C(14)	4048 (3)	440 (2)	6622 (4)	3.9
C(15)	4811 (4)	838 (2)	6630 (4)	4.9
C(16)	4943 (4)	1243 (2)	7458 (5)	5.6
C(17)	4300 (4)	1275 (3)	8270 (5)	6.1
C(18)	3547 (4)	883 (2)	8254 (4)	5.1

observed in the final difference density map; complex neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974); final atomic parameters are presented in Table 1.

Discussion. Fig. 1 shows a perspective drawing of the complex cation. The Co atom is octahedrally coordinated by the two P atoms of dmpe and the four S atoms of the ethyl xanthate* ligands. Interatomic distances and bond angles in the complex cation are listed in Table 2. The five-membered chelate ring formed by the dmpe ligand takes a twisted conformation. The dimensions and the form of dmpe are almost the same as in [Co(dmpe)(en)₂]³⁺ (en, ethylenediamine; Ohba, Saito, Ohishi, Kashiwabara & Fujita, 1983). The Co—P bond distance of the present complex, 2.205 (1) Å, is shorter than in [Co(dmpe)(en)₂]³⁺ [2.248 (3) and 2.264 (3) Å]. The S(1), S(2), C(1), O and C(2) atoms of the xanthate ligand lie in a plane, the out-of-plane distance being less than 0.01 Å. The Co and the terminal C(3) atoms deviate from this plane by 0.14 (1) and -0.18 (1) Å, respectively. The torsion angle C(1)—O—C(2)—C(3) is -172.6 (5)°. Bond lengths and bond angles within the xanthate ligand are almost the same as those in cobalt(III) tris(*O*-ethyl xanthate) (Merlino, 1969). As Merlino noted, the bond angle S(1)—C(1)—O of 126.0 (4)° is greater than S(2)—C(1)—O of 120.3 (4)° because of the steric interaction between S(1) and C(2) (2.99 Å). Values of the Co—S bond distance in Co^{III} ethyl xanthate are 2.276 (4) and 2.277 (4) Å (Merlino, 1969). Those in the present complex are 2.255 (1) and 2.290 (2) Å for Co—S(1) and Co—S(2), respectively.

* Xanthate ≡ dithiocarbonate.

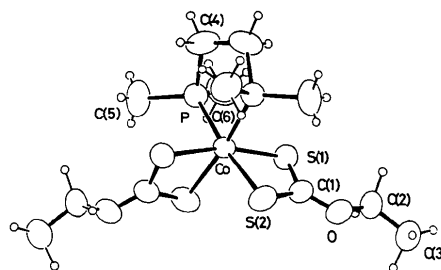


Fig. 1. An ORTEP drawing (Johnson, 1965) of the complex cation with thermal ellipsoids scaled at the 50% probability level. H atoms are represented by circles of radius 0.08 Å.

Table 2. *Bond lengths* (Å) and *bond angles* (°)

Co—S(1)	2.255 (1)	P—C(5)	1.808 (7)
Co—S(2)	2.290 (2)	P—C(6)	1.814 (6)
Co—P	2.205 (1)	O—C(1)	1.323 (6)
S(1)—C(1)	1.677 (5)	O—C(2)	1.473 (7)
S(2)—C(1)	1.680 (5)	C(2)—C(3)	1.505 (9)
P—C(4)	1.823 (6)	C(4)—C(4')	1.499 (8)
S(1)—Co—S(1')	166.1 (1)	Co—P—C(5)	118.1 (2)
S(1)—Co—S(2)	76.4 (1)	Co—P—C(6)	113.9 (2)
S(1)—Co—S(2')	94.1 (1)	C(4)—P—C(5)	105.4 (3)
S(1)—Co—P	96.7 (1)	C(4)—P—C(6)	106.6 (3)
S(1)—Co—P'	93.5 (1)	C(5)—P—C(6)	103.7 (3)
S(2)—Co—S(2')	94.0 (1)	C(1)—O—C(2)	117.6 (4)
S(2)—Co—P	172.1 (1)	S(1)—C(1)—S(2)	113.6 (3)
S(2)—Co—P'	90.1 (1)	S(1)—C(1)—O	126.0 (4)
P—Co—P'	86.6 (1)	S(2)—C(1)—O	120.3 (4)
Co—S(1)—C(1)	85.5 (2)	O—C(2)—C(3)	106.4 (5)
Co—S(2)—C(1)	84.4 (2)	P—C(4)—C(4')	109.3 (4)
Co—P—C(4)	108.3 (2)		

The Co—S bond distance with the S atom in a *trans* position with respect to the P atom of dmpe is longer by 0.035 Å than that with the S atom in a *cis* position, indicating the *trans* influence of the coordinated P atom. The *trans* influence was also observed for the Co—N bond distance in [Co(dmpe)(en)₂]³⁺. The difference in Co—N distances in *cis* and *trans* positions with respect to the coordinated P atom was 0.045 Å (Ohba *et al.*, 1983). These observations show the strong electron-donating effect of the P atom to the Co atom.

Columns of the complex cations and of the BPh₄⁻ anions are arranged alternately along **b**, where the ethoxy moiety of the ethyl xanthate is packed between the phenyl groups of the adjacent BPh₄⁻ ions.* No intermolecular distances are less than the sum of the van der Waals radii of the atoms involved (Bondi, 1964). BPh₄⁻ has a pseudo S₄ axis and the molecular dimensions are almost the same as those in K[BPh₄] (Hoffmann & Weiss, 1974). The mean B—C and C—C bond distances are 1.647 (6) and 1.391 (10) Å, respectively.*

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* See deposition footnote.

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Structure of Bis[*N*-(2-pyrrolylmethylene)-*tert*-butylamine]zinc(II), Zn(C₉H₁₃N₂)₂

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Abstract. $M_r = 363.81$, orthorhombic, *Pbcn*, $a = 17.166$ (5), $b = 7.209$ (5), $c = 15.232$ (3) Å, $V = 1885$ (2) Å³, $Z = 4$, $D_m = 1.25$, $D_x = 1.282$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 13.13$ cm⁻¹, $F(000) = 768$, $T = 294$ K, $R = 0.0398$ for 1591 observed reflections. The Zn atom, which is on a crystallographic twofold axis, is coordinated to four N atoms of the two symmetry-related bidentate pyrrolylmethylene-*tert*-butylamine ligands. These coordinating N atoms form a tetrahedron that is elongated along the bisector of the N–Zn–N ligand angle of the chelating ring.

Introduction. It is well known that Zn^{II} has a catalytic function in substrate reductions by nicotinamide-adenine dinucleotide (NADH) in biological systems and the mechanism of this reduction has been the subject of earlier investigations in polar solvents and often at low pH (Shirai, Chishina & Tanaka, 1975; Branden, Jörnvall, Ekland & Furugren, 1976). From these experiments it has not been possible to decide whether the initial step in the reduction is a proton or an electron transfer.

In order to be able to study substrate reductions in aprotic solvents, it is necessary to have neutral Zn–substrate model compounds available that are soluble in aprotic solvents. The title compound represents such a model and the first aim was to determine accurately its Zn coordination.

Experimental. Synthesized by one of the authors (G. C. van Stein), rod-shaped crystal, $0.58 \times 0.49 \times 0.34$ mm, D_m by flotation, Nonius CAD-4 diffractometer, ω - 2θ scan technique, Zr-filtered Mo *K* α radiation, lattice parameters from ten reflections, one octant of the reflection sphere, 2161 independent intensities measured, h 0–22, k 0–9, l 0–19, $2\theta_{\text{max}} = 55^\circ$, 1591 above $2.5 \sigma(I)$ level; two periodically measured standard reflections showed no significant changes; correction for Lorentz, polarization and absorption (using seven indexed crystal faces, transmission factors 0.591 to 0.640); Patterson and Fourier methods, all H atoms located from difference maps; H atoms, except those of the methyl groups, included in weighted anisotropic full-matrix refinement with constant isotropic thermal parameters equal to those of the carrier atoms, methyl-group H atoms refined in the rigid-rotator model with fixed C–H distances and H–C–H angles, $wR = [\sum w^{1/2}(|F_o| - |F_c|)] / [\sum w^{1/2} F_o] = 0.045$, $w = 1.4515 / [\sigma^2(F_o) + 0.00143 F_o^2]$, $S = 0.70$; refinement of isotropic extinction parameter in the last cycles gave $g = 1.13 \times 10^{-7}$; average and maximum shift/error ratios for non-H parameters were 0.012 and 0.059, respectively, for H parameters 0.018 and 0.034, respectively; final difference map revealed regions of positive and negative densities of about $0.45 \text{ e } \text{Å}^{-3}$ at about 0.8 Å from Zn, the other maxima were below the level of $0.30 \text{ e } \text{Å}^{-3}$; scattering factors from *International Tables for X-ray Crystallography* (1974)