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Structure of [Bis(2-diphenylphosphinoethyl)phenylphosphine-*P,P,P*]carbonyl-(phenylthiolato)cobalt(I), [Co{Ph₂PCH₂CH₂P(Ph)CH₂CH₂PPh₂}(SPh)(CO)]

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Abstract. [Co(C₃₄H₃₃P₃)(C₆H₅S)(CO)], *M_r* = 730.68, monoclinic, *P*2₁, *a* = 11.163 (2), *b* = 15.499 (3), *c* = 10.427 (2) Å, β = 94.18 (3)°, *V* = 1799.34 (93) Å³, *Z* = 2, *D_x* = 1.349 g cm⁻³, λ(Mo *K*α) = 0.71073 Å, μ = 6.928 cm⁻¹, *F*(000) = 760, *T* = 296 K, final *R* = 0.043 for 1866 observed unique reflections. The compound is an asymmetric molecule with a five-coordinate Co atom. The Co—S, Co—C and average value of Co—P bond distances are 2.302 (3), 1.741 (9) and 2.160 (3) Å, respectively.

Introduction. Transition-metal complexes containing phosphino ligands have been studied extensively, not only because of their facile electron-transfer properties and variation of molecular structure but also owing to their potential application as homogeneous or heterogeneous catalysts. Metal thiolato complexes are known as ubiquitous biological electron-transfer mediators (Blower & Dilworth, 1987). Yet complexes blending both poly-phosphino and thiolato ligands have received relatively little attention and only a few reports have been found in this realm (Canich, Cotton, Dunbar & Falvello, 1988), and the structures of complexes blending poly-phosphino, carbonyl and thiolato ligands have not been seen up to now.

In a programme aimed at understanding the synergistic effect between atoms or groups within a molecule, we have explored the coordination chemistry

and the reactivity of metal complexes with both thiolato and ditertiary phosphino ligands (Wei, Liu, Huang, Hong, Huang & Kang, 1991). Herein, we report the synthesis and crystal structure of a cobalt complex blending poly-phosphino, thiolato and carbonyl ligands, [Co(dppep)(SPh)(CO)] [dppep = Ph₂PCH₂CH₂P(Ph)CH₂CH₂PPh₂].

Experimental. [Co(dppep)(SPh)(CO)] was prepared by the reaction of CoCl₂.6H₂O, dppep, NaSPh and Mo(CO)₆ in MeCN at room temperature, and crystals suitable for X-ray analysis were grown by keeping the reaction solution at 263 K. Diffraction intensities were collected from a red plate crystal of 0.30 × 0.30 × 0.15 mm on an Enraf–Nonius CAD-4 diffractometer in the ω–2θ-scan mode [scan rate 1–7° min⁻¹ (in ω); scan width (0.90 + 0.350tanθ)°] using graphite-monochromated Mo *K*α radiation. Cell constants were obtained from least-squares refinement of 25 reflections, using a setting of θ angles from 12 to 18°. Systematic absences: 0*k*0, *k* = 2*n*. A total of 3488 reflections were collected in the range of 2 < 2θ < 50° (0 ≤ *h* ≤ 13, 0 ≤ *k* ≤ 18, –12 ≤ *l* ≤ 12). The intensities were monitored by three representative reflections. The data were corrected for the fluctuation of the monitored reflections (between 1.000 and 1.039), the *L_p* factor, and empirical absorption (*DIFABS*; Walker & Stuart, 1983) (between 1.371 and 0.840), but no extinction correction was made. Of 3134 unique reflections, 1866 with *I* > 3σ(*I*) were used for structure solution and

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Table 1. Positional parameters and equivalent isotropic thermal parameters (\AA^2)
$$B_{eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
Co	0.1702 (1)	0.2223	0.6212 (1)	1.80 (2)
S	0.1367 (2)	0.3568 (2)	0.5322 (3)	3.63 (6)
P1	0.1613 (2)	0.1722 (2)	0.4255 (3)	3.25 (5)
P2	0.1374 (3)	0.0934 (2)	0.6795 (3)	3.57 (6)
P3	0.0372 (2)	0.2597 (2)	0.7527 (3)	3.24 (5)
O	0.4059 (7)	0.2376 (6)	0.7529 (9)	7.1 (2)
C1	0.167 (1)	0.0544 (7)	0.426 (1)	4.4 (3)
C01	0.3146 (8)	0.2339 (8)	0.6942 (9)	3.7 (2)
C2	0.109 (1)	0.0172 (7)	0.546 (1)	5.0 (3)
C3	0.0008 (9)	0.0887 (7)	0.767 (1)	4.2 (2)
C4	0.005 (1)	0.1678 (8)	0.858 (1)	4.5 (3)
C11	0.2855 (8)	0.1970 (6)	0.3217 (9)	3.3 (2)
C12	0.3684 (9)	0.2582 (7)	0.360 (1)	3.9 (2)
C13	0.4606 (9)	0.2752 (9)	0.280 (1)	5.2 (3)
C14	0.4658 (9)	0.233 (1)	0.164 (1)	5.7 (3)
C15	0.378 (1)	0.1739 (8)	0.125 (1)	4.7 (3)
C16	0.2847 (9)	0.1567 (8)	0.203 (1)	4.4 (3)
C21	0.0290 (9)	0.1969 (7)	0.3191 (9)	3.7 (2)
C22	-0.078 (1)	0.1498 (9)	0.319 (1)	5.1 (3)
C23	-0.182 (1)	0.178 (1)	0.244 (1)	6.6 (4)
C24	-0.178 (1)	0.251 (1)	0.171 (1)	6.4 (4)
C25	-0.075 (1)	0.297 (1)	0.168 (1)	6.4 (4)
C26	0.0272 (9)	0.2705 (9)	0.241 (1)	4.5 (3)
C31	0.253 (1)	0.0383 (7)	0.784 (1)	3.9 (2)
C32	0.231 (1)	0.0075 (8)	0.905 (1)	5.3 (3)
C33	0.325 (1)	-0.033 (1)	0.981 (1)	6.6 (4)
C34	0.436 (1)	-0.0421 (9)	0.937 (1)	6.5 (4)
C35	0.456 (1)	-0.012 (1)	0.817 (1)	6.9 (4)
C36	0.366 (1)	0.0287 (8)	0.742 (1)	6.0 (3)
C41	-0.1151 (9)	0.2897 (7)	0.697 (1)	3.7 (2)
C42	-0.205 (1)	0.3082 (9)	0.781 (1)	5.5 (3)
C43	-0.321 (1)	0.324 (1)	0.735 (1)	7.2 (4)
C44	-0.350 (1)	0.325 (1)	0.602 (1)	6.9 (4)
C45	-0.267 (1)	0.306 (1)	0.519 (1)	5.8 (3)
C46	-0.1506 (9)	0.2896 (8)	0.565 (1)	4.1 (2)
C51	0.0829 (9)	0.3458 (7)	0.8646 (9)	3.4 (2)
C52	0.044 (1)	0.4276 (7)	0.852 (1)	4.2 (3)
C53	0.183 (1)	0.4774 (9)	1.020 (1)	5.3 (3)
C54	0.091 (1)	0.4943 (8)	0.929 (1)	5.0 (3)
C55	0.179 (1)	0.3267 (7)	0.959 (1)	4.3 (3)
C56	0.224 (1)	0.3905 (9)	1.036 (1)	5.3 (3)
C61	0.2582 (9)	0.4302 (7)	0.554 (1)	3.7 (2)
C62	0.278 (1)	0.4834 (8)	0.453 (1)	5.6 (3)
C63	0.365 (1)	0.5477 (9)	0.467 (1)	7.7 (4)
C64	0.432 (1)	0.5567 (9)	0.580 (2)	8.6 (4)
C65	0.417 (1)	0.5042 (9)	0.683 (2)	6.8 (4)
C66	0.328 (1)	0.4407 (7)	0.669 (1)	5.2 (3)

refinement. Calculations were performed on a VAX 11/785 computer with the *SDP* program package (Frenz, 1978). The structure was solved by direct methods. All metal, S and P atoms were located from an *E* map. A Fourier map phased by the metal atoms contained most of the remaining non-H atoms. In the last stage of refinement, contributions were included for H atoms with fixed 'idealized' positions of C—H = 0.95 Å. 423 variables were used in refinement. $R_{int} = 0.062$. Full-matrix least-squares refinement with anisotropic thermal parameters for all non-H atoms led to convergence with $R = 0.043$ and $wR = 0.051$. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w^{-1} = 1 + \{[(F_o)^2 + 2\sigma(F_o)|F_o|]^{1/2} - |F_o|\}^2 + (0.01F_o)^2$. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (Cromer & Waber, 1974). The goodness of fit (*S*) was 1.24. The largest Δ/σ value in the final cycle was 0.19, while the extreme peaks in the difference electron density map were 0.72 and

Table 2. Selected interatomic distances (Å) and bond angles (°)

Co—S	2.302 (3)	P2—C2	1.84 (2)
Co—P1	2.179 (3)	P2—C3	1.84 (2)
Co—P2	2.128 (4)	P2—C31	1.83 (2)
Co—P3	2.174 (4)	P3—C4	1.85 (2)
Co—C01	1.741 (9)	P3—C41	1.82 (2)
S—C61	1.77 (2)	P3—C51	1.82 (2)
P1—C1	1.83 (1)	O—C01	1.16 (2)
P1—C11	1.82 (1)	C1—C2	1.56 (2)
P1—C21	1.82 (2)	C3—C4	1.55 (2)
S—Co—P1	87.2 (1)	Co—P1—C1	110.8 (4)
S—Co—P2	160.0 (1)	Co—P1—C11	119.7 (3)
S—Co—P3	85.1 (2)	Co—P1—C21	118.3 (3)
S—Co—C01	101.6 (5)	Co—P2—C2	114.2 (4)
P1—Co—P2	86.3 (1)	Co—P2—C3	110.2 (4)
P1—Co—P3	134.4 (1)	Co—P2—C31	118.6 (4)
P1—Co—C01	115.1 (3)	Co—P3—C4	109.9 (4)
P2—Co—P3	86.0 (1)	Co—P3—C41	122.4 (4)
P2—Co—C01	98.3 (5)	Co—P3—C51	115.3 (3)
P3—Co—C01	110.5 (3)	Co—C01—O	173.3 (9)
Co—S—C61	115.3 (4)		

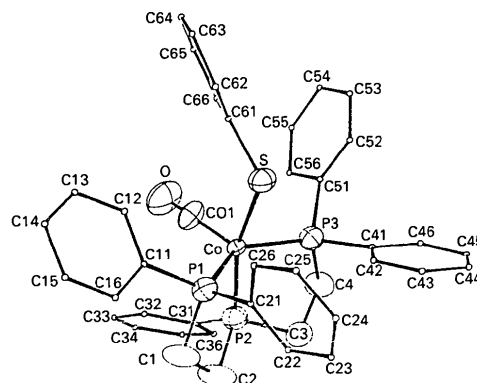


Fig. 1. Molecular structure and atomic labelling scheme for [Co(dppep)(SPh)(CO)].

−0.67 e Å^{−3}. Final positional parameters are given in Table 1, and selected atomic distances and bond angles are listed in Table 2.* The atomic labelling scheme and the molecular structure are shown in Fig. 1.

Discussion. The Co atom in the complex is coordinated by five atoms P, P, P, S, and C, with no symmetric element for the whole molecule. The tridentate ligand dppep chelates to the Co atom forming a CoPPP triangular pyramid with Co—P distances varying from 2.128 to 2.179 Å, while the ligands SPh[−] and CO attach to the Co atom from the other side with Co—S and Co—C distances of 2.302 and 1.741 Å, respectively. The coordination

* Lists of anisotropic thermal parameters, full atomic distances and bond angles, H-atom positional parameters, and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55338 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ASI001]

geometry of the title compound, being similar to that of [Co(dppep)(SPh)₂] (Wei, Hong, Huang & Liu, 1991) is a distorted trigonal bipyramid with a five-coordinate Co atom.

The mean Co—P distance (2.160 Å) in the title compound is significantly shorter than that of 2.345 (6) Å in [Co(dppp)(SPh)₂] [dppp = Ph₂P(CH₂)₃PPh₂] or 2.237 (5) Å in [Co(dppep)(SPh)₂] (Wei, Hong, Huang & Liu, 1991). The Co—S distance in the title compound (2.302 Å) is slightly longer than the mean Co—S distance of 2.256 Å found in [Co(dppep)(SPh)₂].

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Structure du Trihydrogène Hydroxy-1 Ethanedi(phosphonate)-1,1 de Strontium Tétrahydrate

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Abstract. Bis[trihydrogen 1-hydroxy-1,1-ethanediyl-bis(phosphinato)(1-)]strontium tetrahydrate, [Sr(C₂H₇O₇P₂)₂].4H₂O, *M*_r = 569.72, monoclinic, C2/c, *a* = 18.411 (9), *b* = 12.769 (6), *c* = 8.323 (5) Å, β = 100.72 (6)°, *V* = 1922 (25) Å³, *Z* = 4, *D*_m = 1.95, *D*_x = 1.969 Mg m⁻³, λ(Cu Kα) = 1.5418 Å, μ = 7.97 mm⁻¹, *F*(000) = 1152, room temperature, *R* = 0.049 for 1006 independent reflections. The Sr atom is eightfold coordinated to two monodentate and two tridentate hdp⁻ ligands. The structure is made up of chains of edge-sharing SrO₈ polyhedra along the [001] direction. These chains are linked together through hydrogen bonds involving the water molecules.

Introduction. Ce travail entre dans le cadre d'une étude structurale systématique des complexes susceptibles de se former entre cations métalliques et acides organophosphorés à fonction hydroxydiphosphonique.†

Partie expérimentale. Le complexe [Sr{C(CH₃)(OH)(P₂O₆H₃)₂}.4H₂O est obtenu sous forme de monocristaux prismatiques incolores par évaporation lente à température ambiante d'une solution aqueuse résultant de l'attaque de carbonate de strontium par l'acide hydroxyéthylidenediphosphonique (HEDP)

† Etude intégrée dans une Action de Recherche Coordonnée pluridisciplinaire soutenue par le PIRSEM-CNRS et l'AFME portant sur la synthèse et la mise au point de nouveaux extractants hydroxydiphosphonés à hautes performances.

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