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Bis[tricarbonyl(triisopropyl phosphite)-cobalt](*Co*—*Co*) Dichloromethane Solvate

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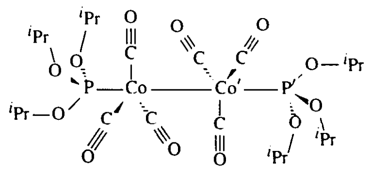
Abstract

The complex of the title compound, $[Co_2(CO)_6(C_9H_{21}O_3P)_2].CH_2Cl_2$, lies about an inversion centre and displays trigonal bipyramidal coordination geometry about each Co atom, with axial phosphite ligands *trans* to the Co—Co bond. The Co—Co bond length of 2.6544 (12) Å in this structure is shorter than Co—Co bond lengths reported for analogous phosphine complexes.

Comment

The $\sigma \rightarrow \sigma^*$ transition in dimetallic carbonyl complexes containing unsupported metal–metal bonds occurs in the visible or near-UV region of the spectrum and provides a quantitative measure of the strength of the metal–metal interaction in these complexes (Levenson, Gray & Ceasar, 1970; Levenson & Gray, 1975; Abrahamson *et al.*, 1977). We have obtained more data for the energies of the $\sigma \rightarrow \sigma^*$ transition in the metal–metal-bonded complexes $[Mn_2(CO)_8L_2]$ and $[Co_2(CO)_6L_2]$ (L is a P-donor ligand) and it is clear that the trends cannot be accounted for on the basis of σ-donicity, π-acidity and steric effects, as had been concluded on the basis of the less complete data. To gain more insight into the metal–metal interactions in these complexes, we undertook the crystal structure determination of the complex $[Co_2(CO)_6\{P(O^iPr)_3\}_2]$, (1).



(1)

The title complex possesses a crystallographically imposed centre of inversion halfway along the Co—Co bond. Each Co atom has the same slightly distorted trigonal bipyramidal arrangement with three carbonyl ligands in the equatorial plane, an axial Co atom and an axial phosphite ligand. The angles subtended at the Co atom in the equatorial plane range from 118.8 (2) to 120.7 (2)°, with the sum of the three angles being 358.9 (1)°. The axial P—Co—Co′ angle is 177.00 (6)°. The presence of the inversion centre at the midpoint of the Co—Co bond ensures that the carbonyl groups attached to the Co atoms adopt a fully staggered conformation. All the carbonyl groups are essentially linear [Co—C—O angles are statistically equivalent with an average value of 176.7 (6)°]. The three O atoms in each phosphite ligand are disordered, each appearing in two positions with site occupancies of 0.5. All distances and angles associated with the phosphite ligands are normal (Allen *et al.*, 1987). The asymmetric unit contains one-half of a disordered dichloromethane solvent molecule. The presence of CH_2Cl_2 is consistent with the ^1H NMR spectrum of a solution of the crystals in $CDCl_3$.

The most interesting feature of the structure is the presence of a non-bridged metal–metal bond. Selected geometric parameters for the complexes $[Co_2(CO)_6L_2]$ are presented in Table 3, where L = $P(O^iPr)_3$ (1), $P(^nBu)_3$ (Ibers, 1968), PMe_3 (Jones, Seeberger, Stuart, Whittlesey & Wright, 1986) and $PPh_2[C_2(Me_2As)(CF_2)_2]$ (Einstein & Kirkland, 1978). The Co—Co and Co—P distances in the three previously reported phosphine structures are equivalent for each type and average 2.666 (2) and 2.175 (1) Å, respectively. The Co—Co bond length in (1), 2.6544 (12) Å, is significantly shorter (9σ) than the values observed in the phosphine-substituted Co—Co dimeric complexes. The

Co—P bond distance in (1) is also less than the average value reported for the phosphine complexes. The Co—Co bond distance reported for the parent cobalt dimer $Co_2(CO)_8$ is 2.524 (2) Å; however, the Co—Co bond in the unsubstituted molecule is supported by two bridging carbonyl ligands (Summer, Klug & Alexander, 1964).

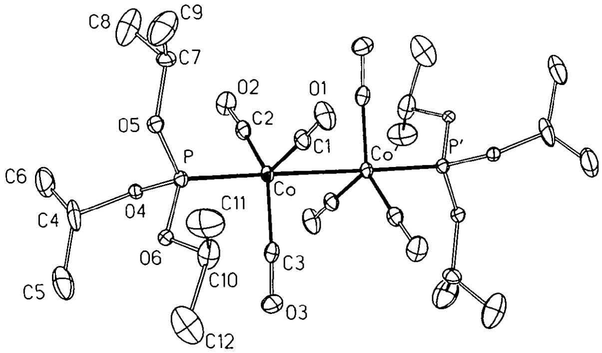


Fig. 1. View of title molecule with the crystallographic numbering scheme and displacement ellipsoids drawn at the 25% probability level. For clarity, H atoms are omitted and disorder is not shown.

Experimental

Complex (1) was synthesized according to the method of Manning (1968) and crystals were grown from a CH_2Cl_2/hexanes mixture.

Crystal data

$[Co_2(CO)_6(C_9H_{21}O_3P)_2]$.-$CH_2Cl_2$
$M_r = 787.34$
Monoclinic
$P2_1/c$
$a = 9.992$ (1) Å
$b = 13.743$ (2) Å
$c = 14.885$ (2) Å
$\beta = 91.35$ (1)°
$V = 2043.4$ (7) Å^3
$Z = 2$
$D_x = 1.280$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 24 reflections
$\theta = 5.0$–20.5°
$\mu = 1.067$ mm^{-1}
$T = 173$ (2) K
Flat plate
0.25 × 0.15 × 0.10 mm
Dark brown

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: seven azimuthal scans (Sheldrick, 1990)
$T_{min} = 0.410$, $T_{max} = 0.553$
4304 measured reflections
4138 independent reflections

2091 observed reflections [$I > 2\sigma(I)$]
$R_{int} = 0.0475$
$\theta_{max} = 26.28°$
$h = -12 \rightarrow 12$
$k = 0 \rightarrow 17$
$l = -18 \rightarrow 0$
2 standard reflections
frequency: 120 min
intensity decay: < 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0472$
$wR(F^2) = 0.1070$
$S = 1.093$
4137 reflections
251 parameters
H atoms refined as riding (C—H 0.96 Å)

$w = 1/[\sigma^2(F_o^2) + (0.0541P)^2 + 1.4036P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.005$
$\Delta\rho_{max} = 0.461$ e Å^{-3}
$\Delta\rho_{min} = -0.401$ e Å^{-3}
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Co	0.07300 (5)	0.00579 (5)	0.07546 (3)	0.0239 (2)
C1	0.1407 (6)	0.1146 (4)	0.0329 (3)	0.0326 (14)
O1	0.1871 (4)	0.1859 (3)	0.0080 (3)	0.0546 (12)
C2	−0.0813 (4)	0.0107 (4)	0.1313 (3)	0.0314 (10)
O2	−0.1777 (3)	0.0153 (3)	0.1713 (2)	0.0521 (10)
C3	0.1422 (6)	−0.1072 (4)	0.0433 (3)	0.0334 (14)
O3	0.1925 (4)	−0.1798 (3)	0.0262 (3)	0.0520 (12)
P	0.18482 (10)	0.00870 (10)	0.19944 (7)	0.0243 (3)
O4†	0.1219 (8)	−0.0648 (6)	0.2694 (6)	0.023 (2)
O4'†	0.1786 (9)	−0.0881 (6)	0.2522 (6)	0.028 (2)
C4	0.2116 (7)	−0.0951 (4)	0.3503 (4)	0.063 (2)
C5	0.2871 (7)	−0.1898 (5)	0.3451 (4)	0.079 (2)
C6	0.0993 (8)	−0.1013 (5)	0.4160 (4)	0.082 (2)
O5†	0.2105 (8)	0.1091 (5)	0.2477 (5)	0.026 (2)
O5'†	0.1339 (9)	0.0829 (5)	0.2743 (5)	0.036 (2)
C7	0.0962 (6)	0.1823 (4)	0.2565 (4)	0.047 (2)
C8	−0.0017 (8)	0.1824 (6)	0.3289 (4)	0.099 (3)
C9	0.1869 (8)	0.2667 (5)	0.2605 (5)	0.096 (3)
O6†	0.3357 (7)	−0.0311 (5)	0.1972 (5)	0.023 (2)
O6'†	0.3354 (7)	0.0417 (7)	0.1997 (5)	0.044 (2)
C10	0.4290 (5)	0.0062 (6)	0.1270 (3)	0.058 (2)
C11	0.5073 (7)	0.0974 (5)	0.1348 (5)	0.088 (3)
C12	0.5152 (7)	−0.0828 (5)	0.1352 (5)	0.086 (3)
C13†	0.461 (4)	0.457 (2)	0.003 (4)	0.145 (19)
Cl1†	0.366 (3)	0.487 (5)	0.086 (2)	0.40 (3)
Cl2†	0.414 (5)	0.394 (3)	−0.010 (4)	0.42 (3)
Cl3†	0.472 (4)	0.565 (3)	0.065 (2)	0.32 (3)

† Disordered (see text).

Table 2. *Selected geometric parameters* (Å, °)

Co—C1	1.766 (5)	C3—O3	1.149 (6)
Co—C2	1.770 (5)	P—O4'	1.547 (9)
Co—C3	1.770 (6)	P—O6'	1.571 (7)
Co—P	2.1350 (12)	P—O5	1.574 (7)
Co—Co^i	2.6544 (12)	P—O4	1.591 (9)
C1—O1	1.149 (6)	P—O5'	1.603 (7)
C2—O2	1.146 (5)	P—O6	1.605 (7)
C1—Co—C2	118.8 (2)	C2—Co—Co^i	86.09 (13)
C1—Co—C3	119.4 (2)	C3—Co—Co^i	85.9 (2)
C2—Co—C3	120.7 (2)	P—Co—Co^i	177.00 (6)
C1—Co—P	95.6 (2)	O1—C1—Co	177.6 (5)
C2—Co—P	92.16 (13)	O2—C2—Co	176.5 (4)
C3—Co—P	92.9 (2)	O3—C3—Co	176.1 (5)
C1—Co—Co^i	87.4 (2)		

Symmetry code: (i) $-x, -y, -z$.

Table 3. *Selected geometric parameters* (Å, °) *for the complexes* $[Co_2(CO)_6L_2]$

L	Co—Co	Co—P	Co—C	Co—Co—P
$P(O^iPr)_3$[a]	2.6544 (12)	2.1350 (12)	1.769 (2)[b]	177.00 (6)
$P(^nBu)_3$[c]	2.665 (14)	2.178 (15)	1.75 (3)	180
PMe_3[d]	2.669 (1)	2.175 (1)	1.772 (3)	180
PPh_2R[e]	2.663 (2)	2.173 (2)	1.767 (3)[b]	177.6 (2)

Notes: (*a*) this work; (*b*) average of equivalent values; (*c*) Ibers (1968); (*d*) Jones *et al.* (1986); (*e*) $R = C_2(Me_2As)(CF_2)_2$, Einstein & Kirkland (1978).

Space group $P2_1/c$ for (1) was determined by the unique systematic absences ($h0l$ absent if $l = 2n + 1$, $0k0$ absent if $k = 2n + 1$). The shape of the anisotropic displacement ellipsoids of the phosphite O atoms suggested the presence of disorder. A difference map showed maxima in positions consistent with an equal disordering of the phosphite atoms O4, O5 and O6, associated with a slight rotation of the ligand O atoms around the P—Co vector. A view of the phosphite ligand down the P—Co vector showing the positions of the six half O atoms has been deposited as supplementary material. The ^{i}Pr groups of the phosphite ligand are ordered. The unit cell was also found to contain two CH_2Cl_2 solvent molecules disordered around inversion centres. A disorder model was used to account for the electron density in these regions of the unit cell. An electron density map showing the positions of the atoms of the solvent molecule, C13 (multiplicity 0.5), Cl1 (0.667), Cl2 (0.667) and Cl3 (0.667), has also been deposited as supplementary material.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CAD*-4 *Software*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL*93.

This research was supported by NSERC, Canada, and the University of Toronto.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, together with a view of the phosphite ligand down the P—Co vector and an electron density map showing the positions of the atoms of the solvent molecule, have been deposited with the IUCr (Reference: FG1073). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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$(CuX)_n$ Helical Chains in $[Pt(S_2CNEt_2)_2Cu_2X_2]$ (X = Br, Cl)

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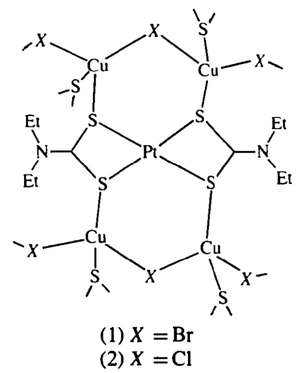
Abstract

In poly[di-μ-bromo-bis(μ_3-N,N-diethyldithiocarbamato)-dicopper(I)platinum(II)], $[Pt(S_2CNEt_2)_2Cu_2Br_2]$, and poly[di-$\mu$-chloro-bis($\mu_3$-$N$,$N$-diethyldithiocarbamato)-dicopper(I)platinum(II)], $[Pt(S_2CNEt_2)_2Cu_2Cl_2]$, a helical chain of $(CuX)_n$ (X = Br, Cl) extends around a 4_1 axis and each $Pt(S_2CNEt_2)_2$ group links two of the helical chains with its four S atoms. Each Cu atom is surrounded by two S and two halogen atoms and has slightly distorted tetrahedral coordination geometry.

Comment

Dithiocarbamato complexes form various types of adducts with copper(I) halides because the bonding capacities of the S atoms are not otherwise fully saturated. $Co(S_2CNR_2)_3$ has three possible interligand S–S chelating sites and reacts with CuBr or CuI utilizing these three chelating sites to give heterobimetallic adducts of 1:1, 1:2 and 1:3 stoichiometries: *e.g.* $[Co\{S_2CN(CH_2)_4\}_3(CuBr)]$ (Engelhardt, Healy, Papasergio & White, 1985), $[Co(S_2CNPr_2)_3(CuI)]$ (Engelhardt, Healy, Skelton & White, 1988), $[Co(S_2CNEt_2)_3(CuBr)_2].2CH_3CN$ and $[Co\{S_2CN(CH_2)_4\}_3(CuI)_3]$ (Engelhardt, Healy, Shephard, Skelton & White, 1988). These mixed-metal complexes have either discrete or one- or three-dimensional polymeric structures in the solid state. We report here the interesting structures of $[Pt(S_2CNEt_2)_2Cu_2Br_2]_n$, (1), and $[Pt(S_2CNEt_2)_2Cu_2Cl_2]_n$, (2), constructed from planar



(1) X = Br
(2) X = Cl

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