nent. However, such a description of this molecule and of other π-cyclic organometallic complexes is of dubious value, because of the limitations of the formal concepts of coordination number and oxidation state.

Registry No. $[(C_4(CH_3)_4)CF_3Pt(P(CH_3)_2C_6H_5)_2]SbF_6$, 39526-70-0.

Acknowledgment. We thank the National Research Council of Canada for financial support of this work.

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Trigonal-Bipyramidal and Square-Pyramidal Five-Coordinate Cobalt(II). Crystal and Molecular Structures of the Red and Green Isomers of Chlorobis[1,2-bis(diphenylphosphino)ethane]cobalt(II) Trichlorostannate(II)[1]

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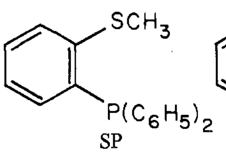
Received October 20, 1972

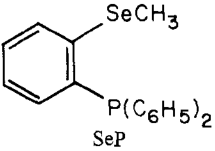
The crystal and molecular structures of two low-spin five-coordinate cobalt(II) complexes containing the same set of donor atoms have been determined from three-dimensional X-ray data collected by counter methods. The red complex [Co(dpe)$_2$Cl]SnCl$_3$ (dpe = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$) crystallizes in space group $C_{2h}{}^5$-$P2_1/c$ of the monoclinic system, with four formula units in a cell of dimensions a = 17.727 (7), b = 16.431 (6), and c = 19.741 (8) Å; β = 122.13 (1)°. The observed and calculated densities are 1.51 and 1.520 g/cm^3, respectively. The green complex [Co(dpe)$_2$Cl]SnCl$_3\cdot C_6H_5Cl$ crystallizes in space group $C_i{}^1$-$P\bar{1}$ of the triclinic system, with two formula units in a cell of dimensions a = 11.781 (11), b = 12.846 (12), and c = 19.893 (19) Å; α = 106.38 (2), β = 93.76 (2), and γ = 101.81 (2)°. The observed and calculated densities are 1.47 and 1.456 g/cm^3, respectively. The structures of both the red and the green complexes have been refined by least-squares techniques to final R factors on F of 0.065 for the red complex and 0.101 for the green complex. The structures both consist of discrete five-coordinate cations and pyramidal SnCl$_3^-$ anions. The difference in color can be ascribed to a difference in the stereochemistry of the cation: the red complex is a tetragonal pyramid with an apical Cl atom and four P atoms in the basal plane, whereas the green complex is based on the trigonal-bipyramidal geometry with two P atoms at the axial positions and two P atoms and one Cl atom in the equatorial plane. Distortions from the two idealized geometries can be attributed to the 81-83° bite of the diphosphine ligand. The Co-Cl distance of 2.398 (2) Å in the tetragonal pyramid is 0.15 Å longer than that in the trigonal bipyramid of 2.251 (5) Å. The average Co-P distances are 2.276 and 2.258 Å in the red and green forms, respectively. The SnCl$_3^-$ anion is pyramidal in both complexes. In organic solvents there is an equilibrium between the red and green forms, with the green form predominating. It is suggested that the interconversion of forms takes place through a four-coordinate intermediate involving rupture of a Co-P bond.

Introduction

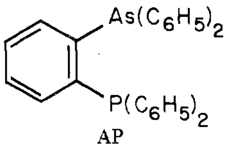
There have been several reports of low-spin five-coordinate cobalt(II) complexes of the type [CoL$_2$X]Y, where L is a neutral bidentate ligand and X a coordinating anion. Dyer and Meek[3] prepared several complexes of this type where L = AP, X = Cl, Br, I, Y = SnX$_3$, ClO$_4$; L = SP, SeP, X = Br, Y = ClO$_4$. All these complexes formed by ligands with *o*-phenylene linkages exhibit a deep red color and have been formulated as square-pyramidal Co(II) complexes.[3] When L = *cis*-1,2-bis(diphenylphosphino)ethylene, a ligand which has steric requirements similar to those of SP, SeP, and AP, a series of dark green complexes has been isolated for X = Cl, Br, I, NCS, Y = B(C$_6$H$_5$)$_4$; X = Cl, Y = SnCl$_3$; and X = NCS, Y = Co(NCS)$_4$.[4] And when L = 1,2-bis(diphenylphosphino)ethane (dpe), Sacco and Gorieri[5] have reported a series of red or orange compounds where X = NO$_3$, Y = NO$_3$, B(C$_6$H$_5$)$_4$; X = I, Y = NO$_3$, I, ClO$_4$, B(C$_6$H$_5$)$_4$; and X = NCS, Y = NCS, ClO$_4$; and a series of green compounds where X = Br, Y = Br, ClO$_4$; X = NCS, Y = Co(NCS)$_4$; and X = Cl, Y = CoCl$_4$. The dark green complex [Co(dpe)$_2$Br]Br had previously been reported by Chatt, *et al.*[6] Horrocks, VanHecke, and Hall also assigned a square-pyramidal geometry to the green series [Co(dpe)$_2$X]X (X = Cl, Br, I) on the basis of the electronic spectra and detailed esr results.[7]



SP



SeP



AP

Several new complexes of empirical composition Co(dpe)$_2\cdot$SnX$_4$ (X = Cl, Br, I) have been isolated from nonaqueous solutions containing a mixture of a cobalt(II) halide, the corresponding stannous halide, and the diphosphine ligand.[4] For the bromide and chloride cases, either a deep red or a deep green crystalline material of identical composition can be isolated depending on the solvent, temperature, and isolation procedures. The analytical, conductance, magnetic, and electronic spectral data indicate that both the red and green series are low-spin, five-coordinate cobalt(II) complexes. The magnetic moments (μ_{eff} = 2.03-2.14 BM) of the red series are somewhat higher than those of the green series (μ_{eff} = 1.89-1.97 BM).[4] However, both ranges are consistent with the values reported previously for five-coordinate cobalt(II) complexes.[3,8] The electronic spectra

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[1] Presented in part at the Symposium on Five-Coordinate Complexes at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971; see Abstracts, No. INORG 96.

[2] Ohio State University Postdoctoral Fellow, July-Dec 1970; Postdoctoral Research Associate, Jan 1971-Sept 1972.

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[5] A. Sacco and F. Gorieri, *Gazz. Chim. Ital.*, 687 (1963).

[6] J. Chatt, F. A. Hart, and D. T. Rosevear, *J. Chem. Soc.*, 5504 (1961).

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[8] L. Sacconi, *J. Chem. Soc. A*, 248 (1970).

of the corresponding red and green complexes in the solid state give the same number of absorption peaks at similar positions. The only significant difference in the spectra of the two series is the greater relative intensity in the bands at ~15,000 cm^{-1} for the green isomer. Both the red and green forms of these complexes convert rapidly (immediately on dissolving) to an equilibrium mixture (predominantly the green form) in all common organic solvents. Three logical possibilities could be proposed to account for the difference in the magnetic and spectral properties of the crystalline compounds: (1) coordination isomerization, *e.g.*, $[\text{Co(dpe)}_2\text{X}]\text{SnX}_3$ and $[\text{Co(dpe)}_2\text{SnX}_3]\text{X}$, (2) bridging halide ligands in the solid state, or (3) different structures for the five-coordinate cations. The $^{119\text{m}}$Sn Mossbauer spectra helped eliminate the possibilities of coordination isomerization and bridging halides;[9] consequently, the X-ray crystal structures of $[\text{Co(dpe)}_2\text{Cl}]\text{SnCl}_3$ (**1**, red) and $[\text{Co(dpe)}_2\text{Cl}]\cdot\text{SnCl}_3\cdot\text{C}_6\text{H}_5\text{Cl}$ (**2**, green) were determined. A preliminary account of this work has appeared.[10]

Experimental Section

$[\text{Co(dpe)}_2\text{Cl}]\text{SnCl}_3$ (1, Red). Unit Cell and Space Group. Crystals of the red form of $[\text{Co(dpe)}_2\text{Cl}]\text{SnCl}_3$ were readily obtained upon mixing stoichiometric amounts of $\text{CoCl}_2\cdot6\text{H}_2\text{O}$ (0.24 g, 1 mmol), $\text{SnCl}_2\cdot2\text{H}_2\text{O}$ (0.23 g, 1 mmol), and dpe (0.81 g, 2 mmol) in 50 ml of boiling 1-butanol. Red crystals immediately precipitated from the dark olive green solution; however, several crystals examined using X-ray and optical means exhibited twinning to mimic orthorhombic symmetry. A large twinned crystal was cleaved, and preliminary precession photographs of the $h0l$, $h1l$, $h2l$, and $hk\bar{h}$ nets indicated monoclinic symmetry with systematic absences for $h0l$, $l \neq 2n$, and $0k0$, $k \neq 2n$, characteristic of space group $C_{2h}{}^5$-$P2_1/c$. The cell dimensions, obtained with Mo Kα_1 radiation (λ 0.70926 Å) at 23° (see below) are $a = 17.727$ (7), $b = 16.431$ (6), and $c = 19.741$ (8) Å; $\beta = 122.13$ (1)°. The calculated density of 1.520 g/cm^3 for four formula units in the unit cell agrees well with the observed value of 1.51 g/cm^3 obtained by flotation in CCl_4–hexane solutions.

Collection and Reduction of Intensity Data. The crystal used for data collection was obtained from a batch containing predominantly green crystals prepared using *o*-dichlorobenzene and ethanol as solvents. An apparently untwinned red crystal of dimensions 0.28 × 0.26 × 0.17 mm in the $[1\bar{1}0]$, [110], and [001] directions, respectively, was mounted on a glass fiber on a eucentric goniometer head and shown to have the same monoclinic symmetry as the fragment used for the space group determination. The crystal was aligned on a Picker FACS-III four-circle diffractometer in conjunction with an EMR Advance 6130 computer control, with the $[1\bar{1}0]$ direction approximately coincident with the diffractometer ϕ axis. The crystal orientation matrix and unit cell parameters were obtained from a least-squares refinement of the setting angles of 18 carefully centered reflections.[11]

Mo Kα radiation was selected for data collection with a graphite monochromator crystal. The data were collected by the θ–2θ scan technique at a takeoff angle of 2.9°. The diffracted beams were counted using a scintillation counter which was placed 22 cm from the crystal and had an aperture of 4.0 × 4.0 mm; when necessary the diffracted beams were attenuated with brass foil to prevent coincidence losses. The pulse height analyzer was set to admit approximately 98% of the maximum intensity of a Mo Kα_1 peak at full window width. A symmetrical scan range of 1.5° about the Kα_1 peak was used at a scan rate of 2.0°/min. Stationary-crystal, stationary-counter background counts of 10 sec were taken at each end of the scan.

A unique data set was initially collected to $\lambda^{-1}\sin\theta = 0.5$, followed by a second shell to $\lambda^{-1}\sin\theta = 0.53$ which still exhibited significant scattering. A second form was then collected to $\lambda^{-1}\sin\theta = 0.53$, followed by the collection of a third shell (both forms) to $\lambda^{-1}\sin\theta = 0.59$. Since relatively few reflections with intensities above background were observed in this shell, data collection was terminated. Eighteen reflections were monitored as standards after every 500 reflections had been processed; all decreased slightly, and nearly linearly with crystal exposure time, in intensity throughout the data collection process. The average total intensity loss was 5%, and the data were corrected for this apparent decomposition. The data were then corrected for background and standard deviations were assigned to the intensities.[12a] A factor $(pI)^2$ was added to the estimated variances of each intensity, I, in an effort to allow for cumulative systematic errors.[12b] A value of 0.05 for p was chosen in the present case. The data were also corrected for Lorentz and polarization effects. A gaussian integration absorption correction was applied,[13] using a calculated absorption coefficient of 12.54 cm^{-1}; transmission coefficients ranged from 0.71 to 0.82. In all, 17,413 reflections were observed; the two equivalent forms collected were averaged to yield 8407 independent observations. Only the 5705 reflections for which $F_o{}^2 \geqslant 3\sigma(F_o{}^2)$ were used in the solution and refinement of the structure.

Solution of the Structure. The structure was solved by the usual combination of Patterson, Fourier, and least-squares methods.[14] One Cl atom and the Sn and Co atoms were found to have $y \simeq {}^1/_4$ from the Patterson function, resulting in a pseudomirror plane at $y = {}^1/_4$; in addition, the four P atoms are symmetrically located above and below this pseudomirror. This led to two possible positions for the Sn and Co atoms, at x, y, z or at $x, y, z + {}^1/_4$. Least-squares refinements of the two solutions led to R_1 values of 0.54 and 0.52 and R_2 values of 0.61 and 0.58, respectively, where $R_1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2)^{1/2}$. In these and succeeding refinements the function $\Sigma w(|F_o| - |F_c|)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and where the weights, w, were taken as $4F_o{}^2/\sigma^2(F_o{}^2)$. The atomic scattering factors for Sn were those of Cromer and Waber,[15] while the usual tabulation was used for Co, Cl, P, and C.[16] The scattering factors for H were from the calculations of Stewart, *et al.*[17] The values of the anomalous terms $\Delta f'$ and $\Delta f''$ were taken from Cromer[18] and were included in F_c.[19]

A difference Fourier map based on the refinement of the Co and Sn atomic positions which resulted in the lower R values clearly indicated the Cl and P atoms. The methylene and phenyl carbon atoms were readily located in a like manner. These were included in two cycles of full-matrix isotropic least-squares refinement, treating the phenyl rings as rigid groups[20] of known geometry and dimension (D_{6h} symmetry, C–C = 1.392 Å) with individual isotropic thermal parameters assigned to group carbon atoms. This was followed by three cycles of refinement with anisotropic thermal parameters assigned to all nongroup atoms, resulting in values of R_1 and R_2 of 0.072 and 0.095. A difference map using only the reflections for which $\lambda^{-1}\sin\theta < 0.35$ gave reasonable positions for all hydrogen atoms. These positions were idealized, assuming C–H = 1.09 Å, H–C–H = 109° 28′ for the methylene hydrogens and C–H = 1.0 Å, C–C–H = 120° for the phenyl group hydrogens; each hydrogen atom was assigned an isotropic thermal parameter corresponding to that of the carbon atom to which it is bonded. The H atom scattering was added as a fixed contribution to the calculated structure factors, and two further cycles of anisotropic refinement reduced the values of R_1 and R_2 to 0.065 and 0.082, respectively. An analysis of $|F_o|$ and $|F_c|$ as a function of scattering angle, magnitude of $|F_o|$, and

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(10) J. K. Stalick, P. W. R. Corfield, and D. W. Meek, *J. Amer. Chem. Soc.*, 94, 6194 (1972).

(11) The following programs by P. W. R. Corfield and G. J. Gainsford were used with the EMR computer: COZLS, for least-squares determination of cell parameters; ASSET, for automatic collection of intensity data; PLPIC, for Lorentz and polarization corrections; PICABS, for gaussian integration absorption corrections; MERGE, for data averaging; and FOUR and FPRNT, for Patterson and Fourier syntheses.

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(14) Programs used in the structure solutions and refinements with the IBM 370/165 computer included local versions of the Busing-Levy ORFFE error function program, Johnson's ORTEP plotting program, Zalkin's FORDAP Fourier program, and the Ibers-Doedens group least-squares program.

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Table I. Final Atomic and Group Parameters

[Co(dpe)$_2$Cl]SnCl$_3$ (1-red)

Atom[a]	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sn	0.26439(5)[b]	0.24259(4)	0.14202(4)	0.00722(4)	0.00420(3)	0.00458(3)	-0.00090(3)	0.00395(3)	-0.00085(2)
Co	0.26736(5)	0.76103(5)	0.27869(4)	0.00232(4)	0.00204(3)	0.00164(3)	-0.00011(3)	0.00066(3)	-0.00004(2)
Cl(1)	0.27620(12)	0.76079(12)	0.40421(9)	0.00428(9)	0.00459(8)	0.00214(5)	0.00047(7)	0.00158(6)	0.00027(5)
Cl(2)	0.10511(22)	0.27205(24)	0.06706(18)	0.00645(16)	0.00911(19)	0.00482(11)	-0.00171(14)	0.00049(11)	0.00127(12)
Cl(3)	0.26381(19)	0.17091(14)	0.25031(15)	0.00728(15)	0.00426(9)	0.00465(9)	-0.00019(9)	0.00293(10)	0.00100(7)
Cl(4)	0.30556(19)	0.37419(13)	0.21061(14)	0.00754(14)	0.00334(8)	0.00456(9)	-0.00075(9)	0.00253(10)	-0.00037(7)
P(1)	0.37670(12)	0.66524(10)	0.31718(10)	0.00301(8)	0.00206(6)	0.00210(6)	0.00016(5)	0.00078(6)	-0.00004(4)
P(2)	0.17755(12)	0.65119(10)	0.23153(10)	0.00304(8)	0.00254(6)	0.00225(6)	-0.00070(6)	0.00087(6)	-0.00009(5)
P(3)	0.15965(11)	0.85894(11)	0.23185(10)	0.00246(7)	0.00266(6)	0.00245(6)	0.00022(5)	0.00083(6)	0.00006(5)
P(4)	0.35599(11)	0.87176(9)	0.30571(9)	0.00249(7)	0.00213(6)	0.00196(5)	-0.00011(5)	0.00079(5)	-0.00021(4)
C(1)	0.3304(6)	0.5632(4)	0.3136(5)	0.0045(4)	0.0023(3)	0.0034(3)	-0.0004(3)	0.0008(3)	0.0003(2)
C(2)	0.2401(6)	0.5705(4)	0.3043(5)	0.0047(4)	0.0027(3)	0.0031(3)	-0.0007(3)	0.0011(3)	0.0007(2)
C(3)	0.2107(5)	0.9431(4)	0.3031(4)	0.0032(3)	0.0031(3)	0.0032(3)	0.0005(2)	0.0013(3)	-0.0007(2)
C(4)	0.3083(5)	0.9556(4)	0.3334(4)	0.0035(3)	0.0029(3)	0.0031(3)	-0.0000(2)	0.0014(3)	-0.0012(2)

Group[c]	x_c	y_c	z_c	δ	ϵ	η	B_1, Å^2	B_2, Å^2	B_3, Å^2	B_4, Å^2	B_5, Å^2	B_6, Å^2
Ring 1	0.4418(3)	0.6679(2)	0.1925(2)	1.876(12)	-1.844(3)	0.869(13)	3.2(1)	3.9(1)	4.8(2)	6.3(2)	5.9(2)	4.8(2)
Ring 2	0.5484(2)	0.6593(2)	0.4974(2)	1.480(4)	2.470(3)	1.863(4)	2.9(1)	4.2(1)	5.0(2)	5.1(2)	4.6(2)	3.6(1)
Ring 3	-0.0175(3)	0.6428(2)	0.2032(2)	-1.541(4)	2.732(3)	1.357(4)	3.3(1)	6.0(2)	6.4(2)	5.2(2)	4.8(2)	4.0(1)
Ring 4	0.1503(3)	0.5816(2)	0.0675(2)	-0.314(10)	-1.950(3)	1.616(10)	3.1(1)	4.7(2)	5.9(2)	5.7(2)	5.6(2)	4.2(1)
Ring 5	-0.0248(3)	0.8561(3)	0.2267(3)	-1.615(5)	2.579(3)	1.324(5)	3.7(1)	5.5(2)	7.1(3)	6.7(2)	6.2(2)	5.0(2)
Ring 6	0.1101(2)	0.9256(2)	0.0597(2)	-2.549(8)	-1.948(3)	-0.623(8)	3.1(1)	4.1(1)	5.2(2)	5.2(2)	4.8(2)	4.2(1)
Ring 7	0.3545(2)	0.9384(2)	0.1515(2)	3.182(10)	-1.914(3)	-1.152(10)	3.0(1)	3.3(1)	4.7(2)	5.7(2)	5.6(2)	3.9(1)
Ring 8	0.5599(2)	0.8833(2)	0.4522(2)	1.652(3)	2.799(2)	-1.385(3)	2.7(1)	3.5(1)	4.4(2)	4.7(2)	4.4(2)	3.6(1)

[Co(dpe)$_2$Cl]SnCl$_3$·C$_6$H$_5$Cl (2-green)

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sn	-0.0572(2)	0.0954(2)	0.0662(1)	0.0264(4)	0.0228(3)	0.0059(1)	0.0165(3)	0.0090(1)	0.0062(1)
Co	0.4579(2)	0.1628(2)	0.3142(1)	0.0033(2)	0.0049(2)	0.0017(1)	-0.0002(1)	0.0005(1)	0.0006(1)
Cl(1)	0.4870(4)	0.2220(4)	0.4331(2)	0.0060(4)	0.0084(4)	0.0018(1)	0.0000(3)	0.0005(2)	0.0007(2)
Cl(2)	-0.2666(11)	0.0511(11)	0.0272(4)	0.0331(17)	0.0347(16)	0.0042(3)	0.0237(15)	-0.0052(6)	-0.0031(5)
Cl(3)	-0.0861(6)	-0.0223(6)	0.1430(4)	0.0114(7)	0.0162(7)	0.0070(3)	0.0052(6)	0.0011(4)	0.0044(4)
Cl(4)	-0.0526(6)	0.2644(7)	0.1606(4)	0.0113(7)	0.0216(9)	0.0050(2)	0.0055(6)	0.0020(3)	0.0044(4)
P(1)	0.3411(4)	0.0000(4)	0.2456(2)	0.0045(4)	0.0046(3)	0.0023(1)	0.0000(3)	0.0004(2)	0.0006(2)
P(2)	0.2873(4)	0.2158(4)	0.3110(2)	0.0039(4)	0.0055(4)	0.0024(1)	0.0009(3)	0.0010(2)	0.0010(2)
P(3)	0.5368(4)	0.2514(4)	0.2384(2)	0.0044(4)	0.0060(4)	0.0023(1)	0.0004(3)	0.0010(2)	0.0011(2)
P(4)	0.6273(4)	0.1072(4)	0.3095(2)	0.0049(4)	0.0057(4)	0.0025(2)	0.0004(3)	0.0010(2)	0.0011(2)
C(1)	0.2297(15)	0.0337(14)	0.1908(8)	0.0055(16)	0.0065(16)	0.0018(5)	0.0001(13)	-0.0004(8)	-0.0011(7)
C(2)	0.2110(14)	0.1497(15)	0.2210(9)	0.0030(14)	0.0097(19)	0.0030(6)	0.0011(13)	0.0012(8)	0.0026(9)
C(3)	0.6232(17)	0.1631(15)	0.1853(9)	0.0088(19)	0.0080(16)	0.0023(6)	0.0011(15)	0.0021(9)	0.0012(8)
C(4)	0.6582(13)	0.0782(13)	0.2194(8)	0.0031(14)	0.0065(14)	0.0021(5)	0.0027(11)	0.0014(7)	0.0009(7)

Group	x_c	y_c	z_c	δ	ϵ	η	B_1 or B, Å^2	B_2, Å^2	B_3, Å^2	B_4, Å^2	B_5, Å^2	B_6, Å^2
Ring 1	0.4365(8)	-0.1894(7)	0.1374(5)	0.524(13)	-2.392(7)	-1.334(12)	3.9(4)	4.5(4)	6.3(5)	7.7(6)	6.0(5)	4.7(4)
Ring 2	0.1869(8)	-0.1377(7)	0.3331(5)	-0.784(10)	2.520(6)	-1.760(11)	3.6(4)	5.0(4)	6.5(5)	5.5(5)	5.0(4)	3.7(4)
Ring 3	0.2976(8)	0.4774(7)	0.3481(4)	3.090(8)	2.929(8)	-0.748(9)	3.5(4)	4.2(4)	5.7(5)	6.0(5)	5.8(5)	4.4(4)
Ring 4	0.1025(7)	0.1354(6)	0.4089(4)	-1.065(10)	2.401(6)	-1.630(11)	2.9(3)	3.8(4)	5.4(5)	5.2(4)	4.7(4)	4.0(4)
Ring 5	0.3843(8)	0.3238(8)	0.1263(5)	-2.363(11)	-2.544(8)	2.192(11)	3.5(4)	4.8(4)	6.1(5)	8.0(6)	6.8(6)	4.7(4)
Ring 6	0.7331(8)	0.4748(7)	0.3186(5)	2.243(9)	2.747(7)	-1.546(9)	3.7(4)	4.7(4)	6.2(5)	6.2(5)	5.2(5)	4.0(4)
Ring 7	0.8573(7)	0.2830(7)	0.4018(4)	2.005(9)	2.689(6)	-1.501(9)	3.5(3)	4.1(4)	5.6(5)	5.8(5)	4.8(4)	4.3(4)
Ring 8	0.6384(8)	-0.1154(8)	0.3511(5)	0.017(9)	2.917(8)	2.118(9)	3.9(4)	4.9(4)	7.0(6)	6.8(6)	7.1(6)	4.5(4)
C$_6$H$_5$Cl	0.2433(16)	0.3970(15)	-0.1043(9)	-1.715(11)	2.913(9)	0.219(24)	19.4(5)					

[a] x, y, and z are fractional coordinates. The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant digits. [c] x_c, y_c, and z_c are the fractional coordinates of the phenyl ring centers. The angles δ, ϵ, and η (in radians) which bring about alignment (except for translation) of an internal coordinate system within the ring with a fixed external coordinate system are those previously described.[20] B_i is the isotropic thermal parameter of atom i in a given ring. The rings are numbered so that C(1) is attached to P; C(4) is para to C(1). The chlorobenzene molecule of structure 2 was refined with a single-group temperature factor, B.

Miller indices indicated that reflections with low values of λ^{-1} sin θ were being slightly overweighted. An empirical correction was applied to the weights, and one final cycle of refinement with 223 variables and 5705 observations gave values of R_1 and R_2 of 0.065 and 0.078. The error in an observation of unit weight was 1.02, and the maximum parameter shift was 0.25σ, which was associated with one of the rigid groups. A final difference Fourier synthesis showed one peak greater than 1.0 e/Å^3 (an average carbon atom peak was 2.4 e/Å^3) of 3.4 e/Å^3 located 1.4 Å away from the Sn atom toward Cl(2). We can offer no definitive explanation for this peak.

Table I presents the final positional, thermal, and group parameters, along with the corresponding standard deviations. Table II gives the positional parameters for the group carbon atoms which may be derived from the data in Table I. The final values of $|F_o|$ and $|F_c|$ (in electrons) are presented in Table IIIA for those reflections used in the refinements.[21]

[Co(dpe)$_2$Cl]SnCl$_3$·C$_6$H$_5$Cl (2, Green). Unit Cell and Space Group. Stoichiometric amounts of CoCl$_2$·6H$_2$O (0.24 g, 1 mmol) and SnCl$_2$·2H$_2$O (0.23 g, 1 mmol) were dissolved in 20 ml of ethanol and added to a solution of dpe (0.8 g, 2 mmol) in 30 ml of chlorobenzene. The resulting dark olive green solution was flushed with nitrogen gas, stoppered, and allowed to stand at room temperature. After several days a few very large olive green crystals were collected. Small fragments exhibited a characteristic red-green pleiochroism and under polarized light appeared alternately red and green as the stage was rotated 90°. Elemental analyses indicated the presence of 1 mol of chlorobenzene per mole of [Co(dpe)$_2$Cl]SnCl$_3$.

A large crystal was cleaved to give a needlelike fragment of dimensions 0.05 × 0.07 × 0.19 mm. The fragment was mounted on a glass fiber parallel to the needle axis, and preliminary precession and Weissenberg photographs failed to yield any special symmetry or systematic absences. Space group C_i^1-$P\bar{1}$ of the triclinic system was assumed and was confirmed by subsequent solution of the structure. Cell dimensions of a = 11.781 (11), b = 12.846 (12), and c = 19.893 (19) Å; α = 106.38 (2), β = 93.76 (2), and γ = 101.81 (2)° (temperature 24°) were obtained by a least-squares refinement of the setting angles of 18 centered reflections using a Picker four-circle diffractometer and Mo Kα_1 radiation.[11] The [100] direction was assigned to be nearly coincident with the diffractometer ϕ axis. The calculated density of 1.456 g/cm^3 for two molecules of complex and two molecules of chlorobenzene in the unit cell agrees well with the

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[21] Tables IIIA and IIIB, listings of observed and calculated structure factor amplitudes for 1 and 2, will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-1668.

Table II. Derived Parameters for Group Carbon Atoms[a]

	1-red			2-green		
Atom	x	y	z	x	y	z
			Ring 1			
C(1)	0.4178(3)	0.6610(3)	0.2491(3)	0.4550(11)	0.2936(10)	0.1729(6)
C(2)	0.4706(11)	0.7257(6)	2.2530(7)	0.4295(20)	0.3983(13)	0.1928(7)
C(3)	0.4946(12)	0.7326(8)	0.1965(7)	0.3588(16)	0.4285(13)	0.1462(5)
C(4)	0.4658(4)	0.6746(4)	0.1362(3)	0.3136(14)	0.3539(11)	0.0797(7)
C(5)	0.4130(12)	0.6099(6)	0.1324(7)	0.3392(21)	0.2493(13)	0.0598(8)
C(6)	0.3890(12)	0.6031(8)	0.1888(7)	0.4099(15)	0.2191(11)	0.1064(5)
			Ring 2			
C(1)	0.4760(2)	0.6652(3)	0.4191(2)	0.6452(10)	0.3807(9)	0.2835(5)
C(2)	0.4626(3)	0.6452(5)	0.4804(3)	0.7193(12)	0.4333(11)	0.2452(5)
C(3)	0.5349(4)	0.6393(4)	0.5588(2)	0.8072(13)	0.5274(12)	0.2802(7)
C(4)	0.6208(3)	0.6533(4)	0.5758(2)	0.8210(11)	0.5689(10)	0.3536(7)
C(5)	0.6342(2)	0.6733(5)	0.5145(3)	0.7470(12)	0.5164(11)	0.3919(5)
C(6)	0.5618(3)	0.6793(3)	0.4362(2)	0.6591(12)	0.4222(11)	0.3569(5)
			Ring 3			
C(1)	0.0676(3)	0.6452(3)	0.2159(3)	0.2915(10)	0.3635(7)	0.3322(6)
C(2)	0.0569(3)	0.6296(5)	0.2795(2)	0.2182(10)	0.4021(10)	0.2921(6)
C(3)	-0.0282(4)	0.6273(4)	0.2670(3)	0.2243(12)	0.5160(11)	0.3080(7)
C(4)	-0.1024(3)	0.6405(4)	0.1908(4)	0.3038(13)	0.5913(7)	0.3640(8)
C(5)	-0.0917(3)	0.6561(5)	0.1271(3)	0.3771(11)	0.5526(10)	0.4040(6)
C(6)	-0.0066(3)	0.6584(3)	0.1397(3)	0.3710(11)	0.4388(11)	0.3881(6)
			Ring 4			
C(1)	0.1605(3)	0.6115(3)	0.1380(2)	0.1811(8)	0.1701(9)	0.3660(5)
C(2)	0.1287(9)	0.5329(4)	0.1126(5)	0.0767(10)	0.0922(11)	0.3357(4)
C(3)	0.1184(11)	0.5029(4)	0.0422(6)	-0.0020(10)	0.0575(14)	0.3787(6)
C(4)	0.1399(5)	0.5516(3)	-0.0028(3)	0.0238(10)	0.1006(11)	0.4519(6)
C(5)	0.1717(9)	0.6302(4)	0.0225(5)	0.1283(11)	0.1786(12)	0.4821(4)
C(6)	0.1820(11)	0.6602(4)	0.0929(6)	0.2069(10)	0.2133(13)	0.4391(5)
			Ring 5			
C(1)	0.0535(3)	0.8528(4)	0.2265(3)	0.4550(10)	0.2936(11)	0.1729(6)
C(2)	0.0550(4)	0.8351(5)	0.2962(3)	0.4295(14)	0.3983(9)	0.1928(5)
C(3)	-0.0233(5)	0.8383(5)	0.2965(3)	0.3588(18)	0.4285(11)	0.1462(8)
C(4)	-0.1031(4)	0.8594(5)	0.2271(4)	0.3136(13)	0.3539(14)	0.0797(7)
C(5)	-0.1047(3)	0.8771(6)	0.1574(3)	0.3392(15)	0.2493(11)	0.0598(5)
C(6)	-0.0264(4)	0.8739(4)	0.1571(3)	0.4099(17)	0.2191(9)	0.1064(7)
			Ring 6			
C(1)	0.1290(3)	0.8998(3)	0.1344(2)	0.6452(10)	0.3807(9)	0.2835(6)
C(2)	0.0898(9)	0.8464(3)	0.0697(4)	0.7193(12)	0.4333(11)	0.2452(5)
C(3)	0.0707(8)	0.8723(4)	-0.0049(3)	0.8072(13)	0.5274(12)	0.2802(7)
C(4)	0.0908(4)	0.9516(3)	-0.0150(2)	0.8210(11)	0.5689(10)	0.3536(7)
C(5)	0.1300(9)	1.0049(3)	0.0497(4)	0.7470(12)	0.5164(10)	0.3919(5)
C(6)	0.1491(8)	0.9790(4)	0.1244(3)	0.6591(12)	0.4222(11)	0.3569(6)
			Ring 7			
C(1)	0.3556(3)	0.9099(3)	0.2185(2)	0.7579(9)	0.2059(9)	0.3620(5)
C(2)	0.3252(12)	0.8599(4)	0.1520(5)	0.8463(11)	0.2514(10)	0.3283(4)
C(3)	0.3241(10)	0.8883(5)	0.0850(4)	0.9456(10)	0.3284(12)	0.3681(6)
C(4)	0.3533(4)	0.9668(3)	0.0846(3)	0.9566(9)	0.3600(10)	0.4416(6)
C(5)	0.3837(12)	1.0168(4)	0.1511(6)	0.8683(11)	0.3145(11)	0.4752(4)
C(6)	0.3849(10)	0.9884(4)	0.2180(5)	0.7689(10)	0.2375(12)	0.4355(6)
			Ring 8			
C(1)	0.4730(2)	0.8769(3)	0.3870(2)	0.6364(12)	-0.0174(8)	0.3347(6)
C(2)	0.5417(3)	0.8955(3)	0.3751(2)	0.5822(13)	-0.0387(11)	0.3911(6)
C(3)	0.6287(3)	0.9020(4)	0.4404(3)	0.5843(13)	-0.1368(13)	0.4075(7)
C(4)	0.6471(2)	0.8899(3)	0.5175(2)	0.6405(15)	-0.2135(10)	0.3675(8)
C(5)	0.5783(3)	0.8712(3)	0.5294(2)	0.6946(15)	-0.1922(11)	0.3111(8)
C(6)	0.4913(3)	0.8647(3)	0.4641(3)	0.6926(11)	-0.0941(12)	0.2547(6)
			Chlorobenzene			
Cl				0.2434(16)	0.3970(15)	-0.1043(9)
C(1)				0.1000(15)	0.3924(14)	-0.0955(7)
C(2)				0.0317(19)	0.3030(20)	-0.0793(17)
C(3)				-0.0857(19)	0.2993(29)	-0.0721(20)
C(4)				-0.1347(17)	0.3850(34)	-0.0811(17)
C(5)				-0.0664(23)	0.4744(32)	-0.0973(20)
C(6)				0.0510(21)	0.4782(23)	-0.1045(17)

[a] Estimated standard deviations are derived from those of the group parameters. Intra-ring distances are fixed (C–C = 1.392 Å).

observed value of 1.47 g/cm^3 obtained by flotation in CCl_4-hexane solutions.

Collection and Reduction of Intensity Data. A unique data set to $\lambda^{-1} \sin \theta = 0.50$ was collected using the θ-2θ scan technique and Mo Kα radiation (graphite monochromator) at a takeoff angle of 3.0°. A symmetrical scan range of 2.0° about the Kα_1 peak was used at a scan rate of 2.0°/min. Stationary-crystal, stationary-counter background counts of 10 sec were taken at each end of the scan. The scintillation counter had an aperture of 6.5 × 6.5 mm and was placed 25 cm from the crystal. The diffracted beams were attenuated with brass foil when necessary to prevent coincidence losses.

The intensities of 18 reflections were monitored as standards throughout the data collection process. Although all reflections remained centered in the scan range, intensity losses of 0–20% were observed (very strong reflections remained essentially constant, weaker reflections exhibited marked intensity losses). The average intensity loss of 10% was corrected for as a function of crystal X-ray exposure time, and the data were corrected for background, with standard deviations assigned as in the red compound. Of the 5868 independent reflections collected, only the 3481 for which $F_o^2 \geq 3\sigma(F_o^2)$ were used in the solution and refinement of the structure. The data were corrected for Lorentz and polarization effects. A gaussian integration absorption correction ($\mu = 11.43$ cm^{-1}) was applied,[13] and transmission coefficients ranged from 0.84 to 0.91.

Solution of the Structure. The structure was solved using the usual combination of Patterson, least-squares, and difference Fourier methods.[14] The Patterson function was readily deconvoluted to give the positions of the Sn, Co, four P, and one Cl atoms. Two difference Fourier maps interspersed with least-squares refinements located the three Cl atoms bonded to the Sn atom and all C atoms, with the exception of those in the chlorobenzene solvent molecule. This model was refined assigning anisotropic thermal parameters to all nongroup atoms and treating the phenyl rings as rigid groups of known geometry and dimensions (D_{6h} symmetry, C–C = 1.392 Å) with individual isotropic thermal parameters for each group carbon atom, resulting in values of R_1 and R_2 of 0.137 and 0.165, respectively. A difference Fourier synthesis clearly indicated the position of the solvent chlorobenzene molecule, and this was included in three cycles of least-squares refinement treating the chlorobenzene molecule as a rigid group (C–C = 1.392 Å, C–Cl = 1.70 Å)[22] with a single group temperature factor, reducing R_1 and R_2 to 0.110 and 0.133. The temperature factor for the chlorobenzene ring was quite high (B = 18.6 (4) Å^2), indicating a probable disorder of the solvent molecule. However, no distinct alternate positions for the chlorobenzene could be located on a difference Fourier map, and refinement of the occupancy parameter of the group did not significantly improve the agreement factors or temperature factor. The positions of all hydrogen atoms in the cation were found on a difference Fourier map, and these were idealized to fit the known geometry (C–H = 1.0 Å for the phenyl rings; for the methylene hydrogens, C–H = 1.09 Å, H–C–H = 109° 28′). Each hydrogen atom was assigned an isotropic thermal parameter corresponding to that of the carbon atom to which it is bonded, and two cycles of least-squares refinement were carried out including the hydrogen atom scattering as a fixed contribution to the calculated structure factors. The values of R_1 and R_2 were reduced to 0.102 and 0.123. An analysis of the weighting scheme as a function of magnitude of $|F_o|$, $\lambda^{-1} \sin \theta$, and Miller indices indicated that (1) the value of 0.05 chosen for p in the assignment of standard deviations was reasonable and (2) reflections at low values of $\lambda^{-1} \sin \theta$ were being overweighted slightly. An empirical correction was applied to the weights, and two final cycles of least-squares refinement using 3481 observations and 230 variables resulted in final values of R_1 and R_2 of 0.101 and 0.121. The error in an observation of unit weight was 1.03 and the maximum parameter shift was $^1/_6\sigma$. A final difference Fourier map showed no peaks greater than 1.0 e/Å^3 except in the area of the solvent chlorobenzene molecule and $SnCl_3^-$ group located nearby. These peaks ranged from 1.23 to 1.86 e/Å^3, compared to an average value of 2.9 for a carbon atom, and gave no good indications of alternate chlorobenzene group positions.

The final positional, thermal, and group parameters, along with their standard deviations, are presented in Table I. Table II gives the derived positional parameters for the group atoms. The final values of $|F_o|$ and $|F_c|$ (in electrons) are presented in Table IIIB for those reflections used in the refinements.[21]

Description of the Structures

The crystal structure of $[Co(dpe)_2Cl]SnCl_3$ (**1**, red) consists of discrete, well-separated $[Co(dpe)_2Cl]^+$ cations and $SnCl_3^-$ anions. The shortest Co–Co, Sn–Sn, and Co–Sn distances are 11.4, 9.9, and 7.6 Å, respectively, indicating that there are no metal–metal interactions, either direct or indirect through bridging groups. All intermolecular contacts are normal, with the closest approaches of phenyl ring hydrogen atoms between adjacent molecules being 2.16 and 2.19 Å. A stereoscopic view of the unit cell is presented in Figure 1.

The structure of $[Co(dpe)_2Cl]SnCl_3 \cdot C_6H_5Cl$ (**2**, green) also is composed of discrete $[Co(dpe)_2Cl]^+$ cations and $SnCl_3^-$ anions, in addition to having a molecule of chlorobenzene located in a large hole in the packing structure near the $SnCl_3^-$ anion. The Co–Co and Co–Sn distances of 9.49 and 7.31 Å are again long enough to rule out metal–metal interactions; however, the $SnCl_3^-$ group is located near a center of symmetry in the unit cell leading to a short Sn–Sn distance of 3.597 (4) Å (see below). The closest H–H interactions are 2.34 and 2.35 Å between phenyl ring hydrogen atoms on adjacent molecules, and all intermolecular contacts appear normal. Figure 2 presents a stereoscopic view of the unit cell.

The Molecular Structure of the $[Co(dpe)_2Cl]^+$ Cation in $[Co(dpe)_2Cl]SnCl_3$ (1, Red). The structure of the $[Co(dpe)_2Cl]^+$ cation is shown in Figure 3; Figure 4 presents a view of the inner coordination sphere about the Co atom, including selected bond lengths. Relevant interatomic bond lengths and angles are presented in Table IV. It can be seen

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(22) *Chem. Soc., Spec. Publ.*, No. 11, S14 (1958).

Table IV. Selected Interatomic Distances and Angles for the $[Co(dpe)_2Cl]^+$ Cation in $[Co(dpe)_2Cl]SnCl_3$ (**1**, Red) and $[Co(dpe)_2Cl]SnCl_3 \cdot C_6H_5Cl$ (**2**, Green)

Atoms	Distance, Å 1-red	 2-green
Co-Cl(1)	2.398(2)	2.251(5)
Co-P(1)	2.291(2)	2.258(5)
Co-P(2)	2.254(2)	2.252(5)
Co-P(3)	2.283(2)	2.268(5)
Co-P(4)	2.274(2)	2.253(6)
P(1)-C(1)	1.853(7)	1.846(19)
P(1)-R1C(1)[a]	1.839(7)	1.818(13)
P(1)-R2C(1)	1.839(3)	1.819(13)
P(2)-C(2)	1.832(7)	1.831(19)
P(2)-R3C(1)	1.806(6)	1.813(11)
P(2)-R4C(1)	1.826(6)	1.829(12)
P(3)-C(3)	1.833(7)	1.838(19)
P(3)-R5C(1)	1.831(7)	1.827(10)
P(3)-R6C(1)	1.827(5)	1.836(15)
P(4)-C(4)	1.844(7)	1.802(15)
P(4)-R7C(1)	1.829(6)	1.820(10)
P(4)-R8C(1)	1.828(3)	1.827(14)
C(1)-C(2)	1.513(12)	1.510(25)
C(3)-C(4)	1.513(10)	1.544(25)

Atoms	Angle, deg 1-red	 2-green
Cl(1)-Co-P(1)	94.47(7)	126.1(2)
Cl(1)-Co-P(2)	93.96(7)	92.1(2)
Cl(1)-Co-P(3)	90.04(7)	128.1(2)
Cl(1)-Co-P(4)	95.85(7)	91.7(2)
P(1)-Co-P(2)	82.77(7)	81.0(2)
P(1)-Co-P(3)	175.33(9)	105.7(2)
P(1)-Co-P(4)	96.58(7)	97.1(2)
P(2)-Co-P(3)	98.16(8)	96.2(2)
P(2)-Co-P(4)	170.19(7)	176.2(2)
P(3)-Co-P(4)	81.71(7)	81.2(2)
Co-P(1)-C(1)	109.1(3)	107.6(6)
Co-P(1)-R1C(1)	112.2(2)	124.5(4)
Co-P(1)-R2C(1)	120.8(2)	112.9(4)
C(1)-P(1)-R1C(1)	106.2(4)	104.1(7)
C(1)-P(1)-R2C(1)	101.0(3)	104.3(7)
R1C(1)-P(1)-R2C(1)	106.2(2)	101.6(6)
Co-P(2)-C(2)	104.8(2)	107.0(6)
Co-P(2)-R3C(1)	125.1(2)	118.5(4)
Co-P(2)-R4C(1)	113.9(2)	117.4(5)
C(2)-P(2)-R3C(1)	104.0(4)	106.8(8)
C(2)-P(2)-R4C(1)	103.8(3)	103.4(7)
R3C(1)-P(2)-R4C(1)	102.9(3)	102.3(6)
Co-P(3)-C(3)	104.8(2)	107.5(6)
Co-P(3)-R5C(1)	126.7(2)	125.9(4)
Co-P(3)-R6C(1)	113.7(2)	112.8(4)
C(3)-P(3)-R5C(1)	99.1(4)	103.5(8)
C(3)-P(3)-R6C(1)	106.2(3)	103.3(7)
R5C(1)-P(3)-R6C(1)	103.8(2)	101.6(6)
Co-P(4)-C(4)	107.4(2)	107.6(5)
Co-P(4)-R7C(1)	113.4(1)	117.5(4)
Co-P(4)-R8C(1)	124.2(2)	118.6(5)
C(4)-P(4)-R7C(1)	104.3(3)	105.1(6)
C(4)-P(4)-R8C(1)	101.1(2)	105.8(7)
R7C(1)-P(4)-R8C(1)	104.2(2)	100.9(6)
P(1)-C(1)-C(2)	110.7(5)	113.7(11)
P(2)-C(2)-C(1)	108.2(5)	111.2(12)
P(3)-C(3)-C(4)	113.4(5)	113.7(11)
P(4)-C(4)-C(3)	113.1(4)	110.9(10)

[a] RiC(1) refers to carbon atom 1 on phenyl ring *i*.

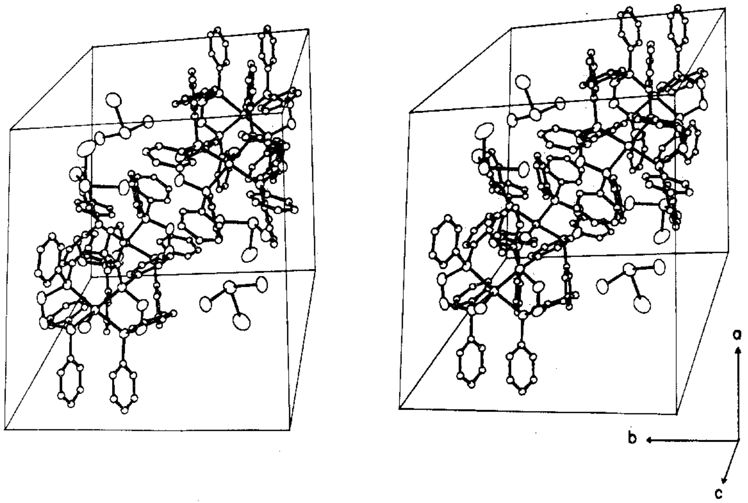

Figure 1. A stereoscopic view of the unit cell of $[Co(dpe)_2Cl]SnCl_3$ (**1**, red). For the sake of clarity hydrogen atoms have been omitted and phenyl ring carbon atoms have been drawn artificially small in this and subsequent figures. All atoms refined anisotropically are shown at 50% electron probability.

that the five-coordinate cation possesses a tetragonal pyramidal geometry, with the four P atoms in the basal plane and the Cl atom occupying the apical position. The cation, including the phenyl rings, has approximate C_{2v} symmetry as shown in the figures. The tetragonal pyramid is slightly distorted owing to the steric requirements of the diphosphine ligand (Table IV). As expected, the Co atom lies 0.141 Å above the plane of the four P atoms, with Cl-Co-P angles ranging from 90.04 to 95.85 (7)°. The Co-Cl(1) distance of 2.398 (2) Å is longer than might be expected from the sum of the covalent radii of 2.3 Å, as is usually the case for apical bonds in a square-pyramidal complex.[23] In the structure of another low-spin $[CoP_4Cl]^+$ complex, $[Co(QP)Cl]B(C_6H_5)_4$ (QP = tris(*o*-diphenylphosphinophenyl)phosphine), Blundell and Powell reported a Co-Cl distance of 2.309 (6) Å, where the Cl atom lies in the axial position of a distorted trigonal bipyramid.[24] The Co-Cl(1) distance is also 0.15 Å longer than that found in the corresponding green cation (see below). The possible sixth coordination site is effectively blocked by the phenyl rings, with the two shortest H atom distances from the Co atom being 2.97 and 2.98 Å to the ortho hydrogen atoms of rings 4 and 7, respectively.

The diphosphine ligands are almost symmetric in their coordination, the Co-P distances ranging from 2.254 to 2.291 (2) Å. The average bond length of 2.276 Å is longer than that usually found with monodentate ligands; for example, distances of 2.18-2.23 (1) Å were reported for the Co-P bonds in $Co(HP(C_6H_5)_2)_3Br_2$,[25] and a value of 2.232 (4) Å was found in *trans*-$[Co(mesityl)_2(P(C_2H_5)_2(C_6H_5))_2]$.[26] With polydentate phosphine ligands, a much wider range of

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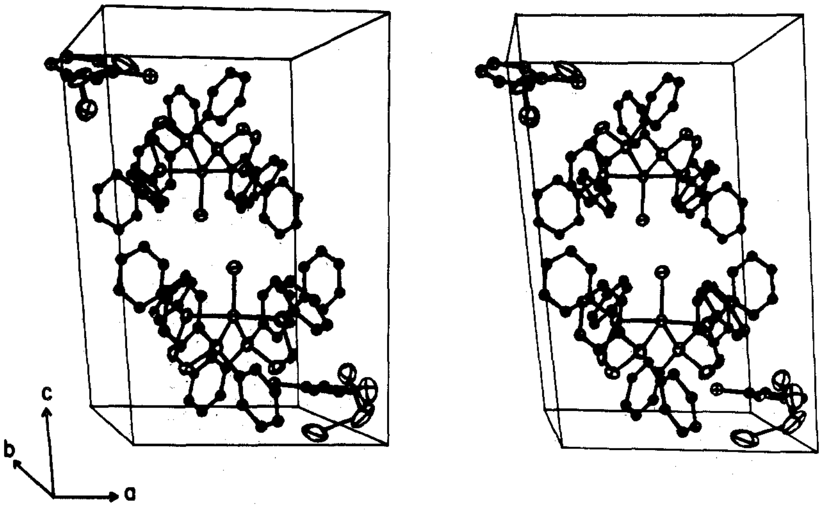
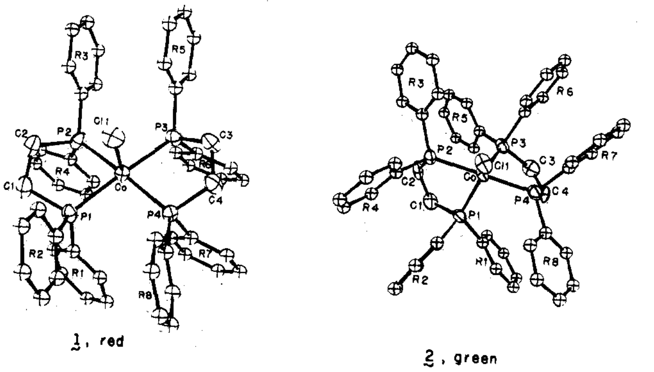


Figure 2. A stereoscopic view of the unit cell of $[Co(dpe)_2Cl]SnCl_3 \cdot C_6H_5Cl$ (2, green). The atoms of the chlorobenzene ring as well as those of the phenyl rings have been drawn artificially small.



1, red

2, green

Figure 3. Perspective views of the $[Co(dpe)_2Cl]^+$ cations in $[Co(dpe)_2Cl]SnCl_3$ (1, red) and $[Co(dpe)_2Cl]SnCl_3 \cdot C_6H_5Cl$ (2, green).

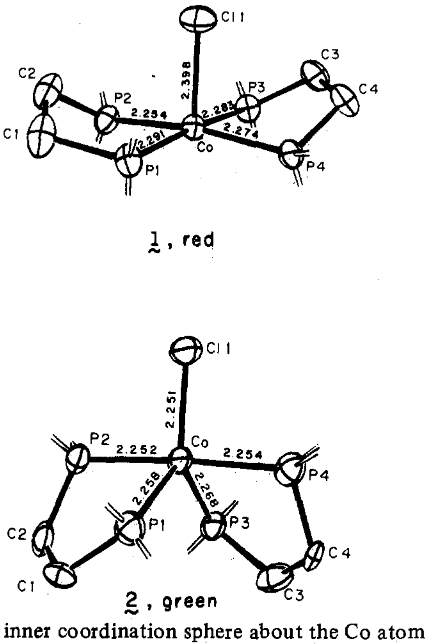


Figure 4. The inner coordination sphere about the Co atom in $[Co(dpe)_2Cl]SnCl_3$ (1, red) and $[Co(dpe)_2Cl]SnCl_3 \cdot C_6H_5Cl$ (2, green).

bond lengths is observed owing to steric requirements of the ligands (*e.g.*, 2.057-2.318 (4) Å in $[Co(QP)Cl]B(C_6H_5)_4$[24] and 2.229-2.279 (8) Å in $[Co(N(CH_2CH_2P(C_6H_5)_2)_3)I]I$[27]). The P-Co-P angles are 82.77 (7) and 81.71 (7)°, similar to the mean value of 82.7° found in $[Rh(dpe)_2]ClO_4$,[28] but less than the 88.8 (1)° found for π-$(CH_2C(CH_3)CH_2)Ni(dpe)Br$[29] and those values found for several other dpe complexes.[30-33]

The P-C and C-C bond distances appear normal for dpe complexes, with average values of 1.840 Å for P-C(alkyl), 1.828 Å for P-C(aryl), and 1.513 Å for C-C. The C-P-C angles average 103.6°, less than the tetrahedral value of 109.45°, as has been previously noted.[34] The average Co-P-C(alkyl) angle is 106.5°, while the Co-P-C(aryl) angles average 118.8°, much greater than the tetrahedral value. The average P-C-C angle is 111.4°.

The Molecular Structure of the $[Co(dpe)_2Cl]^+$ Cation in $[Co(dpe)_2Cl]SnCl_3 \cdot C_6H_5Cl$ (2, Green). The $[Co(dpe)_2Cl]^+$ cation structure in the green complex is shown in Figure 3; Figure 4 presents a view of the inner coordination sphere about the Co atom, including selected bond distances. Other pertinent bond lengths and angles are given in Table IV. The geometry about the Co atom can best be described as a distorted trigonal bipyramid, with two P atoms axial and two P atoms and the Cl atom occupying the equatorial plane. The cation has approximate C_2 symmetry as is evident from Figure 3. There are two major distortions from the ideal D_{3h} symmetry: (1) a 10° tilt of the equatorial plane to accommodate the 81° bite of the diphosphine ligand and (2) angular deviations from threefold symmetry in the equatorial plane, with Cl-Co-P angles of 126.1 (2) and 128.1 (2)° and a P-Co-P angle of 105.7 (2)°. The latter type of distortion has usually been found for trigonal-bipyramidal, low-spin, five-coordinate Co(II) complexes[24,25] and has been attributed to Jahn-Teller effects. The degeneracy of the d_{xy} and $d_{x^2-y^2}$ energy levels can be removed by distorting the threefold axis of the trigonal plane. However, steric factors may be important in this case; there are several close contacts between the equatorial Cl(1) and phenyl H atoms on the same molecule,

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with six Cl(1)-H distances ranging from 2.66 to 2.79 Å (the sum of the van der Waals radii for Cl and H is 3.0 Å). This could result in the increase of the Cl-Co-P angles from the trigonal value of 120° to the angles of 126.1 (2) and 128.1 (2)° that are observed. The tilt of the equatorial plane imposed by the chelating diphosphines can be described as a rotation of the plane about the Co-Cl(1) bond. The P(2)-Co-P(4) (axial) angle of 176.2 (2)° remains nearly linear, and the P(2)-P(4) vector makes an angle of 80.2° with the Co-Cl(1)-P(1)-P(3) equatorial plane. (The Co, Cl(1), P(1), and P(3) atoms are coplanar, with the Co atom 0.001 (5) Å from the plane being the largest deviation.) The Co-Cl(1) distance of 2.251 (5) Å is 0.15 Å shorter than the apical Co-Cl(1) bond in **1**. It is also 0.06 Å shorter than the Co-Cl bond in [Co(QP)Cl]-$B(C_6H_5)_4$,[24] the only other low-spin five-coordinate cobalt(II) complex containing a Cl atom to be studied, but this difference may result from steric effects as QP is a bulky, rigid, tetradentate ligand. The Co-P bond lengths show less variation than in **1**, having a range of 2.252-2.268 (5) Å, and the average Co-P distance of 2.258 Å is 0.02 Å shorter. This could indicate that the distorted trigonal-bipyramidal geometry is sterically more favorable than the tetragonal-pyramidal one (see below). The P-C and C-C bond lengths are within experimental error the same as found for **1**, with average distances P-C(alkyl) = 1.83 Å, P-C(aryl) = 1.82 Å, and C-C = 1.53 Å. The angles about phosphorus are also comparable, with average values of C-P-C = 103.6°, Co-P-C(alkyl) = 107.4°, and Co-P-C(aryl) = 118.5°. The average P-C-C angle is 112.4°.

Conformations of the Five-Membered Rings. The conformations of the five-membered chelate rings in both red and green cations are described in the data presented in Table V. In all four chelate rings the two carbon atoms lie on the same side of the plane formed by the corresponding Co and P atoms, as was found for π-$(CH_2C(CH_3)CH_2)$Ni-(dpe)Br.[29] The torsion angles for the C-C bonds in three of the rings are very similar, with values of 11.0, 9.4, and 10.7°. These small values reflect the partial eclipsing of the P-C bonds in the five-membered ring that occurs when the carbon atoms are both displaced fairly symmetrically on the same side of P-Co-P plane. The chelate ring formed by atoms Co, P(1), C(1), C(2), and P(2) in the red cation has a different conformation from the others, the C-C torsional angle being 41.7°, and this is related to the unsymmetrical displacement of C(1) and C(2) from the P(1)-Co-P(2) plane. The difference in this chelate ring relative to the other three rings extends to some of the bond angles. Thus the P-C-C angles in the unique ring are 110.7 and 108.2°, compared with an average of 112.7° in the other three rings, and the angle at Co in the unique ring is 82.8° compared with an average of 81.3° in the other rings. The reason for the buckling of one of the chelate rings is not clear to us, as there do not appear to be any abnormally short intramolecular or intermolecular contacts involving this ring.

The $SnCl_3^-$ Anions. The $SnCl_3^-$ anions in both **1** and **2** possess a pyramidal geometry, as shown in Figure 5, where the 50% electron probability ellipsoids are drawn. It can be seen that in the $SnCl_3^-$ anion in $[Co(dpe)_2Cl]SnCl_3$ (**1**, red) the Sn atom thermal ellipsoid is fairly isotropic, with the anisotropic thermal ellipsoids of the Cl atoms vibrating perpendicular to the Sn-Cl bonds. The thermal motion in the $SnCl_3^-$ group in $[Co(dpe)_2Cl]SnCl_3 \cdot C_6H_5Cl$ (**2**, green) is much more pronounced and could well indicate a degree of disorder. This $SnCl_3^-$ group is located near the partially disordered chlorobenzene molecule (Figure 2); it is clear that this area of the structure is not as well defined as the structure of the cation or of the $SnCl_3^-$ group in **1**.

Table V. Conformation of the Chelate Rings

Distances from P-Co-P Planes

Plane	Atom	Distance, Å 1, red	 2, green
P(1)-Co-P(2)	C(1)	0.48	−0.99
	C(2)	1.04	−1.11
P(3)-Co-P(4)	C(3)	1.11	−0.96
	C(4)	0.99	−1.09

Torsion Angles about C-C Bonds

Atoms	Angle, deg 1, red	 2, green
C(1)-C(2)	41.71	9.4
C(3)-C(4)	10.97	10.7

Dihedral Angles between Co-P-C Planes

Plane 1	Plane 2	Dihedral angle, deg 1, red	 2, green
Co-P(1)-C(1)	Co-P(2)-C(2)	40.56	54.4
Co-P(3)-C(3)	Co-P(4)-C(4)	53.60	53.7

Table VI. Bond Lengths and Angles for the $SnCl_3^-$ Anion

Atoms	Distance, Å 1, red	 2, green
Sn-Cl(2)	2.440 (4)	2.437 (12)
Sn-Cl(3)	2.445 (2)	2.429 (8)
Sn-Cl(4)	2.447 (2)	2.425 (8)

Atoms	Angle, deg 1, red	 2, green
Cl(2)-Sn-Cl(3)	94.79 (11)	91.4 (4)
Cl(2)-Sn-Cl(4)	93.96 (12)	96.2 (3)
Cl(3)-Sn-Cl(4)	94.64 (9)	93.5 (3)

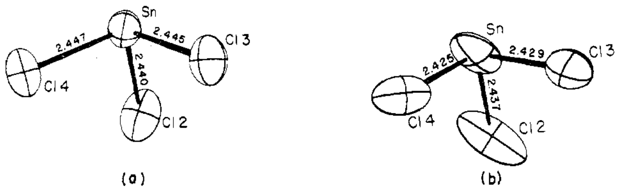

Figure 5. The $SnCl_3^-$ anions: (a) in $[Co(dpe)_2Cl]SnCl_3$ (**1**, red); (b) in $[Co(dpe)_2Cl]SnCl_3 \cdot C_6H_5Cl$ (**2**, green). The 50% probability ellipsoids are shown.

The bond lengths and angles for the two anions are presented in Table VI. The geometry of the $SnCl_3^-$ anion in **1** is obviously more regular, with a mean Sn-Cl distance of 2.444 (2) Å and a mean Cl-Sn-Cl angle of 94.46°. The anion in **2** exhibits a range of bond angles (91.4 (4)-96.2 (3)°), but the mean Cl-Sn-Cl angle of 93.7° is in qualitative agreement with that found in **1**. The Sn-Cl bond lengths are equivalent within the standard deviations given; the mean distance of 2.430 Å is within experimental error of that found in **1**. The bond lengths and angles reported here do not agree with those found in an earlier structure determination of the $SnCl_3^-$ anion in $KCl \cdot KSnCl_3 \cdot H_2O$,[35] in which mirror symmetry was imposed on the $SnCl_3^-$ group. Values of 2.63 and 2.54 Å were reported for the two independent Sn-Cl distances, and Cl-Sn-Cl angles of 87.7 and 90.8° were found. The geometry of the $SnCl_3^-$ group found in the present two structures probably resembles more closely that of the "free" anion, owing to the absence of short-range ionic interactions.

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The $SnCl_3^-$ anion in **2** is located near a center of symmetry, resulting in a short Sn–Sn distance of 3.597 (4) Å; the three Cl atoms bonded to the Sn atom are directed away from the Sn–Sn vector. It seems unlikely that there is any chemical interaction between the two adjacent $SnCl_3^-$ groups, however. The Sn–Sn distance is much larger than the sum of the covalent radii of 2.90 Å;[36] furthermore, the geometry of the $SnCl_3^-$ anion is clearly pyramidal rather than tetrahedral and closely resembles that found in **1**. The ^{119m}Sn Mossbauer parameters also indicate a similar electronic environment for the Sn atom in **1** and **2**, with IS values of 3.10 (6) and 3.08 (6) mm/sec at 77°K *vs.* a $Ba^{119m}SnO_3$ source, respectively.[9] These values lie in the range previously reported for $SnCl_3^-$ and clearly specify the tin as Sn(II).[37]

Discussion

The difference in color between **1** and **2** can be ascribed to a difference in the geometry of the $[Co(dpe)_2Cl]^+$ cations. However, it would be difficult to predict which, if either, of the two idealized configurations—the trigonal bipyramid or the square pyramid—is formed by a particular low-spin cobalt(II) complex on the basis of electronic spectra alone. The solid-state spectra of the red and green forms appear quite similar, as can be seen from Figure 6. The number of bands and their positions are comparable; only the relative intensity of the bands at ~15,000 cm^{-1}, particularly in relation to the intensity of the low-energy band at ~7000 cm^{-1}, serves to distinguish the two types of cations. (Solution spectra are not useful in this regard, owing to the red $\rightleftharpoons$ green equilibrium.) Thus while it is probable that the series of green $[CoL_2X]Y$ complexes discussed in the Introduction are based on a trigonal-bipyramidal geometry and the red $[CoL_2X]Y$ complexes on a square-pyramidal geometry, it is not at all probable that this analogy can be extended to include other classes of five-coordinate cobalt(II) complexes. The assignment of a square-pyramidal geometry to the cation in the green $[Co(dpe)_2Cl]Cl$ complex and similar $[CoL_2X]X$ compounds on the basis of esr and electronic spectra by Horrocks, *et al.*,[7] however, should be reexamined in view of the present structural evidence.

On the basis of qualitative observations it appears that the green trigonal-bipyramidal configuration is favored in these particular complexes. The solution spectra most closely resemble the solid-state spectrum of the green complex (**2**),[4] and the more regular configuration of the chelate rings in **2** also suggests less strain in the trigonal-bipyramidal cation. However, since energy differences between the two idealized geometries are small,[38] slight changes in the molecule can result in quite different geometries. For example, for the complexes $[Co(dpe)_2X]Y$, where X = Cl and Y = BF_4 or ClO_4, only the green complex is isolated.[4] That the red complex crystallizes when Y = $SnCl_3$ is probably due to favorable crystal packing forces.

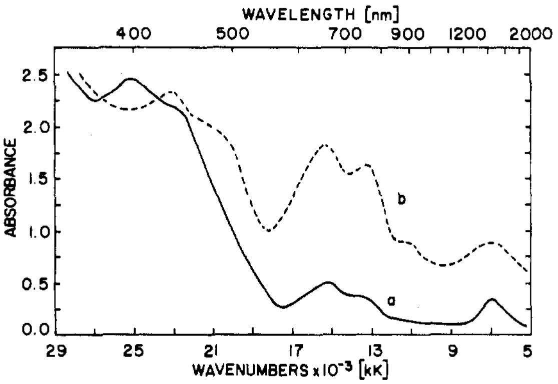

Figure 6. The solid-state electronic spectra of (a) $[Co(dpe)_2Cl]SnCl_3$ (**1**, red) and (b) $[Co(dpe)_2Cl]SnCl_3 \cdot C_6H_5Cl$ (**2**, green) at 77°K (Nujol mull).

The rapid interconversion red $\rightleftharpoons$ green (square pyramid $\rightleftharpoons$ trigonal bipyramid) could occur either by a mechanism involving internal reorganization of bonds, *e.g.*, analogous to conformational changes in a cyclopentane ring, or by the dissociation of one end of a chelating ligand followed by the formation of either the square-pyramidal or trigonal-bipyramidal cation. We favor the latter interpretation, as inspection of molecular models based on the X-ray results indicates considerable steric hindrance to reorganization. As can be seen from Figure 4, in the square pyramid (**1**, red) the diphosphine ethylene bridges are directed toward the Co–Cl bond, whereas they are directed away from this bond in the trigonal bipyramid (**2**, green). Reorganization of **1** to **2** would involve large conformational changes in the ethylene bridge, with concomitant interactions of the phenyl rings.

Not many crystal structures have been determined of five-coordinate complexes of cobalt(II), and these represent the first determinations of the two limiting stereochemistries with the same set of donor atoms. In addition, the structure of the $SnCl_3^-$ group has been determined where it functions as a discrete anion in a transition metal complex rather than as a bonded Sn(IV) ligand.

Registry No. $[Co(dpe)_2Cl]SnCl_3$, 38542-27-7; $[Co(dpe)_2Cl]SnCl_3 \cdot C_6H_5Cl$, 38721-37-8.

Acknowledgments. The authors are grateful for the financial support of the National Science Foundation (Grant GP-23204 and Equipment Grant GP-8534) and The Ohio State University Instruction and Research Computing Center. We thank Professor Derek J. Hodgson for his assistance in providing programs for use on the IBM 360 computer; the programs were converted for use on the IBM 370 computer.

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(36) A value of 1.45 Å for the Sn(II) covalent radius was calculated from the average Sn–Cl bond length.

(37) R. J. H. Clark, L. Maresca, and P. J. Smith, *J. Chem. Soc. A*, 2687 (1970), and references therein.

(38) E. L. Muetterties and R. A. Schunn, *Quart. Rev., Chem. Soc.*, 20, 245 (1966).