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Ditertiary Phosphine Complexes of Cobalt. Spectral, Magnetic, and Electron Paramagnetic Resonance Studies[1]

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Ditertiary phosphine complexes of cobalt(II) of the type $Co[(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2]_mX_2$, where for $n = 3$, $m = 1$ and X = Cl, Br, I and for $n = 2$, $m = 1, 2$, and X = Cl, Br, I, were prepared and studied by spectral and magnetic means. Evidence is presented to show that the high-spin monochelate compounds with $m = 1$ and $n = 2, 3$ involve "tetrahedral" coordination. The epr signals of the low-spin dichelate $Co[(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2]_2X_2$ complexes recorded on polycrystallizing samples show three g values. A satisfactory correlation between the measured electronic spectral, magnetic, and epr data is found. The electronic ground state is $|\overset{+}{(xy)}\overset{-}{(xy)}\overset{+}{(x^2 - y^2)}\rangle$ (vacancy configuration). The energies of the one-electron d orbitals were estimated using the observed optical data and the interelectronic interaction energies calculated for the low-spin d^7 system.

Introduction

In contrast to the large number of cobalt(II) complexes formed with tertiary phosphines that have been prepared and extensively studied,[2] few cobalt(II) complexes prepared with ditertiary phosphines have been reported. Those reported have usually not been studied very extensively. Issleib and Hohlfeld[3] reported some $Co[(C_6H_{11})_2P(CH_2)_nP(C_6H_{11})_2]X_2$ (X = halogen, $n = 3, 4, 5$) compounds. Wymore and Bailar[4] synthesized the compounds $Co[(C_2H_5)_2P(CH_2)_2P(C_2H_5)_2]_nBr_2$ ($n = 1, 2$). Chatt and co-workers[5] have mentioned $Co[(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2]_2Br_2$ as a precursor to the "zerovalent" $Co[(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2]_2$. Sacco and Gorieri[6] reported a variety of complexes of the types: $Co[(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2]_2X_2$ (X = Br, I, NCS, NO_3, ClO_4) and $Co[(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2]_2YZ$ (Y = Br, I, NCS, NO_3; Z = NO_3 ClO_4, $B(C_6H_5)_4$). We report here the preparation, optical spectra, magnetic moments, and, where possible, epr measurements of the compounds $Co[(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2]_mX_2$, where for $n = 2$, $m = 1, 2$ and X = Cl, Br, I, and for $n = 3$, $m = 1$ and X = Cl, Br, I. The ditertiary phosphine ligands will be abbreviated as $(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2$ where $n = 2$ is dpe and $n = 3$ is dpp.

Experimental Section

The ditertiary phosphine 1,2-bis(diphenylphosphino)ethane (dpe) was prepared by the method of Hewerston and Watson.[7] The 1,3-bis(diphenylphosphino)propane (dpp) was prepared as described elsewhere.[8]

Dichlorodi[1,2-bis(diphenylphosphino)ethane]cobalt(II).—To a refluxing solution of dpe (3.00 g, 7.54 mmoles) in 100 ml of isopropyl alcohol was added cobalt(II) chloride hexahydrate (1.34 g, 5.63 mmoles) dissolved in a minimum amount of isopropyl alcohol. An immediate green solution with finely suspended green powder precipitate formed. The reflux was continued for 30 min more, and the solution was cooled; the powder was collected, air dried, and recrystallized as reflecting green microcrystals from 3:1 ethanol-water. *Anal.* Calcd for $Co[(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2]_2Cl_2$: C, 67.38; H, 5.18. Found: C, 67.30; H, 5.28.

Dibromodi[1,2-bis(diphenylphosphino)ethane]cobalt(II).[9]—This was prepared in the same manner as the chloride, yielding on recrystallization from 3:1 ethanol-water a reflecting green microcrystalline product. *Anal.* Calcd for $Co[(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2]_2Br_2$: C, 61.48; H, 4.73. Found: C, 61.46; H, 4.84.

Diiododi[1,2-bis(diphenylphosphino)ethane]cobalt(II).[10]—This was prepared in the same manner by refluxing the ligand dpe and anhydrous cobalt(II) iodide; the isolated brownish green powder was recrystallized from 3:1 ethanol-water. It was observed that while standing overnight dark brown needles crystallized out as well as feathery light green needles. On standing an additional 24 hr, the light green precipitate disappeared and only the dark brown needles remained which were collected and dried *in vacuo* overnight. *Anal.* Calcd for $Co[(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2]_2I_2$: C, 56.25; H, 4.33. Found: C, 56.43; 4.43.

Di[1,2-bis(diphenylphosphino)ethane]cobalt(II) Tetraiodocobaltate.—Cobalt(II) iodide (0.454 g, 1.45 mmoles) dissolved in 50 ml of acetone was diluted with acetone to 350 ml, and dpe (0.566 g, 1.42 mmoles) in 75 ml of acetone was added. An immediate green color formed which paled considerably after 24 hr producing light green crystals. The solution was allowed to stand 4 additional days whereupon the mother liquor became almost colorless. A 1.00-g (99.9%) yield of light green crystals was dried *in vacuo* at 70° and collected. *Anal.* Calcd for $Co[(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2]_2[CoI_4]$: C, 43.88; H, 3.38. Found: 43.60; H, 3.37.

Dichloro[1,2-bis(diphenylphosphino)ethane]cobalt(II).—The ligand dpe (3.00 g, 7.54 mmoles) was dissolved in 300 ml of acetone, and cobalt chloride hexahydrate (1.85 g, 7.76 mmoles) in 50 ml of acetone was added. An immediate dark green solution formed that slowly became blue. After 3 days quantities of blue crystals appeared. After 3 additional weeks of standing, the blue solution yielded a blue powder that was collected, air dried, and recrystallized from a large volume of n-butyl alcohol. The blue microcrystals were dried *in vacuo*. *Anal.* Calcd for $Co[(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2]Cl_2$: C, 59.20; H, 4.55. Found: C, 59.20; H, 4.62.

Dibromo[1,2-bis(diphenylphosphino)ethane]cobalt(II).—Dpe (3.00 g, 7.54 mmoles) was dissolved in 350 ml of acetone to which

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[1] This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, through Contract AF 49(638)-1492.

[2] See G. Booth, *Advan. Inorg. Chem. Radiochem.*, **6**, 1 (1964).

[3] K. Issleib and G. Hohlfeld, *Z. Anorg. Allgem. Chem.*, **312**, 169 (1961).

[4] C. E. Wymore and J. C. Bailar, *J. Inorg. Nucl. Chem.*, **14**, 42 (1960).

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

[6] A. Sacco and F. Gorieri, *Gazz. Chim. Ital.*, **93**, 687 (1963).

[7] W. Hewerston and H. R. Watson, *J. Chem. Soc.*, 1490 (1962).

[8] G. R. Van Hecke and W. D. Horrocks, Jr., *Inorg. Chem.*, **5**, 1960 (1966).

[9] First prepared by Chatt, *et al.*,[5] by a different method.

[10] First prepared by Sacco and Gorieri,[6] in acetone rather than alcohol.

was added cobalt(II) bromide (1.74 g, 7.94 mmoles) in 50 ml of acetone. After 2 days blue and green crystals were observed. Two further days of standing showed an increase of blue product relative to green. The volume of the solution was doubled at the end of 2 weeks and placed in a cold room. Four days later the light blue powder was collected, air dried, and recrystallized from a large amount of *n*-butyl alcohol. *Anal.* Calcd for Co-$[(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2]Br_2$: C, 50.56; H, 3.89. Found: C, 49.92; H, 4.00.

Diiodo[1,2-bis(diphenylphosphino)ethane]cobalt(II).—Cobalt(II) iodide (2.49 g, 7.95 mmoles) dissolved in 60 ml of acetone was filtered into a solution of dpe (3.00 g, 7.54 mmoles) in 350 ml of acetone. After 3 days 5.19 g of light green powder was collected, air dried, and then refluxed in a large quantity (~1 l.) of *n*-butyl alcohol until a blue solution obtained (approximately 4 hr). This was filtered and the light blue crystals that appeared on cooling were collected and dried *in vacuo*.

Anal. Calcd for $Co[(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2]I_2$: C, 43.88; H, 3.38. Found: C, 43.50; H, 3.37.

Dichloro[1,3-bis(diphenylphosphino)propane]cobalt(II).—To a warm solution of dpp (0.510 g, 1.24 mmoles) in 50 ml of isopropyl alcohol was added an isopropyl alcohol solution of cobalt chloride hexahydrate (0.310 g, 1.30 mmoles). The resultant blue solution yielded on cooling brilliant light blue platelike crystals that were dried *in vacuo*. *Anal.* Calcd for $Co[(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2]Cl_2$: C, 59.88; H, 4.81. Found: C, 60.08; H, 4.84.

Dibromo[1,3-bis(diphenylphosphino)propane]cobalt(II).—Cobalt(II) bromide (2.21 g, 10.01 mmoles) dissolved in a minimum amount of isopropyl alcohol was added to dpp (2.93 g, 7.12 mmoles) in 150 ml of isopropyl alcohol. An immediate brilliant green solution and precipitate formed that, when refluxed overnight and collected on a sintered-glass filter while still hot, yielded a bluish green microcrystalline powder. This was washed with isopropyl alcohol and ether and dried *in vacuo* giving finally a 4.17-g (92.8%) yield. *Anal.* Calcd for $Co[(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2]Br_2$: C, 51.36; H, 4.12. Found: C, 51.52; H, 4.40.

Diiodo[1,3-bis(diphenylphosphino)propane]cobalt(II).—To a solution of dpp (1.86 g, 4.52 mmoles) in 20 ml of isopropyl alcohol was added a filtered isopropyl alcohol solution of cobalt(II) iodide (2.16 g, 6.90 mmoles). The immediate reddish brown precipitate that formed appeared to dissolve on heating to reflux. The solution was allowed to cool after refluxing for 1 hr. A 3.16-g (96.8%) yield of light brown powder that became green on standing was collected and dried *in vacuo* for 2 hr.

Anal. Calcd for $Co[(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2]I_2$: C, 44.68; H, 3.59. Found: C, 44.47; H, 3.55.

Iododi[1,2-bis(diphenylphosphino)ethane]cobalt(II) Tetraphenylborate.—This complex was prepared by the method of Sacco and Gorieri.[6]

The magnetic susceptibilities of powder samples were measured using standard Gouy techniques. The susceptibilities were corrected for diamagnetism of the ligands from the tables given by Figgis and Lewis.[11] Solution susceptibilities were checked by the nmr method of Evans.[12] Optical spectra were recorded on a Cary Model 14 recording spectrophotometer. Mull spectra were obtained employing Nujol mulls supported on filter paper. A Varian A-60A instrument with a variable-temperature probe was used for the nmr susceptibilities. The powder epr measurements were obtained using a Varian Q-band (35-kMc) instrument. The low-temperature epr spectra were recorded on an X-band (~9.5-kMc) instrument at the IBM Research Laboratories, San Jose, Calif. The anhydrous cobalt(II) halides were supplied by K & K Chemicals Inc. The microanalyses were performed by Galbraith Laboratories Inc., Knoxville, Tenn.

Results and Discussion

$Co(dpe)X_2$ and $Co(dpp)X_2$ Complexes. Tetrahedral Coordination.—Refluxing an alcoholic solution of dpp and the appropriate cobalt(II) halide yields blue or green microcrystalline powders of composition $Co(dpp)X_2$ (X = Cl, Br, I). No form corresponding to a dichelate complex could be isolated. The analogous tetracoordinate dpe complexes, $Co(dpe)X_2$ (X = Cl, Br, I), are much more difficult to prepare. These compounds will crystallize out on long standing from dilute solutions of the $Co(dpe)_2X_2$ compounds in solvents such as chloroform, methylene chloride, or acetone. Because of the insolubility of these compounds only the optical mull spectra and powder susceptibilities could be recorded.

The spectra recorded for the $Co(dpp)X_2$ complexes $\sim 6 \times 10^{-4}$ *M* in methylene chloride solution are shown in Figure 1. The mull spectra of the $Co(dpe)X_2$ compounds are similar. Table I presents a summary of the data for the $Co(dpp)X_2$ and $Co(dpe)X_2$ compounds.

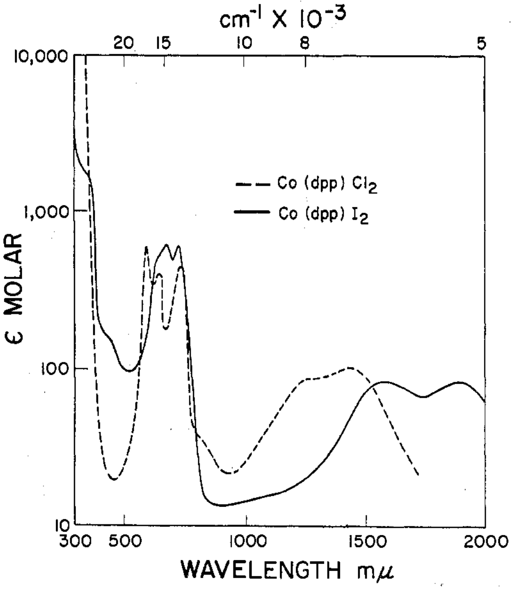

Figure 1.—Optical electronic spectra of $Co(dpp)X_2$ (X = Cl, I) in methylene chloride solution. The spectrum of the bromide has been omitted for clarity.

The spectra are quite similar to those reported for the dihalobis(triphenylphosphine)cobalt(II) complexes and related tertiary phosphine complexes.[13] This is taken as evidence for a pseudo-tetrahedral coordination about the cobalt with the fairly large observed splittings due to the combined effects of the C_{2v} component and spin–orbit coupling. The centers of gravity of the observed bands, with those in the 13,000–17,000-cm^{-1} region assigned to $^4A_2 \rightarrow {}^4T_1(P)$ and those at 6000–8000 cm^{-1} to $^4A_2 \rightarrow {}^4T_1(F)$ of rigorous T_d symmetry, fit the calculated Tanabe–Sugano diagrams for tetrahedral d^7 with $B \cong 710$ cm^{-1} quite well.[14] Average Δ values are larger than for the corresponding tetrahalo complexes, but exact values are probably not very meaningful.

The magnetic moments, corrected for ligand diamagnetism and with a temperature-independent para-

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(11) B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p 403.

(12) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

(13) F. A. Cotton, D. D. Faut, D. M. L. Goodgame, and R. H. Holm, *J. Am. Chem. Soc.*, **83**, 1780 (1961).

(14) F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *ibid.*, **83**, 4690 (1961).

Table I

Optical Data for Tetrahedral Cobalt(II) Ditertiary Phosphine Complexes[a,b]

	$Co(dpp)X_2$	$Co(dpe)X_2$
X	methylene chloride solution	Nujol mull
Cl	16,940 (600), 15,600 (410), 13,800 (440), 12,000 sh, 8000 (~90), 6900 (~100)	28,600 sh, 17,100, 15,400, 14,850, 8700
Br	28,600 sh, 16,100 (670), 14,900 (570), 13,500 (510), 11,400 sh, 8000 (~100), 6900 (~100)	15,900, 14,800, 7700
I	28,600 sh, 15,600 (500), 14,900 (600), 13,900 (600), 9100, 6400 (~80), 5350 (~80)	28,600 sh, 15,050, 13,800, 6150

[a] Energies in cm^{-1}. [b] Molar extinction coefficient ϵ in $l.\ mole^{-1}\ cm^{-1}$ in parentheses. sh = shoulder.

magnetism correction of 500×10^{-6} cgs unit,[13] are, for $Co(dpp)X_2$, 4.43 (X = Cl), 4.47 (Br), and 4.56 (I) BM, and, for $Co(dpe)X_2$, 4.41 (Cl), 4.46 (Br), and 4.63 (I) BM. These are quite similar to those reported[13] for pseudo-tetrahedral cobalt(II) phosphine complexes and increase in the order expected: Cl < Br < I.

$Co(dpe)_2X_2$ Complexes.—Refluxing alcoholic solutions of dpe with the appropriate cobalt(II) halide yields green or brown powders which, when recrystallized from 3:1 ethanol–water, analyze as $Co(dpe)_2X_2$ (X = Cl, Br, I). The same reaction carried out in a nonhydroxylic solvent such as chloroform or acetone leads to the monochelate tetrahedral complexes described above. Certain dichelate complexes of this type were reported by Sacco and Gorieri[6] and, largely on the basis of conductivity and magnetic susceptibility measurements, were assigned a pentacoordinate structure with one ionic halide. The most reasonable geometry for such coordination has the four phosphorus atoms defining the basal plane, and the coordinated halogen, the apex of a rectangular (roughly square) pyramid. Molecular models indicate that structures based on trigonal-bipyramidal coordination would involve a prohibitive amount of steric interaction between phenyl groups on the chelating ligands. In order to obtain more information about the electronic structures of these compounds we have investigated their epr and optical electronic spectra in detail.

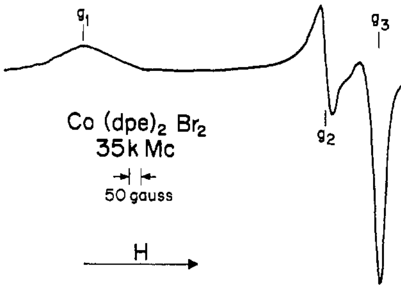

Figure 2.—The room-temperature epr spectrum of a polycrystalline sample of $Co(dpe)_2Br_2$ observed at 35 kMc.

Table II

Observed and Calculated g-Tensor Components for $Co(dpe)_2X_2$ Compounds

	Observed[a]			Calculated[b]		
X	g_1	g_2	g_3	g_{zz}	g_{yy}[c]	g_{xx}[c]
Cl	2.257	2.056	2.041	2.261	2.057	2.040
Br	2.258	2.075	2.037	2.261	2.061	2.042
I	...	...	...	2.298	2.064	2.043

[a] Accurate to ±0.005, obtained from the observed spectra by the method of F. K. Kneubühl, *J. Chem. Phys.*, **33,** 1074 (1960). [b] See text. [c] Assigned arbitrarily.

The room-temperature epr spectrum of a polycrystalline sample of $Co(dpe)_2Br_2$ is shown in Figure 2; that of the chloride is quite similar. The g values obtained for these compounds are presented in Table II. The observation of three distinct g values indicates that the symmetry has been reduced from idealized C_{4v} to C_{2v}. The epr spectrum of $Co(dpe)_2I_2$ was poorly resolved and accurate g values could not be obtained. We will assume in the analysis that follows that the three principal g values correspond to the principal g-tensor components in a molecule-fixed axis system. Room-temperature Gouy susceptibility measurements yield magnetic moments for $Co(dpe)_2X_2$ (X = Cl, Br, I) of $\mu_{eff} = 2.12$, 1.86, and 1.92 BM, respectively; the latter two being somewhat lower than those reported by Sacco and Gorieri,[6] who found $\mu_{eff} = 2.30$ and 2.20 BM for X = Br and I, respectively. These results are consistent with a spin-paired $S = {}^1/_2$ ground state with a significant orbital contribution to the moment. Using the present epr data, μ_{eff} may be calculated from $\mu_{eff} = g_{av}[S(S+1)]^{1/2}$ where $g_{av} = ({}^1/_3)(g_1 + g_2 + g_3)$. For both the chloride and the bromide this yields $\mu_{eff} = 1.84$ BM. The agreement for the bromide is excellent while the discrepancy in the chloride case may indicate a small amount of high-spin impurity in this compound which would not be expected to affect the epr spectrum.

The interpretation of the epr spectra of spin-paired d^7 (three-vacancy) electronic configurations has been discussed by Maki, *et al.*[15] Starting with the strong-field determinantal wave functions correct to first order in the spin–orbit coupling perturbation, $\sum_k \xi \hat{l}_k \cdot \hat{s}_k$, these authors obtained the matrix elements of the Zeeman operator $\beta \mathbf{H} \cdot \sum_k (\hat{l}_k + 2\hat{s}_k)$ for the components of the ground Kramers doublet. The g-tensor components expected for three vacancy configurations were computed for four possible ground states. Of these, only two are in possible agreement with our epr data ($g_1 > g_2 \approx g_3 > 2$): $|\overset{+}{(xy)}\overset{-}{(xy)}\overset{+}{(yz)}\rangle$ and $|\overset{+}{(xy)}\overset{-}{(xy)}\overset{+}{(x^2 - y^2)}\rangle$. Unlike the case of the planar bis(malonitriledithiolato)cobalt(II) where Maki, *et al.*,[15] concluded that $|\overset{+}{(xy)}\overset{-}{(xy)}\overset{+}{(yz)}\rangle$ was the ground state, we find that the best quantitative agreement, considering our observed electronic spectra (*vide infra*), is for the ground configuration: $|\overset{+}{(xy)}\overset{-}{(xy)}\overset{+}{(x^2 - y^2)}\rangle$.

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(15) A. H. Maki, N. Edelstein, A. Davison, and R. H. Holm, *J. Am. Chem. Soc.*, **86,** 4580 (1964). Repeating their calculation we find their eq 7c (our eq 1c) to be in error. This does not affect their conclusions for the MNT complexes; in fact it more clearly argues against the $|\epsilon^2\mu\rangle$ configuration as the ground state in their cobalt case.

For this case the expressions for the principal g-tensor components are

$$g_{xx} = 2 - \{2\xi/[E(|\overset{+}{(xy)}\overset{-}{(xy)}\overset{+}{yz})\rangle) - E(|\overset{+}{(xy)}\overset{-}{(xy)}(x^2 \overset{+}{-} y^2)\rangle)]\} \quad (1a)$$

$$g_{yy} = 2 - \{2\xi/[E(|\overset{+}{(xy)}\overset{-}{(xy)}\overset{+}{(xz)}\rangle) - E(|\overset{+}{(xy)}\overset{-}{(xy)}(x^2 \overset{+}{-} y^2)\rangle]\} \quad (1b)$$

$$g_{zz} = 2 - \{8\xi/[E(|\overset{+}{(xy)}(x^2 \overset{-}{-} y^2)(x^2 \pm y^2)\rangle) - E(|\overset{+}{(xy)}\overset{-}{(xy)}(x^2 \overset{+}{-} y^2)\rangle)]\} \quad (1c)$$

for a coordinate system where the z direction is defined by the Co–X bond and the y axis lies in a plane which bisects both chelate chains. The above expressions were checked by the method of Pryce[16] yielding identical results. Without single-crystal data on crystals of known structure the assignment of g_{xx} and g_{yy} must be arbitrary. We assign g_1 as g_{zz} and, arbitrarily, $g_2 = g_{yy}$ and $g_3 = g_{xx}$.

The ultraviolet–visible–near-infrared spectra of the complexes $Co(dpe)_2X_2$ (X = Cl, Br, I) in both solution and mull are shown in Figures 3–5, respectively. The band positions and molar extinction coefficients are presented in Table III. Of the seven possible excited states (see Table IV), which differ from the ground state by only a single spin orbital, only three contribute to the g values

$$|\overset{+}{(xy)}(x^2 \overset{-}{-} y^2)(x^2 \overset{+}{-} y^2)\rangle,\ g_{zz};\quad |\overset{+}{(xy)}\overset{-}{(xy)}\overset{+}{(xz)}\rangle,\ g_{yy};\quad |\overset{+}{(xy)}\overset{-}{(xy)}\overset{+}{(yz)}\rangle,\ g_{xx}$$

Assuming that these excited states are located at the observed band maxima (X = Cl) of 14,700, 16,680, and 23,800 cm^{-1}, respectively, and employing a spin–orbit

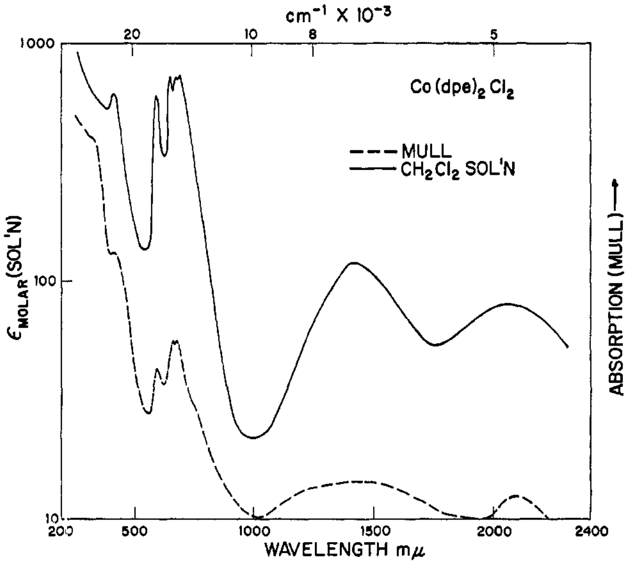

Figure 3.—Optical electronic mull and solution spectra of $Co(dpe)_2Cl_2$.

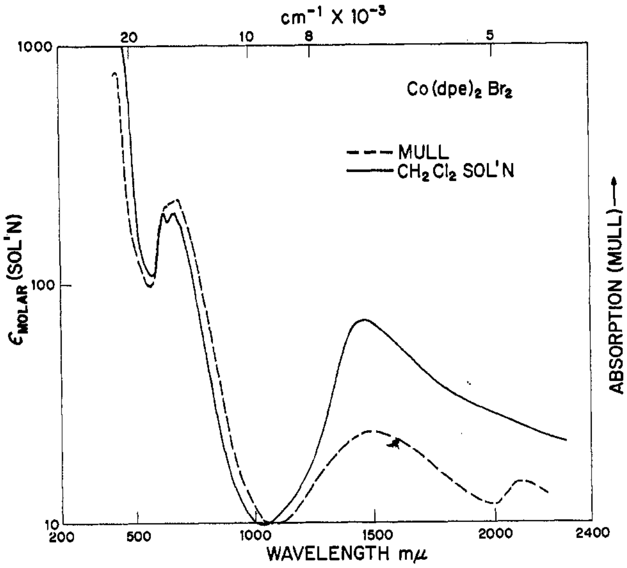

Figure 4.—Optical electronic mull and solution spectra of $Co(dpe)_2Br_2$.

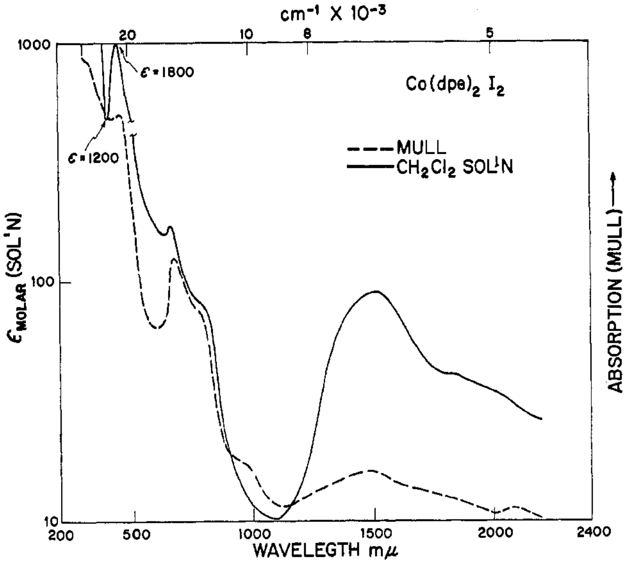

Figure 5.—Optical electronic mull and solution spectra of $Co(dpe)_2I_2$.

TABLE III

SPECTRAL DATA FOR $Co(dpe)_2X_2$ COMPLEXES

X	ν_{max}[a]				
	Methylene Chloride Solution				
Cl	23,800	16,680	14,700	7150	4850
	(600)	(600)	(730)	(120)	(80)
Br	. . .	15,640	14,700	6850	. . .
		(200)	(200)	(80)	
I	22,200	15,100	12,900 sh	6670	. . .
	(1800)	(170)	(80)	(90)	
	Nujol Mull				
Cl	23,800	16,680	14,700	7150[b]	4850
Br	22,750	15,400	14,700	6850[b]	4760
I	22,000	14,700	12,900 sh	6670[b]	4850

[a] Frequencies in cm^{-1}; ϵ in l. mole^{-1} cm^{-1} in parentheses.
[b] Very broad.

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[16] M. H. L. Pryce, *Proc. Phys. Soc.* (London), **A63**, 25 (1950).

TABLE IV

STATE AND TRANSITION ENERGIES FOR THREE-VACANCY CONFIGURATIONS FOR $\overset{+}{(xy)}\overset{-}{(xy)}(x^2 \overset{+}{-} y^2)\,\rangle$ GROUND STATE[a]

State (vacancy configuration)	Co(dpe)$_2$Cl$_2$			Co(dpe)$_2$Br$_2$			Co(dpe)$_2$I$_2$			Interelectronic interaction terms[e]
		Transition energy			Transition energy			Transition energy		
	$\Sigma\epsilon_k$[b]	Calcd[c]	Obsd[d]	$\Sigma\epsilon_k$[b]	Calcd[c]	Obsd[d]	$\Sigma\epsilon_k$[b]	Calcd[c]	Obsd[d]	
$\lvert\overset{+}{(xy)}\overset{-}{(xy)}\langle x^2 \overset{+}{-} y^2)\rangle$	14,700⟩	0	...	14,700	0	...	12,900	0	...	$3F_0 + 12F_2 - 67F_4$ (+7446)
$\lvert\overset{+}{(xy)}\overset{-}{(z^2)}(x^2 \overset{+}{-} y^2)\rangle$	50,150	4,850	4,850	49,850	4,550	4,760	44,470	4,570	4,850	$3F_0 - 12F_2 - 87F_4$ (−23,154)
$\lvert\overset{+}{(xy)}\overset{-}{(xy)}\overset{+}{(z^2)}\rangle$	35,450	7,150	7,150	35,150	6,850	6,850	31,570	6,670	6,670	$3F_0 - 8F_2 + 33F_4$ (−6154)
$\lvert\overset{+}{(xy)}(x^2 \overset{-}{-} y^2)$ $(x^2 \overset{+}{-} y^2)\rangle$	29,400	14,700	14,700	29,400	14,700	14,700	25,800	12,900	12,900	$3F_0 + 12F_2 - 67F_4$ (+7446)
$\lvert\overset{+}{(xy)}\overset{-}{(xz)}(x^2 \overset{+}{-} y^2)\rangle$	56,280	15,060	...[f]	55,240	14,020	...[f]	49,600	13,300	...[f]	$3F_0 - 6F_2 - 151F_4$ (−19,074)
$\lvert\overset{+}{(xy)}\overset{-}{(xy)}\overset{+}{(xz)}\rangle$	41,580	16,680	16,680	40,540	15,640	15,640	36,700	14,800	14,900	$3F_0 - 3F_2 + 8F_4$ (−2754)
$\lvert\overset{+}{(xy)}\overset{-}{(yz)}(x^2 \overset{+}{-} y^2)\rangle$	63,400	22,180	...[f]	62,350	21,130	...[f]	57,000	20,700	...[f]	$3F_0 - 6F_2 - 117F_4$ (−19,074)
$\lvert\overset{+}{(xy)}\overset{-}{(xy)}\overset{+}{(yz)}\rangle$	48,700	23,800	23,800	47,650	22,750	22,750	44,100	22,200	22,200	$3F_0 - 3F_2 + 8F_4$ (−2754)

[a] All energies are in cm^{-1}. [b] The sum of single electron vacancy energies. [c] The sum of single electron vacancy energies and interelectronic interaction terms minus the ground-state energy. [d] Observed electronic transition energies. [e] Condon–Shortley parameters were taken to be F_2 = 1190 cm^{-1} and F_4 = 102 cm^{-1} for Cl and Br (a 15% reduction from the free-ion parameters[19]); F_2 = 1050 cm^{-1} and F_4 = 90 cm^{-1} for I (a 25% reduction). [f] Within the accuracy of these calculations these states lie easily within observed bands.

coupling constant, $\xi = -480$ cm^{-1} (90% of the free ion value), *g* values were calculated. These are shown in Table II; the agreement with experiment is excellent. An analogous assignment (Table IV) was made for the bromide and the agreement is quite satisfactory (Table II).

In order to account for the remaining observed bands in the electronic spectra, the energies of the various excited three vacancy configurations were calculated. The electronic energy may be written as the sum of the energy contributions from the occupied single-electron orbitals and the energy due to the electron–electron interaction. Thus the electronic energy is[17]

$$E(\mathrm{A}) = \sum_i \epsilon_i + \langle \mathrm{A}|1/r_{12}|\mathrm{A}\rangle \qquad (2)$$

where $|\mathrm{A}\rangle$ is the determinantal wave function for the d-orbital configuration and ϵ_i is the energy of a one-electron d orbital appropriate to the Hamiltonian used. $\langle \mathrm{A}|1/r_{12}|\mathrm{A}\rangle$ is given by

$$\langle \mathrm{A}\ 1/r_{12}|\mathrm{A}\rangle = \sum_{k>t=1}^{n} [\langle a_k(1)a_t(2)|1/r_{12}|a_k(1)a_t(2)\rangle - \langle a_k(1)a_t(2)|1/r_{12}|a_t(1)a_k(2)\rangle] \qquad (3)$$

where the first and second terms in the sum are the Coulomb and exchange integrals, respectively, and may be found tabulated[18] for d orbitals in terms of the Condon–Shortley parameters F_0, F_2, and F_4.[19] The values of the electron–electron interaction energies for the various electronic states and the calculated transition energies are given in Table IV. Perfect agreement between the observed and calculated transition energies (Table IV) is obtained for the states used in determining the one-electron orbital energies, ϵ_i, which are given in Table V. The calculations predict a very low energy for the state $|\overset{+}{(xy)}\overset{-}{(z^2)}(x^2 \overset{+}{-} y^2)\rangle$, and the band observed at 4850 and 4760 cm^{-1} for the chloride and bromide, respectively, could be fit quite well using Condon–Shortley parameters decreased by 15% from their free-ion values. The absorption at ~4850 cm^{-1} in the iodide complex is satisfactorily fit with a 25% reduction of these parameters. The increased reduction in the case of the iodide is consistent with its relative position in the nephelauxetic series with respect to the other halides. The remaining levels, $|\overset{+}{(xy)}\overset{-}{(xz)}(x^2 \overset{+}{-} y^2)\rangle$ and $|\overset{+}{(xy)}\overset{-}{(yz)}(x^2 \overset{+}{-} y^2)\rangle$, were calculated with these same parameters to lie near observed bands (Table IV). Thus the present analysis quite satisfactorily accounts for the electronic spectra and *g* values of these complexes.

It should be cautioned that the mixing of levels al-

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[17] M. Tinkham, "Group Theory and Quantum Mechanics," McGraw-Hill Book Co., Inc., New York, N. Y., 1964, p 173.

[18] C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 76.

[19] (a) L. E. Orgel, *J. Chem. Soc.*, 4756 (1952); (b) D. A. Brown, *J. Chem. Phys.*, **28**, 67 (1958).

TABLE V

SINGLE-ELECTRON d-ORBITAL ENERGIES FOR THE Co(dpe)$_2$X$_2$ COMPLEXES[a]

Orbital	Cl	Br	I
xy	48,700	47,650	44,100
x^2-y^2	34,000	32,950	31,100
z^2	13,250	12,500	12,530
xz[b]	7,120	7,110	7,300
yz[b]	0	0	0

[a] Energies in cm^{-1} calculated using interelectronic interaction parameters indicated in footnote *e* to Table IV. [b] Assigned arbitrarily.

lowed by C_{2v} symmetry has been ignored in these calculations, and mixing of metal and ligand orbitals in a molecular orbital formulation of the problem has been accounted for only by reduction of the interelectronic and spin–orbit coupling parameters.

A correlation diagram for the energies of the various states between idealized C_{4v} and C_{2v} symmetries is given in Figure 6 which is drawn to scale for the observed chloride spectrum. A correlation diagram for the one-electron orbital energies (Table V) of Co(dpe)$_2$Cl$_2$ is given in Figure 7. While the present results would be consistent with a planar (tetracoordinate) D_{2h} or tetragonal (hexacoordinate) D_{2h} structure, the dependence of the optical and epr results on the halogen suggest that at least one halide ion is coordinated. The fact that the ground state is $|(\overset{+}{xy})(\overset{-}{xy})(\overset{+}{x^2-y^2})\rangle$ rather than $|(\overset{+}{xy})(\overset{-}{xy})(\overset{+}{z^2})\rangle$ is consistent with a pentacoordinate structure with a smaller axial perturbation than expected for a tetragonal (hexacoordinate) structure. Particularly compelling evidence for the pentacoordinate formulation was the preparation of complexes of the type [Co(dpe)$_2$I$^+$][Y$^-$] where Y is a noncoordinating anion such as perchlorate or, specifically here, tetraphenylborate. The previous authors[6] report identical spectra for the compounds with Y = I, ClO$_4$, and B(C$_6$H$_5$)$_4$. We find bands for methylene chloride solutions of the compound with Y = B(C$_6$H$_5$)$_4$ at 22,330, 15,100, 12,500 (sh), and 6610 cm^{-1}. These values represent slight, but perhaps significant, shifts from those of the analogous compound with Y = I (Table III). This suggests that the iodide ligand in the "sixth" coordination position does have some effect on the energy levels of the complex. A reasonable description of the diiodide might involve one long and one short cobalt–iodine bond. Substantiation of this hypothesis must await an X-ray crystallographic investigation.

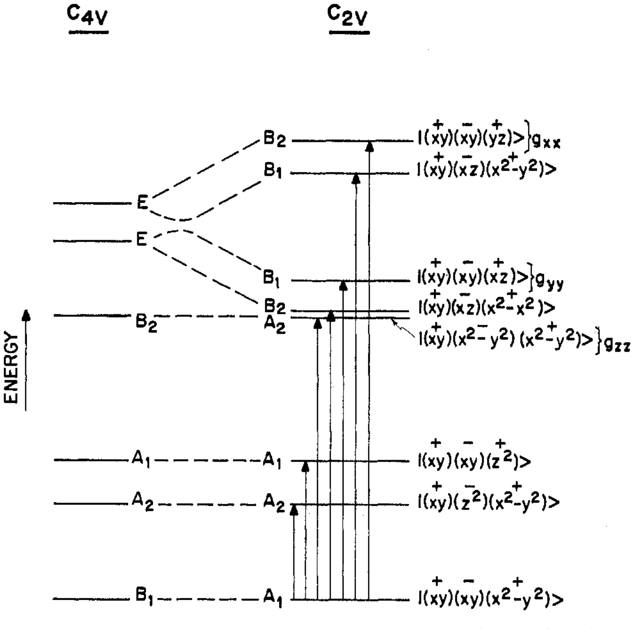

Figure 6.—Electronic energy levels arising from the three-vacancy (d^7) configuration of the Co(dpe)$_2$X$_2$ complexes in C_{4v} and C_{2v} symmetry. The levels under C_{2v} are drawn to scale for the chloride complex.

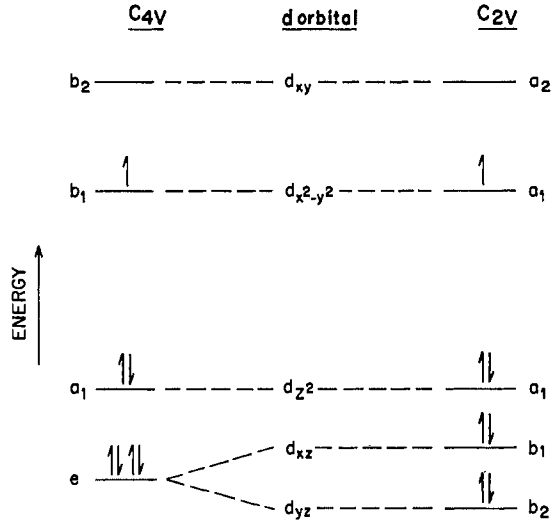

Figure 7.—The one-electron d-orbital energies of Co(dpe)$_2$X$_2$ under C_{4v} and C_{2v} symmetries. The C_{2v} energy separations are drawn to scale for the chloride complex.

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