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Four-Coordinate High-Spin and Five-Coordinate Low-Spin Complexes of Cobalt(II) Chloride with Ethyl Phosphite, Phosphonite, and Phosphinite Ligands. Refinement of the Evans Nuclear Magnetic Resonance Method for the Study of Spin Equilibria[1,2]

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Complexes of cobalt(II) chloride were studied with the ligands L = $(C_2H_5)_nP(OC_2H_5)_{3-n}$, n = 0–2. High-spin complexes $CoCl_2L_2$, n = 0–2, and low-spin five-coordinate complexes $CoCl_2L_3$, n = 1, 2, were obtained in pure form. Their magnetic susceptibilities and electronic spectra are reported. All are monomeric nonelectrolytes in nitrobenzene. The equilibria $CoCl_2L_2 + L \rightleftharpoons CoCl_2L_3$, n = 0–2, were observed in organic solvents. Equilibrium constants and thermodynamic functions were determined in *tert*-butylbenzene by a more detailed application of the Evans NMR shift method than has been used previously in studying high-spin ⇌ low-spin equilibria. Measurements of solution densities as a function of temperature were needed for this application; density data are also reported for the pure phosphorus esters and the solvents. In *tert*-butylbenzene at 30 °C, K_{eq} values are 2.1×10^2 for n = 0, 4.8×10^3 for n = 1, and 5.0×10^2 for n = 2. In spectrophotometric studies, matrix rank analysis confirmed the presence of two absorbing species in equilibrium in each system, and isosbestic points were observed. Determination of equilibrium constants from spectrophotometric data was much less accurate than by the NMR method. In the more polar solvent nitrobenzene, K_{eq} values are smaller by 1–2 orders of magnitude than in *tert*-butylbenzene. Previous work has shown that $CoCl_2L_3$ does not exist when n = 3. The irregular variation in stability of $CoCl_2L_3$ with n is related not only to the ligand steric effect (cone angle) but also to electronic effects on the σ–π balance of the coordinate bond.

Introduction

In the series of ligands $(C_2H_5)_nP(OC_2H_5)_{3-n}$ there is a variation in the steric cone angle, which decreases from 132° for the phosphine to 109° for the phosphite,[3] with intermediate values expected for the phosphonite and phosphinite.[4] A dominant role has been assigned to the steric effect on the relative stabilities of nickel(0) complexes NiL_4[4] and of cobalt(II) complexes CoX_2L_3[5] of similar ligands.

There is also a variation in the electronegativity of the substituents on phosphorus, which would affect its σ-donor ability. Thus, as ethyl groups are replaced by ethoxy groups, there is a monotonic increase in the phosphorus 2s and 2p core electron binding energies[6] indicative of a decrease in electron density on phosphorus. The same inductive effect would enhance the back-π-bonding ability of phosphorus. The relative stabilities of nickel(II) complexes $Ni(CN)_2L_3$ have been interpreted solely in terms of these electronic effects, in contrast to the stabilities of NiL_5^{2+} complexes which were influenced by steric effects.[7]

The combination of these steric and electronic factors may be reflected in the irregularity of the ^{31}P NMR data for these ligands (see Experimental Section, Table II). This has been suggested previously[8] for similar ligands.

The possibility of forming cobalt(II) complexes with these ligands in which the metal ion exhibits differing coordination numbers and spin states offers an opportunity to study the effect of these variables on the autoxidation of the complexes[9] and on the mechanism of cobalt catalysis of the reaction with dioxygen.[10]

The only complex in the triethylphosphine–cobalt(II) chloride system is dichlorobis(triethylphosphine)cobalt(II), according to both solid–vapor[11] and solution[12] equilibrium studies. This compound has spectroscopic and magnetic properties typical of high-spin pseudotetrahedral cobalt(II) species. In related cobalt(II) complexes, five-coordination is attainable by association[13] or by addition of a third phosphine ligand to give $CoX_2(PR_3)_3$ complexes.[5,12,14–18]

No specific cobalt(II) chloride complex with triethyl phosphite appears to have been isolated. Coordination in solution has been postulated on the basis of color changes.[19] Complex solute species $[CoCl_2L_2]$ and $[CoCl_2L_3]$ in benzene, and these plus $[CoL_6]Cl_2$ in ethanol, have been postulated[20–22] on the basis of spectrophotometric, magnetic susceptibility, and conductometric studies. Addition of bases causes disproportionation to give cobalt(I) complexes.[23,24] Apparently, no cobalt(II) halide complexes of dialkyl alkylphosphonites $RP(OR)_2$ or of alkyl dialkylphosphinites $R_2P(OR)$ are known.

We have prepared and characterized the pure compounds dichlorobis(triethyl phosphite)cobalt(II), dichlorobis- and -tris(diethyl ethylphosphonite)cobalt(II), and dichlorobis- and -tris(ethyl diethylphosphinite)cobalt(II). Dichlorotris(triethyl phosphite)cobalt(II) was obtained in solution.

The equilibrium constants and thermodynamic functions have been determined for the reaction

$$\underset{\substack{\text{(four-coordinate,}\\ \text{high-spin)}}}{CoCl_2L_2} + L \rightleftharpoons \underset{\substack{\text{(five-coordinate,}\\ \text{low-spin)}}}{CoCl_2L_3} \qquad (1)$$

in organic solvents, where L = $(C_2H_5)_nP(OC_2H_5)_{3-n}$, n = 0–2. The solubility and reactive properties of these complexes limited the composition range available for study in a single solvent, hindering spectrophotometric determination of the equilibrium constants. The Evans NMR method was found to be uniquely valuable in this situation. Previous applications[17,25,26] of this method to the study of spin equilibria have been semiquantitative, in that assumed values of the magnetic susceptibilities or moments of the individual components have often been used and in that the term involving a density difference has always been neglected. The application of the NMR method with full rigor has been demonstrated in the present work.

Experimental Section

The phosphorus esters and complexes were handled under purified nitrogen in a drybox or in Schlenk ware, or in a standard glass high-vacuum line.

Materials. Cobalt(II) chloride hydrate, reagent grade, was dehydrated by heating in a stream of hydrogen chloride. Anal. Calcd for $CoCl_2$: Cl, 54.61. Found: Cl, 54.50. Chlorobenzene was distilled under nitrogen from phosphorus(V) oxide. Hexane, reagent grade, benzene, Spectroquality grade, and cyclohexane, Spectroquality grade, were distilled under nitrogen from sodium. Ethanol was distilled from magnesium ethoxide. *N,N*-Diethylaniline (MCB) was distilled under nitrogen; bp 91 °C (10 Torr). Nitrobenzene, reagent grade, was washed successively with sulfuric acid, aqueous sodium hydroxide, and water, treated with Drierite, stirred for several days with

Table I. Densities[a] as a Function of Temperature, *d* (g/ml) = *a* − *b*(*t* °C)

	a	$10^4 b$	Linear correln coeff
	Pure ligands		
$P(OC_2H_5)_3$ (L1)	0.9743 ± 0.0002	10.41 ± 0.08	0.9996
$C_2H_5P(OC_2H_5)_2$ (L2)	0.9218 ± 0.0002	9.81 ± 0.06	0.9996
$(C_2H_5)_2POC_2H_5$ (L3)	0.8651 ± 0.0001	9.31 ± 0.06	0.9997
	Solvents		
tert-Butylbenzene (S1)	0.8824 ± 0.0001	8.00 ± 0.03	0.9998
Nitrobenzene + 5.00 vol % cyclohexane (S2)	1.2012 ± 0.0002	9.42 ± 0.05	0.9996
	Solutions		
0.4700 M L1 in S1	0.8906 ± 0.0003	7.91 ± 0.10	0.9991
0.0700 M L2 in S1	0.8820 ± 0.0001	7.73 ± 0.03	0.9999
0.2700 M L3 in S1	0.8809 ± 0.0001	7.97 ± 0.03	0.9999
0.010 00 M $CoCl_2$ + 0.050 00 M L1 in S1	0.8852 ± 0.0001	7.92 ± 0.04	0.9999
0.010 00 M $CoCl_2$ + 0.5000 M L1 in S1	0.8930 ± 0.0004	8.20 ± 0.13	0.9984
0.010 00 M $CoCl_2$ + 0.030 00 M L2 in S1	0.8831 ± 0.0001	7.91 ± 0.02	0.9999
0.010 00 M $CoCl_2$ + 0.1000 M L2 in S1	0.8837 ± 0.0001	7.79 ± 0.03	0.9999
0.010 00 M $CoCl_2$ + 0.025 05 M L3 in S1	0.8837 ± 0.0001	8.08 ± 0.03	0.9999
0.010 00 M $CoCl_2$ + 0.3000 M L3 in S1	0.8822 ± 0.0001	7.96 ± 0.04	0.9998
0.010 00 M $CoCl_2$ + 0.020 00 M L1 in S2	1.2022 ± 0.0001	9.50 ± 0.04	0.9998
0.010 00 M $CoCl_2$ + 0.020 00 M L2 in S2	1.2013 ± 0.0001	9.52 ± 0.03	0.9999
0.010 00 M $CoCl_2$ + 0.020 00 M L3 in S2	1.2017 ± 0.0001	9.58 ± 0.04	0.9999

[a] Errors shown are one standard deviation of the slope and intercept in the linear regression.

phosphorus(V) oxide, and distilled under nitrogen through a Vigreux column; bp 87 °C (10 Torr). The temperature variation of density of a 5.00 vol % solution of cyclohexane in nitrobenzene is given in Table I. *tert*-Butylbenzene (Aldrich), recovered and reused throughout the work, was first distilled, twice thoroughly washed with 6 M hydrochloric acid, water, and 6 M sodium hydroxide, then repeatedly washed with water, stored over Drierite for 2 weeks, refluxed over molten sodium for several hours, distilled under nitrogen through a Vigreux column, bp 166 °C, and stored under nitrogen over molecular sieves. Its purity was checked by GC using SE 30 and Carbowax 20M columns. The temperature variation of density of *tert*-butylbenzene is given in Table I. Phosphorus trichloride, reagent grade, was distilled under nitrogen. Tetraethyllead was used as received from the Ethyl Corp. Ethyldichlorophosphine was in part a research sample from the Ethyl Corp. and in part was prepared[27] (61%, bp 112 °C) from phosphorus trichloride and tetraethyllead. Diethylchlorophosphine was prepared[28] (55%, bp 131–132 °C) from ethyldichlorophosphine and tetraethyllead.

The Phosphorus Ligands. Triethyl phosphite was distilled under nitrogen, bp 52 °C (13 Torr), refluxed over sodium (which reacts with any diethyl hydrogen phosphonate impurity), and distilled under 1 atm of nitrogen. Diethyl ethylphosphonite and ethyl diethylphosphinite have been described[29-31] and were prepared by a modification of the triethyl phosphite synthesis.[32] A mixture of 70.0 g (0.534 mol) of ethyldichlorophosphine and 50 ml of hexane was added dropwise with stirring under nitrogen to a mixture of 62.4 ml (1.068 mol) of ethanol, 170.2 ml (1.068 mol) of *N,N*-diethylaniline, and 200 ml of hexane at 0 °C. The reaction mixture was then refluxed for 3 h and filtered under nitrogen. The *N,N*-diethylaniline hydrochloride precipitate was washed with hexane, and the hexane was removed from the filtrate by distillation under 1 atm of nitrogen. The residue was distilled through a Vigreux column under nitrogen to give diethyl ethylphosphonite (74%, bp 43 °C (15 Torr). In the same way, ethyl diethylphosphinite was prepared (44%, bp 65–66 °C (73 Torr), 83–87 °C (151 Torr),[33,34] n^{25}_D 1.4316) using equimolar quantities of diethylchlorophosphine, ethanol, and *N,N*-diethylaniline. Throughout the work, infrared spectra (tabulated by Studer[2]) were taken of the phosphorus ligands and of their complexes to ensure the absence of hydrolysis or of Arbuzov isomerization to the phosphoryl compounds, for which characteristic infrared frequencies have been reported.[35] The temperature variation of density of the three phosphorus esters is reported in Table I, and their ^{31}P and ^1H NMR data are reported in Table II.

Table II. NMR Data for the Phosphorus Ligands

	^{31}P chem shift, ppm from H_3PO_4	^1H, δ
$(C_2H_5)_3P$	+19.5 m[a]	1.13 m[a]
$(C_2H_5)_2POC_2H_5$	−182 m	1.32 m, 3.94 m
$C_2H_5P(OC_2H_5)_2$	−135 m	1.28 m, 3.84 m
$P(OC_2H_5)_3$	−142[b]	1.19, 3.85[c]

[a] D. D. Axtell and J. T. Yoke, *Inorg. Chem.*, **12**, 1265 (1973). [b] Septet, J_{POCH} = 7.4 Hz. [c] C. E. Jones and K. J. Coskran, *Inorg. Chem.*, **10**, 1536 (1971).

Dichlorobis(triethyl phosphite)cobalt(II). Anhydrous cobalt(II) chloride in a vacuum-line reaction tube dissolved over several days on stirring at room temperature with a benzene solution containing slightly more than 2 mol of triethyl phosphite/mol of cobalt(II) chloride, giving a blue solution. The solvent and slight excess of triethyl phosphite were pumped off, leaving a blue-black solid, mp 59.5–60.5, 60.3–61.0 °C (sealed tube). Anal. Calcd for $CoCl_2(P(OC_2H_5)_3)_2$: C, 31.19; H, 6.54; Co, 12.75. Found: C, 31.06; H, 6.52; Co, 12.66. Molecular weight: calcd, 462; found, 464. A solid with a different melting point and magnetic moment was obtained by dissolving anhydrous cobalt(II) chloride (ca. 0.5 g) under nitrogen in 15 ml of *tert*-butylbenzene containing 3.00 mol of triethyl phosphite/mol of cobalt(II) chloride. When the blue-green solution was diluted with *tert*-butylbenzene, a blue precipitate formed, leaving a green supernatant. The precipitate was filtered under nitrogen, washed with hexane, and dried in vacuo; mp 92–93, 95–96 °C (sealed tube). Anal. Calcd for $CoCl_2(P(OC_2H_5)_3)_2$: C, 31.19; H, 6.54; P, 13.40. Found: C, 31.52; H, 6.13; P, 13.35. The ir spectra of the two forms of the solid were identical. The molar conductance of a 10^{-3} M solution of the complex in nitrobenzene was 0.92 $ohm^{-1}\ cm^2\ mol^{-1}$.

Dichlorobis(diethyl ethylphosphonite)cobalt(II). A 0.9317-g (7.176-mmol) quantity of cobalt(II) chloride dissolved in a solution of 2.1864 g (14.56 mmol) of diethyl ethylphosphonite in 25 ml of benzene in 15 days. All volatile material was then pumped off, leaving a viscous blue-green oil. Anal. Calcd for $CoCl_2(C_2H_5P(OC_2H_5)_2)_2$: C, 33.51; H, 7.03; Co, 13.56. Found: C, 32.47; H, 6.85; Co, 13.29. Molecular weight: calcd, 430; found, 409. This blue-green oil was miscible with an excess of the phosphonite ligand to give a green solution, which returned to the original color when the excess volatile phosphonite was pumped away. The molar conductance of a 10^{-3} M solution in nitrobenzene was 0.67 $ohm^{-1}\ cm^2\ mol^{-1}$.

Dichlorotris(diethyl ethylphosphonite)cobalt(II). A 0.4255-g (3.278-mmol) quantity of cobalt(II) chloride dissolved in a solution of 1.4776 g (9.834 mmol) of diethyl ethylphosphonite in 10 ml of benzene in 4 days. The benzene was carefully distilled from the green solution, leaving a dark green-black solid. This was washed in the drybox with hexane and dried in nitrogen; mp 51.9 °C (sealed tube). Anal. Calcd for $CoCl_2(C_2H_5P(OC_2H_5)_2)_3$: C, 37.26; H, 7.82; P, 16.01. Found: C, 36.87; H, 7.61; P, 15.96. Molecular weight: calcd, 580; found, 567. The molar conductance of a 10^{-3} M solution in nitrobenzene was 0.27 $ohm^{-1}\ cm^2\ mol^{-1}$.

Dichlorobis(ethyl diethylphosphinite)cobalt(II). A 1.4508-g (11.17-mmol) quantity of cobalt(II) chloride with 5.3374 g (39.79 mmol) of ethyl diethylphosphinite in the absence of a solvent gave a green liquid phase and a solid which changed in 12 days from blue to black. When this system was pumped on until constant weight was reached, the nonvolatile residue consisted of a dark blue-green oil. Anal. Calcd for $CoCl_2((C_2H_5)_2POC_2H_5)_2$: C, 36.20; H, 7.59; Cl, 17.81. Found: C, 36.53; H, 7.14; Cl, 17.77. Molecular weight: calcd, 398; found, 386. The molar conductance of a 10^{-3} M solution in nitrobenzene was 0.25 $ohm^{-1}\ cm^2\ mol^{-1}$.

Dichlorotris(ethyl diethylphosphinite)cobalt(II). A 0.2579-g (1.987-mmol) quantity of cobalt(II) chloride dissolved in a solution of 0.7918 g (5.902 mmol) of ethyl diethylphosphinite in 10 ml of benzene in 5 days. The benzene was carefully distilled from the green solution, leaving a dark green-black solid, mp 49.6 °C (sealed tube).

Anal. Calcd for $CoCl_2((C_2H_5)_2POC_2H_5)_3$: C, 40.62; H, 8.52; P, 17.46. Found: C, 40.70; H, 8.48; P, 16.94. Molecular weight: calcd, 532; found, 527. The molar conductance of a 10^{-3} M solution in nitrobenzene was 0.72 ohm^{-1} cm^2 mol^{-1}.

Analyses. Chloride was determined gravimetrically. Cobalt was determined by potentiometric titration.[36] C, H, and P microanalyses were done by Galbraith Laboratories, Knoxville, Tenn.

Densities. Liquid densities were determined dilatometrically under 1 atm of nitrogen. The dilatometer bulb and graduated stem were calibrated using a weighed quantity of freshly boiled distilled water.[37] Typically, 13 points were obtained in the temperature range 10–45 °C, with the temperature controlled to ±0.1 °C. The data were fitted to the equation $d = a - b(t\ °C)$ by linear least squares; the linear correlation coefficients are given in Table I.

Spectrometric Instrumentation. Infrared spectra were obtained using Beckman IR8 and Perkin-Elmer 621 instruments. A Varian HA 100 spectrometer was used for NMR measurements. Visible spectra were obtained with a Cary 15 spectrophotometer with a thermostated cell compartment. Quartz cells of 1- and 0.1-cm nominal path lengths were calibrated using primary standard potassium dichromate in perchloric acid at pH 3.0.[38]

Other Physical Measurements. Molecular weights were determined cryoscopically in nitrobenzene under nitrogen. Conductivities were determined in nitrobenzene under nitrogen with an Industrial Instruments RC16B2 bridge and a cell with a constant of 0.100 cm^{-1}. Melting points were determined with a Mel-Temp apparatus, using tubes sealed under nitrogen.

Solutions. Volumetric flasks were calibrated by weighing distilled water at a known temperature. Solid solutes were weighed on a semimicrobalance under nitrogen. Liquid solutes, whose densities were precisely known at the temperature of solution preparation, were measured volumetrically (±0.02%) using Gilmont S3200A 2.5-ml Ultraprecision micrometer burets. Solutions were prepared at a known temperature in the nitrogen-filled glovebox and were filtered (fine-glass frit) to remove traces of insoluble residue; the weights of such residues were found to be negligible. When samples were taken for NMR and spectrophotometric measurements, solution concentrations were recalculated using the known variation of solution density with temperature.

Paramagnetic Susceptibilities. For pure compounds, these were determined at room temperature by the Gouy method as previously described.[39] The diamagnetic susceptibility of triethyl phosphite was taken from the literature.[40] The susceptibilities of diethyl ethylphosphonite and ethyl diethylphosphinite were calculated by taking 4.6×10^{-6} for each oxygen[41] removed from triethyl phosphite. Diamagnetic corrections were made[41] for $CoCl_2$ but no temperature-independent paramagnetism was assumed. Magnetic moments, calculated by $\mu_{eff} = 2.828(\chi_M{}^{cor}T)^{1/2}$, are given in Table III.

Paramagnetic susceptibilities of solutions were determined by the Evans NMR method,[42] using a Wilmad Precision coaxial cell with an inner sealed capillary of TMS (instrument lock). The diamagnetic susceptibilities of *tert*-butylbenzene, cyclohexane, and nitrobenzene were taken from the literature.[40] The susceptibilities of the dichlorobis(phosphorus ester)cobalt(II) complexes were determined using 10^{-2} M solutions in nitrobenzene containing 5.00 vol % cyclohexane in one chamber of the cell; the other chamber contained only the mixed solvent. The $\Delta\nu$ of the proton resonance of cyclohexane was measured to ±0.04 Hz at 5 °C intervals in the range 11–46 °C. The susceptibilities of the dichlorotris(phosphorus ester)cobalt(II) complexes were determined similarly using 10^{-2} M $CoCl_2$ solutions with added ligand in *tert*-butylbenzene; the $\Delta\nu$ of the *tert*-butyl proton resonance was measured. As the mole ratio of ligand to cobalt(II) chloride was increased in such solutions, $\Delta\nu$ decreased due to the equilibrium shift from the quartet to the doublet cobalt(II) species, leveling off at high mole ratios where essentially all of the cobalt(II) was in the low-spin form. The mole ratios of ligand to cobalt(II) chloride used in determining the susceptibilities of the tris complexes were 50.0 for triethyl phosphite, 10.0 for diethyl ethylphosphonite, and 30.0 for ethyl diethylphosphinite. In these cases, the solvent reference chamber contained solutions of ligand in *tert*-butylbenzene matching the concentration of uncoordinated ligand in the test solutions.

With both classes of complexes, the susceptibility data were fitted by linear least squares to the Curie–Weiss law in the form $T = (\mu_{eff}/2.828)^2(1/\chi_M{}^{cor}) + \Theta$, and the linear correlation coefficients, Weiss constants, and magnetic moments are given in Table III. Errors in the magnetic moments reflect the standard deviations in the slopes of the regression lines. Obviously, the uncertainties in the extrapolated Weiss constants are very great because the susceptibilities were measured only in the narrow temperature range 11–46 °C. However, corrections were made for the thermal variation of solution concentration with density,[43] so this is not a source of error in the Weiss constants. The reported values (Table III) may not differ significantly from zero, with the exception of the value for dichlorotris(ethyl diethylphosphinite)cobalt(II).

Table III. Magnetic Data for the Complexes[a]

Pure compd	μ_{eff}, BM (Curie law, 25 °C)	Pure compd	μ_{eff}, BM (Curie law, 25 °C)
$CoCl_2(P(OC_2H_5)_3)_2$	4.12 (mp 60 °C)	$CoCl_2((C_2H_5)_3P)_2$	4.39[b]
$CoCl_2(P(OC_2H_5)_3)_2$	5.53 (mp 95 °C)	$CoCl_2(C_2H_5P(OC_2H_5)_2)_3$	2.00
$CoCl_2(C_2H_5P(OC_2H_5)_2)_2$	3.51	$CoCl_2((C_2H_5)_2POC_2H_5)_3$	2.54
$CoCl_2((C_2H_5)_2POC_2H_5)_2$	3.40		

Solution	μ_{eff}, BM	Weiss const	Curie–Weiss law linear correln coeff
$CoCl_2(P(OC_2H_5)_3)_2$	4.23 ± 0.22	−78 ± 40	0.9678
$CoCl_2(C_2H_5P(OC_2H_5)_2)_2$	4.48 ± 0.12	+3 ± 16	0.9916
$CoCl_2((C_2H_5)_2POC_2H_5)_2$	4.66 ± 0.03	−16 ± 4	0.9995
$CoCl_2(P(OC_2H_5)_3)_3$	2.03 ± 0.04	+9 ± 12	0.9954
$CoCl_2(C_2H_5P(OC_2H_5)_2)_3$	2.04 ± 0.03	−34 ± 10	0.9972
$CoCl_2((C_2H_5)_2POC_2H_5)_3$	2.48 ± 0.09	−159 ± 34	0.9841

[a] Errors shown are based on one standard deviation of the slope and intercept in the linear regression. [b] Reference 11.

Results and Discussion

The Pure Complexes. These are all monomeric nonelectrolytes (in nitrobenzene solution). The low-spin five-coordinate dichlorotris(phosphorus ester)cobalt(II) complexes are isolable only with the two *middle* members of the ligand series $(C_2H_5)_nP(OC_2H_5)_{3-n}$. The phosphine does not form such a complex[11,12] and the phosphite forms it only in solution in the presence of an excess of ligand. This irregular sequence is in agreement with the trend of the equilibrium constants for eq 1 to be discussed later.

The room-temperature magnetic moments (Gouy method) of the solid tris(diethyl ethylphosphonite) and -(ethyl diethylphosphinite) complexes are in good agreement with the solution moments (Evans method) and are in the general range expected for low-spin five-coordinate complexes of cobalt(II) with phosphorus and halide donor atoms.[17,44,45] When these green-black solids are subjected to lengthy pumping in the high-vacuum line until constant weight is achieved, they reversibly lose 1 mol of phosphorus ligand, giving the dichlorobis(diethyl ethylphosphonite) and -(ethyl diethylphosphinite)cobalt(II) complexes as blue-green oils. When an excess of triethyl phosphite is similarly removed from cobalt(II) chloride, only solid blue-black dichlorobis(triethyl phosphite)cobalt(II) is obtained. Another form of this solid, with a different melting point and magnetic moment,[46] is obtained by precipitation from *tert*-butylbenzene solution. The room-temperature magnetic moments (Gouy method) of the other pure bis(phosphorus ester) complexes do not make much sense and do not agree with the solution moments (Evans method), with the exception of the triethyl phosphite complex prepared by the first method. Similar ambiguous results have been reported previously[47] and may be due to intermolecular association.[48] The solution moments are reasonable for high-spin pseudotetrahedral cobalt(II) complexes.

Table IV. Electronic Spectral Data for the Complexes: λ, nm (ε)[a]

Solvent	$CoCl_2(P(OC_2H_5)_3)_2$	IP[b]	$CoCl_2(P(OC_2H_5)_3)_3$
Nitrobenzene	708[c] (276), 678 (348), 655 (305), 633[c] (247), 586 (325), 535[c] (174), 428[c] (97)	715 (210)	655 (500), 586 (553), 438 (502)[d,e]
tert-Butylbenzene			602 (470), 438 (960), 342 (2800)[f]
Benzene	650[c], 613, 584, 438, 343[c,e]		597 (477), 438 (979), 343 (3050)[g]
Other solvents	679 (286), 654 (279), 632[c] (252), 582 (312), 360 (568)[e,h]		602, 434[f,h] 620, 440, 367[f,i,j] 602 (385), 438 (855)[k]
Solvent	$CoCl_2(C_2H_5P(OC_2H_5)_2)_2$	IP[b]	$CoCl_2(C_2H_5P(OC_2H_5)_2)_3$
Nitrobenzene	667 (281), 617[c] (186), 591[c] (144), 430 (152)	605 (170)	667[c] (260), 654 (285), 591 (342), 430 (906)[e,l]
tert-Butylbenzene		700 (220)	620 (527), 438 (1130)[m]
Benzene	680, 618, 582[i]		
Solvent	$CoCl_2((C_2H_5)_2POC_2H_5)_2$	IP[b]	$CoCl_2((C_2H_5)_2POC_2H_5)_3$
Nitrobenzene	710, 663, 600[i]		
tert-Butylbenzene		722 (270)	675[c] (430), 620 (504), 456 (984)[n]
Benzene	696, 675,[c] 627,[c] 614, 565[i]		

[a] Where extinction coefficients are reported, the applicability of Beer's law had been demonstrated over a range of concentrations. [b] Isobestic point in $CoCl_2L_2 + L \rightleftharpoons CoCl_2L_3$ systems. [c] Shoulder. [d] Limiting spectrum; mole ratio 571. [e] Spectrum taken rapidly on fresh unstable solutions. [f] Limiting spectrum; unspecified large excess of ligand. [g] Limiting spectrum; mole ratio 101. [h] Chlorobenzene. [i] Less accurate data; Beckman DK2 spectrophotometer. [j] Hexane. [k] Neat ligand as solvent. [l] Limiting spectrum; mole ratio >13. [m] Limiting spectrum; mole ratio 10. [n] Limiting spectrum; mole ratio 30.

Solubility Behavior of the Complexes. The observed solubility phenomena are directly related to the equilibria of eq 1. Solubility behavior is related to the effect of the phosphorus ligand:cobalt mole ratio on the position of equilibrium. Solubility behavior also depends on K_{eq}; as discussed later, this is much smaller in nitrobenzene than in *tert*-butylbenzene and smaller for triethyl phosphite than for the phosphonite and phosphinite. Blue or blue-green solutions of the bis(phosphorus ester) complexes in benzene or nitrobenzene can be prepared starting with the complexes or with anhydrous cobalt(II) chloride and a solution of the phosphorus ligand to give a phosphorus:cobalt mole ratio of 2.0. Such solutions cannot be prepared in *n*-hexane or in *tert*-butylbenzene. On addition of extra phosphorus ligand (in the limit using the neat phosphorus ligand itself as solvent), bright green solutions can be prepared in all four solvents as equilibrium 1 shifts to the right. The green solutions are very sensitive to oxygen.[10] In nitrobenzene, such solutions decompose slowly due to oxidation by the solvent of the large amount of free ester present in the equilibrium system. In *tert*-butylbenzene, 10^{-2}–10^{-3} M solutions with a (phosphonite or phosphinite):cobalt mole ratio below about 2.5–2.8 cannot be prepared, and a triethyl phosphite solution with a mole ratio of 3.0 deposits solid bis complex on dilution.

Visible Spectra. Data are given in Table IV. The bis complexes have the structured absorption in the region 580–720 nm typical of high-spin pseudotetrahedral cobalt(II). The tris complexes have an absorption in the same region differing in details of spectral features, as well as more intense absorption near 440 nm which grows in as the phosphorus ligand:cobalt mole ratio is increased above 2. These features are typical of low-spin five-coordinate cobalt(II) halide complexes with distorted square-pyramidal structures.[17,45,47] The transition at about 23 kK has been assigned to $^2A_1 \rightarrow {}^2E(1)$ in C_{4v} symmetry.[49,50]

Equilibrium Constants from NMR Shift Data. The Evans equation[42] written on a molar basis is

$$\chi_M{}^{cor} = \frac{3\Delta\nu(10^3)}{2\pi\nu M} + \chi_0(MW) + \frac{\chi_0(d_0 - d_s)(10^3)}{M} + DC \quad (2)$$

where ν is the spectrometer frequency, $\Delta\nu$ is the observed NMR shift of an inert reference proton, M is the molarity of the paramagnetic species, χ_0 is the gram diamagnetic susceptibility of the solvent, MW is the molecular weight of the paramagnetic complex, d_0 is the density of the solvent, d_s is the density of the solution, and DC is the diamagnetic correction for the complex. Of the four terms on the right-hand side, the first is dominant. The other terms are significant, however, and in particular we find that the third term should *not* be neglected, as has always been done. For example, in the case of 0.01 M cobalt(II) chloride and 0.05 M triethyl phosphite in *tert*-butylbenzene at 26 °C, the magnitudes of the four terms are as shown

$$\chi_M{}^{cor} = 2.285 \times 10^{-3} - 0.460 \times 10^{-3} + 0.229 \times 10^{-3} + 0.358 \times 10^{-3} = 2.412 \times 10^{-3}$$

The application of eq 2 is straightforward to obtain $\chi_M{}^{cor}$ values of the bis and tris complexes, using solutions having phosphorus ester:cobalt chloride mole ratios (MR) of (a) 2.0 in nitrobenzene–cyclohexane solutions and (b) a limiting high value in *tert*-butylbenzene solution (see Experimental Section).

The equilibrium of eq 1 is then to be studied at lower mole ratio (MR) values in *tert*-butylbenzene, where cobalt(II) complexes in both quartet (A) and doublet (B) spin states are present. To simplify the notation, let this be written

$$A + L \rightleftharpoons B \quad (3)$$

The equilibrium constant of eq 3 can be expressed in terms of the solute mole fractions N_A and N_B ($= 1 - N_A$) of the cobalt species A and B as

$$1/K_{eq} = K' = \frac{N_A M(MR + N_A - 3)}{1 - N_A} \quad (4)$$

whence a plot of the function

$$MR + N_A - 3 = K'\left(\frac{1 - N_A}{N_A M}\right) \quad (5)$$

should give a straight line of slope K' and zero intercept.

Following Everett and Holm,[25] we have

$$N_A = \frac{\chi_M{}^{cor}{}_{obsd} - \chi_M{}^{cor}{}_B}{\chi_M{}^{cor}{}_A - \chi_M{}^{cor}{}_B} \quad (6)$$

where $\chi_M{}^{cor}{}_{obsd}$ is the susceptibility of the equilibrium mixture, calculated by eq 2 from the observed $\Delta\nu$ values. The problem is that the values of MW and DC to be used in eq 2 are now

Table V. Equilibrium Constants and Thermodynamic Functions from NMR Shift Data[a]

$CoCl_2L_2 + L \rightleftharpoons CoCl_2L_3$ in *tert*-Butylbenzene

Ligand	K_{eq}(30 °C)	$\Delta H°$, kcal/mol	$\Delta S°$, cal/(mol deg)
$P(OC_2H_5)_3$	$(2.06 \pm 0.19) \times 10^2$	-5.88 ± 0.26	-8.54 ± 0.85
$C_2H_5P(OC_2H_5)_2$	$(4.81 \pm 0.44) \times 10^3$	-8.57 ± 0.10	-11.9 ± 0.3
$(C_2H_5)_2POC_2H_5$	$(4.97 \pm 0.12) \times 10^2$	-13.9 ± 0.2	-33.2 ± 0.7

[a] The errors shown are one standard deviation from the least-squares fit.

weighted averages for the unknown equilibrium mixture of species A and B. The solution is to use only the dominant first term of the Evans equation to calculate a trial value of N_A

$$N_A \approx \frac{\Delta\nu_{obsd} - \Delta\nu_B}{\Delta\nu_A - \Delta\nu_B} \tag{7}$$

This is used to calculate trial weighted-average values of MW and DC which are put into eq 2 to get a trial value of $\chi_M{}^{cor}{}_{obsd}$. An improved value of N_A is then obtained from eq 6, and reiteration is continued until N_A becomes constant. The values of $\chi_M{}^{cor}$ and $\Delta\nu$ for species A in eq 6 and 7 are those determined in nitrobenzene. In the absence of specific solute interaction with each solvent, these values can be used for the *tert*-butylbenzene solutions.[51,52] The K_{eq} values reported in Table V were thus obtained by a linear least-squares fit of the function of eq 5; in all cases the intercepts were zero within one standard deviation. The K_{eq} values at 30 °C in *tert*-butylbenzene are based on studies in the following MR ranges: 5.000–10.00 with triethyl phosphite, 2.813–3.400 with diethyl phosphonite, and 2.505–6.059 with ethyl diethylphosphinite. The $\Delta H°$ and $\Delta S°$ values shown in Table V are based on K_{eq} determinations in the range 11–46 °C for a single value of MR in each system.

Equilibrium Constants from Spectrophotometric Data. In these systems, the major problem with the application of this technique is the solubility behavior described above. In *tert*-butylbenzene at 30 °C, spectrophotometric measurements made on the equilibrium cobalt(II) chloride–phosphonite and –phosphinite systems were limited by the solubility range available. Since the dichlorobis(phosphorus ester)cobalt(II) complexes are relatively insoluble in *tert*-butylbenzene, the conditions of phosphorus ligand:cobalt mole ratio and of concentration of free ligand had to be chosen to give solutions containing cobalt mostly in the form of the tris complexes. This also meant that the extinction coefficients of the bis species were unknown. As the phosphorus ligand:cobalt mole ratios of such solutions were raised well above 3, the growth of the characteristic spectral features of the tris complexes leveled off as equilibrium 1 was shifted nearly completely to the right. Thus, good initial trial values were available for the extinction coefficients of the tris complexes. Equilibrium constants were calculated from data on solutions in the same mole ratio ranges used in the NMR shift studies; such solutions do contain significant concentrations of both types of complex.

First, it was established by the matrix rank method[53] that in each case the absorbance data at several wavelengths were accounted for by an equilibrium involving two absorbing species only. This is supported by the observation of an isosbestic point in each system (Table IV).

Using the notation of eq 3, one can write

$$1/K_{eq} = K' = [A][L]/[B] \tag{8}$$

and knowing the total cobalt concentration M and the total ligand concentration C_L, then the absorbance is given by

$$\text{Abs} = [A](\epsilon_A - \epsilon_B) + \epsilon_B M \tag{9}$$

where ϵ stands for the molar extinction coefficient of the designated species. By algebraic substitution, one obtains

$$\text{Abs} = \left\{\frac{-(K' + C_L - 3M) + [(K' + C_L - 3M)^2 + 4MK']^{1/2}}{2}\right\} \times (\epsilon_A - \epsilon_B) + \epsilon_B M \tag{10}$$

A nonlinear least-squares program[54] was used to fit this function to each set of data consisting of observed absorbance, M, and C_L values by optimizing the values of the three adjustable parameters K', ϵ_A, and ϵ_B. Each data point was given unit weight. In the first round of calculations, ϵ_B values were held constant to obtain optimized initial values of ϵ_A and K'. In the second round, all parameters were allowed to vary. Absorbance data at two different wavelengths were used for each system. The results are shown in Table VI.

The K_{eq} values for *tert*-butylbenzene solutions at 30 °C from Table VI agree grossly with those from NMR shift data in Table V but leave much to be desired quantitatively. For each ligand studied, the K_{eq} value determined at a given wavelength is subject to a large uncertainty, and the K_{eq} values determined at different wavelengths are not in good quantitative agreement. Where the bis and tris complexes show the biggest difference in extinction coefficients, at about 23 kK, the absorbance data were fit mainly in terms of the tris species, and the ϵ_A values are completely uncertain. The optimized ϵ_B values at both wavelengths, however, are in good agreement with the values obtained from solutions with a large excess of ligand present (Table IV), which obey Beer's law for the tris complexes. The most telling criticism is that in various manipulations of the values of the parameters in the nonlinear least-squares calculations, it was found that the goodness of fit between observed and calculated absorbance values is highly insensitive to the value of the equilibrium constant. Because

Table VI. Equilibrium Constants from Spectrophotometric Data[a]

Ligand	λ, nm	ϵ_A	ϵ_B	K_{eq}	Absorbance[b] dev, %
		$CoCl_2L_2 + L \rightleftharpoons CoCl_2L_3$ in *tert*-Butylbenzene at 30 °C			
$C_2H_5P(OC_2H_5)_2$	435	0.01 ± 134	1188 ± 32	$(8.4 \pm 3.3) \times 10^3$	5.2
$C_2H_5P(OC_2H_5)_2$	620	316 ± 22	554 ± 5	$(7.7 \pm 2.4) \times 10^3$	2.1
$(C_2H_5)_2POC_2H_5$	456	20 ± 21	1005 ± 19	$(2.9 \pm 0.4) \times 10^2$	1.3
$(C_3H_5)_2POC_2H_5$	675	79 ± 10	454 ± 7	$(4.2 \pm 0.6) \times 10^2$	1.3
		$CoCl_2L_2 + L \rightleftharpoons CoCl_2L_3$ in Nitrobenzene at 20 °C			
$P(OC_2H_5)_3$	428	89 ± 5	636 ± 28	2.8 ± 0.4	8.7
$P(OC_2H_5)_3$	438	57 ± 6	759 ± 51	2.1 ± 0.3	10.5
$C_2H_5P(OC_2H_5)_2$	430	135 ± 5	906[c]	$(1.4 \pm 0.1) \times 10^3$	2.3
$C_2H_5P(OC_2H_5)_2$	591	145 ± 3	342[c]	$(6.9 \pm 0.7) \times 10^2$	1.1

[a] Errors shown are one standard deviation. [b] Absorbance deviation is the mean of $((|\text{Abs}_{calcd} - \text{Abs}_{obsd}|)/\text{Abs}_{obsd}) \times 100\%$ for each data point. [c] ϵ_B held constant. When all parameters were allowed to vary, the NLLS program failed to converge satisfactorily.

of the controversy[55] involving weighting factors in equilibrium constant calculations based on spectrophotometric data, the limited concentration range available for study in these systems, and the fact that at high ligand mole ratios (used to get initial ϵ_B values) there are nontrivial solvent medium effects on the spectra, elaborate efforts were made to get highly precise data. It is apparent that in the present experimental circumstances, the Evans NMR shift method is greatly to be preferred for obtaining the equilibrium constants.

Also shown in Table VI are equilibrium constants for the phosphite and phosphonite systems in pure nitrobenzene at 20 °C. Measurements with the phosphonite ligand were made difficult by the instability of the solutions due to slow ligand oxidation by the solvent when the ligand:cobalt mole ratio was greater than 2. In the triethyl phosphite system, this problem was compounded by the relatively small value of K_{eq}, requiring that a substantial excess of free ligand be present to shift the equilibrium to the right. A lesser experimental effort was made here, in that spectrophotometer cells and volumetric flasks were not calibrated, and no concentration correction was made for the variation in solution density from the temperature of solution preparation to that of measurement. While the K_{eq} values given for nitrobenzene solutions in Table VI appear to be good to no more than an order of magnitude, they do demonstrate that K_{eq} is 1–2 orders of magnitude less in nitrobenzene than in *tert*-butylbenzene.

Trends in the Equilibrium Constants. That the two *middle* members of the $(C_2H_5)_nP(OC_2H_5)_{3-n}$, $n = 0$–3, ligand series are the only ones for which tris complexes can be prepared in pure form is in agreement with the observed trend in K_{eq} values. The reason for this irregular variation in the series can be rationalized in terms of two opposing tendencies: the proper balancing of σ and π components of the coordinate bond and a steric effect. That the latter effect *can* be dominant is demonstrated by the nonexistence of the tris complex with triethylphosphine as ligand.

The same trend was found by Lukosius and Coskran[7] for equilibrium constants in the system $Ni(CN)_2L_2 + L \rightleftharpoons Ni(CN)_2L_3$, where $L = (CH_3)_nP(OCH_3)_{3-n}$, $n = 0$–3. The results with cobalt(II) and nickel(II) (four-coordinate)–(five-coordinate) equilibria contrast sharply with those for nickel(0) equilibria[3] of the type $NiL_4 + L' \rightleftharpoons NiL_3L' + L$ and for cobalt(II) equilibria[5] of the type $CoX_2L_2 + L \rightleftharpoons CoX_2L_3$ with secondary and tertiary phosphines, where a dominant role was claimed for the steric effect.

For the cobalt(II) systems $CoCl_2L_2 + L \rightleftharpoons CoCl_2L_3$, the K_{eq} values are 1–2 orders of magnitude less in nitrobenzene than in *tert*-butylbenzene (dipole moments 4.27 and 0.83 D, respectively[56]). This manifests the more favorable interaction of the more polar solvent with the four-coordinate complexes. One would expect that the dipole moments of the pseudotetrahedral complexes would be greater than those of the five-coordinate complexes.

The magnitudes of $\Delta H°$ and $\Delta S°$ reported in Table V are reasonable for a reaction in which an additional bond is formed, with a corresponding decrease in the translational entropy of the system. The decrease in spin multiplicity makes a contribution of −2.2 eu to $\Delta S°$.

Several peculiarities are apparent in the comparison of the results for the ethyl diethylphosphinite system with the results for the other two ester systems. These peculiarities suggest that distortion of the tris complex may occur with this, the most sterically hindered of the three $(C_2H_5)_nP(OC_2H_5)_{3-n}$ ligands which do form tris complexes. First, the value of $\Delta S°$ (Table V) for the phosphinite bis → tris reaction seems out of line. Second, the values of the magnetic moment and the Weiss constant of dichlorotris(ethyl diethylphosphinite)cobalt(II) (Table III) differ significantly from the values of the other tris complexes. Third, the characteristic electronic transition (Table IV) is at lower energy (21.9 kK) for the tris(phosphinite) complex than for the corresponding phosphonite and phosphite complexes (23.0 and 22.9 kK, respectively). Finally, a significant difference is observed for the phosphinite complex in the reactions of the three tris complexes with dioxygen.[10]

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Registry No. $CoCl_2(P(OC_2H_5)_3)_2$, 58673-01-1; $CoCl_2(P(OC_2H_5)_3)_3$, 22016-97-3; $CoCl_2(C_2H_5P(OC_2H_5)_2)_2$, 58673-02-2; $CoCl_2(C_2H_5P(OC_2H_5)_2)_3$, 58673-03-3; $CoCl_2((C_2H_5)_2POC_2H_5)_2$, 58673-04-4; $CoCl_2((C_2H_5)_2POC_2H_5)_3$, 58673-05-5; $P(OC_2H_5)_3$, 122-52-1; $C_2H_5P(OC_2H_5)_2$, 2651-85-6; $(C_2H_5)_2POC_2H_5$, 2303-77-7.

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(2) Taken in part from the M.S. thesis of H. V. Studer (1972) and the Ph.D. dissertation of I. B. Joedicke (1976), Oregon State University. The partial support of this research by National Science Foundation Grant MPS75-05782 is gratefully acknowledged.

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Studies of Labile Carbonatocobaltate(III) Complexes. 2. Kinetics of Reactions of Tris(carbonato)cobaltate(III) Species with Ethylenediamine, 1,2-Propanediamine, and 1,3-Propanediamine in Aqueous Sodium Bicarbonate Media. Unusually Stable Half-Bonded Bis(carbonato)diaminecobaltate(III) Intermediates[1,2]

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The kinetics of the title reactions have been investigated by stopped-flow and conventional spectrophotometry in aqueous $NaHCO_3$–$NaClO_4$ media at $8 \lesssim pH \lesssim 10.5$ and ionic strength 1.0 M. Formation of chelated $Co(CO_3)_2(diamine)^-(aq)$ complexes proceeds via unusually stable, brown, half-bonded diamine species with near-uv charge-transfer spectral characteristics. The kinetic data for rapid formation of these half-bonded diamine intermediates at 25.0 °C are consistent with an associative interchange mechanism involving unusually stable reaction precursors with ethylenediamine and 1,2-propanediamine. The rate constant for aquation of half-bonded $Co(CO_3)_2enHCO_3^{2-}(aq)$ to produce a half-bonded aquo analogue with a similar charge-transfer spectrum is $(8.9 \pm 0.1) \times 10^{-2}\ s^{-1}$ at 25.0 °C, with $\Delta H^{\ddagger}_{-2} = 18.2 \pm 1.1$ kcal mol^{-1} and $\Delta S^{\ddagger}_{-2} = 2 \pm 4$ cal $deg^{-1}\ mol^{-1}$ at 25.0 °C. Low rates of ring closure to form $Co(CO_3)_2(diamine)^-(aq)$ (lowest for 1,3-pn) are also consistent with high conformational stability in the half-bonded intermediates, presumably as a result of hydrogen bonding to chelated carbonate. Ring closure in half-bonded $Co(CO_3)_2(diamine)HCO_3^{2-}(aq)$ is considerably faster than in $Co(CO_3)_2(diamine)H_2O^-(aq)$. Available evidence indicates very different solution properties for carbonato- and aquocobalt(III) complexes containing pyridine and saturated diamine ligands.

Introduction

In part 1 of this series[2] we reported a study of the kinetics of the second-order reaction of excess pyridine, py, with solutions of $Na_3[Co(CO_3)_3]{\cdot}3H_2O$ in aqueous sodium bicarbonate. The product of the reaction was found to be *cis*-$Co(CO_3)_2py_2^-(aq)$. Dependences of the reaction rate on acidity and free bicarbonate concentration, $[HCO_3^-]$, were interpreted in terms of equilibria 1 and 2, involving monomeric

$$Co(CO_3)_3^{3-}(aq) + H_3O^+ \rightleftharpoons Co(CO_3)_2(HCO_3)(H_2O)^{2-}(aq) \quad K_h \qquad (1)$$

$$Co(CO_3)_2(HCO_3)(H_2O)^{2-}(aq) + H_2O \rightleftharpoons Co(CO_3)_2(H_2O)_2^-(aq) + HCO_3^-(aq) \quad K_{H_2O} \qquad (2)$$

cobalt(III) species with $Co(CO_3)_2(H_2O)_2^-(aq)$ as the most rapidly substituted by py. Although it was apparent that this complex is a minor component of such solutions at $8 \lesssim pH \lesssim 10$ and analytical bicarbonate concentrations in the range 0.1–1.0 M, it was also noted that the fraction of cobalt(III) in this form would be most significant at low $[HCO_3^-]$ and low pH, conditions which sometimes obtain in syntheses involving reactions of amines with the much more soluble potassium carbonatocobaltate(III) salt in aqueous potassium bicarbonate.[3,4]

During the course of the above studies it was noticed that addition of ethylenediamine, en, 1,2-propanediamine, 1,2-pn, and 1,3-propanediamine, 1,3-pn, to green sodium carbonatocobaltate(III) solutions in 1 M $NaHCO_3$ caused a rapid color change to brown. On standing, these brown solutions slowly became purple and exhibited visible absorption spectra characteristic of carbonato(diamine)cobalt(III) complexes.[3,4] Addition of the above diamines was accompanied by an immediate increase in pH, as was also the case with the strong proton bases ammonia and 1,6-hexanediamine; however, no brown coloration was observed with the latter two ligands, indicating that the rapid initial color change was due to specific interactions of the green carbonatocobaltate(III) complexes with ethylenediamine and 1,2- and 1,3-propanediamines.

In this paper we report that the reactions of the three title ligands with aqueous solutions of $Na_3[Co(CO_3)_3]{\cdot}3H_2O$ consist of at least three separate processes, which have been