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The ligands in the series $Et_nP(OEt)_{3-n}$, n = 0 - 3, all form pseudotetrahedral high-spin bis-complexes with cobalt (II) chloride. Magnetic, spectrophotometric, conductivity, and molecular weight data show that the phosphorus ester ligands (but not the phosphine) also form five-coordinate low-spin tris-complexes; these can be isolated with the phosphonite and phosphinite ligands, while the existence of the tris-phosphite is marginal. At cobalt (II) to phosphorus ester mole ratios of 1:2, a mixture of species is present in all cases. All are non-conducting in nitrobenzene. The ester complexes are much more susceptible to autoxidation than is the phosphine complex.

Some Transition Metal Complexes of Trivalent Phosphorus Esters

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SOME TRANSITION METAL COMPLEXES OF TRIVALENT PHOSPHORUS ESTERS

I. INTRODUCTION

The series of compounds: $:PR_n(OR)_{3-n}$, n = 0 - 3, represents a group of Lewis bases or ligands in which successive replacement of alkyl groups (R) by more electronegative groups (OR) occurs as n decreases from three to zero. This systematic variation in the electronegativity of substituents on the phosphorus donor atom offers the possibility of an experimental assessment of certain features of coordinate bonding in transition metal complexes.

Trivalent phosphorus bases coordinate to transition metal ions by a sigma bond of the regular Lewis acid -base adduct type. In addition, it is commonly supposed that back pi bonding occurs, in which electrons of the metal are in d orbitals of appropriate symmetry to interact with low-lying empty d orbitals of phosphorus. This combination of sigma and pi bonding is described as synergistic, since the two effects together avoid the unfavorable charge distribution which either would lead to alone (Cotton and Wilkinson, 1966).

Changing the electronegativity of the substituents in the phosphorus base should, by the inductive effect, affect the sigma - pi balance of the coordinate bond. Thus the trialkylphosphinés, R_3P,

are fairly strong sigma electron pair donors, and the question of the significance of pi bonding in their complexes is a matter of current controversy. At the other extreme is phosphorus trifluoride, PF_3, which has negligible basic properties. Its complexes are best regarded as derivatives of the metal carbonyls, and the back pi bonding is considered to be of major importance.

Examples of the series $PR_n(OR)_{3-n}$ are known for all values of n. For the specific case $R = C_2H_5$, ethyl (abbreviated Et), the formulas and names are given in Table I.

Table I. Formulas and Names of the Compounds $PEt_n(OEt)_{3-n}$.

Et_3P	Triethylphosphine
Et_2POEt	Ethyl Diethylphosphinite
$EtP(OEt)_2$	Diethyl Ethylphosphonite
$P(OEt)_3$	Triethyl Phosphite

Trialkylphosphines are very common ligands and many metal complexes have been made containing them. Trialkyl phosphite complexes are much less common, and those of dialkyl alkylphosphonites and especially alkyl dialkylphosphinites are very rare.

It is the purpose of this research to study the coordinating behavior of the series of ligands $Et_nP(OEt)_{3-n}$ toward the reference acid cobalt(II) chloride. The work involves synthesis of the complexes,

and their characterization by various physical measurements which will provide information on complex geometry and factors affecting the coordinate bond.

II. HISTORICAL

A. Cobalt Complexes of Trivalent Phosphorus Bases

Developments in the chemistry of transition metal complexes of trialkylphosphines up to 1964 have been comprehensively reviewed (Booth, 1964). The system triethylphosphine - cobalt(II) chloride has been extensively studied, both in this laboratory (Hatfield and Yoke, 1962; Schmidt and Yoke, 1971) and elsewhere (Jensen, 1936; Jensen, Nielsen, and Pedersen, 1963; Jensen and Jørgensen, 1965; Nicolini, Pecile, and Turco, 1965). The only complex in this system, both in organic solvents and in the solid state, is dichlorobis(triethyl phosphine)cobalt(II), $CoCl_2(PEt_3)_2$. This complex has been thoroughly characterized by spectroscopic, magnetochemical, and other techniques. It is monomeric and is a typical example of a high-spin pseudo-tetrahedral cobalt(II) complex.

More complicated behavior has been observed in other trialkylphosphine-cobalt(II) salt systems. For example, $Co(SCN)_2(PEt_3)_2$ is believed (Nicolini, Pecile, and Turco, 1966; idem, 1965) to be polymeric in the solid state, with five- or six-coordinate cobalt. In organic solvents, there is magnetic, spectroscopic, and other evidence for an equilibrium between a dimeric five-coordinate low-spin complex and a monomeric tetrahedral high-spin complex. If an excess of triethylphosphine is added to such a solution, the monomeric

low-spin five-coordinate complex $Co(SCN)_2(PEt_3)_3$ is formed (Boschi, Nicolini, and Turco, 1966). In the analogous tri-n-propylphosphine - thiocyanate system, the monomeric five-coordinate complex is the only one that exists (Boschi et al., 1966), even in the solid state and even if a deficiency of the phosphine ligand is used. However, cobalt(II) halides were found to give only four-coordinate high-spin complexes (Boshi et al., 1966).

With an aliphatic phosphine, Et_2PH, the higher complex $CoCl_2(Et_2PH)_4$ was formed in addition to the bis-complex $CoCl_2(Et_2PH)_2$ (Hatfield and Yoke, 1962). The higher complex represents one of the few examples of low-spin six-coordinate cobalt-(II) (Issleib and Döll, 1960). The aromatic secondary phosphine $(C_6H_5)_2PH$ gave the low-spin five-coordinate complex $CoBr_2[HP(C_6H_5)_2]_3$ (Issleib and Wenschuh, 1960).

No specific cobalt(II) chloride - triethyl phosphite complex appears to have been prepared. Coordination in cobalt(II) halide - trialkyl phosphite mixtures has been postulated (Arbuzov and Zoroastrova, 1952) on the basis of color changes. No solid complexes could be isolated. Other Russian workers (Zgadzai, Naumova, and Troitskaya, 1967) proposed tetrahedral high-spin coordination on the basis of spectrophotometric and magnetic susceptibility studies of ethanol solutions of various trialkyl phosphites with cobalt(II) ion. In concentrated solutions, a decrease in susceptibility was observed and

was attributed to polymer formation. Unfortunately, the anion involved was not mentioned in the abstract, and the original article is not available. With nitrate and perchlorate anions, Verkade and co-workers (1967) found that trialkyl phosphites caused disproportionation of cobalt(II) to the (I) and (III) oxidation states. The disporportionation occurred simply on mixing the reagents in acetone. The cobalt(I) species was five-coordinate, $[Co(P(OR)_3)_5)]^+$. The cobalt(III) product was $[Co(P(OR)_3)_6]^{+3}$, in which a very strong ligand field was observed, comparable to that of cyanide in $[Co(CN)_6]^{-3}$.

With cobalt(II) chloride and trialkyl phosphites, addition of a base (such as triethylamine) causes spontaneous reduction to cobalt(I) (Vol'pin and Kolomnikov, 1966). Whether the oxidation product is cobalt(III) or is derived from the phosphite is not stated. This resembles the coordination of nickel(II) halides by tertiary phosphites (Ginzberg, Zgadzai, and Troitskaya, 1968; Jensen, Nygaard, Elisson, and Nielsen, 1965), followed by their spontaneous reduction to nickel(0) phosphite complexes on addition of base (Vinal and Reynolds, 1964). Starting with cobalt(II) chloride, the d^8 cobalt(I) complexes isolated have been the five-coordinate diamagnetic $CoCl[P(OR)_3]_4$ and the four-coordinate paramagnetic $CoCl[P(OR)_3]_3$ (Vol'pin and Kolomnikov, 1966). These are of interest in that they absorb carbon monoxide and molecular hydrogen, and act as homogeneous hydrogenation catalysts. The complexes $[Co(P(OR)_3)_4]_2$ and $HCo[P(OR)_3]_4$ of cobalt(0) and

cobalt(-1) are formed by hydrogenation of the cobalt(I) complexes (Vol'pin and Kolomnikov, 1966) and can also be obtained from cobalt(II)-phosphite mixtures by hydrogenation (Mullineaux, 1966) or by treatment with potassium graphitate (Jensen et al., 1965).

The relative coordinating abilities of phosphorus bases toward magnesium halides have been placed in the series $Et_3P > Et_2POEt > Et(P(OEt)_2 > P(OEt)_3$ by Sander (1960). He was concerned with breaking up the magnesium halide adducts formed during the Grignard synthesis of the organophosphorus compounds, and did not isolate the complexes in pure form. Since only sigma bonding would be involved in complexes of magnesium, this order would not be applicable to other metal complexes where sigma and pi bonding features shift in the phosphorus base series.

Diethyl ethylphosphonite and ethyl diethylphosphinite have been described by Sander (1960), by Razumov, et al., (1952) and by Arbuzov and Rizpolozhenskii (1953). Part of the classical proof that the structures of these classes of compounds involve trivalent phosphorus was based on their ability to form complexes with metal salts. Usually such complexes were prepared as derivatives for purposes of characterization of the organophosphorus compounds. There has been no systematic study of the coordination chemistry of such ligands. Apparently no cobalt(II) complexes of dialkyl alkylphosphonites or of alkyl dialkylphosphinites have been prepared. A nickel iodide complex

of dimethyl methylphosphonite has been described recently (Coskran, 1969), with the formula $[NiI_2 \cdot 3RP(OR)_2]$. The proposed structure was trigonal bipyramidal with the iodine ligands being equitorial; the analogous cyanide complex was said to have the anionic ligands in axial positions.

B. Spectra and Magnetism of Cobalt(II) Complexes

The cobalt(II) ion has a d^7 configuration, and may have either three or one unpaired electrons, corresponding to quartet or doublet spin states. These give effective magnetic moments of 3.86 and 1.73 Bohr Magnetons, respectively, according to the "Spin-Only" formula. In practice, even if there are considerable deviations from the ideal values, the two spin states are easily distinguished by paramagnetic susceptibility measurements.

The two most common coordination geometries for cobalt(II) complexes are tetrahedral and octahedral. Low-spin tetrahedral complexes are unknown, and even for octahedral complexes the doublet state for cobalt(II) is rare, being found only with a few strong field ligands. Usually tetrahedral and octahedral high-spin cobalt(II) complexes are readily distinguished by their visible spectra (Cotton and Wilkinson, 1966). Commonly, octahedral complexes have a weak absorption in the blue, and look pink; for example, hexaquocobalt(II) ion has an absorption at 18.9 kK, $\log\epsilon$ 1.0, with a shoulder at 20.4 kK,

logϵ 0.7 (Carlin, 1965). The two components of this peak are $^4T_{1g}(F) \rightarrow {}^4A_{2g}$ and $\rightarrow {}^4T_{1g}(P)$ in O_h symmetry. Tetrahedral complexes have a somewhat stronger absorption in the red, and usually look blue. This transition, $^4A_2 \rightarrow {}^4T_1(P)$ in T_d symmetry, is often split into several partly resolved components by spin-orbit coupling and especially by any decrease in symmetry, giving a structured peak in the region 13.5 to 18 kK with log ϵ values of 2.5 to 3. For example, $CoCl_2(PEt_3)_2$ has absorptions at 13.7, 16.1, and 16.5 kK, with log ϵ values of 2.7, 2.8, and 2.8 respectively, and no higher energy transitions in the visible region (Schmidt and Yoke, 1971; Jensen and Jørgensen, 1965). The tetrahedral complexes, having an orbitally non-degenerate ground state, come closer to the spin-only value of effective magnetic moment than the octahedral complexes do. In practice, moments from 4.3 to 4.9 B.M. are observed for tetrahedral complexes, being smaller the larger the ligand field strength is, while moments for octahedral complexes fall in the range 5.0 to 5.5 B.M.

Five coordinate cobalt(II) complexes are known with both trigonal bipyramidal and square pyramidal geometries, and in both doublet and quartet spin states for each geometry. Their spectra have been discussed by Ciampolini (1969). Most of the complexes prepared have actually been of low symmetry, not only because a number of different donor atoms have been involved and because polydentate

chelate ligands have often been used, but also because of severe angular distortions from idealized D_{3h} and C_{4v} symmetry. Illustrated in Ciampolini's review are many of the special polydentate ligands used in early work in the field. These often may give rise to five-coordinate complexes for steric reasons associated with the ligand rather than because of electronic effects associated with the cobalt(II) center. Simple examples of complexes with five identical monodentate ligands are rare, but are now known in three of the four possible cases. Examples are known in all four cases of complexes with five monodentate but not identical ligands.

For the high spin square pyramidal case, there exist pentakis-(trimethylphosphine- and arsine oxide)cobalt(II) perchlorate (Brodie, Hunter, Rodley, and Wilkins, 1968) and perchloratotetrakis(methyldiphenylarsine oxide)cobalt(II) perchlorate (Lions, Dance, and Lewis, 1967). These are characterized by moments of 4.8 to 5.5 B.M. and a series of strong absorption bands in the 16 to 20 kK region. For the high spin trigonal bipyramidal case, there exist pentakis(2-picoline-N-oxide)cobalt(II) perchlorate (Byers, Lever, and Parish, 1968) and μ-dichlorodichlorotetrakis(trimethylamine oxide)dicobalt(II) (Herlocker, 1969). These are characterized by moments of 4.5 to 4.9 B.M. and by a series of absorptions in the 16 to 20 kK region, distinguishable in shape and intensity from the square pyramidal case.

Among the low spin cases, there is for a trigonal bipyramidal

example the complex dibromotris(diphenylphosphine)cobalt(II) (Issleib and Wenschuh, 1960). The magnetic moment has been reported in the range 2.0 to 2.4 B.M., but the spectrum has not been given. The structure shows severe distortions (Bertrand and Plymale, 1966). As square pyramidal examples, there exist pentacyanocobaltate(II) and penta(methyl- or phenyl-isonitrile)cobalt(II) ions (Kimball, Pratt, and Kaska, 1968), and dibromo- or iodo- tris(dimethylaminodifluorophosphine)cobalt(II) and diiodotris(bisdimethylaminofluorophosphine)-cobalt(II) (Nowlin and Cohn, 1971; Nowlin, 1971). These are characterized by moments in the range 1.8 to 2.4 B.M., and by an absorption band in the region 14.3 to 16.2 kK and a stronger peak at 22 to 25 kK.

The 14.3 to 16.2 kK absorption might be taken to indicate high-spin tetrahedral species. Thus, Boschi, Nicolini, and Turco (1966), in studying the equilibrium

$$Co(NCS)_2 \cdot 3PR_3 \rightleftharpoons Co(NCS)_2 \cdot 2PR_3 + PR_3 \ ,$$

associated the variation in intensity of absorption in this region with shifts in the position of equilibrium, an increase meaning a shift to the right. However, Nowlin and Cohn (1971), studying the equilibrium

$$CoX_2 \cdot 3R_2NPF_2 \rightleftharpoons CoX_2 \cdot 2R_2NPF_2 + R_2NPF_2$$

found exactly the opposite effect. Absorption in this typical

"tetrahedral" region was not found for the low-spin five-coordinate complexes dicyanotris(phenyldiethylphosphine)cobalt(II) (Rigo, Bressan, and Turco, 1968) or for $[Co(SP)_2Br]ClO_4$, where SP is diphenyl(o-methylthiophenyl)phosphine, or for its selenium analogue (Dyer and Meek, 1967). However, absorption in this region has been found in most cases, including the examples with monodentate ligands given above, as well as the cases of $[Co(AP)_2X]ClO_4$, where AP is diphenyl(o-diphenylarsinophenyl)phosphine and X is Cl, Br, and I (Dyer and Meek, 1967), and of $[Co(dpe)_2X]X$, where dpe is 1,2-bis (diphenylphosphino)ethane and X is Cl, Br, and I (Horrocks, Van Hecke, and Hall, 1967). The actual structures of many of the complexes are intermediate between the square pyramidal and trigonal bipyramidal extremes, and these distortions may be related to the occasional absence of absorption in the 14.3 to 16.2 region. Any question about the simultaneous presence of high-spin tetrahedral complexes and low-spin five-coordinate complexes is immediately resolved by measurement of the magnetic moment.

The one spectroscopic feature which seems clearly diagnostic of low-spin square pyramidal cobalt(II) complexes is a peak at about 22 to 25 kK, commonly with log ϵ of 2 - 3. (Tetrahedral complexes may also have an observable spin-forbidden transition here, but it is two orders of magnitude weaker.) Low spin trigonal bipyramidal complexes have a similar band at slightly lower energy, about 20 kK,

and of course distorted complexes with intermediate structures can have bands falling anywhere in the 20 to 25 kK region and of even greater intensity.

Finally, relatively rare examples are known of square planar cobalt(II) complexes, of low spin and possibly of high spin; their spectra have not been studied (Carlin, 1965).

III. EXPERIMENTAL

A. Materials

1. Preparation and Purification of Ligands

a. Ethyl Diethylphosphinite. Diethylchlorophosphine (bp 131-132°) was prepared (55% yield) by the reaction of ethyldichlorophosphine with tetraethyl lead (Beeby and Mann, 1951). A 33.3 g quantity of diethylchlorophosphine in 100 ml of absolute ether was added dropwise under nitrogen to a stirred solution of 12.2 g (15.5 ml) of absolute ethanol and 39.6 g (42.3 ml) of N, N-diethylaniline in 400 ml of absolute ether at 0°. The aniline hydrochloride was removed by filtration under nitrogen in a dry box, the solvent was removed from the filtrate by distillation, and the product was purified by trap to trap distillation in the vacuum line; yield ca. 30 ml.

b. Diethyl Ethylphosphonite. Ethyldichlorophosphine (bp 112°) was prepared (61% yield) by the reaction of phosphorus trichloride and tetraethyl lead (Kharasch, Jensen, and Weinhouse, 1949). An additional sample was used as received from the Ethyl Corporation. A 68.1 g quantity of ethyldichlorophosphine in 50 ml of absolute ether was added dropwise under nitrogen to a stirred solution of 48.0 g (60.8 ml) of absolute ethanol and 155 g (166 ml) of N, N-diethylaniline in 30 ml of absolute ether at 0°. The amine hydrochloride was

removed by filtration under nitrogen in a dry box, the solvent was stripped from the filtrate, and the product was distilled at reduced pressure, with a middle fraction taken; bp (uncorr) 43.5-45° (10 torr); (Razumov, Mukhacheva, and Sim-Do-Khen, 1952, bp 137-9°, 760 torr).

c. Triethyl Phosphite. Triethyl phosphite was prepared as follows (Ford-Moore and Perry, 1951). A solution of 34.4 g (21.9 ml) of phosphorus trichloride in 100 ml of light petroleum ether was added dropwise under nitrogen to a cold stirred solution of 34.5 g (43.7 ml) of absolute ethanol and 112 g (119 ml) of N,N-diethylaniline in 250 ml of light petroleum ether. The amine hydrochloride was removed by filtration under nitrogen in a glove box, the solvent was stripped from the filtrate, and the product was distilled at a reduced pressure. A middle fraction was taken up; bp (uncorr) 57-58° (16 torr); redistilled; bp 48-49° (12 torr).

2. Solvents

a. Nitrobenzene. Nitrobenzene (Matheson, Coleman, and Bell) was allowed to stand over Linde Type 4A molecular sieves (Matheson, Coleman, and Bell 4-8 mesh) for a day or more and was subsequently purified by vacuum distillation. The material was degassed on the vacuum line and immediately used, or was stored in a glass-stoppered flask within a nitrogen-filled dry box; bp (uncorr)

96.2° (15 torr); (Chemical Rubber Publishing Company Handbook, 1968, 84.9° (10 torr)).

b. Ethanol. A 250 ml quantity of absolute ethanol and about 5 g of magnesium turnings were maintained at reflux in a 500 ml flask for two hours and then distilled. A short forerun was discarded, and the ethanol was then collected at 77.5-78.0° (uncorr).

c. Other Solvents. Benzene, hexane and ether were distilled from sodium wire. All solvents were degassed on the vacuum line immediately prior to use.

3. Other Materials

Anhydrous cobalt(II) chloride was prepared by the dehydration of the Reagent Grade hexahydrate at approximately 400° in a stream of hydrogen chloride. Phosphorus trichloride (Reagent Grade) was distilled under nitrogen; bp (uncorr) 75-76°. N,N-diethylaniline was distilled; bp (uncorr) 94-95.5° (10 torr).

Unless otherwise noted all other chemicals were of Reagent Grade quality.

4. Preparation of Complexes

a. Dichlorobis(ethyl diethylphosphinite)cobalt(II). A 1.4508 g (11.17 mmole) quantity of cobalt(II) chloride with 5.3374 g (39.79 mmole) of ethyl diethylphosphinite (mole ratio 1:3.56) in a vacuum

line reaction tube in the absence of 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 non-volatile residue consisted of a dark blue green oil. Anal. Calcd. for $CoCl_2(Et_2POEt)_2$: Cl, 17.81; C, 36.20; H, 7.59. Found: Cl, 17.77; C, 36.53; H, 7.14. An additional sample of the bis-complex was prepared by condensing onto 0.5431 g (4.18 mmole) of cobalt(II) chloride a 1.1448 g (8.53 mmole) quantity of ethyl diethylphosphinite (mole ratio 1:2.04). About 10 ml of benzene was then condensed into the vacuum line reaction tube. After 18 days all the blue solid had dissolved to give a green solution. The solvent was then pumped off.

b. Dichlorotris(ethyl diethylphosphinite)cobalt(II). Similarly, a 0.2579 g (1.987 mmole) quantity of cobalt(II) chloride dissolved in a solution of 0.7918 g (5.902 mmole) of ethyl diethylphosphinite (mole ratio 1:2.97) in 10 ml of benzene in five days. The solvent was then pumped off, leaving a dark green black solid, $CoCl_2(Et_2POEt)_3$, m.p. 49.6^{o} (sealed tube).

c. Dichlorobis(diethyl ethylphosphonite)cobalt(II). Similarly, a 0.9317 g (7.176 mmole) quantity of cobalt(II) chloride dissolved in a solution of 2.1864 g (14.56 mmole) of diethyl ethylphosphonite (mole ratio 1:2.028) in 25 ml of benzene in 15 days. All volatile material was then pumped off, leaving a viscous blue-green oil. Anal. Calcd. for $CoCl_2(EtP(OEt)_2)_2$: Co, 13.56; C, 33.51; H, 7.03. Found:

Co, 13.29; C, 32.47; H, 6.85. An additional sample of the bis-complex was obtained similarly when 1.1247 g (8.666 mmole) of cobalt(II) chloride dissolved in five days in a solution of 2.6032 g (17.33 mmole) of diethyl ethylphosphonite in 10 ml of n-hexane, followed by removal of the solvent in vacuo.

d. Dichlorotris(diethyl ethylphosphonite)cobalt(II). Similarly, a 0.4255 g (3.278 mmole) quantity of cobalt(II) chloride dissolved in a solution of 1.4776 g (9.834 mmole) of diethyl ethylphosphonite (mole ratio 1:3.00) in 10 ml of benzene in four days. The solvent was pumped off, leaving a dark green-black solid. This was washed in the dry box with hexane under nitrogen and dried; $CoCl_2[EtP(OEt)_2]_3$, m.p. 51.9° (sealed tube).

e. Dichlorobis(triethyl phosphite)cobalt(II). Mixtures of anhydrous cobalt(II) chloride and triethyl phosphite in benzene with cobalt to phosphorus mole ratios of either 1:2 or of 1:3 gave dichlorobis(triethyl phosphite)cobalt(II) on removal of the solvent and pumping to constant weight. For example, in the dry box under nitrogen, 4.4368 g (26.70 mmole) of triethyl phosphite was added to 1.7315 g (13.33 mmole) of anhydrous cobalt(II) chloride in a reaction tube (mole ratio 1:2.00). The reaction tube was then attached to the vacuum line and 20 ml of benzene was condensed into it. The mixture was allowed to stand at room temperature for one week, and the solvent was pumped off leaving a dark blue-black solid. This was washed with

hexane in a nitrogen-filled dry box, dried and stored under vacuum; m.p. (sealed tube, uncorr) 59.5-60.5°. Anal. Calcd. for $CoCl_2(P(OEt)_3)_2$: Co, 12.75; C, 31.19; H, 6.54. Found: Co, 12.66; C, 30.73; H. 6.51. When, in the same way, cobalt(II) chloride and triethyl phosphite were combined in a mole ratio of 1:3.01 and the system was pumped to constant weight, the bis-complex was again obtained. Anal. Found: Co, 12.73.

Dichlorobis(triethyl phosphite)cobalt(II) was soluble in acetone, alcohol, nitrobenzene, and somewhat soluble in benzene. It was not soluble in hexane, except in the presence of an excess of triethyl phosphite, when it dissolved partially to give a dark green solution.

B. Analytical Methods

The chloride content was determined gravimetrically.

Cobalt content was determined by potentiometric back titration of hexacyanoferrate(III) ion (bright Pt electrode vs. S. C. E.) with standard cobalt(II) chloride solution (Chirnside, Cluley, and Profitt, 1947). Accurately weighed cobalt samples, from 0.20 to 0.25 g, were evaporated to dryness three times with concentrated nitric acid on a steam bath, and then redissolved in water. A buffer, consisting of 75 ml of concentrated aqueous ammonia and 75 ml of concentrated (300 g/l) ammonium monohydrogen citrate, was added next to each sample, followed by a 25.00 ml aliquot of standard potassium

hexacyanoferrate(III) solution. Crushed ice was added to lower the temperature of the solution to about 5°. The excess of hexacyanoferrate(III) ion was back-titrated with standard cobalt(II) chloride solution.

A 0.05 M cobalt(II) solution was standardized by gravimetric chloride analysis, using 25.00 ml aliquots. A 0.05 M potassium hexacyanoferrate(III) solution was then standardized against the cobalt(II) chloride solution by potentiometric titration, as above.

Carbon and hydrogen microanalyses were performed by C. F. Gieger, Ontario, California.

C. Physical Measurements

Spectral and conductivity cells and Gouy and melting point tubes were loaded under nitrogen in a dry box.

1. Infrared Spectra

Infrared spectra, in the range 4000 to 625 cm^{-1}, were recorded on a Beckman Model IR-8 double-beam recording spectrophotometer. Sodium chloride cells were used. Spectra of the neat oils were obtained using thin films. Spectra of the solids were obtained using Nujol mulls. The wavelength scale was calibrated with the spectrum of a polystyrene film.

2. Electronic Spectra

A Beckman Model DK-2 double-beam recording spectrophotometer was used to record solution spectra in the ultraviolet, visible, and near-infrared regions (50,000 to 4,000 cm^{-1}). A pair of one centimeter near-infrared silica cells was used for solution studies. These cells were capped with ground-glass stoppers for studies of air-sensitive solutions.

3. Magnetic Susceptibility Measurements

The effective magnetic moments were obtained at room temperature using the Gouy method. Measurements were made at a field strength of about 5 kgauss, using an Alpha Model AL 7500 water-cooled magnet with 4 inch pole faces and a 1.5 inch air gap. The strength of the magnetic field was controlled by adjusting the current from an Alpha Model 7500 power supply. The Gouy tube used for powders and neat liquids was calibrated with mercury(II) tetrathiocyanatocobaltate(II), prepared according to Figgis and Nyholm, (1958). The gram susceptibility of the calibrant at the temperature of each measurement was calculated from the equations:

$$\chi_g = (\chi_M^{corr} - 137 \times 10^{-6})/491.84$$

$$\chi_M^{corr} = 2.363/(T^oK + 10) + TIP$$

(Stevens and Yoke, 1970). A larger Gouy tube for solution measurements was calibrated with water, as described by Figgis and Lewis (1963).

The gram susceptibility, χ_g, of a complex was calculated from the equation

$$\chi_g = \frac{\beta F'}{W}$$

where β is the tube calibration constant, F' is the weight gain (in mg) of the paramagnetic sample in the magnetic field (corrected for diamagnetic contribution from the tube), and W is the weight of the sample (in g). The molar susceptibility, χ_M, was obtained by multiplying the gram susceptibility by the molecular weight. Pascal's Constants (Figgis and Lewis, 1963), and an experimental value of -104.8×10^{-6} cgsemu/mole for the diamagnetic susceptibility of triethyl phosphite (Chemical Rubber Publishing Company Handbook, 1968), were used to correct the molar susceptibility for diamagnetic contributions from the ligands. No correction for temperature independent paramagnetism was made. Magnetic moments, μ_{eff}, were calculated using the equation

$$\mu_{eff} = 2.828(T \cdot \chi_M^{corr})^{1/2} .$$

4. Conductivity Measurements

Conductivities of nitrobenzene solutions were measured with an Industrial Instruments Model R C 16B2 Conductivity Bridge and an Industrial Instruments conductivity cell. The cell constant of the conductivity cell was determined by the manufacturer to be 0.100 cm^{-1}.

The molar conductance, Λ_M (ohm^{-1} cm^2 $mole^{-1}$), is given by

$$\Lambda_M = (1000/M)(L)$$

where L (ohm^{-1} cm^{-1}) is the measured conductance multiplied by the cell constant and M is the concentration of the solution measured in moles per liter.

5. Cryoscopic Molecular Weight Determinations

Molal freezing point depressions of nitrobenzene solutions of the complexes were determined by use of a Beckman Differential Thermometer. Typically, a solution of about 1 g of complex in about 50 g of nitrobenzene was made up accurately by weight under nitrogen in a glove box and transferred to a dropping funnel with side-arm. The dropping funnel was removed from the glove bag and attached to a four-necked flask fitted with a Beckman Thermometer, glass stirrer, and gas inlet and outlet tubes (Lab Glass Inc. #ML 1660

Reaction Assembly). The system was purged with nitrogen and the solution was drained into the flask. A slow stream of nitrogen was passed through the flask and the contents were stirred vigorously. A slush bath of o-dichlorobenzene (-17°) was then placed around the flask and the change in temperature of the solution with time was recorded. A plot of the data was made and the freezing point was determined, relative to that observed for pure nitrobenzene.

6. Melting Point Determinations

The melting points of the solid complexes were taken in sealed capillary melting point tubes on a Laboratory Devices Mel-Temp melting point apparatus. The tubes were loaded under nitrogen in the dry box, capped with silicone putty, removed, and sealed off with a torch.

IV. RESULTS AND DISCUSSION

Bis-complexes $CoCl_2(Et_nP(OEt)_{3-n})_2$ occur throughout the series $n = 0 - 3$, as blue solids with the two extreme members, the phosphine and the phosphite, and as blue-green oils with the intermediate members, the phosphonite and the phosphinite. A tendency is observed for the coordination of an additional ligand except in the case of the phosphine. This tendency is especially strong in the case of the phosphonite and the phosphinite, where solid tris-complexes can be isolated. With the phosphite, the evidence for higher coordination is limited to spectrophotometric studies in solution.

The infrared spectra of the bis- and tris-complexes do not differ greatly from those of the free ligands. Both Jensen _et al._, (1963) and Miller (1965) make the observation that infrared spectra of phosphines are not changed markedly when they are present as ligands in metal coordination compounds. The similarity ensures that no isomerization of the ligand (Arbuzov Rearrangement) has taken place. Infrared spectra of the phosphonite, phosphinite and phosphite ligands are shown adjacent to those of their respective cobalt chloride complexes in Tables II - IV. Assignments for most of the absorption bands are designated in the tables. These were made by a careful comparison of the spectra of the ligands and their cobalt(II) chloride complexes and by reference to similar correlation studies in the literature. Particular attention was paid to the P-O-C bands. McIvor, Grant, and Hubley

Table II. Infrared Spectra (cm^{-1}) of Ethyl Diethylphosphinite and its $CoCl_2$ Complexes.

$EtOPEt_2$ (thin film)		$CoCl_2(EtOPEt_2)_2$ (thin film)		$CoCl_2(EtOPEt_2)_3$ (Nujol mull)	
3000m	CH_2 stretch	3000m	CH_2 stretch	3000m	CH_2 stretch
2952m		2960m		2955m	
2900m		2910m		2910m	
1460m	CH_3 def., anti-sym.	1462m	CH_3 def., anti-sym.	1460m	CH_3 def., anti-sym.
1415m	CH_2 scissor	1410m	CH_2 scissor	1410m	CH_2 scissor
1380m	CH_3 def., sym.	1385m	CH_3 def., sym.	1382m	CH_3 def., sym.
1275m	CH_2 wag (?)	1275m	CH_2 wag (?)	1273m	CH_2 wag (?)
1245m		1240m		1244m	
1162m	P-O-Et	1159m	P-O-Et	1160m	P-O-Et
1096s	P-O-Et	1095s	P-O-Et	1095s	P-O-Et
1056vs	P-O-C	1055vs	P-O-C	1056vs	P-O-C
1026s	P-O-C	1023s	P-O-C	1025s	P-O-C
950m	P-O-C	955m	P-O-C	950m	P-O-C
770m br	P-C (?) or sym	775m br	P-C (?) or sym	(800-760)m br	P-C (?) or sym
	P-O-Et		P-O-Et		P-O-Et
725w	CH_2 rock	726w	CH_2 rock	726w	CH_2 rock

Abbreviations: w weak, m medium, s strong, vs very strong, br broad.

Table III. Infrared Spectra (cm^{-1}) of Diethyl Ethylphosphonite and its $CoCl_2$ Complexes.

$(EtO)_2PEt$ (thin film)		$CoCl_2((EtO)_2PEt)_2$ (thin film)		$CoCl_2((EtO)_2PEt)_3$ (Nujol mull)	
2994m, 2949m, 2898m	CH_2 Stretch	3003m, 2958m, 2923m	CH_2 Stretch	3000-2000m	CH_2 Stretch
1453m	CH_3 Def., anti-sym.	1457m	CH_3 def., anti-sym.	1455m	CH_3 def., anti-sym.
1439m	CH_2 scissor	1435m	CH_2 scissor	1438m	CH_2 scissor
1385m	CH_3 def., sym.	1390m	CH_3 def., sym.	1392m	CH_3 def., sym.
1290m	CH_2 wag (?)	1282m	CH_2 wag (?)	1284m	CH_2 wag (?)
1160m	P-O-Et	1156m	P-O-Et	1158m	P-O-Et
1099m	P-O-Et	1097m	P-O-Et	1096m	P-O-Et
1050vs, 1031vs	P-O-C	1040vs	P-O-C	1045vs	P-O-C
1024vs	P-O-C	1020vs	P-O-C	1021vs	P-O-C
1003vs	P-O-C	995s	P-O-C	998vs	P-O-C
952s	P-O-C	940s	P-O-C	945s	P-O-C
800-740m br	P-C (?) or sym P-O-Et	793-730m br	P-C (?) or sym P-O-Et	790-735m br	P-C (?) or sym P-O-Et
695w	CH_2 rock	675w	CH_2 rock	680w	CH_2 rock

Abbreviations: w weak, s strong, vs very strong, br broad.

Table IV. Infrared Spectra (cm^{-1}) of Triethyl Phosphite and its $CoCl_2$ Complex.

$(EtO)_3P$ (thin film)		$CoCl_2((EtO)_3P)_2$ (Nujol mull)	
3003m, 2959m, 2915m	CH_2 stretch	3003m, 2959m, 2915m	CH_2 stretch
1479m	CH_3 def., anti-sym.	1479m	CH_3 def., anti-sym.
1445m	CH_2 scissor	1446m	CH_2 scissor
1389m, 1368m	CH_3 def., sym.	1389m, 1368m	CH_3 def. sym.
1290m, 1280m	CH_2 wag (?)	1290m, 1270m	CH_2 wag (?)
1163m	P-O-Et	1158m	P-O-Et
1095m	P-O-Et	1094m	P-O-Et
1030vs	P-O-C	1031vs	P-O-C
943s	P-O-C	950s	P-O-C
770m		765m	
740m	Sym. P-O-Et	725m	Sym. P-O-Et

Abbreviations: w weak, m medium, s strong, vs very strong, br

(1956) observed that a weak band occurs between 1107 and 1099 cm^{-1}, usually at 1105 cm^{-1}, in all EtO-P compounds. Assignments for C-C and C-H skeletal modes and for P-C stretches are extensions of the assignments that Kaesz and Stone (1959) gave to Et_3P.

Molar conductance data, given in Table V, show that the nitrobenzene solutions of the complexes, both at the 2:1 and at the 3:1 phosphorus to cobalt ratios, are all non-conducting. The molar conductance of a typical 1:1 electrolyte in about 10^{-2} Molar concentration in nitrobenzene at 25° is 20 - 30 ohm^{-1} cm^{2} $mole^{-1}$ (Kabesh and Nyholm, 1951). Cryoscopic data in the same solvent, given in Table VI, show that both the bis- and the tris- phosphonite and phosphinite complexes are undissociated and monomeric. Similarly, the bis- phosphite complex is monomeric and molecular, but the cryoscopic data indicate that little association of a third ligand occurs as additional phosphite is added to the bis-complex in solution. The elemental analyses, conductivity data, and molecular weight data thus indicate that the complexes $[CoCl_2(Et_2POEt)_3]$, $[CoCl_2(Et_2POEt)_2]$, $[CoCl_2(EtP(OEt)_2)_3]$, $[CoCl_2(EtP(OEt)_2)_2]$, and $[CoCl_2(P(OEt)_3)_2]$ exist as such in molecular form.

Room temperature magnetic moments for the complexes, as solids or neat liquids, are given in Table VII. These data are particularly important in relating the stoichiometric, conductivity, and molecular weight results to the electronic spectra discussed

Table V. Conductance of the Cobalt(II) Complexes in Nitrobenzene at Room Temperature.

Solution	Concentration (moles/l)	Conductance (ohm^{-1})	Molar Conductance (ohm^{-1} cm^2/mole)
Pure Solvent	---	(1)	---
$CoCl_2((EtO)_3P)_2$	6.716×10^{-3}	0.620×10^{-4}	0.923
$CoCl_2((EtO)_3P)_2$ + Extra $(EtO)_3$ (2)	7.996×10^{-3}	0.790×10^{-4}	0.988
$CoCl_2((EtO)_2PEt)_2$	6.834×10^{-3}	0.460×10^{-4}	0.673
$CoCl_2((EtO)_2PEt)_3$	5.562×10^{-3}	0.150×10^{-4}	0.270
$CoCl_2(EtOPEt_2)_2$	7.267×10^{-3}	0.170×10^{-4}	0.248
$CoCl_2(EtOPEt_2)_3$	6.421×10^{-3}	0.459×10^{-4}	0.715

(1) The conductance of the pure solvent is below the limits of the instrument.

(2) Components were mixed in a 1:1 mole ratio.

Table VI. Cryoscopic Molecular Weight Determinations for the Cobalt(II) Complexes in Nitrobenzene.

Complex	Experimental (g/mole)	Theory (g/mole)
$CoCl_2((EtO)_3P)_2$	463	462.2
$CoCl_2((EtO)_3P)_2$ + Extra $(EtO)_3p$ (1)	315	628.4
$CoCl_2((EtO)_2PEt)_2$	408	430.2
$CoCl_2((EtO)_2PEt)_3$	578	580.4
$CoCl_2(EtOPEt_2)_2$	387	398.2
$CoCl_2(EtOPEt_2)_3$	522	532.4

(1) Components were mixed in a 1:1 mole ratio.

Table VII. Magnetic Moments of the Cobalt(II) Complexes at Room Temperature.

Complex	μ_{eff} (B. M.)
$CoCl_2((EtO)_3P)_2$	4.12 (1)
$CoCl_2((EtO)_2PEt)_2$	3.12
$CoCl_2((EtO)_2PEt)_3$	2.00
$CoCl_2(EtOPEt_2)_2$	3.40
$CoCl_2(EtOPEt_2)_3$	2.54
$CoCl_2(Et_3P)_2$	4.39 (2)

(1) In a 1.17 wt. % solution in $C_6H_5NO_2$, μ_{eff} = 3.83 B.M.

(2) Hatfield and Yoke (1962).

subsequently. These magnetic results greatly resemble previous examples of equilibria between high-spin tetrahedral and low-spin five-coordinate complexes in cobalt(II) - phosphine systems (Nicolini, et al., 1966; Schrauzer and Glockner, 1964; Boschi, et al., 1966; Boschi et al., 1967; Rigo, et al., 1968; Rigo, et al., 1969; Nowlin and Cohn, 1971). The moment of the solid bis-phosphite complex is somewhat low for a high-spin tetrahedral cobalt(II) system, and the moment of a nitrobenzene solution is significantly lower. Both the bis-phosphonite and phosphinite complexes have moments intermediate between those typical of low-spin and high-spin cobalt(II). The tris-phosphonite and phosphinite complexes have moments in the range typical for low-spin five-coordinate cobalt(II) systems, with the latter a little on the high side of this range. The magnetic data suggest strongly that not only do both high-spin four-coordinate and low-spin five-coordinate complexes exist, but also that mixtures of both species are present at the stoichiometric molar ratios of 3:1 and especially 2:1 phosphorus base: cobalt.

Apparently, at the 3:1 ratio the dissociation of the low-spin five-coordinate complex is very slight or negligible in the phosphonite and phosphinite systems. What is more unusual is that a significant amount of low-spin five-coordinate complex is present, mixed in with high-spin tetrahedral species, at the 2:1 ratio in all the phosphorus ester systems studied. For there to be some complex species with

three phosphorus ligands per cobalt, when the stoichiometric amount present corresponds to only two phosphorus ligands per cobalt, means that a corresponding amount of species must be present with only one phosphorus ligand per cobalt. Examples of complexes of the formula $CoX_2 \cdot L$ are well known, where X is Cl, Br, or I and L is triethylamine (Hatfield and Yoke, 1962). In the triethylamine system, coordination of a second amine ligand is precluded for steric reasons; nevertheless the complexes are typical high-spin tetrahedral cobalt(II) species. This four-coordination is achieved by dimerization, using halogen bridges. This suggests that the presence of mixed five-coordinate and four-coordinate species in the $CoCl_2 \cdot 2L$ phosphite, phosphonite, and phosphinite systems can be accounted for by an equation of the type

$$4CoCl_2 \cdot 2L \rightleftharpoons 2CoCl_2 \cdot 3L + [CoCl_2 \cdot L]_2 .$$

If at the 2:1 ratio this equilibrium lay only a little toward the right, it would account for a significant decrease in the paramagnetism without any change in the non-electrolytic character of the system and with only a slight decrease in the number of particles present, within the error of the cryoscopic molecular weight experiments. Moreover, the latter experiments were at a temperature some 20° lower than the other measurements. The presence of a mixture of species would also account for the fact that the bis- phosphonite and phosphinite

systems are oils, while the other complexes are all solids.

Strong support for this reasoning is given by the electronic spectral data, given in Tables VIII and IX and in Figures 1-3. The spectra in nitrobenzene, benzene, and hexane are similar. The two regions of spectral absorption of interest are 13.7 - 18.7 kK (730 - 535 nm) and 22.8 - 23.6 kK (438 - 425 nm). As was pointed out in Chapter II, Section B, the former region is typical of either high-spin tetrahedral or of low-spin square pyramidal cobalt(II) complexes, while the latter region is diagnostic for low-spin square pyramidal cobalt(II).

In the spectrum of $CoCl_2(Et_2POEt)_2$, a small but definite absorption maximum is seen at 23.2 -23.5 kK, in agreement with the suggestion based on magnetic data that a small amount of the 3:1 complex is present at the 2:1 stoichiometric ratio. As shown in Figure 1, the intensity of this absorption is very greatly increased in the spectrum of $CoCl_2(Et_2POEt)_3$. This is in agreement with the conclusion based on magnetic and cryoscopic data that the low-spin five-coordinate complex is not appreciably dissociated.

Exactly the same kind of behavior is shown in Figure 2 for the absorption at 23.4 - 23.6 kK of the $CoCl_2[EtP(OEt)_2]_2$ and $CoCl_2[EtP(OEt)_2]_3$ complexes. The spectra shown in Figure 3, however, indicate that in the phosphite system the equilibrium

Table VIII. Electronic Spectral Data for the Cobalt(II) Complexes in Nitrobenzene.

Complex	Wavelength (nm) (Apparent ε)		Concentration (mole/1)	Color
$CoCl_2(P(OEt)_3)_2$	678(222), 655(197)sh, 586(195), 535(102)sh	428(85)	1.06×10^{-3}	Blue
" + extra $P(OEt)_3$(1)	678(312)sh, 655(325), 586(325), 535(160)sh	428(123)	1.06×10^{-3}	Green
$CoCl_2(EtP(OEt)_2)_2$	720(198), 638(274), 595(254)	425(37)	1.00×10^{-3}	Bl. Gr. (2)
$CoCl_2(EtP(OEt)_2)_3$	678(164), 652(168), 635(143)sh, 590(182), 545(87)sh	428(131)	4.83×10^{-3}	Green (2)
$CoCl_2(Et_2POEt)_2$	720(233), 633(305), 600(289)	425(100)	1.0×10^{-3}	Bl. Gr. (2)
$CoCl_2(Et_2POEt)_3$	685(320), 658(325), 642(284)sh, 598(409), 540(328)sh	430(930)	1.0×10^{-3}	Green (2)

(1) $P(OEt)_3$: $CoCl_2$ = 3.16

(2) Traces of air effect spectrum; rapidly turns blue in air with the disappearance of 425 - 430 nm peak and development of the spectrum of a phosphoryl complex (Schmidt and Yoke, 1970).

Table IX. Electronic Spectral Data for the $CoCl_2(Et_nP(OEt)_{3-n})_2$ Complexes in Benzene.[1]

Complex	Wavelength (nm)		Concentration (mole/1)	Color
$CoCl_2(P(OEt)_3)_2$	682sh, m;653sh, m;626s;584s	430s	1.00×10^{-2}	Blue
$CoCl_2(EtP(OEt)_2)_2$	680sh, m;618m;582m	438s	1.02×10^{-3}	Bl. Gr. (2)
$CoCl_2(Et_2POEt)_2$	696m;675sh, m;627sh, m;614sh, m;565s	435s	1.00×10^{-2}	Bl. Gr. (2)
$CoCl_2(Et_3P)_2$(2) (3)	730m;623m;606m	---		Blue

(1) Abbreviations = s=strong, m=medium, sh=shoulder

(2) Traces of air affect spectrum; rapidly turns blue in air with disappearance of 435 - 438 nm peak and development of the spectrum of the phosphoryl complex (Schmidt and Yoke, 1970).

(3) Schmidt (1970).

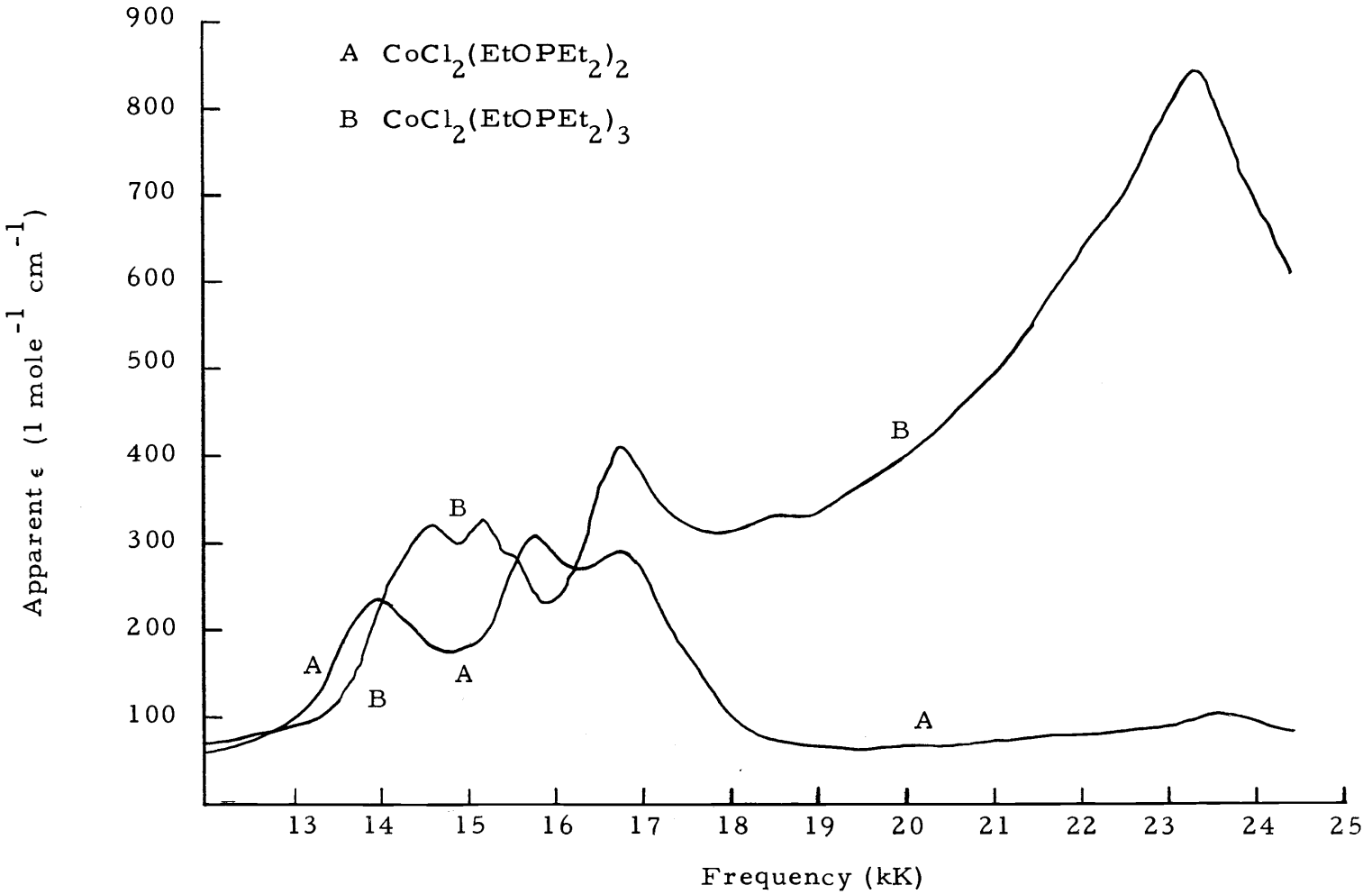

Figure 1. Visible Spectra of $CoCl_2(EtOPEt_2)_2$ and $CoCl_2(EtOPEt_2)_3$ in Nitrobenzene.

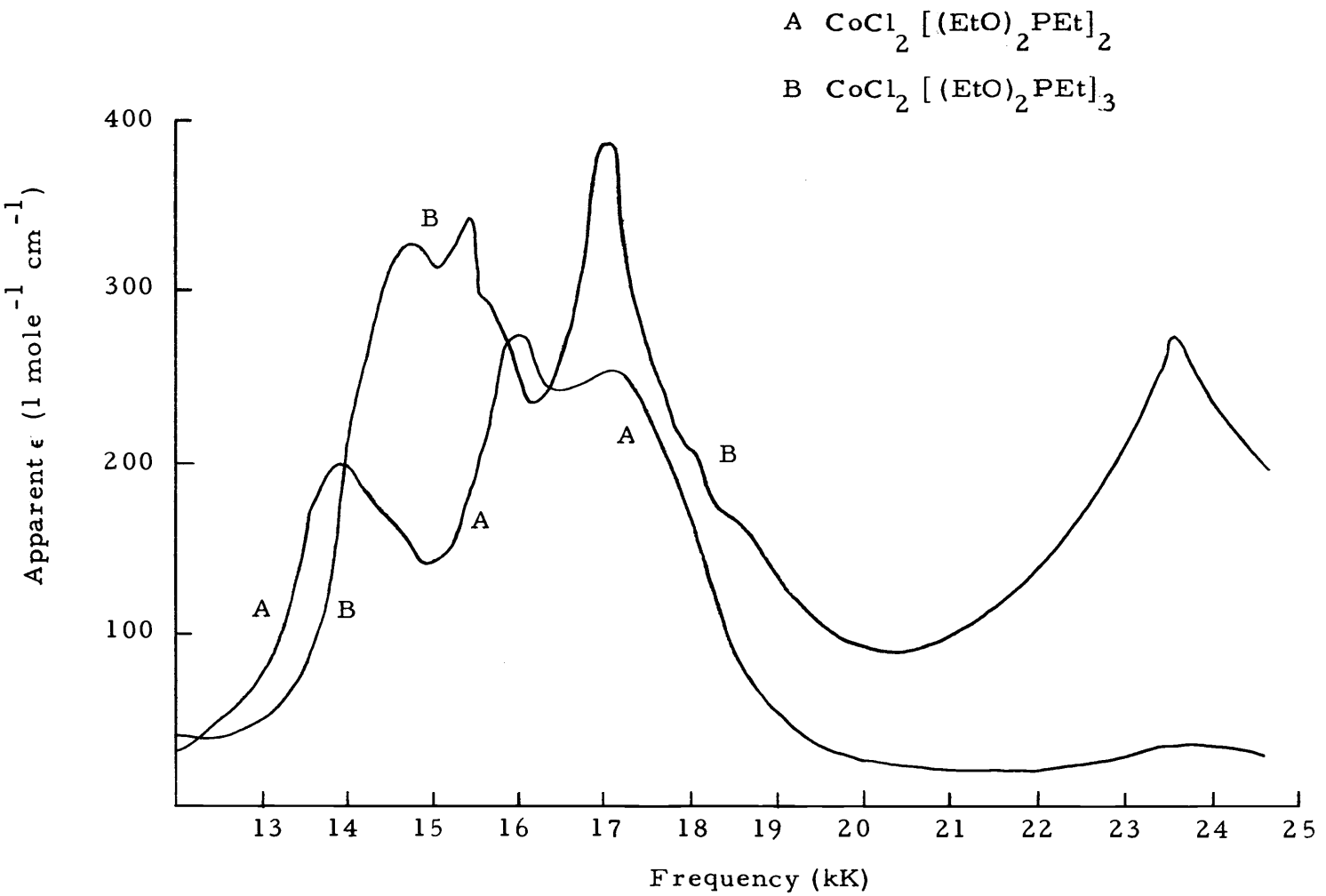

Figure 2. Visible Spectra of $CoCl_2[(EtO)_2PEt]_2$ and $CoCl_2[(EtO)_2PEt]_3$ in Nitrobenzene.

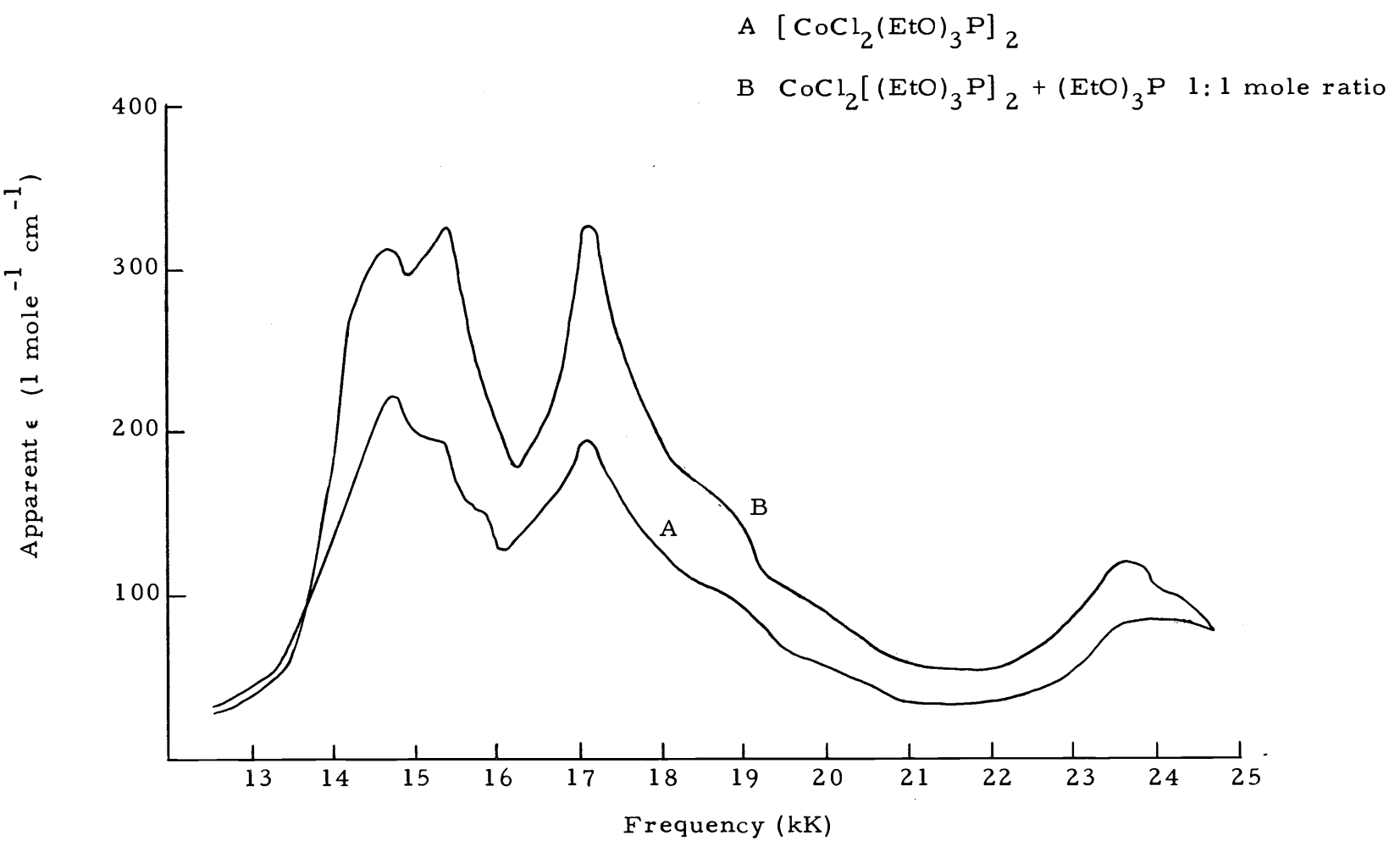

Figure 3. Visible Spectra of $CoCl_2[(EtO)_3P]_2$ and $CoCl_2[(EtO)_3P]_2 + (EtO)_3P$ (1:1 mole ratio) in Nitrobenzene.

$$CoCl_2[P(OEt)_3]_2 + P(OEt)_3 \rightleftharpoons CoCl_2[P(OEt)_3]_3$$

lies mostly toward the left. While it is clear that some low-spin five-coordinate phosphite complex is formed, both at the 2:1 and 3:1 stoichiometric ratios, there is never much of it. Here, the tris-complex cannot be isolated, and a smaller deviation in the magnetic moment of the bis-complex from a typical tetrahedral value is found than in the other ester systems.

As is indicated in Tables VIII and IX, the eye can recognize the low-spin five-coordinate complexes in these systems. The absorption in the low-energy region gives the samples a blue color. With increasing intensity of the absorption in the high energy region, the color becomes blue green and then green.

A definite relation is noticed between the degree to which five-coordinate complexes exist and the sensitivity of the system to oxygen. The phosphonite and phosphinite ester complexes are extremely sensitive to oxygen, and unless precautions are taken for the rigorous exclusion of air, their spectra change rapidly to the corresponding spectra of the phosphonate and phosphinate (phosphoryl) complexes studied by Schmidt and Yoke (1970). This sensitivity also made elemental analysis difficult in these systems. Much less difficulty was found in handling the phosphite system, where formation of a tris-complex is not extensive. In the phosphine system, where only the

high-spin bis-complex exists, the autoxidation reaction was found to be quite slow in solution, to be non-radical in character, and not to take place at all for the pure solid complex (Schmidt and Yoke, 1971). It is an interesting question as to whether it is the five coordinate geometry (square pyramidal or trigonal bipyramidal) or the spin state (doublet or quartet) or both which is responsible for the rapid autoxidation.

V. CONCLUSIONS

The ligands in the series $Et_nP(OEt)_{3-n}$, n = 0 - 3, all form pseudotetrahedral high-spin bis-complexes with cobalt(II) chloride. Magnetic, spectrophotometric, conductivity, and cryoscopic molecular weight data show that the phosphorus ester ligands (but not the phosphine) also form five-coordinate low-spin tris-complexes. These can be isolated in the cases of the phosphonite and phosphinite ligands, while the existence of the tris-phosphite complex is marginal. At phosphorus ester to cobalt(II) mole ratios of 2:1, a mixture of species is present in all cases.

The non-sequential behavior observed in this series no doubt reflects the change in importance of the "synergistic" balance between sigma donor bonding and d-d back pi bonding in the two cobalt geometries and spin states, as the electronegativities of the substituents on phosphorus change.

These results can be compared to those of Boschi, et al. (1966), who found that the reaction

$$CoX_2 \cdot 2PR_3 + PR_3 \rightleftharpoons CoX_2 \cdot 3PR_3$$

would not take place when X = halide, but only when X = thiocyanate, cyanide, or a similar pi-bonding ligand. The results may also be compared to those of Nowlin and Cohn (1971). They first obtained

five-coordinate complexes with X = halide by changing to more electronegative substituents in the phosphorus donor (from $(alkyl)_3P$ to $(dialkylamino)_2PF$ and $(dialkylamino)PF_2$).

It appears that the total sigma and pi bonding balance of all five ligands, the two anions and the three organophosphorus bases, is crucial in determining whether a five-coordinate complex will exist. One question, if it exists, is whether it will be trigonal bipyramidal or square pyramidal. A possible hypothesis is that if the two anions are strongly pi bonding, such as cyanide, they will occupy the axial positions in a trigonal bipyramid. If they are not, such as chloride, they and two phosphorus donors will occupy trans-basal positions in a square pyramid, with the third phosphorus apical. Some epr evidence in support of this hypothesis has been given by Nowlin (1971). A related question, if the five-coordinate complex exists, is whether it will be high-spin or low-spin. In all examples so far, the factors which lead to the existence of five-coordinate $CoX_2 \cdot 3PR_3$ complexes also lead to the doublet spin state.

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