Ethyl Phosphoryl Complexes of Cobalt(II)[1]

BY DONALD D. SCHMIDT[2] AND JOHN T. YOKE[3]

The complete series of complexes $CoCl_2\{OP(C_2H_5)_n(OC_2H_5)_{3-n}\}_2$, $n = 0-3$, has been prepared and characterized by analysis and electronic and infrared spectroscopy. Cobalt is pseudo-tetrahedrally coordinated in each case. On heating, the three complexes with ester ligands undergo the reaction $CoCl_2\{OP(C_2H_5)_n(OC_2H_5)_{3-n}\}_2 \rightarrow 2C_2H_5Cl + Co\{O_2P(C_2H_5)_n(OC_2H_5)_{2-n}\}_2$, the products of which have been characterized. Some magnetic data are reported. A simple method is described for the quantitative synthesis of triethylphosphine oxide from triethylphosphine and mercury(II) oxide.

Introduction

Autoxidation of free tertiary aliphatic phosphines gives not only phosphine oxides but rather a mixture of all the compounds $R_n(RO)_{3-n}PO$.[4] As a part of our work on the autoxidation of a coordinated phosphine,[5] $CoCl_2\{(C_2H_5)_3P\}_2$, the complexes of cobalt(II) chloride with the phosphoryl donors triethylphosphine oxide, ethyl diethylphosphinate, diethyl ethylphosphonate, and triethyl phosphate have been prepared and studied as reference standards. A number of transition metal complexes with organophosphoryl donors have been described previously.[6]

Experimental Section

Ethyl Phosphoryl Ligands.—Practical grade samples of triethyl phosphate (Eastman Kodak) and diethyl ethylphosphonate (J. T. Baker) were distilled at reduced pressure using a Nester–Faust Teflon spinning-band column, and middle fractions were taken: $(C_2H_5O)_3PO$, bp 93° (8 mm); $C_2H_5P(O)(OC_2H_5)_2$, bp 86° (12 mm). Ethyl diethylphosphinate was prepared as follows. Ethyldichlorophosphine (0.2 mol), from the reaction of phosphorus trichloride and tetraethyllead,[7] was added dropwise under nitrogen to a cold stirred solution of 0.4 mol of ethanol and 0.4 mol of N,N-dimethylaniline in 200 ml of light petroleum ether (bp 35–55°). The amine hydrochloride was removed by filtration under nitrogen in a drybox, the solvent was stripped from the filtrate, and the product, diethyl ethylphosphonite, was distilled at a reduced pressure. This was isomerized at 75° with ethyl iodide under nitrogen by the Arbuzov method.[8] The resulting ethyl diethylphosphinate was purified by distillation at a reduced pressure, with a middle fraction taken; $n^{21}D$ 1.4337, lit.[9] $n^{20}D$ 1.4337. Triethylphosphine oxide was prepared by oxidation of triethylphosphine with mercury(II) oxide, using an adaptation of Zingaro's arsine oxide method.[10] Triethylphosphine (22 mmol) was condensed onto 22 mmol of mercury(II) oxide and 10

ml of benzene in a 50-ml flask attached to a high-vacuum line. The reaction mixture was stirred for 2 days at 50°, until all the solid was converted into mercury (appearing as a gray powder). The flask was cooled to room temperature and removed from the vacuum line, and the contents were filtered by gravity through paper in the open air. The benzene was then distilled from the clear filtrate in the vacuum line at room temperature. The white solid product was melted and distilled *in vacuo* with mild application of heat. The yield of triethylphosphine oxide after purification was essentially quantitative. Purity of the four phosphoryl ligands was checked by glpc, using a temperature-programmed Model 700 F & M gas chromatograph.

Other Materials.—Anhydrous cobalt(II) chloride was prepared by dehydration of the reagent grade hydrate at *ca.* 400° in a stream of hydrogen chloride. Absolute ethanol was distilled from magnesium ethoxide. Reagent grade benzene and chloroform were distilled.

Cobalt(II) Chloride Complexes.—In the drybox, stoichiometric amounts of the phosphoryl ligands were added to solutions of 2 g of anhydrous cobalt(II) chloride in 20 ml of absolute ethanol to give a mole ratio of 2.00. The blue solid dichlorobis(triethylphosphine oxide)cobalt(II) separated on cooling; mp 76–77°. The three complexes dichlorobis(ethyl diethylphosphinate)cobalt(II), dichlorobis(diethyl ethylphosphonate)cobalt(II), and dichlorobis(triethyl phosphate)cobalt(II) were recovered as blue oils on evaporation of the solvent *in vacuo* at room temperature. The use of excess amounts of the neat ligands as solvents for anhydrous cobalt(II) chloride did not give higher complexes; oils with identical spectra were obtained. The $CoCl_2\{OP(C_2H_5)_n(OC_2H_5)_{3-n}\}_2$ complexes are all soluble in acetone and alcohol, somewhat soluble in ether and benzene, and insoluble in paraffin hydrocarbons and are decomposed by water. Analytical data for the complexes are given in Table I. Chloride was determined gravimetrically, and cobalt, by potentiometric titration with hexacyanoferrate(III) ion. Carbon and hydrogen microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Thermal Behavior of the Ester Complexes.—The removal of an excess of triethyl phosphate from cobalt(II) chloride in a vacuum-line reaction bulb at room temperature yielded an oil with a negligible dissociation pressure, identical with that of the $CoCl_2\{OP(OC_2H_5)_3\}_2$ described above. However, when the same process was carried out at an elevated temperature, a highly volatile substance was evolved (slowly at 140°, rapidly at 190°) and trapped in the vacuum line. A dark blue-violet solid residue remained. The volatile substance was identified as ethyl chloride by vapor density (mol wt: found, 68; calcd, 64.5) and vapor pressure measurements in the range 0 to −53°, which gave excellent agreement with the literature data.[11] The solid residue gave only a slight turbidity with aqueous silver nitrate. It was purified by dissolution in chloroform, removal of a trace of insoluble material by filtration, and evaporation of the solvent from the filtrate *in vacuo*. The product then gave a negative

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(2) Woodrow Wilson Fellow, 1965–1966; NDEA Fellow, 1966–1969.

(3) To whom inquiries should be addressed.

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(11) "Handbook of Chemistry and Physics," 47th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1966.

TABLE I

ANALYTICAL DATA

Compound	% Co		% Cl		% C		% H	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
CoCl₂{OP(C₂H₅)₃}₂	14.80	14.74	17.81	17.76	36.20	36.23	7.59	7.61
CoCl₂{OP(C₂H₅)₂(OC₂H₅)}₂	13.70	13.57	16.48	16.35	...	...	...	...
CoCl₂{OP(C₂H₅)(OC₂H₅)₂}₂	12.75	12.88	15.34	15.32	...	...	...	...
CoCl₂{OP(OC₂H₅)₃}₂	11.93	11.67	14.35	13.97	...	...	...	...
Co{O₂P(OC₂H₅)₂}₂	16.14	16.19	...	...	26.32	26.65	5.52	5.69
Co{O₂P(OC₂H₅)(C₂H₅)}₂	17.69	18.11	...	...	28.85	27.42	6.05	5.91
Co{O₂P(C₂H₅)₂}₂	19.57	19.35	...	...	31.91	31.72	6.69	6.72

TABLE II

INFRARED SPECTRAL DATA (CM⁻¹)[a]

	940–1060-cm⁻¹ region		P—O—C₂H₅	P=O	Δν_{P=O}
(C₂H₅)₃PO	... ,	997 w, 1010 w, 1024 w, 1040 w	...	1180 s ⎱	81
CoCl₂{OP(C₂H₅)₃}₂	... ,	981 w, 1002 w, 1028 w, 1044 w	...	1099 s ⎰	
(C₂H₅)₂(C₂H₅O)PO	949 s, sh,	1026 s, br, 1047 s, br	1094 w	1202 s ⎱	66
CoCl₂{OP(C₂H₅)₂(OC₂H₅)}₂	954 s, sh,	1021 s, br, 1042 s, br	1096 w	1136 s ⎰	
(C₂H₅)(C₂H₅O)₂PO	954 s, sh,	1013 s, br, 1057 s, br	1095 w	1227, 1250 s, d ⎱	63
CoCl₂{OP(C₂H₅)(OC₂H₅)}₂	965 s, sh,	1013 s, br, 1053 s, br	1095 w	1176 s ⎰	
(C₂H₅O)₃PO	963 s, sh,	1029 s, br	1093 w	1263, 1271 s, d ⎱	40
CoCl₂{OP(OC₂H₅)₃}₂	982 s, sh,	1031 s, br	1099 w	1227 s ⎰	
Co{O₂P(OC₂H₅)₂}₂	971 s, sh,	1058 s, br	1087	1112, 1178 s, d	
Co{O₂P(C₂H₅)(OC₂H₅)₃}₂	958 s, sh,	1050 s, br	1101	1078, 1148 s, d	
Co{O₂P(C₂H₅)₂}₂	... ,	992 w, 1004 w	...	1052, 1119 s, d	

[a] Abbreviations: s, strong; w, weak; sh, sharp; br, broad; d, doublet.

chloride test and was found by analysis (Table I) to be cobalt(II) diethylphosphate; mp 181–182°. It is soluble in chloroform, very slightly soluble in ethers, and insoluble in acetone, carbon tetrachloride, paraffin, and aromatic hydrocarbons and gives pink solutions in water and alcohols.

When pure dichlorobis(diethyl ethylphosphonate)cobalt(II) or dichlorobis(ethyl diethylphosphinate)cobalt(II) was heated at 190–200° in a vacuum-line bulb, ethyl chloride was evolved over several hours and identified as above. With the former, the loss in weight corresponded to 2.13 ± 0.14 mol of ethyl chloride/mol of initial complex, and analysis (Table I) indicated imperfect purity of the product. With the latter complex, exactly 2.00 mol of ethyl chloride was lost per mole of initial complex, and the analysis (Table I) of the product was satisfactory. Cobalt(II) ethyl ethylphosphonate is a dark blue very viscous tar, which solidifies on standing, and cobalt(II) diethylphosphinate is a dark blue gummy solid. They are both soluble in chloroform and slowly give pink solutions in water.

Spectra.—Infrared spectra were measured with Perkin-Elmer 21 and Beckman IR 7 and IR 8 spectrophotometers, using Nujol mulls and potassium bromide pellets for solids and thin films between sodium chloride plates for neat liquid samples. Electronic spectra were measured with Beckman DK 2 and Coleman-Hitachi 124 spectrophotometers using matched 1-cm quartz cells. The wavelength scales were calibrated with a holmium oxide filter.

Magnetic Susceptibilities.—These were determined at room temperature by the Gouy method, using the techniques previously described.[12] For CoCl₂{OP(C₂H₅)₃}₂, μ_{eff} is 4.79 BM, and for Co{O₂P(OC₂H₅)₂}₂, μ_{eff} is 4.62 BM.

Results and Discussion

Some characteristic infrared frequencies of the four phosphoryl donors in the free and coordinated states are given in Table II. The presence or absence of P–O–C ester groups is readily apparent from the intensities of the peaks in the 940–1060-cm⁻¹ region. Triethylphosphine oxide, dichlorobis(triethylphosphine oxide)cobalt(II), and cobalt(II) diethylphosphinate show only weak absorptions in this region, attributed to

(12) J. R. Clifton and J. T. Yoke, *Inorg. Chem.*, **7**, 39 (1968).

TABLE III

ELECTRONIC SPECTRAL DATA FOR COBALT(II) COMPOUNDS

Compound	Wavelength,[a] nm (ϵ)	Solvent
CoCl₂{OP(C₂H₅)₃}₂	662 (375), 640 sh, 614 sh, 596 sh	CHCl₃
CoCl₂{OP(C₂H₅)₂(OC₂H₅)}₂	665 (350), 645 sh, 614 sh, 596 sh	C₆H₆
CoCl₂-{OP(C₂H₅)(OC₂H₅)₂}₂	665, 645 sh, 614 sh, 596 sh	Neat
CoCl₂{OP(OC₂H₅)₃}₂	668, 645 sh, 614 sh, 596 sh	Neat
Co{O₂P(OC₂H₅)₂}₂	623 (280), 600 sh, 580 sh, 550 sh	CHCl₃
Co{O₂P(C₂H₅)(OC₂H₅)}₂	624 (290), 603 sh, 581 sh, 554 sh	CHCl₃
Co{O₂P(C₂H₅)₂}₂	631 (290), 604 sh, 585 sh, 547 sh	CHCl₃

[a] sh = shoulder.

C–CH₃ modes.[13] In marked contrast, all the compounds containing P–O–C ester groups exhibit a sharp strong band in the 949–982-cm⁻¹ region, as well as one or two broad, very strong bands in the 1013–1058-cm⁻¹ region. In addition, a weak P–O–C₂H₅ absorption[14] is seen at about 1095 cm⁻¹. The position of the P=O absorption is seen to vary with the substituents on phosphorus and to shift on coordination. Such shifts in the P=O band have been discussed previously.[15] The increase in $\nu_{P=O}$ with increasing electronegativity of substituents in the series $(C_2H_5)_n(C_2H_5O)_{3-n}PO$ is related to increasing partial positive charge on σ-bonded phosphorus and a resulting increase in $p\pi$–$d\pi$ back-bonding from oxygen to phosphorus (increase in bond strength). The decrease in $\nu_{P=O}$ on coordination of oxygen to cobalt is related to the decrease in availability of oxygen electrons for back-bonding to phosphorus. The decrease in the *shift* $\Delta\nu_{P=O}$ with increasing electronegativity of substituents on phosphorus reflects the competition between the two effects above.

The electronic spectra in the visible region of the cobalt(II) compounds are given in Table III. All the

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(14) R. A. McIvor, G. A. Grant, and C. E. Hubley, *Can. J. Chem.*, **34**, 1611 (1956).

(15) F. A. Cotton, R. D. Barnes, and E. Bannister, *J. Chem. Soc.*, 2199 (1960); J. V. Bell, J. Heisler, H. Tannenbaum, and J. Goldenson, *J. Am. Chem. Soc.*, **76**, 5185 (1954).

compounds contain pseudo-tetrahedrally coordinated cobalt(II) by this criterion, as is also indicated by the magnetic data for two of them. The transition $^4A_2 \rightarrow$ $^4T_1(P)$ in tetrahedral symmetry (as of the CoO_4 chromophore) commonly shows some splitting due to spin–orbit coupling.[16] For the chromophore CoO_2Cl_2 of C_{2v} symmetry, the transition becomes $^4A_2 \rightarrow {}^4A_1 +$ $^4B_1 + {}^4B_2$, and the "average ligand field" approximation applies. Thus the $Co\{O_2PR_2\}_2$ compounds come at higher energy than the $CoCl_2\{OPR_3\}_2$ compounds, and in all cases the band is structured, with shoulders on the high-energy side. It is interesting that although substituent effects are seen on the P=O vibrational frequency and on its shift upon coordination, the four phosphoryl donors seem to have the same ligand field strengths. The visible spectra of their cobalt(II) chloride complexes are virtually identical.

(16) F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Am. Chem. Soc.*, **83**, 4690 (1961).

The complexes of the phosphoryl donors containing ester groups lose all their chloride content on heating to give $Co\{O_2(C_2H_5)_n(OC_2H_5)_{2-n}\}_2$ products. While these could be monomeric, with chelating $O_2PRR'^-$ anionic ligands,[17] their properties suggest association of the type previously found[18] with various polymeric metal phosphinates.

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Force Constants in the Acetylene Molecule in a Cobalt–Carbonyl Complex and in an Excited Electronic State

BY YUJI IWASHITA

An approximate normal-coordinate treatment has been made as a six-body problem for the CH≡CHCo₂ part of the CH≡CHCo₂(CO)₆ molecule. The values of 12 force constants were determined on the basis of 30 observed frequencies of four isotopic molecules (which contain $^{12}CH \equiv {}^{12}CH$, $^{12}CD \equiv {}^{12}CH$, $^{12}CD \equiv {}^{12}CD$, and $^{13}CH \equiv {}^{12}CH$) by the method of least squares. A similar normal-coordinate treatment was made of the acetylene molecule in an excited electronic state (^1A_u). The values of six force constants were estimated on the basis of six observed frequencies. It was found that five of the latter force constant values are nearly equal to the values of the corresponding force constants in the acetylene molecule in the complex.

Introduction

The nature of the coordinate bond has been studied by many investigators and recently some of them have succeeded in elucidating the physical properties of coordination compounds by the use of molecular orbital theory.

As the first approximation, the antibonding and bonding π orbitals of a ligand molecule are taken as the acceptor and donor π orbitals, respectively.[1,2]

The net effect of bond formation on the ligand molecule is assumed to bring the electron of the ligand molecule from the highest bonding π orbital to the lowest antibonding π orbital. That is, the complexed ligand should have an electron configuration analogous to the electronically excited free molecule.

Wilkinson and his coworkers[3] have pointed out that the observed bond lengths and the bond angle in the

coordinated CS_2 in $PtCS_2[P(C_6H_5)_3]_2$ are close to the corresponding values in the first excited state of CS_2.

Recently we have demonstrated a similarity of vibrational spectrum of complexed acetylene to that of an excited acetylene[4] and a similarity of the symmetry of a complexed CO_2 with that of an excited carbon dioxide.[5]

In the present work, the author has attempted to determine the force constants of the complexed and excited acetylenes by an approximate normal vibration treatment and to examine the transferability of the force constants between these two states.

Vibrational Frequencies and Their Assignments

Excited Acetylenes.—Ingold and King[6] gave the geometry and totally symmetric vibrational frequencies of the first excited state (^1A_u) of acetylene.

Innes[7] made a refinement of these data. The results

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(2) A. C. Blizzard and D. P. Santry, *J. Am. Chem. Soc.*, **90**, 5749 (1968).
(3) M. Baird and G. Wilkinson, *Chem. Commun.*, **18**, 93 (1967).
(4) Y. Iwashita, F. Tamura, and A. Nakamura, *Inorg. Chem.*, **8**, 1179 (1969).
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(6) C. K. Ingold and G. W. King, *J. Chem. Soc.*, 2702 (1953).
(7) K. K. Innes, *J. Chem. Phys.*, **22**, 863 (1954).