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Tetraco-ordinated Complexes of Cobalt(I)

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The preparation and properties of cobalt(I)complexes of general formula Co(dp)$_2$X [dp=C$_2$H$_4$(PPh$_2$)$_2$; X=Br, ClO$_4$, BPh$_4$] are reported. The bromide derivative is tetraco-ordinated in polar solvents and pentaco-ordinated in non polar solvents, while the perchlorate and the tetraphenylborate are tetraco-ordinated both in solution and in the solid state. These compounds easily add hydrogen, carbon monoxide and sulfur dioxide. The reactions with benzoyl chloride and nitrogen monoxide are also reported.

Introduction

The cobalt(I) complexes are generally pentaco-ordinated and only a few examples of tetraco-ordinated compounds are reported in the literature, such as [Co(dipy)$_2$]ClO$_4$,[1] K$_2$[Co(CN)$_3$(CO)],[2,3] CoCl[P(O-Et)$_3$]$_3$,[4] and CoH(PEt$_2$Ph)$_3$.[5] Recently, new tetraco-ordinated complexes of cobalt(I) stabilized by tertiary phosphines have been reported by us. They are the paramagnetic compounds of formula CoX(PR$_3$)$_3$[6] (X=Cl, Br, I; PR$_3$=PPh$_3$, PBuPh$_2$, PBzPh$_2$) having a tetrahedral structure, and the diamagnetic compounds of formula [Co(dp)$_2$]X,[7] for which a planar configuration has been suggested. In this paper we report the detailed preparation and the properties of these latter complexes along with their products of reaction with CO, SO$_2$, H$_2$, and NO.

Experimental Section

Unless otherwise specified, all compounds were prepared and manipulated in an atmosphere of pure nitrogen. Samples for decomposition point (d.p.) determination were contained in tubes filled under nitrogen. The I.R. spectra were recorded on a Perkin-Elmer 337 Spectrometer and the electronic spectra on an Optica CF 4NI Spectrophotometer.

Bromobis(1,2–bisdiphenylphosphinoethane)cobalt(I). CoBr(dp)$_2$. a) A suspension of CoBr$_2$(dp)$_2$[8] (2.0 g, 2.0 mmols) and sodium (0.1 g, 4.0 mmols) in anhydrous benzene (50 ml) was stirred at room temperature. The stirring was stopped as soon as the original green suspension produced a brown solution (12-36 hr). After filtration the solvent was evaporated under reduced pressure and the resulting brown powder was washed with n–pentane. The complex is soluble in benzene, ethanol, tetrahydrofuran and acetone, insoluble in n–pentane.

Anal. Calcd for C$_{52}$H$_{48}$BrP$_4$Co: Br, 8.5; P, 13.2; Co, 6.3. Found: Br, 7.9; P, 12.8; Co, 6.4%.

b) A solution of [Co(dp)$_2$][9] (0.5 mmols) in benzene (20 ml) was added to a suspension of CoBr$_2$(dp)$_2$ (0.5 mmols) in benzene (10 ml) and the mixture was stirred at room temperature for 15 minutes to give a brown solution. The solvent was evaporated under reduced pressure and the resulting brown powder was washed with *n*–pentane and dried under vacuum.

Anal. found: Br, 8.6; P, 13.1; Co, 6.3%.

Molar conductance (10^{-3} *M* solution in ethanol at 25°C): 38 ohm^{-1} cm^2 mol^{-1}.

Bis(1,2–bisdiphenylphosphinoethane)cobalt(o). [Co(dp)$_2$]. A suspension of CoBr$_2$(dp)$_2$ (2.0 mmols and sodium (0.2 g, 8.0 mmols) in anhydrous benzene (50 ml) was stirred at room temperature to give at first a brown solution (12-36 hr) and then, after a few hours, a dark-red solution. After filtration the solution was concentrated under reduced pressure. By adding n–hexane dark-red crystals were obtained. The product was crystallised from benzene and ethanol. This compound was identified as the known [Co(dp)$_2$][9] by means of its d.p. and analysis.

Anal. Calcd for C$_{52}$H$_{48}$P$_4$Co: P, 14.5; Co, 6.9. Found: P, 14.3; Co, 7.0%.

Bis(1,2–bisdiphenylphosphinoethane)cobalt(I)perchlorate. [Co(dp)$_2$]ClO$_4$. Crude CoBr(dp)$_2$ (1 g), dissolved in ethanol (20 ml), was treated with an excess of an alcoholic solution of NaClO$_4$. By cooling at –20°C, black crystals, which were crystallised from ethanol, were obtained. D.p. 169-71°C. The complex is soluble in tetrahydrofuran, acetone and warm ethanol, insoluble in benzene and petroleum ether.

Anal. Calcd for C$_{52}$H$_{48}$ClO$_4$P$_4$Co: Cl, 3.7; P, 13.0; Co, 6.2. Found: Cl, 3.7; P, 12.9; Co, 6.1%.

Molar conductance (10^{-3} *M* solution in nitrobenzene at 25°C): 22.4 ohm^{-1} cm^2 mol^{-1}; (10^{-3} *M* solution in ethanol at 25°C): 41 ohm^{-1} cm^2 mol^{-1}.

Bis(1,2–bisdiphenylphosphinoethane)cobalt(I)tetra-

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phenylborate. *[Co(dp)$_2$]BPh$_4$.* This complex was prepared in a manner similar to the perchlorate, except that sodium tetraphenylborate was used instead of sodium perchlorate. The resulting deep purple crystals were filtered, washed with water and ethanol and dried under vacuum. D.p. 204-5°C. The complex is soluble in tetrahydrofuran and acetone; insoluble in ethanol, benzene and petroleum ether.

Anal. Calcd for $C_{76}H_{68}BP_4Co$: P, 10.5; Co, 5.0. Found: P, 10.2; Co, 5.0%.

Carbonylbis(1,2–bisdiphenylphosphinoethane)cobalt(I)bromide. *[Co(CO)(dp)$_2$]Br.* A solution of CoBr(dp)$_2$ (1.0 g) in benzene (20 ml) was stirred under carbon monoxide for 5 minutes at room temperature and atmospheric pressure. The resulting yellow precipitate was washed with benzene and dried under vacuum; m.p. 165-6°C. The complex is soluble in tetrahydrofuran, ethanol, acetone and chloroform, insoluble in benzene and petroleum ether.

Anal. Calcd for $C_{53}H_{48}BrOP_4Co$: Br, 8.3; P, 12.9; Co, 6.1. Found: Br, 8.6; P, 12.9; Co, 6.2%.

I.R. spectrum (nujol mull): $\nu_{CO} = 1902$ cm^{-1}.

Reaction of bromobis(1,2–bisdiphenylphosphinoethane)cobalt(I) with benzoyl chloride. A solution of CoBr(dp)$_2$ (1.0 g) in anhydrous benzene (20 ml) was treated with an excess of benzoyl chloride (0.5 ml) under stirring for 1 hr at room temperature. The resulting precipitate was crystallised from ethanol and water to give yellow crystals. The I.R. spectrum and m.p. of this product is identical to that of the product described above.

Bis(1,2–bisdiphenylphosphinoethane)(sulfur dioxide) cobalt(I) perchlorate. *[Co(dp)$_2$(SO$_2$)]ClO$_4$.* Fine powdered [Co(dp)$_2$]ClO$_4$ | (0.5 g) was kept under an atmosphere of sulfur dioxide at room temperature and atmospheric pressure until the black powder became brown (15 min). The product was washed with benzene and dried under vacuum; d.p. 125-30°C. The complex is soluble in tetrahydrofuran, ethanol and acetone, insoluble in benzene and petroleum ether.

Anal. Calcd for $C_{52}H_{48}ClO_6SP_4Co$: Cl, 3.5; S, 3.1; P, 12.1; Co, 5.8. Found: Cl, 3.6; S, 3.2; P, 11.6; Co, 5.8%.

Reaction of bis(1,2–bisdiphenylphosphinoethane)cobalt(I) perchlorate with hydrogen. (a) Fine powdered [Co(dp)$_2$]ClO$_4$ (0.5 g) was kept under an atmosphere of hydrogen at room temperature and atmospheric pressure for several days to give a yellow product.

(b) A solution of [Co(dp)$_2$]ClO$_4$ (0.5 g) in ethanol (50 ml) was stirred under hydrogen at room temperature and atmospheric pressure for 5 min. The resulting solution was concentrated under reduced pressure to give yellow crystals.

The products obtained under (a) and (b) were identified as the already known cis–[CoH$_2$(dp)$_2$]ClO$_4$[10] by means of their I.R. spectra and d.p.

Reaction of bis(1,2–bisdiphenylphosphinoethane)-cobalt(I) perchlorate with nitrogen monoxide. A suspension of [Co(dp)$_2$]ClO$_4$ (1.0 g) in ethanol (20 ml) was stirred under nitrogen monoxide for 1 hr at room temperature and atmospheric pressure. The resulting red precipitate was washed with cold ethanol and dried. It was identified as the known [Co(dp)(NO)$_2$]ClO$_4$[11] by means of its I.R. spectrum and d.p.

Results and Discussion

Bromobis(1,2–bisdiphenylphosphinoethane)cobalt(I) has been obtained by reduction of the corresponding cobalt(II) complex with sodium metal in benzene, according to the equation:

$$CoBr_2(dp)_2 + Na \rightarrow CoBr(dp)_2 + NaBr \qquad (1)$$

or by reaction of CoBr$_2$(dp)$_2$ with Co(dp)$_2$, according to the equation:

$$CoBr_2(dp)_2 + Co(dp)_2 \rightarrow 2CoBr(dp)_2 \qquad (2)$$

In the first case it is difficult to stop the reaction before the formation of some Co(dp)$_2$, according to the equation:

$$CoBr(dp)_2 + Na \rightarrow Co(dp)_2 + NaBr \qquad (3)$$

Therefore, the product obtained by reduction with sodium metal always contains some Co(dp)$_2$ and we were not able to purify it by recrystallization; however, CoBr(dp)$_2$ has been obtained in pure crystalline form according to the equation (2). This compound is soluble either in polar and non-polar organic solvents. The electronic spectrum of CoBr(dp)$_2$ in non polar solvents, such as benzene (see Table I) is similar to those of pentaco-ordinated low spin d^8 metal complexes of trigonal bipyramidal (actually C_{3v}) symmetry.[12] On the bases of its diamagnetic behaviour and of its electronic spectrum, we assign a pentaco-

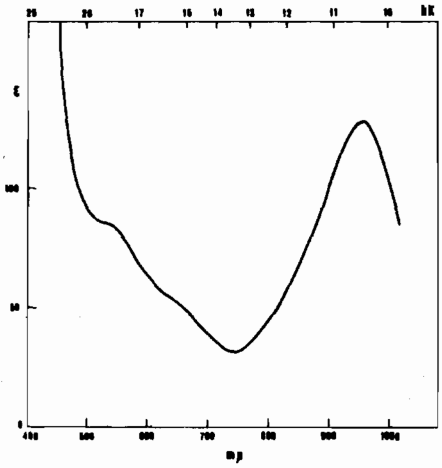

Figure 1. Visible spectrum of Co(dp)$_2$Br in benzene solution.

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Table I. Visible spectra.

Compound	Solvent	Absorption maxima mμ	Absorption maxima cm^{-1}	Molar extinc.
CoBr(dp)$_2$	benzene	~540 (sh)	~18.520	—
		955	10.470	128
[Co(dp)$_2$]Br	ethanol	434	23.040	1725
		563	17.760	1155
		720	13.890	1018
[Co(dp)$_2$]ClO$_4$	ethanol	434	23.040	1710
		563	17.760	1190
		720	13.890	1040
[Ir(dp)$_2$]Cl	ethanol	386	25.910	2450
		440	22.730	2340
		520	19.230	540

ordinated structure to this compound. The brown pentaco-ordinated CoBr(dp)$_2$ readily undergoes solvolysis by polar solvents: in ethanol it gives a green-brown solution, whose electronic spectrum is identical to that of [Co(dp)$_2$]ClO$_4$ (see Table I), and whose molar conductance is in agreement with that expected for an 1:1 electrolyte.

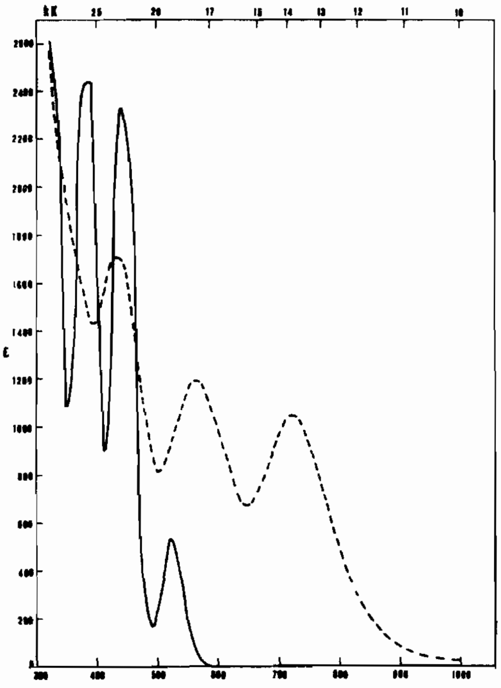

Figure 2. Visible spectra of: ----- [Co(dp)$_2$]ClO$_4$ in ethanol solution; ———— [Ir(dp)$_2$]Cl in ethanol solution.

On treating ethanol solutions of [Co(dp)$_2$]Br with an excess of NaClO$_4$ or of NaBPh$_4$, the corresponding perchlorate or tetraphenylborate were obtained as deep purple, diamagnetic, air unstable crystalline solids. The I.R. spectrum of [Co(dp)$_2$]ClO$_4$ in nujol mull clearly shows that the perchlorate ion is not coordinated to the metal[13,14] (broad asymm. stretching at 1120-1045 cm^{-1}, asymm. bending at 624 cm^{-1}). The electronic spectra in ethanol of both [Co(dp)$_2$]Br and [Co(dp)$_2$]ClO$_4$ show three absorption bands ascribable to *d–d* transitions and they are very similar to that of [Ir(dp)$_2$]Cl (see Table I), whose square planar structure has been confirmed by X rays,[15] and to those of tetracoordinated planar d^8 nickel complexes.[16] The diamagnetism, the conductivity and the electronic and I.R. spectra strongly suggest for [Co(dp)$_2$]ClO$_4$ a tetracoordinated square-planar configuration. The tetracoordinated cation [Co(dp)$_2$]$^+$ readily adds hydrogen and sulfur dioxide both in the solid state and in solution: with hydrogen it gives the known [CoH$_2$(dp$_2$]ClO$_4$[10] and with sulfur dioxide a compound of formula [Co(SO$_2$)(dp)$_2$]ClO$_4$. This latter is a brown powder, moderately air stable. Its I.R. spectrum shows absorption bands at 1322 and 1230 cm^{-1}, ascribable to the asymmetric stretching of the coordinated sulfur dioxide.[17] CoBr(dp)$_2$ readily reacts with carbon monoxide in benzene solution, giving the already known [Co(CO)(dp)$_2$]Br.[18] Moreover, unlike the square planar [Ir(dp)$_2$]$^{+19}$ and the square planar [Rh(dp)$_2$]$^+$,[10] it readily abstracts carbon monoxide from benzoyl chloride to give [Co(CO)(dp)$_2$]Br.

The reaction of [Co(dp)$_2$]ClO$_4$ with nitrogen monoxide gives the already known [Codp(NO)$_2$]ClO$_4$.[11]

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