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Some Cobalt Complexes with a Multidentate Substituted Phosphine

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The quadridentate ligand tris-(o-diphenylphosphinophenyl)phosphine (QP) forms complexes with cobalt(II) of the type$[CoX(QP)]Y$ *which have* $S = 1/2$ *and which have been assigned a distorted trigonal bipyramidal structure. Trigonal-bipyramidal, diamagnetic, complexes of cobalt(I) of the type* $[Co(CO)(L)]^+$ *(L = QP and QAS) and octahedral, diamagnetic complexes of cobalt(III) of the type* $[CoX_2(QP)]^+$ *are also described.*

Introduction

Although the innumerable complexes of cobalt(1) described in the literature have been largely obtained using nitrogen donors, a number of phosphine complexes of cobalt (—I), (O), (I), (II), and (III) have been reported.(2)

We report here the preparation of complexes of cobalt(I), (II) and (III) with the tetratertiary phosphine tris-(*o*-diphenylphosphinophenyl)phosphine, $(o\text{-}Ph_2P\,.\,.\,C_6H_4)_3P$, (QP).

Cobalt(II) complexes. Ethanolic solutions of cobalt(II) halides react with the phosphine to give complexes of the types $[CoX(QP)]_2[CoX_4]$ (X = Cl and Br) and $[CoI(QP)]I$ which react with salts of non-co-ordinating or weakly co-ordinating anions to give compounds of the type $[CoX(QP)]Y$ ($Y = ClO_4$ and BPh_4). The complex $[Co(NCS)(QP)][BPh_4]$ can be prepared by a double exchange reaction from the corresponding chloro-complex. All the perchlorato-salts contain tenaciously held solvent of crystallization and in view of the potentially explosive nature of these derivatives no attempt has been made to obtain them in the unsolvated form by drying them under vacuum at high temperatures. Attempts to prepare complexes with the arsenic ligand QAS, by the use of conditions similar to those which gave the phosphine complexes, led to the recovery of the free ligand.

The complexes prepared and some of their physical properties are given in Table I. Complex ions $[CoX(QP)]^+$, like the analogues $[MX(QP)]^+$ (M = Fe

Table I. General physical data, yields and analyses of cobalt complexes of QP and QAS

Compound	Colour	Decomp. pt.	Λ_M[a] (mho)	$\mu_{eff.}$ (B.M.)	Yield (%)	C		H		P/As		Co	
						Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
$[CoCl(QP)]_2[CoCl_4]$	Blue-black	323-325°	40.2	5.55[b]	69					12.1	12.3	8.6	8.8
$[CoCl(QP)](ClO_4)\,.\,3EtOH$	Blue-black	314-316	28.1	2.05	71	62.5	62.8	4.0	5.0	11.1	10.9	5.3	5.2
$[CoCl(QP)][BPh_4]$	Red-black	262-263	15.2	1.99	65	76.0	76.3	4.8	5.1	10.0	10.1	4.7	4.8
$[CoBr(QP)]_2[CoBr_4]$	Blue-black	335-338	41.3	5.54[c]	73					10.8	10.8	7.7	7.7
$[CoBr(QP)](ClO_4)\,.\,4EtOH$	Blue-black	319-321	27.5	2.00	64					10.0	10.0	4.8	4.8
$[CoBr(QP)][BPh_4]$	Blue-black	258-259	14.9	1.98	63	73.4	73.6	4.7	4.9	9.8	9.7	4.7	4.6
$[CoI(QP)]I$	Blue-black	350-352	24.7	2.09	45	57.4	57.5	3.7	3.7	11.1	11.0	5.2	5.2
$[CoI(QP)](ClO_4)\,.\,4EtOH$	Blue-black	334-335	27.0	2.09	63					9.7	9.7	4.6	4.6
$[CoI(QP)][BPh_4]$	Blue-black	265-267	14.6	1.94	75	70.8	71.0	5.1	4.7	9.3	9.4	4.4	4.5
$[Co(NO_3)(QP)](ClO_4)\,.\,3EtOH$	Blue-black	325-327			54					10.5	10.6	4.8	5.1
$[Co(NO_3)(QP)](ClO_4)$	Blue-black	316-318	21.5		quant.					11.7	12.0	5.5	5.7
$[Co(NO_3)(QP)][BPh_4]$	Red-black	210-212	14.0	2.04	66					9.9	9.9	4.8	4.7
$[Co(NCS)(QP)][BPh_4]$ [d]	Red-brown	240-242	13.5	2.07	42	75.5	75.9	5.4	5.0	10.2	9.9	4.5	4.7
$[Co(CO)(QP)][Co(CO)_4]$ [e]	Orange-yellow	230-233	29.6	diamag.	85					11.4	11.5	10.8	11.0
$[Co(CO)(QP)]Cl$	Yellow	322-325	22.4	diamag.	24					13.0	13.2	6.2	6.3
$[Co(CO)(QP)][BPh_4]$ [f]	Yellow	265-267	15.7	0.5	70	77.4	77.7	5.1	5.1	10.1	10.2	4.8	4.8
$[Co(CO)(QAS)][BPh_4]$ [g]	Red-orange	232-234	15.1	diamag.	72	68.0	68.0	4.9	4.5	21.4	21.5	4.2	4.2
$[CoCl_2(QP)][BPh_4]$	Red	198-199	14.7	0.6	79	73.5	74.2	4.8	4.9	9.7	9.8	4.6	4.7
$[CoBr_2(QP)][BPh_4]$	Rcd	155-158	14.5	0.2	66	70.2	69.2	4.8	4.6	9.1	9.2	4.3	4.3

[a] For $10^{-3}M$ nitrobenzene solutions at 20°. [b] From $\mu_{obs.}^2 = \mu^2[_{CoCl_4}]^{2-} + 2\,\mu^2[_{CoCl(QP)}]^+$ one obtains $\mu_{eff.}[_{CoCl(QP)}]^+ = 1.94$ B.M. taking $\mu_{eff.}[_{CoCl_4}]^{2-} = 4.80$ B.M. (R.H. Holm and F. A. Cotton, *J. Chem. Phys.*, *31*, 788 (1959)). [c] Proceeding as for (*b*) one obtains $\mu_{eff.}[_{CoBr(QP)}]^+ = 1.89$ B.M. [d] The CN-stretch occurs at 2090 cm.$^{-1}$. [e] CO-stretches (in dichloromethane solution) occur at 1980 cm.$^{-1}$ (from $[Co(CO)(QP)]^+$) and at 1890 cm.$^{-1}$ (from $[Co(CO)_4]^-$, see O. Vohler, *Chem. Ber.*, *91*, 1235 (1958)). [f] The CO-stretch occurs at 1980 cm.$^{-1}$. [g] The CO-stretch occurs at 1977 cm.$^{-1}$.

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and Ni)[3] are assigned trigonal bipyramidal structures. This is supported by their electrolytic conductance, corresponding to that of 1:1 electrolytes and their magnetic susceptibility which obeys the Curie-Weiss law and indicates the presence of one unpaired electron. Although cobalt(II) complexes can give rise to S = ½ in a variety of stereochemical arrangements, e.g., octahedral $[Co(das)_3](ClO_4)_2$,[4] (das = *o*-phenylenebisdimethylarsine) has $\mu_{eff.}$ = 1.92 B.M. and square-planar *trans*-$[Co(pentachlorophenyl)_2(PEt_2Ph)_2]$,[5] has $\mu_{eff.}$ = 2.3 B.M. the values of the paramagnetic susceptibilities of our complexes is consistent with a trigonal

Table II. Visible and ultraviolet spectra of cobalt complexes with QP and QAS

Complex	Dichloromethane solution[a]		Tetrahydrofurfuryl alcohol glass[b]		Solid reflection spectrum	
	$E_{max.}$ (cm.$^{-1}$)	$\varepsilon_{max.}$	$E_{max.}$ (cm.$^{-1}$)	$\varepsilon_{max.}$	$E_{max.}$ (cm.$^{-1}$)	«A»[c]
$[CoCl(QP)]_2[CoCl_4]$	36,000	28,000				
	25,000	sh[d]				
	19,600	5,750				
	17,000	sh				
	15,700	sh				
	14,600	sh				
	9,700	450				
$[CoBr(QP)]_2[CoBr_4]$	35,000	sh				
	26,000	sh				
	19,200	5,000				
	16,300	sh				
	15,000	sh				
	14,200	sh				
	9,500	550				
$[CoI(QP)]I$	34,000	sh				
	26,000	sh				
	18,300	2,200				
	15,500	sh				
	9,000	400				
$[CoCl(QP)](ClO_4)$. 3EtOH	36,000	sh				
	25,000	sh				
	19,600	3,000				
	16,500	sh				
	9,700	270				
$[CoBr(QP)](ClO_4)$. 4EtOH	35,000	sh				
	26,000	sh				
	19,200	2,600				
	16,000	sh				
	9,500	300				
$[CoI(QP)](ClO_4)$. 4EtOH	34,000	sh				
	26,000	sh				
	18,300	2,200				
	15,500	sh				
	9,000	400				
$[CoCl(QP)][BPh_4]$	19,600	2,750	20,300	4,150	19,500	0.53
	16,500	sh	16,300	2,075	16,000	sh
	9,600	290	9,400	365	9,500	0.10
$[CoBr(QP)][BPh_4]$	19,200	2,500	19,900	3,460	19,100	0.55
	16,300	sh	16,000	1,900	15,500	sh
	9.400	330	9,300	410	9,400	0.12
$[CoI(QP)][BPh_4]$	18,300	2,140	19,300	3,090	18,200	0.65
	16,400	sh	15,900	1,770	15,000	sh
	9,200	400	9,200	530	9,100	0.15
$[Co(NO_3)(QP)][BPh_4]$	20,100	2,200	20,800	3,380	19,600	0.43
	15,800	850	16,100	1,180	16,000	sh
	9,700	130	9,400	320	9,400	0.04
$[Co(NCS)(QP)][BPh_4]$	21,400	4,020	22,000	5,050	21,000	0.36
	17,200	sh	16,800	1,890	17,000	sh
	9,700	525	9,700	790	9,500	0.10
$[CoCl_2(QP)][BPh_4]$	28,500	18,300	29,000	20,200	28,600	1.35
	20,300	5,400	21,000	6,550	20,200	0.90
$[CoBr_2(QP)][BPh_4]$	28,300	18,600	28,200	29,000	28,200	1.15
	19,500	5,200	20,200	10,200	19,300	0.50
$[Co(CO)(QP)][BPh_4]$	30,400	11,100				
	32,000	sh				
$[Co(CO)(QAS)][BPh_4]$	37,600	sh				
	28,100	8,600				
	21,600	2,950				

[a] At room temperature. [b] At —180°. [c] «A» = Arbitrary absorbance scale. [d] sh = Shoulder.

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bipyramidal structure which gives rise to the *d*-energy level splitting[3] shown in Fig. 1a. The observation that the values of the magnetic moments are close to the spin-only value indicates that the contribution of the orbital angular momentum to the susceptibility has been largely quenched. This quenching is likely to be due to the operation of the Jahn-Teller effect which would distort the trigonal bipyramidal structure to produce the *d*-orbital splitting shown in Fig. 1b.

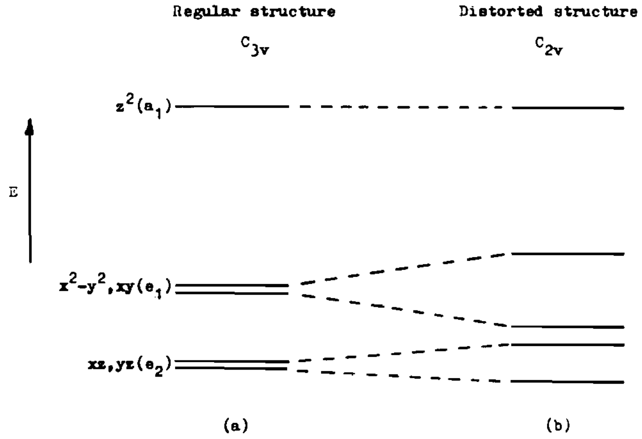

Figure 1. *d*-Energy-level splitting in regular and distorted trigonal bipyramidal complexes [CoX(QP)]$^+$.

The absorption bands expected for trigonal bipyramidal complexes [CoX(QP)]$^+$ in the visible and ultraviolet region of the spectrum have been discussed elsewhere.[6] The data for the complexes given here is summarized in Table II and the ligand-field effects of changes of anionic ligand are shown in Fig. 2. The bands in the region 8,000-12,000 cm.$^{-1}$ are, therefore, assigned to the transition $(e_2)^4(e_1)^3 \rightarrow (e_2)^3(e_1)^4$ and those in the region 14,000-22,000 cm.$^{-1}$ to transitions $(e_2)^4(e_1)^3 \rightarrow (e_2)^4(e_1)^2(a_1)^1$.

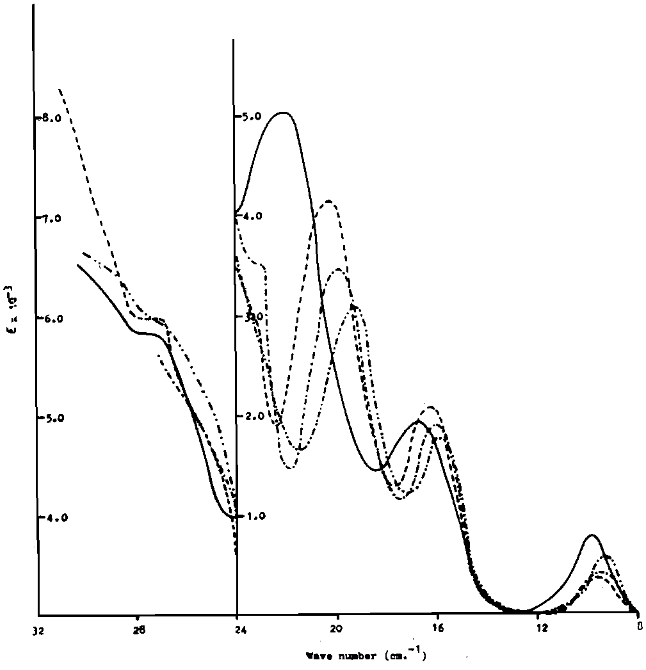

Figure 2. Visible and ultraviolet spectra of complexes [CoX(QP)][BPh$_4$] in a tetrahydrofurfuryl alcohol glass at —180°. ———: X=NCS; — — —: X=Cl; —·—·—: X=Br; —··—··—: X=I.

Cobalt(I) complexes. Reduction of complexes [CoX(QP)](ClO$_4$) (X = Cl, Br and I) either with sodium borohydride or with ethanolic hydrazine gave insoluble, black solids of variable composition. Cobalt(I) complexes of the type [Co(CO)(L)][Co(CO)$_4$] (L = QP and QAS) could, however, be obtained from the reaction of dicobalt octacarbonyl and QP or QAS. The more stable salts [Co(CO)(L)][BPh$_4$] were obtained by a double exchange reaction. Attempts to prepare [CoCl(QP)] either by thermal degradation or by irradiation of [Co(CO)(QP)]Cl led to decomposition, while irradiation of a dichloromethane solution of [Co(CO)(QP)][BPh$_4$] gave the cobalt(III) cationic complex [CoCl$_2$(QP)]$^+$.

The cobalt(I) complexes, as expected for derivatives of a d^8-ion, are diamagnetic, and their spectra are consistent with those of other metal ions of the same electronic configuration.[7] The most unusual property of these compounds is their stability towards air oxidation both in the solid state and in solution. Another interesting feature is the ease of preparation and stability of cobalt(I) complexes with the arsenic ligand QAS. This can be attributed to the low oxidation state of the cobalt atom which produces an expansion of the metal orbitals with consequent improvement of the overlap with the ligand orbitals. Finally, the ease of formation of complexes [RhX(L)], (QP and QAS),[8,9] from the carbonyl derivatives [Rh(CO)(L)]X is in marked contrast to the inertness of complexes [Co(CO)(L)]Cl which do not lose carbon monoxide either by irradiation in refluxing benzene solution or on heating the solids in vacuum below their melting points. As the CO-stretch in the cobalt complex occurs at 1980 cm.$^{-1}$ and in the rhodium complex at 2005 cm.$^{-1}$,[9] it is concluded that the effect is likely to be kinetic in nature.

Cobalt(III) complexes. Oxidation of complexes [CoX(QP)](ClO$_4$) (X=Cl and Br) with the appropriate halogen gives complexes [CoX$_2$(QP)]$^+$ which were isolated as their tetraphenylboron salts. On the other hand, treatment of the iodo-complex with iodine, under similar conditions gave [CoI(QP)]I$_3$ as indicated by the spectrum of the resulting solution which was a superimposition of the spectrum of [CoI(QP)]$^+$ and that of I$_3^-$. As expected, the cobalt(III) complexes are diamagnetic and are assigned octahedral structures similar to that found in [RuBr$_2$(QAS)].[10] The main absorption bands of the cobalt(III) complexes at ca. 20,000 cm.$^{-1}$ and at ca. 28,000 cm.$^{-1}$ are assigned[6] to the transition $^1A_{1g} \rightarrow {}^1T_{2g}$ and $^1A_{1g} \rightarrow {}^1T_{1g}$, in the O$_h$ point group, respectively.

An unusual property of these complexes is the ease with which they are reduced to the correspondig com-

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(7) M. J. Norgett, J. H. M. Thornley and L. M. Venanzi, *Coord. Chem. Revs.* (1967), in the press.

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(9) J. W. Dawson and L. M. Venanzi, unpublished observations.

(10) R. H. B. Mais, H. M. Powell and L. M. Venanzi, *Chem. and Ind.*, 1204 (1963).

plexes of cobalt(II) by mild reducing agents, e.g., ethanol. This is probably due to the trigonal symmetry of the organic ligand which imparts additional stability to complexes which preserve, at least in part, the symmetry of the ligand.

Experimental Section

The tetratertiary phosphine (QP) was prepared by the method of Hartley *et al.*,[11] using the modified procedure described by Chiswell and Venanzi.[12] The tetratertiary arsine (QAS) was prepared by the method of Howell *et al.*,[13] using the modified procedure described by Cannon *et al.*[14] All the complexes, except the perchlorates, were dried in vacuo at 130° for 15 hrs.

Complexes $[CoX(QP)]_2[CoX_4]$ ($X = Cl$ and Br) were prepared by refluxing the hydrated cobalt(II) halide (3.3 mmoles) and the ligand (2 mmoles) in ethanol (30 ml.) for 1 hr., evaporating the solution under reduced pressure and recrystallizing the crude product from ethanol. For the preparation of $[CoI(QP)]I$, which was recrystallized from ethanol, freshly prepared, hydrated cobalt(II) iodide (1.1 moles) and the ligand (1 mole) were used.

Complexes $[CoX(QP)](ClO_4) . xEtOH$ (X = Cl, Br, I and NO_3) were prepared by refluxing the hydrated cobalt(II) salt (1.1 mmoles) and the ligand (1 mmole) in ethanol for 2 hrs., adding sodium perchlorate (1.1 mmoles) in ethanol and filtering off the precipitate which was recrystallized from ethanol/dichloromethane. Complex $[Co(NO_3)(QP)](ClO_4)$ was obtainde by drying the solvated product in vacuo at 150° for 15 hrs.

Complexes $[CoX(QP)][BPh_4]$ (X = Cl, Br, I and NO_3) were prepared by refluxing the hydrated cobalt salt (1.1 mmoles) and the ligand (1 mmole) in ethanol (30 ml.) for 30 min., adding sodium tetraphenylboron (1.1 mmoles) in ethanol (10 ml.), filtering off the product and recrystallizing it from ethanol/acetone. Complex $[Co(NCS)(QP)][BPh_4]$ was prepared by refluxing $[CoCl(QP)][BPh_4]$ (0.6 g.) and sodium thiocyanate (0.1 g.) in ethanol (30 ml.) for 4 hr., evaporating the resulting solution under reduced pressure and recrystallizing the crude product from ethanol/dichloromethane at 0°.

Complexes $[CoX_2(QP)][BPh_4]$ ($X = Cl$ and Br) were prepared by adding the appropriate halogen, in carbon tetrachloride, to a dichloromethane/carbon tetrachloride solution of the appropriate complex $[CoX(QP)](ClO_4)$, evaporating the solution to dryness under reduced pressure, dissolving the solid in ethanol and adding a slight excess of sodium tetraphenylboron in ethanol. The precipitate, after filtration, was recrystallized from ethanol/acetone. In the case of the bromo-complex the latter stages were carried out at 0° and the drying of the product in vacuo was done at room temperature to prevent reduction of cobalt(III) to cobalt(II).

Complexes $[Co(CO)(L)][Co(CO)_4]$ (L = QP and QAS) were prepared by dropwise addition, in a nitrogen atmosphere, of a solution of the organic ligand (1 mmole) in dry tetrahydrofuran (20 ml.) to dicobaltoctacarbonyl (1 mmole) in dry tetrahydrofuran (20 ml.). After the colour of the solution had changed to orange-yellow, it was refluxed for 15 min., cooled and the product was precipitated by addition of dry heptane. The pure product was obtained by recrystallization from hexane/dichloromethane.

Complexes $[Co(CO)(L)][BPh_4]$ were prepared by dissolving the tetracarbonylcobaltate salt in acetone, adding a slight excess of sodium tetraphenylboron in ethanol, reducing the solution to a small volume under reduced pressure and filtering off the precipitate. This was purified by recrystallization from hexane/dichloromethane. For the preparation of complex $[Co(CO)(QP)]Cl$, dry hydrogen chloride was bubbled through a solution of $[Co(CO)(QP)][Co(CO)_4]$ (0.5 mmole) in chloroform (20 ml.), in a nitrogen atmosphere. The resulting pale green solution was evaporated, under reduced pressure giving $[Co(CO)(QP)]_2$-$[CoCl_4]$ (Found: P, 12.5%; Calc.: P, 12.4%). The composition of this intermediate was further confirmed by its visible and ultraviolet spectrum which is the superimposition of that of the cationic and anionic components. This complex (0.35 mmole) in ethanol was refluxed for 12 hr. with a five-fold excesse of tetramethylammonium chloride (50 ml.) and the blue precipitate of $[Me_4N]_2[CoCl_4]$ filtered off. The resulting yellow solution, on evaporation under reduced pressure, gave the product which was recrystallized from heptane/dichloromethane.

Analyses and physical measurements. Cobalt analyses were carried out by an EDTA titration method[15] and phosphorus by a spectrophotometric method.[3b] Analyses for carbon and hydrogen were carried out by Dr. A. Bernhardt, Mikroanalytisches Laboratorium im MaxPlank-Institut, Mülheim, Ruhr. Infrared spectra, in the rock-salt region, were recorded on a Perkin-Elmer 237 spectrometer. The visible and ultraviolet spectra were recorded an a Unicam SP 700 spectrophotometer. The solid reflectance spectra were done by the filter paper techinque[3c] and the low-temperature spectra were recorded using a Research and Industrial Instruments Co., infrared attachment (VLT 2) fitted with silica windows. Tetrahydrofurfuryl alcohol was found to give a satisfactory glass down to liquid nitrogen temperature.

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