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Synthesis, Properties and X-Ray Characterization of Cobalt(I) Complexes with the Tripod Ligand Tris(*o*-diphenylphosphinophenyl)phosphine

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The tripod ligand tris(o-diphenylphosphinophenyl)-phosphine, $P(C_6H_4PPh_2)_3$, QP, forms with cobalt(II) salts in presence of borohydride a series of five-coordinate cobalt(I) complexes of general formula [CoX(QP)], where X = Cl, Br, I, NCS, H. The hydride complex [CoH(QP)] has been studied by X-ray analysis, using diffractometer data. The crystals are orthorhombic, space group Pbca, with the following cell constants: a = 17.040(4), b = 22.312(6), c = 22.581(6) Å, d_m = 1.37 gcm^{-3}, Z = 8, d_c = 1.361 gcm^{-3}. The structure has been solved by three-dimensional Patterson and Fourier syntheses and refined by least-squares techniques to a final R_w factor of 0.048 and R factor of 0.068 for the 1203 observed reflections. The structure consists of discrete trigonal bipyramidal [CoH(QP)] molecules.

Introduction

In previous studies tripod-like ligands containing at least three phosphorus or arsenic as donor atoms have been found to favor low oxidation states (+1 and 0) in cobalt and nickel complexes.[1–3]

Sometimes, such as with the iodide derivative, the reduction of the bivalent ions occurs spontaneously, while in other cases a reducing agent such as borohydride is necessary.

In this paper we report the results of the reactions occurring when cobalt(II) salts are reduced in the presence of the tetratertiary phosphine tris(*o*-diphenylphosphinophenyl)phosphine, QP, with the reducing agent borohydride.

If the initial metal salt contains a halide or thiocyanate, five-coordinate cobalt(I) complexes of general formula [CoX(QP)] where X = Cl, Br, I, NCS, are obtained; if the initial metal salt is a tetrafluoroborate, a hydride complex, [CoH(QP)], is synthesized.

All these complexes were characterized by means of magnetic, spectrophotometric and conductivity measurements.

A complete X-ray structural analysis has been carried out for the [CoH(QP)] compound.

Experimental

Preparation of the Complexes

All preparative operations were carried out in an atmosphere of dry nitrogen and all the complexes were dried off on standing in dry nitrogen current.

The synthesis of the QP ligand has been already reported.[4]

[CoX(QP)] (X = Cl, Br, I)

0.5 mmol of the QP ligand were dissolved by heating in 45 ml glycol ethylenmonomethylether. To this solution was added CoX_2 (0.5 mmol in 10 ml ethanol). To the mixture, cooled at room temperature in dry nitrogen current, were added small bulks of $NaBH_4$ (0.05 gr in 15 ml absolute ethanol). Brown–violet crystals slowly precipitated.

[Co(NCS)(QP)]

The above complex was prepared by an analogous procedure as for [CoX(QP)] complexes, except that the ligand QP and the $Co(NCS)_2$ salt were dissolved in DMF.

[CoH(QP)]

To a hot solution (60°C about) of the QP ligand (0.5 mmol in 15 ml DMF) and of $Co(BF_4)_2$ (0.5 mmol in 10 ml ethanol) was added $NaBH_4$ (0.6 mmol in 10 ml ethanol). From the brown–red solution brown–red crystals separated, which were washed with ethanol and petroleum ether.

Materials and Physical Measurements

All solvents were reagent grade. All physical measurements were carried out as previously described.[5] Table I reports the analytical and physical data. The maxima and extinction coefficients for the electronic spectra of the complexes are given in Table II.

Crystal Data and Data Collection

The regular rhombic shaped crystal, chosen for X-ray work, had approximate dimensions 0.5 × 0.35 × 0.1 mm, parallel to a, c and b respectively. Unit cell

TABLE I. Analytical and Physical Constants.

Compd	Color	% Calcd			% Found			μ_{eff}, μ_B(293 K)	Λ_M[a] cm^{2}ohm^{-1}mol^{-1}
		C	H	M	C	H	M		
[CoCl(QP)][b]	Brown–violet	71.33	4.66	6.48	71.68	4.92	6.34	Diam	Non-conduc.
[CoBr(QP)]	Brown–violet	68.01	4.44	6.18	68.17	5.00	6.00	Diam	Non-conduc.
[CoI(QP)]	Brown–violet	64.81	4.23	5.89	64.68	4.78	5.65	Diam	Non-conduc.
[Co(NCS)(QP)][c]	Brown–violet	70.89	4.54	6.32	69.91	4.81	6.10	Diam	Non-conduc.
[CoH(QP)]	Brown–red	74.14	4.96	6.73	73.92	5.21	6.74	Diam	Non-conduc.

[a] Molar conductance of *ca.* $10^{-3}M$ soln in 1,2-dichloroethane. [b] Cl: calcd, 3.90; found, 3.90. [c] N: calcd, 1.50; found, 1.72.

TABLE II. Maxima and Extinction Coefficients for the Electronic Spectra of the Complexes.

Compd	Absorption max,[a] kK (ε_M for soln)
[CoCl(QP)]	(a) 18.9 (b) 18.3(4350)
[CoBr(QP)]	(a) 19.0 sh (c) 17.9(3760)
[CoI(QP)]	(a) 18.1 sh (b) 17.7(2270)
[Co(NCS)(QP)]	(a) 22.2
[CoH(QP)]	(a) 25.0

[a] Key: a, solid; b, tetrahydrofuran soln; c, 1,2-dichloroethane soln.

parameters obtained by a least-squares refinement of the setting angles of 25 automatically centered reflections are: *a* = 17.040(4), *b* = 22.312(6), *c* = 22.581(6) Å. The systematic absences h00 for h = 2n+1, 0k0 for k = 2n+1, 00l for l = 2n+1, hk0 for h = 2n+1, h0l for l = 2n+1 and 0kl for k = 2n+1 indicated that the space group was the orthorhombic *Pbca*. The density, as measured by flotation, is in good agreement with the value calculated for eight molecules in the unit cell. Thus all the atoms lie in general positions and there are no symmetry conditions imposed on the molecule. The intensity data were collected on an automatic computer-controlled Philips PW 1100 diffractometer, using Mo Kα radiation, monochromatized with a flat graphite crystal. The take-off angle was 4.5°. A total of 1203 observed reflections ($I \geqq 3\sigma(I)$) were collected with the ω–2ϑ scan technique, at a scan rate of 0.07°/sec. A symmetric scan of 1° was used in the range $0° < 2\vartheta \leqq 40°$. Stationary-crystal background counts of 7 sec were taken on each side of the peaks. The intensities of three standard reflections were measured every 170 readings as a check on electronic and crystal stability, but no significant trend was apparent in the intensities of the standards. All data were processed as previously de-

TABLE III. Positional Parameters ($\times 10^4$ for non-hydrogen atoms), Isotropic Temperature Factors, with Estimated Standard Deviations in Parentheses.

Atom	*x/a*	*y/b*	*z/c*	*U*($\times 10^2$, Å^2)
Co	1535(2)	729(1)	1169(1)	a
P(1)	2739(3)	784(3)	928(3)	a
P(2)	1063(3)	24(3)	1706(3)	a
P(3)	742(4)	1414(3)	917(3)	a
P(4)	1771(4)	1199(3)	1933(3)	a
C(1)	3344(14)	97(10)	825(9)	4.6(7)
C(2)	3411(15)	−277(10)	1312(9)	6.7(8)
C(3)	3863(15)	−821(13)	1256(12)	10.8(1.0)
C(4)	4184(15)	−925(12)	746(12)	8.6(1.0)
C(5)	4239(15)	−539(11)	313(11)	7.3(9)
C(6)	3802(14)	−21(11)	321(10)	7.3(8)
C(7)	3022(13)	1216(10)	257(9)	4.4(7)
C(8)	3491(15)	1712(10)	271(10)	5.4(7)
C(9)	3614(15)	2042(10)	−248(12)	8.1(9)
C(10)	3383(16)	1834(10)	−780(10)	7.0(8)

[a] These atoms were refined anisotropically.

TABLE III. (Cont.)

Atom	*x/a*	*y/b*	*z/c*	*U*(×10², Å²)
C(11)	2879(15)	1360(11)	–797(11)	6.5(8)
C(12)	2709(14)	1071(10)	–264(10)	5.8(8)
C(13)	1489(13)	–741(10)	1669(9)	5.4(7)
C(14)	1751(14)	–1071(11)	2152(10)	6.5(9)
C(15)	2050(16)	–1638(12)	2050(12)	10.5(1.1)
C(16)	2066(15)	–1876(11)	1523(11)	9.8(1.0)
C(17)	1885(15)	–1567(12)	1036(11)	8.8(1.0)
C(18)	1560(14)	–975(9)	1068(10)	6.8(7)
C(19)	–4(11)	–168(9)	1716(9)	2.9(6)
C(20)	–522(14)	234(10)	1950(10)	5.9(8)
C(21)	–1321(14)	154(11)	1984(10)	6.8(8)
C(22)	–1587(14)	–370(11)	1744(10)	7.0(8)
C(23)	–1117(14)	–792(11)	1500(10)	6.4(8)
C(24)	–300(14)	–689(11)	1504(10)	6.5(8)
C(25)	867(12)	1894(9)	244(9)	3.1(6)
C(26)	1458(15)	2332(11)	249(10)	6.5(8)
C(27)	1516(16)	2712(11)	–252(11)	8.0(9)
C(28)	1031(14)	2649(11)	–713(10)	8.7(1.0)
C(29)	494(16)	2260(12)	–747(12)	8.9(1.1)
C(30)	378(14)	1878(10)	–249(10)	6.3(9)
C(31)	–302(13)	1184(10)	775(10)	4.0(7)
C(32)	–963(15)	1549(10)	958(11)	6.3(9)
C(33)	–1688(14)	1348(10)	842(10)	6.2(8)
C(34)	–1794(13)	815(11)	550(10)	5.7(8)
C(35)	–1172(15)	452(10)	424(10)	5.8(8)
C(36)	–391(14)	648(11)	527(10)	5.7(8)
C(37)	3269(14)	1155(10)	1512(10)	4.6(7)
C(38)	2830(12)	1410(10)	1969(10)	4.4(7)
C(39)	3164(14)	1735(10)	2452(11)	4.6(7)
C(40)	4000(17)	1809(11)	2422(13)	7.8(9)
C(41)	4415(14)	1545(11)	2006(12)	6.3(8)
C(42)	4106(14)	1249(11)	1539(10)	5.3(8)
C(43)	1175(12)	240(9)	2503(10)	4.2(7)
C(44)	850(13)	–76(10)	2951(10)	5.9(8)
C(45)	955(15)	114(12)	3537(11)	6.7(9)
C(46)	1352(12)	641(10)	3656(9)	5.0(8)
C(47)	1613(13)	967(8)	3186(9)	3.8(7)
C(48)	1509(12)	793(9)	2596(8)	3.5(6)
C(49)	736(12)	2008(9)	1479(9)	3.6(7)
C(50)	1211(13)	1918(10)	1978(10)	4.8(8)
C(51)	1225(11)	2338(9)	2453(10)	3.9(7)
C(52)	782(12)	2832(9)	2385(9)	3.9(7)
C(53)	349(14)	2935(10)	1937(11)	5.1(8)
C(54)	315(12)	2563(11)	1454(10)	5.1(8)
H	.134(11)	.036(7)	.058(7)	7.7(3.2)

TABLE IV. Anisotropic Thermal[a] Parameters (×10³) with Estimated Standard Deviations in Parentheses.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	28(2)	33(2)	39(2)	–3(3)	0(2)	–2(2)
P(1)	32(5)	40(5)	38(5)	5(5)	–1(4)	2(5)
P(2)	34(4)	34(4)	39(4)	–4(4)	–1(4)	–1(4)
P(3)	29(5)	41(5)	37(4)	–6(4)	5(4)	7(4)
P(4)	34(5)	39(4)	35(4)	–3(4)	–2(4)	17(4)

[a] The temperature factor is defined as: $\exp[-2\pi^2 \sum_{i=1} \sum_{j=1} U_{ij} h_i h_j a_i^* a_j^*]$.

scribed.[6,7] The intensities were corrected for Lorentz and polarization effects. An absorption correction was applied to the intensities, the linear absorption coefficient for Mo Kα being 6.07 cm^{-1}.[8] The transmission coefficients for the crystal chosen were found to range from 0.94 to 0.98, so that the absorption correction was relatively small. The effects of anomalous dispersion of the cobalt and phosphorus atoms were included in the calculation of F_c.[9] The atomic scattering factors for cobalt, phosphorus and carbon atoms were taken from ref. 10 and those for hydrogen atoms from ref. 11.

Structure Determination

The position of the cobalt atom was determined from a three-dimensional Patterson function. The locations of the remaining non-hydrogen atoms were obtained from subsequent electron density syntheses. Refinement was then undertaken by means of full-matrix least-squares techniques; the function minimized is $\Sigma w(|F|_o-|F|_c)^2$, where w is taken as $1/\sigma(F_o)$. Two isotropic cycles were followed by several mixed cycles with anisotropic temperature factors for cobalt and phosphorus and isotropic for carbon atoms. The hydrogen atoms were included in the calculation of F_c, with B = 5.5 Å^2, in their idealized positions but were not refined. At this point a delta-F Fourier map was calculated in order to locate the hydride hydrogen atom. This difference Fourier map revealed a peak (0.6 eÅ^{-3}) at bond distance from the metal atom. A final refinement where the hydride hydrogen parameters were allowed to vary led to convergence at the discrepancy indices of R_w = 0.048 and R = 0.068, R_w being defined as $R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w F_o^2]^{1/2}$. Final values of the parameters with their estimated standard deviations are reported in Tables III and IV. A table of structure factors is available from the Editor on request.

Results and Discussion

All the compounds of the series [CoX(QP)] (X = Cl, Br, I, NCS, H) are monomeric and non-electrolytes in 1,2-dichloroethane.

Values of the magnetic moments indicate that all compounds are substantially diamagnetic, so that they should be assigned the low-spin $3d^8$ configuration.

The reflectance spectra of the halide or thiocyanate complexes show an intense band in the range 17.7–22.2 kK, which is assigned as the $^1A_1' \rightarrow {}^1E'$ transition in D_{3h} symmetry.[12] The weak symmetry-forbidden $^1A_1' \rightarrow {}^1E''$ transition, which would be expected at higher frequencies, is not observed, as it is probably masked by the charge-transfer bands.

The values of the band frequencies are in line with the spectrochemical series of the elements (NCS> Cl>Br>I).

The unique intense band at 25 kK present in the spectrum of the hydride complex cannot be safely assigned, but can be well compared to the band exhibited in the range 20–25 kK by analogous hydride complexes.[2,13]

The infrared spectrum of the [CoH(QP)] complex shows a band at *ca.* 1880 and a "doublet" at *ca.* 605 and 588 cm^{-1}, which are absent in the deuterated complex. The first band may be assigned to M–H stretching and the other two bands to bending vibra-

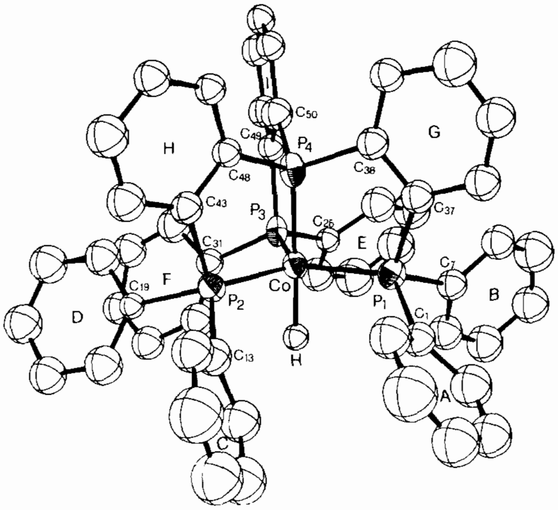

Figure 1. The molecule with labelled atoms.

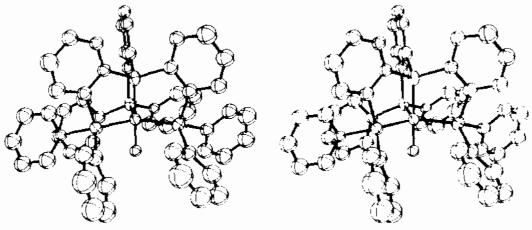

Figure 2. Stereo drawing of the molecule.

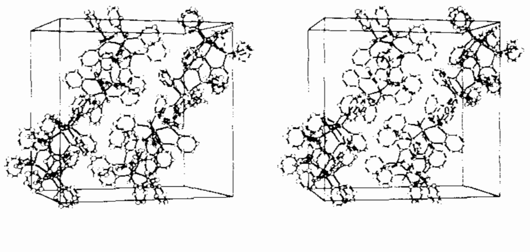

Figure 3. Stereo drawing of the unit cell content.

tions; all can be compared with the analogous frequencies found in other five-coordinate hydride complexes of nickel and cobalt with tripod ligands.[2,3,13]

The hydride complex was characterized also by a quantitative determination of the hydrogen gas liberated on treatment with hydrochloric acid.

The X-ray analysis has shown that the hydride complex has a trigonal bipyramidal structure, consisting of discrete [CoH(QP)] molecules. Figure 1 shows the molecule with labelled atoms. Figures 2 and 3 show stereo drawings of the molecule and of the unit cell content respectively. The metal atom is five-coordinated by the four phosphorus atoms of the ligand and by the hydride atom. Interatomic distances and angles are reported in Table V.

A significant feature of the structure is the value of the axial bond, which is appreciably shorter than the equatorial bonds (2.058(7) *vs.* 2.13 (av.)Å). This fact is not surprising: the repulsions between the valency shell electrons pairs and the oblate core of d^8 electrons, the d_{z^2} orbital being unoccupied, can provide reasonable explanation for that.[14] Similar axial contractions

TABLE V. Bond Lengths (Å) and Angles (deg), with Estimated Standard Deviations in Parentheses.

Co–P(1)	2.126(7)	P(2)–C(19)	1.87(2)
Co–P(2)	2.143(7)	P(2)–C(43)	1.87(2)
Co–P(3)	2.117(7)	P(3)–C(25)	1.87(2)
Co–P(4)	2.058(7)	P(3)–C(31)	1.88(2)
Co–H	1.60(16)	P(3)–C(49)	1.83(2)
P(1)–C(1)	1.86(2)	P(4)–C(38)	1.87(2)
P(1)–C(7)	1.86(2)	P(4)–C(48)	1.81(2)
P(1)–C(37)	1.80(2)	P(4)–C(50)	1.87(2)
P(2)–C(13)	1.86(2)		
P(1)–Co–P(2)	123.3(3)	Co–P(4)–C(48)	113.1(7)
P(1)–Co–P(3)	120.4(3)	Co–P(4)–C(50)	112.5(8)
P(1)–Co–P(4)	89.8(3)	C(38)–P(4)–C(48)	109.2(1.0)
P(1)–Co–H	91(6)	C(38)–P(4)–C(50)	105.9(1.0)
P(2)–Co–P(3)	116.2(3)	C(48)–P(4)–C(50)	104.9(1.0)
P(2)–Co–P(4)	88.4(3)	P(1)–C(1)–C(2)	116.2(1.6)
P(2)–Co–H	91(6)	P(1)–C(1)–C(6)	124.3(1.7)
P(3)–Co–P(4)	89.0(3)	P(1)–C(7)–C(8)	123.5(1.7)
P(3)–Co–H	91(6)	P(1)–C(7)–C(12)	119.4(1.7)
P(4)–Co–H	179(6)	P(2)–C(13)–C(14)	125.3(1.6)
Co–P(1)–C(1)	121.2(8)	P(2)–C(13)–C(18)	113.8(1.5)
Co–P(1)–C(7)	119.2(7)	P(2)–C(19)–C(20)	118.9(1.6)
Co–P(1)–C(37)	108.9(8)	P(2)–C(19)–C(24)	123.7(1.6)
C(1)–P(1)–C(7)	100.4(1.0)	P(3)–C(25)–C(26)	118.2(1.5)
C(1)–P(1)–C(37)	101.1(1.0)	P(3)–C(25)–C(30)	124.5(1.6)
C(7)–P–(1)–C(37)	103.2(1.0)	P(3)–C(31)–C(32)	122.2(1.7)
Co–P(2)–C(13)	120.2(7)	P(3)–C(31)–C(36)	115.2(1.7)
Co–P(2)–C(19)	122.7(7)	P(1)–C(37)–C(38)	117.5(1.7)
Co–P(2)–C(43)	108.4(7)	P(1)–C(37)–C(42)	126.4(1.7)
C(13)–P(2)–C(19)	99.8(1.0)	P(2)–C(43)–C(44)	122.8(1.6)
C(13)–P(2)–C(43)	103.9(9)	P(2)–C(43)–C(48)	114.9(1.6)
C(19)–P(2)–C(43)	98.4(9)	P(3)–C(49)–C(50)	116.7(1.6)
Co–P(3)–C(25)	123.9(7)	P(3)–C(49)–C(54)	126.9(1.6)
Co–P(3)–C(31)	116.9(8)	P(4)–C(38)–C(37)	112.4(1.6)
Co–P(3)–C(49)	109.8(7)	P(4)–C(38)–C(39)	123.2(1.7)
C(25)–P(3)–C(31)	97.1(9)	P(4)–C(48)–C(43)	115.1(1.5)
C(25)–P(3)–C(49)	98.5(9)	P(4)–C(48)–C(47)	128.3(1.5)
C(31)–P(3)–C(49)	108.1(1.0)	P(4)–C(50)–C(49)	112.0(1.6)
Co–P(4)–C(38)	110.8(7)	P(4)–C(50)–C(51)	126.6(1.6)

Mean Bond Lengths (Å) and Angles (deg) in the Benzene Rings

Ring A	1.37(2)	119.7(1.2)	Ring F	1.38(2)	119.9(8)
Ring B	1.37(1)	119.8(1.1)	Ring G	1.39(2)	119.9(1.7)
Ring C	1.38(2)	119.9(1.3)	Ring H	1.38(1)	119.9(1.0)
Ring D	1.37(1)	120.0(1.7)	Ring I	1.37(2)	120.0(1.4)
Ring E	1.37(3)	120.0(1.3)			

have been already found in the [CoH(np$_3$)] and [CoH (pp$_3$)] complexes.[2,13] The value of the Co–H bond length (1.60(16) Å) is reasonable and well comparable with those reported for other hydride complexes of cobalt(I).[15,16] The angles between the equatorial and the axial Co–P bonds (89°(av.)), very close to the value of the regular trigonal bipyramidal geometry, approach those found in d^8 hydride complexes.[3]

It is of interest to compare the structure of the cobalt(I) complex [CoH(QP)] with that of a cobalt(II) complex, containing the same ligand QP, *i.e.* [CoCl(QP)]BPh$_4$.[17] The coordination geometry of the first compound is almost regular trigonal bipyramidal, while that of the second complex shows an appreciable distortion toward the square pyramid. The Jahn–Teller effect could be invoked to explain this difference. In fact in the d^8 configuration of the [CoH(QP)] complex the d_{xy} and $d_{x^2-y^2}$ orbitals are fully occupied, while in the [CoCl(QP)]BPh$_4$ compound (d^7) one of the two orbitals is single occupied: so the orbital degeneracy of the d^7 configuration is removed by the distortion.

An additional explanation for this different stereochemistry can be the steric hindrance of the chlorine atom with respect to the hydride ligand.

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