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The Crystal and Molecular Structure of [Co(QP)Cl]BPh₄ QP = tris(*o*-diphenylphosphinophenyl)phosphine

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The crystal and molecular structure of [Co(QP)Cl]BPh₄ [QP = tris(*o*-diphenylphosphinophenyl)phosphine] is reported. The compound crystallizes in space group *P2₁nb*, $a = 18.85 \pm 0.02$, $b = 18.25 \pm 0.02$, $c = 18.60 \pm 0.02$ Å. The X-ray analysis, involving the use of anomalous scattering techniques in the solution of the phase problem, has shown the cation to have a distorted trigonal bipyramidal coordination of the cobalt in a [Co(QP)Cl]⁺ ion. Although the ligand can have trigonal symmetry, there is a large distortion from threefold axial symmetry, giving an equatorial angle of 137.2°. Arguments are presented to show that this may be a Jahn-Teller effect. The angles between the equatorial and the axial cobalt-phosphorus bonds are 86.5 ± 0.6°, and the axial cobalt-phosphorus bond length, 2.057 Å, is significantly shorter than the equatorial bond lengths of 2.261, 2.280 and 2.318 Å. There are many van der Waals contacts between phenyl groups of the QP ligand and between these and the axial chlorine atom.

Introduction

Although the results of many X-ray crystal structure analyses are now available for pentacoordinate complexes, the stereochemical problem has not yet been fully resolved.

Early theoretical work of Pauling (1939), Daudel & Bucher (1945) and Linnett & Mellish (1954) for instance, gave conflicting predictions about the relative stabilities of the two ideal geometries, the trigonal bipyramid and the square pyramid. It has other shortcomings. Even when different approaches predict the same preferred stereochemistry, the characterization of the bonding is different; the theories often predict the wrong relative strengths for the equatorial and apical

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bonds; and they give no explanation for the many distortions from idealized geometry that are observed in pentaco-ordinate complexes.

In order to explain these anomalies, several factors have been suggested recently by different authors to be important in determining the relative stabilities of the possible geometries. The most important of these appear to be

- (a) valency-shell electron-pair repulsions (Gillespie, 1963).
- (b) crystal field stabilization energy (Basolo & Pearson, 1958).
- (c) steric requirements of the ligands (Venanzi, 1967).
- (d) packing requirements of the complex in the crystal.

It appears that the stereochemistries of most pentaco-ordinate complexes may be considered to result from a delicate balance of these factors.

In order to study the third factor, Venanzi (1967), in an attempt to prepare low spin trigonal bipyramidal complexes of transition metals, has synthesized a series of complexes with the ligand, QP, shown in Fig. 1, and QAS the analogous arsenic ligand. An X-ray analysis proved the complex ion $[\text{Pt}(\text{QAS})\text{I}]^+$ to have only a slightly distorted trigonal bipyramidal geometry (Mair, Powell & Venanzi, 1961). Chemical and spectroscopic data indicated that the analogous QP and QAS complexes with Co(II), Ni(II) and Fe(II) ions were most probably closely trigonal bipyramidal also (Norgett, Thornley & Venanzi, 1967). However, the complexes $[\text{M}(\text{II})(\text{QP})\text{Cl}]\text{BPh}_4$ were not isomorphous, and this was considered a possible indication of slightly differing stereochemistries despite the apparently rigid steric requirements in the platinum complex.

The crystal and molecular structure of the complex $[\text{Co}(\text{QP})\text{Cl}]\text{BPh}_4$ is reported here.

Experimental

Crystal data

$\text{C}_{18}\text{H}_{62}\text{BClCoP}_4$, $M = 1224.5$, orthorhombic; the observed systematic absences $h0l$ for $h+l$ odd and $hk0$ for k odd are consistent with $P2_1nb$ or $Pmnb$; cell dimensions, $a = 18.85 \pm 0.02$, $b = 18.25 \pm 0.02$, $c = 18.60 \pm 0.02$ Å; $U = 6398.6$ Å³, $D_m = 1.25$ (by flotation), $Z = 4$, $D_c = 1.27$, $F(000) = 2556$; Cu $K\alpha$ radiation, $\mu = 36.8$.

Preliminary crystallographic investigation with Cu $K\alpha$ radiation indicated that $F_{hkl} \neq F_{\bar{h}\bar{k}\bar{l}}$ in many cases, suggesting that the crystals were non-centrosymmetric and anomalous scattering was giving rise to a breakdown of Friedel's law. Therefore, 4416 reflexions with indices hkl and $\bar{h}\bar{k}\bar{l}$ were collected with b -axis rotation in order that the Friedel differences might be used in the structure determination if necessary. A further 2300 reflexions were collected with a -axis rotation. Multiple film equi-inclination Weissenberg photographs were used and the intensities were estimated visually.

Accurate cell dimensions were obtained from Weissenberg photographs with superposed aluminum pow-

der lines. A least-squares method was used to make corrections for film shrinkage and eccentricity (Kilbourn, 1965).

The intensities were corrected for absorption by the Busing & Levy (1957) method, and for Lorentz and polarization effects, and then scaled together by means of the least-squares method of Rollett, Hamilton & Sparks (1965), applied to reflexions common between layers.

Observation of large Friedel differences was a strong indication that the structure was non-centrosymmetric. Nevertheless, an analysis of the intensity statistics was made to confirm this. The absolute scale and temperature factors were calculated from a Wilson plot omitting reflexions $0kl$ because of the space group ambiguity.

The intensities were then normalized. The mean value for the reflexions $0kl$ was not abnormally high and $N(z)$ and $N(F)$ plots were close to the acentric distribution (Phillips, Rogers & Wilson, 1950). Further, Foster & Hargreaves's (1963) general moment tests which allow for heavy atoms in general and special positions gave values of 2.22 and 7.09 for $\langle z^2 \rangle$ and $\langle z^3 \rangle$ respectively. (Where the r th moment of z is given by $\langle z^r \rangle = \langle I^r \rangle / \langle I \rangle^r$). The theoretical values are 2 and 6 for $P2_1nb$ and 3 and 15 for $Pmnb$. The non-centrosymmetric space-group $P2_1nb$ is therefore confirmed.

The Patterson function

A three-dimensional, sharpened Patterson function was computed. The interpretation of this was confused by two factors. First, interatomic vectors involving the seventy-nine light atoms confused the identification and precise positioning of the cobalt, phosphorus and chlorine vectors. Second, the arrangement of the four phosphorus atoms and a chlorine around the cobalt atom was a *distorted* trigonal bipyramid with its axis approximately in the direction of the a axis. This gave rise to a partial superposition of the heavy atom vectors. Thus the cobalt, phosphorus and chlorine atom positions were not accurately defined from the Patterson synthesis, and, furthermore, the almost trigonal bipyramidal arrangement gave rise to a pseudo-mirror plane perpendicular to the a axis.

Determination of the position of light atoms

The value of r , where $r = \sum f_4^2 / \sum f_2^2$, was only 0.23 for the cobalt atom (Sim, 1958). Furthermore, the ligand phosphorus and chlorine atoms were both very inaccurately placed and pseudosymmetrical. Thus two different approaches to finding the heavy atoms were developed concurrently. The Bijvoet differences were used in the calculation of phases in addition to the use of the normal heavy atom method.

(i) The heavy atom method

Structure factors were computed using the cobalt and five inaccurate ligand positions. Approximately

75% of the phases were within 20° of 0 and π , and the resulting pseudosymmetric electron density map comprised two superposed structures related by a mirror plane through the cobalt atom. A series of 'difference' Fourier syntheses eventually gave the positions of the seventy-nine light atoms in the ligand and the tetraphenylborate ion.

(ii) *The use of anomalous scattering techniques*

The Bijvoet–Ramachandran–Raman (Ramachandran & Raman, 1956; Peerdeman & Bijvoet, 1956) method was investigated. The phase, α' , is related to the heavy atom phase, α_p , by

$$\alpha' = \alpha_p + \pi/2 - \theta$$

where θ is the angle between the real and imaginary parts of the structure factor. $\cos \theta$ is given by the Bijvoet difference and the real and imaginary parts of the heavy atom structure factor. The ambiguity of deriving θ from $\cos \theta$ is overcome by taking the phase closest to the heavy atom phase, in this case the phase calculated from the cobalt atom. The small imaginary part of the structure factor due to the phosphorus and chlorine atoms was ignored.

For 2100 reflexions where Bijvoet differences had been measured, phases were computed. The resulting electron density map was far superior to that calculated by the heavy atom method. All the light atoms of the cation were easily identified. Peaks of at least two electrons occurred at all of the carbon atom positions finally determined. There was an average difference of 23° between the final calculated phases for the refined structure and the phases calculated by the Bijvoet, Raman–Ramachandran method.

Refinement of the structure

The positional parameters derived from heavy atom phases and Bijvoet difference-phased electron density maps were refined by the method of least squares. Owing to the large number of positional and isotropic vibrational parameters, 339 in all, full-matrix least squares was not possible. Moreover, the program available was limited to 181 parameters in one cycle, and therefore, two cycles were necessary to refine all the parameters. The cobalt positional parameters were included in each cycle and the x coordinate was not refined in order to fix the origin in this direction. In each cycle eight submatrices were used. In the first cycle, the positional parameters for the heavy atoms and the carbon atoms of each of six phenyl rings were refined in separate submatrices. In the second cycle, the positional parameters of the remaining seven phenyl rings were refined in separate matrices, one of which contained the cobalt and boron positional parameters. The overall scale and the isotropic vibrational parameters were included in a further submatrix in both cycles.

This procedure included the most important off-diagonal elements. In particular, it included the param-

eters of the apical phosphorus and chlorine atoms in the same matrix. The positions originally chosen for these atoms were within 0.3 Å of being related by a pseudo-mirror plane. By including them together any 'inverse overlap' (Srinivasan, 1961; Maslen, 1963), resulting from this pseudosymmetry would have been immediately recognized by large standard deviations. However, the refinement proceeded normally.

Structure factor magnitudes were calculated by averaging F_{hkl} and $F_{\bar{h}\bar{k}\bar{l}}$ and were assigned weights, w , according to the relationship

$$1/w = 1 + [(F_o - b)/a]^2$$

where a and b were chosen to remove the dependence of wA^2 on F_o .

Table 1. *Positional parameters ($\times 10^5$) and isotropic vibrational parameters ($\times 10^3$)*

	Y	Z	X	U
Co	727	2077	25000	20
P(1)	11301	8566	24365	27
P(2)	-9004	9579	22262	24
P(3)	2720	-9861	25933	30
P(4)	1683	561	14259	23
Cl	-870	1992	37119	48
C(141)	12787	10671	15148	50
C(142)	18913	14149	12376	61
C(143)	19591	14993	5082	51
C(144)	14771	11964	388	35
C(145)	8911	7746	3197	44
C(146)	7794	6820	10363	12
C(241)	-11765	6926	13664	33
C(242)	-18257	9267	10217	35
C(243)	-20359	6546	3784	45
C(244)	-15514	2144	28	47
C(245)	-8934	-455	3149	27
C(246)	-6949	2171	9881	33
C(341)	7068	-12488	17896	32
C(342)	11042	-19359	16861	60
C(343)	12947	-21268	9461	46
C(344)	11081	-16645	4250	50
C(345)	7468	-10206	5076	38
C(346)	5461	-8043	11808	22
C(111)	10993	17296	28657	36
C(112)	7107	18281	34929	96
C(113)	7317	24089	39255	110
C(114)	9729	30569	34858	120
C(115)	15166	29936	30575	117
C(116)	14803	22982	27028	121
C(121)	19953	4553	27140	29
C(122)	22507	5538	33786	32
C(123)	29110	2025	35997	40
C(124)	32530	-2563	30748	46
C(125)	30252	-3045	24102	61
C(126)	23645	-127	21816	39
C(211)	-9130	19345	21474	32
C(212)	-13463	23904	26050	60
C(213)	-13154	31087	24269	80
C(214)	-9523	33923	18936	72
C(215)	-5318	29744	14683	72
C(216)	-4788	22383	16554	68
C(221)	-16587	7542	27789	38
C(222)	-23012	3527	25970	33
C(223)	-28571	1306	30225	48
C(224)	-28327	3563	37326	49
C(225)	-22059	7833	39998	62
C(226)	-16403	9683	35133	44
C(311)	7394	-14410	33270	48

Table 1 (cont.)

	Y	Z	X	U
C(312)	15905	-13951	32883	68
C(313)	19836	-17185	38525	79
C(314)	15581	-20566	43792	66
C(315)	8769	-21216	43601	70
C(316)	3820	-17743	38236	47
C(321)	-6055	-14714	25955	38
C(322)	-12000	-11590	28609	58
C(323)	-18452	-15553	28633	110
C(324)	-18844	-22665	25601	102
C(325)	-12597	-26386	24136	114
C(326)	-4929	-22387	24144	94
C(11)	6676	55672	18345	48
C(12)	9373	62096	21119	49
C(13)	8801	63426	28616	89
C(14)	5430	58745	33047	72
C(15)	2727	52576	30255	76
C(16)	3120	50367	23104	67
C(21)	-2536	56511	7691	58
C(22)	-7556	51834	6216	64
C(23)	-15952	53159	5250	104
C(24)	-17365	60632	6294	111
C(25)	-12345	66450	6419	94
C(26)	-5067	63700	8124	77
C(31)	12208	59716	5158	43
C(32)	19547	60356	8085	91
C(33)	23846	64272	3554	83
C(34)	20746	67264	-2546	81
C(35)	15149	67463	-5138	109
C(36)	10481	63412	-576	76
C(41)	8161	46308	7052	35
C(42)	11453	41271	11498	48
C(43)	13377	34318	8616	58
C(44)	12123	32461	1926	46
C(45)	8620	37580	-2759	66
C(46)	6463	43960	-111	53
B	6373	54342	9726	42

After two full cycles, the least-squares refinement converged. From these atomic parameters values of the imaginary part of the structure factor were computed,

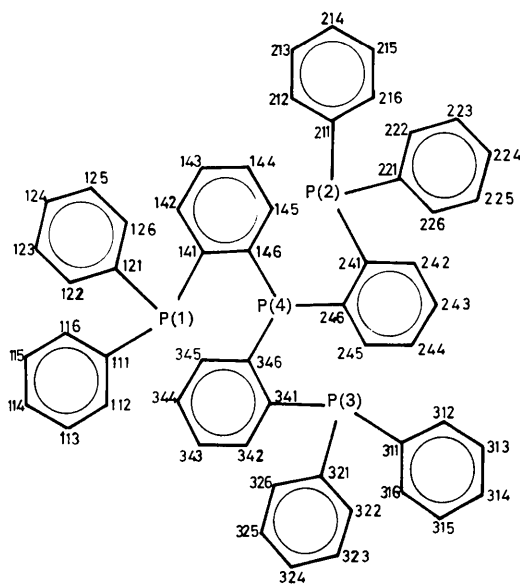


Fig. 1. The ligand, QP.

and the observed values of $|F_{hkl}|$ were adjusted to give an estimate of the real part. These magnitudes were then used in a final cycle of least-squares refinement. The R value converged at 0.11. A final analysis of the largest observed values of $|F|$ showed that they were consistently lower than the calculated values. This was considered to result from extinction and also from an underestimation of scale-factors used in relating the Weissenberg photographs together.

All computer programs were written in C203 auto-code and a symbolic machine code for use on an English Electric KDF9 computer. Except for the Wilson plot, intensity statistics and absorption programs which were written by one of the authors (TLB.) the computer programs were written by Dr J. Rollett and Mr O. J. R. Hodder.

The key to the labelling of the ligand atoms is given in Fig. 1. Table 1 gives the final isotropic vibrational and positional parameters; selected bond lengths and angles with their standard deviations are given in Tables 2 and 3. Tables of observed and calculated structure factors will be made available by the authors on request.

Table 2. Selected bond lengths with their standard deviations in parentheses (\AA)

Co—P(1)	2.280 (4)
Co—P(2)	2.318 (4)
Co—P(3)	2.261 (4)
Co—P(4)	2.057 (4)
Co—Cl	2.309 (6)
P(1)—C(141)	1.81 (3)
P(1)—C(111)	1.82 (2)
P(1)—C(121)	1.82 (2)
P(2)—C(241)	1.77 (2)
P(2)—C(211)	1.83 (2)
P(2)—C(221)	1.78 (2)
P(3)—C(341)	1.78 (2)
P(3)—C(311)	1.83 (2)
P(3)—C(321)	1.84 (2)
P(4)—C(146)	1.77 (2)
P(4)—C(246)	1.80 (2)
P(4)—C(346)	1.80 (2)

Mean values

C—C of phenyl ring	1.40 (4)
C—B of anion	1.67 (4)
P—C of cation	1.80 (2)

Discussion

The structure projected on to (010) is shown in Fig. 2. The main feature is the linear chain of screw-axis related cations running continuously through the crystal in the direction of the a axis. Adjacent cations related by the twofold screw axis fit neatly into each other giving maximum separation of the negatively charged chlorine atoms. Projected on to (100), these chains form a face-centred array with tetraphenylborate ions filling the channels between them.

The stability of this structure combined with a tetraphenylborate ion is probably due both to the large size

and shape of the anion which allows many van der Waals contacts with the very large and irregular shaped complex cations. The use of smaller anions almost always resulted in solvent of crystallization. The tetraphenylborates of the iron and nickel analogues were examined but neither [Fe(QP)Cl]BPh₄ nor [Ni(QP)Cl]BPh₄ proved to be isomorphous with either [Co(QP)Cl]BPh₄ or each other.

The stereochemistry of the pentacoordinate unipositive complex ion [Co(QP)Cl]⁺ is shown in Figs. 3 and 4. The most significant features of the distorted trigonal bipyramidal coordination of the cobalt are:

- the large distortion from threefold axial symmetry giving one equatorial angle of 137.2°.
- the bending of the equatorial Co-P bonds towards the apical phosphorus atom.
- the very short apical Co-P bond length.

(a) *The distortion from threefold symmetry*

One of the equatorial P-Co-P angles is 137.2° compared with the other two of 108.5 and 112.9°. This surprisingly large distortion from trigonal symmetry is not found in the related complexes [Ni(TAP)CN]⁺ (TAP = tris(3-dimethylarsinopropyl)phosphine) or in [Pt(QAS)I]⁺ (QAS = tris(*o*-diphenylarsinophenyl)arsine) (Stevenson & Dahl, 1967) where the largest angle is 122°. However a similar stereochemistry is found in [CoBr₂(PPh₂)₃], a low spin, distorted trigonal bipyramidal complex, with one equatorial angle of 136° (Bertrand & Plymale, 1966). In this complex, two bromine atoms occupy equatorial positions, and so the complex cannot have trigonal symmetry in any case. How-

ever, the ligands TAP, QAS and QP are designed to allow perfect threefold symmetry, and deviations from this symmetry are of particular interest.

Venanzi has attributed the small distortion from trigonal symmetry in [Pt(QAS)I]⁺, *i.e.* the angle of 122° to a gain in crystal field stabilization energy (Dyer & Venanzi, 1965). Crystal field stabilization energy is greater for a square pyramidal than for a trigonal bipyramidal coordination for *d*⁸ and also *d*⁷ electron configurations; the distortion of 122° was described as a distortion towards a square pyramidal geometry. However, crystal field stabilization energy

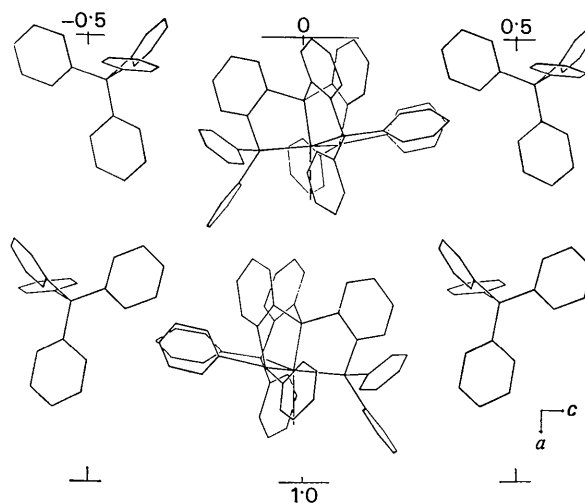


Fig. 2. Arrangement of cations [Co(QP)Cl]⁺, and anions [B(C₆H₅)₄]⁻ seen in projection on (010).

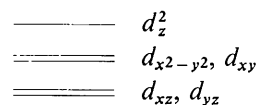
Table 3. Selected bond angles and their standard deviations in parentheses (°)

P(1)-Co-P(2)	108.5 (0.2)	Co—P(3)-C(341)	106.0 (0.6)
P(1)-Co-P(3)	112.9 (0.2)	Co—P(3)-C(311)	125.3 (0.8)
P(2)-Co-P(3)	137.2 (0.2)	Co—P(3)-C(321)	110.1 (0.7)
P(1)-Co-P(4)	87.1 (0.2)	C(341)-P(3)-C(311)	105.3 (1.0)
P(2)-Co-P(4)	85.9 (0.2)	C(341)-P(3)-C(321)	104.8 (1.0)
P(3)-Co-P(4)	85.9 (0.2)	C(311)-P(3)-C(321)	103.7 (1.0)
P(1)-Co-Cl	99.4 (0.2)	Co—P(4)-C(146)	111.9 (0.5)
P(2)-Co-Cl	97.4 (0.2)	Co—P(4)-C(246)	110.8 (0.6)
P(3)-Co-Cl	86.3 (0.2)	Co—P(4)-C(346)	114.0 (0.5)
P(4)-Co-Cl	171.4 (0.2)	C(146)-P(4)-C(246)	104.4 (0.8)
Co—P(1)-C(141)	107.0 (0.8)	C(146)-P(4)-C(346)	103.7 (0.7)
Co—P(1)-C(111)	115.1 (0.6)	C(246)-P(4)-C(346)	111.3 (0.8)
Co—P(1)-C(121)	120.0 (0.6)	P(1)-C(141)-C(146)	113.2 (1.5)
C(141)-P(1)-C(111)	103.9 (1.0)	P(4)-C(146)-C(141)	117.1 (1.3)
C(141)-P(1)-C(121)	103.7 (1.0)	P(2)-C(241)-C(246)	117.0 (1.4)
C(111)-P(1)-C(121)	105.4 (0.8)	P(4)-C(246)-C(241)	114.1 (1.4)
Co—P(2)-C(241)	104.7 (0.6)	P(3)-C(341)-C(346)	115.4 (1.3)
Co—P(2)-C(211)	128.9 (0.7)	P(4)-C(346)-C(341)	112.4 (1.2)
Co—P(2)-C(221)	109.7 (0.6)	C(11)-B-C(21)	102.6 (2.1)
C(241)-P(2)-C(211)	101.5 (0.9)	C(11)-B-C(31)	113.1 (2.1)
C(241)-P(2)-C(221)	104.9 (0.9)	C(11)-B-C(41)	116.3 (2.1)
C(211)-P(2)-C(221)	104.6 (0.9)	C(21)-B-C(31)	109.9 (2.1)
		C(21)-B-C(41)	109.8 (2.1)
		C(31)-B-C(41)	105.1 (2.1)
		Mean value for C-C-C of phenyl rings	120.1 (2.5)

is a more important factor for platinum(II) complexes than for cobalt(II) complexes. It appears unlikely that it would give rise to a distortion of 17.2° in the cobalt(II) case but only 2° in the platinum(II) case. Furthermore, the crystal field stabilization energy should be greater for a square pyramidal $[\text{Ni}(\text{TAP})\text{CN}]^+$ (Stevenson &

Dahl, 1967), but this complex shows no distortion from trigonal symmetry. It is unlikely, therefore, that the distortion in $[\text{Co}(\text{QP})\text{Cl}]^+$ results from a gain in crystal field stabilization in moving towards a square pyramidal geometry.

It appears possible therefore, that the distortion arises from large spin-orbit coupling effects or from the Jahn-Teller effect. In a molecule with C_{3v} symmetry, the five d orbitals split into three groups, two of which are doubly degenerate. The relative energies of the orbitals are given below



Consequently in a low spin complex with a d^8 electron configuration such as $[\text{Pt}(\text{QAS})\text{I}]^+$ or $[\text{Ni}(\text{TAP})\text{CN}]^+$ the two sets of doubly degenerate orbitals would be fully occupied. However, in a complex with a d^7 electron configuration, only one of the $d_{x^2-y^2}$ and d_{xy} orbitals can have two electrons. Thus a Jahn-Teller distortion must result in order that these orbitals should no longer be degenerate; a distortion from threefold symmetry such as that observed in $[\text{Co}(\text{QP})\text{Cl}]^+$ would have this effect.

(b) *The bending of the equatorial Co-P bonds towards the apical phosphorus atom and the non-linear P-Co-P system*

The angles between the three equatorial and the axial Co-P bonds are $86.5 \pm 0.6^\circ$. The stereochemistry of the $[\text{Pt}(\text{QAS})\text{I}]^+$ ion is similar (Mair, Powell & Venanzi, 1961), and angles between the axial and the equatorial Pt-As bonds are bent towards the cyanide group with P-Ni-As angles of $94.7 \pm 0.3^\circ$ (Stevenson & Dahl, 1967).

At first sight these facts appear to be related to the more rigid requirements of the bridging phenyl rings in QP and QAS than in TAP, where the bridging is by an aliphatic chain. However, this is disproved by the geometry of the bridging system in QP. If in fact the bridging span (the distance between two phosphorus atoms bonded to the same benzene ring) was strained so that the equatorial groups are pulled towards the axial phosphorus, then it would be expected that the P-C-P angles of the bridging system would be slightly greater than 120° . In fact the values are $114.9 \pm 2.5^\circ$, very significantly less than 120° . Thus the bending of the equatorial groups tends to increase the distortions from preferred geometry of the ligand.

The explanation for these distortions in QAS and QP complexes seems to be found in the van der Waals energy of intramolecular contacts. QAS and QP are very bulky ligands, and there are van der Waals contacts in $[\text{Co}(\text{QP})\text{Cl}]^+$ between the phenyl rings on adjacent equatorial phosphorus atoms as well as between the phenyl rings of the QP ligand and the axial chlorine atom. A list of intramolecular distances which

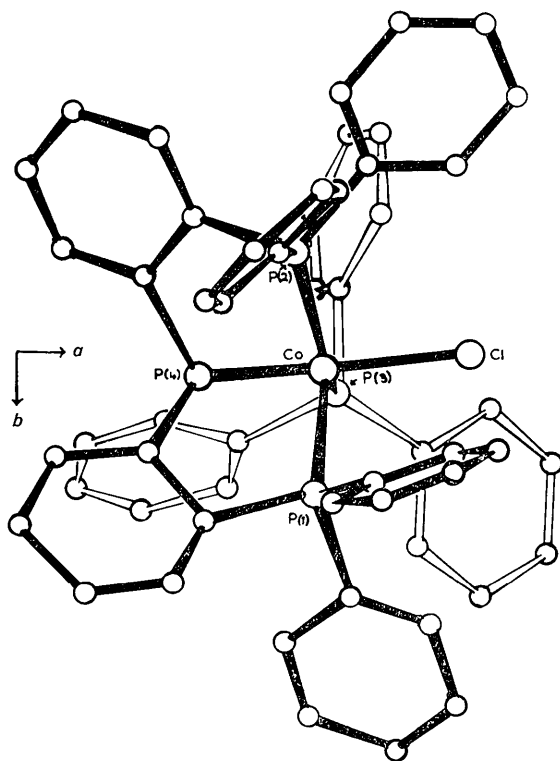


Fig. 3. Detail of the cation, $[\text{Co}(\text{QP})\text{Cl}]^+$, seen in projection on (001).

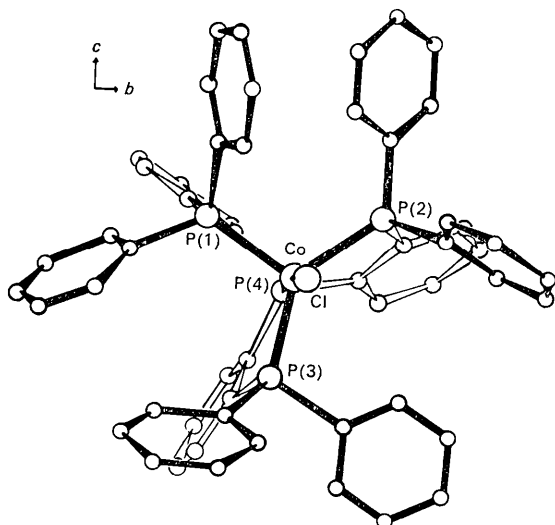


Fig. 4. Detail of the cation, $[\text{Co}(\text{QP})\text{Cl}]^+$, seen in projection on (100).

are less than 4 Å is given in Table 4. In fact the molecule has approximate C_3 symmetry and not C_{3v} symmetry. Fig. 4 shows clearly that of the phenyl rings attached to an equatorial phosphorus atom, one is pushed up and the other down towards the apical chlorine atom, so that their positions alternate around the equatorial plane. This allows close van der Waals packing and a distortion towards C_{3v} symmetry would increase repulsion energies between phenyl rings. Moreover, a distortion such that the angle between the equatorial and axial cobalt phosphorus bonds was 90° would increase repulsion between the axial chlorine and the ligand phenyl ring atoms. The observed angles between these axial and equatorial bonds may then be a result of minimizing the van der Waals repulsion energy of intramolecular contacts; this is consistent with the similar geometry of [Pt(QAS)I]⁺, and the lack of distortions in [Ni(TAP)CN]⁺, where the large phenyl groups are replaced by methyl groups.

Table 4. *Some selected intramolecular distances*

Cl-C(111)	3.65 Å	C(312)-C(121)	3.68 Å
Cl-C(112)	3.39	C(312)-C(122)	3.82
Cl-C(221)	3.51	C(321)-C(123)	3.87
Cl-C(226)	3.20	C(312)-C(124)	3.72
Cl-C(311)	3.48	C(312)-C(125)	3.70
Cl-C(316)	3.78	C(312)-C(126)	3.60
C(111)-C(211)	3.93	C(313)-C(123)	3.98
C(111)-C(216)	3.79	C(313)-C(124)	3.71
C(112)-C(211)	3.94		
C(221)-C(322)	3.66		
C(222)-C(322)	3.49		
C(222)-C(323)	3.68		
C(223)-C(322)	3.87		
C(223)-C(323)	3.65		

The authors can see no mechanism by which similar van der Waals repulsions could lead to a lack of three-fold symmetry as described in the previous section as the three equatorial phosphorus atoms and the adjoining phenyl rings are equivalent. A distortion of three-fold symmetry increases some interactions while decreasing equivalent ones.

(c) *The short axial Co-P bond*

In both [Co(QP)Cl]⁺ and Pt(QAS)I⁺ (Mair, Powell & Venanzi, 1961) the axial metal-ligand bond is much shorter than the equatorial bonds. In the complex cobalt cation, the axial bond length is 2.057 Å while the equatorial bond lengths are 2.261, 2.280 and 2.318 Å, all of standard deviation 0.004 Å. Similarly, in the platinum complex cation the axial bond length is 2.31 Å compared with 2.43, 2.45 and 2.49 Å for the equatorial bonds. By the same argument as that used in the previous section it is easily established that these differences are not due to steric requirements of the ligand bridging groups.

There has been considerable discussion about metal-phosphorus bond-lengths, and it is clear that a mole-

cular orbital treatment including consideration of synergic interaction involving the d orbitals of the phosphorus atom is required for a full explanation of the nature of the bonding. Nevertheless, consideration of the over-simplified crystal field model can sometimes provide a useful insight into the stereochemistry of transition metal complexes. In the case of C_3 symmetry, the d_{z^2} orbital is considerably destabilized compared with other orbitals and thus for the d^7 and d^8 electron configurations of the cobalt(II) and platinum(II) complexes this orbital will be unoccupied. In this situation an increase in the effective dipole in the axial position relative to that in the equatorial positions or, in other words, a decrease in the axial bond length together with an increase in equatorial bond lengths will increase the energy of the d_{z^2} orbital, but stabilize the occupied orbitals. Thus equatorial bonds longer than the axial bond will give a greater crystal field stabilization in both complexes.

Gillespie (1963) has predicted a shorter axial bond in trigonal bipyramidal complexes with a d^7 and d^8 electron configuration. He attributes the distortion to repulsions between the valency-shell electron pairs and the oblate core of d^7 or d^8 electrons. This argument is equivalent to that given above in terms of crystal field stabilization energy.

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