Redetermination of bis(methyltriphenyl-phosphonium) hexachloridorhenate(IV)

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The title compound, $(C_{19}H_{18}P)_2[ReCl_6]$, has been prepared by a new method and its structure redetermined [Hołynska, Korabik & Lis (2006). *Acta Cryst.* E**62**, m3178–m3180]. The previously observed orientational disorder of the $[ReCl_6]^{2-}$ anion (Re site symmetry $\bar{1}$) is reinterpreted as being due to a minor cocrystallized Re^V-containing impurity. Revised magnetic, MS and spectroscopic data are also presented and discussed. The crystal structure involves $C-H\cdots Cl$ hydrogen bonds.

Related literature

For the previous structure, see: Hołyńska *et al.* (2006). For background, see: König (1966); Lis & Jeżowska-Trzebiatowska (1977); Lukas (1978); Takazawa *et al.* (1990).
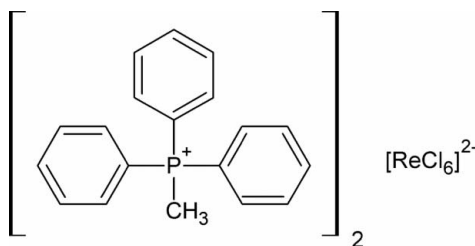
Experimental

Crystal data

$(C_{19}H_{18}P)_2[ReCl_6]$
M_r = 953.52
Monoclinic, $P2_1/n$
a = 9.155 (4) Å
b = 16.429 (5) Å
c = 12.964 (5) Å
β = 101.61 (3)°

V = 1910 (1) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 3.71 mm^{-1}
T = 100 (2) K
$0.23 \times 0.04 \times 0.03$ mm

Data collection

Oxford Diffraction KM-4-CCD diffractometer
Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2006)
T_{min} = 0.597, T_{max} = 0.894

27585 measured reflections
7666 independent reflections
5027 reflections with $I > 2\sigma(I)$
R_{int} = 0.083

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.056
S = 1.00
7666 reflections

214 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.82 e Å^{-3}
$\Delta\rho_{min}$ = −0.98 e Å^{-3}

Table 1
Selected bond lengths (Å).

Re—Cl1	2.3549 (10)	Re—Cl3	2.3644 (12)
Re—Cl2	2.3604 (11)		

Table 2
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C22—H22$\cdots$Cl2^i	0.95	2.74	3.527 (4)	141
C62—H62$\cdots$Cl2^{ii}	0.95	2.81	3.523 (4)	133
C1—H131$\cdots$Cl1^{iii}	0.98	2.71	3.570 (4)	147
C63—H63$\cdots$Cl1^{ii}	0.95	2.83	3.426 (4)	122
C1—H121$\cdots$Cl3	0.98	2.85	3.473 (4)	122
C42—H42$\cdots$Cl3^{iv}	0.95	2.83	3.712 (4)	155
C23—H23$\cdots$Cl3^v	0.95	2.73	3.567 (4)	147

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x-\frac{1}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$; (iii) $x-1, y, z$; (iv) $x+\frac{1}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$; (v) $-x, -y+1, -z+1$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB2601).

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supplementary materials

Redetermination of bis(methyltriphenylphosphonium) hexachloridorhenate(IV)

M. Holynska, M. Korabik and T. Lis

Comment

During our recent unpublished studies on the reaction of gaseous hydrogen chloride with rhenates(VII) (continuation of the work of Lis & Jeżowska-Trzebiatowska, 1977) formation of crystalline products with rhenium at different oxidation states was observed. It was confirmed with a number of physicochemical methods that these products usually contained minor quantity of cocrystallizing impurities, sometimes hardly detectable. This induced us to reinspect all our previous results for compounds obtained by this method.

In our previous paper on the title compound, (I), bis(methyltriphenylphosphonium) hexachlororhenate(IV) we reported the crystal structure of the product obtained from the suspension of methyltriphenylphosphonium rhenate(VII) in acetone exposed to gaseous HCl (Hołyńska *et al.*, 2006). It was assumed that the crystal structure consists of methyltriphenylphosphonium cations and slightly disordered hexachlororhenate(IV) anions. The reinspection showed that one of the three independent Re–Cl bond lengths was slightly shorter than expected based on the literature data [2.323 (3) Å in comparison to 2.3545 (9) reported for potassium hexachlororhenate(IV) by Takazawa *et al.*, 1990]. This work investigates whether this was a result either of minor impurity content or artifact connected with disorder. The other aim is to obtain a pure compound with reliable geometric parameters for the hexachlororhenate(IV) anion.

Therefore recently we used a different method to prepare (I), namely simple precipitation in reaction between methyltriphenylphoshonium chloride and potassium hexachlororhenate(IV). It was assumed that if the different method yields results not arguable from crystallographic point of view, the previous results were affected by impurity content rather than disorder artifacts. The X-ray studies performed on the crystal obtained in recrystallization from ethanol yield different results than in the previous work (Hołyńska *et al.*, 2006). Therefore, the previously reported slightly distorted geometry of the hexachlororhenate(IV) anion, its apparent "disorder" as well as high peaks on the difference Fourier map, could be a result of a co-crystallized impurity, most probably by a Re^V complex. For one thing, it was observed that methyltriphenylphosphonium *trans*-aquatetrachlorooxorhenate(V) monohydrate could be obtained in crystalline form as a second reaction product in the previously investigated system (Hołyńska *et al.*, unpublished). In this salt each anion consists of the central Re^V atom bonded to the oxo ligand and aqua ligand in *trans* position to the oxo ligand and four chlorine ligands lying in the distorted coordination octahedron equatorial plane. The *trans*-aquatetrachlorooxorhenate(V) anion could in small amount cocrystallize with the hexachlororhenate(IV) product. However, the attempt to take such impurity into account during the crystal structure re-refinement was unsuccessful. The reason for this situation could be the very small amounts of the impurity or that the Re^V anion is disordered in many positions in the crystal structure. The position of peaks on the difference Fourier map (Hołyńska *et al.*, 2006) as well as the mode of the hexachlororhenate(IV) anion distortion suggest that the Re atom of the Re^V complex anion is in the same position as the hexachlororhenate(IV) anion Re atom. Moreover, none of the possible anion orientations allows the water molecule coordinated to the Re^V atom to be involved in any strong hydrogen bonds. This is poorly confirmed by the IR spectra obtained in nujol mull in the 3100–3400 cm^{-1} region (hardly detectable bands at 3580 and 3600 cm^{-1}). On the other hand, a weak band at approximately 937 cm^{-1} could be observed which could be

assigned to the Re—O stretching mode. The mass spectra obtained for the pure and impure title compound differ to a small extent, especially with respect to the 200–350 m/Z range where for the latter high noise level is present and some minor peaks could be interpreted as a result of an oxocomplex anion defragmentation [assuming after Lukas (1978) that $ReOCl_3^+$ and $ReOCl_2^+$ ions could be formed]. The previously reported (Hołyńska et al., 2006) magnetic susceptibility data for the impure compound assuming the additivity of gram magnetic susceptibilities (König, 1966) at room temperature allow us to estimate the Re^V impurity amount at about 7–8%.

The structure described here for (I) seems to be more reliable than the structure reported previously (Hołyńska et al., 2006). The title crystal structure consists of hexachlororhenate(IV) anions and methyltriphenylphosphophonium cations (Fig. 1). Each hexachlororhenate(IV) anion is generated by inversion and is of octahedral geometry (Table 1). The geometry of the methyltriphenylphosphonium cation does not differ from our previous results (Hołyńska et al., 2006). The overall crystal structure (Fig. 2) is also as previously reported (Hołyńska et al., 2006). The weak C—H···Cl hydrogen bonding scheme (Table 2) is essentially conserved in comparison to the previously reported structure (Hołyńska et al., 2006) taking into consideration the higher-occupancy component of the hexachlororhenate(IV) anion.

The magnetic susceptibility data collected for the newly obtained compound (Fig. 3) reveal in comparison to the previously published data (Hołyńska et al., 2006) a similar effective magnetic moment temperature dependence with lower values at 300 K (3.54μ_B) in comparison to the here reported 3.71μ_B. This is understandable assuming the diamagnetic properties of the Re^V impurity. The impurity causes lowering of the $\chi_m T$ values in the temperature range $50 - 300$ K (Fig. 3). In the $50 - 300$ K temperature range the $\chi_m T$ values for the "impure" compound are nearly constant which is another effect introduced by the diamagnetic impurity. The new value of the parameter D is 17 (2) cm^{-1} which is higher than 14 (2) cm^{-1} obtained previously (Hołyńska et al., 2006). The remaining fitted parameters are g (perpendicular) and g (parallel). For the 'pure' compound their values are 1.68 and 2.28, respectively (the minimalized $R = 4.0 \times 10^{-4}$). For the 'impure' compound their values are 1.71 and 2.04, respectively (the minimalized value $R = 2.73 \times 10^{-5}$).

Experimental

0.5 g of potassium hexachlororhenate(IV) was dissolved in hot concentrated hydrochloric acid. Stoichiometric quantity of methyltriphenylphosphonium chloride dissolved in concentrated hydrochloric acid was added. As a result, a fine greenish precipitate was formed. The product was recrystallized from hot ethanol to yield green needles of (I). The crystal taken for X-ray measurement was cut from a larger needle. ESI-MS spectrum was collected in acetonitrile for the 'pure' compound as well as for the 'impure' compound obtained with the aid of the method described previously (Hołyńska et al., 2006). The device used was micrOTOF-Q (data for the 'pure' compound (m/Z for negative ions): 363.8 ($ReCl_5^-$); 326.8 ($ReCl_4^-$); (m/Z for positive ions): 277.1 ($PPh_3CH_3^+$); 1230.1 (evidently for the cluster ions formed during the ionization process). IR spectra were collected for suspensions in nujol mull on BRUKER spectrometer. The magnetic measurements were performed for 0.02831 g powdered sample of the title complex, at the magnetic field 0.5 T, using Quantum Design SQUID Magnetometer (type MPMS-XL5), at 1.8 to 300 K temperature range. The corrections introduced for diamagnetism of the constituent atoms were introduced based on the Pascal constants (König, 1966).

Refinement

The non-hydrogen atom coordinates from the previously study (Hołyńska *et al.*, 2006) were used as the starting model for the present refinement. The H atoms were generated geometrically (C—H = 0.95–0.98 Å) and refined as riding with $U_{iso}(H)$ = 1.2$U_{eq}(C)$ or 1.5U_{eq}(methyl C). The highest difference peak is 0.6–0.9Å from Re.
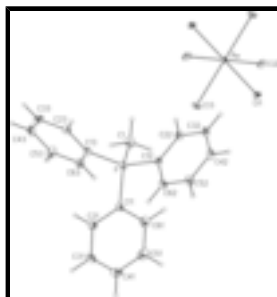
Figures

Fig. 1. View of the molecular structure of (I) with atom labelling scheme adopted from our previous work (Hołyńska *et al.*, 2006). The non-labelled non-hydrogen atoms are related by the symmetry operation: (i) $1 - x$, $1 - y$, $1 - z$.
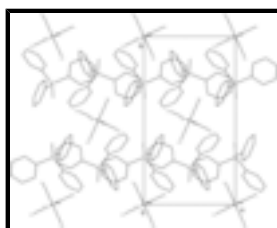

Fig. 2. The packing for (I) viewed along [001] showing cation layers perpendicular to [010]. H atoms were omitted for clarity.
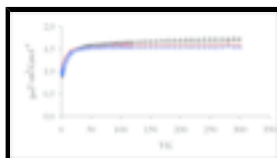
Fig. 3. The $\chi_m T$ temperature dependence (χ_m - the molar magnetic susceptibility) for the "impure" (blue open triangles) and "pure" (black open circles) compounds. The calculated curves are denoted with solid lines (see text). The red squares illustrate the simulated $\chi_m T$ temperature dependence of the "pure" compound with 7% diamagnetic impurity.

bis(methyltriphenylphosphonium) hexachloridorhenate(IV)

Crystal data

$(C_{19}H_{18}P)_2[ReCl_6]$	$F_{000} = 942$
$M_r = 953.52$	$D_x = 1.658$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 12158 reflections
$a = 9.155$ (4) Å	$\theta = 3–35°$
$b = 16.429$ (5) Å	$\mu = 3.71$ mm^{-1}
$c = 12.964$ (5) Å	$T = 100$ (2) K
$\beta = 101.61$ (3)°	Needle, green
$V = 1910$ (1) Å^3	$0.23 \times 0.04 \times 0.03$ mm
$Z = 2$	

Data collection

Oxford Diffraction KM-4-CCD diffractometer	7666 independent reflections
Radiation source: fine-focus sealed tube	5027 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.083$
$T = 100(2)$ K	$\theta_{max} = 35.0°$
ω scans	$\theta_{min} = 3.0°$
Absorption correction: analytical (CrysAlis RED; Oxford Diffraction, 2006)	$h = -14 \rightarrow 13$
$T_{min} = 0.597$, $T_{max} = 0.894$	$k = -26 \rightarrow 25$
27585 measured reflections	$l = -20 \rightarrow 15$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.053$	$w = 1/[\sigma^2(F_o^2) + (0.0084P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.056$	$(\Delta/\sigma)_{max} = 0.002$
$S = 1.00$	$\Delta\rho_{max} = 0.82$ e Å^{-3}
7666 reflections	$\Delta\rho_{min} = -0.98$ e Å^{-3}
214 parameters	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	y	z	U_{iso}*/U_{eq}
Re	0.5000	0.5000	0.5000	0.01104 (4)
Cl2	0.56433 (10)	0.48672 (5)	0.33339 (6)	0.0217 (2)
Cl1	0.60865 (9)	0.63048 (5)	0.51815 (6)	0.01666 (17)
Cl3	0.27081 (9)	0.55985 (5)	0.41870 (7)	0.02034 (19)
P	−0.00563 (10)	0.71920 (5)	0.63598 (7)	0.01511 (18)
C1	0.0052 (4)	0.6349 (2)	0.5511 (3)	0.0254 (8)
H111	0.0669	0.5921	0.5906	0.038*

H121	0.0498	0.6527	0.4922	0.038*
H131	−0.0952	0.6137	0.5240	0.038*
C11	−0.1190 (4)	0.79804 (19)	0.5638 (2)	0.0156 (7)
C21	−0.2431 (4)	0.8290 (2)	0.5957 (3)	0.0207 (8)
H21	−0.2717	0.8081	0.6570	0.025*
C31	−0.3261 (4)	0.8906 (2)	0.5381 (3)	0.0277 (9)
H31	−0.4128	0.9109	0.5592	0.033*
C41	−0.2831 (4)	0.9222 (2)	0.4509 (3)	0.0292 (9)
H41	−0.3381	0.9655	0.4130	0.035*
C51	−0.1599 (5)	0.8910 (2)	0.4182 (3)	0.0328 (10)
H51	−0.1319	0.9122	0.3568	0.039*
C61	−0.0775 (4)	0.8296 (2)	0.4739 (3)	0.0297 (9)
H61	0.0075	0.8086	0.4513	0.036*
C12	0.1785 (4)	0.7612 (2)	0.6796 (2)	0.0158 (7)
C22	0.3037 (4)	0.7143 (2)	0.6761 (2)	0.0183 (7)
H22	0.2928	0.6607	0.6481	0.022*
C32	0.4455 (4)	0.7463 (2)	0.7138 (3)	0.0210 (8)
H32	0.5315	0.7145	0.7114	0.025*
C42	0.4610 (4)	0.8241 (2)	0.7546 (3)	0.0227 (8)
H42	0.5578	0.8455	0.7807	0.027*
C52	0.3353 (4)	0.8715 (2)	0.7577 (3)	0.0236 (8)
H52	0.3463	0.9253	0.7853	0.028*
C62	0.1945 (4)	0.8397 (2)	0.7203 (3)	0.0211 (8)
H62	0.1087	0.8716	0.7224	0.025*
C13	−0.0826 (4)	0.68715 (19)	0.7461 (2)	0.0154 (7)
C23	−0.1450 (4)	0.6100 (2)	0.7468 (3)	0.0190 (8)
H23	−0.1456	0.5740	0.6894	0.023*
C33	−0.2064 (4)	0.5858 (2)	0.8313 (3)	0.0254 (9)
H33	−0.2497	0.5333	0.8317	0.031*
C43	−0.2043 (4)	0.6387 (3)	0.9156 (3)	0.0259 (9)
H43	−0.2451	0.6219	0.9740	0.031*
C53	−0.1429 (4)	0.7155 (2)	0.9143 (3)	0.0266 (9)
H53	−0.1429	0.7515	0.9717	0.032*
C63	−0.0815 (4)	0.7405 (2)	0.8306 (3)	0.0214 (8)
H63	−0.0391	0.7932	0.8302	0.026*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Re	0.01165 (8)	0.00856 (7)	0.01278 (8)	0.00030 (12)	0.00211 (6)	−0.00037 (12)
Cl2	0.0359 (5)	0.0136 (5)	0.0191 (4)	0.0011 (3)	0.0137 (3)	0.0003 (3)
Cl1	0.0174 (4)	0.0103 (4)	0.0209 (4)	−0.0019 (3)	0.0006 (3)	0.0001 (3)
Cl3	0.0143 (4)	0.0141 (4)	0.0295 (5)	0.0028 (3)	−0.0030 (4)	−0.0003 (3)
P	0.0136 (5)	0.0179 (4)	0.0137 (4)	0.0000 (3)	0.0023 (4)	−0.0046 (3)
C1	0.025 (2)	0.027 (2)	0.0229 (18)	−0.0021 (16)	0.0025 (16)	−0.0129 (15)
C11	0.0140 (19)	0.0165 (17)	0.0149 (16)	0.0003 (13)	−0.0005 (14)	−0.0020 (13)
C21	0.022 (2)	0.0181 (19)	0.0225 (19)	0.0001 (15)	0.0070 (17)	−0.0021 (15)
C31	0.019 (2)	0.021 (2)	0.042 (3)	0.0035 (16)	0.0030 (19)	−0.0053 (17)

C41	0.030 (2)	0.023 (2)	0.029 (2)	0.0033 (17)	−0.0055 (18)	−0.0001 (16)
C51	0.044 (3)	0.039 (2)	0.0142 (18)	−0.002 (2)	0.0048 (18)	0.0064 (16)
C61	0.031 (2)	0.040 (2)	0.0193 (19)	0.0048 (18)	0.0084 (17)	0.0040 (17)
C12	0.0136 (18)	0.0188 (18)	0.0144 (16)	−0.0010 (13)	0.0013 (14)	−0.0004 (13)
C22	0.021 (2)	0.0188 (18)	0.0162 (17)	0.0003 (14)	0.0064 (15)	−0.0021 (13)
C32	0.015 (2)	0.032 (2)	0.0172 (17)	0.0011 (15)	0.0057 (15)	0.0004 (15)
C42	0.018 (2)	0.036 (2)	0.0140 (17)	−0.0076 (16)	0.0024 (15)	−0.0033 (15)
C52	0.020 (2)	0.0233 (19)	0.028 (2)	−0.0051 (15)	0.0050 (16)	−0.0071 (15)
C62	0.015 (2)	0.025 (2)	0.0244 (19)	0.0020 (15)	0.0064 (16)	−0.0031 (15)
C13	0.0140 (19)	0.0171 (17)	0.0143 (16)	−0.0019 (13)	0.0007 (14)	−0.0015 (13)
C23	0.0149 (19)	0.0227 (19)	0.0167 (17)	−0.0004 (14)	−0.0033 (14)	−0.0028 (14)
C33	0.023 (2)	0.0218 (19)	0.028 (2)	−0.0073 (15)	−0.0053 (16)	0.0067 (16)
C43	0.015 (2)	0.041 (3)	0.022 (2)	−0.0022 (18)	0.0038 (17)	0.0077 (19)
C53	0.033 (2)	0.029 (2)	0.0191 (19)	−0.0078 (17)	0.0077 (17)	−0.0040 (15)
C63	0.024 (2)	0.0184 (18)	0.0214 (18)	−0.0050 (15)	0.0045 (16)	−0.0028 (14)

Geometric parameters (Å, °)

Re—Cl1	2.3549 (10)	C61—H61	0.95
Re—Cl2	2.3604 (11)	C12—C62	1.389 (5)
Re—Cl3	2.3644 (12)	C12—C22	1.390 (5)
Re—Cl1[i]	2.3549 (10)	C22—C32	1.395 (5)
Re—Cl2[i]	2.3604 (11)	C22—H22	0.95
Re—Cl3[i]	2.3644 (12)	C32—C42	1.380 (5)
P—C1	1.783 (3)	C32—H32	0.95
P—C13	1.793 (3)	C42—C52	1.397 (5)
P—C11	1.800 (3)	C42—H42	0.95
P—C12	1.804 (3)	C52—C62	1.385 (5)
C1—H111	0.98	C52—H52	0.95
C1—H121	0.98	C62—H62	0.95
C1—H131	0.98	C13—C23	1.391 (4)
C11—C21	1.381 (5)	C13—C63	1.401 (4)
C11—C61	1.396 (5)	C23—C33	1.386 (5)
C21—C31	1.390 (5)	C23—H23	0.95
C21—H21	0.95	C33—C43	1.393 (5)
C31—C41	1.371 (5)	C33—H33	0.95
C31—H31	0.95	C43—C53	1.383 (5)
C41—C51	1.380 (5)	C43—H43	0.95
C41—H41	0.95	C53—C63	1.382 (5)
C51—C61	1.376 (5)	C53—H53	0.95
C51—H51	0.95	C63—H63	0.95
Cl1—Re—Cl2	89.85 (3)	C22—C12—P	120.2 (3)
Cl1—Re—Cl3	89.14 (4)	C12—C22—C32	119.7 (3)
Cl2—Re—Cl3	89.60 (4)	C12—C22—H22	120.1
C1—P—C13	110.0 (1)	C32—C22—H22	120.1
C1—P—C11	109.6 (1)	C42—C32—C22	120.0 (3)
C13—P—C11	110.3 (1)	C42—C32—H32	120.0
C1—P—C12	109.0 (1)	C22—C32—H32	120.0

C13—P—C12	110.7 (1)	C32—C42—C52	120.4 (3)
C11—P—C12	107.0 (1)	C32—C42—H42	119.8
P—C1—H111	109.5	C52—C42—H42	119.8
P—C1—H121	109.5	C62—C52—C42	119.5 (3)
H111—C1—H121	109.5	C62—C52—H52	120.3
P—C1—H131	109.5	C42—C52—H52	120.3
H111—C1—H131	109.5	C52—C62—C12	120.3 (3)
H121—C1—H131	109.5	C52—C62—H62	119.9
C21—C11—C61	119.4 (3)	C12—C62—H62	119.9
C21—C11—P	122.2 (3)	C23—C13—C63	120.2 (3)
C61—C11—P	118.4 (3)	C23—C13—P	120.0 (3)
C11—C21—C31	120.1 (4)	C63—C13—P	119.8 (3)
C11—C21—H21	119.9	C33—C23—C13	119.9 (3)
C31—C21—H21	119.9	C33—C23—H23	120.0
C41—C31—C21	120.1 (4)	C13—C23—H23	120.0
C41—C31—H31	120.0	C23—C33—C43	119.8 (3)
C21—C31—H31	120.0	C23—C33—H33	120.1
C31—C41—C51	120.1 (4)	C43—C33—H33	120.1
C31—C41—H41	120.0	C53—C43—C33	120.1 (4)
C51—C41—H41	120.0	C53—C43—H43	120.0
C61—C51—C41	120.4 (4)	C33—C43—H43	120.0
C61—C51—H51	119.8	C63—C53—C43	120.7 (3)
C41—C51—H51	119.8	C63—C53—H53	119.6
C51—C61—C11	119.9 (4)	C43—C53—H53	119.6
C51—C61—H61	120.1	C53—C63—C13	119.2 (3)
C11—C61—H61	120.1	C53—C63—H63	120.4
C62—C12—C22	120.1 (3)	C13—C63—H63	120.4
C62—C12—P	119.7 (3)		
C1—P—C11—C21	123.7 (3)	P—C12—C22—C32	−177.5 (2)
C13—P—C11—C21	2.4 (3)	C12—C22—C32—C42	0.1 (5)
C12—P—C11—C21	−118.2 (3)	C22—C32—C42—C52	−0.5 (5)
C1—P—C11—C61	−57.6 (3)	C32—C42—C52—C62	0.5 (5)
C13—P—C11—C61	−178.8 (3)	C42—C52—C62—C12	−0.2 (5)
C12—P—C11—C61	60.6 (3)	C22—C12—C62—C52	−0.2 (5)
C61—C11—C21—C31	0.4 (5)	P—C12—C62—C52	177.6 (3)
P—C11—C21—C31	179.1 (3)	C1—P—C13—C23	−10.1 (3)
C11—C21—C31—C41	−1.5 (6)	C11—P—C13—C23	111.0 (3)
C21—C31—C41—C51	2.1 (6)	C12—P—C13—C23	−130.7 (3)
C31—C41—C51—C61	−1.5 (6)	C1—P—C13—C63	170.8 (3)
C41—C51—C61—C11	0.4 (6)	C11—P—C13—C63	−68.1 (3)
C21—C11—C61—C51	0.1 (5)	C12—P—C13—C63	50.2 (3)
P—C11—C61—C51	−178.6 (3)	C63—C13—C23—C33	0.0 (5)
C1—P—C12—C62	161.3 (3)	P—C13—C23—C33	−179.1 (3)
C13—P—C12—C62	−77.5 (3)	C13—C23—C33—C43	−0.5 (5)
C11—P—C12—C62	42.8 (3)	C23—C33—C43—C53	0.8 (6)
C1—P—C12—C22	−20.9 (3)	C33—C43—C53—C63	−0.8 (6)
C13—P—C12—C22	100.3 (3)	C43—C53—C63—C13	0.3 (6)
C11—P—C12—C22	−139.4 (3)	C23—C13—C63—C53	0.1 (5)
C62—C12—C22—C32	0.2 (5)	P—C13—C63—C53	179.2 (3)

supplementary materials

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C22—H22···Cl2[i]	0.95	2.74	3.527 (4)	141
C62—H62···Cl2[ii]	0.95	2.81	3.523 (4)	133
C1—H131···Cl1[iii]	0.98	2.71	3.570 (4)	147
C63—H63···Cl1[ii]	0.95	2.83	3.426 (4)	122
C1—H121···Cl3	0.98	2.85	3.473 (4)	122
C42—H42···Cl3[iv]	0.95	2.83	3.712 (4)	155
C23—H23···Cl3[v]	0.95	2.73	3.567 (4)	147

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) *x*−1/2, −*y*+3/2, *z*+1/2; (iii) *x*−1, *y*, *z*; (iv) *x*+1/2, −*y*+3/2, *z*+1/2; (v) −*x*, −*y*+1, −*z*+1.

Fig. 1

Fig. 2

Fig. 3