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Key indicators

Single-crystal X-ray study
 $T = 100$ K
Mean $\sigma(\text{C}-\text{C}) = 0.006$ Å
Disorder in solvent or counterion
 R factor = 0.058
 wR factor = 0.088
Data-to-parameter ratio = 37.2For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

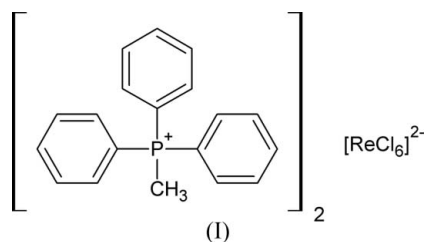
Methyltriphenylphosphonium hexachlororhenate(IV)

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The title compound, $(\text{C}_{19}\text{H}_{18}\text{P})_2[\text{ReCl}_6]$, consists of alternating cationic and anionic layers. Unlike some related materials, the Re^{IV} cations (Re site symmetry $\bar{1}$) of the hexachlororhenate(IV) anions do not order magnetically. Some of the Cl atoms of the anion are disordered over two positions related by rotation with respect to a Cl—Re—Cl axis, which can be correlated with C—H \cdots Cl interactions.

Comment

Numerous crystal structures containing $[\text{ReCl}_6]^{2-}$ hexachlororhenate(IV) anions combined with organic cations have been reported (Cambridge Structural Database, Version 5.27; Allen, 2002). However, phosphonium cations are constituents of only two of these structures, namely the bis(triphenylphosphine)iminium salt (Chau *et al.*, 1988) and the tetraphenylphosphonium salt acetonitrile solvate (Małecka *et al.*, 1998). Magnetic studies performed on compounds of this type have often revealed the presence of antiferromagnetic interactions between neighbouring d^3 Re^{IV} centres (Gonzalez *et al.*, 2005; Mroziński *et al.*, 2002). The possible means of transfer of magnetic interactions was proposed to be *via* hydrogen bonds (Mroziński *et al.*, 2002) or Re—L \cdots L—Re contacts (L denotes a ligand) (Tomkiewicz *et al.*, 2003).



The title compound, (I), is an example of a hexachlororhenate(IV) compound in which the magnetic centres are effectively diluted by the bulky methyltriphenylphosphonium cations, thereby preventing magnetic ordering. Each nearly regular octahedral hexachlororhenate(IV) anion has inversion symmetry, with the Re—Cl bond lengths showing normal values (Table 1; Małecka *et al.*, 1998). The anions are disordered over two orientations (Fig. 1) related by rotation with respect to an axis defined by the atoms Cl1, Re and Cl1ⁱ [symmetry code: (i) $1 - x, 1 - y, 1 - z$]. The two positions differ significantly in occupancy [0.91 (2) and 0.09 (2), respectively]. The methyltriphenylphosphonium cation displays its normal shape (Nelson & Alcock, 1982).

In the crystal structure of (I), well defined cation layers perpendicular to [010] are apparent (Fig. 2). Voids formed

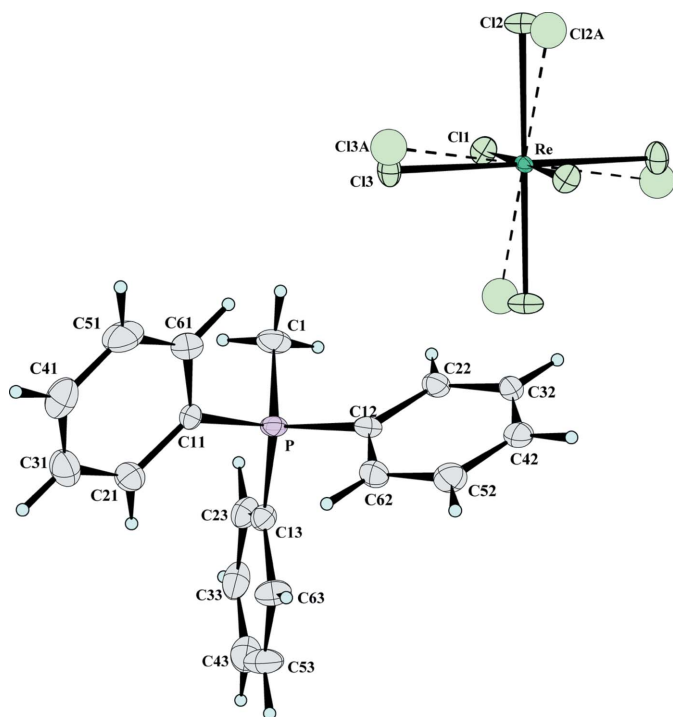


Figure 1

The structure of the constituent ions of (I), showing 50% probability displacement ellipsoids. The bonds for the minor component are dashed. Unlabelled Cl atoms are generated by the symmetry operation $(1 - x, 1 - y, 1 - z)$.

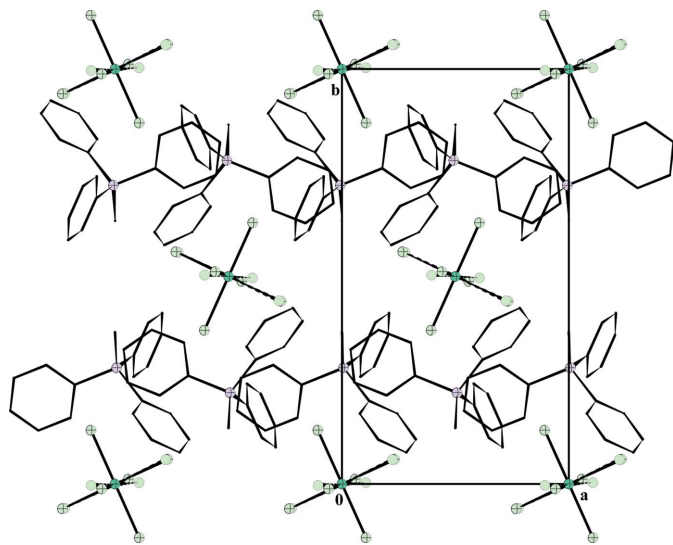


Figure 2

A view of the packing of (I), along $[001]$, showing the cation layers perpendicular to $[010]$. H atoms have been omitted for clarity.

between the layers are occupied by the hexachlororhenate(IV) anions. The distances between the Re centres are considerable, the shortest of these being equal to the a axis length. The crystal structure is stabilized by weak $C-H \cdots Cl$ hydrogen bonds. The hydrogen-bonding schemes are different for the two anion orientations (Fig. 3, Table 2).

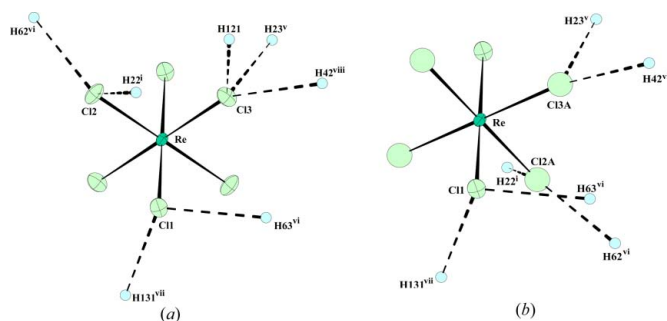


Figure 3

Detail of (I), showing the interaction of the anion with neighbouring H atoms in (a) the major and (b) the minor orientations. Only interactions involving the unique Cl atoms are shown. [Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (v) $-x, 1 - y, 1 - z$; (vi) $\frac{1}{2} + x, \frac{3}{2} - y, -\frac{1}{2} + z$; (vii) $1 + x, y, z$; (viii) $-\frac{1}{2} + x, \frac{3}{2} - y, -\frac{1}{2} + z$.]

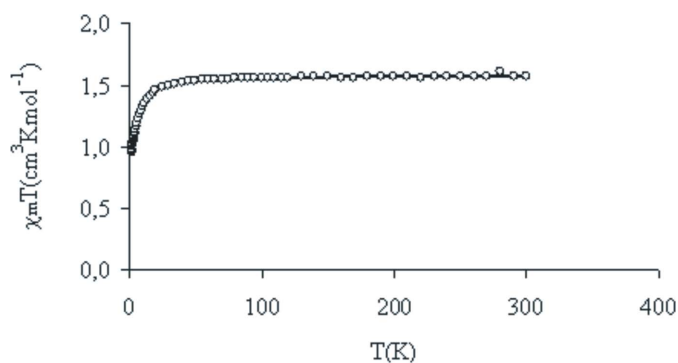


Figure 4

Thermal dependence of $\chi_m T$ for (I) (χ_m is the molar magnetic susceptibility; see text). The solid line is the calculated curve.

The magnetic properties of (I) are illustrated in Fig. 4, with $\chi_m T$ plotted as a function of temperature (χ_m is the magnetic susceptibility). The $\chi_m T$ value remains nearly constant over a wide range of temperatures and decreases smoothly at low temperatures. Taking into account the fact that the hexachlororhenate(IV) anions are practically isolated in the crystal structure, the slight decrease of $\chi_m T$ at low temperatures could be interpreted on the basis of zero-field splitting (ZFS) effects originating from the combined action of the second-order spin-orbit coupling and a slightly distorted octahedral ligand field on the $^4A_{2g}$ ground state for a d^3 ion (Chiozzone *et al.*, 1999).

ZFS effects become important in Re^{4+} complexes when there are no magnetic interactions. D values of 9 and 13 cm^{-1} were found for the tetrabutylammonium and tetraphenylarsonium derivatives, respectively ($|D|$ is the energy gap between the Kramers doublets $|\pm 3/2\rangle$ and $|\pm 1/2\rangle$; Chiozzone *et al.*, 1999). In the case of the title compound, a least-squares fit to the susceptibility data leads to $D = 14(2) \text{ cm}^{-1}$. The value of the effective magnetic moment for (I) at room temperature is 3.55 BM, which is significantly less than the spin-only value of 3.87 BM expected for three unpaired electrons, and this confirms the large spin-orbit coupling for the rhenium(IV) ion (Earnshaw, 1968).

Experimental

Methyltriphenylphosphonium rhenate(VII) (0.2664 g) was suspended in acetone (2.5 ml) and a slow stream of gaseous HCl was bubbled through the mixture. The solid rhenate(VII) dissolved and the reaction mixture underwent colour changes from yellow through orange to brown–red. The resulting solution was placed in a separate vessel where it slowly turned brown–yellow, and after approximately 1 h greenish needles precipitated. The needles were removed from the mixture and washed with acetone [yield 69.6% with respect to rhenate(VII)]. The mixture separated from the needles was left to stand and in 1 d a small number of similar greenish crystals of lower purity were precipitated, which were covered with a brown amorphous substance soluble in acetone. This second crop of crystals was identified as the same compound as that in the first precipitation process, based on unit-cell measurements.

The magnetic measurements were performed in a 0.5 T magnetic field, using a Quantum Design SQUID magnetometer between 1.8 and 300 K. Diamagnetic corrections of the constituent atoms were calculated based on Pascal constants (König, 1966). IR data: Cl–Re–Cl deformation 166 cm⁻¹, Re–Cl stretch 297 cm⁻¹.

Crystal data

(C ₁₉ H ₁₈ P) ₂ [ReCl ₆]	Z = 2
M _r = 953.51	D _x = 1.670 Mg m ⁻³
Monoclinic, P ₂ ₁ /n	Mo K α radiation
a = 9.144 (3) Å	μ = 3.74 mm ⁻¹
b = 16.343 (4) Å	T = 100 (2) K
c = 12.976 (4) Å	Block, green
β = 102.13 (3)°	0.15 × 0.09 × 0.05 mm
V = 1895.8 (10) Å ³	

Data collection

Kuma KM4 CCD area detector diffractometer	31489 measured reflections
ω scans	8322 independent reflections
Absorption correction: numerical (CrysAlis RED; Oxford Diffraction, 2003)	5603 reflections with I > 2 σ (I)
T _{min} = 0.631, T _{max} = 0.902	R _{int} = 0.060
	θ_{max} = 35.0°

Refinement

Refinement on F ²	H-atom parameters constrained
R[F ² > 2 σ (F ²)] = 0.059	w = 1/[$\sigma^2(F_o^2) + (0.0253P)^2$]
wR(F ²) = 0.088	where P = (F _o ² + 2F _c ²)/3
S = 1.09	(Δ/σ) _{max} = 0.001
8322 reflections	$\Delta\rho_{max}$ = 3.23 e Å ⁻³
224 parameters	$\Delta\rho_{min}$ = -1.28 e Å ⁻³

Table 1

Selected geometric parameters (Å, °).

Re–Cl1	2.323 (1)	Re–Cl3	2.364 (2)
Re–Cl2	2.365 (2)		
Cl1–Re–Cl3	89.2 (1)	Cl1–P–Cl3	109.8 (2)
Cl1–Re–Cl2	89.7 (1)	Cl2–P–Cl1	107.0 (2)
Cl3–Re–Cl2	89.7 (1)	Cl1–P–Cl11	109.6 (2)
Cl2–P–Cl1	109.2 (2)	Cl3–P–Cl11	110.3 (2)
Cl2–P–Cl3	110.7 (2)		

Table 2

Hydrogen-bond geometry (Å, °).

D–H...A	D–H	H...A	D...A	D–H...A
C22–H22...Cl2 ⁱ	0.95	2.76	3.535 (4)	139
C62–H62...Cl2 ⁱⁱ	0.95	2.78	3.514 (4)	135
C1–H131...Cl1 ⁱⁱⁱ	0.98	2.67	3.538 (4)	147
C63–H63...Cl1 ⁱⁱ	0.95	2.82	3.404 (4)	121
C1–H121...Cl3	0.98	2.82	3.456 (6)	123
C42–H42...Cl3 ^{iv}	0.95	2.83	3.695 (4)	152
C23–H23...Cl3 ^v	0.95	2.73	3.582 (5)	149
C42–H42...Cl3A ^{iv}	0.95	2.76	3.66 (2)	158
C23–H23...Cl3A ^v	0.95	2.60	3.40 (3)	142
C22–H22...Cl2A ⁱ	0.95	2.71	3.56 (2)	149
C62–H62...Cl2A ⁱⁱ	0.95	2.71	3.35 (2)	126

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.

All H atoms were placed in idealized positions and refined using a riding model, with C–H = 0.95 Å (aromatic C) or 0.98 Å (methyl C) and U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(methyl C). During the refinement, the largest peaks in the difference Fourier map occurred approximately 2.3 Å from the Re atom. The hexachlororhenate(IV) anion was assumed to be disordered over two orientations, in both of which the Re atom coordinates remained constant. During the disorder modelling, restraints were imposed on two pairs of bond lengths (Re–Cl2A equal to Re–Cl2 and Re–Cl3A equal to Re–Cl3). The highest peak and deepest hole were near to atoms Re and Cl1, respectively.

Data collection: KM-4 CCD Software (Kuma Diffraction, 1999); cell refinement: KM-4 CCD Software; data reduction: CrysAlis RED (Oxford Diffraction, 2003); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: DIAMOND (Brandenburg & Putz, 2005); software used to prepare material for publication: SHELXL97.

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