MeOH (20 ml) was added. Brown crystals suitable for X-ray single-crystal diffraction analysis were obtained after 24 h.

Crystal data

$[CuHgBr_2(C_{17}H_{16}N_2O_2)]$
$M_r = 704.277$
Triclinic
$P\overline{1}$
$a = 9.0081\,(10)$ Å
$b = 9.5235\,(10)$ Å
$c = 11.9340\,(13)$ Å
$\alpha = 97.054\,(9)°$
$\beta = 105.340\,(9)°$
$\gamma = 106.471\,(9)°$
$V = 924.90\,(19)$ Å^3
$Z = 2$
$D_x = 2.529$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 9–18°$
$\mu = 13.7$ mm^{-1}
$T = 295$ K
Prismatic
0.125 × 0.100 × 0.075 mm
Brown

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scans (Fair, 1990)
$T_{\min} = 0.222$, $T_{\max} = 0.358$
3547 measured reflections
3370 independent reflections

2713 reflections with $F > 3\sigma(F)$
$R_{\rm int} = 0.012$
$\theta_{\max} = 25.9°$
$h = -11 \rightarrow 10$
$k = -11 \rightarrow 11$
$l = 0 \rightarrow 14$
3 standard reflections
frequency: 120 min
intensity decay: 1%

Refinement

Refinement on F
$R = 0.024$
$wR = 0.032$
$S = 1.14$
2713 reflections
226 parameters
H-atom parameters constrained

$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.817$ e Å^{-3}
$\Delta\rho_{\min} = -0.247$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

Cu···Hg	3.523 (3)	Cu—O1	1.921 (3)
Hg—Br1	2.4489 (8)	Cu—O2	1.919 (4)
Hg—Br2	2.4579 (8)	Cu—N1	1.991 (5)
Hg—O1	2.418 (4)	Cu—N2	1.957 (4)
Hg—O2	2.519 (3)		
Br1—Hg—Br2	152.25 (3)	O1—Cu—N1	90.7 (2)
Br1—Hg—O1	107.9 (1)	O1—Cu—N2	170.7 (2)
Br1—Hg—O2	103.8 (1)	O2—Cu—N1	167.8 (2)
Br2—Hg—O1	99.4 (1)	O2—Cu—N2	91.7 (2)
Br2—Hg—O2	93.5 (1)	N1—Cu—N2	96.5 (2)
O1—Hg—O2	61.4 (1)	Hg—O1—Cu	108.0 (2)
O1—Cu—O2	82.0 (2)	Hg—O2—Cu	104.3 (1)

All H atoms were placed geometrically 0.95 Å from their parent atoms. H-atom displacement parameters were fixed as $U_{\rm iso}(H) = 1.3U_{\rm eq}$(parent) and a riding model was used for all H atoms.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1993). Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *MolEN*. Program(s) used to refine structure: *MolEN*. Molecular graphics: *MolEN* version of *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *MolEN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1060). Services for accessing these data are described at the back of the journal.

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$[ReO_2(dppp)_2]I_x[ReO_4]_{1-x}\cdot xH_2O\cdot CH_3OH$ for $x = 0.17\,(1)$, 0.36 (1) and 1 [dppp is 1,3-bis(diphenylphosphino)propane]

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Abstract

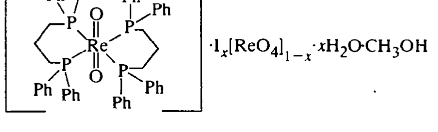
The crystal structures of $[ReO_2(dppp)_2]I_x[ReO_4]_{1-x}\cdot xH_2O\cdot CH_3OH$, where $x = 0.17\,(1)$, 0.36 (1) and 1, *i.e.* dioxo[propane-1,2-diylbis(diphenylphosphine)-*P*,*P*′]-rhenium iodide perrhenate hydrate methanol solvate, with iodide partially substituted by the perrhenate ion,

are described. The compositions studied correspond to $x = 0.17(1)$, $0.36(1)$ and 1. A solvent water molecule participates in the crystallization in a 1:1 stoichiometric ratio with the iodide ion. The iodide ion and the water molecule together occupy nearly the same space and volume as the perrhenate ion and this facilitates their substitution. The three compositions studied are isostructural and crystallize in space group $P2_1/n$. A contraction of the unit cell is detected as the iodide-ion concentration increases.

Comment

Most rhenium(V) chemistry is governed by oxo species and the main factor in the formation of these complexes is believed to be the lowering of the high formal positive charge on the metal(V) atom (Rouschias, 1974). Hence, neutral ligands such as amines or phosphines favour the formation of dioxorhenium(V) species containing the $[ReO_2]^+$ core. The chemistry of these complexes is of great interest because of promising applications in photophysics (Winkler & Gray, 1983; Yam *et al.*, 1992; Ram *et al.*, 1991). Moreover, the development of medically useful radiorheniums, ^{186}Re and ^{188}Re (Deutsch & Jurisson, 1994; Hashimoto & Yoshihara, 1996; Srivastava, 1996), and of their analogous ^{99m}Tc radiopharmaceuticals (Dilworth & Parrott, 1996), has increased interest in elucidation of the crystal structures of these complexes. With this in mind, new studies on Re^V complexes with bidentate phosphine ligands are in progress (Kremer *et al.*, 1999).

This communication describes the evolution of the crystal structure parameters of $[ReO_2(dppp)_2]I_x$-$[ReO_4]_{1-x}{\cdot}xH_2O{\cdot}CH_3OH$ [dppp is 1,3-bis(diphenylphosphino)propane], when the iodide counter-ion is partially substituted by perrhenate. The compositions studied correspond to $x = 0.17(1)$, $0.36(1)$ and 1. A solvent water molecule participates in the crystallization in a 1:1 stoichiometric ratio with the iodide ion. The structural arrangement formed by the iodide and the water molecule occupies nearly the same space and volume as the perrhenate ion, making each system (iodide–water and perrhenate) able to replace the other. A similar replacement of anions in $[ReO_2(dppp)_2]^+$ complexes has been seen previously by Kremer *et al.* (1999) for iodide and perchlorate ions.



$x = 0.17, 0.36, 1$

The three studied compositions are isostructural and belong to space group $P2_1/n$. A contraction of the unit cell is detectable with increasing iodide-ion concentration. The lattice volumes correspond to 5212.6 (9), 5173 (3) and 5095 (4) Å^3 for $x = 0.17(1)$, $0.36(1)$ and 1, respectively. This trend is sustained by a similar evolution of the lattice constants *a*, *b* and *c* with composition. However, no trend is evident for the monoclinic angle β; 91.056 (8), 91.23 (3) and 90.99 (3)° for $x = 0.17(1)$, $0.36(1)$ and 1, respectively.

The coordination polyhedron for these three compositions is a squashed distorted octahedron with the four P atoms defining an equatorial plane and the two O atoms at apical positions. The four P and the central Re atom are not coplanar. The mean planes defined by the four P atoms show r.m.s. deviations of 0.128 (1), 0.129 (1) and 0.127 (1) Å for $x = 0.17(1)$, $0.36(1)$ and 1, respectively. The four P atoms deviate individually from the mean plane by nearly the same distances, with two of them (P1 and P3) on the same side of the plane and the others (P2 and P4) on the opposite side. The Re atom distances from these planes are 0.0186 (11), 0.0207 (13) and 0.0198 (19) Å, respectively. Fig. 1 shows the $x = 1$ composition and the atom-labelling scheme. The distortion of the unit cell produced by perrhenate replacement leads to changes in the rhenium-related distances. While one of the Re—O distances increases with *x*, from 1.780 (6) to 1.808 (8) Å (Re1—O1), the other decreases from 1.759 (5) to 1.748 (7) Å (Re1—O2). The previously reported crystal structure of $[ReO_2(dppp)_2]$-$I_x(ClO_4)_{1-x}{\cdot}CH_3OH$ [$x = 0.414(4)$; Re—O distances 1.782 (5) and 1.747 (5) Å] also exhibited an important difference between the Re—O distances when compared with $[ReO_2(dppp)_2]PF_6{\cdot}CH_3OH$ [Re—O distances 1.768 (6) and 1.754 (5) Å]. Both structures are isostructural with those reported here. In all cases, the differences in Re—O distances are explained by the presence of a hydrogen bond connecting the O1 atom with the H—O group of the methanol solvate present in the structures, which increases the Re1—O1 distance.

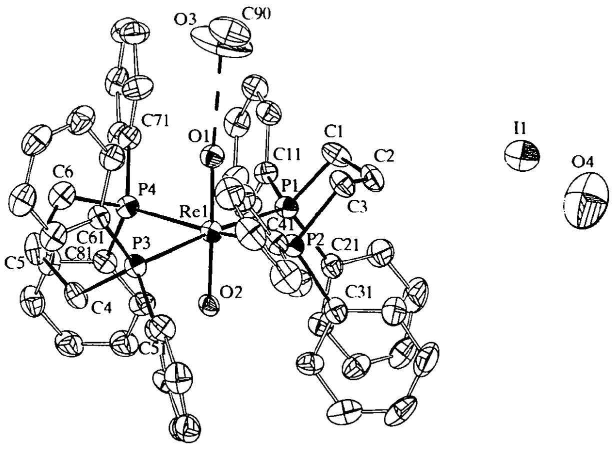
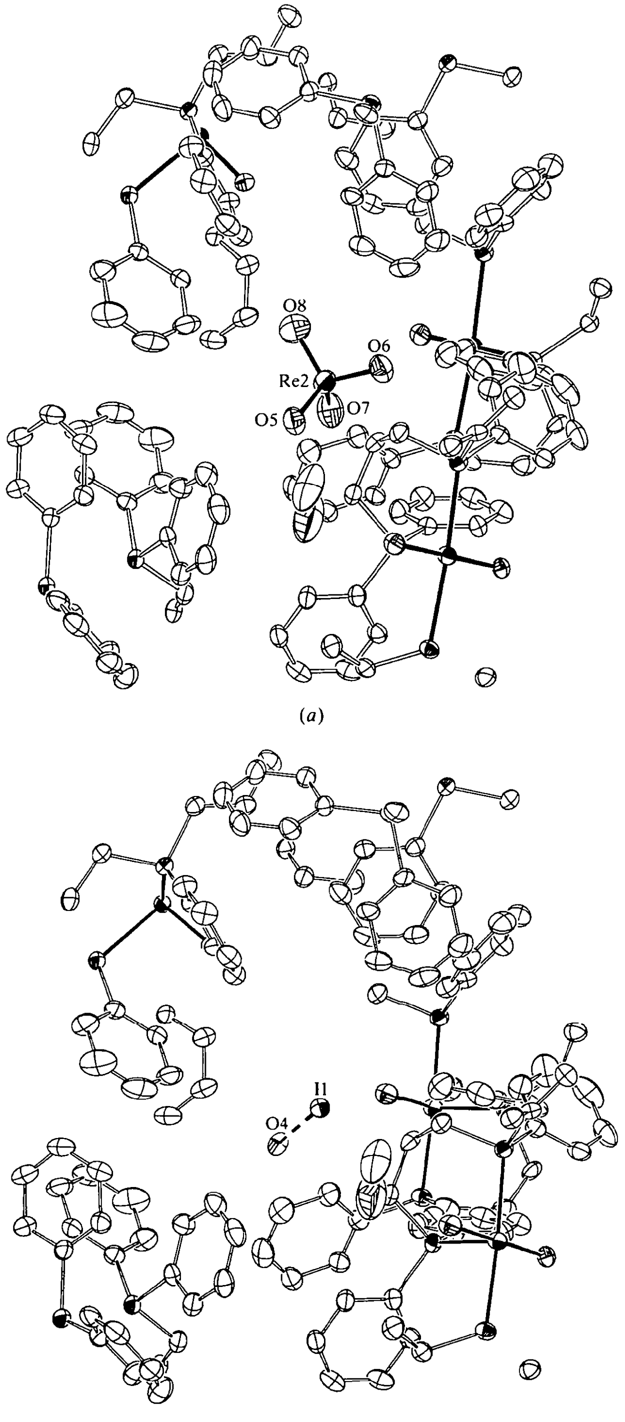


Fig. 1. *ZORTEP* drawing (Zsolnai & Pritzkow, 1995) of the complex of composition $x = 1$. All displacement ellipsoids are drawn at the 30% probability level. H atoms have been excluded for clarity.

The six-membered rings formed by the Re, P and C atoms can adopt different conformations. As in other structures of Re^V complexes with bidentate phosphine ligands (Kremer *et al.*, 1999), these three compositions present a $\lambda\delta$ conformation, where the Re1—P1—C1—C2—C3—P2 ring is in a chair conformation and the Re1—P3—C4—C5—C6—P4 ring is in a twist conformation. This is clearly observed in Fig. 1 (see Table 1 for torsion angles). The dihedral angle between the phenyl groups on the same P atom is greater than 60°. There is no apparent trend in the values of the dihedral angles between the phenyl rings of vicinal P atoms because the angles range from 7.9 (6) [Ph1–Ph7 in x = 1] to 74.1 (6)° [Ph3–Ph5 in x = 0.17 (1)].



(*a*)

(*b*)

Fig. 2. *ZORTEP* view (Zsolnai & Pritzkow, 1995) of (*a*) the perrhenate ion and (*b*) the iodide ion and water molecule and their surroundings within a 10 Å sphere. The I···O4 interaction is indicated by a dashed line.

The packing is mainly dictated by electrostatic interactions and less so by phenyl–phenyl interactions. The shorter intermolecular phenyl–phenyl interaction is between Ph3 of one molecule and $Ph3^i$ of a symmetry-related molecule [symmetry code: (i) $1-x$, $1-y$, $-z$]. The perpendicular distances between both rings are 3.551, 3.566 and 3.602 Å, while the distances between ring centroids are 4.593, 4.585 and 4.519 Å for x = 0.17 (1), 0.36 (1) and 1, respectively. Other contacts between phenyl rings indicate even weaker interactions. No hydrogen bonds are observed involving the participation of O atoms from the perrhenate ion. The interaction between water and the iodide ion in the x = 0.17 (1) and 0.36 (1) compositions may involve hydrogen bonding, as indicated by I···O4 separations of 3.39 (3) and 3.28 (6) Å, respectively. However, for x = 1, the I···O4 separation is 3.64 (2) Å. This could explain the absence of additional destabilization of the structure as x changes (Table 1). Fig. 2 shows the surroundings of both counter-ions.

Experimental

The three compositions were obtained starting from dppp and $[ReO_2(PPh_3)_2]I$ {$[ReO_2(PPh_3)_2]I$ was synthesized according to Kremer *et al.* (1999)} in a 1.1:1 molar ratio in methanol, refluxing the mixture for 10 min. Crystals of the x = 0.36 (1) composition were obtained by cooling slowly the reaction solution in which Re^V was partially oxidized to perrhenate, and recrystallization from dichloromethane/methanol (75/25 *v*/*v*). Crystals of the x = 0.17 (1) composition were obtained by crystallization of $[ReO_2(dppp)_2]I$ from CH_2Cl_2/MeOH in the presence of NH_4ReO_4 by slow evaporation. Crystals of the x = 1 composition were obtained by slow evaporation after adding a small volume of water to the CH_2Cl_2/MeOH mixture. The values of x for the first two compositions were determined by refinement.

Composition x = 0.17 (1)

Crystal data

$[ReO_2(C_{27}H_{26}P_2)_2]I_{0.17}$-
$[ReO_4]_{0.83}\cdot0.17H_2O\cdot CH_4O$
M_r = 1307.1
Monoclinic
$P2_1/n$

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 15.10–16.82°

a = 14.0240 (19) Å
b = 18.8840 (10) Å
c = 19.6861 (16) Å
β = 91.056 (8)°
V = 5212.6 (9) Å^3
Z = 4
D_x = 1.666 Mg m^{-3}
D_m not measured

μ = 4.52 mm^{-1}
T = 293 (2) K
Parallelepiped
0.33 × 0.21 × 0.17 mm
Green

Data collection

Rigaku AFC-7*S* diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (Molecular Structure Corporation, 1993)
$T_{\min}$ = 0.286, $T_{\max}$ = 0.464
12 447 measured reflections
11 967 independent reflections

7482 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.030
$\theta_{\max}$ = 27.5°
$h = 0 \rightarrow 18$
$k = 0 \rightarrow 24$
$l = -25 \rightarrow 25$
3 standard reflections every 150 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.057
$wR(F^2)$ = 0.171
S = 1.041
11 967 reflections
635 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0708P)^2 + 29.8168P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 4.15 e Å^{-3}
$\Delta\rho_{\min}$ = −4.28 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Composition x = 0.36 (1)

Crystal data

$[ReO_2(C_{27}H_{26}P_2)_2]I_{0.36}$-$[ReO_4]_{0.64}\cdot 0.36H_2O\cdot CH_4O$
M_r = 1286.88
Monoclinic
$P2_1/n$
a = 13.943 (5) Å
b = 18.864 (4) Å
c = 19.671 (8) Å
β = 91.23 (3)°
V = 5173 (3) Å^3
Z = 4
D_x = 1.652 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 10.48–12.02°
μ = 4.23 mm^{-1}
T = 293 (2) K
Parallelepiped
0.38 × 0.28 × 0.22 mm
Dark green

Data collection

Rigaku AFC-7*S* diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (Molecular Structure Corporation, 1993)
$T_{\min}$ = 0.256, $T_{\max}$ = 0.394
12 217 measured reflections
11 879 independent reflections

7762 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.056
$\theta_{\max}$ = 27.54°
$h = -18 \rightarrow 18$
$k = -24 \rightarrow 0$
$l = 0 \rightarrow 25$
3 standard reflections every 150 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.064
$wR(F^2)$ = 0.179
S = 1.018
11 879 reflections
635 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0374P)^2 + 65.1515P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 2.61 e Å^{-3}
$\Delta\rho_{\min}$ = −3.95 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Composition x = 1

Crystal data

$[ReO_2(C_{27}H_{26}P_2)_2]I\cdot H_2O\cdot CH_4O$
M_r = 1220.00
Monoclinic
$P2_1/n$
a = 13.832 (7) Å
b = 18.746 (10) Å
c = 19.654 (7) Å
β = 90.99 (3)°
V = 5095 (4) Å^3
Z = 4
D_x = 1.588 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 17.56–21.29°
μ = 3.16 mm^{-1}
T = 293 (2) K
Parallelepiped
0.33 × 0.25 × 0.14 mm
Brown

Data collection

Rigaku AFC-7*S* diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (Molecular Structure Corporation, 1993)
$T_{\min}$ = 0.422, $T_{\max}$ = 0.666
12 145 measured reflections
11 670 independent reflections

7846 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.129
$\theta_{\max}$ = 27.50°
$h = 0 \rightarrow 17$
$k = 0 \rightarrow 24$
$l = -25 \rightarrow 25$
3 standard reflections every 150 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.077
$wR(F^2)$ = 0.247
S = 1.049
11 670 reflections
588 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.1387P)^2 + 34.1853P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 3.12 e Å^{-3}
$\Delta\rho_{\min}$ = −4.54 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °) for the three title compositions*

	x = 0.17	x = 0.36	x = 1
Re1—O2	1.759 (5)	1.756 (6)	1.748 (7)
Re1—O1	1.780 (6)	1.793 (6)	1.808 (8)
Re1—P1	2.511 (2)	2.514 (3)	2.517 (3)
Re1—P2	2.515 (2)	2.514 (3)	2.521 (3)
Re1—P4	2.542 (2)	2.532 (3)	2.536 (3)
Re1—P3	2.629 (3)	2.563 (3)	2.551 (3)

O2—Re1—O1	177.0 (3)	177.3 (3)	178.0 (3)
O2—Re1—P1	93.88 (19)	94.3 (2)	93.3 (2)
O1—Re1—P1	89.1 (2)	88.4 (3)	88.7 (2)
O2—Re1—P2	94.75 (19)	94.9 (2)	94.6 (2)
O1—Re1—P2	85.8 (2)	85.5 (2)	85.8 (2)
P1—Re1—P2	86.58 (7)	86.55 (9)	86.37 (9)
O2—Re1—P4	91.66 (19)	91.7 (2)	91.7 (2)
O1—Re1—P4	87.7 (2)	87.8 (2)	87.9 (2)
P1—Re1—P4	95.60 (8)	95.22 (9)	95.43 (9)
P2—Re1—P4	173.08 (7)	173.06 (8)	173.41 (8)
O2—Re1—P3	81.21 (19)	80.8 (2)	81.7 (2)
O1—Re1—P3	95.8 (2)	96.4 (3)	96.3 (2)
P1—Re1—P3	175.05 (7)	175.09 (8)	174.93 (9)
P2—Re1—P3	94.43 (7)	94.36 (9)	94.19 (9)
P4—Re1—P3	83.96 (7)	84.44 (9)	84.58 (9)
P2—Re1—P1—C1	−48.0 (3)	−47.6 (4)	−47.8 (4)
Re1—P1—C1—C2	67.3 (8)	67.4 (9)	66.7 (9)
P1—C1—C2—C3	−77.1 (10)	−77.0 (11)	−76.6 (13)
C1—C2—C3—P2	76.0 (10)	74.7 (11)	75.4 (13)
C2—C3—P2—Rc1	−65.7 (8)	−64.6 (9)	−64.7 (10)
P1—Re1—P2—C3	47.4 (4)	46.9 (4)	46.6 (4)
P4—Re1—P3—C4	34.1 (3)	33.8 (4)	33.2 (4)
Re1—P3—C4—C5	−82.3 (7)	−81.3 (8)	−81.4 (8)
P3—C4—C5—C6	43.3 (11)	41.5 (13)	44.9 (13)
C4—C5—C6—P4	42.1 (12)	42.1 (13)	37.6 (14)
C5—C6—P4—Re1	−74.4 (8)	−73.8 (9)	−71.3 (9)
P3—Re1—P4—C6	23.7 (4)	23.7 (4)	23.6 (5)

The displacement parameters of the perrhenate atoms of compositions $x = 0.17(1)$ and $0.36(1)$ were refined with restraints to avoid unreal values. The water H atoms were neither found nor calculated in any of the three structures.

For all compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *MSC/AFC Diffractometer Control Software*; program(s) used to solve structures: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ZORTEP* (Zsolnai & Pritzkow, 1995); software used to prepare material for publication: *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1086). Services for accessing these data are described at the back of the journal.

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The salt of the di-μ-chloro-bis[tetrachlorozirconium(IV)] anion with protonated 1,3,5-trimethoxybenzene as cation

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Abstract

The neutrality of the title salt, bis(1,3,5-trimethoxyphenylium) di-μ-chloro-bis[tetrachlorozirconium(IV)], $(C_9H_{13}O_3)_2[Zr_2Cl_{10}]$, is presumably achieved by the addition of a proton to 1,3,5-trimethoxybenzene. This proton was not located crystallographically and is assumed to be disordered over all three methoxy O atoms.

Comment

It is well established that $ZrCl_4$ and other acidic metal species may activate aromatic hydrocarbons to facilitate C—C bond cleavage and intramolecular rearrangement (Solari *et al.*, 1995). The isomerization of methoxy-substituted tetralins *via* $ZrCl_4$-catalysed reactions has also been observed (Harrowven & Dainty, 1996, 1997). In these studies, the formation of η^6-arene intermediates is indicated as being mechanistically significant and is supported by the crystallographic characterization of $[(\eta^6\text{-}C_6Me_6)Zr_2Cl_8]$ (Solari *et al.*, 1995).