Crabtree, R. C. & Lavin, M. (1986). *Inorg. Chem.* **25**, 805–812.
Frenz, B. A. (1978). *The Enraf–Nonius CAD-4 SDP – A Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Solution.* In *Computing in Crystallography*, edited by H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld & G. C. Bassi. Delft Univ. Press.
Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M.M. (1982). *MULTAN11/82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.
Mann, F. G., Wells, A. F. & Purdie, D. (1937). *J. Chem. Soc.* pp. 1828–1836.
Owen, S. M. (1988). *Polyhedron*, **7**, 253–283.
Pursiainen, J., Ahlgrén, M. & Pakkanen, T. A. (1985). *J. Organomet. Chem.* **297**, 391–398.
Pursiainen, J., Pakkanen, T. A. & Jääskeläinen, J. (1985). *J. Organomet. Chem.* **290**, 85–98.
Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.

*Acta Cryst.* (1993). C**49**, 1146–1148

# Structure of *trans*-[Rh(PPh$_3$)$_2$(CO)(OH$_2$)]-[ClO$_4$].CH$_2$Cl$_2$

RONALD J. CROSS, ALAN R. KENNEDY, LJUBICA MANOJLOVIĆ-MUIR AND KENNETH W. MUIR

*Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, Scotland*

(*Received* 26 *August* 1992; *accepted* 1 *December* 1992)

## Abstract

In crystals of *trans*-aquacarbonylbis(triphenylphosphine)rhodium(I) perchlorate dichloromethane solvate, the cations and anions are linked through O—H···O hydrogen bonds to form dimeric [Rh(PPh$_3$)$_2$(CO)(OH$_2$)]$_2$[ClO$_4$]$_2$ units characterized by crystallographically imposed $C_i$ symmetry. The cationic complex displays a slightly distorted square-planar geometry around the Rh atom. The water molecule coordinates the Rh$^{I}$ centre at an Rh—O distance of 2.127 (4) Å.

## Comment

As part of our investigation of complexes of the platinum-group metals with weakly coordinating anions, we attempted to repeat the preparation of *trans*-[Rh(PPh$_3$)$_2$(CO)(ClO$_4$)] using the recommended aerobic filtration (Peone, Flynn & Vaska, 1974). The product was recrystallized from a CH$_2$Cl$_2$/petroleum ether mixture and identified by an X-ray structure analysis as the title compound, in which the metal atom in the cationic complex is coordinated by an H$_2$O molecule rather than by the ClO$_4^-$ ion (Fig. 1). The relatively high displacement parameters of the atoms in the ClO$_4^-$ ion (Table 1) suggest that it may be slightly disordered.

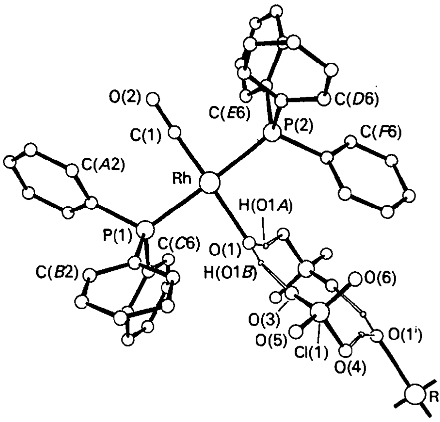

Fig. 1. A view of the structure illustrating hydrogen-bonding interactions of two [Rh(PPh$_3$)$_2$(CO)(OH$_2$)][ClO$_4$] units related by a centre of symmetry, which bisects the O(1)→O(1$^{i}$) vector. In the phenyl rings the atoms are numbered cyclically C(*n*1)···C(*n*6), where *n* = *A*, *B*, *C*, *D*, *E* or *F*, and the C(*n*1) atom is bonded to the P atom; only the C(*n*2) or C(*n*6) labels are shown, for clarity.

The aqua complex [Rh(PPh$_3$)$_2$(CO)(OH$_2$)]$^+$ was previously obtained in the form of SO$_3$CF$_3^-$, BF$_4^-$ and ClO$_4^-$ salts and the crystal structure of [Rh(PPh$_3$)$_2$(CO)(OH$_2$)][BF$_4$].$\frac{1}{2}$H$_2$O.$\frac{1}{4}$C$_6$H$_{12}$ has been determined (Branan, Hoffman, McElroy, Prokopuk, Salazar, Robbins, Hill & Webb, 1991).

In the latter compound, as well as in the ClO$_4^-$ salt reported here, the coordination geometry around the Rh atom is square planar. In the ClO$_4^-$ salt this geometry is subject to a small tetrahedral distortion, which is evident from the bond angles subtended at the Rh centre (Table 2) and from the displacements of the P(1), P(2), O(1) and C(1) atoms by 0.070 (1), 0.068 (1), −0.070 (4) and −0.087 (5) Å, respectively, from the coordination plane of the metal atom. The Rh—P, Rh—O and Rh—C distances (Table 2) are in good agreement with those observed in the BF$_4^-$ salt and in related transition-metal complexes (Alcock, Brown & Jeffery, 1976, 1977; Ceriotti, Ciani & Sironi, 1983; Dahan & Choukroun, 1985; Rheingold & Geib, 1987). The geometrical parameters of the ClO$_4^-$ ion and of the CH$_2$Cl$_2$ solvent molecule are as expected.

In the crystal structure the CH$_2$Cl$_2$ molecules are separated by van der Waals distances from the dimeric [Rh(PPh$_3$)$_2$(CO)(OH$_2$)]$_2$[ClO$_4$]$_2$ units, in which the cations and anions are held together by hydrogen bonding involving H atoms of the coordinated water molecules (Fig. 1, Table 3). The dimeric

0108-2701/93/061146-03$06.00

units are characterized by crystallographically imposed $C_i$ symmetry, the centre of symmetry coinciding with the centre of the twelve-membered $Cl_2O_6H_4$ ring. It has been suggested that hydrogen bonding may also be present in the crystal structure of $[Rh(PPh_3)_2(CO)(OH_2)][BF_4].\frac{1}{2}H_2O.\frac{1}{4}C_6H_{12}$, but the H atoms were not located.

## Experimental

*Crystal data*

$[Rh(C_{18}H_{15}P)_2(CO)(H_2O)]$-$[ClO_4].CH_2Cl_2$
$M_r$ = 857.90
Triclinic
$P\overline{1}$
$a$ = 12.158 (2) Å
$b$ = 12.689 (2) Å
$c$ = 13.822 (1) Å
$\alpha$ = 86.67 (1)°
$\beta$ = 65.15 (1)°
$\gamma$ = 78.65 (1)°
$V$ = 1896.4 (5) Å$^3$
$Z$ = 2
$D_x$ = 1.502 Mg m$^{-3}$

Mo $K\alpha$ radiation
$\lambda$ = 0.71069 Å
Cell parameters from 22 reflections
$\theta$ = 12-14°
$\mu$ = 0.782 mm$^{-1}$
$T$ = 295 K
Prism
0.63 × 0.45 × 0.40 mm
Yellow
Crystal source: recrystallization from $CH_2Cl_2$/petroleum ether mixture

*Data collection*

Enraf-Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical (*DIFABS*; Walker & Stuart, 1983)
$T_{min}$ = 0.698, $T_{max}$ = 1.251
7245 measured reflections
6635 independent reflections

4826 observed reflections $[I \geq 3\sigma(I)]$
$R_{int}$ = 0.069
$\theta_{max}$ = 25°
$h$ = −14 → 1
$k$ = −15 → 15
$l$ = −16 → 16
2 standard reflections
frequency: 120 min
intensity variation: 2.8%

*Refinement*

Refinement on $F$
Final $R$ = 0.0481
$wR$ = 0.0617
$S$ = 2.91
4826 reflections
451 parameters
$w = 1/\sigma^2(|F_o|)$

$(\Delta/\sigma)_{max}$ = 0.026
$\Delta\rho_{max}$ = 0.88 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.96 e Å$^{-3}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å$^2$)

$U_{eq} = \frac{1}{3}\Sigma_{i=1}^{3}\Sigma_{j=1}^{3}U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$. Atoms C(2), Cl(2) and Cl(3) belong to the dichloromethane solvent molecule.

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| Rh | 0.00332 (3) | 0.24250 (3) | −0.23925 (3) | 0.042 |
| Cl(1) | 0.09734 (15) | 0.13293 (12) | 0.11615 (12) | 0.081 |
| Cl(2) | 0.16464 (19) | 0.77017 (20) | −0.53069 (20) | 0.134 |
| Cl(3) | 0.17905 (29) | 0.59069 (18) | −0.39636 (23) | 0.165 |
| P(1) | −0.18982 (12) | 0.35217 (10) | −0.14247 (9) | 0.046 |
| P(2) | 0.20138 (11) | 0.14181 (9) | −0.33841 (9) | 0.042 |
| O(1) | −0.03729 (34) | 0.13554 (26) | −0.10981 (25) | 0.061 |
| O(2) | 0.0401 (4) | 0.3781 (3) | −0.4259 (3) | 0.077 |
| O(3) | 0.0375 (7) | 0.1377 (7) | 0.0510 (5) | 0.223 |
| O(4) | 0.0604 (8) | 0.0514 (5) | 0.1892 (5) | 0.190 |
| O(5) | 0.0717 (9) | 0.2235 (5) | 0.1757 (5) | 0.218 |
| O(6) | 0.2196 (6) | 0.0963 (8) | 0.0597 (6) | 0.214 |
| C(1) | 0.0254 (5) | 0.3271 (4) | −0.3511 (4) | 0.057 |
| C(2) | 0.0926 (8) | 0.7027 (10) | −0.4175 (7) | 0.156 |
| C(*A*1) | −0.2514 (5) | 0.4548 (4) | −0.2145 (4) | 0.053 |
| C(*A*2) | −0.1897 (6) | 0.5388 (5) | −0.2597 (5) | 0.075 |
| C(*A*3) | −0.2359 (6) | 0.6173 (5) | −0.3144 (5) | 0.083 |
| C(*A*4) | −0.3442 (7) | 0.6137 (5) | −0.3222 (5) | 0.090 |
| C(*A*5) | −0.4061 (7) | 0.5319 (5) | −0.2778 (5) | 0.089 |
| C(*A*6) | −0.3607 (6) | 0.4525 (4) | −0.2246 (4) | 0.070 |
| C(*B*1) | −0.1926 (5) | 0.4279 (4) | −0.0333 (4) | 0.058 |
| C(*B*2) | −0.2639 (7) | 0.5295 (5) | 0.0011 (5) | 0.096 |
| C(*B*3) | −0.2613 (9) | 0.5834 (6) | 0.0815 (6) | 0.120 |
| C(*B*4) | −0.1887 (8) | 0.5384 (6) | 0.1328 (6) | 0.116 |
| C(*B*5) | −0.1193 (9) | 0.4368 (6) | 0.1018 (6) | 0.129 |
| C(*B*6) | −0.1200 (7) | 0.3830 (5) | 0.0177 (5) | 0.097 |
| C(*C*1) | −0.3134 (4) | 0.2769 (3) | −0.0815 (3) | 0.047 |
| C(*C*2) | −0.4149 (5) | 0.3098 (4) | 0.0118 (4) | 0.060 |
| C(*C*3) | −0.5118 (5) | 0.2547 (5) | 0.0504 (5) | 0.075 |
| C(*C*4) | −0.5092 (6) | 0.1685 (5) | −0.0022 (5) | 0.083 |
| C(*C*5) | −0.4101 (6) | 0.1340 (5) | −0.0958 (5) | 0.087 |
| C(*C*6) | −0.3103 (5) | 0.1874 (4) | −0.1355 (4) | 0.067 |
| C(*D*1) | 0.3253 (4) | 0.2114 (4) | −0.3548 (3) | 0.048 |
| C(*D*2) | 0.3238 (6) | 0.3137 (4) | −0.3983 (5) | 0.075 |
| C(*D*3) | 0.4201 (6) | 0.3661 (5) | −0.4174 (6) | 0.090 |
| C(*D*4) | 0.5157 (6) | 0.3220 (5) | −0.3930 (5) | 0.084 |
| C(*D*5) | 0.5180 (6) | 0.2227 (6) | −0.3512 (6) | 0.106 |
| C(*D*6) | 0.4238 (6) | 0.1678 (5) | −0.3322 (6) | 0.088 |
| C(*E*1) | 0.2288 (4) | 0.1138 (3) | −0.4752 (3) | 0.045 |
| C(*E*2) | 0.3425 (5) | 0.1091 (4) | −0.5604 (4) | 0.056 |
| C(*E*3) | 0.3574 (6) | 0.0908 (5) | −0.6629 (4) | 0.070 |
| C(*E*4) | 0.2584 (6) | 0.0732 (5) | −0.6808 (4) | 0.081 |
| C(*E*5) | 0.1475 (6) | 0.0758 (5) | −0.5971 (5) | 0.080 |
| C(*E*6) | 0.1308 (5) | 0.0954 (4) | −0.4945 (4) | 0.064 |
| C(*F*1) | 0.2438 (4) | 0.0107 (3) | −0.2892 (4) | 0.048 |
| C(*F*2) | 0.2432 (5) | 0.0045 (4) | −0.1878 (4) | 0.059 |
| C(*F*3) | 0.2777 (6) | −0.0953 (5) | −0.1508 (4) | 0.076 |
| C(*F*4) | 0.3104 (6) | −0.1861 (4) | −0.2103 (5) | 0.086 |
| C(*F*5) | 0.3129 (7) | −0.1796 (4) | −0.3109 (5) | 0.088 |
| C(*F*6) | 0.2782 (6) | −0.0823 (4) | −0.3509 (4) | 0.069 |

Table 2. *Selected bond lengths* (Å) *and angles* (°)

| | | | |
|---|---|---|---|
| Rh—P(1) | 2.352 (2) | Rh—P(2) | 2.351 (2) |
| Rh—O(1) | 2.127 (4) | Rh—C(1) | 1.785 (6) |
| P(1)—C(*A*1) | 1.828 (6) | P(1)—C(*B*1) | 1.821 (5) |
| P(1)—C(*C*1) | 1.813 (5) | P(2)—C(*D*1) | 1.821 (5) |
| P(2)—C(*E*1) | 1.821 (5) | P(2)—C(*F*1) | 1.822 (5) |
| O(2)—C(1) | 1.153 (7) | | |
| P(1)—Rh—P(2) | 176.7 (1) | P(1)—Rh—O(1) | 88.3 (1) |
| P(1)—Rh—C(1) | 89.9 (2) | P(2)—Rh—O(1) | 94.1 (1) |
| P(2)—Rh—C(1) | 88.0 (2) | O(1)—Rh—C(1) | 173.8 (2) |
| Rh—P(1)—C(*A*1) | 117.9 (2) | Rh—P(1)—C(*B*1) | 113.0 (2) |
| Rh—P(1)—C(*C*1) | 113.1 (2) | Rh—P(2)—C(*D*1) | 113.4 (2) |
| Rh—P(2)—C(*E*1) | 112.8 (2) | Rh—P(2)—C(*F*1) | 117.7 (2) |
| Rh—O(1)—H(O1*A*) | 117.5 (3) | Rh—O(1)—H(O1*B*) | 138.6 (4) |
| H(O1*A*)—O(1)—H(O1*B*) | 101.6 | Rh—C(1)—O(2) | 177.1 (5) |

Table 3. *Hydrogen-bond geometry* (Å, °)

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O(1)—H(O1*A*)···O(4$^{i}$) | 1.03 | 1.79 | 2.781 (7) | 161 |
| O(1)—H(O1*B*)···O(3) | 0.84 | 1.94 | 2.735 (8) | 158 |

Symmetry code: (i) $-x, -y, -z$.

An air-sensitive crystal fragment was sealed in a Lindemann capillary. The structure was solved by Patterson and Fourier methods and refined by block-diagonal least squares. All H atoms, except for those in the $CH_2Cl_2$ molecule, were observed in a low-angle $\Delta\rho$ map. Coordinates of $H_2O$ H atoms were determined from this map, while those of the remaining H atoms were geometrically calculated (C—H = 1.00 Å). All H atoms were allowed to ride on the atoms to which they were attached, each with $U(\mathrm{H}) = 1.2U$, where $U$ is the isotropic displacement parameter of the O or C atom in the O—H or C—H bond. All calculations were performed using the *GX* program package (Mallinson & Muir, 1985), which includes a local modification of *ORTEP* (Johnson, 1971).

We thank SERC for an equipment grant and for a studentship (to ARK).

---

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55898 (35 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HU1027]

---

## References

Alcock, N. W., Brown, J. M. & Jeffery, J. C. (1976). *J. Chem. Soc. Dalton Trans.* pp. 583–588.
Alcock, N. W., Brown, J. M. & Jeffrey, J. C. (1977). *J. Chem. Soc. Dalton Trans.* pp. 888–893.
Branan, D. M., Hoffman, N. W., McElroy, E. A., Prokopuk, N., Salazar, A. B., Robbins, M. J., Hill, W. E. & Webb, T. R. (1991). *Inorg. Chem.* **30**, 1200–1207.
Ceriotti, A., Ciani, G. & Sironi, A. (1983). *J. Organomet. Chem.* **247**, 345–350.
Dahan, F. & Choukroun, R. (1985). *Acta Cryst.* C**41**, 704–706.
Johnson, C. K. (1971). *ORTEP*II. Report ORNL-3794, 2nd revision. Oak Ridge National Laboratory, Tennessee, USA.
Mallinson, P. R. & Muir, K. W. (1985). *J. Appl. Cryst.* **18**, 51–53.
Peone, J., Flynn, B. R. & Vaska, L. (1974). *Inorg. Synth.* **15**, 68–72.
Rheingold, A. L. & Geib, S. J. (1987). *Acta Cryst.* C**43**, 784–786.
Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.

---

*Acta Cryst.* (1993). C**49**, 1148–1150

# Di-$\mu$-nitrato-bis[bis(triphenylphosphine)-silver(I)], $[(\mathrm{Ph_3P})_2\mathrm{AgNO_3}]_2$, at 178 K

PETER G. JONES

*Institut für Anorganische und Analytische Chemie der Technischen Universität, Hagenring 30, W-3300 Braunschweig, Germany*

(*Received* 10 *August* 1992; *accepted* 25 *November* 1992)

## Abstract

The title compound possesses crystallographic twofold symmetry. The coordination at silver is distorted tetrahedral, the donor atoms being two phosphine P atoms and one O atom from each of the two nitrate ligands; the O atoms each bridge the two Ag atoms, forming a central $\mathrm{Ag_2O_2}$ ring. The twofold axis passes through each N atom and each coordinating O atom. Most bond lengths and angles are essentially as expected, except that the Ag—O bonds are short (2.34 Å) and the non-coordinated N—O bonds are long (1.29 Å).

## Comment

The title compound (1) arose fortuitously during a study of ylide complexes of silver. Nitratobis(triphenylphosphine)silver(I), the monomeric form corresponding to the dimeric title compound, has previously been studied as two modifications: the unsolvated form (Barron, Dyason, Healy, Engelhardt, Skelton & White, 1986) and a benzene solvate (Harker & Tiekink, 1989). A dimer (2), structurally analogous to the title compound, has also been characterized; this involves trimethylphosphite rather than triphenylphosphine (Meiners, Clardy & Verkade, 1975).

Atomic coordinates of (1) are given in Table 1 with selected bond lengths and angles in Table 2. The molecule (Fig. 1) possesses crystallographic twofold symmetry, the axis passing through the atoms N(1), O(2), N(2) and O(4), whereas the corresponding complex (2) (Meiners *et al.*, 1975) displayed inversion symmetry; in both cases the central four-membered ring is exactly planar. In (1), the nitrate ions are also planar by imposed symmetry and are almost coplanar with the central ring [dihedral angles 6 and 4° for the nitrates at N(1) and N(2), respectively].

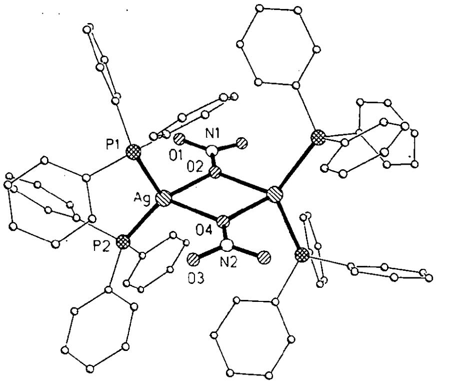

Fig. 1. The molecule of the title compound (1) in the crystal. Radii are arbitrary; H atoms are omitted for clarity.

The nitrate ligands in (1) each bridge both Ag atoms, whereby only one O atom per ligand acts as a donor; this contrasts with the monomeric forms (Barron *et al.*, 1986; Harker & Tiekink, 1989) in which distorted $\eta^2$-coordination by the nitrate ligands is observed. The angles in the four-membered