Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Tetraphenylphosphonium aquatetracyanonitridorhenate(V) pentahydrate

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Received 23 November 2006
Accepted 28 November 2006

Key indicators

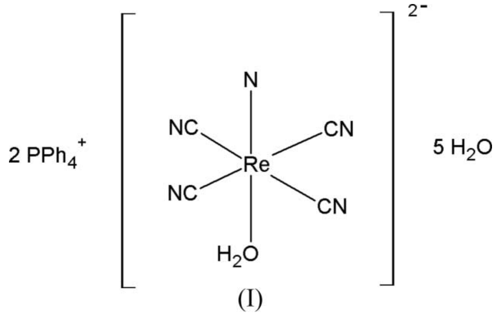
Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.003 Å
R factor = 0.023
wR factor = 0.051
Data-to-parameter ratio = 19.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the title complex, $(C_{24}H_{20}P)_2[Re(CN)_4N(H_2O)]\cdot 5H_2O$, the Re atom is coordinated by one nitride, one aqua and four cyanide ligands in a distorted octahedral geometry. The Re atom is 0.329 (3) Å from the plane formed by the C atoms of the cyanide ligands.

Comment

A number of kinetic and structural studies in the past few years have indicated that the isoelectronic $[MX(H_2O)(CN)_4]^{n-}$ complexes (M = Mo^{IV}, W^{IV}, Tc^{V}, Re^{V} and Os^{VI}, and X = O^{2-} and N^{3-}) are all relatively labile towards monodentate substitution reactions (Leipoldt *et al.*, 1993; Damoense *et al.*, 1994; van der Westhuizen *et al.*, 2002; Mtshali *et al.*, 2006). Our literature search (Cambridge Structural Database; November 2005, Version 5.27; Allen, 2002) revealed two isostructural systems for Re^{V} and Tc^{V} with tetraphenylarsonium as counter-ions and X = N^{3-} (Purcell *et al.*, 1992, Britten *et al.*, 1993; Baldas *et al.*, 1990). We report here the rhenium cyano structure but with tetraphenylphosphonium as the counter-ion.



(I)

The asymmetric unit consists of two discrete PPh_4^+ cations, an $[ReN(CN)_4(H_2O)]^{2-}$ anion and five water molecules (Fig. 1). The bond distances and angles in the cations are all considered normal (Cambridge Structural Database; Version 5.27, August 2006 update; Allen, 2002). The Re—N bond distance of 1.6570 (19) Å and the Re—O bond distance of 2.4429 (15) Å in the anion compare well with those found in other complexes (Purcell *et al.*, 1992), but are shorter than what was found in the isostructural Tc^{V} complex where Tc—N and Tc—O distances of 1.596 (10) and 2.559 (9) Å, respectively, were reported (Baldas *et al.*, 1990).

The large *trans*-influence of the nitrido ligand is once again well illustrated by the mode of distortion from regular octahedral geometry of the $[ReN(CN)_4(H_2O)]^{2-}$ anion. The Re atom is displaced by 0.329 (3) Å out of the plane formed by the four C atoms of the cyano ligands, towards the nitrido ligand. This displacement is similar to those in the structures

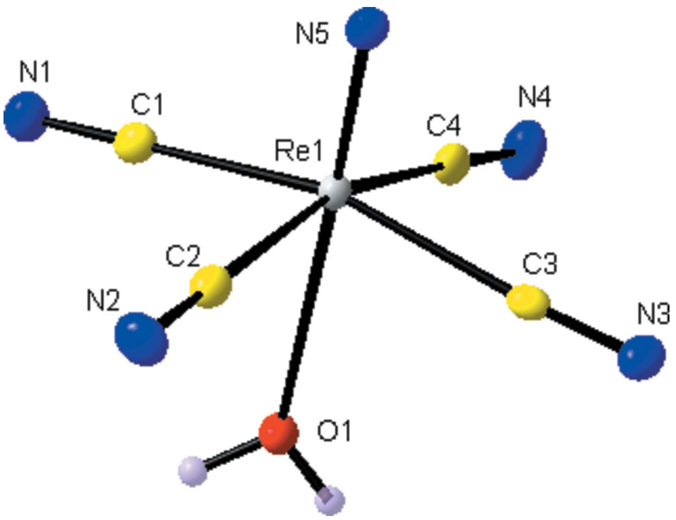


Figure 1
The structure of the anion of (I), showing the atom numbering (50% probability displacement ellipsoids).

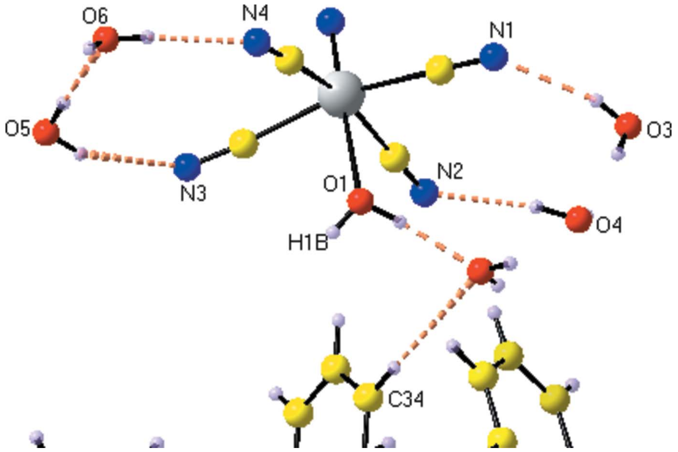


Figure 2
Hydrogen bonding in (I) (illustrated by dashed lines).

previously reported (Purcell *et al.*, 1992; Britten *et al.*, 1993).

The unit cell for (I) is about 2.5% smaller than that reported for the previous Re^{V} structures (Purcell *et al.*, 1992; Britten *et al.*, 1993) and almost 5% smaller than that of the Tc^{V} structure (Baldas *et al.*, 1990). This could be expected if one considers that P—C bonds are generally shorter than As—C bonds.

An extensive network of hydrogen bonds (Table 2) exists, mainly between the anion and the water molecules (Fig. 3). One observation of note is that one of the H atoms of the bonded aqua ligand, H1*B*, does not participate in any hydrogen-bonding interactions due to the fact that it does not lie close to acceptor ligands. However, the stability that is still obtained for this ligand could be attributed to that fact that H1*A* forms a very strong interaction with O2 [1.81 (3) Å].

Experimental

$K_2[ReN(CN)_4]\cdot H_2O$ was prepared by a literature method (Damoense *et al.*, 1994). $(PPh_4)Cl$ (0.04 g, 0.1 mmol) was dissolved in water (3 ml) and added to a solution of $K_2[ReN(CN)_4]\cdot H_2O$ (0.04 g, 0.1 mmol) in H_2O (3 ml). This solution was left at ambient temperature to evaporate. Yellow crystals were obtained after one day. Yield 85%; IR ν(Re—N): 1107 and 1083 cm^{-1}; ν(CN): 2105 cm^{-1}.

Crystal data

$(C_{24}H_{20}P)_2[Re(CN)_4N(H_2O)]\cdot 5H_2O$
$M_r = 1091.14$
Monoclinic, $P2_1/n$
$a = 15.1335$ (9) Å
$b = 19.7216$ (9) Å
$c = 16.7754$ (9) Å
$\beta = 101.576$ (2)°
$V = 4904.9$ (5) Å^3
$Z = 4$
$D_x = 1.478$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 2.59$ mm^{-1}
$T = 100$ (2) K
Cuboid, yellow
0.25 × 0.22 × 0.19 mm

Data collection

Bruker X8 APEXII diffractometer
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
$T_{min} = 0.541$, $T_{max} = 0.613$
49525 measured reflections
12210 independent reflections
10389 reflections with $I > 2\sigma(I)$
$R_{int} = 0.039$
$\theta_{max} = 28.3°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.051$
$S = 1.03$
12210 reflections
643 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0207P)^2 + 1.3302P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.006$
$\Delta\rho_{max} = 0.80$ e Å^{-3}
$\Delta\rho_{min} = -0.62$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Re1—N5	1.6570 (19)	Re1—C2	2.109 (2)
Re1—O1	2.4429 (15)	Re1—C3	2.103 (2)
Re1—C1	2.105 (2)	Re1—C4	2.103 (2)
C1—Re1—O1	79.94 (7)	C1—Re1—C2	88.66 (8)
C2—Re1—O1	79.51 (7)	C3—Re1—C2	92.34 (8)
C3—Re1—O1	81.93 (7)	C4—Re1—C3	83.26 (8)
C4—Re1—O1	82.83 (7)	C3—Re1—C1	161.34 (8)
N5—Re1—O1	177.87 (7)	C4—Re1—C1	90.14 (8)

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

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
O1—H1*A*⋯O2	0.85 (2)	1.804 (11)	2.653 (2)	172 (2)
O5—H5*A*⋯O6	0.847 (19)	1.898 (11)	2.736 (2)	169 (3)
O5—H5*B*⋯N3	0.853 (9)	2.277 (15)	3.083 (3)	158 (2)
O3—H3*B*⋯N1	0.84 (2)	2.054 (13)	2.866 (3)	162 (2)
O4—H4*A*⋯N2	0.85 (2)	2.113 (11)	2.957 (3)	170 (3)
O6—H6*B*⋯N4	0.843 (9)	2.014 (10)	2.849 (2)	171 (2)
C34—H34⋯O2	0.93	2.59	3.482 (3)	161

The phenyl ring H atoms were placed in geometrically idealized positions (C—H = 0.93 Å) and constrained to ride on their parent atoms with $U_{iso}(H) = 1.2U_{eq}C)$. A restrained refinement was applied to the solvent water molecules and bonded aqua ligand using restraints of O—H = 0.85 (1) Å and H⋯H = 1.39 (1) Å.

Data collection: *APEXII* (Bruker, 2004); cell refinement: *SAINT-Plus* (Bruker, 2004); data reduction: *SAINT-Plus* and *XPREP*

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(Bruker, 2004); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

The authors thank the Research Fund of the University of the Free State for financial support and Dr Fanie Muller for the data collection.

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