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Bis(4,4′-dimethyl-2,2′-bipyridinium) hexachlororhenium(IV) dihydrate

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The Re atom in the title compound, $(C_{12}H_{13}N_2)_2[ReCl_6]\cdot 2H_2O$, lies on a crystallographic centre of inversion. The structure consists of discrete anions, cations and solvent water molecules. The solvent water molecule and the pyridinium group form intermolecular O—H···Cl and N—H···O hydrogen bonds, respectively, giving a three-dimensional hydrogen-bonded structure.

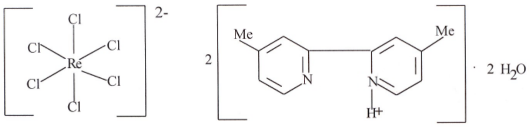
Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.010 Å
R factor = 0.055
wR factor = 0.075
Data-to-parameter ratio = 17.2

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

Comment

The magnetic properties of Re^{4+} complexes are currently being investigated by many groups worldwide. The title rhenium(IV) compound, (I), consists of discrete cations and anions as well as solvent water molecules. The Re atom in the $[ReCl_6]^{2-}$ anion is in the +4 oxidation state and has a $5d^3$ configuration, and is therefore paramagnetic. The Re—Cl bond lengths range from 2.3556 (18) to 2.3695 (18) Å. These values are good agreement with literature values for similar types of salts: 2.353 (2) (Englert *et al.*, 1994) and 2.353 (1)–2.360 (1) Å (Mrozinski & Kochel, 2002). The torsion angles N1—C5—C6—N2 and C4—C5—C6—C7 are 9.6 (2) and 13.7 (3)°, respectively, and indicate some deviation from planarity of the pyridine and pyridinium moieties. Selected bond distances are given in Table 1.



(I)

In the crystal structure of (I), the $[ReCl_6]^{2-}$ anions, on inversion centres, lie in columns along [100] and [010], inside channels formed by the cations and water molecules. In addition, $[ReCl_6]^{2-}$ anions and cations are arranged alternately along [001], forming layers. Furthermore, N—H···O, O—H···Cl and weak C—H···Cl hydrogen bonds form a three-dimensional network (see Table 2). The shortest Re···Re distances are 7.991 (3) Å for Re···Re($x-1$, y, z) and 8.611 (3) Å for Re···Re(x, $y-1$, z). These distances are greater than in both the K_2ReCl_6 salt [6.982 (1) Å; Figgis & Mabbs, 1961] and the (pyridinium)$_2$ReCl$_6$ salt [7.081 (2) Å; Mrozinski & Kochel, 2002], and can probably be attributed to the larger cation in (I).

Experimental

The title compound was prepared according to the following procedure: 0.2 g NH_4ReO_4 was dissolved in 20 ml of water and heated

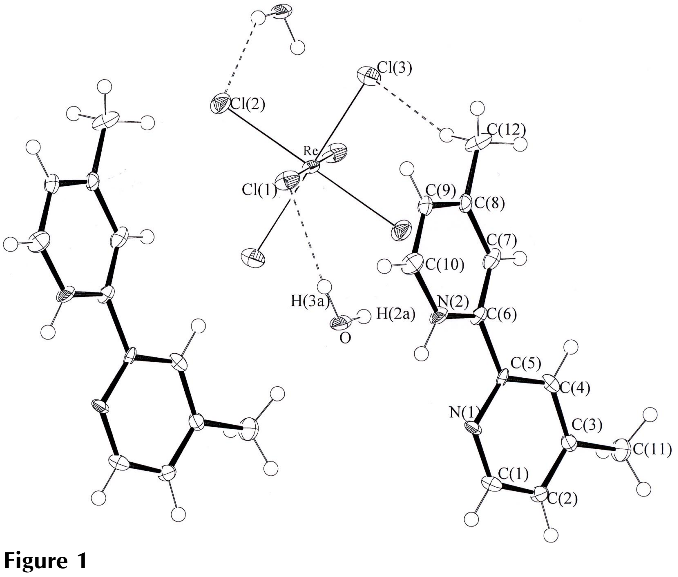


Figure 1
Part of the structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of arbitrary size. Only the asymmetric unit is labelled.

under reflux at 358 K. After a few minutes, a flocculent precipitate of $ReO_2 \cdot nH_2O$ was obtained. The precipitate was filtered off and dissolved in concentrated HCl, resulting in a dark-green solution. The mixture was heated again to 323 K and 0.2 g of 4,4′-dimethyl-2,2′-bipyridyl, dissolved in water, was added. The mixture was heated further for about 6 h. After cooling, the resulting yellow precipitate was filtered off and washed with ethanol and diethyl ether. Crystals suitable for X-ray diffraction study were obtained by slow evaporation of a solution in isobutanol (m.p. 546–467 K). Spectroscopic analysis, IR (KBr, ν cm^{-1}): 3328, 1767, 1645,1400, 1216, 1121, 993, 310, 176, 161. Analysis calculated for $C_{24}H_{30}Cl_6N_4O_2Re$: C 35.79, H 3.75, N 6.95, Cl 26.41%; found: C 34.78, H 3.23, N 6.15, Cl 26.12%.

Crystal data

$(C_{12}H_{13}N_2)_2[ReCl_6] \cdot 2H_2O$
$M_r = 805.43$
Triclinic, $P\bar{1}$
$a = 7.991 (2)$ Å
$b = 8.611 (2)$ Å
$c = 11.007 (2)$ Å
$\alpha = 100.50 (3)^\circ$
$\beta = 98.46 (3)^\circ$
$\gamma = 102.37 (3)^\circ$
$V = 713.6 (3)$ Å^3
$Z = 1$
$D_x = 1.874$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2310 reflections
$\theta = 3.2$–28.3°
$\mu = 4.85$ mm^{-1}
$T = 100 (2)$ K
Prism, yellow
0.08 × 0.05 × 0.05 mm

Data collection

Kuma KM-4-CCD diffractometer
ω scans
Absorption correction: numerical (*CrysAlisRED*; Oxford Diffraction, 1995–2004)
$T_{min} = 0.870$, $T_{max} = 0.987$
5601 measured reflections
3107 independent reflections
2378 reflections with $I > 2\sigma(I)$
$R_{int} = 0.073$
$\theta_{max} = 28.3^\circ$
$h = -9 \rightarrow 10$
$k = -11 \rightarrow 11$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.076$
$S = 0.95$
3107 reflections
181 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0147P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.09$ e Å^{-3}
$\Delta\rho_{min} = -1.23$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Re—Cl3	2.3556 (18)	N2—C6	1.330 (8)
Re—Cl1	2.3647 (19)	N2—C10	1.337 (8)
Re—Cl2	2.3695 (18)	C3—C11	1.505 (8)
N1—C1	1.323 (8)	C5—C6	1.492 (8)
N1—C5	1.348 (7)	C8—C12	1.492 (9)
Cl3—Re—Cl1	90.40 (7)	N1—C1—C2	124.9 (6)
Cl3—Re—Cl2	88.99 (6)	N1—C5—C4	123.6 (6)
Cl1—Re—Cl2	89.74 (7)	N1—C5—C6	114.2 (5)
C1—N1—C5	115.8 (6)	N2—C6—C7	118.2 (6)
C6—N2—C10	123.0 (6)	N2—C6—C5	116.9 (6)

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H1A···O^{i}	1.00 (7)	1.82 (8)	2.808 (8)	168 (6)
O—H2A···Cl2^{ii}	0.95 (7)	2.47 (8)	3.266 (5)	141 (5)
O—H3A···Cl1	0.94 (7)	2.48 (7)	3.231 (5)	138 (6)
C9—H9···Cl1^{iii}	0.95	2.77	3.650 (7)	155
C12—H12A···Cl3	0.98	2.79	3.733 (8)	162

Symmetry codes: (i) $1 - x, -y, -z$; (ii) $1 - x, 1 - y, 1 - z$; (iii) $1 - x, -y, 1 - z$.

Water H atoms were located in a difference Fourier map and refined with a restrained O—H distance of 0.95 (2) Å. The amine H atom was refined independently with an isotropic displacement parameter. H atoms bonded to C atoms were placed in calculated positions (C—H = 0.95 and 0.98 Å) and refined using a riding model, with $U_{iso}(H) = 1.2$ or 1.5 times U_{eq}(parent atom).

Data collection: *KM*-4-*CCD Software* (Oxford Diffraction, 1995–2004); cell refinement: *KM*-4-*CCD Software*; data reduction: *KM*-4-*CCD Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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