

**$\mu$ -Hydroxo-bis[(4,4'-dimethyl-2,2'-bipyridine)-tricarboxylrhenium(I)] perrhenate acetone hemisolvate****Dorothy H. Gibson, Mark S. Mashuta\* and Xiaolong Yin**

Department of Chemistry, University of Louisville, Louisville, KY 40292, USA

Correspondence e-mail: [msmashuta.xray@louisville.edu](mailto:msmashuta.xray@louisville.edu)**Key indicators**Single-crystal X-ray study  
T = 110 K  
Mean  $\sigma(\text{C}-\text{C}) = 0.007 \text{ \AA}$   
H-atom completeness 90%  
Disorder in solvent or counterion  
R factor = 0.027  
wR factor = 0.076  
Data-to-parameter ratio = 17.5For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound,  $[\text{Re}_2(\text{OH})(\text{C}_{12}\text{H}_{12}\text{N}_2)_2(\text{CO})_6][\text{ReO}_4] \cdot 0.5\text{C}_3\text{H}_6\text{O}$ , is the first crystal structure reported for a hydroxo-bridged binuclear rhenium complex containing bipyridine or substituted bipyridine ligands. The cation has distorted octahedral coordination about both rhenium centers, resulting from geometric constraints imposed by the chelating 4,4'-dimethyl-2,2'-bipyridine ligands, which are involved in an intermolecular  $\pi$ - $\pi$  stacking interaction. The distance between the rhenium atoms is  $4.0185(3) \text{ \AA}$ , with no metal-metal bond. The H atom of the bridging hydroxo ligand was directly located in the crystallographic analysis, and is hydrogen-bonded to the perrhenate. The acetone solvent molecule is disordered.

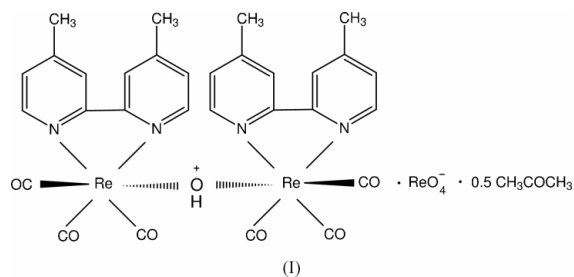
**Comment**

The title compound has been prepared as part of a general study of rhenium complexes bearing polypyridine ligands, which may be intermediates in photocatalytic reductions of  $\text{CO}_2$  (Gibson & Yin, 1998). Surprisingly, only been four crystal structures have been reported for hydroxo-bridged rhenium complexes containing nitrogen donor atoms, and none of these contain the bipyridyl ligand or its substituted derivatives. Böhm *et al.* (1991) observed a metal-metal bond [ $2.528(1) \text{ \AA}$ ] in the doubly-bridged  $[(\text{tacn})_2\text{Re}_2\text{Cl}_2(\mu\text{-Cl})(\mu\text{-OH})]$  ( $\text{tacn} = 1,4,7$ -triazacyclononane) cation, but were unable to locate the H atom of the hydroxy group; thus the assignment of the  $\text{OH}^-$  rather than an  $\text{O}^{2-}$  bridge was based solely on charge. In a study involving the reactivity of rhenium with pyrazolato ligands, Ardizzoia *et al.* (1998) prepared  $(\text{Et}_3\text{NH})[\text{Re}_2(\text{CO})_6(\text{pz})_2\text{OH}]^-$  by hydrolysis of a bromide-bridged species. The crystal structure reported for the bromide complex shows two additional bridging pyrazoles, with an  $\text{Re} \cdots \text{Re}$  separation of  $3.825(1) \text{ \AA}$ . Unfortunately, the structure determination of the hydroxo-bridged compound was an ancillary study for which only unit-cell parameters are available. A third structurally characterized binuclear rhenium complex with N donor atoms is  $\text{Re}_2(\text{CO})_3(\text{NO})_2(\text{SMe})(\mu\text{-}^t\text{BuS})(\mu\text{-OH})$  (Nefedov *et al.*, 1998), which has two nitrosyl groups *trans* to the hydroxo bridge and two bulky *tert*-butylthiolato groups completing the triply-bridged core. Cotton *et al.* (1996) reported the crystal structure of the tetranuclear compound  $[\text{Re}_4(\text{C}_6\text{H}_5\text{NCO-CH}_3)_6(\text{Cl})(\mu\text{-O})(\mu\text{-OH})(\text{MeOH})_3][\text{ReO}_4]_2$ , formed by bridging two dirhenium units with one oxo and one hydroxo ligand.

Compound (I) crystallizes with one hydroxo-bridged  $[\text{Re}_2(\text{CO})_6(4,4'\text{-dmbpy})_2\text{OH}]^+$  cation (dmbpy = dimethyl-2,2'-bipyridine), one perrhenate anion and one-half disordered acetone solvent molecule per asymmetric unit; an *ORTEP*-3 diagram (Farrugia, 1997) of (I) illustrates the structures of the

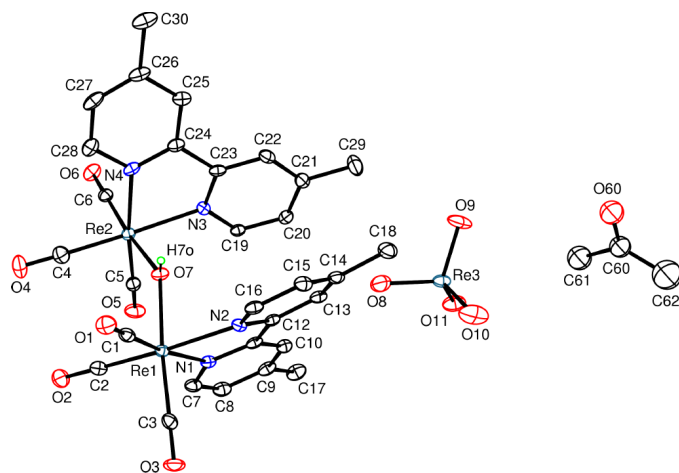
Received 12 August 2003  
Accepted 10 September 2003  
Online 18 September 2003

independent entities in Fig. 1. Each rhenium atom displays distorted octahedral geometry, consistent with rhenium dimethylpyridine compounds that do not contain a hydroxo bridge (Gibson *et al.*, 2003).

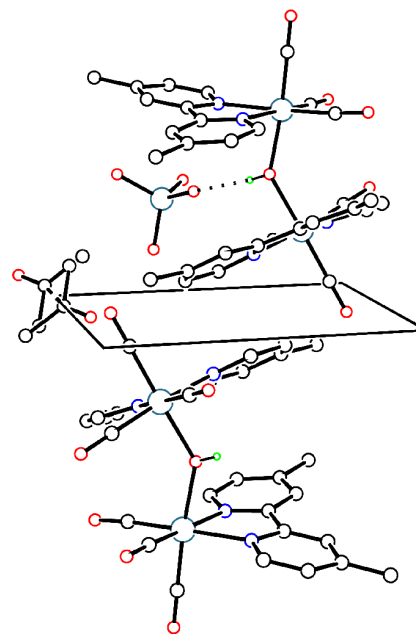


The rhenium atoms are bridged by a single hydroxo ligand, unsupported by a metal–metal bond, as indicated by the large Re...Re separation [4.0185 (3) Å]. In comparison, the multiply bridged complexes described above show strong Re–Re bonds ranging from 2.213 (2) Å to 2.528 (1) for the tetranuclear acetanilide and triazacyclonane complexes, respectively. The position of the H atom of the hydroxo bridge in (I) was determined from an electron density maps and its presence is corroborated by two long Re–O bonds [2.127 (3) and 2.155 (3) Å]. In  $[\text{Re}_4(\text{C}_6\text{H}_5\text{NCOCH}_3)_6(\text{Cl})(\mu\text{-O})(\mu\text{-OH})(\text{MeOH})_3]$ , both Re–O bonds in the oxo bridge are strong [1.88 (2) and 1.94 (2) Å], while its hydroxo bridge has one moderately strong 2.06 (3) and one weak 2.29 (2) Å Re–O bond.

The packing arrangement about the *ac* crystal face for (I) (Fig. 2) shows that the dirhenium cations pack in a three-dimensional network arising from intermolecular  $\pi$ – $\pi$  stacking between dimethylbipyridine ligands of adjacent cations. One six-membered ring (N2 and C12–C16) of the first dmpy stacks together with a second six-membered ring (N2' and C12'–C16') of a neighboring ligand, forming a  $\pi$ – $\pi$  interaction (3.959 Å centroid to centroid). Also seen in this illustration is the hydrogen-bonding interaction between the H



**Figure 1**  
ORTEP-3 (Farrugia, 1997) plot, showing 40% displacement ellipsoids. Aromatic and methyl H atoms are omitted for clarity. The hydroxyl H atom is shown as a small sphere of arbitrary radius.



**Figure 2**

Packing diagram for (I), displaying intermolecular  $\pi$  stacking interactions between neighboring dimethylpyridyl rings, the hydrogen-bonding interaction between the hydroxo-bridged H atom and the perrhenate anion, and disorder of the solvent molecule about an inversion center.

atom of the hydroxo bridge and the perrhenate anion. The O7...O11<sup>i</sup> [2.761 (1) Å] and H7o...O2<sup>i</sup> [2.015 (1) Å] separations, as well as the O7–H7o...O11<sup>i</sup> [169.4 (2)°] angle [symmetry code: (i)  $x, y, z - 1$ ] indicate strong hydrogen bonding.

## Experimental

A mixture of *fac*-Re(dmbpy)(CO)<sub>3</sub>OTf (Gibson & Yin, 1998) and Na<sub>2</sub>CO<sub>3</sub> (1:2) in acetone was stirred for 1 d at 295 K. The reaction mixture was filtered, the filtrate was concentrated and a solution of NH<sub>4</sub>ReO<sub>4</sub> in water was added. After stirring for 19 h, the crude product precipitated from the solution. Repeated recrystallizations from acetone/ether at 273 K gave the pure compound *fac, fac*-Re(dmbpy)(CO)<sub>3</sub>( $\mu$ -OH)Re(dmbpy)(CO)<sub>3</sub>ReO<sub>4</sub> as plate-shaped crystals.

### Crystal data

$[\text{Re}_2(\text{OH})(\text{C}_{12}\text{H}_{12}\text{N}_2)_2(\text{CO})_6] \cdot$   
 $[\text{ReO}_4] \cdot 0.5\text{C}_3\text{H}_6\text{O}$   
 $M_r = 1205.16$   
Monoclinic,  $P2_1/c$   
 $a = 10.6841$  (7) Å  
 $b = 31.649$  (2) Å  
 $c = 10.5758$  (7) Å  
 $\beta = 105.222$  (1)°  
 $V = 3450.7$  (4) Å<sup>3</sup>  
 $Z = 4$

$D_x = 2.320$  Mg m<sup>-3</sup>  
Mo  $K\alpha$  radiation  
Cell parameters from 8716 reflections  
 $\theta = 2.4$ – $28.1^\circ$   
 $\mu = 10.56$  mm<sup>-1</sup>  
 $T = 110$  (2) K  
Rectangular plate, yellow  
0.29 × 0.14 × 0.01 mm

### Data collection

Bruker SMART APEX CCD diffractometer  
 $\omega$  scans  
Absorption correction: multi-scan (SADABS; Sheldrick, 2001)  
 $T_{\text{min}} = 0.180$ ,  $T_{\text{max}} = 0.900$   
29838 measured reflections

7989 independent reflections  
7184 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.042$   
 $\theta_{\text{max}} = 28.3^\circ$   
 $h = -13 \rightarrow 14$   
 $k = -41 \rightarrow 42$   
 $l = -14 \rightarrow 14$

## Refinement

Refinement on  $F^2$  $R[F^2 > 2\sigma(F^2)] = 0.027$  $wR(F^2) = 0.076$  $S = 1.07$ 

7989 reflections

457 parameters

H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.039P)^2 + 1.9625P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.003$$

$$\Delta\rho_{\max} = 3.70 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -1.94 \text{ e } \text{\AA}^{-3}$$

Table 1

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Re1—C1	1.936 (4)	Re1—N2	2.186 (4)
Re1—C2	1.905 (5)	Re1—O7	2.155 (3)
Re1—C3	1.920 (5)	Re2—O7	2.127 (3)
Re1—N1	2.169 (4)		
C2—Re1—C3	89.35 (19)	C1—Re1—N1	171.52 (16)
C2—Re1—C1	89.70 (19)	O7—Re1—N1	83.08 (12)
C3—Re1—C1	88.81 (18)	C2—Re1—N2	171.33 (16)
C2—Re1—O7	94.05 (16)	C3—Re1—N2	96.26 (16)
C3—Re1—O7	175.33 (15)	C1—Re1—N2	97.00 (16)
C1—Re1—O7	94.41 (15)	O7—Re1—N2	80.00 (12)
C2—Re1—N1	98.54 (16)	N1—Re1—N2	74.60 (13)
C3—Re1—N1	93.26 (16)	Re2—O7—Re1	139.63 (17)

Half-occupancy atoms C60—C62 and O60 in the disordered acetone solvent were refined isotropically. A second 50% acetone is generated by the symmetry operator  $-x, -y, 2-z$ , resulting in one full-occupancy disordered solvent located at each corner of the unit cell. Positions for H atoms in the solvent could not be accurately determined and were not included in the model. Aromatic H-atom positions were calculated, and included as fixed contributions, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . Methyl H atoms of the cation were placed in calculated positions and allowed to ride (the torsion angle which defines its orientation was allowed to refine) on the attached C atom,

and these atoms were assigned  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ . The H atom of the hydroxo bridge was located in a difference map and refined isotropically. The highest peak and deepest hole are located at 0.77 and 0.66  $\text{\AA}$  from Re3, respectively.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2001); software used to prepare material for publication: *SHELXTL*.

Support of this work by the National Science Foundation (Grant No. 0203131) is gratefully acknowledged. The X-ray equipment was purchased through a grant from the Kentucky Research Challenge Trust.

## References

- Ardizzoia, G. A., LaMonica, G., Maspero, A., Moret, M. & Masciocchi, N. (1998). *Eur. J. Inorg. Chem.* pp. 1503–1512.
- Bruker (2001). *SAINT* (Version 6.22), *SMART* (Version 5.625) and *SHELXTL* (Version 6.12). Bruker AXS Inc., Madison, Wisconsin, USA.
- Böhm, G., Wieghardt, K., Nuber, B. & Weiss, J. (1991). *Inorg. Chem.* **30**, 3464–3476.
- Cotton, F. A., Lu, J. & Huang, Y. (1996). *Inorg. Chem.* **35**, 1839–1841.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Gibson, D. H. & Yin, X. (1998). *J. Am. Chem. Soc.* **120**, 11200–11201.
- Gibson, D. H., Yin, X., He, H. & Mashuta, M. S. (2003). *Organometallics*, **22**, 337–346.
- Nefedov, S. E., Sidorov, A. A., Berke, H. & Eremenko, I. L. (1998). *Russ. Chem. Bull.* **47**, 1001–1015.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Sheldrick, G. M. (2001). *SADABS*. Version 2.03. University of Göttingen, Germany.