

Tetra- $\mu$ -6-methylpyridin-2-olato-ditungsten toluene sesquisolvate

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The red title compound,  $[\text{W}_2(\text{C}_6\text{H}_6\text{NO})_4] \cdot 1.5\text{C}_7\text{H}_8$ , contains isolated  $\text{W}_2(\text{hmp})_4$  molecules (hmp is 6-methylpyridin-2-olate) in which the W–W separation of 2.1617 (5) Å is consistent with the expected tungsten–tungsten quadruple bond. The complex molecule cocrystallizes with 1.5 molecules of toluene. One toluene molecule is disordered about a crystallographic inversion center, and the other, in a general position, is also disordered.

Received 4 October 2005

Accepted 31 October 2005

Online 5 November 2005

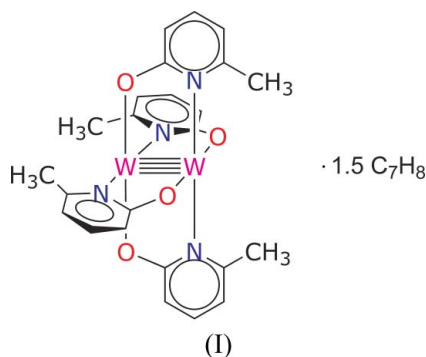
## Key indicators

Single-crystal X-ray study  
 $T = 200\text{ K}$   
 Mean  $\sigma(\text{C}-\text{C}) = 0.010\text{ \AA}$   
 Disorder in solvent or counterion  
 $R$  factor = 0.034  
 $wR$  factor = 0.080  
 Data-to-parameter ratio = 12.5

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

## Comment

$\text{W}_2(\text{hmp})_4$  (hmp is 6-methylpyridin-2-olate) was one of the first structurally characterized compounds containing the quadruply bonded  $\text{W}_2^{4+}$  unit (Cotton *et al.*, 1978).  $\text{W}_2(\text{hmp})_4$  is easily synthesized by the reaction between two equivalents of  $\text{W}(\text{CO})_6$  and four equivalents of Hhmp in the high boiling solvents *o*-dichlorobenzene or diglyme. The current literature preparation calls for purification of the crude product by crystallization from  $\text{CH}_2\text{Cl}_2$ , as the product does not sublime but merely decomposes at high temperatures. However, a molecule of  $\text{CH}_2\text{Cl}_2$  cocrystallizes with the complex molecule, making the purified crystalline compound a poor candidate for reactions with basic or anionic species because of the possible formation of highly reactive dichlorocarbene upon reaction with  $\text{CH}_2\text{Cl}_2$ .



In order to produce a more suitable crystalline precursor for such reactions, we have isolated thin red plates of the title compound, (I), by cooling concentrated solutions of crude  $\text{W}_2(\text{hmp})_4$  dissolved in toluene (approximately  $0.25\text{ g ml}^{-1}$ ) (Fig. 1). As was the case for  $\text{CH}_2\text{Cl}_2$ , crystals of (I) contain intercalated solvent molecules that are not close enough to bond with the dinuclear complex. In fact, as argued previously, the axial sites on the metal are completely blocked by the pyridine methyl substituents, essentially precluding any possibility of axial binding. The W–W bond length in (I) of 2.1617 (5) Å is well within the acceptable range for WW

quadruple bonds and is experimentally indistinguishable from the 2.161 (1) Å bond length reported for  $W_2(\text{hmp})_4 \cdot \text{CH}_2\text{Cl}_2$ . The W—O and W—N bond lengths are also the same for both species within experimental error. We hope that this toluene solvate of  $W_2(\text{hmp})_4$  will be useful in metathetic reactions with carbanion and oxyanion salts.

### Experimental

$W_2(\text{hmp})_4$  was synthesized according to the previously published procedure (Cotton *et al.*, 1978), and small red plates of (I) were obtained by cooling concentrated solutions (0.25 g ml<sup>-1</sup>) of the compound in toluene at 238 K for 14 h.  $M_2(\text{hmp})_4$  compounds (where  $M = \text{Cr}, \text{Mo}$  and  $\text{W}$ ) are known to be relatively stable in air. Nevertheless, standard air- and moisture-sensitive Schlenk techniques were used along with diglyme and toluene solvents that were distilled from appropriate drying agents [Na(s) and K(s), respectively], followed by removal of any dissolved oxygen *via* successive freeze–pump–thaw cycles. Drying the crystals of (I) for 24 h at *ca* 323 K and 80 mTorr removed the toluene to give a dark-red powder with spectroscopic properties identical to those found for unsolvated  $W_2(\text{hmp})_4$  in the original preparation (Cotton *et al.*, 1978).

#### Crystal data

$[\text{W}_2(\text{C}_6\text{H}_6\text{NO})_4] \cdot 1.5\text{C}_7\text{H}_8$	$D_x = 1.884 \text{ Mg m}^{-3}$
$M_r = 938.37$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 6111 reflections
$a = 15.563 (2) \text{ \AA}$	$\theta = 2.0\text{--}25.0^\circ$
$b = 12.975 (2) \text{ \AA}$	$\mu = 6.99 \text{ mm}^{-1}$
$c = 16.486 (3) \text{ \AA}$	$T = 200 (2) \text{ K}$
$\beta = 96.480 (10)^\circ$	Plate, red
$V = 3307.8 (9) \text{ \AA}^3$	$0.19 \times 0.08 \times 0.04 \text{ mm}$
$Z = 4$	

#### Data collection

Nonius KappaCCD diffractometer	5840 independent reflections
$\varphi$ and $\omega$ scans	4480 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SCALEPACK; Otwinowski & Minor, 1997)	$R_{\text{int}} = 0.082$
$T_{\text{min}} = 0.553, T_{\text{max}} = 0.756$	$\theta_{\text{max}} = 25.0^\circ$
51699 measured reflections	$h = -18 \rightarrow 18$
	$k = -15 \rightarrow 15$
	$l = -19 \rightarrow 19$

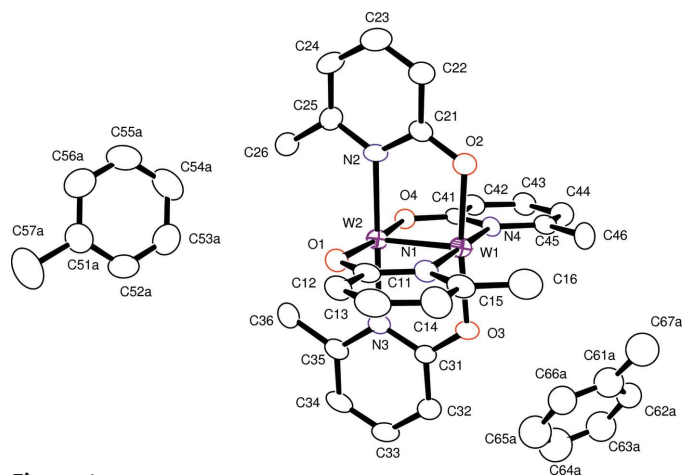
#### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0387P)^2 + 6.3721P]$
$R[F^2 > 2\sigma(F^2)] = 0.034$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.081$	$(\Delta/\sigma)_{\text{max}} = 0.028$
$S = 1.04$	$\Delta\rho_{\text{max}} = 1.43 \text{ e \AA}^{-3}$
5840 reflections	$\Delta\rho_{\text{min}} = -1.30 \text{ e \AA}^{-3}$
466 parameters	
H-atom parameters constrained	

**Table 1**

Selected bond lengths (Å).

W1—W2	2.1617 (5)	W1—N1	2.147 (5)
W2—O1	2.056 (4)	W2—N2	2.142 (5)
W1—O2	2.054 (4)	W2—N3	2.146 (5)
W1—O3	2.063 (4)	W1—N4	2.129 (5)
W2—O4	2.060 (4)		



**Figure 1**

View of (I), showing 30% probability displacement ellipsoids (H atoms have been omitted for clarity). Only one orientation for each disordered toluene molecule is shown.

There are 1.5 molecules of toluene in the asymmetric unit. One toluene molecule (C61A–C67A) is disordered about a crystallographic inversion center. A second toluene molecule is in a general position, but also disordered [orientations C51A–C57A and C51B–C57B in a 0.698 (8):0.302 (8) ratio]. Geometrical restraints were used to ensure reasonable geometrical values and the toluene molecule on the inversion center was refined isotropically. H atoms were positioned geometrically (C–H = 0.95 and 0.98 Å) and refined as riding, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier})$  or  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{methyl carrier})$ . The methyl groups of the main molecule were rotated to fit the electron density. The maximum and minimum electron-density peaks lie 0.75 and 1.32 Å from atoms C63A and W1, respectively.

Data collection: COLLECT (Nonius, 1999); cell refinement: SCALEPACK (Otwinowski & Minor, 1997); data reduction: SCALEPACK and DENZO (Otwinowski & Minor, 1997); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: WinGX (Farrugia, 1999).

MHC and CBH thank the NSF for financial support.

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