Notes

Identification and Structure of $W_2(\mu\text{-}OH)_2[(p\text{-}MeC_6H_4N)_2CH]_4$

F. Albert Cotton,* Lee M. Daniels, and Tong Ren[†]

Texas A&M University, Department of Chemistry,
P.O. Box 30012, College Station, Texas 77842-3012

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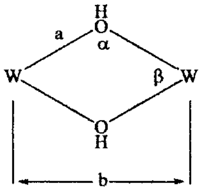
Earlier in this issue, Eglin and co-workers[1] report the isolation and characterization of $W_2(\mu\text{-}OH)_2(\mu\text{-}DCPF)_2(\eta^2\text{-}DCPF)_2$, where $DCPF^-$ represents $\{[(3,5\text{-}Cl_2C_6H_3)N]_2CH\}^-$. This compound arose upon exposure of $W_2(\mu\text{-}DCPF)_4$ to moist air. Their assignment of the two OH bridges as such, rather than as μ-O bridges, was based on the appearance of a peak in the ^1H NMR spectrum as well as on comparison of the metrical parameters of the planar $W_2(\mu\text{-}OH)_2$ core with results for other compounds having $M(\mu\text{-}OH)M$ components. The presence of μ-OH rather than μ-O units was not directly demonstrated by detection of the hydrogen atoms in the X-ray structure, but the conclusion that they are indeed OH and not O seems secure.

We report here that a similar reaction occurs with $W_2(DTolF)_4$ to give $W_2(\mu\text{-}OH)_2(\mu\text{-}DTolF)_2(\eta^2\text{-}DTolF)_2$, where DTolF represents $[(p\text{-}MeC_6H_4N)_2CH]$. We were able to collect a very high quality X-ray data set from which approximate positions of all of the hydrogen atoms were determined experimentally. The hydrogen positions were included as parameters in the structure model and were well-behaved in the refinement process. These results, and the convincing arguments presented by Eglin et al., bolster our conclusion that our compound, like theirs, contains OH bridges. The structural similarities of the two compounds are summarized in the following comparison of the core of $W_2(\mu\text{-}OH)_2(\mu\text{-}DCPF)_2(\eta^2\text{-}DCPF)_2$, **1**, with that of $W_2(\mu\text{-}OH)_2(\mu\text{-}DTolF)_2(\eta^2\text{-}DTolF)_2$, **2**.



	1	2
a (Å)	1.963(3)	1.949[3]
b (Å)	2.3495(3)	2.3499(6)
α °	73.5(1)	74.1(1)
β °	106.5(1)	105.9(1)

The yield of the red, OH-bridged compound was about 10%, when a recrystallization of $W_2(DTolF)_4$[2] from hot toluene was carried out with inadequate protection from laboratory air. When pure $W_2(DTolF)_4$ was subsequently heated with thoroughly deoxygenated H_2O under argon, no observable change occurred, thus confirming that exposure to both H_2O and O_2 is necessary. Treatment of $W_2(DTolF)_4$ with Bu^tOOBu^t did not afford any well-defined product. The sample of **2** displayed a well-resolved ^1H NMR spectrum with signals ($CDCl_3$, ppm) at 2.15 (s), 2.41 (s), 6.45 (d), 6.67 (d), 7.21 (d), 7.56 (d), 8.51 (s), and 8.83 (s).

Table 1. Crystallographic Data for $W_2\ (\mu_8\text{-}OH)_2(DTolF)\cdot C_6H_6$

chemical formula	$W_2O_2N_8C_{60}H_{62}\cdot C_6H_6$
formula weight	1373.0
space group	$P\bar{1}$
a, Å	9.852(1)
b, Å	12.577(1)
c, Å	12.751(2)
α, deg	101.46(1)
β, deg	101.08(2)
γ, deg	92.57(1)
V, Å^3	1513.9(3)
Z	1
d_{calc}, g cm^{-3}	1.506
μ(Cu Kα), mm^{-1}	7.30
λ(Cu Kα), Å	1.54178
T, °C	20 ± 1
transmission coeff: max, min	0.69, 0.33
Final R indices [$I > 2\sigma(I)$][a,b]	$R_1 = 0.025$, $wR_2 = 0.066$
R indices (all data)	$R_1 = 0.029$, $wR_2 = 0.068$

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

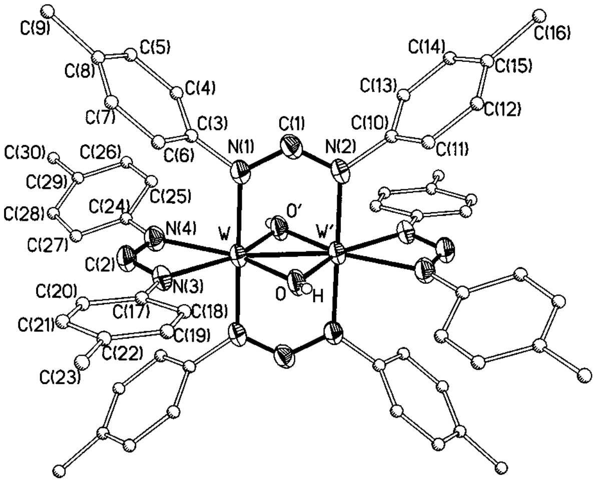


Figure 1. A computer-generated drawing of the molecule, which has a center of inversion. Core atoms are shown as thermal displacement ellipsoids at the 30% level and all carbon atoms as circles of arbitrary size. Hydrogen atoms on the DTolF ligands are not shown.

X-ray Crystallography

General information is given in Table 1. A red plate of dimensions 0.30 × 0.15 × 0.05 mm^3 was attached to a glass fiber with epoxy resin. Indexing on 20 reflections in the 2θ range from 43° to 55° gave a triclinic cell. The dimensions of the cell were confirmed by oscillation photographs. The data were collected on a Rigaku AFC5R diffractometer equipped

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* Corresponding author. E-mail: cotton@tamu.edu.

[†] Current address: The University of Miami, Department of Chemistry, P.O. Box 249118, Coral Gables, FL 33124-0431. E-mail: tren@umiami.ir.miami.edu.

(1) Carlson-Day, K. M.; Eglin, J. L.; Smith, L. T.; Staples, R. J. *Inorg. Chem.* **1999**, *38*, 2216 (preceding paper in this issue).

(2) Cotton, F. A.; Ren, T. *J. Am. Chem. Soc.* **1992**, *114*, 2237.

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Table 2. Selected Bond Lengths [Å] and Angles [deg] for $W_2(\mu\text{-}OH)_2(DTolF)_4$[a]

W−W′	2.3499(6)	W−N(4)	2.182(4)
W−O	1.947(3)	O−H	0.64(7)
W−O′	1.951(3)	N(1)−C(1)	1.319(6)
W−N(2)′	2.113(4)	N(2)−C(1)	1.307(6)
W−N(1)	2.119(4)	N(3)−C(2)	1.322(6)
W−N(3)	2.173(4)	N(4)−C(2)	1.330(6)

O−W−W′	53.0(1)	O−W−N(4)	157.1(2)
O′−W−W′	52.86(9)	O′−W−N(4)	97.1(2)
N(2)′−W−W′	89.6(1)	N(2)′−W−N(1)	177.8(2)
N(1)−W-W′	89.62(9)	N(2)′−W−N(3)	90.8(2)
N(3)−W-W′	149.2(1)	N(1)−W-N(3)	90.9(2)
N(4)−W-W′	149.9(1)	N(2)′−W−N(4)	90.3(2)
O−W−O′	105.9(1)	N(1)−W-N(4)	89.4(2)
O−W−N(1)	90.8(2)	N(3)−W-N(4)	60.9(2)
O′−W−N(1)	88.7(2)	W−O−W′	74.1(1)
O−W−N(2)′	90.3(2)	W−O−H	153(7)
O′−W−N(2)′	89.2(2)	W′−O−H	129(7)
O−W−N(3)	96.2(2)	N(2)−C(1)-N(1)	124.1(4)
O′−W−N(3)	158.0(2)	N(3)−C(2)-N(4)	112.6(4)

[a] Symmetry transformations used to generate equivalent atoms: $-x$, $-y + 1$, $-z + 1$.

with a Cu target. A detailed discussion of the crystallographic procedures that we followed is presented elsewhere.[2] The data set was corrected for decay, Lorentz, and polarization effects. An empirical absorption correction based on the ψ-scan method with 10 reflections having χ near ±90° was applied to the data. The approximate position of the unique W atom was calculated from a three-dimensional Patterson map. Other non-hydrogen atoms were then introduced by alternating series of difference Fourier maps and least-squares refinements, including one molecule of benzene residing on another inversion center. Following convergence of the refinement, a difference Fourier synthesis revealed the positions of all of the expected hydrogen atoms, including one bound to the bridging oxygen atom. Except for those in methyl groups, the hydrogen atom positions and isotropic displacement parameters were included as unconstrained parameters in the final cycles of refinement. Methyl hydrogen atoms were constrained to a tetrahedral geometry, but the group was allowed to rotate about the C−C bond. In the final cycles of refinement, all non-hydrogen atoms were refined with anisotropic displacement parameters. The final figures of merit are collected in Table 1.

Results

A drawing of the molecule of **1** is shown in Figure 1 and principal dimensions are listed in Table 2. The W−O distances are consistent with the bridges being OH rather than O. This, in turn, means that the tungsten atoms are in oxidation state III. In view of the sharp ^{1}H NMR spectrum, the molecule is diamagnetic and the W−W bond must be of order 3, consisting of σ, π, and δ contributions. Our failure to observe the $\mathrm{O}H$ resonance is presumed to be due to its being of only $^1/_{12}$ the total intensity of the $\mathrm{C}H_3$ signals and likely (from Eglin's results) to be in the same region and thus obscured.

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Supporting Information Available: An X-ray crystallographic file, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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