

# Tetranuclear tungsten cyclooctatetraenyl alkoxides $[W_2COT(OR)_4]_2$ , where R = Me, Et and Pr

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Dedicated to Professor E.O. Fischer on the occasion of his 85th birthday

## Abstract

Two equivalents of  $W_2COT(NMe_2)_4$  react with eight equivalents of methanol, ethanol, or *n*-propanol to form the corresponding tetranuclear alkoxide clusters:  $[W_2COT(OR)_4]_2$  where R = Me, Et, or Pr. Single-crystal X-ray diffraction studies on the ethoxide and propoxide compounds reveal centrosymmetric molecules containing two  $[W_2(\mu-\eta^5, \eta^5-COT)(\mu-OR)(OR)_2]$  fragments. Each fragment has a W–W bond length of ca. 2.39 Å and is connected to the other by a pair of symmetrically-bridging alkoxides. These bridging alkoxides are not cleaved in the presence of  $\sigma$ -donors thf and pyridine, or  $\pi$ -acceptor 2-butyne. NMR data suggest that this structure is maintained in solution. Unlike in the related dinuclear alkoxides,  $W_2COT(OR)_4$  [where R =  $CH_2Bu^t$ ,  $Pr^i$  and  $Bu^t$ ], the COT ligands are not fluxional at ambient temperature. The structural similarities between  $[W_2COT(OPr)_4]_2$ ,  $W_2COT(OBu^t)_4$ , and  $W_4(H)_2(OPr^i)_{14}$  are discussed.

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**Keywords:** Tungsten; Cyclooctatetraene; Alkoxide; Tetranuclear

## 1. Introduction

Sandwich compounds of one metal are plentiful [1] and some show very useful reactivity [2], but there are few examples of sandwich compounds containing more than one metal as the sandwich ‘filler’ [3] and only one example of a homoleptic sandwich containing a metal–metal multiple bond [4]. With few exceptions, the bonding interactions between a set of carbocyclic ligands to one metal have been well understood for many years [5], much in part due to the early work of Professor E.O. Fischer [6]. One recent focus of this group has been the synthesis of sandwich and half-sandwich compounds containing metal–metal multiple bonds [7,8]. These efforts, and past efforts of the Cotton group [9] have centered on using the 1,3,5,7-cyclooctatetraenyl (COT) ligand as the sandwich template.

Thus far, we have not been able to sandwich a MM multiple bond between two COT ligands. However, we have recently shown that the COT-substituted dimethylamide,  $W_2COT(NMe_2)_4$ , reacts with four equivalents of neopentanol, isopropanol, or *t*-butanol to give the corresponding tetraalkoxides:  $W_2COT(OR)_4$  [8]. These compounds, and the amide precursor, can be viewed as a four-legged piano stool half-sandwich, with a COT ligand ‘seat’ and amide or alkoxide ‘legs’ (Fig. 1). The work herein was prompted by our suspicion that alcoholysis of  $W_2COT(NMe_2)_4$  with smaller, unbranched alcohols would lead to higher nuclearity species and new types of oligomeric piano stool compounds.

## 2. Results and discussion

### 2.1. Syntheses of $[W_2COT(OR)_4]_2$ compounds

The alcoholysis reactions of  $W_2COT(NMe_2)_4$  employing excess methanol, ethanol, or *n*-propanol in pentane

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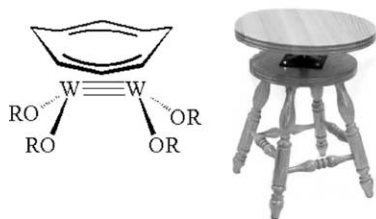
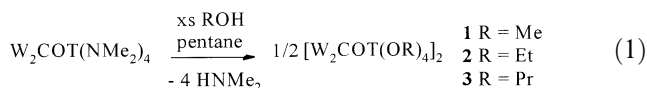


Fig. 1. Comparison of  $W_2COT(OR)_4$  and a piano stool.

proceed to give a good yield of tetranuclear  $[W_2COT(OR)_4]_2$  compounds **1**, **2** or **3** as in Eq. (1). The reaction with methanol is not instantaneous and the solution must be stirred for several hours to reach completion. This may be due to poor solubility of alcoholysis intermediates such as  $W_2COT(OMe)_2(NMe_2)_2$  and can be overcome in part by using neat methanol as solvent. Each of the products is soluble in common ethereal solvents and the solubility in hydrocarbons increases in the order  $1 < 2 \ll 3$ . The reaction is accompanied by an immediate and striking color change from forest green to aqua.



The products are extracted from the crude solids with pentane or hexane giving dark blue powders after drying. At this point, the alkoxydes are analytically pure but can be crystallized from the appropriate solvent. Slow evaporation of benzene solutions of **1** or **2** gives dark, green, rectangular plates. Cooling of a concentrated solution of **3** in glyme gives thin, green plates of **3**. Characterization data for compounds **1**, **2** and **3** are found in Table 1.

## 2.2. Solid-state structures of **3** and $2 \cdot C_6D_6$

The solid-state structure of **3** clearly establishes the tetranuclear nature of the alkoxydes (Fig. 2 and Tables 2 and 3). Compound **3** consists of two  $[W_2(\mu-\eta^5, \eta^5-COT)(\mu-OR)(OR)_2]$  units connected via two bridging alkoxydes (denoted as bridge alkoxydes 'B' in drawing A), and each dinuclear unit is related to the other by a crystallographic inversion center. The COT ligand spans a W–W distance of approximately 2.39 Å in **3**. The alkoxydes bridging the two ditungsten units are essentially symmetric with  $W2-O4$  and  $W2^*-O4$  distances of 2.121(2) Å and 2.111(2) Å, respectively. Within experimental error, they are equal bond lengths, suggesting that alkoxyde bridge B is not the combination of one ionic and one dative bond. In reality, it may be viewed as a three center, four-electron bond. Both tungsten atoms share bridge alkoxydes B equally, much in the same way 'W1' and 'W2' share bridge alkoxyde A. The distance spanned by bridge alkoxyde B in **3** is ca. 3.39 Å,

which is too large a distance for bonding between the two ditungsten units.

All of the alkoxydes in  $W_2COT(OBu^t)_4$  are terminal and have a W–O bond length of ca. 1.92 Å [8]. By comparison, the terminal alkoxydes in **3** have W–O distances that are slightly elongated to 1.961(2) and 1.950(2) Å. This is accompanied by a shortening of the 'W1'–COT distances relative to  $W_2COT(OBu^t)_4$ , and reflects increased 'W1' to COT backbonding in **3**.

The crystals of **2** contain two independent W complexes, each located on a crystallographic inversion center. The asymmetric unit consists of two half W complexes and a molecule of  $C_6D_6$ . The crystals are very thin plates and appear to suffer from non-merohedral twinning. Application of a twin law was not very satisfactory. It was possible to refine only the W atoms anisotropically so that the final R factors were quite high (Fig. 3). However, the structure obtained does corroborate the connectivity found for **3**. The W1–W2 distances are 2.387(1) and 2.391(1) Å in **2** [10].

There are some striking similarities between the solid state structures of **2**, **3** and that of the tetranuclear hydride  $W_4(H)_2(OPr^t)_{14}$  [11].  $W_4(H)_2(OPr^t)_{14}$  has the same arrangement of two isolated ditungsten units connected via a pair of bridging alkoxydes, as in **2** and **3**. The isolated W–W bonds in the hydride complex are 2.45 Å compared to 2.39 Å in **2** and **3**. In fact, replacing three alkoxydes and one hydride (per ditungsten unit) in  $W_4(H)_2(OPr^t)_{14}$  with a COT ligand would give the tetranuclear isopropoxide analogue of **2** and **3** in nearly all respects. According to this analogy, the COT ligand would replace a total of four negatively-charged ligands, and would, therefore, be designated as  $COT^{4-}$ . This is further evidence that  $COT^{2-}$  acts not only as an electron donor to the ditungsten center, but also as a two-electron acceptor as was argued for  $W_2COT(OH)_4$  [8] and  $W_2COT(NMe_2)_4$  [12].

## 2.3. Solution NMR of $[W_2COT(OR)_4]_2$

The solution NMR data for compounds **1–3** fully corroborates the solid state structures of **2** and **3**. The spectroscopic characterization data for **1–3** are found in Table 1. In the  $^1H$ -NMR spectra, the alkoxyde protons are found in a 1:1:2 ratio, representing the two different types of bridge alkoxydes and the one terminal alkoxyde. The COT protons are found as a set of five triplets, which are more accurately described as closely overlapping doublets of doublets. The COT protons are found in the range 5.58–4.62 ppm, in a 2:1:1:2:2 ratio. This fits the pattern anticipated for COT ligands having one mirror plane bisecting two C–H bonds. There is no change in the NMR spectra over the temperature range –60 to 65 °C. This suggests that the alkoxydes do not exchange in this temperature range, and that the COT ligand does not undergo a facile 1,2-shift as in the

Table 1  
Spectroscopic characterization and elemental analysis results for compounds 1–3

	1	2	3
$^1\text{H-NMR}^a$	5.37 (t, 2H, $^3J = 7.2$ , COT-H <sub>d</sub> ), 5.31 (t, 1H, $^3J = 8.1$ , COT-H <sub>c</sub> ), 5.05 (t, 1H, $^3J = 9.1$ , COT-H <sub>a</sub> ), 4.69 (t, 2H, $^3J = 6.6$ , COT-H <sub>b</sub> ), 4.62 (t, 2H, $^3J = 8.4$ , COT-H <sub>c</sub> ), 4.55 (s, 3H, $\mu_A$ -OMe), 4.14 (s, 6H, -OMe), 3.99 (s, 3H, $\mu_B$ -OMe).	5.49 (t, 2H, $^3J = 8.0$ , COT-H <sub>d</sub> ), 5.40 (t, 1H, $^3J = 7.8$ , COT-H <sub>c</sub> ), 5.04 (t, 1H, $^3J = 8.7$ , COT-H <sub>a</sub> ), 4.73 (t, 2H, $^3J = 7.5$ , COT-H <sub>b</sub> ), 4.62 (t, 2H, $^3J = 8.7$ , COT-H <sub>c</sub> ), 4.22 (m, 4H, -OCH <sub>2</sub> Me), 4.15 (m, 2H, $\mu_A$ -OCH <sub>2</sub> Me), 4.04 (m, 2H, $\mu_B$ -OCH <sub>2</sub> Me), 1.59 (t, 3H, $^3J = 7.1$ , $\mu_A$ -OCH <sub>2</sub> Me), 1.32 (t, 6H, $^3J = 6.9$ , -OCH <sub>2</sub> Me), 1.08 (t, 3H, $^3J = 7.0$ , $\mu_B$ -OCH <sub>2</sub> Me).	5.58 (t, 2H, $^3J = 7.8$ , COT-H <sub>d</sub> ), 5.48 (t, 1H, $^3J = 8.0$ , COT-H <sub>c</sub> ), 5.05 (t, 1H, $^3J = 8.7$ , COT-H <sub>a</sub> ), 4.76 (t, 2H, $^3J = 7.1$ , COT-H <sub>b</sub> ), 4.63 (t, 2H, $^3J = 8.6$ , COT-H <sub>c</sub> ), 4.18 (t, 2H, $^3J = 7.4$ , $\mu_A$ -OCH <sub>2</sub> Et), 3.90 (m, 4H, -OCH <sub>2</sub> Et), 3.71 (m, 2H, $\mu_B$ -OCH <sub>2</sub> Et), 2.09 (m, 2H, $\mu_A$ -OCH <sub>2</sub> CH <sub>2</sub> Me), 1.90 (m, 2H, $\mu_B$ -OCH <sub>2</sub> CH <sub>2</sub> Me), 1.59 (m, 4H, -OCH <sub>2</sub> CH <sub>2</sub> Me), 1.21 (t, 3H, $^3J = 7.5$ , $\mu_A$ -OCH <sub>2</sub> CH <sub>2</sub> Me), 1.04 (t, 6H, $^3J = 7.4$ , -OCH <sub>2</sub> CH <sub>2</sub> Me), 0.79 (t, 3H, $^3J = 7.4$ , $\mu_B$ -OCH <sub>2</sub> CH <sub>2</sub> Me).
$^{13}\text{C-NMR}^b$	109.2 (COT-C <sub>a</sub> ), 102.4 (COT-C <sub>b</sub> ), 99.2 (COT-C <sub>c</sub> ), 93.3 (COT-C <sub>d</sub> ), 60.9 ( $\mu_B$ -OMe), 60.7 (-OMe), 55.3 ( $\mu_A$ -OMe), 47.7 (COT-C <sub>c</sub> )	109.0 (COT-C <sub>a</sub> ), 102.7 (COT-C <sub>b</sub> ), 98.4 (COT-C <sub>c</sub> ), 94.0 (COT-C <sub>d</sub> ), 70.0 ( $\mu_B$ -OCH <sub>2</sub> Me), 68.4 (-OCH <sub>2</sub> Me), 62.4 ( $\mu_A$ -OCH <sub>2</sub> Me), 49.1 (COT-C <sub>c</sub> ), 21.0 ( $\mu_B$ -OCH <sub>2</sub> Me), 20.7 (-OCH <sub>2</sub> Me), 20.0 ( $\mu_A$ -OCH <sub>2</sub> Me)	107.1 (COT-C <sub>a</sub> ), 101.9 (COT-C <sub>b</sub> ), 96.8 (COT-C <sub>c</sub> ), 92.6 (COT-C <sub>d</sub> ), 75.2 ( $\mu_B$ -OCH <sub>2</sub> Et), 74.3 (-OCH <sub>2</sub> Et), 67.3 ( $\mu_A$ -OCH <sub>2</sub> Et), 47.5 (COT-C <sub>c</sub> ), 27.0 ( $\mu_B$ -OCH <sub>2</sub> CH <sub>2</sub> Me), 26.4 (-OCH <sub>2</sub> CH <sub>2</sub> Me), 25.0 ( $\mu_A$ -OCH <sub>2</sub> CH <sub>2</sub> Me), 9.98 ( $\mu_B$ -OCH <sub>2</sub> CH <sub>2</sub> Me), 9.92 (-OCH <sub>2</sub> CH <sub>2</sub> Me), 8.23 ( $\mu_A$ -OCH <sub>2</sub> CH <sub>2</sub> Me)
VIS, $\lambda/\text{nm}$ ( $\epsilon / \text{M}^{-1} \text{cm}^{-1}$ )	324 (21,352), 626 (1,473)	326 (20,925), 626 (1,655)	634 (1,732)
EIMS ( $m/z$ ) or microanalysis (%C, H) <sup>c</sup>	C 24.40 (24.18); 3.38 (3.29)	C 29.37 (29.47); 3.79 (4.33)	708.1, [W <sub>2</sub> COT(OPr) <sub>4</sub> ] <sup>+/*</sup> , 665.1, [W <sub>2</sub> COT(OPr) <sub>4</sub> -CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ] <sup>+/*</sup> , 520.9 (100%), [WCOT(OPr) <sub>4</sub> ] <sup>+/*</sup>

<sup>a</sup> 400 MHz, 27 °C, C<sub>6</sub>D<sub>6</sub>,  $\delta$ . All  $J$  couplings are in Hz.

<sup>b</sup> 100 MHz, 27 °C, C<sub>6</sub>D<sub>6</sub>,  $\delta$ .

<sup>c</sup> Calculated values in parenthesis.

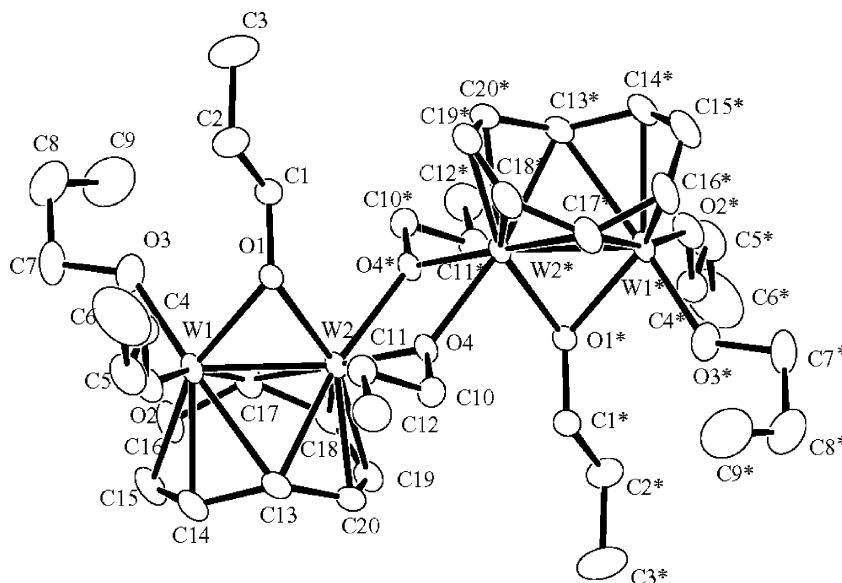


Fig. 2. Molecular structure of **3** showing the atom numbering scheme. Starred atoms are related to the corresponding unstarred atoms by the crystallographic inversion center. Hydrogen atoms are omitted for clarity.

Table 2  
Selected bond lengths (Å) and bond angles (°) for **3**

<i>Bond lengths</i>			
W(1)–W(2)	2.3917(2)	W(2)–C(18)	2.193(3)
W(2)–W(2)*	3.3986(2)	W(2)–C(19)	2.297(3)
W(1)–O(1)	2.138(2)	W(2)–C(20)	2.207(3)
W(1)–O(2)	1.961(2)	C(13)–C(14)	1.468(4)
W(1)–O(3)	1.950(2)	C(14)–C(15)	1.383(5)
W(2)–O(1)	2.132(2)	C(15)–C(16)	1.419(5)
W(2)–O(4)	2.121(2)	C(16)–C(17)	1.463(5)
W(2)–O(4)*	2.111(2)	C(17)–C(18)	1.459(5)
W(1)–C(13)	2.406(3)	C(18)–C(19)	1.404(5)
W(1)–C(14)	2.251(3)	C(19)–C(20)	1.401(5)
W(1)–C(15)	2.330(3)	C(13)–C(20)	1.458(4)
W(1)–C(16)	2.219(3)	O(2)–C(4)	1.412(4)
W(1)–C(17)	2.391(3)	O(3)–C(7)	1.401(4)
W(2)–C(13)	2.339(3)	O(1)–C(1)	1.429(3)
W(2)–C(17)	2.353(3)	O(4)–C(10)	1.432(3)
<i>Bond angles</i>			
W(2)–W(1)–O(3)	116.89(7)	W(2)–O(4)–C(10)	125.9(2)
W(2)–W(1)–O(2)	120.65(7)	W(2)–O(4)*–C(10)*	127.1(2)
W(2)–O(1)–C(1)	123.7(2)	O(2)–W(1)–O(3)	100.7(1)
W(1)–O(1)–C(1)	125.8(2)	O(1)–W(2)–O(4)	83.17(8)
W(1)–O(2)–C(4)	129.2(2)	O(4)–W(2)–O(4) <sup>a</sup>	73.17(8)
W(1)–O(3)–C(7)	133.5(2)		

<sup>a</sup>Symmetry operation used to generate atom:  $-x+1, -y, -z+1$ .

W<sub>2</sub>COT(OR)<sub>4</sub> compounds [8]. Notable in the <sup>13</sup>C-NMR spectra are the resonances for COT-C<sub>c</sub> which appears well upfield of the other COT resonances at ~47–50 ppm, reflecting the fact that it is bonded to two tungsten atoms instead of one.

The bonding in W<sub>2</sub>COT(OH)<sub>4</sub> has been previously explored via relativistic DFT calculations [8]. The

proposed SLUMO for this compound was found to be 42% W–W  $\delta$  bonding in character with most of its nonbonded electron density found opposite the COT ligand. This orbital was also found to be slightly ditungsten–COT bonding. Compounds **1–3** could be construed as two connected [W<sub>2</sub>COT( $\mu$ -OR)(OR)<sub>4</sub>]<sup>1-</sup> molecules, where this SLUMO has interacted with an alkoxide ligand. The incoming alkoxide then becomes bridge alkoxide A. We presume that the slight increase in ditungsten–COT bond order caused by filling this orbital leads to a slightly stronger bonding of the COT ring, and the lack of fluxionality seen in solution for this molecule. We are currently undertaking a full electronic structure calculation of **1** in an effort to explain the subtle difference in COT bonding in the dinuclear and tetranuclear compounds [13].

#### 2.4. Reactions of **1** with Lewis bases (pyridine, thf and 2-butyne)

Solutions of **1** in benzene-*d*<sub>6</sub> were mixed with excess  $\sigma$ -donors thf-*d*<sub>8</sub> or pyridine-*d*<sub>5</sub> in an attempt to establish whether Lewis bases could cleave the bridge alkoxide bonds and form dinuclear species (Eq. (2)). Compound **1** was chosen for this study because of its simple <sup>1</sup>H-NMR spectrum containing only the five COT resonances and three –OMe peaks. It was anticipated that the formation of a dinuclear species would result in a substantial change in the <sup>1</sup>H-NMR spectrum, most likely the coalescence of all three alkoxide peaks into one resonance. The presence of neither thf-*d*<sub>8</sub> nor pyridine-*d*<sub>5</sub> caused any change in the <sup>1</sup>H-NMR spectrum

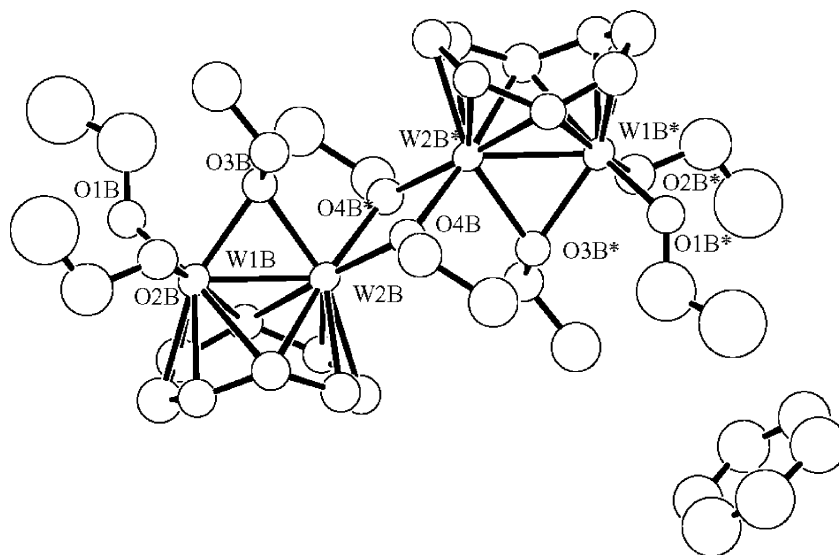


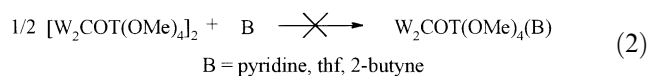
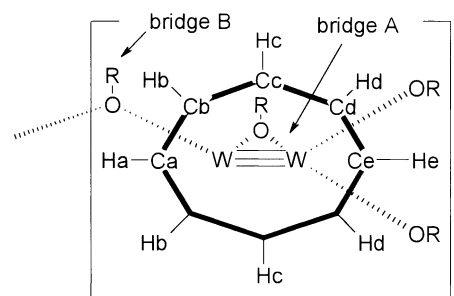
Fig. 3. Isotropic molecular structure of one independent molecule of  $2 \cdot C_6D_6$  showing the numbering scheme for the tungsten and oxygen framework.

of **1**, even when the NMR experiment was conducted at  $> 65^\circ C$  for several hours.

Table 3  
Crystallographic details for **3**

3	
Empirical formula	$C_{40}H_{72}O_8W_4$
Formula weight	1416.38
Temperature (K)	200(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
$a$ (Å)	13.0187(1)
$b$ (Å)	10.3491(1)
$c$ (Å)	17.4327(1)
$\beta$ (°)	109.398(1)
$V$ (Å <sup>3</sup> )	2215.41(3)
$Z$	2
$D_{calc}$ (mg m <sup>-3</sup> )	2.123
Absorption coefficient (mm <sup>-1</sup> )	10.397
Transmission factor range	0.127–0.650
$F(000)$	1.344
Crystal size (mm <sup>3</sup> )	$0.04 \times 0.20 \times 0.24$
Theta range for data collection (°)	2.38–27.47
Index ranges	$-16 \leq h \leq 16, -13 \leq k \leq 13, -22 \leq l \leq 21$
Reflections collected	41 044
Independent reflections	5079 [ $R_{int} = 0.048$ ]
Refinement method	Full-matrix least-squares on $F^2$
Data/restraints/parameters	5079/0/239
Goodness-of-fit on $F^2$	1.097
Final $R$ indices [ $I > 2\sigma(I)$ ] <sup>a</sup>	$R_1 = 0.0197, wR_2 = 0.0431$
$R$ indices (all data)	$R_1 = 0.0231, wR_2 = 0.0441$
Largest difference peak and hole (e Å <sup>-3</sup> )	1.077 and $-1.116$

<sup>a</sup>  $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|, wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$ .



It was shown that  $W_4(H)_2(OPr^i)_{14}$  reacted with several equivalents of ethylene to form saturated alkanes [14]. In the same way, we thought that **1–3** might react with pi-acceptors like alkenes or alkynes to form adducts or possibly dinuclear species as in Eq. (2). To test this theory, a 20-fold excess of 2-butyne was added to benzene- $d_6$  solution of **1** and the <sup>1</sup>H-NMR spectrum monitored over a temperature range of 27–65 °C. The <sup>1</sup>H-NMR resonances for **1** did not change, even at high temperatures, suggesting that compound **1** does not react with 2-butyne. This result, coupled with the fact that the compound does not react with thf or pyridine, suggests that **1** is completely coordinatively saturated, even considering its small *n*-alkoxide ligands.

### 2.5. Visible spectra of **1–3**

The electronic absorption spectra of **1** and **2** show two major absorptions around 325 and 625 nm. Compound **3** shows only the absorption around 625, but it is likely that the absorption at 325 is merely obscured by other

absorptions tailing into the UV. The dinuclear compounds  $W_2COT(OR)_4$  showed an absorption near 580 nm [8], which corresponds closely in molar absorptivity to the absorptions of **1–3** at 625 nm. However,  $W_2COT(OR)_4$  showed much less tailing into the UV around 300 nm. It is this absorption, tailing into the UV region, that gives solutions of the tetranuclear species an aqua color, whereas  $W_2COT(OR)_4$  appear navy blue. We are hopeful that time-dependent DFT calculations on **1** will help elucidate the exact basis of both of these visible transitions.

### 3. Conclusions

$W_2COT(NMe_2)_4$  reacts with excess methanol, ethanol, or propanol to form oligomeric piano stool compounds  $[W_2COT(OR)_4]_2$ . These species have an interesting symmetrical bridge of two alkoxides between the ditungsten centers. This bridge shows no tendency to cleave in the presence of Lewis bases or  $\pi$ -acceptors such as 2-butyne. Structural comparisons with  $W_4(H)_2(O-Pr^i)_{14}$  suggest that the COT ligand is reduced to  $COT^{4-}$  by metal–ligand backbonding, and that the ditungsten center may be viewed as formally  $(W=W)^{8+}$ . This COT ligand is not fluxional on the NMR timescale, unlike the COT ligand found in  $W_2COT(OR)_4$  and many other organometallic compounds. Future DFT calculations on  $[W_2COT(OMe)_4]_2$  should reveal the cause of these differences in bonding in these related dinuclear and tetranuclear alkoxides.

## 4. Experimental

### 4.1. Instrumentation

All NMR spectra were obtained on a Bruker DPX-400 spectrophotometer. Room temperature  $^1H$ -NMR spectra were referenced to the residual protio impurities in benzene- $d_6$  at 7.15 ppm. Room temperature  $^{13}C$ -NMR spectra were referenced to the  $^{13}C$  signal in benzene- $d_6$  at 128.62 ppm. Low temperature  $^1H$ -NMR spectra were recorded in toluene- $d_8$  and referenced to the protio impurity  $C_6D_5CD_2H$  at 2.10 ppm. Mass spectra were obtained on a double-focusing, magnetic sector Kratos MS-890 instrument using either perfluorokerosene or 2,4,6-tris(perfluorononyl)-1,3,5-triazine as the calibrant. Visible spectra were obtained in cuvettes fitted with J-Young valves on a Perkin–Elmer Lambda 900 spectrometer. Elemental microanalysis was performed by Desert Analytics (Tucson, AZ).

### 4.2. Methods and reagents

All manipulations were performed on a standard Schlenk line or in a dry box under an atmosphere of argon or nitrogen respectively.  $W_2COT(NMe_2)_4$  was synthesized as previously reported [8,12]. Pentane was dried over Na/K alloy respectively and stored over molecular sieves. Methanol, ethanol, propanol and glyme were dried by stirring over  $CaH_2$  followed by vacuum transfer to a flask containing activated molecular sieves. NMR solvents benzene- $d_6$  and toluene- $d_8$  were dried and deoxygenated by stirring over sodium or potassium for 12 h followed by vacuum transfer.

### 4.3. Synthesis of $[W_2COT(OR)_4]_2$ compounds

$W_2COT(NMe_2)_4$  (0.5 g, 0.77 mmol) was dissolved in pentane (20 ml) in a 100 ml flask under an atmosphere of argon. The forest green solution was magnetically stirred and methanol (3 ml), ethanol (3 ml), or propanol (3 ml), was added via cannula. The solution underwent an immediate color change from forest green to aqua. The ethanol and propanol mixtures were stirred at ambient temperature for 1 h after which the volatile components were removed under reduced pressure. The methanol solution was stirred longer, ca. 3 h, after which the volatile components were removed. The solids obtained were extracted with hexane ( $3 \times 5$  ml) and the hexane solutions were transferred to another flask via filter cannula. The hexane was removed under reduced pressure and the resultant dark solids were dried under vacuum (80 mtorr, 50 °C, 24 h) to yield fine aqua powders (376 mg, 82% for **1**; 452 mg, 90% for **2**; 404 mg, 74% for **3**). A similar reaction between  $W_2COT(NMe_2)_4$  and methanol using no pentane and 10 ml of methanol, stirring for 1 h, led to the same product **1**. Large, green, rectangular plates of **2**· $C_6D_6$  were obtained by slow evaporation of a concentrated solution of **2** in  $C_6D_6$  in a NMR tube in the drybox. Crystals of **3** suitable for X-ray analysis were grown from a concentrated solution of **3** in glyme that was kept at 30 °C for 1 day.

Unambiguous identification of  $^1H$ -NMR signals arising from bound COT was made possible by a 2D NOESY experiment on **3** showing a positive NOE effect between the terminal propoxide's  $-OCH_2Et$  protons and  $H_d$  (see drawing A). The identification of the remaining COT protons was made by relationships established via  $^1H$ -COSY.  $^1H$ -NMR signals were assigned to bridge A or bridge B based the absence of any NOE between the protons associated with bridge alkoxide A and the COT protons. Assignments for the  $^1H$ -NMR spectra of **1** and **2** were then made based on similarities to the spectra for **3**.  $^{13}C$ -NMR resonances for **1** and **2** were made after HETCOR data on **3** allowed for unambiguous assignment of its  $^{13}C$  resonances.  $^{13}C$ -NMR assignments for **2** and **3** were confirmed using  $^{13}C$

DEPT spectroscopy. The overall features of the  $^1\text{H}$ -NMR spectra of **1**–**3** do not change in the temperature range  $-60$  to  $65$  °C although there are some slight changes in chemical shift.

#### 4.4. Reactions of **1** with Lewis bases and 2-butyne

Approximately 10 mg of **1** was added to an NMR tube fitted with a J-Young valve. Benzene- $d_6$  (1 ml) was added to make an aqua-colored solution. In the first experiment 1 drop of pyridine- $d_5$  was added with no noticeable change in color. The tube was sealed and shaken and a subsequent NMR experiment showed no change in the proton resonances due to **1**. Variable temperature studies on this solution, changing temperature from  $27$  to  $65$  °C, also showed no changes in the proton resonances due to **1**. In the second experiment, 1 drop of thf- $d_8$  was added to the solution. Again, no color change was noted and there was no change in the resonances due to **1**.

The experiment was repeated with 1 drop of 2-butyne, again with the same result. Integration of the methyl resonances of 2-butyne versus those of **1** indicated an approximate 20-fold excess of 2-butyne had been added.

#### 4.5. Crystallographic experimental details

The data collection crystal for **3** was a dark green hexagonal plate. Examination of the diffraction pattern on a Nonius Kappa CCD diffractometer indicated a monoclinic crystal system. All work was done at 200 K using an Oxford Cryosystems Cryostream Cooler. The data collection strategy was set up to measure a quadrant of reciprocal space with redundancy factor of 4.3, which means that 90% of reflections were measured at least 4.3 times. A combination of  $\varphi$  and  $\omega$  scans with a frame width of  $1.0^\circ$  was used. Data integration was done with DENZO [15]. In preparation for an analytical absorption correction, the crystal dimensions were refined with the program EUHEDRAL [16]. The absorption correction was then applied to the data set with PLATON [17]. Merging the data and averaging the symmetry equivalent reflections with SHELXL-97 [18] resulted in a  $R_{\text{int}}$  value of 0.048.

The structure was solved in  $P2_1/n$  by the direct methods in SHELXS-86 [19]. By phasing on the two W atoms, the rest of the molecule was located by standard Fourier methods. This molecule contains a crystallographic inversion center. Full-matrix least-squares refinements based on  $F^2$  were performed in SHELXL-97 [18].

The methyl group hydrogen atoms were added at calculated positions with  $U(\text{H}) = 1.5 \times U_{\text{eq}}$  (bonded carbon atom). For each methyl group, the torsion angle defining the orientation about the C–C bond was refined. The remaining hydrogen atoms were included

in the model at calculated positions using a riding model with  $U(\text{H}) = 1.2 \times U_{\text{eq}}$  (bonded carbon atom). Neutral atom scattering factors were used and include terms for anomalous dispersion [20].

## 5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 206659 and 206658 for **2**· $\text{C}_6\text{D}_6$  and **3**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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