found for the ground state of $Rh_2(O_2CCH_3)_4(H_2O)_2$.[45]

The nature of the HOMO in $Rh_2(O_2CH)_4(PH_3)_2$ also leads to our making a prediction concerning the structural changes upon the formation of cationic species $[Rh_2(O_2CR)_4(PR_3)_2]^+$. A crystal structure of $[Rh_2(O_2CCH_3)_4(H_2O)_2]ClO_4{\cdot}H_2O$ has been reported.[46,47] The Rh–Rh and Rh–OH_2 bonds in the dihydrate cation are 2.317 (2) and 2.22 (1) Å long, respectively, both much shorter than in the neutral species. Even after allowing for a decrease in the effective radius of Rh upon oxidation, the net changes in bond lengths are still negative, viz., Δ(Rh–Rh) = –0.02 Å and Δ(Rh–OH_2) = –0.06 Å, upon forming the cation.[19] The shortening of the Rh–OH_2 bond upon removal of a δ^* electron localized on the Rh atoms is easily rationalized as being due to the now smaller energetic difference of the water lone pairs and the acceptor orbital of the $Rh_2(O_2CCH_3)_4$ framework. The decrease in the Rh–Rh bond length has been attributed to the antibonding nature of the electron involved, although the impact of the antibonding character in a δ^* MO has come under question.[31,32]

We would expect much more pronounced changes in the Rh–Rh and Rh–L bond lengths upon oxidation of, for example, $Rh_2(O_2CCH_3)_4(PPh_3)_2$ to the corresponding cation. The Rh–P bond is expected to shorten considerably upon the removal of an electron from the strongly Rh–P antibonding $17a_g$ MO. The Rh–Rh bond would be expected to lengthen substantially for two reasons. First, electron density would be removed from the Rh–Rh σ-bond framework which is primarily responsible for the shortness of the Rh–Rh bond. Second, the decrease in the Rh–P bond length will be accompanied by increased donation from the phosphine lone pairs into the Rh–Rh σ^* orbital. Thus, from the perspective of the Rh–Rh bond, the oxidation of the system will accomplish a partial charge transfer from the σ to the σ^* orbital. Finally, it is appropriate to address the question of back-bonding once again. To reiterate, we find no evidence in our theoretical results for Rh $\rightarrow$ P donation in $Rh_2(O_2CH)_4(PH_3)_2$, although the applicability of this result to other systems may be considered a moot point. If our prediction that the Rh–P bond will shorten considerably upon oxidation is correct, however, it is expected that the overlap of the Rh–Rh π^* and P 3d orbitals would increase despite the higher formal oxidation state of the Rh atoms. Thus it is not unreasonable to predict more back-bonding in the oxidized cationic species than in the neutral molecule. If the electronic structure of the bis(carbonyl) adduct parallels that of the bis(phosphine) adducts, this prediction would be particularly easy to test, and we eagerly await experimental results.

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Registry No. $Rh_2(O_2CH)_4(PH_3)_2$, 77965-51-6.

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Tetrachlorotetraethoxodi-μ-ethoxo-ditungsten(*W*–*W*). Structure, Bonding, and Improved Preparation

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New methods of preparing the title compound by oxidizing $W_2Cl_4(\mu\text{-OEt})_2(OEt)_2(HOEt)_2$ with silver nitrate or molecular oxygen are described. The crystal and molecular structure have been determined. The molecules, which consist of two distorted octahedra sharing an edge, reside on crystallographic centers of inversion but approximate to D_{2h} symmetry. There is a central $Cl_2W(\mu\text{-OEt})_2WCl_2$ unit which is planar except for the Et groups. Four more EtO groups, two on each tungsten atom above and below this plane, complete the distorted octahedra about each metal atom. The W–W distance is 2.715 (1) Å. The structure and the diamagnetism can be best explained by postulating a single bond between the tungsten atoms. The crystals belong to space group $P2_1/n$ with a = 8.469 (1) Å, b = 9.344 (1) Å, c = 14.815 (1) Å, β = 93.850 (8)°, V = 1169.7 (5) Å^3, and Z = 2. The structure, with hydrogen atoms included but not refined, was refined to R_1 = 0.019 and R_2 = 0.028.

Introduction

A compound of formula $W_2Cl_4(OEt)_6$ appears to have been first reported by Klejnot[2] in 1965. It was later made also by Brubaker et al.,[3] and the *n*-propoxide was reported in 1970 by Reagan and Brubaker.[4] The report by these last workers of NMR spectra with normal characteristics (which we have confirmed for the ethoxide) provided evidence that these are diamagnetic compounds. From the composition, the NMR spectrum, and the diamagnetism, it is a reasonable conjecture that the molecule has OEt bridges between two octahedrally coordinated metal atoms and that the two d electrons supplied by the W^V ions become paired.

However, as the field of binuclear compounds with metal–metal bonds has developed in recent years, this compound took on new interest since it may be regarded as a kind of prototype. We therefore deemed it worthwhile to examine its chemistry further and to provide a definitive structural characterization of it, as a basis for discussing the bonding.

Experimental Section

Reagents. Samples of the tungsten(IV) complex $W_2Cl_4(OEt)_4(EtOH)_2$ were prepared from tungsten(IV) chloride with use of the procedure of Reagan and Brubaker.[4] All solvents were dried and purged with nitrogen prior to use.

Preparation of $W_2Cl_4(OEt)_6$. Method A. A 0.75-g (0.958-mmol), sample of $W_2Cl_4(OEt)_4(EtOH)_2$ and 0.325 g (1.91 mmol) of freshly ground silver nitrate were placed in 75 mL of acetone. The resulting suspension was stirred for 40 min, by which time the color had turned from brown to red. The solution was filtered, and the filtrate was

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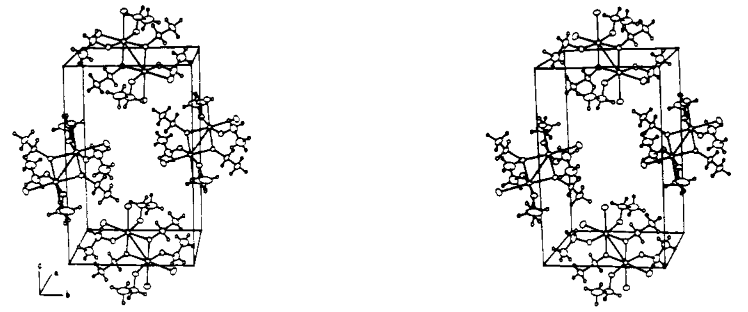

Figure 1. Stereographic representation of the crystal packing in in the unit cell of $W_2Cl_4(OCH_2CH_3)_6$.

evaporated to dryness. The crude red product was recrystallized from benzene-hexane mixtures. The yield (0.47 g) after recrystallization was 62%.

Method B. A 0.67-g sample of $W_2Cl_4(OEt)_4(EtOH)_2$ was dissolved in 50 mL of a 3:1 chloroform-ethanol mixture. Oxygen gas was passed through the solution for 24 h. At the end of this period, the solution had changed from green to red. The solution was filtered and the filtrate was evaporated to dryness; yield 60% (0.40 g).

Preparation of Single Crystals of $W_2Cl_4(OEt)_6$. A sample of $W_2Cl_4(OEt)_6$, prepared by method A, was dissolved in 15 mL of benzene. An excess of hexane was added, and the resulting solution was allowed to stand at 18 °C for 18 h. The resulting crystals were collected, washed with hexane, and vacuum dried.

X-ray Structure Determination. Several well-formed, regularly shaped crystals of approximate 0.2 mm dimensions on a side were mounted on the ends of thin glass fibers with epoxy glue. The crystals were studied individually on an Enraf-Nonius CAD-4 automated diffractometer where automatic location and centering of 25 reflections ($26° \leq 2\theta$ 32°) provided the unit cell parameters presented in Table I. A preliminary study showed systematic absences in $h0l$ for $k + l = 2n$ and $0k0$ for $k = 2n$, indicating the space group $P2_1/n$.

The crystal used in this study was chosen on the basis of peak profile analyses of several strong reflections and because of its optimum size (0.13 × 0.18 × 0.18 mm). Intensities were collected to $2\theta = 45°$ by using the ω–2θ scan method and a scan range determined by $\Delta\omega = (0.50 + 0.35 \tan \theta)°$ with a 25% extension at either end for background determination. Standard data collection procedures have been previously summarized[5] and the specific CAD-4 operating parameters used here are presented in Table I. A total of 1631 intensities were measured; Lorentz and polarization corrections were applied. Of the 1514 unique intensities measured, 1250 had $I > 3\sigma(I)$ and were, therefore, considered observed. Absorption corrections were made by using an empirical method based on Ψ scans (Ψ 0–360° every 10°) for χ values near 90°. A total of 8 sets of scans were used with maximum, minimum, and average relative transmission values of 1.00, 0.85, and 0.93, respectively, with μ(Mo Kα) = 108.85 cm^{-1}.

The structure was solved by Patterson and Fourier methods and refined[6] by full-matrix least squares. A three-dimensional Patterson synthesis provided a single W atom position and thereby indicated that the dinuclear unit is located at a site with crystallographic inversion symmetry. Three cycles of isotropic least-squares refinement gave values of $R_1 = 0.219$ and $R_2 = 0.323$, where the R_i are defined as follows:

$$R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|)^2]^{1/2}$$

The remaining nonhydrogen atoms were located from a difference Fourier synthesis, and isotropic least-squares refinement gave $R_1 = 0.070$ and $R_2 = 0.100$. The absorption-corrected intensity data were introduced, and further refinement led to values of $R_1 = 0.059$ and $R_2 = 0.085$. Convergence of refinement on an anisotropic model produced R_1 and R_2 values of 0.026 and 0.040, respectively. Evidence for the positions of 11 of the 15 hydrogen atoms was present in a difference Fourier. However, attempted refinement produced unsatisfactory results, and the hydrogen atom positions were therefore calculated with the use the conformations of the OCH_2CH_3 groups indicated in the above difference Fourier. Inclusion of these fixed positions in the refinement gave $R_1 = 0.023$ and $R_2 = 0.035$. In the final cycles of refinement, a correction was made for extinction and eventually values of R_1 and R_2 for the 1250 observed reflections of 0.019 and 0.028, respectively, were reached. The error in an observation of unit weight was 0.93, and the largest shift/error ratio in the final cycle was 0.1. A final difference synthesis showed random fluctuations not exceeding ±0.40 e/Å^3.

Table I

Crystallographic Data

formula	$W_2Cl_4O_6C_{12}H_{30}$	M_r	779.88
cryst size, mm	0.12 × 0.18 × 0.18	space group	$P2_1/n$
a, Å	8.469 (1)	β, deg	93.850 (8)
b, Å	9.344 (1)	Z	2
c, Å	14.815 (1)	d_{calcd}, g/cm^3	2.214
V, Å	1169.7 (5)	μ(Mo Kα), cm^{-1}	108.85

Enraf-Nonius CAD-4 Data Collection Procedures

radiation: graphite monochromated Mo Kα (λ_α = 0.710 73 Å)
collectn range: $+h, +k, \pm l$; $0 < 2\theta \leq 45°$
aperture width: $1.50 + 1.0 \tan \theta$
prescan rejectn limit: 2.0
max counting time, s: 30
prescan acceptance limit: 0.02
no. of unique data: 1514
no. of data with $I < 3\sigma(I)$: 1250
p: 0.05
X-ray expos time, h: 12
cryst dec: negligible
no. of variables: 109
$R_1 = 0.019$
$R_2 = 0.028$
esd: 0.93
largest peak, e/Å^3: 0.40
largest shift: 0.10
extinction coeff: 3.29×10^{-7}

Final positional and thermal parameters are given in Table II. Values of F_o vs. F_c for the 1250 observed data are available as supplementary material.

Results and Discussion

Preparative and Chemical Results. In the early preparations yields were low. Even the direct preparation by alcoholysis of W_2Cl_{10} afforded only a 25% yield.[3,4] We describe here new synthetic methods which we believe to be the best now available for the production of $W_2Cl_4(OEt)_6$. These begin with $W_2Cl_4(OEt)_4(EtOH)_2$, a compound that has been mentioned[4] but not definitively characterized before, which we shall describe very thoroughly in a forthcoming paper. This ditungsten(IV) compound may be oxidized easily and in good yield (60% or more) by either nitrate or molecular oxygen to give $W_2Cl_4(OEt)_6$.

The identity of the product, $W_2Cl_4(OEt)_6$, has been verified by comparisons of electronic absorption and NMR spectra, which show it to be identical with the substance previously reported with this formula.[2,4,7,8] We have also recorded the

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(6) All crystallographic computing was performed on a PDP 11/60 computer at the Molecular Structure Corp., College Station, TX, Using a modified version of the Enraf-Nonius structure determination package.

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Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for $W_2Cl_4(OCH_2CH_3)_6$[a,b]

atom	*x*	*y*	*z*	*B*(1,1)	*B*(2,2)	*B*(3,3)	*B*(1,2)	*B*(1,3)	*B*(2,3)
W	0.01434 (3)	0.08320 (3)	0.42588 (1)	3.40 (1)	2.63 (1)	2.40 (1)	0.452 (9)	0.274 (9)	0.122 (8)
Cl(1)	−0.0755 (3)	0.0656 (2)	0.2685 (1)	6.8 (1)	5.52 (9)	2.63 (6)	0.67 (8)	−0.41 (7)	0.30 (7)
Cl(2)	0.1403 (2)	0.3067 (2)	0.3973 (1)	6.45 (9)	4.02 (8)	5.40 (8)	−0.90 (8)	0.80 (8)	1.06 (7)
O(1)	0.1949 (5)	−0.0013 (5)	0.3923 (3)	3.6 (2)	4.8 (2)	3.1 (2)	1.0 (2)	0.9 (2)	0.1 (2)
O(2)	−0.1659 (5)	0.1871 (4)	0.4383 (3)	4.2 (2)	3.0 (2)	3.6 (2)	1.3 (2)	0.5 (2)	0.0 (2)
O(3)	0.0924 (5)	0.1060 (4)	0.5565 (3)	3.8 (2)	2.7 (2)	2.5 (2)	0.2 (2)	0.1 (1)	−0.3 (1)
C(1)	0.3083 (10)	−0.0044 (13)	0.3265 (5)	6.1 (4)	11.1 (6)	4.6 (3)	2.0 (5)	2.7 (3)	0.4 (4)
C(2)	0.4463 (12)	−0.0709 (14)	0.3510 (7)	8.4 (5)	20 (1)	6.3 (5)	7.6 (5)	2.8 (4)	3.4 (5)
C(3)	−0.2639 (11)	0.2962 (9)	0.3985 (6)	7.2 (4)	6.5 (4)	8.2 (5)	4.0 (3)	0.4 (4)	2.5 (4)
C(4)	−0.3712 (12)	0.3580 (12)	0.4561 (7)	11.8 (6)	11.1 (6)	8.4 (5)	8.2 (4)	2.8 (5)	2.4 (5)
C(5)	0.1593 (8)	0.2210 (7)	0.6150 (4)	5.0 (3)	3.1 (3)	4.0 (3)	−0.3 (3)	−0.6 (3)	−1.2 (2)
C(6)	0.0324 (10)	0.3176 (9)	0.6431 (5)	6.9 (4)	5.2 (4)	5.2 (4)	1.2 (3)	0.1 (3)	−2.0 (3)

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
H(11)[c,d]	0.3319 (0)	0.0917 (0)	0.3115 (0)	H42	−0.4399 (0)	0.2861 (0)	0.4762 (0)
H(12)	0.2620 (0)	−0.0518 (0)	0.2746 (0)	H43	−0.3141 (0)	0.3999 (0)	0.5068 (0)
H(21)	0.5139 (0)	−0.0671 (0)	0.3024 (0)	H51	0.2325 (0)	0.2747 (0)	0.5828 (0)
H(22)	0.4960 (0)	−0.0244 (0)	0.4024 (0)	H52	0.2125 (0)	0.1800 (0)	0.6672 (0)
H(23)	0.4261 (0)	−0.1680 (0)	0.3654 (0)	H61	0.0778 (0)	0.3912 (0)	0.6808 (0)
H(31)	−0.3232 (0)	0.2562 (0)	0.3480 (0)	H62	−0.0208 (0)	0.3592 (0)	0.5911 (0)
H(32)	−0.1974 (0)	0.3701 (0)	0.3786 (0)	H63	−0.0408 (0)	0.2644 (0)	0.6755 (0)
H(41)	−0.4316 (0)	0.4296 (0)	0.4241 (0)				

[a] The form of the anisotropic thermal parameter is $\exp[-0.25(h^2a^2B(1,1) + k^2b^2B(2,2) + l^2c^2B(3,3) + 2hkabB(1,2) + 2hlacB(1,3) + 2klbcB(2,3))]$, where *a*, *b*, and *c* are reciprocal lattice constants. [b] Estimated standard deviations in the least significant digits are shown in parentheses. [c] Calculated position $d_{C-H} = 0.95$ Å. [d] *B* for all H atoms is 7.000.

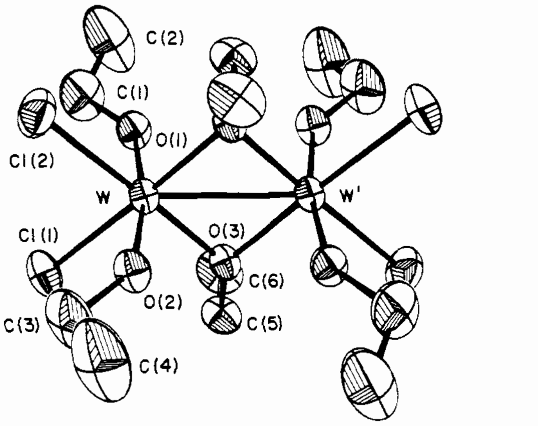

Figure 2. ORTEP diagram of $W_2Cl_4(OCH_2CH_3)_6$ with 40% thermal ellipsoids represented.

mass spectrum at high resolution and shown by comparison with calculated spectra that the parent ion $[W_2Cl_4(OEt)_6]^+$ (the most intense peak is at *m*/*e* 780) is formed.

Structural Characterization. The crystal structure of $W_2Cl_4(OCH_2CH_3)_6$ consists of a well-ordered array of molecules with intermolecular contacts corresponding generally to greater than van der Waals distances (Figure 1). Each molecule has crystallographic inversion symmetry and an overall geometry described by two edge-sharing distorted octahedra. The molecular structure, viewed at right angles to the metal–metal vector, is presented in Figure 2, where the atomic numbering scheme is also defined.

The tungsten atoms are coordinated to a planar arrangement of two cis chlorine ligands and two cis bridging ethoxide groups. The two axial positions of the octahedron are occupied by ethoxide groups. The W–Cl distances differ by 0.014 (3) Å and are therefore not quite equal within the uncertainties; however, the discrepancy is chemically negligible. There is genuine statistical equality of the crystallographically independent pairs of W–O(bridge) and W–O(terminal) distances. The central unit, $W_2(\mu\text{-}O)_2Cl_4O_4$, therefore, has D_{2d} symmetry within the experimental errors.

Table III

Distances, Å			
W–W′	2.715 (1)	O(1)–C(1)	1.414 (9)
W–Cl(1)	2.410 (2)	O(2)–C(3)	1.418 (9)
W–Cl(2)	2.396 (2)	O(3)–C(5)	1.470 (8)
W–O(1)	1.820 (4)	C(1)–C(2)	1.352 (14)
W–O(2)	1.828 (4)	C(3)–C(4)	1.411 (13)
W–O(3)	2.013 (4)	C(5)–C(6)	1.485 (10)
W–O(3)′	2.011 (4)	O(1)–O(2)′	3.075 (6)

Angles, Deg			
W–W–Cl(1)	134.77 (5)	O(1)–W–O(2)	168.6 (2)
W–W–Cl(2)	135.00 (5)	O(1)–W–O(3)	94.6 (2)
W–W–O(1)	95.5 (1)	O(1)–W–O(3)′	92.7 (2)
W–W–O(2)	95.9 (1)	O(2)–W–O(3)	94.0 (2)
W–W–O(3)	47.5 (1)	O(2)–W–O(3)′	93.9 (2)
W–W–O(3)′	47.6 (1)	O(3)–W–O(3)′	95.1 (2)
Cl(1)–W–Cl(2)	90.23 (7)	W–O(1)–C(1)	145.1 (6)
Cl(1)–W–O(1)	85.5 (2)	W–O(2)–C(3)	144.0 (5)
Cl(1)–W–O(2)	85.5 (2)	W–O(3)–W′	84.9 (2)
Cl(1)–W–O(3)	177.7 (1)	W–O(3)–C(5)	137.1 (4)
Cl(1)–W–O(3)′	87.2 (1)	W–O(3)′–C(5)′	136.5 (4)
Cl(2)–W–O(1)	86.4 (2)	O(1)–C(1)–C(2)	116.1 (9)
Cl(2)–W–O(2)	86.5 (2)	O(2)–C(3)–C(4)	115.2 (9)
Cl(2)–W–O(3)	87.5 (1)	O(3)–C(5)–C(6)	110.7 (6)
Cl(2)–W–O(3)′	177.3 (1)		

The mean W–Cl distance (2.403 (7) Å) is considerably longer than the terminal ones found in W_2Cl_{10},[9] which have a mean value of 2.251 ± 0.005 Å. The mean W–O(bridge) distance (2.012 (4) Å) is ca. 0.20 Å longer than the mean W–O(terminal) distance (1.824 (6) Å) which is approximately the sort of difference to be expected. A very similar difference (0.23 Å) was found for $Nb_2(OCH_3)_{10}$.[10] It may be noted that the mean W–O(termial) bond length here is similar to, but a little shorter than, the average of those to similarly positioned

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(8) We find that C_6D_6 solutions exhibit methyl triplets at δ 1.01 and δ 1.40 and methylene quartets at δ 4.57 and δ 5.44 in the ^{1}H NMR. In each case the lower field resonance is due to the OEt bridges. Chloroform solutions of $W_2Cl_4(OEt)_6$ show electronic absorption maxima at 526 and 422 nm.

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(11) Bino, A.; Cotton, F. A.; Dori, Z.; Sekutowski, J. C. *Inorg. Chem.* **1978**, *17*, 2946.

MeO groups in $W_2(\mu\text{-}S)_2(OMe)_4(S_2CNEt_2)_2$, namely, 1.87 ± 0.03 Å.[10]

The W–W distance (2.715 (1) Å) is of special interest. It is very similar to others where a W–W single bond has been assumed to exist. Thus, in the trinuclear species[12] $[W_3O_2(O_2CR)_6(H_2O)_3]^{2+}$ the distances are about 2.75 Å. Similarly, the W–W distance in $W_2(\mu\text{-}S)_2(OMe)_4(S_2CNEt_2)_2$ is 2.791 (1) Å. However, while we may say that the W–W distance is consistent with, and even indicative of, the existence of a W–W single bond, the ambiguities about bonding in bridged systems are well-known, and we therefore turn to other structural criteria for additional support of this view.

As noted several years ago with particular reference to face-sharing octahedra,[13] when two octahedra are joined without distortion, on a common element, face or edge, the metal atoms make a contact that is repulsive in the absence of M–M bond formation. Therefore, if no bond is formed, the repulsion should lead to changes in angles that reflect the repulsive force: the $(\mu\text{-}L)\text{–}M\text{–}(\mu\text{-}L)$ angles should decrease while the $M\text{–}(\mu\text{-}L)\text{–}M$ angles increase. Such a result has been clearly seen in the W_2Cl_{10} structure[9] where the two types of angles just mentioned are respectively 81.5 (instead of 90°) and 98.5° (instead of 90°). The W–W distance is 3.814 (2) Å instead of the 3.56 Å it would be if a rectangular W_2Cl_2 bridge system were maintained.

In the present case we find the angle changes indicative of attraction between the metal atoms: the $(\mu\text{-}O)\text{–}W\text{–}(\mu\text{-}O)$ angles are 95.1 (2)° and the $W\text{–}(\mu\text{-}O)\text{–}W$ angles are 84.9 (2)°. W–W distance of 2.715 (0) Å is shorter than that expected for a rectangular bridge system with the observed $W\text{–}(\mu\text{-}O)$ bond lengths, viz., 2.85 Å. We conclude that the totality of the structural evidence clearly favors the presence of a W–W bond in $W_2Cl_4(OEt)_6$.

It is notable that because of the close approach of the tungsten atoms another distortion is introduced into the octahedra. The repulsive nonbonded contact between O(1) and O(2)′ cannot be as close, and, therefore, the W–O(1) and W′–O(2)′ bonds are bent away from each other, giving a more acceptable O(1)···O(2)′ distance of 3.075 (6) Å. The W′–W–O(1) and W–W′–O(2) angles are therefore 95.5 (1) and 95.9 (1)°, respectively.

It is also interesting to note that the stereochemistry at the bridging oxygen atom O(3) is very nearly flat. The sum of the three bond angles is 358.5 (8)°. This may imply, or at least allow, some participation of the O(3) and O(3)′ lone pairs in a π contribution to the bridge bonding, but the importance of this is probably not great.

Acknowledgment. We thank the National Science Foundation for support of this research at both institutions. B.W.S.K. is the recipient of a NATO postoctoral fellowship from the Natural Science and Engineering Research Council of Canada.

Registry No. $W_2Cl_4(OEt)_6$, 12389-29-6; $W_2Cl_4(OEt_4)(EtOH)_2$, 25365-40-6.

Supplementary Material Available: A table of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

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Structural Characterization of the Octachloroditechnetate(III) Ion in Its Tetra-*n*-butylammonium Salt

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The title compound, $[(n\text{-}C_4H_9)_4N]_2[Tc_2Cl_8]$, has been prepared by the method of Preetz and Peters, and crystals suitable for X-ray study have been obtained. The crystals, isomorphous to those of the rhenium analogue, whose structure was previously determined, have the following parameters: space group $P2_1/c$, $a = 10.915$ (1) Å, $b = 15.382$ (3) Å, $c = 16.409$ (2) Å, $\beta = 122.37$ (1)°, $V = 2327$ (1) Å^3, and $Z = 4$. The structure has been solved and refined to $R_1 = 0.034$ and $R_2 = 0.040$ with the esd of an observation of unit weight equal to 1.021 with the use of 1821 reflections with $F_o^2 > 3\sigma(F_o^2)$ and 209 variables. Hydrogen atoms were included, but not refined, in the final cycles. There is a disorder, with 30.9% of the $[Tc_2Cl_8]^{2-}$ ions oriented perpendicular to the majority (69.1%). The Tc–Tc distances in the major and minor orientations are 2.151 (1) and 2.133 (3) Å, respectively, with a weighted average of 2.147 (4) Å. The mean Tc–Cl distance is 2.320 (4) Å, and the mean Tc′–Tc–Cl angle is 103.8 (4)°. The $[Tc_2Cl_8]^{2-}$ ion resides on a crystallographic inversion center. As in the analogous rhenium compound, the tetra-*n*-butylammonium ions are unusually well-ordered and all atoms in them refined well.

Introduction

From the time that the true character of the $[Re_2Cl_8]^{2-}$ ion was recognized,[2] it has seemed reasonable to anticipate the preparation of technetium compounds homologous to this one and to other multiply bonded dirhenium species. To date this expectation has been rather more honored in the breach than the fulfillment. The earliest development was the characterization[3] of the $[Tc_2Cl_8]^{3-}$ ion, the preparation of which had been described earlier[4] without an identification of the product other than its stoichiometry. The structure of the compound in question, $(NH_4)_3[Tc_2Cl_8]\cdot 2H_2O$, was later described in more detail, including magnetic data that are consistent with the presence of one unpaired electron[5] and a Tc–Tc distance of

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