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Preparation and Characterization of the Heptachlorobis(tetrahydrofuran)ditungstate and Octachloro(tetrahydrofuran)ditungstate Anions: $[Ph_4P][W_2Cl_7(THF)_2]$ and $[Ph_4P][W_2Cl_8(THF)]$

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The anion $W_2Cl_7(THF)_2^-$ has been prepared by the reaction between PPh_4Cl and $NaW_2Cl_7(THF)_5$ and structurally characterized as a PPh_4^+ salt. It contains a confacial bioctahedral unit $OCl_2W(\mu\text{-}Cl)_3WOCl_2$ essentially identical with that seen in the Na^+ salt but without the terminal W–Cl to Na interactions; W–W = 2.409 (4) Å. In solution the $W_2Cl_7(THF)_2^-$ anion is oxidized (CCl_4 + light) to the $W_2Cl_8(THF)^-$ anion, which has also been structurally characterized and shown to retain the confacial bioctahedral moiety with μ-Cl ligands; W–W = 2.520 (1) Å. The new compounds have been characterized by UV–visible spectroscopy and electrochemical studies, and the chemicophysical data are compared to those of related $(\mu_2\text{-}Cl)_3W_2$-containing compounds and to the proposed edge-shared bioctahedral compound $W_2Cl_6(THF)_4$ (Schrock, R. R.; Sturgeoff, L. G.; Sharp, P. R. *Inorg. Chem.* **1983**, *22*, 2801). Crystal data for $[PPh_4][W_2Cl_7(THF)_2]\cdot 2CH_2Cl_2$ at −141 °C: $a = 19.702$ (38) Å, $b = 13.216$ (24) Å, $c = 9.817$ (15) Å, $\alpha = 111.23$ (8)°, $\beta = 66.96$ (9)°, $\gamma = 111.97$ (8)°, $Z = 2$, $d_{calcd} = 1.997$ g cm^{-3}, space group $P\bar{1}$. Crystal data for $[PPh_4][W_2Cl_8(THF)]$ at −155 °C: $a = 11.577$ (4) Å, $b = 14.234$ (6) Å, $c = 11.057$ (2) Å, $\alpha = 112.71$ (2)°, $\beta = 95.78$ (2)°, $\gamma = 92.47$ (2)°, $Z = 2$, $d_{calcd} = 2.119$ g cm^{-3}, space group $P\bar{1}$.

Introduction

In a previous paper we described[2] the synthesis, preparation, and full characterization of the compound $NaW_2Cl_7(THF)_5$. This compound was prepared by the Na/Hg reduction of WCl_4 in tetrahydrofuran according to eq 1 and was shown to be a good

$$2WCl_4 + 2Na \xrightarrow[THF]{0\ °C} NaW_2Cl_7(THF)_5 + NaCl \tag{1}$$

starting material for the synthesis of $X_3W{\equiv}WX_3$ compounds, where X = CH_2CMe_3, NMe_2, and O-*t*-Bu. The green crystalline compound appeared in all respects to mimic the reactivity of a green crystalline compound formulated as $W_2Cl_6(THF)_4$ by Schrock and co-workers,[3] obtained similarly by the Na/Hg reduction of WCl_4 in tetrahydrofuran.

The previous work led us to question whether or not there exists in solution an equilibrium relating $NaW_2Cl_7(THF)_5$ and $W_2Cl_6(THF)_4$, eq 2, and furthermore, whether or not we could isolate $W_2Cl_6(THF)_4$ starting from pure $NaW_2Cl_7(THF)_5$.

$$NaW_2Cl_7(THF)_5 \rightleftharpoons W_2Cl_6(THF)_4 + NaCl + THF \tag{2}$$

Attempts to capture $W_2Cl_6(THF)_4$ in an equilibrium of the type in (2) by the introduction of $TlPF_6$ have failed to yield the desired product.[4] Experiments employing ^{183}W NMR spectroscopy are currently being carried out but as yet have revealed no evidence for (2).[5] Since the compound $NaW_2Cl_7(THF)_5$ showed conductivity in THF solutions intermediate between those of $NaBPh_4$ and $NaW_2(H)(O\text{-}i\text{-}Pr)_8\cdot$diglyme,[6] we were led to question the role of the Na^+ cation in stabilizing the anion $W_2Cl_7(THF)_2^-$. The Na^+ ion is coordinated to three oxygen atoms of three THF molecules and two chloride ligands, which are terminally bonded to tungsten atoms in the confacial bioctahedral $W_2Cl_7(THF)_2^-$ anion. This type of Na^+ binding parallels that in $NaW_2(H)(O\text{-}i\text{-}Pr)_8\cdot$diglyme, where two W-O-*i*-Pr groups substitute for W-Cl moieties and three THF molecules for one molecule of diglyme.

We describe here the preparation of the salt $[Ph_4P][W_2Cl_7(THF)_2]$, which shows that the Na^+ ion is not essential for the existence of the $W_2Cl_7(THF)_2^-$ anion and, in addition, an oxidation product $[Ph_4P][W_2Cl_8(THF)]$. The structural comparisons of the d^3–d^3 dinuclear compounds $NaW_2Cl_7(THF)_5$ and $[Ph_4P][W_2Cl_7(THF)_2]$ with the formally mixed-valence d^3–d^2 compound $[Ph_4P][W_2Cl_8(THF)]$ form an interesting comparison of M–M bonding in trichloro-bridged confacial bioctahedral anions of tungsten.

Results and Discussion

Synthesis. $[Ph_4P][W_2Cl_7(THF)_2]$. $NaW_2Cl_7(THF)_5$ is only slightly soluble in CH_2Cl_2 but dissolves readily upon addition of 1 equiv of PPh_4Cl. The resultant green solution was filtered from NaCl formed during the reaction according to eq 3, giving a clear

$$NaW_2Cl_7(THF)_5 + PPh_4Cl \xrightarrow{CH_2Cl_2} [Ph_4P][W_2Cl_7(THF)_2]\cdot 2CH_2Cl_2 + 3THF + NaCl \tag{3}$$

green filtrate, which was concentrated in vacuo. At lower temperatures (−5 to −20 °C) light brown translucent crystals were formed that readily lost incorporated CH_2Cl_2 and became green to reflected light when isolated and dried in vacuo. The compound is air-stable in the crystalline state for a few hours, but its solutions are air-sensitive.

$[Ph_4P][W_2Cl_8(THF)]$. Addition of CCl_4 to the green reaction mixture obtained according to eq 3 resulted in a color change from green to deep purple-blue after 30 min in the presence of room light. The reaction of CCl_4 with green crystalline $[Ph_4P][W_2Cl_7(THF)_2]$ resulted in the formation of a deep blue solution. Blue crystals of the product were obtained by allowing the blue solution to stand at −20 °C for 2 days. The reaction presumably proceeds according to the stoichiometry shown in eq 4 though C_2Cl_6 was not characterized. The crystalline compound

$$[Ph_4P][W_2Cl_7(THF)_2] + CCl_4 \xrightarrow[h\nu]{CH_2Cl_2} [Ph_4P][W_2Cl_8(THF)] + {}^1/_2C_2Cl_6 + THF \tag{4}$$

is air-stable for a few hours but is air-sensitive in solution. The presence of room light is essential for the oxidation of $[W_2Cl_7(THF)_2]^-$ to $[W_2Cl_8(THF)]^-$ by CCl_4 since the color of the green solution does not change if stored in the dark. The initial step of the reaction is thus probably due to homolytic cleavage of a Cl–C bond in CCl_4 according to eq 5, forming Cl• radicals, which

$$CCl_4 \xrightarrow{h\nu} {}^\bullet CCl_3 + {}^\bullet Cl \tag{5}$$

subsequentialy react with $[W_2Cl_7(THF)_2]^-$ anions. Another example of an oxidation by CCl_4 and formation of C_2Cl_6 was recently found by Dehnicke et al.[7] in the oxidation of $[Ph_4P]_2[Mo_2Cl_2$-

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Table I. Fractional Coordinates and Isotropic Thermal Parameters for $[PPh_4][W_2Cl_7(THF)_2]\cdot 2CH_2Cl_2$

atom	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
W(1)	3257.8 (4)	262 (1)	3754 (1)	17
W(2)	2768.9 (4)	1568 (1)	6086 (1)	17
Cl(3)	2674 (2)	−327 (3)	6197 (4)	20
Cl(4)	2298 (2)	1094 (3)	3902 (4)	25
Cl(5)	4169 (2)	1961 (3)	4826 (4)	21
Cl(6)	3933 (2)	770 (3)	1370 (4)	24
Cl(7)	2477 (2)	−1498 (3)	2663 (4)	22
Cl(8)	1460 (2)	1256 (3)	7580 (5)	27
Cl(9)	2906 (2)	3462 (3)	6216 (5)	27
O(10)	4078 (6)	−576 (9)	3400 (12)	26
C(11)	4916 (9)	−204 (15)	2606 (18)	27
C(12)	5242 (11)	−1029 (16)	2611 (21)	36
C(13)	4604 (12)	−2058 (16)	2812 (25)	42
C(14)	3916 (10)	−1649 (14)	3681 (22)	33
O(15)	3144 (6)	2085 (9)	8108 (12)	29
C(16)	3622 (10)	3243 (14)	8620 (18)	29
C(17)	3121 (12)	3730 (17)	10110 (22)	45
C(18)	2664 (15)	2752 (20)	10785 (21)	65
C(19)	2713 (11)	1674 (16)	9478 (19)	36
P(20)	475 (2)	−3098 (3)	7439 (4)	19
C(21)	−276 (8)	−4180 (12)	8289 (16)	17
C(22)	−876 (9)	−3898 (14)	9575 (17)	25
C(23)	−1471 (11)	−4728 (15)	10171 (17)	32
C(24)	−1479 (10)	−5854 (13)	9553 (19)	26
C(25)	−866 (10)	−6118 (13)	8308 (19)	29
C(26)	−282 (8)	−5306 (12)	7666 (16)	20
C(27)	798 (9)	−1234 (12)	8940 (15)	18
C(28)	317 (9)	−1234 (12)	9854 (18)	24
C(29)	516 (9)	−387 (14)	11069 (18)	26
C(30)	1188 (10)	−236 (13)	11335 (18)	27
C(31)	1666 (10)	−892 (14)	10421 (19)	29
C(32)	1473 (9)	−1757 (13)	9196 (18)	23
C(33)	1246 (8)	−3699 (13)	6128 (17)	22
C(34)	1559 (9)	−4205 (13)	6678 (16)	21
C(35)	2177 (9)	−4631 (12)	5716 (19)	24
C(36)	2479 (9)	−4550 (12)	4205 (18)	23
C(37)	2172 (9)	−4057 (12)	3675 (17)	25
C(38)	1571 (9)	−3592 (13)	4642 (18)	24
C(39)	132 (9)	2594 (13)	6431 (16)	22
C(40)	−611 (9)	−3085 (12)	6264 (16)	20
C(41)	−841 (9)	−2676 (13)	5466 (17)	23
C(42)	−359 (9)	−1790 (14)	4792 (18)	26
C(43)	374 (9)	−1278 (12)	5026 (17)	22
C(44)	610 (9)	−1676 (12)	5834 (16)	22
Cl(45)	4373 (3)	5523 (4)	4402 (7)	50
C(46)	4525 (14)	4219 (160)	3150 (21)	49
Cl(47)	4721 (4)	4197 (6)	1255 (7)	69
Cl(48)	6558 (3)	2116 (6)	2217 (6)	58
C(49)	6131 (10)	2248 (13)	1045 (21)	32
Cl(50)	6443 (3)	3629 (5)	829 (8)	67

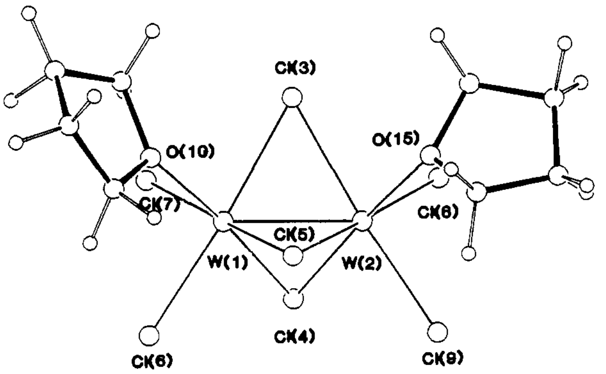

Figure 1. Ball-and-stick drawing of the $W_2Cl_7(THF)_2^-$ anion in the salt $[PPh_4][W_2Cl_7(THF)_2]\cdot 2CH_2Cl_2$, giving the atom-numbering scheme used in the tables.

$(O_2CCH_3)_4]$ to $[Ph_4P]_2[Mo_2Cl_4(O_2CCH_3)_4]$.

Solid-State and Molecular Structures. Atomic positional parameters are given in Tables I and II. $[PPh_4][W_2Cl_7(THF)_2]$ crystallizes from methylene chloride solutions with two molecules of solvent, C(46), Cl(45), Cl(47) and C(49), Cl(48), Cl(50) in Table I. In both structures the molecular parameters of the tetraphenylphosphonium cation are unexceptional. Complete structural details are given in the supplementary material, and attention here is restricted to the ditungsten anions. Ball-and-stick drawings of the $W_2Cl_7(THF)_2^-$ and $W_2Cl_8(THF)^-$ anions giving the atom-numbering schemes are given in Figures 1 and 2, respectively, and pertinent bond distances and bond angles are given in Tables III and IV.

The $W_2Cl_7(THF)_2^-$ anion is seen to be very similar to the ditungsten core in $NaW_2Cl_7(THF)_5$. One striking demonstration

Table II. Fractional Coordinates and Isotropic Thermal Parameters for $[PPh_4][W_2Cl_8(THF)]$

atom	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
W(1)	7510.5 (5)	908.1 (4)	3577 (1)	13
W(2)	6858.2 (5)	2403.2 (4)	5498 (1)	12
Cl(3)	5690 (3)	803 (3)	4458 (3)	18
Cl(4)	7587 (3)	2592 (3)	3524 (4)	20
Cl(5)	8495 (3)	1341 (3)	5837 (3)	18
Cl(6)	9365 (3)	822 (3)	2873 (4)	19
Cl(7)	6434 (3)	340 (3)	1489 (3)	24
O(8)	7537 (8)	−636 (7)	3410 (9)	19
C(9)	6500 (14)	−1408 (12)	2971 (16)	25
C(10)	7040 (17)	−2414 (14)	2553 (20)	40
C(11)	8185 (15)	−2172 (13)	3443 (17)	31
C(12)	8615 (14)	−1125 (13)	3564 (18)	30
Cl(13)	5367 (3)	3265 (3)	5185 (4)	20
Cl(14)	8263 (3)	3853 (3)	6687 (4)	20
Cl(15)	6337 (3)	2424 (3)	7494 (3)	20
P(16)	2198 (3)	2976 (3)	2182 (3)	14
C(17)	2139 (11)	1676 (10)	2010 (13)	14
C(18)	1597 (13)	876 (11)	865 (13)	19
C(19)	1611 (12)	−123 (10)	730 (13)	16
C(20)	2155 (12)	−347 (12)	1744 (15)	22
C(21)	2737 (13)	416 (11)	2897 (14)	20
C(22)	2713 (11)	1428 (10)	3005 (13)	13
C(23)	3497 (12)	3277 (10)	1611 (13)	15
C(24)	3804 (13)	4295 (12)	1755 (14)	22
C(25)	4793 (12)	4498 (11)	1248 (13)	16
C(26)	5483 (13)	3732 (12)	628 (15)	24
C(27)	5205 (14)	2745 (12)	537 (14)	24
C(28)	4216 (13)	2504 (11)	1052 (14)	21
C(29)	2159 (12)	3790 (10)	3900 (14)	16
C(30)	3127 (12)	4440 (10)	4647 (13)	16
C(31)	3089 (12)	5043 (10)	5957 (13)	16
C(32)	2098 (12)	5013 (11)	6551 (14)	17
C(33)	1129 (14)	4376 (12)	5802 (16)	26
C(34)	1162 (13)	3763 (12)	4483 (15)	25
C(35)	960 (12)	3119 (12)	1180 (13)	15
C(36)	1097 (12)	3606 (11)	282 (13)	18
C(37)	115 (14)	3711 (12)	−464 (14)	23
C(38)	−995 (13)	3351 (12)	−337 (15)	23
C(39)	−1113 (13)	2906 (12)	539 (15)	23
C(40)	−150 (12)	2777 (10)	1281 (13)	17

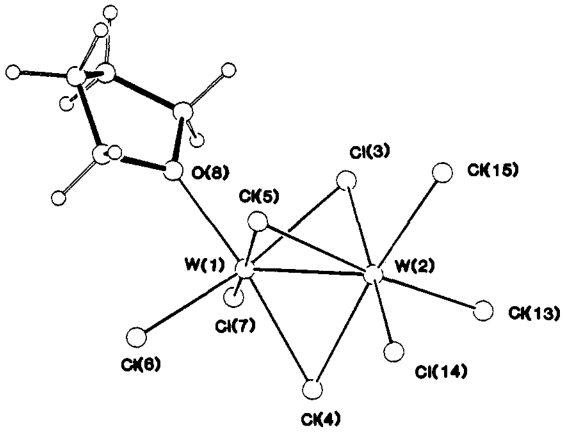

Figure 2. Ball-and-stick drawing for the $W_2Cl_8(THF)^-$ anion found in the salt $[PPh_4][W_2Cl_8(THF)]$, giving the atom-numbering scheme used in the tables.

Table III. Selected Bond Distances (Å) and Angles (deg) for the $[W_2Cl_7(THF)_2]^-$ Anion in $[PPh_4][W_2Cl_7(THF)_2]\cdot 2CH_2Cl_2$

W(1)–W(2)	2.409 (4)	W(1)–O(10)	2.140 (12)
W(1)–Cl(3)	2.491 (5)	W(2)–Cl(3)	2.480 (6)
W(1)–Cl(4)	2.454 (6)	W(2)–Cl(4)	2.448 (5)
W(1)–Cl(5)	2.476 (6)	W(2)–Cl(5)	2.377 (6)
W(1)–Cl(6)	2.393 (5)	W(2)–Cl(8)	2.376 (6)
W(1)–Cl(7)	2.394 (5)	W(2)–O(15)	2.177 (11)

W(2)–W(1)–Cl(3)	60.78 (15)	W(1)–W(2)–Cl(5)	60.86 (14)
W(2)–W(1)–Cl(4)	60.45 (14)	W(1)–W(2)–Cl(8)	124.06 (15)
W(2)–W(1)–Cl(5)	60.92 (16)	W(1)–W(2)–Cl(9)	123.02 (15)
W(2)–W(1)–Cl(6)	122.72 (16)	W(1)–W(2)–O(15)	123.4 (3)
W(2)–W(1)–Cl(7)	123.76 (16)	Cl(3)–W(2)–Cl(4)	101.43 (16)
W(2)–W(1)–O(10)	125.5 (3)	Cl(3)–W(2)–Cl(5)	92.47 (16)
Cl(3)–W(1)–Cl(4)	100.96 (17)	Cl(3)–W(2)–Cl(8)	86.51 (17)
Cl(3)–W(1)–Cl(5)	92.23 (18)	Cl(3)–W(2)–Cl(9)	173.88 (14)
Cl(3)–W(1)–Cl(6)	174.01 (14)	Cl(3)–W(2)–O(15)	81.8 (3)
Cl(3)–W(1)–Cl(7)	86.92 (18)	Cl(4)–W(2)–Cl(5)	100.92 (19)
Cl(3)–W(1)–O(10)	82.4 (3)	Cl(4)–W(2)–Cl(8)	86.05 (20)
Cl(4)–W(1)–Cl(5)	100.76 (20)	Cl(4)–W(2)–Cl(9)	84.69 (17)
Cl(4)–W(1)–Cl(6)	85.00 (18)	Cl(4)–W(2)–O(15)	175.9 (3)
Cl(4)–W(1)–Cl(7)	85.74 (21)	Cl(5)–W(2)–Cl(8)	173.02 (14)
Cl(4)–W(1)–O(10)	174.0 (3)	Cl(5)–W(2)–Cl(9)	86.55 (17)
Cl(5)–W(1)–Cl(6)	85.99 (18)	Cl(5)–W(2)–O(15)	81.4 (3)
Cl(5)–W(1)–Cl(7)	173.45 (14)	Cl(8)–W(2)–Cl(9)	93.73 (18)
Cl(5)–W(1)–O(10)	83.9 (3)	Cl(8)–W(2)–O(15)	91.6 (3)
Cl(6)–W(1)–Cl(7)	94.19 (19)	Cl(9)–W(2)–O(15)	92.0 (3)
Cl(6)–W(1)–O(10)	91.7 (3)	W(1)–Cl(3)–W(2)	57.99 (12)
Cl(7)–W(1)–O(10)	89.6 (3)	W(1)–Cl(4)–W(2)	58.87 (13)
W(1)–W(2)–Cl(3)	61.23 (14)	W(1)–Cl(5)–W(2)	58.22 (14)
W(1)–W(2)–Cl(4)	60.69 (15)		

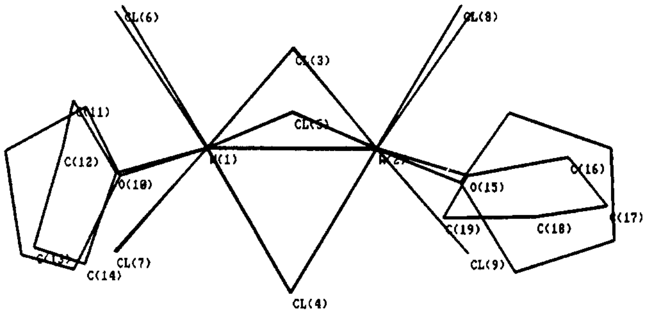

Figure 3. VERSORT drawing of the superposition of the $W_2Cl_7(THF)_2^-$ anion found in $NaW_2Cl_7(THF)_5$ and $[PPh_4][W_2Cl_7(THF)_2)\cdot 2Ch_2Cl_2$.

of this fact is seen in a superposition of the two $W_2Cl_7O_2$ units shown in Figure 3.

The $W_2Cl_8(THF)^-$ anion with its formal W(IV)–W(III) core is closely related to the known $[W_2Cl_9]^{2-}$ anion, first prepared by Saillant and Wentworth[8] from the reaction between $[(n\text{-}Bu)_4N]_3[W_2Cl_9]$ and chlorine and subsequently structurally characterized by Cotton et al.,[9] who prepared it by the reduction of WCl_4 with Na/Hg in THF in the presence of $[Ph_3PNPPh_3]Cl$ in a 40% yield.

Table IV. Selected Bond Distances (Å) and Angles (deg) for the $W_2Cl_8(THF)^-$ Anion in $[PPh_4][W_2Cl_8(THF)_4]$

W(1)–W(2)	2.5199 (13)	W(2)–Cl(3)	2.453 (4)
W(1)–Cl(3)	2.432 (4)	W(2)–Cl(4)	2.474 (4)
W(1)–Cl(4)	2.418 (4)	W(2)–Cl(5)	2.475 (4)
W(1)–Cl(5)	2.470 (4)	W(2)–Cl(13)	2.327 (4)
W(1)–Cl(6)	2.349 (4)	W(2)–Cl(14)	2.347 (4)
W(1)–Cl(7)	2.330 (4)	W(2)–Cl(15)	2.379 (4)
W(1)–O(8)	2.136 (9)		

W(2)–W(1)–Cl(3)	59.36 (9)	W(1)–W(2)–Cl(5)	59.25 (9)
W(2)–W(1)–Cl(4)	60.10 (9)	W(1)–W(2)–Cl(13)	119.73 (10)
W(2)–W(1)–Cl(5)	59.48 (9)	W(1)–W(2)–Cl(14)	121.90 (10)
W(2)–W(1)–Cl(6)	123.38 (10)	W(1)–W(2)–Cl(15)	128.55 (10)
W(2)–W(1)–Cl(7)	121.38 (10)	Cl(3)–W(2)–Cl(4)	100.65 (12)
W(2)–W(1)–O(8)	126.87 (25)	Cl(3)–W(2)–Cl(5)	86.21 (12)
Cl(3)–W(1)–Cl(4)	102.88 (12)	Cl(3)–W(2)–Cl(13)	88.20 (13)
Cl(3)–W(1)–Cl(5)	86.80 (12)	Cl(3)–W(2)–Cl(14)	172.82 (12)
Cl(3)–W(1)–Cl(6)	170.80 (12)	Cl(3)–W(2)–Cl(15)	84.31 (12)
Cl(3)–W(1)–Cl(7)	87.77 (13)	Cl(4)–W(2)–Cl(5)	98.00 (12)
Cl(3)–W(1)–O(8)	82.99 (27)	Cl(4)–W(2)Cl(13)	85.85 (13)
Cl(4)–W(1)–Cl(5)	99.67 (12)	Cl(4)–W(2)–Cl(14)	84.65 (13)
Cl(4)–W(1)–Cl(6)	85.36 (13)	Cl(4)–W(2)–Cl(15)	173.54 (13)
Cl(4)–W(1)–Cl(7)	86.44 (14)	Cl(5)–W(2)–Cl(13)	173.72 (12)
Cl(5)–W(1)–O(8)	172.95 (26)	Cl(5)–W(2)Cl(14)	88.26 (13)
Cl(5)–W(1)–Cl(6)	87.77 (13)	Cl(5)–W(2)–Cl(15)	86.40 (12)
Cl(5)–W(1)–Cl(7)	172.60 (13)	Cl(13)–W(2)–Cl(14)	97.08 (13)
Cl(6)–W(1)–O(8)	84.43 (28)	Cl(13)–W(2)–Cl(15)	90.19 (13)
Cl(6)–W(1)–Cl(7)	96.94 (14)	Cl(14)–W(2)–Cl(15)	90.78 (13)
Cl(6)–W(1)–O(8)	89.09 (27)	W(1)–Cl(3)–W(2)	62.12 (9)
Cl(7)–W(1)–O(8)	89.9 (3)	W(1)–Cl(4)–W(2)	61.99 (9)
W(1)–W(2)–Cl(3)	58.53 (9)	W(1)–Cl(5)–W(2)	61.27 (9)
W(1)–W(2)–Cl(4)	57.91 (9)		

Table V. Metal–Metal Distances of Trichloro-Bridged Confacial Bioctahedral M_2 Dimers

compd	oxidn state	M–M dist, Å	ref
$NaW_2Cl_7(THF)_5$	W(III)–W(III)	2.403	2
$[W_2Cl_7(THF)_2]^-$	W(III)–W(III)	2.409	this work
$[W_2Cl_8(THF)]^-$	W(IV)–W(III)	2.520	this work
$[W_2Cl_9]^{3-}$	W(III)–W(III)	2.418	9
$[W_2Cl_9]^{2-}$	W(IV)–V(III)	2.601	9
$[Re_2Cl_9]^-$	Re(IV)–Re(IV)	2.703	9

A summary of M–M bond distances is given in Table V for the $W_2(\mu\text{-}Cl)_3$-containing compounds. The d^3–d^3 confacial bioctahedral anions have M–M distances of ca. 2.40 Å, while the d^2–d^3 anions have distances of ca. 2.50 Å. The $t_{2g}{}^3$–$t_{2g}{}^3$ interaction in the d^3–d^3 dimers allows for the formal formation of a M–M triple bond, while $t_{2g}{}^3$–$t_{2g}{}^2$ would yield only a bond order of 2.5. In addition to a reduction in bond order, the increased oxidation state of the metal atoms in the d^2–d^3 dinuclear anion will cause a contraction of the d orbitals and a weakening of M–M bonding as a result of poorer d–d overlap. The effect of the increased charge on the metal atoms is seen in the W–Cl distances, which are consistently shorter in the $W_2Cl_8(THF)^-$ anion relative to the $W_2Cl_7(THF)_2^-$ anion. This effect is not localized to one tungsten atom in $W_2Cl_8(THF)^-$, suggesting that the increased charge is indeed delocalized over the W_2 unit, as expected for the removal of an electron from a M–M bonding molecular orbital.

Electrochemical Studies. The facile oxidation of the $W_2Cl_7(THF)_2^-$ anion and reduction of the $W_2Cl_8(THF)^-$ anion were examined by cyclic voltammetry in THF. As soon as the PPh_4^+ salts were added to the THF solutions of the electrolyte Bu_4NPF_6, some white precipitate was formed probably due to the formation of $PPh_4^+PF_6^-$. The electrochemical oxidation of the $W_2Cl_7(THF)_2^-$ anion gives a reversible oxidation at $E_p = +0.61$ V with $\Delta E_p = 200$ mV. Plots of I_p versus $v^{1/2}$ (v = scan rate) yielded straight lines, indicating a diffusion-controlled process. A second oxidation at $E_p = +0.98$ V is chemically irreversible and exhibits no reverse coupled wave over the scan rates studied (20–500 mV/s).

A chemically irreversible reduction was observed at $E_p = -0.24$ V. The electrochemical reduction of the $W_2Cl_8(THF)^-$ anion gives a reversible reduction at $E_p = 0.01$ V with $\Delta E_p = 90$ mV, which is also a diffusion-controlled process, as indicated by plots of I_p versus $v^{1/2}$ yielding straight lines. An irreversible oxidation occurs at $E_p = +0.39$ V.

The peak separations (ΔE_p) between the anodic and cathodic waves can be compared to the values for ferrocene in THF, which were $\Delta E_p = 250$ mV and $E_p = 0.63$ V at a scan rate of 200 mV/s. This suggests that the couples are not completely reversible under the conditions employed here.

As expected, $W_2Cl_7(THF)_2^-$ and $W_2Cl_8(THF)^-$ can easily be oxidized and reduced, respectively. The reversible oxidation of $W_2Cl_7(THF)_2^-$ parallels the reversible reduction of $W_2Cl_8(THF)^-$, and the irreversible second oxidation of $W_2Cl_7(THF)_2^-$ parallels the irreversible oxidation of $W_2Cl_8(THF)^-$.

Magnetic Susceptibility Studies of $[W_2Cl_8(THF)][PPh_4]$. The low moment and the relatively high molecular weight of this

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Table VI. Electronic Absorption Data (UV-Visible Data)

compd	λ, nm	ν, cm^{-1}	ε, L mol^{-1} cm^{-1}	ref
$NaW_2Cl_7(THF)_5$	450	22 200	3 800	6
	634	15 800	290	
	754	13 300	150	
"$W_2Cl_6(THF)_4$"	448	22 330	2 820 (3240)[a]	10
	623	16 000	200 (230)[a]	
	745	13 400	120 (140)[a]	
$[Ph_4P][W_2Cl_7(THF)_2]$	237	42 200	26 300 (Cl)	this work
	262	38 200	9 100	
	268	37 300	9 200 (Ph)	
	276	36 200	7 700	
	454	22 000	2 300	
	632	15 800	220	
	752	13 300	130	
$[Ph_4P][W_2Cl_8(THF)]$	237	42 200	26 100 (Cl)	this work
	262	38 200	14 900	
	268	37 300	15 300 (Ph)	
	275	36 400	14 200	
	525	19 000	1 200	
	580 sh	17 200	930	
	710	14 100	590	
$[PNP]_2[W_2Cl_9]$	390 sh	25 600		9
	580	17 200	1 330	
	740	13 530	875	
$[(n\text{-}Bu)_4N]_2[W_2Cl_9]$	390 sh	25 600	~618	8
	580	17 200	1 700	
	740	13 530	1 040	

[a] The ε values given in parentheses are obtained by using the "correct" molecular mass of 999.401 g/mol for $NaW_2Cl_7(THF)_5$ instead of 868.846 g/mol for "$W_2Cl_6(THF)_4$".

compound meant that at least 200–300 mg was required to prevent the combined value for the diamagnetic container and the paramagnetic sample from becoming negative (diamagnetic) with increasing temperature. Since the magnetization value crossed zero at about 80 K, a few points above and below this temperature are unreliable due to extremely low magnetization. Also, it has been found in previous work that although the slope of a $1/\chi$ versus T plot (and hence the moment) remains reliable above the crossover temperature, the value of Θ does not.

With these considerations in mind, the low- (T = 5–40 K) and high-temperature (T = 130–280 K) regions were fit separately to the Curie–Weiss law. In the low-temperature region, $\mu = 1.70$ μ_B with $\Theta = -2.3$ K for a simultaneous fit of 5- and 40-kG data. Above 130 K, the 5- and 40-kG data follow Curie–Weiss behavior with $\mu = 1.99$ μ_B. The high-temperature data are only mentioned to illustrate that the sample still follows the Curie–Weiss law with approximately the same moment; the lower temperature data are *much* more reliable.

The susceptibility is consistent with one unpaired spin per anion with no appreciable intermolecular interaction.

Electronic Absorption Spectra. The electronic absorption spectra of $[Ph_4P][W_2Cl_7(THF)_2]$ and $[Ph_4P][W_2Cl_8(THF)]$ were recorded in CH_2Cl_2. The λ_{max}, ν, and ε values are shown in Table VI. The absorptions at 237 and 262 nm and at 268 and 275/276 nm are assigned to Cl and Ph absorptions, respectively. They are present for solutions of Ph_4PCl.[10] The absorptions associated with the W(III)–W(III) center in $[W_2Cl_7(THF)_2]^-$ are remarkably similar to those reported for $NaW_2Cl_7(THF)_5$[2] and "$W_2Cl_6(THF)_4$",[11] suggesting that the confacial bioctahedral W(III)–W(III) unit in solution is maintained for all three compounds.

The spectrum of the $W_2Cl_8(THF)^-$ ion shows also three absorptions for the W(III)–W(IV) unit similar to those of the $W_2Cl_9{}^{2-}$ ion.[8,9]

Concluding Remarks. Though we cannot say that $W_2Cl_6(THF)_4$ does not exist, it seems most likely that the compound prepared in the Na/Hg reduction of WCl_4 in THF is $NaW_2Cl_7(THF)_5$ and that the $W_2Cl_7(THF)_2{}^-$ anion has an existence that is not dependent on the presence of the Na^+ countercation.

Experimental Section

General Procedures. All procedures were carried out under a dry-nitrogen atmosphere by using standard Schlenk and glovebox techniques. Carbon tetrachloride, CH_2Cl_2, and CD_2Cl_2 were dried and deoxygenated by refluxing over P_4O_{10} and were distilled prior to use. Tetraphenylphosphonium chloride (Aldrich) was dried 3 h at 100 °C under vacuum. $NaW_2Cl_7(THF)_2$ was prepared by published procedures.[2] Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

^1H NMR spectra were recorded on a Nicolet NT-360 spectrometer. Infrared spectra were obtained as Nujol mulls between CsI plates on a Perkin-Elmer 283 spectrophotometer. Electronic absorption spectra were recorded on a Perkin-Elmer 330 spectrophotometer. Samples were run versus a solvent blank with matched 1.0-cm quartz cells. Electrochemical measurements were obtained by using an EG & G Model 173 potentiostat and programmer along with a Houston Instruments 2000 X-Y recorder. The electrolyte $[Bu_4N][PF_6]$ was made from Bu_4NI and $NaPF_6$. Cyclic voltammograms were referenced to a Ag/Ag^+ electrode. The working electrode was a platinum wire encased in a cobalt glass-tipped electrode. The counter electrode was a platinum-gauze electrode. The CV measurements were carried out in a Vacuum Atmospheres drybox.

Magnetic susceptibility measurements were made by using an SHE Model 905 superconducting magnetometer (SQUID). Sample containers made from tightly fitting KEL-F halves were used for air-sensitive samples; no significant decomposition was noted during the course of measurement, ca. 1 day. In a typical experiment 50–75 mg of the compound to be studied was ground and weighed into a KEL-F container in an argon drybox. The halves of the container were sealed with the aid of a small amount of silicone grease. After removal from the drybox, the container was wired closed with nylon monofilament thread and suspended in the sample chamber by a cotton thread. The sample chamber was then alternately evacuated to 30 μmHg and refilled with high-purity helium three times. Samples were measured automatically at two fields and at temperatures between 5 and 280 K. Measurements were taken at 5 and 40 kG with the following temperature intervals and associated ranges: 3 K, 6–21 K; 5 K, 25–50 K; 10 K, 50–100 K; 20 K, 100–280 K. Sample data were corrected for container (including grease) and sample diamagnetism, the latter correction using Pascal's constants. Samples exhibiting Curie–Weiss behavior were fit to the Curie–Weiss law, $1/\chi = (T - \Theta)/C$, by using a linear-least-squares program written by Dr. E. Gamp. Effective magnetic moments were then calculated as $\mu = 2.828C^{1/2}$.

Preparation of $[Ph_4P][W_2Cl_7(THF)_2]{\cdot}2CH_2Cl_2$. In a Schlenk flask, $NaW_2Cl_7(THF)_5$ (0.50 g, 0.50 mmol) was stirred in 5 mL of CH_2Cl_2. Upon addition of a solution of PPh_4Cl (0.188 g, 0.50 mmol in 5 mL of CH_2Cl_2), the green crystalline starting material dissolved completely. After 5 min the green solution was filtered to remove an olive green precipitate (63 mg), which contained sodium chloride formed during the reaction. The clear green solution was concentrated to ca. 8 mL, and after 12 h at 5 °C, square light brown translucent crystals (120 mg) formed. The crystals lost CH_2Cl_2 very readily under reduced pressure and then became green to reflected light. Further reduction of the volume and cooling to −20 °C yielded additional crops of crystalline product. The total yield of green crystals was 500 mg (79% based on $[PPh_4][W_2Cl_7(THF)_2]{\cdot}2CH_2Cl_2$). IR (CsI, Nujol mull, *anion*): 1580 (w), 1482 (m), 1441 (s), 1336 (w), 1316 (w), 1260 (w), 1105 (vs), 1039 (w), 1003 (m), 920 (w), *845* (*vs*), 766 (w), 758 (m), 742 (w), 723 (vs), 688 (m), 682 (m), 531 (vs), *333* (*s*), *325* (*s*), *308* (*sh*), *300* (*vs*) cm^{-1}. ^1H NMR (23 °C, CD_2Cl_2): δ 7.93 (m, 4 H), 7.77 (m, 8 H), 7.63 (m, 8 H), 4.34 (m, 8 H), 1.94 (m, 8 H). Anal. Calcd for $C_{32}H_{36}Cl_7O_2PW_2{\cdot}2CH_2Cl_2$ (mol wt 1269.35): C, 32.17; H, 3.18; Cl, 30.72. Calcd for $C_{32}H_{36}Cl_7O_2PW_2$ (mol wt 1099.48): C, 34.96; H, 3.30; Cl, 22.57. Found: C, 35.81; H, 3.58; Cl, 29.67.

Preparation of $[Ph_4P][W_2Cl_8(THF)]$. Crystalline $[Ph_4P][W_2Cl_7(THF)_2]{\cdot}2CH_2Cl_2$ (200 mg, 0.158 mmol) was dissolved in 5 mL of CH_2Cl_2. Upon addition of 1 mL of CCl_4 and exposure to room light, the green solution turned purple-blue within 30 min. After 2 days at −20 °C dark blue crystals had formed. Further reduction of the volume and cooling to −20 °C gave an additional crop with a total yield of 125 mg (75%) of blue crystalline product. IR (CsI, Nujol mull, *anion*): 1580 (w), 1482 (m), 1441 (s), 1341 (w), 1310 (w), 1258 (w), 1105 (vs), 1039 (w), 1025 (w), 995 (m), 920 (w), *835* (*vs*), 760 (m), 748 (m), 723 (vs), 688 (m), 682 (m), 530 (vs), *352* (*m*), *330* (*s*), *320* (*vs*) cm^{-1}. Anal. Calcd for $C_{28}H_{28}Cl_8OPW_2$ (mol wt 1062.83): C, 31.64; H, 2.66; Cl, 26.69. Found: C, 33.26; H, 2.9]; Cl, 27.15.

Crystallographic Studies. General operating procedures and listings of programs have been previously described.[12] A summary of crystal-

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(10) Cf. D11/T4 in: *DMS UV Atlas of Organic Compounds*; Verlag Chemie: Weimheim, FRG, 1966; Vol. I.

(11) Sturgeoff, L. G. Ph.D. Thesis, MIT, 1982.

Table VII. Summary of Crystallographic Data[a]

	I	II
empirical formula	$C_8H_{16}O_2Cl_7W_2^-C_{24}H_{20}P^+\cdot 2CH_2Cl_2$	$W_2Cl_8C_4H_8O^-C_{24}H_{20}P^+$
color of cryst	yellow/green	black
cryst dimens, mm	0.08 × 0.16 × 0.16	0.10 × 0.10 × 0.14
space group	$P\bar{1}$	$P\bar{1}$
cell dimens		
temp, °C	−141	−155
a, Å	19.702 (38)	11.577 (4)
b, Å	13.216 (24)	14.234 (6)
c, Å	9.817 (15)	11.057 (4)
α, deg	111.23 (8)	112.71 (2)
β, deg	66.96 (9)	95.78 (2)
γ, deg	111.97 (8)	92.47 (2)
Z, molecules/cell	2	2
V, Å^3	2110.54	1665.70
d_{calcd}, g/cm^3	1.997	2.119
wavelength, Å	0.71069	0.71069
mol wt	1269.35	1062.83
linear abs coeff, cm^{-1}	63.359	77.689
detector to sample dist, cm	22.5	22.5
sample to source dist, cm	23.5	23.5
av ω scan width at half-height, deg	0.25	0.25
scan speed, deg/min	6.0	4.0
scan width, deg + dispersion	1.8	2.0
individual bkgd, s	6	8
aperture size, mm	3.0 × 4.0	3.0 × 4.0
2θ range, deg	6–45	6–45
total no. of reflcns collcd	7821	4442
no. of unique intensities	5569	4373
no. of reflcns with $F > 0.0$	5095	
no. of reflcns with $F > 3.0\sigma(F)$	4420	3630
$R(F)$	0.0554	0.0485
$R_w(F)$	0.0536	0.0475
goodness of fit for last ccle	1.024	1.032
max Δ/σ for last cycle	0.05	0.05

[a] $[PPh_4][W_2Cl_7(THF)_2]\cdot 2CH_2Cl_2$ (I); $[PPh_4][W_2Cl_8(THF)]$ (II).

lographic data is given in Table VII.

$[Ph_4P][W_2Cl_7(THF)_2]\cdot 2CH_2Cl_2$. A small crystal was selected and transferred to the goniostat, where it was cooled to −141 °C for characterization and data collection. A systematic search of a limited hemisphere of reciprocal space yielded a set of reflections that exhibited no symmetry or systematic extinctions. The choice of the centrosymmetric space group $P\bar{1}$ was confirmed by the successful solution and refinement of the structure. No absorption correction was carried out. A total of 7821 reflections were collected. After averaging of equivalent reflections, a unique set of 5569 reflections remained. The R for averaging was 0.060 for 2183 reflections measured more than once.

The structure was solved by the usual combination of direct-methods and Fourier techniques. The W atoms were located by MULTAN and the remaining non-hydrogen atoms were located in successive difference Fourier calculations. The asymmetric unit contains one $W_2Cl_7(THF)_2^-$ anion and one $P(C_6H_5)_4$ cation, as well as two molecules of CH_2Cl_2 solvent. It should be noted that the first batch of crystals, which were dry, appeared to be split, most likely due to loss of solvent molecules. Almost all hydrogen atoms were evident in a difference Fourier map and were included in the final refinement. The full-matrix least-squares refinement was completed by using anisotropic thermal parameters on all non-hydrogen atoms and individual isotropic thermal parameters on the hydrogen atoms. The final residuals were $R(F) = 0.055$ and $R_w(F) = 0.054$ for 4420 reflections having $F > 3.0\sigma(F)$.

The final difference Fourier map contained several peaks of approximately 2 e/Å^3 in the vicinity of the W and Cl atoms; otherwise, it was essentially featureless.

A comparison with the same anion found in the structure report MSC No. 86113 was carried out. The anions are virtually identical except for distortions in the THF rings.

$[PPh_4][W_2Cl_8(THF)]$. A suitable crystal was located and transferred to the goniostat by using standard inert-atmosphere handling techniques employed by the Indiana University Molecular Structure Center and cooled to −155 °C for characterization and data collection. A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with no symmetry or systematic absences, corresponding to one of the triclinic space groups. Subsequent solution and refinement of the structure confirmed the correct choice to be $P\bar{1}$.

Data were collected in the usual manner using a continuous θ–2θ scan with fixed backgrounds. Data were reduced to a unique set of intensities and associated σ's in the usual manner. The structure was solved by a combination of direct-methods (MULTAN78) and Fourier techniques. Many of the hydrogen atom positions were visible in a difference Fourier phased on the non-hydrogen atoms. Positions were calculated for all hydrogens by assuming idealized geometry (with d(C–H) = 0.95 Å), and they were included as fixed-atom contributors in the final cycles.

An absorption correction was applied to the data after initial anisotropic refinement, but the residuals or esd's did not change, and three atoms refined to nonpositive negative thermal parameters. Assuming the difficulty was with the crystal measurement, the uncorrected data were used in the final cycles.

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Registry No. I, 115244-66-1; II, 115244-68-3; $NaW_2Cl_7(THF)_5$, 109764-48-9; CCl_4, 56-23-5; W, 7440-33-7.

Supplementary Material Available: Tables of anisotropic thermal parameters, complete tables of bond distances and bond angles, and VERSORT drawings giving the complete atom-numbering schemes (14 pages); listings of F_o and F_c values (22 pages). Ordering information is given on any current masthead page.

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(12) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kirkpatrick, C. C. *Inorg. Chem.* **1984**, *23*, 1021.