

Synthesis and Structure of a Tungsten Dimer with a W-W Bond Order of 3.5

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Reaction of $W_2(\text{mhp})_4$, where mhp is the anion of 2-hydroxy-6-methylpyridine, with $AlCl_3$ in refluxing diglyme provides the new paramagnetic compound $W_2Cl_2(\text{mhp})_3 \cdot CH_2Cl_2$ in 67 percent yield after recrystallization from dichloromethane. The source of the oxidant for oxidation of tungsten from W(2.0) to W(2.5) was not identified. Orange-brown crystals of the new compound belong to the noncentric orthorhombic space group $P2_12_12_1$ with $a = 13.150(6)$, $b = 21.24(1)$ and $c = 8.738(4)$ Å, $Z = 4$. Refinement of the structure provided $R(R_w) = 0.058(0.080)$ and a W-W bond distance of $2.214(2)$ Å, 0.053 Å longer than that in $W_2(\text{mhp})_4 \cdot CH_2Cl_2$. The W-W bond has a bond order of 3.5 corresponding to the bonding orbital population $\sigma^2\pi^4\delta^1$. Strong bands arising from W-Cl stretching modes occur at 321 and 289 cm^{-1} in the IR spectra, and a weak band at 782 nm ($\epsilon \sim 600$ $M^{-1}cm^{-1}$) in the UV-visible spectrum may correspond to the $\delta \rightarrow \delta^*$ electronic transition. The EPR spectrum shows a strong, nearly symmetric, absorption with $g = 1.842$. Cyclic voltammetry in dichloromethane reveals a quasi-reversible reduction at $E_{1/2} = -0.7$ V vs. SSCE and an irreversible oxidation at $+0.3$ V.

INTRODUCTION

For many years, there has been great interest in the chemistry of compounds with metal-metal bonds of multiple bond order.¹ Some years ago, we developed convenient syntheses of quadruply bonded dimers $Mo_2Cl_4L_4$ and rectangular clusters $Mo_4Cl_8L_4$ by starting with the appropriate carboxylate

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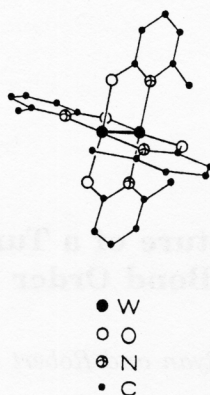
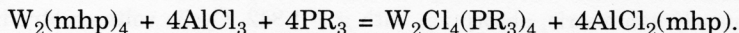


Figure 1. The molecular structure of $W_2(mhp)_4$

dimers $M_2(O_2CR)_4$.²⁻⁵ Reagents like Me_3SiCl and $AlCl_3$ were used both to provide the needed chloride ligands and act as carboxylate acceptor in the presence of the desired donor ligand, primarily alkylphosphines R_3P . However, this approach simply was not practical for the preparation of $W_2Cl_4L_4$ ⁶ or $W_4Cl_8L_4$ ⁷ derivatives because of the lack of a convenient, high yield synthesis of the $W_2(O_2CR)_4$ starting material.

However, Cotton and coworkers showed that the quadruply bonded dimer $W_2(mhp)_4$,⁸ where mhp is the anion of 2-hydroxy-6-methylpyridine, could be prepared in a nearly quantitative yield by reaction of $W(CO)_6$ with Hmhp in refluxing diglyme. A structural drawing of the $W_2(mhp)_4$ molecule is shown in Figure 1. It seemed likely that the mhp ligands could be removed and replaced by Cl^- and donor ligands L by the Me_3SiCl and $AlCl_3$ reagents, as in the reaction



Surprisingly, the $AlCl_3$ was insufficiently robust as a mhp acceptor, and the reaction resulted in removal of only one mhp ligand. A concomitant one-electron oxidation occurred with the formation of $W_2Cl_2(mhp)_3$, the structure and properties of which are reported in this paper.

EXPERIMENTAL

Materials

Organic solvents were dried over CaH_2 or $LiAlH_4$ and distilled under vacuum prior to use on the vacuum manifold. $AlCl_3$ was purified by vacuum sublimation from commercial anhydrous material through a porous fritted-glass disk to prevent par-

ticulate entrainment of Al_2O_3 or AlOCl . $\text{W}_2(\text{mhp})_4$ was prepared from $\text{W}(\text{CO})_6$ and Hmhp in refluxing diglyme by the published procedure,⁸ except for the prescribed volume, the solvent was reduced by 75%. All other materials were of reagent grade and used as received.

Physical Measurements

UV-visible spectra were obtained on a Cary 14 or 219 spectrophotometer on solutions contained in nitrogen-filled cells equipped with rubber septa. Infrared spectra were obtained with nujol mulls prepared and mounted in the drybox between CsI windows and measured on a Beckman IR-4250 instrument.

EPR spectra were measured on a Bruker ER-220 spectrometer at X-band frequency and 25 °C for powdered samples. DPPH was used as a reference standard for field calibration.

Cyclic voltammetry measurements were made using a PAR Model 175 Universal Programmer and a Model 173 Potentiostat/Galvanostat in conjunction with a Moseley Autograph 2D-2 X-Y recorder. Voltages were measured at a platinum disk electrode, and all reported values are in reference to the saturated sodium chloride-calomel electrode (SSCE). Voltammograms were obtained for dry, deaerated $\text{CH}_2\text{-Cl}_2$ solutions which had been made 0.2 M in the supporting electrolyte, tetra-*n*-butylammonium tetrafluoroborate.

Conductivity measurements were made with a Leeds and Northrup Model 4866-60 resistivity bridge connected to the polished platinum electrodes of the conductivity cell. Readings were obtained for acetonitrile solutions of the dimer, which were handled under a nitrogen atmosphere at all times.

Synthesis

AlCl_3 (2.50 g, 18.7 mmol) was placed in a 100 mL flask under a nitrogen atmosphere, and 40 mL diglyme, which had been cooled to 0 °C, was slowly added. $\text{W}_2(\text{mhp})_4$ (3.00 g, 3.75 mmol) was added to the diglyme solution, and the mixture was stirred under nitrogen for 10 hours at 80 °C. A rust-brown solid was filtered from the reaction mixture and washed with a few mL of cyclohexane. This crude product was extracted *in vacuo* with dichloromethane to produce orange-brown crystalline $\text{W}_2(\text{mhp})_3$ in 67% yield.

Anal. Calcd. for $\text{W}_2\text{Cl}_2(\text{C}_6\text{H}_6\text{NO})_3 \cdot \text{CH}_2\text{Cl}_2$: W 43.37, Cl 9.28, C 26.91; N 4.96, H 2.38%; found W 43.33, Cl 8.76, C 27.00, N 4.96 H 2.39%.

The analysis for chlorine includes only the chlorine contributed by $\text{W}_2(\text{mhp})_3\text{Cl}_2$ since the occluded CH_2Cl_2 was not retained when the sample was decomposed for halide analysis.

The oxidation state of tungsten in this compound was determined as follows: A solution 0.6 M in $(\text{NH}_4)\text{Fe}(\text{SO}_4)_2$ and 1.0 M in H_2SO_4 was degassed, and the $\text{W}_2\text{Cl}_2(\text{mhp})_3\text{-CH}_2\text{Cl}_2$ was added under a nitrogen atmosphere. The solution was warmed to about 80 °C for 45 minutes, which resulted in oxidation of all tungsten to W(VI), and the Fe(II) formed was titrated with standard Ce(IV) sulfate solution. The net oxidation state for tungsten was found to be 2.55 ± 0.10 .

X-ray Structure Determination

A crystal of dimensions $0.24 \times 0.26 \times 0.11$ mm was obtained from the preparative reaction, and this was mounted under nitrogen in a glass capillary for the structure determination. Data were collected using an automatic 4-circle diffractometer designed at the Ames Laboratory.⁹ Initial ω -oscillation photographs at various values of χ and ϕ were used to input 12 reflections into an automatic indexing program, ALICE.¹⁰ The indexing indicated orthorhombic symmetry and gave lattice parameters which were confirmed by ω -oscillation photographs about each axis. Eleven intense, high angle reflections were measured on the previously aligned diffractometer, and these were used in a least squares refinement to accurately determine the lattice constants at 25 °C; $a = 13.150(6)$, $b = 21.24(1)$, $c = 8.738(4)$, $V = 2,440(2)$. Mo K α radiation was used, $\lambda = 0.71002$ Å. Flotation density measurements provided a value of $Z = 4$.

Data were collected to $2\theta = 50^\circ$. Four standard reflections which were monitored after every 75 measurements showed negligible decay, and no correction of the data was needed. Many reflections were found to be quite broad, so a scan half width of $0.8^\circ \omega$ was used for data collection to insure that the whole peak was measured. Of the 9,802 reflections collected over four octants ($hkl, \bar{h}\bar{k}l, h\bar{k}l, h\bar{k}\bar{l}$), 1,922 were considered unobserved ($I < 3\sigma_I$), and after averaging 2,122 unique reflections were used in the refinement. The data were corrected for Lorentz-polarization effects, and an absorption correction was made ($\mu = 103.9 \text{ cm}^{-1}$). Systematic extinctions in the data set for $h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; $00l$, $l = 2n + 1$ defined the space group as the noncentric $P2_12_12_1$.

Structure Solution and Refinement

A Patterson function was used to locate the positions of two unique tungsten atoms in the unit cell. The light atom positions were located from electron density maps obtained through successive least-squares refinements. The minimizing function was $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(|F_o|)$. The scattering factors were those of Hanson *et al.*,¹¹ modified for the real and imaginary parts of anomalous dispersion.¹²

TABLE I

Crystallographic data for $W_2Cl_2(mhp)_3 \cdot CH_2Cl_2$

Formula	$W_2Cl_4C_{19}H_{20}N_3O_3$	$\rho(\text{calc.})/(\text{g}/\text{cm}^3)$	2.308
f_w	847.90	$\lambda(\text{Mo K}\alpha)/\text{Å}$	0.71002
Cryst. system	orthorhombic	$\mu(\text{Mo K}\alpha)/\text{cm}^{-1}$	103.9
Space group	$P2_12_12_1$	$t/^\circ\text{C}$	25
$a/\text{Å}$	13.150(6)	total refl. measd.	9802
$b/\text{Å}$	21.24(1)	avg. no. unique refl.	2122
$c/\text{Å}$	8.738(4)	no. parameters	265
$V/\text{Å}^3$	1440(2)	octants measd.	$h \pm k \pm l, -h \pm k \pm l$
Z	4	R^a, R_w^b	0.058, 0.080

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|$$

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

TABLE II

Positional parameters ($x, y, z \times 10^4$) and equivalent isotropic thermal parameters ($U_{\text{eq}}/\text{\AA}^2$) for $\text{W}_2\text{Cl}_2(\text{mhp})_3 \cdot \text{CH}_2\text{Cl}_2^{\text{a}}$

Atom	x	y	z	U_{eq}^{b}
W(1)	8717.6(7)	8839.2(5)	7692(1)	0.041(1)
W(2)	244.3(8)	8423.5(4)	7341(1)	0.040(1)
Cl(1)	7619(6)	8083(4)	8807(8)	0.057(4)
Cl(2)	162(7)	7374(3)	8237(8)	0.060(4)
O(1)	8240(16)	8597(9)	5542(20)	0.057(11)
N(1)	9776(18)	8138(11)	5080(25)	0.048(12)
C(11)	8798(20)	8295(13)	4591(29)	0.045(13)
C(12)	9463(26)	8120(13)	3112(35)	0.061(18)
C(13)	9177(24)	7814(13)	2193(32)	0.058(16)
C(14)	170(20)	7684(15)	2633(34)	0.058(16)
C(15)	453(22)	7857(13)	4093(32)	0.051(16)
C(16)	1497(23)	7739(16)	4664(31)	0.062(22)
O(2)	9084(14)	9193(10)	9812(20)	0.051(11)
N(2)	706(16)	8795(10)	9496(23)	0.042(11)
C(21)	9986(22)	9099(13)	377(31)	0.051(17)
C(22)	257(25)	9336(16)	1858(30)	0.060(17)
C(23)	1186(26)	9214(15)	2386(41)	0.071(19)
C(24)	1927(21)	9907(12)	1529(37)	0.055(15)
C(25)	1662(21)	8704(13)	130(28)	0.042(14)
C(26)	2435(21)	8387(14)	9076(38)	0.069(17)
O(3)	834(14)	9209(11)	6388(23)	0.059(11)
N(3)	9258(22)	9722(10)	6775(28)	0.060(15)
C(31)	272(21)	9714(13)	6243(25)	0.042(13)
C(32)	625(25)	276(14)	5549(38)	0.060(18)
C(33)	00(32)	785(16)	5389(52)	0.086(30)
C(34)	8968(31)	743(16)	5871(38)	0.071(22)
C(35)	8691(25)	212(15)	6599(38)	0.064(20)
C(36)	7579(22)	117(14)	7301(49)	0.039(24)
C(1)	4550(49)	8794(29)	4721(82)	0.14(2)
Cl(3)	5581(17)	8977(11)	5740(29)	0.20(1)
Cl(4)	3505(16)	9220(10)	5113(25)	0.17(1)

^a Estimated standard deviations are given in parentheses for the last significant digits.

^b Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor ($U_{\text{eq}} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^*$).

All atoms were refined anisotropically except for the CH_2Cl_2 solvate whose large isotropic temperature factors were probably due to librational motion of the occluded molecule. Refinement on the atom multipliers for these solvate molecules showed the site to be fully occupied. A final difference map produced areas of $3e^-/\text{\AA}^3$ at the sites of the tungsten atoms, but no other significant features were found. The discrepancy factors were $R = 0.066$ and $R_w = 0.090$. Inversion of the atom coordinates

TABLE III
Bond distances/Å and angles/deg. for $W_2Cl_2(mhp)_3 \cdot CH_2Cl_2$

Distances			
W(1)-W(2)	2.214(2)	O(2)-N(2)	2.31(3)
W(1)-Cl(1)	2.370(8)	O(2)-C(21)	1.30(3)
W(1)-O(1)	2.05(2)	C(21)-N(2)	1.38(4)
W(1)-O(2)	2.06(2)	C(21)-C(22)	1.43(4)
W(1)-N(3)	2.16(2)	C(22)-C(23)	1.33(5)
W(2)-Cl(2)	2.365(7)	C(23)-C(24)	1.39(4)
W(2)-O(3)	2.02(2)	C(24)-C(25)	1.34(4)
W(2)-N(1)	2.16(2)	C(25)-N(2)	1.39(3)
W(2)-N(2)	2.13(2)	C(25)-C(26)	1.53(4)
Cl(1)-Cl(2)	3.70(1)	O(3)-N(3)	2.36(3)
O(1)-N(1)	2.28(3)	O(3)-C(31)	1.31(3)
O(1)-C(11)	1.28(3)	C(31)-N(3)	1.41(4)
C(11)-N(1)	1.40(4)	C(31)-C(32)	1.42(4)
C(11)-C(12)	1.42(4)	C(32)-C(33)	1.37(5)
C(12)-C(13)	1.40(4)	C(33)-C(34)	1.42(6)
C(13)-C(14)	1.39(4)	C(34)-C(35)	1.35(5)
C(14)-C(15)	1.38(4)	C(35)-N(3)	1.29(4)
C(15)-N(1)	1.38(4)	C(35)-C(36)	1.60(5)
C(15)-C(16)	1.48(4)		
Angles			
W(1)-W(2)-Cl(2)	106.8(2)	N(1)-W(2)-O(3)	88.0(8)
W(1)-W(2)-N(1)	88.9(6)	N(2)-W(2)-O(3)	87.1(8)
W(1)-W(2)-N(2)	89.3(6)	W(1)-O(1)-C(11)	123(2)
W(1)-W(2)-O(3)	94.3(6)	O(1)-C(11)-N(1)	117(2)
W(2)-W(1)-Cl(1)	109.8(2)	W(2)-N(1)-C(11)	118(2)
W(2)-W(1)-N(3)	89.8(7)	W(2)-N(1)-C(15)	121(2)
W(2)-W(1)-O(1)	92.9(6)	N(1)-C(15)-C(16)	118(2)
W(2)-W(1)-O(2)	93.3(5)	W(1)-O(2)-C(21)	120(2)
Cl(1)-W(1)-N(3)	160.4(8)	O(2)-C(21)-N(2)	119(2)
Cl(2)-W(2)-O(3)	158.9(6)	W(2)-N(2)-C(21)	118(2)
O(1)-W(1)-O(2)	172.2(8)	W(2)-N(2)-C(25)	124(2)
N(1)-W(2)-N(2)	174.6(8)	N(2)-C(25)-C(26)	115(2)
Cl(1)-W(1)-O(1)	91.2(6)	W(2)-O(3)-C(31)	120(2)
Cl(1)-W(1)-O(2)	91.2(6)	O(3)-C(31)-N(3)	121(2)
O(1)-W(1)-N(3)	88.7(9)	W(1)-N(3)-C(31)	115(2)
O(2)-W(1)-N(3)	86.6(9)	W(1)-N(3)-C(35)	124(2)
Cl(2)-W(2)-N(1)	91.4(6)	N(3)-C(35)-C(36)	112(3)
Cl(2)-W(2)-N(2)	94.0(6)		

from (x, y, z) to $(\bar{x}, \bar{y}, \bar{z})$ gave the correct enantiomorph, as indicated by the improved discrepancy factors of $R = 0.058$ and $R_w = 0.080$. Final full-matrix refinement did not change these values. H-atoms were not located, nor included in the refinement.

Crystallographic data and information about the structure refinement are included in Table I. Positional and equivalent isotropic thermal parameters are given in Table II and an ORTEP drawing of the molecule is shown in Figure 2. Distances and angles are listed in Table III.

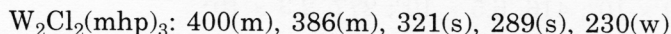
RESULTS

Synthesis and Characterization

The reaction in diglyme of $W_2(mhp)_4$ with a large excess of $AlCl_3$, in 1:5 molar ratio, resulted in removal of only one mhp ligand and formation of the oxidized dimer $W_2Cl_2(mhp)_3$. This product was initially isolated from a reaction mixture of $W_2(mhp)_4$, $AlCl_3$ and trialkylphosphine in an effort to prepare $W_2Cl_4(PR_3)_4$ derivatives. However, when it was found that the phosphine was not coordinated in the product, the phosphine was omitted from the reaction mixture and the $W_2Cl_2(mhp)_3$ was isolated from the reaction.

The crystalline product is moderately air sensitive, darkening after a few minutes of exposure to the laboratory atmosphere. This is in contrast to the $W_2(mhp)_4$ dimer, which is nearly air stable.⁸ Solutions of $W_2Cl_2(mhp)_3$ in tetrahydrofuran, acetonitrile, or methylene chloride are even more air sensitive.

Bands in the infrared spectra and the relative intensity (s = strong, m = medium and w = weak) are as follows:



The bands at 321 and 289 cm^{-1} in $W_2Cl_2(mhp)_3$ probably arise from W-Cl stretching vibrations and the other bands, based on a comparison with those in $W_2(mhp)_4$, probably arise from the mhp ligands.

As indicated by the molecular structure and oxidation state of tungsten (2.5), $W_2Cl_2(mhp)_3 \cdot CH_2Cl_2$ must be paramagnetic. Although magnetic susceptibility measurements were not obtained, the EPR spectrum of the powdered solid showed a strong, nearly symmetric, band devoid of any hyperfine structure. The band had a peak to peak width of *ca* 800 G and was centered at $g = 1.842$.

The low conductivity of acetonitrile solutions ($\Lambda_M = 2 \text{ S cm}^2 \text{ mol}^{-1}$) showed that $W_2Cl_2(mhp)_3$ was not appreciably ionized in solution. In dichloromethane, cyclic voltammograms show a quasi-reversible reduction at $E_{1/2} = -0.7 \text{ V vs. SSCE}$ ($E_{p,c} - E_{p,a} > 60 \text{ mV}$, $i_{p,c}/i_{p,a} = 1$) and an irreversible oxidation at $E_{p,a} \sim 0.3 \text{ V}$. Slow voltage sweep rates have shown that the reduced species is stable for at least 90 seconds.

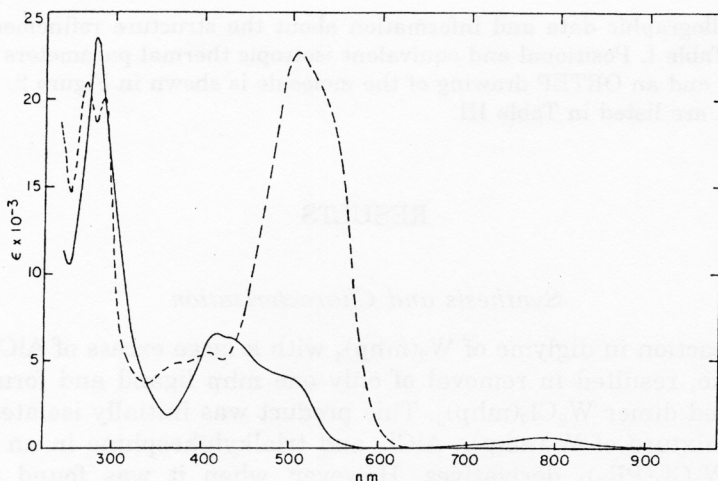


Figure 2. Electronic spectra for solutions of $W_2Cl_2(mhp)_3$ (—) and $W_2(mhp)_4$ (- - -) in dichloromethane.

The UV-visible spectrum of a 3.1×10^{-4} M solution of $W_2Cl_2(mhp)_3$ in dichloromethane is shown in Figure 2. The spectrum of $W_2(mhp)_4$ is shown for comparison. For $W_2Cl_2(mhp)_3$, absorption maxima or shoulders/nm and molar extinction values/ $M^{-1} \text{ cm}^{-1}$ are respectively 782, 6.8×10^2 ; 512(sh), 3.8×10^3 ; 443(sh), 6.0×10^3 ; 416, 6.5×10^3 ; 277, 2.3×10^4 .

Crystal and Molecular Structure

The structure of $W_2Cl_2(mhp)_3$, shown in Figure 3, is like that of $W_2(mhp)_4$, except that one of the mhp ligands has been replaced by two chlorine atoms. The disposition of the remaining three bridging ligands is such that the methyl groups of two mhp ligands are located off one end of the molecule, and the third is held over the opposite end, just as in the parent compound. No symmetry is imposed by the crystallographic site but the $W_2Cl_2(mhp)_3$ molecule has virtual C_s symmetry. The solvent CH_2Cl_2 molecules are trapped in pockets between the dimers and do not interact with them. Bond distances and angles, Table III, in the ligand rings are comparable to those found for $W_2(mhp)_4$.⁸ The average W-O and W-N bond distances, 2.04 and 2.15 Å, respectively, are the same in $W_2Cl_2(mhp)_3$ as in $W_2(mhp)_4$, within the limits of significance. Also, there is no significant difference between the W-O and W-N distances *trans* to the W-Cl bonds as compared to those *trans* to the bonds of another mhp ligand. The W-Cl bond distances, 2.370(8) and 2.365(7) Å, are among the shortest observed in quadruply

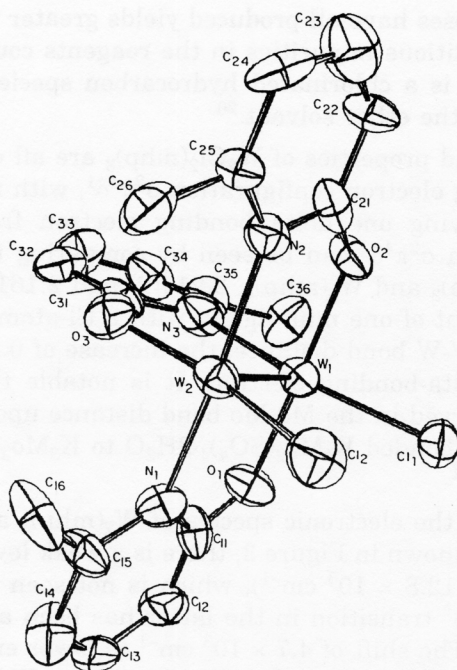


Figure 3. Structure of the $W_2Cl_2(mhp)_3$ molecule with numbering scheme for the atoms. Thermal ellipsoids are scaled to 50% of the electron density.

bonded dimers $W_2Cl_4L_4$ of known structure, where the range is 2.372 to 2.431 Å.¹³⁻¹⁷ However, the W-W bond distance, 2.214(2) Å is 0.053 Å longer than that in $W_2(mhp)_4$, 2.161(1) Å.

DISCUSSION

The strong binding of the mhp ligands in $W_2(mhp)_4$ is reflected in the synthesis of $W_2Cl_2(mhp)_3$, where even a 5:1 molar ratio of $AlCl_3$ to $W_2(mhp)_4$ is unable to remove more than one mhp ligand. Thus, we may conclude that the binding of mhp is much stronger than carboxylate ligands which are readily removed, especially in the more accessible $Mo_2(O_2CR)_4$ compounds. However, this reaction is solvent dependent, as shown by the preparation of $W_2Cl_5H(py)_4$ from $W_2(mhp)_4$ and Me_3SiCl in pyridine containing a small addition of methanol,¹⁸ and by the reaction of $W_2(mhp)_4$ with gaseous HCl in methanol to produce $Cs_3W_2Cl_9 \cdot CH_3OH$ when CsCl is present, or $W_2Cl_4(OCH_3)_2(CH_3OH)_4$ when PEt_3 is added instead of CsCl.¹⁹ In the formation of $W_2Cl_2(mhp)_3$, the nature of the oxidizing agent is not known. Be-

cause several syntheses have all produced yields greater than 50%, it seems unlikely that adventitious impurities in the reagents could be the cause. A more likely oxidant is a chlorinated hydrocarbon species which may form when AlCl_3 attacks the ether solvent.²⁰

The structure and properties of $\text{W}_2\text{Cl}_2(\text{mhp})_3$ are all consistent with the metal-metal bonding electron configuration $\sigma^2\pi^4\delta^1$, with net bond order 3.5. The effect of removing one delta bonding electron from the quadruply bonded configuration $\sigma^2\pi^4\delta^2$ can be seen by comparing the W-W bond distances in $\text{W}_2\text{Cl}_2(\text{mhp})_3$ and $\text{W}_2(\text{mhp})_4$, 2.214(2) and 2.161(1) Å, respectively. Although replacement of one mhp ligand with 2 Cl-atoms might also cause an increase in the W-W bond distance, the increase of 0.053 Å is consistent with loss of one delta-bonding electron. It is notable that an increase of 0.053 Å is also observed in the Mo-Mo bond distance upon one-electron oxidation of quadruply bonded $\text{K}_4\text{Mo}_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ to $\text{K}_3\text{Mo}_2(\text{SO}_4)_4 \cdot 3.5\text{H}_2\text{O}$ having bond order 3.5.²¹

A comparison of the electronic spectra of $\text{W}_2(\text{mhp})_4$ and $\text{W}_2\text{Cl}_2(\text{mhp})_3$ is also instructive. As shown in Figure 3, there is a weak low energy band with $\nu(\text{max.})$ at 782 nm ($12.8 \times 10^3 \text{ cm}^{-1}$), which is not seen in the spectrum of $\text{W}_2(\text{mhp})_4$. The $\delta - \delta^*$ transition in the latter has been assigned at 571 nm ($17.5 \times 10^3 \text{ cm}^{-1}$).²² The shift of $4.7 \times 10^3 \text{ cm}^{-1}$ to lower energy for this transition in $\text{W}_2\text{Cl}_2(\text{mhp})_3$ is consistent with the longer W-W bond and lower bond order. We further note that the $\delta - \delta^*$ transition has been found at lower wavenumbers for $\text{W}_2\text{Cl}_4(\text{PMe}_3)_4$, $15.2 \times 10^3 \text{ cm}^{-1}$;¹³ $\text{W}_2\text{Cl}_4(\text{dppm})_2$ (where dppm = bisdiphenylphosphinomethane), $13.6 \times 10^3 \text{ cm}^{-1}$;¹⁶ and $\text{Na}_4(\text{TMEDA})_4\text{W}_2\text{Cl}_8$ (where TMEDA = tetramethylethylenediamine), $16.7 \times 10^3 \text{ cm}^{-1}$.²³ In these cases, the W-W bond distances are in the range 2.26 to 2.31 Å, all longer than that in $\text{W}_2\text{Cl}_2(\text{mhp})_3$.

In the structure of $\text{W}_2\text{Cl}_2(\text{mhp})_3$, the configuration of ligand atoms about each of the two tungsten atoms is different, namely O(1)O(2)Cl(1)N(3) about W(1), and O(3)N(1)N(2)Cl(2) about W(2). This suggests that the two tungsten atoms could effectively be in different oxidation states, *i.e.* W(1) in the 3+, and W(2) in the 2+ state. This, however, assumes that the mhp ligands are in the tautomeric state with a negative charge on the oxygen atom. However, as noted by Cotton *et al.*,⁸ the other tautomer with negative charge on the nitrogen or some average of the two forms cannot be excluded. The latter averaging could negate any difference in oxidation state between the two tungsten atoms. Nonetheless, the lack of a center of symmetry makes the W-W stretching vibration infrared-allowed. By comparison with $\text{W}_2(\text{mhp})_4$, where $\nu(\text{W-W}) = 295 \text{ cm}^{-1}$,⁸ this vibration should be shifted to lower energy. Thus, only the weak band at 230 cm^{-1} in the IR spectrum of $\text{W}_2\text{Cl}_2(\text{mhp})_3$ would qualify, but this could also be a vibration corresponding to that at 240 cm^{-1} in $\text{W}_2(\text{mhp})_4$. The intensity of the IR-allowed vibration could also be so low that the band is just not observed.

Finally, we note that $W_2Cl_2(mhp)_3$ is only the second example of a compound isolated with the W_2^{5+} core. The first compound $[W_2Cl_4(PBu_3)_4]^+PF_6^-$, prepared from $W_2Cl_4(PBu_3)_4$ by oxidation in acetonitrile with $[Ag(MeCN)_4]^+PF_6^-$,²⁴ has not been structured. An EPR spectrum for $[W_2Cl_4(PBu_3)_4]^+PF_6^-$ in CH_2Cl_2 at $-196^\circ C$ gives $g_{\parallel} = 1.97$, $g_{\perp} = 1.82$.²⁴ These g -values compare favorably with the nearly isotropic $g = 1.842$ found for the powdered $W_2Cl_2(mhp)_3$.

Supplementary Materials. – Crystallographic data (excluding structure factors which are available from the authors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-109/68-769. Copies of the data can be obtained on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. (Fax: 44 (0) 1223-336033; E-mail: teched@chemcrs.cam.ac.uk).

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SAŽETAK

Sinteza i struktura dimera volframa s vezom W-W reda 3.5

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Reakcijom $W_2(\text{mhp})_4$ (mhp = anion 2-hidroksi-6-metilpiridina) s $AlCl_3$ u dime-tilglioksimu, uz refluks, dobiven je paramagentni spoj $W_2Cl_2(\text{mhp})_3 \cdot CH_2Cl_2$ s isko-rištenjem od 67% nakon prekrizalizacije iz diklormetana. Oksidans koji oksidira $W(2.0)$ na $W(2.5)$ nije ustanovljen. Narančastosmeđi kristali novog spoja pripadaju necentrosimetričnoj rombskoj prostornoj grupi $P2_12_12_1$ s $a = 13.150(6)$, $b = 21.24(1)$ i $c = 8.738(4)$ Å, $Z = 4$. Određivanjem kristalne strukture dobiveno je za $R(R_w) = 0.058$ (0.080) i duljinu veze W-W $2.214(2)$ Å, što je za 0.053 duže nego u spoju $W_2(\text{mph})_4 \cdot CH_2Cl_2$. Red veze W-W jest 3.5, što odgovara populaciji veznih orbitala $\sigma^2\pi^4\delta^1$. Jake apsorpcijske vrpce kod 321 i 289 cm^{-1} u infracrvenom spektru odgova-rajaju istezanju veze W-Cl, a slaba vrpca kod 782 nm ($\epsilon \sim 600 M^{-1} cm^{-1}$) u vidljivom spektru može potjecati od elektronskog prijelaza $\sigma \rightarrow \sigma^*$. Spektar elektronske para-magnetske rezonancije pokazuje jaku, skoro simetričnu apsorpciju sa $g = 1.842$. Ci-kličkom voltammetrijom u diklormetanu dobivena je kvazi-reverzibilna redukcija kod $E_{1/2} = -0.7$ V (prema SSCE) i reverzibilna oksidacija kod 0.3 V.