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THE TUNGSTEN-TUNGSTEN TRIPLE BOND. 8.[1] DINUCLEAR ALKOXIDES
OF TUNGSTEN(III) AND STRUCTURAL CHARACTERIZATION OF HEXAKIS-
(ISOPROPOXY)DIPYRIDINODITUNGSTEN, THE FIRST COMPOUND WITH
FOUR-COORDINATED TUNGSTEN ATOMS UNITED BY A TRIPLE BOND.

by

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The Tungsten-Tungsten Triple Bond. 8.[1] Dinuclear Alkoxides

of Tungsten(III) and Structural Characterization of Hexakis-

(isopropoxy)dipyridinoditungsten, the First Compound with

Four-coordinated Tungsten Atoms United by a Triple Bond.

by

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ABSTRACT

$W_2(NMe_2)_6$ reacts with tert-BuOH and Me_3SiOH to yield the crystalline compounds $W_2(OBu-t)_6$ and $W_2(OSiMe_3)_6(HNMe_2)_2$, respectively. The tungsten compounds, unlike their molybdenum analogs, are thermally unstable and can not be sublimed in vacuo. The thermal decomposition which occurs in vacuo appears to be autocatalytic and not stoichiometric. The reaction between $W_2(NMe_2)_6$ and the less bulky alcohols, i-PrOH and Me_3CCH_2OH leads to polynuclear products; this is in contrast to the analogous reactions involving $Mo_2(NMe_2)_6$ which yield $(RO)_3Mo \equiv Mo(OR)_3$ compounds. In pyridine solution $W_2(NMe_2)_6$ reacts with i-PrOH to give the black crystalline compound $W_2(OPr-i)_6(py)_2$, which has been characterized by I.R., NMR, mass spectroscopy and a single crystal X-ray diffraction study. In the crystalline state the molecular structure contains two $W(OPr-i)_3(py)$ units linked by a W-W triple bond with a length of 2.332(1) Å. The rotational conformation is roughly halfway between staggered and eclipsed and the two pyridine ligands are adjacent to each other. Low temperature ^{13}C nmr spectra support the view that this structure is also present in solution. The crystallographic data are: space group, $P2_1$; a = 10.022(2) Å; b = 17.839(4) Å; c = 11.946(2) Å; β = 125.57(1)°; V = 1737.1(6) Å^3; z = 2.

Introduction

Prior work has shown the existence of isostructural M_2X_6 compounds containing non-bridged triple bonds between the metal atoms for M = Mo and W and X = NMe_2[3,4] and CH_2SiMe_3.[5,6] The reaction between $Mo_2(NMe_2)_6$ and alcohols has been shown to lead to structurally related compounds $(RO)_3Mo\equiv Mo(OR)_3$, where R = tert-Bu, i-Pr, Me_3CCH_2 and Me_3Si.[7] We herein report studies of the reactions between $W_2(NMe_2)_6$ and alcohols aimed at the preparation and characterization of analogous dinuclear alkoxides of tungsten(III).[8] For a given alkoxy ligand tungsten is shown to have a marked preference, relative to molybdenum, for increasing its coordination number either by oligomerization, $M_2(OR)_6 \rightarrow [M(OR)_3]_n$ or by coordination with neutral donor ligands as in the stabilization of the $W\equiv W$ unit by coordination of pyridine in the $W_2(OPr-i)_6(py)_2$ molecule.

Results and Discussion

Syntheses. Hydrocarbon solutions of $W_2(NMe_2)_6$ react readily
with tert-butanol and trimethylsilanol at room temperature to
form the crystalline compounds $W_2(OBu-t)_6$ and $W_2(OSiMe_3)_6(HNMe_2)_2$,
respectively. These compounds are extremely oxygen- and moisture-
sensitive and very soluble in hydrocarbon solvents. The spec-
troscopic properties of these tungsten compounds were virtually
identical to those of their molybdenum analogs. Moreover,
$W_2(OBu-t)_6$ reacts reversibly with carbon dioxide to give
$W_2(O_2COBu-t)_2(OBu-t)_4$. Thus we believe that these tungsten
compounds are isostructural with the previously characterized
compounds $(RO)_3Mo \equiv Mo(OR)_3$,[7] $(Me_2NH)(Me_3SiO)_3Mo \equiv Mo(OSiMe_3)_3(HNMe_2)$[8]
and $(OBu-t)_2Mo \equiv Mo(\mu-O_2COBu-t)_2(OBu-t)_2$.[10] The tungsten compounds
differ in only one notable way from their molybdenum analogs,
namely, in their thermal stability. Neither $W_2(OBu-t)_6$ nor
$W_2(OSiMe_3)_6(HNMe_2)_2$ may be purified by vacuum sublimation; both
compounds appear to undergo an autocatalytic and non-stoichio-
metric decomposition.

$W_2(OBu-t)_6$ decomposes at ca. 100°C, 10^{-4} cm Hg with the
evolution of iso-butylene, tert-butanol and water. The tungsten
residue has a grey metallic appearance but is evidently not a
pure oxide since analyses always show small, but significant
quantities of carbon and hydrogen.

$W_2(OSiMe_3)_3(HNMe_2)_2$ when heated in vacuum, $> 80°C$, 10^{-4} cm
Hg, evolves $HNMe_2$ and $(Me_3Si)_2O$. Again, however, the thermolysis

is not clean since the non-volatile tungsten residue contains small quantities of carbon and hydrogen.

Though neither $W_2(OBu-t)_6$ nor $W_2(OSiMe_3)_6(HNMe_2)_2$ may be purified by sublimation, they do give $W_2(OR)_6{}^+$ and many other W_2-containing ions in the mass spectrometer.

Hydrocarbon solutions of $W_2(NMe_2)_6$ react rapidly at room temperature with i-PrOH and Me_3CCH_2OH to give black solid products which, on the basis of elemental analyses, have the empirical formula $W(OR)_3$. These alkoxides are also thermally unstable and in vacuo yield alkenes, alcohols and trace amounts of water. Cryoscopic molecular weight determinations in benzene suggest that both the iso-propoxide and neo-pentoxide are tetrameric, $[W(OR)_3]_4$, in solution. A black crystalline iso-propoxide, obtained from the above reaction, has been the subject of a single crystal X-ray study and found to be a tetranuclear complex of tungsten(IV) resulting from oxidative addition of a PrO-H bond across the W-to-W triple bond. This is the subject of continuing investigations.[11] At this time we emphasize the marked difference between the chemistry of molybdenum and tungsten alkoxides since molybdenum forms thermally stable dinuclear compounds $Mo_2(OR)_6$, where $R = i$-Pr and Me_3CCH_2.

By the reaction of $W_2(NMe_2)_6$ and i-PrOH in pyridine as solvent it has been possible to isolate a black crystalline dinuclear iso-propoxide as a pyridine adduct, $W_2(OPr-i)_6(py)_2$. The compound is again thermally unstable and liberates pyridine,

iso-propanol and propene at $80°C$, 10^{-4} cm Hg. In the mass spectrometer, a weak molecular ion, $W_2(OPr-i)_6(py)_2^+$, is observed, followed by loss of 2 py to give a strong $W_2(OPr-i)_6^+$ ion.

Because of the reactivity of the ditungsten alkoxy compounds, which is quite different from that of their Mo analogs, we considered it important to determine the structures and other properties of the reaction products. We describe here the results for the pyridine adduct.

Solid State Structure of $W_2(OPr-i)_6(py)_2$.

In the space group $P2_1$ with $Z = 2$, the entire molecule is the asymmetric unit and no crystallographic symmetry is imposed on it. The positional and thermal parameters for the atoms constituting one molecule are listed in Table I. Interatomic distances and angles are given in Table II. An ORTEP drawing of the molecule, in which the atom numbering scheme is defined is shown in Figure 1.

The errors on almost all the bond distances and angles not involving the tungsten atoms and the thermal parameters of several of the light atoms are rather large. There are two likely reasons for this, one being the quality of the empirical absorption correction. As this crystal was rather irregular the correction may be accurate only to a first approximation. However, as this crystal did not have well defined faces (nor did any other one we could see) and was embedded in Epoxy

resin, making measurement of its boundary faces impossible,
an empirical correction is the best that could be done. Second,
there is the domination of the scattering by the tungsten atoms.
With just these two atoms anisotropically refined the value of
R_1 was about 0.08. The standard deviations are therefore large
for light atom positions since the differences used in the
least squares refinement are insensitive to shifts in the
light atom parameters. During refinement several of the light
atoms with large temperature factors were removed and replaced
with atoms in positions suggested by new electron density maps.
In each case the atom parameters slowly returned to the former
values. The high temperature parameters for some atoms in the
isopropoxide ligands are not without precedent. In the structure
of bis(nitrosyl)hexakis(isopropoxy)dimolybdenum,[7] where absorption
was quite small, isotropic thermal parameters for the carbon atoms
ranged from 7.7 to 23.8 Å^3.

The molecule consists of two $W(OCHMe_2)_3py$ units linked by
a W-W bond length of 2.332(1) Å. This is slightly longer than
any previously found in a X_3WWX_3 type compound where the range
is from 2.255(2) Å to 2.301(2) Å with the average being about
2.29 Å.[12] The comparison is quite similar to that between the
distance of 2.241(1) Å found in both $Mo_2(OSiMe_3)_6(NHMe_2)_2$[9] and
$Mo_2(O_2COCMe_3)_2(OCMe_3)_4$[10] and the distances of 2.16-2.22 Å found
in X_3MoMoX_3 type compounds.[12]

The W-O distances range from 1.86(2) Å to 2.04(3) Å. In
view of the large esds it is questionable whether there is any

real pattern involved, although the average of the two W-O bond lengths trans to W-N is 2.02 ± 0.02 Å while the average of the other four is 1.91 ± 0.05 Å. The W-N bonds do seem to be longer and weaker than the W-O bonds since the grand average of all W-O bond lengths is 1.95 ± 0.07 Å while the two W-N bond lengths average 2.26 ± 0.03 Å. This is quite analogous to the situation in $Mo_2(OSiMe_3)_6(NHMe_2)_2$ where the mean Mo-O distance is 1.95 ± 0.02 Å and the mean Mo-N distance is 2.282 ± 0.004 Å.

The W-O-C angles show a clear pattern. The four iso-propoxide groups that are trans to each other have angles averaging $121 \pm 2°$ while the two that are trans to the pyridine ligands have angles of $137 \pm 1°$. The reason for this difference cannot be stated with certainty.

The rotational conformation is intermediate between eclipsed and fully staggered. Because of irregularities in the arrangement of the four ligand atoms about each tungsten atom the four smallest independent torsional angles (Table II and Figure 2), are quite disparate; their average value is $28°$. It is interesting that the py groups are in adjacent positions, only $63°$ apart; in this respect the structure differs from that of $Mo_2(OSiMe_3)_6(NHMe_2)_2$. It should be kept in mind that the rotational conformations observed in crystals may be due as much to intermolecular forces as intramolecular forces, though as shown below, there is evidence to support the existence of this conformer in solution.

NMR Studies of $W_2(OPr-i)_6(py)_2$

$W_2(OPr-i)_6(py)_2$ is soluble in hydrocarbon solvents. Unfortunately, however, the compound slowly decomposes with the liberation of pyridine and the formation of as yet unidentified iso-propoxides of tungsten. The most reliable nmr spectroscopic data were consequently obtained by working with freshly prepared samples at low temperatures.

At 100 MHz, $-80°C$, the three pyridine carbon signals were broad, almost embedded in the base line. We attribute this broadening to restricted rotation about the W-N bonds, comparable to that involved in the proximal $\rightleftharpoons$ distal exchange in $M_2(NMe_2)_6$ compounds (M = Mo, W).

The methylene carbon resonances appeared as three sharp signals in the integral ratio 1:1:1. This is exactly what would be expected for the structure found in the solid state. The $W_2O_6N_2$ skeleton has virtual C_2 symmetry (see Figure 2) which leads to the pair-wise equivalence of oxygen atoms and their respective methylene carbon atoms in the following manner: (01, 05), (03, 07) and (02, 06).

The methyl carbon signals are not resolved. This is not surprising since for the $W_2N_2O_6$ conformer with C_2 symmetry there are a total of six different pairs of methyl carbon atoms some of which may appear magnetically degenerate because they are well removed from the dinuclear center.

At $+60°C$, 100 MHz, the three pyridine carbon resonances

are sharp; there is a single methylene carbon resonance and a single methyl carbon resonance. Evidently some fluxional process readily leads to the equivalence of all isoproxy groups on the nmr time scale at this temperature.

Comparisons and Conclusions

The great majority of compounds containing metal-metal triple bonds[12] of the X_3MMX_3 type where X is a monodentate ligand (including some where the ligand atoms are not all the same) have perfectly, or almost perfectly, staggered ethane-like rotational conformations. The great majority of compounds containing metal-metal quadruple bonds[13,14] are of the type X_4MMX_4 (again including those where more than one type of ligand is present) and have essentially eclipsed rotational conformations. The relatively few exceptions to each of these generalizations are of interest because they provide further insight into the nature of metal-metal multiple bonds.

Among molecules with MM triple bonds, those unusual ones which have four ligands bound to each metal atom are of special interest with respect to the research described here. The case of $La_4Re_2O_{10}$[15] is exceptional since eclipsed stereochemistry is enforced by the crystal packing. $Re_2Cl_5(CH_3SCH_2CH_2SCH_3)_2$[16] is also more or less in a class by itself. In addition to these there is a class of compounds in which the triple bond results from cancellation of the δ^2 component of bonding by a δ^{*2} antibonding component. Two structurally characterized representatives of this class are $Re_2(PEt_3)_4Cl_4$[17] and $Re_2(Ph_2PCH_2CH_2PPh_2)Cl_4$.[18]

There are, so far, only a few well characterized representatives of the class of triply-bonded X_4MMX_4 species in which the triple bond is due, simply, to a $\sigma^2\pi^4$ configuration.

The only three whose structures have been reported are
$Mo_2(OSiMe_3)_6(NHMe_2)_2$[9] and $Mo_2(O_2COCMe_3)_2(OCMe_3)_4$,[10] and
$[Mo_2(HPO_4)_4]^{2-}$.[19] In the first, the rotational configuration
(using the method of mean torsional angle introduced in earlier
papers[20,21]) is 24° from eclipsed. In the second, where the
two alkylcarbonato ligands favor an eclipsed configuration,
the angle of twist is only 8°. In the phosphato-bridged
anion the eclipsed configuration is found but this may be
attributed to the steric preference of the bridging groups.
In $W_2(OPr-i)_6(py)_2$ an intermediate conformation with a mean
torsional angle of 28° is seen again.

It seems clear from this work that tungsten, relative to
molybdenum, shows a greater tendency to increase its coordination
number in compounds containing a central $(M\equiv M)^{6+}$ moiety.
$Mo_2(OPr-i)_6$ does not react with amines or pyridine to form
stable adducts $Mo_2(OPr-i)_6L_2$ whereas $W_2(OPr-i)_6$ is reactive
in at least three ways: (i) formation of an adduct of the type
$W_2(OPr-i)_6(py)_2$ in the presence of a donor ligand; (ii) oligo-
merization, which presumably occurs via the formation of
W-OR-W bridges; (iii) attack by RO-H via oxidative addition
across W≡W to give a hydride-bridged W=W bond.

Experimental Section

General procedures including the purification and drying
of alcohols and Me_3SiOH have been previously described.[7]

$W_2(NMe_2)_6$ was prepared from the reaction between WCl_4 and
$4LiNMe_2$.[4]

Preparation of $W_2(OBu\text{-}t)_6$

$W_2(NMe_2)_6$ (2.175 g) was dissolved in benzene (50 ml) in a
round bottomed 100 ml flask containing a magnetic teflon spin
bar. To this yellow solution was added the t-butanol-benzene
azeotrope (40 ml) which contains 36.6% by weight t-butanol.
The solution turned deep red and was stirred for 6 h at room
temperature. The solvent was stripped. Hexane (40 ml) was
added: the red solids dissolved at 40°C. The flask was then
set aside in a large water bath at 40°C which was slowly cooled
to room temperature. The flask was then slowly cooled to 0°C
and finally placed in the refrigerator at -15°C for 12 h.
The resulting dark red crystals were filtered and the
filtrate was concentrated and treated in the manner described
above to obtain a second crop of red needle-like crystals,
$W_2(OBu\text{-}t)_6$. Anal. calcd. for $W_2C_{24}H_{54}O_6$: C, 35.75;
H, 6.75%. Found: C, 35.3; H, 6.07.

Thermal Decomposition of $W_2(OBu\text{-}t)_6$

$W_2(OBu\text{-}t)_6$ (471.9 mg, 0.585 mmole) was placed in a pear-
shaped flask and this was attached to a vacuum line. The

sample was heated in vacuo to 110°C at which temperature trace quantities of a red sublimate formed. On raising the temperature to 120°C there was a sudden increase in pressure and both the bulk sample and the small quantity of sublimate were turned to a black powder which had a metallic sheer. The volatiles were collected in the vacuum line (199.8 mg) and were found to be a mixture of iso-butylene, tert-butanol and water by nmr and g.c. analysis. The non-volatiles (266.3 mg) showed small quantities of carbon and hydrogen, found C, 1.76; H, 0.35%. In this reaction $W_2(OBu-t)_6$ (1 mole) yielded isobutalene (4.0 mole), tert-butanal (1.3 mole) and water (0.9 mole). Similar experiments yielded similar, but not identical results. The differences occurred in (i) the temperature at which decomposition occurred which ranged from 100 to 140° and (ii) the molar equivalents of iso-butylene, tert-butanol and water. The range of the latter, $(CH_3)_2C=CH_2$: $(CH_3)_3C(OH)$: H_2O was (4.0 ± 0.2) : (1.2 ± 0.2) : (0.9 ± 0.2).

Preparation of $W_2(O_2COBu-t)_2(OBu-t)_4$

$W_2(OBu-t)_6$ (0.341 g) was dissolved in toluene (15 ml) in a round bottomed flask (25 ml). CO_2 (2.54 mmol, 6 equiv) was added by use of a calibrated vacuum manifold. The solution darkened (red $\rightarrow$ brown) over a period of ca 1 hr. The flask was placed under 1 atmos of CO_2 and left in the refrigerator at ca -10°C. After 12 hr the solution was dark green and dark green crystals had formed. The latter were collected by filtration (Schlenk-technique) and dried in vacuo at room

temperature to yield $W_2(O_2COBu-t)_2(OBu-t)_4$, ca 100 mg. <u>Anal</u>. Calcd. for $C_{26}H_{54}O_{10}W_2$: C, 34.92; H, 6.09%. Found: C, 34.9; H, 6.16%. Although $W_2(OBu-t)_4(O_2COBu-t)_2$ is stable at room temperature in the solid state it readily looses CO_2 to give $W_2(OBu-t)_6$ in solution in the absence of excess CO_2. Moreover in the mass spectrometer the ion of highest mass corresponds to $W_2(OBu-t)_6^+$.

Preparation of $[W(OPr-i)_3]_n$

$W_2(NMe_2)_6$ (3.989 g, 6.31 mmole) was dissolved in benzene (100 ml) in a 250 ml round bottomed flask fitted with a magnetic follower. To this magnetically stirred solution iso-propanol (15 ml, ca 200 mmole) was added. The solution immediately darkened to a reddish-black color. The solution was stirred for 12 hr at room temperature. The solvent was stripped and the residual black solid was dried at 40-45°C, 10^{-4} cm for 3 hr. Hexane (50 ml) was then added; all the solids dissolved. The black hexane solution was warmed to <u>ca</u> 45°C, concentrated to <u>ca</u> 30 ml and was then left to cool slowly, first to room temperature and then to -10°C. Black crystals (1.5 g) formed in this way were collected by filtration and dried in vacuo. <u>Anal</u>. calcd. for $C_9H_{21}O_3W$: C, 29.93; H, 5.86%. Found: C, 30.28; H, 5.96%.

A cryoscopic molecular weight determination in benzene gave M = 1460 ± 60; for a tetramer $[W(OPr-i)_3]_4$, M would be 1440.

Preparation of $[W(OCH_2CMe_3)_3]_n$

The preparation followed the same procedure as that described above except that neopentanol was added in place of isopropanol. Black crystals of $[W(OCH_2CMe_3)_3]_n$ were obtained. Anal. calcd. for $C_{15}H_{33}O_3W$: C, 40.46; H. 7.47%. Found: C, 40.2; H. 7.28%.

Preparation of $W_2(OPr-i)_6(py)_2$

$W_2(NMe_2)_6$ (470 mg, 0.744 mmole) was dissolved in pyridine (20 ml). Isopropanol (10 ml) was syringed into the flask; the solution turned reddish-black and was left-stirring at room temperature for 12 hr. The volume of the solution was reduced to ca 10 ml and the flask stored in the refrigerator (ca -5°C) for ca 12 hr. Black crystals formed which were collected by Schlenk filtration and dried in vacuo, yielding $W_2(OPr_2)_6(py)_2$ (260 mg, 0.295 mmole). Anal. calcd. for $C_{28}H_{52}O_6N_2W_2$: C, 38.2; H. 5.95; N, 3.18%. Found: C, 39.2; H, 6.17; N, 3.10%. I.r. data obtained from a Nujol mull between CsI plates in the region 4,000 to 200 cm^{-1}: 1602 w, 1338 m, 1262 m, 1216 m, 1162 m, 1114 S br, 1041 m, 992 S, 980 S, 969 S, 845 w, 835 m, 825 m, 805 m, 755 m, 696 m, 603 m br, 535 m, 400 w br, 325 w br. ^{13}C nmr data recorded at 100 MHz in toluene-d_8: At +25°C, single methyl carbon resonance, $\delta = 27.5$; single broad methyne carbon resonance, $\delta = 75.6$; py carbon resonances at $\delta = 150.5$, 135.1 and 122.5 in the intensity ratio 2:1:2, respectively. At -80°C, broad methyl

carbon signals at δ = 29, 28.1 and 25.4 of unequal intensity; methyne carbon resonances at δ = 79.7, 71.25 and 70.3 of equal intensity; py carbon resonances were broad centered at δ = 149.8, 135.3 and 121.7 ppm.

X-ray Crystallography.

Data Collection. A very irregular crystal approximately 0.5 x 0.3 x 0.2 mm was placed in a soft glass capillary immersed in a drop of epoxy resin. The crystal was mounted and data collected on a Syntex PĪ automated diffractometer using crystallographic procedures previously described.[21,22] All operations were performed at 22 ± 1°C using Mo Kα radiation monochromated by a graphite crystal in the incident beam. The cell dimensions based on a least squares fit of fifteen centered reflections in the range 15 < 2θ < 27° were: a = 10.022(2) Å, b = 17.839(4) Å, c = 11.946(2) Å, β = 125.57(1)°, V = 1737.1(6) A^3; Z = 2; d_{calc} = 1.457 g/cm^3.

A total of 1671 reflections were measured using the θ-2θ scan technique in the range 0° < 2θ $\leq$ 45°. A data collection program was used which does not collect data for reflections whose intensity during a rapid prescan is below a preselected threshold. No record is made in the output file for these weak reflections. Variable scan rates from 4° to 24° min^{-1} were used for the collected reflections, depending on their intensities, and the scan width extended from 0.9° below Mo Kα_1 to 0.9° above Mo Kα_2. Three standard reflections were checked after every 97 prescanned reflections and displayed

about a 10% reduction during data collection. A decay

correction was applied to the data.

Solution and Refinement of the Structure.

All calculations were performed using the Enraf-Nonius

structure determination package on the PDP11/45 computer

located at Molecular Structure Corporation, College Station,

Texas. The absorption coefficient of 70.33 cm^{-1} made an

absorption correction necessary. An empirical correction

based on five sets of ψ-scans ($\psi = 0°$ to $360°$ at $10°$ intervals)

at χ $90°$ was used because of the irregular shape of the crystal.

Absences in the data appeared to indicate the space group P2$_1$/c.

For this space group with Z = 2 the molecules must lie on

inversion centers.

Structure refinement was begun in P2$_1$/c using only those

1446 reflections having $F_o^2 > 3\sigma(F_o^2)$. The Patterson map

appeared to be consistent with the chosen space group and

yielded coordinates for the tungsten atom. After three cycles

of least squares refinement the discrepancy indices were

$$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o| = 0.132$$

$$R_2 = [\Sigma w(||F_o|-|F_c||)^2/\Sigma w|F_o|^2]^{\frac{1}{2}} = 0.184$$

The function minimized during all least squares cycles was

$\Sigma w(|F_o|-|F_c|)^2$, where the weighting factor w equals

$4F_o/\sigma(F_o^2)^2$. A value of 0.07 was used for the "ignorance

parameter," ρ, in the calculation[21] of σ. The difference

Fourier map based on this phasing displayed mainly peaks within 1 Å of the tungsten atom. Therefore, this atom was refined anisotropically which lowered the indices to $R_1 = 0.084$ $R_2 = 0.138$. The Fourier maps then indicated eight possible ligand atoms around each tungsten atom. This indication of pseudo-symmetry caused us to reconsider our choice of space group in favor of one with lower symmetry. A Howell-Phillips-Rogers plot was made and it strongly indicated an acentric space group.

Reexamination of the data set showed that while the conditions for the screw axis (oko, $k = 2n$) were never violated, the conditions for the c glide $(h, 0, \ell, \ell = 2n)$ were. The reflections 0, 0, 1 and 1, 0, 1 were both present though weak. Refinement was therefore begun again in $P2_1$. Attempts to leave the tungsten atoms with the same coordinates as in $P2_1/c$ caused their positions to shift drastically. This was probably because of correlation. Direct methods were then run to obtain new positions for these atoms. Solution and refinement then proceeded without problems. During the last least squares cycle no atom moved by more than 0.03 Å. A final difference Fourier map displayed no peak greater than $0.63 e\text{Å}^{-3}$. The final discrepancy indices were $R_1 = 0.040$, $R_2 = 0.053$ and the goodness-of-fit index was 1.19. Two least squares refinement cycles were then run on the enantiomorph of the chosen cell. The discrepancy indices were unchanged so the original cell is reported here.

Supplementary Material Available.

A table of observed and calculated structure factors (7 pages). See any current masthead page for ordering information.

Acknowledgements

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Table I. POSITIONAL AND THERMAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS.[a]

ATOM	X	Y	Z	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
W(1)	0.0885(1)	0.00000(0)	0.35863(9)	3.47(3)	5.80(5)	2.72(3)	-0.41(5)	1.05(2)	-0.52(5)
W(2)	-0.0855(1)	-0.0562(7)	0.14348(10)	4.06(3)	4.65(4)	3.68(3)	-0.52(5)	2.46(2)	-0.30(5)
O(1)	-0.050(2)	0.057(1)	0.382(2)	2.4(5)	10(1)	4.0(6)	2.5(7)	0.2(4)	-3.6(7)
O(2)	0.147(2)	-0.081(1)	0.495(2)	10(1)	3.8(8)	2.8(6)	1.4(8)	3.2(5)	1.8(6)
O(3)	0.297(2)	-0.020(1)	0.396(2)	1.4(5)	12(1)	4.0(7)	2.0(7)	0.0(5)	-2.4(8)
O(5)	-0.064(2)	-0.001(1)	0.023(1)	6.3(6)	5.2(8)	4.1(5)	-2.1(7)	3.3(4)	0.9(6)
O(6)	0.043(3)	-0.147(1)	0.153(2)	9(1)	4.5(9)	8(1)	1.9(9)	5.0(7)	2.4(8)
O(7)	-0.212(2)	-0.125(1)	0.183(1)	6.9(5)	5.6(9)	5.9(5)	-3.9(6)	5.3(3)	-2.7(6)
N(1)	0.087(2)	0.107(1)	0.261(2)	5.2(7)	7(1)	6.5(8)	-0.8(9)	4.2(5)	1.9(9)
N(2)	-0.284(5)	0.039(2)	0.092(3)	20(2)	6(1)	7(2)	7(1)	4(2)	3(1)
C(1)	0.173(3)	0.105(2)	0.209(3)	4.8(6)					
C(2)	0.191(4)	0.170(2)	0.149(3)	6.7(8)					
C(3)	0.094(4)	0.233(2)	0.136(3)	7.3(9)					
C(4)	-0.005(4)	0.232(2)	0.184(4)	8.2(10)					
C(5)	-0.008(3)	0.163(2)	0.254(3)	5.5(7)					
C(11)	-0.018(3)	0.062(2)	0.528(3)	5.4(7)					
C(12)	-0.183(4)	0.078(2)	0.498(3)	7.9(10)					
C(13)	0.113(4)	0.123(2)	0.509(3)	6.7(8)					
C(21)	0.086(3)	-0.156(1)	0.499(2)	3.7(5)					
C(22)	-0.052(4)	-0.147(2)	0.521(3)	6.8(9)					
C(23)	0.231(4)	-0.196(2)	0.613(3)	5.9(7)					
C(31)	0.444(3)	0.007(2)	0.524(3)	5.8(7)					
C(32)	0.527(4)	0.059(3)	0.478(4)	8.8(11)					
C(33)	0.549(9)	-0.067(4)	0.622(7)	18.6(28)					
C(51)	-0.085(7)	-0.053(4)	-0.114(5)	17.9(19)					
C(52)	0.041(5)	-0.090(3)	-0.110(4)	10.5(17)					
C(53)	-0.251(6)	-0.002(3)	-0.223(5)	11.1(16)					

C(61)	0.191(3)	-0.181(2)	0.251(3)	5.0( )
C(62)	0.161(4)	-0.265(2)	0.252(3)	7.2(9)
C(63)	0.303(4)	-0.168(2)	0.209(3)	7.7(10)
C(71)	-0.323(5)	-0.183(3)	0.078(4)	10.1(13)
C(72)	-0.395(5)	-0.225(3)	0.149(4)	9.3(12)
C(73)	-0.430(6)	-0.167(3)	-0.058(5)	12.1(16)
C(81)	-0.366(5)	0.009(2)	0.143(4)	9.1(11)
C(82)	-0.501(4)	0.076(2)	0.095(4)	8.4(10)
C(83)	-0.525(5)	0.125(3)	0.013(4)	9.4(12)
C(84)	-0.422(4)	0.138(2)	-0.035(4)	8.4(11)
C(85)	-0.299(3)	0.083(2)	0.006(3)	6.2(8)

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^aThe form of the anisotropic thermal parameter is:

$$\exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$$

Table II. Interatomic Distances and Angles for $W_2(OCHMe_2)_6Py_2$

BOND DISTANCES($\overset{\circ}{A}$)

W(1)-W(2)	2.332(1)		
W(1)-O(1)	1.86(2)	W(2)-O(5)	1.86(2)
W(1)-O(2)	2.00(2)	W(2)-O(6)	2.04(3)
W(1)-O(3)	1.90(2)	W(2)-O(7)	2.01(2)
W(1)-N(1)	2.23(3)	W(2)-N(2)	2.28(4)
O(1)-C(11)	1.59(4)	O(5)-C(51)	1.63(7)
O(2)-C(21)	1.47(3)	O(6)-C(61)	1.40(4)
O(3)-C(31)	1.45(4)	O(7)-C(71)	1.52(6)
N(1)-C(1)	1.33(4)	N(2)-C(81)	1.32(7)
C(1)-C(2)	1.41(5)	C(81)-C(82)	1.63(6)
C(2)-C(3)	1.45(5)	C(82)-C(83)	1.24(6)
C(3)-C(4)	1.40(6)	C(83)-C(84)	1.47(6)
C(4)-C(5)	1.49(5)	C(84)-C(85)	1.42(5)
C(5)-N(1)	1.35(4)	C(85)-N(2)	1.35(5)
C(11)-C(12)	1.50(5)	C(51)-C(52)	1.39(10)
C(11)-C(13)	1.55(5)	C(51)-C(53)	1.50(9)
C(21)-C(22)	1.55(4)	C(61)-C(67)	1.51(5)
C(21)-C(23)	1.48(4)	C(61)-C(63)	1.50(5)
C(31)-C(32)	1.53(5)	C(71)-C(72)	1.54(7)
C(31)-C(33)	1.68(9)	C(71)-C(73)	1.36(7)

Table II (continued)

BOND ANGLES (Deg).

W(2)-W(1)-O(1)	104.7(6)	W(1)-W(2)-O(5)	106.1(7)
O(2)	105.3(7)	O(6)	103.8(9)
O(3)	101.2(7)	O(7)	99.8(6)
N(1)	91.0(8)	N(2)	89(1)
O(1)-W(1)-O(2)	99(1)	O(5)-W(2)-O(6)	97(1)
O(3)	151(1)	O(7)	152(1)
N(1)	80(1)	N(2)	85(2)
O(2)-W(1)-O(3)	85(1)	O(6)-W(2)-O(7)	88(1)
N(1)	163(1)	N(2)	166(2)
O(3)-W(1)-N(1)	87(1)	O(7)-W(2)-N(2)	84(2)
W(1)-O(1)-C(11)	120(2)	W(2)-O(5)-C(51)	126(3)
W(1)-O(2)-C(21)	138(2)	W(2)-O(6)-C(61)	136(2)
W(1)-O(3)-C(31)	119(2)	W(2)-O(7)-C(71)	120(2)
W(1)-N(1)-C(1)	115(2)	W(2)-N(2)-C(81)	112(3)
W(1)-N(1)-C(5)	118(2)	W(2)-N(2)-C(85)	112(4)
C(1)-N(1)-C(5)	127(3)	C(81)-N(2)-C(85)	136(5)
N(1)-C(1)-C(2)	122(3)	N(2)-C(81)-C(82)	105(4)
C(1)-C(2)-C(3)	114(3)	C(81)-C(82)-C(83)	122(5)
C(2)-C(3)-C(4)	123(4)	C(82)-C(83)-C(84)	124(5)
C(3)-C(4)-C(5)	119(3)	C(83)-C(84)-C(85)	116(4)
C(4)-C(5)-N(1)	114(3)	C(84)-C(85)-N(2)	116(4)
O(1)-C(11)-C(12)	105(2)	O(5)-C(51)-C(52)	104(4)
C(13)	106(3)	C(53)	100(5)

Table II. Bond Angles (continued)

C(12)-C(11)-C(13)	115(3)	C(52)-C(51)-C(53)	115(5)
O(2)-C(21)-C(22)	110(2)	O(6)-C(61)-C(62)	107(3)
C(23)	105(2)	C(63)	105(3)
C(22)-C(21)-C(23)	113(3)	C(62)-C(61)-C(63)	110(3)
O(3)-C(31)-C(32)	105(3)	O(7)-C(71)-C(72)	104(4)
C(33)	108(4)	C(73)	122(5)
C(32)-C(31)-C(33)	118(4)	C(72)-C(71)-C(73)	120(5)

Torsional Angles (deg)

O(1)-W(1)-W(2)-N(2)	16.9
N(1)-W(1)-W(2)-O(5)	21.2
O(3)-W(1)-W(2)-O(6)	35.0
O(2)-W(1)-W(2)-O(7)	37.3
N(1)-W(1)-W(2)-N(2)	63.4
O(1)-W(1)-W(2)-O(7)	67.0
O(2)-W(1)-W(2)-O(6)	53.1
O(3)-W(1)-W(2)-O(5)	66.1

Figure 1. A view of the $W_2(OCHMe_2)_6py_2$ molecule. Projections
of thermal ellipsoids and spheres are drawn at the
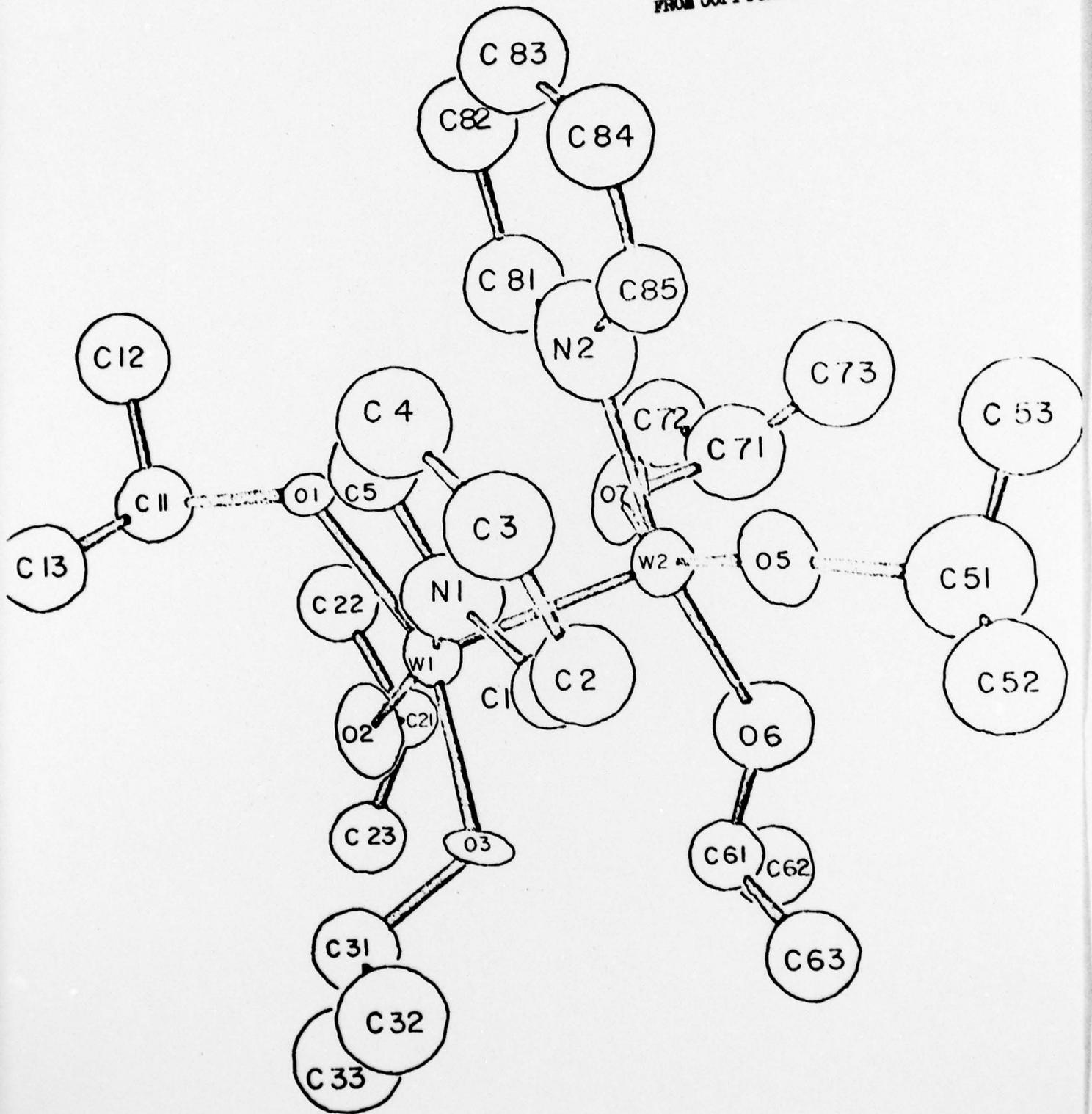50% probability level.

Figure 2. The coordination and rotational conformations as viewed conformation down the W-W axis. Thermal ellipsoids are drawn at the 50% probability level.