real ($\Delta f'$) and the imaginary ($i\Delta f''$) components of anomalous dispersion[45b] were included. The quantity minimized during least-squares analysis was $\sum w(F_o - F_c)^2$ where $w^{-1} = \sigma^2(F) + 0.0003F^2$.

The structure was solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares methods. Hydrogen atom contributions were included by using a riding model with d(C–H) = 0.96 Å and U(iso) = 0.08 Å^2. Refinement of positional and anisotropic thermal parameters led to convergence with R_F = 3.0%, R_{wF} = 3.9%, and GOF = 1.62 for 227 variables refined against those 5038 data with $|F_o| > 1.0\sigma(|F_o|)$ (R_F = 2.4% and R_{wF} = 3.7% for those 4490 data with $|F_o| > 6.0\sigma(|F_o|)$). A final difference Fourier synthesis showed no significant features, ρ(max) = 0.87 e Å^{-3}.

Supplementary Material Available: Tables of complete crystallographic data, positional parameters, bond distances, bond angles, thermal parameters, and H atom coordinates (4 pages); a list of structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

Contribution from Ames Laboratory,[1] U.S. DOE, and Department of Chemistry, Iowa State University, Ames, Iowa 50011

Tetrakis(pyridine)tetrachloro(μ-chloro)(μ-hydrido)ditungsten(W–W) and Its 4-Ethylpyridine Homologue. Compounds Derived from a Quadruply Bonded Dimer by Ligand Exchange and Oxidative Addition of Hydrogen Chloride

Richard T. Carlin and Robert E. McCarley*

Reaction of W$_2$(mhp)$_4$ (mhp = anion of 6-methyl-2-hydroxypyridine) with (CH$_3$)$_3$SiCl and pyridine in the presence of methanol provides the light brown compound W$_2$HCl$_5$(NC$_5$H$_5$)$_4$. The 4-ethylpyridine adduct W$_2$HCl$_5$(NC$_5$H$_4$C$_2$H$_5$)$_4$ is obtained by ligand exchange at 100 °C. Brown crystals of the latter are monoclinic, space group $C2/c$, with a = 11.883 (3) Å, b = 13.213 (3) Å, c = 21.727 (4) Å, β = 96.39 (3)°, and Z = 4. Structure refinement revealed an edge-shared bioctahedral arrangement with one H atom and one Cl atom in bridging positions between the metal atoms. The Cl atoms all occupy positions in the equatorial plane, and the 4-ethylpyridine ligands occupy the axial positions of the dimer. The short W–W distance, 2.516 (2) Å, is consistent with a W–W multiple bond. Comparison of the infrared spectra of the hydride and deuteride derivatives confirms the presence of a bridging H atom and indicates an isostructural arrangement for the pyridine and 4-ethylpyridine derivatives, as do electronic reflectance spectra.

Introduction

The chemistry of quadruply bonded tungsten dimers is a relatively new area of study. Of particular interest is the readily obtained W$_2$(mph)$_4$, where mhp is the anion of 2-hydroxy-6-methylpyridine.[2] This compound has been found to undergo a number of reactions, including ligand exchange with bidentate ligands in which the quadruple bond remains intact[3,4] and metal–metal bond cleavage by π-acceptor ligands to form monomeric tungsten(II) derivatives.[5] Intermediate between these two extremes are the reactions in which the W$_2^{4+}$ core is oxidized to form a compound with a metal–metal bond of order less than four. This has been observed when W$_2$(mhp)$_4$ or W$_2$(dmhp)$_4$ is treated with hydrogen halide in alcohol solutions to form the tungsten(III) compounds W$_2$HCl$_5$(dppm)$_2$[6] and Cs$_3$W$_2$X$_9$,[7] the tungsten(IV) complex W$_2$X$_4$(OR)$_4$(ROH)$_2$,[8] and in this laboratory when W$_2$(mhp)$_4$ is reacted with AlCl$_3$ in diglyme to produce the one-electron-oxidized species W$_2$Cl$_2$(mhp)$_3$ with a bond order of 3.5.[9]

In this paper, we wish to report the synthesis and structure of another W(III) dimer. The preparation involves the oxidation of the quadruple bond to a bond of lower order.

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Experimental Section

Materials. W$_2$(mhp)$_4$ was prepared by the established procedure.[2] Pyridine and 4-ethylpyridine were dried by refluxing over CaH$_2$ followed by distillation. Absolute ethanol and anhydrous diethyl ether were used from the bottles without further purification.

Analyses. Tungsten analyses were performed by decomposing samples with nitric acid and igniting them in tared porcelain crucibles to tungsten trioxide. Chlorine analyses were carried out by first decomposing samples in absolute ethanol by using KOH/H$_2$O$_2$. The resulting solutions were evaporated to near dryness, water was added, and the remainder of the ethanol was boiled off. Following acidification with dilute nitric acid, potentiometric titrations with a standard silver nitrate solution were performed.

Physical Measurements. Standard infrared spectra were obtained on a Beckman IR 4250 spectrometer using both Nujol and fluorocarbon mulls on CsI or KBr plates. Fourier transform infrared spectra were obtained on an IBM IR/90 spectrometer using Nujol mulls on either CsI plates or polyethylene disks. X-ray photoelectron spectra were measured with an AEI-200B instrument using Al Kα radiation (1486.6 eV). Beckman DU and Cary 14 spectrophotometers were used to measure the reflectance and solution UV–visible spectra, respectively.

Synthesis of W$_2$(μ-H)(μ-Cl)Cl$_4$(py)$_4$. In a typical reaction, 3 g (3.75 mmol) of W$_2$(mph)$_4$ and a magnetic stirring bar were introduced under nitrogen atmosphere into a 100-mL reaction flask equipped with a water jacket. Approximately 30 mL of dry pyridine was added either by syringe from a storage flask or by fresh distillation from CaH$_2$. The reaction flask was then evacuated on a vacuum line, and 6 mL (47.2 mmol) of trimethylchlorosilane were vacuum distilled into the flask. The mixture was refluxed under nitrogen for ca. 6 h. It was then cooled to below reflux and 1 mL of methanol was added by syringe while a nitrogen flush was maintained. The mixture was refluxed for an additional 10 h, cooled to room temperature, and filtered. The resulting solid was washed with absolute ethanol and anhydrous diethyl ether and then vacuum-dried, giving the desired product, W$_2$HCl$_5$(py)$_4$, as a light brown powder in ca. 65% yield. Anal. Calcd for W$_2$Cl$_5$C$_{20}$H$_{21}$N$_4$: W, 42.64; Cl, 20.55; C, 27.86; H, 2.45; N, 6.50. Found: W, 42.1; Cl, 20.6; C, 27.80; H, 2.42; N, 6.46.

An oxidation state determination was also performed by decomposing samples in a standard acidic Ce(IV) solution to oxidize tungsten to

Table I. Crystallographic Data for $W_2HCl_5(Etpy)_4$

chem formula: $W_2Cl_5C_{28}H_{37}N_4$	fw = 974.59
a = 11.883 (3) Å	color: brown
b = 13.213 (3) Å	monoclinic
c = 21.727 (4) Å	space group $C2/c$
β = 96.39°	T = 23 °C
V = 3391 (1) Å^3	λ(Mo Kα) = 0.710 34 Å
Z = 4	μ = 77.6 cm^{-1}
ρ_{obsd} = 1.95 g cm^{-3}	$R(F_o)$ = 0.069
ρ_{calcd} = 1.909 g cm^{-3}	$R_w(F_o)$ = 0.091

W(VI) and then titrating the excess Ce(IV) with a standard Fe(II) solution by using ferroin indicator. An average of 7.13 mol of Ce(IV) was needed per mole of compound. Since 1 mol of Ce(IV) is required to oxidize 1 mol of H$^-$ to H$_2$, the average oxidation state of each tungsten is found to be +2.94 compared to the expected +3.0.

The compound is stable in air and showed no signs of decomposition after several days. It is essentially insoluble in most common organic solvents and is only slightly soluble in pyridine, acetonitrile, and methylene chloride; however, acetonitrile and methylene chloride solutions rapidly decompose, changing from faint yellow to light green.

Synthesis of $W_2(\mu$-D)(μ-Cl)Cl$_4$(py)$_4$. The preparation of the deuteride analogue was carried out in the same fashion as the hydride compound except CD$_3$OD was added to the reaction mixture after the initial refluxing step in place of normal methanol. Anal. Found: Cl, 20.64; C, 28.2; H, 2.50; N, 6.64.

Synthesis of $W_2(\mu$-H)(μ-Cl)Cl$_4$(Etpy)$_4$. The 4-ethylpyridine- (Etpy-) substituted compound was obtained by loading a sample of $W_2HCl_5(py)_4$ and ca. 5 mL of 4-ethylpyridine into a 1 × 10 cm Pyrex reaction tube and sealing the tube under vacuum. The tube was then heated to ca. 100 °C in a sand bath for several days. The tube was opened in the air, and the product was washed with anhydrous diethyl ether and dried in the air. The compound was obtained as well-formed brown crystals of parallelepiped geometry suitable for X-ray crystallographic studies.

Synthesis of $W_2(\mu$-D)(μ-Cl)Cl$_4$(Etpy)$_4$. The deuteride analogue was prepared in the same manner as the corresponding hydride compound above except $W_2DCl_5(py)_4$ was used as starting material.

Collection and Treatment of X-ray Data. General procedures used are described elsewhere.[10] Crystal data are summarized in Table I.

Structure Solution and Refinement. The structure was solved in the centric space group $C2/c$. All refinements on positional and thermal parameters were carried out by using a block-matrix least-squares procedure[11] minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma_F^2$. Scattering factors used were those of Hanson et al.,[12] modified for tungsten by the real and imaginary parts of anomalous dispersion.[13]

From the experimentally determined density of 1.95 g/cm^3, it was calculated that the unit cell was composed of four molecules of formula W_2HCl_5(4-Etpy)$_4$. In the space group $C2/c$ the molecule had to reside on a special position (inversion center or 2-fold axis). Examination of a three-dimensional sharpened Patterson map[14] indicated that there was only one unique tungsten atom in the unit cell, and it was related by an inversion center to the other tungsten atom in the dimeric molecule, thus imposing inversion symmetry on the molecule.

Refinement of the positional and thermal parameters of the tungsten atom yielded a conventional residual index of $R = \sum|F_o| - |F_c||/\sum|F_o|$ = 0.219 and $R_w = \sum[w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ = 0.289, where $w = 1/\sigma_F^2$. An electron density map[14] phased on the refined tungsten atom revealed the positions of the chlorine atoms. It became apparent at this stage that there was no true inversion center in the molecule; instead, a pseudoinversion center resulted from disorder in the crystal or from near-inversion symmetry of the molecule. The bridging chlorine atom would refine to a reasonable isotropic thermal parameter only when an atom multiplier of 0.5 was used, indicating only one bridging chlorine atom in the molecule. Each terminal chlorine atom appeared in the electron density map as two overlapping peaks of about equal intensities with separations of ca. 0.8 Å, again showing that the terminal chlorine atoms which should have been equivalent in true $C2/c$ symmetry were

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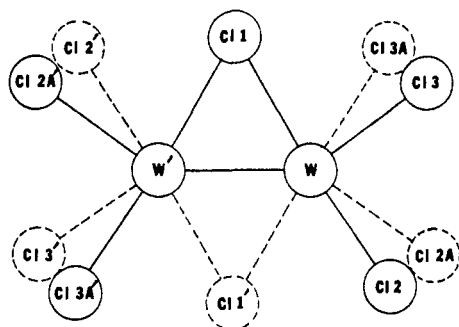
Table II. Positional Parameters[a] for W_2HCl_5(4-Etpy)$_4$

atom	occupation no.	x	y	z
W	1.0	0.42430 (6)	0.52680 (6)	0.45806 (4)
Cl1	0.5	0.5057 (9)	0.3547 (7)	0.4587 (5)
Cl2	0.5	0.3548 (1)	0.693 (1)	0.4445 (8)
Cl2A	0.5	0.298 (1)	0.668 (1)	0.4207 (7)
Cl3	0.5	0.303 (1)	0.467 (1)	0.3679 (7)
Cl3A	0.5	0.338 (1)	0.417 (1)	0.3777 (7)
N1	1.0	0.280 (1)	0.493 (1)	0.5075 (8)
C1	1.0	0.231 (2)	0.403 (2)	0.503 (1)
C2	1.0	0.133 (2)	0.375 (2)	0.534 (1)
C3	1.0	0.089 (2)	0.454 (2)	0.564 (1)
C4	1.0	0.141 (2)	0.544 (2)	0.574 (1)
C5	1.0	0.234 (2)	0.560 (2)	0.542 (1)
C6	1.0	−0.021 (2)	0.421 (2)	0.596 (2)
C7	0.5	−0.009 (7)	0.360 (7)	0.649 (4)
C7A	0.5	−0.012 (6)	0.480 (5)	0.665 (4)
N2	1.0	0.538 (1)	0.579 (2)	0.392 (2)
C21	1.0	0.571 (2)	0.674 (2)	0.392 (1)
C22	1.0	0.637 (2)	0.716 (2)	0.346 (1)
C23	1.0	0.660 (2)	0.643 (2)	0.298 (1)
C24	1.0	0.627 (2)	0.545 (2)	0.299 (1)
C25	1.0	0.568 (2)	0.513 (2)	0.345 (1)
C26	1.0	0.724 (3)	0.683 (4)	0.243 (2)
C27	0.5	0.759 (4)	0.760 (4)	0.246 (2)
C27A	0.5	0.679 (4)	0.797 (4)	0.222 (2)

[a] Estimated standard deviations are in parentheses.

in fact not inversion related. It was necessary to refine the four terminal chlorines separately by using an atomic multiplier of 0.5 for each.

The ring atoms of the 4-ethylpyridine groups were located on an electron density map phased on the tungsten and chlorine atoms. These ring atoms appeared as single peaks, so that it was necessary to refine on only two rings with the other two rings in the molecule being generated by the pseudoinversion center. Upon anisotropic refinement of all ring atoms, larger and/or more anisotropic ellipsoids were obtained for carbon atoms more removed from the nitrogen atoms. Location and refinement of the methylene and methyl carbons proved difficult; however, using isotropic temperature factors and a disordered configuration for the methyl groups, it was possible to account for the electron density in this region reasonably well.

Final convergence was obtained with R = 0.069 and R_w = 0.091 by using full-matrix least-squares refinement. A final difference Fourier synthesis showed no features greater than 0.9 e/Å^3 or less than 0.8 e/Å$_3$ with the largest discrepancies found near the tungsten atom.[15]

Extensive efforts were made to solve the structure in the acentric space group Cc. It was possible to obtain convergence with a model consisting of only the tungsten and chlorine atoms which was essentially the same as that found for the centric model. Attempts to introduce the 4-ethylpyridine ligands, however, resulted in correlation problems and divergence. Use of block-matrix least-squares refinement methods led to unreasonable bond distances and angles within the rings. The pseudoinversion center of the molecule prevented an acentric solution.

Final positional parameters are listed in Table II.

Results and Discussion

Crystal Structure of W_2HCl_5(4-Etpy)$_4$. The pseudoinversion center in the molecule results in two superposed inversion-related images of the dimeric molecule. Since the 4-ethylpyridine ligands and tungsten atoms were refined as truly inversion related, it was necessary only to sort out the chlorine atoms of the two images.

The molecule can be considered as two edge-sharing octahedra bridged by one chlorine atom and one hydride ligand, which was not located in the refined model. All terminal chlorine atoms are in equatorial positions, so that the portion of the dimeric molecule without the axial 4-ethylpyridine ligands is essentially planar. A representation of the planar fragment including all inversion-generated atoms, but excluding the bridging hydride, is shown in Figure 1. Primed atoms are related to their counterpart unprimed atoms by the pseudoinversion center.

(15) The largest peak in the difference map was 0.9 e/Å^3 and was located in the plane of the tungstens and chlorines at distances of 2.6 and 1.5 Å from W and W', respectively. This peak may be due to the hydride although attempts to refine on it were unsuccessful, as might be expected because of the close proximity to the tungstens and the presence of the pseudoinversion center.

Figure 1. Diagram showing the coplanar tungsten and chlorine atoms and the effect of the pseudoinversion center in the structure of $W_2HCl_5(Etpy)_4$.
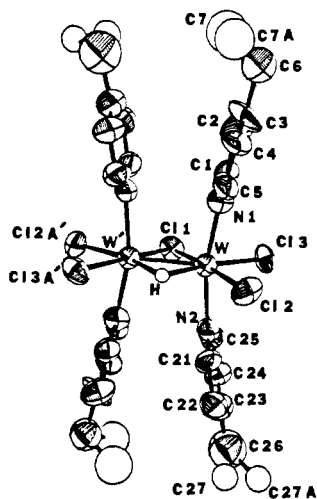

Figure 2. ORTEP drawing of $W_2HCl_5(Etpy)_4$ with the bridging H atom placed in its estimated location. Disordered methyl groups are shown in both half-occupancy positions.

Assuming a chlorine–chlorine van der Waals contact of ca. 3.4 Å,[16] it is found that Cl3A and Cl2′ are much too close to Cl1 at distances of 2.63 (2) and 2.61 (2) Å, respectively, while Cl3 and Cl2A′ are at reasonable distances of 3.29 (2) and 3.32 (2) Å, respectively. This leads to the conclusion that Cl2, Cl2A′, Cl3, and Cl3A′ belong to the image with Cl1 as the bridging atom. This image is a correct one, and bond distances and angles are referred to it. The inverted image composed of Cl1′, Cl2′, Cl2A, Cl3′, and Cl3A (dotted circles) is also correct and would give an identical mirror image structure.

The deconvoluted molecule is shown in Figure 2. The disordered methyl groups are shown in their two half-occupancy sites as unshaded spheres. Also, the hydride ligand has been included in its proposed position. Table III provides the important angles and distances (both bonding and nonbonding) for the skeletal atoms about the two tungsten atoms. As noted, the molecular structure consists of two edge-sharing octahedra distorted in such a manner to allow for a W–W bond distance of 2.516 (2) Å. The tungsten atoms and the five chlorine atoms are essentially coplanar with the greatest deviation from the least-squares plane being only 0.10 Å. The close approach of the two tungsten atoms reduced the W–Cl–W′ angle to 61.3 (2)° while the terminal chlorine atoms are forced toward the hydride-bridged side of the molecule as perceived from viewing the solid circles of Figure 1. The axial nitrogen atoms are tilted away from each other with W–W–N angles of ca. 97° and a N1···N2′ nonbonding distance of 3.05 (2) Å, the approximate distance expected for a van der Waals contact,[16] which is 0.53 Å longer than if the nitrogens were not bent back. The need for this distortion of the axial ligands may explain the occupancy of all axial positions by 4-ethylpyridine, because the chlorine atoms, having a larger van der Waals radius, would

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Table III. Interatomic Distances and Angles around Tungsten Atoms for $W_2HCl_5(4\text{-}Etpy)_4$

Bond Distances (Å)			
W–W′	2.516 (2)	W′–Cl2A′	2.48 (2)
W–Cl1	2.471 (9)	W′–Cl3A′	2.41 (2)
W′–Cl1	2.47 (1)	W–N1	2.17 (2)
W–Cl2	2.35 (2)	W–N2	2.20 (2)
W–Cl3	2.44 (1)		

Intramolecular Nonbonding Distances (Å)			
N1···N2′	3.05 (2)	Cl1···Cl3	3.29 (2)
Cl3···Cl2	3.44 (2)	Cl1···Cl2A′	3.32 (2)
Cl2A′···Cl3′	3.50 (2)		

Bond Angles (deg)			
W–W′–Cl1	59.5 (2)	Cl2A′–W′–Cl3A′	91.5 (5)
W′–W–Cl1	59.3 (2)	W′–W–Cl2	124.6 (4)
W–Cl–W′	61.3 (2)	W–W′–Cl3A′	124.5 (4)
Cl1–W–Cl3	84.3 (4)	W′–W–N1	97.1 (4)
Cl3–W–Cl2	91.9 (5)	W′–W–N2	97.0 (4)
Cl1–W′–Cl2A′	84.5 (4)	N1–W–N2	165.7 (6)

require an even greater axial distortion. Instead, by occupying equatorial positions, the chlorine atoms are able to distort in the manner already described to alleviate steric crowding in the equatorial plane.

The W–W bond distance of 2.516 (2) Å found here, as well those of 2.483 (1) Å in $W_2(\mu\text{-}H)(\mu\text{-}Cl)Cl_4(dppm)_2$,[6] and 2.429 (1) Å (average) in $W_2(\mu\text{-}H)(\mu\text{-}Cl)Cl_2(PhCO_2)_2(PBu_3)_2$,[17] is difficult to reconcile on electronic considerations alone. A formal oxidation state of +3 for each tungsten would seem to require the formulation of a triple bond between the metal atoms; however, the bond is considerably longer than the average W–W triple-bond distance of ca. 2.29 Å found for the W(III) compounds studied extensively by Chisholm.[18] It is also substantially shorter than in the closely related compound $W_2Cl_6(py)_4$, with d(W–W) = 2.737 (3) Å,[19] for which calculations performed by Hoffmann and co-workers[20] lead to the formal assignment of a net single bond resulting from the ordering of the three HOMO's $\sigma^2\pi^2\delta^{*2}$. However, the δ^* is really mostly antibonding with respect to M–Cl, and one may argue that the W–W bond is a double bond. From bond length comparisons, it becomes apparent that the W–W bond in $W_2HCl_5(4\text{-}Etpy)_4$ falls in the range found for a formal double bond. A comparison to W(IV) compounds that are assumed to possess double bonds between tungsten atoms bears this out: $W_2(\mu\text{-}S)_2(\mu\text{-}Et_2NC_2)_2(Et_2NCS_2)_2$, d(W=W) = 2.530 (2) Å;[21] $W_4(OPr^i)_{14}H_2$, d(W=W) = 2.446 (1) Å;[22] $W_2(\mu\text{-}S)(\mu\text{-}EtS)_2Cl_4(SC_4H_8)_2$, d(W=W) = 2.523 (1) Å;[23] $W_2Cl_4(OR)_4(ROH)_2$, d(W=W) = 2.481 (1) Å for R = CH_3 and d(W=W) = 2.483 (1) Å for R = C_2H_5.[8]

The major repulsive forces appear to arise from the axial 4-ethylpyridine ligands, since the Cl···Cl basal repulsions are minimized by the distortion of the chlorine atoms toward the hydride-bridged side of the molecule. Since the effect of N···N axial repulsion will be less than the Cl···N repulsions in $W_2Cl_6(py)_4$,[19] a significant shortening of the metal–metal distance is reasonable. Also, the smaller bridging hydride will tend to pull the metals closer together. Apparently, a compromise is reached in which a distance near that observed for a W(IV)–W(IV) double bond is obtained.

Another noteworthy feature of the structure is that the average W–Cl bond distance of 2.46 Å for the terminal chlorines trans to the bridging hydride ligand is 0.08 Å longer than the average W–Cl distance of 2.38 Å found for the chlorines trans to the bridging chlorine atom. This can be attributed to the stronger trans influence of the hydride ligand. The same trans influence

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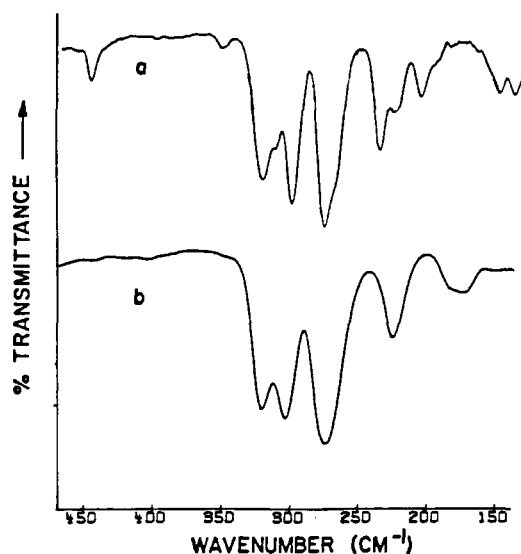
Figure 3. FT-IR spectra of (a) $W_2HCl_5(py)_4$ and (b) $W_2HCl_5(Etpy)_4$.

is observed for $W_4(OPr^i)_{14}H_2$,[22] $(pyH)_3Mo_2Cl_8H$,[24] and $(pyH)_3(H_5O_2)[Mo_2Cl_8H][MoCl_4O(H_2O)]$,[25] in which the W–O and Mo–Cl distances are 0.06 and 0.10 Å longer, respectively, for terminal ligands trans to the bridging hydride ligands. Also, in $W_2[\mu\text{-H}][\mu\text{-Cl}]Cl_2(PhCO_2)_2(P\text{-}n\text{-}Bu_3)_2$ the average W–P and W–Cl bonds and the average W–Cl bond in $W_2(\mu\text{-H})(\mu\text{-Cl})Cl_4(dppm)_2$ trans to the bridging hydride are ca. 0.08 Å longer than the corresponding average W–P and W–Cl distances trans to the bridging chloride.[17] It should be noted, however, that the standard deviations for the W–Cl distances in $W_2HCl_5(Etpy)_4$ are higher than desired as a result of the difficulties encountered in the structure solution. In fact, the difference between the average W–Cl distances for the two types of terminal chlorine atoms is of marginal statistical significance but still highly suggestive that the trans influence is operative.

Infrared Spectra. Infrared spectra were obtained on all compounds by using both Nujol and fluorocarbon mulls. A single, medium-intensity band indicative of a M–H–M stretching mode is found for $W_2HCl_5(py)_4$ at 1510 cm^{-1} and for $W_2HCl_5(Etpy)_4$ at 1545 cm^{-1}. Bands of the corresponding deuteride compounds, $W_2DCl_5(py)_4$ and $W_2DCl_5(Etpy)_4$, show the expected shifts to lower frequencies ($\nu_D = \nu_H/2^{1/2}$) with the respective stretching modes coming at 1082 and 1112 cm^{-1}, thus confirming the assignment. Similar W–H–W stretching wavenumbers were found for $W_2(\mu\text{-H})(\mu\text{-Cl})Cl_4(dppm)_2$. The intensities of these bands imply that they arise from the asymmetric M–H–M stretching mode. Evidently, the weaker band arising from the symmetric stretching mode is not seen because its intensity is too low or it is obscured by other bands in the spectra. However, it is possible that the asymmetric and symmetric modes occur at approximately the same wavenumber, as would happen if the W–H–W bond angle were ca. 90°.[26] Using the W–W bond distance of 2.516 Å and assuming a symmetric hydride bridge bond arrangement with W–H bond distances of ca. 1.8 Å, the W–H–W angle is calculated to be ca. 89°, an angle which would require near coincidence of the two stretching modes. A comparison of the assumed asymmetric M–H–M stretching wavenumber observed here (1510–1545 cm^{-1}) with ν(sym) = 1553 cm^{-1} and ν(asym) = 1248 cm^{-1} found in $Cs_3Mo_2Cl_8H$[26] indicates a much higher wavenumber for ν(asym) in $W_2HCl_5(py)_4$ or $W_2HCl_5(Etpy)_4$. Since this wavenumber approaches that for ν(sym) in $Cs_3Mo_2Cl_8H$, this may be taken as evidence that ν(sym) and ν(asym) are indeed nearly coincident.

Table IV. Chlorine X-ray Photoelectron Spectral Data (Fwhm = 1.4 eV)

| compd | least-squares fit | Cl $2p_{3/2}$ BE,[a] eV | | | ratio | |
		Cl_b	Cl_t	Cl_t'	$Cl_b:Cl_t:Cl_t'$	$10^{-3}\chi^2$
$W_2HCl_5(py)_4$	1	199.4	198.4	197.8	1.0:2.0:2.0	0.47
	2	199.6	198.8	198.0	1.0:2.4:4.5	0.46
$W_2HCl_5(Etpy)_4$	1	199.3	198.3	197.8	1.0:2.0:2.0	1.29
	2	199.4	198.4	197.7	1.0:2.4:2.7	1.15

[a] Spin–orbit splitting is 1.55 eV in all cases.

Above 400 cm^{-1} the spectra of $W_2HCl_5(py)_4$ and $W_2HCl_5(Etpy)_4$ were otherwise essentially those expected for coordinated pyridine and 4-ethylpyridine, respectively.[27] The spectra below 400 cm^{-1}, where W–Cl stretching and deformation and W–N stretching wavenumbers should be found,[28] are shown in Figure 3 for comparison. Assuming exact C_{2v} symmetry, six W–Cl (four terminal and two bridging) stretching modes and three W–N stretching modes should be active for both compounds. The spectrum of $W_2HCl_5(py)_4$ (spectra a) shows five bands (relative intensity in parentheses) at 320 (s), 309 (sh), 299 (s), 275 (s), and 267 (sh) cm^{-1} which are assigned to W–Cl stretching modes. The assignment of the bands at 233 (m), 223 (w), and 203 (w) cm^{-1} is not certain since they may result from bridging W–Cl stretches, Cl–W–Cl deformations, and/or W–N stretches.[28]

The spectrum of $W_2HCl_5(Etpy)_4$ below 400 cm^{-1} is very similar to that of $W_2HCl_5(py)_4$. Bands for the W–Cl stretching modes are found at 322 (s), 304 (s), and 276 (s) cm^{-1}. These bands are slightly broader and the shoulders observed at 309 and 267 cm^{-1} in the spectrum of $W_2HCl_5(py)_4$ are not resolved here. The medium-intensity band at 226 cm^{-1} and the weaker overlapping bands at 185 and 173 cm^{-1} may again be assigned to W–Cl–W bridge-stretching, Cl–W–Cl deformation, and/or W–N stretching modes.

The nearly identical infrared spectra and the method of preparation of $W_2HCl_5(Etpy)_4$ (simple ligand exchange) indicate that $W_2HCl_5(py)_4$ has the same basic structure as that determined for $W_2HCl_5(Etpy)_4$.

X-ray Photoelectron Spectra. Tungsten and chlorine X-ray photoelectron spectra (XPS) were obtained for both $W_2HCl_5(py)_4$ and $W_2HCl_5(Etpy)_4$. Binding energies were referenced to the C 1s binding energy taken as 285.0 eV.[29] Spectra were deconvoluted by using a program developed by Luly.[30]

The W $4f_{5/2}$ and $4f_{7/2}$ energies are at 34.8 and 32.6 eV for $W_2HCl_5(py)_4$ and at 34.6 and 32.4 eV for $W_2HCl_5(Etpy)_4$. The values are in accord with those found for $K_3W_2Cl_9$ (W $4f_{5/2,7/2}$: 34.7, 32.5 eV) and $[Bu_4N]_3W_2Cl_9$ (W $4f_{5/2,7/2}$: 34.4, 32.3 eV).[31]

The chlorine spectra were complex, and efforts to fit one or two types of chlorines to the peak profiles gave poor agreement factors. Using three nonequivalent chlorines for each compound and varying the appropriate parameters gave good fits as shown in Table IV. The χ^2 values provided for each least-squares fit are an indication of the goodness of fit and can only be used to compare fits to the same spectrum since it is dependent on the number of counts.[30] The difference between fits 1 and 2 for each compound is that in fit 1 the $Cl_b:Cl_t$ (trans to Cl):Cl_t' (trans to H) ratios were constrained to 1:2:2, while in fit 2 their ratios were allowed to vary. These structural assignments are based on results obtained for $K_3W_2Cl_9$ and $(Bu_4N)_3W_2Cl_9$ for which bridging Cl $2p_{3/2}$ binding energies are found at 198.2 and 197.9 eV, respectively.[31] The terminal chlorines trans to the hydride ligand should have the lowest binding energy because their longer W–Cl bond distances would increase their effective negative charge; however,

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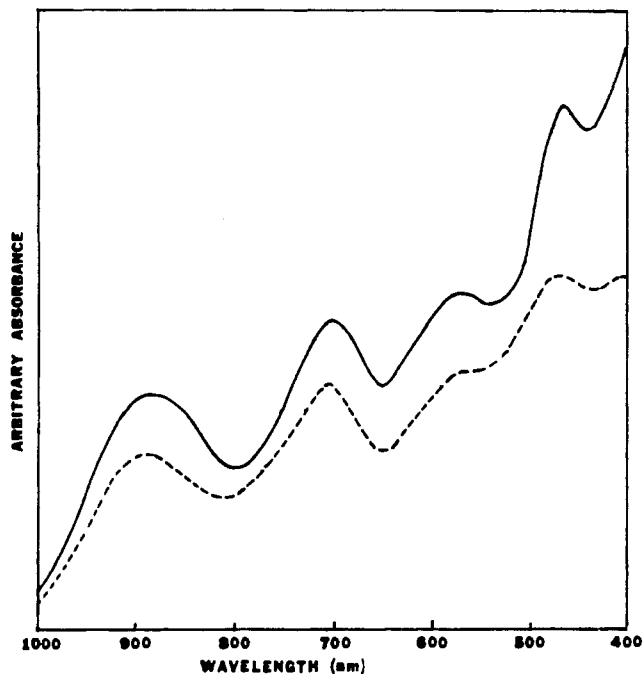
Figure 4. Reflectance electronic spectra for $W_2HCl_5(Etpy)_4$ (upper curve) and $W_2HCl_5(py)_4$ (lower curve).

these assignments for the terminal chlorines are tentative, especially since the terminal chlorine bond distances have a considerable amount of uncertainty associated with them as discussed earlier. When the chlorine ratios are allowed to vary, slight improvements in the fits are seen (lower χ^2's), and the ratios vary somewhat from the ideal 1:2:2, especially for $W_2HCl_5(py)_4$; however, the binding energies change insignificantly.

UV–Visible Spectra. Acquisition of UV–visible spectra was hampered by insolubility and/or decomposition of the pyridine and the 4-ethylpyridine compounds in most common organic solvents. Reflectance spectra were obtained for both compounds and are shown in Figure 4. The spectra are essentially identical. They are also quite similar to the spectra recorded by Wentworth and co-workers for the compounds $W_2Cl_6L_4$ (L = pyridine, 4-picoline, and 4-isopropylpyridine)[32] and by Walton and coworkers for $W_2(\mu\text{-H})(\mu\text{-Cl})Cl_4(dppm)_2$ and $W_2(\mu\text{-Cl})_2Cl_4(dppm)_2$.[6]

Conclusions

The preparation of $W_2HCl_5(py)_4$ can be viewed as the product of the oxidative addition of HCl to a quadruple bond, as previously described in the formation of $Mo_2Cl_8H^{3-}$,[24] $MoWCl_8H^{3-}$,[26] $W_2\text{-}(\mu\text{-H})(\mu\text{-Cl})Cl_2(O_2CPh)_2(P\text{-}n\text{-Bu}_3)_2$,[17] and $W_2(\mu\text{-H})(\mu\text{-Cl})Cl_4\text{-}(dppm)_2$.[6] The reaction, however, is not straightforward in that the HCl generated would exist almost entirely as pyridinium chloride unless it reacted immediately with the ditungsten species in solution. Also, without the generation of HCl, numerous products with incomplete mhp replacement are obtained,[33] indicating the need for HCl in order to completely replace all mhp ligands. Because of these complications, it is not possible at present to formulate a simple reaction scheme for the formation of $W_2HCl_5(py)_4$.

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Contribution from the Department of Chemistry,
Texas A&M University, College Station, Texas 77843

Synthesis and Characterization of a New Series of Zinc Phosphites

C. Yolanda Ortiz-Avila, Philip J. Squattrito, Minghuey Shieh, and Abraham Clearfield*

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Several new zinc phosphites have been synthesized in aqueous solution by reactions of Zn^{2+} with H_3PO_3 and either Na^+, K^+, or Ba^{2+}. The structures were determined by single-crystal X-ray diffraction techniques. $Zn(H_2PO_3)_2\cdot 3H_2O$: $R\bar{3}$, $a = 21.128$ (2) Å, $c = 7.769$ (6) Å, $V = 3003$ (2) Å^3, $Z = 18$, $R(F) = 0.073$ for 494 observations ($I > 3\sigma(I)$), 82 variables. $Zn_2(HPO_3)_2\text{-}(H_2O)_4\cdot H_2O$: $P\bar{1}$, $a = 7.670$ (2) Å, $b = 9.454$ (1) Å, $c = 7.554$ (1) Å, $\alpha = 90.83$ (1)°, $\beta = 92.90$ (1)°, $\gamma = 88.54$ (2)°, $V = 546.9$ (2) Å^3, $Z = 2$, $R(F) = 0.022$ for 1430 observations ($I > 3\sigma(I)$), 175 variables. $Zn_3Na_2(HPO_3)_4$: $Pnma$, $a = 8.331$ (2) Å, $b = 12.243$ (2) Å, $c = 12.669$ (1) Å, $V = 1292.2$ (6) Å^3, $Z = 4$, $R(F) = 0.038$ for 704 observations ($I > 3\sigma(I)$), 103 variables. $Zn_3K_2(HPO_3)_4$: $P2_1/c$, $a = 12.373$ (2) Å, $b = 13.635$ (2) Å, $c = 8.571$ (2) Å, $\beta = 90.24$ (1)°, $V = 1445.9$ (4) Å^3, $Z = 4$, $R(F) = 0.037$ for 1525 observations ($I > 3\sigma(I)$), 206 variables. $Zn_3Ba(HPO_3)_4(H_2O)_6$: $C2/c$, $a = 22.707$ (2) Å, $b = 5.302$ (3) Å, $c = 15.029$ (1) Å, $\beta = 105.28$ (1)°, $V = 1745$ (1) Å^3, $Z = 4$, $R(F) = 0.054$ for 1530 observations ($I > 3\sigma(I)$), 141 variables. Each of the five structures is a new type with the Zn atoms in either octahedral or tetrahedral coordination bridged by phosphite groups to produce a framework of zinc and phosphorus-centered oxygen polyhedra. Several of the frameworks have open channels lined with phosphite H atoms or coordinated water molecules. In some cases, these polyhedra are bridged by alkali-metal or alkaline-earth-metal ions to produce different frameworks. The exact nature of each structure is highly dependent on the identity of the second metal as each adopts a different coordination environment. The coordination numbers of the Na^+, K^+, and Ba^{2+} ions are 6, 7, and 12, respectively. The role of the alkali and alkaline-earth metals in the structures is discussed, and the phosphite structures are compared with similar known phosphates.

Introduction

Transition-metal phosphates are of interest because of their ion exchange and conduction properties.[1] A particularly well-studied family of such compounds are the metal phosphates of groups 4 and 14 as represented by the formula α-$M(HPO_4)_2\cdot H_2O$ (M = Ti, Zr, Hf, Ge, Sn, Pb).[2] These compounds have a layered structure in which the metal atoms are octahedrally coordinated by oxygen atoms from six different tetrahedral phosphate groups.[3]

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* Author to whom correspondence should be addressed.