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Timothy Richard Ryan
Iowa State University

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RYAN, TIMOTHY RICHARD

THE PREPARATION AND CHARACTERIZATION OF DIMERIC AND TETRAMERIC CLUSTERS OF MOLYBDENUM AND TUNGSTEN

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The preparation and characterization of dimeric and tetrameric clusters of molybdenum and tungsten

by

Timothy Richard Ryan

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GENERAL INTRODUCTION

An important aspect of the chemistry of the transition metals lies in their ability to form molecular complexes in which there exist strong metal-metal interactions. These so-called cluster compounds were not thoroughly studied until about 1960 (1). One major reason for the recent intense interest in these compounds was the expectation that metallic cluster complexes might function as homogeneous catalysts or serve as models for processes taking place on heterogeneous catalysts (2-6). Indeed, several cluster compounds have been found to be catalytically active (2, 3, 7-15).

Yet, the study of clusters has been hindered by the fact that most cluster compounds known today were discovered by chance (16, 17). There is a need for the development of synthetic methods which will produce homologous series of cluster complexes which can then be studied for trends in such areas as bonding, reactivity, and physical properties. Eventually, one might hope to synthesize a particular cluster to fulfill a particular need. Work on rational syntheses of clusters has already had some success (16, 18-21) and was a major goal of this thesis research.

The clustering of metal atoms into molecules containing strong metal-metal bonds is principally due to the efficient interaction of the partially filled d orbitals of the metal atoms (1). The requirement that d orbitals must have sufficient radial extension to give good overlap generally limits the metal atoms to low formal oxidation states and explains the greater tendency of second and third row transition elements to engage in metal-metal bonding. The early transition metals in low oxidation states are particularly versatile in forming strongly bonded cluster compounds of high nuclearity.

Molybdenum, for example, forms a complete series of discrete molecular clusters containing 2 to 6 metal atoms which can be visualized as originating from the hexanuclear clusters of the type $Mo_6Cl_8^{4+}$ (22). This cluster consists of an octahedron of strongly bonded metal atoms capped on each face by a triply bridging halide ion. Removal of one molybdenum atom leaves a square pyramid of metal atoms of the type found in $Mo_5Cl_{13}^{2-}$ (23). Removal of two adjacent molybdenum atoms leaves a distorted tetrahedron of the type found for $Mo_4I_{11}^{2-}$ (24). The loss of two apical (trans) metal atoms results in a planar molybdenum cluster not unlike $Mo_4Cl_8(PR_3)_4$ (25). There is also some preliminary evidence (26) for the formation of a metal-metal bonded zig-zag chain of four molybdenum atoms. Removal of three adjacent metal atoms from the octahedron produces a triangular cluster of molybdenum as is present in compounds like $Mo_3O_4(C_2O_4)_3(H_2O)_3^{-2}$. There are numerous examples of this type of trigonal cluster (27-30), including organometallic trimers (31, 32). The loss of four atoms from an octahedron produces dimers of molybdenum. These can roughly be separated into two types: those with single or double bonds between metal atoms (33, 34) and those with strong triple and quadruple bonds (35-37). Usually, it is the latter type which more closely resembles the higher members of the series because of the similarity of oxidation states (+2 to +4) and ligands (halides, alkoxides, amides).

The existence of this series suggests that similar series may exist for other elements of the transition metals, especially since octahedral clusters are known for many transition metals. It also suggests that it may be possible to build higher clusters from fragments which are readily attainable. Such step-wise syntheses would also provide a means to prepare mixed metal clusters. Dimers of Mo, W, Re, and Tc possessing metal-metal bond orders of 3 to 4 seem to be likely candidates for these cluster-building reactions in view of their electronic and structural configurations.

The quadruply bonded dimers typically consist of two metal atoms each situated roughly at the center of a square plane of ligands. A representative example is $Mo_2Cl_8^{4-}$ which is shown in Figure 1. The individual d orbitals on each metal combine in a molecular orbital scheme to give four metal-metal bonding orbitals (1σ, 2π, 1δ) and four antibonding orbitals ($1\delta^*$, $2\pi^*$, $1\sigma^*$) (38). The four bonding orbitals are filled in a quadruply bonded dimer, the HOMO and LUMO being δ and δ^*, respectively. Triply bonded dimers can be obtained by addition of electrons to the δ^* orbital, as in compounds of Re(II) and Tc(II) (37), or removal of electrons from the δ orbital as found in the dimers M_2X_6 (M = Mo, W; X = -OR, $-NR_2$, -R), which have an ethane-like structure (35, 36). Because the metal atoms in these molecules are in low oxidation states and are electronically and coordinatively unsaturated, these dimers might be expected to be highly reactive. It is this potential reactivity which has caused, in part, the interest in the dimers as possible catalysts or precursors to higher clusters.

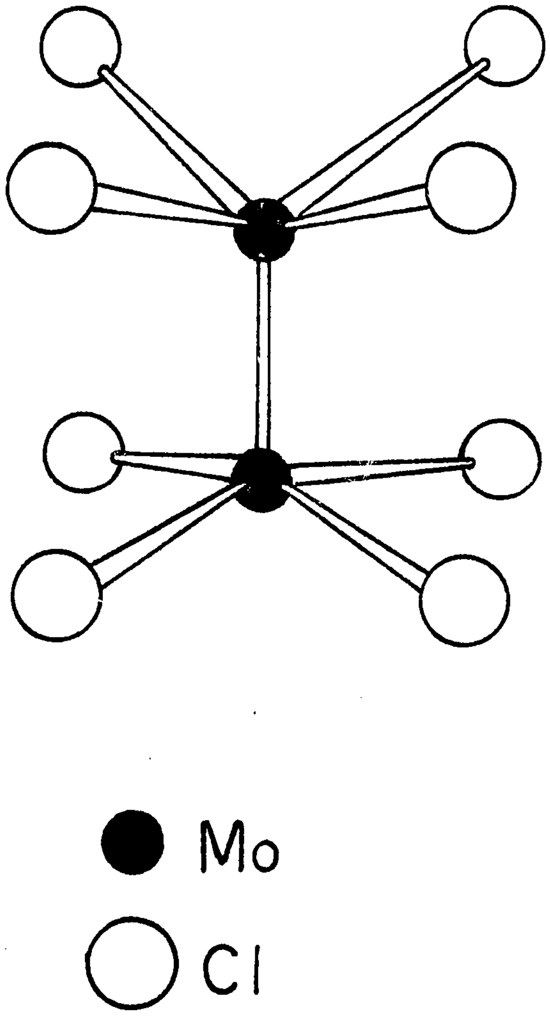

Figure 1. Structure of the $Mo_2Cl_8^{4-}$ anion

Unfortunately, reactions involving multiply bonded dimers frequently lead to irreversible structural degradation thereby producing stable compounds in which the metal-metal bond is greatly weakened or lost altogether (39-50). While this is true for both triply bonded and quadruply bonded complexes, dimers with triple metal-metal bonds have been found to participate in several reversible reactions which are catalytically significant. These include addition of unsaturated molecules across the metal-metal bond (51), carbonylation (26), and insertion of CO_2 into metal-ligand bonds (52-55). The CO_2 insertion, when performed with dimers of the type $M_2R_2(NMe_2)_4$ (M = Mo, W; R = alkyl group containing β-hydrogen), produces alkanes and alkenes by reductive elimination (56).

Unlike triply bonded dimers, the more highly coordinated quadruply bonded dimers are less apt to engage in reversible reactions where the metal-metal bond is retained. Rhenium dimers do show some tendency to be reversibly oxidized or reduced. Cyclic voltametry has produced dimeric species with rhenium in +2, +2.5, and +3 oxidation states (37). Rhenium(II) and rhenium(III) dimers may be reversibly oxidized with HX (57) and X_2 (58), respectively, (X = halide). Additionally, Re(IV) and Re(III) dimers can be reduced by PR_3 (57, 59). The quadruply bonded tungsten and molybdenum dimers undergo only a limited number of reversible oxidations. The molybdenum carboxylates, $Mo_2(O_2CR)_4$ may be oxidized by I_2 to $Mo_2(O_2CR)_4I_3$ in a thermally reversible reaction (60). The mixed metal complex $MoW(O_2CR)_4$ reacts with I_2 to produce $MoW(O_2CR)_4I$ which can be reduced back to the MoW^{4+} dimer (61). The related tetra(dithiocarboxylato) compound, $Mo_2(S_2CR)_4$ (62), and tetrakis(xanthato) compound, $Mo_2(S_2COR)_4$ (41), behave differently in that they are not affected by I_2 and are irreversibly oxidized, respectively. The molybdenum dimers $Mo_2Cl_8{}^{4-}$, $Mo_2(O_2CR)_4$, and $Mo_2(SO_4)_4{}^{4-}$ can undergo one-electron electrochemical oxidation to species with 3.5 order metal-metal bonds (63, 64). Several such oxidized dimers have been isolated as crystalline compounds (65, 66), but only one, $MoW(O_2CR)_4I \cdot CH_3CN$, has been chemically reduced back to a $M\text{-}M^{4+}$ species (62). The dimers, $Mo_2(SO_4)_4{}^{4-}$ and $Mo_2X_8{}^{4-}$ (X = halide) can be photolytically oxidized in acidic solutions, but this process is irreversible under the conditions used (67, 68). The only other well-studied system is the reaction of dimers of molybdenum and tungsten with HX (X = halide) where a variety of products are formed depending upon the reaction conditions and the nature of the metal. Tungsten dimers are irreversibly oxidized to $W_2X_9{}^{3-}$, $W_2X_8H^{3-}$, or $W_2X_4(OR)_2(ROH)$ (69). Molybdenum dimers may react with HX to give simple substitution products, $Mo_2X_8{}^{4-}$ (70, 71), or under different conditions oxidation to MoX_8H^{3-} occurs (72). Unlike the tungsten analog, $Mo_2X_8H^{3-}$ may undergo reduction in the presence of trialkylphosphines or pyridine back to quadruply bonded $Mo_2X_4L_4$ (L = PR_3, py) (73). Reactions of $Mo_2(O_2CCH_3)_4$ with HBr and HI in methanol have produced the clusters $Mo_2Br_6{}^{-}$ and $Mo_4I_{11}{}^{2-}$ (74).

These examples of the reactivity of the metal dimers in which strong metal-metal bonding is retained are not very common, and reversibility of redox reactions is even more unusual, especially for molybdenum and tungsten. Such irreversible behavior would prevent the use of many of the dimers in catalytic cycles. Similarly, the production of monomeric end-products is exactly the opposite effect desired for the building of higher clusters.

The problem faced is then one of finding suitably reactive dimers which retain their strong metal-metal interaction. One method of activating the dimer, so as to initiate reactions under mild conditions, is by the syntheses of derivatives with weakly coordinated ligands. Facile dissociation of the ligands would then open up the coordination sphere about the metal atoms. This thesis will describe just such a compound and how its high reactivity has led to the isolation of a new tetrameric molybdenum cluster. Extension of known principles for the molybdenum syntheses led to the rational synthesis of the tetrameric tungsten analog as well as a new tungsten dimer. The characterization of each of these compounds is described.

Explanation of Thesis Format

The thesis is divided into four sections, each of which is written in a form suitable for publication as a technical paper. While references cited in the general introduction may be found at the end of the thesis, each section contains an independent listing of references and notes which are cited in that section.

SECTION I. STRUCTURE OF THE ACTIVATED QUADRUPLY BONDED DIMER, $Mo_2Cl_4[P(C_6H_5)_3]_2(CH_3OH)_2 \cdot n(CH_3OH)$, AND ITS REACTION TO GIVE A TETRAMERIC MOLYBDENUM CLUSTER

INTRODUCTION

Much attention has been given complexes containing multiple metal-metal bonds primarily because of their potential use as catalysts (1-4). In this regard, it is not surprising that reactions involving the addition of molecular species across the metal-metal bonds have been of particular interest. In quadruply bonded dimeric complexes, such addition reactions are relatively uncommon (5-11). The following report describes the preparation of a unique dimer which undergoes self-addition across the quadruple bond to produce a new tetrameric cluster complex.

It was hoped that the preparation of quadruply bonded dimers with labile ligands would facilitate ligand dissociation in solution. The opening of the coordination sphere about the metal atom would then result in increased reactivity of the dimer. Attempts to prepare the unknown, sterically strained dimer, $Mo_2Cl_4[P(C_6H_5)_3]_4$, resulted in the isolation of the new reactive compound, $Mo_2Cl_4[P(C_6H_5)_3]_2(CH_3OH)_2$ (12), and subsequent investigations have shown that this complex possessed exceptionally labile methanol ligands which readily dissociated upon dissolution of the dimer in benzene. The resulting tetrameric species, $Mo_4Cl_8(PR_3)_4$, can be considered the product of a 2+2 cyclo-addition of two multiply bonded dimers.

EXPERIMENTAL

Materials

The compounds described below were air and moisture sensitive and were handled in Schlenk vessels under nitrogen or on a vacuum line. Samples were stored in a nitrogen-filled drybox. Hydrocarbon solvents were refluxed over $LiAlH_4$ or CaH_2 and vacuum distilled into glass bulbs for storage. Methanol was dried by refluxing with sodium methoxide followed by distillation under nitrogen onto Molecular Sieves (3Å) for storage. Solvent transfers were made by vacuum line distillation or syringe-addition under nitrogen.

Analysis of phosphorus-containing products for molybdenum was performed by digestion of samples in basic peroxide solution followed by precipitation as the molybdenum oxinate (13). Phosphorus-free materials were analyzed gravimetrically by digestion in hot, concentrated nitric acid to give MoO_3. Halides were determined by potentiometric titration with standard $AgNO_3$ solution; carbon, nitrogen and hydrogen analyses were performed by the Ames Laboratory Analytical Services Group, unless otherwise stated.

Physical Measurements

Infrared spectra were measured as nujol mulls on either a Beckman IR-4250 or Aculab-4. Solution uv-visible spectra were measured either on a Cary 14 or Cary 219 spectrophotometer in nitrogen-filled cells equipped with septa.

Syntheses

Molybdenum dimers

$Mo_2(O_2CCH_3)_4$ (14) and $(NH_4)_5Mo_2Cl_9{\cdot}H_2O$ (15) were prepared by established procedures.

$Mo_2Cl_4[P(C_6H_5)]_2(CH_3OH)_2$

In a 100 mL flask $(NH_4)_5Mo_2Cl_9{\cdot}H_2O$ (4.00 g, 6.46 mmol) and triphenylphosphine (3.40 g, 12.96 mmol) were combined with 30 mL of dry, oxygen-free methanol. The mixture was stirred under nitrogen for one day. A purple solid was filtered from the methanol solution and reacted again with 60 mL of methanol for one day. The blue, air-sensitive product was filtered, washed with methanol, and thoroughly vacuum dried. Yield was 76%. The identity of the product was confirmed by comparison of infrared and uv-visible spectra with the previously prepared compound having the following composition (12). *Anal*. Calcd. for $Mo_2Cl_4[P(C_6H_5)_3]_2(CH_3OH)_2$: Mo, 20.80; Cl, 15.37; C 49.48; H, 4.15. Found: Mo, 20.54; Cl, 15.42; C, 50.34; H, 4.45.

$[MoCl(OCH_3)]_n$

Tributylamine (1.20 g, 6.46 mmol) and $(NH_4)_5Mo_2Cl_9{\cdot}H_2O$ (2.00 g, 3.23 mmol) were stirred with 30 mL of dry, oxygen-free methanol under nitrogen for one day. The brown product was filtered under nitrogen and washed with 60 mL methanol. This solid was then extracted for 6 days with methanol to remove the soluble impurities, and the resulting dark brown product was dried *in vacuo*. The material was pyrophoric upon exposure to air. Yield was 60%. Anal. Calcd. for $[MoCl(OCH_3)]_n$: Mo, 59.1; Cl, 21.8. Found: Mo, 57.8; Cl, 21.5.

$Mo_4Cl_8[P(C_2H_5)_3]_4$

In a typical preparation, $Mo_2Cl_4[P(C_6H_5)_3]_2(CH_3OH)_2$ (1.50 g, 1.63 mmol) was placed on a fritted disc filter under a nitrogen atmosphere. Forty mL of benzene were added to give a green solution which was immediately filtered to remove a trace of brown precipitate. The green solution was stirred under nitrogen for 30-60 minutes, during which time a brown precipitate developed which was filtered and dried in vacuo. This material had a composition which was close to $\{MoCl_2[P(C_6H_5)_3]\}_n$, but analyses varied slightly from one preparation to the next (12).

The $\{MoCl_2[P(C_6H_5)_3]\}_n$ (0.50 g) was reacted with triethylphosphine (0.32 g) in 20 mL benzene to produce a yellow precipitate and a blue solution after 12 hours. The yellow product was filtered and washed with toluene. Product identification was confirmed by comparison of infrared and uv-visible spectra with the previously prepared complex having the following composition (12). Anal. Calcd. for $Mo_4Cl_8[P(C_2H_5)_3]_4$: Mo, 33.65; Cl, 24.87; C, 25.28; H, 5.30; P, 10.86. Found: Mo, 33.70; Cl, 24.63; C, 25.50; H, 5.37; P, 10.95. (C, H, P analyses by Galbraith Laboratories, Inc., Knoxville, Tennessee.)

X-ray Structure Determination

Collection and reduction of x-ray data

Crystals of $Mo_2Cl_4[P(C_6H_5)_3]_2(CH_3OH)_2 \cdot nCH_3OH$ were grown by slow evaporation of a saturated methanol solution. The crystal chosen for data collection measured 0.62 x 0.27 x 0.06 mm and was mounted in a thin-walled capillary under an atmosphere of nitrogen saturated with methanol. The crystal was mounted on a 4-circle automatic diffractometer designed at the Ames Laboratory (16). Twelve reflections at various values of chi and phi were input into the automatic indexing program ALICE (17). The cell parameters thus obtained, in conjunction with axial oscillation photographs, indicated a triclinic crystal system. Twenty-two strong, high angle reflections were measured on the previously aligned diffractometer, and these were used to obtain a least-squares refinement on the lattice constants at 25°C: $a = 11.547(6)$, $b = 12.152(5)$, $c = 9.458(4)$, $\alpha = 103.87(5)$, $\beta = 112.47(4)$, $\gamma = 104.33(5)$, $V = 1102.4(7)$. Mo Kα radiation was used, $\lambda = 0.70954$Å. Flotation density measurements provided a value of $z = 1$.

Data were collected to $2\theta = 50°$ using an ω-scan technique. Four unique octants of data showed no systematic extinctions and provided 3346 independent observed reflections ($I > 3\sigma_I$). Data were corrected for Lorentz-polarization effects and an absorption correction was made ($\mu = 9.14\ cm^{-1}$). Three standard reflections were monitored during data collection and showed negligible decay of intensity.

Structure solution and refinement

Solution of the Patterson function revealed the positions of two molybdenum atoms. Subsequent location of lighter atoms in electron density maps was accomplished by successive least-squares refinements using the minimizing function $\Sigma w(|F_o|-|F_c|)^2$ where $w = 1/\sigma_F^2$. The scattering factors were those of Hanson et al. (18) modified for the real and imaginary parts of anomalous dispersion (19).

During refinement, the assumption of space group P_1 led to oscillation of atom positions and chemically unreasonable bond distances. Correction to $P_{\bar{1}}$ resulted in satisfactory refinement. A center of inversion is located midway between the two molybdenum atoms in the molecule. Analysis of the weights was performed with the requirement that $\overline{w\Delta^2}$ should be a constant function of sin θ/λ (20), and the weighting was appropriately adjusted. Refinement of the occupancy factor for solvate methanol (n) showed n = 2.2 molecules per unit cell. Final discrepancy factors were R = 0.066 and R_w = 0.087.

Positional and thermal parameters are given in Tables I-1 and I-2, and bond distances and angles are presented in Table I-3. An ORTEP drawing of the molecule is shown in Figure I-1.

Table I-1. Positional parameters ($\times 10^4$) for $Mo_2Cl_4[P(C_6H_5)_3]_2(CH_3OH)_2 \cdot nCH_3OH$[a]

Atom	x	y	z
Mo	9895.5(5)	735.3(5)	9598.6(6)
Cl(1)	9884(2)	1786(2)	973(2)
Cl(2)	660(2)	594(2)	7549(2)
P	2187(2)	2366(1)	1763(1)
O(1)	7959(5)	207(5)	7363(6)
C(1)	6670(8)	318(9)	7092(11)
C(11)	2760(7)	2601(6)	3948(8)
C(12)	4092(8)	2894(8)	5046(9)
C(13)	4462(9)	3088(9)	6693(10)
C(14)	3501(10)	2977(9)	7228(10)
C(15)	2171(9)	2693(8)	6144(10)
C(16)	1778(8)	2484(7)	4494(9)
C(21)	3686(6)	2474(6)	1465(8)
C(22)	4740(7)	3604(7)	2162(10)
C(23)	5899(8)	3700(8)	1976(12)
C(24)	5972(8)	2681(9)	1063(13)
C(25)	4907(9)	1551(8)	327(13)
C(26)	3768(7)	1433(7)	543(9)
C(31)	2033(6)	3809(6)	1630(9)
C(32)	2183(9)	4745(7)	2920(11)
C(33)	2023(11)	5798(9)	2704(16)
C(34)	1745(9)	6035(9)	1208(17)
C(35)	1620(9)	5001(9)	9932(13)
C(36)	1753(8)	3935(8)	130(10)
O(2)	7597(11)	108(10)	4377(11)
C(2)	7783(27)	1194(17)	4203(31)
O(3)	0	5000	5000
C(3)	9306(55)	4221(50)	4023(68)

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

Table I-2. Thermal parameters ($\times10^4$) for $Mo_2Cl_4[P(C_6H_5)_3]_2(CH_3OH)_2\cdot nCH_3OH$[a,b]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo	50.2(6)	49.1(5)	89(1)	12.7(4)	28.9(5)	30.0(5)
Cl(1)	81(2)	72(1)	140(3)	34(1)	56(2)	38(2)
Cl(2)	91(2)	87(2)	125(3)	24(1)	63(2)	49(2)
P	53(2)	50(1)	91(2)	8(1)	30(2)	25(1)
O(1)	67(5)	97(5)	119(7)	32(4)	14(5)	43(5)
C(1)	75(8)	121(9)	203(16)	44(7)	38(9)	73(10)
C(11)	89(7)	49(5)	92(9)	11(5)	36(7)	24(6)
C(12)	93(8)	95(8)	120(11)	17(6)	23(8)	43(8)
C(13)	121(10)	126(10)	119(12)	30(8)	23(9)	44(10)
C(14)	139(11)	113(9)	111(11)	27(8)	49(9)	45(8)
C(15)	120(9)	102(8)	120(11)	19(7)	55(9)	54(8)
C(16)	96(8)	86(7)	119(11)	12(6)	45(8)	40(7)
C(21)	72(6)	63(6)	113(10)	21(5)	39(7)	38(6)
C(22)	68(7)	80(7)	167(13)	11(6)	50(8)	32(7)
C(23)	76(8)	101(8)	223(16)	25(6)	72(9)	57(9)
C(24)	97(9)	117(9)	271(19)	59(7)	102(11)	100(11)
C(25)	118(10)	100(8)	267(19)	63(8)	116(11)	90(10)
C(26)	91(8)	75(6)	159(12)	40(6)	72(8)	50(7)
C(31)	58(6)	56(5)	147(11)	15(5)	48(7)	35(6)
C(32)	122(10)	63(6)	180(14)	23(6)	71(10)	29(8)
C(33)	141(12)	87(8)	337(25)	48(8)	127(14)	64(12)
C(34)	90(9)	86(8)	374(27)	32(7)	79(13)	102(13)
C(35)	117(10)	109(9)	248(19)	42(8)	67(11)	111(12)
C(36)	97(8)	93(8)	155(13)	23(6)	40(9)	60(8)

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

[b] B_{ij} are defined by $T = \exp[-(h^2\beta_{11} + k^2\beta_{22} + \ell^2\beta_{33} + 2hk\beta_{12} + 2h\ell\beta_{13} + 2k\ell\beta_{23})]$.

Table I-2. (Continued)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(2)	193(13)	156(11)	174(14)	111(10)	120(12)	92(11)
C(2)	444(49)	139(18)	541(61)	163(26)	436(52)	153(29)
	B[c]					
O(3)	16.5(11)					
C(3)	10.7(12)					

[c] Isotropic temperature factors, B, are given in Å^2.

Table I-3. Bond distances (Å) and angles (°) for $Mo_2Cl_4[P(C_6H_5)_3]_2(CH_3OH)_2 \cdot nCH_3OH$[a]

Distances

Mo-Mo'	2.143(1)	C(21)-C(22)	1.388(10)
Mo-Cl(1)	2.411(2)	C(22)-C(23)	1.396(11)
Mo-Cl(2)	2.398(2)	C(23)-C(24)	1.371(13)
Mo-P	2.539(3)	C(24)-C(25)	1.391(13)
Mo-O(1)	2.211(5)		
C(1)-O(1)	1.457(9)	C(25)-C(26)	1.384(11)
P-C(11)	1.836(7)	C(26)-C(21)	1.401(10)
C(11)-C(12)	1.379(10)	P-C(13)	1.835(7)
C(12)-C(13)	1.390(12)	C(31)-C(32)	1.374(11)
C(13)-C(14)	1.376(14)	C(32)-C(33)	1.388(13)
C(14)-C(15)	1.377(13)	C(33)-C(34)	1.388(17)
C(15)-C(16)	1.385(11)	C(34)-C(35)	1.375(16)
C(16)-C(11)	1.405(10)	C(35)-C(36)	1.390(12)
P-C(21)	1.836(7)	C(36)-C(31)	1.385(11)

Angles (middle atom is vertex)

Mo'-Mo-Cl(1)	107.96(6)
Mo'-Mo-Cl(2)	106.44(7)
Mo'-Mo-P	97.58(6)
Mo'-Mo-O(1)	113.70(16)
Cl(1)-Mo-Cl(2)	145.47(7)
P-Mo-O(1)	148.69(15)
Cl(1)-Mo-P	88.04(8)
Cl(2)-Mo-P	90.31(8)
Cl(1)-Mo-O(1)	83.73(15)
Cl(2)-Mo-O(1)	79.97(15)
Mo-O(1)-C(1)	133.83(49)
Mo-P-C(11)	119.85(22)
Mo-P-C(21)	119.85(22)
Mo-P-C(31)	104.26(21)

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[a] Estimated standard deviations are given in parentheses for the last significant figures.

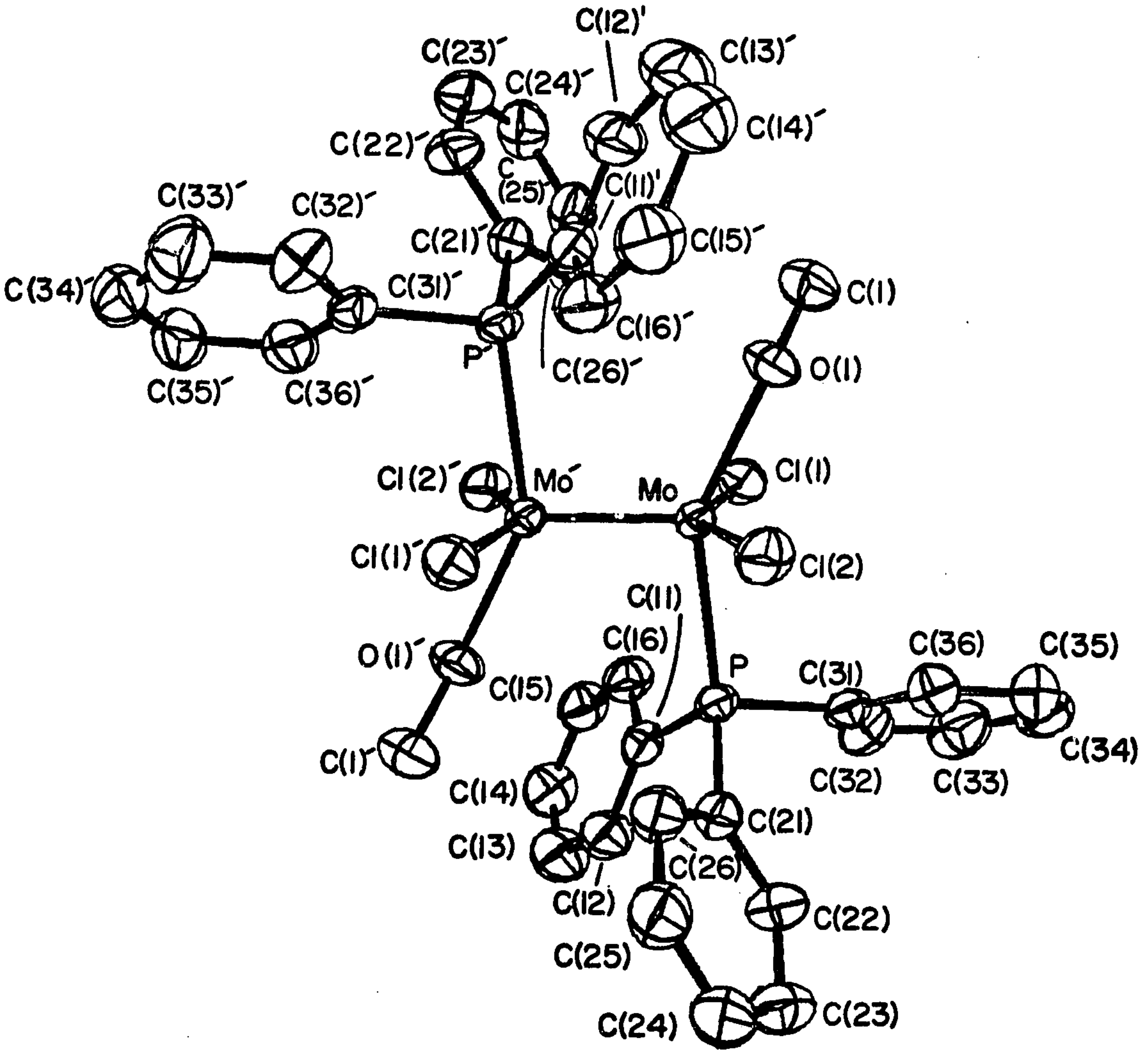

Figure I-1. Structure of the $Mo_2Cl_4[P(C_6H_5)_3]_2(CH_3OH)_2$ molecule with numbering scheme for the atoms shown. Atoms are represented by thermal ellipsoids scaled to 50% of the electron density

RESULTS

Syntheses and Characterizations

The reaction of $Mo_2Cl_8^{4-}$ with phosphines has been a convenient route to $Mo_2Cl_4(PR_3)_4$ dimers (21,22). It was while attempting to prepare $Mo_2Cl_4[P(C_6H_5)_3]_4$ that the dimeric complex, $Mo_2Cl_4[P(C_6H_5)_3]_2(CH_3OH)_2$, was isolated. When four or more equivalents of triphenylphosphine were reacted with the $Mo_2Cl_8^{4-}$ anion in methanol, products could not be obtained free from methanol, and only by washing the products with large amounts of methanol could reproducible compositions be prepared. Later syntheses were simplified by the use of only two equivalents of phosphine per mole $Mo_2Cl_8^{4-}$. Analytical data indicated $Mo_2Cl_4[P(C_6H_5)_3]_2(CH_3OH)_2$ only after thorough vacuum drying at 25°C to remove solvate methanol in the compound.

The attempted preparation of $Mo_2Cl_4(Pcy_3)_2(CH_3OH)_2$ (Pcy_3 = tricyclohexylphosphine) produced a brown, pyrophoric material with only two strong bands in the infrared spectrum at 1035 cm^{-1} and 505 cm^{-1} which suggested that $Mo\text{-}OCH_3$ moieties were present in the compound (23). Since the phosphine had not been incorporated into the product, the reaction was repeated using tri-n-butylamine as a noncoordinating base. An identical product was obtained, and analysis indicated the composition $[MoCl(OCH_3)]_n$. It is likely that this material is polymeric.

The $Mo_2Cl_4[P(C_6H_5)_3]_2(CH_3OH)_2$ dimer was found to be moderately air-sensitive and like the analogous $Mo_2Cl_4(PR_3)_4$ dimers (21) was blue in color. The uv-visible absorption bands are listed in Table I-4. The infrared spectrum exhibited many bands due to triphenylphosphine as well as bands due to methanol at 3380 cm^{-1} (m), 3200 cm^{-1} (m), 1100 cm^{-1} (m) and 996 cm^{-1} (s). Molybdenum-chlorine stretching bands were found at 334 cm^{-1} (s) and 272 cm^{-1} (w).

Solutions of the dimer in methanol were stable in the absence of oxygen, and the compound was insoluble and inert in nonpolar hydrocarbon solvents such as hexane. Quite different behavior was noted when the dimer was dissolved in a noncoordinating solvent such as benzene. The initial blue-green solutions quickly darkened and a fine brown precipitate developed. The composition of the brown compound was variable. Samples isolated from dilute benzene solutions after 30 minutes tended to have analyses corresponding to $[MoCl_2(P\phi_3)]_n$, while longer reaction times and more concentrated solutions produced materials with less triphenylphosphine and more methanol incorporated in the product. The variable composition and insolubility of this product prevented its definitive characterization; however, addition of PR_3 ($R = C_2H_5$, n-C_4H_9) produced more tractable materials and led to their structural characterization as tetrameric clusters (12).

The tetramers, $Mo_4Cl_8(PR_3)_4$, were found to be brown to yellow crystalline powders which were soluble in methylene chloride, tetrahydrofuran, benzene, and hexane. These compounds were only slightly air-sensitive and could be handled in the air for short periods of time. The infrared spectra of these complexes consisted of only PR_3 bands above 400 cm^{-1}, but the Mo-Cl stretching region, 200-400 cm^{-1},

Table I-4. Electronic absorption spectra[a]

$Mo_2Cl_4[P(C_6H_5)_3]_2(CH_3OH)_2$
(1.4×10^{-3} M, methanol solution)

410 ($\sim$360) sh[b]
510 ($\sim$450) sh
565 (610)

$Mo_4Cl_8[P(C_2H_5)_3]_4$
(5.6×10^{-5} M, THF solution)

245 ($\sim 2 \times 10^4$) sh
308 (1.7×10^4) sh
430 (2.2×10^3)

$Mo_4Cl_8[P(n\text{-}C_4H_9)_3]_4$
(6.3×10^{-5} M, hexane solution)

248 ($\sim 2 \times 10^4$) sh
312 (2.8×10^4)
435 (3.5×10^3)
685 ($\sim$100)

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[a] Values are given in nm followed by molar absorptivity, $\varepsilon(M^{-1}\ cm^{-1})$.

[b] sh = shoulder.

exhibited four to five bands which served as characteristic fingerprints for identification of these clusters and are listed in Table I-5. The uv-visible absorption bands are shown in Table I-4.

Crystal Structure

Single crystals of $Mo_2Cl_4[P(C_6H_5)_3]_2(CH_3OH)_2 \cdot nCH_3OH$ were isolated from methanol solutions, but they immediately began to crumble when the compound was dried in vacuo at 25°C. For the x-ray structure determination, it was necessary to include methanol in the sealed capillary to prevent decomposition of the crystal.

The molecule shown in Figure I-1 has a crystallographically imposed symmetry of Ci, but is virtually C_{2h} if one discounts the phenyl rings and methyl groups. The disposition of ligands is typical of quadruply bonded dimers in that each metal has distorted, square-planar coordination to the nonmetallic ligands which maintain an eclipsed configuration as shown by the torsional angles, P'-(Mo',Mo)-O = 1.36° and Cl(1)'-(Mo',Mo)-Cl(2) = 2.97°. The best least-squares fit of a plane through the two molybdenum and four chlorine atoms has no atom more than 0.03Å out of plane. Similarly, the molybdenum, oxygen, and phosphorous atoms are coplanar to within 0.02Å, and the angle between these two planes is 88.4°. The bulky phosphine ligands are situated trans to each other on opposite molybdenum atoms as would be expected for the minimization of nonbonding repulsions. Each molybdenum atom is coordinated to two mutually trans chlorine atoms as is the case in $Re_2Cl_4[P(C_2H_5)_3]_4$ (24). However, the four chlorine atoms in

Table I-5. Infrared spectra (cm^{-1}) 200 cm^{-1} to 400 cm^{-1} (s = strong, m = medium, br = broad)

$Mo_4Cl_8[P(C_2H_5)_3]_4$	$Mo_4Cl_8[P(n\text{-}C_4H_9)_3]_4$
361 (s)	356 (s)
335 (m)	337 (m)
320 (m)	315 (m)
292 (m)	280 (s, br)
257 (s)	

$Mo_2Cl_4[P(C_6H_5)_3]_2(CH_3OH)_2$ are eclipsed while they are staggered in the rhenium dimer. The Mo'-Mo-P angle is 97.6° which is considerably more acute than the Mo'-Mo-O(1) angle of 113.7°. In addition, the Mo-O(1) distance is somewhat long at 2.211(5)Å. The Mo-Mo bond distance of 2.143(1)Å is typical of quadruply bonded molybdenum dimers (25).

Methanol present as solvate is located at two independent crystallographic sites which are partially occupied. The first site has an occupancy of 0.4 molecules/asymmetric unit and has no contacts with other atoms closer than the sums of van der Waals radii. The occupancy of the second site is 0.7 molecules/asymmetric unit. The oxygen atom of the second methanol molecule is rather closely situated to the oxygen atom of the coordinated methanol. The distance, 2.66(1)Å, suggests a hydrogen bond exists between these two methanol molecules (26) and is consistent with the higher occupancy of this site.

DISCUSSION

In spite of the unusual reactivity of $Mo_2Cl_4[P(C_6H_5)_3]_2(CH_3OH)_2$, the spectral properties are not significantly different from other quadruply bonded molybdenum dimers. The two ν(Mo-Cl) bands in the infrared spectrum are similar to those seen for a number of $Mo_2Cl_4L_4$ complexes and are compatible with the presence of mutually trans chlorine atoms coordinated to each metal of the dimer (21). The uv-visible spectrum of the dimer has a strong absorption at 565 nm in methanol. This absorption is comparable to the 588 nm band ($\delta \rightarrow \delta^*$) in $Mo_2Cl_4[P(C_2H_5)_3]_4$ (27). The absorption at 565 nm has a prominent shoulder at 510 nm, and while this is somewhat unusual for quadruply bonded dimers, the $Mo_2Cl_4L_4$ (L = pyridine, dimethylformamide) complexes also display similarly complex spectra (21).

Addition of triphenylphosphine to a methanol solution of $Mo_2Cl_4[P(C_6H_5)_3]_2(CH_3OH)_2$ produces the spectral changes shown in Figure I-2. The strong absorption at 565 nm is shifted to longer wavelengths, and the shoulder at 510 nm becomes less prominent with increasing phosphine concentration. Isosbestic points are maintained at 553 nm and 473 nm. Since steric hindrance would make axial coordination of triphenylphosphine improbable, the phosphine must be replacing methanol in a ligand substitution reaction. Further experimental work is required to confirm the exact identities of the species in solution, but the data clearly show that facile substitution of methanol occurs even in the presence of a large excess concentration of methanol. The

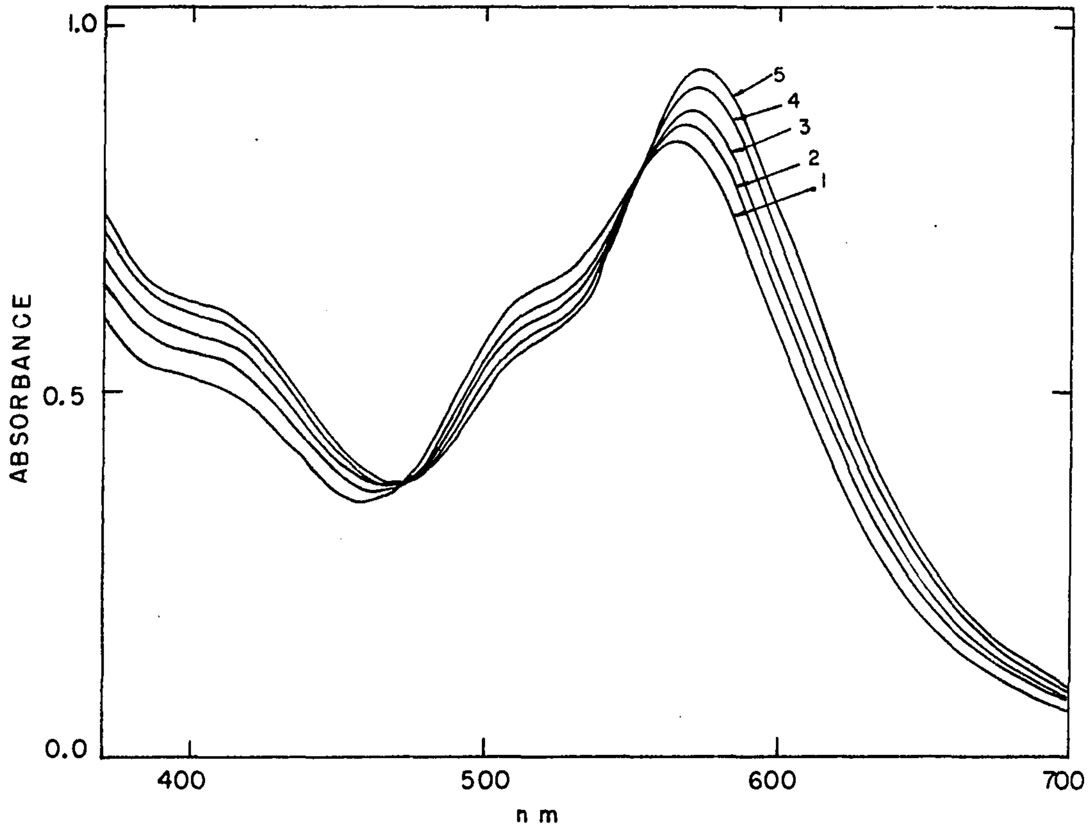

Figure I-2. Visible spectrum of $Mo_2Cl_4[P(C_6H_5)_3]_2(CH_3OH)_2$ (1.4×10^{-3} M, ℓ = 1 cm) with added triphenylphosphine. Concentration of triphenylphosphine: 1 = 0.0 M, 2 = 1.1×10^{-3} M, 3 = 2.3×10^{-3} M, 4 = 4.6×10^{-3} M, 5 = 8.0×10^{-3} M loss of methanol upon dissolution of the dimer in benzene to give $[MoCl_2(P\phi_3)]_n$ is consistent with the lability seen in methanol solution.

The structure of $Mo_2Cl_4[P(C_6H_5)_3]_2(CH_3OH)_2$ is basically the same as other quadruply bonded dimers. Although the hydrogen atoms of the methanol ligands cannot be confirmed crystallographically, the infrared spectrum shows ν(O-H) stretching bands. In addition, the Mo-Mo distance of 2.143(1)Å and the eclipsed ligand configuration are both indicative of a quadruple metal-metal bond and thus Mo(II). The steric congestion caused by triphenylphosphine appears to be the main reason for the dimer's affinity for methanol over additional phosphine ligands.

It is significant that the Mo-O bond is longer than one would expect from the sums of covalent radii. An estimate of 1.41Å is obtained for the covalent radius of molybdenum by subtraction of the radius of chlorine (0.99Å) from the mean Mo-Cl distance (1.40Å). The anticipated Mo-O bond length is then equal to the sum of the molybdenum and oxygen (0.66Å) radii, or approximately 2.07Å. This is 0.14Å shorter than the observed distance (28). Similarly, the large Mo'-Mo-O angle (113.7°) may reflect the weakness of the Mo-O bond as compared to the Mo-P bond whose Mo'-Mo-P angle is more acute (97.6°). The presence of a long, weak molybdenum-methanol bond is consistent with the solution behavior of the dimer. It is interesting to note that the quadruply bonded dimer, $Mo_2Br_6(H_2O)_2^{2-}$, contains a long Mo-O bond of 2.18(1)Å, and the Mo-Mo-O angle (107°) also somewhat larger than the Mo-Mo-Br angle (99.8°) (29). Complete loss of water from this compound can be achieved by heating to 150°C, which also shows the weakness of the Mo-O interaction.

Attempts thus far to prepare analogous $Mo_2Cl_4(PR_3)_2(CH_3OH)_2$ complexes by reacting $Mo_2Cl_8{}^{4-}$ with two equivalents of phosphine in methanol have failed. In the case where R = cyclohexylphosphine, the steric bulk is apparently so great that the phosphine acts merely as a proton acceptor in the production of $[MoCl(OCH_3)]_n$. Another non-coordinating base, tri-n-butylamine, produces the same compound. In cases where R = C_2H_5 or n-C_4H_9, the tetrameric clusters, $Mo_4Cl_8(PR_3)_4$, are the only complexes isolated, although the existence of phosphine-methanol dimer intermediates cannot be discounted (30).

The tetrameric complexes, $Mo_4Cl_8(PR_3)_4$ (R = C_2H_5, n-C_3H_7, n-C_4H_9), were first produced by the substitution of trialkylphosphines for triphenylphosphine in $\{MoCl_2[P(C_6H_5)_3]\}$. The structural data for $Mo_4Cl_8[P(C_2H_5)]_4$ are presented in Tables I-6, 7 and 8 (12). The clusters have a rectangular geometry as shown in Figure I-3 where the short Mo-Mo distance is 2.211(3)Å, and the long distance is 2.901(2)Å. Each long edge of the rectangle is bridged by two chlorine atoms. It is noteworthy that in the triethylphosphine derivative, the two phosphine ligands located along the long edge of the rectangle are both either above or below the plane of the cluster, while in the tri-n-butylphosphine derivative (12), the phosphines alternate up and down around the ring. Thus, the triethylphosphine tetramer has effectively C_{2h} symmetry while the tri-n-butylphosphine tetramer is D_2. The reasons for this discrepancy are not apparent, although the greater space-filling requirements of $P(n\text{-}C_4H_9)_3$ may be involved.

Table I-6. Positional parameters (x10^4) for $Mo_4Cl_8[P(C_2H_5)_3]_4$[a]

Atom	x	y	z
Mo(1)	941(1)	5119(2)	1500(1)
Mo(2)	1391(2)	4809(2)	279(1)
Cl(1)	2281(5)	6290(5)	2955(5)
Cl(2)	2877(5)	3514(5)	947(5)
Cl(3B)	447(5)	6204(4)	8989(4)
Cl(4B)	214(5)	3311(5)	9249(5)
P(1)	2081(5)	3766(5)	3037(5)
P(2)	2982(5)	6136(5)	902(5)
C(1A1)	1639(24)	2335(20)	2881(21)
C(1A2)	1716(21)	1752(21)	1974(22)
C(1B1)	3607(18)	3778(21)	3702(19)
C(1B2)	4268(24)	3093(37)	4754(23)
C(1C1)	1896(23)	4138(23)	4198(19)
C(1C2)	742(27)	4540(30)	3870(25)
C(2A1)	2593(39)	7619(37)	924(36)
C(2A2)	3472(44)	8383(43)	1463(40)
C(2B1)	4288(18)	5866(22)	2240(19)
C(2B2)	5380(25)	6199(38)	2418(28)
C(2C1)	3401(30)	6230(31)	9901(30)
C(2C2)	3054(44)	5510(48)	9097(43)

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

Table I-7. Thermal parameters ($\times 10^4$) for $Mo_4Cl_8[P(C_2H_5)_3]_4$ [a,b]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo(1)	69(2)	69(2)	56(1)	-2(1)	35(1)	-1(1)
Mo(2)	67(2)	67(1)	57(1)	0(1)	34(1)	0(1)
Cl(1)	94(5)	86(5)	81(5)	-18(4)	37(4)	-26(4)
Cl(2)	83(5)	82(5)	70(4)	23(4)	36(4)	3(3)
Cl(3)	74(4)	70(4)	71(4)	-8(3)	37(4)	8(3)
Cl(4)	85(5)	70(4)	82(5)	14(4)	35(4)	14(4)
P(1)	81(5)	86(5)	61(5)	5(4)	36(4)	14(4)
P(2)	81(5)	86(5)	70(5)	-21(4)	34(4)	7(4)
C(1A1)	135(28)	74(19)	110(24)	-9(19)	72(23)	-3(17)
C(1A2)	107(25)	86(21)	124(27)	46(19)	65(22)	51(19)
C(1B1)	58(17)	129(25)	80(19)	24(17)	42(15)	28(17)
C(1B2)	92(28)	293(55)	86(25)	61(33)	35(22)	52(30)
C(1C1)	120(26)	128(26)	80(20)	-6(21)	77(20)	1(18)
C(1C2)	119(31)	184(37)	123(29)	13(27)	79(26)	4(27)
C(2B1)	56(18)	122(24)	82(20)	-7(17)	25(17)	10(18)
C(2B2)	75(24)	329(63)	126(31)	-15(34)	57(24)	-22(37)
	B^c					
C(2A1)	12.0(12)					
C(2A2)	14.2(15)					
C(2C1)	9.5(9)					
C(2C2)	15.2(16)					

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

[b] B_{ij} are defined by $T = \exp[-(h^2\beta_{11} + k^2\beta_{22} + \ell^2\beta_{33} + 2hk\beta_{12} + 2h\ell\beta_{13} + 2K\ell\beta_{23})]$.

[c] Isotropic temperature factors, B, are given in $Å^2$.

Table I-8. Bond distances (Å) and angles (°) for $Mo_4Cl_8[P(C_2H_5)_3]_4$[a]

Distances

Mo(1)-Mo(2)	2.211(3)	P(1)-C(1A1)	1.880(27)
Mo(1)-Mo(2')	2.901(2)	P(1)-C(1B1)	1.845(24)
Mo(1)-Cl(1)	2.425(5)	P(1)-C(1C1)	1.890(35)
Mo(1)-P(1)	2.558(6)	P(2)-C(2A1)	1.947(49)
Mo(1)-Cl(4')	2.417(6)	P(2)-C(2B1)	1.850(19)
Mo(1)-Cl(3')	2.381(6)	P(2)-C(2C1)	1.842(54)
Mo(2)-Cl(2)	2.421(6)	C(1A1)-C(1A2)	1.553(49)
Mo(2)-P(2)	2.556(7)	C(1B1)-C(1B2)	1.542(41)
Mo(2)-Cl(3)	2.373(5)	C(1C1)-C(1C2)	1.532(49)
Mo(2)-Cl(4)	2.422(6)	C(2A1)-C(2A2)	1.431(70)
Cl(3)-Cl(4)	3.687(8)	C(2B1)-C(2B2)	1.495(48)
Cl(3)-Cl(4')	3.212(11)	C(2C1)-C(2C2)	1.334(72)

Angles (middle atom is vertex)

Mo(1)-Mo(2)-Mo(1')	90.58(10)
Mo(2)-Mo(1)-Mo(2')	89.41(8)
Cl(1)-Mo(1)-P(1)	79.60(19)
Cl(2)-Mo(2)-P(2)	83.04(22)
Mo(2)-Cl(3)-Mo(1')	75.21(17)
Cl(1)-Mo(1)-Mo(2)	111.26(23)
Cl(2)-Mo(2)-Mo(1)	111.80(19)
P(1)-Mo(1)-Mo(2)	104.51(21)
P(2)-Mo(2)-Mo(1)	101.04(21)
P(2)-Mo(2)-Cl(3)	79.20(19)
P(2)-Mo(2)-Cl(4)	155.66(30)
P(1)-Mo(1)-Cl(3')	80.19(19)
P(1)-Mo(1)-Cl(4')	152.74(28)
Cl(2)-Mo(2)-Cl(3)	144.19(30)
Cl(2)-Mo(2)-Cl(4)	83.60(20)
Cl(1)-Mo(1)-Cl(3')	145.04(28)
Cl(1)-Mo(1)-Cl(4')	85.36(19)
Mo(1')-Mo(2)-Cl(3)	52.50(14)
Mo(1')-Mo(2)-Cl(4)	53.09(14)
Mo(2)-Mo(1')-Cl(3)	52.27(12)
Mo(2)-Mo(1')-Cl(4)	53.23(13)
Cl(3)-Mo(2)-Cl(4)	100.47(18)
Cl(3)-Mo(1')-Cl(4)	100.40(20)
Mo(2)-Cl(4)-Mo(1')	73.66(17)

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[a] Estimated standard deviations are given in parentheses for the last significant figures.

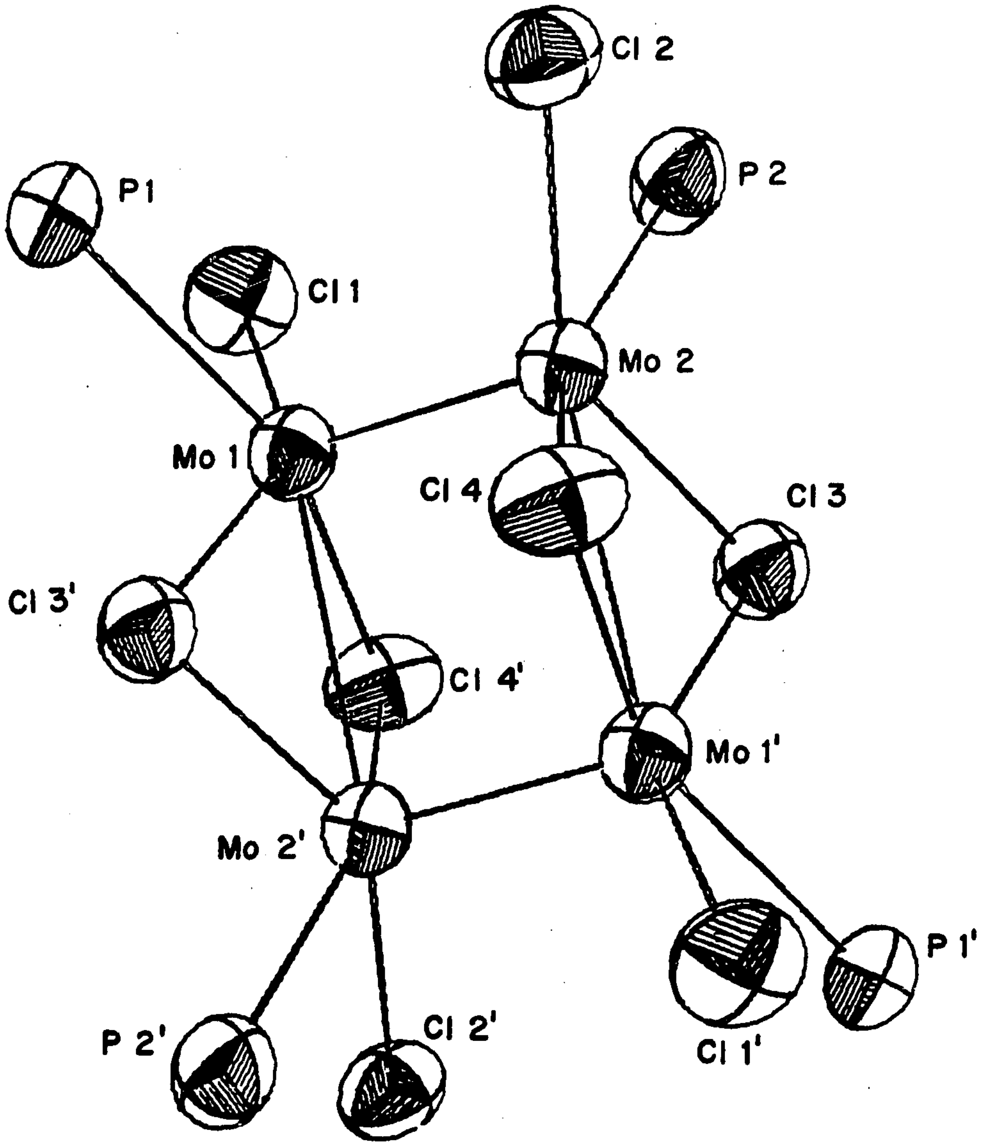


Figure I-3. Structure of the $Mo_4Cl_8[P(C_2H_5)_3]_4$ molecule with carbon atoms omitted. Atoms are represented by thermal ellipsoids scaled to 50% of the electron density

Figure I-3 shows how the two dimers have condensed to form a tetrameric cluster. It is the bond formation between metal atoms across the long edge of the rectangle that distinguishes this molecule as a true cluster compound. The existence of the long metal-metal bond in this diamagnetic molecule is supported by the close approach of the molybdenum atoms, which at 2.901(2)Å is well within the range of 2.5Å to 3.2Å known for Mo-Mo single bonds (31). There is other structural evidence for bonding between metal atoms across the long dimension of the rectangle. First, the Mo-Cl-Mo bridge bond angles are acute and average only 74.4(2)°, while the Cl-Mo-Cl bridge bond angles are quite wide at 100.4(2)°. Second, the nonbonding contacts in the molecule (Figure I-4, Table I-8) are very short. Figure I-4 shows how the bridging chlorine atoms of the tetramers are pinched between the terminal chlorine and phosphine atoms. A comparison with the nonbonding distances in $K_4Mo_2Cl_8$ (32) shown in Figure I-4 reveals the magnitude of the steric crowding in the tetramer. The extremely close contacts are much less than the sums of the van der Waals radii of the atoms (33) and suggest that the terminal ligands are being forced toward the bridging chlorine atoms. This crowding may also be responsible for the unusual situation where the average bridging Mo-Cl distance (2.40Å) is shorter than the average terminal Mo-Cl distance (2.42Å). Finally, Figure I-5 shows how the pairs of dimers are displaced from the centers of the rectangular box of ligand atoms which encloses each dimer unit. The simplest explanation of these facts is that the two dimer units of the cluster are being drawn together by the attractive force of Mo-Mo bonds.

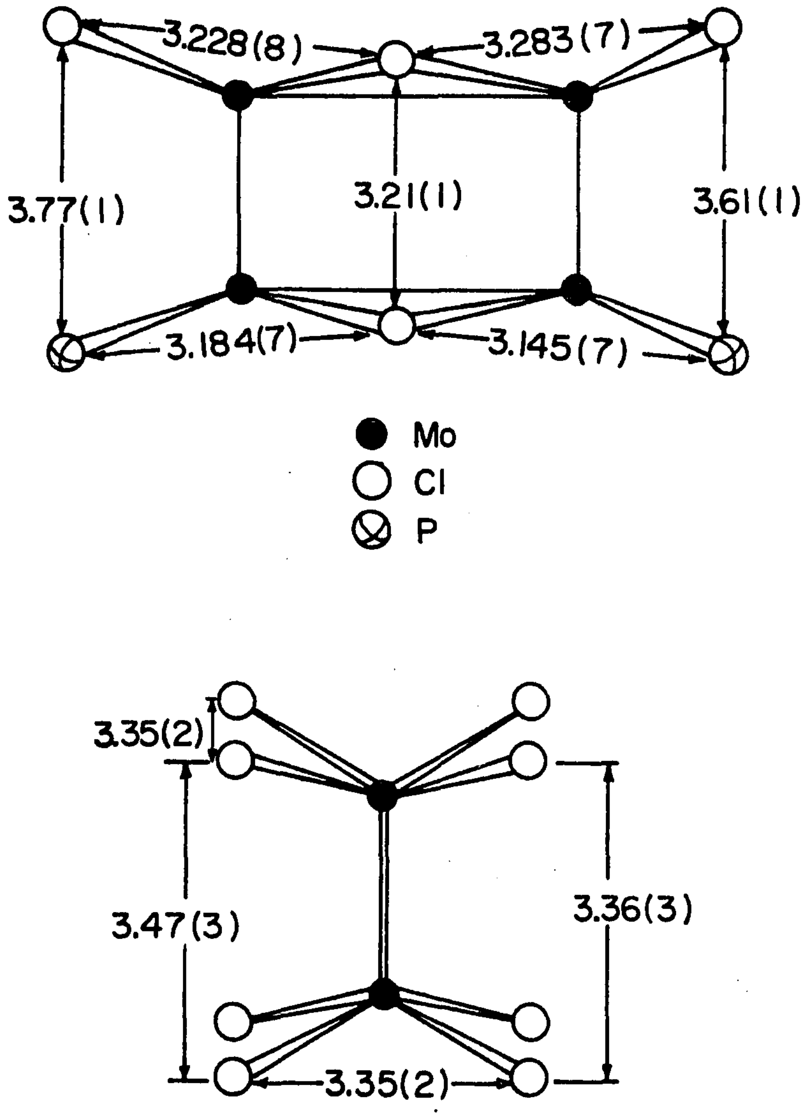


Figure I-4. Nonbonding contacts (Å) in $Mo_4Cl_8[P(C_2H_5)_3]_4$ and $K_4Mo_2Cl_8 \cdot 2H_2O$

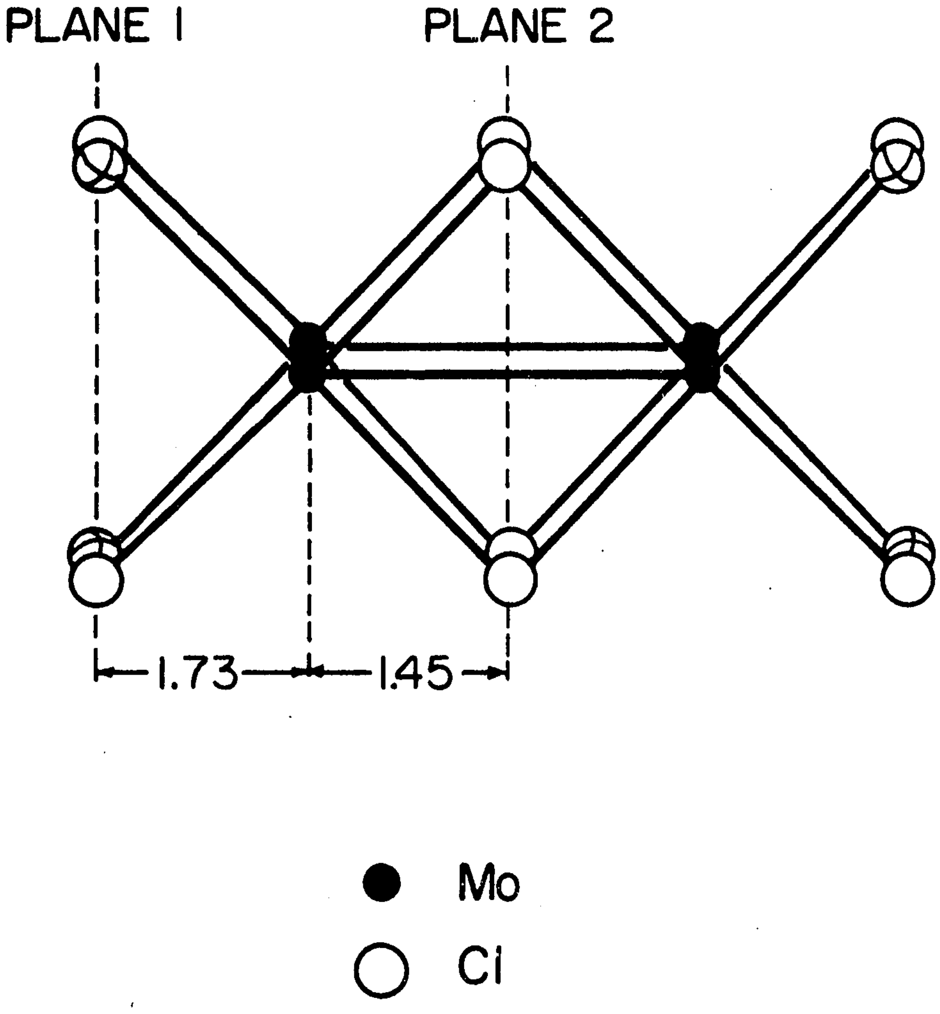


Figure I-5. Distances (Å) of molybdenum atoms from least-squares planes in $Mo_4Cl_8[P(C_2H_5)_3]_4$. Angle between Plane 1 and Plane 2 is 0.7°

In addition to the structural evidence, the visible absorption spectra of the tetramers (Table I-3, Figure I-6) do not exhibit any strong peaks above 450 nm as would be expected for the $\delta \rightarrow \delta^*$ transition in quadruply bonded dimers. In view of the structural similarity of the dimer units in the tetramer to the structures of independent dimers, a $\delta \rightarrow \delta^*$ transition is expected, and its absence suggests that these orbitals have been disrupted in some way.

In fact, the orientation of the δ-type orbitals of the dimer units makes them the most likely orbitals to be involved in Mo-Mo bonding across the long edge of the tetramer. These orbitals are sketched in Figure I-7. On each metal atom, one of the lobes of each orbital extends directly toward the molybdenum atom opposite to it on the long edge of the tetramer. Thus, the poor overlap of a δ bond is exchanged for a stronger σ-type interaction. The σ and π orbitals originally present in the quadruply bonded dimers are assumed to be relatively unchanged in the tetramer. The possible linear combinations for the metal orbitals are shown in Figure I-7. They consist of bonding and antibonding components of σ and δ character. The resulting change in the molecular orbitals on going from dimer to tetramer is diagrammed in Figure I-7. Since the δ component of the bonding is expected to be less important than the σ component, the tetramer is considered to possess a triple metal-metal bond along the short edge of the rectangle ($1\sigma, 2\pi$) and a single metal-metal bond along the long edge (1σ). The short Mo-Mo bond distance of 2.211(3)Å is comparable to the typical triple bond distances known for molybdenum (34), 2.167Å to 2.242Å, and as mentioned

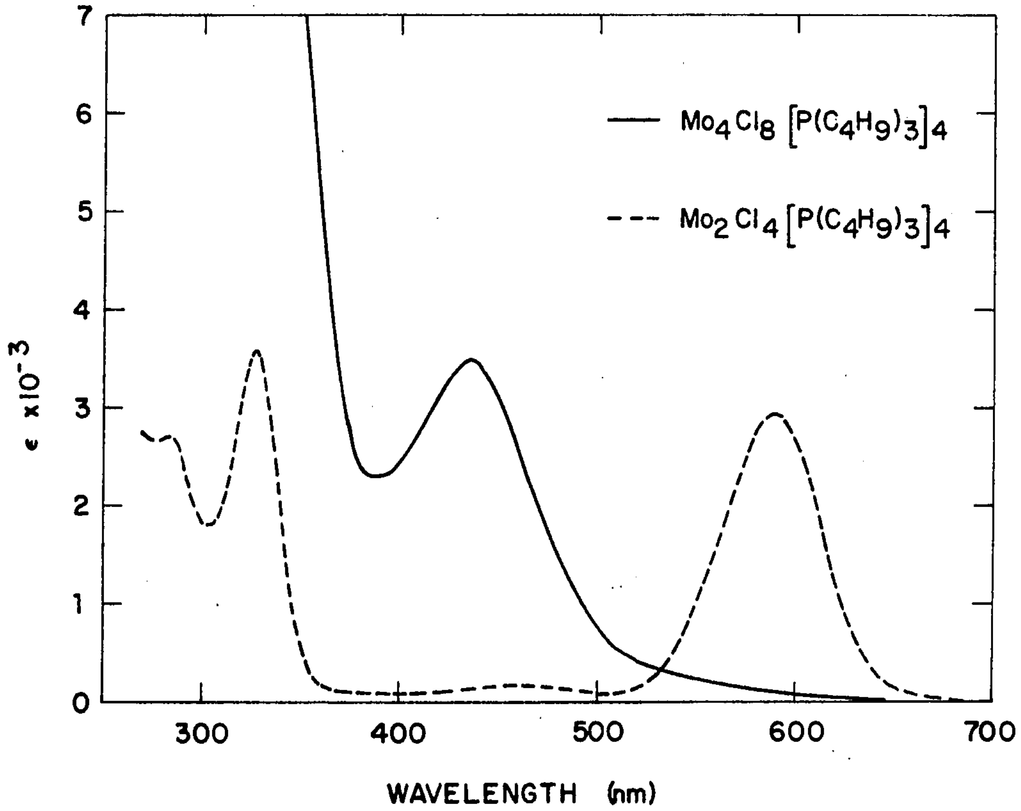


Figure I-6. Electronic absorption spectra of $Mo_2Cl_4[P(n\text{-}C_4H_9)_3]_4$ (---) and $Mo_4Cl_8[P(n\text{-}C_4H_9)_3]_4$ (——)

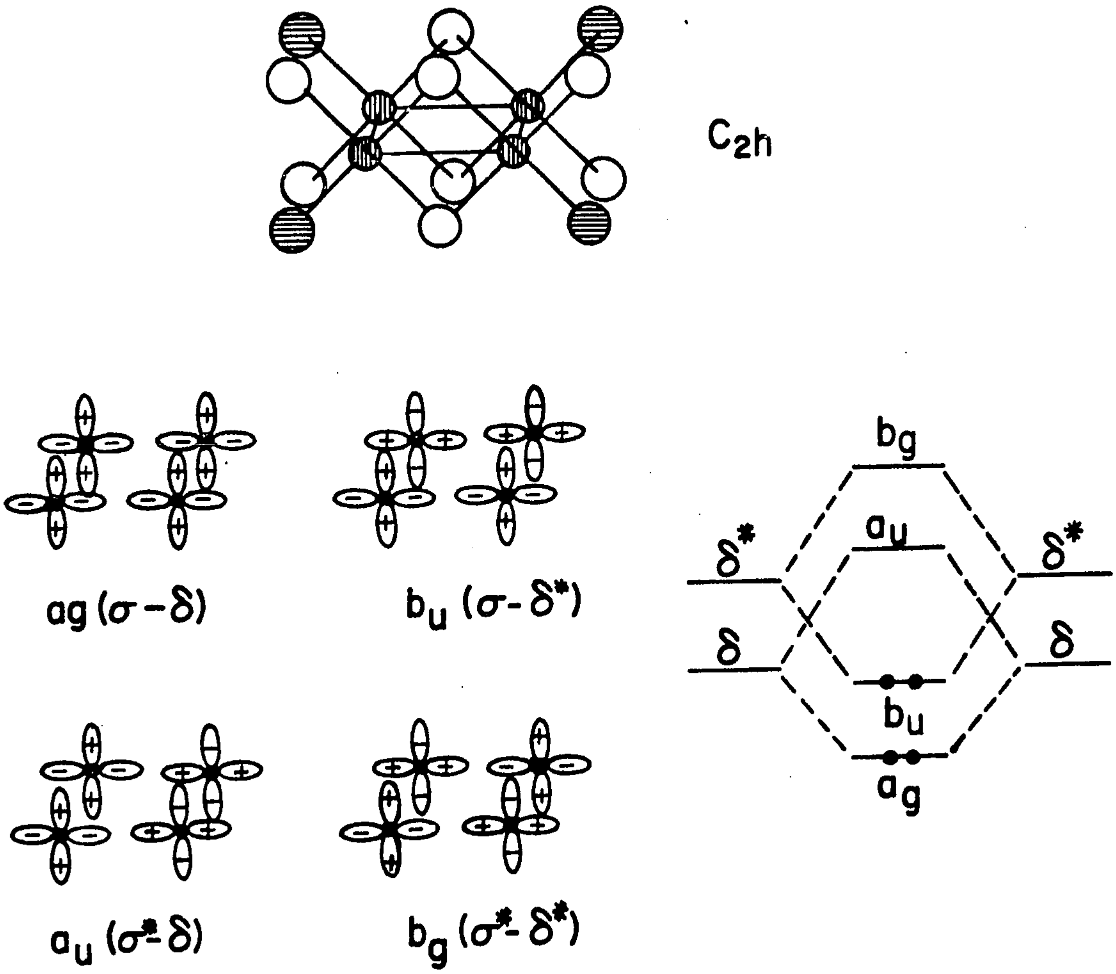
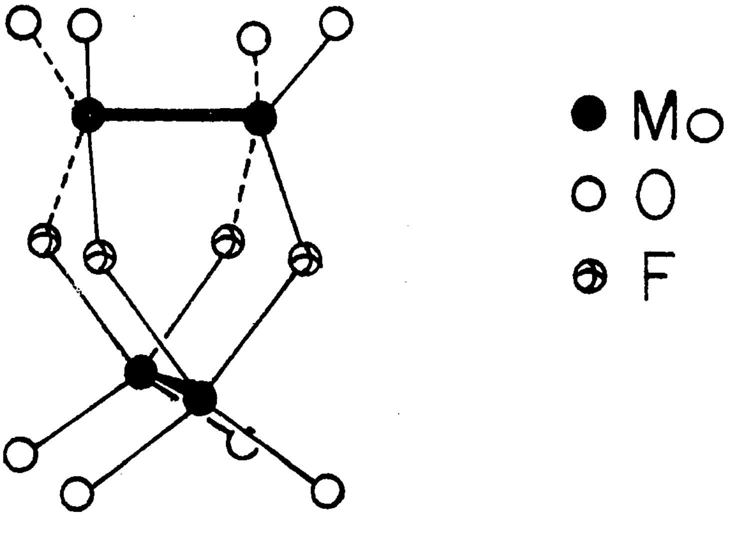


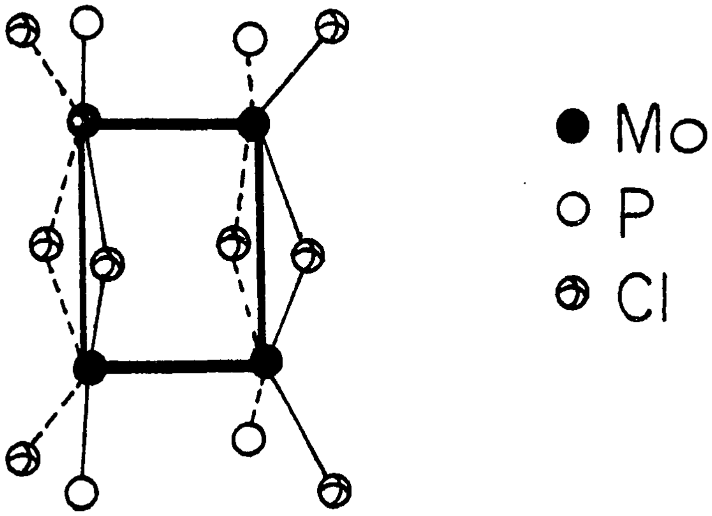
Figure I-7. Molecular orbital scheme for $Mo_4Cl_8L_4$

previously, the long Mo-Mo bond is within the realm of Mo-Mo single bonds. The reason for the loss of the $\delta \rightarrow \delta^*$ transition of the dimers is apparent from the molecular orbital diagram in Figure I-7. The actual band assignments of the complex absorption spectra of the tetramers is currently under investigation.

The stoichiometry of these tetrameric clusters is Mo_4X_{12} where X is a halide or neutral 2 electron donor ligand. Another molybdenum tetramer, $Mo_4F_4(O\text{-}bu^t)_8$, has been isolated (35) with the same stoichiometry, but in this complex X is fluoride or alkoxide. Since the molybdenum has a formal oxidation state of +3, there are four less cluster bonding electrons than in the rectangular Mo(II) tetramers, and if $Mo_4F_4(O\text{-}bu^t)_8$ had a rectangular arrangement of the metal atoms as in $Mo_4Cl_8(PR_3)_4$, the σ bonds along the long edge of the rectangle would necessarily be absent. Actually, $Mo_4F_4(O\text{-}bu^t)_8$ is not rectangular, but rather the metal atoms form a tetrahedron elongated along one of the two-fold axes. The disposition of the ligands is surprisingly similar to that in $Mo_4Cl_8(PR_3)_4$ with eight terminal groups and four bridging groups linking the triply bonded dimers as shown in Figure I-8. The distances between the dimeric units in the Mo(III) compound (av. long Mo-Mo distance is 3.72Å) exclude any bonding interaction between the two dimeric units, and the Mo-F-Mo angles (av. 124°) suggest that the dimeric units may actually repel each other. The minimization of this repulsion can be used as one rational for the tetrahedral structure, which positions the metal atoms further from each other than in a rectangular cluster where the metal atoms are held directly opposite



$Mo_4F_4(O\text{-}bu^t)_8$



$Mo_4Cl_8(PR_3)_4$

Figure I-8. Structures of $Mo_4F_4(O\text{-}bu^t)_8$ and $Mo_4Cl_8(PR_3)_4$. Ligands (o, ▨) in both diagrams have exactly the same placement, only the metal atoms (●) have been changed each other. The geometry of $Mo_4F_4(O\text{-}bu^t)_8$ lends support to the bonding picture suggested for $Mo_4Cl_8(PR_3)_4$ in that the long σ bonds would seem to be responsible for the rectangular geometry in the Mo(II) cluster. It is also interesting to note that the σ and π components of the triple bonds in $Mo_4F_4(O\text{-}bu^t)_8$ do not engage in delocalized cluster bonding even though the smaller van der Waals radii of the ligands would allow closer approach of the dimer units than in $Mo_4Cl_8(PR_3)_4$ (see Figure I-4). This is in accord with the assumption that these same σ and π bonds in the dimeric units of $Mo_4Cl_8(PR_3)_4$ are not greatly involved in bonding across the long edge of the rectangle. This last statement must be tempered by the recognition that the greater orbital extension in the Mo(II) cluster as compared with the Mo(III) species may allow more delocalization of bonding between the orbitals of the triple bonds in $Mo_4Cl_8(PR_3)_4$.

The scheme for the formation of $Mo_4Cl_8(PR_3)_4$ is presented in Figure I-9. The manner in which four ligands are displaced from the dimer and the actual mechanism of the condensation are unknown and probably fairly complex.

This self-addition of the dimer presents some interesting possibilities for further studies. The cyclic-addition of a molybdenum dimer with other unsaturated molecules such as acetylene and ethylene are of considerable interest in view of their catalytic implications. Similar cyclo-additions of other multiply bonded dimers should lead to analogous clusters of metals other than molybdenum, and the synthesis of mixed metal clusters is a likely proposition which deserves some investigation. Some of the problems will be addressed in future work.

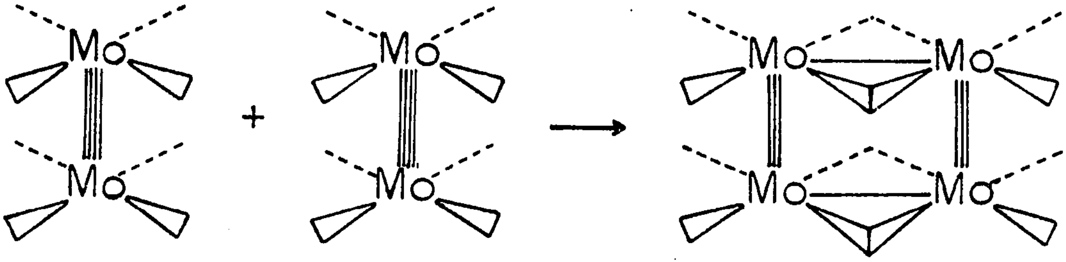


Figure I-9. Scheme for the formation of tetrameric cluster from two dimers

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SECTION II. PREPARATION AND CHARACTERIZATION OF TETRAMERIC CLUSTER COMPLEXES OF MOLYBDENUM

INTRODUCTION

The earlier preparation (1) of $Mo_4Cl_8(PR_3)_4$ from $Mo_2Cl_4[P(C_6H_5)_3]_2(CH_3OH)_2$ has prompted the development of better synthetic routes to these tetrameric clusters. Since the loss of methanol from the quadruply bonded dimer $Mo_2Cl_4[P(C_6H_5)_3]_2(CH_3OH)_2$ initiated the cyclo-addition of two dimers, the syntheses of other dimers containing coordinated methanol were attempted. Failure to isolate any new dimers has nevertheless led to the development of new shorter synthetic routes to known $Mo_4Cl_8(PR_3)_4$ (R = alkyl) clusters as well as preparation of new $Mo_4Cl_8L_4$ derivatives where L = CH_3OH, THF, RCN, $P(C_6H_5)_3$. The physical characterizations of these new clusters showed them to be structurally and electronically similar to the known $Mo_4Cl_8(PR_3)_4$ (R = alkyl) compounds (1).

The action of mild halogenating agents such as $AlCl_3$ and $(CH_3)_3SiX$ (X = Cl, Br, I) on $Mo_2(O_2CCH_3)_4$ has provided an even more direct route to the tetrameric clusters. Halogenation syntheses employ the same notion that in the absence of four strongly bonded ligands, L, in $Mo_2X_4L_4$ (X = halide), condensation to the tetramer readily occurs. These preparations have produced clusters of the type $Mo_4X_8(PR_3)_4$ (X = Cl, Br, I; R = alkyl).

EXPERIMENTAL

Materials

Samples were handled as described earlier (1).

Hydrocarbon solvents and methylene chloride were refluxed over $LiAlH_4$ or CaH_2 and vacuum distilled into glass bulbs for storage. Tetrahydrofuran was refluxed with copper(I) chloride to remove peroxides prior to treatment with CaH_2. Dry THF was then vacuum distilled onto Molecular Sieves (4Å) for storage. Propionitrile was refluxed over phosphorus pentoxide and distilled under a nitrogen atmosphere to a stoppered flask for storage. Methanol was treated as described earlier (1).

Aluminum chloride was purified by sublimation and handled under nitrogen in a drybox. The reagents $(CH_3)_3SiX$ (X = Cl, Br, I), were used as obtained from Aldrich Chemical Co., Milwaukee, Wisconsin.

Analyses were performed as described earlier (1).

Physical Measurements

Infrared and solution uv-visible spectra were obtained as described earlier (1). Diffuse reflectance spectra were obtained on powdered samples with a Beckman DU spectrophotometer fitted with a reflectance cell accessory, and samples were referenced against $MgCO_3$ or $BaSO_4$.

X-ray photoelectron spectra were obtained with an AEI-200B instrument using monochromatic Al Kα radiation (1486.6 ev).

Electrostatic charging of the samples during data collection was controlled with an electron flood gun. Approximately 400 scans were required to produce a spectrum with sufficient signal intensity. The photoelectron binding energy was referenced against the C 1s peak which was assigned a value of 285.0 ev (2). Component peaks in the observed spectra were resolved by least squares curve fitting using a computer program developed in this laboratory (3) which smoothed the data, corrected for inelastic electron scattering and fit the data to a specified number of peaks. The peak shape was governed by the selection or variation of the full width at half maximum and a linear combination of Gaussian and Cauchy functions.

Syntheses

Molybdenum dimers

$Mo_2(O_2CCH_3)_4$ (4), $(NH_4)_5Mo_2Cl_9 \cdot H_2O$ (5), $K_4Mo_2Cl_8$ (6), $(NH_4)_4Mo_2(SO_4)_4 \cdot 2H_2O$ (7), $Mo_2Cl_4[P(C_2H_5)_3]_4$ (8), and $Mo_2Cl_4[P(C_6H_5)_3]_2(CH_3OH)_2$ (1) were prepared by established procedures.

$(NH_4)_4Mo_2Br_8$

This compound was prepared using the method of Brencic *et al.* (7) with slight modification. $(NH_4)_4Mo_2(SO_4)_4 \cdot 2H_2O$ (5.60 g, 8.64 mmol) was added to 47 mL of 48% HBr, and the resulting solution was cooled to -20°C for one hour. The violet product (obtained in 40% yield) was filtered, washed with a few mL of cold 48% HBr solution, and dried under vacuum. A Debye-Scherrer x-ray powder pattern confirmed the identity of the product. Anal. Calcd. for $(NH_4)_4Mo_2Br_8$: Br, 71.6; N, 6.20; H, 1.81. Found: Br, 70.8; N, 6.16; H, 1.78.

$Mo_4Cl_8(CH_3OH)_4$

$Mo_2Cl_4[P(C_6H_5)_3]_2(CH_3OH)_2$ (5.00 g, 5.42 mmol) was added to 50 mL cyclohexane (n-hexane or decalin also have been used). A 20 mL aliquot of anhydrous methanol which had been made 0.40 - 0.50 M in HCl was added to the cyclohexane mixture, and the solution was brought to reflux under a nitrogen atmosphere. After one hour, an insoluble yellow product developed; this was filtered, washed with 30 mL methanol, and dried under vacuum. The yield was 90%. Anal. Calcd. for $Mo_4Cl_8(CH_3OH)_4$: Mo, 48.24; Cl, 35.7; C, 6.03; H, 2.01. Found: Mo, 48.15; Cl, 35.0; C, 6.07; H, 2.08.

The oxidation state of molybdenum in this compound was determined by digestion of a sample in standard acidic Ce(IV) solution followed by titration of excess Ce(IV) with standard Fe(II) solution. A molybdenum oxidation state of 2.1 ± 0.1 was obtained.

$Mo_4Cl_8(CH_3CH_2CN)_4$

$Mo_4Cl_8(CH_3OH)_4$ (2.00 g, 2.51 mmol) was stirred with 20 mL propionitrile under nitrogen for one day to produce a bright yellow solid which was filtered and washed with propionitrile and diethyl ether. The product was vacuum dried at 25°C. The yield was 93%. Anal. Calcd. for $Mo_4Cl_8(CH_3CH_2CN)_4$: Mo, 43.23; Cl, 31.95; C, 16.24; N, 6.31; H, 2.23. Found: Mo, 42.90; Cl, 31.46; C, 16.04; N, 6.10; H, 2.27.

$Mo_4Cl_8(C_4H_8O)_4$

$Mo_4Cl_8(CH_3CH_2CN)_4$ (0.50 g, 0.56 mmol) was extracted *in vacuo* with tetrahydrofuran for four days. The collection flask of the extraction apparatus was then cooled to 0°C for one day in order to distill excess solvent from the residue left undissolved by the tetrahydrofuran. Soluble material which had been transferred to the collection flask was discarded. The insoluble residue was rapidly weighed for analysis to minimize loss of tetrahydrofuran from the sample. *Anal.* Calcd. for $Mo_4Cl_8(C_4H_8O)_4$: Mo, 40.15; Cl, 29.67. Found: Mo, 41.30; Cl, 30.56.

$Mo_4Cl_8[P(C_6H_5)_3]_4$

$Mo_4Cl_8(CH_3CH_2CN)_4$ (0.80 g, 0.90 mmol) was stirred under nitrogen with a solution of triphenylphosphine (2.00 g, 7.62 mmol) in 25 mL tetrahydrofuran. The product was filtered from the solution after 24 hours, and an IR spectrum was obtained in order to monitor the loss of propionitrile from the compound. When propionitrile could no longer be detected (generally 3 to 4 days were required), the orange-yellow product was filtered, washed with THF, and dried under vacuum. The yield was 60%. *Anal.* Calcd. for $Mo_4Cl_8[P(C_6H_5)_3]_4$: Mo, 22.36; Cl, 16.52; C, 50.38; H, 3.33. Found: Mo, 22.45; Cl, 16.50; C, 50.26; H, 3.39.

$Mo_2Cl_2(O_2CCH_3)_2[P(C_6H_5)_3]_2$

$Mo_2(O_2CCH_3)_4$ (1.00 g, 2.33 mmol), aluminum chloride (1.30 g, 9.75 mmol), and triphenylphosphine (6.10 g, 23.0 mmol) were refluxed in

15 mL tetrahydrofuran under nitrogen. After two days, a bright pink compound was filtered from the solution and washed with THF and methanol. The product was dried under vacuum at 25°C. The yield was 80%. Anal. Calcd. for $Mo_2Cl_2(O_2CCH_3)_2[P(C_6H_5)_3]_2$: Cl, 7.83; C, 53.06; H, 4.01. Found: Cl, 7.84; C, 53.00; H, 3.99.

$Mo_4Cl_8(PR_3)_4$

A number of different syntheses have been developed. Product identification was established in some cases by comparison of infrared and uv-visible spectra with authentic samples (1).

(a) The tetramer may be obtained from either $Mo_4Cl_8(CH_3OH)_4$ or $Mo_4Cl_8(CH_3CH_2CN)_4$ by ligand substitution reactions. In a typical preparation, $Mo_4Cl_8(CH_3CH_2CN)_4$ (1.06 g, 1.19 mmol) and triethylphosphine (0.80 g, 6.77 mmol) were stirred at 25°C for six hours in 30 mL cyclohexane. The yellow product was filtered from the blue solution and washed with cyclohexane. The yield was 89%. Anal. Calcd. for $Mo_4Cl_8[P(C_2H_5)_3]_4$: Mo, 33.65; Cl, 24.87; C, 25.28; H, 5.30. Found: Mo, 33.45; Cl, 24.19; C, 24.74; H, 5.10.

(b) $K_4Mo_2Cl_8$ (2.00 g, 3.17 mmol) and tri-n-butylphosphine (1.28 g, 6.33 mmol) were refluxed in 15 mL methanol for one day to produce an orange solid which was filtered and washed with methanol. This was then dissolved in toluene and filtered to separate the soluble cluster from unreacted $K_4Mo_2Cl_8$ and KCl. The toluene solution was evaporated to dryness under vacuum at 25°C to produce a yellow-brown solid which was washed with diethyl ether until the wash was pale yellow. The yield of dry $Mo_4Cl_8[P(C_4H_9)_3]_4$ was 70%. <u>Anal</u>, Calcd. for $Mo_4Cl_8[P(C_4H_9)_3]_4$: C, 39.04; H, 7.37. Found: C, 38.31; H, 7.10.

Substitution of triethylphosphine for tri-n-butylphosphine provided a less soluble product which could not easily be separated from potassium salts left in the reaction. The KCl-$K_4Mo_2Cl_8$ mixture was, therefore, removed by washing the crude product with a 50% methanol-water solution. The product was then washed with methanol and diethyl ether. The yield was 60%. <u>Anal</u>. Found: C, 25.05; H, 5.20.

A preparation of $Mo_4Cl_8[P(n\text{-}C_4H_9)_3]_4$ from $(NH_4)_5Mo_2Cl_9 \cdot H_2O$ and tri-n-butylphosphine was achieved by reaction in methanol at 25°C. The yield was 50% for tri-n-butylphosphine, but the triethylphosphine tetramer could not be isolated under these conditions.

(c) $Mo_2(O_2CCH_3)_4$ (3.00 g, 7.01 mmol), tri-n-butylphosphine (2.84 g, 14.0 mmol), and aluminum chloride (1.87 g, 14.0 mmol) were refluxed in 20 mL tetrahydrofuran for one day. The solution was cooled and 70 mL methanol was added to precipitate a yellow product. After washing well with methanol and diethyl ether, the product was dried under vacuum at 25°C. The yield was 41%.

Substitution of triethylphosphine for tri-n-butylphosphine provided $Mo_4Cl_8[P(C_2H_5)_3]_4$ in 51% yield (9).

(d) $Mo_2(O_2CCH_3)_4$ (1.00 g, 2.33 mmol), triethylphosphine (0.56 g, 4.74 mmol), and $(CH_3)_3SiCl$ (2.03 g, 18.6 mmol) were reacted in 15 mL refluxing tetrahydrofuran for one day. The yellow product obtained in 40% yield was filtered and washed with diethyl ether.

(e) $Mo_2Cl_4[P(n\text{-}C_4H_9)_3]_4$ (0.53 g, 0.46 mmol) and $Mo(CO)_6$ (0.12 g, 0.45 mmol) were dissolved in 10 mL chlorobenzene. Heating the solution rapidly to reflux caused the blue solution to quickly turn brown. After one hour, the chlorobenzene was removed by vacuum distillation at approximately 100°C, and the brown residue was extracted _in vacuo_ with hexane to produce brown crystalline $Mo_4Cl_8[P(n\text{-}C_4H_9)_3]_4$ in the collection flask. The yield was 44%, but the IR spectrum of the product showed that a trace of $Mo(CO)_4[P(n\text{-}C_4H_9)_3]_2$ contaminated this sample.

$Mo_4Br_8[P(n\text{-}C_4H_9)_3]_4$

(a) $(NH_4)_4Mo_2Br_8$ (4.00 g, 4.43 mmol) and tri-n-butylphosphine (1.79 g, 8.85 mmol) were mixed together in 25 mL methanol at 0°C, and after six hours the methanol was removed by vacuum distillation while keeping the solution cool. The residue was stirred with 15 mL benzene and filtered to remove $(NH_4)_4Mo_2Br_8$ and NH_4Br from the soluble product. The benzene was then removed by vacuum distillation, and the dark green solid remaining was redissolved in a minimum of benzene (approximately 4 mL). Twenty mL methanol were added to precipitate a brown solid which was filtered and washed with acetone. The resulting rust-colored product was obtained in 40% yield. _Anal_. Calcd. for $Mo_4Br_8[P(C_4H_9)_3]_4$: Mo, 20.94; Br, 34.89; C, 31.46; H, 5.94. Found: Mo, 20.82; Br, 34.61; C, 31.56; H, 6.01.

(b) $Mo_2(O_2CCH_3)_4$ (1.00 g, 2.33 mmol), tri-n-butylphosphine (0.94 g, 4.66 mmol), and $(CH_3)_3SiBr$ (1.62 g, 10.6 mmol) were stirred together in 15 mL methylene chloride for one day. The solvent was then reduced by vacuum distillation to about 5 mL and 20 mL of methanol was added to precipitate the rust-colored product. The yield was approximately 20%. The uv-visible and infrared spectra of this compound were identical to the spectra obtained for the compound isolated in Part (a).

$Mo_4I_8[P(n\text{-}C_4H_9)_3]_4$

$Mo_2(O_2CCH_3)_4$ (1.00 g, 2.33 mmol) and tri-n-butylphosphine (0.94 g, 4.66 mmol) were stirred in 15 mL methylene chloride which had been cooled to 0°C. After addition of $(CH_3)_3SiI$ (3.66 g, 18.3 mmol), the mixture was stirred under nitrogen for one day at 0°C. Removal of solvent by vacuum distillation produced a dark green residue which was extracted *in vacuo* with diethyl ether for one day. A dark green crystalline product developed in the collection flask and was isolated in 21% yield. *Anal*. Calcd. for $Mo_4I_8[P(C_4H_9)_3]_4$: I, 45.97; C, 26.11; H, 4.93. Found: I, 46.51; C, 25.58; H, 4.53.

RESULTS

Dissociation of coordinated methanol from $Mo_2Cl_4[P(C_6H_5)_3]_2(CH_3OH)_2$ has led to the formation of the tetrameric clusters described earlier

$$2Mo_2Cl_4[P(C_6H_5)_3]_2(CH_3OH)_2 \xrightarrow{\text{benzene}} \xrightarrow{PR_3} Mo_4Cl_8(PR_3)_4 + 4CH_3OH$$

(1). Loss of triphenylphosphine from this same dimer has produced the new cluster, $Mo_4Cl_8(CH_3OH)_4$. Dissociation of the phosphine was

$$2Mo_2Cl_4[P(C_6H_5)_3]_2(CH_3OH)_2 \xrightarrow{\qquad\qquad} Mo_4Cl_8(CH_3OH)_4 + 4P(C_6H_5)_3$$

promoted by carrying out the reaction in a two phase solvent system of methanol-cyclohexane. As the triphenylphosphine was liberated from the dimer, it was removed from the reaction by extraction into the cyclohexane phase while the dimer remained in the methanol phase. The resulting product was found to contain no triphenylphosphine, but solvolysis was a problem, as was shown by the appearance of methoxide bands in the infrared spectrum. Insolubility of the product made purification by recrystallization impossible, but fortunately, it was found that addition of HCl to the reaction effectively inhibited the methoxide formation. The concentration of the HCl was kept in a range that prevented solvolysis, yet did not give triphenylphosphonium salts in the product.

The yellow, microcrystalline product, $Mo_4Cl_8(CH_3OH)_4$, had the same stoichiometry ($Mo_4Cl_8L_4$) as the previously isolated tetramers. An infrared spectrum of the compound showed bands arising from coordinated methanol (10), $\nu(OH)$ 3360 cm^{-1}, 1112 cm^{-1}, $\nu(CO)$ 990 cm^{-1}, and the far infrared spectrum (400 cm^{-1} to 200 cm^{-1}) displayed a number of bands due to Mo-Cl vibrations (Table II-1). It is noteworthy that the tetrameric clusters, $Mo_4Cl_8(PR_3)_4$, also exhibited similarly complex spectra in the far infrared.

The Cl 2p XPS of $Mo_4Cl_8(CH_3OH)_4$ was found to be complicated by the apparent decomposition of the compound in the spectrometer. Loss of methanol from the sample was evidenced by an increase in the pressure in the sample chamber when the sample was irradiated with the x-ray beam. Reliable spectra could not be obtained for this compound. This lability of the methanol was also demonstrated by the loss of methanol from the solid when heated <u>in vacuo</u> at 150-200°C. The residue remaining contained no methanol (shown by its infrared spectrum), and the Debye-Scherrer x-ray powder pattern was identical to the diffuse pattern known for β-$MoCl_2$ (11).

$$Mo_4Cl_8(CH_3OH)_4 \xrightarrow{\Delta} 4\ \beta\text{-}MoCl_2 + 4\ CH_3OH$$

The methanol tetramer was easily converted back to quadruply bonded dimers by reaction with donor ligands. When stirred with pyridine for 12 hours at 25°C, a red precipitate was produced which was identified by infrared and uv-visible spectroscopy as the quadruply bonded dimer $Mo_2Cl_4(C_5H_5N)_4$ (12). Reactions of $Mo_4Cl_8(CH_3OH)_4$ with donor ligands

$$Mo_4Cl_8(CH_3OH)_4 + 8\ C_5H_5N \longrightarrow 2\ Mo_2Cl_4(C_5H_5N)_4 + 4\ CH_3OH$$

could also be limited to simple ligand substitutions. When the amount

Table II-1. Infrared spectra (cm^{-1}) of tetrameric clusters 200 cm^{-1} to 400 cm^{-1} (s = strong, m = medium, w = weak, sh = shoulder)

$Mo_4Cl_8(CH_3OH)_4$	$Mo_4Cl_8(CH_3CH_2CN)_4$	$Mo_4Cl_8(C_4H_8O)_4$
392 (m)	360 (s)	361 (m)
371 (s)	327 (w)	339 (s)
333 (m)	295 (s)	319 (m)
296 (s)	245 (w)	271 (s)
275 (sh)		240 (m)

$Mo_4Cl_8[P(C_6H_5)_3]_4$	$\{MoCl_2[P(C_6H_5)_3]\}_n$
366 (m)	364 (m)
343 (m)	340 (m)
318 (w)	321 (s)
304 (w)	299 (sh)
270 (m)	278 (s)
235 (w)	252 (w)

$Mo_4Cl_8[P(C_2H_5)_3]_4$	$Mo_4Cl_8[P(n\text{-}C_4H_8)_3]_4$
361 (s)	356 (s)
335 (m)	332 (m)
320 (m)	315 (m)
292 (m)	280 (s)
257 (s)	

$$Mo_4Cl_8(CH_3OH)_4 + 4L \longrightarrow Mo_4Cl_8L_4 + 4\ CH_3OH$$

of trialkylphosphine was limited to four equivalents of phosphine per equivalent of tetramer, there was nearly quantitative conversion to $Mo_4Cl_8(PR_3)_4$. Similarly, reactions of the methanol tetramer with weakly coordinating nitriles, RCN, at 25°C also produced tetrameric clusters, $Mo_4Cl_8(RCN)_4$. In the case of acetonitrile, incomplete substitution of CH_3CN for methanol prevented isolation of the pure $Mo_4Cl_8(CH_3CN)_4$ compound.

The $Mo_4Cl_8(CH_3CH_2CN)_4$ cluster was found to possess many of the same properties as $Mo_4Cl_8(CH_3OH)_4$. This yellow, microcrystalline compound was also insoluble in most solvents and only slightly air sensitive. While the compound was found to be soluble to some extent in tetrahydrofuran, substitution of THF for CH_3CH_2CN occurred readily to produce complexes with mixed ligands (vide infra). The infrared spectrum of $Mo_4Cl_8(CH_3CH_2CN)_4$ exhibited the bands for coordinated propionitrile, ν(CN) 2280 cm^{-1}, and several Mo-Cl vibrations between 400 cm^{-1} and 200 cm^{-1} (Table II-1). The XPS data were plagued by the same decomposition problems as observed for $Mo_4Cl_8(CH_3OH)_4$.

Because the nitrile ligands were weakly coordinated, $Mo_4Cl_8(CH_3CH_2CN)_4$ was especially useful for preparing $Mo_4Cl_8L_4$ derivatives where L = trialkylphosphine, triphenylphosphine or tetrahydrofuran. As was the case for the methanol tetramer, trialkylphosphine

$$Mo_4Cl_8(CH_3CH_2CN)_4 + 4L \longrightarrow Mo_4Cl_8L_4 + 4\ CH_3CH_2CN$$

derivatives were obtained in nearly quantitative yields.

The tetrahydrofuran complex was synthesized by long extraction of $Mo_4Cl_8(CH_3CH_2CN)_4$ with THF which caused slow leaching of propionitrile from the compound and eventually produced a material in which THF had replaced the nitrile as the coordinated ligand. Coordinated THF in this complex was very labile, and the compound could not be vacuum dried at 25°C without complete loss of tetrahydrofuran from the compound. The residue remaining after drying in vacuo was identified as β-$MoCl_2$ by its Debye-Scherrer powder pattern. Because of the volatility of THF in $Mo_4Cl_8(C_4H_8O)_4$, analysis of this material was somewhat imprecise. By storing the compound in vacuum over liquid tetrahydrofuran at 0°C (vapor pressure of THF was approximately 65 mm), a dry sample was produced whose composition was close to the stoichiometry expected for a tetrameric cluster, $Mo_4Cl_8(C_4H_8O)_4$. The formulation as a tetramer was based mainly on the analytical data.

The THF derivative was dark brown in color and was slightly soluble in tetrahydrofuran. No trace of propionitrile remaining from the preparative reaction was found in the infrared spectrum, but there were strong bands due to THF at 1025 cm^{-1} and 860 cm^{-1}. The far infrared data are given in Table II-1, and again a complex series of Mo-Cl bonds typical of these tetrameric clusters is evident.

The triphenylphosphine derivative, $Mo_4Cl_8[P(C_6H_5)_3]_4$, could only be prepared via $Mo_4Cl_8(CH_3CH_2CN)_4$. In contrast to the rapid ligand substitution shown by trialkylphosphines, triphenylphosphine was slow to replace propionitrile from the complex. This difficulty in forming the triphenylphosphine derivative can probably be attributed to the lower basicity and increased steric hindrance of triphenylphosphine as compared to trialkylphosphines.

The triphenylphosphine complex was insoluble in noncoordinating solvents such as hexane or benzene. The infrared spectrum confirmed the absence of residual propionitrile in the compound, and only bands due to triphenylphosphine were observed above 400 cm^{-1} while the far infrared spectral data again showed a complex pattern (Table II-1).

The syntheses of the trialkylphosphine clusters, $Mo_4Cl_8(PR_3)_4$, from the quadruply bonded dimer, $Mo_2Cl_4[P(C_6H_5)_3]_2(CH_3OH)_2$, by reaction with benzene was the first method by which the tetrameric clusters were isolated. Unfortunately, this preparation gave low yields of the trialkylphosphine derivatives (e.g., 20-25%). Since the loss of two labile methanol ligands initiated the condensation reaction, the removal of any two strongly bonded neutral ligands from other quadruply bonded dimers also seemed a feasible route to the tetramers. To test this assumption, $Mo_2Cl_4[P(C_2H_5)_3]_4$ was reacted with $Mo(CO)_6$. In this reaction, the production of $Mo(CO)_4[P(C_2H_5)_3]_2$ and carbon monoxide gas were presumed (13), although no product identification was attempted. When a

$$2\ Mo_2Cl_4[P(C_2H_5)_3]_4 + 2\ Mo(CO)_6 \longrightarrow Mo_4Cl_8[P(C_2H_5)_3]_4 + 4\ CO$$
$$+ 2\ Mo(CO)_4[P(C_2H_5)_3]_2$$

stoichiometric amount of $Mo(CO)_6$ was used for the elimination of two equivalents of triethylphosphine per dimer, the product isolated was indeed identified as $Mo_4Cl_8[P(C_2H_5)_3]_4$ by infrared and uv-visible spectroscopy.

Another route to the desired phosphine clusters from $Mo_2Cl_4[P(C_6H_5)_3]_2(CH_3OH)_2$ involved the syntheses of $Mo_4Cl_8L_4$ clusters where L = methanol or propionitrile. Subsequent reaction with trialkylphosphines gave high yields of $Mo_4Cl_8(PR_3)_4$ clusters (80% from $Mo_2Cl_4[P(C_6H_5)_3]_2(CH_3OH)_2$), but this method was rather indirect.

In an effort to shorten the syntheses of the phosphine tetramers, an attempt was made to prepare $Mo_2Cl_4(PR_3)_2(CH_3OH)_2$ dimers where R = alkyl. These could then be conveniently converted to $Mo_4Cl_8(PR_3)_4$ by a reaction analogous to the one known for $Mo_2Cl_4[P(C_6H_5)_3]_2(CH_3OH)_2$.

$$2\ Mo_2Cl_4(PR_3)_2(CH_3OH)_2 \xrightarrow{\text{benzene}} Mo_4Cl_8(PR_3)_4 + 4\ CH_3OH$$

The attempted method of preparation of $Mo_2Cl_4(PR_3)_2(CH_3OH)_2$ was the same as the synthesis of $Mo_2Cl_4[P(C_6H_5)_3]_2(CH_3OH)_2$ where a $Mo_2Cl_8^{4-}$ salt was reacted with two equivalents of phosphine in methanol. However, the mixed ligand dimers were never isolated. Instead, the reaction produced the $Mo_4Cl_8(PR_3)_4$ clusters directly. While the yields of the cluster

$$2\ Mo_2Cl_8^{4-} + 4\ PR_3 \longrightarrow Mo_4Cl_8(PR_3)_4 + 8\ Cl^-$$

compounds were not exceptionally high, the use of readily available octachlorodimolybdate salts made this a major improvement in the syntheses of $Mo_4Cl_8(PR_3)_4$ complexes.

The reaction of trialkylphosphines with $Mo_2Cl_8^{4-}$ salts employed virtually the same conditions used for the preparation of $Mo_2Cl_4(PR_3)_4$ dimers from octachlorodimolybdate anions, except in the dimer syntheses an excess of phosphine had been used (14,15). Lowering the reaction ratio to two equivalents of phosphine per equivalent $Mo_2Cl_8{}^{4-}$ produced quite a dramatic difference in the products isolated. This reduction of the phosphine to dimer ratio has been applied to other reactions which were previously used for the syntheses of tetrakistrialkylphosphine dimers with the same results.

The most direct syntheses of $Mo_4Cl_8(PR_3)_4$ tetramers used $Mo_2(O_2CCH_3)_4$ as the starting material (16). Here, chlorinating agents such as $AlCl_3$ or $(CH_3)_3SiCl$ were used to displace acetate from the dimer and provide a source of halide. In the presence of excess trialkylphosphine, the $Mo_2Cl_4(PR_3)_4$ dimers were isolated in high yields.

$$Mo_2(O_2CCH_3)_4 + 4(CH_3)_3SiCl + 4\ PR_3 \longrightarrow Mo_2Cl_4(PR_3)_4 + 4(CH_3)_3Si(O_2CCH_3)$$

Reduction of the reaction ratio to two equivalents trialkylphosphine per equivalent $Mo_2(O_2CCH_3)_4$ again produced the desired $Mo_4Cl_8(PR_3)_4$ clusters.

$$2\ Mo_2(O_2CH_3)_4 + 8(CH_3)_3SiCl + 4\ PR_3 \longrightarrow Mo_4Cl_8(PR_3)_4 + 8(CH_3)_3Si(O_2CCH_3)$$

Use of triphenylphosphine in this reaction did not result in complete replacement of the acetate groups. Even with excess triphenylphosphine and long reaction times, only the mixed chloride-acetate dimer was produced. The infrared spectrum of the product

$$Mo_2(O_2CCH_3)_4 + 4\ AlCl_3 + 10\ P(C_6H_5)_3 \longrightarrow$$
$$Mo_2Cl_2(O_2CCH_3)_2[P(C_6H_5)_3]_2 + 2\ AlCl_2(O_2CCH_3) + 2\ AlCl_3 + 8\ P(C_6H_5)_3$$

showed the presence of bridging acetate ligands (17), $\nu(CO_2)$ 1480 cm^{-1}, 1435 cm^{-1}, as well as bands due to triphenylphosphine. The visible absorption spectrum in methylene chloride displayed a strong band at 525 nm ($\varepsilon = 2.2 \times 10^3\ M^{-1}\ cm^{-1}$) which was in agreement with the strong absorption at 524 nm known for the similar compound, $Mo_2Cl_2(O_2CC_6H_5)_2[P(C_4H_9)_3]_2$ (18).

The $Mo_4Cl_8(PR_3)_4$, R = alkyl, clusters were only slightly air sensitive and were soluble in a number of organic solvents including tetrahydrofuran, benzene, hexane, and methylene chloride. It appears that the strongly coordinated phosphines have provided these clusters with enhanced thermal stability. For example, the $Mo_4Cl_8[P(C_2H_5)_3]_4$ complex was stable in refluxing xylene (140°C), and a sample sealed in an evacuated tube was stable to 200°C. Accordingly, the problems associated with the XPS of $Mo_4Cl_8L_4$, L = CH_3OH, CH_3CH_2CN, were not important for this compound, and the Cl 2p XPS was obtained without significant decomposition of the sample. The triethyl- and tri-n-butylphosphine derivatives present complex far infrared spectra (400 cm^{-1} to 200 cm^{-1}), which are consistent with the many Mo-Cl and Mo-P stretching vibrations that are IR-active for these molecules (C_{2h}: 4 Au, 4 Bu; D_2: 4 B_1, 4 B_2, 4 B_3).

Some initial investigations into the reactivity of the phosphine tetramers were undertaken. Reactions with donor ligands resulted in the cleavage of the tetramers back to quadruply bonded dimers. When $Mo_4Cl_8[P(C_2H_5)_3]_4$ was refluxed with excess triethylphosphine in benzene, there was rapid formation of the blue $Mo_2Cl_4[P(C_2H_5)_3]_4$ dimer which was easily identified by its infrared and uv-visible spectra (12).

$$Mo_4Cl_8(PR_3)_4 + 4\ PR_3 \longrightarrow 2\ Mo_2Cl_4(PR_3)_4$$

Attempted oxidative cleavage with molecular hydrogen proved unsuccessful. Here, a THF or benzene solution of $Mo_4Cl_8[P(C_2H_5)_3]_4$ was reacted with hydrogen gas at 600 psi in a high pressure bomb at 60°C for 24 hours. No reaction was observed, and the tetramer was recovered nearly quantitatively. The attempted reduction of $Mo_4Cl_8[P(C_2H_5)_3]_4$ with four equivalents of sodium-mercury amalgam resulted in pyrophoric, amorphous products with nonstoichiometric Mo/Cl ratios. These materials were not investigated further.

The preparation of $Mo_4Cl_8(PR_3)_4$ clusters from $Mo_2Cl_8^{4-}$ salts immediately suggested that a simple route to the bromide analogs might be achieved by using $Mo_2Br_8^{4-}$. The bromide tetramer, $Mo_4Br_8[P(n\text{-}C_4H_9)_3]_4$, was isolated from a reaction modeled after the syntheses of tetramers from $Mo_2Cl_8^{4-}$. A major difference, however, was

$$2\ Mo_2Br_8^{4-} + 4\ PR_3 \longrightarrow Mo_4Br_8(PR_3)_4 + 8\ Br^-$$

the need to cool the bromide preparation in order to prevent the formation of molybdenum methoxide species. Isolated yields of

$Mo_4Br_8[P(n\text{-}C_4H_9)_3]_4$ were much smaller than for the chloride analog. The availability of $(CH_3)_3SiBr$ also made direct synthesis of $Mo_4Br_8[P(n\text{-}C_4H_9)_3]_4$ from $Mo_2(O_2CCH_3)_4$ possible. Again, yields were

$$2\ Mo_2(O_2CCH_3)_4 + 8(CH_3)_3SiBr + 4\ PR_3 \longrightarrow Mo_4Br_8(PR_3)_4 + 8(CH_3)_3Si(O_2CCH_3)$$

quite low, but the convenience of this one step synthesis from readily available $Mo_2(O_2CCH_3)_4$ made this the most useful route to the cluster.

As expected, $Mo_4Br_8[P(n\text{-}C_4H_9)_3]_4$ was very similar to the chloride analog in many of its physical properties. The compound was soluble in the same organic solvents, and was only slightly more air sensitive than $Mo_4Cl_8[P(n\text{-}C_4H_9)_3]_4$. The uv-visible spectrum (Figure II-1, Table II-2) was comparable to that of $Mo_4Cl_8[P(n\text{-}C_4H_9)_3]_4$, except for a red shift of about 20 nm. Shoulders at 370 mm and 490 mm in the bromide tetramer have corresponding weak absorptions in the chloride derivative which are more prominent in the single crystal (19) and diffuse reflectance spectra (Figure II-3). There were many bands in the infrared spectrum above 400 cm^{-1} due to the tri-n-butylphosphine, but in the region 400 cm^{-1} to 200 cm^{-1} only one band was observed at 270 cm^{-1}. This confirmed the assumption that for $Mo_4Cl_8(PR_3)_4$ most of the bands in this region were attributable to Mo-Cl vibrations. A Br 3p XPS of the tetramer was obtained, but overlapping of broad peaks did not allow a definitive spectral analysis. The Debye-Scherrer x-ray powder pattern of the bromide complex showed it to be isomorphous with

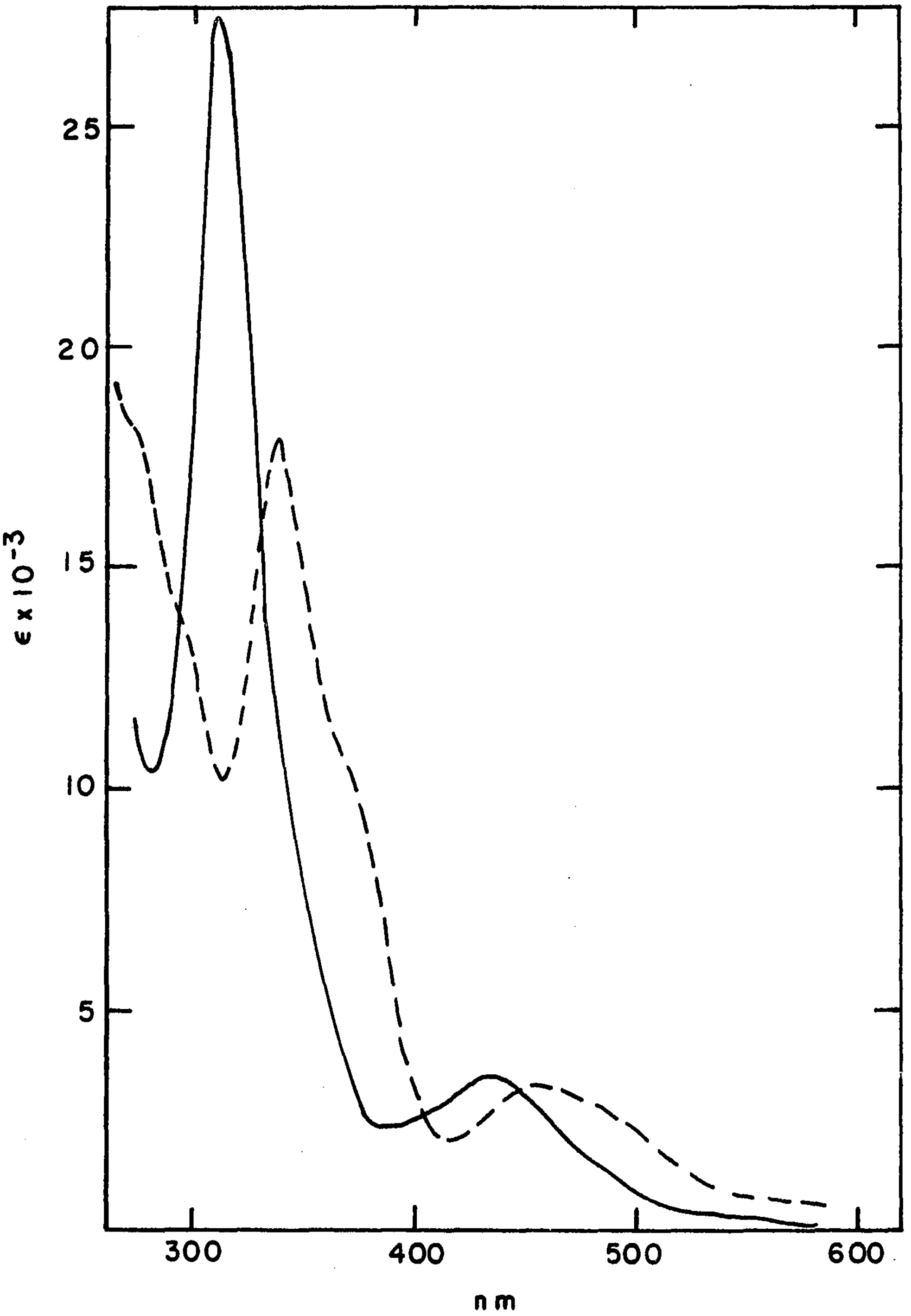

Figure II-1. Electronic absorption spectra of $Mo_4Cl_8[P(n\text{-}C_4H_9)_3]_4$ (——) and $Mo_4Br_8[P(n\text{-}C_4H_9)_3]_4$ (---) in hexane solution

Table II-2. Electronic absorption spectra of $Mo_4Cl_8[P(n\text{-}C_4H_9)_3]_4$ and $Mo_4Br_8[P(n\text{-}C_4H_9)_3]_4$[a]

$Mo_4Cl_8[P(n\text{-}C_4H_9)_3]_4$	$Mo_4Br_8[P(n\text{-}C_4H_9)_3]_4$
312 (2.8×10^4)	338 (1.8×10^4)
435 (3.5×10^3)	458 (3.3×10^3)
685 ($\sim$100)	613 (360)
	685 ($\sim$100)

[a] Values are given in nm followed by molar absorptivity, ε (M^{-1} cm^{-1}).

$Mo_4Cl_8[P(n\text{-}C_4H_9)_3]_4$ and thus was probably the best evidence of its tetrameric structure.

Since a compound containing the $Mo_2I_8^{4-}$ anion has not been isolated, the most feasible route to the $Mo_4I_8[P(n\text{-}C_4H_9)_3]_4$ cluster was by reaction of $Mo_2(O_2CCH_3)_4$ with $(CH_3)_3SiI$. A compound with the

$$2\ Mo_2(O_2CCH_3)_4 + 8(CH_3)_3SiI + 4\ PR_3 \longrightarrow Mo_4I_8(PR_3)_4 + 8(CH_3)_3Si(O_2CCH_3)$$

correct formulation was prepared, yet its physical characteristics were markedly different from the chloride and bromide tetramers. The compound was dark green while the other tetramers were without exception yellow to brown in color. The difference in the colors was due to a fairly strong absorption at 643 nm which was not present in the chloride or bromide tetramers (Figures II-1 and 2). In addition, a Debye-Scherrer powder pattern showed that the iodide derivative was not isomorphous with $Mo_4Cl_8[P(n\text{-}C_4H_9)_3]_4$. The infrared spectrum exhibited no bands in the 400 cm^{-1} to 200 cm^{-1} region.

The $Mo_4I_8[P(n\text{-}C_4H_9)_3]_4$ complex was found to be more air sensitive than either $Mo_4Cl_8[P(n\text{-}C_4H_9)_3]_4$ or $Mo_4Br_8[P(n\text{-}C_4H_9)_3]_4$, and the compound was handled under an inert atmosphere or on a vacuum line at all times. As in the case of $Mo_4Cl_8[P(n\text{-}C_4H_9)_3]_4$, the iodide cluster produced a quadruply bonded dimer, $Mo_2I_4[P(n\text{-}C_4H_9)_3]_4$, when reacted with excess tri-n-butylphosphine. The dimer was formed much more rapidly than in

$$Mo_4I_8(PR_3)_4 + 4\ PR_3 \longrightarrow 2\ Mo_2I_4(PR_3)_4$$

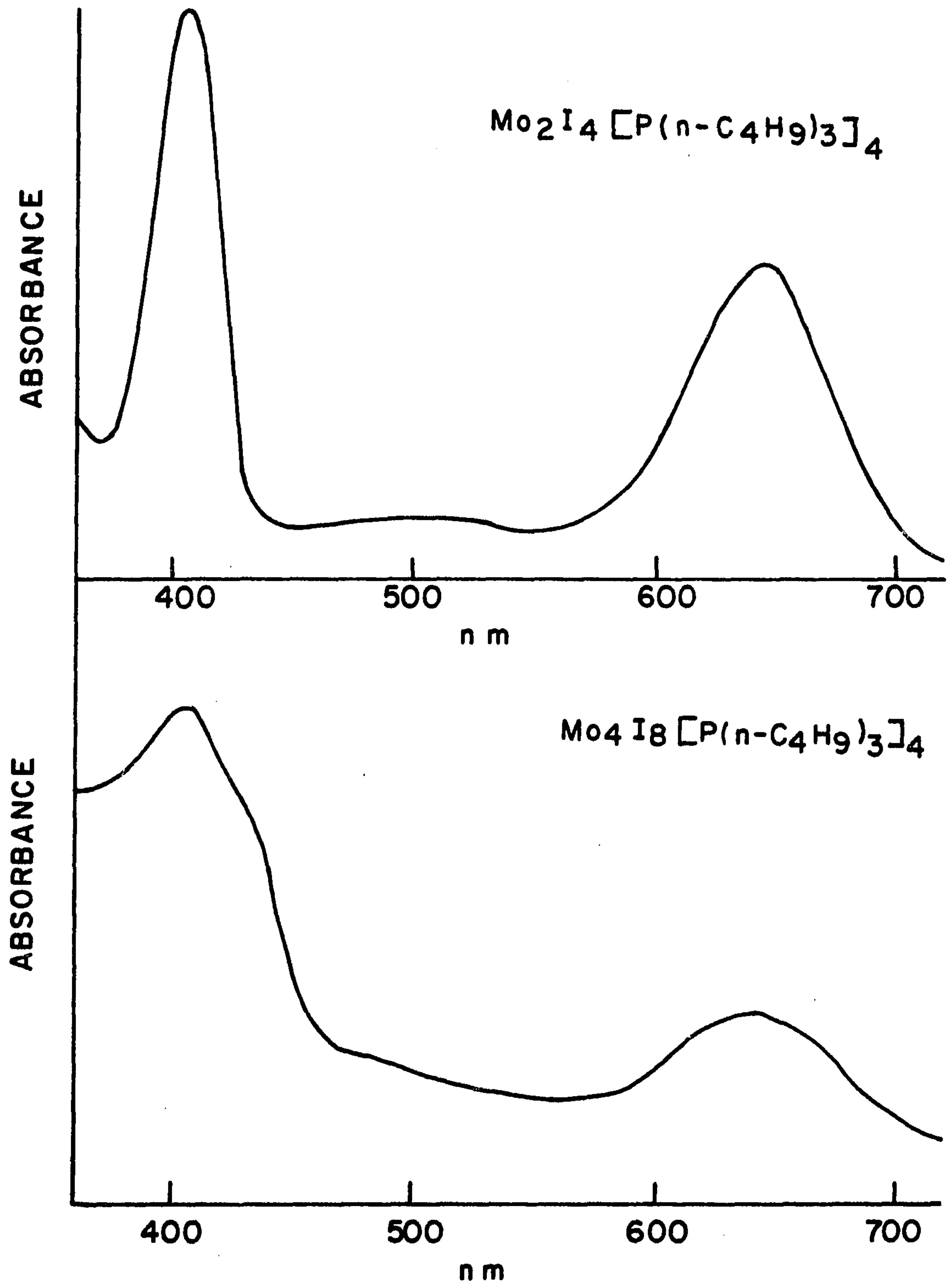

Figure II-2. Electronic absorption spectra of $Mo_4I_8[P(n\text{-}C_4H_9)_3]_4$ and $Mo_2I_4[P(n\text{-}C_4H_9)_3]_4$ in cyclohexane solution the chloride case with complete conversion requiring only a few seconds at 25°C. The dimeric product was identified by its uv-visible spectrum (20).

DISCUSSION

The preparation of tetrameric clusters from quadruply bonded dimers requires the initial loss of coordinated ligands from the dimer. The resulting species of low coordination number are unstable and readily condense to form the cluster compounds. It appears that the manner by which the dimer loses the ligands is not an important factor, as shown by the variety of procedures used for the cluster syntheses.

It was the spontaneous loss of methanol from $Mo_2Cl_4[P(C_6H_5)_3]_2(CH_3OH)_2$ which first led to formation of $Mo_4Cl_8(PR_3)_4$ clusters (1). Likewise, the preparation of $Mo_4Cl_8(CH_3OH)_4$ seems to depend upon the loss of triphenylphosphine from the same dimer. However, since the $Mo_4Cl_8(CH_3OH)_4$ preparation uses methanol as a solvent, simple ligand substitution of methanol for triphenylphosphine could produce a different dimer, $Mo_2Cl_4(CH_3OH)_4$, as a reactive intermediate. This dimer would actually be the reactive species, and again, the loss of weakly coordinated methanol would be responsible for the cycloaddition.

Coordinated methanol in $Mo_4Cl_8(CH_3OH)_4$ also seems to be weakly bonded, and ligand substitutions have led to a number of $Mo_4Cl_8L_4$ complexes where L = propionitrile, tetrahydrofuran, trialkylphosphine, and triphenylphosphine. The $Mo_4Cl_8[P(C_6H_5)_3]_4$ cluster is especially interesting because of the similarity to $\{MoCl_2[P(C_6H_5)_3]\}_n$, which is initially formed when $Mo_2Cl_4[P(C_6H_5)_3]_2(CH_3OH)_2$ is dissolved in benzene. Unfortunately, $\{MoCl_2[P(C_6H_5)_3]\}_n$ is always slightly contaminated with methanol so as to make an unambiguous comparison impossible. For example, the infrared spectra (400 cm^{-1} to 200 cm^{-1}) of the two compounds are very similar except for a band at 323 cm^{-1} in $\{MoCl_2[P(C_6H_5)_3]\}_n$ (Table II-1). Despite these problems, the conversion of $\{MoCl_2[P(C_6H_5)_3]\}_n$ to $Mo_4Cl_8(PR_3)_4$ suggests that n = 4, and this compound is probably an impure form of the $Mo_4Cl_8[P(C_6H_5)_3]_4$ obtained by ligand substitution.

The preparation of $Mo_4Cl_8[P(C_6H_5)_3]_4$ is much more difficult than the corresponding trialkylphosphine tetramers. Complete replacement of propionitrile from $Mo_4Cl_8[CH_3CH_2CN)_4$ requires several days while the trialkylphosphine derivatives are obtained in a few hours. Steric problems and lower basicity of triphenylphosphine seem to inhibit the formation of $Mo_4Cl_8[P(C_6H_5)_3]_4$, and this may be why a methanol solution of $Mo_2Cl_4[P(C_6H_5)_3]_2(CH_3OH)_2$ does not spontaneously give $Mo_4Cl_8[P(C_6H_5)_3]_4$. The fact that the attempted preparations of $Mo_2Cl_4(PR_3)_2(CH_3OH)_2$, R = alkyl, produce the tetrameric clusters from methanol solutions is consistent with this view. Since the tetrameric clusters are easily converted back to quadruply bonded dimers, one can envision the following equilibrium in methanol.

$$2\ Mo_2Cl_4(PR_3)_2(CH_3OH)_2 \rightleftharpoons Mo_4Cl_8(PR_3)_4 + 4\ CH_3OH$$

In the case of triphenylphosphine, the equilibrium lies to the left because of the difficulty in forming the tetramers. In the case of trialkylphosphine, the equilibrium lies far enough to the right to cause pricipitation of the cluster from methanol.

In all the syntheses described so far, the cyclo-addition reaction is initiated by the dissociation of weakly bonded ligands, but this is not the only means by which condensation can occur. In the reaction of $Mo_2Cl_4[P(C_4H_9)_3]_4$ with $Mo(CO)_6$, the metal carbonyl abstracts strongly bound phosphine ligands with subsequent formation of $Mo(CO)_4[P(C_4H_9)_3]_2$ and $Mo_4Cl_8[P(C_4H_9)_3]_4$. This suggests that the cyclo-addition may be generally applicable to almost any quadruply bonded dimer, provided some means is found to remove two coordinated ligands.

In the syntheses involving the use of halogenating agents, the abstraction of acetate ligands is the driving force for cluster formation, but in these reactions there is concurrent replacement of the acetate by halide. Aluminum chloride reacts much more rapidly with $Mo_2(O_2CCH_3)_4$ than trimethylchlorosilane, perhaps reflecting the strong acidity of $AlCl_3$. Since the reactions are run in tetrahydrofuran, it is possible that there is formation of $AlCl_2(OC_4H_8Cl)$, (21), and this may actually be the active halogenating agent.

Proof of the tetrameric structure of $Mo_4Cl_8(PR_3)_4$ was available through an x-ray structure determination. While no direct structural evidence is available for $Mo_4Cl_8L_4$ (L = triphenylphosphine, methanol, propionitrile), the same structure is assumed for these complexes. This is based on several observations. The analyses show that all the compounds have the same stoichiometry, $Mo_4Cl_8L_4$. In addition, when $L = CH_3OH$ or CH_3CH_2CN, reaction with trialkylphosphines gives almost quantitative conversion to $Mo_4Cl_8(PR_3)_4$. The insolubility of many of the compounds does not allow comparison of solution uv-visible spectra, but reflectance spectra on powders are available (Figure II-3), and as expected, the spectrum of $Mo_4Cl_8[P(n-C_4H_9)_3]_4$ agrees well with the other spectra especially in the longer wavelengths. It is not surprising that some differences between the spectra exist in the uv region since these high energy transitions are more likely to involve the ligands. The low energy absorptions listed in Table II-3 show a blue shift for the more weakly bound ligands. A similar blue shift in the low energy transitions of a variety of quadruply bonded molybdenum dimers is attributed to the decreased π-acceptor character of the ligands and subsequent decreased nephelauxetic effect on the metal orbitals (12). Such reasoning may also be applied to the tetramers, and therefore, the general similarity of the reflectance data for these compounds is taken as further proof of their tetrameric structures.

A comparison of the Cl 2p XPS spectra of these clusters is desirable in that relative populations of bridging and terminal chloride can be obtained. Such a ratio would help to confirm the structure of the various tetrameric clusters since the expected ratio is 4:4. Since each type of chlorine produces a pair of peaks in the spectrum due to spin-orbit coupling ($2p^{3/2}$, $2p^{1/2}$), a complex spectrum results which requires deconvolution. Parameters used in the deconvolution of the spectra of $Mo_4Cl_8[P(n-C_4H_9)_3]_4$ and $Mo_4Cl_8(CH_3OH)_4$ are shown in Table II-4, and Figures II-4 and 5 show the spectra resolved into their components. The presence of more than one type of chlorine in $Mo_4Cl_8[P(n-C_4H_9)_3]_4$ is obvious from the shape of the spectrum. Deconvolution using the accepted order of bridging chloride at higher

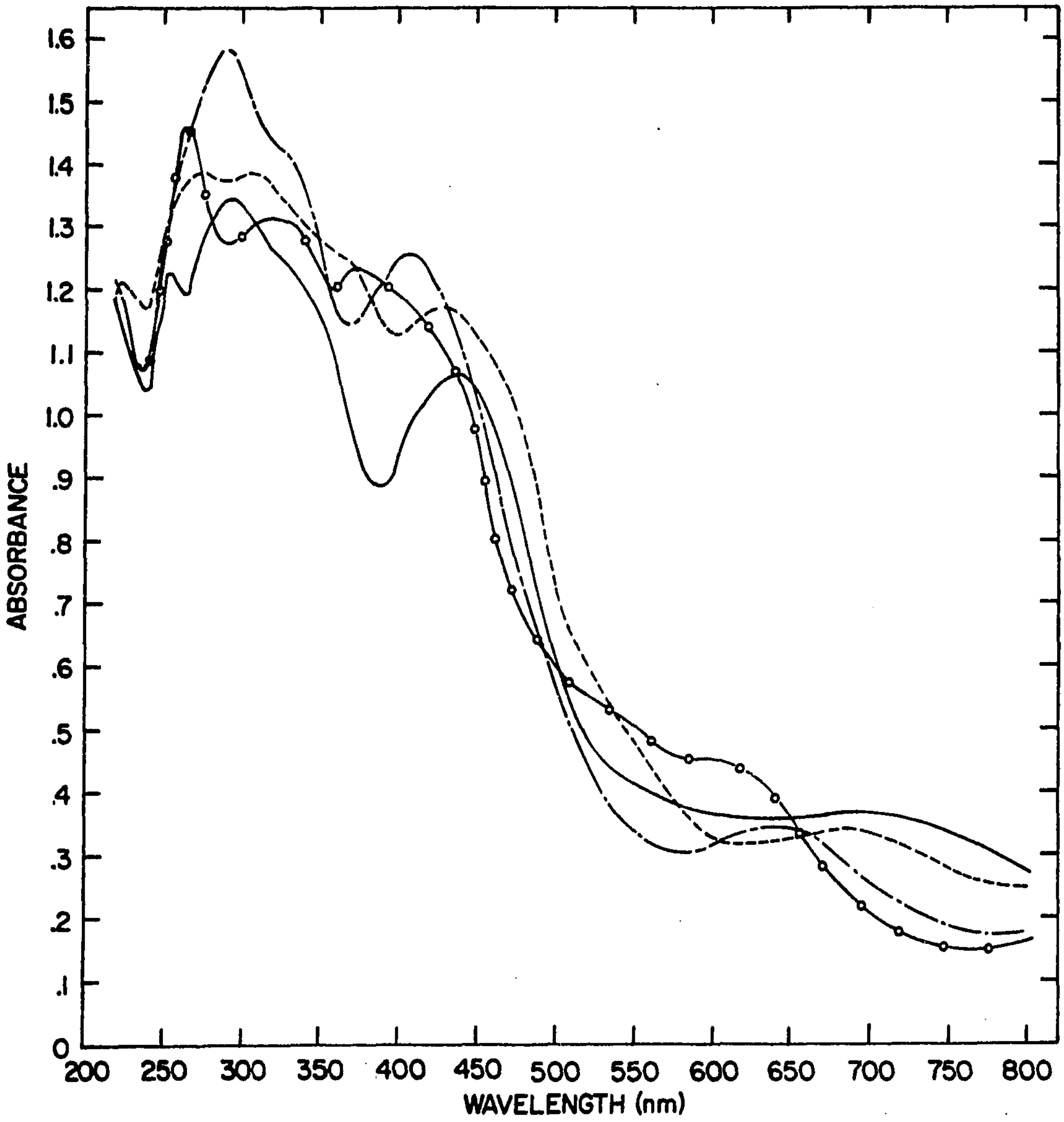

Figure II-3. Reflectance spectra of tetrameric clusters $Mo_4Cl_8[P(n\text{-}C_4H_9)_3]_4$ (——), $Mo_4Cl_8[P(C_6H_5)_3]_4$ (---), $Mo_4Cl_8(CH_3CH_2CN)_4$ (—-—-), and $Mo_4Cl_8(CH_3OH)_4$ (-o-o-o-)

Table II-3. Low energy reflectance bands of $Mo_4Cl_8L_4$ ($\nu_{max} \times 10^{-3}$ cm^{-1})

$P(n\text{-}C_4H_9)_3$	$P(C_6H_5)_3$	CH_3CH_2CN	CH_3OH
14.3	14.5	15.6	16.7
22.7	23.1	24.4	26.7

Table II-4. XPS parameters used in spectra deconvolution

	Fraction Gaussian	Peak Width[a]	Spin Orbit Splitting[a]	Energy[a] (rel. int.)	
				Terminal	Bridging
$Mo_4Cl_8[P(n\text{-}C_4H_9)_3]_4$	0.4	1.2	1.6	198.3 (118.6)	199.6 (157.0)
				199.9 (59.3)	201.4 (78.5)
$Mo_4Cl_8(CH_3OH)_4$	0.9	1.1	1.6	198.6 (382.5)	199.5 (909.0)
				200.2 (191.3)	201.1 (454.5)

[a] Values in eV.

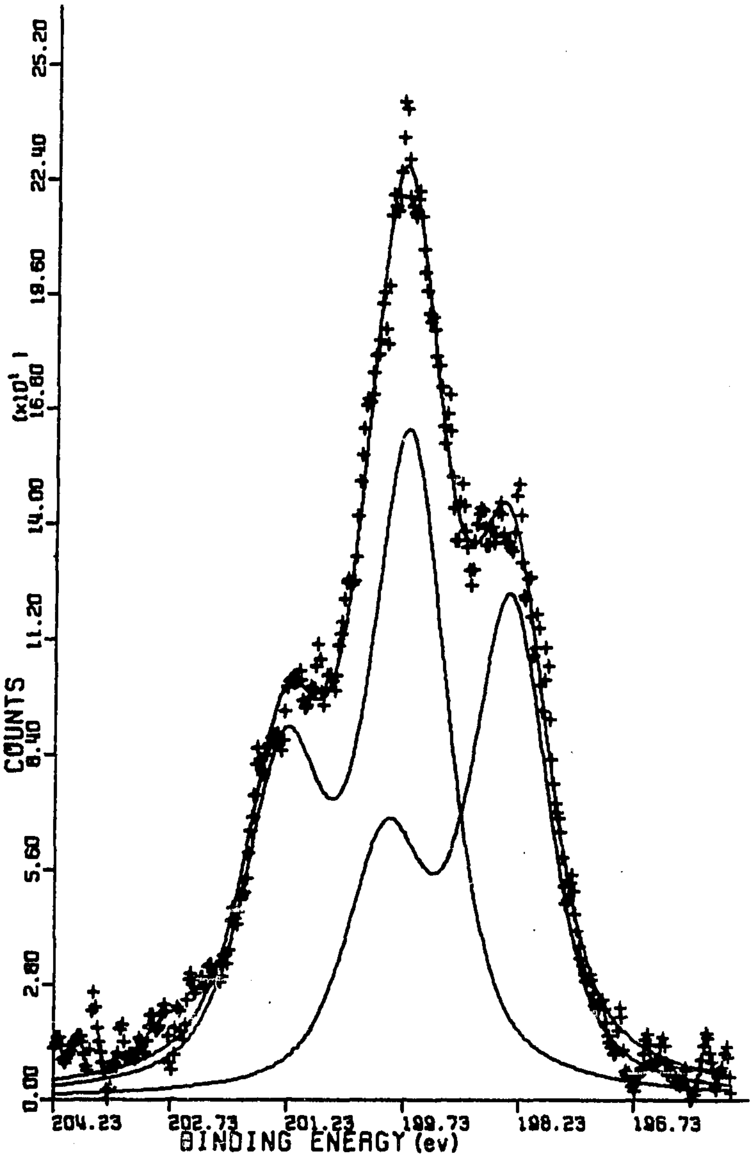

Figure II-4. Cl 2p x-ray photoelectron spectrum of $Mo_4Cl_8[P(n-C_4H_9)_3]_4$. The sum of both components is given by the solid line through the experimental data points, (+)

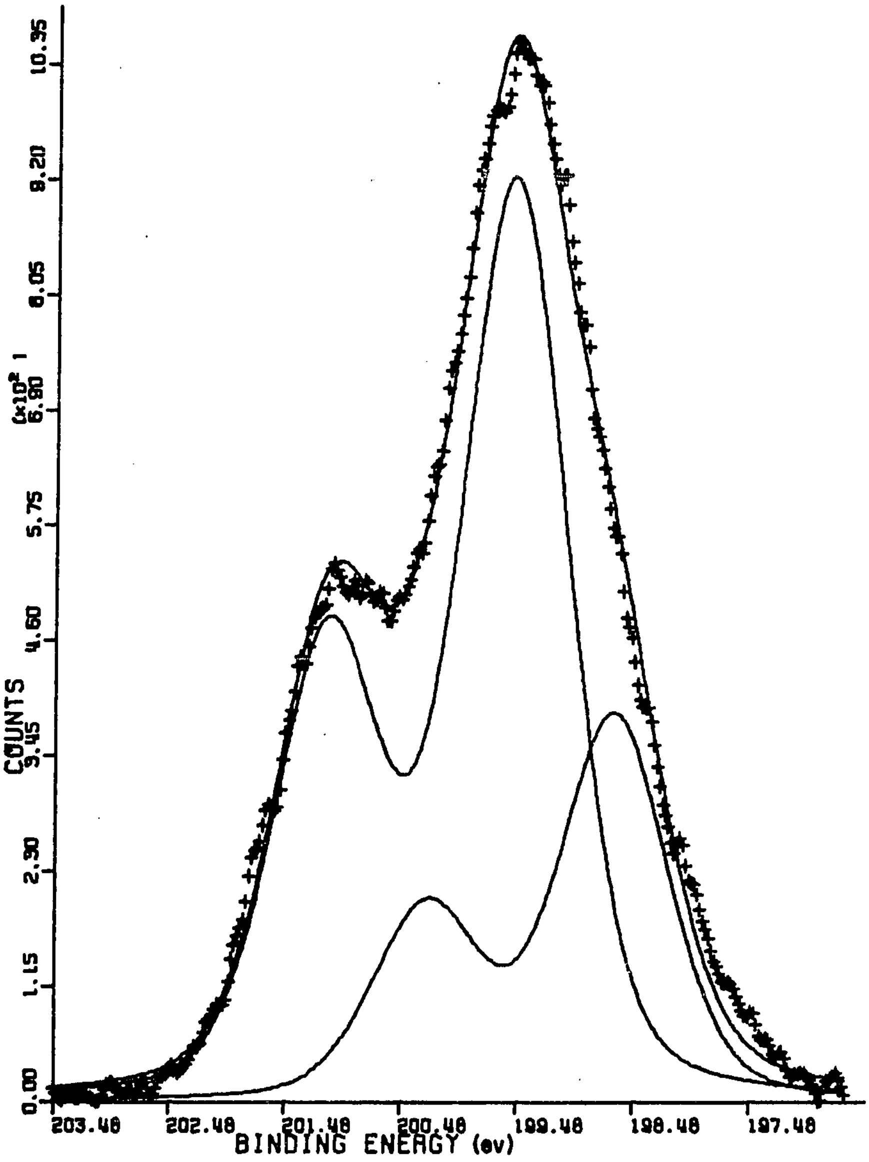

Figure II-5. Cl 2p x-ray photoelectron spectrum of $Mo_4Cl_8(CH_3OH)_4$. The sum of both components is given by the solid line through the experimental data points, (+)

binding energy and terminal chloride at lower binding energy gives a bridging:terminal ratio of 4.5:3.5. While this is slightly higher than the expected 4:4 ratio, it is considerably better than the ratio of 5.6:2.4 obtained for $Mo_4Cl_8(CH_3OH)_4$. In the latter compound, a fit of the data to one type of chlorine gives unreasonable values for the peak widths and intensity ratios of the spin-orbit coupled peaks. It appears then, that the decomposition of the methanol tetramer, as discussed earlier, has caused a conversion of terminal chloride to a bridging mode. During exposure of the sample to x-rays in the high vacuum chamber, loss of methanol from $Mo_4Cl_8(CH_3OH)_4$, as well as loss of some phosphine from $Mo_4Cl_8[P(n\text{-}C_4H_9)_3]_4$, is compensated by the increase in coordination number of the chloride. Because of the decomposition problems, a confirmation of the structure of $Mo_4Cl_8L_4$ compounds by XPS is not possible.

The structure of $Mo_4Br_8[P(n\text{-}C_4H_9)_3]_4$ is undoubtedly the same as the chloride analog as shown by x-ray powder patterns and electronic spectra. However, $Mo_4I_8[P(n\text{-}C_4H_9)_3]_4$ does not appear to have the same electronic structure as the other halogen clusters. The presence of a strong absorption at 643 nm is very much like the 645 nm band of $Mo_2I_4[P(n\text{-}C_4H_9)_3]_4$ (20) shown in Figure II-2 and strongly suggests the existence of a δ bond in the tetramer. The compound might therefore be best considered as a pair of independent quadruply bonded dimers linked by bridging iodide atoms where the large radius of the iodide may prevent the close approach of the dimer units. This is not unexpected since even in $Mo_4Cl_8(PR_3)_4$ there is severe crowding of the smaller chlorine atoms. Two possible structures for the iodide complex are shown in Figure II-6, both of which have some precedence (22,23).

Some of the reactions of these tetrameric clusters include complete loss of coordinated neutral ligands as in $Mo_4Cl_8L_4$ (L = CH_3OH, C_4H_8O) and cleavage of the tetramer to quadruply bonded dimers by donor ligands. The loss of ligands to produce β-$MoCl_2$ may provide some insight into the structure of this material. The amorphous to poorly crystalline β-$MoCl_2$ is usually synthesized by reaction of quadruply bonded $Mo_2(OCCH_3)_4$ with gaseous HCl (15). Since trialkylphosphines react with β-$MoCl_2$ to give back a quadruply bonded dimer, the structure was presumed to contain dimeric units of metal atoms (15). However, the preparation of β-$MoCl_2$ from a tetrameric cluster may indicate that the dimers are present in an arrangement related to the structure of the tetramer, and the β-phase may actually consist of tetrameric units rather than dimers. In reactions of β-$MoCl_2$ with phosphines, the formation of quadruply bonded dimers is consistent with the reactions of tetramers with phosphines in which quadruply bonded dimers are also produced.

The easy cleavage of tetramers by donor ligands suggests that an oxidative cleavage may be possible. Hydrogen was used in an effort to prepare a multiply bonded dimer containing metal hydride bonds, but the tetramer was found to be unreactive under the conditions used.

The availability of this variety of tetrameric clusters will enable investigations into their reactivity and physical properties to

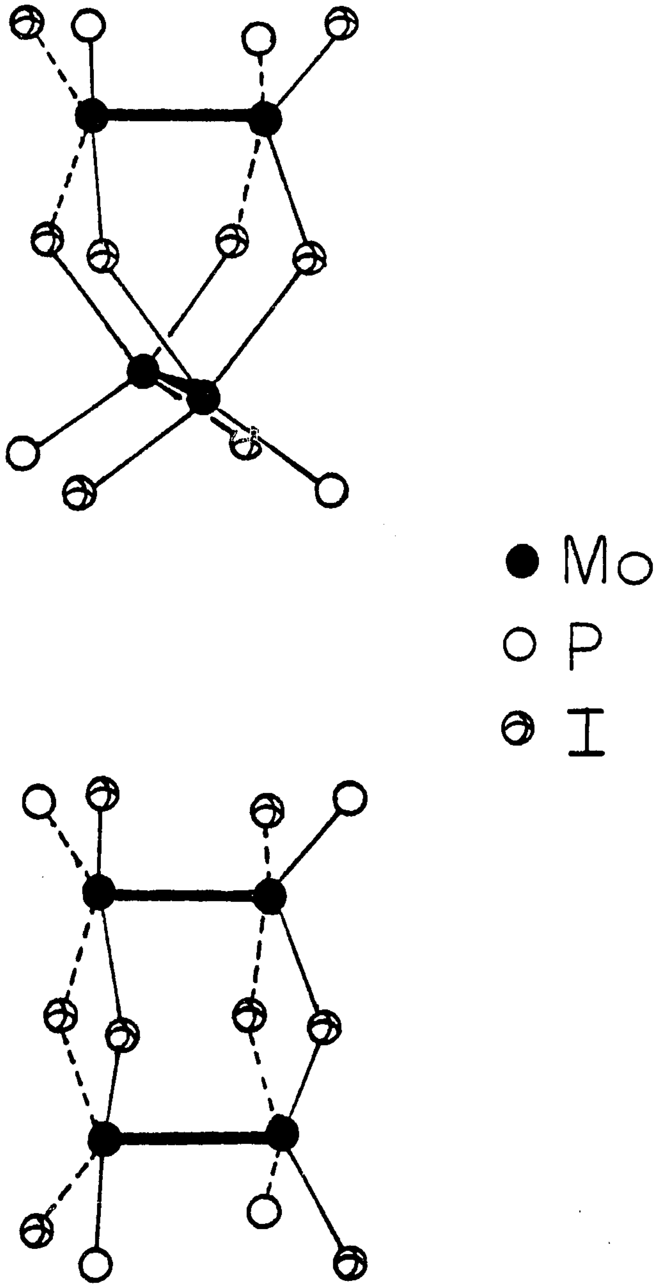

Figure II-6. Possible structures for $Mo_4I_8[P(n\text{-}C_4H_9)_3]_4$

continue. There exist many possibilities for modifying the preparative reactions to prepare higher clusters and for extending the synthetic procedures to metals other than molybdenum.

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SECTION III. PREPARATION AND STRUCTURE OF A RECTANGULAR TETRAMERIC TUNGSTEN CLUSTER

INTRODUCTION

One of the greatest obstacles to the study of metal cluster compounds has been the lack of systematic methods for their preparation (1,2). Because new clusters are almost always discovered by accident, it is difficult to assemble a series of isoelectronic and/or isostructural clusters for investigations into bonding and reactivity trends. A notable exception is the well-studied class of dimers containing quadruple metal-metal bonds. However, even these simple clusters provide an illustration of the frustrating state of affairs. While the carboxylato dimers, $M_2(O_2CR)_4$, of chromium and molybdenum have been known for many years, the tungsten analog has yet to be isolated despite many attempts to do so (3,4). In light of this situation, it was of particular interest to learn whether a stable tungsten analog to the previously synthesized $Mo_4Cl_8[P(n\text{-}C_4H_9)_3]_4$ tetramer (5) could be prepared.

It was hoped that the synthetic principles used in the molybdenum preparation would be directly applicable to the tungsten case. This required the use of quadruply bonded tungsten dimers which could be caused to undergo condensation to tetramers by means of ligand dissociation. The preparation of dimeric $W_2Cl_4[P(n\text{-}C_4H_9)_3]_4$ (4) was therefore modified to achieve this goal, and the desired tetramer, $W_4Cl_8[P(n\text{-}C_4H_9)_3]_4$, was isolated and structurally characterized. This synthesis was especially gratifying in that it represents one of the few cases where a particular cluster was prepared by a rational and systematic method.

EXPERIMENTAL

Materials

The handling of samples and solvents was as described earlier (5). Analysis for tungsten was performed by digestion of samples in basic hydrogen peroxide solution followed by precipitation with nitric acid and gravimetric determination of WO_3 (6). Chlorine, carbon, and hydrogen analyses were performed as described earlier (5), as were spectral measurements.

Syntheses

WCl_4

This compound was prepared by the reduction of WCl_6 with a stoichiometric amount of $W(CO)_6$ in refluxing chlorobenzene (7). The product was stored in a nitrogen filled glove box until needed.

$W_4Cl_8[P(n\text{-}C_4H_9)_3]_4$

WCl_4 (1.10 g, 3.38 mmol) was mixed with 25 mL tetrahydrofuran at 0°C, and 0.29% sodium amalgam (16.9 g, 3.58 mmol Na) was added. Slow warming to 25°C produced a yellow-green solution of $W_2Cl_6(THF)_4$ (4) to which tri-n-butylphosphine (0.65 g, 3.21 mmol) was added. After one hour, the orange-brown reaction mixture was again cooled to 0°C, and sodium amalgam (16.3 g, 3.46 mmol Na) was added. A dark green solution developed as the temperature was slowly raised to 25°C.

The green tetrahydrofuran solution was filtered under nitrogen to remove NaCl and mercury, and the solvent was removed in vacuo leaving a dark green residue. Extraction (under vacuum) of this green solid with n-hexane for a few minutes gave a yellow-green solid and a green solution which was discarded. Further extraction of the yellow-green solid with n-hexane produced dark brown crystals of $W_4Cl_8[P(n\text{-}C_4H_9)_3]_4$ in the collection flask. The air sensitive product was obtained in 18% yield. Anal. Calcd. for $W_4Cl_8[P(n(C_4H_9)_3]_4$: W, 40.22; Cl, 15.51; C, 31.53; H, 5.91. Found: W, 39.82; Cl, 15.50; C, 31.47; H, 5.88.

X-ray Structure Determination

Collection and reduction of x-ray data

Crystals of $W_4Cl_8[P(n\text{-}C_4H_9)_3]_4$ were obtained directly from the preparative reaction. The crystal chosen for x-ray studies measured 0.22 x 0.34 x 0.20 mm and was sealed in a glass capillary under a nitrogen atmosphere. Data were collected using an automatic 4-circle diffractometer designed at Ames Laboratory (8). Fourteen reflections were chosen from ω-oscillation photographs at various values of chi and phi, and these were input into an automatic indexing program ALICE (9). The indexing provided two possible sets of cell parameters, one monoclinic and one orthorhombic. Oscillation photographs about the principal axes in each system showed the orthorhombic cell to be correct. Fourteen intense, high-angle reflections were measured on the previously aligned diffractometer and used in a least squares refinement to obtain lattice constants at 25°C: a = 26.990(9), b = 36.302(9), c = 14.293(6), V = 14,005(8). Mo Kα radiation was used, λ = 0.71002Å.

Data were collected to $2\theta = 50°$ using an ω-scan technique. Standard reflections were monitored after every 75 measurements, and the data were corrected for the 10% decay in intensity. The data were also corrected for Lorentz-polarization effects, and an absorption correction was made based on ϕ-scans of a strong reflection at $\chi = 90°$ ($\mu = 73.3$ cm^{-1}). All reflections in one octant of the reciprocal cell were read until it became obvious that the cell was at least C-centered, after which time only h+k = 2n reflections were sampled. Observation of only reflections of the type $hk\ell$ ($h+k = 2n$, $k+\ell = 2n$); $0k\ell$ ($k+\ell = 4n$); $h0\ell$ ($h+\ell = 4n$); $hk0$ ($h+k = 4n$) uniquely determined the space group as F_{ddd}. Several apparent violations of the extinction conditions were found to be due to the close proximity of very intense reflections which happened to tail into the area sampled as a separate data point. There were 7,831 reflections collected in one octant of which 4674 were symmetry extinct, and an additional 1354 were considered unobserved ($I < 3\sigma_I$). After averaging, 1803 unique reflections were used in the refinement.

Structure solution and refinement

Debye-Scherrer powder patterns of $Mo_4Cl_8[P(n\text{-}C_4H_9)_3]_4$ and $W_4Cl_8[P(n\text{-}C_4H_9)_3]_4$ indicated that the two compounds were probably isomorphous. Additionally, incorrect monoclinic cell parameters known for the molybdenum tetramer closely matched those for the monoclinic cell seen for $W_4Cl_8[P(n\text{-}C_4H_9)_3]_4$. The heavy atom positions known for

$Mo_4Cl_8[P(n\text{-}C_4H_9)_3]_4$ (10) were therefore transformed to orthorhombic coordinates and found to give a satisfactory refinement for $W_4Cl_8[P(n\text{-}C_4H_9)_3]_4$. This produced a unit cell containing eight cluster molecules. Light atoms were located from electron density maps obtained through successive least-squares refinements where the minimizing function was $\Sigma\, w(|F_o|-|F_c|)^2$, and $w = 1/\sigma_F^2$. The scattering factors were those of Hanson et al. (11), modified for the real and imaginary parts of anomalous dispersion (12). Carbon atom positions were generally poorly defined, becoming more so for atoms at the ends of the alkyl chains. This problem was aggravated by the disordering of several of the carbon atoms. Since these light atoms had little bearing on the overall structure refinement and since the heavy atoms were determined precisely, a low temperature structure determination was deemed unnecessary. A final difference map revealed several areas of residual electron density ($\sim 2\ e^-/\text{Å}^3$) near the carbon atom positions and in concentric rings about the tungsten atoms. Neither of these was unexpected nor considered a serious flaw in the solution. The final discrepancy factors were $R = 0.063$ and $R_w = 0.078$.

Positional and thermal parameters are given in Tables III-1 and 2, and an ORTEP drawing of the molecule is shown in Figure III-1. Bond distances and angles are listed in Table III-3.

Table III-1. Positional parameters ($x10^4$) for $W_4Cl_8[P(n-C_4H_9)_3]_4$[a]

Atom	x	y	z
W	3732.9(3)	3359.1(2)	7943.1(5)
Cl(1)	4232(2)	2883(1)	7257(4)
Cl(2)	3054(2)	3762(1)	7600(4)
P	3038(2)	2900(1)	7717(4)
C(11)	2432(9)	2993(7)	8416(16)
C(12)	2018(12)	3028(9)	7752(23)
C(13)	1507(12)	3134(9)	8376(23)
C(14)	1092(19)	3237(12)	7733(34)
C(21)	2876(10)	2865(8)	6503(20)
C(22A)	3252(20)	2866(15)	5916(39)
C(22B)	2975(19)	3135(15)	5839(39)
C(23)	3014(16)	2970(13)	4732(33)
C(24A)	2991(38)	3322(23)	4457(72)
C(24B)	3370(34)	2887(27)	4257(69)
C(31)	3190(7)	2421(5)	8055(14)
C(32)	2745(9)	2146(8)	7763(20)
C(33)	2961(13)	1740(10)	8057(27)
C(34A)	3023(18)	1702(12)	8915(36)
C(34B)	2596(27)	1488(21)	7796(51)

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[a] Estimated standard deviations are given in parentheses for the last significant figures.

Table III-2. Thermal parameters (x10^4) for $W_4Cl_8[P(n\text{-}C_4H_9)_3]_4$[a,b]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
W	21.3(1)	8.76(6)	80.8(5)	-0.40(8)	1.6(2)	-0.4(1)
Cl(1)	29.1(9)	11.2(4)	105(4)	0.5(5)	10(2)	-8(1)
Cl(2)	22.1(7)	10.3(3)	110(4)	-0.5(5)	-10(1)	-1(1)
P	26.9(9)	10.3(4)	97(4)	-2.4(6)	-0.4(17)	-1(1)
	B^c					
C(11)	9.4(6)					
C(12)	14.0(9)					
C(13)	13.2(9)					
C(14)	20.9(15)					
C(21)	11.3(7)					
C(22A)	12.4(14)					
C(22B)	8.6(12)					
C(23)	17.2(12)					
C(24A)	24.7(36)					
C(24B)	15.4(28)					
C(31)	7.3(4)					
C(32)	11.3(7)					
C(33)	14.7(10)					
C(34A)	12.3(13)					
C(34B)	11.9(18)					

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[a] B_{ij} are defined by $T = \exp[-(h^2\beta_{11} + k^2\beta_{22} + \ell^2\beta_{33} + 2hk\beta_{12} + 2h\ell\beta_{13} + 2k\ell\beta_{23})]$.

[b] Estimated standard deviations are given in parentheses for the last significant figures.

[c] Isotropic temperature factors, B, are given in Å^2.

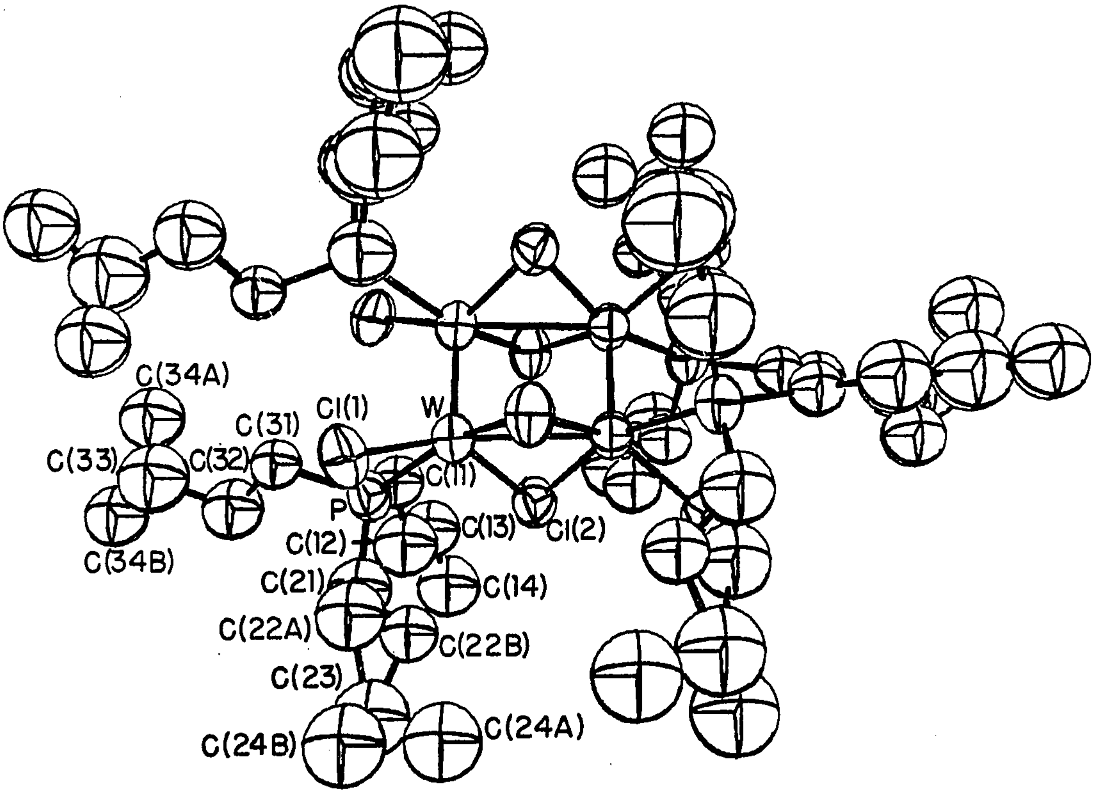

Figure III-1. Structure of the $W_4Cl_8[P(n\text{-}C_4H_9)_3]_4$ molecule with numbering scheme for atoms shown. Atoms are represented by thermal ellipsoids scaled to 50% of the electron density except for C(24A) and C(14) which are shown at B = 15.0. Atoms with letter designations A and B indicate disordered positions with occupancy factors of 0.6 and 0.4, respectively.

Table III-3. Bond distances (Å) and angles (°) for $W_2Cl_4[P(n\text{-}C_4H_9)_3]_4$[a]

Distances

W-W	2.309(2)	C(13)-C(14)	1.50(6)
W-W	2.840(1)	C(21)-C(22A)	1.32(6)
W-Cl(1)	2.400(5)	C(21)-C(22B)	1.39(6)
W-Cl(2)	2.396(5)	C(22A)-C(23)	1.85(7)
W-Cl(2)	2.417(5)	C(22B)-C(23)	1.70(7)
W-P	2.530(5)	C(23)-C(24A)	1.34(10)
P-C(11)	1.95(2)	C(23)-C(24B)	1.21(10)
P-C(21)	1.79(3)	C(31)-C(32)	1.62(3)
P-C(31)	1.85(2)	C(32)-C(33)	1.64(5)
C(11)-C(12)	1.47(4)	C(33)-C(34A)	1.25(7)
C(12)-C(13)	1.69(5)	C(33)-C(34B)	1.40(8)

Angles (middle atom is vertex)

W-W-W	89.93(3)	C(11)-P-C(21)	108(1)
W-W-Cl(1)	112.7(1)	C(21)-P-C(31)	104(1)
W-W-Cl(1)	134.5(1)	C(31)-P-C(11)	102(1)
W-W-Cl(2)	54.2(1)	P-C(11)-C(12)	109(2)
W-W-Cl(2)	53.5(1)	C(11)-C(12)-C(13)	107(2)
W-W-Cl(2)	99.8(1)	C(12)-C(13)-C(14)	110(3)
W-W-Cl(2)	103.6(1)	P-C(21)-C(22A)	115(3)
W-W-P	99.1(1)	P-C(21)-C(22B)	124(3)
W-W-P	133.0(1)	C(21)-C(22A)-C(23)	108(4)
Cl(1)-W-Cl(2)	83.1(2)	C(21)-C(22B)-C(23)	114(4)
Cl(1)-W-Cl(2)	141.7(2)	C(22A)-C(23)-C(24A)	119(6)
Cl(2)-W-Cl(2)	102.8(2)	C(22A)-C(23)-C(24B)	101(6)
Cl(1)-W-P	83.7(2)	C(22B)-C(23)-C(24A)	86(5)
Cl(2)-W-P	79.0(2)	C(22B)-C(23)-C(24B)	131(6)
Cl(2)-W-P	160.0(2)	P-C(31)-C(32)	110(1)
W-Cl(2)-W	72.3(1)	C(31)-C(32)-C(33)	103(2)
W-P-C(11)	116.3(7)	C(32)-C(33)-C(34A)	114(3)
W-P-C(21)	110.6(9)	C(32)-C(33)-C(34B)	106(4)
W-P-C(31)	114.9(6)		

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[a] Estimated standard deviations are given in parentheses for the last significant figures.

RESULTS

Syntheses and Characterizations

In the synthesis of the tungsten tetramer, the reduction of WCl_4 with sodium was carried out in two steps. Initially, the W(III) dimer, $W_2Cl_6(THF)_4$, was formed, and this was reduced further to the W(II) tetramer after the addition of tri-n-butylphosphine. Such a

$$2\ WCl_4 + 2\ Na/Hg \xrightarrow{THF} W_2Cl_6(THF)_4 + 2\ NaCl$$

$$W_2Cl_6(THF)_4 + 2\ PR_3 \longrightarrow W_2Cl_6(THF)_2(PR_3)_2 + 2\ THF$$

$$2\ W_2Cl_6(THF)_2(PR_3)_2 + 4\ Na/Hg \longrightarrow W_4Cl_8(PR_3)_4 + 4\ NaCl + 4\ THF$$

step-wise reduction was not strictly necessary since the tetramer could also be isolated by a one step reaction of WCl_4, tri-n-butylphosphine, and sodium. This procedure, however, produced only about one-half the

$$4\ WCl_4 + 4\ PR_3 + 8\ Na/Hg \longrightarrow W_4Cl_8(PR_3)_4 + 8\ NaCl$$

yield of the two step process. Regardless of the method of preparation, the yield of the tetramer was quite low. The major products of the reactions were therefore unknown, but the intense green color of the solutions suggested that tungsten dimers such as the blue-green $W_2Cl_4(PR_3)_4$ (4) were major side products. Synthesis of the triethylphosphine derivative proceeded in much the same manner, but separation of the tetrameric product from the green contaminant was not achieved because of the similar solubilities of the two materials in most solvents.

The $W_4Cl_8[P(n\text{-}C_4H_9)_3]_4$ cluster was much like $Mo_4Cl_8[P(n\text{-}C_4H_9)_3]_4$ in many of its physical properties. The tungsten cluster was much more reactive than the molybdenum analog, and both solutions and solid samples of $W_4Cl_8[P(n\text{-}C_4H_9)_3]_4$ immediately decomposed upon exposure to air. Like the molybdenum tetramer, the tungsten derivative was very soluble in solvents such as benzene, THF, and hexane. The far infrared spectrum (Table III-4) of the tungsten cluster also displayed many bands due to metal-chloride vibrations just as seen for $Mo_4Cl_8(PR_3)_4$ tetramers (5).

As shown earlier (5), $Mo_4Cl_8(PR_3)_4$ could be prepared directly from $Mo_2Cl_4(PR_3)_4$ by reaction with $Mo(CO)_6$. This procedure was also attempted with $W_2Cl_4(PR_3)_4$, but unfortunately, the tetramer was not produced. Instead, only a material containing carbon monoxide, ν(CO) 1935 cm^{-1}, 1840 cm^{-1}, was isolated, and this was not investigated further. Because $W_2Cl_8^{4-}$ and $W_2(O_2CR)_4$ are unknown, the other established methods (5) of tetramer synthesis were impossible since they require these compounds as starting materials.

Crystal Structure

The structure of $W_4Cl_8[P(n\text{-}C_4H_9)_3]_4$ is essentially the same as the one known for $Mo_4Cl_8[P(n\text{-}C_4H_9)_3]_4$ (10) and shown in Figures III-1 and 2. A pair of strongly bonded tungsten atoms 2.309(2)Å apart are bonded to an identical pair through long W-W bonds of 2.840(1)Å. The nearly planar cluster of metal atoms is bridged across each of the long edges of the rectangle by two chlorine atoms. Four terminal chlorine and

Table III-4. Infrared spectra (cm^{-1}) of tetrameric clusters 200 cm^{-1} to 400 cm^{-1} (s = strong, m = medium)

$W_4Cl_8[P(n\text{-}C_4H_9)_3]_4$	$Mo_4Cl_8[P(n\text{-}C_4H_9)_3]_4$
334 (s)	356 (s)
305 (m)	332 (m)
288 (s)	315 (m)
270 (s)	280 (s)

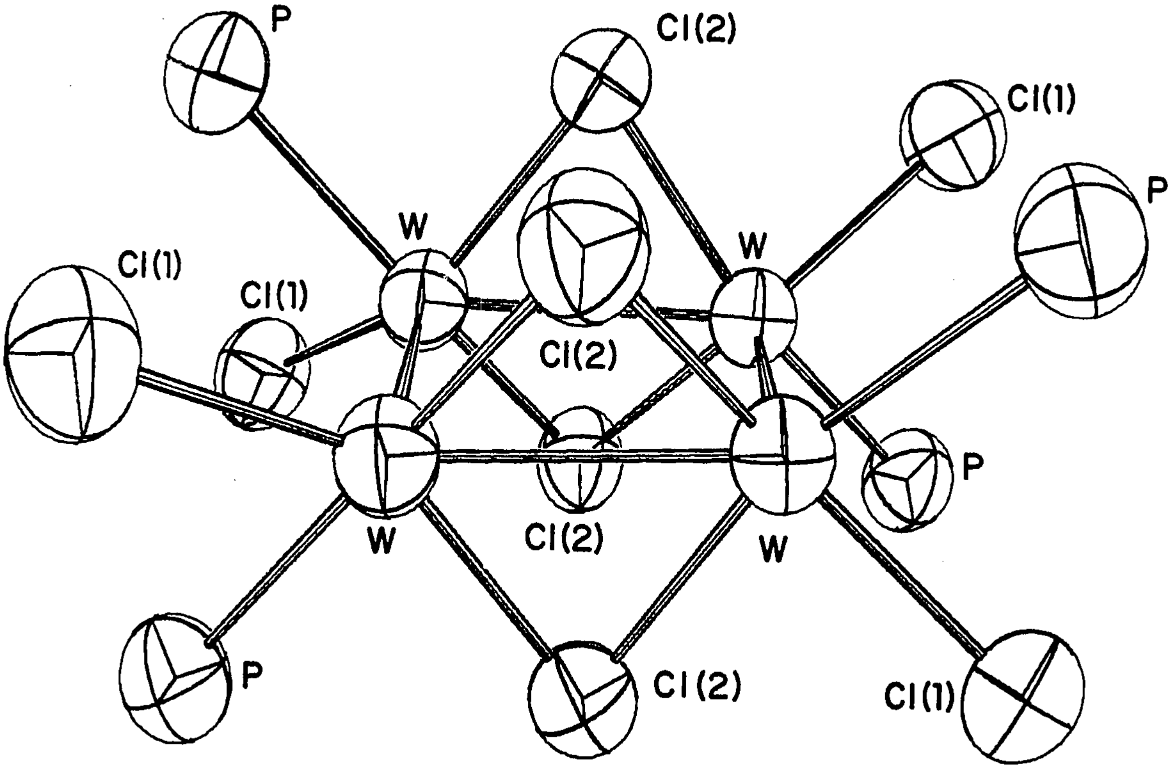

Figure III-2. Structure of the $W_4Cl_8[P(n\text{-}C_4H_9)_3]_4$ molecule with carbon atoms omitted. Atoms are represented by thermal ellipsoids scaled to 50% of the electron density phosphorus atoms are arranged so as to give the molecule D_2 symmetry. The molecule is crystallographically constrained to this D_2 symmetry, and although the tungsten atoms are not required to be coplanar, no metal atom lies more than 0.05Å out of the best least-squares plane through them. As is the case for $Mo_4Cl_8[P(n\text{-}C_4H_9)_3]_4$, the molecule is sterically crowded as shown by the close nonbonding contacts between Cl and P atoms listed in Table III-5.

The poor refinement obtained for the carbon atoms is attributed to high librational movement of the alkyl chains. Given these circumstances, the poor values for distances and angles involving carbon atoms are to be expected. Bond distances and angles for heavier atoms are well within the normal range of values observed in other compounds (Table III-3) and compare well with values obtained in the molybdenum derivatives (10).

Table III-5. Nonbonding contacts (Å) in $W_4Cl_8[P(n\text{-}C_4H_9)_3]_4$[a]

Cl(1)-P[b]	3.290(8)
Cl(1)-P[c]	3.664(8)
Cl(1)-Cl(2)	3.195(5)
Cl(2)-Cl(2)[c]	3.289(8)
Cl(2)-Cl(2)[b]	3.758(8)
Cl(2)-P	3.134(5)

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[a] Estimated standard deviations are given in parentheses for the last significant figures.

[b] Both atoms bonded to the same tungsten atom.

[c] Atoms lie opposite each other across the short dimension of the W_4 rectangle.

DISCUSSION

Earlier work on the tetrameric molybdenum clusters, $Mo_4Cl_8(PR_3)_4$, had revealed that the syntheses of dimeric $Mo_2Cl_4(PR_3)_4$ complexes could be modified to produce tetramers (5). This was accomplished by lowering the PR_3:Mo reaction ratio to that which was needed for the production of tetramers. With the recent isolation of $W_2Cl_4(PR_3)_4$ compounds

$$Mo_2Cl_8^{4-} + 4\ PR_3 \longrightarrow Mo_2Cl_4(PR_3)_4 + 4\ Cl^-$$

$$Mo_2Cl_8^{4-} + 2\ PR_3 \longrightarrow 1/2\ Mo_4Cl_8(PR_3)_4 + 4\ Cl^-$$

by Sharp and Schrock (4), an opportunity arose to apply this same technique to the tungsten tetramer synthesis. The preparation of $W_2Cl_4(PR_3)_4$ was somewhat different from the molybdenum dimer synthesis in that $W_2Cl_4(PR_3)_4$ was prepared by reduction of a W(III) dimer while $Mo_2Cl_4(PR_3)_4$ was prepared by ligand substitution of a Mo(II) dimer. Even so, lowering the PR_3:W reaction ratio produced the desired result.

$$W_2Cl_6(THF)_4 + 4\ PR_3 + 2\ Na(Hg) \longrightarrow W_2Cl_4(PR_3)_4 + 2\ NaCl$$

$$W_2Cl_6(THF)_4 + 2\ PR_3 + 2\ Na(Hg) \longrightarrow 1/2\ W_4Cl_8(PR_3)_4 + 2\ NaCl$$

As expected, the tungsten tetramer exhibited the same structural features already observed in the analogous molybdenum tetramer. The short W-W distances of 2.309(2)Å are appropriate for metal-metal triple bonds, which can range from 2.25 - 2.30 Å in W(III) dimers (13). Even though the long W-W distances of 2.840(1)Å suggest rather weak single bonding interactions between the metal atoms, they are certainly shorter than the known W-W single bond length of 3.222(1)Å found for $(C_5H_5)_2W_2(CO)_6$ (14). Other indications of an attractive force between the triply bonded dimers include the acute W-Cl-W bridge angle of 72.3° and the displacement of the tungsten atoms toward the plane of the four bridging atoms as seen in Figure III-3. Like the molybdenum derivative, the $W_4Cl_8[P(n\text{-}C_4H_9)_3]_4$ molecule contains some very short nonbonding contacts between chlorine and phosphorus atoms (Table III-5), and these seem also to be a result of the bonding interaction along the long edge of the rectangle.

Some interesting structural comparisons can be made between $W_4Cl_8[P(n\text{-}C_4H_9)_3]_4$ and $Mo_4Cl_8[P(C_2H_5)_3]_4$ (Table III-6). The most obvious are the differences in the metal-metal distances in the two compounds. While the short metal-metal bond is lengthened in the tungsten derivatives, the long bond appears to have strengthened and is shorter than in the molybdenum tetramer. These changes in metal-metal bond distances are responsible for several other differences in bonding and nonbonding contacts in the molecules. The shortening of the long metal-metal bond causes the tungsten atoms to lie 1.42Å from the plane of the four bridging chlorine atoms and 1.70Å from the plane of the terminal ligands, while in $Mo_4Cl_8[P(C_2H_5)_3]_4$ these distances are 1.45Å and 1.73Å, respectively (Figure III-3). Narrowing of the M-Cl-M bridge angle from 74° in the molybdenum tetramer to 72° in the tungsten compound is also consistent with the shorter bond between the metal atoms in $W_4Cl_8[P(n\text{-}C_4H_9)_3]_4$. The metal-bridging chlorine distances are the same in both compounds, but the metal-terminal chlorine distances

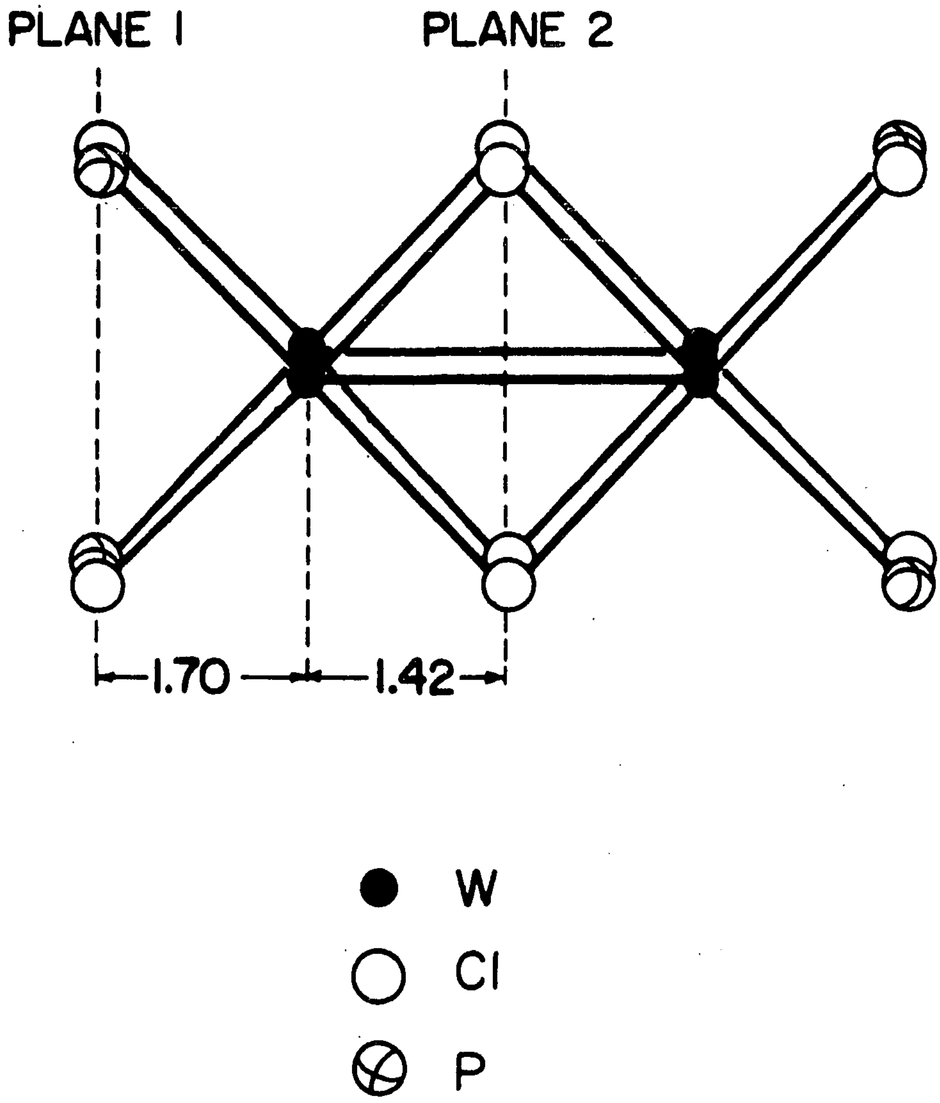

Figure III-3. Distances (Å) of tungsten atoms from least-squares planes in $W_4Cl_8[P(n\text{-}C_4H_9)_3]_4$. Angle between Plane 1 and Plane 2 is 0.0°

Table III-6. Comparisons of molecular dimensions of $W_4Cl_8[P(n\text{-}C_4H_9)_3]_4$ and $Mo_4Cl_8[P(C_2H_5)_3]_4$. Distances in angstroms (Å), angles in degrees (°)

Type bond or angle	$W_4Cl_8P_4$	$Mo_4Cl_8P_4$	
short M-M	2.309(2)	2.211(3)	
long M-M	2.840(1)	2.901(2)	
M-Cl(bridge)	2.396(5) 2.417(5)	2.381(6) 2.417(6)	2.373(5) 2.422(6)
M-Cl(terminal)	2.400(5)	2.425(5)	2.421(6)
M-P	2.530(5)	2.558(6)	2.556(7)
$M\text{-}Cl_b\text{-}M$	72.3(1)	75.2(2)	73.7(2)
$Cl_b\text{-}M\text{-}Cl_b$	102.8(2)	100.5(2)	100.4(2)
M-M-M	89.93(3)	90.6(1)	89.4(1)

have decreased slightly from 2.42Å in the molybdenum tetramer to 2.40Å in the tungsten compound. The metal-phosphorus bond lengths have also decreased slightly in the tungsten compound. It is difficult to say whether these changes in metal-terminal ligand bonds are significant since the molecular symmetry and alkylphosphine ligands are different in the two compounds.

An examination of the nature of the bonding in these tetrameric clusters provides one possible explanation for the observed changes in the metal-metal distances on going from molybdenum to tungsten. As discussed earlier (5), the long metal-metal interactions may be attributed to the σ-type overlap of orbitals formerly involved in δ-type overlap in the quadruply bonded dimers. These orbitals then have both σ and δ character, the δ acting along the short edge of the tetramer and the σ along the long edge (Figure III-4). Because of the contraction of the W-W long bond, the σ bond is presumed to be stronger in the tungsten derivative. Likewise, a strong σ participation necessarily decreases the electron density available for δ bonding, and the short W-W distance is seen to increase slightly in the tungsten tetramer. Apparently, for as yet unknown reasons, δ bonding is not as important for tungsten tetramers as it is for molybdenum tetramers, and therefore, very little δ bonding between tungsten atoms occurs in this compound. This same behavior also manifests itself in the metel-metal bond distances of molybdenum and tungsten dimers. Unbridged dimers are known for both molybdenum and tungsten in +2 and +3 oxidation states (13,15). On going from a Mo(III) dimer, which does not have electrons

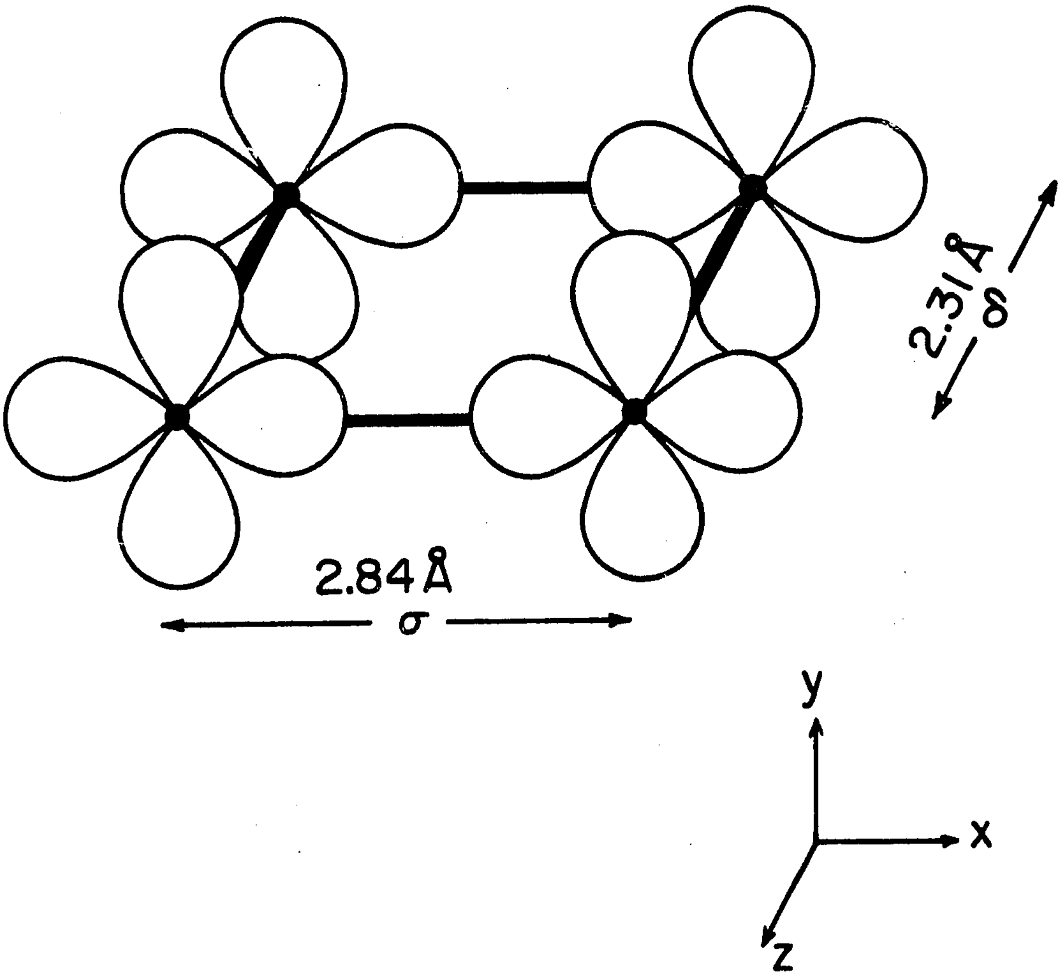

Figure III-4. Metal orbitals involved in δ and σ bonding in tetrameric clusters to populate the δ-bonding orbitals, to Mo(II) dimers containing a δ bond, there is a noticeable contraction in the metal-metal distance from about 2.20Å to 2.14Å (16). Although data are somewhat limited for the tungsten case, a similar contraction is not evident. The bond distances in unbridged W(III) dimers (13) average 2.29Å and contract only slightly to about 2.28Å in unbridged W(II) dimers with a δ bond (17). The inability of tungsten to form strong δ bonds in these dimers is therefore consistent with the stronger σ bonding along the long edge of the tungsten tetramers.

Since the bonding in $W_4Cl_8[P(n\text{-}C_4H_9)_3]_4$ is similar to that of the molybdenum derivative, the uv-visible spectra should also be similar. The spectrum of $W_4Cl_8[P(n\text{-}C_4H_9)_3]_4$ shown in Figure III-5 resembles that of $Mo_4Cl_8[P(n\text{-}C_4H_9)_3]_4$ except for the absence of the prominent band at 435 nm. In the tungsten compound there are, however, shoulders at 315 nm, 410 nm, and 465 nm, one of which may correspond to the 435 band. The changes in the spectra on going from molybdenum to tungsten suggest that the 435 nm band of the molybdenum derivative is due to transitions from the long σ-bonding orbitals since these are the orbitals most perturbed by the structural changes. The complete lack of a strong δ-δ* transition at 500-600 nm lends support to the existence of the long W-W bond, and the possibility of independent quadruply bonded dimers is thus discredited.

The preparation of this tungsten tetramer was especially valuable in that it was shown that techniques used for molybdenum cluster syntheses could be applied to other metals. It now seems possible that

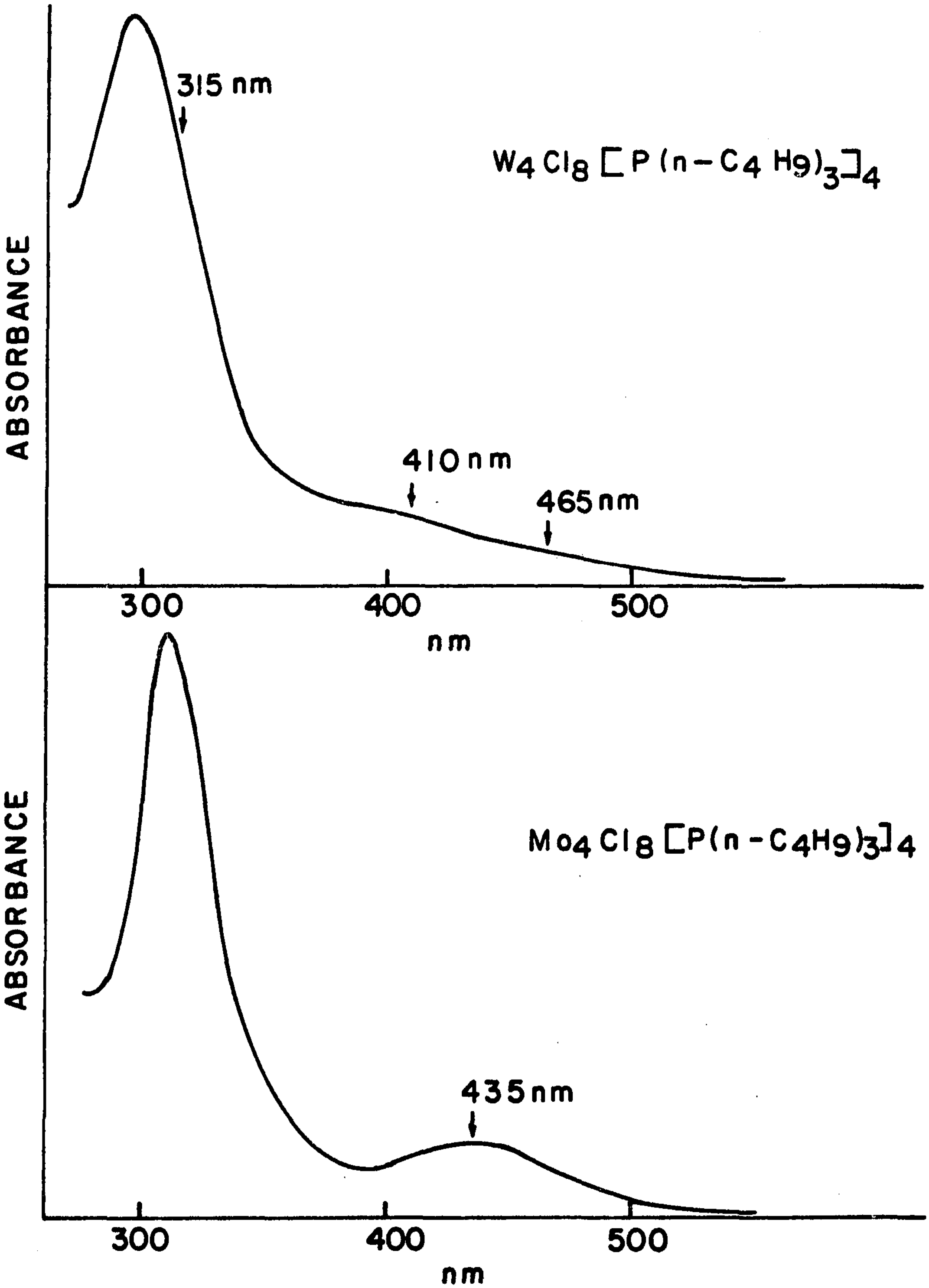

Figure III-5. Electronic absorption spectra of $W_4Cl_8[P(n\text{-}C_4H_9)_3]_4$ and $Mo_4Cl_8[P(n\text{-}C_4H_9)_3]_4$. Solution concentrations not determined tetramers containing still other metals might be prepared by similar techniques. Much work remains to be done on the reactivity of these clusters, especially in regard to possible catalytic activity, which would involve reactions at the multiple metal-metal bond centers.

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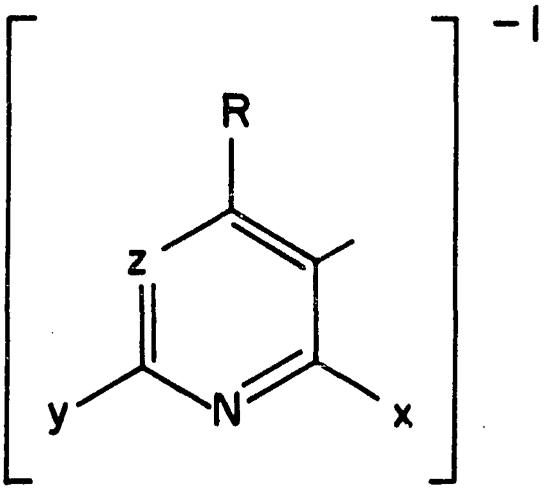
SECTION IV. STRUCTURE OF A TUNGSTEN DIMER WITH A BOND ORDER OF 3 1/2

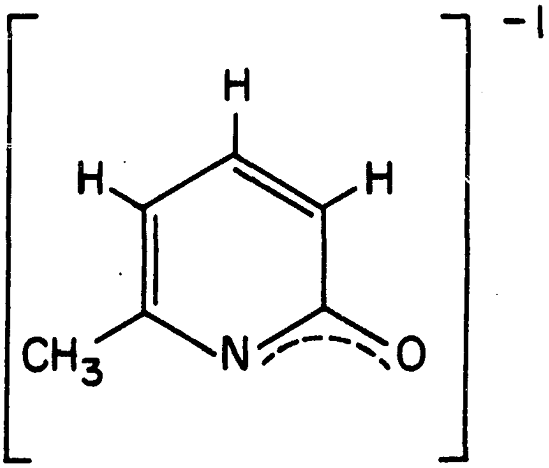
INTRODUCTION

Since 1964 when it was recognized that $Re_2Cl_8^{2-}$ possessed a quadruple Re-Re bond (1), the study of compounds with triple and quadruple metal-metal bonds has increased considerably until today hundreds of such complexes of Cr, Mo, W, Tc, Re and Os are known (2-4). These multiply bonded dimers have electronic configurations of $\sigma^2\pi^4\delta^x\delta^{*y}$ where x and y vary from 0 to 2 to give bond orders of 3 to 4 (3,5). Nonintegral bond orders of 3 1/2 result for Re_2^{5+} and Tc_2^{5+} dimers which have $\sigma^2\pi^4\delta^2\delta^{*1}$ configurations (3). Molybdenum also forms dimers with metal-metal bond orders of 3 1/2, but in these cases, the loss of a δ bonding electron produces the half-filled orbital (2). With the synthesis of the new dimer described here, tungsten can be added to the list of metals which form metal-metal bonds of order 3 1/2.

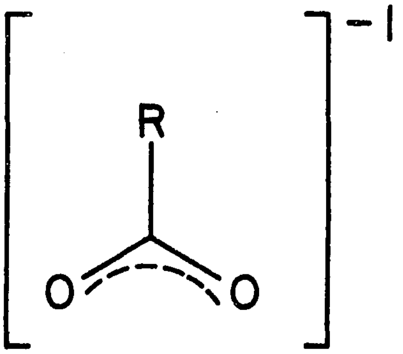
While tungsten is known to form complexes with quadruple metal-metal bonds, these dimers have not been well studied. The unbridged W_2^{4+} dimers characteristically have W-W bond distances which are longer than expected (6), and some, such as $W_2Cl_{8-x}(CH_3)_x$, are thermally unstable as well (7). Other types of tungsten dimers which do possess shorter metal-metal bond lengths utilize ligands of the type shown in Figure IV-1 (8). An example is the anion of 2-methyl-6-hydroxypyridine (mhp) where the bidentate bridging ligands in $W_2(mhp)_4$ (Figure IV-2) produce a dimer with a W-W distance of only 2.161(1)Å (9). The stability of these bridged dimers is due in part to the blocking group y which protects the compound from axial attack.



x = O, NH
y = CH_3, Cl
z = HC, N
R = CH_3, H



mhp



carboxylates

Figure IV-1. Ligand ring systems which produce short W-W bonds compared to carboxylates

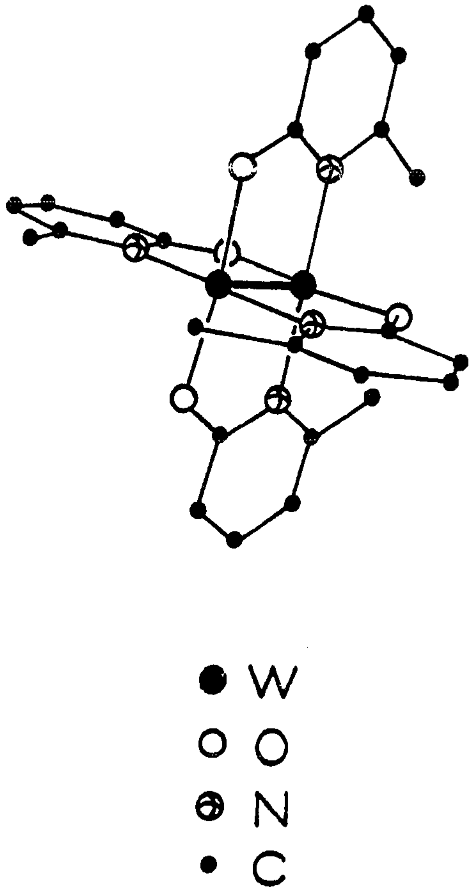


Figure IV-2. Structure of $W_2(mhp)_4$

Since the electronic structure of these tungsten dimers is presumed to be similar to that of quadruply bonded molybdenum dimers, the existence of the new $W_2Cl_2(mhp)_3$ dimer with a $\sigma^2\pi^4\delta^1$ configuration is not surprising. Indeed, tungsten was previously known to participate in such a bonding scheme with molybdenum in the heteronuclear dimer $MoW(O_2CR)_4I$ (10). It is perhaps significant that the tungsten compound was derived from the more stable type of bridged tungsten dimers. Whether the unbridged dimers can also sustain a strong metal-metal bond upon one electron oxidation remains to be seen.

The $W_2Cl_2(mhp)_3$ dimer promises to have an interesting redox chemistry. Cyclic voltammetry studies have shown that a reversible one-electron reduction is possible, and oxidation to a triply bonded species might also be feasible. The cis disposition of the chlorine atoms in $W_2Cl_2(mhp)_3$ is intriguing since displacement of Cl by other ligands might enable chemical reactions to occur at two metal sites simultaneously. Such a situation has very desirable implications for catalytic processes.

EXPERIMENTAL

Materials

Handling of samples and solvents as well as the methods used for elemental analyses were described earlier (11).

Physical Measurements

UV-visible and infrared spectra were obtained in the same manner as set forth earlier (11).

Electron paramagnetic resonance spectra were measured on a Bruker ER-220. X-band spectra (∿3800 G) were obtained at 25° for powdered samples and referenced against a DPPH standard.

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 CH_2Cl_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.

Syntheses

$W_2(mhp)_4$

This dimer was prepared according to published procedures, except about 1/4 the amount of diglyme solvent was used (9).

$W_2Cl_2(mhp)_3 \cdot CH_2Cl_2$

$AlCl_3$ (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. $W_2(mhp)_4$ (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 methylene chloride to produce orange-brown crystalline $W_2Cl_2(mhp)_3 \cdot CH_2Cl_2$ in 67% yield. Anal. Calcd. for $W_2Cl_2(C_6H_6NO)_3 \cdot CH_2Cl_2$: W, 43.37; Cl, 8.36; 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 $W_2(mhp)_3Cl_2$ since the CH_2Cl_2 solvate 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 0.05 M in $(NH_4)Fe(SO_4)_2$ and 1.0 M in H_2SO_4 was degassed, and the $W_2Cl_2(mhp)_3 \cdot CH_2Cl_2$ 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) solution. The net oxidation state for tungsten was found to be 2.55 ± 0.10.

X-ray Structure Determination

Collection and reduction of x-ray data

A crystal of dimensions 0.24 x 0.26 x 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 Ames Laboratory (12). Initial ω-oscillation photographs at various values of chi and phi were used to input 12 reflections into an automatic indexing program, ALICE (13). 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 $K\alpha$ radiation was used, $\lambda = 0.71002$Å. Flotation density measurements provided a value of $z = 4$.

Data were collected to $2\theta = 50°$. 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° ω was used for data collection to insure the whole peak was measured. Of the 9,802 reflections collected over four octants ($hk\ell$, $\bar{h}\bar{k}\ell$, $\bar{h}k\bar{\ell}$, $h\bar{k}\bar{\ell}$), 1,922 were considered unobserved ($I < 3\sigma_I$), and after averaging, 2122 unique reflections were used in the refinement. The data were corrected for Lorentz-polarization effects, and an absorption correction was made ($\mu = 103.9\ \mathrm{cm}^{-1}$). Systematic extinctions in the data set for h00, h = 2n+1; 0k0, k = 2n+1; 00ℓ, ℓ = 2n+1 defined the space group as $P_{2_1 2_1 2_1}$.

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 $\Sigma\, w(|F_o|-|F_c|)^2$ where $w = 1/\sigma_F^2$. The scattering factors were those of Hanson et al. (14) modified for the real and imaginary parts of anomalous dispersion (15).

All atoms were refined anisotropically except 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 $3e^-/\text{Å}^3$ 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 from (x,y,z) to ($\bar{x},\bar{y},\bar{z}$) gave discrepancy factors of R = 0.058 and R_w = 0.080. Final full-matrix refinement did not change these values.

Positional and thermal parameters are given in Tables IV-1 and 2, and an ORTEP drawing of the molecule is shown in Figure IV-3. Distances and angles are listed in Table IV-3.

Table IV-1. Positional parameters ($\times 10^4$) for $W_2Cl_2(mhp)_3\cdot CH_2Cl_2$[a]

Atom	x	y	z
W(1)	8717.6(7)	8839.2(5)	7692(1)
W(2)	244.3(8)	8423.5(4)	7341(1)
Cl(1)	7619(6)	8083(4)	8807(8)
Cl(2)	162(7)	7374(3)	8237(8)
O(1)	8240(16)	8597(9)	5542(20)
N(1)	9776(18)	8138(11)	5080(25)
C(11)	8798(20)	8295(13)	4591(29)
C(12)	9463(26)	8120(13)	3112(35)
C(13)	9177(24)	7814(13)	2193(32)
C(14)	170(20)	7684(15)	2633(34)
C(15)	453(22)	7857(13)	4093(32)
C(16)	1497(23)	7739(16)	4664(31)
O(2)	9084(14)	9193(10)	9812(20)
N(2)	706(16)	8795(10)	9496(23)
C(21)	9986(22)	9099(13)	377(31)
C(22)	257(25)	9336(16)	1858(30)
C(23)	1186(26)	9214(15)	2386(41)
C(24)	1927(21)	9907(12)	1529(37)
C(25)	1662(21)	8704(13)	130(28)
C(26)	2435(21)	8387(14)	9076(38)
O(3)	834(14)	9209(11)	6388(23)
N(3)	9258(22)	9722(10)	6775(28)
C(31)	272(21)	9714(13)	6243(25)
C(32)	625(25)	276(14)	5549(38)
C(33)	00(32)	785(16)	5389(52)
C(34)	8968(31)	743(16)	5871(38)

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

Table IV-1. (Continued)

Atom	x	y	z
C(35)	8691(25)	212(15)	6599(38)
C(36)	7579(22)	117(14)	7301(49)
C(1)	4550(49)	8794(29)	4721(82)
Cl(3)	5581(17)	8977(11)	5740(29)
Cl(4)	3505(16)	9220(10)	5113(25)

Table IV-2. Thermal parameters ($\times 10^4$) for $W_2Cl_2(mhp)_3 \cdot CH_2Cl_2$[a,b]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
W(1)	41.6(6)	21.1(2)	97(1)	2.5(3)	-2.0(8)	-2.9(5)
W(2)	43.5(6)	20.0(2)	90(1)	4.3(3)	-5.0(9)	-3.9(5)
Cl(1)	59(5)	31(2)	126(10)	-10(3)	7(6)	6(4)
Cl(2)	95(6)	21(2)	130(10)	3(3)	-4(7)	10(3)
O(1)	79(14)	31(6)	83(23)	3(8)	-28(17)	-4(9)
N(1)	41(12)	27(6)	120(32)	-3(8)	-27(19)	-4(11)
C(11)	39(15)	26(7)	107(35)	8(9)	12(21)	15(14)
C(12)	99(27)	18(6)	146(45)	-5(10)	5(30)	-2(14)
C(13)	79(21)	28(7)	105(39)	-20(10)	-6(26)	-19(15)
C(14)	41(14)	41(9)	113(39)	-3(10)	-23(26)	14(17)
C(15)	60(20)	23(7)	123(39)	9(10)	25(24)	-17(14)
C(16)	65(22)	42(11)	85(36)	23(12)	20(23)	-1(16)
O(2)	52(12)	33(6)	82(24)	6(7)	8(14)	-6(10)
N(2)	61(14)	16(4)	91(28)	1(7)	-3(17)	6(10)
C(21)	71(24)	25(7)	88(35)	2(10)	25(23)	6(13)
C(22)	75(21)	35(8)	91(36)	-7(13)	-39(25)	-2(15)
C(23)	92(25)	30(8)	171(52)	6(12)	18(39)	-3(19)
C(24)	51(17)	18(6)	205(50)	-10(9)	-42(25)	-7(15)
C(25)	52(16)	23(7)	79(31)	-8(9)	-8(20)	-3(12)
C(26)	46(17)	27(8)	203(52)	-15(10)	20(26)	-24(18)
O(3)	44(11)	38(6)	136(30)	-9(7)	-22(16)	0(12)
N(3)	106(21)	15(5)	135(35)	2(9)	14(24)	-6(11)

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

[b] Bij are defined by $T = \exp[-(h^2\beta_{11} + k^2\beta_{22} + \ell^2\beta_{33} + 2hk\beta_{12} + 2h\ell\beta_{13} + 2k\ell\beta_{23})]$.

Table IV-2. (Continued)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(31)	54(16)	26(7)	53(28)	10(10)	-11(21)	-4(11)
C(32)	77(22)	23(7)	161(48)	-12(11)	-24(29)	-5(16)
C(33)	120(39)	22(8)	277(80)	-19(15)	-12(46)	27(21)
C(34)	117(31)	26(8)	142(49)	10(14)	4(33)	8(17)
C(35)	75(23)	29(9)	157(49)	6(12)	-23(29)	26(18)
C(36)	50(17)	27(8)	29(74)	6(9)	-3(36)	7(23)
	B^c					
C(1)	11.7(18)					
Cl(3)	15.4(7)					
Cl(4)	13.8(6)					

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[c] Isotropic temperature factors, B, are given in $Å^2$.

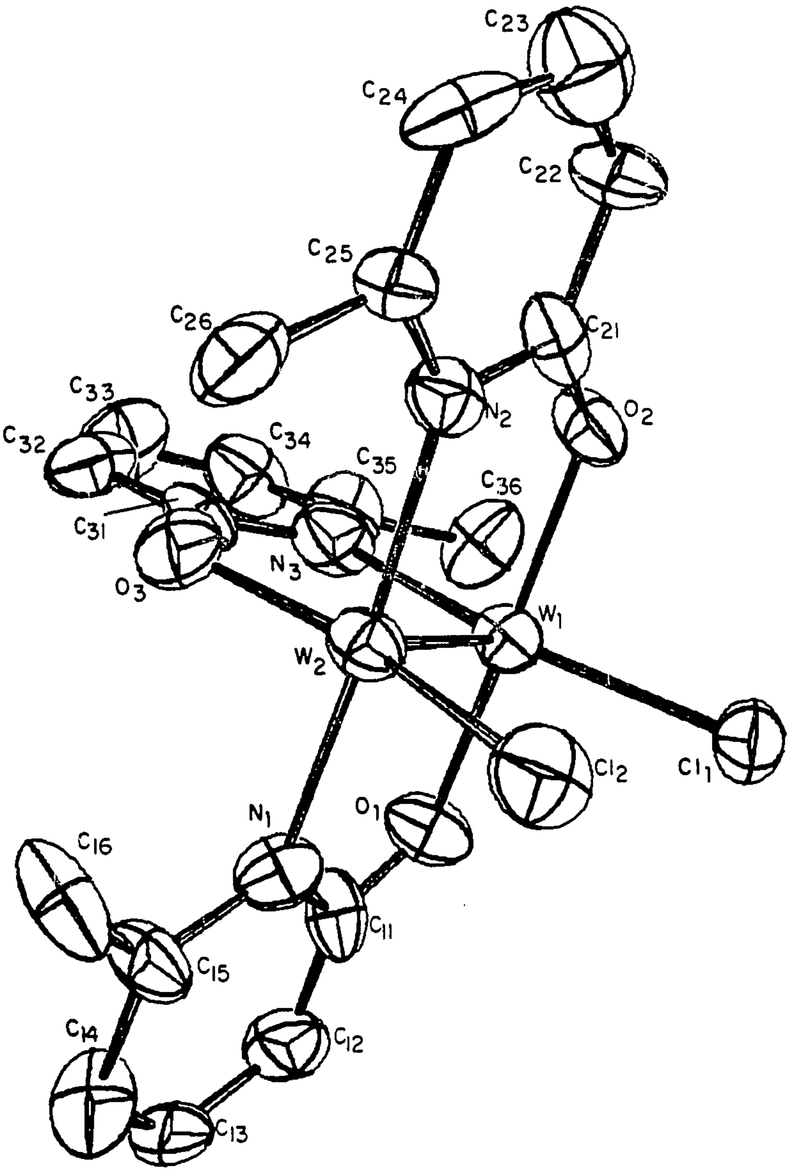


Figure III-3. Structure of the $W_2Cl_2(mhp)_3$ molecule with numbering scheme for atoms shown. Atoms are represented by thermal ellipsoids scaled to 50% of the electron density

Table IV-3. Bond distances (Å) and angles (°) 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)		

RESULTS

Syntheses and Characterizations

Previous work (16) has described methods by which halides may be substituted for acetate groups in $Mo_2(O_2CCH_3)_4$. These methods can be used to prepare trialkylphosphine derivatives of quadruply bonded molybdenum dimers as shown by the equation

$$Mo_2(O_2CCH_3)_4 + 4\ AlCl_3 + 4\ PR_3 \longrightarrow Mo_2Cl_4(PR_3)_4 + 4\ AlCl_2(O_2CCH_4)$$

Since $W_2(O_2CR)_4$ compounds have not yet been isolated, application of this type of synthesis to tungsten compounds is not possible. There does exist, however, a class of compounds with ligands similar to acetates in both electronic structure and chelating geometry which are shown in Figure IV-1. Extension of the chlorine substitution reaction to these compounds seemed an ideal method for the direct preparation of $W_2Cl_4(PR_3)_4$ dimers. Unfortunately, reaction of $W_2(mhp)_4$ with $AlCl_3$ in the presence of trialkylphosphine did not produce the desired complex. Instead, a product containing no trialkylphosphine was isolated. Subsequent syntheses omitted the phosphine from the reaction, and the compound finally obtained was found to be a new dimer, $W_2Cl_2(mhp)_3$.

$$W_2(mhp)_4 + 5\ AlCl_3 \longrightarrow W_2Cl_2(mhp)_3 + ?$$

No products other than the tungsten dimer were characterized.

The crystalline product is moderately air sensitive, darkening after a few minutes exposure to the laboratory atmosphere. This is in contrast to the $W_2(mhp)_4$ dimer which is nearly air stable (9). Solutions of $W_2Cl_2(mhp)_3$ in tetrahydrofuran, acetonitrile, or methylene chloride are even more air sensitive.

Except for an extra band at 321 cm^{-1}, the infrared spectrum of $W_2Cl_2(mhp)_3$ is quite similar to $W_2(mhp)_4$ (Table IV-4). The 321 cm^{-1} band must arise from one of the two W-Cl stretching vibrations which are IR active, and the strong band 289 cm^{-1} suggests the other may lie in this region.

The extremely low conductivity of acetonitrile solutions ($\Lambda_m \sim 2$ ohm^{-1} cm^2 $moles^{-1}$) showed that $W_2Cl_2(mhp)_3$ was not an ionic compound. Therefore, the molecular formula requires that $W_2Cl_2(mhp)_3$ be paramagnetic. Although no magnetic susceptibility data have been obtained to date, the EPR spectrum of the powdered solid did present a strong band with $g = 1.842$. The signal was a featureless band about 800 G wide, which was only slightly asymmetric.

Cyclic voltammograms have been obtained for $W_2Cl_2(mhp)_3$ in methylene chloride. A quasi-reversible reduction occurs at $E_{1/2} \simeq -0.7$ V vs. SSCE ($E_{p,c} - E_{p,a} > 60$ mv, $i_{p,c}/i_{p,a} = 1$). This wave presumably involves addition of an electron to the half-filled δ bonding orbital of the dimer. Slow voltage sweep rates have shown that the reduced species is stable for at least 90 sec. Additionally, an irreversible oxidation occurs at $E_{p,a} \simeq +0.3$ V.

Table IV-4. Infrared spectra (cm^{-1}) of tungsten dimers 200 cm^{-1} to 400 cm^{-1} (s = strong, m = medium, w = weak)

$W_2Cl_2(mhp)_3 \cdot CH_2Cl_2$	$W_2(mhp)_4$
400 (m)	403 (m)
386 (m)	388 (m)
321 (s)	280 (m)
289 (s)	240 (w)
230 (w)	

Crystal Structure

The structure of $W_2Cl_2(mhp)_3$, shown in Figure IV-3, is like that of $W_2(mhp)_4$ (9) (Figure IV-2) except that one of the bridging ligands has been replaced by two chlorine atoms. The disposition of the remaining three bidentate 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. Although no symmetry is imposed upon the molecule by its crystallographic site, the compound has virtual C_s symmetry. Solvate methylene chloride molecules are trapped in pockets between the dimers and do not interact with them.

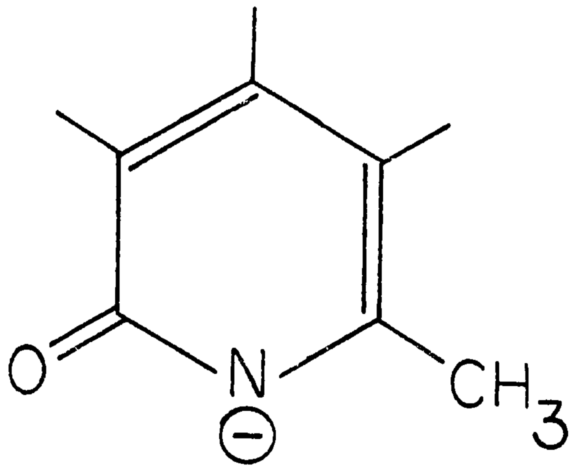
Bond distances and angles (Table IV-3) in the ligand rings are comparable to those found for $W_2(mhp)_4$ (9). The two W-Cl bond distances are within one standard deviation of each other at 2.37Å. A strong metal-metal bond is present in this molecule as shown by the W-W bond distance at 2.214(2)Å.

DISCUSSION

There are two points of interest concerning the synthesis of $W_2Cl_2(mhp)_3$. The first is that while $AlCl_3$ reacts very rapidly with $Mo_2(O_2CCH_3)_4$ to give chloride substituted Mo(II) dimers, complete replacement of mhp ligands is not achieved for the tungsten dimer. The inert substitution behavior of the compound gives an indication of the affinity of the mhp ligands for the dimeric metal unit. In fact, the only known reactions which accomplish complete replacement of mhp-type ligands always result in oxidation of the tungsten dimer as well (17,18). The substitution of one bridging ligand of $W_2(mhp)_4$ by two chlorine atoms is also accompanied by oxidation. The second noteworthy aspect of the synthesis is that the nature of the oxidizing agent is unknown. Since all syntheses have produced yields greater than 50%, it seems unlikely that a contaminant in the reagents could be at fault. A more likely oxidant is a chlorinated hydrocarbon species which may form when $AlCl_3$ attacks the ether solvent (19). Nevertheless, the reproducibility of the preparation has been well established, and further investigation into this question has not been deemed essential at this time.

Proof that $W_2Cl_2(mhp)_3$ indeed possessed the W_2^{5+} unit was of prime importance. The oxidation state determination as well as the non-ionic nature of the compound both agree with this assessment. In addition, the apparent paramagnetism as revealed by the EPR measurements is consistent with a $\sigma^2\pi^4\delta^1$ configuration. Even further evidence is available through comparison of the metal-metal bond length with similar compounds. Loss of one bonding electron from the δ bonding orbital should result in some increase in the W-W distance. This is actually the case as $W_2(mhp)_4$ has a 2.161(1)Å W-W separation (9), while in $W_2Cl_2(mhp)_3$ this has expanded to 2.214(2)Å. In the related isoelectronic $Mo(SO_4)_4{}^{4-,3-}$ dimers, the $Mo_2{}^{5+}$ separation is about 0.054Å longer than in the $Mo_2{}^{4+}$ species (20), which compares well with the 0.053Å increase seen here. Tungsten(III) dimers with a $\sigma^2\pi^4\delta^0$ configuration would be expected to have an even larger metal-metal separation, and although strict comparisons are difficult because known dimers with this electron configuration do not have mhp-type ligands, the metal-metal distances are longer at 2.25 - 2.30Å (3).

The structural features of the ligand ring systems are basically the same as seen in the $W_2(mhp)_4$ compound. The question of which tautomeric form the anionic mhp ligand prefers in these compounds has been addressed previously by Cotton et al. (9). Of the two tautomeric forms shown in Figure IV-4, it was concluded from the bond distance data that an average of both types best described the ligand charge distribution in $W_2(mhp)_4$. Similar conclusions can be drawn from analysis of the structural data of $W_2Cl_2(mhp)_3$. Unlike $W_2(mhp)_4$, however, $W_2Cl_2(mhp)_3$ has the added possibility of charge separation in the molecule since the $W_2{}^{5+}$ unit can be considered as a W^{3+}-W^{2+} dimer. Studies of $Mo_2(SO_4)_4{}^{3-}$ ($\sigma^2\pi^4\delta^1$) and $Te_2Cl_8{}^{3-}$ ($\sigma^2\pi^4\delta^2\delta^{*1}$) have shown that the odd electron resides equally on both metals, and $W_2Cl_2(mhp)_3$ is expected to behave similarly. However, any tendency of the ligands to prefer one tautomer over the other would also induce charge



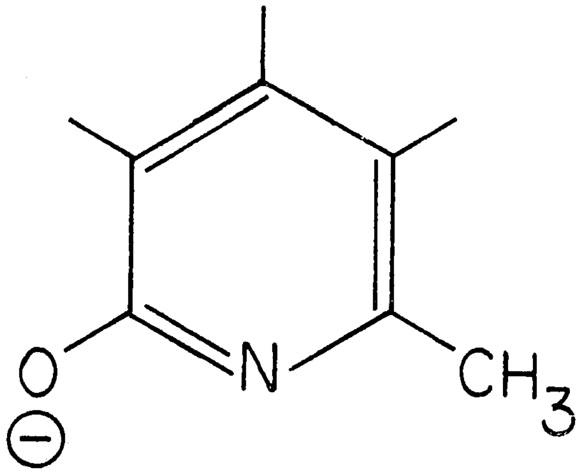


Figure IV-4. Anions of the tautomers of 2-hydroxy-6-methylpyridine separation in the W_2^{5+} dimer. None of the bond distances suggest that any significant charge separation occurs, although it is possible that a partial transfer of charge may not cause observable structural changes.

The differences between the electronic structures of $W_2Cl_2(mhp)_3$ and $W_2(mhp)_4$ are evident from a comparison of the uv-visible spectra of the two compounds in Figure IV-5. No band assignments have been made for either $W_2Cl_2(mhp)_3$ or $W_2(mhp)_4$, and considering the difficulties encountered with the electronically similar metal carboxylates (2), it would be pointless to attempt band assignments with the limited data available here.

There are many features of this dimer that warrant further study. Electrochemical measurements indicate $W_2Cl_2(mhp)_3$ might serve as a redox center where coordinated species could react without destroying the strong metal-metal bond. This robust dimer may, therefore, prove to be well-suited for catalyzing reactions at the metal sites. For this to occur, the chlorine atoms must first be displaced in order for the reactants to coordinate to the tungsten atoms. Substitution of -H, -OR, and -R groups for chlorine would provide the types of compounds known to engage in reductive elimination and insertion reactions (21-23) which are common in catalytic cycles. Additionally, chemical reduction of $W_2Cl_2(mhp)_3$, or substitution of chlorine by a neutral ligand may provide compounds which exhibit unusual reactivity. Another interesting aspect of this dimer is the cis disposition of the nonmhp ligands on each tungsten. Molecules coordinated to the metal atoms in place of the

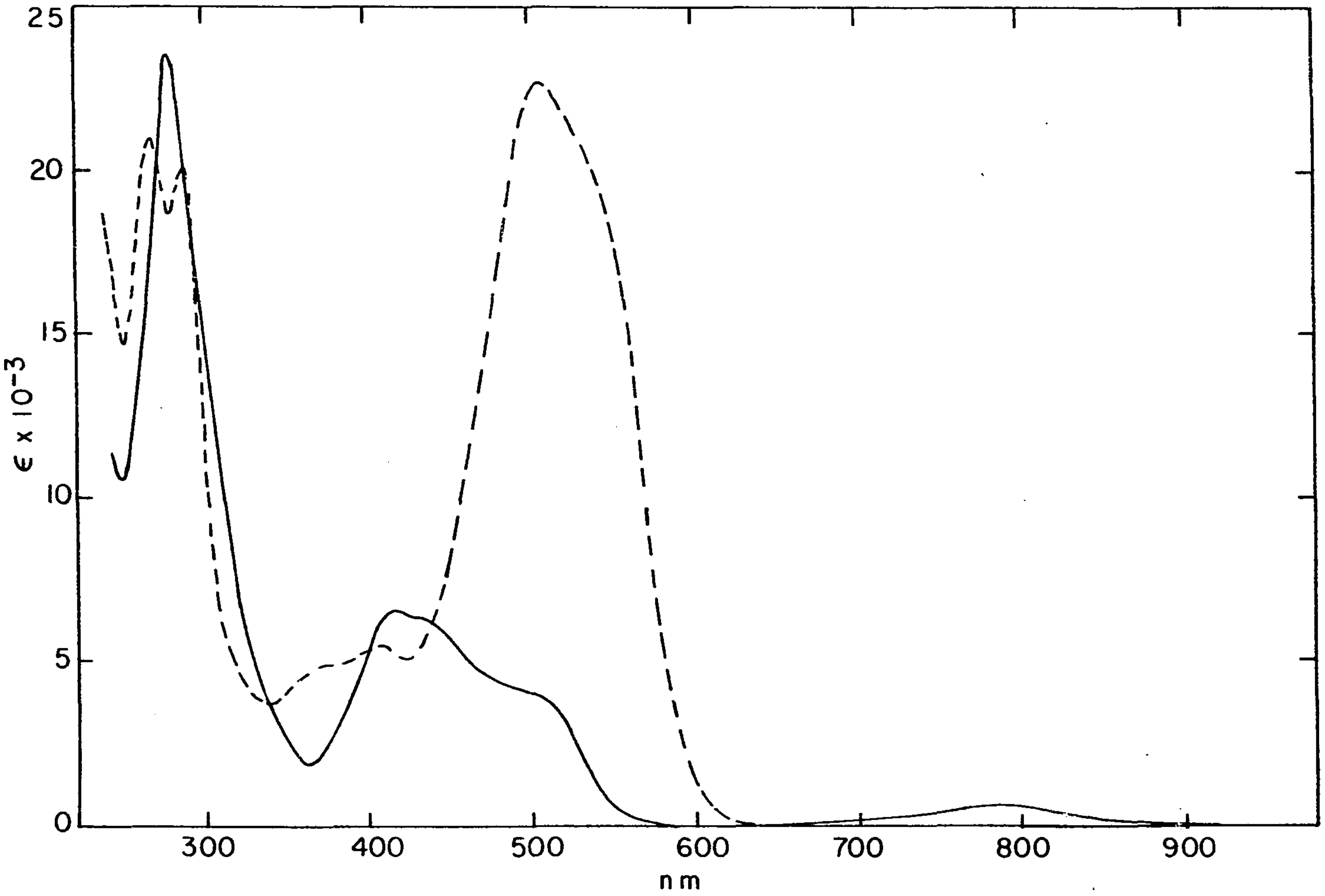


Figure IV-5. Electronic spectra of $W_2Cl_2(mhp)_3$ (——) and $W_2(mhp)_4$ (---)

chlorine atoms would be held in close proximity to each other. Thus, reactions between adjacent groups should be facilitated. All these characteristics will make $W_2Cl_2(mhp)_3$ an interesting subject for further investigations.

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SUMMARY

The original goal of this project was to prepare a reactive quadruply bonded molybdenum dimer. This was accomplished with the synthesis of $Mo_2Cl_4[P(C_6H_5)_3]_2(CH_3OH)_2$, which by self-addition across the multiple metal-metal bond, produced a new type of tetrameric cluster. Exploitation of the same synthetic principles with another quadruply bonded dimer yielded the isostructural tungsten tetramer, thus showing that these preparative techniques should be applicable to syntheses of tetramers containing other metals or even the preparation of larger clusters.

The reaction of $Mo_2Cl_4[P(C_6H_5)_3]_2(CH_3OH)_2$ to produce a new tetrameric cluster was apparently due to the lability of its weakly bound neutral ligands. A number of the $Mo_4Cl_8L_4$ clusters were prepared and characterized. More importantly, new methods were found for the syntheses of the tetrameric molybdenum clusters enabling $Mo_4X_8(PR_3)_4$, X = Cl, Br, I, compounds to be easily prepared. A bonding scheme for these clusters was presented which accounts for the known structural and electronic properties.

The methods of the molybdenum cluster syntheses were applied to tungsten dimers with the expectation that tungsten tetramers could also be prepared. Such a tetrameric cluster compound was indeed isolated. Structural differences between $W_4Cl_8(PR_3)_4$ and $Mo_4Cl_8(PR_3)_4$ were compared and rationalized in terms of the known behavior in dimeric species.

An unsuccessful attempt to prepare the tetrameric tungsten cluster by another route nevertheless led to the preparation of a new and interesting tungsten dimer with a metal-metal bond order of 3.5. The structural and electronic features of this compound were studied, and suggestions were made for future work.

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