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Synthesis and Characterization of Rectangular Tetranuclear Cluster Complexes of Molybdenum(II) by Condensation of Quadruply Bonded Dimers

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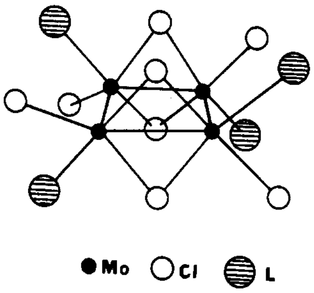
Several new synthetic methods have been developed for preparation of the rectangular tetrameric cluster complexes $Mo_4X_8L_4$ (X = Cl, Br, I; L = neutral donor ligand). $Mo_4Cl_8(CH_3OH)_4$ is prepared efficiently from the dimer $Mo_2Cl_4(PPh_3)_2(CH_3OH)_2$ and subsequently converted in good yield to $Mo_4Cl_8(C_2H_5CN)_4$ by reaction with propionitrile. Reaction of $Mo_4Cl_8(C_2H_5CN)_4$ with triphenylphosphine yields $Mo_4Cl_8(PPh_3)_4$, and with tetrahydrofuran the unstable $Mo_4Cl_8(THF)_4$ is afforded. The trialkylphosphine derivatives $Mo_4Cl_8(PR_3)_4$ (R = C_2H_5 or C_4H_9) may be obtained more conveniently in reactions between (a) $K_4Mo_2Cl_8$ + PR_3 (1:2 mole ratio), (b) $Mo_2(O_2CCH_3)_4$ + PR_3 + $(CH_3)_3SiCl$ (1:2:4 mole ratio), (c) $Mo_2(O_2CCH_3)_4$ + PR_3 + $AlCl_3$ (1:2:2 mole ratio), or (d) $Mo_2Cl_4(PR_3)_4$ + $Mo(CO)_6$ (1:1 mole ratio). The $Mo_4Br_8(P\text{-}n\text{-}Bu_3)_4$ prepared by analogous methods exhibits properties closely related to the chloride derivative; $Mo_4I_8(P\text{-}n\text{-}Bu_3)_4$ however appears to consist of weakly coupled quadruply bonded dimers. The various compounds have been characterized by UV-visible, infrared, and Cl 2p photoelectron spectra which reflect the basic rectangular cluster structure known for $Mo_4Cl_8(PEt_3)_4$.

Introduction

The preparation of tetrakis(phosphine)tetrachlorotetra-μ-chloro-tetramolybdenum(*Mo–Mo*), $Mo_4Cl_8(PR_3)_4$, from bis(methanol)bis(triphenylphosphine)tetrachlorodimolybdenum(*Mo–Mo*), $Mo_2Cl_4(PPh_3)_2(MeOH)_2$, has been described in a preliminary communication.[2] On the basis of the structure found for $Mo_4Cl_8(PEt_3)_4$,[2] the general structural formula for these rectangular clusters can be represented as



where L signifies any potential electron pair donor ligand. Bond distances strongly indicate that the short, unbridged edges of the Mo_4 rectangle are Mo–Mo triple bonds and the doubly bridged, long edges are Mo–Mo single bonds.[2,3] As a result of this structure, the formation of the rectangular clusters can be viewed as the cycloaddition of two quadruply bonded dimers.

Cycloaddition of $Mo_2Cl_4(PPh_3)_2(MeOH)_2$ proceeds with elimination of either methanol or triphenylphosphine ligands and formation of $Mo_4Cl_8(PPh_3)_4$ or $Mo_4Cl_8(MeOH)_4$, respectively. This process is facilitated by the unusual lability of these ligands in this "activated" dimer. It is believed that the addition reaction is initiated by dissociation of ligand from the dimeric complex followed by coupling of coordinately unsaturated dimers through bridging chloride. Although the exact mechanism is not known, the process may be represented by eq 1 and 2.

$$2Mo_2Cl_4L_4 = 2Mo_2Cl_4L_3 + 2L \qquad (1)$$

$$2Mo_2Cl_4L_3 = Mo_4Cl_8L_4 + 2L \qquad (2)$$

The purpose of this work was to develop more general synthetic routes to rectangular clusters of the type $Mo_4X_8L_4$, where X = Cl, Br, or I and L = neutral donor ligands. Several reactions have been devised which lead to formation of the tetranuclear clusters in high yields from easily obtained starting materials.[3] Physical characterization of the new compounds with L = CH_3OH, C_4H_8O (THF), C_2H_5CN, and $P(C_6H_5)_3$ has shown that these are structurally and electronically similar to the known compounds $Mo_4Cl_8(PR_3)_4$ (R = alkyl).

Experimental Section

Materials. 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 (4 Å) for storage. Propionitrile was refluxed over phosphorus pentoxide and distilled under a nitrogen atmosphere to a stoppered flask for storage. Methanol was dried by refluxing with NaOMe followed by distillation under nitrogen onto molecular sieves (–3A) for storage. 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.

$Mo_2(O_2CCH_3)_4$,[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] $Mo_2Cl_4(PEt_3)_4$,[8] and $Mo_2Cl_4(PPh_3)_2(CH_3OH)_2$[2] were prepared by established procedures.

$(NH_4)_4Mo_2Br_8$. This compound was prepared with 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 1 h. The violet product obtained in 40% yield was filtered, washed with a few milliliters 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.

Physical Measurements. Infrared spectra were measured as Nujol mulls on either Beckman IR-4250 or Acculab-4 spectrophotometers. Solution UV-visible spectra were measured on Cary 14 and 219 spectrophotometers in nitrogen-filled cells equipped with septa. 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

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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.[8] Component peaks in the observed spectra were resolved by least-squares curve fitting with use of a computer program developed in this laboratory[9] 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.

$Mo_4Cl_8(CH_3OH)_4$. $Mo_2Cl_4[P(C_6H_5)_3]_2(CH_3OH)_2$ (5.00 g, 5.42 mmol) was added to 50 mL of cyclohexane (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 1 h, an insoluble yellow product developed; this was filtered, washed with 30 mL of 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 of propionitrile under nitrogen for 1 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 4 days. The collection flask of the extraction apparatus was then cooled to 0 °C for 1 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 of tetrahydrofuran. The product was filtered from the solution after 24 h, 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 3–4 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 of tetrahydrofuran under nitrogen. After 2 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.[2]

(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 6 h in 30 mL of 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 of methanol for 1 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%. Anal. 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 $Mo_4Cl_8(PEt_3)_4$ was then washed with methanol and diethyl ether. The yield was 60%. Anal. 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 of tetrahydrofuran for 1 day. The solution was cooled, and 70 mL of methanol was added to precipitate a yellow product. After being washed well with methanol and diethyl ether, the product $Mo_4Cl_8(P\text{-}n\text{-}Bu_3)_4$ 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.

(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 of refluxing tetrahydrofuran for 1 day. The yellow $Mo_4Cl_8(PEt_3)_4$ 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 of chlorobenzene. Heating the solution rapidly to reflux caused the blue solution to quickly turn brown. After 1 h, 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.

$Mo_4Br_8[P(n\text{-}C_4H_9)_3]_4$. The following two methods were devised.

(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 of methanol at 0 °C, and after 6 h the methanol was removed by vacuum distillation while the solution was kept cool. The residue was stirred with 15 mL of 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). Methanol (20 mL) was 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 of methylene chloride for 1 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 with 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 of 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 1 day at 0 °C. Removal of solvent by vacuum distillation produced a dark green residue which was extracted in vacuo with diethyl ether for 1 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

Clusters Derived from $Mo_2Cl_4(PPh_3)_2(MeOH)_2$. As noted previously[2] ligand dissociation from the labile dimer $Mo_2Cl_4(PPh_3)_2(MeOH)_2$ leads to condensation of dimer units, resulting in formation of rectangular clusters. Depending upon

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Table I. Far-Infrared Spectra (cm^{-1}) of Tetrameric Clusters

$Mo_4Cl_8(CH_3OH)_4$[a]	$Mo_4Cl_8(CH_3CH_2CN)_4$	$Mo_4Cl_8(C_4H_8O)_4$
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	

[a] Intensities: s = strong, m = medium, w = weak, sh = shoulder.

reaction conditions, either the phosphine or methanol ligands are lost according to eq 3 or 4.

$$2Mo_2Cl_4(PPh_3)_2(MeOH)_2 = Mo_4Cl_8(PPh_3)_4 + 4MeOH \tag{3}$$

$$2Mo_2Cl_4(PPh_3)_2(MeOH)_2 = Mo_4Cl_8(MeOH)_4 + 4PPh_3 \tag{4}$$

In benzene loss of methanol is favored (eq 3), but this reaction is not suitable for the preparation of pure $Mo_4Cl_8(PPh_3)_4$ because of secondary reaction between this product and the liberated methanol. The preparation of $Mo_4Cl_8(PPh_3)_4$ is more satisfactory when effected from the reaction between $Mo_4Cl_8(EtCN)_4$ and PPh_3 (vide infra).

Loss of PPh_3 and formation of $Mo_4Cl_8(MeOH)_4$ according to eq 4 are prompted in the two-phase solvent system methanol–cyclohexane. Addition of HCl is necessary to suppress methanolysis of the product which precipitates as a yellow microcrystalline solid. Apparently the two-phase solvent system is effective because methanol suppresses dissociation according to eq 3 and promotes eq 4 by removal of PPh_3 into the immiscible cyclohexane phase. The infrared spectrum of $Mo_4Cl_8(MeOH)_4$ shows bands arising from coordinated methanol:[10] ν(OH) 3360, 1112 cm^{-1}; ν(CO) 990 cm^{-1}. Bands arising from Mo–Cl stretching modes are listed in Table I.

The Cl 2p XPS of $Mo_4Cl_8(MeOH)_4$ 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. This lability of the methanol was also demonstrated by the loss of methanol from the solid when heated in vacuo at 150–200 °C (eq 5). The residue remaining contained no methanol (shown

$$Mo_4Cl_8(MeOH)_4 = 4\beta\text{-}MoCl_2 + 4MeOH \tag{5}$$

by its infrared spectrum), and the Debye–Scherrer X-ray powder pattern was identical with the diffuse pattern known for β-$MoCl_2$.[11]

The methanol tetramer was easily converted back to quadruply bonded dimers by reaction with donor ligands. When stirred with pyridine for 12 h at 25 °C, a red precipitate was produced (eq 6) which was identified by infrared and

$$Mo_4Cl_8(MeOH)_4 + 8C_5H_5N = 2Mo_2Cl_4(C_5H_5N)_4 + 4MeOH \tag{6}$$

UV–visible spectroscopy as the quadruply bonded dimer $Mo_2Cl_4(C_5H_5N)_4$.[12] Reactions of $Mo_4Cl_8(MeOH)_4$ with donor ligands could also be limited to simple ligand substitutions (eq 7). When the amount of trialkylphosphine was

$$Mo_4Cl_8(MeOH)_4 + 4L = Mo_4Cl_8L_4 + 4MeOH \tag{7}$$

limited to 4 equiv of phosphine/equiv 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 $Mo_4Cl_8(EtCN)_4$ cluster was found to possess many of the same properties as $Mo_4Cl_8(MeOH)_4$. 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 EtCN occurred readily to produce complexes with mixed ligands (vide infra). The infrared spectrum of $Mo_4Cl_8(EtCN)_4$ exhibited the bands for coordinated propionitrile, ν(CN) 2280 cm^{-1}, and several Mo–Cl vibrations between 400 and 200 cm^{-1} (Table I). An attempt to obtain XPS data was plagued by the same decomposition problems as observed for $Mo_4Cl_8(MeOH)_4$.

Because the nitrile ligands were weakly coordinated and easily displaced, $Mo_4Cl_8(EtCN)_4$ 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 derivatives were obtained in nearly quantitative yields (eq 8).

$$Mo_4Cl_8(EtCN)_4 + 4L = Mo_4Cl_8L_4 + 4EtCN \tag{8}$$

The tetrahydrofuran complex was synthesized by long extraction of $Mo_4Cl_8(EtCN)_4$ 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.[11] Because of the volatility of THF in $Mo_4Cl_8(C_4H_8O)_4$, analysis of this material was somewhat imprecise. When the compound was stored in vacuo over liquid tetrahydrofuran at 0 °C (vapor pressure of THF was approximately 65 torr), 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. 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 and 860 cm^{-1}. The far-infrared data are given in Table I, and again a complex series of Mo–Cl bands typical of these tetrameric clusters is evident.

The triphenylphosphine derivative, $Mo_4Cl_8(PPh_3)_4$, could only be prepared via $Mo_4Cl_8(EtCN)_4$. 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.

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The infrared spectrum confirmed the absence of residual propionitrile in the compound, and only bands due to triphenylphosphine were observed above 400 $\mathrm{cm^{-1}}$ while the far-infrared spectral data again showed a complex pattern (Table I).

Syntheses of the Trialkylphosphine Clusters, $\mathrm{Mo_4Cl_8(PR_3)_4}$. Decomposition of the quadruply bonded dimer, $\mathrm{Mo_2Cl_4[P(C_6H_5)_3]_2CH_3OH)_2}$, in benzene was the first method by which the tetrameric clusters were isolated.[2] 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. So that this assumption could be tested, $\mathrm{Mo_2Cl_4(PEt_3)_4}$ was reacted with $\mathrm{Mo(CO)_6}$. In this reaction, eq 9, the production of

$$\mathrm{2Mo_2Cl_4[P(C_2H_5)_3]_4 + 2Mo(CO)_6 = Mo_4Cl_8[P(C_2H_5)_3]_4 + 4CO + 2Mo(CO)_4[P(C_2H_5)_3]_2} \qquad (9)$$

$\mathrm{Mo(CO)_4(PEt_3)_2}$ and carbon monoxide gas was presumed,[13] although no product identification was attempted. When a stoichiometric amount of $\mathrm{Mo(CO)_6}$ was used for the elimination of 2 mol of triethylphosphine/mol of dimer, the product isolated was indeed identified as $\mathrm{Mo_4Cl_8(PEt_3)_4}$ by infrared and UV–visible spectroscopy.

A major improvement in the synthesis of trialkylphosphine tetramers $\mathrm{Mo_4Cl_8(PR_3)_4}$ resulted from the reaction between $\mathrm{K_4Mo_2Cl_8}$ and phosphine ligand in methanol (eq 10). This

$$\mathrm{2K_4Mo_2Cl_8 + 4PR_3 = Mo_4Cl_8(PR_3)_4 + 8KCl} \qquad (10)$$

reaction was originally investigated as a possible route to the dimers $\mathrm{Mo_2Cl_4(PR_3)_2(MeOH)_2}$, which are still unknown. Instead the reaction led directly to tetramer formation when the molar ratio $\mathrm{PR_3{:}K_4Mo_2Cl_8}$ was maintained as in eq 10. With the use of higher $\mathrm{PR_3{:}K_4Mo_2Cl_8}$ ratios the reaction under these conditions leads to dimers, $\mathrm{Mo_2Cl_4(PR_3)_4}$.[14,15] The use of $\mathrm{(NH_4)_5Mo_2Cl_9{\cdot}H_2O}$ in place of $\mathrm{K_4Mo_2Cl_8}$ for synthesis of tetramer according to eq 10 is less satisfactory because of reduced yields.

The most direct syntheses of $\mathrm{Mo_4Cl_8(PR_3)_4}$ tetramers used $\mathrm{Mo_2(O_2CCH_3)_4}$ as the starting material. Here, chlorinating agents such as $\mathrm{AlCl_3}$ or $\mathrm{(CH_3)_3SiCl}$ were used to displace acetate from the dimer and provide a source of halide. In the presence of excess trialkylphosphine, the $\mathrm{Mo_2Cl_4(PR_3)_4}$ dimers have been isolated in high yields[16] (eq 11). Reduction of the

$$\mathrm{Mo_2(O_2CCH_3)_4 + 4(CH_3)_3SiCl + 4PR_3 = Mo_2Cl_4(PR_3)_4 + 4(CH_3)_3Si(O_2CCH_3)} \qquad (11)$$

reaction ratio to 2 mol of trialkylphosphine/mol of $\mathrm{Mo_2(O_2CCH_3)_4}$ (eq 12) again produced the desired $\mathrm{Mo_4Cl_8(PR_3)_4}$

$$\mathrm{2Mo_2(O_2CH_3)_4 + 8(CH_3)_3SiCl + 4PR_3 = Mo_4Cl_8(PR_3)_4 + 8(CH_3)_3Si(O_2CCH_3)} \qquad (12)$$

clusters. However, 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 (eq 13).

$$\mathrm{Mo_2(O_2CCH_3)_4 + 2AlCl_3 + 10P(C_6H_5)_3 = Mo_2Cl_2(O_2CCH_3)_2[P(C_6H_5)_3]_2 + 2AlCl_2(O_2CCH_3) + 8P(C_6H_5)_3} \qquad (13)$$

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

Table II. Electronic Absorption Spectra of $\mathrm{Mo_4Cl_8[P(\mathit{n}\text{-}C_4H_9)_3]_4}$ and $\mathrm{Mo_4Br_8[P(\mathit{n}\text{-}C_4H_9)_3]_4}$[a]

$\mathrm{Mo_4Cl_8[P(\mathit{n}\text{-}C_4H_9)_3]_4}$	$\mathrm{Mo_4Br_8[P(\mathit{n}\text{-}C_4H_9)_3]_4}$
312 (2.8 × 10^4)	338 (1.8 × 10^4)
435 (3.5 × 10^3)	370 sh
685 (~100)	458 (3.3 × 10^3)
	490 sh
	613 (360)
	685 (~100)

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

The $\mathrm{Mo_4Cl_8(PR_3)_4}$ (R = alkyl) clusters are only slightly air sensitive and 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 $\mathrm{Mo_4Cl_8(PEt_3)_4}$ complex was stable in refluxing xylene (140 °C), and a sample sealed in an evacuated tube was stable at 200 °C. Accordingly, the problems associated with the XPS of $\mathrm{Mo_4Cl_8L_4}$ (L = $\mathrm{CH_3OH}$, $\mathrm{CH_3CH_2CN}$) 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, Table I, which are consistent with the many Mo–Cl and Mo–P stretching vibrations that are IR active for these molecules (for C_{2h}, 4 $\mathrm{A_u}$, 4 $\mathrm{B_u}$; for D_2, 4 $\mathrm{B_1}$, 4 $\mathrm{B_2}$, 4 $\mathrm{B_3}$).

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 $\mathrm{Mo_4Cl_8(PEt_3)_4}$ was refluxed with excess triethylphosphine in benzene (eq 14), there was rapid

$$\mathrm{Mo_4Cl_8(PR_3)_4 + 4PR_3 = 2Mo_2Cl_4(PR_3)_4} \qquad (14)$$

formation of the blue $\mathrm{Mo_2Cl_4(PEt_3)_4}$ dimer which was easily identified by its infrared and UV–visible spectra.[12] Attempted oxidative cleavage with molecular hydrogen proved unsuccessful. Here, a THF or benzene solution of $\mathrm{Mo_4Cl_8(PEt_3)_4}$ was reacted with hydrogen gas at 600 psi in a high-pressure bomb at 60 °C for 24 h. No reaction was observed, and the tetramer was recovered nearly quantitatively. The attempted reduction of $\mathrm{Mo_4Cl_8(PEt_3)_4}$ with 4 equiv of sodium–mercury amalgam resulted in pyrophoric, amorphous products with nonstoichiometric Mo:Cl ratios. These materials were not investigated further.

Synthesis of $\mathrm{Mo_4Br_8(P\text{-}\mathit{n}\text{-}Bu_3)_4}$ and $\mathrm{Mo_4I_8(P\text{-}\mathit{n}\text{-}Bu_3)_4}$. The preparation of $\mathrm{Mo_4Cl_8(PR_3)_4}$ clusters from $\mathrm{Mo_2Cl_8{}^{4-}}$ salts immediately suggested that a simple route to the bromide analogues might be achieved by using $\mathrm{Mo_2Br_8{}^{4-}}$. The bromide tetramer, $\mathrm{Mo_4Br_8(P\text{-}\mathit{n}\text{-}Bu_3)_4}$, was isolated from a reaction (eq 15) modeled after the syntheses of tetramers from $\mathrm{Mo_2Cl_8{}^{4-}}$.

$$\mathrm{2Mo_2Br_8{}^{4-} + 4PR_3 = Mo_4Br_8(PR_3)_4 + 8Br^-} \qquad (15)$$

A major difference, however, was the need to cool the bromide reaction mixture in order to prevent the formation of molybdenum methoxide species. Isolated yields of $\mathrm{Mo_4Br_8(P\text{-}\mathit{n}\text{-}Bu_3)_4}$ were much smaller than for the chloride analogue. The availability of $\mathrm{(CH_3)_3SiBr}$ also made direct synthesis of $\mathrm{Mo_4Br_8(P\text{-}\mathit{n}\text{-}Bu_3)_4}$ from $\mathrm{Mo_2(O_3CCH_3)_4}$ possible (eq 16).

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(13) Poillilanc, R.; Bigorgne, M. *Bull. Soc. Chim. Fr.* **1962**, *7*, 1301.

(14) San Filippo, J. *Inorg. Chem.* **1972**, *11*, 3140.

(15) Glicksman, H. D.; Hammer, A. D.; Smith, T. J.; Walton, R. A. *Inorg. Chem.* **1976**, *15*, 2205.

(16) Klofta, T.; Carlin, R. T.; McCarley, R. E., to be submitted for publication.

(17) Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed.; Wiley: New York, 1978; p 230.

(18) San Filippo, J.; Sniadoch, H. J. *Inorg. Chem.* **1976**, *15*, 2209.

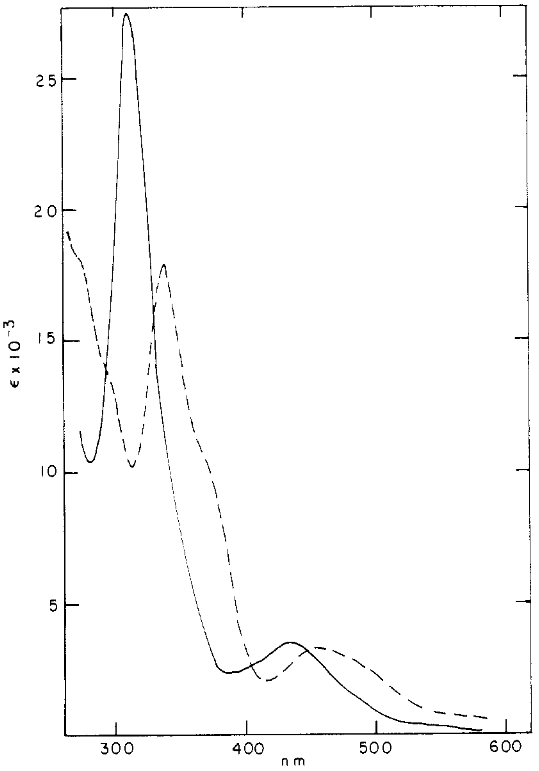

Figure 1. Electronic absorption spectra of $Mo_4Cl_8(P\text{-}n\text{-}Bu_3)_4$ (—) and $Mo_4Br_8(P\text{-}n\text{-}Bu_3)_4$ (---) in hexane solution.

Again, yields were 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 bromide cluster.

$$2Mo_2(O_2CCH_3)_4 + 8(CH_3)_3SiBr + 4PR_3 \rightarrow Mo_4Br_8(PR_3)_4 + 8(CH_3)_3Si(O_2CCH_3) \quad (16)$$

As expected, $Mo_4Br_8(P\text{-}n\text{-}Bu_3)_4$ was very similar to the chloride analogue in many of its physical properties. The compound was soluble in the same organic solvents and was only slightly more air sensitive than $Mo_4Cl_8(P\text{-}n\text{-}Bu_3)$. The UV–visible spectrum (Figure 1, Table II) was comparable to that of $Mo_4Cl_8(P\text{-}n\text{-}Bu_3)_4$, except for a red shift of about 20 nm. Shoulders at 370 and 490 nm 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. There were many bands in the infrared spectrum above 400 cm^{-1} due to the tri-*n*-butylphosphine, but in the region 400–200 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 indicated it to be isomorphous with $Mo_4Cl_8(P\text{-}n\text{-}Bu_3)_4$ 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 $Mo_4I_8(P\text{-}n\text{-}Bu_3)_4$ cluster was by reaction of $Mo_2(O_2CCH_3)_4$ with $(CH_3)_3SiI$ (eq 17).

$$2Mo_2(O_2CCH_3)_4 + 8(CH_3)_3SiI + 4PR_3 \rightarrow Mo_4I_8(PR_3)_4 + 8(CH_3)_3Si(O_2CCH_3) \quad (17)$$

A compound with the 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. The difference in the colors was due to a fairly strong absorption at 643 nm *in the iodide derivative, whereas the chloride or bromide tetramers exhibited only weak bonds in this region* (*cf. Table II*). In addition, a Debye–Scherrer powder pattern showed that the iodide derivative was not isomorphous with $Mo_4Cl_8(P\text{-}n\text{-}Bu_3)_4$. The infrared spectrum exhibited no bands in the 400–200-cm^{-1} region.

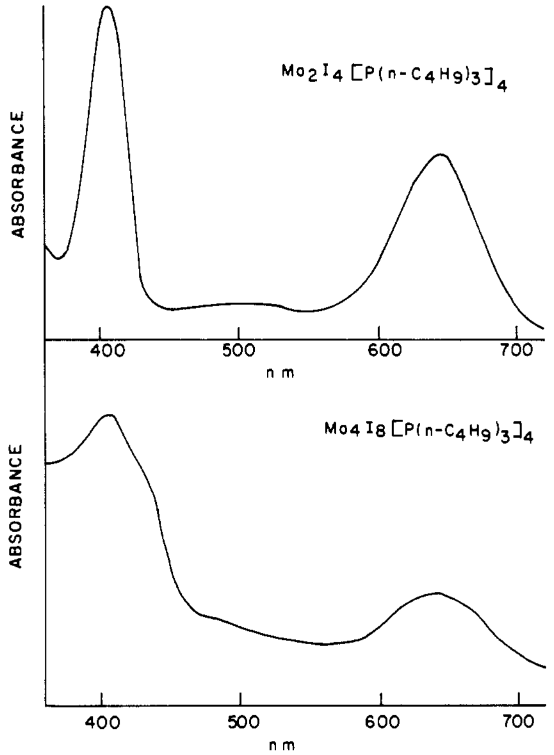

Figure 2. Electronic absorption spectra of $Mo_4I_8(P\text{-}n\text{-}Bu_3)_4$ and $Mo_2I_4(P\text{-}n\text{-}Bu_3)_4$ in cyclohexane solution.

The $Mo_4I_8(P\text{-}n\text{-}Bu_3)_4$ complex was found to be much more air sensitive than either $Mo_4Cl_8(P\text{-}n\text{-}Bu_3)_4$ or $Mo_4Br_8(P\text{-}n\text{-}Bu_3)_4$. As in the case of $Mo_4Cl_8(P\text{-}n\text{-}Bu_3)_4$, the iodide cluster produced a quadruply bonded dimer, $Mo_2I_4(P\text{-}n\text{-}Bu_3)_4$, when reacted with excess tri-*n*-butylphosphine (eq 18). The dimer, identified by its uv–visible spectrum,[20] was formed within a few seconds at 25 °C, much more rapid than in the chloride case (eq 14).

$$Mo_4I_8(PR_3)_4 + 4PR_3 \rightarrow 2Mo_2I_4(PR_3)_4 \quad (18)$$

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 $Mo_2Cl_4(PPh_3)_2(MeOH)_2$ which first led to formation of $Mo_4Cl_8(PR_3)_4$ clusters.[2] Likewise, the preparation of $Mo_4Cl_8(MeOH)_4$ depends upon the loss of triphenylphosphine from the same dimer. However, since the $Mo_4Cl_8(MeOH)_4$ preparation uses methanol as a solvent, simple ligand substitution of methanol for triphenylphosphine could produce a different dimer, $Mo_2Cl_4(MeOH)_4$, as a reactive intermediate. This dimer would actually be the reactive species, and again, the loss of

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(19) A single crystal spectrum of $Mo_4Cl_8[P(n\text{-}C_4H_9)_3]_4$ was kindly provided by Professor D. S. Martin.

(20) Glicksman, H. D.; Walton, R. A. *Inorg. Chem.* **1978**, *17*, 200.

weakly coordinated methanol would be responsible for the cycloaddition.

Coordinated methanol in $Mo_4Cl_8(MeOH)_4$ 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 $Mo_4Cl_8(PPh_3)_4$ cluster is especially interesting because of the similarity to $[MoCl_2(PPh_3)]_n$, which is initially formed when $Mo_2Cl_4(PPh_3)_2(MeOH)_2$ is dissolved in benzene.[2] Unfortunately, $[MoCl_2(PPh_3)]_n$ is always slightly contaminated with methanol so as to make an unambiguous comparison impossible. For example, the infrared spectra (400–200 cm^{-1}) of the two compounds are very similar except for a band at 323 cm^{-1} in $[MoCl_2(PPh_3)]_n$ (Table I). Despite these problems, the conversion of $[MoCl_2(PPh_3)]_n$ to $Mo_4Cl_8(PR_3)_4$ suggests that $n = 4$, and this compound is probably an impure form of the $Mo_4Cl_8(PPh_3)_4$ obtained by ligand substitution.

The preparation of $Mo_4Cl_8(PPh_3)_4$ is much more difficult than that of the corresponding trialkylphosphine tetramers. Complete replacement of propionitrile from $Mo_4Cl_8(EtCN)_4$ 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 $Mo_4Cl_8(PPh_3)_4$, and this may be why a methanol solution of $Mo_2Cl_4(PPh_3)_2(MeOH)_2$ does not spontaneously give $Mo_4Cl_8(PPh_3)_4$. The fact that the attempted preparations of $Mo_2Cl_4(PR_3)_2(MeOH)_2$, 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 equilibrium of eq 19 in methanol. In the case of triphenylphosphine, the

$$2Mo_2Cl_4(PR_3)_2(CH_3OH)_2 \rightleftarrows Mo_4Cl_8(PR_3)_4 + 4CH_3OH \quad (19)$$

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 precipitation of the cluster from methanol.

In all the syntheses described so far, the *addition of dimers* 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 $Mo_2Cl_4(P\text{-}n\text{-}Bu_3)_4$ with $Mo(CO)_6$, the metal carbonyl abstracts strongly bound phosphine ligands with subsequent formation of $Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$ and $Mo_4Cl_8(P\text{-}n\text{-}Bu_3)_4$. This suggests that the *condensation reaction* may be generally applicable to other quadruply bonded dimers, $M_2X_4L_4$ or $M_2X_6L_2$, 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 basic 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 3), and as expected, the spectrum of $Mo_4Cl_8(P\text{-}n\text{-}Bu_3)_4$ 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 III 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 has been 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.

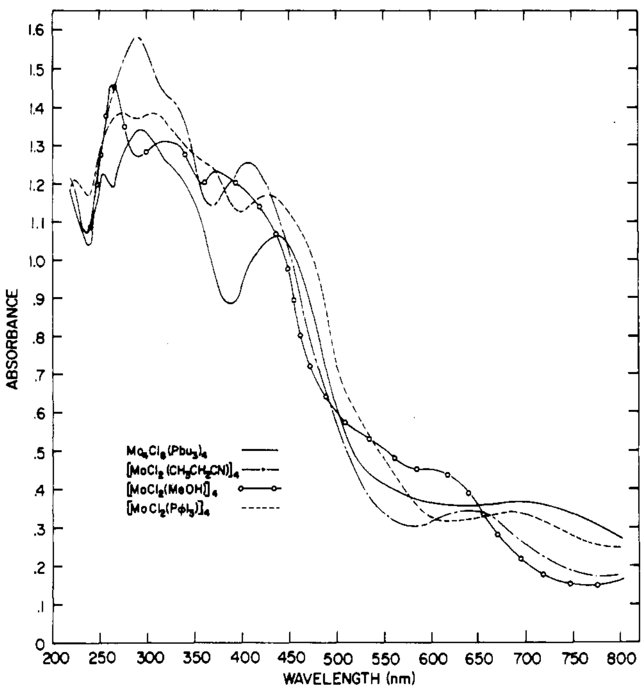

Figure 3. Reflectance spectra of tetrameric clusters $Mo_4Cl_8(P\text{-}n\text{-}Bu_3)_4$ (—), $Mo_4Cl_8(PPh_3)_4$ (- - -), $Mo_4Cl_8(EtCN)_4$ (–●–), and $Mo_4Cl_8(MeOH)_4$ (–○–).

Table III. Low-Energy Reflectance Bands of $Mo_4Cl_8L_4$ ($10^{-3}\nu_{max}$, 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 IV. Parameters Determined from Cl 2p XPS

			BE(Cl $2p_{3/2}$[a])	
	fwhm[a]	spin–orbit splitting[a]	terminal	bridging
$Mo_4Cl_8(P\text{-}n\text{-}Bu_3)_4$	1.2	1.6	198.3 (118.6)[b]	199.6 (157.0)[b]
$Mo_4Cl_8(MeOH)_4$	1.1	1.6	198.6 (382.5)[b]	199.5 (909)[b]

[a] Values in eV. [b] Relative intensity.

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 ($2p_{3/2}$,

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[21] Evans, G. G.; Gibb, T.; Kennedy, K. K.; Del Greco, F. P. *J. Am. Chem. Soc.* **1954**, *76*, 4861.

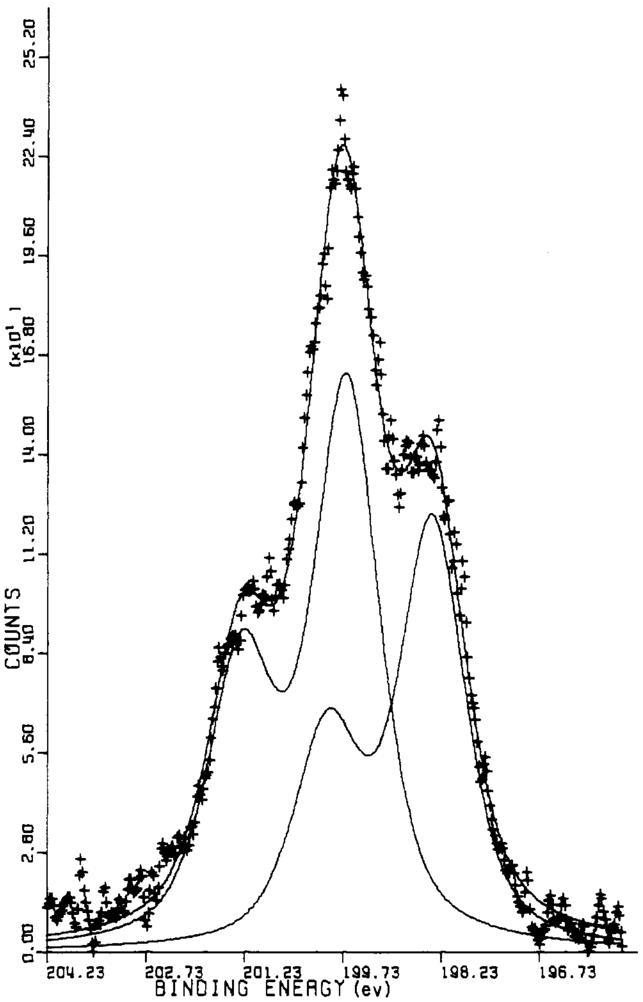

Figure 4. Cl 2p X-ray photoelectron spectrum of $Mo_4Cl_8(P\text{-}n\text{-}Bu_3)_4$. Sum of resolved components is given by the solid line through the data points.

$2p_{1/2}$), a complex spectrum results which requires deconvolution. Parameters used in the deconvolution of the spectra of $Mo_4Cl_8(P\text{-}n\text{-}Bu_3)_4$ and $Mo_4Cl_8(MeOH)_4$ are shown in Table IV, and Figures 4 and 5 show the spectra resolved into their components. The presence of more than one type of chlorine in $Mo_4Cl_8(P\text{-}n\text{-}Bu_3)_4$ is obvious from the shape of the spectrum. Deconvolution using the accepted order of bridging chloride at higher 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 $Mo_4Cl_8(MeOH)_4$, as well as loss of some phosphine from $Mo_4Cl_8(P\text{-}n\text{-}Bu_3)_4$, is compensated by the increase in coordination number of the chloride. Because of these decomposition problems, a confirmation of the structure of $Mo_4Cl_8L_4$ compounds by XPS is not generally possible.

The structure of $Mo_4Br_8(P\text{-}n\text{-}Bu_3)_4$ is undoubtedly the same as that of the chloride analogue as shown by X-ray powder patterns and electronic spectra. However, $Mo_4I_8(P\text{-}n\text{-}Bu_3)_4$ 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 $Mo_2I_4(P\text{-}n\text{-}Bu_3)_4$[20] shown in Figure 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 6. The structure shown in Figure 6 (top) is like that observed recently for $Mo_4(\mu\text{-}F)_4(O\text{-}t\text{-}Bu)_8$ and $Mo_4(\mu\text{-}F)_3(\mu\text{-}NMe_2)(O\text{-}t\text{-}Bu)_8$ by Chisholm et al.[22] In either case the quadruply bonded

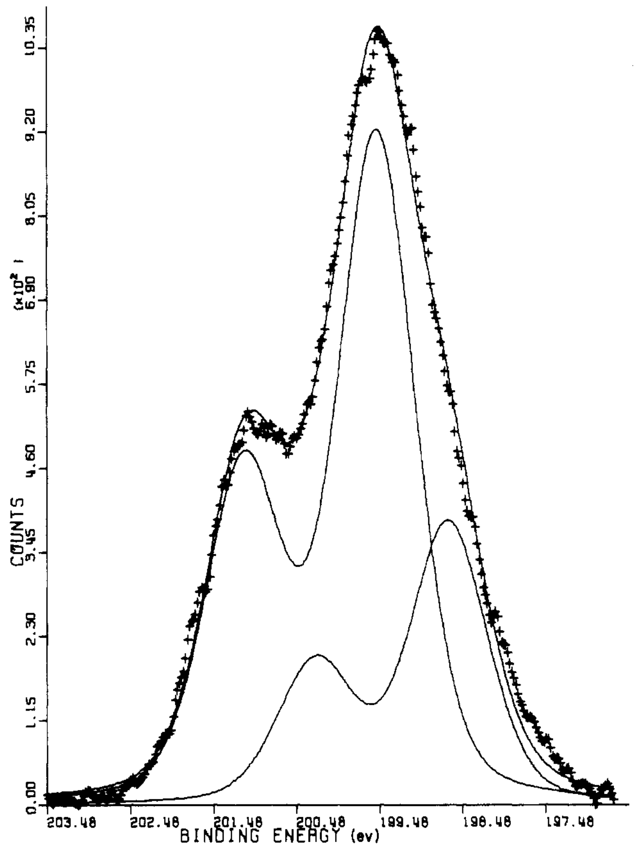

Figure 5. Cl 2p X-ray photoelectron spectrum of $Mo_4Cl_8(MeOH)_4$. Sum of resolved components is given by the solid line through the data points.

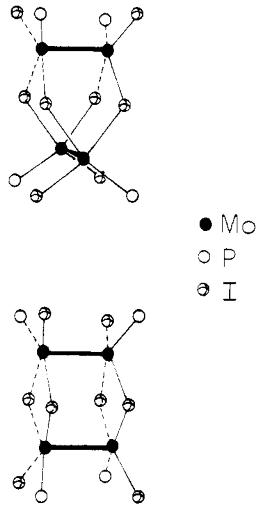

Figure 6. Possible structures for $Mo_4I_8(P\text{-}n\text{-}Bu_3)_4$.

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(22) Chisholm, M. H.; Huffman, J. C.; Kelly, R. L. *J. Am. Chem. Soc.* **1979**, *101*, 7100.

dimer units would be coupled only through the bridging iodide ligands and Mo–Mo interactions between the two coupled dimers would be negligible.

Some insight into the structure of β-$MoCl_2$ may be provided by the formation of this material by loss of ligands from $Mo_4Cl_8L_4$ (L = MeOH, THF). Previous workers[15] postulated that amorphous to poorly crystalline β-$MoCl_2$ contained quadruply bonded dimeric units because (1) the material is usually prepared by reaction of $Mo_2(O_2CCH_3)_4$ with gaseous HCl and (2) the dimeric complexes $Mo_2Cl_4(PR_3)_4$ are obtained upon reaction of β-$MoCl_2$ with excess trialkylphosphine reagent. However, the work reported here establishes that β-$MoCl_2$ may be formed from the tetrameric $Mo_4Cl_8L_4$ clusters under very mild conditions, especially when L = THF, and that the tetrameric clusters also provide $Mo_2Cl_8(PR_3)_4$ dimers upon reaction with excess trialkylphosphine. Thus the new evidence indicates that β-$MoCl_2$ may consist of rectangular tetrameric units rather than dimeric units. Work designed to elucidate the structural features and chemical properties of β-$MoCl_2$ is being continued in this laboratory.

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Registry No. $Mo_4Cl_8(CH_3OH)_4$, 78165-72-7; $Mo_4Cl_8(CH_3CH_2CN)_4$, 78264-81-0; $Mo_4Cl_8(C_4H_8O)_4$, 80822-42-0; $Mo_4Cl_8[P(C_6H_5)_3]_4$, 80822-43-1; $Mo_2Cl_2(O_2CCH_3)_2[P(C_6H_5)_3]_2$, 80822-44-2; $Mo_4Cl_8(PEt_3)_4$, 68568-88-7; $Mo_4Cl_8[P(n\text{-}C_4H_9)_3]_4$, 68568-89-8; $Mo_2Cl_4[P(n\text{-}C_4H_9)_3]_4$, 38832-72-3; $Mo_4Br_8[P(n\text{-}C_4H_9)_3]_4$, 80822-45-3; $Mo_4I_8[P(n\text{-}C_4H_9)_3]_4$, 80822-46-4; $Mo_2Cl_4[P(C_6H_5)_3]_2(CH_3OH)_2$, 68569-21-1; $\{MoCl_2[P(C_6H_5)_3]\}_n$, 80822-56-6; $Mo_2I_4(P\text{-}n\text{-}Bu_3)_4$, 80822-38-4; $(NH_4)_4Mo_2(SO_4)_4 \cdot 2H_2O$, 80822-47-5; $Mo_2(O_2CCH_3)_4$, 14221-06-8; $(NH_4)_5Mo_2Cl_9$, 61583-95-7; $K_4Mo_2Cl_8$, 25448-39-9; $(NH_4)_4Mo_2Br_8$, 61520-69-2; $Mo(CO)_6$, 13939-06-5; $(CH_3)_3SiCl$, 75-77-4; $(CH_3)_3SiBr$, 2857-97-8; $(CH_3)_3SiI$, 16029-98-4; $AlCl_3$, 7446-70-0.

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Monomeric Polymer-Anchored Molybdenum(V) Coordination Complexes

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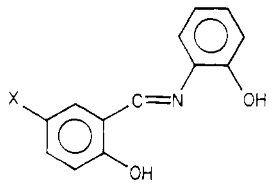
The synthesis and EPR characterization of monomeric, polymer-anchored Mo(V) coordination complexes are described. Tridentate Schiff base ligands derived from 5-X-salicylaldehyde (X = H, NO_2) and 4-amino-3-hydroxybenzoic acid were employed. The Schiff base ligand is covalently attached as an ester through the carboxylic acid function of the ligand to a polystyrene matrix. The polymer-anchored ligand has the same structure and coordination geometry as the analogous free ligand, *N*-(5-H-salicylidene)-2-aminophenol (5-H-SAP-H_2), whose monomeric Mo(V) complex has already been described. $(NH_4)_2MoOCl_5$ is the source of Mo(V) used for the synthesis of the monomeric polymer-anchored Mo(V) coordination complexes. The polymer-anchored Mo(V) complexes are stabilized as monomers for as long as 1 month as is evidenced by no decrease in the intensity of the EPR signal. The anisotropic EPR spectrum and parameters for the polymer-anchored [P]-5-H-SAP-Mo^VOCl (where [P] = polymer-anchored complex) is essentially identical with that observed for the free complex $(Et_4N)MoO(5\text{-}H\text{-}SAP)Cl_2$. The EPR results indicate that the electronic structure and stereochemistry of [P]-5-H-SAP-Mo^VOCl are unchanged from those of the well-characterized $(Et_4N)MoO(5\text{-}H\text{-}SAP)Cl_2$. In DMF, the polymer-anchored Mo(V) complexes are oxidized by NO_3^- with complete loss of the Mo(V) EPR signal.

Introduction

The coordination chemistry of molybdenum has been the subject of intensive study in recent years because of its importance in numerous biochemical redox reactions associated with such enzymes as xanthine oxidase, nitrate reductase, and nitrogenase among others.[1] It is well established that molybdenum is a necessary cofactor for these enzymes.[2] During catalysis, the Mo(V) oxidation state has been identified by electron paramagnetic resonance (EPR) spectroscopy for xanthine oxidase, sulfite oxidase, aldehyde oxidase, and nitrate reductase.[1-3] The EPR signal appears to arise from a monomeric Mo(V) center as a result of electron transfer to or from the substrate. Recent EXAFS studies have established the presence of terminal molybdenum–oxo groups in the oxidized forms of xanthine oxidase[4] and sulfite oxidase.[5] It is also known that in those enzymes that catalyze oxidation reactions, water is the oxygen atom source.

In a previous report,[6] it was shown that stable *cis*-dioxomolybdenum(VI) coordination complexes can be prepared with the tridentate Schiff base ligand 5-X-SAP-H_2 (X = H, Br, NO_2, CH_3O). The cathodic reduction potentials (E_{p_c}) for the Mo(VI) complexes spanned a range of ~200 mV on going from X = NO_2 to X = CH_3O. A linear relationship was observed between E_{p_c} and the Hammet σ_p parameter for the X substituent on the ligand. A logical extension of this work would involve the synthesis and characterization of analogous Mo(V) coordination complexes.



5-X-SAP-H_2 (X = H, **1a**; X = NO_2, **1b**)

In contrast to the molybdenum enzymes, the aqueous chemistry of simple Mo(V) complexes is dominated by EPR silent oxo- or sulfido-bridged dimers.[1] Recently, it has been shown that monomeric Mo(V) complexes can be obtained in solution but only under experimental conditions that rigorously excluded H_2O.[7-10] Spence and co-workers have described the

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