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Synthesis, Structure, and Reactivity of β-$MoCl_2$[1]

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A new synthetic route, utilizing the reaction between $Mo_2(O_2CCH_3)_4$ and $AlCl_3$ in refluxing chlorobenzene, has afforded a reactive form of β-$MoCl_2$. Infrared, UV–visible reflectance, and X-ray photoelectron spectroscopic studies show that β-$MoCl_2$ preparations obtained by both the new and older methods are essentially identical in structural composition. A comparison of spectroscopic properties of β-$MoCl_2$ with those of the tetranuclear rectangular cluster compound $Mo_4Cl_8(PEt_3)_4$ and its coupled condensation product $[Mo_4Cl_8(PEt_3)_2]_x$ suggests the existence of the tetranuclear units in the structure of β-$MoCl_2$. Direct conversion of β-$MoCl_2$ to $Mo_4Cl_8(PEt_3)_4$ by reaction with triethylphosphine at room temperature substantiates this view. Some reactions of the reactive form of β-$MoCl_2$ with acetonitrile, tetrahydrothiophene, and tetraethylammonium chloride are also reported.

Introduction

Although β-$MoCl_2$ was first prepared nearly 20 years ago,[2] its structure remains to be elucidated. Previous workers agree that this material is structurally quite different from $(Mo_6Cl_8)Cl_4$(α-$MoCl_2$) and is probably polymeric.[2–5] The correct structure has been difficult to determine because β-$MoCl_2$ is amorphous or at best semicrystalline when prepared by the usual reaction between $Mo_2(O_2CCH_3)_4$ and gaseous HCl at elevated temperature.[3,5] Allison et al.[3] felt that β-$MoCl_2$ may have a close-packed layer structure because its X-ray powder pattern, consisting of broad, diffuse lines, resembled that of $CdCl_2$. The measured magnetic moment of 0.49 μ_B suggested the presence of metal–metal bonding in this material, and the low Cl/Mo ratio implied that all Cl atoms must bridge between at least two Mo atoms. A later study of the Cl 2p PES supported the bridging nature of the Cl atoms.[5] Peaks in the Cl 2p PES of β-$MoCl_2$ and $CdCl_2$ were reported as having "very similar profiles", emphasing again the possible structural resemblance between these two compounds.

β-$MoCl_2$ is very insoluble in all common solvents and generally has a lower reactivity than α-$MoCl_2$. However, Glicksman et al.[6] have shown that β-$MoCl_2$ (and the related β-$MoBr_2$[6] and β-MoI_2[7]) undergo reactions with pyridine and trialkylphosphines in refluxing ethanol or acetone to produce the derivatives of quadruply bonded dimers, $Mo_2X_4(py)_4$ and $Mo_2X_4(PR_3)_4$. These results led to the conclusion that the β-MoX_2 materials should be thought of as $[Mo_2X_4]_n$, a formulation reflecting the presence of Mo_2 units with Mo–Mo bonds of multiple-bond order.

Our interest in this problem was recently rekindled by observations that inferred a close relationship between the tetranuclear clusters $Mo_4Cl_8L_4$ and β-$MoCl_2$. For example, Ryan and McCarley[8] found that β-$MoCl_2$ was produced upon loss of THF from $Mo_4Cl_8(THF)_4$ in vacuo at room temperature or loss of MeOH from $Mo_4Cl_8(MeOH)_4$ at <100 °C. In more recent work[9] it was found that the tetrameric phosphine derivatives $Mo_4Cl_8(PR_3)_4$ can be coupled by removal of phosphine to produce the condensed products $[Mo_4Cl_8(PR_3)_2]_x$. With certain phosphine ligands linkage does not stop at the earlier stage but proceeds to a product with properties similar to those of β-$MoCl_2$. The initial results of our probe into the structure and properties of β-$MoCl_2$ are presented here.

Experimental Section

Materials. Except where noted otherwise, samples were presumed to be air-sensitive and were handled accordingly. Chlorobenzene and acetonitrile were dried by refluxing with CaH_2. Chlorobenzene was then distilled and stored under nitrogen. The acetonitrile was vacuum distilled onto molecular sieves for storage. Triethylphosphine was used as received. $AlCl_3$ was purified by vacuum sublimation through a sintered-glass frit. Dry Et_4NCl was produced by dissolving it in acetone and precipitating with ether. The product was then dried under vacuum at room temperature for about 1 day.[10] The preparations of $Mo_2(OAc)_4$,[11] $K_4Mo_2Cl_8$,[12] $Mo_4Cl_8(PEt_3)_4$,[8] and $[Mo_4Cl_8(PEt_3)_2]_x$[9] have been described previously.

Analysis. Molybdenum analyses were accomplished by decomposition of the sample in a tared crucible using nitric acid. The resultant MoO_3 was fired at 550 °C before weighing. Decomposition of the samples for chloride analysis was performed in a KOH–H_2O_2 aqueous solution. The chloride content was obtained by potentiometric titration of the solution with standardized $AgNO_3$. Carbon, hydrogen, and nitrogen analyses were performed by the Ames Laboratory Analytical Services.

Physical Measurements. Routine infrared spectra were obtained in a Beckman IR4250 spectrometer. An IBM IR/90 spectrometer was used to measure the Fourier-transform infrared spectra. Instrumentation for the acquisition of reflectance and X-ray photoelectron spectra has been previously described.[9] Resolutions of the Cl 2p3/2,1/2 PE spectra were performed with the computer program APES.[13]

Synthesis. Literature β-$MoCl_2$. Literature β-$MoCl_2$ was prepared from $Mo_2(OAc)_4$ and HCl(g) by following the modified method of Glicksman et al.[6] The infrared spectrum of the product did not contain bands due to the acetate ligand; therefore, the reaction was assumed to be complete.

Reactive β-$MoCl_2$. When $Mo_2(OAc)_4$ and $AlCl_3$ are refluxed in chlorobenzene, a very amorphous form of β-$MoCl_2$ is produced. A typical preparation was performed with use of 2.00 g (4.67 mmol) of $Mo_2(OAc)_4$ and 2.60 g (19.50 mmol) of $AlCl_3$ in about 20 mL of refluxing chlorobenzene. A brown precipitate formed very quickly, but the reaction was usually continued for about 6 h. The precipitate was then filtered and extracted with chlorobenzene until the initially yellow extract became colorless. An infrared spectrum indicated that some form of acetate was still present in the precipitate. Thus the precipitate was extracted for several hours with acetonitrile until the dark green extract became colorless. After vacuum drying at room temperature, a yield of about 90% was realized. The infrared spectrum of this product indicated that some acetonitrile and chlorobenzene were present, but there were no absorptions that could be attributed to an acetate ligand. Anal. Calcd for $MoCl_2$: Mo, 57.50; Cl, 42.50. Found: Mo, 52.53; Cl, 38.22; C, 5.14; H, 0.56; N, 1.21 (Cl/Mo = 2.04, N/Mo = 0.16, C/N = 4.96). When the product was heated under vacuum at 85 °C for 1.5 days, the infrared spectrum indicated that the acetonitrile was eliminated but that a very small amount of chlorobenzene remained. Anal. Found: Mo, 55.44; Cl, 41.82 (Cl/Mo = 2.04). If one assumes the balance of the material to be chlorobenzene, the chlorobenzene/molybdenum ratio is about 0.04. All subsequent experiments were performed with this material, which had been treated for removal of acetonitrile at 85 °C.

Melt β-$MoCl_2$. Although this method for preparing β-$MoCl_2$ was

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Table I. Infrared Absorption Frequencies (cm^{-1}) below 450 cm^{-1} for Two Forms of β-MoCl$_2$ and Related Phosphine Cluster Compounds

reactive β-MoCl$_2$	lit. β-MoCl$_2$	$Mo_4Cl_8(PEt_3)_4$	$[Mo_4Cl_8(PEt_3)_2]_x$
383 s[a]	385 s	449 w	432 m
355 w	354 w	432 m	380 s
332 w	331 w	374 s	357 w
299 s	301 s	348 m	345 m
257 w	260 w	331 m	330 m
b	161 m	306 m	308 s
		273 s	289 s
		234 w	256 w
		177 w	225 w
		140 w	150 m

[a] Relative intensities: s = strong, m = medium, w = weak. [b] Spectrum not measured below 200 cm^{-1}.

originally found by others in this laboratory,[14] this further work led to its inclusion here. A 1:4 mole ratio of $K_4Mo_2Cl_8$ and $AlCl_3$ (2.82 g of $K_4Mo_2Cl_8$ and 2.38 g of $AlCl_3$) were added to a melt composed of 52 mol % $AlCl_3$ and 48 mol % NaCl (6.93 g of $AlCl_3$ and 2.81 g of NaCl). The reactants were sealed in a Pyrex tube and heated to 350 °C for 4 days. The melt was cooled, pulverized in the air, and slowly added to 1 M hydrochloric acid. The mixture was stirred for about 10 min, and then the acid was decanted from the solid. Another extraction of the solid was performed, followed by filtering and washing the solid product with ethanol. The product was air-dried. This form of β-MoCl$_2$, which seems to be fairly air stable, was obtained in about 70% yield. Anal. Found: Mo, 59.52; Cl, 42.77 (Cl/Mo = 1.94).

Results and Discussion

Synthesis. This work was initiated when it was noticed that a product very similar to β-MoCl$_2$ was derived from reactions of the condensed cluster compounds $[Mo_4Cl_8(PR_3)_2]_x$.[9] Synthesis of the latter was based on a two-step process as indicated in eq 1 and 2. In an effort to circumvent this two-step procedure, the

$$2Mo_2(OAc)_4 + 8AlCl_3 + 4PR_3 = Mo_4Cl_8(PR_3)_4 + 8AlCl_2(OAc) \quad (1)$$

$$xMo_4Cl_8(PR_3)_4 + xMo(CO)_6 = [Mo_4Cl_8(PR_3)_2]_x + xMo(CO)_4(PR_3)_2 + 2xCO \quad (2)$$

direct conversion of $Mo_2(OAc)_4$ to the condensation product was attempted via modification of the reaction given in eq 1 such that only 1 mol of PR_3/mol of $Mo_2(OAc)_4$ was added to the mixture. This resulted in the formation of a brown solid with properties like those of β-MoCl$_2$. Elimination of organophosphine from subsequent reactions and establishment of conditions for complete removal of acetate ligands from the product led to the procedure given in the Experimental Section. The β-MoCl$_2$ afforded by this procedure (eq 3) is referred to as reactive β-MoCl$_2$ because of

$$Mo_2(OAc)_4 + 4AlCl_3 = 2\beta\text{-}MoCl_2 + 4AlCl_2(OAc) \quad (3)$$

its enhanced reactivity toward various reagents. It must be admitted, however, that the product labeled as $AlCl_2(OAc)$ in eq 3 has not been definitely established, although the reaction works best when at least a 1:4 mole ratio of $Mo_2(OAc)_4$ to $AlCl_3$ is utilized. There is little doubt that the reactive β-MoCl$_2$ is closely related to β-MoCl$_2$ prepared by other methods, as shown below. This form, however, retains both chlorobenzene and acetonitrile from the preparative and washing procedure. Prolonged heating at 85 °C in vacuo eliminates the acetonitrile, but a persistent residue of chlorobenzene remains, ca. 1 mol/25 mol of MoCl$_2$. At still higher temperatures (250 °C) this chlorobenzene is lost, but the β-MoCl$_2$ then becomes relatively unreactive at a level comparable to that of β-MoCl$_2$ prepared by high-temperature methods. This decrease in reactivity may result from sintering and reduction in surface area as well as an enhancement in crystalline order of the semicrystalline material.

Spectroscopic Characterization. The FT-IR spectra of literature β-MoCl$_2$[2-5] and reactive β-MoCl$_2$ are essentially superimposable in the Mo–Cl stretching region 200–400 cm^{-1}. The absorption band frequencies of these two forms are listed in Table I. These data, combined with UV-visible reflectance and XPS spectra of the materials derived by the three preparative methods, confirm that all must have the same basic structure but differ only in degree of crystallinity and reactivity. A comparison of reflectance spectra for the literature, reactive, and melt β-MoCl$_2$ materials is given in Figure 1. Again, these spectra are almost superimposable and testify to the common origin of electronic transitions within the materials. Thus, on the basis of both the vibrational and electronic spectra, the structural units composing the materials must also be identical.

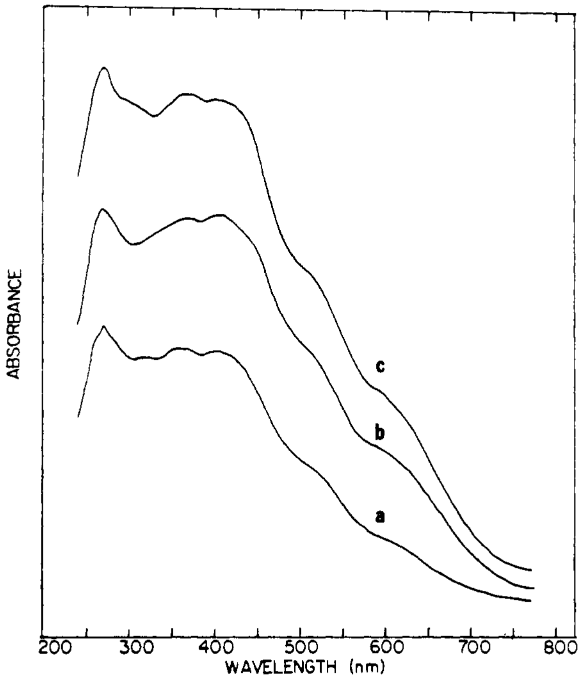

Figure 1. Reflectance spectra of β-MoCl$_2$ prepared by three different methods: (a) literature; (b) reactive; (c) melt.

The three forms of β-MoCl$_2$ also each provide single-component Mo 3d$_{5/2,3/2}$ PES having 3d$_{5/2}$ binding energies of 229.3 ± 0.1 eV with comparable fwhm of 1.62–1.68 eV. The compounds $Mo_4Cl_8[P(n\text{-}Bu)_3]_4$ and $[Mo_4Cl_8(PEt_3)_2]_x$, both containing rectangular cluster units related to those that we believe exist in β-MoCl$_2$, give corresponding Mo 3d$_{5/2}$ binding energies of 229.0 and 229.2 eV, respectively. Resolution of the Cl 2p$_{3/2,1/2}$ PES for these three materials is shown in Figure 2, and the 2p$_{3/2}$ binding energies for the resolved components are given in Table II. Because of the almost featureless shape of the band envelopes, resolution of the spectra into components was approached cautiously. Briefly stated, it was found that a fit to only one component in each case gave fwhm values that were unreasonably large, 1.70–1.77 eV. Two-component fits for literature and reactive β-MoCl$_2$ were judged satisfactory, but for the melt form three components were required. The weak component with a Cl 2p$_{3/2}$ BE of 201.2 eV probably arises from slight contamination of the melt form with $(Mo_4Cl_8)Cl_4$, α-MoCl$_2$, whose formation is promoted by the reaction in molten NaAlCl$_4$ at 350 °C, as previously observed by Jödden and Schäfer at higher temperatures.[15] Hamer and Walton[5] have previously reported a Cl 2p$_{3/2}$ BE of 199.5 eV (referenced to C 1s at 284.0 eV) for the triply bridging Cl atoms in the $Mo_6Cl_8^{4+}$ cluster units of $(Mo_6Cl_8)Cl_4$. Similarly, a Cl 2p$_{3/2}$ BE of 199.4 eV (referenced to C 1s at 284.0 eV) has been reported for the bridging Cl atoms of $(Bu_4N)_2[(Mo_6Cl_8)Cl_6]$.[16] When corrected to the common C 1s BE of 285.0 eV, these values for triply bridging Cl atoms are all in good agreement with BE's > 200.4 eV. In all three forms of β-MoCl$_2$

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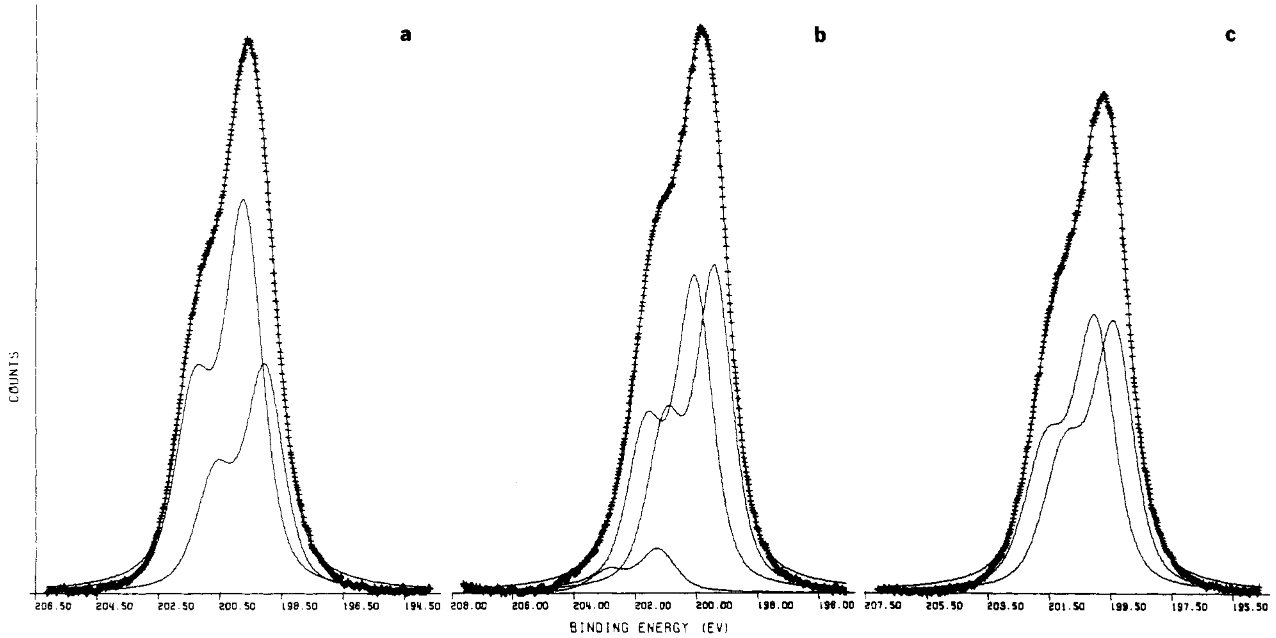

Figure 2. Chlorine 2p photoelectron spectra of β-$MoCl_2$ prepared by three methods: (a) literature; (b) melt; (c) reactive.

Table II. Comparison of Cl $2p_{3/2}$ XPS Data for β-$MoCl_2$ with Those of Related Compounds

	Cl $2p_{3/2}$ BE, eV[a]					
compd	tb[b]	db-1[c]	db-2[d]	t[e]	fwhm, eV	area ratio
lit. β-$MoCl_2$		199.7	199.0		1.44	1.72/1.00
reactive β-$MoCl_2$		200.1	199.4		1.55	1.02/1.00
melt β-$MoCl_2$	201.2	200.0	199.4		1.38	1.00/7.13/7.34
$[Mo_4Cl_8(PEt_3)_2]_x$[f]		199.6	198.9	198.1	1.30	2.72/1.51/1.00
$Mo_4Cl_8(P(n\text{-}Bu)_3)_4$[g]		199.6		198.3	1.2[i]	1.3/1.0
$(Bu_4N)_2Mo_5Cl_{13}$[h]	200.5	199.8		198.3	1.03[i]	1.00/1.00/1.33

[a] Reference to C 1s binding energy of 285.0 eV. [b] Intracluster triply bridging Cl. [c] Intracluster doubly bridging Cl. [d] Intercluster doubly bridging Cl. [e] Terminal Cl. [f] Reference 9. [g] Reference 8. [h] Reference 17. [i] Data was obtained with use of monochromatic radiation.

the BE's in the range 199.7–200.1 eV are assigned to doubly bridging Cl atoms spanning the long edges of coupled rectangular cluster units, in good agreement with the BE's for corresponding Cl atoms in $Mo_4Cl_8[P(n\text{-}Bu)_3]_4$[8] and the doubly bridging Cl atoms of $(Bu_4N)_2Mo_5Cl_{13}$[17] given in Table II. The component with lower BE of 199.0–199.4 eV is assigned to Cl atoms which couple one cluster unit to another through nonmetal-metal-bonded Mo–Cl–Mo bridging. Notably, a component with the same origin also appears in the spectrum of the condensed cluster compound $[Mo_4Cl_8(PEt_3)_2]_x$ with a BE of 198.9 eV.

If β-$MoCl_2$ consists of a polymer of tetramers, as we contend here, then these two types of bridging Cl atoms should occur in the ratio 1:1 as implied by the formulation $[(Mo_4Cl_4)Cl_{8/2}]_\infty$. The PES area ratios for these components are in agreement with this model for the melt and reactive forms but in poor agreement for the literature form. It is possible that only modification or contamination at the surface of the latter is the cause of this discrepancy. However, because of the rather featureless form of the spectra, relatively large errors in area ratios can result from small changes in the fitting parameters, and these data should be interpreted cautiously. Additional uncertainty is introduced in these peak area ratios when spectra for samples from different preparations are compared, although the general features of the spectra and BE of resolved components are reproducible.

A further comparison of spectroscopic properties of β-$MoCl_2$ with those of compounds containing the discrete rectangular cluster units $Mo_4Cl_8L_4$ and with those having a limited degree of coupling of the tetrameric units was sought to substantiate the hypothesis that β-$MoCl_2$ is the end member of a condensation series $\{[(Mo_4Cl_4)Cl_4]_nL_4\}$ containing the rectangular cluster units. Such a comparison is provided by the phosphine-ligated cluster $Mo_4Cl_8(PEt_3)_4$ and its initial condensation product $[Mo_4Cl_8(PEt_3)_2]_x$,[9] believed to be the member with $n = 2$ of the above series. Support for the proposed relationship between these

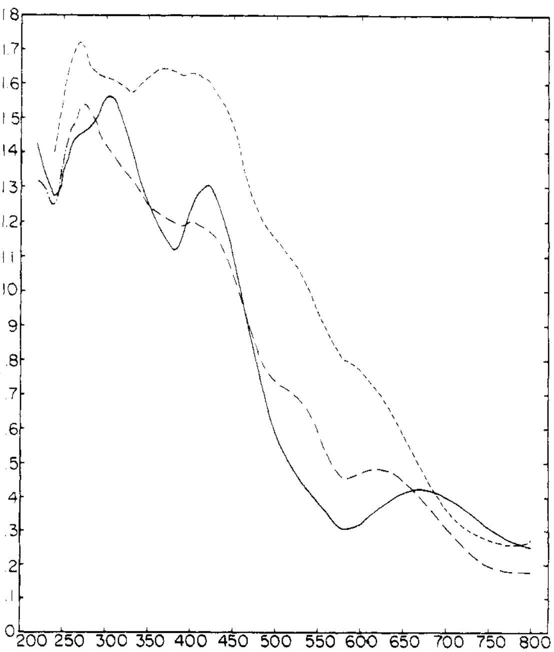

Figure 3. Reflectance spectra of $Mo_4Cl_8(PEt_3)_4$ (—), $[Mo_4Cl_8(PEt_3)_2]_x$ (-·-), and β-$MoCl_2$ (---).

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Table III. Absorption Band Maxima (nm) from Reflectance Spectra

compd	band max				
β-MoCl$_2$	600	520	400	370	270
$[Mo_4Cl_8(PEt_3)_2]_x$	620	520	400		275
$Mo_4Cl_8(PEt_3)_4$	675		420	305	270

compounds based on evidence from photoelectron spectra has been given above. Additional evidence is provided by the reflectance spectra shown in Figure 3 and the resultant absorption band maxima listed in Table III. The striking resemblance of the spectra and close agreement of band maxima for β-MoCl$_2$ and $[Mo_4Cl_8(PEt_3)_2]_x$ indicate that the structural units present in the initial and final stages of condensation are essentially the same. It also appears that the bands in the latter compounds are related to those in the tetramer $Mo_4Cl_8(PEt_3)_4$ by a blue shift of 1200 to 1900 cm^{-1}. An exception may be the band at 520 nm in the spectra of the condensed compounds, which has no obvious counterpart in the spectrum of $Mo_4Cl_8(PEt_3)_4$.

Although no firm conclusion can be drawn from a comparison of vibrational spectra, the infrared spectra of each of these compounds was secured in the region 150–500 cm^{-1}. The resulting absorption band frequencies are listed in Table I. The bands at 432–450 cm^{-1} must arise from coordinated PEt$_3$ since they decrease in intensity in progression from $Mo_4Cl_8(PEt_3)_4$ to β-MoCl$_2$. In the region 200–400 cm^{-1} the bands in all cases must arise from Mo–Cl stretching vibrations. Detailed assignment of these bands is not possible at present. However, the presence of the strong band at 374–385 cm^{-1} in spectra of all three compounds may be attributed to vibrations of the Cl atoms bridging the long edges of the rectangular cluster units. Usually the vibrational frequencies of bridging Cl atoms would be found lower than those of terminal Cl, but in the case of β-MoCl$_2$ it is unlikely that any terminal Cl atoms remain in the structure. Thus the band at 385 cm^{-1} most likely arises from bridging Mo–Cl–Mo vibrational modes.

Reactivity. As previously noted by Walton and co-workers,[6,7] the β-MoX$_2$ (X = Cl, Br, I) compounds react with pyridine and phosphines to form the quadruply bonded dimers $Mo_2X_4(py)_4$ and $Mo_2X_4(PR_3)_4$. This led to the suggestion that β-MoX$_2$ consisted of the polymers of dimers $[Mo_2X_4]_n$, the parent halides of the haloanions $Mo_2X_8^{4-}$. On the other hand, work in this laboratory established that, under the same conditions used in the previously cited work, the rectangular cluster complexes $Mo_4X_8L_4$ react analogously with excess ligand to produce the dimers $Mo_2X_4L_4$. It was also observed[8] that the rectangular cluster derivatives $Mo_4Cl_8(MeOH)_4$ and $Mo_4Cl_8(THF)_4$ readily lose MeOH or THF under very mild conditions to form solids having the properties of β-MoCl$_2$. These observations led to the hypothesis that β-MoCl$_2$ may indeed consist of a polymer of rectangular clusters $[Mo_4Cl_8]_n$. In this work this hypothesis was tested by the following reactions using reactive β-MoCl$_2$ or $Mo_4Cl_8(PEt_3)_4$: (a) reaction of PEt$_3$ with β-MoCl$_2$ (1:1 mole ratio) in refluxing chlorobenzene (131 °C) for 1 h; (b) reaction of PEt$_3$ with β-MoCl$_2$ (1.1:1 mole ratio) in chlorobenzene at room temperature for 3 days; (c) reaction of PEt$_3$ with β-MoCl$_2$ (1.05:1 mole ratio) in chlorobenzene at room temperature for 40 h; (d) reaction of PEt$_3$ with $Mo_4Cl_8(PEt_3)_4$ (4:1 mole ratio) in chlorobenzene at room temperature for 45 h; (e) reaction of acetonitrile under reflux with β-MoCl$_2$ for 6 h; (f) reaction of tetrahydrothiophene with β-MoCl$_2$ (1:1 mole ratio) in refluxing chlorobenzene for 44 h; (g) reaction of $Et_4N^+Cl^-$ with β-MoCl$_2$ (>4:1 mole ratio) in refluxing dichloromethane for 2.5 days.

As expected the vigorous conditions in (a) led to formation of a deep blue solution of $Mo_2Cl_4(PEt_3)_4$. Because of the insolubility of β-MoCl$_2$ the solution in (a) always contains excess PEt$_3$. Thus, if the reaction given in eq 4 is slower than that of eq 5, the only

$$4\beta\text{-MoCl}_2 + 4PEt_3 = Mo_4Cl_8(PEt_3)_4 \qquad (4)$$

$$Mo_4Cl_8(PEt_3)_4 + 4PEt_3 = 2Mo_2Cl_4(PEt_3)_4 \qquad (5)$$

observed product will be $Mo_2Cl_4(PEt_3)_4$. Under the mild conditions of (b) a green solution resulted, from which was recovered $Mo_4Cl_8(PEt_3)_4$ in 32% yield and $Mo_2Cl_4(PEt_3)_4$ in 15% yield, for a total conversion of 47% of the β-MoCl$_2$. In reaction c the results were similar but the shorter reaction period gave a reduced net conversion of ca. 30%. Reaction d provided information about the rate of conversion of tetramer to dimer (eq 5) under the conditions of (b) and (c). In 45 h only ca. 15% of tetramer was converted to dimer, a result consistent with the relative amount of dimer formed in (b) and (c). We conclude from these reactions, made possible by the higher reactivity of reactive β-MoCl$_2$, that the rectangular clusters are the fundamental structural units that can be extracted from β-MoCl$_2$.

Reactions e–g were performed to explore the possible utility of reactive β-MoCl$_2$ as a convenient starting material for preparation of less accessible rectangular cluster derivatives. Under the conditions of (e) only formation of $Mo_2Cl_4(NCCH_3)_4$ was observed, as evidenced by its UV–visible spectrum;[18] ca. 30% conversion of the β-MoCl$_2$ was attained in 6 h. Reaction f was tried since organosulfide derivatives of the rectangular cluster had not previously been prepared. Essentially no reaction was observed, and the infrared spectrum of recovered β-MoCl$_2$ remained unchanged. Earlier work in this laboratory had established that reaction of $Mo_4Cl_8(MeOH)_4$ with excess $Et_4N^+Cl^-$ in dichloromethane produces the purple salt $(Et_4N)_4Mo_4Cl_{12}$.[19] Consequently, it was hoped that reaction g might provide an alternative, more convenient route to this salt. Under the conditions of (g) it was found that a 75% conversion of β-MoCl$_2$ to $(Et_4N)_4Mo_4Cl_{12}$ was attained. However, this encouraging result was tempered by the lack of a suitable method for separation of the mixture. Both β-MoCl$_2$ and the product are insoluble in CH$_2$Cl$_2$, and applications of other solvents to the desired separation either were ineffective or resulted in reaction with the product. Thus, complete conversion of the β-MoCl$_2$ would be required in order for (g) to be a useful synthetic reaction.

Conclusions. The detailed structure of β-MoCl$_2$ (and the related β-MoBr$_2$ and β-MoI$_2$) is still unknown. However, the evidence presented here shows that β-MoCl$_2$ species with substantially identical structural and spectroscopic properties, but with different relative reactivities, can be produced by a variety of methods. The comparison of PES data and UV–visible spectra between β-MoCl$_2$ and model compounds suggests a close relationship of the structural units in β-MoCl$_2$ with those in the rectangular clusters $Mo_4Cl_8(PR_3)_4$ and their condensation products $[Mo_4Cl_8(PR_3)_2]_x$. This relationship is further supported by the direct conversion under mild conditions of β-MoCl$_2$ to the phosphine derivative of the rectangular cluster $Mo_4Cl_8(PEt_3)_4$, and the facile conversion of $Mo_4Cl_8(MeOH)_4$ or $Mo_4Cl_8(THF)_4$ to β-MoCl$_2$. We thus believe there is adequate support for the contention that β-MoCl$_2$ is a polymer of rectangular cluster units coupled through Mo–Cl–Mo bridge bonding, as indicated by the formulation $[(Mo_4Cl_4)Cl_{8/2}]_\infty$. Since β-MoCl$_2$ is amorphous or at best semicrystalline, depending on the method of preparation, there is little prospect that the detailed structure can be elucidated by X-ray diffraction. We have thus undertaken a study of the EXAFS spectra of β-MoCl$_2$ and related model compounds to provide further information about the structure of this compound.

Registry No. $Mo_2(OAc)_4$, 14221-06-8; β-MoCl$_2$, 13478-17-6; AlCl$_3$, 7446-70-0; $Mo_2Cl_4(PEt_3)_4$, 59780-36-8; $Mo_4Cl_8(PEt_3)_4$, 68568-88-7; $Mo_2Cl_4(NCCH_3)_4$, 51731-46-5; $(Et_4N)_4Mo_4Cl_{12}$, 94499-09-9.

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