Table II. Concentration-Independent Rate Constants and Their Temperature Dependence

	25°	17.8°	10°
k_{610}, M^{-1} sec^{-1}	$(1.08 \pm 0.06) \times 10^4$	$(5.44 \pm 0.06) \times 10^3$	$(3.28 \pm 0.01) \times 10^3$
k_{520}, M^{-2} sec^{-1}	$(1.27 \pm 0.04) \times 10^8$	$(6.89 \pm 0.03) \times 10^7$	$(4.18 \pm 0.02) \times 10^7$

gen ion concentrations of 0.015 and 0.0143 *M*. For comparison from Table I at ionic strength 0.1, the rate constant calculated from the equation of this line at 0.0145 M H^+ is 17.9 × 10^5 M^{-1} sec^{-1}. The lack of any ionic strength dependence would support the suggestion of the neutral reactant, MnO_3, although at ionic strengths this high, other explanations are possible.

The manganate disproportionation reaction may be further complicated by still another slow reaction (or reactions) occurring after the two reported here. At both wavelengths studied, long after the D_∞ values have been well established, the optical density begins to increase. The duration of this reaction is 10–20 sec (compared to a few milliseconds for the manganate reaction) before a new final D_∞ value is reached. This new reaction appears to be first order in color appearance and would seem to be the decomposition of the Mn(V) species produced in the first reaction to form a final Mn(IV) species, although it seems unlikely that the Mn(V) reaction can be this slow. At first it was suspected that colloidal MnO_2 was forming at a slow rate. However, no precipitate of MnO_2 is seen in a reasonable length of time. The visible spectrum of the reacted solution shows the pronounced spectrum of permanganate and in addition features that may be attributed to the unknown final product. On prolonged standing, of course, MnO_2 appears, but then the permanganate has also decomposed. The kinetics of this reaction will be investigated when more information on the nature of the reactants and products is known, but at least it is clear that it does not interfere with the kinetics presented here.

Acknowledgment. We wish to acknowledge partial support of this research by NSF grant GP 8097. K. C. received support on an NSF undergraduate participating grant. We also wish to acknowledge Walter Ferguson, who assisted in the very early experiments. He also received support on an NSF undergraduate participating grant.

Registry No. Manganate, 14333-14-3; permanganate, 14333-13-2.

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X-Ray Photoelectron Spectra of Inorganic Molecules. IX.[1,2] Distinction between Bridging and Terminal Metal–Chlorine Bonds in Metal Halide Clusters of Rhenium(III) and Molybdenum(II)

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Received October 2, 1973 AIC30717U

The X-ray photoelectron spectra of chloride clusters of rhenium(III) and molybdenum(II) containing strong metal–metal bonds are reported. Measurements of the chlorine 2p binding energy spectra of the parent chlorides and their derivatives with a variety of donor molecules have shown that for the rhenium and molybdenum compounds the binding energy order is $Cl_b > Cl_t$ and $Cl_b > Cl_b' > Cl_t$, respectively; Cl_b, Cl_b', and Cl_t denote chlorine atoms in intracluster metal–chlorine bridges, intercluster metal–chlorine bridges, and terminal metal–chlorine bonds, respectively. These assignments have been confirmed by recording the binding energy spectra of complexes in which the terminal metal–chlorine bonds have been progressively replaced. The magnitude of the separation between the binding energies associated with Cl_b and Cl_t, ~1.4 eV for rhenium(III) and ~2.3 eV for molybdenum(II), allows this technique to provide definitive structural information on metal chloride clusters. In the present study this is applied to the complexes of molybdenum(II) chloride $[Mo_6Cl_8]Cl_4$ with 1,2-bis(diphenylphosphino)ethane, 2,2′-bipyridyl, 1,10-phenanthroline, and 2,2′,2″-terpyridyl. The X-ray photoelectron spectrum of the phase known as β-molybdenum(II) chloride has also been examined and it is shown that this compound does not have a metal–metal bonded cluster structure related to that of $[Mo_6Cl_8]Cl_4$.

Introduction

In our recent studies on the redox behavior of rhenium(III) chloride toward monodentate heterocyclic tertiary amines,[3,4] we isolated a new class of polymeric rhenium(II) derivatives of the type $[Re_3Cl_6L_3]_n$, where L = pyridine, β- or γ-picoline, isoquinoline, quinaldine, or benzimidazole, together with the acridinium salt $\{[AcrH]_2Re_3Cl_8\}_n$. Since these products were amorphous to X-rays and a structure solution was not feasible by a single-crystal X-ray structure analysis, we resorted to X-ray photoelectron spectroscopy (ESCA)[5] as a possible means of providing definitive structural information on these derivatives. From a preliminary study of the chlorine 2p binding energies of these complexes, together with related measurements on several adducts of rhenium(III) chloride of the type $Re_3Cl_9L_3$, L = pyrazine, triphenylphosphine, or dimethylformamide, and the complex anions $Re_3Cl_{11}^{2-}$ and $Re_3Cl_{12}^{3-}$,[3,4] we were able to establish that the rhenium(II) derivatives possessed two types of rhenium–chlorine bonds, terminal (or intercluster bridges) and intracluster bridges. The separation between the binding energies

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of these two types of chlorine atoms was ~1.4 eV and we tentatively assigned the higher energy chlorine 2p components to the bridging (Cl_b) chlorine atoms.

In view of the magnitude of the binding energy separation between the different types of chlorine environment (~1.4 eV) it appeared to us that ESCA was capable of providing important structural information on many metal halide clusters and that this was particularly useful when a single-crystal X-ray structure analysis was either impossible or inappropriate. Accordingly we felt it essential to carry out the following investigations: (1) provide unambiguous evidence that our previous assignments[3,4] for the binding energy order $Cl_b > Cl_t$ for rhenium chloride clusters were in fact correct; (2) investigate the chlorine 2p binding energy pattern for another type of metal chloride cluster, preferably one whose structure was different from that of trinuclear rhenium(III) chloride; we chose the hexanuclear molybdenum(II) chloride cluster $[Mo_6Cl_8]Cl_4$ and its derivatives for this purpose; (3) apply the technique to a system which possessed, at least potentially, a cluster structure but for which no definitive structural information was available. The phase described as β-molybdenum(II) chloride[6-8] seemed particularly appropriate in this regard. The results of these investigations are now reported in detail and provide, we believe, clear evidence for the general usefulness of ESCA in the structural characterization of metal chloride clusters.

Experimental Section

Preparation of Metal Chlorides and Their Complexes. Rhenium(III) chloride was prepared by the thermal decomposition of rhenium(V) chloride in a nitrogen stream[9] or obtained commercially from the S. W. Shattuck Co., Denver, Colo. Molybdenum(II) chloride, $[Mo_6Cl_8]Cl_4$, was prepared by the method of Sheldon, as modified by Jolly.[10] The compound β-molybdenum(II) chloride was prepared by Sheldon's method[7] of heating molybdenum(II) acetate at 300° in a stream of dry hydrogen chloride for 4 hr. The resulting brown powder was analyzed. *Anal.* Calcd for $MoCl_2$: C, 0.0; Cl, 42.5; Mo, 57.5. Found: C, 1.4; Cl, 40.9; Mo, 57.7. The microanalyses indicated a small amount of contamination by a carbon-containing material.

The molybdenum(II) complexes of stoichiometries (i) $Mo_6Cl_{12}L_2$, where L = dimethylformamide (DMF), dimethyl sulfoxide (DMSO), pyridine (py), triethylamine (NEt_3), triphenylphosphine (PPh_3), $^1/_2$-[1,2-bis(diphenylphosphino)ethane] (dppe), or $^1/_2$[2,2′,2″-terpyridyl] (terpy), (ii) $Mo_6Cl_{12}B_2$, where B = 2,2′-bipyridyl (bipy) or 1,10-phenanthroline (phen), (iii) $[H_3O]_2Mo_6Cl_{14}\cdot 6H_2O$, (iv) $[(C_2H_5)_4N]_2Mo_6Cl_{14}$, and (v) $[(C_4H_9)_4N]_2[(Mo_6Cl_8)X_6]$, where X = Br or I, were prepared by standard literature procedures.[11-14] Their identity was established by infrared spectroscopy (4000–200 cm^{-1}) and molybdenum analysis. Samples of the complexes $Re_3Cl_9(pyz)_3$ (pyz = pyrazine) and $[Re_3Cl_6(py)_3]_n$ were synthesized as described previously.[3] The diethyldithiocarbamato complex of rhenium(III), $Re_3Cl_6(S_2CNEt_2)_3$, was prepared as a brown powder by the procedure of Colton, *et al.*[15] Acetone solutions of the complexes $Re_3Cl_6(acac)_3$ (acacH = acetylacetone) and $Re_3Cl_3(SCN)_3(S_2CNEt_2)_3$ were generated as described by Robinson and Fergusson.[16] These solutions were evaporated to dryness to afford the desired complexes (see below).

Spectral Measurements. The X-ray photoelectron spectra were recorded using a Hewlett-Packard 5950A ESCA spectrometer. The aluminum $K\alpha_{1,2}$ line (1486.6 eV) was used as the X-ray excitation source and the electron binding energies were calculated from the expression $E_b = E_x - E_k - \phi_s$ where E_x is the incident X-ray energy (1486.6 eV), E_k is the kinetic energy of the emitted electrons, and ϕ_s is the spectrometer work function.

Samples were generally rubbed into a gold-plated copper surface, taking care to remove excess material which was not in good electrical contact with the gold surface. However for the complexes $Mo_6Cl_{12}(DMF)_2$ and $Mo_6Cl_{12}(DMSO)_2$, an evaporation technique similar to that of Larsson, *et al.*,[17] was used. A small drop of a dilute (~10^{-6} *M*) solution of the sample was allowed to evaporate on the sample plate. The solvents used in this sampling procedure were dimethylformamide and dimethyl sulfoxide, respectively. A similar procedure was used on acetone solutions of the rhenium(III) complexes $Re_3Cl_6(acac)_3$ and $Re_3Cl_3(SCN)_3(S_2CNEt_2)_3$. Using this method it was possible to form thin sample films and this helped to eliminate charging effects.

Surface charging effects throughout the course of these studies were found to be negligible, except for $Mo_6Cl_{12}(PPh_3)_2$ which charged appreciably. Charging effects were eliminated in this case by use of an electron "Floodgun," supplied by the Hewlett-Packard Co., which bathes the sample surface in a flux of "zero" volt electrons. The "Floodgun" was routinely used to check for surface charging. The advantages of this method, as opposed to the graphite dilution technique we have previously used.[1,18-20] are discussed in part VIII of this series.[2]

As before, we have used the carbon 1s binding energy of graphite at 284.0 eV as a reference standard. When appropriate a Du Pont 310 Curve Resolver was used for peak deconvolutions using a gaussian shape fit.

Binding energy measurements were usually carried out in triplicate on different samples of the compounds. The binding energies were generally located with a precision of ±0.1 eV and are considered accurate to ±0.2 eV relative to a carbon 1s binding energy of graphite at 284.0 eV.

Results and Discussion

(a) Rhenium Chloride Clusters. In a previous paper,[3] we compared the chlorine 2p binding energy spectra of the complexes $[Re_3Cl_6(py)_3]_n$ and $Re_3Cl_9L_3$ (L = pyz, DMF, or PPh_3) and concluded that the observed *three*-component spectra could only be explained by the overlap of the chlorine 2p binding energies of two types of chlorine atom. For $Re_3Cl_9L_3$ this was consistent with the known structure of complexes of this type[21] and for $[Re_3Cl_6(py)_3]_n$ supported our suggestion[3,22] that it was a polymeric phase containing both "strong" intracluster and "weak" intercluster Re-Cl-Re bridges. We have argued[3,4] that in such strongly metal-metal bonded clusters, a chlorine atom in an *intracluster* Re-Cl_b-Re bond should possess a significantly higher positive charge than that in a terminal Re-Cl_t bond or "weak" *intercluster* Re-Cl---Re bridging unit. Accordingly, we would anticipate a chlorine 2p electron binding energy order of $Cl_b > Cl_t$.

In our previous study of the ESCA spectrum of $[Re_3Cl_6(py)_3]_n$,[3] the chlorine 2p binding energy spectrum was not of sufficiently good quality to justify a detailed comparison of relative peak intensities with those obtained for the com-

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Table I. Rhenium 4f and Chlorine 2p Binding Energies (eV) for Trinuclear Rhenium Chloride Clusters[a]

Compd	Re $4f_{5/2,7/2}$[b]	Cl $2p_{1/2,3/2}$
$[Re_3Cl_6(py)_3]_n$	44.6 (1.6), 42.4 (1.2)	200.8, 199.2, 197.8
$Re_3Cl_9(pyz)_3$	45.0 (1.0), 42.6 (0.9)	201.0, 199.5, 198.0
$Re_3Cl_6(acac)_3$	44.6 (1.3), 42.1 (1.4)	200.5, 199.0, 197.7
$Re_3Cl_6(S_2CNEt_2)_3$	44.1 (1.8), 41.7 (1.7)	200.5, 199.2, 197.8
$Re_3Cl_3(SCN)_3(S_2CNEt_2)_3$	44.5 (1.7), 42.1 (1.3)	(200.2), 198.9

[a] All spectra are referenced to the C 1s binding energy of graphite taken as 284.0 eV. Shoulders are quoted in parentheses. [b] FWHM values are given in parentheses.

plexes of the type $Re_3Cl_9L_3$. In particular, the rhenium 4f and chlorine 2p binding energies had FWHM values approaching twice those observed for the latter complexes. At the time,[3] we attributed this pronounced broadening to the amorphous nature of $[Re_3Cl_6(py)_3]_n$. More recently, following improvement in our sampling procedures and instrumental resolution we have remeasured the rhenium 4f and chlorine 2p spectra of $[Re_3Cl_6(py)_3]_n$ and $Re_3Cl_9(pyz)_3$. The spectral quality was sufficiently good that we are now able to draw some further conclusions. The rhenium 4f and chlorine 2p binding energies (Table I) were similar to those reported previously[3] but the peaks were significantly narrower in the present work although, as before, their widths were greater for $[Re_3Cl_6(py)_3]_n$ than $Re_3Cl_9(pyz)_3$.

Deconvolution of the chlorine 2p binding energy spectra now seemed appropriate (see Experimental Section). First we checked the chlorine $2p_{3/2}$:$2p_{1/2}$ intensity ratio for several rhenium chloride complexes containing one type of chlorine environment. Complexes such as $[C_5H_5NH]_2Re_2Cl_8$, K_2ReCl_6, and $[(C_2H_5)_4N]ReCl_5(DMF)$ seemed convenient for this purpose, and using data already accumulated in this laboratory for such species,[23] we found a $Cl(2p_{3/2})$:$Cl(2p_{1/2})$ intensity ratio of 1.9 ± 0.2, fairly close to the expected value of 2.0. It is also apparent that the spin-orbit separation $E_b[Cl(2p_{1/2})-Cl(2p_{3/2})]$ is invariably 1.5 ± 0.1 eV.[23] Accordingly, deconvolution of the chlorine 2p binding energy spectra of $[Re_3Cl_6(py)_3]_n$ and $Re_3Cl_9(pyz)_3$ were carried out keeping within the above limits for $I[Cl(2p_{3/2})$:$Cl(2p_{1/2})]$ and $E_b[Cl(2p_{1/2})-Cl(2p_{3/2})]$ (Figure 1). These deconvolutions were helped by the realization that the middle component of the three-peak spectrum arises from a coincidence in the energies of $Cl(2p_{3/2})$ of one type of chlorine atom with the $Cl(2p_{1/2})$ component of the other type. From these deconvolutions we found the relative peak intensities within the three-component spectra to be 1.2:3.4:2.0 and 1.1:4.9:4.0 for $[Re_3Cl_6(py)_3]_n$ and $Re_3Cl_9(pyz)_3$, respectively. Deconvolution of the related spectra of $Re_3Cl_9(DMF)_3$ and $Re_3Cl_9(PPh_3)_3$ gave ratios of 0.9:4.0:4.0 and 1.0:4.0:4.0, respectively. These values are in good agreement with the theoretical ratios of 1.0:3.0:2.0 and 1.0:4.0:4.0, which are expected for "ideal" systems with $Cl(2p_{3/2})$:$Cl(2p_{1/2})$ intensity ratios of 2.0. Furthermore, the change in peak intensities for these two types of complex is in keeping with the proposed change in relative numbers of intracluster rhenium-chlorine bridges and rhenium-chlorine terminal bonds (or intercluster rhenium-chlorine bridges).[24]

To confirm our assignments we have utilized the observations of Fergusson and Robinson,[16] that the Re-Cl_t bonds are much more readily substituted than Re-Cl_b, in order to study the rhenium 4f and chlorine 2p binding energy spectra of cluster species in which the Re-Cl_t bonds have been progressively substituted. The rhenium(III) complexes of diethyldithiocarbamate and acetylacetone, $Re_3Cl_6(S_2CNEt_2)_3$ and $Re_3Cl_6(acac)_3$,[16] were ideal for this purpose and afforded chlorine 2p spectra (Table I) which closely resembled that of the rhenium(II) complex $[Re_3Cl_6(py)_3]_n$. For $Re_3Cl_6(acac)_3$ the three-peak spectrum of intensity ratio 1.2:3.2:2.0, confirmed that the Cl_b:Cl_t ratio in this complex was 1.0. $Re_3Cl_6(S_2CNEt_2)_3$ has been reported[16] to react with thiocyanate ion to afford a derivative $Re_3Cl_3(SCN)_3(S_2CNEt_2)_3$ in which all the *terminal* chlorine atoms of the parent Re_3Cl_9 cluster have been replaced. The X-ray photoelectron spectrum of this complex (Table I) confirmed this conclusion and in addition proved our previous contention that in such a cluster species the binding energy order is $Cl_b > Cl_t$, since the chlorine 2p binding energies assigned to Cl_t are now absent.

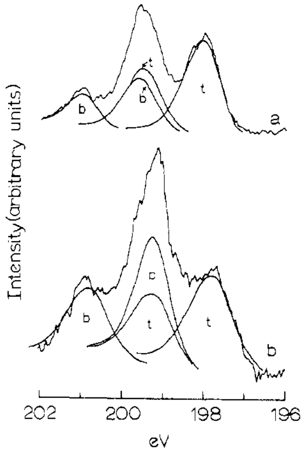

Figure 1. Chlorine 2p binding energy spectra of (a) $Re_3Cl_9(pyz)_3$ and (b) $[Re_3Cl_6(py)_3]_n$ showing deconvolutions into two Cl $2p_{1/2,3/2}$ doublets; Cl_b and Cl_t components are distinguished by the labels b and t.

A problem which can arise in interpreting the binding energy spectra of certain cluster compounds is the presence of more than two types of metal-chlorine bond. This is the situation in rhenium(III) chloride itself,[25] where in addition to Re-Cl_t and Re-Cl_b, weak intercluster Re-Cl---Re bridges are also present. This is reflected by a broad unresolved chlorine 2p band envelope, centered at ~199.0 eV (FWHM = 2.4 eV), containing the six overlapping chlorine 2p spin-orbit components. It has been noted[25] that this halide will take up water from a moist atmosphere to afford a material which when dehydrated is more reactive than the freshly prepared halide. This has been attributed[25] to a disruption of the intercluster Re-Cl---Re bridges by the water molecules, which are not regenerated when the water molecules are removed. This does in fact seem to be the case, since when we carried out this water treatment and then pumped the product at 100° for 12 hr, the chlorine 2p spectrum now showed the characteristic three-component

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(24) Since we do not necessarily expect chlorine atoms in weak intercluster Re-Cl- - -Re bridges to have binding energies very different from those in Re-Cl_t bonds, we do not normally anticipate being able to distinguish between these two possibilities (see later).

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Table II. Molybdenum 3d and Chlorine 2p Binding Energies (eV) for Molybdenum(II) Chloride Clusters

		Mo		Cl_b		Cl_t		
Compd[a]	No.	$3d_{3/2}$	$3d_{5/2}$	$2p_{1/2}$	$2p_{3/2}$	$2p_{1/2}$	$2p_{3/2}$	Other BE's
Mo_6Cl_{12}	I	232.0	228.7	201.0	199.5		197.0	
$[H_3O]_2Mo_6Cl_{14}\cdot 6H_2O$	II	231.9	228.7	201.2	199.6	(198.8)[b]	197.4	
$[(C_2H_5)_4N]_2Mo_6Cl_{14}$	III	232.4	229.3	201.7	200.1	(199.4)[b]	197.8	
$[(C_4H_9)_4N]_2[(Mo_6Cl_8)Br_6]$	IV	232.3	229.2	201.7	200.1			Br $3d_{3/2,5/2}$, ~69.2, ~68.2; C 1s, 284.7
$[(C_4H_9)_4N]_2[(Mo_6Cl_8)I_6]$	V	232.2	229.0	201.4	199.9			I $3d_{3/2,5/2}$, 630.2, 618.6
$Mo_6Cl_{12}(py)_2$	VI	231.9	228.8	201.2	199.6	(198.8)[b]	197.4	C 1s, 286.0, 284.0; N 1s, ~400.6[c]
$Mo_6Cl_{12}(DMF)_2$	VII	232.0	228.9	201.2	199.6	(198.8)[b]	197.4	N 1s, ~400.0[c]
$Mo_6Cl_{12}(DMSO)_2$	VIII	231.9	228.8	201.0	199.4	(198.8)[b]	197.2	C 1s, 284.3
$Mo_6Cl_{12}(PPh_3)_2$	IX	232.2	229.0	201.3	199.8	(198.9)[b]	197.4	C 1s, 284.2
$Mo_6Cl_{12}(NEt_3)_2$	X	232.1	228.9	201.3	199.7	(198.9)[b]	197.4	
$Mo_6Cl_{12}(dppe)$	XI	232.3	229.0	201.3	199.8	(199.1)[b]	197.6	C 1s, 285.9, 283.9
$Mo_6Cl_{12}(bipy)_2$	XII	232.2	228.9	201.3	199.7	(198.9)[b]	197.4	
$Mo_6Cl_{12}(phen)_2$	XIII	232.2	229.0	201.4	199.9	(199.3)[b]	197.8	C 1s, 284.6
$Mo_6Cl_{12}(terpy)$	XIV	232.5	229.3	201.6	200.1	(199.4)[b]	197.8	

[a] Ligand abbreviations: py, pyridine; DMF, dimethylformamide; DMSO, dimethyl sulfoxide; dppe, 1,2-bis(diphenylphosphino)ethane; bipy, 2,2'-bipyridyl; phen, 1,10-phenanthroline; terpy, 2,2',2''-terpyridyl. [b] Chlorine 2p binding energies given in parentheses were obtained by deconvolution of the three-peak spectra using a Du Pont 310 curve analyzer (see Experimental Section). [c] These nitrogen 1s binding energy peaks were rather poorly defined (±0.3 eV) due to the low nitrogen content of the complexes and the proximity of the broad (FWHM ~2 eV) molybdenum $2p_{3/2}$ peak at ~395 eV.

spectrum (*albeit* broad) with peaks at ~200.4, 199.0, and 198.1 eV.

(b) Molybdenum Chloride Clusters. Molybdenum(II) chloride and its derivatives seemed particularly ideal systems for extending our studies. The dichloride contains the $[Mo_6Cl_8]^{4+}$ cluster, in which a chlorine atom (Cl_b) lies above each face of the Mo_6 octahedron and is bonded to *three* molybdenum atoms, together with six "external" chlorine atoms, four of which (Cl_b') occupy intercluster bridging positions between molybdenum atoms of two different clusters and the remaining two (Cl_t) are each bound to one molybdenum atom.[26] This halide is accordingly best represented as $[Mo_6Cl_8]Cl_{4/2}Cl_2$. In derivatives of this halide with monodentate donor molecules, the *intercluster* bridges (Cl_b') are disrupted and products of stoichiometry $[Mo_6Cl_8]Cl_4L_2$, where L represents a neutral donor molecule, and $[(Mo_6Cl_8)X_6]^{2-}$, where X = Cl, Br, or I, can be isolated.[27] The molybdenum 3d and chlorine 2p binding energies for complexes of these types are listed in Table II, together with other binding energies which are characteristic of the individual complexes. Related data are also included in this table for complexes with the bidentate donors 2,2'-bipyridyl, 1,10-phenanthroline, and 1,2-bis(diphenylphosphino)ethane and the terdentate 2,2',2''-terpyridyl. The molybdenum 3d and chlorine 2p spectra were well resolved with typical signal to noise ratios for molybdenum $3d_{5/2}$ and chlorine $2p_{3/2}$ of 18.0 and signal to background ratios of 6.0 and 3.0, respectively. FWHM values for the molybdenum 3d and chlorine 2p peaks were 1.1 ± 0.2 and 1.3 ± 0.3 eV, respectively.

Molybdenum 3d Binding Energies. As expected, the molybdenum $3d_{3/2,5/2}$ binding energies (Table II) vary very little within this series of molybdenum(II) complexes. Formally, the only change which occurs is the variation in the nature of the ligand bound in a "centrifugal" position to each of the molybdenum atoms of the $[Mo_6Cl_8]^{4+}$ cluster. Even within the series $[(Mo_6Cl_8)X_6]^{2-}$, where X = Cl, Br, or I, there is no significant variation in the molybdenum 3d binding energies, which contrasts with the situation in $RhX_3(C_4H_8OS)_3$[19] and $ReX_6{}^{2-}$,[23] where X = Cl, Br, or I. For the latter complexes the metal binding energies are markedly dependent upon the ligand electronegativity since respectively three and six of the ligands about the metal center are being changed.

Chlorine 2p Binding Energies. The chlorine 2p binding energy spectra for all compounds listed in Table II, with the exception of compounds IV and V, have a three-peak profile caused by the overlap of the 2p doublets of chlorine atoms in two different environments (Figure 2).

The assignment of the spectra can be simplified by observing the series of complex halide anions $[(Mo_6Cl_8)X_6]^{2-}$ (where X = Cl, Br, I). The replacement of the chlorine atoms in terminal Mo-Cl_t bonds by bromine or iodine removes the low-energy chlorine 2p doublet. This confirms, as for the rhenium chloride clusters, the binding energy order $Cl_b > Cl_t$. For these two types of chlorine environment (Cl_b and Cl_t) in complexes II, III, and VI-XIV, the energy difference is 2.3 ± 0.2 eV (Table II), significantly greater than the corresponding value of ~1.4 eV for the rhenium chloride clusters (Table I). This suggests that chlorine atoms bridging three or two metal centers in metal-metal bonded clusters may be distinguished by the binding energy order $Cl_{b(3)} > Cl_{b(2)}$.[28] It is apparent from the magnitude of this energy separation that the chlorine $2p_{1/2}$ component of the lower energy spin-orbit doublet is not coincident with the more intense chlorine $2p_{3/2}$ component of the higher energy doublet. This is reflected by a marked asymmetry on the low binding energy side of this $2p_{3/2}$ component (Figure 2). For the mixed halide clusters $[(Mo_6Cl_8)X_6]^{2-}$, where X = Br or I, the separation of the chlorine 2p doublets of Cl_b is within the expected range of 1.5 ± 0.1 eV (Table II). Furthermore the $Cl(2p_{3/2})$:$Cl(2p_{1/2})$ intensity ratios are 1.9 (X = Br) and 1.8 (X = I) eV, which are within the expected experimental range of 1.9 ± 0.2 eV (see Results and Discussion, section a). Accordingly, deconvolutions of these spectra were carried out, as for the rhenium chloride clusters, within the above limits. The deconvolution of chlorine 2p spectra for $[(C_2H_5)_4N]_2Mo_6Cl_{14}$ (Figure 2) was consistent with a Cl_b:Cl_t intensity ratio[29] of 1.2, close to that expected for

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[26] H. Schafer, H. G. von Schnering, J. Tillack, F. Kuhnen, H. Wohrle, and H. Baumann, *Z. Anorg. Allg. Chem.*, 353, 281 (1967).

[27] D. L. Kepert, "The Early Transition Metals," Academic Press, New York, N. Y., 1972, pp 354, 355.

[28] Where there is a need to distinguish chlorine atoms bridging two or more metal centers we will use the symbol $Cl_{b(n)}$, where *n* is the number of metal centers bridged by chlorine.

[29] Intensity ratios can be computed by either considering the total peak areas of the chlorine $2p_{1/2,3/2}$ doublets or comparing the intensities of the well-resolved components at either end of the chlorine 2p binding energy spectra, *i.e.*, $2p_{1/2}$ of Cl_b and $2p_{3/2}$ of Cl_t. Both approaches gave the same results.

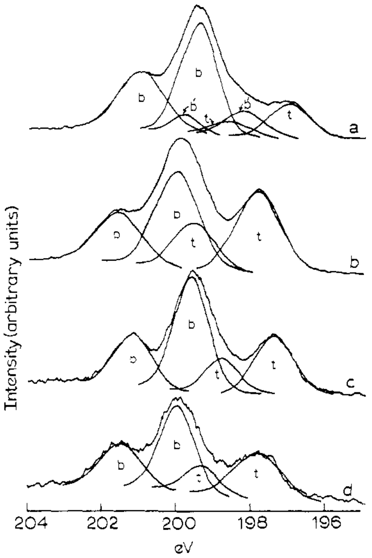

Figure 2. Chlorine 2p binding energy spectra of (a) $[(Mo_6Cl_8)Cl_{4/2}Cl_2]$, (b) $[(C_2H_5)_4N]_2[(Mo_6Cl_8)Cl_6]$, (c) $[(Mo_6Cl_8)Cl_4(py)_2]$, and (d) $Mo_6Cl_{12}(phen)_2$ showing deconvolutions; Cl_b, Cl_b', and Cl_t components are distinguished by the labels b, b', and t.

eight bridging and six terminal chlorines.[30,31] For the complexes with neutral monodentate donors of the type $Mo_6Cl_{12}L_2$ (complexes VI-X), the Cl_b:Cl_t ratios are 2.0 ± 0.2 and are therefore in accord with proposed nonionic structural formulation $[(Mo_6Cl_8)Cl_4L_2]$,[13] in which the six "external" coordination sites of the cluster (one per molybdenum atom) are occupied by four chlorines and two neutral ligands L.

From a comparison of the spectra of molybdenum(II) chloride and its derivatives $[(C_2H_5)_4N]_2Mo_6Cl_{14}$ and $Mo_6Cl_{12}L_2$ (Figure 2), the lowest energy component of the three peak spectrum of molybdenum(II) chloride is clearly much less intense than might have been anticipated and the tail of the low-energy side of the most intense component (199.5 eV) much more pronounced than in the corresponding spectra of $[Mo_6Cl_{14}]^{2-}$ and $Mo_6Cl_{12}L_2$. The explanation for this probably lies in the presence of three types of chlorine environment as expected by the formulation $[(Mo_6Cl_8)Cl_{4/2}Cl_2]$.[26] This spectrum may be readily deconvoluted using three chlorine 2p doublets (Figure 2). Since the extra doublet is intermediate in energy between that of $Cl_{b(3)}$ and Cl_t, it is apparent that for the molybdenum(II) chloride cluster system the binding energy order is $Cl_{b(3)} > Cl_b' > Cl_t$, where Cl_b' is the symbol for an intercluster bridging chlorine atom. When this halide reacts with donor molecules to afford species such as $[Mo_6Cl_{14}]^{2-}$ and $Mo_6Cl_{12}L_2$, the intercluster bridges are disrupted and the intensity of the chlorine 2p peaks due to Cl_t are correspondingly enhanced. Our failure to resolve clearly three types of chlorine environment in the spectra of Re_3Cl_9 (see Results and Discussion, section a) reflects the expected closer overlap of the three sets of chlorine 2p binding energies. Also, in molybdenum(II) chloride the intercluster bridging chlorines Cl_b' are equidistant (at 2.49 ± 0.03 Å)[26] from the molybdenum atoms of different clusters, whereas in Re_3Cl_9, the Re-Cl---Re bridges are unsymmetrical.[25] Such differences will probably affect the binding energy difference between Cl_t and Cl_b'.

Although the chlorine 2p binding energy spectra of the complexes with bidentate donors (complexes XI-XIII in Table II) and the potentially terdentate donor 2,2′2″-terpyridyl (complex XIV) have a pattern which resembles that of the dichloride and its derivatives with *monodentate donors*, the intensities of the peaks are not in all instances in accord with a Cl_b:Cl_t ratio of 2.0 (Figure 2). Previous characterizations[13] of these derivatives using more classical physical techniques has led to the suggestion[13] that some structural adaption of the $[Mo_6Cl_8]^{4+}$ cluster must occur, such as the displacement of certain cluster halogens from their normal positions, to accommodate the chelate characteristics of the ligand molecules. Evidence sited[13] in favor of this was an increase in the complexity of the *solid-state* electronic spectra of these complexes relative to that of molybdenum(II) chloride and its derivatives with monodentate donors. Conductance and molecular weight data obtained[13] on solutions of these complexes in polar solvents, such as dimethyl sulfoxide and acetone, were interpreted in terms of the structures $[(Mo_6Cl_8)Cl_3(dppe)]Cl$, $[(Mo_6Cl_8)Cl_2B_2]Cl_2$, where B = bipy or phen, and $[(Mo_6Cl_8)Cl_3(terpy)]Cl$. Our conclusions on the nature of the complexes in the *solid state* suggests that there is a structure change following dissolution in polar solvents.

The chlorine 2p binding energy spectrum of $Mo_6Cl_{12}(dppe)$ so closely resembles that of the complexes $Mo_6Cl_{12}L_2$ (Table II), with a Cl_b:Cl_t intensity ratio of 1.9, that we conclude that in this molecule the $[(Mo_6Cl_8)Cl_4L_2]$ type structure is preserved. This would be accomplished if the dppe molecules bridge adjacent $[Mo_6Cl_8]^{4+}$ clusters, in a similar fashion to that proposed in the related complex with rhenium(III) chloride, $Re_3Cl_9(dppe)_{1.5}$.[32] This possibility is given further credence by recent crystal structure analyses[33,34] on certain dppe complexes of copper, which have unambiguously established the presence of these ligand molecules in the bridging trans conformation. Previous work by us[19] on ionic rhodium(III) derivatives of the type $[RhCl_2L_4]Cl$ has shown that the chlorine 2p binding energies of Cl^- are ~1.5 eV lower than that of Cl_t in Rh-Cl_t bonds. No low binding energy peaks characteristic of Cl^- were observed in the spectrum of $Mo_6Cl_{12}(dppe)$. So unless these binding energies for Cl^- and Cl_t are fortuitously coincident for this derivative, we can find no evidence to substantiate the formulation $[(Mo_6Cl_8)Cl_3(dppe)]Cl$[13] in the *solid state.*

The spectra of complexes XII and XIII cannot be unambiguously interpreted in terms of a specific structure. Although the characteristic three-peak pattern was observed (Figure 2), deconvolution of the spectra using two chlorine 2p doublets gave a Cl_b:Cl_t intensity ratio of 1.4. This certainly suggests that some structural change has occurred relative to the complexes with monodentate donors. Since there is no evidence for Cl^-, we do not believe that these complexes have the ionic structure $[(Mo_6Cl_8)Cl_2B_2]Cl_2$, where B = bipy or phen,[13] in the *solid state.* Rather surprisingly the intensity data approach that expected for the $[Mo_6Cl_{14}]^{2-}$ anion.[35]

Finally, the spectrum of $Mo_6Cl_{12}(terpy)$ closely resembles that of $Mo_6Cl_{12}(dppe)$ and the derivatives with monodentate donors. The Cl_b:Cl_t intensity ratio is ~1.8, and there is no clear evidence for the presence of Cl^- in the lattice, so that

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(30) H. G. von Schnering, *Z. Anorg. Allg. Chem.*, **385**, 75 (1971).

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(33) A. P. Gaughan, R. F. Ziolo, and Z. Dori, *Inorg. Chem.*, **10**, 2776 (1971).

(34) V. G. Albano, P. L. Bellon, and G. Ciani, *J. Chem. Soc., Dalton Trans.*, 1938 (1972).

the *solid-state* structure is apparently not $[(Mo_6Cl_8)Cl_3(terpy)]Cl$.

Although we have presented evidence that the solid-state structures of complexes XI-XIV are probably not the same as the species in polar solvents,[13] the question still remains as to their exact structural details. While binding energy measurements have confirmed the suspicion[13] that a structural modification must have occurred in the bipyridyl and phenanthroline derivatives, it is difficult for this technique to draw unambiguous structural conclusions from small changes in the relative proportions of large numbers of chlorine atoms in different environments. It is hoped that this intriguing structural problem will be solved in the near future by a single-crystal X-ray structure analysis.

(c) β-Molybdenum(II) Chloride. This phase has been investigated by several groups,[6-8] but no definitive structural information is yet available. However, Allison, *et al.*,[7] have contended, on the basis of reactivity differences between β-$MoCl_2$ and $[Mo_6Cl_8]Cl_{4/2}Cl_2$ and their strikingly different X-ray powder photographs, that they are not structurally related. Measurement of the molybdenum 3d (231.3 and 228.2 eV) and chlorine 2p (199.9 and 198.4 eV) binding energies of β-$MoCl_2$ confirms this contention. The single chlorine $2p_{1/2,3/2}$ spin-orbit doublet rules out the presence of a cluster structure involving different types of chlorine environment. It has further been noted[7] that the X-ray powder pattern for β-$MoCl_2$ shows a distinct resemblance to the stronger lines of the $CdCl_2$ pattern. Indeed, we have found that the chlorine 2p binding energy peaks of β-$MoCl_2$ and $CdCl_2$, which for the latter chloride are at 199.5 and 198.0 eV, have a very similar profile, so that β-$MoCl_2$ may adopt a close-packed layer structure like $CdCl_2$.

The X-ray photoelectron spectrum of β-$MoCl_2$ also exhibits a broad carbon 1s binding energy at 284.0 eV. This is presumably due to a small amount of carbon contaminant. It does not, however, arise from contamination by the molybdenum(II) acetate starting material which has a characteristic two-component carbon 1s acetate spectrum,[36] with peaks at 287.4 and 284.6 eV. The molybdenum 3d binding energies for $Mo_2(O_2CCH_3)_4$, at 231.6 and 228.4 eV, are similar to those of the other molybdenum(II) derivatives described herein.

(d) Comparisons with Other Systems Containing Metal-Chlorine Bridging Bonds. At the start of this work we were surprised by the magnitude of the binding energy differences between the different types of chlorine environment, but it soon became clear that these spectral features were characteristic of metal-metal bonded cluster compounds. We have previously suggested[4] that in metal halides such as Mo_2Cl_{10}, which contain both Cl_b and Cl_t environments but *no* metal-metal bond, there should be little difference between the two sets of chlorine 2p binding energies. Some recent results[37] for the chlorine-bridged platinum(II) complex *trans*-$[Et_3P]_2Pt_2Cl_4$ indicate that the chlorine 2p binding energies for Cl_b are ~1 eV less than those for Cl_t in this complex. On the other hand, related measurements on the polymeric $\{[ReCl_5]^-\}_n$ anion[23] show that there is little difference in binding energies between Cl_b and Cl_t. It is clearly difficult in this type of system to predict with any certainty the relative ordering of the binding energies for Cl_b and Cl_t. Available evidence at present suggests that in contrast to our results for the metal chloride clusters the binding energy order will usually be $Cl_t \gtrsim Cl_b$ for systems which do not contain *strong* metal-metal bonds.

Acknowledgments. This work was supported by the National Science Foundation (Grant No. GP-19422 and MRL Program GH-33574). The award of a Camille and Henry Dreyfus Foundation Teacher-Scholar Grant to R. A. W. is gratefully acknowledged.

Registry No. $[Re_3Cl_6(py)_3]_n$, 27614-34-2; $Re_3Cl_9(pyz)_3$, 27988-08-5; $Re_3Cl_6(acac)_3$, 17787-16-5; $Re_3Cl_6(S_2CNEt_2)_3$, 17442-30-7; $Re_3Cl_3(SCN)_3(S_2CNEt_2)_3$, 21360-04-3; Mo_6Cl_{12}, 9021-81-2; $[H_3O]_2Mo_6Cl_{14}\cdot 6H_2O$, 12187-16-5; $[Et_4N]_2Mo_6Cl_{14}$, 51056-19-0; $[Bu_4N]_2[(Mo_6Cl_8)Br_6]$, 12367-10-1; $[Bu_4N]_2[(Mo_6Cl_8)I_6]$, 12367-11-2; $Mo_6Cl_{12}(py)_2$, 12170-24-0; $Mo_6Cl_{12}(DMF)_2$, 12128-03-9; $Mo_6Cl_{12}(DMSO)_2$, 12123-07-8; $Mo_6Cl_{12}(PPh_3)_2$, 18307-01-2; $Mo_6Cl_{12}(NEt_3)_2$, 51108-03-3; $Mo_6Cl_{12}(dppe)$, 12172-16-6; $Mo_6Cl_{12}(bipy)_2$, 17926-51-1; $Mo_6Cl_{12}(phen)_2$, 12172-04-2; $Mo_6Cl_{12}(terpy)$, 17926-54-4; β-$MoCl_2$, 13478-17-6.

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(35) Since this article was submitted for publication we have been interested to learn from Dr. J. E. Fergusson that the compounds he formulated[13] as $Mo_6Cl_{12}(bipy)_2$ and $Mo_6Cl_{12}(phen)_2$ are probably the salts $[BH^+]_2[(Mo_6Cl_8)Cl_6{}^{2-}]$. It is believed that the protons arise from the reaction of the $[Mo_6Cl_8]Cl_4$ cluster with species containing the hydroxyl group, such as traces of water or the solvent ethanol. Our ESCA results apparently substantiate these conclusions since the observed $Cl_b:Cl_t$ intensity ratios of ~1.4 could be interpreted to mean that the $[Mo_6Cl_{14}]^{2-}$ anion is a major component of these reaction products.

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