the energy of the dσ-MLCT transition in these compounds is primarily related to the energy of the ligand-based acceptor orbital, and $\Delta_{\pi-\sigma}$ is related to the extent of metal-to-ligand π bonding. From the dσ-MLCT data shown in Table V, the ordering of the stability of the ligand acceptor orbitals is P-donor > CNR ~ olefin > CO. The energy difference between the most stable (lowest energy) P-donor ligands and the least stable CO is 0.5–0.6 μm^{-1} and is not exceptionally large. This result may imply a significant amount of metal $(n + 1)\mathrm{p}_z$ character in the acceptor MO, since greater $(n + 1)\mathrm{p}_z$ character would reduce the sensitivity of the orbital to the nature of the ligand. The magnitude of $\Delta_{\pi-\sigma}$ shows the order olefin > CO > PR_3 ~ CNR and suggests the olefin ligands are the best acceptor ligands of those represented in Table V. Their participation in metal-to-ligand bonding (back-bonding) causes the largest "splitting" of the occupied *n*d orbitals. Again the energy difference between the olefins and CNR is not large, amounting to only 0.40–0.42 μm^{-1}. The small "splitting" of the occupied orbitals by π-acceptor ligands has been noted previously and appears characteristic of electron-rich low coordination number complexes.[3,4,6,27]

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Registry No. $[RhCl(CO)_2]_2$, 14404-25-2; $[RhCl(CO)_2(CH_3CN)]$, 68474-99-7; $[RhCl(COD)]_2$, 12092-47-6; $[RhCl(COD)(CH_3CN)]$, 68475-00-3; $[RhCl(NBD)]_2$, 12257-42-0; $[RhCl(NBD)(CH_3CN)]$, 68525-24-6; $[RhCl(C_2H_4)_2]_2$, 12081-16-2; $[RhCl(COT)_2]_2$, 12279-09-3; $[IrCl(COD)]_2$, 12112-67-3; $[IrCl(COD)(CH_3CN)]$, 68475-01-4; $[IrCl(COT)_2]_2$, 12246-51-4.

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X-ray Photoelectron Spectra of Inorganic Molecules. 22.[1] Halogen Core Electron Binding Energies of Low Oxidation State Molybdenum Bromide and Molybdenum Iodide Clusters and Niobium and Tantalum Chlorides Containing the $[M_6Cl_{12}]^{n+}$ Cores

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The Br 3p and I 3d binding energy spectra of α-molybdenum bromide and iodide, $(Mo_6X_8)X_4$, and the bromide derivatives $(Mo_6Br_8)Br_4L_2$ and $(Et_4N)_2[(Mo_6Br_8)X_6]$, where X = Cl or Br, show that bridging (X_b) and terminal (X_t) halogen environments are readily differentiated by X-ray photoelectron spectroscopy (XPS). Values of $\Delta E(X_b–X_t)$ were in the range of 1.8–2.4 eV for the bromide complexes and 1.3 eV for $(Mo_6I_8)I_4$. XPS data for the complex $(Bu_4N)_2Mo_4I_{11}$ show the presence of two sets of I $3d_{3/2,5/2}$ doublets which differ in binding energy by 1.2 eV. The energies and relative intensities of these latter peaks are in accord with a stoichiometric ratio $I_b{:}I_t$ equal to 7:4. These studies constitute the first examples of the use of XPS to successfully distinguish different halogen environments in transition-metal bromides and iodides and their complexes. The Cl 2p spectra of the niobium and tantalum chloride clusters which contain the $(M_6Cl_{12})^{n+}$ cores have also been measured and show that, like Re_3Cl_9 and $(Mo_6Cl_8)Cl_4$ and their derivatives, the binding energy order is $Cl_b > Cl_t$, with $\Delta E(Cl_b–Cl_t)$ being between 1.4 and 2.1 eV.

Introduction

The steadily increasing accumulation of data on the X-ray photoelectron spectra (XPS) of metal halides and their complexes has prompted two recent reviews on this subject.[2,3] Largely as a result of work carried out in our laboratory, it has been demonstrated that for metal–metal bonded dimers and clusters which contain both bridging (Cl_b) and terminal (Cl_t) metal–chlorine bonds the Cl 2p binding energy order is $Cl_b > Cl_t$.[4–7] The chemical shift differences between $E(Cl_b)$ and $E(Cl_t)$ depend upon the system in question, ranging from ~2.3 eV for $(Mo_6Cl_8)Cl_4$ and its derivatives[6] to ~1.4 eV for Re_3Cl_9 and its derivatives[4–6] to a value between 0.5 and 1.2

Table I. X-ray Photoelectron Spectra of Molybdenum Bromide and Iodide Clusters and Their Complexes[a]

	Mo		Br_b		Br_t	
complex	$3d_{3/2}$	$3d_{5/2}$	$3p_{1/2}$	$3p_{3/2}$	$3p_{1/2}$	$3p_{3/2}$
$(Mo_6Br_8)Br_4$	232.5	229.5 (1.0)	190.4	183.9 (2.5)	188.5	181.8 (2.5)
$(Et_4N)_2[(Mo_6Br_8)Br_6]$	232.6	229.5 (1.2)	190.5	184.1 (2.1)	188.6	182.1 (2.5)
$(Et_4N)_2[(Mo_6Br_8)Cl_6]$[b]	232.5	229.4 (1.5)	190.5	184.0 (2.4)		
$(Mo_6Br_8)Br_4(py)_2$	233.0	229.9 (1.1)	190.7	184.2 (2.2)	188.6	181.8 (2.1)
$(Mo_6Br_8)Br_4(PPr^n{}_3)_2$	232.6	229.5 (1.1)	190.4	183.8 (2.1)	188.4	181.7 (2.1)
$(Mo_6Br_8)Br_4(PBu^n{}_3)_2$	232.4	229.3 (1.1)	190.5	183.8 (2.2)	188.7	182.0 (2.2)
$(Mo_6Br_8)Br_4(dppe)$	233.1	230.0 (1.0)	190.7	184.1 (2.1)	188.6	181.9 (2.2)
$(Mo_6I_8)I_4$	232.1	229.0 (1.0)	632.2[c]	620.8[c] (1.2)	630.8[c]	619.5[c] (2.0)
$(Bu_4N)_2Mo_4I_{11}$	232.5[d]	229.2[d] (1.0)	631.7[c]	620.2[c] (1.3)	630.5[c]	619.0[c] (1.2)

[a] Binding energies in eV are referenced to C 1s binding energy of 285.0 eV for carbon contaminant and/or the carbon atoms of the organic ligands; full width at half maximum (fwhm) values given in parentheses. [b] Cl $2p_{1/2,3/2}$ binding energies at 199.8 and 198.4 eV. [c] I $3d_{3/2,5/2}$ binding energies. [d] These Mo 3d binding energies have been reported previously.[15]

eV for chloro anions of the type $M_2Cl_9{}^{n-}$, where M = Cr(III), Mo(III), W(III), and Re(IV).[7] These results, coupled with data for certain complex salts of the type $[ML_4Cl_2]Cl$, where M = Cr or Rh and L = pyridine, $^1/_2$(2,2′-bipyridyl), $^1/_2$-(2,5-dithiahexane), $^1/_2$(1,2-bis(diphenylphosphino)ethane), or $^1/_2$(1,2-bis(diphenylarsino)ethane),[7-9] which show a chemical shift of ~1.5 eV between $E(Cl_t)$ and $E(Cl^-)$, mean that an unexpectedly large energy difference (up to ~4 eV) can exist between the Cl 2p binding energies of Cl_b and Cl^-.

In previous extensions of these studies to include F 1s and Br 3p binding energies of certain metal fluorides[10] and bromides,[11] the binding energy differences between halogens in terminal and bridging metal–halogen bonds, i.e., $\Delta E(F_b–F_t)$ and $\Delta E(Br_b–Br_t)$, were rather small, and it did not appear at the time that the XPS technique would be a useful means of structurally characterizing such phases. However, recent measurements of the halogen binding-energy spectra of molybdenum(II) bromide and iodide, $(Mo_6X_8)X_4$, and certain of their derivatives, together with related data for the salt $(Bu_4N)_2Mo_4I_{11}$, demonstrate that $M–X_t$ and $M–X_b$ environments in these phases can indeed be differentiated.[12] Details of this study are now reported, together with the results of our XPS investigations of niobium and tantalum chloride clusters which contain the $[M_6Cl_{12}]^{n+}$ cores. This work completes our detailed investigations of the XPS of transition-metal halide clusters.

Experimental Section

A. Preparation of Molybdenum Bromide and Iodide Complexes. $(Mo_6Br_8)Br_4$ and $(Mo_6I_8)I_4$ were prepared by the reaction of $(Mo_6Cl_8)Cl_4$ (obtained by Jolly's modification of Sheldon's method[13]) with an excess of fused LiBr or LiI.[14] The following complexes were available from previous studies in our laboratory and were supplied by Victoria A. Ozimec: $(Et_4N)_2[(Mo_6Br_8)X_6]$, where X = Cl or Br; $(Mo_6Br_8)Br_4(py)_2$; $(Mo_6Br_8)Br_4(PPr^n{}_3)_2$; $(Mo_6Br_8)Br_4(PBu^n{}_3)_2$, and $(Mo_6Br_8)Br_4(dppe)$, where dppe = 1,2-bis(diphenylphosphino)ethane.

Samples of the salt $(Bu_4N)_2Mo_4I_{11}$ were prepared by the reaction of HI gas with a suspension of molybdenum(II) acetate, $Mo_2(O_2CCH_3)_4$, in ethanol followed by the addition of tetra-*n*-butylammonium iodide.[15]

B. Preparation of Niobium and Tantalum Chloride Complexes. The following complexes were prepared by literature methods:[16-19] $(M_6Cl_{12})Cl_2(H_2O)_4·4H_2O$, $(Et_4N)_3[(Nb_6Cl_{12})Cl_6]$, $(Et_4N)_2[(Ta_6Cl_{12})Cl_6]$, and $(Nb_6Cl_{12})Cl_2(Me_2SO)_4$, where Me_2SO = dimethyl sulfoxide. The purity of these complexes was checked by IR spectroscopy and/or elemental microanalyses.

The mixed-halide complexes $(Bu_4N)_2[(Nb_6Cl_{12})Br_6]$ and $(Bu_4N)_2[(Ta_6Cl_{12})Br_6]$ were prepared using the following procedure. $(M_6Cl_{12})Cl_2(H_2O)_4·4H_2O$ (0.2 g) was dissolved in 20 mL of absolute ethanol, and the solution was purged with nitrogen gas for about 30 min. An ice bath was then placed around the reaction flask, the nitrogen flow stopped, and the HBr gas bubbled through the solution for 15 min. An excess of $(Bu_4N)Br$ was dissolved in 20 mL of absolute ethanol and then added to the reaction mixture. The HBr flow was continued for an additional 10 min, and the solution was then purged with nitrogen gas to remove excess HBr. The resulting solution was evaporated to half its volume and filtered. The resulting dark red crystalline product was washed with ethanol and ether and dried in vacuo. Yield ≈65%. Anal. Calcd for $C_{32}H_{72}Br_6Cl_{12}N_2Nb_6$: C, 19.72; H, 3.70; Br, 24.62. Found: C, 20.03; H, 4.00; Br, 24.32. Calcd for $C_{32}H_{72}Br_6Cl_{12}N_2Ta_6$: C, 15.52; H, 2.91; Br, 19.37. Found: C, 15.80; H, 3.05; Br, 19.36. An interesting feature concerning our isolation of $(Bu_4N)_2[(M_6Cl_{12})Br_6]$ is that the reaction conditions we used would not have been expected[16] to ensure complete oxidation to $[(M_6Cl_{12})Br_6]^{2-}$. Instead, salts of $[(M_6Cl_{12})Br_6]^{3-}$ might have been expected. Nonetheless, it is apparent that the addition of Bu_4N^+ favors the further oxidation to $[(M_6Cl_{12})Br_6]^{2-}$. The microanalytical data reported for $(Bu_4N)_2[(Nb_6Cl_{12})Br_6]$ are consistent with the presence of a small amount of $(Bu_4N)_3[(Nb_6Cl_{12})Br_6]$ contaminant.

$(Nb_6Cl_{12})Cl_2(PPr^n{}_3)_4$ was prepared by the following procedure. $(Nb_6Cl_{12})Cl_2(H_2O)_4·4H_2O$ (0.1 g) and 1 mL of tri-*n*-propylphosphine were refluxed in 20 mL of absolute ethanol for 6 h. The resulting black crystals were washed with ethanol and ether and dried in vacuo. Yield: 79%. Anal. Calcd for $C_{36}H_{84}Cl_{14}Nb_6P_4$: C, 25.50; H, 4.96; Cl, 29.34. Found: C, 25.37; H, 4.82; Cl, 28.98.

C. 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 excitation source. Sample preparation and full details of the experimental procedure are described fully elsewhere.[6,20] Deconvolutions were carried out using the procedure we have described previously,[6] namely, a Du Pont 310 curve resolver employing a Gaussian-shape fit.

Results and Discussion

The appropriate XPS data are presented in Tables I and II. In all instances, the Mo $3d_{3/2,5/2}$ binding energies (Table I) occur in a range which is characteristic of the molybdenum(II) halides and their complexes,[21] while the values of the related Nb $3d_{3/2,5/2}$ and Ta $4f_{5/2,7/2}$ energies of the niobium and tantalum chloride clusters are reasonable in comparison with other low-oxidation-state niobium and tantalum systems.[22,23] A 0.7 eV decrease in Mo 3d binding energies is evident in the different halide clusters $(Mo_6X_8)X_4$, corresponding to the electronegativity order Cl > Br > I, i.e., Mo $3d_{5/2}$ of 229.7 eV for $(Mo_6Cl_8)Cl_4$[6,24] vs. 229.0 eV for $(Mo_6I_8)I_4$. This result is expected since the less electronegative iodine atoms will create a smaller positive charge at the metal centers of the Mo_6 octahedron. These metal binding energies will not be considered further.

(a) Nomenclature and Structures of the Metal Halide Clusters. These aspects need to be briefly discussed prior to our interpretation of the halogen binding energy data. As before,[2,6] we will use the symbols X_t, X_b, and $X_{b'}$ to distinguish between halogen atoms in terminal, intracluster bridging, and intercluster bridging metal–halogen bonds, respectively.

The molybdenum(II) halides are isomorphous.[25] A crystallographic study on Mo_6Cl_{12} shows[26] the presence of the $(Mo_6Cl_8)^{4+}$ cluster in which the eight chlorine atoms (Cl_b) are located above the faces of the Mo_6 octahedron. Of the six remaining chlorine atoms, four occupy intercluster bridging positions ($Cl_{b'}$) between molybdenum atoms of two different clusters, while the remaining two (Cl_t) are bound to mo-

Table II. X-ray Photoelectron Spectra of Niobium and Tantalum Chloride Clusters and Their Complexes[a]

	metal[b]		Cl_b		Cl_t	
complex	$3d_{3/2}(4f_{5/2})$	$3d_{5/2}(4f_{7/2})$	$2p_{1/2}$	$2p_{3/2}$	$2p_{1/2}$	$2p_{3/2}$
$(Nb_6Cl_{12})Cl_2(H_2O)_4 \cdot 4H_2O$	207.7	204.9 (1.1)	201.0	199.5 (1.0)	199.9	198.1 (1.0)
$(Et_4N)_3[(Nb_6Cl_{12})Cl_6]$	207.7	204.9 (1.3)	201.0	199.6 (1.0)	199.3	197.7 (1.0)
$(Bu_4N)_2[(Nb_6Cl_{12})Br_6]$[c]	207.7	204.9 (1.6)	201.0	199.6 (1.4)		
$(Nb_6Cl_{12})Cl_2(PPr^n_3)_4$	207.6	204.8 (1.3)	201.0	199.5 (1.1)	199.3	197.7 (1.0)
$(Nb_6Cl_{12})Cl_2(Me_2SO)_4$	207.6	204.8 (1.1)	201.0	199.5 (1.1)	199.3	197.7 (1.0)
$(Ta_6Cl_{12})Cl_2(H_2O)_4 \cdot 4H_2O$	26.0	24.2 (1.2)	201.1	199.5 (1.0)	200.0	198.0 (1.1)
$(Et_4N)_2[(Ta_6Cl_{12})Cl_6]$	26.4	24.4 (1.0)	201.4	199.8 (1.0)	199.3	197.7 (1.0)
$(Bu_4N)_2[(Ta_6Cl_{12})Br_6]$[d]	26.5	24.5 (1.0)	201.5	199.9 (1.1)		

[a] Binding energies in eV are referenced to a C 1s binding energy of 285.0 eV for carbon contaminant and/or the carbon atoms of the organic ligands; full width at half maximum (fwhm) values given in parentheses. [b] Nb $3d_{3/2}$ and Nb $3d_{5/2}$ or Ta $4f_{5/2}$ and Ta $4f_{7/2}$. [c] Br $3p_{1/2,3/2}$ binding energies at 188.1 and 181.5 eV. [d] Br $3p_{1/2,3/2}$ binding energies at 188.7 and 182.1 eV.

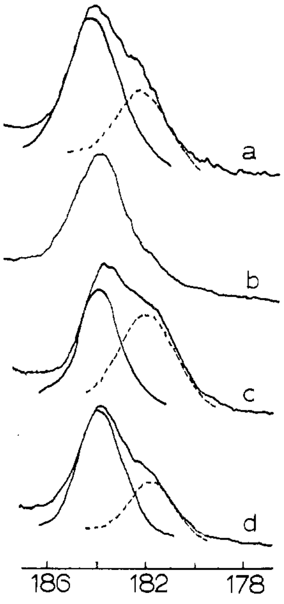

Figure 1. Bromine Br $3p_{3/2}$ binding energy spectra of (a) $(Mo_6Br_8)Br_4$, (b) $(Et_4N)_2[(Mo_6Br_8)Cl_6]$, (c) $(Et_4N)_2[(Mo_6Br_8)Br_6]$, and (d) $(Mo_6Br_8)Br_4(PPr^n_3)_2$ showing deconvolutions into Br_b (—) and Br_t (- - -) components.

lybdenum atoms in the axial positions of the cluster. These halides are accordingly best represented as $(Mo_6X_8)X_{4/2}X_2$, but, for convenience, we will write them as $(Mo_6X_8)X_4$ (see Table I). In their reactions with donor molecules (L), the *intercluster* bridges are broken, and products of stoichiometry $(Mo_6X_8)X_4L_2$ result,[27] in which X_t and X_b environments are present.

Preliminary details of the crystal structure of $(Bu_4N)_2Mo_4I_{11}$ reveal[28] that the four molybdenum atoms form a distorted tetrahedron, and both terminal (four) and bridging (seven) Mo–I bonds are present.

The hydrated niobium and tantalum chloride clusters $M_6Cl_{14} \cdot 8H_2O$ contain the $(M_6Cl_{12})^{2+}$ cores, with the chlorine atoms bridging the 12 edges of the M_6 octahedra.[18,29,30] The six remaining coordination sites of the clusters are occupied by two chloride and four water ligands. The structures of these phases are therefore represented as $(M_6Cl_{12})Cl_2(H_2O)_4 \cdot 4H_2O$.[29,30] In their reactions to form the complexes $(M_6Cl_{12})Cl_2L_4$, where L = Me_2SO, pyridine *N*-oxide etc.,[18] and $(Nb_6Cl_{12})Cl_6^{n-}$, where *n* = 2, 3, or 4,[19,31] this basic structure, containing only Cl_t and Cl_b environments, is retained.

(b) Molybdenum Bromide and Iodide Clusters. In all instances, the Br 3p and I 3d binding energy spectra of the molybdenum bromide and iodide clusters (Table I and Figures 1 and 2) reveal the presence of at least two different halogen environments in these phases.[32] Deconvolution of the spectra for $(Mo_6Br_8)Br_4$ and $(Mo_6I_8)I_4$ gave two sets of spin-orbit doublets with the intensity ratio of the higher energy to the lower energy doublet being 2:1 in each case.[33] In view of this information, and the known structures of these halides,[26] it is clear that the higher energy doublet is assigned to the intracluster bridging halogen atoms and that the lower energy set arises from a *combination* of halogen atoms in intercluster bridging and terminal metal–halogen bonds.

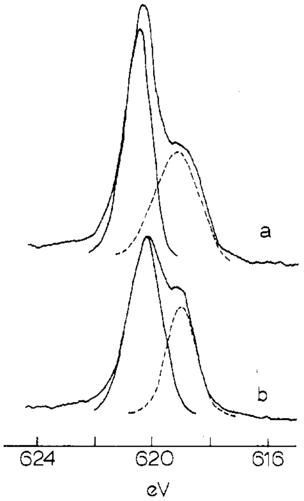

Figure 2. Iodine I $3d_{5/2}$ binding energy spectra of (a) $(Mo_6I_8)I_4$ and (b) $(Bu_4N)_2Mo_4I_{11}$ showing deconvolutions into I_b (—) and I_t (- - -) components.

The Cl 2p spectrum of the corresponding chloride cluster $(Mo_6Cl_8)Cl_4$ produced *three* distinct doublets upon deconvolution.[6] Intensity ratios of 4:1:1 were obtained,[6] thereby fitting the stoichiometric ratio expected for $(Mo_6Cl_8)Cl_{4/2}Cl_2$. The highest energy Cl $2p_{3/2}$ peak at 200.5 eV was assigned[24] to the intracluster bridging chlorines (Cl_b). The Cl $2p_{3/2}$ peak at 198.5 eV was assigned[24] to the intercluster bridging sites ($Cl_{b'}$), and a Cl $2p_{3/2}$ peak at 198.0 eV was assigned[24] to the terminally bound chlorines (Cl_t). From this and other studies[2] on metal–metal bonded clusters and dimers which contain both terminal and bridging metal–chlorine bonds, the Cl 2p binding energy order is $Cl_b > Cl_{b'} > Cl_t$. In contrast, the corresponding binding energy order for $(Mo_6Br_8)Br_4$ and $(Mo_6I_8)I_4$ is $X_b > X_{b'} \approx X_t$.

The spread of halogen binding energies (i.e., $\Delta E(X_b - X_t)$) within the series $(Mo_6X_8)X_4$ is seen to decrease in the order Cl (2.5 eV) > Br (2.1 eV) > I (1.3 eV). This trend may be a direct reflection of the corresponding decreasing charge to radius ratio of the halogens. This leads to a decreasing sensitivity of the charge residing on the larger halogen atoms to the nature of their binding to a metal ion (i.e., X_b, $X_{b'}$, or X_t). Similar effects have been noted for the trimeric rhenium complexes $Re_3X_9(pyz)_3$ and $(Re_3X_6L_3)_n$, where X = Cl or Br, pyz = pyrazine, and L = pyridine or γ-picoline. The chloride

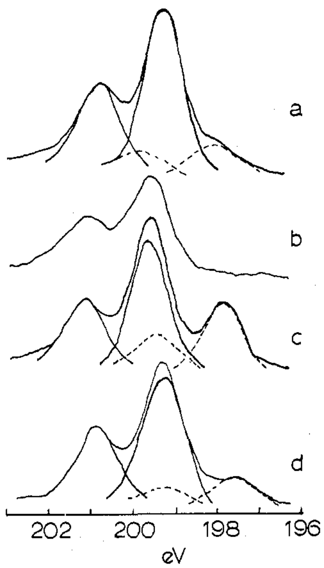

Figure 3. Chlorine Cl $2p_{1/2,3/2}$ binding energy spectra of (a) $(Nb_6Cl_{12})Cl_2(H_2O)_4{\cdot}4H_2O$, (b) $(Bu_4N)_2[(Nb_6Cl_{12})Br_6]$, (c) $(Et_4N)_3[(Nb_6Cl_{12})Cl_6]$, and (d) $(Nb_6Cl_{12})Cl_2(PPr^n{}_3)_2$ showing deconvolutions into Cl_b (—) and Cl_t (- - -) components.

derivatives of rhenium show clearly resolved bridging and terminal peaks, with an energy difference $\Delta E(Cl_b\text{–}Cl_t)$ of between 1.1 and 1.4 eV.[4,11] In contrast, the bromide systems do not show two sets of well-separated binding energies associated with Br_b and Br_t.[11] While the Br 3p peaks of $Re_3Br_9(pyz)_3$ and $(Re_3Br_6L_3)_n$ are significantly broader than those exhibited by complexes which contain only a single type of bromine environment, there is insufficient difference to justify their deconvolution into bridging and terminal components.

To aid in the full interpretation of the Br 3p spectrum of $(Mo_6Br_8)Br_4$, this molecule was reacted with Et_4NCl and Et_4NBr to afford the salts $(Et_4N)_2[(Mo_6Br_8)X_6]$, and several derivatives of the type $(Mo_6Br_8)Br_4L_2$ were also prepared. With $(Et_4N)_2[(Mo_6Br_8)Cl_6]$, all terminal and intercluster bridging bromine atoms have been replaced by terminal Mo–Cl bonds, and only the intracluster bridging bromines remain intact. Figure 1 shows the resultant Br 3p spectrum which is obtained. The full width at half maximum (fwhm) of the $3p_{3/2}$ peak of $(Et_4N)_2[(Mo_6Br_8)Cl_6]$ is similar to that used in the deconvolution of the bromine 3p spectrum of $(Mo_6Br_8)Br_4$. The intensity ratios $(Br_b{:}Br_t)$ of the Br 3p peaks of $(Et_4N)_2[(Mo_6Br_8)Br_6]$ and $(Mo_6Br_8)Br_4L_2$ (Table I) were very close to the expected stoichiometric ratios of 4:3 and 2:1, respectively.

$(Bu_4N)_2Mo_4I_{11}$ possesses an I 3d spectrum in which the two sets of doublets (Table I) have energies corresponding to I_b and I_t environments. Deconvolution of this spectrum shows that the $I_b{:}I_t$ intensity ratio is 7:4, which is in excellent agreement with the known structure of this complex.[28] Although two different types of *bridging* iodide environments are present (doubly and triply bridging),[28] we were unable to resolve them by XPS.

(c) Niobium and Tantalum Chloride Clusters. The general features of the chlorine XPS of these octahedral clusters (Table II and Figure 3) resemble closely the related spectra of $(Mo_6Cl_8)Cl_4$ and its derivatives.[6] The three-peak Cl 2p spectra (Figure 3) which are obtained for all the complexes listed in Table II, with the exception of the mixed halides $(Bu_4N)_2[(M_6Cl_{12})Br_6]$, where M = Nb or Ta, are readily deconvoluted via the usual procedure[6] to produce the two sets of Cl $2p_{1/2,3/2}$ doublets. In all instances, the intensity ratios of the two doublets (Figure 3) were very close to the expected stoichiometric ratios for the different chlorine environments, i.e., $Cl_b{:}Cl_t$ = 6:1 for $(M_6Cl_{12})Cl_2L_4$ and 2:1 for $[(M_6Cl_{12})Cl_6]^{n-}$. The absence of binding energies associated with Cl_t environments in the XPS of $(M_6Cl_{12})Br_6{}^{2-}$ confirms our structural formulation for these complexes.

A comparison of the XPS data for the salts containing the $[(Nb_6Cl_{12})Cl_6]^{3-}$, $[(Nb_6Cl_{12})Br_6]^{2-}$, $[(Ta_6Cl_{12})Cl_6]^{2-}$, and $[(Ta_6Cl_{12})Br_6]^{2-}$ anions with that for derivatives of the type $(M_6Cl_{12})Cl_2L_4$, where L represents a neutral ligand molecule (see Table II), shows no discernible variation in the metal core electron binding energies with change in the metal oxidation state. This result is in accord with our previous observation[5] that small variations in charge associated with metal halide clusters are not reflected by any significant changes in the metal binding energies because these charge variations are delocalized over several metal atom centers.

Field and Kepert[18] have reported that upon reacting $(Nb_6Cl_{12})Cl_2(H_2O)_4{\cdot}4H_2O$ with various oxygen-containing ligands, compounds of the type $(Nb_6Cl_{12})Cl_2L_4$, where L = dimethyl sulfoxide (Me_2SO), dimethylformamide (DMF), triphenylphosphine oxide, and pyridine *N*-oxide, are formed. The product of the reaction of $(Nb_6Cl_{12})Cl_2(H_2O)_4{\cdot}4H_2O$ with tri-*n*-propylphosphine is believed to be the first reported *neutral* complex of this cluster without an oxygen-containing ligand. Its chlorine 2p spectrum (Table II and Figure 3) is virtually the same as that obtained for the Me_2SO adduct. Since the $Cl_b{:}Cl_t$ intensity ratio is ~6:1, it is clear that this molecule has the same structural characteristics as the oxygen-containing ligand adducts reported by Fields and Kepert.[18]

The binding energy difference $\Delta E(Cl_b\text{–}Cl_t)$ for the complexes listed in Table II spans the range 1.4–2.1 eV, the lowest values (1.4 and 1.5 eV) being characteristic of the hydrates $(M_6Cl_{12})Cl_2(H_2O)_4{\cdot}4H_2O$. Whether these differences are reflected by variations in the $M\text{–}Cl_b$ and $M\text{–}Cl_t$ bond lengths of these clusters remains to be seen. Present structural data are insufficient to draw any such conclusions. $\Delta E(Cl_b\text{–}Cl_t)$ values for Re_3Cl_9 and its derivatives (~1.4 eV)[6] and for $(Mo_6Cl_8)Cl_4$ and its derivatives (2.1–2.4 eV)[6] reveal much smaller variations within these two groups of complexes.

(d) Concluding Remarks. The XPS of the molybdenum bromide and iodide clusters $(Mo_6X_8)X_4$ and their derivatives and of $(Bu_4N)_2Mo_4I_{11}$ constitute the first examples of the successful use of this technique to distinguish different bromine and iodine environments in metal halides and their complexes. The Br 3p data for $(Mo_6Br_8)Br_4$, when taken in conjunction with some recent XPS results we have obtained[9] on the bromide complexes $[RhBr_2(LL)_2]Br$, where LL = 1,2-bis(diphenylphosphino)ethane or 1,2-bis(diphenylarsino)ethane, show that a Br 3p chemical shift of ~3.5 eV is possible between Br_b and Br^-. This is only ~0.5 eV less than the corresponding maximum value of the Cl 2p chemical shift associated with transition-metal chlorides.[6,7]

The XPS of the phases β-$MoBr_2$ and β-MoI_2, which unlike $(Mo_6X_8)X_4$ are believed to contain a dimeric $[Mo_2X_4]$ unit,[34,35] reveal the presence of one Br $3p_{1/2,3/2}$ and one I $3d_{3/2,5/2}$ doublet,[36] thereby supporting our structural conclusions. This is in keeping with similar differences which exist[6] between the XPS of α-$MoCl_2$ (i.e., $(Mo_6Cl_8)Cl_4$) and β-$MoCl_2$ (i.e., $[Mo_2Cl_4]_n$).

The Cl 2p binding-energy spectra of $(M_6Cl_{12})Cl_2L_4$, where M = Nb or Ta, provide further proof of the usefulness of the XPS technique in the structural characterization of transition-metal chlorides.[2]

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Registry No. $(Mo_6Br_8)Br_4$, 12234-30-9; $(Et_4N)_2[(Mo_6Br_8)Br_6]$, 12365-73-0; $(Et_4N)_2[(Mo_6Br_8)Cl_6]$, 12365-71-8; $(Mo_6Br_8)Br_4(py)_2$, 62185-92-6; $(Mo_6Br_8)Br_4(PPr_3\text{-}n)_2$, 62185-93-7; $(Mo_6Br_8)Br_4(PBu_3\text{-}n)_2$, 68813-07-0; $(Mo_6Br_8)Br_4$(dppe), 68757-62-0; $(Mo_6I_8)I_4$, 12175-58-5; $(Bu_4N)_2Mo_4I_{11}$, 68024-65-7; $(Nb_6Cl_{12})Cl_2(H_2O)_4\cdot 4H_2O$, 12766-39-1; $(Et_4N)_3[(Nb_6Cl_{12})Cl_6]$, 12128-45-9; $(Bu_4N)_2[(Nb_6Cl_{12})Br_6]$, 68867-04-9; $(Nb_6Cl_{12})Cl_2(PPr_3\text{-}n)_4$, 68813-06-9; $(Nb_6Cl_{12})Cl_2(Me_2SO)_4$, 12335-06-7; $(Ta_6Cl_{12})Cl_2(H_2O)_4\cdot 4H_2O$, 51269-64-8; $(Et_4N)_2[(Ta_6Cl_{12})Cl_6]$, 12556-09-1; $(Bu_4N)_2[(Ta_6Cl_{12})Br_6]$, 68758-52-1.

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Electrical and Optical Properties of the System $TiO_{2-x}F_x$

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A convenient method for preparing compounds in the system $TiO_{2-x}F_x$ has been developed. The electronic and photoelectric properties of samples prepared accordingly have been studied. The fluorine content was found to be an essentially linear function of the reaction temperature over the range 575–700 °C. The saturation photocurrent increased with decreasing fluorine content, because of increased response at the longer wavelengths. This improved response may be attributed to the increase in depletion-layer width arising from the observed increase in resistivity. A significantly larger saturation photocurrent was obtained from samples of $TiO_{2-x}F_x$ than from comparable samples of TiO_{2-x} under the same conditions. The increased output may be attributed to a decrease in the recombination rate brought about by the filling of oxygen vacancies. The long-term stability was studied, and a sample of $TiO_{2-x}F_x$ was found to be at least as stable, in a suitable electrolyte, as comparable TiO_{2-x}.

Introduction

In most of the previous studies dealing with oxides which have served as n-type electrodes, increased conductivity was achieved by the production of oxygen deficiencies. Whereas earlier publications on n-type anodes such as TiO_{2-x} indicated that they were stable, there has been recent evidence[1] that these compounds do not show long-term stability in the presence of the production of oxygen at their surfaces. An alternate method of producing conducting electrodes is by the chemical substitution of fluorine for oxygen, rather than the creation of oxygen vacancies. Both methods result in the formation of $3d^1$ titanium, which would account for the relatively high conductivity obtained.

In a recent publication, Derrington et al.[2] reported on the photoelectrolytic behavior of $WO_{3-x}F_x$. It was found that the substitution of fluorine for oxygen in WO_3 did not adversely affect the photoelectric properties of WO_3 but increased the stability of the compound when used as a photoanode. One might expect members of the system $TiO_{2-x}F_x$ also to show increased stability over TiO_{2-x}, since all of the anion sites would be occupied. It is the purpose of this study to prepare members of the series $TiO_{2-x}F_x$ and to determine their photocurrents and stability as photoanodes in photoelectrolysis cells.

Sample Preparation

Wafers 1 mm thick were sliced from a single-crystal boule obtained from National Lead Industries, South Amboy, N.J., using a water-cooled diamond saw. Each wafer was sandblasted in order to produce homogeneous surfaces, cleaned in an ultrasonic bath, and then wrapped in a piece of platinum gauze. The gauze and wafer were inserted into a sleeve made from 0.005 in. thick titanium foil

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