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# X-ray Photoelectron Spectra of Inorganic Molecules. XVII [1, 2]. Differences in the Binding Energies of Bromine Atoms in Bridging and Terminal Metal–Bromine Bonds of the Molybdenum(II) Bromide Cluster

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We have recently established [3, 4] that for metal–metal bonded clusters and dimers which contain both terminal ($Cl_t$) and bridging ($Cl_b$) metal–chlorine bonds, the Cl 2p binding energy order is $Cl_b < Cl_t$. The magnitudes of the separations between the binding energies associated with $Cl_b$ and $Cl_t$ are as follows: ~1.4eV for $Re_3Cl_9$ and its derivatives [3], ~2.3eV for $(Mo_6Cl_8)Cl_4$ and its derivatives [3], and between 0.5 and 1.2eV for chloro-anions of the type $M_2Cl_9^{n-}$, where M = Cr(III), Mo(III), W(III), and Re(IV) [4]. The increase in this energy separation on going from $Re_3Cl_9$ to $(Mo_6Cl_8)Cl_4$ has been attributed to an increase in the coordination number of the *bridging* chlorines (from two to three) [3]. In an extension of these studies to include the F 1s and Br 3p binding energies of certain metal fluorides [5] and bromides [6], the related binding energy differences $\Delta E(F_b - F_t)$ and $\Delta E(Br_b - Br_t)$ were found to be rather small. Accordingly, it appeared that the XPS technique would be much less useful as a structure probe for such phases. However, recent measurements on the Br 3p binding energies of derivatives of molybdenum(II) bromide $(Mo_6Br_8)Br_4$ indicate that different bromine environments in metal bromide clusters may be readily differentiated. We now report preliminary details of these results.

The Mo 3d and Br 3p binding energies of the complexes were recorded using a Hewlett–Packard 5950A ESCA spectrometer with aluminum $K_{\alpha 1,2}$ radiation (1486.6eV). Our experimental procedure has been described fully elsewhere [3]. The appropriate data are presented in Table I and representative Br 3p spectra shown in Figure 1. The Mo 3d binding energies occur in a range which is characteristic of molybdenum(II) halides and their complexes [7]. Bromine 3p binding energies were obtained by deconvolution of the spectra using the same procedures we have described previously [3]. The relative intensities of the Br 3p peaks whose energies are listed in Table I, are in accord with the binding energy order $Br_b > Br_t$. For $(Et_4N)_2[(Mo_6Br_8)Br_6]$, the $Br_b:Br_t$ intensity ratio is almost exactly 4:3, which is in excellent agreement with the stoichiometric ratio of $Br_b$ to $Br_t$. For $(Mo_6Br_8)Br_4$, $(Mo_6Br_8)Br_4(py)_2$ and $(Mo_6Br_8)Br_4(PPr^n_3)_2$ the $Br_b:Br_t$ intensity ratio increases to 2:1 as the number of terminal Mo–Br bonds decreases to four.

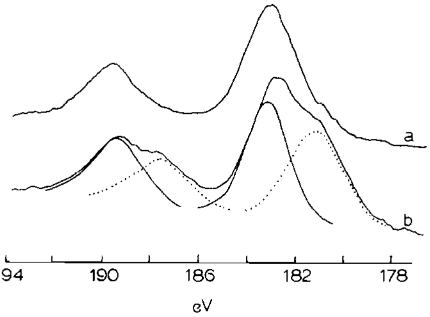

Figure 1. Bromine 3p binding energy spectra of (a) $(Et_4N)_2[(Mo_6Br_8)Cl_6]$ and (b) $(Et_4N)_2[(Mo_6Br_8)Br_6]$.

Our binding energy assignments have been confirmed by recording the Br 3p spectrum of $(Et_4N)_2[(Mo_6Br_8)Cl_6]$ (see Table I and Figure 1). In

TABLE I. X-ray Photoelectron Spectra of Molybdenum(II) Bromide and its Complexes.[a]

| Complex | Mo | | $Br_b$ | | $Br_t$ | |
|---|---|---|---|---|---|---|
| | $3d_{3/2}$ | $3d_{5/2}$ | $3p_{1/2}$ | $3p_{3/2}$ | $3p_{1/2}$ | $3p_{3/2}$ |
| $(Mo_6Br_8)Br_4$ | 231.5 | 228.5(1.0) | 189.4 | 182.9(2.5) | 187.5 | 180.8(2.5) |
| $(Et_4N)_2[(Mo_6Br_8)Br_6]$ | 231.6 | 228.5(1.2) | 189.5 | 183.1(2.1) | ~187.6 | 181.1(2.5) |
| $(Et_4N)_2[(Mo_6Br_8)Cl_6]^b$ | 231.5 | 228.4(1.5) | 189.5 | 183.0(2.4) | – | – |
| $(Mo_6Br_8)Br_4(py)_2$ | 232.0 | 228.9(1.1) | 189.7 | 183.2(2.2) | ~187.6 | 180.8(2.1) |
| $(Mo_6Br_8)Br_4(PPr^n_3)_2$ | 231.6 | 228.5(1.1) | 189.4 | 182.8(2.1) | 187.4 | 180.7(2.1) |

[a] Binding energies (in eV) are quoted relative to a carbon 1s value of 284.0eV for graphite and are considered accurate to at least ±0.2eV; fwhm values given in parentheses. [b] Cl $2p_{1/2,3/2}$ binding energies at 198.8 and 197.4eV.

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this case, the lower energy Br $3p_{1/2,3/2}$ spin–orbit doublet was absent, in keeping with the replacement of bromine in the terminal Mo–Br bonds by chlorine.

These results contrast with those reported previously [6] for the Br 3p binding energy spectra of $Re_3Br_9(pyz)_3$ and $[Re_3Br_6L_3]_n$, where pyz = pyrazine and L = pyridine, γ-picoline, 3-chloropyridine or benzimidazole. These systems do not show two sets of well separated binding energies associated with $Br_b$ and $Br_t$. While these peaks are significantly broader than those exhibited by complexes which contain only a single type of bromine environment, the binding energy differences are clearly much less than those observed for $(Mo_6Br_8)Br_4$ and its derivatives.

Studies on these and related systems are continuing and will be reported in full at a later date.

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