Supplementary Material Available: Tables of positional and thermal parameters and bond distances and angles of the structure of **5** (6 pages). Ordering information is given on any current masthead page.

Intermolecular Influences on M–M Multiple Bonds from Thin-Film UPS Studies of Group VI $M_2(O_2CCH_3)_4$ Complexes

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Dimetal tetracarboxylate complexes have provided a rich arena for study of metal–metal bonding since the presence of σ-, π-, and δ-orbital symmetry interactions was first explained in 1964.[1] The title compounds have proven particularly fruitful for investigating these interactions because the volatility of these compounds makes them suitable for gas-phase photoelectron studies, thus allowing detailed experimental examination of the theoretical principles of bonding.[2-10] Development of the basic bonding description for these complexes has been accompanied by numerous studies of the effects of bridging ligands and axial interactions on the metal–metal bond strength and bond length. The Cr–Cr bond length is especially sensitive to the bridging ligand type and axial interactions.[11] The importance of axial interactions is illustrated by comparison of the hydrous and anhydrous single-crystal[12] structures of $Cr_2(O_2CCH_3)_4$ and by a further comparison of these structures to the recent gas-phase electron diffraction results of Fink and Ketkar.[13] These structures yield Cr–Cr bond lengths of 2.362 (1), 2.288 (2), and 1.966 (14) Å, respectively. In contrast, the Mo_2^{4+} and W_2^{4+} cores show minimal change in metal–metal bond length despite the use of a wide variety of bridging and axial ligands.[14,15] As one step to examining the electronic effects of axial occupation on the metal–metal bond, we have obtained the

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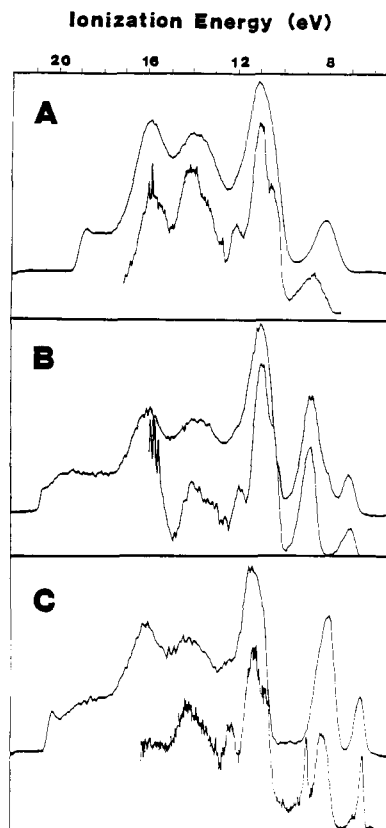
Ionization Energy (eV)

Figure 1. Valence He I photoelectron spectra of $M_2(O_2CCH_3)_4$ for (A) M = chromium, (B) M = molybdenum, and (C) M = tungsten. In each case the top spectrum is from the thin film and the bottom spectrum is from the gas phase.
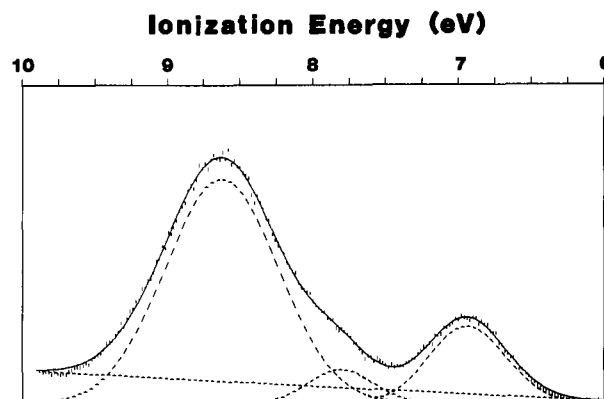
Ionization Energy (eV)

Figure 2. Close-up He I spectra of the $Mo_2(O_2CCH_3)_4$ metal ionization region for the thin film. The vertical lines indicate experimental data. The solid line is the sum of three asymmetric Gaussian peaks, shown as dashed lines.

photoelectron spectra of thin films of anhydrous group VI tetraacetates. In these thin films the axial positions of the metal–metal bonds are occupied by neighboring molecules. With appropriate preparation[16] of these films in ultrahigh vacuum conditions, we are able to obtain spectra which exhibit only slight broadening as compared to the gas-phase spectra, indicating that each molecule contributing to the observation is in a similar electronic environment. The axial positions of the metal–metal
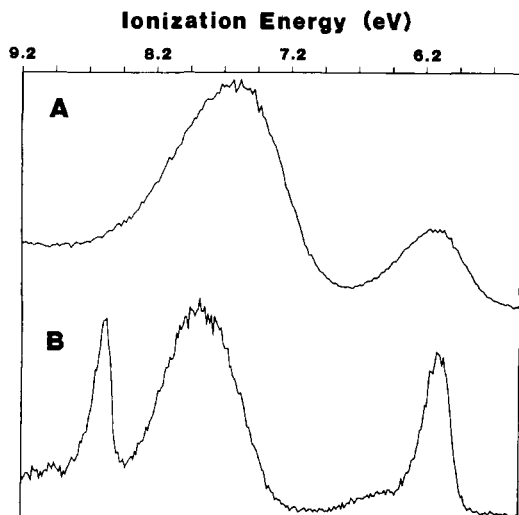
Ionization Energy (eV)

Figure 3. Close-up He I spectrum of the $W_2(O_2CCH_3)_4$ metal ionization region from thin-film (A) and gas-phase (B) experiments.

bonds are most likely occupied by the oxygen atoms of the neighboring complexes, as found in the single-crystal structures.

Valence ionizations of these complexes in the gas phase[6] and in thin films are shown in Figure 1. The general features of the gas-phase and thin-film spectra are seen to correlate closely. In the case of the molybdenum complex (Figure 1B), all of the major ionization features in the gas-phase spectrum are also observed in the thin-film spectrum with no significant relative ionization energy shifts (<0.1 eV).[17] Assignment of the leading ionization band to the δ and the second ionization band to the π (and perhaps the σ[18]) carries over to the solid from the gas-phase data. We do, however, observe a shoulder at $\approx$7.8 eV on the low binding energy side of the π band (Figure 2). This shoulder was reproduced for a variety of experimental conditions with this complex, and it was also observed for the formate analogue, $Mo_2(O_2CH)_4$. Comparison with the results of the W_2 study (vida infra) indicates that this shoulder corresponds to the σ ionization, which is destabilized from the π-ionization band by axial interactions in the thin film.

The analogous chromium compound (Figure 1A) also provides a close correlation of spectral features between the gas and thin-film spectra.[5] The leading ionization band in the gas-phase spectrum (8–9 eV) reveals broad overlapping ionization features assignable to predominantly metal orbitals.[19] This ionization band is shifted approximately 0.5 eV to lower energy relative to predominantly acetate ionizations in going to the thin film. The sensitivity of the energy of the leading ionization band of the chromium complex parallels the observed sensitivity of the chromium–chromium bond length to its environment, in particular to axial interactions.[11] The higher relative binding energy for this band in the gas-phase spectrum provides support for the shortened metal–metal distance found in the recent gas-phase electron diffraction structure.[13]

Comparison of the tungsten spectra in the gas phase and the thin film (Figure 1C) also reveals a one-to-one correspondence of ionization envelopes except for the sharp σ ionization at 8.56 eV in the gas-phase spectrum (Figure 3B).[9] The σ ionization is not independently observed in the thin-film spectrum. The increase in the intensity of the π-ionization region ($\sim$8 eV) relative to the δ-ionization region ($\sim$6 eV) in the thin film ($\sim$5:1) com-

pared to the gas phase ($\sim$3:1) indicates that the σ ionization has shifted into the π-ionization band region. This observation is consistent with the disappearance of the sharp σ ionization with axial alkylation[15] and is understandable since the σ ionization would be expected to be more affected by axial interactions. This shift is also consistent with that proposed for the σ ionization of the molybdenum complex, indicating that these spectra have provided the first observation of the σ ionization in the region of the π ionization for a quadruply bonded Mo_2 dimer.

Heterogeneous Sonocatalysis with Nickel Powder

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We have discovered that ultrasonic irradiation of Ni powder increases its activity as a hydrogenation catalyst by >10^5. In order to probe the origin of this dramatic enhancement, the surface composition has been examined. We find that ultrasonic irradiation of Ni powder causes remarkable changes in particle aggregation, surface morphology, and thickness of the surface oxide coating.

The use of high-intensity ultrasound to initiate or enhance both homogeneous and heterogeneous chemical reactions has been under intense investigation,[1–7] and a detailed understanding of the mechanism of *homogeneous* sonochemistry has recently been developed.[8] Our knowledge about the reaction conditions created

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