

## The Photoelectron Spectrum of Quadruply Bonded $W_2(O_2CCF_3)_4$

G. Michael Bancroft,<sup>a\*</sup> Emmanuel Pellach,<sup>a</sup> Alfred P. Sattelberger,<sup>b\*</sup> and Kevin W. McLaughlin<sup>b</sup>

<sup>a</sup> Department of Chemistry, University of Western Ontario, London, Ontario N6A 5B7, Canada

<sup>b</sup> Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109, U.S.A.

We have resolved photoelectron peaks from the ionization of all three metal–metal molecular orbitals [ $b_{2g}(\delta)$ ,  $e_u(\pi)$ , and  $a_{1g}(\sigma)$ ] that form the metal–metal quadruple bond in  $W_2(O_2CCF_3)_4$ .

There has been considerable recent debate about the bonding descriptions and photoelectron assignments for Cr, Mo, and W compounds containing quadruple metal–metal bonds.<sup>1–13</sup> In the dimolybdenum and ditungsten complexes, the photoelectron spectra and M.O. calculations are consistent with the low binding energy peak (labelled A as in ref. 4) being assigned to the  $2b_{2g}(\delta)$  molecular orbital; the assignment of the second band is in dispute, however.<sup>4,6,7</sup> In the dimolybdenum carboxylates, the SCF X $\alpha$ –SW results<sup>8,9</sup> assign band B to the  $6e_u(\pi)$  orbital, whereas the *ab initio* calculations<sup>10–13</sup> suggest that band B be assigned to both the  $6e_u(\pi)$  and the  $5a_{1g}(\sigma)$  orbitals. In the  $M_2(mhp)_4$  ( $M = Mo, W$ ;  $mhp$  = anion of 2-hydroxy-6-methylpyridine) complexes, the interpretation of band B is further complicated by overlap of ligand orbitals.<sup>6</sup> The assignment problems are even more difficult for the dichromium compounds. The calculations<sup>3,9–13</sup> indicate that the  $\delta, \pi$ , and  $\sigma$  orbitals are much closer in energy in the chromium than in the molybdenum compounds, and the spectra are most readily interpreted on the basis of a configuration interaction wavefunction with the quadruply bonding configuration  $\sigma^2\pi^4\delta^2$  as the leading term contributing to the first band (A).

Because of the increase in metal–metal orbital energy spread from Cr to Mo compounds, we felt that the spectrum of a ditungsten dicarboxylate might lead to resolution of the three peaks in the photoelectron spectra. The recent synthesis of the first such ditungsten compounds,  $W_2(O_2CCF_3)_4$  [designated  $W_2(tfa)_4$ ] with a very long W–W bond length of 2.21 Å† provided an excellent compound for a photoelectron study.

Both  $Mo_2(tfa)_4$  and the air-sensitive  $W_2(tfa)_4$  were doubly sublimed *in vacuo*, handled in an  $N_2$  glove box, and transferred in our vacuum lock to the photoelectron spectrometer under  $N_2$ . He I and He II spectra of both compounds were obtained using our hollow cathode lamp<sup>15</sup> and heated inlet system<sup>16</sup> at

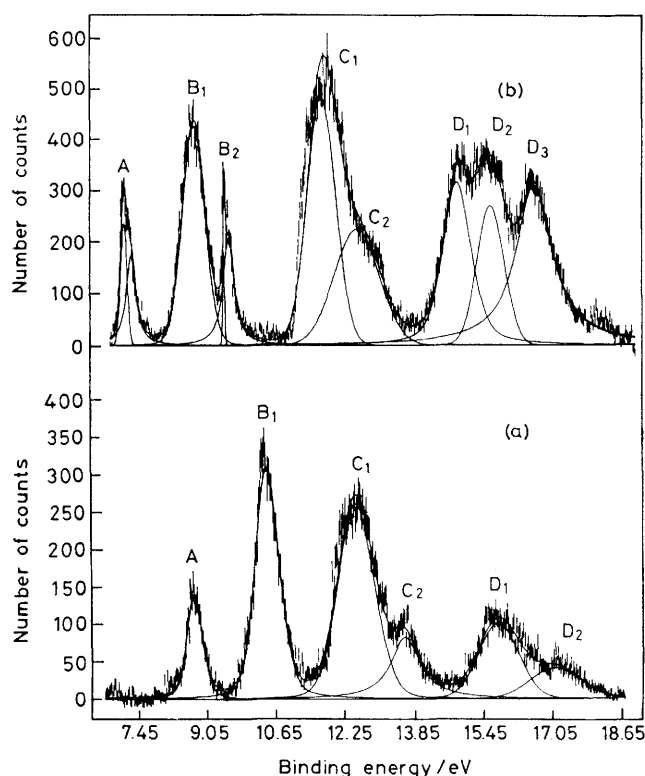


Figure 1. He I photoelectron spectra of (a)  $Mo_2(tfa)_4$  and (b)  $W_2(tfa)_4$ . The spectra have been computer-fitted to combination Lorentzian–Gaussian peaks. Bands A and B<sub>2</sub> in  $W_2(tfa)_4$  have been fitted to two peaks to obtain a reasonable fit to the data.

† Compared with the Mo–Mo bond length of 2.09 Å in the  $Mo_2(tfa)_4$  analogue (F. A. Cotton and J. G. Norman, *J. Coord. Chem.*, 1971, 1, 161) and the W–W bond length of 2.16 Å in  $W_2(mhp)_4$  (ref. 6).

probe temperatures between 140 and 180 °C. The spectra did not change between these temperatures, and the He I instrument resolution was always better than 30 meV. He I and He II spectra of the ligand,  $CF_3CO_2H$ , were also recorded.

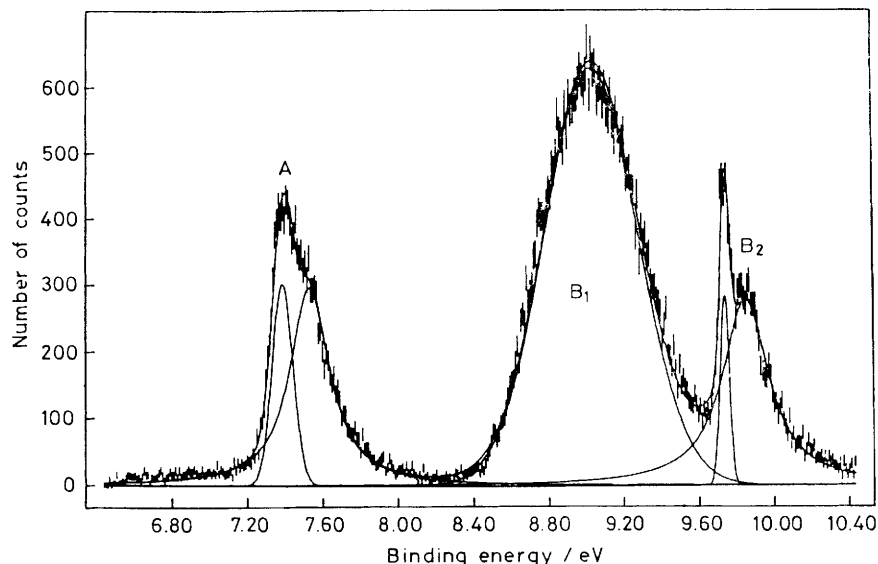


Figure 2. High resolution He I spectrum of the low binding energy region in  $W_2(tfa)_4$ .

Table 1. Ionization energies (eV) for  $M_2(tfa)_4$  complexes.<sup>a</sup>

Band	$Mo_2(tfa)_4$ <sup>b</sup>	$W_2(tfa)_4$
A	8.76	7.39
B <sub>1</sub>	10.46	9.01
B <sub>2</sub>		9.71
		9.81
C <sub>1</sub>	12.51	11.96
C <sub>2</sub>	13.63	12.75
D <sub>1</sub>	15.78	15.07
D <sub>2</sub>	17.09	15.82
D <sub>3</sub>		16.83

<sup>a</sup> Calibrated relative to the Ar 3p<sub>3/2</sub> line at 15.759 eV. <sup>b</sup> These values are within 0.1 eV of those reported earlier (refs. 1, 2, 4).

The He I spectra of the two quadruply bonded compounds are shown in Figures 1 and 2, and the ionization or binding energies are given in Table 1. The spectra of  $Mo_2(tfa)_4$  and  $tfa$  are in good agreement with those published previously,<sup>1,2,4</sup> and peaks A and B<sub>1</sub> lie well below the lowest lying ligand orbital at 12.1 eV. It is important to note that peak B<sub>1</sub> in  $Mo_2(tfa)_4$  shows no signs of asymmetry as reported earlier, and that the separation of these two peaks is *ca.* 1.7 eV, as it is for all the Mo-carboxylate complexes.<sup>4</sup> However, the spectrum of  $W_2(tfa)_4$  shows three distinct bands (A, B<sub>1</sub>, and B<sub>2</sub>) at considerably lower binding energies than in the Mo analogue, and with a spread of 2.4 eV. These bands can be assigned to ionizations from the three component M.O.s of the quadruple bond: band A to  $b_{2g}(\delta)$ , band B<sub>1</sub> to  $e_u(\pi)$ , and band B<sub>2</sub> to  $a_{1g}(\sigma)$ . The area ratios A : B<sub>1</sub> : B<sub>2</sub> of 1 : 2.3 : 1 are rather close to 1 : 2 : 1 based on the degeneracies of the molecular orbitals, and compare with the A : B<sub>1</sub> area ratio in  $Mo_2(tfa)_4$  of 1 : 3.2.<sup>‡</sup> The decrease in binding energy from Mo to W is expected,<sup>6,17</sup> but the decrease is substantially greater than that between

$Mo_2(mhp)_4$  and  $W_2(mhp)_4$ .<sup>6</sup> The intensity changes between the He I and He II spectra of  $W_2(tfa)_4$  are consistent with those seen<sup>4</sup> for  $Mo_2(tfa)_4$ : bands B<sub>1</sub> and B<sub>2</sub> decrease in intensity relative to C and A.

The higher resolution spectrum of  $W_2(tfa)_4$  (Figure 2) reveals more clearly some interesting additional features not present in the  $Mo_2(tfa)_4$  spectrum. Band A is markedly asymmetric, and band B<sub>2</sub> shows a distinct splitting of 0.1 eV (*ca.* 800 cm<sup>-1</sup>). Both features are probably vibrational in origin, with the W-W stretching vibration at 313 cm<sup>-1</sup>, and the vibrational modes at 746 cm<sup>-1</sup> and 874 cm<sup>-1</sup><sup>14</sup> being probably the most important contributors to bands A and B<sub>2</sub>, respectively. Another possible origin could be configuration interaction in the ground state leading, for example, to two  $\delta$  configurations.<sup>18</sup>

It might be tempting to assign B<sub>1</sub> and B<sub>2</sub> to the spin-orbit components of the <sup>2</sup>E state of  $W_2(tfa)_4^+$ , but the splitting of *ca.* 0.75 eV between B<sub>1</sub> and B<sub>2</sub> is larger than the 0.3–0.6 eV splitting expected from the spin-orbit interaction.<sup>6</sup> Also, it is unlikely, even taking 0.75 eV as an acceptable spin-orbit splitting, that the photoionization cross-sections, widths, and structure of the two levels would be so different.

Since the molecular orbital calculations show that the  $\delta$ - $\pi$ - $\sigma$  orbital energy spread does not increase dramatically (*e.g.* by a factor of two) from W to Mo analogues, our  $W_2(tfa)_4$  spectra support the interpretation of the dimolybdenum spectra from *ab initio* calculations; band B is assigned to an overlap of the  $6e_u(\pi)$  and  $5a_{1g}(\sigma)$  orbital ionizations.

After submission of this note, we read the paper by Cotton *et al.*<sup>19</sup> which reports the photoelectron spectra of  $Mo_2Cl_4(PMe_3)_4$  and  $W_2Cl_4(PMe_3)_4$ . They also observe three low energy bands in the  $W_2Cl_4(PMe_3)_4$  spectrum (at 5.81, 7.05, and 7.45 eV), but assign B<sub>1</sub> and B<sub>2</sub> to spin-orbit split components of the <sup>2</sup>E state. The B<sub>1</sub>-B<sub>2</sub> separation of 0.4 eV is within the expected range of W spin-orbit splitting, but the band areas are anomalous even considering mixing with the  $\delta$  and  $\sigma$  state. Taken together with our spectra of  $W_2(tfa)_4$ , it would seem more reasonable to assign the spectra of both  $Mo_2Cl_4(PMe_3)_4$  and  $W_2Cl_4(PMe_3)_4$  as we have done above for our carboxylate complexes.

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<sup>‡</sup> This intensity agreement does not constitute conclusive evidence, because the intensity ratios fluctuate considerably between Mo complexes, and between He I and He II spectra (ref. 4).

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