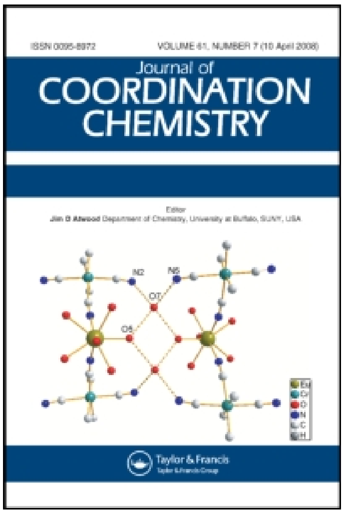

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# THE PREPARATION AND CRYSTAL STRUCTURE OF DIMOLYBDENUM TETRAFORMATE; PHOTOELECTRON SPECTRA OF THIS AND SEVERAL OTHER DIMOLYBDENUM TETRACARBOXYLATES

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# THE PREPARATION AND CRYSTAL STRUCTURE OF DIMOLYBDENUM TETRAFORMATE; PHOTOELECTRON SPECTRA OF THIS AND SEVERAL OTHER DIMOLYBDENUM TETRACARBOXYLATES

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The compound $Mo_2(O_2CH)_4$ is described in detail for the first time and its crystal structure is reported. Crystallographic parameters are: Space group: $P2_12_12_1$; $a = 12.288(4)$Å; $b = 12.930(5)$Å; $c = 5.500(1)$Å, and $Z = 4$. Using 952 reflections for which $I > 3\sigma(I)$ the structure has been solved and refined to $R_1 = 0.063$ and $R_2 = 0.071$. The molecule has virtual symmetry $D_{4h}$ and all comparable dimensions are virtually identical to those of $Mo_2(O_2CCH_3)_4$; for example, the Mo–Mo distance is 2.091(2)Å. The Raman spectrum has a band at 403 cm$^{-1}$ due mainly to Mo–Mo stretching. The photoelectron spectra of the $Mo_2(O_2CR)_4$ compounds with R = H, $CH_3$ and $CF_3$ are reported. The spectra are qualitatively similar and exhibit trends in accord with the relative electronegativities of the *R* groups, in harmony with the results of an earlier study which also included the formate and acetate.

## INTRODUCTION

Since the earliest reports[1] of the preparation of dimolybdenum tetracarboxylates, they have been the subjects of much study.[2,3] Although Wilkinson and coworkers pointed out the generality of this class of compounds, i.e., to the fact that in $Mo_2(O_2CR_4)$, R could apparently be any alkyl or aryl group, they did not prepare, or mention having made any attempt to prepare, the compound with R = H, that is, the formate. For certain purposes, such as theoretical treatment of the bonding or vibrational spectroscopy, the ultimate simplicity of the formate offers significant advantages. Thus, we were motivated to undertake the preparation of the formate and to so characterize it structurally as to be assured that it is truly representative of the general class, $Mo_2(O_2CR)_4$, to which it belongs.

During the time we were engaged in this work, the compound has been mentioned several times in the literature. Abbot and his coworkers[4] stated that $Mo_2(O_2CH)_4$ forms virtually instantaneously when 90% formic acid is added to a concentrated solution of $Mo_2(O_2S(O)CF_3)_4$ in anhydrous ethanol.[4a] They have also reported the mass spectrum,[4b] but have not otherwise described or characterized the compound in the literature. We have confirmed their procedure. Still more recently, the photoelectron spectrum of $Mo_2(O_2CH)_4$ was reported[5] without any indication of the source, or any description whatever of the properties of the compound. We have also been informed by E. H. Abbot[6] that the formate can be prepared directly from $Mo(CO)_6$ and formic acid in a manner similar to that used for the acetate.

In this paper we report a preparative procedure, the crystal structure and numerous other properties of dimolybdenum tetraformate, including a comparison of its structural and spectroscopic properties with those of the acetate and the trifluoroacetate.

## EXPERIMENTAL

### *Preparation*

Molybdenum(II) acetate[1,3] (0.80 g) was stirred in 100 ml formic acid under nitrogen while the mixture was heated to boiling, at which point all the acetate had dissolved. The solution was filtered under nitrogen and cooled at 10°C overnight, care being taken not to allow it to freeze (formic acid melts at 8°C).

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The yellow crystals were filtered in air and washed with absolute ethanol and ether. Two further crops were usually obtained by concentrating the filtrate *in vacuo* and cooling it. The compound thus obtained is quite pure, but may be recrystallized from hot formic acid under nitrogen or sublimed at 150°C/$10^{-3}$ torr. *Yield* of $Mo_2(O_2CH)_4$: 0.50 g, 72%.

*Anal.* Calcd for $C_4H_4Mo_2O_8$: C, 12.92; H, 1.08; Mo, 51.59. Found: C, 12.93; H, 1.06; Mo, 51.31. Elemental analyses were obtained from Spang Microanalytical Laboratory, Ann Arbor, Michigan.

Ir spectrum (fluorolube and Nujol mulls, 4000–350 $cm^{-1}$): 2970w, 2820w, 1630s, 1615s, 1360s, 1350s, 1325s, 1010w, 770s, 470s, 440s, 410m, 370m $cm^{-1}$.

The absence of residual acetate groups was conclusively shown by the mass spectrum in which there was no peak above m/e 380 ($^{100}Mo_2(O_2CH)_4{}^+$); the mass spectrum we have observed is in agreement with that reported by Hochberg, Walks and Abbot.[4b]

The Raman spectrum of the solid was recorded on a Cary Model 82 spectrometer using the 568.2 nm line of a krypton laser. Lines were observed with the following shifts in $cm^{-1}$ and the relative intensities given in parentheses: 84(31), 95(31), 132(100), 147(89), 195(92), 215(62), 293(12), 302(23), 333(7, sh), 350(62), 371(58), 393(15, sh) 406(90), 420(15), 782(15), 795(20), 1325 (v.v. strong, ≈1000).

Photoelectron spectra were recorded on a Perkin–Elmer Model PS-18 spectrometer.

The electronic spectrum was measured in 90% formic acid solution:

$\lambda_{max} = 438$ nm($\epsilon = 100 \pm 10$ $M^{-1}$ $cm^{-1}$);
$\lambda_{sh} = 330$ nm;
$\lambda_{max} = 291$ nm($\epsilon = 8000 \pm 500$ $M^{-1}$ $cm^{-1}$).

### *X-ray Data Collection*

$Mo_2(O_2CH)_4$ forms tabular crystals. Examination of numerous crystals from several different batches on a Syntex $P\bar{1}$ autodiffractometer showed that the crystals are generally poor in quality. Complete sets of intensity data were recorded on two different crystals. The first crystal, measuring approximately 0.50 x 0.13 x 0.02 mm and having omega scans with half-height peak widths from 0.25° to 0.30°, was mounted on a glass fiber with the long crystal direction tilted 30° from the diffractometer $\phi$ axis. Although the structure was solved and refined using this first data set, giving a result of the anticipated type, difficulties encountered in the structural solution, questionable aspects of the refinement and poor agreement in equivalent structural parameters, such as Mo–O distances ranging from 2.07Å to 2.17Å, prompted the collection of a second data set.[7] A second crystal measuring 0.268 x 0.076 x 0.018 nm was mounted on a glass fiber with the long crystal dimension only slightly tipped from the $\phi$ axis. Data collection and refinement results for the second crystal will be described in detail. Omega scans for several strong reflections showed this crystal to be of better quality than the first, having average half-height peak widths from 0.20° to 0.23°. The unit cell dimensions and orientation matrix for the orthorhombic cell were determined from least-squares refinement of the diffraction geometry of fifteen high-angle reflections, $17° < MoK\alpha < 30°$, giving $a = 12.288(4)$Å, $b = 12.930(5)$Å, $c = 5.500(1)$Å and $V = 872.9(5)$Å$^3$. The observed systematically absent reflections ($h00, h = 2n + 1$; $0k0, k = 2n + 1$; $00l, l = 2n + 1$) identified the space group as $P2_12_12_1$. For $Z = 4$ and a formula weight of 371.95, the calculated density of 2.82 $gcm^{-3}$ is in excellent agreement with the observed density of 2.83 ± 0.02 g $cm^{-3}$ measured by flotation in a $CCl_4/CHBr_3$ mixture.

Data were collected at 23° ± 2° using MoK$\alpha$ radiation filtered by a graphite-crystal monochromator. The $\theta$–$2\theta$ scan technique utilizing scan ranges from $MoK\alpha_1 - 1.0°$ to $MoK\alpha_2 + 1.1$ and scan rates from 2.0° to 24.0° per min. were used to collect the 933 unique data in the range $0° < 2\theta < 50.0°$. Scan rates from 1.0 to 24.0°/min were used to collect the 599 reflections in the range $50.0 < 2\theta < 60.4°$. In addition 100 Friedel pair reflections, $0° < 2\theta < 25.0°$, were collected. No significant change in the intensities of four standard reflections, measured every 150 reflections, were observed. Additional details of the data collection have been given previously.[8] In addition to corrections for Lorentz and polarization effects a numerical absorption correction was applied to all data. The absorption coefficient for MoK$\alpha$ radiation is 28.34 $cm^{-1}$. The calculated transmission coefficients range from 0.811 to 0.950 with the average being 0.915. A value of 0.05 was used for $p$ in the calculation of $\sigma(I)$.[8]

### *Structure Solution and Refinement*

The positions of the two independent molybdenum atoms were derived from an $E$ map utilizing the set of phases having the highest figures of merit from the direct methods program MULTAN.[9] The positions and isotropic thermal parameters for the two molybdenum atoms were subjected to two cycles of least-squares refinement. The following discrepancy indices were obtained.. $R_1 = \Sigma\,||F_o| - |F_c||/\Sigma\,|F_o| = 0.247$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w\,|F_o|^2)^{1/2} = 0.301$. In these and all subsequent cycles of least-squares refinement the scattering factors for the neutral atoms were those of Cromer and Waber.[10] Anomalous dispersion effects were included in the calculated structure factors for the molybdenum atoms.[11] The carbon and oxygen atoms were located from a difference Fourier synthesis. Refinement of the positional and isotropic thermal parameters gave $R_1 = 0.104$ and $R_2 = 0.123$. Two cycles of refinement utilizing anisotropic thermal parameters for all atoms resulted in $R_1 = 0.068$ and $R_2 = 0.079$ for the 952 reflections having $I > 3\sigma(I)$. At this stage of refinement a structure factor calculation for the Friedel pair data clearly indicated that that correct absolute configuration had been selected. To verify this a structure factor calculation for the other enantiomorph showed it to be incorrect. Attempts to locate the four hydrogen atoms in difference maps were unsuccessful; these atoms were therefore introduced at idealized positions during the final cycles of least-squares refinement as a fixed contribution and not refined. The structure was refined to convergence in two additional cycles of full-matrix least-squares refinement to give $R_1 = 0.063$ and $R_2 = 0.071$. During the final cycle of the refinement no parameter shifted by more than $0.3\sigma$, where $\sigma$ is the estimated standard deviation of that parameter.

A table of the observed and calculated structure factors is available upon request from F. A. Cotton, Texas A & M University.

## RESULTS

### *Preparation*

Evidently dimolybdenum tetraformate can be prepared in various ways. The simplest ones known are by direct reaction of $Mo(CO)_6$ with formic acid[4b] and by reaction of the tetraacetate with formic acid, as described here. Our method affords a good yield while requiring relatively little effort. It gives a product which appears to be quite pure even without recrystallization. The compound is obtained as small, pale yellow crystals which are stable to air for many weeks, although the solution in formic acid is rapidly attacked by air. The compound is not appreciably soluble in common nonpolar solvents, but it is slightly volatile.

TABLE I

Positional and thermal parameters and their estimated standard deviations for $Mo_2(O_2CH)_4$[a]

| Atom | $x$ | $y$ | $z$ | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Mo(1) | 0.4081(1) | 0.2752(1) | 0.3907(3) | 0.00364(8) | 0.00361(8) | 0.0081(3) | −0.0004(2) | −0.0015(3) | −0.0011(4) |
| Mo(2) | 0.3396(1) | 0.2132(1) | 0.0746(3) | 0.00365(8) | 0.00345(8) | 0.0077(3) | −0.0003(2) | −0.0010(4) | −0.0005(4) |
| O(1) | 0.290(1) | 0.394(1) | 0.411(3) | 0.0053(9) | 0.0043(9) | 0.017(4) | 0.000(2) | 0.003(4) | −0.005(4) |
| O(2) | 0.215(1) | 0.321(1) | 0.073(3) | 0.0042(9) | 0.0054(10) | 0.024(5) | −0.001(2) | −0.003(4) | −0.004(5) |
| O(3) | 0.308(1) | 0.178(1) | 0.606(2) | 0.0075(11) | 0.0054(9) | 0.004(3) | 0.001(2) | −0.003(4) | −0.003(3) |
| O(4) | 0.238(1) | 0.112(1) | 0.271(3) | 0.0045(9) | 0.0050(10) | 0.022(5) | −0.002(2) | 0.001(4) | 0.003(4) |
| O(5) | 0.535(1) | 0.166(1) | 0.394(3) | 0.0039(8) | 0.0050(9) | 0.013(4) | 0.002(2) | 0.001(4) | 0.006(4) |
| O(6) | 0.461(1) | 0.101(1) | 0.052(3) | 0.0059(10) | 0.0035(8) | 0.019(5) | 0.002(2) | 0.004(4) | −0.002(4) |
| O(7) | 0.512(1) | 0.377(1) | 0.195(3) | 0.0035(9) | 0.0048(10) | 0.019(5) | −0.001(2) | 0.005(4) | 0.003(4) |
| O(8) | 0.437(1) | 0.314(1) | −0.142(2) | 0.0037(8) | 0.0049(9) | 0.012(4) | 0.000(2) | 0.002(3) | −0.003(3) |
| C(1) | 0.215(2) | 0.390(2) | 0.251(4) | 0.005(1) | 0.007(2) | 0.017(6) | −0.002(3) | 0.007(6) | 0.003(6) |
| C(2) | 0.243(2) | −0.117(1) | 0.503(4) | 0.005(1) | 0.002(1) | 0.025(7) | 0.001(2) | 0.003(5) | 0.0011(5) |
| C(3) | 0.532(2) | 0.102(2) | 0.210(5) | 0.004(1) | 0.003(1) | 0.035(8) | 0.003(2) | 0.010(6) | 0.007(6) |
| C(4) | 0.502(2) | 0.372(2) | −0.044(3) | 0.006(1) | 0.005(1) | 0.005(5) | −0.002(3) | 0.003(5) | −0.005(5) |

[a] The form of the anisotropic thermal parameter is: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

### *Crystal and Molecular Structures*

The atomic coordinates and anisotropic thermal vibration parameters are listed in Table I. The coordinates assumed for the hydrogen atoms were as follows, where the $x, y$, and $z$ coordinates are listed for each one in that order: H(1), 0.116, 0.440, 0.262; H(2), 0.196, 0.074, 0.601; H(3), 0.589, 0.052, 0.200; H(4), 0.548, 0.416, –0.142. These hydrogen atoms were treated as fixed in the least squares refinement, each one being assigned an isotropic thermal parameter of 5.0 Å$^3$. Table II lists the bond distances and bond angles. The molecular structure is shown in Figure 1.

The entire molecule, $Mo_2(O_2CH)_4$, constitutes the asymmetric unit in the space group $P2_12_12_1$ and thus no crystallographic symmetry is imposed. However, the molecular symmetry is very close to the expected, idealized $D_{4h}$. Each five-membered $\overline{\text{Mo—Mo—O—C—O}}$ ring is essentially planar, as shown in Table III. The mean dimensions of the $Mo_2(O_2C)_4$ central unit of the formate, averaged according to $D_{4h}$ symmetry, are listed and compared with the similarly averaged dimensions in the other three $Mo_2(O_2CR)_4$ species which have been studied crystallographically, viz., $Mo_2(O_2CCH_3)_4$,[12] $Mo_2(O_2CCF_3)_4$,[13] and $Mo_2(O_2CCH_2NH_3)_4(SO_4)_2 \cdot 2H_2O$,[14] in Table IV.

As in the $Mo_2(O_2CCH_3)_4$[12] and $Mo_2(O_2CCF_3)_4$[13] structures the closest inter-molecular contacts are such as to place an oxygen atom from one molecule

TABLE II
Bond distances and bond angles[a,b]

| | Distances, Å | | |
|---|---|---|---|
| Mo(1)–Mo(2) | 2.091(2) | C(1)–O(1) | 1.29(2) |
| Mo(1)–O(1) | 2.112(13) | –O(2) | 1.34(3) |
| –O(3) | 2.122(14) | C(2)–O(3) | 1.27(2) |
| –O(5) | 2.100(12) | O(4) | 1.30(2) |
| –O(7) | 2.125(14) | C(3)–O(5) | 1.31(3) |
| | | –O(6) | 1.24(3) |
| Mo(2)–O(2) | 2.072(13) | C(4)–O(7) | 1.32(2) |
| | | –O(8) | 1.23(2) |
| –O(4) | 2.112(14) | C(1)–H(1) | 0.98 |
| –O(6) | 2.087(13) | C(2)–H(2) | 0.97 |
| –O(8) | 2.140(13) | C(3)–H(3) | 0.96 |
| | | C(4)–H(4) | 0.96 |

| | Angles, degrees | | |
|---|---|---|---|
| Mo(1)–Mo(2)–O(2) | 92.3(4) | O(1)–Mo(1)–O(3) | 90.1(5) |
| –O(4) | 93.2(4) | –O(5) | 174.4(5) |
| –O(6) | 91.6(4) | –O(7) | 89.3(5) |
| O(8) | 90.2(3) | O(3)–Mo(1)–O(5) | 91.7(5) |
| Mo(2)–Mo(1)–O(1) | 92.6(4) | O(7) | 176.3(5) |
| –O(3) | 90.4(3) | O(5)–Mo(1)–O(7) | 88.7(5) |
| –O(5) | 92.7(4) | O(2)–Mo(2)–O(4) | 89.1(6) |
| –O(7) | 93.3(4) | –O(6) | 176.0(6) |
| | | –O(8) | 90.0(5) |
| Mo(1)–O(1)–C(1) | 117(1) | O(4)–Mo(2)–O(6) | 91.2(6) |
| –O(3)–C(2) | 119(1) | –O(8) | 176.5(5) |
| –O(5)–C(3) | 114(1) | O(6)–Mo(2)–O(8) | 89.6(5) |
| –O(7)–C(4) | 115(1) | | |
| Mo(2)–O(2)–C(1) | 118(1) | H(1)–C(1)–O(1) | 118 |
| –O(4)–C(2) | 117(1) | –O(2) | 119 |
| –O(6)–C(3) | 117(1) | H(2)–C(2)–O(3) | 120 |
| –O(8)–C(4) | 120(1) | –O(4) | 120 |
| | | H(3)–C(3)–O(5) | 117 |
| O(1)–C(1)–C(2) | 120(2) | –O(6) | 118 |
| O(3)–C(2)–C(4) | 120(2) | H(4)–C(4)–O(7) | 118 |
| O(5)–C(3)–C(6) | 124(2) | –O(8) | 120 |
| O(7)–C(4)–C(8) | | | |

[a] Figures in parentheses are the estimated deviations in the least significant figures.

[b] Bond distance and angles involving hydrogen atoms are given without esd's since the hydrogen atoms were not refined.

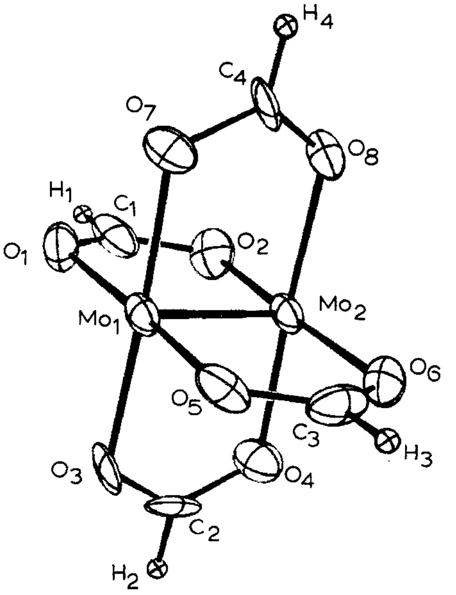

FIGURE 1 An ORTEP drawing of the molecule in which each atom is represented by an ellipsoid proportional to its thermal vibrational amplitude as given in Table I. The hydrogen atoms are represented by artificially small spheres for clarity purposes. The atom labeling scheme is indicated.

along the extended Mo–Mo axis of another at a distance which is too short to be a simple nonbonded contact. In the present case the two ends of the molecule are not crystallographically equivalent, but the two Mo· · · O distances, 2.643 Å and 2.646 Å are effectively identical. These distances are very similar to those found in the other structures namely 2.645 Å in the acetate and 2.71 in the trifluoroacetate.

### *Photoelectron Spectra*

The spectra recorded in this work are displayed in Figure 2. Excitation was by the He(I) resonance line. The spectrum of the formate has been illustrated

TABLE III
Least-squares mean planes

| Plane | Equation of mean plane |
|---|---|
| I | $0.5619x + 0.6030y - 0.5662z = 3.7643$ |
| II | $0.7111x - 0.7030y - 0.0128z = 1.0312$ |
| III | $0.5575x - 0.6199y - 0.5522z = 3.8107$ |
| IV | $0.7114x - 0.7019y - 0.0344z = 1.0066$ |

| Displacement of atoms from mean plane, Å | | |
|---|---|---|
| Plane I | Mo(1) | −0.017 |
| | Mo(2) | 0.011 |
| | O(1) | 0.027 |
| | C(1) | −0.022 |
| | O(2) | 0.001 |
| Plane II | Mo(1) | 0.005 |
| | Mo(2) | −0.008 |
| | O(3) | 0.000 |
| | C(2) | 0.009 |
| | O(4) | 0.011 |
| Plane III | Mo(1) | 0.004 |
| | Mo(2) | −0.002 |
| | O(5) | −0.008 |
| | C(3) | 0.009 |
| | O(6) | −0.003 |
| Plane IV | Mo(1) | −0.011 |
| | Mo(2) | 0.013 |
| | O(7) | 0.006 |
| | C(4) | 0.008 |
| | O(8) | −0.016 |

| Dihedral angles between planes, degrees | |
|---|---|
| I–II | 89.0 |
| I–III | 1.3 |
| I–IV | 89.8 |
| II–III | 88.1 |
| II–IV | 1.2 |
| III–IV | 88.9 |

TABLE V
Peak energies (eV) in the photoelectron spectra of dimolybdenum tetracarboxylates

| $Mo_2(O_2CCF_3)_4$ | $Mo_2(O_2CH)_4$ | $Mo_2(O_2CCH_3)_4$ |
|---|---|---|
| 8.7 | 8.0 | 7.0 |
| 10.4 | 9.7 | 8.8 |
| 12.5 | 11.1 | 10.5 |
| | 11.7 | 11.0 |
| 13.4 | 12.8 | 12.0 |
| | | 13.3 |
| | | 14.0 |

TABLE IV
Comparison of mean dimensions for four dimolybdenum tetracarboxylates

| | Distances, Angstroms | | | Angle, deg. |
|---|---|---|---|---|
| Compound | Mo–Mo[a] | Mo–O | C–O | MoMoO |
| $Mo_2(O_2CH)_4$ | 2.091(2) | 2.11 | 1.29 | 92.0 |
| $Mo_2(O_2CCH_3)_4$ | 2.093(1) | 2.12 | 1.28 | 91.8 |
| $Mo_2(O_2CCF_3)_4$ | 2.090(4) | 2.06 | 1.26 | 92.2 |
| $Mo_2(O_2CCH_2NH_3)_4^{4+}$ | 2.115(1) | 2.13 | 1.26 | 91.5 |

[a] E.s.d. in parenthesis.

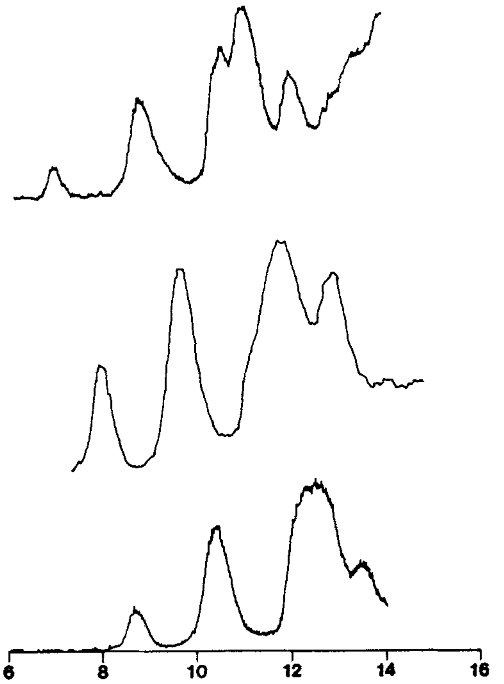

FIGURE 2 The photoelectron spectra of $Mo_2(O_2CH_3)_4$ (upper), $Mo_2(O_2CCH)_4$ (middle), and $Mo_2(O_2CCF_3)_4$ (lower) recorded on gaseous samples using the He(I) resonance line (21.1 eV) for excitation.

previously[5] and all of the same essential features are evident in both cases. Numerical values of the peak positions are listed in Table V. There appears to be a small systematic difference between our values and those of Green and Hayes such that their values are about 0.1 eV below ours.

## DISCUSSION

Dimolybdenum tetraformate is homologous to the other members of the class of $Mo_2(O_2CR)_4$ compounds. The molecular structure is typical for the class, with the $Mo_2O_8$ skeleton having nearly ideal $D_{4h}$ symmetry and the Mo–Mo distance not significantly different from the Mo–Mo distances in the acetate and the trifluoroacetate.

The electronic absorption spectrum is very similar to those of the acetate[15] and the glycinate,[16] indicating that the electronic structures of all the $Mo_2(O_2CR)_4$ compounds are qualitatively the same. However, the qualitative similarity pertains only to the *differences* between the energies of ground and excited states, since the photoelectron spectra clearly show that the absolute values vary significantly. It is evident from Figure 2 and Table V that while the pattern of excitation energies is the same for all three compounds, the actual energies change appreciably with the electronegativity of the group R in $Mo_2(O_2CR)_4$. The trend is such that all ionization energies shift to higher values as the group R becomes more electronegative. While such a trend is not, in a general way, surprising, its detailed explanation must await a complete presentation and analysis of the SCF–Xα–SW calculations, which have thus far been reported only in preliminary and incomplete form.[17] Suffice it to say, for the present, that the first two peaks, at 8.0 and 9.7 eV in the formate, appear to correspond to the $2b_{2g}$ (δ bonding) and $6e_u(\pi)$ levels shown in the published[17] energy level diagram, although two nonbonding levels (not shown on the diagram) centered mainly on oxygen atoms also contribute to the high-energy side of the 9.7 eV peak. Photoelectron intensity from such ligand levels might be expected to be lower than that from levels with large amounts of metal character because of the greater charge localization in the latter.[18]

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