A Comparison of the Electronic Structure of Some Group 6A Dimetal Tetracarboxylates using Photoelectron Spectroscopy

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He(I) and He(II) photoelectron spectra are presented for $[Cr_2(O_2CR)_4]$ (R = Me or Et), $[CrMo(O_2CMe)_4]$, and $[Mo_2(O_2CR)_4]$ (R = H, Me, CMe$_3$, or CF$_3$). Ionization energies and intensities are discussed in relation to *ab initio* and SCF-Xα-SW calculations. A $\sigma^2\pi^4\delta^2$ configuration for the metal electrons gives the most plausible explanation for all spectra, but the $^2\Sigma$, $^2\Pi$, and $^2\Delta$ ion states lie much closer in energy for the dichromium tetracarboxylates than for the molybdenum analogues.

PRELIMINARY gas-phase photoelectron studies of dimolybdenum tetracarboxylates [1,2] and anhydrous dichromium tetra-acetate [3] have shown that in the low-ionization energy (i.e.) region the ionization pattern of the chromium compound differs substantially from that of the molybdenum compounds. Whereas the photoelectron (p.e.) spectra of the molybdenum compounds are readily interpreted in terms of conventional quadruple bonds, that of anhydrous chromium acetate poses considerable assignment problems.

Various procedures have been used to calculate the electronic structure of these large molecules. These include *ab initio* treatments [3-7] and SCF-Xα-SW calculations.[8,9] The calculations on $[Mo_2(O_2CH)_4]$ confirm the previous postulates of quadruple bonding and are in general agreement with the experimental data, although the detailed assignments of the p.e. spectra differ. The calculations on chromium carboxylates give a variety of results. An *ab initio* SCF calculation reported in a preliminary note [3] predicts a non-bonded ground state for the eight *d* electrons ($\sigma^2\delta^2\sigma^{*2}\delta^{*2}$) of $[Cr_2(O_2CH)_4(OH_2)_2]$, but further calculations including correlation effects [4-6] show that, although this is the lowest-energy single configuration, configuration interaction accessible to a $\sigma^2\pi^4\delta^2$ configuration lowers the energy of this state below that of the non-bonded one, thus allowing some degree of multiple bonding character in the chromium dimer. A SCF-Xα-SW calculation [9] supports the presence of a quadruple bond qualitatively similar to that of the molybdenum analogue but weaker.

In this paper we present details of the p.e. results communicated previously [1,3] and further He(I) and He(II) spectra of Group 6 metal carboxylates.

EXPERIMENTAL AND RESULTS

Samples of $[Cr_2(O_2CMe)_4(OH_2)_2]$,[10] $[Cr_2(O_2CEt)_4(OH_2)_2]$,[11] and $[CrMo(O_2CMe)_4]$ [12] were prepared according to the literature or by analogous methods. The dimolybdenum tetracarboxylates were prepared by literature methods [13,14] and also by a previously unreported route. This is exemplified below for $[Mo_2(O_2CH)_4]$. All compounds were characterized by their mass spectra, i.r. spectra, and C, H, and O analysis where possible.

Dimolybdenum Tetraformate.—Anhydrous sodium formate (0.21 g, 3 mmol) was mixed with di-μ-chloro-bis[(η-allyl)(η-toluene)molybdenum], $[\{Mo(\eta\text{-}C_6H_5Me)(\eta\text{-}C_3H_5)Cl\}_2]$ [14] (0.75 g, 1.5 mmol) in ethanol (20 cm^3). The mixture was stirred at 50 °C for 1 h after which time all the solid dimer had disappeared giving a dark purple solution. This solution was filtered and the filtrate was treated with an excess of formic acid (1 cm^3). After 5 min the solution became yellow-brown and after 30 min yellow crystals had separated. The brown solution was then concentrated to one quarter of its original volume and the yellow crystals were filtered off, washed with toluene and diethyl ether, and finally dried under vacuum, yield *ca.* 82%.

Spectra.—Most of the photoelectron spectra shown here were obtained using a Perkin-Elmer PS16/18 instrument fitted with an Helectros lamp capable of producing both He(I) and He(II) radiation, although some were obtained on an instrument with an earlier lamp. No significant differences were found between spectra obtained with different lamps. The spectra are given in Figures 1—7. All samples had to be heated to produce a sufficient counting rate and the conditions of measurement are given in Table 1.

TABLE 1

Experimental conditions for obtaining spectra

Compound	Temperature range (θ_c/°C)	Counting rate (counts s^{-1}) He(I)	He(II)
$[Mo_2(O_2CH)_4]$	209—223	800	*ca.* 300
$[Mo_2(O_2CMe)_4]$	175—206	10^3	*ca.* 300
$[Mo_2(O_2CCMe_3)_4]$	142—158	10^3	*ca.* 300
$[Mo_2(O_2CCF_3)_4]$	120—125	*ca.* 10^3	*ca.* 50
$[CrMo(O_2CMe)_4]$	187—202	800	300
$[Cr_2(O_2CMe)_4]$	220—286	*ca.* 2×10^3	350
$[Cr_2(O_2CEt)_4]$	248—257	2×10^3	200

All spectra were calibrated with reference to xenon, nitrogen, and the helium self-ionization band (apparent i.e. 4.99 eV).† The ionization energies obtained are given in Table 2. Agreement between values obtained in the two investigations is generally within 0.05 eV.

The spectrum of chromium(II) acetate was obtained in a number of ways; the vapour was obtained by dehydrating hydrated chromium(II) acetate in the spectrometer and then subliming, or by subliming a previously dehydrated sample, or by subliming a previously sublimed sample. The constancy of the spectrum obtained by the various procedures and over the temperature range indicates only one species in the gas phase. Such variations as were found between spectra were those of quality rather than i.e. pattern. Both the signal-to-noise ratio and the amount of background appeared very dependent on the sample pre-

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† Throughout this paper: 1 eV ≈ 1.60×10^{-19} J.

TABLE 2

Ionization energies (eV)

Region	$[Mo_2(O_2CH)_4]$	$[Mo_2(O_2CMe)_4]$	$[Mo_2(O_2CCMe_3)_4]$	$[Mo_2(O_2CCF_3)_4]$	$[CrMo(O_2CMe)_4]$ [a]
A	7.60	6.92	6.75	8.67	7.06
B	9.37	8.77	8.54	10.44	8.82
C_1	10.95	10.47	10.22	12.59	10.59
	11.56	10.94	10.97		11.12
	11.89 (sh)		11.61		
C_2	12.69	11.99	13.14	13.53	12.08
D	14.92	13.31	14.48	15.95	13.31
	16.16	14.09	15.74	17.21	14.16
	16.68	15.56 [b]	17.25	18.63	15.83
E	19.68 [b]	15.93 [b]		20.78 [b]	18.20 [b]
		16.57 [b]			
		18.15 [b]			

Region	$[Cr_2(O_2CMe)_4]$	$[Cr_2(O_2CEt)_4]$	CF_3CO_2H
A	8.65	8.104 [b] (sh)	12.08
	9.10 (sh)	8.55	13.17
		8.92 (sh)	
C_1	10.2		14.85
	10.51	10.50	15.84
	11.04	10.80	16.59
C_2	12.08	12.04	17.41
D	13.33	16.06 [b]	17.84
	14.11	17.96 [b]	19.7 [b]
	15.68 [b]	21.08 [b]	20.8 [b]
	16.21 [b]		22.6 [b]
	18.43 [b]		

[a] See text for discussion on nature of vapour-phase species. [b] Value obtained from He(II) spectrum.

paration, indicating that with some samples decomposition was occurring. Independent evidence that the p.e. spectrum recorded is that of $[Cr_2(O_2CMe)_4]$ is that a peak assigned to $[Cr_2(O_2CMe)_4]^+$ is present in the mass spectrum as the highest *m/e* peak and that crystals of anhydrous $[Cr_2(O_2CMe)_4]$ have been grown by vacuum sublimation.[15]

Obtaining good quality spectra for the molybdenum carboxylates was more straightforward, but most samples degraded the instrumental resolution. Samples of the mixed-metal carboxylate $[CrMo(O_2CMe)_4]$ for which analytical data are good give mass spectra with a *m/e* peak corresponding to $[Mo_2(O_2CMe)_4]^+$ which may be due to an ion–molecule reaction, as well as the parent-ion peak.[16] Both previously sublimed and unsublimed samples were used for p.e. spectral measurement.

Spectra obtained on the two instruments were very similar to each other and to the spectrum of $[Mo_2(O_2CMe)_4]$, so we were concerned as to whether complete decomposition was occurring and whether there was any significant deviation at all from the spectrum of the dimolybdenum compound. Small amounts of involatile residue remained after running the sample but the weight of this was $<20\%$ of the sample loaded. The volatile material in such a spectrometer eventually deposits on the cold electron-analyser plates. Analysis of the deposited material after one run gave a Cr : Mo ratio of 1 : 3 which suggests that the vapour in the ionization region was about a 1 : 1 mixture of $[Mo_2(O_2CMe)_4]$ and $[CrMo(O_2CMe)_4]$. An alternative 1 : 3 mixture of $[Cr_2(O_2CMe)_4]$ and $[Mo_2(O_2CMe)_4]$ can be ruled out on the grounds of differing volatilities and the spectra themselves, since such a mixture would not account for the form of the spectra in the region <10 eV. There are slight differences from the dimolybdenum spectrum, in particular the first band has a different shape and an i.e. which is just significantly different. It is difficult to draw any detailed conclusions about the form of the spectrum of $[CrMo(O_2CMe)_4]$ but it seems that it is likely to be rather similar to that of the dimolybdenum compound.

We have attempted to measure the areas under certain bands. The methods employed included use of a curve analyser, tracing and weighing, and counting of squares (the spectra were obtained on graph paper). Uncertainty was introduced by the choice of base line under bands at >10 eV when some background was suspected. In general, we found that relative areas were reproducible to $\pm10\%$. Values for relative areas divided by the electron energy (to compensate for the sensitivity of the analyser) are given in Table 3.

DISCUSSION

Interest in the electronic structure of these Group 6 metal dimeric carboxylates centres on the description of

TABLE 3

Relative intensities of bands for metal carboxylates

	$[Mo_2(O_2CH)_4]$		$[Mo_2(O_2CMe)_4]$		$[Mo_2(O_2CCMe_3)_4]$		$[Mo_2(O_2CCF_3)_4]$		$[CrMo(O_2CMe)_4]$ *	
Region	He(I)	He(II)	He(I)	He(II)	He(I)	He(II)	He(I)	He(II)	He(I)	He(II)
A	0.18	0.38	0.21	0.36	0.32	0.43	0.31	0.60	0.33	0.37
B	1	1	1	1	1	1	1	1	1	1
C	3.17	4.26	3.92	4.21			3.51	3.48	4	

	$[Cr_2(O_2CMe)_4]$	
Region	He(I)	He(II)
A	1	1
C	5.5	4.8

* See text for discussion of nature of vapour-phase species.

the eight metal electrons. On a simple quadruple-bond theory these are allocated to bonding molecular orbitals (m.o.s) of primarily metal *d* character and of σ, π, and δ symmetry with respect to the metal–metal axis. Symmetry treatment of the anhydrous dimetal tetracarboxylates results in the labelling of these orbitals as $a_{1g}(\sigma)$, $e_u(\pi)$, and $b_{2g}(\delta)$.

In the discussion below we first investigate whether

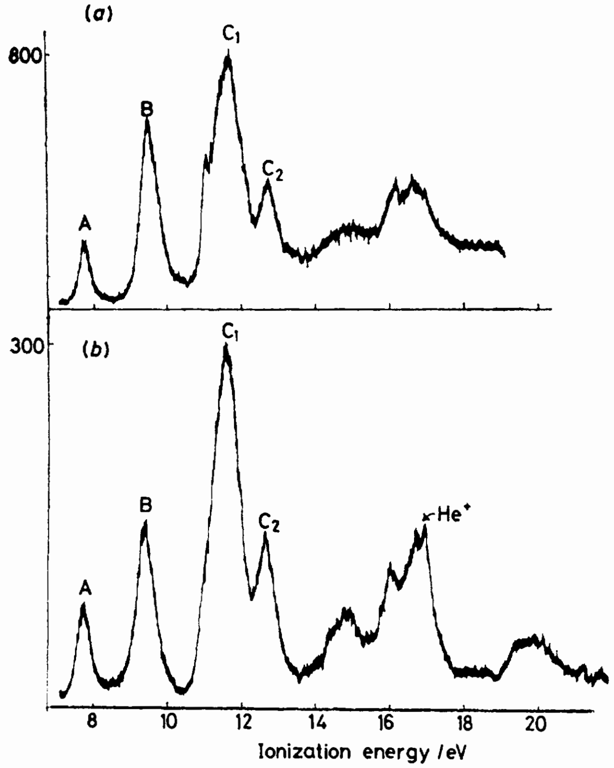

FIGURE 1 He(I) (*a*) and He(II) (*b*) spectra of $[\mathrm{Mo_2(O_2CH)_4}]$. Units of the vertical axis are counts $\mathrm{s^{-1}}$, similarly for all the Figures

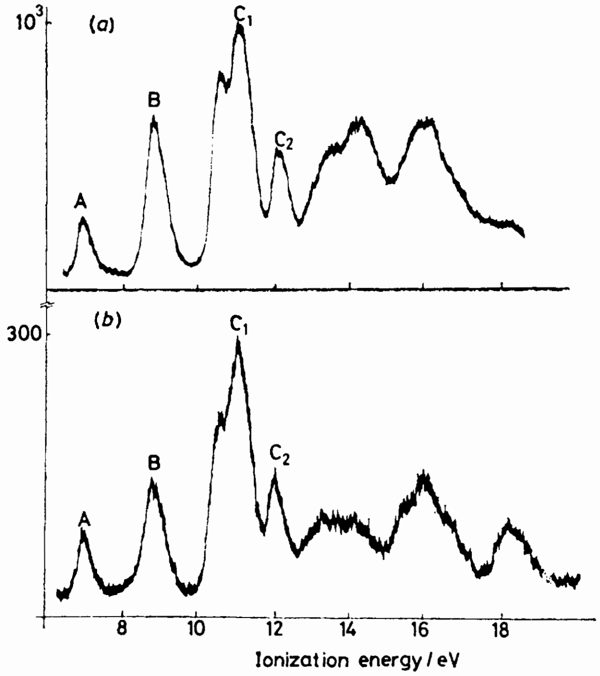

FIGURE 2 He(I) (*a*) and He(II) (*b*) spectra of $[\mathrm{Mo_2(O_2CMe)_4}]$

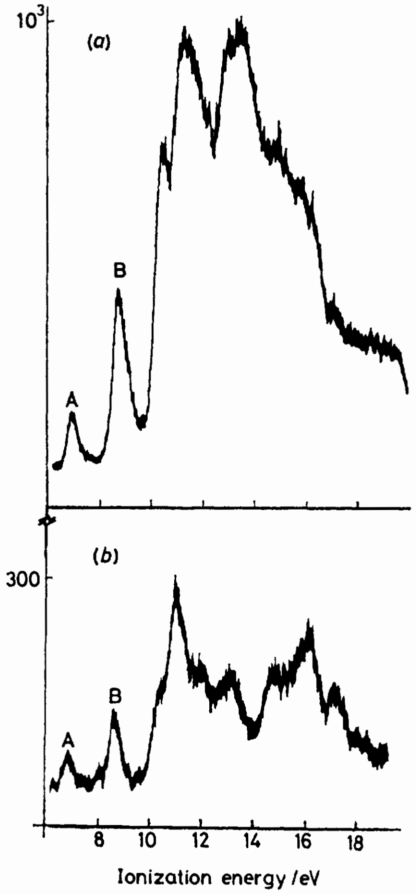

FIGURE 3 He(I) (*a*) and He(II) (*b*) spectra of $[\mathrm{Mo_2(O_2CCMe_3)_4}]$

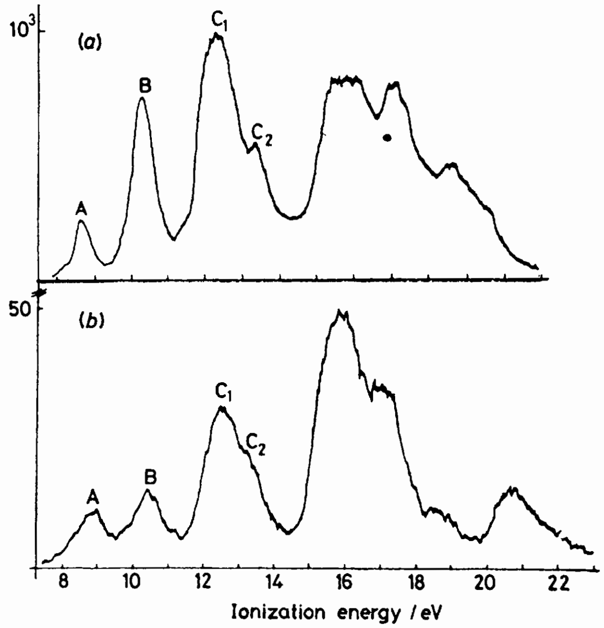

FIGURE 4 He(I) (*a*) and He(II) (*b*) spectra of $[\mathrm{Mo_2(O_2CCF_3)_4}]$

this simple model provides an adequate basis for interpretation of the photoelectron spectra of this class of molecules. We then discuss the relationship of more sophisticated valence calculations to the spectroscopic data.

$[Mo_2(O_2CR)_4]$.—The spectra of the dimolybdenum tetracarboxylates (see Figures 1—3 and Tables 2 and 3) resemble each other in the low i.e. region in that they both exhibit two bands A and B ($R = CF_3$ 8.67, 10.44; R = H 7.60, 9.37; R = Me 6.92, 8.77; $R = CMe_3$ 6.75, 8.54 eV). The variation in the i.e. of these bands follows the inductive effect of the group R. When R = H, Me, and CF_3 the region C is also very similar in profile. No analogous region C can be identified for the pivalate compound, presumably because ionization of electrons localized on the CMe_3 group occurs in this region. The region D at >13 eV differs for all four carboxylates, and has some resemblance to the corresponding regions in the spectra of the carboxylic acids.[17] However, the spectra of the free acids are more structured in this region partly because of the lower symmetry produced by the acid proton, and detailed comparison has not been illuminating.* Spectra of the acetate ion in the solid phase have been reported recently;[18] there is considerable similarity between the high-i.e. region of the acetate spectrum and region D of both $[Cr_2(O_2CMe)_4]$ and $[Mo_2(O_2CMe)_4]$, so we assume that in all the metal compounds region D is essentially due to ligand-localized ionizations.

There is a substantial body of empirical evidence which demonstrates that changes in the relative intensities of p.e. bands with photon energy give information on the localization of electrons which gives rise to these bands. This localization has often been expressed, in the LCAO approximation, in terms of the atomic orbitals contributing to the m.o. from which the ionized electron originates.

Both Mo 4*d* and Cr 3*d* cross sections increase relative to C 2*p* on changing the ionizing radiation from He(I) to He(II).[19] However, evidence from the study of transition-metal pentane-2,4-dionates suggests very little relative change between metal *d* and oxygen 2*p* cross sections.[20] This is borne out by the fact that, whereas there are substantial changes in the relative intensities of bands in the metal pivalates which have high carbon content, those detected in the spectrum of molybdenum formate are small. In fact the He(II) spectrum of molybdenum pivalate has a similar profile at <13 eV to the spectra of the formate and acetate compounds because the metal- and oxygen-localized ionizations are now dominating this region.

For all four carboxylates there is a change in the relative intensities of regions C and D on changing from He(I) to He(II) radiation. For R = H, Me, and CMe_3, D has less intensity relative to C in the He(II) spectrum, which parallels observations on the free acetate and the free acids. This can be associated with a large O 2*p* character for orbitals giving rise to C, and corresponding C 2*p*, H 1*s* character for D. The increase in intensity of D relative to C for $R = CF_3$ can be ascribed to substantial F 2*p* character in the corresponding orbitals. Although region C changes slightly in appearance between the different compounds, there is no evident change on changing photon energy, except that for R = H the shoulder at 10.95 eV is less evident in He(II), and for the other compounds there may be some slight intensity loss in the leading component of band C.

In the spectra of all four dimolybdenum tetracarboxylates band A increases in intensity relative to band B on changing from He(I) to He(II) photons. In the spectrum of $[Mo_2(O_2CH)_4]$ there is also an increase in intensity of band C relative to B.

Theoretical Treatments.—The original assignment of these spectra was that band A corresponds to ionization of the metal δ electrons and band B to ionization of metal π electrons.[1] The band due to ionization of the metal σ electrons was proposed to occur somewhere in the complex band C and it was suggested that it may give rise to the low-energy shoulder on this band (10.95 eV, R = H; 10.47 eV, R = Me). The thesis underlying this assignment is that electrons occupying orbitals of high metal character should have relatively low ionization energies. This assignment is presented as (IV) in Table 5.

An SCF-Xα-SW calculation on $[Mo_2(O_2CH)_4]$[8] has already been used to interpret its p.e. spectrum. We summarize the results in Tables 4 and 5. The agreement between theory and experiment is encouraging, although several assignments are possible (Table 5). We now comment on some minor points. Norman *et al.*[8] suggest that a shoulder is evident at 10.1 eV in our published spectra.[1] We would dispute this and suggest that this region is occupied by the high i.e. tail of band B. This leads to the supposition that the ion states ^2E_g and $^2A_{1u}$ assigned to this shoulder in fact form part of the complex band C. We propose a new assignment of region C labelled (II) in Table 5. This leaves unchanged the essential feature of this calculation with respect to assignment of the i.e. of the metal–metal quadruple-bonding electrons. To summarize the Xα-SW results: band A originates from ionization of δ electrons and B from π electrons; both the $4a_{1g}$ and $5a_{1g}$ m.o.s have metal–metal σ-bonding character, the former at lower energy having the higher metal content; the corresponding ionization energies are 11.56 eV ($5a_{1g}$) and 12.69 eV ($4a_{1g}$).

Ab initio calculations[5,7] have yielded a different spectral assignment. We also summarize these results in Tables 4 and 5. Good agreement is not expected between the quantitative predictions of Koopmans' theorem and the experimental results. Four ionization energies have been calculated by ΔSCF methods,[7] which suggest that the $\sigma(5a_{1g})$ and $\pi(6e_u)$ orbitals have comparable i.e. An assignment following this calculation,

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* He(I) and He(II) spectra of the free acids are available as Supplementary Publication No SUP 22473 (13 pp.). For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue. Ionization energies for CF_3CO_2H, which have not been reported previously, are given in Table 2; intensity changes suggest that the band at 14.9 eV has a similar origin to the third band of HCO_2H.[17]

labelled (III) in Table 5, places both these ionizations under band B. Band A is again assigned to ionization of $\delta(2b_{2g})$ electrons. Other minor differences between the two assignments, upon which we do not wish to comment, may be seen from Tables 4 and 5.

TABLE 4

Theoretical predictions of ionization energies

	$[Mo_2(O_2CH)_4]$				$[Cr_2(O_2CH)_4]$		$[CrMo(O_2CH)_4]$
			Koopmans' theorem		(Koopmans' theorem [5])		(Koopmans' theorem [5])
Orbital	Xα–SW *,[8]	ΔSCF [7]	ref. 7	ref. 5			
$2b_{2g}$	8.00	8.6	9.4	7.45	8.24	$3b_2$	11.65
$6e_u$	9.68	10.4	11.6	9.93	8.43	$10e$	10.1
$4e_g$	(10.2)		12.7	12.68	12.65	$9e$	12.82
$1a_{1u}$	10.23	11.9	12.2	12.24	12.08	$2a_2$	12.30
$5e_u$	(10.6)		13.7	13.82	13.69	$8e$	13.47
$5a_{1g}$	(10.9)	10.3	11.5	9.87	9.76	$8a_1$	12.11
$3e_g$	(10.7)		13.9	13.41	13.65	$7e$	13.80
$3a_{2u}$	(11.0)		14.3	13.71	13.90	$7a_1$	13.88
$3b_{2u}$	11.29		14.2	13.71	13.63	$7b_1$	13.61
$1b_{1u}$	(11.6)		14.4	13.93	14.12	$2b_2$	14.50
$4b_{1g}$	(12.0)		15.6	14.77	13.9	$6b_1$	14.56
$4a_{1g}$	13.06		15.7	14.99	14.67	$6a_1$	15.05
$1a_{2g}$	(12.7)		17.4				
$4e_u$	(13.0)		17.9				
$1b_{2g}$	(13.7)		18.8				
$3b_{1g}$	(16.2)		19.9				
$2e_g$	(16.3)		18.2				
$3a_{1g}$	(16.2)		20.2				
$3e_u$	(16.3)		20.1				
$2a_{2u}$	(16.9)		19.6				
$2b_{2u}$	(16.9)		19.5				
$2e_u$			23.5				
2_{1g}			24.2				
$2a_{1g}$			24.4				

* Values in parentheses are estimates which only represent the eigenvalues found in explicit transition-state calculations of other levels.

TABLE 5

Suggested assignments for the p.e. spectrum of $[Mo_2(O_2CH)_4]$

Experimental (eV)	i.e.	(I)	(II)	(III)	(IV)
7.6	A	$2b_{2g}$ (δ)	$2b_{2g}$ (δ)	$2b_{2g}$ (δ)	$2b_{2g}$ (δ)
9.37	B	$6e_u$ (π), $4e_g$, $1a_{1u}$	$6e_u$ (π)	$5a_{1g}$ (σ), $6e_u$ (π)	$6e_u$ (π)
10.95	C_1	$5e_u$, $5a_{1g}$, $3e_g$, $3a_{2u}$	$4e_g$, $1a_{1u}$	$1a_{1u}$, $4e_g$	$4e_g$, $1a_{1u}$, $5a_{1g}$ (σ)
11.56	C_1	$3b_{2u}$, $1b_{1u}$	$5e_u$, $5a_{1g}$, $3e_g$, $3a_{2u}$, $3b_{2u}$	$5e_u$, $3e_g$, $3b_{2u}$, $3a_{2u}$, $1b_{1u}$	$5e_u$, $3e_g$, $3a_{2u}$, $3b_{2u}$
11.89	C_1	$4b_{1g}$	$1b_{1u}$		$1b_{1u}$
12.69	C_2	$4a_{1g}$ (σ), $1a_{2g}$, $4e_u$	$4a_{1g}$ (σ), $4b_{1g}$	$4b_{1g}$, $4a_{1g}$	$4b_{1g}$, $4a_{1g}$
14.92	D	$1b_{2g}$	$1a_{2g}$, $4e_u$, $1b_{2g}$	$1a_{2g}$, $4e_u$, $2e_g$	as (II)
16.16	D	$3b_{1g}$, $2e_g$, $3a_{1g}$, $3e_u$	$3b_{1g}$, $2e_g$, $3a_{1g}$, $3e_u$	$1b_{2g}$	
16.68	D	$2a_{2u}$, $2b_{2u}$	$2a_{2u}$, $2b_{2u}$	$2b_{2u}$, $2a_{2u}$, $3b_{1g}$, $3e_u$, $3a_{1g}$	
19.68	E		$2e_u$, $2b_{1g}$, $2a_{1g}$	$2e_u$, $2b_{1g}$, $2a_{1g}$	

I = the assignment based on the Xα–SW calculation of ref. 8, II the modification of (I) as discussed in text, and III is an assignment based on SCF calculations.[7] IV is a variation where $5a_{1g}(\sigma)$ at 11.56 eV may also be considered [denoted (IV′) in text]: these assignments of the metal electrons were proposed in ref. 1.

Although the two different calculations concur in confirming the localized bond model of a quadruple metal–metal bond, they differ in the assignments of the i.e. associated with the $a_{1g}(\sigma)$ component of the band. Both assignments pose problems in fitting the experimental data. The *ab initio* calculations indicate that band B arises from two ionizations but there is no evidence of any splitting or even variation of band profile in any of the four carboxylates. Also the band profile is unchanged on varying the photon energy, while the first band of the chromium compounds shows some slight profile changes. On the other hand, if band B is assigned exclusively to a ${}^2E_u$ ion state, on degeneracy grounds, it might be expected to be twice as intense as band A. However, in both He(I) and He(II) spectra the B : A intensity ratio is greater than this (Table 3). Since the ratio changes substantially with photon energy, the simple model is breaking down as is discussed further below and these values should not be taken as very significant.

The Xα calculation assigns band C_2 to an a_{1g} orbital with 75% metal content. Since intensity variations occur in bands A and B it might be expected that there would be variations in the $C_1 : C_2$ ratio if this were the case. For both the formate and the acetate, where this region is free from interferences, this ratio, as assessed from peak heights, is essentially constant.

The leading edge of C_1 changes appreciably between the four carboxylates. Changes are also found for the spectra of chromium(II) acetate and chromium(II) propionate where it is probable (see below) that all the metal ionizations occur within the first band. Variations in the leading edge on changing the photon energy occur for all the carboxylates studied and cannot be taken as evidence of metal character.

Since band C_1 is very intense it is possible that the metal a_{1g} orbital ionization lies within this band as originally suggested [assignment (IV′) in Table 5].

We have made efforts to rationalize the observed He(II) intensities in terms of the Gelius model [21] which relies on summing calculated orbital characters weighted by atomic cross sections. The results, which are inconclusive, are given in Table 6. They do, however, represent a considerable improvement on a simple degeneracy model. Indeed, from the substantial changes in the A : B ratios with photon energy when both bands presumably arise from orbitals of mainly metal character, it seems likely that more than atomic terms will be necessary for a full description of the intensities. Neglect of these other terms will be more significant in the He(I) than the He(II) case.

TABLE 6

Predicted relative intensities of the photoelectron spectrum of $[Mo_2(O_2CH)_4]$ using the Gelius model

Assignment *	A	B	C
(II_a)	0.57	1	4.77
(II_b)	0.49	1	3.74
(II_c)	0.49	1	3.93
(II_d)	0.5	1	6.5
(III_b)	0.34	1	2.29
(III_c)	0.33	1	2.28
(III_d)	0.33	1	4
Experimental	0.38	1	4.26

* (II) and (III) refer to the assignments of Table 5. $(P_{A\lambda})_i$ values were obtained from (a) ref. 8, (b) ref. 7, (c) ref. 5, and (d) intensities predicted by orbital degeneracies. Cross-section values from ref. 20: $\sigma_{O2p} = 1.3$, $\pi_{C2s} = 1.0$, $\sigma_{Mo4d} = 2.5$.

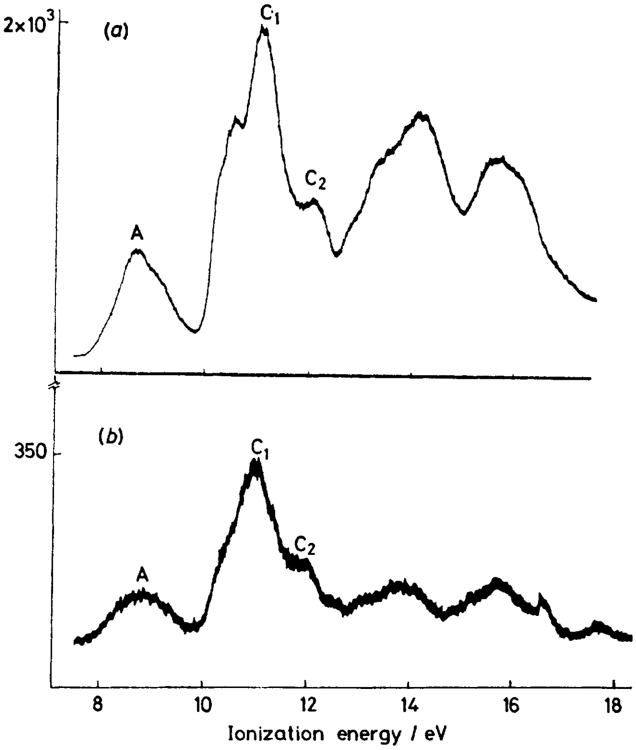

FIGURE 5 He(I) (*a*) and He(II) (*b*) spectra of $[Cr_2(O_2CMe)_4]$

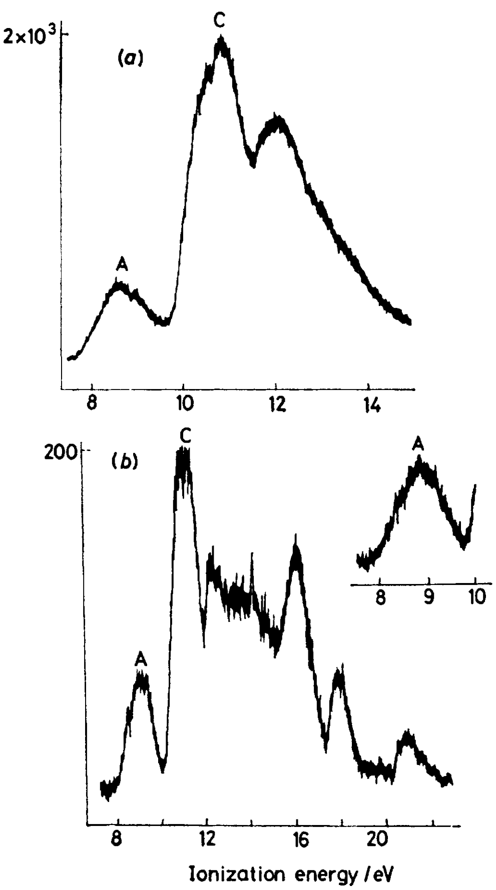

FIGURE 6 He(I) (*a*) and He(II) (*b*) spectra of $[Cr_2(O_2CEt)_4]$

On the available experimental evidence we are unable to decide which of the assignments (II)—(IV) is correct, although (II) and (III) seem rather less probable than the original assignments (IV) or (IV′). The main objection to assignment (II) is a theoretical one in that the σ ionization ($4a_{1g}$) which is mainly metal localized is said to have a rather high ionization energy (12.69 eV). The chief disadvantage of assignment (III) is that it requires the π and σ ionizations to remain unresolved through a wide variation in inductive effect from CF_3 to CMe_3 and with change in photon energy. However, whichever assignment is correct it seems likely that the same assignment holds for all the dimolybdenum tetracarboxylates.

Dichromium Tetracarboxylates.—The spectra of $[Cr_2(O_2CR)_4]$ (R = Me or Et) show a complex band A in the region <10 eV. Perhaps the spectra which give most information are those of the propionate. In the He(I) spectrum of $[Cr_2(O_2CEt)_4]$, Figure 6, two vertical ionization energies are discernible at 8.55 and 8.92 eV and there is a suspicion of a shoulder on the leading edge. In the He(II) spectrum this first shoulder is clearly evident at 8.04 eV. We may conclude that this first band contains at least three ionizations. In the case of $[Cr_2(O_2CMe)_4]$ (Figure 5) a change of gradient on the leading edge is just detectable in the best spectrum, suggesting a similar shoulder but the low signal-to-noise ratio with He(II) and lower resolution do not improve the position. The detection of three bands in this region suggests an assignment to δ, π, and σ ionizations. The intensity pattern, so far as it can be discerned, would parallel that of [Mo$_2$(carboxylate)$_4$] on this assignment, the π ionization decreasing relative to δ on changing the incident radiation from He(I) to He(II).

The chief difference in the remaining part of the spectrum between [Mo$_2$(O$_2$CMe)$_4$] and [Cr$_2$(O$_2$CMe)$_4$] is the band C$_2$ at 11.99 eV in the former and 12.08 eV in the latter. For [Mo$_2$(O$_2$CMe)$_4$] the band is better defined, especially on the leading edge, and more intense in both He(I) and He(II) spectra. From 12 eV onwards the spectrum of [Mo$_2$(O$_2$CMe)$_4$] shows slightly better definition than that of [Cr$_2$(O$_2$CMe)$_4$] but the general forms are very similar.

A comparison with calculations again presents some problems. Application of Koopmans' theorem to Benard's *ab initio* calculation for [Cr$_2$(O$_2$CH)$_4$] [5] gives the i.e. prediction of $2b_{2g}$ (8.24) $<$ $6e_u$ (8.43) $<$ $5a_{1g}$ (9.76 eV). Cotton and Stanley [9] report an Xα-SW calculation on [Cr$_2$(O$_2$CH)$_4$] which gives a $\sigma^2\pi^4\delta^2$ ground state. Ionization energies have not yet been reported but the orbital-energy ordering is $2b_{2g} > 6e_u > 5a_{1g}$ with a spread of 1.55 eV. Their paper assigns $2b_{2g}$ and $6e_u$ to band A and $5a_{1g}$ to the leading edge of C. We consider that reconciliation of both calculations with the experiments is best achieved if all three ionizations are assigned to band A with their ionization energies lying closer than the calculations would suggest, but in an order in agreement with both calculations.

The change of appearance of band C$_2$ between the two acetates is compatible with the calculations if C$_2$ is correctly assigned as $4b_{1g} + 4a_{1g}$ in the molybdenum compound. The smaller stabilization of $5a_{1g}$ in the chromium compound leads to less stabilization of $4a_{1g}$ and this will readily account for the loss of definition of the leading edge of C$_2$ and the loss of intensity.

Ab initio calculations at the SCF and CI levels have been performed on [Cr$_2$(O$_2$CH)$_4$],[4,5] [Cr$_2$(O$_2$CH)$_4$(OH$_2$)$_2$],[3,6] [Mo$_2$(O$_2$CH)$_4$],[4,5] and [CrMo(O$_2$CH)$_4$].[5] The ground state of all these systems is best described by a CI wavefunction with the quadruply bonding configuration $\sigma^2\pi^4\delta^2$ as the leading term. The CI expansion included all the configurations (from di- to octa-excited, corresponding to the excitations $a^2 \rightarrow a^{*2}$ where a denotes one of the σ, π, and δ orbitals and a^* the corresponding antibonding orbital). The percentage of the leading term varies considerably: [Cr$_2$(O$_2$CH)$_4$], 18%; [Mo$_2$(O$_2$CH)$_4$], 66%.[5]

If a single configuration description fails significantly for the ground state of a molecule the p.e. spectrum of the molecule should reflect this initial-state configuration interaction, ISCI,[22] by the presence of satellite ionizations. Unfortunately, estimates of correlation effects in the ion are not available but rough estimates using Benard's unoccupied orbital energies [5] suggest that several satellites should appear before 21 eV. It is possible that some of the lack of definition in the [Cr$_2$(O$_2$CMe)$_4$] spectrum beyond 12 eV could be due to the presence of such satellites but it is still surprising that the satellites are not more in evidence if the leading term is as low as 20%.

We conclude that the most satisfactory interpretation of the dichromium tetra-acetate spectrum is on the basis of a single configuration with δ, π, and σ metal–metal bonding electrons contributing to the first complex band. The other chromium carboxylates are similarly assigned.

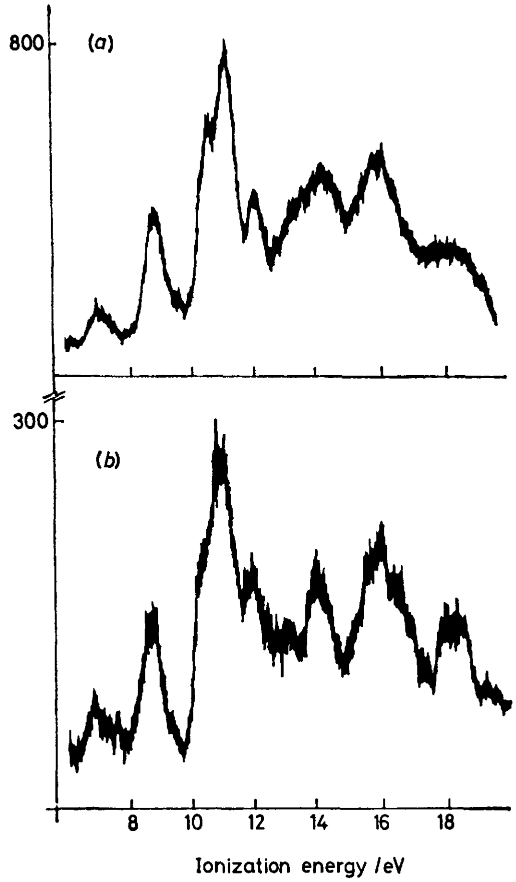

FIGURE 7 He(I) (*a*) and He(II) (*b*) spectra obtained from a sample of [CrMo(O$_2$CMe)$_4$]. (For a discussion of the nature of the vapour-phase species see text.)

[CrMo(O$_2$CMe)$_4$].—As noted above, the spectra shown in Figure 7 result from at least as much [Mo$_2$(O$_2$CMe)$_4$] as [CrMo(O$_2$CMe)$_4$]. However, it seems unlikely that the spectrum of the mixed compound is greatly different from that of the dimolybdenum compound. This is not suggested by a Koopmans' theorem prediction from SCF calculations [5] (see Table 4) where metal-localized orbitals are found to have orbital energies *ca.* 2 eV less in the mixed compound than in the molybdenum dimer, while the oxygen-based orbital energies are similar.

Conclusions.—The photoelectron spectra of the dichromium and dimolybdenum tetracarboxylates are most readily interpreted on experimental grounds as showing that the ion states $^2B_{2g}$, ^2E_u, and $^2A_{1g}$, which result from ionization of the metal–metal bonding δ, π, and σ orbitals, lie much closer in energy in the chromium than in the molybdenum compounds. Calculations by both Xα-SW and *ab initio* methods are in qualitative agreement with this, and suggest that this drawing together of orbital energies results from lengthening of the metal–metal bond. However, there are difficulties in fitting either set of calculations to the spectra. If our assignments are correct the energy separations of the metal levels are overestimated by the Xα calculations for both molybdenum and chromium compounds. Also it is difficult to find evidence in the spectrum of the chromium(II) carboxylates for the extensive configuration interaction predicted by the *ab initio* method.

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