

$2 \rightarrow 1$ isomerization to be within ± 5 kcal of our single point DZP-CI result of 39.1 kcal.

It appears that aluminum, or possibly other metals, may be useful in isolating and identifying vinylidene. As discussed by Trenary,³ the features exhibited in the energy surface of $\text{Al} + \text{C}_2\text{H}_2$ are likely to be important in other hydrocarbon rearrangements where a metal is introduced. A rather interesting result in this regard is found here in comparison with the naked vinylidene \rightarrow acetylene rearrangement, which (as noted) has a negligible barrier. In contrast, Figure 1 shows (follow arrows in reverse direction) that the Al-vinylidene complex **1** has a substantial barrier (~ 52 kcal) for rearrangement to the Al-acetylene complex. Thus the

attachment of the aluminum atom, while reducing the barrier height relative to non-interacting $\text{Al} + \text{HCCH} \rightarrow \text{Al} + \text{CCH}_2$, effectively introduces an inhibitive barrier to a reaction [**1** \rightarrow **2**] which otherwise proceeds very rapidly.

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Theoretical Study on the Quadruple Metal Bond in d^4-d^4 Binuclear Tetracarboxylate Complexes of Chromium, Molybdenum, and Tungsten by the Hartree-Fock-Slater Transition-State Method

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Abstract: Hartree-Fock-Slater calculations are presented on the metal-metal bond distance R_{M}^0 and metal-metal stretch force constant k_{MM}^0 for $\text{M}_2(\text{CO}_2\text{H})_4$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) as well as the three states ${}^2\text{B}_{2g}$ ($\sigma^2\pi^4\delta$), ${}^2\text{E}_u$ ($\sigma^2\pi^3\delta^2$), and ${}^2\text{A}_{1g}$ ($\sigma\pi^4\delta^2$) of $\text{M}_2(\text{CO}_2\text{H})_4^+$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$). The three states ${}^2\text{B}_{2g}$, ${}^2\text{E}_u$, and ${}^2\text{A}_{1g}$ corresponding to the ionization of an electron out of the δ , π , and σ metal-metal bonding orbitals, respectively, were calculated to be at lower energy than the ion states corresponding to ionizations from the ligand-based orbitals. It is shown from calculations on $\text{W}_2(\text{CO}_2\text{CF}_3)_4$ that the photoelectron spectrum of this molecule is consistent with σ , π , δ being at higher energy than the ligand-based orbitals, and a similar interpretation is offered, based on HFS calculations, for $\text{Cr}_2(\text{CO}_2\text{CH}_3)_4$ and $\text{Mo}_2(\text{CO}_2\text{H})_4$. The ionization of an electron from δ results in a modest (0.04 Å) elongation of the metal-metal bond, whereas the increase in metal-metal bond length is more substantial (0.10 Å) for an ionization out of the π orbital. The ionization of an electron out of the strongly metal-metal bonding σ orbital does on the other hand not significantly change the metal-metal bond distance contrary to what one might have expected. This surprising result is explained in qualitative terms. It is finally shown that σ , π , δ in $\text{M}_2(\text{PH}_3)_4\text{Cl}_4$ ($\text{M} = \text{Mo}, \text{W}$) and σ , π in $\text{Mo}_2(\text{OH})_6$, as for the tetracarboxylates, are at higher energy than the ligand-based orbitals, and this result is reconciled with the recorded photoelectron spectra of $\text{M}_2(\text{PMe}_3)_4\text{Cl}_4$ ($\text{M} = \text{Mo}, \text{W}$) and $\text{Mo}_2(\text{OCH}_2\text{CMe}_3)_6$. The change in R_{M}^0 on ionization of an electron from σ , π , δ in $\text{M}_2(\text{PH}_3)_4\text{Cl}_4$ ($\text{M} = \text{Mo}, \text{W}$) and π , σ in $\text{Mo}_2(\text{OH})_6$ was calculated to follow the same trend as for the tetracarboxylates.

I. Introduction

The structure of the dimolybdenum tetracarboxylate complex $\text{Mo}_2(\text{CO}_2\text{CH}_3)_4$ was determined¹ shortly after the recognition of a quadruple metal-metal bond by Cotton in $\text{Re}_2\text{Cl}_8^{2-}$. Cotton accounted for the quadruple bond in $\text{Re}_2\text{Cl}_8^{2-}$ in terms of metal-metal bonding orbitals of local σ , π , δ axial symmetry, and the same bonding scheme was adopted for $\text{Mo}_2(\text{CO}_2\text{CH}_3)_4$.³ The complex $\text{Mo}_2(\text{CO}_2\text{CH}_3)_4$ has according to Cotton's bonding picture the electron configuration $\sigma^2\pi^4\delta^2$ with the same formal bond order of four as $\text{Re}_2\text{Cl}_8^{2-}$.

The neutral dimolybdenum tetracarboxylates $\text{Mo}_2(\text{CO}_2\text{CH}_3)_4$ and $\text{Mo}_2(\text{CO}_2\text{H})_4$ have^{4,5} been used widely to further our understanding of the quadruple metal-metal bond since their volatility makes them well suited for experimental investigations even in the gas phase, and $\text{Mo}_2(\text{CO}_2\text{H})_4$ is further amiable for theo-

retical treatments.⁶ One of the experimental techniques with the strongest bearings on the nature of the quadruple metal-metal bond is low-energy photoelectron spectroscopy^{5a} which in conjunction with theoretical calculations⁶ can provide information on the states generated from ionizations of electrons out of the σ , π , δ and metal-metal bonding orbitals. Different interpretations of the recorded photoelectron spectra on $\text{Mo}_2(\text{CO}_2\text{R})_4$ systems^{5a,b} have, however, been provided by the HF ab initio^{6a,b} method and the SCF- $X\alpha$ -SW scheme^{6c} in connection with theoretical calculations on $\text{Mo}_2(\text{CO}_2\text{H})_4$. A recent ab initio calculation by Atha et al.^{6d} seems, however, in our view, to have resolved the controversy.

The nature of the quadruple metal-metal bond has also been probed by low-energy photoelectron experiments on the homologous and equally volatile dichromium^{5a} and tungsten tetracarboxylates.⁷ The interpretation of the recorded spectra of $\text{Cr}_2(\text{CO}_2\text{R})_4$ systems by theoretical calculations^{6a,8} has, however,

- (1) Lawton, D.; Mason, R. *J. Am. Chem. Soc.* **1965**, *87*, 921.
- (2) Cotton, F. A. *Inorg. Chem.* **1965**, *4*, 334.
- (3) Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982.
- (4) Reference 3, pp 84-135 and pp 390-435.
- (5) (a) Coleman, A. W.; Green, J. C.; Hayes, A. J.; Seddon, E. A.; Lloyd, D. R.; Niwa, Y. *J. Chem. Soc., Dalton Trans.* **1979**, *75*, 485. (b) Green, J. C.; Hayes, A. *J. Chem. Phys. Lett.* **1975**, *31*, 306. (c) Hino, K.; Saito, Y.; Benard, M. *Acta Crystallogr.* **1981**, *B37*, 2164. Lichtenberger, D. L.; Blevine, C. H., II *J. Am. Chem. Soc.* **1984**, *106*, 1936.

- (6) (a) Benard, M. *J. Am. Chem. Soc.* **1978**, *100*, 2354. (b) Hillier, I. H.; Garner, C. D.; Mitcheson, G. R.; Guest, M. F. *J. Chem. Soc., Chem. Commun.* **1978**, 204. (c) Norman, J. G.; Kolari, H. J.; Gray, H. B.; Troglor, W. C. *Inorg. Chem.* **1977**, *12*, 987. (d) Atha, P. M.; Hillier, I. H.; Guest, M. F. *Mol. Phys.* **1982**, *46*, 437.
- (7) Bancroft, G. M.; Pellach, E.; Sattelberger, A. P.; McLaughlin, K. W. *J. Chem. Soc., Chem. Commun.* **1982**, 752.
- (8) Cotton, F. A.; Stanley, G. G. *Inorg. Chem.* **1977**, *16*, 2668.

Table I. Calculated and Experimental Ionization Potentials (eV) for HCOOH

assignment ^a	IP(calcd)	IP(calcd) ^b
7a'	11.63	11.51
2a''	12.59	12.5
6a'	13.90	14.7
1a''	15.57	15.7
5a'	16.7	17.1

^aThe symmetry point group of HCOOH is C_s . ^bFrom ref 5b.

been hampered by lack of experimental information on the length of the Cr–Cr bond,⁹ and no calculations have to date been presented to aid the interpretation of the photoelectron spectra⁷ of $W_2(CO_2R)_4$ complexes.

We present in the first part of this study Hartree–Fock–Slater calculations on the energies of $M_2(CO_2H)_4$ and the three states of $M_2(CO_2H)_4^+$ corresponding to the ionization of a single electron out of the σ , π , δ orbitals as a function¹⁰ of the metal–metal bond distance for the entire triad $M = Cr, Mo, W$. The calculated potential energy curves provide not only information on the relative energies of the three states but also equilibrium metal–metal bond distances R_M^0 and metal–metal stretching frequencies ν_{MM} . The relative energies as well as the spectroscopic constants R_M^0 and ν_{MM} can be determined experimentally from low-energy photoelectron spectroscopy, but the constants R_M^0 and ν_{MM} have to date only been inferred^{5d} for one tetracarboxylate ion state, namely the state $\sigma^2\pi^4\delta$ of $Mo_2(CO_2H)_4^+$. An assignment of the recorded low-energy photoelectron spectra of $Cr_2(CO_2CH_3)_4$,^{5a} $Mo_2(CO_2H)_4$,^{5a} and $W_2(CO_2CF_3)_4$ ⁷ is given in the second part based on HFS calculations on the three molecules. We compare finally in the last part the results from the present study on the tetracarboxylates to theoretical¹¹ and experimental^{11a,c} investigations on other binuclear complexes of group 6 metals with a quadruple or triple metal–metal bond.

II. Computational Details

All calculations were based on the HFS method as implemented by Baerends et al.¹² The relativistic calculations were based on the method due to Snijders et al.¹³ The many electron wave functions for the binuclear complexes were represented as discussed in ref 11b. The computational details for $Mo_2Cl_4(PH_3)_4$ and $W_2Cl_4(PH_3)_4$ can be found in ref 11b and those of $Mo_2(OH)_6$ in ref 11d. All atoms on the carboxylate ligands were represented by an uncontracted double- ζ STO basis set.¹⁴ The 1s orbitals on C, O, F were taken as core and frozen according to the procedure by Baerends et al.¹² On the metal atoms ns and np were represented by an uncontracted double- ζ STO basis¹⁴ whereas nd , $(n+1)s$, $(n+1)p$ were represented by an uncontracted triple- ζ STO basis.¹⁴ Orbitals of lower energy were frozen according to the method by Baerends et al.¹²

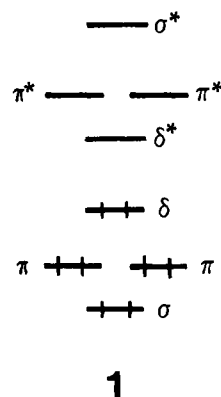
The experimentally determined geometries were adopted for calculations on $Cr_2(CO_2CH_3)_4$,¹⁵ $Mo(CO_2H)_4$,¹⁶ and $W_2(CO_2CF_3)_4$.¹⁷ The CO_2H^- ligand was in the calculations on $M_2(CO_2H)_4$

($M = Cr, Mo, W$) given the same geometry as determined experimentally in $Mo_2(CO_2H)_4$, and the metal–oxygen distances were the same as determined in $Cr_2(CO_2CH_3)_4$, $Mo_2(CO_2H)_4$, and $W_2(CO_2CF_3)_4$, respectively. A standard value of $\alpha = 0.70$ was used for the exchange scale factor.¹²

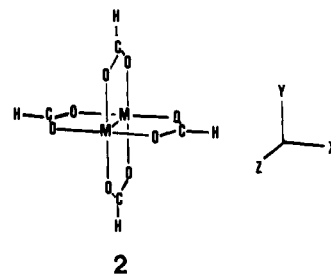
We give in Table I, in order to demonstrate the adequacy of the HFS method and assess the quality of the basis set, a comparison between calculated and experimental ionization potentials for HCOOH. It follows that the accord between theory and experiment is fair in particular for the two ionizations of lowest energy.

III. $M_2(CO_2R)_4$ ($M = Cr, Mo, W$).

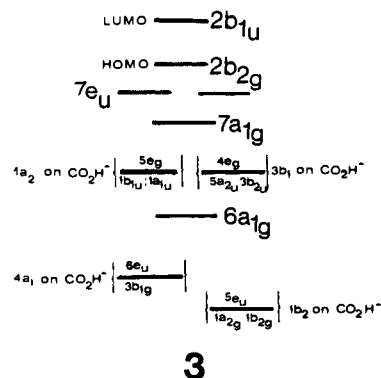
(a) **The Bonding in $M_2(CO_2H)_4$ ($M = Cr, Mo, W$).** The metal–metal bond in binuclear complexes was first accounted for by Cotton² in terms of metal–metal bonding orbitals with local σ , π , δ axial symmetry **1** as well as the corresponding metal–metal antibonding orbitals σ^* , π^* , δ^* . The order of energy for the orbitals was assumed based on overlap considerations to be $\epsilon(\sigma) < \epsilon(\pi) < \epsilon(\delta) < \epsilon(\delta^*) < \epsilon(\pi^*) < \epsilon(\sigma^*)$, **1**.



The d^4 – d^4 tetracarboxylates $M_2(CO_2H)_4$ ($M = Cr, Mo, W$) of D_{4h} point group symmetry **2** have in Cotton's original model the quadruple metal–metal bonded configuration $(\sigma)^2(\pi)_4(\delta)^2$ with δ^* as the unoccupied orbital of lowest energy (LUMO).



The metal–metal bonded orbitals of σ , δ , π symmetry are in our HFS calculations identified as the $7a_{1g}$, $7e_u$, and $2b_{2g}$ orbitals respectively **3** whereas $2b_{1u}$ represents the δ^* orbital.



(17) Sattelberger, A. P.; McLaughlin, K. W.; Huffman, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 2880.

(9) (a) Reference 3, pp 150–159 and p 177. (b) Wiest, R.; Benard, M. *Chem. Phys. Lett.* **1983**, *98*, 102.

(10) The metal–metal distance R_{MM} was varied under the constrain of fixed M–O distances, with the rest of the molecule rigid. We note that a variation without this constrain in which R_{MM} is changed with the rest of the molecule fixed relative to the center of mass gave nearly the same potential curve for $Mo_2(CO_2H)_4$. Thus the exact way in which the “free movement” of the two metal atoms is defined is not crucial.

(11) (a) Cotton, F. A.; Hubbard, J. L.; Lichtenberger, D. L.; Shim, I. *J. Am. Chem. Soc.* **1982**, *679*. (b) Ziegler, T. *J. Am. Chem. Soc.* **1984**, *106*, 5901. (c) Bursten, B. E.; Cotton, F. A.; Green, J. C.; Seddon, E. A.; Stanley, G. G. *J. Am. Chem. Soc.* **1980**, *102*, 4579. (d) Ziegler, T. *J. Am. Chem. Soc.* **1983**, *105*, 7543.

(12) Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys.* **1973**, *2*, 41.

(13) (a) Snijders, J. G.; Baerends, E. J.; Ros, P. *Mol. Phys.* **1979**, *38*, 1909. (b) Relativistic calculations were only carried out on 5d complexes.

(14) Snijders, G. J.; Baerends, E. J.; Vernooijs, P. *At. Nucl. Data Tables* **1983**, *26*, 483 and private communication.

(15) Ketkar, S. N.; Fink, M. *J. Am. Chem. Soc.*, in press.

(16) Cotton, F. A.; Norman, J. G., Jr.; Stults, B. R.; Webb, T. R. *J. Coord. Chem.* **1976**, *5*, 217.

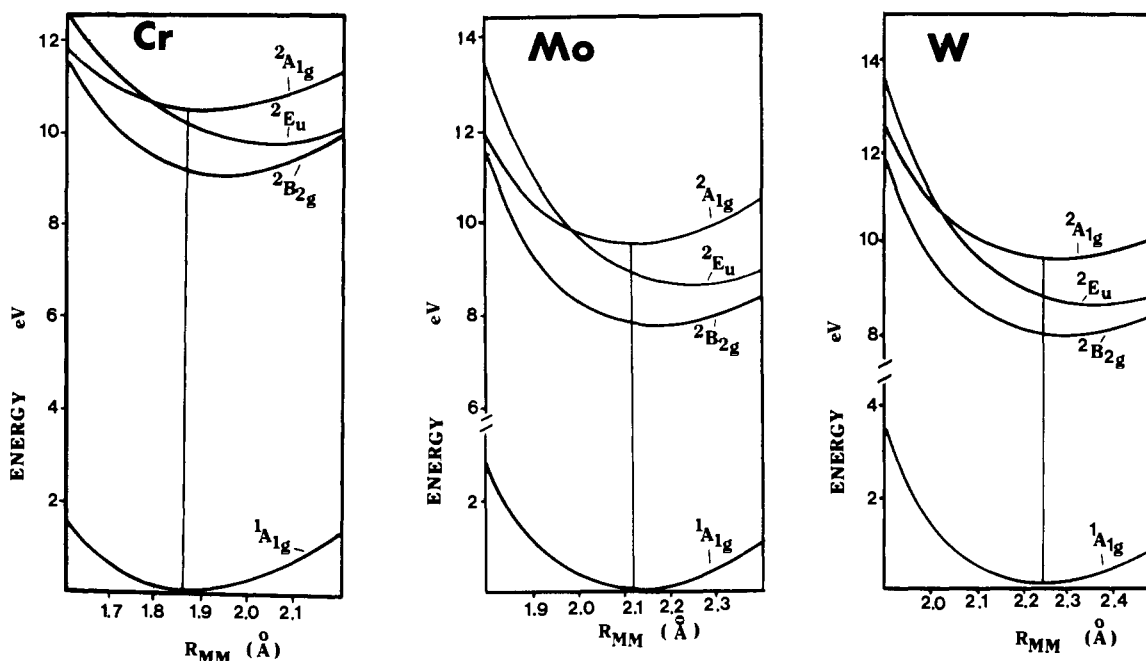


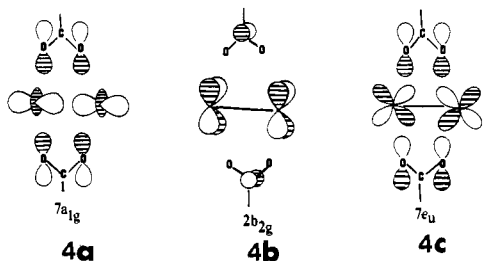
Figure 1. Energies (eV) of the $1A_{1g}$ ground state for $M_2(\text{CO}_2\text{H})_4$ ($M = \text{Cr, Mo, W}$) and the three states $2B_{2g}$ ($\delta^2\pi^4\sigma^2$), $2E_u$ ($\delta^2\pi^3\sigma^2$), and $2A_{1g}$ ($\delta^2\pi^4\sigma$) of $M_2(\text{CO}_2\text{H})_4^+$ ($M = \text{Cr, Mo, W}$) as a function of the metal-metal bond distance R_{MM} (Å).

Table II. Calculated Spectroscopic Constants^{a-c} for $M_2(\text{CO}_2\text{H})_4$ ($M = \text{Cr, Mo, W}$) and the $2B_{2g}$, $2E_u$, and $2A_{1g}$ States of $M_2(\text{CO}_2\text{H})_4^+$ ($M = \text{Cr, Mo, W}$)

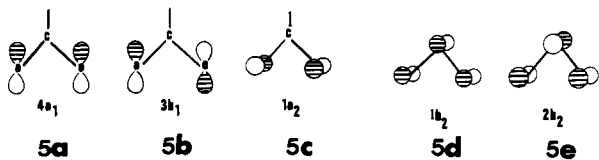
state	$\text{Cr}_2(\text{CO}_2\text{H})_4$			$\text{Mo}_2(\text{CO}_2\text{H})_4$			$\text{W}_2(\text{CO}_2\text{H})_4$		
	R_M^0	k_{MM}^0 ^b	ν_{MM}^0 ^c	R_M^0	k_{MM}^0	ν_{MM}^0	R_M^0	k_{MM}^0	ν_{MM}^0
$1A_{1g}$	1.87	5.26	586	2.12	5.83	454	2.26	5.68	324
$2B_{2g}$	1.92	4.84	562	2.16	5.80	453	2.30	5.37	315
$2E_u$	2.03	2.90	435	2.23	3.93	373	2.37	3.89	268
$2A_{1g}$	1.87	3.92	505	2.10	5.72	450	2.26	4.29	282

^a R_M^0 is the calculated metal-metal equilibrium distance in Å. ^b k_{MM}^0 is the calculated metal-metal stretching force constant in mdyn/Å. ^c ν_{MM}^0 is the calculated metal-metal stretching frequency in cm^{-1} .

The $7a_{1g}$ orbital **4a** is an in-phase combination between d_{z^2} on the two metals, antibonding with respect to the $4a_1$ orbital **5a** on CO_2H^- .



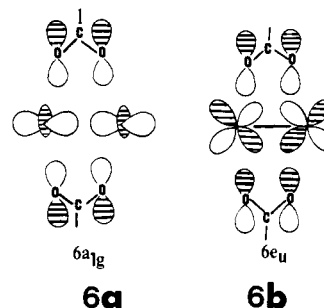
The $2b_{2g}$ orbitals **4b** consists of an in-phase combination between d_{xy} on the two metals, bonding with respect to the unoccupied $2b_2$ ligand orbital **5e** of CO_2H^- and antibonding with respect to the occupied $1b_2$ orbital **5d** of CO_2H^- .



The orbital pair $7e_{ux}$, $7e_{uy}$ is made up from in-phase combinations between d_{xz} or d_{yz} on the two metals, respectively, antibonding with respect to the occupied $4a_1$ orbital **5a** on CO_2H^- , **4c**.

The $7a_{1g}$, $2b_{2g}$ orbitals **4a**, **4b**, metal-metal bonding, and metal-ligand antibonding have more than 75% metal character. The $6a_{1g}$ orbital **6a** is metal-metal bonding as well as metal-ligand bonding with less than 15% metal character, whereas $3a_{1g}$ to $5a_{1g}$

and $1b_{2g}$ primarily are ligand based with $1a_{1g}$, $2a_{1g}$ representing in-phase combinations of ns and np_z on the metal centers, respectively. The $7e_u$ orbitals **4c**, antibonding with respect to $4a_1$ on CO_2H^- **5a** and the in-phase $d_{\pi}-d_{\pi}$ combination, has more than 60% metal character whereas $6e_u$, **6b**, the corresponding metal-ligand bonding orbital, has less than 25% metal character. The orbitals $2e_1$ to $5e_u$ are primarily ligand based, and $1e_u$ is the $np_{\pi}-np_{\pi}$ metal combination.



It is perhaps interesting to note that the $X\alpha$ model without the muffin-tin approximation, as it is used here in the implementation by Baerends et al.,¹² provides level orderings and orbital compositions in accord with recent HF ab initio calculations,^{6a,b,d} whereas previous $X\alpha$ calculations in which the muffin-tin approximation was applied gave quite different orderings and compositions.^{6c}

(b) The Energy of $M_2(\text{CO}_2\text{H})_4$ ($M = \text{Cr, Mo, W}$) and $M_2(\text{CO}_2\text{H})_4^+$ as a Function of the Metal-Metal Bond Distance R_{MM} . We present in Figure 1 the ground-state energy of $M_2(\text{CO}_2\text{H})_4$ as well as the energies corresponding to the $2A_{1g}$, $2B_{2g}$, and $2E_u$ states of $M_2(\text{CO}_2\text{H})_4^+$ as a function of the metal-metal bond

distance R_{MM} , where ${}^2A_{1g}$, ${}^2B_{2g}$, and 2E_u are the states resulting from an ionization of one electron out of the σ , δ , and π metal bonding orbitals of $M_2(CO_2H)_4$, respectively.

It follows from Figure 1 and Table II that the ionization of one electron from the weakly bonding δ orbital results (${}^2B_{2g}$) in a modest elongation of the metal-metal bond distance (0.04 Å) and a modest change in the force constant k_{MM}^0 , whereas an ionization from the stronger bonding π orbital gives rise to (2E_u) a substantial elongation of the metal-metal bond distance as well as a considerable reduction in the force constant k_{MM}^0 (see Table II). Ionization of one electron from the strongly metal-metal bonded σ orbital gives rise to (2E_u) a substantial elongation of the metal-metal bond distance as well as a considerable reduction in the force constant k_{MM}^0 (see Table II). Ionization of one electron from the strongly metal-metal bonded σ orbital $7a_{1g}$ does, on the other hand, not, according to our calculations, elongate the metal-metal bond distance as $M_2(CO_2H)_4^+$ in the ${}^2A_{1g}$ state is calculated to have nearly the same equilibrium distance as $M_2(CO_2H)_4$ in the ground state (Table II). We note in order to explain this somewhat surprising result that the in-phase d_σ combination **4a** in contrast to the d_δ and d_π combinations **4b**, **4c** has strong overlaps with metal orbitals of lower energy, notably ns , np_z . Such overlaps will weaken the metal-metal quadruple bond of $M_2(CO_2H)_4$ through repulsive interactions (exchange repulsion) between the electron pair of the in-phase d_σ combination and the electrons in ns , np_z . The removal of one electron from the σ -orbital $7a_{1g}$ will reduce the σ bond order as well as the exchange repulsion. The reduction of the σ bond order and the exchange repulsion have adverse effects on the metal-metal bond distance of the ${}^2A_{1g}$ state, which largely cancels according to our calculations.

The calculated metal-metal bond distances R_M^0 for the two quadruple bonded species $Mo_2(CO_2H)_4$ and $W_2(CO_2H)_4$ are $R_{Mo}^0 = 2.12$ Å and $R_W^0 = 2.26$ Å, respectively, in fair agreement with $R_{Mo}^0 = 2.09$ Å observed for $Mo_2(CO_2H)_4$ ¹⁶ and $R_W^0 = 2.21$ Å observed for $W_2(CO_2CF_3)_4$.¹⁷ The chromium-chromium bond distance in dichromium tetracarboxylates was until recently only known from $Cr_2(CO_2CH_3)_4L_2$ systems⁹ with two axial ligands. The observed distance⁹ in $Cr_2(CO_2CH_3)_4(H_2O)_2$ at $R_{Cr}^0 = 2.37$ is rather large, and Cotton⁹ has suggested that R_{Cr}^0 in $Cr_2(CO_2CH_3)_4$ should be much shorter and at the same order of magnitude as the "super short" bond in $Cr_2(PhNC(CH_3)O)_4$ with $R_{Cr}^0 = 1.87$ Å. Fink et al.¹⁵ have now shown from electron-diffraction experiments that the metal-metal distance in $Cr_2(CO_2CH_3)_4$ is close to "super short" at $R_{Cr}^0 = 1.97$ Å. Our calculated value at $R_{Cr}^0 = 1.87$ Å for $Cr_2(CO_2H)_4$ also indicates a very short bond in the dichromium tetracarboxylate systems.

Information on the geometries of binuclear systems involving Cr, Mo, and W with a bond order less than 4 as in $M_2(CO_2H)_4^+$ ($M = Cr, Mo, W$) is scant. Cotton et al.²¹ have structurally characterized $Mo_2(SO_4)_4^{4-}$ ($\sigma^2\pi^4\delta^2$) and $Mo_2(SO_4)_4^{3-}$ ($\sigma^2\pi^4\delta$). The metal-metal bond distances were $R_{Mo}^0 = 2.11$ Å for $Mo_2(SO_4)_4^{4-}$ and $R_{Mo}^0 = 2.16$ Å for $Mo_2(SO_4)_4^{3-}$, corresponding to a lengthening of the bond by 0.04 Å as one electron is removed from the δ orbital of $Mo_2(SO_4)_4^{4-}$. We have, as already mentioned, calculated a similar elongation for all three metals as one electron is removed from the δ orbital **1** to produce the ${}^2B_{2g}$ state of $M_2(CO_2H)_4^+$ (see Table II).

Lichtenberg et al.^{5d} have, however, inferred from an important work on the photoelectron spectrum of $Mo_2(CO_2CH_3)_4$ that the removal of one electron from the δ orbital of $Mo_2(CO_2CH_3)_4$ gives rise to an elongation in the range 0.13 to 0.18 Å. Lichtenberg et al. also inferred a considerable reduction in the metal-metal stretch (40 cm^{-1}) in going from $Mo_2(CO_2CH_3)_4$ to the ${}^2B_{2g}$ state of $Mo_2(CO_2CH_3)_4$, in contrast to our results for $Mo_2(CO_2H)_4$ and $Mo_2(CO_2H)_4^+$ as well as experimental findings on $Mo_2(SO_4)_4^{4-}$ and $Mo_2(SO_4)_4^{3-}$ where a metal-metal stretch of 370 cm^{-1} has been found for both species. We can certainly not exclude that

Table III. Experimental Spectroscopic Constants for $Cr_2(COCH_3)_4$,^a $Mo_2(CO_2CH_3)_4$,^b and $W_2(CO_2CF_3)_4$.^c

complex	R_M^0 (Å)	k_{MM}^0 (mdyn/Å)	ν_{MM}^0 (cm^{-1})
$Cr_2(COCH_3)_4$	1.97	3.8 ^d	498 ^e
$Mo_2(COCH_3)_4$	2.08	4.6 ^f	404
$W_2(CO_2CF_3)_4$	2.21	5.3 ^f	313

^aReference 15. ^bReference 23. ^cReference 17. ^dDetermined from the mean amplitude of the metal-metal stretch in ref 15. ^eEstimated here from k_{CrCr} given in ref 15 by assuming a pure metal-metal stretch. ^fEstimated here from ν_{MM}^0 assuming a pure metal-metal stretch.

R_{Mo}^0 calculated for $Mo_2(CO_2H)_4^+$ in the ${}^2B_{2g}$ state is too short compared with R_{Mo}^0 calculated for $Mo_2(CO_2H)_4$. We note, however, that $Re_2Cl_4(PMe_2Ph)_4^{2+}$ ($\sigma^2\pi^4\delta^2$) and $Re_2Cl_4(PMe_2Ph)_4^+$ ($\sigma^2\pi^4\delta$) both are observed²² to have a metal-metal bond distance of $R_{Re}^0 = 2.22$ Å, and that we in reasonable agreement with this observation in a previously HFS study^{11b} have calculated R_{Re}^0 for $Re_2Cl_4(PH_3)_4^{2+}$ at $R_{Re}^0 = 2.24$ Å only to be 0.01 Å shorter than R_{Re}^0 for $Re_2(PH_3)_4Cl_4^+$ at $R_{Re}^0 = 2.25$ Å.

The calculated metal-metal stretching force constants k_{MM}^0 and frequencies ν_{MM}^0 seem somewhat large in comparison with the experimental values for k_{MM}^0 and ν_{MM}^0 compiled in Table III for $Cr_2(CO_2CH_3)_4$, $Mo_2(CO_2CH_3)_4$, and $W_2(CO_2CF_3)_4$, respectively. The complexity of the tetracarboxylate excludes a complete experimental force field analysis, and it is assumed in the comparison that the observed frequencies ν_{MM}^0 correspond to a pure metal-metal stretch without significant couplings from other vibrational modes.

The three states of $W_2(CO_2H)_4^+$, corresponding to ionizations of an electron out of the δ , π , σ metal-metal bonding orbitals, have in Figure 1 and Table II been classified according to their symmetries in the D_{4h} single point group as ${}^2B_{2g}$, 2E_1 , and ${}^2A_{1g}$, respectively, although $W_2(CO_2H)_4^+$ as well as $W_2(CO_2H)_4$ are subject to relativistic calculations.¹³ It is of importance for the subsequent discussion in the next sections to note that the doubly degenerate state 2E_u in the relativistic calculation is split into the two states E_{2u} and E_{3u} of different energies by the spin-orbit coupling interaction and that the splitting according to our calculations is $\Delta E_{so} = 0.21$ eV at R_W^0 . Thus, the potential curve in Figure 1 for the 2E_u state of $W_2(CO_2H)_4^+$ represents the average energies of E_{2u} and E_{3u} . Arratia-Perez and Case²⁴ have carried out a full relativistic calculation on $W_2Cl_8^{4-}$ within the SCF-X α -SW approximation in which they find $\Delta E_{so} = 0.33$ eV. The two ΔE_{so} values can be reconciled by observing that if the metal-metal bonding π orbital is written in terms of its metal and ligand components as $\pi = C_1(d_\pi) + C_2(L_\pi)$ then ΔE_{so} can, to a good approximation, be related to the spin-orbit constant λ_W of the W atom by

$$\Delta E_{so} = C_1^2 \lambda_W \quad (1)$$

We have calculated $\lambda_W = 0.41$ eV and find with $C_1^2 = 0.61$ for $W_2(CO_2H)_4^+$ that $\Delta E_{so} = 0.25$ eV in comparison to $\Delta E_{so} = 0.21$ eV from the full treatment. Arratia-Perez and Case²⁴ give $C_1^2 = 0.8$ for $W_2Cl_8^{4-}$ corresponding to $\Delta E_{so} = 0.33$ eV, in good accord with $\Delta E_{so} = 0.33$ eV from the full relativistic treatment of $W_2Cl_8^{4-}$. The difference in the calculated spin-orbit splittings of $W_2Cl_8^{4-}$ and $W_2(CO_2H)_4^+$ is thus seen to be a consequence of a different participation (C_1) from the in-phase d_π combination in the metal-metal bonding π orbitals of the two molecules, and we note further that 0.4 eV should be an upper bound for ΔE_{so} in the quadruple bonded binuclear complexes of tungsten.

(c) **The Photoelectron Spectra of $Cr_2(CO_2CH_3)_4$, $Mo_2(CO_2H)_4$, and $W_2(CO_2CCF_3)_4$.** The orbital level diagram 3 given for $M_2(CO_2H)_4$ has above $2b_{2g}$, $7e_u$, and $7a_{1g}$ a nest of 16 levels represented by symmetrized combinations of the parent $4a_1$, $3b_1$, a_2 , and b_2 CO_2H^- ligand orbitals **5**, with $1a_{1u}$ at the lower energy edge. We would, in conjunction with the present study on $M_2(CO_2H)_4$ ($M = Cr, Mo, W$) and the ${}^2B_{2g}$, 2E_u , and ${}^2A_{1g}$ states of $M_2(CO_2H)_4^+$, like to present a limited assignment of the recorded photoelectron spectra of $Cr_2(CO_2CH_3)_4$, $Mo_2(CO_2H)_4$, and $W_2(CO_2CF_3)_4$ in which the bands due to ionizations from the δ ,

(18) Slater, J. C. *Adv. Quantum Chem.* **1972**, 6, 1.

(19) Johnson, K. H. *Phys. Lett.* **1968**, 27a, 138.

(20) Baerends, E. J.; Ros, P. *Chem. Phys.* **1975**, 8, 412.

(21) Cotton, F. A.; Frenz, B. A.; Webb, T. R. *Inorg. Chem.* **1975**, 14, 391.

Table IV. Assignment for the Photoelectron Spectra of $\text{Cr}_2(\text{CO}_2\text{CH}_3)_4$, $\text{Mo}_2(\text{CO}_2\text{H})_4$, and $\text{W}_2(\text{CO}_2\text{CF}_3)_4$

$\text{Cr}_2(\text{CO}_2\text{CCH}_3)_4^a$			$\text{Mo}_2(\text{CO}_2\text{H})_4^b$			$\text{W}_2(\text{CO}_2\text{CF}_3)_4^c$					
region	IP(exptl)	assignm	IP(calcd)	region	IP(exptl)	assignm	IP(calcd)	region	IP(exptl)	assignm	IP(calcd)
A	8.65	δ	7.97	A	7.60	δ	7.82	A	7.3		7.79
	9.10(sh)	π	8.89								
B				B	9.37	π	8.91	B ₁	9.01	π^d	8.74,8.94
								B ₂	9.71	σ	9.38
C ₁	10.2			C ₁	10.95			C ₁	12.51	L ^e	10.22
	10.51	L ^e	9.87		11.56	L ^e	10.02				
	11.04				11.89(sh)						

^a Calculate at $R_{\text{MM}} = 1.97 \text{ \AA}$. ^b Calculated at $R_{\text{MM}} = 2.12 \text{ \AA}$. ^c Calculated at $R_{\text{MM}} = 2.21 \text{ \AA}$. ^d The calculated ionization potentials at 8.74 and 8.94 correspond to the two spin-orbit components of the π orbitals. ^e First ionization from ligand-based orbital.

π , σ metal-metal bonding orbitals are identified and located relative to the peak representing the ionization of lowest energy from the nest of ligand-based orbitals, 3.

Binuclear tetracarboxylate complexes of group 6 metals were prior to 1980 only known for $M = \text{Cr}$, Mo , and all interpretations⁶ of their recorded⁵ photoelectron spectra agreed that the ionization of lowest energy from the ligand-based orbitals should be assigned to the region classified as C₁ (See Table IV). The interpretations differed, however, with respect to an assignment of the region at lower energy than C₁. This region was based on ab initio^{6a,b} HF calculations assigned ionizations for all three metal-metal bonding δ , π , σ orbitals whereas only ionizations from δ , π should be assigned to this region according to SCF-X α -SW calculations.^{6c}

Bancroft et al.⁷ have, following the successful synthesis after 1980 of $\text{W}_2(\text{CO}_2\text{R})_4$ systems by Sattelberger et al.¹⁷ as well as Cotton²⁵ and Wang, recorded the photoelectron spectrum of $\text{W}_2(\text{CO}_2\text{CF}_3)_4$, where three bands can be clearly identified in the region below C₁ (see Table IV). Bancroft et al. assigned δ to A (7.3 eV) and π , σ to B₁ (9.01 eV), B₂ (9.71 eV), respectively, and this assignment is supported by the present HFS calculation on $\text{W}_2(\text{CO}_2\text{CF}_3)_4$ where ionizations from δ , π , σ are calculated to be at lower energy than the first ionization from a ligand-based orbital (Table IV). Bancroft et al. found that the large splitting (0.7 eV) and difference in intensities (2:1) between B₁ and B₂ ruled out an assignment of the two bands as due to ionizations from the spin-orbit components of the two π -orbitals, and we note that the calculated spin-orbit splitting of the two π -orbitals at 0.20 eV is much smaller than the observed splitting (0.7 eV) between B₁ and B₂. It is of interest to note that B₁ is much broader than either A or B₂. The broadening of B₁ can aside from the spin-orbit splitting be accounted for when we observe that an ionization from the π -orbitals in section IIIb was calculated to result in a much larger elongation of the metal-metal bond than ionizations from the δ and σ orbitals.

We calculate, as in the case of $\text{W}_2(\text{CO}_2\text{CF}_3)_4$, the ionizations from δ , π , σ to be at lower energy than the ionization from the first ligand based orbital for both $\text{Cr}_2(\text{CO}_2\text{CH}_3)_4$ and $\text{Mo}_2(\text{CO}_2\text{H})_4$ and offer the same assignment, Table IV, for the photoelectron spectra of the two molecules as given previously based on ab initio^{6a,b,d} calculations on $\text{Cr}_2(\text{CO}_2\text{H})_4$ and $\text{Mo}_2(\text{CO}_2\text{H})_4$.

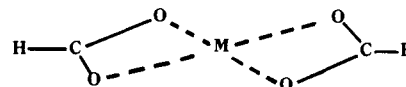
Our relativistic calculations on $\text{W}_2(\text{CO}_2\text{CF}_3)_4$ thus indicate that the assignment of the three first ionization potentials to δ , π , σ for tetracarboxylate complexes of Molybdenum, based on ab initio calculations^{6d} on $\text{Mo}_2(\text{CO}_2\text{H})_4$, can be extended to tungsten systems as well. The assignment of the first three ionization potentials to δ , π , σ for $\text{Cr}_2(\text{CO}_2\text{R})_4$ systems has been based on ab initio calculations on the model system $\text{Cr}_2(\text{CO}_2\text{H})_4$ corresponding to a metal bond distance (2.20–2.36 Å) much larger than that observed (1.97 Å)¹⁵ in $\text{Cr}_2(\text{CO}_2\text{CH}_3)_4$ for which a photoelectron spectrum in fact has been recorded. However, HFS calculations on $\text{Cr}_2(\text{CO}_2\text{CH}_3)_4$ with $R_{\text{MM}}^0 = 1.97 \text{ \AA}$, Table IV, confirm the original^{6d} assignment of δ , π , σ to the first three ionization potentials of $\text{Cr}_2(\text{CO}_2\text{R})_4$ systems.

(d) $\text{V}_2(\text{CO}_2\text{H})_4$, $\text{Nb}_2(\text{CO}_2\text{H})_4$, $\text{Mn}_2(\text{CO}_2\text{H})_4$, and $\text{Tc}_2(\text{CO}_2\text{H})_4$. We have also carried out calculations on the unknown d^3-d^3 systems $\text{V}_2(\text{CO}_2\text{H})_4$, $\text{Nb}_2(\text{CO}_2\text{H})_4$ of configuration $\sigma^2\pi^4$ as well as the unknown d^3-d^5 systems $\text{Mn}_2(\text{CO}_2\text{H})_4$, $\text{Tc}_2(\text{CO}_2\text{H})_4$ of

Table V. Calculated Metal-Metal Bond Distances (Å) R_{MM}^0 for Various $\text{M}_2(\text{CO}_2\text{H})_4$ Complexes

R_{MM}^0	M					
	V	Cr	Mn	Nb	Mo	Tc
	1.95	1.87	1.87	2.35	2.12	2.16

configuration $(\sigma)_2(\pi)^4(\delta)^2(\delta^*)^2$, all with a triple metal-metal bond. The two metals V and Nb in the d^3-d^3 systems have relatively diffuse d orbitals and the calculated metal-metal bond distances are as a consequence somewhat larger than the calculated distances for the corresponding d^4-d^4 and d^5-d^5 complexes (Table V). It is not easy to define the metal-metal bonding energy for the tetracarboxylate systems $\text{M}_2(\text{CO}_2\text{H})_4$. We have for the various metals compared the energy of $\text{M}_2(\text{CO}_2\text{H})_4$ with the energy of two $\text{M}(\text{CO}_2\text{H})_2$ units of structure 7 in their electronic high-spin configuration. The d^3-d^3 complexes have according to this comparison a somewhat stronger metal-metal bond, and the d^5-d^5 complexes a somewhat weaker metal-metal bond, than the corresponding d^4-d^4 systems, indicating perhaps that at least $\text{V}_2(\text{CO}_2\text{R})_4$ and $\text{Nb}_2(\text{CO}_2\text{R})_4$ systems might be isolated. The calculated metal-metal bonding energies according to the procedure given above were 207 and 486 kJ mol⁻¹ for $\text{Cr}_2(\text{CO}_2\text{H})_4$ and $\text{Mo}_2(\text{CO}_2\text{H})_4$, respectively.



7

IV. $\text{Mo}_2\text{Cl}_4(\text{PH}_3)_4$, $\text{W}_2\text{Cl}_4(\text{PH}_3)_4$, and $\text{Mo}_2(\text{OH})_6$

We have in previous studies investigated the quadruple bond^{11b} of $\text{M}_2\text{Cl}_4(\text{PH}_3)_4$ ($M = \text{Mo}$, W) as well as the triple bond^{11d} in $\text{Mo}_2(\text{OH})_6$ by way of our energy-decomposition scheme. We present in Figure 2, as a function of R_{MM} , the energies for the $^2\text{B}_1$, ^2E , and $^2\text{A}_1$ states of $\text{M}_2\text{Cl}_4(\text{PH}_3)_4^+$ ($M = \text{Mo}$, W), corresponding to ionizations out of the δ , π , σ orbitals, respectively, as well as the energies for $^2\text{E}_1$ ($\sigma^2\pi^3$) and $^2\text{A}_{1g}$ ($\sigma\pi^4$) of $\text{Mo}_2(\text{OH})_6^+$. It follows from Figure 2 and Table VI that the changes in the metal-metal bond distances on ionization of an electron out of the δ , π , σ orbitals in $\text{M}_2\text{Cl}_4(\text{PH}_3)_4$ ($M = \text{Mo}$, W) and the σ , π orbitals in $\text{Mo}_2(\text{OH})_6$ give rise to the same trends as calculated for the tetracarboxylates in section IIIb, and we expect in general for binuclear complexes with a multiple metal-metal bond that the removal of one electron from the δ orbital will result in a modest elongation of the metal-metal bond length, whereas the removal of an electron from the π orbital will give rise to a larger increase in R_{MM}^0 . The ionization of an electron from the σ orbital should, on the other hand, in contrast to what one might expect, not significantly increase the metal-metal bond length for reasons given in Scheme IIIb. It is in this respect interesting to note that

- (22) Cotton, F. A.; Dunbar, K. R.; Falvello, L. R.; Tomas, F.; Walton, R. A. *J. Am. Chem. Soc.* **1983**, *105*, 4950.
 (23) Kelley, M. H.; Fink, M. *J. Chem. Phys.* **1982**, *76*, 1407.
 (24) Arratia-Perez, R.; Case, D. A. *Inorg. Chem.* **1984**, *23*, 3271.
 (25) Cotton, F. A.; Wang, W. *Inorg. Chem.* **1982**, *21*, 3859.

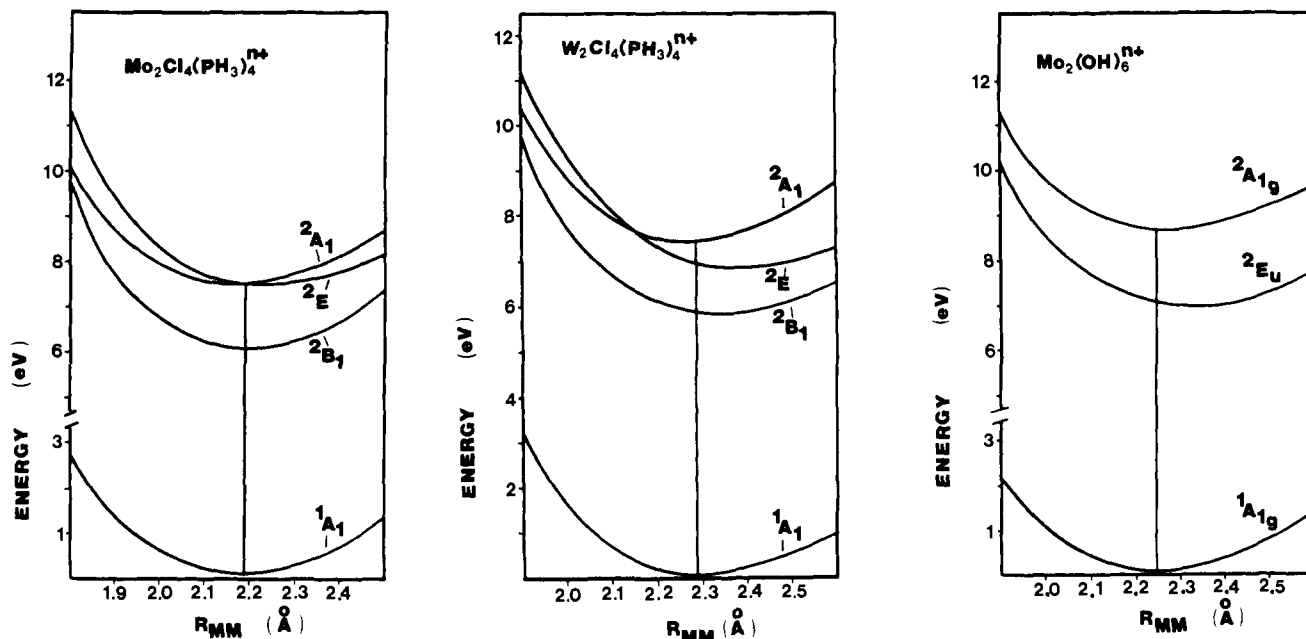


Figure 2. Energies of the 1A_1 ground state for $M_2Cl_4(PH_3)_4$ ($M = Mo, W$) and the $^1A_{1g}$ ground state of $Mo_2(OH)_6$ as well as the 2B_1 ($\delta\pi^4\sigma^2$), 2E ($\delta^2\pi^3\sigma^2$), and 2A_1 ($\delta_2\pi^4\sigma$) states of $M_2Cl_4(PH_3)_4^{n+}$ and the 2E_1 ($\pi^3\sigma^2$) and $^2A_{1g}$ ($\pi^4\sigma$) states of $Mo_2(OH)_6^{n+}$ as a function of the metal-metal bond distance R_{MM} (Å).

Table VI. Calculated Spectroscopic Constants^{a,b} for $Mo_2Cl_4(PH_3)_4^{n+}$, $W_2Cl_4(PH_3)_4^{n+}$, and $Mo_2(OH)_6^{n+}$, with $n = 0, 1$

n	$Mo_2Cl_4(PH_3)_4^{n+}$			$W_2Cl_4(PH_3)_4^{n+}$			$Mo_2(OH)_6^{n+}$		
	state	R_M^0	k_{MM}^0	state	R_M^0	k_{MM}^0	state	R_M^0	k_{MM}
0	1A_1	2.18 (2.13) ^c	5.18 (3.46) ^c	1A_1	2.28 (2.26) ^d	4.76 (3.65) ^d	$^1A_{1g}$	2.24 (2.22) ^e	3.81
1	2B_1	2.18	5.01	2B_1	2.31	4.54			
1	2E	2.22	4.05	2E	2.38	3.70	2E_u	2.33	3.67
1	2A_1	2.14	4.99	2A_1	2.26	4.65	$^2A_{1g}$	2.25	3.05

^a R_M^0 is the calculated metal-metal equilibrium distance in Å. ^b k_{MM}^0 is the calculated metal-metal stretching force constant in mdyn/Å. ^c Experimental values for $Mo_2Cl_4(PMe_3)_4$ from ref 3. ^d Experimental values for $W_2Cl_4(PMe_3)_4$ from ref 3. ^e Experimental values for $Mo_2(OCH_2CMe_3)_6$ from ref 3.

Table VII. Assignment for the Photoelectron Spectra of $Mo_2Cl_4(PMe_3)_4$,^a $W_2Cl_4(PMe_3)_4$,^a and $Mo_2(OCH_2CMe_3)_6$ ^b

$Mo_2Cl_4(PMe_3)_4$				$W_2Cl_4(PMe_3)_4$				$Mo_2(OCH_2CMe_3)_6$			
region	IP(exptl)	assignm	IP(calcd) ^d	region	IP(exptl)	assignm	IP(calcd) ^e	region	IP(exptl)	assignm	IP(calcd) ^f
A	6.44	δ	6.05	A	5.81	δ	5.89	A	7.40	π	7.07
B	7.70	π	7.50	B ₁	7.05	π	7.27, 7.45 ^g	B	8.23	σ	8.69
		σ	7.52	B ₂	7.45	σ	7.57				
C	8.41	L ^h	7.83	C	8.36	L ^h	7.76	C	9.46	L ^h	9.21

^a Reference 11a. ^b Reference 11c. ^c Calculated and experimental ionization potentials (IP) are all in eV. ^d From calculations on $Mo_2Cl_4(PH_3)_4$. ^e From calculations on $W_2Cl_4(PH_3)_4$. ^f From calculations on $Mo_2(OH)_6$. ^g Ionization potentials for the two spin-orbit components of the π orbital. ^h First calculated ionization potential from ligand-based orbital.

N_2^+ of configuration $\sigma^2\pi^3$ has²⁸ a longer bond than N_2 , whereas N_2^+ of configuration $\sigma\pi^4$ has nearly the same bond length as N_2 .

We present in Table VII a limited assignment of the recorded photoelectron spectra of $Mo_2Cl_4(PMe_3)_4$, $W_2Cl_4(PMe_3)_4$,^{11a} and $Mo_2(OCH_2CMe_3)_6$ ^{11c} in which we, as for the tetracarboxylates, identify and locate bands due to ionizations from the δ , π , σ metal-metal bonding orbitals relative to the peak representing the ionization of lowest energy from the nest of ligand-based orbitals. The assignments are made on the basis of calculations on $Mo_2(PH_3)_4Cl_4$, $W_2(PH_3)_4Cl_4$, and $Mo_2(OH)_6$.

For $Mo_2(OCH_2CMe_3)_6$ we offer the assignment, Table VII, already given by Bursten, Cotton et al.,^{11c} in which C is attributed to ionizations from ligand-based orbitals and the bands A and B at lower energies to ionizations from the π and σ metal-metal bonding orbitals, respectively.

We are in the interpretation of the recorded^{11a} spectra for $Mo_2Cl_4(PMe_3)_4$ and $W_2Cl_4(PMe_3)_4$, as for the tetracarboxylates,

faced with the task of assigning the region at lower energy than the band C, due to the first ionization from the ligand-based orbitals, to two or three of the metal-metal bonding orbitals δ , π , σ . The region has, as in the case of the tetracarboxylates, for $M = Mo$ two bands A and B and for $M = W$ three bands A, B₁, and B₂, where the splitting between B₁ and B₂ is 0.4 eV (see Table VII). Cotton et al.^{11a} have from SCF-X α -SW calculations on $M_2Cl_4(PH_3)_4$ ($M = Mo, W$) found σ to be of lower energy than δ , π as well as several of the ligand-based orbitals and assigned for this reason only δ , π to the contested region, with B₁ and B₂ for $M = W$ representing the two spin-orbit components of the π -orbitals. We find from our calculations on $M_2(PH_3)_4Cl_4$ ($M = Mo, W$), Table VII, the two orbitals π , σ to be of nearly the same energy and the three ionizations of lowest energy to correspond to δ , π , σ , respectively. We offer, as for the tetracarboxylates, the assignments A(δ), B(π, σ) and A(δ), B₁(π), B₂(σ) for $M = Mo, W$ respectively (Table VII). The relative intensities (2:1) and shapes of B₁ and B₂ are closely the same for $W_2Cl_4(PMe_3)_4$ and $W_2(CO_2CF_3)_4$ with B₁ being much broader than B₂. The different shapes of B₁ and B₂ make an assignment of the two bands to the spin-orbit components of the two π -orbitals unlikely.²⁹

(26) Ziegler, T.; Rauk, A. *Theor. Chim. Acta* 1977, 46, 1.

(27) Noodleman, L.; Post, D.; Baerends, E. J. *Chem. Phys.* 1982, 64, 159.

(28) Cade, P. E.; Sales, K. D.; Wahl, A. C. *J. Chem. Phys.* 1966, 44, 1973.

The observed splitting between B_1 and B_2 of 0.4 eV is further larger than the calculated spin-orbit splitting of $\Delta E_{so} = 0.18$ eV for $W_2Cl_4(PH_3)_4$ (Table VII). A spin-orbit splitting of 0.4 eV would, according to the discussion in section IIIc, require that the π -orbital is almost pure d_π ($C_1^2 = 1$). We find, however, $C_1^2 = 0.57$ in close agreement with the value of $C_1^2 = 0.6$ from the SCF- $X\alpha$ -SW calculations on $W_2Cl_4(PH_3)_4$.^{11a}

V. Concluding Remarks

We have in this study explored the σ , π , δ orbitals, used by Cotton^{2,3} to account for the multiple metal-metal bond in binuclear complexes, by calculating the energies for the ${}^2B_{2g}$, 2E_u , and ${}^2A_{1g}$ states of $M_2(CO_2H)_4^+$ ($M = Cr, Mo, W$), corresponding to ionization of one electron out of the σ , π , δ orbitals, respectively, as a function of the metal-metal bond distance R_{MM} . The energies for the three states were calculated in the order $E({}^2B_{2g}) < E({}^2E_u)$

(29) It is argued in ref 11a where B_1 and B_2 are assigned to the π orbitals that the different shapes of B_1 and B_2 are due to differences in the coupling between the two π orbitals with σ , δ as one spin-orbit component of π will interact with δ and the other with σ . We do not in our full relativistic treatment find any significant coupling between π and σ , δ . In fact, such a coupling would only be important if either δ or σ was degenerate in energy with the π orbitals. In ref 11a π is separated from δ and σ by 2 eV from above and below, respectively.

(30) The calculated trend in R_M^0 for the doublet states of the bridged $M_2(CO_2R)_4^+$ systems, Table II and Figure 1, seems not possible to rationalize in terms of changing metal-ligand overlaps with variations in the metal-metal bond distance, as the same trend was calculated for the nonbridged $M_2Cl_4(PH_3)_4^+$ systems, Table VI and Figure 2.

$\sim E({}^2A_{1g})$, indicating with out energy-decomposition analysis on several $M_2Cl_4(PH_3)_4^{n+}$ complexes^{11b} of group 6 and group 7 metals. We have found in line with the δ bond being weaker than the π bond that ionization of one electron out of the π -orbital results in a larger elongation of the metal-metal bond than the ionization of an electron out of the δ -orbital. The ionization of an electron from the σ -orbital does, on the other hand, not change the metal-metal bond distance substantially, and this somewhat surprising result³⁰ is explained in section IIIb.

The HFS calculations indicate, in contrast to previous studies⁴ based on the $X\alpha$ model, that ionizations from the δ , π , σ orbitals occur at lower energy than ionizations from the ligand-based orbitals and that the ionization potentials for σ , π are close in energy. We have attempted to reconcile the HFS results with record photoelectron spectra of tetracarboxylate complexes^{5,7} and other binuclear systems^{11a} with a quadruple metal-metal bond and find that the spectra of $W_2(CO_2CF_3)_4$ and $W_2Cl_4(PMe_3)_4$ clearly show three bands that can be assigned to the metal-metal bonding orbitals δ , π , σ , at lower energy than the first peak due to ionizations from ligand-based orbitals.

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Registry No. $Cr_2(CO_2H)_4$, 63448-51-1; $Mo_2(CO_2H)_4$, 51329-49-8; $W_2(CO_2H)_4$, 96482-79-0; $W_2(CO_2CF_3)_4$, 77479-85-7; $Cr_2(CO_2CH_3)_4$, 15020-15-2; $Mo_2(Ph_3)_4Cl_4$, 80485-12-7; $W_2(Ph_3)_4Cl_4$, 80485-13-8; $Mo_2(OH)_6$, 64438-94-4.

Comparative Studies on the Electronic Structures of $W_2(O_2CH)_4$ and $W_2(O_2CH)_4(CH_3)_2$ by the Relativistic $X\alpha$ -SW Method: A d^3 - d^3 Metal Dimer with a Quadruple Metal-Metal Bond?

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Abstract: The bonding in $W_2(O_2CR)_4$ and in the recently characterized $W_2(O_2CR)_4R'_2$ molecules is compared via $X\alpha$ -SW calculations with quasi-relativistic corrections on the model system $W_2(O_2CH)_4$ (I) and $W_2(O_2CH)_4(CH_3)_2$ (II). Several questions concerning the electronic structure of II have been addressed; in particular, the apparently strong W-W bond in the presence of strong W-C bonds was of interest. It has been found that II is best considered as a $W_2(O_2CH)_4$ fragment interacting with two CH_3 radicals, a description consistent with the photochemical decomposition of $W_2(O_2CET)_4(CH_2Ph)_2$. The resulting W-W bond still retains the essential components of the quadruple bond in I. The W-W bonding remains strong in spite of strong axial ligation because of involvement of a higher-lying s-s σ -bonding orbital, an orbital whose contribution is more important in II than in I. It is the presence of this orbital, which is lower-lying for third-row metals than for first, which is believed to account for the structural differences between $Cr_2(O_2CR)_4L_2$ and the $W_2(O_2CR)_4R_2$ systems.

The rapid growth is the synthetic and structural chemistry of dinuclear transition-metal complexes containing strong metal-metal bonds has provided a wealth of information about the nature of metal-ligand and metal-metal interactions.² The elegant story of the Cr-Cr quadruple bond as told by Cotton and Walton³ beautifully emphasizes this point. The general conclusion gained through the structural studies of these Cr compounds is that it is not the electronic properties of the chelating ligands that determines the Cr-Cr bond lengths but rather the presence of or absence of axial ligands. Indeed, the unflinching occurrence of axial

ligation in the dichromium tetracarboxylates and the enormous range of Cr-Cr distances has posed exceptional challenges to the theory of the electronic structure of these compounds. Numerous electronic structural calculations have appeared in the literature³⁻¹⁰

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(2) Cotton, F. A. *Acc. Chem. Res.* **1978**, *11*, 225.

(3) Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982; Chapter 4.

(4) Benard, M. *J. Am. Chem. Soc.* **1978**, *100*, 2354.

(5) Benard, M.; Veillard, A. *Nouv. J. Chim.* **1977**, *1*, 97.

(6) Garner, C. D.; Hillier, I. H.; Guest, M. F.; Green, J. C.; Coleman, A. *W. Chem. Phys. Lett.* **1976**, *41*, 91.

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