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Strong Metal-to-Metal Quadruple Bonds in a Series of Five Isostructural Compounds as Indicated by Photoelectron Spectroscopy

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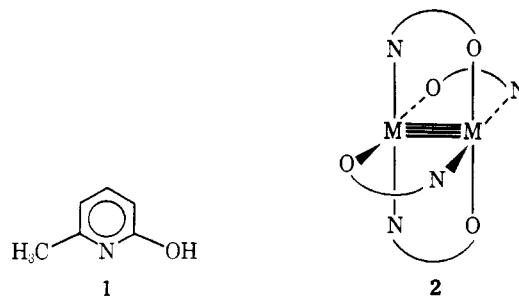
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Abstract: The He(I) photoelectron spectra of five homologous compounds, $MM'(mhp)_4$, where mhp is the 2-oxo-6-methylpyridine ion and $MM' = Cr_2, CrMo, Mo_2, MoW$, and W_2 , have been measured; the spectra of the gaseous Hmhp and Hhp (2-hydroxypyridine) molecules are also reported. The oxidation potentials of the complexes have been recorded by cyclic voltammetry and the Raman spectra of all five compounds are also tabulated ($\nu_{Cr-Mo} 504 \pm 3 \text{ cm}^{-1}$). On the basis of all of this information, with guidance from MO calculations (not given in detail here), we are able to suggest consistent assignments of the PE spectra leading to the conclusion that the M-M δ bonding electrons have ionization energies of 6.8–5.3 eV (through the series from Cr_2 to W_2) and that these energies correlate well with the voltammetrically measured $E_{1/2}$ values. The ionization energies for the molecular orbitals principally responsible for M-M π bonding are fairly constant at about 7.7 eV and the principal σ -bonding orbitals have ionization energies in the range 10.2–10.6 eV. We do not believe that an assignment that places the π and σ ionizations very close together, as suggested by others, is tenable on the basis of all of the evidence available from our experimental studies.

Introduction

Photoelectron (PE) spectroscopy has proven to be a powerful source of data on the electronic structures of both organic and inorganic² compounds. It has already been employed in connection with compounds containing triple and quadruple bonds between metal atoms.^{3–5} The interpretation of the spectra for compounds containing $Mo \equiv Mo$ bonds⁵ has not provoked controversy, but the bonding details and, hence, the interpretation of PE spectra for compounds containing quadruple bonds have aroused considerable differences of opinion.^{6–8}

The recent discovery^{9,10} and characterization of a series of five homologous, quadruply bonded compounds of the type $MM'(mhp)_4$, where mhp is the anion of 2-hydroxy-6-methylpyridine, **1**, and MM' represents $Cr_2, CrMo, Mo_2, MoW$, and W_2 , presents us with an unusually good opportunity for a study of the PE spectra by a procedure based on comparisons between similar, homologous molecules in which only the metal atoms are changed. The structures of all these molecules are as shown schematically in **2**, and the idealized point symmetry (which presumably is the actual symmetry when the



molecules are in the gas phase or in nonpolar solvents) is D_{2d} .

We report here the photoelectron spectra of these five molecules and of the free protonated ligand, Hmhp, as well as various other data which bear on the interpretation of the PE spectra and an understanding of the metal-to-metal bonds in these molecules. The compounds studied are listed in Table I.

Table I. Structural Parameters and M-M' Bond Force Constants

M ₂ in M ₂ (mhp) ₄	distances, Å ^a			Raman ^b ν, cm ⁻¹	force constant k, mdyn/Å
	M-M	M-O	M-N		
Cr-Cr	1.889 (1)	1.969 (10)	2.067 (5)	556 (3)	4.73
Mo-Cr				504 (3)	5.04
Mo-Mo	2.065 (1)	2.086 (8)	2.167 (16)	425 (3)	5.10
W-Mo	2.091 (1)	2.063 (9)	2.156 (19)	384 (3)	5.47 ^c
W-W	2.161 (1)	2.037 (8)	2.12 (3)	295 (3)	4.71

^a The M-O and M-N distances are averages with the standard σ(n) values given. There are only single M-O and M-N distances for W-Mo because the Mo and W positions in the crystal structure are disordered and cannot be uniquely defined as W or Mo. ^b The Raman values refer to the M-M stretching frequency. ^c Recalculated from ref 10.

Table II. Conditions for Recording Photoelectron Spectra

compd	temp, °C ^a	resolution, meV ^b
Hhp	96	50
Hmhp	96	35
Cr ₂ (mhp) ₄	212-221, 248-251	40
MoCr(mhp) ₄	243-247	30
Mo ₂ (mhp) ₄	207-210, 244-249	30
WMo(mhp) ₄	232-237	30
W ₂ (mhp) ₄	250-280	40

^a Where more than one temperature range is given similar spectra were obtained. ^b These values represent the approximate resolutions and in all cases are the upper limits.

Experimental Section

The compounds Cr₂(mhp)₄,⁹ Mo₂(mhp)₄,⁹ Mo(mhp)₄,¹⁰ and W₂(mhp)₄⁹ were prepared by methods described in the literature. The compound MoCr(mhp)₄ has never been obtained completely free of Mo₂(mhp)₄. The impure sample used was prepared by reaction of MoCr(O₂C₂H₃)₄¹¹ that was ca. 80 mol % pure with Na(mhp) in ethanol.

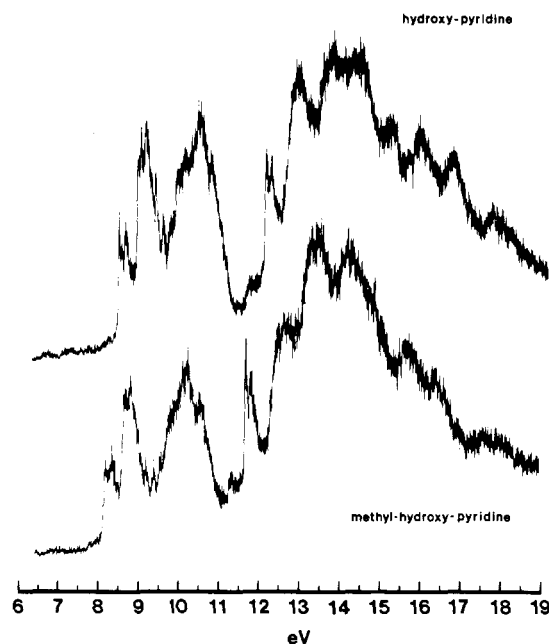
Photoelectron Spectra. The photoelectron spectra were obtained using a Perkin-Elmer PS18 instrument. The spectra were all calibrated with xenon and argon reference ionizations. The temperatures and instrument resolutions for each species are listed in Table II.

Cyclic Voltammograms. Electrochemical measurements were made with a Beckman Electroscan 30. All solutions were 0.001 M in substrate and 0.1 M in (*n*-Bu)₄NClO₄. Acetonitrile, distilled from P₂O₅ under N₂, was the solvent for all measurements.

Results and Discussion

Ligand PE Spectra. The He(I) photoelectron spectra of the protonated ligand, 6-methyl-2-hydroxypyridine (Hmhp), and the related compound 2-hydroxypyridine (Hhp) are shown in Figure 1. The vertical ionization potentials in the 8-13-eV range are listed in Table III. The two spectra are essentially identical except for a 0.3-eV shift to lower energy for the Hmhp spectrum. This is entirely consistent with the expected inductive effect upon adding a methyl group to Hhp.

To facilitate the assignment of the ligand PE spectra, it is instructive to compare them to the parent compounds phenol¹² and pyridine.¹³ The assignments for both of these have been firmly established, as labeled in Figure 2. π₁ and π₂ are the two π orbitals derived from the degenerate e_{1g} orbitals of benzene upon symmetry lowering. π₁ is the member of the pair which has a node passing through the heteroatom, whereas the node in π₂ cuts the two α-β carbon-carbon bonds. Thus, it is expected, and found, that there is extensive heteroatom involvement in π₂ and none in π₁. It should be noted that in pyridine the replacement of a CH group by a more electronegative N atom stabilizes π₂ relative to π₁.¹⁴ In phenol the destabilizing influence of the O pπ orbital will manifest itself

**Figure 1.** He(I) photoelectron spectra for 2-hydroxypyridine (top) and 2-hydroxy-6-methylpyridine (bottom).**Table III.** Photoelectron Data for the Ligand Molecules, Hhp and Hmhp

compd	vertical ionizations, eV ^a						
Hhp	8.62	9.12	10.08 (sh)	10.48	10.78 (sh)	12.18	12.92
Hmhp	8.33	8.81	9.9 (sh)	10.22	10.58 (sh)	11.75	12.6

^a sh = shoulder.

in π₂, destabilizing π₂ relative to π₁. In both molecules, the π₁ ionization is only slightly different than the e_{1g} ionization in benzene (adiabatic IP 9.24 eV). In addition to the π peaks, there are ionizations below 12 eV in both the pyridine and phenol spectra which have been assigned to ejection from in-plane heteroatom lone pairs perturbed somewhat by the σ system of the ring. As one would expect on the basis of electronegativity, the oxygen lone pair of phenol, n(O), has a significantly higher IP than does the nitrogen lone pair of pyridine, n(N).

In assigning the spectrum of hydroxypyridine, we shall be concerned only with ionizations corresponding to those discussed for phenol and pyridine, i.e., the four bands below 12.5 eV. The sharp peaks at 8.62 and 12.18 eV are assigned to the in-plane n(N) and n(O), respectively. The destabilization of n(N) and the stabilization of n(O) relative to pyridine and phenol are consistent with the expected inductive shifts for adding a destabilizing hydroxy substituent or a stabilizing ring nitrogen. The assignment of the two π ionizations, centered at 9.12 and 10.48 eV, is not as straightforward owing to the different orderings of π₁ and π₂ in phenol and pyridine. On the basis of electronegativity it might be expected that the oxygen of the hydroxy group would have a larger effect than the ring nitrogen. We have confirmed this by nonempirical Fenske-Hall calculations¹⁵ on all three molecules, which predict a nodal structure in Hhp identical with that in phenol, i.e., the node in π₁ passes through the oxygen atom and the 2- and 5-carbon atoms. Thus, we assign the ionization of 9.12 eV to an orbital similar to the π₂ orbital of phenol, while the 10.48-eV band is assigned to π₁. The Fenske-Hall calculation also supports the assignment of the first and fourth ionizations to n(N) and n(O).

The third band in each spectrum is unusually broad (~1 eV at half-height) and it seems doubtful that vibrational structure

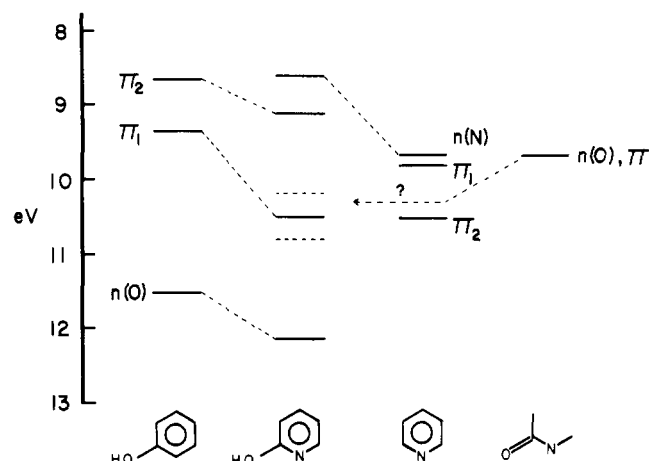


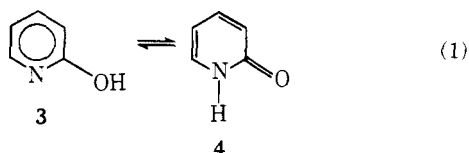
Figure 2. Vertical ionization potentials for phenol, 2-hydroxypyridine, pyridine, and *N*-methylacetamide. π_1 and π_2 refer to ionizations from the asymmetric π system, and $n(X)$ refers to lone-pair ionizations. Dashed ionizations for 2-hydroxypyridine are discussed in the text.

Table IV. Photoelectron Data for the $M_2(mhp)_4$ Molecules

$M_2(mhp)_4$	vertical ionizations, eV						
	A	X	B	C	D	E	F
Cr-Cr	6.8		7.75	8.1	9.8	10.2	11.1
Mo-Cr	6.0		7.73	8.15	9.7	10.5	11.2
Mo-Mo	5.89		7.69	8.20	9.6	10.5	11.2
W-Mo	5.60		7.70	8.15	9.6	(10.4-11.2) ^a	
W-W	5.3	7.30	7.70	8.0	9.6	10.6	11.3

^a Not able to resolve distinct peaks.

alone could account for so much broadening, since the corresponding peaks in pyridine and phenol have half-widths of only ~ 0.3 eV. In fact, the band appears to have shoulders on both the high- and low-energy sides of the maximum, as indicated by the dashed lines in Figure 2. We suggest the following explanation for this structure. It has been established that gaseous Hhp (3) exists in equilibrium with its keto tautomer, α -pyridone (4)¹⁶ (eq 1). The equilibrium constant $K_T = [3]/[4]$ has



been found to be 2.0–2.5 at 130 °C;¹⁶ it is to be expected that a smaller but still significant proportion of this keto tautomer exists at 96 °C (the PE analyzer temperature) as well. We feel that the broad structure of the third band is due to ionizations from the α -pyridone tautomer. This is corroborated by the PE spectrum of *N*-methylacetamide,¹⁷ which can serve as a model of the N-C-O framework. The first two ionizations of *N*-methylacetamide, one from the in-plane oxygen lone pair and one from the primarily oxygen and nitrogen nonbonding π orbital, are both assigned to 9.68 eV. It seems reasonable that the more extensive π system of α -pyridone would split these peaks and account for the high- and low-energy shoulders of the third band in Hhp. Clearly this conjecture could be better established by a comparison of the PE spectra of *N*-methyl-2-pyridone and 2-methoxypyridine in which complications due to tautomerization are not possible.

$M_2(mhp)_4$ PE Spectra. The He(I) photoelectron spectra for the five $M_2(mhp)_4$ compounds with $M_2 = \text{Cr-Cr}$, Mo-Cr, Mo-Mo, W-Mo, and W-W are shown in Figure 3. The peak positions in the 5–12-eV region are listed in Table IV. Except for the Mo-Cr species,¹⁸ the crystal structures of all the

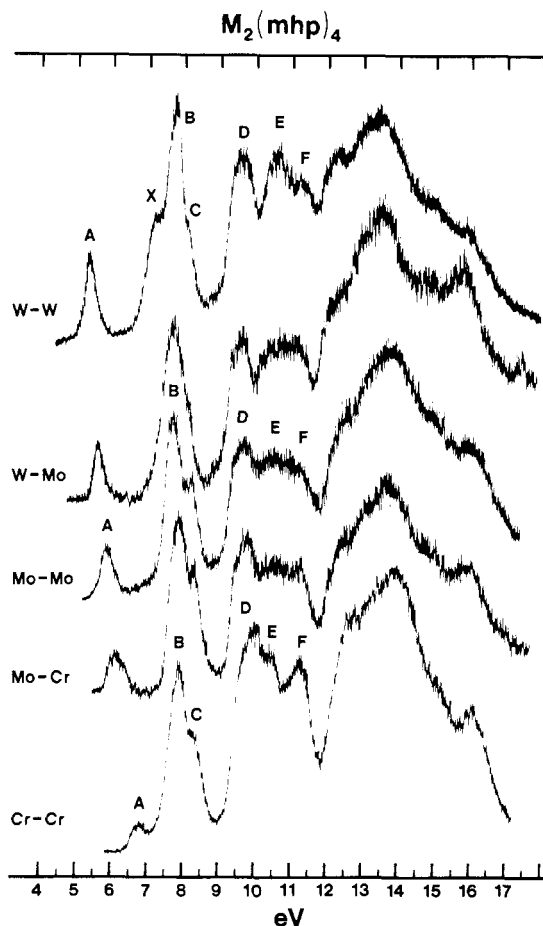


Figure 3. He(I) photoelectron spectra for the series of $MM'(mhp)_4$ compounds. Hatch marks on the top correspond to the integral eV values at the bottom.

compounds have been determined and all are isostructural.^{9,10} The metal-metal and average metal-ligand bond distances along with the energies of the Raman bands associated primarily with the M-M stretch and the calculated force constant for this vibration using the harmonic oscillator approximation are all listed in Table I.^{9,10}

For each PE spectrum the first peak, A, is due to ionization of electrons from the δ metal-metal bonding orbital. As one proceeds through the series from Cr_2 to W_2 the peaks move to lower energy and increase in intensity. Both effects are expected as the metal atoms become progressively heavier and, therefore, have lower electronegativities and larger photoelectron cross sections. Peak A in the Mo-Cr spectrum is markedly asymmetric when compared to the other spectra. This results from the approximately 10–15% contamination by $\text{Mo}_2(mhp)_4$ ¹⁸ which contributes to the spectrum, skewing the Mo-Cr δ band to slightly lower energy, creating the odd band shape (see Figure 4 for details of this lower region).

The position of peak B remains virtually constant at 7.72 ± 0.03 eV throughout the entire series. We assign this as one of the two asymmetric ligand π orbitals. The first π ionization in Hmhp occurs at 8.81 eV and it is reasonable to expect that the partial negative charge present on the complexed ligand will shift this peak to lower energy, corresponding to the observed value of 7.7 eV.

There are four such π orbitals, one from each ligand, that form bases for the e, b_1 , and a_2 irreducible representations under D_{2d} point symmetry. An SCF-X α -SW calculation that we have performed on $\text{Cr}_2(\text{hp})_4$ ¹⁹ shows that the ligand a_2 orbital, which has the same symmetry as the unoccupied M-M δ^* orbital, is interacting with the δ^* level causing a stabilization

of the ligand a_2 orbital relative to the e and b_1 components. Based on this, shoulder C on the high-energy side of peak B is assigned to the ionization from this a_2 orbital. The calculated splitting from the $X\alpha$ calculation between the b_1-e ligand set (essentially degenerate in energy) and the a_2 orbital is 0.4 eV, which compares nicely with the experimental value of 0.35 eV for $\text{Cr}_2(\text{mhp})_4$. The presence of this interaction is not particularly surprising since the metal d_{xy} orbital making up the δ and δ^* levels is directed between the ligand planes allowing a potentially strong overlap with the ligand π system. This allows the filled ligand π level to transfer some of its electron density into the empty metal δ^* orbital, a process analogous to the well-established π back-bonding in metal carbonyls.

The position of shoulder C is affected somewhat differently by changes in the metal atoms via several factors. One is the increased spatial extension of the metal d orbitals which, as one proceeds from 3d to 5d, will favor better overlap and increased stabilization of the ligand a_2 orbital. This, however, will be countered by two other electronic effects, viz., the increased energetic spacing between the ligand a_2 and metal δ^* orbitals and the decreasing electronegativities of the heavier metals. Thus, proceeding from Cr to W these effects should result in a decreased interaction between the ligand π system and the δ^* orbital, and the reduced ability of the metal to accept electron density from the ligand. The spectra indicate that the net result of the simultaneous operation of all these effects is rather small, with the B-C splitting ranging from 0.3 to 0.5 eV.

A most interesting feature of the W-W spectrum is the presence of a distinct low-energy shoulder on peak B. This shoulder, labeled X, is clearly unique to the W-W spectrum as emphasized by the expanded low-energy region for Mo-Cr, W-Mo, and W-W in Figure 4. This feature provides strong evidence that the metal-metal π bonding orbital (of e symmetry) is also located under the B-C envelope since it is expected that, for a third-row element, a degenerate metal level such as this should exhibit spin-orbit splitting. On the basis of previously measured and calculated spin-orbit splittings for third-row metals,^{20,21} one would expect the e orbital to be split into $^2E_{1/2}$ and $^2E_{3/2}$ states of $\text{W}_2(\text{mhp})_4^+$ with a separation of 0.3–0.6 eV. This suggests an alternate assignment for shoulder C in the W-W spectrum; viz., it could result from the higher energy component of the spin-split metal π orbital, rather than from the ligand a_2 π orbital as discussed previously. The relatively low intensity of shoulder C in the W-W spectrum compared to peak B and the other spectra rules out a combination of the two possibilities. Based on the increase in the intensity of peak B despite the spin-orbit splitting which removes roughly half of the metal π ionization (shoulder X) from beneath peak B, we are inclined to believe that for the $\text{W}_2(\text{mhp})_4$ compound the ligand a_2 level has moved back underneath peak B and that C is due to the higher energy spin-split metal π component. A more definitive assignment of this X-B-C envelope may be possible when the appropriate spin-orbit coupling parameters are calculated. For the rest of the spectra the metal π ionizations are apparently right under peak B or slightly to the high-energy side of B.

Peak D is assigned to the lower set of asymmetric ligand π levels. The upper ligand π orbitals under peak B (and shoulder C) have the nodal plane passing, approximately, through the nitrogen and 4-carbon atoms. This lower set has the nodal plane perpendicular to the upper set. These ionizations also hold fairly constant ranging only from 9.6 to 9.8 eV. The separation between the π orbitals in the free ligand, Hmhp, is 1.41 eV and in the $\text{M}_2(\text{mhp})_4$ series 2.0 ± 0.1 eV. This increased splitting is in line with the additional perturbation introduced by the coordination to the metal atoms through the nitrogen and oxygen atoms which are responsible for the 1.4-eV splitting in Hmhp.

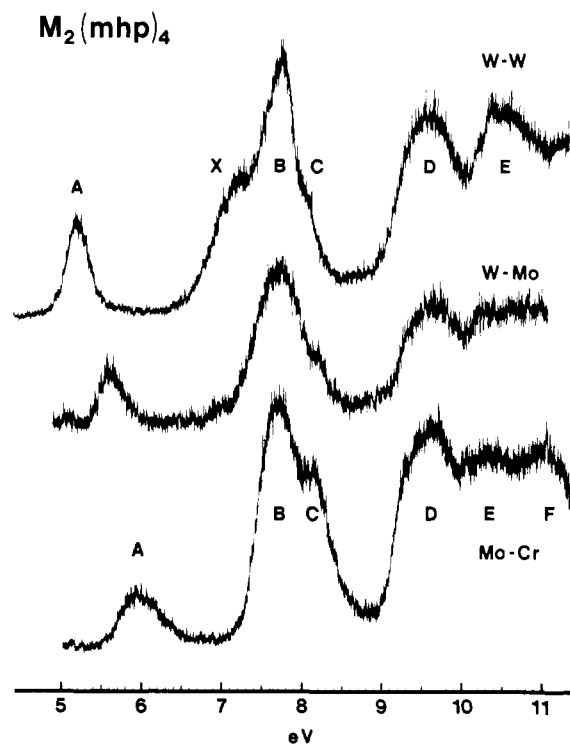


Figure 4. He(I) PES for Mo-Cr, W-Mo, and $\text{W}_2(\text{mhp})_4$ showing the expanded lower ionization region in detail. The W-Mo spectrum was recorded with a different vertical sensitivity causing the peaks to look smaller relative to the other spectra.

Peak E, although not very well resolved, can be seen to shift to slightly higher energy and gradually increase in intensity as one proceeds from Cr-Cr through W-W. The intensities point to a metal-based orbital(s) and as expected, it is most striking in the W-W spectrum. Based upon the intensity changes, the peak position shifts, and our $X\alpha$ calculation on $\text{Cr}_2(\text{hp})_4$, we assign peak E as the metal-metal σ bonding orbital.

Hillier et al.⁸ note the change in this region in their PES on the Cr_2 and $\text{Mo}_2(\text{mhp})_4$ compounds and suggest that metal-ligand bonding orbitals are causing the changes. Furthermore, based on their single determinantal minimal basis set Hartree-Fock calculations on $\text{Mo}_2(\text{O}_2\text{CH})_4$,⁷ they assign both the π and σ metal-metal ionizations to peak B. It is apparent, however, that the consistent increase in intensity, energy shifts, and the broad nature of the ionization for this series of five (rather than two) PES all point strongly to peak E arising from the principal σ component of the M-M quadruple bond.

Peak E is particularly broad and unresolved in the W-Mo spectrum. This is quite interesting as $\text{WMo}(\text{mhp})_4$ has the largest force constant in this series (or for any metal-metal bond so far studied) for M-M bond stretching. If E is the ionization resulting from the σ metal-metal bond one might expect it to have a peak shape reflecting the strength of the M-M bond, that is, a sharper ionization for a weaker bond and vice versa, exactly as observed for the shape of peak E in this series of PE spectra. The force constants and Raman frequencies for the M-M stretches are listed in Table I. The shape of peak E parallels these force constants with the Cr_2 and W_2 bands being clearly resolved and, as far as can be observed from the spectra, considerably sharper than the Mo-Cr and Mo_2 peaks, with the W-Mo ionization being the least resolved and hence probably the broadest of the series. The correlation of the "broadness" of peak E with the force constants could, of course, be coincidental, but we feel that it is general and that it further supports our assignment of peak E arising from the principal metal-metal bonding σ orbital.

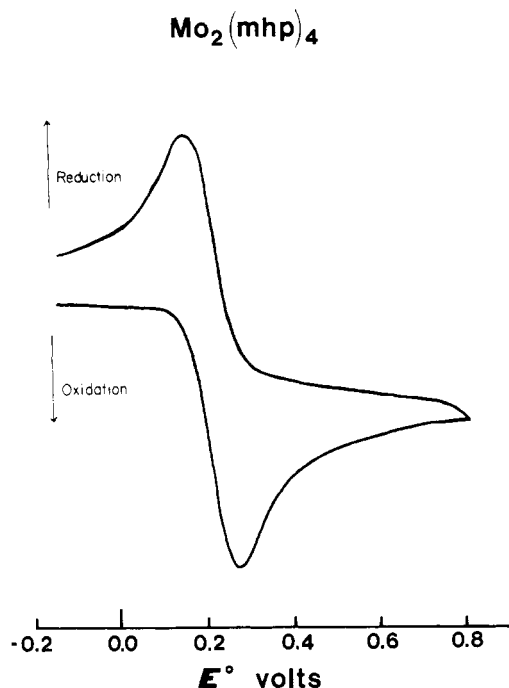


Figure 5. Cyclic voltammogram of a 0.001 M solution of $\text{Mo}_2(\text{mhp})_4$ in acetonitrile which was 0.1 M in $(n\text{-Bu})_4\text{NClO}_4$. The reference electrode was saturated calomel. A platinum electrode was the working electrode.

Table V. Reversible One-Electron Oxidation Potentials for $\text{MM}'(\text{mhp})_4$ Molecules

molecule	$E_{1/2}$, vs. SCE	solvent	electrolyte ^a
$\text{Cr}_2(\text{mhp})_4$		acetonitrile	TBAC
$\text{CrMo}(\text{mhp})_4$	0.35	acetonitrile	TBAC
$\text{Mo}_2(\text{mhp})_4$	0.20	acetonitrile	TBAC
$\text{MoW}(\text{mhp})_4$	-0.16	acetonitrile	TBAC
$\text{W}_2(\text{mhp})_4$	-0.35	acetonitrile	TBAC

^a TBAC = $(n\text{-Bu})_4\text{NClO}_4$.

Peak F, like D, is constant in position and intensity and is assigned to orbitals of mostly ligand character. The $X\alpha$ calculations indicate that this peak is due to levels which are mainly composed of oxygen and nitrogen $p\pi$. The metal-ligand bonding apparently perturbs the nitrogen and oxygen bonding in the π system causing these orbitals to split off from the totally symmetric π orbitals, shifting them to lower ionization potentials. Most of the metal-ligand orbitals are predicted from the calculation to occur just below 12 eV, and, while this is quite low for the nitrogen levels, the changes in this lower region on substituting heavier metals would seem to support this assignment.

Electrochemistry. The cyclic voltammogram for $\text{Mo}_2(\text{mhp})_4$ is shown in Figure 5. It is representative of the reversible one-electron waves of $\text{MM}'(\text{mhp})_4$ compounds, for $\text{MM}' = \text{CrMo}, \text{MoMo}, \text{MoW}$, and WW . The reversible $E_{1/2}$ values are listed in Table V. In addition, each of these compounds exhibits an irreversible oxidation (presumably $+1 \rightarrow +2$) at 1.0–1.15 V vs. SCE. The first oxidation for $\text{Cr}_2(\text{mhp})_4$ occurs at 1.01 V vs. SCE and is irreversible in nature. Free Hmhp was found to oxidize irreversibly at 1.30 V vs. SCE.

Although a relationship between the first oxidation half-potential and the energy of the highest occupied molecular orbital has been established for some mononuclear transition metal complexes,^{22,23} the present work is the first homologous series of $E_{1/2}$ values obtained for multiply bonded transition

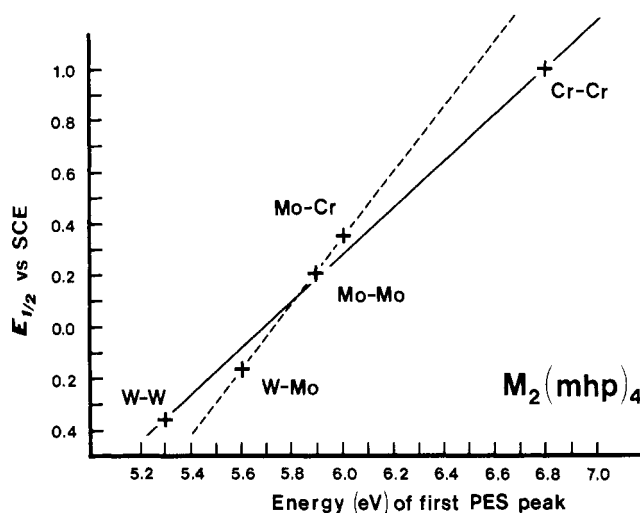


Figure 6. A plot of cyclic voltammogram $E_{1/2}$ values vs. the ionization potentials for the first peaks in the PES for a series of $\text{MM}'(\text{mhp})_4$ compounds. The Cr_2 value represents an irreversible oxidation while the others are all reversible.

metal dimers. It is not unreasonable to suppose that the first oxidation wave would correlate with the first ionization potential (from the δ M–M bonding orbital) of these compounds. Indeed, this is the case as emphasized in Figure 6, in which the reversible $E_{1/2}$ values for MoCr –, Mo_2 –, WMo –, and $\text{W}_2(\text{mhp})_4$, as well as the irreversible oxidation for $\text{Cr}_2(\text{mhp})_4$, are plotted against the first ionization potentials of the compounds. That the relationship is virtually linear is not very surprising since solvation effects should be essentially constant throughout the series, and should cause a fixed increment in the ionization energies relative to those for the gas phase, assuming that the first redox potentials do correspond to the same process as the first ionization potentials in the gas phase.

In $\text{Cr}_2(\text{mhp})_4$ the first oxidation occurs at 1.01 V and is irreversible, contrasting with the reversible first oxidations observed for the other compounds. One possible explanation for this is that the δ orbital in $\text{Cr}_2(\text{mhp})_4$ is close enough to the ligand or metal π levels (cf. the PES) that there is substantial ligand or metal π character mixing into the electrochemical redox reaction, spoiling the normally reversible nature of the process. Another possibility is that the ligand levels are being raised slightly in energy relative to the metal δ orbital through solvation effects and the observed oxidation is primarily due to ligand levels. In either case, it would appear that a good energetic isolation of the δ orbital is crucial for a cleanly reversible $0 \rightarrow +1$ oxidation. The rest of the compounds also have irreversible waves occurring between 1.0 and 1.15 V which are presumably due to the $+1 \rightarrow +2$ oxidation from the upper ligand π levels. It is expected that the metal-metal π bonding levels will be stabilized greatly relative to the ligand π levels by the removal of an electron from the metal-localized δ orbital. Assignment of the second oxidation wave primarily to the ligand π levels is suggested by the fairly constant position of the electrochemical values and the occurrence of an irreversible wave in free Hmhp at 1.30 V vs. SCE, which would be expected to shift to lower E° values in the $\text{M}_2(\text{mhp})_4$ compounds owing to the partial negative charge on the complexed ligands.

Thus, the electrochemistry appears to be completely consistent with the photoelectron spectra and further supports the assignment of the first peak (and redox wave) as resulting from the M–M δ bonding orbital and the second ionization as arising partially from the ligand π levels.

Heteronuclear Quadruple Bonds. There have been four heteronuclear quadruply metal-metal bonded species charac-

terized so far, two of which are discussed in this paper, MoCr- and WMo(mhp)₄, and the two mixed carboxylates, MoCr(O₂CCH₃)₄¹¹ and WMo(O₂CC(CH₃)₃)₄.²⁴ Each of these compounds has physical properties which are far from representing the average of the properties from the homonuclear parent species.

MoCr(O₂CCH₃)₄ is a dramatic example of this: Cr₂(O₂CCH₃)₄ has a Cr–Cr bond length of 2.288 (2) Å²⁵ while Mo₂(O₂CCH₃)₄ has a Mo–Mo distance of 2.093 (1) Å,²⁶ both of which are longer than that in the mixed species, which has a Mo–Cr distance of 2.050 (1) Å.¹¹ The photoelectron spectrum³ of MoCr(O₂CCH₃)₄ is quite similar to that of Mo₂(O₂CCH₃)₄ but vastly different from that of Cr₂(O₂CCH₃)₄. WMo(O₂CC(CH₃)₃)₄ has a W–Mo bond length of 2.080 (1) Å, which is slightly shorter than that for Mo₂(O₂CC(CH₃)₃)₄ at 2.088 (1) Å²⁷ despite the presence of the larger tungsten atom. No W₂(O₂CR)₄ compounds have yet been characterized but it would seem safe to expect a W–W distance longer than 2.09 Å.

The mixed MM'(mhp)₄ compounds show similar trends, with the W–Mo bond distance closer to that of the Mo₂ than that of the W₂ species (cf. Table I). The force constant for W–Mo is larger than the values for either Mo₂ or W₂, but, once again, it is closer to the Mo₂ value. Although we do not have a bond distance in the MoCr case, it is probably closer to that for Mo₂ than for Cr₂, with the force constant for MoCr essentially identical with that of Mo₂(mhp)₄.

While we are not prepared to offer a detailed explanation for these nonlinear relationships, it seems fairly clear that the various changes are all weighted toward the Mo₂ properties as compared to the parent Cr₂ and W₂ compounds. For group 6 quadruple M–M bonds, it is fairly well established^{28,29} that molybdenum forms the most stable metal–metal quadruple bonds. This extremely favorable situation seems to be carried over into the heteronuclear bonding between Mo and Cr or W. A manifestation of this can be seen in Figure 6, where the best line (solid) through the five data points passes through the W₂, Mo₂, and Cr₂ values with the heteronuclear points both off the line. One can, however, draw another straight line (dotted) through the heteronuclear points which also intercepts the Mo₂ value with the Cr₂ and W₂ values now substantially off the line. While the validity of drawing conclusions based on only three data points is admittedly questionable, we feel that this is consistent with the available data presented above and that the physical properties of these mixed M–M' bonds are indeed dominated by Mo relative to Cr or W.

Although these trends appear definite, it is appropriate to offer a caveat as to their generality. What appears to be true for group 6 metals in the +2 oxidation state need not apply to the same elements in a different oxidation state,²⁴ much less

those in a different triad. This is, however, an area of rapidly increasing importance owing to the recent discovery of mixed metal cluster compounds,^{30,31} which are proving to be of considerable interest both in terms of fundamental bonding and reactivities.

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References and Notes

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- (19) The detailed results of the SCF-X α -SW calculation on Cr₂(hp)₄ will be reported in a future publication along with PES spectra of Mo₂(hp)₄ and Mo₂(map)₄, where map = 6-methyl-2-aminopyridine.
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