On the role of PES data in the identification of metal–metal charge transfer bands in clusters of clusters[1]

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Abstract

The clusters of clusters $M_2[O_2CCCo_3(CO)_9]_{4-n}[O_2CR]_n$, where M is Cr, $n = 0$; where M is Mo, $n = 0$, 1, R is CH_3; where M is W, $n = 0$; exhibit allowed transitions with absorbance maxima that correlate with the lowest ionization energy of $M_2(O_2CMe)_4$. An analysis of this correlation, in conjunction with molecular orbital models of electronic structure, allows these absorptions to be assigned to charge transfer transitions between the group 16 dimetal center and the tricobalt cluster substituent on the carboxylate ligand functionality. The characteristics of this metal–metal charge transfer transition should be amenable to further control by variation in substituent cluster properties.

Introduction

Although the continuous development of quantum chemical methods permits the treatment of ever larger problems with chemically useful accuracy, there are still many problems which are just too large to be dealt with by state-of-the-art methods. For molecular problems requiring a knowledge of valence electronic states, ultraviolet photoelectron spectroscopy (PES) provides an alternative of considerable usefulness. Indeed, being experimental it provides real-world information that is exact (within the accuracy of measurements). However, the data primarily reflect properties of the radical cation states relative to the ground state of the molecule of interest. In addition, for large systems, the technique provides only limited spectroscopic detail. In short, a chemically useful interpretation of the data often requires both quantum chemical calculations and the examination of series of related compounds. The former provides the molecular orbital (MO) language for the description of the pertinent electronic states via Koopmans' theorem as well as considerable detail on intramolecular electronic interactions in the molecule of interest. An examination of related compounds reduces the complexity of the problem by focusing on relative changes in series of structurally related molecules rather than on absolute quantities such as ionization energies.

One purpose of this short contribution is to stress the continuing value of the data generated in these experiments. Not only is the PES experiment a primary source of information on new systems of bonding, but the educational value of PES data in presenting concepts of electronic structure to beginning students is becoming more and more appreciated [1]. Moreover, the PES data already in the literature constitute an important resource in the solution of electronic structural problems. The typical preparative chemist is quite prepared these days to carry out reasonably sophisticated spectro-

[1] Dedicated to Professor David Turner for his services to electron spectroscopy.

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SSDI 0368-2048(93)01823-W

scopic experiments, e.g. multinuclear NMR, in the characterization of new compounds. It is rare for such a person to look to the PES experiment for additional useful information. The obvious reasons are that the appropriate equipment is only available in a few laboratories and large molecules require considerably more effort than small gaseous molecules to measure. However, in some instances, data already available can be helpful. Indeed, the dearth of accurate thermodynamic quantities in inorganic chemistry gives ionization data even greater value.

The second purpose served by this paper is to celebrate, in a real sense, the seminal contributions of David Turner in the development of the technique [2]. It was in his laboratory that I was introduced to PES and the ingenuity of his spectrometer designs. On returning to Notre Dame I constructed a version of his photoelectron spectrometer with my own sampling devices. It was applied to various cluster structure problems generated by our synthetic work using the empirical approach learned at Oxford. Although I am no longer a practitioner of the method, I continue to find the data invaluable.

Clusters of clusters

Recently, we have been pursuing the idea of a metal cluster as a substituent with unusual steric and electronic properties [3]. When used, for example, to replace a methyl group in the acetate ligand, a metal cluster substituent allows the synthesis of large and complex metal carboxylates [4,5]. These constitute a type of cluster of clusters in which coordinate covalent bonding holds the cluster units together. Among other things, we are interested in characterizing the nature of the interaction between the cluster substituents and the central metal core. For small molecules such questions constitute ideal subjects for theoretical studies. But, even though mononuclear transition metal complexes have yielded to sophisticated quantum chemical techniques [6], large transition metal clusters remain in the realm of much more approximate theories. That is, on a qualitative level, e.g. counting electrons, theory has provided systemization of the metal cluster area [7]. However, more detailed considerations present formidable obstacles. It is here where PES data can be an invaluable aid.

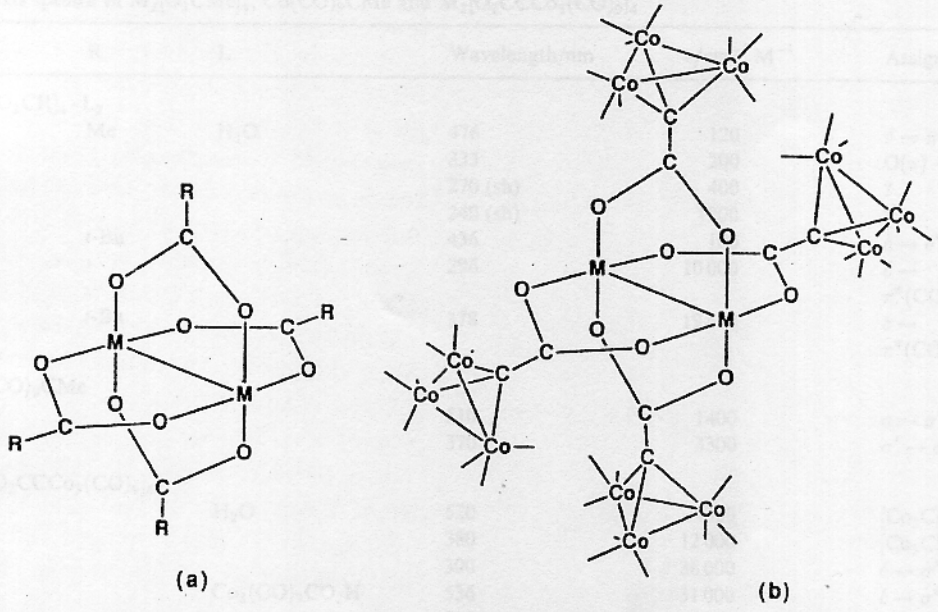

Fig. 1. Schematic drawings of the structures of (a) $M_2[O_2CMe]_4$ and (b) $M_2[O_2CCCo_3(CO)_9]_4$, where M is Mo. The 3 CO ligands have been omitted from each Co for clarity.

A type of complex with fascinating properties are the $M_2(O_2CR)_4$ carboxylates where M is a group 16 metal (Fig. 1a) [8]. In an electronic structural sense, the focus of attention here is the quadruple bond between the metal centers. Hence, these compounds have been the subject of intense scrutiny including PES studies [9]. One current problem is to define the nature of the interaction between the carboxylate ligands and the quadrupole bond. It is this interaction that is addressed here when the R group on the carboxylate is a metal cluster rather than an alkyl or aryl substituent.

We have already communicated the synthesis of $Mo_2[O_2CCCo_3(CO)_9]_4$ (Fig. 1b) [10]. We noted at that time the intense absorption in the visible and tentatively assigned it to a metal-to-ligand charge transfer band which is moved into the visible by virtue of the action of the metal cluster substituent on the bridging carboxylate ligands. In the following we present a more detailed analysis of this interaction including new results on chromium and tungsten analogs. These data empirically define the origin of the observed transition.

Optical properties of $M_2[O_2CCCo_3(CO)_9]_{4-n}[O_2CR]_n$

The absorptions observed for $M_2[O_2CCCo_3(CO)_9]_{4-n}[O_2CR]_n$, where M is Cr, $n = 0$; where M is Mo, $n = 0, 1$, R is CH_3; where M is W, $n = 0$; in the UV-vis region, as well as those for the parent compounds are given in Table 1 and a representative example is shown in Fig. 2. Note that when M is Mo there is no significant difference in the intensity or energy of the lowest energy absorption for $n = 0$ and $n = 1$, R is CH_3. These data present an interesting problem. Both $M_2(O_2CMe)_4$ and $(CO)_9Co_3CMe$ exhibit absorptions in the UV-vis region but the extinction coefficients are fairly small. However, the cluster substituted compounds, $M_2[O_2CR]_4$, where M is Mo, W, but not Cr, have very intense absorptions in this range ($\epsilon = 6000-8000$ per $[(CO)_9Co_3C]$ frag-

Table 1
UV-vis spectra of $M_2[O_2CMe]_4$, $Co(CO)_9CMe$ and $M_2[O_2CCCo_3(CO)_9]_4$

M	R	L	Wavelength/nm	ϵ/cm^{-1} M^{-1}	Assignment	Ref.
$M_2[O_2CR]_4 \cdot L_2$						
Cr	Me	H_2O	476	120	$\delta \rightarrow \pi^*$	21
			333	200	$O(\pi) \rightarrow \pi^*$	
			270 (sh)	400	?	
			240 (sh)	1200	?	
Mo	*t*-Bu		436	100	$\delta \rightarrow \delta^*$	20
			296	10 000	$\delta \rightarrow \pi^*(CO_2)$	
W	*t*-Bu		378	19 400	$\delta \rightarrow \pi^*(CO_2)$	20
$Co(CO)_9CMe$						
			510	1400	$\sigma \rightarrow \sigma^*$	
			370	3300	$\sigma' \rightarrow \sigma^*$	
$M_2[O_2CCCo_3(CO)_9]_4$						
Cr		H_2O	520	4300	$[Co_3C]$	This work
			380	12 000	$[Co_3C]$	This work
			300	36 000	$\delta \rightarrow \sigma^*$	This work
Mo		$Co_3(CO)_9CO_2H$	536	31 000	$\delta \rightarrow \sigma^*$	This work
W			800	36 000	$\delta \rightarrow \sigma^*$	This work
$M_2[O_2CCCo_3(CO)_9]_3[O_2CMe]$						
Mo			572	22 000	$\delta \rightarrow \sigma^*$	This work

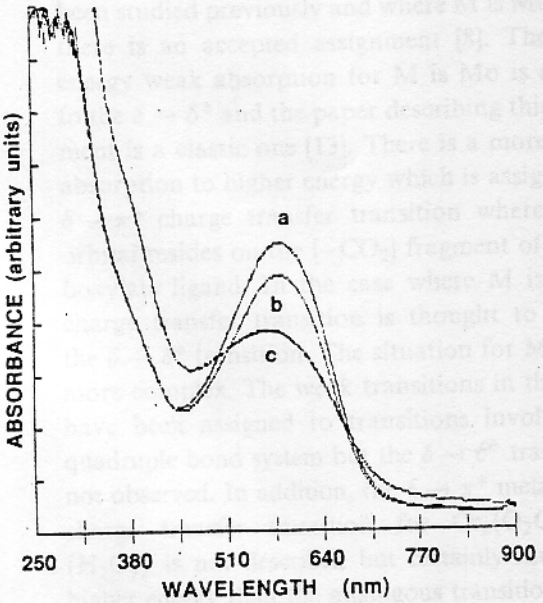

Fig. 2. The UV-vis spectra of (curve a) $Mo_2[O_2CCCo_3(CO)_9]_3[O_2CMe]$, (curve b) $Mo_2[O_2CCCo_3(CO)_9]_4$, and (curve c) $Mo_2[O_2CCCo_3(CO)_9]_4 \cdot [HO_2CCCo_3(CO)_9]_2$.

ment). Clearly, these are allowed transitions as opposed to the weak transitions of largely d–d character exhibited by the two parent compounds. How is one to understand these transitions?

The calculational challenge for these compounds is a formidable one. However, there is no real difficulty in applying approximate methods such as the Fenske–Hall treatment [11,12]. The result is an expression of the electronic structures of the component parts and the complete molecule in terms of a set of filled MOs. One might expect a comparison of MO energies and compositions to yield insight on the nature of the observed transition, but there are two fundamental problems with such an analysis. First, the virtual orbitals are exceedingly poor representations of the excited states and, second, there is a real possibility that two different transition metal centers may be directly involved in the excitation. Therefore, the choice of metal basis function exponents becomes crucial if energy differences are to be meaningful. In the Fenske–Hall method, choice of "oxidation state" is not well defined. Thus, for our purposes the calculations alone are even qualitatively ambiguous. In order to use the detail of the calculations, we need a source of accurate information on the energetics. Photoelectron spectroscopy, with an MO interpretation, provides such information for the two components of our complex system. For clarity, a brief review of the published PES data and MO models for the parent molecules is first presented.

The electronic structures of $M_2(O_2CCMe)_4$, M = Cr, Mo, W and $MeCCo_3(CO)_9$

The qualitative MO model for the quadruple bond is well known [8] and, as expected, the MOs associated with this bonding feature constitute the highest filled orbitals in $Mo_2(O_2CCMe)_4$. The highest filled MO (HOMO) and lowest unfilled MO (LUMO) are the δ bonding and δ^* antibonding orbitals (Fig. 3). The former is associated with the lowest ionizations in the molecule. This description is deceptively simple. For example, the results of PES studies [9] have shown that the primary bonding orbitals are the δ and π while the σ has a significant non-bonding component and lies at higher energy than expected. However, for our discussions the simple description is sufficient.

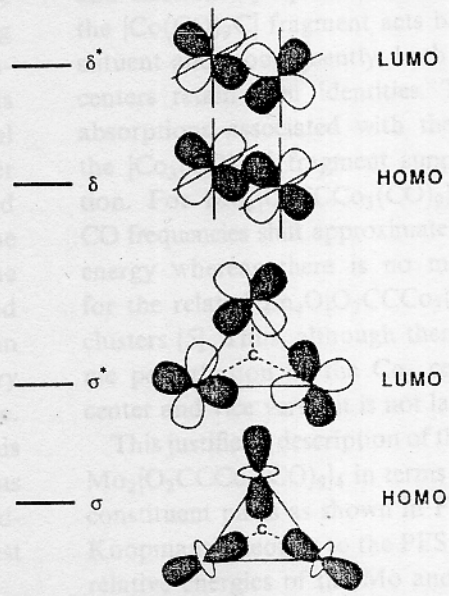

Fig. 3. A representation of the frontier orbitals of $Mo_2[O_2CMe]_4$ (top) and $Co_3(CO)_9CMe$ viewed down the C_3 axis (bottom).

The UV-visible spectra of these compounds have been studied previously and where M is Mo and W there is an accepted assignment [8]. The lowest energy weak absorption for M is Mo is assigned to the $\delta \rightarrow \delta^*$ and the paper describing this assignment is a classic one [13]. There is a more intense absorption to higher energy which is assigned to a $\delta \rightarrow \pi^*$ charge transfer transition where the π^* orbital resides on the $[-CO_2]$ fragment of the carboxylate ligand. In the case where M is W, the charge transfer transition is thought to obscure the $\delta \rightarrow \delta^*$ transition. The situation for M is Cr is more complex. The weak transitions in the visible have been assigned to transitions involving the quadruple bond system but the $\delta \rightarrow \delta^*$ transition is not observed. In addition, the $\delta \rightarrow \pi^*$ metal–ligand charge transfer transition for $Cr_2(O_2CCMe)_4 \cdot (H_2O)_2$ is not described but certainly must lie at higher energy than the analogous transitions of the heavier metals.

The situation with the tricobalt nonacarbonyl akylidyne complexes is a similar one. Although not to be found in undergraduate textbooks, the MO description of the bonding in compounds of this type is also thoroughly discussed in the literature [14]. Again the highest lying MOs are associated with the metal centers. There are two basic types of filled MOs lying at high energy having large metal character. One type is largely nonbonding with respect to the cluster core and is derived from the "t_{2g}" type orbitals on the metal centers. The other type is associated with cluster bonding including the trimetal cluster base and apical carbon to trimetal base, i.e. bonding of the CM_3 tetrahedron. The HOMO is a member of the second type being an a_1 symmetry MO involved substantially with M_3 bonding as indicated in Fig. 3. The LUMO is related but has a_2 symmetry and is antibonding with respect to the M_3 triangle. The results of several PES studies agree with this general analysis but do not give an unambiguous assignment of the two types of metal based bonding MOs that lie in the complex band at lowest ionization potential in the PE spectrum [15–18].

The UV-vis spectra are not as well understood as those for the quadruple bond compounds. It has been argued on an empirical basis that both the absorption at 510 nm and that at 370 nm in $Co_3(CO)_9CMe$ have the same final state which is represented by the LUMO (Fig. 3) [19]. The lowest energy transition is said to originate from the HOMO (substantially Co–Co bonding) whereas the latter originates from a related MO (substantially Co–C bonding). This interpretation is consistent with the observations on $H_3Fe(CO)_9CMe$ [18]. In this compound the orbital corresponding to the HOMO of $Co_3(CO)_9CMe$ is greatly stabilized by the FeHFe interactions and only a single well-defined absorption, shifted to the blue relative to the low energy absorption of the cobalt cluster, is observed. In any case, although we adopt this interpretation for the purposes of the discussion below, the conclusions arrived at below do not depend on the validity of the detailed assignment.

Empirical assignment of the intense $Mo_2[O_2CCCo_3(CO)_9]_4$ visible absorption

In $Mo_2[O_2CCCo_3(CO)_9]_4$ the $[Co_3(CO)_9C]$ cluster fragment replaces the Me group on $Mo_2[O_2CMe]_4$. Although possessing different steric and electronic properties than the methyl group, the $[Co(CO)_9C]$ fragment acts basically as a substituent and, consequently, both it and the $[Mo_2]$ centers retain their identities. The observed IR absorptions associated with the CO ligands on the $[Co_3(CO)_9C]$ fragment support this assumption. For $Mo_2[O_2CCCo_3(CO)_9]_4$ the Co bound CO frequencies shift approximately 2 cm^{-1} to lower energy whereas there is no measurable change for the related $Zn_4O[O_2CCCo_3(CO)_9]_6$ cluster of clusters [5]. Thus, although there is some electronic perturbation of the Co_3 center by the Mo_2 center and vice versa, it is not large.

This justifies a description of the frontier orbitals $Mo_2[O_2CCCo_3(CO)_9]_4$ in terms of the MOs of its constituent parts as shown in Fig. 4. By applying Koopmans' theorem to the PES data (Table 2) the relative energies of the Mo and Co levels can be fixed as shown. The UV-vis data on the parent

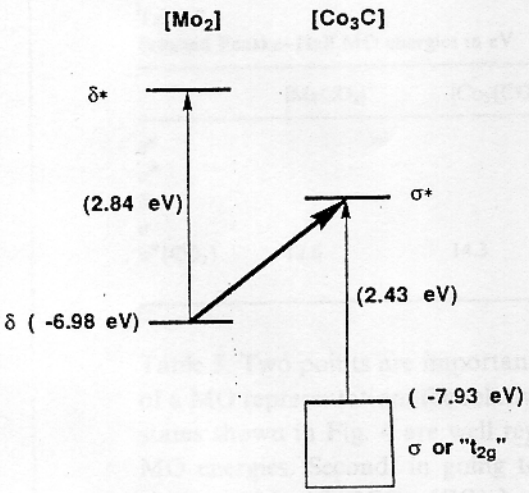

Fig. 4. A schematic energy level diagram for $Mo_2[O_2CCCo_3(CO)_9]_4$ using the data for the parent metal compounds given in Tables 1 and 2.

compounds are then used to fix the excited state energies relative to the ground state. As noted above, the latter are associated with the LUMOs of the two parent molecules but the energies are empirical and do not depend on the identification of any MOs with the transition. The ambiguity of the location of the ionization corresponding to the HOMO of $[Co_3(CO)_9C]$ fragment within the complex band is noted on the diagram. With these assumptions, the σ^* level lies between the δ and δ^* levels whereas the δ level lies between the σ and σ^* levels. This suggests that the allowed transition giving rise to the intense visible absorption of $Mo_2[O_2CCCo_3(CO)_9]_4$ may be due to a $\delta \rightarrow \sigma^*$ transition between the two different clusters. For purposes of comparing energies, the σ level is taken

Table 2
Lowest vertical ionization potentials in the gas phase for $M_2[O_2CMe]_4$, where M is Cr, Mo and W, and $Co_3(CO)_9CMe$

M	IP/eV	Assignment	Ref.
$M_2[O_2CMe]_4$			
Cr	8.69	δ	22
Mo	6.98	δ	23
W	6.04	δ	24
$Co_3(CO)_9CMe$			
	7.93	σ or "t_2g"	18

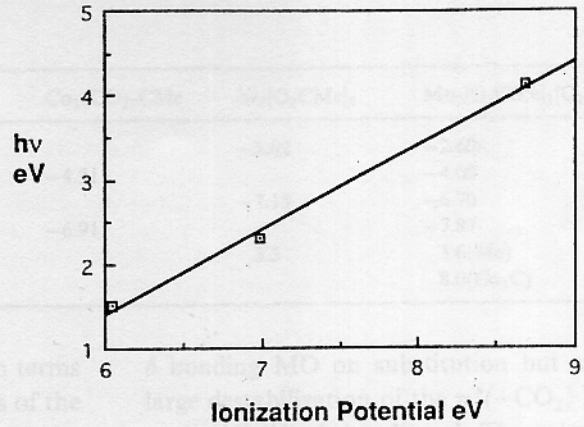

Fig. 5. A plot of $\delta \rightarrow \sigma^*$ band maxima vs. δ ionization potential for $M_2[O_2CMe]_4$, where M is Cr, Mo and W.

to correspond to the lowest ionization defined by a shoulder on the first band of the $[Co_3(CO)_9C]$ fragment. This gives a calculated energy of 1.48 eV for the transition versus the observed band position of 2.17 eV. Obviously, the agreement is not very good and this emphasizes the fact that in applying a Koopmans' theorem to the metal ionizations one assumes a cancellation of errors, e.g. differences in relaxation behavior are minor. This raises a question of whether such errors invalidate the assignment.

One way of reducing these errors and thereby checking the assignment is to empirically vary the energy of one cluster manifold with respect to the other. Hence, as will be described elsewhere, we have synthesized related Cr and W derivatives of $Mo_2[O_2CCCo_3(CO)_9]_4$ namely $Cr_2[O_2CCCo_3(CO)_9]_4$ and $W_2[O_2CCCo_3(CO)_9]_4$. Now if the above assignment is correct, one would expect to see a linear correlation between the ionization potential of the $M_2[O_2CCCo_3(CO)_9]_4$ molecules and the energy of the cluster–cluster ligand charge transfer band. Just such a correlation is demonstrated in Fig. 5. Clearly, the data are consistent with the assignment.

Another test is to compare the observations with calculated eigenvalues for the parent molecules as well as the cluster-of-clusters itself. The pertinent values resulting from the application of the Fenske–Hall method for M is Mo are given in

Table 3
Selected Fenske–Hall MO energies in eV

	$[MeCO_2]^-$	$[Co_3(CO)_9CCO_2]^-$	$Co_3(CO)_9CMe$	$M_2[O_2CMe]_4$	$Mo_2[O_2CMe]_3[O_2CCCo_3(CO)_9]$
δ^*				−3.02	−2.60
σ^*			−4.31		−4.08
δ				−7.15	−6.70
σ			−6.91		−7.87
$\pi^*(CO_2)$	12.6	14.3		3.3	3.6(Me) 8.0(Co_3C)

Table 3. Two points are important. First, in terms of a MO representation, the relative energies of the states shown in Fig. 4 are well represented by the MO energies. Second, in going to the cluster-of-clusters, $Mo_2[O_2CCCo_3(CO)_9]_4$, there are no large changes in the MO energies (or compositions for that matter) associated with the component clusters.

However, there is alternative assignment of the visible absorption in $Mo_2[O_2CCCo_3(CO)_9]_4$ that is reasonable and, as will be pointed out, a variation on the one just discussed. That is, $Mo_2[O_2CMe]_4$ compounds exhibit an intense metal–ligand charge transfer band at higher energies which has been assigned to a $\delta \rightarrow \pi^*$ metal-to-ligand charge transfer (see Table 1 and above) [8]. Further, on using the oxylate ligand to form bridged species, this absorption is considerably red-shifted and appears in the visible [20]. This is reasonable as $H_2C_2O_2$ is a stronger acid than CH_3COOH and the π manifold of the anion of the former will be at lower energy. Hence, an alternative assignment for $Mo_2[O_2CCCo_3(CO)_9]_4$ is $\delta \rightarrow \pi^*(-CO_2)$ with a red shift caused by a substituent effect resulting from the replacement of an alkyl group with the $[Co_3(CO)_9C]$ fragment. The correlation of the absorption maxima with the PES data is consistent with this interpretation as the energy of this absorption should also track the $[M_2]$ fragment ionization energy for a given carboxylate ligand. There is a problem with this assignment, however, as for MO the replacement of an alkyl group with the $[Co_3(CO)_9C]$ fragment requires a red-shift of 1.88 eV. As shown in Table 3, the MO calculations do show a small destabilization of the δ bonding MO on substitution but also show a large destabilization of the $\pi^*(-CO_2)$ MO associated with the cluster ligand. The calculations are consistent with the fact that the substitution of the $[Co_3(CO)_9C]$ fragment for the Me fragment leads to a significant reduction in the acidity of $Co_3(CO)_9CO_2H$, i.e. the π manifold of the $[-CO_2]$ fragment is raised in energy [5]. These points suggest that the large red-shift required by this assignment may be unreasonable.

There is certainly electronic coupling between the $[Mo_2]$, $[-CO_2]$, and $[Co_3C]$ fragments in $Mo_2[O_2CCCo_3(CO)_9]_4$. It is perhaps incorrect, then, to describe the excited state associated with the intense absorption in terms of MOs exclusively associated with either the $[-CO_2]$ or $[Co_3C]$ fragments. That is, both of the two suggested assignments for the intense absorption exhibited by the clusters of clusters require the participation of the $[Co_3(CO)_9C]$ fragment. In one case it is direct whereas in the other it is indirect.

Conclusions

The analysis of the UV-vis absorption spectrum of the clusters-of-clusters, $M_2[O_2CCCo_3(CO)_9]_4$, with the aid of PES and UV-vis data on the parent clusters supports the assignment of this intense observed absorption to a new type of metal-to-ligand charge transfer transition. It is a transition which originates in a state associated with the $[M_2]$ core but ends up in a state associated with the $[M'_3C]$ core of the cluster substituent. The energy of this absorption can be varied in a predictable fashion by changing the identity of the M metal.

It is logical to expect, then, that change in the $[M_3'C]$ core should also change the energy of the charge transfer absorption. To test this prediction further synthetic work is required.

Acknowledgments

The support of the National Science Foundation and the Petroleum Research Foundation administered by the American Chemical Society are gratefully acknowledged.

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