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Gas-Phase UV Photoelectron Spectra of Some Edge-Bridged Decacarbonyltriosmium Clusters

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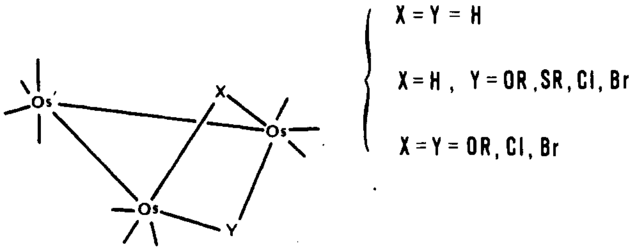
The gas-phase He I and He II excited UV PE spectra of several $(X)(Y)Os_3(CO)_{10}$ cluster derivatives (X, Y = H, OR, SR, Cl, Br) are reported. A qualitative discussion of the spectral data has been made on the basis of MOs that predominantly represent Os–Os bonds, t_{2g}-like nonbonding metallic pairs, or $(\mu\text{-}X)(\mu\text{-}Y)Os_2$ bridge bonds. Investigation of the He II spectrum was crucial for assignment. The similarity found between the spectrum of $H_2Os_3(CO)_{10}$ and those of the two series $(H)(Y)Os_3(CO)_{10}$ and $(Y)_2Os_3(CO)_{10}$ points to a very similar bonding pattern in all the compounds. Evidence for a direct weak interaction between the two bridged osmium atoms via the t_{2g}-like set has been reported. This source of Os–Os bonding progressively reduces its importance on going from $H_2Os_3(CO)_{10}$ to $(H)(Y)Os_3(CO)_{10}$ and $(Y)_2Os_3(CO)_{10}$.

Introduction

Trinuclear osmium clusters of formula $(X)(Y)Os_3(CO)_{10}$ (where X, Y = H or three-electron-donor group) can be easily prepared via oxidative addition of several ligands to trimetallic osmium carbonyl clusters.[2] High yields and short reaction times are obtained when $H_2Os_3(CO)_{10}$[2c] or $Os_3(CO)_{10}$ (c-C_6H_8)[2d] replace $Os_3(CO)_{12}$ as starting material.

Single-crystal structural investigations (both X-ray and neutron diffraction) have been carried out extensively, and the same edge-bridging arrangement has been found for a large set of ligands.[3]



The synthetic and diffractometric efforts on this class of molecules have not been paralleled by adequate attention from the spectroscopic and theoretical points of view. As a consequence, the bonding scheme in these compounds is far from being well understood, in particular when the $(\mu\text{-}X)(\mu\text{-}Y)Os_2$ moiety is concerned. The empirical EAN rule dictates a formal double bond (A), a single bond (B), and no bond (C) between the two metallic centers, depending on the number of electrons that the bridging ligands donate to the cluster.

The experimental Os–Os distances parallel the expected trend, but the differences among A, B, and C can also be related to the steric requirements of the bridging ligand. However, it is likely that the dimensions of the $(\mu\text{-}X)(\mu\text{-}Y)Os_2$ moiety are determined by both the steric and electronic properties of the bridging ligands. On the other hand, recent IR studies provided indirect support for the hypothesis that there is not a direct Os–Os bond in such bridges.[4]

Recently we have shown that the gas-phase UV photoelectron spectroscopy (UV PES) can be a useful tool in describing the electronic properties of cluster compounds, especially when it is coupled with quantum-mechanical calculations.[5] Two different PE studies on $H_2Os_3(CO)_{10}$ have been reported recently,[6,7] both discarding the hypothesis of an Os–Os double bond in favor of a diborane-like structure. Sherwood and Hall[6] have also reported theoretical results, and on this basis they claimed the existence of a weak Os–Os direct interaction arising from in-phase contributions of t_{2g}-like metallic orbitals.

Herein we report a comprehensive PES study on a series of derivatives with several bridging ligands, namely H, OR, SR, Cl, and Br; the purpose of this paper is to relate the PE spectral changes along a series of ligands differing in their atomic dimensions and donor properties.

Experimental Section

The (H)(Y)–Os_3 (hereafter $Os_3 = Os_3(CO)_{10}$) derivatives (Y = OEt, SEt, S-*i*-Bu, S-*t*-Bu, Cl) have been prepared with (c-C_6H_8)–Os_3 as an intermediate.[2d] The $(Y)_2$–Os_3 complexes (Y = OEt, Cl, Br) have been synthesized by direct reaction of $Os_3(CO)_{12}$ with ethanol[2a] or a halogen.[2b] Their purity was checked by IR and mass spectroscopy.

He I (21.217 eV) and He II (40.814 eV) excited PE spectra were run on a Perkin-Elmer PS-18 spectrometer using a heated inlet probe system. They were taken in the 85–100 °C temperature range, and no decomposition evidence has been observed. The spectrometer was connected on-line with a Minc-23 computer (Digital Equipment) by an interface built in our laboratory. Data acquisition was carried out by several sweeps (3–7) over 500 distinct channels. Typical sweep time amounts to 5–10 min. The ionization energy (IE) scale was calibrated by reference to peaks due to admixed inert gases (Xe, Ar) and to the $1s^{-1}$ He ionization.

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(1) (a) University of Padova. (b) CNR of Padova. (c) University of Torino.

(2) (a) Azam, K. A.; Deeming, A. J.; Kimber, R. E.; Shukla, P. R. *J. Chem. Soc., Dalton Trans.* **1976**, 1853. (b) Deeming, A. J.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc. A* **1970**, 897. (c) Jackson, W. G.; Johnson, B. F. G.; Lewis, J.; Kelland, J. W.; Schorpp, K. T. *J. Organomet. Chem.* **1975**, *88*, C17. (d) Bryan, E. G.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1977**, 1328.

(3) (a) Broach, R. W.; Williams, J. M. *Inorg. Chem.* **1979**, *18*, 314. (b) Churchill, M. R.; Hollander, F. J.; Hutchinson, J. P. *Ibid.* **1977**, *16*, 2697. (c) Allen, V. F.; Mason, R.; Hitchcock, P. B. *J. Organomet. Chem.* **1977**, *140*, 297. (d) Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* **1980**, *19*, 2391. (e) Churchill, M. R.; Lashewycz, R. A. *Ibid.* **1979**, *18*, 1926. (f) Churchill, M. R.; Lashewycz, R. A. *Ibid.* **1979**, *18*, 3261. (g) Einstein, F. W. B.; Jones, T.; Tyers, K. G. *Acta Crystallogr., Sect. B* **1982**, *B38*, 1272. (h) Aleksandrov, G. G.; Zol'nikova, G. P.; Krickaja, I. I.; Struchkov, Ju. T. *Koord. Khim.* **1980**, *6*, 626.

(4) (a) Oxton, I. A. *J. Mol. Struct.* **1982**, *79*, 243. (b) Kettle, S. F. A.; Stanghellini, P. L. *Inorg. Chem.* **1982**, *21*, 1447.

(5) (a) Ajò, D.; Granozzi, G.; Tondello, E.; Fragalà, I. *Inorg. Chim. Acta* **1979**, *37*, 191. (b) Granozzi, G.; Tondello, E.; Ajò, D.; Casarin, M.; Aime, S.; Osella, D. *Inorg. Chem.* **1982**, *21*, 1081. (c) Granozzi, G.; Casarin, M.; Aime, S.; Osella, D. *Ibid.* **1982**, *21*, 4073. (d) Granozzi, G.; Tondello, E.; Ajò, D.; Faraone, F. *J. Organomet. Chem.* **1982**, *240*, 191. (e) Granozzi, G.; Tondello, E.; Casarin, M.; Aime, S.; Osella, D. *Organometallics* **1983**, *2*, 430. (f) Granozzi, G.; Tondello, E.; Bertoncello, R.; Aime, S.; Osella, D. *Inorg. Chem.* **1983**, *22*, 744. (g) Granozzi, G.; Bertoncello, R.; Acampora, M.; Ajò, D.; Aime, S.; Osella, D. *J. Organomet. Chem.* **1983**, *244*, 383.

(6) Sherwood, D. E.; Hall, M. B. *Inorg. Chem.* **1982**, *21*, 3458.

(7) (a) Green, J. C.; Mingos, D. M. P.; Seddon, E. A. *Inorg. Chem.* **1981**, *20*, 2595. (b) Green, J. C.; Seddon, E. A.; Mingos, D. M. P. *J. Chem. Soc., Chem. Commun.* **1979**, 94.

0020-1669/83/1322-3899$01.50/0

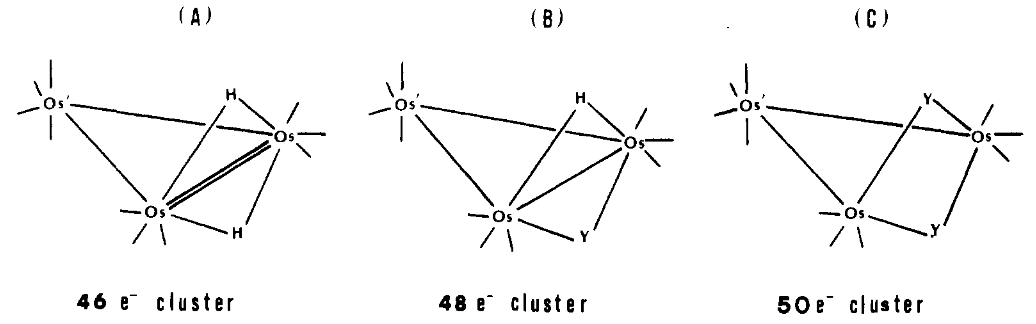

Table I. Ionization Energies (eV) of the $(X)(Y)Os_3(CO)_{10}$ Clusters

$(H)_2$	(H)(SEt)	(H)(S-*i*-Bu)	(H)(S-*t*-Bu)	(H)(OEt)	$(OEt)_2$	(H)(Cl)	$(Cl)_2$	$(Br)_2$
7.82 (A)	7.64 (A)	7.63 (A)	7.58 (A)	7.62 (A)	7.50 (A)	7.80 (A)	7.78 (A)	7.70 (A)
8.51 (A′)	8.17 (A′)	8.19 (A′)	8.17 (A′)	8.19 (A′)	8.00 (A′)	8.40 (A′)	8.34 (A′)	8.25 (A′)
8.86 (B)	8.54 (B)	8.57 (B)	8.58 (B)	8.64 (B)	8.50 (B)	8.87 (B)	8.90 (B)	8.75 (B)
9.36 (B′)	9.23 (B′)	9.22 (B′)	9.23 (B′)	9.24 (B′)	9.30 (B′)	9.35 (B′)	9.73 (B′)	9.33 (B′)
10.40 (B″)	9.77 (B″)	9.80 (B″)	9.76 (B″)	9.94 (B″)	9.94 (B″)	9.81 (B″)	10.35 (B″)	9.90 (B″)
10.61 (B‴)	10.06 (B‴)	10.00 (B‴)	9.98 (B‴)	10.49 (B‴)	10.13 (B‴)	10.23 (B‴)	11.17 (C)	10.40 (B‴)
10.84 (B⁗)	10.53 (C)	10.47 (C)	10.43 (C)	11.10 (C)	11.12 (C)	10.72 (C)	12.27 (C′)	11.60 (C)
11.91 (C)	10.93 (C′)	10.85 (C′)	10.79 (C′)	12.04 (C′)	12.97 (D)	12.23 (C′)	13.09 (C″)	12.47 (C′)
12.58 (C′)	12.20 (C″)	11.90 (C″)	11.88 (C″)	12.91 (D)		13.00 (C″)		

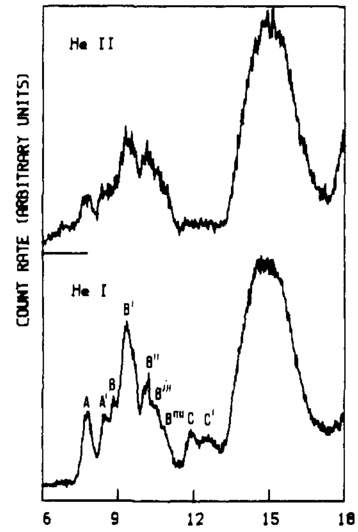

Figure 1. He I and He II excited PE spectra of $H_2Os_3(CO)_{10}$.

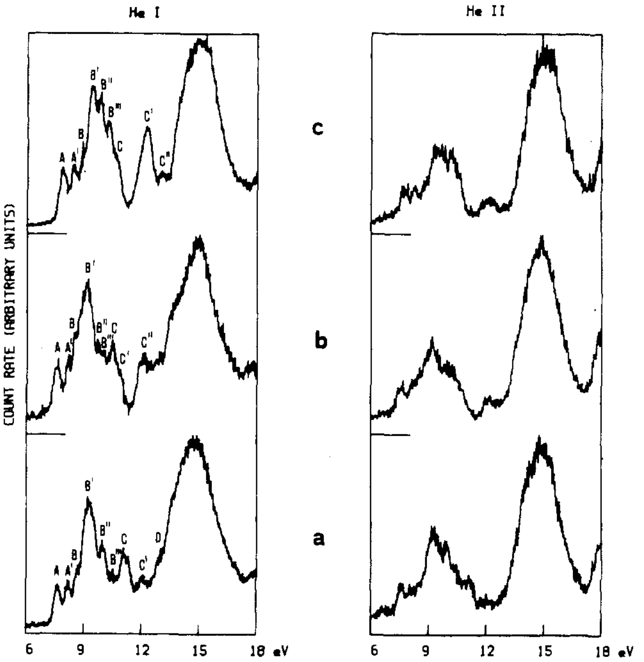

Figure 2. He I and He II excited PE spectra of $(H)(Y)Os_3(CO)_{10}$ clusters: (a) Y = OEt; (b) Y = SEt; (c) Y = Cl.

Results

The He I and He II excited spectra of $(H)_2$–Os_3, (H)-(Y)–Os_3, and $(Y)_2$–Os_3 are reported in Figures 1, 2, and 3, respectively. The pertinent IE values of the reported spectra and other derivatives not shown in the figures are collected in Table I. The gas-phase spectrum of $(H)_2$–Os_3 (Figure 1) has already been reported in two different papers,[6,7] and our results are in agreement. The condensed-phase UV PE spectra of several bridged osmium cluster derivatives have also been recently reported;[8] however, their low resolution ($\simeq$0.3 eV) and solid-state effects do not allow an accurate comparison with our gas-phase results; their results on the spectrum of $(H)(OCH_3)$–Os_3 roughly reproduce our high-resolution ones.

Reference to the previous results of $Os_3(CO)_{12}$[5f,6,7] and $(H)_2$–Os_3[6,7] suggests dividing the spectra into four distinct IE regions for discussion purposes (i.e.: a, 6–8.5 eV; b, 8.5–10.5 eV; c, 10.5–13.0 eV; d, 13.0–18 eV). The bands in each region are labeled accordingly. Along the studied series, no significant changes are observed in region a (two well-resolved bands A and A′) and in region d, which shows a broad envelope centered around 15 eV in all the cases. On the contrary, marked spectral differences are clearly evident in regions b and c, reflecting the nature of the various bridging ligands. The He II excited spectra show very pronounced relative intensity variations that will assist us in determining the participation of ligand and/or metallic AOs to the corresponding MOs.

In this context it is useful to recall the empirical arguments (within the Gelius model[9]) that will be adopted in the following discussion:[10] the ligand 3p and 4p and hydrogen 1s valence AOs decrease their photoionization cross sections with respect to the ligand 2p AOs on going from the He I to the He II source whereas metallic 5d AOs behave in the opposite manner. The low-IE region (6.5–8.0 eV) of the He II spectra suffers from high noise and low resolution because of the photoelectrons originating from the same orbitals at 15 eV by

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(8) Brucker, C. F.; Rhodin, T. N.; Wijeyesekera, S.; St. George, G.; Shapley, J. R. *J. Chim. Phys. Phys.-Chim. Biol.* **1981**, *78*, 897.

(9) Gelius, U. In "Electron Spectroscopy"; Shirley, D. A., Ed.; North-Holland Publishing Co.: Amsterdam, 1972; p 311.

(10) Rabalais, J. W. "Principles of Ultraviolet Photoelectron Spectroscopy"; Wiley: New York, 1977; p 335.

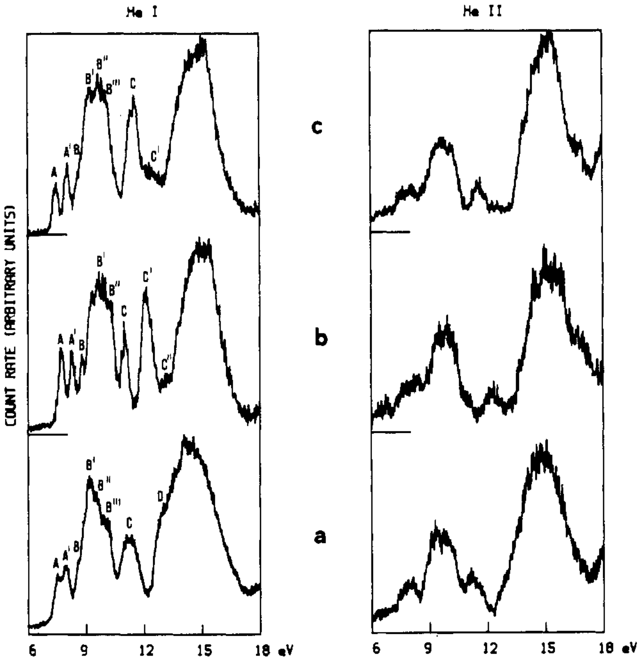

Figure 3. He I and He II excited PE spectra of $(Y)_2Os_3(CO)_{10}$ clusters: (a) Y = OEt; (b) Y = Cl; (c) Y = Br.

operation of a small amount of the He IIβ radiation (48.40 eV).

Discussion

In order to get more insight into the discussion of these spectra, we find it useful to recall the results obtained for the triangulo $M_3(CO)_{12}$ (M = Ru, Os), for which a satisfactory description of the electronic structure has been attained through the use of the PE[5a,5f,6,7] and theoretical (EHT,[11] CNDO,[5a] Fenske–Hall,[6] DV-Xα[12]) techniques.

A qualitative valence-level diagram of $M_3(CO)_{12}$ based on the PE findings is reported in Figure 4, indicating the parentage of the cluster MOs with the $M(CO)_4$ (C_{2v}) fragment orbitals (indicated as split in e_g-like and t_{2g}-like orbitals). The M–M bonding MOs (a_1' and e' in D_{3h}) arise from the high-lying "e_g" components whereas the "t_{2g}" nonbonding set (which includes back-bonding interactions with the carbonyl framework) is split into two subsets ("$t_{2a}{}^{a}$" and "$t_{2g}{}^{b}$"), antibonding and bonding with respect to the M–M interactions.

The PE spectrum of $(H)_2$–Os_3 can be easily interpreted (see level diagram in Figure 4) when two three-center two-electron Os–H–Os bonds are associated to bands C and C′ in Figure 1 (note the intensity decrease of these bands in the He II spectrum). Bands A and A′ in region a represent the two remaining Os′–Os bonding levels, and in region b the "$t_{2g}{}^{a}$–$t_{2g}{}^{b}$" splitting is still evident; the presence of several resolved components associated with "$t_{2g}{}^{b}$" ionizations (bands B″, B‴, and B⁗ in Figure 1 and Table I) probably reflects different "t_{2g}–t_{2g}" bonding interactions induced by the different Os′–Os and Os–Os distances. The common parentage of these bands and the "$t_{2g}{}^{b}$" ones of $Os_3(CO)_{12}$ is demonstrated by their similar He I/He II behavior (i.e. "$t_{2g}{}^{b}$" components increase their intensity vs. the "$t_{2g}{}^{a}$" ones at the He II wavelength).

As a starting point for the discussion of the spectra reported in this paper, we can assume that spectral regions a and b maintain their predominant character in the whole series; i.e., they contain ionizations from Os′–Os bonding MOs and from t_{2g}-like nonbonding MOs, respectively. This is equivalent to assuming that the bonding MOs of the $(X)(Y)Os_2$ bridge are restricted to region c. This hypothesis is summarized in the qualitative bonding schemes reported in Figure 4 for the two cases $(H)(Y)$–Os_3 and $(Y)_2$–Os_3. The subsequent analysis of the different spectral regions will test this assumption and will provide an indication of the relative energies of the Os–H–Os and Os–Y–Os bonding MOs.[13]

Os′–Os Bonding Levels. There is no doubt in assigning bands A and A′ of all the spectra (Figures 2 and 3) to ionizations from the two Os′–Os bonding MOs. The energy difference between them is almost unchanged along the examined series ($\overline{\Delta IE} \simeq 0.6$ eV). The small perturbations of these bands along the series (Figure 5) probably indicate different electron densities in the trimetallic triangles, depending on the donor properties of the bridging ligands. In particular, the lowest IE values pertain to the $(OEt)_2$–Os_3 derivative, in agreement with the very large donor power expected for the OEt ligand. Similarly, but in an opposite way, the $(H)_2$–Os_3 complex shows the highest IE values for the Os′–Os bonding levels. These long-range transmissions of the electronic effects of the bridging ligands to the Os′–Os bonds are related to second-order perturbations induced by electron transfer from the donor ligand to metal–metal antibonding MOs.

t_{2g}-like Nonbonding Levels. A detailed assignment of region b is an impossible task because of the large number of overlapping bands (at least nine t_{2g}-like ionizations) expected within 2 eV. A reasonable qualitative assignment relates bands B and B′ of all the spectra to the "$t_{2g}{}^{a}$" ionizations and the higher IE components to the "$t_{2g}{}^{b}$" ones. The He I/He II intensity changes support these assignments since the higher IE components of region b invariably increase their intensity with respect to the lower IE ones in the same way as in $(H)_2$–Os_3 (Figure 1). A trend toward a progressive reduction of the "$t_{2g}{}^{a}$–$t_{2g}{}^{b}$" splitting on going from $(H)_2$–Os_3 to $(H)(Y)$–Os_3 and $(Y)_2$–Os_3 is clearly evident (Figures 1, 2, and 3 and Table I) coupled with a reduction of the number of resolved "$t_{2g}{}^{b}$" components. This is particularly true for $(Cl)_2$–Os_3 and $(Br)_2$–Os_3, where an unresolved "t_{2g}" broad band is found (Figure 3). Since it has been proposed that an extra source of Os–Os bonding in $(H)_2$–Os_3 is related to the "$t_{2g}{}^{a}$–$t_{2g}{}^{b}$" splitting,[6] the observed trend could be taken as an indication of a progressive reduction of the Os–Os direct interaction; this view is consistent with the trend of the experimental Os–Os distances. Furthermore, since these bonding contributions are expected to be small, the mentioned difficulty concerning the interpretation of the diffractometric data in terms of the EAN rule is dismissed. This behavior does relate to the charge transfer for the bridging ligand to the cluster, but the actual mechanism cannot be extracted from the reported PE data. As a tentative explanation, we suggest that this charge transfer would be assisted by virtual Os–Os antibonding levels and that some mixing of the donor orbitals with occupied "t_{2g}" levels occurs. Both mechanisms should lead to a decrease in the energy differences between the "$t_{2g}{}^{a}$–$t_{2g}{}^{b}$" sets: an electron enrichment of the metallic centers would produce a more marked back-donation to the carbonyl framework with a consequent stabilization of the "$t_{2g}{}^{a}$" set (which is the preferential set to back-bond). On the contrary, the "$t_{2g}{}^{b}$" set would be more destabilized by the mixing with the inner ligand orbitals than the outer "$t_{2g}{}^{a}$" one.

Bridge-Bonding Levels. Region c of all the spectra includes ionizations from MOs that are mainly localized on the bridging atoms. This statement is clearly supported by (i) the strong spectral changes along the examined series and (ii) the marked

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(11) Schilling, B. E. R.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3456.

(12) Manning, M. C.; Trogler, W. C. *Coord. Chem. Rev.* **1981**, *38*, 89.

(13) The spectral region d consists of a very broad and featureless envelope containing the ionizations from inner levels primarily localized on the carbon groups (5σ, 1π, and 4σ of free CO) and on the bridging ligands. The analysis of this region will be omitted in the following discussion since it does not furnish useful information.

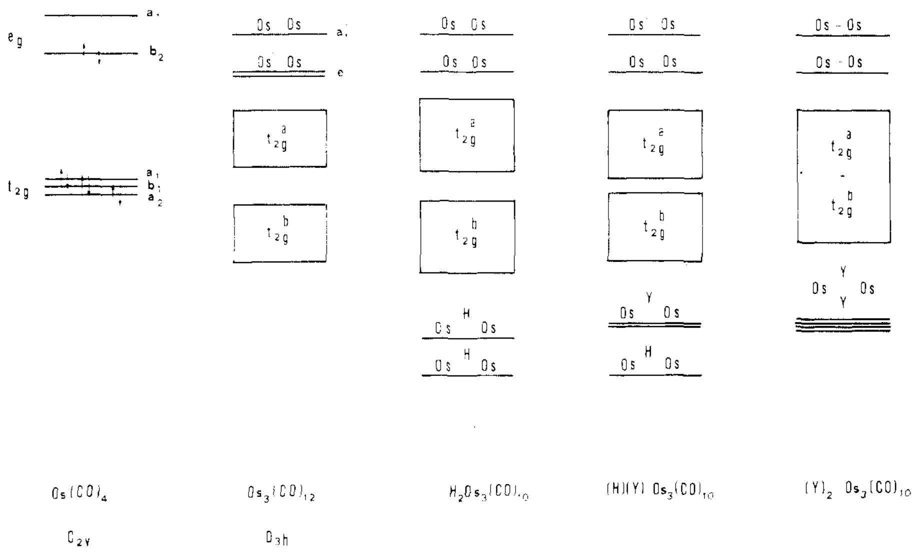

Figure 4. Qualitative outer-level diagram for the Os(CO)$_4$ fragment and for Os$_3$(CO)$_{12}$, H$_2$Os$_3$(CO)$_{10}$, (H)(Y)Os$_3$(CO)$_{10}$, and (Y)$_2$Os$_3$(CO)$_{10}$ clusters.

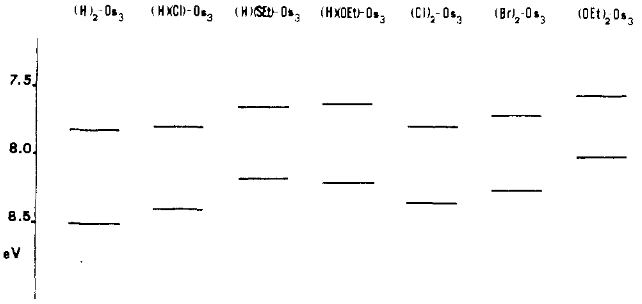

Figure 5. Experimental correlation diagram for outer A and A′ PE bands of the studied cluster.

intensity decrease of the bands contained in this region when the He II source is adopted. The second point is most evident for the halogen-bridged derivatives (Figures 2 and 3). Furthermore, the trend of the IEs of these bands parallels that expected on the basis of the electronegativity character of the bridging atoms; actually, bromine-based MOs are destabilized with respect to the chlorine ones (see Figure 3) in a similar way as the sulfur-based MOs behave with respect to the oxygen ones (see Figure 2). The above-mentioned electronegativity arguments coupled with an accurate analysis of the He I/He II changes allow us to propose the following assignment. In (H)(OEt)–Os$_3$ (Figure 2) we suggest relating band C and its shoulder C′ to the ionizations from the two MOs representing the three-center four-electron Os–O–Os bond whereas band C″ we take to represent the two-electron Os–H–Os bond; this latter statement is supported by intensity arguments and by comparison with the data for (H)$_2$–Os$_3$ (Figure 1). On the other hand, the analysis of the spectrum of (OEt)$_2$–Os$_3$ (Figure 3) eliminates any doubt about the proposed assignment since band C″ disappears in favor of a broadening of band C, representing now two Os–O–Os bonds. The same comparison also suggests relating the shoulders D in both spectra to inner MOs of the OEt groups, probably the C–O and C–H bonding σ MOs. According to these data the two Os–O–Os bonds are very close in energy and are mainly composed of the two 2p oxygen lone pairs (the third oxygen lone pair has predominant 2s character and does not interact significantly with the metallic centers). Similarly, band C and its shoulder C′ of the spectra of the (H)(SR)–Os$_3$ derivatives are related to the two Os–S–Os bonding MOs; their IE values lie very close to the "t$_{2g}^{b}$" ionizations, but their He II behavior allows us to distinguish them with enough confidence. The He I trend of the bands C and C′ along the series (H)(SEt)–Os$_3$, (H)(S-*i*-Bu)–Os$_3$, and (H)(S-*t*-Bu)–Os$_3$ (Table I) is in line with the expected one on the basis of the electronic effect of the substituent; along the same series the broad and ill-resolved band C″ increases in intensity and shifts toward lower IEs (Table I), suggesting a relationship to ionization localized in the σ framework of the SR bridging ligand. Accordingly, it is not possible to detect separately the band representing the Os–H–Os band in the (H)(SR)–Os$_3$ derivatives.

A complication is encountered when the spectra of the halogen-bridged derivatives are considered: in the same region c, ionizations are expected deriving from the additional electron pair that each halogen atom carries. Qualitatively, this electron pair should not be heavily involved in the bonding with the metallic centers and should behave as a pure lone pair. The real situation is much more complicated as it can be seen by the analysis of the theoretical (SCF-Xα-SW) and PE results[14] obtained for the related system (μ-Cl)$_2$–[Rh(CO)$_2$]$_2$: the PE data, in excellent agreement with the theoretical results, unequivocally show that the six MOs having predominant Cl 3p character split into three subsets (1:4:1), the first of them being the only one with scarce metal participation (essentially 3p nonbonding pair).

These results fit with our data on (Cl)$_2$–Os$_3$ (Figure 3): bands C, C′, and C″ (at 11.17, 12.27, and 13.09 eV, respectively) are to be related with the bands found at 11.29, 12.39, and 13.41 eV in the spectrum of the Rh dimer.[14] The He II data, which dictate the largest intensity decrease for band C, are also similar in the two cases. The (Br)$_2$–Os$_3$ case (Figure 3) can be easily related to the (Cl)$_2$–Os$_3$ one if it is assumed that the 4p lone-pair bromine band (that corresponding to band C in the chlorine derivative) is located (and not separately visible) under the broad t$_{2g}$-like envelope. On the other hand, this shift toward lower IE is clearly seen for the two remaining bands C and C′; as a further consequence of this shift, the higher IE component of the 4p bromine-based MOs (band C′) is better resolved than the corresponding 3p chlorine one. The assignment of the spectrum of (H)(Cl)–Os$_3$ is consistent with the above results: we regard shoulder C and band C′ (Figure 2) as chlorine-based MOs whereas band C″ should be associated to the Os–H–Os bonding MO. If this latter assignment is correct, it would imply that the IE of the Os–H–Os bonding

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(14) (a) Nixon, J. F.; Suffolk, R. J.; Taylor, M. J.; Norman, J. G., Jr.; Hoskins, D. E.; Gmur, D. J. *Inorg. Chem.* **1980**, *19*, 810. (b) Norman, J. G., Jr.; Gmur, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 1446.

MO suffers significant changes (i.e. 12.04 eV in (H)(OEt)–Os_3 and 13.00 eV in (H)(Cl)–Os_3) according to the nature of the bridgehead atom.

Conclusion

The cluster derivatives reported in this study are probably the most complicated molecular systems so far studied by gas-phase PES. In our opinion, this study represents a challenge to the PE technique, from both the experimental and the interpretative points of view.

In spite of the high molecular complexity (about 15–20 MOs in the higher valence region), a qualitative discussion of the spectral data is possible on the basis of molecular orbitals that predominantly represent Os′–Os bonds, t_{2g}-like nonbonding pairs, or (μ-X)(μ-Y)Os_2 bridge bonds. In this respect the use of the He II ionizing source was of crucial importance in order to discern between bands relating to MOs having high metal "d" contribution and those mainly localized on the bridging heteroatoms.

The most interesting result deriving from this study is the similarity found between the PE spectra of $(H)_2$–Os_3, (H)(Y)–Os_3, and $(Y)_2$–Os_3 derivatives, which points to very similar bonding schemes. This would imply, in contrast to the simple EAN arguments, that there is not a net direct interaction between the bridged Os atoms in either case, but it allows the existence of a weak extra source of Os–Os interaction via the t_{2g}-like set that progressively reduces its importance on going from $(H)_2$–Os_3 to (H)(Y)–Os_3 and $(Y)_2$–Os_3. In our opinion, the present data support the "t_{2g}–t_{2g}" bond theory proposed by Sherwood and Hall[6] for $(H)_2$–Os_3. Furthermore, the experimental data clearly show that the bridge-bonding MOs are essentially composed of the AOs of the bridging atoms with their typical IEs.

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Registry No. $(H)_2Os_3(CO)_{10}$, 41766-80-7; $(H)(SEt)Os_3(CO)_{10}$, 23733-18-8; $(H)(S\text{-}i\text{-}Bu)Os_3(CO)_{10}$, 87569-04-8; $(H)(S\text{-}t\text{-}Bu)Os_3(CO)_{10}$, 59088-69-6; $(H)(OEt)Os_3(CO)_{10}$, 64489-41-4; $(OEt)_2Os_3(CO)_{10}$, 64387-08-2; $(H)(Cl)Os_3(CO)_{10}$, 12557-93-6; $(Cl)_2Os_3(CO)_{10}$, 28109-18-4; $(Br)_2Os_3(CO)_{10}$, 28109-19-5.

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Redox Chemistry of Iron Tetraphenylporphyrin, Imidazolate-Chelated Protoheme, and Thiolate-Chelated Protoheme and of Their Iron(II)–Superoxide Adducts in Dimethyl Sulfoxide

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Cyclic voltammetry, controlled-potential coulometry, and UV–visible spectroscopy have been used to characterize the redox reactions in dimethyl sulfoxide of iron(III) *meso*-tetraphenylporphyrin, iron(III) protohemin monomethyl ester mono-(3-(1-imidazolyl)propyl)amide, and iron(III) protohemin monomethyl ester mono(3-(benzoylmercapto)propyl)amide and of the iron(II) thiolate that results from reduction and hydrolysis by addition of OH^-. All of these iron–porphyrin systems exhibit three reduction peaks [Fe(III)/Fe(II), Por/$Por^{-}\cdot$, and $Por^{-}\cdot/Por^{2-}$]; the last two are identical with those observed for zinc(II) *meso*-tetraphenylporphyrin. Addition of superoxide ion to the iron(II) state of these porphyrins yields an Fe(III)–(O_2^{2-}) adduct. In the case of iron(II) thiolated protoheme, the resulting peroxide complex may provide an effective model for the monooxygenase mechanism of cytochrome P-450.

Hemoproteins provide a variety of biological functions via their iron–porphyrin centers.[1] These include dioxygen transport by the myoglobin–hemoglobin proteins,[2–4] monooxygenase catalysis by cytochrome P-450,[5,6] four-electron reduction of dioxygen by cytochrome oxidase,[7–10] and the disproportionation and activation of peroxides by the catalase/peroxidase proteins.[11,12] The reversible binding of dioxygen occurs at a five-coordinate iron(II)–protoporphyrin molecule with its axial position occupied by an imidazole.[3] Cytochrome P-450 also has a five-coordinate structure, but as an iron(III) porphyrin with the axial position occupied by a thiolate anion.[5,13] Peroxidases such as horseradish peroxidase and cytochrome *c* peroxidase contain iron(III) protoporphyrin IX with the fifth ligand position on the iron occupied by an imidazole.[14]

The most extensively studied model systems involve the iron tetraphenylmeso- and octaethylprotoporphyrin complexes.

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(1) James, B. R. "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. 5; p 205, 253.

(2) Rifkin, J. M. "Inorganic Biochemistry"; Eichhorn, G., Ed.; Elsevier: Amsterdam, 1973; Vol. 2, p 832.

(3) Antonini, E.; Bennori, M. "Hemoglobin and Myoglobin in Their Reactions with Ligands"; North-Holland Publishing Co.: Amsterdam, 1971.

(4) Collman, J. P. *Acc. Chem. Res.* **1977**, *10*, 265.

(5) White, R. E.; Coon, M. J. *Ann. Rev. Biochem.* **1980**, *49*, 315 (and ref 1–15 therein).

(6) Collman, J. P.; Sorrell, T. N.; Dawson, J. H.; Trudell, J. R.; Bunnenberg, E.; Djerrasi, C. *Proc. Natl. Acad. Sci. U.S.A.* **1976**, *73*, 6.

(7) Hayaishi, O., Ed. "Molecular Oxygen in Biology"; North-Holland Publishing Co.: Amsterdam, 1974.

(8) Bennett, L. E. *Prog. Inorg. Chem.* **1973**, *18*, 1.

(9) Wharton, D. C. "Inorganic Biochemistry"; Eichhorn, G., Ed.; Elsevier: Amsterdam, 1973; Vol. 2.

(10) Wilson, D. F.; Erecinska, M. "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1979; Vol. 7, p. 1.

(11) Hewson, W. D.; Hager, L. P. "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1979; Vol. 7.

(12) Dunford, H. B.; Stillman, J. S. *Coord. Chem. Rev.* **1976**, *19*, 187.

(13) Dawson, J. H.; Cramer, S. P. *FEBS Lett.* **1978**, *88*, 127.

(14) Yonetani, J.; Yamamoto, H.; Erman, J. E.; Leigh, J. S., Jr.; Reed, G. H. *J. Biol. Chem.* **1972**, *247*, 2447.