LiF and LiOH are very similar to the corresponding values seen for the tetramers. Purely electrostatic estimates indicate a large decrease in the binding energy on going from $(LiF)_6$ to $(LiOH)_6$. The inadequacy of electrostatic considerations suggests that multicenter covalent bonding may be important for the oligomers of LiOH and $LiNH_2$.

For the planar structure of $(LiNH_2)_6$, an asymmetric structure was investigated, where six alternate Li–N bonds were optimized separately from the other six. The geometry optimization led to the equalization of all the Li–N bonds, ruling out the possibility of a "lithium bond"[37] between lithium and the nitrogen of the next monomer, different from the intramolecular lithium–nitrogen bond.

In previous studies,[10–14] the smaller oligomers of LiF, LiOH, and $LiNH_2$ have been studied in detail. It is of interest to see how the binding energy per monomer increases as the cluster size increases. Table V lists the binding energies (per monomer) of the dimers, trimers, tetramers, and hexamers of these compounds. These values were all calculated at a uniform level of theory by using the 6-31G+sp+d basis set. It should be remembered that zero-point vibrational effects would decrease these binding energies (per monomer) by $\simeq$1–2 kcal/mol. Comparison of the tetramers with the hexamers in Table V shows that the binding energy per monomer in the hexamer is about 3–5 kcal/mol higher than that in the tetramer. In addition, the binding energy per monomer in the solid is known experimentally[38] for LiF and LiOH, and these values are also listed in the last column of Table V. Comparison between the hexamers and the solid shows that there is still a significant difference, not unexpected for these predominantly ionic molecules.

Other Isomeric Structures

In addition to the octahedral and planar ring arrangements considered above, other geometries are also possible for these hexamers. In particular, we have performed preliminary explorations of two such geometrical arrangements, viz. (1) a geometry based on the NaCl lattice, i.e. a 3 × 2 × 2 rectangular solid (D_{2h} symmetry) closely related to the geometry expected in the solid state, and (2) a similar geometry but only in 2-dimensions, i.e. a 6 × 2 planar framework (C_{2h} symmetry). Analogous structures for the hexamer of LiH have been considered previously by Kato et al.[16] who referred to these two structures as "fence dimer" and "fence" geometries, respectively. Our preliminary results indicate that both these geometrical arrangements represent local minima on the potential surface but that neither of these structures is as stable as the octahedral arrangement considered in detail in this study. In fact, these additional calculations strongly suggest that the octahedral structures **1a**, **2a**, and **3a** are probably the global minima for the hexamers of LiF, LiOH, and $LiNH_2$, respectively.

Conclusions

The structures and energies of the hexamers of LiF, LiOH, and $LiNH_2$ have been investigated with accurate ab initio molecular orbital techniques. Large basis sets including diffuse and polarization functions have been used in these calculations. For all three systems, distorted octahedral forms (D_{3d}) are found to be considerably more stable than planar (D_{6h}) forms. These results are quite different from the corresponding results involving the tetramers. Electrostatic factors appear to contribute significantly to these differences. The binding energies of $(LiF)_6$ and $(LiOH)_6$ are about 310 kcal/mol and that of $(LiNH_2)_6$ is about 270 kcal/mol.

Acknowledgment. The authors are indebted to Prof. P. v. R. Schleyer for some valuable suggestions.

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Contribution from the Dipartamento di Chimica Inorganica, Metallorganica ed Analitica, Università di Padova, I-35131 Padova, Italy, and Laboratoire de Chimie Quantique, ER 139 du CNRS, Institut Le Bel, Université Louis Pasteur, 67000 Strasbourg, France

UV Photoelectron Spectrum and Electronic Structure of $\{Fe(\eta^5\text{-}C_5H_5)(\mu\text{-}NO)\}_2$: An Interpretation by means of ab Initio CI Calculations

Gaetano Granozzi,[1a] Pierre Mougenot,[1b] Jean Demuynck,[1b] and Marc Benard*[1b]

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The He I photoelectron spectrum of $\{Fe(\eta^5\text{-}C_5H_5)(\mu\text{-}NO)\}_2$ is reported and interpreted by means of ab initio SCF and CI calculations. An original quantum-chemical treatment accounts for the relaxation and the relocalization of the metal 3d and ligand outer valence electrons. Part of the correlation effects are also included. The calculations yield four well-separated clusters of levels that can be consistently correlated with the four resolved band systems (A′, A″, B, and C) of the experimental spectrum. The degree of matching between the groups of computed levels and the experimental bands appears excellent, especially for this class of molecules. The analysis of the SCF wave function obtained for the neutral complex confirms the existence of two molecular orbitals (MO's) delocalized over the $[FeNO]_2$ fragment responsible for the stabilization of the system. A considerable charge transfer from the Cp ring (Cp = C_5H_5) toward the NO ligands through the metal atoms is noticed from the Mulliken population analysis. The very labile character of the Cp π electrons is confirmed by an analysis of the 12 computed ionized states. More specifically, the positive hole created in Fe by the ionization of a localized metal 3d electron is almost quantitatively compensated by a transfer of charge originating in the Cp rings.

Introduction

Binuclear clusters with two π-acceptor bridging ligands such as CO or NO have recently been the subject of several experimental[2–5] and theoretical[2–10] studies that have brought to light the unexpected character of their metal–metal interaction. It now appears that the low-lying π^* orbitals of the bridging ligands

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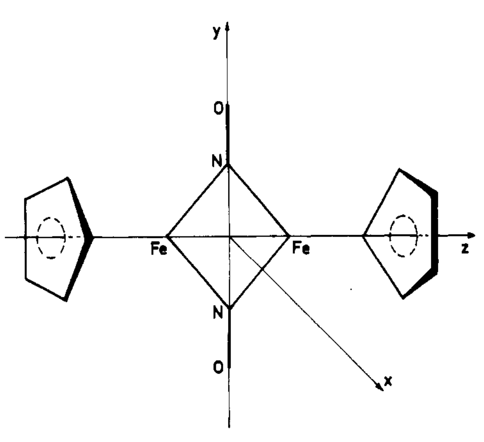

Figure 1. Schematic view of $\{Fe(\eta^5\text{-}C_5H_5)(\mu\text{-}NO)\}_2$ with the axis system adopted in the calculations.

interact with the metal d orbitals of proper symmetry to form molecular orbitals delocalized over four centers.[3-9] The strong stabilization and the important electron delocalization obtained from these multicentered interactions are in contrast with the weak overlap and the slight electron reorganization associated with direct metal–metal bonds, at least for the first transition series.[2,9] This explains why the bond order deduced from the 18-electron rule appears purely formal for this class of complexes and has apparently no relation with the balance between metal–metal *direct* bonding and antibonding interactions. Such four-center interactions have been proposed by Pinhas and Hoffmann[6] and by Bottomley[7] to account for the metal–metal distance variations and conformational preferences observed for complexes of the type $Cp_2M_2(CO)_x(NO)_{2-x}$ (with Cp = C_5H_5). In a previous study,[3] we reported the ultraviolet photoelectron (UV-PE) spectra of $\{Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)\}_2$, a d^9–d^9 complex with a planar $Ni_2(CO)_2$ core and a formally single metal–metal bond. The UV-PE spectra were interpreted in agreement with the qualitative bonding scheme proposed in ref 6. The present work reports the gas-phase UV-PE spectrum of $\{Fe(\eta^5\text{-}C_5H_5)(\mu\text{-}NO)\}_2$, a complex with similar geometrical conformation but with d^8 metal atoms and a formally double metal–metal bond (Figure 1). The second purpose of the present study was to develop and test an original quantum-chemical treatment based on ab initio calculations and provide a quantitative interpretation of the PE spectrum of large organometallic molecules. This treatment is expected to account at a reasonable cost for the electron relaxation for the relocalization of the positive hole and for part of the correlation effects in each valence ionized state.

Experimental Section

PE Spectroscopy. The He I (21.217 eV) PE spectrum in the gas phase was obtained on a Perkin-Elmer PS-18 spectrometer. The ionization energy (IE) scale was calibrated by reference to peaks due to admitted inert gases (Xe–Ar) and to He $1s^{-1}$ self-ionization. A heated inlet probe system was adopted at 110 °C. Pertinent IEs are reported in Figure 2.

Methodology and Computational Details. The "real" orbital energies obtained from photoelectron spectroscopy are inaccessible to standard theoretical treatments because of the well-documented failure of Koopmans' theorem.[11] More sophisticated and sometimes computationally expensive treatments, such as the transition-state method (used in conjunction with $X\alpha$ calculations), ab initio ΔSCF or ΔSCF/CI, or Green's function methods, are necessary to obtain a semiquantitative estimate of ionization energies.[12] The problem of interpreting the experimental spectra is of special importance and difficulty in the field of organometallic chemistry for several reasons:

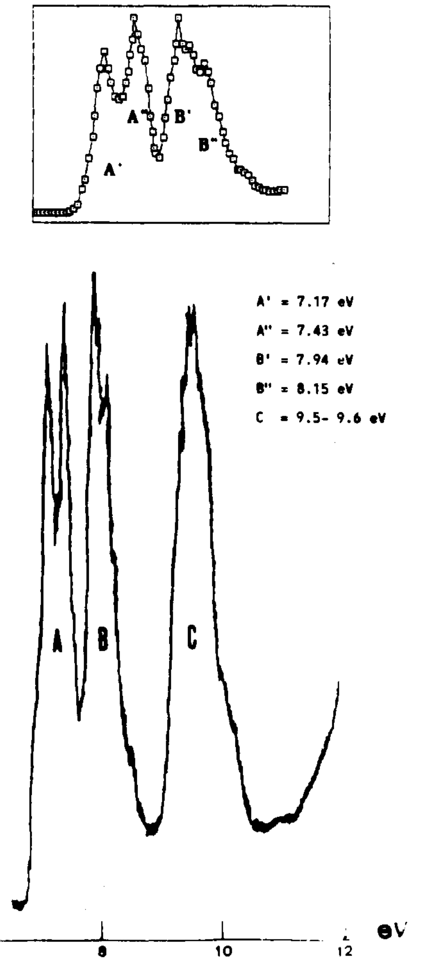

Figure 2. He I PE spectrum of $\{Fe(\eta^5\text{-}C_5H_5)(\mu\text{-}NO)\}_2$. An expanded-scale view of the first two bands is reported at the top of the figure.

(i) The orders of magnitude of the relaxation energy are markedly different for the electrons localized on the metal d shells (6–10 eV) and for those localized on the organic ligands (0.5–2 eV).[13] As a consequence, the ionization energy of the electrons ensuring the metal–metal, metal–ligand, or metal–ligand–metal bonding is affected by relaxation effects in a quite unpredictable way within these extreme values.

(ii) In symmetric molecules the ionization energies computed from ab initio ΔSCF calculations can be biased by the constraints associated with the space symmetry of the system. This effect is well-documented for the d electrons localized on the metal atoms, for which the bias can reach several electronvolts: a symmetry-adapted SCF wave function yields an unrealistic description of the d hole delocalized over two[14,15a] or three[15b] equivalent metals. A similar, though quantitatively less important, error can also affect the ionization energies originating from symmetric ligands.[16]

(iii) The influence of electron correlation can modify and partly cancel the effect of relaxation with respect to Koopmans's values. The methods accounting for relaxation only, such as ΔSCF, can therefore lead to a wrong sequence of ionization energies.[12b]

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The method used for the present calculations is aimed to obtain the complete set of outer valence ionization energies. These computed ionization energies must account for relaxation effects, including the relocalization of the positive holes generated either in the metal 3d shell or in the C_5H_5 π or NO π^* systems. Part of the difference in correlation energy between the ionized states will also be included. We could not afford however to use for such a large molecule the computationally expensive ΔSCF or ΔSCF/CI[12b] methods associated with Boys' technique to relocalize the nonbonding electrons on individual atoms.[17] We started from an all-electron calculation[18] of the ground state of $(\mu\text{-NO})_2(\text{FeCp})_2$ carried out using the experimental geometry[20] with a coplanar Fe–$(\mu\text{-NO})_2$–Fe moiety and with cyclopentadienyl cycles staggered with respect to each other, thus ensuring a perfect C_{2h} symmetry. It must be noted that the C_2 axis corresponds to the direction of the NO ligands (y axis in Figure 1).[21] The Gaussian basis set was triplet-ζ for metal d shells and double-ζ for the valence orbitals of first-row atoms. The basis set for iron was taken from the (13,7,5) set of Hyla-Kryspin et al.[22] incremented with one p function of exponent 0.15 and one d function of exponent 0.09 and then contracted to [5,3,3]. Basis sets (9,5) and (4) were used for first-row atoms and hydrogen, respectively, and contracted to split valence.[23]

Instead of computing the energy of the ionized states accounting for relaxation through separate SCF calculations, we started from a unique set of molecular orbitals, the one optimized for the neutral molecule. This set of MO's is not optimum for any of the ionized states, but the relaxation associated with a specific Koopmans theorem configuration can be accounted for through a CI expansion restricted to *single excitations* with respect to this configuration.[24] Since ionizations arising from several valence MO's have to be considered, a *multireference* CI expansion can be carried out, each root configuration corresponding to a Koopmans theorem configuration of interest. This expansion can be split into several subsets, each associated with a different irreducible representation. The multiplicity of the reference configurations introduces some account of the difference in correlation effects between the ionized states.[24] The use of such CI expansions to account for both the relaxation and part of the correlation effects has been advocated by Doran et al. and successfully applied to assign the photoelectron spectrum of $CrOCl_3$.[24]

The complete set of configurations resulting from a single electron transfer with respect to *one specific ionized configuration* (with use of the MO set of the neutral complex) would relax the energy of this configuration as a *symmetry-adapted* SCF minimization carried out on the same state. As discussed above, this relaxation is not complete in the case of symmetric molecules, especially for core or nonbonding metal d-electron ionizations. It has been shown that a convenient relocalization will be obtained in this case through one-electron excitations with respect to *couples* of reference configurations associating the symmetry-adapted bonding and antibonding counterparts of the localized MO's.[25] In the C_{2h} symmetry, the individual configurations belonging to such couples are distributed either among the a_g/b_u and a_u/b_g representations (for the ionizations originating from metal d and Cp π MO's) or among the b_g/b_u representations for the NO π and π^* combinations. It is therefore essential to consider all the ionized states of any symmetry as reference configurations for each of the four CI expansions respectively associated with the a_g, b_u, a_u, and b_g irreducible representations.

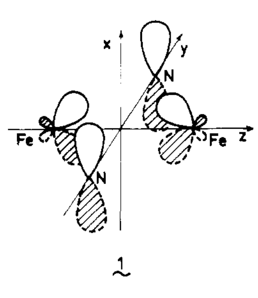
The set of MO's involved in the CI expansions included 64 orbitals, 26 of them being doubly occupied in the neutral complex. The ionized states associated with each of these 26 MO's were considered as reference configurations in all four CI expansions. The 38 virtual MO's involved in these expansions included the frontier orbitals and the high-energy MO's with important metal character (4d virtual shell). The four multireference CI expansions limited to single excitations on this basis of 64 MO's respectively generated 6559, 6558, 6301, and 6296 configurations for the a_g, b_u, b_g, and a_u representations.

Results and Discussion

1. Computed Ground State. The theoretical calculations[6,8] as well as photoelectron data obtained on related bridged dimers[3,4] suggest that the low-energy region of the spectrum should be assigned to 12 outer valence energy levels. Four of them are expected to arise from MO's describing the metal–Cp π-bonding interactions. These four MO's correspond to the highest occupied orbital of each irreducible representation, namely $23b_u$, $25a_g$, $13b_g$, and $15a_u$ (see the sequence of the occupied valence SCF MO's for the neutral molecule given in Table I). These four MO's have predominant Cp character and Koopmans' theorem is expected in this case to provide a reasonable estimate for the ionization energy.

According to the earlier studies of Pinhas and Hoffmann,[6] Bottomley,[7] Fenske,[8] and others,[10] all complexes of the type $Cp_2M_2(CO)_x(NO)_{2-x}$ are expected to display a bulk of six "t_{2g}-like" MO's with high metal character resulting from the interaction between the two MCp fragments. These MO's are expected to be globally nonbonding and therefore to maintain 3d atom like character. According to the symmetry constraints, they are distributed into three couples of orbitals with respective metal–metal bonding and antibonding character. In Table I, these couples of MO's are labeled as ($21b_u$, $24a_g$), ($11b_g$, $14a_u$), and ($17b_u$, $20a_g$). In some cases, the metal weight is distributed among several MO's. For this reason, molecular orbitals $19b_u$ and $8b_g$ also display an important metal character. Previous experience in computing the ionization energy of such localized metal electrons has shown that the relaxation energy—including the electron relocalization energy—is generally more than 5 eV and sometimes close to 10 eV.[12-14]

The two remaining MO's of interest describe the bonding between the FeCp moieties and the nitrosyl ligands. Their identification in the PE spectrum is therefore of special importance for understanding the electronic structure of this complex. Assuming the traditional electron-counting formalism for the ligands i.e. Cp^- and NO^+, the iron atoms are in the oxidation state 0. The complex is therefore "d^8–d^8",[4] and a formal bond order of 2 is requested in order to comply with the 18-electron rule. Earlier studies on dinuclear complexes with π-acceptor bridging ligands[2-10] have shown however that the two moieties of the complex and the bridging ligands are held together by one or several interactions delocalized over the central metallacycle rather than by direct metal–metal bonds. The specific case of the $Cp_2M_2(CO)_x(NO)_{2-x}$ class of complexes has been more thoroughly investigated by Pinhas and Hoffmann[6] and by Bottomley.[7] According to these studies, the two delocalized combinations responsible for the bonding are expected to have the form $[(d_{xz} - d_{xz}) + \pi^*_x(\text{NO})]$ for **1** and $[(d_{yz} + d_{yz}) + \pi^*_z(\text{NO})]$ for **2** (see Figure 1 for the definition of the axes).



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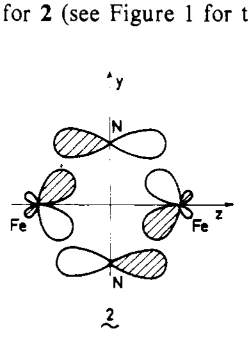

2

The situation is not quite the same in the present molecule. At variance from the occupied frontier orbitals represented by Pinhas and Hoffmann for bis(μ-carbonyl) complexes, the low-lying π^*

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Table I. Ground-State MO's of $\{Fe(\eta^5\text{-}C_5H_5)(\mu\text{-}NO)\}_2$ from ab Initio SCF Calculations

orbital	fragment populn, %; character: Fe	Cp	NO	Koopmans IE, eV	ref configns[a]
$23b_u$	15; $x^2 - y^2$	70; π	15; π^* (x)	9.6	*
$25a_g$	22; $x^2 - y^2$	78; π	0	9.8	*
$13b_g$	18; xy	67; π	15; π^* (z)	9.8	*
$15a_u$	17; xy, yz	82; π	1	10.1	*
$22b_u$	23; xz	14	63; π^* (x,z)	10.9	*
$12b_g$	20; yz	10	70; π^* (x,z)	10.9	*
$21b_u$	40; $2y^2 - x^2 - z^2$	11	49; π (z)	13.6	*
$11b_g$	41; xy	9	50; π (x)	14.2	*
$24a_g$	73; $x^2 - y^2$, xz	24	3	14.2	*
$14a_u$	58; xy	36; σ	6	14.6	*
$20b_u$	11	87; σ	2	14.9	*
$10b_g$	1	95; σ	4	15.0	
$23a_g$	3	97; σ	0	15.0	
$19b_u$	44; $z^2 - x^2$	53; σ, π	3	15.1	*
$13a_u$	25; xy	72; σ	3	15.2	*
$22a_g$	22; $z^2 - x^2$	77; π	1	15.5	*
$9b_g$	3	91; σ	6	15.7	
$18b_u$	5	83; σ	12	15.8	
$12a_u$	3	93; σ	4	15.9	
$21a_g$	16; $z^2 - x^2$	82; σ	2	16.0	*
$17b_u$	52; $2z^2 - x^2 - y^2$	48; π	0	16.3	*
$20a_g$	60; $z^2 - y^2$	17	23; σ	16.4	*
$16b_u$	27; $x^2 - y^2$, xy	8	65; π (x)	17.3	*
$8b_g$	46; xy	8	46; π (x)	17.4	*
$7b_g$	2	3	95; π (x,z)	18.4	*
$11a_u$	16; xy, yz	3	81; σ	18.6	*
$15b_u$	8	17	75; π (z)	18.9	*
$19a_g$	19; $2z^2 - x^2 - y^2$	20	61; σ	19.4	*
$14b_u$	9	90	1	20.4	*
$18a_g$	4	94	2	20.5	
$10a_u$	3	97	0	20.6	
$6b_g$	4	95	1	20.6	
$17a_g$	15	80	5	20.6	*
$13b_u$	8	83	9	20.7	*

[a] The asterisk means that the electronic configuration with one electron in the corresponding orbital has been taken as one of the reference states in the CI expansion.

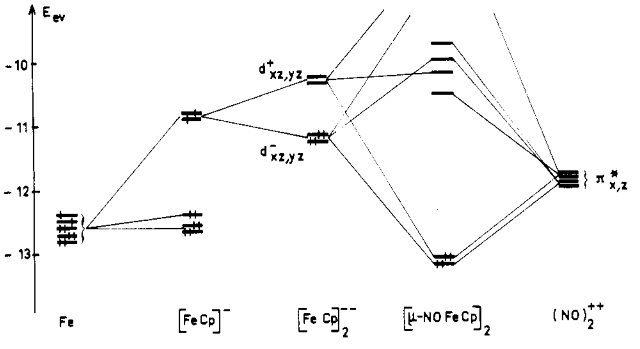

Figure 3. Simplified interaction diagram displaying the frontier orbitals of $Fe(\eta^5\text{-}C_5H_5)$, $\{Fe(\eta^5\text{-}C_5H_5)\}_2$, and $\{Fe(\eta^5\text{-}C_5H_5)(\mu\text{-}NO)\}_2$ (from extended Hückel calculations). The orbital occupancy of the fragments corresponds to the traditional electron-counting formalism (Cp^-, NO^+, and Fe(0)).

orbitals of the bridging NO ligands are by far the major contributors to these molecular orbitals in the present calculation (63% for $22b_u$ and 70% for $12b_g$), in agreement with the result of Fenske–Hall calculations by Schugart and Fenske.[8] An increase of the π^* weight for NO ligands with respect to that for CO was predictable in relation with the higher acidity of NO making the π^* orbitals more energetically accessible. The weight of NO becomes dominant with respect to the metal contribution as a result of the Fe–Cp interaction pushing the metal π orbital combinations to high energy with regard to the low-lying nitrosyl π^* combinations (Figure 3). As a consequence, each nitrosyl presents a negative charge of −0.73 e equally distributed between the nitrogen and oxygen atoms. The high polarity of the free NO has therefore disappeared in the complex, due to a considerable increase of the population on nitrogen ($q_N = -0.36$ e instead of +0.50 e in the free NO). In the opposite way, the negative net charge on oxygen has been slightly diminished (Table II). This excess of charge on nitrogen is not equally distributed between the p_x and p_z orbitals. In fact, the contribution of p_z(N) as acceptor orbital is about twice as important as that of p_x (Table II). This can be related to the fact that orbital $22b_u$, which is the equivalent of **1** in the present calculation, becomes under the C_{2h} symmetry constraints a more complex combination of $d_{z^2-x^2}$ and d_{xz} on the metal atoms and π^*_x and π^*_z on the NO ligands (**3**). Since orbital

Table II. Net Atomic Charge and π-Orbital Populations of NO in $(\mu\text{-}NO)_2(FeC_5H_5)_2$ Compared to Those of an Isolated Neutral NO Fragment

	free NO	NO in $(\mu\text{-}NO)_2(FeCp)_2$
q_N, e	+0.50	−0.36
q_O, e	−0.50	−0.37
π_x(N)	0.83	1.19
π_x(O)	1.67	1.49
π_z(N)	0.83	1.44
π_z(O)	1.67	1.66

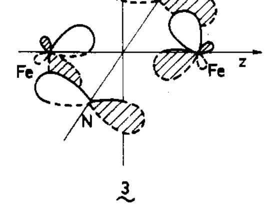

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Table III. Electron Transfer from the C_5H_5 (Cp) Rings to Bridging π-Acceptor Ligands in $(\mu\text{-}C_2H_2)(NiC_5H_5)_2$, $(\mu\text{-}CO)_2(C_5H_5FeCO)_2$, and $(\mu\text{-}NO)_2(FeC_5H_5)_2$ from ab Initio SCF Calculations

	net charge, e		
molecule	Cp	bridging ligand (per ligand)	metal
FeCp[a]	−1.00		+1.00
$(\mu\text{-}C_2H_2)(NiCp)_2$[9]	−0.54	−0.56 (one ligand only)	+0.82
$(\mu\text{-}CO)_2(CpFeCO)_2$[9]	−0.40	−0.36	+0.76
$(\mu\text{-}NO)_2(FeCp)_2$[a]	+0.25	−0.72	+0.47

[a] This work.

$12b_g$ remains very similar to **2** in spite of a minor admixture of the NO π^*_x orbitals, both MO's responsible for the metal–ligand–metal linkage involve a major contribution from the nitrosyl π^*_z orbitals.[26]

The presence of a large negative charge on the nitrosyls illustrates the ambiguity of classically assuming closed-shell NO^+ fragments in the interaction scheme when the supposedly empty NO π^* orbitals are lower in energy than the doubly degenerate HOMO of the complex (Figure 3). It is more realistic and rewarding in the present case to consider *neutral* FeCp and NO fragments, each populated with one electron in its doubly degenerate HOMO. SCF calculations on the neutral FeCp molecule confirm that the metal charge is almost exactly +1 e and the Cp^- π system is populated with six electrons (Table III). When the bis(μ-nitrosyl) complex is formed, a huge amount of charge is withdrawn *from the cyclopentadienyl ion and mainly* (but not exclusively) *from its π system.* The π population of the Cp ring decreases from 6 to 4.98 e, resulting in a positive net charge of *+0.25 e for each Cp fragment* (Table III). A small part of this charge is retained by the metal, but the major part flows through the metal toward the bridging nitrosyls. Similar though less dramatic electron transfers from a cyclopentadienyl ion to bridging π-acceptor ligands can be noticed from the result of previous ab initio calculations on binuclear complexes (Table III). The mechanism is the same for the three considered molecules $(\mu\text{-}C_2H_2)(NiCp)_2$, $(\mu\text{-}CO)_2\{Fe(Cp)CO\}_2$, and the presently investigated dinitrosyl complex: a more or less important fraction of the Cp π-electron population is removed. The net Cp charge remains however negative except for the dinitrosyl complex. About 20% of the transferred electrons are retained by the metal in its oxidation state 1 and the metal positive charge decreases accordingly. Finally, 80% of the charge removed from the Cp rings is transferred back to the bridging ligands.[29]

2. Photoelectron Spectrum. The low-IE region (6–12 eV) of the PE spectrum is reported in Figure 2. Five bands are resolved, belonging to three well-separated groups labeled alphabetically. An expanded view of the first two bands is also reported in Figure 2. As for the complex $(\mu\text{-}CO)_2(NiCp)_2$ investigated in a previous work,[3] the region at higher energies consists of two broad composite structures. These envelopes, centered at 12.9 and 16.7 eV (instead of 13.4 and 16.7 eV for the nickel carbonyl complex[3]) correspond to ionizations deriving from the σ and π nitrosyl MO's and from the Cp rings. Koopmans' values for this latter block of MO's range from 14.9 to 16.3 eV. The deeper MO block localized on the nitrosyl ligands extends from 17.3 to 20.7 eV (Table I). It is however noteworthy that two relatively high-lying MO's ($21b_u$ at 13.6 eV and $11b_g$ at 14.2 eV) display an important nitrosyl π character (Table I). These orbitals are the antibonding counterparts of the respective interactions of the metal d_{y^2} and d_{xy} orbitals with the nitrosyl π_z and π_x orbitals.

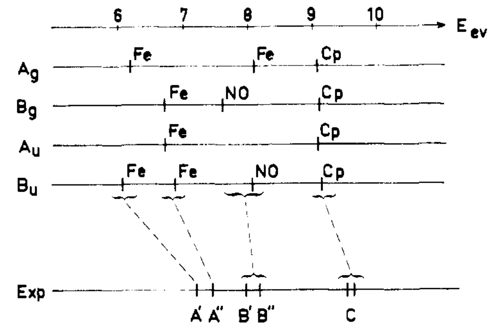

Figure 4. Energy values of the 12 ionized states computed from the CI expansion and proposed assignment of the experimental spectrum.

The energies, Mulliken fragment charges, and natural-orbital analysis of the 12 ionized states computed from the CI expansion are reported in Table IV. Figure 4 displays the relative energy ordering of the computed ionized states as a function of their symmetry, showing that the 12 computed states are clustered into 4 groups. The proposed assignment of the experimental spectrum is also indicated.

The four lowest levels according to the calculations correspond to the ionization of nonbonding metal 3d electrons. The natural orbitals describing the positive hole are all more than 65% metal with some contribution from the NO π^* orbitals when allowed by symmetry (Table IV). These four levels are clustered two by two according to the nature of the ionized metal d electron: mainly localized on d_{y^2} metal orbitals for the lowest couple of levels (6.03 and 6.18 eV, with respective b_u and a_g symmetries) and on d_{xy} orbitals for the second couple (6.69 eV (b_g) and 6.70 eV (a_u)). The two experimental bands A′ and A″ of similar intensity separated by 0.26 eV (Figure 2) could be assigned to these two couples of ion states (Figure 4).

The third pair of computed ionized states with high metal d contribution behaves somewhat differently. The corresponding ion states, of symmetry b_u and a_g, are split by more than 1 eV at 6.84 and 8.08 eV, respectively (Table IV). The corresponding orbitals, with more than 85% metal weight, are mainly oriented along the z axis. At variance from the four other ion states associated with atom-localized d electrons, these two states are connected to a couple of metal–metal bonding/antibonding orbitals. This four-electron repulsive interaction is enhanced by the short metal–metal bond length. At 6.84 eV, the antibonding MO probably contributes to the experimental band A″. Such a hypothesis is well in tune with the experimental intensity ratio between the two A′ and A″ bands (see top of Figure 2), the A″ band showing a higher intensity compatible with a third component. The bonding counterpart is pushed down in energy, and the corresponding ionization (8.08 eV) falls in the region of band system B (7.9–8.2 eV).

Between these two metal 3d levels, respectively at 7.60 and 8.06 eV, we find the two ion states arising from the b_g and b_u MO's responsible for the stabilizing interactions between the metal Cp dimer and the bridging nitrosyls. The natural-orbital analysis confirms that the ionized electrons are delocalized over the $Fe_2(NO)_2$ molecular fragment with major weight on the NO π^*

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(26) The respective orientation of the metal and nitrosyl orbitals in **3**, confirmed by plots of the electron deformation density, appears very puzzling since it makes the character of the metal–NO–metal linkage dependent upon the symmetry point group of the molecule, i.e. upon the eclipsed or staggered conformation of the Cp cycles. We rather suspect this deviation from the ideal D_{2h} symmetry of the $Fe_2(NO)_2$ fragment and the consecutive population of the NO π^*_z orbital to minimize important correlation effects involving the occupied and empty couples of NO π^* orbitals.[27] The SCF wave function with C_2h symmetry could therefore correspond to a "broken symmetry solution"[28] relieving the space symmetry constraints associated with the C_{2v} symmetry. This important theoretical problem concerning the description of the ground state of $\{CpFe(NO)\}_2$ and related molecules will be investigated in a subsequent paper.

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Table IV. Sequence of the Computed Ionized States of $\{Fe(\eta^5\text{-}C_5H_5)(\mu\text{-}NO)\}_2$[a]

		fragment charge anal.			character of the natural-orbital major contrib to the positive hole					
state	energy, eV	q_{Fe}, e	q_{Cp}, e	q_{NO}, e	sym	populn, e	% Fe	% Cp	% NO	assignt
^1A_g[b]	0.0	+0.47	+0.25	−0.72						
^2B_u	6.03	+0.44	+0.62	−0.56	b_u	1.12	72; $y^2 - z^2$	7	21; π^* (x)	A′
					a_g	1.90	97; $y^2 - z^2$	3	0	
^2A_g	6.18	+0.47	+0.63	−0.60	a_g	1.12	87; $y^2 - x^2$	12	1	A′
					b_u	1.88	90; $y^2 - x^2$	5	5	
^2B_g	6.69	+0.45	+0.61	−0.56	b_g	1.16	65; xy	11	24; π^* (z)	A″
					a_u	1.89	92; xy	7	1	
^2A_u	6.70	+0.46	+0.63	−0.59	a_u	1.14	89; xy	10	1	A″
					b_g	1.86	90; xy	6	4	
^2B_u	6.84	+0.46	+0.62	−0.58	b_u	1.15	85; $z^2 -x^2$	10	5	A″
					a_g	1.87	87; $z^2 - x^2$	9	4	
^2B_g	7.60	+0.44	+0.54	−0.48	b_g	1.17	26; xy	1	73; π^* (x,z)	B′
					b_u	1.87	16; xz	7	77; π^* (x,z)	
^2B_u	8.06	+0.45	+0.54	−0.49	b_u	1.20	24; $z^2 - y^2$	9	73; π^*(x,z)	B′ or B″
					b_u	1.89	48; $z^2 - y^2$	27; π	25; π^* (x), π (z)	
					b_g	1.84	6	10	84; π^* (z)	
^2A_g	8.08	+0.48	+0.61	−0.59	a_g	1.20	91; z^2	4	5	B″
					b_u	1.81	94; z^2	3	3	
^2A_g	9.05	+0.45	+0.71	−0.66	a_g	1.08	24; xz	76; π	0	C
^2B_g	9.07	+0.42	+0.71	−0.66	b_g	1.09	28; yz	72; π	0	C
^2A_u	9.07	+0.42	+0.75	−0.67	a_u	1.07	18; yz	82; π	0	C
^2B_u	9.10	+0.43	+0.73	−0.66	b_u	1.09	22; xz	78; π	0	C

[a] The electronic charges for the fragments (from the Mulliken population analysis), the character of the positive hole (from the natural-orbital analysis), and the proposed assignment are displayed. [b] Ground state.

orbitals (Table IV). The band system B′–B″ (see top of Figure 2) can be assigned to these molecular orbitals with the probable contribution to B″ from the a_g metal–metal-bonding MO. The large intensity of the B′–B″ band envelope, when compared with that of band A′–A″, is justified by the composition of the corresponding MO's. Actually, the bands B′–B″ are related to MO's mainly composed of NO-based atomic orbitals, and it is well-known that He I photoionization cross sections are larger for first-row atomic orbitals than for 3d metal orbitals.[31]

Finally, the broad band centered at 9.5–9.6 eV can be assigned to the four lowest Cp π orbitals that appear in the calculation at 9.05–9.10 eV. These four levels, scattered over 0.5 eV according to Koopmans' theorem, have been nicely gathered within 0.05 eV by the CI expansion in agreement with the almost unresolved structure of the experimental band. These MO's retain an important metal character (20–25%, see Table IV), which confirms the special importance of the Cp–metal interaction for this molecule. As discussed above, this interaction initiates the electron flow from the Cp π system to the NO π^* orbitals, mainly through the metal d_{xz} and d_{yz} orbitals.

A comparison between the ionization energies obtained from Koopman's theorem and from the CI expansion shows that the relaxation effects obey the trends already noticed from previous studies on transition-metal complexes: about 8 eV for the globally nonbonding metal 3d electrons, 3 eV for the delocalized electrons ensuring the metal–ligand–metal linkage, and less than 1 eV for the π Cp electrons. As a consequence, the Cp π orbitals, highest in energy according to Koopmans' theorem, are associated with the third band envelope.

3. Electronic Structure of the Ionized Molecule. Although the positive hole created in these 12 ionized states can originate from various parts of the molecule (Cp rings, metal atoms, Fe_2N_2 metallacycle), the electronic structure of the $Fe_2(NO)_2$ fragment maintains throughout these ionization processes a surprising similarity with the ground state of the neutral complex. The most striking indication comes from the net metal charge that remains for *all* ionized states practically equal to its ground-state value (+0.47 e) with a general trend to slightly *reduce* the positive charge (Table IV). When the ionization involves a localized metal 3d electron, this represents a considerable reorganization of the wave function. A similar, though less drastic, relaxation had been noticed already by Van Dam et al.[14] for metal 3d ionizations in $Fe_2(CO)_6S_2$ and $Co_2(CO)_6C_2H_2$. Concerning more specifically dicyclopentadienyl complexes, similar relaxation effects have been discussed by Sherwood and Hall for $(\mu\text{-}Ph_2P(CH_2)_nPPh_2)\{Fe(CO)Cp\}_2$[32] and by Bagus et al. for ferrocene.[33] An important delocalization of the metal 3d positive holes has also been pointed out by Hillier et al. in nitrosylmetal complexes.[34] In the present case, a large fraction of the removed 3d electron is recovered from the cyclopentadienyl π orbitals: the positive net charge of each Cp ring increases from +0.25 to +0.62 e (Table IV). This confirms the very labile character of the Cp π electrons: the Cp π system seems to be used as an electron tank available upon request to the rest of the molecule. The reverse effect is not operative, however: upon ionization of a Cp π electron, the positive hole does not delocalize over the rest of the molecule and the net charge of each Cp ring increases from +0.25 e to the range of +0.71 to +0.75 e. The ionization of an electron delocalized over the metallacycle (but with major NO π^* character) also results in a depopulation of the Cp π system. The effect is less drastic in this case since the positive net charge of each Cp cycle increases by 0.29 e only. The other half of the positive hole remains localized on the NO π^* system as the net metal charge is practically unchanged (Table IV).

To summarize, the CI expansion restricted to single excitations with respect to a multiple-reference basis of Koopmans theorem configurations provides a consistent interpretation of the UV PE spectrum of the title compound. The band system of lowest energy (A) corresponds to ionizations from localized metal d orbitals. Band system B is assigned to ionizations from the two delocalized orbitals responsible for the bonding of the Fe_2N_2 metallacycle. A third contribution to band B comes, however, from a pure metal orbital, stabilized by a σ-bonding Fe–Fe interaction. As in other related molecules, band C is attributed to the four ionizations arising from the cyclopentadienyl π orbitals. In agreement with former studies,[6–9] the formal metal–metal double bond assumed to account for an 18-electron environment of the Fe atoms in the neutral molecule and for the short observed Fe–Fe bond length (2.326 Å) does not appear as a direct metal–metal-bonding in-

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teraction. The dimer is stabilized by two two-electron–four-center interactions delocalized over the Fe_2N_2 metallacycle and with major contribution from the NO π^*_z orbitals. The population of the nitrosyl π^* orbitals originates in charge transfer from the π system of the Cp ring to the nitrosyl ligands through the metal atoms. As a consequence, the net charge of each Cp ring becomes positive (+0.25 e). The lability of the Cp π electrons is confirmed by the electron reorganization occurring upon the ionization of the localized metal 3d electrons: the positive hole is shielded by electron transfers originating from the Cp rings and isotropically directed toward all five metal d orbitals. The net metallic charge in the ionized states therefore remains globally identical with its value in the neutral molecule.

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Contribution from the Department of Chemistry,
Princeton University, Princeton, New Jersey 08544

Electrochemical and Resonance Raman Spectroscopic Characterization of Polyaniline and Polyaniline–Metalloporphyrin Electrode Films

Kathleen A. Macor, Y. Oliver Su,† Lisa A. Miller, and Thomas G. Spiro*

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Characteristics of electropolymerized aniline and metallotetrakis(2-aminophenyl)porphine (metallo–2-TAPP) films are described. Aniline polymerized from methylene chloride solution by oxidative cycling at a platinum electrode shows characteristic two-wave or one-wave cyclic voltammograms when scanned in pH 1 aqueous solution, depending on the positive potential sweep limit. Similar CV's are produced when the solution contains metallo–TAPP's, except that additional waves associated with metalloporphyrin redox processes are superimposed. The absorption spectra of the films formed on transparent SnO_2 electrodes showed characteristic metalloporphyrin Soret absorption bands, with red shifts relative to the solution spectra, due to axial coordination and/or excitonic effects. Raman spectra are reported for films polymerized from aniline, aniline-^{15}N, aniline-*N*,*N*-d_2, and aniline-d_5. The replacement of strong aniline bands at 1000 and 1029 cm^{-1} with bands in the films at 1190 and 1200 cm^{-1} is diagnostic for para-substituted aniline units in the polymer. The films show a strong ^{15}N-sensitive band at 1525 cm^{-1}, which is absent in aniline but present in *p*-phenylenediamine. It is assigned to a Fermi resonance between a phenyl ring mode and a combination mode involving an out-of-plane ring motion with substantial N involvement. This band also appears in the TAPP films, superimposed on the strong resonance Raman spectra of the metalloporphyrins. Thus the electrochemical and spectroscopic characteristics of the TAPP films are fully consistent with unmodified porphyrin units contained within a polyaniline polymer. No film formation is observed when a methylene chloride solution of Zn(2-TAPP) is cycled to 0.9 V, just beyond the porphyrin radical cation oxidation wave, but extending the sweep to 1.2 V does lead to polymer formation. Thus, porphyrin radical cation formation is insufficient to induce polymerization if the potential is lower than that required for aniline oxidation. Films containing Mn(2-TAPP) show a Mn$^{3+/2+}$ wave at $\sim$−0.2 V, negative of the polyaniline redox waves, when the electrode is in contact with nonaqueous or aqueous electrolyte. The metalloporphyrin redox process does not require electronic conduction through the polyaniline framework. When polyaniline or polyaniline–porphyrin films are scanned to positive potentials (1.4 V) in contact with aqueous electrolyte, electroactivity is abolished for both the aniline and metalloporphyrin redox waves.

Introduction

Metalloporphyrins are attractive agents for electrode modification[1] because of their favorable electron transfer characteristics and the possibilities for electrocatalysis associated with the redox reactions of coordinated ligands. Moreover, the strong light absorption in the visible–near-ultraviolet region of the porphyrin π electronic system may prove useful in photoelectrochemical processes.[2] We have previously demonstrated formation of metalloporphyrin electrode films via oxidative electropolymerization of metalloprotoporphyrins from nonaqueous solution.[3] The peripheral vinyl groups of protoporphyrin provide a convenient route for cationic polymerization via the oxidized porphyrin ring. These films showed reversible electroactivity in nonaqueous solvents, but were rapidly inactivated by oxidation when in contact with aqueous solution.[4]

We were attracted to the use of (aminophenyl)porphyrins in electrode film formation because of the known propensity of aniline to form electroactive polymers.[5] During the course of our work Murray and coworkers[6,7] have shown that tetrakis(aminophenyl)porphines do indeed form electroactive polymer films upon oxidative cycling of the electrode potential. Redox processes for the metalloporphyrin units as well as the polyaniline backbone were characterized for a number of systems. Herein we demonstrate via Raman spectroscopy on electrode films that aniline oxidative polymerization proceeds via para substitution, as is commonly supposed, and that electrode films formed by oxidation of tetrakis(2-aminophenyl)porphines (TAPP) contain a polyaniline backbone with pendant and unaltered metalloporphyrin groups. We also show that polymerization requires oxidation of the aniline groups. In contrast to protoporphyrin,[3] (aminophenyl)porphine does not polymerize if only the porphyrin ring is oxidized.

Experimental Section

meso-Tetrakis(2-aminophenyl)porphines (2-TAPP) (Mid-Century Chemicals, Posen, IL) were metalated by refluxing them in DMF with

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* To whom correspondence should be addressed.

† Present address: Department of Chemistry, National Taiwan University, Taipei, Taiwan, Republic of China.

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