An INDO MO Study on the Ground State and the Cationic States of Cyclopentadienyl Nickel Nitrosyl

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The electronic structure of cyclopentadienyl nickel nitrosyl (**1**) in the ground state as well as the cationic states of **1** are investigated by means of a semiempirical INDO Hamiltonian and many body perturbation theory. It is demonstrated that the nature of the NiNO coupling is largely covalent while the interaction between the 3d center and the cyclopentadienyl ligand is predominantly of ionic type. The ground state MO sequence of the Ni 3d orbitals is $4e_2(3d_{x^2-y^2}/3d_{xy})$ below $7e_1(3d_{xz}/3d_{yz})$ and $15a_1(3d_{z^2})$. The sequence of the ionization potentials is $8e_1(\text{Cp}-\pi) < 15a_1 < 4e_2 < 7e_1$. The ionization energies have been determined by means of the Green's function formalism; the self-energy part has been calculated by a second order and a renormalized approximation. Both procedures predict the correct sequence of ionization events.

1. Introduction

Photoelectron (PE) spectra of transition metal compounds cannot be assigned on the basis of Koopmans' theorem ($I^K_{v,j} = -\varepsilon_j$) [1] as a result of strong electronic reorganization in the case of ionization events of electrons which are strongly localized at the transition metal center. Computational methods beyond the picture of the Koopmans' configurations can be devided into two classes. In relaxational procedures (e.g. ΔSCF approximation [2]) only deviations from the one-particle energies ($-\varepsilon_j$) in the Hartree-Fock (HF) framework are considered. In recent years PE spectra of transition metal compounds were often assigned on the basis of the ΔSCF approach [3, 4]. In computational procedures beyond the HF picture not only relaxation effects but also correlation contributions are taken into account.

Several ΔSCF ab initio studies in organometallic systems have shown large deviations between calculated ionization energies and measured ones [5, 6] as a result of the neglected correlation effects. Cyclopentadienyl nickel nitrosyl (**1**) is such an example where one needs guidance from computational procedures taking into account relaxation and correlation [7].

In previous publications we have demonstrated that PE spectra of transition metal compounds can be reproduced by means of an improved INDO Hamiltonian [8] in combination with many body perturbation theory based on the Green's function formalism [9, 10]. Therefore we felt it of interest to reinvestigate the electronic structure of **1** in the ground state as well as in the various cationic states by means of the semiempirical INDO procedure of Reference [8]. We intend to test the reliability of the perturbational Green's function method within a simplified LCAO model in a molecule where ΔSCF ab initio calculations were insufficient to allow the interpretation of PE data.

2. Ground State Properties of 1

The molecular geometry of **1** [11] corresponds to the geometrical parameters of recent ab initio studies [7, 12]. In Table 1 we have summarized the outer valence orbitals of the Ni complex; a graphical display of the MO's is given in Figure 1. The highest occupied MO ($8e_1$) is predominantly of cyclopentadienyl (Cp) π-type destabilized by Ni $3d_{xz}/3d_{yz}$ contributions. The ligand π amplitude (78.6%) clearly dominates the Ni 3d admixture (9.1%). $15a_1$ is separated 2.95 eV from the complex HOMO; this MO is of $3d_{z^2}$ type with antibonding contributions from the 5σ donor of the nitrosyl group. In the case of $7e_1$ at -11.13 eV comparable contributions from the transition metal center and from the fivemembered ring are predicted. The degenerate $4e_2$ linear combination is strongly localized (96.8%) at the Ni center and is of $3d_{x^2-y^2}/3d_{xy}$ type. The INDO results differ from recent ab initio findings where a ground state MO sequence of $8e_1 > 7e_1 > 4e_2 > 15a_1$ is predicted [12].

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Table 1. Valence orbitals of cyclopentadienyl nickel nitrosyl according to an INDO calculation. The orbital energies (ε_i) are given in eV. The composition (%), the type, as well as the irreducible representation (Γ_i) of the MO wave function are displayed.

MO	Γ_i	MO-Type	ε_i	Ni %	Cp %	NO %
22/23	$8e_1$	e_1''(Cp), $3d_{xz}/3d_{yz}$, π^*(NO)	− 8.00	9.1	78.6	12.3
21	$15a_1$	$3d_{z^2}$	− 10.95	89.5	2.8	7.7
19/20	$7e_1$	$3d_{xz}/3d_{yz}$, e_1''(Cp), π^*(NO)	− 11.13	45.5	48.9	5.6
17/18	$4e_2$	$3d_{x^2-y^2}/3d_{xy}$	− 11.80	96.8	3.2	

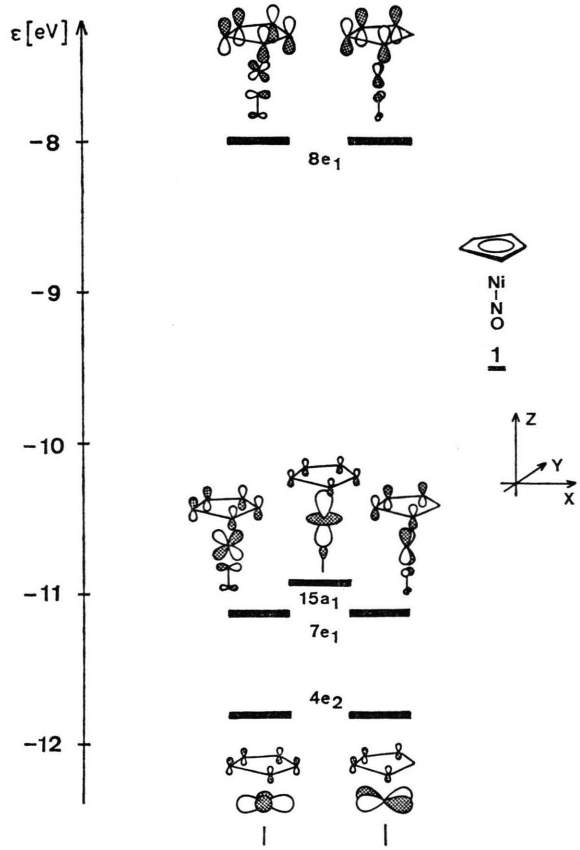

Fig. 1. Schematical representation of the outer valence orbitals of cyclopentadienyl nickel nitrosyl **1**.

Table 2. AO population and net charges in cyclopentadienyl nickel nitrosyl according to an INDO calculation.

AO	Ni	AO	C_{Cp}	N	O	AO	H
4s	0.043	2s	1.042	1.869	1.884	1s	0.877
$4p_x$	0.012	$2p\sigma$	2.071	0.969	1.269		
$4p_y$	0.012	$2p\pi$	1.160	1.576	3.190		
$4p_z$	0.034						
$3d_{z^2}$	1.979						
$3d_{xz}$	1.720						
$3d_{yz}$	1.720						
$3d_{x^2-y^2}$	1.988						
$3d_{xy}$	1.988						
Net charge	0.505		−0.273	0.586	−0.342		0.123

Table 3. Wiberg bond indices of cyclopentadienyl nickel nitrosyl according to an INDO calculation.

Bond	Bond Index
NiN	0.755
NiC	0.047
CC	1.374
NO	1.938

In Table 2 the results of a population analysis [13] are collected, Wiberg bond indices [14] are displayed in Table 3. The Ni 3d population in $3d_{z^2}$ and $3d_{x^2-y^2}/3d_{xy}$ is near $2e$ while the AO population of $3d_{xz}/3d_{yz}$ is reduced to about $1.72e$ as a result of metal to ligand charge transfer. The 3d center has a charge deficit of $0.505e$ while each carbon atom in the Cp moiety has a surplus of $0.273e$. Table 2 shows that the negative carbon net charges are the result of charge accumulation in the π AO's. In the case of the NO ligand a predominance of the σ-donor properties in comparison to the π-acceptor capabilities is recognized.

The Wiberg indices in Table 3 demonstrate that the NiN interaction is strongly covalent leading to a bond index of 0.755. On the other hand the covalent coupling to the C_5H_5 moiety is very small (0.047). Thus the nature of the NiCp interaction is primarily of ionic type leading to the VB representation $Cp^{\ominus}$ $(NiNO)^{\oplus}$ for the half-sandwich. The theoretically predicted ionic character is in line with experimental findings [15] and corresponds to interatomic ab initio populations calculated by Hillier et al. [12]. The charge accumulation in the Cp unit leads to a significant destabilization of the ligand π linear combination $8e_1$ (see Table 1) and should result in a low ionization potential for the degenerate π orbital.

3. Basic Theory

The principles of the Green's function method and its application in molecules without 3d atoms has been described in several references [16, 17].

Ionization potentials in the Green's function formalism are related to the zeros of the inverse Dyson equation (1) [18]:

$$G^{-1} = \omega I - \varepsilon - \Sigma(\omega) = \sigma . \tag{1}$$

$(\omega I - \varepsilon)$ is the inverse of the free Green's function (G^0) which is associated to the HF ansatz with canonical molecular orbital energies ε_j. ε in (1) symbolizes the diagonal matrix of these one-electron functions. I is the unit matrix and ω represents the energy coordinates that have to be determined. $\Sigma(\omega)$ is the self-energy part which is expanded in a series (2) according to different orders of perturbation.

$$\Sigma(\omega) = \Sigma^{(2)} + \Sigma^{(3)} + \Sigma^{(4)} + \ldots + \Sigma^{(\infty)} . \tag{2}$$

On the basis of Kelly's geometrical approximation [19] Cederbaum has derived a renormalized potential for the self-energy part which is given by the second order contributions and a single third order element [20]. The effective self-energy operator is defined in Eq. (3), the nomenclature corresponds to [20].

$$\Sigma^{\text{eff}} = \Sigma^{(2)} + \text{D}4 . \tag{3}$$

As $\Sigma^{(2)}$ and D4 have only first order poles the renormalized Σ^{eff} ansatz has the same analytical behaviour as the exact self-energy part $\Sigma(\omega)$ which can be written as sum of a constant part $\Sigma(\infty)$ and a ω-dependent part $M(\omega)$ with simple poles (Eq. (4)) [21].

$$\Sigma(\omega) = \Sigma(\infty) + M(\omega) . \tag{4}$$

The approximations used for the determination of the zeros in Eq. (1) are described in detail in [9].

4. The PE Spectrum and the Cationic States of 1

The low energy He(I) PE spectrum of **1** as well as the PE spectrum of the monomethyl derivative have been measured by Evans et al. [7]. Both spectra show four bands in the lower energy region below 12 eV. The first two maxima of the parent compound are found at 8.29 and 8.48 eV within two strongly overlapping bands. In the methyl derivative the two IP's are shifted to 8.09 and 8.32 eV, respectively. The center of gravity has been destabilized by about 0.18 eV. This shift is typical for $e_1(\pi)$ orbitals in a Cp unit as a result of methyl substitution and has been detected in various sandwich and half-sandwich complexes [22]. The assumption that the first two band maxima correspond to the degenerate $8e_1$ HOMO is supported if one takes into account the Jahn-Teller activity of the $^2\text{E}_1$ hole-state. In the case of topologically related CpBeX derivatives Jahn-Teller splits of about 0.2 eV have been observed for the degenerate Cp π linear combination [23]. The PE spectra of **1** and its methyl derivative show a shoulder at the high energy side of the two strongly overlapping bands ① and ②. Considering the relative cross sections of ligand MO's and metal 3d functions [24] it is evident that this shoulder can only arise from an ionization event of a nondegenerate metal 3d orbital ($= 15a_1$).

The third band in the Ni complexes is only destabilized by 0.07 eV due to the methyl group. The bandshape [7] is similar to peak ① and ② and shows a steep onset. According to the Franck-Condon principle [25] a weakly bonding or nonbonding MO is to be expected for this ionization event. Methyl shift and bandshape therefore suggest to assign the third maximum to the nonbonding $4e_2$ combination predominantly localized at the Ni site. Band ④ thus must be assigned to the $7e_1$ linear combination with comparable Ni 3d and Cp π amplitudes. The observed methyl shift (0.12 eV), which lies between the $8e_1$ and the $4e_2$ destabilization, is in line with the calculated MO localization properties.

The assignment $^2\text{E}_1 < {}^2\text{A}_1 < {}^2\text{E}_2 < {}^2\text{E}_1$ is the only combination that corresponds to the observed methyl shifts and to the integrated band intensities of Evans et al. [7] (see below).

	① + ② + (sh)	③	④	
1	3.1	1.9	2.1	
methyl derivative of **1**	3.3	1.9	2.1	relative intensities

ΔSCF ab initio calculations on the other hand predicted the following (incorrect) sequence for the cationic hole-states: $^2\text{E}_2 < {}^2\text{A}_1 < {}^2\text{E}_1 < {}^2\text{E}_1$. In Table 4 and Fig. 2 we have summarized the Green's function results based on the semiempirical INDO Hamiltonian. 12 hole-states and 13 particle-functions have been taken into account in the perturbational summation. It is seen that the Koopmans' configurations break down if relaxation and correlation effects are considered by means of the perturbational approach. The ionization sequence is even reproduced by the second order approximation to

Table 4. Comparison between the measured vertical ionization potentials ($I_{v,j}^{\text{exp}}$) of cyclopentadienyl nickel nitrosyl and the calculated ones, assuming the validity of Koopmans' theorem ($I_{v,j}^{K}$) and using the inverse Dyson equation ($I_{v,j}^{K} + \Sigma^{(2)}$ and $I_{v,j}^{K} + \Sigma^{\text{eff}}$, respectively). All values in eV (sh = shoulder).

Band	MO(Γ_j)	$I_{v,j}^{K}$	$I_{v,j}^{K} + \Sigma^{(2)}$	$I_{v,j}^{K} + \Sigma^{\text{eff}}$	$I_{v,j}^{\text{exp}}$
①	$8e_1$	8.00	7.71	7.83	8.29
②					8.48
(sh)	$15a_1$	10.95	8.13	8.89	8.70 sh
③	$4e_2$	11.80	8.19	9.26	9.30
④	$7e_1$	11.13	9.65	9.93	10.27

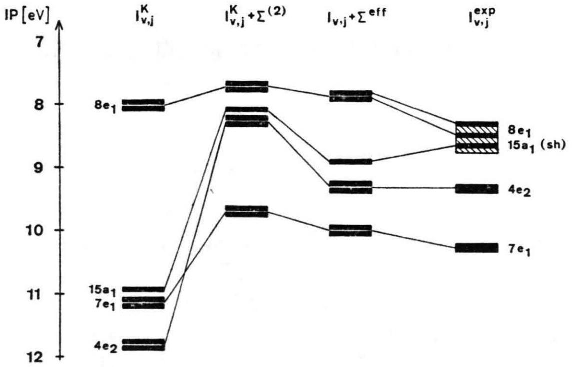

Fig. 2. Comparison between the measured vertical ionization potentials ($I_{v,j}^{\text{exp}}$) of cyclopentadienyl nickel nitrosyl and calculated ones assuming the validity of Koopmans' theorem ($I_{v,j}^{K}$) and using the inverse Dyson equation. $I_{v,j}^{K}+\Sigma^{(2)}$ symbolizes the second order approximation to the self-energy operator, $I_{v,j}^{K}+\Sigma^{\text{eff}}$ represents the renormalized ansatz (sh = shoulder).

the self-energy part ($\Sigma^{(2)}$) and the results are improved by means of the Σ^{eff} ansatz. The first IP is due to the $8e_1$ HOMO; the Koopmans' value of 8.00 eV is lowered in second order to 7.71 eV and is renormalized by 0.12 eV due to D4. Measured and calculated IP for the ligand π combination differ by 0.56 eV.

In the case of $15a_1$ 8.7 eV (experiment) must be compared with 8.89 eV (Eq. (3), $\Sigma^{(2)}$ gives 8.13 eV). As expected for a strongly localized MO large Koopmans' defect are predicted. The largest deviations between $I_{v,j}^{K}$ and the Green's function approach is encountered in $4e_2$ with the most pronounced localization properties at the 3d center. In second order a reorganization energy of 3.61 eV is predicted; the renormalization term amounts to 1.07 eV.

The Koopmans' defect of $7e_1$ lies between the two extremes $8e_1$ on one side (validity of Koopmans' theorem) and the strongly localized $15a_1/4e_2$ linear combinations on the other side. In second order the IP is reduced from 11.13 eV to 9.65 eV. The modification due to D4 contributes with 0.28 eV to the net defect.

In comparison to other Cp sandwich compounds the IP of the ligand π HOMO is lowered by about 1–2 eV.

Cp_2Fe: 9.05 (center of gravity e_{1u}/e_{1g}) [22]
$CpMn(CO)_3$: 10.10 eV [26]

On the other hand this IP is close to observed ionization energies of typical ionic cyclopentadienyl complexes. In Cp_2Mg the e_{1g} ligand π IP is found at 8.26 eV [22]. In the slip sandwich Cp_2Be the center of gravity between $a''(\pi)$ and $a'(\pi)$ lies at 7.94 eV [27]. The electronic structure in the Cp moiety of **1** therefore is similar to the sandwich complexes with Be and Mg. The position of the Ni 3d ionization events in the nitrosyl complex is close to the 3d ionization energies in nickelocene [24].

5. Conclusion

In the present study the electronic structure of cyclopentadienyl nickel nitrosyl in its ground state and its various cationic states has been investigated by means of a semiempirical INDO Hamiltonian. Ionization energies have been determined in the framework of many body perturbation theory based on the Green's function formalism. As a result of large electronic reorganization, differences between the sequence of the one-electron energies in the ground state and the measured ionization potentials have been verified.

As a result of the covalent coupling between the 3d center and the nitrosyl ligand, and the ionic interaction between Ni and the Cp ring the sequence of the 3d orbitals in **1** differs from the frontier orbital pattern generally accepted for these conical Cp fragments [28, 29]. In Fig. 3 we have displayed the two controverse bonding capabilities in half-sandwich complexes. On the top of Fig. 3 the 3d MO sequence of the transition metal center (M) is developed under the assumption that the MCp interaction (covalent) is predominant. The degenerate M 3d levels split under the influence of the

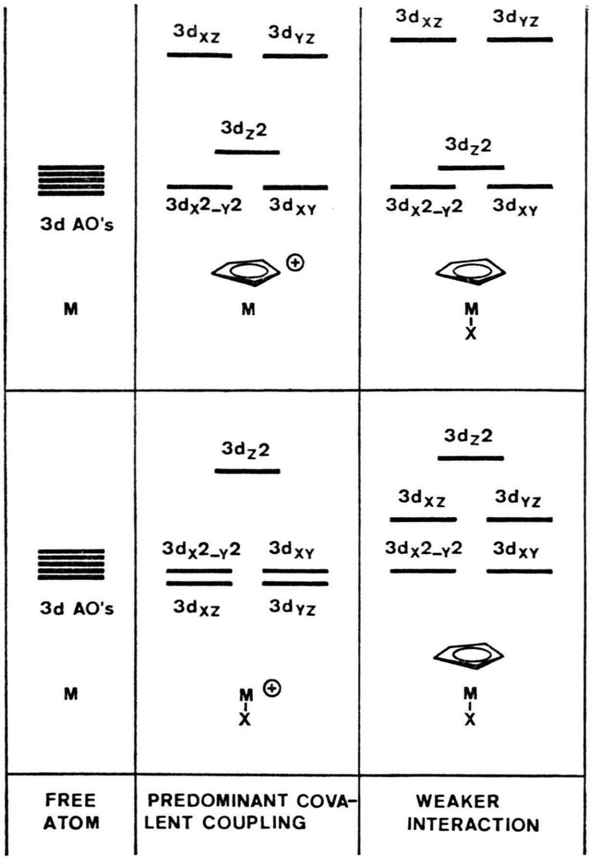

Fig. 3. Possible splitting patterns of the 3d orbitals in cyclopentadienyl transition metal X complexes. Top: predominace of the covalent coupling to the Cp moiety, weaker interaction with the X ligand. Bottom: strong interaction with the ligand X and weaker covalent coupling with the Cp ring. In **1** the latter splitting pattern is realized (M = transition metal center, X = hetero ligand).

Cp moiety into an e_2, an a_1 and an e_1 combination. Within the e_2 set ($3d_{x^2-y^2}/3d_{xy}$) the metal-ligand interaction is negligible. $3d_{z^2}$ (a_1) is destabilized by the filled $a_1(\pi)$ MO of the fivemembered ring. $e_1(3d_{xz}/3d_{yz})$ is strongly destabilized by filled Cp π orbitals of proper symmetry. The X ligand leads to a destabilization of the a_1 fragment orbital by means of the σ donor and to a stabilization of e_1 due to the π^* acceptor functions.

In the NO complex **1** (M = Ni, X = NO) the MO sequence differs from this pattern as a result of the predominant NiNO coupling. Here in the first step the fragment orbitals of the NiNO$^+$ moiety (MX$^+$) must be constructed (bottom of Figure 3). $3d_{z^2}$ is strongly destabilized by the donor function of the NO group while the degenerate e_1/e_2 linear combinations are close in energy. Due to the weaker covalent coupling with the Cp fragment the MO sequence $(e_2)^4(e_1)^4(a_1)^2$ is not modified. As a result of the stronger reorganization of e_2 during the ejection e_2 has a lower ionization energy than e_1. Therefore the sequence of the Ni 3d ionization events in **1** ($a_1 < e_2 < e_1$) differs from the IP's in nickelocene where $3d_{xz}/3d_{yz}$ on top of $3d_{x^2-y^2}/3d_{xy}$ and $3d_{z^2}$, respectively, is encountered [24].

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