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THE ELECTRONIC STRUCTURE OF CARBONYL METAL CLUSTERS

I. AN INDO INVESTIGATION OF MONO-, DI- AND TRINUCLEAR NICKEL COMPLEXES

GIANFRANCO PACCHIONI, PIERCARLO FANTUCCI
Istituto di Chimica Generale e Inorganica dell'Università, Centro CNR, Via Venezian 21, I-20133 Milano (Italy)

and VENANZIO VALENTI
Istituto Chimico dell'Università, Via S. Agostino 1, I-62032 Camerino (Italy)

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Summary

A series of mono-, di- and trinuclear nickel carbonyl complexes has been investigated by means of the MO-LCAO method. The total molecular energies, one-electron energies and electron distributions have been computed and their variations along the series are discussed. The wavefunction of the complex has been considered in terms of contributions of the individual MO's of the free CO molecule in order to compute the variations of the σ-donor and π-accepting ability of the carbonyl ligand.

Introduction

The increasing interest in the study of molecular clusters centers on the hypothesis that they can be considered as good models of the metal surfaces for certain chemisorption processes. A recent review [1] has pointed out that this hypothesis, if used with care, provides a useful tool for investigations since it is based on several interesting similarities between, for instance, the coordination to a metal center and the surface adsorption process of certain small molecules. In particular, on the basis of the theory of the "surface molecule" it can be concluded that the electronic mechanism of catalytic activation is the same on a surface as in a molecular cluster.

In recent years problems connected with the electronic activation of the small molecules have been investigated extensively by a variety of theoretical methods. However, this effort has been mainly directed toward the case of bare metal clusters. Molecular clusters, in contrast, have been little studied by theoretical methods, the only exceptions being qualitative treatments directed towards deriving general rules for the stoichiometry and shape of molecular clusters. The results of the most relevant of those studies are compared with those from the present study in the 'Conclusions' section below. The aim of this paper is to contribute to the knowledge of the electronic structure of nickel carbonyl clusters of low nuclearity. To this end we performed MO-LCAO calculations using an INDO-like method which can, in principle, overcome some inadequacies of the Hückel method, which is the most widely used for MO calculations on large metal clusters. In particular, we wish to establish the change of the electronic distribution at the nickel atoms and on carbonyl ligands upon formation of Ni—CO and Ni—Ni bonds. The commonly accepted synergic σ—π process is investigated in detail, since it is one of the most important contributors to the stability of a molecular cluster.

Computational method

We used a modified version of the INDO method, originally proposed by Pople et al. [2]. In this approximation the elements of the Fock matrix for a closed shell system are defined as follows:

$$F_{\mu\mu} = H_{\mu\mu} + \sum_{\nu \in A} R_{\nu\nu}[2(\mu\mu/\nu\nu) - (\mu\nu/\mu\nu)] + \sum_{B \neq A} \sum_{\nu \in B} 2R_{\nu\nu}(\mu\mu/\nu\nu); \qquad \mu \in A$$

$$F_{\mu\nu} = R_{\mu\nu} 3[(\mu\nu/\mu\nu) - (\mu\mu/\nu\nu); \qquad \mu, \nu \in A$$

$$F_{\mu\nu} = H_{\mu\nu} - R_{\mu\nu}(\mu\mu/\nu\nu); \qquad \mu \in A, \ \nu \in B$$

In the above expressions $R_{\mu\nu}$ and $H_{\mu\nu}$ stand for elements of the one particle density matrix and the core matrix, respectively, while $(\mu\nu/\lambda\sigma)$ is the usual notation for two-electron integrals. The core matrix elements are evaluated according to:

$$H_{\mu\mu} = U_{\mu\mu} - \sum_{B \neq A} \sum_{\nu \in B} n_\nu^0 (\mu\mu/\nu\nu) \tag{1}$$

$$H_{\mu\nu} = \tfrac{1}{2} S_{\mu\nu}(\beta_\mu + \beta_\nu) \tag{2}$$

In eq. 1, $U_{\mu\mu}$ represents the one-center empirical parameter which can be determined, for instance, by reproducing the experimental ionization energies of the neutral atom [3]; n_ν^0 is the orbital occupation number of the free atom in its reference valence state.

Since the second term of the r.h.s. of eq. 1 is used instead of the nuclear attraction integral, our method neglects all penetration effects. This is done, as in other INDO or CNDO methods, in order to avoid too large binding energies or too high ionization potentials.

The β_μ parameters in eq. 2 have been optimized in the present work only for Ni, C and O atoms, as described later. The one-center (F^0 Slater Condon parameters) and two-center Coulomb integrals are evaluated analytically using Slater orbitals expanded in three Gaussian functions of s type. This procedure produces rotationally invariant matrix elements, but with use of Slater exponents $\xi_{4s} = \xi_{4p} \neq \xi_{3d}$ for the nickel atom our method is not invariant with respect to the hybridization. In order to have a rotational invariant method, the one-center exchange integrals must be subjected to some specific constraints. If only the integrals of type $(\mu\nu/\mu\nu)$ are retained the rotational ivnariance condition is no longer fulfilled [3]. In order to overcome this difficulty it has been suggested that all the one-center integrals $(\mu\nu/\lambda\sigma)$ [4] should be considered or, more simply, mean values should be used for the $(\mu\nu/\mu\nu)$ integrals [3]. Using the second approach, the necessary exchange integrals are of the type (sp/sp), (sd/sd), (pp'/pp'), (pd/pd) and (dd'/dd'), which can be evaluated by means of Slater-Condon parameters tabulated, for instance, in ref. [4]. The atomic basis set used for the nickel carbonyl complexes includes the 2*s*, 2*p* orbitals on the carbon and oxygen atoms, with exponents determined by the Slater rules, while the exponents for the 3*d*, 4*s* and 4*p* orbitals of the nickel atom are taken from ref. [5].

The SCF iterative calculation was carried out according to the level-shifting procedure [6] in order to force the convergence.

Since the complexes studied here present high symmetry, there is considerable saving of computer time by working with the HF matrix factorized in symmetry blocks. The symmetry adapted functions are automatically generated using a new algorithm [7] implemented in a very efficient program. Besides the time saving, working with symmetry allows evaluation of the energy of different electronic configurations of well defined occupation number of each irreducible representation. This is an important point since our experience has shown that the aufbau principle applied within the level-shifting scheme does not necessarily produce the lowest energy configuration (see Table 2).

In order to discuss the σ donation-π back donation mechanism in relation to the coordination of the CO molecule, each occupied MO of the complex, Ψ_I, can be considered in terms of the occupied and virtual MO's, φ_i, of the free CO molecule. By projecting each Ψ_I on the space spanned by the φ_i's (with proper orientation) the following quantities can be evaluated:

$$n_i = 2 \sum_I \langle \varphi_i | \Psi_I \rangle^2$$

These have the obvious meaning of formal occupation numbers of the φ_i orbitals within the complex. The deviation of the n_i values from 2 or 0, which are the characteristic values of the free molecule, is a measure of the distortion of the wavefunction of the CO molecule upon coordination. For brevity, in the results section only the sums $N_\sigma = \Sigma n_\sigma$, $N_\pi = \Sigma n_\pi$ and $N_{\pi\star} = \Sigma n_{\pi\star}$ are reported. For instance, a value of N_σ lower than 6 indicates that the CO molecule donates electrons via a σ mechanism. However, N_σ includes also the electrons which occupy the $\sigma^\star$ virtual orbital of the free CO molecules. This occupation, for certain types of coordination, is by no means negligible, as it will be shown in the next section. It should be noted that the $n_{\pi\star}$ and $n_{\sigma\star}$ quantities strongly depend upon the shape and energy of the vacant MO's. We are aware that a semiempirical method probably cannot produce virtual orbitals of the correct shape and energy, and so our computed occupation numbers of the ligand are meaningful only for comparisons within a class of similar molecular systems.

The INDO results for the free CO molecule in its equilibrium geometry of 1.128 Å (see Table 1) were obtained by optimizing the parameters $\beta_{2s_C} = \beta_{2p_C}$ and $\beta_{2s_O} = \beta_{2p_O}$ in order to reproduce at the best corresponding "ab initio"

TABLE 1

MO ENERGIES AND NET CHARGES FOR THE CO MOLECULE [a]

	"ab initio" [b]	INDO
3σ	−1.533	−1.392
4σ	−0.759	−0.732
1π	−0.612	−0.575
5σ	−0.507	−0.484
Net atomic charges		
C	0.17	0.14
O	−0.17	−0.14
Total energy		
−112.28882		

[a] Energies in atomic units (1 a.u. = 27.21 eV). [b] Present work with STO-6G basis. The Slater exponents are taken from Clementi and Roetti [44]. In the "ab initio" work [10] a double-zeta basis set is used for the C atom. This produces for the free CO molecule a total energy of −112.550 a.u. and a net charge $q_c = 0.37$.

results, with the constraint that the computed binding energy (251.4 kcal/mol) is close in value to the experimental value (256.2 kcal/mol) [8]. The best β_c and β_0 parameters are found to be 8.0 and 27.0 eV, respectively. These results can be considered satisfactory in the sense that the computed charge distribution and the one-electron energies are closer to the "ab initio" values than those computed by the CNDO/2 method [9]. This method is known to underestimate the ionic character of the bond and generally to indicate too large values of the ionization potentials.

We obtained the corresponding β parameters of the nickel atom by applying a similar procedure to the $Ni(CO)_4$ complex, using as a reference "ab initio" calculation that of Veillard et al. [10]. The results, presented in the next section, correspond to values $\beta_{4s} = \beta_{4p} = 1.0$ eV and $\beta_{3d} = 18.0$ eV. For the dissociation process $Ni(CO)_4 \rightarrow Ni + 4\ CO$ we computed an energy of 142.2 kcal/mol, the experimental estimated value being 140.0 kcal/mol [11].

In the case of hydride complexes a Slater exponent of 1.2 for the 1s orbital of the hydrogen atom was adopted and the β_H parameter was kept equal to the CNDO/2 value of 9.0 eV. The MO calculations were carried out with a new computer program which can handle metallic cluster compounds with up to 150 atomic basis functions with low core memory occupation (64 kwords) and at small computational cost. For the largest cluster considered in the present work, $Ni_3(CO)_6(\mu_2\text{-}CO)_3$, the computer time required by the generation of the 99 symmetry adapted functions is 5 sec while the whole INDO calculation required 121 sec (CPU times on UNIVAC 1100/80).

Results and discussion

Before presenting the results of our INDO calculations it is appropriate to consider the general reliability of the theoretical approach used. In addition to the well known limitations of such an empirical method, there is a limitation connected with the determination of the β parameters, to which the spectrum of the one-electron energies and the binding energy are strictly related. As

TABLE 2

FORMULA, POINT GROUP SYMMETRY, ELECTRONIC CONFIGURATION AND DISSOCIATION ENERGY FOR MONO-, DI- AND TRINUCLEAR NICKEL CARBONYL COMPLEXES

Complex	Point group	Configuration [a]	E_D [b]
I, $Ni(CO)_4$	T_d	$3a_1, 4e, 3t_1, 15t_2$	142.2 [c]
II, $[Ni(CO)_3H]^-$	C_{3v}	$6a_1, 1a_2, 14e$	172.9 [c]
III, $[Ni(CO)_3]^{2-}$	C_{3v}	$6a_1, 1a_2, 14e$	5.2 [c]
IV, $Ni_2(CO)_6$	D_{3h}	$5a'_1, 1a''_1, 1a'_2, 5a''_2, 14e', 14e''$	275.5
V, $Ni_2(CO)_6H_2$	C_{2v}	$13a_1, 8a_2, 12b_1, 8b_2$	352.6
VI, $[Ni_2(CO)_6H]^-$	C_{2v}	$13a_1, 8a_2, 12b_1, 8b_2$	342.9
VII, $[Ni_2(CO)_6]^{2-}$	D_{3h}	$5a'_1, 1a''_1, 1a'_2, 6a''_2, 14e', 14e''$	170.5
		$5a'_1, 1a'', 2a'_2, 5a''_2, 14e', 14e''$	—78.8 [c]
VIII, $Ni_3(CO)_3(\mu_2CO)_3$	D_{3h}	$8a'_1, 1a''_1, 3a'_2, 3a''_2, 22e', 8e''$	430.9
		$9a'_1, 1a''_1, 3a'_2, 2a''_2, 22e', 8e''$	191.8
IX, $[Ni_3(CO)_3(\mu_2CO)_3]^{2-}$	D_{3h}	$9a'_1, 1a''_1, 3a'_2, 3a''_2, 22e', 8e''$	311.2
X, $[Ni_3(CO)_6]^{2-}$	D_{3h}	$7a'_1, 2a''_1, 5a'_2, 2a''_2, 22e', 8e''$	376.0
		$7a'_1, 2a''_1, 4a'_2, 3a''_2, 22e', 8e''$	119.1
		$6a'_1, 2a''_1, 5a'_2, 3a''_2, 22e', 8e''$	102.1 [c]
		$5a'_1, 2a''_1, 4a'_2, 3a''_2, 24e', 8e''$	—176.2
XI, $Ni_3(CO)_3(\mu_2CO)_3(\mu_3CO)_2$	D_{3h}	$11a'_1, 1a''_1, 3a'_2, 6a''_2, 24e', 10e''$	368.7
		$12a'_1, 1a''_1, 2a'_2, 6a''_2, 24e', 10e''$	225.4
XII, $[Ni_3(CO)_3(\mu_2CO)_3(\mu_3CO)_2]^{2-}$	D_{3h}	$12a'_1, 1a''_1, 3a'_2, 6a''_2, 24e', 10e''$	274.1
		$11a'_1, 1a''_1, 3a'_2, 5a''_2, 26e', 10e''$	205.0
		$11a'_1, 1a''_1, 4a'_2, 6a''_2, 24e', 10e''$	57.1
XIII, $[Ni_3(CO)_6(\mu_3CO)_2]^{2-}$	D_{3h}	$10a'_1, 2a''_1, 5a'_2, 5a''_2, 24e', 10e''$	344.9
		$10a'_1, 2a''_1, 4a''_2, 4a''_2, 26e', 10e''$	233.6
XIV, $Ni_3(CO)_9$	C_{3v}	$12a_1, 8a_2, 40e$	110.6
		$13a_1, 7a_2, 40e$	67.1
XV, $[Ni_3(CO)_9]^{2-}$	C_{3v}	$13a_1, 8a_2, 40e$	42.1
		$12a_1, 7a_2, 42e$	—18.7
XVI, $Ni_3(CO)_6(\mu_2CO)_3$	D_{3h}	$9a'_1, 2a''_1, 3a'_2, 6a''_2, 24e', 16e''$	291.8
XVII, $[Ni_3(CO)_6(\mu_2CO)_3]^{2-}$	D_{3h}	$10a'_1, 2a''_1, 3a'_2, 6a''_2, 24e', 16e''$	199.8
		$8a'_1, 2a''_1, 3a'_2, 6a''_2, 26e', 16e''$	145.8

[a] Numbers of occupied MO's of each irreducible representation. The MO's belonging to the degenerate representations have been counted as many times as the degree of degeneration. [b] E_D is the dissociation energy in kcal/mol relative to the process $[Ni_n(CO)_m]^{p-} \rightarrow n\ Ni + m\ CO + pe^-$. Similar definition holds for hydride derivatives. The nickel atom produced by the dissociation is supported to be in the $3d^94s^1$ valence state. [c] Auf bau principle results.

pointed out above, we carried out an optimization of the β parameters, which is unsatisfactory in some respects. In particular, the β values for the nickel atom, derived from calculations on the $Ni(CO)_4$ complex, correctly describe the Ni—C and Ni—O interactions, but may be incorrect for the Ni—Ni interactions. This clearly affects the computed strength of the Ni—Ni bond, which in all cases seems to be considerably overestimated. This implies that we cannot use our results to discern trends in the stability of clusters of different nuclearities, while the comparison between clusters of the same Ni_n class remains valid. The seventeen nickel carbonyl compounds we have studied are listed in Table 2. The anionic species II and III derived from the tetracarbonyl nickel have never been isolated but probably exist as intermediates in the reduction of I with alkaline metals [12—15]. These species containing nickel atoms with formal oxidation number —2 can react with the neutral complex I to give dinuclear complexes (V, VI, VII), of which only VI has been completely characterized in the solid state [16]. The forms V and VII are assumed only to be present in solution [12—15], and V has been postulated as an ammonolysis product of VII but its formation was not confirmed by recent investigations [16]. No experimental evidence is available for the existence of the neutral dinuclear complex IV or the neutral trinuclear clusters VIII, XI, XIV and XVI. The existence of other trinuclear clusters, even as dianions in solution, is a matter of controversy [17—20]. However, there is general agreement [20] that the trinuclear species may be present as intermediates in the reduction of I, or as intermediates in the cluster growth which produces the well characterized five and six metal species $[Ni_5(CO)_{12}]^{2-}$ and $[Ni_6(CO)_{12}]^{2-}$ [20,22].

These observations indicate that accurate information is not available on the molecular structure of most of the cluster compounds studied here. The exceptions are those of I [23], VI [16] and of the clusters with high nuclearity [24]. All the geometry parameters that we need for the MO calculations are derived from these three basic structures. For the complex V we assumed that both hydrogen atoms are in bridging positions with a local geometry identical to that determined for the complex VI.

Mononuclear complexes

Among the mononuclear species listed in Table 2 only form I has been extensively studied experimentally [26,27] or by theoretical methods [10,28—32]. As mentioned above, in order to determine the optimum β parameters of the nickel atom it was necessary that the INDO results should be close to the "ab initio" results of Veillard et al. [10]. In Table 3 the eigenvalues of the occupied MO's and some selected values of the electron distribution are reported. The ordering of the occupied MO's, as determined by our INDO method, shows some inversions with respect to that obtained by the more rigorous calculation. Also our charge distribution does not completely fit that from the "ab initio"

TABLE 3

MO ENERGIES AND ATOMIC NET CHARGES FOR THE $Ni(CO)_4$ COMPLEX [a]

	"ab initio", [10]		Present work
$5t_2$	—1.530	$6a_1$	—1.390
$6a_1$	—1.530	$5t_2$	—1.384
$7a_1$	—0.809	$7a_1$	—0.777
$6t_2$	—0.793	$6t_2$	—0.744
$8a_1$	—0.693	$1e$	—0.582
$1e$	—0.665	$7t_2$	—0.576
$7t_2$	—0.662	$1t_1$	—0.562
$1t_1$	—0.653	$8a_1$	—0.534
$8t_2$	—0.644	$8t_2$	—0.533
$2e$	—0.471	$2e$	—0.346
$9t_2$	—0.395	$9t_2$	—0.291
Net atomic charges			
Ni	0.24		0.20
C	0.29		0.12
O	—0.35		—0.17

[a] Energies in atomic units.

TABLE 4

ELECTRONIC DISTRIBUTION ON NICKEL ATOM AND CARBONYL LIGANDS IN MONONUCLEAR COMPLEXES

	$Ni(CO)_4$ (I)	$[Ni(CO)_3H]^-$ (II)	$[Ni(CO)_3]^{2-}$ (III)
$4s$	0.1916	1.6666	1.9402
$4p$	0.0807	0.0855	0.0682
$3d$	9.5291	9.0112	9.2568
q_{Ni} [a]	0.1986	−0.7633	−1.2652
q_{C}	0.1203	0.2000	0.2160
q_{O}	−0.1699	−0.3069	−0.4608
q_{H}	—	0.0840	—
N_σ [a]	5.9624	6.0074	6.0414
N_π	3.9963	3.9899	3.9810
$N_{\pi^\star}$	0.0908	0.1067	0.2197

[a] q_i = net charge of the atom i. [b] See text for definitions.

method. However, the agreement is satisfactory, at least qualitatively, since the wrong ordering of the occupied MO's occurs for groups of levels closely spaced in energy and the error in charge distribution does not affect, for example, the description of the changes experienced by the CO ligand. In fact, we have found that coordination produces a metal to ligand net transfer of 0.05 electrons for each CO group, while the corresponding "ab initio" value is 0.06. Finally, as already mentioned, our method has the advantage of reproducing very satisfactorily the experimental binding energy of the $Ni(CO)_4$ complex.

The Ni—C and C—O bond lengths used for the anionic complexes II and III are assumed to be equal to the experimental values observed for VI [16]. The Ni—H distance ranges from 1.47 Å in Ni—H molecule [8] to 1.70 Å as estimated in VI. Calculations performed on II for both Ni—H distances gave nearly identical charge distribution on nickel atom, CO ligands and hydrogen atom which carries a very small positive charge, 0.084 and 0.047, respectively.

The results of Table 4, which refer to the shortest Ni—H distance for II, show that in the three complexes the increase in the negative molecular charge is accompanied by an increase of the electron occupancy of the 4*s* orbital and thus by a more negative charge on the nickel atoms, for which we computed a total charge of 0.199, −0.076 and −1.265, respectively. The fact that a nickel atom carries a negative charge is not surprising, since some "ab initio" calculations [31,32] reached the same result for the neutral species I.

On going from I to III, we have an increase in electron density on the CO ligands, the negative charges on which are −0.050, −0.107 and −0.244, respectively. Interestingly, the increase in the molecular negative charge does not parallel the metal 3*d* orbital occupancy, which is lower in the anionic than in the neutral species. This can be explained by assuming that the electron accumulation in the nickel 4*s* orbitals increases the one-center Coulomb repulsion and raises the energy of the MO's with large metal components. Related to this is the fact that the nickel atom is more available for π back donation, as it is evident when one considers the variation of the $N_{\pi^\star}$ quantities of Table 4. However, we also obtained evidence that the virtual σ^* MO of the CO ligand has an occupation number which is not negligible: 0.036, 0.064 and 0.080 for I, II and III, respectively. This result, obtained by semiempirical method, is largely confirmed by a very recent "ab initio" investigation on $Ni(CO)_4$ [32] carried out with careful optimization of the 4*s* and 4*p* nickel orbital at the molecular level: it was found that π^* and σ^* vacant orbitals of the CO group are involved in the coordination to comparable extents.

On the basis of the dissociation energy values of the three mononuclear species, we conclude that the INDO method predicts the complex II to be more stable than the neutral species I. However, this result may be influenced by the inadequacy of the INDO parameters for the hydrogen atom which probably overestimates the Ni—H interaction. In contrast, we have confidence in the prediction of the very low stability of the dianion III.

Dinuclear complexes

We have studied the four species dinuclear nickel carbonyl complexes IV, V, VI and VII (see Table 2). The population analyses relative to this group of compounds are reported in Table 5. The electron distribution in the neutral species IV can be conveniently compared with that of I.

On going from a mononuclear to a dinuclear complex there is an increase in the nickel 4*s* orbital population. This can be explained by assuming that in I this oribtal is involved only in the metal—ligand σ interaction and can have a large component only in virtual MO's. In contrast, in a dinuclear complex the 4*s* orbital is strongly involved also in the metal—metal interaction. Bonding combinations (a_1' symmetry) and antibonding combinations (a_2'' symmetry) of the 4*s* orbitals contribute to occupied MO's of energy ranging from —8.54 to —21.70 eV (see Fig. 1). The highest energy must be compared with the eigenvalue of the 4*s* orbital of the free atom in the $3d^9\ 4s^1$ valence state which is

TABLE 5

ELECTRONIC DISTRIBUTION ON NICKEL ATOMS AND CARBONYL LIGANDS IN DINUCLEAR COMPLEXES

		$Ni_2(CO)_6$ (IV)	$Ni_2(CO)_6H_2$ [a] (V)	$[Ni_2(CO)_6H]^-$ [a] (VI)	$[Ni_2(CO)_6]^{2-}$ (VII)
4*s*		0.2975	0.3441	0.6082	1.1945
4*p*		0.0831	0.1151	0.0941	0.0803
3*d*		9.4382	9.3475	9.3700	9.2766
	q_{Ni}	0.1812	0.1933	—0.0723	—0.5514
CO	q_C	0.1268	0.0970	0.1220	0.2042
	q_O	—0.1814	—0.1842	—0.2736	—0.3527
CO'	q_C	—	0.1024	0.1258	—
	q_O	—	—0.1768	—0.2704	—
	q_H	—	0.0435	0.0467	—
CO	N_σ	5.9330	5.9838	6.0108	6.0191
	N_π	3.9931	3.9940	3.9924	3.9864
	N_{π^*}	0.1316	0.1092	0.1480	0.1846
CO'	N_σ	—	5.9612	6.0000	—
	N_π	—	3.9930	3.9916	—
	N_{π^*}	—	0.1200	0.1441	—

[a] For the complexes of C_{2v} symmetry there are four (CO) and two (CO') equivalent carbonyl groups.

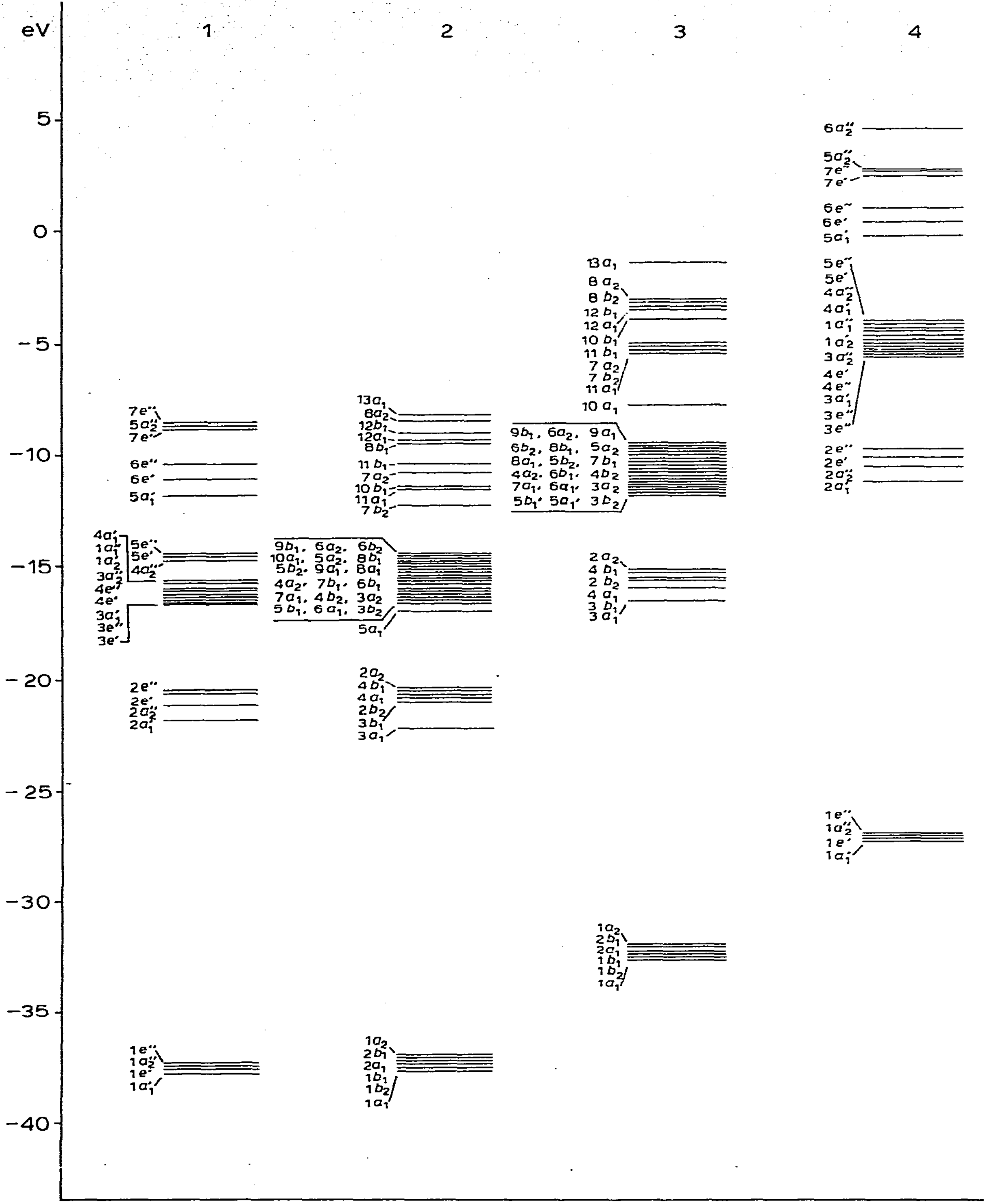

Fig. 1. One-electron energy spectrum of dinuclear nickel compounds. 1: $Ni_2(CO)_6$; 2: $Ni_2(CO)_6H_2$; 3: $[Ni_2(CO)_6H]^-$; 4: $[Ni_2(CO)_6]^{2-}$.

equal to —6.84 eV. It must be noted that the contribution of the a_1 MO's to the 4*s* orbital occupancy is slightly higher than that of the a_2 MO's. Moreover, the energy of each MO of a_1 symmetry is lower than the corresponding energy of the a_2 symmetry, thus producing a net binding effect.

As already observed for the mononuclear complexes, the increased 4*s* orbital occupancy is accompanied by a reduced 3*d* orbital population of the nickel atoms, and so by a variation of the energy of the MO's to which these orbitals mainly contribute. We conclude that on going from a mononuclear to a dinuclear complex there is a variation of both the energy and the composition of the occupied MO's which describe the metal—ligand interaction. This reflects, for instance, the ability of the carbonyl ligand to act as a stronger σ donor group (see Table 5): the transferred σ electrons to each nickel atom amount to 0.201, while the corresponding value computed in the case of the complex I is 0.150.

A similar variation is encountered also in the N_{π^*} values: each nickel atom of the dinuclear species IV donates 0.395 electrons to the π^* MO's of the CO groups. This quantity is slightly higher than that computed for the complex I (0.362). The dinuclear complexes V, VI and VII all contain nickel atoms in formal oxidation state —1 but differ markedly in stability and charge distribution. As for their stability, the data of Table 2 suggest that the hydride forms are much more stable than the dianion VII. In particular, the reaction $[Ni_2(CO)_6]^{2-} + H^+ \rightarrow [Ni_2(CO)_6H]^-$ can take place with high probability, being accompanied by a loss of energy of about 170 kcal/mol. The second reaction with a proton to give the dihydride complex $[Ni_2(CO)_6H]^- + H^+ \rightarrow Ni_2(CO)_6H_2$ is not very likely to occur in the condensed phase in polar solvents, since solvation of the charged species will largely compensate for the difference in stability between V and VI, which is computed to be only 9.6 kcal/mol. Our results indicate that V cannot be formed in basic solvents such as liquid ammonia [14,15], in agreement with recent experimental observations [16].

On the basis of the results reported in Table 5 we suggest an electronic mechanism for the formation of the hydride VI. We note that the negative charge of VII is largely localized on the nickel atoms, in particular in their 4*s* orbitals. This can be easily explained by assuming (see Fig. 1) that the HOMO of the dianion VII has a high energy, corresponding, to a first approximation, to a very pronounced basic character of the complex, and by taking account of the fact that the largest components in the HOMO are those of the nickel 4*s* orbitals. We conclude that the basic site of the complex is at the nickel 4*s* orbitals which can interact strongly with an incoming proton.

Similar reasoning can be used to explain the formation of the complex V, but in this case the above effects of interaction between a proton with the nickel 4*s* orbitals are less evident since the negative charge is largely delocalized on the ligands. Such a description is equivalent to the statement that in the Ni—H bond the contribution of the 3*d* orbitals of the nickel atom is negligible, and is confirmed by "ab initio" calculations on the diatomic Ni—H [33] or model studies of the chemisorption of hydrogen atoms on nickel surfaces [34].

Finally, (see Fig. 1 and Table 5) our results show a regular trend in the series V, VI and VII. As the molecular charge increases, the HOMO energy increases from —8.19 to —1.84 and 4.47 eV, respectively, while the 4*s* and 3*d* nickel orbital density associated with the HOMO vary according to 0.08, 0.33, 0.84 and 0.41, 0.28, 0.04, respectively.

The data in Table 5 relative to the occupation numbers of the MO's of the CO ligands merit comment. As expected, an increase of negative charge on the nickel atom (in the series IV, V, VI, VII) is accompanied by a more pronounced back donation toward the π^* MO's of the CO groups. In the same series, however, there is a regular increase of occupation of the σ^* virtual MO's, which amounts to 0.039, 0.041, 0.056 and 0.080 electrons, respectively (average values for non-equivalent carbonyl ligands in V and VI). When this contribution is taken into account, the electrons actually donated by each CO ligand are 0.145, 0.072, 0.053, 0.061, respectively, showing that the donor ability is effectively reduced in the presence of a negative charge on the complex, which makes the nickel atoms weaker acid centers.

Trinuclear complexes

The trinuclear clusters which we considered (VIII—XVII of Table 2) can be thought of as a small part of the cluster $[Ni_5(CO)_9(\mu_2\text{-}CO)_3]^{2-}$. In the case of the clusters XI, XII, XIII we also consider the presence of μ_3-type carbonyls in order to see whether the present INDO approach correctly differentiates the three types of CO coordination.

The trinuclear clusters can be conveniently partitioned into three groups of complexes, having six, eight and nine carbonyl ligands, respectively. As mentioned in the previous section, our SCF procedure allowed us to compute different electronic configurations. Some of these, corresponding to the lowest energy, are listed in Table 2, while Tables 6, 7 and 8 show the electron population data relative to the electronic ground state of the complexes.

The first group of clusters includes the species VIII and the dianions IX and X, which differ for the presence of the μ_2-type CO groups. We take the neutral complex VIII as an example in discussing the formation of the metal—metal

TABLE 6

-ELECTRONIC DISTRIBUTION ON NICKEL ATOMS AND CARBONYL LIGANDS IN TRINUCLEAR COMPLEXES

		$Ni_3(CO)_3(\mu_2CO)_3$ (VIII)	$[Ni_3(CO)_3(\mu_2CO)_3]^{2-}$ (IX)	$[Ni_3(CO)_6]^{2-}$ (X)
4*s*		0.5574	1.1845	1.2494
4*p*		0.0184	0.0798	0.0552
3*d*		9.3343	9.1649	9.1825
	q_{Ni}	0.0270	—0.4302	—0.4871
CO	q_C	0.1660	0.2487	0.2102
	q_O	—0.1495	—0.2806	—0.2996
μ_2CO	q_C	0.1649	0.1822	—
	q_O	—0.2077	—0.3861	—
CO	N_σ	5.9300	5.9387	5.9976
	N_π	3.9965	3.9930	3.9933
	N_{π^*}	0.0570	0.0998	0.0985
μ_2CO	N_σ	5.8334	6.0226	—
	N_π	3.9697	3.9714	—
	N_{π^*}	0.2396	0.2098	—

TABLE 7

ELECTRONIC DISTRIBUTION ON NICKEL ATOMS AND CARBONYL LIGANDS IN TRINUCLEAR COMPLEXES

		$Ni_3(CO)_3(\mu_2CO)_3(\mu_3CO)_2$ (XI)	$[Ni_3(CO)_3(\mu_2CO)_3(\mu_3CO)_2]^{2-}$ (XII)	$[Ni_3(CO)_6(\mu_3CO)_2]^{2-}$ (XIII)
$4s$		0.3619	0.9378	1.0053
$4o$		0.1100	0.1094	0.0898
$3d$		9.3851	9.2568	9.2786
	q_{Ni}	0.1430	−0.3040	−0.3737
CO	q_C	0.1618	0.2251	0.1950
	q_O	*−0.1366*	*−0.2677*	*−0.2821*
μ_2CO	q_C	0.1137	0.1550	—
	q_O	−0.2009	−0.3601	—
μ_3CO	q_C	0.0893	0.1959	0.2109
	q_O	−0.2085	−0.3672	−0.3879
CO	N_σ	5.9198	5.9501	5.9938
	N_π	3.9962	3.9939	3.9940
	$N_{\pi\star}$	0.0588	0.0985	0 .0992
μ_2CO	N_σ	5.9906	6.0182	—
	N_π	3.9730	3.9710	—
	$N_{\pi\star}$	0.2136	0.2157	—
μ_3CO	N_σ	5.9711	6.0278	6.0218
	N_π	3.9752	3.9662	3.9674
	$N_{\pi\star}$	0.1725	0.1770	0.1876

bond. As in the case of the dinuclear complex IV, we assume that the bond is formed mainly by interaction of the nickel 4*s* orbitals. In D_{3h} symmetry, these span the irreducible representations a_1' and e'. The a_1' representation contains the nodeless combination which has fully bonding character. The occupied MO's in which the 4*s* linear combination has appreciable weight (at least 4 percent) have energies ranging from —21.8 eV to —8.5 eV. All these levels are more stable

TABLE 8

ELECTRONIC DISTRIBUTION ON NICKEL ATOMS AND CARBONYL LIGANDS IN TRINUCLEAR COMPLEXES

	Ni	$Ni_3(CO)_9$ (XIV)	$[Ni_3(CO)_9]^{2-}$ (XV)	Ni [illegible]$CO)_6(\mu_2CO)_3$ (XVI)	$[Ni_3(CO)_6(\mu_2CO)_3]^{2-}$ (XVII)
$4s$		0.2425	0.8243	0.3512	0.7978
$4p$		0.0904	0.0879	0.1023	0.0992
$3d$		9.4899	9.3281	9.4131	9.3427
	q_{Ni}	0.1771	−0.2403	0.1334	−0.2397
CO	q_C	0.1012	0.1474	0.1108	0.1767
	q_O	−0.1597	−0.2887	−0.1457	−0.2749
μ_2CO	q_C	—	—	0.1287	0.1275
	q_O	—	—	−0.1916	−0.3574
CO	N_σ	5.9796	6.0364	5.9810	6.0042
	N_π	3.9930	3.9932	3.9957	3.9948
	$N_{\pi\star}$	0.1057	0.1330	0.0582	0.1010
μ_2CO	N_σ	—	—	5.8399	6.0199
	N_π	—	—	3.9668	3.9662
	$N_{\pi\star}$	—	—	0.2561	0.2438

than the 4*s* orbital in the free atom because of the ligand contribution, but those of a'_1 symmetry have larger 4*s* components and lower energy than the corresponding MO's of e' symmetry. This situation produces a net Ni—Ni bonding effect, which is also reflected by an increase in the 4*s* orbital occupancy in the complex VIII compared with that in the neutral mono- and dinuclear complexes (see Table 5). It is important to note, however, that a too large accumulation of electrons into the 4*s* orbitals would increase the energy of some of the corresponding a'_1 and e' MO's above the level of the 4*s* orbital in the free atom, thus producing a loss of stability of the metal cluster. This is exactly what happens for the complex VIII on going from the configuration ($8a'_1$, $1a''_1$, $3a'_2$, $3a''_2$, $22e'$, $8e''$) to the configuration ($9a'_1$, $1a''_1$, $3a'_2$, $2a''_2$, $22e'$, $8e''$). This change is equivalent to the excitation of an electron pair from a MO of a''_2 symmetry (which does not contain nickel 4*s* orbitals) to a MO of a'_1 symmetry. Correspondingly, the nickel 4*s* orbital population increases from 0.557 to 0.709 and the dissociation energy decreases by 239.1 kcal/mol.

The two anionic clusters IX and X are less stable than the neutral one VIII. However, the form X with terminal carbonyls only is preferred over the form IX with μ_2-type ligands. Both forms differ from the neutral one by a fairly strong localization of the negative charge on the nickel atoms, a result which parallels that found in the case of mono- and dinuclear complexes (see Table 6). The nickel atoms in IX carry a smaller negative charge than those in X because in the former complex the charge is more delocalized onto the ligands. This is related to the π accepting ability of the μ_2-type carbonyls, whose $N_{\pi\star}$ value is twice as large as that of the terminal carbonyls. On the other hand, the lower stability of IX with respect to X can be explained in terms of the fact that in IX the σ^* occupation number for both type of carbonyls is considerably higher than in X.

The clusters XI, XII and XIII contain eight CO ligands, two of which are assumed to be face-bridging. For this type of ligands there are no X-ray structural data available, and we assume the Ni—C and C—O distances equal to 2.0 and 1.20 Å, respectively, derived from the molecular structure of $[Co_6(CO)_{16}]^{2-}$ [35] and $[Co_6(CO)_{14}]^{2-}$ [36]. As discussed later, these bond distances were varied slightly in order to determine their influence on the electronic distribution of the CO ligands. The data reported in Tables 2 and 7 refer to the above structural parameters.

For the neutral species XI, which is the most stable of this group, we computed two different configurations (see Table 2). The second corresponds to a nickel 4*s* orbital population equal to 0.709, which is greater than that (0.361) for the first configuration (see Table 7). This confirms our findings for the previously discussed trinuclear clusters. Both dianions XII and XIII are less stable than the neutral cluster, but in this case also the form without bridging ligands is preferred over the form XII with μ_2-CO groups. The electron distribution in this group of clusters deserves particular attention.

It is usually accepted on the basis of IR C—O stretching frequencies that the π^* orbital occupation of the carbonyl ligand increases going from terminal to μ_2- and μ_3-CO. The data in Table 7, however, indicate that the bridged ligands are much more effective π accepting groups than the terminal ones, but are very similar to each other. To show how these results depend upon the geometry parameters assumed for the μ_3-CO ligands we carried out calculations with different bond lengths.

For the cluster XII, chosen as an example, we computed the charge distribution for a Ni—C distance of 2.0 and 1.90 Å, and for corresponding C—O distances of 1.20 and 1.22 Å. Such a small variation in CO geometry has a marked effect only on the charge distribution of the μ_3-CO ligands, the other types of ligands retaining electron densities almost the same as those reported in Table 7. In particular we find that the decrease of the Ni—C distance is accompanied by an increase of the $N_{\pi*}$ value. A similar effect is produced by an increase in the C—O bond length, although to a smaller extent. For Ni—C = 2.0 Å we have $N_{\pi*}$ equal to 0.177, 0.185 corresponding to C—O = 1.20 and 1.22 Å, respectively. For Ni—C = 1.90 Å the corresponding values for $N_{\pi*}$ are 0.230 and 0.242.

We can conclude that variations of the order of 0.1 Å in the Ni—C distance, and even smaller in the C—O distance, are still very important in producing changes in the charge distribution of the μ_3-CO ligand, which for acceptable geometry becomes more π accepting than the μ_2-type carbonyl. However, we observe that our INDO method indicates a low π accepting character for the μ_3-CO ligand. This may be due to the fact that the π^* CO orbitals in our calculation are higher in energy than those indicated by "ab initio" methods, and, by consequence, less able to interact with $3d$ nickel orbitals than they actually are.

The last group of trinuclear clusters we consider comprises the species XIV and XV, with all the nine carbonyls in terminal arrangement, and the species XVI and XVII with three bridged carbonyls. A general consideration is that each element of this group of clusters is characterized by a lower stability than the other trinuclear clusters with fewer CO ligands. Within the group, however, the forms XIV and its dianion XV are less stable than the corresponding forms XVI and XVII which have bridged carbonyls. This clearly represents an important difference from the previously discussed clusters and may be tentatively explained by considering that the μ_2-CO ligands seem in this case to be much better σ donors and π acceptors than the terminal ones (see Table 7). However, there may be an important contribution to the cluster stability from the ligand—ligand interaction. For the geometry arrangement characteristic of the forms XVI and XVII we have a lower total nuclear repulsion than with XIV and XV. Of course, this effect is expected to be more important as the ratio between the number of carbonyls and metal atoms increases.

Little need be said about the relative energies of the different electron configurations (and the associated charge distributions) shown in Table 2, since they are similar to those for the other trinuclear clusters.

Conclusions

The main features of the INDO results obtained for a quite large series of nickel carbonyl complexes can be summarized as follows. First, we find that the neutral forms should always be more stable than the dianions. This seems to be in contrast with the experimental evidence, since the few isolated nickel carbonyl clusters are always in the anionic form. However, this anionic form exists in solution in polar solvents in the presence of strong reducing agents, or in the solid state where the ionic lattice energy may produce an overstabilization. In contrast, MO-LCAO calculations refer to isolated gas phase molecules. In this case, the prediction of a low electron affinity favouring the neutral species of this class of clusters, seems reasonable.

A few comments can be made on the comparison of our results with those of others. The only example of MO calculation on transition metal clusters with a theoretical approach similar to that we used is the work of Freund and Hohlneicher [29], but they did not comment on the cluster stability. Other theoretical approaches make use of the Hückel theory in its iterative [37] or non-iterative version [38]. The latter seems useful only for a qualitative description of the orbital splitting due to the metal—metal and metal—ligand overlap, or for producing a visual picture of the MO energy spectrum depending upon the nodal character of the one-electron wavefunction. Nevertheless, such theoretical approaches have produced interesting results relative to the shape of the metal cage, and the electron-count model proposed by Mingos [39] and Lauher [38] are examples. Special mention must be made of the work of Stone [40], which seems the best attempt to explain not only the energy spectrum of the bare metal cluster orbitals but also of the ligand orbitals. However, also this last approach does not overcome the inadequacies inherent in the non-iterative Hückel theory. In our opinion, this theoretical method cannot give satisfactory explanations when important electron redistributions occur, or when the bond formation must be described in terms of donation-back donation as is the case for the carbonyl complexes.

Our MO calculations, in contrast, are aimed at defining in more detail the electron distribution within the clusters, and in particular to delineate the electron modifications experienced by the CO ligands in different coordination positions. To underline the nature of our theoretical approach we consider the Ni_3 clusters. In Lauher's theory for a trinuclear cluster (D_{3h} symmetry) a cluster valence electron (CVE) number equal to 48 should correspond to a fully stable electronic configuration. We have presented INDO results for ten clusters with D_{3h} symmetry, but with different CVE numbers. According to this, the trinuclear clusters can be grouped as follows: VIII, 42 CVE; IX, X, 44; XI, 46; XII, XIII, XIV, XVI, 48; XV, XII, 50. Only for the last two clusters is the "magic" number of 48 CVE's exceeded and in this case we can safely apply the Lauher's prediction that a low stability should be associated with a too electron-rich character of the cluster itself.

For the other clusters with CVE numbers less or equal to 48, we did not obtain evidence for preferred ratios between the number of the electrons formally associated with the ligand groups or the molecular charge and the number of atoms. We conclude that the stability of a cluster also depends strongly upon the geometry of the coordinated ligands and not only upon their number. On the other hand, prediction of the stability of a molecular cluster on the basis only of an MO energy spectrum for a bare metal cage should be taken with care, since our INDO calculations have shown that this spectrum changes markedly under the influence of the ligand contributions.

Concerning the charge distribution within the nickel compounds studied, we note that the INDO method indicates a trend in the σ-donor π-accepting properties of the CO ligand: which is in agreement with chemical intuition. In order to discuss satisfactorily the σ-π synergetic mechanism of carbonyl coordination it is important to determine the MO occupation number of the CO group, as we have done by breaking down the cluster wavefunction. In this respect our approach seems to be a chemically interesting tool for investigation which, while computationally very easy, has not been widely applied before. For instance in ref. [29] the π accepting ability of the CO ligand is measured on the basis of the negativation of the oxygen atom with respect to the free molecule. Our results of Tables 6, 7 and 8 show, on the contrary, that this kind of correlation cannot be considered as satisfactory in all cases, and that it is wrong in the particular case of the dianion. We believe that the negative charge on the ligand atoms is largely determined not only by the N_{π^*} quantities, but also by the N_σ. The second important point refers just to these N_σ quantities. As shown in the previous section, the N_σ quantities measure both the loss of electrons due to σ donation and of the electrons which occupy the σ^* vacant orbital. While the π^* orbital population can be easily explained by symmetry arguments relative to the metal—ligand interaction [41,42], the σ^* occupation cannot. It can only be explained on the basis of a more general theory describing the coordination of a ligand as a weighted superposition of ground and excited configurations of the metal and ligand groups. If, as we believe, in certain cases the σ^* occupation is by no means negligible, the commonly accepted theory relating to the red-shift of the stretching frequencies of the coordinated carbonyls [43] must be revised. We assume that the lower-frequency shift is proportional only to the N_{π^*} value, while the σ^* occupation may play an even greater role in the weakening of the C—O bond. Due to the limitations of our present theoretical approach we can only suggest the existence of this effect, and cannot depict it quantitatively. More rigorous investigations by the configuration interaction method will probably clarify this problem.

The present computational method will be applied in a later paper to the nickel carbonyl clusters with higher nuclearity to further investigate the stabilizing role of the CO ligand compared with the bare metal cage.

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