Bonding in nickel cluster carbonyls

G. Pacchioni and P. Fantucci
Dipartimento di Chimica Inorganica e Metallorganica, Centro CNR, Università di Milano,
via Venezian 21 I-20133 Milano, Italy

Received 4 July 1988

Semiempirical (INDO) and ab initio valence only calculations of the electronic structure of Ni_n and Ni_n(CO)_m clusters support the idea that the bonding with the CO ligands destabilizes the 4s-like MOs of the Ni_n fragment thus eliminating their contribution to the metal-metal bonding in the carbonylated form. This process is accompanied by a complete quenching of the magnetic moment of the bare cluster.

PACS: 36.40; 31.20.R

Introduction

Inorganic clusters with ligands have been proposed as a bridge between organometallic and surface chemistry [1]. This idea is based on the hypothesis that similar electronic mechanisms govern the bonding of small molecules on surfaces and on clusters. However, the nature of the metal-metal bonding and in particular the role of metal d electrons in transition-metal organometallic clusters is far from being completely understood and the assumed similarity with the bonding in bulk metals has still to be proved. Qualitative arguments [2] support the view of a metal-metal bond arising entirely from interactions involving the metal d orbitals in bare and in carbonylated metal clusters. It has been suggested [2a] that the role of the ligands is basically that of inducing a considerable d-p hybridization, thus maximizing metal-metal and metal-ligand overlaps.

Only recently it became possible to perform more rigorous quantum-mechanical studies [3] on organometallic clusters because of the difficulties connected with the treatment of transition metal atoms. These studies [3] provide first evidences of the very different metal-metal interaction in clusters with ligands (in particular CO) with respect to the bare counterparts. It is now clear that in small naked clusters of atoms of the first transition series (e.g. Fe, Co, Ni) the bonding originates mainly from 4s-4s interactions [4–6]. The 3d electrons belong to orbitals strongly contracted around the metal centers and characterized by small interatomic 3d-3d overlap. The appearance of typical ferromagnetic spin ordering [4–6] is the consequence of the weak coupling between unpaired electrons on different centers.

In a preliminary investigation performed at semiempirical level of theory [7] we have shown that the effect of adding CO ligands to a bare paramagnetic Ni_n cluster is that of reducing the number of unpaired electrons per atom leading to low-spin (for coordinatively unsaturated) or diamagnetic (for coordinatively saturated) XNi_n(CO)_m clusters.

Here we present an extension of our previous INDO investigation focused on the metal-metal bond changes caused by the carbonylation. In addition, we further support our conclusions reporting the results of preliminary non empirical Effective Core Potential (ECP) calculations on Ni_3 and Ni_3(CO)_6 systems.

Results of semiempirical INDO calculations

Previous INDO investigations on Ni_3, Ni_5, Ni_3(CO)_8 and Ni_3(CO)_6 systems [7] have been extended to Ni_6 and Ni_6(CO)_12 clusters (Fig. 1). The details of the computational procedure are given elsewhere [7]. The
The geometry of the carbonylated system has been derived from the experimental X-ray structure of [(Ni₆(CO)₁₂)²⁻] [8]. For the bare Ni₆ cluster the same geometry of the metal core of Ni₆(CO)₁₂ has been assumed. We found for Ni₆ at least six states in an energy range of less than 2 eV; all these states are paramagnetic containing two to six unpaired electrons. An attempt of precisely defining the ground state of Ni₆ on the basis of a semiempirical method can be questionable. Nevertheless, it is significative that the present method gives the lowest closed shell singlet state lying at about 3.3 eV above the lowest paramagnetic state (³A₂_u). The singlet state corresponding to three 3d1⁰ Ni atoms lies 8 eV above the ground state, i.e. much higher than the dissociation limit.

The existence of several low-lying states, a typical feature of clusters of metal atoms [9], originates from 3d → 3d and 3d → 4s excitations. Accurate ab initio CI calculations on Ni₃ [5] have shown the existence of four almost degenerate states which differ only for the position of the 3d-holes, i.e. 3dδ or 3dπ. When we consider the Ni₆(CO)₁₂ cluster, we found that the ground state is a ³A₁g well separated from the lowest paramagnetic configuration (³A₂₃, (a₂₃ → a₁₉, LUMO), ΔE = 2.2 eV). The a₁₉ LUMO in Ni₆(CO)₁₂ is the bonding combination of the 4s Ni orbitals and the ³A₂₃ state arises indeed from a 3d → 4s excitation. The change in the magnetic moment due to the bonding with the CO ligands reflects the electronic rearrangements occurred in the metal fragment. To follow these modifications we adopted three criteria (Table I): a) the average atomic Ni population, b) the values of the Wiberg indices [10] (the sum of the squares of the elements in the interatomic blocks of the one-particle density matrix, roughly proportional to the bond order) and c) the Ni-Ni two-center energy contribution obtained by partitioning the total energy of the system as sum of one- and two-center terms: E_{tot} = Σ̃E_a + Σ̃ab E_{ab}.

The effect of the carbonylation of the Ni₆ cluster is that to change the atomic Ni configuration from 4s0.3 3d⁹.⁷ (in the triplet state) to 4s0.⁰ 3d⁹.⁴. The reduced 4s population is due to the destabilization of the 4s-derived MOs caused by repulsion of the 4s and CO 5σ charge distributions (Pauli repulsion) [11], with the consequent promotion of the Ni electrons from 4s to 3d. The 4s-4s contribution to the metal-metal bonding is therefore completely removed in the carbonylated cluster. All the fifteen 3d-like MOs are doubly occupied in the Ni₆(CO)₁₂ complex, but the Ni 3d population is only 9.4 because of the metal-CO back-donation mechanism. The electronic redistribution following the interaction with the CO ligands has a direct effect on the strength of the metal-metal bond. This is shown by the values of the two-center contributions to the total energy, E_{Ni–Ni}, and by the Wiberg indices: both these quantities decrease significantly on going from the naked to the carbonylated form (Table I).

### Results of ECP calculations

These conclusions, deduced from semiempirical calculations, need to be substantiated by more rigorous quantum-mechanical approaches. For this reason we performed ab initio ECP Hartree-Fock calculations on Ni₃ and Ni₆(CO)₁₂ clusters. The calculations use the non-relativistic ECP developed by Hay and Wadt [12] which replaces the Ne core but leaves the 3s, 3p, 3d, 4s and 4p as valence orbitals. The Ni basis set is the same as reported by Hay and Wadt [12], except that the most diffuse p function has been eliminated because it originates nearly-linear dependency problems when combined with the analogous functions on different Ni atoms. The basis for Ni was contracted to [3s2p2d]. C and O atoms where treated at all electron level adopting a minimal basis set of Gaussian type orbitals [7s3p/2s1p] [13].

The Ni₃ was considered in a fixed equilateral triangular geometry with r(Ni-Ni) = 2.38 Å, the same distance observed in the Ni₃(CO)₆ subunit of the [Ni₆(CO)₁₂]²⁻ cluster [8]. As discussed by Basch et al. [4] and more recently by Walch [5], the dominant 

### Table 1. Analysis of the strength of the metal-metal bond in Ni₆ and Ni₆(CO)₁₂ clusters (INDO results)

<table>
<thead>
<tr>
<th></th>
<th>Ni₆(D₃h)</th>
<th>Ni₆(CO)₁₂ (D₃h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground state</td>
<td>³A₂₃</td>
<td>³A₁g</td>
</tr>
<tr>
<td>Total energy (au)</td>
<td>-233.5032</td>
<td>-492.6723</td>
</tr>
<tr>
<td>De (eV)</td>
<td>1.15⁷</td>
<td>1.43⁹</td>
</tr>
<tr>
<td>average Ni configuration</td>
<td>4s₀ / ³A₂₃  / 3d⁹ / ³A₁₉</td>
<td>4s₀ / ³A₂₃  / 3d⁹ / ³A₁₉</td>
</tr>
<tr>
<td>E_{Ni–Ni} (au)</td>
<td>-0.241</td>
<td>-0.133</td>
</tr>
<tr>
<td>E_{Ni–Ni} (au)</td>
<td>-0.093</td>
<td>-0.028</td>
</tr>
<tr>
<td>Wiberg index Ni–Ni</td>
<td>0.229</td>
<td>0.026</td>
</tr>
<tr>
<td>Wiberg index Ni–Ni’</td>
<td>0.114</td>
<td>0.005</td>
</tr>
</tbody>
</table>

* Defined as [6E(Ni)−E(Ni₆)]/6
* Defined as [(12E(CO) + E(Ni₆)−E(Ni₆(CO)₁₂))/12

---

Fig. 1. Geometry of Ni₆ and Ni₆(CO)₁₂ clusters