Carbonylated Nickel Clusters: From Molecules to Metals

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Introduction

What is a metal cluster? The question has been around in organometallic chemistry for at least 30 years, the time which has passed since the first examples of polynuclear metal complexes were reported.[1] In Figure 1 the structure of a "classical" cluster compound, $[Ni_6(CO)_{12}]^{2-}$, is shown.[2] In this structure two different Ni–Ni distances can be observed; the one within the triangular $Ni_3(CO)_6$ unit is about 0.1 Å shorter than in metallic Ni (2.49 Å) while the second one, separating the $Ni_3(CO)_6$ monomers, is considerably longer, 2.77 Å. Despite this substantial difference in bond lengths, solid lines are drawn to connect all the Ni atoms in the compound. According to the Lewis notation, lines between atoms indicate the existence of a chemical bond. The idea of drawing solid lines among the metal atoms in the cluster cage has a 2-fold origin. On the one hand, it is the simplest way to display the connectivity and the topology of the cluster; on the other hand, it refers to the original definition of a cluster, i.e., to "a compound containing a finite group of metal atoms which are held together entirely, mainly or at least to a significant extent by bonds directly between metal atoms".[1] This latter view is widely accepted in the chemical community and has found its way into textbooks or review articles where often an organometallic cluster is defined as a microscopic piece of metal, with adsorbed species on its surface.[3,4]

Unfortunately, the situation is not so simple. It is only in the last decade that accurate physical measurements have been performed on well-characterized metal clusters with the main purpose of better understanding their electronic structure.[5] The picture that emerges from these measurements is quite different from the original view.[3,4] A rather clear indication for this diversity comes from the response of metal clusters to external magnetic fields. Let us consider in particular Ni, a ferromagnetic metal for which several examples of cluster compounds are known.[6]
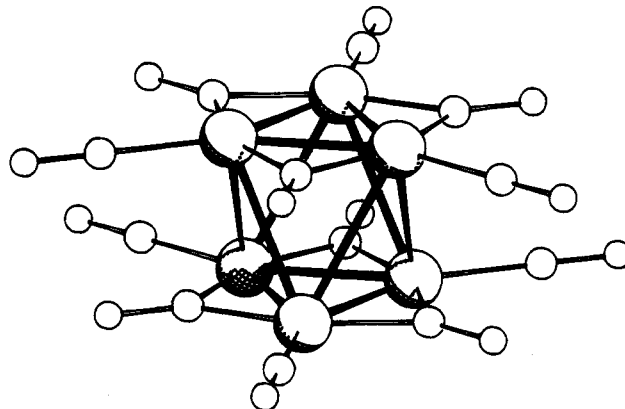

Figure 1. Structure of the cluster $[Ni_6(CO)_{12}]^{2-}$.

Bulk Ni has an average magnetization of 0.6 Bohr magnetons per atom, μ_B/atom.[7] Free gas phase Ni clusters of a nuclearity ranging from 50 to 180 atoms show a similar behavior and exhibit high magnetic moments corresponding to 0.8–0.9 μ_B/atom.[8] One may expect that also small (naked) Ni clusters containing a few metal atoms, for which experiments are not available, will show a high magnetization. Indeed, there is enough theoretical evidence that this is the case.[9] The temperature dependence of magnetic susceptibility has been studied for several organometallic clusters; the measured effective moments are close to 0 for the small carbonylated Ni clusters $[Ni_9(CO)_{18}]^{2-}$ and $[Ni_{12}(CO)_{21}H_2]^{2-}$, while values of ~4–9 μ_B/cluster have been measured for the larger clusters $[Ni_{38}C_6(CO)_{42}H]^{5-}$ and $[Ni_{38}Pt_6(CO)_{48}H]^{5-}$.[10] Assuming the same magnetization as in the bulk, a cluster of 38 Ni

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atoms should have a magnetic moment of about 22–23 μ_B; thus, powdered polynuclear Ni clusters exhibit an effective magnetic moment per atom corresponding to only 10–20% of the bulk value. More recent measurements on single crystals indicate that the magnetic moments are even smaller, close to 0 (see below).

Besides magnetic susceptibility, other physical measurements,[5a] like NMR line shapes and relaxation times, specific heat, the Mössbauer effect, etc., point toward a difference, at least a partial one, between a cluster surrounded by ligands and a naked metal particle of the same size. The reason is that the ligand shell induces a strong change in the properties of the metal atoms at the surface of the cluster. Magnetic quenching[11] is a macroscopically observable consequence of the presence of the ligands; an indirect, but not easily measurable effect is that the metal–metal interaction is substantially weaker in carbonylated than in free Ni clusters. A general, simple model may be formulated to explain these effects. This model, along with its quantum-mechanical foundation, is the subject of this Account.

Theoretical Treatment of Metal Clusters: Molecules or Metallic Particles?

Three general questions arise from the preceding discussion: Are the metal–metal bonds in organometallic clusters similar to those of the corresponding bulk metals? How is it possible to characterize the nature and strength of the metal–metal bonds? And, finally, how does this metal–metal interaction evolve as one goes from low- to high-nuclearity clusters and to colloidal particles containing hundreds or thousands of metal atoms?

To address these questions one needs a theoretical framework and a computational method capable of describing at the same level of accuracy the electronic structure of a small cluster like $[Ni_6(CO)_{12}]^{2-}$, which has clearly a molecular nature, and that of an aggregate with metallic properties in "embryonic" form. Two methodological approaches are generally used in quantum chemistry, Hartree–Fock (HF) plus post-HF "ab initio" methods based on the determination of the many-body wave function of a system and methods derived from density functional theory (DFT). DFT is based on the Hohenberg–Kohn theorem which asserts that the energy of a system is a unique functional of the electron density $\varrho(r)$. From a historical point of view DFT was developed in the physical community for the study of solids,[12] but in recent years it has been successfully applied to typical molecular problems.[13] Nowadays wave function based as well as density-based methods may both be considered as established computational schemes and the use of one or the other approach is, to a certain extent, a matter of convenience. The treatment of a large and complex system like a Ni particle with a highly magnetic

ground state (GS) is very difficult in a wave function based scheme; even for a small system like octahedral Ni_6 the number of electronic configurations arising from the different spin-coupling schemes is very large.[9a] This problem is more conveniently treated within DFT. A particularly useful way to solve the Schrödinger equation in DFT is the all-electron linear combination of Gaussian-type orbital density functional, LCGTO-DF, method.[14] In this method one solves effective one-electron equations derived in the Kohn–Sham approach[15] to DFT using Gaussian-type expansions for pertinent quantities:

$$[-(1/2)\nabla^2 + v(r)]\psi_i(r) = \epsilon_i\psi_i(r)$$

The local potential

$$v(r) = v_n(r) + v_{coul}(r) + v_{xc}(r)$$

is composed of the electron–nuclear attraction, $v_n(r)$, the electron–electron repulsion, $v_{coul}(r)$, and the exchange-correlation potential, $v_{xc}(r)$. An approximate form of $v_{xc}(r)$, used in most of the calcuations underlying this work, is the Xα variant of the local density approximation (LDA),

$$v_{xc}(r) = (3/2)\alpha[(3/\pi)\varrho(r)]^{1/3}$$

where $\alpha = 0.7$ and $\varrho(r)$ is the charge density:

$$\varrho(r) = \sum_i n_i|\psi_i(r)|^2$$

Two features of the method are of particular importance in the present context. First, the use of the spin-polarized version of the formalism (the local spin density approach) allows one to determine the magnetic nature of the GS by assigning different spatial orbitals for the two spin orientations. Second, the filling of the one-electron levels can be done according to the Aufbau principle[12] modified by the fractional occupation number (n_i) technique[14] where one formally broadens each one-electron level by a Gaussian and fills the resulting density of states, DOS, by the appropriate number of electrons. The cluster Fermi energy E_F is thus determined in a self-consistent way; for a closed-shell system featuring a reasonable gap, the Fermi energy reduces to the energy of the highest occupied molecular orbital, HOMO. The resulting total energy and charge density may be viewed as an average over several close-lying electronic configurations. When heavy atoms are involved, like Pt, a scalar-relativistic version of the method has been employed.[14c]

Using this approach it has been possible to compute the electronic structure of systems ranging from the

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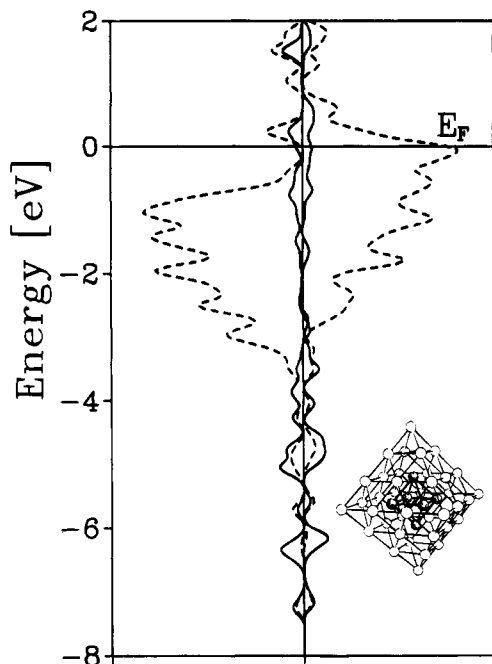
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Figure 2. Density of states (DOS) (in arbitrary units) of the octahedral Ni₃₈Pt₆ cluster. The six Pt atoms occupy the cavity of the octahedral cage. The DOS curves have been generated by Gaussian broadening (by 0.1 eV) of the one-electron spectrum. Left side: majority spin. Right side: minority spin. Energies are with respect to the Fermi level. The contributions from surface Ni atoms (- - -) and from core Pt atoms (—) are shown separately.

mononuclear Ni—CO complex to clusters of about 150 Ni atoms and 180 ligands at the all-electron level without reference to empirical parameters.[16] For clusters comprising several dozens of metal atoms the language of molecular orbitals is no longer convenient. The average level spacing, δ, in a metallic particle with N valence electrons and a valence band width W can be roughly estimated as $\delta \sim 2W/N$ assuming that each level is doubly occupied and nondegenerate. The valence band width in a Ni cluster of 147 atoms is about 5 eV, and $\delta \sim 7$ meV is much smaller than the thermal energy at room temperature ($k_BT = 24$ meV); even if one takes the degeneracy in case of icosahedral symmetry into account, δ does not exceed this thermal energy value. In such a system the one-electron energy levels are so closely spaced that the spectrum is better approximated by a near-continuum. Therefore, the following discussion will be based on a solid-state language more than on a MO language. For the clusters considered, the one-electron energy spectrum has been broadened by Gaussian functions; in this way a DOS is obtained (e.g., see Figure 2) which can be directly related to the DOS obtained in a solid-state approach from the "band structure" of a periodic system. Clearly, low-nuclearity clusters containing 10—20 or fewer metal atoms exhibit a one-electron spectrum and the nature of the compound is still "molecular", even if level broadening is used as a convenient device to emphasize qualitative features of a level spectrum. As the cluster size increases, however, the "solid state" language becomes more appropriate[17] and the evolution of the one-electron

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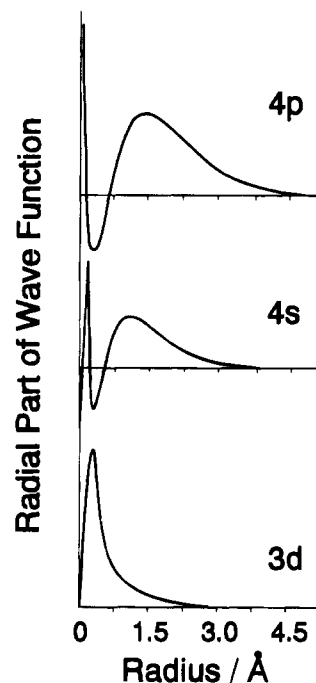

Figure 3. Schematic representation of the radial extension of 3d, 4s, and 4p orbitals for a first-row transition metal atom.

Table 1. Total number, N_s, and Average Distribution of Unpaired Electrons per Atom, N_e/atom, between Core and Surface Ni Atoms in Free and Ligand-Stabilized Ni Clusters

cluster	N_s	N_e/atom core	surface
Ni₆	6.8		1.14
Ni₉	8.1		0.90
Ni₃₂	26.4	0.74	0.86
Ni₃₈Pt₆	29.9	0.22 (Pt)	0.76
Ni₄₄	32.7	0.72	0.75
Ni₁₄₇	94.8	0.60	0.67
[Ni₆(CO)₁₂]²⁻	0.0	0.0	0.0
[Ni₉(CO)₁₈]²⁻	0.0	0.0	0.0
[Ni₃₂(CO)₃₆]⁶⁻	3.8	0.50	0.0
[Ni₄₄(CO)₄₈]⁶⁻	3.4	0.56	0.0
[Ni₃₂(CO)₃₆C₆]⁶⁻	0.0	0.0	0.0
[Ni₃₈Pt₆(CO)₄₈]⁶⁻	0.0	0.0	0.0
Ni₄₄He₄₈	7.1	0.64	0.08
Ni₁₄₇He₁₈₀	41.6	0.61	0.09

spectrum toward the metal valence DOS becomes quite evident.

Magnetic and Metallic Properties of Free Ni Clusters

Free Ni clusters have a high-spin GS, irrespective of the cluster size.[8,9] For instance, a Ni₆ cluster with the same trigonal antiprism structure as [Ni₆(CO)₁₂]²⁻, Figure 1, is predicted to have about one unpaired electron associated with each Ni atom.[11c] This magnetization is larger than in bulk Ni because (a) the average coordination of the Ni atoms in a cluster is much smaller than in the metal and (b) the magnetization strongly depends on the intermetallic separation; in particular it is higher for an elongated Ni—Ni distance as in the example reported.[16d] Going to larger Ni clusters, comprising a few tens of metal atoms, the number of unpaired electrons/atom approaches the bulk value; see Table 1. The high spin polarization of the cluster electrons can be clearly seen from the

DOS plot of $Ni_{38}Pt_6$, Figure 2. This cluster has the same octahedral structure as the metallic core in $[Ni_{38}Pt_6(CO)_{48}]^{6-}$.[6f] The majority and minority spin components show a considerable asymmetry and an exchange splitting of about 1 eV. The magnetization originates from the partial filling of the minority 3d manifold which extends above the Fermi level while the majority spin component is completely filled. The reason for the strong magnetization is that the Ni atoms in a cluster assume a $3d^9 4s^1$-like configuration similar to atoms in the bulk metal. The 4s orbitals are very diffuse, Figure 3, and their mutual overlap gives rise to a wide band which completely "envelops" the 3d band on the energy scale.[18] The 3d orbitals, on the other hand, are much more localized, Figure 3, and their mutual overlap is concomitantly much weaker. The bonding is thus dominated by the more itinerant 4s electrons with little 3d contribution; the 3d band is relatively narrow, and the unpaired 3d electrons are only weakly coupled.

These general features are common to very small Ni clusters as well as to relatively large aggregates. The DOS plot of a Ni_{13} cluster has many features in common with that of an icosahedral Ni_{147} cluster,[16f] for instance, the absence of a well-defined gap between occupied and virtual states; see also Figure 2. The width of the 3d band in clusters containing more than 40–50 Ni atoms is about 5 eV, close to the 4.7 eV value from DFT band structure calculations;[18] furthermore, the DOS curve of Ni_{147} shows a high similarity to that of the bulk metal.[16f] All these data point toward a bonding mechanism in finite size free clusters similar to that in the bulk metal.[16f]

Why Small Carbonylated Ni Clusters are Diamagnetic

Of course, in a low-nuclearity cluster like Ni_6 the 4s–4s interaction does not result in the formation of a band, but rather in a set of discrete MOs with the filled part exhibiting strong or partial bonding character. In particular, the total-symmetric bonding combination of 4s orbitals is well below the 3d manifold and substantially contributes to the cluster stability.[11c] The addition of the 12 CO ligands to Ni_6 has dramatic consequences for the electronic structure, and as a first result, the GS of $[Ni_6(CO)_{12}]^{2-}$ becomes diamagnetic. A closer look at the one-electron level structure reveals that the total-symmetric bonding combination is no longer occupied and has been pushed above the cluster Fermi level; furthermore, the 4s and the 4p orbitals, as a result of the interaction with the CO orbitals, are considerably mixed in with the 3d orbitals (differently from the bare Ni_6 cluster).

The quenching of the magnetism in the cluster $[Ni_6(CO)_{12}]^{2-}$ is not too surprising if one considers that a similar effect is well-known on surfaces: when CO or other adsorbates are interacting with a Ni surface, a local reduction of the magnetic moment is observed.[19] Indeed, the mechanism of the interaction of a lone pair ligand like CO and a Ni atom, cluster, or
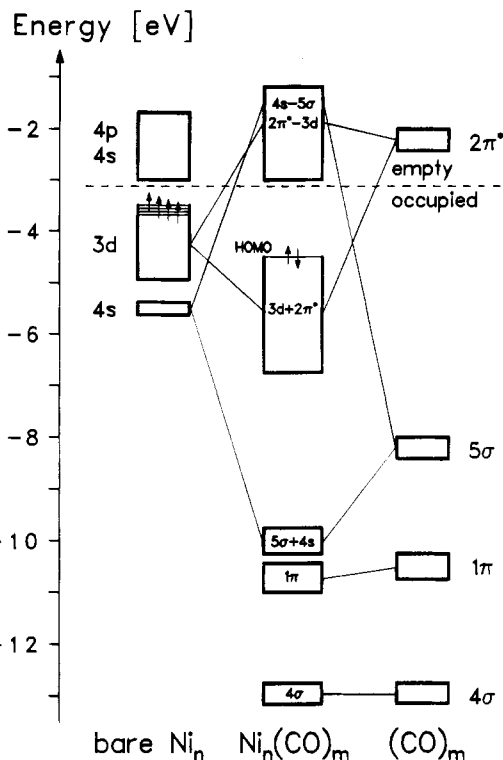

Figure 4. Schematic MO diagram for the interaction of *m* CO ligands with a bare Ni_n cluster to give the carbonylated Ni_n-$(CO)_m$ cluster.

metal is quite similar. Ideally, one can divide the Ni–CO interaction into three steps (see also Figure 4). The electronic configuration of the Ni atoms in the metal or in a cluster is close to $3d^9 4s^1$; when CO approaches a Ni atom (or cluster), the first interaction occurs between the 5σ orbital of CO, a carbon lone pair, and the Ni diffuse 4s orbital (or 4s-derived MOs).[20] As a consequence, three or more electrons occupy the same region of space in violation of the Pauli exclusion principle. This results in a strong repulsive interaction. In order to reduce the repulsion and to allow the CO molecule to come closer to the metal atom, hence to efficiently overlap with the 3d orbitals, the 4s levels are destabilized and pushed above the Fermi level, and the corresponding electrons are redistributed into the partially filled 3d shell (or 3d band).

Formally, this second step corresponds to a configuration change from $3d^9 4s^1$ to $3d^{10}$. All the electrons in the 3d shell are now spin-paired and the system becomes diamagnetic. The last step completes the formation of a classical σ-donation, π-back-donation bond between the CO 5σ and $2\pi^*$ MOs, respectively, and the Ni 3d orbitals of proper symmetry. Thereby the Ni 3d orbitals undergo a substantial hybridization with the 4s and 4p orbitals in order to overlap more efficiently with the CO MOs and to form a stronger bond. The dominating back-donation mechanism removes charge from the 3d levels which become energetically more stable (because of the reduced Coulomb repulsion), and a well-defined HOMO–LUMO gap of about 1–2 eV appears in the DOS curves.[11c,16c] It is worth noting that this magnetic quenching mechanism in Ni clusters is reminiscent

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Table 2. Computed and Measured Bond Lengths (Å) for Ni Clusters with a Cubic Core and Formula $Ni_8(\mu_4\text{-PR})_6(L)_{8(4)}$
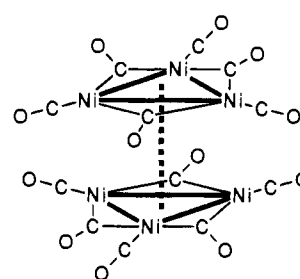
	distances				
cluster	Ni-Ni	Ni-C	Ni-P	ref	
Ni_8	2.19			16e	theory
$Ni_8(CO)_8$	2.27	1.72		16e	theory
$Ni_8(\mu_4\text{-PH})_6$	2.37		2.19	16e	theory
$Ni_8(\mu_4\text{-PH})_6(CO)_8$	2.64	1.83	2.17	16e	theory
$Ni_8(\mu_4\text{-PPh})_6(CO)_8$	2.65	1.78	2.18	6b	expt
$Ni_8(\mu_4\text{-PPh})_6(PPh_3)_4(CO)_4$	2.67	1.80	2.19	6c	expt
$Ni_8(\mu_4\text{-PPh})_6(PPh_3)_4$	2.53		2.20	6d	expt
bulk Ni	2.49				

of the high-spin/low-spin transition in mononuclear metal complexes as described in ligand field theory.
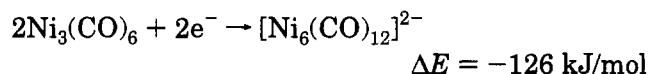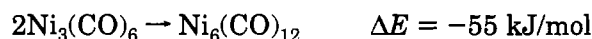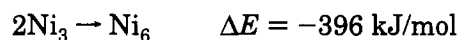
Strength of the Ni-Ni Bonds

The different effective magnetic moment of free and carbonylated Ni clusters is a macroscopic manifestation of the different bonding. A second, less visible effect of the ligand shell is the change in the strength of the metal-metal bond. The determination of the strength of a bond within a molecular compound is not straightforward. Qualitative theoretical evaluations based on bond orders or total energy partitioning have been reported,[21] but the resulting values do not correspond to any physical observable and, therefore, are of little help. One indirect indication of the strength of a bond is its length. If the addition of the ligands to the bare Ni cluster weakens the metal-metal bond, this should result in longer distances. Let us consider a series of Ni clusters: Ni_8, $Ni_8(CO)_8$, Ni_8-$(PH)_6$, and $Ni_8(CO)_8(PH)_6$. The last cluster differs from the experimentally isolated cluster $Ni_8(CO)_8(PPh)_6$[6b] only by the substituent R of the phosphinidine ligands, PR (R = Ph), which in the calculation have been simplified to R = H. The other systems of the series are hypothetical, and selected distances have been optimized assuming cubic symmetry in all cases, Table 2. Excellent agreement is found with the available experimental data.[6b] Upon addition of the ligands the Ni-Ni distance, which in bare Ni_8 is 2.19 Å, i.e., 0.3 Å shorter than in the bulk, increases considerably. In the coordinatively saturated $Ni_8(CO)_8(PH)_6$ cluster the metal-metal distance, 2.64 Å, is significantly longer than in Ni_8, but also than in the bulk metal; see Table 2. These values strongly suggest that the addition of the ligand shell considerably weakens the Ni-Ni interaction. The reason, as discussed above, is the promotion of the 4sp electrons into the contracted 3d shell; the 4s-bonding contribution is partially lost and is not compensated by any significant increase due to 3d-3d bonding. The same trend can be deduced from experimental X-ray diffraction data.[6c,d] The cluster $Ni_8(CO)_4(PPh_3)_4(PPh)_6$,[6c] where four CO ligands are replaced by PPh_3 groups, shows essentially the same Ni-Ni distance, 2.67 Å, as in $Ni_8(CO)_8(PPh)_6$; see Table 2. Notice that the Ni atoms in the two clusters have the same coordination. When the four terminal CO ligands are removed to give $Ni_8(PPh_3)_4(PPh)_6$,[6d] some of the Ni atoms remain coordinatively unsaturated and the Ni-Ni distances decrease by 0.14 Å! Thus, a clear correlation is established between the

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Scheme 1

number of ligands and the length (and the strength) of the Ni-Ni bonds.

Let us go back now to the compound $[Ni_6(CO)_{12}]^{2-}$ of Figure 1. One can directly compute the strength of the Ni-Ni bonds between the two $Ni_3(CO)_6$ units and compare it to the dimerization energy of two bare Ni_3 (the structure of the Ni_3 and Ni_6 units is the same as in $[Ni_6(CO)_{12}]^{2-}$):[11c]

$$2Ni_3 \rightarrow Ni_6 \qquad \Delta E = -396 \text{ kJ/mol}$$

$$2Ni_3(CO)_6 \rightarrow Ni_6(CO)_{12} \qquad \Delta E = -55 \text{ kJ/mol}$$

$$2Ni_3(CO)_6 + 2e^- \rightarrow [Ni_6(CO)_{12}]^{2-}$$
$$\Delta E = -126 \text{ kJ/mol}$$

It is clear that a large contribution to the stabilization of $[Ni_6(CO)_{12}]^{2-}$ comes from the two extra electrons which enter a bonding 4sp MO (see ref 11c and references therein for a more detailed discussion of the bonding in this cluster); nevertheless, the stability of Ni_6 toward fragmentation into Ni_3 monomers is 3 times larger than that of the carbonylated cluster. If we now divide the value obtained from the calculations, 126 kJ/mol, by the number of interunit Ni-Ni bonds, 6, we obtain an average value of about 20 kJ/mol for each Ni-Ni bond. Given that the LDA approximation tends to overestimate binding energies,[13] one may conclude that the strength of an interunit Ni-Ni bond in $[Ni_6(CO)_{12}]^{2-}$ is closer to that of a hydrogen bond than to that of a metal-metal bond. Probably a better representation of this cluster in terms of a Lewis structure should be as depicted in Scheme 1.

Magnetic Behavior of High-Nuclearity Carbonylated Ni Clusters

In small clusters, where all the metal atoms are at the surface, the ligands induce a complete quenching of the cluster magnetic moment; see Table 1. On the other hand, for clusters containing a few tens of metal atoms it is possible to distinguish between internal and external atoms of the metal cage. Just a few examples of Ni clusters of this size have been synthesized, like $[Ni_{38}C_6(CO)_{42}H_n]^{(6-n)-}$ (**1**)[6e] or $[Ni_{38}Pt_6$-$(CO)_{48}H_n]^{(6-n)-}$ (**2**).[6f] To what extent does the interaction with the ligands affect the properties of the metal atoms in the interior of these clusters?

To answer this question we consider two idealized models of **1** and **2**, $[Ni_{32}(CO)_{36}]^{n-}$ and $[Ni_{44}(CO)_{48}]^{n-}$. These models differ significantly from the real structures. $[Ni_{32}(CO)_{36}]^{n-}$ is derived from **1** by eliminating six capping Ni-CO groups and the six interstitial C atoms. In $[Ni_{44}(CO)_{48}]^{n-}$ six Ni atoms replace the core
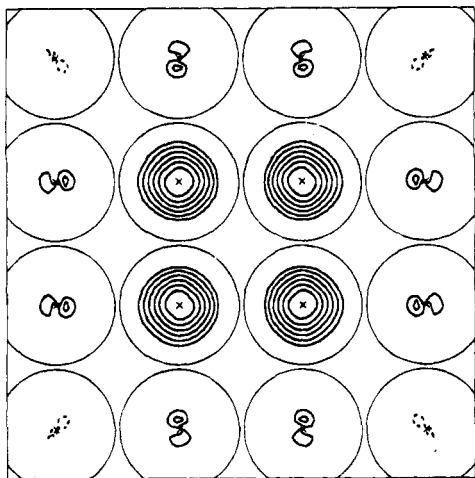
Figure 5. Electron density contour map of the difference between majority and minority spin in $[Ni_{44}(CO)_{48}]^{6-}$ determined in one of the σ_d mirror planes of the cluster. The circles indicate the size of the Ni atoms; solid lines indicate positive values of the spin density which is localized on the core Ni atoms. Reprinted with permission from ref 16b. Copyright 1992 American Chemical Society.

Pt atoms of **2** and the distribution of the ligands has been symmetrized to some extent. At this point, it should be mentioned that the net charge on **1** and similarly large clusters is not known with certainty.[6f] To test the sensitivity of the model results, calculations for various values n of the cluster charge have been performed, but no significant differences with respect to the conclusions to be discussed in the following have been found for the range $n = 0-6$.[16b]

Later on we will consider more realistic models of **1** and **2**. Here it is important that in both model clusters, $[Ni_{32}(CO)_{36}]^{n-}$ and $[Ni_{44}(CO)_{48}]^{n-}$, some Ni atoms are in the core and not in direct contact with the ligand coordination sphere. The bare Ni_{32} and Ni_{44} counterparts are highly magnetic with a spin distribution and a DOS structure not too different from those of other Ni clusters.[16b] In particular, Ni_{32} has a total of 26 unpaired electrons, Ni_{44} about 33; see Table 1. When the CO ligands are added the total magnetization is strongly reduced but, different from small clusters, not completely eliminated. In particular, 3–4 unpaired electrons are still present on each carbonylated cluster. The unpaired electrons are localized entirely on the internal Ni atoms (see Figure 5), while the surface metal atoms have lost their original magnetic moments (see Table 1), an effect which is independent of the total charge of the cluster anions.[16b] At first glance, the small magnetic moments computed for $[Ni_{32}(CO)_{36}]^{n-}$ and $[Ni_{44}(CO)_{48}]^{n-}$ seem to be in agreement with the values of 4–9 μ_B/cluster,[5a,10] obtained from powder samples of **1** and **2**; this agreement, however, is accidental since more recent measurements[22] on a single crystal of **2** have shown that the actual cluster magnetization is close to 0. The residual magnetism is probably due to contaminations occurring at the surface of the powder samples (as a consequence of oxidation or reduction).

As previously mentioned, $Ni_{32}(CO)_{36}$ and $Ni_{44}(CO)_{48}$ differ substantially from the real clusters **1** and **2**. Spin-polarized calculations on the more realistic mod-

(22) van Leeuwen, D. A.; van Ruitenbeek, J. M.; de Jongh, L. J.; Ceriotti, A.; Pacchioni, G.; Häberlen, O. D.; Rösch, N. *Phys. Rev. Lett.* **1994**, *73*, 1432.

els $[Ni_{32}C_6(CO)_{36}]^{n-}$ and $[Ni_{38}Pt_6(CO)_{48}]^{n-}$ show that these systems, differently from $Ni_{32}(CO)_{36}$ and $Ni_{44}(CO)_{48}$, are totally diamagnetic; see Table 1. The origin of the diamagnetism, however, is not the same. In **1** the C atoms couple their valence electrons to the unpaired 3d electrons of the internal Ni atoms to form strong covalent bonds. Thus, not only the ligands but also the interstitial C atoms have a marked effect on the total magnetic moment. The diamagnetism of **2** is due to the substitution of the internal atoms of a ferromagnetic metal like Ni with atoms of a nonmagnetic metal, here Pt.

The experimental situation is somewhat more complicated.[22] The temperature dependence of the magnetic susceptibility of a $[Ni_{38}Pt_6(CO)_{48}H_n]^{(6-n)-}$ single crystal shows that this system can be described as a diluted Heisenberg ferromagnet where one out of five clusters carries a spin of 1 μ_B, while the other clusters are diamagnetic. This behavior is quite peculiar: it can be understood only in terms of disorder in the structure (the presence of paramagnetic impurities in the sample has clearly been excluded). The surprising result that only one out of every five clusters exhibits a small magnetic moment can be understood by assuming that in some of the clusters one surface Ni atom exchanges its position with a core Pt atom. In fact, spin-polarized calculations of an isomer of $[Ni_{38}Pt_6(CO)_{48}]^{n-}$ where the six internal Pt atoms have been exchanged with six surface (corner) Ni atoms show a magnetic moment of about 3 unpaired electrons. As in $[Ni_{44}(CO)_{48}]^{n-}$, the spin density is localized in the core region.[22] This result has a 2-fold significance. It shows that every time that, in a large carbonylated Ni cluster stabilized by ligands, some of the Ni atoms are in the core, surrounded only by other Ni atoms as in the bulk metal, a permanent magnetic moment will appear. Furthermore, it provides a simple explanation (although not necessarily the only one) for the behavior of $[Ni_{38}Pt_6(CO)_{48}]^{n-}$ as a diluted Heisenberg antiferromagnet.

The difference between core and surface Ni atoms can also be seen from DOS curves of an isomer of $[Ni_{38}Pt_6(CO)_{48}]^{n-}$ where the contributions from the surface and core atoms have been distinguished; see Figure 6. While in the surface component the majority and minority DOS mirror each other, resulting in a complete spin pairing, the core component exhibits a residual magnetic moment. Even more important, the Fermi level (the chemical potential) is well above the surface component of the 3d manifold (which is stabilized by back-donation) so that the surface Ni atoms become Cu-like and do not contribute to the DOS at the Fermi level. Therefore, all the physical properties which are directly connected to the DOS near E_F, like the Knight shift in NMR[5a] or the electronic contribution to the specific heat,[5a] depend only on the number of core atoms in the cluster.

From Clusters to Colloids

$[Ni_{38}Pt_6(CO)_{48}]^{n-}$ is the largest Ni carbonyl cluster characterized in the solid state by X-ray diffraction.[6f] Larger metal particles stabilized by ligands have been obtained as colloids, and their structure and stoichiometry are known only approximately.[5b] To model one of these colloidal particles, let us consider an icosa-
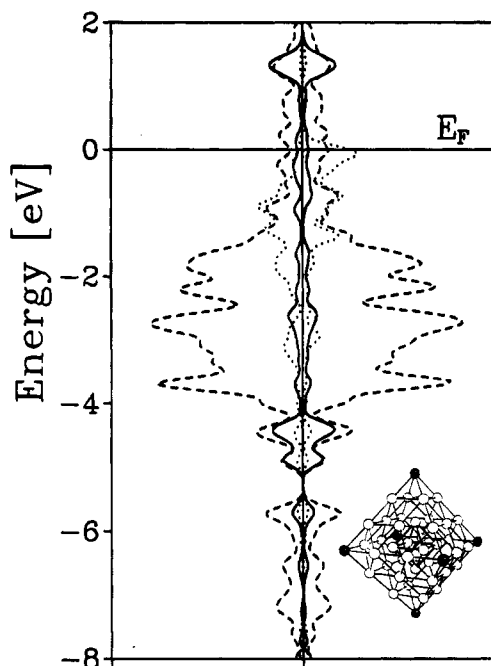
Figure 6. Density of states (DOS) (in arbitrary units) of an isomer of $[Ni_{38}Pt_6(CO)_{48}]^{6-}$ where the six Pt atoms are at the vertices of the external octahedron and are replaced by six Ni atoms in the cluster core; the CO ligands are not shown for clarity. The DOS curves have been generated by Gaussian broadening (by 0.1 eV) of the one-electron spectrum. Left side: majority spin. Right side: minority spin. Energies are with respect to the Fermi level. The contributions from surface Ni atoms (- - -), from Pt atoms (—), and from the core Ni atoms (···) are shown separately.
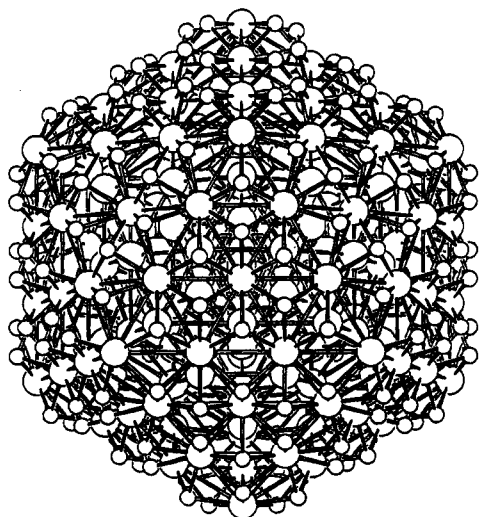

Figure 7. Structure of the icosahedral cluster $Ni_{147}He_{180}$.

hedral Ni cluster of 147 atoms: this is a small particle of about 15 Å diameter. Four shells of Ni atoms can be distinguished, a total of 92 surface and 55 core atoms. This cluster has a high magnetic moment corresponding to about 95 unpaired electrons. To represent the ligand shell, 180 He atoms have been added to give the cluster $Ni_{147}He_{180}$, Figure 7.

Of course, He is not a ligand in organometallic chemistry, and the choice to simulate a lone-pair ligand like CO by He is dictated also by the necessity to keep the size of the all-electron calculations within acceptable limits: still, $Ni_{147}He_{180}$ has 4476 electrons, and the orbital basis set used consists of 5229 con-

tracted Gaussian-type functions. However, there is another reason to use He. The mechanism responsible for the magnetic quenching is the repulsive interaction between the 4s-like states of the cluster and the CO 5σ lone pair. If the conclusion about the origin of the magnetic quenching is correct, the repulsive interaction with rare-gas atoms should induce a similar effect.

Indeed, the total number of unpaired electrons decreases from 95 in Ni_{147} to 42 in $Ni_{147}He_{180}$, Table 1. Most important, the spin density is almost entirely localized on the 55 internal atoms while the 92 surface atoms carry an average of about 0.09 unpaired electrons/atom. This small residual magnetization is due to the fact that He is less "efficient" than CO in quenching the magnetic moment.[16f] The He 1s orbital is much more contracted than the CO 5σ lone pair; since He does not bind to a Ni cluster, the He–Ni bond length in these models had to be fixed at a smaller bond distance (1.70 Å) after comparing the effect of a He matrix with that of carbonyl ligands on a Ni_6 cluster. Another obvious distinction is that no back-donation occurs to the He atoms. This leads to some changes in the DOS curves, in particular in the position of the surface component of the 3d band which is closer to the Fermi level than in carbonylated clusters.[16f] Despite these differences, the model shows that the magnetic quenching occurs also with He for the simple reason that a He matrix provides a crude representation of the Pauli repulsion between the metal particle and the ligand shell.

Conclusions

The generalization of these results to other metals and ligands leads to the conclusion that two kinds of metal atoms can be distinguished in high-nuclearity clusters and colloidal particles stabilized by organic ligands: the atoms at the particle surface, with only "partial" metallic character, and the core or "bulk" atoms which retain most of the free metal particle character. Two recent experiments fully support this conclusion. An average magnetic moment of 0.48 μ_B/atom has been measured for colloidal Ni particles of about 4 nm of diameter (3500–4000 atoms) surrounded by organic molecules.[23] This value, which is ~80% of the bulk value, can be easily rationalized assuming a complete quenching of the magnetic moments of the surface atoms, approximately 20% of the total for a spherical particle of this size. Another, completely different, experiment is the [195]Pt NMR of $Pt_{309}Phen_{36}O_{30}$,[24] a colloidal particle characterized by electron microscopy where the 309 Pt atoms have a cuboctahedral structure.[24] The [195]Pt NMR line shape shows two peaks with Knight shifts and nuclear-spin lattice relaxation times typical of metals and insulators, respectively. This is consistent with a contribution to the signal due to the 162 "surface" Pt atoms, with insulator behavior, and a "metallic" term due to the 147 "bulk" Pt atoms.[24]

All these data indicate that the bonding with the ligands induces deep changes in the electronic struc-

(23) Duteil, A.; Schmid, G.; Meyer-Zeika, W. *J. Chem. Soc., Chem. Commun.* **1995**, 31.
(24) van der Putten, D.; Brom, H. B.; Witteveen, J.; de Jongh, L. J.; Schmid, G. *Z. Phys. D* **1993**, *26*, 21.
(25) Rösch, N.; Pacchioni, G. In ref 5b, p 5.

ture of the surface metal atoms which lose part of their "metallic" character. For small clusters, where all the atoms are at the cluster surface, this means that in no way can the system be described as "a little piece of metal with chemisorbed species on the periphery".[4] The fact that nevertheless many similarities exist between organometallic ligands and adsorbed species on surfaces (the so-called cluster-surface analogy)[4] has its origin in the very local nature of the metal–ligand interaction which, to a first approximation, involves only the metal atoms in direct contact with the ligands,[25] but some care is necessary when this analogy is extended beyond its phenomenological value.