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Notes

Metal–Metal Bonding in Free and Ligated Nickel Clusters

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One fundamental question in cluster chemistry is whether the metal–metal interaction in organometallic clusters resembles that of the bulk metal or not. Molecular metal clusters have been proposed as models for the study of chemisorption phenomena, mainly because of the similarity of the ligand stereochemistry on clusters and surfaces.[1] For a long time, it has also been assumed that the metal–metal bonding in inorganic clusters and small metal particles is not too dissimilar,[1,2] and only recently it has been shown that the ligands induce strong rearrangements in the electronic structure of a bare metal cluster with consequent large changes in the metal–metal bonding.[3–7] In this note we will demonstrate this effect for a series of bare and ligated Ni$_8$ clusters with a cubic metal core using results from all-electron local density functional calculations.

The determination of the strength of a bond within a molecular compound is not straightforward. Qualitative theoretical evaluations of the metal bond strength in metal clusters have been based on overlap populations,[8] or on total energy partitioning.[9] These schemes, however, do not correspond to observable quantities. One, albeit indirect, indicator for the strength of a bond is its length. The change of a metal–metal bond length in a ligand-free, bare metal cluster compared to its ligated counterpart reflects, to some extent, the change of the interaction in the two cases. Unfortunately, while the bond lengths of organometallic clusters are known with remarkable accuracy from X-ray diffraction measurements, there is no experimental information on the bond distances for ligand-free, gas-phase, metal clusters other than the diatomics.[10]

The objective of this note is to show that, when the ligands are added to a bare nickel cluster, the metal–metal bonds, judged by their length, are weakened as expected from the change in the electronic configuration of the metal atoms.[3–5] This effect has already been established in inorganic chemistry, although a direct comparison of the optimal metal–metal distances in a bare cluster and in its ligated counterpart is not possible experimentally for the reasons mentioned above. Nevertheless, considerable advances in the theoretical description of transition metal compounds make it possible nowadays to compute and predict, with reasonable accuracy, the equilibrium bond distances of coordination compounds. We report the results of all-electron linear combination of Gaussian-type orbitals, LCGTO, local density functional, LDF,[11,12] calculations on free and ligated Ni$_8$ clusters with a cubic core: Ni$_8$ (**1**), Ni$_8$(CO)$_8$ (**2**), Ni$_8$(μ_4-PH)$_6$ (**3**), and Ni$_8$(μ_4-PH)$_6$(CO)$_8$ (**4**) (see Figure 1). For each structure, the optimal Ni–Ni, Ni–P, and Ni–C distances have been determined within the O_h symmetry constraint; see Table I. (For the bare cluster **1**, a cubic arrangement will most probably not be the energetically favored structure,[13] but it serves as a useful reference for the clusters **2**–**4**.) To the best of our knowledge, this is the first time that a geometry optimization is performed with a "first principles" method for a transition metal compound of this size. The results are compared with the experimental data for the Ni$_8$(μ_4-PPh)$_6$(CO)$_8$ (**5**) cluster;[14] this latter cluster differs from **4** only for the μ_4-PPh group which in the calculation has been replaced by a μ_4-PH ligand. To further reduce the computational effort in the case of **4**, the C–O distance was kept at the average experimental value found in **5**, 1.13 Å. Relaxing this constraint would certainly lead to an increase in r(C–O), accompanied by a decrease of r(Ni–C), which is currently somewhat overestimated (see below). However, when this hypothesis was tested for **2**, r_e(C–O) = 1.14 Å was found, leading only to negligible changes in r_e(Ni–C) and r_e(Ni–P).

The optimized distances in **4**, r_e(Ni–Ni) = 2.64 Å, r_e(Ni–C) = 1.83 Å, and r_e(Ni–P) = 2.17 Å, are remarkably close to the mean experimental values in **5**,[14] 2.65, 1.78, and 2.18 Å, respectively; see Table I. This excellent agreement provides compelling evidence that the computational method used is reliable for predicting the bond lengths of the bare as well as of the ligated unknown clusters **1**–**3**.

The cubic form of Ni$_8$ has a high-spin ground state arising from the interaction of the Ni atoms in a 3d^{9}4s^1 atomic configuration.[15] Various configurations have been considered, but configurations with more or less than eight unpaired electrons are unfavorable. The 3d orbitals are rather contracted and, in fact, do not overlap significantly; one hole is localized on each 3d shell. The 4s electrons are spin-coupled and completely fill a set of bonding a_{1g} and t_{1u} MOs; they largely contribute to the stabilization of the structure. The large stability of the cluster is shown by the atomization energy, 2.84 eV/atom, and by the very short Ni–Ni distances, 2.19 Å. For comparison, the average Ni–Ni distance in larger clusters is about 2.30 Å,[16] and in bulk Ni it is 2.49 Å.[17] The low average coordination of the Ni atoms in a cluster with respect to the bulk is partially compensated by a contraction of the bond distances. The addition of the eight terminal CO ligands, **2**, has the main effect to completely quench the cluster magnetic moment and to change the formal Ni

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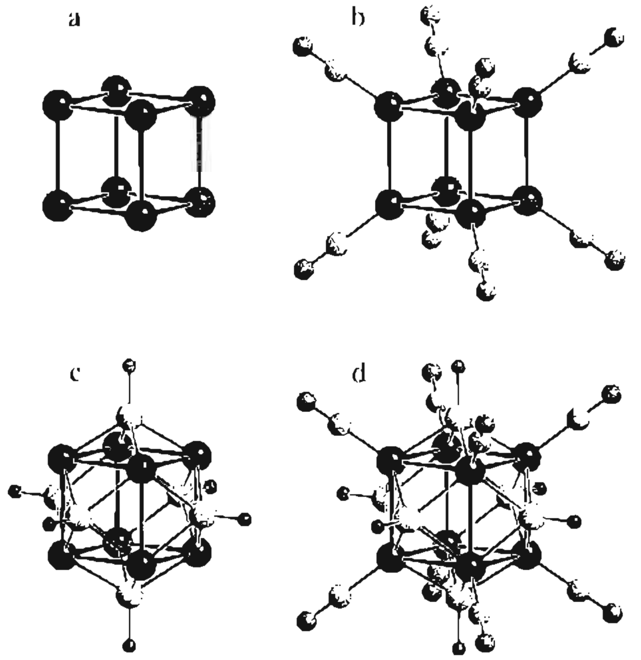

Figure 1. Geometry of the clusters which have been investigated by LCGTO-LDF calculations: (a) Ni_8, (b) $Ni_8(CO)_8$, (c) $Ni_8(\mu_4\text{-}PH)_6$, and (d) $Ni_8(\mu_4\text{-}PH)_6(CO)_8$. In all cases O_h symmetry was assumed.

Table I. Computed and Measured Mean Bond Lengths, in Å, for Ni Clusters with a Cubic Core and Generic Formula $Ni_{8(9)}(\mu_4\text{-}E)_6(R)_{8(4)}$

			distances			
no.	cluster	CVEs[a]	Ni–Ni	Ni–C	Ni–E	ref
	Theory					
1	Ni_8	80	2.19			
2	$Ni_8(CO)_8$	96	2.27	1.72		
3	$Ni_8(\mu_4\text{-}PH)_6$	104	2.37		2.19	
4	$Ni_8(\mu_4\text{-}PH)_6(CO)_8$	120	2.64	1.83	2.17	
	Experiment					
5	$Ni_8(\mu_4\text{-}PPh)_6(CO)_8$	120	2.65	1.78	2.18	14
6	$Ni_8(\mu_4\text{-}PPh)_6(PPh_3)_4(CO)_4$	120	2.67	1.80	2.19	20
7	$Ni_8(\mu_4\text{-}PPh)_6(PPh_3)_4$[b]	112	2.53		2.20	21
8	$Ni_8(\mu_4\text{-}S)_6(PPh_3)_6Cl_2$	118	2.68		2.21	22
9	$Ni_8(\mu_4\text{-}PPh)_6(PPh_3)_4Cl_4$	116	2.61		2.21	20
10	$Ni_9(\mu_4\text{-}GeEt)_6(CO)_8$	124	2.67		2.36	23
11	$Ni_9(\mu_4\text{-}Te)_6(PEt_3)_8$	130	2.86		2.55	24
12	$Ni_9(\mu_4\text{-}As)_6(PPh_3)_5Cl_3$	121	2.81		3.32	25

[a] Cluster valence electrons: the electron count is done by assuming that the contribution of each moiety is Ni = 10, CO = PR_3 = 2, Cl = 1, and μ_4-PR = μ_4-GeEt = μ_4-S(Te) = 4. [b] Distorted cube.

configuration from $3d^94s^1$ to $3d^{10}$-like.[3-5,7,15] Open-shell configurations, in fact, are higher in energy with respect to the diamagnetic ground state. A similar magnetic quenching was found for CO adsorbed on Ni surfaces.[18,19] The repulsive interaction of the 4s electrons with the CO lone pairs induces a 4s → 3d promotion leading to a complete filling of the 3d shell. The destabilization of the 4s-derived bonding MOs, which are empty in the carbonylated cluster, has important consequences on the Ni–Ni bond lengths which increase by about 0.1 Å; see Table I. Even larger is the effect of the addition of the μ_4-PH ligands to Ni_8: in **3**, which also has a diamagnetic ground state, the Ni–Ni bond lengths are about 0.2 Å larger than in **1**. In **3** the 4s electrons become involved in the bonding with the PH ligands and are no longer available for metal–metal bonding. The simultaneous addition of the CO and μ_4-PH ligands causes a dramatic elongation of the Ni–Ni distance, from 2.19 Å in **1** to 2.64 Å in **4**. This latter distance is 0.15 Å longer than in bulk Ni and 0.45 Å longer than in bare Ni_8. This is a very large change; it cannot be simply due to steric effects of the ligand sphere and reflects the strong electronic redistribution which has occurred in the metal frame.

These conclusions are fully consistent with the trend of the measured Ni–Ni bond distances in a series of ligated Ni clusters with a cubic core; see Table I.[14,20-25] One common feature to all these cubic clusters, **5**–**12**, is that the Ni–Ni distances are larger than in the bulk. However, it is not easy to find a simple correlation between the average Ni–Ni bond lengths and other electronic or steric parameters, like the number of cluster valence electrons, CVEs. Clearly, a detailed understanding of the relationships between the valence electron concentration, type of ligands, and bond lengths is not at all simple and would require a much more extended analysis of the electronic structure of these systems.

What is relevant in the present context, however, is that when the cluster is coordinatively saturated, the Ni–Ni distances are rather long, typically about 0.15 Å or more longer than in the bulk. The calculations help to understand the reason for these changes. The ligands induce strong modifications in the metal–metal interaction, in particular reducing the 4s–4s contribution to the metal–metal bonding, and remove almost completely the "metallic" character of the bare cluster.[3-5,15] Thus, the origin of the long Ni–Ni distances is primarily electronic, although steric effects do also play a role. The calculations predict also that coordinatively unsaturated Ni clusters, **2** and **3**, exhibit short Ni–Ni distances, intermediate between Ni_8 and $Ni_8(\mu_4\text{-}PH)_6(CO)_8$. This is fully consistent with the experimental observations. Compound **7** is the only known case where the Ni_8 cage is ligated to four terminal ligands instead of eight as for the other clusters of the series; hence, in **7** four Ni atoms are low coordinated. As a consequence, the average Ni–Ni distance is 0.14 Å shorter than in the coordinatively saturated counterpart **6**. Apparently, there is a direct relationship between the number of ligands in the coordination sphere and the metal–metal bond lengths: the cluster loses its metallic character as the number of the ligands increases, and this is reflected in a substantial elongation of the intermetallic bonds.

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