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Influence of Single Impurity Atoms on the Structure, Electronic, and Magnetic Properties of Ni_5 Clusters

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With a gradient-corrected density functional method, we have studied computationally the influence of single impurity atoms on the structure, electronic, and magnetic properties of Ni_5 clusters. The square−pyramidal isomer of bare Ni_5 with six unpaired electrons was calculated 23 kJ/mol more stable than the trigonal bipyramid in its lowest-energy electronic configuration with four unpaired electrons. In a previous study on the cluster Ni_4, we had obtained only one stable isomer with an O or an H impurity, but we located six minima for ONi_5 and five minima for HNi_5. In the most stable structures of HNi_5, the H atom bridges a Ni−Ni edge at the base or the side of the square pyramid, similarly to the coordination of an H atom at the tetrahedral cluster Ni_4. The most stable ONi_5 isomers exhibit a trigonal bipyramidal structure of the Ni_5 moiety, with the impurity coordinated at a facet, $(\mu_3\text{-O})Ni_5$, or at an apex edge, $(\mu\text{-O})Ni_5$. We located four stable structures for a C impurity at a Ni_5 cluster. As for CNi_4, the most stable structure of the corresponding Ni_5 complex comprises a four-coordinated C atom, $(\mu_4\text{-C})Ni_5$, and can be considered as insertion of the impurity into a Ni−Ni bond of the bare cluster. All structures with C and five with O impurity have four unpaired electrons, while the number of unpaired electrons in the clusters HNi_5 varies between 3 and 7. As a rough trend, the ionization potentials and electron affinities of the clusters with impurity atoms decrease with the coordination number of the impurity. However, the position of the impurity and the shape of the metal moiety also affect the results. Coordination of an impurity atom leads to a partial oxidation of the metal atoms.

1. Introduction

Impurities of nonmetal atoms on small metal clusters, either in the gas phase or on support, can considerably affect the structure, electronic, and magnetic properties of the metal moiety. Such "ligated" clusters can be produced by the interaction of bare metal clusters with gas molecules,[1] by reactions of supported metal clusters with surface active sites, e.g., OH groups,[2,3] or by the decomposition of molecular ligands (e.g., CO) adsorbed on the metal moiety.[4−6] The latter approach is routinely applied in the preparation of supported metal species on oxide surfaces or in zeolite cages when carbonylated transition metal clusters are used as precursors.[6−8] In several computational studies, complementing available experimental information, we have concluded that supported metal clusters produced in this way are not free of heteroatoms.[2,3,5] Despite the importance of such impurity atoms for the behavior of metal clusters, experimental information about the presence of heteroatoms and their influence on the properties of clusters is rather scarce due to difficulties with preparing and characterizing such samples in a reproducible way. This lack of essential experimental information provides one of the motivations for the theoretical model studies of small transition metal clusters. Various computational approaches have been applied to clarify bonding in and magnetic properties of bare metal clusters;[9−24] alternatively, one characterizes clusters with impurity atoms via spectral features.[2,3,5,25−31]

Recently, we reported a computational study of Ni_4 clusters containing single impurity atoms H, C, or O.[32] These impurity atoms were selected not only according to their importance for the gas-phase chemistry of size-selected clusters, but also with regard to heterogeneous catalytic systems where supported transition metal clusters often are utilized as components of active multifunctional catalysts.[33,34] We determined unique stable isomers of the species HNi_4 and ONi_4 where the impurity atom adopts a 2-fold coordinated position at an edge of the tetrahedral Ni_4 cluster. We also located three structures for the cluster CNi_4 where C exhibits a preference for 4-fold coordination. The bonding of the impurity atoms H, C, or O to the cluster causes a partial oxidation of the metal atoms.

In the present work, we considered how single impurity atoms, H, C, or O, affect the structure and other properties of the cluster Ni_5. As mentioned above, these impurities often are present in heterogeneous catalytic systems, either from the preparation process of the catalyst or from catalytic reactions. We determined the magnetic states of such clusters, their spin and electron density distribution as well as their ionization potential (IP) and electron affinity (EA).

2. Computational Details

All calculations were carried out with the linear combination of Gaussian-type orbitals fitting-functions density functional method (LCGTO-FF-DF)[35] as implemented in the program ParaGauss.[36,37] We applied the unrestricted Kohn−Sham procedure with the gradient-corrected exchange-correlation functional suggested by Becke (exchange) and Perdew (correlation).[38,39] A recent extensive study on transition metal

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TABLE 1: Calculated Characteristics of Bare Ni_5 and Ni_5 Clusters with H, C, and O Impurity Atoms:[a] Number Ns of Unpaired Electrons, Binding Energy BE per Atom of Bare Ni_5, BE of Impurity Atoms at Ni_5 (Both in kJ/mol), Interatomic Distances (in pm)

structures	Ns	BE	Ni−Ni[b]	Ni−X[c]
$\mathrm{Ni}_5/C_{4v}\text{-sp}$	6	231	231 aa ab	
$\mathrm{Ni}_5/C_{3v}\text{-bp}$	4	226	237 ab, 229 bb, 236 bc	
$(\mu\text{-H})\mathrm{Ni}_5/C_s\text{-sp1}$	5	273	231 ab ac, 234 bc, 225 bb, 234 cc	167 b
$(\mu\text{-H})\mathrm{Ni}_5/C_s\text{-sp2}$	5	266	242 ab, 232 ac, 231 ad, 235 bd, 233 cd	166 a, 163 c
$(\mu_3\text{-H})\mathrm{Ni}_5/C_s\text{-bp}$	5	262	232 ab, 243 ad, 233 bc, 236 bd, 234 dc, 225 dd	163 a, 179 d
$(\eta\text{-H})\mathrm{Ni}_5/C_s\text{-bp}$	3	234	239 ab, 234 ad, 231 bc, 231 bd, 235 cd, 230 dd	149 a
$(\eta\text{-H})\mathrm{Ni}_5/C_s\text{-sp}$	7	209	234 ab, 235 ac, 231 cd	152 a
$(\mu_4\text{-C})\mathrm{Ni}_5/C_s\text{-sp}$	4	660	232 ab, 253 ad, 231 bd, 241 cd	181 a, 182 c, 182 d
$(\mu_3\text{-C})\mathrm{Ni}_5/C_s\text{-sp}$	4	646	237 ab, 235 ac, 237 ad, 231 bd, 243 cd	206 b, 184 c, 181 d
$(\eta\text{-C})\mathrm{Ni}_5/C_s\text{-bp}$	4	403	234 ab, 228 ac, 233 ad, 227 bd, 246 cd	162 c
$(\eta\text{-C})\mathrm{Ni}_5/C_s\text{-sp}$	4	378	230 ab, 230 ac, 230 ad, 234 bd, 234 cd	160 a
$(\mu_3\text{-O})\mathrm{Ni}_5/C_s\text{-bp}$	4	436	242 ab, 261 ad, 238 bc, 230 bd, 235 cd, 260 dd	177 a, 187 d
$(\mu\text{-O})\mathrm{Ni}_5/C_s\text{-bp}$	4	412	236 ab, 231 ad, 249 bc, 231 bd, 243 dd	179 b, 174 c
$(\mu\text{-O})\mathrm{Ni}_5/C_1\text{-sp}$	6	402	241 ab, 238 ac, 230 ad ae, 237 bc, 239 de, 230 bd	178 b c
$(\mu_3\text{-O})\mathrm{Ni}_5/C_s\text{-sp}$	4	390	255 ab, 230 ac, 232 bc, 296 bb, 231 cc	190 a, 180 b
$(\mu_4\text{-O})\mathrm{Ni}_5/C_s\text{-sp}$	4	340	238 ab, 235 ac, 236 ad, 238 bd, 238 cd	192 b c d
$(\eta\text{-O})\mathrm{Ni}_5/C_s\text{-sp}$	4	313	232 ab, 239 ac, 231 ad, 230 bd, 226 cd	163 c

[a] For the notation of the atoms in the clusters, see Figures 1−4. [b] The types of Ni atoms involved are indicated after the value; see Figures 1−4. [c] The type of the Ni atom bound to the impurity X is indicated after the value; see Figures 2−4.

compounds concluded that this exchange-correlation potential furnishes very satisfactory accuracy, in particular when one considers the computational effort.[40] For all open-shell systems, we checked the spin contamination of the underlying Kohn−Sham determinant; the contamination of the ground states of all local minima of Ni_5 in bare form and with an impurity was below 4%.

The Kohn−Sham orbitals were represented by Gaussian-type basis sets contracted in generalized fashion: (15s11p6d) → [6s5p3d] for Ni,[10,41] (9s5p2d) → [5s4p2d] for C and O, and (6s1p) → [3s1p] for H.[42] The auxiliary basis set used in the LCGTO-FF-DF method to describe the Hartree part of the electron−electron interaction was derived from the orbital basis set in the usual fashion[35] and augmented by five p-type and five d-type "polarization" exponents for each atom. These exponents were constructed as geometric series with a factor 2.5, starting with 0.1 and 0.2 for p- and d-exponents, respectively.[35,43]

Gas-phase Ni_5 clusters with and without an impurity were optimized with the help of analytical energy gradients invoking various symmetry constraints (C_{4v}, D_{3h}, C_{3v}, C_{2v}, C_s or C_1).[44] The stability of bare clusters was characterized by the binding energy (BE) per Ni atom (in $3d^9 4s^1$ configuration; Table 1):

$$\mathrm{BE} = -[E_{\mathrm{tot}}(\mathrm{Ni}_5) - 5E(\mathrm{Ni})]/5$$

For clusters with an impurity atom, we determined the binding energy of the impurity X═C, O, H with respect to the most stable isomer of bare Ni_5:

$$\mathrm{BE} = -[E_{\mathrm{tot}}(\mathrm{XNi}_5) - E_{\mathrm{stab}}(\mathrm{Ni}_5) - E(\mathrm{X})]$$

Thus, the larger a BE value, the more stable are the species Ni_5 or XNi_5, respectively. For the optimized configurations, we carried out a normal-mode analysis without symmetry constraints, to corroborate that the structures represent local minima of the potential energy surface (Table S1 of Supporting Information). For this purpose, the second-order energy derivatives were estimated as finite differences of analytic displacement gradients. In cases with at least one imaginary vibrational frequency, the original symmetry constraint was reduced and the structure was re-optimized.

TABLE 2: Vertical Ionization Potential IP, Electron Affinity EA, HOMO Energy ϵ_{HOMO} and Spin Character of the HOMO (α − Majority, β − Minority), HOMO−LUMO Gap $\Delta\epsilon_{\mathrm{HL}}$ of Bare Ni_5 and Ni_5 Clusters with a H, C, or O Impurity Atom (Energies in eV)

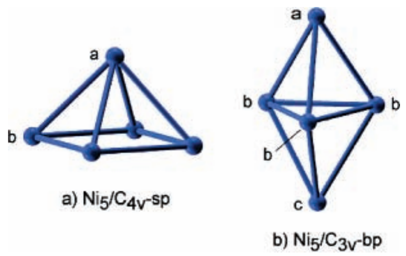
structures[a]	IP	EA	ϵ_{HOMO}	$\Delta\epsilon_{\mathrm{HL}}$[b]
Ni_5 exp.	6.18 ± 0.24[c] 6.22 ± 0.05[d] 6.17 ± 0.02[e]	1.57 ± 0.06[f]		
$\mathrm{Ni}_5/C_{4v}\text{-sp}$	6.64/6.46[g]	1.64	−4.45 α	0.75
$\mathrm{Ni}_5/C_{3v}\text{-bp}$	6.41/6.24[g]	1.39	−4.03 β	0.51
$(\mu\text{-H})\mathrm{Ni}_5/C_s\text{-sp1}$	6.95	1.62	−4.32 α	0.69
$(\mu\text{-H})\mathrm{Ni}_5/C_s\text{-sp2}$	6.56	1.79	−4.40 α	0.51
$(\mu_3\text{-H})\mathrm{Ni}_5/C_s\text{-bp}$	6.45	1.51	−4.11 α	0.36
$(\eta\text{-H})\mathrm{Ni}_5/C_s\text{-bp}$	6.77	1.71	−4.31 β	0.66
$(\eta\text{-H})\mathrm{Ni}_5/C_s\text{-sp}$	7.08	2.03	−4.79 α	1.98
$(\mu_4\text{-C})\mathrm{Ni}_5/C_s\text{-sp}$	6.59	1.68	−4.31 β	0.45
$(\mu_3\text{-C})\mathrm{Ni}_5/C_s\text{-sp}$	6.69	1.79	−4.37 β	0.38
$(\eta\text{-C})\mathrm{Ni}_5/C_s\text{-bp}$	6.73	2.08	−4.50 α	0.35
$(\eta\text{-C})\mathrm{Ni}_5/C_s\text{-sp}$	7.07	2.09	−4.82 α	0.56
$(\mu_3\text{-O})\mathrm{Ni}_5/C_s\text{-bp}$	6.53	1.30	−4.39 β	1.02
$(\mu\text{-O})\mathrm{Ni}_5/C_s\text{-bp}$	6.80	1.94	−4.44 β	0.34
$(\mu\text{-O})\mathrm{Ni}_5/C_1\text{-sp}$	6.90	1.77	−4.58 α	0.79
$(\mu_3\text{-O})\mathrm{Ni}_5/C_s\text{-sp}$	6.54	1.62	−4.29 α	0.57
$(\mu_4\text{-O})\mathrm{Ni}_5/C_s\text{-sp}$	6.34	1.47	−3.95 β	0.32
$(\eta\text{-O})\mathrm{Ni}_5/C_s\text{-sp}$	7.04	2.06	−4.77 β	0.68

[a] For the notation of the clusters with impurity atoms see Section 3.2; for the structures, see Figures 1−4. [b] HOMO−LUMO gap calculated within one spin manifold. [c] Ref 47. [d] Ref 48. [e] Ref 49. [f] Ref 53. [g] Calculated adiabatic IP.

The vertical IP and EA values of bare and ligated clusters (Table 2) were estimated as differences of total energies (ΔSCF procedure). We also determined atomic charges, both with a Mulliken analysis and by fitting the electrostatic potential[45] (potential derived charges, PDC) (Tables S2−S5 of Supporting Information). We characterized the local spin s of an atomic center by the difference between majority and minority charge contributions of that center as obtained in a Mulliken analysis (Tables S2−S5 of Supporting Information).

3. Results and Discussion

3.1. Bare Cluster Ni_5. We started our studies with the bare cluster Ni_5 as reference, exploring four topologies: (i) a square pyramid (Ni_5-sp, Figure 1a), (ii) a trigonal bipyramid (Ni_5-bp, Figure 1b), (iii) a tetrahedral cluster with the fifth Ni atom bound to a Ni−Ni bond (Ni_5-t); and (iv) a square-planar cluster with the fifth Ni atom bound to a Ni−Ni bond (Ni_5-e). The



a) Ni_5/C_{4v}-sp

b) Ni_5/C_{3v}-bp

Figure 1. Structures of the bare Ni_5 cluster. Also shown are the labels for the different types of Ni atoms; see text and tables.

optimization of the square pyramid structure with C_{4v} and C_1 symmetry constraints lead to the same geometry, binding energy, and spin state of the cluster; the C_{4v} symmetry of the ground state was confirmed by normal-mode analysis. The trigonal bipyramid structure was optimized with D_{3h}, C_{3v}, and C_s symmetry constraints. The bipyramidal structure Ni_5/D_{3h}-bp features one imaginary frequency in the vibrational analysis, while the structure with lower symmetry, Ni_5/C_{3v}-bp, represents an energy minimum.[46] The last two isomers, Ni_5-t and Ni_5-e, were optimized in C_{2v} and C_s symmetry constraints and are less stable than the square pyramid by 50 and 90 kJ/mol, respectively; however, each of these structures exhibit imaginary vibrational frequencies. Release of the symmetry constraints from the initial Ni_5-e and Ni_5-t geometries results in the square pyramidal and bipyramidal structures, respectively. Thus, the only stable structures of the neutral Ni pentamer are the clusters Ni_5/C_{4v}-sp and Ni_5/C_{3v}-bp.

The stability of the obtained spin states of the bare Ni_5 isomers was checked by single-point calculations (at fixed geometry) where the number of unpaired electrons, Ns, was varied by ± 2. In the square pyramid structure, the number of unpaired electrons in the ground state is $Ns = 6$, while the trigonal bipyramid, Ni_5/C_{3v}-bp, has two unpaired electrons less, $Ns = 4$. The square pyramid structure of Ni_5 (Figure 1a) is 23 kJ/mol more stable than the trigonal bipyramid structure (Figure 1b).

As square pyramidal and triangular bipyramidal structures of Ni_5 differ very little in energy, we reoptimized them using an uncontracted basis set (15s,11p,6d). We obtained the same structures; nearest-neighbor distances changed less than 1 pm. Also the relative stability of the two stable isomers remained the same as with the contracted basis set; the energy difference changed very little, 1 kJ/mol for the whole cluster.

None of the modeled high-symmetry structures, Ni_5/C_{4v}-sp or Ni_5/C_{3v}-bp, has partially occupied degenerate spin orbitals. In both cases the HOMO is a doubly occupied e-type spin-orbital.

The Ni−Ni distances of the isomer Ni_5/C_{4v}-sp are 231 pm (Figure 1a and Table 1), close to the values in the tetrahedral structure of Ni_4, 230 pm.[32] In the bipyramidal structure, Ni_5/C_{3v}-bp, the distances between the Ni atoms in the triangular base of the bipyramid are 229 pm, while the Ni−Ni distances involving one atom at an apex are longer, 236 and 237 pm (Figure 1b and Table 1).

The tetrahedral Ni_4/C_s cluster[32] has a very small HOMO−LUMO gap, 0.09 eV, but the gap of the most stable structure of Ni_5, the cluster Ni_5/C_{4v}-sp, is much larger, 0.75 eV (Table 2). Ni 3d Mulliken populations dominate to more than 80% the six unpaired majority spin orbitals of the square pyramidal cluster Ni_5/C_{4v}-sp; the remaining contributions exhibit 4s character. The two highest occupied MOs have majority spin character and exhibit dominant 4s contributions of the four Ni atoms at the base of the pyramid, while the 4s AO of the apex atom Ni_a contributes to an unoccupied molecular orbital (LUMO+2).

The apex Ni atom of Ni_5/C_{4v}-sp has the effective valence electronic configuration $s^{0.72}p^{0.34}d^{8.93}$, the Ni atoms at the base of the pyramid have the configuration $s^{0.93}p^{0.24}d^{8.84}$. A somewhat higher d population is determined for the Ni atoms of Ni_5/C_{3v}-bp which are $s^{0.71}p^{0.28}d^{8.95}$ (base) and $s^{1.04}p^{0.12}d^{8.94}$ (apex). In both structures of Ni_5, the metal atoms with three nearest neighbors (apex atoms in bp and base atoms in sp) have higher 4s populations than the atoms with four neighbors (base atoms in bp and apex in sp). In both structures the spin population s per atom is higher on Ni atoms with three neighbors and smaller for atoms with four neighbors. The variation of s for different atoms is larger for the Ni_5 square pyramid, 0.35 e, than that for the bipyramidal structure, 0.14 e (Table S2).

The vertical ionization potential of the square pyramid structure of bare Ni_5 cluster is 6.64 eV (Table 2), ~0.4 eV higher than the experimental values 6.18 ± 0.24,[47] 6.22 ± 0.05,[48] and 6.17 ± 0.02 eV.[49] The vertical IP of Ni_5/C_{3v}-bp is smaller, 6.41 eV (Table 2), hence closer to the experimental values. As the calculated vertical IP value overestimates the experimental ionization potential, we calculated the adiabatic IP of the square pyramid structure without symmetry restrictions (Table 2). The resulting value, 6.46 eV, is 0.18 eV smaller than the vertical IP value because the structure of the final state cation differs from that of the initial state (square pyramid) which was used in the evaluation of the vertical IP. The same effect is calculated for Ni_5/C_{3v}-bp (Table 2). The structure of Ni_5^+ can be considered as intermediate between bipyramidal and square pyramid structures.[50] The estimated adiabatic IP values of the square pyramid and bipyramidal structures are 6.46 and 6.24 eV, respectively. The former value is ~0.3 eV higher than experiment, while the latter one essentially coincides with experiment.[51] The vertical EA of the square pyramid structure, 1.64 eV (Table 2), is very close to the experimental value 1.57 ± 0.06 eV,[53] while the vertical EA of the bipyramidal isomer Ni_5/C_{3v}-bp, 1.39 eV, is ~0.2 eV lower. Thus, both Ni_5 isomers show reasonable agreement of calculated IP and EA values with experimental results and either of them could correspond to the experimentally studied Ni_5 clusters. The calculated vertical IP and EA values of the stable Ni_5 clusters are higher than the corresponding values calculated for the tetrahedral Ni_4 cluster by 0.75 and 0.24 eV, respectively. This trend fits the experimental values of Ni_5 which are also larger, by 0.47 (IP) and 0.07 eV (EA), than the corresponding experimental values of Ni_4.[49,53]

The vibrational frequencies of the stable structures Ni_5/C_{4v}-sp and Ni_5/C_{3v}-bp fall into the intervals 78−312 cm^{-1} and 61−334 cm^{-1}, respectively (Table S1 of Supporting Information). The vibrational frequencies of the tetrahedron-like cluster Ni_4 were calculated in the same region, 61−329 cm^{-1}.[32]

Previous computational studies of bare Ni_5 clusters yielded two isomers (Table 3), square pyramid and/or trigonal bipyramid structures with six and four unpaired electrons, respectively,[21,54−56] as obtained in the present work (Table 1). Also, the relative stability of the two isomers had been calculated to be very similar; the overall energy difference was at most 20 kJ/mol. The local density approximation (LDA) combined with triple-ζ quality basis set[54] gives a BE per Ni atom of 275 kJ/mol for the trigonal bipyramid and 271 kJ/mol for the square pyramid (Table 3). Calculations using the Perdew's exchange[57] and correlation[39] functional yielded only 1 kJ/mol difference per atom between the two isomers[21] with structures optimized at the highest symmetries, D_{3h} and C_{4v}, respectively. Recent DF

TABLE 3: Results from Previous Calculations for the Cluster Ni_5: Binding Energy per Ni Atom BE in kJ/mol, Number of Unpaired Electrons Ns, and Ni−Ni Distances in pm

method, basis set	symmetry, shape	BE	Ns	distances
LSDA, TZ[a]	D_{3h}-bp	275	4	231, 239
	C_{4v}-sp	271	6	226, 228
P91/P86, TZ[b]	D_{3h}-bp	213	4	231, 239
	C_{4v}-sp	214	6	234, 235
BLYP, DNP[c]	D_{3h}-bp	341	4	
	C_{2v}-bp	343	4	<237>[d]
	C_{4v}-sp	346	6	
	C_{2v}-sp	347	6	<235>[d]
VWN, DZVP2[e]	Bp	296	4	
PW86/P86, DZVP2[e]	Bp	241	4	231, 236
GGA-NS[e]	Bp	197	4	

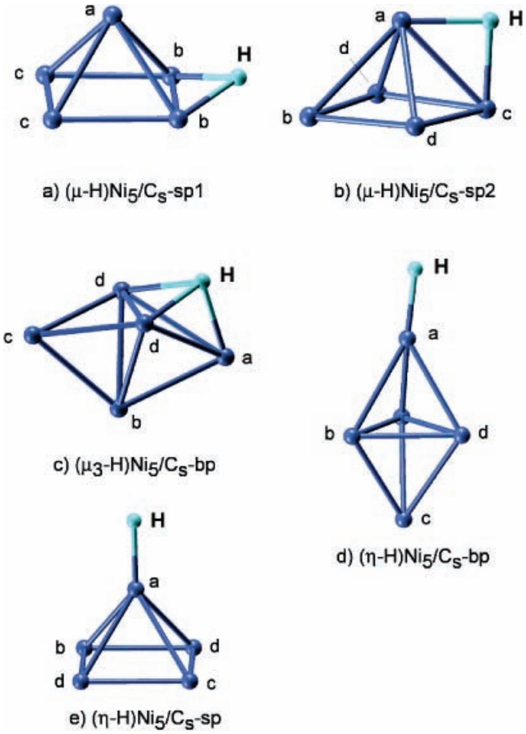
[a] Ref 54. [b] Ref 21; P91/P86 denotes a combination of Perdew's exchange, ref 57, and correlation, ref 39, functionals. [c] Ref 56, DNP denotes a double numerical basis with polarization functions where the 1s, 2s and 2p orbitals are kept "frozen." [d] Averaged value. [e] Ref 55, PW86/P86 denotes a combination of the exchange functional suggested by Perdew and Wang, ref 59, and the correlation functional of ref 39.

modeling using the BLYP functional[56] found the square pyramid isomer to be overall 20 kJ/mol more stable than trigonal bipyramid, where both structures had been optimized with a C_{2v} symmetry constraint (Table 3). However, the calculated BE per Ni atom was rather high for a GGA exchange-correlation functional, 347 kJ/ mol,[58] compared to calculations with other GGA functionals including the present results which yielded a BE per Ni atom of 231 kJ/mol.

The Ni−Ni distances that we obtained for the bipyramidal structure are shorter than the values reported in previous works. The equatorial distances are up to 2 pm shorter; this holds for previous calculations with various exchange-correlation functionals (LDA,[54] GGA[21,39,55,57,59]) while the bonds involving an apex atom differ by up to 3 pm (Table 3). All studies suggest close values for the Ni−Ni bonds at the base and the apex edges for the cluster with square pyramidal shape; the distances differ at most 2 pm. The average Ni−Ni distance, 227 pm, from LDA calculations[54] is slightly shorter than that from our BP calculations, 231 pm, while optimization with P91/P86[39,57] or BLYP[38,60] functionals gives slightly longer distances,[21,56] 235 pm.

Finally, we note that the reliability of the exchange-correlation functional and the basis set used in the present work for reproducing experimental values of binding energy and interatomic distances[61] was recently confirmed for Ni_2.[40,62]

As direct experimental information about the structure of small neutral nickel clusters is not available, we may compare our results with structural information derived from experiments with cations. Parks et al.[63] used the saturation coverage of Ni_x cluster cations with N_2 ligands to deduce the structure. For Ni_5^+ they found five and eight N_2 molecules adsorbed at low and high N_2 pressure, respectively, and concluded that the structure of the cluster should be a trigonal bipyramid. This agrees with our finding that the stable structure of Ni_5^+ resembles that of a distorted bipyramid with a single extended equatorial Ni−Ni distance (see endnote 50). However, the adsorption energy of a N_2 molecule on a small Ni cluster, estimated at 116 kJ/mol per ligand for the neutral complex $Ni_3(N_2)_3$ and at 86 kJ/mol per ligand for the corresponding cation,[62] is much larger than the total energy difference between square pyramidal and bipyramidal conformations of the bare Ni_5 cluster, 23 kJ/mol. Therefore, N_2 coordination could easily change the structure of the metal moiety.

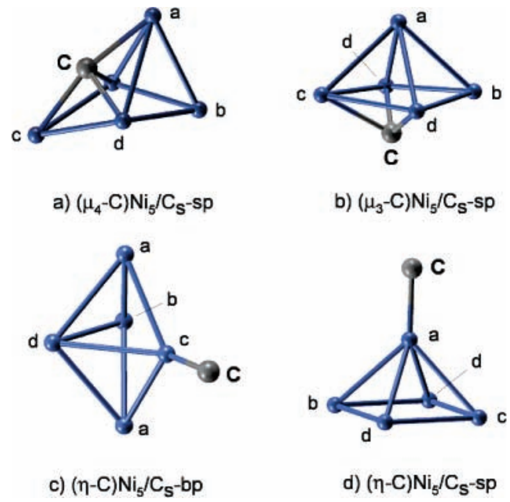


a) $(\mu\text{-H})Ni_5/C_S$-sp1 b) $(\mu\text{-H})Ni_5/C_S$-sp2

c) $(\mu_3\text{-H})Ni_5/C_S$-bp d) $(\eta\text{-H})Ni_5/C_S$-bp

e) $(\eta\text{-H})Ni_5/C_S$-sp

Figure 2. Stable structures of HNi_5 clusters. Also shown are the labels for the different types of Ni atoms; see text and tables.



a) $(\mu_4\text{-C})Ni_5/C_S$-sp b) $(\mu_3\text{-C})Ni_5/C_S$-sp

c) $(\eta\text{-C})Ni_5/C_S$-bp d) $(\eta\text{-C})Ni_5/C_S$-sp

Figure 3. Stable structures of CNi_5 clusters. Also shown are the labels for the different types of Ni atoms; see text and tables.

3.2. Clusters with Impurity Atoms. *3.2.1. Localization of Stable Minima.* To locate the preferred positions of the impurity atoms H, C, and O on Ni_5, we selected various initial positions of the heteroatoms at square pyramid and trigonal bipyramid metal frameworks (Figure S1 of the Supporting Information). To identify the bonding mode of the impurity, we use a nomenclature adapted from that common for inorganic complexes, that has served already well for XNi_4 isomers.[32] Direct coordination of an impurity atom to a single Ni atom is denoted by the prefix η (Figures 2d,e; 3c,d; 4f), coordination to a Ni−Ni bond is denoted by the prefix μ (Figures 2a,b and 4b,c), and simultaneous coordination to three or four Ni atoms by the prefixes μ_3 (Figures 2c, 3b, and 4a,d) or μ_4 (Figures 3a and 4e), respectively.

Thirteen initial structures of the clusters with impurities were constructed in the following way. For the square pyramid structure, the impurity atom X was located (i) in on-top fashion at the apex and base Ni atoms, (η-X)Ni_5-sp1 and (η-X)Ni_5-sp2, respectively; (ii) inside the cluster, (μ_5-X)Ni_5-sp; (iii) below the base of the pyramid, (μ_4-X)Ni_5-sp; (iv) at a side facet, (μ_3-X)Ni_5-sp; (v) over a Ni−Ni bond at the base, (μ-X)Ni_5-sp1; (vi) over a Ni−Ni bond at a side facet, (μ-X)Ni_5-sp2 (see Supporting Information Figure S1a−g). For the bipyramidal structure, the impurity atom X was located (vii) on-top at the apex and base Ni atoms, (η-X)Ni_5-bp1 and (η-X)Ni_5-bp2, respectively; (viii) over a Ni−Ni bond involving an apex atom, (μ-X)Ni_5-bp1; (ix) over a facet, (μ_3-X)Ni_5-bp1; and (x) over an equatorial Ni−Ni bond (μ-X)Ni_5-bp2; and (xi) inside the cluster, (μ_3-X)Ni_5-bp2 (see Supporting Information Figure S1 h-m).

All these structures were optimized applying pertinent symmetry constraints. To check the stability of the resulting structures, we carried out a normal-mode analysis without any symmetry restriction as described in Section 2 and proceeded at a lower symmetry constraint if necessary.

The stability of the obtained spin states was checked by single-point calculations (at fixed geometry) where the number of unpaired electrons was varied by ± 2. For nearly degenerate structures, where we found a BE difference with respect to the initial multiplicity below 10 kJ/mol, we subsequently optimized the cluster geometry, keeping the spin multiplicity fixed.

In the following, we discuss the geometry and some features of the electronic structure of the obtained stable minima.

3.2.2. Clusters with H Impurity. We identified five minima for an H impurity atom at the Ni_5 cluster: (μ-H)Ni_5/C_s-sp1, (μ-H)Ni_5/C_s-sp2, (μ_3-H)Ni_5/C_s-bp, (η-H)Ni_5/C_s-bp, and (η-H)Ni_5/C_s-sp (Figure 2a−e). In the most stable structures, the first two of this series, the H atom bridges one of the two types of Ni−Ni bonds of the square pyramid, similarly to the coordination of an H atom at the tetrahedral Ni_4 cluster.[32] In (μ-H)Ni_5/C_s-sp1 (Figure 2a) with BE(H) = 273 kJ/mol, the impurity atom is coordinated at the base of the pyramid, while in the (μ-H)Ni_5/C_s-sp2 isomer with BE(H) = 266 kJ/mol, the H atom is bound at an edge involving an apex of the pyramid (Figure 2b). Both structures are sextets, i.e., the number of unpaired electrons decreases by one with respect to the bare square pyramidal Ni_5 cluster. The binding energy of H in the most stable isomer, (μ-H)Ni_5/C_s-sp1, is 12 kJ/mol smaller than the BE of this impurity atom at the cluster Ni_4.[32] Coordination of H to an edge at the base of the square pyramid shortens this Ni−Ni distance by 6 pm compared to the bare Ni_5/C_{4v}-sp cluster. A similar effect had been determined for an H impurity at tetrahedral Ni_4.[32] In the other isomer with bridge-coordinated H, (μ-H)Ni_5/C_s-sp2, the impurity does not affect the length of the Ni_a−Ni_c bond to which it is coordinated (Figure 2b), but the Ni_a-Ni_b bond in trans position at the same apex is elongated by 11 pm.

In addition to bridge-coordinated H, which was the only stable structure of the HNi_4 cluster,[32] for HNi_5 we also found mono- and three-coordinated positions to be local minima. In the isomer (μ_3-H)Ni_5/C_s-bp the heteroatom is three-coordinated. This structure has 5 unpaired electrons and a BE(H) value of 262 kJ/mol (Table 1, Figure 2c). The impurity H atom, coordinated at a facet of the trigonal bipyramid, is notably closer to the apex Ni_a, 163 pm, than to the two equatorial centers Ni_d, 179 pm. In the structures (η-H)Ni_5/C_s-bp and (η-H)Ni_5/C_s-sp (Figure 2d,e), the H atom is coordinated on top to an apex Ni_a atom of each of the two fundamental framework topologies, bipyramid and square pyramid, respectively. The corresponding BE(H) values are quite a bit smaller, 234 and 209 kJ/mol, respectively. The former cluster is stable with three unpaired electrons, by one less than bare Ni_5/C_{3v}-bp, while the latter isomer is an octet, i.e., it has one unpaired electron more than the corresponding bare Ni_5/C_{4v}-sp cluster.

In four of the five reported structures, variation of the number of unpaired electrons by 2 resulted in a reduced stability of the isomer, by more than 25 kJ/mol. Only the cluster (μ_3-H)Ni_5/C_s-bp has similar stability when optimized with three and five unpaired electrons: 259 and 262 kJ/mol, respectively (Table 1). This small energy difference does not allow us to assign the ground state configuration. However, on the basis of the estimated spin contamination, 18% for Ns = 3 and 1% for Ns = 5, we expect the higher spin multiplicity to represent the ground state.

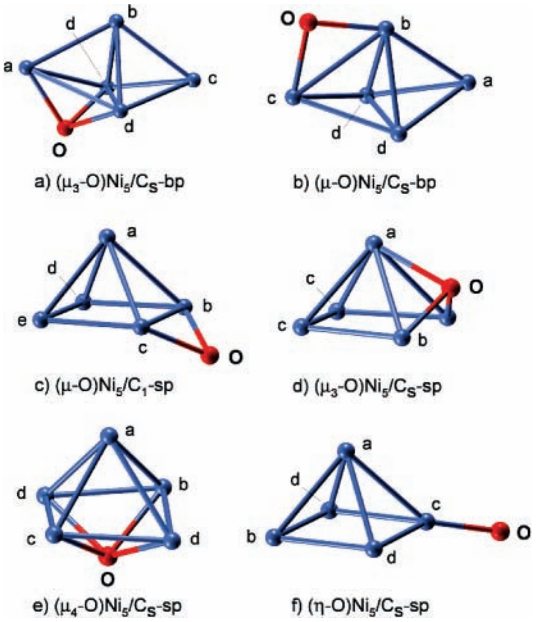
Extended Hückel calculations[64] suggested also bridge coordination of H to be most stable for Ni_5, yet at an edge involving the apex of trigonal bipyramidal Ni_5. Spin-polarized DF-GGA studies, directed to hydrogen adsorption on different surfaces of metallic nickel[65] suggested slightly smaller binding energies (by 2−18 kJ/mol) than calculated here for bridge coordinated H at Ni_5. The BE(H) values were 252−264 kJ/mol for Ni(100) and 255−264 kJ/mol for Ni(111). Periodic slab model calculations also showed that H adsorption on 3-fold sites (fcc or hcp) of low-index single-crystal surfaces is 12−21 kJ/mol more stable than adsorption on bridge sites.[65] This trend is opposite to the results reported here for H adsorption at Ni_5, where the isomer with bridge-coordinated H is 11 kJ/mol more stable than the isomer with a 3-fold coordinated impurity.

In the most stable structure (μ-H)Ni_5/C_s-sp1 the HOMO is a majority spin orbital. Both HOMO energy, −4.32 eV, and the HOMO−LUMO gap, 0.69 eV, of this complex are very similar to the analogous quantities of bare Ni_5/C_{4v}-sp (Table 2). A notable deviation in effective electron configuration with respect to the bare cluster was found only for the 4s population of atoms Ni_b, bound to H, which decreases by 0.19 e.

In all HNi_5 structures, the H atom features a small spin, s = −0.02 to 0.14 e. In the most stable structure (μ-H)Ni_5/C_s-sp1, the maximum difference between the spins s on the various types of Ni atoms is reduced from 0.35 e in the bare cluster to 0.18 e in the ligated cluster (Tables S2, S3 of the Supporting Information). This reduction occurs due to smaller s values of the Ni_b and Ni_c atoms at the base of the square pyramid where H is bound in the ligated cluster, 1.00 and 1.07 e, while the corresponding s values in bare Ni_5/C_s-sp are 1.27 e. The s of the apex Ni_a atoms, 0.89 e, remains almost at value in the corresponding bare cluster, 0.92 e. On the other hand, the second isomer (μ-H)Ni_5/C_s-sp2 with H coordinated at the apex bond Ni_a−Ni_c, features a larger difference between s values of the Ni atoms in the cluster, 0.56 e, because the impurity is bound to the apex Ni_a atom and reduces that s value by 0.27 e. In the structure with a three-coordinated H atom (Ns = 5) at the trigonal bipyramidal cluster Ni_5/C_{3v}-bp (Ns = 4), the additional unpaired electron increases the atomic spin s mainly on the atoms Ni_b and Ni_c which are distant from the impurity.

The calculated atomic charges for various conformations of the HNi_5 cluster are shown in Table S3 of the Supporting Information. Both types of charges of the H atom of HNi_5 were determined to be negative: PDC from −0.51 e to −0.39 e and Mulliken charges from −0.25 e to −0.18 e.

Similarly to the trend calculated for the HNi_4 cluster,[32] the vertical ionization potential of the most stable structure with an H impurity, (μ-H)Ni_5/C_s-sp1, is higher than for the bare nickel cluster, by 0.31 eV. In contrast, the IP of the second most stable structure, (μ-H)Ni_5/C_s-sp2, is 0.08 lower than the vertical IP of the bare Ni_5/C_{4v}-sp cluster (Table 2). The calculated IP values (Figure 5a) roughly follow a trend to smaller values with



a) (μ_3-O)Ni$_5$/C$_s$-bp b) (μ-O)Ni$_5$/C$_s$-bp

c) (μ-O)Ni$_5$/C$_1$-sp d) (μ_3-O)Ni$_5$/C$_s$-sp

e) (μ_4-O)Ni$_5$/C$_s$-sp f) (η-O)Ni$_5$/C$_s$-sp

Figure 4. Stable structures of ONi$_5$ clusters. Also shown are the labels for the different types of Ni atoms; see text and tables.

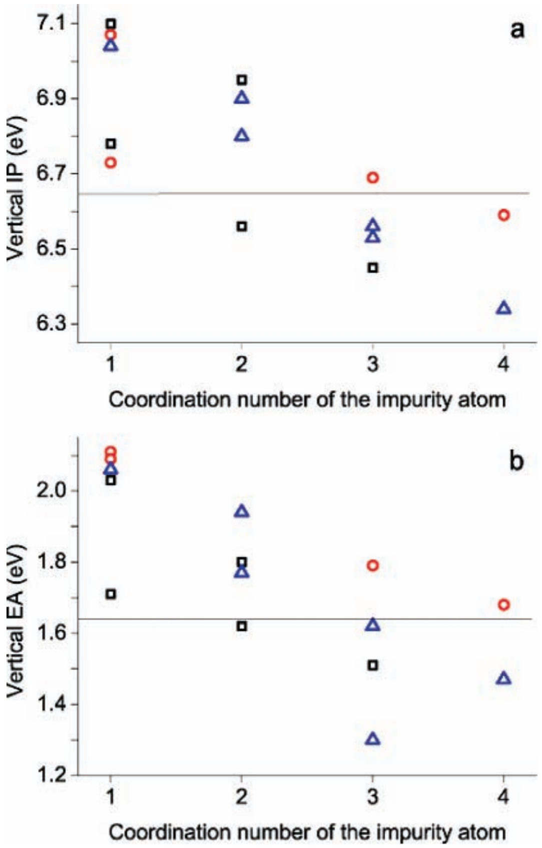


Figure 5. Dependence of IP (a) and EA (b) on the coordination number of the impurity atom. Squares, HNi$_5$; circles, CNi$_5$; triangles, ONi$_5$; straight line, bare Ni$_5$.

increasing coordination number of H, but this correlation is not strict, as can be seen both for η and μ coordinated impurities. The calculated electron affinity of four of the HNi$_5$ structures varies in the interval 1.51−1.79 eV, which is close to the value of the bare cluster, 1.64 eV (Table 2). The only larger change in the EA is calculated for the least stable complex, (η-H)Ni$_5$/C_s-sp, with EA = 2.03 eV. The EA values also decrease qualitatively with the coordination number of the impurity (Figure 5b).

As previously done for Ni$_4$,[32] we tried to rationalize how a hydrogen impurity affects the magnetism of a Ni$_5$ moiety. We used a simple model which focuses on the HOMO and the LUMO of the bare metal cluster[25−27] and assumes that the HOMO−LUMO gap of the cluster is small. In a simplified two-orbital three-electron picture, the 1s orbital of the H impurity interacts with the most appropriate filled orbital of the cluster, resulting in a pair of bonding and antibonding MOs of HNi$_5$. If the energy of that antibonding MO is above that of the LUMO of the (bare) cluster, the extra electron of H will occupy the LUMO of the bare cluster. The spin multiplicity of the cluster will decrease (increase) if the LUMO of the bare cluster belongs to the minority (majority) spin manifold. If the antibonding orbital is situated below the HOMO of the bare metal cluster, then it will be filled by an electron of the HOMO of the (bare) cluster and the spin character of the HOMO will affect the number of unpaired electrons in HNi$_5$.

Both HOMO and LUMO orbitals of the reference bipyramidal structure Ni$_5$/C_{3v}-bp belong to the minority spin manifold. Thus, one expects a decrease of the number of unpaired electrons if the Ni$_5$−H antibonding orbital lies above the LUMO, or an increase if the antibonding orbital lies below the HOMO. (η-H)Ni/C_s-bp follows the former situation (ΔNs = −1), while (μ_3-H)Ni$_5$/C_s-bp, corresponds to the latter situation (ΔNs = 1). Hence, the simple orbital model does not allow a clear prediction. HOMO and LUMO of the Ni$_5$/C_{4v}-sp isomer of the bare cluster belong to majority and minority spin manifolds, respectively. Hence, both variants of the simple orbital argument predict a decrease of the number of unpaired electrons. Indeed, we found both (μ-H)Ni$_5$/C_s-sp1 and (μ-H)Ni$_5$/C_s-sp2 isomers to be stable with Ns = 5 whereas the bare Ni$_5$/C_{4v}-sp has Ns = 6 (Table 1). However, the result for the structure (η-H)Ni$_5$/C_s-sp (with Ns = 7) does not fit to the above orbital argument. Thus, the latter case is another example that demonstrates the limitations of the simplified orbital model for rationalizing the spin multiplicity. In this context, note that compared to Ni$_4$, which has a small HOMO−LUMO gap of 0.09 eV,[32] Ni$_5$ structures feature considerably larger gaps: 0.75 eV for Ni$_5$/C_{4v}-sp and 0.51 eV for Ni$_5$/C_{3v}-bp (Table 2).

3.2.3. Clusters with C Impurity. We found four stable structures for the cluster CNi$_5$, two of them with C at a terminal position, and one each with C three- and four-coordinated (Figure 3); the stability of these structures increases in that order. All structures have four unpaired electrons. In the most stable structure (μ_4-C)Ni$_5$/C_s-sp (Figure 3a), BE(C) is 660 kJ/mol, which is by 20 kJ/mol higher than the BE of C at the Ni$_4$ cluster.[32] Similarly to the 4-fold coordinated C atom at Ni$_4$, the optimized structure of (μ_4-C)Ni$_5$/C_s-sp (Figure 3a) can be considered as insertion of the impurity in a Ni−Ni bond − either into an apex bond of the square pyramid or an equatorial bond of the trigonal bipyramid structure of Ni$_5$. The bonds of the C impurity to the four neighboring Ni atoms, 181−182 pm (Table 1), are very similar to the distances determined for (μ_4-C)Ni$_4$, 181−184 pm. In fact, the cluster (μ_4-C)Ni$_5$/C_s-sp can formally be constructed from (μ_4-C)Ni$_4$ simply by adding a Ni atom to a facet of an open tetrahedron.

In the complex (μ_3-C)Ni$_5$/C_s-sp, the BE is 646 kJ/mol. The impurity is bound at the base of the square pyramid, close to three of the Ni atoms, at 181−184 pm, while the distance to the fourth metal center, Ni$_\mathrm{b}$, is 206 pm.

In the last two local minima, the C atom is coordinated at the apex Ni$_\mathrm{a}$ of the square pyramid or to an equatorial Ni atom of a bipyramid which has been distorted toward a square pyramid. In both cases the BE of C, 378 and 403 kJ/mol, is considerably lower than for the previous two isomers. As expected from the lower coordination of C, the C−Ni bond is rather short, 160−162 pm (Table 1).

While the C impurity on Ni_4 leads to a stabilization of the HOMO with respect to the bare cluster in all observed structures, in the case of CNi_5 the stabilization of the HOMO depends on the coordination of the impurity atom. In the stable isomers with a high coordination number of C, $(\mu_4\text{-C})Ni_5/C_s$-sp and $(\mu_3\text{-C})Ni_5/C_s$-sp, the HOMO energy is essentially the same as in the bare cluster Ni_5/C_{4v}-sp, while for η-coordination the stabilization depends on the shape of the Ni moiety. The main change in the effective electronic configuration of the Ni centers in the most stable isomer $(\mu_4\text{-C})Ni_5/C_s$-sp with respect to the bare cluster Ni_5/C_{4v}-sp is the reduction of the occupation of 4s AOs of the metal atoms bound to C by 0.06−0.14.

The spin s in CNi_5 isomers (Table S4 of the Supporting Information) is not equally distributed on the nonequivalent types of Ni atoms. In the structures $(\mu_4\text{-C})Ni_5/C_s$-sp and $(\mu_3\text{-C})Ni_5/C_s$-sp the spin s on the C atom is low, −0.01 and 0.12 e, respectively, while in one of the structures with top-coordinated C atom $(\eta\text{-C})Ni_5/C_s$-sp the spin on C is higher (by absolute value), −0.45 e. In all CNi_5 clusters Ni atoms bound to carbon show some spin quenching compared to the bare Ni_5 cluster.

In all locally stable structures of CNi_5, the C center has a strong "carbidic" character, with PDCs ranging from −0.54 e for $(\eta\text{-C})Ni_5/C_s$-sp to −0.89 e and −0.90 e in the more stable structures $(\mu_3\text{-C})Ni_5/C_s$-sp and $(\mu_4\text{-C})Ni_5/C_s$-sp, respectively (Table S4 of the Supporting Information). In both latter complexes, the positive counter charge is almost equally distributed over the four Ni atoms bound to C, while the farther Ni atom is neutral or slightly negative.

The presence of a C heteroatom in the cluster does not significantly change the IP of the two stable structures $(\mu_4\text{-C})Ni_5/C_s$-sp and $(\mu_3\text{-C})Ni_5/C_s$-sp compared to the bare square pyramid cluster (Table 2). The EA values of these isomers of CNi_5 are 0.04 and 0.15 eV higher, respectively, than the EA of the bare cluster, 1.64 eV. As for the H impurity complexes, the IP and EA values of the clusters with a C impurity tend to lower values with increasing coordination number of the impurity atom (Figure 5). However, comparing the complexes $(\eta\text{-C})Ni_5/C_s$-bp and $(\eta\text{-C})Ni_5/C_s$-sp, one can conclude that the structure of the Ni_5 moiety and the coordination site of the impurity also affect the IP value.

3.2.4. Clusters with O Impurity. At variance with the ONi_4 complex,[32] where we determined only one stable structure, $(\mu\text{-O})Ni_4/C_{2v}$, for the Ni_5 cluster we found six local minima with an O impurity. The coordination of O in these complexes varies between 1- and 4-fold. The most stable isomers are based on the trigonal bipyramid structure of the Ni_5 moiety with the impurity coordinated to a facet, $(\mu_3\text{-O})Ni_5/C_s$-bp, or apex edge, $(\mu\text{-O})Ni_5/C_s$-bp, (Figure 4a,b; Table 1). The former isomer is more stable with a BE(O) of 436 kJ/mol; for the isomer with bridge-coordinated O we calculated a smaller value, 412 kJ/mol. Both isomers are quintets, as the bipyramidal isomer of bare Ni_5. In the most stable structure, the Ni_a−O bond to the apex Ni atom is calculated at 177 pm, while the Ni_d−O bonds to the metal atoms at the base of the bipyramid are 10 pm longer. All Ni−Ni distances of the facet, where the impurity is coordinated, are extended by ∼24 pm compared to the bare cluster. The structural changes in the Ni_5 moiety of $(\mu\text{-O})Ni_5/C_s$-bp with bridge-coordinated O are smaller; the Ni_b-Ni_c bond closest to O elongates only by 13 pm (Table 1, Figure 4b).

In the other four isomers of the ONi_5 complex the Ni_5 moiety has a square pyramidal shape. The O impurity atom is coordinated at the base or a side of the pyramid, to a Ni−Ni bond of the base, or to a Ni atom of the base, forming the complexes $(\mu_4\text{-O})Ni_5/C_s$-sp (Figure 4e), $(\mu_3\text{-O})Ni_5/C_s$-sp (Figure 4d), $(\mu\text{-O})Ni_5/C_1$-sp (Figure 4c), or $(\eta\text{-O})Ni_5/C_s$-sp (Figure 4f), respectively. The BE of the impurity to the square pyramid increases with decreasing coordination number: 340, 390, and 402 kJ/mol for four-, three-, and two-coordinated O. However, the mono-coordinated O ligand of the cluster $(\eta\text{-O})Ni_5/C_s$-sp forms an exception with the lowest value, BE(O) = 313 kJ/mol. The complex $(\mu\text{-O})Ni_5/C_1$-sp has six unpaired electrons, as the bare Ni_5/C_{4v}-sp cluster, whereas all other complexes with an O impurity have 4 unpaired electrons. The Ni−O distances increase with increasing coordination number of O, from 163 pm for $(\eta\text{-O})Ni_5/C_s$-sp to 192 pm for $(\mu_4\text{-O})Ni_5/C_s$-sp (Table 1).

The energy of the HOMO of four of the structures with an O impurity is similar to that of the most stable bare cluster; the difference ranges from −0.13 to 0.14 eV (Table 2). In the structure with highest coordination of the impurity, $(\mu_4\text{-O})Ni_5/C_s$-sp, the energy of the HOMO is 0.50 eV higher than for the bare cluster, while in the isomer with on-top bonded O, $(\eta\text{-O})Ni_5/C_s$-sp (Figure 4f), the HOMO is stabilized by 0.32 eV.

The effective configurations of the Ni atoms of the most stable isomer $(\mu_3\text{-O})Ni_5/C_s$-bp suggest a strong decrease of the 4s population of the centers Ni_a and Ni_d compared to the bare cluster, due to Ni−O bonding which results in a positive potential-derived charge on these centers (Table S5 of the Supporting Information, Mulliken charges are given in brackets), $q(Ni_a) = 0.23$ [0.22] e and $q(Ni_d) = 0.30$ [0.29] e, while the Ni_b and Ni_c atoms, far from O, are essentially neutral, $q(Ni_{b,c}) = -0.05$ [0.02, −0.05] e. The high electronegativity of the O atom is reflected in its large negative charge, ranging from −0.71 [−0.62] e to −0.76 [−0.78] e on the clusters with μ and μ_3 coordination of the ligand and from −0.52 [−0.78] e to −0.64 [−0.51] e for μ_4 and η coordination, respectively. The O atom features a spin s of 0.01−0.25 e in the isomers with four unpaired electrons and 0.33 e in the structure $(\mu\text{-O})Ni_5/C_1$-sp with six unpaired electrons. That spin is associated with the O 2p contribution to the HOMO of the cluster. The remaining spin s is not equally distributed over the Ni atoms.

Depending on the location of the O impurity on the cluster, the vertical IP of ONi_5 isomers varies from 6.34 to 7.04 eV. The IP of the most stable structure $(\mu_3\text{-O})Ni_5/C_s$-bp is only 0.12 eV higher than the vertical IP of the bare Ni_5/C_{3v}-bp cluster. Calculated EA values vary from 1.30 to 2.06 eV. As can be seen in Figure 5, both the IP and EA values roughly decrease with the increasing coordination number of the impurity atom, similarly as for the clusters HNi_5 and CNi_5.

The calculated binding energies of an oxygen impurity at a single-crystal nickel surface, calculated with respect to $1/2O_2$, are 163 kJ/mol for adsorption at a bridge site of Ni(111) and 221 kJ/mol for adsorption at an fcc site of that surface.[66] For comparison with these values, we recalculated the BE of O in the relevant structures of the ONi_5 cluster with respect to $1/2O_2$ using the calculated energy of the reaction $1/2O_2(g) \rightarrow O(g)$ of 196 kJ/mol; the resulting values were 216 kJ/mol for $(\mu\text{-O})Ni_5/C_s$-sp and 240 kJ/mol for $(\mu_3\text{-O})Ni_5/C_s$-bp. This comparison suggests that oxygen atoms bind stronger at small metal clusters than on a regular close-packed surface; this observation was already made for the Ni_4 cluster.[32]

3.2.5. Detachment Energy of Ni Atoms from the Clusters. To evaluate the influence of the impurity atom on the stability of

TABLE 4: Calculated and Experimental[a] Detachment Energy DE (kJ/mol) for a Ni Atom from the Ni_5 Cluster with and without Impurity

reaction	DE(calc)	DE(exp)
$Ni_5^+ \rightarrow Ni_4^+ + Ni$	256	206 ± 23
$Ni_5 \rightarrow Ni_4 + Ni$	320	256 ± 22
(μ-H)Ni_5/C_s-sp1 → (μ-H)Ni_4/C_1(5) + Ni	306	
(μ_4-C)Ni_5/C_s-sp → (μ_4-C)Ni_4/C_{2v} + Ni	313	
(μ_3-O)Ni_5/C_s-bp → (μ-O)Ni_4/C_{2v} + Ni	340	

[a] Ref 67.

small nickel clusters, we calculated the detachment energy (DE) of a Ni atom from the Ni_5 cluster with impurity and compared it with the DE of bare Ni_5 and Ni_5^+ clusters (Table 4). For both latter values, experimental estimates are available.[67] For the evaluation of the calculated DE, we used the energies of the most stable structures of the corresponding clusters with five and four Ni atoms, reported here and in ref 32. The calculated DE of a Ni atom from neutral Ni_5 is 320 kJ/mol, while a Ni atom is detached much easier from the cationic cluster Ni_5^+, where the DE is 256 kJ/mol. These values are about 50−64 kJ/mol overestimated[68] compared to experimental results which were determined with an accuracy of ±22 kJ/mol. However, the difference between calculated DE values for Ni_5 and Ni_5^+, 64 kJ/mol, is quite close to the difference between the values derived from experiment, 50 kJ/mol. According to experiment[67] the difference in the DE of the neutral and cationic clusters of the same nuclearity depends strongly on the size of the cluster.

On the other hand, the presence of an impurity atom on the cluster modifies only slightly the detachment energy of a Ni atom, at most by 20 kJ/mol. H or O impurities facilitate the detachment of a Ni atom by 14 and 7 kJ/mol, respectively, compared to bare Ni_5. A C impurity has the opposite effect: it slightly stabilizes the cluster as the DE value increases by 20 kJ/mol. On the basis of this result, one may speculate that a C impurity would foster the growth of a nickel cluster, while a H impurity would assist in its decomposition.

Comparison of the DE of a Ni atom from the clusters with impurity with the BE of the impurity to Ni_5 (Table 1) suggests that the cluster HNi_5 will easier release the H impurity. The corresponding energies are 273 kJ/mol for the removal of H and 306 kJ/mol for the removal of a Ni atom. It requires less energy to remove a Ni atom from CNi_5 and ONi_5 clusters, with DE values of 340 and 313 kJ/mol, respectively, whereas the detachment of the impurity atom requires much more energy, 660 kJ/ mol for a C atom and 436 kJ/mol for a O atom.

3.2.6. Evaluation of the Reactivity of the Clusters. To evaluate the influence of impurity atoms on the reactivity of the Ni_5 cluster, we estimated[69] the total hardness[70] $\eta \approx (IP - EA)/2$ using the calculated values of IP and EA (Table 2). The hardness concept was previously applied to analyze the relative stability and the reactivity of small sodium and coinage metal clusters.[71] The calculated values of the total hardness of both stable Ni_5 structures and all Ni_5X clusters are presented in Figure 6. The values are ordered according to the type of coordination of the impurity at the metal cluster, as in Figure 5. The two isomers of Ni_5 yield essentially the same hardness, 2.5 eV. Impurity atoms hardly change the hardness (Figure 6) and hence the reactivity of the cluster; values vary within ±10% around the result for Ni_5. As both IP and EA tend to decrease with increasing coordination number of the impurity atom, the total hardness of the cluster changes neither with the coordination number nor the type of the impurity atom.

For comparison we included in Figure 6 also the η values of the stable structures of Ni_3, Ni_4 and Ni_6,[32,62,72] calculated in analogous way. The hardness of Ni_4 is 0.25 eV smaller than that of Ni_5, while the values of Ni_3 and Ni_6 are larger, by 0.22 and 0.10 eV, respectively. Thus, the effect of impurities H, C, or O on the hardness of the cluster is comparable with the changes caused by addition to or removal of metal atoms from the cluster. The variations of the hardness of Na_n, $n = 3-6$, clusters (determined also from calculated IP and EA values) with their nuclearity were reported larger, 0.5−0.7 eV, and exhibited an odd−even oscillation, typical for sodium clusters.[71a]

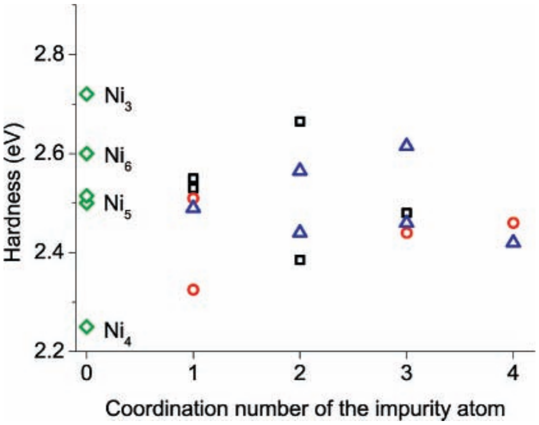


Figure 6. Estimated total hardness η of bare Ni_n clusters (n = 3−6) and Ni_5X clusters (X = H, C, and O) with different coordination numbers of the impurity atom. Squares, HNi_5; circles, CNi_5; triangles, ONi_5; rhombus, bare clusters.

Following Pearson's principle,[70] Ni_5 and Ni_5X clusters should react preferably with reactants with similar total hardness, i.e., with η between 2 and 3 eV. These values are much smaller than the hardness of molecules considered as soft, as CO and N_2 with η values above 7 eV. As the difference between the hardness of these ligand molecules and the cluster Ni_5 is much larger than the variations of η from Ni_5 to Ni_5X, one should not expect substantial changes in ligand binding energy due to addition of a single impurity atom to Ni_5. According to the estimated total hardness, the reactivity of the modeled metal clusters, both with and without impurities, is expected to be higher with softer reactants, e.g., with other metal clusters, suggesting a propensity to cluster aggregation.

4. Summary

In agreement with earlier studies, the square pyramid and the trigonal bipyramid have been calculated as the more stable structures of Ni_5. In the square pyramid structure, the bare Ni_5 cluster has six unpaired electrons, Ns = 6, while the trigonal bipyramid has two unpaired electrons less, Ns = 4. In the square pyramid structure (Figure 1a), the cluster is 23 kJ/mol more stable than in the trigonal bipyramid structure (Figure 1b).

The binding energy of the impurity (relative to an isolated impurity atom) increases in the order H (273 kJ/mol), O (436 kJ/mol), and C (660 kJ/mol; values quoted for the most stable isomers). Comparison with calculated atomization energies of H_2 or O_2 in the gas-phase suggests that the reactions 2 Ni_5 + X_2 → 2 Ni_5X (X = H, O) are exothermic with 90 kJ/mol (X = H) and 480 kJ/mol (X = O).

The adsorption positions of H and C atoms at a nickel pentamer are essentially the same as those at a Ni_4 tetramer. The preferred coordination of O on Ni_5 is 3-fold, while on the smaller Ni_4 cluster it was coordinated to a Ni−Ni bond. The structural distortions of the nickel moiety due to impurity coordination correlate with the BE of the impurity atom. The H impurity has the lowest BE and causes small changes in the

Ni−Ni bond lengths, at most ±6 pm for the most stable isomer. The C atom, featuring a more than twice larger BE, induces a considerable distortion of the nickel cluster; one of the Ni−Ni bonds of Ni$_5$ is broken in the energetically preferred structure.

As expected, inclusion of an impurity atom H, C, or O in the cluster causes a partial oxidation of the metal atoms, as shown by a charge analysis, based either on potential derived or Mulliken charges.

As a rough trend, the values of the IP and EA of the clusters with impurity atoms decrease with the coordination number of the impurity. In the most stable isomers of the clusters with C and O impurity the IP of the cluster is almost the same as for bare Ni$_5$/C_{4v}-sp, while the IP of the most stable HNi$_5$ cluster is 0.3 eV higher. The EA values of the most stable isomers of the HNi$_5$ and CNi$_5$ clusters are close to the EA of the bare cluster, whereas the EA of the most stable ONi$_5$ isomer is 0.3 eV lower than that of Ni$_5$/C_{4v}-sp.

Comparison of the detachment energy of a Ni atom from the neutral and ionized Ni$_5$ clusters suggested that it costs less energy to remove a Ni atom from the cationic species than from the neutral Ni$_5$ cluster. Impurity atoms change the Ni removal energies in either way. A C impurity stabilizes the bonding of the Ni atoms in the cluster, whereas H or O impurities reduce the Ni detachment energy. From the calculated detachment energies one can conclude that it costs less energy to remove an H impurity from a HNi$_5$ cluster than a Ni atom, while the clusters with a C or an O impurity lose much easier a Ni atom than the impurity atom.

The estimates of the total hardness η as measure of the reactivity of the clusters with and without impurity atoms showed only small variations due to presence of an impurity atom (±10%) around the value of bare Ni$_5$, $\eta = 2.50$ eV. These variations are much smaller than the difference to the hardness of CO or N$_2$ ligand molecules; therefore, one should not expect substantial differences in the binding energy of these ligands due to the presence of single impurity atoms on the nickel cluster.

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Supporting Information Available: We provide a figure with initial structures of the clusters with impurities and tables with calculated vibrational frequencies, potential derived charges (PDC), Mulliken charges (MC), the corresponding spin densities per atom, and the electronic configurations of the isomers of bare Ni$_5$ and the clusters with impurity atoms. This material is available free of charge via the Internet at http://pubs.acs.org.

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pm for the diagonals of the Ni_5/C_{4v}-sp structure. The resulting structure can also be considered as distorted trigonal bipyramid where one of the equatorial Ni−Ni bonds is considerably extended to 273 pm, while the other Ni−Ni distances are 233 pm (equatorial) and 231, 236 pm (axial). The deviation of the cationic cluster from both high symmetry structures can be rationalized as Jahn−Teller distortion. The HOMO, occupied by only one electron, originally is a degenerate e-type set, which splits upon distortion. The stability of the ionized species Ni_5^+ with respect to 4 Ni atoms and 1 Ni^+ ion is 603 kJ/mol on average per mononuclear species.

(51) The IP values were calculated also taking into account scalar relativistic effects as implemented in ParaGauss.[52] The obtained values are: IP(vertical) = 6.52 eV, IP(adiabatic) = 6.29 eV for Ni_5/C_{3v}-bp; IP(vertical) = 6.81 eV, IP(adiabatic) = 6.63 eV for Ni_5/C_{4v}-sp. These relativistic values are by 0.05−0.17 eV higher than the non-relativistic results, and thus increase slightly the deviation from experiment compared to the non-relativistic approach.

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