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considerably more complicated. These "intermediate hapticity" systems will be the subject of a separate manuscript.

Relationship of Main-Group Annulene Complexes to Polyhedral Carbocations, Carboranes, and Boranes

Finally, we comment that annulene complexes of the main-group elements are related conceptually to polyhedral carbocations[40] and hence to familiar main-group clusters such as the carboranes and boranes.[41] These interrelationships can be illustrated by starting with the polyhedral carbocation $[C_6H_6]^{2+}$ (**1**) (Scheme I). This dication is unknown; however, the corresponding permethylated cation $[C_6Me_6]^{2+}$ is known and believed to possess a nido (η^5) structure on the basis of NMR spectroscopic data.[42]

If the capping group of **1** is regarded as CH^{2+}, then this moiety contributes one electron to interstitital bonding and obeys the six-electron rule like the isoelectronic molecule $(\eta^5\text{-}C_5H_5)BeH$. Replacement of the apical CH by an isoelectronic BH^- group generates the carborane cation **2**. As mentioned earlier, some B–halogen analogues of **2** are known[37] and believed to possess η^5 structures on the basis of NMR spectroscopic data. Like **1**, **2** also conforms to the six-electron rule. A further CH/BH^- replacement produces the known neutral carborane **3**.[43] In order to maintain neutrality, it is necessary to replace further basal CH groups with H–B–H moieties. Such replacements generate sequentially the carboranes $C_3B_3H_7$, $C_2B_4H_8$, and CB_5H_9 and finally the polyhedral borane B_6H_{10}. Relationships to a host organometallic system are made possible by use of the isolobal concept.[44]

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Registry No. CpLi, 16733-97-4; CpIn, 34822-89-4; CpBeH, 50293-77-1; CpBeCl, 36346-97-1.

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Electronic Structure of Metal Carbonyl Clusters. 2. An INDO Investigation of Tetra-, Penta-, and Hexanuclear Nickel Complexes

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Tetra-, penta-, and hexanuclear nickel carbonyl clusters have been theoretically investigated by means of a MO–LCAO INDO method. Qualitative correlations have been found between the molecular stability and the electron density on metal atoms and ligand groups. The electronic density on the carbonyls has been described by means of the occupation numbers of the MO's of the free CO molecule, thereby giving a systematic description of the variations in donor–acceptor properties of the coordinated carbonyls. The cluster stability has been analyzed in terms of two-atom interaction energies for evaluating the separate contributions of metal–metal, metal–ligand, and ligand–ligand interactions. The main contribution is the direct interaction between a nickel atom and its ligand groups, but significant bonding interactions occur also between a metal atom and the ligand groups not directly bonded and between different ligand groups. All these intramolecular interactions are even more important than the direct metal–metal ones. These latter interactions do not give the most important contribution to the cluster stability.

1. Introduction

In a previous paper,[1] hereafter referred to as part 1, the electronic structure of carbonyl clusters having up to three nickel atoms was investigated by means of semiempirical MO–LCAO INDO calculations. The most important result of part 1 is that the INDO method suggests that the stability of the metal clusters cannot be accounted for by simplified electron-count models.[2]

In this paper, the theoretical approach outlined in part 1 is applied to the nickel carbonyl clusters of higher nuclearity, with the aim of obtaining more detailed information on the different electronic contributions to the overall cluster stability. As pointed out in a recent review paper,[3] the cluster stability problem is still far from being solved, mainly because the rigorous quantum-chemical methods cannot be applied to molecular clusters of high nuclearity. On the other hand, the results of different semiempirical methods are difficult to compare because of their basic approximations.

A widely discussed aspect of the cluster stability is the contribution of the metal–metal bond, which according to the classic definition of a metal cluster compound is supposed to play an important role.[4] However, the problematic nature

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Table I. Formula, Symmetry, Electronic Configuration, and Dissociation Energy[a] for Tetra-, Penta-, and Hexanuclear Nickel Clusters

formula	symmetry	electronic confign	D, kcal·mol^{-1}
$Ni_4(CO)_6(\mu\text{-}CO)_3$ (I)	C_{3v}	$16a_1, 5a_2, 44e$	518.2
$(Ni_4(CO)_6(\mu\text{-}CO)_3)^{2-}$ (II)	C_{3v}	$17a_1, 5a_2, 44e$	420.6
		$16a_1, 4a_2, 46e$	345.5
		$15a_1, 5a_2, 46e$	335.4
$(Ni_4(CO)_6(\mu\text{-}CO)_3H)^-$ (III)	C_{3v}	$17a_1, 5a_2, 44e$	500.8
		$16a_1, 4a_2, 46e$	353.2
$Ni_5(CO)_9(\mu\text{-}CO)_3$ (IV)	C_{3v}	$21a_1, 6a_2, 58e$	601.5
$(Ni_5(CO)_9(\mu\text{-}CO)_3)^{2-}$(V)	C_{3v}	$22a_1, 6a_2, 58e$	519.5
		$23a_1, 5a_2, 58e$	414.9
		$24a_1, 6a_2, 56e$	405.9
$Ni_6(CO)_6(\mu\text{-}CO)_6$ (VI)	D_{3d}	$11a_{1g}, 4a_{2g}, 4a_{1u}, 11a_{2u}, 30e_g, 30e_u$	681.1
		$10a_{1g}, 4a_{2g}, 4a_{1u}, 10a_{2u}, 32e_g, 30e_u$	393.9
$(Ni_6(CO)_6(\mu\text{-}CO)_6)^{2-}$ (VII)	D_{3d}	$12a_{1g}, 4a_{2g}, 4a_{1u}, 11a_{2u}, 30e_g, 30e_u$	625.8
		$11a_{1g}, 4a_{2g}, 4a_{1u}, 10a_{2u}, 32e_g, 30e_u$	433.6

[a] The dissociation energy D (kcal·mol^{-1}) is computed with respect to the process $(Ni_m(CO)_n)^{p-} \rightarrow m\text{Ni} + n\text{CO} + pe^-$, with free nickel atoms in the $3d^94s^1$ reference valence state.

of the metal–metal bond in molecular metal clusters is well recognized and has been a matter of considerable discussion in the last few years.[5] Up to now a well-grounded theoretical evaluation of the metal–metal interaction in metal carbonyl compounds has been reported only for a few dinuclear[6] and trinuclear metal complexes.[7]

Of the approaches taken to estimate the strength of the metal–metal bond, particularly worthy of note are the electron-pair counting methods,[8] the empirical metal–metal interaction potential,[9] and the derivation of the bond energies from the fitting of thermochemical data for a series of clusters of increasing nuclearity.[10]

Besides the above-mentioned studies, a clear picture of the metal–metal bond is lacking, and one main problem remains unsolved: Is the metal cage structure determined by the geometry of the vacancies left in a regular arrangement of the carbonyl ligands,[11] or are the spatial position and the number of CO groups determined by the free coordination sites of a metal cage with its own important stability?[4]

The purpose of the present investigation is to contribute to the solution of this problem by analyzing the electronic structure of some tetra-, penta-, and hexanuclear nickel carbonyl clusters. The details of the theoretical method used are given in part 1.[1]

In the next section the energy data for different electronic configurations and the associated charge distributions are presented and discussed for the following seven clusters: $Ni_4(CO)_6(\mu\text{-}CO)_3$ (I), $(Ni_4(CO)_6(\mu\text{-}CO)_3)^{2-}$ (II), $(Ni_4(CO)_6(\mu\text{-}CO)_3H)^-$ (III), $Ni_5(CO)_9(\mu\text{-}CO)_3$ (IV), $(Ni_5(CO)_9(\mu\text{-}CO)_3)^{2-}$ (V), $Ni_6(CO)_6(\mu\text{-}CO)_6$ (VI), and $(Ni_6(CO)_6(\mu\text{-}CO)_6)^{2-}$ (VII).

In section 3 the analysis of some factors affecting the cluster stability are examined. The metal–metal, metal–ligand, and ligand–ligand contributions are discussed in section 4. Relations to other studies will be presented in the concluding section.

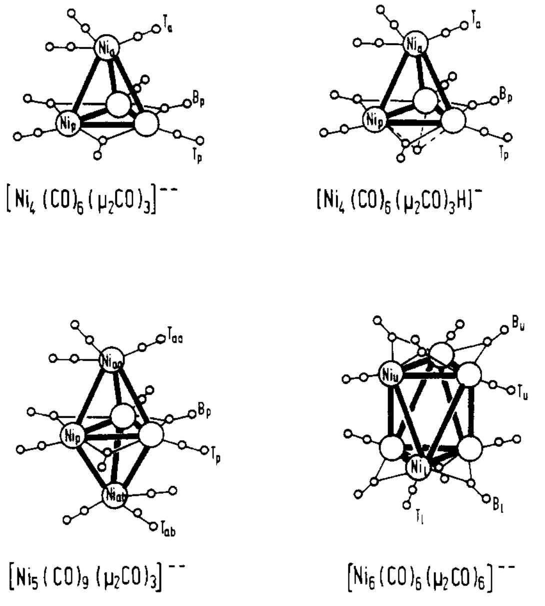

Figure 1. Schematic structures of tetra-, penta-, and hexanuclear nickel clusters.

2. Electronic Structure of Tetra-, Penta-, and Hexanuclear Nickel Carbonyl Clusters

Among the nickel clusters considered here (see Table I and Figure 1), the penta- and hexanuclear anionic complexes are the most widely studied.[12] These are the only species isolated in the solid state for which the molecular structure is known.[12b,c] By contrast, the existence of the neutral clusters has never been proved and they have been included in our investigation merely to illustrate some important differences in charge distribution and stability between neutral and anionic species.

The tetranuclear clusters have been postulated to form during the reduction of $Ni(CO)_4$ with alkali metals in liquid ammonia or with alkali-metal amalgams in THF.[13,14] The

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Table II. Electronic Distribution in Tetranuclear Nickel Clusters[a]

		$Ni_4(CO)_6(\mu\text{-}CO)_3$	$(Ni_4(CO)_6\text{-}(\mu\text{-}CO)_3)^{2-}$	$(Ni_4(CO)_6\text{-}(\mu\text{-}CO)_3H)^-$
Nip	4s	0.4679	0.6215	0.4723
	4p	0.0865	0.0836	0.0968
	3d	9.3792	9.3229	9.3760
	q	0.0574	−0.0280	0.0548
Ni_a	4s	0.2161	1.9137	1.4012
	4p	0.0828	0.0777	0.0979
	3d	9.5073	9.1138	9.1116
	q	0.1938	−1.1053	−0.6106
T_p	N_σ	5.9438	5.9847	5.9278
	N_π	3.9962	3.9960	3.9960
	$N_{\pi*}$	0.0562	0.0844	0.0745
	q_C	0.1473	0.1741	0.1843
	q_O	−0.1436	−0.2392	−0.1827
T_a	N_σ	5.9629	5.9959	6.0175
	N_π	3.9942	3.9982	3.9902
	$N_{\pi*}$	0.1152	0.1208	0.0773
	q_C	0.1049	0.2471	0.1709
	q_O	−0.1774	−0.3520	−0.2558
B_p	N_σ	5.8306	5.8319	5.9221
	N_π	3.9668	3.9636	3.9720
	$N_{\pi*}$	0.2526	0.3013	0.2343
	q_C	0.1448	0.2026	0.1289
	q_O	−0.1950	−0.2994	−0.2573
q_H				0.0959

[a] See part 1 for definitions of N_σ, N_π, and $N_{\pi*}$. The nickel atoms and the ligand groups are identified as in Figure 1.

hydride species III has been hypothesized as a product of the reaction between II and water.[14] However, the existence of this and other tetranuclear species has not been confirmed by a more recent experimental investigation,[12b,c] in which it was found that the most reduced form obtainable is the pentanuclear cluster V.

Tetranuclear Clusters. The geometrical parameters for the tetranuclear clusters have been derived from the X-ray data of the pentanuclear cluster V.[12b] We assume that the tetranuclear species belong to the C_{3v} point group, being composed of a planar $Ni_3(CO)_3(\mu\text{-}CO)_3$ fragment (the cluster VIII of part 1) and an apical $Ni(CO)_3$ group. A Ni–H distance equal to 1.84 Å derived from the literature data[15] has been taken for the hydride derivative III. The hydrogen atom is placed on the threefold axis and below the Ni_3 basal plane (see Figure 1).

The 130 valence electrons of the ground-state configuration of the cluster I are distributed in 16, 5, and 44 MO's of a_1, a_2, and e symmetry, respectively, and its dissociation energy $D = -(E_{Ni_n(CO)_m} - nE_{Ni} - mE_{CO})$ is equal to 518.2 kcal·mol^{-1} (see Table I). The Ni atom of the apical group (Ni_a, see Figure 1 for definition) carries a higher positive charge than the nickel atoms of the basal plane (Ni_p). However, the positive charge on Ni_a is completely balanced by the excess of electron density on the apical terminal carbonyls (T_a). Thus the $Ni(CO)_3$ group carries a very small negative charge and behaves as a very weak Lewis acid with respect to the planar Ni_3 fragment. When compared with the corresponding free cluster (VIII of part 1), the Ni_3 fragment shows very small variations in the charge distribution: even the N_σ, N_π, and $N_{\pi*}$ values computed for the in-plane terminal (T_p) and bridged (B_p) carbonyls are nearly identical in the two cases (compare Table II of this work and Table VI of part 1).

In Table I the different electronic configurations considered for the dianion cluster II are reported. The ground state (D = 420.6 kcal·mol^{-1}) is described by the following MO occupancy: $17a_1$, $5a_2$, 44e. With respect to the neutral cluster, the two extra electrons occupy an HOMO of a_1 symmetry mainly composed of the 4s orbital of the Ni_a atom. The electron distribution corresponds to a strong localization of negative charge on the apical $Ni(CO)_3$ group. In other words, the hypothetical formation of the cluster II by the addition of a neutral $Ni(CO)_3$ group to the dianion $(Ni_3(CO)_3(\mu\text{-}CO)_3)^{2-}$ is accompanied by a large charge transfer toward the apical group (1.42 electrons). In contrast, if the cluster is supposed to be formed by a dianion $(Ni(CO)_3)^{2-}$ reacting with a neutral $Ni_3(CO)_3(\mu\text{-}CO)_3$ cluster, then the charge transfer to this latter fragment is largely reduced (0.58 electron) (see Tables IV and VI of part 1). On the basis of these results, it may be suggested that the $Ni(CO)_3$ group is a stronger Lewis acid than the $Ni_3(CO)_3(\mu\text{-}CO)_3$ group, although the acid–base properties are much less evident when the two competing groups are both neutral, as in the case of the formation of the cluster 1.

Other interesting observations can be made by comparing the $Ni_3(CO)_3(\mu\text{-}CO)_3$ fragment of the cluster II with the corresponding free dianionic cluster IX of part 1. The 4s orbitals of the Ni_p atoms show a reduced occupancy in the tetranuclear dianion II, from 1.185 to 0.621. Since the electrons lost by the Ni_p atoms are nearly coincident with those transferred to the apical $Ni(CO)_3$ group, the formation of the cluster II can be described in terms of charge transfer between the frontier orbitals of the two fragments: a totally symmetric combination of 4s orbitals on Ni_p atoms (the HOMO of $(Ni_3(CO)_3(\mu\text{-}CO)_3)^{2-}$) and the 4s orbital on the Ni_a atom (the LUMO of the $Ni(CO)_3$ group).

As one passes from neutral to anionic forms, the back-donation into the π^* CO orbitals increases (see Table II). This is true for all the three types of ligands present in the clusters I and II. However, the T_a carbonyls seem to behave quite differently because their $N_{\pi*}$ index is markedly higher than the corresponding index of the T_p carbonyls. A plausible interpretation of this effect is that the π-accepting ability of the T_p groups is reduced because these are in competition with the bridged groups B_p.

The third tetranuclear cluster considered here is the monohydride derivative III. Due to steric requirements the hydrogen atom is supposed to lie below the Ni_3 plane (see Figure 1). The ground-state configuration of the cluster is identical with that of the dianion II (see Table I) but is more stable by 80 kcal·mol^{-1}. In part 1 we found that in the case of mono- and dinuclear species the formation of the hydride derivative may be rationalized in terms of direct interaction between the incoming proton and the negative charge cloud associated with the 4s nickel orbitals. In this respect the hydride III is somewhat different from the cases encountered in part 1, because the proton cannot interact with the Ni_a atom, where the negative charge is highly localized. The results of Table II show that the proton–cluster interaction produces a decrease of negative charge on all the atoms of the basal plane and, at the same time, an electron removal of 0.54 electron from the apical $Ni(CO)_3$ group. Therefore, the formation of a Ni–H bond is also due to an electron flow from the 4s nickel orbitals toward the hydrogen 1s orbital, with the difference that this process is less favored, requiring an important charge redistribution within the cluster. This is reflected in the reaction energy values: the proton attachment to a triangle of nickel atoms with low and diffuse negative charge is characterized by a lower energy gain (80 kcal·mol^{-1}) compared with the case of a single nickel atom (168 kcal·mol^{-1}) or a pair of nickel atoms (172.0 kcal·mol^{-1}) having strong localized negative charge (see part 1).

Pentanuclear Clusters. The two pentanuclear forms IV and V (see Figure 1) are composed of a planar $Ni_3(CO)_3(\mu\text{-}CO)_3$ group and two axial $Ni(CO)_3$ groups. The two apical groups

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(15) See, for instance, ref 5g and references therein.

Table III. Electronic Distribution in Pentanuclear Nickel Clusters[a]

		$Ni_5(CO)_9(\mu\text{-}CO)_3$	$(Ni_5(CO)_9(\mu\text{-}CO)_3)^{2-}$
Ni_p	4s	0.4630	0.9669
	4p	0.0922	0.0893
	3d	9.3894	9.2697
	q	0.0554	−0.3259
Ni_a	4s	0.2165	0.2846
	4p	0.0827	0.0809
	3d	9.5072	9.4341
	q	0.1937	0.2004
T_p	N_σ	5.9399	5.9450
	N_π	3.9959	3.9944
	$N_{\pi*}$	0.0540	0.0900
	q_C	0.1448	0.2209
	q_O	−0.1347	−0.2502
T_a	N_σ	5.9599	5.9826
	N_π	3.9940	3.9942
	$N_{\pi*}$	0.1144	0.1452
	q_C	0.1046	0.1268
	q_O	−0.1749	−0.2502
B_p	N_σ	5.8324	5.9905
	N_π	3.9663	3.9674
	$N_{\pi*}$	0.2498	0.2316
	q_C	0.1361	0.1503
	q_O	−0.1847	−0.3399

[a] See part 1 for definitions of N_σ, N_π, and $N_{\pi*}$. Nickel atoms and carbonyls are identified as in Figure 1.

are in an arrangement of symmetry C_{3v}. The small distortion from this symmetry observed in the solid state[12b] is therefore ignored.

The ground-state configuration ($21a_1$, $6a_2$, $58e$) of the neutral cluster IV ($D = 601.5$ kcal·mol^{-1}) can be easily derived by summing up the MO occupancies of the two separated fragments (the cluster I and the group $Ni(CO)_3$) (see Table I). For the corresponding anionic cluster V, the ground state has the two extra electrons associated with a totally symmetric MO, in agreement with all the previous cases. Its stability is lowered by 82 kcal·mol^{-1} with respect to the neutral form. Since the two apical $Ni(CO)_3$ groups have very similar charge distribution, for brevity only the mean values are reported in Table III. From these results it is apparent that the two axial groups in the neutral complex carry a very small negative charge, being similar to the unique apical group of the neutral tetranuclear species. On the other hand, when the anionic form V is considered, the Lewis acid character of the two axial groups seems to be strongly reduced with respect to the corresponding tetranuclear case. In fact, the total negative charge shared by the two $Ni(CO)_3$ groups is equal to 0.72 electron, the remaining charge being associated with atomic centers of the equatorial plane. In particular, going from the neutral to the anionic cluster, a large charge accumulation occurs on Ni_p atoms and B_p ligands. The hypothetical reaction $(Ni_4(CO)_6(\mu\text{-}CO)_3)^{2-} + Ni(CO)_3$ leading to the cluster V can be considered as a base–acid reaction similar to that producing the monohydride species.

The B_p ligands, despite their whole negative charge, have a weaker π-accepting and σ-donating ability compared to that of the corresponding B_p ligands of the neutral form IV. This confirms the results of part 1, where it was found that the negative charge accumulation on the carbonyls, and in particular on the oxygen atoms, cannot be assumed as a measure of the metal–ligand back-donation.

Hexanuclear Clusters. The molecular structure of the hexanuclear clusters reported in Figure 1 belongs to the D_{3d} point group. The clusters are formed by two $Ni_3(CO)_3(\mu\text{-}CO)_3$ fragments, with the metal atoms at the vertices of a trigonal antiprism.[13] The data of Table I show that the neutral form VI has a dissociation energy of 681.1 kcal·mol^{-1}, while the corresponding value of the dianion is 626.8 kcal·mol^{-1}. Also in this case the anion VII is formed by adding the two electrons to a totally symmetric MO that is delocalized over all the six metallic centers. Each of them increases its negative charge by 0.164 electron. This means that one of the two electrons is associated with the metal centers while the other is delocalized over the ligands, particularly the B_u and B_l carbonyls (see Figure 1).

Table IV. Electronic Distribution in Hexanuclear Nickel Clusters[a]

		$Ni_6(CO)_6(\mu\text{-}CO)_6$	$(Ni_6(CO)_6(\mu\text{-}CO)_6)^{2-}$
Ni	4s	0.5006	0.7342
	4p	0.0922	0.0903
	3d	9.3750	9.3073
	q	0.0321	−0.1318
T	3σ	1.9907	1.9918
	4σ	1.9637	1.9694
	1π	3.9944	3.9934
	5σ	1.9000	1.9219
	2π	0.0982	0.1313
	6σ	0.0273	0.0332
	q_C	0.1713	0.1999
	q_O	−0.1456	−0.2410
B	3σ	1.9824	1.9854
	4σ	1.9607	1.9761
	1π	3.9785	3.9773
	5σ	1.9172	1.9701
	2π	0.1859	0.1962
	6σ	0.0318	0.0541
	q_C	0.1361	0.1448
	q_O	−0.1927	−0.3041

[a] Nickel atoms and carbonyls are identified as in Figure 1.

In Table IV, the individual occupation numbers of the valence MO's of the coordinated CO are reported to show the role of the σ^* MO. The contribution of this orbital does not change the classic qualitative description of the donation–back-donation mechanism. The terminal carbonyls in neutral and anionic clusters are better σ-donors and poorer π-acceptors than the bridged ones, even though in certain cases the differences are too small to be considered chemically meaningful.

3. Cluster Stability and Intramolecular Interactions

Let us consider now the trend in stability of the nickel carbonyl clusters investigated in this work and in part 1 (Table V). As expected, the atomization and dissociation energies increase in a regular way with increase of the cluster size. A model of the cluster-growth process can be represented by a reaction occurring between a cluster, a nickel atom, and a suitable number of free CO molecules (see Table VI). In this picture, all the clusters are stable with respect to their precursor system, with reaction energies falling into the range 80–165 kcal·mol^{-1}. It must be observed that, in the case of clusters of high nuclearity, the growth of the anionic species is accompanied by an energy gain larger than that of the corresponding process involving neutral species. In other words, the stability of the anionic clusters approaches that of the neutral ones as the nuclearity increases. In fact, the differences in stability between neutral and anionic forms (see Table V) are nearly halved in going from small to hexanuclear species. An explanation of this effect may be easily found in the relatively high electron affinity of a molecular system of large size, containing groups of delocalized electrons. If the Koopmans theorem is considered as approximately valid for ionization or electron attachment processes involving delocalized orbitals (i.e. with small electronic relaxation energy), then the trend in cluster stability may be correlated with the variation in electron affinity of the neutral clusters and the ionization potential of the anionic clusters. Table V shows that this view is consistent, despite the fact that the computed

Table V. Stability of Nickel Carbonyl Clusters: Energies of HOMO and LUMO

cluster	atomization energy,[a] kcal·mol^{-1}	dissociation energy, kcal·mol^{-1}	HOMO energy, eV	LUMO energy, eV
$Ni(CO)_4$ (A)	1147.9	142.2		
$(Ni(CO)_3)^{2-}$ (B)	759.4	5.2		
$Ni_2(CO)_6$ (C)	1783.8	275.5		8.26
$(Ni_2(CO)_6)^{2-}$ (D)	1678.8	170.5 (105.0)[b]	4.48	
$Ni_3(CO)_3(\mu\text{-}CO)_3$ (E)	1939.1	430.9		8.85
$(Ni_3(CO)_3(\mu\text{-}CO)_3)^{2-}$ (F)	1819.4	311.2 (119.7)	4.34	
$Ni_4(CO)_6(\mu\text{-}CO)_3$ (G)	2780.6	518.2		8.19
$(Ni_4(CO)_6(\mu\text{-}CO)_3)^{2-}$ (H)	2683.0	420.6 (97.6)	3.65	
$Ni_5(CO)_9(\mu\text{-}CO)_3$ (I)	3618.1	601.5		7.87
$(Ni_5(CO)_9(\mu\text{-}CO)_3)^{2-}$ (L)	3552.9	519.5 (82.0)	2.92	
$Ni_6(CO)_6(\mu\text{-}CO)_6$ (M)	3697.5	681.1		7.75
$(Ni_6(CO)_6(\mu\text{-}CO)_6)^{2-}$ (N)	3642.3	625.8 (55.3)	2.74	

[a] Atomization energies are defned as $-(E_{Ni_n(CO)_m} - nE_{Ni} - mE_C - mE_O)$. E_{Ni}, E_C, and E_O are the energies of the free atoms in their ground valence configuration. [b] Difference in stability between neutral and corresponding anionic cluster.

Table VI. Energy Changes Occurring in the Cluster-Growing Reaction[a]

$$(Ni_x(CO)_y)^{n-} + Ni + (z - y)CO \rightarrow (Ni_{x+1}(CO)_z)^{n-}$$

clusters	x	y	z	n	ΔE, kcal·mol^{-1}
A → C	1	4	6	0	−133.1
B → D	1	3	6	2	−165.1
C → E	2	6	6	0	−155.3
D → F	2	6	6	2	−140.6
E → G	3	6	9	0	−87.2
F → H	3	6	9	2	−109.4
G → I	4	9	12	0	−83.3
H → L	4	9	12	2	−115.6
I → M	5	12	12	0	−79.4
L → N	5	12	12	2	−89.3

[a] The clusters are identified with the lettering of Table V.

Table VII. Energy Changes Occurring in the Reaction Producing Clusters of Lower Nuclearity[a]

$$(Ni_x(CO)_y)^{2-} + (4 - z)CO \rightarrow (Ni_{x-1}(CO)_{y-z})^{2-} + Ni(CO)_4$$

clusters	x	y	z	ΔE, kcal·mol^{-1}
N → L	6	12	0	−52.9
L → H	5	12	3	−26.6
H → F	4	9	3	−32.8
F → D	3	6	0	−1.6
D → B	2	6	3	22.9

[a] The clusters are identified with the lettering of Table V.

HOMO and LUMO energies are not completely meaningful from a physical viewpoint.

Finally, we wish to briefly discuss the behavior of the nickel carbonyl clusters with respect to the reaction producing clusters of lower nuclearity. This point is of some interest because it is experimentally well-known[12a,c] that the hexanuclear cluster VII reacts with carbon monoxide to produce the pentanuclear cluster V and $Ni(CO)_4$. This kind of reaction can in principle be considered as applicable to clusters of any nuclearity:

$$(Ni_x(CO)_y)^{n-} + (4 - z)CO \rightarrow (Ni_{x-1}(CO)_{y-z})^{n-} + Ni(CO)_4$$

In Table VII are reported the reaction energies for all the anionic clusters considered in the present work and in part 1. The highest energy gain is associated with the production of the pentanuclear species. The reaction seems less and less favored as the cluster size decreases. Typically, the mononuclear species $(Ni(CO)_3)^{2-}$ is unlikely to be obtainable by the decomposition of the dinuclear species.

4. Metal-Metal, Metal-Ligand, and Ligand-Ligand Interactions

Usually two methods are employed to evaluate theoretically the bond strength within a molecule. The first is based on Mulliken overlap population indexes[16] while the second requires partitioning of the total molecular energy into one- and many-center contributions. As an alternative to the Mulliken analysis, hardly applicable in the framework of the ZDO methods, Wiberg[17] suggested that the interatomic energies are proportional to the sum of squared nondiagonal elements of the bond order matrix. Being always positive, the Wiberg indexes are unable to describe repulsive interatomic interactions. Examples of the use of Wiberg's indexes as an estimate of the metal–metal bond strength in dinuclear carbonyl complexes have been reported.[18] In order to describe the intramolecular interactions, the energy partitioning is a better tool, especially because the INDO energy may be written exactly as $E_T = \sum_A E_A + \sum'_{AB} E_{AB}$. The term $\sum_A E_A$ does not equal the sum of the energies of the separated atoms because the valence configurations in the molecule are different from the reference configurations of the free atomic state. As a consequence, the sum $\sum'_{AB} E_{AB}$ is different from the atomization energy. Nevertheless, these quantities can be assumed as a qualitative measure of the two-atom interaction energy.

For the sake of simplicity, we report in the following only the values of the metal–metal (M–M) interaction, the value of the interaction between a metal and a carbonyl group directly bonded to it (M–L: M–T or M–B), the corresponding interaction between non directly bonded groups (M–L′: M–T′ or M–B′), and the ligand–ligand interaction L–L′.

Further simplification is achieved by reporting under M–M, M–L, M–L′, and L–L′ the sum of the contributions of the symmetry-related groups.

The above analysis has been performed for clusters containing three to six nickel atoms. For space saving, we report in Tables VIII and IX the results of only the penta- and hexanuclear species. The first observation is that the M–M interaction within the triangle $Ni_3(CO)_3(\mu\text{-}CO)_3$ has repulsive character (5.1 and 8.5 kcal·mol^{-1} in V and VII, respectively). The in-plane repulsive interactions are not compensated by the small and attractive indirect M–L′ interactions with carbonyl groups belonging to the Ni_3 plane (−0.2 and −2.2 kcal·mol^{-1} in V and VII, respectively). Therefore, the stability of the $Ni_3(CO)_3(\mu\text{-}CO)_3$ fragments may be mainly attributed to the bonding L–L′ in-plane interactions, which amount to about −14 kcal·mol^{-1} in both clusters.

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Table VIII. Intramolecular Interactions in $(Ni_5(CO)_9(\mu\text{-}CO)_3)^{2-}$ [a]

	metal-carbonyls		
metal-metal	directly bonded	nonbonded	ligand-ligand
Ni_p-Ni_p: 5.1	Ni_p-T_p: −113.4	Ni_p-T_p': −6.9	T_p-T_p: 0.1
Ni_p-(Ni_{aa} + Ni_{ab}): −68.1	Ni_p-B_p: −103.2	Ni_p-B_p': 6.1	T_p-B_p: −14.2
Ni_{aa}-Ni_{ab}: 2.2	Ni_{aa}-T_{aa} = Ni_{ab}-T_{ab}: −102.7	Ni_p-(T_{aa} + T_{ab}): 7.9	T_p-(T_{aa} + T_{ab}): 1.7
		(Ni_{aa} + Ni_{ab})-T_p: 1.1	B_p-B_p: 3.5
		(Ni_{aa} + Ni_{ab})-B_p: −46.9	B_p-(T_{aa} + T_{ab}): 22.0
		Ni_{aa}-T_{ab} = Ni_{ab}-T_{aa}: −3.1	T_{aa}-T_{aa} = T_{ab}-T_{ab}: −9.9
			T_{aa}-T_{ab}: 4.5
Ni-Ni: −60.8	Ni-L: −422.0	Ni-L: −44.9	L-L: −2.2

[a] Nickel atoms and carbonyls are identified as in Figure 1. Interaction energies are in kcal·mol^{-1}.

Table IX. Intramolecular Interactions in $(Ni_6(CO)_6(\mu\text{-}CO)_6)^{2-}$ [a]

	metal-carbonyls		
metal-metal	directly bonded	nonbonded	ligand-ligand
Ni_u-Ni_u = Ni_l-Ni_l: 8.5	Ni_u-T_u = Ni_l-T_l: −135.6	Ni_u-T_u' = Ni_l-T_l': −1.3	T_u-T_u = T_l-T_l: −0.1
Ni_u-Ni_l: −22.9	Ni_u-B_u = Ni_l-B_l: −136.6	Ni_u-B_u' = Ni_l-B_l': −0.9	T_u-B_u = T_l-B_l: −13.3
		Ni_u-T_l = Ni_l-T_u: −1.0	T_u-T_l: 1.3
		Ni_u-B_l = Ni_l-B_u: −0.1	T_u-B_l = T_l-B_u: 1.3
			B_u-B_u = B_l-B_l: 2.7
			B_u-B_l: 10.0
Ni-Ni: −5.9	Ni-L: −544.4	Ni-L′: −6.6	L-L: −8.8

[a] Nickel atoms and carbonyls are identified as in Figure 1. Interaction energies are in kcal·mol^{-1}.

The out-of-plane interactions are significantly different for the penta- and hexanuclear clusters. In the former, a quite strong M–M bond is formed between the in-plane and the apical nickel atoms (−68.1 kcal·mol^{-1}), while in the hexanuclear species the corresponding value is only −22.9 kcal·mol^{-1}. Even the indirect M–L′ out-of-plane bonding interactions are stronger in the cluster V than in the cluster VII. This means that the bond between the two Ni_3 fragments of the cluster VII is weaker than that existing between the unique Ni_3 fragment and the two $Ni(CO)_3$ groups in the cluster V. The hexanuclear species VII is characterized by a greater dissociation energy only because the direct M–L bonding interactions are stronger than in the pentanuclear cluster V.

The trend in sign and magnitude of the interatomic interactions is confirmed by the results relative to $(Ni_3(CO)_6)^{2-}$, $(Ni_3(CO)_3(\mu\text{-}CO)_3)^{2-}$, and $(Ni_4(CO)_6(\mu\text{-}CO)_3)^{2-}$. For these compounds the M–M interactions between the in-plane atoms amount to 24.6, 20.4, and 18.5 kcal·mol^{-1}, respectively. For the tetranuclear cluster the value of −21.4 kcal·mol^{-1} for the interaction Ni_p/Ni_a confirms the result already presented for the pentanuclear cluster V.

Important considerations may be derived from the above results. First of all, for some coordination geometries the stability of a metal polyhedron is mainly due to the possibility of fitting it into the vacancies left in a regular arrangement of carbonyls. This arrangement is characterized by an important internal stability, which is not due, of course, to the ability of the CO molecules to form stable clusters but only to the electrostatic stabilization induced by coordination to metal centers. Moreover, the stabilization due to the ligand groups may not be assumed as a general rule applicable to every cluster, since we have shown that it is a peculiar feature of a $Ni_3(CO)_3(\mu\text{-}CO)_3$ fragment.

The second consideration is that our results predict a repulsive energy between pairs of metal atoms separated by short distances. This is the case for the $Ni_3(CO)_3(\mu\text{-}CO)_3$ basal fragment, where the Ni–Ni internuclear separation, 2.36 Å, is shorter than the nearest-neighbor contact in metallic nickel (2.50 Å). On the other hand, the attractive but relatively weak interactions found between in-plane and apical metal atoms occur for a larger Ni–Ni separation (about 2.80 Å in both V and VI). This is in evident disagreement with the classical idea that a metal–metal bond is said to exist only for short distances. Our results parallel the situation found by Heijser et al.[6] in $Mn_2(CO)_{10}$ and $Fe_2(CO)_6(\mu\text{-}CO)_3$ complexes. In fact, the existence of a real metal–metal bond is found in $Mn_2(CO)_{10}$, where the Mn–Mn bond length, 2.93 Å, is much larger than the corresponding value for the bulk metal (2.74 Å). In contrast, the conclusion that no metal–metal bond is present in the dinuclear iron complex holds for a Fe–Fe distance of 2.523 Å, nearly coincident with the bulk-metal value (2.52 Å).

On the basis of these results, the effect of the bridging carbonyls seems therefore that of forcing the orbitals of the metal centers to interact strongly with those of the CO ligands, so that only a weak metal–metal bond can be formed. As pointed out by Hoffmann,[19] the donor orbitals of the CO bridging groups are usually quite low in energy with respect to the acceptor orbitals of the metal atoms. The consequence is that the resulting low-energy orbital has a character more similar to that of the CO orbitals and therefore "the bonds are mostly on the bridging groups with slight metal character".[19] Finally, our model does not fit the results of a simple MO scheme[20] proposed some years ago for the complex $(M_2Ni_3(CO)_{13}(\mu\text{-}CO)_3)^{2-}$. This qualitative treatment assigns a localized electron pair to short M–M bonds with high bonding character and a much less important role to delocalized electron pairs between metal atoms separated by long distances, while we have found that important bonding contributions occur just between Ni_p and Ni_a atoms and between carbonyls not directly bonded. In both cases a description in terms of localized electron pairs is clearly unapplicable.

5. Relations to Other Works and Conclusions

The results reported here predict that the neutral forms of the nickel carbonyl clusters are more stable than the corresponding anionic forms, even in the case of clusters of relatively high nuclearity. As already pointed out in part 1, the fact that experimentally only negatively charged clusters, containing

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only carbonyl ligands, have been isolated is not due to energetic factors related to the electronic structure of the cluster itself but more probably to extra stabilization supplied by the solvation sphere or by the ionic lattice in the solid state. The anionic clusters gain in stability more than the neutral ones as the nuclearity increases, and this is probably the reason anionic clusters of only relatively high nuclearity have been successfully isolated.

The results concerning the two-atom contributions to the cluster stability are to be compared with other suggestions made on the basis of different approaches. In the review paper of Connor,[10] the thermochemical data for a series of iron and cobalt carbonyl clusters were analyzed and relations between the strength of different bonds within the cluster have been established. These relations, assumed to be valid also for other transition-metal clusters, may be summarized as follows: (a) the strength of the unique M–T bond and the sum of the two M–B bond strengths are similar; (b) the mean value of the energy of the M–L bond (L = T, B) is independent of the nuclearity; (c) the empirical relation M–M = 0.68(M–T) is assumed as approximately valid.

The experimental data available for nickel clusters are insufficient to obtain a set of relations similar to those presented above. Nevertheless, from the trend observed in ref 10, bond energy values for nickel compounds may be estimated to be as follows: M–T, 30–40 kcal·mol^{-1}; M–B, 15–20 kcal·mol^{-1}; M–M, 20–27 kcal·mol^{-1}. On the basis of the results of Table VIII (and other results not reported here for brevity) the M–T and M–B values fall into ranges wider than those reported above and are dependent on the molecular charge and structure. Furthermore, our computed values for the M–M contributions are definitely smaller than those obtainable by extrapolation to the nickel case of the data of ref 10.

Another attempt to evaluate the M–M energy interaction has been made by Housecroft et al.[9] In this case the metal–metal interaction is smaller than in Connor's treatment but the qualitative description of the bond remains unaltered. In the approach of ref 9, it must be noted that an interaction potential of the type $E(\text{M–M}) = AR_{\text{M-M}}^{-k}$, where A and k are determined from length and strength of the bonds in the bulk metal, cannot be transferred to a molecular cluster without significant modifications. In particular, the analytical form of this potential is such that the contribution of the metal–metal interaction is always of bonding character, while when a more flexible potential is used (as is the INDO one, even if approximate), such terms may be either attractive or repulsive. Finally, the model of ref 9 seems to neglect every energy variation accompanying changes in coordination mode and valence configuration of the metal atoms. We have shown, on the contrary, that M–M interactions are strongly influenced by the particular geometric and electronic situation of each metal atom.

We note that the results of the present theoretical investigation are not in disagreement with those of other theoretical investigations,[5,6] in which the contribution of the direct M–M interaction is found to be much less important than that required by the usual qualitative arguments.

Moreover, in very recent X-ray diffraction studies, the presence of a strong metal–metal bond has not been confirmed for several cluster compounds of nickel,[21] cobalt,[22] and osmium.[23]

All these aspects considered, we feel that a more careful analysis of the commonly accepted concepts used in the description of the bonds within the clusters is in order.

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Notes

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Molecular Structure of (μ-Oxo)bis[oxobis(8-quinolinolato)vanadium(V)]

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The structural chemistry of vanadium(V), like that of the other early transition metals in higher oxidation state, is dominated by the presence of oxo complexes. However, oxo-bridged V(V) species are rare compared to those of Ti(IV), Mo(V), and Mo(VI), where binuclear species are found bridged by one or two oxo or oxygen ligands.[1,2]

Vanadium(V) reacts with 8-quinolinol (HQ) to give a 1:2 water-insoluble complex in weakly acidic media. It has been known that the black solution of this complex dissolved in organic solvents causes a pronounced color change in the presence of various types of substances by forming the corresponding monomeric derivatives.[3] Among them, the structures have been established crystallographically for a red isopropyl ester[4] and yellow sodium[5] and tetrabutylammonium[5,6] salts. On the other hand, for the black complex dried at about 130 °C, the conflicting formulas of $V_2O_3Q_4$[7,8] and $VO(OH)Q_2$[9-11] have been assigned from the elemental analysis. Extensive studies involving the black complex have been carried out with the monomeric composition assumed for this complex.[3,9-19]

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