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Nickel Carbonyl Clusters in Molecular Beams: A Reinterpretation of the Results Which Gives Circumstantial Evidence for a Face-Capping Cluster-Growth Sequence

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Abstract: Nickel cluster ions, size selected by quadrupole mass spectrometry, have been reacted with carbon monoxide to yield in the gas phase nickel carbonyl clusters of the type $Ni_n(CO)_k{}^+$ and $Ni_nC(CO)_l{}^+$, where n ranges from 1 to 13 and k and l vary as a function of cluster size n. Fayet et al. have interpreted these results using EHMO calculations on bare nickel clusters previously reported by Lauher. A reinterpretation of these results in terms of the *polyhedral skeletal electron pair theory* not only provides a more complete account of the stoichiometries of these clusters but also provides strong circumstantial evidence for a face-capping growth sequence based on a pentagonal bipyramidal Ni_7 cluster.

I. Introduction

In some recent very elegant molecular beam experiments Fayet, McGlinchey, and Wöste have mass selected individual Ni_n (n = 1–20) cluster ions and studied their reactions with carbon monoxide.[1] A range of cluster ions was formed with varying numbers of carbonyl ligands and the following sets of primary reactions were identified:

$$Ni_n{}^+ + k\text{CO} \rightarrow Ni_n(CO)_k{}^+$$

$$Ni_n{}^+ + l\text{CO} \rightarrow Ni_nC(CO)_l{}^+$$

$$Ni_n{}^+ + m\text{CO} \rightarrow Ni_{n-1}(CO)_m{}^+$$

The limiting number of carbonyls for each of these reactions as a function of the number of metal atoms is summarized in Table I. These have been related to the closed-shell requirements of the related neutral molecular clusters $Ni_n(CO)_k$ and $Ni_nC(CO)_l$. The closed-shell requirements of the neutral clusters were evaluated by reference to metal carbonyl clusters that had been structurally characterized and to the molecular orbital calculations reported for bare metal clusters by Lauher.[2] For example, $Ni_4(CO)_{10}$, which has a total of 60 valence electrons, was assigned a tetrahedral structure by analogy with the isoelectronic clusters $M_4(CO)_{12}$ (M = Co, Rh, or Ir). Similarly $Ni_5(CO)_{12}$ and $Ni_6(CO)_{13}$ were assigned square-pyramidal (74 cluster valence electrons) and octahedral (86 cluster valence electrons) structures, respectively. It was proposed that $Ni_7(CO)_{15}$ could have either a pentagonal-bipyramidal or capped-octahedral structure. For clusters with more than eight nickel atoms the observed stoichiometries were at variance with those predicted for deltahedral structures and Fayet et al.[1] suggested that "as one goes to larger clusters, the metal cluster/boron analogy begins to break down, and the metal complexes (sic) are perhaps better described as metal crystallites with a peripheral coating of ligands".

II. Reinterpretation

It was established many years ago[3] that the analogy between metal carbonyl clusters and borane polyhedra results because both sets of molecules have the same number of inaccessible molecular orbitals that cannot be utilized for either metal–metal or metal–ligand bonding. The number of these orbitals depends on the skeletal geometry, and this obviates the necessity of performing detailed molecular orbital calculations on specific bare metal clusters.[4] For example, main group and transition-metal deltahedral clusters are both characterized by $2n - 1$ (n = number of metal atoms) inaccessible molecular orbitals and consequently are characterized by $4n + 2$ $(2(4n - (2n - 1))$ and $14n + 2$ $(2(9n - (2n - 1))$ cluster valence electrons, respectively. The relevant deltahedral structures are illustrated on the left-hand side of Figure 1.[5] These principles can be applied also to *nido*- and *arachno*-deltahedral structures that are characterized by $2n - 2$ and $2n - 3$ inaccessible molecular orbitals.[5] The molecular orbital calculations of Lauher[2] on bare metal clusters have provided a justification for these generalizations.

Table I. Limiting Stoichiometries of Clusters Formed between Nickel Cluster Cations and Carbon Monoxide in the Molecular Beam Experiments Described in Reference 1

	no. of valence electrons		predicted structure
$Ni_4(CO)_{10}$	60	$15n$	tetrahedral
$Ni_5(CO)_{12}$	74	$14n + 4$	square pyramid
$Ni_6(CO)_{13}$	86	$14n + 2$	octahedral
$Ni_7(CO)_{15}$	100	$14n + 2$	pentagonal bipyramid
$Ni_8(CO)_{16}$	112	$14n$	capped pentagonal bipyramid
$Ni_9(CO)_{17}$	124	$14n - 2$	bicapped pentagonal bipyramid
$Ni_{10}(CO)_{18}$	136	$14n - 4$	tricapped pentagonal bipyramid
$Ni_{11}(CO)_{19}$	148	$14n - 6$	tetracapped pentagonal bipyramid
$Ni_{12}(CO)_{20}$	160	$14n - 8$	pentacapped pentagonal bipyramid
$Ni_{13}(CO)_{20}$	170	$14(n - 1) + 2$	centered icosahedron

An additional important structural generalization in cluster chemistry is the *capping principle*,[6] which states that the number of skeletal molecular orbitals of a cluster remains unaffected when capping atoms are added. Families of structures based on the capping principle have been confirmed in particular by the X-ray crystallographic studies of McPartlin.[7] These capped structures are always associated with increments in the cluster valence electron counts of 12.[8]

These simple principles derived from the *polyhedral skeletal electron pair theory*[9] provide an illuminating interpretation of the molecular beam experiments of Fayet et al.[1] It is apparent from Table I that $Ni_6(CO)_{13}$ and $Ni_7(CO)_{15}$ both have $14n + 2$ cluster valence electrons, but the subsequent clusters with 8 to 12 metal atoms deviate from the closed-shell requirements for deltahedral clusters. These members of the series do, however, involve successive increments of 12 in the total number of valence electrons. This pattern when taken as a whole suggests the successive addition of five caps to the parent structure. Since the parent structure

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(1) Fayet, M.; McGlinchey, M. J.; Wöste, L. H. *J. Am. Chem. Soc.* **1987**, *109*, 1733.

(2) Lauher, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 5305.

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(7) McPartlin, M. *Polyhedron* **1984**, *3*, 1279.

(8) McPartlin, M.; Mingos, D. M. P. *Polyhedron* **1984**, *3*, 1321.

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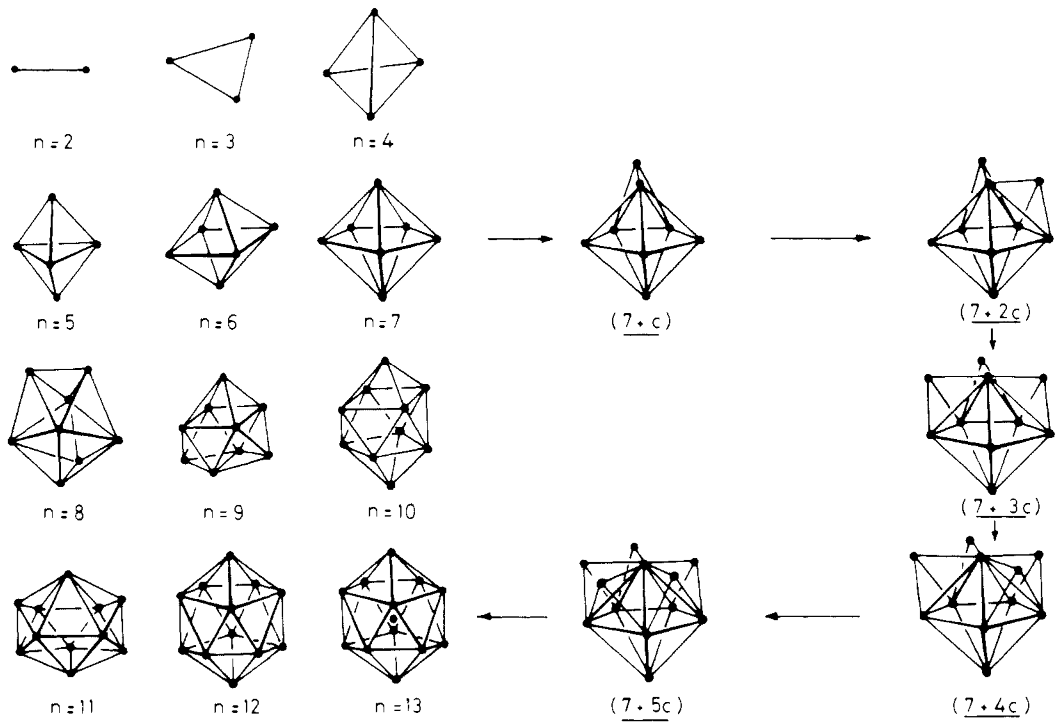

Figure 1. On the left-hand side the deltahedral structures with $n = 4$–12 are illustrated together with the centered icosahedron with $n = 13$. On the right-hand side capped structures connecting the pentagonal bipyramid and the centered icosahedron are illustrated.

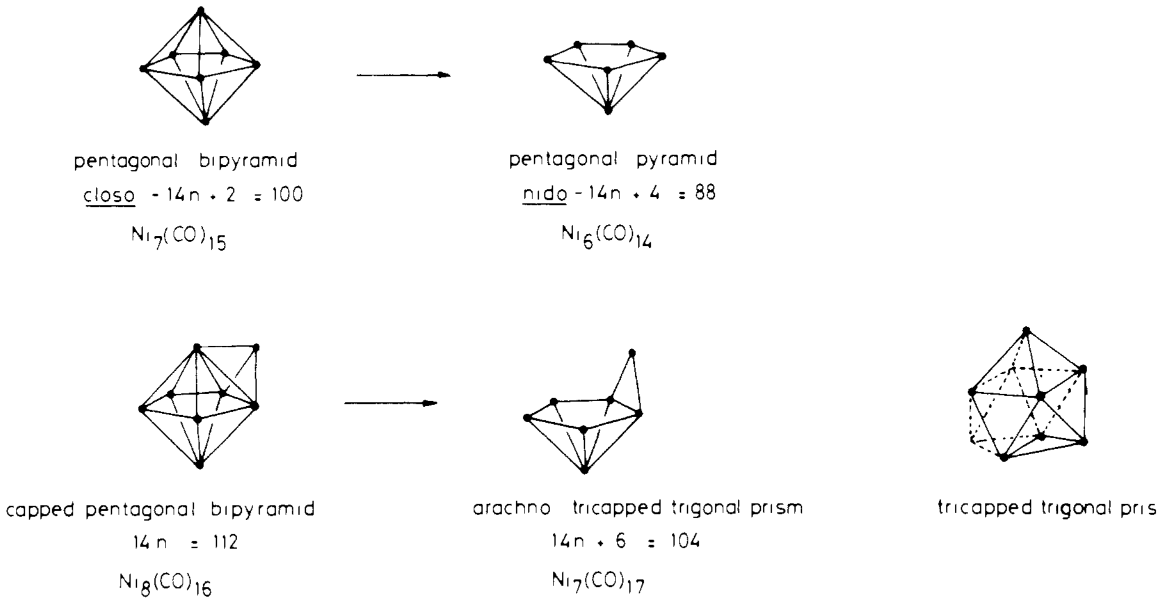

Figure 2. Possible fragmentation process based on a pentagonal bipyramid and a capped pentagonal bipyramid. In each case an apical atom of the pentagonal-bipyramidal moiety is removed and leads in the first instance to a nido pentagonal pyramid and in the second case an arachno tricapped trigonal prism, which can also be described as an edge bridged pentagonal prism. Capped structures based on this fragment can be generated by adding capping atoms to the five triangular faces in the lower half of the molecule.

has a cluster valence electron count consistent with a pentagonal bipyramid with 5-fold symmetry this pattern suggests the growth sequence illustrated on the right-hand side of Figure 1. The pentacapped pentagonal bipyramid (7 + 5c) in Figure 1 is geometrically ideally set up to form an icosahedron with an interstitial nickel atom by the addition of one more nickel atom (see Figure 1). According to the *polyhedral skeletal electron pair theory* this centered geometry should be associated with a total of 170 valence electrons, i.e. 14 × 12 + 2, because the interstitial atom stabilizes the basic molecular orbital pattern associated with an uncentered icosahedron and does not create any additional accessible molecular orbitals.[10] The limiting molecular species observed by Fayet et al.,[1] $Ni_{13}(CO)_{20}$, has just this electron count. Therefore, the pattern of molecular ions observed in these experiments provides strong circumstantial evidence for a cluster-growth sequence based on face capping of the pentagonal bipyramid. Such growth sequences have been proposed previously on the basis of theoretical calculations,[11] and this reinterpretation provides additional experimental support for these ideas.

Further support for this proposal comes from an examination of the growth sequence in the fragmentation reaction

$$Ni_n^+ + mCO \rightarrow Ni_{n-1}(CO)_m^+$$

The limiting stoichiometries of the ions observed in this process

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Table II. Limiting Stoichiometries of Clusters Formed in the Fragmentation Process $Ni_n^+ + mCO \rightarrow Ni_{n-1}(CO)_m^+$

	no. of valence electrons		predicted structure
$Ni_5(CO)_{11}$	72	$14n + 2$	trigonal bipyramid
$Ni_6(CO)_{14}$	88	$14n + 4$	pentagonal pyramid
$Ni_7(CO)_{17}$	104	$14n + 6$	arachno tricapped trigonal prism
$Ni_8(CO)_{18}$	116	$14n + 4$	capped arachno tricapped trigonal prism
$Ni_9(CO)_{19}$	128	$14n + 2$	bicapped arachno tricapped trigonal prism
$Ni_{10}(CO)_{20}$	140	$14n$	tricapped arachno tricapped trigonal prism
$Ni_{11}(CO)_{21}$	152	$14n - 2$	tetracapped arachno tricapped trigonal prism
$Ni_{12}(CO)_{22}$	164	$14n - 4$	pentacapped arachno tricapped trigonal prism

are summarized in Table II. The $Ni_6(CO)_{14}$ species has an electron count consistent with a nido structure ($14n + 4$) and could most readily be accounted for in terms of a pentagonal pyramid derived from the pentagonal bipyramid by the loss of an apical atom (see Figure 2). The next member in the series $Ni_7(CO)_{17}$ has an electron count consistent with an *arachno* electron count and a geometry based on a tricapped-trigonal prism with two adjacent vertices missing.[12] This structure that is illustrated in Figure 2 could also be generated from a capped pentagonal bipyramid by the loss of the highest connected apical vertex, i.e. the same vertex as that lost for the pentagonal bipyramid above. Interestingly, the next five members of the series given in Table II have limiting electron counts that represent an increment of 12 valence electrons for each metal atom. This, of course, again suggests a series of capped molecules based on the *arachno*-$Ni_7(CO)_{17}$ structure illustrated at the bottom of Figure 2. These could all be derived from the capped structures illustrated in Figure 1 by the removal of a highly connected nickel vertex. The important fact is that the fragmentation pattern reinforces the growth sequence based on a pentagonal bipyramid proposed above.

Face capping and polytetrahedral growth sequences[13] have also been proposed to account for experimental results derived from molecular beam and electron microscopy results on other cluster systems. For example, the lowest energy calculated Ar_8 and Ar_{14} clusters are a capped pentagonal bipyramid and a capped icosahedron, respectively.[14] Computed growth sequences for copper and gold clusters, where the metal–metal bonding interactions are largely isotropic, also result in polytetrahedral capped structures.[15]

In summary the *polyhedral skeletal electron pair theory* provides a consistent and unified account of the molecular beam experiments reported by Fayet el al.[1] and increases one's confidence for applying it to related molecular beam problems.

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Registry No. Ni, 7440-02-0; CO, 630-08-0.

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