

Interstitial nickel carbonyl clusters

Giuliano Longoni

Dipartimento di Chimica Fisica ed Inorganica, viale del Risorgimento 4,
40136 Bologna, Italy

Abstract - Systematic efforts to synthesize interstitial tridecanuclear clusters of general formula $[\text{Ni}_{12}(\text{CO})_n(\mu_{12}\text{-E})]^{2-}$, where E is either a different transition metal atom or a main group element of suitable size, led to isolation and characterization of a series of new nickel carbonyl clusters containing up to 44 metal atoms. Those containing main group elements, although not necessarily as interstitial atoms, systematically show icosahedral geometries, whereas those involving different transition metals as heteroatoms invariably present metal frameworks related to close-packed metal lattices. These structural differences are often to ascribe to a subtle interplay of electronic and steric factors.

Calculations on bare metal clusters systematically show that the most favorable geometries for an aggregate of twelve and thirteen metal atoms respectively are the non-centered and the centered icosahedron (ref. 1); Frameworks related to the metal close-packed lattices should become more favorable only with much higher nuclearities of the metal aggregates. Indeed, pseudo-alkaline metals such as gold and silver give rise to homo-metallic gold and bi-metallic silver-gold molecular clusters whose geometries invariably are based on either incomplete (e.g. $[\text{Au}_8\text{L}_8]^{3+}$ (ref. 2) and $\text{Au}_{11}\text{L}_7\text{I}_3$ (ref. 3)), or centered (e.g. $[\text{Au}_{13}\text{L}_{10}\text{Cl}]_2^{3+}$ (ref. 4)), or mono-, bi- and tri-dimensionally condensed icosahedra such as documented by the spectacular series of compounds isolated and characterized by Teo (ref. 5-8) (e.g. $[\text{Ag}_{12}\text{Au}_{13}\text{L}_{12}\text{Cl}_6]^{m+}$, $[\text{Ag}_{19}\text{Au}_{18}\text{L}_{12}\text{Br}_{11}]^{2+}$ and $\text{Ag}_{20}\text{Au}_{18}\text{L}_{12}\text{Cl}_{14}$) and Schmid (ref. 9,10).

In the field of transition metal carbonyl clusters the situation is less straightforward: thus, the overwhelming majority of the highly-condensed high-nuclearity clusters displays metal frames related either to the hexagonal or the face-centered cubic close packing (ref. 11, 12). The only notable exceptions are $[\text{Rh}_{12}\text{Sb}(\text{CO})_{27}]^{3-}$ (ref. 13) and $[\text{Pt}_{19}(\text{CO})_{22}]^{4-}$ (ref. 14), which display pseudo C_5 symmetry; however, while the metal framework of the former consists in a very distorted icosahedron centered by the unique antimony atom, the metal geometry of the latter may be described as deriving from two interpenetrating bicapped pentagonal prisms. The only other reported examples of icosahedral carbonyl clusters are the non-centered $[\text{Ni}_{10}(\text{AsMe})_2(\text{CO})_{18}]^{2-}$ and $[\text{Ni}_9(\text{AsPh})_3(\text{CO})_{15}]^{3-}$ (ref. 15), in which respectively two and three vertices of the icosahedron are constituted by AsR moieties.

Most of the cluster bonding theories agree in indicating 170 valence electrons as necessary in order to stabilize both a centered and a non-centered dodecanuclear polyhedron, regardless of its icosahedral, cuboctahedral or anticuboctahedral geometry (ref. 16-19). Therefore, the factors driving the metal aggregate to the choice of one of the above frameworks are rather ill-defined. In the attempt to gain some better understanding of this problem, we have undertaken systematic efforts to synthesize tridecanuclear carbonyl clusters of general formula $[\text{Ni}_{12}(\mu_{12}\text{-E})(\text{CO})_n]^{2-}$. The main reason for the above choice stems from the following considerations: first of all, it has been reported that the condensation of two $[\text{Ni}_6(\text{CO})_{12}]^{2-}$ units gives rise to the dodecanuclear $[\text{Ni}_{12}(\text{CO})_{21}\text{H}_{4-n}]^{n-}$ ($n=2,3,4$) clusters (ref. 20,21), whose geometry is based on the $3,6,3\text{-D}_{3h}$ stack of nickel atoms schematically represented in Figure 1a. It appeared conceivable that the central Ni_6 triangle of frequency 2 could formally derive from collapse of a central Ni_6 hexagon such as present in the icosahedral, cuboctahedral and anticuboctahedral polyhedra, respectively shown in Fig. 1b-d; the driving force for this transformation could originate from the tendency of the metal aggregate to achieve the highest possible metal connectivity, being not hindered by the steric request of the carbonyl

groups and/or the presence of an interstitial atom of suitable size to fill the cavities of the above polyhedra. Indeed, the metal frame schematized in Fig. 1a displays an average metal connectivity intermediate between those of the centered and non-centered dodecanuclear polyhedra of Fig. 1b-d. It is worth mentioning that cluster geometries corresponding to those shown in Fig. 1b and 1d are documented by the already cited $[\text{Rh}_{12}\text{Sb}(\text{CO})_{27}]^{3-}$ and $[\text{Rh}_{13}(\text{CO})_{24}\text{H}_{5-n}]^{n-}$ or $[\text{Rh}_{12}\text{Pt}(\text{CO})_{24}]^{4-}$ (ref. 22,23), respectively.

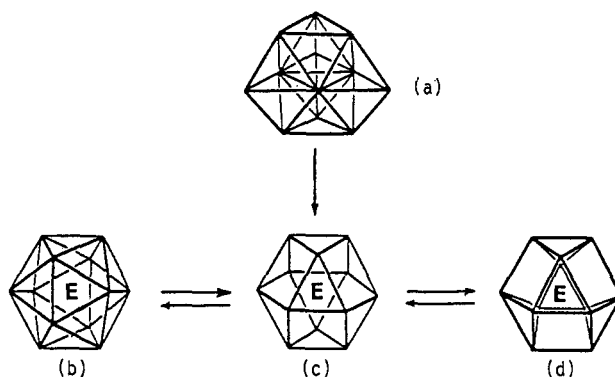


Fig. 1. The geometry of some selected dodecanuclear clusters: interconversion is readily obtained by shrinking or edge-stretching or layer twisting.

It appeared, therefore, possible to stabilize polyhedra 1b-d, rather than 1a, by performing the condensation of two $[\text{Ni}_6(\text{CO})_{12}]^{2-}$ moieties in conditions suitable to give rise to interstitial derivatives of general formula $[\text{Ni}_{12}(\mu_{12}\text{-E})(\text{CO})_n]^{2-}$, where the heteroatom E is either a different transition metal or a main group element of suitable size with the purpose to test their effect on cluster geometry. As a result of this investigation, we have isolated and characterized a series of new bimetallic Ni-Rh, Ni-Ir, Ni-Pd, Ni-Pt and hetero-metallic Ni-Ge, Ni-Sn and Ni-Sb carbonyl clusters. The compounds so far structurally characterized and of some relevance for the present discussion are collected in Table 1, together with previously known species already reported in the literature.

TABLE 1. Nickel carbonyl clusters containing a different transition metal atom or a main group element (other than carbon) as interstitial or pseudo-interstitial atom

E=transition metal	E=main group element
$[\text{Ni}_6\text{Rh}_5(\text{CO})_{21}]^{3-}$, (ref. 24)	$[\text{Ni}_{10}\text{Ge}(\text{CO})_{20}]^{2-}$, (ref. 25)
$[\text{Ni}_6\text{Ir}_3(\text{CO})_{17}]^{3-}$, (ref. 26)	$[\text{Ni}_{12}\text{Ge}(\text{CO})_{22}]^{2-}$, (ref. 25)
$[\text{Ni}_9\text{Pt}_3(\text{CO})_{21}\text{H}_{4-n}]^{n-}$, (ref. 27)	$[\text{Ni}_{12}\text{Sn}(\text{CO})_{22}]^{2-}$, (ref. 25)
$[\text{Ni}_6\text{Pt}_6(\text{CO})_{21}]^{4-}$, (ref. 28)	$[\text{Ni}_{13}\text{Sb}_2(\text{CO})_{24}]^{2-}$, (ref. 29)
$[\text{Ni}_{36}\text{Pt}_4(\text{CO})_{44}]^{6-}$, (ref. 28)	$[\text{Ni}_{13}\text{Sb}_2(\text{CO})_{24}]^{3-}$, (ref. 29)
$[\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}\text{H}_{6-n}]^{n-}$, (ref. 28,30)	

As shown in Table 1, no tridecanuclear cluster containing a different transition metal as heteroatom has yet been isolated; in spite of that, a significant trend seems to emerge. All the compounds collected in the left column of Table 1, which only involve transition metals, generally show metal frameworks related to close packed metal lattices. In particular, the $[\text{Ni}_{12-x}\text{Pt}_x(\text{CO})_{21}\text{H}_{4-n}]^{n-}$ derivatives adopt the metal geometry represented in Fig. 1a, whereas the $[\text{Ni}_6\text{Ir}_3(\text{CO})_{17}]^{3-}$ cluster represents a fragment of the above polyhedron, being based on a 3,3,3 stack of atoms with the three iridium atoms allocated at the vertices of the central triangle. The structures of the $[\text{Ni}_{36}\text{Pt}_4(\text{CO})_{44}]^{6-}$ and $[\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}\text{H}_{6-n}]^{n-}$ ($n=4,5,6$) clusters are models of the so-called "cherry crystallites" (ref. 31) respectively deriving from

an incomplete Ni_{36} tetrahedron of frequency 5 and a complete Ni_{38} octahedron of frequency 3 encapsulating a platinum kernel.

In contrast the nickel clusters collected in the right side of Table 1, and containing main group elements as heteroatoms, invariably present metal frameworks displaying pseudo C_5 symmetry. Thus, both the $[\text{Ni}_{12}\text{Ge}(\text{CO})_{22}]^{2-}$ and $[\text{Ni}_{12}(\text{CO})_{22}]^{2-}$ dianions show slightly distorted icosahedral arrangements of twelve nickel atoms interstitially lodging the unique germanium and tin atoms, as schematically shown in Fig. 1b; accordingly the $[\text{Ni}_{10}\text{Ge}(\text{CO})_{20}]^{2-}$ cluster presents a pentagonal antiprismatic geometry which formally and chemically derives from the above polyhedron by loss of two opposite vertices. A possible explanation for the choice of an icosahedral geometry by $[\text{Rh}_{12}\text{Sb}(\text{CO})_{27}]^{3-}$, rather than the anticuboctahedral packing chosen by $[\text{Rh}_{13}(\text{CO})_{24}\text{H}_{4-n}]^{n-}$, has been recently suggested by Mingos on the basis of EHM0 calculations on a $\text{Rh}_{13}\text{H}_{36}$ model (ref. 19); this also applies to the above derivatives.

Also the $[\text{Ni}_{13}\text{Sb}_2(\text{CO})_{24}]^{n-}$ ($n=2,3,4$) clusters contain icosahedral moieties: at difference with those previously described, these consist of $\text{Ni}_{10}\text{Sb}_2$ icosahedra encapsulating an unique nickel atom. The failure in encapsulating the antimony atom, which has a size comparable to that of tin, is probably to ascribe to its greater electronegativity which contrasts a positive polarization of the atom and the consequent shrinking, necessary in order to be lodged in an icosahedral cavity. The two antimony atoms are located on opposite vertices of the icosahedron and the whole $\text{Ni}_{10}\text{Sb}_2$ moiety may be considered to behave as a fully inorganic distibine bridge-binding two $\text{Ni}(\text{CO})_3$ fragments. These compounds, from one side, represent additional examples of the growing family of "cluster ligands" already documented by lower nuclearity Fe-P, Fe-As, Fe-Sb and Fe-Bi clusters such as for instance $[\text{HFe}_3(\text{CO})_9(\mu_3\text{-PFe}(\text{CO})_4)]^{2-}$ (ref. 32) and $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-SbFe}(\text{CO})_4)_2]^{2-}$ (ref. 33). On the other side, they are closely related to the $[\text{Ni}_{10}(\text{AsMe})_2(\text{CO})_{18}]^{2-}$ derivative, the major difference being the absence in the latter of an interstitial nickel atom. Once one considers the interstitial atom simply as a source of valence electrons, which is common practice in most cluster bonding theories, the Ni-Sb species contain from 8 to 10 valence electrons in excess with respect to the number thought necessary for an icosahedral cluster. Nevertheless, they show completely normal M-M interactions and, moreover, the individual molecular parameters are barely affected by the change in the number of valence electrons, as shown by a comparison between the structure of the di- and tri-anion. A further hint that tridecanuclear carbonyl clusters could accommodate more than 170 valence electrons stems from the results of the reaction of carbon monoxide with a quadrupole mass selected Ni_{13}^+ molecular beam (ref. 34). Indeed, these unexpectedly showed formation of $\text{Ni}_{13}(\text{CO})_{21}^+$ and $\text{Ni}_{13}(\text{CO})_{22}^+$ ions which had respectively 2 and 4 valence electrons in excess with respect to the more abundant electron-precise $\text{Ni}_{13}(\text{CO})_{20}^+$ ion. Even if the structure of these ions is unknown, their observation and, above all, the structures of the Ni-Sb clusters seem to imply that at least in an icosahedral cluster there are available low lying cluster orbitals which may become cluster valence orbitals depending on the nature of the interstitial atom.

Although at this stage it is rather unsafe to try to draw conclusions, particularly in view of our failure in synthesizing a wider set of clusters belonging to the structural archetypes of Fig. 1c-d, it appears reasonable to suggest that different combination of electronic and steric factors operating in the inside or at the surface of the metallic core can explain the results so far available. However, the interplay between these factors often appears so subtle and unpredictable to greatly hamper cluster design.

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