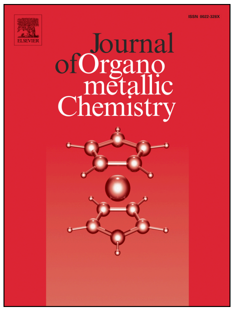

Molecular nickel poly-carbide carbonyl nanoclusters: the octa-carbide $[HNi_{42}C_8(CO)_{44}(CuCl)]^{7-}$ and the deca-carbide $[Ni_{45}C_{10}(CO)_{46}]^{6-}$

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Molecular nickel poly-carbide carbonyl nanoclusters: the octa-carbide $[HNi_{42}C_8(CO)_{44}(CuCl)]^{7-}$ and the deca-carbide $[Ni_{45}C_{10}(CO)_{46}]^{6-}$

In Memoriam of Professor Jack Lewis

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Abstract: The reaction of $[Ni_{10}(C_2)(CO)_{16}]^{2-}$ with CuCl in thf affords $[Ni_{45}C_{10}(CO)_{46}]^{6-}$ as the major product. This represents the first deca-carbide carbonyl cluster and this is the highest number of C-atoms found in a molecular cluster. Besides, the new octa-carbide $[HNi_{42}C_8(CO)_{44}(CuCl)]^{7-}$ and the previously reported tetra-carbide $[Ni_{34+x}C_4(CO)_{38+x}]^{6-}$ (x = 0,1) have been obtained as side-products. Whilst studying the reactions of miscellaneous Ni carbide clusters with Cu(I) salts in the search for a better synthesis of $[HNi_{42}C_8(CO)_{44}(CuCl)]^{7-}$, the homoleptic $[Ni_{32+x}C_6(CO)_{36+x}]^{6-}$ (x = 0-2) and the heteroleptic $[Ni_{38}C_6(CO)_{36}(MeCN)_6(CuMeCN)_{2x}]^{2-}$ clusters have been isolated in low yields. By analyzing the Ni carbide clusters herein reported as well as those previously described in the literature, it results that they are built-up starting from four fundamental building blocks: octahedral Oh-Ni_6C, trigonal prismatic TP-Ni_6C, capped trigonal prismatic cTP-Ni_7C and square anti-prismatic SA-Ni_8C. These may be joined into larger Ni_xC_y metal-carbide frameworks by sharing vertices, edges or faces. Even though infinite combinations are possible, some Ni_xC_y motives are common to two or more clusters, envisioning a possible rationale behind their building-up.

1. Introduction

Since the discovery of $Ru_6C(CO)_{17}$ and $Ru_6C(CO)_{14}$(arene),[1-3] several metal carbonyl clusters (MCCs) containing fully interstitial carbide atoms have been reported.[4-10] Nowadays, the stabilizing effect of interstitial main group elements (*e.g.* B, C, N, Si, P, As, Bi, Sb, Sn, Ge) in MCCs is well established.[11-15] Among these, carbide carbonyl clusters represent the largest class of MCCs containing interstitial main group atoms.[4-10] Carbide MCCs are known for several transition metals, but Nickel is the element which displays the largest variety of carbide clusters.[16-21]

Nickel carbonyl clusters containing one, two, four, six and eight isolated carbide atoms are known.[17-19] These are usually enclosed within trigonal prismatic (TP), mono-capped trigonal prismatic (cTP) and square anti-prismatic (SA) cavities, whereas (highly distorted) octahedral (Oh) cages are rarer. This is due to the fact that carbon is too large in order to fit in a regular octahedral Ni_6C-cage. As a result, Ni carbonyl poly-carbide clusters usually display rather complex and irregular structures, compared to homometallic MCCs and carbides of larger transition metals.[22,23]

In addition, Nickel carbonyl clusters containing one, two and four tightly bonded C–C (acetylide) units have been described.[20,21] Recently, we have reported the $[Ni_{12}(C)(C_2)(CO)_{17}(AuPPh_3)_3]^-$ cluster, which is the first molecular MCC containing at the same time one carbide atom and one tightly bonded C_2-unit. These display sub-van der Waals contacts, suggesting the incipient formation of more extended C-C bonding within the metal cage of MCCs.[24] At this regard, the study of molecular carbide clusters can help to a better understanding of the interaction between metal cages and carbide atoms or C_2-units. It must be remarked that metal surfaces, metal crystallites and metal nanoparticles are active catalysts in several chemical reactions as well as for the preparation of carbon nanotubes and other nanostructured carbon-based materials.[25-28]

Generally speaking, carbide MCCs are interesting both at the molecular level and as precursors for the preparation of metal nanoparticles with controlled composition.[11,29,30] At the molecular level, carbide MCCs often display rather different properties than analogous homometallic species, and can more easily reach higher nuclearities.[7a,11,12b,13,31] In addition, high nuclearity molecular MCCs containing a few tenths or more of metal atoms and possessing diameters of *ca.* 1-3 nm can be viewed as atomically defined ultra-small metal nanoparticles.[11] Thus, their study may contribute to a better understanding of the chemical, structural and physical properties of metal nanoparticles. Therefore, it would be helpful to obtain larger molecular clusters containing a higher number of carbide atoms and/or acetylide units, in order to get a better insight into their structures and organization of the C-atoms.

Herein, we report the synthesis and structural characterization of the first Ni deca-carbide carbonyl cluster, *i.e.*, $[Ni_{45}C_{10}(CO)_{46}]^{6-}$. This has been obtained in good yields from the reaction of $[Ni_{10}(C)_2(CO)_{16}]^{2-}$ with CuCl. As a side product, the bimetallic Ni-Cu octa-carbide $[HNi_{42}C_8(CO)_{44}(CuCl)]^{7-}$ has been isolated. This species is isostructural to the previously reported

Ni-Cd octa-carbides $[Ni_{42}C_8(CO)_{44}(CdCl)]^{7-}$ and $[HNi_{42}C_8(CO)_{44}(CdBr)]^{6-}$.[19c] In addition, whilst studying the reactions of miscellaneous Ni carbide clusters with Cu(I) salts in the search for a better synthesis of $[HNi_{42}C_8(CO)_{44}(CuCl)]^{7-}$, the homoleptic $[Ni_{32+x}C_6(CO)_{36+x}]^{6-}$ (x = 0-2) and the heteroleptic $[Ni_{38}C_6(CO)_{36}(MeCN)_6(CuMeCN)_{2x}]^{2-}$ clusters have been isolated. The structures of these clusters will be discussed in details, giving particular emphasis to the role of the interstitial carbide atoms and the building-up of their final metal-carbide cages.

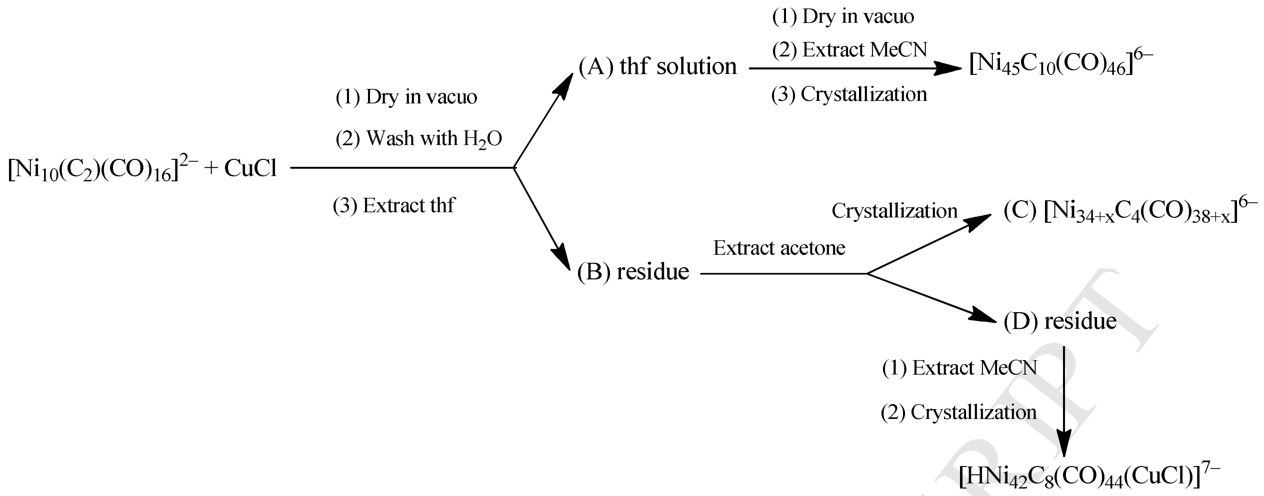
2. Results and Discussion

2.1 Synthesis.

The reaction of $[NMe_4]_2[Ni_{10}(C_2)(CO)_{16}]$ with a slight excess of CuCl in thf affords a new species displaying ν(CO) at 2021(vs) and 1849(m) cm^{-1} with concomitant formation of $Ni(CO)_4$ and a Cu(s) mirror. $Ni(CO)_4$ was eliminated by removing the solvent under reduced pressure and the residue washed with water to eliminate unreacted Cu(I) salts. The solid was treated with thf resulting in a dark-brown solution (A) (major component) and a reddish brown solid (B) (minor component), which were separated by filtration (Scheme 1). The thf solution (A) was dried *in vacuo* and the residue completely solubilised in MeCN. Slow diffusion of n-hexane and di-iso-propyl ether on this MeCN solution in the presence of traces of CH_2Cl_2 afforded crystals of $[NMe_4]_6[Ni_{45}C_{10}(CO)_{46}]·2MeCN·2CH_2Cl_2$ suitable for X-ray analyses.

The solid (B) was further extracted with acetone (C) and MeCN (D). Slow diffusion of iso-propanol on the acetone solution (C) resulted in crystals of $[NMe_4]_6[Ni_{34+x}C_4(CO)_{38+x}]·2MeCOMe$, whereas a few crystals of $[NMe_4]_7[HNi_{42}C_8(CO)_{44}(CuCl)]·5.5MeCN$ were obtained from the MeCN solution (D). It must be remarked that $[NMe_4]_6[Ni_{45}C_{10}(CO)_{46}]·2MeCN·2CH_2Cl_2$ is the main product of the reaction, whereas only minor amounts of $[NMe_4]_6[Ni_{34+x}C_4(CO)_{38+x}]·2MeCOMe$ and just a few crystals of $[NMe_4]_7[HNi_{42}C_8(CO)_{44}(CuCl)]·5.5MeCN$ have been obtained.

Scheme 1



The crystals of $[NMe_4]_6[Ni_{45}C_{10}(CO)_{46}]\cdot 2MeCN\cdot 2CH_2Cl_2$ display ν(CO) in nujol mull at 2013(vs) and 1850(m) cm^{-1}. These crystals are soluble in organic solvents such as thf (ν(CO) 2020(vs) and 1847(m) cm^{-1}), acetone (ν(CO) 2019(vs) and 1844(m) cm^{-1}) and MeCN (ν(CO) 2013(vs) and 1844(m) cm^{-1}), where they show very similar IR spectra. This compound is unstable under CO atmosphere resulting in $Ni(CO)_4$ as the major decomposition product. Its cyclic voltammetric profile displays only ill-defined irreversible processes.

$[NMe_4]_6[Ni_{34+x}C_4(CO)_{38+x}]\cdot 2MeCOMe$ (x = 0.09) contains a mixture of the previously reported $[Ni_{34}C_4(CO)_{38}]^{6-}$ (91%) and $[Ni_{35}C_4(CO)_{39}]^{6-}$ (9%).[18d] The crystals show ν(CO) in nujol mull at 1998(m), 1961(vs), 1932(m) and 1829(ms) cm^{-1}, and at 1993(vs) and 1853 cm^{-1} in MeCN solution. Since these species have been already fully characterized, they will not be further discussed. The CIF file has been deposited within the Cambridge Crystallographic Data Centre for sake of completeness.

$[NMe_4]_7[HNi_{42}C_8(CO)_{44}(CuCl)]\cdot 5.5MeCN$ show ν(CO) in nujol mull at 1990(s), 1953(sh), 1847(m), 1825(w) cm^{-1}, and ν(CO) in MeCN at 2006(vs), 1880(m) cm^{-1}, in agreement with the solid state structure which displays both terminal and edge bridging carbonyls.

The formation of the major species $[Ni_{45}C_{10}(CO)_{46}]^{6-}$ from $[Ni_{10}(C_2)(CO)_{16}]^{2-}$ and CuCl may be formally explained on the basis of equation (1), which is in agreement with the fact that the main by-products observed are $Ni(CO)_4$ and copper metal.

$$5[Ni_{10}(C_2)(CO)_{16}]^{2-} + 4Cu^{+} \rightarrow [Ni_{45}C_{10}(CO)_{46}]^{6-} + 5Ni(CO)_4 + 4Cu + 14CO \qquad (1)$$

We have previously reported that $[Ni_9C(CO)_{17}]^{2-}$ reacts with the halide-free $[Cu(MeCN)_4][BF_4]$ salt resulting in the Ni-Cu bimetallic tetra-carbide

$[H_2Ni_{30}C_4(CO)_{34}\{Cu(MeCN)\}_2]^{4-}$.[18a] The same compound is formed using $[Ni_{10}(C_2)(CO)_{16}]^{2-}$ and $[Cu(MeCN)_4][BF_4]$, even if the yields are lower. Conversely, the reaction of $[Ni_9C(CO)_{17}]^{2-}$ with CuCl affords a mixture of oxidation products, among which $[Ni_{34}C_4(CO)_{38}]^{6-}$, $[Ni_{38}C_6(CO)_{42}]^{6-}$, $[Ni_{32}C_6(CO)_{36}]^{6-}$ and $Ni(CO)_4$ have been spectroscopically identified. These oxidized clusters do not further react with stoichiometric amounts of CuCl, whereas complete decomposition to $Ni(CO)_4$ and Ni^{2+} is observed with a larger amount of CuCl. Whilst studying the reaction of $[Ni_{32}C_6(CO)_{36}]^{6-}$ with CuCl, crystals of its $[NMe_4]_8[Ni_{32+x}C_6(CO)_{36+x}][Cl]_2\cdot 10MeCN$ salt have been isolated, confirming that this species is almost unreactive under these conditions.

The presence in the structure of $[NMe_4]_8[Ni_{32+x}C_6(CO)_{36+x}][Cl]_2\cdot 10MeCN$ of two Ni(CO) capping fragments with fractional occupancy factors (see next Section) indicates that, actually, a mixture of $[Ni_{32}C_6(CO)_{36}]^{6-}$ (featuring only edge bridging CO's), $[Ni_{33}C_6(CO)_{37}]^{6-}$ (36 μ-CO and one terminal t-CO) and $[Ni_{34}C_6(CO)_{38}]^{6-}$ (36 μ-CO and two t-CO) is present. Since the refined occupancy factors are very low (ca. 0.08), $[Ni_{32}C_6(CO)_{36}]^{6-}$ is the major species. This agrees very well with the IR spectrum of $[NMe_4]_8[Ni_{32+x}C_6(CO)_{36+x}][Cl]_2\cdot 10MeCN$ in MeCN, which displays a strong ν(CO) at 1896 cm^{-1} corresponding to μ-CO, and a weak ν(CO) at 1990 cm^{-1} due to the terminal carbonyls.

The formation of such a mixture is due to the fact that the reaction of $[Ni_{32}C_6(CO)_{36}]^{6-}$ with CuCl leads to partial decomposition of the cluster with concomitant formation of $Ni(CO)_4$. This, in turn, reacts with the unreacted $[Ni_{32}C_6(CO)_{36}]^{6-}$ resulting into $[Ni_{33}C_6(CO)_{37}]^{6-}$ and $[Ni_{34}C_6(CO)_{38}]^{6-}$, as described by reactions (2) and (3):

$$[Ni_{32}C_6(CO)_{36}]^{6-} + Ni(CO)_4 \rightarrow [Ni_{33}C_6(CO)_{37}]^{6-} + 3CO \qquad (2)$$

$$[Ni_{33}C_6(CO)_{37}]^{6-} + Ni(CO)_4 \rightarrow [Ni_{34}C_6(CO)_{38}]^{6-} + 3CO \qquad (3)$$

Condensation of further Ni(CO) fragments would have resulted in $[Ni_{38}C_6(CO)_{42}]^{6-}$, as previously described in the literature.[19a,19b] This indicates that a series of structurally related clusters of general formula $[Ni_{32+x}C_6(CO)_{36+x}]^{6-}$ (x = 0-6) may be obtained, by the step-wise addition or removal of Ni(CO) fragments.

Similarly, $[Ni_{34}C_4(CO)_{38}]^{6-}$, $[Ni_{38}C_6(CO)_{42}]^{6-}$ and $[Ni_{32}C_6(CO)_{36}]^{6-}$ do not react with stoichiometric amounts of $[Cu(MeCN)_4][BF_4]$ whereas a complex mixture of decomposition products, dominated by $Ni(CO)_4$ and Ni^{2+}, is obtained with a larger amount of Cu(I). Whilst studying the reaction of $[Ni_{38}C_6(CO)_{42}]^{6-}$ with increasing amounts of $[Cu(MeCN)_4][BF_4]$ in MeCN, among the decomposition products, we have been able to isolate in a crystalline form and structurally characterize the $[NMe_4]_2[Ni_{38}C_6(CO)_{36}(MeCN)_6(CuMeCN)_{2x}]\cdot 2(1\text{-}x)MeCN$ salt, which contain the unprecedented $[Ni_{38}C_6(CO)_{36}(MeCN)_6(CuMeCN)_{2x}]^{2-}$. Since only a few crystal of these new species have been obtained, it has not been possible to further proceed with its characterization. Nonetheless, this species is rather interesting since it represents a rare case of heteroleptic MCCs in which several CO ligands have been replaced by MeCN molecules. This is favoured by its low negative charge, in view of the greater basicity of MeCN compared to CO.[18a]

2.2 Crystal structures.

Crystal structures have been determined for $[NMe_4]_6[Ni_{45}C_{10}(CO)_{46}]\cdot 2MeCN\cdot 2CH_2Cl_2$, $[NMe_4]_6[Ni_{34+x}C_4(CO)_{38+x}]\cdot 2MeCOMe$, $[NMe_4]_7[HNi_{42}C_8(CO)_{44}(CuCl)]\cdot 5.5MeCN$, $[NMe_4]_2[Ni_{38}C_6(CO)_{36}(MeCN)_6(CuMeCN)_{2x}]\cdot 2(1\text{-}x)MeCN$ and $[NMe_4]_8[Ni_{32+x}C_6(CO)_{36+x}][Cl]_2\cdot 10MeCN$. Since $[NMe_4]_6[Ni_{34+x}C_4(CO)_{38+x}]\cdot 2MeCOMe$ contains a mixture of $[Ni_{34}C_4(CO)_{38}]^{6-}$ and $[Ni_{35}C_4(CO)_{39}]^{6-}$, which have been previously reported, its structure will not be discussed.[18d] $[NMe_4]_8[Ni_{32+x}C_6(CO)_{36+x}][Cl]_2\cdot 10MeCN$ contains the $[Ni_{32+x}C_6(CO)_{36+x}]^{6-}$ (x = 0-2) anions closely related to the previously reported $[Ni_{32}C_6(CO)_{36}]^{6-}$ [19a,19b] and, thus, its structure will be only briefly commented at the end of this section. Conversely, the other three structures containing new species will be discussed in detail.

The molecular structure of the $[Ni_{45}C_{10}(CO)_{46}]^{6-}$ deca-carbide has been determined as its $[NMe_4]_6[Ni_{45}C_{10}(CO)_{46}]\cdot 2MeCN\cdot 2CH_2Cl_2$ salt (Figure 1 and Table1). It is the first molecular cluster containing ten interstitial carbide atoms reported in the literature. Its structure is composed by a $Ni_{45}C_{10}$ metal-carbide core coordinated on the surface to 46 CO ligands, 22 terminal and 24 edge bridging. Its 155 Ni-Ni contacts are rather spread [2.379(3)-2.976(3) Å; average 2.61(4) Å] and the average Ni-Ni connectivity is 6.89, as previously found in MCCs with analogous nuclearities.[19] The CO/Ni ratio is 1.022 which, considering that nine Ni-atoms are fully interstitial, corresponds to a surface coverage $CO/Ni_{surface}$ of 1.28.

Considering the ten interstitial carbides, five are enclosed within distorted Oh-Ni_6C octahedral cavities, two within TP-Ni_6C trigonal prismatic cavities and three inside cTP-Ni_7C mono-capped trigonal prismatic cavities. Even though the Ni-C contacts in the octahedral cavities [1.832(17)-2.133(15) Å; average 1.92(9) Å] are rather more spread than those of the trigonal prismatic cages [1.867(18)-1.960(16) Å; average 1.92(6) Å], their average values are almost identical. This indicates that the average Ni-C contacts within these hexa-coordinated cages are similar, but the octahedral cages are very distorted whereas the trigonal prismatic ones are more regular. In the case of the cTP-Ni_7C cavities [1.890(16)-2.205(17) Å; 2.01(8) Å], the apparent larger value of the Ni-C contacts is due to the fact that the six contacts with the vertices of the prism are as above, whereas the Ni-C distances involving the capping atoms are considerably longer.

Figure 1

Molecular structure of $[Ni_{45}C_{10}(CO)_{46}]^{6-}$ *(green, Ni; grey, C; red, O).*

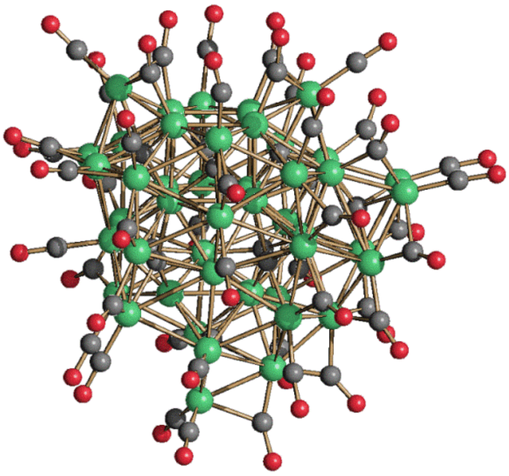


Table1

Main bonding distances (Å) of $[Ni_{45}C_{10}(CO)_{46}]^{6-}$, $[HNi_{42}C_8(CO)_{44}(CuCl)]^{7-}$ *and* $[Ni_{38}C_6(CO)_{36}(MeCN)_6(CuMeCN)_{2x}]^{2-}$.

	$[Ni_{45}C_{10}(CO)_{46}]^{6-}$	$[HNi_{42}C_8(CO)_{44}(CuCl)]^{5-}$	$[Ni_{38}C_6(CO)_{36}(MeCN)_6(CuMeCN)_{2x}]^{2-}$
Ni-Ni	2.379(3)-2.976(3) Average 2.61(4)	2.356(2)-2.989(3) Average 2.58(4)	2.389(2)-2.969(2) Average 2.568(11)
Ni-C (TP)	1.867(18)-1.960(16) Average 1.92(6)	1.879(17)-2.069(16) Average 1.93(5)	-
Ni-C (cTP)	1.890(16)-2.205(17) Average 2.01(8)	1.884(15)-2.131(15) Average 1.99(9)	-
Ni-C (SA)	-	1.967(16)-2.203(17) Average 2.05(6)	1.991(10)-2.111(10) Average 2.05(4)
Ni-C (Oh)	1.832(17)-2.133(15) Average 1.92(9)	-	-
Ni-Cu	-	2.582(3)-2.691(3) Average 2.624(7)	2.400(15)-2.846(8) Average 2.78(2)

The cluster possesses a very complex $Ni_{45}C_{10}$ kernel with idealized m (C_s) symmetry, which may be rationalized as depicted in Figures 2-4. The core of the cluster is based on a $Ni_{32}C_8$ framework, which has been previously found also in the $[Ni_{36}C_8(CO)_{36}(Cd_2Cl_3)]^{5-}$ and $[Ni_{36}C_8(CO)_{34}(MeCN)_3(Cd_2Cl_3)]^{3-}$ octa-carbides.[19c] This, in turn, is composed by two different (A and B) $Ni_{18}C_4$ fragments sharing a Ni_4-square face (Figures 2 and 3).

Fragment (A)-$Ni_{18}C_4$ is based on a cubic Ni_8C_4 unit, in which four adjacent (related by a 4-fold axis) faces are capped by carbide atoms (Figure 2). Two carbides (on opposite faces) are enclosed within trigonal prismatic cages, after the addition of two further Ni-atoms on each carbide. Conversely, the remaining two carbides are encapsulated within mono-capped trigonal prismatic cages after the addition of three further Ni-atoms on each carbide. These operations result in the (A)-$Ni_{18}C_4$ fragment.

Fragment (B)-$Ni_{18}C_4$ is composed by four Ni_6C octahedra disposed in a square arrangement (Figure 3) and sharing two triangular faces (four Ni-atoms). Fragments (A) and (B) are joined by a common square face (in purple in Figures 2-4) resulting in a $Ni_{32}C_8$ unit (Figure 4a). The $Ni_{36}C_8$ framework common to $[Ni_{45}C_{10}(CO)_{46}]^{6-}$, $[Ni_{36}C_8(CO)_{36}(Cd_2Cl_3)]^{5-}$ and $[Ni_{36}C_8(CO)_{34}(MeCN)_3(Cd_2Cl_3)]^{3-}$ is, then obtained, by adding four further Ni-atoms (not bonded to any carbide; Figure 4b).

In the case of the two Ni-Cd hexa-carbides, the clusters are completed by the coordination of a $[Cd_2Cl_3]^+$ unit below the $Ni_{36}C_8$ framework to fragment (B). Conversely, in the case of $[Ni_{45}C_{10}(CO)_{46}]^{6-}$, the same side of the cluster is completed by a fifth Oh-Ni_6C octahedron sharing two Ni-atoms with fragment (B), and resulting in a $Ni_{40}C_9$ unit (Figure 4c). The tenth carbide is enclosed within a cTP-Ni_7C mono-capped trigonal prism sharing two Ni atoms with fragment (A) and one with fragment (B). This results in a $Ni_{44}C_{10}$ framework (Figure 4d), from which the final $Ni_{45}C_{10}$ cage of the cluster is obtained after the addition of a further Ni atom (not bonded to any carbide) connected to three Ni's of fragment (B), two of the cTP-Ni_7C mono-capped trigonal prism and one of the Oh-Ni_6C octahedron (Figure 4e). $[Ni_{45}C_{10}(CO)_{46}]^{6-}$ possesses 588 Cluster Valence Electrons (CVE) and 294 (6n+24) Cluster Valence Molecular Orbitals (CVMO).

Figure 2

The fragment (A)-$Ni_{18}C_4$ composing the structure of $[Ni_{45}C_{10}(CO)_{46}]^{6-}$ (a) and its cubic Ni_8C_6 core (b) (Ni atoms composing the inner Ni_8 cube are in purple; Ni atoms completing the two trigonal prismatic cages in yellow; Ni atoms completing the two mono-capped trigonal prismatic cages in orange; carbides in black).

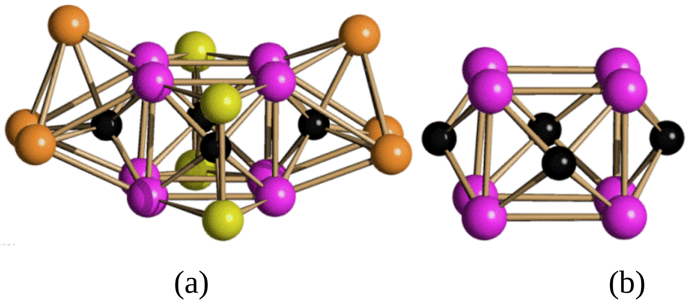

(a) (b)

Figure 3

The fragment (B)-$Ni_{18}C_4$ composing the structure of $[Ni_{45}C_{10}(CO)_{46}]^{6-}$ (a) and the four Ni_6C octahedral units constituting (B) (b) (Ni atoms in common with (A)-$Ni_{18}C_4$ in purple; other Ni atoms in green; carbides in grey).

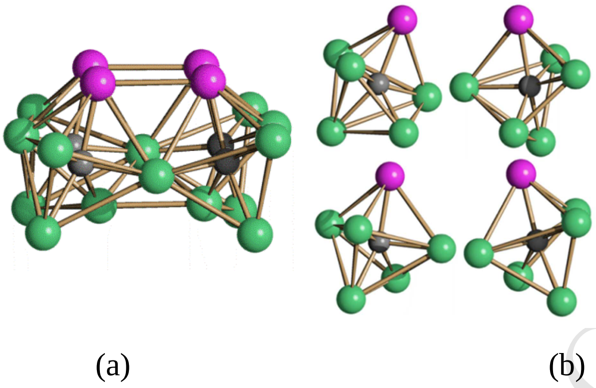
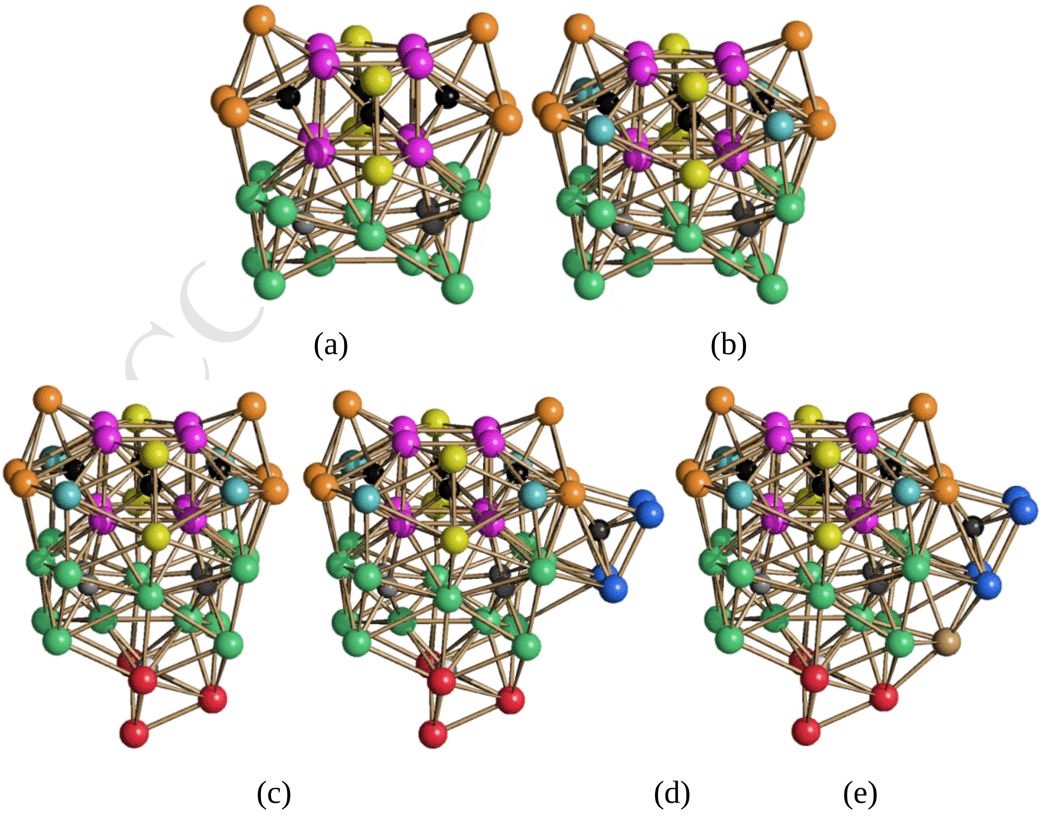

(a) (b)

Figure 4

Formal building up of the metal carbide cage of $[Ni_{45}C_{10}(CO)_{46}]^{6-}$. (a) The $Ni_{32}C_8$ fragment obtained by joining (A) and (B)-$Ni_{18}C_4$ (colours as in Figures 2 and 3). (b) $Ni_{36}C_8$ framework obtained by adding four Ni atoms (light blue) to (a). (c) $Ni_{40}C_9$ unit obtained by adding a Ni_6C octahedron sharing with (b) two Ni's (other Ni atoms in red, C in white). (d) $Ni_{44}C_{10}$ framework obtained by adding a Ni_7C mono-capped trigonal prismatic unit sharing with (c) three Ni's (other Ni atoms in blue, C in dark grey). (e) The final $Ni_{45}C_{10}$ cage of the cluster resulting from the addition of a further Ni (brown).

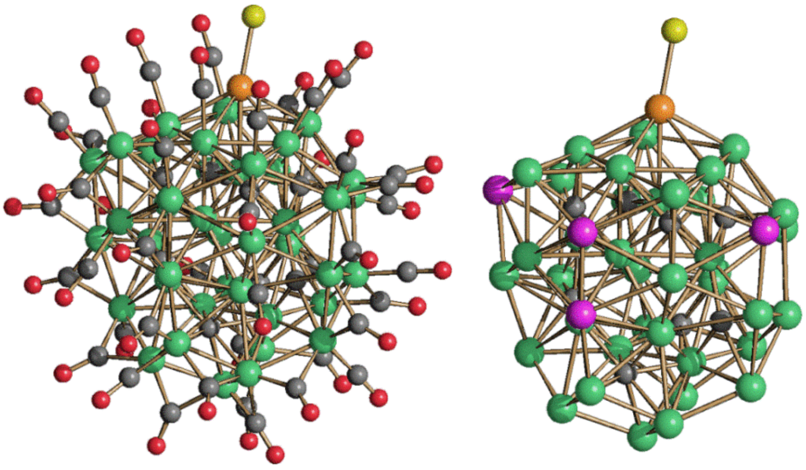

(a) (b)

(c) (d) (e)

The molecular structure of $[HNi_{42}C_8(CO)_{44}(CuCl)]^{7-}$ has been determined as its $[NMe_4]_7[HNi_{42}C_8(CO)_{44}(CuCl)]\cdot5.5MeCN$ salt (Figure 5 and Table 1). The structure of this cluster is almost identical to those previously reported for $[Ni_{42}C_8(CO)_{44}(CdCl)]^{7-}$ and $[HNi_{42}C_8(CO)_{44}(CdBr)]^{6-}$.[19c] It is noteworthy that the replacement of the $[CdX]^+$ (X = Cl, Br) fragment with [CuCl] does not cause any significant structural change regarding the bonding parameters, coordination of the carbide atoms and stereochemistry of the CO ligands. These $Ni_{42}C_8$ clusters display rather complex metal cages, which cannot be described in terms of simple polyhedrons. They are, in fact, the result of the condensation of two C-centred TP-Ni_6C trigonal prisms, four C-centred cTP-Ni_7C mono-capped trigonal prisms and two C-centred SA-Ni_8C square-antiprisms. This generates a rather irregular and non-symmetrical $Ni_{38}C_8$ metal carbido cage (Figure 5), in which all Ni atoms are bonded to at least one interstitial carbide atom. The structure is completed by the addition of four Ni atoms not bonded to any carbide and 44 CO ligands. The unique [CuCl] unit is coordinated to an almost planar pentagonal face of the $Ni_{42}C_8$ cage. The cluster has been formulated as a mono-hydride $[HNi_{42}C_8(CO)_{44}(CuCl)]^{7-}$, in order to be isoelectronic with $[Ni_{42}C_8(CO)_{44}(CdCl)]^{7-}$ and $[HNi_{42}C_8(CO)_{44}(CdBr)]^{6-}$. Overall, these clusters possess 548 CVE which correspond to 274 (6n+22) CVMO.

Figure 5

(a) Molecular structure of $[HNi_{42}C_8(CO)_{44}(CuCl)]^{6-}$ (green, Ni; orange Cu; yellow, Cl; grey, C; red, O) and (b) its $Ni_{42}C_4CuCl$ core (purple, Ni not bonded to any carbide).


(a) (b)

The molecular structure of $[Ni_{38}C_6(CO)_{36}(MeCN)_6(CuMeCN)_{2x}]^{2-}$ has been determined as its $[NMe_4]_2[Ni_{38}C_6(CO)_{36}(MeCN)_6(CuMeCN)_{2x}]\cdot2(1-x)MeCN$ salt (Figure 6). The cluster anion possesses crystallographic $\bar{3}$ (D_{3d}) symmetry and the two $[CuMeCN]^+$ fragments have partial occupancy factors, which refine as 0.174(11). The structure of $[Ni_{38}C_6(CO)_{36}(MeCN)_6(CuMeCN)_{2x}]^{2-}$ is closely related to those of $[Ni_{38}C_6(CO)_{42}]^{6-}$ and $[Ni_{32}C_6(CO)_{36}]^{6-}$,[19a,19b] and shows some resemblances also to $[Ni_{36}Co_8C_8(CO)_{48}]^{6-}$.[19d] The core of the cluster is based on a cubic Ni_8C_6 unit whose six square faces are capped by six carbide atoms (Figure 7). These carbides are encapsulated within six square anti-prismatic cages, after the addition of further four Ni-atoms on each carbide. This results in a $Ni_{32}C_6$ framework, identical to the one found in $[Ni_{32}C_6(CO)_{36}]^{6-}$, which possesses eight centred hexagonal Ni_7-faces. Six of these faces, related by $\bar{3}$, are capped by the remaining Ni-atoms, resulting in a $Ni_{38}C_6$ unit. These six Ni-atoms are bonded to six MeCN molecules in $[Ni_{38}C_6(CO)_{36}(MeCN)_6(CuMeCN)_{2x}]^{2-}$, and to six terminal CO ligands in $[Ni_{38}C_6(CO)_{42}]^{6-}$. The remaining 36 CO ligands are all edge bridging. The two $[CuMeCN]^+$ fragments (with partial occupancy factors) are bonded to the two hexagonal Ni_7-faces (related by an inversion centre) not bonded to any Ni atom.

Figure 6

Two views of the molecular structure of $[Ni_{38}C_6(CO)_{36}(MeCN)_6(CuMeCN)_{2x}]^{2-}$ (green, Ni; orange Cu; blue, N; grey, C; red, O; white, H).

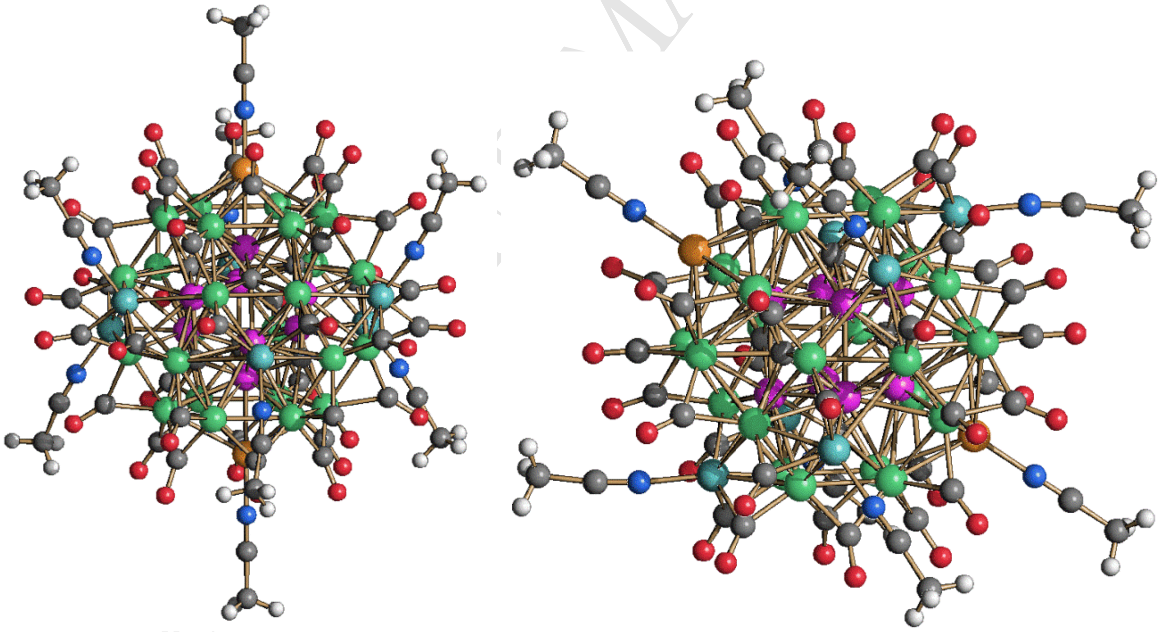
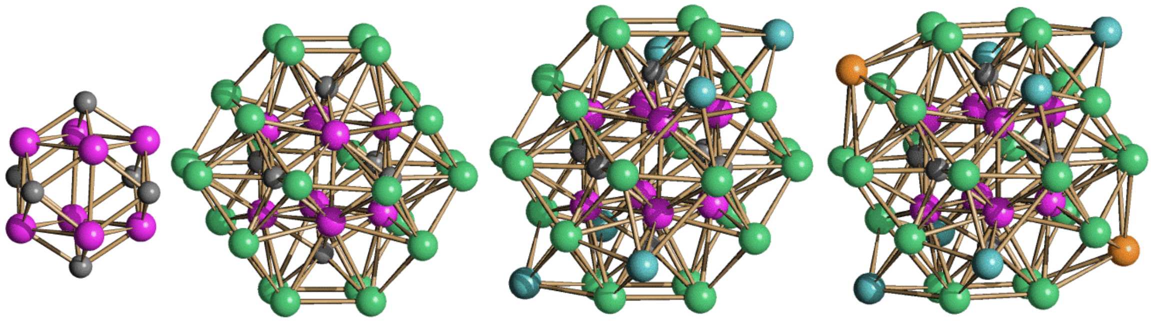


Figure 7

The metal core of $[Ni_{38}C_6(CO)_{36}(MeCN)_6(CuMeCN)_{2x}]^{2-}$*: (a) inner cubic* Ni_8C_6 *unit (purple, Ni; grey, C); (b)* $Ni_{32}C_6$ *framework in which the six carbides are encapsulated within square anti-prismatic cages (added Ni's in green); (c)* $Ni_{38}C_6$ *unit from the addition of six Ni atoms (light blue) not bonded to any carbide; (d)* $Ni_{38}C_6Cu_2$ *framework (orange, Cu).*



(a) (b) (c) (d)

The $[NMe_4]_8[Ni_{32+x}C_6(CO)_{36+x}][Cl]_2\cdot 10MeCN$ salt contains the $[Ni_{32+x}C_6(CO)_{36+x}]^{6-}$ anion closely related to the previously reported $[Ni_{32}C_6(CO)_{36}]^{6-}$. The additional Ni(CO) fragment (refined occupancy factor 0.083(4)) caps one of the centred hexagonal Ni_7-faces of the cluster (light blue in Figure 7c). Since the anion is located in an inversion centre, the additional Ni(CO) fragment is present in two opposite faces. Since its occupancy factor is very low, $[Ni_{32}C_6(CO)_{36}]^{6-}$ is the main species present within the crystal. In addition, there are minor amounts of $[Ni_{33}C_6(CO)_{37}]^{6-}$ (two different orientation) and/or $[Ni_{34}C_6(CO)_{38}]^{6-}$. Capping a cluster face with a Ni(CO) group does not alter the electron counting of the molecule, and the possibility of having species that differ only in the presence/absence of such a group is quite common in the chemistry of Ni MCCs.[18a] Indeed, $[Ni_{38}C_6(CO)_{42}]^{6-}$ results from capping six faces of $[Ni_{32}C_6(CO)_{36}]^{6-}$ with Ni(CO) groups. The present work indicates the existence of intermediate species of general formula $[Ni_{32+x}C_6(CO)_{36+x}]^{6-}$ ($x = 0$-6).

3. Conclusions

The syntheses and structures of the new $[Ni_{45}C_{10}(CO)_{46}]^{6-}$ and $[HNi_{42}C_8(CO)_{44}(CuCl)]^{7-}$ poly-carbide carbonyl clusters have been reported in this paper. The former represents the first deca-carbide MCC and this is the highest number of C-atoms found in a molecular cluster. The latter is isostructural to the Ni-Cd bimetallic $[Ni_{42}C_8(CO)_{44}(CdCl)]^{7-}$ and $[HNi_{42}C_8(CO)_{44}(CdBr)]^{6-}$ octa-carbides.[19c] Besides, the homoleptic $[Ni_{32+x}C_6(CO)_{36+x}]^{6-}$ hexa-anion and the heteroleptic $[Ni_{38}C_6(CO)_{36}(MeCN)_6(CuMeCN)_{2x}]^{2-}$ di-anion, closely related to the previously reported $[Ni_{32}C_6(CO)_{36}]^{6-}$ and $[Ni_{38}C_6(CO)_{42}]^{6-}$,[19a,19b] have been described.

Several homo- and hetero-metallic Ni carbonyl mono- and poly-carbide species are known. All the homo-metallic clusters as well as the bi-metallic ones presenting carbide atoms mainly bonded to Ni are reported in Table 2. Overall, these species present rather complex and often irregular metal-carbide cages, which result from the subtle balance between Ni-Ni, Ni-CO and Ni-$C_{carbide}$ interactions, as well as Ni-M bonds in the case of bimetallic species. Nonetheless, by analyzing all the entries of Table 2, it results that in all these MCCs the carbide atoms are enclosed within four types of cages: 1) ocathedral Oh-Ni_6C; 2) trigonal prismatic TP-Ni_6C; 3) capped trigonal prismatic cTP-Ni_7C; 4) square anti-prismatic SA-Ni_8C. All these cages have been found isolated in mono-carbide clusters (entries 1-6 of Table 2) or combined in poly-carbide species (entries 7-30). Poly-carbide clusters may contain just one type of cage as well as two or three different cages.

Thus, Oh-Ni_6C, TP-Ni_6C, cTP-Ni_7C and SA-Ni_8C may be viewed as the fundamental building-blocks of all Ni carbide clusters reported so far. It is noteworthy that the overall Ni-Ni and the Ni-C distances within a single type of carbide cage are almost identical in all the clusters. This indicates that these building-blocks are quite rigid and their structures are not significantly altered after that they are joined into larger Ni_xC_y metal-carbide frameworks. These may result from sharing vertices, edges or faces between two or more Oh-Ni_6C, TP-Ni_6C, cTP-Ni_7C and SA-Ni_8C cages. These Ni_xC_y frameworks may be further decorated on the surface by Ni atoms or other metals not directly connected to the carbides.

We can expect infinite combinations of these four building-blocks. Nonetheless, some Ni_xC_y frameworks are common to two or more Ni carbide clusters. For instance, a $Ni_{30}C_4$ framework composed of two TP-Ni_6C and two cTP-Ni_7C cages has been found in several Ni, Ni-Cd and Ni-Cu clusters (entries 7-20 of Table 2). A $Ni_{42}C_8$ cage composed of two TP-Ni_6C, four cTP-Ni_7C and two SA-Ni_8C is common to Ni-Cd and Ni-Cu octa-carbides (entries 26-28). Similarly, a cubic $Ni_{32}C_6$ framework based on six SA-Ni_8C cages is common to $[Ni_{32+x}C_6(CO)_{36+x}]^{6-}$ (x = 0-6), $[Ni_{38}C_6(CO)_{36}(MeCN)_6(CuMeCN)_{2x}]^{2-}$ and the bimetallic Ni-Co $[Ni_{36}Co_8C_8(CO)_{48}]^{6-}$ (entries 21-23,29; the latter contains also two cTP-Ni_7C cages). Finally, a $Ni_{36}C_8$ framework composed of four Oh-Ni_6C, two TP-Ni_6C and two cTP-Ni_7C cages has been found in $[Ni_{36}C_8(CO)_{36}(Cd_2Cl_3)]^{5-}$, $[Ni_{36}C_8(CO)_{34}(MeCN)_3(Cd_2Cl_3)]^{3-}$ and $[Ni_{45}C_{10}(CO)_{46}]^{6-}$ (entries 24,25,30; the latter contains also one further Oh-Ni_6C and one cTP-Ni_7C). Moreover, the $Ni_{32}C_6$ and $Ni_{36}C_8$ frameworks just described are both based on cubic Ni_6 cages capped by 6 and 4 C-atoms, respectively.

As a general conclusion, the study of larger Ni poly-carbide carbonyl clusters seems very fascinating since, from one side, they display a rich structural diversity but, from the other, some general building-up principles and motives might be found. This, in turn, might help to a better understanding of the growth and structure of carbon rich Ni nanoparticles which are fundamental in several catalytic processes.[25-28]

Table 2

Average Ni-Ni and Ni-C$_{carbide}$ distances (Å) of miscellaneous Ni carbide carbonyl clusters.

	Ni–Ni	**Ni–C (Oh)** [a]	**Ni–C (TP)** [b]	**Ni–C (cTP)** [c]	**Ni–C (SA)** [d]
(1) $Ni_6C(CO)_9(AuPPh_3)_4$[e]	2.678	1.893	-	-	-
(2) $[Ni_6C(CO)_8(AuPPh_3)_8]^{2+}$[f]	2.695	1.902	-	-	-
(3) $[Ni_7C(CO)_{16}]^{2-}$[g]	2.570	-	-	1.99	-
(4) $[Ni_8C(CO)_{16}]^{2-}$[h]	2.552	-	-	-	2.08
(5) $[Ni_9C(CO)_{17}]^{2-}$[h]	2.545	-	-	-	2.09
(6) $[Ni_{10}C(CO)_{18}]^{2-}$[h]					
(7) $[H_2Ni_{30}C_4(CO)_{34}\{Cu(CH_3CN)\}_2]^{4-}$ [i]	2.580	-	1.95	2.02	-
(8) $[H_3Ni_{30}C_4(CO)_{34}\{Cu(NCC_6H_4CN)\}_2]^{3-}$ [i]	2.573	-	1.94	2.00	-
(9) $[H_2Ni_{29}C_4(CO)_{32}(CH_3CN)_2\{Cu(CH_3CN)\}_2]^{2-}$ [i]	2.583	-	1.95	2.01	-
(10) $[H_2Ni_{29}C_4(CO)_{34}\{Cu(CH_3CN)\}_2]^{2-}$ [i]	2.572	-	1.94	2.01	-
(11) $[H_2Ni_{30}C_4(CO)_{34}(CdI)_2]^{4-}$ [j]	2.581	-	1.96	2.00	-
(12) $[HNi_{30}C_4(CO)_{34}(CdBr)_2]^{5-}$ [j]	2.583	-	2.00	2.02	-
(13) $[H_2Ni_{32}C_4(CO)_{36}(CdBr)]^{5-}$ [j]	2.587	-	1.94	2.01	-
(14) $[HNi_{33}C_4(CO)_{37}(CdCl)]^{6-}$ [j]	2.584	-	1.94	2.02	-
(15) $[H_2Ni_{30}C_4(CO)_{34}(CdCl)_2]^{4-}$ [k]	2.593	-	1.94	2.01	-
(16) $[HNi_{30}C_4(CO)_{34}(CdCl)_2]^{5-}$ [k]	2.596	-	1.95	2.01	-
(17) $[Ni_{30}C_4(CO)_{34}(CdCl)_2]^{6-}$ [k]	2.599	-	1.92	2.02	-
(18) $[HNi_{34}C_4(CO)_{38}]^{5-}$ [l]	2.597	-	1.94	2.01	-
(19) $[Ni_{35}C_4(CO)_{39}]^{6-}$ [l]	2.596	-	1.94	2.03	-
(20) $[Ni_{34}C_4(CO)_{38}]^{6-}$ [m]	2.58	-	1.940	2.015	-
(21) $[Ni_{32}C_6(CO)_{36}]^{6-}$ [n]					
(22) $[Ni_{38}C_6(CO)_{44}]^{6-}$ [n]					
(23) $[Ni_{38}C_6(CO)_{36}(MeCN)_6(CuMeCN)_{2x}]^{2-}$ [m]	2.568	-	-	-	2.05

(24) $[Ni_{36}C_8(CO)_{36}(Cd_2Cl_3)]^{5-}$ [o]	2.67	1.90	1.92	2.01	
(25) $[Ni_{36}C_8(CO)_{34}(MeCN)_3(Cd_2Cl_3)]^{3-}$ [o]	2.67	1.90	1.92	2.01	
(26) $[Ni_{42}C_8(CO)_{44}(CdCl)]^{7-}$ [o]	2.63	-	1.93	2.00	2.06
(27) $[HNi_{42}C_8(CO)_{44}(CdBr)]^{6-}$ [o]	2.62	-	1.93	1.99	2.05
(28) $[HNi_{42}C_8(CO)_{44}(CuCl)]^{5-}$ [m]	2.58	-	1.93	1.99	2.05
(29) $[Ni_{36}Co_8C_8(CO)_{48}]^{6-}$ [p]	2.55	-	-	2.02	2.07
(30) $[Ni_{45}C_{10}(CO)_{46}]^{6-}$ [m]	2.61	1.92	1.92	2.01	-

[a] Average Ni-C distance in octahedral cavities;[b] Average Ni-C distance in trigonal prismatic cavities;[c] Average Ni-C distance in capped trigonal prismatic cavities; [d] Average Ni-C distance in square anti-prismatic cavities; [e] See ref [17c];[f] See ref [24[;[g] See ref [17a];[h] See ref [17b];[i] See ref [18a];[j] See ref [18b];[k] See ref [18c];[l] See ref [18d];[m] this work; [n] See ref [19a,19b];[o] See ref [19c];[p] See ref [19d].

4. Experimental Section

4.1 General procedures.

All reactions and sample manipulations were carried out using standard Schlenk techniques under nitrogen and in dried solvents. All the reagents were commercial products (Aldrich) of the highest purity available and used as received, except $[NMe_4]_2[Ni_{10}(C_2)(CO)_{16}]$ [21a] and $[Cu(CH_3CN)_4][BF_4]$ [32] which have been prepared according to the literature. Analysis of Ni and Cu were performed by atomic absorption on a Pye-Unicam instrument. Analyses of C, H and N were obtained with a ThermoQuest FlashEA 1112NC instrument. IR spectra were recorded on a Perkin Elmer Spectrum One interferometer in CaF_2 cells. Structure drawings have been performed with SCHAKAL99.[33]

4.2 Synthesis of $[NMe_4]_6[Ni_{45}C_{10}(CO)_{46}]\cdot 2MeCN\cdot 2CH_2Cl_2$ and its side-products $[NMe_4]_6[Ni_{34+x}C_4(CO)_{38+x}]\cdot 2MeCOMe$ and $[NMe_4]_7[HNi_{42}C_8(CO)_{44}(CuCl)]\cdot 5.5MeCN$.

CuCl (0.30 g, 3.06 mmol) was added as solid to a solution of $[NMe_4]_2[Ni_{10}(C_2)(CO)_{16}]$ (1.19 g, 0.99 mmol) in thf (30 mL) over a period of 2 hours. The resulting mixture was further stirred at room temperature for 6 hours and, then, the solvent removed *in vacuo*. The residue was washed with water (40 mL), dried under vacuum and extracted with thf (20 mL). The thf solution was, then, evaporated to dryness and the residue completely solubilised in MeCN (20 mL). Crystals of $[NMe_4]_6[Ni_{45}C_{10}(CO)_{46}]\cdot 2MeCN\cdot 2CH_2Cl_2$ suitable for X-ray analyses were obtained by layering n-hexane (3 mL) and di-iso-propyl ether (40 mL) on the MeCN solution in the presence of traces of CH_2Cl_2 (2 mL) (yield 0.51 g, 49 % based on Ni).

$C_{86}H_{82}Cl_4N_8Ni_{45}O_{46}$ (4747.35): calcd. C 21.76, H 1.74, N 2.36, Ni 55.64; found: C 22.08, H 1.51, N 2.63, Ni 55.93. IR (nujol, 293 K) $\nu(CO)$: 2013(vs), 1850(m) cm^{-1}. IR (thf, 293 K) $\nu(CO)$: 2020(vs), 1847(m) cm^{-1}. IR (acetone, 293 K) ν(CO): 2019(vs), 1844(m) cm^{-1}. IR (MeCN, 293 K) ν(CO): 2013(vs), 1844(m) cm^{-1}.

The solid left after the extraction in thf, was further extracted in acetone (15 mL) and, then, MeCN (10 mL). Crystals of $[NMe_4]_6[Ni_{34+x}C_4(CO)_{38+x}]\cdot 2MeCOMe$ suitable for X-ray analyses were obtained by layering iso-propanol (40 mL) on the acetone solution. Similarly, crystals of $[NMe_4]_7[HNi_{42}C_8(CO)_{44}(CuCl)]\cdot 5.5MeCN$ suitable for X-ray analyses were obtained by layering n-hexane (2 mL) and di-iso-propyl ether (20 mL) on the MeCN solution.

$[NMe_4]_6[Ni_{34+x}C_4(CO)_{38+x}]\cdot 2MeCOMe$: IR (nujol, 293 K) ν(CO): 1998(m), 1961(vs), 1932(m), 1829(ms) cm^{-1}. IR (MeCN, 293 K) ν(CO): 1993(vs), 1853(m) cm^{-1}.

$[NMe_4]_7[HNi_{42}C_8(CO)_{44}(CuCl)]\cdot 5.5MeCN$:IR (nujol, 293 K) ν(CO): 1990(s), 1953(sh), 1847(m), 1825(w) cm^{-1}.IR (MeCN, 293 K) ν(CO): 2006(vs), 1880(m) cm^{-1}.

4.3 Synthesis of $[NMe_4]_2[Ni_{38}C_6(CO)_{36}(MeCN)_6(CuMeCN)_{2x}]\cdot 2(1\text{-}x)MeCN$.

$[Cu(MeCN)_4][BF_4]$ (0.36 g, 1.14 mmol) was added as a solid to a solution of $[NMe_4]_6[Ni_{32}C_6(CO)_{38}]$ (0.36 g, 0.106 mmol) in MeCN (20 mL) over a period of 4 hours. The resulting mixture was further stirred at room temperature for two days and, then, the solvent removed *in vacuo*. The residue was washed with water (40 mL), thf (20 mL), acetone (20mL), and extracted with MeCN (20 mL). A few crystals of $[NMe_4]_2[Ni_{38}C_6(CO)_{36}(MeCN)_6(CuMeCN)_{2x}]\cdot 2(1\text{-}x)MeCN$ suitable for X-ray analyses were obtained by layering n-hexane (5 mL) and di-iso-propyl ether (40 mL) on the MeCN solution. These crystals have been found in mixture with unreacted $[NMe_4]_6[Ni_{32}C_6(CO)_{38}]$ and other decomposition products, hampering any further characterization.

IR (nujol, 293 K) ν(CO): 2010(m), 1865(vs) cm^{-1}. IR (MeCN, 293 K) ν(CO): 2005(s), 1866(ms) cm^{-1}.

4.4 Synthesis of $[NMe_4]_8[Ni_{32+x}C_6(CO)_{36+x}][Cl]_2\cdot 10MeCN$.

CuCl (0.28 g, 2.83mmol) was added as a solid to a solution of $[NMe_4]_6[Ni_{32}C_6(CO)_{36}]$ (0.36 g, 0.106 mmol) in MeCN (20 mL) over a period of 1 hour. The resulting mixture was further stirred at room temperature for one night and, then, the solvent removed *in vacuo*. The residue was washed with water (40 mL), thf (20 mL), acetone (20mL), and extracted with MeCN (20 mL). Crystals of $[NMe_4]_8[Ni_{32+x}C_6(CO)_{36+x}][Cl]_2\cdot 10MeCN$ suitable for X-ray analyses were obtained by layering n-hexane (5 mL) and di-iso-propyl ether (40 mL) on the MeCN solution. These crystals are formed in mixture with other amorphous species.

IR (MeCN, 293 K) ν(CO): 1990(w), 1896(vs) cm^{-1}.

4.4 X-ray Crystallographic Study.

Crystal data and collection details for $[NMe_4]_6[Ni_{45}C_{10}(CO)_{46}]\cdot 2MeCN\cdot 2CH_2Cl_2$, $[NMe_4]_6[Ni_{34+x}C_4(CO)_{38+x}]\cdot 2MeCOMe$, $[NMe_4]_7[HNi_{42}C_8(CO)_{44}(CuCl)]\cdot 5.5MeCN$, $[NMe_4]_2[Ni_{38}C_6(CO)_{36}(MeCN)_6(CuMeCN)_{2x}]\cdot 2(1\text{-}x)MeCN$ and $[NMe_4]_8[Ni_{32+x}C_6(CO)_{36+x}][Cl]_2\cdot 10MeCN$ are reported in Table 3. The diffraction experiments were carried out on a Bruker APEX II diffractometer equipped with a CCD detector using Mo–Kα radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS).[34] Structures were solved by direct methods and refined by full-matrix least-squares based on all data using F^2.[35] Hydrogen atoms were fixed at calculated positions and refined by a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters, unless otherwise stated.

$[NMe_4]_6[Ni_{45}C_{10}(CO)_{46}]\cdot 2MeCN\cdot 2CH_2Cl_2$: The asymmetric unit of the unit cell contains one cluster anion, six $[NMe_4]^+$ cations, two MeCN and two CH_2Cl_2 molecules (all located on general positions). Two $[NMe_4]^+$ cations and two CH_2Cl_2 molecules are disordered, and therefore they have been split into two positions each and refined isotropically using one occupancy parameter per disordered group. Because of this disorder as well as the presence of several small solvent and cation molecules containing lighter atoms, only the cluster anion, which contains heavier metal atoms, has been refined anisotropically. Some C and O atoms of the cluster anion have been restrained to isotropic behaviour (ISOR line in SHELXL, s.u. 0.01). The $[NMe_4]^+$ cations and the solvent molecules were restrained to have similar geometries (SAME line in SHELXL, s.u. 0.02) and similar U parameters (SIMU line in SHELXL, s.u. 0.01). Restraints to bond distances were applied as follow: 1.47 Å for C–N in $[NMe_4]^+$ (s.u. 0.02); 1.47 Å for C–C and 1.14 Å for C–N in MeCN (s.u. 0.01); 1.75 Å for C–Cl in CH_2Cl_2 (s.u. 0.01). Some high residual electron density remain in the structure close to C(611) (ALERT A in the checkcif) probably due to $MeCN/CH_2Cl_2$ disorder; in view of the complexity of the structure it has not been possible to deal further with this disorder.

$[NMe_4]_6[Ni_{34+x}C_4(CO)_{38+x}]\cdot 2MeCOMe$: The asymmetric unit of the unit cell contains one half of a cluster anion (located on an inversion centre), three $[NMe_4]^+$ cations and one MeCOMe molecule (all located on general positions). One $[NMe_4]^+$ cation is disordered, and therefore it has been split into two positions and refined isotropically using one occupancy parameter per disordered group. Ni(18) displays a refined occupancy factor of 0.054(3); since this value is quite small, it has not been possible to locate the CO ligand bonded to Ni(18). Some C and O atoms of the cluster anion

have been restrained to isotropic behaviour (ISOR line in SHELXL, s.u. 0.01). The $[NMe_4]^+$ cations were restrained to have similar geometries (SAME line in SHELXL, s.u. 0.01) and similar *U* parameters (SIMU line in SHELXL, s.u. 0.02). The acetone molecule was restrained to have similar distances (SADI line in SHELXL; s.u. 0.02) and similar *U* parameters (SIMU line in SHELXL, s.u. 0.02).

$[NMe_4]_7[HNi_{42}C_8(CO)_{44}(CuCl)]\cdot 5.5MeCN$: The asymmetric unit of the unit cell contains one cluster anion, seven $[NMe_4]^+$ cations, five MeCN molecules (all located on general positions) and half of a MeCN molecule (on an inversion centre). The latter is disordered over two symmetry related positions and has been refined isotropically with 0.5 occupancy factor. Because of this disorder as well as the presence of several small solvent and cation molecules containing lighter atoms together with a large cluster anion, which contains heavier metal atoms, the MeCN molecules and three $[NMe_4]^+$ cations have been refined isotropically. Some C and O atoms of the cluster anion have been restrained to isotropic behaviour (ISOR line in SHELXL, s.u. 0.01). The $[NMe_4]^+$ cations and the MeCN molecules were restrained to have similar geometries (SAME line in SHELXL, s.u. 0.02) and similar *U* parameters (SIMU line in SHELXL, s.u. 0.01). Restraints to bond distances were applied as follow (s.u. 0.01): 1.47 Å for C–N in $[NMe_4]^+$; 1.47 Å for C–C and 1.14 Å for C–N in MeCN.

$[NMe_4]_2[Ni_{38}C_6(CO)_{36}(MeCN)_6\{Cu(MeCN)\}_{2x}]\cdot 2(1\text{-}x)MeCN$: The asymmetric unit of the unit cell contains one sixth of cluster anion (on $\bar{3}$), one third of a $[NMe_4]^+$ cation (on 3) and one third of the disordered MeCN molecule (on 3). Once applied all relevant symmetry operations, the unit cell results to contain four cluster anions, eight $[NMe_4]^+$ cations and 1.65 MeCN molecules. The $Cu(CH_3CN)$ fragment coordinated to the cluster and the free CH_3CN molecule are disordered in the sense that when the former is present the latter is absent and *vice versa*. Thus, they have been refined including the former in PART 1 of the model and the latter in PART 2 and using an occupancy factor for the former which refined as 0.174(11). Because of the presence of an inversion centre, these disordered Cu(MeCN)/MeCN fragments are present twice per cluster anion. The $[NMe_4]^+$ cation and the disordered Cu(MeCN)/MeCN fragments have been refined isotropically, apart Cu which has been refined anisotropically. Some C and O atoms of the cluster anion and the MeCN molecule bonded to Ni have been restrained to isotropic behaviour (ISOR line in SHELXL, s.u. 0.01). The geometries of the free and coordinated MeCN molecules were restrained to be similar (SAME line in SHELXL; s.u. 0.02). Similar *U* restraints were applied to the MeCN molecules and $[NMe_4]^+$ cation (SIMU line in SHELXL, s.u. 0.01). Restraints to bond distances

were applied as follow (s.u. 0.01): 1.47 Å for C–N in $[NMe_4]^+$; 1.47 Å for C–C and 1.14 Å for C–N in MeCN.

$[NMe_4]_8[Ni_{32+x}C_6(CO)_{36+x}][Cl]_2\cdot 10MeCN$: The asymmetric unit of the unit cell contains half of a cluster anion (located on an inversion centre), four $[NMe_4]^+$ cations, one Cl^- anion and five MeCN molecules (all located on general positions). Ni(21) in the cluster anion has a refined occupancy factor of 0.083(4); because of this, it has not been possible to locate the CO ligand bonded to it and this originates an ALERT A in the checkcif. The N-C distances of the $[NMe_4]^+$ cations have been restrained to be similar (SADI line in SHELXL, s.u. 0.02). The MeCN molecules have been restrained to have similar geometries (SAME line in SHELXL; s.u. 0.02) and similar thermal parameters (SIMU line in SHELXL, s.u. 0.02).

CCDC 1053620-1053624 contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 3

Crystal data and experimental details for $[NMe_4]_6[Ni_{45}C_{10}(CO)_{46}]\cdot 2MeCN\cdot 2CH_2Cl_2$, $[NMe_4]_6[Ni_{34+x}C_4(CO)_{38+x}]\cdot 2MeCOMe$, $[NMe_4]_7[HNi_{42}C_8(CO)_{44}(CuCl)]\cdot 5.5MeCN$, $[NMe_4]_2[Ni_{38}C_6(CO)_{36}(MeCN)_6(CuMeCN)_{2x}]\cdot 2(1-x)MeCN$ and $[NMe_4]_8[Ni_{32+x}C_6(CO)_{36+x}][Cl]_2\cdot 10MeCN$.

	$[NMe_4]_6[Ni_{45}C_{10}(CO)_{46}]\cdot 2MeCN\cdot 2CH_2Cl_2$	$[NMe_4]_6[Ni_{34+x}C_4(CO)_{38+x}]\cdot 2MeCOMe$
Formula	$C_{86}H_{82}Cl_4N_8Ni_{45}O_{46}$	$C_{72}H_{84}N_6Ni_{34.09}O_{40}$
Fw	4747.35	3675.17
T, K	100(2)	100(2)
λ, Å	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space Group	$P\bar{1}$	$P2_1/n$
a, Å	15.7528(14)	15.6852(16)
b, Å	16.4623(15)	19.234(2)
c, Å	28.274(3)	16.6430(17)
α, °	87.0760(10)	90

β, °	81.7140(10)	90.3350(10)
γ, °	66.0600(10)	90
Cell Volume, Å^3	6631.3(10)	5021.0(9)
Z	2	2
D_c, g cm^{-3}	2.378	2.431
μ, mm^{-1}	6.365	6.298
F(000)	4700	3665
Crystal size, mm	0.16×0.13×0.11	0.19×0.16×0.12
θ limits, °	1.35–25.03	1.62–26.00
Index ranges	$-18\leq h \leq 18$ $-19\leq k \leq 19$ $-33\leq l \leq 33$	$-19\leq h \leq 19$ $-23\leq k \leq 23$ $-20\leq l \leq 20$
Reflections collected	62606	51455
Independent reflections	23337 [R_{int} = 0.1045]	9868 [R_{int} = 0.0368]
Completeness to θ max	99.6%	99.9%
Data / restraints / parameters	23337 / 1595 / 1557	9868/ 232 / 672
Goodness on fit on F^2	0.946	1.018
R_1 ($I > 2\sigma(I)$)	0.0751	0.0324
wR_2 (all data)	0.2560	0.0817
Largest diff. peak and hole, e Å^{-3}	3.927 / –1.827	1.357/ –1.017

	$[NMe_4]_7[HNi_{42}C_8(CO)_{44}(CuCl)]\cdot 5.5MeCN$	**$[NMe_4]_2[Ni_{38}C_6(CO)_{36}(MeCN)_6(CuMeCN)_{2x}]\cdot 2(1\text{-}x)MeCN$**
Formula	$C_{91}H_{100.5}ClCuN_{12.5}Ni_{42}O_{44}$	$C_{66}H_{48}Cu_{0.35}N_{10}Ni_{38}O_{36}$
Fw	4638.15	3810.36
T, K	100(2)	293(2)
λ, Å	0.71073	0.71073
Crystal system	Monoclinic	Cubic
Space Group	$P2_1/n$	$Pa\bar{3}$
a, Å	20.5131(16)	21.5680(13)
b, Å	23.8768(19)	21.5680(13)
c, Å	26.996(2)	21.5680(13)
a, °	90	90

β, °	94.1580(10)	90
γ, °	90	90
Cell Volume, Å^3	13187.3(18)	10033.0(10)
Z	4	4
D_c, g cm^{-3}	2.336	2.523
μ, mm^{-1}	6.084	7.082
F(000)	9232	7505
Crystal size, mm	0.18×0.15×0.12	0.16×0.15×0.12
θ limits, °	1.31–25.03	1.64–25.02
Index ranges	$-24 \leq h \leq 24$ $-28 \leq k \leq 28$ $-32 \leq l \leq 32$	$-25 \leq h \leq 25$ $-25 \leq k \leq 25$ $-25 \leq l \leq 25$
Reflections collected	125804	92642
Independent reflections	23305 [R_{int} = 0.1794]	2962 [R_{int} = 0.1634]
Completeness to θ max	100.0%	99.8%
Data / restraints / parameters	23305 / 1137 / 1573	2962/ 89 / 226
Goodness on fit on F^2	1.007	1.028
R_1 ($I > 2\sigma(I)$)	0.0663	0.0476
wR_2 (all data)	0.1997	0.1588
Largest diff. peak and hole, e Å^{-3}	2.592 / –1.244	2.941/ –1.064

	$[NMe_4]_8[Ni_{32+x}C_6(CO)_{36+x}][Cl]_2$ ·10MeCN
Formula	$C_{94}H_{126}Cl_2N_{18}Ni_{32.16}O_{36}$
Fw	4042.85
T, K	100(2)
λ, Å	0.71073
Crystal system	Monoclinic
Space Group	$P2_1/n$
a, Å	15.57387(6)
b, Å	15.9603(6)
c, Å	27.1180(10)
a, °	90

β, °	104.187(2)
γ, °	90
Cell Volume, Å^3	6534.9(4)
Z	2
D_c, g cm^{-3}	2.055
μ, mm^{-1}	4.621
F(000)	4077
Crystal size, mm	0.16×0.13×0.10
θ limits, °	1.38–26.00
Index ranges	$-19 \le h \le 19$ $-19 \le k \le 19$ $-33 \le l \le 33$
Reflections collected	99025
Independent reflections	12840 [R_{int} = 0.0895]
Completeness to θ max	100.0%
Data / restraints / parameters	12840 / 174 / 830
Goodness on fit on F^2	1.076
R_1 ($I > 2\sigma(I)$)	0.0495
wR_2 (all data)	0.1603
Largest diff. peak and hole, e Å^{-3}	2.574 / –1.415

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Graphical Abstract

Molecular nickel poly-carbide carbonyl nanoclusters: the octa-carbide $[HNi_{42}C_8(CO)_{44}(CuCl)]^{7-}$ and the deca-carbide $[Ni_{45}C_{10}(CO)_{46}]^{6-}$

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Keywords: Cluster compound / Carbonyl ligand / Structure elucidation / Nickel / Carbide

The first molecular deca-carbide cluster $[Ni_{45}C_{10}(CO)_{46}]^{6-}$ is described together with the bimetallic octa-carbide $[HNi_{42}C_8(CO)_{44}(CuCl)]^{7-}$. Their structures are compared to other Ni poly-carbide clusters.