Polycarbide nickel clusters containing interstitial $Ni(\eta^2-C_2)_4$ and $Ni_2(\mu-\eta^2-C_2)_4$ acetylide moieties: mimicking the supersaturated Ni–C solutions preceding the catalytic growth of CNTs with the structures of $[HNi_{25}(C_2)_4(CO)_{32}]^{3-}$ and $[Ni_{22}(C_2)_4(CO)_{28}Cl]^{3-}$ †

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Reaction of $[Ni_6(CO)_{12}]^{2-}$ with CCl_4 in CH_2Cl_2 gives the $[HNi_{25}(C_2)_4(CO)_{32}]^{3-}$ and $[Ni_{22}(C_2)_4(CO)_{28}Cl]^{3-}$ carbonyl clusters containing interstitial $Ni(\eta^2-C_2)_4$ and $Ni_2(\mu-\eta^2-C_2)_4$ acetylide moieties.

Nickel nanoparticles are active catalysts for the preparation of single- and multi-wall carbon nanotubes (SW-CNTs and MW-CNTs) and carbon fibers from miscellaneous C_1–C_n feedstocks.[1–4] The suggested catalytic mechanism involves decomposition of the feedstock onto the surface of the nanoparticle and formation of a Ni–C solid solution. As the solution becomes supersaturated, carbon atoms precipitate and assemble in graphene sheets with tubular structure.[5] During this process, the addition of C_2 moieties to the growing carbon nanotube is suggested to play a significant role.[6] Consequently, well-defined nickel carbonyl polycarbide and polyacetylide molecular clusters, besides being potential precursors of active catalysts, may provide snapshots of the steps preceding formation of CNTs.

These considerations prompted a re-investigation of the chemistry of carbonyl polycarbide Ni clusters. Herein, we report the $[HNi_{25}(C_2)_4(CO)_{32}]^{3-}$ (**1**) and $[Ni_{22}(C_2)_4(CO)_{28}Cl]^{3-}$ (**2**) clusters, which contain interstitial $Ni(\eta^2-C_2)_4$ and $Ni_2(\mu-\eta^2-C_2)_4$ acetylide moieties, respectively.

Both compounds have been obtained by reaction of CCl_4 with $[NEt_4]_2[Ni_6(CO)_{12}]$ in CH_2Cl_2 and refluxing under nitrogen; which compound is formed depends on the $[NEt_4]_2[Ni_6(CO)_{12}]/CCl_4$ ratio (experimental details are given in ESI†). With a ratio of *ca.* 0.9, the reaction leads to a waxy precipitate containing the new $[NEt_4]_3$[**1**] salt. The compound has been purified by washing the precipitate with water and THF, extraction of the residue in acetone and crystallization by diffusion of *n*-hexane. **1** shows ν(CO) absorptions in CH_3CN at 2017(s) and 1886(m) cm^{-1}. The compound is deprotonated to $[Ni_{25}(C_2)_4(CO)_{32}]^{4-}$ by dissolution into a more basic solvent such as DMF [ν(CO) 2010(s) and 1875(m) cm^{-1}]. Its attempted isolation has been hindered by ready re-protonation during the work-up. Although we do not have a direct ^{1}H NMR proof of the presence of the hydride in **1**, and its presence can be inferred only from the chemical behaviour, this is a general problem for metal carbonyl clusters exceeding a nuclearity of *ca.* 20, as previously discussed.[7] The formulation of **1** is further supported by its ESI-MS in MeCN, which displays multiplets centred at *m*/*z* (relative intensity in parentheses): 1295 (*20*) ($\{[NEt_4][HNi_{25}(C_2)_4(CO)_{32}]\}^{2-}$), 1230 (*35*) ($[HNi_{25}(C_2)_4(CO)_{32}]^{2-}$) and 820 (*100*) ($[HNi_{25}(C_2)_4(CO)_{32}]^{3-}$).

Decreasing the $[NEt_4]_2[Ni_6(CO)_{12}]/CCl_4$ ratio to *ca.* 0.65 leads to the related tetraacetylide cluster **2**, which shows ν(CO) in MeCN at 2016(s) and 1852(m) cm^{-1}, and multiplets centred at *m*/*z* (relative intensity in parentheses): 1168 (*75*) ($\{[NEt_4][Ni_{22}(C_2)_4(CO)_{28}Cl]\}^{2-}$), 1103 (*40*) ($[Ni_{22}(C_2)_4(CO)_{28}Cl]^{2-}$) and 735 (*100*) ($[Ni_{22}(C_2)_4(CO)_{28}Cl]^{3-}$) in the ESI-MS in MeCN. $[NEt_4]_3$[**1**] and $[NEt_4]_3$[**2**]$\cdot 0.5Me_2CO$ have been characterized by single-crystal X-ray analysis.[8] Both anions display metal frameworks deriving from the square-orthobicupola (Johnson solid J28)[9] shown in Fig. 1.

In the case of **1** the above 16-vertex polyhedron of idealized D_{4h} symmetry encapsulates the $Ni(\eta^2-C_2)_4$ moiety [C–C_{av} 1.368 Å] shown in Fig. 2(a). The metal framework of the cluster is completed by capping with a Ni atom all eight lateral square faces (Fig. 2(b)). Each carbon atom is hepta-coordinated, displaying one C–C, and six Ni–C bonding contacts. The whole structure comprises thirty-two CO ligands, of which twenty-two are terminal and ten edge bridging, and is shown in Fig. 2(c). Despite the fact that the unique hydride atom has not been located by X-ray diffraction, calculations with the program XHYDEX[10] indicate the two square faces orthogonal to the C_4 axis as the most suited sites for the unique hydride atom. This would result in a semi-interstitial hydride located in a square-pyramidal cavity, as previously found in $[H_2Rh_{13}(CO)_{24}]^{3-}$.[11]

The crystals of $[NEt_4]_3$[**2**]$\cdot 0.5Me_2CO$ contain two independent $[Ni_{22}(C_2)_4(CO)_{28}Cl]^{3-}$ anions showing almost identical

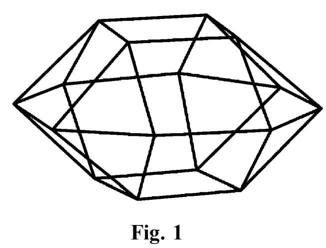

Fig. 1

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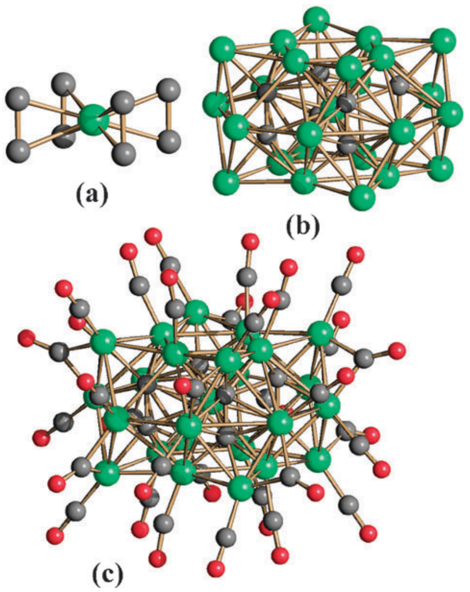

Fig. 2 The Ni(η^2-C_2)$_4$ interstitial moiety (a), the metal framework (b) and the complete structure (c) of **1** (colour legend: Ni green, C grey, O red).

geometry and very similar bonding parameters. The metal framework is related to that of **1** being also based on the 16-vertex square-orthobicupola of Fig. 1. However, it differs in that it encapsulates the Ni_2(μ-η^2-C_2)$_4$ moiety [Ni–Ni 2.398(2), C–C 1.365(17)–1.422(17) Å] shown in Fig. 3(a) and is capped by four additional Ni atoms on four alternate lateral square faces (Fig. 3(b)) arranged with idealized T_d symmetry.

Further departures from the idealized symmetry of the 16-vertex square-orthobicupola of Fig. 1 are due to distortions of the top and bottom square faces. These distortions are mainly explained by the encapsulation of a Ni_2(μ-η^2-C_2)$_4$ moiety which is bulkier than the interstitial Ni(η^2-C_2)$_4$ fragment of **1**. Each carbon atom displays five or six Ni–C and one C–C bond. As shown in Fig. 3(c), the structure of the cluster is completed by fourteen terminal and fourteen edge-bridging CO ligands, and one chloride atom bridging the loose Ni–Ni contact [2.918(4) and 2.948(4) Å for the two independent molecules, respectively] of the bottom face.

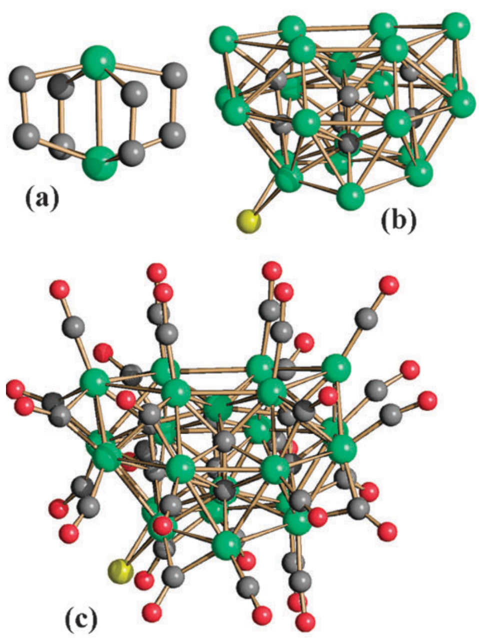

Fig. 3 The Ni_2(μ-η^2-C_2)$_4$ interstitial moiety (a), the metal framework (b) and the complete structure (c) of **2** (colour legend: Ni green, Cl yellow, C grey, O red).

Several Co, Ni and Co–Ni carbonyl clusters containing interstitial C_2 moieties displaying short C–C contacts are known,[12–16] and also a species containing two C_2 moieties, *viz*. $[Ni_{16}(C_2)_2(CO)_{23}]^{4-}$, has already been reported.[17] The title compounds represent the first examples of molecular clusters encapsulating four C_2 moieties and featuring Ni/C ratios (3.125 and 2.75, respectively) crossing the composition of the only reported metastable binary Ni–C phase (Ni_3C).[18] Such a low Ni/C ratio favours the approach of carbide atoms within the metallic frame and enables C–C bond formation giving rise to interstitial C_2 moieties.

The length of the C–C bonds of both **1** and **2** suggests a bond order of *ca*. 2, which is in keeping with the overlap population inferable from EHMO calculations with CACAO.[19] Such a bond order of acetylide moieties is justified by the covalent nature of their bonds. For instance, analysis of $[Co_6Ni_2C_2(CO)_{16}]^{2-}$ has shown that the C_2 moiety is involved in synergic bonding and back-bonding interactions with the skeletal MOs of the cage *via* its σ_p, π and π^* orbitals.[20] This is confirmed by our EHMO analyses on the title compounds, which point out the covalent interaction of the C_2 units with the whole metal cages. Moreover, analysis of the overlap population points out that the carbon atomic orbitals become less available for interaction with the metal atoms of the cage, as the C–C bond length decreases (see ESI†). Consequently, the metal cluster frame becomes increasingly destabilised. Such a conclusion is in keeping with the experimental observation that both **1** and **2** are completely degraded by carbon monoxide at atmospheric pressure, in contrast with most mono- and poly-carbide clusters.[21] Therefore, C_2 moieties are less effective than isolated carbide atoms in stabilising a metal cluster. At this regard, it is worth mentioning that the growth of CNT promoted by Ni-nanoparticles *via* C_2 addition has been proposed on the basis of theoretical calculations and experimental observations.[6] Experiments to test molecular clusters **1** and **2** as potential precursors of carbidized Ni nanoparticles for the catalytic growth of CNTs are underway, since it has been shown that molecular cluster precursors may enable preparation of SW-CNTs of uniform size.[22]

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