

# Polycarbide Nickel Clusters Containing Interstitial $\text{Ni}(\eta^2\text{-C}_2)_4$ and $\text{Ni}_2(\mu\text{-}\eta^2\text{-C}_2)_4$ Acetylide Moieties: Mimicking the Supersaturated Ni-C Solutions Preceding the Catalytic Growth of CNTs with the Structures of $[\text{HNi}_{25}(\text{C}_2)_4(\text{CO})_{32}]^{3-}$ and $[\text{Ni}_{22}(\text{C}_2)_4(\text{CO})_{28}\text{Cl}]^{3-}$ .

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## Electronic Supplementary Information

### General experimental 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. The  $[\text{NEt}_4]_2[\text{Ni}_6(\text{CO})_{12}]$  salt has been prepared according to the literature.<sup>1</sup> Analyses of Ni 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 SpectrumOne interferometer in  $\text{CaF}_2$  cells. Structure drawings have been performed with SCHAKAL99.<sup>2</sup>

### Synthesis of $[\text{NEt}_4]_3[\text{HNi}_{25}(\text{C}_2)_4(\text{CO})_{32}]$

A solution of  $\text{CCl}_4$  (150  $\mu\text{L}$ , 1.57 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL) was added dropwise over a period of 30 minutes to a suspension of  $[\text{NEt}_4]_2[\text{Ni}_6(\text{CO})_{12}]$  (1.35 g, 1.42 mmol) in  $\text{CH}_2\text{Cl}_2$  (40 mL), and the resulting mixture was, then, refluxed for 2 hours. The solvent was removed *in vacuo* and the residue washed with water (40 mL) and THF (40 mL), and extracted in acetone (20 mL). Crystals of  $[\text{NEt}_4]_3[\text{HNi}_{25}(\text{C}_2)_4(\text{CO})_{32}]$  suitable for X-ray analysis were obtained by slow diffusion of n-hexane (40 mL) on the acetone solution (yield 0.386 g, 42% based on Ni).

The salt is soluble in acetone and acetonitrile, insoluble in non-polar solvents, THF and alcohols. Dissolution in DMF results in a sensible lowering of the  $\nu(\text{CO})$  frequencies [2017(s) and 1886(m)  $\text{cm}^{-1}$  in  $\text{CH}_3\text{CN}$ ; 2010(s) and 1875(m)  $\text{cm}^{-1}$  in DMF] consistent with a net charge change from 3- to 4-. The tri-anion is regenerated after addition of acids but not with oxidants, suggesting the formulation of the tri-anion as a mono-hydride  $[\text{HNi}_{25}(\text{C}_2)_4(\text{CO})_{32}]^{3-}$ . All attempts to confirm directly the presence of the hydride by  $^1\text{H}$  NMR have failed. A detailed discussion on the problem of directly detect hydride atoms in high nuclearity metal carbonyl clusters and how their presence can be indirectly deduced by chemical and IR data has recently appeared.<sup>3</sup>

C<sub>64</sub>H<sub>61</sub>N<sub>3</sub>Ni<sub>25</sub>O<sub>32</sub> (2851.505): calcd. C 26.96, H 2.16, N 1.47, Ni 51.46; found: C 26.85, H 2.22, N 1.55, Ni 51.34. ESI-MS (CH<sub>3</sub>CN) multiplets centred at m/z (relative intensity in parentheses): 1295(20) ( $\{[\text{NEt}_4][\text{H}\text{Ni}_{25}(\text{C}_2)_4(\text{CO})_{32}]\}^{2-}$ ), 1230(35) ( $[\text{H}\text{Ni}_{25}(\text{C}_2)_4(\text{CO})_{32}]^{2-}$ ) and 820(100) ( $[\text{H}\text{Ni}_{25}(\text{C}_2)_4(\text{CO})_{32}]^{3-}$ ).

IR (293 K):  $[\text{H}\text{Ni}_{25}(\text{C}_2)_4(\text{CO})_{32}]^{3-}$  in CH<sub>3</sub>CN: 2017(s) and 1886(m) cm<sup>-1</sup>;  $[\text{Ni}_{25}(\text{C}_2)_4(\text{CO})_{32}]^{4-}$  in DMF 2010(s) and 1875(m) cm<sup>-1</sup>.

### Synthesis of $[\text{NEt}_4]_3[\text{Ni}_{22}(\text{C}_2)_4(\text{CO})_{28}(\mu\text{-Cl})]\cdot 0.5\text{Me}_2\text{CO}$

A solution of CCl<sub>4</sub> (210 μL, 2.20 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was added dropwise over a period of 1 hour to a suspension of  $[\text{NEt}_4]_2[\text{Ni}_6(\text{CO})_{12}]$  (1.35 g, 1.42 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) kept at 40 °C. The resulting mixture was, then, stirred at room temperature for 3 hours. The solvent was removed *in vacuum* and the residue washed with water (40 mL) and THF (40 mL), and extracted in acetone (20 mL). Crystals of  $[\text{NEt}_4]_3[\text{Ni}_{22}(\text{C}_2)_4(\text{CO})_{28}(\mu\text{-Cl})]\cdot 0.5\text{Me}_2\text{CO}$  suitable for X-ray analysis were obtained by slow diffusion of n-hexane (40 mL) on the acetone solution (yield 0.459 g, 45% based on Ni).

The salt is soluble in acetone, acetonitrile and DMF, insoluble in non-polar solvents, THF and alcohols.

C<sub>61.5</sub>H<sub>63</sub>ClN<sub>3</sub>Ni<sub>22</sub>O<sub>28.5</sub> (2626.87): calcd. C 28.12, H 2.42, N 1.60, Ni 49.16; found: C 28.18, H 2.25, N 1.82, Ni 49.32. ESI-MS (CH<sub>3</sub>CN) multiplets centred at m/z (relative intensity in parentheses): 1168(75) ( $\{[\text{NEt}_4][\text{Ni}_{22}(\text{C}_2)_4(\text{CO})_{28}\text{Cl}]\}^{2-}$ ), 1103(40) ( $[\text{Ni}_{22}(\text{C}_2)_4(\text{CO})_{28}\text{Cl}]^{2-}$ ) and 735(100) ( $[\text{Ni}_{22}(\text{C}_2)_4(\text{CO})_{28}\text{Cl}]^{3-}$ ).

IR (CH<sub>3</sub>CN, 293 K): 2016(s) and 1852(m) cm<sup>-1</sup>.

### X-ray Crystallographic Study

Crystal data and collection details for  $[\text{NEt}_4]_3[\text{H}\text{Ni}_{25}(\text{C}_2)_4(\text{CO})_{32}]$  and  $[\text{NEt}_4]_3[\text{Ni}_{22}(\text{C}_2)_4(\text{CO})_{28}(\mu\text{-Cl})]\cdot 0.5\text{Me}_2\text{CO}$  are reported in Table 1. 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).<sup>4</sup> Structures were solved by direct methods and refined by full-matrix least-squares based on all data using  $F^2$ .<sup>5</sup> 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.

$[\text{NEt}_4]_3[\text{H}\text{Ni}_{25}(\text{C}_2)_4(\text{CO})_{32}]$ : The asymmetric unit contains half of the cluster anion (located on a 2 axis), one  $[\text{NEt}_4]^+$  cation located on a general position and half of a  $[\text{NEt}_4]^+$  cation located on a 2

axis. Similar *U* restraints were applied to all the C and O atoms (s.u. 0.01). Restraints to bond distances were applied as follow: 1.47 Å for C–N and 1.53 Å for C–C in [NEt<sub>4</sub>]<sup>+</sup> (s.u. 0.01).

**[NEt<sub>4</sub>]<sub>3</sub>[Ni<sub>22</sub>(C<sub>2</sub>)<sub>4</sub>(CO)<sub>28</sub>(μ-Cl)]·0.5Me<sub>2</sub>CO:** The asymmetric unit contains two independent cluster anions, five [NEt<sub>4</sub>]<sup>+</sup> cations located on general positions and two halves of [NEt<sub>4</sub>]<sup>+</sup> cations located on inversion centres. Similar *U* restraints were applied to all the N, C and O atoms (s.u. 0.005), and ISOR restraints were applied to most the O atoms of the carbonyl ligands (s.u. 0.005). Two of the [NEt<sub>4</sub>]<sup>+</sup> cations located on general positions are disordered; therefore, they have been split into two positions each and isotropically refined using one occupancy parameter per disordered group. Moreover, the two halves of [NEt<sub>4</sub>]<sup>+</sup> cations located on inversion centres are disordered over two positions related by symmetry; the independent part of each cation has been refined isotropically with 50% occupancy factor. Restraints to bond distances were applied as follow: 1.47 Å for C–N and 1.53 Å for C–C in [NEt<sub>4</sub>]<sup>+</sup>; 1.21 Å for C–O and 1.53 Å for C–C in Me<sub>2</sub>CO (s.u. 0.005).

**Table 1**

*Crystal data and experimental details for [NEt<sub>4</sub>]<sub>3</sub>[HNi<sub>25</sub>(C<sub>2</sub>)<sub>4</sub>(CO)<sub>32</sub>] and [NEt<sub>4</sub>]<sub>3</sub>[Ni<sub>22</sub>(C<sub>2</sub>)<sub>4</sub>(CO)<sub>28</sub>(μ-Cl)]·0.5Me<sub>2</sub>CO*

	<b>[NEt<sub>4</sub>]<sub>3</sub>[HNi<sub>25</sub>(C<sub>2</sub>)<sub>4</sub>(CO)<sub>32</sub>]</b>	<b>[NEt<sub>4</sub>]<sub>3</sub>[Ni<sub>22</sub>(C<sub>2</sub>)<sub>4</sub>(CO)<sub>28</sub>(μ-Cl)]·0.5Me<sub>2</sub>CO:</b>
Formula	C <sub>64</sub> H <sub>60</sub> N <sub>3</sub> Ni <sub>25</sub> O <sub>32</sub>	C <sub>61.5</sub> H <sub>63</sub> ClN <sub>3</sub> Ni <sub>22</sub> O <sub>28.5</sub>
<i>F</i> <sub>w</sub>	2850.90	2627.22
<i>T</i> , K	295(2)	295(2)
<i>λ</i> , Å	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	<i>C</i> 2/ <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> , Å	19.5647(14)	13.6790(16)
<i>b</i> , Å	25.8822(18)	23.876(3)
<i>c</i> , Å	17.7927(13)	27.991(3)
<i>α</i> , °	90	65.368(2)
<i>β</i> , °	100.6780(10)	82.239(2)
<i>γ</i> , °	90	88.296(2)
Cell Volume, Å <sup>3</sup>	8853.8(11)	8230.1(17)
<i>Z</i>	4	4
<i>D</i> <sub>c</sub> , g cm <sup>-3</sup>	2.139	2.120

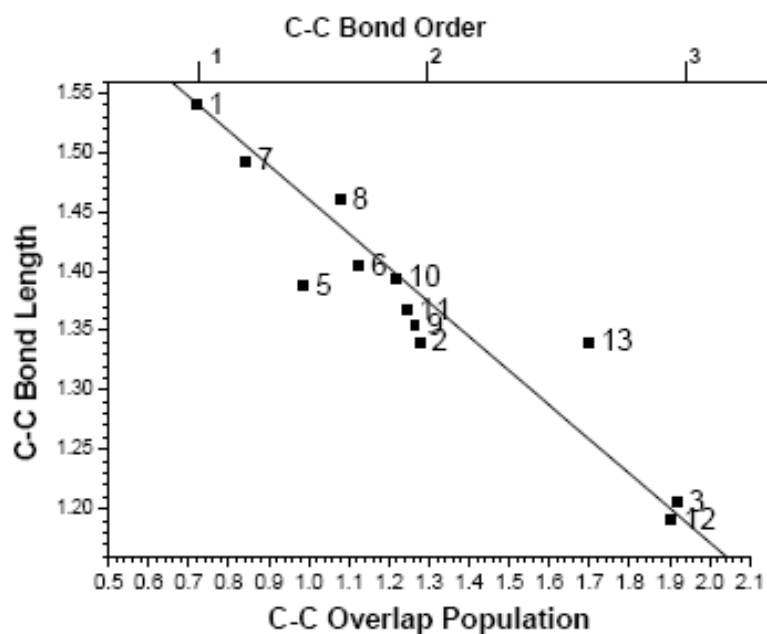
$\mu$ , mm <sup>-1</sup>	5.246	5.004
F(000)	5684	5256
Crystal size, mm	0.21×0.16×0.12	0.21×0.14×0.11
$\theta$ limits, °	1.32–27.00	1.47–25.03
Index ranges	-24 ≤ h ≤ 24 -33 ≤ k ≤ 33 -22 ≤ l ≤ 22	-16 ≤ h ≤ 16 -28 ≤ k ≤ 28 -33 ≤ l ≤ 33
Reflections collected	49325	77938
Independent reflections	9664 [ $R_{\text{int}} = 0.0472$ ]	28968 [ $R_{\text{int}} = 0.1012$ ]
Completeness to $\theta = 25.03^\circ$	100.0%	99.6%
Data / restraints / parameters	9664 / 44 / 560	28968 / 554 / 2049
Goodness on fit on $F^2$	1.000	0.985
$R_1$ ( $I > 2\sigma(I)$ )	0.0372	0.0674
$wR_2$ (all data)	0.1115	0.2165
Largest diff. peak and hole, e Å <sup>-3</sup>	0.627 / -0.466	1.318 / -0.877

### EHMO analysis

EHMO calculations on the title compounds were carried out by means of the program CACAO<sup>6</sup> using their crystallographic coordinates. These results were used in order to extract both C-C and M-C overlap populations, which have been compared with those of other Ni, Co and Ni-Co carbide clusters previously reported in the literature (CIF files were obtained from the Cambridge Structural Database). A comparison between C-C bond length, C-C overlap population and C-C bond order is reported in figure 1, whereas figure 2 reports a plot of M-C overlap population versus C-C overlap population. These calculations clearly indicate that as the C-C overlap population increases, the M-C overlap population decreases.

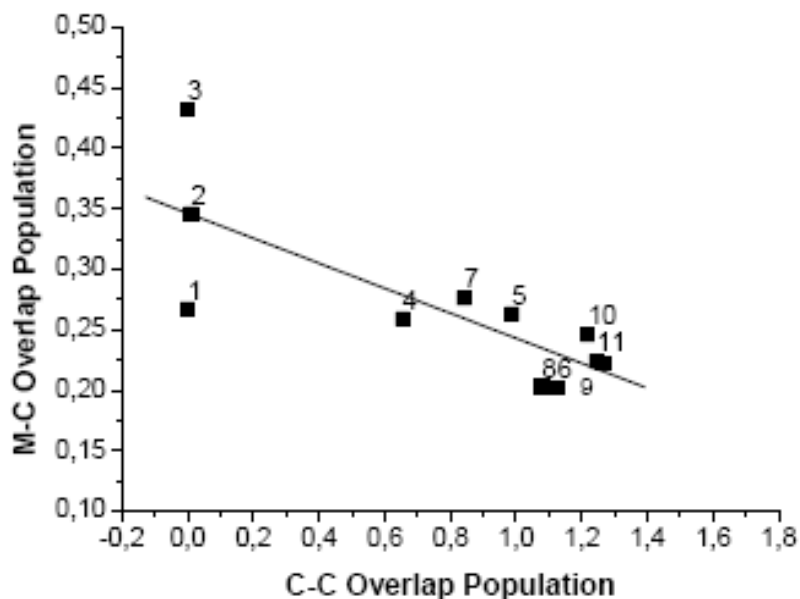
**Figure 1**

Comparison between C-C bond length, C-C overlap population and C-C bond order in a series of molecular acetylide clusters, ionic bulk acetylides and  $C_2H_{2n}$  ( $n = 1-3$ ) molecules [1-  $C_2H_6$ ; 2-  $C_2H_4$ ; 3-  $C_2H_2$ ; 4-  $[Co_{11}C_2(CO)_{22}]^{3-}$ ; 7-  $[Co_9C_2(CO)_{19}]^{3-}$ ; 8-  $[Ni_{10}C_2(CO)_{16}]^{2-}$ ; 9-  $[Co_6Ni_2C_2(CO)_{16}]^{2-}$ ; 10-  $[Ni_{12}C_2(CO)_{16}]^{4-}$ ; 11-  $[Ni_{16}(C_2)_2(CO)_{23}]^{4-}$ ; 12-  $[Ni_{22}(C_2)_4(CO)_{28}(\mu-Cl)]^{3-}$ ; 13-  $[HfNi_{25}(C_2)_4(CO)_{32}]^{3-}$ ; 12-  $C_2^{2-}$  ( $CaC_2$ ); 13-  $C_2^{2-}$  ( $UC_2$ )].



**Figure 2**

Plot of M-C overlap population versus C-C overlap population in acetylide cluster and comparison with the M-C overlap population of octahedral, trigonal prismatic and square antiprismatic monocarbides: 1-  $[Ni_8C(CO)_{16}]^{2-}$ ; 13- 2-  $[Co_6C(CO)_{15}]^{2-}$ ; 14- 3-  $[Fe_6C(CO)_{16}]^{2-}$ ; 15- 4-  $[Co_{11}C_2(CO)_{22}]^{3-}$ ; 7- 5-  $[Co_9C_2(CO)_{19}]^{3-}$ ; 8- 6-  $[Ni_{10}C_2(CO)_{16}]^{2-}$ ; 9- 7-  $[Co_6Ni_2C_2(CO)_{16}]^{2-}$ ; 10- 8-  $[Ni_{12}C_2(CO)_{16}]^{4-}$ ; 11- 9-  $[Ni_{16}(C_2)_2(CO)_{23}]^{4-}$ ; 12- 10-  $[Ni_{22}(C_2)_4(CO)_{28}(\mu-Cl)]^{3-}$ ; 11-  $[HfNi_{25}(C_2)_4(CO)_{32}]^{3-}$ .



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