



Cadmium-substitution promoted by nucleophilic attack of $[\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdX})_2]^{6-}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) carbido carbonyl clusters: Synthesis and characterization of the new $[\text{H}_{7-n}\text{Ni}_{32}\text{C}_4(\text{CO})_{36}(\text{CdX})]^{n-}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}; n = 5, 6, 7$) polycarbide

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ABSTRACT

The reaction of $[\text{Ni}_9\text{C}(\text{CO})_{17}]^{2-}$ with $\text{CdX}_2 \cdot x\text{H}_2\text{O}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) affords the tetra-carbide carbonyl clusters $[\text{H}_{6-n}\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdX})_2]^{n-}$ ($n = 3-6; \text{X} = \text{Cl}, \text{Br}, \text{I}$), which are transformed into the closely related $[\text{H}_{7-n}\text{Ni}_{32}\text{C}_4(\text{CO})_{36}(\text{CdX})]^{n-}$ ($n = 5, 6, 7; \text{X} = \text{Cl}, \text{Br}, \text{I}$) by reaction with OH^- or X^- ions. A detailed crystal analysis clearly indicates that the latter is actually obtained in mixture with $[\text{H}_{7-n}\text{Ni}_{31}\text{C}_4(\text{CO})_{37}(\text{CdX})]^{n-}$ and $[\text{H}_{7-n}\text{Ni}_{33}\text{C}_4(\text{CO})_{37}(\text{CdX})]^{n-}$, which differ only by the presence or the absence of $\text{Ni}(\text{CO})$ fragments. The above mixture can be considered to represent a fully characterized molecular example of “mono-dispersed colloids” of ligand-protected metal nanoparticles.

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1. Introduction

We have previously reported the first examples of bimetallic Ni–Cd polycarbide carbonyl clusters, *i.e.* $[\text{H}_{6-n}\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdCl})_2]^{n-}$ ($n = 3-6$) [1]. These species, as well as other high nuclearity metal carbonyl clusters (MCC) [2] and among them large nickel polycarbides [3], are multivalent, in the sense that they can be reversibly oxidized and reduced without structural alterations. Therefore, it has been proposed that multivalent MCC can behave as molecular nanocapacitors and ideal quantum dots [4,5]. Moreover, their capacitance of ca. 0.7 aF per molecule is comparable to that of quasi mono-dispersed gold colloids stabilized by thiols [6]. The appearance of new electronic properties on nanometric molecular clusters has suggested that metal clusters stabilized in a ligand shell are valid candidates to assemble functional devices for data storage and could potentially represent the ultimate solution for miniaturization in microelectronics and nanolithography [7]. For these purposes, the presence of CdX fragments on the clusters might be exploited for further functionalization and to assist MCC assembly, as recently demonstrated for the $\{\text{Cd}_2\text{Cl}_3[\text{Ni}_6(\text{CO})_{12}]_2\}^{3-}$ dimer [8], or the $\{[\text{Pt}_9(\text{CO})_{18}(\text{CdCl}_2)_2]^{2-}\}_\infty$ infinite chains [9].

From a structural point of view, nickel polycarbide MCC are a quite fascinating class of compounds. The carbide atom is, in fact, too large to fit in an octahedral cavity within a nickel compact metal packing. Thus, larger cavities, such as trigonal prismatic or square anti-prismatic, are needed, resulting in strong deformations of the metal cores of the clusters. These deformations are probably possible since molecular MCC possess quite soft metal cores. Conversely, the periodical conditions imposed by the extended crystal lattices in bulk phases make them more rigid, and this, in addition to electronic reasons, might explain the very low solubility of carbon atoms in bulk nickel, being the ill-defined metastable Ni_3C the only phase reported to date [10]. High nuclearity MCC are at the border between molecules and colloidal metal nanoparticles and, hence, their properties could help in understanding the behaviour in the nanoscale regime. At this regard, it is noteworthy that nickel nanoparticles are among the best catalysts for the preparation of carbon nanotubes, and it has been suggested that both the formation of nickel–carbon species and the low solubility of carbon in nickel metal play a fundamental role in this process [11].

The above considerations prompted a detailed study on the reactivity of $[\text{H}_{6-n}\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdCl})_2]^{n-}$ ($n = 3-6$) with strong bases and nucleophiles, in order to establish their maximum charge and investigate the reactivity of the CdCl functionality and the possibility to obtain unsubstituted $[\text{H}_{6-n}\text{Ni}_{30}\text{C}_4(\text{CO})_{34}]^{n-}$ ($n = 3-6$) species. These findings are reported in this paper,

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together with an extension of our previous work to other halides such as bromine and iodine.

2. Experimental

2.1. 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. The $[\text{NR}_4]_2[\text{Ni}_9\text{C}(\text{CO})_{17}]$ [12], and $[\text{NR}_4]_n[\text{H}_{6-n}\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdCl})_2]$ [1] [$\text{NR}_4 = \text{NEt}_4, \text{NMe}_4, \text{NMe}_3(\text{CH}_2\text{Ph})$; $n = 3-6$] salts have been prepared according to the literature. The analogous $[\text{NR}_4]_n[\text{H}_{6-n}\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdX})_2]$ [$\text{NR}_4 = \text{NEt}_4, \text{NMe}_4, \text{NMe}_3(\text{CH}_2\text{Ph})$; $n = 3-6$; $\text{X} = \text{Br}, \text{I}$] salts have been prepared in a similar way, employing $\text{CdX}_2 \cdot x\text{H}_2\text{O}$ instead of $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$. Analysis of Ni and Cd 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 CaF_2 cells. Structure drawings have been performed with SCHAKAL99 [13].

2.2. Synthesis of $[\text{NMe}_4]_4[\text{H}_2\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdI})_2] \cdot 2\text{COMe}_2$

$\text{CdI}_2 \cdot x\text{H}_2\text{O}$ (0.754 g, 2.06 mmol) was added in portions to a solution of $[\text{NMe}_4]_2[\text{Ni}_9\text{C}(\text{CO})_{17}]$ (1.85 g, 1.59 mmol) in THF (30 mL) with stirring. The mixture was left to react for 3 h, until all the starting $[\text{NMe}_4]_2[\text{Ni}_9\text{C}(\text{CO})_{17}]$ was disappeared by IR monitoring and, then, the resulting dark-brown suspension was evaporated to dryness. The residue was washed with water (40 mL) and THF (30 mL), in order to remove all Ni^{II} and Cd^{II} salts and minor quantities of lower nuclearity Ni–C carbonyl clusters, and finally extracted in acetone (30 mL) resulting in a dark-brown solution of the target compound. Precipitation by slow diffusion of $^i\text{PrOH}$ (60 mL) gave a dark-brown crystalline precipitate composed of crystals of $[\text{NMe}_4]_4[\text{H}_2\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdI})_2] \cdot 2\text{COMe}_2$, (yield 1.15 g, 66.0% based on Ni). The salt is soluble in acetone, acetonitrile, DMF, DMSO, sparingly soluble in THF and alcohols, insoluble in non-polar solvents.

Calc. for $\text{C}_{60}\text{H}_{60}\text{Cd}_2\text{I}_2\text{N}_4\text{Ni}_{30}\text{O}_{36}$ (3653.02): C, 19.73; H, 1.66; N, 1.53; Ni, 48.21; Cd, 6.16. Found: C, 19.92; H, 1.51; N, 1.37; Ni, 48.05; Cd, 6.03%. IR (acetone, 293 K) $\nu(\text{CO})$: 2018(s), 1873(m) cm^{-1} .

The related compounds $[\text{NR}_4]_4[\text{H}_2\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdX})_2]$ [$\text{NR}_4 = \text{NMe}_4, \text{NEt}_4, \text{NBU}_4$; $\text{X} = \text{Br}, \text{I}$], can be obtained following the same procedure as above employing the relative $[\text{NR}_4]_2[\text{Ni}_9\text{C}(\text{CO})_{17}]$ and CdX_2 salts.

2.3. Synthesis of $[\text{NMe}_4]_5[\text{HNI}_{30}\text{C}_4(\text{CO})_{34}(\text{CdBr})_2] \cdot 6\text{MeCN}$

$\text{CdBr}_2 \cdot x\text{H}_2\text{O}$ (0.664 g, 2.44 mmol) was added in portions to a solution of $[\text{NMe}_4]_2[\text{Ni}_9\text{C}(\text{CO})_{17}]$ (1.85 g, 1.59 mmol) in THF (30 mL) with stirring. The mixture was left to react for 3 h, until all the starting $[\text{NEt}_4]_2[\text{Ni}_9\text{C}(\text{CO})_{17}]$ was disappeared by IR monitoring and, then, the resulting dark-brown suspension was evaporated to dryness. The residue was washed with water (40 mL) and THF (30 mL), in order to remove all Ni^{II} and Cd^{II} salts and minor quantities of lower nuclearity Ni–C carbonyl clusters, and finally extracted in acetonitrile (30 mL) resulting in a dark-brown solution of the target compound. Precipitation by slow diffusion of diisopropyl ether (60 mL) gave a dark-brown crystalline precipitate composed of crystals of $[\text{NMe}_4]_5[\text{HNI}_{30}\text{C}_4(\text{CO})_{34}(\text{CdBr})_2] \cdot 6\text{MeCN}$ (yield 1.16 g, 64.7% based on Ni). The salt is soluble in acetonitrile, DMF, DMSO, sparingly soluble in acetone, insoluble in less-polar solvents.

Calc. for $\text{C}_{70}\text{H}_{78}\text{Br}_2\text{Cd}_2\text{N}_{11}\text{Ni}_{30}\text{O}_{34}$ (3763.35): C, 22.34; H, 2.09; N, 4.09; Ni, 46.79; Cd, 5.97. Found: C, 22.56; H, 1.92; N, 4.19; Ni,

46.58; Cd, 5.78%. IR (acetonitrile, 293 K) $\nu(\text{CO})$: 2008(s), 1868(m) cm^{-1} .

The related compounds $[\text{NR}_4]_5[\text{HNI}_{30}\text{C}_4(\text{CO})_{34}(\text{CdX})_2]$ [$\text{NR}_4 = \text{NMe}_4, \text{NEt}_4, \text{NBU}_4$; $\text{X} = \text{Br}, \text{I}$], can be obtained following the same procedure as above employing the relative $[\text{NR}_4]_2[\text{Ni}_9\text{C}(\text{CO})_{17}]$ and CdX_2 salts.

2.4. Synthesis of $[\text{NEt}_4]_5[\text{H}_2\text{Ni}_{32-y}\text{C}_4(\text{CO})_{36-y}(\text{CdBr})] \cdot 2\text{MeCN}$ ($y = 0.22$)

$[\text{NEt}_4]_5[\text{HNI}_{30}\text{C}_4(\text{CO})_{34}(\text{CdBr})_2]$ (1.72 g, 0.505 mmol) was stirred in MeCN (30 mL) for 1 h; IR indicated that the penta-anion $[\text{HNI}_{30}\text{C}_4(\text{CO})_{34}(\text{CdBr}_2)]^{5-}$ partially deprotonated to $[\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdBr}_2)]^{6-}$ under these conditions. $[\text{NEt}_4]\text{Br}$ (0.446 g, 2.12 mmol) was, then, added, and the resulting suspension stirred overnight. The solvent was removed in vacuum, the residue washed with water (40 mL) and THF (40 mL), and finally extracted in MeCN (20 mL). Precipitation by slow diffusion of diisopropyl ether (60 mL) gave a dark-brown crystalline precipitate composed of crystals of $[\text{NEt}_4]_5[\text{H}_2\text{Ni}_{32-y}\text{C}_4(\text{CO})_{36-y}(\text{CdBr})] \cdot 2\text{MeCN}$ ($y = 0.22$) (yield 0.775 g, 42.3% based on Ni). The salt is soluble in acetonitrile, DMF, DMSO, sparingly soluble in acetone, insoluble in less-polar solvents.

Calc. for $\text{C}_{83.79}\text{H}_{106}\text{BrCdN}_7\text{Ni}_{31.78}\text{O}_{35.78}$ (3842.14): C, 26.20; H, 2.78; N, 2.55; Ni, 48.56; Cd, 2.93. Found: C, 26.08; H, 2.59; N, 2.22; Ni, 48.72; Cd, 3.05%. IR (acetonitrile, 293 K) $\nu(\text{CO})$: 2005(s), 1873(m) cm^{-1} .

2.5. Synthesis of $[\text{NMe}_3(\text{CH}_2\text{Ph})]_6[\text{HNI}_{33-y}\text{C}_4(\text{CO})_{37-y}(\text{CdCl})] \cdot 5\text{MeCN}$ ($y = 0.86$)

NaOH (0.58 g, 14.5 mmol) was added to a solution of $[\text{NMe}_3(\text{CH}_2\text{Ph})]_5[\text{HNI}_{30}\text{C}_4(\text{CO})_{34}(\text{CdCl})_2]$ (1.85 g, 0.551 mmol) in MeCN (30 mL) and the resulting suspension stirred overnight before filtration. The solvent was removed in vacuum from the filtrate, the residue washed with water (40 mL) and THF (40 mL), and finally extracted in MeCN (20 mL). Precipitation by slow diffusion of diisopropyl ether (60 mL) gave a dark-brown crystalline precipitate composed of crystals of $[\text{NMe}_3(\text{CH}_2\text{Ph})]_6[\text{HNI}_{33-y}\text{C}_4(\text{CO})_{37-y}(\text{CdCl})] \cdot 5\text{MeCN}$ ($y = 0.86$) (yield 0.821 g, 38.0% based on Ni). The salt is soluble in acetonitrile, DMF, DMSO, sparingly soluble in acetone, insoluble in less-polar solvents.

Calc. for $\text{C}_{110.14}\text{H}_{111}\text{CdClN}_{11}\text{Ni}_{32.14}\text{O}_{36.14}$ (4201.81): C, 31.49; H, 2.66; N, 3.67; Ni, 44.90; Cd, 2.68. Found: C, 31.22; H, 3.85; N, 3.42; Ni, 45.02; Cd, 2.79%. IR (acetonitrile, 293 K) $\nu(\text{CO})$: 1995(s), 1860(m) cm^{-1} .

2.6. X-ray crystallographic study

Crystal data and collection details for $[\text{NMe}_4]_4[\text{H}_2\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdI})_2] \cdot 2\text{COMe}_2$, $[\text{NMe}_4]_5[\text{HNI}_{30}\text{C}_4(\text{CO})_{34}(\text{CdBr})_2] \cdot 6\text{MeCN}$, $[\text{NEt}_4]_5[\text{H}_2\text{Ni}_{32-y}\text{C}_4(\text{CO})_{36-y}(\text{CdBr})] \cdot 2\text{MeCN}$ ($y = 0.22$) and $[\text{NMe}_3(\text{CH}_2\text{Ph})]_6[\text{HNI}_{33-y}\text{C}_4(\text{CO})_{37-y}(\text{CdCl})] \cdot 5\text{MeCN}$ ($y = 0.86$) are reported in Table 1. The diffraction experiments were carried out on a Bruker APEX II diffractometer equipped with a CCD detector using $\text{Mo K}\alpha$ radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS) [14]. Structures were solved by direct methods and refined by full-matrix least-squares based on all data using F^2 [15]. 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.

2.6.1. $[\text{NMe}_4]_4[\text{H}_2\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdI})_2] \cdot 2\text{COMe}_2$

The asymmetric unit contains half of a cluster anion (located on an inversion centre), two $[\text{NMe}_4]^+$ cations and one COMe_2 molecule. These crystals appear to be non-merohedrally twinned. The

Table 1

Crystal data and experimental details for $[\text{NMe}_4]_4[\text{H}_2\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdI})_2] \cdot 2\text{COMe}_2$, $[\text{NMe}_4]_5[\text{HNi}_{30}\text{C}_4(\text{CO})_{34}(\text{CdBr})_2] \cdot 6\text{MeCN}$, $[\text{NET}_4]_5[\text{H}_2\text{Ni}_{32-y}\text{C}_4(\text{CO})_{36-y}(\text{CdBr})] \cdot 2\text{MeCN}$ ($y = 0.22$) and $[\text{NMe}_3(\text{CH}_2\text{Ph})]_6[\text{HNi}_{33-y}\text{C}_4(\text{CO})_{37-y}(\text{CdCl})] \cdot 5\text{MeCN}$ ($y = 0.86$)

	$[\text{NMe}_4]_4[\text{H}_2\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdI})_2] \cdot 2\text{COMe}_2$	$[\text{NMe}_4]_5[\text{HNi}_{30}\text{C}_4(\text{CO})_{34}(\text{CdBr})_2] \cdot 6\text{MeCN}$	$[\text{NET}_4]_5[\text{H}_2\text{Ni}_{32-y}\text{C}_4(\text{CO})_{36-y}(\text{CdBr})] \cdot 2\text{MeCN}$	$[\text{NMe}_3(\text{CH}_2\text{Ph})]_6[\text{HNi}_{33-y}\text{C}_4(\text{CO})_{37-y}(\text{CdCl})] \cdot 5\text{MeCN}$
Formula	$\text{C}_{60}\text{H}_{60}\text{Cd}_2\text{I}_2\text{N}_4\text{Ni}_{30}\text{O}_{36}$	$\text{C}_{70}\text{H}_{78}\text{Br}_2\text{Cd}_2\text{N}_{11}\text{Ni}_{30}\text{O}_{34}$	$\text{C}_{83.79}\text{H}_{106}\text{BrCdN}_7\text{Ni}_{31.78}\text{O}_{35.78}$	$\text{C}_{110.14}\text{H}_{111}\text{CdClN}_{11}\text{Ni}_{32.14}\text{O}_{36.14}$
Fw	3653.02	3763.35	3842.14	4201.81
T (K)	293(2)	294(2)	291(2)	100(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	triclinic	triclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	Cc	$P\bar{1}$
a (Å)	15.116(13)	15.6721(9)	21.3756(15)	14.410(2)
b (Å)	15.098(13)	16.2315(10)	21.0348(15)	14.877(2)
c (Å)	15.520(13)	24.1526(14)	26.4772(19)	18.969(4)
α (°)	116.216(11)	72.0350(10)	90	96.072(3)
β (°)	93.054(12)	78.2020(10)	98.1170(10)	106.007(3)
γ (°)	119.387(10)	66.4070(10)	90	117.543(2)
Cell volume (Å ³)	2598(4)	5332.7(5)	11785.7(15)	3333.6(9)
Z	1	2	4	1
D_{calc} (g cm ⁻³)	2.335	2.344	2.165	2.093
μ (mm ⁻¹)	6.346	6.362	5.524	4.664
F(000)	1778	7556	7668	2103
Crystal size (mm)	0.24 × 0.16 × 0.12	0.22 × 0.15 × 0.11	0.19 × 0.15 × 0.14	0.19 × 0.14 × 0.11
θ limits (°)	1.56–25.02	1.41–25.03	1.36–25.03	1.61–25.03
Index ranges	–17 ≤ h ≤ 17 –17 ≤ k ≤ 17 –18 ≤ l ≤ 18	–18 ≤ h ≤ 18 –19 ≤ k ≤ 19 –28 ≤ l ≤ 28	–25 ≤ h ≤ 25 –25 ≤ k ≤ 25 –31 ≤ l ≤ 31	–17 ≤ h ≤ 17 –17 ≤ k ≤ 17 –22 ≤ l ≤ 22
Reflections collected	21 552	51 494	56 355	31 258
Independent reflections (R_{int})	9080 (0.0845)	18 806 (0.0496)	20 823 (0.1293)	23 058 (0.0411)
Completeness to $\theta = 25.03^\circ$ (%)	99.2	99.7	100.0	99.6
Data/restraints/parameters	9080/761/585	18 806/339/1252	20 823/2516/1322	23 058/2838/1605
Goodness of fit on F^2	1.274	1.023	1.025	1.015
R_1 ($I > 2\sigma(I)$)	0.1122	0.0444	0.0859	0.0559
wR_2 (all data)	0.1268	0.1197	0.2617	0.1465
Largest difference in peak and hole (e Å ⁻³)	4.941/–1.721	0.927/–1.209	2.431/–2.559	2.273/–1.363

TwinRotMat routine of PLATON [16] was used to determine the twinning matrix (–0.001 1.000 –0.001 0.999 0.000 –0.001 –0.999 –1.000 –0.999; two-axis (1 1 –1) [1 1 0]) and to write the reflection data file (.hkl) containing the two twin components. Refinement was performed using the instruction HKLF 5 in SHELX and one BASF parameter, which refined as 0.49909. Because of this heavy twinning and the contemporary presence of many heavy atoms together with light ones, several restraints were applied in order to obtain a satisfactory model, and in particular: similar U restraints were applied to the C and O atoms; rigid bond restraints were applied to the anion and the two independent cations. Restraints to bond distances were applied as follow: 1.15 Å for C–O in the cluster anion; 1.47 Å for C–N in $[\text{NMe}_4]^+$; 1.21 Å for C–O and 1.51 Å for C–C in COMe₂.

2.6.2. $[\text{NMe}_4]_5[\text{HNi}_{30}\text{C}_4(\text{CO})_{34}(\text{CdBr})_2] \cdot 6\text{MeCN}$

The asymmetric unit contains two halves of two independent cluster anions (located on inversion centres), five $[\text{NMe}_4]^+$ cations and six MeCN molecules. The latter were refined isotropically and assuming similar geometries (SAME restraint in SHELX) because of problems in refining these small molecules in the presence of the large metal cluster anions. Similar U restraints were applied to all the C and O atoms, and ISOR restraints were applied to most the O atoms of the carbonyl ligands. Restraints to bond distances were applied as follow: 1.47 Å for C–N in $[\text{NMe}_4]^+$; 1.14 Å for C–N and 1.47 Å for C–C in MeCN.

2.6.3. $[\text{NET}_4]_5[\text{H}_2\text{Ni}_{32-y}\text{C}_4(\text{CO})_{36-y}(\text{CdBr})] \cdot 2\text{MeCN}$ ($y = 0.22$)

The asymmetric unit contains one cluster anion, five $[\text{NET}_4]^+$ cations and two MeCN molecules. The latter were refined isotropically, as above. The crystals appeared to be racemically twinned with a refined Flack parameter of 0.28(4) [17]. The Ni(32) atom with the attached C(40)O(40) carbonyl ligand has a refined occu-

pancy factor of 0.78213. Because of twinning and the contemporary presence of many heavy atoms together with light ones, several restraints were applied in order to obtain a satisfactory model, and in particular: similar U restraints were applied to the Ni, C and O atoms; rigid bond restraints were applied to the anion; the ISOR restraint of SHELX was applied to almost all the O atoms in the anion; similar geometries (SAME restraint in SHELX) were imposed to the $[\text{NET}_4]^+$ cations. Restraints to bond distances were applied as follow: 1.15 Å for C–O in the cluster anion; 1.47 Å for C–N and 1.53 Å for C–C in $[\text{NET}_4]^+$; 1.14 Å for C–N and 1.47 Å for C–C in MeCN.

2.6.4. $[\text{NMe}_3(\text{CH}_2\text{Ph})]_6[\text{HNi}_{33-y}\text{C}_4(\text{CO})_{37-y}(\text{CdCl})] \cdot 5\text{MeCN}$ ($y = 0.86$)

The asymmetric unit contains one cluster anion, six $[\text{NMe}_3(\text{CH}_2\text{Ph})]^+$ cations and five MeCN molecules. The crystals appeared to be racemically twinned with a refined Flack parameter of 0.49(3) [17], generating a pseudo-inversion centre detected by PLATON. A satisfactory solution was obtained, only, in the non-centrosymmetric space group $P\bar{1}$. The Ni(32) atom with the attached C(40)O(40) carbonyl ligand as well as Ni(33), C(41) and O(41) have refined occupancy factors of 0.69410 and 0.44629, respectively. The partial presence of the latter Ni(CO) group generates disorder in one of the six $[\text{NMe}_3(\text{CH}_2\text{Ph})]^+$ cations. This has been split into two positions and refined isotropically using the same occupancy factor of Ni(33)C(41)O(41). Also one of the five MeCN molecules appears to be disordered; its atoms have been split into two positions and refined isotropically with one independent occupancy factor (0.40757 after refinement). Because of twinning, partial disorder and the contemporary presence of many heavy atoms together with light ones, several restraints were applied in order to obtain a satisfactory model, and in particular: similar U restraints were applied to the N, C and O atoms; rigid bond restraints were applied to the anion and to the non-disordered $[\text{NMe}_3(\text{CH}_2\text{Ph})]^+$ cations; the ISOR

restraint of SHELX was applied to the O atoms in the anion; similar geometries (SAME restraint in SHELX) were imposed to the $[\text{NMe}_3(\text{CH}_2\text{Ph})]^+$ cations and to the MeCN molecules. Restraints to bond distances were applied as follow: 1.15 Å for C–O in the cluster anion; 1.14 Å for C–N and 1.47 Å for C–C in MeCN.

3. Results and discussion

3.1. Synthesis and Characterization of the $[\text{H}_{6-n}\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdX})_2]^{n-}$ ($n = 3-6$; $X = \text{Cl, Br, I}$) and $[\text{H}_{7-n}\text{Ni}_{32}\text{C}_4(\text{CO})_{36}(\text{CdX})]^{n-}$ ($X = \text{Cl, Br, I}$; $n = 5, 6, 7$) clusters

It has been previously shown that the reaction of $[\text{Ni}_9\text{C}(\text{CO})_{17}]^{2-}$ with $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ results in the formation of the tetra-carbide clusters $[\text{H}_{6-n}\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdCl})_2]^{n-}$ ($n = 3-6$) [1]. In a similar way, we report here that other Cd(II) hydrated halide salts, such as $\text{CdBr}_2 \cdot x\text{H}_2\text{O}$ and $\text{CdI}_2 \cdot x\text{H}_2\text{O}$, but not $\text{CdF}_2 \cdot x\text{H}_2\text{O}$, give an analogous reaction affording the related clusters $[\text{H}_{6-n}\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdX})_2]^{n-}$ ($n = 3-6$; $X = \text{Br, I}$). These species display IR spectra in solution very similar to the chloride analogues, as well as identical protonation–deprotonation behaviour as a function of the basicity of the solvent or addition of acids or bases (Scheme 1). The crystal structures of the tetra-anion $[\text{H}_2\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdI})_2]^{4-}$ and the penta-anion $[\text{H}\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdBr})_2]^{5-}$, in their $[\text{NMe}_4]_4[\text{H}_2\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdI})_2] \cdot 2\text{COMe}_2$ and $[\text{NMe}_4]_5[\text{H}\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdBr})_2] \cdot 6\text{MeCN}$ salts, have been deliberately determined in order to further demonstrate the possibility to decrease the charge of the parent hexa-anion by protonation. It is noteworthy that whereas addition of acids to the hexa-anions $[\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdX})_2]^{6-}$ ($X = \text{Cl, Br, I}$) results in a progressive lowering (5–, 4– and 3–, as described in Scheme 1) of the charge of the anion, electrochemical studies only disclosed one reversible 6–/5– oxidation step [1]. Accordingly, chemical oxidation of $[\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdX})_2]^{6-}$ ($X = \text{Cl, Br, I}$) with stoichiometric amounts of oxidizing agents such as I_2 , Ag^+ and $[\text{C}_7\text{H}_7][\text{BF}_4]$ only leads to $\text{Ni}(\text{CO})_4$, Ni metal, Ni(II) and Cd(II) salts decomposition products. These results further implements the previous suggestion that the different charges of the anion are due to progressive neutralization of the charge owing to protonation, even if the direct ^1H NMR proof could not be obtained.

The occurrence in solution of the protonation–deprotonation equilibria reported in Scheme 1 prompted a detailed study of the reactivity of these anions with strong bases in order to verify whether $[\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdX})_2]^{6-}$ ($X = \text{Cl, Br, I}$) is completely deprotonated or not. Addition of NaOH to solutions in MeCN or DMF of the hexa-anions $[\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdX})_2]^{6-}$ ($X = \text{Cl, Br, I}$) led to complex mixtures of products, which appeared to arise from attack of the OH^- nucleophile to Cd(II), followed by elimination of the latter from the cluster. In agreement with this hypothesis, it has been possible to separate from the above mixture the $[\text{Ni}_{34}\text{C}_4(\text{CO})_{38}]^{6-}$ cluster [18], which has a structure very closely related to $[\text{H}_{6-n}\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdX})_2]^{n-}$, being the replacement of the two CdX moieties with two $\text{Ni}_2(\text{CO})_2$ fragments the only difference. A more detailed study of the reaction between $[\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdX})_2]^{6-}$ ($X = \text{Cl, Br, I}$) and OH^- has led, now, to the characterization of other

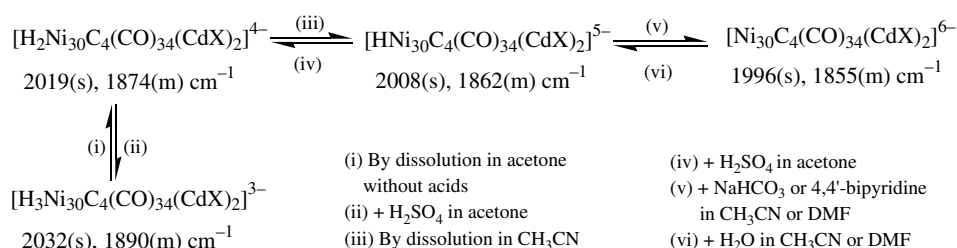
products probably resulting from the nucleophilic attack of OH^- to Cd(II) and elimination of the latter, i.e. the $[\text{Ni}_{31}\text{C}_4(\text{CO})_{35}(\text{CdX})]^{7-}$, $[\text{Ni}_{32}\text{C}_4(\text{CO})_{36}(\text{CdX})]^{7-}$ and $[\text{Ni}_{33}\text{C}_4(\text{CO})_{37}(\text{CdX})]^{7-}$ ($X = \text{Cl, Br, I}$) tetra-carbide clusters. These compounds are always obtained in mixtures and are hardly spectroscopically distinguishable, since they display almost overlapping IR and little diagnostic ESI-MS spectra. All attempted crystallizations of these colloidal solutions of “quasi mono-dispersed ligand-protected metal nanoparticles” afforded single crystals which, as it will be shown in the next Section, contain within the single crystal a mixture of different species. Since in all examined crystals a $[\text{H}_{7-n}\text{Ni}_{32}\text{C}_4(\text{CO})_{36}(\text{CdX})]^{n-}$ species is always present, from now on we will refer to this formula for sake of simplicity.

In the attempt to isolate the homometallic unsubstituted $[\text{H}_{8-n}\text{Ni}_{30}\text{C}_4(\text{CO})_{34}]^{n-}$ cluster, the reaction of halide ions (in the form of $[\text{NR}_4]\text{X}$ salts) with $[\text{H}_{6-n}\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdX})_2]^{n-}$ has been investigated. These reactions resulted in a more convenient synthesis of $[\text{H}_{7-n}\text{Ni}_{32}\text{C}_4(\text{CO})_{36}(\text{CdX})]^{n-}$. The use of X^- nucleophiles enable the sequential removal of Cd(II) yielding $[\text{H}_{7-n}\text{Ni}_{32}\text{C}_4(\text{CO})_{36}(\text{CdX})]^{n-}$ ($X = \text{Cl, Br, I}$; $n = 5-7$) and $[\text{H}_{6-n}\text{Ni}_{34}\text{C}_4(\text{CO})_{38}]^{n-}$ ($n = 4-6$), as a function of their added amounts. This further implements the view that after removal of all hydride atoms, the OH^- nucleophile attacks also the Cd(II) site of $[\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdX})_2]^{6-}$. Since in no instance we could gather evidence of formation of partially or completely Cd(II) depleted $[\text{H}_{7-n}\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdX})]^{n-}$ and $[\text{H}_{8-n}\text{Ni}_{30}\text{C}_4(\text{CO})_{34}]^{n-}$ species, it appears conceivable to think that these species are unstable and Cd(II) removal is accompanied by partial decomposition, which sets free $\text{Ni}(\text{CO})$ fragments. These fragments are intercepted by yet undecomposed $[\text{H}_{7-n}\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdX})]^{n-}$ (or $[\text{H}_{8-n}\text{Ni}_{30}\text{C}_4(\text{CO})_{34}]^{n-}$) species yielding the stable $[\text{H}_{7-n}\text{Ni}_{32}\text{C}_4(\text{CO})_{36}(\text{CdX})]^{n-}$ ($X = \text{Cl, Br, I}$; $n = 5, 6, 7$) (or $[\text{H}_{6-n}\text{Ni}_{34}\text{C}_4(\text{CO})_{38}]^{n-}$) final products. These probably arise from protonation (and eventual oxidation) during the work up of the reaction mixtures. Among these, the $[\text{H}_2\text{Ni}_{32}\text{C}_4(\text{CO})_{36}(\text{CdBr})]^{5-}$ and $[\text{H}\text{Ni}_{32}\text{C}_4(\text{CO})_{36}(\text{CdCl})]^{6-}$ cluster anions have been crystallographically characterized in their $[\text{NET}_4]_5[\text{H}_2\text{Ni}_{32-y}\text{C}_4(\text{CO})_{36-y}(\text{CdBr})] \cdot 2\text{MeCN}$ ($y = 0.22$) and $[\text{NMe}_3(\text{CH}_2\text{Ph})]_6[\text{H}\text{Ni}_{33-y}\text{C}_4(\text{CO})_{37-y}(\text{CdCl})] \cdot 5\text{MeCN}$ ($y = 0.86$) salts, respectively. The fractionary indexes in the crystallographic formula are due to co-crystallization of $[\text{H}_{7-n}\text{Ni}_{32}\text{C}_4(\text{CO})_{36}(\text{CdX})]^{n-}$ with minor amounts of $[\text{H}_{7-n}\text{Ni}_{31}\text{C}_4(\text{CO})_{35}(\text{CdX})]^{n-}$ and $[\text{H}_{7-n}\text{Ni}_{33}\text{C}_4(\text{CO})_{37}(\text{CdX})]^{n-}$ (see next Section).

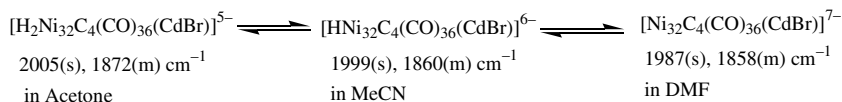
As the related $[\text{H}_{6-n}\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdX})_2]^{n-}$ ($n = 3-6$) and $[\text{H}_{6-n}\text{Ni}_{34}\text{C}_4(\text{CO})_{38}]^{n-}$ ($n = 3-6$) carbonyl clusters, also the new $[\text{H}_{7-n}\text{Ni}_{32}\text{C}_4(\text{CO})_{36}(\text{CdX})]^{n-}$ ($X = \text{Cl, Br, I}$; $n = 5, 6, 7$) tetra-carbides display protonation–deprotonation equilibria depending on the solvent (see Scheme 2). Also in this case, all attempts to directly detect the hydride atoms by means of ^1H NMR or ESI-MS have failed.

3.2. X-ray structures of $[\text{NMe}_4]_4[\text{H}_2\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdI})_2] \cdot 2\text{COMe}_2$, $[\text{NMe}_4]_5[\text{H}\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdBr})_2] \cdot 6\text{MeCN}$, $[\text{NET}_4]_5[\text{H}_2\text{Ni}_{32-y}\text{C}_4(\text{CO})_{36-y}(\text{CdBr})] \cdot 2\text{MeCN}$ ($y = 0.22$) and $[\text{NMe}_3(\text{CH}_2\text{Ph})]_6[\text{H}\text{Ni}_{33-y}\text{C}_4(\text{CO})_{37-y}(\text{CdCl})] \cdot 5\text{MeCN}$ ($y = 0.86$)

The crystal structures of $[\text{NMe}_4]_4[\text{H}_2\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdI})_2] \cdot 2\text{COMe}_2$, $[\text{NMe}_4]_5[\text{H}\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdBr})_2] \cdot 6\text{MeCN}$, $[\text{NET}_4]_5[\text{H}_2\text{Ni}_{32-y}\text{C}_4(\text{CO})_{36-y}(\text{CdBr})] \cdot 2\text{MeCN}$ ($y = 0.22$) and $[\text{NMe}_3(\text{CH}_2\text{Ph})]_6[\text{H}\text{Ni}_{33-y}\text{C}_4(\text{CO})_{37-y}(\text{CdCl})] \cdot 5\text{MeCN}$ ($y = 0.86$)



Scheme 1.



Scheme 2.

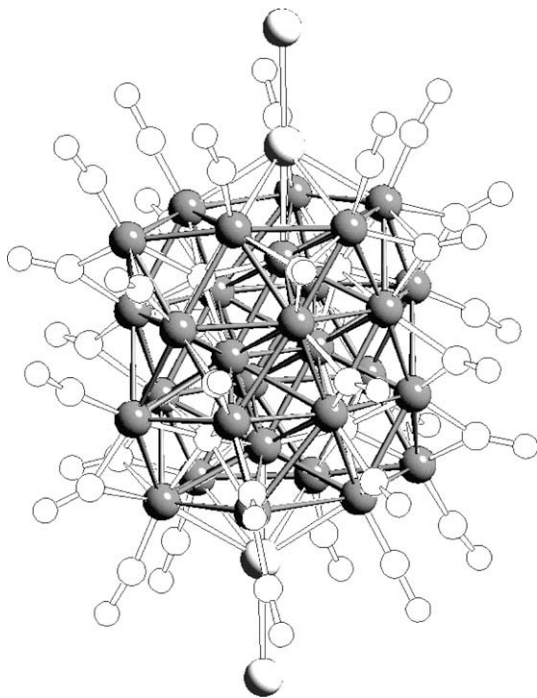


Fig. 1. Molecular structure common to $[\text{H}_2\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdI})_2]^{4-}$ and $[\text{HNi}_{30}\text{C}_4(\text{CO})_{34}(\text{CdBr})_2]^{5-}$.

(CdBr) · 2MeCN ($y = 0.22$) and $[\text{NMe}_3(\text{CH}_2\text{Ph})]_6[\text{HNi}_{33-y}\text{C}_4(\text{CO})_{37-y}(\text{CdCl})] \cdot 5\text{MeCN}$ ($y = 0.86$) have been determined by X-ray diffraction on single crystals (Figs. 1 and 2, Table 2).

The molecular structures of the tetra-anion $[\text{H}_2\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdI})_2]^{4-}$ and the penta-anion $[\text{HNi}_{30}\text{C}_4(\text{CO})_{34}(\text{CdBr})_2]^{5-}$ (Fig. 1 and Table 2) are identical to the ones previously reported for $[\text{H}_2\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdCl})_2]^{4-}$, $[\text{HNi}_{30}\text{C}_4(\text{CO})_{34}(\text{CdCl})_2]^{5-}$ and $[\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdCl})_2]^{6-}$ [1]. Therefore, they are only presented for sake of comparison with those of $[\text{NEt}_4]_5[\text{H}_2\text{Ni}_{32-y}\text{C}_4(\text{CO})_{36-y}(\text{CdBr})] \cdot 2\text{MeCN}$ ($y = 0.22$) and $[\text{NMe}_3(\text{CH}_2\text{Ph})]_6[\text{HNi}_{33-y}\text{C}_4(\text{CO})_{37-y}(\text{CdCl})] \cdot 5\text{MeCN}$ ($y = 0.86$). As shown in Fig. 1, their structure consists of a Ni_{30}C_4 metal carbide core to which are coordinated two CdX fragments condensed on two opposite pentagonal faces.

The crystal structures of $[\text{NEt}_4]_5[\text{H}_2\text{Ni}_{32-y}\text{C}_4(\text{CO})_{36-y}(\text{CdBr})] \cdot 2\text{MeCN}$ ($y = 0.22$) and $[\text{NMe}_3(\text{CH}_2\text{Ph})]_6[\text{HNi}_{33-y}\text{C}_4(\text{CO})_{37-y}(\text{CdCl})] \cdot 5\text{MeCN}$ ($y = 0.86$) (Fig. 2) are described in some more detail. Both salts contain the $[\text{H}_2\text{Ni}_{32-y}\text{C}_4(\text{CO})_{36-y}(\text{CdBr})]^{5-}$ and $[\text{HNi}_{33-y}\text{C}_4(\text{CO})_{37-y}(\text{CdCl})]^{6-}$ anions, which are closely structurally related to $[\text{H}_{6-n}\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdX})_2]^{n-}$ ($n = 3-6$) [1], as well as $[\text{HNi}_{34}\text{C}_4(\text{CO})_{38}]^{5-}$ and $[\text{Ni}_{35}\text{C}_4(\text{CO})_{39}]^{6-}$ [18]. All these carbide clusters, in fact, possess a common Ni_{30}C_4 core, in which two of the four carbide atoms are encapsulated in trigonal prismatic cages and the other two in mono-capped trigonal prismatic cages. Therefore, the coordination numbers of carbon are 6 and 7, respectively. The Ni_{30}C_4 core possesses two opposite pentagonal faces, which are capped by two CdX moieties in $[\text{H}_{6-n}\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdX})_2]^{n-}$. Conversely, addition of two $\text{Ni}_2(\text{CO})_2$ groups onto the pentagonal faces results in the formation of the $[\text{HNi}_{34}\text{C}_4(\text{CO})_{38}]^{5-}$ penta-anion. Further addition of a $\text{Ni}(\text{CO})$ group on a butterfly face of the

cluster (whose addition does not alter the number of cluster valence electrons) gives the related $[\text{Ni}_{35}\text{C}_4(\text{CO})_{39}]^{6-}$ cluster.

The here reported $[\text{H}_2\text{Ni}_{32}\text{C}_4(\text{CO})_{36}(\text{CdX})]^{5-}$ is obtained by adding a CdX group onto one pentagonal face and a $\text{Ni}_2(\text{CO})_2$ onto the other and formally represents the fusion of one half $[\text{H}_2\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdX})_2]^{6-}$ with one half $[\text{H}_2\text{Ni}_{34}\text{C}_4(\text{CO})_{38}]^{4-}$. In the crystal structures of $[\text{NEt}_4]_5[\text{H}_2\text{Ni}_{32-y}\text{C}_4(\text{CO})_{36-y}(\text{CdBr})] \cdot 2\text{MeCN}$ ($y = 0.22$), the $\text{Ni}(\text{CO})$ fragment of the latter $\text{Ni}_2(\text{CO})_2$ moiety not directly bonded to the pentagonal face displays a refined occupancy factor of 0.78. This indicates that the crystal is actually a mixture of $[\text{H}_2\text{Ni}_{32}\text{C}_4(\text{CO})_{36}(\text{CdBr})]^{5-}$ (78%) and $[\text{H}_2\text{Ni}_{31}\text{C}_4(\text{CO})_{35}(\text{CdBr})]^{5-}$ (22%). The two clusters only differs for the presence or absence of a $\text{Ni}(\text{CO})$ fragment on a butterfly face of the cluster surface, which in Fig. 2a is shown with a hatched sphere.

The $[\text{NMe}_3(\text{CH}_2\text{Ph})]_6[\text{HNi}_{33-y}\text{C}_4(\text{CO})_{37-y}(\text{CdCl})] \cdot 5\text{MeCN}$ ($y = 0.86$) is closely related to the above and differs by the following facts. First of all, the $\text{Ni}(\text{CO})$ fragment belonging to the bottom $\text{Ni}_2(\text{CO})_2$ moiety not directly bonded to the pentagonal face displays a refined occupancy factor of 0.69. Secondly, as shown in Fig. 2b, there is a further $\text{Ni}(\text{CO})$ fragment displaying an occupancy factor of 0.45 located on a butterfly face comprising the Cd atom and three vicinal Ni atoms. The most likely interpretation of this crystal structure involves the presence of a mixture of $[\text{HNi}_{33}\text{C}_4(\text{CO})_{37}(\text{CdX})]^{6-}$ (45%), $[\text{HNi}_{32}\text{C}_4(\text{CO})_{36}(\text{CdX})]^{6-}$ (24%) and $[\text{HNi}_{31}\text{C}_4(\text{CO})_{35}(\text{CdX})]^{6-}$ (31%). This would perfectly match the experimental occupancy factors. Conversely, other possible alternative disorder models do not match sufficiently well the experimental occupancy factors.

All these species are systematically obtained as co-crystallized mixtures with variance of compositions, probably because of their very close steric hindrances. Nickel carbonyl clusters differing by the presence of one or more $\text{Ni}(\text{CO})$ fragment are well documented [19]. Consider, for instance the following series of mono-, di-, tetra- and hexa-carbides: $[\text{Ni}_8\text{C}(\text{CO})_{16}]^{2-}$, $[\text{Ni}_9\text{C}(\text{CO})_{17}]^{2-}$ and $[\text{Ni}_{10}\text{C}(\text{CO})_{18}]^{2-}$ [12]; $[\text{Ni}_{11}\text{C}_2(\text{CO})_{15}]^{4-}$ and $[\text{Ni}_{12}\text{C}_2(\text{CO})_{16}]^{4-}$ [20]; $[\text{Ni}_{34}\text{C}_4(\text{CO})_{38}]^{6-}$ and $[\text{Ni}_{35}\text{C}_4(\text{CO})_{39}]^{6-}$ [18]; $[\text{Ni}_{38}\text{C}_6(\text{CO})_{42}]^{6-}$ and $[\text{Ni}_{32}\text{C}_6(\text{CO})_{36}]^{6-}$ [3].

3.3. EHMO analysis

It should be noticed that $[\text{H}_{7-n}\text{Ni}_{31}\text{C}_4(\text{CO})_{35}(\text{CdX})]^{n-}$, $[\text{H}_{7-n}\text{Ni}_{32}\text{C}_4(\text{CO})_{36}(\text{CdX})]^{n-}$, $[\text{H}_{7-n}\text{Ni}_{33}\text{C}_4(\text{CO})_{37}(\text{CdX})]^{n-}$ ($X = \text{Cl}, \text{Br}, \text{I}; n = 5, 6, 7$) and the parent $[\text{H}_{6-n}\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdX})_2]^{n-}$ ($n = 3-6; X = \text{Cl}, \text{Br}, \text{I}$) exhibit $6n + 16$ cluster valence molecular orbitals (CVMO) and feature one more skeletal electron pair SEP than the related $[\text{H}_{6-n}\text{Ni}_{34}\text{C}_4(\text{CO})_{38}]^{n-}$ ($n = 3-6$) and $[\text{Ni}_{35}\text{C}_4(\text{CO})_{39}]^{6-}$ ($6n + 15$ CVMO). The different number of SEPs can be explained on the basis of Extended Hückel molecular orbital (EHMO) analysis [1]. Previous calculations carried out with CACAO [21] by using the crystallographic coordinates of $[\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdI})_2]^{6-}$ and $[\text{Ni}_{34}\text{C}_4(\text{CO})_{38}]^{6-}$ indicated that the two additional electrons present in the former species were due to filling of a weakly-stabilized CVMO essentially originating from interaction of one LUMO of the $[\text{ClCd} \cdots \text{CdCl}]^{2+}$ fragment with an MO of the $[\text{Ni}_{30}\text{C}_4(\text{CO})_{34}]^{8-}$ core. In contrast, owing to the higher energy of the LUMO orbitals of the $[(\text{CO})_2\text{Ni} \cdots \text{Ni}_2(\text{CO})_2]$ fragment, their weak interactions with orbitals of suitable symmetry of the $[\text{Ni}_{30}\text{C}_4(\text{CO})_{34}]^{6-}$ fragment only increase the multitude of empty antibonding energy levels of $[\text{Ni}_{34}\text{C}_4(\text{CO})_{38}]^{6-}$.

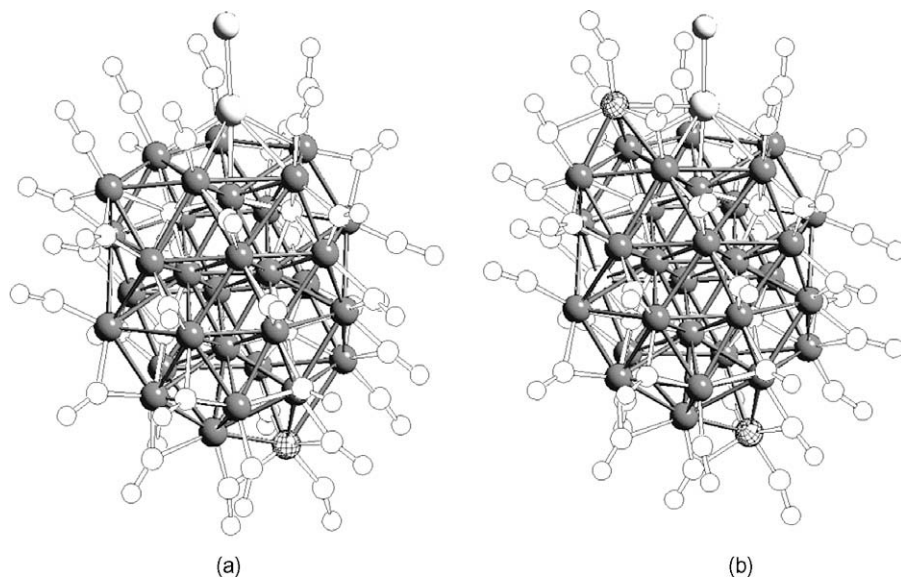


Fig. 2. Molecular structure of (a) $[\text{H}_2\text{Ni}_{32-y}\text{C}_4(\text{CO})_{36-y}(\text{CdBr})]^{5-}$ ($y = 0.22$) and (b) $[\text{HNi}_{33-y}\text{C}_4(\text{CO})_{37-y}(\text{CdCl})]^{6-}$ ($y = 0.86$). [Ni atoms with full occupancy factor are in grey, whereas those with fractionary occupancy factor are hatched; Cd, Cl and Br are shadowed. Distances used for drawing: Ni–Ni 2.34–3.10 Å; Ni–Cd 2.57–2.92 Å.]

Table 2

Average bond distances (Å) in $[\text{H}_2\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdI})_2]^{4-}$, $[\text{HNi}_{30}\text{C}_4(\text{CO})_{34}(\text{CdBr})_2]^{5-}$, $[\text{H}_2\text{Ni}_{32-y}\text{C}_4(\text{CO})_{36-y}(\text{CdBr})]^{5-}$, $[\text{HNi}_{33-y}\text{C}_4(\text{CO})_{37-y}(\text{CdCl})]^{6-}$, $[\text{H}_2\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdCl})_2]^{4-}$, $[\text{HNi}_{30}\text{C}_4(\text{CO})_{34}(\text{CdCl})_2]^{5-}$, $[\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdCl})_2]^{6-}$, $[\text{HNi}_{34}\text{C}_4(\text{CO})_{38}]^{5-}$ and $[\text{Ni}_{35}\text{C}_4(\text{CO})_{39}]^{6-}$.

	Ni–Ni	Ni–C (6) ^a	Ni–C (7) ^b	Ni–Cd
$[\text{H}_2\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdI})_2]^{4-c}$	2.581	1.96	2.00	2.772
$[\text{HNi}_{30}\text{C}_4(\text{CO})_{34}(\text{CdBr})_2]^{5-c}$	2.583	2.00	2.02	2.765
$[\text{H}_2\text{Ni}_{32-y}\text{C}_4(\text{CO})_{36-y}(\text{CdBr})]^{5-c}$	2.587	1.94	2.01	2.766
$[\text{HNi}_{33-y}\text{C}_4(\text{CO})_{37-y}(\text{CdCl})]^{6-c}$	2.584	1.94	2.02	2.728
$[\text{H}_2\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdCl})_2]^{4-d}$	2.593	1.94	2.01	2.764
$[\text{HNi}_{30}\text{C}_4(\text{CO})_{34}(\text{CdCl})_2]^{5-d}$	2.596	1.95	2.01	2.768
$[\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdCl})_2]^{6-d}$	2.599	1.92	2.02	2.757
$[\text{HNi}_{34}\text{C}_4(\text{CO})_{38}]^{5-e}$	2.597	1.94	2.01	2.768
$[\text{Ni}_{35}\text{C}_4(\text{CO})_{39}]^{6-e}$	2.596	1.94	2.03	

^a Average Ni–C distance in the trigonal prismatic cavities.

^b Average Ni–C distance in the capped trigonal prismatic cavities.

^c This work.

^d See Ref. [1].

^e See Ref. [18].

Similar calculations carried out on $[\text{Ni}_{32}\text{C}_4(\text{CO})_{36}(\text{CdCl})]^{7-}$, combining the molecular orbitals of a $[\text{Ni}_{30}\text{C}_4(\text{CO})_{34}]^{8-}$ fragment (Fig. 3, left side) with those of a $[(\text{CO})_2\text{Ni}_2\cdots\text{CdCl}]^+$ fragment (Fig. 3, right side), points out a related interaction between the lower energy LUMO of the $[(\text{CO})_2\text{Ni}_2\cdots\text{CdCl}]^+$ fragment (FMO 576), which is mainly composed by Cd-based orbitals (Fig. 4a). Its combination with orbitals of the $[\text{Ni}_{30}\text{C}_4(\text{CO})_{34}]^{8-}$ fragment originates a low-lying CVMO. Conversely, the second LUMO, centred on the $\text{Ni}_2(\text{CO})_2$ group (FMO 575, Fig. 4b), mainly combines to give an empty antibonding orbitals. Therefore, a single $[\text{CdCl}]^+$ fragment is enough to increase the overall number of SEPs from 15, as in $[\text{Ni}_{34}\text{C}_4(\text{CO})_{38}]^{6-}$, to 16, as in $[\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdCl})_2]^{6-}$ and $[\text{Ni}_{32}\text{C}_4(\text{CO})_{36}(\text{CdCl})]^{7-}$. Similar considerations apply to the closely related $[\text{Ni}_{31}\text{C}_4(\text{CO})_{35}(\text{CdCl})]^{7-}$ and $[\text{Ni}_{33}\text{C}_4(\text{CO})_{37}(\text{CdCl})]^{7-}$ species, since on the basis of the capping principle [22] the addition or elimination of Ni(CO) fragments does not influence the number of SEPs of the cluster. Moreover, an inspection of Fig. 3 shows that the molecular orbitals of the $[\text{Ni}_{30}\text{C}_4(\text{CO})_{34}]^{8-}$ fragment slightly decrease in energy after combination with the $[(\text{CO})_2\text{Ni}_2\cdots\text{CdCl}]^+$ fragment,

resulting in the stabilization of the molecule compared to the free fragments.

Finally, the frontier region of the EHMO diagram (in the -11.2 to -9.3 eV interval of energy) for $[\text{Ni}_{32}\text{C}_4(\text{CO})_{36}(\text{CdCl})]^{7-}$ displays 18 closely spaced MOs in an energy interval of less than 2 eV, and a well defined HOMO–LUMO gap can be hardly identified, as previously found for the analogous $[\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdCl})_2]^{6-}$ and $[\text{Ni}_{34}\text{C}_4(\text{CO})_{38}]^{6-}$ [1]. In keeping with these semi-empirical calculations,

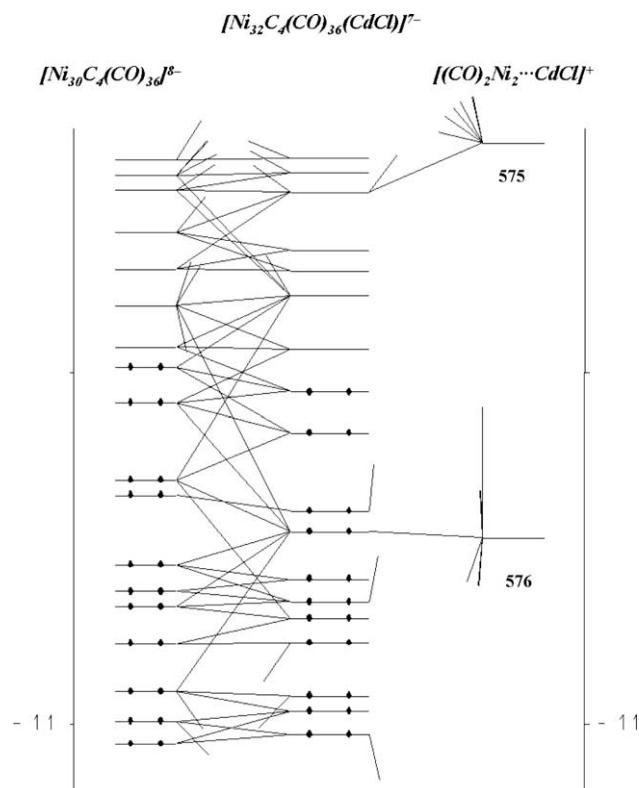


Fig. 3. Frontier region (in the -11.2 to -9.3 eV interval of energy) of the EHMO diagram of $[\text{Ni}_{32}\text{C}_4(\text{CO})_{36}(\text{CdCl})]^{7-}$.

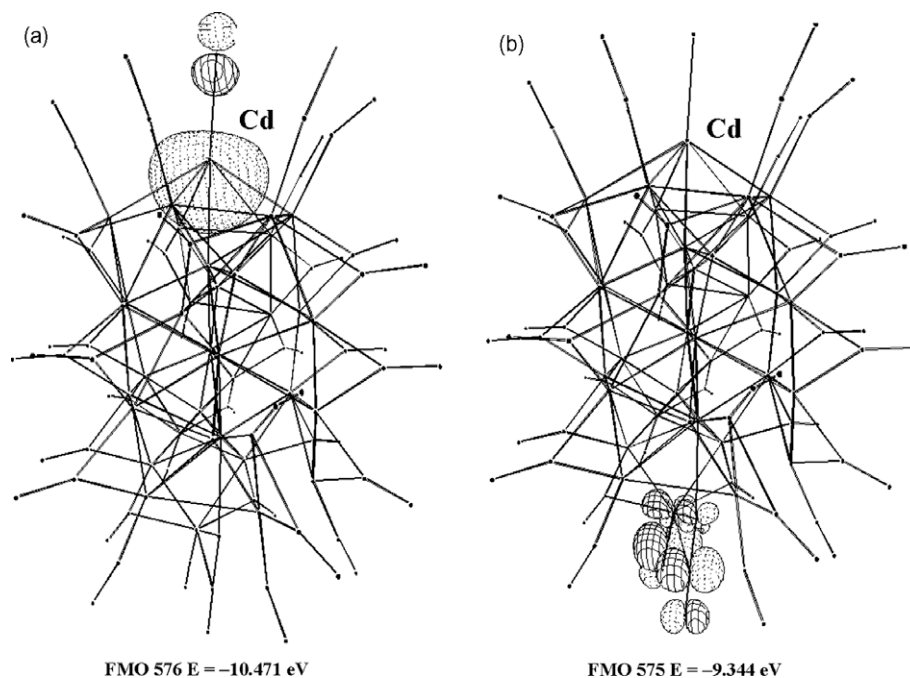


Fig. 4. First (a) and second (b) LUMO of the $[(\text{CO})_2\text{Ni}_2 \cdots \text{CdCl}]^+$ fragment.

both $[\text{H}_{6-n}\text{Ni}_{34}\text{C}_4(\text{CO})_{38}]^{n-}$ and $[\text{H}_{6-n}\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdX})_2]^{n-}$ displayed several electrochemically reversible redox processes. As previously reported [1], observation of both their oxidation and reduction steps were hampered by occurrence of protonation–deprotonation equilibria in the miscellaneous solvents and could be clarified only by studying the completely deprotonated species. Related complications, further enhanced by the fact that the $[\text{H}_{7-n}\text{Ni}_{32}\text{C}_4(\text{CO})_{36}(\text{CdX})]^{n-}$ cluster is always a mixture of the former with $[\text{H}_{7-n}\text{Ni}_{31}\text{C}_4(\text{CO})_{35}(\text{CdCl})]^{7-}$ and $[\text{H}_{7-n}\text{Ni}_{33}\text{C}_4(\text{CO})_{37}(\text{CdCl})]^{7-}$, so far hindered reliable interpretations of their cyclic voltammetric behaviour.

4. Conclusions

The full series of $[\text{H}_{6-n}\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdX})_2]^{n-}$ ($n = 3–6$; $X = \text{Cl}, \text{Br}, \text{I}$) carbonyl polycarbide cluster has been completely characterized, showing that the nature of the halide coordinated to Cd(II) does not alter the chemistry and structures of these clusters. The reaction of $[\text{H}_{6-n}\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdX})_2]^{n-}$ ($X = \text{Cl}, \text{Br}, \text{I}$) with NaOH affords the new $[\text{Ni}_{32}\text{C}_4(\text{CO})_{36}(\text{CdX})]^{7-}$ ($X = \text{Cl}, \text{Br}, \text{I}$) species, whereas X^- ions lead to the corresponding protonated $[\text{H}_{7-n}\text{Ni}_{32}\text{C}_4(\text{CO})_{36}(\text{CdX})]^{n-}$ ($X = \text{Cl}, \text{Br}, \text{I}$; $n = 5, 6, 7$) species. First of all, these results confirm our previous hypothesis on the total number of hydride atoms contained in $[\text{H}_{6-n}\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdX})_2]^{n-}$ ($n = 3–6$; $X = \text{Cl}, \text{Br}, \text{I}$). Indeed, after formation of the hexa-anion no further deprotonation occurs and nucleophilic attack of Cd(II) takes place. As previously discussed [1], detection of the number or even the presence of hydride atoms in high nuclearity Ni clusters is not trivial. ^1H NMR is, in fact, completely silent for these species and, therefore, hydrides have to be indirectly detected on the basis of circumstantial chemical evidence, eventually supported by electrochemical studies.

Secondly, the fact that $[\text{H}_{7-n}\text{Ni}_{32}\text{C}_4(\text{CO})_{36}(\text{CdX})]^{n-}$ ($X = \text{Cl}, \text{Br}, \text{I}$; $n = 5, 6, 7$) species is always obtained in mixture with $[\text{H}_{7-n}\text{Ni}_{31}\text{C}_4(\text{CO})_{35}(\text{CdX})]^{n-}$ and $[\text{H}_{7-n}\text{Ni}_{33}\text{C}_4(\text{CO})_{37}(\text{CdX})]^{n-}$ sheds some more light on the reaction course between $[\text{H}_{6-n}\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdX})_2]^{n-}$ ($X = \text{Cl}, \text{Br}, \text{I}$) and nucleophiles. Overall, it seems that addition of X^- to $[\text{H}_{6-n}\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdX})_2]^{n-}$ ($X = \text{Cl}, \text{Br}, \text{I}$) results, first, in the removal of one $[\text{CdX}]^+$ fragment leading to an unstable

$[\text{H}_{7-n}\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdX})]^{n-}$ species. The latter partially decomposes generating Ni(CO) fragments, which can be intercepted by yet undecomposed $[\text{H}_{7-n}\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdX})]^{n-}$ species to give the new $[\text{H}_{7-n}\text{Ni}_{31}\text{C}_4(\text{CO})_{35}(\text{CdX})]^{n-}$, $[\text{H}_{7-n}\text{Ni}_{32}\text{C}_4(\text{CO})_{36}(\text{CdX})]^{n-}$ and $[\text{H}_{7-n}\text{Ni}_{33}\text{C}_4(\text{CO})_{37}(\text{CdX})]^{n-}$ carbide clusters. Such a reaction course would justify the relatively low yields of the reaction and the systematic formation of colloidal mixtures of quasi mono-dispersed molecular clusters. Removal of the second CdX unit by NaOH or X^- , causes further decomposition, which generates the Ni(CO) fragments necessary in order to stabilize $[\text{Ni}_{34}\text{C}_4(\text{CO})_{38}]^{6-}$.

From a structural point of view, it is noteworthy that all the $[\text{H}_{6-n}\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdX})_2]^{n-}$ ($n = 3–6$; $X = \text{Cl}, \text{Br}, \text{I}$) and $[\text{H}_{7-n}\text{Ni}_{32}\text{C}_4(\text{CO})_{36}(\text{CdX})]^{n-}$ ($X = \text{Cl}, \text{Br}, \text{I}$; $n = 5, 6, 7$) species here described, as well as the previously reported $[\text{HNi}_{34}\text{C}_4(\text{CO})_{38}]^{5-}$ and $[\text{Ni}_{35}\text{C}_4(\text{CO})_{39}]^{6-}$ carbide clusters [18], have in common the same Ni_{30}C_4 metal carbide framework, suggesting a remarkable stability of this moiety. So far, we did not obtain any clue of the possible existence of an unsubstituted $[\text{H}_{6-n}\text{Ni}_{30}\text{C}_4(\text{CO})_{34}]^{n-}$ species. It seems conceivable to suggest that such a lack of evidence is favoured by the fact that removal of Cd(II) with X^- (or OH^-) from $[\text{H}_{6-n}\text{Ni}_{30}\text{C}_4(\text{CO})_{34}(\text{CdX})_2]^{n-}$ would generate an electron-rich $[\text{H}_{6-n}\text{Ni}_{30}\text{C}_4(\text{CO})_{34}]^{(n+2)-}$ species displaying $6n + 16$, rather than $6n + 15$, filled CVMO and two coordinatively-unsaturated pentagonal faces.

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Appendix A. Supplementary material

CCDC 682380, 682381, 682382 and 682383 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary

data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2008.06.010.

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