Electron-Sink Behaviour of the Carbonylnickel Clusters $[Ni_{32}C_6(CO)_{36}]^{6-}$ and $[Ni_{38}C_6(CO)_{42}]^{6-}$: Synthesis and Characterization of the Anions $[Ni_{32}C_6(CO)_{36}]^{n-}$ (n = 5–10) and $[Ni_{38}C_6(CO)_{42}]^{n-}$ (n = 5–9) and Crystal Structure of $[PPh_3Me]_6[Ni_{32}C_6(CO)_{36}] \cdot 4\ MeCN$

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The hexacarbide clusters $[H_{6-n}Ni_{38}C_6(CO)_{42}]^{n-}$ (n = 3, 4, 5, or 6) have been directly obtained from the reaction of $[Ni_6(CO)_{12}]^{2-}$ with C_3Cl_6, whereas the related anions, $[H_{6-n}Ni_{32}C_6(CO)_{36}]^{n-}$ (n = 5 or 6), have been obtained by degradation under carbon monoxide of $[Ni_{38}C_6(CO)_{42}]^{6-}$, or upon thermal treatment at ca. 110 °C of $[Ni_{10}C_2(CO)_{16}]^{2-}$ salts. The compound $[PPh_3Me]_6[Ni_{32}C_6(CO)_{36}] \cdot 4$ MeCN is triclinic, space group $P\bar{1}$ (No 2), with a = 15.974(3), b = 17.474(3), c = 18.200(4) Å, α = 61.37(2), β = 69.31(2), γ = 72.35(2)° and Z = 1; final R = 0.033. The structure of $[Ni_{32}C_6(CO)_{36}]^{6-}$ has an idealised O_h symmetry and is based on a truncated octahedral $Ni_{32}C_6$ framework, with all edges spanned by bridging carbonyl groups. The six interstitial carbide atoms are lodged in square-antiprismatic cavities. The overall geometry of the $Ni_{32}C_6$ core is very similar to that found previously in $[HNi_{38}C_6(CO)_{42}]^{5-}$, and shows very close interatomic separations. Both $[Ni_{32}C_6(CO)_{36}]^{6-}$ and $[H_{6-n}Ni_{38}C_6(CO)_{42}]^{n-}$ (n = 5 or 6) display electron-sink behaviour. Thus, they have been chemically and electrochemically reduced to their corresponding $[Ni_{32}C_6(CO)_{36}]^{n-}$ (n = 7–10), $[Ni_{38}C_6(CO)_{42}]^{n-}$ (n = 7–9) and $[HNi_{38}C_6(CO)_{42}]^{n-}$ (n = 6–8) derivatives, and several of the involved redox changes show features of electrochemical reversibility. In contrast, both $[Ni_{32}C_6(CO)_{36}]^{6-}$ and $[H_{6-n}Ni_{38}C_6(CO)_{42}]^{n-}$ (n = 5 or 6) support only one partially reversible oxidation step. Their different behaviour upon protonation or oxidation is an indirect, but unambiguous, proof of the hydride nature of $[HNi_{32}C_6(CO)_{36}]^{5-}$ and $[H_{6-n}Ni_{38}C_6(CO)_{42}]^{n-}$ (n = 3, 4, or 5), which could not be validated by ^{1}H-NMR spectroscopy.

Introduction

Homoleptic carbonyl transition metal clusters show little propensity for multiple redox changes.[1−3] Only some exceptional compounds feature different (three or more) oxidation states which are stable, or sufficiently long-lived, to permit isolation or spectroscopic characterisation of the species. Among these exceptions there are examples of both homo-, e.g. $[Ir_{14}(CO)_{27}]^{n-}$ (n = 0, 1, 2),[4] and heterometallic clusters, e.g. $[Fe_3Pt_3(CO)_{15}]^{n-}$ (n = 0, 1, 2),[5,6] $[Ag_{13}Fe_8(CO)_{32}]^{n-}$ (n = 3, 4, 5),[7] and $[AuFe_4(CO)_{16}]^{n-}$ (n = 1, 2, 3);[8] a few more associate group 14−16 elements, e.g. $[Co_{13}C_2(CO)_{30}]^{n-}$ (n = 3, 4, 5, 6),[9,2c] $[Co_9Si(CO)_{23}]^{n-}$ (n = 2, 3, 5),[10] $[Ni_{11}Bi_2(CO)_{18}]^{n-}$ (n = 2, 3, 4),[11] $[Ni_{13}Sb_2(CO)_{24}]^{n-}$ (n = 2, 3, 4),[12] and $[Fe_5S_2(CO)_{14}]^{n-}$ (n = 0, 1, 2),[13] in their cluster cores. EHMO[6,7b,8] as well as LDF[14] calculations suggest that the redox aptitude of some clusters descends from ad hoc electronic conditions such as the presence within the HOMO-LUMO gap of a low-lying delocalised orbital, non-bonding or slightly antibonding in character; this can be filled or depleted of electrons without significant destabilisation of the cluster. In other cases, such as $[Co_{13}C_2(CO)_{30}]^{n-}$ and $[Co_9Si(CO)_{23}]^{n-}$, a synergy between steric (good fit of the cavity) and electronic (extra-stabilisation arising from Co−C or Co−Si bonds) effects seems to be operative.

Only very few homoleptic carbonyl clusters, viz. $[Pt_{19}(CO)_{22}]^{4-}$,[15,2c] $[Pt_{24}(CO)_{30}]^{2-}$,[16] and $[HFe_6Pd_6(CO)_{24}]^{3-}$[17] display a wider redox aptitude. In particular the former two homometallic clusters undergo two consecutive pairs of close-spaced one-electron reductions, as well as two close-spaced one-electron oxidations. Several of the above redox changes display features of electrochemical reversibility, even if most electrogenerated species are only stable on the timescale of cyclic voltammetry.

Multivalent carbonyl metal clusters are of interest for several reasons. First of all, the knowledge of their structural parameters and/or spectroscopic behaviour can validate their theoretical analysis (a procedure defined by L. F. Dahl as ‘experimental quantomechanics’). Secondly, the intrinsically paramagnetic odd-electron species are molecular quantum dots.[14] Finally, anionic multivalent clusters in conjunction with cationic multivalent counterparts may give rise to ionic materials, hopefully with interesting electronic and magnetic behaviour. Ionic solids in which both

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the cation and the anion are organometallic clusters have already been prepared.[18]

In the search for new multivalent anionic systems we reinvestigated the chemistry of the nickel carbido-carbonyl clusters.[19] As a result, we report the synthesis and chemical and structural characterisation of the $[Ni_{32}C_6(CO)_{36}]^{6-}$ and $[HNi_{32}C_6(CO)_{36}]^{5-}$ clusters. The study of the electrochemical redox behaviour of both $[Ni_{32}C_6(CO)_{36}]^{6-}$ and $[H_{6-n}Ni_{38}C_6(CO)_{42}]^{n-}$ (n = 5 or 6) points out that these clusters show electron-sink features. Both compounds withstand several reversible electrochemical and chemical reduction steps. In contrast, they feature only a single one-electron oxidation step and the resulting species of this exhibits a limited stability. This lack of propensity for oxidation provides indirect but unambiguous proof of the hydride nature of $[HNi_{32}C_6(CO)_{36}]^{5-}$ and $[H_{6-n}Ni_{38}C_6(CO)_{42}]^{n-}$ (n = 3, 4, or 5), which could not be validated by proton NMR experiments.

Preliminary reports on the synthesis and structure of $[Ni_{32}C_6(CO)_{36}]^{6-}$ and $[HNi_{38}C_6(CO)_{42}]^{5-}$ have already appeared.[20][21]

Results and Discussion

Synthesis, Chemical Reactivity, and Spectroscopic Behaviour of $[HNi_{32}C_6(CO)_{36}]^{5-}$, $[Ni_{32}C_6(CO)_{36}]^{n-}$ (n = 5−8), $[H_{6-n}Ni_{38}C_6(CO)_{42}]^{n-}$ (n = 3−5), and $[Ni_{38}C_6(CO)_{42}]^{n-}$ (n = 5−8)

Previous work carried out showed that the reaction of the $[Ni_6(CO)_{12}]^{2-}$ dianion with C_3Cl_6 in THF or acetone as solvent leads to the formation of the $[HNi_{38}C_6(CO)_{42}]^{5-}$ hexacarbide cluster in low yields.[20] A re-investigation of the above reaction has shown that slight modifications of the reaction procedure have beneficial effects on the yields. In particular, the changes include: i) the use of a dild. THF solution of C_3Cl_6 which is slowly added in small portions to a THF solution of $[NEt_4]_2[Ni_6(CO)_{12}]$ up to a 1:2 molar ratio, ii) the continuous removal of the reaction atmosphere with a slow stream of nitrogen to avoid the build-up of a carbon monoxide partial pressure, and iii) the cooling of the reaction solution at ca. −15°C to minimise the stripping of $Ni(CO)_4$ vapour. Under these conditions, IR monitoring of the reaction shows that $[Ni_6(CO)_{12}]^{2-}$ is initially oxidised by C_3Cl_6 to $[Ni_7(CO)_{15}]^{2-}$ and $[Ni_9(CO)_{18}]^{2-}$; this step requires ca. 0.3 moles of C_3Cl_6 per mol of $[Ni_6(CO)_{12}]^{2-}$. The subsequent addition of a similar amount of C_3Cl_6 gives rise to a solution containing $Ni(CO)_4$, a yet uncharacterised brown species [ν_{CO} in THF at 2019 (s), 1856 (mw), and 1829 (sh) cm^{-1}] and a dark precipitate. At this stage the reaction mixture is left to stand for 24−48 hours at room temp. under a static nitrogen atmosphere. During this period it precipitates further. Extraction of the precipitate with acetone, acetonitrile, and DMSO sequentially affords three fractions containing $[H_2Ni_{38}C_6(CO)_{42}]^{4-}$, $[HNi_{38}C_6(CO)_{42}]^{5-}$, and $[Ni_{38}C_6(CO)_{42}]^{6-}$ respectively. Formation of the $[H_{6-n}Ni_{38}C_6(CO)_{42}]^{n-}$ (n = 4, 5) hydrides, in addition to the parent $[Ni_{38}C_6(CO)_{42}]^{6-}$ hexaanion, can probably be ascribed to the intrinsic acidity of the reaction solution owing to formation of Ni^{2+} salts during the reaction, and the presence of humidity. The above mixture can be converted into pure $[NEt_4]_6[Ni_{38}C_6(CO)_{42}]$ by direct extraction of the residue in DMSO and precipitation with water. Other quaternary ammonium or phosphonium salts of $[Ni_{38}C_6(CO)_{42}]^{6-}$ have been isolated by metathesis with their corresponding halides in DMSO and precipitation with water.

Addition of stoichiometric amounts of acids yields further products, e.g. dild. H_2SO_4, to an acetonitrile solution of $[Ni_{38}C_6(CO)_{42}]^{6-}$ sequentially, affords $[HNi_{38}C_6(CO)_{42}]^{5-}$ and $[H_2Ni_{38}C_6(CO)_{42}]^{4-}$, as shown by a progressive shift to higher wavenumbers of the carbonyl absorptions. The latter is obtained in a spectroscopically pure form only on switching to acetone as solvent. In this latter solvent addition of a further amount of acid leads to the formation of $[H_3Ni_{38}C_6(CO)_{42}]^{3-}$, which slowly decomposes to an (as yet) uncharacterised species. The $[H_{6-n}Ni_{38}C_6(CO)_{42}]^{n-}$ (n = 3−5), as well as the related $[Ni_{38}C_6(CO)_{42}]^{n-}$ (n = 5−8) species (see below), share a common characteristic infrared pattern consisting of three equally intense bands, one in the terminal and two in the edge bridging region; the absorptions wavenumbers of all above compounds are collected in Table 1. We have been unable to directly and unambiguously demonstrate the presence of hydride atoms by ^1H NMR spectroscopy in any of the $[H_{6-n}Ni_{38}C_6(CO)_{42}]^{n-}$ (n = 3−5) derivatives, probably as a result of the too low molar concentrations which can be obtained in both acetone and acetonitrile. However, as previously reported, the apparent partial or quantitative reduction occurring on dissolving the $[H_{6-n}Ni_{38}C_6(CO)_{42}]^{n-}$ (n = 3−5) salts in organic solvents with increasing dielectric constants can only be reasonably interpreted as due to the occurrence in solution of protonation-deprotonation equilibria, such as those reported in Eq. (1) and (2).

Table 1. Infrared carbonyl absorptions (± 2 cm^{-1}) of the $[H_{6-n}Ni_{38}C_6(CO)_{42}]^{n-}$ (n = 3−6) and $[Ni_{38}C_6(CO)_{42}]^{n-}$ (n = 5−8) derivatives

Compound	Solvent	ν_{CO} [cm^{-1}]
$[H_3Ni_{38}C_6(CO)_{42}]^{3-}$	acetone	2031 (s), 1920 (s), 1902 (s)
$[H_2Ni_{38}C_6(CO)_{42}]^{4-}$	acetone	2016 (s), 1909 (s), 1892 (s)
$[HNi_{38}C_6(CO)_{42}]^{5-}$	acetone	2006 (s), 1891 (s), 1878 (s)
$[HNi_{38}C_6(CO)_{42}]^{5-}$	acetonitrile	2005 (s), 1890 (s), 1876 (s)
$[Ni_{38}C_6(CO)_{42}]^{5-}$	acetonitrile	2006 (s), 1889 (s), 1875 (s)
$[Ni_{38}C_6(CO)_{42}]^{6-}$	acetonitrile	1992 (s), 1877 (s), 1862 (s)
$[Ni_{38}C_6(CO)_{42}]^{6-}$	DMF	1989 (s), 1874 (s), 1859 (s)
$[Ni_{38}C_6(CO)_{42}]^{7-}$	DMF	1978 (s), 1858 (s), 1847 (s)
$[Ni_{38}C_6(CO)_{42}]^{8-}$	DMF	1960 (s), 1845 (s), 1832 (s)

$$[H_2Ni_{38}C_6(CO)_{42}]^{4-} \underset{}{\overset{MeCN}{\rightleftharpoons}} [HNi_{38}C_6(CO)_{42}]^{5-} + H^+ \quad (1)$$

$$[HNi_{38}C_6(CO)_{42}]^{5-} \overset{DMSO}{\rightleftharpoons} [Ni_{38}C_6(CO)_{42}]^{6-} + H^+ \quad (2)$$

Moreover, the presence of hydride atoms has now been indirectly, but unambiguously, proved by the electrochemical experiments (see below).

The $[Ni_{38}C_6(CO)_{42}]^{6-}$ hexaanion in DMF is sequentially reduced by the addition of a sodium/naphthalene solution to the corresponding $[Ni_{38}C_6(CO)_{42}]^{7-}$ and $[Ni_{38}C_6(CO)_{42}]^{8-}$ polyanions. Both these two new derivatives show the characteristic IR pattern of the parent compound and are apparently stable in solution under a nitrogen atmosphere for several hours. Nevertheless, their attempted isolation by precipitation with quaternary ammonium or phosphonium salts failed owing to their partial or complete reoxidation to the hexaanion. Addition of a further amount of the reducing agent to $[Ni_{38}C_6(CO)_{42}]^{8-}$ causes a further shift of the carbonyl absorptions to lower wavenumber; however, the IR pattern appears less distinctive and this can probably be attributed to a $[Ni_{38}C_6(CO)_{42}]^{9-}$ species, as in this instance the band due to the stretching of edge bridging carbonyls is too close to the carbonyl infrared band of DMF.

The $[Ni_{38}C_6(CO)_{42}]^{8-}$ is sequentially oxidised by stoichiometric amounts of tropylium tetrafluoroborate to $[Ni_{38}C_6(CO)_{42}]^{7-}$, $[Ni_{38}C_6(CO)_{42}]^{6-}$, and $[Ni_{38}C_6(CO)_{42}]^{5-}$. The $[Ni_{38}C_6(CO)_{42}]^{5-}$ pentaanion shows infrared carbonyl absorptions practically coincident with those of $[HNi_{38}C_6(CO)_{42}]^{5-}$; however, the different nature of the two is pointed out by the fact that the former is observed in a highly ionising medium such as DMF, where the latter undergoes a ready deprotonation. Addition of one further equiv. of tropylium tetrafluoroborate to $[Ni_{38}C_6(CO)_{42}]^{5-}$ results in its complete decomposition to $Ni(CO)_4$ and an insoluble amorphous black material. The failure to obtain infrared spectroscopic evidence for the possible existence of $[Ni_{38}C_6(CO)_{42}]^{n-}$ (n = 3, 4) upon oxidation with tropylium tetrafluoroborate can also be taken as circumstantial evidence of the hydride nature of the $[H_{6-n}Ni_{38}C_6(CO)_{42}]^{n-}$ (n = 3, 4, 5) derivatives resulting upon addition of protonic acids to $[Ni_{38}C_6(CO)_{42}]^{6-}$. The enhanced stability of $[H_{6-n}Ni_{38}C_6(CO)_{42}]^{n-}$ (n = 3−5) with respect to their corresponding $[Ni_{38}C_6(CO)_{42}]^{n-}$ (n = 3−5) anions can probably be ascribed to the fact that protonation, in contrast to oxidation, leaves unchanged the number of valence electrons of the cluster.

The $[H_{6-n}Ni_{38}C_6(CO)_{42}]^{n-}$ (n = 4 and 5) derivative is unstable with respect to carbon monoxide at atmospheric pressure and decomposes principally to a mixture of $Ni(CO)_4$ and an insoluble black material. Only minor amounts of the new $[Ni_{32}C_6(CO)_{36}]^{6-}$ hexaanion could be recovered. For n = 4, the decomposition above is probably favoured by the instability of the corresponding $[H_2Ni_{32}C_6(CO)_{36}]^{4-}$ species (vide infra). In contrast, the $[Ni_{38}C_6(CO)_{42}]^{6-}$ hexaanion affords $[Ni_{32}C_6(CO)_{36}]^{6-}$ almost quantitatively according to Eq. (3).

$$[Ni_{38}C_6(CO)_{42}]^{6-} + 18\,CO \underset{CO\ (1\ atm)}{\overset{MeCN}{\rightleftharpoons}} [Ni_{32}C_6(CO)_{36}]^{6-} + 6\,Ni(CO)_4 \qquad (3)$$

The equilibrium (Eq. 3) is shifted to the right by removal of $Ni(CO)_4$ under vacuum and re-exposure of the solution to a carbon monoxide atmosphere. IR monitoring of the reaction initially shows the appearance of $Ni(CO)_4$ and a change in the pattern of the carbonyl absorptions. As the reaction proceeds, the absorption attributed to the terminal carbonyl groups progressively weakens and the two bands attributed to the edge bridging carbonyls collapse into a single absorption centred at slightly higher wavenumber. The intermediate IR patterns are suggestive of the possible formation of $[Ni_{38-x}C_6(CO)_{42-x}]^{6-}$ (x = 1−5) species by stepwise loss of Ni(CO) moieties. It should be noted that members of the $[Ni_{38-x}C_6(CO)_{42-x}]^{6-}$ (x = 0−6) series of compounds would always have $6N + 19$ filled cluster valence orbitals; therefore each one of them is sterically and electronically feasible. Previously reported examples of such behaviour include the $[Ni_{10}C(CO)_{18}]^{2-}$−$[Ni_8C(CO)_{16}]^{2-}$,[19a] $[Ni_{12}C_2(CO)_{16}]^{4-}$−$[Ni_{11}C_2(CO)_{15}]^{4-}$,[19e] $[Ni_{12}Ge(CO)_{22}]^{2-}$−$[Ni_{10}Ge(CO)_{20}]^{2-}$,[22] and $[Ni_{35}C_4(CO)_{39}]^{6-}$−$[Ni_{34}C_4(CO)_{38}]^{6-}$[19d] sets of compounds. The resulting $[Ni_{32}C_6(CO)_{36}]^{6-}$ hexaanion shows a single sharp carbonyl absorption in the region of edge-bridging carbonyls (see Table 2). Although the $[Ni_{32}C_6(CO)_{36}]^{6-}$ hexaanion is also not indefinitely stable under a carbon monoxide atmosphere, its decomposition is slow. As a result, it has been isolated in yields of ca. 80% by monitoring the reaction with IR, and removal of the carbon monoxide atmosphere and $Ni(CO)_4$ as soon as the equilibrium (Eq. 3) has shifted to the right.

Table 2. Infrared carbonyl absorptions (± 2 cm^{-1}) of the $[HNi_{32}C_6(CO)_{36}]^{5-}$ and $[Ni_{32}C_6(CO)_{36}]^{n-}$ (n = 5−8) derivatives

Compound	Solvent	ν_{CO} [cm^{-1}]
$[HNi_{32}C_6(CO)_{36}]^{5-}$	acetone	1911 (s)
$[Ni_{32}C_6(CO)_{36}]^{5-}$	DMF	1905 (s)
$[Ni_{32}C_6(CO)_{36}]^{6-}$	acetonitrile	1888 (s)
$[Ni_{32}C_6(CO)_{36}]^{6-}$	DMF	1889 (s)
$[Ni_{32}C_6(CO)_{36}]^{7-}$	DMF	1872 (s)
$[Ni_{32}C_6(CO)_{36}]^{8-}$	DMF	1851 (s)

Formation of small amounts of $[Ni_{32}C_6(CO)_{36}]^{6-}$ often occurs upon thermal treatment of the majority of nickel carbide clusters, including monocarbides such as $[Ni_9C(CO)_{17}]^{2-}$. However, the best results have been obtained by using the $[Ni_{10}C_2(CO)_{16}]^{2-}$ dicarbide as the starting material.[19b] Thermal decomposition of this dicarbide in diglyme affords $[Ni_{32}C_6(CO)_{36}]^{6-}$, approximately according to Eq. 4.

$$5\,[Ni_{10}C_2(CO)_{16}]^{2-} \xrightarrow{110\ °C} [Ni_{16}C_4(CO)_{23}]^{4-} + [Ni_{32}C_6(CO)_{36}]^{6-} + 2\,Ni(CO)_4 + 13\,CO \qquad (4)$$

The salts of $[Ni_{32}C_6(CO)_{36}]^{6-}$ separate out from the reaction solution, together with some insoluble inorganic material, owing to their very low solubility in diglyme. Their tetrasubstituted ammonium and phosphonium salts have been purified by extraction in MeCN and precipitated by layering di-isopropyl ether.

The chemical reactivity of $[Ni_{32}C_6(CO)_{36}]^{6-}$ is similar but not coincident with that of the parent $[Ni_{38}C_6(CO)_{42}]^{6-}$.

The major difference is represented by the decreased propensity of $[Ni_{32}C_6(CO)_{36}]^{6-}$ to partially substitute its free negative charge with hydrogen atoms upon protonation. Thus, addition of acid to an acetonitrile solution of $[Ni_{32}C_6(CO)_{36}]^{6-}$ gives rise only to trace amounts of $[HNi_{32}C_6(CO)_{36}]^{5-}$. This arises from the fact that in acetonitrile the equilibrium (Eq. 5) is shifted to the right, and can be moved to the left only on using acetone as the solvent.

$$[HNi_{32}C_6(CO)_{36}]^{5-} \overset{MeCN}{\rightleftharpoons} [Ni_{32}C_6(CO)_{36}]^{6-} + H^+ \qquad (5)$$

In this solvent $[HNi_{32}C_6(CO)_{36}]^{5-}$ is stable and has been isolated in the solid state by precipitation with isopropyl alcohol. Attempts to further protonate $[HNi_{32}C_6(CO)_{36}]^{5-}$ only resulted in decomposition to $Ni(CO)_4$ and as yet uncharacterised materials. The instability of the $[H_{6-n}Ni_{32}C_6(CO)_{36}]^{n-}$ (n = 3−5) hydrides is in keeping with the reported failures above to degrade the corresponding $[H_{6-n}Ni_{38}C_6(CO)_{42}]^{n-}$ salts with carbon monoxide.

As with $[Ni_{38}C_6(CO)_{42}]^{6-}$, the $[Ni_{32}C_6(CO)_{36}]^{6-}$ hexaanion is progressively reduced by a solution of sodium/naphthalene in DMF to the corresponding $[Ni_{32}C_6(CO)_{36}]^{7-}$ and $[Ni_{32}C_6(CO)_{36}]^{8-}$ polyanions, as shown by a concomitant shift to lower wavenumber of their unique carbonyl absorption (see Table 2). IR monitoring shows that both species are stable at room temp. for at least several hours. The reaction is perfectly reversible upon addition of a DMF solution of tropylium tetrafluoroborate. The $[Ni_{32}C_6(CO)_{36}]^{7-}$ intermediate and the parent $[Ni_{32}C_6(CO)_{36}]^{6-}$ hexaanion are regenerated quantitatively. So far, all attempts to isolate the $[Ni_{32}C_6(CO)_{36}]^{7-}$ and $[Ni_{32}C_6(CO)_{36}]^{8-}$ salts have met with little success owing to their partial or complete reoxidation to $[Ni_{32}C_6(CO)_{36}]^{6-}$ during the workup. Addition of a further equiv. of tropylium tetrafluoroborate to $[Ni_{32}C_6(CO)_{36}]^{6-}$ causes the appearance of an infrared absorption practically coincident with that of $[HNi_{32}C_6(CO)_{36}]^{5-}$; however, this is assigned to $[Ni_{32}C_6(CO)_{36}]^{5-}$, in view of the fact that Eq. 5 is already shifted to the right in acetonitrile. Furthermore, $[HNi_{32}C_6(CO)_{36}]^{5-}$ salts obtained as above are instantaneously and completely deprotonated to the parent hexaanion once dissolved in DMF.

All $[Ni_{32}C_6(CO)_{36}]^{n-}$, as well as $[Ni_{38}C_6(CO)_{42}]^{n-}$ species with an odd n value contain an odd number of electrons and should, therefore, be paramagnetic. However their solutions in organic solvents such as DMF and *N*-methylpyrrolidinone do not display any significant EPR signal at any temperature (150−300 K). It is worth mentioning that such an unfortunate behaviour is featured by several previously reported odd-electron clusters, e.g. $Ni_3Cp_3S_2$[23] and $[Ni_{11}Bi_2(CO)_{18}]^{3-}$;[11] the latter does exhibit an enormously broad EPR signal but only in the solid state. As a result, their formulation is based exclusively upon their chemical and electrochemical behaviour.

X ray Crystal Structure of $[PPh_3Me]_6[Ni_{32}C_6(\mu\text{-}CO)_{36}]\cdot 4$ MeCN

The unit cell of $[PPh_3Me]_6[Ni_{32}C_6(\mu\text{-}CO)_{36}]\cdot 4$ MeCN contains one molecular anion located on a crystallographic inversion centre, six cations, and four acetonitrile molecules. A view of the structure of the $[Ni_{32}C_6(CO)_{36}]^{6-}$ hexaanion is reported in Figure 1. Selected interatomic distances and angles are given in Table 3. The truncated octahedral $Ni_{32}C_6$ framework of $[Ni_{32}C_6(CO)_{36}]^{6-}$, which shows an overall idealized O_h symmetry (Figure 2), is identical to the corresponding fragment previously found in $[HNi_{38}C_6(CO)_{42}]^{5-}$,[20] with very close interatomic separations. A formal stepwise construction of the metal skeletons of the two is shown in Figure 3. The inner part of both clusters constitutes a Ni_8 empty cube ($Ni-Ni_{av}$ = 2.397 Å, vs. 2.402 Å in $[HNi_{38}C_6(CO)_{42}]^{5-}$) with all six faces capped by carbon atoms, which describe a nonbonded C_6 octahedron. This inner Ni_8C_6 moiety is surrounded by a truncated-octahedral Ni_{24} shell {$Ni-Ni_{av}$ = 2.461 Å vs. 2.459 Å in $[HNi_{38}C_6(CO)_{42}]^{5-}$} in such a way as to generate six square-antiprismatic cavities lodging the six carbide atoms ($Ni-C_{av}$ = 2.062 Å). Each nickel atom of the inner cube lies ca. 0.93 Å underneath the centre of each hexagonal face of the outer Ni_{24} shell {av. $Ni_{inner}-Ni_{outer}$ = 2.634 Å vs. 2.633 Å in $[HNi_{38}C_6(CO)_{42}]^{5-}$} and is 12-coordinate being at a bond distance from 6 nickel atoms of the outer shell, 3 nickel atoms of the inner cube and 3 carbide atoms.

In the solid state, $[Ni_{32}C_6(CO)_{36}]^{6-}$ shows the presence of edge-bridging carbonyl groups only ($Ni-C_{av}$ = 1.917; $C-O_{av}$ = 1.152 Å), which span all Ni−Ni edges of the outer Ni_{24} shell. The above carbonyl stereochemistry is also retained in solution, as shown by the infrared spectrum of $[Ni_{32}C_6(CO)_{36}]^{6-}$, which only consists of one strong absorption in the bridging region.

An interesting structural feature of $[Ni_{32}C_6(CO)_{36}]^{6-}$ is represented by the presence of eight distorted hexagonal cups formed by subsequent concentric rings of oxygen, carbon, and nickel atoms, and ending with a unique nickel atom belonging to the inner cube. Addition of six Ni(CO) fragments to six of the above eight cups generates $[Ni_{38}C_6(CO)_{42}]^{6-}$. It may be questioned as to why two opposite cups have been left empty and whether a $[Ni_{40}C_6(CO)_{44}]^{6-}$ species could be possible or not. It is conceivable that the existence of the latter is unlikely owing to the shrinking of the carbonyl groups on those two empty cups, which releases the steric pressure brought about by the progressive entrance of the six Ni(CO) fragments in the others.

Electrochemical Behaviour of $[Ni_{38}C_6(CO)_{42}]^{6-}$ and $[Ni_{32}C_6(CO)_{36}]^{6-}$

The high redox aptitude of $[Ni_{32}C_6(CO)_{36}]^{6-}$ in acetonitrile solution is illustrated in Figure 4. The cyclic voltammogram displays five sequential electron transfer steps possessing features of chemical reversibility. Voltammetry at a platinum electrode with periodical renewal of the diffusion

Table 3. Interatomic distances [Å] and angles [deg.] within the $[Ni_{32}C_6(CO)_{36}]^{6-}$ anion[a]

a) Metal-metal distances

i) within the inner cubic Ni_8 moiety

Ni1−Ni2	2.391(1)	Ni2−Ni3	2.400(1)
Ni1−Ni3′	2.403(1)	Ni2−Ni4′	2.399(1)
Ni1−Ni4	2.398(1)	Ni3−Ni4	2.392(1)
<Ni−Ni>	2.397		

ii) from the inner cubic Ni_8 moiety to the external Ni_{24} shell

Ni1−Ni7	2.633(1)	Ni3−Ni5	2.650(1)
Ni1−Ni8	2.646(1)	Ni3−Ni6	2.633(1)
Ni1−Ni10	2.630(1)	Ni3−Ni11′	2.640(1)
Ni1−Ni11	2.633(1)	Ni3−Ni12′	2.617(1)
Ni1−Ni13	2.647(1)	Ni3−Ni13′	2.652(1)
Ni1−Ni14	2.614(1)	Ni3−Ni16′	2.620(1)
Ni2−Ni5	2.630(1)	Ni4−Ni6	2.625(1)
Ni2−Ni8	2.639(1)	Ni4−Ni7	2.646(1)
Ni2−Ni9′	2.615(1)	Ni4−Ni9	2.620(1)
Ni2−Ni12′	2.647(1)	Ni4−Ni10	2.634(1)
Ni2−Ni14	2.642(1)	Ni4−Ni15′	2.652(1)
Ni2−Ni15	2.628(1)	Ni4−Ni16′	2.636(1)
<Ni−Ni>	2.634		

iii) within the external Ni_{24} shell

Ni5−Ni6	2.466(1)	Ni9−Ni12	2.464(1)
Ni5−Ni8	2.449(1)	Ni9−Ni15′	2.469(1)
Ni5−Ni12′	2.460(1)	Ni10−Ni11	2.462(1)
Ni6−Ni7	2.457(1)	Ni11−Ni12	2.451(1)
Ni6−Ni16′	2.468(1)	Ni11−Ni13	2.460(1)
Ni7−Ni8	2.468(1)	Ni13−Ni14	2.455(1)
Ni7−Ni10	2.471(1)	Ni13−Ni16	2.465(1)
Ni8−Ni14	2.453(1)	Ni14−Ni15	2.458(1)
Ni9−Ni10	2.464(1)	Ni15−Ni16	2.462(1)
<Ni−Ni>	2.461		

b) Ni−C(carbide)

Ni1−C_a	2.017(4)	Ni9−C_b	2.104(4)
Ni2−C_a	2.009(4)	Ni10−C_b	2.115(3)
Ni3−C_a	2.014(4)	Ni11−C_b	2.119(4)
Ni4−C_a	2.000(4)	Ni12−C_b	2.115(4)
Ni5−C_a	2.115(4)	Ni1−C_c	2.004(4)
Ni6−C_a	2.096(4)	Ni2−C_c	2.016(4)
Ni7−C_a	2.116(4)	Ni3′−C_c	1.999(4)
Ni8−C_a	2.136(4)	Ni4′−C_c	2.031(4)
Ni1−C_b	2.005(4)	Ni13−C_c	2.119(4)
Ni2′−C_b	2.021(4)	Ni14−C_c	2.115(4)
Ni3′−C_b	2.004(3)	Ni15−C_c	2.113(4)
Ni4−C_b	2.007(4)	Ni16−C_c	2.105(4)

c) Ni−C−O(carbonyl)

Ni5−C1	1.923(4)	Ni11−C6	1.929(4)
Ni5−C4	1.926(4)	Ni11−C7	1.903(4)
Ni5−C13	1.888(4)	Ni11−C18	1.915(4)
Ni6−C1	1.923(4)	Ni12−C7	1.910(4)
Ni6−C2	1.918(5)	Ni12−C8′	1.911(4)
Ni6−C14′	1.914(5)	Ni12−C13′	1.906(4)
Ni7−C2	1.926(5)	Ni13−C9	1.933(5)
Ni7−C3	1.907(5)	Ni13−C12	1.912(5)
Ni7−C15	1.921(5)	Ni13−C18	1.895(5)
Ni8−C3	1.942(5)	Ni14−C9	1.922(5)
Ni8−C4	1.919(4)	Ni14−C10	1.902(5)
Ni8−C16	1.893(5)	Ni14−C16	1.910(5)
Ni9−C5′	1.906(5)	Ni15−C10	1.944(5)
Ni9−C8′	1.915(4)	Ni15−C11	1.924(5)
Ni9−C17′	1.936(5)	Ni15−C17	1.902(4)
Ni10−C5′	1.930(5)	Ni16−C11	1.932(5)
Ni10−C6	1.930(4)	Ni16−C12	1.916(4)
Ni10−C15	1.911(5)	Ni16−C14	1.910(5)
C1−O1	1.154(5)	C10−O10	1.145(5)
C2−O2	1.157(5)	C11−O11	1.148(5)

Table 3. *(continued)*

C3−O3	1.160(5)	C12−O12	1.149(5)
C4−O4	1.159(5)	C13−O13	1.152(5)
C5−O5	1.148(5)	C14−O14	1.135(5)
C6−O6	1.152(5)	C15−O15	1.134(5)
C7−O7	1.164(5)	C16−O16	1.164(5)
C8−O8	1.154(5)	C17−O17	1.145(5)
C9−O9	1.161(5)	C18−O18	1.150(5)
Ni5−C1−Ni6	79.8(2)	Ni14−C10−Ni15	79.4(2)
Ni5−C1−O1	140.6(4)	Ni14−C10−O10	140.5(4)
Ni6−C1−O1	139.6(4)	Ni15−C10−O10	140.1(4)
Ni6−C2−Ni7	79.5(2)	Ni15−C11−Ni16	79.4(2)
Ni6−C2−O2	139.6(4)	Ni15−C11−O11	140.2(4)
Ni7−C2−O2	140.9(4)	Ni16−C11−O11	140.4(4)
Ni7−C3−Ni8	79.8(2)	Ni13−C12−Ni16	80.2(2)
Ni7−C3−O3	140.7(4)	Ni13−C12−O12	141.0(4)
Ni8−C3−O3	139.5(4)	Ni16−C12−O12	138.8(4)
Ni5−C4−Ni8	79.1(2)	Ni5−C13−Ni12′	80.8(2)
Ni5−C4−O4	139.1(4)	Ni5−C13−O13	140.6(3)
Ni8−C4−O4	141.6(4)	Ni12′−C13−O13	138.6(3)
Ni9′−C5−Ni10′	79.9(2)	Ni6′−C14−Ni16	80.4(2)
Ni9′−C5−O5	139.7(4)	Ni6′−C14−O14	139.7(4)
Ni10′−C5−O5	140.3(4)	Ni16−C14−O14	139.9(4)
Ni10−C6−Ni11	79.3(2)	Ni7−C15−Ni10	80.3(2)
Ni10−C6−O6	140.0(4)	Ni7−C15−O15	139.6(4)
Ni11−C6−O6	140.6(4)	Ni10−C15−O15	140.1(4)
Ni11−C7−Ni12	80.0(2)	Ni8−C16−Ni14	80.3(2)
Ni11−C7−O7	140.1(4)	Ni8−C16−O16	140.2(4)
Ni12−C7−O7	139.8(4)	Ni14−C16−O16	139.4(4)
Ni9′−C8−Ni12′	80.2(2)	Ni9′−C17−Ni15	80.1(2)
Ni9′−C8−O8	139.3(4)	Ni9′−C17−O17	139.1(4)
Ni12′−C8−O8	140.6(4)	Ni15−C17−O17	140.8(4)
Ni13−C9−Ni14	79.1(2)	Ni11−C18−Ni13	80.4(2)
Ni13−C9−O9	140.8(4)	Ni11−C18−O18	138.5(4)
Ni14−C9−O9	140.0(4)	Ni13−C18−O18	141.0(4)

[a] Primed atoms are related to the unprimed ones by the symmetry operation 1 − *x*, 1 − *y*, 2 − *z*.

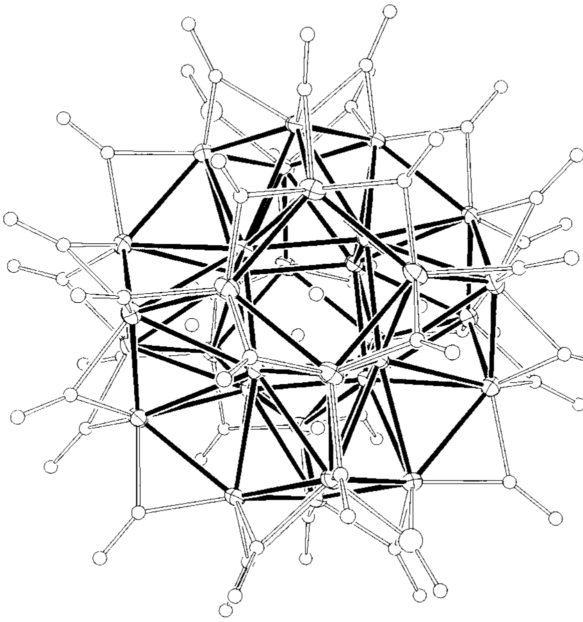

Figure 1. The structure of $[Ni_{32}C_6(CO)_{36}]^{6-}$ (Ni−Ni bonds are black; Ni−$C_{carbide}$ bonds have been omitted for clarity)

layer[24] (direct-current voltammogram) proves that the less cathodic peak-system involves an oxidation process, whereas the subsequent four-peak system is due to reduction processes. Controlled potential coulometric tests

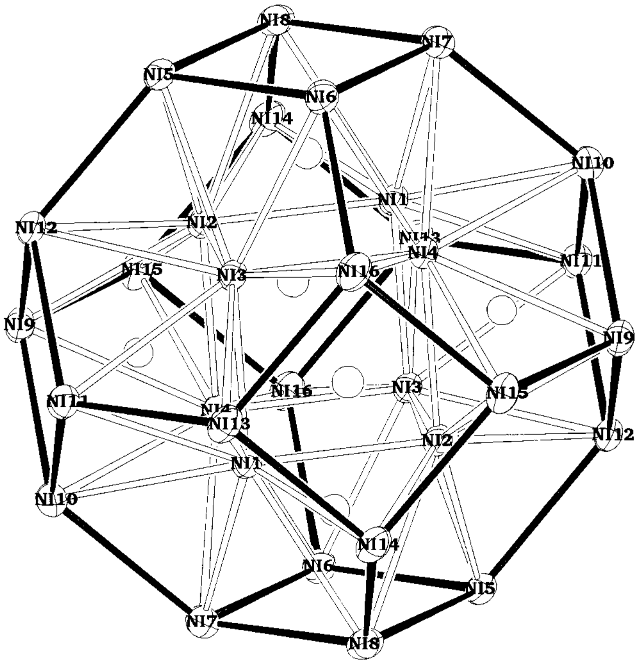

Figure 2. Metal skeleton of $[Ni_{32}C_6(CO)_{36}]^{6-}$ with the atom numbering scheme

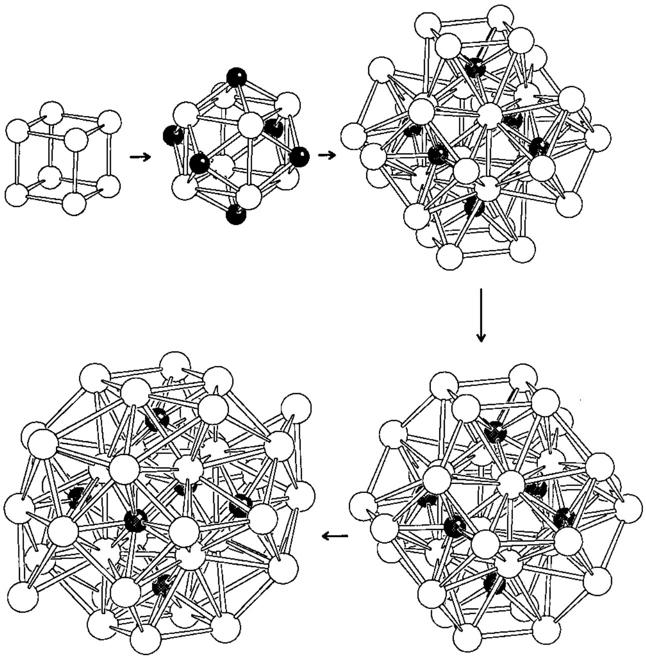

Figure 3. Formal construction of the metal skeletons of $[Ni_{32}C_6(CO)_{36}]^{6-}$ and $[HNi_{38}C_6(CO)_{42}]^{5-}$

performed in correspondence to the first reduction process (E_w = −0.9 V) show that it consumes one electron/molecule. The resulting solution displays a cyclic voltammetric profile complementary to the original one, thus testifying to the chemical reversibility of the $[Ni_{32}C_6(CO)_{36}]^{6-/7-}$ redox change. Further exhaustive reduction at the potential of the second reduction process (E_w = −1.2 V) also consumes one electron/molecule, but the subsequent cyclic voltammetric monitoring already indicates the partial occurrence of some degradation of the electrogenerated $[Ni_{32}C_6(CO)_{36}]^{8-}$. Based on these results we assume that all the electron transfer processes exhibited by $[Ni_{32}C_6(CO)_{36}]^{6-}$ are one-electron steps generating the corresponding redox congeners (namely $[Ni_{32}C_6(CO)_{36}]^{5-}$, $[Ni_{32}C_6(CO)_{36}]^{7-}$, $[Ni_{32}C_6(CO)_{36}]^{8-}$, $[Ni_{32}C_6(CO)_{36}]^{9-}$, $[Ni_{32}C_6(CO)_{36}]^{10-}$), which are stable under the short times of cyclic voltammetry, but under the longer times of macroelectrolysis only $[Ni_{32}C_6(CO)_{36}]^{7-}$ appears perfectly stable.

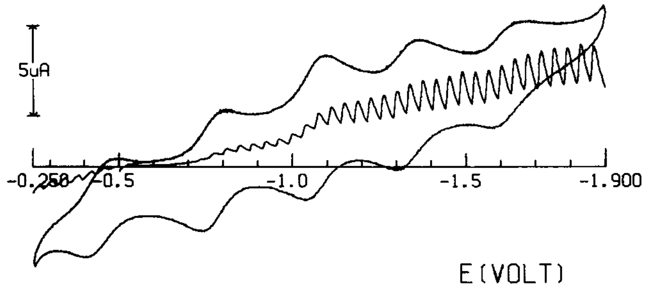

Figure 4. Cyclic and d.c. voltammograms recorded at a platinum electrode on a MeCN solution containing $[Ni_{32}C_6(CO)_{36}]^{6-}$ ($6 \cdot 10^{-4}$ mol dm^{-3}) and $[NEt_4][ClO_4]$ (0.1 mol dm^{-3}). Scan rates: cyclic voltammogram, 0.2 Vs^{-1}; d.c.voltammogram, 0.02 Vs^{-1}

Figure 5 compares the electrochemical response of $[Ni_{38}C_6(CO)_{42}]^{6-}$ in acetonitrile solution with that of its protonated species $[HNi_{38}C_6(CO)_{42}]^{5-}$. The hexaanion gives rise to four well-defined redox processes, all of which possess features of chemical reversibility in the cyclic voltammetric timescale. In this case too, direct-current voltam-

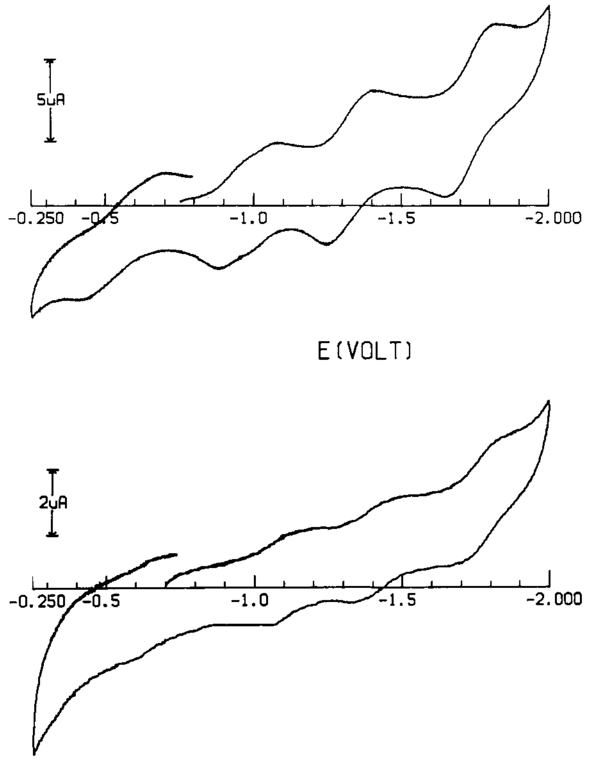

Figure 5. Cyclic voltammograms recorded at a mercury electrode on MeCN solutions containing $[NEt_4][ClO_4]$ (0.1 mol dm^{-3}). Top: $[Ni_{38}C_6(CO)_{42}]^{6-}$ ($4 \cdot 10^{-4}$ mol dm^{-3}). Bottom: $[HNi_{38}C_6(CO)_{42}]^{5-}$ ($5 \cdot 10^{-4}$ mol dm^{-3}). Scan rate 0.2 Vs^{-1}

metry shows the occurrence of one oxidation and three subsequent reduction processes. The protonated pentaanion also exhibits an analogous sequence of redox processes, encompassing the $[HNi_{38}C_6(CO)_{42}]^{4-/8-}$ oxidation states; they are, however, less well defined and shifted by about 400 mV towards more negative potential values. To our knowledge, the highest nuclearity clusters which have been previously studied to determine the influence of hydride incorporation on the electrochemical redox behaviour are $[Ru_{10}C(CO)_{24}]^{2-}$ and $[HRu_{10}C(CO)_{24}]^{-}$.[25] These, however, only exhibit a two-electron electrochemically irreversible reduction.

Step-by-step controlled potential coulometry shows that both $[Ni_{38}C_6(CO)_{42}]^{7-}$ and $[Ni_{38}C_6(CO)_{42}]^{8-}$ are stable, whereas $[Ni_{38}C_6(CO)_{42}]^{5-}$ tends to decompose slowly.

Finally, as illustrated in Figure 6, the redox change $[Ni_{38}C_6(CO)_{42}]^{8-/9-}$ in DMF solution is probably masked by the solvent discharge, because of the shift of the redox processes of $[Ni_{38}C_6(CO)_{42}]^{6-}$ towards negative potential values. Furthermore, one more anodic process becomes detectable, even if the instantaneously generated $[Ni_{38}C_6(CO)_{42}]^{4-}$ species is very unstable.

The formal electrode potentials of the redox changes exhibited by the present complexes are compiled in Table 4. From the electrochemical viewpoint it is noteworthy that all the redox changes concerned with the Ni_{38} species exhibit peak-to-peak separations which largely depart from the value of 60 mV, which is the theoretical prediction for electrochemically reversible one-electron processes. It could be speculated that the quasi-reversibility of such redox processes, i.e. their rather slow electron transfer rate, suggests that the Ni_{38} electron exchanges are accompanied by some geometric reorganisations, which are more significant than those accompanying the Ni_{32} redox processes.[2d]

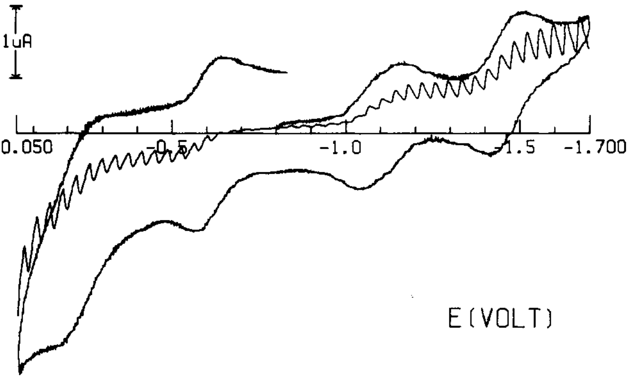

Figure 6. Cyclic and d.c. voltammograms recorded at a mercury electrode on a DMF solution containing $[Ni_{38}C_6(CO)_{42}]^{6-}$ ($3\cdot10^{-4}$ mol dm^{-3}) and $[NEt_4][ClO_4]$ (0.1 mol dm^{-3}). Scan rates: cyclic voltammogram, 0.2 Vs^{-1}; d.c.voltammogram, 0.02 Vs^{-1}.

Conclusion

The most notable property of the $[H_{6-n}Ni_{32}C_6(CO)_{36}]^{n-}$ (n = 5, 6) and $[H_{6-n}Ni_{38}C_6(CO)_{42}]^{n-}$ (n = 4, 5, 6) derivatives is represented by their electron-sink behaviour encompassing up to six different electrochemically reversible oxidation states. Their redox features resemble those of higher valent clusters such the Fe−S cubanes,[2] or fullerenes.[26] In the nickel clusters mentioned above such behaviour probably arises from the presence of highly connected nickel atoms belonging to the inner cube and the extra-stability of the metal core granted by the interstitial carbide atoms. Indeed, the nickel atoms of the inner cubic core of $[Ni_{32}C_6(CO)_{36}]^{6-}$ display coordination number 12, being coordinated to 9 nickel and 3 carbide atoms, whereas the coordination number of six out of eight corresponding nickel atoms of $[Ni_{38}C_6(CO)_{42}]^{6-}$ increases to 13 by intervention of the additional six Ni(CO) fragments. LDF calculations, carried out on $[Ni_{32}C_6(CO)_{36}]^{6-}$ prior to its isolation and characterisation, indicate that its electronic structure begins to bear some qualitative resemblance to that of a metal. In particular, almost degenerate t_{1u}, a_{2g}, and t_{2g} levels, holding a total of ten electrons, were found close to the Fermi energy.[27] This finding is in perfect agreement with the redox behaviour of $[Ni_{32}C_6(CO)_{36}]^{6-}$. Indeed, the progressive one-electron reduction of the latter to the corresponding decaanion corresponds to complete filling of the energy levels mentioned above. Moreover, the differences between the formal electrode potentials of consecutive redox couples of $[Ni_{32}C_6(CO)_{36}]^{6-}$ (range 0.26−0.33 V) is indicative of the presence in the frontier region of almost equally spaced one-electron energy levels with an average energy separation of ca. 0.3 eV. It may be concluded therefore that a metalisation process begins to emerge due to the presence of eight highly-connected nickel atoms.

Experimental Section

General Remarks: All reactions including sample manipulations were carried out under a well ventilated hood with standard Schlenk techniques under nitrogen and in carefully dried solvents.

Table 4. Formal electrode potentials (in V, vs. S.C.E.) and peak-to-peak separations (in mV) for the redox changes exhibited by $[Ni_{32}C_6(CO)_{36}]^{6-}$, $[Ni_{38}C_6(CO)_{42}]^{6-}$, and $[HNi_{38}C_6(CO)_{42}]^{5-}$

Cluster	$E°'_{4-/5-}$	ΔEp[a]	$E°'_{5-/6-}$	ΔEp	$E°'_{6-/7-}$	ΔEp	$E°'_{7-/8-}$	ΔEp	$E°'_{8-/9-}$	ΔEp	$E°'_{9-/10-}$	ΔEp	Solvent
$[Ni_{32}C_6(CO)_{36}]^{6-}$			−0.45	70	−0.77	66	−1.06	66	−1.33	66	−1.61	64	MeCN
$[Ni_{38}C_6(CO)_{42}]^{6-}$			−0.49	160	−0.98	190	−1.33	160	−1.73	178			MeCN
$[Ni_{38}C_6(CO)_{42}]^{6-}$	−0.24b	b	−0.60	85	−1.10	130	−1.47	112					DMF
$[HNi_{38}C_6(CO)_{42}]^{5-}$	−0.6b	b	−1.11	100	−1.42	150	−1.77	120					MeCN

[a] Measured at 0.2 Vs^{-1} − [b] Difficult to be measured.

The $[Ni_6(CO)_{12}]^{2-}$ salts were prepared according to literature.[28] − Elemental analyses: atomic absorption on a Pye-Unicam instrument (Ni), gravimetrically as BPh_4^- salts for the tetrasubstituted ammonium cations. − IR: Perkin-Elmer 1605 interferometer using CaF_2 cells. Materials and apparatus for the electrochemical measurements have been described elsewhere.[29] Potential values are referred to the saturated calomel electrode (SCE).

Synthesis of $[NEt_4]_6[Ni_{38}C_6(CO)_{42}]$: $[NEt_4]_2[Ni_6(CO)_{12}]$ (2.58 g, 2.72 mmol) was dissolved in THF (40 mL) in a 100 mL three-necked round-bottomed flask cooled at −15°C and equipped with a microburette charged with C_3Cl_6 (0.51 g, 2.05 mmol) in THF (5 mL). The C_3Cl_6 solution (4 mL) was added dropwise over a period of six h into the stirred $[NEt_4]_2[Ni_6(CO)_{12}]$ solution while continuously removing the reaction atmosphere with a slow stream of nitrogen. The resulting dark brown suspension was left standing for 2 d at room temp. and under a static nitrogen atmosphere, and then evaporated to dryness under vacuum. The residue was washed in portions with water (30 mL), methanol (20 mL), and THF (20 mL) and extracted with DMSO (30 mL). $[NEt_4]_6[Ni_{38}C_6(CO)_{42}]$ was precipitated from the DMSO solution by addition of a solution of $[NEt_4]Cl$ (1.5 g) in water (30 mL) with stirring, it was then filtered, and washed with methanol (20 mL). The resulting dark brown material was extracted with acetonitrile (20 mL) and filtered. Precipitation by layering of diisopropyl ether (40 mL) gave black crystals of $[NEt_4]_6[Ni_{38}C_6(CO)_{42}]\cdot x$ MeCN (0.61 g). The salt is soluble in acetonitrile, DMF and DMSO, and sparingly soluble or insoluble in acetone, THF, alcohols, and nonpolar solvents. − $[NEt_4]_6[Ni_{38}C_6(CO)_{42}]$: calcd. $[NEt_4]^+$ 18.31, Ni 52.38; found $[NEt_4]^+$ 16.9, Ni 49.07. − Ni/$[NEt_4]^+$ calcd 6.33; found 6.43.

The corresponding $[NBu_4]^+$, $[NMe_3CH_2Ph]^+$, $[PPh_3Me]^+$, $[PPh_3CH_2Ph]^+$, and $[PPh_4]^+$ salts of $[Ni_{38}C_6(CO)_{42}]^{6-}$ have been similarly prepared by metathesis in DMSO with the appropriate quaternary salt.

Synthesis of $[PPh_3Me]_6[Ni_{32}C_6(CO)_{36}]$: A solution of $[PPh_3Me]_6[Ni_{38}C_6(CO)_{42}]$ (0.35 g, 0.067 mmol) in acetonitrile (20 mL) was stirred under a carbon monoxide atmosphere for 15 min and evaporated under vacuum to dryness. The residue was dissolved in acetonitrile (20 mL) and stirred under a carbon monoxide atmosphere for 10 min and dried under vacuum. The resulting dark brown residue was extracted with acetonitrile (20 mL) and filtered. Precipitation by layering of diisopropyl ether (40 mL) gave black crystals of $[PPh_3Me]_6[Ni_{32}C_6(CO)_{36}]\cdot 4$ MeCN (210 mg, 0.043 mmol). The salt is soluble in acetone, acetonitrile, DMF, and DMSO, and insoluble in THF, alcohols, and nonpolar solvents. − $[PPh_3Me]_6[Ni_{32}C_6(CO)_{36}]\cdot 4$ MeCN: calcd. $[PPh_3Me]^+$ 34.74, Ni 39.26; found $[PPh_3Me]^+$ 34.12, Ni 38.87. − Ni/$[PPh_3Me]^+$: calcd 5.33, found 5.37.

The corresponding $[NEt_4]^+$, $[NBu_4]^+$, $[NMe_3CH_2Ph]^+$, $[PPh_3CH_2Ph]^+$, and $[PPh_4]^+$ salts have been similarly prepared using the appropriate starting material.

Synthesis of $[NBu_4]_5[HNi_{38}C_6(CO)_{42}]$: $[NBu_4]_6[Ni_{38}C_6(CO)_{42}]$ (0.91 g) was dissolved in acetonitrile (30 mL), treated with 2.5 mL of a solution obtained by diluting 1 mL of H_2SO_4 (20% in aqueous solution) in acetonitrile (25 mL), and evaporated to dryness under vacuum. The resulting residue was extracted in acetone (20 mL) and precipitated by layering with isopropyl alcohol (45 mL) to give black crystals of $[NBu_4]_5[HNi_{38}C_6(CO)_{42}]$. Yields 0.64 g. The salt is soluble in acetone, sparingly soluble in THF, and insoluble in alcohols and nonpolar solvents. $[NBu_4]_5[HNi_{38}C_6(CO)_{42}]$ is very soluble in acetonitrile, DMF, and DMSO with partial or complete conversion into the corresponding $[Ni_{38}C_6(CO)_{42}]^{6-}$ hexaanion. − $[NBu_4]_5[HNi_{38}C_6(CO)_{42}]$: calcd. $[NBu_4]^+$ 25.80, Ni 47.57; found $[NBu_4]^+$ 25.12, Ni 47.2. − Ni/$[NBu_4]^+$: calcd. 7.6, found 7.74.

Synthesis of $[PPh_3Me]_5[HNi_{32}C_6(CO)_{36}]$: $[PPh_3Me]_6[Ni_{32}C_6(CO)_{36}]$ (0.31 g) was dissolved in acetonitrile (10 mL), treated with 1 mL of a solution obtained by diluting 1 mL of H_2SO_4 (20% in aqueous solution) in acetonitrile (25 mL) and evaporated to dryness under vacuum. The resulting residue was extracted in acetone (15 mL) and precipitated by layering with isopropyl alcohol (30 mL) to give black crystals of $[PPh_3Me]_5[HNi_{32}C_6(CO)_{36}]$. Yields 0.24 g. The salt is soluble in acetone, sparingly soluble in THF, and insoluble in alcohols and nonpolar solvents. $[PPh_3Me]_5[HNi_{32}C_6(CO)_{36}]$ is also soluble in acetonitrile, DMF, and DMSO with complete conversion into the parent $[Ni_{32}C_6(CO)_{36}]^{6-}$ hexaanion. − $[PPh_3Me]_5[HNi_{32}C_6(CO)_{36}]$: calcd. $[PPh_3Me]^+$ 31.88, Ni 43.24; found $[PPh_3Me]^+$ 30.79, Ni 41.57. − Ni/$[PPh_3Me]^+$: calcd 6.4, found 6.37.

X-ray Data Collection and Crystal Structure Determination: Crystal data for $[PPh_3Me]_6[Ni_{32}C_6(CO)_{36}] \cdot 4$ MeCN: triclinic, space group $P\bar{1}$ (No. 2), a = 15.974(3), b = 17.474(3), c = 18.200(4) Å, α = 61.37(2), β = 69.31(2), γ = 72.35(2)°, V = 4115(1) Å^3, Z = 1, D_c = 1.93 gcm^{-3}, Mo-K_α radiation (λ = 0.71073 Å), μ (Mo-K_α) = 37.1 cm^{-1}, T = 298 K. 14585 reflections with 3°< θ < 25° were measured on a CAD4 diffractometer at room temp. using a crystal with approximate dimensions 0.20 × 0.15 × 0.35 mm. Data were corrected for Lorentz polarisation and absorption effects (empirical absorption, transmission factors in the range 0.56−1.00[30]). The structure was solved by direct methods (SIR 89) and refined using 10639 independent reflections having $I > 3\sigma(I)$, minimising the function $\Sigma w(|Fo|-|Fc|)^2$. Scattering factors were taken from Cromer and Waber.[31] Anomalous dispersion corrections were included.[32] Anisotropic displacement parameters were assigned to all non-hydrogen atoms.The hydrogen atoms were placed at calculated positions (C−H 0.95 Å). The final R value was 0.033 (R_w = 0.043). All the calculations were performed using Personal SDP software.[33]

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-179-79 Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44 (1223) 336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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[1] [1a] P. Lemoine, *Coord. Chem. Rev.* **1982**, *47*, 55. − [1b] P. Lemoine, *Coord. Chem. Rev.* **1988**, *83*, 169.

[2] [2a] P. Zanello, *Coord. Chem. Rev.* **1988**, *83*, 199. − [2b] P. Zanello, *Coord. Chem. Rev.* **1988**, *87*, 1. − [2c] P. Zanello, in *Stereochemistry of Organometallic and Inorganic Compounds,* (Ed.: P. Zanello), Elsevier, Amsterdam, **1994**, *5*, 163. − [2d] P. Zanello, *Structure and Bonding*, Spinger-Verlag, Berlin, **1992**, *79*, 101.

[3] G. Longoni, C. Femoni, M. C. Iapalucci, P. Zanello, in *Metal Clusters in Chemistry* (Eds.: P. Braunstein, L. Oro, P. Raithby), Wiley-VCH Verlag, Weinheim, submitted.

[4] R. Della Pergola, L. Garlaschelli, M. Manassero, N. Masciocchi, P. Zanello, *Angew. Chem.* **1993**, *105*, 1415; *Angew. Chem. Int. Ed.* **1993**, *32*, 1347.

[5] [5a] G. Longoni, M. Manassero, M. Sansoni, *J. Am. Chem. Soc.* **1980**, *102*, 7973. − [5b] R. D. Adams, I. Arafa, G. Chen, J-C. Lii, J-G. Wang, *Organometallics* **1990**, *9*, 2350.

[6] R. Della Pergola, L. Garlaschelli, C. Mealli, D. M. Proserpio, P. Zanello, *J. Cluster Sci.* **1990**, *1*, 93.

[7] [7a] V. G. Albano, F. Calderoni, M. C. Iapalucci, G. Longoni, M. Monari, P. Zanello, *J. Cluster Sci.*, **1995**, *6*, 107. – [7b] V. G. Albano, L. Grossi, G. Longoni, M. Monari, S. Mulley, A. Sironi, *J. Am. Chem. Soc.* **1992**, *114*, 5708.

[8] V. G. Albano, R. Aureli, M. C. Iapalucci, F. Laschi, G. Longoni, M. Monari, P. Zanello, *J. Chem Soc., Chem. Comm.* **1993**, 1501.

[9] V. G. Albano, D. Braga, P. Chini, G. Ciani, S. Martinengo, *J. Chem Soc., Dalton Trans.*, **1982**, 645.

[10] [10a] K. M. MacKay, B. K. Nicholson, W. T. Robinson, A. W. Sims, *J. Chem Soc., Chem. Comm.* **1984**, 1276. – [10b] G. C. Barris, D. Phil. Thesis, University of Waikato, New Zealand.

[11] V. G. Albano, F. Demartin, M. C. Iapalucci, G. Longoni, M. Monari, P. Zanello, *J. Chem Soc., Dalton Trans.* **1992**, 497.

[12] V. G. Albano, F. Demartin, M. C. Iapalucci, F. Laschi, G. Longoni, A. Sironi, P. Zanello, *J. Chem Soc., Dalton Trans.* **1991**, 739.

[13] F. Calderoni, F. Demartin, M. C. Iapalucci, G. Longoni, P. Zanello, *Inorg. Chem.* **1996**, *35*, 898.

[14] J. Sinzig, L. J. de Jongh, A. Ceriotti, R. Della Pergola, G. Longoni, M. Stener, K. Albert, N. Rösch, *Phys. Rev. Lett.* **1998**, *81*, 3211.

[15] D. M. Washecheck, E. J. Wucherer, L. F. Dahl, A. Ceriotti, G. Longoni, M. Manassero, M. Sansoni, P. Chini, *J. Am. Chem. Soc.* **1979**, *101*, 6110.

[16] [16a] G. J. Lewis, J. D. Roth, R. A. Montag, L. K. Safford, X. Gao, S-C. Chang, L. F. Dahl, M. J. Weaver, *J. Am. Chem. Soc.* **1990**, *112*, 2831. – [16b] J. D. Roth, G. J. Lewis, L. K. Safford, X. Jiang, L. F. Dahl, M. J. Weaver, *J. Am. Chem. Soc*. **1992**, *114*, 6159

[17] E. Brivio, A. Ceriotti, R. Della Pergola, L. Garlaschelli, F. Demartin, M. Manassero, M. Sansoni, P. Zanello, F. Laschi, B. T. Heaton, *J. Chem Soc., Dalton Trans.* **1994**, 3237.

[18] [18a] J. Podlahová, J. Podlaha, A. Jegorov, J. Hašek, *J. Organomet. Chem*. **1989**, *359*, 401. – [18b] P. Baird, J. A. Bandy, M. L. H. Green, A. Hamnett, E. Marseglia, D. S. Orbetelli, K. Prout, J. Qin, *J. Chem Soc., Dalton Trans.*, **1991**, 2377. – [18c] M. J. Scott, R. H. Holms, *Angew. Chem. Int. Ed. Engl.*, **1993**, *32*, 564. – [18d] V. G. Albano, C. Femoni, M. C. Iapalucci, G. Longoni, M. Rauccio, S. Zacchini, *Inorg. Chim. Acta*, submitted.

[19] [19a] A. Ceriotti, G. Longoni, M. Manassero, M. Perego, M. Sansoni, *Inorg. Chem.* **1985**, *24*, 117. – [19b] A. Ceriotti, G. Longoni, M. Manassero, L. Resconi, M. Sansoni, *J. Chem Soc., Chem. Comm.* **1985**, 181. – [19c] A. Ceriotti, G. Longoni, M. Manassero, N. Masciocchi, G. Piro, L. Resconi, M. Sansoni, *J. Chem Soc., Chem. Comm.* **1985**, 1402. – [19d] A. Ceriotti, A. Fait, G. Longoni, G. Piro, L. Resconi, F. Demartin, M. Manassero, N. Masciocchi, M. Sansoni, *J. Am. Chem. Soc.* **1986**, *108*, 5370. – [19e] A. Ceriotti, G. Longoni, G. Piro, M. Manassero, N. Masciocchi, M. Sansoni, *New J. Chem.* **1988**, *12*, 501.

[20] A. Ceriotti, A. Fait, G. Longoni, G. Piro, F. Demartin, M. Manassero, N. Masciocchi, M. Sansoni, *J. Am. Chem. Soc.* **1986**, *108*, 8091

[21] F. Calderoni, F. Demartin, M. C. Iapalucci, G. Longoni, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2225.

[22] A. Ceriotti, F. Demartin, B. T. Heaton, P. Ingallina, G. Longoni, M. Manassero, M. Marchionna, N. Masciocchi, *J. Chem Soc., Chem. Comm.* **1989**, 786.

[23] [23a] H. Vahrenkamp, V. A. Uchtman, L. F. Dahl, *J. Am. Chem. Soc.* **1968**, *90*, 3272. – [23b] L. F. Dahl, J. E. North, J. B. Thoden, B. Spencer, *Organometallics* **1993**, *12*, 1299.

[24] S. Lo Schiavo, G. Bruno, P. Zanello, F. Laschi. P. Piraino, *Inorg. Chem.* **1997**, *36*, 1004.

[25] M. P. Cifuentes, M. G. Humphrey, G. A. Heath, *Inorg. Chim. Acta* **1997**, 259, 273.

[26] I. Noviandri, R. D. Bolskar, P. A. Lay, C. A. Reed, *J. Phys. Chem.* **1997**, *B101*, 6350.

[27] N. Rösch, L. Ackermann, G. Pacchioni, *J. Am. Chem. Soc.* **1992**, *114*, 3549.

[28] A. Ceriotti, G. Longoni, G. Piva, *Inorg. Synth.* **1989**, *26*, 312.

[29] C. Bianchini, F. Laschi, D. Masi, F. M. Ottaviani, A. Pastor, M. Peruzzini, P. Zanello, F. Zanobini, *J. Am. Chem. Soc.* **1993**, *115*, 2723.

[30] A. C. T. North, D. C. Phillips, F. S. Mathews, *Acta Crystallogr.* **1968**, A24, 351.

[31] D. T. Cromer, J. T. Waber, *International Tables for X-ray Crystallography,* Vol IV, Kynoch Press, Birmingham, UK, **1974**, Table 2.2B.

[32] D. T. Cromer, *International Tables for X-ray Crystallography,* Vol IV, Kynoch Press, Birmingham, UK, **1974**, Table 2.3.1.

[33] [33a] B. Frenz, *Comput. Phys.* **1988**, *3*, 42. – [33b] B. Frenz, *Crystallographic Computing*, 5, Oxford University Press, **1991**, Chapter 11, pp. 126–135.

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