penheimer approximation). Rather, as Jameson has noted,[21] the chief contribution to $\Delta\delta$ arises from the anharmonic segment of the expression for chemical shielding. The effect of a shorter C-D bond is to deshield C5, C6, and C7 because these atomic centers are particularly responsive to the charge redistribution that accompanies the difference in zero-point vibrational energy.

Acknowledgment. We are indebted to the National Institutes of Health for generous financial support of our research (Grant CA-12115).

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Synthesis and X-ray Structure of the $[HNi_{38}(CO)_{42}C_6]^{5-}$ Cluster: An Extended Fragment of the $Cr_{23}C_6$ Lattice Stabilized in a Molecular Carbonyl Nickel Cluster

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Although close structural ties between molecular carbide clusters and interstitial carbide alloys were earlier pointed out,[1-5] owing to a greater degree of freedom of the former,[6] the above structural analogy is generally restricted to the stereochemistry of the interstitital carbide atom. We wish to report here the synthesis and structural characterization of $[HNi_{38}(CO)_{42}C_6]^{5-}$, which to our knowledge represents the first example of stabilization with carbonyl ligands of an extended fragment of a metal–carbide lattice, such as that shown by $Cr_{23}C_6$.[7]

The $[HNi_{38}(CO)_{42}C_6]^{5-}$ pentaanion has been obtained by reaction of $[NBu_4]_2[Ni_6(CO)_{12}]$ with hexachloropropene in a ca. 1.7:1 molar ratio in tetrahydrofuran (THF) and under a nitrogen atmosphere. After evaporation to dryness of the resulting suspension, the residue was thoroughly washed with water, methanol, and THF; subsequent extraction of the residue with acetone gives a dark brown solution containing $[HNi_{38}(CO)_{42}C_6]^{5-}$ in a fairly pure state.[8] Isolation of a hexacarbide cluster in the above conditions is in keeping with the previously reported synthesis of tetracarbide clusters, viz., $[H_{6-n}Ni_{34}(CO)_{38}C_4]^{n-}$ ($n = 6, 5$) and $[Ni_{16}(CO)_{23}(C_2)_2]^{4-}$,[9,10] in addition to the $[Ni_{10}(CO)_{16}C_2]^{2-}$ dicarbide,[11] in the related reaction of $[Ni_6(CO)_{12}]^{2-}$ salts with C_2Cl_6.

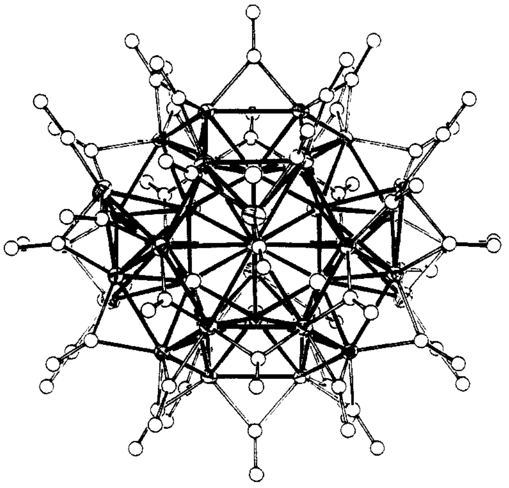

Figure 1. ORTEP drawing of the $[HNi_{38}(CO)_6(\mu_2\text{-}CO)_{36}C_6]^{5-}$ anion.

As in the case of $[H_{6-n}Ni_{34}(CO)_{38}C_4]^{n-}$,[9] the presence of a hydride atom in $[HNi_{38}(CO)_{42}C_6]^{5-}$ is only suggested by the reversible protonation–deprotonation equilibrium (1).[8] Crystals of

$$[Ni_{38}(CO)_{42}C_6]^{6-} \xrightleftharpoons[Me_2SO]{H^+,\ MeCN} [HNi_{38}(CO)_{42}C_6]^{5-} \qquad (1)$$

$[NBu_4]_5[HNi_{38}(CO)_{42}C_6]$ were grown from acetone by precipitation with isopropyl alcohol and the structure was determined by X-ray diffraction studies.[12]

The overall structure of the $[HNi_{38}(CO)_{42}C_6]^{5-}$ pentaanion, which shows idealized D_{3d} and crystallographic $\bar{1}$ symmetry, is shown in Figure 1. Figure 2 shows the $Ni_{38}C_6$ core of the $[HNi_{38}(CO)_{42}C_6]^{5-}$ cluster (Figure 2b), as well as the truncated octahedral $Ni_{32}C_6$ moiety contained in the above (Figure 2a). The inner core of the cluster consists in a Ni_8 empty cube ($Ni\text{-}Ni_{av}$ = 2.402 Å) capped onto the six square faces by six carbide atoms which are at the corners of a nonbonded C_6 octahedron (range of interatomic C...C separations = 3.25–3.32 Å). The six carbide atoms are caged into six Ni_8 square-antiprismatic moieties (Figure 2a, $Ni\text{-}C_{av}$ = 2.061, $Ni\text{-}Ni_{interlayer(av)}$ = 2.633 Å), originating from the inner cube and giving rise to an outer truncated octahedron of frequency 1[13] with an average edge length of 2.459 Å. The outer polyhedron recalls the structure of $[H_2Pt_{38}(CO)_{44}]^{2-}$,[1,14] but in contrast to the latter the $Ni_{32}C_6$ moiety does not have a close-packed inner core. Moreover, the central nickel atom of each hexagonal face, which belongs to the inner Ni_8 cube, lies well underneath the Ni_6–ring plane and, as a result, the eight hexagonal faces are clearly concave. The remaining six nickel atoms are μ_3-capping six out of the above eight hexagonal faces ($Ni\text{-}Ni_{av}$ = 2.488 Å), giving rise to a D_{3d} idealized symmetry (Figure 2b; the idealized threefold axis comprises the central nickel atoms of the two uncapped hexagonal faces).

As shown in Figure 1, of the 42 carbonyl groups six are terminally bound to the six μ_3-capping nickel atoms, whereas the remaining 36 are μ_2-edge-bridging ligands. This carbonyl stereochemistry is probably maintained in solution and is likely to be shown also by the $[Ni_{38}(CO)_{42}C_6]^{6-}$ hexaanion, as suggested by the close resemblance of the IR pattern of the two anions and

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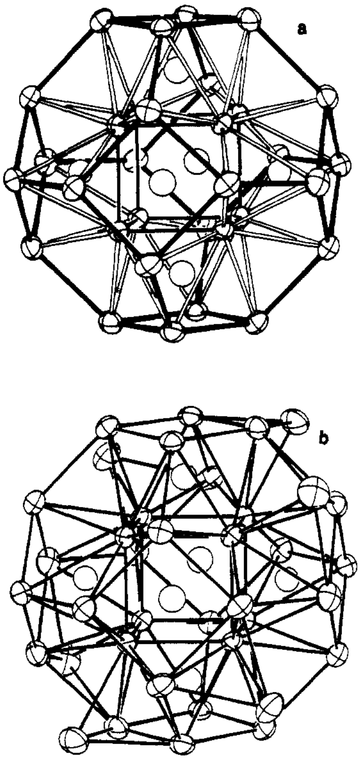

Figure 2. $Ni_{38}C_6$ metal frame (b) and the truncated-octahedral $Ni_{32}C_6$ moiety (a), which represents a fragment of the structure of $Cr_{23}C_6$ (solid lines depict the inner Ni_8 cube and the outer truncated-octahedral polyhedron; open circles represent the interstitial carbide atoms).

by the presence of strongest absorptions in the edge-bridging carbonyl stretching region.[8]

The $Ni_{32}C_6$ inner core of the $[HNi_{38}(CO)_{42}C_6]^{5-}$ cluster (Figure 2a) is closely related to a fragment of the structure of $Cr_{23}C_6$.[7] The $Cr_{23}C_6$ interstitial alloy has a $Fm3m$ structure which conforms to the No. 24 of Andreini's space-filling models[15,16] and derives from a regular sequence of $Cr_{32}C_6$ truncated octahedra of frequency 1[13] and Cr_{13} cuboctahedra three-dimensionally fused through their square faces. The truncated-octahedral $Cr_{32}C_6$ moiety has a structure identical with that shown by the $Ni_{32}C_6$ moiety of $[HNi_{38}(CO)_{42}C_6]^{5-}$ and also shows very similar molecular parameters. It is worth noting that the only well-defined Ni-C interstitial alloy, viz., Ni_3C,[2,17] shows a hexagonal close-packed nickel lattice encapsulating the carbide atoms in octahedral cavities.[18,19]

To our knowledge $[HNi_{38}(CO)_{42}C_6]^{5-}$ represents the first example of stabilization in a molecular cluster of an extended fragment of the structure of a metal-carbide alloy and is suggestive of the possibility of a molecular approach to new Ni-C binary phases.

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Supplementary Material Available: Lists of atomic coordinates (Table I), thermal factors (Table II), and bond distances and angles (Table III) and a figure with labeling of $[NBu_4]_5[HNi_{38}(CO)_{42}C_6]$ (36 pages). Ordering information is given on any current masthead page.

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Synthesis of Organometallic Heterodinuclear μ-Oxo Complexes by Extrusion of Alkenes from Zirconium/Tungsten Oxaalkyl Complexes

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Because of the role they have played in structural inorganic[1] and bioinorganic chemistry,[2] many μ-oxo complexes have been prepared and studied. Nearly all the complexes in this class which are presently known contain identical metal centers (M-O-M);[3] a much smaller number having two different metals (M-O-M′) have been prepared.[4] We wish to report the synthesis and unusual chemical properties of organometallic heterodinuclear μ-oxo complexes containing a zirconium and tungsten atom bound to oxygen.

Dinuclear oxaalkyl complexes **3** in Scheme I were obtained in good yield by treatment of the appropriate carbon-bound tungsten enolates[5] **1** with hydridozirconium complex **2** under rigorously air- and moisture-free conditions.[6-8] Complex **3d** exists as two diastereomers which are separable by recrystallization. Spectral data showed no evidence for W-Zr interaction in any of these

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(8) Full experimental, spectroscopic, and analytical data are provided in the supplementary material.

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