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STRUCTURAL SYSTEMATICS IN NICKEL CARBONYL CLUSTER ANIONS

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CONTENTS

1. INTRODUCTION

The first report of the structural characterisation of a nickel carbonyl cluster anion was that of $[Ni_6(CO)_6(\mu_2\text{-}CO)_6]^{2-}$ in 1974.[1] Since then, the structures of an additional 16 homonuclear nickel cluster anions with combinations of only carbonyl, hydride and carbide ligands have been reported.[2–19] The structures of these clusters have been discussed individually or in small groups in a variety of texts,[20–25] and the crystal structure of $[NMe_4]_2[Ni_6(CO)_{12}]$ as a molecular aggregate has recently been described.[25] However, the structures of the known homonuclear nickel carbonyl anions have not been compared as a group.

Herein, we discuss the structures of those homometallic nickel carbonyl cluster anions in which the only ancillary ligands are hydrides and/or carbides.

Heterometallic nickel carbonyl clusters and cluster anions are also well known,[8,26–36] but are outside the scope of this discussion, as are computational studies on the structures of the theoretical neutral nickel clusters, with or without carbonyl ligands.[37]

Selected crystallographic parameters for those derivatives which have been structurally charac-

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terised are collected in Table 1 and descriptions of the idealised cluster geometries and important bond distances are summarised in Table 2. Although the structures of the salts of Tables 1 and 2 have been reported, most reports have been in communication form, only limited metric data have been reported and the positional parameters can be difficult to access.

The Ni—Ni bonds in nickel metal and in the Ni_3C binary phase are 2.50 and 2.62 Å, respectively. The carbide atom of Ni_3C is at the centre of an octahedron of nickel atoms with a Ni—C bond length of 1.86 Å.[38–40] Mingos and Wales[41] propose that metal–metal distances less than 115% of the sum of the covalent radii be formally considered as bonds. In the case of nickel, for which the metallic radius for 12 co-ordination is 1.25 Å,[42] this definition would suggest an upper limit for Ni—Ni bond distances of 2.9 Å. Accordingly, we consider below only Ni—Ni distances less than 3.1 Å.

2. HOMOLEPTIC NICKEL CARBONYL CLUSTER ANIONS

$[Ni_5(CO)_{12}]^{2-}$

This 76 electron cluster conforms to Mingos and co-workers' $(14m+6)$ classification $(m = 5)$[41,43] and is an example of the simplest polar cluster.[44–46] The $[Ni_5(CO)_{12}]^{2-}$ dianion (Fig. 1) exists as a trigonal bipyramid consisting of a planar $Ni_3(CO)_3(\mu_2\text{-}CO)_3$ fragment, symmetrically capped by two $Ni(CO)_3$ groups.[2] The Ni—Ni distances within the triangle (av. 2.36 Å, spread 0.02 Å) are less than those between the triangle and the apical atoms (av. 2.81 Å, spread 0.09 Å). The apical atoms are connected to the triangle by Ni—Ni bonds only. The shortest Ni—Ni bonds from the two apical nickel atoms connect to the same nickel atom within the triangle, indicative of a distortion of the Ni_5 core from an idealised D_{3h} towards a C_{2v} geometry. Due to crystal disorder, the structure was solved with half weighted terminal carbonyl carbon atoms of the central $Ni_3(CO)_3(\mu_2\text{-}CO)_3$ fragment being completely superimposed on half-weighted bridging carbonyl oxygen atoms. Accordingly, the distances involving these atoms should be treated with caution.

$[Ni_6(CO)_{12}]^{2-}$

The $[Ni_6(CO)_{12}]^{2-}$ dianion (Fig. 2) has been structurally characterised as its NMe_4^+ and PPN^+ salts.[1,18,19] It exists as a trigonal antiprism formed from two $[Ni_3(CO)_3(\mu_2\text{-}CO)_3]$ triangles, separated by 2.49 Å (NMe_4^+ salt)[13] and joined to each other only by Ni—Ni bonds. The intratriangle Ni—Ni bond lengths (2.38 Å, NMe_4^+ salt; 2.390 Å, PPN^+ salt) are identical and are approximately the same as those in the $[Ni_5(CO)_{12}]^{2-}$ dianion, but are considerably less than those between the triangles (av. 2.760 Å, PPN^+ salt). The intertriangle Ni—Ni bond distances fall into three significantly different, symmetry related pairs of lengths 2.734(1), 2.755(1) and 2.791(1) Å, as illustrated in Fig. 3. This distortion lowers the symmetry from C_{3v} to C_i. The terminal carbonyl ligands lie approximately within the plane of the $[Ni_3(CO)_3(\mu_2\text{-}CO)_3]$ triangles and eclipse the μ_2-CO ligands of the other triangle. The carbon atoms of each μ_2-CO ligand are oriented away from the other Ni_3 triangle by approximately 0.5 Å, an effect attributed to carbonyl–carbonyl repulsions.[13] Within experimental error, the μ_2-CO ligands bridge symmetrically.

The structure contrasts with that of the trigonal prismatic analogue, $[Pt_3(CO)_3(\mu_2\text{-}CO)_3]_2^{2-}$.[47] It has been suggested that the intertriangle repulsions are sufficiently greater at the shorter Ni—Ni separations to induce a staggered (trigonal antiprism) rather than an eclipsed (trigonal prism) configuration of metal atoms.[1]

$[Ni_9(CO)_{18}]^{2-}$

The structure of $[AsPh_4]_2[Ni_9(CO)_{18}]$ was first reported in 1975.[3,48] A crystal disorder obscured the true conformation of the dianion and the structure of $[Ni_9(CO)_{18}]^{2-}$ was suggested to be two face sharing octahedra. In 1986 a redetermination of the structure was reported.[13] The $[Ni_9(CO)_{18}]^{2-}$ dianion (Fig. 4) consists of an essentially parallel stack of three planar $[Ni_3(CO)_3(\mu_2\text{-}CO)_3]$ fragments joined only by Ni—Ni bonds to generate a distorted trigonal antiprism sharing a face with a distorted trigonal prism. It can be thought of as a condensation of a $[Ni_3(CO)_3(\mu_2\text{-}CO)_3]$ unit onto the $[Ni_6(CO)_{12}]^{2-}$ dianion in an eclipsed fashion. The structure is illustrated schematically in Fig. 5

Table 1. Crystal data for nickel carbonyl cluster anions

Cluster type (cations stated only when multiple determinations have been performed)	System[a]	S.G.[b]	Cell constants from X-ray diffraction data						R	R_w	Ref.
			a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)			
Dianions											
$[Ni_5(CO)_{12}]^{2-}$	T	$A\bar{1}$	13.309(7)	23.804(14)	12.577(7)	91.73(5)	95.30(4)	77.63(4)	0.075	0.097	2,3
$[Ni_6(CO)_{12}]^{2-}[NMe_4^+]_2$	Trig	$P\bar{3}$	11.003(1)	11.003(1)	7.045(1)				0.039	0.040	1
$[Ni_6(CO)_{12}]^{2-}[PPN^+]_2$	T	$P\bar{1}$	13.024(2)	13.270(2)	13.319(3)	81.38(2)	73.68(2)	60.94(2)	0.069	0.066	19
$[Ni_6(CO)_{12}]^{2-}[PPN^+]_2$	T	$P\bar{1}$	13.299(4)	13.343(4)	13.051(5)	106.24(3)	119.04(2)	84.1(3)	0.033	–	18
$[Ni_9(CO)_{18}]^{2-}$	M	$P2_1/n$	20.347(4)	15.758(5)	22.820(8)		114.380(2)		0.085	0.070	12,13
$[Ni_{12}(CO)_{21}]^{4-}$	M	$C2/c$	20.398(6)	12.812(5)	26.142(8)		119.62(4)				17
Carbonyl hydrides											
$[HNi_2(CO)_6]^-$	M	$P2_1/c$	13.44(1)	21.09(1)	14.46(1)		90.45(5)		0.054		7
$[HNi_{12}(CO)_{21}]^{3-}$	T	$P\bar{1}$	15.057(4)	25.479(5)	12.891(3)	91.57(2)	91.93(2)	76.25(2)	0.084	0.083	5
$[H_2Ni_{12}(CO)_{21}]^{2-}[AsPh_4^+]_2$	T	$P\bar{1}$	14.872(4)	25.480(5)	9.652(3)	101.11(2)	96.77(2)	89.37(2)	0.062	0.073	5,6
$[H_2Ni_{12}(CO)_{21}]^{2-}[PPN^+]_2$	T	$P\bar{1}$	16.248(5)	25.523(5)	11.589(3)	103.67(2)	92.16(2)	91.17(2)	0.057	0.078	5
$[H_2Ni_{12}(CO)_{21}]^{2-}[PPh_4^+]_2$	M	$P2_1/c$	9.738(2)	25.662(9)	28.611(6)		97.09(2)		0.083	0.088	5
Monocarbides											
$[Ni_7(CO)_{12}C]^{2-}$	O	$Pbca$	20.186(5)	15.881(5)	35.225(9)				0.066	0.085	16
$[Ni_8(CO)_{16}C]^{2-}$	Tet	$P4/nnc$	13.664(4)	13.664(4)	17.013(6)				0.057	0.084	11
$[Ni_9(CO)_{17}C]^{2-}$	Tet	$P4nc$	14.115(3)	14.115(3)	16.195(4)				0.055	0.063	11
Dicarbides											
$[Ni_{10}(CO)_{16}C_2]^{2-}$	M	Pc	11.762(4)	13.404(4)	22.948(8)		113.5(4)		0.042	0.043	10
$Ni_{11}(CO)_{15}C_2]^{4-}$	T	$P\bar{1}$	12.660(4)	12.667(2)	13.932(5)	111.45(2)	109.65(2)	91.00(2)	0.056	0.070	16
$[Ni_{12}(CO)_{16}C_2]^{4-}$	M	$P2_1/c$	13.381(3)	22.112(9)	19.106(8)		105.97(3)		0.080	0.117	16
Tetracarbides											
$[Ni_{16}(CO)_{23}C_4]^{4-}$	M	$P2_1/n$	12.772(4)	21.245(5)	23.317(9)		99.73(3)		0.065	0.077	9
$[HNi_{34}(CO)_{38}C_4]^{5-}$	M	$P2_1/c$	16.779(4)	23.898(6)	18.886(7)		93.70(2)		0.057	0.084	15
$[Ni_{35}(CO)_{39}C_4]^{6-}$	M	$C2/c$	25.443(33)	16.812(6)	32.811(13)		109.35(6)		0.070	0.096	15
Hexacarbides											
$[HNi_{38}(CO)_{42}C_6]^{5-}$	M	$P2_1/c$	29.208(17)	18.436(9)	32.821(7)		104.14(4)		0.047	0.059	14

[a] System; T = triclinic, Trig = trigonal, Tet = tetragonal, M = monoclinic, O = orthorhombic.

[b] S.G. = space group.

Table 2. Summary data for nickel carbonyl cluster anions

Cluster ion	Number of cluster valance electrons	Idealised symmetry of nickel frame	Description of idealised nickel framework	Range of Ni–Ni bonds (Å)	Av. Ni—Ni bond length (Å)	Av. Ni—CO$_t$ bond length (Å)	Av. Ni—CO$_b$ bond length (Å)	Av. Ni—carbide bond length (Å)	Av. C—C (carbide) bond length (Å)	Av. CO$_t$ bond length (Å)	Av. CO$_b$ bond length (Å)	Ref.
$[Ni_5(CO)_{12}]^{2-}$	76	D_{3h}	Trigonal bipyramid	2.36–2.87	2.66	1.79	1.84	NA	NA	1.10	1.13	2,3
$[Ni_6(CO)_{12}]^{2-}$	86	C_{3d}	Trigonal antiprism	2.391–2.788	2.57	1.76	1.90	NA	NA	1.11	1.16	1,18,19
$[Ni_9(CO)_{18}]^{2-}$	128	C_{3v}	Face sharing trigonal prism and trigonal antiprism	2.367–2.989	2.60	1.75	1.89	NA	NA	1.14	1.17	12,13
$[Ni_{12}(CO)_{21}]^{4-}$	166	D_{3h}	Two face-shared octahedra with nickel atoms bridging the shared edges	2.42–2.80	2.56	1.73	1.89	NA	NA	1.14	1.16	4
$[HNi_2(CO)_6]^{-}$	34	C_{2v}	Two vertex-shared tetrahedra	NA	2.864	1.73	NA	NA	NA	1.18	NA	7
$[HNi_{12}(CO)_{21}]^{3-}$	166	C_{3v}	Two face-shared octahedra with nickel atoms bridging the shared edges	2.404–3.031	2.66	1.75	1.88	NA	NA	1.14	1.17	5,6
$[H_2Ni_{12}(CO)_{21}]^{2-}$	166	D_{3h}	Two face-shared octahedra with nickel atoms bridging the shared edges	2.424–2.909	2.67[a]	1.77	1.91	NA	NA	1.14	1.15	5,6
$[Ni_7(CO)_{12}C]^{2-}$	100	C_{2v}	Mono capped trigonal prism	2.382–3.056	2.57	1.65	1.85	1.99	NA	1.19	1.21	16
$[Ni_8(CO)_{16}C]^{2-}$	118	D_{4d}	Square antiprism	2.477–2.641	2.55	1.72	1.92	2.085	NA	1.14	1.15	11

$[Ni_9(CO)_{17}C]^{2-}$	130	C_{4v}	Mono capped square antiprism	2.485–2.617	2.55	1.71	1.98	2.09	NA	1.14	1.17	11
$[Ni_{10}(CO)_{18}C]^{2-}$	142	C_{4v}	Bicapped square antiprism	Presumed[b]	NA	NA	NA	NA	NA	NA	NA	11
$[Ni_{10}(CO)_{16}C_2]^{2-}$	142	C_{2h}	Two nickel triangles on either side of a planar nickel quadrilateral	2.38–3.00	2.62	1.71	1.94	2.08	1.405	1.15	1.16	10
$[Ni_{11}(CO)_{15}C_2]^{4-}$	152	C_s	Mono capping of one of the triangles of $[Ni_{10}(CO)_{16}C_2]^{2-}$[c]	2.34–2.87	2.57	1.76	1.90	2.07	1.46	1.14	1.17	16
$[Ni_{12}(CO)_{16}C_2]^{4-}$	164	C_{2v}	Capping of both triangles of $[Ni_{10}(CO)_{16}C_2]^{2-}$	2.334–3.033	2.56	1.75	1.90	2.07	1.43	1.11	1.20	16
$[Ni_{16}(CO)_{23}C_4]^{4-}$	226	C_{2h}	Distorted tetra capped cubo-octahedron	2.355–3.330	2.604	1.67	1.88	2.07	1.39	1.20	1.21	9
$[HNi_{34}(CO)_{38}C_4]^{5-}$	438	C_i	Ring of four Ni_7 units, capped by six nickel atoms	2.350–2.975	2.501	1.70	1.75–2.12	2.01	>3.0	1.17	1.17	15
$[Ni_{35}(CO)_{39}C_4]^{6-}$	450	C_i	Ring of four Ni_7 units, capped by seven nickel atoms	2.359–2.940	2.59	1.78	1.91	2.01	>3.0	1.12	1.22	15
$[HNi_{38}(CO)_{42}C_6]^{5-}$	494	D_{3d}	Hexa capped truncated octahedron with an Ni_8 cube core	2.380–3.034	2.57	1.70	1.87	2.06	>3.0	1.17	1.20	14

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[a] Calculated for PPh_4^+ salt.

[b] The structure of $[Ni_{10}(CO)_{18}C]^{2-}$ as either its NMe_4^+ or NBu_4^+ salts could not be determined because of the poor quality of the crystals. However, on the basis of the infrared spectrum, the dianion was suggested to have a μ_4-Ni bicapped square antiprismatic structure, similar to that of $[Ni_9(CO)_{17}C]^{2-}$.

[c] The unique Ni(CO) is disordered over two sites.

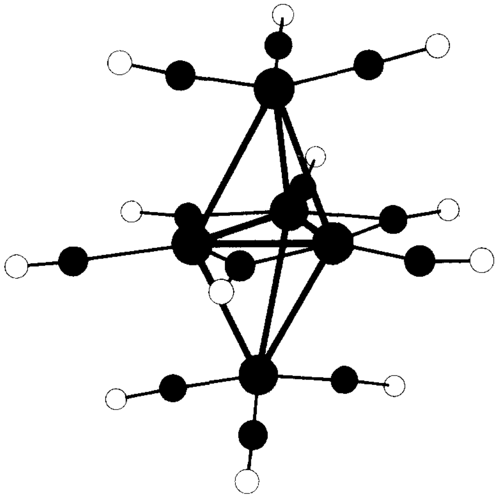

Fig. 1. Illustration of the structure of the $[Ni_5(CO)_{12}]^{2-}$ dianion.[2,3] ●, nickel atoms; ●, carbon atoms; ●, oxygen atoms.

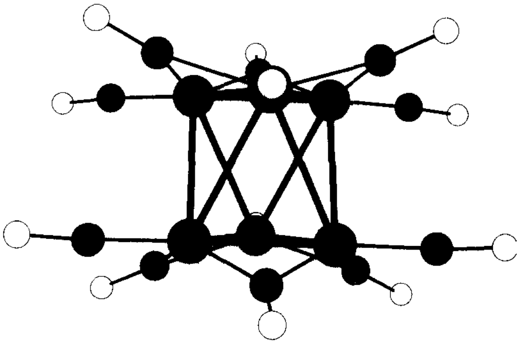

Fig. 2. Illustration of the structure of the $[Ni_6(CO)_{12}]^{2-}$ dianion.[1,18,19] ●, nickel atoms; ●, carbon atoms; ●, oxygen atoms.

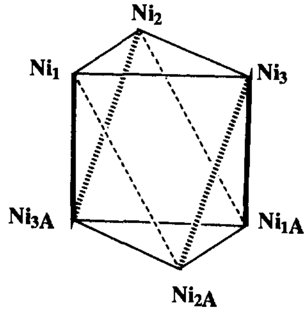

Fig. 3. Schematic illustration of the trigonal antiprismatic nickel architecture of the $[Ni_6(CO)_{12}]^{2-}$ dianion, showing the equivalent sets of Ni—Ni bonds (solid lines, 2.390 Å; dashed lines, 2.734 Å; hatched lines, 2.755 Å; bold lines, 2.791 Å).

and contrasts with those of the face-sharing bi(trigonal prismatic) polyhedron of $[Pt_9(CO)_{18}]^{2-}$ (i.e. simple hexagonal packing)[3,47,49] and the cofacial bioctahedral (or face-shared bi(trigonal antiprismatic) $[Rh_9(CO)_{19}]^{3-}$ (i.e. a hexagonal close packed fragment).[50] Layer A, the outer layer of the trigonal antiprism, is laterally displaced slightly relative to the central layer (B) and the outer layer (C) and the outer layers are rotated by ~11° from a centrosymmetric configuration. The Ni—Ni bond lengths within layer are equal (av. 2.400(3) Å) and are not significantly different from the intratriangle Ni—Ni bonds of $[Ni_6(CO)_{12}]^{2-}$.[1,18,19] Those of the middle layer B (the other triangle of

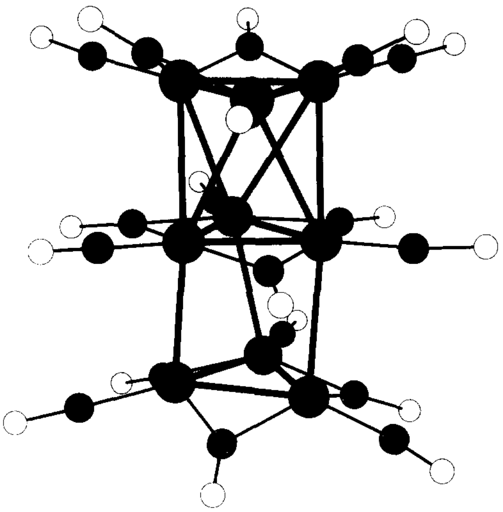

Fig. 4. Illustration of the structure of the $[Ni_9(CO)_{18}]^{2-}$ dianion.[12,13] ●, nickel atoms; ●, carbon atoms; ●, oxygen atoms.

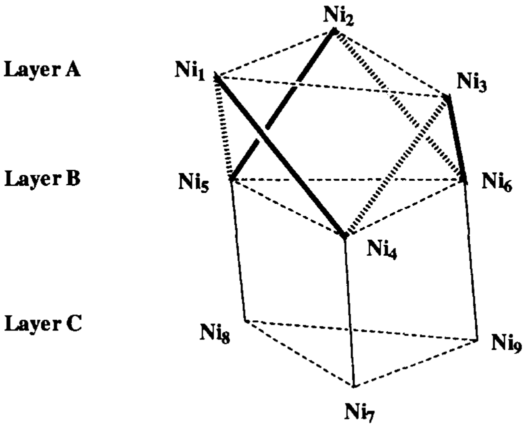

Fig. 5. Schematic illustration of the trigonal antiprismatic nickel architecture of the $[Ni_9(CO)_{18}]^{2-}$ dianion, showing the equivalent sets of Ni—Ni bonds [dashed lines, 2.387 Å (av.); solid lines, 2.719 Å (av.); hatched lines, 2.766 Å (av.); bold lines, 2.941 Å (av.)].

the trigonal antiprism) are effectively all the same (av. 2.371 Å) but are significantly shorter than those within layer A (and, hence, than those of $[Ni_6(CO)_{12}]^{2-}$).

Layers A and B are separated by 2.49 Å (as are the Ni_3 triangles of $[Ni_6(CO)_{12}]^{2-}$). However, there are two groups of three interplanar (AB) Ni—Ni bond lengths, one of which (av. 2.766 Å) is approximately the same as that in $[Ni_6(CO)_{12}]^{2-}$. The other group is significantly longer (av. 2.941 Å), the increase being attributed to interlayer repulsions of the carbonyl ligands.

The average Ni—Ni bond length within layer C (2.389 Å) is intermediate between those within layers A and B. The Ni—Ni distances between layers B and C (av. 2.719 Å) are significantly shorter than those between layers A and B and the BC interlayer distance (2.66 Å) is greater than that (2.49 Å) between layers A and B.

The carbon atoms of the ligands on the outer layers are bent away from the central layer by significant amounts (terminal 0.22 Å, bridging ~0.5 Å). The carbon atoms of the terminal carbonyls of layer B are displaced ~0.1 Å towards layer A, those of the bridging carbonyls are displaced ~0.1 Å towards layer C. All μ_2-CO ligands bridge symmetrically.

Such distortions have been attributed to a combination of steric repulsions between carbonyl ligands, similar to those in $[Ni_6(CO)_{12}]^{2-}$ and a strengthening of interlayer Ni—Ni bonds by changing the nickel hybridisation.[51]

The 128 cluster valence electrons are as predicted for the observed condensed trigonal antiprism and trigonal prism. The alternative bitrigonal prismatic (*cf* $[Pt_9(CO)_{18}]^{2-}$) or bitrigonal antiprismatic (*cf* $[Rh_9(CO)_{19}]^{3-}$) geometries require 132 and 124 cluster valence electrons, respectively.[13]

On the basis of the structures of $[Ni_6(CO)_{12}]^{2-}$ and $[Ni_9(CO)_{18}]^{2-}$, an homologous series, $[Ni_3(CO)_6]_n^{2-}$, analogous to the platinum carbonyl dianions, might be expected. The next member would be $[Ni_{12}(CO)_{24}]^{2-}$; however, the known homoleptic dodeca cluster is $[Ni_{12}(CO)_{21}]^{4-}$.[4,17]

$[Ni_{12}(CO)_{21}]^{4-}$

The details of this structure have been reported only at a meeting and have not otherwise been published.[4,17] The atomic co-ordinates of the tetraanion are collected in Table 3.

The $[Ni_{12}(CO)_{21}]^{4-}$ tetraanion is illustrated in Fig. 6 and consists of an *aba* hexagonal close packed stack of three near parallel planar nickel arrays, 2.35 Å apart, disposed about a common C_3 axis and joined only by Ni—Ni bonds. The two outer layers consist of $[Ni_3(CO)_3(\mu_2\text{-}CO)_3]$ fragments. A $[Ni_6(CO)_3(\mu_2\text{-}CO)_6]$ triangle makes up the inner layer. In contrast to $[Ni_9(CO)_{18}]^{2-}$, the outer triangles are eclipsed and the structure can be thought of as two cofacial trigonal antiprisms with nickel atoms bridging the shared edges. The bi(trigonal antiprismatic) geometry presumably

Table 3. Positional-parameters and estimated standard deviations for the $[Ni_{12}(CO)_{21}]^{4-}$ tetraanion[17]

Atom	*x*	*y*	*z*	*B* (Å^2)
Ni(1)	0.00000	0.15477(18)	0.250	
Ni(2)	0.00000	−0.18446(17)	0.250	
Ni(3)	0.02181(8)	−0.00417(12)	0.30750(6)	
Ni(4)	0.03905(9)	−0.17519(13)	0.35373(6)	
Ni(5)	0.12664(8)	0.04758(13)	0.27212(6)	
Ni(6)	0.10803(8)	−0.11707(13)	0.22126(6)	
Ni(7)	0.14663(8)	−0.11478(13)	0.32514(6)	
O(1)	0.00000	0.3804(11)	0.250	7.40
O(2)	0.08291(55)	−0.2985(10)	0.45759(39)	7.20
O(3)	0.18023(61)	0.2563(8)	0.28400(50)	7.50
O(4)	0.12169(58)	−0.2129(11)	0.12777(42)	8.60
O(5)	0.23607(60)	−0.2180(9)	0.43587(43)	7.80
O(6)	0.04609(69)	0.1892(9)	0.37047(42)	7.80
O(7)	0.07444(68)	−0.0057(9)	0.43177(37)	8.40
O(8)	0.03249(87)	−0.3818(9)	0.30998(44)	10.80
O(9)	0.13223(54)	0.0591(9)	0.16319(38)	7.00
O(10)	0.18346(60)	−0.3036(9)	0.28467(43)	7.40
O(11)	0.21831(55)	0.0651(8)	0.39930(39)	7.30
C(1)	0.00000	0.2892(15)	0.250	5.90
C(2)	0.06528(73)	−0.2491(11)	0.41633(55)	5.00
C(3)	0.15425(73)	0.1736(11)	0.27732(55)	4.90
C(4)	0.11068(78)	−0.1785(13)	0.16250(59)	6.90
C(5)	0.19653(70)	−0.1802(11)	0.39295(55)	5.40
C(6)	0.03180(74)	0.1341(11)	0.33254(52)	5.00
C(7)	0.05320(73)	−0.0383(11)	0.38416(48)	4.50
C(8)	0.02461(75)	−0.2894(11)	0.30358(52)	5.00
C(9)	0.12377(67)	0.0181(11)	0.19926(49)	5.70
C(10)	0.15684(69)	−0.2212(11)	0.27878(52)	4.50
C(11)	0.18147(69)	0.0204(11)	0.35598(52)	4.30

$[NMe_4]_4[Ni_{12}(CO)_{21}] \cdot CH_3CN$—space group *C*2/*c* (no. 15), $a = 20.398(6)$, $b = 12.812(5)$, $c = 26.142(8)$ Å, $\beta = 119.62(4)°$, $Z = 4$.

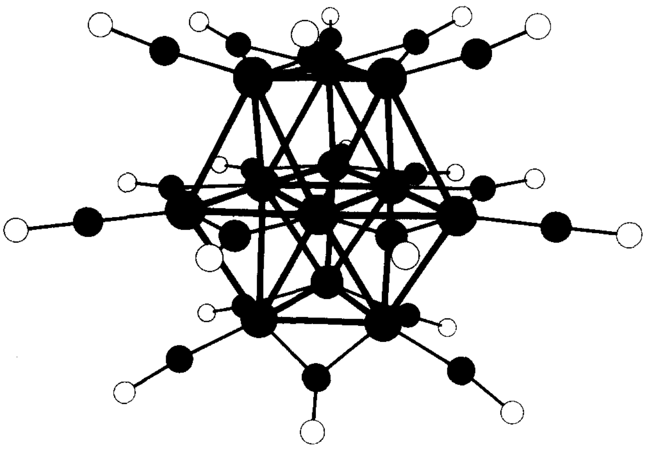

Fig. 6. Illustration of the structure of the $[Ni_{12}(CO)_{21}]^{4-}$ tetraanion.[17] ●, nickel atoms; ●, carbon atoms; ●, oxygen atoms.

becomes possible with the loss of interlayer carbonyl–carbonyl repulsions as the μ_2-CO ligands of the middle layer of $[Ni_9(CO)_{18}]^{2-}$ are replaced by nickel atoms. The structure contains an unfilled distorted octahedral hole between each pair of layers.

Within the outer layers, the Ni—Ni bond lengths are all equal (2.421 Å). Whilst the Ni—Ni bonds within the central layer are longer, having an average length of 2.514 Å, they fall into two groups, shorter bonds, bridged by carbonyls on the periphery of the triangle (av. 2.434 Å) and longer bonds, not bridged by carbonyls, across the triangle (av. 2.674 Å).

The interlayer Ni—Ni bonds fall into two groups, those from apical atoms (with terminal carbonyl ligands) of the middle triangle and those from central atoms of the middle triangle. The former average 2.744 Å in length, the latter 2.780 Å, with the average interlayer Ni—Ni bond length being 2.768 Å.

All carbonyl carbon atoms of the central $[Ni_6(CO)_3(\mu_2\text{-}CO)_6]$ triangle are situated on the plane defined by the six nickel atoms. However, the carbonyl carbons of the outer layers are located ~0.5 Å on the opposite side of the Ni_3 plane from the central layer. There are no carbonyls bridging between layers, the shortest Ni—C distance being 2.85 Å.

3. NICKEL CARBONYL HYDRIDE CLUSTER ANIONS

$[HNi_2(CO)_6]^-$

The simplest of the carbonyl hydride nickelates is the dimer, $[HNi_2(CO)_6]^-$, which contains two eclipsed tetrahedral $Ni(CO)_3$ fragments, joined by a Ni—Ni bond, which supports a bridging hydride ligand.[7] The hydride was located on the basis of potential energy maps calculations and the consistency of the results of these calculations with distortions in the $Ni_2(CO)_6$ framework. The Ni—H bond length is estimated to be *ca* 1.70 Å, with the hydrogen atom randomly occupying two symmetry related bridging sites. The atomic positional parameters for this species are no longer available. The PPN^+ counterion adopts a linear conformation.

$[H_{4-n}Ni_{12}(CO)_{21}]^{n-}$ ($n = 2,3$)

The $[H_{4-n}Ni_{12}(CO)_{21}]^{n-}$ ($n = 2,3$) anions were amongst the first interstitial hydrides to be structurally characterised by diffraction techniques. The structures of the $[HNi_{12}(CO)_{21}]^{3-}$ trianion as its $[AsPh_4]^+$ salt and of the $[H_2Ni_{12}(CO)_{21}]^{2-}$ dianion as its $[PPh_4]^+$ salt were established by both X-ray and neutron diffraction.[5,6] The structures of the $[PPN]^+$ and $[AsPh_4]^+$ salts of the $[H_2Ni_{12}(CO)_{21}]^{2-}$ dianion have also been determined by X-ray crystallography.[5]

Both anions, $[H_{4-n}Ni_{12}(CO)_{21}]^{n-}$ ($n = 2,3$), are based on the same general motif as that of the $[Ni_{12}(CO)_{21}]^{4-}$ tetraanion, i.e. three parallel layers of two planar $[Ni_3(CO)_3(\mu_2\text{-}CO)_3]$ moieties flanking a planar $[Ni_6(CO)_3(\mu_2\text{-}CO)_6]$ fragment to form a hexagonal close packed array of nickel atoms. This dodecanickel array contains two octahedral and six tetrahedral holes (Fig. 7). When the hydride positions are considered, the series of anions, $[Ni_{12}(CO)_{21}]^{4-}$, $[HNi_{12}(CO)_{21}]^{3-}$, and $[H_2Ni_{12}(CO)_{21}]^{2-}$ have idealised geometries D_{3h}, C_{3v} and D_{3h}, respectively. The average distances within the nickel frameworks are collected in Table 4 for comparison. The nickel atoms of the central layers of all anions define a plane which also contains the terminal carbonyls of that layer. The carbon atoms of the bridging carbonyl ligands of the central layers are on average ~0.24 Å out of that plane.

As in the structure of the $[Ni_{12}(CO)_{21}]^{4-}$ tetraanion, the carbonyl groups of the outer triangles of both the $[HNi_{12}(CO)_{21}]^{3-}$, and $[H_2Ni_{12}(CO)_{21}]^{2-}$ anions are displaced ~0.5 Å out of the outer Ni_3 planes on the side opposite the central layer.

Some of the bridging carbonyl ligands are bound asymmetrically to the nickel atoms. There are no carbonyl ligands bridging between layers. The hydrides of the $[HNi_{12}(CO)_{21}]^{3-}$ and $[H_2Ni_{12}(CO)_{21}]^{2-}$ anions are assigned to non-central positions in the octahedral holes between the hexagonal close packed layers. The hydrogen atoms are closer to the central (0.73 Å in $[HNi_{12}(CO)_{21}]^{3-}$; 1.04 Å in

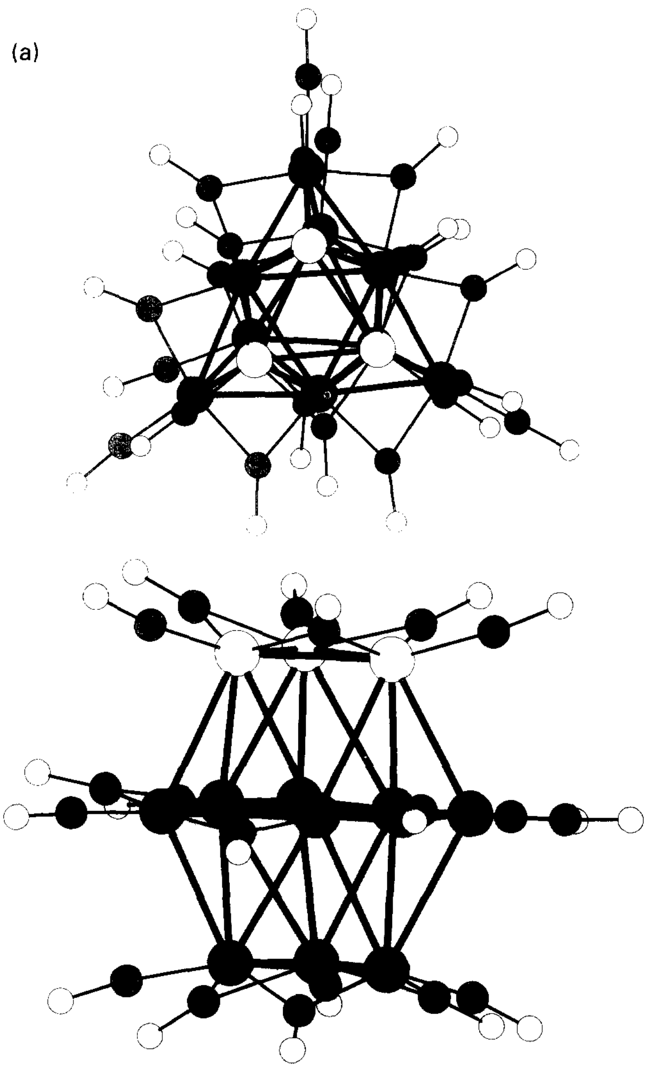

Fig. 7. Illustrations of the structure of the $[HNi_{12}(CO)_{21}]^{3-}$ trianion, (a) viewed down the C_3 axis and (b) viewed perpendicular to the C_3 axis.[5] Large spheres, nickel atoms; medium spheres, carbon atoms; small spheres, oxygen atoms.

Table 4. Comparison of average nickel framework distances in the dodecanickel anions[5,6,17]

Average distance (Å)	$[Ni_{12}(CO)_{21}]^{4-}$	$[HNi_{12}(CO)_{21}]^{3-}$	$[H_2Ni_{12}(CO)_{21}]^{2-}$
Ni—Ni bond length in outer triangles	2.421	2.435(near H) 2.421	2.439
Ni—Ni bond lengths in inner triangle	2.674 (Ni_C—Ni_C) 2.434 (Ni_B—Ni_C)	2.682 (Ni_C—Ni_C) 2.416 (Ni_B—Ni_C)	2.659 (Ni_C—Ni_C) 2.431 (Ni_B—Ni_C)
Av. interlayer distance	2.35	2.43 (near H) 2.39	2.43
Interlayer Ni_A—Ni_B bond length	2.780	2.848(near H) 2.812	2.851
Interlayer Ni_A—Ni_C bond length	2.744	2.823 (near H) 2.750	2.808

$[H_2Ni_{12}(CO)_{21}]^{2-}$), than to the outer (1.69 Å in $[HNi_{12}(CO)_{21}]^{3-}$; 1.40 Å in $[H_2Ni_{12}(CO)_{21}]^{2-}$) layers.† The average Ni—H distances in the monohydride are 2.22 Å (to the nickel atoms of the outer layer) and 1.72 Å. Those in the dihydride are 2.00 Å (to the nickel atoms of the outer layer) and 1.84 Å. The hydrogen atom in the $[HNi_{12}(CO)_{21}]^{3-}$ anion is sufficiently far from the outer layer that it can be regarded as triply bridging to only the three Ni_C atoms of the central layer.

These structures contain layers of nickel triangles. Within the triangles, the carbonyl-bridged Ni—Ni bond lengths fall in the range 2.36–2.43 Å. The unbridged Ni—Ni bond lengths within the triangles are significantly longer, falling in the range 2.66–2.68 Å. The unbridged Ni—Ni bonds between layers are longer still, with lengths in the range 2.73–2.99 Å.

4. CARBIDE AND CARBIDE HYDRIDE CARBONYL CLUSTER ANIONS

4.1. *Monocarbide anions*

Just over half of the structurally characterised nickel carbonyl cluster anions contain at least one carbide carbon atom. Examples with one, two, four and six interstitial carbide carbons have been reported. Although several nickel carbide cluster anions have been isolated as hydrides, the locations of the hydride atoms have not been reported. King has commented that the increased volume necessary to accommodate non-hydrogen interstitial atoms can be generated within deltahedra by conversion of a pair of edge-sharing triangular faces into a single quadrilateral face by an elongation and hence rupture of the common edge.[20] Thus, whereas the non-carbide clusters, $[H_nNi_x(CO)_y]^{z-}$, discussed above, have structures based on the stacking of layers of nickel triangles and condensed triangles, the structures of the carbide cluster anions incorporate nickel quadrilaterals. In many cases, these are stacked in layers with nickel triangles.

In this context, the $[Ni_7(CO)_{12}C]^{2-}$ cluster dianion can be thought of at least formally as the structural precursor of a range of carbide clusters as shown in the following discussion.

$[Ni_7(CO)_{12}C]^{2-}$

The nickel polyhedron of this cluster anion (Fig. 8) has been described as approximating a trigonal prism, capped on a square face by a $Ni(CO_t)_2$ (t = terminal carbonyl, b = bridging carbonyl) fragment (Ni_4 of Fig. 9) or as a layer of three nickel atoms [Ni(1), Ni(4), Ni(6) of Fig. 9 (or Ni(2), Ni(4), Ni(5) by symmetry)] stacked above a layer of four nickel atoms [Ni(2), Ni(5), Ni(3), Ni(7) (or Ni(1), Ni(3), Ni(7), Ni(6)) of Fig. 9], with the two layers encapsulating a carbide atom.[16]

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† Note that the available co-ordinates for the neutron diffraction data for $[Ph_4As]_3[HNi_{12}(CO)_{21}] \cdot Me_2CO$ (ref. 5) are inconsistent with the Ni—H bond lengths in the published account (ref. 6). Good agreement is obtained if the *x* co-ordinate of the hydrogen atom is changed from 0.774 to 0.747.

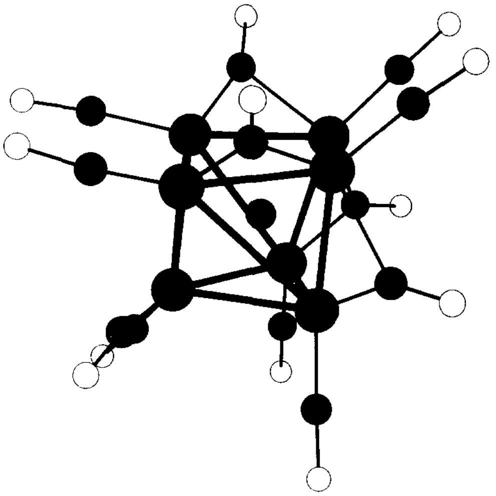

Fig. 8. Illustration of the structure of the $[Ni_7(CO)_{12}C]^{2-}$ dianion[16] emphasising the stacking of the nickel triangle and quadrilateral and the approximate mirror symmetry. ●, nickel atoms; ●, carbon atoms; ●, oxygen atoms.

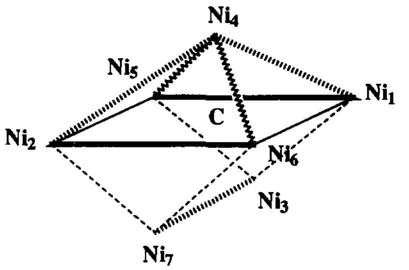

Fig. 9. Schematic illustration of the capped trigonal prismatic nickel frame of the $[Ni_7(CO)_{12}C]^{2-}$ dianion, showing the five sets of Ni—Ni bonds [dashed lines, 2.389(6) Å (av.); zig-zag lines 2.475(6) Å (av.); solid lines 2.54(2) Å(av.); hatched lines 2.62(3) Å (av.); bold lines 2.98(7) Å (av.)].

The symmetry of the anion approximates C_{2v}, with the nickel atom of the $Ni(CO_t)_2$ fragment, two of the $Ni(CO_t)$ groups and the encapsulated carbide defining a plane and the $Ni(CO_t)_2$ nickel atom and the carbide carbon lying on the C_2 axis, as illustrated in Fig. 8. The atoms Ni(3), Ni(4), Ni(7), and C (Fig. 9) are planar to within 0.05 Å. The carbonyls of the capping group are displaced slightly to opposite sides of the {Ni(3), Ni(4), Ni(7), C} plane (defined in Fig. 9). Figure 9 schematically illustrates the five groups of Ni—Ni bonds which make up the structure. As a capped trigonal prism, this anion is an example of a C_2 polar deltahedron. However, the two long Ni—Ni bonds allow an alternative description of the nickel frame as a square layer of four nickel atoms overlaid by a triangle of nickel atoms. The only bridging carbonyl ligands are the four within the two triangles of the trigonal prism. They occur in two pairs, related by the C_2 axis. In both pairs the bonding of the carbon to the nickel frame is asymmetric. Those carbonyls bridging the Ni(1)—Ni(3) and Ni(2)—Ni(7) bonds have average Ni—C bond lengths of 2.05(3) and 1.755(4) Å, those bridging Ni(3)—Ni(5) and Ni(6)—Ni(7) bonds have average Ni—C bond lengths of 1.736(1) and 1.84 Å. The carbide carbon is co-ordinated to all seven nickel atoms in two sets of near equivalent Ni—C bonds, one to Ni(1), Ni(2), Ni(4) and Ni(6), of average length 1.947(6) Å and the other to Ni(3), Ni(5) and Ni(7), of average length 2.04(3) Å.

The description of the structure as the stacking of a nickel triangle and nickel quadrilateral is particularly instructive in considering the structural similarities of a range of nickel carbide cluster anions. The $[Ni_7(CO)_{12}C]^{2-}$ structure is unique amongst the nickel carbonyl clusters in having a $Ni(CO_t)_2$ fragment and, unlike the homoleptic carbonyls and carbonyl hydrides above, has bridging carbonyl ligands between the layers of nickel atoms.

$[Ni_8(CO)_{16}C]^{2-}$

The nickel frame of the octanuclear $[Ni_8(CO)_8(\mu\text{-}CO)_8C]^{2-}$ dianion, of idealised D_{4h} symmetry, is formally derived by bridging and rupturing an edge of the nickel triangle of $[Ni_7(CO)_{12}C]^{2-}$, thereby forming a distorted square antiprism, formed from two parallel, staggered, square, planar $[Ni_4(CO)_4(\mu\text{-}CO)_4]$ fragments (each with Ni—Ni distances of 2.477(2) Å) encapsulating a carbide carbon atom.[11] The Ni—Ni interplanar distances are 2.641(2) and 2.612(2) Å (av. 2.627 Å), and all nickel atoms are 2.084(1) Å from the carbide carbon atom. The two tetranickel planes are connected by Ni—Ni and Ni—C bonds only, with no bridging carbonyl ligands between planes. The cluster dianion is illustrated in Fig. 10. All Ni—CO_t bond lengths are 1.72(1) Å, and any symmetry in the Ni—CO_b [1.93(1) and 1.91(1) Å] bonding is within experimental error. The terminal carbonyl ligands have C—O bond lengths of 1.14(1) Å and those of the bridging carbonyl ligands are 1.15(1) Å. The carbon atoms of the terminal carbonyl ligands lie slightly out of each $[Ni_4(CO)_4(\mu\text{-}CO)_4]$ plane (by ~0.15 Å) towards the other tetranickel plane whereas the bridging carbonyl carbon atoms are on the outer side of the structure by approximately 1.23 Å. The bridging carbonyl ligands of one plane eclipse the terminal carbonyl ligands of the other.

$[Ni_9(CO)_{17}C]^{2-}$

The structure of this dianion, illustrated in Fig. 11, is a distorted capped square antiprism.[11] It is derived from that of $[Ni_8(CO)_{16}C]^{2-}$ by capping one of the square faces with an Ni(CO) group and converting the four μ_2 carbonyl ligands of that plane into triply bridging carbonyl ligands. The structure is then formally $[Ni_9(CO)_9(\mu\text{-}CO)_4(\mu_3\text{-}CO)_4C]^{2-}$. The dimensions of the $[Ni_7(CO)_{12}C]^{2-}$, $[Ni_8(CO)_{16}C]^{2-}$ and $[Ni_9(CO)_{17}C]^{2-}$ dianions are compared in Table 5. Most of the dimensions of the $[Ni_9(CO)_{17}C]^{2-}$ dianion are not significantly different from those of the $[Ni_8(CO)_{16}C]^{2-}$ dianion. The dimensions suggest that the Ni—Ni, Ni—CO and C—O bonds and the displacements of the

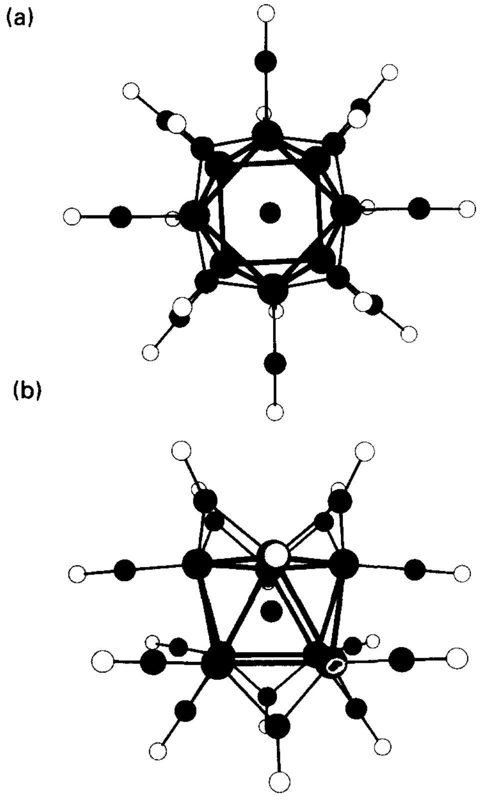

Fig. 10. Illustrations of the structure of the $[Ni_8(CO)_{16}C]^{2-}$ dianion[11] viewed (a) down the C_4 axis and (b) perpendicular to the C_4 axis. ●, nickel atoms; ●, carbon atoms; ●, oxygen atoms.

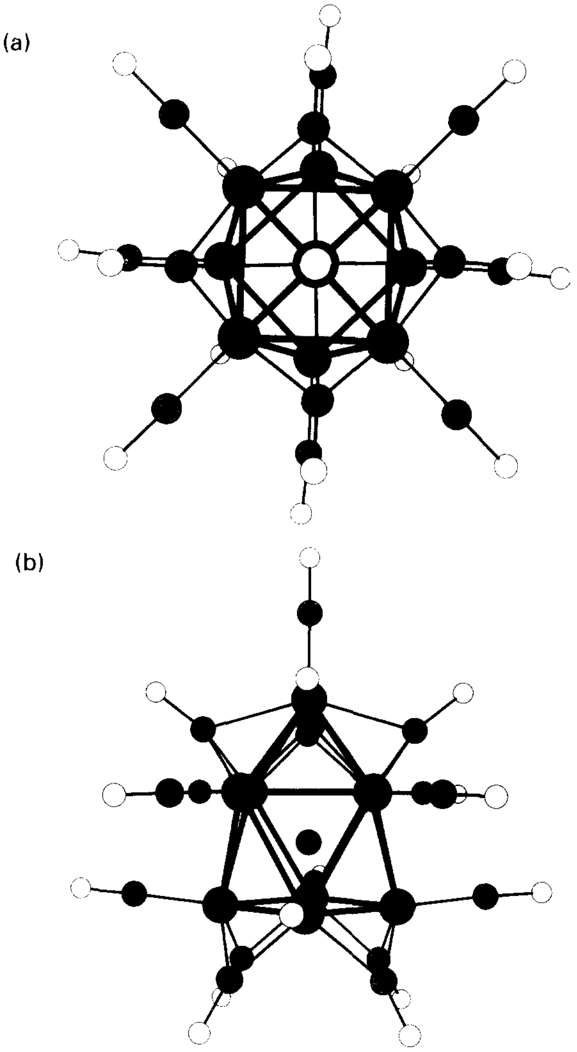

Fig. 11. Illustrations of the structure of the $[Ni_9(CO)_{17}C]^{2-}$ dianion[11] viewed (a) down the C_4 axis and (b) perpendicular to the C_4 axis. ●, nickel atoms; ●, carbon atoms; ●, oxygen atoms.

carbonyl ligands from the tetranickel plane within the $[Ni_8(CO)_{16}C]^{2-}$ cluster are approximately the same as those within the uncapped tetranickel plane of the $[Ni_9(CO)_{17}C]^{2-}$ cluster. The capped $[Ni_4(CO)_4(\mu\text{-}CO)_4]$ moiety has slightly longer Ni—Ni, NiC_t—O and NiC_b—O bonds and slightly shorter Ni—C_tO and Ni—C_bO bonds (Table 5). The interplanar Ni—Ni bonds and the interplanar separation are slightly shorter in the $[Ni_9(CO)_{17}C]^{2-}$ cluster. The Ni—$C_{carbide}$ distances within the square antiprismatic $[Ni_8(CO)_{16}C]^{2-}$ frames of both dianions are about the same.

The Ni—Ni bonds to the capping nickel atom of $[Ni_9(CO)_{17}C]^{2-}$ are considerably shorter than the interplanar Ni—Ni bonds and not very much longer than those within the tetranickel planes. The distance between the capping nickel atom and the carbide carbon is considerably longer than the Ni—$C_{carbide}$ "bonding" distances of those clusters structurally characterised to date (Table 6). Similarly, the bonds between the capping nickel atom and the μ_3-CO ligands are relatively long.

Thus, the square antiprismatic $[Ni_8(CO)_{16}C]$ units of the two dianions are almost identical, with the $[Ni_9(CO)_{17}C]^{2-}$ structure being derived from that of the $[Ni_8(CO)_{16}C]^{2-}$ structure by the capping of a square face of the latter with a Ni(CO) fragment, held to the $[Ni_8(CO)_{16}C]^{2-}$ unit predominantly by Ni—Ni bonds. The terminal carbonyl ligands of the capped tetranickel plane move into that plane and the oxygens of the now triply bridging carbonyl ligands move towards that plane.

Table 5. Comparison of the dimensions of the $[Ni_7(CO)_{12}C]^{2-}$, $[Ni_8(CO)_{16}C]^{2-}$ and $[Ni_9(CO)_{17}C]^{2-}$ dianions

Dimension	$[Ni_7(CO)_{12}C]^{2-}$ [16] (Å)	$[Ni_8(CO)_{16}C]^{2-}$ [11] (Å)	$[Ni_9(CO)_{17}C]^{2-}$ [11] (Å)
Ni—Ni quadrilateral intraplane	av. 2.48	2.477(2)	2.485(2) (uncapped) 2.493(2) (capped)
Ni—Ni interplane	av. 2.64	2.641(2), 2.612(2) av. 2.627	2.627(2), 2.608(2) av. 2.618
Ni—Ni_{cap}	–	–	2.526(3)
Ni—$C_{carbide}$	av. 1.987	2.084(1)	2.03(2) (capped) 2.15(2) (uncapped) 2.81(3) (capping atom)
Interplane separation	2.64	2.26	2.23
Ni—C_tO	1.646	1.72(1)	1.75(2) (uncapped) 1.69(2) (capped) 1.69(3) (capping atom)
C_t—O	1.187	1.14(1)	1.11(2) (uncapped) 1.19(2) (capped) 1.07(3) (capping atom)
Ni—C_bO	1.847	1.91(1), 1.93(1)	1.90(2) (uncapped) 1.93(2) (uncapped) 1.88(2) (capped) 2.18(2) (capping atom) 1.99(2)
C_b—O	1.213	1.15(1)	1.13(3) (uncapped) 1.20(2) (capped) 1.20(2) (capping atom)
Displacement of C_tO from Ni_4 plane	–	0.15(C) 0.24(O)	0.21(C) (uncapped) 0.29(O) (uncapped) 0(C), 0(O) (capped)
Displacement of C_bO from Ni_4 plane	–	1.23(C), 2.18(O)	1.23(C), 2.13(O) (uncapped) 1.21(C), 1.95(O) (capped)

$[Ni_{10}(CO)_{18}C]^{2-}$

This cluster has been isolated as its NMe_4^+ and NBu_4^+ salts and characterised by elemental analysis and infrared spectroscopy.[11] On the basis of the observation of only bands attributable to terminal and μ_3-CO ligand vibrations in the infrared spectrum, the structure was suggested to be a μ_4-Ni bicapped square antiprism. If these assignments are correct, this dianion would represent the *closo* member of a *closo*, *nido* ($[Ni_9(CO)_{17}C]^{2-}$) and *arachno* ($[Ni_8(CO)_{16}C]^{2-}$) series of cluster dianions.

4.2. *Dicarbide anions*

$[Ni_{10}(CO)_{16}C_2]^{2-}$

The structure of this dianion is illustrated in Fig. 12 and has been described as being formally derived by condensation of two $[Ni_7(CO)_{12}C]^{2-}$ clusters about a square face.[10] This description is equivalent to regarding the nickel polyhedron as two staggered isosceles nickel triangles layered either side of a planar nickel quadrilateral. Carbide carbon atoms occupy interstitial positions between the layers and lie 0.7 Å out of the tetranickel plane, on an axis approximately perpendicular to that plane. The average interplanar spacing is 2.12 Å. The central nickel quadrilateral has two bonds of moderate length and two of the longest bonds in the structure. Four short Ni—Ni bonds, each bridged by a carbonyl ligand, connect the nickel triangles with the nickel quadrilateral. Each

Table 6. Summary of Ni—$C_{carbide}$ bond distances

Carbide cluster	Range of Ni—$C_{carbide}$ bond lengths (Å)	Av. Ni—$C_{carbide}$ (Å)	Ref.
Ni_3C	1.86	1.86	39,40
$[Ni_7(CO)_{12}C]^{2-}$	1.940–2.085	1.988	16
$[Ni_8(CO)_{16}C]^{2-}$	2.085	2.085	11
$[Ni_9(CO)_{17}C]^{2-}$	2.022–2.155[a]	2.089	11
$[Ni_{10}(CO)_{16}C_2]^{2-}$	2.025–2.154	2.082	10
$[Ni_{11}(CO)_{15}C_2]^{4-}$	1.963–2.182	2.069	16
$[Ni_{12}(CO)_{16}C_2]^{4-}$	1.960–2.142	2.065	16
$[Ni_{16}(CO)_{23}C_4]^{4-}$	1.932–2.175	2.070	9
$[HNi_{34}(CO)_{38}C_4]^{5-}$	1.836–2.146[b]	2.012	15
$[Ni_{35}(CO)_{39}C_4]^{6-}$	1.817–2.382[c]	2.009	15
$[HNi_{38}(CO)_{42}C_6]^{5-}$	1.978–2.128	2.061	14

[a] There are four Ni—$C_{carbide}$ distances of 2.155 Å and four of 2.022 Å, with an average Ni—$C_{carbide}$ distance of 2.089 Å. The capping atom is 2.800 Å from the carbide carbon atom. The average distance of the carbide carbon atom from all nickel atoms is then 2.168 Å.

[b] There are 28 Ni—$C_{carbide}$ distances in the range 1.836–2.146 Å (av. 2.012 Å). A further three pairs of nickel atoms are 2.674, 2.678 and 2.845 Å from the carbide carbon atom, making the overall average Ni—$C_{carbide}$ distance 2.139 Å.

[c] There are 28 Ni—$C_{carbide}$ distances in the range 1.817–2.382 Å (av. 2.009 Å). A further three pairs of nickel atoms are 2.668, 2.753 and 2.895 Å from the carbide carbon atom, making the overall average Ni—$C_{carbide}$ distance 2.143 Å.

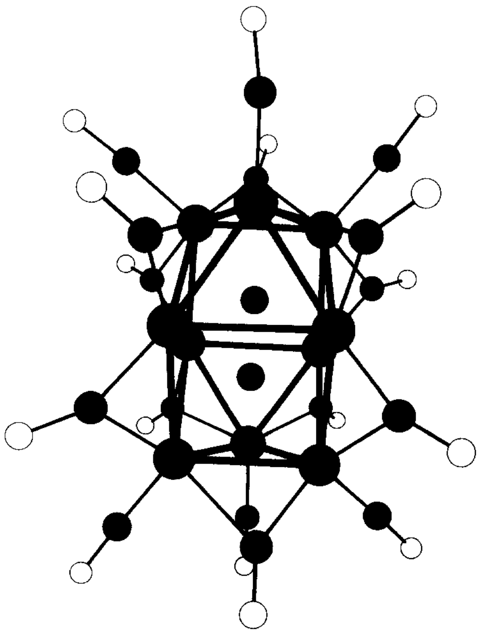

Fig. 12. Illustration of the structure of the $[Ni_{10}(CO)_{16}C_2]^{2-}$ dianion,[10] emphasising the description as a stack of two nickel triangles about a nickel quadrilateral and the disposition of the carbide atoms on either side of the quadrilateral. ●, nickel atoms; ●, carbon atoms; ●, oxygen atoms.

nickel triangle is oriented with its vertices approximately eclipsing a vertex and the midpoints of two edges of the nickel quadrilateral. One edge of each triangle is unique in this series in being bridged by a carbonyl ligand. The structure is then formally $[\{Ni_3(CO)_3(\mu\text{-}CO)\}_2(Ni_4)(\mu\text{-}CO)_8C_2]^{2-}$. The Ni—Ni bonds fall broadly into four groups as illustrated in Fig. 13. The longest are those between the layers. Each carbide atom is surrounded by seven nickel atoms at between 2.032 and 2.154 Å (av. $Ni\text{—}C_{carbide}$ 2.082 Å, *cf* $[Ni_7(CO)_{12}C]^{2-}$, range 1.940–2.085, av. 1.988). The two carbide carbon atoms are separated by 1.40 Å, a distance consistent with the presence of an interstitial C_2 fragment, rather than of two isolated carbide atoms. The $Ni\text{—}C_tO$ bond distances average 1.71 Å, whilst the bridging carbonyls around the edges of each layer are bound unsymmetrically, averaging $Ni\text{—}C_bO$ distances of 1.82 and 2.06 Å.

$[Ni_{11}(CO)_{15}C_2]^{4-}$

The preparation and identification of this cluster were reported briefly in a communication.[16] The cluster anion was isolated as its $NEt_3CH_2Ph^+$ salt, presumably from a solution from which $[Ni_{12}(CO)_{16}C_2]^{4-}$ was isolated as its NBu_4^+ salt. The salt, $[NEt_3CH_2Ph]_4[Ni_{11}(CO)_{15}C_2]$, was characterised by absorptions assigned to ν_{CO} vibrations in the infrared spectrum (apparently at low resolution), and by single crystal X-ray diffraction. The structure was disordered, with the disorder of the anion not stated, but presumably being half occupancy of each of two of the 12 nickel atoms listed in the deposited atomic parameters.‡

The structure of this tetraanion (Fig. 14) is formally derived from that of $[Ni_{10}(CO)_{16}C_2]^{2-}$ by loss of the two carbonyl ligands bridging the two nickel triangles and by capping of one of these triangles with a Ni(CO) moiety which converts the terminal carbonyl ligands of that triangle into bridging carbonyls in $[Ni_{11}(CO)_{15}C_2]^{4-}$ (in a manner similar to the formal conversion of $[Ni_8(CO)_{16}C]^{2-}$ into $[Ni_9(CO)_{17}C_2]^{2-}$). The four nickel atoms of the central quadrilateral again lie in a plane containing two Ni—Ni bonds of intermediate length and the two longest bonds within the cluster. Each carbide atom is 0.73 Å out of the plane of the nickel quadrilateral. The terminal carbonyl ligand, the capping nickel atom and the two carbide carbons are collinear, being situated on an axis perpendicular to the tetranickel plane.

$[Ni_{12}(CO)_{16}C_2]^{4-}$

This structure is illustrated in Fig. 15. It is formally derived from that of $[Ni_{11}(CO)_{15}C_2]^{4-}$ by the capping of the remaining triangular plane with a Ni(CO) moiety which is collinear with the other

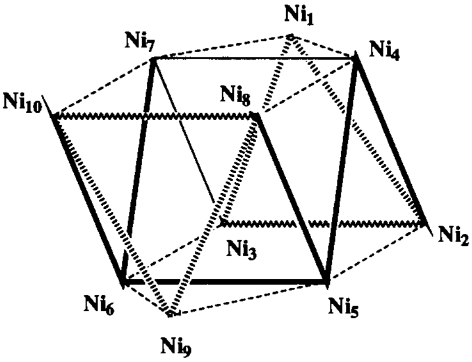

Fig. 13. Schematic representation of the nickel polyhedron of the $[Ni_{10}(CO)_{16}C_2]^{2-}$ dianion, showing the four sets of similar Ni—Ni bonds (dashed lines, ~2.4 Å; zig-zag lines, ~2.5 Å; hatched lines, ~2.6 Å; solid lines, ~2.7 Å; bold lines, ~2.9 Å).

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‡ The published ORTEP illustration of the structure of the $[Ni_{11}(CO)_{15}C_2]^{4-}$ tetraanion is accompanied by a figure legend referring to the $[Ni_{12}(CO)_{16}C_2]^{4-}$ tetraanion and *vice versa*. The information within each legend appears to be correct and self consistent.

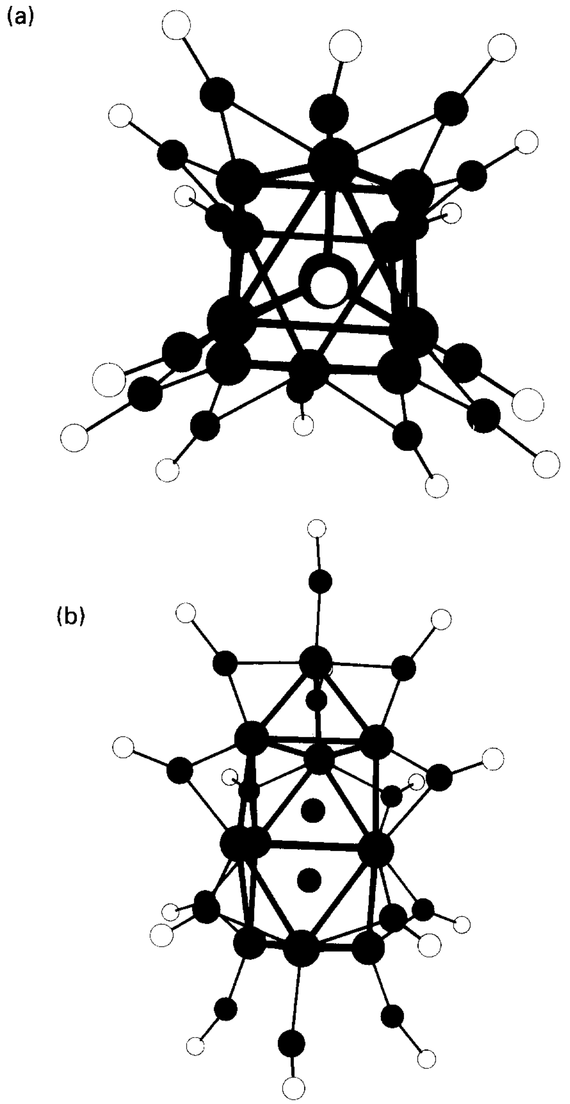

Fig. 14. Illustrations of the structure of the $[Ni_{11}(CO)_{15}C_2]^{4-}$ tetraanion[16] viewed (a) down the axis defined by the two carbide atoms and the capping Ni(CO) fragment (which hides the carbide atoms in this orientation) and (b) perpendicular to this axis emphasising the stacking of the nickel triangles on either side of the nickel quadrilateral. ●, nickel atoms; ●, carbon atoms; ●, oxygen atoms.

Ni(CO) moiety and the two carbide atoms.[16] The axis containing these atoms is perpendicular to the central tetranickel plane. The three terminal carbonyl ligands of the uncapped triangular plane of $[Ni_{11}(CO)_{15}C_2]^{4-}$ bridge unsymmetrically to the new capping Ni(CO) unit of $[Ni_{12}(CO)_{16}C_2]^{4-}$. Similarly to the structures of the deca- and undeca-nickel carbides, the carbide atoms are 0.71 Å either side the tetranickel plane (Table 7).

4.3. *Tetracarbide anions*

$[Ni_{16}(CO)_{23}C_4]^{4-}$

In this structure (Fig. 16) the carbide atoms are situated in pairs.[9] Each pair has a C—C bond length of 1.38 Å and the two pairs are separated by approximately 2.9 Å. The metal polyhedron can be described as a distorted bis truncated equatorially edge-centred octahedron or as a tetracapped cubooctahedron. The idealised symmetry of the metal array is C_{2h}, with the C_2 axis passing through

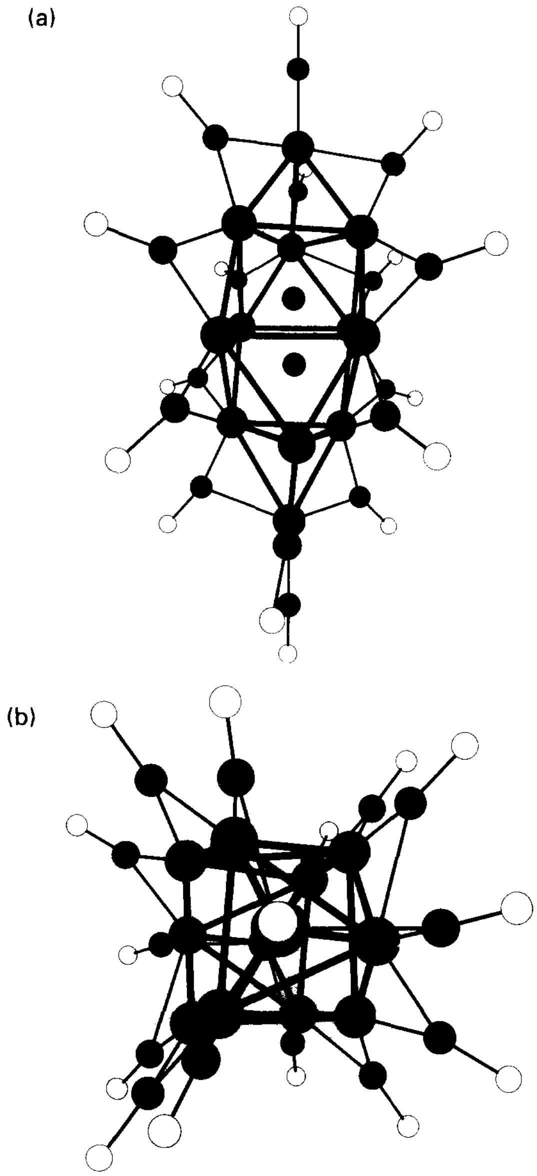

Fig. 15. Illustration of the structure of the $[Ni_{16}(CO)_{16}C_2]^{4-}$ tetraanion[16] viewed (a) perpendicular to, and (b) down the axis defined by the two carbide atoms, emphasising the stacking of the nickel triangles on either side of the nickel quadrilateral. ●, nickel atoms; ●, carbon atoms; ●, oxygen atoms.

Ni(1) and Ni(16) (Fig. 17). The structure is formally produced from the condensation of two $[Ni_{10}(CO)_{16}C_2]^{2-}$ clusters at one vertex from each nickel layer in each structure and the loss of what would be an interstitial nickel atom formed from the condensation of the quadrilaterals of the two $[Ni_{10}(CO)_{16}C_2]^{2-}$ clusters. The two "vertex sharing" tetranickel planes then become a planar hexagon perpendicular to the axes of the two C_2 fragments, the carbon atoms of which are approximately 0.70 Å out of the hexanickel plane. The tetraanion is then $[Ni_{16}(CO)_{12}(\mu\text{-}CO)_{10}(\mu_3\text{-}CO)(C_2)_2]^{4-}$.

The common structural features of the $[Ni_{10}(CO)_{16}C_2]^{2-}$, $[Ni_{11}(CO)_{15}C_2]^{4-}$, $[Ni_{12}(CO)_{16}C_2]^{4-}$ and $[Ni_{16}(CO)_{23}C_4]^{4-}$ anions are a stack of two staggered nickel isosceles triangles surrounding a planar nickel quadrilateral with carbide atoms between the layers, approximately 0.7 Å out of the central plane and on an axis perpendicular to that plane. This axis includes any Ni(CO) fragments capping the structure. The structure of the $[Ni_{16}(CO)_{23}C_4]^{4-}$ cluster is derived from two such decanickel clusters (with loss of an otherwise interstitial nickel atom). The metal polyhedra of all structures are formally derived by the addition of a nickel triangle, capping Ni(CO) units and a carbide atom

Table 7. Comparison of selected bond distances within nickel mono- and di-carbide carbonyl cluster anions

Bond	$[Ni_7(CO)_{12}C]^{2-}$ [16] (Å)	$[Ni_{10}(CO)_{16}C_2]^{2-}$ [10] (Å)	$[Ni_{11}(CO)_{15}C_2]^{4-}$ [16] (Å)	$[Ni_{12}(CO)_{16}C_2]^{4-}$ [16] (Å)
Ni—Ni within triangle	2.481	2.504, 2.521	2.580	2.547
	2.560	2.605, 2.614	2.616	2.578
	2.580	2.645, 2.641	2.628	2.585
Ni—Ni within quadrilateral	2.395, 2.395	2.682, 2.700	2.720	2.743
	2.526, 2.604	2.850, 2.892	2.821	2.797
C-quadrilateral plane	1.06	0.70	0.73	0.71
Triangle-quadrilateral				
	long			
	3.056, 2.908,	3.001, 2.867	2.839	3.033
	2.668	2.935, 2.956	2.866	2.732
	short			
	2.382, 2.383,	2.412, 2.399	2.394, 2.406	2.334, 2.342
	2.469	2.402, 2.384	2.341, 2.347	2.349, 2.513
		2.403, 2.390		
		2.393, 2.398		
Cap-triangle	–	–	2.408, 2.350	2.473, 2.468
			2.249	2.398

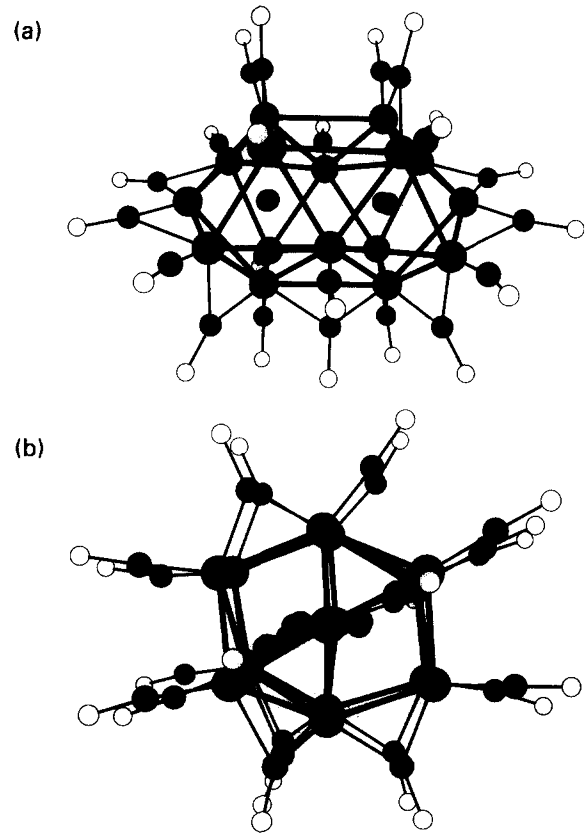

Fig. 16. Illustrations of the structure of the $[Ni_{16}(CO)_{23}C_4]^{4-}$ tetraanion[9] viewed (a) along the axis defined by one C_2 ligand and (b) approximately perpendicular to this axis. ●, nickel atoms; ●, carbon atoms; ●, oxygen atoms.

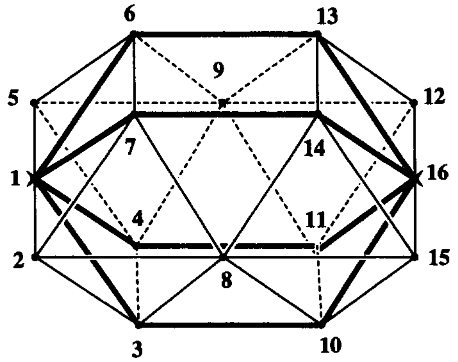

Fig. 17. Schematic illustration of the nickel polyhedron of $[Ni_{16}(CO)_{23}C_4]^{4-}$. The longest Ni—Ni bonds (2.739–3.330 Å) are those between nickel atoms defining the planes [Ni(1), Ni(6), Ni(13), Ni(16), Ni(10), Ni(3)] and [Ni(1), Ni(4), Ni(11), Ni(16), Ni(14), Ni(7)]. The shortest bonds between nickel atoms are between these planes [i.e. Ni(6)–Ni(7), Ni(13)–Ni(14), Ni(3)–Ni(4) and Ni(10)–Ni(11), 2.355–2.369 Å].

to the $[Ni_7(CO)_{12}C]^{2-}$ dianion which can also be viewed as the formal structural precursor of the $[Ni_8(CO)_{16}C]^{2-}$ and $[Ni_9(CO)_{17}C]^{2-}$ monocarbides.

In this context, capping the $[Ni_{16}(CO)_{23}C_4]^{4-}$ cluster with Ni(CO) fragments on the two axes defined by the dicarbide ligands would produce the hypothetical anions, $[Ni_{17}(CO)_8(\mu\text{-}CO)_{16}(C_2)_2]^{4-}$, $[Ni_{18}(CO)_6(\mu\text{-}CO)_{19}(C_2)_2]^{4-}$, $[Ni_{19}(CO)_5(\mu\text{-}CO)_{20}(\mu_3\text{-}CO)(C_2)_2]^{4-}$ and $[Ni_{20}(CO)_4(\mu\text{-}CO)_{21}(\mu_3\text{-}CO)_2(C_2)_2]^{4-}$.

$[HNi_{34}(CO)_{38}C_4]^{5-}$

The carbides of this anion define a planar rhombus with edges of 3.64 Å.[15] The carbide atoms are therefore well separated and the structure is analogous to the mono-, rather than di-carbide structures discussed above.

Figure 18 illustrates the structure of the cluster anion, the nickel/carbide frame of which has C_i symmetry and which has been described as conceptually derived from three cubic close packed

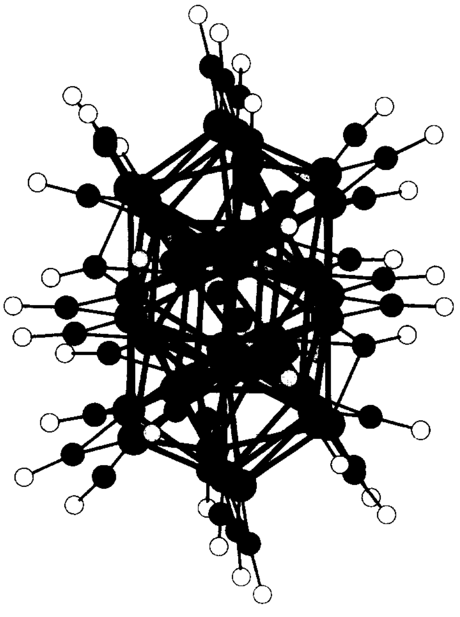

Fig. 18. Illustration of the structure of the $[Ni_{34}(CO)_{38}C_4]^{6-}$ hexaanion.[15] ●, nickel atoms; ●, carbon atoms; ●, oxygen atoms.

layers of eight, four and eight nickel atoms (Fig. 19).[15] The layers are approximately 2.04 Å apart. Figure 20 illustrates that this arrangement produces two quadrilateral faces between adjacent layers. Carbide atoms have been shown to exhibit a preference for quadrilateral faces. Thus, the four carbide atoms cap the quadrilateral faces and are in turn each capped by two nickel atoms such that the carbide atoms are each in trigonal prismatic cavities. This arrangement generates two symmetry related concave centred pentagonal faces, each with two adjacent quadrilateral faces. Nickel atoms cap the pentagonal and two of the quadrilateral faces. The resultant structure then has a stepped "belt" with four butterfly and two quadrilateral faces. To complete the structure, two nickel atoms condense onto the butterfly faces between the capped pentagon and the capped quadrilateral faces.

An alternative useful conceptual view of the structure, relating it to the structures of other nickel carbides, is as the condensation of two halves of the molecules about a centre of symmetry. Each half is based on two monocapped Ni_7C units, each capped over a square face. A comparison between the dimensions of these Ni_7C moieties and those of $[Ni_7(CO)_{12}C]^{2-}$ (structurally characterised some

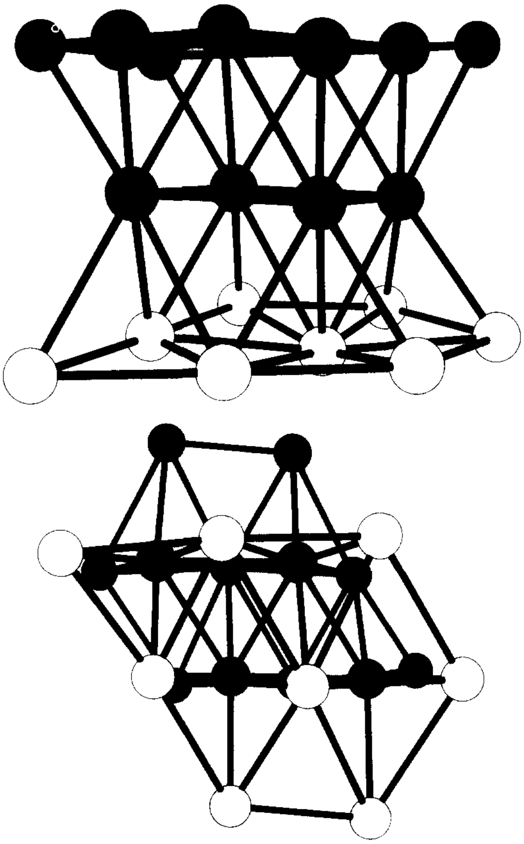

Fig. 19. Approximately perpendicular illustrations of the cubic close packed core of the $[Ni_{34}(CO)_{38}C_4]^{6-}$ hexaanion.[15]

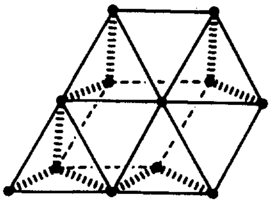

Fig. 20. Schematic illustration of two layers of a cubic close packed nickel fragment of the $[HNi_{34}(CO)_{38}C_4]^{5-}$ anion (solid lines, Ni—Ni bonds of the outer layer; dotted lines, Ni—Ni bonds of the middle layer; hatched lines, interlayer Ni—Ni bonds).

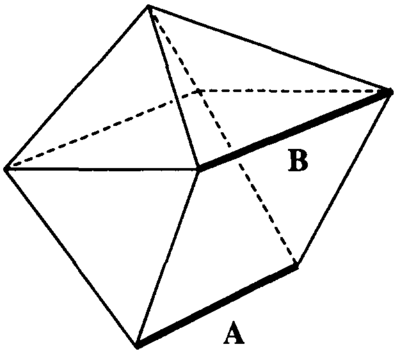

Fig. 21. The Ni_7C unit common to $[HNi_{34}(CO)_{38}C_4]^{5-}$, $[Ni_{35}(CO)_{39}C_4]^{6-}$ and $[Ni_7(CO)_{12}C]^{2-}$.

Table 8. Comparison between the dimensions of the Ni_7C units of $[HNi_{34}(CO)_{38}C_4]^{5-}$, $[Ni_{35}(CO)_{39}C_4]^{6-}$ and $[Ni_7(CO)_{12}C]^{2-}$

Bond distance	$[HNi_{34}(CO)_{38}C_4]^{5-}$[15] (Å)		$[Ni_{35}(CO)_{39}C_4]^{6-}$[15] (Å)		$[Ni_7(CO)_{12}C]^{2-}$[16] (Å)
(Å)	Site 1	Site 2	Site 1	Site 2	
av. Ni—$C_{carbide}$	2.009[a]	2.015[b]	2.005[c]	2.012[d]	1.987[e]
av. Ni—Ni	2.569[f]	2.578[g]	2.575[h]	2.572[i]	2.569[j]

[a] Individual distances 1.836, 1.872, 1.910, 1.938, 2.025, 2.075, 2.404.

[b] Individual distances 1.935, 1.945, 1.962, 1.970, 2.057, 2.092, 2.146.

[c] Individual distances 1.817, 1.897, 1.924, 1.933, 2.033, 2.049, 2.382.

[d] Individual distances 1.916, 1.940, 2.001, 2.031, 2.039, 2.071, 2.089.

[e] Individual distances 1.940, 1.942, 1.951, 1.953, 2.014, 2.028, 2.085.

[f] Individual distances 2.429, 2.450, 2.455, 2.490, 2.498, 2.470, 2.479, 2.561, 2.591, 2.689, 2.731, 2.734, 2.815.

[g] Individual distances 2.376, 2.410, 2.486, 2.493, 2.559, 2.574, 2.584, 2.587, 2.594, 2.628, 2.658, 2.736, 2.831.

[h] Individual distances 2.359, 2.414, 2.465, 2.486, 2.540, 2.575, 2.577, 2.586, 2.614, 2.652, 2.655, 2.728, 2.818.

[i] Individual distances 2.435, 2.438, 2.478, 2.483, 2.491, 2.494, 2.495, 2.532, 2.598, 2.670, 2.749, 2.756, 2.821.

[j] Individual distances 2.382, 2.383, 2.395, 2.395, 2.469, 2.481, 2.526, 2.560, 2.580, 2.604, 2.668, 2.908, 3.056.

2 years later) is made in Table 7. The capping atom to carbide distance is outside the range expected for Ni—C interactions (Table 5), suggesting a description as a monocapped Ni_7C unit, rather than as a bicapped Ni_6C trigonal prism. The two Ni_7C fragments share a common vertex and are joined to each other by bonds between the two triangular faces of each Ni_7C moiety which are adjacent to the common vertex. The common vertex is one of the four members of the middle layer of the cubic close packed array, two other members of which define edges A and B of the Ni_7C units (Fig. 21). Thus, the two Ni_7C units which make up the core of the half cluster differ in their orientations, such that one (site 1) presents a quadrilateral face to the exterior of the $Ni_{28}C_4$ core,§ whereas the other (site 2) presents the apical atom of the Ni_7C unit to the periphery (Table 8). Figure 22 illustrates the two capped Ni_7C fragments. Of the three remaining pairs of nickel atoms, one pair completes the two symmetry related concave pentagonal faces referred to above, a second pair caps these two faces and a third pair caps the two resultant butterfly faces as discussed above.

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§The $Ni_{28}C_4$ core described in this manner differs slightly from that of Fig. 18.

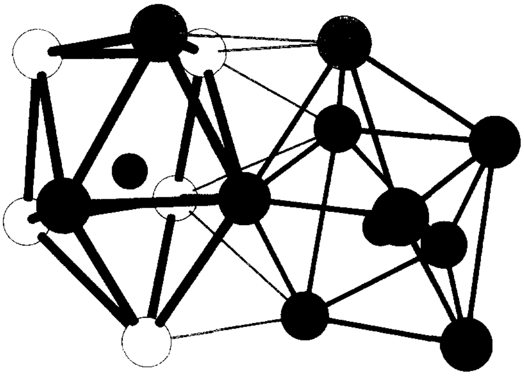

Fig. 22. The two corner-sharing capped Ni_7C fragments on which the structures of $[HNi_{34}(CO)_{38}C_4]^{5-}$ and $[Ni_{35}(CO)_{39}C_4]^{6-}$ are based (thick bonds, site 1; medium bonds, site 2).

In addition to triangular faces of the nickel polyhedron, this arrangement leaves two symmetry related butterfly faces and two symmetry related quadrilateral faces (from sites 1) on the "belt" of the structure (i.e. approximately perpendicular to the outer layers of the cubic close packed array).

The hydride atom of $[HNi_{34}(CO)_{38}C_4]^{5-}$ was not located. Given the presence of several interstitial octahedral holes the hydride might, by analogy with $[H_{4-n}Ni_{12}(CO)_{21}]^{n-}$ ($n = 2, 3$), be expected to occupy an interstitial position(s), possibly near the centre of the triangle of three of the four intestitial nickel atoms, where the interlayer distance is greatest. The average interlayer spacing (2.04 Å) is not significantly different from that of $[Ni_{35}(CO)_{39}C_4]^{6-}$ (2.03 Å), however, the outer layers of the cubic close packed core are significantly buckled in both structures.

There are three sets of carbonyl ligands, ten terminal, on four of the six nickel atoms capping the belt of the structure and on six of the external nickel atoms of the carbide cages (Ni—C 1.64–1.74 Å, av. 1.70 Å; C—O 1.12–1.21 Å, av. 1.17 Å), 26 edge bridging (Ni—C 1.77(3)–2.12(3) Å, av. 1.90 Å; C—O 1.11–1.19 Å, av. 1.17 Å) and two triply bridging (Ni—C 1.89–2.14 Å, av. 2.01 Å; av. C—O 1.17 Å) ligands, with several of the ligands exhibiting unsymmetrical or semi-bridging bonding modes.

$[Ni_{35}(CO)_{39}C_4]^{6-}$

The structure of this cluster anion is illustrated in Fig. 23.[15] Similarly to $[HNi_{34}(CO)_{38}C_4]^{5-}$, the four carbides of $[Ni_{35}(CO)_{39}C_4]^{5-}$ define a planar rhombus with edges 3.62 and 3.72 Å, making the cluster a homologue of the monocarbide clusters. It has overall statistical C_i symmetry, the nickel/carbide polyhedron being derived from that of $[HNi_{34}(CO)_{38}C_4]^{5-}$ by placing a Ni(CO) moiety in two half occupied positions capping the two remaining butterfly faces of the belt of the structure. The other carbonyl ligands (eight terminal, av. Ni—C 1.79 Å, av. C—O 1.10 Å; 26 doubly bridging, av. Ni—C 1.89 Å, av. C—O 1.22 Å and three triply bridging, av. Ni—C 2.00 Å, av. C—O 1.23 Å) are oriented similarly to those of $[HNi_{34}(CO)_{38}C_4]^{5-}$.

4.4. *Hexacarbide anions*

$[HNi_{38}(CO)_{42}C_6]^{5-}$

The carbide atoms of the capped Ni_7C fragments of $[HNi_{34}(CO)_{38}C_4]^{5-}$ and $[Ni_{35}(CO)_{39}C_4]^{6-}$ are situated close to the quadrilateral base of the fragment and closer to the apical atom of the Ni_7C unit than to the extra capping atom. If, however, the carbide atom is located equidistant from the triangular and quadrilateral faces, such that the capping of the central trigonal prism of the capped Ni_7C unit becomes symmetric and the Ni—Ni bond perpendicular to their axis is ruptured, the capped Ni_7C moiety becomes a square antiprismatic Ni_8C fragment.[52] Whereas the nickel frames of $[HNi_{34}(CO)_{38}C_4]^{5-}$ and $[Ni_{35}(CO)_{39}C_4]^{6-}$ are based on condensation of Ni_7C units around a central rhombohedron, four vertices of which are on the periphery of the nickel frame, that of

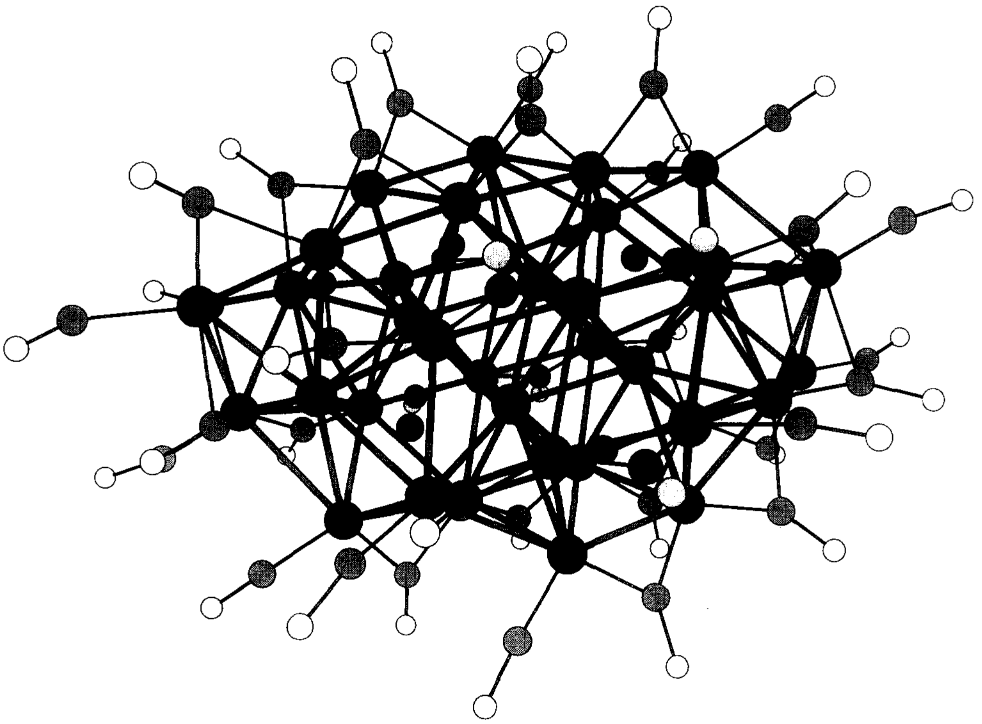

Fig. 23. Illustration of the structure of the $[Ni_{35}(CO)_{39}C_4]^{6-}$ hexaanion.[15] ●, nickel atoms; ●, carbon atoms; ●, oxygen atoms.

$[HNi_{38}(CO)_{42}C_6]^{5-}$ is derived by the vertex-sharing condensation of six Ni_8C square antiprisms (av. N—C 2.061 Å, av. Ni—Ni interlayer bonds 2.633 Å, av. Ni—Ni edge bonds 2.459 Å) to produce an empty cube (av. Ni—Ni 2.402 Å) within a truncated octahedron (Fig. 24).[14] The resultant nickel polyhedron has six vertex sharing square faces and eight concave centred hexagonal faces. Six Ni(CO) units μ_3-cap six of these hexagonal faces producing a polyhedron of D_{3d} idealised geometry (Fig. 25). The structure is formally $[HNi_{38}(CO)_6(\mu\text{-}CO)_{36}C_6]^{5-}$.[14]

The six carbide atoms define the vertices of a non-bonded octahedron with edges between 3.25 and 3.32 Å long. The hydride atom was not located.

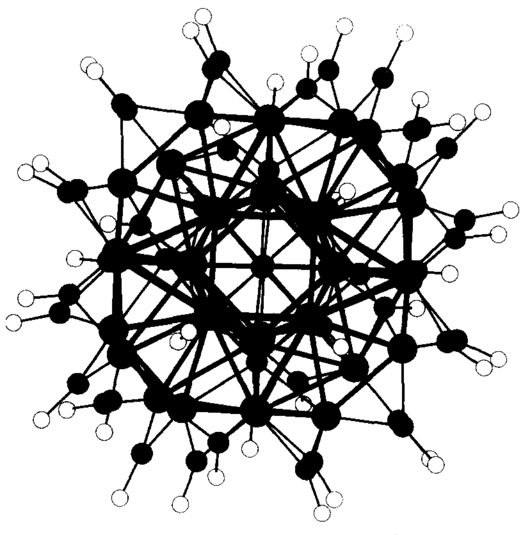

Fig. 24. Illustration of the structure of the $[HNi_{38}(CO)_{42}C_6]^{5-}$ pentaanion.[14] ●, nickel atoms; ●, carbon atoms; ●, oxygen atoms.

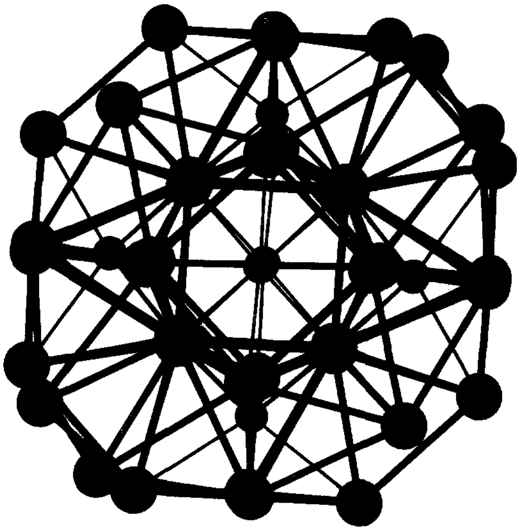

Fig. 25. The nickel/carbide polyhedron of the $[HNi_{38}(CO)_{42}C_6]^{5-}$ pentaanion.[14]

5. CONCLUSIONS

The simple homoleptic nickel carbonyl cluster anions are derived by stacking of planar nickel arrays consisting of nickel triangles or condensed nickel triangles (or $Ni(CO)_3$ groups in $[Ni_5(CO)_{12}]^{2-}$). The Ni—Ni distances between the layers are significantly greater than those within the layers. The interlayer Ni—Ni bonds are not bridged by carbonyl ligands. Those hydrides that have been located in hydrido carbonyl nickel clusters occupy interstitial sites.

The nickel carbide carbonyl clusters and their hydrido analogues can be thought of as being based on the stacking of planes of nickel triangles and nickel quadrilaterals. The cluster nuclearity can be extended by capping the outer layers with Ni(CO) units. In those structures containing an interstitial C_2 group, the C_2 unit is disposed perpendicular to a nickel quadrilateral plane, with each carbon atom equidistant from that plane. Hydrides have not been located in any of the carbide cluster anions. The two common structural motifs in the known carbide cluster anions are Ni_7C and Ni_8C moieties and each of these forms the structural basis of large (Ni_{34}, Ni_{38}) cluster anions.

The Ni—Ni distances within all of these clusters are generally between 2.33 and 3.03 Å (however, there is a 3.330 Å separation in $[Ni_{16}(CO)_{23}C_4]^{4-}$). The average Ni—Ni bond distance within a cluster anion is generally between 2.5 and 2.7 Å. Nickel–carbide bond distances are within the range 1.84–2.38 Å, with an average value within a cluster anion of about 2.0–2.1 Å.

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