Formation of Tetra- and Tri-nuclear Nickel Acetylene Complexes; Crystal and Molecular Structures of Tris-μ_3-(η^2-hexafluorobut-2-yne)-tetrakis-(carbonylnickel) and Tricarbonyl-μ_3-(η-cyclo-octatetraene)-μ_3-(η^2-hexafluorobut-2-yne)-*triangulo*-trinickel with Evidence for a Nickel-stabilised Cyclo-octatetraenyl Dication

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Reaction of $[Ni(CO)_4]$ with hexafluorobut-2-yne gives initially $[Ni(CO)_2(\eta^2\text{-}CF_3C_2CF_3)]$, which decomposes to afford the cluster complex $[Ni_4(CO)_4\{\mu_3\text{-}(\eta^2\text{-}CF_3C_2CF_3)\}_3]$, the structure of which has been established by single-crystal *X*-ray diffraction studies. It crystallises in the monoclinic space group $P2_1/m$, with two molecules in a unit cell of dimensions a = 8.506(2), b = 16.055(12), c = 9.011(4) Å, and β = 100.52(3)°. The structure has been elucidated *via* analysis of 1 033 significant reflections, and refined to R 0.13, R' 0.165. The molecule has essentially C_{3v} symmetry consisting of a trigonal pyramid of nickel atoms [Ni(basal)–Ni(basal) 2.670, Ni(basal)–Ni(apical) 2.382 Å] each carrying a terminally bonded carbonyl group, and three face-bridging, $\mu_3(\eta^2\text{-}\perp)$, acetylenic ligands. Reactions of the tetranuclear nickel cluster with 1,2-bis(diphenylphosphino)ethane (dppe) or Bu^{t}NC gives the mononuclear complexes $[NiL_2(\eta^2\text{-}CF_3C_2CF_3)]$ (L_2 = dppe, L = CNBu^t). In contrast, cyclo-octatetraene affords $[Ni_3(CO)_3\{\mu_3\text{-}(\eta^2\text{-}CF_3C_2CF_3)\}\{\mu_3\text{-}(\eta^2\text{-}C_8H_8)\}]$, the structure of which has also been determined by *X*-ray crystallography. Crystals are monoclinic, space group $P2_1/n$, with four molecules in a unit cell of dimensions a = 9.5915(19), b = 11.994(3), c = 14.876(4) Å, and β = 99.57(2)°. Least-squares refinement using 2 114 reflections has converged at R 0.040, R' 0.048. An isosceles triangle of nickel atoms [Ni(basal)–Ni(basal) 2.702, Ni(basal)–Ni(apical) 2.457 Å], each carrying a terminal carbonyl ligand, is sandwiched between a planar cyclo-octatetraene ring and a face-bonding acetylene molecule whose orientation with respect to the metal triangle is complementary, $\mu_3(\eta^2\text{-}||)$, to that observed in the tetranuclear complex. Evidence is presented for regarding the C_8H_8 ligand as a co-ordinated 6-π-electron $[C_8H_8]^{2+}$ species.

THERE is an expanding class of organometallic cluster complexes containing nickel, including the species $[Ni_4(\mu_2\text{-}CO)_6\{P(C_2H_4CN)_3\}_4]$,[1] $[Ni_4(CNBu^t)_7]$,[2] $[\{Ni_3(CO)_3(\mu_2\text{-}CO)_3\}_2]^{2-}$ (ref. 3), $[\{Ni_3(CO)_3(\mu_2\text{-}CO)_3\}_3]^{2-}$ (ref. 4), $[\{Ni_5(CO)_9(\mu_2\text{-}CO)_3\}]^{2-}$ (ref. 5), and $[Ni_8(CO)_8(\mu_4\text{-}PPh)_6]$.[6] As part of a general study [7] of reactions of acetylenes with d^{10} complexes of the nickel triad the reaction [8] of hexafluorobut-2-yne with tetracarbonylnickel was re-examined,[9] and found to provide a synthetic path to a novel Ni_4 cluster complex. Following our communication,[9] a related complex $[Ni_4(CNBu^t)_4(\eta^2\text{-}PhC_2Ph)_3]$ was reported [10] as a product of the reaction of $[Ni_4(CNBu^t)_7]$ with diphenylacetylene. Herein we provide details of our work including single-crystal *X*-ray diffraction studies.

RESULTS AND DISCUSSION

Hexafluorobut-2-yne reacts in a sealed vessel with tetracarbonylnickel at 50—60 °C provided the presumed equilibrium is disturbed by periodically cooling (−196 °C) and pumping off carbon monoxide. The product of the reaction, a liquid at room temperature, is stable in the presence of hexafluorobut-2-yne, and its i.r. spectrum showed terminal carbonyl bands at 2 122s and 2 076s cm^{-1} together with a band at 1 905m cm^{-1} which is assigned to a ν(C≡C) stretching frequency. This suggested that the product (1) is dicarbonyl(hexafluorobut-2-yne)nickel, which was supported by the observation of a singlet resonance in the ^{19}F n.m.r. spectrum at 55.3 p.p.m. (relative to CCl_3F, 0.0 p.p.m.), characteristic [11] of co-ordinated hexafluorobut-2-yne. It has been established [12] that Ni–CO dissociation is rate-determining in substitution reactions of $[Ni(CO)_4]$ and it is likely that with the removal of carbon monoxide the 16-electron species $[Ni(CO)_3]$ is captured by the good π acceptor hexafluorobut-2-yne; the resulting 18-electron species $[Ni(CO)_3(\eta^2\text{-}CF_3C_2CF_3)]$ losing carbon monoxide to give complex (1).

On standing at room temperature in a nitrogen atmosphere the colourless mononuclear species (1) forms a deep red-violet crystalline complex (2), whose i.r. spectrum shows bands due to terminal carbonyl ligands at 2 115ms and 2 102s cm^{-1}. The ^{19}F n.m.r. spectrum was temperature-invariant and showed two singlet resonances at 53.6 and 56.9 p.p.m. Elemental analysis and a mass spectrum suggested a tetranuclear structure, and in order to define the molecular geometry of this potentially interesting molecule a single-crystal *X*-ray diffraction study was undertaken.

Complex (2) crystallises as discrete molecules, separated by normal van der Waals contacts. Figure 1 gives a perspective view of one molecule parallel to the mirror plane about which it is disposed and the atomic numbering scheme. Table 1 lists the important molecular parameters of the complex. The molecular geometry is constructed from a trigonal pyramid of nickel atoms [Ni(2) apical] each of which carries a terminal carbonyl group. Three hexafluorobut-2-yne ligands are distributed around the pyramid, each linked, *via* its unsaturated central carbon atoms, to one non-basal pyramidal face.

Complex (2) has crystallographically required C_s symmetry about the plane defined by atoms Ni(1), Ni(2), C(1), O(1), C(2), O(2), F(201), C(20), C(21), C(22), C(23), and F(231). In an alternative view (Figure 2),

TABLE 1

Interatomic distances (Å) and angles (°) for the complex $[Ni_4(CO)_4(\mu_3\text{-}CF_3C_2CF_3)_3]$ (2)

(*a*) Distances			
Ni(1)–Ni(2)	2.377(7)	C(10)–F(101)	1.32(6)
Ni(1)–Ni(3)	2.670(6)	C(10)–F(102)	1.29(7)
Ni(2)–Ni(3)	2.385(7)	C(10)–F(103)	1.37(7)
Ni(3)–Ni(3′) *	2.670(10)	C(10)–C(11)	1.51(6)
Ni(1)–C(1)	1.76(6)	C(11)–C(12)	1.27(4)
C(1)–O(1)	1.16(7)	C(12)–C(13)	1.53(6)
Ni(2)–C(2)	1.79(9)	C(13)–F(131)	1.27(6)
C(2)–O(2)	1.16(10)	C(13)–F(132)	1.29(6)
Ni(3)–C(3)	1.82(5)	C(13)–F(133)	1.35(6)
C(3)–O(3)	1.14(7)	C(20)–F(201)	1.34(11)
Ni(1)–C(11)	2.17(3)	C(20)–F(202)	1.23(6)
Ni(1)–C(12)	1.97(3)	C(20)–C(21)	1.55(8)
Ni(2)–C(11)	1.99(3)	C(21)–C(22)	1.29(6)
Ni(3)–C(11)	2.16(3)	C(22)–C(23)	1.54(9)
Ni(3)–C(12)	1.93(3)	C(23)–F(231)	1.43(8)
Ni(2)–C(21)	2.01(4)	C(23)–F(232)	1.27(5)
Ni(3)–C(21)	2.22(3)		
Ni(3)–C(22)	1.96(3)		
(*b*) Angles			
Ni(1)–Ni(2)–Ni(3)	68.2(2)	Ni(2)–Ni(1)–C(1)	175(2)
Ni(3)–Ni(2)–Ni(3′)	68.1(2)	Ni(2)–Ni(3)–C(3)	176(2)
Ni(2)–Ni(1)–Ni(3)	56.0(2)	Ni(1)–Ni(2)–C(2)	140(3)
Ni(2)–Ni(3)–Ni(1)	55.8(2)	Ni(3)–Ni(2)–C(2)	139.8(13)
Ni(2)–Ni(3)–Ni(3′)	56.0(2)	C(10)–C(11)–C(12)	126(3)
Ni(1)–Ni(3)–Ni(3′)	60.00(14)	C(11)–C(12)–C(13)	136(3)
Ni(3)–Ni(1)–Ni(3′)	60.00(18)	C(20)–C(21)–C(22)	134(4)
		C(21)–C(22)–C(23)	130(4)

* Primed atoms are the result of reflection in the crystallographic mirror plane at $y = 0.25$.

however, the effective molecular symmetry can be seen to be C_{3v}, thus rendering equivalence to the two distinct basal nickel atoms, their carbonyl groups, and the face-bonding alkynes. In terms of the bond lengths and angles calculated for the complex, this C_{3v} symmetry is good to within two standard deviations and therefore our discussion will employ the weighted mean of all the corresponding molecular parameters.

The trigonally distorted tetrahedron of nickel atoms has a basal–basal separation of 2.670 Å, complemented by a basal–apical distance of 2.382 Å.* These values may be set against the corresponding distances of 2.686 and 2.374 Å in the related complex $[Ni_4(CNBu^t)_4(\eta^2\text{-}PhC_2Ph)_3]$,[10] and against the average metal–metal lengths of 2.508 and 2.414 Å, respectively, in the essentially tetrahedral cluster complexes $[Ni_4(CO)_6\{P(C_2H_4CN)_3\}_4]$ [1] and $[Ni_4(\eta\text{-}C_5H_5)_4H_3]$.[13]

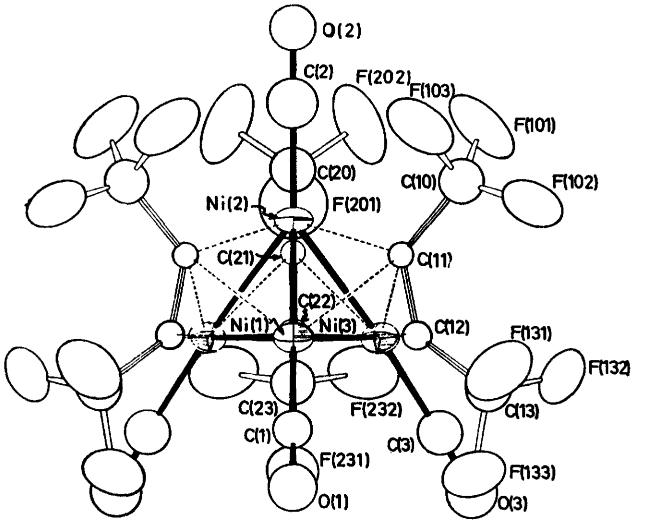

FIGURE 1 View of the complex $[Ni_4(CO)_4(\mu_3\text{-}CF_3C_2CF_3)_3]$ (2), along the crystallographic mirror plane it bestrides

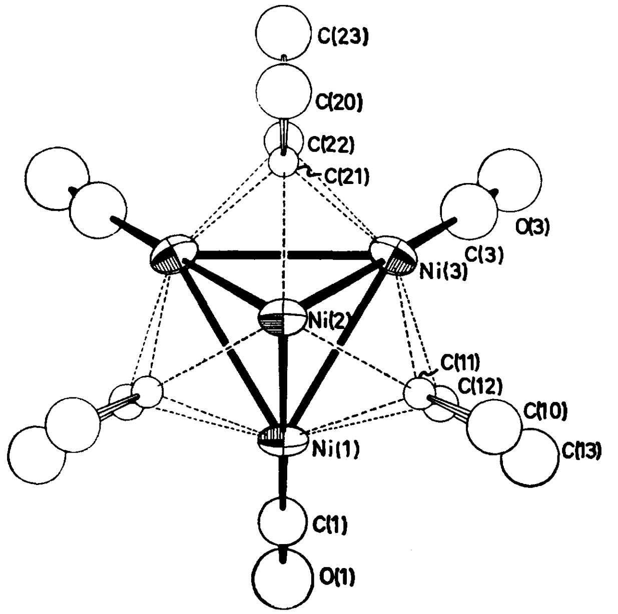

FIGURE 2 Complex (2) from above, demonstrating the effective C_{3v} symmetry. The C(2)O(2) carbonyl group and all the fluorine atoms are omitted for clarity

The Ni–CO and C–O distances in (2) are unexceptional, averaging 1.80 and 1.15 Å, respectively. The apical carbonyl group complies with the approximate C_{3v} symmetry of the complex since the Ni(2)–CO sequence is linear [179(7)°], and all Ni(basal)–Ni(apical)–CO angles are 140°. The Ni(basal)–CO moieties, on the other hand, may be regarded as linear extensions of the Ni(apical)→Ni(basal) vectors to within one standard deviation of the angles at Ni and C.

A most interesting aspect of the structure of (2) is the mode of bonding of the acetylenic units. Figure 3 compares projections of the two crystallographically independent hexafluorobut-2-yne ligands on to the faces of the respective metal triangles. Two other examples of similar acetylene co-ordination to M_3 faces are known. The tetranuclear $[Ni_4(CNBu^t)_4(\eta^2\text{-}PhC_2Ph)_3]$ complex was mentioned above, and is formally analogous to (2) in every respect, but the complex $[Fe_3(CO)_9(\eta^2\text{-}PhC_2Ph)]$ also features [14] an acetylene–metal μ_3-interaction of this type. At the relevant positions in the text below, therefore, the corresponding molecular parameters of these two species are presented, respectively, in square brackets.

In (2) atoms C(11) and C(21) are clearly associated with all three nickel atoms of the appropriate trigonal face. Links to the apical metal average 2.00 [1.972, 2.05] Å,

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* The magnitude of the three types of Ni–Ni–Ni angles follows naturally from these dimensions. Thus Ni(basal)–Ni(apical)–Ni(basal) is *ca.* 68.1°, whilst Ni(apical)–Ni(basal)–Ni(basal) is *ca.* 56.0°. Ni(basal)–Ni(basal)–Ni(basal) angles, of course, are exactly 60.0°.

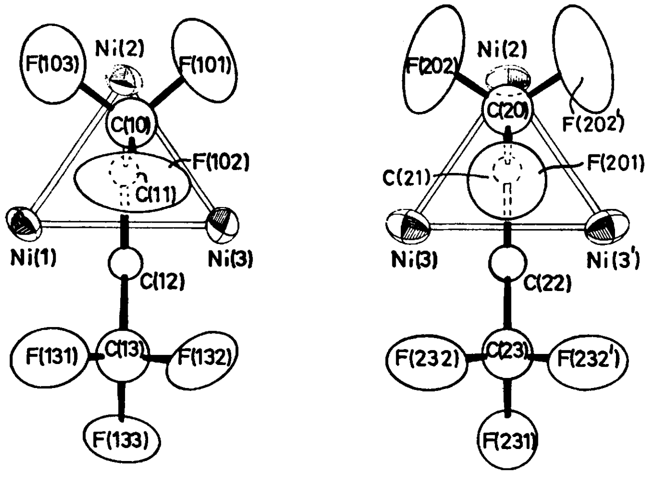

FIGURE 3 Projections of the co-ordinated acetylene molecules of (2) on to their respective nickel triangles

whilst their mean distance from the basal nickel is somewhat longer at 2.18 [2.203, 2.07] Å. The second unsaturated carbon of the acetylene [C(12) and C(22) respectively] is symmetrically bonded to the basal metal atoms only, at an average Ni–C distance of 1.95 [1.977, 1.95] Å. The central C–C bond is 1.28 [1.344, 1.41] Å, and the terminal CF_3 groups bend away from the nickel face to subtend an average angle of 131° at carbon, no individual measurement differing by more than 2σ from this figure.* The C(10)—C(13) unit is planar to within 0.02 Å. [Atoms C(20)—C(23) are constrained by symmetry to be coplanar.]

Dahl and his co-workers [14] have discussed this bonding mode in terms of a localised σ interaction between the apical metal and triply bridging carbon [C(11), C(21)], complemented by a two-electron three-centre μ-bond involving the remaining π electrons of the (then) alkene with the basal metal atoms, the vacant (sp^2) orbital of the doubly bridging carbon [C(12),C(22)] participating in a three-centre ' bent ' M–C–M bond. The $[Ni_4L_4]$ cores of the nickel clusters are 48-electron systems, and therefore require an additional 12 electrons to complete a closed-shell configuration. The Dahl model allows each acetylenic ligand to employ all four π electrons in cluster bonding, and is, therefore, a plausible hypothesis. It predicts the length of the C–C bond to be typically that observed for a co-ordinated olefin as opposed to a co-ordinated acetylene. Indeed, the order of the central C–C link is critical in any discussion of the bonding in these complexes.

In $[Fe_3(CO)_9(PhC_2Ph)]$ and $[Ni_4(CNBu^t)_4(PhC_2Ph)_3]$ the appropriate distances are 1.41 and 1.344 Å, respectively.† The former is consistent with a co-ordinated olefin, but the latter is barely distinguishable from the accepted unco-ordinated length. In (2) there are two central C–C bond lengths of 1.27(4) Å and one of 1.29(6) Å. Although appearing anomalously short, their standard deviations are unfortunately high enough ‡ to bring both within the normal statistical equivalence of those previously mentioned, and we therefore refrain from any conclusions based on distances. It is interesting to note that ν(C≡C) for (2) (at 1 552 cm^{-1}) is not inconsistent with a four-electron donor model. In acetylene complexes of $[Co_2(CO)_6]$, $[Co_4(CO)_{10}]$, and their derivatives,[15] where the acetylenic and metal–metal vectors are also orthogonal, ν(C≡C) occurs typically at 1 500—1 600 cm^{-1}. Clearly, more accurate work in this area is required, preferably with a range of acetylene substituents of differing electronegativities, before the applicability of a simple transposition of the Dahl scheme for a metal triangle to a metal cluster may be adequately tested.

With the establishment of the structural identity of (2), the question as to how such a species is formed from the mononuclear complex (1) is raised. In separate studies [7] we have shown that bridged acetylene complexes such as $[Pt_2\{\mu_2\text{-}(\eta^2\text{-}RC_2R)\}(\eta^2\text{-}RC_2R)L_2]$ and $[Pt_3\text{-}\{\mu_2\text{-}(\eta^2\text{-}RC_2R)\}_2L_4]$ can be built up stepwise by a successive attack of platinum(0) (d^{10}) species on an η^2-bonded acetylene, and it seems likely that carbon monoxide is lost dissociatively from $[Ni(CO)_2(CF_3C_2CF_3)]$ to give the formally 14-electron species $[Ni(CO)(CF_3C_2CF_3)]$, which then builds as in the platinum system to form an open-chain (*arachno*) Ni_4 species. If this path is followed then there must be a strong driving force for rearrangement to occur with loss of hexafluorobut-2-yne and formation of the isolated *closo*-species (2).

Reaction of (2) with 1,2-bis(diphenylphosphino)ethane (dppe) or t-butyl isocyanide led to complete disruption of the Ni_4 cluster and the formation of the mononuclear complexes $[Ni(CF_3C_2CF_3)(dppe)]$ (3) and $[Ni(CF_3C_2\text{-}CF_3)(CNBu^t)_2]$ (4), which were characterised by analysis and i.r. and n.m.r. spectroscopy. In contrast, cyclooctatetraene, which has versatile bonding capabilities,[16] reacted slowly with (2) in refluxing hexane to form in high yield the black crystalline complex (5). Elemental analysis and mass spectroscopy suggested the unusual molecular formula $[Ni_3(CO)_3(CF_3C_2CF_3)(C_8H_8)]$. The i.r. spectrum supported this formulation showing three terminal carbonyl bands at 2 065, 2 047, and 2 040 cm^{-1}. Of particular interest was the occurrence in the ^{1}H n.m.r. spectrum of a temperature-invariant singlet at τ 5.5 implying an interesting bonding mode for the co-ordinated C_8H_8. In addition, the ^{19}F spectrum showed a single resonance typical of a trifluoromethyl group

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* For the complex $[Ni_4(CNBu^t)_4(PhC_2Ph)_3]$ no equivalent data have been given. For $[Fe_3(CO)_9(PhC_2Ph)]$ the angles at C differ substantially, being 118° at the carbon associated with three metal atoms and 131° at the other.

† Given an M(apical)–C σ bond, with $\hat{\mathrm{M}}$(apical) and M-(apical)–C–C angles of reasonably fixed dimensions, together with the apparent preference of the acetylenic carbons to bind equally to the basal metal atoms, the observed variation in C–C distances may represent an interesting reflection of the ease of compressibility of a $\mathrm{C} \overset{\cdot\cdot\cdot}{\equiv} \mathrm{C}$ system as a function of the basal–apical metal–metal bond lengths.

‡ The crystallographic determination of the structure of (2) is generally of low accuracy, as evidenced by the final R index, and the high standard deviations of all the bond lengths and angles. We attribute this primarily to the poor quality of the crystalline sample, and to our inability to correct accurately for the substantial crystal decay in the X-ray beam.

bonded to an unsaturated system. It was clear that the structural identity of this complex would only be established by single-crystal *X*-ray crystallography, and therefore such a study was undertaken.

A single molecule of the trinuclear complex (5) is presented and numbered in Figure 4, a projection on to the best (least-squares) plane of the co-ordinated cyclo-octatetraene ring. Interatomic distances (uncorrected for thermal effects) and interbond angles appear in Tables 2 and 3, respectively.

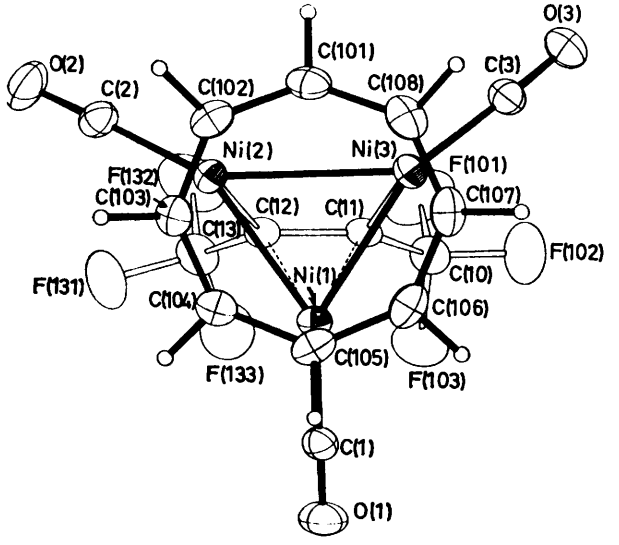

FIGURE 4 View of the complex $[Ni_3(CO)_3(\mu_3\text{-}CF_3C_2CF_3)(\mu_3\text{-}C_8H_8)]$ (5) normal to the plane of the cyclo-octatetraene ligand. Hydrogen atoms (small circles) carry the same number as the carbon to which they are bound

The nickel atoms define an isosceles triangle in which Ni(1) is apical. Each metal carries a terminal carbonyl group which, in projection, radiates outward from the centre of the triangle. The basal nickel atoms Ni(2) and Ni(3) are σ,σ-bridged by the central carbon atoms of a previously acetylenic (hexafluorobut-2-yne) ligand, now functioning as a co-ordinated olefin to the apical nickel. On the opposite side of the Ni_3 sequence is an η^8-bonded (with respect to the triangle) cyclo-octatetraene ring. The molecule as a whole has an approximate-mirror plane passing through Ni(1) and the midpoint of the Ni(2)–Ni(3) bond, and Tables 2 and 3

TABLE 2

Interatomic distances (Å) for the complex $[Ni_3(CO)_3(\mu_3\text{-}CF_3C_2CF_3)(\mu_3\text{-}C_8H_8)]$ (5)

	Ni(2)–Ni(3)	2.701 7(13)	
Ni(1)–Ni(2)	2.458 3(12)	Ni(1)–Ni(3)	2.4560(12)
	Ni(1)–C(105)	1.996(7)	
Ni(1)–C(104)	2.357(6)	Ni(1)–C(106)	2.315(8)
Ni(2)–C(103)	2.077(6)	Ni(3)–C(107)	2.088(8)
Ni(2)–C(102)	2.090(7)	Ni(3)–C(108)	2.067(7)
Ni(2)–C(101)	2.585(8)	Ni(3)–C(101)	2.565(8)
	Ni(1)–C(1)	1.798(7)	
Ni(2)–C(2)	1.781(8)	Ni(3)–C(3)	1.771(8)
	C(1)–O(1)	1.129(10)	
C(2)–O(2)	1.128(10)	C(3)–O(3)	1.137(10)
C(101)–C(102)	1.408(12)	C(101)–C(108)	1.403(13)
C(102)–C(103)	1.421(11)	C(108)–C(107)	1.414(13)
C(103)–C(104)	1.406(11)	C(107)–C(106)	1.426(12)
C(104)–C(105)	1.426(10)	C(106)–C(105)	1.407(12)
Ni(1)–C(12)	2.013(6)	N(1)–C(11)	1.989(6)
Ni(2)–C(12)	1.898(5)	Ni(3)–C(11)	1.889(6)
	C(11)–C(12)	1.381(9)	
C(12)–C(13)	1.489(10)	C(11)–C(10)	1.501(9)
C(13)–F(131)	1.317(10)	C(10)–F(102)	1.324(10)
C(13)–F(132)	1.306(11)	C(10)–F(101)	1.287(10)
C(13)–F(133)	1.336(10)	C(10)–F(103)	1.328(10)

TABLE 3

Important interbond angles (°) for complex (5)

	Ni(2)–Ni(1)–Ni(3)	66.70(4)	
Ni(1)–Ni(2)–Ni(3)	56.61(3)	Ni(1)–Ni(3)–Ni(2)	56.69(3)
	Ni(1)–C(1)–O(1)	176.0(6)	
Ni(2)–C(2)–O(2)	177.7(8)	Ni(3)–C(3)–O(3)	176.8(7)
	C(102)–C(101)–C(108)	137.5(8)	
	C(104)–C(105)–C(106)	133.6(7)	
C(101)–C(102)–C(103)	132.2(7)	C(101)–C(108)–C(107)	133.5(8)
C(102)–C(103)–C(104)	134.3(7)	C(108)–C(107)–C(106)	133.6(8)
C(103)–C(104)–C(105)	135.7(7)	C(107)–C(106)–C(105)	135.1(7)
Ni(2)–Ni(1)–C(1)	145.0(2)	Ni(3)–Ni(1)–C(1)	143.2(2)
Ni(1)–Ni(2)–C(2)	145.1(3)	Ni(1)–Ni(3)–C(3)	148.7(2)
Ni(3)–Ni(2)–C(2)	146.1(2)	Ni(2)–Ni(3)–C(3)	139.0(2)
Ni(1)–Ni(2)–C(12)	53.18(18)	Ni(1)–Ni(3)–C(11)	52.54(18)
Ni(3)–Ni(2)–C(12)	69.09(19)	Ni(2)–Ni(3)–C(11)	70.06(18)
Ni(2)–C(12)–C(13)	121.4(5)	Ni(3)–C(11)–C(10)	123.0(5)
Ni(2)–C(12)–C(11)	111.0(4)	Ni(3)–C(11)–C(12)	109.8(4)
C(13)–C(12)–C(11)	126.6(5)	C(10)–C(11)–C(12)	125.8(6)
C(12)–C(13)–F(131)	113.9(6)	C(11)–C(10)–F(102)	113.1(6)
C(12)–C(13)–F(132)	112.7(7)	C(11)–C(10)–F(101)	114.0(7)
C(12)–C(13)–F(133)	113.4(7)	C(11)–C(10)–F(103)	114.3(6)
F(131)–C(13)–F(132)	108.85(8)	F(102)–C(10)–F(101)	106.0(6)
F(131)–C(13)–F(133)	101.4(7)	F(102)–C(10)–F(103)	101.5(7)
F(132)–C(13)–F(133)	106.1(6)	F(101)–C(10)–F(103)	106.9(7)

TABLE 4

Nickel–nickel distances in cluster complexes

Complex	Geometry	Bond type	Length (average) (Å)	Ref.
$[Ni_3(CO)_3(CF_3C_2CF_3)(C_8H_8)]$	Isosceles triangle	Basal	2.702	This work
		Apical	2.457	
$[Mo_2Ni_3(CO)_{16}]^{2-}$	Trigonal bipyramid (Ni atoms equatorial)	Equatorial	2.341	18
$[W_2Ni_3(CO)_{16}]^{2-}$	Trigonal bipyramid (Ni atoms equatorial)	Equatorial	2.339	18
$[Ni_4(CO)_6\{P(CH_2CN)_3\}_4]$	Tetrahedron		2.508	1
$[Ni_4(\eta\text{-}C_5H_5)_4H_3]$	Tetrahedron		2.464	13
$[Ni_4(CO)_4(CF_3C_2CF_3)_3]$	Trigonal pyramid	Basal–basal	2.670	This work
		Basal–apical	2.382	
$[Ni_4(CNBu^t)_4(PhC_2Ph)_3]$	Trigonal pyramid	Basal–basal	2.686	10
		Basal–apical	2.374	
$[Ni_4(CNBu^t)_7]$	Trigonal pyramid	Basal–apical	2.338	2
$[Ni_5(CO)_9(\mu_2\text{-}CO)_3]^{2-}$	Trigonal bipyramid	Equatorial	2.36	5
		Apical	2.81	
$[\{Ni_3(CO)_3(\mu_2\text{-}CO)_3\}_2]^{2-}$	Trigonal antiprism	Facial	2.38	3
		Prismatic	2.77	
$[Ni_8(CO)_8(\mu_4\text{-}PPh)_6]$	Cube		2.648	6

are arranged such that molecular parameters thus related are presented together. We shall again employ the average value of corresponding lengths and angles in our discussion.

The base of the nickel triangle [Ni(2)–Ni(3)] is *ca.* 2.702 Å, whilst its basal–apical dimension is *ca.* 2.457 Å. Some Ni–Ni distances in binuclear complexes have recently been given,[17,18] and emphasize the wide range of lengths (*ca.* 2.3—2.8 Å) that may be taken as indicative of a significant metal–metal interaction. In Table 4 we extend the list to triangular and cluster complexes, and note that although the overall range here is much the same as for the binuclear species, multinuclear complexes of relatively low symmetry (in terms of the number of nickel vertices) consistently show a separation of their metal–metal lengths into the comparatively narrow bands of *ca.* 2.35—2.45 and *ca.* 2.7—2.8 Å. The inequality and dimensions of the Ni–Ni distances we have observed in complexes (2) and (5) are, therefore, not without precedent.

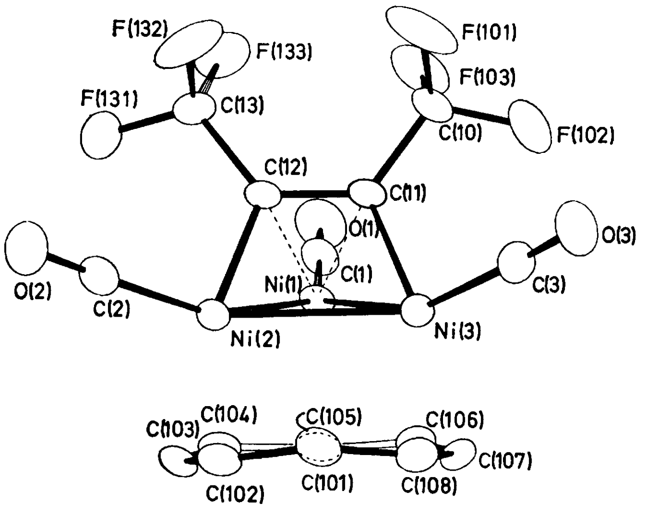

FIGURE 5 Side-on view of the complex $[Ni_3(CO)_3(\mu_3\text{-}CF_3C_2CF_3)(\mu_3\text{-}C_8H_8)]$ (5). Hydrogen atoms are omitted for clarity

In an alternative, nearly orthogonal, view (Figure 5) of the structure of the triangular complex (5), the Ni(CO) sequences may clearly be seen to point towards a position below the nickel plane. All three sequences are linear to within 4°, and subtend elevation angles with respect to the triangle of *ca.* 16° (apical metal atom) and *ca.* 22° (basal metal atoms). The Ni(1)–CO bond [1.798(7) Å] is slightly longer than the others (mean 1.776 Å) but barely significantly so.

TABLE 5

Molecular planes for complex (5) represented by $px + qy + rz = s$, where x, y, and z are the atomic fractional co-ordinates in direct space, and deviations (Å) from the planes (in square brackets)

Plane (A): C(13), C(10), Ni(2), Ni(3)

$$0.694x + 10.423y - 7.358z = -0.706$$

[C(13) 0.021, C(10) −0.020, Ni(2) −0.024, Ni(3) 0.024, C(11) −0.160, C(12) −0.144, Ni(1) −1.831]

Plane (B): C_8 ring

$$7.981x - 3.176y + 5.090z = 4.835$$

[C(101) −0.121, C(102) 0.030, C(103) 0.081, C(104) −0.050, C(105) 0.000, C(106) −0.058, C(107) 0.088, C(108) 0.029, Ni(1) −1.975, Ni(2) −1.879, Ni(3) −1.876]

Plane (C): The three-atom triangle Ni(1), Ni(2), Ni(3)

Dihedral angles (°): (A)–(B) 65.9; (A)–(C) 63.2; and (B)–(C) 2.7

The single ' acetylenic ' ligand of (5) is linked to the basal nickel atoms *via* two σ bonds of average length 1.894 Å, a distance close to the value of the Ni(apical)–C σ length in (2). The least-squares plane (Table 5) through atoms Ni(2), Ni(3), C(10), and C(11) is inclined at *ca.* 63° to the nickel triangle, thus placing the olefinic [C(11)–C(12)] fragment in an ideal orientation to co-ordinate to the apical Ni(1). The efficiency of its co-ordination is demonstrated by the relevant Ni–C distance of *ca.* 2.00 Å, the extended C(11)–C(12) length [1.381 (9) Å], and by the observation that atoms C(11) and C(12) are rehybridised *ca.* 0.15 Å out of the aforementioned plane, towards Ni(1). This mode of acetylene to metal-triangle bonding is complementary to that observed in (2), and Muetterties and his co-workers[10] have termed the respective types $\mu_3(\eta^2\text{-}\|)$ and $\mu_3(\eta^2\text{-}\perp)$.

The $\mu_3(\eta^2\text{-}\|)$ bonding mode between an acetylene and a triangle of metals is already established for the complexes $[Fe_3(CO)_8(PhC_2Ph)_2]$ (violet isomer),[19] $[Os_3(CO)_7(PhC_2Ph)(C_4Ph_4)]$,[20] $[Os_3(CO)_{10}(PhC_2Ph)]$,[21] and $[Rh_3(\eta\text{-}C_5H_5)_3(CO)(RC_2R)]$ (R = Ph or C_6F_5).[22] A doubly linking $\mu_3(\eta^2\text{-}\|)$ mode is present[23] in the ' butterfly ' complex $[Co_4(CO)_{10}(EtC_2Et)]$. With the exception of $[Os_3(CO)_7(PhC_2Ph)(C_4Ph_4)]$ in which the basal[*] metal atoms are additionally linked *via* an osmacyclopentadienyl ring, a general feature of the complexes $[Fe_3(CO)_8(PhC_2Ph)_2]$, $[Os_3(CO)_{10}(PhC_2Ph)]$, and $[Rh_3(\eta\text{-}C_5H_5)_3(CO)(RC_2R)]$ is that the basal–basal bond is longer than the average basal–apical link by *ca.* 0.03—0.13 Å (such a difference will be defined as Δ). In $[Fe_3(CO)_8(PhC_2Ph)_2]$ and $[Os_3(CO)_{10}(PhC_2Ph)]$ the metal oxidation states are formally IV for the basal and II for the apical atoms; in $[Rh_3(\eta\text{-}C_5H_5)_3(CO)(RC_2R)]$ the respective states are V and III. On the basis of oxidation states alone, therefore, the direction of the difference (Δ) in lengths between the two types of metal–metal bond appears initially surprising. On the other hand, the co-ordination number of the basal metals is one more than the apical atoms, but it is unlikely that this small difference in co-ordination numbers could offset the effect of the difference in oxidation states and still further lengthen the basal–basal bond. A more plausible hypothesis is that the dimensions within the triangles are sensitive to the geometrical requirements of the $\mu_3(\eta^2\text{-}\|)$-bonded ' acetylene ' ligand.

In the case of complex (5), we consider the skeleton of the molecule with the cyclo-octatetraene ligand removed. The formal oxidation state for the basal nickel atoms is III, and II for the apical nickel. Metal co-ordination

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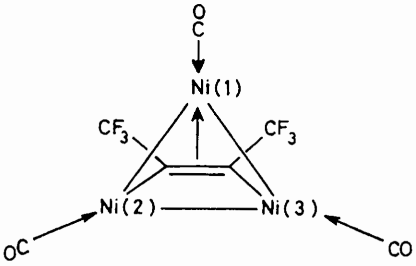
[*] ' Basal ' and ' apical ' here refer to the metal atoms which are σ- and π-bonded to the ' acetylene,' respectively.

numbers in the framework, however, are all four, and if we assume that these changes with respect to $[Fe_3(CO)_8(PhC_2Ph)_2]$, $[Os_3(CO)_{10}(PhC_2Ph)]$, and $[Rh_3(\eta\text{-}C_5H_5)_3(CO)(RC_2R)]$ mutually cancel, a Δ of, say, 0.05—0.15 Å might be expected for (5). The observed value is almost 0.25 Å. Clearly this large Δ value is most simply explained if the oxidation states described for complex (5) are altered on co-ordination of the C_8H_8 ligand; either the apical oxidation state must formally increase or the basal states formally decrease. This point will be discussed below.



(5)

The nickel to cyclo-octatetraene-carbon distances in (5) fall into three distinct groups, whose disposition is consistent with the approximate mirror symmetry of the complex. There are five short bonds [Ni(1)–C(105) 1.996, Ni(2)–C(103) or Ni(3)–C(107), mean 2.083, and Ni(2)–C(102) or Ni(3)–C(108), mean 2.079 Å], two intermediate bonds [Ni(1)–C(104) and Ni(1)–C(106), mean 2.366 Å], and two long bonds [Ni(2)–C(101) and Ni(3)–C(101), mean 2.575 Å]. The near planarity of the C_8 ring [Table 5, the standard deviation of the ring atoms from the best (least-squares) plane through them is 0.07 Å] and the statistical equivalence of the eight C–C distances (the maximum disagreement is only 2σ) suggest an aromatic system.

Raymond and his co-workers [24-26] have successfully demonstrated the ability of large, highly positive, rare-earth metal cations to stabilise the 10-π-electron cyclo-octatetraenyl dianion. Crystallographic studies of $[U(C_8H_8)_2]$ and $[Th(C_8H_8)_2]$,[24] $[\{Ce(C_8H_8)Cl\cdot 2thf\}_2]$,[25] and $[Ce(C_8H_8)_2]^-$ (ref. 26) have consistently revealed planar C_8 rings with a mean C–C distance of 1.386—1.394 Å. In the nickel triangle of complex (5) the corresponding distance is 0.020—0.030 Å longer at 1.414(10) Å. Although clearly only on the verge of a statistical significance, this difference may nevertheless imply stabilisation in (5) of the 6-π-electron cyclo-octatetraenyl dication, a species which has only recently [27] been identified in the unco-ordinated form.

As mentioned above, the skeleton of (5) requires modification to its metallic oxidation states to rationalise the observed Δ value of *ca.* 0.25 Å. There are two ways in which this may be done. A formal two-electron oxidation of the apical nickel by the C_8H_8 ligand produces the $[C_8H_8]^{2-}$ dianion, and an oxidation-state pattern for the triangle of IV : III : III (apical : basal : basal). Alternatively, a one-electron reduction of each basal metal atom leads to a II : II : II pattern for the nickel atoms and the presence of the $[C_8H_8]^{2+}$ dication. In view of the long C–C distances in the ring, and of the near equivalence of the three Ni–CO bond lengths, albeit unfortunately the only secondary standard available, we tentatively suggest that the latter description is more appropriate.

Figure 6 reproduces the crystal packing of (5) projected on to the *bc* plane, and numbers selected atoms of the molecule defined by the co-ordinates of Table 7. There are no intermolecular contacts less than the appropriate van der Waals sum of atomic radii. Finally, the observation of only one ^1H n.m.r. resonance for the C_8H_8 ring down to −90 °C requires that a dynamic process is involved. The simplest explanation would be a rotation of the planar C_8H_8 ring relative to the Ni_3 triangle.

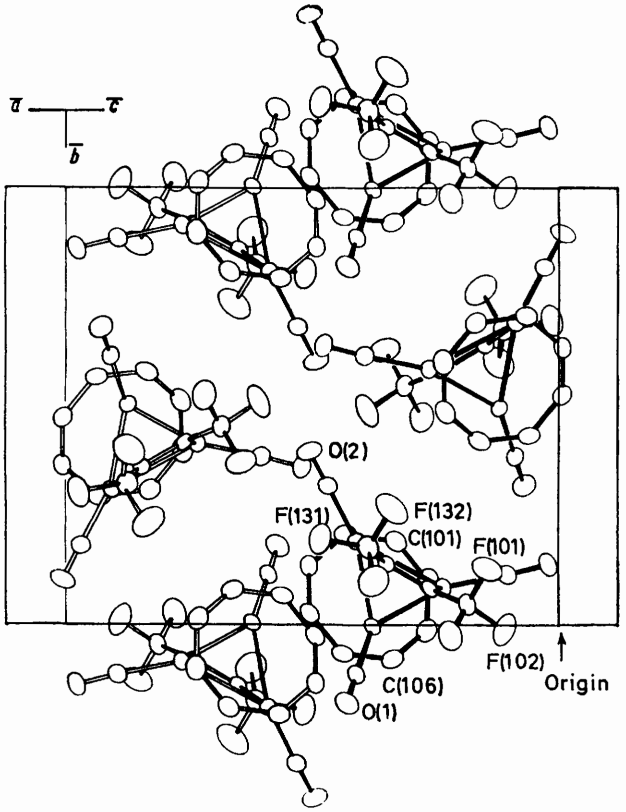


FIGURE 6 The crystal packing of (5) projected on to the crystallographic *bc* plane. Hydrogen atoms are omitted for clarity

EXPERIMENTAL

Hydrogen-1 and ^{19}F n.m.r. spectra were recorded using Varian Associates HA100 and JEOL PFT-100 spectrometers, respectively. Fluorine chemical shifts are relative to CCl_3F (0.0 p.p.m., external). Infrared spectra were obtained on a Perkin-Elmer 457 spectrophotometer, mass spectra on an A.E.I. MS902 spectrometer operating at 70 eV.* Reactions were carried out either in sealed tubes

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* 1 eV ≈ 1.60 × 10^{-19} J.

fitted with Westef high-pressure stopcocks or under a dry oxygen-free nitrogen atmosphere.

Reaction of Hexafluorobut-2-yne with Tetracarbonylnickel.—Tetracarbonylnickel (1.5 g, 1.1 mmol) and hexafluorobut-2-yne (2.5 g, 1.5 mmol) were condensed (−196 °C) into a thick-walled glass tube (80 cm^3) fitted with a Westef stopcock. The tube and contents were allowed to warm to room temperature, and then placed in an oven at 50—60 °C for 15 h. The tube was then cooled (−196 °C) and the evolved carbon monoxide pumped off. This procedure was repeated a number of times over a period of 4 d, when no more carbon monoxide was evolved. In the later stages of the reaction off-white crystals formed. The tube and contents were cooled to 0 °C and the excess of hexafluorobut-2-yne allowed to escape slowly. The colourless liquid product was carefully decanted to the top of the tube thus allowing extraction of a small quantity, for spectroscopic examination, of *dicarbonyl(hexafluorobut-2-yne)nickel* (1). Infrared spectrum in hexane: 2 122ms (CO), 2 076s (CO), 1 905m ($C\equiv C$), 1 276ms, 1 270(sh), 1 215s, 1 176vs, and 1 153ms (CF) cm^{-1}. Fluorine-19 n.m.r. spectrum in $CDCl_3$: 55.3(s) p.p.m. The remainder of the liquid was removed from the tube. It rapidly turned dark brown-purple as it was transferred to a nitrogen-filled Schlenk tube. The liquid was stirred (10 min) under nitrogen, and then extracted with diethyl ether (40 cm^3). After filtration the volume of the solvent was reduced *in vacuo* and hexane added, which on cooling (−20 °C) gave red-violet air-sensitive *crystals* of (2) (0.63 g, 35%), m.p. 119—121 °C (decomp.) (Found: C, 25.5; C, 38.6. $C_{16}F_{18}Ni_4O_4$ requires C, 25.7; F, 38.8%). Infrared spectrum in hexane: 2 115ms (CO), 2 102s (CO), 1 552wm ($C\equiv C$), 1 540wm ($C\equiv C$), 1 230m, 1 200s, 1 162ms, and 1 148ms (CF) cm^{-1}. Fluorine-19 n.m.r. spectrum in [$^2H_8$]toluene: 53.6 (s, 9 F, CF_3) and 56.9 p.p.m. (s, 9 F, CF_3); temperature invariant down to −90 °C.

Reactions of the Tetranuclear Cluster Complex (2).—(*a*) *With* 1,2-*bis(diphenylphosphino)ethane.*—Addition of a solution of dppe (0.04 g, 0.07 mmol) in diethyl ether (10 cm^3) to a stirred (room temperature) solution of (2) (0.05 g, 0.06 mmol) in hexane (30 cm^3) led to a rapid change in colour. After 0.5 h, partial (10 cm^3) removal of solvent *in vacuo* and cooling (−20 °C) afforded yellow crystals of (3) [1,2-*bis(diphenylphosphino)ethane*](*hexafluorobut*-2-*yne*)*nickel* (3) (0.07 g, 90%) (Found: C, 58.2; H, 3.9. $C_{30}H_{24}F_6NiP_2$ requires C, 58.0; H, 4.0%). Infrared spectrum in $CHCl_3$: 1 795wm ($C\equiv C$), 1 270ms, 1 200s, and 1 126s (CF) cm^{-1}. Fluorine-19 n.m.r. spectrum in $(CD_3)_2CO$: 53.5 p.p.m. [dd, 6 F, CF_3, J(PF) = J(PF) 4.4 Hz].

(*b*) *With t-butyl isocyanide.* A solution of Bu^tNC (0.2 g) in hexane (5 cm^3) was added dropwise with stirring (room temperature) to a solution of (2) (0.04 g, 0.05 mmol) in hexane (20 cm^3). An immediate reaction occurred and on cooling (−20 °C) pale yellow crystals of *hexafluorobut*-2-*ynebis(t-butyl isocyanide)nickel* (4) were deposited (0.03 g, 45%) (Found: C, 41.3; H, 4.4. $C_{14}H_{18}F_6N_2Ni$ requires C, 41.3; H, 4.4%). Infrared spectrum in hexane: 2 158s (NC), 2 125s (NC), 1 848w ($C\equiv C$), 1 262s, 1 201vs, and 1 130s (CF) cm^{-1}.

(*c*) *With cyclo-octatetraene.* A solution of (2) (0.10 g, 1.2 mmol) and freshly distilled cyclo-octatetraene (0.40 g, 4.0 mmol) in hexane (20 cm^3) was heated under reflux for 18 h. Filtration followed by cooling (−20 °C) gave black *crystals* of (5) (0.045 g, 71%), m.p. 157 °C (decomp.) (Found: C, 34.0; H, 1.7. $C_{15}H_8F_6Ni_3O_3$ requires C, 34.2; H, 1.5%). Infrared spectrum in hexane: 2 065m (CO), 2 047vs (CO), 2 040vs (CO), 1 442w, 1 250w, 1 240w, 1 212m, and 1 150m cm^{-1}. N.m.r. spectra: ^1H in CD_2Cl_2, τ 5.5 (s, temperature-invariant down to −80 °C); ^{19}F in $CDCl_3$, 55.9 p.p.m. (s, 6 F, CF_3). The mass spectrum showed a parent ion at m/e 524 and a triple nickel-isotope pattern.

Crystal-structure Determinations.—The collection of reflection intensities and the solution and refinement of the structures of complexes (2) and (5) followed similar lines, and are therefore described for (2) only. Data in braces correspond to that for complex (5).

Crystals, prepared as above, were obtained from hexane as dark purple needles {small black parallelepipeds}. A single crystal, mounted on a thin glass fibre with a quick-setting epoxy-resin adhesive, was used to establish the unit cell *via* oscillation and equi-inclination Weissenberg *X*-ray photographs (Cu-K_α radiation). Thereafter the specimen was transferred to a Syntex four-circle auto-diffractometer; accurate setting and intensity-data collection followed an established procedure [28] in which the following pertinent details applied: 15 reflections, $18 > 2\theta > 11°$ $\{22 > 2\theta > 14°\}$ (Mo-K_α), were taken from a 30-min rotation photograph and accurately centred in 2θ, ω, and χ. The unit cell was chosen (by inspection of the real-space vectors and intervector cosines produced by the auto-indexing routine) to correspond to that determined photographically. The orientation matrix and the cell dimensions and their associated errors were calculated by a least-squares fit. For data collection the 2θ range was 2.9—50.0° using graphite-monochromated Mo-K_α X-radiation ($\lambda_{\alpha 1}$ 0.709 26, $\lambda_{\alpha 2}$ 0.713 54 Å), $T \simeq 298$ K. Peaks were scanned (θ—2θ in 96 steps) from 1.0° below $K_{\alpha 1}$ to 1.0° above $K_{\alpha 2}$ at speeds between 0.048 8 {0.033 7} and 0.488 3° s^{-1}, the precise rate dependent on an initial 2-s peak count in which 150.0 and 1 500.0 counts were used as minimum and maximum thresholds, respectively. All the net counts were thereafter adjusted to a common 0.016 7° s^{-1} scan rate. Three check reflections, chosen to have near-orthogonal scattering vectors, were re-monitored once every batch of 40{75} reflections. For the crystal of complex (5), no significant variation in any of their net intensities as individual functions of time was discovered throughout the 81 h of X-ray exposure. For (2), however, analysis of all the three standards implied that considerable sample decay due to the incident beam had occurred in the 60 h of data collection, the final net intensities of the checks averaging only *ca.* 65% of their initial values. Using the Fortran program DRSYN,[29] an exponential decay analysis was found to successfully fit the data and the appropriate correction was applied.

Of 2 220 {3 123} independent reflections ($+h + k \pm l$, $0 + k + l$) measured, 1 033 {2 114} had $I \geqslant 2.5\sigma(I)$ and were retained for structure solution and refinement. No absorption correction was applied.

Crystal data. Complex (2), $C_{16}F_{18}Ni_4O_4$, $M = 883.0$, Monoclinic, $a = 8.506(2)$, $b = 16.055(12)$, $c = 9.011(4)$ Å, $\beta = 100.52(3)°$, $U = 1\ 209.9(14)$ Å^3, D_m not measured, $Z = 2$, $D_c = 2.286$ g cm^{-3}, $F(000) = 804$, μ(Mo-K_α) = 30.4 cm^{-1}, space group $P2_1(C_2^2$, no. 4) or $P2_1/m$ (C_{2h}^2, no.11) from the systematic absence (0k0) $k = 2n + 1$.

Complex (5), $C_{15}H_8F_6Ni_3O_3$, $M = 526.4$, Monoclinic, $a = 9.591\ 5(19)$, $b = 11.994(3)$, $c = 14.876(4)$ Å, $\beta = 99.57(2)°$, $U = 1\ 687.5(7)$ Å^3, D_m not measured, $Z = 4$, $D_c = 2.071$ g cm^{-3}, $F(000) = 1\ 040$, μ(Mo-K_α) = 33.8 cm^{-1}, space group $P2_1/n$ (alternative setting of $P2_1/c$, C_{2h}^5, no. 14) from the systematic absences $(0k0)$ $k = 2n + 1$ and $(h0l)$ $h + l = 2n + 1$.

Data were corrected for Lorentz and polarisation effects and a three-dimensional Patterson synthesis was computed. Although the density of neither complex was measured only two formula units for (2) and four formula units for (5) are reasonable. Accordingly, the tetranuclear molecule must either lie in a general position in $P2_1$, or bestride a crystallographic mirror in $P2_1/m$ (assuming an essentially tetrahedral Ni_4 skeleton). Analysis of the Patterson function implied the latter, and nothing occurred under subsequent refinement to suggest that this was not a valid description. The vector map for (5) was straightforwardly solved for a triangle of heavy atoms in general positions.

The C, O, and F atoms were located from a difference electron-density synthesis produced after three cycles of full-matrix least-squares refinement of the relevant nickel positional and isotropic thermal parameters. F_o moduli were weighted such that $w = (xy)^{-1}$ with $x = b/\sin\theta$, if $\sin\theta < b$, $x = 1$ if $\sin\theta \geqslant b$, $y = F_o/a$, if $F_o > a$, and $y = 1$ if $F_o \leqslant a$ with a and b set at 60.0 and 0.25 {40.0 and 0.22}, respectively.

For (2) all the nickel atoms, together with those fluorine atoms not located on the crystallographic mirror plane, were allowed anisotropic thermal motion. In the case of (5) all the non-hydrogen atoms were treated anisotropically. Hydrogen atoms were introduced into calculated positions [r(C–H) 1.00 Å, U_H 0.07 Å^2] updated after every third cycle. It was necessary to divide the 245 variables describing this molecule into three least-squares blocks.

Refinement converged at R 0.130, R' 0.165 {R 0.040, R' 0.048}. A final difference-Fourier of 0.37 {0.30} Å resolution revealed a maximum residue of *ca.* 1.62 e Å^{-3} near −0.16, 0.32, −0.34 {*ca.* 0.74 e Å^{-3} near 0.39, 0.22, 0.88}. The scattering factors of refs. 30 (Ni, F) and 31 (C, O) were used, all sets being appropriately corrected for both components of anomalous dispersion.[32] For (5) the hydrogen-atom factors of Stewart *et al.*[33] were also used.

TABLE 6

Final atomic positional parameters (fractional co-ordinates: Ni, × 10^4; C, O, and F, × 10^3) for complex (2)

Atom	x	y	z
Ni(1)	2 172(7)	2 500	2 787(6)
Ni(2)	−303(6)	2 500	1 063(6)
Ni(3)	1 685(5)	3 332(3)	177(5)
C(1)	409(7)	250	392(6)
O(1)	533(6)	250	472(6)
C(2)	−241(11)	250	108(9)
O(2)	−376(6)	250	112(5)
C(3)	326(6)	391(3)	−45(5)
O(3)	428(5)	422(3)	−90(4)
F(101)	−190(4)	429(2)	151(4)
F(102)	−15(4)	478(3)	327(6)
F(103)	−148(4)	371(3)	359(4)
C(10)	−69(6)	410(3)	259(5)
C(11)	55(3)	353(3)	212(3)
C(12)	203(3)	369(2)	226(3)
C(13)	315(6)	437(4)	301(6)
F(131)	309(4)	447(2)	440(4)
F(132)	277(4)	507(2)	232(4)
F(133)	468(3)	424(2)	285(4)
F(201)	−152(9)	250	−352(8)
F(202)	−266(5)	313(2)	−205(5)
C(20)	−186(9)	250	−212(8)
C(21)	−16(4)	250	−114(4)
C(22)	127(5)	250	−143(5)
C(23)	184(8)	250	−296(8)
F(231)	354(5)	250	−260(5)
F(232)	151(3)	317(3)	−369(3)

TABLE 7

Final atomic positional parameters (fractional co-ordinates; Ni, × 10^5; C, O, and F, × 10^4) for complex (5)

Atom	x	y	z
Ni(1)	13 241(8)	−400(6)	35 173(5)
Ni(2)	19 860(8)	19 080(6)	38 829(5)
Ni(3)	25 319(8)	8 529(7)	23 749(5)
C(1)	127(8)	−1 146(6)	3 681(4)
O(1)	−688(7)	−1 803(5)	3 761(4)
C(2)	1 461(8)	3 179(6)	4 349(5)
O(2)	1 083(8)	3 968(5)	4 642(5)
C(3)	2 580(8)	1 151(6)	1 215(5)
O(3)	2 572(8)	1 384(5)	473(4)
C(101)	4 476(8)	1 908(7)	3 433(6)
C(102)	4 164(7)	2 064(6)	4 317(5)
C(103)	3 564(7)	1 348(6)	4 911(5)
C(104)	3 013(7)	259(6)	4 838(5)
C(105)	3 083(7)	−668(6)	4 247(5)
C(106)	3 507(8)	−790(6)	3 392(6)
C(107)	4 295(8)	−131(8)	2 856(5)
C(108)	4 670(7)	1 010(8)	2 862(6)
F(101)	−1 192(8)	1 282(5)	1 171(4)
F(102)	46(6)	−102(6)	988(4)
F(103)	−1 464(6)	−245(6)	1 811(4)
C(10)	−508(8)	469(7)	1 604(5)
C(11)	570(6)	826(5)	2 402(4)
C(12)	290(6)	1 395(5)	3 159(4)
C(13)	−1 120(7)	1 770(7)	3 334(6)
F(131)	−1 170(5)	1 962(6)	4 200(4)
F(132)	−1 576(7)	2 656(6)	2 865(5)
F(133)	−2 130(5)	1 000(6)	3 132(5)

Table 6 {Table 7} lists the atomic co-ordinates and Appendix A {Appendix C} * the thermal parameters obtained. A list of observed and calculated structure factors (× 10) is deposited as Appendix B {Appendix D}. Calculated hydrogen-atom positions for (5) appear as Appendix E. Apart from the preliminary data treatment, all the crystallographic calculations employed programs of the ' X-RAY ' 72 ' package [34] made available on the University of London CDC 7600 computer.

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* All Appendices may be recovered from Supplementary Publication No. SUP 22387 (20 pp.). For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

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