Iridium–Nickel Mixed-metal Carbonyl Clusters. Part 2.[1] Synthesis and Chemical Behaviour of $[IrNi_8(CO)_{18}]^{3-}$. Crystal and Molecular Structure of $[NBu_4]_3[IrNi_8(CO)_{18}]$†

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The mixed-metal carbonyl cluster $[IrNi_8(CO)_{18}]^{3-}$ was obtained by treating $[Ni_6(CO)_{12}]^{2-}$ with $[Ir(CO)_2Cl_2]^-$ in MeCN (molar ratio 2:1). It is rapidly degraded by carbon monoxide, at room temperature and atmospheric pressure, to $[Ni_5(CO)_{12}]^{2-}$, $[Ni(CO)_4]$ and $[Ir(CO)_4]^-$. The salt $[NBu_4]_3[IrNi_8(\mu\text{-}CO)_9(CO)_9]$ crystallizes in the monoclinic space group $C2/c$, with $a = 20.525(9)$, $b = 18.877(5)$, $c = 42.713(4)$, $\beta = 95.13(2)°$, and $Z = 8$. The structure was solved by conventional Patterson and Fourier methods and refined by full-matrix least squares to $R = 0.045$ and $R' = 0.054$ for 4545 independent reflections having $I > 3.0\sigma(I)$. The cluster consists of three almost parallel stacked triangles; the central unit contains the iridium atom, which achieves the highest metal–metal connectivity by rotating and translating the internal triangle. Each metal atom is bonded to one terminal CO and each intratriangular edge is spanned by one bridging carbonyl ligand. Average bond distances are Ir–Ni_{inter} 2.945, Ir–Ni_{intra} 2.522, Ni–Ni_{inter} 2.891 and Ni–Ni_{intra} 2.401 Å.

In a previous paper[1] dealing with the chemistry of Ni–Ir mixed-metal carbonyl clusters we described the synthesis of the trianion $[Ir_3Ni_6(CO)_{17}]^{3-}$. This compound was obtained by condensation of $[Ni(CO)_4]$ with $[Ir(CO)_4]^-$ in refluxing tetrahydrofuran (thf). We also outlined that no mixed-metal carbonyl clusters could be obtained by treating preformed nickel carbonyl clusters with iridium halide and/or carbonyl complexes. This behaviour seems rather peculiar because the reaction of $[Ni_6(CO)_{12}]^{2-}$ with metal halide complexes is a general method for the synthesis of mixed-metal nickel-containing carbonyl clusters.[2–6]

As a continuation of our studies on the chemistry of Ni–Ir carbonyl clusters we decided to explore more deeply these strategies, testing different combinations of reactants and solvents and eventually obtained a very selective synthesis of $[IrNi_8(CO)_{18}]^{3-}$. We report here the synthesis, the chemical behaviour of $[IrNi_8(CO)_{18}]^{3-}$ and a complete account of the crystal structure determination of its tetrabutylammonium salt $[NBu_4]_3[IrNi_8(CO)_{18}]$. The metal framework of the enneanuclear cluster is very irregular; its geometry can be described as three $M_3(\mu\text{-}CO)_3(CO)_3$ stacked units which do not conform to a common idealized three-fold axis. A comparison of $[IrNi_8(CO)_{18}]^{3-}$ with other enneanuclear clusters having a related metal array, formed by face-fused regular polyhedra, is also made.

Results and Discussion

Preparation of $[IrNi_8(CO)_{18}]^{3-}$.—The trianion $[IrNi_8(CO)_{18}]^{3-}$ is the only cluster obtained from $[PPh_4]_2[Ni_6(CO)_{12}]$ and $[PPh_4][Ir(CO)_2Cl_2]$ when the two complexes are allowed to react in MeCN solution at room temperature in 2:1 molar ratio. It is almost impossible to monitor by IR spectroscopy the reaction course, since the final product has ν(CO) bands almost identical to that of the starting $[Ni_6(CO)_{12}]^{2-}$;[7] thus, $[IrNi_8(CO)_{18}]^{3-}$ shows in the carbonyl stretching region bands at 1985vs and 1810m cm^{-1} (MeCN), while $[Ni_6(CO)_{12}]^{2-}$ shows bands at 1981vs, 1808m and 1783 ms cm^{-1} (MeCN).[7] In order to be sure to drive the reaction to completeness, the mixture was stirred at room temperature for 72 h under a nitrogen atmosphere. At the end the colour of the reaction mixture is darker and the IR spectrum shows the presence of a small amount of $[Ni(CO)_4]$. According to the molar ratio of the reagents the stoicheiometry of the process is described by equation (1).

$$2[Ni_6(CO)_{12}]^{2-} + [Ir(CO)_2Cl_2]^- \longrightarrow [IrNi_8(CO)_{18}]^{3-} + 2[Ni(CO)_4] + 2Ni + 2Cl^- \quad (1)$$

The product was recovered by removing the solvent and the $[Ni(CO)_4]$ formed *in vacuo*; the insoluble brown residue of $[PPh_4]_3[IrNi_8(CO)_{18}]$ was suspended in MeOH, collected by filtration, extracted with acetone and crystallized by addition of propan-2-ol. Salts with different tetrasubstituted bulky ammonium or phosphonium cations are only sparingly soluble in tetrahydrofuran and MeOH, but very well soluble in acetone or MeCN.

The mixed-metal nature of the product was recognized from its reaction with carbon monoxide (atmospheric pressure, room temperature), equation (2), which produces well known

$$[IrNi_8(CO)_{18}]^{3-} + 10CO \longrightarrow [Ni_5(CO)_{12}]^{2-} + 3[Ni(CO)_4] + [Ir(CO)_4]^- \quad (2)$$

homonuclear species of nickel and iridium. An analogous instability toward carbon monoxide had been described for $[Ir_3Ni_6(CO)_{17}]^{3-}$,[1] and for some homo- and hetero-metallic carbonyl clusters containing Ni.[8] All these derivatives react with carbon monoxide with degradation to carbonyl complexes of low nuclearity. For $[Ir_3Ni_6(CO)_{17}]^{3-}$, where the number of

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

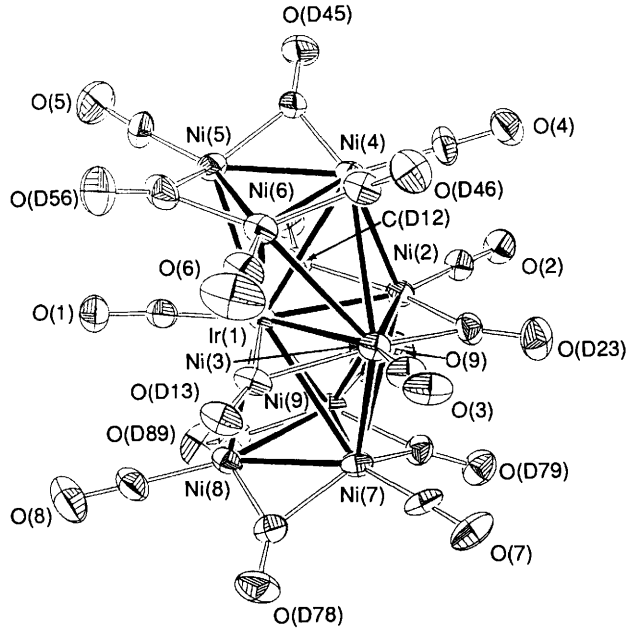

Fig. 1 ORTEP drawing of $[IrNi_8(CO)_{18}]^{3-}$. Thermal ellipsoids are drawn with 30% probability

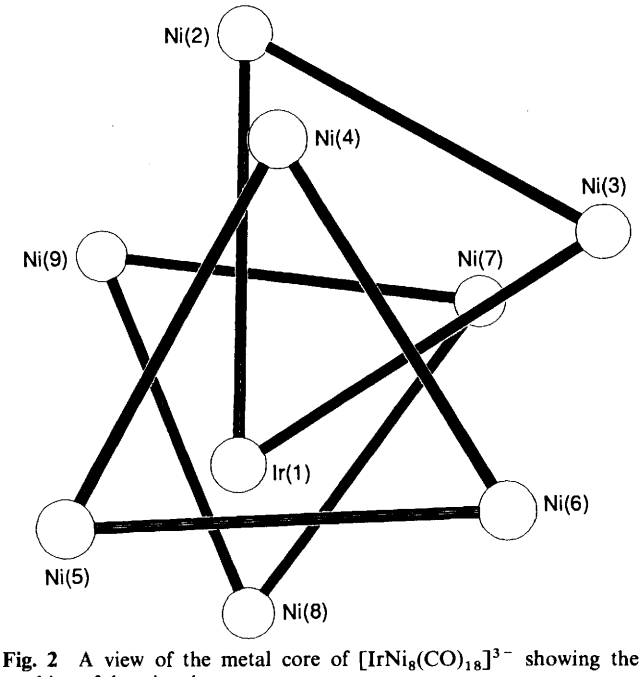

Fig. 2 A view of the metal core of $[IrNi_8(CO)_{18}]^{3-}$ showing the stacking of the triangles

negative charges and iridium atoms is coincident, only mononuclear fragments are obtained,[1] while in the present case the cluster $[Ni_5(CO)_{12}]^{2-}$ (ref. 9) is one of the final products.

The complex $[IrNi_8(CO)_{18}]^{3-}$ reacts with acids but, owing to instability, the product could never be characterized since it was impossible to recover it in a crystalline form suitable for an X-ray analysis. However, during the work-up of the product, compounds of high nuclearity are probably formed as can be deduced from their infrared spectra (2000vs and 1860s cm^{-1} acetone solution) and from their scarce solubility.

Crystal Structure of $[NBu_4]_3[IrNi_8(\mu\text{-}CO)_9(CO)_9]$.—The solid-state structure, determined by X-ray single-crystal diffraction techniques, consists of a packing of discrete cations and anions in the molar ratio 3:1 with normal van der Waals contacts between atoms of different ionic fragments. The structure of the $[IrNi_8(\mu\text{-}CO)_9(CO)_9]^{3-}$ trianion is represented

Table 1 Selected distances (Å) in the trianion $[IrNi_8(CO)_{18}]^{3-}$ with estimated standard deviations (e.s.d.s) on the last figure in parentheses

Metal–Metal			
Ir(1)–Ni(2)	2.521(1)	Ni(2)–Ni(9)	2.897(2)
Ir(1)–Ni(3)	2.523(1)	Ni(3)–Ni(4)	2.972(2)
Ir(1)–Ni(4)	3.048(1)	Ni(3)–Ni(6)	2.940(2)
Ir(1)–Ni(5)	2.780(2)	Ni(3)–Ni(7)	2.727(2)
Ir(1)–Ni(6)	3.001(2)	Ni(4)–Ni(5)	2.414(2)
Ir(1)–Ni(7)	3.005(2)	Ni(4)–Ni(6)	2.385(2)
Ir(1)–Ni(8)	2.762(2)	Ni(5)–Ni(6)	2.400(2)
Ir(1)–Ni(9)	3.074(1)	Ni(7)–Ni(8)	2.410(2)
Ni(2)–Ni(3)	2.420(2)	Ni(7)–Ni(9)	2.377(2)
Ni(2)–Ni(4)	2.748(2)	Ni(8)–Ni(9)	2.402(2)
Ni(2)–Ni(7)	3.061(2)		
$M–C_{terminal}$			
Ir(1)–C(1)	1.78(1)	Ni(6)–C(6)	1.75(1)
Ni(2)–C(2)	1.70(1)	Ni(7)–C(7)	1.72(1)
Ni(3)–C(3)	1.70(1)	Ni(8)–C(8)	1.73(1)
Ni(4)–C(4)	1.72(1)	Ni(9)–C(9)	1.75(1)
Ni(5)–C(5)	1.68(2)		
$M–C_{bridging}$			
Ir(1)–C(D12)	2.02(1)	Ni(5)–C(D56)	1.83(1)
Ir(1)–C(D13)	2.00(1)	Ni(6)–C(D46)	1.86(1)
Ni(2)–C(D12)	2.10(1)	Ni(6)–C(D56)	1.84(1)
Ni(2)–C(D23)	1.88(1)	Ni(7)–C(D78)	1.90(1)
Ni(3)–C(D13)	2.16(1)	Ni(7)–C(D79)	1.85(1)
Ni(3)–C(D23)	1.88(1)	Ni(8)–C(D78)	1.84(1)
Ni(4)–C(D45)	1.85(1)	Ni(8)–C(D89)	1.85(1)
Ni(4)–C(D46)	1.87(1)	Ni(9)–C(D79)	1.85(1)
Ni(5)–C(D45)	1.85(1)	Ni(9)–C(D89)	1.87(1)
$C–O_{terminal}$			
C(1)–O(1)	1.22(1)	C(6)–O(6)	1.10(1)
C(2)–O(2)	1.15(1)	C(7)–O(7)	1.16(1)
C(3)–O(3)	1.14(1)	C(8)–O(8)	1.14(1)
C(4)–O(4)	1.13(1)	C(9)–O(9)	1.13(1)
C(5)–O(5)	1.16(1)		
$C–O_{bridging}$			
C(D12)–O(D12)	1.17(1)	C(D56)–O(D56)	1.19(1)
C(D13)–O(D13)	1.13(1)	C(D78)–O(D78)	1.19(1)
C(D23)–O(D23)	1.17(1)	C(D79)–O(D79)	1.17(1)
C(D45)–O(D45)	1.21(1)	C(D89)–O(D89)	1.19(1)
C(D46)–O(D46)	1.19(1)		

in Fig. 1, together with the atom labelling scheme; selected bond distances and angles are listed in Tables 1 and 2, respectively.

The metal skeleton of the anion $[IrNi_8(CO)_{18}]^{3-}$ is formed by three almost parallel triangles of metal atoms with the Ir atom located in the central unit. Different enneametal cores constructed from three superimposed metal triangles with different rotational sequences have been found in the homonuclear carbonyl clusters $[Rh_9(CO)_{19}]^{3-}$,[10] $[Ir_9(CO)_{20}]^{3-}$,[11] $[Ni_9(CO)_{18}]^{2-}$,[12] and $[Pt_9(CO)_{18}]^{2-}$,[13] in some mixed-metal clusters $[Ir_3Ni_6(CO)_{17}]^{3-}$ (ref. 1) and $[PtRh_8(CO)_{19}]^{2-}$,[14] and, from a more general point of view, also in the $[Co_9C_2(CO)_{19}]^{2-}$ anion,[15] swollen by the interstitial dicarbide unit. All these clusters have been described as formed by face-fused regular polyhedra, either octahedral, trigonal prismatic or antiprismatic; accordingly they all possess different numbers of cluster valence electrons (c.v.e.s) ranging from 122 to 129.[16]

The structure of $[IrNi_8(CO)_{18}]^{3-}$ can easily be related to that of $[Ni_9(CO)_{18}]^{2-}$, of idealized C_{3v} symmetry: when a nickel atom of the latter is substituted by an isoelectronic iridato(1−) group the exact stoichiometry, charge and ligand distribution of the former complex are generated. An analogous replacement of iridium atoms with isoelectronic ferrate(1−) groups has been described for several mixed-metal Fe–Ir

Table 2 Selected angles (°) in $[IrNi_8(CO)_{18}]^{3-}$ with e.s.d.s on the last figure in parentheses

Metal–Metal–Metal			
Ir(1)–Ni(2)–Ni(3)	61.37(5)	Ni(5)–Ni(4)–Ni(6)	60.02(7)
Ir(1)–Ni(3)–Ni(2)	61.29(5)	Ni(7)–Ni(8)–Ni(9)	59.20(6)
Ni(2)–Ir(1)–Ni(3)	57.34(5)	Ni(7)–Ni(9)–Ni(8)	60.57(6)
Ni(4)–Ni(5)–Ni(6)	59.39(7)	Ni(8)–Ni(7)–Ni(9)	60.24(6)
Ni(4)–Ni(6)–Ni(5)	60.59(7)		
M–C(terminal)–O			
Ir(1)–C(1)–O(1)	177(1)	Ni(6)–C(6)–O(6)	178(2)
Ni(2)–C(2)–O(2)	178(1)	Ni(7)–C(7)–O(7)	175(1)
Ni(3)–C(3)–O(3)	178(1)	Ni(8)–C(8)–O(8)	176(2)
Ni(4)–C(4)–O(4)	175(2)	Ni(9)–C(9)–O(9)	175(1)
Ni(5)–C(5)–O(5)	178(2)		
M–C(bridging)–M			
Ir(1)–C(D12)–Ni(2)	75.5(5)	Ni(5)–C(D56)–Ni(6)	81.7(6)
Ir(1)–C(D13)–Ni(3)	74.6(4)	Ni(7)–C(D78)–Ni(8)	80.1(6)
Ni(2)–C(D23)–Ni(3)	80.2(5)	Ni(7)–C(D79)–Ni(9)	80.0(5)
Ni(4)–C(D45)–Ni(5)	81.4(6)	Ni(8)–C(D89)–Ni(9)	80.5(5)
Ni(4)–C(D46)–Ni(6)	79.4(6)		
M–C(bridging)–O			
Ir(1)–C(D12)–O(D12)	152(1)	Ni(6)–C(D46)–O(D46)	142(1)
Ni(2)–C(D12)–O(D12)	132(1)	Ni(5)–C(D56)–O(D56)	140(1)
Ir(1)–C(D13)–O(D13)	156(1)	Ni(6)–C(D56)–O(D56)	138(1)
Ni(3)–C(D13)–O(D13)	130(1)	Ni(7)–C(D78)–O(D78)	137(1)
Ni(2)–C(D23)–O(D23)	139(1)	Ni(8)–C(D78)–O(D78)	143(1)
Ni(3)–C(D23)–O(D23)	141(1)	Ni(7)–C(D79)–O(D79)	139(1)
Ni(4)–C(D45)–O(D45)	141(1)	Ni(9)–C(D79)–O(D79)	140(1)
Ni(5)–C(D45)–O(D45)	137(1)	Ni(8)–C(D89)–O(D89)	140(1)
Ni(4)–C(D46)–O(D46)	138(1)	Ni(9)–C(D89)–O(D89)	140(1)

carbonyl clusters.[17] In this system the carbonyl disposition is driven by the predominance of iridium in the metallic cage and is reminiscent of those of the homometallic clusters of that metal, whereas the topology of the CO ligands in $[IrNi_8(CO)_{18}]^{3-}$ is identical to that of the homometallic $[Ni_9(CO)_{18}]^{2-}$ dianion. Each metal atom possesses one terminal ligand, and each intralayer edge is bridged by a carbonyl ligand almost coplanar with the metal atoms; none of the interlayer edges is spanned by bridging carbonyls as found, on the contrary, in $[Ir_9(CO)_{20}]^{3-}$ (ref. 11) and $[Ir_3Ni_6(CO)_{17}]^{3-}$.[1]

However, the central triangle of $[IrNi_8(CO)_{18}]^{3-}$, containing the Ir atom, is significantly translated in the same plane and rotated by about 30°, when compared with the central triangle of $[Ni_9(CO)_{18}]^{2-}$. As a result of this displacement the idealized symmetry of the metallic cage, which is also reflected by the carbonyl disposition, is C_2 only, with the two-fold axis passing through Ir and bisecting the Ni(2)–Ni(3) edge. It is rather difficult to define the limit between bonding and non-bonding metal-to-metal distances in this structure, and in the following discussion we have arbitrarily assumed a maximum value of 3.10 Å for bonding, although weak, interactions; accordingly, this value was chosen also for drawing metal–metal bonds in Fig. 1.

Within this assumption, Ir(1) is bonded to all nickel atoms. As a main consequence of the aforementioned lateral shift and rotation, the slightly distorted regular trigonal-prismatic and antiprismatic units, forming the cage of $[Ni_9(CO)_{18}]^{2-}$,[12] cannot be recognized in $[IrNi_8(CO)_{18}]^{3-}$. A small superposition of atoms along the stacking direction is retained, as can be easily observed in Fig. 2, where the metal cage of the cluster is represented in a different orientation. On the contrary, the whole metal framework might be envisaged as a fragment of an iridium-centred cluster of nickel, either cuboctahedral or icosahedral. However, the distortions found in $[IrNi_8(CO)_{18}]^{3-}$, which are also reflected by the large scattering of metal–metal bond distances, are incompatible with the above-mentioned polyhedra. Nickel was found to form icosahedral clusters, both centred or empty, such as $[Ni_{12}(CO)_{22}E]^{2-}$ (E = Ge or Sn),[4] $[Ni_{13}Sb_2(CO)_{24}]^{3-}$ (ref. 5) and $[Ni_9(CO)_{15}(AsPh_3)]^{2-}$.[18] Cuboctahedral cores of nickel clusters are unknown, but some neutral platinum[19] and palladium[20] carbonyl clusters containing also phosphorus-donor ligands show this arrangement.

The presence of the iridium atom in the site of highest connectivity is in keeping with the situation observed in other mixed-metal carbonyl clusters containing third-row transition elements such as Pt–Rh,[21,22] Fe–Pt[23] and Ni–Pt[2,3] and reflects the higher metal–metal bond energy of the heavier elements (as measured, for example, by the sublimation enthalpies of the elements).[24] We consider the structure of $[IrNi_8(CO)_{18}]^{3-}$ as derived from a compromise between the tendency of nickel to reproduce $[Ni_9(CO)_{18}]^{2-}$ and the tendency of iridium to generate more compact clusters. This idea is substantiated by the structure of $[Ir_3Ni_6(CO)_{17}]^{3-}$:[1] when two nickel atoms of $[IrNi_8(CO)_{18}]^{3-}$ are substituted by two iridium atoms the metal cage becomes a regular fragment of a hexagonal close-packed lattice. It is worth noting that the geometry of the metallic cage of $[IrNi_8(CO)_{18}]^{3-}$ is such that the iridium atom is somewhat hidden in a pocket dictated by the irregular envelope of the eight nickel atoms, and their directly attached carbonyl groups; in spite of this, and thanks to the significant bend of the CO ligands of the homometallic layers away from the central layer, Ir is allowed to bear also a terminal carbonyl.

The Ni–Ni bond distances of the two external triangles, supported by bridging ligands, are in the range 2.377(2)–2.414(2) Å; their average value of 2.398 Å is in good agreement with those found in the two dianions $[Ni_6(CO)_{12}]^{2-}$ and $[Ni_9(CO)_{18}]^{2-}$ (2.387 and 2.39 Å,[12] respectively) where $Ni_3(\mu\text{-}CO)_3(CO)_3$ units are present. The slightly longer Ni–Ni distance in the central triangle [2.420(2) Å] is probably due to the presence of the iridium atom. The Ir–Ni distances can be divided into two distinct groups: the first set consists of two intralayer distances of the central triangle averaging 2.522 Å; this value is even shorter than the average (2.599 Å) found for

the bridged Ni–Ir distances of $[Ir_3Ni_6(CO)_{17}]^{3-}$.[1] The second set consists of six Ni–Ir interlayer distances with an average value of 2.945 Å; this value is greater than the unbridged interlayer distances (2.688 Å) in $[Ir_3Ni_6(CO)_{17}]^{3-}$.[1] Two Ir–Ni distances are definitely shorter (< 2.8 Å) than the remaining four (> 3.0 Å) and reflect the observation that the iridium atom does not lie exactly on the axis passing through the centres of the external triangles and some distortion from idealized symmetry is present. The average Ni–$C_{terminal}$ and Ni–$C_{bridging}$ bond lengths of 1.72 and 1.89 Å in $[IrNi_8(CO)_{18}]^{3-}$ are in agreement with the corresponding separations found in $[Ni_6(CO)_{12}]^{2-}$ and $[Ni_9(CO)_{18}]^{2-}$.[7,12] The Ir–C distances involving the linear as well as the bridging carbonyl groups fall in the usual range found in other iridium-containing clusters. The C–O distances are slightly different in the linear and bridging mode (averages 1.15 and 1.18 Å, respectively) and in good agreement with those found in other nickel clusters.[7,12]

Table 3 Crystal and data collection parameters for $[NBu_4]_3[IrNi_8(CO)_{18}]$

Formula	$C_{66}H_{108}IrN_3Ni_8O_{18}$
M	1893.49
Crystal system	Monoclinic
Space group	$C2/c$ (no. 15)
a/Å	20.525(9)
b/Å	18.877(5)
c/Å	42.713(4)
β/°	95.13(3)
U/Å^3	16 482(13)
Z	8
D_c/g cm^{-3}	1.526
μ(Mo-Kα)/cm^{-1}	34.5
Minimum transmission factor	0.80
Crystal dimensions/mm	0.10 × 0.12 × 0.20
ω Scan width/°	1.20 + 0.35 tan θ
Octants of reciprocal space explored	$+h, +k, \pm l$
No. of variables	610

Experimental

All reactions were carried out in an atmosphere of nitrogen or carbon monoxide with Schlenk-tube and vacuum-line techniques.[25] Solvents were purified and dried by distillation under a nitrogen atmosphere as follows: thf, sodium–benzophenone;

Table 4 Positional parameters for $[NBu_4]_3[IrNi_8(CO)_{18}]$ with e.s.d.s in the last figure in parentheses

Atom	x	y	z	Atom	x	y	z
Ir(1)	0.135 92(3)	0.110 30(3)	0.143 28(1)	C(111)	0.723 8(8)	0.033 8(9)	0.706 6(4)
Ni(2)	0.120 07(8)	0.174 0(1)	0.091 30(4)	C(112)	0.687 1(9)	−0.021(1)	0.724 8(4)
Ni(3)	0.222 74(8)	0.113 9(1)	0.105 07(4)	C(113)	0.623(1)	−0.031(1)	0.702 1(5)
Ni(4)	0.198 05(9)	0.254 2(1)	0.133 25(4)	C(114)	0.581(1)	−0.083(1)	0.720 3(6)
Ni(5)	0.164 7(1)	0.222 8(1)	0.184 22(4)	C(121)	0.786 2(8)	0.076 6(9)	0.759 0(4)
Ni(6)	0.264 07(9)	0.176 4(1)	0.166 70(5)	C(122)	0.745(1)	0.145(1)	0.758 6(5)
Ni(7)	0.131 85(8)	0.012 7(1)	0.087 55(4)	C(123)	0.769(1)	0.171(2)	0.796 5(7)
Ni(8)	0.077 23(9)	−0.020 3(1)	0.133 03(5)	C(124)	0.740(2)	0.216(2)	0.798(1)
Ni(9)	0.026 69(8)	0.059 8(1)	0.094 46(5)	C(131)	0.825 5(8)	0.104 5(9)	0.704 3(4)
O(1)	0.090 2(6)	0.066 3(6)	0.205 1(2)	C(132)	0.895(1)	0.129(1)	0.718 9(5)
O(2)	0.032 9(4)	0.252 8(5)	0.048 7(2)	C(133)	0.912(1)	0.190(1)	0.698 6(5)
O(3)	0.354 7(5)	0.085 3(6)	0.093 7(3)	C(134)	0.953(1)	0.233(2)	0.713 6(7)
O(4)	0.196 2(6)	0.342 2(6)	0.079 1(3)	C(141)	0.834 9(8)	−0.019(1)	0.729 8(4)
O(5)	0.077 8(7)	0.250 1(8)	0.231 1(3)	C(142)	0.847(1)	−0.057(1)	0.698 6(5)
O(6)	0.385 3(6)	0.103 8(8)	0.180 0(4)	C(143)	0.908(1)	−0.112(1)	0.712 3(6)
O(7)	0.231 0(5)	−0.015 0(7)	0.045 7(3)	C(144)	0.916(2)	−0.149(2)	0.687 9(7)
O(8)	0.066 9(7)	−0.101 9(7)	0.189 1(3)	C(211)	0.589 5(7)	0.275 4(9)	0.478 9(4)
O(9)	−0.084 4(5)	0.137 3(6)	0.066 5(3)	C(212)	0.650 7(8)	0.236(1)	0.471 3(4)
O(D12)	0.015 3(4)	0.209 8(5)	0.133 7(2)	C(213)	0.665 4(9)	0.182(1)	0.499 4(4)
O(D13)	0.249 9(4)	0.006 7(5)	0.156 8(3)	C(214)	0.623 1(9)	0.119(1)	0.497 9(4)
O(D23)	0.205 5(5)	0.169 6(7)	0.042 1(3)	C(221)	0.498 9(8)	0.359 7(9)	0.460 0(4)
O(D45)	0.113 9(6)	0.355 3(6)	0.160 5(3)	C(222)	0.444 6(8)	0.312(1)	0.470 6(4)
O(D46)	9.335 2(5)	0.261 4(7)	0.124 6(3)	C(223)	0.392 9(9)	0.360(1)	0.481 9(4)
O(D56)	0.252 0(6)	0.161 0(8)	0.232 0(3)	C(224)	0.332 3(9)	0.317(1)	0.491 8(4)
O(D78)	0.170 4(6)	−0.123 0(6)	0.114 4(3)	C(231)	0.607 3(8)	0.365 0(9)	0.434 7(4)
O(D79)	0.057 1(5)	0.049 7(6)	0.030 8(2)	C(232)	0.635 7(8)	0.420(1)	0.457 6(4)
O(D89)	−0.061 9(5)	−0.009 8(7)	0.133 1(3)	C(233)	0.682 7(9)	0.464(1)	0.438 4(4)
C(1)	0.109 5(7)	0.085 8(8)	0.180 3(3)	C(234)	0.716(1)	0.514(1)	0.459 5(5)
C(2)	0.067 4(6)	0.221 0(8)	0.066 3(3)	C(241)	0.534 1(8)	0.259 0(9)	0.423 0(4)
C(3)	0.301 5(6)	0.095 7(8)	0.098 1(4)	C(242)	0.494 5(9)	0.286(1)	0.393 7(5)
C(4)	0.194 2(8)	0.307 6(9)	0.100 4(3)	C(243)	0.479(1)	0.210(2)	0.375 5(6)
C(5)	0.113 5(8)	0.238(1)	0.212 2(3)	C(244)	0.437(2)	0.227(2)	0.359(1)
C(6)	0.338 2(7)	0.130 9(9)	0.174 7(4)	C(311)	0.474 3(8)	0.130 1(9)	0.600 2(4)
C(7)	0.193 3(7)	−0.003 0(8)	0.063 6(3)	C(312)	0.499 6(9)	0.051(1)	0.602 7(5)
C(8)	0.073 1(8)	−0.069 8(9)	0.166 9(4)	C(313)	0.567(1)	0.058(1)	0.589 8(5)
C(9)	−0.040 6(7)	0.109 0(8)	0.078 5(4)	C(314)	0.602(1)	−0.013(1)	0.595 9(6)
C(D12)	0.061 8(6)	0.176 2(7)	0.129 2(3)	C(321)	0.359 7(9)	0.092(1)	0.574 6(4)
C(D13)	0.215 6(6)	0.049 1(7)	0.146 3(4)	C(322)	0.367(1)	0.128(1)	0.542 6(6)
C(D23)	0.191 3(7)	0.159 0(8)	0.067 5(3)	C(323)	0.386(1)	0.080(2)	0.520 6(6)
C(D45)	0.145 9(8)	0.301 9(8)	0.159 4(3)	C(324)	0.392(1)	0.100(1)	0.487 2(6)
C(D46)	0.288 5(6)	0.238 2(8)	0.135 8(4)	C(331)	0.379 1(8)	0.212(1)	0.603 4(4)
C(D56)	0.234 6(8)	0.180 3(9)	0.206 2(4)	C(332)	0.305(1)	0.225(1)	0.606 2(5)
C(D78)	0.140 4(7)	−0.069 0(8)	0.113 6(3)	C(333)	0.297(1)	0.305(1)	0.605 0(5)
C(D79)	0.068 1(7)	0.046 5(8)	0.058 1(3)	C(334)	0.227(1)	0.318(2)	0.603 7(7)
C(D89)	−0.009 8(6)	0.004 7(8)	0.124 7(3)	C(341)	0.381 2(9)	0.093(1)	0.633 1(4)
N(1)	0.793 1(6)	0.050 1(8)	0.725 6(3)	C(342)	0.416(1)	0.128(1)	0.663 1(5)
N(2)	0.557 5(5)	0.314 8(6)	0.449 0(3)	C(343)	0.415(1)	0.075(1)	0.689 3(5)
N(3)	0.399 9(7)	0.132 8(8)	0.603 4(3)	C(344)	0.445(1)	0.100(1)	0.717 1(6)

methanol, Mg; propan-2-ol, $Al(OPr^i)_3$; MeCN, Na_2CO_3. Infrared spectra were recorded on a Perkin-Elmer 781 grating spectrophotometer using calcium fluoride cells previously purged with nitrogen or carbon monoxide. The compounds $[PPh_4][Ir(CO)_2Cl_2]$[26] and $[PPh_4]_2[Ni_6(CO)_{12}]$[7] were prepared as described.

Preparation of $[NBu_4]_3[IrNi_8(CO)_{18}]$.—A round-bottomed flask (100 cm^3), equipped with a magnetic stirring bar, was evacuated, filled with nitrogen and charged with $[PPh_4]_2[Ni_6(CO)_{12}]$ (1.17 g, 0.85 mmol) and $[PPh_4][Ir(CO)_2Cl_2]$ (0.29 g, 0.44 mmol). The two solids were dissolved in MeCN (30 cm^3) and the red solution was gently swirled for 72 h; thereafter the solvent and $[Ni(CO)_4]$ were removed *in vacuo*. The brown residue was suspended in MeOH (20 cm^3), stirred for 1 h and then the microcrystalline product was recovered by filtration. It was dissolved in acetone (15 cm^3) on the frit, leaving undissolved a very small amount of metallic residue, and crystallized by adding propan-2-ol. Crystals of $[NBu_4]_3[IrNi_8(CO)_{18}]$ suitable for X-ray analysis were obtained as follows. The $[PPh_4]^+$ salt of $[IrNi_8(CO)_{18}]^{3-}$ was dissolved in acetone and treated with a stoichiometric amount of $Na[BPh_4]$. After 20 min the solution was dried *in vacuo* and the residue dissolved in MeOH. By filtration, the sodium salt of the cluster was separated from the microcrystalline precipitate of PPh_4BPh_4. The methanolic solution was then layered with a 5% solution of NBu_4Br in propan-2-ol. Yield 0.540 g, 65%. Any other combination of tetrasubstituted ammonium salts and solvents resulted in the formation of tacky products (Found: C, 41.4; H, 5.5; N, 2.0. $C_{66}H_{108}IrN_3Ni_8O_{18}$ requires C, 41.8; H, 5.7; N, 2.2%).

X-Ray Structure Analysis for $[NBu_4]_3[IrNi_8(CO)_{18}]$.—A dark prismatic specimen was mounted on the tip of a thin glass fibre for X-ray examination and data collection. All data were collected, at room temperature, on a CAD4 diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). Unit-cell parameters were obtained by least-squares refinement of the angular settings of 25 reflections, well distributed in reciprocal space and lying in the range θ 8–12°. Crystal data and intensity collection parameters are reported in Table 3. Intensity data were collected in the ω scan mode with θ 3–21°. Three standard reflections were monitored every 300 and showed a gradual decrease in intensity which was evaluated as about 47% decay at the end of the data collection. The data were corrected for Lorentz and polarization effects. An empirical absorption correction[27] was applied using three reflections with ψ values near to 90°. All crystallographic computations were carried out by using the SDP Structure Determination Package[28] and a PDP 11/73 computer.

Solution and refinement of the structure. Of a total of 8884 reflections measured, 4545 independent reflections with intensities $I > 3.0\sigma(I)$ were used in the structure solution and refinement. The structure was solved by a combination of Patterson and Fourier difference syntheses: the positions of the three metal atoms defining the central triangle were found by Patterson synthesis; the remaining Ni atoms and all non-hydrogen atoms were found by subsequent Fourier difference synthesis. Full-matrix least-squares refinement minimizing the function $\Sigma w(F_o - k|F_c|)^2$ was carried out using anisotropic thermal parameters for all atoms of the anion, isotropic ones for all atoms of the cations, and was continued until the largest shift in any parameter was less than 0.5σ. Owing to the high thermal parameters of the aliphatic chains of the cations (9–30 Å^2) the contribution of the hydrogen atoms to the structure factors was omitted. Individual weights were assigned according to the formula $w = 1/\sigma^2(F_o)$, where $\sigma(F_o) = \sigma(F_o^2)/2F_o$, $\sigma(F_o^2) = [\sigma^2(I) + (pI)^2]^{\frac{1}{2}}/L_p$ and p the 'ignorance factor' was equal to 0.04. Scattering factors and anomalous dispersion corrections were taken from ref. 29. The full-matrix least-squares refinement converged with $R = [\Sigma(F_o - k|F_c|)/\Sigma F_o] = 0.045$, $R' = [\Sigma w(F_o - k|F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}} = 0.054$ and e.s.d. = $[\Sigma w(F_o - k|F_c|)^2/(N_o - N_v)]^{\frac{1}{2}} = 1.630$ where N_o = number of observations and N_v = number of variables. Final atomic positional parameters for non-hydrogen atoms are given in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Acknowledgements

We thank the Italian Consiglio Nazionale delle Ricerche (CNR) for financial support.

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Received 27*th March* 1991; *Paper* 1/01474I