New Icosahedral Heterometallic Nickel Carbonyl Clusters containing Bismuth *

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The new $[Ni_{11}Bi_2(CO)_{18}]^{n-}$ (n = 2 or 3) cluster anions have been obtained as a mixture by reaction of $[Ni_6(CO)_{12}]^{2-}$ with 0.5–0.7 equivalents of $BiCl_3$ in tetrahydrofuran. Subsequent controlled oxidation or reduction of this mixture selectively affords the two anions. They have been isolated in the solid state as tetrasubstituted ammonium salts. The corresponding $[Ni_{11}Bi_2(CO)_{18}]^{4-}$ tetraanion has only been obtained in solution by chemical or electrochemical reduction of the parent di- or tri-anion. All these compounds have been chemically and spectroscopically characterized, and the structure of $[NEt_4]_3[Ni_{11}Bi_2(CO)_{18}]$ has been ascertained by X-ray diffraction [orthorhombic, space group *Pccn*, a = 14.573(2), b = 19.638(4), c = 21.248(3) Å, Z = 4, R = 0.0501]. The geometry of the trianion is based on a nickel-centred $Ni_{10}Bi_2(\mu_{12}\text{-}Ni)(CO)_{18}$ icosahedral core. Relevant average bond distances are $Ni\text{-}Ni_{intrapentagonal}$ 2.810 Å, $Ni\text{-}Ni_{interpentagonal}$ 2.506 Å, $Ni\text{-}Ni_{inner\text{-}outer}$ 2.595 Å, $Bi\text{-}Ni_{inner}$ 2.507 Å and $Bi\text{-}Ni_{outer}$ 2.819 Å. The corresponding di- and tetra-anions probably possess a closely related structure as shown by the electrochemical reversibility of their electron-transfer processes and by the similarity of the IR patterns of the three compounds.

In previous papers[1,2] we have reported the synthesis and structural characterization of a series of cluster anions of general formula $[Ni_{13}Sb_2(CO)_{24}]^{n-}$ (n = 1–4). On the basis of their structure, these compounds were described as nickel-centred $[Ni_{11}Sb_2(CO)_{18}]^{n-}$ icosahedral moieties behaving as bidentate cluster-ligands[3,4] toward two dangling $Ni(CO)_3$ unsaturated groups. The electronic structure within the $[Ni_{11}Sb_2(CO)_{18}]^{n-}$ unit was analysed by extended Hückel molecular orbital (EHMO) calculations under the above assumption. However, an attempt to set free the $[Ni_{11}Sb_2(CO)_{18}]^{2-}$ cluster-ligand, by reaction with CO of $[Ni_{13}Sb_2(CO)_{24}]^{2-}$, was unsuccessful.[2] This was rather surprising in view of the known equilibria between $[Ni(CO)_3L]$ (L = trisubstituted phosphine) and $[Ni(CO)_4]$ species under CO, and the expected decreased stability of the corresponding stibine complexes,[5] which in the case of nickel are rather rare.[6]

In order to demonstrate the validity of the above assumptions, we have undertaken similar investigations with bismuth hoping that its substantial 6s–6p separation[7] would favour the formation of nickel-centred $[Ni_{11}Bi_2(CO)_{18}]^{n-}$ icosahedral cluster-ligands, rather than their adducts with $Ni(CO)_3$ groups.

Results and Discussion

Synthesis and Spectroscopic Characterization of the $[Ni_{11}Bi_2(CO)_{18}]^{n-}$ (n = 2–4) *Anions.*—Explorative reactions between $BiCl_3$ and $[Ni_6(CO)_{12}]^{2-}$ revealed a substantial difference from the corresponding reaction with $SbCl_3$.[2] For instance, reactions run in acetonitrile solution, where most of the $[Ni_6(CO)_{12}]^{2-}$ salts are well soluble, led only to formation of Ni and Bi metals and clear solutions containing $[Ni(CO)_4]$ and $[Ni(CO)_3Cl]^-$.[8] No heterometallic Ni–Bi carbonyl compound was detected. However, when the reaction of $[Ni_6(CO)_{12}]^{2-}$ with $BiCl_3$ is run in tetrahydrofuran (thf) with either NEt_4^+ or NBu_4^+ as counter ion, black precipitates are obtained; subsequent extraction with acetone or acetonitrile affords dark brown solutions, which show infrared carbonyl absorptions in the 1990–1960 and 1850–1800 cm^{-1} regions indicating the presence of $[Ni_{11}Bi_2(CO)_{18}]^{2-}$ or $[Ni_{11}Bi_2(CO)_{18}]^{3-}$, or mixtures of the two anions. The relative composition of the mixture depends on the $BiCl_3/[Ni_6(CO)_{12}]^{2-}$ ratio adopted. This has been investigated within the range 0.5–1 : 1, also in order to maximize the yields. With molar ratios close to 0.5 : 1 the conversion of $[Ni_6(CO)_{12}]^{2-}$ is not complete and the $[Ni_{11}Bi_2(CO)_{18}]^{3-}$ salts prevail in the precipitate. On increasing the ratio to 0.8–1 : 1 only the corresponding salts of the dianion are obtained; however the yields are very poor owing to a greater formation of Ni and Bi metals, and $[Ni(CO)_4]$. The best yields, which never exceed *ca.* 30% of the amount expected on the basis of the formal stoichiometry (1), have been obtained by adopting a 0.65–0.75 : 1

$$3[Ni_6(CO)_{12}]^{2-} + 2BiCl_3 \longrightarrow [Ni_{11}Bi_2(CO)_{18}]^{2-} + 3[Ni(CO)_4] + 2[Ni(CO)_3Cl]^- + Ni + Ni^{2+} + 4Cl^- \quad (1)$$

ratio which, on the other hand, generally leads to a mixture of $[Ni_{11}Bi_2(CO)_{18}]^{2-}$ and $[Ni_{11}Bi_2(CO)_{18}]^{3-}$ salts. The reaction mixture was worked up depending on its actual composition, to afford selectively either $[Ni_{11}Bi_2(CO)_{18}]^{2-}$ or $[Ni_{11}Bi_2(CO)_{18}]^{3-}$, as well as the corresponding $[Ni_{11}Bi_2(CO)_{18}]^{4-}$ tetraanion according to the redox interconversion reactions shown in Scheme 1.

$$\begin{array}{ccccc} & E^{\circ\prime} = -0.67\ \text{V} & & E^{\circ\prime} = -1.42\ \text{V} & \\ [Ni_{11}Bi_2(CO)_{18}]^{2-} & \underset{-e}{\overset{+e}{\rightleftharpoons}} & [Ni_{11}Bi_2(CO)_{18}]^{3-} & \underset{-e}{\overset{+e}{\rightleftharpoons}} & [Ni_{11}Bi_2(CO)_{18}]^{4-} \end{array}$$

Scheme 1

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Non-SI unit employed: G = 10^{-4} T.

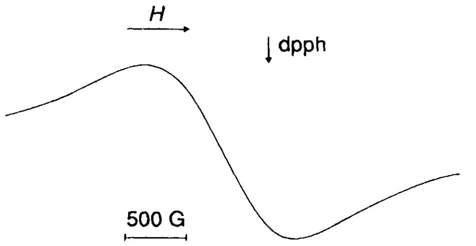

Fig. 1 X-Band ESR spectrum recorded at 100 K on a powdered solid sample of $[NEt_4]_3[Ni_{11}Bi_2(CO)_{18}]$

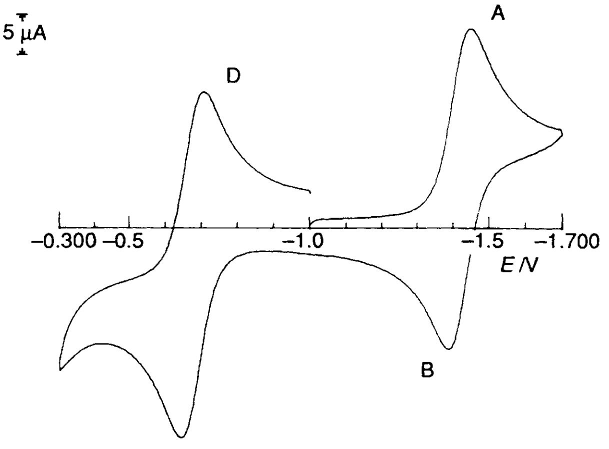

Fig. 2 Cyclic voltammogram recorded at a platinum electrode on an acetonitrile solution containing $[NEt_4]_3[Ni_{11}Bi_2(CO)_{18}]$ (1.72×10^{-3} mol dm^{-3}) and NEt_4ClO_4 (0.2 mol dm^{-3}). Scan rate 0.2 V s^{-1}

The $[Ni_{11}Bi_2(CO)_{18}]^{4-}$ tetraanion was obtained in solution by reduction of the above mixture with sodium metal in $P(NMe_2)_3O$ where it shows infrared carbonyl absorptions at 1921s, 1750m and 1705(sh) (br) cm^{-1}. Attempted precipitations by addition of water solutions of tetrasubstituted ammonium halides systematically resulted in separation of waxy precipitates of the corresponding salts of the $[Ni_{11}Bi_2(CO)_{18}]^{3-}$ trianion. Microcrystalline samples of $[Ni_{11}Bi_2(CO)_{18}]^{4-}$ were isolated by reduction of $[Ni_{11}Bi_2(CO)_{18}]^{3-}$ with sodium diphenylketyl in thf as a result of their very low solubility in this solvent. However, as shown by IR monitoring, dissolution of these precipitates in acetone or acetonitrile results in regeneration of the parent trianion, probably owing to the unavoidable presence of traces of moisture, which behaves as an oxidizing agent.

The $[Ni_{11}Bi_2(CO)_{18}]^{2-}$ dianion is quantitatively obtained by controlled oxidation of the above reaction mixture with several oxidizing agents including $BiCl_3$, $[Fe(\eta^5\text{-}C_5H_5)_2]^+$ and $FeCl_3$, as well as protonic acids such as 32% H_2SO_4 and 48% H_3PO_4 in acetone or acetonitrile. Several tetrasubstituted ammonium salts of $[Ni_{11}Bi_2(CO)_{18}]^{2-}$ have been precipitated in the crystalline state by slow diffusion of isopropyl alcohol or diisopropyl ether in their acetone or acetonitrile solutions, in the presence of a slight amount of oxidizing agent to prevent regeneration of the parent trianion. In acetonitrile solution the $[Ni_{11}Bi_2(CO)_{18}]^{2-}$ dianion shows infrared carbonyl absorptions at 1995s, 1840m and 1780(sh) (br) cm^{-1}.

The $[Ni_{11}Bi_2(CO)_{18}]^{3-}$ trianion, which is the most stable of the three $[Ni_{11}Bi_2(CO)_{18}]^{n-}$ (n = 2–4) derivatives and remains unaltered in solution over a period of weeks, is obtained by controlled reduction of the reaction mixture with sodium diphenylketyl in thf and has been crystallized from acetone–isopropyl alcohol. In acetonitrile solution it shows infrared carbonyl absorptions at 1963s, 1807m and 1740(sh) (br) cm^{-1}, which can be attributed to terminal, edge- and face-bridging carbonyls, in agreement with its solid state structure (see later).

The ready conversion of $[Ni_{11}Bi_2(CO)_{18}]^{4-}$ into $[Ni_{11}Bi_2(CO)_{18}]^{3-}$ by action of water, and the corresponding transformation of the latter in $[Ni_{11}Bi_2(CO)_{18}]^{2-}$ with protonic acids, as well as the failure to observe an ESR signal in solution for the odd-electron $[Ni_{11}Bi_2(CO)_{18}]^{3-}$ derivative, suggested the possibility that the tri- and di-anions could contain respectively one and two μ_6-BiH capping groups. Proton NMR spectra of their salts were inconclusive and only showed signals attributable to the counter ions and the crystallization solvents. However, an X-band ESR spectrum recorded at 100 K on a powdered solid sample of $[NEt_4]_3[Ni_{11}Bi_2(CO)_{18}]$ showed a very large absorption ($\Delta H = 1190 \pm 5$ G) at $g = 2.283 \pm 0.005$ (see Fig. 1). Such a line shape is clearly indicative of the metal character of the unpaired spin density, which is likely delocalized over the whole metal framework. No structural change in the shape of the signal is observed on increasing the temperature to 300 K, except for a significant decrease in intensity, likely attributable to the increase in the cluster vibrational modes. This could also account for the lack of a signal in dilute solution at room temperature.

A further confirmation of the given formulations stems from the cyclic voltammetric response exhibited by $[Ni_{11}Bi_2(CO)_{18}]^{3-}$ in acetonitrile solution, which is shown in Fig. 2. The trianion undergoes both a reduction (peak A) and an oxidation (peak C) process, each displaying a directly associated response in the reverse scan (peaks B and D, respectively). Controlled-potential coulometry showed that both the redox steps involve a one-electron transfer, according to the reversible sequence shown in Scheme 1. Analysis of cyclic voltammograms with scan rates varying from 0.02 to 51.2 V s^{-1} revealed the substantial reversibility of the electron transfer:[9] (*i*) the peak current ratio $i_{p(backward)}/i_{p(forward)}$ is constantly equal to unity; (*ii*) the relevant peak-to-peak separation remains in the range 60–70 mV up to 5.12 V s^{-1}, then tends to increase (about 130 mV at the highest scan rate), likely because of the occurrence of some uncompensated solution resistance; (*iii*) the ratio $i_{p(forward)}/v^{\frac{1}{2}}$ remains substantially constant. Macroelectrolysis tests showed that both the redox congeners $[Ni_{11}Bi_2(CO)_{18}]^{2-}$ and $[Ni_{11}Bi_2(CO)_{18}]^{4-}$ are quite stable. On the basis of the electrochemical reversibility of the relevant electron transfers,[10] we may presume that the geometry of the parent trianion is maintained. This conclusion is in keeping with the close similarity of IR patterns in the carbonyl stretching region.

The propensity of the present $[Ni_{11}Bi_2(CO)_{18}]^{n-}$ family of compounds to change stepwise from $n = 2$ to $n = 4$ without structural reorganization parallels that of $[Ni_{13}Sb_2(CO)_{24}]^{n-}$.[2] Furthermore, the values of the redox potentials, which are very close in the two systems, suggest that replacement of μ_6-Sb–$Ni(CO)_3$ with μ_6-Bi moieties has only a very minor effect on the energy and composition of the highest occupied molecular orbital. It was of interest to verify the substantial lack of residual basicity of the Bi atoms in these compounds, as suggested by their ready oxidation, rather than protonation, upon treatment with protonic acids. As expected, the reaction of $[Ni_{11}Bi_2(CO)_{18}]^{4-}$ with 2 equivalents of methyl iodide gives quantitatively $[Ni_{11}Bi_2(CO)_{18}]^{2-}$, rather than a $[Ni_{11}(BiMe)_2(CO)_{18}]^{2-}$ congener of the previously isolated $[Ni_{11}(SbMe)_2(CO)_{18}]^{2-}$ derivative.[2] The nature of the product reactions was confirmed by coincidence of its infrared and redox behaviour with that of a genuine sample of $[Ni_{11}Bi_2(CO)_{18}]^{2-}$ obtained by a different route, as well as from the completely different electrochemical behaviour of $[Ni_{11}(SbMe)_2(CO)_{18}]^{2-}$. As shown in Fig. 3, the $[Ni_{11}(SbMe)_2(CO)_{18}]^{2-}$ dianion in thf solution undergoes an irreversible reduction ($E_p = -1.80$ V), as well as a one-electron oxidation ($E^{\circ\prime} = +0.14$ V, $\Delta E_p = 121$ mV at 0.2 V s^{-1}), complicated by the relatively slow decomposition of the $[Ni_{11}(SbMe)_2(CO)_{18}]^-$ monoanion. The minor redox couples asterisked in Fig. 3 are due to the

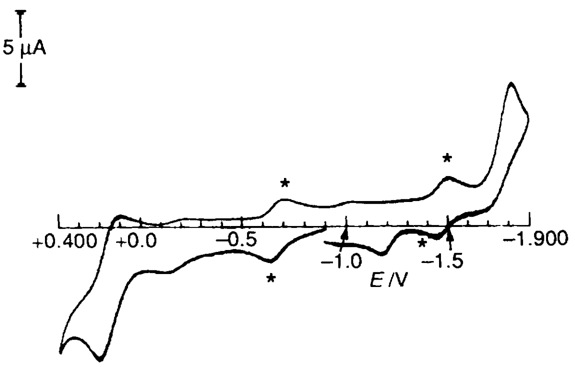

Fig. 3 Cyclic voltammogram recorded at a platinum electrode on a thf solution of $[NBu_4]_2[Ni_{11}(SbMe)_2(CO)_{18}]$ mixed with $[NBu_4]_2[Ni_{13}Sb_2(CO)_{24}]$. Supporting electrolyte NBu_4ClO_4 (0.2 mol dm^{-3}). Scan rate 0.1 V s^{-1}

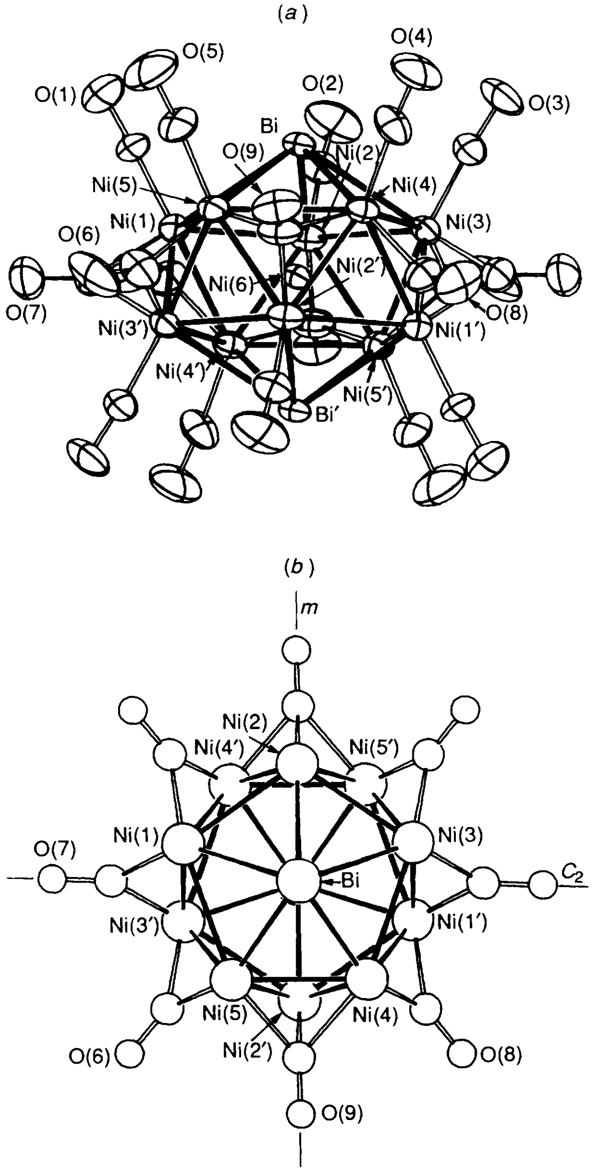

Fig. 4 (*a*) ORTEP[12] view of the $[Ni_{11}Bi_2(CO)_{18}]^{3-}$ anion. The carbon atoms of the carbonyl ligands are labelled in accord with the corresponding oxygens. (*b*) View of the anion perpendicular to the Bi–Bi′ axis showing the idealized C_{2h} arrangement of the bridging ligands (terminal ligands omitted for clarity), crystallographic symmetry C_i

Table 1 Selected bond lengths (Å) and angles (°) for $[NEt_4]_3[Ni_{11}Bi_2(CO)_{18}]$

Ni–Bi			
Ni(1)–Bi	2.851(1)	Ni(4)–Bi	2.808(1)
Ni(2)–Bi	2.769(1)	Ni(5)–Bi	2.818(1)
Ni(3)–Bi	2.851(1)	Average	2.82
Ni (interstitial)–Bi			
Ni(6)–Bi	2.507(1)		
Ni–Ni (intrapentagonal)			
Ni(1)–Ni(2)	2.782(2)	Ni(4)–Ni(5)	2.700(2)
Ni(2)–Ni(3)	2.799(2)	Ni(1)–Ni(5)	2.881(2)
Ni(3)–Ni(4)	2.890(1)	Average	2.81
Ni–Ni (interpentagonal)			
Ni(1)–Ni(3′)	2.513(1)	Ni(4)–Ni(2′)	2.486(2)
Ni(4)–Ni(1′)	2.521(2)	Ni(5)–Ni(2′)	2.494(1)
Ni(3)–Ni(5′)	2.516(1)	Average	2.51
Ni (surface)–Ni (interstitial)			
Ni(1)–Ni(6)	2.611(1)	Ni(4)–Ni(6)	2.585(1)
Ni(2)–Ni(6)	2.575(1)	Ni(5)–Ni(6)	2.586(1)
Ni(3)–Ni(6)	2.620(1)	Average	2.59
Other distances			
Ni(1)–C(1)	1.742(9)	Ni(5)–C(6)	1.85(1)
Ni(1)–C(7)	1.90(1)	Ni(5)–C(9)	2.14(1)
Ni(1′)–C(8)	1.95(1)	C(1)–O(1)	1.16(1)
Ni(2)–C(2)	1.73(1)	C(2)–O(2)	1.15(1)
Ni(2′)–C(9)	1.86(1)	C(3)–O(3)	1.16(1)
Ni(3)–C(3)	1.74(1)	C(4)–O(4)	1.13(1)
Ni(3′)–C(6)	1.95(1)	C(5)–O(5)	1.14(1)
Ni(3′)–C(7)	1.88(1)	C(6)–O(6)	1.19(1)
Ni(4)–C(4)	1.75(1)	C(7)–O(7)	1.17(1)
Ni(4)–C(8)	1.87(1)	C(8)–O(8)	1.17(1)
Ni(4)–C(9)	2.16(1)	C(9)–O(9)	1.17(1)
Ni(5)–C(5)	1.73(1)	N(1)–C(10)	1.52(1)
Cation			
N–C Average	1.51(1)	C–C Average	1.49(1)
Bi–Ni(1)–C(1)	85.0(3)	Ni(3)–C(3)–O(3)	177(1)
Bi–Ni(2)–C(2)	90.7(4)	Ni(4)–C(4)–O(4)	176(1)
Bi–Ni(3)–C(3)	84.8(4)	Ni(5)–C(5)–O(5)	176(1)
Bi–Ni(4)–C(4)	87.5(4)	Ni(5)–C(6)–O(6)	142(1)
Bi–Ni(5)–C(5)	87.0(4)	Ni(1)–C(7)–O(7)	137(1)
Ni(1)–C(1)–O(1)	176(1)	Ni(4)–C(8)–O(8)	142(1)
Ni(2)–C(2)–O(2)	176(1)		

$[Ni_{13}Sb_2(CO)_{24}]^{n-}$ system, which has been introduced for comparison. It is worthy of note that a related failure in the synthesis of non-centred icosahedral $[Ni_{10}(BiR)_2(CO)_{18}]^{2-}$, corresponding to the known $[Ni_{10}(SbR)_2(CO)_{18}]^{2-}$, has been reported.[11]

The Molecular Structure of $[Ni_{11}Bi_2(CO)_{18}]^{3-}$ *as its* $[NEt_4]^+$ *Salt*.—The unit cell contains four cluster trianions sitting around inversion centres, eight cations in general positions and four around two-fold axes; the independent part of the structural pattern is half of the formula unit. A view of the anion is shown in Fig. 4(*a*) and relevant bond values are listed in Table 1. The $Ni_{11}Bi_2$ polyhedron is similar to that in the analogous antimony derivatives, *i.e.* a nickel-centred $Ni_{10}Bi_2$ triangulated polyhedron very close to the icosahedron in which the Bi atoms occupy opposite vertices. The idealized symmetry of the metal atom cluster is D_{5d} and therefore it is better described as a bicapped pentagonal antiprism. The distinctive feature of the present anion is the lack of outer groups bonded to the Bi atoms.

The eighteen CO ligands are co-ordinated to the Ni atoms in a variety of geometries, ten linearly, one per surface nickel atom, and eight bridging in the equatorial region of the cluster [Fig.

4(*b*)]. Two ligands cap opposite faces (and are contained in an idealized mirror plane), and the remaining six span the interbasal edges other than those belonging to the capped faces. The basal edges of the Ni_{10} prism do not support ligands.

The idealized symmetry of the anion as a whole is C_{2h} but only the inversion centre is retained in the crystal. The ligand arrangement realizes three connections for all the nickel atoms but two [Ni(2) and Ni(2′)]. Nevertheless an even distribution of charge among the metal atoms is obtained by a stronger Ni(2′)–μ_3-C(9) interaction [1.86 against 2.15 Å (average) for Ni(4,5)–μ_3-C(9)]. A slightly different mechanism of charge equalization operates in the antimony analogues[2] in which four face-bridging ligands are found which allow three connections for all the nickel atoms. These differences in ligand geometries are more apparent than real because they can interconvert by slight rotations of the bridging ligands, as surely they do when not in the solid state. Therefore, the geometries observed in the crystals can be considered instantaneous images of a roundabout fluxionality of all the bridging ligands along the equator of the metal atom polyhedron.

The average bond distances in the metal atom core are reported in Table 2 together with corresponding values in related polyhedra. The Ni–Ni distances belong to three different sets under D_{5d} symmetry, *i.e.* ten pentagonal edges (2.810 Å), ten inter-pentagonal edges (2.506 Å) and ten centre–surface distances (2.595 Å, Table 1). These figures are substantially equivalent (on average 0.02 Å longer) to the corresponding values in the $Ni_{11}Sb_2$ trianion. The two kinds of nickel–bismuth distances exhibit distinctly different values; the ten Ni–Bi distances on the polyhedron surface average 2.819 Å, while the centre–surface distance is only 2.507(1) Å. The corresponding Ni–Sb values are as expected some 0.09 Å shorter. The deviation of the metal atom core from the icosahedral geometry consists in a compression along the Bi–Ni–Bi′ axis accompanied by lengthening of the Ni–Ni pentagonal edges. Two factors contribute to this effect: (*i*) the localization of all the bridging ligands in the interbasal region which causes shortening of the implied Ni–Ni distances; (*ii*) the polarization of the interaction among the interstitial and surface atoms towards the more electronegative Bi heteroatoms. The consistence of the latter factor can be checked in the antimony analogues where the Sb–$Ni(CO)_3$ distance [2.539(1) Å in the trianion] can be assumed as a reference value for the Sb–Ni interaction. The significantly shorter Sb–$Ni_{interstitial}$ distance [2.403(1) Å] is a strong indication of localization of the centre–surface interactions towards the heteroatoms in the $Ni_{11}E_2$ polyhedra (E = Sb or Bi). It should be noted that an even more significant compression is present in the $Ni_{10}E_2$ polyhedra[11] (E = P, As or Sb) in which the absence of the interstitial atom eliminates the just described bond polarization effect, but at the same time permits some degree of inward collapsing of the heteroatoms. On extending the comparison to the nickel icosahedra $[Ni_{12}E(CO)_{22}]^{2-}$ (E = Ge or Sn),[13] in which the heteroatom is now in the cavity, one would expect greater regularity in the metal atom core. Instead the icosahedral symmetry is removed in these species as well, this time by some stretching of the metal atom polyhedron along one of the five-fold axes. Completing this survey of the icosahedral clusters, in both $[Rh_{12}Sb(CO)_{27}]^{3-}$ (ref. 14) and $[Au_{13}(PMe_2Ph)_{10}Cl_2]^{3+}$ (ref. 15), one finds that the metal atom cores exhibit extensive deviations from icosahedral symmetry. In conclusion no regular icosahedral metal atom cluster has yet been found, not even in the case of like atoms at the polyhedron vertices. One could explain this in terms of lower symmetry of the bonding interactions of the ligands in combination with some steric pressure on the part of the interstitial atom. However, it is true that polyhedra based on close packings of atoms deviate much less from their idealized symmetries, even though the surface ligands conform to lower symmetries. In $[PtRh_{12}(CO)_{24}]^{4-}$,[16] for example, in which the ligands exhibit a C_{3v} arrangement on the anticuboctahedral metal core, the edges free from bridging ligands do not show elongations comparable to those seen in icosahedral polyhedra. At this point one might suspect that the degree of degeneracy of the frontier orbitals of the icosahedral cage plays a role and induces ligand stereogeometries of low symmetry in order to split the degenerate levels. Molecular orbital calculations, which could help in explaining these experimental findings, are in progress.

Finally, the isolation of a $[Ni_{11}Bi_2(CO)_{18}]^{3-}$ molecular ion, almost identical to the $[Ni_{11}Sb_2(CO)_{18}]^{n-}$ moiety found in the $[Ni_{13}Sb_2(CO)_{24}]^{n-}$ (*n* = 2–4) clusters, provides further support to the conclusions drawn by EHMO calculations on $[Ni_{11}As_2(CO)_{18}]^{n-}$ model compounds, and confirms that clusters interstitially lodging a late-transition metal may accommodate up to ten electrons in excess due to the progressive deepening of the d orbitals of the latter.[1,2]

Experimental

All reactions including sample manipulations were carried out with standard Schlenk techniques under nitrogen in dried solvents. The $[Ni_6(CO)_{12}]^{2-}$ salts were prepared according to literature methods,[17] and analyses performed as previously described.[18] Infrared spectra were recorded on a Perkin-Elmer 257 grating spectrophotometer using CaF_2 cells, proton NMR spectra on a Bruker WP-200 spectrometer. Materials and apparatus for the electrochemical and ESR measurements (dpph = diphenylpicrylhydrazyl) have been described elsewhere.[19] Potential values are referred to the saturated calomel electrode. Under the present experimental conditions the ferrocenium–ferrocene couple is located at + 0.38 V in acetonitrile solution and + 0.54 V in thf solution.

Synthesis of $[NEt_4]_3[Ni_{11}Bi_2(CO)_{18}]$.—A solution of $BiCl_3$ (0.51 g, 1.55 mmol) in thf (20 cm^3) was added in portions (2 cm^3) to a stirred solution of $[NEt_4]_2[Ni_6(CO)_{12}]$ (2.2 g, 2.32 mmol) in thf (20 cm^3) over 2 h. The resulting brown suspension was filtered. The precipitate was washed several times with water and extracted with several portions of thf (60 cm^3 in 10 portions) to obtain a brown solution containing a mixture of $[Ni_{11}Bi_2(CO)_{18}]^{2-}$ and $[Ni_{11}Bi_2(CO)_{18}]^{3-}$ anions. The volume of the solution was reduced to *ca.* 30 cm^3 by evaporation under vacuum and $[Ni_{11}Bi_2(CO)_{18}]^{2-}$ reduced to $[Ni_{11}Bi_2(CO)_{18}]^{3-}$ by addition of a thf solution of sodium diphenylketyl (0.5 mol dm^{-3}) in portions while monitoring by IR spectroscopy. The resulting brown solution was evaporated to dryness under vacuum and the residue washed with toluene and suspended in methanol. The precipitation of $[NEt_4]_3[Ni_{11}Bi_2(CO)_{18}]$ was completed by addition of an excess of solid NEt_4Cl and water. After filtration, the solid material was dissolved in acetone (20 cm^3) and precipitated by slow diffusion of isopropyl alcohol (40 cm^3) to give 0.57 g of well shaped black crystals of $[NEt_4]_3[Ni_{11}Bi_2(CO)_{18}]$. These are soluble in acetone and acetonitrile, less soluble in thf and insoluble in non-polar solvents {Found: Ni, 32.1; NEt_4^+, 19.4. Calc. for $[NEt_4]_3[Ni_{11}Bi_2(CO)_{18}]$: Ni, 32.50; NEt_4^+, 19.65%}.

The corresponding salt $[NBu_4]_3[Ni_{11}Bi_2(CO)_{18}]$ was similarly obtained starting from $[NBu_4]_2[Ni_6(CO)_{12}]$.

Synthesis of $[NEt_4]_2[Ni_{11}Bi_2(CO)_{18}]$.—Starting from $[NEt_4]_2[Ni_6(CO)_{12}]$ (2.71 g) a procedure completely identical to the above was followed up to the brown suspension. This was filtered and the precipitate was washed with water and then extracted with acetone (30 cm^3) to obtain a brown solution containing a mixture of the $[Ni_{11}Bi_2(CO)_{18}]^{2-}$ and $[Ni_{11}Bi_2(CO)_{18}]^{3-}$ anions. The latter was converted into the former by addition of a few drops of a dilute solution of H_3PO_4 (48%) in acetone, while monitoring by IR spectroscopy. The resulting brown solution, only showing infrared carbonyl absorptions of $[Ni_{11}Bi_2(CO)_{18}]^{2-}$, was concentrated to *ca.* 20 cm^3 and by slow diffusion of isopropyl alcohol (40 cm^3) gave 0.54 g of well shaped black crystals of $[NEt_4]_2[Ni_{11}Bi_2(CO)_{18}]$. These are

Table 2 Average bond distances (Å) in the icosahedral nickel carbonyl clusters

Cluster core	Ref.	Ni–Ni			Ni–E		E···E[a]	Ni···Ni
Nickel-centred $Ni_{11}E_2$ and non-centred $Ni_{10}E_2$								
		Intrapentagonal	Interpentagonal	Inner–outer	Inner	Outer		
$Ni_{11}Bi_2$		2.810	2.506	2.595	2.507	2.819	5.014	5.19
$Ni_{11}Sb_2$[b]	2	2.780	2.519	2.578	2.403	2.737	4.806	5.16
$Ni_{10}Sb_2$	11	2.78	2.50			2.55	3.905	5.15
E-centred $Ni_{12}E$								
				$Ni–Ni_{cap}$	E–Ni	$E–Ni_{cap}$		
$Ni_{12}Ge$	12	2.553	2.791	2.622	2.493	2.691	5.38	4.98
$Ni_{12}Sn$	12	2.606	2.956	2.641	2.575	2.745	5.49	5.15
$Ni_{10}Ge$	12	2.548	2.721		2.470			4.94

[a] E–E represents the distance between the heteroatoms in the first data set and the related Ni–Ni distance in the second data set. [b] Only the data relative to the trianion are reported.

Table 3 Crystal data and experimental details for $[NEt_4]_3[Ni_{11}Bi_2(CO)_{18}]$

Formula	$C_{42}H_{60}Bi_2N_3Ni_{11}O_{18}$
Crystal size/mm	0.23 × 0.31 × 0.39
System	Orthorhombic
Space group	*Pccn*
a/Å	14.573(2)
b/Å	19.638(4)
c/Å	21.248(3)
U/Å^3	6080.7
Z	4
D_c/g cm^{-3}	2.14
$F(000)$	3803
μ(Mo-Kα)/cm^{-1}	88.20
Scan mode	ω–2θ
θ limits/°	2–25
ω Scan width/°	0.8 + 0.35 tanθ
Prescan rate/° min^{-1}	10
Prescan acceptance $\sigma(I)/I$	0.5
Required $\sigma(I)/I$	0.01
Maximum scan time/s	100
Standard reflections	Three remeasured periodically; no decay
Reflections collected	6583
Unique observed reflections (N_{obs}) $[F_o > 4\sigma(F_o)]$	3813
No. of refined parameters (N_{par})	351
R, R'	0.0501, 0.0514
Quality-of-fit indicator	1.31

$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R' = \Sigma||F_o| - |F_c||w^{\frac{1}{2}}/\Sigma|F_o|w^{\frac{1}{2}}$, quality-of-fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{par})]^{\frac{1}{2}}$, $w = K/[\sigma^2(F) + |g|F^2]$ where $K = 1.3$ and $g = 0.0024$.

Table 4 Fractional atomic coordinates for $[NEt_4]_3[Ni_{11}Bi_2(CO)_{18}]$

Atom	x	y	z
Bi	0.143 28(3)	−0.058 53(2)	−0.036 53(2)
Ni(1)	0.142 42(10)	0.080 67(8)	0.001 59(7)
Ni(2)	0.056 41(11)	0.039 43(8)	−0.108 92(6)
Ni(3)	−0.031 11(10)	−0.086 06(7)	−0.091 77(6)
Ni(4)	0.010 04(10)	−0.125 47(7)	0.036 21(6)
Ni(5)	0.111 90(10)	−0.027 15(8)	0.091 09(6)
Ni(6)	0.000 00	0.000 00	0.000 00
C(1)	0.260 3(6)	0.077 3(7)	−0.011 9(6)
O(1)	0.339 1(7)	0.075 6(7)	−0.017 1(7)
C(2)	0.133 1(8)	0.025 7(6)	−0.169 9(5)
O(2)	0.179 5(9)	0.014 9(6)	−0.212 8(5)
C(3)	0.028 5(8)	−0.145 5(6)	−0.137 1(6)
O(3)	0.064 5(8)	−0.185 5(5)	−0.168 7(5)
C(4)	0.075 7(11)	−0.199 5(5)	0.028 1(6)
O(4)	0.113 2(9)	−0.249 8(6)	0.022 2(7)
C(5)	0.222 3(7)	−0.056 0(7)	0.105 5(6)
O(5)	0.296 5(8)	−0.071 5(7)	0.115 9(7)
C(6)	0.091 1(11)	0.032 1(7)	0.157 1(5)
O(6)	0.107 7(11)	0.040 5(6)	0.211 2(5)
C(7)	0.137 3(9)	0.137 3(7)	0.074 1(7)
O(7)	0.181 4(8)	0.181 2(6)	0.096 3(6)
C(8)	−0.108 7(9)	−0.154 6(7)	0.055 1(6)
O(8)	−0.149 0(7)	−0.199 0(6)	0.079 7(6)
C(9)	0.029 0(9)	−0.103 7(7)	0.135 2(6)
O(9)	0.047 3(7)	−0.142 1(5)	0.175 2(4)
N(1)	0.281 3(8)	0.7500	0.2500
N(2)	0.045 2(7)	0.388 3(5)	0.126 0(4)
C(10)	0.340 3(8)	0.686 4(5)	0.252 2(6)
C(11)	0.413 3(9)	0.686 3(7)	0.301 9(6)
C(12)	0.224 0(8)	0.748 2(7)	0.191 2(5)
C(13)	0.169 7(9)	0.684 1(8)	0.181 0(7)
C(14)	0.024 7(15)	0.458 3(7)	0.099 0(7)
C(15)	0.024 2(15)	0.517 7(7)	0.143 3(8)
C(16)	−0.021 0(10)	0.370 4(10)	0.178 5(6)
C(17)	−0.120 6(11)	0.376 2(13)	0.161 9(10)
C(18)	0.140 8(9)	0.390 7(10)	0.154 0(7)
C(19)	0.172 2(15)	0.327 0(10)	0.183 1(10)
C(20)	0.037 1(12)	0.336 4(8)	0.075 1(6)
C(21)	0.098 3(15)	0.341 8(11)	0.019 2(8)

well soluble in acetone and acetonitrile, less soluble in thf and insoluble in non-polar solvents {Found: Ni, 34.3; NEt_4^+, 14.3. Calc. for $[NEt_4]_2[Ni_{11}Bi_2(CO)_{18}]$: Ni, 34.80; NEt_4^+, 14.00%}.

Attempted Preparation of $[Ni_{11}Bi_2(CO)_{18}]^{4-}$.—The salt $[NEt_4]_3[Ni_{11}Bi_2(CO)_{18}]$ (0.21 g) was dissolved in $P(NMe_2)_3O$ (10 cm^3) and treated with 1.2 equivalents of sodium. Infrared monitoring showed a *ca.* 40 cm^{-1} shift of the carbonyl absorptions to lower wavenumbers due to quantitative formation of $[Ni_{11}Bi_2(CO)_{18}]^{4-}$. Addition of a water solution of NEt_4Cl (1 g in 50 cm^3) gave a waxy solid which was separated by decantation and dried. Extraction with acetonitrile afforded a brown solution of the starting material.

X-Ray Data Collection and Structure Determination.—Crystal data and details of the data collection for the anion $[Ni_{11}Bi_2(CO)_{18}]^{3-}$ as its $[NEt_4]^+$ salt are given in Table 3. The diffraction experiments were carried out at room temperature on a fully automated Enraf-Nonius CAD-4 diffractometer using a crystal mounted on a glass fibre. Graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å) was used. The unit cell was determined from 25 randomly selected strong reflections by using automatic search, indexing and least-squares routines. Data were corrected for Lorentz polarization effects. Empirical absorption corrections were applied by using the Walker and Stuart method.[20] All calculations were performed using the SHELX 76 system of programs.[21] The metal atom positions were determined by direct methods and all non-hydrogen atoms located from Fourier difference syntheses. The structure was refined by full-matrix least-squares calculations in the space group *Pncc* (non-standard setting of *Pccn*, no. 56). Hydrogen atoms were added in calculated positions (d_{CH} = 1.08 Å) and their positions were not refined but continuously updated with respect to their carbon atoms. The final refinement of all positional and thermal parameters proceeded using anisotropic thermal parameters. The final Fourier difference map showed peaks not exceeding 1.1 e Å^{-3}. Final fractional coordinates for the non-hydrogen atoms are presented in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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