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A high-nuclearity Ni–Sb carbonyl cluster displaying unprecedented metal stereochemistries: synthesis and X-ray structure of $[NEt_4]_6[Ni_{31}Sb_4(CO)_{40}]\cdot 2\ Me_2CO$

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The mild oxidation of $[NEt_4]_2[Ni_{15}Sb(CO)_{24}]$ in acetone solution with $SbCl_3$ in a *ca.* 3 : 1 molar ratio leads to the new high-nuclearity $[Ni_{31}Sb_4(CO)_{40}]^{6-}$ hexaanion, which displays two interstitial Ni and four semi-interstitial Sb atoms with unprecedented stereochemistries.

Several low-nuclearity Ni–Sb carbonyl clusters have been reported.[1–4] All adopt an icosahedral geometry which can be Sb-centred, *viz.* $[Ni_{15}(\mu_{12}\text{-}Sb)(CO)_{24}]^{2-}$ $\mathbf{1}^{2-}$,[1] or Ni-centred, *viz.* $[Ni_{10}Sb_2(\mu_{12}\text{-}Ni)(CO)_{18}]^{n-}$ $\mathbf{2}^{n-}$,[1] and $[Ni_{10}(Sb \rightarrow Ni(CO)_3)_2(\mu_{12}\text{-}Ni)(CO)_{18}]^{n-}$ $\mathbf{3}^{n-}$, (n = 2–4),[2,3] as well as non-centred, *e.g.* $[Ni_{10}(SbR)_2(CO)_{18}]^{2-}$ $\mathbf{4}^{2-}$, (R = alkyl or aryl substituent).[4] Notably, only the Ni-centred $\mathbf{2}^{n-}$ and $\mathbf{3}^{n-}$ species are multivalent and display three stable oxidation states.[1–6] It has been later shown that the presence of interstitial or highly connected nickel or platinum atoms triggers multivalence in several carbonyl metal clusters.[5,6] Icosahedral species such as $\mathbf{1}^{2-}$, $\mathbf{2}^{n-}$ and $\mathbf{3}^{n-}$ are potential building blocks of poly-icosahedral *supra*-clusters,[7] related to $[Ag_{12}Au_{13}(PPh_3)_{10}Br_8]^-$,[8,9] $Ag_{20}Au_{18}[P(C_6H_4Me)_3]_{12}Cl_{14}$,[10] or $Pd_{59}(CO)_{32}(PMe_3)_{21}$.[11] The above consideration, as well as our interest in redox-active[5,6] and paramagnetic metal carbonyl clusters,[12] led us to investigate the chemical behaviour of $\mathbf{1}^{2-}$, $\mathbf{2}^{n-}$ and $\mathbf{3}^{n-}$ with the aim to synthesise polyicosahedral Ni–Sb carbonyl clusters of higher nuclearity. We now report our first result consisting in the synthesis and structural characterisation of the $[Ni_{31}Sb_4(CO)_{40}]^{6-}$ $\mathbf{5}^{6-}$, hexaanion, which displays unprecedented stereochemical features.

The $\mathbf{5}^{6-}$ salts were spectroscopically detected among the by-products of the synthesis of $\mathbf{1}^{2-}$ by reaction of $[Ni_6(CO)_{12}]^{2-}$ with $SbCl_3$. The best synthesis of $\mathbf{5}^{6-}$ consists in the mild oxidation of $[NEt_4]_2\mathbf{1}$ in acetone solution with $SbCl_3$ in a *ca.* 3:1 molar ratio. $[NEt_4]_6\mathbf{5}\cdot 2\ Me_2CO$ [ν_{CO} in acetonitrile at 2040vw, 2001s, 1980(sh), 1894m, 1861m, 1846m and 1812(sh) cm^{-1}; no hydride signal in the ^1H NMR spectrum in the range δ +25 to −50; diamagnetic] separates out from the reaction solution on standing as well shaped black crystals (yields up to 30% based on Sb) and has been characterised by X-ray diffraction studies.† The by-products of the above reaction are $[Ni(CO)_3Cl]^-$, $Ni(CO)_4$ and $[NEt_4]_3$ **3**. As shown by separated experiments, a mixture of $Ni(CO)_4$ and $[NEt_4]_3$ **3** also results from degradation of $\mathbf{5}^{6-}$ salts under a carbon monoxide atmosphere.

The overall structure of $\mathbf{5}^{6-}$ is shown in Fig. 1 and a formal reconstruction of its metal framework is given in Fig. 2(a). The central $Ni_{19}Sb_4$ moiety of the metal frame is based on two interpenetrating Ni-centred $Ni_{11}Sb_3(\mu_{14}\text{-}Ni)$ 14-hedron displaying a distorted bicapped hexagonal antiprismatic geometry. One of the two 14-hedrons has been emphasised out with filled in bonds; its idealised C_6 axis is almost orthogonal to the plane of the paper and the in-plane idealised C_6 axis of the other moiety. Each of the two 14-coordinated nickel atoms behaves at the same time as an interstitial atom of one unit and as an *ortho* atom of the Ni_5Sb hexagonal ring of the second unit. The second hexagonal ring of the above 14-hedra displays a *para*-Sb_2Ni_4 geometry. The major deviation of the centred $Ni_{11}Sb_3(\mu_{14}\text{-}Ni)$ 14-hedron from the idealised bicapped hexagonal antiprism is due to departure from the mid-point of the Sb–Sb diagonal of the Ni atoms capping the Ni_4Sb_2 hexa-rings. These caps become closer to one of the two pairs of nickel atoms and show Ni···Ni contacts with the second pair which are beyond the usually accepted limit for a Ni–Ni bond [3.350(2) and 3.426(2) Å].

The metal framework of $\mathbf{5}^{6-}$ is completed by condensing two Ni_6 moieties [Ni–Ni range 2.373(2)–2.944(2) Å], displaying a polytetrahedral metal arrangement having the architecture of the $Os_6(CO)_{18}$ prototype,[13,14] on two opposite sides of the central $Ni_{19}Sb_4$ kernel. These Ni_6 moieties bind to the two Sb and surrounding Ni atoms through their butterfly face. As

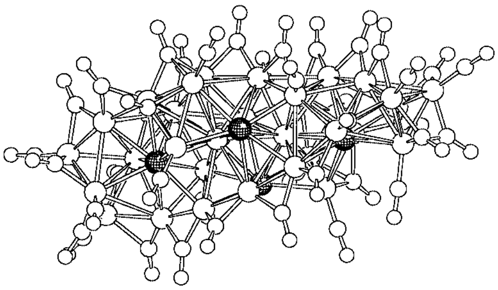

Fig. 1 The molecular structure of the $[Ni_{31}Sb_4(CO)_{12}(\mu\text{-}CO)_{24}(\mu_3\text{-}CO)_4]^{6-}$ $\mathbf{5}^{6-}$ ion. The Ni–Ni and Ni–Sb bonding interactions are spread over the ranges 2.357(1)–3.090(1) and 2.496(1)–2.782(1) Å respectively.

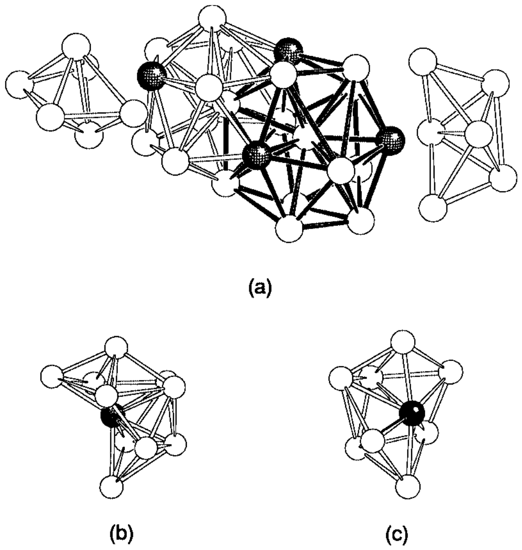

Fig. 2 Formal reconstruction of the metal framework of $\mathbf{5}^{6-}$ with omission of the bonds between the two outer Ni_6 moieties with the central $Ni_{19}Sb_4$ kernel (a) and the two coordination stereogeometries shown by the Sb atoms [(b) and (c)].

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pointed out in Fig. 2(b) and (c), the four Sb atoms display two pairs of different stereogeometries, being semi-interstitially lodged in Ni_{10} and Ni_8 incomplete icosahedral moieties, which are related to the $[B_{10}H_{14}]^{2-}$ and B_8H_{14} *arachno*-boranes, respectively.[15,16] Semi-interstitial lodging of Sb atoms in a nickel cluster is not surprising because it has been shown that a Sb atom is oversized for a Ni_{12} icosahedral cage.[1] In contrast, the coordination of the two interstitial nickel atoms is more unexpected and unprecedented in molecular clusters. A metal coordination number of 14 has been found in intermetallic phases such as the Ni–V σ and Ni–Mo δ phases.[15] These alloys also involve 12-coordinated sites of icosahedral geometry, as partially displayed by $\mathbf{5}^{6-}$, as well as 15- and 16-coordinated sites. Besides, these intermetallic phases show a tendency to segregate the bulkiest metal atoms in the highest coordinated sites (14–16), while the other metal atoms occupy the 12- and 14-coordinated sites.[15] In this regard, an ideal 14-hedron having a bicapped hexagonal antiprismatic geometry provides two 6-fold vertices and the interstice as the most suitable sites for the bulkiest Sb atoms of a centred $Ni_{12}Sb_3$ moiety. Therefore, centring of the above by the least bulky nickel atom and segregation of Sb in the two hexagonal rings may appear odd. However, the segregation observed in $\mathbf{5}^{6-}$ could probably be due to its molecular nature and the need to accommodate the carbonyl ligand shell. The forty carbonyl ligands can be approximately classified as terminal (12), edge-bridging (24) and face-bridging (4).

In conclusion, the condensation of $\mathbf{1}^{2-}$ into $\mathbf{5}^{6-}$ does not lead to polyicosahedral *supra*-clusters, as for the Ag–Au system.[7–10] An alternative and unprecedented growth pathway has been observed, which shows that high nuclearity nickel carbonyl clusters can be stabilised not only by interstitially lodging small main group elements such as carbon, *e.g.* $[Ni_{32}C_6(CO)_{36}]^{6-}$ and $[Ni_{38}C_6(CO)_{42}]^{6-}$,[17] but also bulkier atoms such as antimony. Studies of the chemical and physical behaviour of $\mathbf{5}^{6-}$ are underway.

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Notes and references

† *Crystal data* for $[NEt_4]_6[Ni_{31}Sb_4(CO)_{40}]\cdot 2Me_2CO$: M = 4325, monoclinic, space group $P2_1/n$, a = 20.9876(6), b = 14.6084(4), c = 44.1418(11) Å, β = 93.707(1)°, U = 13505.4(6) Å^3, T = 298 K, Z = 4, μ(Mo-Kα) = 50.59 cm^{-1}, 94623 reflections measured, 23779 unique (R_{int} = 0.0492) which were used in all calculations. The final $wR2$ was 0.1166 [$I > 2\sigma(I)$]. CCDC 182/1573. See http://www.rsc.org/suppdata/cc/b0/b000783h/ for crystallographic files in .cif format.

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