

Synthesis and X-Ray Structure of the $[\text{Ni}_{13}\text{Sb}_2(\text{CO})_{24}]^{n-}$ ($n = 2,3,4$) Cluster Anions containing an Icosahedral $[\text{Ni}_{11}\text{Sb}_2(\text{CO})_{18}]^{n-}$ Moiety behaving as a Distibine Ligand and displaying an Unexpected Electron Count

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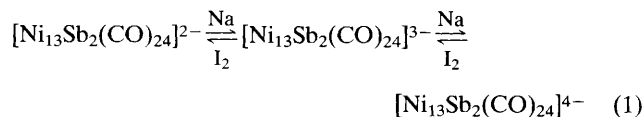
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The new $[\text{Ni}_{13}\text{Sb}_2(\text{CO})_{24}]^{n-}$ ($n = 2,3,4$) cluster anions have been isolated from the reaction of $[\text{Ni}_6(\text{CO})_{12}]^{2-}$ with SbCl_3 ; their structures ($n = 2,3$) have been elucidated by X-ray diffraction studies and consist of Ni-centred icosahedral $[\text{Ni}_{11}\text{Sb}_2(\text{CO})_{18}]^{n-}$ moieties which display an unexpected electron count and formally behave as 'exotic' distibine bridging ligands.

Several examples of carbonyl metal clusters possessing an icosahedral framework are already known and they are either non-centred {e.g., $[\text{Ni}_{10}(\mu_5\text{-ER})_2(\text{CO})_{18}]^{2-}$ ($\text{E} = \text{P}, \text{As}, \text{Sb}; \text{R} = \text{Me}, \text{Ph}$)}^{1,2} or encapsulate a non-transition element {e.g., $[\text{Rh}_{12}\text{Sb}(\text{CO})_{27}]^{3-}$ and $[\text{Ni}_{12}\text{E}(\text{CO})_{22}]^{2-}$ ($\text{E} = \text{Ge}, \text{Sn}$)}.^{3,4} We report here the synthesis and characterization of a series of new Ni-Sb carbonyl clusters of general formula $[\text{Ni}_{13}\text{Sb}_2(\text{CO})_{24}]^{n-}$ ($n = 2,3,4$), which represent the first examples of icosahedral carbonyl clusters containing a transition metal as the interstitial atom: these consist of Ni-centred icosahedral $[\text{Ni}_{11}\text{Sb}_2(\text{CO})_{18}]^{n-}$ cluster moieties, which show a puzzling electron count and behave as 'exotic' distibine ligands by co-ordinating two $\text{Ni}(\text{CO})_3$ fragments. The $[\text{Ni}_{13}\text{Sb}_2(\text{CO})_{24}]^{n-}$ ($n = 2,3,4$) clusters have been obtained by addition of SbCl_3 to a tetrahydrofuran (THF) solution of $[\text{Ni}_6(\text{CO})_{12}]^{2-}$ in up to a ca. 0.5 : 1 molar ratio, as a mixture with other yet unidentified products. After evaporation of the reaction solvent, the residue was extracted with acetone and reacted with carbon monoxide (1 atm) to obtain a mixture of the $[\text{Ni}_{13}\text{Sb}_2(\text{CO})_{24}]^{n-}$ ($n = 3,4$) anions; the components of the series have been synthesized selectively from the above mixture according to the interconversion reactions (1), for instance.



The tetra-anion is unstable and only the salts of the tri- and di-anion could be isolated in a crystalline state.† Crystals of

† IR ν_{CO} (cm^{-1}) in THF for $[\text{Ni}_{13}\text{Sb}_2(\text{CO})_{24}]^{4-}$: 2035s, 1980s, 1970s, sh, 1775m, br., and 1730sh; $[\text{Ni}_{13}\text{Sb}_2(\text{CO})_{24}]^{3-}$: 2042s, 2000s, sh, 1990s, 1810m, br., and 1760sh; $[\text{Ni}_{13}\text{Sb}_2(\text{CO})_{24}]^{2-}$: 2060s, 2030s, sh, 2020s, 1845m, br., and 1805sh.

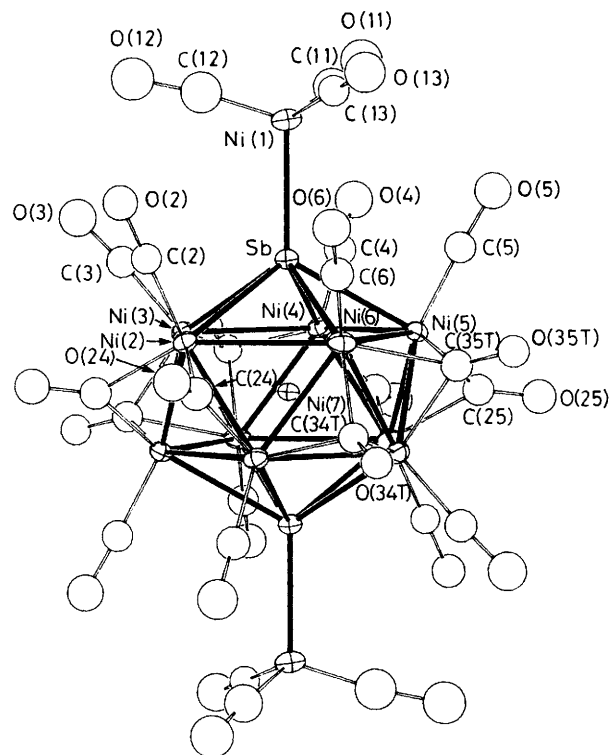


Figure 1. ORTEP drawing of the $[\text{Ni}_{13}\text{Sb}_2(\text{CO})_{24}]^{2-}$ dianion. Important bond lengths (\AA) in the dianion and trianion [in square brackets] are: Sb-Ni(1) 2.522(1) [2.539(1)], Sb-Ni(2,3,4,5,6)_{av.} 2.730 [2.738], Sb-Ni(7) 2.399(1) [2.403(1)], Ni-Ni_{intrapentagonal} 2.673(1)—2.870(1) [2.698(1)—2.857(1)], Ni-Ni_{interpentagonal} 2.394(1)—2.585(1) [2.420(1)—2.558(1)], Ni(7)—Ni(2,3,4,5,6) 2.560(1)—2.581(1) [2.403(1)—2.593(1)].

$[N(PPh_3)_2]_2[Ni_{13}Sb_2(CO)_{24}]$ and $[NMe_3CH_2Ph]_4[Ni_{13}Sb_2(CO)_{24}]\cdot[Cl]$ have been grown by slow diffusion of propan-2-ol and di-isopropyl ether, respectively, into acetone and acetonitrile solutions of the appropriate cluster salt, and their crystal structures have been determined by X-ray diffraction analysis.‡

The geometries of the $[Ni_{13}Sb_2(CO)_{24}]^{2-}$ and $[Ni_{13}Sb_2(CO)_{24}]^{3-}$ anions are very similar and only the ORTEP drawing of the former is reported in Figure 1, together with the most significant parameters of both compounds. The anions have crystallographically imposed C_i and idealized C_{2h} symmetry. They consist of a central $Ni_{10}Sb_2(\mu_{12}-Ni)(CO)_{10}(\mu-CO)_4(\mu_3-CO)_4$ icosahedral moiety with the two antimony atoms lying on opposite vertices of the icosahedron; moreover, each antimony atom binds a dangling $Ni(CO)_3$ fragment. The eight bridging carbonyl groups are distributed in alternating pairs of doubly and triply bridging ligands on adjacent interpentagonal edges and faces, respectively. The nickel atoms of the two dangling $Ni(CO)_3$ fragments require donation of an electron pair by the antimony atom in order to attain the effective atomic number. Therefore, the central $[Ni_{11}Sb_2(CO)_{18}]^{n-}$ cluster unit can be considered as a distibine bridging cluster-ligand. Related complexes featuring tetra-co-ordinate main group elements are known,⁵ e.g., $[Fe_5Sb_2(CO)_{17}]^{2-}$,⁶ whereas the $Fe_3(CO)_9(\mu_3-E)_2$ ($E = As, Bi$)^{7,8} derivative containing trico-ordinate heteroatoms can be seen as examples of free cluster-ligands.

The Ni-centred icosahedral $[Ni_{11}Sb_2(CO)_{18}]^{n-}$ moieties, contained in the $[Ni_{13}Sb_2(CO)_{24}]^{n-}$ ($n = 2, 3, 4$) clusters, respectively possess 4 and 5 extra filled cluster valence orbitals (CVO) with respect to the non-centred $[Ni_{10}(\mu_5-ER)_2(CO)_{18}]^{2-}$ ($E = As, Sb; R = Me, Ph$),^{1,2} whereas the E-centred $[Ni_{12}E(CO)_{22}]^{2-}$ ($E = Ge, Sn$)⁴ and $[Rh_{12}Sb(CO)_{27}]^{3-}$ (ref. 3) would be isoelectronic with the former or the latter, whether or not the inner d electrons of E are considered.§ The assumption that interstitial atoms can be

considered as 'internal ligands' contributing cluster valence electrons (CVE) but not altering the number of filled CVO,⁹ seems questionable unless the interstitial nickel atom is considered to have an inert d^{10} configuration and, consequently, it only contributes s-p valence orbitals and no electrons. A possible rationalization of the electron count of $[Ni_{11}Sb_2(CO)_{18}]^{n-}$ lies in the failure of an over-generalized assumption of strong interactions between the orbitals of the interstitial atom and the cluster cage, affording an even number of occupied bonding and unoccupied antibonding orbitals, which leaves the CVO number unchanged. From a perturbational point of view, strong interactions are due to large overlap integrals and small energy separations between the interacting orbitals; with the parameters normally used in EHMO computations the d orbitals of Ge, Sn, As, and Sb belong to the core, and those of Ni are still too contracted and low in energy to afford five high-energy antibonding orbitals. A direct EHMO computation on $[Ni_{11}Sb_2(CO)_{18}]^{n-}$ shows good HOMO – LUMO gaps only in correspondence with $n = 4$ (-10.73 vs. -9.87 eV), that is 90 CVO, and $n = 2$ (-11.15 vs. -10.73 eV), that is 89 CVO, in agreement with our experimental data.

A further hint that tridecanuclear clusters could accommodate more electrons than expected is also provided by an investigation of the reaction of a quadrupole mass selected beam of the Ni_{13}^+ cluster with carbon monoxide: in this experiment, in addition to the expected $[Ni_{13}(CO)_{20}]^+$ species, evidence of the presence of the more electron-rich $[Ni_{13}(CO)_x]^+$ ($x = 21, 22$) has been observed.¹⁰

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‡ Crystal data for $[N(PPh_3)_2]_2[Ni_{13}Sb_2(CO)_{24}]$: $C_{96}H_{60}N_2Ni_{13}O_{24}P_4Sb_2$, $M = 2756.17$, triclinic, space group $P\bar{1}$, $a = 13.134(3)$, $b = 13.546(2)$, $c = 15.416(2)$ Å, $\alpha = 109.54(1)$, $\beta = 91.47(2)$, $\gamma = 101.68(1)^\circ$, $U = 2518$ Å³, $Z = 1$, $D_c = 1.817$ g cm⁻³, $F(000) = 1368$, $\mu(Mo-K\alpha) = 30.44$ cm⁻¹. Final R and R_w are 0.036 and 0.050, for 2135 absorption-corrected reflections having $I \geq 3\sigma(I)$. For $[NMe_3CH_2Ph]_4[Ni_{13}Sb_2(CO)_{24}]\cdot[Cl]$: $C_{64}H_{64}ClN_4Ni_{13}O_{24}Sb_2$, $M = 2315.42$, monoclinic, space group $C2/c$, $a = 20.615(4)$, $b = 15.508(3)$, $c = 25.805(19)$ Å, $\beta = 99.21(4)^\circ$, $U = 8143$ Å³, $Z = 4$, $D_c = 1.888$ g cm⁻³, $F(000) = 4604$, $\mu(Mo-K\alpha) = 37.04$ cm⁻¹. Final R and R_w are 0.039 and 0.048 respectively, for 3610 absorption-corrected reflections having $I \geq 3\sigma(I)$. The structures have been solved by standard Patterson and difference Fourier methods and refined by full-matrix least-squares with anisotropic temperature factors for all the atoms of the anionic moieties. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Data Centre. See Notice to Authors, Issue No. 1.

§ It is worth noting that on formal consideration of the inner d electrons of the heteroatoms E (interstitial or surfacial) all the above centred-icosahedral clusters are isoelectronic, whereas the non-centred ones have a lower electron count.

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