

A New Family of Metal-centred and Noncentred Icosahedral Cages with Transition Metal and Main Group VI Atoms: Synthesis and Structural-bonding Analysis of the Nickel-centred $[\text{Ni}_{11}\text{Se}_2(\text{CO})_{18}]^{2-}$, Nickel-centred $[\text{Ni}_{10}\text{Te}_3(\text{CO})_{15}]^{2-}$ and Noncentred $[\text{Ni}_8\text{Te}_4(\text{CO})_{12}]^{2-}$ Icosahedral Dianions

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Three new dianions possessing Ni-centred $\text{Ni}_{10}\text{Se}_2$ **1**, Ni-centred Ni_9Te_3 **2** and noncentred Ni_8Te_4 **3** cages were synthesized and crystallographically characterized; a structural-bonding analysis indicates that the extra ten cluster valence electrons (CVEs) arising in **1** and **2** from the filled 3d atomic orbitals (AOs) of the centred interstitial Ni(i) atom occupy antibonding radial Ni(i)-cage molecular orbitals (MOs) (in violation of current electron-counting rules) such that the icosahedral frameworks of **1**, **2** and **3** possess the expected 13 skeletal electron pairs.

Work from our laboratories has shown that the icosahedron is a dominant polyhedron for nickel carbonyl clusters containing main group atoms. Initial studies have produced a large transition metal-group V family of clusters with noncentred icosahedral $\text{Ni}_{12-x}\text{E}_x$ cages—*viz.* Ni_{10}P_2 , Ni_9P_3 , Ni_8P_4 ,¹ $\text{Ni}_{10}\text{As}_2$, Ni_9As_3 ² and $\text{Ni}_{10}\text{Sb}_2$.³ Extended investigations with main group IV reagents have given rise to clusters with Ni-centred Ni_{10}E_2 icosahedral cages (E = Sn,⁴ Ge⁵). Complementary work by Longoni and coworkers^{6–8} has resulted in several important related clusters including $[\text{Ni}_{12}\text{E}(\text{CO})_{22}]^{2-}$

(E = Sn, Ge)⁷ with E-centred Ni_{12} icosahedral cages and the recently isolated $[\text{Ni}_{11}(\text{SbNi}(\text{CO})_3)_2(\text{CO})_{18}]^{n-}$ anions ($n = 2, 3, 4$)⁸ which contain Ni-centred $\text{Ni}_{10}\text{Sb}_2$ cages.

Here we report the first successful incorporation of transition metal and main group VI atoms into nonboron-containing icosahedral cages. Reactions of the $[\text{Ni}_6(\text{CO})_{12}]^{2-}$ dianion⁹ with chalcogen main group reagents result in the formation of $[\text{Ni}_{11}\text{Se}_2(\text{CO})_{18}]^{2-}$ **1**, $[\text{Ni}_{10}\text{Te}_3(\text{CO})_{15}]^{2-}$ **2** and $[\text{Ni}_8\text{Te}_4(\text{CO})_{12}]^{2-}$ **3** with Ni-centred 1,12- $\text{Ni}_{10}\text{Se}_2$, Ni-centred 1,2,12- Ni_9Te_3 and noncentred 1,2,11,12- Ni_8Te_4 icosahedral

cages, respectively (Figs. 1 and 2).^{†,‡} The metal-centred M_9E_3 icosahedral cage in **2** is unprecedented. This new family of icosahedral clusters highlights geometrical effects related to the presence or absence of the centred interstitial Ni(i) atom and thereby furnishes further insight into the subtle bonding nature of the Ni(i) to the cage surface Ni(s) and main group cage E(s) atoms in two different types of $Ni_{12-x}E_x$ cages ($x = 2$, E = Se **1**; $x = 3$, E = Te **2**).

A comparison of the Ni-centred 1,12- $Ni_{10}Se_2$ cage in the 160-electron **1** with the similar-sized empty 1,12- $Ni_{10}As_2$ cage in the 150-electron $[Ni_{10}(AsMe)_2(CO)_{18}]^{2-}$ **4** [*i.e.*, covalent radii are nearly identical for Ni (1.20 Å), As (1.20 Å) and Se (1.16 Å)¹⁰] indicates that the formal addition of a d^{10} Ni(i) into the $Ni_{10}E_2$ cage (with concomitant transmutation of two AsR fragments into two isolobal¹¹ Se atoms) causes a 0.68 Å elongation of the markedly compressed icosahedral cage along the principal fivefold $E \cdots E'$ axis together with an increase of the mean Ni(s)-E distance by 0.18 Å; this cage-enlargement in **1** relative to **4** results in two short identical Ni(i)-Se distances of 2.19 Å, which indicate strong radial bonding interactions. Of significance is that the accompanying increases in the mean radial inversion centre-Ni(s), intrapentagonal Ni(s)-Ni(s') and interpentagonal Ni(s)-Ni(s') distances of 0.05, 0.05 and 0.03 Å, respectively, are relatively small. These geometrical differences parallel those between the Ni-centred $Ni_{10}Sn_2$ cages in the 158-electron $[Ni_{11}(SnR)_2(CO)_{18}]^{2-}$ (R = Buⁿ **5**, Me **6**) and the similar-sized noncentred $Ni_{10}Sb_2$ cage in the 150-electron $[Ni_{10}(SbPh)_2(CO)_{18}]^{2-}$. From bonding considerations discussed elsewhere for the $[Ni_{11}(SbNi(CO)_3)_2(CO)_{18}]^{n-}$ anions ($n = 2, 3, 4$)⁸ and for **5**, **6**,⁴ it follows that the 160-electron **1** provides further persuasive support that current electron-counting rules¹² do not work in general when applied to icosahedral cage clusters containing interstitial Ni(i) atoms.

[†] *Synthesis*: Preparation of $[Ni_{11}Se_2(CO)_{18}]^{2-}$ **1** as the $[PPh_3Me]^+$ salt: PhSeCl (0.20 g, 1.04 mmol) in 50 ml of tetrahydrofuran (THF) was added dropwise at ambient temperature under N_2 to $[PPh_3Me]_2[Ni_6(CO)_{12}]^{2-}$ (0.65 g, 0.52 mmol) in THF (150 ml). After being stirred for 2 h, the red solution was concentrated by a N_2 stream and then loaded onto a silica gel column. Compound **1** (20% yield) was eluted with THF as the fourth band; dark-brown crystals were grown from a layering of diisopropyl ether over a concentrated solution of **1** in THF. IR (THF) ν/cm^{-1} : 2004(s), 1840(m); cyclic voltammetry (THF): at least one quasi-reversible oxidation and reduction. Preparation of $[Ni_{10}Te_3(CO)_{15}]^{2-}$ **2** and $[Ni_8Te_4(CO)_{12}]^{2-}$ **3** as $[PPh_3Me]^+$ salts: Te_2Ph_2 (0.24 g, 0.59 mmol) in THF (50 ml) was added dropwise at ambient temperature under N_2 to $[PPh_3Me]_2[Ni_6(CO)_{12}]^{2-}$ (0.72 g, 0.58 mmol) in THF (200 ml). After being stirred for 3 h, the solution was concentrated by a N_2 stream and loaded onto a silica gel column; elution with THF gave **3** (15% yield) as the third band and **2** (25% yield) as the fifth band. Deep-red crystals of **3** and dark-greenish-brown crystals of **2** were obtained from a layering of diisopropyl ether over concentrated solutions of **2** and **3** in THF. IR (THF) ν/cm^{-1} of **2**: 1975(s), 1770(m). IR (THF) ν/cm^{-1} of **3**: 1991(s), 1818(m, br).

[‡] *Crystal data*: Crystal structures were determined and refined by use of SHELXTL PLUS. X-Ray data were obtained at the indicated temperatures *via* a Siemens diffractometer with Mo-K α radiation. For $[PPh_3Me]_2[Ni_{11}Se_2(CO)_{18}]^{2-}$: $M = 1862.3$, triclinic, $P\bar{1}$; $a = 10.317(3)$, $b = 11.870(6)$, $c = 12.621(5)$ Å, $\alpha = 88.33(7)$, $\beta = 76.02(5)$, $\gamma = 84.60(4)^\circ$, $V = 1493.1(3)$ Å³; $Z = 1$. $R(F) = 6.09\%$, $R_w(F) = 4.50\%$ for 3487 absorption-corrected reflections ($T = -100^\circ C$). For $[PPh_3Me]_2[Ni_{10}Te_3(CO)_{15}]^{2-}$: $M = 1944.5$, monoclinic, $P2_1/n$; $a = 17.513(6)$, $b = 17.442(9)$, $c = 19.125(5)$ Å, $\beta = 95.20(3)^\circ$, $V = 5817.8(4)$ Å³; $Z = 4$. $R(F) = 6.32\%$, $R_w(F) = 5.83\%$ for 3232 independent absorption-corrected reflections ($T = -100^\circ C$). For $[PPh_3Me]_2[Ni_8Te_4(CO)_{12}]^{2-} \cdot 2C_4H_8O$: $M = 2014.9$, triclinic, $P\bar{1}$, $a = 9.144(4)$, $b = 13.160(3)$, $c = 15.575(6)$ Å, $\alpha = 113.12(4)$, $\beta = 101.96(5)$, $\gamma = 95.02(4)^\circ$, $V = 1656.3(6)$ Å³; $Z = 1$. $R(F) = 5.08\%$, $R_w(F) = 4.51\%$ for 4428 absorption-correction reflections ($T = 17^\circ C$). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

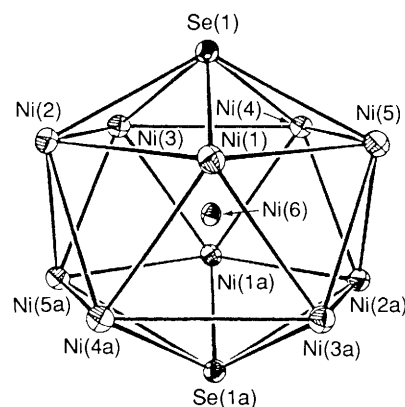


Fig. 1 Configuration of the Ni(i) centred 1,12- $Ni_{10}Se_2$ icosahedral cage in $[Ni_{11}Se_2(CO)_{18}]^{2-}$ **1** of crystallographic C_{2v} and pseudo D_{5h} symmetry. This Se,Se-bicapped pentagonal antiprism of 10 surface Ni(s) with an interstitial Ni(i) has the following mean distances (Å) (where the number of averaged distances is denoted within square brackets): Ni(i)-Se, [2] 2.19; Ni(i)-Ni(s), [10] 2.55; Ni(s)-Se, [10] 2.61; intrapentagonal Ni(s)-Ni(s'), [10] 2.74; interpentagonal Ni(s)-Ni(s'), [10] 2.52.

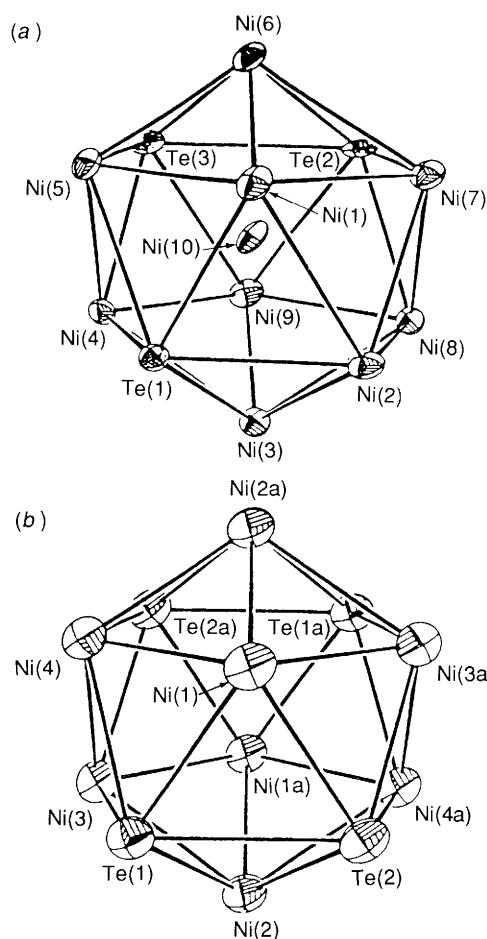


Fig. 2 Configurations of (a) the Ni-centred 1,2,12- Ni_6Te_3 icosahedral cage in $[Ni_{10}Te_3(CO)_{15}]^{2-}$ **2** of crystallographic C_{2v} and pseudo C_{2v} symmetry [with the mirror plane passing through Te(1), Te(2), Te(3), Ni(2) and Ni(10)]; and (b) the noncentred 1,2,11,12- Ni_8Te_4 icosahedral cage in $[Ni_8Te_4(CO)_{12}]^{2-}$ **3** of crystallographic C_{2v} and pseudo D_{2h} symmetry. The Ni(i)-centred Ni(s)₆Te(s)₃ cage of **2** has the following mean distances (Å): centrosymmetrically related Te(1)-Te(2), 4.87; adjacent Te(2)-Te(3), 3.13; Ni(i)-Te(*n*), 2.49, 2.39, 2.56 for $n = 1, 2, 3$ (mean, 2.48 Å); Ni(i)-Ni(s), [9] 2.59; Ni(s)-Te(s), [13] 2.71; Ni(s)-Ni(s'), [16] 2.65. The empty Ni(s)₈Te(s)₄ cage of **3** has the following mean distances (Å): centrosymmetrically related Ni(s)-Ni(s'), [4] 4.94 and Te(s)-Te(s'), [2] 5.02; adjacent Te(s)-Te(s'), [2] 2.88; Ni(s)-Te(s), [16] 2.61; Ni(s)-Ni(s'), [12] 2.58.

Fig. 2 shows that the formal interconversion of **3** into **2** is a two-step process involving (i) a replacement of the Te(2) atom of the empty 1,2,11,12-Ni₈Te₄ cage in **3** with the Ni(2) atom [as an isolobal Ni(CO)₃ fragment] to give a 1,2,12-Ni₉Te₃ cage in an electronically equivalent but still unknown cluster; and (ii) the addition of a d¹⁰ Ni(i) into the cage. Two striking bonding implications which emanate from a geometrical examination of **2** and **3** are: (i) In **2** the mean of 2.48 Å for the three radial Ni(i)-Te(s) distances in the Ni(i)-centred Ni₉Te₃ cage is considerably shorter than the mean of 2.71 Å for the Ni(s)-Te(s) cage distances. That the mean radial Ni(i)-Te(s) distance is also 0.11 Å smaller than the mean radial Ni(i)-Ni(s) distance of 2.59 Å in **2** is consistent with the premise that radial Ni(s)-Te(s) bonding interactions predominate over Ni(i)-Ni(s) bonding interactions. (ii) The mean bonding Te(s)-Te(s'), Ni(s)-Te(s) and Ni(s)-Ni(s') cage distances in **2** (3.13, 2.71 and 2.65 Å) are significantly longer than the corresponding ones in **3** (2.88, 2.61 and 2.58 Å). These bond-length differences are entirely consistent with the radial Ni(i)-cage bonding interactions in **2** producing markedly weaker tangential cage bonding interactions in **2** relative to those in the noncentred **3**.

We conclude that the interstitial Ni(i) in **2** as well as in **1** contributes its empty 4s, 4p atomic orbitals (AOs) but not its filled core-like 3d AOs in stabilizing the Ni₁₀E₂ and Ni₉E₃ cages by preferential radial bonding interactions with the main group E(s) atoms. These radial bonding interactions involving the interstitial Ni(i) provide increased stabilization of an icosahedral cage but are accompanied by decreased tangential cage bonding interactions. This model, in which the extra ten cluster valence electrons (CVEs) arising in **1** or **2** from the 3d¹⁰ Ni(i) are accommodated in five antibonding radial Ni(i)-cage cluster valence orbitals (CVOs), results in the modified electron-counting view that the icosahedral cage frameworks in **1**, **2** and **3** possess the expected 13 skeletal electron pairs. §

§ Note added in proof: the dark brown Ni-centred Ni₁₀Te₂ [Ni₁₁Te₂(CO)₁₈]²⁻, which is isostructural with **1**, has been synthesized and characterized (X-ray diffraction; IR spectroscopy) as the [PPh₃Me]⁺ salt from the reaction of [PPh₃Me]⁺₂[Ni₆(CO)₁₂]²⁻ with Et₃PTe.

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