

ARTICLE

[Ni₃₀S₁₆(PEt₃)₁₁]: An Open-shell Nickel Sulfide Nanocluster with a “Metal-like” Core

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Reaction of [Ni(1,5-cod)₂] (30 equiv) with PEt₃ (46 equiv) and S₈ (1.9 equiv) in toluene, followed by heating at 115 °C for 16 h, results in formation of the atomically precise nanocluster (APNC), [Ni₃₀S₁₆(PEt₃)₁₁] (**1**), in 14% isolated yield. Complex **1** represents the largest open shell Ni APNC yet isolated. In the solid state, **1** features a compact “metal-like” core indicative of a high degree of Ni-Ni bonding. Additionally, SQUID magnetometry suggests that **1** possesses a manifold of closely-spaced electronic states near the HOMO-LUMO gap. *In situ* monitoring by ESI-MS and ³¹P{¹H} NMR spectroscopy reveal that **1** forms via the intermediacy of smaller APNCs, including [Ni₈S₅(PEt₃)₇] and [Ni₂₆S₁₄(PEt₃)₁₀] (**2**). The latter APNC was also characterized by X-ray crystallography and features a nearly identical core structure as found in **1**. This work demonstrates that large APNCs with a high degree of metal-metal bonding are isolable for nickel, and not just the noble metals.

Introduction

Atomically-precise nanoclusters (APNCs) are an emerging class of materials that feature properties found in both metal complexes and bulk metal.¹ Unlike traditional nanoparticles, APNCs are perfectly mono-disperse and feature a well-defined arrangement of their capping ligands.^{2, 3} This high level of chemical precision makes them attractive for a variety of applications,⁴ including catalysis,⁵⁻⁷ sensing,⁸ and imaging.^{8, 9} Magnetic APNCs, in particular, have been touted as alternatives to larger ferromagnetic nanoparticles for use in existing technologies, like magnetic data storage,¹⁰ and frontier technologies, like quantum computing.^{11, 12} However, very little APNC research has focused on ferromagnetic metals, such as Fe, Co, and Ni, and so these applications have yet to be realized. Indeed, the vast majority of APNC work has focused on the group 11 metals, which tend to generate diamagnetic APNCs.^{5, 13}

Nonetheless, some past work has shown that open-shell APNCs of Ni are isolable.¹⁴ For example, [Ni₉Te₆(PEt₃)₈], first reported in 1989,¹⁵ features an $S = 2$ ground state.¹⁶⁻¹⁸ Similarly, the mixed-metal cluster [NBu₄]₄[Ni₁₆Pd₁₆(CO)₄₀], features a $J = 2$ ground state.¹⁹ In addition, we recently reported the isolation of [Ni₂₃Se₁₂Cl₃(PEt₃)₁₀],²⁰⁻²² which features an $S = 3/2$ ground state according to an Evans' method determination. Also notable are calculations of [Ni₄₄(CO)₄₈]^{6, 23-25} which predict an open shell ground state. Notably, the unpaired electron density in [Ni₄₄(CO)₄₈]⁶ was calculated to reside exclusively on the six

core Ni atoms, which exhibit fcc-type packing. Intriguingly, [Ni₂₃Se₁₂Cl₃(PEt₃)₁₀] also features fcc packing of its central Ni₁₃ core.^{20, 21} While its electronic structure is not entirely understood, we propose that its paramagnetism is related to this metal-like core structure. Moreover, we hypothesize that larger nickel chalcogenide APNCs will feature greater structural similarity to bulk Ni, potentially resulting in the emergence of superparamagnetic or ferromagnetic behaviour. The resulting APNCs would be potentially useful in a number of magnetic applications.^{12, 26}

In an effort to test this hypothesis, we endeavoured to synthesize and characterize even larger open-shell Ni APNCs. Herein, we report the largest open shell Ni APNC yet known, namely, [Ni₃₀S₁₆(PEt₃)₁₁] (**1**). X-ray crystallography reveals a compact “metal-like” core indicating a high degree of Ni-Ni bonding. Additionally, SQUID magnetometry shows that **1** possesses an open shell ground state.

Results and Discussion

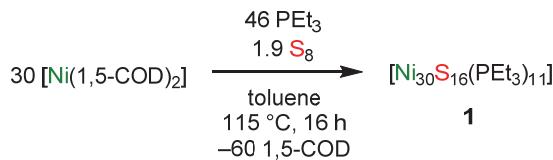
Previous attempts by our research group to form large Ni APNCs demonstrated that low-valent Ni nanoclusters are incompatible with Ph₃P, which is too easily reduced.²⁷ Additionally, past work by Jin and co-workers has shown that NaBH₄ cannot reduce Ni²⁺ salts to Ni(0).²⁸⁻³⁰ Given these considerations, we chose PEt₃ as our supporting ligand and [Ni(1,5-cod)₂] as our Ni source. Thus, heating a mixture of [Ni(1,5-cod)₂] (30 equiv), PEt₃ (46 equiv), and S₈ (1.9 equiv) in toluene at 115 °C for 16 h generated a deep brown solution. Work-up of the reaction mixture afforded [Ni₃₀S₁₆(PEt₃)₁₁] (**1**) as a black crystalline solid in 14% yield (Scheme 1). Air-sensitive **1** is soluble in toluene, benzene, and THF, very sparingly soluble in hexanes, pentane, methylene chloride, diethyl ether, and 1,2-dimethoxyethane, and insoluble in acetonitrile. C₆D₆ solutions of **1** exhibit complete

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[†] Electronic supplementary information (ESI) available: Experimental procedures, crystallographic details (as CIF files), computational results, and spectral data for complexes **1**:Et₂O and **2**:C₆H₁₂. CCDC 2150613–2150614. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

decomposition upon exposure to air and water after 18 h (Figures S44-S45).

Curiously, the highest yields of **1** were achieved with an Ni:PEt₃ ratio of ca. 1:1.5. When the Ni:PEt₃ ratio was decreased to 3:1 (the rational stoichiometry, given the formula of **1**) the isolated yields were reduced substantially. Previous work by our group suggests that the first step in APNC formation involves formation of [Ni(1,5-cod)(PEt₃)₂] by ligand substitution.³⁰ Thus, we surmise that a large excess of PEt₃ is required to completely form [Ni(1,5-cod)(PEt₃)₂], which is much more thermally stable than [Ni(1,5-cod)₂], and subsequently functions as a better Ni(0) source at these elevated temperatures. However, the excess PEt₃ unavoidably sequesters some of the S₈ (see below), which likely contributes to the low isolated yield.



Single crystals of **1** were grown by slow evaporation of a cold (–25 °C) toluene/Et₂O solution over the course of three weeks. Complex **1** crystallizes in monoclinic space group *P*2₁/n, as the diethyl ether solvate, **1**·Et₂O (Fig. 1). The solid-state structure of **1** consists of a densely packed core with extensive Ni–Ni bonding. The core is anchored by two interpenetrating Ni₁₃ “kernels” (Fig. 1A–B). Curiously, neither kernel adopts the archetypal cuboctahedral (fcc) and anti-cuboctahedral (hcp) geometries observed for many Au APNCs.¹³ Instead, they adopt an irregular arrangement of their Ni atoms. The resulting Ni₂₁ polyhedron is capped by three “[cyclo-{Ni(μ-S)(PEt₃)₃}₃]” units (Fig. 1C–D). Two of these units are equivalent by symmetry. Similar “[cyclo-{Ni(μ-E)(PEt₃)₃}₃]” units are found in [Ni₂₃Se₁₂Cl₃(PEt₃)₁₀].²⁰ The addition of these three capping units brings the total metal nuclearity to 30 (Fig. 1E–F). Also appended to the Ni₂₁ polyhedron are two PEt₃ ligands (at Ni28 and Ni15), five μ₄-S²⁻ ligands, and two μ₅-S²⁻ ligands, giving this Ni₃₀ cluster an overall *C*₅ symmetric structure (Figures 1G–H, S46).

As a result of this arrangement, five Ni atoms (Ni1, Ni2, Ni3, Ni4, Ni5) feature coordination numbers of 11 or greater, and two Ni atoms are solely bonded to other Ni atoms (Ni1 and Ni3) (Figure S46). The high coordination numbers exhibited by these atoms is reminiscent of bulk Ni, which features coordination number of 12.^{31, 32} No other Ni APNC features comparable amounts of “metal-like” character. For comparison, only two other reported Ni nanoclusters feature compact “metal-like” cores, namely, [Ni₂₁Se₁₄(PEt₂Ph)₁₂] and [Ni₂₃Se₁₂Cl₃(PEt₃)₁₀], which each have just one fcc and hcp Ni₁₃ “kernel”, respectively.^{20, 33} This paucity of examples lies in stark contrast to the broad landscape of “metal-like” structures observed for Ag and Au. Indeed, over 250+ high-nuclearity, low-valent group 11 APNCs have been structurally characterized over the last 10 years.³⁴

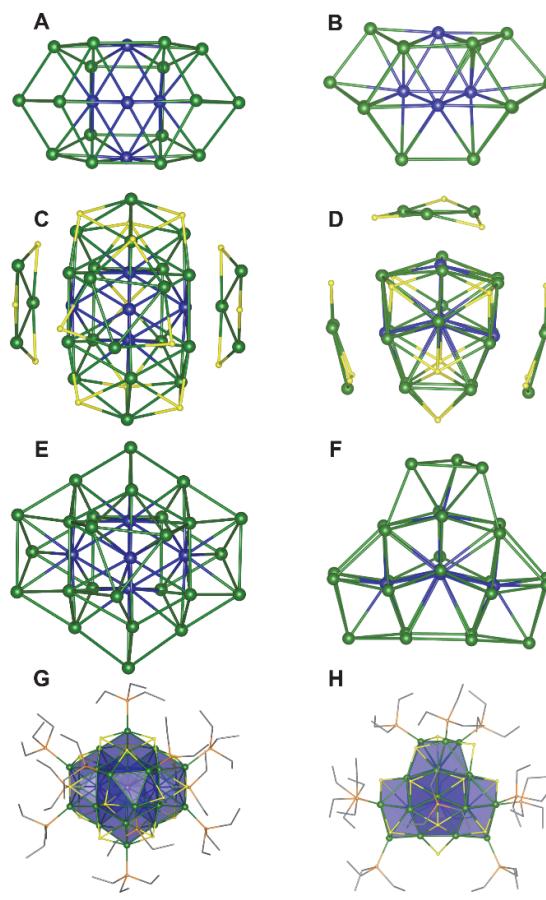


Fig. 1 Solid-state structure of [Ni₃₀S₁₆(PEt₃)₁₁]·Et₂O (**1**·Et₂O) from two different orientations. (A–B) Ni₂₁ core. (C–D) The three “[cyclo-{Ni(μ-S)}₃]” units attached to the Ni₂₁S₇ core. (E–F) Ni-only structure of **1**. (G–H) Full molecular structure. Color scheme: Ni_{shell}, green; Ni_{core}, blue; S, yellow; P, orange; C, grey. Carbon atoms are shown in wireframe. Diethyl ether solvate molecule and hydrogen atoms were omitted for clarity.

The 99 Ni–Ni distances in **1** span a large range (2.401(3) – 2.911(3) Å), which is typical of APNCs,^{7, 35} and the average Ni–Ni distance is 2.58 Å. A histogram of these distances (Fig. S1) shows the highest frequency from 2.40 and 2.55 Å, which compares well to the Ni–Ni distance in bulk Ni metal (2.49 Å).^{31, 32} The 68 Ni–S distances in **1** also span a large range (2.104(5) – 2.759(4) Å) with an average of 2.24 Å. A histogram of these distances (Fig. S2) shows the highest frequency between 2.20 Å and 2.25 Å. For comparison, the average Ni–S distances observed in [Ni₅S₂(SPh)₂(PEt₃)₅] and [Ni₅S₅(PEt₃)₇] are shorter (2.04 and 2.19 Å, respectively), perhaps reflecting the lower average coordination number of their S²⁻ ligands.³⁰ For further comparison, the average Ni–P distance in **1** is 2.18 Å, which is similar to Ni–P distances in [Ni₈S₅(PEt₃)₇], [Ni₂₁Se₁₄(PEt₂Ph)₁₂], and [Ni₂₃Se₁₂Cl₃(PEt₃)₁₀].^{20, 30, 33}

The average Ni oxidation state in **1** is 1.067, making it among the most reduced Ni chalcogenide cluster yet isolated, and highlighting its large “metal-like” character. For comparison,

$[\text{Ni}_{32}\text{S}_{24}(\text{PPh}_3)_{10}]$, $[\text{Ni}_8\text{S}_5(\text{PEt}_3)_7]$, $[\text{Ni}_{21}\text{Se}_{14}(\text{PEt}_2\text{Ph})_{12}]$, and $[\text{Ni}_{23}\text{Se}_{12}\text{Cl}_3(\text{PEt}_3)_{10}]$ have average oxidation states of 1.5, 1.25, 1.33, and 1.17, respectively.^{20, 30, 33, 38} Despite its low average oxidation state, the disparate coordination geometries of the interior Ni atoms vs. the surface Ni atoms in **1** suggest that the oxidation load is not distributed evenly over all 30 Ni atoms. In this regard, we hypothesize that the oxidation states of five interior Ni atoms approach 0, whereas the oxidation states of surface Ni atoms are closer to 2+.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1** in toluene- d_8 displays resonances at 30, 246, 842, and 2054 ppm, in a 4:2:3:2 ratio, respectively (Fig. 2A, S18–S20).³⁹ While these results confirm the presence of 11 PEt₃ ligands, they contrast with the pattern expected for a complex with C_s symmetry, which should feature seven peaks in a 1:1:1:2:2:2:2 ratio. To explain this discrepancy, we propose that the unique “[cyclo- $\{\text{Ni}(\mu\text{-S})(\text{PEt}_3)\}_3\}$ ” unit (comprised of Ni26, Ni29, and Ni30), can rotate with respect to the Ni₂₁ polyhedron, giving **1** an effective symmetry of C_{2v} . Cooling a sample of **1** in toluene- d_8 to $-25\text{ }^\circ\text{C}$ results in shifting of four PEt₃ resonances (Fig. S21–S23), but no decoalescence of these peaks was observed. However, plots of these shifts vs. T^{-1} are linear, demonstrating the Curie-Weiss behavior expected for a paramagnet (Fig. 2B, S24).⁴⁰ The electrospray ionization mass spectrum (ESI-MS) of **1**, recorded in THF in positive ion mode, features two major peaks at $3572.43\text{ }m/z$ and $1786.20\text{ }m/z$ (Fig. 2D, S26–S28), which correspond to $[\text{Ni}_{30}\text{S}_{16}(\text{PEt}_3)_{11}]^+$ (calcd 3572.57 m/z) and $[\text{Ni}_{30}\text{S}_{16}(\text{PEt}_3)_{11}]^{2+}$ (calcd 1787.30 m/z), respectively. Overall, these results further confirm our proposed formulation.

To further probe its magnetic properties, we measured the moment of **1** in solution via Evans' method and in the solid state via variable-temperature SQUID magnetometry. Complex **1** exhibits a magnetic moment of $2.70\text{ cm}^3\text{ K/mol}$ at 298 K in C_6D_6 .^{41, 42} In the solid state, its magnetic moment is $2.53\text{ cm}^3\text{ K/mol}$ at 300 K (Fig. 2C, S43). This value drops to $1.38\text{ cm}^3\text{ K/mol}$ on cooling to 100 K , briefly plateaus, then drops to $0.33\text{ cm}^3\text{ K/mol}$ at 2 K . These data are consistent with the field-induced mixing of a triplet ground state with a low-lying quintet excited state and can be rationalized by a manifold of closely-spaced electronic states near the HOMO-LUMO gap, as expected for an APNC with a high degree of metal-metal bonding. Additionally, zero-field-cooled (ZFC) and field-cooled (FC) magnetization vs. temperature curves indicate no magnetic blocking down to 1.8 K , while no hysteresis is seen when cycling magnetization vs. applied field (Fig. S42–S43).

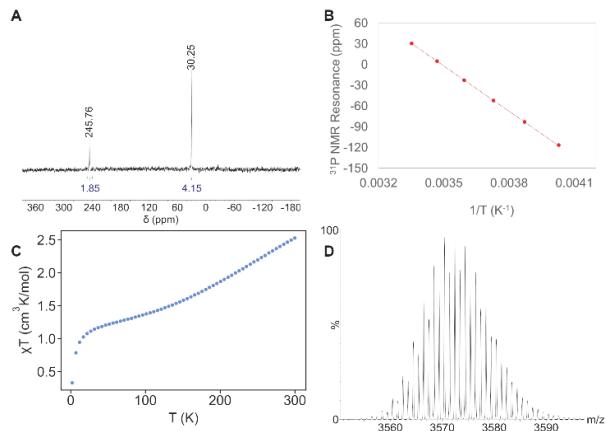


Fig. 2 Characterization data for **1**. (A) Partial $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **1** in toluene- d_8 . (B) A plot of $^{31}\text{P}\{^1\text{H}\}$ NMR chemical shift versus T^{-1} for the 30 ppm ($25\text{ }^\circ\text{C}$) resonance. (C) Variable temperature magnetic susceptibility (χT) for **1** collected at 10,000 Oe. (D) Partial ESI-MS mass spectrum of **1** in THF (capillary voltage of 2.50 kV, positive ion mode) showing a peak at $3572.43\text{ }m/z$ assignable to $[\text{Ni}_{30}\text{S}_{16}(\text{PEt}_3)_{11}]^+$ (calcd 3572.57 m/z).

To better understand its synthesis, we monitored the *in situ* formation of **1** by ESI-MS, as well as by $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectroscopies (Fig. S5–S15). A mass spectrum of a reaction aliquot, collected immediately after mixing the reagents, features a major peak at $1456.0\text{ }m/z$ that is assignable to $[\text{Ni}_8\text{S}_5(\text{PEt}_3)_7]^+$ (calcd 1455.9733 m/z).³⁰ A mass spectrum recorded after heating the reaction mixture to $115\text{ }^\circ\text{C}$ for 105 min also features the peak assignable to $[\text{Ni}_8\text{S}_5(\text{PEt}_3)_7]^+$. However, this spectrum features several additional peaks, which are assignable to $[\text{Ni}_{20}\text{S}_{12}(\text{PEt}_3)_7]^+$, $[\text{Ni}_{21}\text{S}_{14}(\text{PEt}_3)_7]^+$, $[\text{Ni}_{21}\text{S}_{14}(\text{PEt}_3)_8]^+$, $[\text{Ni}_{23}\text{S}_{14}(\text{PEt}_3)_9]^+$, $[\text{Ni}_{26}\text{S}_{14}(\text{PEt}_3)_{10}]^+ ([2]^+)$, and $[\text{Ni}_{30}\text{S}_{16}(\text{PEt}_3)_{11}]^+ ([1]^+)$. Heating of the reaction mixture for 17 h results in a sharp decrease of the peaks assignable to the Ni₈–Ni₂₆ clusters in the ESI-MS, leaving **1** as the major remaining high molecular weight material.⁴³ The *in situ* $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectra corroborate the reaction trajectory suggested by the ESI-MS data (Fig. S10–S15). The NMR spectra reveal that Et₃PS is also formed in the reaction. Overall, these data suggest that $[\text{Ni}_8\text{S}_5(\text{PEt}_3)_7]^+$, $[\text{Ni}_{20}\text{S}_{12}(\text{PEt}_3)_7]^+$, $[\text{Ni}_{21}\text{S}_{14}(\text{PEt}_3)_7]^+$, $[\text{Ni}_{21}\text{S}_{14}(\text{PEt}_3)_8]^+$, $[\text{Ni}_{23}\text{S}_{14}(\text{PEt}_3)_9]^+$, and $[\text{Ni}_{26}\text{S}_{14}(\text{PEt}_3)_{10}]^+$ are likely intermediates in the formation of **1**, and that cluster growth is promoted by longer reaction times and high temperatures. We next sought to isolate one of the intermediately-sized Ni nanoclusters that we observed in the *in situ* ESI mass spectra. To target these intermediates, we decreased the reaction temperature and shortened the reaction time. Thus, thermolysis of a mixture of $[\text{Ni}(1,5\text{-cod})_2]$ (30 equiv), PEt₃ (31 equiv), and S₈ (1.9 equiv) in toluene at $95\text{ }^\circ\text{C}$ for 5 h provided a complex mixture containing **1**, **2**, $[\text{Ni}_8\text{S}_5(\text{PEt}_3)_7]$, and Et₃PS, as assayed by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy (Fig. S37). Work-up of this mixture afforded relatively pure $[\text{Ni}_{26}\text{S}_{14}(\text{PEt}_3)_{10}]$ (**2**) in 5% yield via selective crystallization. However, the isolated material also contained a small amount of complex **1**, which precluded its complete characterization. Complex **2** is very soluble in tetrahydrofuran, toluene, and benzene, but is sparingly soluble in pentane, hexanes, and diethyl ether.

Single crystals of **2** were grown by slow evaporation of a cold (-25°C) toluene/pentane solution over the course of one week. They crystallizes in the monoclinic space group $P2_1/n$ as the pentane solvate, $\mathbf{2}\cdot\text{C}_5\text{H}_{12}$ (Figures 3, S47). The solid-state structure of **2** is remarkably similar to that of complex **1** and can be derived from that of **1** by removal of one “[cyclo- $\{\text{Ni}(\mu\text{-S})(\text{PEt}_3)\}_3$]” unit and substitution of Ni5 with a $\mu_6\text{-S}^2$ -ligand. The positions of the remaining Ni atoms are unchanged. Not surprisingly, then, the metrical parameters of **2** are similar to those of **1**. For example, the average Ni-Ni distance in **2** (2.56 \AA) is similar to that of **1**, and the values span a similar range ($2.399(6)\text{ \AA} - 2.889(7)\text{ \AA}$).

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2** in C_6D_6 features resonances at 5730, 912, 606, and 179 ppm (Fig. S35-S36). The latter three resonances are present in a 2:2:4 ratio. The number and intensities of the resonances are consistent with the C_{2v} symmetry observed in the solid state, while the large downfield chemical shifts are suggestive of a paramagnetic ground state. The ^1H NMR spectrum of **2** in C_6D_6 is also indicative of a paramagnetic cluster, as revealed by a resonance at 21.38 ppm that is assignable to a PEt_3 methylene environment (Fig. S30). Finally, the ESI-MS of **2** in THF (positive ion mode) features a major peak at $3155.05\text{ }m/z$ (Fig. S34), which corresponds to $[\text{Ni}_{26}\text{S}_{14}(\text{PEt}_3)_{10}]^+$ (calcd $3154.80\text{ }m/z$), further confirming our formulation.

Formally, conversion of **2** into **1** requires addition of 4 equiv of “Ni(0)”, 2 equiv of “S”, and 1 equiv of PEt_3 . Surprisingly, however, this change results in minimal rearrangement of the Ni_{26} core. The similarity of their structures supports our contention that **2** is an intermediate in the formation of **1**. Additionally, the similar core structures in **1** and **2** suggests that it is an especially stable fragment and may form a good “seed” for further cluster growth.

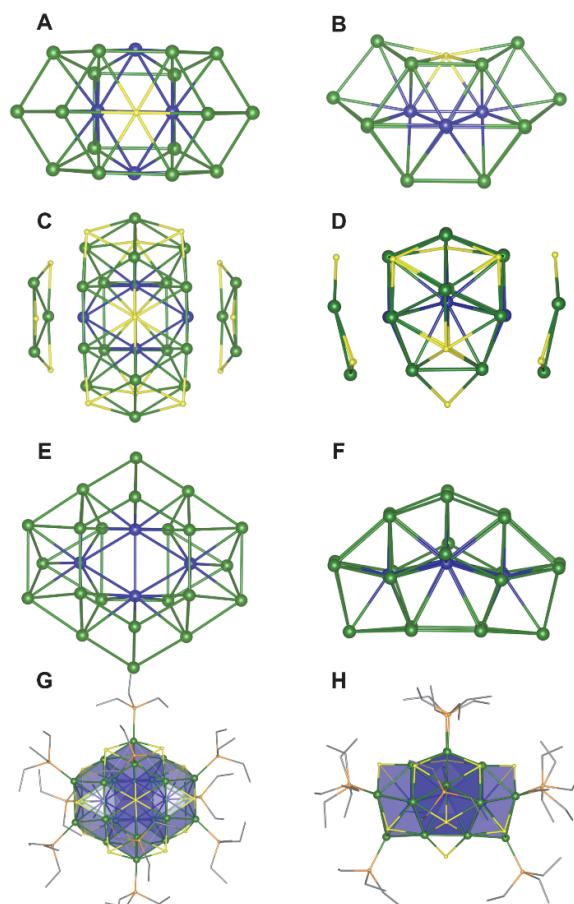


Fig. 3 Solid-state structure of $[\text{Ni}_{26}\text{S}_{14}(\text{PEt}_3)_{10}]\cdot\text{C}_5\text{H}_{12}$ ($2\cdot\text{C}_5\text{H}_{12}$) from two different orientations. (A-B) Ni_{26}S core. (C-D) The two “[cyclo- $\{\text{Ni}(\mu\text{-S})\}_3$]” units attached to the Ni_{26}S core. (E-F) Ni-only structure of **2**. (G-H) Full molecular structure. Color scheme: Ni_{shell}, green; Ni_{ore}, blue; S, yellow; P, orange; C, grey. Carbon atoms are shown in wireframe. Pentane solvate molecule and hydrogen atoms were omitted for clarity.

Conclusions

In summary, we have isolated the largest open-shell Ni chalcogenide APNC reported to date. X-ray crystallography reveals that this nanocluster contains a compact “metal-like” core that is unprecedented for the group 10 elements. Additionally, SQUID magnetometry measurements suggest a manifold of closely-spaced electronic states near the HOMO-LUMO gap, further corroborating the nanocluster’s “metal-like” nature. Importantly, this work shows that large APNCs with a high degree of metal-metal bonding are possible for nickel, and not just the noble metals, opening the door to the synthesis of a much more chemically diverse array of APNCs. These new group 10 APNCs offer promise for their unique, and potentially useful, magnetic properties.

Author Contributions

A. J. T. performed the synthesis and characterization. G. W. assisted with the crystallography. A. J. T. and T. W. H. jointly wrote the manuscript. T. W. H. secured funding for the research.

Data availability

All of the experimental data have been included in the ESI. Crystallographic data can be obtained from the CCDC (2150613 and 2150614).

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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