

**An Enneanuclear Nickel Sulphide with a Confacial Bi-octahedral Geometry:
X-Ray Crystal Structure of $[\text{Ni}_9(\mu_4\text{-S})_3(\mu_3\text{-S})_6(\text{PEt}_3)_6][\text{BPh}_4]_2$**

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Summary An X-ray analysis of $[\text{Ni}_9\text{S}_9(\text{PEt}_3)_6][\text{BPh}_4]_2$ shows that the nine nickel atoms in the $[\text{Ni}_9\text{S}_9(\text{PEt}_3)_6]^{2+}$ cluster lie in a confacial bi-octahedral arrangement and are held together by bridging sulphur atoms, while six phosphine groups complete the co-ordination around the nickel atoms.

ATOMIC sulphur has been found as a multiple-bridging ligand in several bi-, tri-, and tetra-nuclear transition-metal

complexes¹ and in some ternary metal chalcogenides.² We have prepared a nickel cluster containing nine metal atoms bridged by nine sulphur atoms and surrounded by six triethylphosphines. Black crystals of $[\text{Ni}_9\text{S}_9(\text{PEt}_3)_6][\text{BPh}_4]_2$ are obtained on bubbling H_2S through a solution of $\text{Ni}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$, NaBPh_4 , and an excess of PEt_3 in methylene dichloride-ethanol. Red crystals of the previously reported compound $[\text{Ni}_3\text{S}_2(\text{PEt}_3)_6][\text{BPh}_4]_2$,³ which were also formed, were separated by repeated recrystallizations from

methylene dichloride-ethanol solutions. The compound, obtained in a yield of *ca.* 20%, is air stable, diamagnetic, and soluble in all the common, polar organic solvents; it behaves as a 2:1 electrolyte in nitroethane solution. The ^{31}P n.m.r. spectrum of the compound in CDCl_3 solution at room temperature exhibits a singlet at -32.96 p.p.m. (H_3PO_4), indicative of six equivalent PET_3 groups.

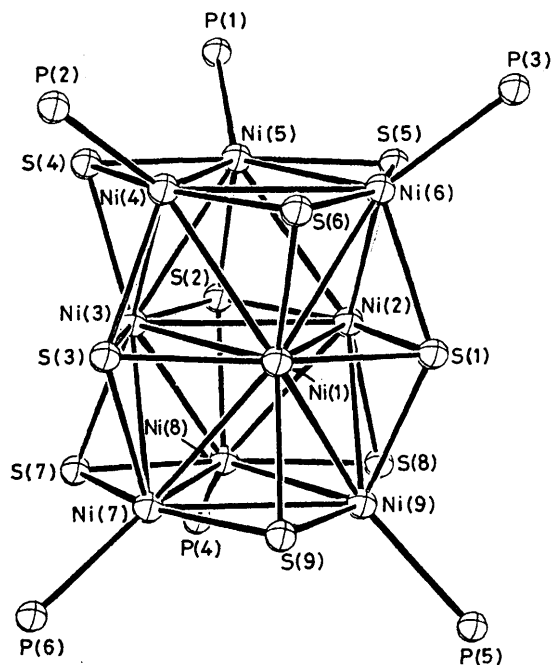


FIGURE. Inner core of $[\text{Ni}_9\text{S}_9(\text{PET}_3)_6]^{2+}$. Selected bond distances: Ni-Ni (1)-(2) 2.960(8), (1)-(3) 2.954(8), (1)-(4) 2.702(8), (1)-(6) 2.685(8), (1)-(7) 2.681(8), (1)-(9) 2.711(8), (2)-(3) 2.954(8), (2)-(5) 2.711(8), (2)-(6) 2.694(8), (2)-(8) 2.681(8), (2)-(9) 2.692(8), (3)-(4) 2.671(8), (3)-(5) 2.681(8), (3)-(7) 2.709(8), (3)-(8) 2.701(8), (4)-(5) 2.848(8), (4)-(6) 2.857(8), (5)-(6) 2.868(8), (7)-(8) 2.856(8), (7)-(9) 2.888(8), (8)-(9) 2.867(8); Ni-S (1)-(1) 2.20(1), (1)-(3) 2.19(1), (1)-(6) 2.23(1), (1)-(9) 2.22(1), (2)-(1) 2.19(1), (2)-(2) 2.21(1), (2)-(5) 2.23(1), (2)-(8) 2.20(1), (3)-(2) 2.20(1), (3)-(3) 2.20(1), (3)-(4) 2.23(1), (3)-(7) 2.22(1), (4)-(3) 2.27(1), (4)-(4) 2.15(1), (4)-(6) 2.16(1), (5)-(2) 2.27(1), (5)-(4) 2.16(1), (5)-(5) 2.17(1), (6)-(1) 2.24(1), (6)-(5) 2.14(1), (6)-(6) 2.16(1), (7)-(3) 2.25(1), (7)-(7) 2.15(1), (7)-(9) 2.13(1), (8)-(2) 2.26(1), (8)-(7) 2.14(1), (8)-(8) 2.16(1), (9)-(1) 2.26(1), (9)-(8) 2.14(1), (9)-(9) 2.17(1); Ni-P (4)-(2) 2.18(1), (5)-(1) 2.19(1), (6)-(3) 2.21(1), (7)-(6) 2.22(2), (8)-(4) 2.18(1), (9)-(5) 2.20(1).

Crystal data: $\text{C}_{34}\text{H}_{130}\text{B}_2\text{Ni}_9\text{P}_6\text{S}_9$, $M = 2164.4$, monoclinic, space group $P2_1/a$, $a = 19.784(4)$, $b = 34.159(8)$, $c = 14.595(4)$ Å, $\beta = 92.41(5)^\circ$, $U = 9854.6$ Å 3 , $Z = 4$, $D_m =$

1.44, $D_c = 1.458$ g cm $^{-3}$, $\mu(\text{Mo-K}\alpha) = 20.07$ cm $^{-1}$. Intensity data were collected on a Philips computer-controlled PW 1100 diffractometer using the ω - 2θ scan technique and graphite-monochromatized Mo- $K\alpha$ radiation. The structure was solved by heavy-atom techniques. Several Fourier maps were necessary to locate the carbon atoms of the ethyl chains which are affected by disorder. The phenyl rings of the two tetraphenylborate anions were treated as rigid groups. The hydrogen atoms were not included. Full-matrix least-squares refinement converged at R and R_w values of 0.074 and 0.068, respectively, for the 2246 reflections ($2\theta \leq 40^\circ$) with $I \geq 3\sigma(I)$.†

The structure of the complex consists of discrete $[\text{Ni}_9\text{S}_9(\text{PET}_3)_6]^{2+}$ cations and BPh_4^- anions. The Figure shows a perspective view of the inner core of the cation. The enneanickel dication has no crystallographic symmetry; however, the inner core may be considered to possess idealized D_{3h} symmetry. The nine nickel atoms lie at the vertices of an ideal confacial biotetrahedron. The octahedron faces which are not parallel to the shared one are all capped by sulphur atoms. All the nickel and sulphur atoms lie on three parallel planes which are 2.1 Å apart. The six sulphur atoms of the outer layers triply bridge three nickel atoms, while the three sulphur atoms of the central plane quadruply bridge four nickel atoms. Finally, the six nickel atoms of the outer layers are co-ordinated by the six phosphorus atoms of the six triethylphosphine ligands.

The average values† of the intralayer Ni-Ni distances, 2.956(2) Å within the internal layer and 2.864(6) Å within the external layers, as well as the interlayer value, 2.693(4) Å, are considerably larger than the sum of the nickel covalent radii (2.30 Å).⁴ These values are close to those found in the trinuclear species $(\eta^5\text{-C}_5\text{H}_5)_3\text{Ni}_3\text{S}_2$ [2.801(5) Å]⁵ and $[(\text{PET}_3)_6\text{Ni}_3\text{S}_2]^{2+}$ [2.91(2) Å],³ for which a weak Ni-Ni linkage and no significant Ni-Ni interaction, respectively, have been assumed. Thus, only weak, direct metal to metal interactions can be invoked here.

The average values of the Ni-S bond lengths, equal to 2.175(8) and 2.230(9) Å for the triply and quadruply bridging sulphur atoms, respectively, fall in the range observed for analogous 3d metal-bridging sulphur linkages.^{3,5,6} The main interactions which cement the atoms in the cluster are those between Ni and S species. The compression of the two trigonal antiprisms along the pseudo-threefold axis with consequent shorter Ni-Ni interlayer distances is probably due to these strong Ni-S interactions.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

‡ The estimated errors on the means were calculated using the formula $[\Sigma_n(d_n - \bar{d})^2/n(n-1)]^{0.5}$.

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