A Quindecanuclear Nickel–Sulphur Cluster: Synthesis and Crystal Structure of Ni$_{15}$(μ$_3$-S)$_6$(μ$_4$-S)$_9$(PPh$_3$)$_6$

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A quindecanuclear nickel–sulphur cluster compound with triphenylphosphine, Ni$_{15}$(μ$_3$-S)$_6$(μ$_4$-S)$_9$(PPh$_3$)$_6$, is obtained from the reaction of NiCl$_2$, PPh$_3$, and Na$_2$S in dimethylformamide–tetrahydrofuran and has been shown by X-ray single crystal structural analysis to be co-facial quater-octahedra in a chain.

High-nuclearity metal-cluster compounds have attracted attention because of their novel structural features and potential uses as heterogeneous catalysts.[1] The structural characterization of such clusters is important in establishing a relationship between geometry and electronic structure. Moreover, recognition of the high nuclearity metal clusters suggests that they may provide a clue to understanding the relevance of molecular compounds and the infinite lattice in metal sulphide and metal clusters, and that they may pave ways for the discovery of novel materials with unusual physical or chemical properties.

Recently, several cobalt- or nickel-chalcogen clusters with face-sharing octahedra have been characterized.[2] However, nickel–sulphur clusters containing more than two face-sharing octahedra have not yet been reported. In the studies of transition metal complexes, we have successively obtained a series of high-nuclearity metal-cluster compounds, [M$_2$Cu$_5$S$_6$X$_2$(R$_2$dtc)$_3$]$^{2-}$ (M=Mo, W; X=O, S; R=Me, Et; dtc = dithiocarbamato),[3] Co$_6$X$_8$(PR$_3$)$_6$ (X=S, Se; R=Ph, Et),[4] and [Au$_{13}$Ag$_{12}$(PPh$_3$)$_{10}$Cl$_8$]$^{1+}$.[5] Herein, we report the synthesis and X-ray crystal structure of a quindecanuclear nickel–sulphur cluster with triphenylphosphine ligand, Ni$_{15}$(μ$_3$-S)$_6$-(μ$_4$-S)$_9$(PPh$_3$)$_6$.

To a solution of anhydrous NiCl$_2$ (10 mmol) and triphenylphosphine (20 mmol) in dimethylformamide (DMF)–tetrahydrofuran (THF) (45 ml) at room temperature under N$_2$ was added a solution of Na$_2$S·9H$_2$O (10 mmol) in DMF (25 ml). After stirring the mixture for two days, a black solid was collected, and washed with water, acetone, and THF–hexane (1 : 1, v/v). The black solid was then treated with THF (50 ml). The resulting solution was filtered and the filtrate was covered with a layer of hexane. After leaving the filtrate to stand at ambient temperature for several weeks, dark-red crystals of the title compound were collected. The X-ray crystallographic study established the structure of the giant fused cluster.† Figure 1 shows a perspective view of the core. The central core
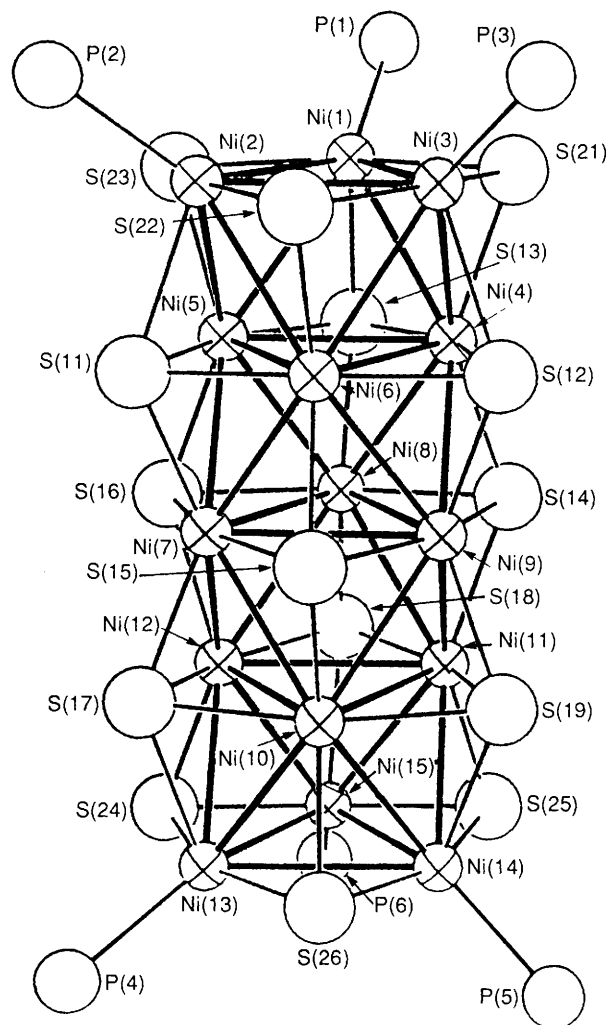
Figure 1. Structure of Ni$_{15}$(μ$_3$-S)$_6$(μ$_4$-S)$_9$(PPh$_3$)$_6$. Selected atomic distances (Å): Ni–Ni: (1)–(2) 2.881(1), (1)–(3) 2.873(1), (1)–(4 2.751(2),(1)–(5) 2.686(2), (2)–(3) 2.896(1), (2)–(5) 2.754(1), (2)–(6 2.670(1), (3)–(4) 2.665(1), (3)–(6) 2.776(2), (4)–(5) 2.893(2), (4)–(6 2.891(1), (4)–(8) 2.665(2), (4)–(9) 2.685(2), (5)–(6) 2.887(1), (5)–(7 2.665(2), (5)–(8) 2.712(1), (6)–(7) 2.709(2), (6)–(9) 2.648(1), (7)–(8 2.907(1), (7)–(9) 2.884(2), (7)–(10) 2.662(1), (7)–(12) 2.701(1 (8)–(9) 2.876(1), (8)–(11) 2.719(2), (8)–(12) 2.664(1), (9)–(1(2.712(2), (9)–(11) 2.644(1), (10)–(11) 2.911(1), (10)–(12) 2.894(1 (10)–(13) 2.735(2), (10)–(14) 2.691(1), (11)–(12), 2.918(2), (11)–1· 2.732(2), (11)–(15) 2.687(2), (12)–(13) 2.683(2), (12)–(15) 2.795(1 (13)–(14) 2.935(2), (13)–(15) 2.879(1), (14)–(15) 2.901(1); Ni–(μ$_3$-S 2.146–2.219; Ni–(μ$_4$-S): 2.201–2.282, 2.334–2.401; Ni–P: 2.16(2.205.

may be considered to possess D_{3h} symmetry and consists of five layers of Ni_3S_3 planes with an average‡ separation of 2.10(2) $\pm$ 0.02 Å between the planes. The five Ni_3 triangles in the planes are parallel and staggered with respect to each other. The nickel atoms are in different environments: each Ni atom in the central layer [Ni(7)–Ni(8)–Ni(9)] is co-ordinated to four μ_4-S atoms; those in the second and fourth layers [Ni(4)–Ni(6), Ni(10)–Ni(12)] are co-ordinated to one μ_3-S and three μ_4-S atoms; the Ni atom in the basal faces [Ni(1)–Ni(3), Ni(13)–Ni(15)] is bonded to two μ_3-S, one μ_4-S atoms, and one triphenylphosphino ligand. Each of the Ni atoms of the three inner layers is surrounded by four sulphur atoms of the nearest sphere and six nickel atoms of the second sphere, while that of the basal layers is surrounded accordingly by three sulphur and one phosphorus, and four nickel atoms. Alternatively, the cluster can also be viewed as four Ni_6-octahedra sharing three triangular faces in a nearly linear chain, which is similar to the torsional chain[2c] of $Ni_{15}Se_{15}(PPh_3)_6$. The octahedral faces which are not parallel to the shared faces are all capped by sulphur atoms as μ_3- or μ_4-S.

The average value of Ni–Ni distances within each of the five layers (2.895 $\pm$ 0.017 Å) is larger than the average value of those between layers (2.700 $\pm$ 0.040 Å). The average distance of Ni–(μ_3-S) [2.173(14) Å within each layer and 2.210(9) Å between layers] is slightly shorter than that of Ni–(μ_4-S) [2.229(9) Å within each layer and 2.240(26) Å between layers]. The values mentioned above are close to those found in the $[Ni_9S_9(PEt_3)_6]^{2+}$,[2a] $Ni_8S_6Cl_2(PPh_3)_7$ and $Ni_8S_5(PPh_3)_6^{2b}$ clusters, but distinctly shorter than that in $Ni_{15}Se_{15}(PPh_3)_6$.[2c]

Essentially, the sulphur atoms are in the extending triangular Ni_3 planes and bridge Ni atoms are in a layer with an average bridging angle ($\angle$Ni–S–Ni) of 83.6 $\pm$ 1.1° for the basal faces and of 81.2 $\pm$ 0.4° for the three inner planes. Each of the nine sulphur atoms of the inner layers [S(11)–S(13), S(14)–S(16), and S(17)–S(19)] also bridges the nickel atoms of the alternative layers with an average bridging angle of 135.9 $\pm$ 0.7°.

It is interesting that each of the nine nickel atoms in the three inner layers is co-ordinated by S or Ni atoms in a hemisphere and is practically bare in the other hemisphere, which is similar to a metal atom in a heterogeneous catalyst surface. This type of structure might provide a favourable geometrical environment for catalysis.

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‡ The average value (X) and standard deviation (sd) were calculated based on a group of similar data sd = $[(\Sigma X_i^2 - nX^2)/(n - 1)]^{1/2}$.