Hexacapped Mixed-metal Cubic $[M_8S_6]$ Clusters. Formation and Structures of $[Fe_6Ni_2S_6I_6(PMePh_2)_2]^{2-}$ and $[Fe_4Ni_4S_6I_4(PMePh_2)_4]$

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On a novel synthetic pathway to mixed-metal $[M_8S_6]$ clusters the compounds $[PhCH_2NEt_3]_2[Fe_6Ni_2S_6I_6(PMePh_2)_2]$ and $[Fe_4Ni_4S_6I_4(PMePh_2)_4]$ were isolated and characterised by single-crystal X-ray crystallography.

Cubic $[M_8S_6]$ clusters are found not only in naturally occurring sulfides, such as in the pentlandites,[1] but also, as a molecular counterpart, in synthetic compounds.[2–6] Several authors have analysed the electronic structures of these species by extended Hückel-methods.[7–9] According to calculations of Halet, Saillard and coworkers,[9] $[M_8S_6]$ clusters are stable within a wide number of electron counts (metallic valence electrons, MVE) ranging from 76 to 120. The electronic configuration and hence the properties can be varied with the kinds of ligands and/or metals.

We have found a novel synthetic pathway to mixed-metal cubic $[M_8S_6]$ clusters. Reactions of the easily accessible $[Fe_4S_4I_4]^{2-}$ [10] with appropriate mononuclear complexes and posphanes or with phosphane-coordinated complexes give $[Fe_{8-x}M_xS_6]$ clusters (x = 1–4). Here we report the isolation and characterisation of $[PhCH_2NEt_3]_2[Fe_6Ni_2S_6I_6(PMePh_2)_2]$ **1** and $[Fe_4Ni_4S_6I_4(PMePh_2)_4]$ **2**.

Cluster **1** is obtained from a mixture of NiI_2 (2 mmol) $PMePh_2$ (4 mmol) and $[PhCH_2NEt_3]_2[Fe_4S_4I_4]$ (1 mmol) in acetonitrile (80 ml). After filtration of a precipitate formed within the first 3 days, rhombic black crystals of analytically pure **1** (0.33 g) are isolated after another 3 days. No initial precipitate is observed when half the concentration of the reaction mixture is used but black needles of **2** begin to crystallize after 10 days, solvated with two acetonitrile molecules and contaminated with a small amount of **1**.

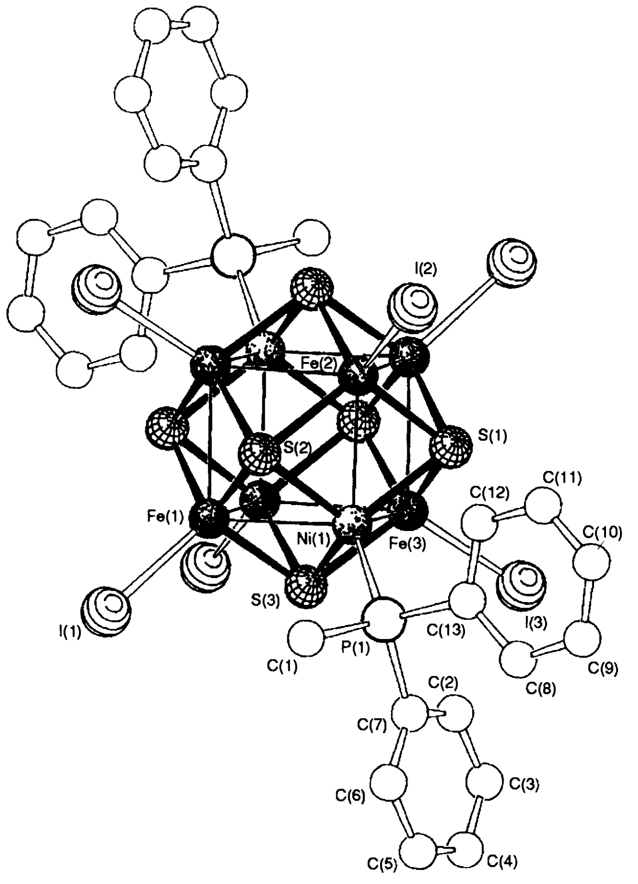

Fig. 1 Molecular structure of the anion of **1** (H atoms omitted for clarity). The complex exhibits C_i-symmetry. Selected distances (Å, range) and mean values (in parentheses): Fe–S 2.276(3)–2.301(3) (2.289), Ni–S 2.257(3)–2.265(3) (2.262), Fe–I 2.551(2)–2.570(2) (2.563), Ni–P 2.259(3), Fe–Fe 2.708(2)–2.762(2) (2.719), Fe–Ni 2.624(2)–2.658(2) (2.645).

This suggests that the reaction proceeds *via* a stepwise incorporation of nickel into the $[M_8S_6]$ cluster. However, it was not possible to isolate compounds with one or three nickel atoms as a part of the $[M_8S_6]$ core.

The structures of the anion of **1** and of the neutral complex of **2** are shown in Fig. 1 and 2, respectively, as the result of X-ray crystal structure determinations.†

In contrast to $[Fe_3Ni_5S_6I_8]^{4-}$ [6] where iron and nickel are randomly distributed among the eight metal positions of the $[M_8S_6]$ cluster, the metal atoms of **1** and **2** can be located unambiguously by means of the ligation. As expected, the phosphanes are coordinated to the electron-richer nickel atoms. Due to the shorter Fe–Ni and Ni–S distances compared with Fe–Fe and Fe–S bond lengths, the M_8 cubes are slightly distorted [M–M–M between 88.0 and 93.5 **1** and 87.7–92.5 **2**, respectively]. The overall oxidation state of the metals is +II and hence the number of metallic valence electrons are 104 for **1** and 108 for **2** (see also ref. 11).

In the reactions described here the phosphane not only acts as ligand but is also necessary to reduce the iron from oxidation state +III to +II, itself being oxidized to phosphanesulfide. As it was not possible to react a thiolate ligated cluster $[Fe_4S_4(SR)_4]^{2-}$ in the same manner, the substitution of iodide of $[Fe_4S_4I_4]^{2-}$ by phosphane with concomitant destabilisation of the $[Fe_4S_4]^{2+}$ core seems to be the first step in this reaction. This is supported by the observation that a cluster with different subsites, like $[Fe_4S_4(SR)_2L_2]$ [L = $Me_2N)_2CS$][12] where the thiourea derivative is readily substituted can be

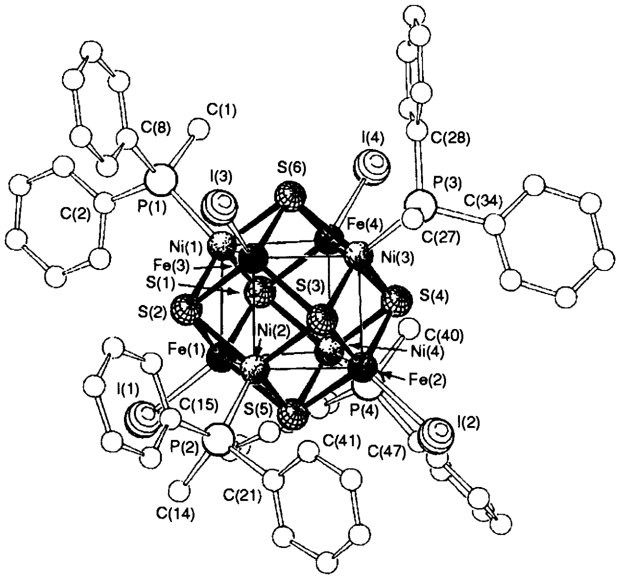

Fig. 2 Molecular structure of **2** (H atoms omitted for clarity). Selected distances (Å, range) and mean values (in parentheses): Fe–S 2.267(2)–2.282(2) (2.275), Ni–S 2.238(2)–2.258(2) (2.248), Fe–I 2.534(1)–2.559(1) (2.547), Ni–P 2.228(2)–2.243(2) (2.236), Fe–Ni 2.627(1)–2.672(1) (2.650).

reacted with phosphanes leading to $[Fe_6S_6(SR)_2(PR_3)_4]$ in the absence of heterometals.[13]

The specific variation of the mononuclear complexes enables the synthesis of compounds with different $[M_8S_6]$ units. Thus, nearly the whole range of stable MVE configurations calculated for this cluster geometry should be accessible.

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Footnote

† *Crystal data* for **1**: $C_{52}H_{70}Fe_6I_6N_2Ni_2P_2S_6$ M = 2191.3, monoclinic, space group $P2_1/n$, a = 14.588(1), b = 15.344(1), c = 16.287(1) Å, β = 97.67(1)°, U = 3613.0 Å^3, (T = 296 K), Z = 2, D_c = 2.014 g cm^{-3}, μ(Mo-Kα) = 4.46 mm^{-1}. A crystal was mounted on a AED2 Siemens four-circle diffractometer. Data collection using Mo-Kα radiation (π = 0.71073 Å) and ω–2θ scans gave 5660 independent reflections ($2\theta_{max}$ 48°) of which 3536 with $I \geqslant 2\sigma(I)$ were used in all calculations. The structure was solved by direct methods and the solution developed using full-matrix least-squares refinement and difference Fourier syntheses. Anisotropic displacement parameters were refined for non-H atoms, H atoms were included in fixed calculated positions.[14] At convergence, R = 0.048, R_w = 0.043, GOF = 1.40 for 331 parameters.

Crystal data for **2**·2MeCN: $C_{56}H_{58}Fe_4I_4N_2Ni_4P_4S_6$, M = 2041.1, triclinic, space group $P\bar{1}$, a = 12.507(3), b = 15.912(3), c = 20.058(5) Å, α = 91.77(1), β = 102.27(2), γ = 112.48 (2)°, U = 3567.3 Å^3, (T = 295 K), Z = 2, D_c = 1.895 g cm^{-3}, μ(Mo-Kα) = 3.84 mm^{-1}. A needle-like crystal was treated as described above, ω–2θ scans gave 12564 independent reflections ($2\theta_{max}$ 50°). The structure was solved by direct methods[14] and the solution developed using the described procedure, but SHELXL-93[15] instead for refinement (H atoms of the MeCN solvate could not be located). At convergence, R = 0.041, $wR2$ = 0.080 (for 12561 data and 721 parameters) GOF on F^2 = 1.05.

Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

1 S. Geller, *Acta Crystallogr.*, 1962, **15**, 1195; S. R. Hall and J. M. Stewart, *Can. Miner.*, 1973, **12**, 169; V. Rajamani and C. T. Prewitt, *Can. Miner.*, 1975, **13**, 75.

2 D. Fenske, J. Hachgenei and J. Ohmer, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 706; D. Fenske and J. Magull, *Z. Naturforsch., Teil B*, 1990, **45**, 121.

3 G. Christou, K. S. Hagen, J. K. Bashkin and R. H. Holm, *Inorg. Chem.*, 1985, **24**, 1010.

4 S. A. Al-Ahmad, A. Salifoglou, M. G. Kanatzidis, W. R. Dunham and D. Coucouvanis, *Inorg. Chem.*, 1990, **29**, 927.

5 S. Pohl and W. Saak, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 907; S. Pohl and U. Opitz, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 863; S. Pohl, W. Barklage, W. Saak and U. Opitz, *J. Chem. Soc. Chem. Commun.*, 1993, 1251.

6 W. Saak and S. Pohl, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 881.

7 J. K. Burdett and G. Miller, *J. Am. Chem. Soc.*, 1987, **109**, 4081.

8 G. G. Hoffman, J. K. Bashkin and M. Karplus, *J. Am. Chem. Soc.*, 1990, **112**, 8705.

9 E. Furet, A. Beuze, J.-F. Halet and J.-Y. Saillard, *J. Am. Chem. Soc.*, 1994, **116**, 274.

10 W. Saak and S. Pohl, *Z. Naturforsch. Teil B*, 1985, **40**, 1105.

11 R. L. Johnston and D. M. P. Mingos, *J. Organomet. Chem.*, 1985, **280**, 407.

12 U. Bierbach, W. Saak, D. Haase and S. Pohl, *Z. Naturforsch., Teil B*, 1991, **46**, 1629.

13 S. Pohl and B. Bahlmann, in preparation.

14 G. M. Shedrick, SHELXTL-PLUS, Siemens Analytical Systems, Madison, WI, 1989.

15 G. M. Sheldrick, *J. Appl. Crystallogr.*, in preparation.