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Communication

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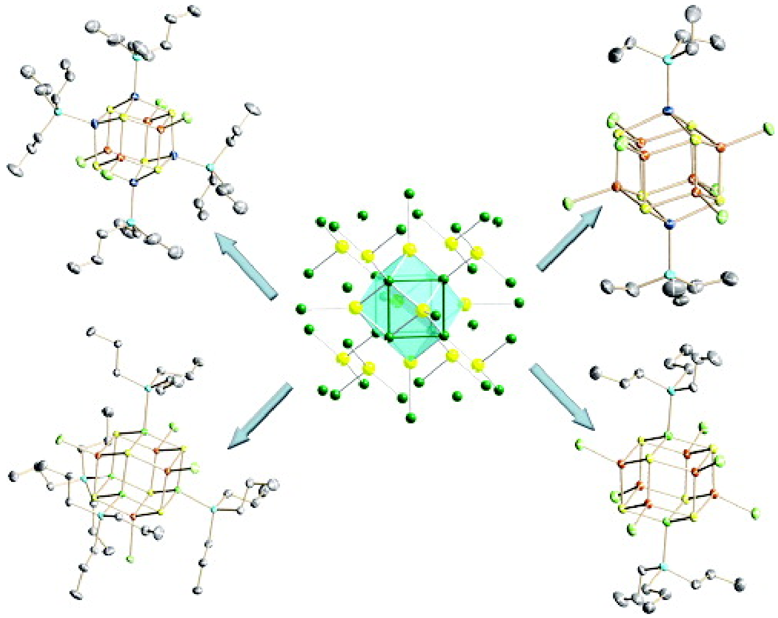

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Systematic Synthesis of Heterometallic Ni/Fe/S and Cu/Fe/S Clusters with a Pentlandite-like M_8S_6 Core

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Included among the plethora of metal sulfide minerals are the cubic pentlandites, $(M')M_8S_8$, represented by such examples as argentopentlandite ($M' = Ag$, $M = Fe, Ni$), cobalt pentlandite ($M' = M = Co$), and Fe and Ni pentlandite.[1] The major repeating units in these minerals are cubic M_8 clusters stabilized by six quadruply bridging sulfide ligands, one on each of the M_8 cube faces (Figure 1). Synthetic, molecular, pentlandite analogues are known and include clusters with the Fe_8S_6,[2] Ni_8S_6,[3] and Co_8S_6[4] cores.

The Fe_8S_6[2] and $Mo_2Fe_6S_6$[5] clusters can be envisioned as derivatives of the known Fe_6S_6 pentlandite "prismane" fragment (Figure 2A).[5] The latter is theoretically obtainable by the removal of two Fe atoms from the body diagonal of the Fe_8S_6 pentlandite cubes. The removal of two metal atoms from a face diagonal of the Fe_8S_6 unit leads to the Fe_6S_6 isomer (Figure 2B). Examples of **2A**[5] and **2B**[6] have been obtained independently and structurally characterized. Further removal of two more metal atoms leads, *hypothetically*, to the two tetranuclear isomeric fragments, Fe_4S_6, with either a planar or a tetrahedral Fe_4 array. Molecular examples of either of these two isomers (Figure 2C,D) are not known, although an adamantane Fe_4S_6 cage, with μ_3-RS^- ligands, exists in the $[Fe_4(SR)_6Cl_4]^{2-}$ [7] and $[Fe_4(SR)_{10}]^{2-}$ [8] clusters. The $[Fe_4S_6L_4]$ isomer, with a square arrangement of four Fe atoms (Figure 2D), can be envisioned as a result of the coupling of two $Fe_2S_2L_4$[9] dimers that could be accomplished by the following synthetic procedure (eq 1).

$$2\,[\mathrm{Cl_2Fe_2S_2Cl_2}]^{2-} + 2\,[((\mathrm{CH_3})_3\mathrm{Si})_2]\mathrm{S} \rightarrow [\mathrm{Fe_4S_6Cl_4}]^{4-} + 4\,(\mathrm{CH_3})_3\mathrm{SiCl} \quad (1)$$

The other $[Fe_4S_6L_4]$ isomer (Figure 2C) can possibly be obtained by a structural rearrangement, following reduction of **2D**. The real and hypothetical structures shown in Figure 2 possess an important common feature that makes them viable precursors in the synthesis of heterometallic $(M')_{8-x}(Fe)_xS_6(L')_{8-x}(L)_x$ clusters. They all contain six, octahedrally arranged, μ-sulfido ligands and trihapto sites poised for coordination to $M'L'$ units and generation of $L'M'S_3$ tetrahedral subunits. Distinct thermodynamically stable isomers are expected to form with different terminal ligands (L') and specific $M'-L'$ coordination preferences.

In this communication, we report a systematic approach toward the synthesis of heterometallic "pentlandite-like" clusters. The general methodology in the synthesis of $M'_4L'_4M_4L_4S_6$ clusters is based on the addition of $M'L'$ units to the in situ generated, *hypothetical*, "dimer of dimers" or "adamantane" $[Fe_4L_4S_6]$ structures (Figure 2C,D).

The stoichiometric addition of an acetonitrile solution of a $Cu(CH_3CN)_4PF_6/R_3P$ 2:2 mixture to a 1:1 mixture of $(Et_4N)_2[Fe_2S_2Cl_4]/(CH_3Si)_2S$, also in acetonitrile solution at ambient temperature, leads to the formation of $[Cu_4Fe_4S_6(P^nPr_3)_4Cl_4]$, **1**, in 40% yield. The corresponding $[Ni_4Fe_4S_6(P^nPr_3)_4Cl_4]$, **3** (35% yield), is obtained by a similar reaction using $[Ni(CH_3CN)_6](BF_4)_2$.[10] When a deficit of Cu or Ni with PR_3 is used ($^2/_3$ equiv), $[Cu_2Fe_6S_6(PEt_3)_2Cl_6]_2(Bu_4N)_2$, **2** (25% yield), or $[Ni_2Fe_6S_6(P^nPr_3)_2Cl_6](Et_4N)_2$, **4** (28% yield), is isolated. The structures of all four compounds were crystallographically determined[11] and are shown in Figure 3.[12,13]

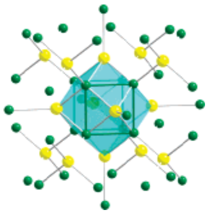

Figure 1. Part of the repeating framework of the M_9S_8 pentlandites that contain a metal cube and sulfur atoms in an octahedron (Ni and Fe atoms are depicted in green, whereas S atoms are yellow).

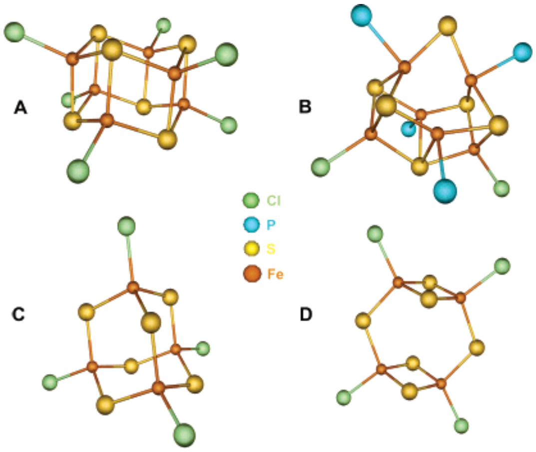

Figure 2. Schematic representations of various pentlandite, $M_nS_6L_n$ fragments. Examples of A and B have been obtained and structurally characterized. C and D are only hypothetical.

The core structure of all compounds deviates only slightly from the one in naturally occurring pentlandites. Coordination of one terminal chloride (in the case of the iron atoms) or one terminal phosphine (in the case of the copper or nickel atoms) completes tetrahedral coordination and results in a trigonally distorted, local C_{3v} symmetry, $(\mu_4\text{-S})_3ML$ sites. Compounds **2** and **3** are isostructural and exhibit similar average Fe−S and Fe−Cl distances (see Table 1).

The M_8S_6 cores in **1** and **2** are larger than those in **3** and **4**, with M−M body diagonals of 4.810, 4.808, 4.576, and 4.642 Å, respectively. These differences undoubtedly are mainly due to the longer Cu−S bonds in **1** and **2** at 2.336 and 2.385 Å, respectively, when compared to the Ni−S bonds in **3** and **4** at 2.243 and 2.255 Å, respectively. Clusters **1** and **3** are two different structural isomers with the same M/M′ ratio. In **1**, the 4Fe and the 4Cu atoms define

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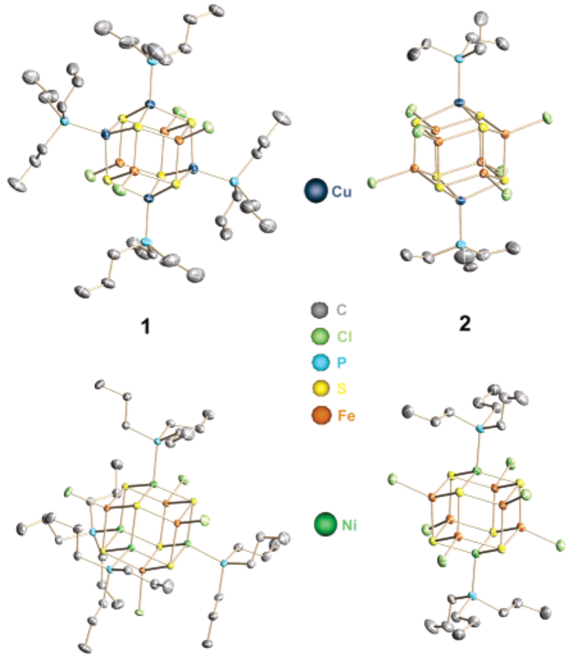

Figure 3. Ortep diagrams of the $[Cu_4Fe_4S_6(P^nPr_3)_4Cl_4]$ (**1**), $[Cu_2Fe_6S_6Cl_6(PEt_3)_2](Bu_4N)_2$ (**2**), $Ni_4Fe_4S_6(P^nPr_3)_4Cl_4$ (**3**), and $[Ni_2Fe_6S_6(P^nPr_3)_2Cl_6](Et_4N)_2$ (**4**) clusters, showing the thermal ellipsoids at 50% probability. The Et_4N^+, Bu_4N^+ cations of **2** and **4**, as well as the hydrogen atoms, have been omitted for clarity.

Table 1. Selected Bond Distances (Å)[a]

	1	**2**	**3**	**4**
Cu−Cu	2.733			
Ni−Ni			3.630(6, 6)	
Cu−Fe	2.787(15, 4)	2.784(8, 6)		
Ni−Fe			2.636(3, 12)	2.616(1, 3)
Fe−Fe	2.784	2.772(8, 6)	3.820(5, 6)	2.752(4, 3)
Cu−S	2.366(4, 6)	2.385(2, 6)		
Ni−S			2.243(1, 6)	2.255(8, 3)
Fe−S	2.269(2, 6)	2.307(2, 18)	2.281(2, 6)	2.296(4, 9)
Cu−P	2.252(3, 2)	2.243(4, 2)		
Ni−P			2.218(9, 2)	2.222
Fe−Cl	2.197(2, 2)	2.229(3, 6)	2.221(7, 2)	2.232(4, 3)

[a] The first number in parentheses is the standard deviation from the mean, and the second number is the number of equivalent distances averaged out. The numbering scheme follows the one in Figure 3.

interpenetrating squares, whereas in **3**, the 4Fe and the 4Ni define interpenetrating tetrahedra.

In the Mössbauer spectra of **1**, **2**, **3**, and **4** (at room temperature, vs Fe metal), isomer shifts and quadruple splittings are found at 0.341(5), 0.64 mm/s; 0.345(5), 0.39 mm/s; 0.395(5), 0.70 mm/s; and 0.355(5), 0.68 mm/s, respectively. The values are consistent with a delocalized system where the Fe(II) atoms are partially oxidized ($Fe^{+(2+n)}$), while the Cu(II) or Ni(II) sites are partially reduced ($Cu^{+(2-n)}$, $Ni^{+(2-n)}$). Not unexpectedly, the Fe atoms in **3** and **4** appear to be more reduced than those in **1** and **2**. Similar delocalization of charge has been previously observed with naturally occurring $(Fe,Ni)_8S_6$ pentlandites.[14]

Cyclic voltammetry[15] of **1** shows two reversible reductions at −10 and −616 mV and one irreversible oxidation at 672 mV. In contrast, **3** shows a reversible reduction at −245 mV and a reversible oxidation at 883 mV. **2** and **4** reveal single reversible reduction waves at −555 and −585 mV and two irreversible oxidation waves at 384, 854 mV, and 342, 1058 mV, respectively. The magnetic moments for **2** at 5, 40, and 300 K are 0.90, 1.46, and 3.69 μ_B, respectively, whereas the corresponding moments for **3** at the same temperatures are 1.87, 2.05 and 3.10 μ_B. These moments suggest strong antiferromagnetic coupling. Clusters **1** and **4** are diamagnetic at either 5 °C or room temperature.

Although a structure similar to **3** has been previously reported,[16] it was not fully characterized, and its chemical properties and electronic structure were not addressed or investigated in any detail. Specifically functionalized MM′/S heterometallic clusters potentially can be building blocks for extended solids with unusual magnetic and electronic properties. The clusters reported in this communication represent examples of molecules of unique utility for the synthesis of new materials.

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Supporting Information Available: X-ray crystallographic file in CIF format, as well as synthesis and characterization for $[Cu_4Fe_4S_6(P^nPr_3)_4Cl_4]$ (**1**), $[Cu_2Fe_6S_6Cl_6(PEt_3)_2](Bu_4N)_2$ (**2**), $Ni_4Fe_4S_6(P^nPr_3)_4Cl_4$ (**3**), and $[Ni_2Fe_6S_6(P^nPr_3)_2Cl_6](Et_4N)_2$ (**4**). This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Diffraction data were collected on a Bruker SMART CCD-based X-ray diffractometer operated at 150 K ($2\theta_{max}$ = 56.52, 56.71, 56.58, and 52.84 for **1**, **2**, **3**, and **4**, respectively). The space groups, *Pbca*, orthorhombic for **1**; *P*2(1)/*m*, monoclinic for **2**; $R\bar{3}c$, trigonal for **3**; and *P*1, triclinic for **4**, were determined based on systematic absences and intensity statistics. Cell dimensions (Å, deg) are for [**1**]: $a = 16.947(2)$, $b = 16.975(2)$, $c = 20.846(3)$ with $\alpha = \beta = \gamma = 90.00$ and $V = 5996.7(13)$ Å^3, $z = 4$; for $(Bu_4N)_2$ [**2**]: $a = 13.936(2)$, $b = 15.934(2)$, $c = 15.719(2)$ with $\beta = 96.004(2)$ and $V = 3471.6(8)$ Å^3, $z = 2$; for [**3**]: $a = 19.9487(16)$, $b = 19.9487(16)$, $c = 26.536(5)$ with $\alpha = \beta = 90.00$, $\gamma = 120$, and $V = 9145.2(19)$ Å^3, $z = 6$; for $(Et_4N)_2$ [**4**]: $a = 12.420(3)$, $b = 12.547(3)$, $c = 12.710(3)$ with $\alpha = 94.592(4)$, $\beta = 117.208(4)$, $\gamma = 115.894(4)$, and $V = 1484.6(6)$ Å^3, $z = 1$. Full-matrix least-squares refinement based on F^2 converged to an $R1$ [$I > 2\sigma$] value of 0.0336, 0.0428, 0.0157, and 0.0669, and a $wR2$ value of 0.0792, 0.0844, 0.0413, and 0.1974; GoF = 1.018, 1.010, 1.083, and 1.074 for [**1**], $(Bu_4N)_2$ [**2**], [**3**], and $(Et_4N)_2$ [**4**], respectively.
(12) Compounds **2**, **3**, and **4** were also synthesized from the reaction of M/PPr_3 with the single $[Fe_4S_4Cl_4]^{2-}$ cubanes, albeit in smaller yields. The induced rearrangement of the $[Fe_4S_4L_4]^{2-}$ cubanes is not unknown and has previously resulted in the synthesis of cubic metal sulfur clusters, as in the case of the $[Fe_8S_6I_8]^{4-}$ and $[(CO)_3Mo]_2[Fe_6S_6CL_6]$ compounds.
(13) In all cases, the ratio of Cu to Fe or Ni to Fe was confirmed by microprobe analysis (The University of Michigan Electron Microbeam Analysis Laboratory).
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