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# Heteronuclear metal cluster complexes with a new coordination mode of the $Fe_2S_2(CO)_6$ unit. Synthesis, structure and possible reaction pathway of the first Fe–Cu–S cluster compound, $[Fe_6Cu_5S_6(CO)_{18}(PPh_3)_2]^-$

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**Abstract**

The first iron–copper–sulfur cluster compound $[Et_4N][Fe_6Cu_5(\mu_4\text{-}S)_6(CO)_{18}(PPh_3)_2]$ (**1**) is prepared by the reaction of $[Et_4N][CuCl_2PPh_3]$ with $Li_2[Fe_2S_2(CO)_6]$ in mixed solvents of MeCN–$CH_3OH$. **1**·MeCN crystallizes in the monoclinic, space group *Pn* with $a=12.426(3)$, $b=15.572(4)$, $c=20.709(4)$ Å; $\beta=90.14(2)°$; $V=4007.2$ Å$^3$; $Z=2$, $D_c=1.80$ g cm$^{-3}$, and $R_1=0.032$, $R_2=0.037$ for 3319 independent reflections ($I>3\sigma(I)$). The anion of **1** contains an undeca-nuclear Fe–Cu–S core with $Fe^I$ and $Cu^I$, $[Fe_6Cu_5(\mu_4\text{-}S)_6]^-$, which consists of a central trigonal bipyramid composed of five copper atoms in the center and three 'butterfly' type $Fe_2S_2$ units chelating to the copper atoms of the central $Cu_5$ trigonal bipyramid along the pseudo-$D_3$ axis resulting in pseudo-$D_3$ symmetry. All the sulfur atoms in **1** are $\mu_4$-S, linking to two iron and two copper atoms. Around the core, twelve terminal carbonyls, six bridging CO groups and two $PPh_3$ ligands meet the requirement of four-coordination of the copper atoms and five-coordination of the iron atoms. Fe–S and Cu–S distances are 2.28–2.36 and 2.24–2.51 Å, respectively. There are fifteen M–M bonds in **1**, including three Fe–Fe of 2.5 Å, six Cu–Fe of 2.7 Å and six Cu–Cu of 2.6 Å. The $Fe_2S_2(CO)_6$ units in **1** take a new coordination mode in that each unit coordinates to four metal atoms by its two sulfur atoms in a $\mu_4$-type fashion. A possible reaction pathway for **1** via the formation of two reactive fragments is proposed and discussed.

*Keywords:* Crystal structures; Iron complexes; Copper complexes; Sulfur complexes; Cluster complexes

## 1. Introduction

Interest in transition metal–sulfur clusters has arisen from their significance as possible models for the active center of metal enzyme [1–5] and heterogeneous catalysts [6–13] and their unusual electronic properties and structural chemistry. Recently, an important synthetic route to produce heteronuclear metal clusters using the iron–sulfur cluster $Fe_2S_2(CO)_6$ or its dianion [14] as the source of iron and sulfur bridges has been increasingly used and many mixed-metal clusters containing the $Fe_2S_2(CO)_6$ unit have been reported [4,15–27]. In the reported clusters, the coordination modes of the $Fe_2S_2(CO)_6$ unit are of three types: (i) the 'butterfly' type $Fe_2S_2$ unit coordinated to one metal atom by $\mu_3$-S or two metal atoms by $\mu_4$-S [4,17–21] (A); (ii) a near planar $Fe_2S_2$ unit coordinated to a metal atom leading to a square pyramid with the metal atom at the apex [4,19,22–26] (B); (iii) a planar $Fe_2S_2$ unit linking two metal atoms on two sides by the $\mu_4$-S atoms [26,27] (C); the metals are Fe, Co, Ni, Pt, Pd, Mo, W, Zn and Cr. Herein we report a new iron–copper–sulfur cluster compound containing $Fe_2S_2(CO)_6$ units which are in a new coordination mode (D). The 'butterfly' type $Fe_2S_2(CO)_6$ unit coordinates to four metal atoms by the $\mu_4$-S atoms.

## 2. Experimental

### 2.1. Materials and methods

Acetonitrile and methanol were dried by distillation with $CaH_2$ and magnesium methoxide, respectively.

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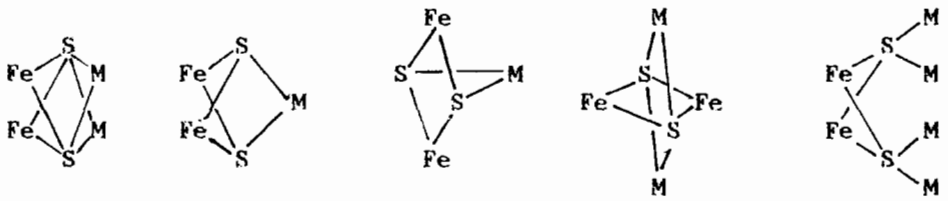



Compounds, $[Fe_2S_2(CO)_6]$ [14] and $[Et_4N][CuCl_2PPh_3]$ [28] were prepared by literature methods. $LiB(C_2H_5)_3H$ was purchased from Aldrich.

All synthetic reaction procedures, crystal growth and preparation of the sample for X-ray determination and spectroscopy measurements were carried out under a nitrogen atmosphere, using the Schlenk technique and degassed solvents, and all reactants were also degassed before used.

IR spectra were recorded on a Perkin-Elmer 577 spectrophotometer in the range 200–4000 $cm^{-1}$ using KBr pellets. Elemental analysis for carbon, hydrogen and nitrogen was conducted on a Carlo Erba Strumentazion elemental analyser MOD 1106.

### 2.2. Synthesis of $[Et_4N][Fe_6Cu_5(\mu_4\text{-}S)_6(\mu\text{-}CO)_6(CO)_{12}(PPh_3)_2]$ (1)

To a solution of $Fe_2S_2(CO)_6$ (0.25 g, 0.73 mmol) in 20 ml $CH_3OH$ at −78 °C were added dropwise 1.5 ml of a 1 M solution of $LiB(C_2H_5)_3H$ in THF. After stirring for a while, to the dark brown resulting reaction solution was added 0.40 g (0.73 mmol) of $[Et_4N][CuCl_2PPh_3]$ in 20 ml MeCN and the reaction temperature was raised gradually to room temperature. The reaction mixture was then stirred for 2 days at room temperature. After filtering off a small amount of brown residue, the brown–green filtration was cooled to 4 °C, and 0.22 g of dark red crystalline product **1** was collected by filtering and dried in vacuo; yield 73% (based on the $[Et_4N][CuCl_2PPh_3]$ used). *Anal.* Calc. for $C_{64}H_{50}NCu_5Fe_6S_6P_2O_{18}\cdot CH_3CN$: C, 37.58; H, 2.59; N, 1.37; Cu, 15.54; Fe, 16.40; S, 9.39; P, 3.03. Found: C, 36.65; H, 2.75; N, 1.81; Cu, 14.90; Fe, 16.70; S, 9.85; P, 2.89%. IR (KBr pellet): 2050s, 2020s, 1990s, 1910s ($\nu$MC=O), 351w, 339w ($\nu$Fe–S), 312w, 254w ($\nu$Cu–S).

### 2.3. X-ray analysis

Crystal data and details of data collection and refinement procedures for **1**·MeCN are summarized in Table 1. The structure was solved by direct methods. A total of 11 atoms was located from an *E*-map and the remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were not included in the calculations. The structure was refined

Table 1
Crystal data and details of data collection and refinement procedures for **1**·MeCN

| | |
|---|---|
| Compound | $[Cu_5Fe_6S_6(PPh_3)_2(CO)_{18}][Et_4N]\cdot MeCN$ |
| Formula | $C_{64}H_{53}Cu_5Fe_6N_2O_{18}P_2S_6$ |
| Formula weight | 2044.5 |
| Crystal system | monoclinic |
| Space group | *Pn* (No. 7) |
| *a* (Å) | 12.426(3) |
| *b* (Å) | 15.572(4) |
| *c* (Å) | 20.709(4) |
| $\beta$ (°) | 90.14(2) |
| *V* (Å$^3$) | 4007.2 |
| *Z* | 2 |
| $\rho$ (g $cm^{-3}$) | 1.80 |
| $\mu$ ($cm^{-1}$) | 26.1 |
| Crystal dimensions (mm) | 0.30×0.30×0.20 |
| Temp. (°C) | 23±1 |
| Diffractometer | Enraf-Nonius CAD4 |
| Radiation, (Å) | Mo K$\alpha$, 0.71073 |
| Monochromator | graphite |
| Scan technique | $\omega$–2$\theta$ |
| Scan speed (°/min) | 2 to 7 (in $\omega$) |
| Data collected, 2$\theta$ max (°) | 50.0 ($+h+k\pm l$) |
| $\omega$ scan width (°) | 1.40+0.35 tan $\theta$ |
| Unique data | 7037 |
| Data used in refinement with $I>3.0\sigma(I)$ | 3319 |
| Corrections | Lorentz–polarization<br>line decay (0.981–1.142)<br>DIFABS absorption (0.578–1.718) |
| Solution | direct methods |
| $R_a$ | 0.032 |
| $R_w$[b] | 0.037 |

[a] $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$.
[b] $R_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

in full-matrix least-squares where the function minimized was $\Sigma w(|F_o|-|F_c|)^2$ and the weight $w$ is as defined by Killean and Lawrence with terms of 0.020 and 1.0 [29]. The final cycle of refinement included 596 variable parameters for 3319 reflections with $I>3.0\sigma(I)$ and converged to $0.01\sigma$ with unweighted and weighted agreement factors of 0.032 and 0.037, respectively. The standard deviation of an observation of unit weight was 0.41. There were five correlation coefficients greater than 0.50. The highest peak in the final difference Fourier had a height of 0.40 e Å$^{-3}$ with an estimated error based on $\delta F$ [30] of 0.09 The minimum negative

peak had a height of $-0.12$ e Å$^{-3}$. All calculations were performed on a VAX computer using SDP/VAX [31]. The final positional and thermal parameters with e.s.d.s are listed in Table 2. Selected bond distances and bond angles are shown in Tables 3 and 4,respectively.

## 3. Results and discussion

### 3.1. Structure of $[Et_4N][Fe_6Cu_5S_6(CO)_{18}(PPh_3)_2]$ (1)

**1** contains two discrete fragments, a cation $Et_4N^+$ and an undeca-nuclear mixed-metal anion $[Fe_6Cu_5S_6(CO)_{18}(PPh_3)_2]^-$. An ORTEP drawing of the anion of **1** and a view of the Fe–Cu–S core in $[Fe_6Cu_5S_6(CO)_{18}(PPh_3)_2]^-$ are depicted in Figs. 1 and 2, respectively. The structure of the anion of **1** comprises a novel undeca-nuclear iron–copper–sulfur cluster core $[Fe_6Cu_5(\mu\text{-}S)_6]^-$ (Fig. 2), which consists of a central $Cu_5$ in a trigonal bipyramid arrangement with the equatorial plane Cu(1)Cu(2)Cu(3), and three puckering 'butterfly' type $Fe_2S_2$ units chelating to the copper atoms of the central $Cu_5$ along the pseudo-$D_3$ axis through the Cu(4) and Cu(5) atoms of the trigonal bipyramid resulting in pseudo-$D_3$ symmetry. Around the $[Fe_6Cu_5(\mu\text{-}S)_6]^-$ core, there are twelve terminal CO, six bridging CO and two $PPh_3$ ligands coordinated to the Fe and Cu atoms, resulting in five-coordination geometry of each Fe atom, and tetra-coordination geometry of each Cu atom in the cluster. The Fe–Fe bond lengths of 2.517(4)–2.532(4) Å, Fe–S bond distances of 2.292(5)–2.353(6) Å and FeSFe angles of 65.5(1)–66.3(1)° of the $Fe_2S_2(CO)_6$ units in **1** are comparable with those observed in $Fe_2S_2(CO)_6$ and other 'butterfly' type $Fe_2S_2(CO)_6$-containing complexes (see Table 5) indicating that the $Fe_2S_2(CO)_6$ units in cluster **1** are similar to those in $Fe_2S_2(CO)_6$ and related complexes with a puckered $Fe_2S_2$ ring in which the oxidation states of the Fe atoms are Fe(I). Each S atom of the $Fe_2S_2(CO)_6$ unit becomes $\mu_4$-S, connecting with 2 copper atoms, thus the coordination mode of the $Fe_2S_2(CO)_6$ unit in the cluster is a new type, found here for the first time. It is worth pointing out that each of the six bridging carbonyls is unsymmetrically connected with each pair of Fe and Cu atoms with Fe–$C_b$ ($C_b$ is the carbon atom of the bridging carbonyl) of 1.81–1.89 Å and Cu–$C_b$ of 2.6075–2.6635 Å. The fact that Fe–$C_b$ of 1.84 (av.) Å and Fe–$C_b$–$O_b$ ($O_b$ is the oxygen atom of the bridging carbonyl) of 166–170° are very close to the Fe–$C_t$ ($C_t$ is the carbon atom of the terminal carbonyl) and Fe–$C_t$–$O_t$ ($O_t$ is the oxygen atom of the terminal carbonyl) values implies that two of the carbonyls in each $Fe_2S_2(CO)_6$ unit converted to two bridging carbonyls in order to complete the four-coordination geometries of the Cu atoms in the cluster **1**, but still maintain the characteristics of terminal CO ligands.

Table 2
Positional and thermal parameters of $[Cu_5Fe_6S_6(CO)_{18}(PPh_3)_2]$-$[Et_4N]$·MeCN

| Atom | x | y | z | B (Å²) |
|---|---|---|---|---|
| Cu(1) | 1.070 | 0.1559(1) | 0.781 | 2.84(4) |
| Cu(2) | 0.8588(1) | 0.1605(1) | 0.82841(9) | 2.79(4) |
| Cu(3) | 0.8968(1) | 0.1645(1) | 0.69409(9) | 2.77(4) |
| Cu(4) | 0.9336(2) | 0.0310(1) | 0.76404(9) | 2.83(4) |
| Cu(5) | 0.9473(2) | 0.2922(1) | 0.7711(1) | 3.00(4) |
| Fe(1) | 0.6540(2) | 0.1997(1) | 0.7970(1) | 2.45(4) |
| Fe(2) | 0.6812(2) | 0.1394(1) | 0.6847(1) | 2.40(4) |
| Fe(3) | 1.0456(2) | 0.1913(2) | 0.6023(1) | 2.86(5) |
| Fe(4) | 1.1871(2) | 0.1206(1) | 0.6721(1) | 2.73(4) |
| Fe(5) | 1.1320(2) | 0.1762(1) | 0.9044(1) | 2.58(4) |
| Fe(6) | 0.9549(2) | 0.1163(1) | 0.9423(1) | 2.45(4) |
| S(1) | 0.7457(3) | 0.0716(3) | 0.7755(2) | 2.59(8) |
| S(2) | 0.7725(3) | 0.2598(3) | 0.7249(2) | 2.53(8) |
| S(3) | 1.0168(3) | 0.0657(3) | 0.6604(2) | 2.66(8) |
| S(4) | 1.0997(3) | 0.2494(2) | 0.6999(2) | 2.45(8) |
| S(5) | 1.0486(3) | 0.0571(3) | 0.8588(2) | 2.38(8) |
| S(6) | 0.9726(3) | 0.2451(3) | 0.8840(2) | 2.70(8) |
| P(1) | 0.9252(3) | −0.1140(2) | 0.7666(2) | 2.85(9) |
| P(2) | 0.9532(3) | 0.4392(2) | 0.7713(2) | 2.89(9) |
| O(11) | 0.5017(9) | 0.3304(8) | 0.7611(6) | 6.4(3) |
| O(12) | 0.489(1) | 0.0943(9) | 0.8514(7) | 6.8(4) |
| O(13) | 0.707(1) | 0.280(1) | 0.9205(5) | 6.8(3) |
| O(21) | 0.5853(8) | 0.2644(8) | 0.5971(5) | 4.8(3) |
| O(22) | 0.4930(9) | 0.0232(8) | 0.6855(7) | 6.0(3) |
| O(23) | 0.7825(9) | 0.0507(8) | 0.5750(6) | 5.6(3) |
| O(31) | 1.044(1) | 0.080(1) | 0.4930(6) | 7.3(4) |
| O(32) | 1.183(1) | 0.3186(8) | 0.5402(6) | 6.3(3) |
| O(33) | 0.849(1) | 0.2811(8) | 0.5640(6) | 5.7(3) |
| O(41) | 1.3709(9) | 0.2287(9) | 0.6478(7) | 6.2(3) |
| O(42) | 1.263(1) | −0.0141(8) | 0.5844(5) | 6.0(3) |
| O(43) | 1.2887(9) | 0.0307(7) | 0.7808(5) | 4.6(3) |
| O(51) | 1.163(1) | 0.3012(8) | 1.0062(6) | 6.2(3) |
| O(52) | 1.2855(9) | 0.0517(9) | 0.9569(7) | 7.3(4) |
| O(53) | 1.2994(9) | 0.253(1) | 0.8207(6) | 6.3(4) |
| O(61) | 1.0383(9) | −0.0212(7) | 1.0254(6) | 5.3(3) |
| O(62) | 0.913(1) | 0.2244(9) | 1.0533(6) | 6.3(4) |
| O(63) | 0.7356(8) | 0.0486(9) | 0.9376(6) | 4.8(3) |
| C(11) | 0.557(1) | 0.283(1) | 0.7740(8) | 3.6(3)* |
| C(12) | 0.552(1) | 0.1325(9) | 0.8318(7) | 2.4(3)* |
| C(13) | 0.697(1) | 0.248(1) | 0.8738(9) | 4.7(4)* |
| C(21) | 0.617(1) | 0.216(1) | 0.6314(7) | 2.9(3)* |
| C(22) | 0.567(1) | 0.072(1) | 0.6865(8) | 4.1(4)* |
| C(23) | 0.755(1) | 0.090(1) | 0.6194(9) | 4.8(4)* |
| C(31) | 1.047(1) | 0.124(1) | 0.5344(7) | 2.9(3)* |
| C(32) | 1.135(1) | 0.272(1) | 0.5626(7) | 3.1(3)* |
| C(33) | 0.920(1) | 0.247(1) | 0.5838(8) | 3.8(3)* |
| C(41) | 1.303(1) | 0.190(1) | 0.6570(8) | 3.9(4)* |
| C(42) | 1.234(1) | 0.039(1) | 0.6146(8) | 4.2(4)* |
| C(43) | 1.246(1) | 0.072(1) | 0.7446(7) | 3.0(3)* |
| C(51) | 1.152(1) | 0.255(1) | 0.9681(8) | 4.2(4)* |
| C(52) | 1.222(1) | 0.104(1) | 0.9368(8) | 3.8(3)* |
| C(53) | 1.232(1) | 0.225(1) | 0.8471(7) | 3.1(3)* |
| C(61) | 1.009(1) | 0.030(1) | 0.9906(7) | 3.2(3)* |
| C(62) | 0.925(1) | 0.183(1) | 1.0085(8) | 4.0(4)* |
| C(63) | 0.816(1) | 0.074(1) | 0.9351(7) | 3.3(3)* |
| C(111) | 0.808(1) | −0.162(1) | 0.7287(7) | 2.9(3)* |
| C(112) | 0.778(1) | −0.125(1) | 0.6715(8) | 4.6(4)* |
| C(113) | 0.681(2) | −0.160(2) | 0.641(1) | 6.7(5)* |
| C(114) | 0.621(2) | −0.224(2) | 0.667(1) | 8.3(6)* |
| C(115) | 0.659(2) | −0.261(2) | 0.722(1) | 7.4(6)* |

(continued)

Table 2 (*continued*)

| Atom | x | y | z | B (Å²) |
|---|---|---|---|---|
| C(116) | 0.751(2) | −0.225(1) | 0.757(1) | 6.0(5)* |
| C(121) | 0.925(1) | −0.158(1) | 0.8454(7) | 2.6(3)* |
| C(122) | 0.841(1) | −0.132(1) | 0.8884(7) | 3.1(3)* |
| C(123) | 0.837(1) | −0.159(1) | 0.9500(7) | 3.6(3)* |
| C(124) | 0.918(2) | −0.213(1) | 0.980(1) | 5.9(5)* |
| C(125) | 1.004(1) | −0.235(1) | 0.9396(9) | 4.7(4)* |
| C(126) | 1.009(2) | −0.210(1) | 0.8719(9) | 5.4(4)* |
| C(131) | 1.042(1) | −0.169(1) | 0.7239(8) | 4.4(4)* |
| C(132) | 1.139(1) | −0.131(1) | 0.7372(8) | 3.8(3)* |
| C(133) | 1.234(2) | −0.171(1) | 0.711(1) | 5.8(5)* |
| C(134) | 1.219(2) | −0.236(1) | 0.671(1) | 6.5(5)* |
| C(135) | 1.119(2) | −0.273(2) | 0.659(1) | 8.1(6)* |
| C(136) | 1.028(1) | −0.241(1) | 0.686(1) | 5.3(4)* |
| C(211) | 0.845(1) | 0.494(1) | 0.8204(7) | 3.0(3)* |
| C(212) | 0.866(1) | 0.562(1) | 0.855(1) | 5.4(4)* |
| C(213) | 0.774(1) | 0.603(1) | 0.8831(8) | 4.1(4)* |
| C(214) | 0.679(1) | 0.572(1) | 0.8820(8) | 3.7(3)* |
| C(215) | 0.662(2) | 0.494(1) | 0.849(1) | 5.7(5)* |
| C(216) | 0.748(1) | 0.459(1) | 0.8182(8) | 4.2(4)* |
| C(221) | 0.935(1) | 0.487(1) | 0.6916(7) | 2.9(3)* |
| C(222) | 0.983(2) | 0.449(2) | 0.642(1) | 7.7(6)* |
| C(223) | 0.985(2) | 0.480(2) | 0.580(2) | 11.4(9)* |
| C(224) | 0.907(1) | 0.553(1) | 0.5682(9) | 5.3(4)* |
| C(225) | 0.857(2) | 0.591(1) | 0.621(1) | 6.4(5)* |
| C(226) | 0.873(1) | 0.558(1) | 0.6847(8) | 4.1(4)* |
| C(231) | 1.081(1) | 0.485(1) | 0.7987(8) | 3.9(3)* |
| C(232) | 1.145(1) | 0.429(1) | 0.8366(9) | 4.7(4)* |
| C(233) | 1.241(2) | 0.463(2) | 0.863(1) | 8.0(6)* |
| C(234) | 1.272(2) | 0.545(2) | 0.849(1) | 7.1(6)* |
| C(235) | 1.211(2) | 0.598(2) | 0.809(1) | 6.9(5)* |
| C(236) | 1.111(1) | 0.570(1) | 0.7848(7) | 3.1(3)* |
| N(1) | 0.944(1) | 0.498(1) | 0.0912(9) | 7.3(5)* |
| C(71) | 0.371(2) | 0.440(1) | 0.624(1) | 6.0(5)* |
| C(72) | 0.333(3) | 0.474(2) | 0.692(2) | 13(1)* |
| C(73) | 0.490(2) | 0.452(2) | 0.531(1) | 8.8(7)* |
| C(74) | 0.564(2) | 0.502(2) | 0.481(1) | 11.2(9)* |
| C(75) | 0.036(2) | 0.460(2) | 0.131(1) | 10.9(8)* |
| C(76) | 0.616(2) | 0.477(2) | 0.645(1) | 11.5(9)* |
| C(77) | 0.890(2) | 0.419(2) | 0.071(2) | 11.7(9)* |
| C(78) | 0.769(3) | 0.449(3) | 0.025(2) | 15(1)* |
| N(2) | 0.432(2) | 0.261(2) | 0.975(1) | 10.7(7)* |
| C(81) | 0.463(2) | 0.206(2) | 1.006(1) | 9.8(8)* |
| C(82) | 0.513(2) | 0.125(2) | 0.024(1) | 7.8(6)* |

Starred atoms were refined isotropically.

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B(1,1)+b^2B(2,2)+c^2B(3,3)+ab(\cos\gamma)B(1,2)+ac(\cos\beta)B(1,3)+bc(\cos\alpha)B(2,3)]$.

Table 3
Selected bond distances (Å) of $[Cu_5Fe_6S_6(CO)_{16}(PPh_3)_2][Et_4N]\cdot MeCN$

| | | | |
|---|---|---|---|
| Cu(1)–Cu(2) | 2.809(3) | Fe(3)–C(31) | 1.75(2) |
| Cu(1)–Cu(3) | 2.799(3) | Fe(3)–C(32) | 1.87(2) |
| Cu(1)–Cu(4) | 2.602(3) | Fe(3)–C(33) | 1.84(2) |
| Cu(1)–Cu(5) | 2.619(3) | Fe(4)–S(3) | 2.294(4) |
| Cu(1)–Fe(4) | 2.734(3) | Fe(4)–S(4) | 2.353(5) |
| Cu(1)–Fe(5) | 2.697(3) | Fe(4)–C(41) | 1.84(3) |
| Cu(1)–S(4) | 2.246(5) | Fe(4)–C(42) | 1.84(2) |
| Cu(1)–S(5) | 2.252(5) | Fe(4)–C(43) | 1.83(2) |
| Cu(2)–Cu(3) | 2.823(3) | Fe(5)–Fe(6) | 2.517(4) |
| Cu(2)–Cu(4) | 2.590(3) | Fe(5)–S(5) | 2.326(5) |
| Cu(2)–Cu(5) | 2.613(4) | Fe(5)–S(6) | 2.292(5) |
| Cu(2)–Fe(1) | 2.696(3) | Fe(5)–C(51) | 1.82(2) |
| Cu(2)–Fe(6) | 2.729(3) | Fe(5)–C(52) | 1.72(2) |
| Cu(2)–S(1) | 2.256(5) | Fe(5)–C(53) | 1.89(2) |
| Cu(2)–S(6) | 2.247(5) | Fe(6)–S(5) | 2.283(4) |
| Cu(3)–Cu(4) | 2.574(3) | Fe(6)–S(6) | 2.352(5) |
| Cu(3)–Cu(5) | 2.623(3) | Fe(6)–C(61) | 1.81(2) |
| Cu(3)–Fe(2) | 2.714(3) | Fe(6)–C(62) | 1.76(3) |
| Cu(3)–Fe(3) | 2.688(3) | Fe(6)–C(63) | 1.85(2) |
| Cu(3)–S(2) | 2.235(4) | P(1)–C(111) | 1.81(2) |
| Cu(3)–S(3) | 2.255(5) | P(1)–C(121) | 1.77(2) |
| Cu(4)–S(1) | 2.431(4) | P(1)–C(131) | 1.90(2) |
| Cu(4)–S(3) | 2.444(5) | P(2)–C(211) | 1.89(2) |
| Cu(4)–S(5) | 2.457(4) | P(2)–C(221) | 1.82(2) |
| Cu(4)–P(1) | 2.261(5) | P(2)–C(231) | 1.83(2) |
| Cu(5)–S(2) | 2.424(4) | O(11)–C(11) | 1.04(2) |
| Cu(5)–S(4) | 2.493(4) | O(12)–C(12) | 1.06(2) |
| Cu(5)–S(6) | 2.470(5) | O(13)–C(13) | 1.09(2) |
| Cu(5)–P(2) | 2.291(5) | O(21)–C(21) | 1.11(2) |
| Fe(1)–Fe(2) | 2.532(4) | O(22)–C(22) | 1.20(3) |
| Fe(1)–S(1) | 2.341(5) | O(23)–C(23) | 1.16(2) |
| Fe(1)–S(2) | 2.300(5) | O(31)–C(31) | 1.10(2) |
| Fe(1)–C(11) | 1.83(2) | O(32)–C(32) | 1.06(2) |
| Fe(1)–C(12) | 1.80(2) | O(33)–C(33) | 1.10(2) |
| Fe(1)–C(13) | 1.84(2) | O(41)–C(41) | 1.05(2) |
| Fe(2)–S(1) | 2.299(5) | O(42)–C(42) | 1.10(3) |
| Fe(2)–S(2) | 2.344(5) | O(43)–C(43) | 1.12(2) |
| Fe(2)–C(21) | 1.80(2) | O(51)–C(51) | 1.07(3) |
| Fe(2)–C(22) | 1.77(2) | O(52)–C(52) | 1.21(2) |
| Fe(2)–C(23) | 1.81(2) | O(53)–C(53) | 1.09(2) |
| Fe(3)–Fe(4) | 2.526(3) | O(61)–C(61) | 1.14(2) |
| Fe(3)–S(3) | 2.326(5) | O(62)–C(62) | 1.14(3) |
| Fe(3)–S(4) | 2.312(5) | O(63)–C(63) | 1.08(2) |

Numbers in parentheses are e.s.d.s in the least significant digits.

This is consistent with the IR data of **1** (2050, 2020, 1990, 1910 $cm^{-1}$), which indicate the presence of the $Fe_2S_2(CO)_6$ unit [14,17,35,36]. There are fifteen metal–metal bonds including three Fe–Fe bond lengths of 2.521 Å, six Fe–Cu of 2.710 Å and six Cu–Cu of 2.604 Å in the cluster for stabilizing the structure of **1** with 168 skeleton electrons in accordance with the 9N-L (N, number of nuclear; L, number of M–M bonds) rule [37]. The two groups of Cu–S distances corresponding to two apical copper atoms ($Cu_A$–S) and the three copper atoms (Cu(1), Cu(2), Cu(3)) of the triangle in the central trigonal bipyramid ($Cu_T$–S) are 2.453 and 2.249 Å, respectively, reflecting that the two kinds of copper atoms with a different coordination environment possess a different electron density although their formal oxidation state is +1. By carefully inspecting the six Cu–S distances of the Cu atoms located in the triangle of the central trigonal bipyramid, it can be seen that the values of the Cu–S distances are divided into two groups, three of 2.243 Å and three of 2.254 Å, indicating the vestiges of fragment construction in the formation of cluster **1** (see following section).

Table 4
Selected bond angles (°) of $[Cu_5Fe_6S_6(CO)_{18}(PPh_3)_2][Et_4N]\cdot MeCN$

| | | | |
|---|---|---|---|
| Cu(2)–Cu(1)–Cu(3) | 60.45(7) | Cu(5)–Cu(2)–Fe(1) | 96.4(1) |
| Cu(2)–Cu(1)–Cu(4) | 57.05(7) | Cu(5)–Cu(2)–Fe(6) | 114.02(9) |
| Cu(2)–Cu(1)–Cu(5) | 57.41(8) | Cu(5)–Cu(2)–S(1) | 121.5(1) |
| Cu(2)–Cu(1)–Fe(4) | 142.60(9) | Cu(5)–Cu(2)–S(6) | 60.5(1) |
| Cu(2)–Cu(1)–Fe(5) | 85.74(8) | Fe(1)–Cu(2)–Fe(6) | 132.6(1) |
| Cu(2)–Cu(1)–S(4) | 113.7(1) | Fe(1)–Cu(2)–S(1) | 55.6(1) |
| Cu(2)–Cu(1)–S(5) | 69.6(1) | Fe(1)–Cu(2)–S(6) | 125.7(2) |
| Cu(2)–Cu(1)–S(6) | 47.0(2) | Fe(6)–Cu(2)–S(1) | 122.5(1) |
| Cu(3)–Cu(1)–Cu(4) | 56.78(7) | Fe(6)–Cu(2)–S(6) | 55.4(1) |
| Cu(3)–Cu(1)–Cu(5) | 57.79(7) | S(1)–Cu(2)–S(6) | 177.8(2) |
| Cu(3)–Cu(1)–Fe(4) | 83.94(8) | Cu(1)–Cu(3)–Cu(2) | 59.94(7) |
| Cu(3)–Cu(1)–Fe(5) | 145.12(9) | Cu(1)–Cu(3)–Cu(4) | 57.76(7) |
| Cu(3)–Cu(1)–S(4) | 67.7(1) | Cu(1)–Cu(3)–Cu(5) | 57.66(7) |
| Cu(3)–Cu(1)–S(5) | 113.7(1) | Cu(1)–Cu(3)–Fe(2) | 142.8(1) |
| Cu(3)–Cu(1)–S(6) | 97.5(2) | Cu(1)–Cu(3)–Fe(3) | 85.98(8) |
| Cu(4)–Cu(1)–Cu(5) | 102.49(9) | Cu(1)–Cu(3)–S(2) | 112.3(1) |
| Cu(4)–Cu(1)–Fe(4) | 95.15(9) | Cu(1)–Cu(3)–S(3) | 69.9(1) |
| Cu(4)–Cu(1)–Fe(5) | 113.37(9) | Cu(2)–Cu(3)–Cu(4) | 57.15(7) |
| Cu(4)–Cu(1)–S(4) | 119.7(1) | Cu(2)–Cu(3)–Cu(5) | 57.19(8) |
| Cu(4)–Cu(1)–S(5) | 60.3(1) | Cu(2)–Cu(3)–Fe(2) | 84.29(8) |
| Cu(4)–Cu(1)–S(6) | 100.7(1) | Cu(2)–Cu(3)–Fe(3) | 144.78(9) |
| Cu(5)–Cu(1)–Fe(4) | 114.4(1) | Cu(2)–Cu(3)–S(2) | 67.4(1) |
| Cu(5)–Cu(1)–Fe(5) | 98.10(9) | Cu(2)–Cu(3)–S(3) | 113.7(1) |
| Cu(5)–Cu(1)–S(4) | 61.1(1) | Cu(4)–Cu(3)–Cu(5) | 103.17(9) |
| Cu(5)–Cu(1)–S(5) | 122.6(1) | Cu(4)–Cu(3)–Fe(2) | 95.6(1) |
| Cu(5)–Cu(1)–S(6) | 53.7(2) | Cu(4)–Cu(3)–Fe(3) | 113.69(9) |
| Fe(4)–Cu(1)–Fe(5) | 130.85(9) | Cu(4)–Cu(3)–S(2) | 119.8(1) |
| Fe(4)–Cu(1)–S(4) | 55.4(1) | Cu(4)–Cu(3)–S(3) | 60.5(1) |
| Fe(4)–Cu(1)–S(5) | 121.2(1) | Cu(5)–Cu(3)–Fe(2) | 112.81(9) |
| Fe(4)–Cu(1)–S(6) | 161.9(1) | Cu(5)–Cu(3)–Fe(3) | 98.6(1) |
| Fe(5)–Cu(1)–S(4) | 125.8(1) | Cu(5)–Cu(3)–S(2) | 59.3(1) |
| Fe(5)–Cu(1)–S(5) | 55.2(1) | Cu(5)–Cu(3)–S(3) | 123.2(1) |
| Fe(5)–Cu(1)–S(6) | 48.9(1) | Fe(2)–Cu(3)–Fe(3) | 130.7(1) |
| S(4)–Cu(1)–S(5) | 176.4(2) | Fe(2)–Cu(3)–S(2) | 55.5(1) |
| S(4)–Cu(1)–S(6) | 108.4(2) | Fe(2)–Cu(3)–S(3) | 122.2(1) |
| S(5)–Cu(1)–S(6) | 74.9(1) | Fe(3)–Cu(3)–S(2) | 125.1(1) |
| Cu(1)–Cu(2)–Cu(3) | 59.61(6) | Fe(3)–Cu(3)–S(3) | 55.3(1) |
| Cu(1)–Cu(2)–Cu(4) | 57.46(7) | S(2)–Cu(3)–S(3) | 177.6(2) |
| Cu(1)–Cu(2)–Cu(5) | 57.65(7) | Cu(1)–Cu(4)–Cu(2) | 65.49(8) |
| Cu(1)–Cu(2)–Fe(1) | 143.4(1) | Cu(1)–Cu(4)–Cu(3) | 65.48(8) |
| Cu(1)–Cu(2)–Fe(6) | 83.79(8) | Cu(1)–Cu(4)–S(1) | 114.8(1) |
| Cu(1)–Cu(2)–S(1) | 113.2(1) | Cu(1)–Cu(4)–S(3) | 70.9(1) |
| Cu(1)–Cu(2)–S(6) | 67.0(1) | Cu(1)–Cu(4)–S(5) | 52.8(1) |
| Cu(3)–Cu(2)–Cu(4) | 56.59(7) | Cu(1)–Cu(4)–P(1) | 140.7(2) |
| Cu(3)–Cu(2)–Cu(5) | 57.56(7) | Cu(2)–Cu(4)–Cu(3) | 66.28(8) |
| Cu(3)–Cu(2)–Fe(1) | 85.24(8) | Cu(2)–Cu(4)–S(1) | 53.3(1) |
| Cu(3)–Cu(2)–Fe(6) | 141.58(9) | Cu(2)–Cu(4)–S(3) | 115.7(1) |
| Cu(3)–Cu(2)–S(1) | 68.9(1) | Cu(2)–Cu(4)–S(5) | 70.8(1) |
| Cu(3)–Cu(2)–S(6) | 112.7(1) | Cu(2)–Cu(4)–P(1) | 138.5(2) |
| Cu(4)–Cu(2)–Cu(5) | 103.01(9) | Cu(3)–Cu(4)–S(1) | 71.1(1) |
| Cu(4)–Cu(2)–Fe(1) | 113.04(9) | Cu(3)–Cu(4)–S(3) | 53.3(1) |
| Cu(4)–Cu(2)–Fe(6) | 95.27(9) | Cu(3)–Cu(4)–S(5) | 114.7(1) |
| Cu(4)–Cu(2)–S(1) | 59.7(1) | Cu(3)–Cu(4)–P(1) | 144.2(2) |
| Cu(4)–Cu(2)–S(6) | 119.7(1) | S(1)–Cu(4)–S(3) | 115.9(2) |
| S(1)–Cu(4)–S(5) | 115.9(2) | Fe(1)–Fe(2)–S(2) | 56.1(1) |
| S(1)–Cu(4)–P(1) | 102.3(2) | Fe(1)–Fe(2)–C(21) | 105.0(5) |
| S(3)–Cu(4)–S(5) | 114.7(1) | Fe(1)–Fe(2)–C(22) | 95.2(6) |
| S(3)–Cu(4)–P(1) | 105.1(2) | Fe(1)–Fe(2)–C(23) | 156.2(6) |
| S(5)–Cu(4)–P(1) | 100.0(2) | S(1)–Fe(2)–S(2) | 84.8(2) |
| Cu(1)–Cu(5)–Cu(2) | 64.94(8) | S(1)–Fe(2)–C(21) | 162.7(5) |
| Cu(1)–Cu(5)–Cu(3) | 64.55(8) | S(1)–Fe(2)–C(22) | 89.4(6) |
| Cu(1)–Cu(5)–S(2) | 112.5(1) | S(1)–Fe(2)–C(23) | 103.8(7) |
| Cu(1)–Cu(5)–S(4) | 52.0(1) | S(2)–Fe(2)–C(21) | 84.4(5) |

(continued)

Table 4 (*continued*)

| | | | |
|---|---|---|---|
| Cu(1)–Cu(5)–S(6) | 67.5(1) | S(2)–Fe(2)–C(22) | 148.8(6) |
| Cu(1)–Cu(5)–P(2) | 142.2(2) | S(2)–Fe(2)–C(23) | 111.3(7) |
| Cu(2)–Cu(5)–Cu(3) | 65.25(9) | C(21)–Fe(2)–C(22) | 92.9(9) |
| Cu(2)–Cu(5)–S(2) | 68.8(1) | C(21)–Fe(2)–C(23) | 92.7(8) |
| Cu(2)–Cu(5)–S(4) | 112.3(1) | C(22)–Fe(2)–C(23) | 100(1) |
| Cu(2)–Cu(5)–S(6) | 52.4(1) | Cu(3)–Fe(3)–Fe(4) | 90.40(9) |
| Cu(2)–Cu(5)–P(2) | 142.8(2) | Cu(3)–Fe(3)–S(3) | 52.9(1) |
| Cu(3)–Cu(5)–S(2) | 52.4(1) | Cu(3)–Fe(3)–S(4) | 69.1(1) |
| Cu(3)–Cu(5)–S(4) | 67.6(1) | Cu(3)–Fe(3)–C(31) | 118.7(5) |
| Cu(3)–Cu(5)–S(6) | 112.4(1) | Cu(3)–Fe(3)–C(32) | 145.5(5) |
| Cu(3)–Cu(5)–P(2) | 140.1(2) | Cu(3)–Fe(3)–C(33) | 68.5(5) |
| S(2)–Cu(5)–S(4) | 113.1(2) | Fe(4)–Fe(3)–S(3) | 56.3(1) |
| S(2)–Cu(5)–S(6) | 115.1(2) | Fe(4)–Fe(3)–S(4) | 58.0(1) |
| S(2)–Cu(5)–P(2) | 103.7(2) | Fe(4)–Fe(3)–C(31) | 101.0(5) |
| S(4)–Cu(5)–S(6) | 112.7(2) | Fe(4)–Fe(3)–C(32) | 97.7(6) |
| S(4)–Cu(5)–P(2) | 104.1(2) | Fe(4)–Fe(3)–C(33) | 157.0(6) |
| S(6)–Cu(5)–P(2) | 106.9(2) | S(3)–Fe(3)–S(4) | 85.5(2) |
| Cu(2)–Fe(1)–Fe(2) | 90.56(9) | S(3)–Fe(3)–C(31) | 85.0(6) |
| Cu(2)–Fe(1)–S(1) | 52.6(1) | S(3)–Fe(3)–C(32) | 152.6(5) |
| Cu(2)–Fe(1)–S(2) | 69.1(1) | S(3)–Fe(3)–C(33) | 112.0(6) |
| Cu(2)–Fe(1)–C(11) | 147.7(5) | S(4)–Fe(3)–C(31) | 158.8(5) |
| Cu(2)–Fe(1)–C(12) | 116.0(5) | S(4)–Fe(3)–C(32) | 87.1(5) |
| Cu(2)–Fe(1)–C(13) | 67.2(6) | S(4)–Fe(3)–C(33) | 104.1.(6) |
| Fe(2)–Fe(1)–S(1) | 56.2(1) | C(31)–Fe(3)–C(32) | 92.6(8) |
| Fe(2)–Fe(1)–S(2) | 57.9(1) | C(31)–Fe(3)–C(33) | 97.1(8) |
| Fe(2)–Fe(1)–C(11) | 96.5(6) | C(32)–Fe(3)–C(33) | 95.4(8) |
| Fe(2)–Fe(1)–C(12) | 104.5(5) | Cu(1)–Fe(4)–Fe(3) | 90.65(9) |
| Fe(2)–Fe(1)–C(13) | 155.2(6) | Cu(1)–Fe(4)–S(3) | 70.7(1) |
| S(1)–Fe(1)–S(2) | 84.8(2) | Cu(1)–Fe(4)–S(4) | 51.7(1) |
| S(1)–Fe(1)–C(11) | 150.8(6) | Cu(1)–Fe(4)–C(41) | 116.3(6) |
| S(1)–Fe(1)–C(12) | 85.8(5) | Cu(1)–Fe(4)–C(42) | 147.3(6) |
| S(1)–Fe(1)–C(13) | 112.0(7) | Cu(1)–Fe(4)–C(43) | 67.8(5) |
| S(2)–Fe(1)–C(11) | 88.2(6) | Fe(3)–Fe(4)–S(3) | 57.5(1) |
| S(2)–Fe(1)–C(12) | 162.1(6) | Fe(3)–Fe(4)–S(4) | 56.5(1) |
| S(2)–Fe(1)–C(13) | 102.1(6) | Fe(3)–Fe(4)–C(41) | 101.2(6) |
| C(11)–Fe(1)–C(12) | 92.7(7) | Fe(3)–Fe(4)–C(42) | 98.9(6) |
| C(11)–Fe(1)–C(13) | 97.2(9) | Fe(3)–Fe(4)–C(43) | 157.6(5) |
| C(12)–Fe(1)–C(13) | 95.4(9) | S(3)–Fe(4)–S(4) | 85.3(2) |
| Cu(3)–Fe(2)–Fe(1) | 90.83(9) | S(3)–Fe(4)–C(41) | 158.4(7) |
| Cu(3)–Fe(2)–S(1) | 70.4(1) | S(3)–Fe(4)–C(42) | 88.3(6) |
| Cu(3)–Fe(2)–S(2) | 51.8(1) | S(3)–Fe(4)–C(43) | 107.4(5) |
| Cu(3)–Fe(2)–C(21) | 112.4(5) | S(4)–Fe(4)–C(41) | 84.6(7) |
| Cu(3)–Fe(2)–C(22) | 151.4(6) | S(4)–Fe(4)–C(42) | 153.7(6) |
| Cu(3)–Fe(2)–C(23) | 67.4(6) | S(4)–Fe(4)–C(43) | 109.6(5) |
| Fe(1)–Fe(2)–S(1) | 57.7(1) | C(41)–Fe(4)–C(42) | 92.5(8) |
| C(41)–Fe(4)–C(43) | 94.0(8) | Cu(5)–S(2)–Fe(2) | 137.7(2) |
| C(42)–Fe(4)–C(43) | 96.8(8) | Fe(1)–S(2)–Fe(2) | 66.1(1) |
| Cu(1)–Fe(5)–Fe(6) | 90.29(9) | Cu(3)–S(3)–Cu(4) | 66.3(1) |
| Cu(1)–Fe(5)–S(5) | 52.7(1) | Cu(3)–S(3)–Fe(3) | 71.8(2) |
| Cu(1)–Fe(5)–S(6) | 68.5(1) | Cu(3)–S(3)–Fe(4) | 108.9(2) |
| Cu(1)–Fe(5)–C(51) | 143.8(6) | Cu(4)–S(3)–Fe(3) | 135.0(2) |
| Cu(1)–Fe(5)–C(52) | 118.5(6) | Cu(4)–S(3)–Fe(4) | 112.5(2) |
| Cu(1)–Fe(5)–C(53) | 68.5(5) | Fe(3)–S(3)–Fe(4) | 66.3(1) |
| Fe(6)–Fe(5)–S(5) | 56.1(1) | Cu(1)–S(4)–Cu(5) | 66.9(1) |
| Fe(6)–Fe(5)–S(6) | 58.3(1) | Cu(1)–S(4)–Fe(3) | 110.4(2) |
| Fe(6)–Fe(5)–C(51) | 98.2(6) | Cu(1)–S(4)–Fe(4) | 72.9(1) |
| Fe(6)–Fe(5)–C(52) | 101.7(6) | Cu(5)–S(4)–Fe(3) | 113.7(2) |
| Fe(6)–Fe(5)–C(53) | 157.7(5) | Cu(5)–S(4)–Fe(4) | 136.4(2) |
| S(5)–Fe(5)–S(6) | 85.1(2) | Fe(3)–S(4)–Fe(4) | 65.5(1) |
| S(5)–Fe(5)–C(51) | 153.4(6) | Cu(1)–S(5)–Cu(4) | 66.9(1) |
| S(5)–Fe(5)–C(52) | 85.6(6) | Cu(1)–S(5)–Fe(5) | 72.2(1) |
| S(5)–Fe(5)–C(53) | 111.2(5) | Cu(1)–S(5)–Fe(6) | 109.3(2) |
| S(6)–Fe(5)–C(51) | 86.2(6) | Cu(4)–S(5)–Fe(5) | 135.6(2) |
| S(6)–Fe(5)–C(52) | 159.8(6) | Cu(4)–S(5)–Fe(6) | 112.1(2) |

(continued)

Table 4 (*continued*)

| | | | |
|---|---|---|---|
| S(6)–Fe(5)–C(53) | 105.3(5) | Fe(5)–S(5)–Fe(6) | 66.2(1) |
| C(51)–Fe(5)–C(52) | 94.2(9) | Cu(1)–S(6)–Cu(2) | 66.0(1) |
| C(51)–Fe(5)–C(53) | 95.4(9) | Cu(1)–S(6)–Cu(5) | 58.8(2) |
| C(52)–Fe(5)–C(53) | 95.0(8) | Cu(1)–S(6)–Fe(5) | 62.5(1) |
| Cu(2)–Fe(6)–Fe(5) | 91.05(9) | Cu(1)–S(6)–Fe(6) | 90.6(2) |
| Cu(2)–Fe(6)–S(5) | 70.7(1) | Cu(2)–S(6)–Cu(5) | 67.1(1) |
| Cu(2)–Fe(6)–S(6) | 51.9(1) | Cu(2)–S(6)–Fe(5) | 111.3(2) |
| Cu(2)–Fe(6)–C(61) | 145.8(6) | Cu(2)–S(6)–Fe(6) | 72.8(1) |
| Cu(2)–Fe(6)–C(62) | 115.6(7) | Cu(5)–S(6)–Fe(5) | 114.9(2) |
| Cu(2)–Fe(6)–C(63) | 67.3(5) | Cu(5)–S(6)–Fe(6) | 136.7(2) |
| Fe(5)–Fe(6)–S(5) | 57.7(1) | Fe(5)–S(6)–Fe(6) | 65.7(1) |
| Fe(5)–Fe(6)–S(6) | 56.0(1) | Fe(6)–C(61)–O(61) | 174(2) |
| Fe(5)–Fe(6)–C(61) | 97.3(5) | Fe(6)–C(62)–O(62) | 176(2) |
| Fe(5)–Fe(6)–C(62) | 102.0(6) | Fe(6)–C(63)–O(63) | 173(2) |
| Fe(5)–Fe(6)–C(63) | 157.1(5) | Cu(4)–P(1)–C(111) | 116.1(6) |
| S(5)–Fe(6)–S(6) | 84.7(2) | Cu(4)–P(1)–C(121) | 114.0(6) |
| S(5)–Fe(6)–C(61) | 86.0(6) | Cu(4)–P(1)–C(131) | 113.7(6) |
| S(5)–Fe(6)–C(62) | 159.5(7) | C(111)–P(1)–C(121) | 103.6(7) |
| S(5)–Fe(6)–C(63) | 105.9(6) | C(111)–P(1)–C(131) | 103.1(8) |
| S(6)–Fe(6)–C(61) | 152.5(5) | C(121)–P(1)–C(131) | 105.2(8) |
| S(6)–Fe(6)–C(62) | 85.1(6) | Cu(5)–P(2)–C(211) | 115.5(6) |
| S(6)–Fe(6)–C(63) | 110.3(6) | Cu(5)–P(2)–C(221) | 113.6(6) |
| C(61)–Fe(6)–C(62) | 95.1(8) | Cu(5)–P(2)–C(231) | 114.6(6) |
| C(61)–Fe(6)–C(63) | 97.1(8) | C(211)–P(2)–C(221) | 102.7(7) |
| C(62)–Fe(6)–C(63) | 94.2(8) | C(211)–P(2)–C(231) | 105.9(8) |
| Cu(2)–S(1)–Cu(4) | 67.1(1) | C(221)–P(2)–C(231) | 103.3(8) |
| Cu(2)–S(1)–Fe(1) | 71.8(1) | Fe(1)–C(11)–O(11) | 179(3) |
| Cu(2)–S(1)–Fe(2) | 109.3(2) | Fe(1)–C(12)–O(12) | 178(2) |
| Cu(4)–S(1)–Fe(1) | 135.1(2) | Fe(1)–C(13)–O(13) | 169(2) |
| Cu(4)–S(1)–Fe(2) | 112.0(2) | Fe(2)–C(21)–O(21) | 175(2) |
| Fe(1)–S(1)–Fe(2) | 66.1(1) | Fe(2)–C(22)–O(22) | 176(2) |
| Cu(3)–S(2)–Cu(5) | 68.5(1) | Fe(2)–C(23)–O(23) | 167(2) |
| Cu(3)–S(2)–Fe(1) | 111.1(2) | Fe(3)–C(31)–O(31) | 178(2) |
| Cu(3)–S(2)–Fe(2) | 72.7(1) | Fe(3)–C(32)–O(32) | 179(2) |
| Cu(5)–S(2)–Fe(1) | 113.8(2) | Fe(3)–C(33)–O(33) | 170(2) |
| Fe(5)–C(51)–O(51) | 179(3) | Fe(4)–C(41)–O(41) | 179(2) |
| Fe(5)–C(52)–O(52) | 177(2) | Fe(4)–C(42)–O(42) | 174(2) |
| Fe(5)–C(53)–O(53) | 170(2) | Fe(4)–C(43)–O(43) | 166(2) |

Numbers in parentheses are e.s.d.s in the least significant digits.

### 3.2. *Synthesis of 1 and possible reaction pathway for the formation of 1 in solution*

Cluster **1** was synthesized by the reaction of $Li_2[Fe_2S_2(CO)_6]$ with $[Et_4N][CuCl_2PPh_3]$ in MeCN/THF as shown in Eq. (1). It is obvious that the reaction

$$5[Et_4N][CuCl_2PPh_3] + 3Li_2[Fe_2S_2(CO)_6] \rightleftharpoons [Et_4N][Fe_6Cu_5S_6(CO)_{18}(PPh_3)_2] + 6LiCl + 4Et_4NCl + 3PPh_3 \quad (1)$$

only involves condensation with elimination of LiCl and substitution of Cl and $PPh_3$ ligands because the Fe and Cu atoms in cluster **1** maintain the same oxidation states as in the starting materials.

A careful examination of the structural parameters of cluster **1**, reveals several traces which indicate its formation process. (i) Cluster **1** contains two kinds of Cu–S bond distances (Table 6) for the copper atoms at the apex and on the triangle of the central trigonal bipyramid, and the Cu–S bond lengths (2.453 Å) for the apex Cu are much greater than those for the Cu atoms on the triangle (2.249 Å). This indicates that the core of cluster **1** consists of two kinds of moieties, one is $Fe_6S_6Cu_3$ (Fig. 3, F) which is composed of three $Fe_2S_2(CO)_6$ units and three Cu atoms located on the triangle of a trigonal bipyarmid, and the other is two apex Cu atoms with the $PPh_3$ ligand. (ii) The six Cu–S bond distances in the moiety F are divided into two groups of values (three of 2.243 Å and three of 2.254 Å) in a regular arrangement. This is evidence that the moiety F should come from three identical $Fe_2S_2Cu$ moieties (Fig. 3, G). Therefore on the basis of the structural traces seen in cluster **1** it is suggested that a possible reaction pathway for its formation in solution includes steps of condensation, trimerization and capping via the formation of two reactive fragments **H** and **I** which possess the same cores as the moieties G and F, respectively.

$$3Li_2[Fe_2S_2(CO)_6] + 3[Et_4N][CuCl_2PPh_3] \xrightleftharpoons{\text{condensation}} 3[Et_4N]Li[Fe_2CuS_2(CO)_6ClPPh_3] + 3LiCl \quad (2)$$

**H**

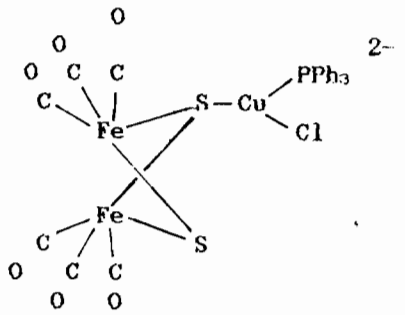
$$3[Et_4N]Li[Fe_2CuS_2(CO)_6ClPPh_3] \xrightleftharpoons{\text{trimerization}} [Et_4N]_3[Fe_6Cu_3(CO)_{18}S_6] + 3LiCl + 3PPh_3 \quad (3)$$

**I**

$$[Et_4N]_3[Fe_6Cu_3(CO)_{18}S_6] + 2[Et_4N][CuCl_2PPh_3] \xrightleftharpoons{\text{capping}} [Et_4N][Fe_6Cu_5(CO)_{18}S_6(PPh_3)_2] + 4Et_4NCl \quad (4)$$

**1**

As shown in Eqs. (2), (3) and (4), the reaction of $Li_2[Fe_2S_2(CO)_6]$ with $[Et_4N][CuCl_2PPh_3]$ by elimination of LiCl results in a condensation product, reactive fragment **H**, and three **H** undergo further trimerization by elimination of LiCl, substitution of $PPh_3$ and conversion of some of the terminal carbonyls to bridging carbonyls affording the nona-nuclear reactive




The anion of **H**

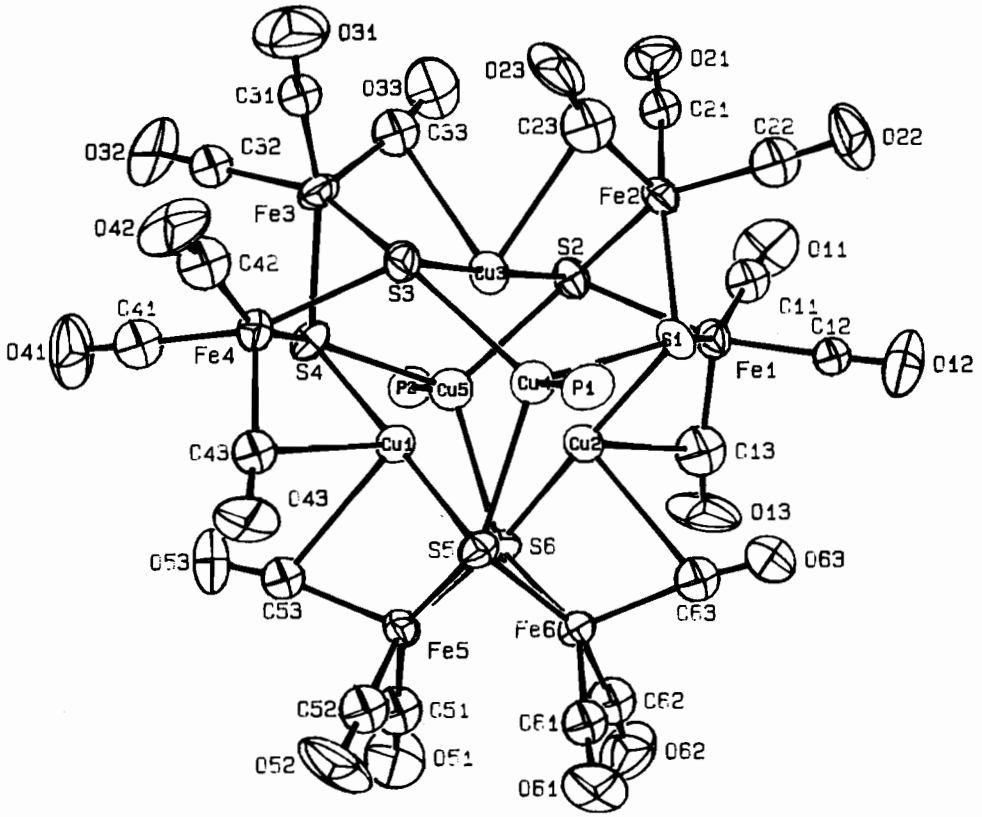
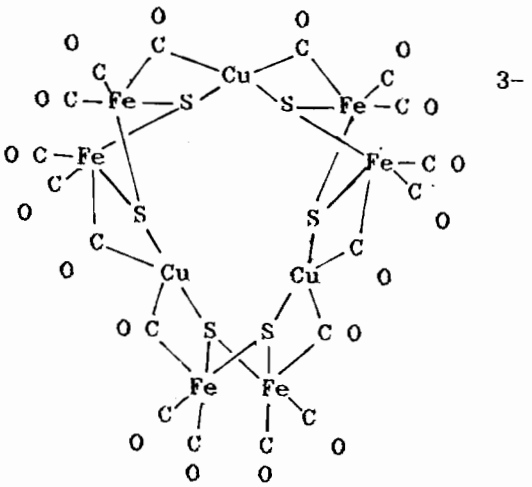



Fig. 1. The ORTEP drawing of the anion of $[Et_4N][Fe_6Cu_5(CO)_{18}S_6(PPh_3)_2]$ (**1**) with omission of benzene rings in the $PPh_3$ group.




The anion of **I**

fragment **I**. **I** reacts with $[Et_4N][CuCl_2PPh_3]$ by capping two $CuPPh_3$ moieties leading to the final cluster **1**. Thus, although cluster **1** was prepared by a spontaneous self-assembly reaction of simple starting materials, it should actually form via a 'unit construction' [38] using the reactive fragments as building blocks.

## 4. Conclusions

The first Fe–Cu–S cluster compound $[Et_4N][Fe_6Cu_5(CO)_{18}S_6(PPh_3)_2]$ (**1**) was prepared by the reaction of

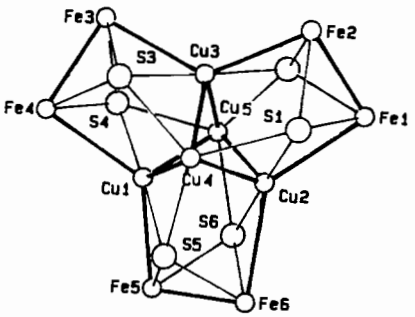



Fig. 2. The Fe–Cu–S core in $[Fe_6Cu_5(CO)_{18}S_6(PPh_3)_2]^-$.

$[Fe_2S_2(CO)_6]^{2-}$ with $[CuCl_2PPh_3]^-$. A structural study reveals that **1** contains a *closo*-type undeca-nuclear core with a new coordination mode of the $Fe_2S_2(CO)_6$ units and it retains the vestiges of the formation process of the cluster. A possible reaction pathway including condensation, trimerization and capping steps via the formation of two reactive fragments is suggested.

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Table 5
Selected structural parameters of $Fe_2S_2(CO)_6$-containing complexes

| Complexes | Fe–Fe (Å) | Fe–S (Å) | Fe–S–Fe (°) | |
|---|---|---|---|---|
| $[Fe_2S_2(CO)_6]$ | 2.552(2) | 2.222(3)–2.238(4) | 69.67(12)–70.08(11) | [32] |
| $[MoOFe_5S_6(CO)_{12}]^{2-}$ | 2.480(3)–2.434(3) | 2.246(5)–2.286(5) | 65.9(5)–67.3(5) | [17] |
| $[MoFe_5S_6(CO)_6(PEt_3)_3]$ | 2.564(5) | | | [33] |
| $[MoFe_4S_3(CO)_{13}(PEt_3)_3]^{2-}$ | 2.553(3) | 2.274(5)–2.286(5) | 68.1(1) | [26] |
| $[MoFe_3S_6(CO)_6]^{2-}$ | 2.491(4) | 2.301(6)–2.318(6) | | [34] |
| $[Fe_6Cu_5S_6(CO)_{18}(PPh_3)_2]^-$ | 2.517(4)–2.532(4) | 2.292(5)–2.353(6) | 65.5(1)–66.3(1) | this work |
| $[Fe_6S_6(CO)_{12}]^{2-}$ | 2.499(1) | 2.315(2)–2.337(2) | | [17b] |

Table 6
Bond distances (Å) of Cu–S in cluster compound **1**

| | |
|---|---|
| $Cu_A$–S | 2.431(4); 2.444(5); 2.457(4)<br>2.493(4); 2.470(4); 2.424(4) |
| $Cu_T$–S | 2.246(5); 2.247(5); 2.235(4)<br>2.252(5); 2.256(5); 2.255(5) |

$Cu_A$–Cu atoms at the apex of the central trigonal bipyramid $Cu_5$.
$Cu_T$–Cu atoms on the triangle of the central trigonal bipyramid $Cu_5$.

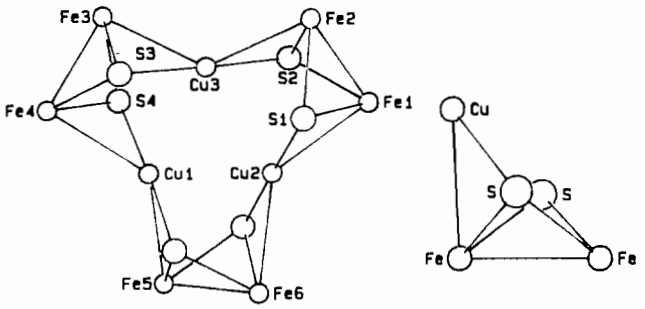


Fig. 3. The $Fe_6C_6Cu_3$ (F) and $Fe_2CuS_2$ (G) moieties of the core in cluster **1**.

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