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# Synthesis and characterization of new heterometallic iron sulfur nitrosyl clusters

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Dedicated to Professor Dieter Fenske on the occasion of his 65th Birthday

#### Abstract

The reactivity of the (PPN)<sub>2</sub>[Fe<sub>8</sub>S<sub>6</sub>(NO)<sub>8</sub>] and (PPN)<sub>2</sub>[Fe<sub>6</sub>S<sub>6</sub>(NO)<sub>6</sub>] clusters is explored and new derivative clusters have been synthesized and structurally characterized. The unique (PPN)<sub>2</sub>Fe<sub>4</sub>S<sub>4</sub>(NO)<sub>6</sub> "open-cubane" cluster with a chair like Fe<sub>4</sub>S<sub>4</sub> core is obtained along with the mixed metal pentandite-like clusters (PPN)<sub>2</sub>[Mo<sub>2</sub>Fe<sub>6</sub>S<sub>6</sub>(NO)<sub>6</sub>(CO)<sub>6</sub>], (PPr<sub>3</sub>)<sub>2</sub>Cu<sub>2</sub>Fe<sub>6</sub>S<sub>6</sub>(NO)<sub>6</sub>, (PPr<sub>3</sub>)<sub>4</sub>Cu<sub>4</sub>Fe<sub>4</sub>S<sub>6</sub>(NO)<sub>4</sub>, (PPr<sub>3</sub>)<sub>2</sub>Ni<sub>2</sub>-Fe<sub>6</sub>S<sub>6</sub>(NO)<sub>6</sub>, (PPr<sub>3</sub>)<sub>3</sub>Ni<sub>3</sub>Fe<sub>4</sub>S<sub>6</sub>(NO)<sub>4</sub>. The rich electrochemistry of the mixed metal clusters is presented as well. Published by Elsevier Ltd.

Keywords: Iron sulfur clusters; Nitrosyl coordination

# 1. Introduction

The diversity of Fe/S cluster chemistry is expressed in a multitude of stoichiometries, ligand (L) types and structures and in a general broad sense the Fe/S/L clusters can be classified as Fe/S/X (X = halogens, thiols), Fe/S/CO, Fe/S/PR<sub>3</sub> and Fe/S/NO species. Examples of these clusters (Scheme 1) include the [Fe<sub>4</sub>S<sub>4</sub>(L)<sub>4</sub>]<sup>*n*</sup> cubanes [1,2], the sulfur voided [Fe<sub>4</sub>S<sub>3</sub>] cube of (Ph<sub>4</sub>As)[Fe<sub>4</sub>S<sub>3</sub>(NO)<sub>7</sub>] [3], the iron voided [Fe<sub>3</sub>S<sub>4</sub>] cube in (Et<sub>4</sub>N)<sub>3</sub>[Fe<sub>3</sub>S<sub>4</sub>(LS<sub>3</sub>)], (LS<sub>3</sub> = 1,3,5-Tris((4,6-dimethyl-3-mercaptophenyl)thio)-2, 4,6-tris(*p*-tolylthio)benzene) [4], the Fe<sub>6</sub>S<sub>6</sub> prism in the [Fe<sub>6</sub>S<sub>6</sub>(L)<sub>6</sub>]<sup>*n*</sup> prismanes (L = halogens, MeOC<sub>6</sub>H<sub>4</sub>O or nitrosyl) [5–7], the "bow-tie" [Fe<sub>6</sub>S<sub>6</sub>] core in (PPN)<sub>2</sub>-[Fe<sub>6</sub>S<sub>6</sub>(CO)<sub>12</sub>] [8] (PPN = Bis(triphenylphospine)iminium), the edge-fused double cubane [Fe<sub>8</sub>S<sub>8</sub>] core in Fe<sub>8</sub>S<sub>8</sub>(PCy<sub>3</sub>)<sub>6</sub> [9] (PCy<sub>3</sub> = Tricyclohexylphosphine).

Interest in the coordination chemistry of metal-nitrosyl clusters stems from the recognition of the important role

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nitric oxide plays in living systems as a vasodilator and a signaling molecule [10–12]. Various iron sulfur nitrosyl clusters are known and  $(NH_4)$ [Fe<sub>4</sub>S<sub>3</sub>(NO)<sub>7</sub>][13] also known as the Roussin black salt is the oldest and the most well studied member of this class. This molecule is also recognized as an important physiological NO donor due to its ability to penetrate membranes of cells and slowly release NO [14–16].

In a recent communication [17] we have reported the synthesis of  $(PPN)_2[Fe_8S_6(NO)_8]$ ,  $(PPN)_2[Fe_6S_6(NO)_6]$  and  $(PPN)_2[Fe_4S_4(NO)_4]$  and in this article we report further on the reactivity and derivatives of the  $PPN^+$  salts of the  $[Fe_8S_6(NO)_8]^{2-}$  and  $[Fe_6S_6(NO)_6]^{2-}$  clusters and the isolation of the unique  $(PPN)_2[Fe_4S_4(NO)_6]$  "opencubane" cluster with a chair like  $Fe_4S_4$  core, and also we report the synthesis of new M/Fe/S/NO clusters (M=Ni, Cu, Mo) with a cubeoctahedral  $M_8S_6$  core.

The cubeoctahedral  $M_8S_6$  "pentandite-like" core with a cubic array of metal atoms inscribed in an  $S_6$  octahedron of  $\mu_4$ -sulfido ligands has been observed in minerals [18] and also in molecular clusters with halides [19–23] as terminal ligands.

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Scheme 1. Examples of different arrangements of Fe/S clusters.

# 2. Experimental

All Reactions have been performed under a dinitrogen atmosphere in a glove box and standard shlenck line techniques. All solvents have been distilled and degassed, except of DMF that was not distilled.

 $(NH_4)$ [Fe<sub>4</sub>S<sub>3</sub>(NO)<sub>7</sub>][24], (PPN)<sub>2</sub>[Fe<sub>4</sub>(CO)<sub>13</sub>][25], Benzyl trisulfide (Bz<sub>2</sub>S<sub>3</sub>) [26], Mo(CO)<sub>3</sub>(MeCN)<sub>3</sub> [27], [Ni-(MeCN)<sub>6</sub>](BF<sub>4</sub>)<sub>2</sub> [28] were synthesized according to published procedures. [Cu(MeCN)<sub>4</sub>]PF<sub>6</sub>, Fe(CO)<sub>5</sub>, SCl<sub>2</sub> and Bu<sub>4</sub>NSH were purchased from commercial sources.

IR spectra were obtained on a Perkin–Elmer BX FT-IR spectrometer (mid-IR) and a Nicolet 740 FT-IR spectrometer (Far-IR) in KBr pellets. Mass Spectra were collected on a Micromass LCT Time-of-Flight mass spectrometer. Elemental analyses were performed by the Microanalytical Laboratory at the University of Michigan. Microbeam Electron Analysis was performed at The University of Michigan Electron Microbeam Analysis Laboratory (EMAL). and Cyclic Voltammetry experiments were carried out on a Glass Carbon working electrode and Ag/ AgCl reference electrode with 0.1 M  $Bu_4NPF_6$  supporting electrolyte on a EG&G Princeton Potentiostat/Galvanostat model 263 A. The reduction potentials are reported against a standard calomel electrode SCE.

# 2.1. Bis(Bis(triphenylphospine)iminium) hexasulfidooctairon-octanitrosyl, $(PPN)_2[Fe_8S_6(NO)_8)]$

An amount of  $(NH_4)[Fe_4S_3(NO)_7]$  (0.50 g, 0.87 mmol) and  $(PPN)_2[Fe_4(CO)_{13}]$  (2.17 g 1.30 mmol) were dissolved in 20 ml MeCN and allowed to stir for 24 h. The precipitate obtained by filtration was washed with 5 ml MeCN, dissolved in 15 ml DMF and the resulting solution layered with ca. 150 ml ether, affording 0.80 g of a black crystalline product. Yield 0.41 mmol 94% of (PPN)<sub>2</sub>[Fe<sub>8</sub>S<sub>6</sub>(NO)<sub>8</sub>] yield based on [Fe<sub>4</sub>S<sub>3</sub>(NO)<sub>7</sub>]<sup>-</sup> as the only source of Fe. Elemental *Anal.* Calc. for (PPN)<sub>2</sub>[Fe<sub>8</sub>S<sub>6</sub>(NO)<sub>8</sub>] · DMF C<sub>75</sub>H<sub>67</sub>N<sub>11</sub>O<sub>9</sub>P<sub>4</sub>S<sub>6</sub>-Fe<sub>8</sub>: C, 44.39; H, 3.33; N, 7.59. Found: C, 44.75, H, 3.48, N, 7.36%. IR: 3054(w), 2690(m), 2928(m), 2868(w), 1684(vs)(v<sub>N-O</sub>), 1427(m), 1263(m), 1113(m), 797(w), 744(w), 723(m), 690(m), 550(m), 532(m), 526(w), 495(w). MS: (ESI –) 878.6 Fe<sub>8</sub>S<sub>6</sub>(NO)<sub>8</sub><sup>-</sup>, 788.2 Fe<sub>8</sub>S<sub>6</sub>(NO)<sub>5</sub><sup>-</sup>, 707.2 Fe<sub>6</sub>S<sub>6</sub>(NO)<sub>6</sub><sup>-</sup>, 647.3 Fe<sub>6</sub>S<sub>6</sub>(NO)<sub>4</sub><sup>-</sup>, 617.3 Fe<sub>6</sub>S<sub>6</sub>-(NO)<sub>3</sub><sup>-</sup>, 587.3 Fe<sub>6</sub>S<sub>6</sub>(NO)<sub>2</sub><sup>-</sup>, 471.5 Fe<sub>4</sub>S<sub>4</sub>(NO)<sub>4</sub><sup>-</sup>, 441.5 Fe<sub>4</sub>S<sub>4</sub>(NO)<sub>3</sub><sup>-</sup>, 411.52 Fe<sub>4</sub>S<sub>4</sub>(NO)<sub>2</sub><sup>-</sup>. MS: (ESI +) 537.8 (PPN<sup>+</sup>). CV: (DMF solution, 0.017 M)  $E_{1(rev)} = -482$  mV,  $E_{2(rev)} = -616$  mV,  $E_{3(rev)} = -1202$  mV,  $E_{4(rev)} = -1295$  mV.

# 2.2. Bis(Bis(triphenylphospine)iminium) hexasulfidohexairon-hexanitrosyl, $(PPN)_2[Fe_6S_6(NO)_6)]$

#### 2.2.1. Method A (Scheme 2, Reaction 2)

An amount of (PPN)[Fe<sub>4</sub>S<sub>3</sub>(NO)<sub>7</sub>] (0.50 g, 0.47 mmol) and (PPN)<sub>2</sub>[Fe<sub>4</sub>(CO)<sub>13</sub>] (0.78 g, 0.47 mmol) were dissolved in 20 ml MeCN, and Bz<sub>2</sub>S<sub>3</sub> (0.39 g, 1.40 mmol) was added. The resulting mixture was heated under reflux for 24 h. The precipitate formed was washed with 5 ml MeCN, dissolved in 15 ml DMF and layered with ca. 150 ml ether, affording 0.88 g of a black crystalline product. Yield 0.49 mmol, 79% of (PPN)<sub>2</sub>[Fe<sub>6</sub>S<sub>6</sub>(NO)<sub>6</sub>], based on total Fe content.

## 2.2.2. Method B (Scheme 2, Reaction 4)

An amount of  $(PPN)_2[Fe_8S_6(NO)_8]$  (0.23 g, 0.12 mmol) was dissolved in 10 ml DMF and Bz<sub>2</sub>S<sub>3</sub> (0.1 g, 0.36 mmol) was added and the solution stirred for 24 h. The solution was filtered and layered with ca. 100 ml ether, affording 0.18 g of crystalline product. Yield 0.10 mmol, 84% of (PPN)<sub>2</sub>[Fe<sub>6</sub>S<sub>6</sub>(NO)<sub>6</sub>]. Elemental Anal. Calc. for (PPN)<sub>2</sub>- $[Fe_6S_6(NO)_6], C_{72}H_{60}N_8O_6P_4S_6Fe_6: C, 48.46; H, 3.39; N,$ 6.28. Found: C, 47.90; H, 3.65; N, 7.33%. IR: 2690(m), 2928(m), 2868(w), 1679(vs) ( $v_{N-O}$ ), 1669(vs) ( $v_{N-O}$ ), 1435(m), 1262(m), 1116(m), 803(w), 743(w), 723(m), 692(m), 687(m), 546(m), 531(m), 523(w), 498(w). MS: (ESI –) m/z 1245.31 (PPN)Fe<sub>6</sub>S<sub>6</sub>(NO)<sub>6</sub><sup>-</sup>, 707.26 Fe<sub>6</sub>S<sub>6</sub>- $(NO)_{6}^{-}$ , 647.27  $Fe_{6}S_{6}(NO)_{4}^{-}$ , 617.28  $Fe_{6}S_{6}(NO)_{3}^{-}$ , 587.28 Fe<sub>6</sub>S<sub>6</sub>(NO)<sub>2</sub><sup>-</sup>, 557.31 Fe<sub>6</sub>S<sub>6</sub>(NO)<sup>-</sup>, 471.49 Fe<sub>4</sub>S<sub>4</sub>(NO)<sub>4</sub><sup>-</sup>, 441.49  $\text{Fe}_4\text{S}_4(\text{NO})_3^-$ , 411.52  $\text{Fe}_4\text{S}_4(\text{NO})_2^-$  and several smaller molecular weight fragments were observed below 400. MS: (ESI +): 537.78 (PPN<sup>+</sup>). CV: (DMF solution, 0.019 M)  $E_{1(rev)} = -690 \text{ mV}, E_{2(rev)} = -1521 \text{ mV}.$ 

# 2.3. Bis(Bis(triphenylphospine)iminium) tetrasulfidotetrairon-tetranitrosyl, $(PPN)_2[Fe_4S_4(NO)_4]$

#### 2.3.1. Method A (Scheme 2, Reaction 3)

An amount of (PPN)[Fe<sub>4</sub>S<sub>3</sub>(NO)<sub>7</sub>] (0.50 g, 0.47 mmol) and (PPN)<sub>2</sub>[Fe<sub>4</sub>(CO)<sub>13</sub>] (1.17 g, 0.70 mmol) were dissolved in 20 ml MeCN, followed by the addition of Bu<sub>4</sub>NSH (0.13 g, 0.47 mmol) in 5 ml MeCN and the mixture was heated under reflux for 24 h. After cooling at room temper-



Scheme 2. Schematic representations of the transformations of Fe/S/NO clusters discussed in this article.

ature the mixture was filtered, and the precipitate was washed with MeCN and extracted with ca. 15 ml DMF and layered with ca. 100 ml ether, affording 0.35 g of microcrystalline product. Yield 0.23 mmol 48.9% of  $(PPN)_2$ -Fe<sub>4</sub>S<sub>4</sub>(NO)<sub>4</sub> based on Fe<sub>4</sub>S<sub>3</sub>(NO)<sub>7</sub><sup>-</sup>. Elemental *Anal.* Calc. for  $(PPN)_2$ [Fe<sub>4</sub>S<sub>4</sub>(NO)<sub>4</sub>] C<sub>72</sub>H<sub>60</sub>N<sub>6</sub>O<sub>4</sub>P<sub>4</sub>S<sub>4</sub>Fe<sub>4</sub>: C, 55.39; H, 3.90; N, 5.43. Found: C, 51.49; H, 3.49; N, 5.96%.

## 2.3.2. Method B (Scheme 2, Reaction 5)

An amount of  $(PPN)_{2}[Fe_{8}S_{6}(NO)_{8}]$  (0.20 g, 0.10 mmol) and Bu<sub>4</sub>NSH (0.17 g, 0.62 mmol) were dissolved in 10 ml DMF and heated at 80 °C for 24 h. The resulting mixture was cooled at room temperature, filtered, and the solution was layered with ca. 100 ml ether, affording 0.22 g of microcrystalline product. Yield 0.14 mmol, 68.75% of (PPN)<sub>2</sub>Fe<sub>4</sub>S<sub>4</sub>(NO)<sub>4</sub>. Elemental Anal. Calc. for (PPN)<sub>2</sub>- $[Fe_4S_4(NO)_4] C_{72}H_{60}N_6O_4P_4S_4Fe_4$ : C, 55.39; H, 3.90; N, 5.43. Found: C, 52.04; H, 4.10; N, 5.88%. IR:, 2960(m), 2928(m), 2868(w), 1652(vs) ( $v_{N-O}$ ), 1435(m), 1262(m), 1116(m), 803(w), 743(w), 723(m), 692(m), 687(m), 546(m), 531(m), 523(w), 498(w). MS: (ESI –) m/z 471.5 Fe<sub>4</sub>S<sub>4</sub>- $(NO)_4^-$ , 441.5 Fe<sub>4</sub>S<sub>4</sub> $(NO)_3^-$ , 411.5 Fe<sub>4</sub>S<sub>4</sub> $(NO)_2^-$  and several smaller molecular weight fragments were observed below 400. MS: (ESI +): 537.7 (PPN<sup>+</sup>). CV: (DMF solution, 0.022 M)  $E_{1(rev)} = -202 \text{ mV}, E_{2(rev)} = -1279 \text{ mV}.$ 

# 2.4. Bis(Bis(triphenylphospine)iminium) tetrasulfidotetrairon-hexanitrosyl, $(PPN)_2[Fe_4S_4(NO)_6]$

An amount of  $(NH_4)[Fe_4S_3(NO)_7]$  (0.20 g, 0.35 mmol) and  $(PPN)_2[Fe_4(CO)_{13}]$  (0.87 g 0.52 mmol) were dissolved in 15 ml MeCN, the mixture was cooled at -20 °C and a solution of Bu<sub>4</sub>NSH (0.05 g, 0.19 mmol) in 2 ml MeCN was added. The mixture was stirred for 8 h at -20 °C, filtered, and the precipitate was washed with MeCN and extracted with ca. 5 ml DMF and layered with ca. 50 ml ether, left for 2 days in the freezer, filtered again to remove any (PPN)<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>(NO)<sub>4</sub>] that formed and the filtrate layered with additional 100 ml ether, affording 0.08 g of green brown microcrystalline product. Yield 0.07 mmol, 14% of (PPN)<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>(NO)<sub>6</sub>] based on [Fe<sub>4</sub>S<sub>3</sub>(NO)<sub>7</sub>]<sup>-</sup>. Elemental *Anal.* Calc. for (PPN)<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>(NO)<sub>6</sub>]  $\cdot$  2DMF C<sub>78</sub>H<sub>74</sub>N<sub>10</sub>-O<sub>8</sub>P<sub>4</sub>S<sub>4</sub>Fe<sub>4</sub>: C, 53.38; H, 4.25; N, 7.98. Found: C, 53.92; H, 4.20; N, 7.33%. IR: 2962(w), 2930(w), 2861(w), 1700(vs) ( $v_{N-O}$ ), 1668(vs) ( $v_{N-O}$ ), 1435(m), 1262(m), 1115(m), 840(w), 746(w), 723(m), 692(m), 687(m), 546(m), 531(m), 523(w), 496(w). MS: (ESI –): m/z 525.4 Fe<sub>4</sub>S<sub>4</sub>(NO)<sub>6</sub><sup>-</sup>, 495.6 Fe<sub>4</sub>S<sub>4</sub>(NO)<sub>5</sub><sup>-</sup>, 467.8 Fe<sub>4</sub>S<sub>4</sub>(NO)<sub>4</sub><sup>-</sup> 438.1 Fe<sub>4</sub>S<sub>4</sub>(NO)<sub>3</sub><sup>-</sup>. MS: (ESI +): m/z 535.3 (PPN<sup>+</sup>).

# 2.5. Bis(Bis(triphenylphospine)iminium) hexasulfidohexairon-hexanitrosyl bis(tricarbonyl-molybdenum) (PPN)<sub>2</sub>[Mo<sub>2</sub>Fe<sub>6</sub>(NO)<sub>6</sub>(CO)<sub>6</sub>]

An amount of (PPN)<sub>2</sub>[Fe<sub>6</sub>S<sub>6</sub>(NO)<sub>6</sub>] (0.5 g, 0.28 mmol) and Mo(CO)<sub>3</sub>(MeCN)<sub>3</sub> (0.17 g, 0.56 mmol) were dissolved in 15 ml dichloroethane and the solution stirred overnight. The mixture was filtered, and the filtrate layered with ca. 60 ml ether, affording 0.45 g of crystalline material. Yield 0.20 mmol, 71.3% of (PPN)<sub>2</sub>[(CO)<sub>6</sub>Mo<sub>2</sub>Fe<sub>6</sub>S<sub>6</sub>(NO)<sub>6</sub>]. Elemental *Anal.* Calc. for (PPN)<sub>2</sub>[(CO)<sub>6</sub>Mo<sub>2</sub>Fe<sub>6</sub>S<sub>6</sub>(NO)<sub>6</sub>]. Elemental *Anal.* Calc. for (PPN)<sub>2</sub>[(CO)<sub>6</sub>Mo<sub>2</sub>Fe<sub>6</sub>S<sub>6</sub>(NO)<sub>6</sub>]. C<sub>78</sub>H<sub>60</sub>N<sub>8</sub>O<sub>12</sub>P<sub>4</sub>S<sub>6</sub>Fe<sub>6</sub>Mo<sub>2</sub>: C, 43.68; H, 2.82; N, 5.22. Found: C, 43.48; H, 2.70; N, 5.16%. IR:, 3055(w), 2957(w), 2926(w), 2861(w), 1926(vs) ( $v_{C-O}$ ), 1877( $v_{C-O}$ ), 1723(sh) ( $v_{N-O}$ ), 1695(vs) ( $v_{N-O}$ ), 1670(sh) ( $v_{N-O}$ ), 1437(m), 1384(m), 1258(m), 1113(m), 744(w), 723(m), 691(m), 690(m), 594(m) ( $v_{Mo-C}$ ), 548(m), 532(m), 498(w). CV: (DMF solution, 0.031 M)  $E_{1(rev)} = -$  641 mV,  $E_{2(rev)} = -1247$  mV. 2.6. Hexasulfido-hexairon-hexanitrosyl bis(tripropylphosphino-copper)  $(PPr_3)_2Cu_2Fe_6S_6(NO)_6$ and Hexasulfido-tetrairon-tetranitrosyl tetrakis(tripropylphosphino-copper)  $(PPr_3)_4Cu_4Fe_4S_6(NO)_4$ 

In 5 ml MeCN, [Cu(MeCN)<sub>4</sub>]PF<sub>6</sub> (0.21 g, 0.56 mmol) was dissolved and tripropyl phosphine (PPr<sub>3</sub>) (0.12 ml, 0.60 mmol) was added dropwise and the solution stirred for 30 min. This solution was added dropwise to a dichloroethane solution (15 ml) containing  $(PPN)_2[Fe_6S_6(NO)_6]$ (0.5 g, 0.28 mmol) and the mixture was stirred overnight. The mixture was filtered and the precipitate was washed with small amounts of ether, extracted with a THF/Ether 1:1 mixture and layered with hexanes affording 0.2 g of crystalline (PPr<sub>3</sub>)<sub>2</sub>Cu<sub>2</sub>Fe<sub>6</sub>S<sub>6</sub>(NO)<sub>6</sub>. The filtrate was taken to dryness and the residue stirred in ether affording a colored solution and a white powder identified as PPNPF<sub>6</sub>. Following filtration, the ether solution was dried affording approx. 0.05 g of oily (PPr<sub>3</sub>)<sub>4</sub>Cu<sub>4-</sub>  $Fe_4S_6(NO)_4$ . Crystals suitable for X-ray diffraction were obtained by redissolving in ether and allowing for slow evaporation to occur.

 $\begin{array}{ll} (\mathrm{PPr}_3)_2\mathrm{Cu}_2\mathrm{Fe}_6\mathrm{S}_6(\mathrm{NO})_6 & \mathrm{Elemental} & Anal. & \mathrm{Calc.} & \mathrm{for} \\ (\mathrm{PPr}_3)_2\mathrm{Cu}_2\mathrm{Fe}_6\mathrm{S}_6(\mathrm{NO}) & \mathrm{C}_{18}\mathrm{H}_{42}\mathrm{N}_6\mathrm{O}_6\mathrm{P}_2\mathrm{S}_6\mathrm{Fe}_6\mathrm{Cu}_2 : & \mathrm{C}, \ 18.72 ; \\ \mathrm{H}, \ 3.67 ; \ \mathrm{N}, \ 7.28 . & \mathrm{Found:} \ \mathrm{C}, \ 18.51 ; \ \mathrm{H}, \ 3.63 ; \ \mathrm{N}, \ 7.05\%. & \mathrm{Yield} \\ 0.17 \ \mathrm{mmol}, \ 60\% & \mathrm{of} \ (\mathrm{PPr}_3)_2\mathrm{Cu}_2\mathrm{Fe}_6\mathrm{S}_6(\mathrm{NO})_6 \ \mathrm{based} \ \mathrm{on} \ \mathrm{Fe}. \\ \mathrm{IR}:, \ 2957(\mathrm{m}), \ 2927(\mathrm{m}), \ 2867(\mathrm{w}), \ 1766(\mathrm{sh}) \ (v_{\mathrm{N-O}}), \ 1750(\mathrm{sh}) \\ (v_{\mathrm{N-O}}), \ \ 1729(\mathrm{vs}) \ (v_{\mathrm{N-O}}), \ \ 1660(\mathrm{sh}) \ (v_{\mathrm{N-O}}), \ \ 1450(\mathrm{m}), \\ 1410(\mathrm{m}), \ 1080(\mathrm{m}), \ 1000(\mathrm{m}), \ 851(\mathrm{w}), \ 736(\mathrm{w}). \ \mathrm{Microprobe} \\ \mathrm{analysis \ confirms \ the \ 2:6 \ ratio \ of \ \mathrm{Cu \ to} \ \mathrm{Fe}. \ \mathrm{CV}: \ (\mathrm{THF \ solution}, \\ 0.029 \ \mathrm{M}) \ \ E_{1(\mathrm{rev})} = -169 \ \mathrm{mV}, \ \ E_{2(\mathrm{rev})} = -1035 \ \mathrm{mV}, \\ E_{3(\mathrm{rev})} = -1667 \ \mathrm{mV}. \end{array}$ 

 $(PPr_3)_4Cu_4Fe_4S_6(NO)_4$  Elemental *Anal.* Calc. for  $(PPr_3)_4Cu_4Fe_4S_6(NO)_4 C_{36}H_{84}N_4O_4P_4S_6Fe_4Cu_4$ : C, 30.22; H, 5.92; N, 3.92%. Found: C, 32.90; H, 6.35; N, 3.08%. Yield 0.04 mmol 28.5%  $(PPr_3)_4Cu_4Fe_4S_6(NO)_4$  based on Cu. IR: 2957(m), 2928(m), 2869(w), 1724(vs) ( $v_{N-O}$ ), 1712(vs) ( $v_{N-O}$ ), 1457(m), 1080(m), 840(w). Microprobe analysis confirms the 1:1 ratio of Cu to Fe. CV: (THF solution, 0.011 M)  $E_{1(rev)} = -153 \text{ mV}, E_{2(rev)} = -1021 \text{ mV}, E_{3(rev)} = -1537 \text{ mV}, E_{4(irr)} = -2077 \text{ mV}.$ 

#### 2.7. Hexasulfido-hexairon-hexanitrosyl

 $bis(tripropylphosphino-nickel)(PPr_3)_2Ni_2Fe_6S_6(NO)_6$  and Hexasulfido-tetrairon-tetranitrosyl tris(tripropylphosphinonickel) (PPr\_3)\_3Ni\_3Fe\_4S\_6(NO)\_4

In 5 ml MeCN,  $[Ni(MeCN)_6](BF_4)_2$  (0.27 g, 0.56 mmol) was dissolved and PPr<sub>3</sub> (0.12 ml, 0.60 mmol) was added dropwise and the solution stirred for 30 min. This solution was added dropwise to a dichloroethane solution (15 ml) containing (PPN)<sub>2</sub>[Fe<sub>6</sub>S<sub>6</sub>(NO)<sub>6</sub>] (0.5 g, 0.28 mmol) and the mixture was stirred overnight. The mixture was filtered and the precipitate was washed with small amounts of ether and extracted with a THF/Ether 1:1 mixture and layered with hexanes affording 0.15 g of crystalline (PPr<sub>3</sub>)<sub>2</sub>Ni<sub>2</sub>-

 $Fe_6S_6(NO)_6$ . The filtrate was taken to dryness and the residue stirred in ether affording a colored solution and a white powder identified as PPNBF<sub>4</sub>. The resulting ether solution was dried and washed with hexanes and ether and extracted with THF using silica gel as a filtration agent, affording approx. 0.04 g of oily (PPr<sub>3</sub>)<sub>3</sub>Ni<sub>3</sub>-Fe<sub>4</sub>S<sub>6</sub>(NO)<sub>4</sub>. Crystals suitable for X-ray diffraction were obtained by recrystalization from THF/Hexanes.

 $(PPr_3)_2Ni_2Fe_6S_6(NO)_6$  Elemental *Anal.* Calc. for  $(PPr_3)_2Ni_2Fe_6S_6(NO)_6$   $C_{18}H_{42}N_6O_6P_2S_6Fe_6Ni_2$  C, 18.88; H, 3.70; N, 7.34. Found: C, 19.12; H, 3.77; N, 7.26%. Yield 0.13 mmol, 46% of  $(PPr_3)_2Ni_2Fe_6S_6(NO)_6$  based on Fe. IR: 2958(m), 2927(m), 2868(w), 1763(s) ( $v_{N-O}$ ), 1745(sh) ( $v_{N-O}$ ), 1725(vs) ( $v_{N-O}$ ), 1663(sh) ( $v_{N-O}$ ), 1449(m), 1405(m), 12181(m), 1076(m), 1041(m), 851(m), 762(w), 731(m), 586(w), 435(w). Microprobe analysis confirms the 2:6 ratio of Ni to Fe. CV: (THF solution, 0.029 M)  $E_{1(rev)} = -1 \text{ mV}, E_{2(rev)} = -717 \text{ mV}, E_{3(rev)} = -1431 \text{ mV}.$ 

 $(PPr_3)_3Ni_3Fe_4S_6(NO)_4$  Elemental *Anal.* Calc. for  $(PPr_3)_3Ni_3Fe_4S_6(NO)_4C_{27}H_{63}N_4O_4P_3S_6Fe_4Ni_3$  C, 27.19; H, 5.32; N, 4.70. Found: C, 31.57; H, 5.91; N, 5.31%. Yield 0.033 mmol, 17.83%  $(PPr_3)_3Ni_3Fe_4S_6(NO)_4$  based on Ni. IR: 2957(m), 2927(m), 2868(w), 1720(s) ( $v_{N-O}$ ), 1698(vs) ( $v_{N-O}$ ), 1679(s) ( $v_{N-O}$ ), 1452(m), 1404(m), 1221(m), 1073(m), 1038(m), 849(m), 724(m), 584(w), 440(w). Microprobe analysis confirms the 3:4 ratio of Ni to Fe.

2.8. Reactions of  $(PPN)_2[Fe_6S_6(NO)_6]$  with  $Fe^{2+}$  or  $Fe^0$ 

2.8.1. With  $Fe(H_2O)_6(BF_4)_2$  / PPr<sub>3</sub> (Scheme 2, Reaction 7)

An amount of  $(PPN)_2[Fe_6S_6(NO)_6]$  (0.2 g, 0.11 mmol) and  $Fe(H_2O)_6(BF_4)_2$  (0.08 g, 0.24 mmol) were suspended in 20 ml of THF/MeCN 1:1 ratio, and PPr<sub>3</sub> (0.05 ml, 0.25 mmol) was added dropwise. The mixture was stirred overnight, filtered, and the solution layered with ether affording 0.12 g of crystalline material. The material was identified as  $(PPN)_2[Fe_8S_6(NO)_8]$  by IR, MS and cyclic voltammetry, without any evidence suggesting the presence of a different species. Yield 0.06 mmol, 55% of  $(PPN)_2[Fe_8S_6(NO)_8]$ .

# 2.8.2. With $Fe(CO)_5$

An amount of  $(PPN)_2[Fe_6S_6(NO)_6]$  (0.2 g, 0.11 mmol) was dissolved in a solution of 20 ml THF/MeCN 1:1 ratio and Fe(CO)<sub>5</sub> (0.03 ml, 0.23 mmol) was added dropwise. The mixture was stirred overnight, filtered, and the filtrate layered with ether affording 0.10 g of a microcrystalline material. The material was identified as  $(PPN)_2$ -[Fe<sub>8</sub>S<sub>6</sub>(NO)<sub>8</sub>] by IR and MS. Yield 0.05 mmol, 46% of  $(PPN)_2$ [Fe<sub>8</sub>S<sub>6</sub>(NO)<sub>8</sub>].

2.9. Reactions of  $(PPN)_2[Fe_8S_6(NO)_8]$  with oxidizing agents

#### 2.9.1. With $O_2$

An amount of  $(PPN)_2[Fe_8S_6(NO)_8]$  (0.2 g, 0.11 mmol) was dissolved in 10 ml DMF and O<sub>2</sub> was bubbled through

	$[Fe_4S_4(NO)_6]^{2-}$	$\left[(CO)_{6}Mo_{2}Fe_{6}S_{6}(NO)_{6}\right]^{2-}$	$(PPr_3)_2Cu_2Fe_6S_6(NO)_6$	$(PPr_3)_4Cu_4Fe_4S_6(NO)_4$	$(PPr_3)_2Ni_2Fe_6S_6(NO)_6$	$(PPr_3)_3Ni_3Fe_4S_6(NO)_4$
Color	brown	black	black	black	black	black
Habit	needle	needle	polyhedron	plate	polyhedron	block
Size (mm)	$0.60\times0.04\times0.04$	$044 \times 0.44 \times 0.34$	$0.44 \times 0.40 \times 036$	$0.30 \times 0.28 \times 0.05$	$0.38 \times 0.34 \times 030$	$0.40 \times 0.24 \times 0.16$
Formula	C <sub>78</sub> H <sub>74</sub> Fe <sub>4</sub> N <sub>10</sub> O <sub>8</sub> P <sub>4</sub> S <sub>4</sub>	$C_{90}H_{86}Fe_6Mo_2N_{12}O_{16}P_4S_6$	$C_{18}H_{42}Cu_2Fe_6N_6O_6P_2S_6$	$C_{36}H_{84}Cu_4Fe_4N_4O_4P_4S_6$	C <sub>18</sub> H <sub>42</sub> Fe <sub>6</sub> Ni <sub>2</sub> N <sub>6</sub> O <sub>6</sub> P <sub>2</sub> S <sub>6</sub>	$C_{24}H_{63}Fe_4N_4Ni_3O_4P_3S_6$
Weight	1754.99	2434.93	1155.06	1430.87		1192.61
Crystal system	triclinic	triclinic	cubic	monoclinic	cubic	cubic
Space group	$P\bar{1}$	$P\overline{1}$	$Pa\bar{3}$	P21/c	$Pa\bar{3}$	$Pa\bar{3}$
Unit cell dimensions						
a (Å	10.951(6)	12.373(2)	15.9081(9)	11.299(3)	15.7773(10)	21.3741(18)
b (Å)	12.345(7)	14.386(3)	15.9081(9)	15.292(5)	15.7773(10)	21.3741(18)
c (Å)	28.632(15)	15.495(3)	15.9081(9)	17.404(5)	15.7773(10)	21.3741(18)
α (°)	90.021(9)	97.037(3)	90.00	90.00	90.00	90.00
β (°)	94.034(9)	91.936(3)	90.00	98.193(4)	90.00	90.00
γ (°)	90.127(9)	110.014(2)	90.00	90.00	90.00	90.00
Volume	3861(4)	2563.4(8)	4025.8(4)	2976.4(15)	3927.3(4)	9764.8(14)
Ζ	2	1	4	2	4	8
Temperature (K)	123(2)	123(2)	108(2)	123(2)	108(2)	108(2)
Absorption coefficient	0.991	1.311	3.563	2.700	3.528	2.675
F(000)	1808	1234	2320	1472	2312	4912
θ Range (°)	1.80-19.27	1.88-28.39	2.22-28.29	1.78-26.43	2.24-28.30	1.65-28.32
Reflections	32467	81 490	82778	51 829	85115	194707
Limiting indices	-10 < h < 10,	-16 < h < 16,	-21 < h < 21,	-14 < h < 14,	-21 < h < 21,	-28 < h < 28,
	-11 < k < 11,	-19 < k < 19,	-21 < k < 21,	-19 < k < 19,	-20 < k < 20,	-28 < k < 28,
	-26 < l < 26	-20 < l < 20	-21 < l < 21	-21 < l < 21	-21 < l < 21	-28 < l < 28
R <sub>int</sub>	0.1486	0.0292	0.0332	0.0806	0.0383	0.0571
Data/restraints/ parameters	6428/0/978	12725/0/617	1671/0/72	6079/0/286	1636/0/71	4069/0/157
$R_1, wR_2 [I > 2\sigma(I)]$	0.0573, 0.1372	0.0396, 0.1050	0.0134, 0.0343	0.0738, 0.1753	0.0147, 0.0395	0.0199, 0.0413
$R_1$ , $wR_2$ (all data)	0.1235, 0.1781	0.0456, 0.1098	0.0142, 0.0348	0.1290, 0.2281	0.0158, 0.0399	0.0345, 0.0497
Goodness-of-fit $(F^2)$	1.029	1.024	1.090	0.990	1.139	1.239

 Table 1

 Crystallographic and refinement table of the compounds presented herein

the solution for 5 min. the mixture was stirred for 1 h and filtered to remove a light brown powder and layered with ether affording 0.10 g of crystalline material. The material was identified as  $[Fe(DMF)_6][Fe_6S_6(NO)_6]$  by IR, MS and Unit Cell determination. Yield 0.08 mmol, 75.64% of  $[Fe(DMF)_6][Fe_6S_6(NO)_6]$ .

## 2.9.2. With $[Fe(Cp)_2]PF_6$

An amount of  $(PPN)_2[Fe_8S_6(NO)_8]$  (0.2 g, 0.11 mmol) was dissolved in 10 ml DMF and  $[Fe(Cp)_2]PF_6$  (0.14 g, 0.42 mmol) was added. The mixture was stirred overnight, filtered, and the filtrate layered with ether affording 0.05 g of crystalline  $[Fe(DMF)_6][Fe_6S_6(NO)_6]$  as identified by IR and MS. Yield 0.04 mmol, 37.8% of  $[Fe(DMF)_6]-[Fe_6S_6(NO)_6]$ .

# 2.9.3. With SCl<sub>2</sub>

An amount of  $(PPN)_2[Fe_8S_6(NO)_8]$  (0.2 g, 0.11 mmol) was dissolved in 20 ml dichloroethane and a 10% SCl<sub>2</sub> solution in dichloroethane (0.07 ml, 0.11 mmol) was added dropwise and the solution was stirred for 1 h. The mixture was filtered and the precipitate was dissolved in DMF and layered with ether affording a powder that was identified by IR as  $[Fe(DMF)_6]$ - $[Fe_6S_6(NO)_6]$ .

The filtrate of this solution was layered with ca. 20 ml ether, filtered to remove a white powder of PPNCl, and then layered with additional 40ml ether to obtain 0.08 g light green needle shaped crystals.

The unit cell was identical to the known (PPN)-[Fe(CO)<sub>3</sub>(NO)] complex [29], and IR showed characteristic peaks at 1794 cm<sup>-1</sup> ( $\nu_{N-O}$ ) and 350 cm<sup>-1</sup> ( $\nu_{Fe-Cl}$ ). Elemental analysis confirmed that the crystals are (PPN)-[FeCl<sub>3</sub>(NO)], apparently isomorphous to the (PPN)[Fe-(CO)<sub>3</sub>(NO)] complex. Yield 0.17 mmol, 80% of (PPN)[FeCl<sub>3</sub>(NO)].

Elemental *Anal.* Calc. for (PPN)[FeCl<sub>3</sub>(NO)]C<sub>36</sub>H<sub>30</sub>-N<sub>2</sub>OP<sub>2</sub>Cl<sub>3</sub>Fe C, 59.17; H, 4.14; N, 3.83. Found: C, 58.86; H, 3.99; N, 3.66%. IR:, 3052(w), 2917(w), 2848(w), 1794(vs) ( $v_{N-O}$ ), 1436(s), 1244(s), 1114(s), 998(w), 795(w), 749(m), 723(s), 692(s), 550(s), 533(m), 500(m), 350(s) ( $v_{Fe-Cl}$ ).

## 2.10. Crystallographic data

Diffraction data were collected on a Siemens SMART CCD-based X-ray diffractometer, equipped with a Mo K $\alpha$  probe on a wavelength of 0.71073 Å. Space groups were determined on systematic absences and intensity statistics. Full Matrix least-squares refinement based on F<sup>2</sup> was performed. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in ideal positions and refined as rigid atoms with individual isotropic thermal displacement parameters. The specific crystallographic data for each compound are presented in Table 1.

#### 3. Results and discussion

The synthesis of the octanuclear iron sulfur nitrosyl cluster  $(PPN)_2[Fe_8S_6(NO)_8]$  proceeds through the reaction of  $(NH_4)[Fe_4S_3(NO)_7]$  with  $(PPN)_2[Fe_4(CO)_{13}]$  in a 2:3 molar ratio affording  $(PPN)_2[Fe_8S_6(NO)_8]$  in high yields. The byproducts of this reaction, that were isolated and verified by IR and MS are mainly (PPN)[Fe(CO)<sub>3</sub>(NO)] and a small amount of  $(PPN)[Fe_4N(CO)_{12}]$ . The reaction appears to proceed through the abstraction of nitrosyl ligands from  $[Fe_4S_3(NO)_7]^-$  by the  $[Fe_4(CO)_{13}]^{2-}$  cluster and the possible formation of an  $[Fe_4S_3(NO)_4]^-$  intermediate which subsequently self couples to form the  $[Fe_8S_6(NO)_8]^{2-}$  cluster. (PPN)[Fe(CO)<sub>3</sub>(NO)] seems to be the main product formed by the reaction of the  $[Fe_4(CO)_{13}]^2$ -cluster with NO<sup>+</sup>. The generation of the  $[Fe_4N(CO)_{12}]^-$  cluster also is possible considering the reported synthesis of this cluster by the reaction of  $Fe_3(CO)_{12}$  with  $[Fe(CO)_3(NO)]^-$  [30,31].

In the synthesis of  $(PPN)_2[Fe_6S_6(NO)_6]$  (Reaction 2, Scheme 2), the yield of the Fe<sub>6</sub>S<sub>6</sub> "prismane" is unreasonably high, assuming that  $[Fe_4S_3(NO)_7]^-$  is the only source of Fe. It appears therefore that the  $[Fe_4(CO)_{13}]^{2-}$  cluster also provides Fe in the formation of  $(PPN)_2[Fe_6S_6(NO)_6]$ . In addition, it is known that  $[Fe(CO)_3(NO)]^-$  upon reaction with S<sup>0</sup> produces  $[Fe_4S_4(NO)_4]^-$  [32] so the pathway to the formation of  $(PPN)_2[Fe_6S_6(NO)_6]$  through reaction 2 may be more complicated than the initial formation of  $(PPN)_2[Fe_8S_6(NO)_8]$  and further reaction with Bz<sub>2</sub>S<sub>3</sub> as shown by reactions 1 and 4 (Scheme 2). The  $[Fe_6S_6-(NO)_6]^{2-}$  cluster has been synthesized previously with different counter ions but in lower yields [7].

The  $[Fe_4S_4(NO)_4]^{2-}$  cluster has not been isolated in this oxidation level previously. The IR spectrum shows a NO stretching vibration at 1652 cm<sup>-1</sup> which is lower when compared to the 1760 cm<sup>-1</sup> and 1700 cm<sup>-1</sup> reported for Fe<sub>4</sub>S<sub>4</sub>(NO)<sub>4</sub> and  $[Fe_4S_4(NO)_4]^-$  respectively [32]. The lower frequency of the NO stretching vibration in (PPN)<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>(NO)<sub>4</sub>] is consistent with the expected increase in the Fe–NO backbonding in the dianionic (PPN)<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>(NO)<sub>4</sub>]. Elemental analysis also is consistent with the (PPN)<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>(NO)<sub>4</sub>] formula, however we were not able to obtain a satisfactory crystal structure due to high distortion of the PPN<sup>+</sup> cations in the crystal lattice. Nevertheless, the presence of a  $[Fe_4S_4(NO)_4]^{2-}$  cluster and two PPN<sup>+</sup> cations has been confirmed.

The synthesis of the  $[{\rm Fe}_4{\rm S}_4({\rm NO})_6]^{2-}$  (Fig. 1) and  $[{\rm Fe}_4{\rm S}_4({\rm NO})_4]^{2-}$  clusters from the Roussin anion is not unexpected. The reactions of  $[{\rm Fe}_4{\rm S}_3({\rm NO})_7]^-$  with SH<sup>-</sup>, in polar solvents (L), may well lead in cluster fragmentation and generation of dimeric species such as  $\{{\rm Fe}_2{\rm S}_2({\rm NO})_3(L)\}^-$  and  $\{{\rm Fe}_2{\rm S}_2({\rm NO})_2(L)_2\}^-$ . Coupling of these units can lead to the formation of the  $[{\rm Fe}_4{\rm S}_4({\rm NO})_6]^{2-}$  and  $[{\rm Fe}_4{\rm S}_4({\rm NO})_4]^{2-}$  clusters respectively. As in the case of all  $[{\rm Fe}_4{\rm S}_4({\rm NO})_7]^-/$   $[{\rm Fe}_4({\rm CO})_{13}]^{2-}$  reactions, the main byproduct in the synthesis of either  $[{\rm Fe}_4{\rm S}_4({\rm NO})_4]^{2-}$  or  $[{\rm Fe}_4{\rm S}_4({\rm NO})_6]^{2-}$  is  $[{\rm Fe}({\rm CO})_3({\rm NO})]^-$ . The apparent role of  $[{\rm Fe}_4({\rm CO})_{13}]^{2-}$  as a



Fig. 1. Ortep diagram of  $[Fe_4S_4(NO)_6]^{2-}$  with 50% probability ellipsoids.

NO abstracting reagent is affected by both time and temperature and this explains the formation and isolation of  $[Fe_4S_4(NO)_6]^{2-}$  at low temperatures.

The formation of  $Fe_4S_4(NO)_4$  from the reaction of  $[Fe_4S_3(NO)_7]^-$  and elemental sulfur has been reported [32] and this cluster was studied several years ago, although the mechanism of this reaction is not clear. Based on experimental observations and theoretical calculations by Glidewell and Hoffmann [33,34] the formation of Fe\_4S\_4(NO)\_4 from  $[Fe_4S_3(NO)_7]^-$  could proceed through a mechanism of fragmentation and reassembly of the latter cluster.

The isolation of  $(PPN)_2[Fe_4S_4(NO)_6]$  has been achieved by repeating the reaction that yields  $(PPN)_2[Fe_4S_4(NO)_4]$ but at low temperatures. According to the formal oxidation levels, there is a two electron oxidation from  $[Fe_4S_3(NO)_7]^$ to  $[Fe_4S_4(NO)_6]^{2-}$  and an additional two electron oxidation to  $[Fe_4S_4(NO)_4]^{2-}$ . The isolation of this edge fused double dimer can be envisioned as the coupling product of two  $\{Fe_2S_2(NO)_3^-\}$  fragments while the cubane as the product of two  $\{Fe_2S_2(NO)_2^-\}$  fragments.

The procedure reported here for the synthesis of  $(PPN)_2[Fe_4S_4(NO)_6]$  is not an easily reproducible process and seems to be sensitive to time and temperature of crystallization. Both the hypothetical  $\{Fe_2S_2(NO)_3(L)\}^-$  and  $\{Fe_2S_2(NO)_2(L)\}^-$  fragments possibly involved in the formation of  $[Fe_4S_4(NO)_6]^{2-}$  and  $[Fe_4S_4(NO)_4]^{2-}$  respectively, may be preset at the same time in various amounts. Therefore isolation of  $[Fe_4S_4(NO)_6]^{2-}$  or the more stable  $[Fe_4S_4(NO)_4]^{2-}$  will depend on the exact conditions of the experiment, and such conditions are not easily reproduced/ obtained. Although  $[Fe_4S_4(NO)_6]^{2-}$  has been detected several times in mixtures obtained from this reaction, analytically pure crystalline material has only been obtained once thus far.

# 3.1. Transformations of $(PPN)_2[Fe_8S_6(NO)_8]$

The  $(PPN)_2[Fe_8S_6(NO)_8]$  cluster, stable at high temperatures, upon oxidation transforms to the  $[Fe_6S_6(NO)_6]^{2-1}$ "prismane". This occurs using O<sub>2</sub>, SCl<sub>2</sub> and [Fe(Cp)<sub>2</sub>]PF<sub>6</sub>. In all three cases it seems that there is loss of two  $\{Fe(NO)\}$ fragments rather than rearrangement of the clusters. In coordinating solvents, the main product isolated is  $[Fe^{II}(L)_6][Fe_6S_6(NO)_6]$  (L = DMF, THF, MeCN). The  $[Fe_6S_6(NO)_6]^{2-}$  anion is structurally related to the  $[Fe_8S_6 (NO)_8$ <sup>2-</sup> pentlandite. The former is obtained from the latter when two {Fe(NO)} moieties are removed from the body diagonal of the pentlandite cube. In addition to the  $[Fe_6S_6(NO)_6]^{2-}$  prismane, a yellow brown powder also forms. In the case of the SCl<sub>2</sub> reaction this byproduct was identified and characterised as (PPN)[FeCl<sub>3</sub>(NO)] both analytically and spectroscopically (by the NO stretch at  $1794 \text{ cm}^{-1}$ , the Fe–Cl stretch at  $350 \text{ cm}^{-1}$  and characteristic PPN stretches in the  $800-500 \text{ cm}^{-1}$  region). The unit cell dimensions of this byproduct were nearly identical to those of the known (PPN)[Fe(CO)<sub>3</sub>(NO)] complex [29]. Although this particular complex has not been synthesized previously, its crystallographic structure determination and further characterizations were not of particular interest in this study and were not further pursued. The  $[Fe(L)_6]$ - $[Fe_6S_6(NO)_6]$  complex isolated has exactly the same infrared spectral pattern for the NO stretching vibrations as the pattern for the previously reported [Fe(DMF)<sub>6</sub>]- $[Fe_6S_6(NO)_6]$  [7]. A counter-ion exchange of  $[Fe(DMF)_6]^{n+1}$ with  $PPN^+$  gives  $(PPN)_2[Fe_6S_6(NO)_6]$ . The latter is verified by elemental analysis and confirms that the iron in the  $[Fe(L)_6]^{n+}$  counter-ion is divalent (n = 2).

For the reaction of  $(PPN)_2[Fe_8S_6(NO)_8]$  with eight equivalents of  $NOBF_4$  the products isolated are  $Fe(DMF)_6[Fe_6S_6(NO)_6]$ ,  $(PPN)[Fe_4S_3(NO)_7]$  and  $PPNBF_4$  suggesting that in order to form the more reduced  $[Fe_4S_3(NO)_7]^-$  cluster some of the  $[Fe_8S_6(NO)_8]^{2-}$  cluster has to be oxidized to produce the necessary electrons since  $NO^+$  cannot act as a reducing agent.

In contrast, when gaseous NO is used both  $[Fe_8S_6-(NO)_8]^{2-}$  and  $[Fe_6S_6(NO)_6]^{2-}$  produce  $[Fe_4S_3(NO)_7]^{-}$  in nearly quantitative yields.

# 3.2. Reactivity of $(PPN)_2[Fe_6S_6(NO)_6]$

The cyclohexane-like  $Fe_3S_3$  units of the  $[Fe_6S_6]$  core can serve as ligands for two additional metal ions and form  $[M_2Fe_6S_6]$  clusters, [19,35,36]. The latter were obtained in reactions carried out with coordinatively-unsaturated complexes containing Fe, Mo, Cu and Ni.

In the reaction of  $(PPN)_2[Fe_6S_6(NO)_6]$  with  $[Fe_{H_2O}_6]^{2+}/PPr_3$ , or  $Fe(CO)_5$ , the only product isolated was  $[Fe_8S_6(NO)_8]^{2-}$ . The formation of  $[Fe_8S_6(NO)_8]^{2-}$  even at NO deficient conditions can be explained if fragmentation of the cluster to  $\{Fe(NO)\}$  units occurs. The later under reducing conditions form the  $[Fe_8S_6(NO)_8]^{2-}$  preferentially.

In order to increase the yield of  $[Fe_8S_6(NO)_8]^{2-}$  the reaction of  $(PPN)_2[Fe_6S_6(NO)_6]$  with  $[Fe(H_2O)_6]^{2+}$  was carried out in the presence of NOBF<sub>6</sub>. The only products isolated were  $(PPN)[Fe_4S_3(NO)_7]$  and  $[Fe(DMF)_6][Fe_6S_6(NO)_6]$  suggesting that the formation of  $[Fe_4S_3(NO)_7]^-$  is more favorable in the presence of  $NO^+$ .

As in the case of  $(Et_4N)_2[Fe_6S_6Cl_6]$ , [35] the reaction of  $(PPN)_2[Fe_6S_6(NO)_6]$  with  $Mo(CO)_3(MeCN)_3$  yields  $(PPN)_2[(CO)_6Mo_2Fe_6S_6(NO)_6]$  (Fig. 2) even in molar ratios less than 1:1 suggesting that the [MoFe\_6S\_6] core, if it forms at all, disproportionates to the [Mo\_2Fe\_6S\_6] and [Fe\_6S\_6] clusters.

The reaction of  $(PPN)_2[Fe_6S_6(NO)_6]$  with  $[Cu(Me-CN)_4]^+/PPr_3$  affords  $(PPr_3)_2Cu_2Fe_6S_6(NO)_6$  (Fig. 3) as the main product, and in a lower yield the  $(PPr_3)_4Cu_4$ -Fe\_4S\_6(NO)\_4 (Fig. 4) cluster. Formation of the  $(PPr_3)_4Cu_4$ -Fe\_4S\_6(NO)\_4 cluster could be explained in terms of fragmentation of the  $[Fe_6S_6(NO)_6]^{2-}$  cluster to smaller Fe/S/NO units (i.e.  $\{Fe_2S_2(NO)_2\}$  units), The latter in the presence of Cu(PR\_3) form (PR\_3)CuS\_2Fe(NO) units which couple to form the final product. In both cases the Fe\_6Cu\_2 and Fe\_4Cu\_4 clusters form due to the superior thermodynamic stability of the Cu–S bond relative to the Fe–S bond. Previously, we have reported on the substitution of Fe atoms by Cu atoms in Fe/S clusters [19,37].

These two products form regardless of the ratio of the Cu used, and their separation was achieved due to their slightly different solubilities. Similar reactions of  $[Fe_6S_6-(NO)_6]^{2-}$  with  $[Ni(MeCN)_6]^{2+}/PPr_3$ , give the neutral  $(PPr_3)_2Ni_2Fe_6S_6(NO)_6$  (Fig. 5) cluster as the main product, but unlike the case of copper where the byproduct formed



Fig. 3. Ortep diagram of  $(PPr_3)_2Cu_2Fe_6S_6(NO)_6$  showing ellipsoids with 50% probability. The carbons of the phosphines have been omitted for clarity.





Fig. 2. Ortep diagram of  $[(CO)_6Mo_2Fe_6S_6(NO)_6]^{2-}$  showing ellipsoids with 50% probability.

Fig. 4. Ortep diagram of  $(PPr_3)_4Cu_4Fe_4S_6(NO)_4$  showing ellipsoids with 50% probability. The carbons of the phosphines have been omitted for clarity.

is  $(PPr_3)_4Cu_4Fe_4S_6(NO)_4$ , with nickel the other isolable byproduct is the unique Ni/Fe/S cluster  $(PPr_3)_3Ni_3$ -Fe<sub>4</sub>S<sub>6</sub>(NO)<sub>4</sub> (Fig. 6). This cluster contains the "voided– cubic" M<sub>7</sub>S<sub>6</sub> core which previously has been found in  $(PPr_3)_4Fe_7S_6Cl_3$  [38], Co<sub>7</sub>S<sub>6</sub>I<sub>3</sub>(PEt<sub>3</sub>)<sub>4</sub> [39], and Co<sub>7</sub>S<sub>6</sub>-



Fig. 5. Ortep diagram of  $(PPr_3)_2Ni_2Fe_6S_6(NO)_6$  showing ellipsoids with 50% probability. The carbons of the phosphines have been omitted for clarity.

 $X_3(PPh_3)_4$  (X=Cl<sup>-</sup> [23], Br<sup>-</sup> [40]) but not in mixed metal systems. The  $(PPr_3)_3Ni_3Fe_4S_6(NO)_4$  is the only byproduct isolated from a mixture that appears to contain three compounds. The separation of these species is relatively difficult as their solubilities are relatively similar, with  $(PPr_3)_3Ni_3Fe_4S_6(NO)_4$  being less soluble in ether and hexanes than the other two species. Unfortunately we ware not able to obtain any crystals from the other two byproducts as they seem relatively unstable. Nevertheless these two species also contain phosphine and nitrosyls as shown by infrared spectroscopy, with the main N-O stretching peak at  $1696 \text{ cm}^{-1}$  for  $(PPr_3)_3Ni_3Fe_4S_6(NO)_4$  (THF fraction),  $1739 \text{ cm}^{-1}$  (Ether fraction) and  $1711 \text{ cm}^{-1}$  (Hexanes Fraction). The IR spectra of the Ether fraction is very similar to the pattern of (PPr<sub>3</sub>)<sub>4</sub>Cu<sub>4</sub>Fe<sub>4</sub>(NO)<sub>4</sub> and since the  $[Ni_4Fe_4S_4]$  core is known for  $(PPr_3)_4Ni_4Fe_4S_4Cl_4$  [19] and (PPh<sub>2</sub>Me)<sub>4</sub>Ni<sub>4</sub>Fe<sub>4</sub>S<sub>4</sub>I<sub>4</sub> [20], we expect the nitrosyl cluster to have a similar structure.

# 3.3. Structures

Crystallographic determination of  $(PPN)_2[Fe_4S_4(NO)_6]$ reveals a Fe<sub>4</sub>S<sub>4</sub> core that can be described as the fusion of two  $[(NO)_2Fe(\mu-S)_2Fe(NO)]^-$  dimers to give a *nido*  $[Fe_4S_4(NO)_6]^{2-}$  cluster (Fig. 1) with an inter-dimer Fe–Fe distance of 2.77 Å and an average intra-dimer Fe–Fe distance of 2.68 Å. The Fe–NO distances are almost equivalent at 1.66 Å (1.65–1.67 Å) with average Fe–N–O bond angles of 167° within a range of 163°–171°.

In the (PPN)<sub>2</sub>[(CO)<sub>6</sub>Mo<sub>2</sub>Fe<sub>6</sub>S<sub>6</sub>(NO)<sub>6</sub>] cluster, the M<sub>8</sub>S<sub>6</sub> cuboctahedral core exhibits average Mo–Fe and Fe–Fe distances are at 2.89 Å and 2.69 Å, respectively, and Mo–S and Fe–S distances at 2.58 Å and 2.25 Å, respectively. As expected, by comparison to  $[Fe_8S_6(NO)_8]^{2-}$ , the Mo<sub>2</sub>Fe<sub>6</sub> cluster is elongated along the three-fold axis that contains



Fig. 6. Ortep diagram of  $(PPr_3)_3Ni_3Fe_4S_6(NO)_4$  (side and top view) showing ellipsoids with 50% probability. The carbons of the phosphines have been omitted for clarity.

the Mo atoms (Fig. 2). The cluster topology is identical to the MoFe/S/Cl analogues  $(Et_4N)_3[(CO)_6Mo_2Fe_6S_6Cl_6]$  and  $(Et_4N)_4[(CO)_6Mo_2Fe_6S_6Cl_6]$  [35].

Both of the Cu/Fe/S/NO structures exhibit the typical cubic arrangement of metals capped by sulfur atoms and have structures similar to those of their Cu/Fe/S/Cl analogues  $(Bu_4N)_2[(PPr_3)_2Cu_2Fe_6S_6Cl_6]$  and  $(PPr_3)_4Cu_4$ -Fe<sub>4</sub>S<sub>6</sub>Cl<sub>6</sub> [19]. In the case of  $(PPr_3)_2Cu_2Fe_6S_6(NO)_6$  (Fig. 3) the average Cu–Fe and Fe–Fe distances are 2.70 Å and 2.65 Å and the Cu–S and Fe–S bonds are found at 2.38 Å and 2.24 Å. In  $(PPr_3)_4Cu_4Fe_4S_6(NO)_4$  (Fig. 4) the metals in the Cu<sub>4</sub>Fe<sub>4</sub> core are arranged in D<sub>2h</sub> geometry (mutually perpendicular Fe<sub>4</sub> and Cu<sub>4</sub> squares) with average metal–metal distances of 2.74 Å and average Cu–S and Fe–S bond structures and Fe–S bond structures are 2.76 Å and 2.26 Å respectively.

The neutral  $(PPr_3)_2Ni_2Fe_6S_6(NO)_6$  (Fig. 5) possesses the same core structure as the copper analogue, but is slightly more compact with average Ni–S and Fe–S distances of 2.25 Å and 2.26Å, respectively, and Ni–Fe and Fe–Fe distances at 2.59Å and 2.65Å, respectively. A similar Ni<sub>2</sub>Fe<sub>6</sub> core is also found in the Ni/Fe/S/halide analogues,  $(Et_4N)_2[(PPr_3)_2Ni_2Fe_6S_6Cl_6]$  [19] and  $[PhCH_2NEt_3]_2[(Ph_2-MeP)_2Ni_2Fe_6S_6I_6]$  [20].

The  $(PPr_3)_3Ni_3Fe_4S_6(NO)_4$  (Fig. 6) cluster can be viewed as a Fe<sub>4</sub>S<sub>3</sub>(NO)<sub>4</sub> unit coupled with a nearly trigonal planar Ni<sub>3</sub>S<sub>3</sub>(PPr<sub>3</sub>)<sub>3</sub> unit. In this structure the Iron atoms show a tetrahedral coordination geometry while the Nickel atoms show a trigonal pyramidal geometry. The Fe–Fe distances in the equatorial triangle (defined by Fe1, Fe2 and Fe3) have a mean value of 3.82 Å. These irons are located 2.74 Å from the capping iron. The Ni–Fe distances and Ni–Ni distances are at found at 2.61 and 2.79 Å, respectively, and the Fe–S and Ni–S distances are 2.23 Å and 2.25 Å, respectively.

As shown in Table 2, the M/Fe/S (M=Mo,Cu,Ni) clusters reported in this paper have shorter metal-metal and ironsulfur distances in a more compact overall structure than their corresponding analogues with halogens. An exception is the (PPr<sub>3</sub>)<sub>3</sub>Ni<sub>3</sub>Fe<sub>4</sub>S<sub>6</sub>(NO)<sub>4</sub> cluster which is of similar size to the structurally similar [Fe<sub>7</sub>S<sub>6</sub>] and [Co<sub>7</sub>S<sub>6</sub>] clusters. In the M<sub>7</sub>S<sub>6</sub> clusters the "uncapped" M<sub>3</sub>S<sub>3</sub> unit shows a triangular M<sub>3</sub> array with distances nearly 1 Å shorter than the distances found in the hexagonal faces of the M<sub>6</sub>S<sub>6</sub> prismanes. At present we are exploring the possible function of the "uncapped" unit as a ligand to other metal atoms.

Table 2

Comparison of selected bond distances between different M/Fe/S clusters with the range of distances given in parenthesis along with esd's

Selected bond distances (in Å)	$[(CO)_6Mo_2Fe_6S_6(NO)_6]^2$	$[(CO)_6Mo_2Fe_6S_6Cl_6]^{3-}$	$[(CO)_6Mo_2Fe_6S_6Cl_6]^{4-}$		
Mo–Fe	2.893(2.884(6)-2.906(6))	2.930(2)	3.005(2.980(1)–3.031(2)) 2.7(1(2.740(2), 2.781(2))		
Fe–Fe	2.672(2.669(6)-2.674(6))	2.742(3)	2.761(2.740(2) - 2.781(2))		
Octahedron Volume	21.535	22.810	23.983		
Mo–S	2.580(2.576(8)-2.674(8))	2.582(3)	2.619(2.611(2) - 2.625(2))		
Fe–S	2.247(2.230(8)-2.279(8))	2.292(2.280(4)-2.312(4))	2.353 (2.279(2)-2.336(3))		
	$(PPr_3)_2Cu_2Fe_6S$	$S_6(NO)_6$	$\left[(PEt_{3})_{2}Cu_{2}Fe_{6}S_{6}Cl_{6}\right]^{2-}$		
Cu–Fe	2.699(3)		2.784(2.756(10)-2.811(10))		
Fe–Fe	2.647(3)		2.772(2.750(11)-2.791(10))		
M <sub>8</sub> volume	19.098		21.435		
Cu–S	2.381(3)		2.385(2.384(15)-2.392(15))		
Fe–S	2.240(2.230(3)-	2.247(3))	2.310(2.297(16)-2.322(16))		
	$(PPr_3)_4Cu_4Fe_4S$	$S_6(NO)_4$	$(PPr_3)_4Cu_4Fe_4S_6Cl_6\\$		
Cu–Cu	2.747(16)		2.733(6)		
Cu–Fe	2.747(2.765(17)	-2.739(19))	2.787(2.765(6)-2.823(6))		
Fe–Fe	2.710(19)		2.784(6)		
M <sub>8</sub> volume	20.593		21.431		
Cu–S	2.236(2.341(29)	2.366(2.351(8)-2.380(8))			
Fe–S	2.264(2.251(29)	2.269(2.265(8)-2.275(8))			
	$(PPr_3)_2Ni_2Fe_6S_6(NO)_6$	$[(PPr_3)_2Ni_2Fe_6S_6Cl_6]^{2-}$	$\left[(Ph_2MeP)_2Ni_2Fe_6S_6I_6\right]^{2-}$		
Ni–Fe	2.586(3)	2.615(2.613(15)-2.617(15))	2.645(2.624(2)-2.658(2))		
Fe–Fe	2.649(3)	2.752(2.747(18)-2.759(19))	2.719(2.707(2)-2.726(2))		
M <sub>8</sub> volume	17.933	19.328	19.281		
Ni–S	2.250(3)	2.255(2.245(25)-2.267(25))	2.261(2.257(1)-2.265(1))		
Fe–S	2.257(2.236(3)-2.271(3))	2.296(2.297(26)-2.309(26))	2.289 (2.277(2)-2.300(2))		
	$(PPr_3)_3Ni_3Fe_4S_6(NO)_4$	$(PEt_3)_4Fe_7S_6Cl_3$	$Co_7S_6Br_3(PPh_3)_4$		
Ni–Ni <sup>a</sup>	2.790(4)	2.746(3)	2.883(4)		
Ni–Fe	2.618(2.605(4)-2.630(4))	2.624(2.622(2)-2.626(2))	2590 (2.583(3)-2.596(4))		
Fe-Fe <sup>b</sup> <sub>(planar)</sub>	3.823(4)	4.148(2)	3.955(4)		
Fe-Fe <sub>(capping)</sub>	2.744(4)	2.584(2)	2.607(3)		
Ni-S <sub>(equatorial)</sub>	2.144(2.140(5)-2.148(5))	2.179(3)	2.139 (2.129(6)-2.149(5))		
Ni-S <sub>(axial)</sub>	2.470(5)	2.231(3)	2.197(6)		
Fe-S <sub>(capping)</sub>	2.223(5)	2.193(2)	2.168(4)		
Fe-S <sub>(equatorial)</sub>	2.242(5)	2.363(2.361(3)-2.366(3))	2.254 (2.249(5)-2.258(5))		
Fe-S <sub>(axial)</sub>	2.204(5)	2.276(3)	2.184(5)		

The volume of the metal formed cuboidal unit has been calculated approximating it as a cube, using average metal-metal distances.

<sup>a</sup> The distances of interest are denoted as shown in Fig. 6 using the equivalent metal positions for  $Fe_7S_6$  and  $Co_7S_6$  since in the case of  $Ni_3Fe_4S_6$  they are more easily defined and recognized.

<sup>b</sup> The Fe–Fe plane is the trigonal plane defined by Fe1–Fe2–Fe3, and the Fe–Fe(capping) is the distance of Fe4 to the trigonal Fe plane. Fe–S (capping) is the Fe4–S3 distance, Fe–S (equatorial) is the Fe3–S3 distance and Fe–S (axial) is the Fe3–S4 distance.

Compound	$v_{\mathrm{N-O}}~(\mathrm{cm}^{-1})$	Fe-N distances (Å)	N-O distances	Fe-N-O angles	Nitrosyl oxidatio	n state		
			(A)	( <sub>0</sub> )	$NO^+$	.ON	-ON	Enemark-Feltham
$[Fe_4S_3(NO)_7]^{-a}$	1731	1.646(2)	1.177(2)	163.4(2)-178.3(2)	Fe(I), 3Fe(-1)	3Fe(I), Fe(II)	4Fe(III)	${\rm FeNO}^{7}3{\rm Fe(NO)}^{9}$
$[Fe_4S_4(NO)_4]^{2-}$	1652				2 Fe(0), 2Fe(I)	2Fe(I), 2Fe(II)	2Fe(II),	$2{\rm [FeNO]}^7 2{\rm [FeNO]}^8$
							2Fe(III)	
$[Fe_4S_4(NO)_6]^{2-}$	1700, 1668	1.66(11)	1.18(11)	163(1) - 171(1)	4Fe(0)	2Fe(I), 2Fe(II)	4Fe(III)	2{FeNO} <sup>8</sup>
								$2{\rm [Fe(NO)_2]}^8$
$[Fe_8S_6(NO)_8]^{2-}$	1684	1.674(2)	1.181(2)	174.6(2)-178.8(2)	6Fe(0), 2Fe(I)	6Fe(I), 2Fe(.II)	6Fe(II),	$6{\rm FeNO}^{\rm S}2{\rm FeNO}^7$
							2Fe(III)	
$[Fe_6S_6(NO)_6]^{2-}$	1679, 1669	1.669(1)	1.181(2)	172.9(2)-177.0(2)	2Fe(0), 4Fe(I)	2Fe(I), 4Fe(II)	2Fe(II),	$2{\rm [FeNO]}^{8} 4{\rm [FeNO]}^{7}$
							4Fe(III)	
(PPr) <sub>2</sub> Cu <sub>2</sub> Fe <sub>6</sub> S <sub>6</sub> (NO) <sub>6</sub> <sup>b</sup>	1766, 1750, 1729,	1.676(1)	1.171(1)	171(0.1)	2Fe(0), 4Fe(I)	2Fe(I), 4Fe(II)	2Fe(II),	$2{\rm [FeNO]}^{8} 4{\rm [FeNO]}^{7}$
	1660						4Fe(III)	
(PPr) <sub>4</sub> Cu <sub>4</sub> Fe <sub>4</sub> S <sub>6</sub> (NO) <sub>4</sub> <sup>b</sup>	1724, 1712	1.709(9)	1.14(12)	175 - 177(1.1)	4Fe(I)	4Fe(II)	4Fe(III)	$4{\rm [FeNO]}^7$
(PPr) <sub>2</sub> Ni <sub>2</sub> Fe <sub>6</sub> S <sub>6</sub> (NO) <sub>6</sub> <sup>b</sup>	1763, 1745, 1725,	1.676(1)	1.172(1)	173(0.1)	4Fe(0), 2Fe(I)	4Fe(I), 2Fe(II)	4Fe(II),	$4{\rm [FeNO]}^8 2{\rm [FeNO]}^7$
	1663						2Fe(III)	
(PPr) <sub>3</sub> Ni <sub>3</sub> Fe <sub>4</sub> S <sub>6</sub> (NO) <sub>4</sub> <sup>b</sup>	1720, 1698, 1679	1.668(2)	1.184(3)	168 - 180 (0.2)	2Fe(0), 2Fe(I)	2Fe(I), 2Fe(II)	2Fe(II),	$2{\rm [FeNO]}^8 2{\rm [FeNO]}^7$
							2Fe(III)	
$[(CO)_6Mo_2Fe_6$	1723, 1695, 1670	1.678(2)	1.166(3)	175.5(2)-178.2(3)	2Fe(0), 4Fe(I)	2Fe(I), 4Fe(II)	2Fe(II),	$2{\rm FeNO}^{8} 4{\rm FeNO}^{7}$
$S_6(NO)_6 \int_{z=0}^{z=0}$							4Fe(111)	
<sup>a</sup> Crystal structure of ( <sup>b</sup> The heterometals are	$Et_4N)[Fe_4S_3(NO)_7]$ taken assigned as Cu(I), Ni(II)	from Ref. [46]. and Mo(0) assuming the	hat they did not unde	ergo change of oxidati	on state during th	e reaction.		

Table 3

# 3.4. The NO ligands

In metal nitrosyl complexes it is difficult to determine precise oxidation states for the metal atoms since NO could be described as NO<sup>+</sup>, NO or NO<sup>-</sup>. Thus, in  $[Fe_4S_3(NO)_7]^-$  two descriptions have been proposed for the cluster based on the assignment of the NO ligand state. These are:  $4Fe^{3+}/NO^-$  [41] and  $3Fe^{-1}$ ,  $Fe^+/NO^+$  [42].

Spectroscopic and structural data for the Fe/S/NO and M/Fe/S/NO clusters (Table 3) show the N-O stretching vibrations in the range from 1652 to 1766  $\text{cm}^{-1}$ , the M-N-O angle in the range from 171.8° to 180.0°, the Fe-N bond in the range from 1.67 Å to 1.71 Å and the N–O bond between 1.14 Å and 1.18 Å. Within  $3\sigma$  (at times as high as .01-.02 Å) the N-O and Fe-NO distances are nearly indistinguishable. The Fe-NO bond is short enough consistent with a considerable amount of multiple bond character. The high standard deviations often associated with the N-O bonds make the bond order difficult to evaluate. The M-N-O angles are all near 180° which is expected for  $NO^+$  coordination as opposed to 120° for  $NO^-$  taken in extreme cases, but on the basis of the IR data the NO ligands may be even considered as NO<sup>-</sup> given that the typical range for lineal NO is  $1450-1950 \text{ cm}^{-1}$  and 1400-1720 cm<sup>-1</sup> for bent NO [10]. Unfortunately there is great overlap in ranges, and given that in a series of  $[M(NO)(CN)_5]^{n-}$  complexes (M=V, Cr, Mn, Fe and n = 2, 3) the position of  $v_{NO}$  depends upon the cation present and variations up to  $100 \text{ cm}^{-1}$  have been observed for a given anion [43,44]. This makes the  $v_{N-O}$  vibration unreliable for determining NO oxidation. As described by Enemark and Feltham [45] the transition metal-nitrosyl systems are better described as highly covalent entities using a {M-NO}<sup>*n*</sup> notation with *n* the sum of metal d and NO  $\pi^*$ electrons. Any reference to change of oxidation states of the clusters in this article is in accordance with this notation.

An examination of the structural parameters in the  $\{[(R_3P)M]_x Fe_{8-x}(L)_{8-x}S_6\}^{n-}$  clusters for L = NO vs  $Cl^{-1}$ (Table 2) shows that the NO clusters are characterized by significantly shorter Fe-M, Fe-Fe and Fe-S bond lengths. The data are consistent with the expected  $\pi$  back bonding from the Fe atoms into the NO  $\pi^*$  orbital which in turn results in electron deficient Fe atoms, significant M-Fe and Fe-Fe bonding and Fe-S multiple bonding. At present <sup>57</sup>Fe Moessbauer spectroscopy appears to be needed for an assignment of oxidation states to the Fe metals and the NO ligands, by a comparison of the Moessbauer spectra of the NO clusters to those of the corresponding chloro clusters. The Moessbauer spectra of the Cu<sub>2</sub>Fe<sub>6</sub>, Cu<sub>4</sub>Fe<sub>4</sub> and Ni<sub>2</sub>Fe<sub>6</sub> clusters  $(L = Cl^{-})$ , with isomer shifts of 0.345 mm/s, 0.341 mm/s and 0.355 mm/s, respectively, are consistent with an Fe oxidation state around +3 and Cu<sup>+1</sup>, Ni<sup>o</sup> or Ni<sup>+1</sup>.

# 3.5. Electrochemistry

Electrochemical studies of the clusters reported here, show mainly reversible, multielectron reductions (Table 4).

Reduction potentials of the four	$M_2 \operatorname{Fe}_6 S_6 \operatorname{Cl}$	usters a	na compa	arison with th	eir Fe/s	s/CI equiv	alents					
Compound	0/-1 couple			-1/-2 couple		-2/-3 couple			-3/-4 couple			
	$E_{1/2}$ (mV)	$\Delta E$	$i_{\rm pc}/i_{\rm pa}$	$E_{1/2}$ (mV)	$\Delta E$	$i_{\rm pc}/i_{\rm pa}$	$E_{1/2} ({ m mV})$	$\Delta E$	$i_{\rm pc}/i_{\rm pa}$	$E_{1/2} ({ m mV})$	$\Delta E$	$i_{\rm pc}/i_{\rm pa}$
$(PPr_3)_2Cu_2Fe_6S_6(NO)_6$	-169	152	0.84	-1035	148	0.99	-1667	152	1.02			
$(Bu_4N)_2[(PPr_3)_2Cu_2Fe_6S_6Cl_6]$							-228	26		-555	120	
$(PPr_3)_4Cu_4Fe_4S_6(NO)_4$	-153	172	0.39	-1021	156	0.57	-1537	116	0.73	-2065		irr
(PPr <sub>3</sub> ) <sub>4</sub> Cu <sub>4</sub> Fe <sub>4</sub> S <sub>6</sub> Cl <sub>6</sub>	-17	124		-635	130							
$(PPr_3)_2Ni_2Fe_6S_6(NO)_6$	-1	168	1.10	-717	156	0.61	-1431	334	0.71			
$(Et_4N)_2[(PPr_3)_2Ni_2Fe_6S_6Cl_6]$							-585	156				
$(PPN)_2[(CO)_6Mo_2Fe_6S_6(NO)_6]$							-641	192	0.70	-1247	176	0.68
(Et N) [(CO) Mos FecS (C1)]										+50	92	1.00

Table 4 Reduction potentials of the four  $M_2$  Fe<sub>6</sub>S<sub>6</sub> clusters and comparison with their Fe/S/Cl equivalents

All reductions are reversible unless denoted otherwise.

The  $(PPr_3)_2Cu_2Fe_6S_6(NO)_6$  cluster shows three reversible reduction waves (Fig. 7) at -169 mV, -1035 mV, -1667 mV. Following a cyclic scan from 1.8 V to -2 V, the voltammetry shows the appearance of an additional reduction wave at about -633 mV, which suggest that the small peak that appears in that region in the 0 to -2.0 V scan is due to partial oxidation of the cluster during the experiment rather than to the presence of an impurity.

In the case of  $(PPr_3)_4Cu_4Fe_4S_6(NO)_4$ , although the CV appears to be very similar to  $(PPr_3)_2Cu_2Fe_6S_6(NO)_6$  as the first two reductions coincide, (Fig. 8) at high potentials there are different peaks. In addition when two consecutive full scans from -2 V to 1.8 V are performed, there is no appearance of the peak at -0.5 V indicating that it is not a mixture of two species.

For  $(PPr_3)_2Ni_2Fe_6S_6(NO)_6$  the cyclic voltammogram (Fig. 9) shows only two reductions at -717 mV and -1431 mV but there is also a reversible wave at -1 mV (not shown), and overall the voltammogram of  $(PPr_3)_2Ni_2$ -Fe<sub>6</sub>S<sub>6</sub>(NO)<sub>6</sub> is similar to that of  $(PPr_3)_2Cu_2Fe_6S_6(NO)_6$  shifted by approx 0.2 V towards more positive potentials. Again after a full range scan there is an emergence of a new reversible wave at -235 V which is also evident in the initial scan but with smaller intensity suggesting that part of the sample had been oxidized during the experimental process.

Contamination of the  $(PPr_3)_3Ni_3Fe_4S_6(NO)_4$  cluster with the other unidentified Ni/Fe/S species, did not allow for conclusive electrochemical measurements of this cluster.

For  $(PPN)_2[(CO)_6Mo_2Fe_6S_6(NO)_6]$ , there are two reduction waves observed at -641 mV and -1247 mV (Fig. 10). In addition there is no significant effect of oxidation as there are no new peaks appearing but the two reductions change in intensity after a full range scan.

As shown in Table 4, by comparison to the corresponding M/Fe/S/Cl species and equivalent couples, the clusters presented herein are more difficult to reduce which is reasonable given that these clusters appear to be more electron rich than their corresponding halogen analogues due to the more covalent nature of the Fe–NO bond that eventually



Fig. 7. Cyclic voltammogram of (PPr<sub>3</sub>)<sub>2</sub>Cu<sub>2</sub>Fe<sub>6</sub>(NO)<sub>6</sub>.



Fig. 8. Cyclic voltammogram of  $(PPr_3)_4Cu_4Fe_4S_6(NO)_6$  in comparison with  $(PPr_3)_2Cu_2Fe_6S_6(NO)_6.$ 



Fig. 9. Cyclyc voltammogram of (PPr<sub>3</sub>)<sub>2</sub>Ni<sub>2</sub>Fe<sub>6</sub>(NO)<sub>6</sub>.



Fig. 10. Cyclyc voltammogram of (PPN)<sub>2</sub>[(CO)<sub>6</sub>Mo<sub>2</sub>Fe<sub>6</sub>(NO)<sub>6</sub>].

disturbs the ability of the metals to accept additional electrons.

## 4. Conclusions

In this article we have explored the syntheses and reactivities of the Fe/S/NO clusters. These clusters were found structurally similar to their halo and phosphino analogues, exhibiting similar interconversions between their core structures, and the reactivity of  $(PPN)_2[Fe_6S_6(NO)_6]$ towards thiophilic metals such as Mo, Cu and Ni, provides almost identical core structures as the Fe/S/Cl clusters.

The reactivity of the Fe/S/NO clusters presented in this paper are in line with the fragmentation/reassembly mechanism proposed by Glidewell and Hoffmann, as the products obtained through various reactions seem to be the four basic and thermodynamically stable core topologies of Fe<sub>4</sub>S<sub>3</sub>, Fe<sub>4</sub>S<sub>4</sub> Fe<sub>6</sub>S<sub>6</sub> and Fe<sub>8</sub>S<sub>6</sub>, however the isolation of the unique (PPN)<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>(NO)<sub>6</sub>], "open-cubane" and the (PPr<sub>3</sub>)<sub>3</sub>Ni<sub>3</sub>Fe<sub>4</sub>S<sub>6</sub>(NO)<sub>4</sub> clusters provides additional evidence that it is possible to obtain new core topologies by varying reaction conditions and stabilizing inherently metastable structures.

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## Appendix A. Supplementary material

CCDC 643468, 643469, 643470, 643471, 643472 and 643473 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2007.06.015.

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