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# Attachment of cyanometal units to the $Fe_4S_4$ cluster[1]

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**Abstract**

Treatment of $[Fe_4S_4Cl_4]^{2-}$ with anionic cyano-metal carbonyls leads to the octanuclear complexes $[Fe_4S_4(NC-ML_n)_4]^{2-}$ for M = Cr, Mo, W, Mn. Likewise with neutral organometal cyanides bearing phosphine or cyclopentadienyl ligands the octanuclear complexes $[Fe_4S_4(NC-M'L_n)_4]^{2+}$ for M′ = Fe, Ru, Cu, Ag are obtained. The crystal structures of the anionic clusters with $ML_n = W(CO)_5$ and $MnCp(CO)_2$ have been determinated. Electrochemical data and UV–vis spectra of the complexes can be correlated with a metal–metal charge transfer from the cyanometal units to the $[Fe_4S_4]^{2+}$ cluster. © 1998 Elsevier Science S.A. All rights reserved.

*Keywords:* $Fe_4S_4$ clusters; Cyano-organometallics; Octanuclear clusters; Charge transfer spectra; Electrochemistry

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## 1. Introduction

There is currently an upsurge of activity in the chemistry and physics of coordination compounds having redox-active metal centers linked by cyanide bridges. The reason for this is that modern spectroscopic and magnetic equipment has allowed to find and study attractive phenomena of electron transfer and metal–metal interaction in these compounds which possibly allow applications in optical, electrical and magnetic devices. Several recent reviews have outlined the features and attractions of this field [1–4].

We have been interested in M–CN–M′ systems for about 10 years, resulting from our work in organometallic electrochemistry [5] and in the use of organometallic Lewis bases to attach metal containing ligands to clusters [6]. We found that electron-rich organometallic cyano complexes, when attached to mononuclear [7–9] or cluster entities [10,11], provide a fertile extension of the chemistry and spectroscopy of the polynuclear metallocyanides which previously were mostly constructed from classical metal complex building blocks.

In this context it seemed attractive to us to combine the redox activity of both cyanometal complexes and transition metal clusters. For this purpose some purely inorganic clusters seemed to be more suitable than the polynuclear metal carbonyls [10,11]. Shriver had already shown that six cyanomanganese units can be attached to the $[Mo_6Cl_8]$ and $[Ta_6Cl_{12}]$ clusters [12,13]. We opted for the $[Fe_4S_4]^{2+}$ system. Its ubiquity as a biological electron-transfer agent [14] and the extensive work on the modelling of its biological function [15] have provided a solid basis of its chemistry, electrochemistry, spectroscopy and magnetism. We wanted to build on this basis by attaching cyanometal units to the $Fe_4S_4$ core and exploiting the spectroscopic and physical properties of the resulting polynuclear com-

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[1] Dedicated to Professor Michael Bruce on the occasion of his 60th birthday in recognition of his important contribution to organometallic chemistry.

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plexes. In a short communication we have already presented some results including an unusual magnetic behaviour of $[Fe_4S_4(NC{-}ML_n)_4]^{2-}$ species [16]. This paper reports the preparation, spectroscopy and electrochemistry of the $Fe_4S_4$-derived compounds.

## 2. Preparations

The starting material of the syntheses was $[Fe_4S_4Cl_4]^{2-}$ as the $Et_4N$ or $Ph_4P$ salt [17]. Its reactions with the anionic organometallic cyanides $[NC{-}M(CO)_5]^-$ with M = Cr, Mo, W and $[NC{-}MnCp(CO)_2]^-$ produced the octanuclear anionic complexes **1**–**4** in excellent yields. Compounds **1**–**4** are thermally quite stable and easy to handle. Using the neutral metallocyanides $Cp(CO)_2Fe{-}CN$, $Cp(dppe)Fe{-}CN$, $Cp(PPh_3)_2Ru{-}CN$, $(PPh_3)_2Cu{-}CN$ and $(PPh_3)_3Ag{-}CN$ yielded the cationic complexes **5**–**9**. These were difficult to obtain in a pure state and thermally so labile that they decomposed upon attempts at recrystallization. In all cases an essential part of the driving force for the formation of the complexes is salt precipitation. Thus complexes **1**–**4** could only be obtained from the sodium salts of the cyanometalates (the PPN salts did not react), and complexes **5**–**9** had to be supported in their formation by addition of $NH_4PF_6$ or $NaSbF_6$.

$[Ph_4P]_2[Fe_4S_4\{NC{-}Cr(CO)_5\}_4]$
**1**
$[Ph_4P]_2[Fe_4S_4\{NC{-}Mo(CO)_5\}_4]$
**2**
$[Ph_4P]_2[Fe_4S_4\{NC{-}W(CO)_5\}_4]$
**3**
$[Et_4N]_2[Fe_4S_4\{NC{-}MnCp(CO)_2\}_4]$
**4**

$[Fe_4S_4\{NC{-}FeCp(CO)_2\}_4](SbF_6)_2$
**5**
$[Fe_4S_4\{NC{-}FeCp(dppee)\}_4](PF_6)_2$
**6**
$[Fe_4S_4\{NC{-}RuCp(PPh_3)_2\}_4](SbF_6)_2$
**7**
$[Fe_4S_4\{NC{-}Cu(PPh_3)_2\}_4](PF_6)_2$
**8**
$[Fe_4S_4\{NC{-}Ag(PPh_3)_3\}_4](PF_6)_2$
**9**

All compounds **1**–**9** are deeply coloured. As expected, their paramagnetism is reflected in the non-obtainability of simple $^1$H-NMR spectra. IR-spectroscopy allows, however, to assign all constituents of the compounds. Table 1 lists the data. Of these the $\nu$(CN) values are worth discussing. Firstly the CN bands are quite intense, being comparable in height to the CO bands. Secondly in all cases except **5** the $\nu$(CN) band positions are lowered by 40–70 cm$^{-1}$ relative to those of the free metallocyanide 'ligands'. This is unusual when compared to the data for dinuclear complexes of the same 'ligands' [7]. Normally $\nu$(CN) rises upon coordination of a second metal complex unit at the N terminus. However, when this second complex is oxidized, i.e. becomes a stronger electron acceptor, then $\nu$(CN) is loweeredd [7]. From this it can be concluded that the $Fe_4S_4$ core is a rather strong electron acceptor, as is borne out by the electronic spectra discussed below. A third notable phenomenon of the IR spectra is the fact that there is always just one set of $\nu$(CN) and $\nu$(CO) bands which means that neither the overall molecular symmetry nor the mixed-valent nature of the $Fe_4S_4$ core are effective in modifying the vibrational energies of the four $NC{-}ML_n$ units.

Table 1
IR spectra (KBr, cm$^{-1}$) of the complexes

| | $\nu$(CN) | $\nu$(CO) | $\nu$(anion) |
|---|---|---|---|
| **1** | 2036m | 2099w, 1985w, 1944s | |
| **2** | 2038m | 2102w, 1991w, 1925s | |
| **3** | 2034m | 2105w, 1981w, 1916s | |
| **4** | 2015s | 1911s, 1861s | |
| **5** | 2142m | 2062s, 2015s | 658s($SbF_6$) |
| **6** | 2016s | | 839s($PF_6$) |
| **7** | 2023s | | 658s($SbF_6$) |
| **8** | 2093w | | 839s($PF_6$) |
| **9** | 2092w | | 838s($PF_6$) |

## 3. Structure determinations

While the lability of the cationic octanuclear complexes did not allow the growth of good single crystals, two of the anionic ones, **3** and **4**, could be subjected to structure determinations. Figs. 1 and 2 display the molecular shapes of the clusters, Table 2 lists some bond lengths and angles. Cluster **3** has 2-fold crystallographic symmetry with the axis passing through the centers of two opposing faces of the $Fe_4S_4$ cube.

Both complexes contain the $Fe_4S_4$ core with its typical shape, i.e. significantly distorted from ideal cube symmetry with angles at the iron atoms approaching the tetrahedral angle and angles at the sulfur atoms well below 90° [15]. In both complexes there exist several values for each bond length or angle which are equivalent due to molecular but not due to crystallographic symmetry. Table 2 shows that there is a remarkable uniformity of all such bond lengths with the overall spread being in the order of the individual standard deviations. The Fe–N, N–C, and C–M bond lengths compare well with those in simple Fe–N–C–M complexes [7].

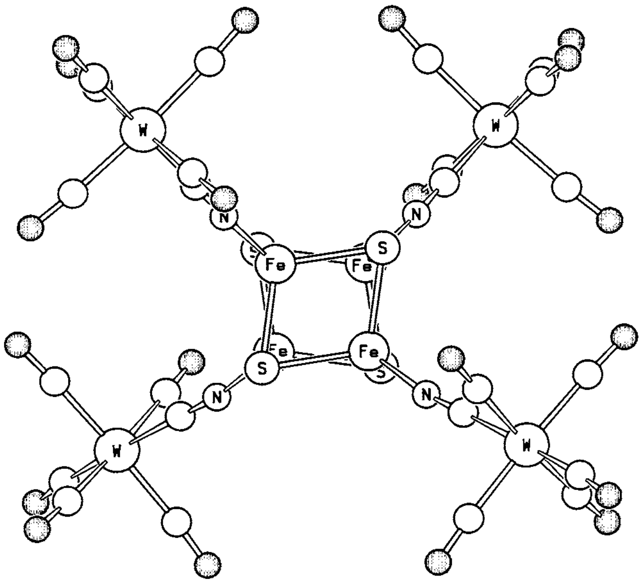

Fig. 1. Molecular structure of the octanuclear anion of complex **3**.

compare well with those in simple Fe–N–C–M complexes [7].

The only bonding parameters which show a noticeable spread are the angles involving the bridging cyanide ligands. The Fe–N–C angles range from 163.7 to 176.3°, the N–C–M angles from 175.5 to 179.1°. This reflects the general softness of angles near 180°, but also the weaker linearizing efficiency across the CN nitrogen due to weaker M–NC $\pi$ bonding at this end of the cyanide ligand. While the crystallographic data do not allow to assign the orientation of the cyanide ligands as Fe–NC–M or Fe–CN–M (see discussion in ref. [4]), the observed Fe–N–C and N–C–M angles provide a clear distinction. The nearer-to-180° value of N–C–M and the higher variability of Fe–N–C confirm the given Fe–N–C–M arrangement.

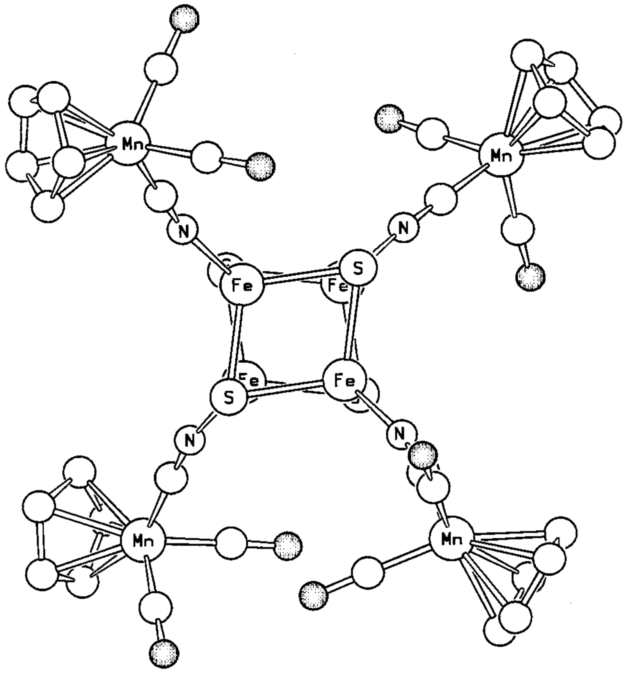

Fig. 2. Molecular structure of the octanuclear anion of complex **4**.

Table 2
Selected bond lengths [Å] and angles [°] for **3** and **4**

| | **3** | **4** |
|---|---|---|
| Fe–Fe(avg.) | 2.733 ± 0.012 | 2.756 ± 0.008 |
| Fe–S(avg.) | 2.275 ± 0.025 | 2.283 ± 0.009 |
| Fe–N(avg.) | 1.915 ± 0.005 | 1.937 ± 0.006 |
| N–C(avg.) | 1.160 ± 0.005 | 1.155 ± 0.013 |
| C–M(avg.) | 2.143 ± 0.001 | 1.881 ± 0.006 |
| Fe–N–C(avg.) | 173.4 ± 2.9 | 167.3 ± 4.0 |
| N–C–M(avg.) | 177.3 ± 1.1 | 177.7 ± 1.9 |

## 4. Redox behaviour

Except for **5**, **8** and **9** all complexes were amenable to cyclic voltammetry. In each case a reversible reduction and an irreversible oxidation were observed. The difference of the two redox potentials is relatively constant around 1.5 V, indicating that both redox steps involve the complexes as a whole and not the $Fe_4S_4$ core or the $L_nM$–CN 'ligand' alone. Table 3 lists the data together with those of two reference compounds.

All redox potentials of the octanuclear complexes are shifted to more positive values relative to those of the reference compounds. This reflects in a semiquantitative way the electron-donating abilities of the metallocyanide 'ligands'. Both thiolate and chloride are stronger electron donors than the metallocyanides. Due to the $\pi$-acceptor properties of the organometallic units at the C terminus of the bridging cyanides the electron donation is reduced at the N terminus. This is most noticeable for the pure metal carbonyls in **1**–**3** and least pronounced for the very electron rich $Cp(CO)_2Mn$–CN 'ligand' (see below).

Table 3
Cyclic voltammetriy of the complexes[a]

| Complex | $E_{\frac{1}{2}}$(red) | Ep(ox) |
|---|---|---|
| $[Fe_4S_4(SPh)_4]^{2-}$ | −1.07 | +0.07 |
| $[Fe_4S_4Cl_4]^{2-}$ | −0.87 | +0.53 |
| **1** | −0.46 | +0.96 |
| **2** | −0.45 | +0.98 |
| **3** | −0.46 | +1.00 |
| **4** | −0.75 | +0.40 |
| **6** | −0.64 | +0.70 |
| **7** | −0.57 | +1.20 |

[a] Measured in $CH_2Cl_2$ using 0.1 M $Bu_4NPF_6$ as electrolyte. Referenced against Ag/AgCl. Peak potentials for the irreversible oxidations. Values in volts.

The reversible reduction responses induced us to carry out chemical reductions with cobaltacene. These seemed to work in dichloromethane for complexes **3** and **4**. Their solutions turned dark brown upon treatment with one equivalent of $CoCp_2$. However, the reduced products were extremely air-sensitive and persisted only for a few hours in solution or in the solid state.

## 5. Electronic spectra

The electronic spectra of complexes **1**–**7** differ significantly from those of the reference compounds $[Fe_4S_4Cl_4]^{2-}$ and $[Fe_4S_4(SR)_4]^{2-}$ [18]. While the intense absorption of the latter in the upper visible or near UV range, assigned to intracore charge transfers [19], appears in the near UV for the octanuclear clusters as well, the visible or near IR range which shows only weak features for the reference compounds is dominated by intense and very broad bands for complexes **1**–**7**. Table 4 lists these intense bands, Fig. 3 gives a visualization.

We assign the broad bands to metal–metal charge transfer (MMCT) transitions from the cyanometal units to the $Fe_4S_4$ core. This is consistent with the fact that bands of this intensity and shape are also observed for dinuclear complexes in which the same cyanometal units are linked to partly oxidized organometallic units [7]. The strongest indication is, however, the nearly linear relation between the MMCT energies and the oxidation potentials of the free metallocyanides. Table 4 lists these $E_{\frac{1}{2}}$(ox) values measured by us. The easier the 'ligand' $L_nM$–CN is to oxidize (maximum $Cp(CO)_2Mn$–$CN^-$) the lower the MMCT energy. It is for this reason that the MMCT bands of **8** and **9** are not clearly observed as they may be hidden under other bands in the near UV. Similarly the MMCT band of presumably highest energy for **5** may be incorrectly assigned. Further support for the MMCT assignment comes from the observation that solutions of the trianionic cluster, which is obtained by one-electron reduction of **3** with cobaltacene, show the intervalence transfer band at higher energy ($\lambda = 466$ nm, $\varepsilon = 14.000$ l $mol^{-1}$ $cm^{-1}$) than **3**.

Table 4
MMCT bands of the octanuclear complexes and redox potentials of their free metallocyanides M–CN[a]

| Complex | M | $\lambda$(MMCT) | $\varepsilon$ | $E_{\frac{1}{2}}$(ox) |
|---|---|---|---|---|
| **1** | $Cr(CO)_5^-$ | 520 | 18.000 | 0.58 |
| **2** | $Mo(CO)_5^-$ | 508 | 20.000 | 0.64 |
| **3** | $W(CO)_5^-$ | 506 | 17.500 | 0.62 |
| **4** | $Mn(CO)_2Cp^-$ | 602 | 15.000 | 0.11 |
| **5** | $Fe(CO)_2Cp$ | 344 | 2.000 | 1.8 |
| **6** | Fe(dppe)Cp | 526 | 12.000 | 0.48 |
| **7** | $Ru(PPh_3)_2Cp$ | 440 | 11.000 | 0.79 |
| **8** | $Cu(PPh_3)_2$ | n.o. | – | 0.86 |
| **9** | $Ag(PPh_3)_3$ | n.o. | – | 1.23 |

[a] Band positions in nm, $\varepsilon$ values in l $mol^{-1}$ $cm^{-1}$, potentials in V. All measurements in $CH_2Cl_2$. Conditions for electrochemistry as in Table 3.

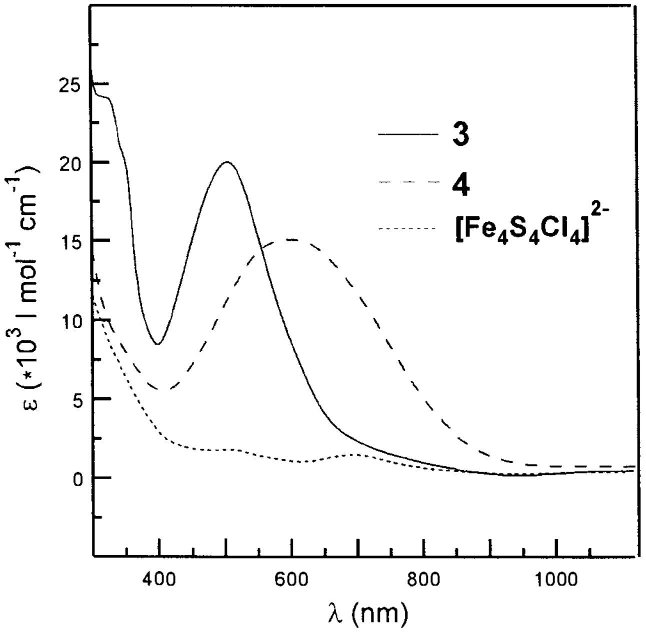

Fig. 3. UV–vis/NIR spectra of $[PPN]_2[Fe_4S_4Cl_4]$ and of complexes **3** and **4**.

In conclusion it can be stated that the redox activity and the optical properties of these octanuclear clusters add a new facet to the very well established chemistry and physics of the $Fe_4S_4$ system. The first results on their magnetism [16] indicate that there are also interactions between the unpaired electrons in these compounds which deserve a more detailed investigation.

## 6. Experimental

The general experimental and measuring techniques were as described before [7]. All starting materials were prepared according to the published procedures.

### 6.1. Preparations

**1**: 115 mg (0.10 mmol) of $[Ph_4P]_2[Fe_4S_4Cl_4]$ and 110 mg (0.46 mmol) of $Na[Cr(CO)_5CN]$ were dissolved in 15 ml of $CH_2Cl_2$ and stirred for 30 min.. After filtration the filtrate was layered with 10 ml of benzene and then 30 ml of hexane. After 2 days at −27°C, filtration, washing with hexane and drying yielded 186 mg (97%) of **1** as dark violet crystals, m.p. 97°C (dec.). Anal. Found: C, 45.68; H, 2.41; N, 2.57. $C_{72}H_{40}Cr_4Fe_4N_4O_{20}P_2S_4$ (1902.68) Calc.: C, 45.45; H, 2.12; N, 2.94%.

**2**: Like **1** from 116 mg (0.10 mmol) of $[Ph_4P]_2[Fe_4S_4Cl_4]$ and 115 mg (0.41 mmol) of $Na[Mo(CO)_5CN]$. Yield 170 mg (82%) of **2** as dark violet crystals, m.p. 121°C (dec.). Anal. Found: C, 41.82; H, 1.95; N, 2.59. $C_{72}H_{40}Fe_4Mo_4N_4O_2P_2S_4$ (2078.46) Calc.: C, 41.62; H, 1.94; N, 2.70%.

**3**: Like **1** from 120 mg (0.11 mmol) of $[Ph_4P]_2[Fe_4S_4Cl_4]$ and 180 mg (0.48 mmol) of $Na[W(CO)_5CN]$. Yield 233 mg (92%) of **3** as dark violet crystals, m.p. 128°C (dec.). Anal. Found: C, 35.43; H, 1.86; N, 2.19. $C_{72}H_{40}Fe_4N_4O_2P_2S_4W_4$ (2430.10) Calc.: C, 35.59; H, 1.66; N, 2.31%.

**4**: Like **1** from 45 mg (0.055 mmol) of $[Et_4N]_2[Fe_4S_4Cl_4]$ and 65 mg (0.28 mmol) of $Na[MnCp(CO)_2CN]$. Yield 66 mg (85%) of **4** as dark blue crystals, m.p. 121°C (dec.). Anal. Found: C, 38.46; H, 4.12; N, 5.54. $C_{48}H_{60}Fe_4Mn_4N_6O_8S_4$ (1420.42) Calc.: C, 40.59; H, 4.26; N, 5.92%.

**5**: 101 mg (0.134 mmol) of $[Et_4N]_2[Fe_4S_4Cl_4]$, 110 mg (0.54 mmol) of $Cp(CO)_2Fe–CN$, and 165 mg (0.64 mmol) of $NaSbF_6$ in 30 ml of acetonitrile were stirred for 12 h. After filtration the solvent was removed in vacuo and the residue picked up in 10 ml of $CH_2Cl_2$. After layering with 10 ml of ether the mixture was kept at −27°C for a week. Filtration, washing with ether and drying yielded 29 mg (12%) of **5** as an impure red–brown powder, m.p. 103°C (dec.). Anal. Found: C, 27.29; H, 3.31; N, 3.87. $C_{32}H_{20}F_{12}Fe_8N_4O_8S_4Sb_2$ (1635.05) Calc.: C, 23.51; H, 1.23; N, 3.43%.

**6**: Like **5** from 60 mg (0.050 mmol) of $[Ph_4P]_2[Fe_4S_4Cl_4]$, 113 mg (0.20 mmol) of Cp(dppe)Fe–CN and 60 mg (0.36 mmol) of $NH_4PF_6$. The $CH_2Cl_2$ extract was treated with 40 ml of hexane to precipitate 35 mg (25%) of **6** as a blue powder, m.p. 87°C (dec.). Anal. Found: C, 52.99; H, 4.21; N, 1.92. $C_{128}H_{116}F_{12}Fe_8N_4P_{10}S_4$ Calc.: C, 54.46; H, 4.14; N, 1.98%.

**7**: Like **5** from 60 mg (0.05 mmol) of $[Ph_4P]_2[Fe_4S_4Cl_4]$, 150 mg (0.20 mmol) of $Cp(PPh_3)_2Ru–CN$, and 65 mg (0.25 mmol) of $NaSbF_6$. The $CH_2Cl_2$ extract was treated with 50 ml of ether and 20 ml of hexane, kept at −27°C for 2 days and then filtered to yield 42 mg (23%) of impure **7** as a partially oily brown solid. Anal. Found: C, 48.41; H, 3.55; N, 1.25. $C_{168}H_{140}F_{12}Fe_4N_4P_8Ru_4S_4Sb_2$ Calc.: C, 54.68; H, 3.82; N, 1.52%.

**8:** 71 mg (0.061 mmol) of $[Ph_4P]_2[Fe_4S_4Cl_4]$, 152 mg (0.247 mmol) of $(PPh_3)_2Cu–CN$, and 81 mg (0.49 mmol) of $NH_4PF_6$ were stirred for 12 h in a mixture of 15 ml of $CH_2Cl_2$ and 15 ml of acetonitrile. After filtration the solvent was removed in vacuo. The residue was picked up in 10 ml of $CH_2Cl_2$, the solution layered with 20 ml of hexane and kept for 2 days at 7°C. Filtration and washing with hexane yielded 96 mg (51%) of **8** as a green powder, m.p. 148°C (dec.). Anal. Found: C, 59.30; H, 4.14; N, 1.68. $C_{148}H_{120}Cu_4F_{12}Fe_4N_4P_{10}S_4$ (3098.15) Calc.: C, 57.38; H, 3.90; N, 1.81%.

**9:** Like **8** from 55 mg (0.047 mmol) of $[Ph_4P]_2[Fe_4S_4Cl_4]$, 176 mg (0.191 mmol) of $(Ph_3P)_3Ag–CN$, and 64 mg (0.394 mmol) of $NH_4PF_6$. Yield 71 mg (38%) of **9** as a brown powder, m.p. 155°C (dec.). Anal. Found: C, 58.29; H, 4.24; N, 1.75. $C_{220}H_{180}Ag_4F_{12}Fe_4N_4P_{14}S_4$ (4324.60) Calc.: C, 61.10; H, 4.20; N, 1.30%.

### 6.2. Structure determinations

Crystals of **3** and **4** were obtained by slow diffussion of hexane into their dichloromethane (**3**) and chlorobenzene solutions (**4**). Diffraction data were obtained on a Nonius CAD4 diffractometer with graphite-filtered Mo–$K_\alpha$ radiation by the $\omega/2\theta$ technique in the $\theta$ range 3–26°. They were treated with an absorption correction based on psi scans. The structures were solved with direct methods and refined anisotropically with the SHELX program suite [20]. Drawings were produced with SCHAKAL [21]. The crystallographic data of the structures were deposited at the Cambridge Crystallographic Data Centre, (those of **3** already with the short communication [16]) with deposition numbers CSD-404693 for **3** and 100870 for **4**. Copies of these data are available free of charge from the following address: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +12 23/3 36 0 33; e-mail: teched@chemcrys.cam.ac.uk).

### 6.3. Crystal data

**3**: Monoclinic, space group C2/c, $Z = 4$, $a = 27.743(6)$, $b = 16.906(3)$, $c = 19.169(4)$ Å, $\beta = 92.75(3)°$, $V = 8980(3)$ Å$^3$, $d_{calc} = 1.85$ g cm$^{-3}$, $\mu = 5.95$ mm$^{-1}$, 8787 independent reflections, 4996 observed reflections ($I \geq 2\sigma(I)$), 532 variables, $R = 0.048$.

**4**: Monoclinic, space group C2, $a = 22.933(5)$, $b = 11.438(2)$, $c = 22.464(4)$ Å, $\beta = 90.99(3)°$, $V = 5892(2)$ Å$^3$, $d_{calc} = 1.58$ g cm$^{-3}$, $\mu = 1.98$ mm$^{-1}$, 7792 independent reflections, 5669 observed reflections ($I \geq 2\sigma(I)$), 593 variables, $R = 0.051$.

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