Cyclotriveratrylene models for [4Fe–4S] proteins: 3:1 subsite differentiation and modulation of the redox potential †

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The potential of cyclotriveratrylene (ctv) (2,3,7,8,12,13-hexamethoxy-10,15-dihydro-5*H*-tribenzo[*a,d,g*]cyclononene) trithiols as ligands that can easily be functionalised and show subsite differentiation in their complexes with [4Fe–4S] clusters has been explored. The cluster complexes of tris(2-sulfanylethoxy)- and tris(3-sulfanyl-methylbenzyloxy)-functionalised ctvs have been studied by core-extrusion experiments, spectroscopy and electrochemical techniques. With $[Fe_4S_4Cl_4]^{2-}$ as starting material a cluster complex was obtained in which the unique Fe and its co-ordinating Cl was turned into the cavity and show no reactivity. Starting with the more bulky $[Fe_4S_4(SBu^t)_4]^{2-}$ the unique iron points outwards and is susceptible to substitution reactions. The effects of hydrogen bonding and electron density on the redox potential of the cluster complex have been investigated. The redox potential becomes more negative when the length of the spacer between the ctv and cluster core is increased, which is explained by the longer distance between the cluster and the electron-withdrawing phenoxy moiety of the ctv. The synthesis of ctv derivatives with one thiol and one alcohol functionality per phenyl unit, and comparison with corresponding derivatives where hydrogen bonding is not possible, showed that no significant differences were found. The effects of a substituent in an aromatic amide group that could hydrogen bond to the co-ordinated thiol were investigated. A weak effect, in the direction expected, was found upon substitution of methyl for H.

The iron sites in naturally occurring [4Fe–4S] clusters are necessarily inequivalent because of the asymmetric protein mantle which surrounds them. Recently, evidence has been presented that [4Fe–4S] centres in certain proteins and enzymes indeed have subsites with different structural and reactivity properties.[1] This has evoked interest in the development of synthetic models that mimic this feature. To avoid the formation of polymers, Holm's group used Cram's cavitand concept[2] and synthesized a tripodal ligand, which has the ideal preorganisation for binding of a [4Fe–4S]²⁺ cluster.[3] In order to investigate the effects of the size and conformation of the ligand, Holm's group also synthesized a cluster based on a macrocyclic polyether trithiol.[4] Evans *et al.*[5] used a more accessible triazacyclane-based trithiol to obtain site-differentiated iron–sulfur clusters.

In order to have possibilities to vary the parameters which are important for modulation of the redox potential of the cluster compounds, *viz.* the number of hydrogen bonds, the hydrophobicity of the environment, and the electron density on the [4Fe–4S] core, we designed a tripodal ligand system based on the building block cyclotriveratrylene (2,3,7,8,12,13-hexamethoxy-10,15-dihydro-5*H*-tribenzo[*a,d,g*]cyclononene **I**). This molecule has a rigid, bowl-like shape and possesses three-fold symmetry.[6] The functionalisation of the cyclotriveratrylene framework with arms having terminal thiol groups provides a suitable ligand system. These trithiols are chiral because the conformational inversion of their nine-membered ring is very slow at room temperature.[6] By varying the arms we may be able to modulate the redox potential of the cluster.

We have recently reported the synthesis and characterisation of trithiol **IIa** and the more acidic trithiol **IId** and their use in the preparation of 3:1 subsite-differentiated cluster com-


I

IIa   IId
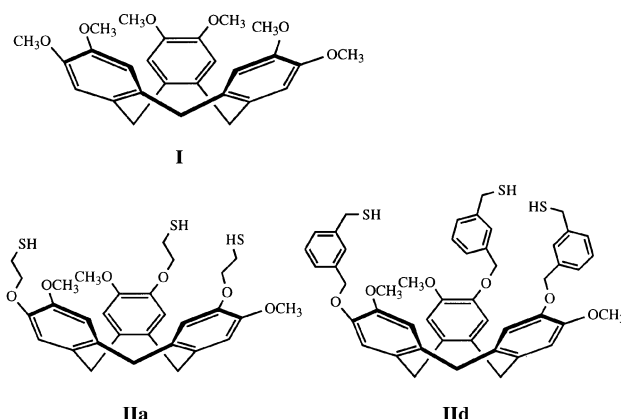
pounds[7a,b] and others have reported on a similar approach.[7c] In this paper we elaborate on our work and also describe how the reduction potential can be modulated by modifying the tridentate ligand. To that purpose we first changed the spacer between the cluster core and the cyclotriveratrylene (ctv) unit. Secondly we investigated whether hydrogen bonds could cause a change in electron donation of the tridentate ligand to the cluster core. Two kinds of hydrogen-bridging functionalities were introduced, *viz.* a hydroxy group and an amide group, in both cases by modifying the methoxy group of the ctv unit. For reasons of efficiency and in order to investigate whether indeed a modulation of the redox potential can be expected for the ctv-based trithiols, the corresponding monothiols were synthesized first and tested.

Results and Discussion

Synthesis of the cyclotriveratrylene trithiol

Derivatives of compound **II** were conveniently prepared as
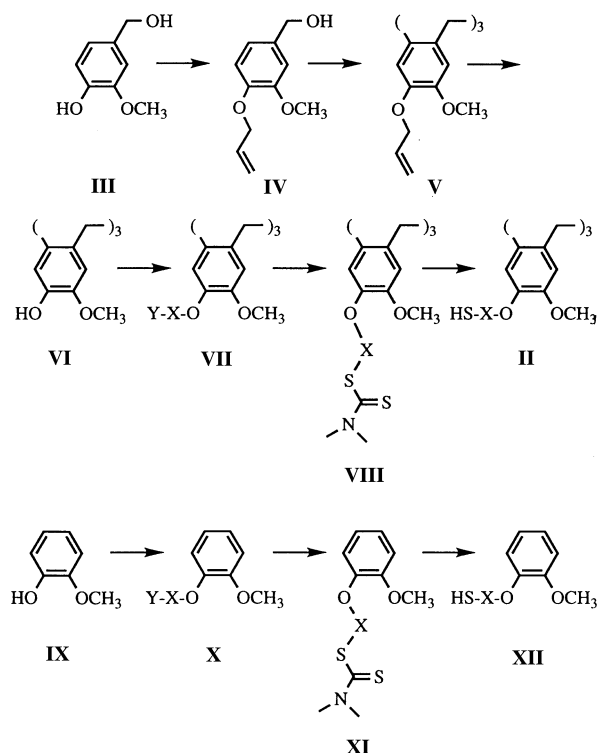
Scheme 1 Y = Br, X = CH$_2$CH$_2$ **a**, CH$_2$CH$_2$CH$_2$ **b**, CH$_2$CH$_2$CH$_2$CH$_2$ **c**, *m*-CH$_2$C$_6$H$_4$CH$_2$ **d** or *p*-CH$_2$C$_6$H$_4$CH$_2$ **e**; Y = Cl, X = *p*-CH$_2$CH$_2$-OC$_6$H$_4$CH$_2$ **f**, 4-(CH$_2$CH$_2$O)-2-(CH$_3$O)C$_6$H$_4$CH$_2$ **g** or CH$_2$CH$_2$OCH$_2$-CH$_2$ **h**

Scheme 2 *n* = 2, *m* = 3 **a**; *n* = 3, *m* = 2 **b** or 3 **c**; *n* = 4, *m* = 2 **d** or 3 **e**

shown in Scheme 1. The tris(*O*-allyl) ether **V** of cyclotriguaia-cylene **VI** was prepared according to the literature,[8] but was deprotected by using Pd(O$_2$CMe)$_2$, with higher yields (96%) than reported[8] using Pd/C (80%).

The length of both alkyl and aryl spacers between the ctv unit and the iron–sulfur cluster was varied. First we alkylated cyclotriguaiacylene with dibromo compounds. In our hands, the use of dithiocarbamate[9] as the reagent to introduce the sulfur into **VIIa**–**VIIe** turned out to be the most convenient method. Subsequent reduction with lithium aluminium hydride followed by acidic work-up gave the desired trithiols **IIa–IIe**. The yields were relatively low, probably because the thiolates are able to cleave aryl ethers.[10] Acidic deprotection,[11] however, did not improve the yields, probably because of the acid labile aryl ether functionality. In the case of **IId** the relatively low yield is due to the acid lability of the benzyl aryl ether linkage, which is partly hydrolysed during purification by column chrom-atography. Other purification methods were not successful. The monothiols **XIIa–XIIe** were prepared in a similar way as described for the corresponding trithiols **IIa–IIe**, *viz.* starting from guaiacol **IX** instead of cyclotriguaiacylene **VI** (Scheme 1). Compounds **XIIb** and **IIb** were obtained in lower yields than the other compounds. This is due to a β-elimination reaction, resulting in a stable allyl ether, in both the step where the alkyl-ation of the phenolates takes place and the thiol-deprotection step. An additional complication is that in the latter case the intermediate thiol is capable of cleaving the alkyl aryl ether bond.[10] As found for compound **XIIa**, this gave rise to side products which could, however, be separated from the desired product by column chromatography. From the intermediate **VIIa** we prepared compounds **IIf** and **IIg** by simple alkylation reactions. The corresponding monothiols (**XIIf** and **XIIg**) were not synthesized. Compounds **XIIh** and **IIh** were prepared from the chloro analogues of **Xh** and **VIIh**, respectively, and the thiol functionality was introduced *via* a thioacetate.[12]

To study the effect of hydrogen bonds a number of com-pounds with the general structure *o*-HS(CH$_2$)$_n$OC$_6$H$_4$O(CH$_2$)$_m$-OH **XVII** were sy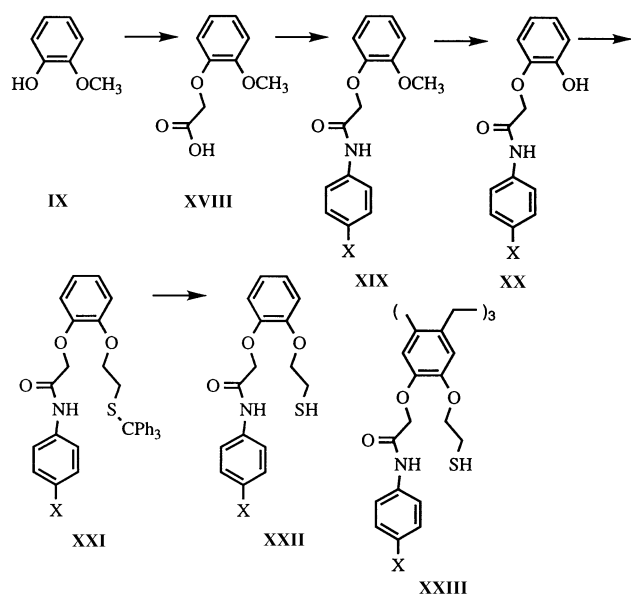nthesized. By varying the spacer lengths we hoped to optimise the values of *m* and *n* which would give the best match for a hydrogen bond. In order to be able to use the same strategy for the synthesis of the corresponding ctv thiols, the reaction sequence in Scheme 2 was employed. For the key step, the cleavage of the methyl aryl ether linkage **XIII** ⟶ **XIV**, lithium diphenylphosphide was used,[13] which gave the desired products in reasonable yields (30–55%). However, as the studies with **XVII** gave no evidence of hydrogen bonding (see below) we did not prepare the corresponding ctv thiols.
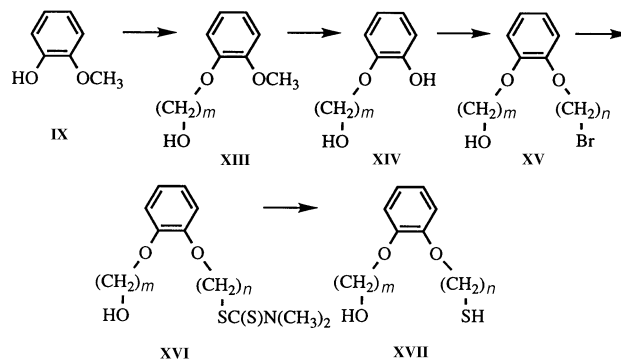
The compounds **XXII** were prepared in order to mimic the hydrogen bonds between amides and iron–sulfur clusters in proteins. Corey–Pauling–Koltun (CPK) models showed that the geometry and rigidity of the ethyl spacer is optimal for the formation of a hydrogen bond between the amide and the co-ordinating thiolate sulfur. By varying the *para* substituent X, the strength of the hydrogen bond can be modulated and thus the redox potential of the cluster. There are two possible strat-egies for the preparation of the amide-containing thiols. The first one starts with the introduction of the protected thiol func-tionality, subsequent removal of the methyl group, and finally the amide spacer is connected. An advantage of this strategy is that the amide is introduced in one of the last steps. This means that for the preparation of a variety of thiols the same precursor can be treated with different substituted anilines. The second strategy involves the introduction of the amide spacer, followed by demethylation, and attachment of the thiol spacer. The bottleneck in both strategies is the demethylation step.

First bromide **Xa** was synthesized. It was not possible to demethylate this compound with LiPPh$_2$, used earlier for the preparation of the hydroxy-containing thiols, because the phosphide was found to substitute the bromide. We therefore had to introduce the sulfanyl ethyl group first. The trityl group was chosen to protect the thiol because it is known that this group can be removed in the presence of an amide. Unfortu-nately, we were not able to remove the methyl group selectively from this compound.[14]

In the second strategy (Scheme 3) compound **IX** was first alkylated with chloroacetic acid to give **XVIII**. After this step aniline and *p*-methylaniline were introduced.[15] It appeared to be impossible to demethylate **XVIII** first and subsequently intro-duce these groups.[14] Aluminium chloride in toluene proved to be a good choice to demethylate **XIX**. In this reaction more than 2 equivalents of reagent were required; 1 equivalent gave no demethylated product at all. The reaction temperature was very critical: below 40 °C no reaction took place, between 40 and 50 °C the product **XX** was formed, between 50 and 65 °C, a mixture of **XX** and guaiacol was obtained and above 65 °C only guaiacol could be detected. The yield of the reaction amounted to 35%, which could be improved further by using aluminium iodide in refluxing carbon sulfide (56%). Introduction of the ethylene spacer using 1,2-dibromoethane and subsequently treating the product with a protected thiol caused cleavage of the amide functionality, so we first substituted 1,2-dibromo-ethane with 1 equivalent of trityl thiolate and afterwards treat-

Scheme 3 structures (compounds IX, XVIII, XIX, XX, XXI, XXII, XXIII)

Scheme 3 X = H **a** or CH₃ **b**

Cluster structures:

1a X = CH₂CH₂
1d X = m‑CH₂C₆H₄CH₂

2a X = CH₂CH₂
2d X = m‑CH₂C₆H₄CH₂

ed this with the alkylated phenol **XX**, to give **XXI**. Finally, thiol **XXII** could be obtained by deprotecting **XXI** with silver acetate and acidic work-up. The route followed appeared to be limited to certain amides, *e.g.* with X = H and CH₃. The use of an electron-withdrawing substituent (*e.g.* NO₂) resulted in cleavage of the amide functionality during the demethylation step.

In contrast to guaiacol, cyclotriguaiacylene did not react with chloroacetic acid under various conditions to give the ctv analogue of **XVIII**. Therefore, chloroacetic acid was first coupled to aniline and the resulting product treated with cyclotriguaiacylene to give the ctv analogue of **XIX**. This compound could be demethylated with aluminium iodide to give the ctv analogue of **XX**. This compound, however, could not be alkylated with 1-bromo-2-tritylsulfanylethane so we were not yet able to prepare ctv thiol **XXIII**. The thiols were fully characterised by spectroscopic methods and elemental analyses.

Cluster complexes 1a, 1d, 2a and 2d

In this section we describe the preparation of the cluster complexes from the compounds **IIa** and **IId**, and the experiments which were performed to investigate whether the products obtained, **1a**, **1d**, **2a** and **2d**, are the desired 3:1 subsite-differentiated clusters or random polymers.

Preparation. Thiolate-ligated cubane type [4Fe–4S] clusters can be synthesized from elemental sulfur, iron(III)chloride and thiolate in a process called self-assembly. Other clusters can be synthesized from these clusters *via* ligand-exchange reactions which in fact are acid–base equilibrium reactions. A volatile thiol-forming precursor such as Bu^{t}S$^-$ is most commonly used,[16] because it can be removed *in vacuo*, thus driving the reaction to completion. It is also possible to start from a tetrachloro-ligated cluster, *viz.* [Fe₄S₄Cl₄]²⁻, which is prepared by the reaction of a thiolate cluster with an acid chloride. This procedure is especially useful when less acidic alkanethiols are involved.[17]

Exchange reactions of [Fe₄S₄Cl₄]²⁻ with 1 equivalent of compound **IIa** or **IId** and 3 equivalents of a base (tetrabutylammonium hydroxide) were conducted under a nitrogen atmosphere in dilute dimethylformamide (dmf) (10⁻³ mol dm⁻³), to avoid the formation of polymers. Upon mixing of the reactants the mixtures immediately changed from purple-brown to yellow-brown. After the addition of diethyl ether black solids precipitated, which were identified as **1a** and **1d**, respectively (see below). In a similar way black precipitates of **2a** and **2d** were formed by treating [Fe₄S₄(SBu^t)₄]²⁻ with 1 equivalent of **IIa** or **IId** under dynamic vacuum.
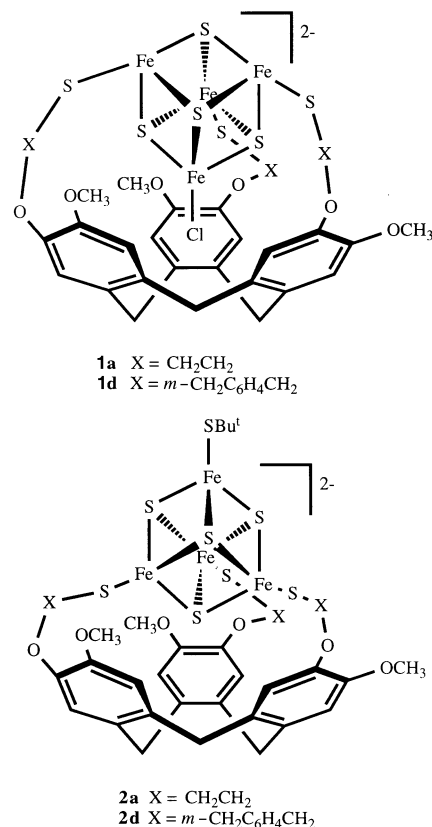
The four complexes are very soluble in dimethyl sulfoxide (dmso) and reasonably soluble in dmf but insoluble in most common organic solvents such as chloroform, toluene, acetonitrile, acetone, diethyl ether, tetrahydrofuran and hexane. The counter ions used were either tetrabutylammonium or tetraphenylphosphonium cations. In the case of tetraethylammonium cations the products were completely insoluble. Carrying out the reactions with an excess of trithiol in more concentrated solutions resulted in the formation of an insoluble, probably polymeric product. When acetonitrile was used as the solvent to perform the exchange reactions the product precipitated with ether was no longer soluble in acetonitrile. Remarkably, no spectroscopic differences were observed between the reaction mixture in acetonitrile and the precipitate dissolved in dmf or dmso. The reason may be that precipitation from acetonitrile induces the formation of aggregates. The observed change in solubility may also be due to some unknown interaction of the solvent with the cluster. In this context it is worth mentioning that according to Holm and co-workers[18] a large excess of chloride ions is required to obtain a sharp wave in the cyclic voltammogram of [Fe₄S₄Cl₄]²⁻ in dmso, indicating that there is an equilibrium between co-ordinating solvent and chloride ions. Furthermore it should be noted that we were never able to remove all the acetonitrile or dmf from the clusters, as indicated by NMR spectroscopy. Evidence of strong solvent cluster interactions also comes from electrochemical measurements. At low temperature the dependence of the half-wave potentials of cluster compounds on temperature is no longer linear, which points to an equilibrium reaction between the clusters and solvent molecules (see below). Blonk[19] has shown that the reaction entropies for the reduction of [Fe₄S₄(SR)₄]²⁻ are considerably less negative in dmso and dmf than in dichloromethane.

Characterisation. *Core extrusion.* In biochemistry the presence of a [4Fe–4S] core is often demonstrated by an experiment in which the cluster core is extruded. To do this an excess of benzenethiol is added which results in the formation of the known compound [Fe₄S₄(SPh)₄]²⁻.[20] When we performed such

Table 1 Proton NMR isotropic shifts of cluster compounds in $(CD_3)_2SO$

Cluster	T/K	Isotropic shift [a]/ppm
$[Fe_4S_4L_4]^{2-}$		
L = SBu^t	298	-1.3 [C(CH$_3$)$_3$]
L = SCH$_2$Ph [b]	298	-10.1 (SCH$_2$)
	325	-10.7 (SCH$_2$)
L = SCH$_2$CH$_3$ [b]	298	-10.0 (SCH$_2$)
1a	298	-10.6 (SCH$_2$)
1d	298	-10.1 (SCH$_2$)
2a	298	-10.5 (SCH$_2$), -1.2 [C(CH$_3$)$_3$]
2d	298	-9.8 (SCH$_2$), -1.2 [C(CH$_3$)$_3$]
	324	-10.6 (SCH$_2$), -1.3 [C(CH$_3$)$_3$]

[a] $\delta^{iso} = \delta^{dia} - \delta^{obs}$. [b] Taken from ref. 24.

an experiment with our complexes cyclic voltammetry (CV) and the NMR spectra indicated that indeed $[Fe_4S_4(SPh)_4]^{2-}$ was formed. One should note, however, that this result does not unequivocally prove the presence of a cubane [4Fe–4S] core since it is known[21] that also prismane-like [6Fe–6S] clusters react with benzenethiol resulting in the formation of $[Fe_4S_4(SPh)_4]^{2-}$.

UV/VIS. Upon reaction with the thiol **IIa** or **IId** the UV/VIS spectrum of $[Fe_4S_4Cl_4]^{2-}$ changed to one typical of a thiolate-ligand cluster and showed absorption maxima at *ca.* 300 (shoulder) and 420 nm.[17,22] The product formed in the corresponding reactions with $[Fe_4S_4(SBu^t)_4]^{2-}$ showed the same electronic spectra.

NMR. In the ^{1}H NMR spectra of ferredoxins the CH$_2$S protons of the cysteinyl residues directly bonded to the cluster are visible as broadened resonances at about δ 10–17.[23] Our complexes had temperature-dependent isotropic shifts* in accordance with the shifts reported by Holm *et al.*[24] for comparable ligands (see Table 1).

In the NMR spectra of complexes **2a** and **2d** the resonances of the corresponding ligands **IIa** and **IId** were clearly visible as was the Bu^{t}S$^-$ group. For **2d** this is shown in Fig. 1. Complexes **1a** and **1d** displayed slightly different isotropic shifts when compared to **2a** and **2d**. This sensitivity of the isotropic shift to changes in ligation at the unique site was also found for cluster compounds derived from other trithiols.[3–5] The fact that all complexes showed only one ^{1}H NMR signal for the CH$_2$S protons is indicative of a single product with trigonal symmetry. When $[Fe_4S_4Cl_4]^{2-}$ was titrated with the reference thiolate $^-$SCH$_2$C$_6$H$_4$-CH$_2$OPh-*m* we observed different resonances for the CH$_2$S protons in the NMR spectra for less than 4 equivalents of added thiolate because a mixture of products is formed. After the addition of 4 equivalents only one resonance remained with an isotropic shift comparable to that of compound **2d**. The NMR spectra of the four complexes revealed that even after exposure to high vacuum some dmf was always retained by the clusters (resonances at δ 2.72, 2.91 and 7.94). This was also found for the macrocyclic [4Fe–4S] cluster compounds of Okuno and co-workers.[25]

Carbon-13 NMR data for several synthetic $[Fe_4S_4(SR)_4]^{2-}$ clusters have been reported.[26] Owing to broadening not all the expected resonances in the ^{13}C NMR spectra of our clusters could be observed. The signals belonging to the carbons adjacent to the sulfur atoms of the ligand were shifted, implying that the thiolate groups are co-ordinating to iron centres.

IR. Compounds **1a** and **1d** displayed their IR spectra at Fe–Cl vibration at 351 cm^{-1}. The intensity of the band was less intense than for the tetrachloro cluster (Fig. 2).

* Defined as $\delta^{iso} = \delta^{dia} - \delta^{obs}$. The diamagnetic reference shifts are those of the thiols.
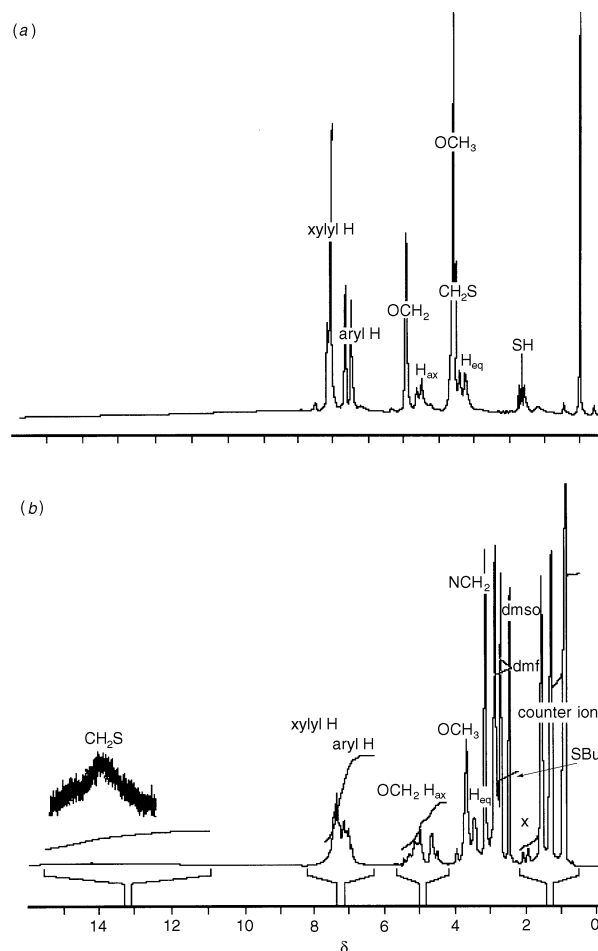
Fig. 1 Proton NMR spectra of compound **IId** in CDCl$_3$ (*a*) and of cluster compound **2d** in $(CD_3)_2SO$ (*b*). Spectrum (*b*) was recorded at 324 K. Signal assignments are indicated. X = impurity
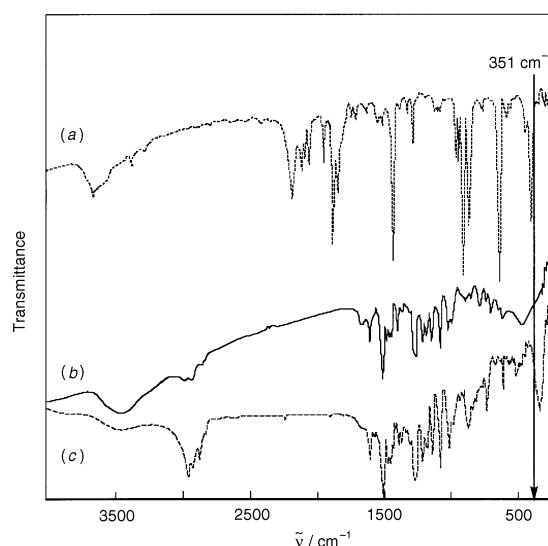
Fig. 2 Infrared spectra of $[PPh_4]_2[Fe_4S_4Cl_4]$ (*a*), **2d** (*b*) and **1d** (*c*)
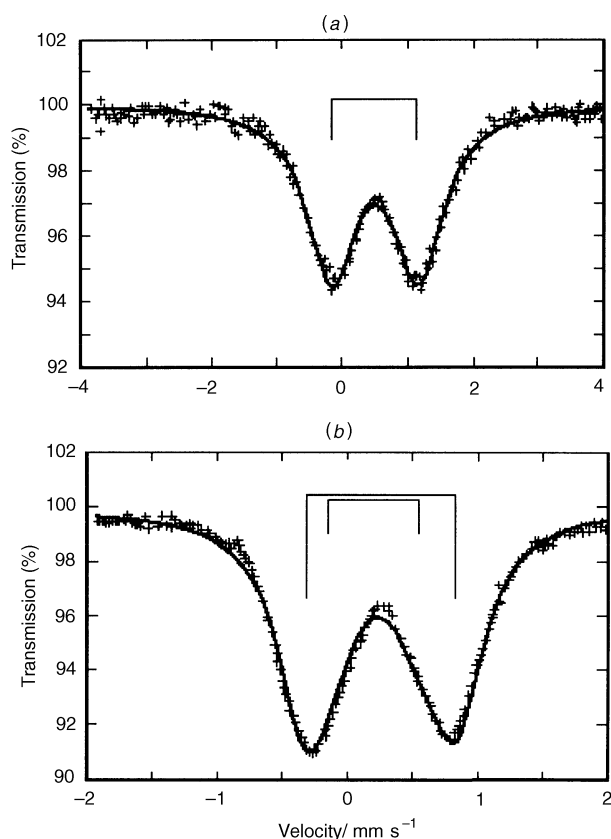
Mössbauer. The 3 : 1 differentiation of the iron sites in the solid state is reflected in the ^{57}Fe Mössbauer spectrum of complex **1d**. At 77 K this compound showed two quadrupole doublets, one at 0.32 ($\Delta E_Q = 1.15$) and one at 0.29 mm s^{-1} ($\Delta E_Q = 0.69$ mm s^{-1}), in a 3 : 1 ratio. Product **2d** exhibited only one quadrupole doublet with an isomer shift of 0.51 mm s^{-1} and a quadrupole splitting of 1.33 mm s^{-1} (Fig. 3).

Electrochemistry. Half-wave potentials. The electrochemical behaviour of the four clusters was studied using different elec-
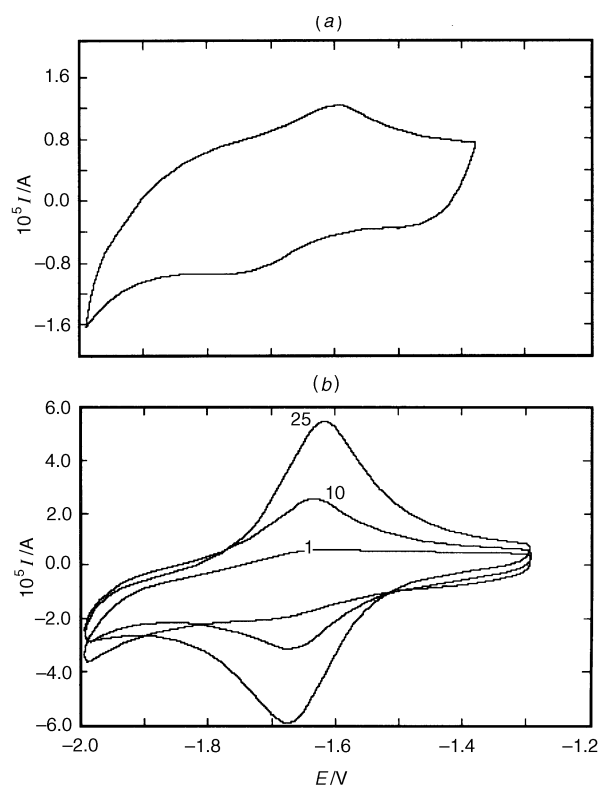
Table 2 Electrochemical properties of cluster compounds in dmf

Compound	$E_{\frac{1}{2}}*/V$ (ΔE_p/mV)			Response improvement after addition of Ba²⁺
	0 mmol dm⁻³ Ba²⁺	2.5 mmol dm⁻³ Ba²⁺	20 mmol dm⁻³ Ba²⁺	
$[Fe_4S_4L_4]^{2-}$				
L = SPh	−1.52 (60)	−1.52 (60)	−1.52 (60)	No
L = S(CH₂)₃OPh	−1.80 (80)	−1.80 (75)	−1.80 (75)	No
HL = **XIIb**	−1.80 (120)	−1.77 (105)	−1.77 (100)	No
HL = **XVIIb**	−1.82 (160)	−1.77 (120)	−1.77 (120)	No
1a	−1.68 (60)	−1.64	−1.61 (20)	Yes
1d	−1.69 (70)	−1.65	−1.62 (5)	Yes
2a	−1.80 (70)	−1.77	−1.72 (10)	Yes
2d	−1.78 (80)	−1.74	−1.70 (30)	Yes

* 2−/3− Reduction at 25 °C *vs.* ferrocene–ferrocenium, using an edge-plane graphite working electrode, ΔE_p = peak separation. Peak-current ratios of the forward and backward scans are approximately unity.

Fig. 3 Mössbauer spectra of cluster compounds **2d** (*a*) and **1d** (*b*) at 77 K

Fig. 4 Cyclic voltammograms of complex **2d** in dmf without a promoter present (*a*) and with a promoter (20 mmol dm⁻³ Ba²⁺) after 1, 10 and 25 scans (*b*). Platinum working electrode, 0.1 mol dm⁻³ NBu₄PF₆ as supporting electrolyte and 0.5 mmol dm⁻³ **2d** at a scan rate of 100 mV s⁻¹. Potentials are *vs.* ferrocene–ferrocenium

trodes, *viz.* platinum, gold, edge-plane graphite and basal-plane graphite. With a platinum or gold working electrode hardly any current response was observed in the cyclic voltammograms [Fig. 4(*a*)]. With the use of an edge-plane graphite electrode the current response improved considerably and for the 2−/3− redox transition of **1d** a half-wave potential ($E_{\frac{1}{2}}$) of −1.69 V (dmf, *vs.* ferrocene–ferrocenium) was determined. This potential is in between the redox potential measured for the reduction of $[Fe_4S_4Cl_4]^{2-}$ (−1.35 V) and that measured for $[Fe_4S_4(SCH_2-C_6H_4CH_2OPh)_4]^{2-}$ (−1.80 V) under the same conditions. Also with a basal-plane graphite working electrode a measurable current response was obtained, although less than with an edge-plane electrode. Compound **1d** showed only one reduction peak in the differential pulse voltammogram, indicative of a single substance, whereas $[Fe_4S_4Cl_4]^{2-}$ which had partly reacted with the analogous monothiolate ⁻SCH₂C₆H₄CH₂OPh gave rise to more than one reduction peak, due to the occurrence of a mixture of mono-, di-, tri- and tetra-substituted products. For a polymer such an intramolecular mixture of various substituted

clusters would result in a differential pulse voltammogram with a multiplet of waves.

The half-wave potential of compound **2d** was observed at −1.78 V. The current response showed the same behaviour as that of **1d**. The redox behaviour of the clusters with the alkyl spacers (**1a** and **2a**) was very similar to that of the clusters with the xylylic spacers (Table 2).

Promoter effect. A considerable increase in the current response and a decrease in the cathodic-to-anodic peak separation (ΔE_p) in the cyclic voltammograms of cluster compounds **1a**, **1d**, **2a** and **2d** was observed after the addition of a promoter[27] like Ba²⁺ (Fig. 4).

With a promoter present we could also use a platinum or a gold working electrode. With the graphite electrodes a promoter is not strictly needed as without it there is a reasonable current response. This observation may indicate that specific interactions, *e.g.* π–π interactions, between the electrode surface and the cluster compounds are operative.[28] The response of the basal-plane electrode may be ascribed to structural defects

introduced in the manufacturing of this electrode or during the polishing process. In line with results reported for some negatively charged metalloproteins[29] and a semi-encapsulated cluster based on diphenylglucoluril 3a,4,6,6a-tetrahydro-3a,-6a-diphenylimidazo[4,5-d]imidazole-2(1H),5(3H)-dione[30] the optimum promoter concentration for Ba^{2+} was found to be approximately 20 mmol dm^{-3} for all four electrodes used. To obtain the same effect with Na^+, a 50 times larger amount of this ion was required. This is also in accordance with results found for proteins[27,31] and is as expected for a cation with a lower charge. With the promoter present the redox reactions were chemically reversible as could be deduced from the anodic-to-cathodic peak-current ratio of 1.0:1. All compounds showed an irreversible oxidation at approximately −0.2 V, immediately followed by a multielectron oxidation.

Modulation effect. The redox potential of complexes **1a**, **1d**, **2a** and **2d** shifted 70 mV when Ba^{2+} was added. This means that the promoter also has a modulating effect and hence must also be located in the neighbourhood of the cluster compounds. This positive shift is probably due to the electron-withdrawing effect of the barium ions, forming a complex with the cluster compounds. As can be seen in Table 2, the presence of oxygen atoms is important for the formation of this complex. Furthermore, one can conclude from this table and the studies of Hill and co-workers[29] and Martens *et al.*[31] that an improvement in the response only occurs if the redox-active species possesses a dipole. For the spherically ligated cluster compounds in Table 2 no improvement of the current response is visible after the addition of the promoter. For the oxygen-containing clusters a decrease of the peak separation was observed, probably because after the addition of Ba^{2+} a radial diffusion, due to a limited number of active sites on the electrode, changes to a more linear diffusion process, due to a homogeneous covered electrode. The addition of barium cations had no observable effect on the NMR and UV/VIS spectra of the clusters.

Adsorption. The redox reactions of the complexes, both with and without promoter, were controlled by adsorption. This was indicated by the linear responses of i_{pc} on the scan rate, the small ΔE_p values, and the higher current response when the number of scans was increased [Fig. 4(b)]. Owing to a lateral interaction between the electroactive species the peak separation (ΔE_p) will never become the theoretical zero value. Hill and co-workers[29] interpreted the promotion of the cyclic voltammetric response of 2[4Fe–4S] ferrodoxin from *Clostridium pasteurianum* in terms of two processes: first the formation of a 1:1 protein–promoter complex in the bulk and secondly the transfer of an electron to this complex at the electrode surface. From the magnitude of the calculated standard Gibbs energies of adsorption a reversible weak physical adsorption of the complex was suggested.

EPR. The clusters were EPR silent as expected for compounds with a [4Fe–4S]$^{2+}$ core. After reduction in dmf typical [4Fe–4S]$^+$ core signals could be detected. From the presence of a signal in both the $g = 2$ (axial-like) and 5 regions (Table 3) we can conclude that the reduced compounds are physical mixtures of pure $S = \frac{1}{2}$ and $\frac{3}{2}$ clusters, as has been reported for other synthetic [Fe$_4$S$_4$(SR)$_4$]$^{3-}$ clusters in frozen solution.[25] Variation of the ligand at the unique iron site (Cl *vs.* SBu^t) resulted in a slight variation of the g values (Table 3).

Orientation of the cluster core with respect to the ctv cavity. To investigate whether the unique ligand is pointing toward or away from the cavity of the ctv unit we performed exchange reactions at the unique iron site. The reactions were monitored by CV and ^{1}H NMR spectroscopy. Addition of sodium benzenethiolate or sodium dimethyldithiocarbamate to either complex **1a** or **1d** ($E_{\frac{1}{2}}$ = −1.64 and −1.65 V respectively) gave, according to CV, no reaction, even when a large excess of reagent was used.

Reaction of complex **2d** with 1 equivalent of benzenethiol

Table 3 The g values of the reduced cluster compounds **1d** and **2d** in dmf

Compound	g
[Fe$_4$S$_4$(SBu^t)$_4$]$^{3-}$	1.92, 2.05, 5.04
[Fe$_4$S$_4$(SCH$_2$Ph)$_4$]$^{3-}$	1.92, 2.05, 4.36
1d	2.10, 2.46, 4.23
2d	2.06, 2.15, 4.30

yielded a product with a redox potential of −1.68 V (20 mmol dm^{-3} Ba^{2+}), indicative of substitution of the SBu^t group by SPh. Reaction of **2d** with 1 equivalent of benzoyl chloride gave a product which showed a redox potential at −1.63 V (20 mmol dm^{-3} Ba^{2+}). This result suggests that the Bu^{t}S$^-$ group of **2d** is substituted by a chloride. Support for this comes from the disappearance of the *tert*-butyl resonance in the NMR spectrum and the appearance of a Fe–Cl vibration at 351 cm^{-1} in the IR spectrum. In contrast to **1d**, the newly formed chloro complex did react with sodium benzenethiolate and sodium dimethyldithiocarbamate to give products with redox potentials of −1.68 and −1.75 V (both 20 mmol dm^{-3} Ba^{2+}), respectively. From these results we may conclude that reactions of the tripodal ligands with [Fe$_4$S$_4$Cl$_4$]$^{2-}$ give products in which the chloride ligands point toward the cavity of the ctv units. This suggests the formation of a complex before the co-ordination takes place. It is known that ctv derivatives can form complexes with halogen-containing compounds, *e.g.* chloroform. Apparently, the unique iron is shielded. Reaction of **IIa** and **IId** with [Fe$_4$S$_4$(SBu^t)$_4$]$^{2-}$ yields compounds with the unique iron outside the cavity, probably because the Bu^t group cannot fit in the cavity.

The reaction of complex **2a** with benzenethiol or benzoyl chloride resulted in a mixture of products, indicating that these reactants do not fully discriminate between the different subsites of **2a**. This suggests that the fit of the cluster core in ligand **IIa** is not as good as in **IId**, giving rise to strain which means that **IIa** is relatively easily removed. Another explanation may be that the alkanethiolate co-ordination of **2a** is less stable than the *m*-CH$_2$C$_6$H$_4$CH$_2$S co-ordination of **2d**.

Modulation of the redox potential

Preparation of the cluster compounds. The cluster compounds of **IIa–IIh**, **XIIa–XIIh**, **XVIIa–XVIIe** and **XXIIa–XXIIb** were synthesized from [Fe$_4$S$_4$Cl$_4$]$^{2-}$ and [Fe$_4$S$_4$(SBu^t)$_4$]$^{2-}$ as described for **1** and **2**. The monothiols **XIIa–XIIh**, **XVIIa–XVIIe** and **XXIIa** and **XXIIb** were treated with 1 equivalent of hydroxide and 0.25 equivalent of [Fe$_4$S$_4$Cl$_4$]$^{2-}$ in acetonitrile. All products were characterised by UV/VIS and NMR spectroscopy. The chloride ligand present in the products obtained from the reaction of [Fe$_4$S$_4$Cl$_4$]$^{2-}$ with the ctv thiols was identified by IR spectroscopy (351 cm^{-1}).

Electrochemical characterisation. The electrochemical measurements showed typical half-wave potentials for the expected products (see below). The current response for all subsite-differentiated clusters was promoted and modulated by the addition of metal ions like Ba^{2+}, as found earlier for the clusters ligated by the trithiols **IIa** and **IId** (see above). When [Fe$_4$S$_4$Cl$_4$]$^{2-}$ was titrated with less than 4 equivalents of monothiolate the differential pulse voltammogram showed five peaks, indicating the presence of unsubstituted, mono-, di-, tri- and tetra-substituted cluster compounds. After addition of 4 equivalents all sites were substituted. Titration of [Fe$_4$S$_4$Cl$_4$]$^{2-}$ with the ctv thiolates resulted in a decrease in the current attributed to the reduction of the starting material and the rise of one new reduction signal. The reaction was completed after the addition of 1 equivalent of ctv thiolate. From these results we may conclude that the clusters formed are analogous to those described in the previous section. The orientation of the

Table 4 Half-wave potentials * of $[Fe_4S_4L(L')]^{2-/3-}$ in dmf *vs.* ferrocene–ferrocenium

		$E_{\frac{1}{2}}/V$	
H_3L	L'	No modulator	$20\ mmol\ dm^{-3}\ Ba^{2+}$
IIa	Cl	−1.68	−1.61
IIb	Cl	−1.74	−1.65
IIc	Cl	−1.78	−1.70
IId	Cl	−1.70	−1.62
IIe	Cl	−1.69	−1.62
IIf	Cl	—	−1.65
IIg	Cl	—	−1.70
IIh	Cl	−1.74	−1.67
IIa	SBu^t	−1.80	−1.72
IIb	SBu^t	−1.82	−1.75
IIc	SBu^t	−1.84	−1.77
IId	SBu^t	−1.82	−1.76
IIe	SBu^t	−1.82	−1.75
IIf	SBu^t	—	−1.70

* Without modulator an edge-oriented pyrolytic graphite working electrode was employed. With modulator a platinum working electrode was used.

Table 5 Half-wave potentials for the 2+/1+ core reduction of $[Fe_4S_4L_4]^{2-}$ clusters ^{a}

	$E_{\frac{1}{2}}/V$	
HL	dmf	CH_2Cl_2
XIIa	−1.72	−1.67
XVIIa	−1.72	−1.68
XIIb	−1.80	−1.76
XVIIb	−1.82	−1.76
XIIc	−1.85	−1.80
XVIIc	−1.82	−1.75
XIId	−1.80	b
XVIId	−1.86	−1.79
XIIe	−1.79	b
XVIIe	−1.88	−1.82
XIIh	−1.82	b

^{a} *versus* ferrocene–ferrocenium. ^{b} Not determined.

cluster cores with respect to the ctv cavity was not further investigated.

Effect of the spacer. The results of electrochemical experiments on clusters with ctv ligands **IIa**–**IIh** are presented in Table 4. As shown, the redox potential can be modulated by varying the spacer between the ctv unit and the cluster compound. In general we can say that the values of the half-wave potentials are in line with the electronic properties of the ligands. The half-wave potential for the 2+/1+ core reduction is expected to become more negative when the alkyl spacer becomes longer. This is indeed found for the ctv ligands **II** (Table 4, L = **IIa**–**IIc**) and the ligands **XII** (Table 5, L = **XIIa**–**XIIc**). This trend can be explained as an effect of the electron-withdrawing phenoxy moiety which is sensed less by the cluster core when the length of the spacer is increased. The difference between a *p*- and an *m*-xylylic spacer is small as can be concluded from both the NMR spectra of the clusters and their electrochemical properties (Table 4, data for **IId** and **IIe**; Table 5, **XIId** and **XIIe**). This indicates that despite the different ligand geometries no structural differences between the cluster cores exist in solution. Compared to **IIf**, the electron-donating methoxy substituent of ligand **IIg** forces the reduction potential to a more negative value. As already noticed in the previous section, the half-wave potential of the clusters with ligands of the types **II** and **XII** can also be changed by adding a modulator, and in the case of **II** by substitution of the unique ligand.[7b]

Effect of hydroxy hydrogen bonds. Iron–sulfur clusters of the type $[Fe_4S_4(SR)_4]^{2-}$ with R = CH_2CH_2OH and C_6H_4OH-*o* have

in principle the possibility to form intramolecular hydrogen bonds with the co-ordinating sulfur atoms *via* their hydroxy groups. In addition they can exhibit an electronic effect as compared to the cluster compounds with R = Pr^n or Ph. For the cluster compound with R = C_6H_4OH-*o* Holm *et al.*[32] measured in dmf a shift of the redox potential for the 2−/3− transition of approximately 0.15 V in the positive direction, which was ascribed to an intramolecular hydrogen bond. It has been suggested earlier[19] that the deviation of the half-wave potential of the cluster compound with R = CH_2CH_2OH relative to R = Pr^n is the result of the presence of a hydrogen bond. We now believe, however, that this deviation is due to the electron-withdrawing properties of the hydroxy group because the cluster perfectly fits the Taft equation.[7b] The trends observed in the reaction entropies have also been ascribed to intramolecular hydrogen bonding,[19] but they can equally well be explained in terms of interactions between the solvent and the cluster core and between the solvent and the free hydroxy groups.

In order to get more insight into the effects of hydrogen bonding the electrochemical properties of the cluster compounds $[Fe_4S_4(SR)_4]^{2-}$ with R = *o*-$(CH_2)_nOC_6H_4O(CH_2)_mOH$ were investigated. In Table 5 the half-wave potentials for the 2+/1+ core reduction of the hydroxy-containing cluster compounds with the ligands **XVII** are compared with those of the corresponding cluster compounds with the ligands **XII** which cannot form hydrogen bonds. From these data we may conclude that hydrogen bonds play no role in the solvents used. This could be due to the fact that the $RO\cdots H\cdots S$ bonds in the clusters are not strong enough or that the ligands are too flexible, which would allow interactions with the solvent.

To check whether hydrogen bonding occurs at lower temperatures we measured half-wave potentials in the temperature range 210–295 K. No significant differences between the clusters with L = **XIIb** and **XVIIb** are observed both in dmf and in dichloromethane. At temperatures lower than 240 K a deviation from the linear relationship between the half-wave potential and the temperature is visible. This could point to an interaction between the solvent and the cluster core.

By using the relation $\Delta G^\circ = -nFE^\circ = \Delta H^\circ - T\Delta S^\circ$, we are able to determine[19] the reaction entropy ΔS°_{rc} for the half-reaction $[Fe_4S_4L_4]^{2-} + e^- \longrightarrow [Fe_4S_4L_4]^{3-}$ *via* the relation $\Delta S^\circ_{rc} = nF\cdot dE_{\frac{1}{2}}/dT$, measuring $E_{\frac{1}{2}}$ with a non-isothermal cell. In such a cell the reference electrode is held at 298 K, so the measured potential includes a non-isothermal liquid junction. In order to compare the results free from the contribution of the thermal liquid junction we used ΔS°, which is defined as $\Delta S^\circ = \Delta S^\circ_{rc}(\text{cluster}^{2-/3-}) - \Delta S^\circ_{rc}(\text{ferrocenium–ferrocene})$. The values of ΔS° found for the clusters with L = **XIIb** and **XVIIb** are listed in Table 6. In dichloromethane all reaction entropies, including the one for L = Pr^{n}S$^-$ which is known,[19] are essentially the same. In dmf a wider range of values is observed. This feature has also been reported for other thiolate iron–sulfur clusters and is probably caused by a difference in specific interactions between dmf molecules and the clusters as mentioned above.

Effect of amide hydrogen bond. For both iron–sulfur cluster-containing enzymes[33] and synthetic model systems[34] it is known that $NH\cdots S$ hydrogen bonds can influence the redox behaviour of the cluster core. In this section we will investigate the possibilities of modulation of the redox potential of subsite-differentiated [4Fe–4S] clusters with amide bonds.

In order to investigate whether $NH\cdots S$ hydrogen bonds are present in our clusters, thiols **XXIIa** and **XXIIb** were treated with $[Fe_4S_4Cl_4]^{2-}$ in acetonitrile. Based on the UV/VIS spectra (λ_{max} at *ca.* 300 and 420 nm, acetonitrile) we concluded that the expected thiolate-ligated clusters were formed. When these compounds were dissolved in CDCl$_3$ a change from yellow-brown to brown-red occurred. The NMR and UV/VIS spectra indicated that the cluster compounds had been partially decomposed to $[Fe_4S_4Cl_4]^{2-}$. We encountered the same problem

Table 6 Reaction entropies for the reduction of $[Fe_4S_4L_4]^{2-/3-}$ complexes

	$\Delta S^c/J\,K^{-1}\,mol^{-1}$	
HL	dmf	CH_2Cl_2
Pr^{n}SH *	−108	−126
XIIb	−85	−127
XVIIb	−96	−124

* Taken from ref. 19. The entropies with **XIIb** and **XVIIb** were determined between 240 and 300 K.

in the reaction of $[Fe_4S_4(SBu^t)_4]^{2-}$ with a ctv thiol in $CHCl_3$ (see above). After evaporation of the solvent and dissolution of the residue in acetonitrile or dmf the original thiolate cluster was not formed again. We tentatively conclude that clusters with thiolate ligands can undergo exchange reactions with chloroform to form $[Fe_4S_4Cl_4]^{2-}$ and a thioether in an analogous way to the reaction of thiolate clusters with acid chlorides which gives a thioester and $[Fe_4S_4Cl_4]^{2-}$.[17a] From differential pulse voltammograms in dichloromethane the half-wave potentials of the tetrathiolate clusters were estimated to be *ca.* −1.50 and −1.53 V for **XXIIa** and **XXIIb**, respectively. This means that the redox potential is shifted to more positive potentials when compared with cluster $[Fe_4S_4L_4]^{2-}$ (L = **XIIa**). As expected, the shift is smaller for the more electron-donating amide **XXIIb** (140 mV) than for **XXIIa** (170 mV). In dmf a half-wave potential of −1.66 V was measured for the cluster obtained from thiol **XXIIa**. Upon the addition of barium ions this changed to −1.60 V. The difference in half-wave potentials of this compound and that of **XIIa** is 60 mV, less than found in dichloromethane. It is known that dmf and dichloromethane have different acceptor properties and that possible intramolecular hydrogen bonds can be destabilised in the former solvent.

Conclusion

From the results presented here we may conclude that the reactions of the ctv thiols **IIa** and **IId** with $[Fe_4S_4X_4]^{2-}$ give 1:1 products. For these preorganised trithiols, tripodal binding seems to be preferred over binding that leads to polymeric structures. The preorganisation is not too critical as complexes could be prepared with spacers of different geometry. Interestingly, reaction of the trithiolates with $[Fe_4S_4Cl_4]^{2-}$ gives clusters in which the chloride ligand points toward the cavity of the ctv unit. We have also presented novel ctv-based ligand systems which are capable of holding a [4Fe–4S] core in a 3:1 site-differentiated fashion. By varying the spacer between the cluster and the ctv unit it was possible to modulate the redox potential of the cluster core. We were unable to tune the redox potential of these compounds with hydroxy hydrogen bonds, but preliminary evidence suggests that it is possible to achieve this using amide hydrogen bonds.

The reaction of compounds **IIa** and **IId** with $[Fe_4S_4(SBu^t)_4]^{2-}$ yields complexes with the unique iron pointing away from the cavity, probably because the *tert*-butyl group cannot fit in the cavity of the ligand. Only with compound **2d** it was possible to perform ligand-exchange reactions exclusively at the unique iron site. This regioselectivity opens the possibility to prepare complexes with a great variety of unique ligands. This in turn enables one to investigate the effect of the unique ligand on *e.g.* the half-wave potential of the clusters.[7b]

Experimental

Materials

Unless otherwise indicated, commercial chemicals were used as received. All manipulations involving compounds containing a [4Fe–4S] cluster core were carried out under an inert atmosphere. All solvents were distilled under a nitrogen atmosphere. Dimethylformamide was predried over activated BaO and distilled under reduced pressure. Diethyl ether was washed with a solution of $FeSO_4$ (6 g) and concentrated H_2SO_4 (6 cm^3) in water (100 cm^3), predried over $CaCl_2$ and distilled from sodium–benzophenone. Acetonitrile was purified by distillation from CaH_2. Dichloromethane was washed with concentrated H_2SO_4, water, 5% aqueous KOH, water, and subsequently dried over $CaSO_4$ and distilled from P_2O_5. Carbon disulfide was dried over phosphorus pentaoxide prior to distillation. Elemental sulfur was purified by sublimation under reduced pressure. Ferrocene was sublimed before use. For column chromatography Merck silica gel 60H was used. The TLC analyses were performed on Merck Kieselgel 60 F_{254} plates.

Physical measurements

The UV/VIS spectra were recorded on a Perkin-Elmer Lambda 5 spectrometer, ^{1}H and ^{13}C NMR spectra on a Bruker WH-90, WM-400 or AC-100 instrument. Chemical shifts are given relative to tetramethylsilane. The FAB mass spectra were recorded on a VG 7070E instrument using 3-nitrobenzyl alcohol as the matrix, IR spectra (CsI pellet technique) on a Perkin-Elmer 1720-X Fourier-transform spectrometer. Melting points were measured on a Reichert–Jung hot stage mounted on a microscope and are reported uncorrected. Mössbauer spectra were recorded at the Kamerlingh Onnes Institute of the University of Leiden with a constant-acceleration spectrometer equipped with a ^{57}Co source in a rhodium matrix. Powder samples were dispersed in boron nitride and sealed in brass rings with kapton windows. Isomer shifts were reported relative to iron metal at 298 K. Cyclic voltammetry and differential pulse voltammetry (DPV) measurements were performed with an EG&G Princeton Applied Research model 273 electrochemistry system, using a conventional three-electrode configuration with a platinum auxiliary electrode, and either a platinum or gold, edge-plane graphite, or basal-plane graphite working electrode. The working electrodes were polished before use, using 0.3 mm aluminium oxide, followed by sonication. In dmf an Ag–AgCl (0.1 mol dm^{-3} LiCl) reference electrode was used, in acetonitrile a Ag–Ag$^+$ (0.1 mol dm^{-3} AgNO$_3$) electrode and in dichloromethane a Ag–AgI (0.02 mol dm^{-3} NBu$_4$I–0.1 mol dm^{-3} NBu$_4$PF$_6$) electrode. The half-wave potentials are reported relative to the ferrocene–ferrocenium couple measured under the same conditions. In all solvents tetrabutylammonium hexafluorophosphate (0.1 mol dm^{-3}) was used as the supporting electrolyte. The concentration of the electroactive species was between 0.1 and 1 mmol dm^{-3}. Unless otherwise indicated the scan rates for the CV and the DPV measurements were 100 and 10 mV s^{-1}, respectively. Elemental analyses were carried out on a EA 1108 Carlo Erba instrument; iron analysis was carried out at the Analytical Laboratory, Engelskirchen, Germany. The EPR spectra of 0.1–1 mmol dm^{-3} solutions in dmf were measured at X-band frequencies on a Bruker ESP 300 spectrometer equipped with a helium continuous-flow cryostat. For these experiments a two-electrode electrochemical EPR cell (SEERS cell) was constructed as published.[35] The working electrode was a gold helix (1 m length, 0.56 mm diameter) and the combined reference–auxiliary electrode a platinum wire. The cell was used in combination with a PAR 174A polarographic analyser. Outside the EPR cavity a V_a–$E_{\frac{1}{2}}$ test line was made for the SEERS cell by the method published,[36] where V_a is the maximum of the DP voltammogram as obtained with this cell, and $E_{\frac{1}{2}}$ the half-wave potential as obtained from a normal three-electrode cell. Temperature-dependent half-wave potentials were measured with a non-isothermal cell identical to that described earlier.[19]

Preparations

(±)-2,7,12-Trimethoxy-3,8,13-tris(prop-2-enyloxy)-10,15-dihydro-5*H*-tribenzo[*a,d,g*]cyclononene **V** was synthesized

according to a literature procedure.[8] Full details of the syntheses and characterisation of all thiols are given in SUP 57195.

(±)-2,7,12-Trihydroxy-3,8,13-trimethoxy-10,15-dihydro-5*H*-tribenzo[*a,d,g*]cyclononene (cyclotriguaiacylene VI).

A solution of compound **V** (24.3 g, 0.046 mol), triphenylphosphine (300 mg), trimethylammonium formate (22 g) and a catalytic amount of palladium(II) acetate in acetonitrile (350 cm^3) and water (80 cm^3) was refluxed for 2 h until the solution became clear. After evaporation of the acetonitrile, the solution was extracted with ethyl acetate and subsequently washed with water, then brine, dried (Na$_2$SO$_4$), filtered, and concentrated *in vacuo* to *ca.* 80 cm^3. The product was precipitated with hexane and after filtration recrystallised from CH$_2$Cl$_2$ yielding 96% of a white product. The NMR spectrum of the compound was in agreement with the literature.[8]

(±)-2,7,12-Tris(2-bromoethoxy)-3,8,13-trimethoxy-10,15-dihydro-5*H*-tribenzo[*a,d,g*]cyclononene VIIa.

A solution of potassium hydroxide (18.0 g, 0.32 mol), 1,2-dibromoethane (15.0 g, 80.7 mmol), cyclotriguaiacylene (3.0 g, 6.15 mmol) and benzyltriethylammonium chloride (1.0 g, 4.4 mmol) in water (100 cm^3) was stirred for 1 week at room temperature, then extracted with CH$_2$Cl$_2$. After evaporation of the solvent and the excess of 1,2-dibromoethane the product was purified by column chromatography (silica, eluent CH$_2$Cl$_2$), giving 2.96 g (4.06 mmol, 66%) of a white solid. NMR (CDCl$_3$): ^{1}H (100 MHz), δ 3.56 (t, 6 H, CH$_2$Br, $J = 6$), 3.45 (d, 3 H, H$_{eq}$, $J = 14$), 3.62 (s, 9 H, OCH$_3$), 4.27 (t, 6 H, OCH$_2$, $J = 6$), 4.58 (d, 3 H, H$_{ax}$, $J = 14$ Hz), 6.78 (s, 3 H, aryl H) and 6.82 (s, 3 H, aryl H); ^{13}C, δ 29.1 (CH$_2$Br), 36.4 (CH$_2$), 56.2 (OCH$_3$), 69.8 (OCH$_2$), 113.8 (aryl CH), 117.8 (aryl CH), 131.7 (aryl CCH$_2$), 133.8 (aryl CCH$_2$), 145.9 (aryl CO) and 148.9 (aryl CO) (Found: C, 49.9; H, 4.55. Calc. for C$_{30}$H$_{33}$O$_6$S$_3$: C, 49.4; H, 4.55%). FAB mass spectrum: $m/z = 730$ (M^+).

(±)-2,7,12-Tris(3-bromomethylbenzyloxy)-3,8,13-trimethoxy-10,15-dihydro-5*H*-tribenzo[*a,d,g*]cyclononene VIId.

A solution of cyclotriguaiacylene (1.0 g, 2.5 mmol) in acetone (50 cm^3) was added to a solution of α,α'-dibromo-*m*-xylene (6 g, 23 mmol) and potassium carbonate (5 g) in acetone (100 cm^3). After refluxing for 8 h the solvent was evaporated. The resulting solid was boiled in hexane for 5 min, filtered off while hot, and subsequently extracted with dichloromethane. After evaporation of the solvent the product was purified by column chromatography (silica, eluent CH$_2$Cl$_2$; short column), giving 1.05 g (4.81 mmol, 45%) of a white solid. ^{1}H NMR (90 MHz, CDCl$_3$): δ 3.46 (d, 3 H, H$_{eq}$, $J = 14$), 3.71 (s, 9 H, OCH$_3$), 4.46 (s, 6 H, aryl CH$_2$Br), 4.70 (d, 3 H, H$_{ax}$, $J = 14$ Hz), 5.08 (s, 6 H, OCH$_2$ aryl), 6.68 (s, 3 H, aryl H), 6.82 (s, 3 H, aryl H), 7.33 (s, 9 H, xylyl H) and 7.42 (s, 3 H, xylyl H) (Found: C, 59.45; H, 5.0. Calc. for C$_{48}$H$_{45}$Br$_3$O$_6$: C, 60.2; H, 4.75%). FAB mass spectrum: $m/z = 958$ (M^+). UV/VIS (CH$_3$CN): λ_{max}/nm (ε/l mol^{-1} cm^{-1}) 247 (108 000) and 292 (68 400).

(±)-2,7,12-Tris[2-(dimethyldithiocarbamoylsulfanyl)ethoxy]-3,8,13-trimethoxy-10,15-dihydro-5*H*-tribenzo[*a,d,g*]cyclononene VIIIa.

To a solution of compound **VIIa** (2.2 g, 3.0 mmol) in acetonitrile (50 cm^3) was added sodium dimethyldithiocarbamate dihydrate (2.15 g, 15.0 mmol). The resulting mixture was stirred for 8 h at room temperature. After evaporation of the solvent the product was purified by column chromatography (silica, eluent ethyl acetate–hexane, 4:1 v/v; $R_f = 0.32$), giving 2.01 g (2.37 mmol, 79%) of a white solid, m.p. 84 °C. NMR (CDCl$_3$): ^{1}H (90 MHz), δ 3.38 (s, 9 H, NCH$_3$), 3.55 (s, 9 H, NCH$_3$), 3.55 (d, 3 H, H$_{eq}$, $J = 14$), 3.66 (t, 6 H, CH$_2$S, $J = 6$), 3.81 (s, 9 H, OCH$_3$), 4.26 (t, 6 H, OCH$_2$, $J = 6$), 4.74 (d, 3 H, H$_{ax}$, $J = 14$ Hz), 6.95 (s, 3 H, aryl H) and 7.22 (s, 3 H, aryl H); ^{13}C, δ 35.5 (CH$_2$S), 36.3 (CH$_2$), 41.6 (NCH$_3$), 45.5 (NCH$_3$), 56.5 (OCH$_3$), 67.4 (OCH$_2$), 113.7 (aryl CH), 115.2 (aryl CH),

131.7 (aryl CCH$_2$), 132.5 (aryl CCH$_2$), 146.3 (aryl CO), 147.9 (aryl CO) and 196.4 [SC(S)] (Found: C, 54.15; H, 5.8; N, 4.8; S, 22.0. Calc. for C$_{39}$H$_{51}$N$_3$O$_6$S$_6$: C, 55.1; H, 6.05; N, 4.95; S, 22.5%). FAB mass spectrum: $m/z = 850$ ([$M + $H]$^+$).

(±)-2,7,12-Tris[3-(dimethyldithiocarbamoylsulfanylmethyl)benzyloxy]-3,8,13-trimethoxy-10,15-dihydro-5*H*-tribenzo[*a,d,g*]cyclononene VIIId.

To a solution of compound **VIId** (1.0 g, 1.04 mmol) in acetonitrile (25 cm^3) was added NaS$_2$CNMe$_2$·2H$_2$O (1.0 g, 7.0 mmol). The resulting mixture was stirred for 8 h at room temperature. After evaporation of the solvent the product was purified by column chromatography (silica, eluent ethyl acetate–hexane, 1:1 v/v; short column), giving 0.76 g (0.73 mmol, 72%) of a white solid. ^{1}H NMR (90 MHz, CDCl$_3$): δ 3.25 (s, 9 H, NCH$_3$), 3.42 (s, 9 H, NCH$_3$), 3.3 (d, 3 H, H$_{eq}$), 3.71 (s, 9 H, OCH$_3$), 4.55 (s, 6 H, CH$_2$S), 4.6 (d, 3 H, H$_{ax}$), 5.07 (s, 6 H, OCH$_2$), 6.89 (s, 3 H, aryl H), 6.99 (s, 3 H, aryl H), 7.46 and 7.64 (s, 12 H, xylyl H).

(±)-2-{7,12-Bis(2-sulfanylethoxy)-3,8,13-trimethoxy-10,15-dihydro-5*H*-tribenzo[*a,d,g*]cyclononen-2-yloxy}ethanethiol IIa.

Under a dinitrogen atmosphere compound **VIIIa** (0.75 g, 1.06 mmol) was dissolved in dichloromethane (25 cm^3). To this solution was added diethyl ether (75 cm^3) and lithium aluminium hydride (1.2 g, 31.6 mmol). After refluxing for 2 h the solution was acidified using 6 mol dm^{-3} aqueous HCl solution. The mixture was extracted with dichloromethane and the organic layer washed with water (3×), dried (Na$_2$SO$_4$) and evaporated to dryness. The product was purified by column chromatography (silica, eluent chloroform–methanol, 98:2 v/v; $R_f = 0.66$), giving 266 mg (0.46 mmol, 43%) of a white solid, m.p. 58 °C. NMR (CDCl$_3$): ^{1}H (400 MHz), δ 1.64 (t, 3 H, SH, $J = 8$), 2.85 (dt, 6 H, CH$_2$S, $J = 6, 8$), 3.54 (d, 3 H, H$_{eq}$, $J = 14$), 3.84 (s, 9 H, OCH$_3$), 4.10 (t, 6 H, OCH$_2$, $J = 6$), 4.75 (d, 3 H, H$_{ax}$, $J = 14$ Hz), 6.78 (s, 3 H, aryl H) and 6.82 (s, 3 H, aryl H); ^{13}C, δ 23.8 (CH$_2$S), 36.4 (CH$_2$), 56.2 (OCH$_3$), 71.5 (OCH$_2$), 113.8 (aryl CH), 116.7 (aryl CH), 131.8 (aryl CCH$_2$), 132.2 (aryl CCH$_2$), 146.4 (aryl CO) and 148.7 (aryl CO) (Found: C, 61.05; H, 6.2; S, 16.15. Calc. for C$_{30}$H$_{36}$O$_6$S$_3$: C, 61.2; H, 61.5; S, 16.35%). FAB mass spectrum: $m/z = 588$ (M^+). UV/VIS (CH$_3$CN): λ_{max}/nm (ε/l mol^{-1} cm^{-1}) 234 (29 000) and 288 nm (10 300).

(±)-(3-{7,12-Bis(3-sulfanylmethylbenzyloxy)-3,8,13-trimethoxy-10,15-dihydro-5*H*-tribenzo[*a,d,g*]cyclononen-2-yloxymethyl}phenyl)methanethiol IId.

Under a dinitrogen atmosphere compound **VIIId** (1.0 g, 0.93 mmol) was dissolved in dichloromethane (25 cm^3). To this solution was added diethyl ether (75 cm^3) and LiAlH$_4$ (0.5 g, 13.1 mmol). After refluxing for 2 h the solution was acidified with 6 mol dm^{-3} aqueous HCl. The mixture was extracted with dichloromethane and the organic layer was washed with water (3×), dried (Na$_2$SO$_4$), and evaporated to dryness. After digestion in ether the product was purified by column chromatography using a short column (silica, eluent chloroform–methanol, 97:3 v/v; $R_f = 0.40$), giving 515 mg (0.63 mmol, 68%) of a white solid. NMR (CDCl$_3$): ^{1}H (90 MHz), δ 1.72 (t, 3 H, SH), 3.43 (d, 3 H, H$_{eq}$), 3.73 (d, 6 H, CH$_2$S), 3.72 (s, 9 H, OCH$_3$), 4.68 (d, 3 H, H$_{ax}$), 5.07 (s, 6 H, OCH$_2$), 6.68 (s, 3 H, aryl H), 6.83 (s, 3 H, aryl H), 7.27 and 7.34 (m, 12 H, xylyl H); ^{13}C (100 MHz), δ 28.6 (CH$_2$S), 36.4 (CH$_2$), 56.2 (OCH$_3$), 72.0 (OCH$_2$), 110–116 (aryl CH), 127.4 (aryl CCH$_2$), 128.2 (aryl CCH$_2$), 146.0 (aryl CO) and 148.4 (aryl CO) (Found: C, 75.05; H, 6.2; S, 12.3. Calc. for C$_{48}$H$_{48}$O$_6$S$_3$: C, 74.95; H, 6.3; S, 12.5%). FAB mass spectrum: $m/z = 816$ (M^+).

1-(2-Bromoethoxy)-2-methoxybenzene Xa.

A solution of potassium hydroxide (6.0 g, 0.12 mmol), 1,2-dibromoethane (5 cm^3), guaiacol (3.0 g, 24.2 mmol) and [NEt$_3$(CH$_2$Ph)]Cl (1.0 g, 4.4 mmol) in water (30 cm^3) was stirred for 1 week at room temperature. The solution was extracted with CH$_2$Cl$_2$. After evaporation of the solvent and the excess of 1,2-dibromoethane

the product was obtained as a colourless oil in 80.6% (4.50 g) yield. ^{1}H NMR (90 MHz, CDCl$_3$): δ 3.50 (t, 2 H, CH$_2$Br, $J = 6$), 3.87 (s, 3 H, OCH$_3$), 4.40 (t, 2 H, OCH$_2$, $J = 6$ Hz) and 6.90 (m, 4 H, aryl H).

1-[2-(Dimethyldithiocarbamoylsulfanyl)ethoxy]-2-methoxy-benzene XIa. To a solution of compound **Xa** (4.5 g, 19.5 mmol) in acetonitrile (75 cm^3) was added NaS$_2$CNMe$_2$·2H$_2$O (3.6 g, 25.0 mmol). The resulting mixture was stirred for 8 h at room temperature. After evaporation of the solvent the product was purified by column chromatography (silica, eluent ethyl acetate–hexane, 1:4 v/v; $R_f = 0.6$), giving 4.2 g (15.5 mmol, 79%) of a white solid, m.p. 64 °C. NMR (CDCl$_3$): ^{1}H (100 MHz), δ 3.35 (s, 3 H, NCH$_3$), 3.52 (s, 3 H, NCH$_3$), 3.75 (t, 2 H, CH$_2$S, $J = 6$), 3.84 (s, 3 H, OCH$_3$), 4.27 (t, 2 H, OCH$_2$, $J = 6$ Hz) and 6.95 (m, 4 H, aryl H); ^{13}C, δ 35.9 (CH$_2$S), 41.3 (NCH$_3$), 45.2 (NCH$_3$), 55.7 (OCH$_3$), 111.7 (aryl CH), 113.8 (aryl CH), 120.7 (aryl CH), 121.3 (aryl CH), 147.6 (aryl CO), 149.2 (aryl CO) and 196.1 [SC(S)] (Found: C, 52.7; H, 6.3; N, 6.25; S, 23.95. Calc. for C$_{12}$H$_{17}$NO$_2$S$_2$: C, 53.1; H, 6.3; N, 6.3; S, 23.6%).

2-(2-Methoxyphenoxy)ethanethiol XIIa. Under a dinitrogen atmosphere compound **XIa** (0.5 g, 1.84 mmol) was dissolved in diethyl ether (75 cm^3) and LiAlH$_4$ (0.7 g, 18.4 mmol). After refluxing for 2 h the solution was cooled to 4 °C and acidified using 6 mol dm^{-3} aqueous HCl. It was extracted with dichloromethane and the organic layer washed with water (3×), dried (Na$_2$SO$_4$) and evaporated to dryness. The product was purified by column chromatography (silica, eluent ethyl acetate–hexane, 1:4 v/v; $R_f = 0.6$), giving 153 mg (0.83 mmol, 45%) of a colourless oil. ^{1}H NMR (90 MHz, CDCl$_3$): δ 1.66 (t, 1 H, SH, $J = 8$), 2.83 (dt, 2 H, CH$_2$S, $J = 6, 8$), 3.84 (s, 3 H, OCH$_3$), 4.10 (t, 2 H, OCH$_2$, $J = 6$ Hz) and 6.95 (s, 4 H, aryl H) (Found: C, 59.0; H, 6.25; S, 17.15. Calc. for C$_9$H$_{12}$O$_2$S: C, 58.65; H, 6.55; S, 17.4%).

2-(2-Methoxyphenoxy)ethanol XIIIb. A mixture of guaiacol (15 g, 0.121 mol), 2-bromoethanol (45 g, 0.36 mol), aliquat 336 (7 g) and potassium hydroxide (30 g) in water (100 cm^3) was stirred for 4 d at 60 °C. After cooling to room temperature the solution was extracted with dichloromethane (3 × 50 cm^3). The organic layer was washed with water (3×), dried (Na$_2$SO$_4$) and evaporated to dryness. The product was purified by distillation (0.2 mmHg, *ca.* 26.6 Pa; 84–88 °C) yielding 13 g (65%) of 2-(2-methoxyphenoxy)ethanol. ^{1}H NMR (90 MHz, CDCl$_3$): δ 3.80 (s, 3 H, OCH$_3$), 4.00 (m, 4 H, CH$_2$CH$_2$) and 6.90 (m, 4 H, aryl H).

2-(2-Hydroxyethoxy)phenol IVb. Under a dinitrogen atmosphere diphenylphosphine (9.1 g, 0.049 mol) was dissolved in tetrahydrofuran (thf) (50 cm^3). To this solution was added dropwise a 15% butyllithium solution (22 cm^3, 0.052 mol) in hexane. The deep red solution was stirred for 30 min. This solution was added slowly to a solution of 2-(2-methoxyphenoxy)-ethanol (7.5 g, 0.045 mol) and butyllithium (0.047 mol) in thf (50 cm^3). After stirring for 3 h the yellow solution was poured into 3% potassium hydroxide solution (200 cm^3). The aqueous layer was extracted with diethyl ether (4 × 75 cm^3). The ether layers were collected and extracted with 15% aqueous potassium hydroxide solution (2 × 50 cm^3). The collected water layers were cooled on ice and acidified to pH 5 with concentrated HCl. The acidic water layer was extracted with diethyl ether (3 × 75 cm^3). The combined ether layers were dried (Na$_2$SO$_4$) and evaporated to dryness. The product was purified by column chromatography (silica, eluent methanol–chloroform, 2:98 v/v), yielding 3.1 g (45%) of a colourless oil. ^{1}H NMR (90 MHz, CDCl$_3$): δ 4.00 (m, 4 H, CH$_2$CH$_2$) and 6.90 (m, 4 H, aryl H).

[2-(3-Bromopropoxy)phenoxy]ethanol XVb. To a solution of compound **XIVb** (0.66 g, 4.3 mmol) in acetone (100 cm^3) was added 1,3-dibromopropane (2.6 g, 12.8 mmol) and potassium

carbonate (1.8 g). This mixture was refluxed for 24 h. After evaporation of the solvent, the product was dissolved in dichloromethane and subsequently washed with water (3×) and brine. The organic layer was dried and evaporated to dryness. After purification by column chromatography (silica, eluent methanol–chloroform, 2:98 v/v) 0.95 g (81%) of product was isolated. ^{1}H NMR (90 MHz, CDCl$_3$): δ 2.2 (m, 2 H, CH$_2$), 3.6 (t, 2 H, CH$_2$Br), 4.1 (m, 6 H, OCH$_2$ and CH$_2$OH) and 6.90 (m, 4 H, aryl H).

2-[(3-Dimethyldithiocarbamoylsulfanyl)phenoxy]ethanol XVIb. To a solution of compound **XVb** (0.88 g, 3.2 mmol) in acetonitrile (20 cm^3) was added NaS$_2$CNMe$_2$·2H$_2$O (1.15 g, 6.4 mmol). After evaporation of the solvent the mixture was dissolved in dichloromethane, washed with water and brine and dried (Na$_2$SO$_4$). The solvent was removed *in vacuo* and the product purified by column chromatography (silica, eluent methanol–chloroform, 1:99 v/v) yielding 0.80 g (79%) of product as an off-white solid. ^{1}H NMR (90 MHz, CDCl$_3$): δ 2.0 (m, 2 H, CH$_2$), 3.4 (s, 3 H, NCH$_3$), 3.5 (s, 3 H, NCH$_3$), 3.5–4.4 (m, 8 H, OCH$_2$, CH$_2$S and CH$_2$OH) and 6.9 (m, 4 H, aryl H).

2-[2-(3-Sulfanylpropoxy)phenoxy]ethanol XVIIb. Under a dinitrogen atmosphere compound **XVIb** (0.70 g, 2.2 mmol) and LiAlH$_4$ (1.29 g, 7.6 mmol) were dissolved in thf (80 cm^3). After stirring for 2 h at 40 °C the solution was cooled to 4 °C and acidified with 6 mol dm^{-3} aqueous HCl. The mixture was extracted with dichloromethane and the organic layer washed with water (3×), dried (Na$_2$SO$_4$), and evaporated to dryness. The product was purified by column chromatography (silica, eluent methanol–chloroform, 1:99 v/v) and 0.333 g (66%) of product was isolated as an oil. ^{1}H NMR (90 MHz, CDCl$_3$): δ 1.49 (t, 1 H, SH, $J = 8$), 2.09 (m, 2 H, CH$_2$), 2.74 (dt, 2 H, CH$_2$S, $J = 6, 8$ Hz), 3.75–4.25 (m, 6 H, OCH$_2$ and CH$_2$OH) and 6.9 (m, 4 H, aryl H) (Found: C, 58.1; H, 6.9; S, 12.05. Calc. for C$_{11}$H$_{16}$O$_3$S: C, 57.85; H, 7.05; S, 14.05%). Electron impact mass spectrum: $m/z = 228$, $[M + H]^+$; 154, $[M − (CH_2)_3SH + H]^+$ and 110, $[M − (CH_2)_3SH(CH_2)_2OH + H]^+$.

(2-Methoxyphenoxy)acetic acid XVIII. To a solution of sodium hydride (1.16 g, 43.8 mmol) in dmf (125 cm^3) was added guaiacol (2.5 g, 20.1 mmol) and chloroacetic acid (2.0 g, 21.2 mmol). After stirring for 5 d at ambient temperature water (75 cm^3) was added. The resulting mixture was acidified to pH < 5 with 6 mol dm^{-3} aqueous HCl then extracted with toluene. The organic layer was washed with brine and dried (MgSO$_4$). After evaporation of the solvent, the product was crystallised from CHCl$_3$, giving 2.8 g (76%) of a white solid. ^{1}H NMR (100 MHz, CDCl$_3$): δ 3.81 (s, 3 H, OCH$_3$), 4.62 [s, 2 H, OCH$_2$C(O)], 6.9–7.1 (m, 4 H, aryl H) and 10.25 [br, 1 H, C(O)OH].

2-(2-Methoxyphenoxy)-*N*-phenylacetamide XIXa. To a solution of compound **XVIII** (1.5 g, 8.23 mmol) and pentafluoro-phenol (1.67 g, 9.09 mmol) in ethyl acetate (175 cm^3) was added dicyclohexylcarbodiimide (1.70 g, 8.23 mmol) at 0 °C. After stirring for 1 h at 0 °C and 30 min at room temperature the mixture was filtered. To this filtrate aniline (0.828 cm^3, 9.07 mmol) was added and the mixture was stirred overnight. After evaporation of the solvent the product was crystallised from Pr^{i}OH, yielding 1.7 g (80%) of a white solid. ^{1}H NMR (100 MHz, CDCl$_3$): δ 3.94 (s, 3 H, OCH$_3$), 4.66 [s, 2 H, OCH$_2$C(O)], 6.9–7.7 (m, 9 H, aryl H) and 8.96 (br, 1 H, NH).

2-(Phenylcarbamoylmethoxy)phenol XXa. To aluminium (0.92 g, 34 mmol) in dry, oxygen-free CS$_2$ (125 cm^3) was added iodine (9.05 g, 36 mmol) and the mixture was refluxed for 2 h. After cooling to room temperature compound **XIXa** (1.57 g, 6.1 mmol) was added and the resulting mixture was refluxed overnight. After the addition of ice–water (100 cm^3) the mixture was extracted with diethyl ether. The organic layer was washed with

5% aqueous sodium thiocarbonate and then extracted with 1 mol dm^{-3} aqueous sodium hydroxide. The resulting mixture was acidified to pH < 5 with 6 mol dm^{-3} aqueous HCl. The mixture was extracted with diethyl ether. The organic layer was washed with brine, dried (MgSO$_4$), and the solvent removed under reduced pressure. After crystallisation from chloroform, 0.84 g (56%) of a white solid was isolated. ^{1}H NMR (100 MHz, CDCl$_3$): δ 4.71 [s, 2 H, OCH_2C(O)], 5.95 (br, 1 H, OH), 6.9–7.7 (m, 9 H, aryl H) and 8.15 (br, 1 H, NH).

N-Phenyl[2-(2-tritylsulfanylethoxy)phenoxy]acetamide XXIa.

To a solution of compound **XXa** (0.75 g, 3.1 mmol) and 1-bromo-2-tritylsulfanylethane (1.19 g, 3.1 mmol) in acetonitrile (175 cm^3) was added potassium carbonate (2.3 g). After refluxing for 72 h the solvent was removed and the residue redissolved in dichloromethane. The mixture was washed with water (3×), 1 mol dm^{-3} aqueous NaOH, water and brine. After drying (Na$_2$SO$_4$) and evaporation of the solvent, the product was purified by column chromatography (silica, eluent dichloromethane) followed by crystallisation from hexane, giving 0.09 g (5.3%) of a white solid, m.p. 124 °C. ^{1}H NMR (100 MHz, CDCl$_3$): δ 2.70 (t, 2 H, CH$_2$S, $J = 6.6$), 3.82 (t, 2 H, OCH$_2$, $J = 6.6$ Hz), 4.59 [s, 2 H, OCH_2C(O)], 6.9–7.7 (m, 24 H, aryl H) and 8.8 (br, 1 H, NH) (Found: C, 74.8; H, 5.55; N, 2.55; S, 5.8. Calc. for C$_{35}$H$_{31}$NO$_3$S: C, 77.05; H, 5.55; N, 2.55; S, 5.85%). Electron impact mass spectrum: m/z 302 (M − CPh$_3$).

2-[2-(Phenylcarbamoylmethoxy)phenoxy]ethanethiol XXIIa.

Under a nitrogen atmosphere compound **XXIa** (60 mg, 0.11 mmol) and silver acetate (100 mg, 0.33 mmol) were dissolved in methanol (5 cm^3). After stirring for 18 h the solution was acidified with degassed 1 mol dm^{-3} aqueous HCl solution (5 cm^3). The mixture was extracted with degassed diethyl ether and the organic layer washed with degassed brine, dried (Na$_2$SO$_4$) and evaporated to dryness. The product was purified by column chromatography (silica, eluent methanol–chloroform, 1:99 v/v), to give a white solid. ^{1}H NMR (100 MHz, CDCl$_3$): δ 1.68 (t, 1 H, SH, $J = 8.2$), 2.95 (m, 2 H, CH$_2$S), 4.21 (t, 2 H, OCH$_2$, $J = 6.3$ Hz), 4.64 [s, 2 H, OCH_2C(O)], 6.9–7.7 (m, 9 H, aryl H) and 8.8 (br, 1 H, NH).

Cluster complexes. The complexes [NBu$_4$]$_2$[Fe$_4$S$_4$(SBu^t)$_4$], [PPh$_4$]$_2$[Fe$_4$S$_4$(SBu^t)$_4$], [NMe$_4$]$_2$[Fe$_4$S$_4$(SBu^t)$_4$], [NBu$_4$]$_2$[Fe$_4$S$_4$Cl$_4$] and [PPh$_4$]$_2$[Fe$_4$S$_4$Cl$_4$] were prepared as described in the literature.[17a,37] All thiolate-ligated cluster compounds showed in the UV/VIS spectra (dmf) absorption maxima at *ca.* 290 (50 000), 300 (sh, 25 000) and 420 nm (15 000 l mol^{-1} cm^{-1}).

Exchange reactions with the monothiols. To a stirred solution of 100 mg of either [NBu$_4$]$_2$[Fe$_4$S$_4$Cl$_4$] or [PPh$_4$]$_2$[Fe$_4$S$_4$Cl$_4$] in acetonitrile (25 cm^3) were added 4.1 mol equivalents of the appropriate monothiol and 4.1 mol equivalents of 0.81 mol dm^{-3} NBu$^n_4$OH solution in methanol. Subsequently, diethyl ether (50 cm^3) was added. After diffusion of the diethyl ether in the acetonitrile layer a black precipitate was formed in 80–90% yield.

Product with compound **XIIb**: ^{1}H NMR [90 MHz, 298 K, (CD$_3$)$_2$SO] δ 0.9 (24 H, NCH$_2$CH$_2$CH$_2$CH_3), 1.3 (16 H, NCH$_2$CH$_2$CH_2CH$_3$), 1.6 (16 H, NCH$_2$CH_2CH$_2$CH$_3$), 2.8 (8 H, CH$_2$), 3.2 (16 H, NCH_2CH$_2$CH$_2$CH$_3$), 3.8 (12 H, OCH$_3$), 4.6 (8 H, OCH$_2$), 6.9 (16 H, aryl H) and 13.5 (br, 8 H, CH$_2$S) (Found: C, 51.8; H, 7.35; N, 1.6; S, 15.7. Calc. for C$_{72}$H$_{124}$Fe$_4$N$_2$O$_8$S$_8$: C, 53.2; H, 7.7; N, 1.7; S, 15.8%).

Product with compound **XIId**: ^{1}H NMR δ 0.9 (24 H, NCH$_2$-CH$_2$CH$_2$CH_3), 1.3 (16 H, NCH$_2$CH$_2$CH_2CH$_3$), 1.6 (16 H, NCH$_2$CH_2CH$_2$CH$_3$), 3.2 (16 H, NCH_2CH$_2$CH$_2$CH$_3$), 3.8 (9 H, OCH$_3$), 5.1 (6 H, OCH$_2$), 7.0 (16 H, aryl H), 7.4 (16 H, xylyl H) and 13.7 (8 H, CH$_2$S).

The products with thiols **XVIIa–XVIIe** were characterised by ^{1}H NMR spectroscopy. All signals, except the spacer signals,

were found at approximately the same shift values as those for the corresponding thiol compounds. For the spacer resonances isotropic shifts were observed in agreement with those reported[24] (a-CH$_2$, 10.3; γ-CH$_2$, 0.5 ppm; the β-CH$_2$ signals were obscured by signals of the counter ion).

Exchange reactions of the ctv thiolates with [Fe$_4$S$_4$Cl$_4$]$^{2-}$. To a stirred solution of 100 mg of either [NBu$_4$]$_2$[Fe$_4$S$_4$Cl$_4$] or [PPh$_4$]$_2$[Fe$_4$S$_4$Cl$_4$] in dmf (100 cm^3) was added 1.0 mol equivalent of the appropriate ctv thiol and 3.0 mol equivalents of 0.081 mol dm^{-3} NBu$^n_4$OH solution in methanol. Subsequently diethyl ether (100 cm^3) was added. After diffusion of the diethyl ether in the dmf layer a black precipitate was formed in 80–90% yield. All products were characterised by UV/VIS spectroscopy, cyclic voltammetry and differential pulse voltammetry. The characteristic features are given in the text.

Product with compound **IIa** (NBu$_4^+$ salt of **1a**): ^{1}H NMR [90 MHz, 298 K, (CD$_3$)$_2$SO] δ 0.9 (24 H, NCH$_2$CH$_2$-CH$_2$CH_3), 1.3 (16 H, NCH$_2$CH$_2$CH_2CH$_3$), 1.6 (16 H, NCH$_2$CH_2CH$_2$CH$_3$), 3.2 (16 H, NCH_2CH$_2$CH$_2$CH$_3$), 3.5 (3 H, H$_{eq}$), 3.7 (9 H, OCH$_3$), 4.1 (6 H, OCH$_2$), 4.5 (3 H, H$_{ax}$), 7.1 (6 H, aryl H) and 13.5 (br, 6 H, CH$_2$S) (Found: C, 50.8; H, 6.55; N, 1.6; S, 14.1. Calc. for C$_{62}$H$_{105}$ClFe$_4$N$_2$O$_6$S$_7$: C, 51.1; H, 7.25; N, 1.9; S, 15.4%); N:S:C:H = 1.9:7.1:68.1:105. Visual examination of the sample showed it to be contaminated with iron oxide.

Product with compound **IIb** (NBu$_4^+$ salt of **1b**): ^{1}H NMR δ 0.9 (24 H, NCH$_2$CH$_2$CH$_2$CH_3), 1.3 (16 H, NCH$_2$CH$_2$CH_2CH$_3$), 1.6 (16 H, NCH$_2$CH_2CH$_2$CH$_3$), 2.8 (6 H, CH$_2$), 3.2 (16 H, NCH_2CH$_2$CH$_2$CH$_3$), 3.6 (3 H, H$_{eq}$), 3.7 (9 H, OCH$_3$), 4.6 (6 H, OCH$_2$), 4.8 (3 H, H$_{ax}$), 7.1 (6 H, aryl H) and 12.9 (br, 6 H, CH$_2$S); ^{13}C NMR (CDCl$_3$) δ 13.5 (CH$_3$), 19.3 (NCH$_2$-CH$_2$CH_2CH$_3$), 23.1 (NCH$_2$CH_2CH$_2$CH$_3$), 35.0 (CH$_2$ bridge), 55.8 (NCH$_2$), 57.6 (OCH$_3$), 66.8 (OCH$_2$), 113.8 (aryl CH), 115.3 (aryl CH), 131.9 (aryl CCH$_2$), 132.3 (aryl CCH$_2$), 146.2 (aryl CO), 147.6 (aryl CO); the broadened CH$_2$S resonance was not observed (Found: C, 52.75; H, 6.75; N, 1.55; S, 13.75. Calc. for C$_{65}$H$_{111}$ClFe$_4$N$_2$O$_6$S$_7$: C, 52.05; H, 7.45; N, 1.85; S, 14.95%).

Product with compound **IId** (NBu$_4^+$ salt of **1d**): ^{1}H NMR δ 0.9 (24 H, NCH$_2$CH$_2$CH$_2$CH_3), 1.3 (16 H, NCH$_2$CH$_2$CH_2CH$_3$), 1.6 (16 H, NCH$_2$CH_2CH$_2$CH$_3$), 3.2 (16 H, NCH_2CH$_2$CH$_2$CH$_3$), 3.4 (3 H, H$_{eq}$), 3.7 (9 H, OCH$_3$), 4.6 (3 H, H$_{ax}$), 5.1 (6 H, OCH$_2$), 7.0–7.3 (18 H, aryl and xylyl H) and 13.8 (6 H, CH$_2$S).

Product with compound **IIe** (NBu$_4^+$ salt of **1e**): ^{1}H NMR δ 0.9 (24 H, NCH$_2$CH$_2$CH$_2$CH_3), 1.3 (16 H, NCH$_2$CH$_2$CH_2CH$_3$), 1.6 (16 H, NCH$_2$CH_2CH$_2$CH$_3$), 3.2 (16 H, NCH_2CH$_2$CH$_2$CH$_3$), 3.4 (3 H, H$_{eq}$), 3.7 (9 H, OCH$_3$), 4.6 (3 H, H$_{ax}$), 5.0 (6 H, OCH$_2$), 7.0–7.3 (18 H, aryl and xylyl H) and 13.8 (6 H, CH$_2$S) (Found: C, 56.5; H, 7.25; N, 3.25; S, 12.5. Calc. for C$_{80}$H$_{117}$ClFe$_4$N$_2$O$_6$S$_7$·2dmf: C, 56.4; H, 7.2; N, 3.05; S, 12.25%).

Product with compound **IIg** (NBu$_4^+$ salt of **1g**): the CH$_2$S protons were found at δ 14.2 in the ^{1}H NMR spectrum.

Product with compound **IIh** (NBu$_4^+$ salt of **1h**) (Found: C, 52.65; H, 6.75; N, 1.55; S, 13.75. Calc. for C$_{65}$H$_{111}$ClFe$_4$N$_2$O$_6$S$_7$: C, 52.05; H, 7.45; N, 1.85; S, 14.95%).

Exchange reactions of the ctv thiols with [Fe$_4$S$_4$(SBu^t)$_4$]$^{2-}$. A solution of [Fe$_4$S$_4$(SBu^t)$_4$]$^{2-}$ (0.1 mmol) and 0.1 mmol of trithiol **IIa** or **IId** in dmf (100 cm^3) was stirred for 3 h under reduced pressure. Subsequently the complexes were isolated as described for **1a** and **1d** in 80–90% yield.

NBu$_4^+$ salt of **2a**: ^{1}H NMR [90 MHz, 298 K, (CD$_3$)$_2$SO] δ 0.9 (24 H, NCH$_2$CH$_2$CH$_2$CH_3), 1.3 (16 H, NCH$_2$CH$_2$-CH_2CH$_3$), 1.6 (16 H, NCH$_2$CH_2CH$_2$CH$_3$), 2.7 [9 H, SC(CH$_3$)$_3$], 3.2 (16 H, NCH_2CH$_2$CH$_2$CH$_3$), 3.5 (3 H, H$_{eq}$), 3.7 (9 H, OCH$_3$), 4.1 (6 H, OCH$_2$), 4.7 (3 H, H$_{ax}$), 7.1 (6 H, aryl H) and 13.4 (br, 6 H, CH$_2$S).

PPh$_4^+$ salt: ^{1}H NMR δ 2.7 [9 H, SC(CH$_3$)$_3$], 3.4 (3 H, H$_{eq}$),

3.7 (9 H, OCH$_3$), 4.7 (3 H, H$_{ax}$), 5.3 (6 H, OCH$_2$), 7.0–7.2 and 7.3 (18 H, aryl and xylyl H), 7.6–7.9 [40 H, P(C$_6$H$_5$)$_4$] and 13.5 (6 H, CH$_2$S); ^{1}H NMR (400 MHz, 330 K) δ 2.8 [9 H, SC(CH$_3$)$_3$], 3.6 (3 H, H$_{eq}$), 3.9 (9 H, OCH$_3$), 4.7 (3 H, H$_{ax}$), 5.2 (6 H, OCH$_2$), 6.9–7.1 and 7.4 (18 H, aryl and xylyl H), 7.6–7.9 [40 H, P(C$_6$H$_5$)$_4$] and 14.3 (6 H, CH$_2$S); ^{13}C NMR of NBu$_4^+$ salt [100 MHz, 298 K, (CD$_3$)$_2$SO] δ 16.8 (CH$_3$, counter ion), 22.8 (CH$_2$, counter ion), 26.6 (CH$_3$, counter ion), 38.5 (CH$_2$ bridge), 59.5 (CCH$_3$), 61.4 (NCH$_2$), 66.6 (OCH$_3$), 74.0 (OCH$_2$), 117.8 (aryl CH), 119.4 (aryl CH), 130–140 (aryl CCH$_2$, CO) [Found: C, 57.1; H, 4.6; N, 0.9; S, 11.3. Calc. for C$_{100}$H$_{94}$Fe$_4$O$_6$P$_2$S$_8$·1.5dmf (NMR): C, 61.45; H, 5.15; N, 1.05; S, 12.55%]; N : S : C : H = 1.6 : 8.1 : 109.1 : 104.5 (calc. 1.5 : 8 : 104.5 : 104.5). Visual inspection of the sample showed it to be contaminated with iron oxide.

Substitution reactions. The exchange reactions were all performed in the electrochemical cell or in an NMR tube, and spectra recorded *in situ*. The products obtained were not isolated, except for that described below.

To a solution of complex **2d** (0.1 mmol) in dmf (100 cm^3) was added, while stirring, benzoyl chloride (0.1 mmol). Ether (100 cm^3) was added and the complex was isolated as described for **1a** and **1d**. Yield 80–90%. ^{1}H NMR [400 MHz, 298 K, (CD$_3$)$_2$SO]: δ 3.4 (3 H, H$_{eq}$), 3.7 (9 H, OCH$_3$), 4.6 (3 H, H$_{ax}$), 5.1 (6 H, OCH$_2$), 7.0–7.3 (18 H, aryl and xylyl H), 7.6–7.9 [40 H, P(C$_6$H$_5$)$_4$] and 13.5 (6 H, CH$_2$S) [Found: C, 60.65; H, 5.3; N, 0.95; Fe, 9.2; S, 11.25. Calc. for C$_{96}$H$_{85}$ClFe$_4$O$_6$P$_2$S$_7$·1.5dmf (from NMR): C, 60.65; H, 4.85; Fe, 11.25; N, 1.05; S, 11.3%]; N : S : C : Fe : H = 1.3 : 6.4 : 92.1 : 3.1 : 95.5 (calc. 1.5 : 7 : 104.5 : 95.5).

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