Subsite-Specific Reactions of a Cyclotriveratrylene [4Fe−4S] Cluster Complex

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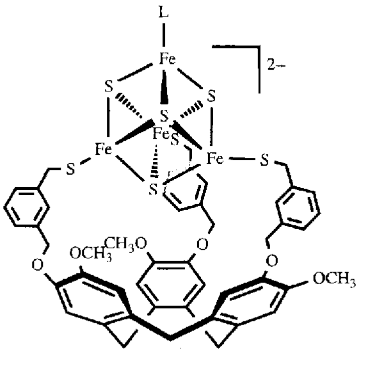
Received January 20, 1997

Keywords: Iron-sulfur clusters / S ligands / Cyclotriveratrylene / Subsite-specific reactions / Electrochemistry

Ligand exchange reactions are carried out exclusively at the unique iron site of a subsite-differentiated cyclotriveratrylene [4Fe−4S] cluster complex. The effect of a variety of thiolate, phenolate, bidentate, and bridging ligands on the redox potential of the subsite-differentiated [4Fe−4S] cluster complex is studied and compared with the effects of such ligands on an $[Fe_4S_4Cl_4]^{2-}$ cluster. The redox potential can be modulated within the range of −1.60 to −1.80 V (vs. $Fc^{0/+}$) by varying the ligand. The introduction of an electron releasing substituent shifts the redox potential to more negative values, whereas an electron withdrawing substituent has the opposite effect. A linear relationship exists between the number of substituted sites and the reduction potential of the cluster.

Introduction

$[Fe_4S_4L_4]$ cluster compounds can easily undergo ligand substitution with nucleophiles. These reactions can be used to prepare new cubane cluster compounds with various kinds of ligands in high yields[1]. The ligand exchange reactions are equilibria and can be driven to completion in various ways, viz. by using a volatile leaving ligand, by using an excess of incoming ligand, or by effectively removing the leaving ligand from the equation by trapping it as a stable product, which is not reactive towards the newly formed cluster compound. The substitutional lability of the clusters, and the fact that the reactions are almost independent of the nature of the other ligands present, means that it is not possible to limit the substitutions to only one iron site. In recent years, however, subsite-differentiated cluster compounds have been described in the literature[2]. We have recently shown that such a differentiation is possible when trithiol ligands based on cyclotriveratrylene (CTV) are used, as in the cluster compound **1**, and that such complexes can be selectively substituted at the unique site[3]. This regiospecificity can be exploited for several purposes. For example, it can be used to introduce a second center of chirality in compounds of type **1**, to immobilise them on a support or in vesicles, or to make them water soluble. It is also worthwhile to investigate the catalytic properties of the site-differentiated compounds. A site-differentiated cluster occurs in the enzyme *cis*-aconitase[4], where the differentiated iron takes citrate as a ligand and acts as a Lewis acid catalyst in its isomerization to isocitrate. Another interesting possibility is to bridge two cubane clusters, or to bridge a cubane cluster with another metal-containing moiety. In this way it is possible to design catalysts that are mimics of the P-cluster in nitrogenase[5], and the siroheme-FeS cluster couple in sulfite reductase[6], respectively.



L = Cl, $[1\text{-}Cl]^{2-}$; L = S^{t}Bu, $[1\text{-}S^tBu]^{2-}$

In this paper, we report on ligand substitution reactions which have been carried out with the cluster compound $[Fe_4S_4(CTVS_3)Cl]^{2-}$ ($[\mathbf{1}\text{-}Cl]^{2-}$). We have investigated the type of ligands that can be bound and have probed the effect of a unique ligand on the redox potential. For this purpose, we used complex $[\mathbf{1}\text{-}Cl]^{2-}$ instead of $[\mathbf{1}\text{-}S\mathit{t}Bu]^{2-}$, because the chloro ligand in the former compound is a better leaving group than the thiolate ligand in the latter. We did, however, prepare $[\mathbf{1}\text{-}Cl]^{2-}$ from $[\mathbf{1}\text{-}S\mathit{t}Bu]^{2-}$ in order to ensure that the chloride ligand is not turned into the cavity but is available for substitution[3].

Results and Discussion

Exchange Reactions

As a fast screening method, the following procedure was followed: different ligand L′ were added to a $7.8 \cdot 10^{-4}$ M

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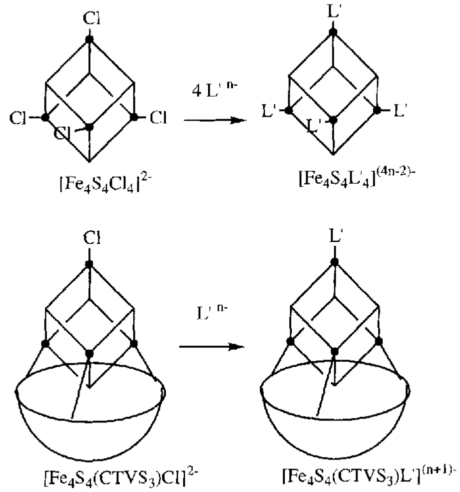
solution of cluster [**1**-Cl]$^{2-}$ in dimethylformamide (DMF) containing 0.1 M tetrabutylammonium hexafluorophosphate (supporting electrolyte) and 20 mM barium perchlorate (promoter[3]). Where appropriate, a base was added to deprotonate the ligand. Subsequently, a differential pulse voltammogram (DPV) was measured. This technique proved to be more effective than cyclic voltammetry (CV) because of the small differences in half-wave potentials of the 2−/3− redox reactions of the resulting products. For comparison, most ligands were also reacted with [Fe$_4$S$_4$Cl$_4$]$^{2-}$ in a similar procedure. The reactions are proposed to proceed as shown in Scheme 1. No indications of incomplete substitution or of cluster degradation were observed, unless specifically noted.

In the discussion of the electrochemical characterization we will concentrate on the 2−/3− (2+/1+ for the cluster core) redox reactions. Although we were sometimes able to observe the mainly irreversible 3−/4− (1+/0) redox transitions, the corresponding reduction potentials are not reported. Because of the solvent used, no well-defined oxidation to the 1− (3+) level would be expected to take place. Therefore, we did not investigate the 2−/1− transitions of the cluster compounds. A more detailed electrochemical and spectroscopic characterization of selected isolated cluster compounds was reported earlier[3a,b].

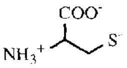
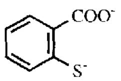
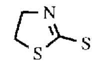
Scheme 1



Thiolates

In biological systems, proteins are almost exclusively bound to [4Fe−4S] clusters via cysteinyl residues. As a consequence, thiolates are the most extensively investigated class of ligands for iron-sulfur clusters. Various kinds of thiolates have been bound to the cluster core, with the aim of establishing the parameters that govern the redox potential, e.g. the electron-donating capacity[7] and the hydrophobicity[8] of the ligand L′. In Table 1, the half-wave potentials of the first core reduction step (2+/1+) are reported for a series of thiolate-ligand cluster compounds. These half-wave potentials are all more negative than the potentials found for the corresponding chloro clusters and lie in the range reported for other thiolate-coordinated [4Fe−4S] cores[1]. The variation in the potential is larger for the [Fe$_4$S$_4$L′$_4$] clusters than for the [Fe$_4$S$_4$(CTVS$_3$)L′] clusters, since in the former case all four ligands are substituted, whereas in the latter case only one ligand is replaced. The bulky trityl thiol ligand (entry 7, Table 1) did not react with even one of the iron sites of the [Fe$_4$S$_4$Cl$_4$]$^{2-}$ cluster, whereas it was reactive towards [Fe$_4$S$_4$(CTVS$_3$)Cl]$^{2-}$. We have no explanation for this behaviour.

Table 1. Half-wave potentials (vs. Fc$^{0/+}$) for the reduction of [4Fe−4S]$^{2+}$ clusters in DMF

	L	$E_{1/2}$ / V [Fe$_4$S$_4$L′$_4$]$^{2-/3-}$	$E_{1/2}$ / V[a] [Fe$_4$S$_4$(CTVS$_3$)L′]$^{2-/3-}$
1.	Cl$^-$	-1.35	-1.62
2.	(CH$_3$)$_3$CS$^-$	-1.85	-1.70
3.	PhS$^-$	-1.52	-1.68
4.	HS$^-$	not measured	-1.69
5.	 (D, L)	-1.76	-1.71
6.		not measured	-1.74[b]
7.	Ph$_3$CS$^-$	no reaction observed	-1.71
8.		-1.74	-1.67

[a] 20 mM Ba(ClO$_4$)$_2$ was added. − [b] 3−/4− reduction.

p-Substituted Phenolates

[4Fe−4S] clusters with phenolate ligands are known in the literature[9]. As phenols with various substituents and functionalities are readily available, they are suitable substrates for studying the influence of substituents on the half-wave potential of cluster compounds. A series of phenols, deprotonated with tetrabutylammonium hydroxide in methanol, was added to both compound [**1**-Cl]$^{2-}$ and [Fe$_4$S$_4$Cl$_4$]$^{2-}$ (Table 2). In the case of the latter compound, the tetrasubstituted products were obtained. For [**1**-Cl]$^{2-}$, the product resulting from substitution of the chloro ligand was observed, as well as a small amount of the tetrasubstituted cluster. This indicates that the CTV ligand can only be replaced as a single entity.

In Figure 1, Hammett plots of the half-wave potential, measured in DMF, vs. the Hammett substituent constant σ_p, are given for the two types of cluster compounds. The introduction of an electron-releasing substitutent shifts the reduction potential to more negative values, whereas an electron-withdrawing substituent has the opposite effect. The tetraphenolate-ligated clusters obey the following Hammett equation: $E_{1/2}$ (vs. Fc$^{0/+}$) = 0.435 σ_p − 1.64 V (R = 0.99). The relationship found for the site-differentiated clusters is: $E_{1/2}$ (vs. Fc$^{0/+}$) = 0.114 σ_p − 1.69 V (R =

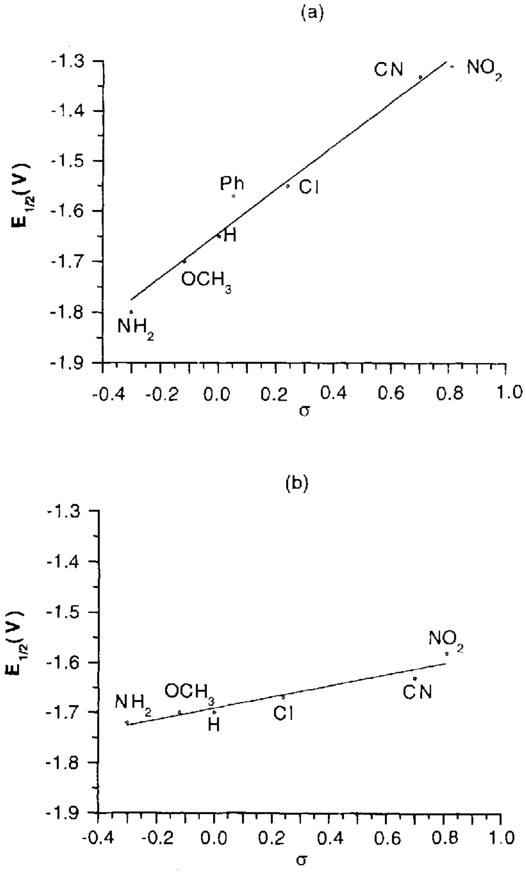
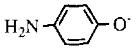
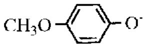
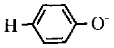
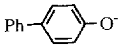
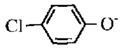
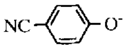
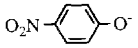


Figure 1. Hammett plots for $[Fe_4S_4(p\text{-}X\text{-}C_6H_4O)_4]^{2-/3-}$ (a) and $[Fe_4S_4(CTVS_3)(p\text{-}X\text{-}C_6H_4O)]^{2-/3-}$ (b); X is indicated in the plot

Table 2. Half-wave potentials (vs. $Fc^{0/+}$) for the reduction of $[4Fe-4S]^{2+}$ clusters in DMF

	L'	$E_{1/2}$ / V $[Fe_4S_4L'_4]^{2-/3-}$	$E_{1/2}$ / V[a] $[Fe_4S_4(CTVS_3)L']^{2-/3-}$
9.		-1.80	-1.72
10.		-1.70	-1.70
11.		-1.65	-1.70
12.		-1.57	not measured
13.		-1.55	-1.67
14.		-1.33	-1.63
15.		-1.31	-1.58

[a] 20 mM $Ba(ClO_4)_2$ was added.

0.97). As expected, the effect for the site-differentiated cluster is approximately 1/4 of the effect measured for the tetrasubstituted clusters.

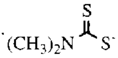
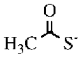
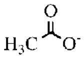
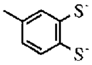
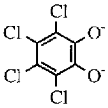
It is known that thiolate-ligated [4Fe−4S] clusters also display a linear correlation between the half-wave potential ($E_{1/2}$) of the 2−/3− redox process and the Hammett σ_p or Taft σ^* constants[7]. In DMF, the following relationships have been reported for $[Fe_4S_4(SR)_4]^{2-/3-}$: $E_{1/2}$ (vs. SCE) = $0.411\ \sigma^* - 1.30$ V and $E_{1/2}$ (vs. SCE) = $0.295\ \sigma_p - 1.04$ V. Similar linear relationships are found in other solvents[10].

The reaction constant ρ is slightly more positive for the *para*-substituted phenols than for the thiophenolates. This means that it is easier to modulate the redox potential of the former cluster compounds than that of the latter. The inherently more feebly electron donating phenolates (Table 2) gave rise to more negative shifts compared to the analogous thiophenolates[9]. These results are comparable to those reported in the literature for other clusters and have been explained in terms of greater covalency of the iron−phenolate bond[9].

Bidentate Ligands

Certain ligands are capable of binding to the iron sites of a $[4Fe-4S]^{2+}$ cluster in a bidentate fashion, e.g. dithiocarbamates, for which this was proven by X-ray crystallography[11]. Holm et al. studied the effect of the coordination number at a single subsite on the electron distribution and reduction potential of the [4Fe−4Se] core[2c]. Compared to monodentate ligands, bidentate ligands increase the electron density in the cluster and thus decrease the reduction potential. From Mössbauer spectroscopy it was concluded that the unique, pentacoordinated iron sites tend to have a more ferric character. We investigated whether the electrochemical findings also hold for our CTV-based cluster compounds.

Table 3. Half-wave potentials (vs. $Fc^{0/-}$) for the reduction of $[4Fe-4S]^{2+}$ clusters with bidentate ligands in DMF

	L'	$E_{1/2}$, V $[Fe_4S_4L'_4]$	$E_{1/2}$, V[a] $[Fe_4S_4(CTVS_3)L']$
16.		-1.78	-1.75
17.		-1.66	not measured
18.		-1.37	-1.63
19.		not measured	-1.83
20.		-1.80	-1.75

[a] 20 mM $Ba(ClO_4)_2$ was added.

In Table 3, we present the half-wave potentials of [4Fe−4S] clusters obtained after reaction of either $[\mathbf{1}\text{-Cl}]^{2-}$ or $[Fe_4S_4Cl_4]^{2-}$ with bidentate ligands and the appropriate amount of base to deprotonate the ligands (except for entry 16, where the sodium salt was used). From this table, we conclude that the previously observed trend[2c], that a bidentate mode of binding results in lower reduction potentials than a monodentate mode of binding, is evident for both the CTV-based clusters and the clusters coordinated by four bidentate ligands.

DP voltammograms recorded from the reaction mixtures of $[Fe_4S_4Cl_4]^{2-}$ showed that the intensity of the product peaks decreased when more than four equivalents of the bidentate ligands were added, and other peaks appeared. From this we conclude that reaction of the tetrachloro compound with the bidentate ligands, especially the dianions, leads to core degradation.

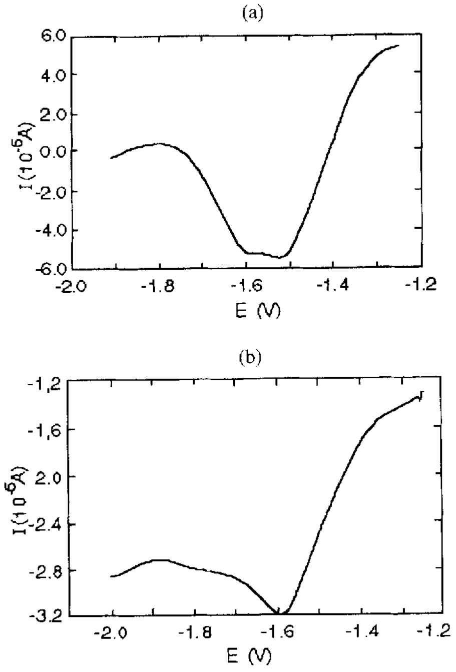
Bridging Ligands

In iron-sulfur proteins containing two or more [4Fe−4S] cores, a magnetic interaction is often found between these cluster cores in the 1+ state[11]. If two identical electroactive centers are present in one molecule, we may observe either a one-electron transition with double current amplitude or, if the centers influence each other, two one-electron transitions. This influence may be electrostatic in nature or be the result of an overlap of cluster orbitals. Holm synthesized a series of dithiolate-bridged bis-cluster compounds based on a tripodal ligand and investigated this cluster interaction by electrochemical means[2c]. For these compounds, the interactions between the cluster cores, measured as the peak separations of the successive reductions ($\Delta E_{1/2}$), were found to be distance dependent. The maximum effect was obtained with a sulfide bridge, which resulted in the smallest separation (7.5 Å). When the distance exceeded 11 Å, no interaction could be measured. A similar result has been reported by Coucouvanis[12].

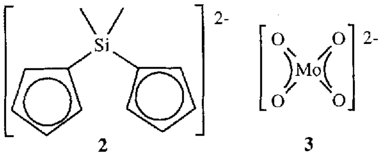
The DP voltammogram of a reaction mixture of lithium sulfide and [**1**-Cl]$^{2-}$ showed the appearance of two reduction potentials, one at −1.57 V and one at −1.64 V, indicating the formation of a sulfide-bridged cluster compound with two one-electron transitions. However, after few scans, the two reduction peaks coalesced to a single peak at −1.59 V, as shown in Figure 2. After cleaning the electrode, we again obtained a voltammogram with two separate peaks. The coalescence of the peaks may be caused by an intermolecular interaction, i.e. between adsorbed molecules, which overrules the intramolecular interaction. From the values of the half-wave potentials, we were sure that no starting compound was present. Furthermore, there was a pronounced difference between the infrared spectra of [**1**-S*t*Bu]$^{2-}$ and [**1**-Cl]$^{2-}$ on the one hand, and of the sulfide-bridged compound on the other. The latter showed broader peaks and an intense absorption at 453 cm^{-1}. The aforementioned results are similar to those reported for the sulfide-bridged cluster [(Fe$_4$S$_4$Cl$_3$)$_2$S]$^{4-}$, the bridged structure of which has been proven by X-ray crystallography[12]. Such cluster assemblies with a single sulphur bridge can be considered as an important step towards the synthesis of models for the P-clusters found in nitrogenase, in which two [4Fe−4S] clusters are bridged by 2 sulphurs[5].

Our sulfide-bridged cluster compound displayed a peak separation $\Delta E_{1/2}$ of 70 mV in DMF solution. A peak separation of 300 mV has been reported for [(Fe$_4$S$_4$Cl$_3$)$_2$S]$^{4-}$ in acetonitrile[12], while in DMF, we measured a $\Delta E_{1/2}$ value of 220 mV for the same cluster. The sulfide-bridged cluster prepared by Holm from a hexasubstituted benzene ligand exhibited a peak separation of 220 mV in DMSO[2c]. For the sulfide-bridged macrocyclic polyether trithiolate-based cluster, a peak separation of 130 mV in DMSO has been reported[2f]. From this list of data it is clear that the cluster interaction, as measured by the peak separation, is dependent on the solvent and on the other ligands present.

Figure 2. DPV of [(Fe$_4$S$_4$(CTVS$_3$))$_2$S]$^{4-/5-}$ in DMF after 1 scan (a) and after 10 scans (b); *E* is given vs. Fc$^{0/+}$



Scheme 2



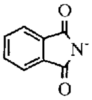
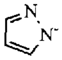
2 **3**

In order to investigate the effect of bridging ligands other than dithiolates, compounds **2** and **3** (Scheme 2) were added to [**1**-Cl]$^{2-}$. Cyclopentadienyl reacts with the site-differentiated cluster [**1**-Cl]$^{2-}$ (vide infra), hence we used ligand **2** to connect two clusters. The resulting product showed only one reduction wave at −1.76 V, indicating the formation of new complex and, moreover, that the cluster cores do not influence each other electrochemically. Molybdate, the oxygen analogue of molybdenum tetrasulfide used by Holm to bridge two clusters, did not react with [**1**-Cl]$^{2-}$ under the experimental conditions. The addition of molybdenum tetrasulfide resulted in a broad reduction wave at −1.79 V. This broadening may have been caused by a slow electron transfer, or otherwise may have been the result of a superposition of two peaks, indicating a small interaction between the cluster cores.

Other Types of Ligands

In Table 4, the effect of various other types of ligands on the reduction potential of the [4Fe−4S]$^{2+}$ clusters is shown. The reduction potentials of the products obtained from the reactions with potassium phthalimide (entry 26) were difficult to determine accurately since they appeared as shoulders on the reduction peak of phthalimide at −1.94 V. It is clear from Table 4 that the electron-donating and -accepting properties determine the potentials. For example, with π acceptor ligands like cyanide, the reduction potential of the resulting clusters is less negative than for those with electron-donating ligands.

Table 4. Half-wave potentials (vs. $Fc^{0/+}$) for the reduction of $[4Fe-4S]^{2+}$ clusters with different ligands L′ in DMF

	L′	$E_{1/2}$ / V $[Fe_4S_4L'_4]^{2-/3-}$	$E_{1/2}$ / V[a] $[Fe_4S_4(CTVS_3)L']^{2-/3-}$
1.	Cl^-	-1.35	-1.62
21.		[b]	-1.81
22.	NCO^-	-1.24	-1.59
23.	HO^-	-1.94	-1.77
24.	N_3^-	-1.23	-1.59
25.	NC^-	-1.34	-1.62
26.		-1.84	-1.81
27.		-1.45	[c]

[a] 20 mM $Ba(ClO_4)_2$ was added. − [b] No reaction was observed. [c] Not measured.

Under the experimental conditions, no detectable reaction of $[Fe_4S_4Cl_4]^{2-}$ with $(H_3C)_3NBH_3$, indole or triphenylphosphane was observed within a period of 5 minutes. Reaction with pyridine resulted in a complex mixture, indicative of cluster core degradation. The addition of cyanide did not lead to any difference in the reduction potential, but from the change in colour we concluded that the cyanide had reacted.

None of the chloro ligands of the tetrachloro cluster could be substituted by cyclopentadienyl (Cp^-) ligands, in contrast to the chloro ligand of the site-differentiated cluster, which could easily be replaced by this ligand (entry 21 of Table 4). This result is not surprising since $[Fe_4S_4Cp_4]$ compounds are only stable in higher oxidation states[13]. We assume that the product formed after reaction of $[\mathbf{1}\text{-Cl}]^{2-}$ with Cp^- owes its stability to the presence of the trithiolate ligand. This suggests that the tridentate ligand not only directs substitution to the unique site, but in some cases also stabilizes the product.

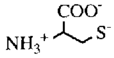
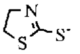
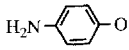
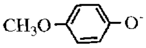
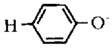
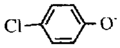
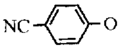
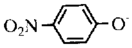
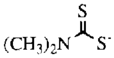
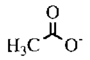
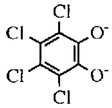
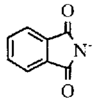
Comparison of Calculated and Measured $E_{1/2}$ Values

Data from ligand substitution reactions in the literature and our own data indicate that there is a nearly linear relationship between the number of substituted sites and the half-wave potential of the reduction of the mixed $[Fe_4S_4L_{(4-n)}L'_n]^{2-}$ cluster compounds. This additivity of ligand contributions is also found for other electroactive species[14]. For a given solvent, the half-wave potential is composed of an intrinsic part (the cluster core), and a contribution that depends upon the ligands. The effect of the tridentate ligand can be calculated from the half-wave potential for the reduction of $[Fe_4S_4(m\text{-}SCH_2C_6H_4CH_2OPh)_4]^{2-}$, which is −1.80 V. This compound contains the same "arms" as the tridentate ligand. If we assume that there is no additional effect of the cavity, the tridentate CTV ligand will affect the redox potential in the same way as three corresponding monothiolate ligands. The contribution of the unique ligand L′ in the CTV-based cluster $[Fe_4S_4(CTVS_3)L')]$ will be 1/4 of the value it has in the $[Fe_4S_4L'_4]^{2-}$ cluster. We do not know the intrinsic redox potential of the [4Fe−4S] core, but if the potential for $[Fe_4S_4L'_4]^{2-}$ $[E_{1/2}(L'_4)]$ is known, we can calculate the difference in effect of one L′ and one "arm" ($-m\text{-}SCH_2C_6H_4CH_2O-$) on the half-wave potential of the clusters. If we add this difference to the value found for the standard cluster with four "arms", we can calculate the theoretical half-wave potential $[E_{1/2}(\mathrm{CTVL'})]$ of the $[Fe_4S_4(CTVS_3)(L')]^{2-}$ clusters [Equation (1)].

$$E_{1/2}(\mathrm{CTVL'}) = -1.80 + 0.25\,[(E_{1/2}(L'_4) - (-1.80)] + 0.07\ \mathrm{V} \qquad (1)$$

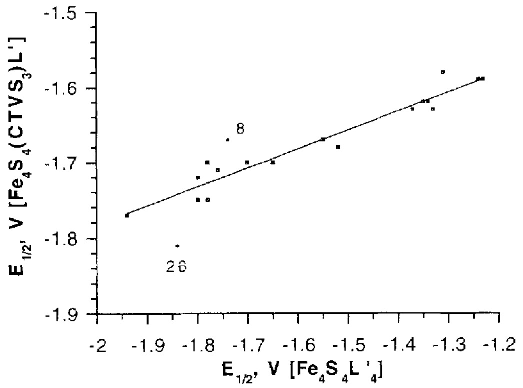
The constant 0.07 is used to compensate for the effect of barium modulation[3]. If we assume that the additivity rule holds for the reduction of $[4Fe-4S]^{2+}$ cores, we can compare calculated $E_{1/2}$ values with measured $E_{1/2}$ values.

Table 5. Measured and calculated half-wave potentials (vs. $Fc^{0/+}$) for the reduction of $[4Fe-4S]^{2+}$ clusters in DMF

	L′	$E_{1/2}$ / V	
		measured	calculated
1.	Cl^-	-1.62	-1.62
2.	$(CH_3)_3CS^-$	-1.70	-1.73
3.	PhS^-	-1.68	-1.66
5.		-1.71	-1.72
8.		-1.67	-1.72
9.		-1.72	-1.73
10.		-1.70	-1.71
11.		-1.70	-1.69
13.		-1.67	-1.67
14.		-1.63	-1.61
15.		-1.58	-1.61
16.		-1.75	-1.73
18.		-1.63	-1.62
20.		-1.75	-1.73
22.	NCO^-	-1.59	-1.59
23.	HO^-	-1.77	-1.77
24.	N_3^-	-1.59	-1.59
25.	NC^-	-1.62	-1.62
26.		-1.81	-1.74

The results are presented in Table 5. In general, it can be seen that the calculated and measured values are in good agreement. In Figure 3, a plot of the half-wave potentials of $[Fe_4S_4(CTVS_3)L']$ versus the half-wave potentials of the corresponding $[Fe_4S_4L'_4]$ cluster is shown. It is clear that there is a linear relationship between the half-wave potential of a cluster and the ligand substitution.

Figure 3. Plots of the half-wave potentials of $[Fe_4S_4(CTVS_3)L']$ versus $[Fe_4S_4Li'_4]$; solid line, $y = -1.2812 + 0.25066 \times x$, $R = 0.97033$; the ligands with the largest deviation from linearity are indicated with their entry numbers



Conclusions

Cluster $[\mathbf{1}\text{-Cl}]^{2-}$ displays subsite-specific reactions with different ligands. This gives access to a wide variety of interesting new compounds. It is possible to modulate the redox potentials within the range of −1.60 to −1.80 V (vs. $Fc^{0/+}$) by varying the ligand. The value of the redox potential depends on the electron-donating and electron-withdrawing properties of the ligands. A linear relationship exists between the number of sites that are substituted and the reduction potential of the cluster.

Experimental Section

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 dinitrogen atmosphere. DMF was predried over activated BaO and distilled under reduced pressure. Diethyl ether was washed with a solution of 6 g of $FeSO_4$ and 6 ml of concentrated H_2SO_4 in 100 ml of water, predried over $CaCl_2$ and distilled from sodium benzophenone ketyl. Elemental sulfur was purified by sublimation under reduced pressure. Ferrocene was sublimed before use.

Physical Measurements: UV/Vis spectra were recorded on a Perkin-Elmer Lambda 5 spectrometer. − ^1H- and ^{13}C-NMR spectra were obtained on Bruker WH-90, Bruker WM-400 or Bruker AC-100 instruments. Chemical shifts are given relative to tetramethylsilane. − The IR spectra (CsI pellets) were measured on a Perkin-Elmer 1720-X Infrared Fourier Transform spectrometer. − Cyclic voltammetry and differential pulse voltammetry 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 a platinum working electrode. The working electrode was polished before use, using 0.3-mm aluminium oxide, followed by sonication. In DMF, an Ag/AgCl (0.1 M LiCl) reference electrode was used. The half-wave potentials are reported relative to the ferrocene/ferrocenium couple measured under the same conditions. Tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) was used as the supporting electrolyte (0.1 M). The concentration of the electroactive species was between 0.1 and 1 mM. Unless otherwise indicated, the scan rate for the cyclic voltammetry measurements was 100 mV/s and for the differential pulse voltammetry measurements 10 mV/s.

Preparation of the Compounds: Dilithium dicyclopentadienyldimethylsilane was prepared by a published method[15]. Derivatives of **1** were prepared from cyclotriguaiacylene as described elsewhere[3a,b].

Substitution Reactions: A $7.78 \cdot 10^{-4}$ M solution of $[\mathbf{1}\text{-S}t\text{Bu}]^{2-}$ in DMF was prepared as described elsewhere[3]. To 2 ml of this solution was added 2 ml of a solution containing 40 mM of $Ba(ClO_4)_2$ and 0.2 M of Bu_4NPF_6 in DMF. Subsequently, 1.1 equivalents of pivaloyl chloride were added. This solution was checked with DPV for the presence of $[\mathbf{1}\text{-Cl}]^{2-}$ (characteristic redox potentials of $[\mathbf{1}\text{-Cl}]^{2-}$ and $[\mathbf{1}\text{-S}t\text{Bu}]^{2-}$ are −1.672 and −1.70 V, respectively, cf. Table 1) and directly used for an exchange reaction. The products from the substitution reactions were not isolated unless otherwise stated and DPV was performed in situ. For each reaction, a fresh solution of $[\mathbf{1}\text{-Cl}]^{2-}$ was prepared. The substitution reactions with $[Fe_4S_4Cl_4]^{2-}$ were performed in an analogous manner using a $5 \cdot 10^{-4}$ M solution of cluster and a 0.1 M stock solution of Bu_4NPF_6 in DMF. DPV's were measured from −1.2 to −2.1 V vs. $Fc^{0/+}$. In separate electrochemical experiments, the redox properties of the free ligands in this potential window were defined.

Thiolates: To a DMF solution of either $[\mathbf{1}\text{-Cl}]^{2-}$, prepared as mentioned above, or $[Fe_4S_4Cl_4]^{2-}$ was added an excess (ca. 2 equivs.) of the appropriate thiol in DMF. The latter reagent was deprotonated with 0.9 equivs. of tetrabutylammonium hydroxide in methanol. In the case of thiophenolate, a slight excess of sodium thiophenolate, prepared from thiophenol and sodium in THF, was added as a solid.

Phenolates: To a DMF solution of either $[\mathbf{1}\text{-Cl}]^{2-}$, prepared as mentioned above, or $[Fe_4S_4Cl_4]^{2}$ was added a large excess (ca. 50 equivs.) of the appropriate phenol in DMF. The latter reagent was deprotonated with 0.9 equivs. of tetrabutylammonium hydroxide in methanol. In the case of ammonium phenolate, 2 equivs. of base were used.

Bridging Ligands: To a freshly prepared solution of $[\mathbf{1}\text{-Cl}]^{2-}$ in DMF, 0.5 equivalents of one of the following reagents were added: dilithium dicyclopentadienyldimethylsilane, lithium sulfide, diammonium molybdenum tetrasulfide, or potassium molybdate. Subsequently, DPV's were recorded as described above.

Miscellaneous: To a DMF solution of $[\mathbf{1}\text{-Cl}]^{2-}$, prepared as mentioned above, one of the following compounds was added (1.1 equivalents in the case of $[\mathbf{1}\text{-Cl}]^{2-}$, 4.4 equivalents in the case of $[Fe_4S_4Cl_4]^{2-}$): sodium dimethyldithiocarbamate trihydrate, potassium cyanide, sodium cyclopentadienyl, potassium cyanate, or sodium azide. In the case of triphenylphosphane, lithium amide, sodium acetate, sodium hydrogen sulfide, borane trimethylamine complex, potassium phthalimide, and indole, an excess of reagent was used. The following compounds were added as solutions: tetrabutylammonium hydroxide (excess in methanol) or pyrazole (excess in DMF with an excess of sodium hydroxide).

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