Kinetic Studies on $[\{MFe_3S_4(SR)_3\}_2(\mu\text{-}SR)_3]^{3-}$ (M = Mo or W, R = Et or Ph): Influence of Mo or W on the Mechanism of Substitution at the Iron Centres within the Cluster†

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Kinetic studies on the acid-catalysed substitution of $[\{MFe_3S_4(SR)_3\}_2(\mu\text{-}SR)_3]^{3-}$ (M = Mo or W, R = Et or Ph) have shown that the heterometal influences the intimate mechanism of substitution at the iron sites. Whereas $[Fe_4S_4(SR)_4]^{n-}$ (n = 2 or 3) react exclusively by a dissociative mechanism, the Mo- or W-containing clusters usually exhibit an additional associative pathway. In addition the heterometal influences the ability of the iron centres to bind a variety of small molecules. The possible relevance of these studies to the binding of substrates by certain metalloenzymes is discussed.

In the previous paper[1] a general system was described by which the details of the acid-catalysed substitution of $[Fe_4S_4(SR)_4]^{n-}$ (R = alkyl or aryl, n = 2 or 3) can be delineated. Although the substrate-binding sites of several metalloenzymes are based on simple 4Fe–4S cores,[2] there is for some the additional necessity of another metal within the cluster framework (Mo or V for the nitrogenases,[3] Ni for the hydrogenases[4]). It is still not clear what the role for these heterometals may be; it has always been assumed, at least for the nitrogenases, that Mo or V was the site of substrate binding. In the context of understanding the action of metalloenzymes at the atomic level it is important to understand all the influences that a heterometal may have on the substitution and binding characteristics of the entire cluster. To this end studies on $[\{MFe_3S_4(SR)_3\}_2(\mu\text{-}SR)_3]^{3-}$ (M = Mo or W, R = Et or Ph) are reported herein. These complexes have already been shown to have some of the structural characteristics associated with the iron–molybdenum cofactor of the Mo-based nitrogenases.[5] However, they do not show any of the characteristic reactivity (such as formation of NH_3 from N_2, *etc.*) associated with this enzyme.[3]

Earlier studies[5b,6] on $[\{MFe_3S_4(SR)_3\}_2(\mu\text{-}SR)_3]^{3-}$ showed that only the terminal thiolate ligands (*i.e.* those bound to iron) are substitutionally labile. Mechanistically then these clusters present the opportunity to study substitution at the iron centres, and the way in which their reactivity is perturbed by the heterometal. It is a little surprising that, despite the wealth of kinetic studies on cluster complexes of all types, the influence of one metal on substitution at another has not been investigated before.

Experimental

All manipulations were routinely performed under an atmosphere of dinitrogen or argon using standard Schlenk and syringe techniques as appropriate. The complexes $[NBu^n_4]_3[\{MoFe_3S_4(SPh)_3\}_2(\mu\text{-}SPh)_3]$,[7] $[NEt_3(CH_2Ph)]_3[\{MoFe_3S_4(SEt)_3\}_2(\mu\text{-}SEt)_3]$[8] and $[NEt_4]_3[\{WFe_3S_4(SEt)_3\}_2(\mu\text{-}SEt)_3]$[9] were prepared by the literature methods.

Table 1 Temperature dependence of the ^1H NMR spectral chemical shifts for $[NBu^n_4]_3[\{WFe_3S_4(SPh)_3\}_2(\mu\text{-}SPh)_3]$ in CD_3CN (relative to $SiMe_4$)

	Chemical shift[a] (δ)					
T/°C	o_T	m_T	p_T	o_B	m_B	p_B
23	−2.70	13.62	−3.31	8.20	5.60	5.96
40	−1.93	13.21	−2.67	8.20	5.72	6.10
55	−1.56	12.94	−2.24	8.23	5.79	6.20
70[b]	−1.01	12.68	−1.85	8.25	5.84	6.22

[a] Chemical shifts and temperature dependence are very similar to those of $[\{MoFe_3S_4(SPh)_3\}_2(\mu\text{-}SPh)_3]^{3-}$; o = *ortho*, m = *meta*, p = *para*, T = terminal, B = bridge. Spectrum also shows characteristic peaks of $[NBu^n_4]^+$ at δ 0.96, 1.35, 1.61 and 3.06. [b] Some free PhS observed at δ 7.53–7.34 upon going to this temperature.

$[NBu_4]_3[\{WFe_3S_4(SPh)_3\}_2(\mu\text{-}SPh)_3]$.—Since the 'normal' synthetic route to this type of complex gives $[NBu^n_4]_3[\{WFe_3S_4(SPh)_3\}_2(\mu\text{-}OMe)_3]$[5b,7] the desired complex was prepared in the following manner. To a solution of $[NBu^n_4]_2[Fe_4(SPh)_{10}]$[10] (4.5 g, 2.61 mmol) in MeCN (*ca.* 50 cm^3) was added $[NBu^n_4]_2[WS_4]$ (1.98 g, 1.1 equivalents, 2.73 mmol). The solution immediately turned dark red, and slowly became more brown-red upon stirring overnight. The following day all volatiles were removed *in vacuo*, and then methanol (*ca.* 20 cm^3) was added and the solution stirred for *ca.* 0.5 h. The solid was filtered off, washed with methanol until the washings were colourless and then the black solid was dried *in vacuo*. Recrystallisation from hot MeCN–MeOH and allowing to cool slowly to −5 °C overnight gave the product as well formed black cubes. Yield 40–60% (Found: C, 45.5; H, 5.85; N, 1.55; S, 21.0. Calc. for $C_{102}H_{153}Fe_6N_3S_{17}W_2$: C, 45.8; H, 5.75; N, 1.55; S, 20.4%). The ^1H NMR spectrum was as expected for this type of complex;[6,7] the positions of the various signals vary with temperature as shown in Table 1.

All other reagents were prepared as described before, and the kinetic measurements and analysis of the data were as described in the previous paper.[1] All kinetic studies monitored the absorbance change of the cluster, usually at λ = 420 or 500 nm. The absorbance *vs.* time curves observed correspond to the consecutive substitution of all the thiolate ligands, and are consequently *at least* two exponentials. We have restricted our attention to the initial (*ca.* 50% of total absorbance change) exponential part, corresponding to substitution of the first

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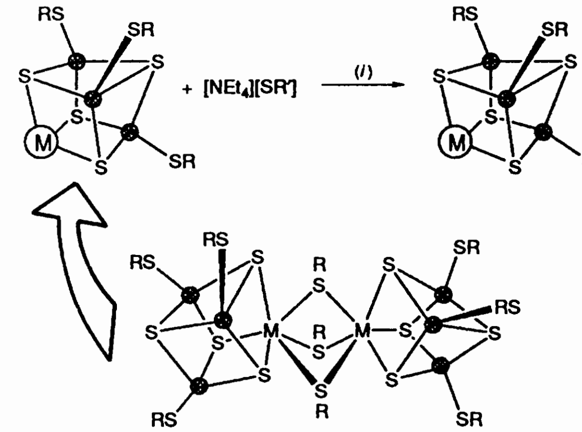
† *Supplementary data available* (No. SUP 56938, 8 pp.): first-order rate constants. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.



Scheme 1 (*i*) $[NHEt_3][BPh_4]$, MeCN

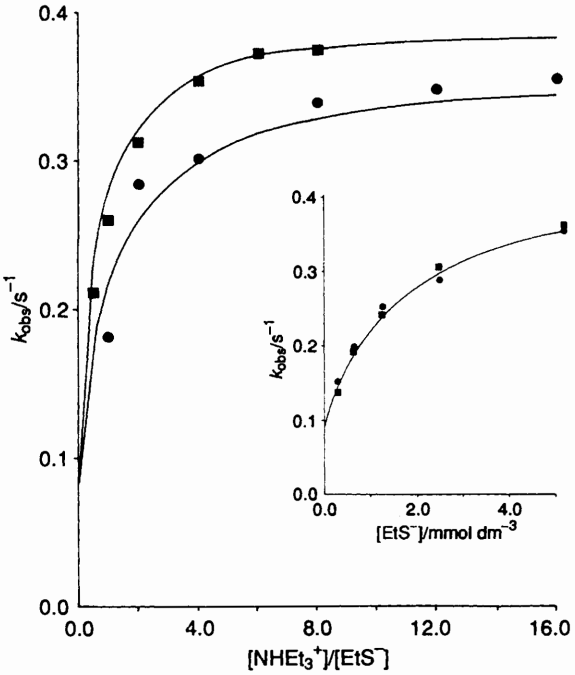


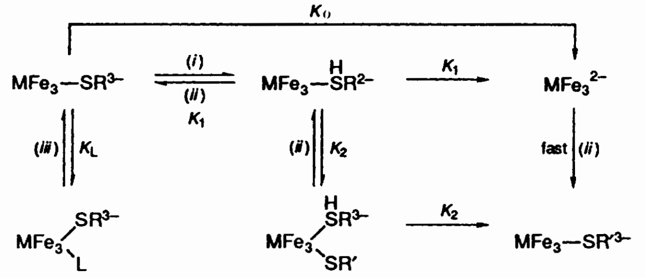
Fig. 1 Kinetic data for the reaction between $[\{MoFe_3S_4(SPh)_3\}_2(\mu\text{-}SPh)_3]^{3-}$ (0.1 mmol dm^{-3}) and $[NEt_4][SPh]$ with $[NHEt_3][BPh_4]$ in MeCN at 25.0 °C. In the main plots the data points correspond to: $[EtS^-]$ = 2.5, $[NHEt_3^+]$ = 2.5–40 (●); $[EtS^-]$ = 5.0, $[NHEt_3^+]$ = 2.5–40 mmol dm^{-3} (■). Curves drawn are those defined by equation (3) and the constants listed in Table 2. For the insert $[NHEt_3^+]/[EtS^-]$ = 6.0 (●) and 10.0 (■). The curve drawn is that defined by equation (2)

thiolate ligand. The method of analysis was analogous to that described before.[1]

Results and Discussion

We described in the previous paper[1] the general system for establishing the mechanisms of acid-catalysed substitution at iron–sulfur-based clusters: the use of $[NHEt_3][BPh_4]$ as the acid and $[NEt_4][SR']$ as the nucleophile or base. The application of this system to the dicubanes $[\{MFe_3S_4(SR)_3\}_2(\mu\text{-}SR)_3]^{2-}$ is shown in Scheme 1.

The processing of the data to establish the relationships between the rate of the reaction and the concentrations of the various reagents was similar to that described[1] for $[Fe_4S_4(SR)_4]^{n-}$. However, analysis of the dependence of the observed rate constants or the concentrations of $[NHEt_3]^+$ and RS^- is not as simple as before. We will start by describing the analysis of the most complicated system, $[\{MoFe_3S_4(SPh)_3\}_2(\mu\text{-}SPh)_3]^{3-}$, and then show how the kinetics observed with the other systems is a limiting form of this general behaviour.



Scheme 2 (*i*) $[NHEt_3]^+$; (*ii*) $R'S^-$; (*iii*) L

Substitution at $[\{MoFe_3S_4(SPh)_3\}_2(\mu\text{-}SPh)_3]^{3-}$.—In the absence of acid the substitution of the first thiolate ligand in this cluster occurs at a rate which shows a simple first-order dependence on the concentration of the cluster, $[Mo_2]$, but is independent of $[EtS^-]$ as described by equation (1). In the

$$-d[Mo_2]/dt = (8.0 \pm 0.2) \times 10^{-2}[Mo_2] \qquad (1)$$

presence of acid the rate increases as shown in Fig. 1. These data show the following characteristics. The observed first-order rate constant, k_{obs}, exhibits a complicated dependence on the ratio $[NHEt_3^+]/[EtS^-]$ [Fig. 1 (main)]: a first-order dependence at low ratios but independence at high ratios. Superimposed on this effect there is a dependence on $[EtS^-]$. This effect is shown in Fig. 1 (insert), where (at a large, constant value of $[NHEt_3^+]/[EtS^-]$) the rate of the reaction exhibits a non-linear dependence on $[EtS^-]$. Analysis of this curve by the normal method[11] gives the rate equation (2). It is important to note at

$$k'_{obs} = (k_{obs} - 0.08) = (3.3 \pm 0.1) \times 10^{-2}[EtS^-]/\{1 + (1.13 \pm 0.1) \times 10^3[EtS^-]\} \qquad (2)$$

this stage, as we did in the previous paper,[1] that the absence of a pK_a for RSH in MeCN means that we cannot distinguish between a dependence on $[RS^-]$ or $[RSH]$. However, we have established in these reactions, as in the previous paper,[1] that RSH does not act as a proton source. For this system it is not possible to arrive at a single equation which describes the dependence of the reaction rate on $[NHEt_3^+]/[EtS^-]$, because the dependence on this ratio and $[EtS^-]$ are coupled.

There is no contribution to the overall rate from any EtSH generated in solution. Studies on the reaction between $[\{MFe_3S_4(SPh)_3\}_2(\mu\text{-}SPh)_3]^{3-}$ and EtSH show that in the concentration range $[EtSH]$ = 1–10 mmol dm^{-3} the thiol does not contribute to the rate of the acid-catalysed pathway. Similarly PhSH, in the same concentration range, does not contribute to the rate of the acid-catalysed substitution of $[\{MFe_3S_4(SEt)_3\}_2(\mu\text{-}SEt)_3]^{3-}$. Similar behaviour was observed in the reaction of $[Fe_4S_4(SR)_4]^{n-}$.[1]

From our knowledge of the mechanism of acid-catalysed substitution at $[Fe_4S_4(SR)_4]^{n-}$ clusters[1] it is clear that the data shown in Fig. 1 are consistent with the mechanism in Scheme 2. The rate law associated with this mechanism is shown in equation (3) and is derived assuming that K_1 and K_2 are rapidly

$$-\frac{d[Mo_2]}{dt} = \left\{k_0 + \frac{(k_1 + k_2K_2[RS^-])K_1[NHEt_3^+][RS^-]^{-1}}{1 + K_1[NHEt_3^+][RS^-]^{-1}(1 + K_2[RS^-])}\right\}[Mo_2] \qquad (3)$$

established equilibria and k_1 and k_2 are the rate-limiting steps. When $[NHEt_3^+]/[RS^-]$ is large then k'_{obs} derived from this equation simplifies to equation (4). Comparison of equations (2)

Table 2 Summary of elementary rate constants and equilibrium constants for substitution of $[\{MFe_3S_4(SR)_3\}_2(\mu\text{-}SR)_3]^{3-}$ in MeCN at 25.0 °C[a]

Cluster	Nucleophile	$10^2k_0/s^{-1}$	K_1	k_1/s^{-1}	$K_2/dm^3\ mol^{-1}$	k_2/s^{-1}	$K_3/dm^3\ mol^{-1}$
$[Fe_4S_4(SPh)_4]^{2-}$	EtS^-	1.0 ± 0.2	1.20 ± 0.1	(8.0 ± 0.2) × 10^{-2}	—	—	—
$[\{MoFe_3S_4(SPh)_3\}_2(\mu\text{-}SPh)_3]^{3-}$	EtS^-	8.0 ± 0.3	0.26 ± 0.03	—	(1.1 ± 0.1) × 10^3	0.29 ± 0.03	—
$[\{WFe_3S_4(SPh)_3\}_2(\mu\text{-}SPh)_3]^{3-}$	EtS^-	0.6 ± 0.1	>4	—	(5.5 ± 0.6) × 10^2	0.19 ± 0.02	—
$[Fe_4S_4(SEt)_4]^{2-}$	PhS^-	—	0.29 ± 0.03	2.48 ± 0.1	—	—	67.6 ± 0.5
$[\{MoFe_3S_4(SEt)_3\}_2(\mu\text{-}SEt)_3]^{3-}$	PhS^-	—	0.41 ± 0.05	1.6 ± 0.2	<20[b]	—	—
$[\{WFe_3S_4(SEt)_3\}_2(\mu\text{-}SEt)_3]^{3-}$	PhS^-	—	0.72 ± 0.06	3.4 ± 0.3	>2[b]	—	(1.29 ± 0.06) × 10^2

[a] λ = 500 nm. [b] $K_2k_2 = 40.5 \pm 1\ dm^3\ mol^{-1}\ s^{-1}$.

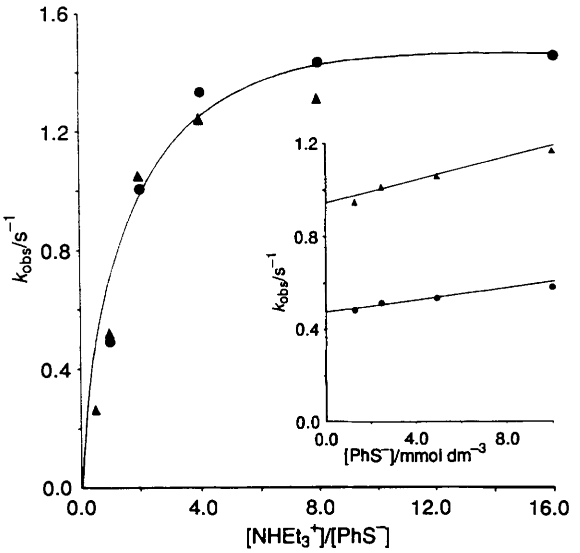


Fig. 2 Kinetic data for the reaction between $[\{MoFe_3S_4(SEt)_3\}_2(\mu\text{-}SEt)_3]^{3-}$ (0.1 mmol dm^{-3}) and $[NEt_4][SPh]$ with $[NHEt_3][BPh_4]$ in MeCN at 25.0 °C. In the main plot the data points correspond to: $[PhS^-] = 2.5$, $[NHEt_3^+] = 2.5$–40.0 (●); $[PhS^-] = 5.0$, $[NHEt_3^+] = 2.5$–40.0 mmol dm^{-3} (▲). The curve drawn is that defined by equation (6). For the insert $[NHEt_3^+]/[PhS] = 1.0$ (●) and 2.0 (▲). The lines drawn are those defined by equation (6)

$$k'_{obs} = (k_{obs} - 0.08) = (k_1 + k_2K_2[EtS^-])/(1 + K_2[EtS^-]) \quad (4)$$

and (4) gives the values $k_1 = 0$, $k_2 = 0.29 \pm 0.03\ s^{-1}$, $K_2 = (1.13 \pm 0.1) \times 10^3\ dm^3\ mol^{-1}$. Using these values to analyse the data in Fig. 1 (main) permits the calculation of $K_1 = 0.26 \pm 0.03$. These equilibrium constants and elementary rate constants are summarised in Table 2.

The mechanism shown in Scheme 2 is entirely general and, as indicated above, follows the behaviour we have established for $[Fe_4S_4(SR)_4]^{n-}$. In the uncatalysed pathway (k_0) rate-limiting dissociation of the thiolate ligand occurs to give a cluster where one iron centre has a vacant site which is subsequently rapidly attacked by the excess of RS^- present. The acid-catalysed pathways both involve initial, rapid protonation of the cluster, probably at an iron-bound thiolate-ligand, followed by either dissociative loss of the thiol (k_1 route) and rapid capture of the cluster by RS^-, or associative attack by RS^- at the cluster, then rate-limiting dissociation of the thiol (K_2k_2 route).

The substitution reactions of the other clusters investigated in this study show behaviour consistent with Scheme 2, but the kinetics has simplifying features which makes the analysis less tortuous than that for $[\{MoFe_3S_4(SPh)_3\}_2(\mu\text{-}SPh)_3]^{3-}$.

Substitution at $[\{WFe_3S_4(SPh)_3\}_2(\mu\text{-}SPh)_3]^{3-}$.—Studies analogous to those described for $[\{MoFe_3S_4(SPh)_3\}_2(\mu\text{-}SPh)_3]^{3-}$ show a dependence on $[EtS^-]$ as described by equation (5), similar to that observed for the molybdenum analogue. Although this system requires acid to react rapidly, it shows no dependence on $[NHEt_3^+]/[EtS^-]$. This we interpret as a rapid and stoichiometric protonation of the cluster, complete within the dead-time of the stopped-flow apparatus ($K_1 > 4$). The derived elementary rate constant and equilibrium constants are summarised in Table 2.

$$\frac{-d[W_2]}{dt} = [(1.05 \pm 0.1) \times 10^2[EtS^-]/\{1 + (5.47 \pm 0.2) \times 10^2[EtS^-]\}][W_2] \quad (5)$$

Substitution at $[\{MoFe_3S_4(SEt)_3\}_2(\mu\text{-}SEt)_3]^{3-}$.—In the studies with ethanethiolate clusters the kinetics is simplified by the absence of the uncatalysed pathway, k_0. Similar behaviour[1] was observed in the reactions of $[Fe_4S_4(SR)_4]^{n-}$. Another simplifying feature of the kinetics with $[\{MoFe_3S_4(SEt)_3\}_2(\mu\text{-}SEt)_3]^{3-}$ is that the dependence of the reaction rate on $[PhS^-]$ is linear as shown in Fig. 2 (insert). Analysis of the data in Fig. 2 allows the derivation of the rate law (6). The derived elementary rate constants obtained by comparison of equations (3) and (6) are shown in Table 2.

$$\frac{-d[Mo_2]}{dt} = \left\{(0.66 + 0.02) + \frac{(1.66 \pm 0.05)[NHEt_3^+]}{\{1 + (0.41 \pm 0.05)[NHEt_3^+][PhS^-]^{-1}\}}\right\}[Mo_2] \quad (6)$$

Substitution at $[\{WFe_3S_4(SEt)_3\}_2(\mu\text{-}SEt)_3]^{3-}$.—The substitution kinetics observed in this system is similar to that for $[Fe_4S_4(SEt)_4]^{2-}$: the rate of the reaction shows saturation dependence on $[NHEt_3^+]/[PhS^-]$, but is inhibited by $[PhS^-]$, giving the rate law (7). This rate law demonstrates that in this system the substitution proceeds entirely by the dissociative route, with the derived constants listed in Table 2. The inhibition of the reaction afforded by PhS^- is attributable to this anion binding to the intact cluster. Consistent with this interpretation we observe (see below) that other small molecules bind at this cluster.

$$\frac{-d[Mo_2]}{dt} = \left[\frac{(2.44 \pm 0.2)[NHEt_3^+][PhSt^-]^{-1}}{\{1 + (0.72 \pm 0.06)[NHEt_3^+][PhS^-]^{-1}\}\cdot\{1 + (1.29 \pm 0.01) \times 10^2[PhS^-]\}}\right][W_2] \quad (7)$$

General Trends in the Substitution Characteristics.—Before discussing the general substitution patterns associated with the iron–sulfur-based clusters it is important to remind ourselves that the reactions being studied are the substitution of the first thiolate ligand bound to an iron site, the same reaction as was observed in the studies[1] on $[Fe_4S_4(SR)_4]^{n-}$. However, now the presence of a Mo or W atom within the cluster framework changes the reactivity of the iron centres. Of course, at this stage in the development of the understanding of the reactivity of these clusters we cannot be absolutely sure that changes in the

Table 3 Binding constants, K_L, for the interaction of small molecules with $[Fe_4S_4(SEt)_4]^{2-}$(FeFe$_3$) and $[\{MFe_3S_4(SEt)_3\}_2(\mu\text{-}SEt)_3]^{3-}$ (M = Mo, MoFe$_3$; or M = W, WFe$_3$) in MeCN at 25.0 °C

	K_1/dm^3 mol^{-1} [a]	
L	FeFe$_3$	MoFe$_3$
Cl^- [b]	202	1550
Br^-	96.2	850
PhS^-	67.6	129
CO [c]	*ca.* 300	*ca.* 800
N_2O [c]	*ca.* 380	*ca.* 1030

[a] Independent of [cluster] = 0.1–0.01 mmol dm^{-3} and of $[NHEt_3^+]/[PhS^-]$ = 2.0–4.0. [b] 563 dm^3 mol^{-1} for WFe$_3$. [c] Limited solubility of gases precludes extensive study.

mechanism between the two types of clusters $[Fe_4S_4(SR)_4]^{n-}$ and $[\{MFe_3S_4(SR)_3\}_2(\mu\text{-}SR]_3]^{3-}$ are attributable solely to the presence of the heterometal. However, we have seen before[1] that changing the redox level of $[Fe_4S_4[SPh)_4]^{n-}$ (n = 2 or 3) changes the intrinsic reactivity but not the fundamental mechanism.

All of the systems $[\{MFe_3S_4(SR)_3\}_2(\mu\text{-}SR)_3]^{3-}$ (M = Mo or W, R = Et or Ph) undergo acid-catalysed substitution reactions the mechanisms of which are accommodated by Scheme 2. Comparison of the data in Table 2 reveals an important general feature. Although $[Fe_4S_4(SR)_4]^{n-}$ react by a dissociative mechanism, the Mo- or W-containing clusters often show an additional pathway which we ascribe to the binding of RS^- to the cluster prior to loss of the leaving group. With $[\{MFe_3S_4(SPh)_3\}_2(\mu\text{-}SPh)_3]^{3-}$ this associative-type mechanism is the exclusive substitution route, whereas for the clusters $[\{MFe_3S_4(SEt)_3\}_2(\mu\text{-}SEt)_3]^{3-}$ the associative pathway is less important and dissociative pathways are also evident. This is because the value of K_2 is much smaller for the alkanethiolate clusters than for their arenethiolate analogues.

Binding of Small Molecules.—We have demonstrated before[1] how the perturbation of the kinetics of substitution of iron–sulfur clusters can be used to show that small molecules such as L = Cl^-, Br^-, CO *etc.* can bind, albeit transiently, to $[Fe_4S_4(SEt)_4]^{2-}$. In adopting the same strategy to $[\{MFe_3S_4(SR)_3\}_2(\mu\text{-}SR)_3]^{2-}$ the approach was to study the rate of substitution of the cluster at constant $[NHEt_3^+]/[R'S^-]$ and $[R'S^-]$, and observe the way in which k_{obs} is effected by varying concentrations of L. It is important to emphasise that L is not incorporated into the product.

The same general features are evident for $[\{MFe_3S_4(SR)_3\}_2(\mu\text{-}SR)_3]^{3-}$ as observed in the analogous studies on $[Fe_4S_4(SR)_4]^{2-}$: when R = Ph the clusters show no tendency to bind L, but for R = Et binding of L is indicated. For $[\{MFe_3S_4(SEt)_3\}_2(\mu\text{-}SEt)_3]^{3-}$ with L = N_2, H_2, C_2H_4 or PhCCH no binding is evident, but as shown by the data in Table 3 the addition of L = Cl^-, Br^-, CO or N_2O results in an inhibition of k_{obs} as given by the general expression (8). Where k'

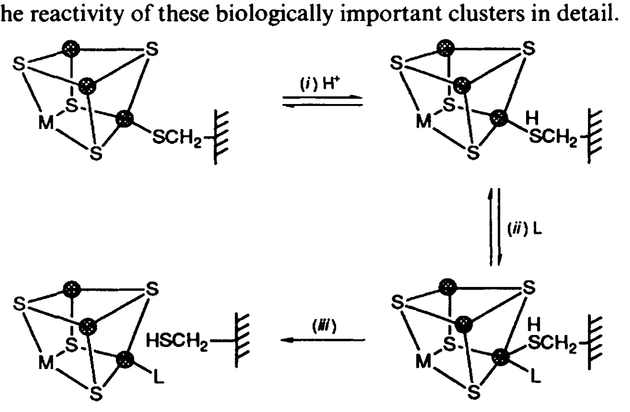
$$k_{obs} = k'/(1 + K_L[L]) \qquad (8)$$

is the observed rate constant in the absence of L. A feature of the data in Table 3 is that *irrespective of the nature of* L (CO *or* Cl^-) *the* Mo-*containing cluster has a greater affinity to bind* L *than does the simple* $[Fe_4S_4(SEt)_4]^{2-}$ *cluster.* This leads us to propose that the presence of the heterometal within the cluster makes the iron sites behave as if they were more co-ordinatively unsaturated; that is the electronic influence of the heterometal is to make the iron sites more likely to bind molecules.

Controlling Substrate Binding in Metalloenzymes.—It is often assumed that the Mo or V atoms in the nitrogenases are the substrate-binding sites. Whilst this may be the case, the results of the studies presented here suggest another role for these atoms, within a cluster. It could be that all nitrogenases bind N_2 at an iron site. However, the presence of the heterometal atom within the cluster changes (*i*) the binding characteristics and (*ii*) the substitution mechanisms at the iron centres. This proposal may be more in keeping with the existence of a nitrogenase containing only Fe.[12]

By favouring an associative mechanism of substitution in clusters containing iron, molybdenum and sulfur and, in addition, coupling this substitution to a rapid protonation reaction (Scheme 3) the enzyme has two degrees of control on substrate binding. In this model three important features are evident. (*a*) Substrate binding only occurs when sufficient protons are around to activate the substrate. (*b*) Protonation and substrate binding are necessary before the enzyme is committed to activating the substrate. (*c*) Opening the site to bind the substrate is always productive. Recently it has been suggested that dinitrogen binds initially to molybdenum and then transfers the substrate to an iron centre.[13] This then is a third possible role for the Mo or V atoms in the active-site cluster.

Of course, these are still models in their infancy and further studies on related systems are necessary before we understand the reactivity of these biologically important clusters in detail.



Scheme 3 (*i*) Labilisation; (*ii*) associative interaction; (*iii*) committal to activation

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Received 29*th October* 1992; *Paper* 2/05788C