Associative Substitution Mechanisms of Clusters: the Relationship between Sites of Nucleophilic Attack and Leaving Group Dissociation

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The associative substitution mechanism of $[Fe_4S_4Cl_4]^{2-}$ with $4\text{-}RC_6H_4S^-$ involves initial, rapid binding of the thiolate to an iron atom (Fe_a), followed by rate-limiting dissociation of a chloro-ligand; however, the origin of the leaving group changes with the electron-releasing capability of the thiolate and when R = Cl, F, H or Me, the chloro-group at Fe_a is labilised, whereas when R = Me, MeO or NH_2 the chloro-group at a remote iron site (Fe_r) is labilised.

In the reactions of transition metal clusters, the presence of more than one metal site means that mechanisms may operate which have no parallel in mononuclear systems. In particular, a general feature of the reactivity of clusters is the modulation of the reactivity of all sites by changes to only one atom within the framework.[1,2] Herein studies on simple homonuclear iron–sulfur-based clusters demonstrate, for the first time, that in the associative substitution mechanism the site of nucleophile attack need not be the site of dissociation of the leaving group.

The substitution of the first chloro-group in $[NBu_4]_2[Fe_4S_4Cl_4]$ by $[NEt_4][4\text{-}RC_6H_4S]$ (R = Cl, F, H, Me, MeO or NH_2), as shown in eqn. (1), have been studied in MeCN on a stopped-flow apparatus, and all obey the generalised rate law shown in eqn. (2).[3]

$$[Fe_4S_4Cl_4]^{2-} + RC_6H_4S^- \rightarrow [Fe_4S_4Cl_3(SC_6H_4R)]^{2-} + Cl^- \tag{1}$$

$$\frac{-d[Fe_4S_4Cl_4{}^{2-}]}{dt} = \frac{\{k_1 + K_2{}^{R}k_3{}^{R}[RC_6H_4S^-]\}\,[Fe_4S_4Cl_4{}^{2-}]}{1 + K_2{}^{R}[RC_6H_4S^-]} \tag{2}$$

The first term in this rate law is associated with a pathway involving rate-limiting dissociation of a chloro-group from $[Fe_4S_4Cl_4]^{2-}$ ($k_1 = 2 \pm 0.3\ s^{-1}$), followed by rapid attack of the thiolate ion at the vacant site, and will not be considered further here. The second term describes an associative pathway, involving rapid attack of the nucleophile at an iron atom ($K_2{}^R$), followed by rate-limiting dissociation of the chloro-leaving group ($k_3{}^R$). Over an extended nucleophile concentration range, the rate of the reaction exhibits a non-linear dependence on the concentration of the nucleophile, as shown in Fig. 1, and analysis[4] of these data permits the calculation of the values of $K_2{}^R$ and $k_3{}^R$ as listed in Table 1. The values of the binding constants of $4\text{-}RC_6H_4S^-$ to $[Fe_4S_4Cl_4]^{2-}$ ($K_2{}^R$) steadily decrease along the series, R = Cl > F > H > Me > MeO > NH_2, as expected from the relative electron-releasing capabilities of these groups.[5] However, the corresponding dissociation constants ($k_3{}^R$), decrease, R = Cl > F > H > Me, and then increase, R = Me < MeO < NH_2, as illustrated in Fig. 2. This discontinuity is a consequence of a change in the nature of the dissociation of the chloro-group.†

Upon binding of the thiolate, the iron sites within the cluster become differentiated: there is the iron atom bound to the thiolate (Fe_a) and the three equivalent remote sites (Fe_r); as shown in Scheme 1. Either Fe_a or Fe_r can be the origin of the leaving group. For the more electron-withdrawing arylthiolates (R = Cl, F, H or Me), subsequent dissociation of the chloro-group bound to Fe_a dominates the reaction (Hammett $\rho = +2.1$). The electronic origin of this labilisation is presumably the nucleophile and the leaving group, both bound to Fe_a, competing for the π-bonding orbitals associated with the d electrons on the iron atom.

With nucleophiles that are more electron-releasing (R = Me, MeO or NH_2) the labilisation of the chloro-group bound to Fe_a must become less marked. However, the increased electron density imparted by these nucleophiles to the cluster labilises chloro-groups on the Fe_r sites. The electronic origin of the labilisation of the remote iron sites is presumably the stabilisation of the incipient positive charge on the cluster as the leaving group departs (Hammett $\rho = -0.7$).

The mechanism shown in Scheme 1 has the same form of rate law as shown in eqn. (2) except, $k_3{}^R = \{(k_3{}^a)^R + (k_3{}^r)^R\}$. Consequently the origin of the leaving group is not discernible from studies with a single nucleophile.

Consideration of the two linear portions of the Hammett plot for the reactions of $[Fe_4S_4Cl_4]^{2-}$ in Fig. 2, permits an estimate of the values of $(k_3{}^a)^R$ and $(k_3{}^r)^R$ for all the arylthiolates, and reveals that, even at the extremes of this plot, the values of $(k_3{}^a)^R$ and $(k_3{}^r)^R$ differ by less than a factor of twenty. Clearly, in the intermediate region (R = Me, H or F), both pathways are operating.

It seems likely that the behaviour exhibited by $[Fe_4S_4Cl_4]^{2-}$ is general, and that all iron–sulfur-based clusters (and possibly all metal clusters) show this behaviour. However, the point at which there is a change in the origin of the leaving group will

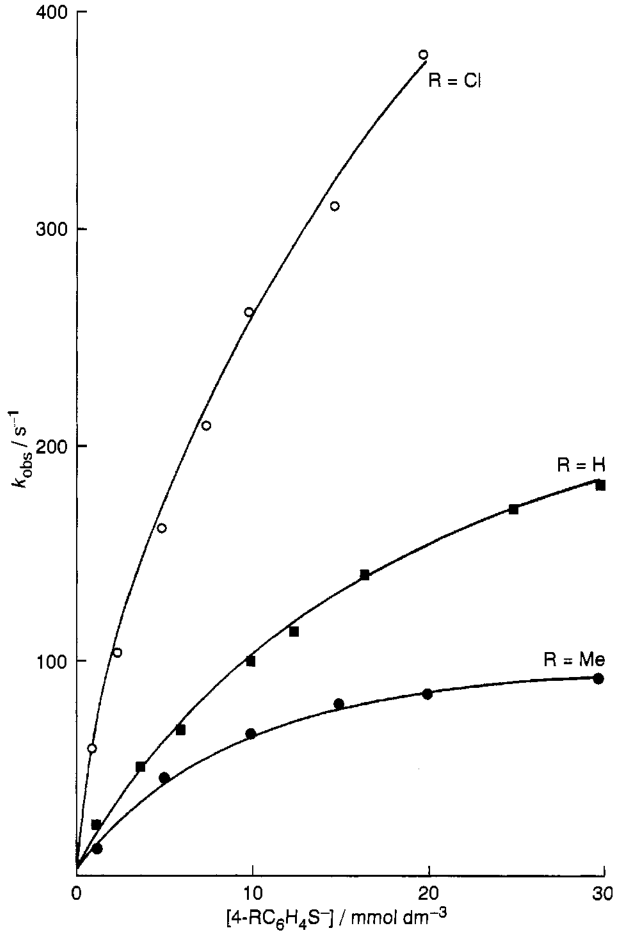


Fig. 1 Dependence of k_{obs} (pseudo-first-order observed rate constant) on the concentration of arylthiolate ion for the reactions of $[Fe_4S_4Cl_4]^{2-}$ with $4\text{-}RC_6H_4S^-$ {R = Cl (○), H (■) or Me (●)} in MeCN at 25 °C, $I = 0.1$ mol dm^{-3} ($[NBu_4]BF_4$). Curves drawn are those defined by eqn. (2), and the values presented in Table 1.

Table 1 Summary of the nucleophile binding constants (K_2^R) and leaving group dissociation constants (k_3^R) for the substitution reactions of $[NBu_4]_2[Fe_4S_4Cl_4]$ or $[NEt_4]_2[MoFe_3S_4Cl_3(catCl_4)(NCMe)]$ with $[NEt_4][4\text{-}RC_6H_4S]$ (R = Cl, F, H, Me, MeO or NH_2) in MeCN at 25 °C, I = 0.1 mol dm^{-3} {$[NBu_4]BF_4$}

Cluster	R	$K_2^R/dm^3\ mol^{-1}$	k_3^R/s^{-1}
$[Fe_4S_4Cl_4]^{2-}$	Cl	51.2[a]	794[b]
	F	63.0	339
	H	68.4	250
	Me	149	108
	MeO	355	200
	NH_2	> 1000[c]	220
$[MoFe_3S_4Cl_3(catCl_4)(NCMe)]^{2-}$	Cl	123	159
	F	130	140
	H	133	126
	Me	179	79.4
	MeO	400	51.2
	NH_2	> 1000[c]	27

[a] Errors in K_2^R are, in all cases, ±5%. [b] Errors in k_3^R are ±5–8%, except for R = Cl with $[Fe_4S_4Cl_4]^{2-}$ where the error is ±10%, because of the rapidity of the reaction. [c] Rate of reaction independent of the concentration of thiolate in the concentration range, $[4\text{-}RC_6H_4S^-]$ = 1–50 mmol dm^{-3}

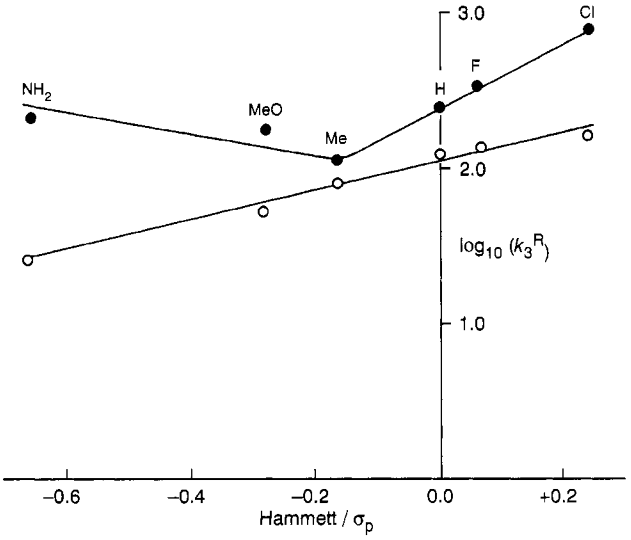
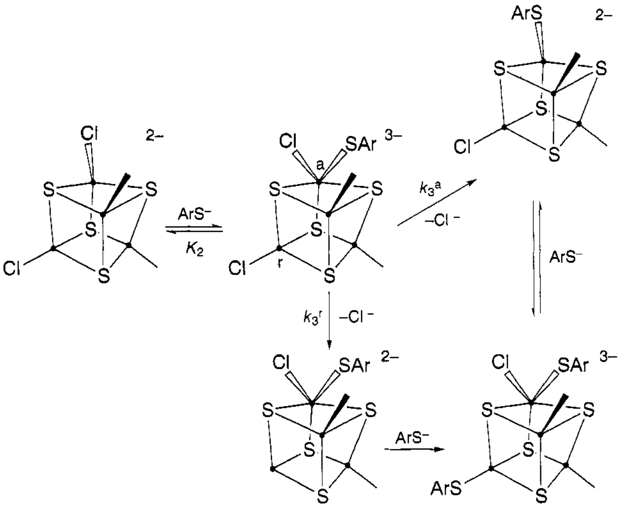


Fig. 2 Hammett correlation for the dissociation rate constant of the chloro-ligands (k_3^R) in the associative substitution pathway for the reactions of $4\text{-}RC_6H_4S^-$ (R = Cl, F, H, Me, MeO or NH_2) with $[Fe_4S_4Cl_4]^{2-}$ (●) or $[MoFe_3S_4Cl_3(catCl_4)(NCMe)]^{2-}$ (○) in MeCN at 25 °C, I = 0.1 mol dm^{-3} ($[NBu_4]BF_4$).

vary depending on the cluster. In studies of the heteronuclear cluster, $[NEt_4]_2[MoFe_3S_4Cl_3(catCl_4)(NCMe)]$‡ {$catCl_4$ = $C_6Cl_4O_2$, tetrachlorocatecholate(2−)}[6] with $4\text{-}RC_6H_4S^-$, a uniform increase in the binding constants (K_2^R), and a uniform decrease in the dissociation constants (k_3^R) is observed along the series, R = Cl > F > H > Me > MeO > NH_2 (Hammett ρ = +1.2), as shown in Table 1 and Fig. 2. It seems likely that for the molybdenum-based cluster the change from one pathway to the other occurs with more electron-releasing nucleophiles, outside the range of this study. Certainly this is consistent with the characteristic reactivity of the iron sites in $\{MoFe_3S_4\}^{3+}$ cubes which, as has been noted before,[1] behave as though they are more electron-deficient than in $\{Fe_4S_4\}^{2+}$ clusters.



Scheme 1 Associative substitution mechanisms for the reactions of $[Fe_4S_4Cl_4]^{2-}$ with arylthiolate ions (Ar = $4\text{-}RC_6H_4$); Only the chloro-groups pertinent to the discussion are shown

In general, the kinetics of substitution reactions of transition metal clusters are very simple and exhibit a zero- and/or a first-order dependence on the concentration of the nucleophile interpreted in terms of dissociative and associative mechanisms, respectively.[7] This work indicates that in many of these studies the relationship between the sites of nucleophilic attack and leaving group dissociation is incompletely defined. The important point is that the addition of a nucleophile to a metal site even in a symmetrical, homonuclear cluster need not necessarily labilise that particular site to substitution, but rather may labilise another metal site within the framework. This complexity cannot be established from the rate law, but only by correlations of the dissociation constants, k_3^R, with either a linear free energy parameter as shown in Fig. 2 or, possibly the activation enthalpy, $\Delta H^‡$. Even the application of such correlations with the second-order rate constants, $K_2^R k_3^R$, may not reveal a change in mechanism if the electronic influence of the nucleophile effects K_2^R and k_3^R differently.

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Footnotes

† This discontinuity is not a consequence of the substituent, R, binding to the cluster, since the values of the binding constants (K_2^R) vary uniformly with the nature of the arylthiolate. In addition, the stopped-flow absorbance-time traces for all the arylthiolates are very similar, consisting of a single exponential, whose initial absorbance is that of the parent cluster. Finally, linear Hammett plots with the same range of nucleophiles have been observed for $[MoFe_3S_4Cl_3(catCl_4)(NCMe)]^{2-}$ (Fig. 2), $[Fe_2S_2Cl_4]^{2-}$ and $[Y_2MoS_2FeCl_2]^{2-}$ (Y = S or O).[8]

‡ In this cluster the molybdenum is substitutionally inert and, again, displacement of a chloro-group on an iron site is being monitored.

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