A New Kinetic Pattern for the Substitution Reactions of Inorganic Complexes: Studies on $[Fe_2S_2Cl_4]^{2-}$

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Kinetic studies on the substitution reactions of $[Fe_2S_2Cl_3(NCMe)]^-$ with the nucleophiles L = Br^- or RS^- (R = Et or Bu^t) to form $[Fe_2S_2Cl_3L]^{2-}$ show that the rate of the reaction is inhibited by increasing the concentration of the nucleophile; this is a consequence of L binding to the iron atom not undergoing substitution.

The kinetics of substitution reactions of mono- and polynuclear transiton metal complex are well defined.[1,2] Two limiting rate laws have been identified. (*i*) The rate of the reaction is independent of the concentration and nature of the nucleophile, consistent with rate-limiting dissociation of the leaving group, or rate-limiting attack by solvent. (*ii*) The rate of the reaction increases with an increase in the concentration of the nucleophile, consistent with either rate-limiting attack by the nucleophile or rapid outer-sphere association of the nucleophile with the complex prior to dissociation of the leaving group.

We now report studies on the substitution reactions of $[Fe_2S_2Cl_4]^{2-}$ in MeCN which exhibits the novel kinetic behaviour that the rate of the substitution reaction decreases with an increase in the concentration of the nucleophile.

Earlier studies[3] on $[Fe_2S_2Cl_4]^{2-}$ in solution showed that this dimer is labile towards chloride dissociation. In the course of these studies we have quantified this behaviour and shown that the dominant and reactive solution species is $[Fe_2S_2Cl_3(NCMe)]^-$.† This has the important ramification that the two iron atoms are differentiated by their coordination sphere and hence their reactivity.

Upon mixing solutions of $[Fe_2S_2Cl_3(NCMe)]^-$ and an excess of L (L = Br^-, EtS^- or Bu^tS^-) in MeCN in a stopped-flow spectrophotometer an exponential absorbance–time curve is observed,‡ with an initial absorbance corresponding to that of the parent dimer and a final absorbance which varies with the concentration of L. This is consistent with the equilibrium reaction shown in eqn. (1).

$$[Fe_2S_2Cl_3(NCMe)]^- + L^- \rightleftharpoons [Fe_2S_2Cl_3L]^{2-} + MeCN \quad (1)$$

The dependence of the reaction rate on the concentration of nucleophile is complicated as typified by the data with L = Bu^tS^- in Fig. 1, and for all L in Fig. 1 (insert). All three nucleophiles show the same behaviour: a decrease in the rate of the reaction as the concentration of L is increased. At low concentrations of L the observed pseudo first order rate constant, $k_{obs} = 1.7 \pm 0.2\ s^{-1}$, is the same for all nucleophiles, and at high concentrations of L the rate limits to a small but finite value, k_{lim}; the value of k_{lim} depends on the nature of L. It must be emphasised that this kinetic behaviour is directly related to the substitution process and is not due to general or specific medium effects. All reactions were studied using only $[NEt_4]^+$ salts, at a constant ionic strength of 0.1 mol dm^{-3} ($[NEt_4]BF_4$). In addition, studies with $[Br^-]$ = 2.5 mmol dm^{-3} but varying the ionic strength $[NEt_4]BF_4$ = 0–50 mmol dm^{-3}, showed no significant effect on $k_{obs} = 0.43 \pm 0.02\ s^{-1}$. Finally, the kinetics of the reaction between $[Fe_2S_2Cl_3(NCMe)]^-$ and other nucleophiles§ show a very different behaviour, over the same concentration range as used with Br^-, EtS^- or Bu^tS^-. As shown in Fig. 1, with L = PhS^- [6] the rate of substitution is independent of the concentration of the nucleophile, and with L = p-$MeC_6H_4O^-$ [7] the rate increases with increasing concentration of nucleophile. At low concentrations of PhS^- or p-$MeC_6H_4O^-$ the rate of substitution is the same as with the other nucleophiles, $k_{obs} = 1.4 \pm 0.2\ s^{-1}$.

The kinetics observed with all the nucleophiles can be rationalised in terms of the mechanism shown in Scheme 1.

For all nucleophiles, at low concentrations of L, the dominant pathway involves rate-limiting dissociation of the coordinated MeCN followed by rapid attack of the nucleophile at the, thus generated, vacant site. At high concentrations of nucleophile, rapid binding of L can occur at either of the electron-deficient, formally 13-electron, iron centres. The rapid binding of anions to these electron-deficient sites is a mechanistic pattern we have observed before[8] for the related clusters, $[Fe_4S_4Cl_4]^{2-}$.

Binding of L to the substitutionally active iron (right hand side of Scheme 1) results in the 'usual' kinetic behaviour, typified by L = p-$MeC_6H_4O^-$, in which the rate of substitution increases with increase in the concentration of the nucleophile. However, with Br^-, EtS^- and Bu^tS^- competitive binding of L to the non-active iron (left hand side of Scheme 1) results in an inhibition to the rate of substitution. In binding to the 'wrong' iron site, the nucleophile produces a species which is less labile to substitution than $[Fe_2S_2Cl_3(NCMe)]^-$. An alternative mechanism, in which binding of nucleophiles occurs only at the substitutionally active iron, but for L = Br^-, EtS^- and Bu^tS^- the intermediate is less labile than when L =

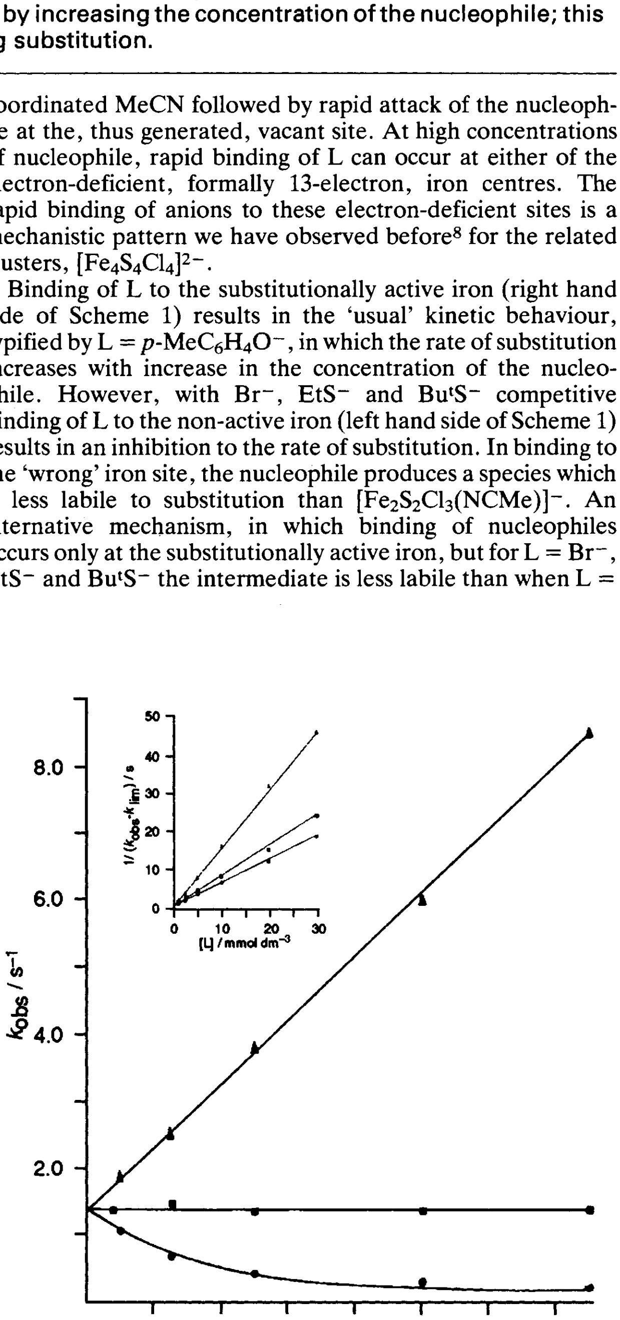
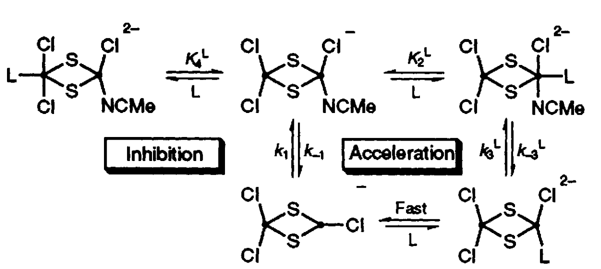


Fig. 1 Kinetics for the reactions of $[Fe_2S_2Cl_3(NCMe)]^-$ with various nucleophiles, L in MeCN at 25.0 °C, ionic strength = 0.1 mol dm^{-3} ($[NEt_4]BF_4$), concentration of $[Fe_2S_2Cl_3(NCMe)]^-$ = 0.1 mmol dm^{-3}; L = p-$MeC_6H_4O^-$ (▲), L = PhS^- (■), L = Bu^tS^- (●). Lines drawn are those defined by eqn. (3) and the values in the text. *Insert*: Graph of $1/(k_{obs}$-$k_{lim})$ {k_{lin} is the observed rate constant at high concentrations of nucleophile = $(k_3 + k_{-3})K_2{}^L/(K_2{}^L + K_4{}^L)$} against the concentration of L for the reactions of $[Fe_2S_2Cl_3(NCMe)]^-$ with L = Br^- (■), L = EtS^- (●) or L = Bu^tS^- (▲) in MeCN at 25.0 °C, ionic strength = 0.1 mol dm^{-3} ($[NEt_4]BF_4$). Concentration of $[Fe_2S_2Cl_3(NCMe)]^-$ = 0.1 mmol dm^{-3}. Lines drawn are those defined by eqn. (3) and the values in the text.



Scheme 1 Pathways for the substitution reactions of $[Fe_2S_2Cl_3(NCMe)]^-$ with various nucleophiles, L in MeCN; iron atoms shown as ●

p-$MeC_6H_4O^-$, seems unlikely. The general rate law for the equilibrium reactions shown in Scheme 1 is given by eqn. (3).[9]

$$-\mathrm{d}[Fe_2S_2Cl_3(NCMe)^-]/\mathrm{d}t = \frac{\{(k_1+k_{-1}+k_{-3}^{L})+(k_3^{L}+k_{-3}^{L})K_2^{L}[L]\}\,[Fe_2S_2Cl_3(NCMe)^-]}{1+(K_2^{L}+K_4^{L})[L]} \qquad (3)$$

The first term in eqn. (3) describes the common dissociative pathway observed at low concentrations of nucleophile, while the second term describes the associative pathway with L binding to the substitutionally labile iron centre. The binding of L to the non-labile iron site is reflected only in the denominator term, and hence only if this binding constant is large will it perturb the kinetics, resulting in inhibition of the reaction rate. Analysis of the data in Fig. 1 gives the following values. L = Br^-: $(k_1 + k_{-1} + k_{-3}^{Br}) = 1.7 \pm 0.2\ s^{-1}$, $(k_3^{Br} + k_{-3}^{Br})K_2^{Br} = (2.1 \pm 0.1) \times 10^2\ dm^3\ mol^{-1}\ s^{-1}$, $(K_2^{Br} + K_4^{Br}) = (1.3 \pm 0.2) \times 10^3\ dm^3\ mol^{-1}$; L = EtS^-: $(k_1 + k_{-1} + k_{-3}^{EtS}) = 1.7 \pm 0.2\ s^{-1}$, $(k_3^{EtS} + k_{-3}^{EtS})K_2^{EtS} = (2.6 \pm 0.1) \times 10^2\ dm^3\ mol^{-1}\ s^{-1}$, $(K_2^{EtS} + K_4^{EtS}) = (1.1 \pm 0.2) \times 10^3\ dm^3\ mol^{-1}$; L = Bu^tS^-: $(k_1 + k_{-1} + k_{-3}) = 1.7 \pm 0.2\ s^{-1}$, $(k_3^{BuS} + k_{-3}^{BuS})K_2^{BuS} = (1.5 \pm 0.1) \times 10^2\ dm^3\ mol^{-1}\ s^{-1}$, $(K_2^{BuS} + K_4^{Bus}) = (2.6 \pm 0.2) \times 10^3\ dm^3\ mol^{-1}$. For the non-equilibrium reactions, where k_{-1} and k_{-3} are negligable, L = p-$MeC_6H_4O^-$: $k_1 = 1.4 \pm 0.2\ s^{-1}$, $(k_3K_2)^{ArO} = (4.7 \pm 0.2) \times 10^2\ dm^3\ mol^{-1}\ s^{-1}$, $K_2^{ArO} \leqslant 7\ dm^3\ mol^{-1}$; L = PhS^-: $k_1 = 1.4 \pm 0.2\ s^{-1}$.

There are two important points about these data which must be emphasised. First, the values for the binding constants, K_2^L and K_4^L indicate that the various nucleophiles have markedly different affinities for the two iron sites. Secondly, the apparent independence of the rate of substitution on the concentration of PhS^- is consistent with the reaction proceeding exclusively by the dissociative, k_1 pathway. However, if $k_3^L/k_1 \approx (1 + K_4^L/K_2^L)$ then $k_{obs} \approx k_1$. Under these conditions an associative pathway may be operating, with L binding to both iron centres, but it is not reflected in the kinetics. This may be an important consideration in the interpretation of the kinetics of substitution reactions of other polynuclear complexes.

The mechanistic conclusion from this work is that polynuclear complexes may be susceptible to nucleophilic attack at several sites. However, in order for other complexes to exhibit the kinetic behaviour described herein they must fulfil certain rather stringent requirements. First, the complex must be polynuclear with at least one metal site distinct from the rest. Secondly, the nucleophiles must be capable of binding to more than just the substitutionally active site and in addition, the influence they impart to the reactive site must be quite distinct. Using kinetic studies alone it would certainly be difficult to identify multiple nucleophile binding sites in polynuclear complexes if the effect of the nucleophile was merely to accelerate the rate of substitution irrespective of the site to which it bound.

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Footnotes

† The molar conductivity of $[NEt_4]_2[Fe_2S_2Cl_4]$ (0.5 mmol dm^{-3}) in MeCN is $\Lambda_M = 150\ \Omega^{-1}\ cm^2\ mol^{-1}$, which is more consistent with the 1:1 electrolyte,[4] $[Fe_2S_2Cl_3(NCMe)]^-$. This formulation is confirmed by the kinetic studies. Studies on the reaction between $[Fe_2S_2Cl_4]^{2-}$ (0.1 mmol dm^{-3}) and $[EtS^-]$ = 5.0 mmol dm^{-3} in the presence of various concentrations of $[Cl^-]$ = 0–1.0 mmol dm^{-3} showed that the rate of the reaction is unaffected by the Cl^- ($k_{obs} = 0.43 \pm 0.02$) but the magnitude of the absorbance change associated with the formation of $[Fe_2S_2Cl_3(SEt)]^{2-}$ progressively decreases until at $[Cl^-]$ = 1.0 mmol dm^{-3} no absorbance change is observed. This is consistent with the coupled equilibria in eqn. (2).

$$[Fe_2S_2Cl_4]^{2-} \underset{K_{Cl}}{\overset{Cl^-}{\rightleftharpoons}} [Fe_2S_2Cl_3(NCMe)]^- \underset{K_{EtS}}{\overset{EtS^-}{\rightleftharpoons}} [Fe_2S_2Cl_3(SEt)]^{2-} \qquad (2)$$

Consequently, $K_0^{EtS} = K_{Cl}K_{EtS} = [Fe_2S_2Cl_3(SEt)^{2-}][Cl^-]/[Fe_2S_2Cl_4^{2-}][EtS^-]$. Analysis[5] of the effect of the Cl^- concentration on the magnitude of the absorbance changes gives $K_0^{EtS} = (1.3 \pm 0.3) \times 10^{-2}$. Using this value, and analysing the effect of various concentrations of EtS^- on the magnitude of the absorbance change, in the absence of added Cl^-, we can calculate that one mole-equivalent of Cl^- is released from dilute solutions of $[Fe_2S_2Cl_4]^{2-}$. Similar analysis of the spectrophotometric data with other nucleophiles gives: $K_0^{BuS} = (1.8 \pm 0.4) \times 10^{-2}$ and $K_0^{Br} = (3.4 \pm 0.4) \times 10^{-2}$.

‡ The first-order dependence on the concentration of the dimer is evident from the exponential fit of the absorbance–time traces over at least three halflives. This is confirmed by studies with $[EtS^-]$ = 10.0 mmol dm^{-3} and $[Fe_2S_2Cl_4^{2-}]$ = 0.03–0.5 mmol dm^{-3} where the observed rate constant did not vary, $k_{obs} = 0.40 \pm 0.02\ s^{-1}$.

¶ With L = PhS^- or p-$MeC_6H_4O^-$ stoichiometric amounts of $[Fe_2S_2L_4]^{2-}$ are formed as demonstrated by: (*i*) the larger absorbance changes associated with these nucleophiles; (*ii*) the insensitivity of the absorbance change to the concentration of L and; (*iii*) the *in situ* ^1H NMR spectra of the products in excellent agreement with those in the literature[6,7] {L = PhS^-: δ 9.3 (*m*-H), δ 4.9 (*o*-H), δ 3.4 (*p*-H): L = p-$MeC_6H_4O^-$; δ 10.8 (*m*-H), δ 6.8 (*p*-Me)}.

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