Inorg. Chem. **2002**, *41*, 5487–5494

Inorganic Chemistry
Article

Substitution Reactions of $[Fe_4S_4Cl_4]^{2-}$ with Bu^tNC or $Et_2NCS_2^-$: Trapping Intermediates and Detecting New Pathways

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Received March 19, 2002

Kinetic studies on the substitution reaction between $[Fe_4S_4Cl_4]^{2-}$ and Bu^tNC or $Et_2NCS_2^-$ are reported. The binding of small molecules and ions to Fe–S clusters is a fundamental step in substitution reactions but can be difficult to follow directly because these reactions are rapid and often associated with small spectroscopic changes. A novel kinetic method is reported which allows the time course of molecule and ion binding to Fe–S clusters to be followed by monitoring the lability of the cluster. Using a stopped-flow, sequential-mix apparatus, $[Fe_4S_4Cl_4]^{2-}$ and L (L = $Et_2NCS_2^-$ or Bu^tNC) are rapidly mixed, and after a known time (δ) the resulting solution is mixed with a solution of PhS^-. The thiolate substitutes for the chloro ligands on the cluster, in a reaction which is easy to follow because of the large change in the visible absorption spectrum. The rate of this substitution is extremely sensitive to whether L is bound to the cluster or not. By correlation of δ with the rate of the reaction with PhS^-, the time course of the reaction between $[Fe_4S_4Cl_4]^{2-}$ and L can be mapped out. In studies where L = Bu^tNC this technique has allowed the detection of an intermediate $\{[Fe_4S_4Cl_4(CNBu^t)]^{2-}\}$ which cannot be detected spectrophotometrically. In further studies, the substitution reactions of $[Fe_4S_4Cl_4]^{2-}$ with PhS^-, $Et_2NCS_2^-$, or Bu^tNC are all perturbed by the addition of Cl^-. In all cases a common pathway for substitution is evident, but with $Et_2NCS_2^-$ an additional, slower pathway becomes apparent under conditions where the common pathway is completely inhibited by Cl^-.

Introduction

In biology, Fe–S clusters are most commonly associated with the storage and transfer of electrons. However, over the past few years new roles for these clusters have emerged including their involvement in biosynthesis, sensing, and regulation.[1] In enzymes such as nitrogenases, hydrogenases, and aconitase, Fe–S-based clusters are the sites at which molecules and ions (hereafter referred to as substrates) bind and are transformed.[2,3] Although the structures of several of these Fe–S-based active sites have been determined by X-ray crystallography, our understanding of how substrates bind and transform to these clusters is still rudimentary. In particular, we do not know where, or how rapidly, the substrates bind to these large clusters. The sheer size and complexity of enzymes make it difficult to define the details of these binding reactions on the enzyme itself. Thus, it is essential to study simpler systems such as synthetic Fe–S-based clusters,[4] but even with synthetic clusters our understanding of how substrates bind is poorly developed. Clusters such as $[Fe_4S_4(SPh)_4]^{2-}$, $[MoFe_3S_4Cl_3(NCMe)(Cl_4cat)]^{2-}$ (Cl_4cat = tetrachlorocatecholate), and $[VFe_3S_4Cl_3(L)_3]^{n-}$ (L = dmf, PEt_3, etc.) convert acetylene into ethylene[5−7] or hydrazine into ammonia[8,9] in the presence of weak acids and a reducing agent. However, no intermediates have been detected in these reactions. In only a few cases have clusters been isolated with substrates or products bound and the structure determined.[10,11] Even in structurally well-defined

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10.1021/ic0202110 CCC: $22.00

systems there is the nagging doubt that the structure determined by crystallography may not represent the *initial* binding configuration of the substrate. *Whether it is a synthetic Fe−S-based cluster or a cluster in an enzyme there is little doubt that substrates can bind and be transformed on these sites, but how this happens is still obscure.*

A major obstacle in investigating the mechanism of binding substrates to Fe−S-based clusters is that these reactions are often associated with small spectroscopic changes.[12] It is important to distinguish between the simple binding of substrate to the intact cluster, as indicated in eq 1, and substitution reactions of these clusters where the substrate displaces a ligand on the cluster, as shown in eq 2. While substitution reactions are invariably associated with an appreciable spectroscopic change, the binding reactions are often not. Thus, in associative mechanisms $[Fe_4S_4Cl_4(L)]^{2-}$ must be intermediates in the substitution reaction, but no direct spectroscopic evidence for such species has been obtained. *Clearly, it is crucial to develop a time-resolved method for studying the binding of molecules and ions to Fe−S-based clusters which avoids the poor spectroscopic response generally associated with these reactions.*

$$[Fe_4S_4Cl_4]^{2-} + L \rightleftharpoons [Fe_4S_4Cl_4(L)]^{2-} \qquad (1)$$

$$[Fe_4S_4Cl_4]^{2-} + L \rightleftharpoons [Fe_4S_4Cl_3(L)]^{-} + Cl^{-} \qquad (2)$$

Herein, we report kinetic studies on the reaction of $[Fe_4S_4Cl_4]^{2-}$ with Bu^tNC or $Et_2NCS_2^-$, including a sequential-mix approach aimed at detecting the spectroscopically silent binding of these substrates. We also present studies on the effect of Cl^- on the rate of substitution reactions of this cluster with PhS^-, Bu^tNC, and $Et_2NCS_2^-$. A common pathway of substitution for all three nucleophiles is established.[13−23] However, at high concentrations of Cl^-, this pathway is completely inhibited, revealing another (previously hidden) pathway for substitution with $Et_2NCS_2^-$.

Experimental Section

All manipulations were routinely performed under an atmosphere of dinitrogen using Schlenk and syringe techniques as appropriate. The compounds $[NEt_4]SPh$, $[NHEt_3]BPh_4$, $[Fe_4S_4Cl_2(CNBu^t)_6]$, and $[NEt_4]_2[Fe_4S_4Cl_4]$ were prepared by the literature methods.[24−27] Bu^tNC (Aldrich) was stored at 5 °C under dinitrogen and used as received. $[Et_4N]Cl$, $[Et_4N]Br$, and $[Et_4N]CN$ (Aldrich) were used without purification but dried under vacuum at 80 °C for 24 h. $[NBu_4^n][S_2CNEt_2]$ and $[NEt_4]_2[Fe_4S_4Cl_2(S_2CNEt_2)_2]$ were prepared by the methods described in the literature.[28] The solvents, MeCN (CaH_2), thf (sodium−benzophenone), and diethyl ether (sodium), were dried over the appropriate drying agents and distilled immediately prior to use.

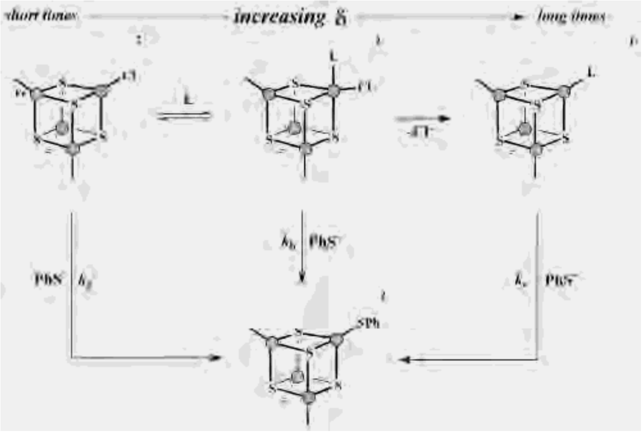

Figure 1. Diagrammatic representation of the sequential-mix experiment. The time course of the reaction between $[Fe_4S_4Cl_4]^{2-}$ and L is followed by rapidly mixing solutions of these two reactants, leaving them together for a known time (δ) and then introducing an acidic solution of PhS^- and measuring the rate of substitution of the terminal chloro ligands.

Kinetic Studies. All kinetic studies were performed using an Applied Photophysics SX.18MV stopped-flow spectrophotometer, modified to handle air-sensitive solutions. The temperature was maintained at 25.0 ± 0.1 °C using a Grant LT D6G thermostated recirculating pump.

All solutions were prepared under an atmosphere of dinitrogen and transferred by gastight, all-glass syringes into the stopped-flow spectrophotometer. Solutions of mixtures of reagents were prepared from freshly prepared stock solutions and used within 1 h. Kinetics were studied under pseudo-first-order conditions with all reagents in a large excess (>10-fold) over the concentration of the cluster.

The absorbance−time curves were fitted using the Applied Photophysics computer program, and the values of the observed rate constants (k_{obs}) were obtained from the analysis. The stopped-flow, sequential-mix apparatus is an integral part of the instrumentation and allows a delay time of greater than 2 ms.

To follow the time course of reactions of Fe−S-based clusters which are not associated with an appreciable spectroscopic change the kinetic method described below, and illustrated in Figure 1, has been employed. Briefly, to follow the time course for the reaction of small molecules or ions (L) with $[Fe_4S_4Cl_4]^{2-}$, solutions of the cluster and L are mixed using a stopped-flow, sequential-mix apparatus. After a known time (δ), the resulting mixture is reacted with a solution of PhS^- resulting in substitution of the terminal chloro ligands. The rate of substitution depends on the

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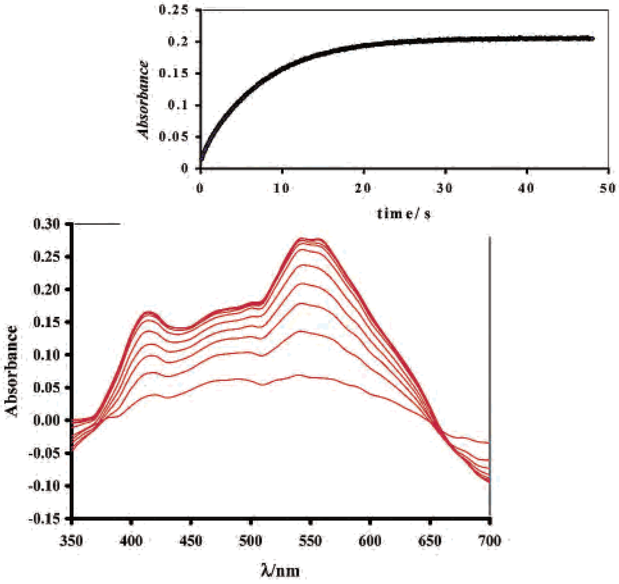

Figure 2. Main: Rapid-scan visible absorption difference spectrum for the reaction of $[Fe_4S_4Cl_4]^{2-}$ (0.15 mmol dm^{-3}) with Bu^{t}NC (12.5 mmol dm^{-3}) in MeCN at 25.0 °C. Each curve was recorded after 1.25 s, and the total reaction time is 50 s. Insert: Typical absorbance−time stopped-flow trace of the same reaction, measured at $\lambda = 560$ nm, under conditions identical to those used in the rapid scan experiment. Superimposed on this trace is a single curve defined by the equation absorbance $= 0.205 - 0.20 \exp(-0.14t)$.

status of the cluster, and by variation of δ and measurement of the corresponding rate of substitution, the time course for the reaction between L and $[Fe_4S_4Cl_4]^{2-}$ can be constructed. The approach makes use of two earlier observations[13,14] concerning the reactivity of synthetic Fe−S-based clusters. First, the substitution of terminal ligands on the Fe sites in the cluster is associated with a large change in the electronic spectrum, and second, the rate of substitution depends on whether L is bound to the cluster or not. Thus, the rate of substitution of the terminal ligands effectively “reports” on the status of the cluster.The substitution of the terminal chloro groups in $[Fe_4S_4Cl_4]^{2-}$ by PhS^- is followed at a single wavelength ($\lambda = 560$ nm). The absorbance−time traces were fitted to an exponential curve using a computer curve-fitting program.

The stopped-flow, sequental-mix data were fitted to exponential curves by an iterative method using Microsoft Excel program. The detailed equations used in the fits to the data for the reactions of $[Fe_4S_4Cl_4]^{2-}$ with Bu^{t}NC or $Et_2NCS_2^-$ are described in the legends to Figures 5 and 8, respectively.

Results and Discussion

Reaction between Bu^{t}NC and $[Fe_4S_4Cl_4]^{2-}$. (a) Stopped-Flow Spectrophotometric Studies. The reaction of $[Fe_4S_4Cl_4]^{2-}$ with an excess of Bu^{t}NC in MeCN produces $[Fe_4S_4Cl_2(CNBu^t)_6]$ (eq 3).[24] This is a well-defined reaction with the structures of both the reactant[25] and product[28] having been established by X-ray crystallography.

$$[Fe_4S_4Cl_4]^{2-} + 6Bu^tNC \rightarrow [Fe_4S_4Cl_2(CNBu^t)_6] + 2Cl^- \quad (3)$$

We have studied the reaction shown in eq 3 using conventional stopped-flow spectrophotometry. Rapid scan experiments (Figure 2) show that at all wavelengths in the range $\lambda = 350-700$ nm the time course is simple: the change in absorbance is monotonic with a well-defined isosbestic point maintained at $\lambda = 670$ nm. When studied at a single wavelength ($\lambda = 560$ nm), the absorbance−time curves are excellent fits to a single exponential (Figure 2, insert) with initial and final absorbances corresponding to $[Fe_4S_4Cl_4]^{2-}$ and $[Fe_4S_4Cl_2(CNBu^t)_6]$, respectively. The kinetics of the reaction exhibit first-order dependences on the concentrations of the cluster and Bu^{t}NC, as described by eq 4 and shown in Figure 3 (insert).

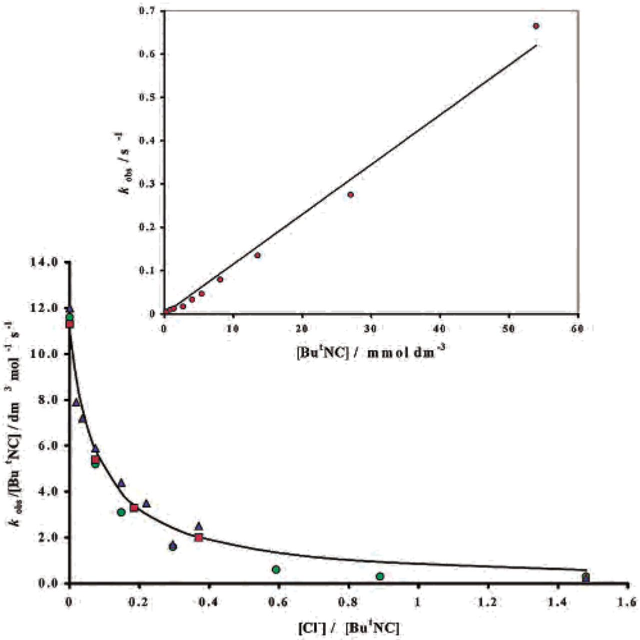

Figure 3. Main: Dependence of k_{obs}/[Bu^{t}NC] on [Cl$^-$]/[Bu^{t}NC] for the reaction between $[Fe_4S_4Cl_4]^{2-}$ (0.15 mmol dm^{-3}) and Bu^{t}NC in the presence of Cl$^-$, in MeCN at 25 °C. Data points correspond to [Bu^{t}NC] = 6.75 mmol dm^{-3} (■), 13.5 mmol dm^{-3} (●), and 27 mmol dm^{-3} (▲). The curve drawn is that defined by eq 5. Insert: Graph showing dependence of k_{obs} on the concentration of Bu^{t}NC for the same reaction. The line drawn is that defined by eq 4.

$$\frac{-d[Fe_4S_4Cl_4{}^{2-}]}{dt} = (11.5 \pm 0.5)[Bu^tNC][Fe_4S_4Cl_4{}^{2-}] \quad (4)$$

Addition of Cl$^-$ perturbs the kinetics of the reaction between $[Fe_4S_4Cl_4]^{2-}$ and Bu^{t}NC. Figure 3 (main) shows that the rate of the inhibition depends on the ratio [Cl$^-$]/[Bu^{t}NC]. Analysis of the data shows that in the presence of Cl$^-$ the rate law for the reaction is described by eq 5.

$$\frac{-d[Fe_4S_4Cl_4{}^{2-}]}{dt} = \frac{(11.0 \pm 0.5)[Bu^tNC][Fe_4S_4Cl_4{}^{2-}]}{1 + (11.0 \pm 0.4)[Cl^-]/[Bu^tNC]} \quad (5)$$

Equation 5 is consistent with the mechanism shown in Figure 4. Initial binding of Bu^{t}NC to $[Fe_4S_4Cl_4]^{2-}$ is followed by rate-limiting dissociation of Cl$^-$ and subsequent binding of a second Bu^{t}NC. The remaining elementary reactions which result in the formation of $[Fe_4S_4Cl_2(CNBu^t)_6]$ are fast and thus kinetically hidden but presumably involve dissociation of a second Cl$^-$ and binding of four Bu^{t}NC’s.

Assuming that both $[Fe_4S_4Cl_4(CNBu^t)]^{2-}$ and $[Fe_4S_4Cl_3(CNBu^t)]^-$ are steady-state intermediates, the rate law shown in eq 6 can be derived, and comparison with eq 5 gives $k_1k_2/(k_{-1} + k_2) = 11.0 \pm 0.5$ dm^3 mol^{-1} s^{-1} and

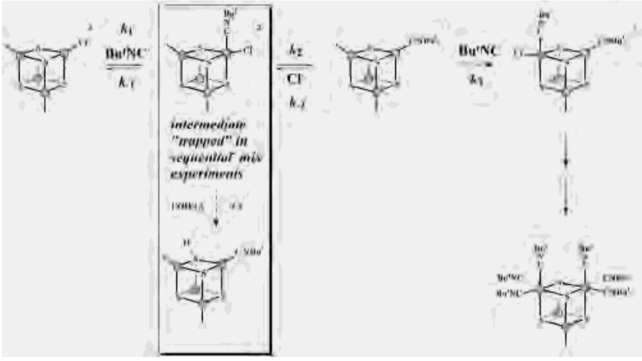

Figure 4. Proposed mechanism for the formation of $[Fe_4S_4Cl_2(CNBu^t)_6]$ in the reaction between $[Fe_4S_4Cl_4]^{2-}$ and BuᵗNC in MeCN.

$k_{-1}k_{-2}/k_3(k_{-1} + k_2) = 11.0 \pm 0.4$. At low concentrations of Cl^-, $k_{-1}k_{-2}[Cl^-]/k_3(k_{-1} + k_2)[Bu^tNC] < 1$ and eq 6 simplifies to eq 7, consistent with the experimental observation (eq 4).

$$\frac{-d[Fe_4S_4Cl_4{}^{2-}]}{dt} = \frac{\{k_1k_2/(k_{-1} + k_2)\}[Bu^tNC][Fe_4S_4Cl_4{}^{2-}]}{1 + \{k_{-1}k_{-2}/k_3(k_{-1} + k_2)\}[[Cl^-]/[Bu^tNC]} \quad (6)$$

$$\frac{-d[Fe_4S_4Cl_4{}^{2-}]}{dt} = \frac{k_1k_2[Bu^tNC][Fe_4S_4Cl_4{}^{2-}]}{k_{-1} + k_2} \quad (7)$$

The mechanism shown in Figure 4, and described by eq 6, is identical to that proposed in earlier studies on Fe−S clusters.[13−23] The effect of Cl^- on the kinetics of the reaction between $[Fe_4S_4Cl_4]^{2-}$ and BuᵗNC is consistent with rate-limiting dissociation of Cl^- from $[Fe_4S_4Cl_4(CNBu^t)]^{2-}$.

When the reaction between $[Fe_4S_4Cl_4]^{2-}$ and BuᵗNC is studied spectrophotometrically, there is no spectroscopic evidence for the accumulation of either $[Fe_4S_4Cl_4(CNBu^t)]^{2-}$ or $[Fe_4S_4Cl_3(CNBu^t)]^-$. We have also studied the reaction of BuᵗNC with $[Fe_4S_4Cl_4]^{2-}$ using FTIR spectroscopy. $[Fe_4S_4Cl_2(CNBu^t)_6]$ exhibits two IR stretches ($\nu_{CN} = 2130$ and 2152 cm^{-1}) of essentially the same intensity [$\epsilon = (3.2 \pm 0.3) \times 10^3$ dm^3 mol^{-1} cm^{-1} $cluster^{-1}$ or $\epsilon = 5 \times 10^2$ dm^3 mol^{-1} cm^{-1} $isonitrile^{-1}$]. Following the appearance of these bands allows the reaction between $[Fe_4S_4Cl_4]^{2-}$ and BuᵗNC to be followed. While the reaction is too rapid to be studied by conventional FTIR spectroscopy, quantitative studies using equimolar concentrations of cluster and BuᵗNC showed that only 1/6 of the cluster is converted to $[Fe_4S_4Cl_2(CNBu^t)_6]$. No partially substituted species are observable.

In a later section a complete quantitative description of the mechanism will be presented which explains why no intermediate accumulates in the reaction between $[Fe_4S_4Cl_4]^{2-}$ and BuᵗNC. However, first we will show how, using the stopped-flow, sequential-mix method, it has been possible to "trap" $[Fe_4S_4Cl_4(CNBu^t)]^{2-}$.

(b) Sequential-Mix Studies. The reaction between $[Fe_4S_4Cl_4]^{2-}$ and BuᵗNC can be followed by a stopped-flow, sequential-mix approach, in which changes in the rate of substitution of the terminal chloro ligands of the cluster are used to follow the reaction of the cluster with BuᵗNC (Experimental Section and Figure 1). When the reaction between $[Fe_4S_4Cl_4]^{2-}$ and BuᵗNC is followed using PhS^- to substitute the chloro ligands, no intermediate is observed, consistent with the results obtained when following the reaction spectroscopically. However, when the reaction between $[Fe_4S_4Cl_4]^{2-}$ and BuᵗNC is followed by monitoring the rate of substitution of the cluster with PhS^- in the presence of an excess of $[NHEt_3]^+$, an intermediate is observed, as shown in Figure 5. In Figure 5, one axis shows the time $[Fe_4S_4Cl_4]^{2-}$ and BuᵗNC are held together (δ) before being mixed with the solution of $[NHEt_3]^+$ and PhS^-. The observed rate constant (k_{obs}) for the substitution reaction of the cluster with the $[NHEt_3]^+/PhS^-$ mixture is shown on the other axis. Simplistically, k_{obs} is a measure of the status of the cluster. When δ is small, the rate of the reaction with PhS^- ($k_{obs} = 150$ s^{-1}) corresponds[29] to substitution of $[Fe_4S_4Cl_4]^{2-}$. When δ is large, the rate of the reaction with PhS^- ($k_{obs} = 5$ s^{-1}) corresponds to the rate of substitution of $[Fe_4S_4Cl_2(CNBu^t)_6]$, which we have measured independently.[30] Notably, an intermediate is evident in the early stages of the reaction (Figure 5, insert).

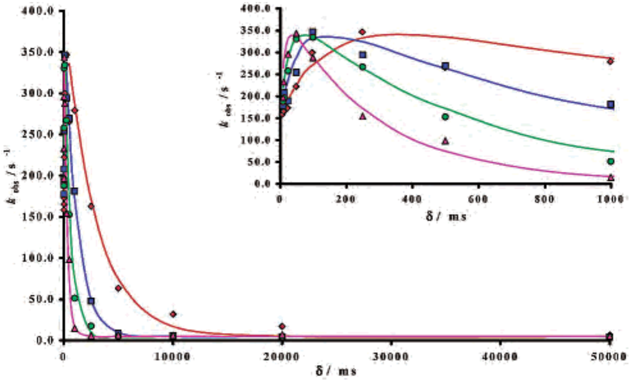

Figure 5. Time course for the reaction between $[Fe_4S_4Cl_4]^{2-}$ (0.15 mmol dm^{-3}) and BuᵗNC {[BuᵗNC] = 5.0 mmol dm^{-3} (♦), 12.5 mmol dm^{-3} (■), 25.0 mmol dm^{-3} (●), and 50.0 mmol dm^{-3} (▲)} as established by a sequential-mix experiment. The reaction was followed by monitoring the change in the rate of substitution of the terminal chloro ligands using an acidic solution of PhS^- ($[PhS^-] = 5.0-10.0$ mmol dm^{-3}, $[NHEt_3{}^+] = 15.0-60.0$ mmol dm^{-3}). The abscissa corresponds to the time (δ) that $[Fe_4S_4Cl_4]^{2-}$ and BuᵗNC are left together before mixing with the acidic PhS^- solution. The ordinate is the corresponding observed rate constant (k_{obs}) for the reaction with PhS^-. The curves are the best fit to the data and comprise two exponentials. The equations of the curves are given by the general equation $k_{obs} = 5.0 - 250 \exp(-1700[Bu^tNC]\delta) + 400 \exp(-70[Bu^tNC]\delta)$.

While the sequential-mix experiments allow the detection of a species which is not detected spectroscopically, clues to the identity of the intermediate can only be obtained from consideration of the kinetics of its formation and decay. It is important to appreciate that the intermediate is not observed, either in the absence of acid or when $[NHEt_3]^+$ is

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(30) Stopped-flow studies on the substitution reaction between $[Fe_4S_4Cl_2(CNBu^t)_6]$ and an excess of PhSH, in the presence of $[NHEt_3]^+$ or $[lutH]^+$ (lut = 2,6-dimethylpyridine), to form $[Fe_4S_4(SPh)_2(CNBu^t)_6]$ occurs at a rate ($k_{obs} = 5.0 \pm 0.5$ s^{-1}) which is independent of the concentration of acid. It seems likely that protonation of $[Fe_4S_4Cl_2(CNBu^t)_6]$ cannot occur because of the bulky *tert*-butyl groups. Similar behavior[16] has been observed with $[Fe_4S_4\{P(C_6H_{11})_3\}_4]$, containing the bulky phosphine ligands.

added to the cluster at the same time as the Bu^{t}NC, only when the $[NHEt_3]^+$ is included with the PhS^-. Thus, the acid effectively "traps" the intermediate. Simulation of the data in Figure 5 shows that the intermediate is produced at a rate which exhibits first-order dependences on the concentrations of both Bu^{t}NC and $[Fe_4S_4Cl_4]^{2-}$ (k = ca. $(1.7 \pm 0.5) \times 10^3$ dm^3 mol^{-1} s^{-1}). The decay of the intermediate can be fitted to a single exponential, exhibiting a first-order dependence on the concentration of Bu^{t}NC ($k = 70 \pm 10$ dm^3 mol^{-1} s^{-1}).

The first-order dependences on Bu^{t}NC in both the formation and decay of the intermediate mirrors the overall second-order dependence on the concentration of Bu^{t}NC observed in eq 6. Consideration of the mechanism of the reaction between $[Fe_4S_4Cl_4]^{2-}$ and Bu^{t}NC shown in Figure 4 indicates that the intermediate detected is $[Fe_4S_4Cl_4(CNBu^t)]^{2-}$. Thus, formation of the intermediate corresponds to the binding of Bu^{t}NC to $[Fe_4S_4Cl_4]^{2-}$ ($k_1 = (1.7 \pm 0.5) \times 10^3$ dm^3 mol^{-1} s^{-1}). We have also determined k_1 by another method,[31] and the value is in good agreement with that reported herein ($k_1 = (2.1 \pm 0.5) \times 10^3$ dm^3 mol^{-1} s^{-1}). The decay of the intermediate corresponds to $k_3 = 70 \pm 10$ dm^3 mol^{-1} s^{-1}.

Knowing the values of k_1 and k_3, we can now present a more detailed analysis of the kinetics of the reaction between $[Fe_4S_4Cl_4]^{2-}$ and Bu^{t}NC (eq 6). Since $k_1 = 1.7 \times 10^3$ dm^3 mol^{-1} s^{-1} and $k_3 = 70$ dm^3 mol^{-1} s^{-1}, we can calculate $k_{-1}/k_2 = 100$ and $k_{-2}/k_3 = 10$. Thus, for every 1000 molecules of $[Fe_4S_4Cl_4(CNBu^t)]^{2-}$ produced (Figure 4), approximately 990 will revert to $[Fe_4S_4Cl_4]^{2-}$ and only 10 form $[Fe_4S_4Cl_3(CNBu^t)]^-$. Of these 10 molecules of $[Fe_4S_4Cl_3(CNBu^t)]^-$, only 1 binds another Bu^{t}NC and goes on to form product, whereas the other 9 revert to $[Fe_4S_4Cl_4(CNBu^t)]^{2-}$. It is no surprise, therefore, that neither $[Fe_4S_4Cl_4(CNBu^t)]^{2-}$ nor $[Fe_4S_4Cl_3(CNBu^t)]^-$ accumulates in the reaction between $[Fe_4S_4Cl_4]^{2-}$ and Bu^{t}NC. It is only the addition of the acid that "traps" the intermediate.

Previous studies have shown that the rate of proton transfer from $[NHEt_3]^+$ to $[Fe_4S_4Cl_4]^{2-}$ is rapid ($2 \times 10^5 \leq k \leq 4.8 \times 10^6$ dm^3 mol^{-1} s^{-1}).[21] Thus, in the stopped-flow, sequential-mix experiments, it is reasonable that protonation of $[Fe_4S_4Cl_4(CNBu^t)]^{2-}$ occurs within the time of mixing the acidic solution of PhS^- with the cluster. Protonation has been shown to labilize Fe−S clusters toward dissociation.[13] For example, with $[Fe_4S_4Cl_4]^{2-}$ substitution of the chloro ligand by PhS^- increases by a factor of ca. 200 in the presence of $[NHEt_3]^+$. Recent studies[31] have shown that protonation also has a minor effect on the rate of binding nucleophiles to $[Fe_4S_4Cl_4]^{2-}$ (factor of 4). In considering the effect of acid on the elementary reactions of Figure 4, it is likely that $[NHEt_3]^+$ has little effect on k_1 and k_3 but appreciably increases k_2. Consequently, it seems likely that, in the presence of $[NHEt_3]^+$, $[Fe_4S_3(SH)Cl_3(CNBu^t)]$ is formed by rapid protonation and dissociation of Cl^- from $[Fe_4S_4Cl_4(CNBu^t)]^{2-}$. The reason we detect $[Fe_4S_3(SH)Cl_3(CNBu^t)]$ must be because the rate of substitution of the chloro ligands in this species is markedly different from that of either $[Fe_4S_4Cl_4]^{2-}$ or $[Fe_4S_4Cl_2(CNBu^t)_6]$. Clearly, the necessity that the substitution lability of the intermediate differs appreciably from that of reactant or product limits the general applicability of the sequential-mix method we have described here.

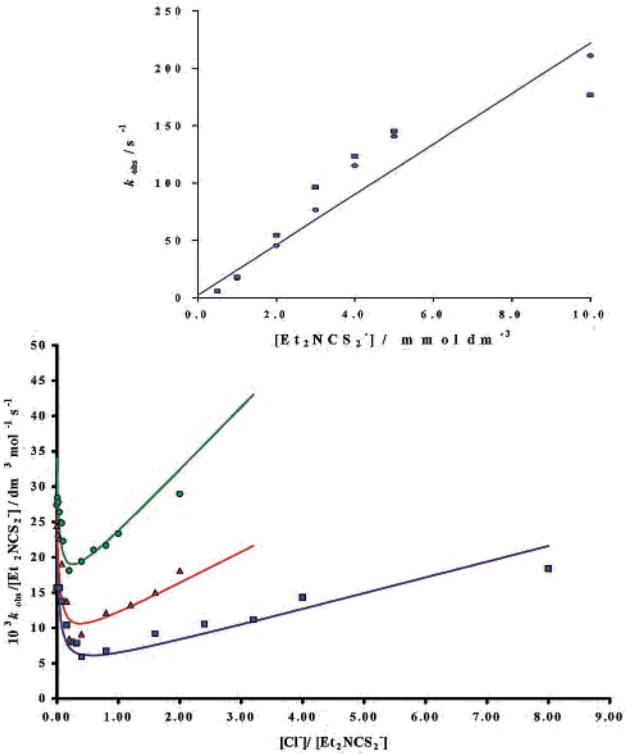

Figure 6. Kinetics for the reaction between $[Fe_4S_4Cl_4]^{2-}$ (0.15 mmol dm^{-3}) and $Et_2NCS_2^-$ in MeCN at 25.0 °C. Main: Dependence of $k_{obs}/[Et_2NCS_2^-]$ on $[Cl^-]/[Et_2NCS_2^-]$. Data points correspond to $[Et_2NCS_2^-] = 1.25$ mmol dm^{-3} (■), 2.50 mmol dm^{-3} (▲), and 5.0 mmol dm^{-3} (●). Curves drawn are those defined by eq 10. Insert: For the same reaction, dependence on the concentration of $Et_2NCS_2^-$ in the absence of Cl^-. The line drawn is that defined by eq 9.

Reaction between $Et_2NCS_2^-$ and $[Fe_4S_4Cl_4]^{2-}$. (a) Stopped-Flow Spectrophotometric Studies. The reaction between $Et_2NCS_2^-$ and $[Fe_4S_4Cl_4]^{2-}$ produces $[Fe_4S_4Cl_2(S_2CNEt_2)_2]^{2-}$ as shown in eq 8. As with the Bu^{t}NC reaction, this is a structurally well-defined reaction with both the reactant[25] and the product[32] having been characterized by X-ray crystallography.

When studied using stopped-flow spectrophotometry the reaction between $[Fe_4S_4Cl_4]^{2-}$ and an excess of $Et_2NCS_2^-$ exhibits first-order dependences on the concentrations of both $[Fe_4S_4Cl_4]^{2-}$ and $Et_2NCS_2^-$ [eq 9, Figure 6 (insert)].

$$[Fe_4S_4Cl_4]^{2-} + 2Et_2NCS_2^- \rightarrow [Fe_4S_4Cl_2(S_2CNEt_2)_2]^{2-} + 2Cl^- \quad (8)$$

$$\frac{-d[Fe_4S_4Cl_4{}^{2-}]}{dt} = (2.2 \pm 0.2) \times 10^3[Fe_4S_4Cl_4{}^{2-}][Et_2NCS_2^-] \quad (9)$$

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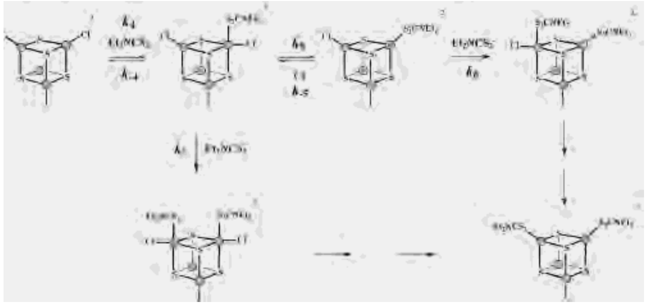

Figure 7. Proposed mechanism for the formation of $[Fe_4S_4Cl_2(S_2CNEt_2)_2]^{2-}$ in the reaction between $[Fe_4S_4Cl_4]^{2-}$ and $Et_2NCS_2^-$ in MeCN. For simplicity the Cl^--catalyzed pathway (k_7) is not shown but is analogous to the k_8 route.

The effect of Cl^- on the reaction between $[Fe_4S_4Cl_4]^{2-}$ and $Et_2NCS_2^-$ is shown in Figure 6 (main). The behavior is clearly complicated and is only consistent with a multiple substitution pathway. At low concentrations of Cl^-, the rate of substitution with $Et_2NCS_2^-$ is inhibited by Cl^- (in an analogous fashion to that observed with Bu^tNC). However, at high concentrations of Cl^-, the rate of the reaction increases with increasing concentration of Cl^-. Analysis of the data yields the rate law shown in eq 10, which was arrived at by an iterative, trial and error method. Equation 10 explains the following features of the kinetics. (i) In the absence of Cl^-, the reaction exhibits a first-order dependence on the concentration of $Et_2NCS_2^-$, but at high concentrations of Cl^- the rate exhibits a second-order dependence on the concentration of $Et_2NCS_2^-$. (ii) At high concentrations of Cl^-, the rate increases with increasing concentration of Cl^-.

$$\frac{-d[Fe_4S_4Cl_4{}^{2-}]}{dt} = \left\{\frac{(2.2 \pm 0.5) \times 10^3[Et_2NCS_2{}^-]^2}{[Et_2NCS_2{}^-] + 25 \pm 5[Cl^-]} + (2.8 \pm 0.5) \times 10^3[Et_2NCS_2{}^-]^2 + (1.8 \pm 0.5) \times 10^3[Cl^-][Et_2NCS_2{}^-]\right\}[Fe_4S_4Cl_4{}^{2-}] \quad (10)$$

The three terms in eq 10 indicate three pathways for substitution, as illustrated in Figure 7. The dominant substitution mechanism in the reaction between $[Fe_4S_4Cl_4]^{2-}$ and $Et_2NCS_2^-$ is described by the first term of eq 10 and is analogous to that observed in the reaction with Bu^tNC. The other two pathways indicated in eq 10 only become important at high concentrations of $Et_2NCS_2^-$ and Cl^- and involve the binding of $Et_2NCS_2^-$ or Cl^-, respectively, to $[Fe_4S_4Cl_4(S_2CNEt_2)]^{3-}$. It seems that the binding of either anion ($Et_2NCS_2^-$ or Cl^-) to $[Fe_4S_4Cl_4(S_2CNEt_2)]^{3-}$ labilizes the chloro ligand to dissociation. Consequently, it seems likely that the dissociation of the chloro ligand in the k_5 step involves the monodentate $Et_2NCS_2^-$ ligand in $[Fe_4S_4Cl_4(S_2CNEt_2)]^{3-}$ becoming bidentate. In the final product of the reaction, $[Fe_4S_4Cl_2(S_2CNEt_2)_2]^{2-}$, the $Et_2NCS_2^-$ ligands are bidentate.

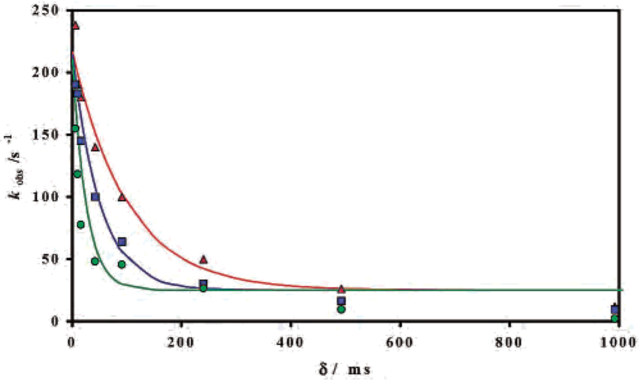

Figure 8. Results of sequential-mix experiments on the reaction between $[Fe_4S_4Cl_4]^{2-}$ (0.15 mmol dm^{-3}) and $Et_2NCS_2^-$. Data points correspond to $[Et_2NCS_2^-]$ = 0.5 mmol dm^{-3} (■), 1.0 mmol dm^{-3} (▲), and 2.5 mmol dm^{-3} (●). The reaction was followed by monitoring the change in the rate of substitution of the terminal chloro ligands using solutions of PhS^- ($[PhS^-]$ = 25.0 mmol dm^{-3}). The abscissa corresponds to the time (δ) that $[Fe_4S_4Cl_4]^{2-}$ and $Et_2NCS_2^-$ are left together before mixing with the PhS^- solution. The ordinate is the corresponding observed rate constant (k_{obs}) for the substitution reaction with PhS^-. The curves drawn are those defined by eq 9.

Assuming both $[Fe_4S_4Cl_4(S_2CNEt_2)]^{3-}$ and $[Fe_4S_4Cl_3(S_2CNEt_2)]^{2-}$ are steady-state intermediates, the rate law associated with the mechanism in Figure 7 is that shown in eq 11. As shown in Appendix 1, the full rate law is more complex than eq 11 but simplifies to this form. Comparison of eqs 10 and 11 gives $k_4k_5/(k_{-4} + k_5) = (2.2 \pm 0.5) \times 10^3$ dm^3 mol^{-1} s^{-1}, $k_{-5}/k_6 = 25 \pm 5$, $k_4k_7/(k_{-4} + k_5) = (1.8 \pm 0.5) \times 10^3$ dm^3 mol^{-1} s^{-1}, and $k_4k_8/(k_{-4} + k_5) = (2.8 \pm 0.5) \times 10^3$ dm^3 mol^{-1} s^{-1}.

$$\frac{-d[Fe_4S_4Cl_4{}^{2-}]}{dt} = \frac{k_4[Et_2NCS_2{}^-]}{k_{-4} + k_5}\left\{\frac{\{k_5k_6[Et_2NCS_2{}^-]}{k_{-5}[Cl^-] + k_6[Et_2NCS_2{}^-]} + k_7[Cl^-] + k_8[Et_2NCS_2{}^-]\right\}[Fe_4S_4Cl_4{}^{2-}] \quad (11)$$

In the absence of Cl^-, eq 11 simplifies to eq 12. Studies in the absence of Cl^- are consistent with eq 12, but the $[Et_2NCS_2^-]^2$-dependent term makes an insignificant contribution to the total rate until $[Et_2NCS_2^-] \geq 0.79$ mol dm^{-3}. Only at high concentrations of Cl^-, where the dominant substitution pathway (first term of eq 11) is completely inhibited, is the slower $[Et_2NCS_2^-]^2$-dependent pathway revealed.

$$\frac{-d[Fe_4S_4Cl_4{}^{2-}]}{dt} = \left(\frac{k_4k_5[Et_2NCS_2{}^-]}{k_{-4} + k_5} + \frac{k_4k_8[Et_2NCS_2{}^-]^2}{k_{-4} + k_5}\right)[Fe_4S_4Cl_4{}^{2-}] \quad (12)$$

(b) Sequential-Mix Studies. The reaction between $[Fe_4S_4Cl_4]^{2-}$ and $Et_2NCS_2^-$ can be followed by monitoring the lability of the cluster in its reaction with PhS^- using the stopped-flow, sequential-mix method described above for the studies with Bu^tNC. When the reaction between $[Fe_4S_4Cl_4]^{2-}$ and $Et_2NCS_2^-$ is studied by the sequential-mix method, a simple behavior is observed as shown in Figure 8. Analysis of the sequential-mix data reveals behavior identical to that observed in the conventional stopped-flow experiments: first-order dependences on the concentrations of both $Et_2NCS_2^-$ and $[Fe_4S_4Cl_4]^{2-}$ with an associated rate constant, $k = 2.2 \times 10^3$ dm^3 mol^{-1} s^{-1}. Thus, the curves drawn in Figure 8 are exponential with rate constants derived from eq 9. The rate constant for the reaction between $[Fe_4S_4Cl_4]^{2-}$ and $Et_2NCS_2^-$ is independent of the concentration of PhS^- used and did not vary if mixtures of PhS^- and $[NHEt_3]^+$ are used.

In the studies on the reaction between $[Fe_4S_4Cl_4]^{2-}$ and $Et_2NCS_2^-$ we have shown that the reaction can be followed by both conventional stopped-flow spectrophotometry and the stopped-flow, sequential-mix method, with excellent agreement in the rate constants between the two methods. However, for this system no intermediates could be “trapped”.

Summary

In this paper, we have described kinetic studies on the reactions between $[Fe_4S_4Cl_4]^{2-}$ and Bu^{t}NC or $Et_2NCS_2^-$ in MeCN with a particular emphasis on the effect Cl^- has on the kinetics and the development of a stopped-flow, sequential-mix approach to detect intermediates in these reactions.

Earlier work[18−22] has proposed that species such as $[Fe_4S_4X_4(L)]^{n-}$ (X = halide or thiolate; L = X, CN^-, N_3^-, N_2O, CO, or alkyne) are formed in solution. For example, in the reaction of PhS^- with $[Fe_4S_4Cl_4]^{2-}$ to form $[Fe_4S_4(SPh)_4]^{2-}$, $[Fe_4S_4Cl_4(SPh)]^{3-}$ has been invoked as an intermediate. The spectroscopic evidence for the intermediate is poor: there is no appreciable change in the visible absorption spectrum between $[Fe_4S_4Cl_4]^{2-}$ and $[Fe_4S_4Cl_4(SPh)]^{3-}$, presumably because the $\{Fe_4S_4\}^{2+}$ chromophore dominates the electronic spectrum. The evidence that $[Fe_4S_4Cl_4(SPh)]^{3-}$ accumulates in appreciable concentrations is only kinetic: deviation of the kinetics from strict first-order dependence on the concentration of PhS^-. Similarly, the binding of a variety of molecules and ions (e.g. CN^-, N_3^-, halide, N_2O, or CO) to intact Fe−S-based clusters is indicated by perturbation of the rate of substitution of the cluster.[14,16,20−23]

Recently, time-resolved FTIR spectroscopy has been used to study the binding of CO to nitrogenase and extracted FeMo-cofactor of nitrogenase.[33] While this technique is ideally suited to substrates such as CO, its applicability is limited since it requires a substrate that has *intense* IR absortion. Reactions such as the binding of thiolate ions to $[Fe_4S_4Cl_4]^{2-}$, which can be followed by sequential-mix approach described in this paper, *cannot* conveniently be followed by the FTIR spectroscopic technique.

In the studies described herein the rates of binding of Bu^{t}NC ($k_1 = (1.7 \pm 0.5) \times 10^3$ dm^3 mol^{-1} s^{-1}) and $Et_2NCS_2^-$ ($k_4 \geq 3 \times 10^5$ dm^3 mol^{-1} s^{-1}) to $[Fe_4S_4Cl_4]^{2-}$ can be estimated. Although rapid, these rate constants are markedly slower than the diffusion-controlled limit, indicating (not unexpectedly) there is a significant barrier for binding substrates to the cluster. The origin of this barrier is probably (at its most rudimentary level) the buildup of charge as the substrate approaches the anionic cluster, a feature which we have demonstrated quantitatively recently.[34] A further barrier must be the necessary geometrical and electronic reorganization of the coordination sphere of the site(s) to which the substrate binds. Because the binding site is a cluster, any reorganization at one metal will be transmitted to other atoms in the cluster core. A similar proposal has been used to explain why protonation of Fe−S-based clusters occurs at rates significantly slower than the diffusion-controlled limit.[21]

Theoretical and experimental studies[35−40] have indicated that, in general, adsorption of molecules on metal surfaces is followed by relaxation of the surface.[41] Recent theoretical studies[42] on the binding of molecules to the natural Fe−S-based cluster, FeMo-cofactor, indicate that, after binding of dinitrogen, repulsive interactions between the bound molecule and the sulfur atoms of the cluster cause the structure of the cluster to “relax” in an manner analogous to that of surfaces. While it is only speculation at this stage, it could be that the binding of molecules and ions to $[Fe_4S_4Cl_4]^{2-}$ involves initial “adsorption” on to the face of the cuboidal cluster, followed by rearrangement (“relaxation”) to the final binding site of the substrate. Certainly, it seems intuitively reasonable that the “adsorption” would involve minimal structural reorganization of the cluster.

Finally, the effect of Cl^- on the reaction between $[Fe_4S_4Cl_4]^{2-}$ and $Et_2NCS_2^-$ reveals that in the absence of Cl^- substitution occurs by two pathways. However, while one pathway is inhibited by Cl^-, the other is unaffected by Cl^-. The pathway inhibited by Cl^- is shown in the center of Figure 7. An analogous pathway is observed in the reactions with Bu^{t}NC (Figure 4), and we believe that the pathway inhibited by Cl^- is general for all nucleophiles. Previously[19] this mechanism has been proposed for the reaction between $[Fe_4S_4Cl_4]^{2-}$ and PhS^-. Unfortunately, we cannot confirm the identity of the mechanism with PhS^- because the addition of Cl^- reveals the substitution is an equilibrium reaction with associated rate law shown in eq 13.

$$\frac{-d[Fe_4S_4Cl_4{}^{2-}]}{dt} = (1.7 \times 10^4[PhS^-] + 3.1 \times 10^3[Cl^-])[Fe_4S_4Cl_4{}^{2-}] \quad (13)$$

Appendix 1

Derivation of Eq 11. Consider the mechanism shown in Figure 7 (using the abbreviation dtc = $Et_2NCS_2^-$).

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$$\frac{d[Fe_4S_4Cl_2(dtc)_2{}^{2-}]}{dt} = k_6[Fe_4S_4Cl_3(dtc)^{2-}][dtc] + k_7[Fe_4S_4Cl_4(dtc)^{3-}][Cl^-] + k_8[Fe_4S_4Cl_4(dtc)^{3-}][dtc] \quad (A.1)$$

Applying the steady-state treatment to $[Fe_4S_4Cl_3(dtc)]^{2-}$ gives (A.2).

$$k_5[Fe_4S_4Cl_4(dtc)^{3-}] = (k_6[dtc] + k_{-5}[Cl^-])[Fe_4S_4Cl_3(dtc)^{2-}] \quad (A.2)$$

Applying the steady-state treatment to $[Fe_4S_4Cl_4(dtc)]^{3-}$ gives (A.3).

$$k_4[Fe_4S_4Cl_4{}^{2-}][dtc] + k_{-5}[Fe_4S_4Cl_3(dtc)^{2-}][Cl^-] = (k_{-4} + k_5 + k_7[Cl^-] + k_8[dtc])[Fe_4S_4Cl_4(dtc)^{3-}] \quad (A.3)$$

Substituting (A.2) and (A.3) into (A.1), eliminating $[Fe_4S_4Cl_4(dtc)^{3-}]$ and $[Fe_4S_4Cl_3(dtc)^{2-}]$, and rearranging gives (A.4).

$$\frac{d[Fe_4S_4Cl_2(dtc)_2{}^{2-}]}{dt} = \frac{\dfrac{k_4[dtc]}{(k_{-4} + k_5)}\dfrac{\{k_5k_6[dtc]}{k_{-5}[Cl^-] + k_6[dtc]} + k_7[Cl^-] + k_8[dtc]\}[Fe_4S_4Cl_4{}^{2-}]}{1 + \dfrac{k_7[Cl^-] + k_8[dtc]}{k_{-4} + k_5} - \dfrac{k_5k_{-5}[Cl^-]}{(k_{-4} + k_5)(k_{-5}[Cl^-] + k_6[dtc])}} \quad (A.4)$$

If $1 > (k_7[Cl^-] + k_8[dtc])/(k_{-4} + k_5) - (k_5k_{-5}[Cl^-])/\{(k_{-4} + k_5)(k_{-5}[Cl^-] + k_6[dtc])\}$, then (A.4) simplifies to (A.5).

$$\frac{d[Fe_4S_4Cl_2(dtc)_2{}^{2-}]}{dt} = \frac{k_4[dtc]}{(k_{-4} + k_5)}\left\{\frac{k_5k_6[dtc]}{k_{-5}[Cl^-] + k_6[dtc]} + k_7[Cl^-] + k_8[dtc]\right\}[Fe_4S_4Cl_4{}^{2-}] \quad (A.5)$$

An algebraically simpler analysis considers that the initial binding of dtc to $[Fe_4S_4Cl_4]^{2-}$ is a rapid equilibrium step, K_4. This leads to the expression shown in (B.1), and when $1 > K_4[dtc]$, the simpler expression (B.2) results, which is identical in form to that shown in (A.5).

$$\frac{d[Fe_4S_4Cl_2(dtc)_2{}^{2-}]}{dt} = \frac{K_4[dtc]\left\{\dfrac{k_5k_6[dtc]}{k_{-5}[Cl^-] + k_6[dtc]} + k_7[Cl^-] + k_8[dtc]\right\}[Fe_4S_4Cl_4{}^{2-}]}{1 + K_4[dtc]} \quad (B.1)$$

$$\frac{d[Fe_4S_4Cl_2(dtc)_2{}^{2-}]}{dt} = K_4[dtc]\left\{\frac{k_5k_6[dtc]}{k_{-5}[Cl^-] + k_6[dtc]} + k_7[Cl^-] + k_8[dtc]\right\}[Fe_4S_4Cl_4{}^{2-}] \quad (B.2)$$

Supporting Information Available: Tables of kinetic data. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0202110