

Binding Nucleophiles to $[\text{Fe}_4\text{Y}_4\text{Cl}_4]^{2-}$ (Y = S or Se) can Increase or Suppress the Rate of Proton Transfer to the Cluster

Katie Bates and Richard A. Henderson*

Chemistry, School of Natural Sciences, Newcastle University, Newcastle upon Tyne, NE1 7RU, U.K.

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In the proton transfer reactions between $[\text{Fe}_4\text{Y}_4\text{Cl}_4]^{2-}$ (Y = S or Se) and $[\text{pyrH}]^+$ (pyr = pyrrolidine) in the presence of a variety of nucleophiles (L = I^- , Br^- , PhS^- , EtS^- or Bu^tNC), initial binding of the nucleophile can occur to generate $[\text{Fe}_4\text{Y}_4\text{Cl}_4(\text{L})]^{n-}$. The subsequent rate of proton transfer depends markedly on the nature of L. Stopped-flow kinetic studies show that proton transfer from $[\text{pyrH}]^+$ to $[\text{Fe}_4\text{Y}_4\text{Cl}_4]^{2-}$ ($^{\text{S}}k_4 = (2.1 \pm 0.5) \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$; $^{\text{Se}}k_4 = (8.0 \pm 0.5) \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) is increased by prior binding of L = PhS^- or Bu^tNC to form $[\text{Fe}_4\text{Y}_4\text{Cl}_4(\text{L})]^{n-}$ ($^{\text{S}}k_7^{\text{L}} \sim 1 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$), but prior binding of L = I^- , Br^- , or EtS^- to the clusters inhibits the rate of proton transfer {e.g. $^{\text{S}}k_7^{\text{I}} = (6.0 \pm 0.8) \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$; $^{\text{Se}}k_7^{\text{I}} = (4.5 \pm 0.5) \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ }. This behavior is correlated with the bonding characteristics of L and the effect this has on bond length reorganization within the cluster upon proton transfer.

Introduction

Proton transfer is one of the most fundamental and prevalent reactions found in chemical and biological processes. Numerous kinetic and mechanistic studies have established that the rates of proton transfer are controlled by relatively few factors.¹ Thus, thermodynamically favorable proton transfer to sites on a molecule containing lone pairs of electrons usually occur at the diffusion-controlled limit. However, thermodynamically unfavorable proton transfer reactions are slower and occur with a rate constant defined by the Brønsted relationship, $k = G_A K^\alpha$ (G_A and α are constants for a series of similar acids, and K is the equilibrium constant for the protonation reaction). Two general exceptions to this simple picture have been identified.² Proton transfer involving carbon or metal sites are usually inherently slower than the diffusion-controlled limit, even when the reaction is thermodynamically favorable. It has been proposed that for carbon sites the change in hybridization and for the metal sites the necessary movement of the coligands are the origin of the slow rates of proton transfer in these cases.

Protonation of natural Fe–S-based clusters is implicated³ in the action of certain enzymes. Whereas there have been a number of theoretical investigations exploring the protonation chemistry of these natural Fe–S-based clusters,⁴ the experimental measurement of proton transfer to natural or synthetic Fe–S-based clusters is poorly developed. Studies to date have shown that the rates of proton transfer to synthetic Fe–S-based clusters occur slower than the diffusion-controlled limit⁵ and are modulated by the metal composition⁶ and the ligands bound to the cluster.⁷ In this article, we describe how the rates of proton transfer to

* To whom correspondence should be addressed. E-mail: r.a.henderson@ncl.ac.uk.

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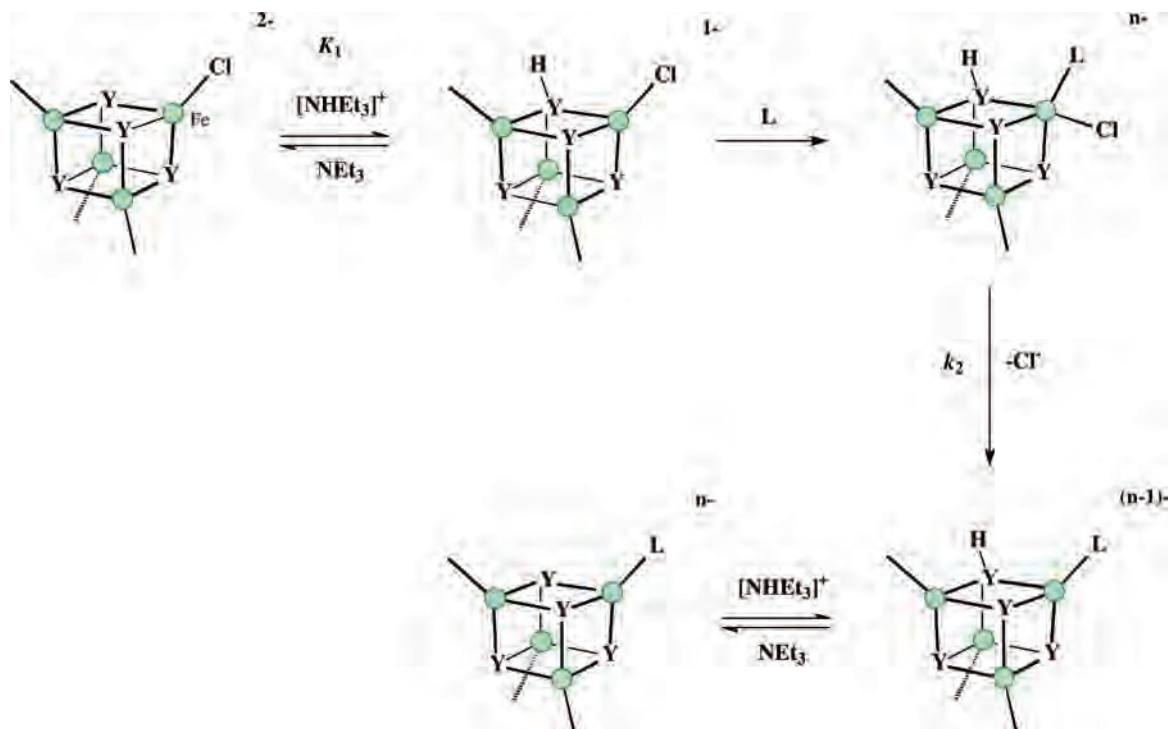


Figure 1. Mechanism for the acid-catalyzed reaction between $[\text{Fe}_4\text{Y}_4\text{Cl}_4]^{2-}$ ($\text{Y} = \text{S}$ or Se) and nucleophile L in the presence of $[\text{NHEt}_3]^+$ in MeCN as solvent.

synthetic Fe–S-based clusters are modulated by the prior binding of L ($\text{L} = \text{I}^-$, Br^- , PhS^- , EtS^- , or ButNC) to the cluster. Notably, we report that binding of $\text{L} = \text{I}^-$, Br^- , or EtS^- to $[\text{Fe}_4\text{Y}_4\text{Cl}_4]^{2-}$ ($\text{Y} = \text{S}$ or Se) inhibits the rate of subsequent proton transfer. These studies complement our earlier studies and allow us to discuss, for the first time, how the $\text{p}K_{\text{a}}$ and binding of various molecules or ions to the cluster affects the rates of proton transfer. That binding nucleophiles to a complex inhibits protonation of that complex is a reactivity that is unprecedented, not only for synthetic Fe–S-based clusters but also for protonation of any compounds. In this study, as in previous work, we use $[\text{pyrH}]^+$ ($\text{pyr} = \text{pyrrolidine}$) as the acid. By using the same acid, we ensure that the comparison of the rates of proton transfer between different clusters can be made.

Results and Discussion

Measuring the Rates of Proton Transfer. Protonation of Fe–S-based clusters is rapid but is not associated with an appreciable spectroscopic change and so is difficult to study directly. To study the protonation chemistry of synthetic Fe–S-based clusters (in MeCN as solvent) we have made use of the observation that protonation affects the rate of substitution of the cluster. Substitution reactions of Fe–S-based clusters are associated with large spectrophotometric changes. In the presence of $[\text{NHEt}_3]^+$ ($\text{p}K_{\text{a}} = 18.46$ in MeCN),⁸ the acid-catalyzed substitution reactions of Fe–S-

based clusters occur by a mechanism involving initial, rapid protonation of the cluster followed by rate-limiting substitution (Figure 1). Studies on a wide range of Fe–S-based clusters have shown that in MeCN the $\text{p}K_{\text{a}}$ of all synthetic Fe–S-based clusters fall in the narrow range of 17.9–18.9. The constancy of this $\text{p}K_{\text{a}}$ indicates that the protonation site is common to all clusters and is most likely the bridged sulfur atoms.⁹

In the acid-catalyzed substitution reactions with $[\text{NHEt}_3]^+$, protonation is invariably rapid and the act of substitution is rate-limiting. Consequently, in the acid-catalyzed substitution reactions involving $[\text{NHEt}_3]^+$, it is not possible to determine the rate constant for proton transfer. However, by changing to the much weaker acid, $[\text{pyrH}]^+$ ($\text{pyr} = \text{pyrrolidine}$, $\text{p}K_{\text{a}} = 21.5$ in MeCN)⁸ protonation of the synthetic Fe–S-based clusters becomes thermodynamically unfavorable and consequently slow. The result is that, in acid-dependent substitution reactions of the Fe–S-based clusters, proton transfer can become rate limiting, allowing investigation of the factors affecting the rates of proton transfer to these clusters.⁵

Earlier, kinetic studies on the substitution reactions between $[\text{Fe}_4\text{S}_4\text{Cl}_4]^{2-}$ and $4\text{-RC}_6\text{H}_4\text{S}^-$ ($\text{R} = \text{MeO}$, Me , H , CF_3) in the presence of $[\text{pyrH}]^+$ showed that the reaction operated by the mechanism shown in Figure 2 ($\text{L} = 4\text{-RC}_6\text{H}_4\text{S}^-$).⁵ In this mechanism, because protonation of the cluster by $[\text{pyrH}]^+$ is slow ($k_0 = (2.4 \pm 0.4) \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, vide infra), binding of thiolate to the cluster occurs preferentially to form $[\text{Fe}_4\text{S}_4\text{Cl}_4(\text{SC}_6\text{H}_4\text{R-4})]^{3-}$. Subsequently, the substitution reaction to form $[\text{Fe}_4\text{S}_4\text{Cl}_3(\text{SC}_6\text{H}_4\text{R-4})]^{2-}$ can occur by the simple (acid-independent) dissociation of

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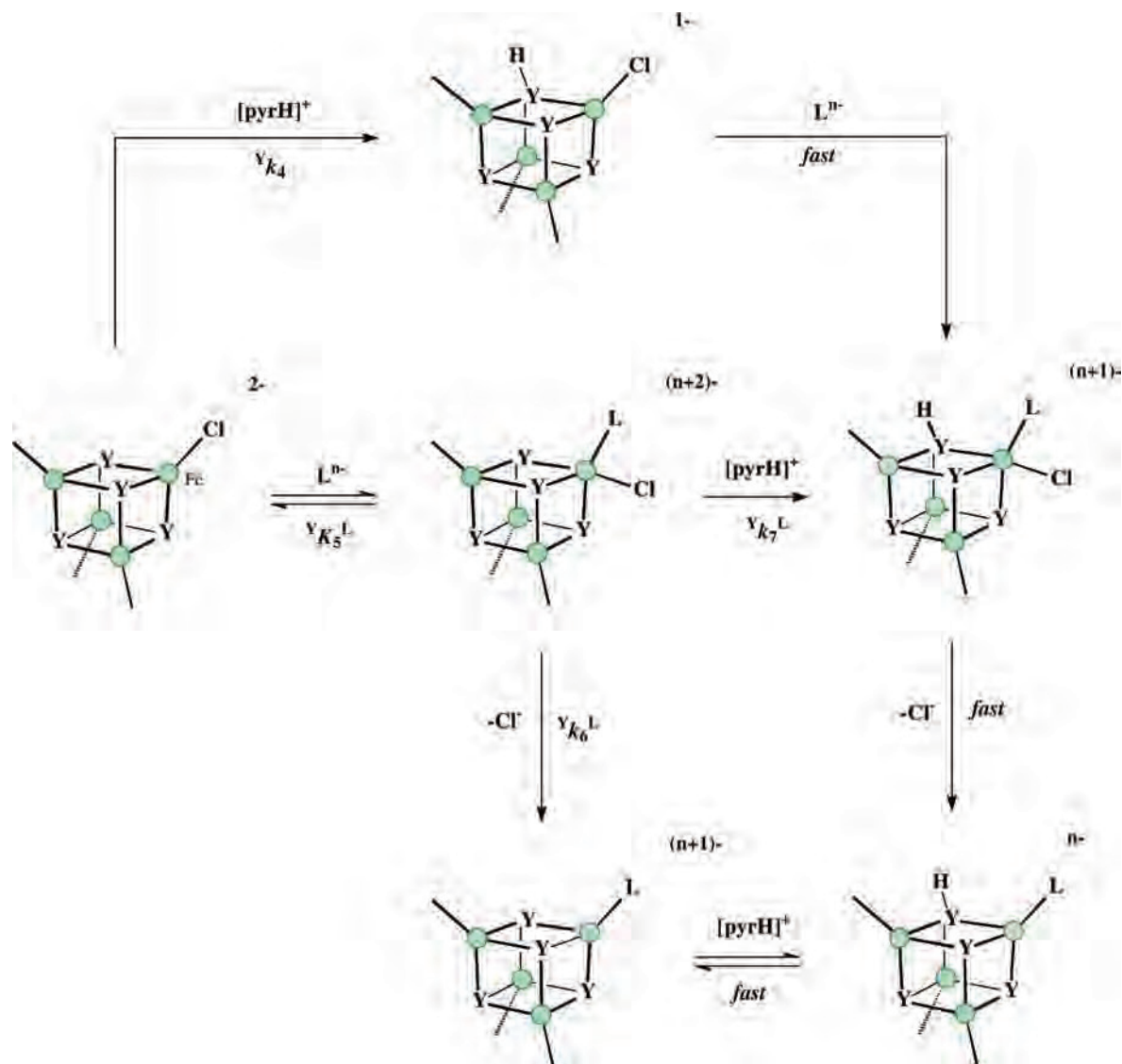


Figure 2. Pathways for the reaction between $[\text{Fe}_4\text{Y}_4\text{Cl}_4]^{2-}$ ($\text{Y} = \text{S}$ or Se) and nucleophile L in the presence of $[\text{pyrH}]^+$ in MeCN as solvent.

chloride ($^{\text{S}}k_6^{\text{L}}$). However, as the concentration of $[\text{pyrH}]^+$ is increased the rate of proton transfer to $[\text{Fe}_4\text{S}_4\text{Cl}_4(\text{SC}_6\text{H}_4\text{R}-4)]^{3-}$ becomes faster than the rate of dissociation of the chloride, and so progressively more of the reaction occurs by the acid-dependent route ($^{\text{S}}k_7^{\text{L}}$). Analysis of the data for the reaction with $\text{C}_6\text{H}_5\text{S}^-$ gives $^{\text{S}}k_7^{\text{PhS}} = (1.8 \pm 0.2) \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Analogous kinetics and mechanism operate in the reaction between $[\text{Fe}_4\text{S}_4\text{Cl}_4]^{2-}$ and $\text{Bu}^t\text{NC}^{10}$ in the presence of $[\text{pyrH}]^+$. Thus, in the reactions of $[\text{Fe}_4\text{S}_4\text{Cl}_4]^{2-}$ with $4\text{-RC}_6\text{H}_4\text{S}^-$ or Bu^tNC in the presence of $[\text{pyrH}]^+$, binding of the nucleophile to the cluster increases the rate of proton transfer to the cluster. This seems intuitively reasonable because it would be anticipated that binding of a nucleophile (particularly an anionic nucleophile) would increase the basicity of the cluster. However, the kinetics of the reaction between $[\text{Fe}_4\text{Y}_4\text{Cl}_4]^{2-}$ ($\text{Y} = \text{S}$ or Se) and Br^- or I^- in the presence of $[\text{pyrH}]^+$ shows that binding nucleophiles to these clusters does not facilitate proton transfer per se but can suppress proton transfer.

Studies with I^- . The kinetics of the reaction between $[\text{Fe}_4\text{Se}_4\text{Cl}_4]^{2-}$ and I^- in the presence of $[\text{pyrH}]^+$ is shown in Figure 3. Thus, in experiments performed at a constant concentration of $[\text{pyrH}]^+$, increasing the concentration of I^- leads to a decrease in the rate of the reaction. However, at high concentrations of I^- the rate does not go to zero but limits at a finite value. In experiments performed at a constant concentration of I^- , the rate of the reaction increases as the concentration of $[\text{pyrH}]^+$ increases as shown in Figure 3 (inset). Analogous kinetics are observed in the reaction of $[\text{Fe}_4\text{S}_4\text{Cl}_4]^{2-}$ and I^- in the presence of $[\text{pyrH}]^+$ (Supporting Information).

The kinetics shown in Figure 3 are consistent with the mechanism shown in Figure 2, and the associated rate law presented in eq 1 ($\text{L} = \text{I}^-$). Thus, at low concentrations of I^- , the predominant species present is $[\text{Fe}_4\text{Se}_4\text{Cl}_4]^{2-}$ and the pathway for substitution involves rate-limiting protonation of this cluster by $[\text{pyrH}]^+$ ($^{\text{Se}}k_4$) followed by rapid substitution of a chloro-ligand by I^- . Because proton transfer of the parent cluster is rate-limiting, it is not possible to establish whether the intimate mechanism of the substitution step is associative

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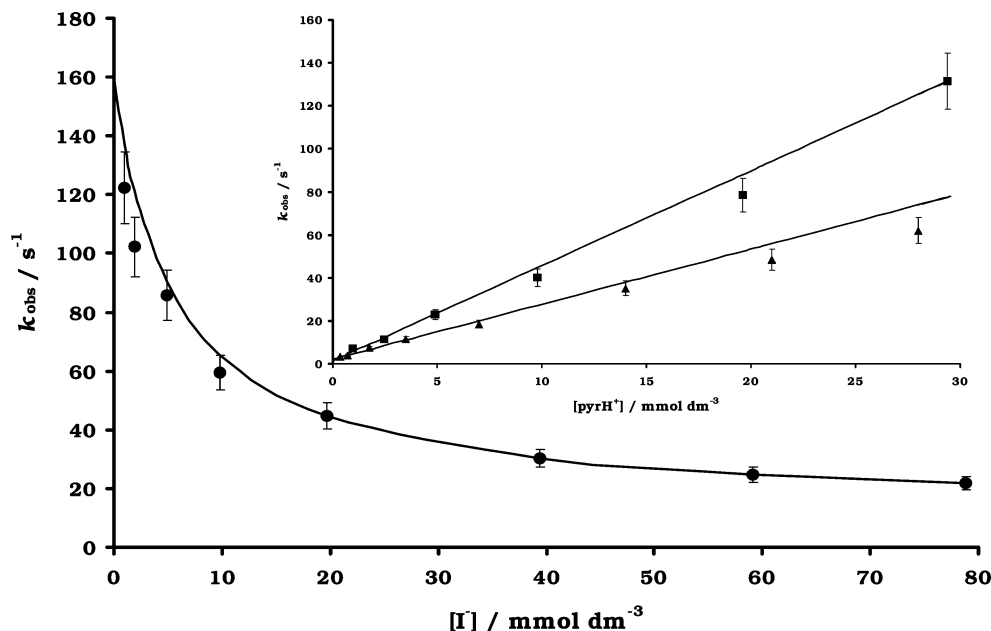


Figure 3. Kinetic data for the reaction of $[\text{Fe}_4\text{Se}_4\text{Cl}_4]^{2-}$ with I^- in the presence of $[\text{pyrH}^+]$. Main: Variation of k_{obs} with $[\text{I}^-]$ when $[\text{pyrH}^+] = 20.0 \text{ mmol dm}^{-3}$ (\bullet). Inset: Variation of k_{obs} with $[\text{pyrH}^+]$ when $[\text{I}^-] = 5.0 \text{ mmol dm}^{-3}$ (\blacksquare) and $[\text{I}^-] = 14.3 \text{ mmol dm}^{-3}$ (\blacktriangle). The fits to the data are those defined by eq 1 and the parameters presented in the text.

or dissociative. As the concentration of I^- is increased, rapid binding of I^- to the parent cluster produces increasing amounts of $[\text{Fe}_4\text{Se}_4\text{Cl}_4\text{I}]^{3-}$ (${}^{\text{Se}}K_5^{\text{I}}$) in solution. Consequently, the rate of proton transfer measured at high concentrations of I^- corresponds to proton transfer from $[\text{pyrH}^+]$ to $[\text{Fe}_4\text{Se}_4\text{Cl}_4\text{I}]^{3-}$ (${}^{\text{Se}}k_7^{\text{I}}$). It is worth emphasizing that proton transfer to $[\text{Fe}_4\text{Se}_4\text{Cl}_4]^{2-}$ (${}^{\text{Se}}k_4$) is observed in this system at low concentrations of I^- , either because the rate of I^- binding to this cluster is slower than the rate of proton transfer from $[\text{pyrH}^+]$ or because the rate of I^- binding to $[\text{Fe}_4\text{Se}_4\text{Cl}_4]^{2-}$ is faster than proton transfer, but rapid dissociation of I^- from $[\text{Fe}_4\text{Se}_4\text{Cl}_4\text{I}]^{3-}$ means that high concentrations of I^- are necessary to produce appreciable amounts of $[\text{Fe}_4\text{Se}_4\text{Cl}_4\text{I}]^{3-}$ in solution.

Analysis of the kinetic data gives the following values. For $[\text{Fe}_4\text{Se}_4\text{Cl}_4]^{2-}$: ${}^{\text{Se}}k_4 = (8.0 \pm 0.5) \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, ${}^{\text{Se}}K_5^{\text{I}} = 180 \pm 20 \text{ dm}^3 \text{ mol}^{-1}$, ${}^{\text{Se}}k_6^{\text{I}} = 3 \pm 1 \text{ s}^{-1}$, and ${}^{\text{Se}}k_7^{\text{I}} = (4.5 \pm 0.5) \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$; and for $[\text{Fe}_4\text{S}_4\text{Cl}_4]^{2-}$: ${}^{\text{S}}k_4 = (2.1 \pm 0.5) \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, ${}^{\text{S}}K_5^{\text{I}} = 220 \pm 20 \text{ dm}^3 \text{ mol}^{-1}$, ${}^{\text{S}}k_6^{\text{I}} = 7 \pm 1 \text{ s}^{-1}$, and ${}^{\text{S}}k_7^{\text{I}} = (6.0 \pm 0.8) \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

$$k_{\text{obs}} = \frac{{}^{\text{Y}}k_4[\text{pyrH}^+] + {}^{\text{Y}}K_5^{\text{L}}({}^{\text{Y}}k_6^{\text{L}} + {}^{\text{Y}}k_7^{\text{L}}[\text{pyrH}^+])[\text{L}]}{1 + {}^{\text{Y}}K_5^{\text{L}}[\text{L}]} \quad (1)$$

An important characteristic of the data shown in Figure 3 (inset) is the intercept on the graph. This small but finite intercept shows that, in the presence of I^- , there is a substitution pathway that is independent of the concentration of $[\text{pyrH}^+]$. This observation necessitates the need to include the ${}^{\text{Y}}k_6^{\text{L}}$ pathway in the mechanism (Figure 2).

From the calculated rate and equilibrium constants associated with the elementary steps in Figure 2, we can determine that the binding of I^- to $[\text{Fe}_4\text{Y}_4\text{Cl}_4]^{2-}$ results in a significant decrease in the rate of proton transfer to the cluster

(${}^{\text{S}}k_7^{\text{I}}/{}^{\text{S}}k_4 = 0.029$; ${}^{\text{Se}}k_7^{\text{I}}/{}^{\text{Se}}k_4 = 0.056$). We will discuss the significance of these observations later in this article.

Before discussing the effect that coordinated L has on the rate of proton transfer from $[\text{pyrH}^+]$ to $[\text{Fe}_4\text{Y}_4\text{Cl}_4\text{L}]^{n-}$, we need to consider further the interpretation of the kinetic data presented above. An alternative interpretation of the results presented in Figure 3 is that the inhibition is attributable to ion pairing between I^- and $[\text{Fe}_4\text{Y}_4\text{Cl}_4]^{2-}$, but this seems untenable, purely on charge terms. However, at first sight, the inhibition could be due to ion-pairing of I^- with $[\text{pyrH}^+]$ and that the ion-pair $[\text{pyrH}^+]\text{I}^-$ is a weaker acid than the free $[\text{pyrH}^+]$. There are three lines of evidence (presented below) that indicate that this interpretation is not correct and that the inhibition is due to the effect that the coordinated I^- is having on the rate of proton transfer.

First, we have tried to fit the experimental data (exemplified by that shown in Figure 3) to a system in which the cluster reacts with both $[\text{pyrH}^+]$ and the ion-pair $[\text{pyrH}^+]\text{I}^-$. However, we cannot get satisfactory fits to the data. For example, in the reaction of $[\text{Fe}_4\text{Se}_4\text{Cl}_4]^{2-}$, the effect that the increasing concentration of I^- has on the rate of the reaction between $[\text{Fe}_4\text{Se}_4\text{Cl}_4]^{2-}$ and $[\text{pyrH}^+]$ (20 mmol dm^{-3}) is shown by the data points in Figure 4. This is the same data that is presented in Figure 3 (main).

The concentrations of both free $[\text{pyrH}^+]$ and ion-pair $[\text{pyrH}^+]\text{I}^-$ {eq (2)} were calculated by successive estimation of the value of K_{IP} in an attempt to get a good fit to the experimental data. The curves presented in Figure 4 are those defined with $K_{\text{IP}} = 3 \times 10^2 \text{ dm}^3 \text{ mol}^{-1}$ (solid line) and $K_{\text{IP}} = 1 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$ (dashed line). In these simulations, the rate constants for the protonation of $[\text{Fe}_4\text{Se}_4\text{Cl}_4]^{2-}$ were $k = 8 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for free $[\text{pyrH}^+]$ (the same value as determined from the analysis shown in Figure 3) and $k = 4.5 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for the ion-pair (the same rate

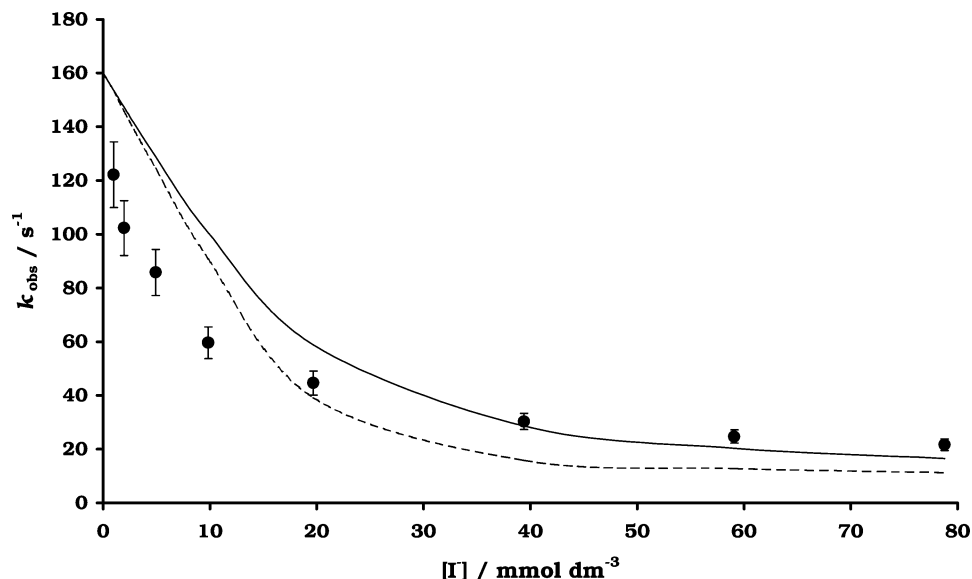


Figure 4. Kinetic data for the reaction of $[\text{Fe}_4\text{Se}_4\text{Cl}_4]^{2-}$ with I^- in the presence of $[\text{pyrH}]^+$, showing the variation of k_{obs} with $[\text{I}^-]$ when $[\text{pyrH}^+] = 20.0 \text{ mmol dm}^{-3}$ (●), the poor fits to these data assuming that there is ion-pairing between $[\text{pyrH}]^+$ and I^- {eq (2)}, and that free $[\text{pyrH}]^+$ and the ion pair protonate the cluster at different rates. The curves are those predicted when $K_{\text{IP}} = 300 \text{ dm}^3 \text{ mol}^{-1}$ (solid line) and $K_{\text{IP}} = 1000 \text{ dm}^3 \text{ mol}^{-1}$ (dashed line). The parameters are described in the text.

constant at high concentrations of I^- as determined from the analysis shown in Figure 3). It is clear that the fits to the experimental data are poor, particularly at low concentrations of $[\text{I}^-]$ where the formation of the ion-pair $[\text{pyrH}^+]\text{I}^-$ predicts an appreciably smaller degree of inhibition than is observed experimentally. Indeed, it is impossible to fit the data at low concentrations of I^- , assuming the reactivity is attributable to formation of ion-pairs. For example, consider the value of k_{obs} when $[\text{pyrH}^+] = 20 \text{ mmol dm}^{-3}$ and $[\text{I}^-] = 10 \text{ mmol dm}^{-3}$. If all of the I^- is ion-paired to $[\text{pyrH}]^+$, then the concentration of free $[\text{pyrH}^+] = 10 \text{ mmol dm}^{-3}$ and the concentration of ion-pair $= 10 \text{ mmol dm}^{-3}$. This would predict that under these conditions $k_{\text{obs}} = 90 \text{ s}^{-1}$, which is appreciably higher than the experimentally observed value of $k_{\text{obs}} = 59.6 \text{ s}^{-1}$. A similar argument when $[\text{pyrH}^+] = 20 \text{ mmol dm}^{-3}$ and $[\text{I}^-] = 5 \text{ mmol dm}^{-3}$ predicts $k_{\text{obs}} = 125 \text{ s}^{-1}$, whereas the experimentally observed value is $k_{\text{obs}} = 85.8 \text{ s}^{-1}$.



The second line of argument against the involvement of ion pairs is as follows. The reaction between $[\text{Fe}_4\text{Y}_4\text{Cl}_4]^{2-}$ and $[\text{pyrH}]^+$ is also inhibited by Br^- (vide infra). However, earlier studies have shown that over similar concentration ranges to the studies presented herein, the rate of the reaction between $[\text{Fe}_2\text{S}_2\text{Cl}_4]^{2-}$ and Br^- in the presence of $[\text{pyrH}]^+$ is independent of the concentration of Br^- .¹⁶ Because ion pairing is independent of the cluster, it would be expected that inhibition effects would be observed in the reactions of all clusters if ion-pairing were occurring.¹⁶

In the reaction between $[\text{Fe}_4\text{S}_4\text{Cl}_4]^{2-}$ and PhS^- in the presence of $[\text{pyrH}]^+$, the rate of reaction is increased by increasing the concentration of PhS^- . This behavior is inconsistent with the formation of a less-reactive ion pair

$[\text{pyrH}^+]\text{PhS}^-$. It seems unreasonable to argue that Br^- and I^- form unreactive ion pairs with $[\text{pyrH}]^+$, but PhS^- forms an ion pair that is more reactive than $[\text{pyrH}]^+$.

Finally, although a constant ionic strength has not been maintained in the reactions of $[\text{Fe}_4\text{Y}_4\text{Cl}_4]^{2-}$ with $[\text{pyrH}]^+$ in the presence of various nucleophiles, two observations indicate that ionic strength is not a major factor in controlling how the various nucleophiles affect the rates of proton transfer. First, both a charged and neutral nucleophile (PhS^- and $\text{Bu}^{\text{N}}\text{C}$) accelerate protonation and second, two anionic thiolates (PhS^- and EtS^- , vide infra) have different effects on the rates of proton transfer,

Studies with Br^- . The kinetics of the reaction between $[\text{Fe}_4\text{Se}_4\text{Cl}_4]^{2-}$ and Br^- in the presence of $[\text{pyrH}]^+$ show the same characteristics as in the analogous reactions with I^- (Figure 5). Analysis of the kinetic data gives ${}^{\text{Se}}k_4 = (10.0 \pm 2) \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$; ${}^{\text{Se}}K_5^{\text{Br}} = 200 \pm 20 \text{ dm}^3 \text{ mol}^{-1}$ ${}^{\text{Se}}k_6^{\text{Br}} = 5 \pm 1 \text{ s}^{-1}$; and ${}^{\text{Se}}k_7^{\text{Br}} = (4.0 \pm 0.5) \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. It is evident that whereas Br^- and I^- both inhibit the rate of proton transfer to $[\text{Fe}_4\text{Se}_4\text{Cl}_4]^{2-}$, the effect of Br^- is much smaller (${}^{\text{Se}}k_7^{\text{Br}}/{}^{\text{Se}}k_4 = 0.40$).

We earlier reported⁶ that the reaction between $[\text{Fe}_4\text{S}_4\text{Cl}_4]^{2-}$ and Br^- in the presence of $[\text{pyrH}]^+$ occurred at a rate that was independent of the concentration of Br^- . In the light of the results from the studies in the presence of I^- we now reconsider the results with Br^- . Over an extended concentration range of Br^- , there is a small decrease in the rate of the reaction. The decrease is so slight that we were originally hesitant to credit it with any mechanistic significance. Rather, it was attributed to a medium effect.¹¹ However, because proton transfer to $[\text{Fe}_4\text{Se}_4\text{Cl}_4]^{2-}$ is inhibited by I^- or Br^- , and proton transfer to $[\text{Fe}_4\text{S}_4\text{Cl}_4]^{2-}$ is also inhibited by I^- , it seems likely that proton transfer to $[\text{Fe}_4\text{S}_4\text{Cl}_4]^{2-}$ is also

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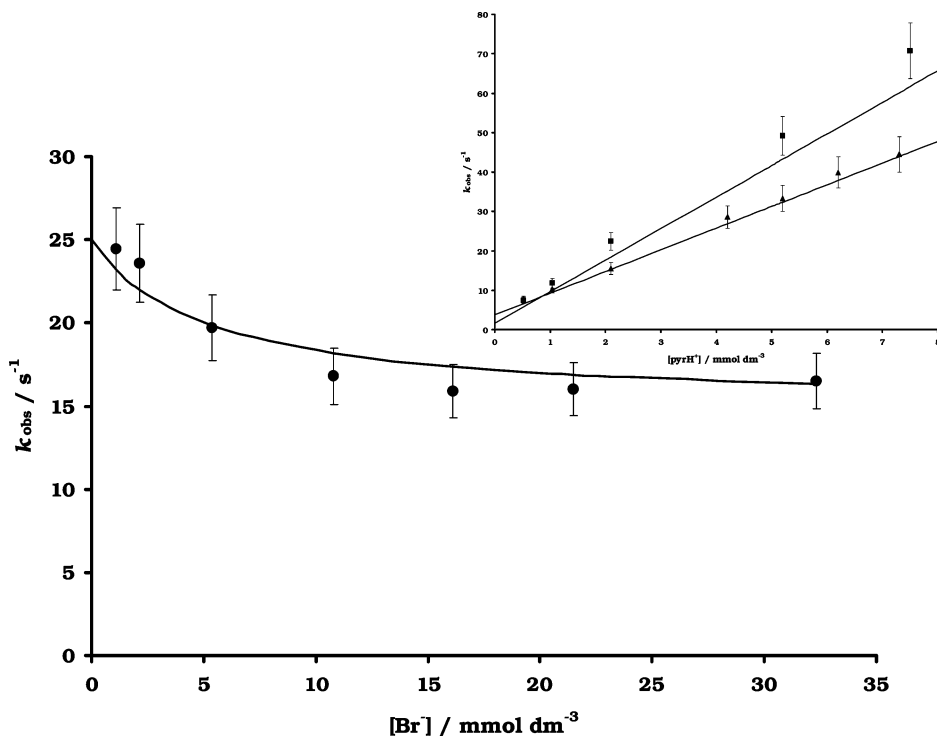


Figure 5. Kinetic data for the reaction of $[\text{Fe}_4\text{Se}_4\text{Cl}_4]^{2-}$ with Br^- in the presence of $[\text{pyrH}]^+$. MAIN. Variation of k_{obs} with $[\text{Br}^-]$ when $[\text{pyrH}^+] = 2.5 \text{ mmol dm}^{-3}$ (\bullet). Inset: Variation of k_{obs} with $[\text{pyrH}^+]$ when $[\text{Br}^-] = 5.0 \text{ mmol dm}^{-3}$ (\blacksquare) and $[\text{Br}^-] = 15.0 \text{ mmol dm}^{-3}$ (\blacktriangle). The fits to the data are those defined by eq 1 and the parameters presented in the text.

inhibited by Br^- . Assuming the effect that Br^- has on the rate of the reaction between $[\text{Fe}_4\text{S}_4\text{Cl}_4]^{2-}$ and $[\text{pyrH}]^+$ is due to Br^- binding to the cluster, analysis of the kinetic data using eq 1 gives $^S k_4 = (2.2 \pm 0.5) \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$; $^S K_5^{\text{Br}} = 200 \pm 20 \text{ dm}^3 \text{ mol}^{-1}$ and $^S k_7^{\text{Br}} = (1.8 \pm 0.2) \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. However, because the effect that Br^- has on the rate of proton transfer to $[\text{Fe}_4\text{S}_4\text{Cl}_4]^{2-}$ is so small ($^S k_7^{\text{Br}} / ^S k_4 = 0.82$), we treat this analysis with some caution.

It is worth emphasizing that the values of $^Y k_4$ obtained from the studies with Br^- and I^- are in excellent agreement. This is to be expected because $^Y k_4$ corresponds to protonation of the parent clusters prior to the binding of the halide. Furthermore, the value of $^S k_4$ for $[\text{Fe}_4\text{S}_4\text{Cl}_4]^{2-}$ reported herein is in excellent agreement with that reported earlier $\{^S k_4 = (2.4 \pm 0.4) \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}\}$.⁶

We have also shown that binding EtS^- to $[\text{Fe}_4\text{S}_4\text{Cl}_4]^{2-}$ suppresses the rate of proton transfer to the cluster. The kinetics of the reaction between $[\text{Fe}_4\text{S}_4\text{Cl}_4]^{2-}$ and EtS^- in the presence of $[\text{pyrH}]^+$ are shown in Figure 6. The data shows that the rate of the reaction exhibits a linear dependence on the concentration of $[\text{pyrH}]^+$ and is inhibited by increasing concentrations of EtS^- .

Although the inhibitory effect of EtS^- is small ($^S k_7^{\text{EtS}} / ^S k_4 = 0.31$, vide infra), the error bars on the data points indicate that the trend is significant. Analysis of the data shown in Figure 6 yields the experimental rate law shown in eq 3. This rate law is consistent with the pathways shown in Figure 2 and the associated rate law shown in eq 1. Comparison of eqs 1 and 3 gives the values $^S k_4 = (3.5 \pm 0.8) \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $^S K_5^{\text{EtS}} = 50 \pm 10 \text{ dm}^3 \text{ mol}^{-1}$, and $^S k_7 = (1.1 \pm 0.2) \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The value of $^S k_4$ is in reasonable

agreement with the value obtained in the analogous studies with Br^- or I^- described above.

$$k_{\text{obs}} = \frac{2 + (3.5 \times 10^4)[\text{pyrH}^+] + (5.5 \times 10^5)[\text{pyrH}^+][\text{EtS}^-]}{1 + 50[\text{EtS}^-]} \quad (3)$$

Effect of Nucleophile on Rates of Proton Transfer.

Binding of $4\text{-RC}_6\text{H}_4\text{S}^-$ and Bu^iNC to $[\text{Fe}_4\text{Y}_4\text{Cl}_4]^{2-}$ increases the rates of proton transfer^{5-7,10} (for $\text{C}_6\text{H}_5\text{S}^-$ with $[\text{Fe}_4\text{S}_4\text{Cl}_4]^{2-}$, $^S k_7^{\text{PhS}} / ^S k_4 = 75$), whereas binding Br^- or I^- decreases the rates of proton transfer. Consideration of the properties of all these nucleophiles allows us to propose the origin of these different effects. First, consider charge. Three of the nucleophiles (Br^- , I^- , and $4\text{-RC}_6\text{H}_4\text{S}^-$) are anionic, but binding $4\text{-RC}_6\text{H}_4\text{S}^-$ and the halides to the clusters have diametrically opposite effects on the rates of proton transfer. Consequently, charge on the nucleophile is not a controlling factor. Second, consider size. The sizes of the donor atoms for the thiolate and halides are too similar to be the distinguishing factor [ionic radii: S^{2-} (1.84 Å), Br^- (1.96 Å), I^- (2.06 Å)].¹⁴ Furthermore, studies on the reaction between $[\text{Fe}_4\text{S}_4\text{Cl}_4]^{2-}$ and $[\text{pyrH}]^+$ in the presence of EtS^- indicate that binding this thiolate inhibits proton transfer to the cluster, demonstrating that the way the coordinated nucleophile modulates the rate of proton transfer to the cluster is more subtle than size or type of donor atom.

Because of the arguments presented above, we propose that the origin of the different effects that nucleophiles have on the rates of proton transfer is associated with the structure of the transition state for the protonation reaction. Earlier studies on the reaction between $[\text{Fe}_4\text{S}_4\text{Cl}_4]^{2-}$ and $[\text{pyrH}]^+$ in

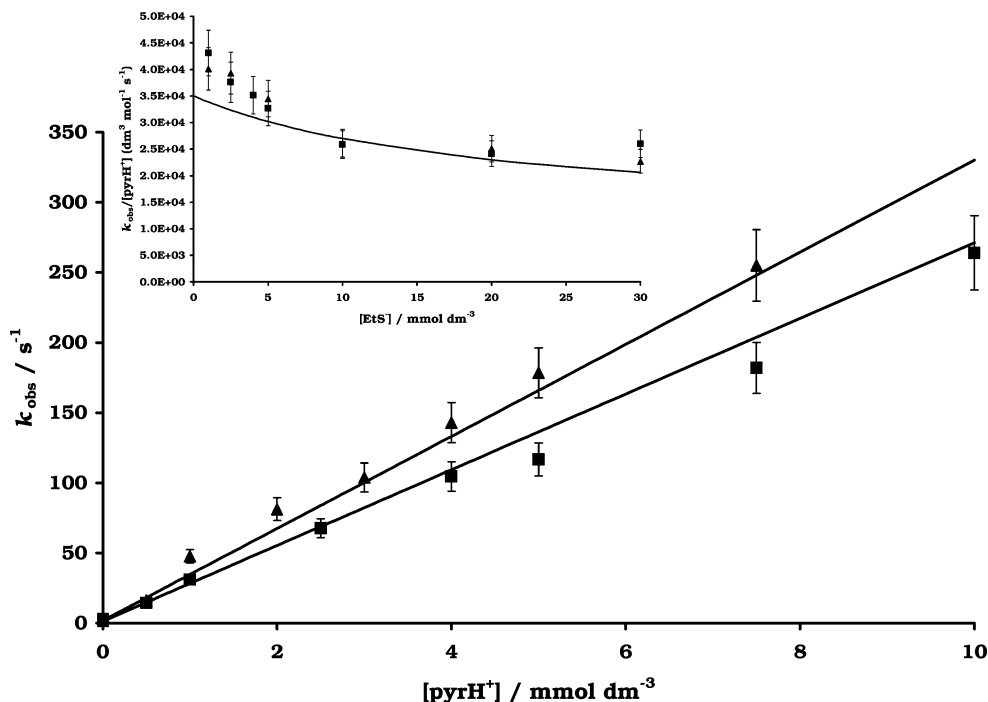


Figure 6. Kinetic data for the reaction between $[\text{Fe}_4\text{S}_4\text{Cl}_4]^{2-}$ and $[\text{pyrH}]^+$ in the presence of EtS^- . Main: Variation of k_{obs} with $[\text{pyrH}^+]$ when $[\text{EtS}^-] = 2.5 \text{ mmol dm}^{-3}$ (\blacktriangle) and $[\text{EtS}^-] = 10.0 \text{ mmol dm}^{-3}$ (\blacksquare). Inset: Variation of $k_{\text{obs}}/[\text{pyrH}^+]$ with $[\text{EtS}^-]$ when $[\text{pyrH}^+] = 1.0 \text{ mmol dm}^{-3}$ (\blacktriangle) and $[\text{pyrH}^+] = 2.0 \text{ mmol dm}^{-3}$ (\blacksquare). The fits to the data are those defined by eq 3 and the parameters presented in the text.

the presence of $4\text{-RC}_6\text{H}_4\text{S}^-$ showed that, after initial binding of the thiolate to the cluster, the subsequent rate of proton transfer from $[\text{pyrH}]^+$ to cluster is modulated by the 4-R-substituent in an unexpected manner. Proton transfer from $[\text{pyrH}]^+$ to $[\text{Fe}_4\text{S}_4\text{Cl}_4(\text{SC}_6\text{H}_4\text{R}-4)]^{3-}$ is facilitated by electron-withdrawing 4-R-substituents $\{k = 0.47 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ($\text{R} = \text{MeO}$); $k = 26.4 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ($\text{R} = \text{CF}_3$)}. Upon transfer of the proton to the cluster, the bond lengths within the cluster have to adjust by shortening, and it would be anticipated that the bond lengths in the cluster (and principally those around the protonation site) would shorten. As the $\text{Fe-SC}_6\text{H}_4\text{R-4}$ bond shortens in the transition states for these proton transfer reactions, there is an unfavorable build up of negative charge, which can be dissipated by electron-withdrawing 4-R-substituents.⁷

Consider now the protonation of $[\text{Fe}_4\text{S}_4\text{Cl}_4(\text{L})]^{n-}$ ($^{\text{S}}k_7^{\text{L}}$; $\text{L} = \text{C}_6\text{H}_5\text{S}^-$, $\text{Bu}^{\text{t}}\text{NC}$, EtS^- , Br^- , or I^-). In line with the earlier argument, the transition state for the protonation of $[\text{Fe}_4\text{S}_4\text{Cl}_4(\text{L})]^{n-}$ would involve shortening of the Fe-ligand bonds within the cluster. However, shortening of the Fe-L bond would be resisted by the build up of negative charge as L and the anionic cluster get closer. Hence, any ligand that can dissipate the unfavorable accumulation of negative charge as the bonds shorten will facilitate Fe-L bond shortening and lead to an increase in $^{\text{S}}k_7^{\text{L}}$. Simplistically, the ability of L to dissipate the increased negative charge upon bond length compression is related to the way in which L bonds to the metal (i.e., its π -bonding capabilities).

Lever¹⁵ has described the E_{L} scale, which is a quantitative description of whether the ligand is a σ -/ π -donor (negative

E_{L} values) or a σ -donor/ π -acceptor (positive E_{L} values). For the reaction¹⁰ with $\text{L} = \text{Bu}^{\text{t}}\text{NC}$, where protonation of $[\text{Fe}_4\text{S}_4\text{Cl}_4(\text{CNBu}^{\text{t}})]^{2-}$ is faster than protonation of the parent cluster, shortening of the Fe-CN Bu^{t} bond must be facilitated. For $\text{L} = \text{Bu}^{\text{t}}\text{NC}$, this ligand is a reasonable π acceptor ($E_{\text{L}} = +0.45$), and any unfavorable increase in electron density at iron could be dissipated by π backbonding from iron to the $\text{Bu}^{\text{t}}\text{NC}$ ligand. However, for all of the other nucleophiles $\{\text{L} = \text{C}_6\text{H}_5\text{S}^-$ ($E_{\text{L}} = -0.53$), EtS^- ($E_{\text{L}} = -0.56$), Br^- ($E_{\text{L}} = -0.22$), or I^- ($E_{\text{L}} = -0.24$)\} these ligands are anionic and good σ -/ π -donors but poor π -acceptors. Yet, whereas binding $\text{C}_6\text{H}_5\text{S}^-$ to $[\text{Fe}_4\text{S}_4\text{Cl}_4]^{2-}$ facilitates proton transfer, binding EtS^- , Br^- , or I^- to the cluster inhibits proton transfer. Clearly, the E_{L} scale alone cannot rationalize the effect that binding L to the cluster has on the rate of subsequent proton transfer. It seems likely that for $\text{C}_6\text{H}_5\text{S}^-$ the unfavorable charge repulsion experienced as the Fe- SC_6H_5 bond shortens is not so significant as with the other anions (EtS^- , Br^- , or I^-) because the anionic charge on the thiolate is not localized on the sulfur but is delocalized around the phenyl group. $\text{L} = \text{EtS}^-$, Br^- , and I^- are good σ -/ π -donors with no means of dissipating the anionic charge. Consequently, the Fe- SEt , Fe- Br , or Fe- I bond shortening is opposed by the unfavorable charge repulsion, leading to an increase in the transition-state energy and a consequent decrease in the rate of proton transfer.

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Effect of $\text{p}K_{\text{a}}$ on Rates of Proton Transfer. Earlier studies showed that the metal composition and structure of the cluster affects the rates of proton transfer.⁶ Consequently, it has not been possible to describe the effect that changes in the $\text{p}K_{\text{a}}$ of the clusters have on the rates of proton transfer. For example, in cuboidal clusters, where changes to terminal ligation or metal composition have only a minor effect on the $\text{p}K_{\text{a}}$, the rates of proton transfer differ by several orders of magnitude.^{6,16} It is only in the studies with the structurally analogous $[\text{Fe}_4\text{Y}_4\text{Cl}_4]^{2-}$ ($\text{Y} = \text{S}$ or Se) reported herein that allow us, for the first time, to gauge the effect that changes to the basicity of the cluster have on the rates of proton transfer. Using $[\text{pyrH}]^+$, the rate of proton transfer to $[\text{Fe}_4\text{Se}_4\text{Cl}_4]^{2-}$ is slower than that of $[\text{Fe}_4\text{S}_4\text{Cl}_4]^{2-}$ ($^{\text{S}}k_4/^{\text{Se}}k_4 = 2.6$). As would be anticipated, this difference in rates of proton transfer is similar to the difference in the basicities of the clusters calculated from their $\text{p}K_{\text{a}}$ ($^{\text{S}}K_{\text{a}}/^{\text{Se}}K_{\text{a}} = 3.2$).^{12,13} The Brønsted relationship ($k = G_{\text{A}}K^{\alpha}$) describes the relationship between the rate constant and the corresponding equilibrium constant for thermodynamically unfavorable proton-transfer reactions.¹⁷ Using the values of $^{\text{S}}k_4/^{\text{Se}}k_4$ and $^{\text{S}}K_{\text{a}}/^{\text{Se}}K_{\text{a}}$, we can estimate that Brønsted $\alpha \sim 0.82$. The simple interpretation of Brønsted α is that when $\alpha \sim 1.0$ the transition state is product-like with essentially complete proton transfer, whereas $\alpha \sim 0$ indicates a transition state that is reactant-like, with little proton transfer. Clearly, the Brønsted α estimated for $[\text{Fe}_4\text{Y}_4\text{Cl}_4]^{2-}$ indicates that proton transfer is well advanced in the transition state. This conclusion is consistent with our not observing a significant deuterium kinetic isotope effect in the proton transfer reactions with synthetic Fe–S-based clusters.¹⁶ Maximal deuterium kinetic isotope effects are observed when the proton is half-transferred in the transition state, corresponding to Brønsted $\alpha = 0.5$. When Brønsted $\alpha = 0$ or 1.0 , only a small deuterium kinetic isotope effect will be observed.

Conclusions

In this article, we have shown that the rates of proton transfer to $[\text{Fe}_4\text{Y}_4\text{Cl}_4]^{2-}$ are inhibited by the prior binding of $\text{L} = \text{EtS}^-$, Br^- , or I^- to the cluster. Such an effect is unprecedented. Whereas it is not unusual for the rates of proton transfer to the ligands on metal complexes to be modulated by the nature of other coligands, what makes the studies reported in this article unique is that some nucleophiles ($\text{L} = 4\text{-RC}_6\text{H}_4\text{S}^-$ or $\text{Bu}^{\text{t}}\text{NC}$) facilitate the rates of proton transfer to $[\text{Fe}_4\text{Y}_4\text{Cl}_4]^{2-}$, whereas others ($\text{L} = \text{EtS}^-$, Br^- , or I^-) suppress the reaction. Clearly, this observation is not consistent with the simple description that binding L affects the basicity of the cluster. Rather, we propose that Fe–L bond reorganization in the transition state for protonation of these clusters modulates the rates of proton transfer. To some extent, our argument is similar to that for why a proton transfer at carbon and metal sites is slow: reorganization of the ligands is a controlling factor. The difference with

these studies on the Fe–S clusters is that the reorganization cost to the proton transfer step depends on the type of ligand that binds to the cluster.

Finally, the question arises as to whether the effects reported in this article for $[\text{Fe}_4\text{Y}_4\text{Cl}_4]^{2-}$ are more widespread. Certainly, studies on the kinetics of the reactions between $[\{\text{MFe}_3\text{S}_4\text{Cl}_3\}_2(\mu\text{-SEt})_3]^{3-}$ ($\text{M} = \text{Mo}$ or W)¹⁸ and halides in the presence of $[\text{pyrH}]^+$ show that the binding of halides to the clusters also inhibits the rates of proton transfer. However, the effects described in this article are unique to synthetic Fe–S-based clusters, and have yet to be observed in any other area of chemistry.

Experimental Section

All manipulations were routinely performed under an atmosphere of dinitrogen using standard Schlenk or syringe techniques as appropriate. All solvents were dried and distilled under dinitrogen immediately prior to use. Acetonitrile was distilled from calcium hydride and methanol from $\text{Mg}(\text{OMe})_2$. Tetrahydrofuran and diethyl ether were dried in a two stage process; the bulk of the water was removed by addition of sodium wire to the solvent as supplied, and then the predried solvents were distilled from sodium/benzophenone or sodium, respectively. Ethanol was used as received.

NMR spectra was recorded on a 300 MHz Bruker NMR spectrometer fitted with a wide bore cavity to hold larger NMR tubes, operating at 121.5 MHz.

The following chemicals were purchased from Aldrich and used as received: FeCl_3 , pyrrolidine, sodium tetraphenylborate, sulfur, selenium, and sodium. $[\text{NEt}_4]\text{Br}$ was purchased from Aldrich and dried prior to use by heating to 80°C under vacuum for 24 h. $[\text{NBu}_4]\text{I}$ was purchased from Aldrich; recrystallized from methanol/diethyl ether and stored under dinitrogen prior to use.

The clusters $[\text{NBu}_4]_2[\text{Fe}_4\text{Se}_4\text{Cl}_4]$ ^{19,20} and $[\text{NEt}_4]_2[\text{Fe}_4\text{S}_4\text{Cl}_4]$ ^{21,22} were prepared by the methods described in the literature, and characterized by elemental analysis (calculated values shown in parentheses) and comparison of the UV–vis spectrum with that in the literature.

$[\text{NBu}_4]_2[\text{Fe}_4\text{Se}_4\text{Cl}_4]$: C, 33.1 (33.0); H, 6.3 (6.4); N, 2.4 (2.4). ($\lambda_{\text{max}} \sim 320$ nm, shoulder, $\epsilon_{\text{max}} \sim 2100$ $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$), ($\lambda_{\text{max}} \sim 530$ nm, shoulder, $\epsilon_{\text{max}} \sim 500$ $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$).

$[\text{NEt}_4]_2[\text{Fe}_4\text{S}_4\text{Cl}_4]$: C, 25.4 (25.5); H, 5.4 (5.4); N, 3.8 (3.7); ($\lambda_{\text{max}} = 505$ nm, shoulder, $\epsilon_{\text{max}} = 2300$ $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$); $\lambda_{\text{max}} = 690$ nm, $\epsilon_{\text{max}} = 1790$ $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$).

The $[\text{pyrH}]\text{BPh}_4$ used in the studies reported herein was prepared by the methods described in the literature and characterized by elemental analysis and ^1H NMR spectroscopy.²³

$[\text{pyrH}]\text{BPh}_4$: C, 86.0 (85.9); H, 7.6 (7.7); N, 3.6 (3.6); NMR δ 1.9 (m, $\text{CH}_2\text{CH}_2\text{N}$), 3.20 (t, $\text{CH}_2\text{CH}_2\text{N}$, $J_{\text{HH}} = 7.5$ Hz), 6.6 (br, NH_2), 6.8–7.3 (m, Ph).

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[NEt₄][EtS] was prepared by the method described in the literature and characterized by elemental analysis: C, 62.6 (62.8); H, 13.3 (13.2); N, 6.8 (6.9).

Characterization of Products of Reactions. The cuboidal cluster, [Fe₄S₄Cl₄]²⁻, has previously been shown to undergo a facile ligand exchange in the presence of benzoyl bromide, forming the bromo-ligated cluster, [Fe₄S₄Br₄]²⁻ or sodium iodide to give the iodo-ligated cluster, [Fe₄S₄I₄]²⁻.²⁴ Analogous reaction conditions have been reported for the formation of [Fe₄Se₄Br₄]²⁻ and [Fe₄Se₄I₄]²⁻ from [Fe₄Se₄Cl₄]²⁻.²⁰ For the kinetic studies reported herein, the source of exchanging halides are tetraalkylammonium salts; however, comparison of the visible absorption spectrum (reported below) indicates that identical products are formed.

[Fe₄S₄Br₄]²⁻ ($\lambda_{\max} = 370$ nm, $\epsilon_{\max} = 8300$ dm³ mol⁻¹ cm⁻¹; $\lambda_{\max} \sim 420$ nm, shoulder, $\epsilon_{\max} \sim 2900$ dm³ mol⁻¹ cm⁻¹; $\lambda_{\max} = 480$ nm, $\epsilon_{\max} = 4500$ dm³ mol⁻¹ cm⁻¹; $\lambda_{\max} \sim 505$ nm, shoulder, $\epsilon_{\max} \sim 3500$ dm³ mol⁻¹ cm⁻¹; $\lambda_{\max} = 600$ nm, $\epsilon_{\max} = 2500$ dm³ mol⁻¹ cm⁻¹).

[Fe₄S₄I₄]²⁻ ($\lambda_{\max} = 415$ nm, $\epsilon_{\max} = 11\,700$ dm³ mol⁻¹ cm⁻¹; $\lambda_{\max} \sim 460$ nm, shoulder, $\epsilon_{\max} \sim 5900$ dm³ mol⁻¹ cm⁻¹; $\lambda_{\max} = 525$ nm, $\epsilon_{\max} = 6190$ dm³ mol⁻¹ cm⁻¹; $\lambda_{\max} = 625$ nm, $\epsilon_{\max} = 2700$ dm³ mol⁻¹ cm⁻¹).

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[Fe₄Se₄Br₄]²⁻ ($\lambda_{\max} = 560$ nm, $\epsilon_{\max} = 2900$ dm³ mol⁻¹ cm⁻¹; $\lambda_{\max} = 750$ nm, $\epsilon_{\max} = 2020$ dm³ mol⁻¹ cm⁻¹).

[Fe₄Se₄I₄]²⁻ ($\lambda_{\max} \sim 600$ nm, shoulder, $\epsilon_{\max} \sim 1900$ dm³ mol⁻¹ cm⁻¹; $\lambda_{\max} \sim 650$ nm, shoulder, $\epsilon_{\max} \sim 3150$ dm³ mol⁻¹ cm⁻¹).

Kinetic Studies. All kinetic studies were performed using an Applied Photophysics SX.18MV stopped-flow spectrophotometer modified to handle air-sensitive solutions connected to a RISC pc. The temperature was maintained at 25.0 ± 0.1 °C using a Grant LTD 6G thermostat tank with a combined recirculating pump. The solutions of the cluster and reactants were prepared under an atmosphere of dinitrogen and transferred to the spectrophotometer via gastight, all-glass syringes. The solutions of all reagents were prepared by dilution from freshly made stock solutions in acetonitrile and used within 1 h of preparation.

The absorbance-time traces were fitted to exponential curves using the *Applied Photophysics* software. The observed rate constants (k_{obs}) presented in the figures are the average of at least three experiments. The error bars presented in the figures show a 10% reproducibility. All experiments were performed under pseudo-first-order conditions with the concentration of all reagents in an excess over the concentration of the cluster.

Acknowledgment. We acknowledge EPSRC for a grant to K.B.

Supporting Information Available: Listings of tables containing the observed rate constants for all the reactions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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