Electronic Supplementary Material (ESI) for Dalton Transactions.

Exploring the acid-catalyzed substitution mechanism of $[Fe_4S_4Cl_4]^{2-}$

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SUPPLEMENTARY INFORMATION

Supplementary Information

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FIG S1 Absorbance-time curve for the reaction of $[Fe_4S_4Cl_4]^{2-}$ (0.2 mmol dm^{-3}) with PhS^- (5.0 mmol dm^{-3}) in the presence of $NHMe_3^+$ (10.0 mmol dm^{-3}) in MeCN at 25.0 °C (λ = 550 nm). The experimental trace is shown in black and the exponential curves fit is in grey. The curve is defined by the equation $A_t = 0.38 - (0.19e^{-13.2t}) - (0.079e^{-1.45t})$.

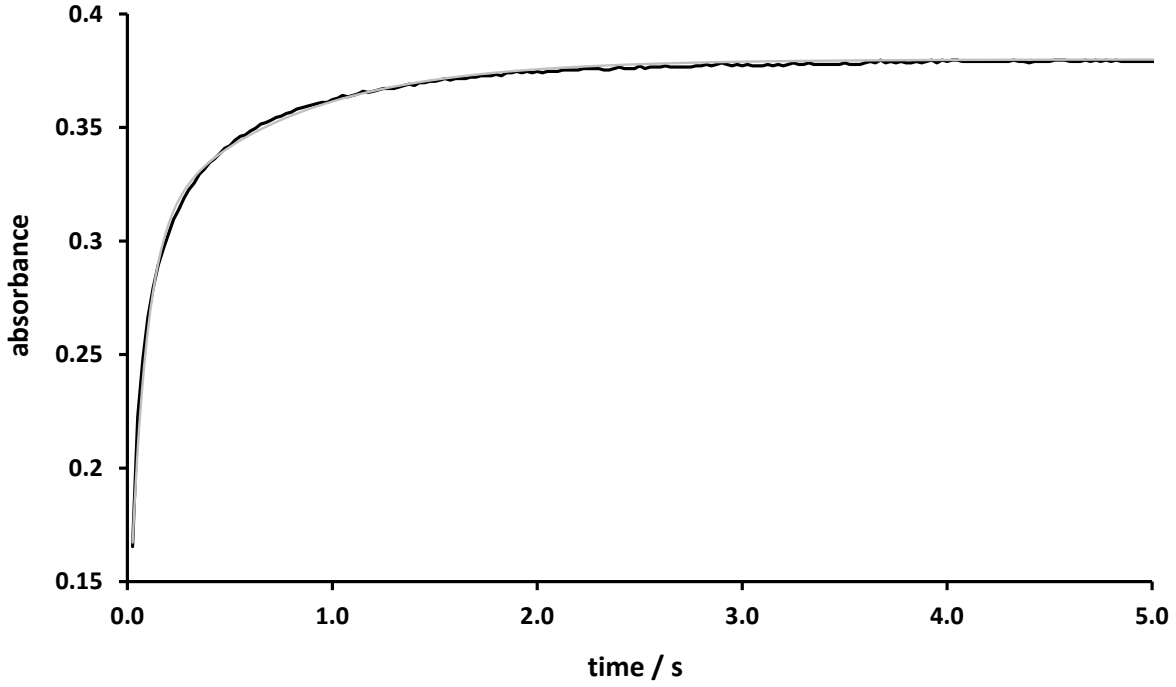


TABLE S1

Kinetic data for the Reaction of $[Fe_4S_4Cl_4]^{2-}$ (0.2 mmol dm^{-3}) with PhSH in the Presence of $NHPr^n{}_3^+$ in MeCN at 25.0 °C (λ = 550 nm).

$[NHPr^n{}_3^+]_i$ / mmol dm^{-3}	$[NPr^n]_i$ / mmol dm^{-3}	$[PhS^-]_i$ / mmol dm^{-3}	$[NHPr^n{}_3^+]_i/[NPr^n]_i$	$k_{obs}(1)$ / s^{-1}	$k_{obs}(1)/[PhSH]_i$ / dm^3 mol^{-1} s^{-1}	$k_{obs}(2)$ / s^{-1}
2.50		1.25	1	11.4	9120	2.1
5.00		2.50	1	27.5	11000	3.0
5.00		1.25	3	15.0	12000	2.6
10.0		2.50	3	35.0	14000	4.9
10.0		1.25	7	15.4	12300	2.2

TABLE S2

Kinetic data for the Reaction of $[Fe_4S_4Cl_4]^{2-}$ (0.2 mmol dm^{-3}) with PhSH in the Presence of $NHMe_3^+$ in MeCN at 25.0 °C (λ = 550 nm).

$[NHMe_3^+]_i$ / mmol dm^{-3}	$[NMe_3]_i$ / mmol dm^{-3}	$[PhS^-]_i$ / mmol dm^{-3}	$[NHMe_3^+]_e/[NMe]_e$	$k_{obs}(1)$ / s^{-1}	$k_{obs}(1)/[PhSH]_i$ / dm^3 mol^{-1} s^{-1}	$k_{obs}(2)$ / s^{-1}
2.50	0.0	1.25	1.0	2.2	1760	0.37
5.00		2.50	1.0	6.2	2480	0.63
10.0		5.00	1.0	13.2	2640	1.4
15.0		5.00	2.0	14.9	2980	1.0
5.00		1.25	3.0	3.4	2720	0.76
10.0		2.50	3.0	7.0	2784	0.90
20.0		5.00	3.0	15.6	3120	1.4
25.0		5.00	4.0	20.0	4000	1.5
15.0		2.50	5.0	12.3	4920	1.9
10.0		1.25	7.0	6.1	4880	1.9
20.0		2.50	7.0	14.3	5720	1.8
15.0		1.25	11.0	8.9	7120	1.5
30.0		2.50	11.0	17.5	7000	2.0
20.0		1.25	15	10.5	8400	1.7
25.0		1.25	19	12.3	9800	2.5

TABLE S3

Kinetic data for the Reaction of $[Fe_4S_4Cl_4]^{2-}$ (0.2 mmol dm^{-3}) with PhSH in the Presence of $NHBu^n{}_3^+$ in MeCN at 25.0 °C (λ = 550 nm).

$[NHBu^n{}_3^+]_i$ / mmol dm^{-3}	$[PhS^-]_i$ / mmol dm^{-3}	$[NHBu^n{}_3^+]_e/[NBu^n{}_3]_e$	$[NHBu^n{}_3^+]_e$ / mmol dm^{-3}	$k_{obs}(1)$ / s^{-1}	$10^{-3}k_{obs}(1)/[PhSH]_i$ / dm^3 mol^{-1} s^{-1}	$k_{obs}(2)$ / s^{-1}
1.25	0.625	1	0.625	1.2	1.92	0.3
2.50	1.25	1	1.25	2.0	1.60	0.41
2.50	0.625	3	1.88	1.9	3.04	0.40
5.0	2.50	1	2.50	2.2	0.88	0.44
5.0	1.25	3	3.75	3.3	2.64	0.55
5.0	0.625	7	4.38	2.8	4.48	0.50
10.0	5.0	1	5.0	5.0	1.0	0.75
10.0	2.50	3	7.5	4.8	1.9	0.70
10.0	1.25	7	8.75	5.2	4.16	0.88
10.0	0.625	15	9.38	5.3	8.48	0.90
15.0	5.0	2	10.0	6.2	1.24	0.92
15.0	2.50	5	12.5	7.3	2.92	0.95
15.0	1.25	11	13.75	7.7	6.16	0.95
15.0	0.625	23	14.38	9	14.4	1.2

Temperature Dependence Studies

All temperature dependence studies were performed over the temperature range 15 – 35 ^{o}C.

The data was analysed using the Eyring equation shown below.

$$\log_{10}(k/T) = \{10.32 + (\Delta S^{\ddagger}/R)\} - \{\Delta H^{\ddagger}/RT\}$$

Where k = rate or equilibrium constant measured at temperature T (^{o}K), R = gas constant and both $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are in cals.

TABLE S4

Kinetic data for the Effect of Temperature on the Reaction of $[Fe_4S_4Cl_4]^{2-}$ (0.2 mmol dm^{-3}) with PhSH in the Presence of $NHBu^n{}_3^+$ in MeCN.

Temperature / ^oK	$[NHBu^n{}_3^+]_i$ / mmol dm^{-3}	$[PhS^-]_i$ / mmol dm^{-3}	$k_{obs}(1)$ / s^{-1}	$k_{obs}(2)$ / s^{-1}
288	3.50	2.50	6.1	0.69
	4.50	2.50	6.5	0.80
	6.50	2.50	7.5	0.98
	10.5	2.50	9.5	1.1
	14.5	2.50	10.5	1.1
293	3.50	2.50	6.0	0.75
	4.50	2.50	6.5	1.0
	6.50	2.50	7.8	1.07
	10.5	2.50	9.5	1.1
	14.5	2.50	11.3	1.1
308	3.50	2.50	6.5	0.85
	4.50	2.50	7.0	1.0
	6.50	2.50	8.0	1.18
	10.5	2.50	9.5	1.3
	14.5	2.50	12.2	1.3

FIG. S2

Eyring plot the Reaction of $[Fe_4S_4Cl_4]^{2-}$ (0.2 mmol dm^{-3}) with PhSH in the Presence of $NHBu^n{}_3{}^+$ in MeCN.

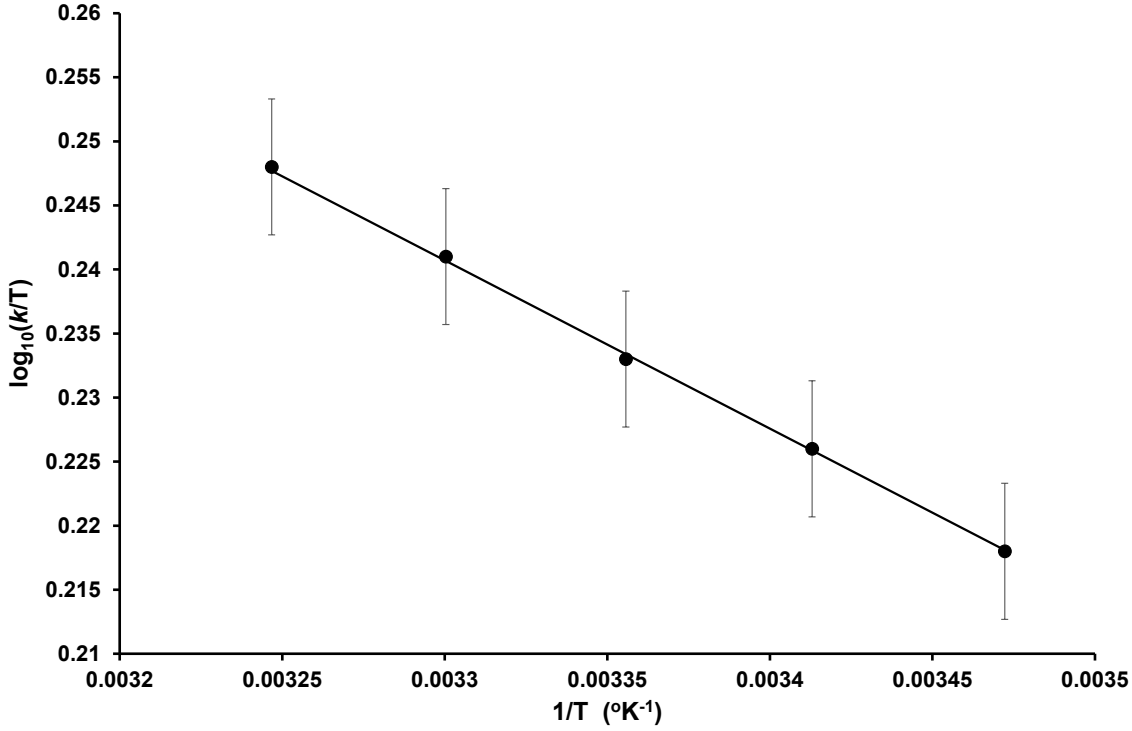


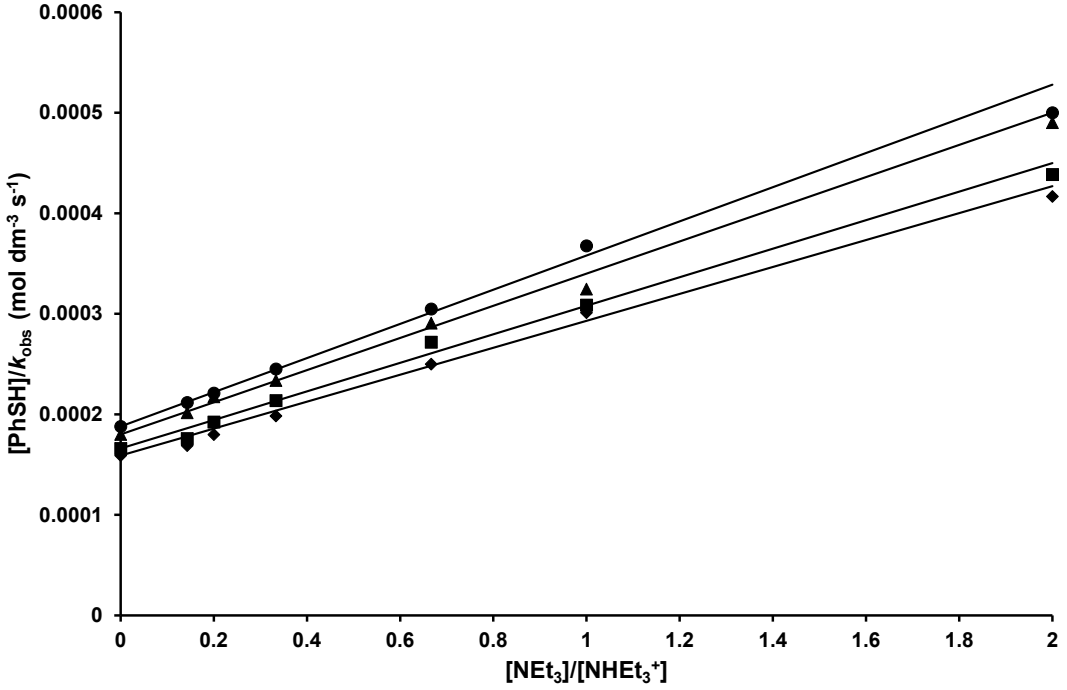
TABLE S5

Kinetic data for the Effect of Temperature on the Reaction of $[Fe_4S_4Cl_4]^{2-}$ (0.2 mmol dm^{-3}) with PhSH in the Presence of $NHEt_3^+$ in MeCN.

Temperature / ^oK	$[NHEt_3^+]_i$ / mmol dm^{-3}	$[PhS^-]_i$ / mmol dm^{-3}	$[NHEt_3^+]_i/[NEt_3]_i$	$k_{obs}(1)$ / s^{-1}	$k_{obs}(2)$ / s^{-1}
288	3.80	2.5	0.50	5.0	0.48
	5.0	2.5	1.0	6.8	0.67
	6.2	2.5	1.5	8.2	0.80
	10.0	2.5	3.0	10.2	0.90
	15.0	2.5	5.0	11.3	1.08
	20.0	2.5	7.0	11.8	1.2
293	3.80	2.5	0.50	5.1	0.49
	5.0	2.5	1.0	7.7	0.57
	6.2	2.5	1.5	8.6	0.89
	10.0	2.5	3.0	10.7	1.17
	15.0	2.5	5.0	11.5	1.26
	20.0	2.5	7.0	12.4	1.55
303	3.80	2.5	0.50	5.7	0.73
	5.0	2.5	1.0	8.1	0.9
	6.2	2.5	1.5	9.2	1.01
	10.0	2.5	3.0	11.7	1.37
	15.0	2.5	5.0	13.0	1.7
	20.0	2.5	7.0	14.2	2.6
308	3.80	2.5	0.50	6.0	0.83
	5.0	2.5	1.0	8.3	0.96
	6.2	2.5	1.5	10.0	1.6
	10.0	2.5	3.0	12.6	1.8
	15.0	2.5	5.0	13.9	2.45
	20.0	2.5	7.0	14.8	3.6

FIG. S3

Graphs of $[PhSH]/k_{obs}$ versus $[NEt_3]/[NHEt_3^+]$ for the Reaction of $[Fe_4S_4Cl_4]^{2-}$ (0.2 mmol dm^{-3}) with PhSH (2.5 mmol dm^{-3}) in the Presence of $NHEt_3^+$ in MeCN at Various Temperatures. Data points correspond to: T = 288 ^oK (♦); T = 293 ^oK (■); T = 303 ^oK (▲); T = 308 ^oK (●).



Each line is that defined by the equation below and the associated rate and equilibrium constants.

$$\frac{[PhSH]}{k_{obs}} = \frac{1}{kK_0}\frac{[NEt_3]}{[NHEt_3^+]} + \frac{1}{k}$$

temperature / ^oK	K_0 / dm^3 mol^{-1}	k / s^{-1}
288	1.103	5.33×10^3
293	1.124	5.56×10^3
303	1.168	6.03×10^3
308	1.190	6.27×10^3

FIG. S4

Eyring plot the Reaction of $[Fe_4S_4Cl_4]^{2-}$ (0.2 mmol dm^{-3}) with PhSH in the Presence of $NHEt_3^+$ in MeCN: Variation of K_0

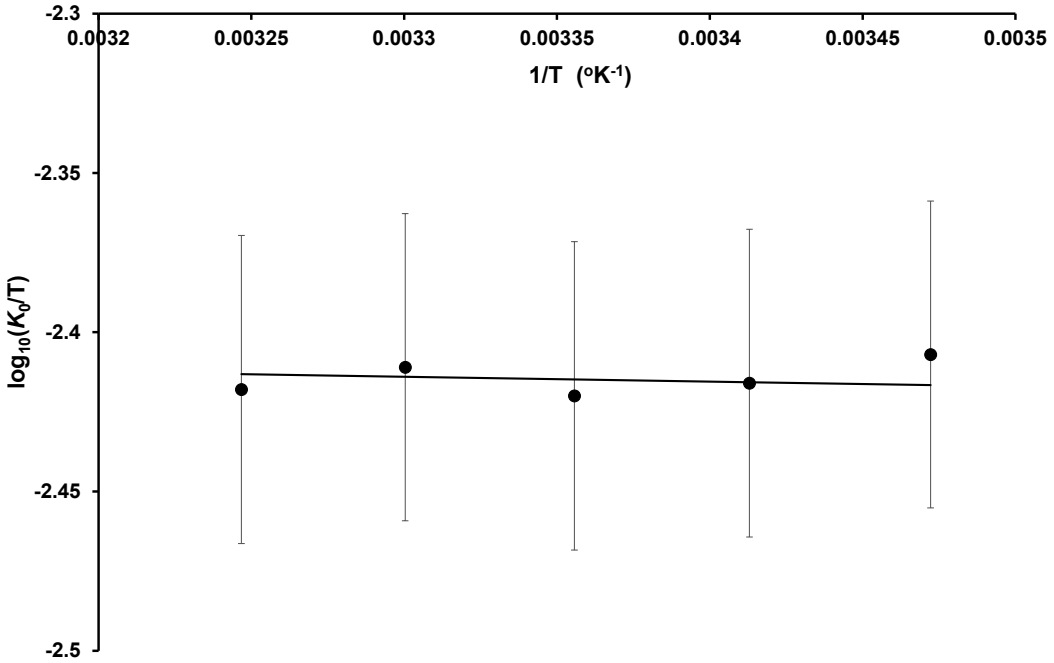


FIG. S5

Eyring plot the Reaction of $[Fe_4S_4Cl_4]^{2-}$ (0.2 mmol dm^{-3}) with PhSH in the Presence of $NHEt_3^+$ in MeCN: Variation of k

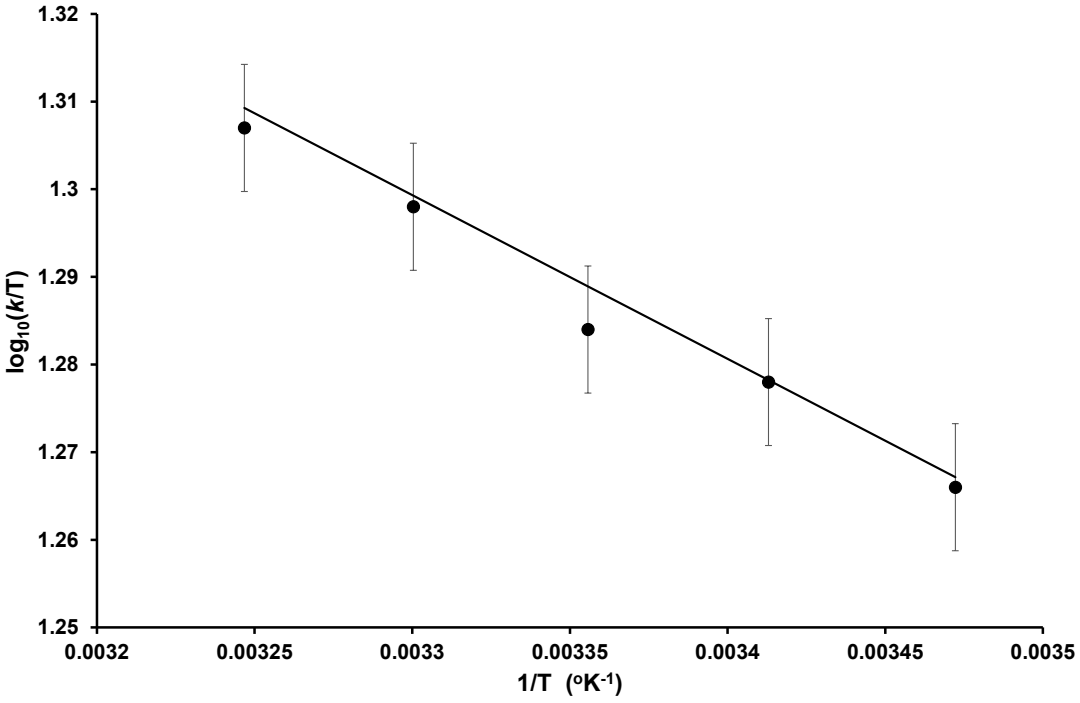


TABLE S6

Kinetic data for the Effect of Temperature on the Reaction of $[Fe_4S_4(SEt)_4]^{2-}$ (0.2 mmol dm^{-3}) with PhSH in the Presence of $NHEt_3^+$ in MeCN.

Temperature / ^oK	$[NHEt_3^+]_i$ / mmol dm^{-3}	$[PhS^-]_i$ / mmol dm^{-3}	$[NHEt_3^+]_i/[NEt_3]_i$	$k_{obs}(1)$ / s^{-1}	$k_{obs}(2)$ / s^{-1}
288	10.0	1.0	9.0	1.80	0.2
293	10.0	1.0	9.0	1.88	0.17
298	10.0	1.0	9.0	2.0	0.18
303	10.0	1.0	9.0	2.1	0.2
308	10.0	1.0	9.0	2.2	0.18

FIG. S6

Eyring plot the Reaction of $[Fe_4S_4(SEt)_4]^{2-}$ (0.2 mmol dm^{-3}) with PhSH in the Presence of $NHEt_3^+$ in MeCN.