Electronic Supplementary Material (ESI) for Dalton Transactions.

Binding small molecules and ions to $[Fe_4S_4Cl_4]^{2-}$ modulates rate of protonation of the cluster

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SUPPLEMENTARY INFORMATION

Supplementary Information

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Kinetic Data

FIG S1 Absorbance-time curve for the reaction of $[Fe_4S_4Cl_4]^{2-}$ (0.2 mmol dm^{-3}) with PhS^- (1.25 mmol dm^{-3}) in the presence of $NHBu^n{}_3^+$ (5.0 mmol dm^{-3}) in the presence of Bu^tNC (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 $A_t = 0.313 - (0.15e^{-7.4t}) - (0.068e^{-1.1t})$.

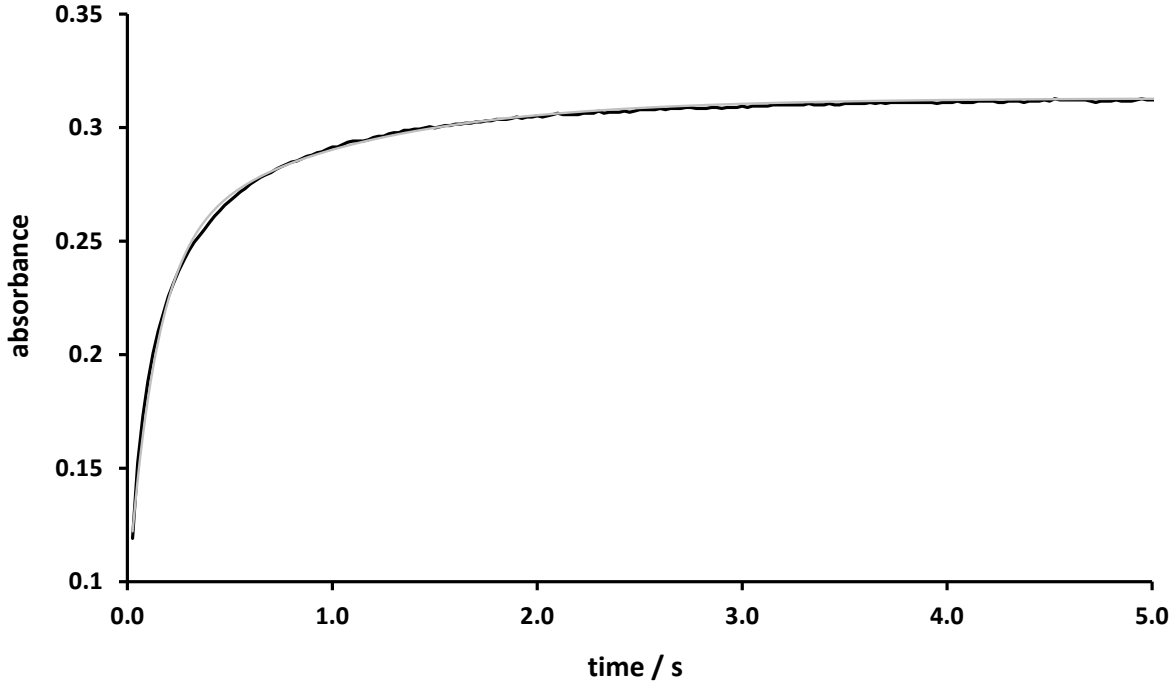

TABLE S1

Kinetic data for the Reaction of $[Fe_4S_4Cl_4]^{2-}$ with PhSH in the Presence of $NHBu^n_3{}^+$ and X^- (X = Cl, Br or I) in MeCN at 25.0 °C (λ = 550 nm).

$[PhS^-]_i$ / mmol dm^{-3}	$[NHBu^n_3{}^+]_i$ / mmol dm^{-3}	$[NHBu^n_3{}^+]_e$ / mmol dm^{-3}	$[X^-]$ / mmol dm^{-3}	$k_{obs}(1)$ / s^{-1}	$k_{obs}(2)$ / s^{-1}
X = Cl					
1.25	5.0	3.75	0.0	5.4	0.62
			1.0	3.7	0.57
			2.5	1.8	0.25
			5.0	2.0	0.27
			10.0	2.2	0.3
			20.0	2.95	0.39
			30.0	3.7	0.52
			40.0	4.4	0.64
			50.0	5.7	0.76
X = Br					
1.25	5.0	3.75	0.0	5.2	0.68
			1.0	5.1	0.72
			2.5	5.0	0.68
			5.0	5.2	0.66
			10.0	4.8	0.65
			20.0	4.7	0.64
X = I					
1.25	5.0	3.75	0.0	5.3	0.69
			1.0	5.5	0.70
			2.5	5.1	0.70
			5.0	5.1	0.67
			10.0	5.0	0.63
			20.0	4.8	0.62

TABLE S2

Kinetic data for the Reaction of $[Fe_4S_4Cl_4]^{2-}$ with PhSH in the Presence of $NHBu^n_3{}^+$ and N_3^- in MeCN at 25.0 °C (λ = 550 nm).

$[PhS^-]_i$ / mmol dm^{-3}	$[NHBu^n_3{}^+]_i$ / mmol dm^{-3}	$[NHBu^n_3{}^+]_e$ / mmol dm^{-3}	$[N_3^-]$ / mmol dm^{-3}	$k_{obs}(1)$ / s^{-1}	$k_{obs}(2)$ / s^{-1}
1.25	5.0	3.75	0.0	5.1	0.60
			1.0	16	1.5
			2.5	20.1	1.9
			5.0	24.9	1.5
			10.0	34.6	1.2
			20.0	39.6	1.9
			30.0	45.6	1.2
			40.0	50.0	1.5
			50.0	50.0	1.6

TABLE S3

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

$[PhS^-]_i$ / mmol dm^{-3}	$[NHBu^n{}_3^+]_i$ / mmol dm^{-3}	$[NHBu^n{}_3^+]_e$ / mmol dm^{-3}	$[NCS^-]$ / mmol dm^{-3}	$k_{obs}(1)$ / s^{-1}	$k_{obs}(2)$ / s^{-1}
1.25	5.0	3.75	0	4.1	0.43
			1.0	11.9	1.2
			2.5	21.3	2.06
			5.0	26.6	2.7
			10.0	29.3	3.3
			20.0	37.5	3.6
			30.0	42.1	3.8
			40.0	44.1	3.9
			50.0	45.0	3.9
1.25	2.5	1.25	5.0	11.9	1.17
	5.0	3.75		25.4	2.4
	7.5	6.25		39.8	3.9
	10.0	8.75		45.6	4.8
	15.0	13.75		99.0	8.9
	25.0	23.75		116.0	12.2
	30.0	28.75		133.0	13.2
	40.0	38.75		146.0	12.9

TABLE S4

Kinetic data for the Reaction of $[Fe_4S_4Cl_4]^{2-}$ with PhSH in the Presence of $NHBu^n_3{}^+$ and Bu^tNC in MeCN at 25.0 °C (λ = 550 nm).

$[PhS^-]_i$ / mmol dm^{-3}	$[NHBu^n_3{}^+]_i$ / mmol dm^{-3}	$[NHBu^n_3{}^+]_e$ / mmol dm^{-3}	$[Bu^tNC]$ / mmol dm^{-3}	$k_{obs}(1)$ / s^{-1}	$k_{obs}(2)$ / s^{-1}
1.25	5.0	3.75	0.0	5.2	0.60
			1.0	5.2	0.47
			2.5	5.6	0.47
			5.0	6.2	0.60
			10.0	7.4	1.1
			20.0	10.5	1.6
			30.0	12.9	1.6
			40.0	17.7	1.7
			50.0	19.3	1.7

TABLE S5

Kinetic data for the Reaction of $[Fe_4S_4Cl_4]^{2-}$ with PhSH in the Presence of $NHBu^n_3{}^+$ and pyridine in MeCN at 25.0 °C (λ = 550 nm).

$[PhS^-]_i$ / mmol dm^{-3}	$[NHBu^n_3{}^+]_i$ / mmol dm^{-3}	$[NHBu^n_3{}^+]_e$ / mmol dm^{-3}	[pyridine] / mmol dm^{-3}	$k_{obs}(1)$ / s^{-1}	$k_{obs}(2)$ / s^{-1}
1.25	5.0	3.75	0.0	5.5	0.74
			1.0	7.0	0.90
			2.5	7.5	0.95
			5.0	8.5	1.09
			10.0	9.3	1.20
			20.0	10.9	1.48
			30.0	11.4	1.52
			40.0	13.0	1.8
			50.0	13.0	1.8

TABLE S6

Kinetic data for the Reaction of $[Fe_4S_4Cl_4]^{2-}$ with PhSH in the Presence of $NHBu^n_3{}^+$ and substituted hydrazines ($PhNHNH_2$, $MeNHNH_2$ and Me_2NNH_2) in MeCN at 25.0 °C (λ = 550 nm).

$[PhS^-]_i$ / mmol dm^{-3}	$[NHBu^n_3{}^+]_i$ / mmol dm^{-3}	$[NHBu^n_3{}^+]_e$ / mmol dm^{-3}	[hydrazine] / mmol dm^{-3}	$k_{obs}(1)$ / s^{-1}	$k_{obs}(2)$ / s^{-1}
hydrazine = $PhNHNH_2$					
1.25	5.0	3.75	0.0	5.1	0.60
			1.0	6.7	0.91
			2.0	5.4	0.76
			3.0	6.0	0.88
			4.0	7.7	0.97
			5.0	8.2	1.09
			7.5	9.2	1.10
			10.0	10.5	1.59
			15.0	10.5	1.62
			25.0	10.5	1.65
hydrazine = $MeNHNH_2$					
1.25	5.0	3.75	0.0	5.0	0.60
			1.0	27.6	3.3
			2.0	36.0	4.2
			3.0	45.9	3.9
			4.0	53.3	5.6
			5.0	59.4	6.5
			7.5	70.0	11.6
hydrazine = Me_2NNH_2					
1.25	5.0	3.75	0.0	5.0	0.6
			1.0	15.0	1.7
			2.0	17.0	2.1
			3.0	19.5	2.2
			4.0	21.0	2.6
			5.0	22.5	2.6
			7.5	24.5	3.2
			10.0	28.0	3.2
			15.0	30.0	3.5
			25.0	32.5	3.9

TABLE S7

Kinetic data for the Reaction of $[Fe_4S_4Cl_4]^{2-}$ with PhSH in the Presence of $NHBu^n_3{}^+$ and CN^- in MeCN at 25.0 °C (λ = 550 nm).

$[PhS^-]_i$ / mmol dm^{-3}	$[NHBu^n_3{}^+]_i$ / mmol dm^{-3}	$[NHBu^n_3{}^+]_e$ / mmol dm^{-3}	$[CN^-]_i$ / mmol dm^{-3}	$[CN^-]_e$ / mmol dm^{-3}	$[HCN]_e$ / mmol dm^{-3}	$k_{obs}(1)$ / s^{-1}	$k_{obs}(2)$ / s^{-1}
$[NHBu^n_3{}^+]_i \leq ([PhS^-]_i + [CN^-]_i)$							
1.25	2.5	0.0	1.75	0.50	1.25	34.4	3.7
			2.0	0.75		47.3	3.1
			2.25	1.00		61.7	4.7
2.50	5.0	0.0	3.0	0.5	2.50	43	3.7
			3.5	1.0		61	4.4
			3.75	1.25		93.7	7.0
			4.0	1.50		97.5	8.4
			4.25	1.75		128.5	13.7
			4.5	2.00		159.8	25.1
5.0	10.0	0.0	5.50	0.50	5.0	33.4	3.2
			5.75	0.75		50.1	5.4
			6.0	1.00		70.4	7.3
			6.25	1.25		83.3	8.2
			6.5	1.50		118.2	11.2
			6.75	1.75		138.4	12.5
			7.0	2.00		145.0	13.2

$[PhS^-]_i$ / mmol dm^{-3}	$[NHBu^n{}_3^+]_i$ / mmol dm^{-3}	$[NHBu^n{}_3^+]_e$ / mmol dm^{-3}	$[CN^-]_i$ / mmol dm^{-3}	$[CN^-]_e$ / mmol dm^{-3}	$[HCN]_e$ / mmol dm^{-3}	$k_{obs}(1)$ / s^{-1}	$k_{obs}(2)$ / s^{-1}
$[NHBu^n{}_3^+]_i \geq ([PhS^-]_i + [CN^-]_i)$							
1.25	2.50	0.25	1.0	0.0	1.0	1.92	0.23
	5.00	2.75				4.0	0.50
	10.0	7.75				6.0	0.71
	15.0	12.75				8.5	0.88
	25.0	22.75				11.5	1.18
	30.0	27.75				13.5	1.34
	40.0	37.75				18.7	1.60
1.25	10.0	5.75	3.0	0.0	3.0	5.5	0.64
	15.0	10.75				9.4	0.90
	25.0	20.75				13.2	1.47
	30.0	25.75				15.1	1.60
	40.0	35.75				18.0	2.15