ELECTRONIC SUPPORTING INFORMATION

Reduction mechanism of a coordinated superoxide by thiols in acidic media

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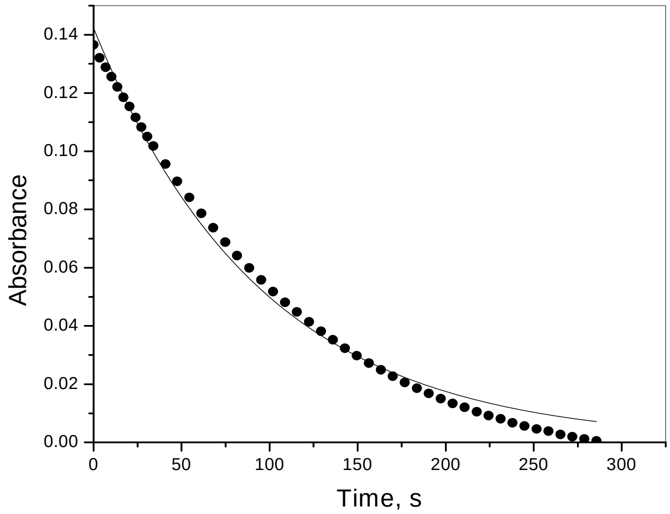

Fig. S1 Kinetic profile at 700 nm for the reduction of **1** (0.50 mM) with cys (5.0 mM) without dipicolinic acid. $[H^+]$ = 0.05 M, $[Cu^{2+}]$ = 5.0 μM (added as perchlorate salt), I = 0.50 M ($NaClO_4$), T = 25.0 ^{o}C. The solid line is the attempted first-order fit (visibly unacceptable) of the experimental values (solid circles).

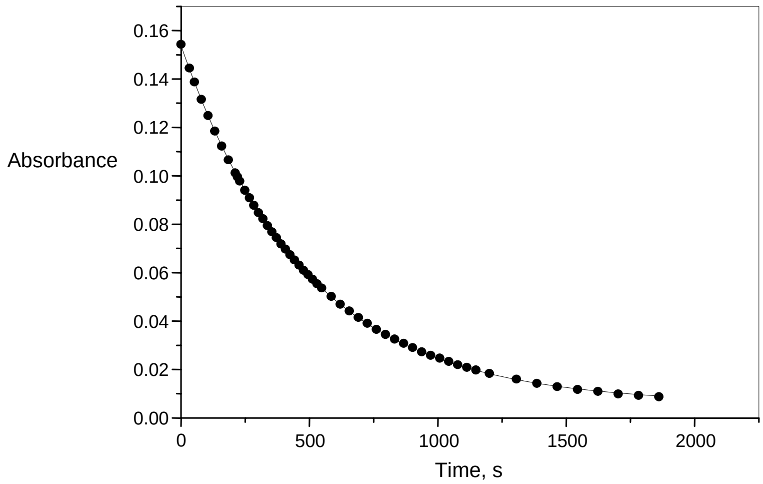

Fig. S2 Excellent first-order fit (solid line) to the experimental values (solid circles) for the reduction of **1** (0.50 mM) with cys (5.0 mM). $[H^+]$ = 0.05 M, [dipicolinic acid] = 2.0 mM, I = 0.50 M ($NaClO_4$), T = 25.0 ^oC.

Table S1. Cu^{2+} catalysis and its suppression by dipicolinic acid, in the reduction of **1** (0.50 mM) with cys (5.0 mM) in acid perchlorate media ($[H^+]$ = 50.0 mM, I = 0.50 mM ($NaClO_4$)).

$10^6[Cu^{2+}]$, M	[dipic], mM	$t_{1/2}$, s[a]
2.2 (present as impurity in the reaction media[b])	0.0	164
2.2 (present as impurity in the reaction media[b])	2.0	330
5.0 (Cu^{2+} added as perchlorate)	1.0	130
5.0 (Cu^{2+} added as perchlorate)	2.0	330
5.0 (Cu^{2+} added as perchlorate)	4.0	330
5.0 (Cu^{2+} added as perchlorate)	0.0	65

[a]Time required for initial absorbance of **1** to become half.

[b]As determined by AAS.

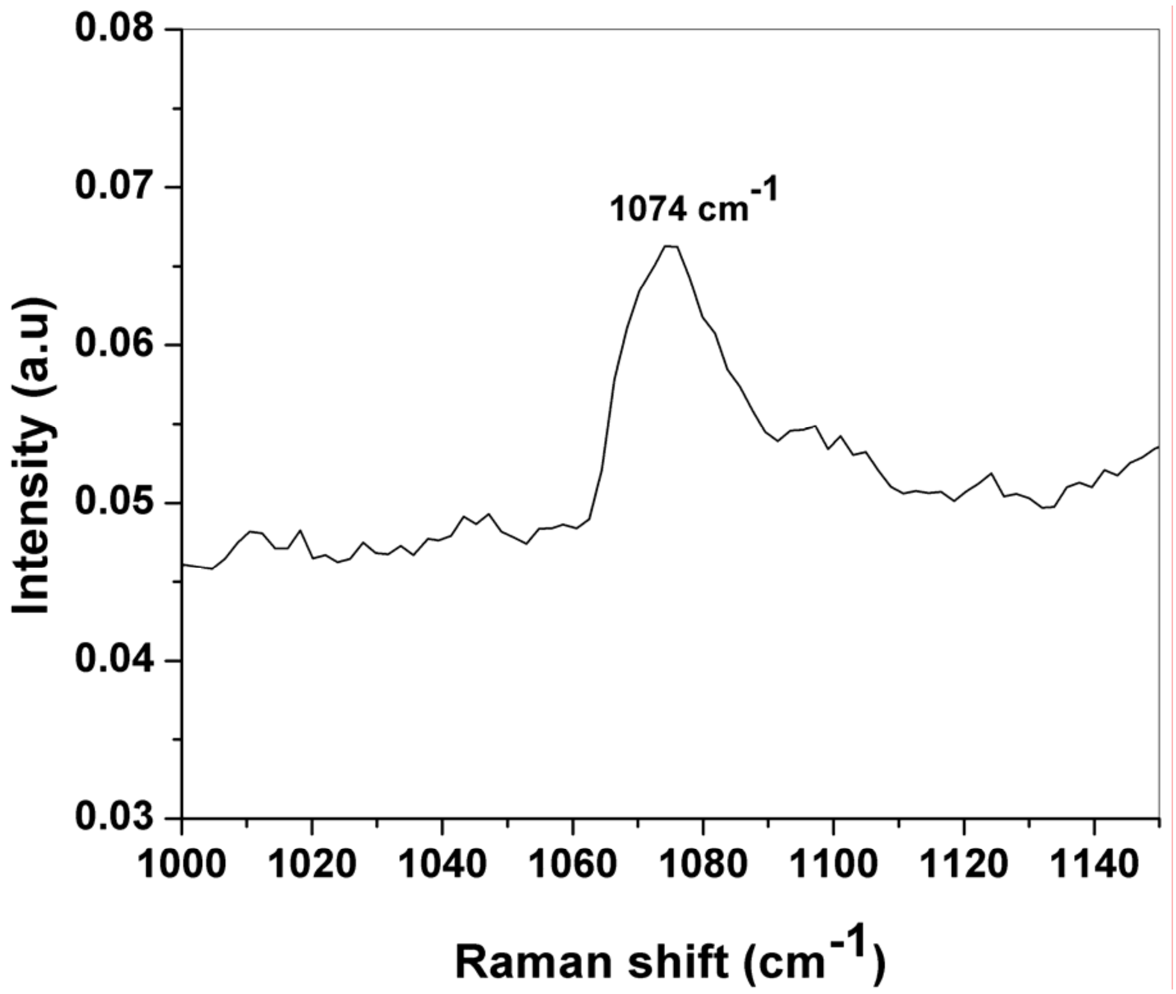

Fig. S3 Observed Raman Spectrum for complex **1.** Peak position expected[1] at 1075 ± 10 cm^{-1} for superoxo stretching of a pure sample.

Reference

1. C. G. Barraclough, G. A. Lawrance and P. A. Lay, *Inorg. Chem.*, 1978, **17**, 3317.

Table S2. Variation of k_o with [thiol], [**1**] = 0.50 mM, $[H^+]$ = 0.05 M for cys, 0.030 M for mercap and tga, [dipicolinic acid] = 2.0 mM, I = 0.50 M ($NaClO_4$), T = 25.0 ºC.

[thiol], M	10^3k_o, s^{-1}		
	for cys	for mercap	for tga
0.005	2.4	1.2	3.7
0.010	4.9	2.5	6.8
0.013	6.3	3.6	8.8
0.015	7.3	4.1	9.7
0.018	9.2	4.7	11.4
0.020	10.4	5.6	12.5

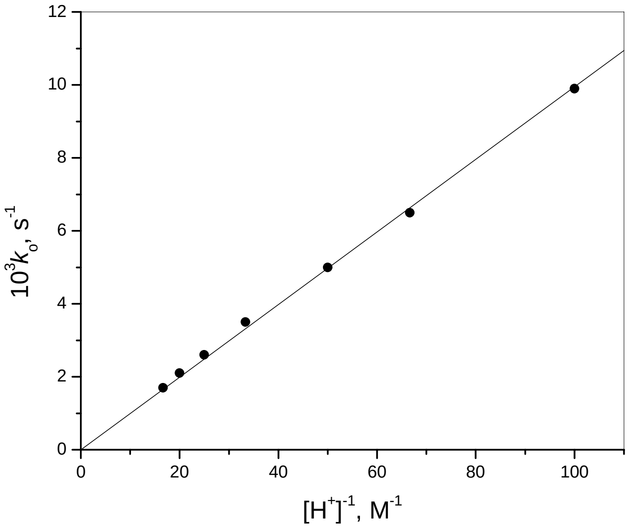

Fig. S4 Variation of k_o with $[H^+]^{-1}$. [tga] = 5.0 mM, [**1**]= 0.50 mM, [dipicolinic acid] = 2.0 mM, I = 0.5 M ($NaClO_4$), T = 25.0 ^oC.

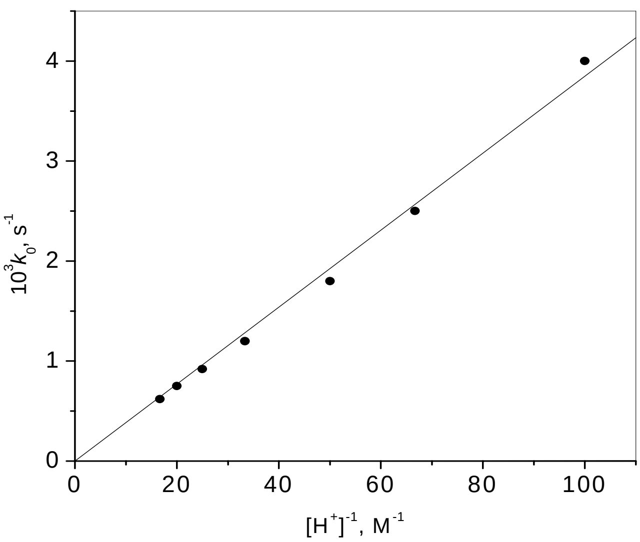

Fig. S5 Variation of k_o with $[H^+]^{-1}$. [mercap] = 5.0 mM, [**1**] = 0.50 mM, [dipicolinic acid] = 2.0 mM, I = 0.50 M ($NaClO_4$), T = 25.0 °C.

Table S3. Effect of $[H^+]$ on k_o: [**1**] **=** 0.50 mM, [thiol] = 5.0 mM, [dipicolinic acid] = 2.0 mM, I = 0.5 M ($NaClO_4$), T = 25 °C.

$[H^+]$, M	$10^3 k_o$, s^{-1}		
	mercap	tga	cys
0.010	4.0	9.9	12.4
0.015	2.7	6.5	8.3
0.020	1.8	5.0	6.2
0.030	1.2	3.5	4.1
0.040	0.92	2.6	3.1
0.050	0.75	2.1	2.4
0.060	0.62	1.7	1.9

Table S4. Stoichiometric results for the oxidation of thiols by **1**, $[H^+]$ = 0.05 M for cys, 0.030 M for mercap and tga, [dipicolinic acid] = 2.0 mM, I = 0.50 M ($NaClO_4$), T = 25.0 ºC.

[**1**], mM	Δ[thiol], mM			Δ[**1**]/ Δ[thiol]	Av. Δ[**1**]/Δ[thiol]
	mercap	tga	cys		
3.0	2.8			1.07	1.02
4.0	4.5			0.97	
2.0		1.9		1.05	1.04
5.0		4.8		1.04	
3.0			1.8	1.67	1.64
5.0			3.1	1.61	

Table S5. Estimation of cystine sulfinic acid, $[H^+]$ = 0.05 M, [dipicolinic acid] = 2.0 mM, I = 0.50 M ($NaClO_4$), T = 25.0 ºC.

[**1**], mM	[cys], mM	unreacted cys, mM	cys oxidized, mM	(unreacted cys + sulfinic acid), mM	[cystine sulfinic acid], mM	% cys converted to sulfinic acid
2.0	2.5	1.3	1.2	1.55	0.25	20.8%
3.0	1.5	0.0	1.5	0.29	0.29	19.3%