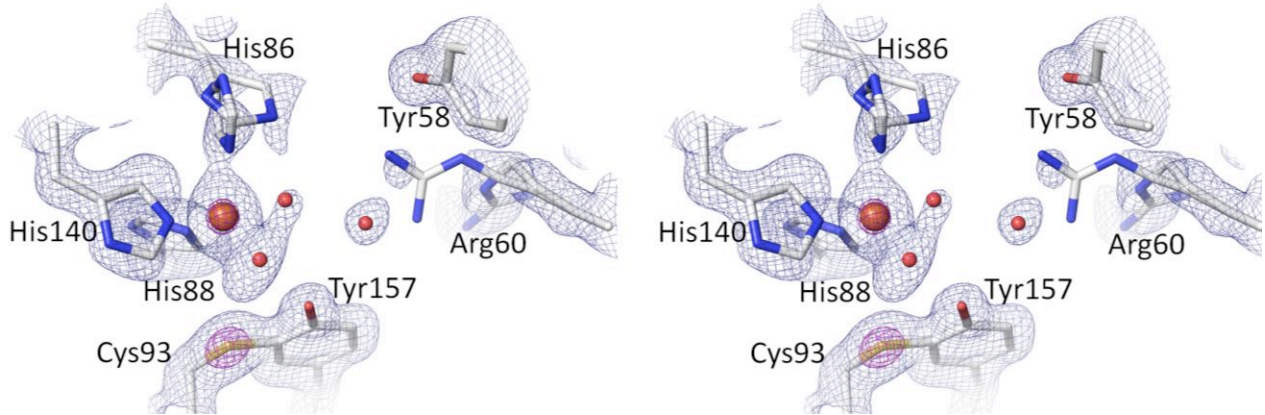


# 1 Supplementary Information

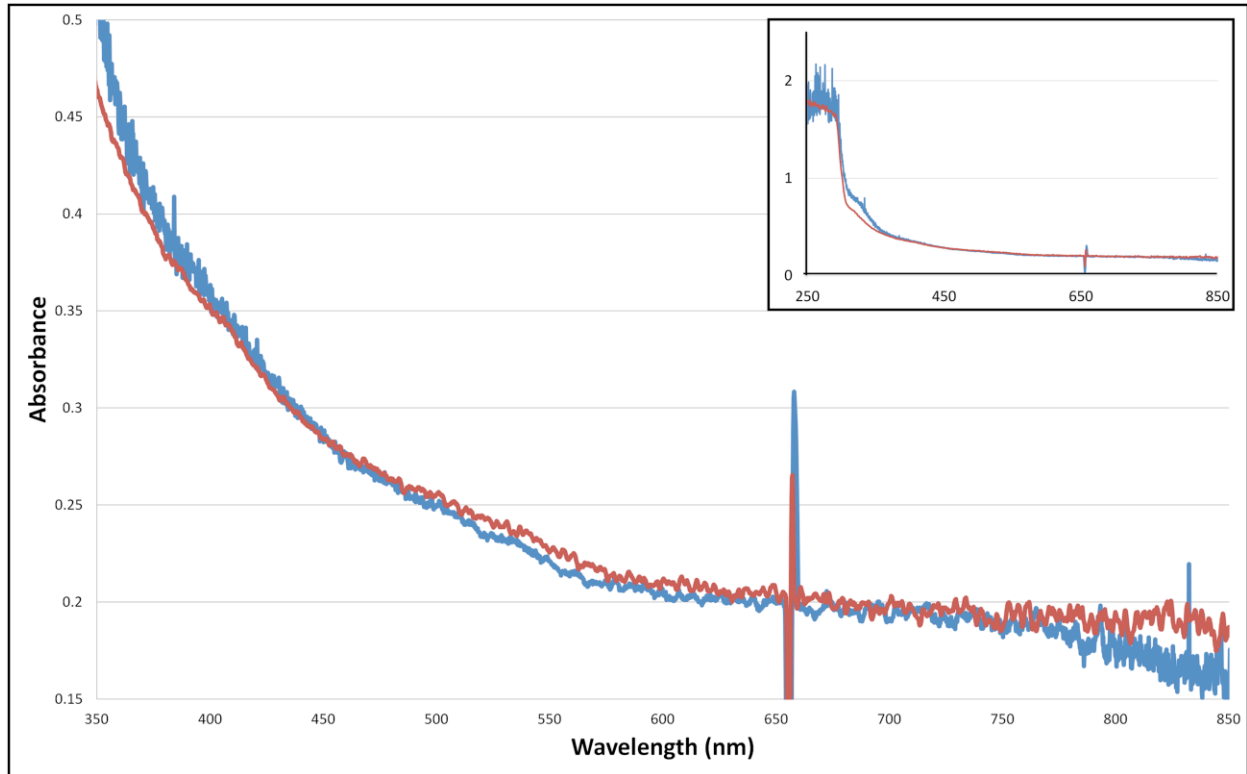
## 2 Supplementary Figure S1



3 Figure S1. Partial iron loss in the pH=4.0 Cys structure. Stereo figure showing the active site  
4 density contoured at  $1.2 \rho_{rms}$  (blue) and  $5.0 \rho_{rms}$  (purple) shows weak complex density for the  
5 His86 side chain density that is weaker than that of the Cys93  $S_{\gamma}$ , consistent with the iron having  
6 decreased occupancy. We modeled the occupancy at 80% by selecting occupancy that yields a  
7 B-factor that matches that expected based on a fully liganded structure. The refined model is  
8 shown including alternate conformations for the His86 and Arg60 side chains. Our interpretation  
9 is that the side chain of His86 becomes partially protonated at this pH, weakening iron ligation  
10 and allowing His86 to adopt an alternative conformation (shown).

11

1 Supplemental Figure S2.



2

3 Figure S2. UV/VIS spectra of select CDO crystals before data collection. Shown are the spectra  
4 of a crystal containing a Cys-only complex (red trace; pH=8.0 + Cys soak) and a crystal  
5 containing a bound cys-persulfenate/persulfenic acid complex (blue trace; pH 6.2 + Cys soak).  
6 To facilitate comparisons, the blue trace shown has been origin shifted (by subtracting 0.207  
7 absorbance units) from the original data so that its absorbance at 750 nm matches that of the red  
8 trace. The main panel shows no significant difference exists in the spectra surrounding the 640  
9 nm region where an absorbance band would be expected for an Fe(III)-Cys complex. The inset  
10 shows the full spectral range collected. Diffraction data collected for each of these crystals after  
11 the spectra were taken confirmed the content of the structures. The one visible difference is a  
12 small additional absorbance that occurs for the CDO:Cys-persulfenate containing crystal at 325  
13 nm. The spike at 650 nm is due to a technical aspect of how the spectra were collected. To test  
14 for dichroic absorption bands, spectra were taken for all crystal orientations around a 360°  
15 rotation axis with kappa 0 and using a kappa offset of 90° (i.e. a crystal tilt of 45°). All the  
16 spectra were similar to the ones shown. Spectra were collected at National Synchrotron Light  
17 Source beamline X26C.