Table S1. Ni EXAFS Fitting Results for Model Compounds and for the

C.N.	R (Å)	$\sigma^2(10^{-3}\text{\AA}^2)$	F
4S	2.192(2)	6.47	522.4
1Cl	2.484(10)	4.53	
4S	2.183(2)	6.26	
1Cl	2.486(9)	4.34	391.1
1Fe	3.295(7)	3.04	
4S	2.132(2)	2.55	776.9
4C	3.086(13)	5.30	
4S	2.187(4)	6.35	558.2
38	2.187(3)	4.50	483.1
3S	2.182(3)	4.23	425.2
1N	1.887(7)	2.35	
2S	2.190(2)	2.39	398.2
2N	1.929(11)	6.55	
3S	2.182(2)	4.27	374.9
1N	1.886(7)	2.35	
1Fe	2.963(7)	6.26	
2S	2.191(3)	2.41	
2N	1.932(10)	6.67	345.3
1Fe	2.969(8)	6.62	
	C.N. 4S 1Cl 4S 1Cl 1Fe 4S 4C 4S 3S 3S 1N 2S 2N 3S 1N 1Fe 2S 2N 1Fe 2S 2N 1Fe	C.N.R (Å)4S2.192(2)1Cl2.484(10)4S2.183(2)1Cl2.486(9)1Fe3.295(7)4S2.132(2)4C3.086(13)4S2.187(4)3S2.187(3)3S2.182(3)1N1.887(7)2S2.190(2)2N1.929(11)3S2.182(2)1N1.886(7)1Fe2.963(7)2S2.191(3)2N1.932(10)1Fe2.969(8)	C.N.R (Å) $\sigma^2 (10^{-3} Å^2)$ 4S2.192(2)6.471Cl2.484(10)4.534S2.183(2)6.261Cl2.486(9)4.341Fe3.295(7)3.044S2.132(2)2.554C3.086(13)5.304S2.187(4)6.353S2.187(3)4.503S2.182(3)4.231N1.887(7)2.352S2.190(2)2.392N1.929(11)6.553S2.182(2)4.271N1.886(7)2.351Fe2.963(7)6.262S2.191(3)2.412N1.932(10)6.671Fe2.969(8)6.62

ACDS β Subunit Using Integer Coordination Numbers

	3S 1N	2.174(3) 1.846(7)	3.73 1.68	618.2
ACDS β subunit Ti ³⁺ -reduced	2S 2N	2.176(3) 1.879(13)	1.85 7.50	626.0
	3S 1N 1Fe	2.176(3) 1.847(7) 2.982(10)	3.71 1.76 6.01	607.2



Figure S1. Long and short range Ni EXAFS Fourier transforms show persistence of the ~3.0 Å feature, most likely due to a Ni-Ni interaction. Upper, Ni FT EXAFS of as-isolated ACDS β subunit. Middle, Ti³⁺-reduced β subunit. Lower, Ni FT EXAFS of the Ni-Fe compound [Fe{N(CH₂CH₂S)₃}(NO)NiCl(dppe)]. FT range is k = 1 to 12.5 Å⁻¹ (---) and k = 1 - 16.0 Å⁻¹ (----). The ~3.0 Å peak persists regardless of the *k* range over which the transform was

performed. This feature also shifts to a longer average distance upon reduction with Ti³⁺ in both cases, suggesting an increased Ni-Ni distance in the reduced enzyme.