n	Fe	L	R	$2\sigma^2$	R_{Cx}(Å)	*EF*	Φ
			Å	Å^2	Å	eV	x10^3
jHmd-wt							
2	Fe	C[a]	1.776(3)	0.0053(8)	1.16(1)	-1.9(7)	0.1691
1	Fe	C	1.91(1)	0.0053(8)			
1	Fe	O	2.49(7)	0.004(4)			
1	Fe	N	2.05(1)	0.0053(8)			
1	Fe	S	2.304(7)	0.008(3)			
2	Fe	O[a]	2.936(8)	0.004(1)			
jHmd-CN							
2	Fe	C[a]	1.76(1)	0.005(1)	1.16(2)	-5(1)	0.4754
1	Fe	C[b]	2.10(2)	0.0246(1)	1.04(3)		
1	Fe	O	1.88(6)	0.004(2)			
1	Fe	S	2..33(2)	0.019(2)			
2	Fe	O[a]	2.920(9)	0.009(1)			
1	Fe	N[b]	3.14(1)	0.003(1)			
(A): $Fe(II)(edt)(CO)_2(PMe3)_2$							
2	Fe	C[a]	1.782(6)	0.006(1)	1.16(1)	-5.3(5)	0.1902
2	Fe	S	2.32(3)	0.004(7)			
2	Fe	P	2.26(4)	0.004(7)			
2	Fe	O[a]	2.946(6)	0.007(1)			
(B): $K_2[Fe(0)(CN)_2(CO)_3]$							
3	Fe	C[a]	1.764(3)	0.0010(8)	1.163(9)	-1.8(4)	0.1578
2	Fe	C[b]	1.865(6)	0.0010(8)	1.18(1)		
3	Fe	O[a]	2.927(3)	0.0010(4)			
2	Fe	N[b]	3.048(6)	0.0010(4)			
(C): $K[Fe(0)(CN)(CO)_4]$							
4	Fe	C[a]	1.797(4)	0.0068(8)	1.156(9)	-1.2(5)	0.1830
1	Fe	C[b]	1.94(2)	0.0068(8)	1.16(3)		
4	Fe	O[a]	2.952(5)	0.0080(6)			
1	Fe	N[b]	3.10(2)	0.0080(6)			
(D): $K_3[Fe(III)CN_6]$							
6	Fe	C[b]	1.932(2)	0.0040(4)	1.163(5)	-4.6(4)	0.1535
6	Fe	N[b]	3.095(3)	0.0057(4)			
(E): $K_4[Fe(II)CN_6]$							
6	Fe	C[b]	1.911(3)	0.0045(5)	1.168(6)	-3.6(4)	0.1972
6	Fe	N[b]	3.079(3)	0.0047(4)			

Tab. S1 The table shows the parameter extracted from the structure-based EXAFS modeling of jHmd-wt and the compounds A-F. The numbers (n) of donor atoms (L), their distance to the iron ion (R), the corresponding Debye-Waller factor ($2\sigma^2$), the C–O or C–N bond length (R_{CX}), the Fermi energy for all shells (EF), and the fit index (Φ), indicating the quality of the model. The model of jHmd-CN obtained from the crystallographic data reported by Shima et al. does not contain the acyl-carbon ligand. Therefore its spectrum is not included in the XANES analysis

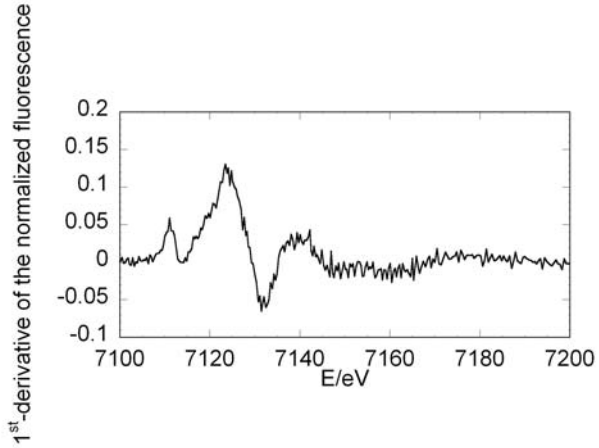

Fig. S1 jHmd-CN: 1st derivative of the experimental XANES.

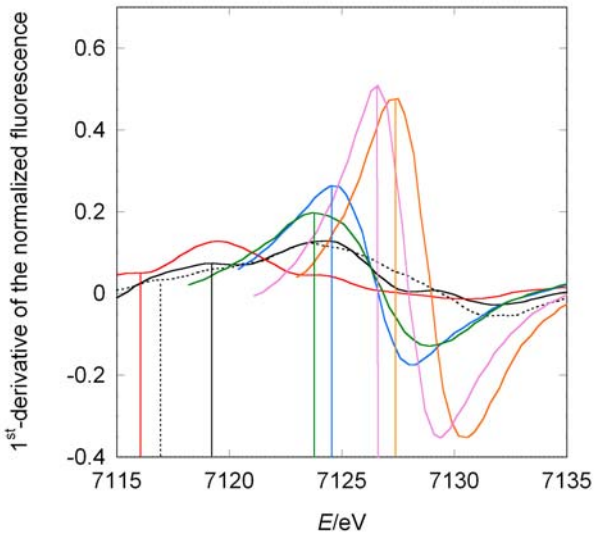

Fig. S2 First derivative of the XANES for the model compounds, jHmd-wt and jHmd-CN. The edge positions are indicated by vertical lines. Black line: jHmd-wt; black broken line: jHmd-CN; red line: **A**; blue line: **B**; green line: **C**; orange line: **D**; purple line: **E**.

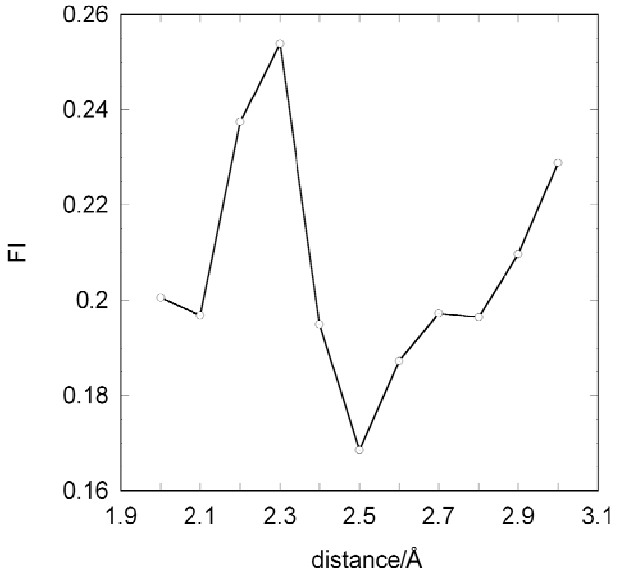

Fig. S3 The figure shows the dependency of the Fit Index (FI) on the Fe-O distance. Apart from the Fe-O distance all parameters were refined as indicated in Tab S1. Two local minima, one at 2.1 Å the other at 2.5 Å, can be identified. The assumption of an oxygen atom at 2.5 Å, representing a potential water ligand, results in the best fit.

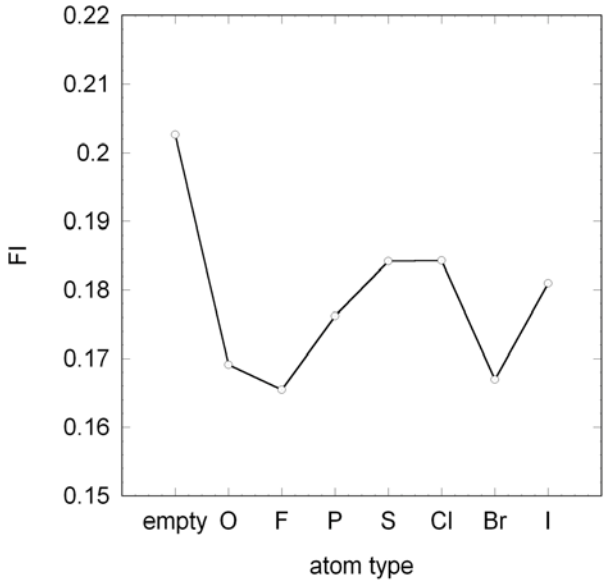

Fig. S4 The figure shows the trend of the Fit Indexes (FI) with respect to the atom type at the "solvent-oxygen" position. All parameters were refined as indicated in Tab S1, but no ligand (empty) or an O, F, P, S, Cl, Br or I ligand were modelled. The atom types are ordered according to their atomic number. For fluorine we obtain a rather small Debye-Waller factor (0.003 Å^2), for bromine a quite large one (0.016 Å^2) similar to other ligands and for oxygen a moderate one (0.005 Å^2) similar to the carbon of the CO-groups. Therefore, we stick to the assumption of an oxygen ligand.

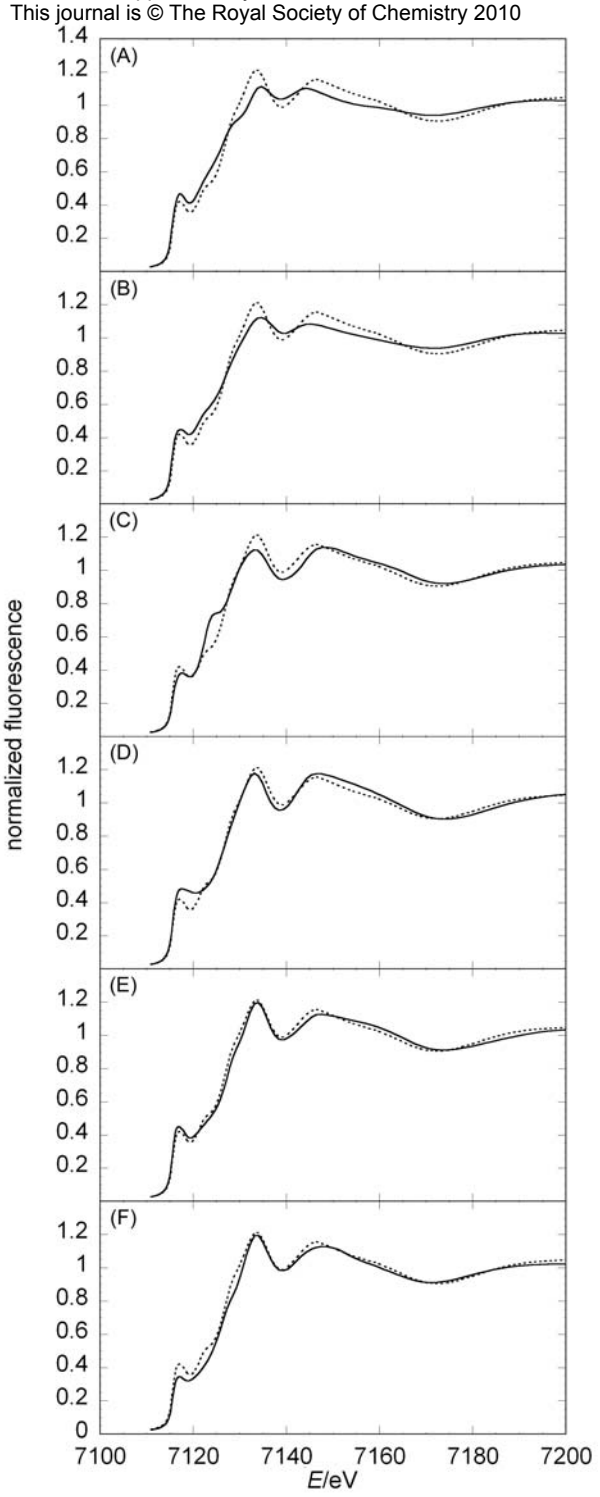

Fig. S5 Comparison between jHmd-wt XANES simulation in the full coordination and omission of single ligands in the simulations. (A) CO1 omitted, (B) CO2 omitted, (C) acyl-C of the cofactor omitted, (D) pyridol-N of the cofactor omitted, (E) cys176-S omitted, (F) Oxygen omitted

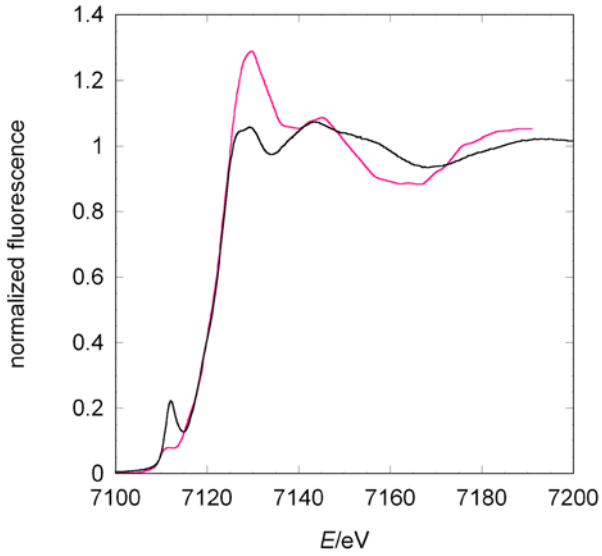

Fig. S6 Comparison between the XANES spectra of jHmd-wt and HoxC subunit. (NiFe(II)-hydrogen-sensing protein from *Ralstonia eutropha*). jHmd-wt rising edge is overlapping with HoxC's. XANES data for isolated HoxC subunit of the hydrogen-sensing hydrogenase from *Ralstonia eutropha* were extracted from [37] by DataThief III (http://www.datathief.org).

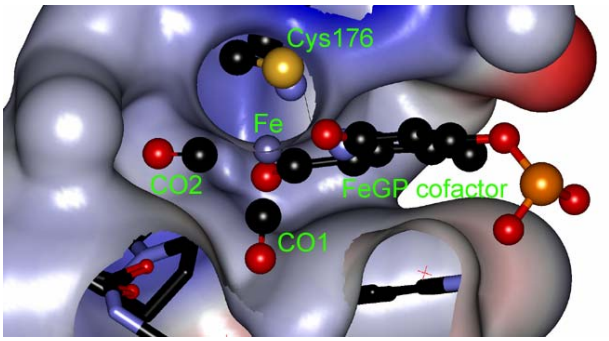

Fig. S7 FeGP binding pocket in jHmd-wt. The iron ion and the ligands are shown in ball and stick representation, while the surrounding aminoacids are shown as electrostatic potential surface. The carbon monoxide CO1 is encircled by Cys204, Val205, Pro206, Trp148 and His14. CO2 is encircled by His201, Pro202 and Gly203.