Electronic Supplementary Information for Dalton Transactions

SUPPORTING INFORMATION FOR

Experimental charge density in an oxidized trinuclear iron complex using 15 K synchrotron and 100 K conventional single crystal X-ray diffraction

by

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Residual density maps

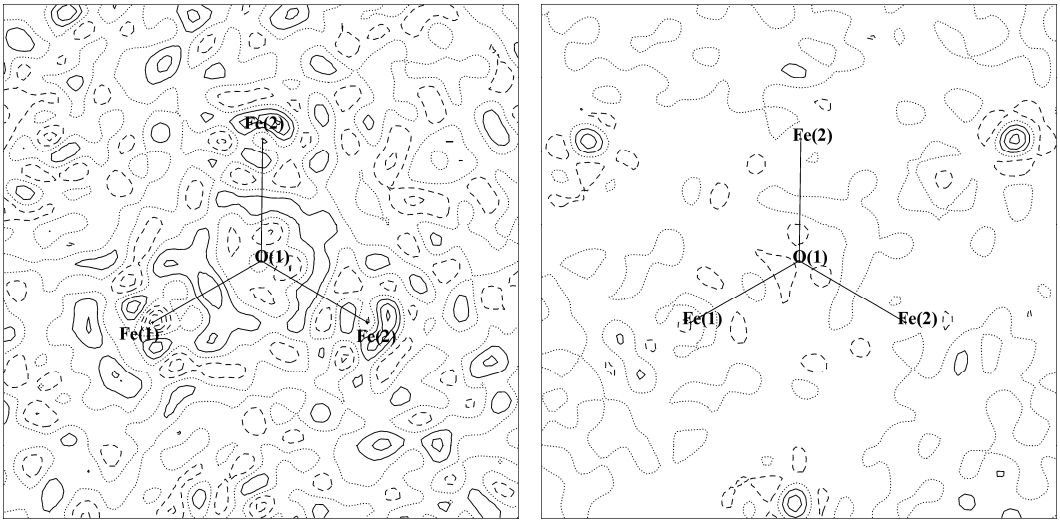

Figure S1. Residual density maps from synchrotron (left) and conventional (right) models using a resolution of 0.9 Å^{-1}. Contours as in Figure 2a.

Topological analysis

Table S1A. Synchrotron model. The values shown are: the density at the bcp, $\rho_b(r)$ in e Å^{-3}; the Laplacian at the bcp, $\nabla^2\rho(r)$, in e Å^{-5}; the inter-nuclear distance, $d_{1\text{-}2}$, in Å; the distance from the first atom to the bcp, $d_{1\text{-bcp}}$, in Å; the three eigenvalues of the Hessian matrix, $\lambda_{1\text{-}3}$, in e Å^{-5}; the ellipticity, ε.

Bond	$\rho_b(r)$	$\nabla^2\rho(r)$	d_{1-2}	d_{1-bcp}	d_{2-bcp}	λ_1	λ_2	λ_3	ε
FE(1)-O(1)	0.576(8)	12.88(1)	1.945	0.994	0.951	-3.78	-3.5	20.16	0.08
FE(1)-O(11)	0.469(4)	10.30(1)	2.035	1.021	1.015	-3.02	-2.87	16.19	0.05
FE(1)-O(21)	0.478(5)	10.53(1)	2.015	1.012	1.003	-3.05	-2.85	16.43	0.07
FE(1)-O(1A)	0.493(3)	10.95(1)	1.999	1.001	0.998	-3.02	-2.95	16.92	0.02
FE(2)-O(1)	0.620(5)	14.41(1)	1.916	0.969	0.947	-3.99	-3.77	22.18	0.06
FE(2)-O(12)	0.434(4)	9.87(1)	2.036	1.018	1.019	-2.65	-2.48	15	0.07
FE(2)-O(22)	0.463(4)	10.37(1)	2.032	1.017	1.016	-2.87	-2.77	16.01	0.04
FE(2)-O(31)	0.469(4)	10.48(1)	2.022	1.014	1.008	-2.89	-2.76	16.13	0.05
FE(2)-O(41)	0.425(4)	9.93(1)	2.031	1.017	1.015	-2.56	-2.34	14.82	0.1
FE(2)-O(2A)	0.448(4)	10.17(1)	2.035	1.020	1.015	-2.69	-2.57	15.43	0.05
O(11)-C(11)	2.76(4)	-24.9(2)	1.255	0.755	0.500	-25.83	-23.49	24.41	0.1
O(12)-C(11)	2.78(4)	-26.3(2)	1.255	0.760	0.495	-25.93	-24.2	23.85	0.07
O(21)-C(21)	2.82(4)	-31.1(2)	1.253	0.768	0.486	-27.05	-26.84	22.84	0.01
O(22)-C(21)	2.74(4)	-27.1(2)	1.259	0.766	0.493	-27.16	-23.65	23.75	0.15
O(31)-C(31)	2.81(2)	-26.95(8)	1.260	0.747	0.513	-26.93	-24.28	24.25	0.11
O(41)-C(41)	2.84(2)	-33.1(1)	1.253	0.759	0.495	-29.46	-25.96	22.33	0.13
O(1A)-C(1A)	2.48(3)	-18.4(1)	1.288	0.771	0.517	-21.94	-20.57	24.07	0.07
O(1B)-C(1A)	2.91(3)	-26.0(1)	1.229	0.739	0.490	-27.02	-24.42	25.46	0.11
O(2A)-C(2A)	2.79(4)	-27.7(2)	1.265	0.745	0.520	-26.05	-25.61	23.96	0.02
O(2B)-C(2A)	2.79(4)	-26.6(2)	1.247	0.761	0.486	-27.25	-23.69	24.3	0.15
N(4)-C(4A)	2.44(3)	-20.1(1)	1.352	0.751	0.601	-21.17	-19.25	20.3	0.1
N(4)-C(4E)	2.30(3)	-18.5(1)	1.347	0.786	0.562	-18.98	-17.19	17.64	0.1
C(4A)-C(4B)	2.31(3)	-19.18(8)	1.379	0.717	0.662	-18.98	-15.78	15.58	0.2
C(4B)-C(4C)	2.24(3)	-18.79(9)	1.399	0.734	0.665	-18.11	-15.99	15.31	0.13
C(4C)-C(4D)	2.28(3)	-18.03(9)	1.390	0.733	0.657	-18.36	-15.48	15.82	0.19
C(4D)-C(4E)	2.21(3)	-16.45(8)	1.394	0.709	0.686	-17.88	-14.7	16.13	0.22
C(4E)-C(4F)	1.76(3)	-9.51(7)	1.494	0.800	0.694	-12.26	-12.09	14.84	0.01

Table S1B. Conventional model. The values shown are: the density at the bcp, $\rho_b(r)$ in e Å^{-3}; the Laplacian at the bcp, $\nabla^2\rho(r)$, in e Å^{-5}; the inter-nuclear distance, $d_{1\text{-}2}$, in Å; the distance from the first atom to the bcp, $d_{1\text{-bcp}}$, in Å; the three eigenvalues of the Hessian matrix, $\lambda_{1\text{-}3}$, in e Å^{-5}; the ellipticity, ε.

Bond	$\rho_b(r)$	$\nabla^2\rho(r)$	d_{1-2}	d_{1-bcp}	d_{2-bcp}	λ_1	λ_2	λ_3	ε

FE(1)-O(1)	0.639(3)	11.704(7)	1.947	0.984	0.962	-4.37	-4.06	20.14	0.08
FE(1)-O(11)	0.519(2)	10.132(3)	2.033	1.016	1.016	-3.27	-2.88	16.28	0.14
FE(1)-O(21)	0.533(3)	10.448(3)	2.013	1.007	1.007	-3.37	-2.93	16.75	0.15
FE(1)-O(1A)	0.587(2)	10.867(3)	2.001	1.007	0.995	-3.87	-3.56	18.29	0.09
FE(2)-O(1)	0.697(2)	13.506(7)	1.916	0.971	0.945	-4.57	-4.47	22.55	0.02
FE(2)-O(12)	0.486(2)	9.860(5)	2.038	1.011	1.027	-2.84	-2.63	15.33	0.08
FE(2)-O(22)	0.495(2)	10.025(5)	2.032	1.012	1.019	-2.99	-2.61	15.63	0.15
FE(2)-O(31)	0.499(2)	10.239(5)	2.021	1.008	1.013	-3.02	-2.66	15.92	0.14
FE(2)-O(41)	0.489(2)	10.314(5)	2.030	1.004	1.026	-2.84	-2.53	15.69	0.12
FE(2)-O(2A)	0.525(2)	9.828(5)	2.035	1.013	1.022	-3.20	-3.05	16.08	0.05
O(11)-C(11)	2.71(2)	-26.1(1)	1.252	0.816	0.436	-24.89	-23.73	22.48	0.05
O(12)-C(11)	2.71(2)	-28.1(1)	1.254	0.814	0.441	-24.50	-23.66	20.02	0.04
O(21)-C(21)	2.69(2)	-24.1(1)	1.251	0.821	0.430	-24.94	-24.14	24.93	0.03
O(22)-C(21)	2.71(2)	-29.2(1)	1.258	0.815	0.443	-25.06	-23.43	19.26	0.07
O(31)-C(31)	2.729(6)	-29.40(5)	1.257	0.816	0.441	-25.15	-23.72	19.46	0.06
O(41)-C(41)	2.713(6)	-27.56(5)	1.251	0.814	0.437	-25.60	-23.69	21.73	0.08
O(1A)-C(1A)	2.57(1)	-29.48(6)	1.287	0.807	0.480	-22.54	-20.31	13.37	0.11
O(1B)-C(1A)	2.91(1)	-30.48(8)	1.230	0.794	0.436	-27.48	-24.19	21.18	0.14
O(2A)-C(2A)	2.74(2)	-31.2(1)	1.262	0.815	0.447	-24.84	-23.65	17.30	0.05
O(2B)-C(2A)	2.80(2)	-29.0(1)	1.245	0.809	0.436	-26.04	-24.38	21.41	0.07
O(99)-H(99A)	2.51(2)	-32.2(1)	0.969	0.734	0.235	-36.40	-35.83	39.99	0.02
O(99)-H(99B)	2.328(7)	-23.65(2)	0.969	0.719	0.250	-32.70	-30.87	39.92	0.06
N(4)-C(4A)	2.41(2)	-23.98(1)	1.350	0.765	0.585	-20.52	-17.93	14.46	0.14
N(4)-C(4E)	2.39(2)	-25.66(8)	1.345	0.788	0.557	-20.33	-17.63	12.30	0.15
N(4)-H(4)	1.94(5)	-29.6(4)	1.036	0.807	0.230	-29.77	-27.42	27.57	0.09
C(11)-H(11)	1.80(1)	-18.34(5)	1.083	0.755	0.328	-18.53	-17.32	17.51	0.07
C(21)-H(21)	1.80(1)	-18.54(2)	1.083	0.756	0.327	-18.72	-17.32	17.51	0.08
C(31)-H(31)	1.86(1)	-19.92(5)	1.083	0.768	0.315	-19.67	-18.40	18.14	0.07
C(41)-H(41)	1.76(1)	-18.13(2)	1.083	0.754	0.330	-18.28	-16.94	17.09	0.08
C(1A)-H(1A)	1.70(1)	-16.18(2)	1.083	0.747	0.336	-17.18	-15.90	16.90	0.08
C(2A)-H(2A)	1.79(1)	-17.90(2)	1.083	0.755	0.329	-18.55	-16.92	17.57	0.10
C(4A)-C(4B)	2.26(2)	-21.66(5)	1.376	0.729	0.647	-17.78	-14.53	10.66	0.22
C(4A)-H(4A)	1.80(1)	-18.12(2)	1.083	0.765	0.318	-19.08	-17.74	18.70	0.08
C(4B)-C(4C)	2.24(2)	-22.05(5)	1.394	0.742	0.651	-18.23	-14.74	10.91	0.24
C(4B)-H(4B)	1.75(1)	-16.75(3)	1.083	0.759	0.324	-18.09	-17.09	18.43	0.06
C(4C)-C(4D)	2.27(2)	-22.78(8)	1.388	0.802	0.586	-17.46	-14.56	9.24	0.20
C(4C)-H(4C)	1.74(1)	-17.21(3)	1.083	0.753	0.330	-17.98	-16.81	17.59	0.07
C(4D)-C(4E)	2.23(2)	-20.03(4)	1.393	0.699	0.693	-17.43	-14.22	11.61	0.23
C(4D)-H(4D)	1.78(1)	-16.96(3)	1.083	0.764	0.319	-18.00	-17.80	18.83	0.01
C(4E)-C(4F)	1.76(2)	-12.71(6)	1.491	0.857	0.634	-11.72	-11.20	10.21	0.05
C(4F)-H(4FA)	1.75(2)	-14.01(7)	1.061	0.722	0.339	-16.77	-15.63	18.39	0.07
C(4F)-H(4FB)	1.70(2)	-13.66(4)	1.061	0.712	0.349	-16.25	-14.76	17.35	0.10
C(4F)-H(4FC)	1.73(2)	-14.23(3)	1.061	0.716	0.345	-16.80	-15.11	17.68	0.11

XDFFT output

Table S2A. Synchrotron model

	PK(1)	is 0.07 A from Fe(2)	0.2809	0.3340	0.8507	0.71
	PK(2)	is 1.00 A from Fe(1)	0.0193	0.2500	1.0299	0.65
	PK(3)	is 0.39 A from O(22)	0.4624	0.3876	1.0187	0.62
44	PK(4)	.....	0.3019	0.2404	0.1645	0.60
	PK(5)	is 0.97 A from Fe(1)	0.1873	0.2500	1.0158	0.60
45	PK(6)	.....	0.4722	0.2500	0.7172	0.60
46	PK(7)	.....	0.1408	0.0188	0.4536	0.53
	PK(8)	is 1.26 A from Fe(2)	0.2519	0.3049	0.7527	0.53
	PK(9)	is 0.47 A from Fe(1)	0.1895	0.2500	1.1150	0.52
	PK(10)	is 0.64 A from C(41)	0.6177	0.2500	0.8485	0.52
47	HL(1)	.....	0.3012	0.2500	0.1986	-0.97
	HL(2)	is 0.69 A from Fe(2)	0.2542	0.3001	0.8523	-0.62
48	HL(3)	.....	0.2744	0.2500	0.7632	-0.61
49	HL(4)	.....	0.4432	0.2500	0.6177	-0.56
	HL(5)	is 0.70 A from Fe(2)	0.3362	0.3609	0.8350	-0.55
50	HL(6)	.....	0.6939	0.2500	0.3691	-0.54
	HL(7)	is 0.84 A from Fe(1)	0.2526	0.2500	1.0976	-0.53
51	HL(8)	.....	0.1958	0.2500	0.3648	-0.52
52	HL(9)	.....	0.3933	0.2500	0.2565	-0.51
53	HL(10)	.....	0.8306	0.2500	0.5306	-0.50

Table S2B. Conventional model

44	PK(1)	.....	0.4451	0.2500	0.6142	0.61
45	PK(2)	.....	0.1338	0.0860	0.0937	0.39
	PK(3)	IS 0.40 A FROM O(11)	-0.0841	0.3044	1.0317	0.31
	PK(4)	IS 0.45 A FROM O(21)	0.2780	0.3287	1.1369	0.27
	PK(5)	IS 0.19 A FROM O(1B)	-0.1982	0.2500	1.4177	0.26
46	PK(6)	.....	0.6684	0.2500	0.3204	0.25
	PK(7)	IS 0.41 A FROM H(41)	0.8138	0.2500	0.8016	0.25
47	PK(8)	.....	0.7451	0.2056	0.4500	0.22
48	PK(9)	.....	0.4473	0.0840	0.6128	0.21
	PK(10)	IS 0.76 A FROM Fe(1)	0.0215	0.2500	1.1118	0.21
	HL(1)	IS 0.54 A FROM O(21)	0.3825	0.3015	1.1780	-0.33
	HL(2)	IS 0.32 A FROM O(1)	0.1922	0.2500	0.9159	-0.29
49	HL(3)	.....	0.0818	0.0819	0.0692	-0.28
50	HL(4)	.....	0.2152	0.2500	0.4022	-0.26
	HL(5)	IS 0.74 A FROM Fe(2)	0.3041	0.3252	0.9187	-0.26
51	HL(6)	.....	0.3212	0.2500	0.2316	-0.25
	HL(7)	IS 0.55 A FROM O(11)	-0.1431	0.3047	1.0370	-0.25
	HL(8)	IS 0.72 A FROM Fe(1)	0.1102	0.2500	1.0294	-0.25
	HL(9)	IS 0.76 A FROM Fe(1)	0.2408	0.2500	1.1000	-0.23
52	HL(10)	.....	0.4466	0.2317	0.5963	-0.22

Atomic charges

Table S3A. Atomic charges, synchrotron model.

Atom	q(Ω)	V001	Atom	q(Ω)	V001
Fe(1)	1.734	54.13	C(4B)	-0.091	79.81
Fe(2)	1.745	54.79	C(4C)	-0.058	76.04
O(1)	-0.777	86.03	C(4D)	-0.143	79.30
O(11)	-1.058	105.03	C(4E)	0.328	55.77
O(12)	-1.115	101.24	C(4F)	-0.214	78.22
O(21)	-1.045	100.50	H(11)	0.194	34.48
O(22)	-1.047	98.36	H(21)	0.190	35.92
O(31)	-1.089	102.55	H(31)	0.103	39.84
O(41)	-0.994	102.62	H(41)	0.095	44.84
O(1A)	-1.014	91.03	H(1A)	0.104	41.01
O(1B)	-0.921	113.73	H(2A)	0.191	35.41
O(2A)	-1.018	96.09	H(4)	0.420	17.73
O(2B)	-1.064	108.46	H(4A)	0.177	35.60
O(99)	-1.141	145.29	H(4B)	0.184	37.15
N(4)	-0.942	82.30	H(4C)	0.175	38.67
C(11)	1.204	46.15	H(4D)	0.180	37.27
C(21)	1.311	48.04	H(4FA)	0.217	35.35
C(31)	1.221	43.92	H(4FB)	0.206	37.41
C(41)	1.434	46.17	H(4FC)	0.198	36.82
C(1A)	1.225	47.62	H(99A)	0.551	14.51
C(2A)	1.289	47.47	H(99B)	0.570	13.59
C(4A)	0.082	71.71			

Table S3B. Atomic charges, conventional model.

Atom	q(Ω)	V_{001}	Atom	q(Ω)	V_{001}
Fe(1)	+1.767	54.79	C(4B)	-0.232	86.48
Fe(2)	+1.773	55.63	C(4C)	-0.221	81.49
O(1)	-0.672	85.09	C(4D)	-0.139	83.58
O(11)	-1.239	108.08	C(4E)	+0.251	56.30
O(12)	-1.190	103.60	C(4F)	-0.271	84.72
O(21)	-1.177	102.55	H(11)	+0.235	37.88
O(22)	-1.189	102.39	H(21)	+0.232	37.46
O(31)	-1.220	105.14	H(31)	+0.238	38.91
O(41)	-1.184	106.06	H(41)	+0.231	45.64
O(1A)	-1.088	92.54	H(1A)	+0.252	40.96
O(1B)	-1.216	118.76	H(2A)	+0.241	39.03
O(2A)	-1.185	98.01	H(4)	+0.591	11.70

O(2B)	-1.236	113.71	H(4A)	+0.280	33.07
O(99)	-1.330	148.23	H(4B)	+0.284	35.21
N(4)	-1.029	84.95	H(4C)	+0.263	41.13
C(11)	+1.500	45.48	H(4D)	+0.291	35.30
C(21)	+1.520	47.40	H(4FA)	+0.265	35.50
C(31)	+1.445	43.96	H(4FB)	+0.241	37.35
C(41)	+1.560	48.16	H(4FC)	+0.242	36.04
C(1A)	+1.353	49.78	H(99A)	+0.540	14.47
C(2A)	+1.419	49.68	H(99B)	+0.548	15.53
C(4A)	+0.074	74.93			

Static deformation maps

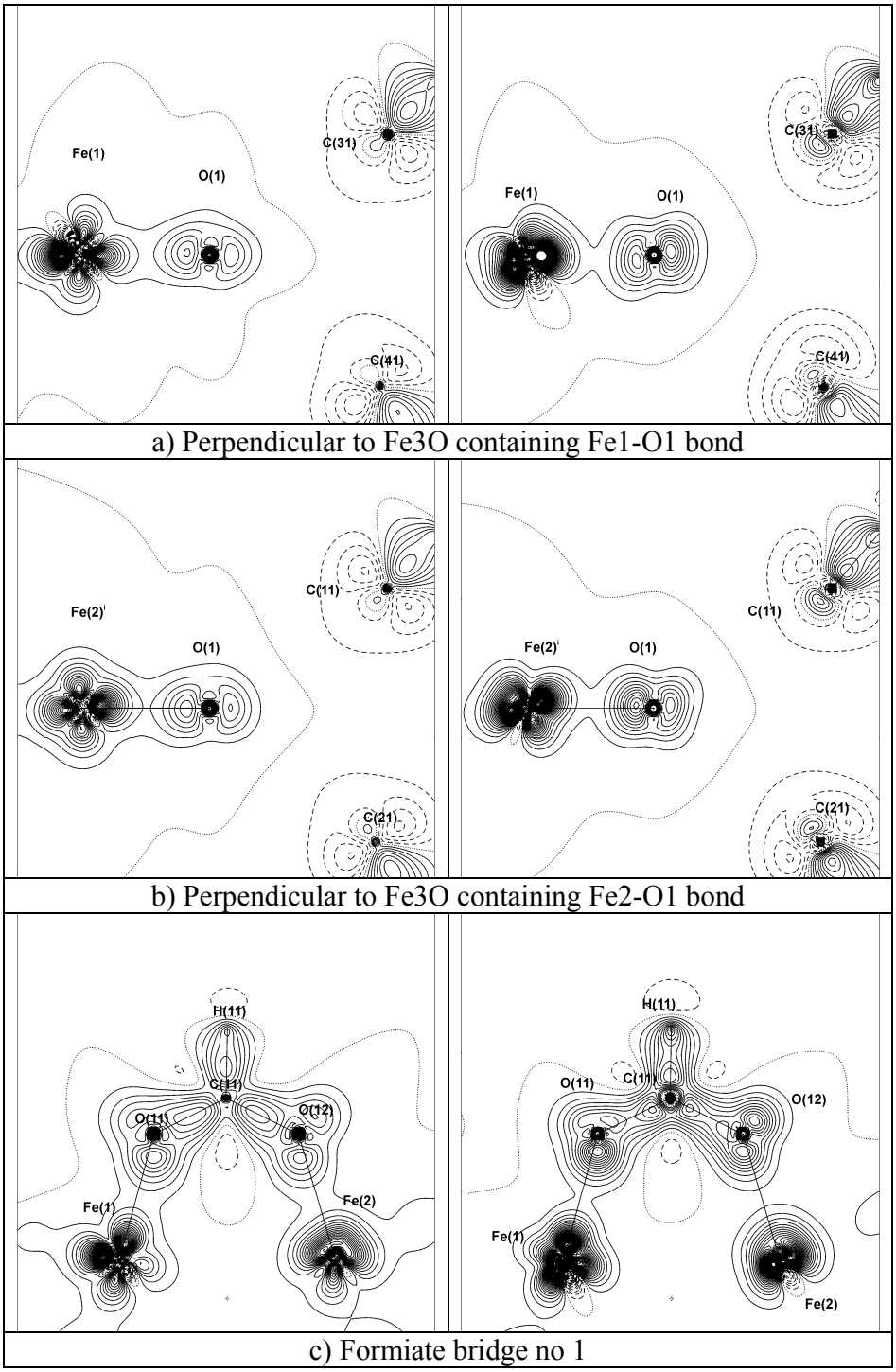

Figure S2. Static deformation density maps in selected planes for conventional model (left) and synchrotron model (right). The contours are as in Figure 2a.

Charge concentrations near O and Fe

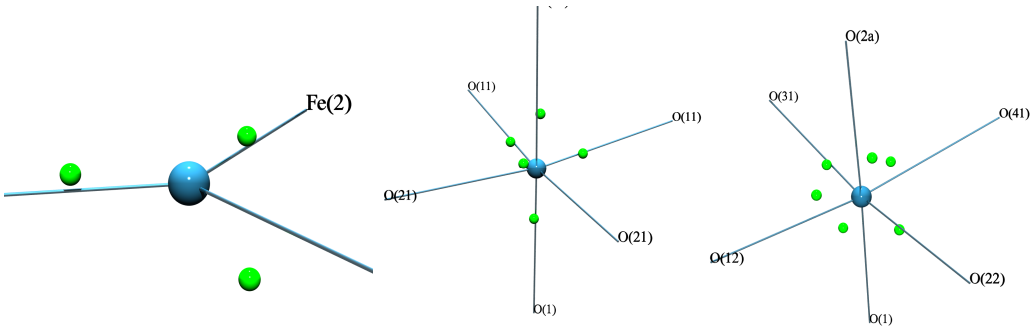

Figure S3A. Distribution of critical points in the Laplacian distribution for O(1), Fe(1) and Fe(2), synchrotron model. Only the (3,-3) critical points in the Laplacian distribution are shown.

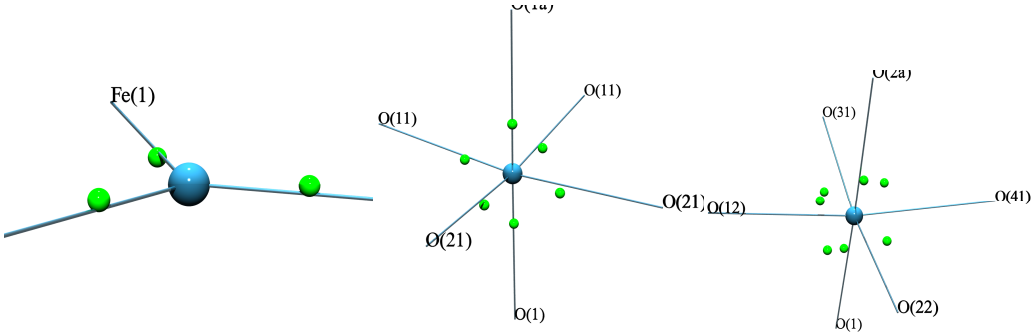

Figure S3B. Distribution of critical points in the Laplacian distribution for O(1), Fe(1) and Fe(2), conventional model.

Plots of energy density vs bond length

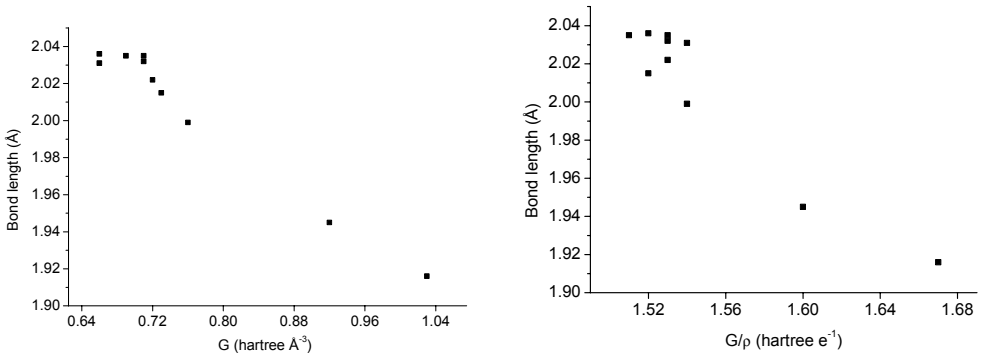

Figure S4A. Synchrotron model, (left) d(Fe-O) vs G and (right) d(Fe-O) vs (G/ρ).

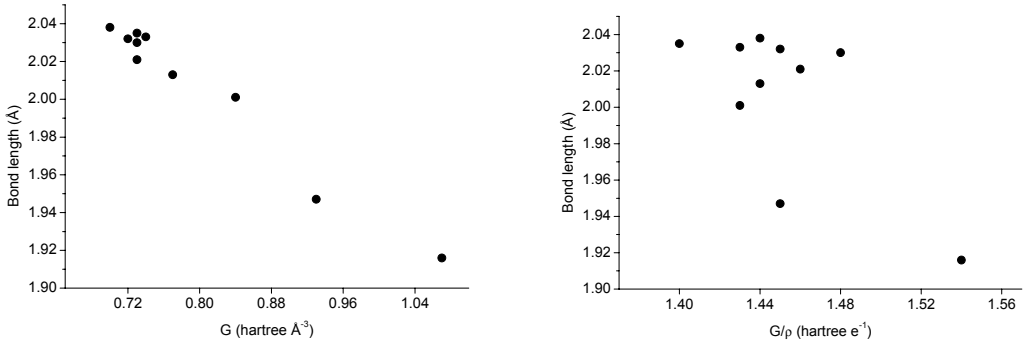

Figure S4B. Conventional model, (left) d(Fe-O) vs G and (right) d(Fe-O) vs (G/ρ).

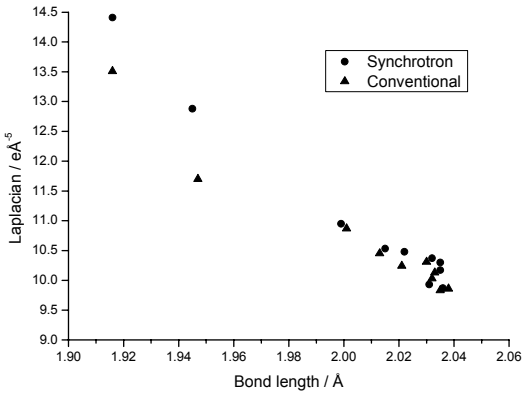

Figure S4C. Laplacian values in the Fe-ligand bcp's for both models.

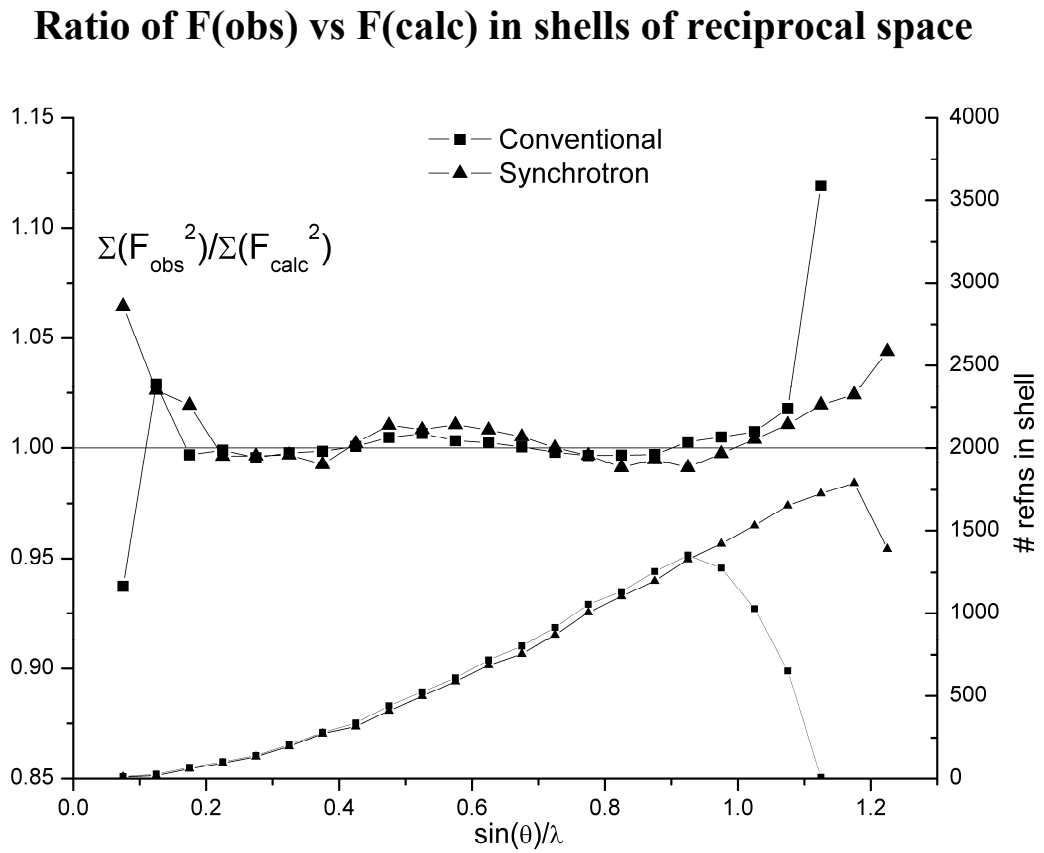

Figure S5. Ratio of the sum of F^2(obs) over the sum of F^2(calc) in shells of reciprocal space. The lower curves show the number of reflections in each shell which is read on the right Y-axis.

It is clear that the ratio stays close to 1 in most of the range. In the LO regime a couple of reflections perturb the curves in different directions for both data sets. In the HO range, the conventional data curve creeps slightly up but the statistics is based on only a small number of reflections and the average values are furthermore small. The number of reflections in the synchrotron data shells at high angle is larger than for the conventional data, and so there is a small but significant increase in this curve with a maximum of around 4-5% for the outermost shell. The synchrotron data was for this calculation truncated to reflections less than 1.25 $Å^{-1}$ in $\sin(\theta)/\lambda$. Above this value, the number of reflections decrease quickly while the ratio increases.

d-orbital populations – synchrotron model

Table S4 d-orbital populations from synchrotron model.

Atom[a]	$d(z^2)$	d(xy)	$d(x^2-y^2)$	d(yz)	d(xz)	SUM
Fe(1)	1.41	1.39	1.00	1.14	1.14	6.08
Fe(2)	1.31	1.06	1.30	1.18	1.23	6.06

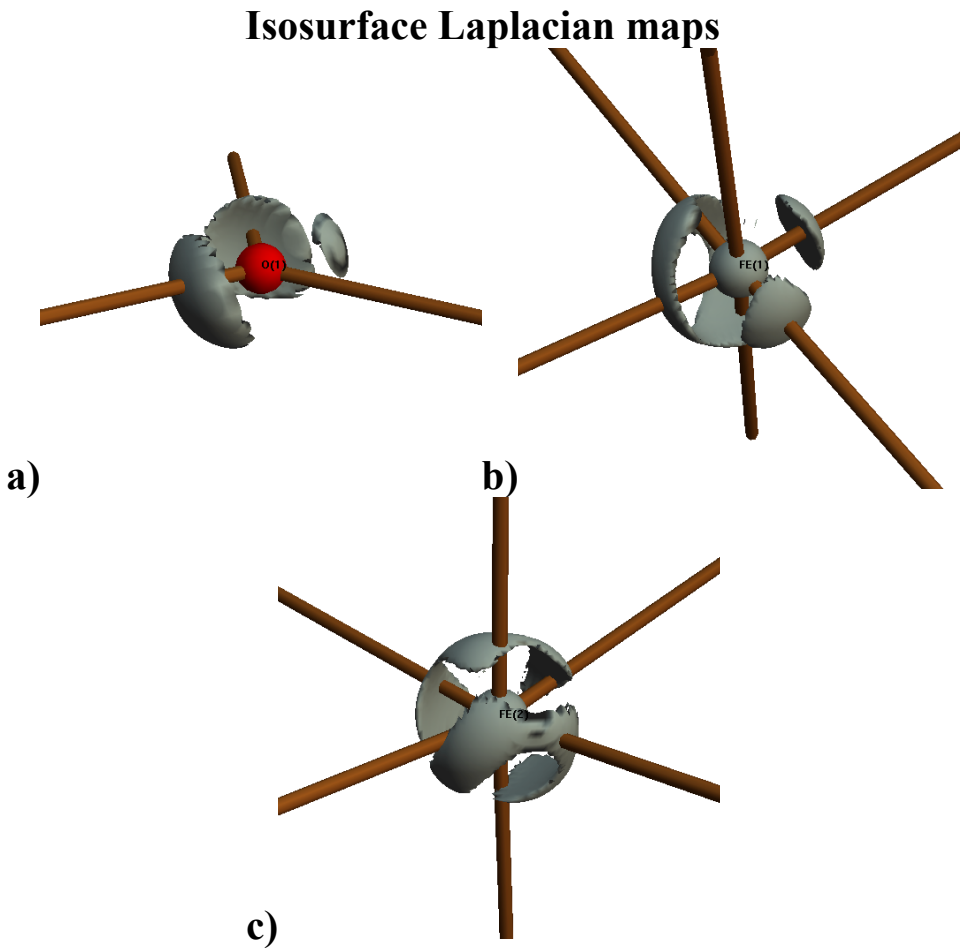

Figure S6. Isosurface Laplacian maps of (a) the central O(1), (b) Fe(1) and (c) Fe(2) from the synchrotron model. The surfaces were drawn at a contour of L(r) = -110 eÅ^{-5} for (a) and L(r) = -750 eÅ^{-5} for (b) and (c).