

# Structure and Population of Complex Ionic Species in FeCl<sub>2</sub> Aqueous Solution by X-Ray Absorption Spectroscopy

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**Table S1.** Parameters of photoelectron multiple scattering paths on the neighbours in the nearest coordination shells around Fe cations in the FeCl<sub>2</sub> samples. All multiple (triangular and linear) scattering paths with a total length up to 5 Å in the two in FeCl<sub>2</sub> (aq) species ( [FeCl(H<sub>2</sub>O)<sub>5</sub>]<sup>+</sup> and [FeCl<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>] schematically presented in Figure 2.) were included in the FEFF model. Following parameters are listed in the table: path degeneracy (N), relative amount of each path (N<sub>rel</sub>), based on relative amount of of the two FeCl<sub>2</sub> (aq) species (uncertainty ±0.3) , half-path length (R), and Debye-Waller factor of each path (σ<sup>2</sup>). Uncertainty of the last digit is given in parentheses. The parameters of multiple scattering paths within the distorted octahedra of nearest neighbors were constrained with the values of structural parameters obtained by modeling the single scattering paths on the same neighbors, listed in Table 1. The best fit is obtained with a total number of O and Cl neighbors constrained to 6, the amplitude reduction factor S<sub>0</sub><sup>2</sup>=0.85, and the shift of the energy origin ΔE<sub>0</sub> = -4 ±1 eV.

MS paths	N* N <sub>rel</sub>	R [Å]	σ <sup>2</sup> [Å <sup>2</sup> ]
1 molL <sup>-1</sup> FeCl <sub>2</sub> aq. solution measured at RT			
Fe-O-O-Fe	16*1.0	3.63(1)	0.011(1)
Fe-O-Cl-Fe	16*0.1	3.80(3)	0.026 (6)
Fe-O-O-Fe	4*1.0	4.20(1)	0.011(1)
Fe-O-Fe-O-Fe	4*1.0	4.20(1)	0.008(1)
Fe-O-Fe-O-Fe	5*1.0	4.20(1)	0.008(1)
Fe-Cl-Cl-Fe	2*0.0	4.62(4)	0.015(3)
Fe-Cl-Fe-Cl-Fe	2*0.0	4.62(4)	0.015(3)

MS paths	N* N <sub>rel</sub>	R [Å]	σ <sup>2</sup> [Å <sup>2</sup> ]
1 molL <sup>-1</sup> FeCl <sub>2</sub> aq. solution measured at T = 30 °C			
Fe-O-O-Fe	16*0.9	3.63(1)	0.011(1)
Fe-O-Cl-Fe	16*0.2	3.83(3)	0.026 (6)
Fe-O-O-Fe	4*1.0	4.20(1)	0.011(1)
Fe-O-Fe-O-Fe	4*1.0	4.20(1)	0.008(1)
Fe-O-Fe-O-Fe	5*1.0	4.20(1)	0.008(1)
Fe-Cl-Cl-Fe	2*0.1	4.68(4)	0.015(3)
Fe-Cl-Fe-Cl-Fe	2*0.1	4.68(4)	0.015(3)
MS paths	N* N <sub>rel</sub>	R [Å]	σ <sup>2</sup> [Å <sup>2</sup> ]
1 molL <sup>-1</sup> FeCl <sub>2</sub> aq. solution measured at T = 40 °C			
Fe-O-O-Fe	16*0.9	3.63(1)	0.011(1)
Fe-O-Cl-Fe	16*0.3	3.82(3)	0.026 (6)

Fe-O-O-Fe	4*1.0	4.20(1)	0.011(1)
Fe-O-Fe-O-Fe	4*1.0	4.20(1)	0.008(1)
Fe-O-Fe-O-Fe	5*1.0	4.20(1)	0.008(1)
Fe-Cl-Cl-Fe	2*0.2	4.68(4)	0.015(3)
Fe-Cl-Fe-Cl-Fe	2*0.2	4.68(4)	0.015(3)

MS paths	N* N <sub>rel</sub>	R [Å]	σ <sup>2</sup> [Å <sup>2</sup> ]
1 molL <sup>-1</sup> FeCl <sub>2</sub> aq. solution measured at T = 50 °C			
Fe-O-O-Fe	16*0.8	3.63(1)	0.011(1)
Fe-O-Cl-Fe	16*0.5	3.82(3)	0.028 (6)
Fe-O-O-Fe	4*1.0	4.20(1)	0.011(1)
Fe-O-Fe-O-Fe	4*1.0	4.20(1)	0.008(1)
Fe-O-Fe-O-Fe	5*0.9	4.20(1)	0.008(1)
Fe-Cl-Cl-Fe	2*0.4	4.68(4)	0.017(3)
Fe-Cl-Fe-Cl-Fe	2*0.4	4.68(4)	0.017(3)
MS paths	N* N <sub>rel</sub>	R [Å]	σ <sup>2</sup> [Å <sup>2</sup> ]
1 molL <sup>-1</sup> FeCl <sub>2</sub> aq. solution measured at T = 60 °C			
Fe-O-O-Fe	16*0.9	3.63(1)	0.012(1)
Fe-O-Cl-Fe	16*0.6	3.82(3)	0.029 (6)
Fe-O-O-Fe	4*1.0	4.20(1)	0.012(1)
Fe-O-Fe-O-Fe	4*1.0	4.20(1)	0.008(1)
Fe-O-Fe-O-Fe	5*0.9	4.20(1)	0.008(1)
Fe-Cl-Cl-Fe	2*0.5	4.68(4)	0.018(3)
Fe-Cl-Fe-Cl-Fe	2*0.5	4.68(4)	0.018(3)

MS paths	N* N <sub>rel</sub>	R [Å]	σ <sup>2</sup> [Å <sup>2</sup> ]
1 molL <sup>-1</sup> FeCl <sub>2</sub> aq. solution measured at T = 80 °C			
Fe-O-O-Fe	16*0.8	3.63(1)	0.012(1)
Fe-O-Cl-Fe	16*0.6	3.82(3)	0.029 (6)
Fe-O-O-Fe	4*1.0	4.20(1)	0.011(1)
Fe-O-Fe-O-Fe	4*1.0	4.20(1)	0.008(1)
Fe-O-Fe-O-Fe	5*0.9	4.20(1)	0.008(1)
Fe-Cl-Cl-Fe	2*0.5	4.68(4)	0.017(3)
Fe-Cl-Fe-Cl-Fe	2*0.5	4.68(4)	0.017(3)
MS paths	N* N <sub>rel</sub>	R [Å]	σ <sup>2</sup> [Å <sup>2</sup> ]
2 molL <sup>-1</sup> FeCl <sub>2</sub> aq. solution measured at RT			
Fe-O-O-Fe	16*0.8	3.63(1)	0.009(1)
Fe-O-Cl-Fe	16*0.6	3.83(3)	0.029 (6)
Fe-O-O-Fe	4*1.0	4.21(1)	0.009(1)
Fe-O-Fe-O-Fe	4*1.0	4.21(1)	0.007(1)
Fe-O-Fe-O-Fe	5*0.9	4.21(1)	0.007(1)
Fe-Cl-Cl-Fe	2*0.5	4.71(4)	0.021(3)
Fe-Cl-Fe-Cl-Fe	2*0.5	4.71(4)	0.021(3)
MS paths	N* N <sub>rel</sub>	R [Å]	σ <sup>2</sup> [Å <sup>2</sup> ]
3 molL <sup>-1</sup> FeCl <sub>2</sub> aq. solution measured at RT			

Fe-O-O-Fe	16*0.5	3.63(1)	0.009(1)
Fe-O-Cl-Fe	16*1.0	3.86(3)	0.030(6)
Fe-O-O-Fe	4*1.0	4.20(1)	0.009(1)
Fe-O-Fe-O-Fe	4*1.0	4.20(1)	0.007(1)
Fe-O-Fe-O-Fe	5*0.8	4.20(1)	0.007(1)
Fe-Cl-Cl-Fe	2*1.0	4.75(4)	0.019(3)
Fe-Cl-Fe-Cl-Fe	2*1.0	4.75(4)	0.019(3)

MS paths	N* Nrel	R [Å]	$\sigma^2$ [Å <sup>2</sup> ]
4 molL <sup>-1</sup> FeCl <sub>2</sub> aq. solution measured at RT			
Fe-O-O-Fe	16*0.5	3.63(1)	0.009(1)
Fe-O-Cl-Fe	16*1.0	3.86(3)	0.030(6)
Fe-O-O-Fe	4*1.0	4.20(1)	0.009(1)
Fe-O-Fe-O-Fe	4*1.0	4.20(1)	0.007(1)
Fe-O-Fe-O-Fe	5*0.8	4.20(1)	0.007(1)
Fe-Cl-Cl-Fe	2*1.0	4.75(4)	0.019(3)
Fe-Cl-Fe-Cl-Fe	2*1.0	4.75(4)	0.019(3)