1 Tables

The tables show the total energies and selected bond distances of the optimised structures.

Table 1: Selected bond distances and total energies of the optimised structures of the different states of $[Fe_2(OCH(CH_2N)_2(CH_2CO_2)_4(H_2O)_3Cl]\cdot H_2O$ (B3LYP functional, SVP basis set)

r/pm	$^{(1)}A$	^{11}A	$^{(1)}A^{low-spin}$	$^{3}A^{low-spin}$
Fe^1-Fe^2	369.1	370.4	360.1	361.0
Fe^1-O^1	207.5	208.6	196.4	196.6
Fe^2-O^1	201.7	202.6	191.7	192.1
Fe^1-N^1	226.2	226.4	199.7	199.7
Fe^1-O^2	194.9	194.9	184.0	184.0
Fe^1-O^4	193.6	193.4	187.8	187.8
Fe^1-O^{10}	210.5	210.6	200.4	200.3
Fe^1-O^{11}	208.5	208.5	204.9	204.9
Fe^2-N^2	231.9	232.2	205.0	205.1
Fe^2-O^6	199.7	199.7	191.8	191.9
Fe^2-O^8	192.2	192.2	190.2	190.1
Fe^2-O^{12}	227.5	226.9	205.6	205.8
Fe^2-Cl	231.7	231.7	230.1	229.9
$H^{20}-O^6$	182.6	182.6	249.5	247.4
$H^{21}-O^7$	225.0	225.3	180.6	181.0
$H^{14}-Cl$	208.3	208.5	200.7	200.7
E/Hartree	−4504.631877	−4504.630037	−4504.590991	−4504.590877
E/eV	0.0	0.050	1.113	1.116

Table 2: Selected bond distances and total energies of the optimised structures of the different states of $[Fe_2(OCH(CH_2N)_2(CH_2CO_2)_4(H_2O)_3Cl]\cdot H_2O$ (BP functional, SVP basis set)

r/pm	$^{(1)}A$	^{11}A	$^{(1)}A^{low-spin}$	$^{3}A^{low-spin}$
Fe^1-Fe^2	365.3	369.3	352.5	354.4
Fe^1-O^1	206.1	210.1	193.0	193.8
Fe^2-O^1	200.3	202.0	189.5	190.2
Fe^1-N^1	228.9	229.7	197.8	197.7
Fe^1-O^2	197.0	197.3	185.2	185.1
Fe^1-O^4	194.4	194.1	188.6	188.5
Fe^1-O^{10}	212.5	212.9	201.9	202.0
Fe^1-O^{11}	207.0	207.2	205.1	205.2
Fe^2-N^2	234.1	235.2	202.3	202.8
Fe^2-O^6	201.7	201.4	191.7	191.7
Fe^2-O^8	193.2	193.2	191.2	190.9
Fe^2-O^{12}	230.2	229.7	206.7	206.6
Fe^2-Cl	231.7	231.2	231.0	230.3
$H^{20}-O^6$	185.4	187.0	257.0	257.5
$H^{21}-O^7$	195.7	194.9	173.4	173.6
$H^{14}-Cl$	204.8	206.2	196.3	197.3
E/Hartree	−4506.197071	−4506.192413	−4506.196589	−4506.195595
E/eV	0.0	0.127	0.013	0.040

Table 3: Selected bond distances and total energies of the optimised structures of the different states of $[Fe_2(OCH(CH_2N)_2(CH_2CO_2)_4(H_2O)_3Cl]\cdot H_2O$ (B3LYP functional, TZVP basis set)

r/pm	$^{(1)}A$	^{11}A	$^{(1)}A^{low-spin}$	$^{3}A^{low-spin}$
Fe^1-Fe^2	370.8	372.1	365.1	365.7
Fe^1-O^1	206.6	207.7	197.9	198.1
Fe^2-O^1	202.8	203.9	193.1	193.5
Fe^1-N^1	224.9	225.3	199.1	199.2
Fe^1-O^2	194.5	194.4	183.8	183.7
Fe^1-O^4	193.8	193.6	188.0	188.1
Fe^1-O^{10}	210.6	210.7	200.5	200.5
Fe^1-O^{11}	211.9	211.9	206.9	206.9
Fe^2-N^2	229.1	229.4	203.9	204.0
Fe^2-O^6	199.1	199.0	191.9	192.0
Fe^2-O^8	192.4	192.4	190.2	190.0
Fe^2-O^{12}	232.9	232.2	207.1	207.5
Fe^2-Cl	231.2	231.1	230.0	229.9
$H^{20}-O^6$	176.7	176.8	266.3	264.6
$H^{21}-O^7$	351.2	351.1	188.3	188.7
$H^{14}-Cl$	211.7	212.0	201.4	201.4
E/Hartree	−4506.826000	−4506.824105	−4506.779918	−4506.779909
E/eV	0.0	0.052	1.254	1.254

Table 4: Selected bond distances and total energies of the optimised structures of the different states of $[Fe_2(OCH(CH_2N)_2(CH_2CO_2)_4(H_2O)_3Cl]\cdot H_2O$ (BP functional, TZVP basis set)

r/pm	$^{(1)}A$	^{11}A	$^{(1)}A^{low-spin}$	$^{3}A^{low-spin}$
Fe^1-Fe^2	367.4	371.1	358.0	360.5
Fe^1-O^1	205.5	208.8	194.0	194.9
Fe^2-O^1	201.3	203.5	190.6	191.7
Fe^1-N^1	227.0	228.0	197.3	197.3
Fe^1-O^2	196.2	196.4	185.1	184.8
Fe^1-O^4	194.6	194.3	188.8	188.8
Fe^1-O^{10}	212.7	213.0	201.4	201.3
Fe^1-O^{11}	210.7	211.0	207.1	207.4
Fe^2-N^2	230.4	231.2	201.5	202.1
Fe^2-O^6	201.1	200.8	191.8	192.0
Fe^2-O^8	193.6	193.6	191.3	190.9
Fe^2-O^{12}	235.4	234.7	207.9	208.0
Fe^2-Cl	230.7	230.2	230.5	229.7
$H^{20}-O^6$	169.8	170.7	268.9	266.6
$H^{21}-O^7$	333.4	334.9	180.0	180.9
$H^{14}-Cl$	207.2	208.5	196.8	197.5
E/Hartree	−4508.380194	−4508.375498	−4508.378122	−4508.377324
E/eV	0.0	0.128	0.056	0.078

Table 5: Selected bond distances and total energies of the optimised structures of the different states of $[Fe_2(OCH(CH_2N)_2(CH_2CO_2)_4(H_2O)_3Cl]\cdot H_2O$ (TPSS functional, TZVP basis set)

r/pm	$^{(1)}A$	^{11}A	$^{(1)}A^{low-spin}$	$^{3}A^{low-spin}$
Fe^1-Fe^2	366.5	369.6	359.9	361.4
Fe^1-O^1	205.1	207.7	194.6	195.4
Fe^2-O^1	200.7	202.8	191.0	191.9
Fe^1-N^1	223.7	224.6	197.1	197.2
Fe^1-O^2	195.2	195.8	184.5	184.3
Fe^1-O^4	194.4	194.1	188.3	188.4
Fe^1-O^{10}	211.4	211.7	200.3	200.2
Fe^1-O^{11}	210.7	210.8	205.8	206.1
Fe^2-N^2	227.3	227.9	200.9	201.2
Fe^2-O^6	200.3	200.0	191.6	191.8
Fe^2-O^8	193.4	193.4	190.9	190.6
Fe^2-O^{12}	232.3	231.7	206.2	206.6
Fe^2-Cl	230.9	230.5	229.6	229.2
$H^{20}-O^6$	171.9	172.7	272.7	270.1
$H^{21}-O^7$	344.3	344.5	181.3	182.1
$H^{14}-Cl$	207.9	208.8	198.1	198.3
E/Hartree	−4508.094844	−4508.090570	−4508.106980	−4508.106777
E/eV	0.0	0.116	−0.330	−0.325

Table 6: Selected bond distances and total energies of the optimised structures of the different states of $[Fe_2(OCH(CH_2N)_2(CH_2CO_2)_4(H_2O)_3Cl]\cdot H_2O$ (HCTH functional, TZVP basis set)

r/pm	$^{(1)}A$	^{11}A	$^{(1)}A^{low-spin}$	$^{3}A^{low-spin}$
Fe^1-Fe^2	373.1	375.6	363.6	365.7
Fe^1-O^1	207.7	209.3	195.2	197.1
Fe^2-O^1	205.0	207.0	193.9	193.9
Fe^1-N^1	229.9	230.5	198.5	198.1
Fe^1-O^2	194.7	194.8	184.4	184.1
Fe^1-O^4	194.4	194.3	189.2	188.7
Fe^1-O^{10}	216.8	217.2	203.3	203.9
Fe^1-O^{11}	219.4	219.4	214.9	215.1
Fe^2-N^2	234.5	235.2	203.3	204.1
Fe^2-O^6	199.2	199.1	192.4	192.2
Fe^2-O^8	193.0	193.0	191.3	190.8
Fe^2-O^{12}	252.0	249.9	217.2	215.3
Fe^2-Cl	231.2	231.0	231.5	230.3
$H^{20}-O^6$	188.0	188.5	283.5	283.4
$H^{21}-O^7$	340.6	340.6	200.9	203.2
$H^{14}-Cl$	216.9	218.0	200.0	202.4
E/Hartree	−4508.609883	−4508.607119	−4508.520701	−4508.519664
E/eV	0.0	0.075	2.427	2.455

Table 7: Selected bond distances and total energies of the optimised structures of the different states of $[Fe_2(OCH(CH_2N)_2(CH_2CO_2)_4(H_2O)_3Cl]\cdot H_2O$ (B3LYP functional, TZVPP basis set)

r/pm	$^{(1)}$A	^{11}A
Fe^1-Fe^2	369.9	371.2
Fe^1-O^1	206.1	207.2
Fe^2-O^1	202.3	203.5
Fe^1-N^1	225.1	225.4
Fe^1-O^2	193.5	193.5
Fe^1-O^4	192.9	192.8
Fe^1-O^{10}	210.6	210.8
Fe^1-O^{11}	212.3	212.3
Fe^2-N^2	229.5	229.9
Fe^2-O^6	197.9	197.9
Fe^2-O^8	191.7	191.6
Fe^2-O^{12}	235.5	234.7
Fe^2-Cl	230.5	230.4
$H^{20}-O^6$	178.4	178.5
$H^{21}-O^7$	350.4	350.1
$H^{14}-Cl$	209.9	210.3
E/Hartree	−4506.913181	−4506.911245
E/eV	0.0	0.053