

## SUPPLEMENTARY INFORMATION

*Table S1. Caresian co-ordinates (Å).*

### 1 Fe<sub>4</sub><sup>+</sup>

4				
Fe	1	-0.051490	-1.192099	0.019741
Fe	2	-2.293985	0.025066	-0.019697
Fe	3	2.294624	-0.028178	-0.019683
Fe	4	0.050851	1.195212	0.019639

### 2 NH<sub>3</sub>

4				
N	1	-0.020960	-0.017726	-0.043489
H	2	0.956412	-0.111342	-0.274330
H	3	-0.405067	-0.679644	0.613499
H	4	-0.404623	0.915066	-0.034748

### 3 Fe<sub>4</sub>(NH<sub>3</sub>)<sup>+</sup>

8				
Fe	1	0.028221	0.929482	-0.029805
Fe	2	-2.276118	-0.255144	-0.025425
Fe	3	2.252348	-0.374999	-0.025716
Fe	4	-0.054636	-1.506532	0.051750
N	5	0.125167	3.033318	0.070364
H	6	0.968313	3.367918	-0.407851
H	7	0.159575	3.336209	1.049789
H	8	-0.699243	3.449661	-0.375355

### 4 Fe<sub>4</sub>(NH<sub>2</sub>)H<sup>+</sup>

8				
Fe	1	-0.903009	-1.009942	1.673114
Fe	2	1.154999	1.444630	-1.550997
Fe	3	-0.207659	-0.607261	-1.042870
Fe	4	0.417054	0.892868	0.843459
N	5	-1.245813	-2.004901	-0.018821
H	6	-2.238759	-2.081523	-0.274203
H	7	-0.843600	-2.950686	-0.045954
H	8	-0.192970	0.338850	2.461568

### 5 Fe<sub>4</sub>(NH)(H<sub>2</sub>)<sup>+</sup>

8				
Fe	1	0.021992	-0.608414	1.377169
Fe	2	1.416656	1.046441	-0.005680
Fe	3	0.435134	-1.107831	-1.055172
Fe	4	-1.324682	0.841312	-0.282688
N	5	-1.210056	-1.126752	0.000770
H	6	-2.009127	-1.769022	-0.008032
H	7	-1.528871	2.710319	-0.491879
H	8	-2.268224	2.486750	-0.379824

**6 Fe<sub>4</sub>(NH)<sup>+</sup>**

6				
Fe	1	-0.677714	-0.676566	1.280661
Fe	2	1.703286	-0.040320	0.357935
Fe	3	-0.100020	-0.660982	-1.452188
Fe	4	-0.387273	1.396231	-0.072500
N	5	-1.624101	-0.053999	-0.343666
H	6	-2.626562	-0.099453	-0.555946

**7 H<sub>2</sub>**

2				
H	1	0.000000	0.000000	0.3715
H	2	0.000000	0.000000	-0.3715

**8 TS 3/4**

8				
Fe	1	-0.137314	1.005817	0.034643
Fe	2	-2.002337	-0.725333	-0.245927
Fe	3	2.246444	0.183849	-0.212318
Fe	4	0.372497	-1.443490	0.314439
N	5	-1.101089	2.605868	0.270018
H	6	-1.888647	1.073443	0.237957
H	7	-1.567532	3.126043	-0.475909
H	8	-1.297725	3.017545	1.186078

**9 TS 4/5**

8				
Fe	1	-0.403742	-0.450084	1.353684
Fe	2	1.789005	-0.191568	-0.020719
Fe	3	-0.508649	-0.956921	-1.093542
Fe	4	-0.131433	1.519187	-0.235575
N	5	-1.841042	-0.121415	0.109976
H	6	-2.828164	-0.385960	0.230128
H	7	-1.937605	1.170792	-0.375518
H	8	-1.721615	2.129106	-0.724482

**10 Fe<sub>4</sub>(H<sub>2</sub>)<sup>+</sup>**

6				
Fe	1	0.768716	-0.983248	-0.056573
Fe	2	1.529052	1.242637	-1.146284
Fe	3	-1.420284	-1.360419	1.179505
Fe	4	-0.739781	0.898530	0.014502
H	5	-1.562146	2.745834	0.399238
H	6	-2.018113	2.519178	-0.169137

**11** *endo*-Fe<sub>4</sub>N<sup>+</sup>

5				
Fe	1	-0.621312	1.668855	-0.626605
Fe	2	-0.136376	-0.081703	1.882875
Fe	3	-1.022050	-1.373784	-0.766917
Fe	4	1.783557	-0.215811	-0.491982
N	5	-0.014186	0.009072	0.009767

**12** Fe<sub>4</sub>N(H<sub>2</sub>)<sup>+</sup>

7				
Fe	1	-0.114870	1.837138	0.392356
Fe	2	-0.028974	-1.017876	1.564629
Fe	3	-1.436134	-0.643183	-1.058412
Fe	4	1.580905	-0.450074	-0.916257
N	5	-0.008179	-0.020273	-0.019807
H	6	-0.144951	3.672056	0.656446
H	7	0.178106	3.593748	-0.057995

**13** TS 12/14

7				
Fe	1	-0.69961	-1.74813	0.97922
Fe	2	1.40751	-0.12561	0.18754
Fe	3	-0.40438	-0.20355	-1.7596
Fe	4	-0.01513	1.9824	0.51466
N	5	-0.60965	-0.04221	0.15003
H	6	-1.49207	0.85322	0.60097
H	7	-1.77775	1.84779	0.90514

**14** Fe<sub>4</sub>(NH)H<sup>+</sup>

7				
Fe	1	0.206180	1.346445	-0.780775
Fe	2	1.534341	-0.761909	-0.126732
Fe	3	-0.168754	0.265915	1.372397
Fe	4	-1.138979	-1.123149	-0.499202
N	5	-1.472757	0.727654	0.033438
H	6	1.476169	0.876721	0.620306
H	7	-2.419347	1.119845	0.037747

**15** TS 14/16

7				
Fe	1	0.676908	1.128755	0.676245
Fe	2	-1.289081	0.624402	-0.940793
Fe	3	0.841593	-0.907831	-0.761031
Fe	4	-1.000211	-0.827056	1.026196
N	5	2.135805	0.130689	-0.042643
H	6	1.931890	-1.511977	0.284397
H	7	3.158049	0.122111	-0.001932

**16 Fe<sub>4</sub>(NH<sub>2</sub>)<sup>+</sup>**

7

Fe	1	-0.058725	-0.777528	-1.179853
Fe	2	-1.228548	1.197374	-0.006089
Fe	3	0.058326	-0.746614	1.199862
Fe	4	1.228360	1.197635	-0.025341
N	5	0.001457	-2.382292	0.031284
H	6	0.828741	-2.982924	-0.054039
H	7	-0.823697	-2.983589	0.132004