Electronic Supplementary Information

Counterintuitive noncovalent interactions of ammonia with all metal rings of cyclic trinuclear Ag(I) clusters: A DFT study

Athanassios C. Tsipis[a]

[a] Laboratory of Inorganic Chemistry, Department of Chemistry, University of Ioannina 45110, Greece

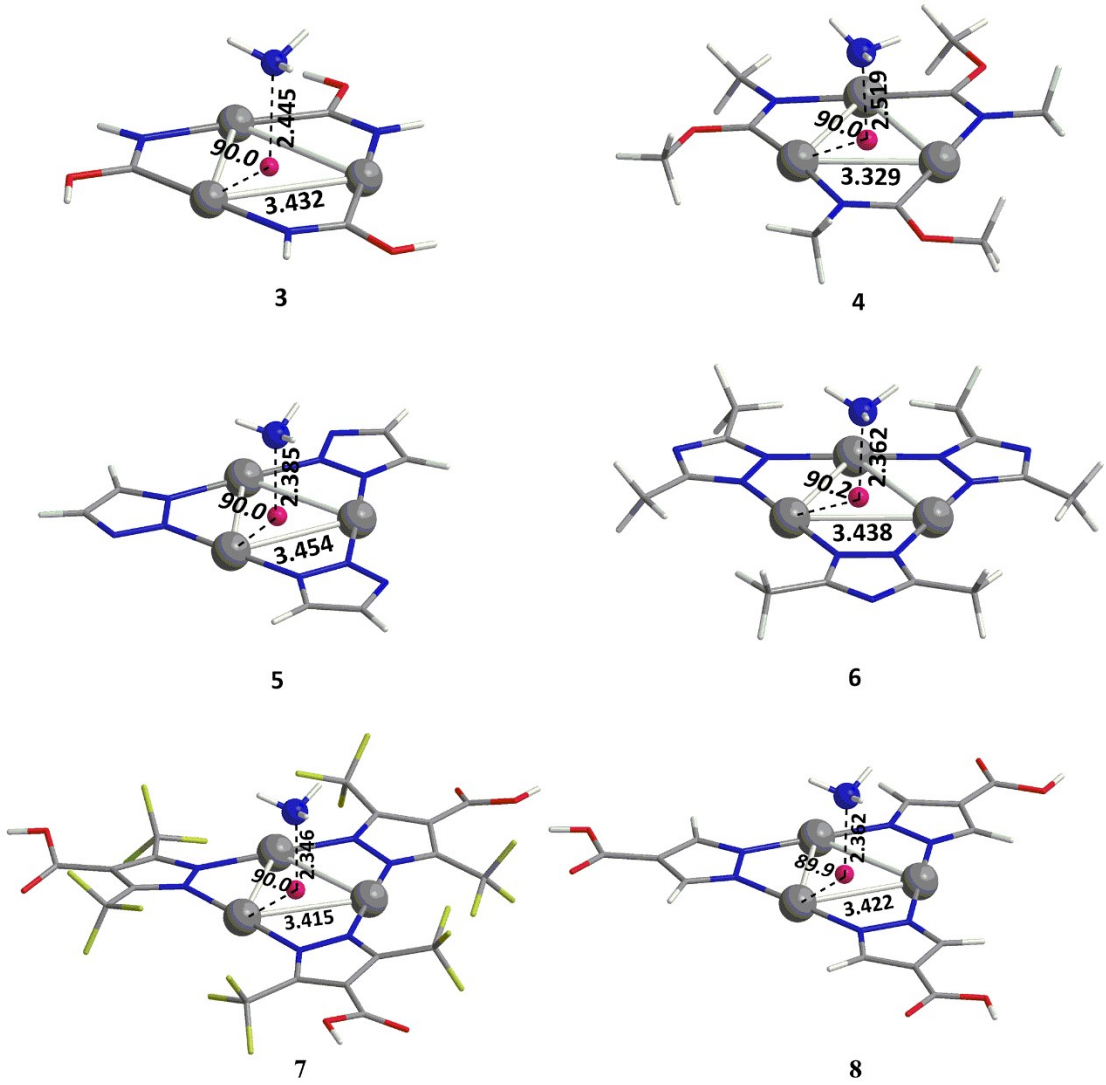

Fig. S1 Selected structural parameters of the optimized geometries of complexes **3** – **8**.

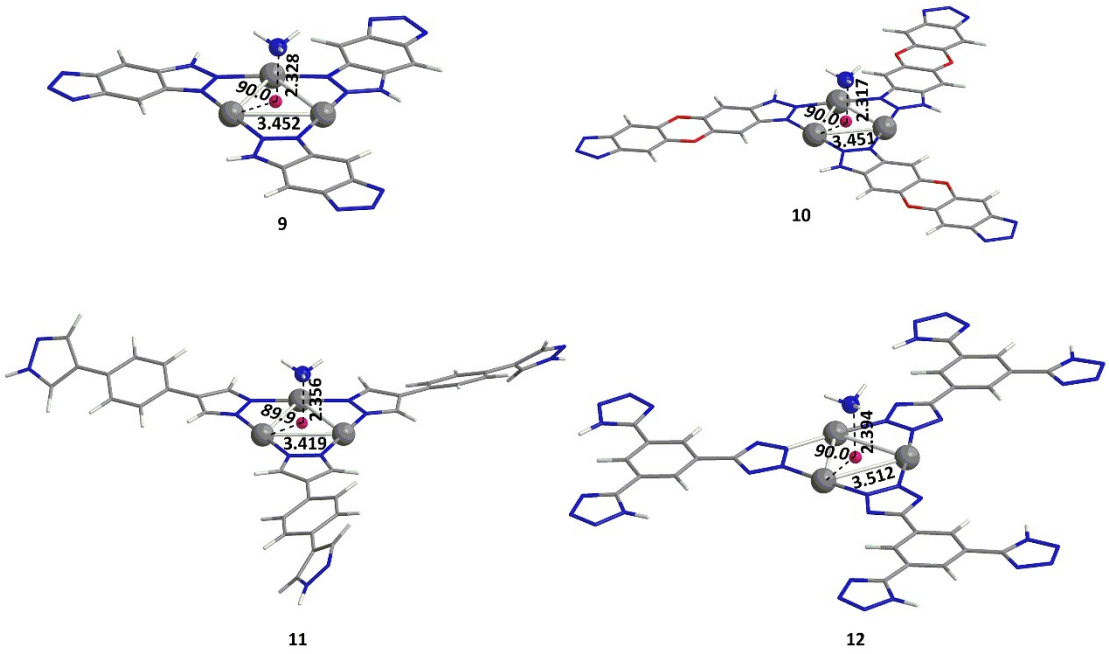

Fig. S2 Selected structural parameters of the optimized geometries of complexes **9** – **12**.

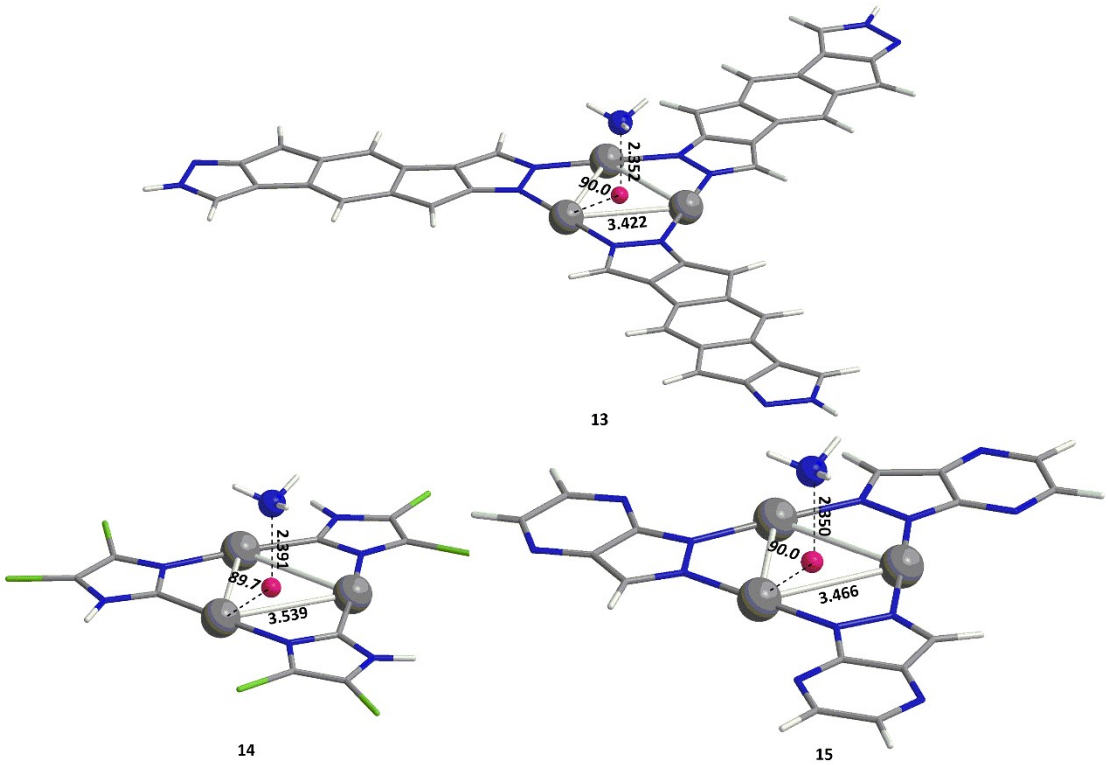

Fig. S3 Selected structural parameters of the optimized geometries of complexes **13** – **15**.

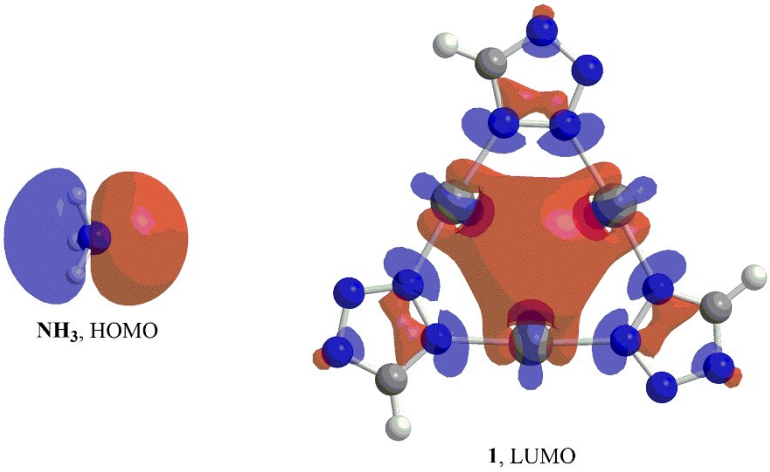

Fig. S4 3D surfaces plot of HOMO of NH_3 and LUMO of cluster **1**.

Table S1 Topological and energetic properties of ρ(r) calculated at the (3,–1) bond critical point (BCP) of the complexes **1 – 15.**

Species	ρ_{BCP}[a]	$\nabla\rho_{BCP}$[b]	G_{BCP}[c]	V_{BCP}[c]	$\lvert V_{BCP}\rvert/G_{BCP}$	H_{BCP}[c]	G_{BCP}/ρ_{BCP}	H_{BCP}/ρ_{BCP}[d]
1	0.012	0.037	0.009	-0.008	0.889	0.0006	0.750	0.050
2	0.014	0.044	0.010	-0.010	1.000	0.0004	0.714	0.029
3	0.012	0.035	0.008	-0.008	1.000	0.0010	0.667	0.083
4	0.015	0.047	0.012	-0.011	0.917	0.0003	0.800	0.020
5	0.012	0.038	0.009	-0.008	0.889	0.0006	0.750	0.050
6	0.013	0.041	0.010	-0.009	0.900	0.0005	0.769	0.038
7	0.013	0.041	0.010	-0.009	0.900	0.0005	0.769	0.038
8	0.013	0.040	0.009	-0.009	1.000	0.0005	0.692	0.038
9	0.013	0.041	0.010	-0.009	0.900	0.0005	0.769	0.038
10	0.014	0.042	0.010	-0.009	0.900	0.0005	0.714	0.036
11	0.013	0.041	0.010	-0.009	0.900	0.0005	0.769	0.038
12	0.012	0.036	0.008	-0.008	1.000	0.0006	0.667	0.050
13	0.013	0.040	0.010	-0.009	0.900	0.0005	0.769	0.038
14	0.012	0.036	0.008	-0.008	1.000	0.0006	0.667	0.050
15	0.013	0.039	0.009	-0.009	1.000	0.0006	0.692	0.046

[a] in eÅ^{-3}

[b] in eÅ^{-5}

[c] in kJ mol^{-1} (atomic unit volume)$^{-1}$.

[d] in kJ mol^{-1} electron^{-1}. The bond degree parameter H_{BCP}/ρ_{BCP} represents either the covalence (H_{BCP}<0) or the softening (H_{BCP}>0) degree of the interaction.

Table S2 Calculated parameters used for molecular structure – property correlations.[1]

Species	Q_{zz}	Q_{xx}	E_{HOMO}[2]	E_{LUMO}[2]	μ	η	ω	χ	α	q_{Ag} Mul.
1	-137.550	-173.880	-0.3069	-0.0668	0.187	0.24	0.004	-0.187	226.61	0.248
2	-260.502	-299.350	-0.3144	-0.0826	0.199	0.232	0.005	-0.199	325.57	0.260
3	-113.289	-99.277	-0.2360	-0.0184	0.127	0.218	0.002	-0.127	180.83	0.108
4	-150.518	-133.432	-0.2214	-0.0054	0.113	0.216	0.001	-0.113	278.75	0.067
5	-144.241	-135.499	-0.2758	-0.0415	0.159	0.234	0.003	-0.159	242.05	0.223
6	-183.416	-180.167	-0.2546	-0.0365	0.146	0.218	0.002	-0.146	335.49	0.168
7	-312.177	-328.484	-0.3012	-0.0801	0.191	0.221	0.004	-0.191	428.23	0.284
8	-192.403	-187.498	-0.2766	-0.0506	0.164	0.226	0.003	-0.164	357.02	0.195
9	-258.854	-438.13	-0.2447	-0.1366	0.191	0.108	0.002	-0.191	623.21	0.301
10	-394.153	-939.93	-0.2166	-0.1672	0.192	0.049	0.001	-0.192	1647.69	0.296
11	-331.963	-368.73	-0.2158	-0.0346	0.125	0.181	0.001	-0.125	825.13	0.171
12	-404.95	-567.02	-0.2914	-0.0925	0.192	0.199	0.004	-0.192	890.28	0.297
13	-375.484	-305.22	-0.2054	-0.0984	0.152	0.107	0.001	-0.152	1234.41	0.172
14	-218.54	-205.117	-0.238	-0.0191	-0.129	0.219	0.002	0.129	375.61	0.172
15	-210.08	-200.142	-0.2609	-0.0766	-0.169	0.184	0.003	0.169	439.46	0.178

[1]Data refer to the Ag(I) clusters.

[2]HOMO and LUMO energies are given in a.u.

Table S3 Calculated parameters used for molecular structure – property correlations.[1]

Species	p (D)	Q_{zz}	Q_{xx}	E_{HOMO}[2]	E_{LUMO}[2]	μ	η	ω	χ	q_{Ag} Mul	q_N Mul	q_{Ag}	q_N	R_e	D_0
1	2.577	-137.550	-173.880	-0.29661	-0.04988	0.173	0.247	0.004	-0.173	0.248	-0.727	0.622	-1.072	2.399	8.7
2	2.640	-259.251	-311.766	-0.30441	-0.06652	0.185	0.238	0.004	-0.185	0.260	-0.727	0.623	-1.066	2.358	9.7
3	2.027	-113.675	-109.120	-0.22714	-0.01097	0.119	0.216	0.002	-0.119	0.108	-0.709	0.400	-1.061	2.445	4.6
4	1.900	-150.876	-143.914	-0.20973	-0.00391	0.107	0.206	0.001	-0.107	0.067	-0.692	0.400	-1.048	2.519	4.2
5	2.347	-143.749	-146.512	-0.26691	-0.02574	0.146	0.241	0.003	-0.146	0.223	-0.720	0.608	-1.068	2.385	7.4
6	2.339	-179.952	-195.183	-0.24948	-0.02110	0.135	0.228	0.002	-0.135	0.168	-0.718	0.575	-1.061	2.362	7.0
7	3.486	-311.156	-341.768	-0.29287	-0.06556	0.179	0.227	0.004	-0.179	0.284	-0.725	0.626	-1.063	2.346	9.7
8	3.704	-192.403	-187.498	-0.27167	-0.03587	0.154	0.236	0.003	-0.154	0.195	-0.722	0.609	-1.068	2.362	7.9
9	3.032	-256.517	-453.995	-0.24119	-0.13143	0.186	0.110	0.002	-0.186	0.301	-0.739	0.575	-1.094	2.328	12.2
10	6.062	-391.490	-962.712	-0.21416	-0.16353	0.189	0.051	0.001	-0.189	0.296	-0.738	0.638	-1.079	2.317	12.4
11	3.830	-331.963	-368.730	-0.21327	-0.02846	0.121	0.185	0.001	-0.121	0.171	-0.720	0.598	-1.067	2.356	7.3
12	1.927	-403.034	-582.044	-0.28901	-0.09059	0.190	0.198	0.004	-0.190	0.309	-0.729	0.628	-1.073	2.394	9.0
13	2.239	-374.720	-322.084	-0.20311	-0.09643	0.150	0.107	0.001	-0.150	0.172	-0.719	0.597	-1.066	2.352	7.2
14	1.877	-218.583	-216.583	-0.23389	-0.01210	0.123	0.222	0.002	-0.123	0.030	-0.712	0.469	-1.057	2.391	5.2
15	2.345	-209.501	-212.720	-0.25635	-0.07283	0.165	0.184	0.002	-0.165	0.190	-0.721	0.605	-1.066	2.350	7.7

[1]Data refer to the ammonia complexes.

[2]HOMO and LUMO energies are given in a.u.