Electronic Supplementary Information

Aromaticity in all-metal annular systems: The counter-ion effect

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Table S1. Atomic charge distribution on the different atoms of Na_2Mg_3 molecule with the variation of distance of the Na^+ ion computed at HF/aug-cc-pVDZ and B3LYP/aug-cc-pVDZ levels of theory

HF/aug-cc-pVDZ		B3LYP/aug-cc-pVDZ			MP2/aug-cc-pVDZ		QCISD/aug-cc-pVDZ	
Singlet		Singlet		Distance (Å)	Singlet		Singlet	
Mg	Na	Mg	Na		Mg	Na	Mg	Na
0.311	-0.467	0.294	-0.441	1.0	0.339	-0.509	0.329	-0.493
0.280	-0.420	0.293	-0.440	1.1	0.310	-0.466	0.299	-0.449
0.252	-0.378	0.300	-0.450	1.2	0.286	-0.429	0.274	-0.411
0.229	-0.343	0.307	-0.460	1.3	0.269	-0.403	0.255	-0.328
0.212	-0.318	0.301	-0.452	1.4	0.259	-0.389	0.243	-0.364
0.197	-0.296	0.282	-0.423	1.5	0.250	-0.375	0.232	-0.349
0.184	-0.275	0.260	-0.389	1.6	0.239	-0.359	0.221	-0.331
0.170	-0.255	0.242	-0.362	1.7	0.229	-0.343	0.209	-0.314
0.157	-0.236	0.229	-0.344	1.8	0.219	-0.329	0.198	-0.298
0.146	-0.218	0.221	-0.332	1.9	0.212	-0.318	0.189	-0.283
0.135	-0.203	0.218	-0.327	2.0	0.210	-0.315	0.182	-0.274
0.128	-0.192	0.220	-0.331	2.1	0.217	-0.326	0.183	-0.274
0.126	-0.189	0.225	-0.338	2.2	0.231	-0.347	0.192	-0.288
0.128	-0.192	0.222	-0.333	2.3	0.234	-0.351	0.203	-0.305

0.132	-0.197	0.208	-0.311	2.4	0.222	-0.332	0.201	-0.302
0.128	-0.192	0.189	-0.283	2.5	0.199	-0.299	0.184	-0.276
0.112	-0.169	0.171	-0.257	2.6	0.170	-0.256	0.157	-0.235
0.087	-0.130	0.155	-0.233	2.7	0.136	-0.204	0.124	-0.186
0.054	-0.081	0.140	-0.210	2.8	0.098	-0.148	0.087	-0.130
0.017	-0.025	0.125	-0.188	2.9	0.058	-0.087	0.047	-0.070
-0.023	0.034	0.109	-0.164	3.0	0.016	-0.024	0.005	-0.008
-0.064	0.096	0.093	-0.140	3.1	-0.027	0.041	-0.038	0.057
-0.105	0.157	0.076	-0.114	3.2	-0.071	0.106	-0.081	0.122
-0.145	0.218	0.057	-0.086	3.3	-0.114	0.170	-0.124	0.186
-0.183	0.275	0.039	-0.059	3.4	-0.155	0.232	-0.164	0.246
-0.218	0.327	0.020	-0.029	3.5	-0.194	0.291	-0.202	0.304
-0.247	0.371	0.001	-0.001	3.6	-0.229	0.343	-0.236	0.355
-0.271	0.407	-0.017	0.026	3.7	-0.259	0.388	-0.265	0.398
-0.288	0.433	-0.034	0.051	3.8	-0.283	0.425	-0.288	0.431
-0.299	0.448	-0.048	0.073	3.9	-0.301	0.452	-0.303	0.455
-0.302	0.452	-0.060	0.090	4.0	-0.312	0.469	-0.312	0.469
-0.299	0.448	-0.069	0.103	4.1	-0.317	0.476	-0.315	0.472
-0.291	0.436	-0.075	0.113	4.2	-0.316	0.475	-0.311	0.467
-0.278	0.418	-0.079	0.119	4.3	-0.311	0.466	-0.303	0.454
-0.263	0.395	-0.081	0.122	4.4	-0.301	0.452	-0.290	0.436
-0.246	0.369	-0.082	0.123	4.5	-0.288	0.433	-0.275	0.413
-0.228	0.342	-0.081	0.122	4.6	-0.274	0.411	-0.258	0.388
-0.210	0.314	-0.081	0.121	4.7	-0.258	0.388	-0.240	0.361
-0.191	0.287	-0.079	0.119	4.8	-0.243	0.364	-0.222	0.333
-0.173	0.260	-0.078	0.117	4.9	-0.226	0.340	-0.204	0.306
-0.155	0.233	-0.076	0.114	5.0	-0.211	0.316	-0.187	0.280
-0.032	0.048	-0.050	0.075	6.0	-0.090	0.135	-0.063	0.094
0.004	-0.006	-0.023	0.035	7.0	-0.031	0.046	-0.018	0.027
0.007	-0.011	-0.009	0.013	8.0	-0.009	0.014	-0.004	0.005
0.006	-0.009	-0.004	0.005	9.0	-0.001	0.002	0.001	-0.001
0.004	-0.006	-0.002	0.003	10	0.001	-0.002	0.002	-0.003
0.280	-0.420	-0.001	0.002	11	0.002	-0.002	0.002	-0.003
0.001	-0.002	-0.001	0.001	12	0.001	-0.002	0.001	-0.002
0.001	-0.001	0.000	0.001	13	0.001	-0.001	0.001	-0.001
0.000	0.000	0.000	0.000	14	0.000	-0.001	0.000	-0.001
0.000	0.000	0.000	0.000	15	0.000	0.000	0.000	0.000
0.000	0.000	0.000	0.000	16	0.000	0.000	0.000	0.000
0.000	0.000	0.000	0.000	17	0.000	0.000	-----a-----	-----a----
0.000	0.000	0.000	0.000	18	0.000	0.000	0.000	0.000
0.000	0.000	0.000	0.000	19	0.000	0.000	0.000	0.000
0.000	0.000	0.000	0.000	20	0.000	0.000	-----a-----	-----a----
0.000	0.000	0.000	0.000	21	0.000	0.000	-----a-----	-----a----
0.000	0.000	0.000	0.000	22	0.000	0.000	-----a-----	-----a----
0.000	0.000	0.000	0.000	23	0.000	0.000	-----a-----	-----a----
0.000	0.000	0.000	0.000	24	0.000	0.000	-----a-----	-----a----
0.000	0.000	0.000	0.000	25	0.000	0.000	-----a-----	-----a----

-----a----- indicates that the calculations on the Na_2Mg_3 molecule in their respective spin states do not converge at the above level of theory.

Table S2 Atomic charge distribution on the different atoms of Na_2Mg_3 molecule with the variation of distance of the Na^+ ion computed at MP2/aug-cc-pVDZ and QCISD/ aug-cc-pVDZ levels of theory

HF/aug-cc-pVDZ		B3LYP/aug-cc-pVDZ			MP2/aug-cc-pVDZ		QCISD/aug-cc-pVDZ	
Triplet		Triplet		Distance (Å)	Triplet		Triplet	
Mg	Na	Mg	Na		Mg	Na	Mg	Na
0.196	-0.293	0.153	-0.230	1.0	0.184	-0.457	-----a-----	-----a-----
0.195	-0.293	0.136	-0.204	1.1	0.327	-0.304	-----a-----	-----a-----
0.126	-0.188	0.123	-0.185	1.2	0.196	-0.293	0.186	-0.279
0.092	-0.139	0.113	-0.170	1.3	0.161	-0.241	0.151	-0.226
0.063	-0.095	0.104	-0.156	1.4	0.131	-0.196	0.120	-0.181
0.038	-0.058	0.094	-0.141	1.5	0.106	-0.160	0.095	-0.143
0.018	-0.027	0.082	-0.124	1.6	0.087	-0.130	0.075	-0.112
0.001	-0.002	0.071	-0.107	1.7	0.070	-0.106	0.058	-0.086
-0.013	0.019	0.062	-0.093	1.8	0.040	-0.060	0.043	-0.065
-0.025	0.037	0.054	-0.080	1.9	0.058	-0.087	0.032	-0.047
-0.035	0.052	0.046	-0.069	2.0	0.048	-0.072	0.021	-0.032
-0.042	0.064	0.040	-0.060	2.1	0.035	-0.053	0.012	-0.018
-0.049	0.073	0.035	-0.053	2.2	0.042	-0.062	0.004	-0.007
-0.052	0.079	0.032	-0.048	2.3	0.068	-0.103	-0.002	0.003
-0.054	0.081	0.031	-0.047	2.4	0.051	-0.076	-0.007	0.011
-0.052	0.078	0.068	-0.102	2.5	0.030	-0.044	0.011	-0.017
-0.007	0.012	0.086	-0.129	2.6	0.027	-0.041	0.025	-0.037
-0.003	0.004	0.103	-0.154	2.7	0.066	-0.099	0.084	-0.126
-0.002	0.003	0.120	-0.180	2.8	0.096	-0.145	0.095	-0.143
-0.002	0.002	0.133	-0.200	2.9	0.094	-0.142	0.091	-0.137
-0.002	0.003	0.140	-0.210	3.0	0.081	-0.121	0.078	-0.117
-0.002	0.002	0.138	-0.207	3.1	0.062	-0.094	0.060	-0.091
-0.002	0.002	0.128	-0.192	3.2	0.042	-0.063	0.041	-0.061
-0.001	0.002	0.112	-0.168	3.3	0.021	-0.032	0.021	-0.031
-0.001	0.002	0.093	-0.140	3.4	0.002	-0.003	0.002	-0.003
-0.001	0.002	0.073	-0.110	3.5	-0.015	0.022	-0.015	0.022
-0.029	0.043	0.054	-0.081	3.6	-0.029	0.043	-0.029	0.043
-0.001	0.002	0.036	-0.054	3.7	-0.040	0.059	-0.040	0.059
-0.001	0.002	0.020	-0.030	3.8	-0.047	0.071	-0.047	0.070
-0.001	0.002	0.006	-0.010	3.9	-0.052	0.078	-0.051	0.077
-0.001	0.002	-0.004	0.010	4.0	-0.053	0.080	-0.052	0.079
-0.001	0.002	-0.013	0.019	4.1	-0.053	0.079	-0.051	0.077
-0.001	0.002	-0.019	0.028	4.2	-0.051	0.076	-0.048	0.073
-0.001	0.002	-0.023	0.034	4.3	-0.047	0.070	-0.045	0.067
-0.001	0.002	-0.025	0.037	4.4	-0.042	0.064	-0.040	0.060
-0.001	0.002	-0.026	0.038	4.5	-0.038	0.056	-0.035	0.053
-0.001	0.002	-0.026	0.038	4.6	-0.033	0.049	-0.030	0.044
-0.002	0.002	-0.025	0.037	4.7	-0.028	0.043	-0.026	0.039
-0.002	0.002	-0.024	0.036	4.8	-0.024	0.036	-0.022	0.033
-0.002	0.002	-0.023	0.034	4.9	-0.020	0.031	-0.019	0.028

-0.002	0.002	-0.021	0.032	5.0	-0.017	0.026	-0.016	0.024
-0.002	0.003	-0.011	0.016	6.0	-0.003	0.005	-0.003	0.005
-0.001	0.002	-0.005	0.008	7.0	-0.001	0.002	-0.001	0.002
-0.001	0.001	-0.003	0.004	8.0	-0.001	0.001	0.000	0.001
0.000	0.001	-0.001	0.002	9.0	0.000	0.000	0.000	0.000
0.000	0.000	-0.001	0.002	10	0.000	0.000	0.000	0.000
0.000	0.000	-0.001	0.001	11	0.000	0.000	0.000	0.000
0.000	0.000	-0.001	0.001	12	0.000	0.000	0.000	0.000
0.000	0.000	0.000	0.001	13	0.000	0.000	0.000	0.000
0.000	0.000	0.000	0.000	14	0.000	0.000	0.000	0.000
0.000	0.000	0.000	0.000	15	0.000	0.000	0.000	0.000
0.000	0.000	0.000	0.000	16	0.000	0.000	0.000	0.000
0.000	0.000	0.000	0.000	17	0.000	0.000	0.000	0.000
0.000	0.000	0.000	0.000	18	0.000	0.000	0.000	0.000
0.000	0.000	0.000	0.000	19	0.000	0.000	-----a-----	-----a-----
0.000	0.000	0.000	0.000	20	0.000	0.000	-----a-----	-----a-----
0.000	0.000	0.000	0.000	21	0.000	0.000	-----a-----	-----a-----
0.000	0.000	0.000	0.000	22	0.000	0.000	-----a-----	-----a-----
0.000	0.000	0.000	0.000	23	0.000	0.000	-----a-----	-----a-----
0.000	0.000	0.000	0.000	24	0.000	0.000	-----a-----	-----a-----
0.000	0.000	0.000	0.000	25	0.000	0.000	-----a-----	-----a-----

-----a----- indicates that the calculations on the Na_2Mg_3 molecule in their respective spin states do not converge at the above level of theory.

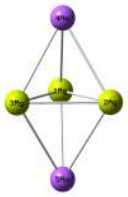
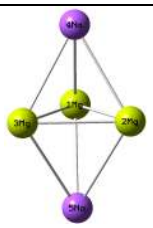
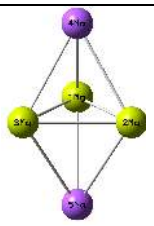
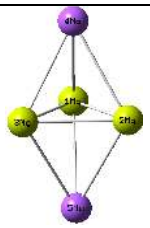
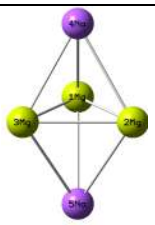
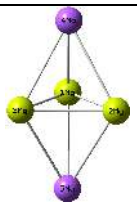
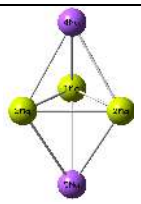
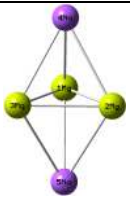
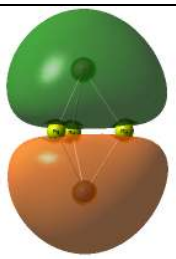
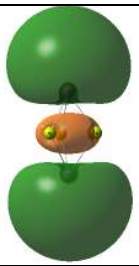
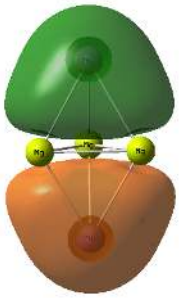
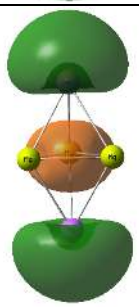
Na_2Mg_3 (D_{3h})_Singlet		Na_2Mg_3 (D_{3h})_Triplet	
Levels	Figures	Levels	Figures
HF/aug-cc-pVDZ (NIMAG=0)	 Mg-Mg=3.36 Mg-Na=3.46 Na-Na=5.74	HF/aug-cc-pVDZ	---@---
B3LYP/aug-cc-pVDZ (NIMAG=0)	 Mg-Mg=3.14 Mg-Na=3.30 Na-Na=5.51	B3LYP/aug-cc-pVDZ (NIMAG=2)	 Mg-Mg=3.17 Mg-Na=3.70 Na-Na=6.42
MP2/aug-cc-pVDZ (NIMAG=0)	 Mg-Mg=3.05 Mg-Na=3.36 Na-Na=5.71	MP2/aug-cc-pVDZ (NIMAG=2)	 Mg-Mg=3.07 Mg-Na=3.21 Na-Na=5.34
QCISD/aug-cc-pVDZ (NIMAG=0)	 Mg-Mg=3.15 Mg-Na=3.37 Na-Na=5.67	QCISD/aug-cc-pVDZ (NIMAG=2)	 Mg-Mg=3.17 Mg-Na=3.65 Na-Na=6.31
CASSCF(8,8)/aug-cc-pVDZ (NIMAG=0)	 Mg-Mg=3.15 Mg-Na=3.48 Na-Na=5.94	CASSCF(8,8)/aug-cc-pVDZ	---@---

Fig. S1 Geometries of the Na_2Mg_3 molecule (singlet and triplet) optimized at different levels of theory. --@-- implies that no convergence is achieved.

Levels	HOMO	LUMO
HF/aug-cc-pVDZ		
B3LYP/aug-cc-pVDZ		

Singlet

Fig. S2 Frontier molecular orbitals (FMOs) generated for the optimized geometry of the Na_2Mg_3 system in its singlet state computed at HF and B3LYP levels of theory.

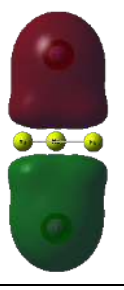
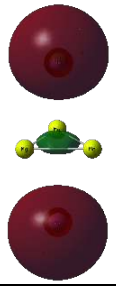
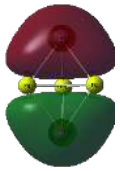
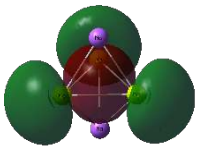
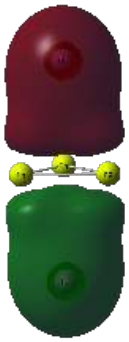
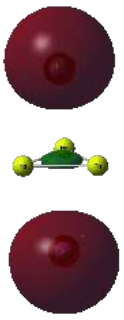
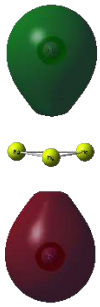
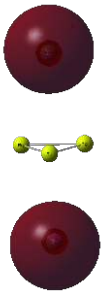
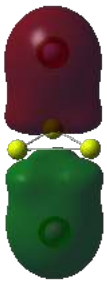
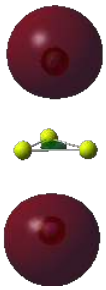
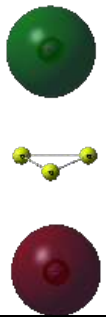
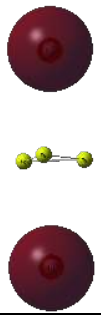
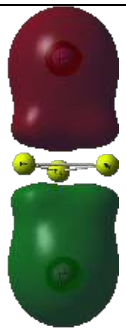
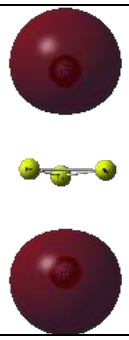
Isomer-I(Mg_3^{2-}) (3.22)			Isomer-II(Mg_3^{2-}) (3.37)		
Distances	HOMO	LUMO	Distances	HOMO	LUMO
Na-Na (8.0) Mg-Mg (3.20)			Na-Na (4.8) Mg-Mg (3.36)		
Na-Na (8.2) Mg-Mg (3.21)			Na-Na (10.0) Mg-Mg (3.32)		
Na-Na (8.4) Mg-Mg (3.22)			Na-Na (12.0) Mg-Mg (3.42)		
Na-Na (8.6) Mg-Mg (3.24)					

Fig. S3 Frontier molecular orbitals (FMOs)** of some of the intermediate structures of the Na_2Mg_3 molecule in their singlet state where the Mg – Mg distance corresponds closely to their bond-stretch isomers in the free $[Mg_3]^{2-}$ system.
**All computations are at B3LYP/aug-cc-pVDZ level of theory