Supporting Information file

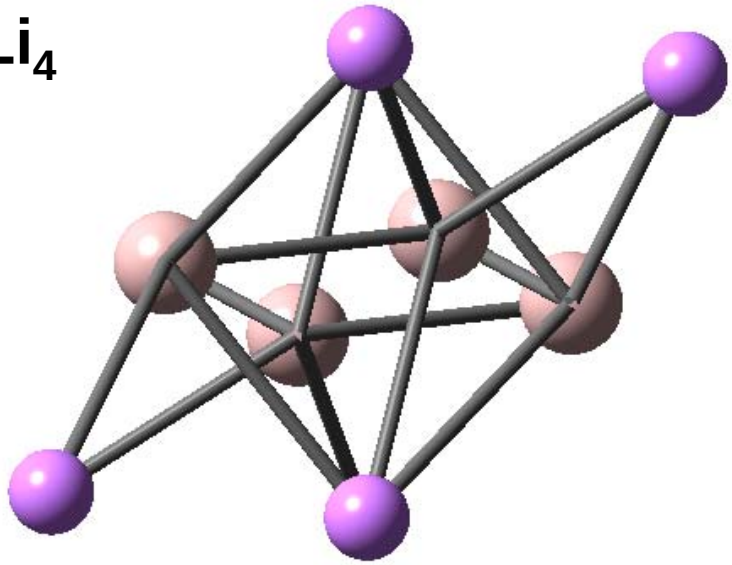
New examples of metalloaromatic Al-clusters: $(Al_4M_4)Fe(CO)_3$ (M=Li, Na and K) and $(Al_4M_4)_2Ni$: Rationalization for possible synthesis

Ayan Datta and Swapan K. Pati

Information available:

1. Structures and coordinates of the molecules.
2. Energies in Hartree for Ground State structures.
3. HOMO orbital plots $(Al_4Li_4)Fe(CO)_3$ and $(Al_4Li_4)_2Ni$

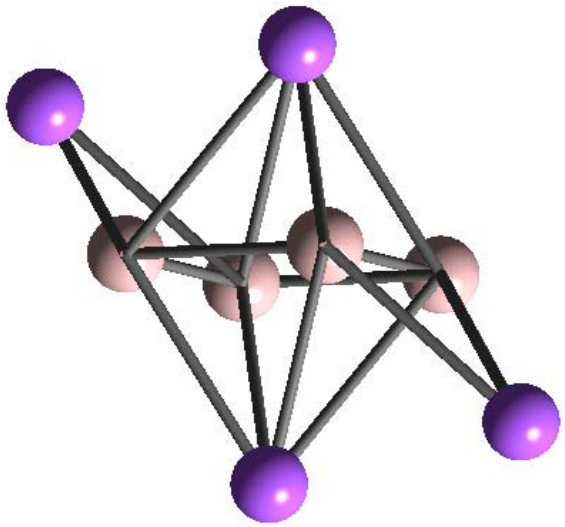
Al_4Li_4



Atomic Number	Coordinates (Angstroms) X	Y	Z
13	-1.124051	0.732993	1.278122
13	1.124051	-0.732993	1.278122
13	1.124051	-0.732993	-1.278122
13	-1.124051	0.732993	-1.278122
3	1.124051	1.822781	0.000000
3	3.444435	-0.317229	0.000000
3	-3.444435	0.317229	0.000000
3	-1.124051	-1.822781	0.000000

Energy (RB3LYP/6-311G++(d,p)) level: -999.9329739. Hartree

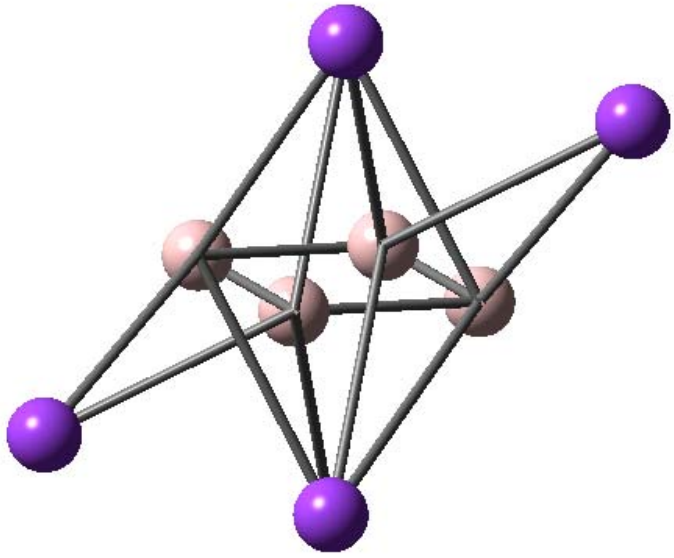
Al_4Na_4



Atomic Number	Coordinates (Angstroms) X	Y	Z
13	0.526184	1.245963	1.296408
13	-0.526184	-1.245963	1.296408
13	-0.526184	-1.245963	-1.296408
13	0.526184	1.245963	-1.296408
11	-0.526184	3.819469	0.000000
11	-2.404722	0.927235	0.000000
11	2.404722	-0.927235	0.000000
11	0.526184	-3.819469	0.000000

Energy (RB3LYP/6-311G++(d,p)) level: -1619.0386804 Hartree

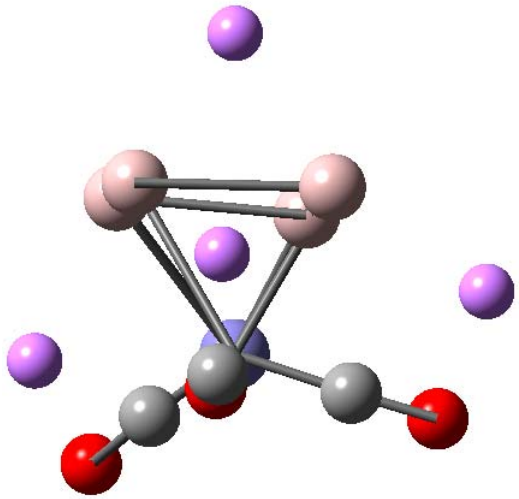
Al_4K_4



Atomic Number	Coordinates (Angstroms) X	Y	Z
13	0.438465	1.261327	1.288506
13	-0.438465	-1.261327	1.288506
13	-0.438465	-1.261327	-1.288506
13	0.438465	1.261327	-1.288506
19	-0.438465	4.420901	0.000000
19	-3.019563	0.815458	0.000000
19	0.438465	-4.420901	0.000000
19	3.019563	-0.815458	0.000000

Energy (RB3LYP/6-311G++(d,p)) level: -3369.5869271 Hartree

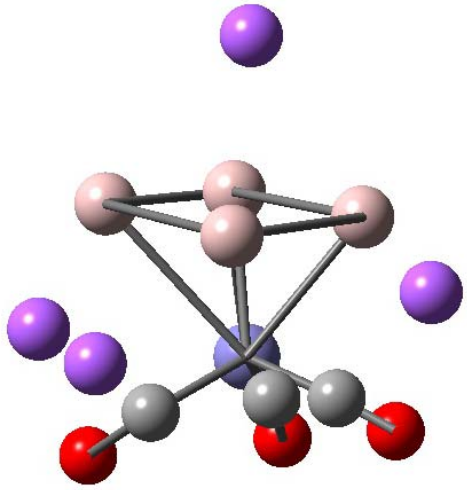
$(Al_4Li_4)Fe(CO)_3$



Atomic Number	Coordinates (Angstroms) X	Y	Z
26	0.251137	-0.657195	-0.262571
8	-1.882479	-2.452586	-1.182356
6	-1.004643	-1.674750	-0.810004
8	1.727981	-1.878943	1.953013
6	1.071476	-1.393136	1.028739
8	2.330517	-0.105646	-2.252107
6	1.403746	-0.340866	-1.473140
13	-0.933105	0.396268	2.084654
13	-2.305136	0.943173	-0.053475
13	-0.301378	1.967005	-1.295590
13	1.162701	1.599584	0.920819
3	-1.128161	3.186714	1.259385
3	1.509536	-0.441647	3.131270
3	-3.355645	-1.401612	-0.851900
3	2.353859	1.742740	-1.981569

Energy (RB3LYP/6-311G++(d,p)) level: -2603.8843801 Hartree

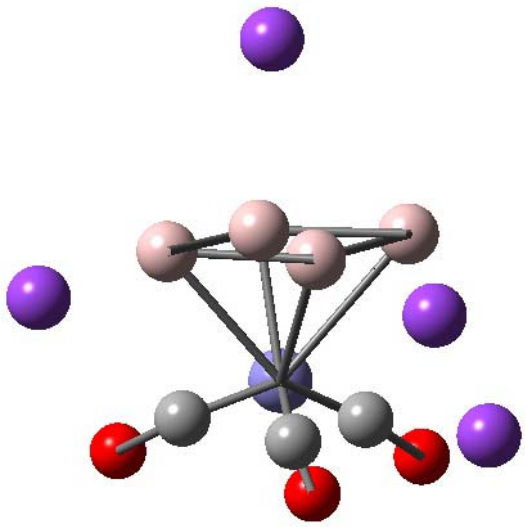
$(Al_4Na_4)Fe(CO)_3$



Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
26		-0.447598	-0.702076	-0.275499
8		-2.089303	-1.419101	-2.570938
6		-1.364157	-1.070652	-1.709441
8		-2.069389	-1.013759	2.121802
6		-1.436710	-0.828069	1.115151
8		1.323179	-2.973265	0.079385
6		0.619876	-2.022658	-0.105300
13		-0.587386	2.096876	0.695501
13		-0.219237	1.696572	-1.822913
13		1.741713	0.148897	-1.352655
13		1.344745	0.467820	1.266484
11		-2.957554	0.651094	-0.643240
11		-0.942348	0.608652	3.335503
11		3.268538	-1.769634	0.470981
11		2.246795	3.027988	-0.427327

Energy (RB3LYP/6-311G++(d,p)) level: -3222.998702 Hartree

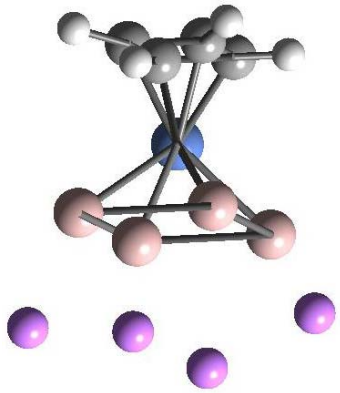
$(Al_4K_4)Fe(CO)_3$



Atomic Number	Coordinates (Angstroms) X	Y	Z
26	-0.417686	-0.588717	-0.686013
8	-2.257535	-0.293186	-2.897557
6	-1.403477	-0.326657	-2.068837
8	-2.291548	-1.756948	1.199103
6	-1.495550	-1.207876	0.474616
8	1.258219	-2.874776	-1.317836
6	0.623265	-1.893509	-1.071697
13	-0.734378	1.527964	1.224862
13	-0.357006	2.095455	-1.263878
13	1.777996	0.722545	-1.324494
13	1.397527	0.059077	1.196764
19	3.612771	-2.051692	-0.387660
19	-0.909765	-1.165864	3.429599
19	2.214133	3.543606	0.675276
19	-3.667270	0.621774	-0.552484

Energy (RB3LYP/6-311G++(d,p)) level: -4973.5638068 Hartree

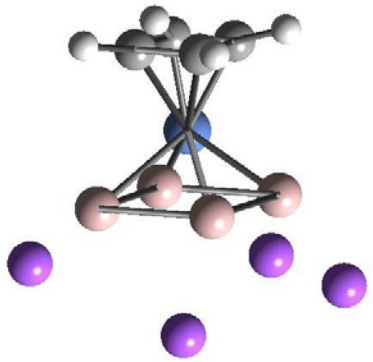
$(Al_4Li_4)(C_4H_4)Ni$



Atomic Number	Coordinates (Angstroms) X	Y	Z
28	-0.576066	-0.001429	-0.005730
6	-2.295778	-0.712901	0.746768
6	-2.300758	-0.743633	-0.716997
6	-2.300401	0.710963	-0.747946
6	-2.295348	0.742300	0.715911
1	-2.464536	-1.514813	-1.455633
1	-2.458262	-1.451386	1.518301
1	-2.464810	1.449803	-1.518774
1	-2.458482	1.513080	1.455160
13	0.879279	-1.312665	1.332947
13	0.892137	-1.312152	-1.329719
13	0.888327	1.313011	-1.330290
13	0.874827	1.313375	1.333478
3	2.666820	-2.802136	0.008747
3	3.208397	0.004096	-1.680986
3	2.657027	2.809012	0.009117
3	3.194503	0.003206	1.693639

Energy (RB3LYP/6-311G++(d,p)) level: -2663.098208 Hartree

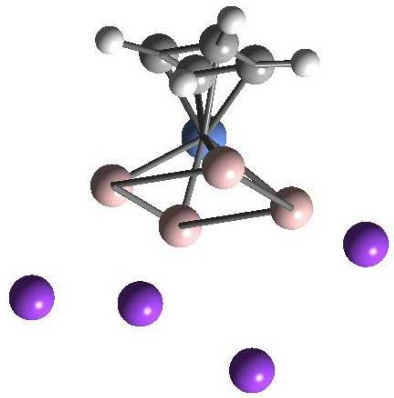
$(Al_4Na_4)(C_4H_4)Ni$



Atomic Number	Coordinates (Angstroms) X	Y	Z
28	-1.116451	0.001460	0.075037
6	-2.666643	0.726443	1.145462
6	-2.664862	-0.726359	1.146730
6	-2.948720	-0.730481	-0.288867
6	-2.950432	0.727369	-0.290270
1	-2.658029	-1.482564	1.918192
1	-2.661677	1.483992	1.915604
1	-3.260674	-1.485791	-0.995796
1	-3.265581	1.480523	-0.998064
13	0.558147	1.348358	1.017117
13	0.553848	-1.351318	1.015004
13	-0.025291	-1.293683	-1.638585
13	-0.023644	1.296644	-1.635890
11	1.682090	3.547991	-0.687069
11	2.613996	-0.007055	2.710402
11	1.681952	-3.544617	-0.694308
11	2.810212	0.001963	-1.153452

Energy (RB3LYP/6-311G++(d,p)) level: -3282.2117134 Hartree

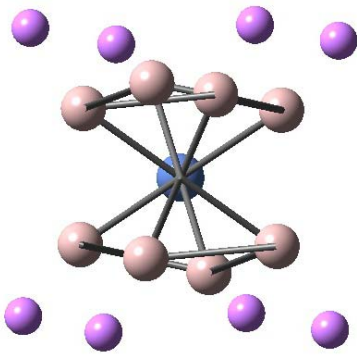
$(Al_4K_4)(C_4H_4)Ni$



Atomic Number	Coordinates (Angstroms) X	Y	Z
28	1.636318	-0.005165	0.000022
6	3.365899	0.725165	0.728129
6	3.368297	0.712340	-0.734550
6	3.363484	-0.747009	-0.721684
6	3.361027	-0.734133	0.740996
1	3.539197	1.459119	-1.496890
1	3.533920	1.485397	1.477712
1	3.529397	-1.508321	-1.470639
1	3.524455	-1.482015	1.503902
13	0.314323	1.345388	1.397289
13	0.318060	1.345561	-1.400638
13	0.309273	-1.347886	-1.400058
13	0.306539	-1.347913	1.397851
19	-1.316465	4.048201	-0.002592
19	-2.799006	0.009250	-2.294044
19	-1.344054	-4.038843	-0.003320
19	-2.799562	0.008513	2.298913

Energy (RB3LYP/6-311G++(d,p)) level: -5032.7487654 Hartree

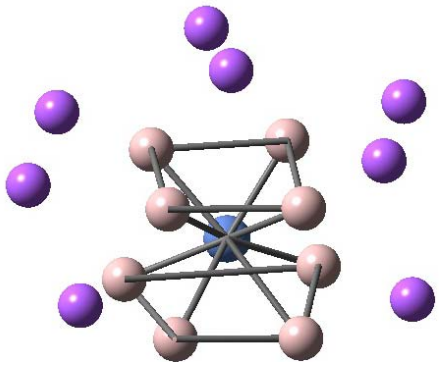
$(Al_4Li_4)_2Ni$



Atomic Type	Coordinates (Angstroms) X	Y	Z
28	0.000878	-0.000500	-0.004409
13	-1.431528	2.060570	0.013049
13	-1.746181	-0.068889	1.741935
13	-1.275012	-2.167199	0.002189
13	-1.774630	-0.048490	-1.706670
13	1.424829	-2.040658	-0.021417
13	1.779516	0.047202	1.701187
13	1.268951	2.152124	0.002913
13	1.709732	0.065417	-1.718099
3	-2.673244	-2.503549	2.338383
3	-2.718619	-2.476228	-2.309841
3	-2.955422	2.263377	2.286216
3	-2.999572	2.284282	-2.222758
3	2.777348	2.494661	2.237223
3	2.714454	2.508577	-2.265855
3	3.051316	-2.299827	2.137864
3	2.987605	-2.266959	-2.225453

Energy (RB3LYP/6-311G++(d,p)) level: -3508.3288233 Hartree

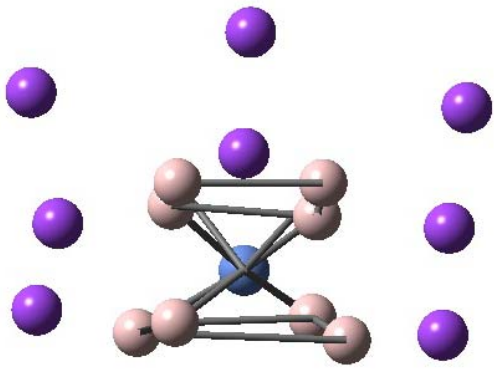
$(Al_4Na_4)_2Ni$



Atomic Number	Coordinates (Angstroms) X	Y	Z
28	-0.001946	-0.000062	-0.000937
13	-1.413539	-2.361877	0.000784
13	-1.668720	0.007020	-1.927937
13	-1.407950	2.369390	-0.000794
13	-1.669482	0.007867	1.925572
13	1.411615	2.359045	0.000435
13	1.668774	-0.007375	-1.926157
13	1.406046	-2.366858	-0.000315
13	1.666723	-0.007653	1.926268
11	3.420430	2.649718	2.557691
11	3.420406	2.651784	-2.556244
11	3.343867	-2.709366	-2.600507
11	3.337838	-2.711189	2.603998
11	-3.416248	-2.653429	-2.561862
11	-3.419532	-2.650505	2.561473
11	-3.335388	2.713208	2.607651
11	-3.338697	2.710457	-2.607281

Energy (RB3LYP/6-311G++(d,p)) level: -4746.5120699 Hartree

$(Al_4K_4)_2Ni$

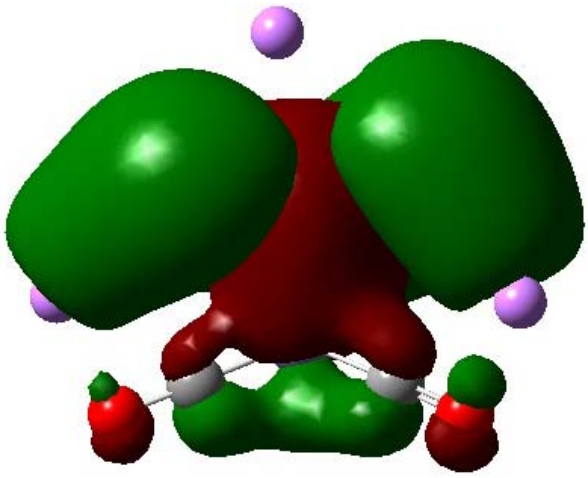


Atomic Number	Coordinates (Angstroms) X	Y	Z
28	-0.003058	-0.003661	-0.439019
13	-1.410663	2.909580	-0.077968
13	-1.680728	0.677381	2.423806
13	-0.744821	-1.895840	1.212007
13	-1.587719	0.853490	-2.172749
13	1.405847	-2.917300	-0.110689
13	1.705750	-0.723525	2.390671
13	0.741796	1.871122	1.226830
13	1.590613	-0.843582	-2.176402
19	-4.375190	-1.736567	2.871766
19	-1.658393	-2.661751	-2.076162
19	-3.689696	-0.593653	-0.084569
19	-4.793273	2.229707	-1.330647
19	4.358867	1.733147	2.882753
19	1.651404	2.674011	-2.053455
19	3.699857	0.618272	-0.092751
19	4.797195	-2.210783	-1.327937

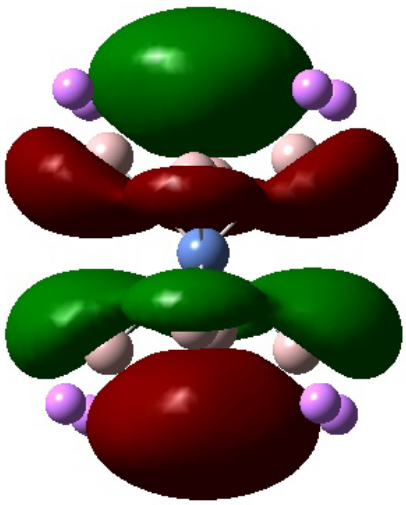
Energy (RB3LYP/6-311G++(d,p)) level: -8247.5384351 Hartree

HOMO orbital plots for (a) $(Al_4Li_4)Fe(CO)_3$ and (b)$(Al_4Li_4)_2Ni$

(a)



(b)



The ligand group orbitals (LGOs) in Al_4Li_4 interact more strongly with the $Fe(CO)_3$ fragment in $(Al_4Li_4)Fe(CO)_3$ compared to that with the d-orbitals for Ni in $(Al_4Li_4)_2Ni$.