

Supplementary Information

Multiple d-d bonds between early transition metals in TM_2Li_n (TM = Sc, Ti) superatomic molecule clusters

By

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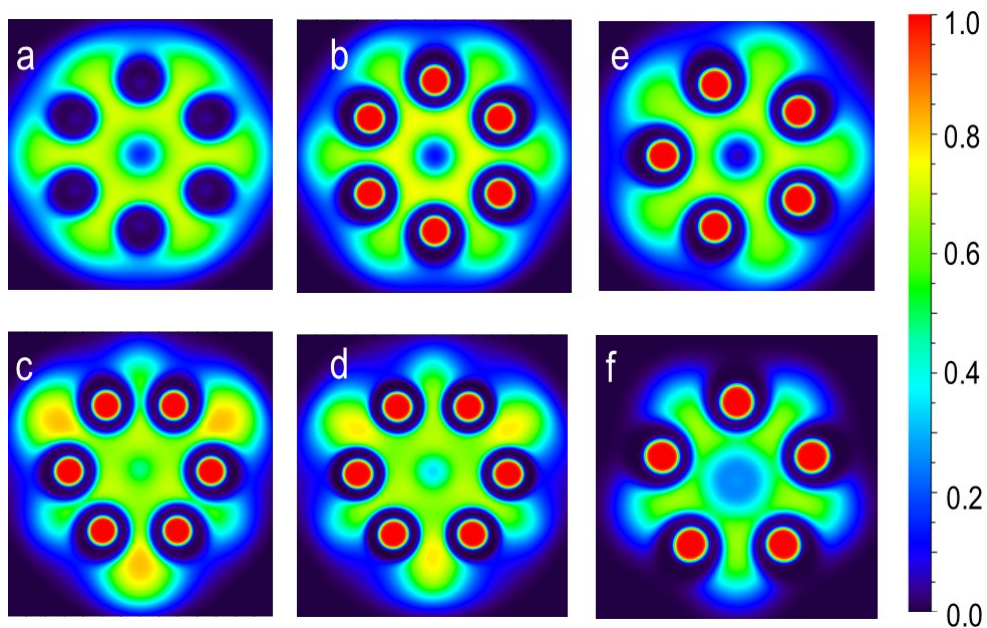


Figure S1. ELFs for $\text{Li}_{18}\text{Ti}_2$ (a), $\text{Li}_{20}\text{Sc}_2$ (b), $\text{Li}_{24}\text{Sc}_2$ (c), Li_{24}Y_2 (d), $[\text{Li}_{17}\text{Ti}_2]^-$ (e), and $[\text{Li}_{17}\text{V}_2]^+$ (f) in color and shape. The scale is labeled aside. All cross sections are perpendicular to the double transition metal. ELF values are between 0 (no localization, blue) and 1 (complete localization, red).

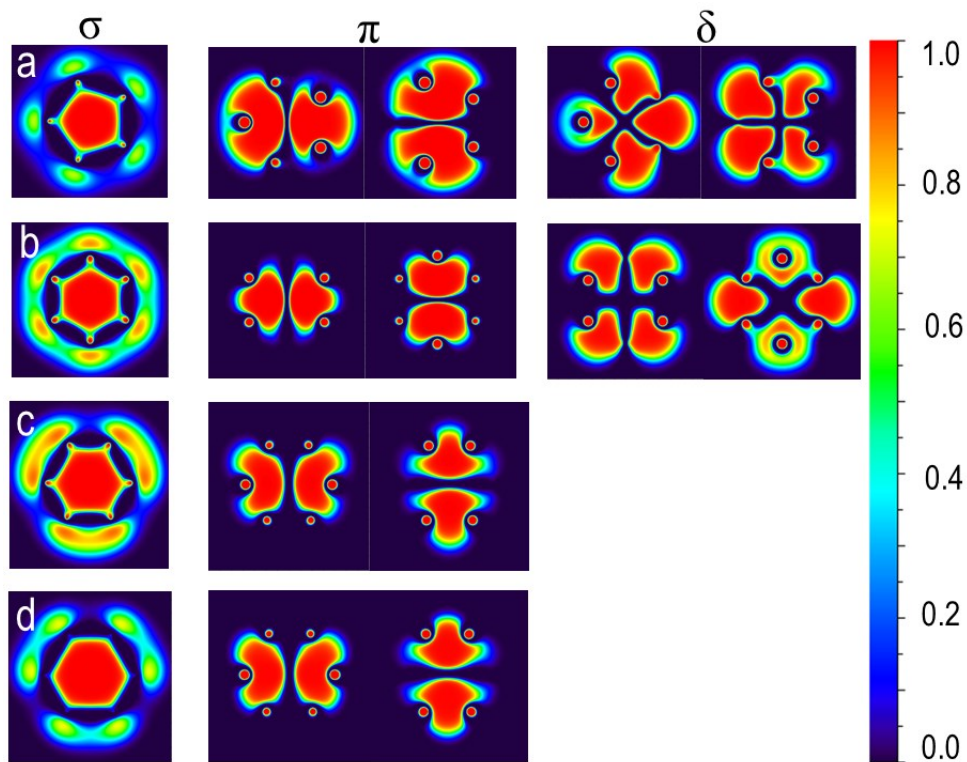


Figure S2. ELFs of multiple bonding $\text{Li}_{18}\text{Ti}_2$ (a), $\text{Li}_{20}\text{Sc}_2$ (b), $\text{Li}_{24}\text{Sc}_2$ (c) and Li_{24}Y_2 (d) in color and shape. The scale is labeled aside. All cross sections are perpendicular to the double transition metal. ELF values are between 0 (no localization, blue) and 1 (complete localization, red)

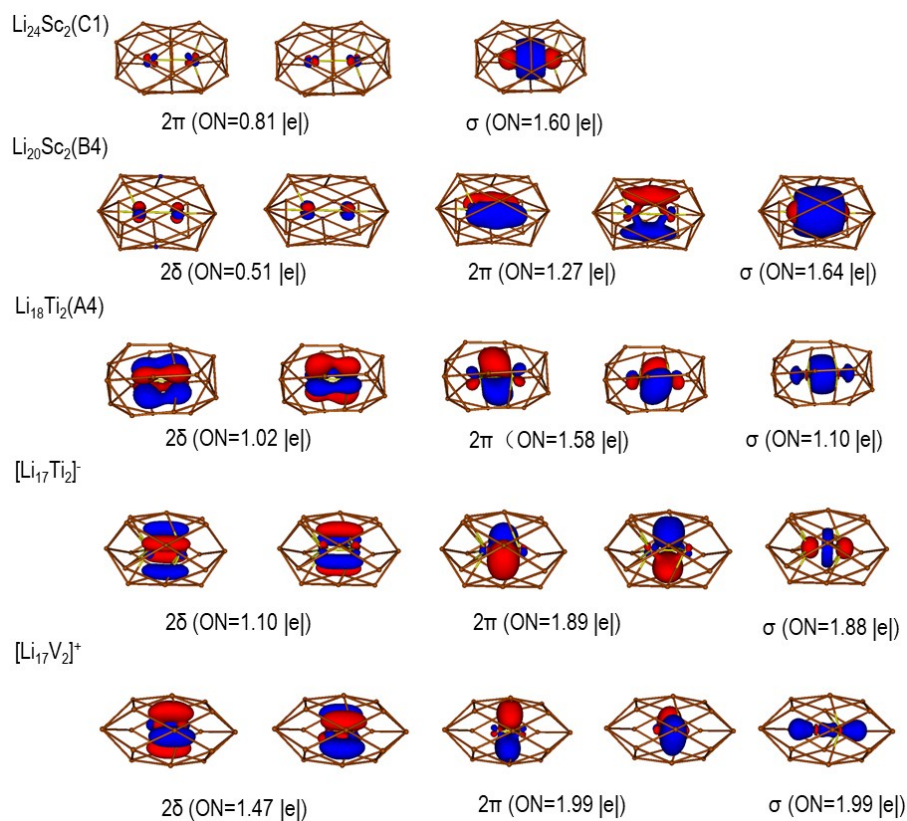


Figure S3. Localization on TM_2 atoms of the delocalized multiple super-bonding orbitals in $\text{Li}_{24}\text{Sc}_2$ (**C1**), $\text{Li}_{20}\text{Sc}_2$ (**B4**), $\text{Li}_{18}\text{Ti}_2$ (**A4**), $[\text{Li}_{17}\text{Ti}_2]^-$, and $[\text{Li}_{17}\text{V}_2]^+$ clusters. ON represents the occupancy number on TM_2 atoms of the delocalized bond.

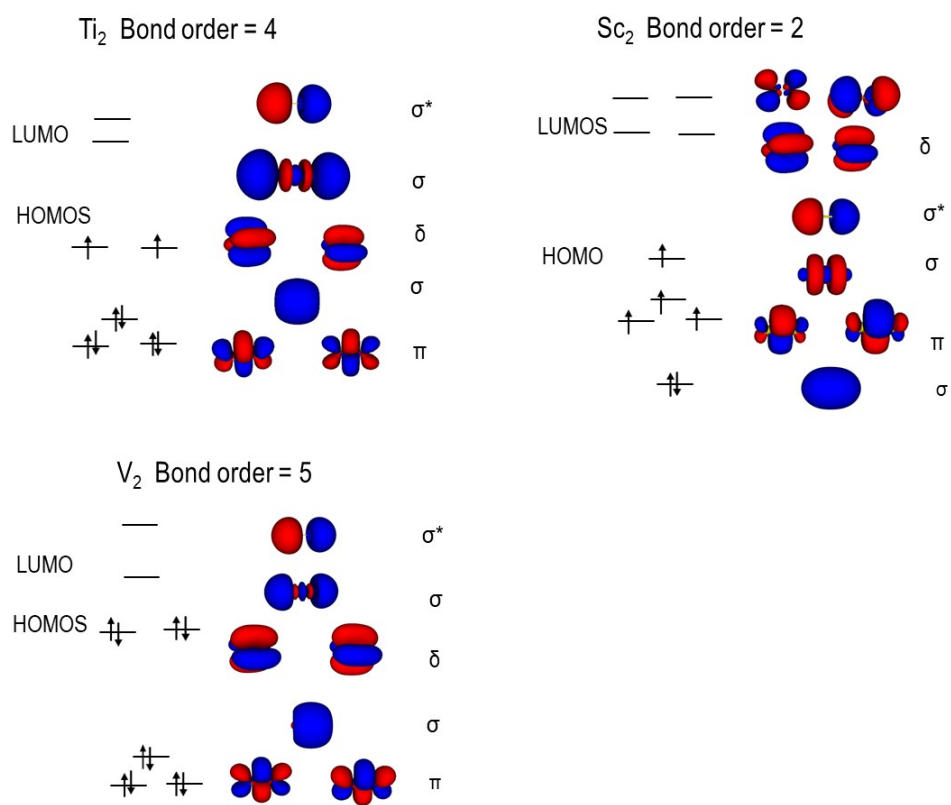


Figure S4. Kohn-Sham MO diagrams of Ti_2 , Sc_2 , and V_2 molecules (PBE0/def2-TZVP)

Cartesian coordinates (in angstrom) of the structures:

Li₁₈Ti₂ (A1)

Li	0.130154	-2.425519	-1.366187
Li	-0.273384	-3.521492	1.269065
Li	2.298858	-1.428030	-0.438582
Li	2.030344	-2.007003	2.415853
Li	-2.152852	-1.306030	-1.093139
Li	0.535651	-0.714814	-3.648930
Li	-0.605680	-1.973952	3.753892
Li	-2.737474	-1.895317	1.708557
Li	2.811900	0.717966	-2.359418
Li	2.342787	0.921333	0.909673
Li	-1.953635	0.829845	-3.078504
Li	0.598102	2.226557	-3.609286
Li	0.980920	0.526050	3.546183
Li	-2.456719	1.049340	0.196084
Li	1.727301	3.128985	-1.017525
Li	-1.947283	0.594264	3.109680
Li	-0.133282	2.304087	1.291393
Li	-1.201534	3.199792	-1.461368
Ti	-0.166938	-0.598021	1.013181
Ti	0.167732	0.567194	-1.030559

Li₁₈Ti₂ (A2)

Li	-2.356458	1.954840	2.151762
Li	-3.529673	-0.688618	2.320626
Li	-3.063960	-2.112062	-0.293158
Li	1.367103	0.950583	2.177516
Li	-1.296795	2.049923	-1.317943
Li	-3.672355	0.758895	-0.232278
Li	-1.403441	-2.763382	2.086712
Li	0.049133	2.643828	0.783355
Li	-0.860561	-0.211035	3.580115
Li	-1.361284	-0.465207	-2.257867
Li	2.492083	2.728064	-0.715258
Li	0.995331	1.770060	-3.112806
Li	1.340710	-1.694116	1.577556
Li	3.695915	0.349618	0.546796
Li	-0.075473	-2.552212	-0.766060
Li	1.319611	-1.209619	-3.265545
Li	3.550678	0.514851	-2.377669
Li	2.942132	-2.051100	-0.945319
Ti	-0.990718	-0.190730	0.649849

Ti	0.972623	0.194369	-0.641740
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Li₁₈Ti₂ (A3)

Li	-0.612110	-0.993980	2.420578
Li	-2.616282	1.136608	2.048404
Li	-3.157966	-1.591165	0.686180
Li	2.074340	0.260032	3.077179
Li	1.830190	-2.536170	1.875721
Li	-5.663570	-1.023779	-1.348837
Li	0.190213	2.099839	1.826045
Li	-0.359772	-2.620772	-0.181472
Li	-3.451066	0.795808	-0.772082
Li	-2.508476	-1.487802	-2.115911
Li	2.510037	-2.425965	-1.055997
Li	-1.600359	3.079235	-0.256016
Li	2.982031	2.212765	0.775182
Li	0.529536	-0.810202	-2.506722
Li	3.210114	0.444185	-1.826392
Li	-1.465773	1.322182	-2.903766
Li	0.939158	2.221847	-1.400825
Li	3.900676	-0.599286	0.881080
Ti	1.191619	-0.100335	0.272533
Ti	-0.745836	0.170783	-0.166490

Li₁₈Ti₂ (A4)

Li	1.461365	0.843719	3.737520
Li	2.310686	1.334075	0.674856
Li	0.000000	2.807865	2.175389
Li	-1.461365	0.843719	3.737520
Li	-0.000000	-1.687439	3.737520
Li	2.431683	-1.403933	2.175389
Li	0.000000	1.687439	-3.737520
Li	2.431683	1.403933	-2.175389
Li	-0.000000	-2.668150	0.674856
Li	-1.461365	-0.843719	-3.737520
Li	2.310686	-1.334075	-0.674856
Li	0.000000	2.668150	-0.674856
Li	-2.431683	-1.403933	2.175389
Li	-2.431683	1.403933	-2.175389
Li	-2.310686	1.334075	0.674856
Li	-0.000000	-2.807865	-2.175389
Li	1.461365	-0.843719	-3.737520
Li	-2.310686	-1.334075	-0.674856
Ti	0.000000	0.000000	1.226356

Ti	0.000000	-0.000000	-1.226356
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Li₂₀Sc₂ (B1):

Li	-2.329924	2.709391	-1.460263
Li	0.014610	1.312835	-2.539271
Li	-4.306961	1.377956	0.243535
Li	-2.051621	2.732861	1.533514
Li	0.390324	2.762086	-0.179863
Li	-3.238514	0.001907	-2.443037
Li	0.000710	-1.318213	-2.539156
Li	3.108496	1.579484	-2.146861
Li	-4.312737	-1.364071	0.247571
Li	-2.345182	-2.708800	-1.455756
Li	-2.724924	0.003518	2.742395
Li	-2.060675	-2.728188	1.534677
Li	0.382037	-2.762936	-0.182664
Li	3.100482	-1.558277	-2.165030
Li	0.367453	1.383838	2.411792
Li	3.266344	2.412648	0.865201
Li	4.707962	-0.002103	-0.114460
Li	0.365691	-1.391695	2.408264
Li	3.265533	-2.423616	0.840787
Li	3.279831	-0.013136	2.611146
Sc	-1.412904	0.000511	0.014090
Sc	1.573056	-0.001295	-0.044450

Li₂₀Sc₂ (B2)

Li	2.985797	-0.083990	-2.600956
Li	2.043968	-2.760185	-1.520037
Li	4.405652	1.184158	0.006644
Li	-3.178928	0.789607	-2.522580
Li	-0.481419	-2.727945	0.001316
Li	-0.265484	-1.240537	-2.510646
Li	2.040669	-2.755895	1.530665
Li	2.384660	2.667494	-1.499302
Li	4.227393	-1.548123	0.007169
Li	-3.192526	-2.087106	-1.565034
Li	2.971183	-0.073457	2.608965
Li	-3.193800	-2.092545	1.553860
Li	-4.715886	-0.035274	-0.002649
Li	-0.269924	-1.232490	2.512469
Li	-0.110353	1.449610	-2.439001
Li	2.375013	2.676320	1.493575
Li	-3.327785	2.564261	0.009784

Li	-0.122725	1.461630	2.427963
Li	-3.185118	0.774503	2.525718
Li	-0.239576	2.803937	-0.010771
Sc	-1.578076	0.047648	-0.001272
Sc	1.413674	-0.009644	0.000250

Li₂₀Sc₂ (B3)

Li	1.950915	0.824083	-4.054902
Li	2.491328	-1.804165	-2.960816
Li	0.028977	-3.003530	-1.692799
Li	3.257946	0.653003	-1.035034
Li	-0.322123	-1.159878	-4.194344
Li	2.613588	-0.063981	2.119401
Li	-2.614756	0.069993	-2.117917
Li	-0.861603	1.782988	-3.844356
Li	2.032093	-1.866878	0.095751
Li	1.250298	2.952223	-2.066251
Li	1.377686	2.216394	0.753626
Li	-1.367067	2.262291	-0.625469
Li	-0.039106	-3.092460	1.517983
Li	-3.254170	0.606319	1.070078
Li	-2.037657	-1.849874	-0.204402
Li	0.867545	1.555849	3.940711
Li	0.313089	-1.398645	4.123484
Li	-1.237722	2.834481	2.232170
Li	-2.499743	-1.960497	2.850624
Li	-1.950348	0.599214	4.095445
Sc	0.363295	0.029277	-1.452301
Sc	-0.363176	-0.051696	1.451875

Li₂₀Sc₂ (B4)

Li	1.417323	2.454875	-2.861819
Li	0.000000	0.000000	-4.452916
Li	-1.417323	2.454875	-2.861819
Li	2.834645	-0.000000	-2.861819
Li	-2.834645	0.000000	-2.861819
Li	1.417323	-2.454875	-2.861819
Li	-0.000000	2.800232	-0.000000
Li	-1.417323	-2.454875	-2.861819
Li	2.425072	1.400116	-0.000000
Li	-2.425072	1.400116	-0.000000
Li	-2.425072	-1.400116	-0.000000
Li	-1.417323	2.454875	2.861819
Li	-0.000000	-2.800232	-0.000000

Li	1.417323	2.454875	2.861819
Li	-2.834645	0.000000	2.861819
Li	2.834645	-0.000000	2.861819
Li	2.425072	-1.400116	-0.000000
Li	1.417323	-2.454875	2.861819
Li	-1.417323	-2.454875	2.861819
Li	-0.000000	0.000000	4.452916
Sc	0.000000	0.000000	-1.467610
Sc	-0.000000	0.000000	1.467610

Li₂₄Sc₂ (C1)

Li	-0.000000	2.930441	2.804222
Li	1.466195	0.846508	4.518871
Li	-1.466195	0.846508	4.518871
Li	-2.836695	1.637767	2.265656
Li	2.836695	1.637767	2.265656
Li	1.305625	2.414240	-0.000000
Li	-0.000000	-1.693016	4.518871
Li	-0.000000	-3.275534	2.265656
Li	-1.305625	2.414240	0.000000
Li	2.537836	-1.465220	2.804222
Li	-2.537836	-1.465220	2.804222
Li	2.743605	-0.076415	0.000000
Li	-2.743605	-0.076415	-0.000000
Li	-2.836695	1.637767	-2.265656
Li	0.000000	2.930441	-2.804222
Li	-1.437980	-2.337824	0.000000
Li	2.836695	1.637767	-2.265656
Li	1.437980	-2.337824	-0.000000
Li	-2.537836	-1.465220	-2.804222
Li	1.466195	0.846508	-4.518871
Li	2.537836	-1.465220	-2.804222
Li	-1.466195	0.846508	-4.518871
Li	-0.000000	-1.693016	-4.518871
Li	-0.000000	-3.275534	-2.265656
Sc	-0.000000	-0.000000	1.751545
Sc	0.000000	-0.000000	-1.751545

Li₂₄Sc₂ (C2)

Li	0.000000	-3.289252	2.338141
Li	0.000000	-1.674885	4.530365
Li	2.848576	-1.644626	-2.338141
Li	-1.450493	0.837443	4.530365
Li	1.450493	0.837443	4.530365

Li	1.365254	-2.364689	-0.000000
Li	2.546834	-1.470416	2.768070
Li	-2.546834	-1.470416	2.768070
Li	-1.365254	-2.364689	-0.000000
Li	-0.000000	2.940831	2.768070
Li	2.730507	-0.000000	-0.000000
Li	-2.848576	1.644626	2.338141
Li	-1.365254	2.364689	0.000000
Li	2.848576	1.644626	2.338141
Li	-2.848576	-1.644626	-2.338141
Li	0.000000	-2.940831	-2.768070
Li	-2.730507	0.000000	0.000000
Li	1.450493	-0.837443	-4.530365
Li	1.365254	2.364689	0.000000
Li	-1.450493	-0.837443	-4.530365
Li	2.546834	1.470416	-2.768070
Li	-0.000000	1.674885	-4.530365
Li	-0.000000	3.289252	-2.338141
Li	-2.546834	1.470416	-2.768070
Sc	-0.000000	0.000000	1.760298
Sc	-0.000000	-0.000000	-1.760298

Li₂₄Sc₂ (C3)

Li	-4.796758	-0.275245	-0.525738
Li	-3.659883	-2.814807	-1.239856
Li	-3.424140	-1.835631	1.558359
Li	-0.938752	-0.486254	2.164072
Li	-3.179659	1.222809	1.547879
Li	1.135877	-2.386735	2.119008
Li	-3.677379	2.188885	-1.253936
Li	-3.256458	-0.452587	-3.362992
Li	-1.133236	-3.183340	0.259802
Li	-1.328345	-2.862010	-2.813148
Li	1.584799	3.628020	0.684585
Li	1.330695	0.055133	4.012174
Li	0.048308	2.238703	2.719722
Li	-1.587751	2.012512	-3.093618
Li	-0.996266	2.444598	0.012359
Li	0.939833	-1.898742	-1.144929
Li	-0.049045	-0.416676	-3.497009
Li	3.426971	-2.391692	0.247157
Li	3.662259	-1.047236	2.888813
Li	3.256484	2.120216	2.650537
Li	3.675080	2.423325	-0.717259

Li	0.994427	1.683045	-1.775723
Li	3.178796	-0.269810	-1.954560
Li	4.795723	0.194742	0.560271
Sc	-1.630852	-0.326798	-0.783261
Sc	1.630626	0.342338	0.776694

Li₂₄Y₂ (**D1**):

Li	-1.492120	0.861476	4.636969
Li	-0.000000	-1.722952	4.636969
Li	2.874322	1.659491	2.333496
Li	-2.610295	-1.507054	2.890373
Li	1.492120	0.861476	4.636969
Li	2.610295	-1.507054	2.890373
Li	-2.874322	1.659491	2.333496
Li	1.348122	2.501203	-0.000000
Li	-0.000000	-3.318981	2.333496
Li	2.840166	-0.083093	0.000000
Li	2.610295	-1.507054	-2.890373
Li	-0.000000	-3.318981	-2.333496
Li	1.492120	0.861476	-4.636969
Li	-1.348122	2.501203	0.000000
Li	0.000000	3.014109	2.890373
Li	1.492044	-2.418109	-0.000000
Li	-1.492044	-2.418109	0.000000
Li	2.874322	1.659491	-2.333496
Li	-2.840166	-0.083093	-0.000000
Li	0.000000	-1.722952	-4.636969
Li	0.000000	3.014109	-2.890373
Li	-2.610295	-1.507054	-2.890373
Li	-2.874322	1.659491	-2.333496
Li	-1.492120	0.861476	-4.636969
Y	-0.000000	0.000000	1.814235
Y	0.000000	0.000000	-1.814235

Li₂₄Y₂ (**D2**):

Li	0.000000	3.332027	-2.405502
Li	0.000000	1.706030	-4.651320
Li	-2.619578	1.512414	-2.859517
Li	2.619578	1.512414	-2.859517
Li	1.412053	2.445748	0.000000
Li	-1.412053	2.445748	0.000000
Li	1.477465	-0.853015	-4.651320
Li	-1.477465	-0.853015	-4.651320
Li	-2.824107	-0.000000	-0.000000

Li	2.824107	-0.000000	0.000000
Li	2.885620	-1.666013	-2.405502
Li	2.885620	1.666013	2.405502
Li	-2.885620	1.666013	2.405502
Li	-1.412053	-2.445748	-0.000000
Li	2.619578	-1.512414	2.859517
Li	-0.000000	-3.024828	-2.859517
Li	-2.619578	-1.512414	2.859517
Li	-2.885620	-1.666013	-2.405502
Li	1.412053	-2.445748	0.000000
Li	-0.000000	3.024828	2.859517
Li	-0.000000	-3.332027	2.405502
Li	-0.000000	-1.706030	4.651320
Li	1.477465	0.853015	4.651320
Li	-1.477465	0.853015	4.651320
Y	-0.000000	-0.000000	-1.824261
Y	-0.000000	0.000000	1.824261

Li₂₄Y₂ (**D3**):

Li	-0.997857	3.318898	-2.183723
Li	-1.334216	0.576884	-3.897713
Li	-1.944320	-2.348096	-2.726438
Li	3.521899	-0.362694	-2.057845
Li	-3.570173	2.331219	-2.463466
Li	-2.769459	3.031019	0.523376
Li	-4.083837	-0.579884	-2.774105
Li	1.200776	1.421213	-2.092922
Li	0.790852	-1.354646	-2.391890
Li	-1.232704	-1.517954	2.001515
Li	-0.776288	1.253852	2.387456
Li	-3.612322	-2.095364	-0.050751
Li	-0.356514	-2.823302	-0.289700
Li	-4.907977	0.840453	-0.292886
Li	-3.534159	0.316009	2.054110
Li	1.078175	-3.274457	2.269560
Li	3.560433	2.119159	-0.002208
Li	0.430773	2.749951	0.302663
Li	4.913263	-0.709028	0.311472
Li	1.888172	2.409723	2.775837
Li	2.844433	-3.055412	-0.452332
Li	3.663852	-2.262820	2.505411
Li	1.340717	-0.595902	3.907661
Li	4.025709	0.658760	2.769349
Y	-1.655114	0.321909	-0.734182

Y	1.644404	-0.325569	0.723995
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[Li₁₇Ti₂]⁻:

Li	0.000000	0.000000	4.179599
Li	0.000000	-2.550556	2.628878
Li	2.425723	-0.788165	2.628878
Li	1.499179	2.063443	2.628878
Li	-1.499179	2.063443	2.628878
Li	-2.425723	-0.788165	2.628878
Li	-0.000000	2.619724	-0.000000
Li	1.539835	-2.119402	-0.000000
Li	-1.539835	-2.119402	-0.000000
Li	2.491506	0.809539	-0.000000
Li	-2.491506	0.809539	-0.000000
Li	0.000000	-2.550556	-2.628878
Li	2.425723	-0.788165	-2.628878
Li	-2.425723	-0.788165	-2.628878
Li	1.499179	2.063443	-2.628878
Li	-1.499179	2.063443	-2.628878
Li	0.000000	0.000000	-4.179599
Ti	0.000000	0.000000	1.141322
Ti	0.000000	0.000000	-1.141322

[Li₁₇V₂]⁺:

Li	0.000000	0.000000	4.922462
Li	-0.000000	-2.356836	2.733633
Li	2.241484	-0.728302	2.733633
Li	1.385313	1.906720	2.733633
Li	-1.385313	1.906720	2.733633
Li	-2.241484	-0.728302	2.733633
Li	0.000000	2.627714	-0.000000
Li	1.544531	-2.125865	-0.000000
Li	-1.544531	-2.125865	-0.000000
Li	2.499104	0.812008	-0.000000
Li	-2.499104	0.812008	-0.000000
Li	0.000000	-2.356836	-2.733633
Li	2.241484	-0.728302	-2.733633
Li	-2.241484	-0.728302	-2.733633
Li	1.385313	1.906720	-2.733633
Li	-1.385313	1.906720	-2.733633
Li	0.000000	0.000000	-4.922462
V	0.000000	0.000000	0.876226
V	0.000000	0.000000	-0.876226