Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Planar Pentacoordinate Carbon in CGa_5^+ Derivatives

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Supporting Information

Table S1. EDA results for **5A**, **5B** and **5C** isomers of CGa_3Be_2Li cluster at the PBE-D3(BJ)/TZ2P//PBE0-D3/def2-TZVPP level taking $CGa_3Be_2^-$ and Li^+ in singlet ground states as interacting fragments. Energy values are in kcal/mol.

Fragments	**5A**	**5B**	**5C**
ΔE_{int}	-128.8	-135.4	-126.7
ΔE_{elstat}[a]	-107.6 (72.0%)	-116.3 (74.0%)	-102.5 (70.3%)
ΔE_{Pauli}	20.8	21.8	19.1
ΔE_{orb}[a]	-40.8 (27.3%)	-39.7 (25.3%)	-42.3 (29.0%)
ΔE_{disp}[a]	-1.1 (0.7%)	-1.2 (0.8%)	-1.0 (0.7%)

[a]The values within the parentheses show the contribution towards the total attractive interaction $\Delta E_{elstat} + \Delta E_{orb} + \Delta E_{disp}$.

Table S2. The natural charge on each atomic center (q, au), total WBI values for C center (WBI_C), valence orbital population of C center, HOMO-LUMO energy gap (Δ_{H-L}, eV), the lowest frequency (ν, cm^{-1}) and the related frequency for the out-of-plane mode of vibration of C (ν_C, cm^{-1}) at the PBE0-D3/def2-TZVPP level.

Clusters	***q***				**WBI_C**	**Pop**	**Δ_{H-L}**	**ν_{min}**	**ν_C**
	C	**Ga**	**Be**	**Li**					
CGa_4Be, **1A**	-2.41	0.49, 0.55	0.33		2.52	$2s^{1.56}\ 2p_x^{1.76}\ 2p_y^{1.63}\ 2p_z^{1.45}$	2.79	41	224
$CGa_3Be_2^-$, **2A**	-2.33	0.33, 0.35	0.16		2.61	$2s^{1.50}\ 2p_x^{1.77}\ 2p_y^{1.62}\ 2p_z^{1.42}$	2.93	73	283
CGa_3Be_2Li, **5A**	-2.30	0.46, 0.53, 0.29(Li)	0.34, -0.10(Li)	0.78	2.64	$2s^{1.50}\ 2p_x^{1.77}\ 2p_y^{1.59}\ 2p_z^{1.42}$	2.96	32	288
$CGa_2Be_3Li_2$, **6B**	-2.21	0.48	0.05, -0.39	0.78	2.73	$2s^{1.44}\ 2p_x^{1.73}\ 2p_y^{1.64}\ 2p_z^{1.38}$	2.96	57	305
$CGaBe_4Li_3$, **7A**	-2.15	0.54	-0.02, -0.30	0.74, 0.76	2.77	$2s^{1.39}\ 2p_x^{1.73}\ 2p_y^{1.65}\ 2p_z^{1.36}$	2.64	49	343

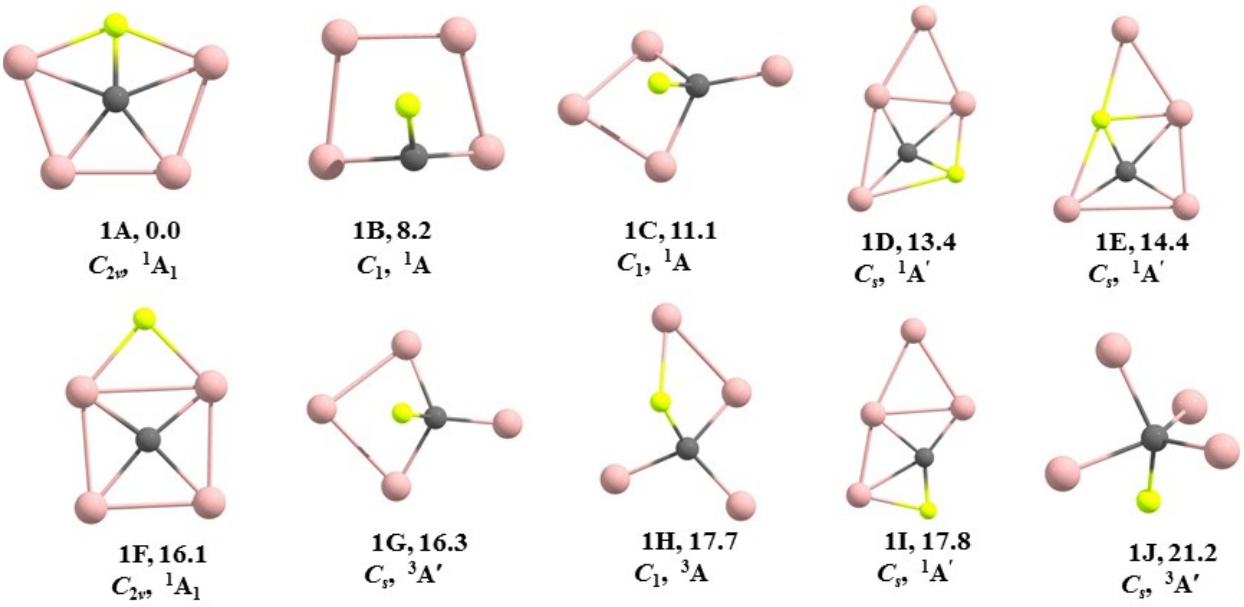

Fig. S1 Low-lying isomers of CGa_4Be cluster studied at the CCSD(T)/def2-TZVPP//PBE0-D3/def2-TZVPP level. Relative energies are in kcal/mol.

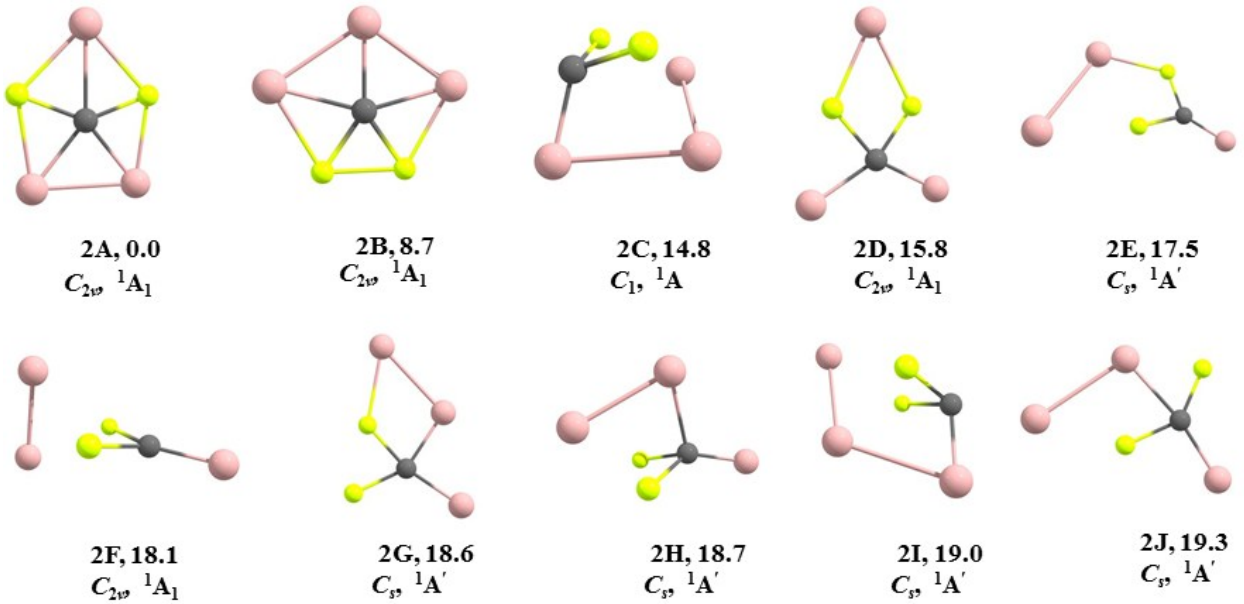

Fig. S2 Low-lying isomers of $CGa_3Be_2^-$ clusters studied at the CCSD(T)/def2-TZVPP//PBE0-D3/def2-TZVPP level. Relative energies are in kcal/mol.

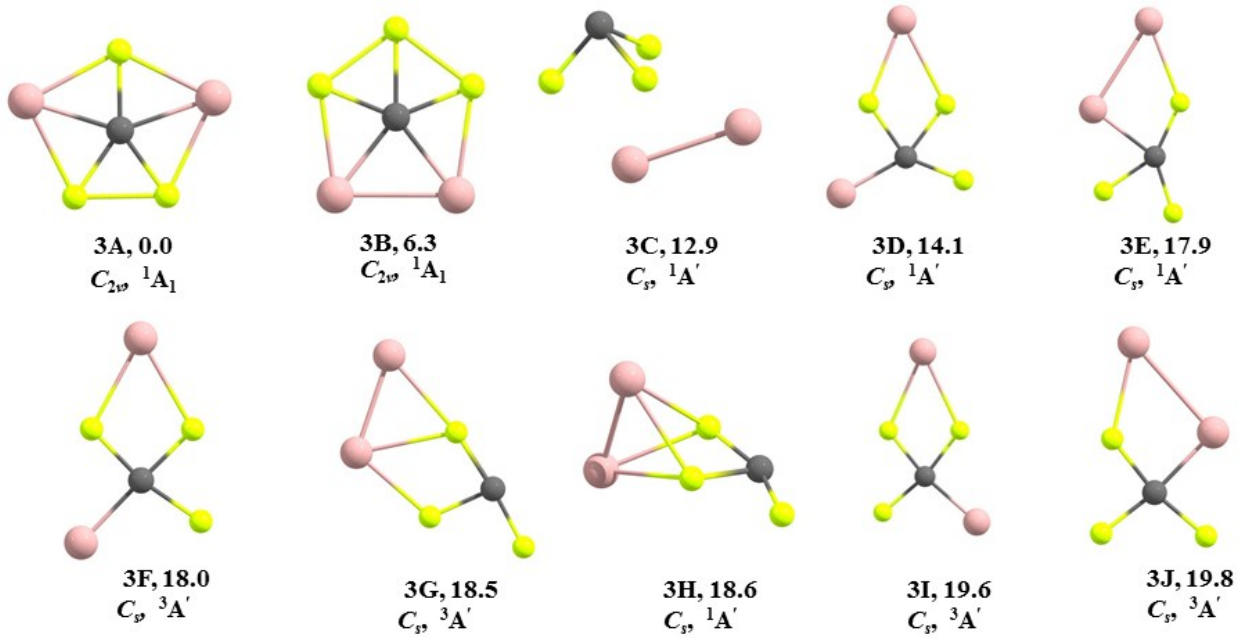

Fig. S3 Low-lying isomers of $CGa_2Be_3^{2-}$ clusters studied at the CCSD(T)/def2-TZVPP//PBE0-D3/def2-TZVPP level. Relative energies are in kcal/mol.

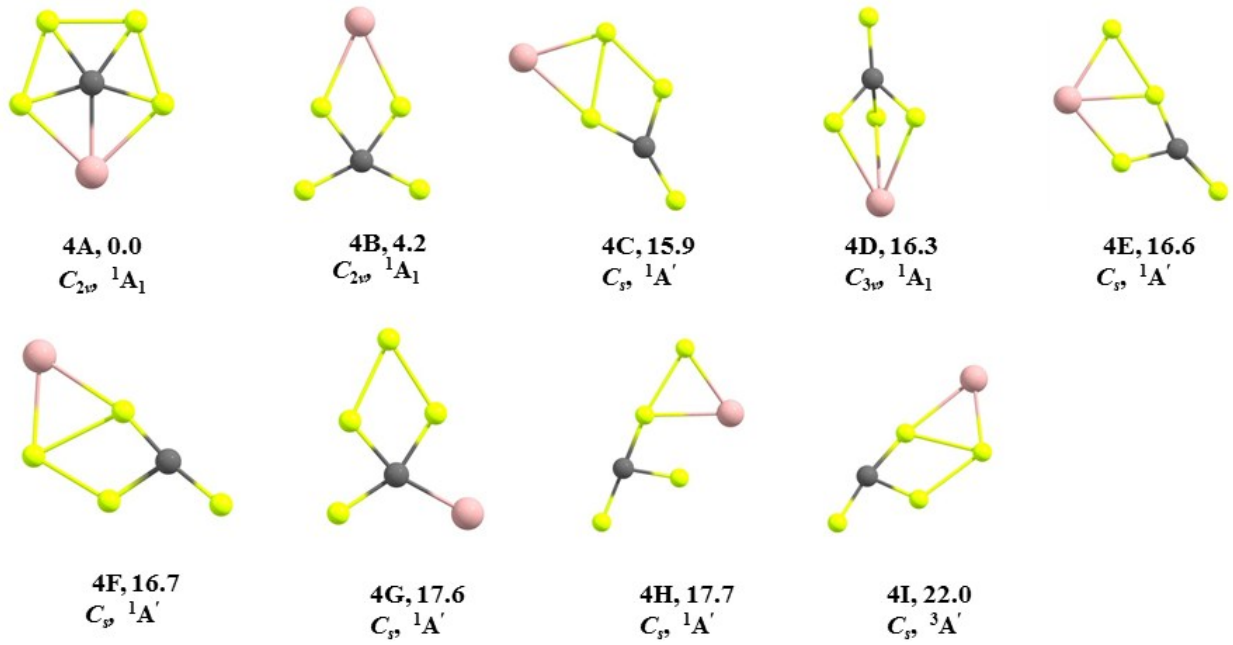

Fig. S4 Low-lying isomers of $CGaBe_4^{3-}$ clusters studied at the CCSD(T)/def2-TZVPP//PBE0-D3/def2-TZVPP level. Relative energies are in kcal/mol.

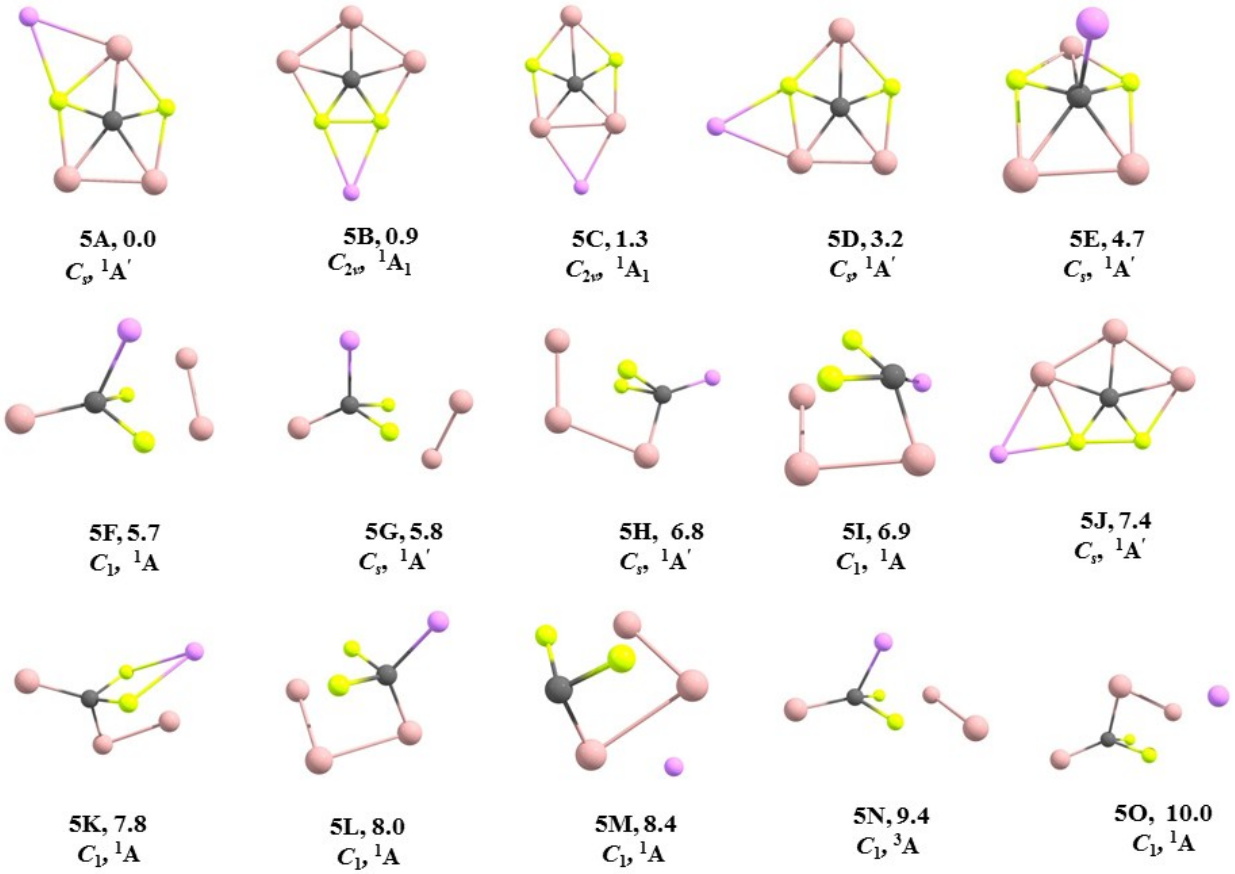

Fig. S5 Low-lying isomers of CGa_3Be_2Li clusters studied at the CCSD(T)/def2-TZVPP//PBE0-D3/def2-TZVPP level. Relative energies are in kcal/mol.

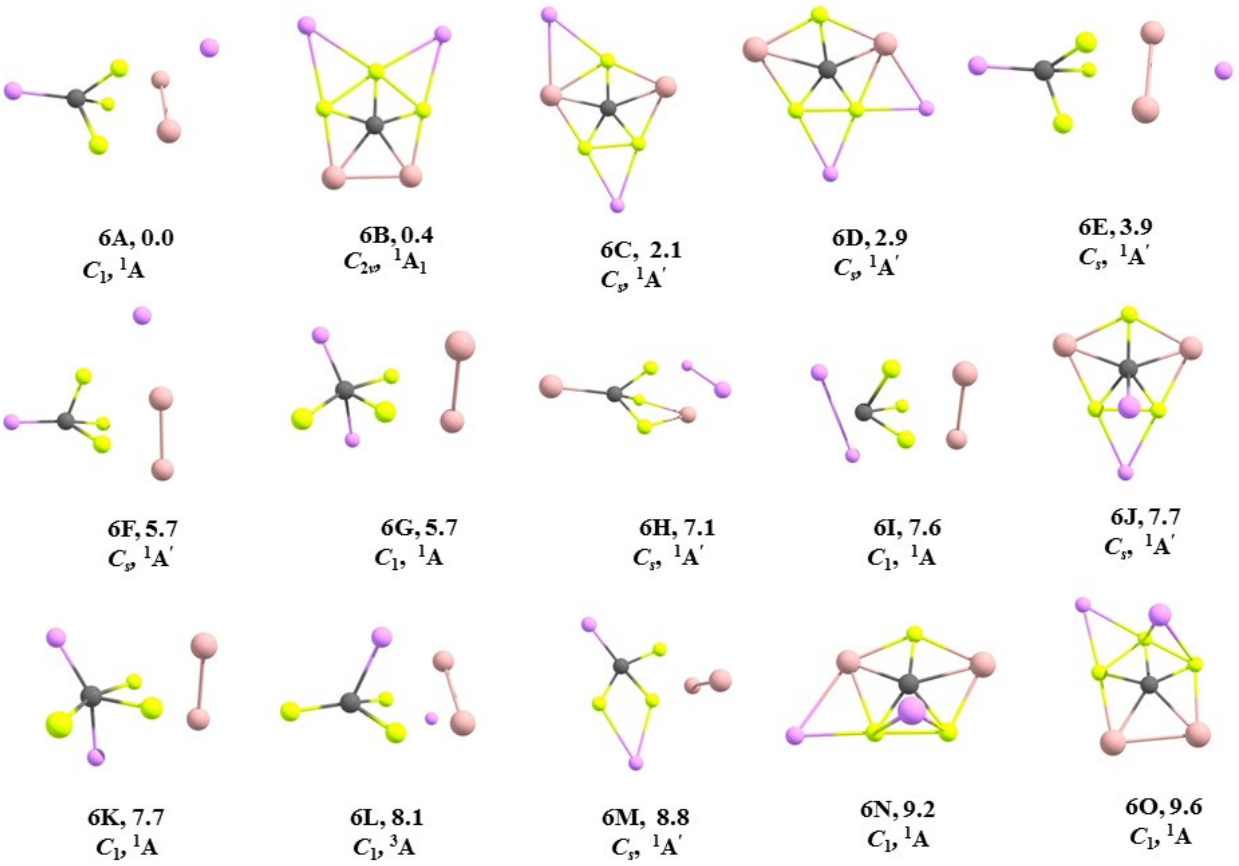

Fig. S6 Low-lying isomers of $CGa_2Be_3Li_2$ clusters studied at the CCSD(T)/def2-TZVPP//PBE0-D3/def2-TZVPP level. Relative energies are in kcal/mol.

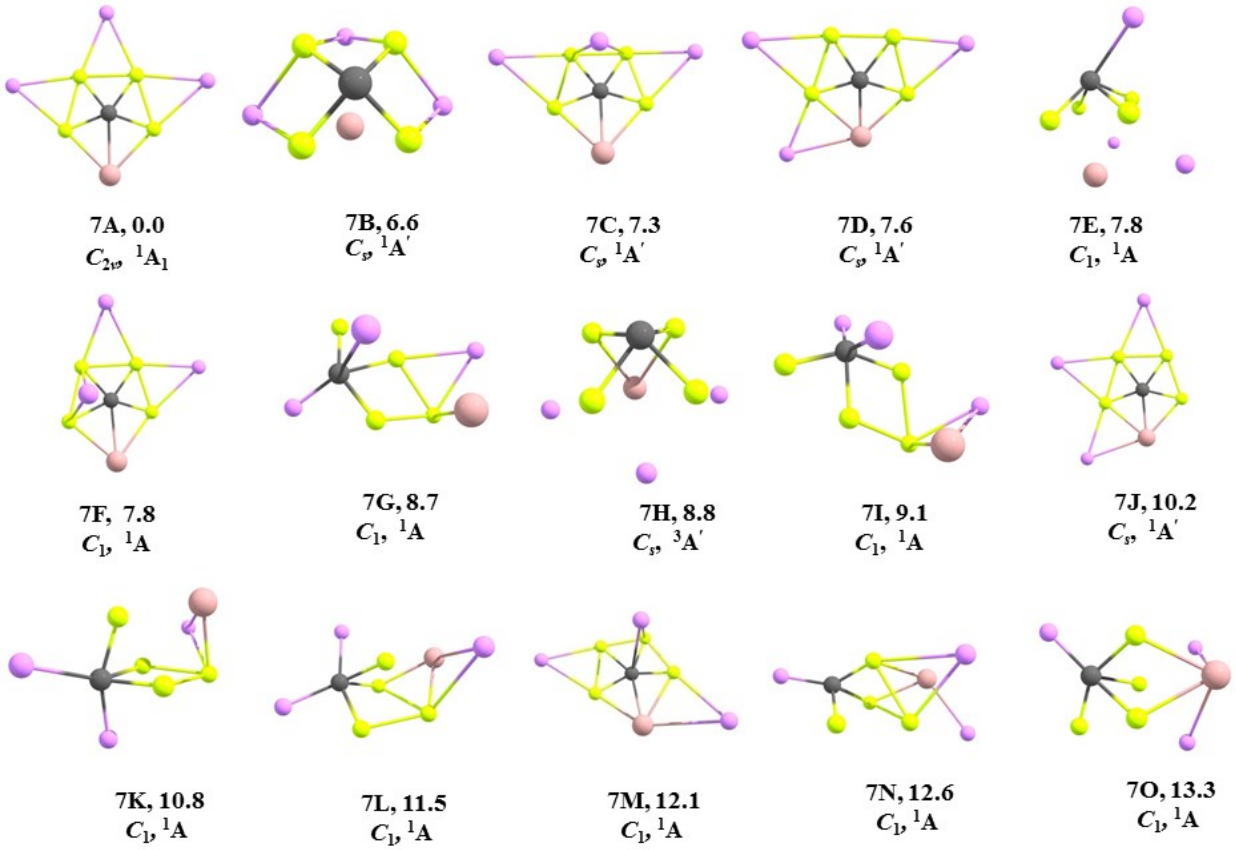

Fig. S7 Low-lying isomers of $CGaBe_4Li_3$ clusters studied at the CCSD(T)/def2-TZVPP//PBE0-D3/def2-TZVPP level. Relative energies are in kcal/mol.

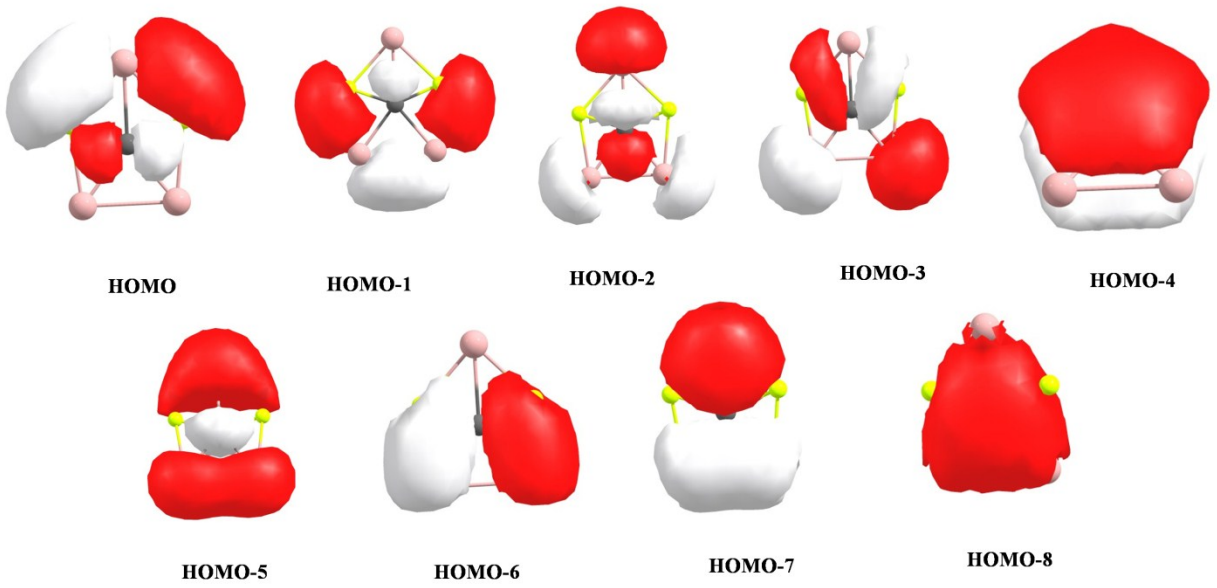

Fig. S8 The occupied valence molecular orbitals of **2A**, $CGa_3Be_2^-$.

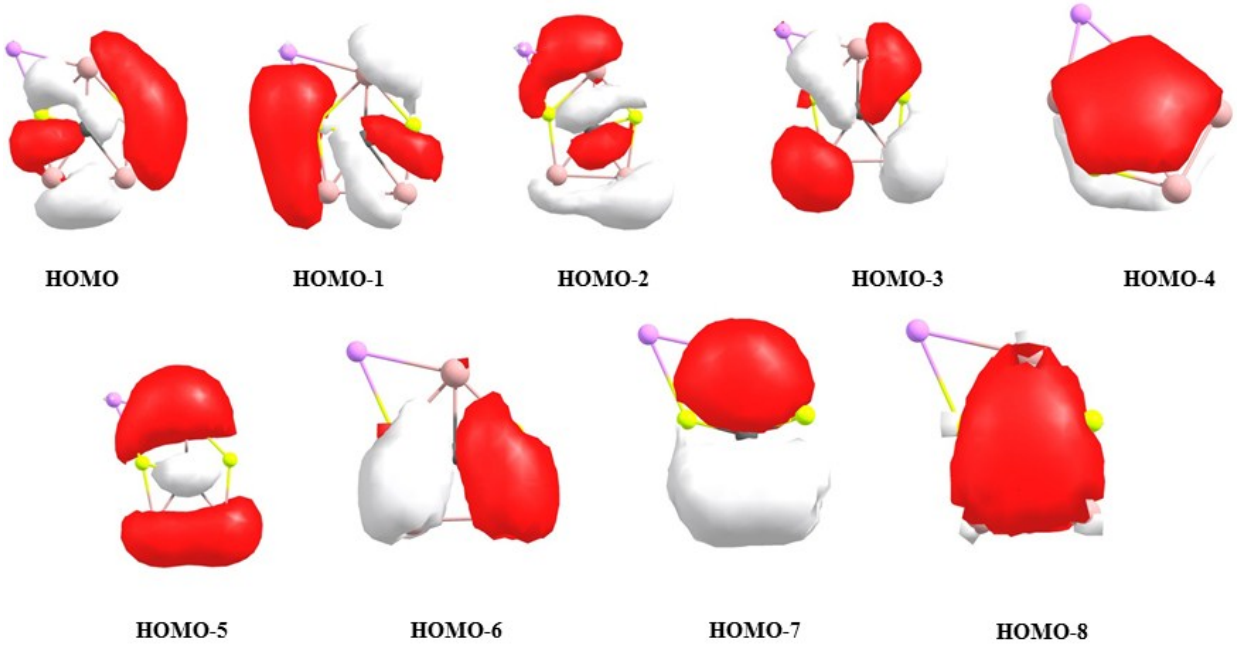

Fig. S9 The occupied valence molecular orbitals of **5A**, CGa_3Be_2Li.

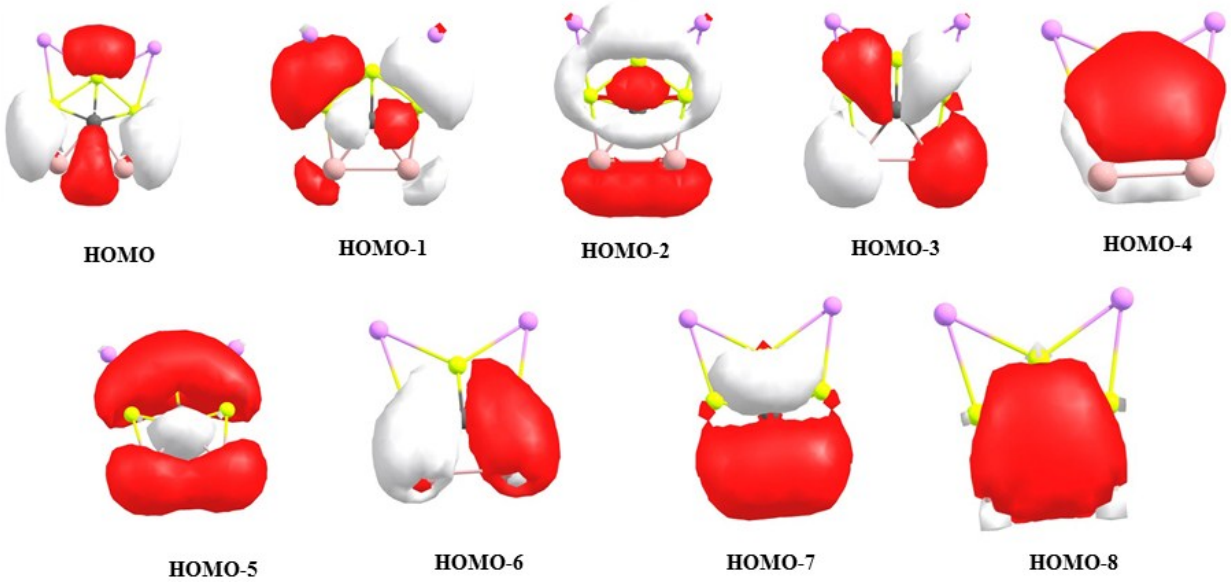

Fig. S10 The occupied valence molecular orbitals of **6B**, $CGa_2Be_3Li_2$.

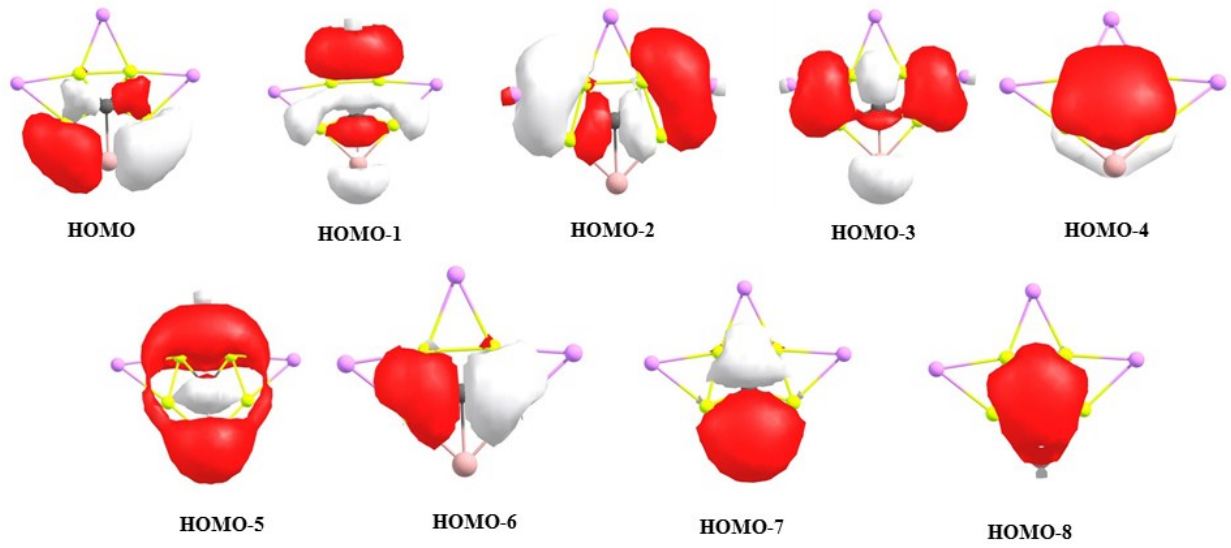

Fig. S11 The occupied valence molecular orbitals of **7A**, $CGaBe_4Li_3$.

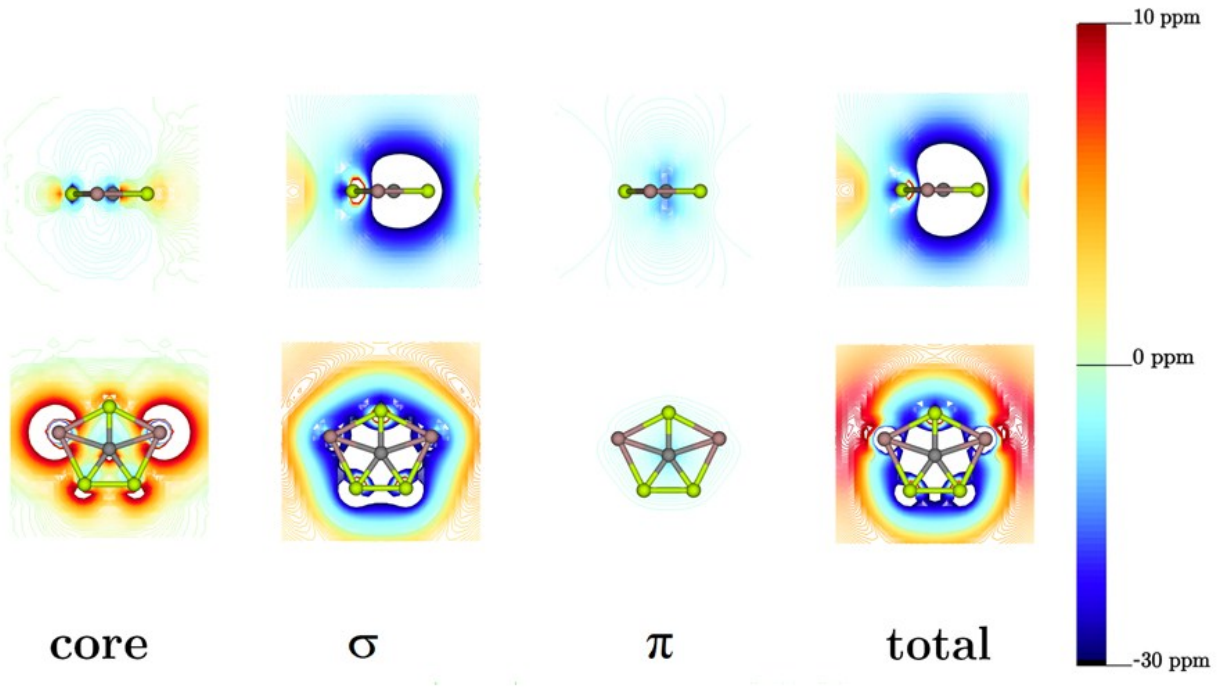

Fig. S12 The isolines of B_z^{ind} of **2A**, $CGa_3Be_2^-$.

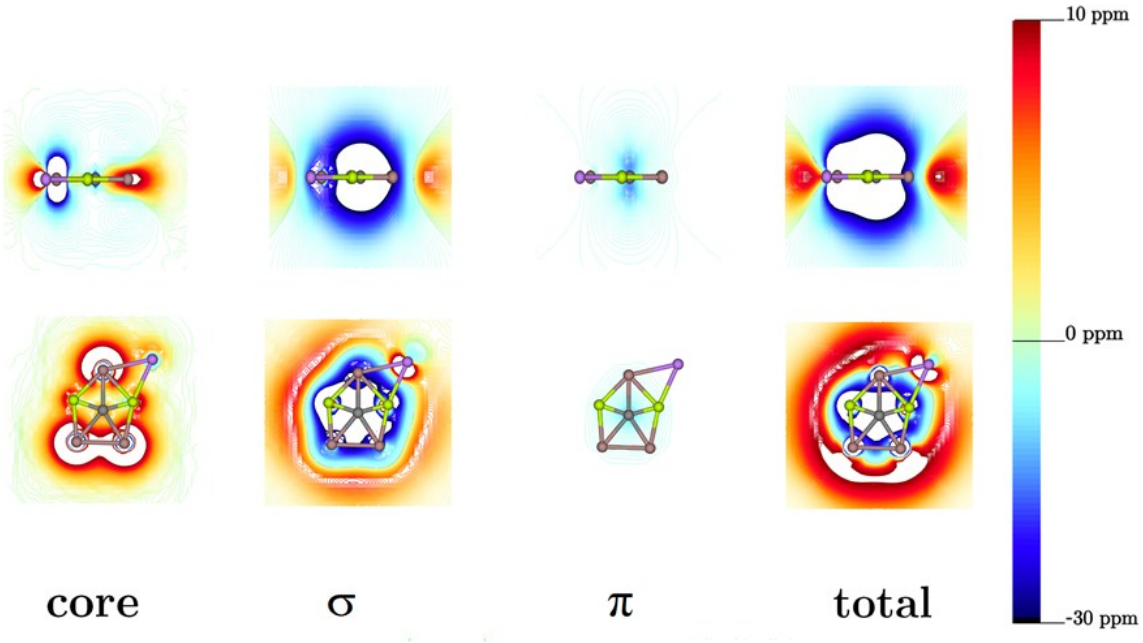

Fig. S13 The isolines of B_z^{ind} of **5A**, CGa_3Be_2Li.

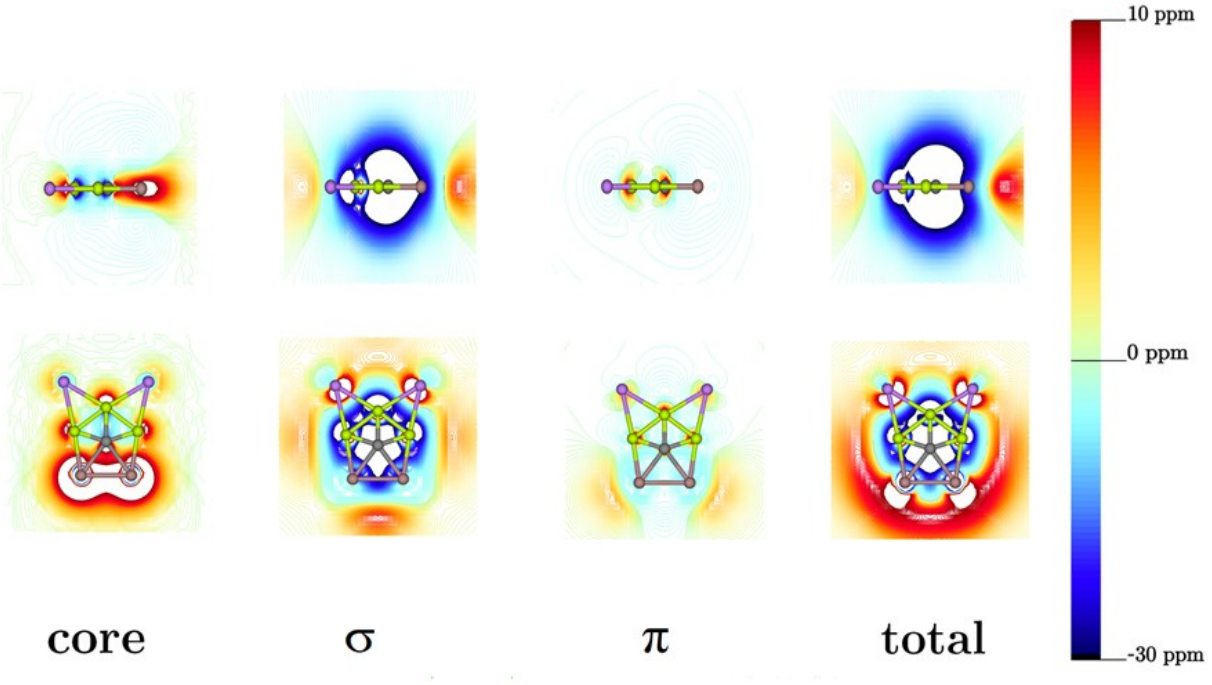

Fig. S14 The isolines of B_z^{ind} of **6B**, $CGa_2Be_3Li_2$.

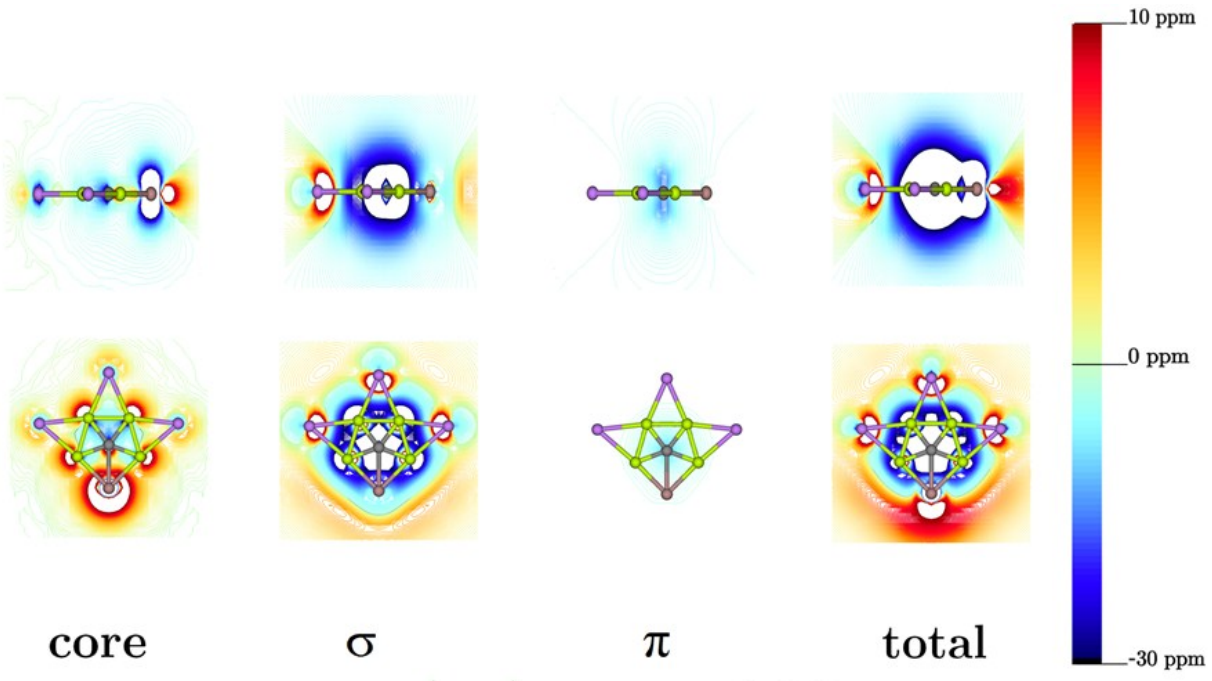

Fig. S15 The isolines of B_z^{ind} of **7A**, $CGaBe_4Li_3$.

PBE0-D3/def2-TZVPP Coordinates for five low-lying isomers of the studied clusters

CGa_4Be

1A

0 1

C	0.00000000	0.00000000	0.32262000
Ga	0.00000000	1.27785500	-1.29009300
Ga	0.00000000	-1.27785500	-1.29009300
Be	0.00000000	0.00000000	1.95665500
Ga	0.00000000	2.10956200	1.13263600
Ga	0.00000000	-2.10956200	1.13263600

1B

0 1

Ga	-1.35635800	-1.60572900	-0.02866900
Be	-0.17831700	0.25975900	1.63495600

Ga	-1.57938000	1.07219200	-0.19130600
C	0.32352900	-1.01525500	0.78987000
Ga	2.02455000	-0.88646500	-0.19730200
Ga	0.87157900	1.58298600	0.05343800

1C

0 1

Be	-0.14594200	-0.36044800	1.52126700
Ga	-0.57136200	-1.58465700	-0.43090000
Ga	-0.07192600	1.68194500	-0.37098800
Ga	2.76786300	-0.17664000	0.19712000
C	0.80129700	-0.02996100	0.22552300
Ga	-2.26083400	0.13166100	0.36482700

1D

0 1

Ga	3.09206300	0.35790400	0.00000000
Be	1.30625200	-2.09820400	0.00000000
Ga	-0.76237700	-1.53512800	0.00000000
Ga	-2.74002900	0.53397800	0.00000000
C	1.24927200	-0.48285400	0.00000000
Ga	0.00000000	1.00743800	0.00000000

1E

0 1

31	0.840464000	-1.145889000	0.000000000
4	-1.189221000	-0.183998000	0.000000000
6	0.000000000	0.941272000	0.000000000
31	1.955848000	1.264991000	0.000000000
31	-1.190360000	2.539678000	0.000000000
31	-1.452504000	-2.817220000	0.000000000

$CGa_3Be_2^-$

2A

-1 1

C	0.00000000	0.00000000	0.26139400
Ga	0.00000000	1.29375400	-1.38899300
Ga	0.00000000	-1.29375400	-1.38899300
Be	0.00000000	-1.56122400	0.87457900
Ga	0.00000000	0.00000000	2.50169500
Be	0.00000000	1.56122400	0.87457900

2B

-1 1

Ga	0.00000000	2.10642100	-0.23680100
Be	0.00000000	-0.97736300	-2.22909900
C	0.00000000	0.00000000	-0.80900100
Ga	0.00000000	0.00000000	1.20543400
Be	0.00000000	0.97736300	-2.22909900
Ga	0.00000000	-2.10642100	-0.23680100

2C

-1 1

Ga	2.07634300	-0.22894400	-0.26667600
Ga	-0.39966400	1.43125100	0.10751900
Be	-0.22474400	-0.26777400	1.64413900
C	0.86127300	-1.21152000	0.91639200
Ga	-1.77073900	-0.64636900	-0.28878300
Be	-0.33819900	-2.22346400	0.45280900

2D

-1 1

Be	0.00000000	1.02255100	0.85073100
Be	0.00000000	-1.02255100	0.85073100
C	0.00000000	0.00000000	-0.52828900
Ga	0.00000000	-1.67979100	-1.52290900
Ga	0.00000000	1.67979100	-1.52290900
Ga	0.00000000	0.00000000	2.92852500

2E

-1 1

Be	0.00000000	0.51780000	0.00000000
C	1.57858600	0.21025700	0.00000000
Ga	-1.16852500	-1.65998700	0.00000000

Be	1.08244600	-1.32897200	0.00000000
Ga	-2.51564500	0.56058500	0.00000000
Ga	3.23896700	1.16337400	0.00000000

$CGa_2Be_3^{2-}$

3A

-2 1

Be	0.00000000	0.99907700	1.86729200
Ga	0.00000000	2.02670500	-0.20494100
Be	0.00000000	-0.99907700	1.86729200
C	0.00000000	0.00000000	0.45543500
Ga	0.00000000	-2.02670500	-0.20494100
Be	0.00000000	0.00000000	-1.24114800

3B

-2 1

Ga	-1.28390100	-0.52244600	0.00000600
C	0.00090700	1.10404800	-0.00134200
Be	0.00218400	2.94385500	0.00089600
Ga	1.28309200	-0.52371700	0.00012900
Be	1.61115900	1.75288200	-0.00034200
Be	-1.60843400	1.75495700	0.00041600

3C

-2 1

Be	-0.71284400	1.25462200	1.01280500
Be	-0.71240200	1.25511100	-1.01249100
Ga	-0.64254700	-1.01425600	-0.00011200
C	-1.83606700	1.88093600	0.00005700
Be	-2.59967600	0.46627600	-0.00004300
Ga	1.51726000	0.26620300	0.00006600

3D

-2 1

Be	-0.16266200	-0.42461700	0.00090100
Be	1.02770500	2.56142700	0.00021000
Ga	2.31960300	-0.41482700	-0.00000800
C	0.90098800	0.93008700	-0.00063900
Ga	-2.51126600	-0.23681300	-0.00006300
Be	-0.73113600	1.51827100	0.00039300

3E

-2 1

Ga	0.75612900	-0.84367600	0.00004500
Be	3.14931500	1.84021500	-0.00007800
Be	0.14029700	1.47631000	0.00037800
C	1.72242500	1.06272300	0.00001100
Be	2.90788600	-0.15195500	-0.00023400
Ga	-1.88917800	0.22965600	-0.00005600

$CGaBe_4^{3-}$

4A

-3 1

C	0.00000000	0.00000000	-1.08186500
Be	0.00000000	1.66612800	-0.58336200
Be	0.00000000	-1.66612800	-0.58336200
Be	0.00000000	1.03535200	-2.52270100
Ga	0.00000000	0.00000000	1.01095800
Be	0.00000000	-1.03535200	-2.52270100

4B

-3 1

Be	0.81131100	1.01355300	0.00066900
Be	0.81190400	-1.01107500	-0.00056400
Be	2.94685900	-1.46913800	0.00006500
C	2.20108500	-0.00017400	0.00053700
Be	2.94582500	1.46858300	-0.00078500
Ga	-1.39581000	-0.00021400	-0.00002400

4C

-3 1

Be	-2.10319200	1.35009000	-0.00078300
Be	-0.98407900	-0.42847400	0.00040300
Be	-4.11202200	-0.87030400	0.00097000
Ga	1.43109400	-0.18060200	-0.00004800
C	-2.59831500	-0.21360900	-0.00083800
Be	0.00578900	1.66876800	0.00104100

4D

-3 1

Ga	-0.00000000	0.00000000	1.26718834
Be	1.10606173	0.63823814	-0.98597077
Be	-0.00000000	-0.00000000	-3.73839466
Be	-0.00030042	-1.27699662	-0.98597077
Be	-1.10576131	0.63875848	-0.98597077
C	0.00000000	-0.00000000	-2.07450066

4E

-3 1

Ga	1.08577700	0.28544900	0.00064300
Be	-3.90466000	0.22202800	0.00662500
Be	1.03491300	-2.03823800	0.00350300
C	-2.29949400	-0.17499500	-0.00065900
Be	-0.96686700	-1.11062800	-0.00856100
Be	-1.12891800	0.97710400	-0.00556300

CGa_3Be_2Li

5A

0 1

C	0.00000000	0.26796700	0.00000000
Ga	1.14319700	-1.50595800	0.00000000
Ga	0.00658700	2.40333300	0.00000000
Be	1.60041800	0.69981200	0.00000000
Li	2.64165200	2.98591100	0.00000000
Be	-1.57133800	0.80344900	0.00000000
Ga	-1.40918000	-1.43216800	0.00000000

5B

0 1

Be	0.00000000	0.97482900	-2.08501700
Ga	0.00000000	-2.07916000	-0.12023200
C	0.00000000	0.00000000	-0.70163200
Ga	0.00000000	2.07916000	-0.12023200
Ga	0.00000000	0.00000000	1.34272500

Li	0.00000000	0.00000000	-4.42672600
Be	0.00000000	-0.97482900	-2.08501700

5C

0 1

Ga	0.00000000	0.00000000	2.64567900
Be	0.00000000	1.49627100	0.98998900
Ga	0.00000000	-1.35831600	-1.29764600
Ga	0.00000000	1.35831600	-1.29764600
Li	0.00000000	0.00000000	-3.58149000
C	0.00000000	0.00000000	0.21042600
Be	0.00000000	-1.49627100	0.98998900

5D

0 1

Ga	0.34316700	2.51613000	0.00000000
Ga	-1.61975700	-1.15487300	0.00000000
Be	1.61401900	0.63983900	0.00000000
Ga	0.90776200	-1.54952100	0.00000000
Li	3.56257500	-0.93524500	0.00000000
Be	-1.42753300	1.12486000	0.00000000
C	0.00000000	0.26384900	0.00000000

5E

0 1

Ga	0.60803300	2.42146500	0.00000000
Be	-0.11836600	0.88967000	1.52958900
Ga	-0.11836600	-1.39754900	-1.29764300
Be	-0.11836600	0.88967000	-1.52958900
Li	-2.43062000	0.88077900	0.00000000
C	-0.54526000	0.30382500	0.00000000
Ga	-0.11836600	-1.39754900	1.29764300

$CGa_2Be_3Li_2$

6A

0 1

31	0.116068000	1.255934000	-0.110274000
31	-1.391722000	-0.777839000	-0.138492000
4	2.358389000	0.663892000	-0.135434000
3	3.883882000	-2.000108000	0.014756000
4	1.101439000	-0.702259000	1.178283000
3	-1.192307000	0.303651000	2.124281000
4	0.948366000	-0.963626000	-0.841225000
6	2.306298000	-0.953931000	0.081355000

6B

0 1

Be	0.00000000	0.00000000	2.60768300
Be	0.00000000	1.59896800	1.40751800
Ga	0.00000000	1.27025200	-0.81275700
Li	0.00000000	-2.14414600	3.88988200
C	0.00000000	0.00000000	0.89346000
Li	0.00000000	2.14414600	3.88988200
Ga	0.00000000	-1.27025200	-0.81275700
Be	0.00000000	-1.59896800	1.40751800

6C

0 1

4	0.154028000	-1.284713000	0.000000000
3	-0.054029000	4.083442000	0.000000000
4	-1.003857000	1.730758000	0.000000000
31	2.110359000	-0.157131000	0.000000000
31	-1.960701000	-0.306971000	0.000000000
3	-1.646272000	-3.002680000	0.000000000
4	0.965205000	1.786404000	0.000000000
6	0.000000000	0.369179000	0.000000000

6D

0 1

4	0.936533000	1.666358000	0.000000000
6	0.000000000	0.292640000	0.000000000
4	-0.200710000	-1.376109000	0.000000000
31	-2.187621000	-0.359245000	0.000000000
31	1.899825000	-0.489756000	0.000000000
4	-1.071812000	1.597586000	0.000000000
3	3.424345000	1.723236000	0.000000000

3	-0.002465000	3.947380000	0.000000000

6E

0 1

4	-0.591540000	-1.164437000	0.997167000
4	-0.591540000	-1.164437000	-0.997167000
6	-1.740123000	-1.814675000	0.000000000
3	-2.930754000	-3.286227000	0.000000000
31	-0.591540000	1.086900000	0.000000000
3	1.983395000	2.129769000	0.000000000
4	-2.406439000	-0.325456000	0.000000000
31	1.483182000	-0.281263000	0.000000000

$CGaBe_4Li_3$

7A

0 1

Be	0.00000000	1.02083000	-2.05615000
Li	0.00000000	0.00000000	-4.34990900
Be	0.00000000	1.58437500	-0.12636100
Li	0.00000000	-3.50395600	-1.78368100
Li	0.00000000	3.50395600	-1.78368100
Be	0.00000000	-1.58437500	-0.12636100
Be	0.00000000	-1.02083000	-2.05615000
C	0.00000000	0.00000000	-0.71829700
Ga	0.00000000	0.00000000	1.46844100

7B

0 1

6	-1.013914000	-1.722416000	0.000000000
4	-1.637022000	-0.550268000	0.995969000
4	0.217249000	-1.471107000	1.045016000
3	-1.749160000	1.780391000	0.000000000
3	0.217249000	0.533146000	-2.601717000
4	-1.637022000	-0.550268000	-0.995969000
31	0.689860000	0.579531000	0.000000000
4	0.217249000	-1.471107000	-1.045016000
3	0.217249000	0.533146000	2.601717000

7C

0 1

6	0.635663000	0.648328000	0.000000000
4	0.972162000	1.980516000	-1.020002000
4	0.263628000	0.169338000	1.595109000
3	-1.085460000	2.310608000	0.000000000
4	0.972162000	1.980516000	1.020002000
3	0.263628000	1.953533000	-3.405120000
4	0.263628000	0.169338000	-1.595109000
3	0.263628000	1.953533000	3.405120000
31	-0.387925000	-1.281994000	0.000000000

7D

0 1

4	-0.938998000	2.411256000	0.000000000
4	1.044484000	2.278357000	0.000000000
4	-1.687174000	0.564502000	0.000000000
4	1.565034000	0.325611000	0.000000000
6	0.000000000	0.917665000	0.000000000
3	-3.405607000	2.417208000	0.000000000
3	3.509363000	1.909842000	0.000000000
3	2.358186000	-1.976704000	0.000000000
31	-0.236104000	-1.125030000	0.000000000

7E

0 1

6	1.795035000	-0.481546000	0.181831000
3	-0.824529000	1.223765000	2.058912000
4	1.111567000	0.200612000	-1.222162000
31	-1.071197000	-0.168646000	-0.153409000
3	-0.321636000	2.204728000	-1.133895000
4	0.670183000	-1.583551000	-0.308981000
3	3.457614000	0.380671000	-0.435332000
4	1.314867000	1.126440000	0.579716000
4	0.779020000	-0.571053000	1.500333000