

Supporting Information

Endohedral C_3 $Ca@B_{39}^+$ and C_2 $Ca@B_{39}^+$: Axially Chiral Metalloborospherenes Based on $B_{39}^{-□}$

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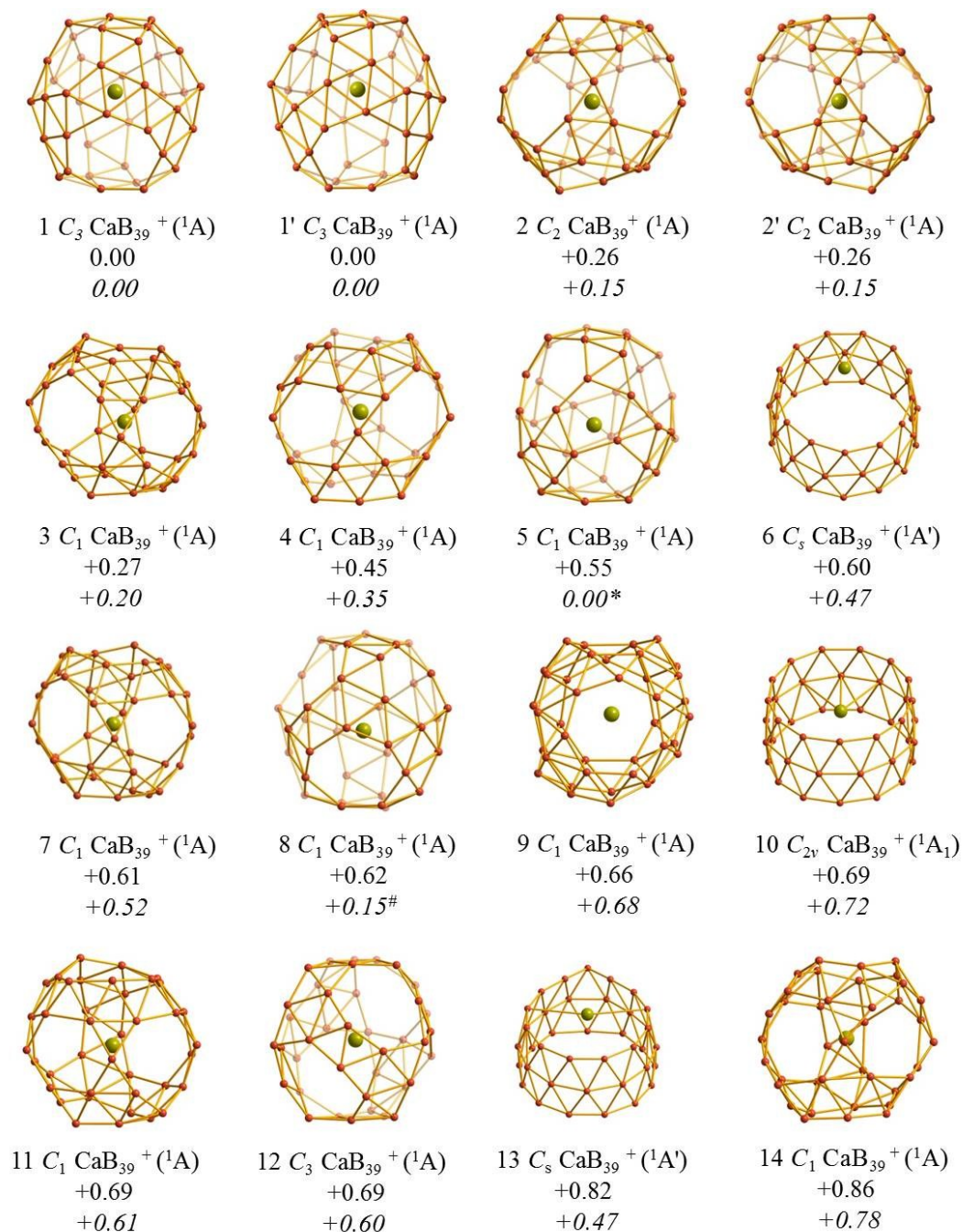
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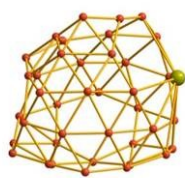
Fig. S1 Low-lying isomers of CaB_{39}^+ with their relative energies (with zero-point corrections included) indicated in eV at PBE0/6-311+G(d) and CAM-B3LYP/6-311+G(d) (in *italic*) levels.



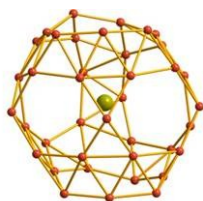
The isomer 5 marked with * is automatically converted to the isomer 1 during structural optimization at CAM-B3LYP/6-311+G(d) level.

The isomer 8 marked with # is automatically converted to the isomer 2 during structural optimization at CAM-B3LYP/6-311+G(d) level.

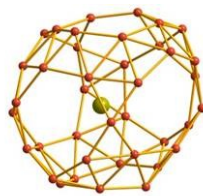
(Continued)



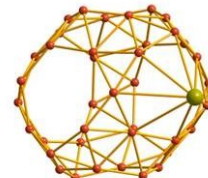
15 C_1 $\text{CaB}_{39}^+ (^1A)$
+0.91



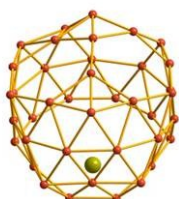
16 C_1 $\text{CaB}_{39}^+ (^1A)$
+0.93



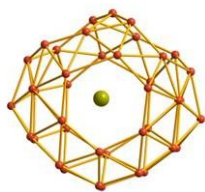
17 C_1 $\text{CaB}_{39}^+ (^1A)$
+0.95



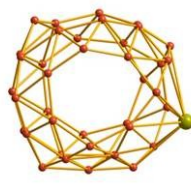
18 C_1 $\text{CaB}_{39}^+ (^1A)$
+0.98



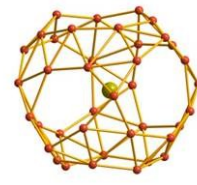
29 C_1 $\text{CaB}_{39}^+ (^1A)$
+0.99



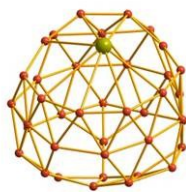
20 C_1 $\text{CaB}_{39}^+ (^1A)$
+1.01



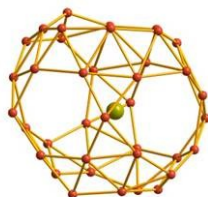
21 C_1 $\text{CaB}_{39}^+ (^1A)$
+1.03



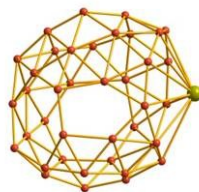
22 C_1 $\text{CaB}_{39}^+ (^1A)$
+1.03



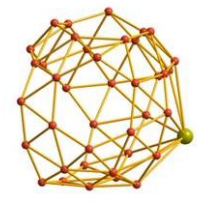
23 C_1 $\text{CaB}_{39}^+ (^1A)$
+1.03



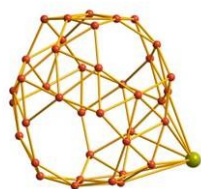
24 C_1 $\text{CaB}_{39}^+ (^1A)$
+1.05



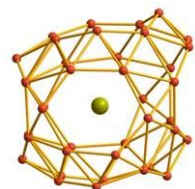
25 C_1 $\text{CaB}_{39}^+ (^1A)$
+1.08



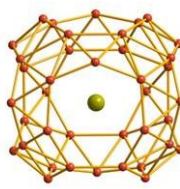
26 C_1 $\text{CaB}_{39}^+ (^1A)$
+1.09



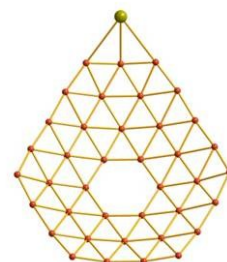
27 C_1 $\text{CaB}_{39}^+ (^1A)$
+1.09



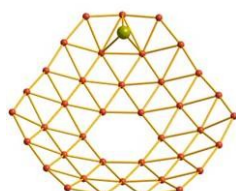
28 C_1 $\text{CaB}_{39}^+ (^1A)$
+1.10



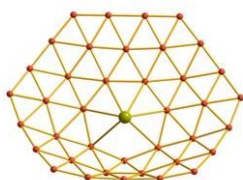
29 C_s $\text{CaB}_{39}^+ (^1A')$
+1.10



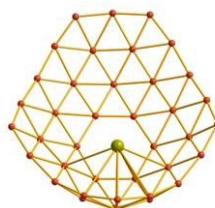
30 C_s $\text{CaB}_{39}^+ (^1A')$
+1.52



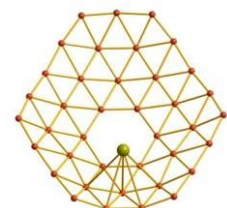
31 C_s $\text{CaB}_{39}^+ (^1A')$
+1.77



32 C_s $\text{CaB}_{39}^+ (^1A')$
+1.91



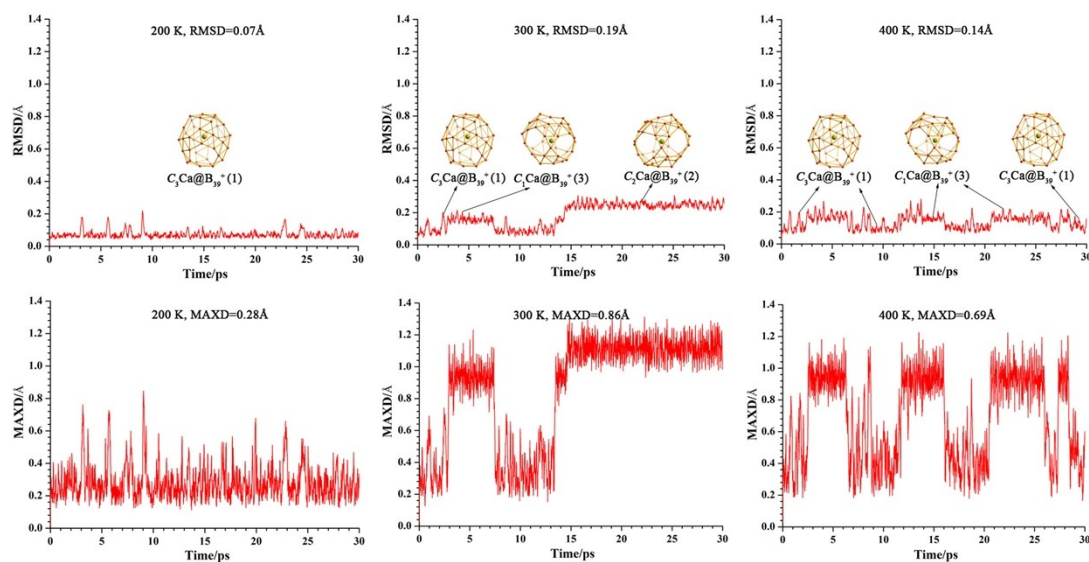
33 C_1 $\text{CaB}_{39}^+ (^1A)$
+2.14



34 C_s $\text{CaB}_{39}^+ (^1A')$
+2.19

Fig. S2 Born-Oppenheimer molecular dynamics simulations of (a) C_3 Ca@B_{39}^+ (**1**) and (b) C_2 $\text{Ca@B}_{39}\text{Ca}^+$ (**2**) at 200K, 300K, and 400K for 30 ps, with the average root-mean-square-deviation (RMSD) values and maximum bond length deviation (MAXD) values indicated in Å. The approximate symmetries of typical structures picked up during the simulations are shown.

(a) C_3 Ca@B_{39}^+ (**1**)



(b) C_2 $\text{Ca@B}_{39}\text{Ca}^+$ (**2**)

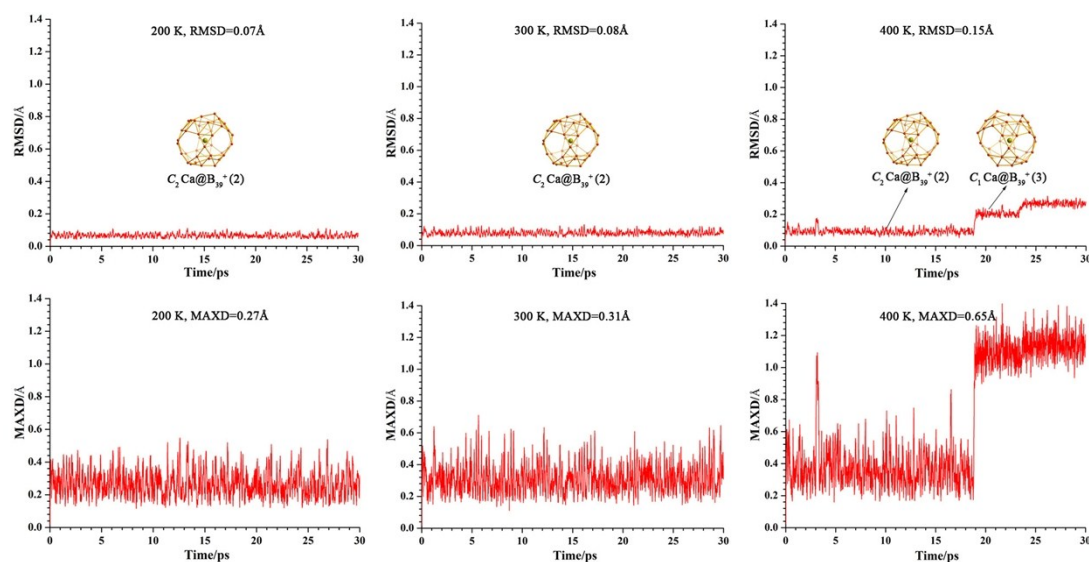


Table S1. Optimized coordinates (Å) of the five lowest-lying isomers of B₃₉Ca⁺ at PBE0/6-311+G(d).

1. C₃ CaB₃₉⁺ (1)

B	0.94877600	-1.60760600	-2.72998200
B	2.87776000	-0.04303100	0.75673400
B	1.32087900	-2.27919100	-1.30057600
B	-1.32824600	1.96974200	2.25264600
B	-2.47467900	1.42602400	-0.27585400
B	0.91784000	1.62546700	-2.72998200
B	-1.53503700	-2.64383100	-0.85452300
B	0.39670000	-1.82084100	2.84686000
B	0.00236700	-2.85614600	-0.27585400
B	1.51989100	2.63497300	0.29344900
B	2.07359200	1.59474900	1.38935800
B	-0.19951500	1.01331700	3.09025400
B	-1.40161400	2.51372900	0.75673400
B	-0.49526000	-0.89831700	-2.92895700
B	-1.52210600	2.65129600	-0.85452300
B	1.37854500	1.25397200	2.84686000
B	2.15973000	-0.85173400	-1.91596300
B	3.05714300	-0.00746500	-0.85452300
B	2.47231200	1.43012300	-0.27585400
B	1.02559500	0.02025000	-2.92895700
B	1.31339800	2.28351000	-1.30057600
B	0.97731500	-0.33387400	3.09025400
B	2.36996900	0.16542300	2.25264600
B	0.00000000	2.82844200	-0.25075600
B	-0.34224200	2.29624800	-1.91596300
B	-1.81748800	-1.44451400	-1.91596300
B	0.34429700	-2.59315700	1.38935800
B	2.44950200	-1.41422100	-0.25075600
B	-0.53033500	0.87806600	-2.92895700
B	1.52200800	-2.63375100	0.29344900
B	-3.04190000	-0.00122200	0.29344900
B	-1.86661600	-0.01786100	-2.72998200
B	-2.63427600	-0.00431900	-1.30057600
B	-0.77780100	-0.67944300	3.09025400
B	-1.04172400	-2.13516500	2.25264600
B	-1.47614600	-2.47069800	0.75673400
B	-1.77524400	0.56686900	2.84686000
B	-2.44950200	-1.41422100	-0.25075600
B	-2.41788800	0.99840900	1.38935800
Ca	0.00000000	0.00000000	-0.27951700

2. $C_2 CaB_{39}^+$ (2)

B	-2.56252000	1.78866200	1.09355400
B	0.79560200	0.05813600	3.03848000
B	-1.06604600	2.33571500	1.50401700
B	1.80296700	-1.91562500	-1.72571600
B	-0.96663800	-2.46387800	-1.24446300
B	-2.86696100	-1.37247500	0.61716800
B	-0.59097300	2.89280800	-1.29682100
B	2.86696100	1.37247500	0.61716800
B	0.00000000	2.92150700	0.22279500
B	-0.52104100	-2.65753800	1.74583300
B	1.06604600	-2.33571500	1.50401700
B	2.88419300	-1.29195700	-0.44470400
B	0.15553500	-1.53579300	-2.21289400
B	-2.88419300	1.29195700	-0.44470400
B	0.59097300	-2.89280800	-1.29682100
B	2.56252000	-1.78866200	1.09355400
B	-1.81479500	0.85333400	2.19748300
B	-0.79560200	-0.05813600	3.03848000
B	0.07787800	-1.40428300	2.58889800
B	-2.86828600	0.19031100	0.97435800
B	-1.62988900	-2.45354300	0.58795800
B	2.86828600	-0.19031100	0.97435800
B	1.81479500	-0.85333400	2.19748300
B	0.00000000	-2.92150700	0.22279500
B	-2.41716300	-1.93314700	-0.80846600
B	-1.80296700	1.91562500	-1.72571600
B	1.62988900	2.45354300	0.58795800
B	-0.07787800	1.40428300	2.58889800
B	-3.04580400	-0.39513800	-0.74464500
B	0.52104100	2.65753800	1.74583300
B	0.00000000	0.00000000	-2.98119100
B	-2.85142000	0.67465100	-1.95169800
B	-1.45790300	0.58823800	-2.75554000
B	3.04580400	0.39513800	-0.74464500
B	2.41716300	1.93314700	-0.80846600
B	0.96663800	2.46387800	-1.24446300
B	2.85142000	-0.67465100	-1.95169800
B	-0.15553500	1.53579300	-2.21289400
B	1.45790300	-0.58823800	-2.75554000
Ca	0.00000000	0.00000000	0.05250000

3. C_1 CaB_{39}^+ (3)

B	2.81548900	-0.71731500	-1.62083800
B	1.88302600	1.24764200	1.96190700
B	2.85238000	-1.22241300	-0.06646600
B	-3.02823800	0.74158900	0.70220100
B	-2.91520500	0.65026200	-1.12623500
B	1.18009700	2.04062600	-2.14617700
B	0.67463600	-3.00932100	-0.71053700
B	1.10698300	-2.13037400	1.98627900
B	1.71906600	-2.46830100	0.41242100
B	-0.03952500	3.09258600	0.67245800
B	0.32626300	2.17706800	1.96157900
B	-2.09799800	0.39705200	2.19509100
B	-2.61268500	2.01285000	-0.21555700
B	1.41615200	-0.83061000	-2.43999300
B	-1.97724100	1.91241400	-1.67245500
B	-0.87583800	1.29546000	2.69558600
B	3.00023800	0.47720000	-0.51471100
B	2.82640500	1.58332700	0.66970900
B	1.49375200	2.51967300	0.73179100
B	2.12504000	0.72189500	-1.98911600
B	0.57549700	2.74835500	-0.79969500
B	0.63401500	0.82299100	2.88713300
B	-0.48480100	-0.41761800	2.71471800
B	-1.12232100	2.71177200	-0.45576000
B	-0.44113300	2.01757900	-2.10371600
B	0.24523900	-2.05698600	-1.98017300
B	-0.44997900	-2.06491700	2.31267100
B	2.83663300	0.01054700	1.18453000
B	0.49170300	0.65930800	-2.72024800
B	2.54129700	-1.55455000	1.52036900
B	-2.81242900	-0.81563900	-1.77957100
B	-0.14036700	-0.81976400	-2.97605800
B	-1.37717600	-1.49380800	-2.18367400
B	-1.84459700	-1.30670600	2.28563900
B	0.01037300	-2.65708500	0.78351100
B	-0.90701100	-2.71305800	-0.70013100
B	-3.10202800	-0.67836500	1.48688100
B	-2.34828900	-2.05783300	-0.90874000
B	-3.15354300	-0.78516100	-0.15029000
Ca	0.24403000	-0.01009400	0.02391600

4. C_1 CaB_{39}^+ (4)

B	-3.25844000	-0.68782600	-1.45650800
B	-0.88389000	-2.17586000	1.81559900
B	-3.12412000	-0.21627300	0.11809400
B	3.33159300	-0.71304100	-0.65103200
B	1.74031300	1.81872600	-1.96791400
B	-0.26421400	-1.57659900	-2.33972600
B	-1.72891000	2.42135300	0.35049500
B	-0.35633200	1.42255500	2.81413400
B	-2.85218300	1.32731000	0.70390500
B	1.51338300	-2.87482400	0.17551700
B	0.93370800	-2.33309300	1.58344200
B	3.05176300	0.49050000	0.36724100
B	2.70790800	0.63661700	-1.44984600
B	-2.40493300	0.31973900	-2.34609100
B	2.72660200	-0.88216700	-2.11244100
B	1.68557700	-1.11792000	2.41396300
B	-2.63330200	-1.77169600	-0.45644500
B	-1.75372300	-2.72867600	0.54803400
B	-0.12610000	-2.91966800	0.34541000
B	-1.79666900	-1.23458600	-2.02240200
B	0.59658000	-2.37609800	-1.13598000
B	0.65369400	0.14758100	2.86860800
B	0.17075800	-1.45715400	2.80109000
B	2.28967100	-2.03805600	-0.96005800
B	1.32325300	-1.54756700	-2.42905400
B	-1.46752600	1.59029400	-2.50885700
B	-1.72564400	1.44522000	1.95404400
B	-2.32080100	-1.37889300	1.27609700
B	-0.70719600	0.07889400	-2.54694700
B	-2.67755900	0.11283200	1.72310500
B	0.76461800	2.64361900	-0.95632800
B	0.15122900	1.64112900	-2.31730000
B	-0.95957400	2.45710100	-1.21170100
B	2.24383700	0.30058700	1.93078700
B	1.12490200	1.67954300	2.18142700
B	-0.37685200	2.47533900	1.56348000
B	2.43821400	1.74649600	1.21701500
B	-0.32843800	3.21122500	0.11020200
B	2.23467700	1.91684400	-0.41000900
Ca	0.01603200	0.03662300	0.10423700

5. C_1 CaB_{39}^+ (5)

B	-2.95503900	1.22771200	-1.22288200
B	0.70077900	3.10741000	-0.08791000
B	-1.53259600	1.97731200	-1.58306200
B	2.11141100	-1.68863900	1.39614800
B	-0.63479900	-2.02711900	1.94122300
B	-2.79578300	0.29850900	1.90370000
B	-0.77067300	-1.51333200	-2.41600100
B	2.62937000	1.02329300	-1.71891700
B	0.15123900	-0.03878300	-2.79922200
B	-0.29014900	1.64872400	2.66292200
B	1.27177500	1.46652800	2.24155600
B	2.96741700	-0.32237000	0.83544400
B	0.74699800	-2.65159300	1.55504100
B	-3.11745100	-0.34634200	-0.93987000
B	0.88014400	-1.36159200	2.50595700
B	2.69976100	1.12007900	1.53199400
B	-2.37112100	2.23389900	-0.13285700
B	-0.89472000	2.83097800	0.00827800
B	0.16941600	2.52725900	1.35061600
B	-3.12869200	0.82125600	0.37674700
B	-1.42533100	0.51588900	2.72570100
B	2.84260300	1.16176200	-0.10579100
B	1.80848500	2.26923200	0.76435800
B	0.23732700	0.11537000	2.87190500
B	-1.86568500	-1.00175700	2.10920900
B	-2.26233300	-1.47821900	-1.85540400
B	1.16639500	1.34530900	-2.34904100
B	0.12020200	2.46679400	-1.49257000
B	-3.04456700	-0.86621300	0.79676000
B	-0.43368200	1.47265100	-2.66230900
B	-0.17772400	-2.89682000	0.21176800
B	-2.81753800	-1.90206200	-0.43255000
B	-1.32494600	-2.48327700	-0.85626100
B	2.94021800	-0.38464400	-0.96847200
B	1.84461700	-0.29210900	-2.31245300
B	0.82820900	-1.52413200	-2.60231000
B	2.84256000	-1.72951800	-0.07703300
B	0.33466500	-2.45613000	-1.31128100
B	1.48522600	-2.62575000	-0.01185700
Ca	0.26600300	-0.00989200	0.03718100