SUPPLEMENTARY INFORMATION

Ternary CE_2Ba_2 (E = As, Sb) Clusters: New Pentaatomic Planar Tetracoordinate Carbon Species with 18 Valence Electrons

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Table S1. Calculated lowest vibrational frequencies (ν_{min}, cm^{-1}) and natural atomic charges (q, in |e|) for the CE_2M_2 (E = N–Bi; M = Be–Ba) clusters at the PBE0-D3/def2-TZVPP level. There are twelve minima (in blue).

System	Symm.	ν_{min}	E	Symm.	ν_{min}	E
CN_2Be_2	D_{2h}	471i(4)	-176.706254	**C_{2v}**	**272**	**-176.875515**
CN_2Mg_2	D_{2h}	240i(3)	-547.353880	**C_{2v}**	**131**	**-547.430180**
CN_2Ca_2	D_{2h}	155i(3)	-1502.267885	C_{2v}	51i(1)	-1502.158734
CN_2Sr_2	D_{2h}	120i(3)	-208.877612	C_{2v}	83i(1)	-208.763080
CN_2Ba_2	D_{2h}	78i(2)	-198.451513	C_{2v}	119i(1)	-198.338596
CP_2Be_2	D_{2h}	345i(2)	-749.808395	C_{2v}	277i(2)	-749.783728
CP_2Mg_2	D_{2h}	96i(2)	-1120.428798	C_{2v}	45i(1)	-1120.455658
CP_2Ca_2	D_{2h}	30i(1)	-2075.348112	C_{2v}	249i(1)	-2075.291771
CP_2Sr_2	**D_{2h}**	**34**	**-781.951592**	C_{2v}	199i(1)	-781.894416
CP_2Ba_2	**D_{2h}**	**55**	**-771.542348**	C_{2v}	119i(2)	-771.466572
CAs_2Be_2	D_{2h}	321i(3)	-4538.572386	C_{2v}	63i(1)	-4538.614859
CAs_2Mg_2	D_{2h}	88i(3)	-4909.181337	C_{2v}	194i(1)	-4909.125861
CAs_2Ca_2	D_{2h}	21i(1)	-5864.102880	C_{2v}	241i(1)	-5864.052169
CAs_2Sr_2	**D_{2h}**	**36**	**-4570.706892**	C_{2v}	188i(1)	-4570.654082
CAs_2Ba_2	**D_{2h}**	**45**	**-4560.300440**	C_{2v}	103i(1)	-4560.224978
CSb_2Be_2	D_{2h}	311i(2)	-547.903684	C_{2v}	441i(2)	-547.891523
CSb_2Mg_2	D_{2h}	95i(3)	-918.489269	C_{2v}	331i(1)	-918.454975
CSb_2Ca_2	**D_{2h}**	**29**	**-1873.419587**	C_{2v}	245i(1)	-1873.372145
CSb_2Sr_2	**D_{2h}**	**40**	**-580.023010**	C_{2v}	190i(1)	-579.972231
CSb_2Ba_2	**D_{2h}**	**41**	**-569.615865**	C_{2v}	99i(1)	-569.540280

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System	Symm.	ν_{min}	E	Symm.	ν_{min}	E
CBi_2Be_2	D_{2h}	336i(2)	-496.666014	C_{2v}	399i(2)	-496.659355
CBi_2Mg_2	D_{2h}	96i(3)	-867.246137	C_{2v}	343i(1)	-867.221164
CBi_2Ca_2	**D_{2h}**	**29**	**-1822.172265**	C_{2v}	282i(2)	-1822.131366
CBi_2Sr_2	**D_{2h}**	**37**	**-528.775595**	C_{2v}	223i(2)	-528.730575
CBi_2Ba_2	**D_{2h}**	**37**	**-518.368349**	C_{2v}	129i(2)	-518.297513

Note: The numbers of imaginary frequencies are listed in parentheses in ν_{min} column.

Table S2. Cartesian coordinates for the global-minimum structure of CE_2Ba_2 (E = As, Sb), and four low-lying isomers at the PBE0-D3/def2-TZVPP level.

CAs_2Ba_2 (**1**)

C	0.00000000	0.00000000	0.00000000
Ba	0.00000000	2.48975700	0.00000000
Ba	0.00000000	-2.48975700	0.00000000
As	1.83700800	0.00000000	0.00000000
As	-1.83700800	0.00000000	0.00000000

1B

C	0.00000000	0.00000000	1.38804100
As	0.00000000	1.75790800	1.15838300
As	0.00000000	-1.75790800	1.15838300
Ba	1.95256800	0.00000000	-0.75697800
Ba	-1.95256800	0.00000000	-0.75697800

1C

Ba	0.00000000	2.20809800	-0.52236600
Ba	0.00000000	-2.20809800	-0.52236600
C	0.00000000	0.00000000	1.01912000
As	-1.79108000	0.00000000	0.79379200
As	1.79108000	0.00000000	0.79379200

1D

Ba	-2.62886100	-0.30178500	0.00000000
Ba	2.62891200	0.30152700	0.00000000
C	0.00000000	0.00018500	0.00000000
As	0.20542800	-1.78660000	0.00000000

As	-0.20551400	1.78700500	0.00000000

1E

C	0.00000000	0.00000000	0.82620000
Ba	0.00000000	2.45623200	0.44371200
Ba	0.00000000	-2.45623200	0.44371200
As	1.22231300	0.00000000	-0.82807400
As	-1.22231300	0.00000000	-0.82807400

CSb_2Ba_2 (**2**)

C	0.00000000	0.00000000	0.00000000
Sb	2.05863500	0.00000000	0.00000000
Sb	-2.05863500	0.00000000	0.00000000
Ba	0.00000000	2.52950500	0.00000000
Ba	0.00000000	-2.52950500	0.00000000

2B

C	0.00164900	0.94456400	0.00000000
Sb	-1.40993800	-0.82879500	0.00000000
Sb	1.40612300	-0.83500800	0.00000000
Ba	0.00164900	0.70702300	2.48002400
Ba	0.00164900	0.70702300	-2.48002400

2C

Ba	0.00000000	2.25458600	-0.63613700
Ba	0.00000000	-2.25458600	-0.63613700
C	0.00000000	0.00000000	0.85456500
Sb	2.02720600	0.00000000	0.64823400
Sb	-2.02720600	0.00000000	0.64823400

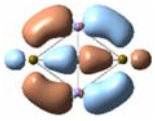
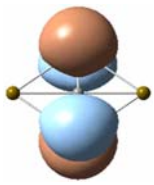
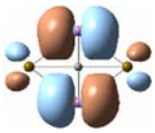
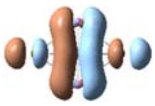
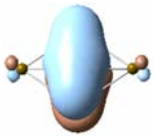
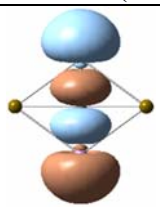
2D

C	0.00000000	0.00000000	1.19885900
Sb	0.00000000	1.97758000	1.00563200
Sb	0.00000000	-1.97758000	1.00563200
Ba	1.95852700	0.00000000	-0.98006800
Ba	-1.95852700	0.00000000	-0.98006800

2E

Ba	0.76361200	-0.63118900	2.37385100
Ba	0.76361200	-0.63118900	-2.37385100
C	0.76361200	0.10129700	0.00000000
Sb	-1.51053700	-0.56271500	0.00000000
Sb	-0.25625200	1.93693800	0.00000000

Table S3. Orbital composition analysis for occupied canonical molecular orbitals (CMOs) of CAs_2Ba_2 GM (D_{2h}, ^1A_g) cluster.

CMO	C (%)		As_2 (%)		Ba_2 (%)	
	s/p	total	s/p	total	s/p/d	total
 HOMO (b_{1u})	0.00/16.64	16.64	0.00/42.41	42.41	10.52/0.20/28.45	39.17
 HOMO−1 (b_{1g})	0.00/0.00	0.00	0.00/89.46	89.46	0.00/0.00/9.99	9.99
 HOMO−2 (b_{3g})	0.00/0.00	0.00	0.00/84.60	84.60	0.00/1.67/12.18	13.85
 HOMO−3 (b_{1u})	0.00/50.58	50.58	0.00/27.65	27.65	2.59/7.75/6.13	16.47
 HOMO−4 (b_{3u})	0.00/59.58	59.58	0.00/35.48	35.48	0.00/0.95/3.34	4.29
 HOMO−5 (b_{2u})	0.00/22.39	22.39	22.88/49.68	72.56	0.00/0.17/0.51	0.68

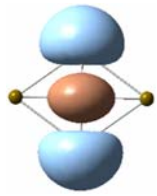
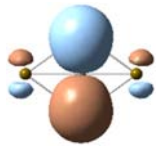
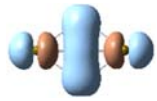
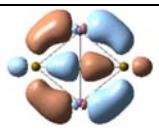
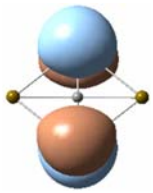
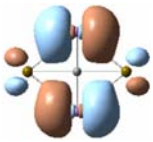
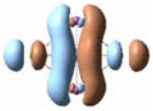
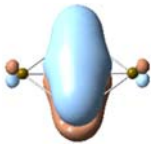
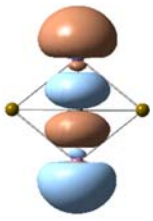
 HOMO−6 (a_g)	18.22/0.00	18.22	53.35/22.18	75.53	0.78/0.73/1.68	3.19
 HOMO−7 (b_{2u})	0.00/39.53	39.53	48.93/0.45	49.38	0.00/5.28/1.28	6.56
 HOMO−8 (a_g)	28.37/0.00	28.37	24.43/3.97	28.40	1.00/37.39/1.55	39.94

Table S4. Orbital composition analysis for occupied canonical molecular orbitals (CMOs) of CSb_2Ba_2 GM (D_{2h}, ^1A_g) cluster.

CMO	C (%)		Sb_2 (%)		Ba_2 (%)	
	s/p	total	s/p	total	s/p/d	total
 HOMO (b_{1u})	0.00/18.35	18.35	0.00/47.16	47.16	6.83/0.36/26.29	33.48
 HOMO−1 (b_{1g})	0.00/0.00	0.00	0.00/87.70	87.70	0.00/0.00/11.75	11.75
 HOMO−2 (b_{3g})	0.00/0.00	0.00	0.00/84.58	84.58	0.00/1.39/11.90	13.29
 HOMO−3 (b_{1u})	0.00/52.14	52.14	0.00/26.79	26.79	3.49/6.39/5.70	15.58
 HOMO−4 (b_{3u})	0.00/60.39	60.39	0.00/33.57	33.57	0.00/0.87/4.44	5.31
 HOMO−5 (b_{2u})	0.00/28.94	28.94	20.43/45.87	66.30	0.00/0.26/0.09	0.35

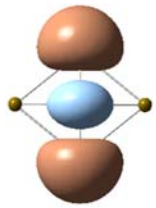
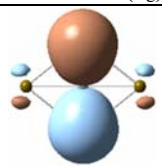
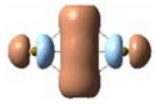
 HOMO−6 (a_g)	18.34/0.00	18.34	58.26/15.51	73.77	0.80/0.51/2.01	3.32
 HOMO−7 (b_{2u})	0.00/34.87	34.87	52.80/0.13	52.93	0.00/3.16/1.92	5.08
 HOMO−8 (a_g)	39.73/0.00	39.73	23.87/5.20	29.07	1.02/23.38/1.97	26.37

Figure S1. Optimized structures of C_{2v} CN_2M_2 (M = Be, Mg) clusters at the PBE0-D3/def2-TZVPP level. Bond distances (in Å), Wiberg bond indices (WBIs; blue color), and natural atomic charges (in |e|; red color) are shown.

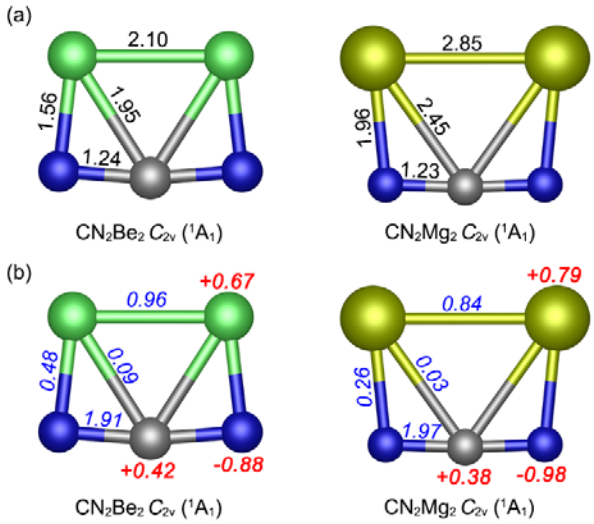


Figure S2. AdNDP bonding schemes of the ptC cluster CSb_2Ba_2(**2**) with 18ve.

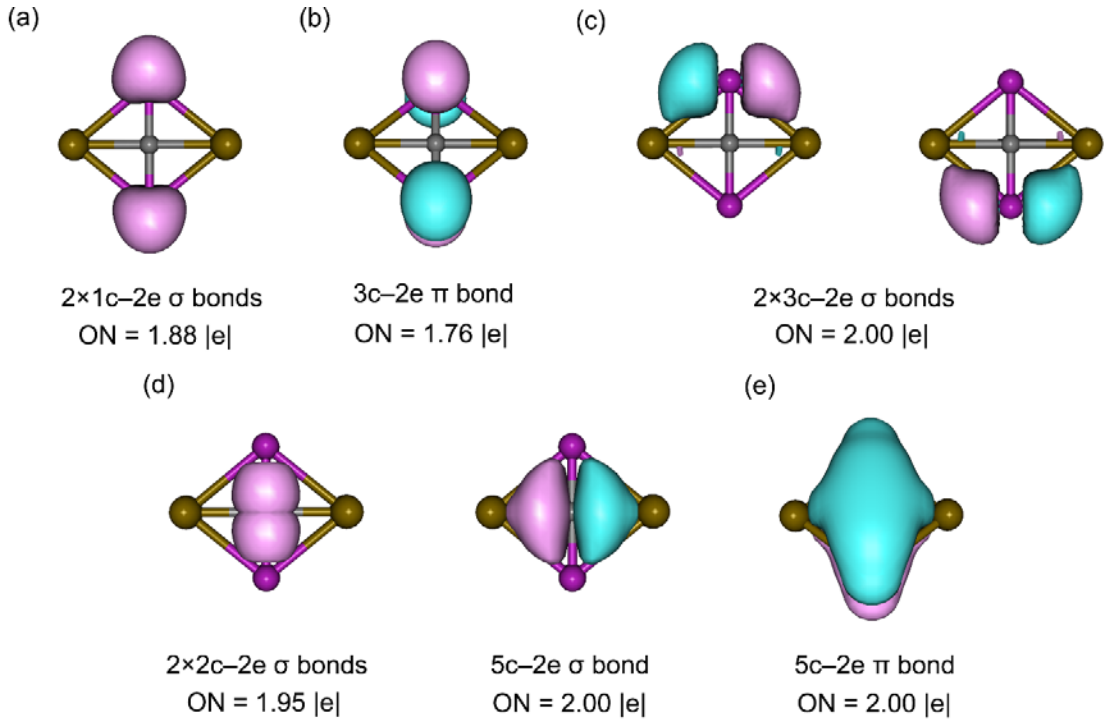


Figure S3. Simulated infrared spectra of CE_2Ba_2 (E = As, Sb) at PBE0-D3/def2-TZVPP.