Electronic Supplementary Information

A planar pentacoordinate oxygen in the experimentally observed $[Be_5O_6]^{2-}$ dianion

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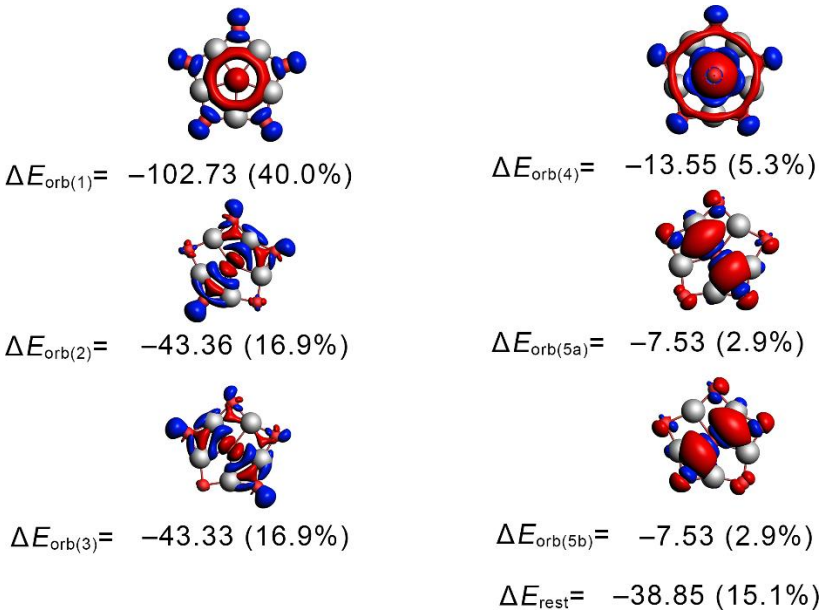
Fig. S1: The shapes of deformation densities ($\Delta\rho$) for EDA-NOCV analysis of $[Be_5O_6]^{2-}$ cluster. The isovalues of the surfaces are 0.003 for $\Delta\rho_{orb(1)}$, 0.001 for $\Delta\rho_{orb(2)–(3)}$, 0.0003 for $\Delta\rho_{orb(4)}$, and 0.0005 for $\Delta\rho_{orb(5)}$. The direction of charge flow is from red to blue. Energy values are given in kcal/mol.

Cartesian Coordinates for the structures shown in **Fig. 1**.

Table S1: The EDA results of $[Be_5O_6]^{2-}$ cluster using different charged fragments at the B3LYP-D3(BJ)/TZ2P level. The most favourable fragments which are given by the smallest ΔE_{orb} value are shown in red. $\Delta E_{steric} = \Delta E_{pauli} + \Delta E_{elstat}$. Energy values are given in kcal/mol. (S: singlet; D: doublet; T: triplet)

Energy	O^{2-} (S) + Be_5O_5 (S)	O^{2-} (T) + Be_5O_5 (T)	O^{-} (D) + $Be_5O_5^{-}$ (D)
ΔE_{int}	–441.27	–2209.80	–223.57
ΔE_{pauli}	475.19	163.94	410.53
ΔE_{elstat}	–656.69	–542.89	–330.34
ΔE_{orb}	–256.88	–1827.97	–300.88
Energy	O (T) + $Be_5O_5^{2-}$ (T)	O^{3-} (S) + $Be_5O_5^{+}$ (S)	O^{3-} (T) + $Be_5O_5^{+}$ (T)
ΔE_{int}	–344.15	–1465.85	–6109.33
ΔE_{pauli}	294.43	480.46	355.31
ΔE_{elstat}	–120.87	–1208.55	–1261.48
ΔE_{orb}	–514.84	–734.87	–5200.28

Fig. S1: The shapes of deformation densities ($\Delta\rho$) for EDA-NOCV analysis of $[Be_5O_6]^{2-}$ cluster. The isovalues of the surfaces are 0.003 for $\Delta\rho_{orb(1)}$, 0.001 for $\Delta\rho_{orb(2)-(3)}$, 0.0003 for $\Delta\rho_{orb(4)}$, and 0.0005 for $\Delta\rho_{orb(5)}$. The direction of charge flow is from red to blue. Energy values are given in kcal/mol.



Cartesian Coordinates for the structures shown in **Fig. 1**.

B2PLYP-D3(BJ)/aug-cc-pVTZ-optimized structures (in Cartesian coordinates) shown in **Fig. 1**.

0

O	0.00000000	0.00000000	7.14759300
Be	0.00000000	0.00000000	2.86369100
Be	0.00000000	0.00000000	-5.75350500
Be	0.00000000	0.00000000	0.00000200
Be	0.00000000	0.00000000	-2.86369200
Be	0.00000000	0.00000000	5.75350400
O	0.00000000	0.00000000	-4.26291000
O	0.00000000	0.00000000	4.26290900
O	0.00000000	0.00000000	1.42029900
O	0.00000000	0.00000000	-7.14759400
O	0.00000000	0.00000000	-1.42029600

1a

O	0.00000000	0.00000000	0.00000000
Be	0.00000000	1.76451200	0.00000000
Be	-1.67815100	0.54526400	0.00000000
Be	-1.03715400	-1.42752000	0.00000000
Be	1.03715400	-1.42752000	0.00000000
Be	1.67815100	0.54526400	0.00000000
O	1.48087200	2.03824600	0.00000000
O	-1.48087200	2.03824600	0.00000000
O	-2.39610200	-0.77854100	0.00000000
O	0.00000000	-2.51941100	0.00000000
O	2.39610200	-0.77854100	0.00000000

1b

O	-1.35937000	-0.78483300	1.42614700
Be	0.00000000	1.77056600	0.00000000
Be	0.00000000	0.00000000	1.60003000
Be	-1.53335600	-0.88528300	0.00000000
Be	1.53335600	-0.88528300	0.00000000
Be	0.00000000	0.00000000	-1.60003000
O	-1.35937000	-0.78483300	-1.42614700
O	1.35937000	-0.78483300	-1.42614700
O	0.00000000	1.56966600	1.42614700
O	0.00000000	1.56966600	-1.42614700
O	1.35937000	-0.78483300	1.42614700

1c

O	-0.17525500	-1.31917600	0.00000000
Be	0.27882000	1.81402700	1.02352800
Be	0.27882000	1.81402700	-1.02352800
Be	0.27882000	-0.18770200	-1.03473300
Be	0.27882000	-0.18770200	1.03473300
Be	-0.61384700	-2.76018700	0.00000000
O	-0.94827900	-4.11287900	0.00000000
O	1.14295500	0.68704100	0.00000000
O	-0.01161700	2.89546800	0.00000000
O	-0.12926000	0.80165700	-2.09435300
O	-0.12926000	0.80165700	2.09435300

1d

O	0.00000000	1.36372800	-2.06613100
Be	0.00000000	0.00000000	-1.18999600
Be	0.00000000	-1.02468300	-3.43658900

Be	0.00000000	0.00000000	1.72314400
Be	0.00000000	0.00000000	4.62789800
Be	0.00000000	1.02468300	-3.43658900
O	0.00000000	0.00000000	-4.50292800
O	0.00000000	0.00000000	6.03463300
O	0.00000000	0.00000000	3.15088500
O	0.00000000	0.00000000	0.30573900
O	0.00000000	-1.36372800	-2.06613100

PBE0-D3/aug-cc-pVTZ-optimized structures (in Cartesian coordinates) shown in **Fig. 1**.

0

O	0.00000000	0.00000000	-7.11386400
Be	0.00000000	0.00000000	-2.85236000
Be	0.00000000	0.00000000	5.73032200
Be	0.00000000	0.00000000	0.00000000
Be	0.00000000	0.00000000	2.85236000
Be	0.00000000	0.00000000	-5.73032200
O	0.00000000	0.00000000	4.24609800
O	0.00000000	0.00000000	-4.24609800
O	0.00000000	0.00000000	-1.41485400
O	0.00000000	0.00000000	7.11386400
O	0.00000000	0.00000000	1.41485400

1a

O	-0.00001900	0.00000000	0.00000000
Be	-1.75112900	0.00000000	0.00000000
Be	-0.54112800	1.66542900	0.00000000
Be	1.41670000	1.02929200	0.00000000
Be	1.41670000	-1.02929200	0.00000000
Be	-0.54112800	-1.66542900	0.00000000
O	-2.02873900	-1.47397400	0.00000000
O	-2.02873900	1.47397400	0.00000000
O	0.77491600	2.38492500	0.00000000
O	2.50765800	0.00000000	0.00000000
O	0.77491600	-2.38492500	0.00000000

1b

O	-1.35454900	-0.78204900	1.42225700
Be	0.00004300	1.74911800	0.00000000

Be	0.00000000	0.00000000	1.58824700
Be	-1.51480200	-0.87452200	0.00000000
Be	1.51475900	-0.87459600	0.00000000
Be	0.00000000	0.00000000	-1.58824700
O	-1.35454900	-0.78204900	-1.42225700
O	1.35454900	-0.78204900	-1.42225700
O	0.00000000	1.56409900	1.42225700
O	0.00000000	1.56409900	-1.42225700
O	1.35454900	-0.78204900	1.42225700

1c

O	0.17396100	1.31296500	0.00000000
Be	-0.27366900	-1.80072400	1.01351100
Be	-0.27366900	-1.80072400	-1.01351100
Be	-0.27366900	0.18399500	-1.02785200
Be	-0.27366900	0.18399500	1.02785200
Be	0.60552800	2.75024000	0.00000000
O	0.93061300	4.09334500	0.00000000
O	-1.14114300	-0.68782600	0.00000000
O	0.01654000	-2.88255500	0.00000000
O	0.13230000	-0.79715900	-2.08428100
O	0.13230000	-0.79715900	2.08428100

1d

O	0.00000000	1.35857300	-2.05465900
Be	0.00000000	0.00000000	-1.18693200
Be	0.00000000	-1.01579300	-3.41724900
Be	0.00000000	0.00000000	1.71433600
Be	0.00000000	0.00000000	4.60741300
Be	0.00000000	1.01579300	-3.41724900
O	0.00000000	0.00000000	-4.48325000
O	0.00000000	0.00000000	6.00310800
O	0.00000000	0.00000000	3.13595200
O	0.00000000	0.00000000	0.30335100
O	0.00000000	-1.35857300	-2.05465900