Supporting Information

D_{4h} $OMg_4S_4^{2-}$: a global minimum featuring a planar tetracoordinate oxygen

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Contents

Computational methods

Cluster $OMg_4S_4^{2-}$ with a planar tetracoordinate oxygen (ptO) was considered for geometry optimization and vibrational frequency calculations at the B3LYP/aug-cc-pVTZ, B2PLYP[1]-D3(BJ)[2]/aug-cc-pVTZ, and B2PLYP-D3(BJ)/def2-TZVPP levels. Remarkably, these three levels yielded nearly identical molecular structures and vibrational frequencies. Consequently, the geometries obtained from the B2PLYP/D3(BJ) functional were reported in the text and used for energy improvement at the CCSD(T) level, while the B3LYP functional was used for various electronic structure analyses. For the designed ptO cluster $OMg_4S_4^{2-}$, the extensive exploration of potential energy surfaces (PESs) was performed at the B3LYP/6-31G* level using stochastic search algorithm[3]. During the search process, both singlet and triplet states were systematically evaluated, yielding 2000 singlet and 1300 triplet structures. The structures generated by the stochastic search were sorted according to their energy. The ten lowest-energy isomers were further calculated at the B2PLYP-D3(BJ)/aug-cc-pVTZ level, and then the eight lowest-energy isomers were further improved at the CCSD(T)/aug-cc-pVTZ level. The relative energies of the isomers were compared by the CCSD(T)/aug-cc-pVTZ energies plus the B2PLYP-D3(BJ)/aug-cc-pVTZ zero-point energy corrections. To assess the dynamic stability, Born-Oppenheimer Molecular Dynamics (BOMD) simulations[4] were carried out at the PBE/DZVP level under the considered temperatures. Meanwhile, electronic structure analyses were carried out to better understand chemical bonding. Firstly, the adaptive nature density partitioning (AdNDP) analyses[5] were done at the B3LYP/6-31G* level using AdNDP program[11]. Moreover, natural bond orbital (NBO) analyses[7] were performed at the B3LYP/aug-cc-pVTZ level using NBO 3.0[8]. Furthermore, nucleus independent chemical shifts (NICS)[9] analyses were performed at the B3LYP/aug-cc-pVTZ level. Lastly, vertical detachment energies (VDEs) were calculated using the outer valence Green's function (OVGF) procedure at the OVGF/aug-cc-pVTZ level[10]. The representation of cross sections of NICS (CS-NICS) and simulated photoelectron spectroscopy were generated with the Multiwfn 3.8 code[11]. The stochastic search algorithm was realized using the GXYZ 2.0 program[12], the EDA-NOCV[13] were performed at the B3LYP-D3(BJ)/TZ2P level using the ADF 2019 program package[14], the CCSD(T) calculations were carried out using the MolPro 2012.1 package[15], and all other calculations were performed using the Gaussian 16 package[16].

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Table 1 The EDA results of $OMg_4S_4^{2-}$ 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. $\Delta E_{attr} = \Delta E_{pauli} + \Delta E_{elstat} + \Delta E_{disp}$. Energy values are given in kcal·mol^{-1}. (S: singlet; D: doublet; T: triplet; Q: quartet)

Energy	O^{2-} (S) + Mg_4S_4 (S)	O^- (D) + $Mg_4S_4^-$ (D)	O (S) + $Mg_4S_4^{2-}$ (S)
ΔE_{int}	–468.4	–225.6	–386.2
ΔE_{pauli}	345.9	285.2	220.6
ΔE_{elstat}	–595.2	–282.6	–168.6
ΔE_{orb}	–215.6	–224.6	–434.6
ΔE_{disp}	–3.5	–3.5	–3.5
Energy	O (T) + $Mg_4S_4^{2-}$ (T)	O^+ (D) + $Mg_4S_4^{3-}$ (D)	O^+ (Q) + $Mg_4S_4^{3-}$ (Q)
ΔE_{int}	–331.6	–830.2	–788.3
ΔE_{pauli}	195.4	196.5	192.2
ΔE_{elstat}	–92.4	–175.8	–178.3
ΔE_{orb}	–431.1	–847.4	–798.7
ΔE_{disp}	–3.5	–3.5	–3.5

Fig. S1 Optimized structure of cluster $OMg_4S_4^{2-}$ (**1**) at the B2PLYP-D3(BJ)/aug-cc-pVTZ level, along with the Wiberg bond indices (WBIs, blue fonts) and natural population analysis (NPA) charges (|e|, purple fonts) are shown.

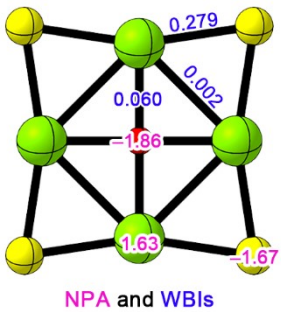


Fig. S2 The shapes of deformation densities ($\Delta\rho$) for EDA-NOCV analysis of $OMg_4S_4^{2-}$ cluster. The isovalues of the surfaces are 0.003 for $\Delta\rho_{orb(1)-(3)}$, and 0.0002 for $\Delta\rho_{orb(4)}$. The direction of charge flow is from red to blue. Energy values are given in kcal/mol.

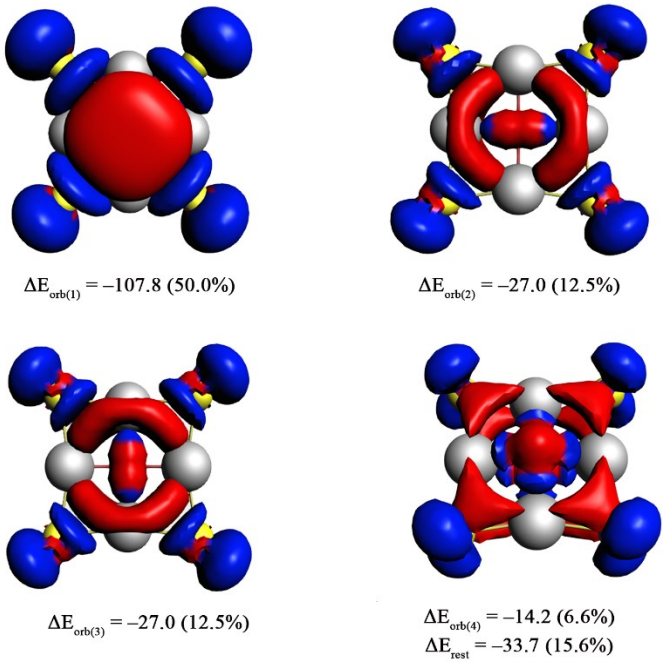


Fig. S3 The distribution of $NICS_{zz}$ values for $OMg_4S_4^{2-}$ (**1**). CS-$NICS(0)_{zz}$ correspond to the molecular plane, while CS-$NICS(1)_{zz}$ correspond to the plane parallel to and located 1 Å above the molecular plane. The NICS values that are negative, positive, and close to zero indicate aromaticity, antiaromaticity, and non-aromaticity, respectively.

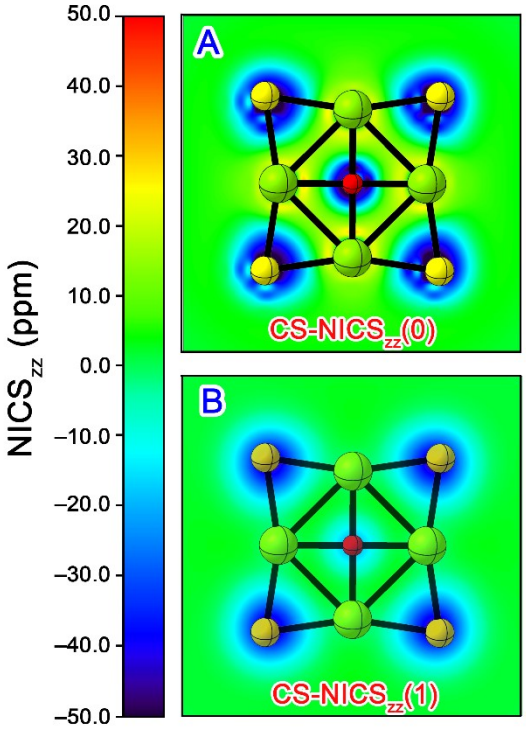


Fig. S4 RMSD (in Å) *versus* simulation time (in ps) for the BOMD simulations of $OMg_4S_4^{2-}$ (**1**) at 298, 500, and 1000 K.

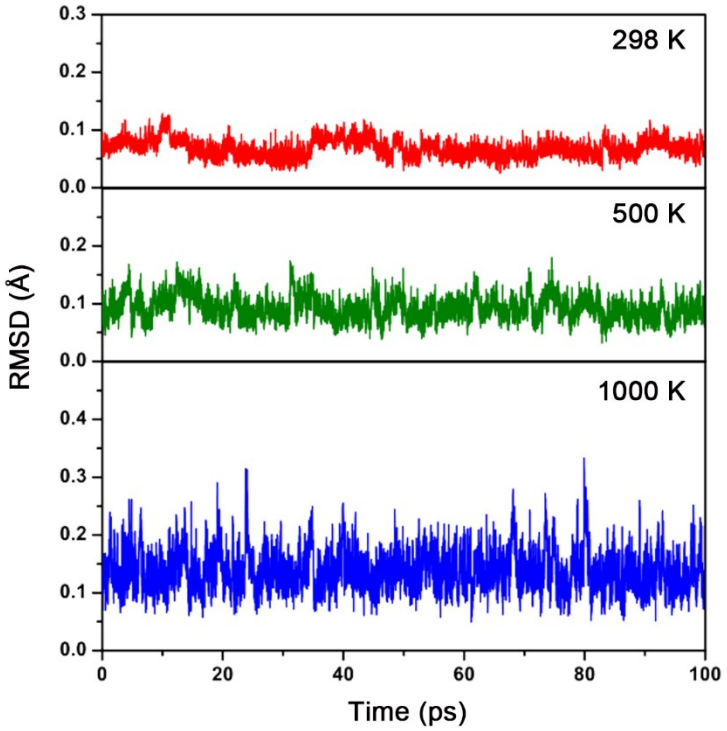


Fig. S5 Simulated PES of cluster $OMg_4S_4^{2-}$(**1**).

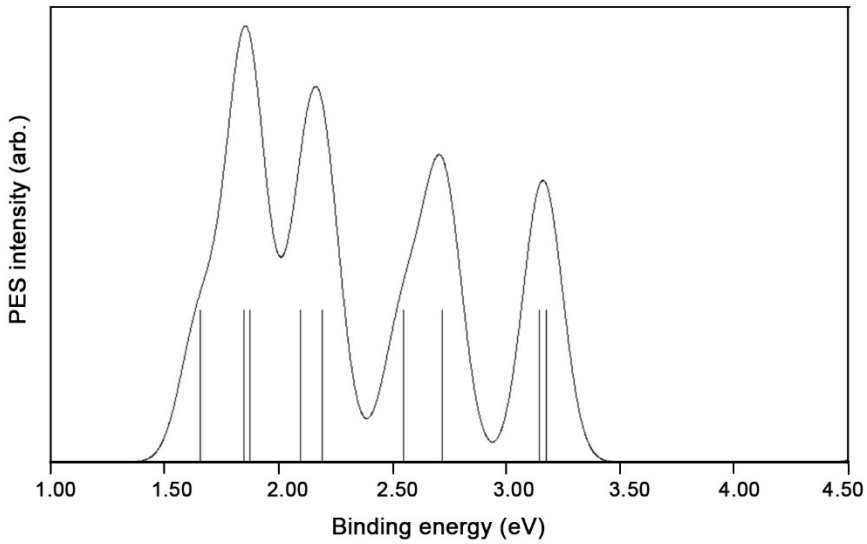
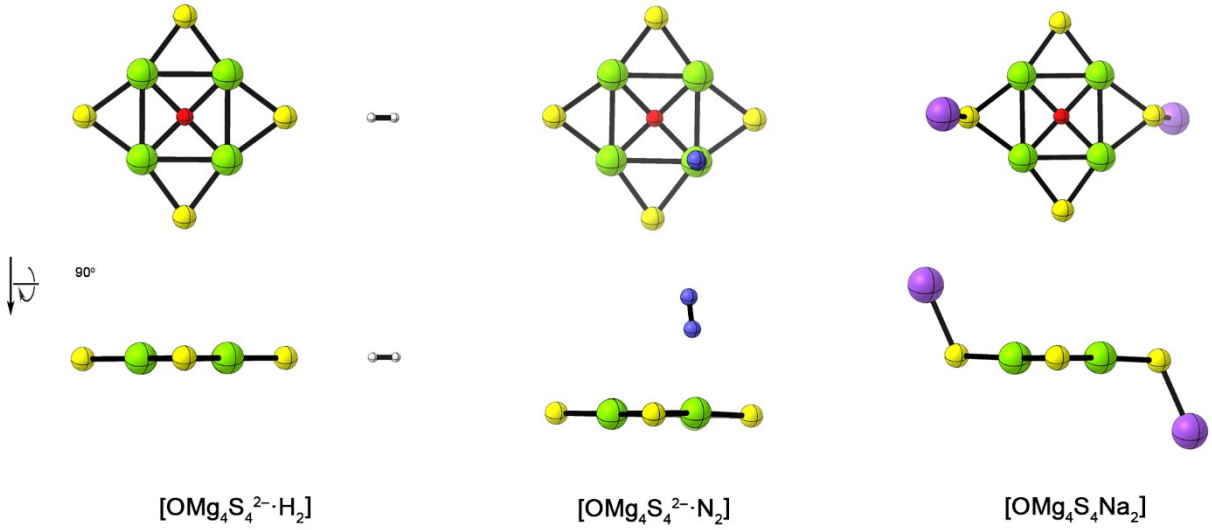


Fig. S6 Optimized structures of $[OMg_4S_4^{2-}\cdot H_2]$, $[OMg_4S_4^{2-}\cdot N_2]$, and $[OMg_4S_4Na_2]$ at the B2PLYP-D3(BJ)/aug-cc-pVTZ level.



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

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

1

Mg	0.00000000	1.98949800	0.00000000
Mg	1.98949800	0.00000000	0.00000000
Mg	0.00000000	-1.98949800	0.00000000
Mg	-1.98949800	0.00000000	0.00000000
O	0.00000000	0.00000000	0.00000000
S	-2.34219000	2.34219000	0.00000000
S	2.34219000	2.34219000	0.00000000
S	-2.34219000	-2.34219000	0.00000000
S	2.34219000	-2.34219000	0.00000000

1a

O	-0.66680700	-2.86104500	0.00000000
Mg	0.35271400	1.18704600	1.48753800
Mg	-0.64672200	-1.61273500	-1.39770800
Mg	0.35271400	1.18704600	-1.48753800
Mg	-0.64672200	-1.61273500	1.39770800
S	1.54003000	2.59884300	0.00000000
S	-1.47104100	0.37206000	0.00000000
S	0.35271400	-0.45092300	-3.20440100
S	0.35271400	-0.45092300	3.20440100

1b

O	0.00000000	0.00000000	0.40768800
Mg	0.00000000	0.00000000	2.29213900
Mg	0.00000000	1.61063600	-0.83057700
Mg	1.39485200	-0.80531800	-0.83057700
Mg	-1.39485200	-0.80531800	-0.83057700
S	0.00000000	-2.59944600	-1.52069500
S	2.25118600	1.29972300	-1.52069500
S	-2.25118600	1.29972300	-1.52069500
S	0.00000000	0.00000000	4.50793500

1c

O	1.49889600	-0.74189500	0.00000000
Mg	1.08701300	-2.66276500	0.00000000
Mg	0.25108100	-0.50585600	1.42522700
Mg	-0.82235700	3.14925500	0.00000000
Mg	0.25108100	-0.50585600	-1.42522700
S	0.25108100	-2.71845800	2.27088900
S	-0.53066100	5.34607000	0.00000000
S	-1.29606200	0.85571100	0.00000000
S	0.25108100	-2.71845800	-2.27088900

1d

O	-1.87296000	1.08344900	0.00000000
Mg	-3.78922800	1.07929000	0.00000000
Mg	0.00000000	1.24535700	0.00000000
Mg	2.61087600	-0.08043500	0.00000000
Mg	-1.84723200	-0.89155400	0.00000000

S	-4.15061800	-1.30353600	0.00000000
S	4.73061500	-1.21920400	0.00000000
S	0.50935100	-1.25973700	0.00000000
S	2.11632000	2.22626100	0.00000000

B2PLYP-D3(BJ)/def2-TZVPP-optimized structures (in Cartesian coordinates) shown in **Fig. 1**.

1

Mg	0.00000000	1.98643100	0.00000000
Mg	1.98643100	0.00000000	0.00000000
Mg	0.00000000	-1.98643100	0.00000000
Mg	-1.98643100	0.00000000	0.00000000
O	0.00000000	0.00000000	0.00000000
S	-2.33807200	2.33807200	0.00000000
S	2.33807200	2.33807200	0.00000000
S	-2.33807200	-2.33807200	0.00000000
S	2.33807200	-2.33807200	0.00000000

1a

O	-0.67744600	-2.84814500	0.00000000
Mg	0.35551400	1.18186100	1.48287000
Mg	-0.65244300	-1.60376000	-1.39434200
Mg	0.35551400	1.18186100	-1.48287000
Mg	-0.65244300	-1.60376000	1.39434200
S	1.54830700	2.58623500	0.00000000
S	-1.47521900	0.37860500	0.00000000
S	0.35551400	-0.45396000	-3.19581400
S	0.35551400	-0.45396000	3.19581400

1b

O	0.00000000	0.00000000	0.40362000
Mg	0.00000000	0.00000000	2.28893700
Mg	0.00000000	1.60770400	-0.82798600
Mg	1.39231200	-0.80385200	-0.82798600
Mg	-1.39231200	-0.80385200	-0.82798600
S	0.00000000	-2.59665100	-1.51526500
S	2.24876600	1.29832600	-1.51526500
S	-2.24876600	1.29832600	-1.51526500
S	0.00000000	0.00000000	4.49025200

1c

O	1.46519700	-0.73729300	0.00000000
Mg	1.05851200	-2.65383300	0.00000000
Mg	0.22051000	-0.50291200	1.42151300
Mg	-0.76476000	3.14345700	0.00000000
Mg	0.22051000	-0.50291200	-1.42151300
S	0.22051000	-2.71161700	2.26506700
S	-0.40000800	5.31533900	0.00000000
S	-1.32468800	0.86369200	0.00000000
S	0.22051000	-2.71161700	-2.26506700

1d

O	-1.86788900	1.07527700	0.00000000
Mg	-3.79368800	1.08690400	0.00000000
Mg	0.00000000	1.23970200	0.00000000
Mg	2.60609400	-0.07771300	0.00000000
Mg	-1.84971000	-0.89137700	0.00000000
S	-4.13866000	-1.31164600	0.00000000

S	4.72830000	-1.20596800	0.00000000
S	0.51166300	-1.26260200	0.00000000
S	2.11061900	2.22444100	0.00000000

B2PLYP-D3(BJ)/aug-cc-pVTZ-optimized structures (in Cartesian coordinates) of OGa_4 (**2**) and its second lower-lying isomer (**2a**).

2

O	0.00000000	0.00000000	0.00000000
Ga	0.00000000	2.04111200	0.00000000
Ga	2.04111200	0.00000000	0.00000000
Ga	-2.04111200	0.00000000	0.00000000
Ga	0.00000000	-2.04111200	0.00000000

2a

Ga	0.00000000	1.19897900	-2.14874700
Ga	0.00000000	-1.19897900	-2.14874700
Ga	0.00000000	0.00000000	0.11482000
Ga	0.00000000	0.00000000	3.69544000
O	0.00000000	0.00000000	1.88802800

B2PLYP-D3(BJ)/aug-cc-pVTZ-optimized structures (in Cartesian coordinates) of $[OMg_4S_4^{2-}\cdot H_2]$, $[OMg_4S_4^{2-}\cdot N_2]$, and $[OMg_4S_4Na_2]$.

$[OMg_4S_4^{2-}\cdot H_2]$

Mg	0.00000000	1.40825300	-1.29836400
Mg	0.00000000	-1.40825300	-1.29836400
Mg	0.00000000	-1.40685700	1.51381200
Mg	0.00000000	1.40685700	1.51381200
O	0.00000000	0.00000000	0.10545800
S	0.00000000	3.31242400	0.10693700
S	0.00000000	0.00000000	-3.20432300
S	0.00000000	0.00000000	3.41835400
S	0.00000000	-3.31242400	0.10693700
H	0.00000000	0.00000000	-6.80444100
H	0.00000000	0.00000000	-6.05645300

$[OMg_4S_4^{2-}\cdot N_2]$

Mg	-0.29498800	-1.81266000	0.00000000
Mg	-0.38012300	0.17567700	1.98978100
Mg	-0.32574000	2.16490500	0.00000000
Mg	-0.38012300	0.17567700	-1.98978100
O	-0.31453800	0.17648000	0.00000000
S	-0.38012300	-2.16356600	-2.34578200
S	-0.38012300	-2.16356600	2.34578200
S	-0.35794600	2.51786700	-2.34148600
S	-0.35794600	2.51786700	2.34148600
N	2.50726900	-1.59949500	0.00000000
N	3.59361300	-1.42803000	0.00000000

$[OMg_4S_4Na_2]$

Mg	0.00000000	1.37517100	1.44114800
Mg	0.00000000	1.37517100	-1.44114800
Mg	0.00000000	-1.37517100	-1.44114800

Mg	0.00000000	-1.37517100	1.44114800
O	0.00000000	0.00000000	0.00000000
S	0.00000000	0.00000000	3.31263300
S	0.10158500	3.28422300	0.00000000
S	-0.10158500	-3.28422300	0.00000000
S	0.00000000	0.00000000	-3.31263300
Na	2.40148500	4.27595300	0.00000000
Na	-2.40148500	-4.27595300	0.00000000