Method validation. A number of density functional were tested on the diatomic molecules FeS, CoS and S_2, Table 1S. Experimental data are available for FeS and S_2, while for CoS only the bond length and the ground electron state were reported. B3LYP provides accurate results for the dissociation energies and electron affinities of FeS and S_2; vibrational frequencies are also predicted with minor deviation, bond lengths are slightly overestimated, by 0.6% for FeS and CoS and by 1% for S_2. More accurate FeS bond length is provided by the B3PW91 functional, but the dissociation energy is calculated too high, while electron affinity is too low. MO6 overestimates bond lengths of FeS and S_2, the dissociation energies as well, while providing more accurate CoS bond length; electron affinities are either overestimated (FeS) or underestimated (S_2); in general the MO6 calculated binding energies and electon affinities do not match well the experimental data. The TPSS and BLYP calculated electron affinities are similar and underestimate experimental measurements, for CoS they provide higher values than all other density functionals.

Table 1S. Bond Length, Dissociation Energy (Dzpe) Corrected for Zero-Point Energy, Vibrational Frequency (ω) and Electron Affinity (EA) for FeS, CoS, S_2, as Calculated by DFT

Cluster/Method	R_{M-O}, Å	D_{zpe}, kJ mol^{-1}	ω, cm^{-1}	EA, eV
FeS; $^5\Delta$				
B3LYP [(1)]	2.029	327.7	515.6	1.717
B3PW91 [(2)]	2.014	360.5	528.2	1.578
BLYP [(3)]	2.031	378.5	499.0	1.541
TPSS [(4)]	2.009	387.7	523.3	1.433
M06 [(5)]	2.033	393.2	530.1	1.835
Exp.	2.017 [a]	328.9±14.6 [b]	523.2 [c]	1.725 ± 0.010 [d]
CoS; $^4\Delta$				
B3LYP	1.989	323.4	520	1.293

B3PW91	1.977	326.6	533	1.273
BLYP	1.999	322.1	497	1.810
TPSS	1.982	376.3	522	1.780
M06	1.976	345.9	548	1.597
Exp.	1.978 [e]			
S_2; $^3\Sigma_g^-$				
B3LYP	1.909	423.2	712.4	1.682
B3PW91	1.897	435.7	735.9	1.666
BLYP	1.936	442.0	663.7	1.516
TPSS	1.913	447.6	703.8	1.568
M06	1.899	438.4	739.7	1.532
Exp.	1.889 [b]	421.6 [b]	725.7 [b]	1.670 ± 0.015 [f]

Experimental data are from references in the paper: [a] – ref. 43; [b] – ref. 67; [c] – ref. 68; [d] – ref. 13; [e] – ref. 42; [f] – ref. 69

(1) A. D. Becke, "Density-functional thermochemistry. III. The role of exact exchange," *J. Chem. Phys.*, **98** (1993) 5648-52; C. Lee, W. Yang, R. G. Parr, Phys. Rev. B, **37**, 785 (1988); B. Miehlich, A. Savin, H. Stoll, H. Preuss, Chem. Phys. Lett., 157, 200 (1989)

(2) J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, "Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation," *Phys. Rev. B*, **46** (1992) 6671-87.

(3) A. D. Becke, "Density-functional exchange-energy approximation with correct asymptotic-behavior," *Phys. Rev. A*, **38** (1988) 3098-100.

(4) J. M. Tao, J. P. Perdew, V. N. Staroverov, and G. E. Scuseria, "Climbing the density functional ladder: Nonempirical meta-generalized gradient approximation designed for molecules and solids," *Phys. Rev. Lett.*, **91** (2003) 146401. Gaussian Keyword TPSSTPSS.

(5) Y. Zhao and D. G. Truhlar, "The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements" *Theor. Chem. Acc.*, **120** (2008) 215-41.

Table 2S. Natural charges (q, e) and natural orbital population for sulfides bonded to cations.

Cluster	q_M	q_S	q cat/lig [a]	M 3d	M 4s	M 4p	Cation/Ligand
CoS_2	0.54	-0.27		7.62	0.49	0.33	
$Co(S_2)$	0.22	-0.11		7.90	0.47	0.41	
Co_2S_2, afm [b]	0.61	-0.61		7.71	0.37	0.26	
Co_2S_2 npl [c], $^3A_2$	0.69	-0.69		7.72	0.35	0.23	
$Co_2(S_2)$ npl [c], $^7A_1$	0.43	-0.43		7.84	0.51	0.20	
FeS_2	0.52	-0.26		6.58	0.41	0.35	
$Fe(S_2)$	0.50	-0.25		6.85	0.40	0.22	
Fe_2S_2; afm [b]	0.66	-0.66		6.79	0.43	0.31	
$Fe_2(S_2)$ $^5\mathbf{A_1}$	0.26	-0.26		6.93	0.59	0.21	
FeSSFe, C_{2h} $^5\mathbf{A_u}$	0.31	-0.31		6.86	0.75	0.07	
$ClCo(S_2)$	0.80	-0.12	-0.55	7.68	0.45	0.04	3p(5.58)
$ClCoS_2$	0.55	-0.09	-0.36	7.86	0.49	0.06	3p(5.39)
$ClCo(S_2)$-Li^+	0.98	-0.62	0.90 Li	7.49	0.45	0.05	2s(0.05) Li
$(CO)Co(S_2)$	0.78	-0.33	0.32 C/ -0.43 O	7.75	0.38	0.07	2p(2.22)C 2p(4.70)O
$(CO)CoS_2$	0.69	-0.39	0.50 C/ -0.40 O	7.82	0.40	0.07	2p(2.16)C 2p(4.67)O
Co_2S_2-Li^+	0.79	-0.76	0.94	5.53	0.42	0.28	2s(0.04)
Co_2S_2-Li^+,e^-	0.44	-0.89	0.90	7.74	0.44	0.36	2s(0.07)
Co_2S_2-Na^+	0.60	-0.53	0.94	7.65	0.61	0.14	3s(0.06)
Co_2S_2-Na^+,e^-	0.44	-0.90	0.92	7.73	0.44	0.37	3s(0.07)

$Co(S_2)$-Li^+	0.91	-0.43	0.94	7.67	0.25	0.16	2s(0.03)
CoS_2-Li^+	0.93	-0.43	0.93	7.67	0.34	0.05	2s(0.04)
CoS_2-Li^+,e^-	0.54	-0.72	0.90	7.59	0.42	0.42	2s(0.06)
$Co(S_2)$-Li^+,e^-	0.30	-0.52	0.75	7.38	0.99	0.35	2p(0.17)Li
$Co(S_2)$-Na^+	0.86	-0.42	0.97	7.71	0.25	0.16	3s(0.02)
$Co(S_2)$-Na^+,e^-	0.34	-0.59	0.86	7.38	0.95	0.39	3s(0.12)
CoS_2-Zn^{2+}	1.00	-0.15	1.29	7.50	0.28	0.19	4s(0.52) 4p(0.20) Zn
$Co(S_2)$-Zn^{2+}	1.20	-0.27	1.35	7.52	0.18	0.10	4s(0.46) 4p(0.19) Zn
CoS_2-Zn^{2+},$2e^-$	0.61	-0.75	0.89	7.70	0.34	0.32	4s(0.67) 4p(0.44) Zn
$Co(S_2)$-Zn^{2+},$2e^-$	0.30	-0.26	0.28	7.86	0.66	0.17	4s(1.50) 4p(0.21) Zn
Co_2S_2-Zn^{2+}	1.03	-0.60	1.15	7.42	0.33	0.20	4s(0.58) 4p(0.27) Zn
Co_2S_2-Zn^{2+},e^-	0.50	-0.74	0.50	7.72	0.42	0.34	4s(1.21) 4p(0.29) Zn
Co_4S_4-Li^+	0.23	-0.22	0.94	8.15	0.35	0.44	2s(0.05)Li
Co_4S_4-Li^+,e^-	0.49	-0.79	0.91	7.58	0.42	0.40	2s(0.06)Li
FeS_2-Li^+	0.72	-0.33	0.94	6.55	0.36	0.34	2s(0.04)
$Fe(S_2)$-Li^+	0.99	-0.42	0.85	6.56	0.27	0.17	2p(0.11)Li
FeS_2-Li^+,e^-	0.41	-0.65	0.88	6.96	0.40	0.21	2s(0.07)
$Fe(S_2)$-Li^+,e^-	0.33	-0.53	0.74	6.32	1.00	0.34	2p(0.18)Li
$Fe(S_2)$-Na^+,e^-	0.26	-0.57	0.89	6.35	0.99	0.38	3s(0.10)

$(CO)Fe(S_2)$	0.71	-0.31	0.34 C/ -0.43 O	6.82	0.39	0.04	2p(2.20)C 2p(4.69)O
$(CO)FeS_2$	0.72	-0.38	0.42 C/ -0.39 O	6.75	0.43	0.04	2p(2.09)C 2p(4.65)O
$ClFeS_2$	0.79	-0.19	-0.41	6.67	0.43	0.07	3p(5.44)
$ClFe(S_2)$	0.85	-0.14	-0.57	6.58	0.49	0.04	3p(5.60)
$ClFe(S_2)$-Li^+	1.03	-0.65	0.90 Li	6.48	0.41	0.05	2s(0.06) Li
Fe_2S_2-Li^+	0.70	-0.67	0.94	6.72	0.33	0.23	2s(0.04)
Fe_2S_2-Li^+,e^-	0.43	-0.88	0.90	6.74	0.45	0.35	2s(0.06)
Fe_2S_2-Na^+	0.68	-0.66	0.96	6.72	0.33	0.24	2s(0.03)
Fe_2S_2-Na^+,e^-	0.30	-0.76	0.91	6.95	0.40	0.32	3s(0.08)
FeS_2-Zn^{2+}	0.97	-0.16	1.35	6.41	0.23	0.18	4s(0.50) 4p(0.21) Zn
$Fe(S_2)$-Zn^{2+}	1.18	-0.25	1.32	6.39	0.21	0.13	4s(0.48) 4p(0.18) Zn
FeS_2-Zn^{2+},$2e^-$	0.69	-0.73	0.77	6.55	0.33	0.31	4s(0.61) 4p(0.25) Zn
$Fe(S_2)$-Zn^{2+},$2e^-$	0.46	-0.42	0.40	6.49	0.82	0.22	4s(1.28) 4p(0.32) Zn
Fe_2S_2-Zn^{2+}	0.92	-0.52	1.16	6.65	0.29	0.19	4s(0.59) 4p(0.24) Zn
Fe_2S_2-Zn^{2+},e^-	0.50	-0.75	0.51	6.75	0.41	0.31	4s(1.09) 4p(0.40) Zn

a – cat/lig =cation or ligand; b – afm = antiferromagnetic ordering; c – npl = non-planar cluster

Table 3S. Bond Lengths, Bond Angles, Magnetic Moments on Atoms (μ, Bohr Magnetons), and Energies for disulfides XMS_2 and persulfides $XM(S_2)$, with X=CO,Cl^- and M=Co,Fe

Cluster Model	State	R_{M-S} Å	R_{S-S} Å	∠SCoS, deg	R_{X-M} Å	μ_M	μ_S	$\Delta E_{tot,}$ eV B3LYP	$\Delta E_{tot,}$ eV CCSD(T)
$Co(S_2)$	$^4\mathbf{A_1}$	2.141	2.155	60.4		2.17	0.41	0	0
	$^2\mathbf{A_2}$	2.149	2.064	57.4		1.30	-0.15	0.57	0.59
CoS_2	$^4\mathbf{B_2}$	1.980		110.7		2.02	0.49	0.50	0.38
	$^6\mathbf{A_1}$	2.120		155.9		2.62	1.18	0.56	0.64
	$^2\mathbf{A_1}$	1.996		120.7		1.95	-0.47	0.82	0.87
	$^4\mathbf{\Sigma_g}$	2.103		180.0		2.24	0.38	1.90	1.81
$(CO)Co(S_2)$	$^4\mathbf{B_1}$	2.196	2.085	56.7	1.888	2.14	0.40	0	0
$(CO)CoS_2$	$^4\mathbf{A_1}$	2.037		154.8	1.795	1.49	0.80	0.96	1.33
$Cl\text{-}Co(S_2)$	$^3\mathbf{B_2}$	2.173	2.024	55.5	2.108	2.00	-0.04	0	0
$Cl\text{-}CoS_2$	$^3\mathbf{B_2}$	1.983		113.6	2.094	1.77	0.05	1.72	1.89
$Fe(S_2)$	$^5\mathbf{A_1}$	2.166	2.186	60.6		3.33	0.33	0	0
	$^3\mathbf{B_2}$	2.185		57.2		2.35	-0.17	0.58	0.79

	$^{1}\mathbf{A_1}$	2.095	2.040	58.3		0.00	0.00	1.98	1.58
FeS_2	$^{5}\mathbf{B_2}$	2.015		113.5		3.34	0.33	0.13	0.14
	$^{3}\mathbf{B_1}$	2.015		122.4		2.94	-0.47	0.39	0.54
	$^{1}\mathbf{A_1}$	1.940		116.6		0.00	0.00	1.81	1.21
$(CO)Fe(S_2)$	$^{5}\mathbf{A}$	2.238	2.074	55.2	1.884	3.10	0.48	0	0
$(CO)FeS_2$	$^{5}\mathbf{A}$	2.044		107.6	2.053	3.09	0.54	0.97	0.93
Cl-Fe (S_2)	$^{4}\mathbf{B_2}$	2.239	2.053	54.5	2.138	3.27	-0.18	0	0
$Cl\text{-}FeS_2$	$^{4}\mathbf{A_1}$	2.040		113.8	2.134	3.17	-0.12	1.25	1.40

[a] ΔE_{tot}: total energy difference relative to the ground state energy for a given composition; for $Co(S_2)$ E_{tot} = -2179.226190 Hartree (B3LYP); for $Fe(S_2)$ E_{tot} = -2060.174869 Hartree (B3LYP); zero-point and dispersion correction included. CCSD(T) E_{tot} = -2177.080007 for $Co(S_2)$ and -2058.068628 for $Fe(S_2)$

Table 4S. Bond Lengths, Bond Angles, Magnetic Moments on Atoms (μ, Bohr Magnetons), Spin Contamination Expectation Value ‹S^2› and Energies for Neutral $(CoS)_2$ and for the Persulfo-isomers $Co_2(S_2)$.

Cluster Model	State	R_{Co-S} Å	R_{S-S} Å	R_{Co-Co} Å	∠SCoS, ∠CoSS [a] deg	Dihedral ∠SCoSCo deg	μ_{Co}	μ_{S}	‹S^2›	ΔE_{tot}, eV B3LYP	ΔE_{tot},eV CCSD(T)
Co_2S_2, D_{2h}	^{1}A	2.183	3.655	2.388	113.7		2.46 -2.46	0.00 0.00		0	0
	$^7\mathbf{A_u}$	2.181	3.652	2.385	113.6		2.36	0.64	12.048	0.54	0.41
	$^5\mathbf{B_{2u}}$	2.120	3.549	2.319	113.7		1.91	0.09	6.147	1.88	1.51
	$^3\mathbf{B_{3u}}$	2.047	3.385	2.303	111.5		1.09	-0.09	2.066	2.42	2.44
	$^1\mathbf{A_g}$	2.026	3.355	2.271	111.8		0.00	0.00		2.82	2.71
Co_2S_2, C_{2v}	$^3\mathbf{A_2}$	2.105	3.153	2.496	97.0	33.7	0.86	0.14	2.118	2.95	2.81
	$^7\mathbf{A_1}$	2.260	2.302	3.508	61.2	43.2	2.80	0.20	12.102	3.01	2.88
	$^1\mathbf{A_1}$	2.151	2.106	2.735	58.6	62.5	0.00	0.00		4.62	4.31
$Co_2(S_2)$	$^5\mathbf{A_2}$	2.130	2.169	2.330	92.2		1.87	0.13	6.105	2.48	2.57
	$^7\mathbf{B_1}$	2.210	2.096	2.142	90.6		2.62	0.38	12.055	2.69	2.60
	$^3\mathbf{A_1}$	2.077	2.102	2.165	90.9		0.91	0.09	2.059	3.97	3.79

	$^{1}\mathbf{A_1}$	2.023	2.102	2.087	89.8	0.00	0.00		4.58	n.c.
CoSSCo, C_{2h}	$^{3}\mathbf{A_u}$	2.184	2.056		116.5	1.48	-0.48	2.297	3.75	3.83
$Co_2S_2Cl_2$, C_{2v}	^{1}A	2.133	3.462	2.494	108.5	2.47 -2.47	0.00			

[a] – ∠SCoS for sulfide clusters with separated sulfur atoms and for non-planar disulfide clusters; ∠CoSS for planar clusters with bridging or side-on bonded S_2. ΔE_{tot} – total energy difference relative to the ground state energy of neutral Co_2S_2: E_{tot} = -3562.050919 Hartree for B3LYP, zero-point and dispersion correction included; -3558.797034 Hartree for CCSD(T).

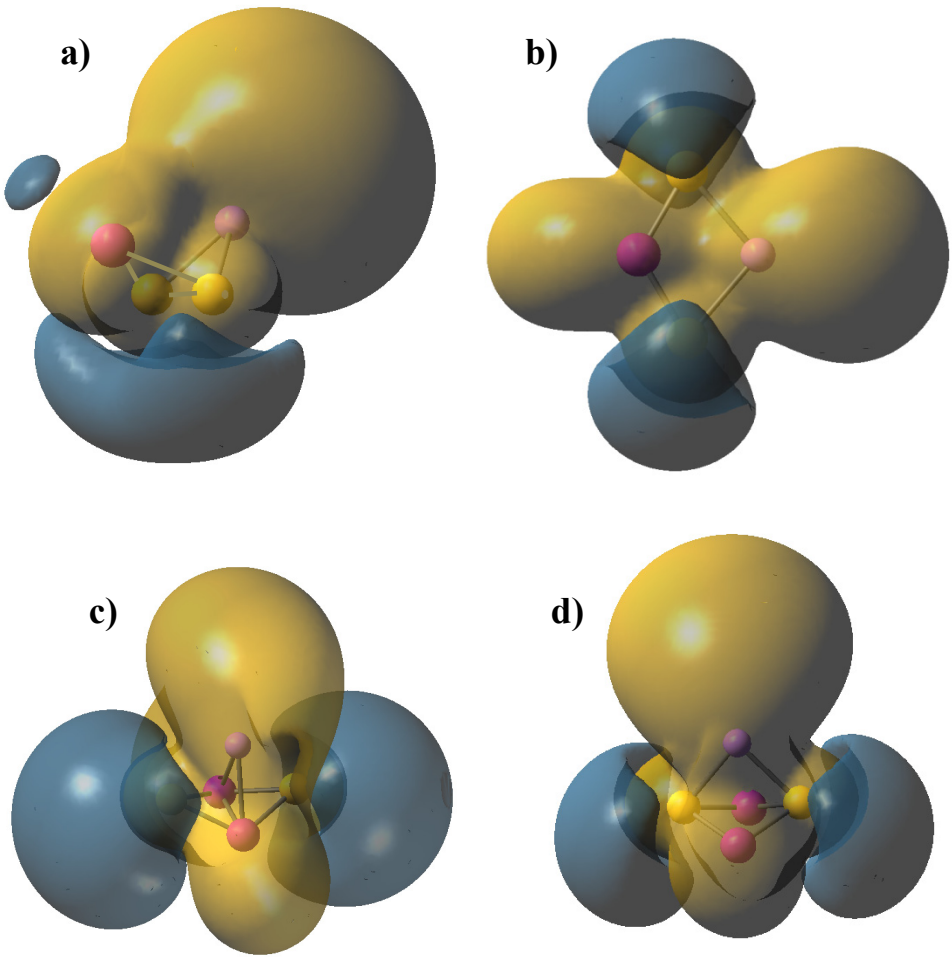

Figure 1S. Molecular electrostatic potential (MEP) map of a) $Co(S_2)$-Li^+,e^-; b) CoS_2- Li^+,e^-; and c) Co_2S_2- Li^+,e^- in ^6A state; d)Co_2S_2- Li^+,e^- in $^6B_1$ state. Sulphur atoms are yellow, cobalt – pink, lithium ions – small pink balls. Electropositive area is golden yellow, electronegative areas – dark blue. Contour lines are drawn at 0.085 a.u. for a), b) and at 0.2 a.u. for c). Colour legend as Figure 1S.

Li^+ binding to $Co(S_2)$ yields a rhomboid boat-shaped cluster in which all local charges increase, Co and Li bear nearly equal charge of +0.91 and +0.94 and the charge on S becomes less negative, see Table 2S. Chloride and carbonyl ligands have minor effect on the relative stability of cation-coordinated clusters, as the cations have a dominant effect on the electron distribution: they create a strong field of positive electrostatic potential and increase Co-S and Fe-S bond polarization

Table 5S. Bond Lengths, Bond Angles, Magnetic Moments on Atoms [a] (μ, Bohr Magnetons), for $[M_4S_4]X_4$ clusters, with M=Fe,Co and X=CO, Cl^-

Cluster Model	R_{M-S} Å	R_{M-X} Å	μ_M	μ_S
Fe_4S_4	2.221		1.70/-1.70	-0.20/0.20
Co_4S_4	2.220		1.47/-1.47	0.03/-0.03
$Fe_4S_4Cl_4$	2.177	2.110	2.11 -2.11	0.00 0.00
$Co_4S_4Cl_4$	2.182	2.120	2.53 -2.53	0.24/-0.24
$Co_2Fe_2S_4Cl_4$	2.140 (Co) 2.142 (Fe)	2.110 (Co) 2.103 (Fe)	2.12/-2.12 (Co) 3.16/-3.16 (Fe)	0.00 0.00
$Fe_4S_4(CO)_4$	2.250	1.978	3.21 -3.21	0.00 0.00
$Co_4S_4(CO)_4$	2.230	1.861	2.18 -2.18	0.04/-0.04
$Co_2Fe_2S_4(CO)_4$	2.259 (Co) 2.247 (Fe)	1.923 (Co) 1.998 (Fe)	2.27/-2.27 (Co) 3.39/-3.39 (Fe)	0.07/-0.07

[a] – negative sign in magnetic moment denotes antiferromagnetic coupling

Table 6S. Bond Lengths, Bond Angles, Magnetic Moments on Atoms (μ, Bohr Magnetons), and Energies for disulfides MS_2, M_2S_2 and persulfides $M(S_2)$, bonded to Li^+ cations and upon $1e^-$ reduction

Cluster Model	State	R_{M-S} Å	R_{S-Cat} Å	∠S-M-S, deg	μ_M	μ_S	ΔE_{tot} eV [a] B3LYP
$Co(S_2)$-Li^+	^{4}**A'**	2.198	2.377	59.4	2.33	0.33	0.0
CoS_2-Li^+	^{4}**B$_2$**	2.029	2.421	97.4	2.13	0.41	0.66
	^{6}**A$_1$**	2.129	2.507	117.5	2.58	1.19	0.86
CoS_2- Li^+,e^-	^{5}**A$_1$**	2.081	2.360	120.3	2.50	0.75	0.0
$Co(S_2)$-Li^+,e^-	^{5}**A'**	2.349	2.253	54.6	3.57	0.19	1.26
Cl-$Co(S_2)$-Li^+	^{4}**A'**	2.269	2.271	61.2	2.50	0.20	0.0
Cl-CoS_2-Li^+	^{4}**B$_2$**	2.056	2.277	100.7	2.18	0.28	0.74
Co_2S_2-Li^+	^{7}**A**	2.223	2.505	98.1	2.53	0.43	
Co_2S_2- Li^+,e^- (Li-S; Li-Co_2) bonds	^{6}**A**	2.245	2.420 (S) 2.519 (Co)	107.7	2.27	0.23	0.0
Co_2S_2- Li^+,e^- (Li-S) bond	^{6}**B$_1$**	2.239	2.306	86.6	2.71	-0.23	2.20
$Fe(S_2)$-Li^+	^{5}**A'**	2.228	2.369	54.3	3.47	0.26	0.0
FeS_2-Li^+	^{5}**B$_2$**	2.043	2.426	102.3	3.33	0.31	0.35
	^{3}**B$_1$**	2.061	2.424	101.2	3.10	-0.58	0.70
FeS_2- Li^+,e^-	^{6}**A$_1$**	2.110	2.357	118.8	3.72	0.64	0.0
$Fe(S_2)$-Li^+,e^-	^{6}**A'**	2.368	2.257	57.5	4.62	0.17	1.34
Cl-$Fe(S_2)$-Li^+	^{5}**A'**	2.309	2.268	58.0	3.58	0.16	0.0
Cl-FeS_2-Li^+	^{5}**B$_2$**	2.102	2.281	100.6	3.42	0.18	0.41
Fe_2S_2-Li^+	^{7}**A**	2.197	2.502	100.4	3.12	-0.12	
Fe_2S_2-Li^+,e (Li-S; Li-Fe_2) bond	^{8}**A**	2.271	2.442 (S) 2.574 (Fe)	106.8	3.30	0.20	0.0

Fe_2S_2-Li^+,e (Li-S) bond	^{6}**A**	2.207	2.390	100.5	2.69	-0.16	0.91

[a] $-\Delta E_{tot}$ – total energy difference relative to the ground state energy, zero-point and dispersion corrections included.

Table 7S. Bond Lengths, Bond Angles, Magnetic Moments on Atoms (μ, Bohr Magnetons), and Energies for disulfides MS_2, M_2S_2 and persulfides $M(S_2)$, $M_2(S_2)$ bonded to Na^+ and upon $1e^-$ reduction

Cluster Model	State	R_{M-S} Å	R_{S-Cat} Å	∠S-M-S, deg	μ_M	μ_S	ΔE_{tot}, eV B3LYP
$Co(S_2)$-Na^+	^{4}**A'**	2.181	2.778	57.9	2.28	0.35	0.0
CoS_2-Na^+	^{4}**B$_2$**	2.012	2.831	102.4	2.10	0.43	0.64
CoS_2-Na^+,e^-	^{5}**A$_1$**	2.081	2.727 2.876 Co-Na	128.9	2.51	0.75	0.0
$Co(S_2)$-Na^+,e^-	^{5}**A'**	2.304	2.650	55.4	3.51	0.21	1.32
Co_2S_2-Na^+	^{7}**A**	2.231	2.903	101.7	2.53	0.45	0.0
$Co_2(S_2)$-Na^+	^{7}**A$_1$**	2.324	2.804	65.3	2.80	0.16	2.63
Co_2S_2-Na^+,e^-	^{6}**A**	2.241	2.805	111.5	2.27	0.24	
$Fe(S_2)$-Na^+	^{5}**A'**	2.212	2.760	59.8	3.45	0.27	0.0
FeS_2-Na^+	^{5}**B$_2$**	2.037	2.828	105.6	3.33	0.31	0.30
FeS_2-Na^+,e^-	^{6}**A$_1$**	2.111	2.722 2.913 Fe-Na	126.5	3.72	0.64	0.0
$Fe(S_2)$-Na^+,e^-	^{6}**A'**	2.340	2.652	57.1	4.56	0.19	1.38
Fe_2S_2-Na^+	^{7}**A$_2$**	2.219	2.817	103.2	3.14	-0.14	
Fe_2S_2-Na^+,e^-	^{8}**B$_2$**	2.299	2.736	100.4	3.28	0.23	0.0
Fe_2S_2-Na^+,e^-	^{6}**A$_1$**	2.196	2.735	99.1	2.52	0.00	1.36

[a] $-\Delta E_{tot}$ – total energy difference relative to the ground state energy.

Table 8S. Adsorption energies E (kJ mol^{-1}) of N_2 and O_2 at alkali cations in FeS_2 and Fe_2S_2

Cluster	E (N_2)	E (O_2)
Fe_2S_2- Li^+	14.9	9.1
Fe_2S_2- Li^+,e^-	10.8	6.3
FeS_2- Li^+	40.1	25.3
FeS_2- Li^+,e^-	23.8	12.2
FeS_2- Na^+	24.1	17.2
FeS_2- Na^+,e^-	15.4	11.3

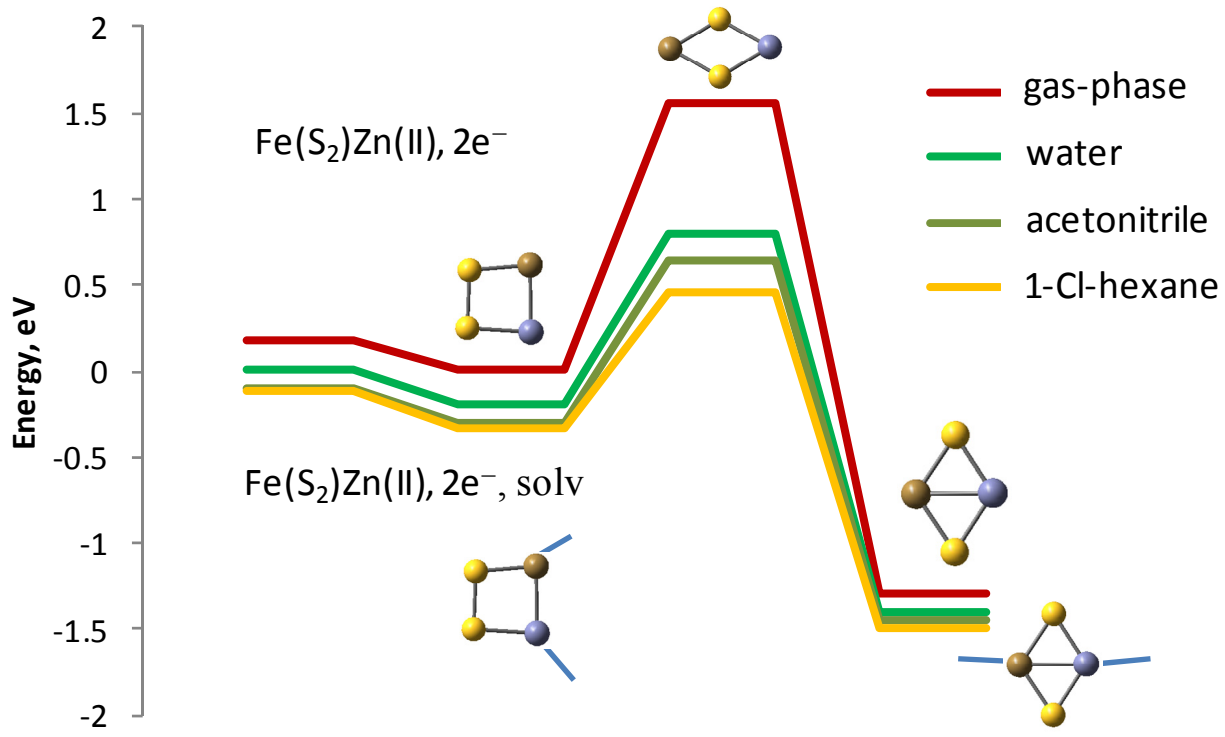

Figure 2S IRC Reaction path following of persulphide to disulphide isomerisation in reduced clusters Fe(S_2)-Zn(II),$2e^-$. Acetonitrile and water molecule coordination to the clusters is denoted by blue lines.