Electronic Supporting Information for the Article:

Catalytic effect of a second H_3PO_2 molecule in the mechanism of stabilisation of the unstable pyramidal tautomer of H_3PO_2 coordinated at $[Mo_3S_4M']$ clusters (M'= Ni, Pd)

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1. Synthesis of the clusters

The green starting trinuclear cluster $[Mo_3S_4(H_2O)_9]^{4+}$ cluster was prepared according to published procedures [1, 2] and purified by Dowex-50W-X2 cation exchange chromatography. The cluster was obtained in 2M HCl aqueous solution at concentrations close to 0.01 M (UV-vis band positions λ/nm (ε/$M^{-1}cm^{-1}$): 370(4995), 616(326)).

The blue $[Mo_3(PdCl)S_4(H_2O)_9]^{3+}$ complex was prepared according to the published procedure[3, 4] by reacting Pd black with $[Mo_3S_4(H_2O)_9]^{4+}$. (UV- Vis peak positions λ/nm (ε/$M^{-1}cm^{-1}$) (450(1013) and 580(1382)). Although this complex crystallises as an edge-linked double cube[4] from concentrated solutions of Hpts, its elution behaviour indicates that in solution it exists as a single cube. When eluted with HCl, the cube has 3+ charge, consistent with Cl^- coordination to Pd, and it elutes prior to $[Mo_3S_4(H_2O)_9]^{4+}$. Elution is also possible with 2 M Hpts, and in this case the behaviour is typical of 4+ charge, consistent with the existence of a water molecule at the Pd coordination site, i.e. $[Mo_3PdS_4(H_2O)_{10}]^{4+}$.

A similar behaviour is observed for the green $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ cluster (UV-Vis band at 677 nm (ε = 610 $M^{-1}cm^{-1}$)), which was prepared by reacting Ni metal with $[Mo_3S_4(H_2O)_9]^{4+}$ at 90 º for 2 days.[5]

2. Kinetic and NMR experiments

Solutions of $[Mo_3PdS_4(H_2O)_{10}]^{4+}$ and $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ were stored at low temperature under N_2 to avoid reaction with O_2. Standard Schlenck and manifold procedures were used to maintain an N_2 atmosphere during the preparation of the solutions and the kinetic runs. The kinetic experiments were carried out with a Cary 50 Bio UV-Vis spectrophotometer by mixing stock solutions of $[Mo_3PdS_4(H_2O)_{10}]^{4+}$ or $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ and H_3PO_2. The experiments were carried out at 25.0 ± 0.1 ºC under pseudo first order conditions of H_3PO_2 excess, with the ionic strength adjusted to I = 2.00 ± 0.01 M with Hpts/Lipts mixtures. The complex solutions were prepared at concentrations of (2.0-2.4)×10^{-3} M in Hpts 2.0 M, and preliminary experiments at two different complex concentrations were carried out to confirm the first-order dependence of the observed rate constants on the complex concentration. The complex concentration was estimated from the UV-Vis spectra and the Hpts concentration was determined by titration with KOH (Phenolphthalein indicator). Stock H_3PO_2 solutions were prepared in water and titrated with KOH (Phenolphthalein indicator). These stock solutions were then mixed with Hpts/Lipts solutions whose acidity was also determined by KOH titration. A similar procedure was used for the experiments with H_3PO_4.

The reaction kinetics were monitored by recording the spectral changes with time and analysing the data with the SPECFIT. [6] The analysis required the use of a two-step kinetic model and provided the rate constants for both steps as well as the calculated spectra for reagents, intermediate and reaction products. Reported rate constants are the average of at least three separate experiments.

The NMR experiments were carried out with a Varian Unity 400 spectrometer using the standard pulse sequences provided by the manufacturer. The chemical shifts in

the ^{31}P NMR spectra are reported with respect to external H_3PO_4. The samples were prepared under an inert atmosphere of N_2 by adding different aliquots of a H_3PO_2 solution to an NMR tube containing a solution of the starting complex.

3. Computational Details

All calculations were performed using the GAUSSIAN 03 series of programs[7] together with B3LYP functional.[8, 9] Two kinds of basis set systems were used. In the geometry optimization, the basis set system used (BS-I) was the double-ξ pseudo-orbital basis set LanL2DZ, in which the inner electrons of Mo, Pd and P atoms are represented by the relativistic core LanL2 potential of Los Alamos,[7, 10] and its associated double-ξ basis set for the outer ones. In the case of the P atoms, polarization and diffuse functions were added to the standard basis functions.[11] All other atoms were described with the double-ξ D95v basis set.[12] All geometry optimizations were performed without any symmetry constrains and for compounds that have multiple conformations, efforts were made to find the lowest energy conformation by comparing the structures optimized from different starting geometries.

Solvent effects were taken into account by means of polarised continuum model (PCM)[13, 14] calculations using standard options.[7] The reported energies correspond to Gibbs free energies ΔG in aqueous solution (ε= 78,39) and were computed by single-point calculations with a better basis set system (BS-II), using the geometries optimized in the gas phase by the B3LYP/BS-I method. In BS-II, the same basis set and ECPs as those of BS-I were used for Mo and Pd atoms. The 6-311+G(3df,2p) basis set was used for P, O and H atoms.

The nature of each stationary point was checked by diagonalizing the Hessian matrix to determine the number of imaginary frequencies (zero for the local minima and one for the TSs). The intrinsic reaction coordinate (IRC)[16] pathways from the TSs down to the two lower energy structures have been traced using the second-order González-Schelegel integration method[17, 18] in order to verify that each saddle point links the two putative minima.

4. References

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Table S1. Summary of total energies calculated for the different species involved in the proposed mechanism.

Species	gas phase	aqueous solution
	E (hartrees)	*E* (hartrees)
tet-H_3PO_2	-493.7405206	-493.7664040
pyr-H_3PO_2	-493.7313513	-493.7531565
H_3PO_2-TS[a]	-493.6411556	-493.6623655
$H_4PO_2^+$	-494.0609353	-494.1823255
1	-1133.3670102	-1134.3192327
I	-1550.6758967	-1551.5989257
TS (**I** to $\mathbf{I_3}$)[b]	-1550.5725241	-1551.4982605
$\mathbf{I_2}$	-1550.5436534	-1551.1473050
$\mathbf{I_3}$	-1550.6570159	-1551.5927540
TS ($\mathbf{I_3}$ to **2**)	-1550.6449943	-1551.5887665
2	-1550.6828827	-1551.6209159

[a] Transition state for tautomerization in free H_3PO_2. [b] Transition state for direct conversion of **I** to $\mathbf{I_3}$ without participation of a second H_3PO_2 molecule.

5. Tables of the Cartesian Coordinates (in Å) for the different species discussed in the text.

tet-H_3PO_2

O	0.000000	0.000000	0.000000
P	0.000000	0.000000	1.489502
O	1.447730	0.000000	2.243817
H	-0.669194	1.104645	2.064070
H	-0.547825	-1.123526	2.138357
H	2.108980	0.550099	1.797406

pyr-H_3PO_2

O	0.000000	0.000000	0.000000
P	0.000000	0.000000	1.694411
O	1.644057	0.000000	2.103955
H	-0.202743	-0.856595	-0.425289
H	-0.083230	1.425722	1.759438
H	2.008272	-0.856104	2.404218

H_3PO_2-TS

O	0.000000	0.000000	0.000000
P	0.000000	0.000000	1.665568
O	1.491671	0.000000	2.306132
H	0.469689	0.725557	-0.459545
H	-0.634385	-1.283525	1.771161
H	0.419150	0.845668	2.835286

$H_4PO_2^+$

O	0.000000	0.000000	0.000000
P	0.000000	0.000000	1.583449
O	1.419008	0.000000	2.286246
H	-0.532605	1.254726	1.914093
H	-0.786852	-1.070662	2.071843
H	0.142601	-0.699094	-0.668677
H	2.081653	-0.699270	2.453930

1

S	0.000000	0.000000	0.000000
Mo	0.000000	0.000000	2.458032
S	2.330806	0.000000	3.116046
Pd	1.413246	2.367672	3.164796
O	2.171296	3.618827	4.796335
Mo	2.159600	0.831344	0.851235
O	4.349010	1.082960	1.078607
Mo	-0.241977	2.294917	0.838090
S	-1.078140	2.081356	3.111361

O	2.979718	-1.086311	0.101423
S	1.988385	3.248872	0.848637
O	-0.836304	4.421887	0.918716
O	-2.432153	2.246064	0.321557
O	-2.136180	-0.732642	2.431465
O	0.086075	-2.207121	2.282799
O	-0.422346	2.830126	-1.308354
O	2.831180	1.193212	-1.270151
O	-0.291910	-0.705999	4.539928
H	-2.384326	-1.599637	2.047336
H	-2.922649	-0.271454	2.788487
H	-1.182703	-0.908557	4.896304
H	0.356080	-0.609913	5.270589
H	0.110886	-2.796428	1.501666
H	0.207925	-2.709709	3.118093
H	-3.194955	2.144975	0.926512
H	-2.720666	2.234688	-0.615731
H	-0.344526	2.260840	-2.101442
H	-0.488812	3.780769	-1.546409
H	-0.264838	5.174217	1.182514
H	-1.783654	4.673547	0.960794
H	2.927021	2.060874	-1.714648
H	3.078364	0.456549	-1.868142
H	4.888433	1.495541	0.370383
H	4.841712	1.070693	1.926363
H	2.533534	-1.846668	-0.324438
H	3.914366	-1.293152	0.322007
H	3.115834	3.786092	4.988599
H	1.601109	4.079732	5.444477

I

S	0.000000	0.000000	0.000000
Mo	0.000000	0.000000	2.464424
O	2.250139	0.000000	2.434379
Mo	-0.612307	-2.237757	0.849281
O	1.405059	-3.048991	0.289685
Mo	-2.307588	0.025589	0.875457
O	-3.073414	0.003139	-1.250584
S	0.300325	-2.307566	3.102839
Pd	-2.145704	-1.726395	3.107860
O	-3.117041	-3.212083	4.353251
P	-3.390943	-4.723147	4.413432
O	-2.767314	-5.439737	3.030629
S	-3.040433	-2.263980	0.821851
O	-0.723757	-2.871562	-1.277832
S	-2.167247	0.847149	3.152173
O	-4.436982	0.586372	1.128938
O	0.508789	0.526719	4.555731
O	0.678616	2.118339	2.316954
O	-2.372870	2.137048	0.183313
O	-0.948395	-4.389550	1.168456
H	-0.569290	-2.342001	-2.086891
H	-1.100180	-3.753587	-1.487719
H	-0.223764	-5.033748	1.031481
H	-1.643396	-4.748490	1.799745
H	1.669813	-3.146340	-0.648947
H	2.134086	-3.302822	0.890997
H	-3.467512	-0.755011	-1.728249
H	-3.026542	0.800403	-1.818793

H	-1.699546	2.690568	-0.261200
H	-3.148917	2.669387	0.464508
H	-4.892810	0.702314	1.989621
H	-5.086307	0.450627	0.406766
H	0.824687	2.695476	1.540656
H	0.704442	2.629406	3.155420
H	-0.137460	0.627577	5.286677
H	1.413447	0.385670	4.907381
H	2.738195	0.804914	2.161233
H	2.861100	-0.745018	2.603464
H	-2.750432	-5.371199	5.496801
H	-3.015193	-6.371739	2.823495
H	-4.765210	-5.066460	4.417777

I_2

S	-0.008767	0.024103	0.023055
Mo	-0.062359	0.104398	2.505948
S	2.263809	0.115491	3.232713
Pd	1.263216	2.443664	3.204574
S	-1.195178	2.191294	3.069544
Mo	-0.272217	2.337974	0.843544
S	1.934966	3.376399	0.882188
Mo	2.090505	0.936126	0.948768
O	4.251086	1.444415	1.142291
O	3.121369	-1.008745	0.475962
O	-0.884661	4.483167	0.903953
O	-2.465349	2.237376	0.273062
O	-2.100726	-0.787897	2.403238
O	0.229665	-2.132208	2.573214
O	1.668938	3.264955	5.046676
P	0.845402	3.031625	6.408753
O	0.433254	1.288141	6.370246
O	-0.465786	-0.242393	4.604881
O	2.822813	1.048931	-1.180728
O	-0.431792	2.932395	-1.310978
H	-2.645265	-1.043971	1.633739
H	-2.608914	-0.773000	3.241632
H	-0.457962	-1.161643	4.938791
H	-0.141242	0.451012	5.365669
H	-0.426250	-2.763485	2.215732
H	1.001224	-2.584885	2.966746
H	-3.218253	2.103233	0.881401
H	-2.743286	2.269176	-0.664380
H	-0.331025	2.407484	-2.128260
H	-0.379635	3.897033	-1.479746
H	-0.302187	5.185079	1.262163
H	-1.828920	4.727828	0.988604
H	2.357251	0.889790	-2.024160
H	3.650221	1.560155	-1.306559
H	4.567292	2.293540	1.515410
H	4.906569	0.729741	1.278330
H	3.307953	-1.240602	-0.456167
H	3.287914	-1.753658	1.085208
H	-0.493614	3.407616	6.027857
H	0.770192	0.812263	7.159409

I_3

O	0.000000	0.000000	0.000000
Mo	0.000000	0.000000	2.211510
O	2.161989	0.000000	1.729793
S	-2.418706	-0.352325	1.950121
Mo	-1.787824	-0.437275	4.322447
O	-1.914622	-2.696927	4.275498
Mo	-1.972903	1.940006	2.783542
O	-2.350175	2.764078	0.722976
S	0.603870	-0.891645	4.398547
Pd	0.188480	1.617886	4.559837
O	1.127376	3.251269	5.783722
P	0.896354	4.961166	5.530167
O	-0.820900	4.966578	5.277242
S	0.322746	2.395612	2.169376
O	-4.145191	2.318842	2.642806
S	-2.257443	1.761020	5.179681
O	-3.903001	-0.991665	4.663523
O	-2.080289	4.049680	3.260753
O	0.354153	-2.131246	1.562006
O	-1.849516	-0.989458	6.468576
H	0.847943	0.160371	-0.468265
H	-0.759424	-0.024593	-0.617336
H	2.664022	-0.835073	1.617845
H	2.773841	0.753138	1.870744
H	0.103204	-2.437675	0.665215
H	0.734838	-2.860684	2.091951
H	-3.254589	2.827211	0.350810
H	-1.684303	3.144807	0.114369
H	-4.890709	1.751775	2.359181
H	-4.461060	3.143284	3.074208
H	-2.775014	-3.149968	4.151310
H	-1.178047	-3.339998	4.312404
H	-4.653311	-1.063392	4.039467
H	-4.200670	-1.059672	5.596980
H	-1.672179	-1.912391	6.749385
H	-1.759895	-0.373552	7.225927
H	1.140274	4.852198	4.127838
H	-1.607523	4.456636	4.098660
H	-2.198285	4.715492	2.552292
H	-1.333756	5.429832	5.977337
H	1.578314	3.026414	6.627855

2

S	0.000000	0.000000	0.000000
Mo	0.000000	0.000000	2.457267
O	2.245082	0.000000	2.386948
Mo	-0.610529	-2.234475	0.862651
O	1.430635	-3.005472	0.360013
Mo	-2.296100	0.033776	0.900111
O	-2.907533	0.291768	-1.196192
S	0.253470	-2.297720	3.149073
Pd	-2.174802	-1.808730	3.177092
P	-3.255295	-3.631549	4.263586
O	-4.861631	-3.587823	4.102424

S	-3.037888	-2.249170	0.885451
O	-0.754275	-2.909153	-1.241890
S	-2.193249	0.772154	3.218101
O	-4.477951	0.436524	1.022607
O	0.563965	0.572755	4.519562
O	-2.654711	-4.901146	3.320575
O	0.633207	2.118241	2.243100
O	-2.393686	2.274271	0.558640
O	-0.973355	-4.374264	1.220940
H	-1.190397	-3.769963	-1.423749
H	-0.542346	-2.437679	-2.072826
H	-0.340767	-5.087257	0.999294
H	-1.629802	-4.657947	1.934368
H	1.774776	-3.038519	-0.556906
H	2.057159	-3.423166	0.985590
H	-3.869726	0.250104	-1.388777
H	-2.374211	0.353044	-2.014248
H	-2.461456	2.680531	-0.330921
H	-2.415458	2.950553	1.267149
H	-5.152399	-0.215918	1.308402
H	-4.816953	1.350516	1.131229
H	0.717669	2.660802	1.432662
H	0.745858	2.653729	3.058398
H	-0.058409	0.711853	5.264336
H	1.477467	0.430995	4.847438
H	2.730905	0.785411	2.058246
H	2.851736	-0.752165	2.538849
H	-3.019428	-4.119757	5.582479
H	-2.885578	-5.835483	3.537369
H	-5.541862	-4.092162	4.601995

TS (**I** to **I**$_3$)

S	-0.000907	0.002694	0.008029
Mo	-0.017313	-0.000522	2.471780
O	2.238736	0.015807	2.462096
Mo	-0.606526	-2.237514	0.855377
O	1.425941	-3.028823	0.324780
Mo	-2.310323	0.011979	0.874489
O	-3.053359	-0.030515	-1.259102
S	0.283278	-2.306192	3.116626
Pd	-2.180280	-1.750849	3.103922
O	-2.996791	-3.277859	4.416130
P	-3.622826	-4.799652	4.294095
O	-2.838362	-5.462401	2.953113
S	-3.042979	-2.282666	0.830412
O	-0.693997	-2.867094	-1.271580
S	-2.192193	0.824613	3.161775
O	-4.443308	0.580523	1.110229
O	0.487476	0.527807	4.562565
O	0.644813	2.123482	2.319100
O	-2.388134	2.122167	0.182079
O	-0.936215	-4.393375	1.161481
H	-0.541168	-2.332546	-2.077425
H	-1.048061	-3.757017	-1.486660
H	-0.204634	-5.034780	1.049611
H	-1.643677	-4.750965	1.776829

H	1.715043	-3.109001	-0.608276
H	2.136772	-3.300450	0.940103
H	-3.453715	-0.789004	-1.730932
H	-2.993261	0.759708	-1.835752
H	-1.717922	2.685659	-0.254457
H	-3.174842	2.642911	0.454932
H	-4.901905	0.704589	1.968069
H	-5.089703	0.441100	0.386140
H	0.802549	2.692530	1.539082
H	0.661164	2.643134	3.152410
H	-0.155965	0.632071	5.295071
H	1.394437	0.390588	4.909379
H	2.724173	0.823107	2.191338
H	2.852808	-0.727689	2.627031
H	-3.011239	-4.112614	5.548181
H	-3.036559	-6.401353	2.720262
H	-4.976180	-4.729613	3.825776

TS (**I_3** to **2**)

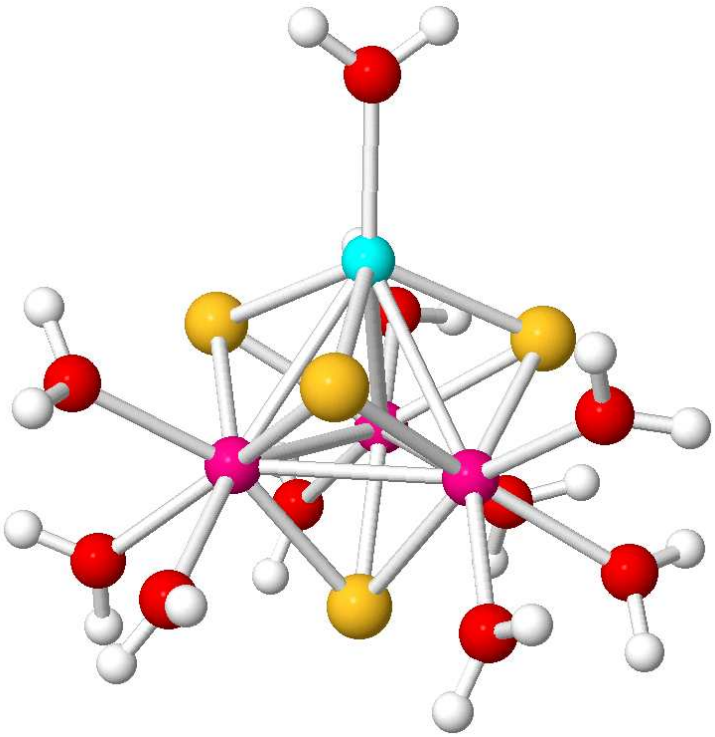
O	0.000000	0.000000	0.000000
Mo	0.000000	0.000000	2.209403
O	2.161308	0.000000	1.545447
Pd	-1.560065	0.409982	4.586393
S	-2.092904	-1.978596	5.186729
Mo	-2.236402	-1.639786	2.795909
O	-3.077979	-1.881814	0.718038
S	0.994833	0.438200	4.381985
Mo	0.155397	-1.845067	4.333154
O	0.372344	-4.016299	4.679926
S	-0.047156	-2.445734	1.961417
O	0.345601	2.131041	1.719842
S	-2.312099	0.692681	2.175294
O	2.363704	-2.321744	4.268276
O	-2.967559	-3.719880	2.644214
O	-4.336048	-1.433298	3.251836
O	-5.092353	-0.023642	5.201184
P	-4.216883	1.450025	5.476098
O	-3.165294	1.095729	6.723583
O	0.691026	-1.977702	6.480260
H	-0.019059	0.866708	-0.461259
H	-0.108184	-0.748404	-0.621954
H	1.250814	2.494420	1.616691
H	-0.301444	2.855415	1.856960
H	2.411512	-0.291393	0.643497
H	2.950092	0.245428	2.070026
H	-3.293465	-2.767269	0.357154
H	-3.342511	-1.168265	0.101955
H	-2.526727	-4.555739	2.389949
H	-3.844305	-3.881101	3.058394
H	2.678518	-3.242436	4.148961
H	3.112970	-1.693460	4.304624
H	0.314931	-4.771778	4.060597
H	0.398485	-4.315116	5.615224
H	1.628331	-1.949966	6.768637
H	0.093350	-1.768856	7.229048
H	-5.264133	2.140228	6.169497
H	-4.688536	-0.899420	4.091248

H	-4.986208	-1.406340	2.519391
H	-5.878545	-0.262211	5.742756
H	-3.375685	1.145616	7.683685

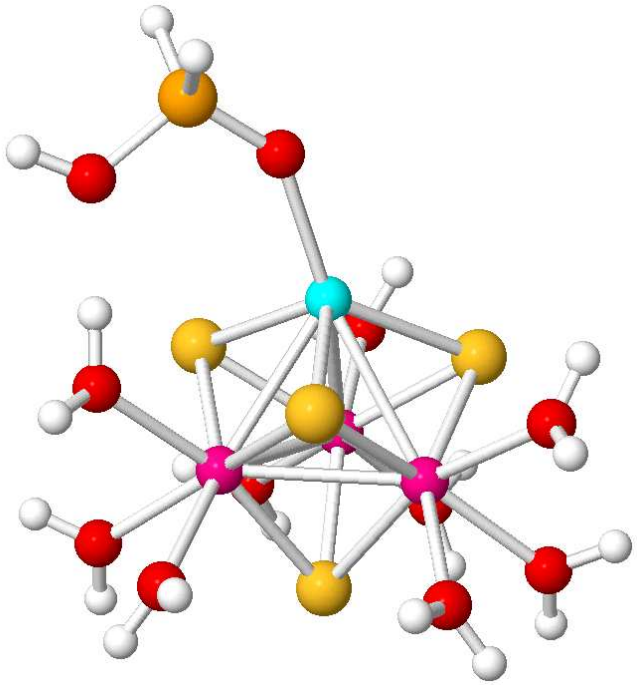
6. Optimized geometries for the different cluster species

H
O
S
P
Mo
Pd

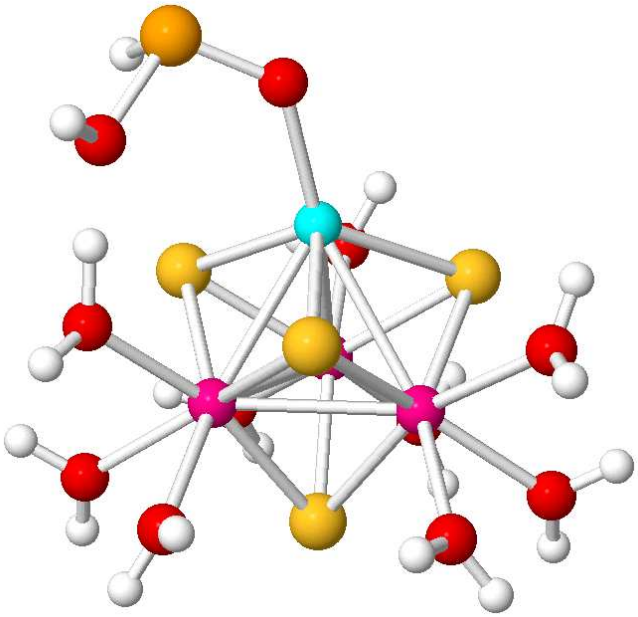
1



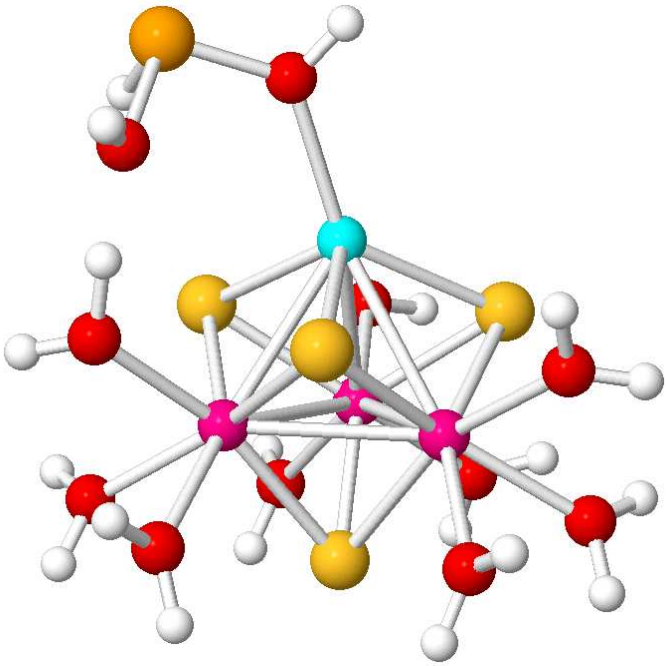
I



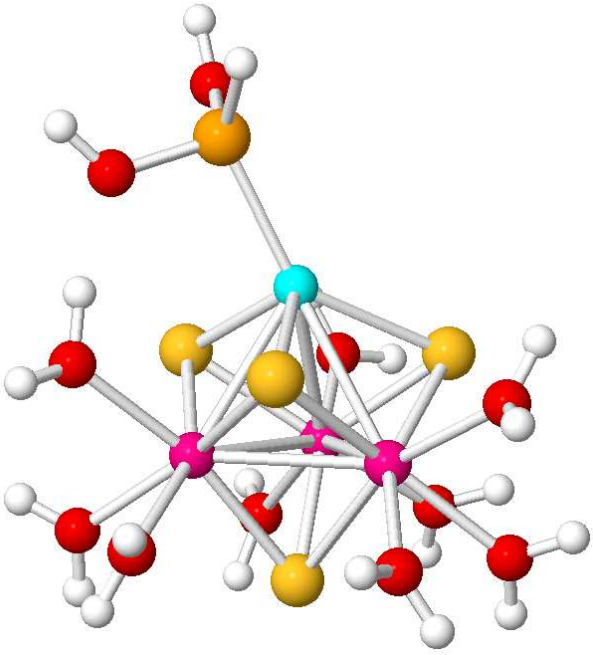
I_2



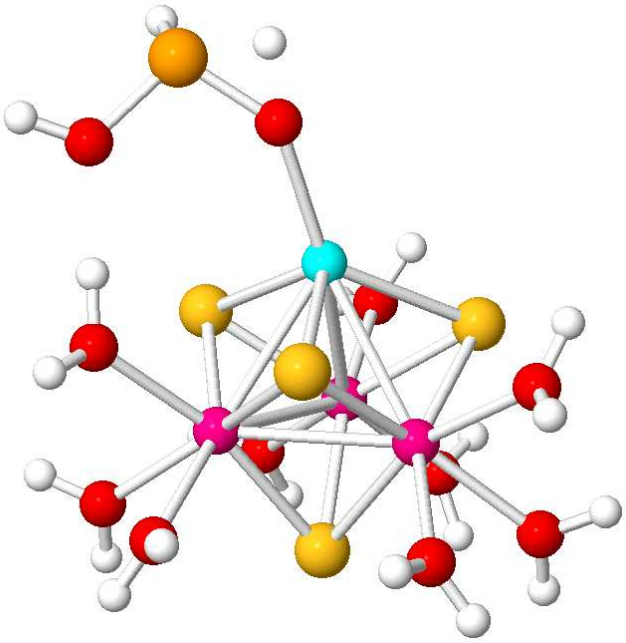
I_3



2



TS (**I** to **I_3**)



TS (**I_3** to **2**)