Supplementary Information

Enhancing the Double Exchange Interaction in Mixed Valence $\{V^{III}\text{-}V^{II}\}$ Pair: A Theoretical Perspective

Soumen Ghosh, Saurabh Kumar Singh and Gopalan Rajaraman*[a]

Computational Details

The magnetic interaction between V(II)-V(II) is calculated using the Hamiltonian,

$$\hat{H} = -2J\hat{S}_{V^{2+}}\hat{S}_{V^{2+}}$$

J is the isotropic coupling constant and $S_{v^{2+}}$ is the spin of V(II) centres. *J* values are computed from the energy differences between the high spin (HS) state, which is calculated using single determinant wave functions and low spin (BS) state, determined using Broken Symmetry (BS) approach developed by Noodleman.[1,2] The BS approach was proved to be handy in evaluating the *J* values to a good estimate in variety of complexes. All the calculations for $V^{2+}\text{-}V^{2+}$ complex has been done using B3LYP3 functional and TZV4 basis set.

For the mixed valence V (II)-V (III) complex all the single point energy calculation has been done using B3LYP functional and TZV basis set. For optimizing different spin states B3LYP functional is used with LANL2DZ ECP5 basis set for Vanadium atom and all electron 6-31G6 basis set for all other atoms. For excited state calculation TD-DFT method available in Gaussian097 is used. For excited state calculations also B3LYP functional has been used with TZV basis set for all the atoms. Here all the calculations have been done with Gaussian 097 code.

The following equation used for calculating percentage contribution of a single particle excitation in a particular excited state,[8]

$$y\% = \frac{x_i^{\,2}}{\sum_{i=1}^{n} x^2{}_i} X100$$

Excited state with highest contribution of HOMO to LUMO transition has been used to calculate all the parameter. For calculating exact energy of transition, % contribution of the energy is taken. Example: 2β for S=5/2 state= =.6808ev X .7282 = .4957ev = 3998cm^{-1}.

Table-S1. Overlap integral computed between the d orbitals for complex **1**.

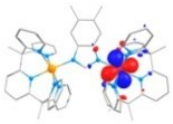
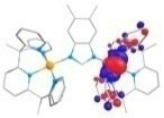
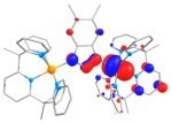
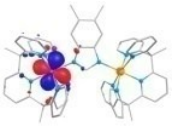
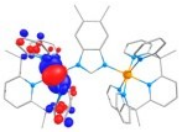
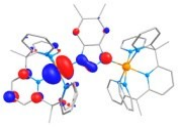
			
	$1.24X10^{-2}$	$5.41X10^{-3}$	$9.82X10^{-4}$
	$5.31X10^{-3}$	$9.51X10^{-3}$	$7.83X10^{-4}$
	$1.83X10^{-3}$	$5.90X10^{-4}$	$\mathbf{3.83X10^{-2}}$

Table S2: DFT computed energies of high spin (HS) and broken symmetry (BS) state, $<S^2>$ values for different value of V-N bond in the magneto structural correlation

V-N distance(Å)	HS energy	BS energy	$<S^2>$ value	
1.8	-5132.56116667	-5132.56394150	12.0316	2.9728
1.9	-5132.60105132	-5132.60248969	12.0301	2.9813
2.0	-5132.62217502	-5132.62291454	12.0285	2.9939
2.2	-5132.63308843	-5132.63328884	12.0261	3.0239
2.3	-5132.630323220	-5132.63033863	12.0256	3.0246
2.4	-5132.62471832	-5132.62477548	12.0251	3.0249
2.5	-5132.61773954	-5132.61777083	12.0247	3.0245
2.6	-5132.61009750	-5132.61011495	12.0243	3.0246

For fig 2a exponential equation has been used and the equation is,

$$y = A1*\exp(-x/t1) + y0$$

Where y0=-0.06368, A1=$-7.41644x1E^6$ and t1=0.1514

Table S3: DFT computed energies of high spin (HS) and broken symmetry (BS) state, $<S^2>$ values for different value of V-N-C angle in the magneto structural correlation

Angle	HS Energy	BS Energy	$<S^2>$ value	
115°	-5132.53458529	-5132.53529502	12.0265	3.0187
117°	-5132.58063438	-5132.58118919	12.0267	3.0202
119°	-5132.60558154	-5132.60605127	12.0268	3.0210
121°	-5132.61962354	-5132.62004841	12.0269	3.0215
123°	-5132.62755962	-5132.62794880	12.0276	3.0225
127°	-5132.63133035	-5132.63106388	12.0269	3.0222
129°	-5132.62549911	-5132.62586468	12.0282	3.0236

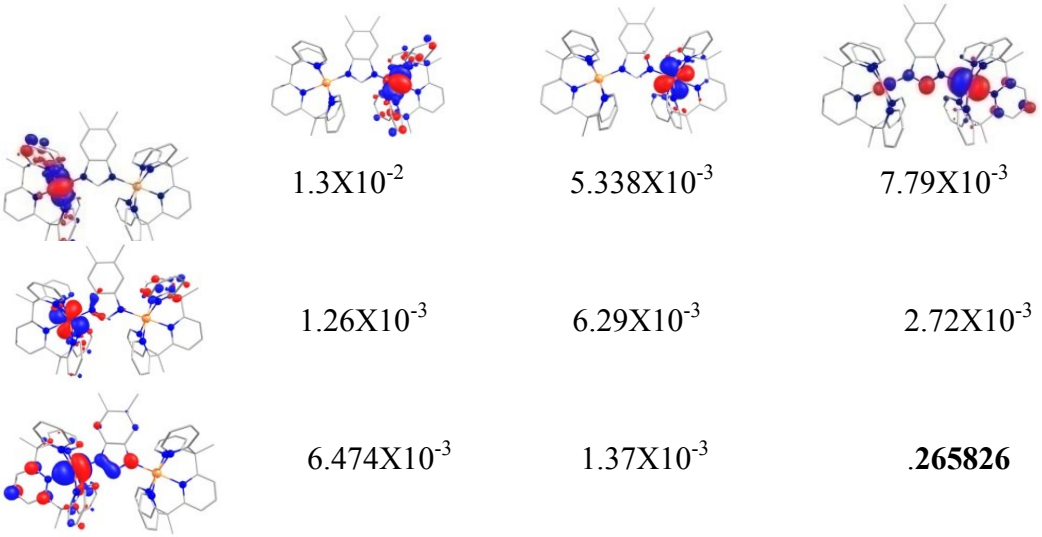
131°	-5132.61351326	-5132.61387490	12.0305	3.0259
133°	-5132.59338507	-5132.59373385	12.0344	3.0301
135°	-5132.56483783	-5132.56516670	12.0371	3.0359

For fig 2b polynomial equation has been used and the equation is,

$$y = Intercept + B1*x^1 + B2*x^2 + B3*x^3 + B4*x^4$$

Where Intercept=-22381.8385, B1=674.47635, B2=-7.61324, B3=0.03813 and B4=-7.14839x1E^{-5}

Table S4. Overlap integral for d orbital of complex 1_{ox}.



1.3X10^{-2}	5.338X10^{-3}	7.79X10^{-3}
1.26X10^{-3}	6.29X10^{-3}	2.72X10^{-3}
6.474X10^{-3}	1.37X10^{-3}	**.265826**

Optimized Geometries

Table S5. Cartesian co-ordinates for the optimized structures.

a) Optimized structure for S=5/2 state.

V	-3.151000	-0.093100	-0.001000
V	3.151100	-0.093000	0.000800
C	-0.000300	-0.130100	-0.000300
H	-0.000300	-1.207700	-0.000400
C	-0.706400	1.960900	0.026800
C	0.705500	1.960900	-0.027000
C	-1.413300	3.168800	0.072600
H	-2.492400	3.182000	0.134000
C	1.412500	3.168700	-0.072700
H	2.491600	3.181700	-0.134000
C	-0.713000	4.383000	0.041300
C	0.712400	4.383000	-0.041200
C	-1.471900	5.688000	0.089800
H	-1.179900	6.295200	0.955400
H	-2.550500	5.520500	0.151200
H	-1.279900	6.301400	-0.799200
C	1.471300	5.687900	-0.089500

H	1.179300	6.295300	-0.954800
H	2.550000	5.520300	-0.151200
H	1.279600	6.301000	0.799700
N	-1.154700	0.605000	0.025900
N	1.153800	0.605000	-0.026400
C	-5.435500	-2.173100	-0.135100
C	-6.741800	-2.669500	-0.094200
H	-6.945900	-3.722000	-0.204000
C	-7.807800	-1.793200	0.093500
H	-8.825100	-2.165400	0.131200
C	-7.548900	-0.432300	0.228500
H	-8.376300	0.243600	0.369800
C	-6.230900	0.034500	0.177400
C	-4.229300	-3.131400	-0.333300
C	-4.737300	-4.585300	-0.498700
H	-3.902600	-5.272500	-0.653300
H	-5.409500	-4.675800	-1.352900
H	-5.286700	-4.917200	0.383000
C	-5.921600	1.548500	0.304400
C	-7.244000	2.341500	0.454400
H	-7.791500	2.034300	1.346700
H	-7.899100	2.185300	-0.403800
H	-7.047800	3.412300	0.535400
C	-3.319800	-3.046100	0.921600
C	-3.115300	-4.152900	1.759600
H	-3.564300	-5.107400	1.535200
C	-2.336700	-4.036100	2.913700
H	-2.204800	-4.889900	3.568400
C	-1.743600	-2.806900	3.204400
H	-1.135200	-2.668300	4.088800
C	-1.960700	-1.747700	2.330400
H	-1.505100	-0.786500	2.508000
C	-3.446800	-2.720000	-1.607600
C	-3.396000	-3.542100	-2.744200
H	-3.909000	-4.490600	-2.766200
C	-2.687300	-3.140500	-3.879500
H	-2.678500	-3.767400	-4.764000
C	-1.994500	-1.928700	-3.849000
H	-1.428200	-1.579500	-4.704100
C	-2.068300	-1.158600	-2.693700
H	-1.530300	-0.226500	-2.615100
C	-5.182000	2.025800	-0.976500
C	-5.741600	2.980400	-1.838600
H	-6.713100	3.404200	-1.639800
C	-5.048800	3.403900	-2.976500
H	-5.492700	4.134800	-3.642600
C	-3.779500	2.881000	-3.226200
H	-3.196000	3.196400	-4.082200
C	-3.270500	1.940300	-2.338700
H	-2.277300	1.544200	-2.475500
C	-5.033000	1.800200	1.552900
C	-5.468300	2.592900	2.625500
H	-6.452100	3.034600	2.624800
C	-4.630500	2.830400	3.718800
H	-4.977200	3.437300	4.547400
C	-3.343800	2.289000	3.713500

H	-2.651900	2.469800	4.526700
C	-2.963400	1.510600	2.627100
H	-1.964100	1.108600	2.560700
N	-5.188100	-0.834600	0.005000
N	-2.741000	-1.845700	1.221700
N	-2.804400	-1.515900	-1.608000
N	-3.953400	1.493600	-1.250200
N	-3.787800	1.240300	1.579200
C	6.230900	0.034500	-0.177500
C	7.548900	-0.432400	-0.228700
H	8.376300	0.243500	-0.370100
C	7.807800	-1.793200	-0.093700
H	8.825100	-2.165500	-0.131500
C	6.741800	-2.669500	0.094200
H	6.945900	-3.722000	0.204000
C	5.435500	-2.173100	0.135200
C	5.921700	1.548600	-0.304400
C	7.244100	2.341400	-0.454400
H	7.791600	2.034200	-1.346700
H	7.899200	2.185100	0.403700
H	7.048000	3.412300	-0.535400
C	4.229300	-3.131400	0.333500
C	4.737300	-4.585200	0.499200
H	5.409600	-4.675600	1.353300
H	5.286600	-4.917200	-0.382600
H	3.902600	-5.272400	0.654000
C	5.033200	1.800300	-1.553000
C	5.468500	2.593100	-2.625500
H	6.452400	3.034700	-2.624800
C	4.630800	2.830600	-3.718900
H	4.977600	3.437500	-4.547400
C	3.344200	2.289300	-3.713700
H	2.652300	2.470100	-4.526900
C	2.963600	1.510900	-2.627300
H	1.964300	1.108900	-2.561000
C	5.182100	2.025900	0.976400
C	5.741800	2.980300	1.838700
H	6.713400	3.404000	1.640000
C	5.049100	3.403900	2.976600
H	5.493100	4.134600	3.642800
C	3.779600	2.881100	3.226200
H	3.196300	3.196600	4.082200
C	3.270600	1.940600	2.338600
H	2.277300	1.544500	2.475400
C	3.319800	-3.046200	-0.921300
C	3.115300	-4.153200	-1.759200
H	3.564100	-5.107700	-1.534500
C	2.336800	-4.036500	-2.913400
H	2.205000	-4.890400	-3.568000
C	1.744100	-2.807300	-3.204500
H	1.135900	-2.668700	-4.089200
C	1.961100	-1.747900	-2.330700
H	1.505800	-0.786700	-2.508600
C	3.446800	-2.719800	1.607800
C	3.396100	-3.541600	2.744600
H	3.909300	-4.490100	2.766800

C	2.687500	-3.139900	3.879900
H	2.678900	-3.766600	4.764500
C	1.994500	-1.928100	3.849100
H	1.428300	-1.578800	4.704300
C	2.068200	-1.158200	2.693700
H	1.530200	-0.226200	2.614900
N	5.188200	-0.834600	-0.005000
N	3.787900	1.240500	-1.579400
N	3.953400	1.493800	1.250100
N	2.741100	-1.845900	-1.221800
N	2.804200	-1.515800	1.608100

b) Optimized structure for S=3/2 state.

V	-3.164548	-0.096734	-0.005210
V	3.177320	-0.093634	-0.002647
C	-0.086432	-0.127344	-0.025128
H	-0.084312	-1.205033	-0.031560
C	-0.821318	1.968676	0.017882
C	0.590370	1.961481	-0.033834
C	-1.517494	3.183747	0.064606
H	-2.596736	3.212784	0.122206
C	1.309519	3.160907	-0.074198
H	2.388860	3.156148	-0.134180
C	-0.804695	4.391013	0.039311
C	0.621697	4.380543	-0.039437
C	-1.551913	5.702714	0.090341
H	-1.255930	6.304145	0.958508
H	-2.632559	5.545866	0.148602
H	-1.351460	6.317454	-0.795711
C	1.391377	5.679394	-0.080664
H	1.107513	6.292568	-0.944710
H	2.468340	5.501771	-0.140040
H	1.203200	6.290431	0.810672
N	-1.268808	0.610630	0.007764
N	1.040240	0.607172	-0.043535
C	-5.421661	-2.211411	-0.126498
C	-6.720763	-2.724511	-0.084541
H	-6.909678	-3.780205	-0.191643
C	-7.799069	-1.862526	0.100542
H	-8.811302	-2.248475	0.138901
C	-7.558256	-0.497815	0.232005
H	-8.393840	0.168641	0.370659
C	-6.247337	-0.013954	0.180422
C	-4.204465	-3.149957	-0.322755
C	-4.686921	-4.612947	-0.481201
H	-3.840928	-5.285985	-0.635423
H	-5.359095	-4.718697	-1.333675
H	-5.227776	-4.950674	0.403683
C	-5.956668	1.500582	0.302925
C	-7.284985	2.282502	0.453545
H	-7.829545	1.970499	1.345954
H	-7.938753	2.121151	-0.404846
H	-7.097726	3.354822	0.535170
C	-3.292434	-3.039576	0.926832

C	-3.050272	-4.141115	1.760223
H	-3.475668	-5.106684	1.537167
C	-2.262084	-4.006499	2.905981
H	-2.098646	-4.858227	3.556312
C	-1.698361	-2.762719	3.192113
H	-1.078048	-2.610292	4.065746
C	-1.953799	-1.707029	2.325295
H	-1.516791	-0.738129	2.501654
C	-3.428283	-2.727800	-1.595892
C	-3.351705	-3.555784	-2.725668
H	-3.848918	-4.512709	-2.745354
C	-2.634523	-3.152033	-3.854839
H	-2.603953	-3.785134	-4.734363
C	-1.956477	-1.931981	-3.821555
H	-1.375592	-1.584239	-4.667155
C	-2.057672	-1.153235	-2.675103
H	-1.524900	-0.219168	-2.595159
C	-5.220044	1.977948	-0.977704
C	-5.777285	2.935951	-1.835598
H	-6.748104	3.360115	-1.634155
C	-5.083528	3.363465	-2.971951
H	-5.526294	4.097473	-3.635478
C	-3.814102	2.841255	-3.221861
H	-3.227912	3.161406	-4.074154
C	-3.305600	1.896239	-2.339292
H	-2.311528	1.505130	-2.476311
C	-5.064408	1.760669	1.545131
C	-5.499455	2.550381	2.618552
H	-6.489339	2.978533	2.624720
C	-4.653994	2.804326	3.702616
H	-5.000752	3.409045	4.532752
C	-3.358515	2.285141	3.683032
H	-2.657938	2.483994	4.484385
C	-2.977256	1.507112	2.597223
H	-1.970091	1.129834	2.519146
N	-5.191247	-0.868663	0.010713
N	-2.744180	-1.823018	1.223508
N	-2.807760	-1.511376	-1.597039
N	-3.991809	1.443196	-1.253833
N	-3.811843	1.214439	1.561279
C	6.248160	0.080167	-0.178661
C	7.572787	-0.369287	-0.233164
H	8.391475	0.316271	-0.378839
C	7.849870	-1.726245	-0.095506
H	8.871948	-2.084790	-0.135472
C	6.796747	-2.616657	0.097477
H	7.016073	-3.665962	0.209232
C	5.483698	-2.136815	0.140662
C	5.917091	1.592028	-0.307146
C	7.231235	2.399052	-0.457588
H	7.780504	2.099177	-1.351226
H	7.889532	2.247432	0.398944
H	7.024147	3.468087	-0.535782
C	4.287878	-3.111443	0.342059
C	4.818758	-4.556728	0.513618
H	5.492354	-4.632663	1.368041

H	5.374178	-4.883223	-0.366274
H	3.995113	-5.256800	0.670637
C	5.027609	1.836372	-1.558300
C	5.457524	2.636447	-2.628716
H	6.435859	3.090291	-2.624314
C	4.621893	2.864487	-3.725339
H	4.964793	3.476675	-4.551538
C	3.342976	2.304777	-3.727954
H	2.654481	2.474614	-4.546522
C	2.968705	1.520385	-2.643366
H	1.976762	1.097426	-2.584051
C	5.174274	2.065326	0.974990
C	5.732976	3.018944	1.840339
H	6.704168	3.444384	1.643662
C	5.039780	3.438781	2.978847
H	5.482816	4.168482	3.646846
C	3.771377	2.912672	3.227843
H	3.188827	3.223790	4.086188
C	3.265033	1.972867	2.337659
H	2.274253	1.569006	2.475973
C	3.378927	-3.048119	-0.915960
C	3.200335	-4.161423	-1.752695
H	3.667049	-5.106477	-1.524336
C	2.426994	-4.062504	-2.911874
H	2.317433	-4.919923	-3.566101
C	1.813261	-2.845081	-3.210299
H	1.214272	-2.719208	-4.103496
C	2.004354	-1.780332	-2.336498
H	1.538686	-0.824370	-2.520916
C	3.498536	-2.709875	1.616832
C	3.466496	-3.528403	2.757699
H	3.996109	-4.467777	2.782165
C	2.757802	-3.133586	3.895212
H	2.765044	-3.756545	4.782491
C	2.047944	-1.931409	3.864979
H	1.487474	-1.584438	4.725176
C	2.103633	-1.165733	2.705284
H	1.559374	-0.236398	2.627396
N	5.219506	-0.802932	-0.001410
N	3.789118	1.262352	-1.590547
N	3.946500	1.530730	1.247182
N	2.777805	-1.860467	-1.222433
N	2.835717	-1.516862	1.615887

c) Optimized structure for S=1/2

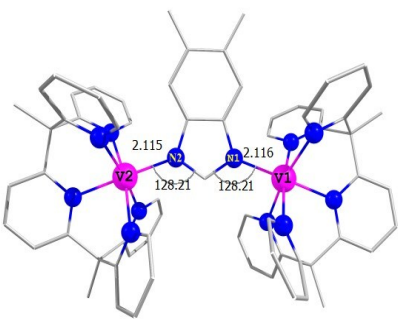
V	-3.183567	-0.097162	-0.006222
V	3.209262	-0.095953	-0.003638
C	-0.109602	-0.118472	-0.033224
H	-0.107813	-1.196231	-0.045136
C	-0.850981	1.977440	0.021248
C	0.560949	1.968809	-0.030442
C	-1.544594	3.194423	0.071532
H	-2.623992	3.226719	0.128156
C	1.283440	3.165481	-0.066507

H	2.362946	3.156072	-0.126959
C	-0.828275	4.400058	0.050586
C	0.598265	4.386948	-0.027496
C	-1.572361	5.713382	0.105381
H	-1.275343	6.311202	0.975676
H	-2.653478	5.559209	0.162399
H	-1.369648	6.330505	-0.778487
C	1.370794	5.684021	-0.064064
H	1.088731	6.300640	-0.926283
H	2.447288	5.504005	-0.123453
H	1.183504	6.292578	0.829185
N	-1.298275	0.621007	0.004727
N	1.010514	0.615474	-0.047809
C	-5.434552	-2.225237	-0.122593
C	-6.731502	-2.743951	-0.081126
H	-6.915672	-3.800873	-0.184203
C	-7.814104	-1.886027	0.097924
H	-8.824635	-2.276547	0.135507
C	-7.580171	-0.519605	0.224375
H	-8.419270	0.143393	0.358246
C	-6.271389	-0.029848	0.174305
C	-4.213168	-3.159960	-0.314462
C	-4.689838	-4.625413	-0.467711
H	-3.841016	-5.295665	-0.618267
H	-5.360518	-4.737239	-1.320584
H	-5.230238	-4.961815	0.417969
C	-5.988846	1.487011	0.293517
C	-7.321315	2.262721	0.439204
H	-7.866517	1.950287	1.331061
H	-7.972299	2.096332	-0.420347
H	-7.139214	3.336100	0.518689
C	-3.300347	-3.042373	0.933860
C	-3.053107	-4.139704	1.771313
H	-3.477847	-5.107021	1.554645
C	-2.259235	-3.998493	2.912394
H	-2.090557	-4.847206	3.565340
C	-1.695421	-2.752755	3.190232
H	-1.069149	-2.596202	4.058869
C	-1.957636	-1.701042	2.320704
H	-1.520457	-0.730815	2.490068
C	-3.437558	-2.739418	-1.588761
C	-3.354186	-3.572575	-2.714198
H	-3.844851	-4.532943	-2.729552
C	-2.638026	-3.169789	-3.844424
H	-2.601046	-3.807771	-4.720178
C	-1.969574	-1.944270	-3.817576
H	-1.390185	-1.596930	-4.664308
C	-2.077549	-1.160139	-2.675434
H	-1.552657	-0.221168	-2.601157
C	-5.250888	1.966510	-0.985353
C	-5.810388	2.918347	-1.848440
H	-6.785755	3.335312	-1.653915
C	-5.112359	3.349236	-2.981067
H	-5.556576	4.078643	-3.648717
C	-3.836966	2.837233	-3.221987
H	-3.247713	3.161407	-4.070626

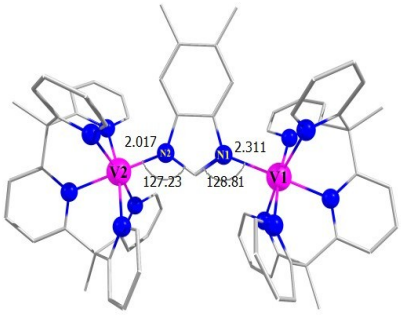
C	-3.326661	1.897298	-2.334942
H	-2.328258	1.514002	-2.463859
C	-5.100659	1.754191	1.537090
C	-5.541670	2.542835	2.608704
H	-6.533470	2.966605	2.612324
C	-4.699484	2.801215	3.694457
H	-5.050639	3.405338	4.523202
C	-3.401970	2.287034	3.678934
H	-2.704403	2.488871	4.482145
C	-3.014529	1.509953	2.594485
H	-2.005780	1.136198	2.519849
N	-5.211403	-0.880826	0.010126
N	-2.753247	-1.824123	1.223442
N	-2.823974	-1.519773	-1.595405
N	-4.017437	1.441094	-1.253861
N	-3.845625	1.214600	1.556740
C	6.274139	0.094892	-0.184358
C	7.600928	-0.348364	-0.240480
H	8.416285	0.340504	-0.389337
C	7.884590	-1.703750	-0.100187
H	8.908311	-2.057426	-0.141202
C	6.836298	-2.598994	0.096733
H	7.061121	-3.646952	0.210401
C	5.520895	-2.125263	0.141179
C	5.934632	1.605382	-0.315037
C	7.244947	2.417972	-0.469358
H	7.793610	2.119135	-1.363733
H	7.905704	2.270382	0.385987
H	7.033130	3.486013	-0.548594
C	4.328993	-3.104828	0.345890
C	4.867405	-4.547064	0.520020
H	5.542188	-4.617512	1.374003
H	5.423710	-4.872461	-0.359747
H	4.047653	-5.251189	0.679322
C	5.041561	1.845056	-1.564958
C	5.465722	2.646666	-2.636710
H	6.442293	3.104349	-2.634924
C	4.626643	2.870954	-3.731432
H	4.965188	3.484201	-4.558632
C	3.350163	2.305519	-3.731288
H	2.659585	2.471589	-4.548916
C	2.982001	1.519360	-2.645811
H	1.992843	1.089511	-2.585230
C	5.192158	2.078414	0.967835
C	5.749287	3.035286	1.830892
H	6.718804	3.463550	1.631996
C	5.056841	3.454412	2.970039
H	5.498661	4.186557	3.636157
C	3.790989	2.923728	3.222692
H	3.209634	3.233223	4.082471
C	3.286493	1.980560	2.334934
H	2.298482	1.570844	2.477609
C	3.417282	-3.049688	-0.910988
C	3.241508	-4.166668	-1.743656
H	3.714484	-5.108379	-1.514258
C	2.462866	-4.075865	-2.899907

H	2.355412	-4.936014	-3.550889
C	1.841516	-2.862568	-3.200019
H	1.238909	-2.742746	-4.091747
C	2.031373	-1.793673	-2.330996
H	1.562269	-0.839647	-2.518040
C	3.537268	-2.705782	1.620519
C	3.508439	-3.523501	2.762228
H	4.044189	-4.459373	2.788652
C	2.795073	-3.132329	3.898070
H	2.804646	-3.754527	4.785854
C	2.078056	-1.934322	3.865797
H	1.514679	-1.589879	4.725187
C	2.132022	-1.168813	2.705863
H	1.584392	-0.241250	2.626899
N	5.250770	-0.793153	-0.003180
N	3.805438	1.265678	-1.594463
N	3.966655	1.540024	1.243099
N	2.809197	-1.865917	-1.219419
N	2.867613	-1.516466	1.617793

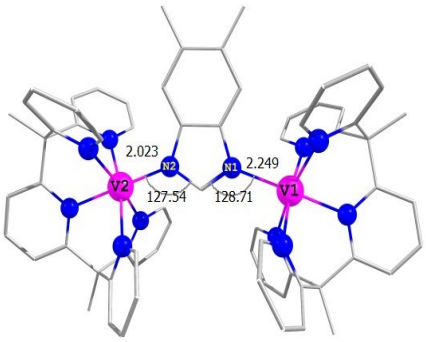
Figure S1. Optimized structures of different spin states.



S=5/2

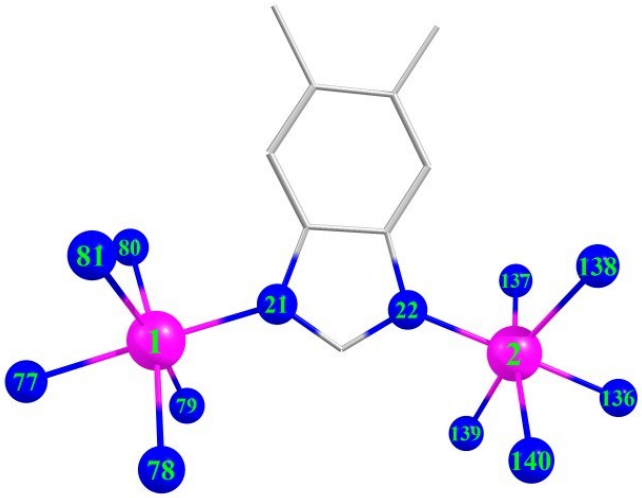


S=3/2



S=1/2

Table S6. Spin densities on all the atoms for optimized structure of different spin states.



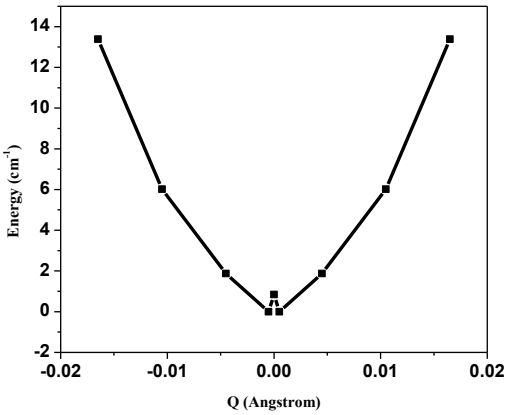
for S=5/2 state	for S=3/2 state	for S=1/2 state
1 V 2.548601	1 V 0.098690	1 V -2.117863
2 V 2.550294	2 V 2.814676	2 V 2.873044
3 C 0.133912	3 C 0.076070	3 C 0.035922
4 H -0.003016	4 H -0.002985	4 H -0.001977
5 C 0.016930	5 C -0.001642	5 C -0.023454
6 C 0.016898	6 C 0.014000	6 C 0.010094
7 C -0.017507	7 C -0.010693	7 C 0.012965
8 H 0.001007	8 H -0.000880	8 H -0.000660
9 C -0.017483	9 C -0.004459	9 C 0.010506
10 H 0.001011	10 H 0.001234	10 H 0.001454
11 C -0.006108	11 C -0.003944	11 C -0.004926
12 C -0.006143	12 C -0.002111	12 C 0.005739
13 C 0.000869	13 C 0.000611	13 C 0.000750
14 H -0.000609	14 H -0.000354	14 H -0.000251
15 H -0.000003	15 H 0.000000	15 H -0.000004
16 H -0.000597	16 H -0.000343	16 H -0.000241
17 C 0.000873	17 C 0.000042	17 C -0.001211
18 H -0.000611	18 H -0.000123	18 H 0.000686
19 H -0.000003	19 H -0.000013	19 H -0.000028
20 H -0.000599	20 H -0.000116	20 H 0.000672
21 N -0.109592	21 N -0.022637	21 N 0.067180
22 N -0.109547	22 N -0.073899	22 N -0.032821
23 C 0.022031	23 C 0.005272	23 C -0.006502
24 C -0.011200	24 C -0.002615	24 C 0.002037
25 H 0.000713	25 H -0.000224	25 H -0.000281
26 C 0.017497	26 C 0.004607	26 C -0.000749
27 H -0.000894	27 H -0.000193	27 H 0.000006
28 C -0.011169	28 C -0.002765	28 C 0.001990
29 H 0.000687	29 H -0.000245	29 H -0.000240
30 C 0.022584	30 C 0.004451	30 C -0.006773
31 C 0.004509	31 C -0.007641	31 C -0.003225

32 C 0.000524	32 C -0.000040	32 C -0.000358
33 H -0.000078	33 H -0.000029	33 H 0.000045
34 H -0.000082	34 H -0.000012	34 H 0.000056
35 H -0.000084	35 H -0.000013	35 H 0.000059
36 C 0.003046	36 C -0.004746	36 C -0.002568
37 C 0.000531	37 C 0.000016	37 C -0.000328
38 H -0.000084	38 H -0.000013	38 H 0.000059
39 H -0.000088	39 H -0.000018	39 H 0.000056
40 H -0.000078	40 H -0.000033	40 H 0.000050
41 C 0.023287	41 C 0.007960	41 C -0.015587
42 C -0.013609	42 C -0.004357	42 C 0.008816
43 H 0.000656	43 H 0.000331	43 H -0.000421
44 C 0.024263	44 C 0.009062	44 C -0.016206
45 H -0.001236	45 H -0.000443	45 H 0.000801
46 C -0.014803	46 C -0.005322	46 C 0.010226
47 H 0.000587	47 H 0.000037	47 H -0.000519
48 C 0.029028	48 C 0.011026	48 C -0.019347
49 H -0.000227	49 H 0.000109	49 H -0.000081
50 C 0.023741	50 C 0.010475	50 C -0.015621
51 C -0.013579	51 C -0.004539	51 C 0.009026
52 H 0.000665	52 H 0.000298	52 H -0.000423
53 C 0.024525	53 C 0.010227	53 C -0.016677
54 H -0.001225	54 H -0.000501	54 H 0.000824
55 C -0.014931	55 C -0.005770	55 C 0.010462
56 H 0.000634	56 H 0.000156	56 H -0.000435
57 C 0.030420	57 C 0.012490	57 C -0.019649
58 H -0.001053	58 H -0.000226	58 H 0.000241
59 C 0.022995	59 C 0.007379	59 C -0.015646
60 C -0.012832	60 C -0.003987	60 C 0.008363
61 H 0.000627	61 H 0.000323	61 H -0.000385
62 C 0.022927	62 C 0.008358	62 C -0.016228
63 H -0.001141	63 H -0.000388	63 H 0.000796
64 C -0.014108	64 C -0.005139	64 C 0.010582
65 H 0.000603	65 H 0.000143	65 H -0.000455
66 C 0.029257	66 C 0.011474	66 C -0.018738
67 H -0.000543	67 H -0.000116	67 H 0.000673
68 C 0.023754	68 C 0.009512	68 C -0.016459
69 C -0.013440	69 C -0.004927	69 C 0.009258
70 H 0.000665	70 H 0.000306	70 H -0.000410
71 C 0.024239	71 C 0.010509	71 C -0.018523
72 H -0.001193	72 H -0.000499	72 H 0.000898
73 C -0.015040	73 C -0.006133	73 C 0.011894
74 H 0.000600	74 H 0.000191	74 H -0.000459
75 C 0.031668	75 C 0.013953	75 C -0.020476
76 H -0.001199	76 H -0.000307	76 H 0.000577
77 N -0.048077	77 N -0.002378	77 N 0.035996
78 N -0.046662	78 N -0.006803	78 N 0.042627
79 N -0.047530	79 N -0.008326	79 N 0.042898
80 N -0.049368	80 N -0.008037	80 N 0.042724
81 N -0.051148	81 N -0.009524	81 N 0.044568

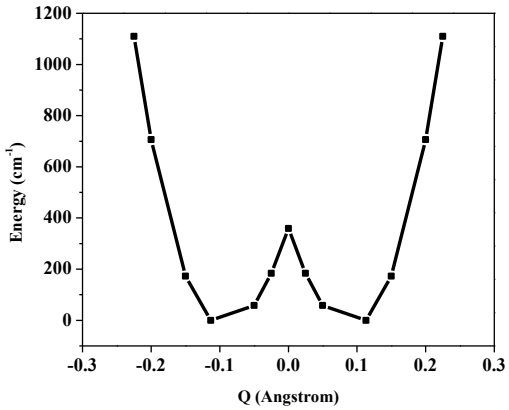
82 C 0.022643	82 C 0.033414	82 C 0.036053
83 C -0.011207	83 C -0.018044	83 C -0.019978
84 H 0.000689	84 H 0.001079	84 H 0.001198
85 C 0.017566	85 C 0.030265	85 C 0.033818
86 H -0.000898	86 H -0.001569	86 H -0.001761
87 C -0.011238	87 C -0.017919	87 C -0.019788
88 H 0.000714	88 H 0.001097	88 H 0.001220
89 C 0.022086	89 C 0.032712	89 C 0.035415
90 C 0.003062	90 C 0.005624	90 C 0.006888
91 C 0.000532	91 C 0.000714	91 C 0.000764
92 H -0.000084	92 H -0.000104	92 H -0.000109
93 H -0.000088	93 H -0.000112	93 H -0.000119
94 H -0.000079	94 H -0.000101	94 H -0.000107
95 C 0.004527	95 C 0.007394	95 C 0.008597
96 C 0.000525	96 C 0.000720	96 C 0.000785
97 H -0.000082	97 H -0.000110	97 H -0.000120
98 H -0.000084	98 H -0.000113	98 H -0.000122
99 H -0.000078	99 H -0.000101	99 H -0.000108
100 C 0.023784	100 C 0.030811	100 C 0.032970
101 C -0.013460	101 C -0.017869	101 C -0.019339
102 H 0.000666	102 H 0.000914	102 H 0.000995
103 C 0.024268	103 C 0.031270	103 C 0.033779
104 H -0.001195	104 H -0.001580	104 H -0.001719
105 C -0.015054	105 C -0.018174	105 C -0.019241
106 H 0.000600	106 H 0.000840	106 H 0.000926
107 C 0.031707	107 C 0.038655	107 C 0.040441
108 H -0.001200	108 H -0.001255	108 H -0.001167
109 C 0.023020	109 C 0.029299	109 C 0.031089
110 C -0.012850	110 C -0.016980	110 C -0.018265
111 H 0.000628	111 H 0.000852	111 H 0.000922
112 C 0.022952	112 C 0.029719	112 C 0.031939
113 H -0.001143	113 H -0.001505	113 H -0.001626
114 C -0.014121	114 C -0.017256	114 C -0.018294
115 H 0.000604	115 H 0.000816	115 H 0.000889
116 C 0.029289	116 C 0.036511	116 C 0.038402
117 H -0.000542	117 H -0.000792	117 H -0.000902
118 C 0.023320	118 C 0.031850	118 C 0.034681
119 C -0.013633	119 C -0.019250	119 C -0.021161
120 H 0.000658	120 H 0.000960	120 H 0.001066
121 C 0.024298	121 C 0.033794	121 C 0.037204
122 H -0.001238	122 H -0.001757	122 H -0.001944
123 C -0.014820	123 C -0.019113	123 C -0.020428
124 H 0.000589	124 H 0.000893	124 H 0.000986
125 C 0.029069	125 C 0.038767	125 C 0.041840
126 H -0.000230	126 H -0.000736	126 H -0.000939
127 C 0.023772	127 C 0.032513	127 C 0.035392
128 C -0.013599	128 C -0.019199	128 C -0.021124
129 H 0.000666	129 H 0.000985	129 H 0.001101
130 C 0.024556	130 C 0.034059	130 C 0.037464
131 H -0.001227	131 H -0.001747	131 H -0.001938

132 C -0.014945	132 C -0.019051	132 C -0.020332
133 H 0.000635	133 H 0.000888	133 H 0.000970
134 C 0.030460	134 C 0.040237	134 C 0.043165
135 H -0.001057	135 H -0.001509	135 H -0.001583
136 N -0.048111	136 N -0.053041	136 N -0.053711
137 N -0.051163	137 N -0.052919	137 N -0.053117
138 N -0.049380	138 N -0.051107	138 N -0.051231
139 N -0.046674	139 N -0.048533	139 N -0.048990
140 N -0.047540	140 N -0.049590	140 N -0.050113

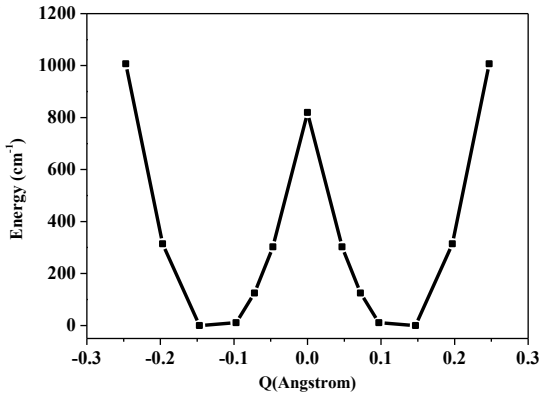
Figure S2. Potential Energy surface for all the spin states



S=5/2



S=3/2



S=1/2

TD-DFT calculation:-

Table S7. TD-DFT computed energies of excited states

a) TDDFT computed energies of excited state with maximum percentage contribution of HOMO -> LUMO transition and the percentage contribution of HOMO -> LUMO transition.

Spin state	Structure	Energy of the excited state with maximum contribution from HOMO ⟶ LUMO transition (ev).	Percentage contribution from HOMO ⟶ LUMO transition.	$<S^2>$
S=5/2	Crystal structure	.6584	76%	8.768
S=5/2	Optimized structure	.6809	72.7%	8.766
	For Q=0 point	.6808	72.8%	8.766
S=3/2	Optimized structure	.6221	98.8%	4.816
	For Q=0 point	.5759	88.83%	4.783
S=1/2	Optimized structure	.9815	97.2%	2.886
	For Q=0 point	.6362	93.8%	2.952

b) TD-DFT computed energies of excited state with maximum contribution of HOMO -> LUMO transition and the percentage contribution of HOMO -> LUMO for magneto structural correlation.

i) TDDFT results for double exchange vs. V-N bond length

V-N Bond length (Å)	Energy of the excited state with maximum contribution from HOMO⟶ LUMO transition (ev).	Percentage contribution from HOMO⟶ LUMO transition
2.61	0.3900	75.2%
2.41	0.4570	77.4%
2.31	0.5054	66.3%
2.21	0.5654	55.7%
2.01	0.7922	84.5%
1.91	0.9420	92.7%
1.81	1.1449	95.4%
1.71	1.4203	97.5%
1.61	1.7852	96.9%

ii) TDDFT results for double exchange vs V-N-C bond angle

V-N-C bond angle (°)	Energy of the excited state with maximum contribution from HOMO ⟶ LUMO transition (ev).	Percentage contribution from HOMO⟶ LUMO transition
133	.6959	77.8%
132	.6930	77.2%
131	.6900	76.9%
130	.6870	76.0%
129	.6839	74.5%
127	.6775	70.9%
126	.6741	68.9%
124	.6674	62.9%
123	.6640	59.4%

Formula for calculating energy barrier:-

To calculate activation energy for different S=3/2 and S=1/2 we have used the formula,

$$E_\theta = \frac{\lambda}{2} + \frac{\beta_{eff}^{\ 2}}{2\lambda} - \beta_{eff}$$

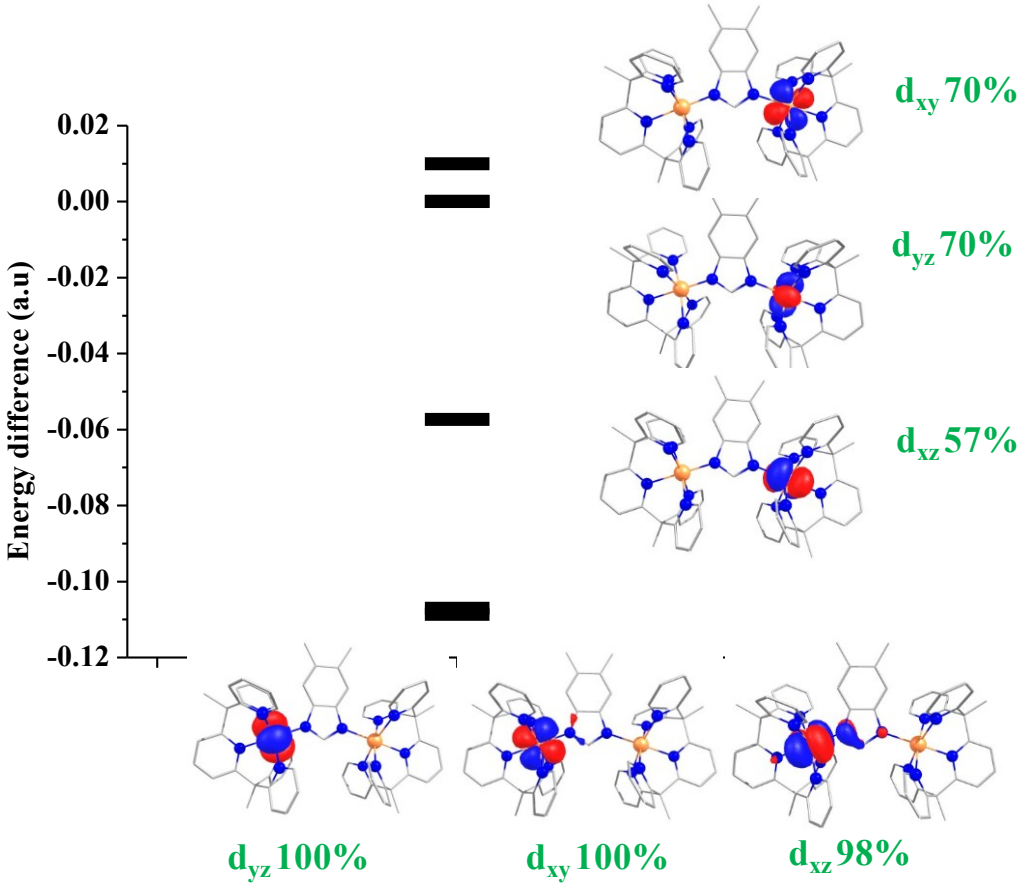
Where E_θ is the activation energy for a particular spin state.

CASSCF calculation:-

To check the exact electronic configuration for S=3/2 state, we have performed the state average CASSCF calculations for S=3/2 state. The calculations have been performed using ORCA code, where we have taken five active electrons in the six active orbitals (t_{2g} set of both V) with (CAS(5,6)). We have chosen nine roots which includes all the possibility for this spin state. The electronic configuration generated from the CASSCF calculations are in the context with the DFT predicted ground state and this provides us more confidence and reliability on DFT computed various parameters. The CASSCF computed ground state for S=3/2 is similar to DFT predicted S=3/2 and the first excited state for S=3/2 found to be ~ 3000 cm^{-1} far from the ground state configuration of S=3/2. The CASSCF computed spin densities on metal ions are found to be 0.48 and 2.47 which are in reasonable agreement with with the 0.1 and 2.81 predicted from the DFT. This reflects that single determinant DFT computed S=3/2 spin states are reliable for estimation of these excited states.

Lowlying States for S=3/2 With electronic configuration and occupancy	Energies (hartrees)	Energy difference (cm^{-1})
$(d_{yz})^1(d_{xy})^1(d_{xz})^1(d_{xy})^1(d_{yz})^1(d_{xz})^0$ 99%,	-5107.6509307282	0
$(d_{yz})^1(d_{xy})^1(d_{xz})^1(d_{xy})^0(d_{yz})^1(d_{xz})^1$ 98%,	-5107.6373331169	2984.3
$(d_{yz})^1(d_{xy})^1(d_{xz})^1(d_{xy})^1(d_{yz})^0(d_{xz})^1$ 98%,	-5107.6331356284	3905.6
$(d_{yz})^1(d_{xy})^1(d_{xz})^1(d_{xy})^1(d_{yz})^1(d_{xz})^0$ 99%,	-5107.5886591923	13667.0
$(d_{yz})^1(d_{xy})^1(d_{xz})^1(d_{xy})^2(d_{yz})^0(d_{xz})^0$ 52%,	-5107.5884424134	13714.6
$(d_{yz})^1(d_{xy})^1(d_{xz})^1(d_{xy})^0(d_{yz})^1(d_{xz})^1$ 83%,	-5107.5788818149	15812.9
$(d_{yz})^1(d_{xy})^1(d_{xz})^1(d_{xy})^1(d_{yz})^0(d_{xz})^1$ 83%,	-5107.5782768017	15945.7
$(d_{yz})^1(d_{xy})^1(d_{xz})^1(d_{xy})^0(d_{yz})^0(d_{xz})^2$ 60%,	-5107.5756825902	16515.1
$(d_{yz})^2(d_{xy})^1(d_{xz})^0(d_{xy})^1(d_{yz})^1(d_{xz})^0$ 55%,	-5107.5731935209	17061.3

FigS3. The CASSCF computed molecular orbitals for S=3/2 ground state. The red color shows the positive spin density while, the blue color represents the negative spin density.



FigS3. CASSCF computed molecular orbitals for S=3/2 states. The energy spectrum is given above along with the corresponding occupancies of the orbitals.

Fitting for Figure 5

a) Double exchange bond length

y=A1*exp(-x/t1)+y0

Where y0=209.41229, A1=265232.16638 and t1=0.3371

b) Double exchange bond angle

y=A1*exp(-x/t1)+y0

Where y0=780.67739, A1=-85.6776 and t1=6.27233

References:

1. L. Noodleman, *J. Chem. Phys.*, 1981, **74**, 5737.
2. E. Ruiz, S. Alvarez, A. Rodriguez-Fortea, P. Alemany, Y. Pouillon and C. Massobrio, in *"Magnetism:Molecules toMaterials"*, Vol. II ed J. S. Miller and M. Drillon, Wiley-VCH, Weinheim, 2001, pp 227.
3. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
4. (a) A. Schafer, H. Horn and R. Ahlrichs, *J. Chem. Phys*., 1992, **97**, 2571; (b) A. Schafer, C. Huber and R. Ahlrichs, *J.Chem. Phys.,* 1994, **100**, 5829.
5. a) P. J. Hay, W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 270. b) P. J. Hay, W. R. Wadt, *J. Chem. Phys*., 1985, **82**, 284. c) P. J. Hay, W. R. Wadt, *J. Chem. Phys*., 1985, **82**, 299.
6. J.D. Dill, J. A. Pople, *J. Chem. Phys.,* 1975, 62, 2921.
7. Gaussian 09, Revision **A.02**, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B.Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
8. R. A. Vogt, T. G. Gray, C. E. Crespo-Hernandez, *J. Am. Chem. Soc,* 2012, **134**, 14808.