Supporting Information

Basis Sets. The Karlsruhe split-valence basis set (SV)[31,33] for Cr was first augmented with two p functions that were obtained by minimizing the MCSCF energy of the ^{7}F state with $4s^1\ 3d^4\ 4p^1$ configurations. In a second step, this basis set was augmented by a d function via minimization of the ^{6}S ground state energy. It is denoted as sv(p). The svp basis set was obtained by adding a f function to sv(p). The ground state energy was minimized via a configuration interaction singles-doubles (CISD) calculation (the 1-3s and 2p, 3p core MOs were kept frozen), whereby the 4s and 3d MOs were correlated with all of the empty MOs. The MCSCF and CISD calculations were performed with the occupation-restricted multiple active space (ORMAS) method.[35] Likewise, the tzvp basis set of Cr was constructed by supplementing the Karlsruhe triple-zeta valence basis set (TZV)[32,33] with two p, then one d, and finally with one f function as described for sv(p)/svp.

The p polarization function of H for svp and tzvp was optimized for the ground state CISD energy of the H_2 molecule at its experimental geometry (d(H–H) = 0.74611 Å). The d polarization function of O for sv(p)/svp and tzvp was obtained via the minimization of the multi-reference CISD (MR-CISD) energy of the ^{3}P ground state. For Cl, the d polarization function for sv(p)/svp was obtained likewise. The first d polarization function of tzvp for Cl was calculated analogously. Then, the core d polarization function of tzvp was added via optimization with MR-CISD, whereby, in addition to the 3s and 3p MOs, also the 2p MOs were correlated with all of the empty MOs. The MCSCF and MR-CISD calculations were performed using the ORMAS technique.[35]

Basis sets in GAMESS format

svp (in sv(p), p of H and f of Cr are omitted):

```
H   1.
S   3
1   .13010701000E+02   0.33485484813E-01
2   .19622572000E+01   0.23472187088E+00
3   .44453796000E+00   0.81377028526E+00
S   1
1   .12194962000E+00   0.10000000000E+01
P   1
1   0.737              1.


O   8.
S   5
1   .22661767785E+04   -.53893503922E-02
2   .34087010191E+03   -.40234721389E-01
3   .77363135167E+02   -.18008184206E+00
4   .21479644940E+02   -.46828857658E+00
5   .66589433124E+01   -.44692617160E+00
S   1
1   .80975975668E+00   0.10000000000E+01
S   1
1   .25530772234E+00   0.10000000000E+01
P   3
1   .17721504317E+02   0.62630248763E-01
2   .38635505440E+01   0.33331138482E+00
3   .10480920883E+01   0.74148638308E+00
P   1
1   .27641544411E+00   0.10000000000E+01
D   1
1   1.182              1.
```

```
Cl  17.
 S   5
 1   .10449827566E+05   0.54265953789E-02
 2   .15717365221E+04   0.40626378129E-01
 3   .35712065523E+03   0.18359747853E+00
 4   .10025185935E+03   0.47438948768E+00
 5   .30812727554E+02   0.43735181104E+00
 S   3
 1   .51923789434E+02   -.92754154848E-01
 2   .57045760975E+01   0.56380825544E+00
 3   .23508376809E+01   0.50367044630E+00
 S   1
 1   .44605124672E+00   0.10000000000E+01
 S   1
 1   .16848856190E+00   0.10000000000E+01
 P   5
 1   .30766790569E+03   -.88797025589E-02
 2   .72102015515E+02   -.64284071721E-01
 3   .22532680262E+02   -.24288739736E+00
 4   .78991765444E+01   -.48340836370E+00
 5   .28767268321E+01   -.38952563876E+00
 P   1
 1   .77459363955E+00   0.10000000000E+01
 P   1
 1   .21037699698E+00   0.10000000000E+01
 D   1
 1   0.605              1.
```

```
Cr  24.
 S   6
 1   .51528086349E+05   0.17695545769E-02
 2   .77372103487E+04   0.13556436258E-01
 3   .17603748470E+04   0.67162645785E-01
 4   .49687706544E+03   0.23295905919E+00
 5   .16146520598E+03   0.47040576983E+00
 6   .55466352268E+02   0.35733072607E+00
 S   3
 1   .10754732999E+03   -.10605255447E+00
 2   .12408671897E+02   0.62543981484E+00
 3   .50423628826E+01   0.44878820794E+00
 S   3
 1   .85461640165E+01   -.21819012081E+00
 2   .13900441221E+01   0.70422525668E+00
 3   .56066602876E+00   0.42488555413E+00
 S   1
 1   .71483705972E-01   0.10000000000E+01
 S   1
 1   .28250687604E-01   0.10000000000E+01
 P   5
 1   .64048536096E+03   0.93555063747E-02
 2   .15069711194E+03   0.68993338492E-01
 3   .47503755296E+02   0.26341189593E+00
 4   .16934120165E+02   0.51034501652E+00
 5   .62409680590E+01   0.33195512954E+00
 P   3
 1   .30885463206E+01   0.32917682677E+00
 2   .11791047769E+01   0.55491385190E+00
 3   .43369774432E+00   0.23818412856E+00
 P   1
 1   0.224              1.
 P   1
 1   0.0597             1.
 D   4
 1   .27559479426E+02   0.36950140314E-01
 2   .74687020327E+01   0.18821519783E+00
 3   .24345903574E+01   0.44641244240E+00
 4   .78244754808E+00   0.56816173032E+00
 D   1
 1   .21995774311E+00   0.10000000000E+01
 D   1
 1   0.0552             1.
 F   1
 1   1.098              1.
```

tzvp:

```
H   1.
S   3
1   .34061341000E+02   0.25439307209E-01
2   .51235746000E+01   0.19008594890E+00
3   .11646626000E+01   0.85244113011E+00
S   1
1   .32723041000E+00   0.10000000000E+01
S   1
1   .10307241000E+00   0.10000000000E+01
P   1
1   0.724              1.


O   8.
S   6
1   .27032382631E+05   0.57227335211E-03
2   .40523871392E+04   0.44353233493E-02
3   .92232722710E+03   0.23020107706E-01
4   .26124070989E+03   0.92822490668E-01
5   .85354641351E+02   0.29378500010E+00
6   .31035035245E+02   0.67401604502E+00
S   2
1   .12260860728E+02   0.63839937026E+00
2   .49987076005E+01   0.39534587126E+00
S   1
1   .11703108158E+01   0.10000000000E+01
S   1
1   .46474740994E+00   0.10000000000E+01
S   1
1   .18504536357E+00   0.10000000000E+01
P   4
1   .63274954801E+02   0.12018332223E-01
2   .14627049379E+02   0.83005421790E-01
3   .44501223456E+01   0.31991743926E+00
4   .15275799647E+01   0.70715542916E+00
P   1
1   .52935117943E+00   0.10000000000E+01
P   1
1   .17478421270E+00   0.10000000000E+01
D   1
1   1.164              1.
```

```
Cl  17.
 S   7
 1   .69507990945E+05   0.51457389646E-03
 2   .10426156880E+05   0.39781344807E-02
 3   .23732334061E+04   0.20456178671E-01
 4   .67156420071E+03   0.80148102888E-01
 5   .21841999790E+03   0.23454770318E+00
 6   .77572249714E+02   0.44543368582E+00
 7   .28888815277E+02   0.35466842499E+00
 S   3
 1   .12710527185E+03   0.11293688055E+00
 2   .39339582961E+02   0.48373514210E+00
 3   .76740679989E+01   -.12292297390E+01
 S   2
 1   .38745627630E+01   0.67296821636E+00
 2   .18385832573E+01   0.34956051409E+00
 S   1
 1   .50229057542E+00   0.10000000000E+01
 S   1
 1   .17962723420E+00   0.10000000000E+01
 P   6
 1   .66650423284E+03   0.24420743816E-02
 2   .15764241690E+03   0.19508869633E-01
 3   .50262520978E+02   0.90114416816E-01
 4   .18536078105E+02   0.26128813953E+00
 5   .72940532777E+01   0.44957990746E+00
 6   .29433248995E+01   0.36194544581E+00
 P   1
 1   .10404970818E+01   0.10000000000E+01
 P   1
 1   .38456415080E+00   0.10000000000E+01
 P   1
 1   .13069642732E+00   0.10000000000E+01
 D   1
 1   9.721              1.
 D   1
 1   0.598              1.
```

```
Cr  24.
 S   8
 1   .25447780704E+06   0.24290477637E-03
 2   .38131797054E+05   0.18843523609E-02
 3   .86752930607E+04   0.98009584389E-02
 4   .24550099848E+04   0.39825008653E-01
 5   .79916217787E+03   0.12940543735E+00
 6   .28690021489E+03   0.30629001808E+00
 7   .11125413232E+03   0.43462834976E+00
 8   .43864152636E+02   0.22469562869E+00
 S   4
 1   .27932669173E+03   -.24363357906E-01
 2   .86274732376E+02   -.11511495394E+00
 3   .13555756113E+02   0.55092266281E+00
 4   .56978112751E+01   0.53611354691E+00
 S   2
 1   .85636582615E+01   -.37123017689E+00
 2   .13988296768E+01   0.11681169458E+01
 S   1
 1   .57288171116E+00   0.10000000000E+01
 S   1
 1   .90096171317E-01   0.10000000000E+01
 S   1
 1   .34125885135E-01   0.10000000000E+01
 P   6
 1   .13064398864E+04   0.28292800655E-02
 2   .30925311441E+03   0.22776629200E-01
 3   .98996273963E+02   0.10564561899E+00
 4   .36756916451E+02   0.29949944921E+00
 5   .14566657077E+02   0.47706245357E+00
 6   .58739937432E+01   0.27654234377E+00
 P   3
 1   .22890999695E+02   -.19412106077E-01
 2   .30855001822E+01   0.38618875825E+00
 3   .12132329118E+01   0.67623908895E+00
 P   1
 1   .44931680699E+00   0.10000000000E+01
 P   1
 1   0.130              1.
 P   1
 1   0.0420             1.
 D   4
 1   .43720074476E+02   0.22093259256E-01
 2   .12391242652E+02   0.12801438775E+00
 3   .42639442006E+01   0.38652910276E+00
 4   .15525221790E+01   0.64103301437E+00
 D   1
 1   .53761929485E+00   0.10000000000E+01
 D   1
 1   .16493173074E+00   0.10000000000E+01
 D   1
 1   0.0418             1.
 F   1
 1   1.131              1.
```

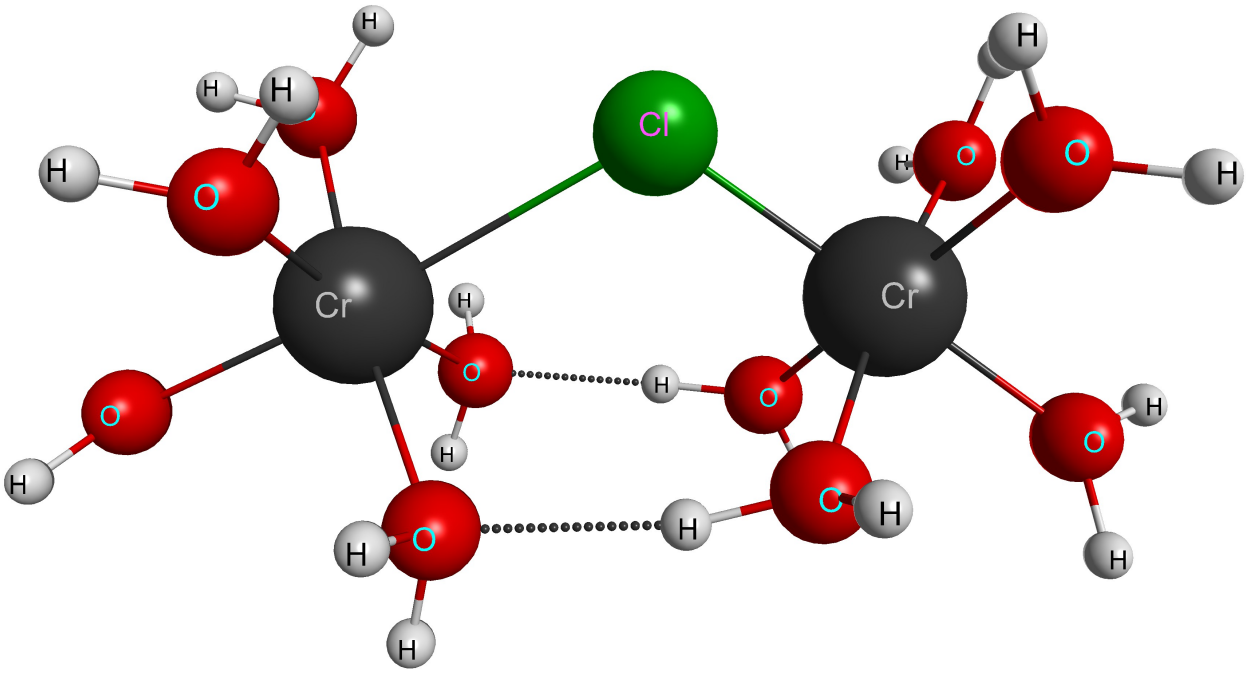

Figure S1. Structure of the bent P/S with asymmetric hydrogen bonds, whereby two water molecules coordinated to Cr^{III} are H-bond donors, and two waters coordinated to Cr^{II} are H-bond acceptors (LC-BOP(μ=0.33)-CPCM/tzvp calculation).

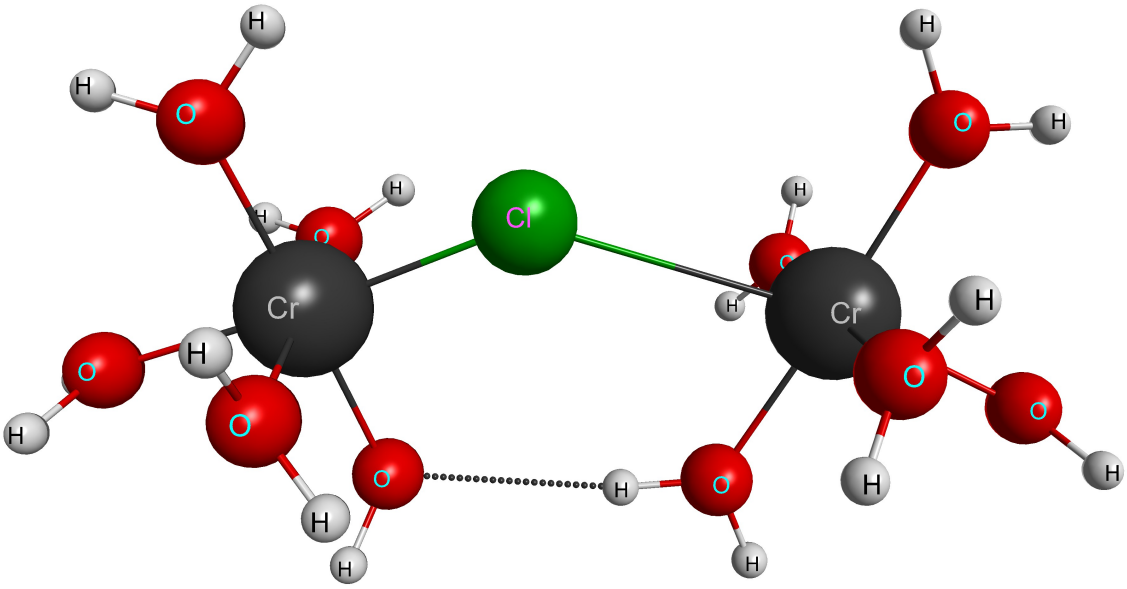

Figure S2. Structure of the bent P/S with a single hydrogen bond, whereby the water molecule coordinated to Cr^{III} is the H-bond donor (LC-BOP(μ=0.33)-CPCM/tzvp calculation).

Table S1. Atomic Coordinates (Å) of the Transition State $(H_2O)_5CrClCr(OH_2)_5^{4+\ddagger}$ (TS)

(a) Bent Isomer, LC-BOP(μ=0.33)-CPCM/tzvp Geometry

ATOM	CHARGE	X	Y	Z
CR	24.0	-0.0029399871	-0.1637276437	-2.1350701687
CR	24.0	-0.0473078979	-0.0757911002	2.2323251342
CL	17.0	-0.0561456779	-1.1018678302	0.0693028963
O	8.0	-1.4880028793	-1.2880842510	2.8973286120
O	8.0	1.3348809206	-1.5099249534	-2.7594349640
O	8.0	-1.3270309280	1.1698550219	-1.4494336039
O	8.0	1.3781417098	1.1252167450	1.5034519992
H	1.0	-1.8836664037	-2.0339903649	2.4107256787
H	1.0	1.6537398956	-2.2804477982	-2.2552318722
H	1.0	-1.5595060612	1.2377707473	-0.4982800418
H	1.0	1.6244210779	1.1431080073	0.5537741918
H	1.0	-1.8128730894	-1.2983595883	3.8163614413
H	1.0	1.6639921714	-1.5687690189	-3.6751485331
H	1.0	-1.7258514959	1.9056263171	-1.9477621658
H	1.0	1.8433187617	1.8317481073	1.9864357148
O	8.0	1.3611131748	-1.2875588662	2.9770887908
O	8.0	-1.5081097243	-1.2947727688	-2.8159183028
O	8.0	1.5811608604	1.0268531645	-1.4804850897
O	8.0	-1.5065804600	1.2317244088	1.5187245586
H	1.0	2.2834601951	-1.2575234144	2.6626296701
H	1.0	-2.4198070521	-1.1780700258	-2.4907304928
H	1.0	2.4650036610	0.6688623981	-1.7017046971
H	1.0	1.1715716286	-2.1935462961	3.2826527611
H	1.0	-1.4048482414	2.1852896051	1.7103623723
H	1.0	1.6044035873	1.9736081093	-1.7233420281
H	1.0	-1.3923952777	-2.2276168416	-3.0737195153
H	1.0	-2.4240029193	0.9998981534	1.7695319620
O	8.0	-0.0098550964	0.7609985256	-4.0377167579
O	8.0	0.0307932613	0.9251020605	4.0955179953
H	1.0	-0.4928117828	1.6541747353	4.4709010025
H	1.0	0.5629356841	1.4399196037	-4.4346823148
H	1.0	-0.6694950263	0.5070672141	-4.7076856052
H	1.0	0.6563618092	0.6316103872	4.7818376796

(b) Linear Isomer, LC-BOP(μ=0.33)-CPCM/tzvp Geometry

ATOM	CHARGE	X	Y	Z
CR	24.0	-0.0166885109	-0.1598071820	-2.3641050438
CR	24.0	-0.0295179308	-0.0611896384	2.4624493529
CL	17.0	-0.0304844040	-0.1130535085	0.0490344160
O	8.0	-1.4983540234	-1.4189332592	2.5064880787
O	8.0	1.3368753986	-1.6327158441	-2.3373646809
O	8.0	-1.3679995979	1.3145990625	-2.4186334604
O	8.0	1.4423254144	1.2937399894	2.4469440881
H	1.0	-1.9333529450	-1.8293130668	1.7385556384
H	1.0	1.7218015617	-2.0498197907	-1.5466198567
H	1.0	-1.7729680530	1.7626796491	-1.6553479783
H	1.0	1.8734320064	1.6724756072	1.6608559928
H	1.0	-1.8944143638	-1.7642166890	3.3267952123
H	1.0	1.7151471581	-2.0406800295	-3.1369449782
H	1.0	-1.7304634525	1.6871555571	-3.2425585069
H	1.0	1.8403575609	1.6733709858	3.2508910273
O	8.0	1.3249406837	-1.5361339362	2.6206811713
O	8.0	-1.4956255504	-1.5155031037	-2.4732324944
O	8.0	1.4645845886	1.1909911919	-2.5056365438
O	8.0	-1.3846195484	1.4191770622	2.5491050119
H	1.0	2.2734660380	-1.4092477434	2.4392111548
H	1.0	-2.4256945391	-1.2912468427	-2.2897920292
H	1.0	2.3931204961	0.9663753268	-2.3150203598
H	1.0	1.1022069655	-2.4719310110	2.4678156690
H	1.0	-1.1515501682	2.3486146972	2.3736783118
H	1.0	1.3352794380	2.1407751770	-2.3321036940
H	1.0	-1.3619108542	-2.4596245258	-2.2737740292
H	1.0	-2.3272959659	1.2916220871	2.3395965940
O	8.0	-0.0012167581	-0.1976342384	-4.4836655419
O	8.0	-0.0335995969	-0.0082356520	4.5812462373
H	1.0	-0.5770591253	0.5831856630	5.1301285917
H	1.0	0.5826185768	0.3290075421	-5.0565612866
H	1.0	-0.5758445482	-0.7423315091	-5.0489298255
H	1.0	0.4979565489	-0.5714647965	5.1699907458

Table S2. Atomic Coordinates (Å) of the Precursor/Successor Complex $(H_2O)_5Cr^{III}ClCr^{II}(OH_2)_5^{4+}$ (P/S)

(a) Bent Isomer, LC-BOP(μ=0.33)-CPCM/tzvp Geometry

ATOM	CHARGE	X	Y	Z
CR	24.0	0.0118531830	-0.1746735294	-2.1355024763
CR	24.0	-0.0680177769	-0.0149842766	2.3126010324
CL	17.0	0.1275908095	-1.3322551427	-0.2088142730
O	8.0	-1.5746304045	-1.2080829169	2.9773275841
O	8.0	1.2288647307	-1.4740448092	-2.9787588054
O	8.0	-1.1905861770	1.1370926472	-1.3297618730
O	8.0	1.3811466625	1.1789888829	1.5378899090
H	1.0	-1.9263424894	-2.0169587366	2.5657297878
H	1.0	1.5881788493	-2.2615099680	-2.5281748272
H	1.0	-1.4174314008	1.1716127503	-0.3624630594
H	1.0	1.7677989338	1.0734034553	0.6494244453
H	1.0	-1.8906692320	-1.1701614380	3.8977903699
H	1.0	1.4935849757	-1.4755643022	-3.9179421715
H	1.0	-1.6301889916	1.8565184737	-1.8196431317
H	1.0	1.8660060972	1.8751066833	2.0152509041
O	8.0	1.3459683195	-1.2682536834	3.0877506780
O	8.0	-1.5515011104	-1.1863729934	-2.7970049749
O	8.0	1.6011744344	0.9562403595	-1.6092325191
O	8.0	-1.5447744067	1.2207023688	1.4055950632
H	1.0	2.2878333198	-1.2313958353	2.8461198722
H	1.0	-2.4163209831	-1.0945549419	-2.3523434225
H	1.0	2.4836508001	0.6109833652	-1.8547982751
H	1.0	1.1590519361	-2.1594476271	3.4305786584
H	1.0	-1.4957307798	2.1748850420	1.6169700882
H	1.0	1.6132616626	1.9201349724	-1.7720773274
H	1.0	-1.4588030740	-2.1123074983	-3.0938346120
H	1.0	-2.4560533385	0.9452146073	1.6360306647
O	8.0	-0.1214637321	0.7893122419	-3.8783968536
O	8.0	-0.0764073935	1.0220862665	4.3239379237
H	1.0	-0.5674952617	1.7761373847	4.6907220238
H	1.0	0.4676137649	1.4639046147	-4.2632382780
H	1.0	-0.8224415753	0.5746461535	-4.5230443717
H	1.0	0.5626473703	0.7515491998	5.0048312143

(b) Linear Isomer, LC-BOP(μ=0.33)-CPCM/tzvp Geometry

ATOM	CHARGE	X	Y	Z
CR	24.0	-0.0168091215	-0.1617782225	-2.6005149624
CR	24.0	-0.0306877230	-0.0576846110	2.5916016762
CL	17.0	-0.0255225673	-0.1098616139	0.3461148559
O	8.0	-1.4940501033	-1.3728342107	2.6446750955
O	8.0	1.3755194179	-1.6453882397	-2.5036086428
O	8.0	-1.4101881576	1.3231363187	-2.5450565663
O	8.0	1.4350563366	1.2549566144	2.5970134445
H	1.0	-1.9015326055	-1.7692704433	1.8524564170
H	1.0	1.7630766761	-2.0475106600	-1.7075549677
H	1.0	-1.7952663597	1.7419268247	-1.7564074525
H	1.0	1.8512715514	1.6265352217	1.7973729972
H	1.0	-1.8968657817	-1.7402178506	3.4534854460
H	1.0	1.7609879084	-2.0728851000	-3.2880558264
H	1.0	-1.7923559422	1.7411211665	-3.3362405912
H	1.0	1.8224748209	1.6532105957	3.3986659161
O	8.0	1.2907317662	-1.5235855339	2.7912732516
O	8.0	-1.5049893845	-1.5491258504	-2.5756979173
O	8.0	1.4728766416	1.2248846386	-2.6222085456
O	8.0	-1.3542726824	1.4156410995	2.7134696352
H	1.0	2.2272710153	-1.3846916496	2.5536165304
H	1.0	-2.4381002267	-1.3358297650	-2.4030604426
H	1.0	2.4061655613	1.0086118461	-2.4541457018
H	1.0	1.0505026517	-2.4420313176	2.5645035304
H	1.0	-1.1170009249	2.3172478578	2.4240787995
H	1.0	1.3418609830	2.1721632248	-2.4444971720
H	1.0	-1.3678609192	-2.4943327531	-2.3917831279
H	1.0	-2.2902490131	1.2604327555	2.4832021192
O	8.0	0.0118586054	-0.2232492066	-4.8509729756
O	8.0	-0.0374374133	-0.0069218618	4.5874804973
H	1.0	-0.5834614518	0.5965574006	5.1243268262
H	1.0	0.5705159487	0.3167631421	-5.4342299589
H	1.0	-0.5850729353	-0.7348897788	-5.4217603401
H	1.0	0.4878231578	-0.5894623776	5.1665199198

(c) Bent Isomer with Asymmetric Hydrogen Bonds, LC-BOP(μ=0.33)-CPCM/tzvp

Geometry

ATOM	CHARGE	X	Y	Z
CR	24.0	-0.0165327624	-0.1185086360	-2.0146068252
CR	24.0	0.1065778776	-0.0535791144	2.2973516928
CL	17.0	-1.2868130946	-0.1792078560	0.5168516560
O	8.0	-0.9717641200	-1.3899427508	3.2618012904
O	8.0	1.5169778812	-1.3532341774	-1.2428709753
O	8.0	-1.5837147066	1.0777525917	-2.5453751758
O	8.0	1.1739639086	1.3240604969	1.3981939043
H	1.0	-1.7539707735	-1.8341969750	2.8842602525
H	1.0	1.3353254607	-2.2768413515	-1.5172600369
H	1.0	-2.3752817696	1.1931241351	-1.9885840477
H	1.0	1.0855976644	1.5768362952	0.4440174741
H	1.0	-0.8218410335	-1.6949226627	4.1762473429
H	1.0	2.4497892723	-1.1932440669	-1.4928158179
H	1.0	-1.8635684105	1.1901012330	-3.4720629364
H	1.0	2.0149824250	1.6548515276	1.7648214503
O	8.0	1.2908548009	-1.4739368386	1.5946628866
O	8.0	-0.9769889312	-1.8850626475	-2.3814942283
O	8.0	0.8995645784	1.6706203272	-1.3414684021
O	8.0	-0.9046176041	1.3935675025	3.1944546640
H	1.0	1.4961050821	-1.4809016064	0.6269528787
H	1.0	-1.2195333031	-2.1878168173	-3.2756095688
H	1.0	1.7709067216	1.9304586905	-1.7043093677
H	1.0	1.1388657931	-2.3967851226	1.8756502457
H	1.0	-0.8638988017	2.3058613100	2.8488651764
H	1.0	0.3124036328	2.4355416410	-1.5186868254
H	1.0	-1.6458219773	-2.2411273348	-1.7680195203
H	1.0	-1.7953646386	1.2413788670	3.5633969183
O	8.0	0.8421775592	0.0531424120	-4.0900531488
O	8.0	1.3496150466	0.0362901568	3.8452576753
H	1.0	1.2416908577	0.6326930139	4.6095839465
H	1.0	0.9665397764	0.8644818881	-4.6115564785
H	1.0	1.2282093160	-0.6628661137	-4.6230613487
H	1.0	2.1802791793	-0.4675473255	3.9301540446

Table S3. Atomic Coordinates (Å) of the Ion-Aggregate of the Reactants, $Cr(H_2O)_6{\cdot}CrCl(OH_2)_5^{4+}$ (IAR), LC-BOP(μ=0.33)-CPCM/tzvp Geometry

ATOM	CHARGE	X	Y	Z
CR	24.0	0.1411689390	0.0294761175	-2.6006164373
CR	24.0	-0.2668630256	0.4348171768	2.4473520179
CL	17.0	-1.9344841054	1.1931698378	1.1239073739
O	8.0	-1.5921359132	-0.3692975629	3.6726532784
O	8.0	1.9411566918	0.0522071632	-3.5499094951
O	8.0	-1.6774154051	-0.0750318152	-1.7044205897
O	8.0	1.0758903298	1.2150060009	1.2708546359
H	1.0	-2.5558415464	-0.3673660504	3.5242280064
H	1.0	2.6638584174	0.6904957420	-3.4141323664
H	1.0	-1.8842162182	0.2521465019	-0.7964212868
H	1.0	0.8709473205	1.6408379920	0.3735192806
H	1.0	-1.3742663540	-0.8712308524	4.4797268019
H	1.0	2.1771377550	-0.4893550974	-4.3238060031
H	1.0	-2.5008632019	-0.4098566172	-2.0999617116
H	1.0	2.0171861371	1.2932041989	1.5078799371
O	8.0	-0.0708941970	-1.2774368454	1.4926463740
O	8.0	-0.1702760680	-2.3625516956	-3.1324928982
O	8.0	0.3936888226	2.1018849521	-1.0766889592
O	8.0	-0.2536163622	2.0740044388	3.5716965914
H	1.0	0.2713449745	-1.3152514854	0.5587839297
H	1.0	-1.0377516142	-2.7979308580	-3.0570432088
H	1.0	1.0071281406	2.7691289328	-1.4402137879
H	1.0	-0.6853542538	-2.0172124956	1.6527531406
H	1.0	0.0242068730	2.9291482268	3.1919785059
H	1.0	-0.4537427024	2.5764676011	-0.9710889753
H	1.0	0.2960027488	-2.8480455046	-3.8358044861
H	1.0	-0.9832091282	2.2439415975	4.1976949086
O	8.0	-0.6366497016	1.1507767863	-4.0929028031
O	8.0	1.1682877058	-0.2162457689	3.6690205885
H	1.0	1.5449503713	0.2992533137	4.4058058412
H	1.0	-1.5211607682	1.5551338900	-4.1112521798
H	1.0	-0.1248362441	1.4989787186	-4.8435734119
H	1.0	1.6563413154	-1.0531711058	3.5610533769
O	8.0	0.9433710403	-1.2134103385	-1.0632299788
H	1.0	0.7343034717	-2.0718087371	-1.5164454442
H	1.0	1.9150570803	-1.1979057317	-0.9531843059

Table S4. Atomic Coordinates (Å) of the Transition State for Water Substitution at $Cr(OH_2)_6^{2+}$ via the I_d Mechanism, $(H_2O)_5Cr\cdots(OH_2)[ClCr(OH_2)_5]^{4+\ddagger}$ (I_d-TS), LC-BOP(μ=0.33)-CPCM/tzvp Geometry

ATOM	CHARGE	X	Y	Z
CR	24.0	0.0562096312	0.1936430176	-2.3515048496
CR	24.0	-0.0873258370	0.4161081824	2.9244538834
CL	17.0	-1.3280745571	-0.3207212442	1.1977005690
O	8.0	-1.3527615004	-0.4257179992	4.1769577997
O	8.0	1.8592312228	-0.5885593501	-2.9203090046
O	8.0	-1.5623841827	1.2015030644	-1.6464054781
O	8.0	1.2060070706	1.2524764121	1.7110212791
H	1.0	-2.1457348879	-0.9194192092	3.8962805397
H	1.0	2.2103130547	-1.4392895702	-2.6054317171
H	1.0	-1.9977773530	0.9842348951	-0.8001748103
H	1.0	1.1845760467	1.2279675531	0.7211371826
H	1.0	-1.2940521894	-0.4020854357	5.1501886115
H	1.0	2.1685529597	-0.4538295337	-3.8341026634
H	1.0	-2.1874789573	1.7022649975	-2.1991744133
H	1.0	1.9843428378	1.7453566664	2.0305835120
O	8.0	1.0523659204	-1.2015700037	3.0278570126
O	8.0	-1.0505139210	-1.2115687614	-3.3601355006
O	8.0	1.2145601543	1.4549264729	-1.1015580678
O	8.0	-1.0634982907	2.1307322087	3.1100538272
H	1.0	1.8098156512	-1.3574179985	2.4335980546
H	1.0	-1.9464837819	-1.0846793986	-3.7161832489
H	1.0	2.1573993280	1.3927238848	-1.3605510657
H	1.0	0.7059344482	-2.0610251933	3.3332761262
H	1.0	-0.9378912133	2.8612397585	2.4753462472
H	1.0	0.9766601631	2.4015543539	-1.1729426169
H	1.0	-1.0553406798	-1.9992845514	-2.7725666979
H	1.0	-1.9907578622	2.1453429755	3.4147929261
O	8.0	0.1629725733	1.2912788825	-4.3493483607
O	8.0	0.9926260757	1.0632344504	4.4704111770
H	1.0	0.8476569631	1.9037353612	4.9430015635
H	1.0	0.3638848688	2.2254157185	-4.5269217441
H	1.0	-0.1834337847	0.9257393657	-5.1807220506
H	1.0	1.6980071861	0.5497179309	4.9055399965
O	8.0	-0.0008103845	-2.1679491344	-1.1494228521
H	1.0	-0.4457337808	-2.0760448832	-0.2872328784
H	1.0	0.5154189193	-2.9899178902	-1.0914979945

Table S5. Atomic Coordinates (Å) of the Water Adduct of the Precursor/Successor Complex, $(H_2O)_5Cr^{III}ClCr^{II}(OH_2)_5{\cdot}OH_2]^{4+}$ (P/S·H_2O), LC-BOP(μ=0.33)-CPCM/tzvp Geometry

ATOM	CHARGE	X	Y	Z
CR	24.0	-0.0974857547	-0.0490647802	-2.1595568299
CR	24.0	0.0046018928	0.1129639291	2.1618409079
CL	17.0	-1.3986630135	-0.0169016364	0.3986611312
O	8.0	-1.0431720735	-1.2566571474	3.1193961037
O	8.0	1.3942087354	-1.2915080589	-1.3414580714
O	8.0	-1.6290026012	1.1730657006	-2.7470591645
O	8.0	1.0280380837	1.5339567316	1.2781527901
H	1.0	-1.8087873596	-1.7193414769	2.7309096780
H	1.0	1.2401507025	-2.2590713130	-1.6137192814
H	1.0	-2.4780446638	1.3322051168	-2.2984067760
H	1.0	0.9580254207	1.7364274781	0.3094741152
H	1.0	-0.8859579553	-1.5713728467	4.0290009647
H	1.0	2.3200101046	-1.1014179199	-1.5914587445
H	1.0	-1.7274681649	1.4039460470	-3.6886494675
H	1.0	1.8789953632	1.8511743802	1.6334456461
O	8.0	1.2149210932	-1.2666246525	1.4266446443
O	8.0	-1.0555530206	-1.7098697979	-2.7937091807
O	8.0	0.8098697989	1.7451141312	-1.4659754030
O	8.0	-1.0321913100	1.5276619264	3.0894532765
H	1.0	1.3595495269	-1.2991171678	0.4416075464
H	1.0	-2.0079511658	-1.7836116723	-2.9707779149
H	1.0	1.6872742484	2.0161731025	-1.8043012596
H	1.0	1.1184378370	-2.1840351902	1.7453677649
H	1.0	-1.0099681130	2.4434059807	2.7514400574
H	1.0	0.2100033862	2.4873071783	-1.6914551905
H	1.0	-0.6576398286	-2.6117365619	-2.6778545342
H	1.0	-1.9247555006	1.3507375684	3.4424142527
O	8.0	0.5868307681	0.2385948539	-4.3164264412
O	8.0	1.2520628138	0.2177895113	3.7112778282
H	1.0	1.1248177857	0.8048257899	4.4796594815
H	1.0	1.2932846578	0.7764394596	-4.7116587088
H	1.0	0.3983066036	-0.4713748627	-4.9535933913
H	1.0	2.0982436304	-0.2592182674	3.7949078856
O	8.0	0.6512437219	-3.6435471788	-2.2044336181
H	1.0	0.4418120474	-4.3618589897	-1.5800512331
H	1.0	1.1571596433	-4.0498776011	-2.9316944211

Calculation of λ_{ou}. r (in eq 9) is the Cr···Cr distance in P/S. r_{III} and r_{II} were estimated on the basis of CPCM cavity volumes (V_{CPCM}) of the $Cr^{III}(OH_2)_5Cl^{2+}$, $Cr^{III}(OH_2)_5^{3+}$, $Cr^{II}(OH_2)_5Cl^{+}$, and $Cr^{II}(OH_2)_5^{2+}$ fragments of P/S (Table S6) using GEPOL-AS tessalation. r_{III} is the average radius of $Cr^{III}(OH_2)_5Cl^{2+}$ and $Cr^{III}(OH_2)_5^{3+}$, and r_{II} that of $Cr^{II}(OH_2)_5Cl^{+}$ and $Cr^{II}(OH_2)_5^{2+}$, respectively, since the Cl^- bridge is shared by the Cr^{III} and the Cr^{II} centers. The fragments were considered as spherical, and the individual radii (ρ) were estimated as

$$\rho = \left(\frac{3}{4\pi} V_{CPCM}\right)^{1/3}$$

Table S6. Parameters for Equation 9

geometry	basis set	r, Å	r_{II}, Å	r_{III}, Å	λ_{ou}, kJ/mol
(i) bent structure					
LC-BOP(μ=0.33)	sv(p)	4.364	3.434	3.372	48.73
LC-BOP(μ=0.33)	svp	4.385	3.433	3.369	49.73
LC-BOP(μ=0.33)	tzvp	4.452	3.435	3.369	52.21
(ii) linear structure					
LC-BOP(μ=0.33)	tzvp	5.193	3.432	3.364	76.63
LC-BOP(μ=0.37)	tzvp	5.226	3.433	3.363	77.57