Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information

Catalysis of CO_2 reduction by diazapyridinophane complexes of Fe, Co, and Ni: CO_2 binding triggered by combined frontier MO associations involving a SOMO

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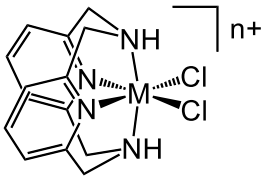
Computational Method

Density functional theory (DFT) calculations were performed using the Gaussian 09 software package.[1] The structures of M(dapp) derivatives and related compounds were fully optimized using the B3P86 density functional[2] with the effect of solvation in DMF taken into consideration using the conductor-like polarizable continuum model (C-PCM) method.[3] The B3P86/6-31+G(d,p) basis set was applied to all atoms. The use of B3P86/6-31+G(d,p) level of DFT was reported to show good consistency with theoretical and experimental results for first row transition metal complexes.[4] The redox potentials and pK_a values are calculated as described in Scheme S1. The graphical representations of geometry, molecular orbital, and Mulliken spin distribution were generated using GaussView 6.1.1.[5]



$[M(dapp)Cl_2]^{n+}$
M = Fe,Co,Ni

Scheme S1. Isodesmic reaction methods[6,7] for calculating redox potentials and pK_a values based on the experimentally determined values for the reduction potential of $Zn(dapp)Cl_2$ (−2.36 V *vs.* Fc/Fc^+) and pK_a for benzoic acid (pK_a = 12.2 in DMF), respectively. *F* is Faraday constant, *R* is the gas constant, and *T* is temperature (298.15 K). The solvent free energies of proton in DMF ($\Delta G_{sol}(H^+)$) is 264.5 kcal/mol.[8]

(1) Determination of the redox potential for $Ox + e^- \rightarrow Red$

$Ox + e^- \rightarrow Red$ $\quad \Delta G^0 = -FE^0$

$Zn(dapp)Cl_2 + e^- \rightarrow [Zn(dapp^{-\bullet})Cl_2]^-$

$\Delta G^0_{ref} = -FE^0_{ref}$ $\quad E^0_{ref} = -2.36$ V *vs.* Fc/Fc^+

$Ox + [Zn(dapp^{-\bullet})Cl_2]^- \rightarrow Red + Zn(dapp)Cl_2$

$\Delta G^0_r = G(Red)_{solv} + G(Zn(dapp)Cl_2)_{solv} - G(Ox)_{solv} - G([Zn(dapp^{-\bullet})Cl_2]^-)_{solv}$

$\Delta G^0_r = -\Delta G^0_{ref} + \Delta G^0 = FE^0_{ref} - FE^0$

$E^0 = -\Delta G^0_r/F + E^0_{ref}$

(2) Determination of pK_a value for $AH \rightarrow A^- + H^+$

$AH \rightarrow A^- + H^+$ $\quad \Delta G^0 = RT\ln(10)pK_a$

$PhCOOH \rightarrow PhCOO^- + H^+$

$\Delta G^0_{ref} = RT\ln(10)pK_{a,ref}$ $\quad pK_{a,ref} = 12.2$ in DMF

$A^- + PhCOOH \rightarrow AH + PhCOO^-$

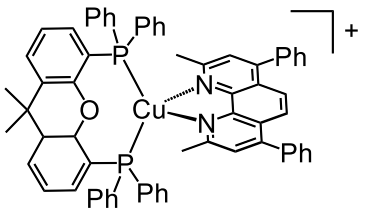
$\Delta G^0_r = G(AH)_{solv} + G(PhCOO^-)_{solv} - G(A^-)_{solv} - G(PhCOOH)_{solv}$

$\Delta G^0_r = -RT\ln(10)pK_a + RT\ln(10)pK_{a,ref}$

$pK_a = -\Delta G^0_r/RT\ln(10) + pK_{a,ref}$

Photocatalytic Experiments.

In the photocatalytic experiments shown in Fig. 1B, a DMF:TEOA (4:1 v/v) mixed solution (5 mL) containing **Cu-PS**(PF_6)[9] (0.5 mM), BIH (50 mM), xantphos (1.0 mM), and {[Fe^{III}(dapp)Cl]$_2$(μ-O)}Cl_2[9] (0.25 mM), [Co^{III}(dapp)Cl_2]Cl[9] (0.5 mM) or [Ni^{II}(dapp)(μ-Cl)]$_2Cl_2$[9] (0.25 mM) was purged with CO_2 (purity ≥ 99.995 %) for 15 min prior to irradiation. Photoirradiation experiments were carried out by an ILC Technology CERMAX LX-300 Xe lamp (179 mW·cm^{-2}) equipped with a CM-1 cold mirror which reflects lights in the range of 400 < λ < 800 nm. The photolysis vial (21 mL) was immersed in a 25 ºC water bath to remove IR radiation and to eliminate the temperature effects.



Cu-PS

The quantification of gases was done by using Shimadzu GC-14A equipped with a molecular sieve 13X-S Å column of 2 m x 3 mm *i.d.*, at 30 ºC. The injection of the sample gas (200 μL) was performed manually using a gas-tight syringe and the output signal from the thermal conductivity detector of the gas chromatograph was analyzed using a Shimadzu C-R8A integrator. The CO peaks were determined using calibration curves which had been previously obtained using standard CO and H_2 gas.

Table S1. Comparisons of the redox potentials (V *vs.* Fc/Fc^{+}), the bond distances (Å), and angles (degree) of $M^{II}(dapp)Cl_2$ (M = Fe, Co, Ni, and Zn) between computational and experimental values.[9]

	B3P86	B3LYP	BP86	M06	B3P86	Experimental
	6-31+G**				6-311+G**	
$Fe^{II/I}$	-2.161	-2.162	-1.947	-2.327	-2.162	-2.15
$Co^{II/I}$	-1.981	-1.968	-1.566	-1.784	-1.969	-1.96
$Ni^{II/I}$	-2.059	-2.047	-1.774	-1.869	-2.058	-2.01
$Sum(\lvert\Delta_{potential}\rvert)$	**0.103**	**0.057**	0.833	0.871	0.068	-
$Zn\text{-}N_{py}$	2.165	2.194	2.186	2.191	2.168	2.128(1)
$Zn\text{-}N_{amine}$	2.290	2.318	2.313	2.297	2.293	2.276(1)
Zn-Cl	2.393	2.432	2.147	2.373	2.394	2.386(1)
$Sum(\lvert\Delta_{distance}\rvert)$	**0.040**	0.090	0.249	0.068	0.044	-
$N_{py}\text{-}Zn\text{-}N_{py}$	79.5	79.3	79.4	78.3	79.5	81.0(1)
$N_{am}\text{-}Zn\text{-}N_{am}$	142.5	141.5	142.4	142.0	142.1	144.3(1)
Cl-Zn-Cl	97.7	97.9	97.9	98.3	97.8	93.5(1)
$Sum(\lvert\Delta_{angle}\rvert)$	**4.8**	5.5	5.1	6.0	5.1	-

Table S2. Comparison of the bond distances (Å) and angles (degree) of $[Co^{III}(dapp)Cl_2]^{+}$ between DFT-optimized and crystal structures.[9]

	Structure optimized by DFT	Crystal structure
$Co\text{-}N_{py}$	1.868	1.875(1) 1.873(1)
$Co\text{-}N_{amine}$	1.977	1.987(1) 1.978(1)
Co-Cl	2.250	2.263(1) 2.255(1)
$N_{py}\text{-}Co\text{-}N_{py}$	89.84	89.8(1)
$N_{amine}\text{-}Co\text{-}N_{amine}$	164.2	163.3(1)
Cl-Co-Cl	92.4	91.5(1)

Table S3. Comparison of the geometries around the M-C bonds (M = Fe, Co, Ni) in the optimized structures of the species involved in the proposed photocatalytic CO_2 reduction cycle. Selected bond distances (Å) and angles (degree) are listed.

Compound	Bond distance (Å)	Angle (°)	Geometry
$Fe^{III}(dapp)(CO_2^{2-})Cl$	Fe35-C37 = 1.962 C37-O38 = 1.246 C37-O39 = 1.228	O38-C37-O39 = 137.33	**Table S11**
$HCOO^-$ (deprotonated formate)	C1-O2 = 1.258 C1-O3 = 1.257	O2-C1-O3 = 128.17	
$Co^{III}(dapp)(CO_2^{2-})Cl$	Co1-C37 = 1.951 C37-O38 = 1.235 C37-O39 = 1.219	O38-C37-O39 = 140.46	**Table S28**
$Ni^{III}(dapp)(CO_2^{2-})Cl$	Ni1-C37 = 2.000 C37-O38 = 1.230 C37-O39 = 1.230	O38-C37-O39 = 137.20	**Table S48**

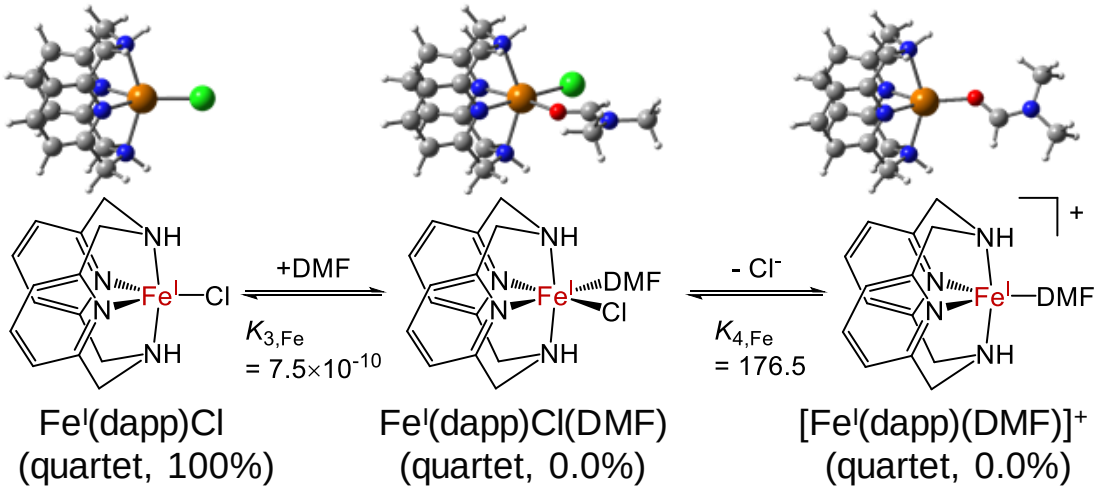


Fig. S1 Ligand substitution profile of Fe^I(dapp) derivatives at [DMF] = 10.4 M.

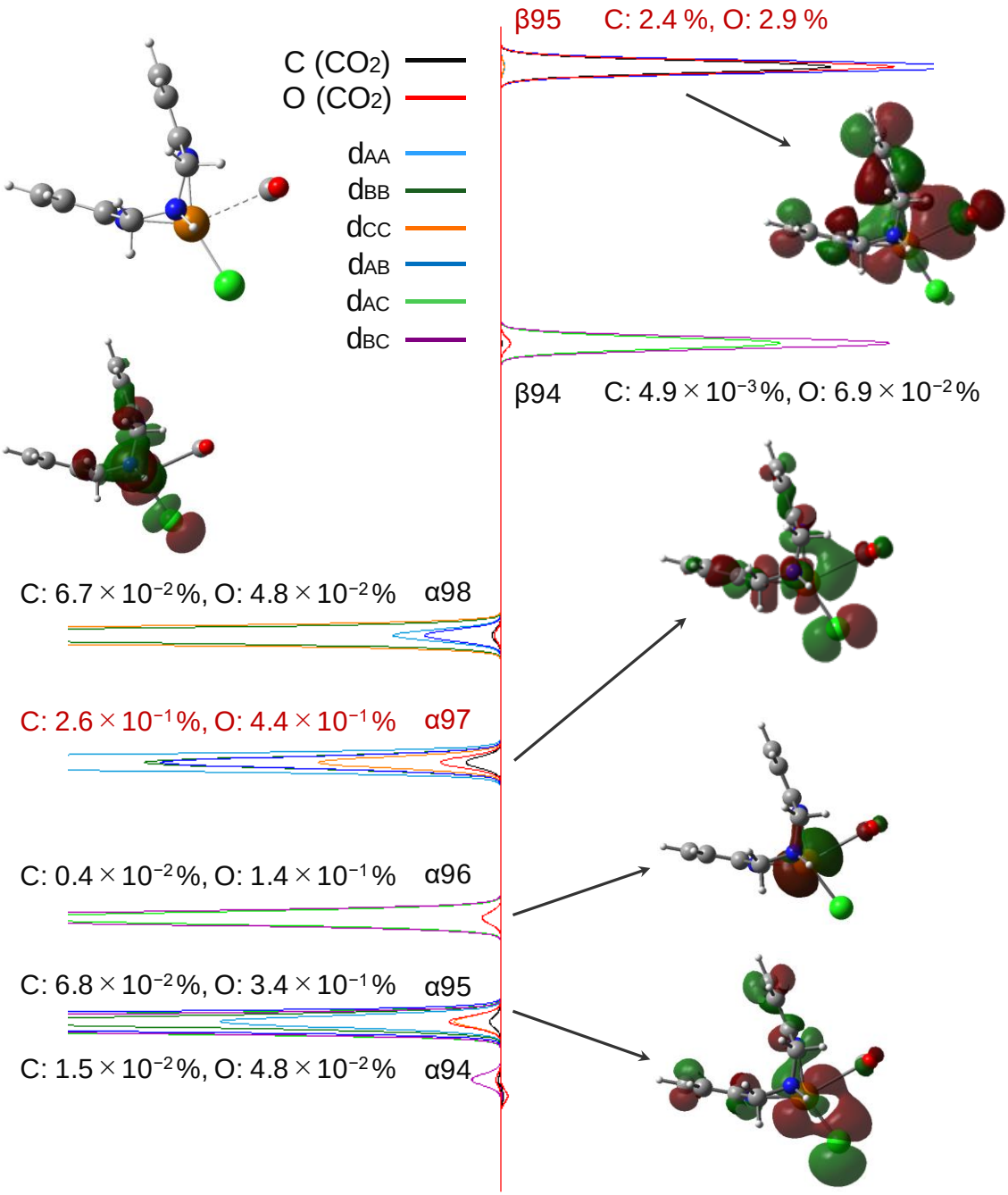


Fig. S2 The projected density of states clarifying the contributions of each atomic orbital (AO) in the transition state of CO_2 binding for the Fe^{I}(dapp) derivative, [Fe^{I}(dapp)Cl---CO_2]‡ (quartet, S = 3/2). Contributions of all the AOs for C atom (black) and two O atoms (red) in CO_2, and all the d-based AOs for Fe atom (light blue, green, orange, blue, light green, purple) are shown. A, B, and C in the description of d-based orbitals (i.e., d_{AA}, d_{BB}, d_{CC}, d_{AB}, d_{AC}, d_{BC}) correspond to the x, y, and z axes, respectively, on the basis of the definition by its DFT calculation.

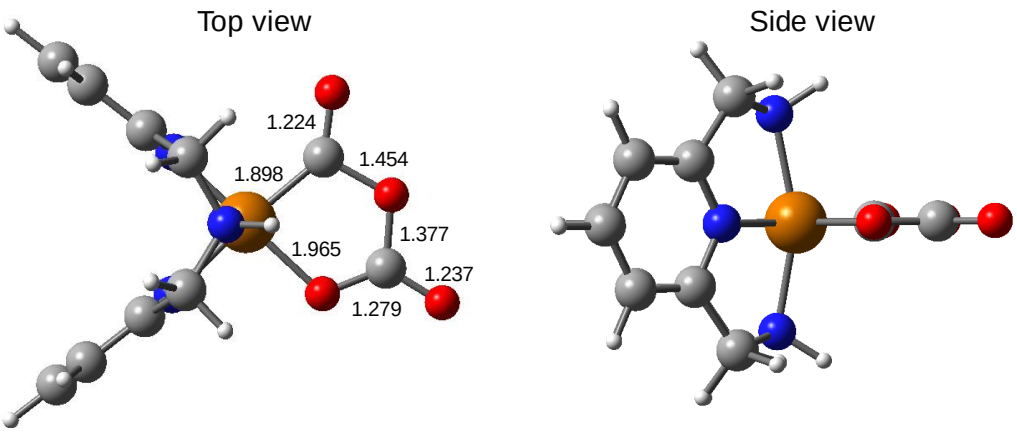


Fig. S3 The structure of Fe^{II}(dapp)($CO_2CO_2^{2-}$-*C,O*) (singlet). The selected bond distances (Å) are also shown.

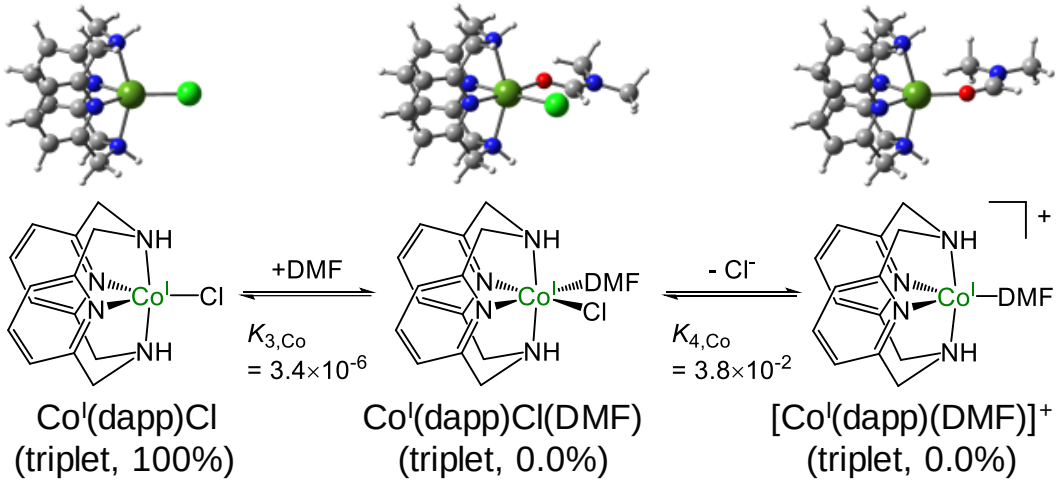


Fig. S4 Ligand substitution profile of Co^I(dapp) derivatives at [DMF] = 10.4 M.

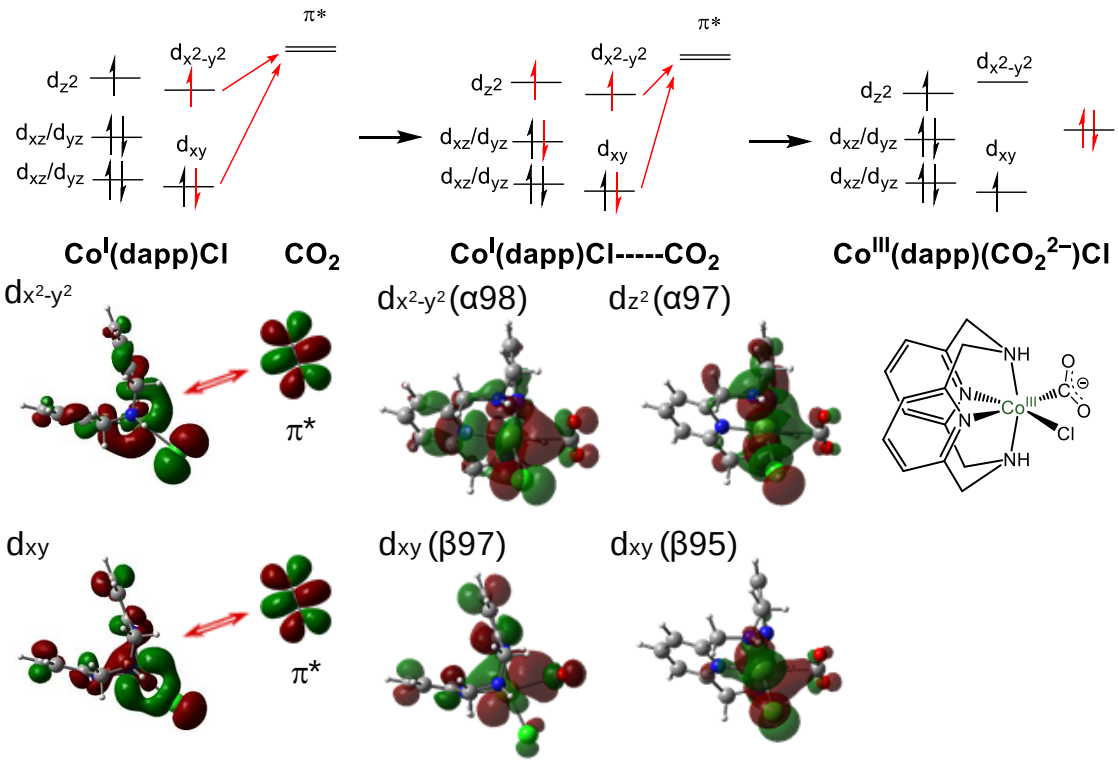


Fig. S5 Molecular orbital (MO) diagrams correlated with the CO_2 binding into Co^{I}(dapp)Cl (triplet).

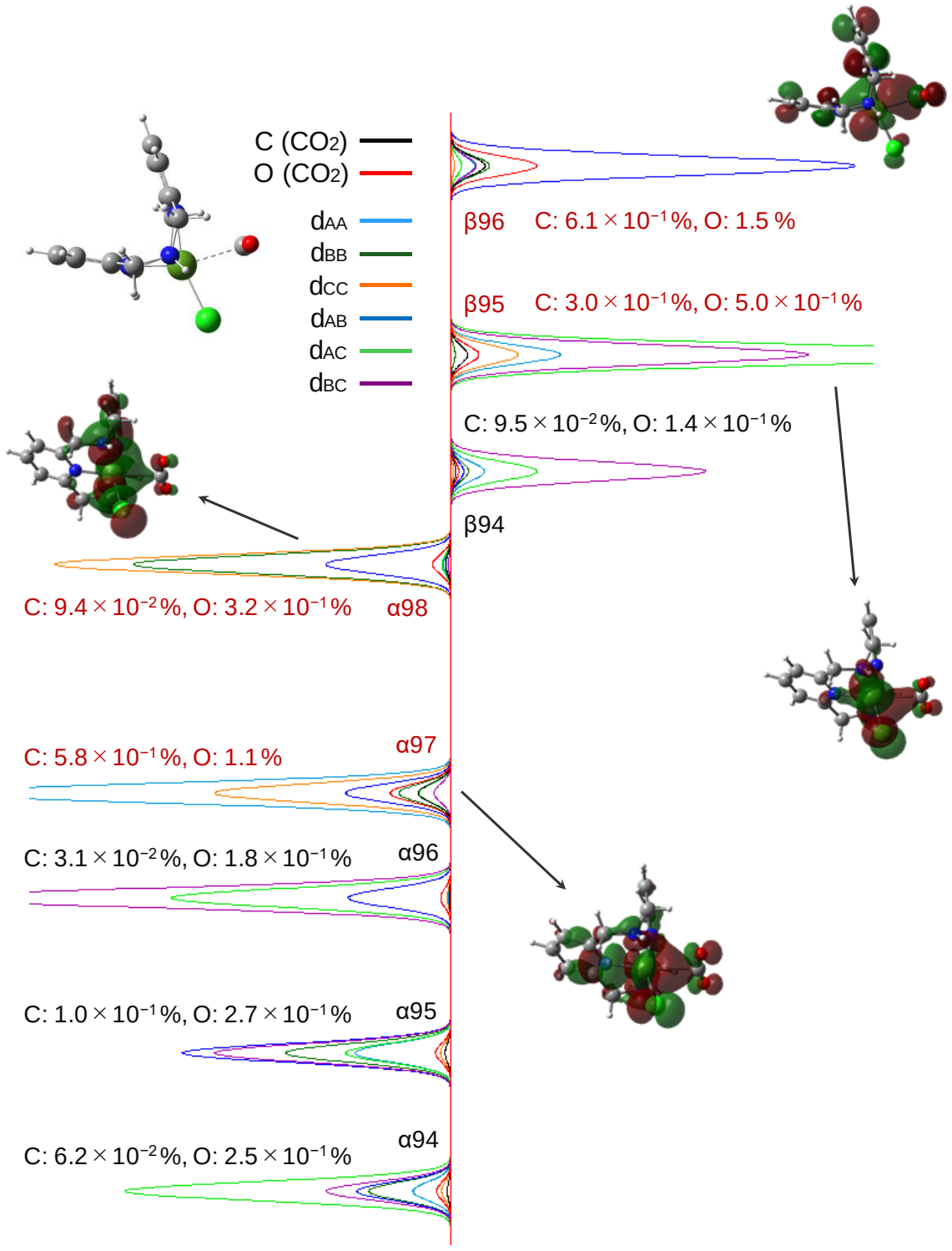


Fig. S6 The projected density of states clarifying the contributions of each atomic orbital (AO) in the transition state of CO_2 binding for the Co^{I}(dapp) derivative, [Co^{I}(dapp)Cl---CO_2]‡ (triplet, S = 1). Contributions of all the AOs for C atom (black) and two O atoms (red) in CO_2, and all the d-based AOs for Co atom (light blue, green, orange, blue, light green, purple) are shown. A, B, and C in the description of d-based orbitals (i.e., d_{AA}, d_{BB}, d_{CC}, d_{AB}, d_{AC}, d_{BC}) correspond to the x, y, and z axes, respectively, on the basis of the definition by its DFT calculation.

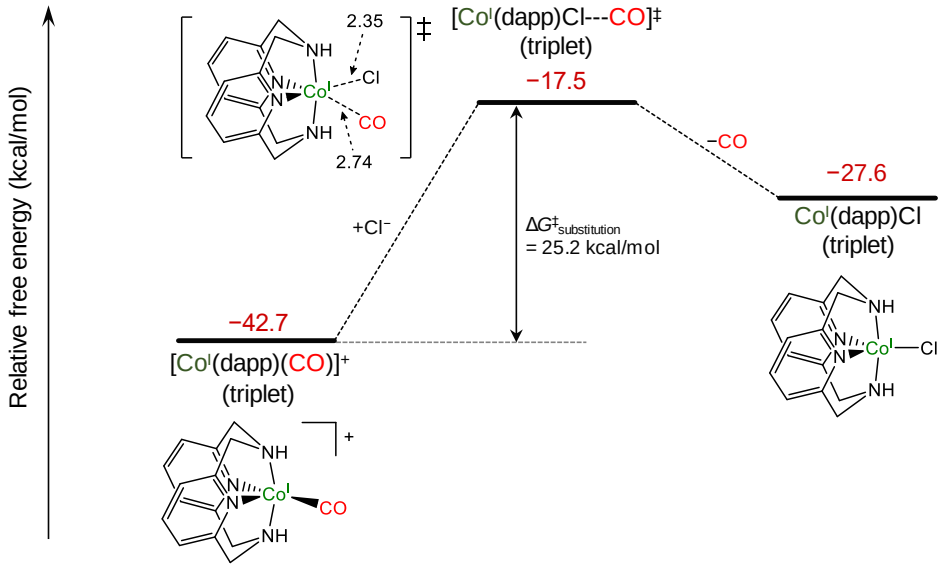


Fig. S7 Free energy diagram computed by DFT for the CO releasing step of [Co^{I}(dapp)(CO)]$^{+}$.

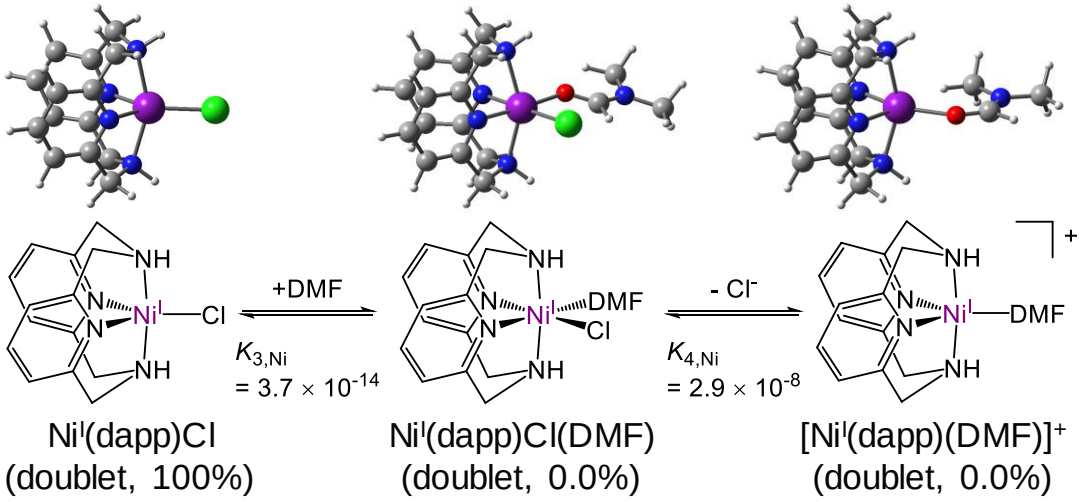


Fig. S8 Ligand substitution profile of Ni^{I}(dapp) derivatives at [DMF] = 10.4 M.

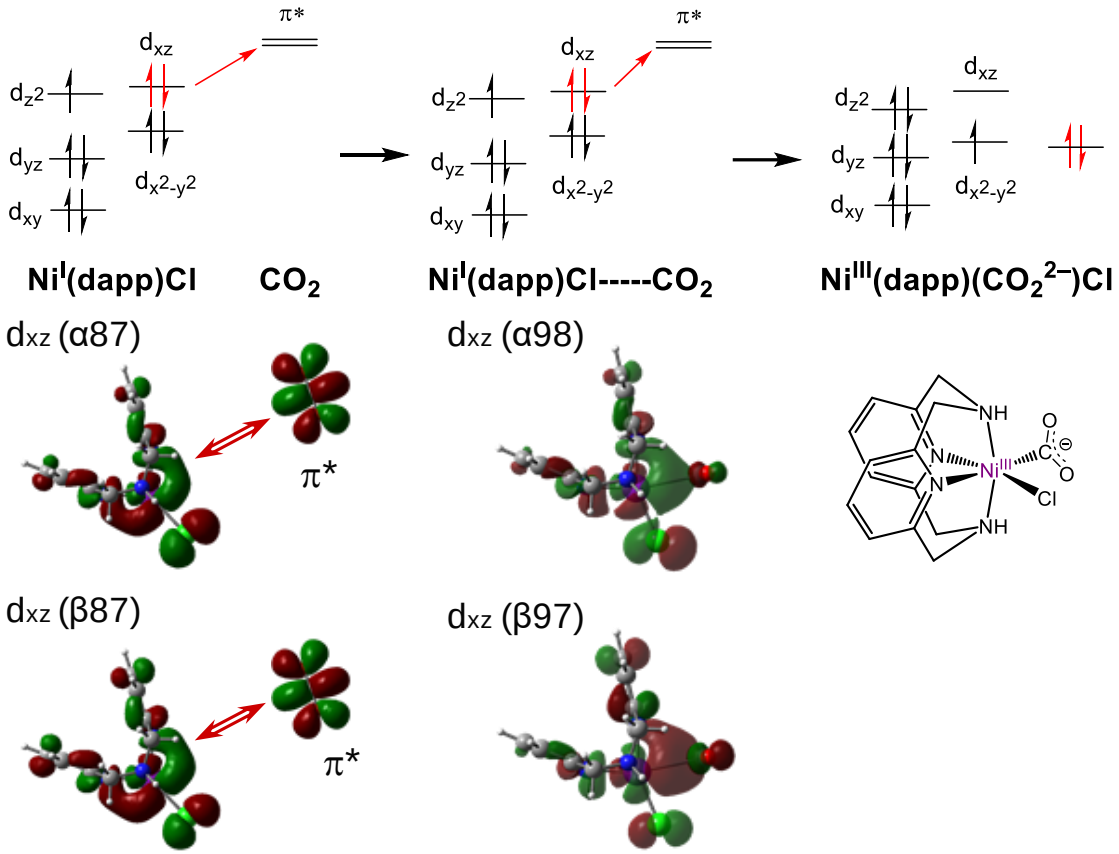


Fig. S9 MO diagrams correlated with the CO_2 binding into Ni^{I}(dapp)Cl (doublet).

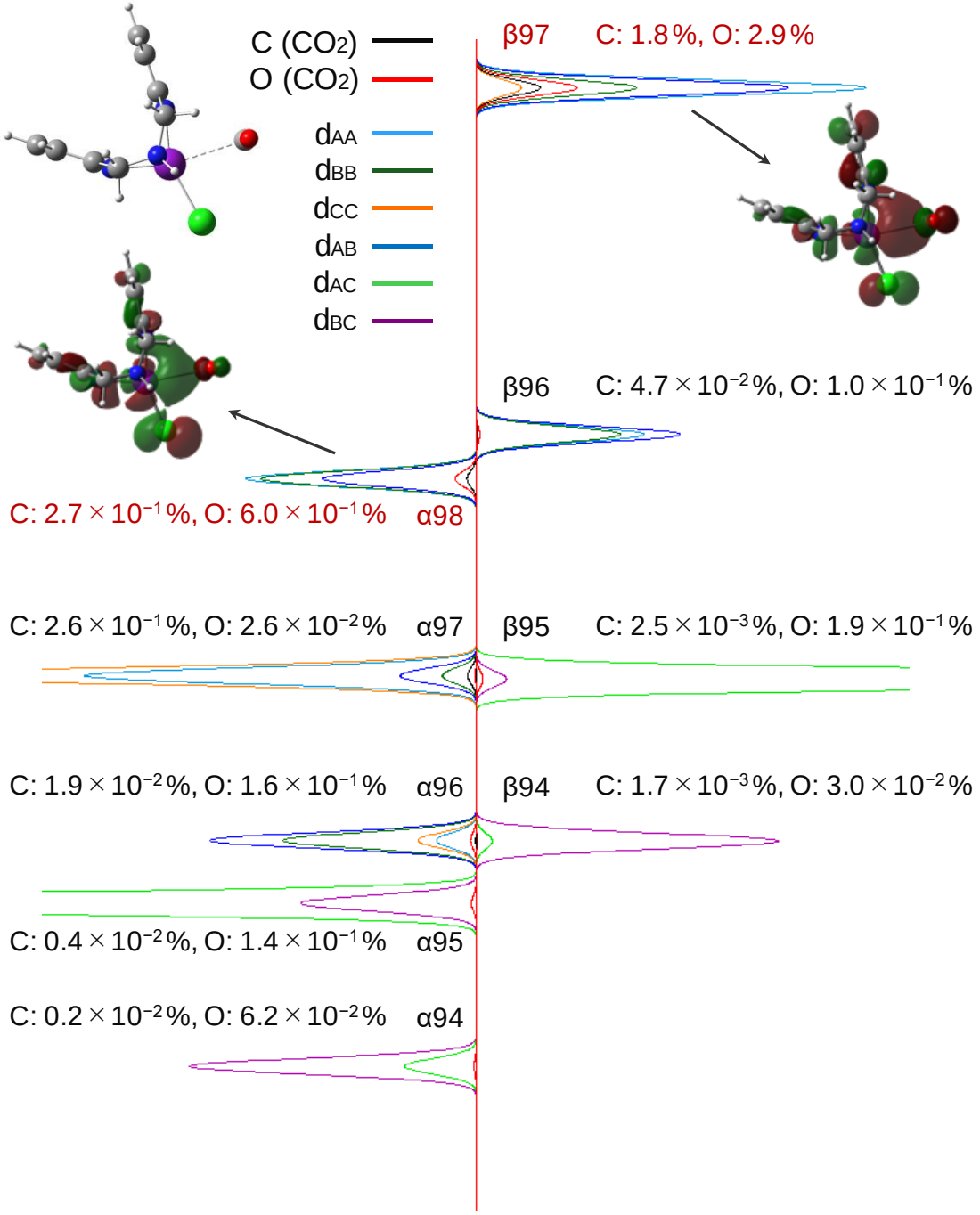


Fig. S10 The projected density of states clarifying the contributions of each atomic orbital (AO) in the transition state of CO_2 binding for the Ni^{I}(dapp) derivative, [Ni^{I}(dapp)Cl---CO_2]‡ (doublet, S = 1/2). Contributions of all the AOs for C atom (black) and two O atoms (red) in CO_2, and all the d-based AOs for Ni atom (light blue, green, orange, blue, light green, purple) are shown. A, B, and C in the description of d-based orbitals (i.e., d_{AA}, d_{BB}, d_{CC}, d_{AB}, d_{AC}, d_{BC}) correspond to the x, y, and z axes, respectively, on the basis of the definition by its DFT calculation.

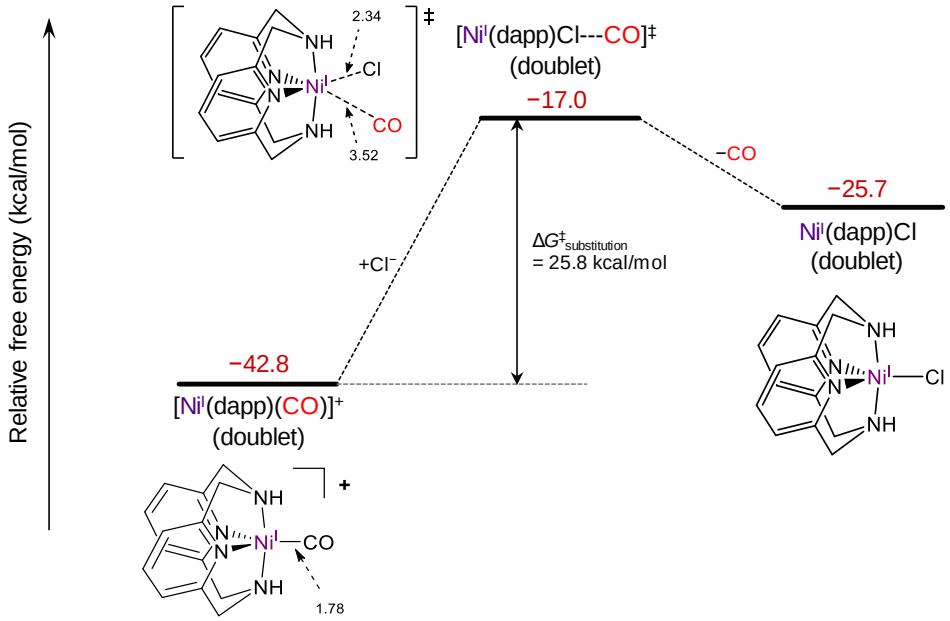


Fig. S11 Free energy diagram computed by DFT for the CO releasing step of [Ni^{I}(dapp)(CO)]$^{+}$.

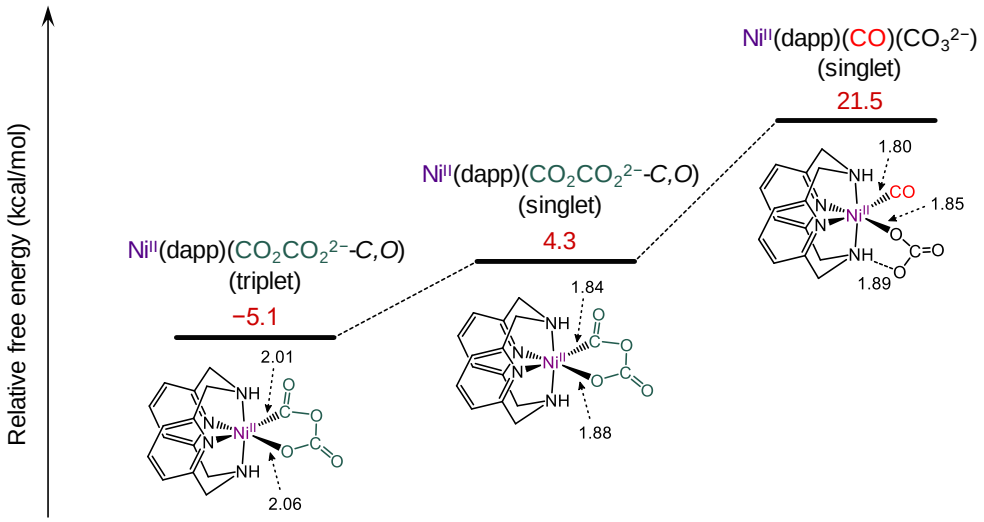


Fig. S12 Free energy diagram computed by DFT for the spin state and structural change from Ni^{II}(dapp)(CO$_2$CO$_2^{2-}$-*C,O*) (triplet) into Ni^{II}(dapp)(CO)(CO$_3^{2-}$) (singlet).

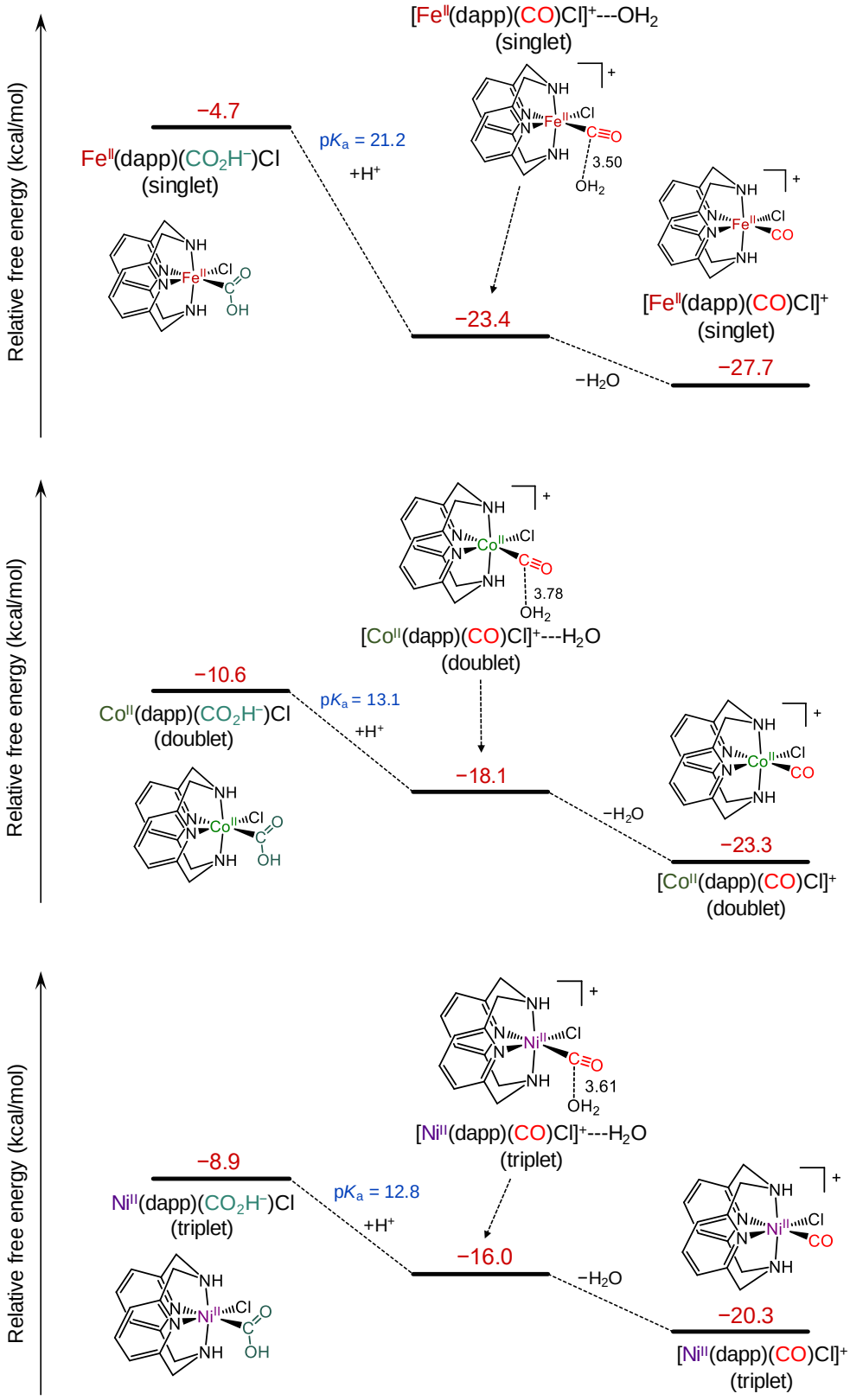
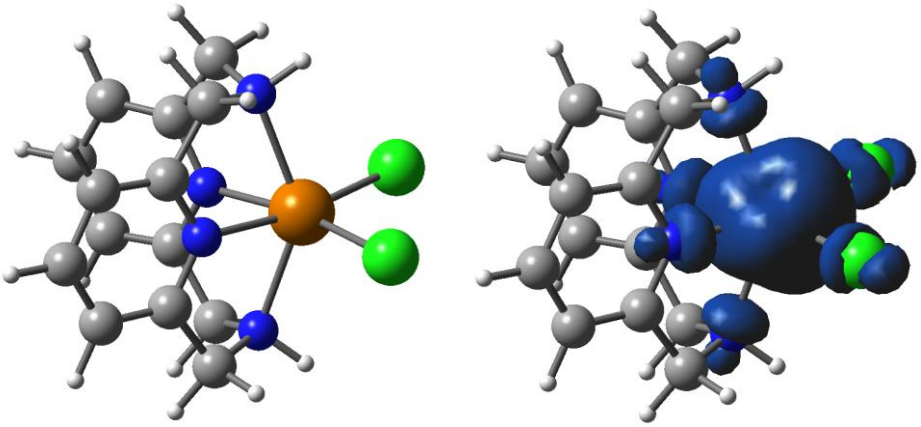


Fig. S13 Free energy diagram for the OH^- dissociation coupled with protonation to release H_2O, computed for all the M(dapp) catalysts (M = Fe, Co, and Ni), revealing that these steps can be ruled out as the paths limiting the overall kinetic rate.

Table S4. DFT-optimized geometry of $Fe^{II}(dapp)Cl_2$ (quintet), computed at the UB3P86/6-31+G(d,p) level using C-PCM.



Spin Density Distribution

atom	x	y	z	Mulliken charge	Spin density
C1	-2.15055	-2.55793	-0.98937	-0.31127	-0.01015
C2	-0.97469	-1.81249	-1.00695	-0.12153	0.001078
C3	-0.99885	-1.58701	1.308143	-0.07126	0.007558
C4	-2.17644	-2.32351	1.409371	-0.22596	-0.01065
C5	-2.74827	-2.82205	0.241113	-0.25549	0.003712
H6	-2.59417	-2.90832	-1.91525	0.185458	0.000841
H7	-2.63989	-2.48952	2.376005	0.185521	0.000867
H8	-3.66938	-3.39416	0.28705	0.189332	-0.00015
C9	-2.17658	2.323424	-1.40934	-0.22601	-0.01065
C10	-0.99899	1.586918	-1.30813	-0.07117	0.007556
C11	-0.97481	1.812415	1.006968	-0.12147	0.001074
C12	-2.15067	2.557858	0.989398	-0.31136	-0.01015
C13	-2.7484	2.821961	-0.24108	-0.25547	0.003711
H14	-2.64004	2.489444	-2.37597	0.185521	0.000867
H15	-2.59427	2.908255	1.91528	0.185459	0.000841
H16	-3.66951	3.394076	-0.28701	0.189332	-0.00015
N17	-0.4194	-1.37011	0.124959	0.348429	0.027712
N18	-0.41954	1.370026	-0.12495	0.348455	0.027715
N19	0.50124	-0.19191	-2.14924	-0.41125	0.008461
H20	1.314987	-0.23418	-2.75421	0.382672	0.00021
N21	0.501267	0.191901	2.149211	-0.41126	0.008461
H22	1.315045	0.234226	2.754131	0.382674	0.00021
C23	-0.27672	1.006373	-2.50155	-0.06687	-0.01322
H24	-0.99038	0.807782	-3.31089	0.173849	0.001206
C25	-0.27658	-1.00645	2.501558	-0.06679	-0.01322
H26	-0.99021	-0.80793	3.310947	0.173849	0.001206
C27	-0.22554	-1.4661	-2.2714	-0.0224	0.004432
H28	0.520219	-2.24828	-2.44923	0.211139	0.000092
H29	-0.91142	-1.46692	-3.12771	0.173439	0.001048
C30	-0.22562	1.466043	2.2714	-0.02246	0.004434
H31	-0.91148	1.466787	3.127716	0.173441	0.001048
H32	0.520084	2.248274	2.449231	0.21114	0.000092

H33	0.427198	1.759241	-2.87293	0.206343	-0.00003
H34	0.427432	-1.75925	2.872884	0.206342	-0.00003
Fe35	1.271808	0.000038	-1.7E-05	0.028263	3.823716
Cl36	2.867298	1.815018	0.058193	-0.58434	0.065115
Cl37	2.867402	-1.81482	-0.05821	-0.58432	0.06512

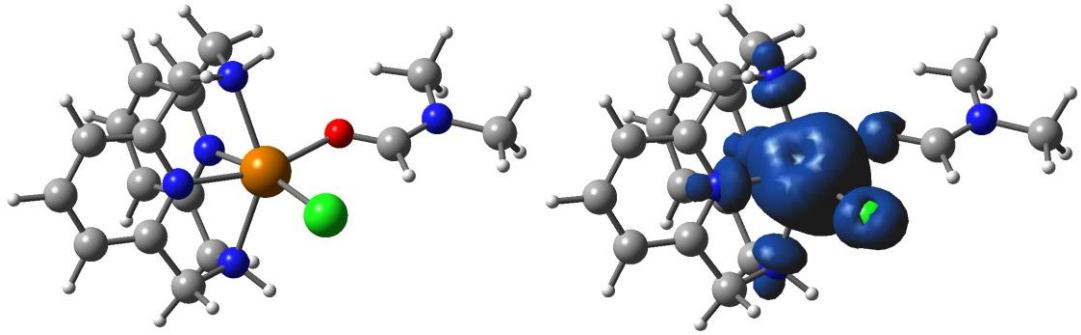
SCF Done: E(UB3P86) = −2949.93552848 A.U. after 2 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation 6.0086, after 6.0000

	1	2	3
	A	A	A
Frequencies --	41.8476	43.0983	50.2021
Red. masses --	5.1756	16.7738	8.5681

Zero-point correction= 0.292824 (Hartree/Particle)
Thermal correction to Energy= 0.312141
Thermal correction to Enthalpy= 0.313085
Thermal correction to Gibbs Free Energy= 0.242981
Sum of electronic and zero-point Energies= −2949.642704
Sum of electronic and thermal Energies= −2949.623387
Sum of electronic and thermal Enthalpies= −2949.622443
Sum of electronic and thermal Free Energies= −2949.692547

Item	Value	Threshold	Converged?
Maximum Force	0.000013	0.000450	YES
RMS Force	0.000004	0.000300	YES

Table S5. DFT-optimized geometry of $[Fe^{II}(dapp)(DMF)Cl]^{+}$ (quintet), computed at the UB3P86/6-31+G(d,p) level using C-PCM.



Spin Density Distribution

atom	x	y	z	Mulliken charge	Spin density
Fe1	-0.39587	-0.66407	-0.00962	0.092821	3.920764
C2	0.874407	1.635342	1.542253	-0.04603	-0.00316
N3	0.377638	1.329078	0.340046	0.315991	0.03201
N4	0.007291	0.164516	-2.09248	-0.40079	0.009474
H5	-0.76226	-0.1196	-2.69014	0.382251	-0.00021
C6	1.565601	2.824947	1.754584	-0.21441	-0.01941
H7	1.967912	3.058435	2.734514	0.186524	0.000809
N8	1.707755	-1.01479	-0.32297	0.116801	0.018992
C9	1.74214	3.691485	0.678304	-0.24747	0.003573
H10	2.281725	4.623468	0.812388	0.19068	-0.000052
C11	1.254445	3.340324	-0.57844	-0.5346	-0.01863
H12	1.410793	3.980102	-1.44029	0.187259	0.00076
N13	0.493267	-0.74468	2.095402	-0.46653	0.004962
H14	-0.16109	-1.26192	2.673449	0.3856	0.000111
C15	0.576946	2.131561	-0.71134	0.101909	-0.0133
C16	0.007259	1.636143	-2.01862	-0.0258	0.008983
H17	0.545966	2.087968	-2.86034	0.176348	0.001332
H18	-1.03546	1.963476	-2.08556	0.208208	0.000159
C19	1.244935	-0.43756	-2.61637	-0.05275	-0.01492
H20	1.714386	0.195341	-3.37928	0.176612	0.001392
C21	2.237486	-0.74585	-1.52016	-0.05251	0.003087
C22	3.614566	-0.77719	-1.72123	-0.29557	-0.00927
H23	4.032334	-0.55401	-2.69708	0.187564	0.000816
C24	4.436166	-1.08175	-0.63826	-0.19608	0.005415
H25	5.513855	-1.10735	-0.76309	0.190693	-0.000035
C26	3.871659	-1.32085	0.612655	-0.42546	-0.02059
C27	2.486052	-1.26906	0.734372	0.094274	-0.00476
C28	0.614169	0.62063	2.63086	-0.03231	-0.01064
H29	1.392035	0.690405	3.401051	0.176954	0.00156
H30	4.491964	-1.52587	1.478487	0.187364	0.000743
C31	1.750435	-1.50973	2.030399	-0.12036	0.010143
H32	1.484583	-2.57127	2.079795	0.215913	-0.000005
H33	2.406085	-1.29558	2.883202	0.175958	0.001217
H34	-0.33746	0.871596	3.112049	0.203757	-0.00006

Cl35	-1.16744	-2.91469	0.072797	-0.54478	0.071686
H36	0.971814	-1.37949	-3.10452	0.206484	-0.00014
O37	-2.34321	0.148564	-0.1507	-0.5518	0.002515
C38	-3.4414	-0.41794	0.047104	0.317804	0.013051
H39	-3.47911	-1.48268	0.304405	0.156838	0.001379
N40	-4.61938	0.189006	-0.03518	0.087982	-0.00066
C41	-4.73266	1.597225	-0.37207	-0.35928	0.000055
C42	-5.85437	-0.53479	0.213236	-0.27779	0.000705
H43	-5.32659	1.712462	-1.28327	0.185301	0.000022
H44	-5.22787	2.133747	0.442382	0.184499	0.000004
H45	-3.73686	2.007844	-0.5289	0.198764	0.000015
H46	-5.6314	-1.57507	0.452989	0.178734	-0.000003
H47	-6.39061	-0.08236	1.052214	0.187162	0.000089
H48	-6.49303	-0.50215	-0.67397	0.187258	0.000019

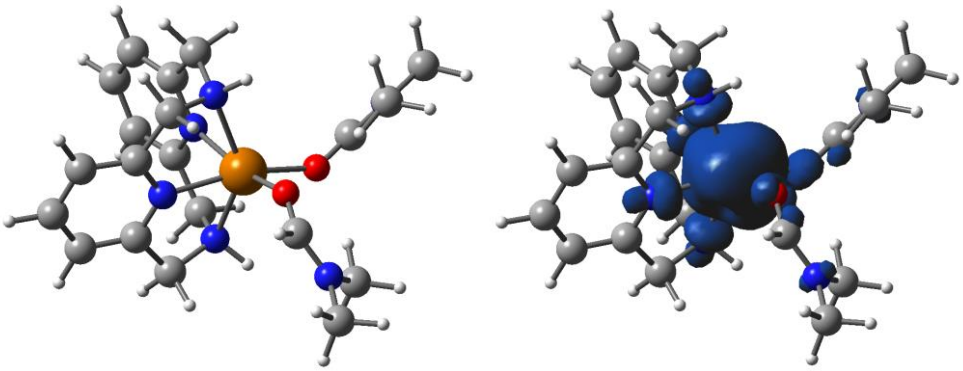
SCF Done: E(UB3P86) = −2738.47089068 A.U. after 1 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation 6.0123, after 6.0000

	1	2	3
	A	A	A
Frequencies --	15.9704	21.9312	28.3521
Red. masses --	5.5978	3.1803	4.3197

Zero-point correction= 0.396570 (Hartree/Particle)
Thermal correction to Energy= 0.421693
Thermal correction to Enthalpy= 0.422638
Thermal correction to Gibbs Free Energy= 0.337525
Sum of electronic and zero-point Energies= −2738.074321
Sum of electronic and thermal Energies= −2738.049197
Sum of electronic and thermal Enthalpies= −2738.048253
Sum of electronic and thermal Free Energies= −2738.133366

Item	Value	Threshold	Converged?
Maximum Force	0.000016	0.000450	YES
RMS Force	0.000002	0.000300	YES

Table S6. DFT-optimized geometry of $[Fe^{II}(dapp)(DMF)_2]^{2+}$ (quintet), computed at the UB3P86/6-31+G(d,p) level using C-PCM.



Spin Density Distribution

atom	x	y	z	Mulliken charge	Spin density
Fe1	-0.321759	0.000603	-0.000591	0.155342	3.97672
C2	1.861925	-1.461925	-1.489841	0.209847	-0.014049
N3	1.301294	-1.368606	-0.278279	0.203873	0.022132
N4	0.396966	-0.430373	2.107474	-0.426526	0.010804
H5	-0.419491	-0.566623	2.694981	0.387089	-0.000096
C6	3.044365	-2.169311	-1.684343	-0.454185	-0.011419
H7	3.488963	-2.235067	-2.671452	0.18825	0.000656
N8	1.302305	1.368142	0.278253	0.202469	0.02228
C9	3.648387	-2.767043	-0.580491	-0.27662	-0.002291
H10	4.574662	-3.319739	-0.699092	0.192139	0.000214
C11	3.077629	-2.622607	0.681879	-0.428208	-0.011336
H12	3.548726	-3.046315	1.562297	0.188864	0.000726
N13	0.398479	0.430633	-2.107983	-0.426864	0.010788
H14	-0.417431	0.567549	-2.696101	0.387149	-0.000093
C15	1.893048	-1.901264	0.796115	0.093639	-0.008219
C16	1.181105	-1.677601	2.108754	-0.090465	-0.004485
H17	1.901196	-1.702521	2.935084	0.179385	0.001606
H18	0.482539	-2.506183	2.267532	0.205303	-0.000206
C19	1.111196	0.764194	2.59817	-0.0874	0.005198
H20	1.790791	0.521125	3.423219	0.178793	0.001452
C21	1.862251	1.461035	1.490151	0.209984	-0.01398
C22	3.045115	2.167538	1.685337	-0.453656	-0.011272
H23	3.489201	2.232953	2.6727	0.188247	0.000656
C24	3.650201	2.76485	0.58184	-0.276467	-0.002303
H25	4.576813	3.316865	0.700985	0.192131	0.000214
C26	3.080062	2.620888	-0.680872	-0.426228	-0.011334
C27	1.89503	1.900401	-0.795793	0.093277	-0.008227
C28	1.112145	-0.764449	-2.59832	-0.086064	0.005288
H29	1.792495	-0.521774	-3.422861	0.178828	0.00145
H30	3.551965	3.044315	-1.560992	0.188868	0.000726
C31	1.1836	1.677293	-2.108808	-0.090489	-0.004474
H32	0.485744	2.506403	-2.267956	0.205321	-0.000205
H33	1.904116	1.70163	-2.934778	0.179406	0.001605

H34	0.355838	-1.452548	-2.990282	0.213788	-0.000093
H35	0.355107	1.452909	2.98946	0.21377	-0.000093
O36	-1.763202	-1.222109	-0.871779	-0.464836	0.001709
C37	-2.323591	-2.337666	-0.773912	0.221939	0.004848
H38	-2.156474	-3.104468	-1.539395	0.157823	0.001637
N39	-3.1554	-2.698218	0.192367	0.063139	0.009707
C40	-3.511301	-1.800219	1.278825	-0.381748	0.000951
C41	-3.753439	-4.023813	0.210878	-0.278788	-0.000469
H42	-4.599981	-1.717926	1.336144	0.18869	0.000513
H43	-3.137606	-2.198228	2.226792	0.189087	0.000567
H44	-3.078956	-0.817307	1.096854	0.189077	0.000228
H45	-3.412376	-4.597184	-0.651588	0.180014	0.000002
H46	-3.464884	-4.54846	1.12569	0.18972	0.000763
H47	-4.842969	-3.940252	0.177889	0.190118	0.000381
O48	-1.760236	1.225391	0.873353	-0.465128	0.001752
C49	-2.323499	2.339414	0.775029	0.22197	0.004824
H50	-2.160139	3.105944	1.541599	0.157781	0.001646
N51	-3.154126	2.698768	-0.192748	0.063038	0.009661
C52	-3.506077	1.800682	-1.280413	-0.381921	0.000965
C53	-3.754478	4.023311	-0.211922	-0.278951	-0.000465
H54	-4.594582	1.719432	-1.342244	0.188621	0.000508
H55	-3.128062	2.197864	-2.227033	0.189094	0.000565
H56	-3.075567	0.817358	-1.096197	0.18888	0.00023
H57	-3.416443	4.596819	0.651646	0.179987	0.000002
H58	-3.464686	4.549004	-1.125748	0.189726	0.00076
H59	-4.843932	3.937818	-0.181565	0.19008	0.000377

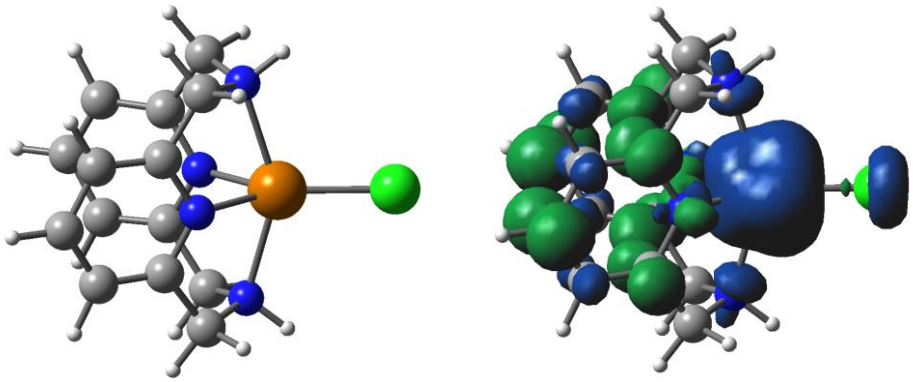
SCF Done: E(UB3P86) = −2678.31294332 A.U. after 1 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation 6.0152, after 6.0000

	1	2	3
	A	A	A
Frequencies --	15.2463	19.1274	27.9541
Red. masses --	4.5347	3.7568	4.1063

Zero-point correction= 0.500930 (Hartree/Particle)
Thermal correction to Energy= 0.531525
Thermal correction to Enthalpy= 0.532470
Thermal correction to Gibbs Free Energy= 0.434535
Sum of electronic and zero-point Energies= −2526.492167
Sum of electronic and thermal Energies= −2526.461571
Sum of electronic and thermal Enthalpies= −2526.460627
Sum of electronic and thermal Free Energies= −2526.558562

Item	Value	Threshold	Converged?
Maximum Force	0.000015	0.000450	YES
RMS Force	0.000002	0.000300	YES

Table S7. DFT-optimized geometry of Fe^{I}(dapp)Cl (quartet), computed at the UB3P86/6-31+G(d,p) level using C-PCM.



Spin Density Distribution

atom	x	y	z	Mulliken charge	Spin density
C1	2.025539	-1.20551	-2.12998	-0.1528	0.090413
C2	0.747839	-1.17076	-1.59266	-0.01781	-0.15138
C3	0.748037	1.165694	-1.59618	-0.01792	-0.15128
C4	2.025729	1.1986	-2.13362	-0.15279	0.090389
C5	2.677355	-0.00396	-2.42932	-0.29776	-0.22855
H6	2.510023	-2.16217	-2.30074	0.16473	-0.00132
H7	2.510396	2.154649	-2.30729	0.164731	-0.00132
H8	3.677633	-0.00467	-2.84892	0.170647	0.010335
C9	2.024699	-1.19871	2.134547	-0.15323	0.090334
C10	0.747383	-1.16572	1.5962	-0.01799	-0.15121
C11	0.747332	1.170709	1.592678	-0.01787	-0.15135
C12	2.024658	1.205393	2.130907	-0.15317	0.090353
C13	2.676172	0.003806	2.430705	-0.29751	-0.22836
H14	2.509195	-2.15478	2.308554	0.164745	-0.00132
H15	2.509099	2.162021	2.301984	0.164746	-0.00132
H16	3.676143	0.004454	2.851037	0.170658	0.010325
N17	0.096027	-0.00212	-1.36062	0.171553	0.003751
N18	0.095626	0.002118	1.360215	0.172114	0.00378
N19	-0.80432	-2.19963	0.00313	-0.38605	0.033847
H20	-1.60026	-2.82975	0.004079	0.363946	-0.00142
N21	-0.80421	2.199641	-0.00372	-0.38605	0.033856
H22	-1.60011	2.829826	-0.0049	0.363959	-0.00142
C23	-0.04137	-2.39811	1.248613	-0.15283	-0.00157
H24	0.619898	-3.2734	1.199478	0.162445	0.001687
C25	-0.04095	2.398049	-1.24907	-0.15279	-0.00157
H26	0.620128	3.273476	-1.1999	0.162446	0.001686
C27	-0.04139	-2.40188	-1.24181	-0.15281	-0.00155
H28	-0.78089	-2.58987	-2.0301	0.189303	-0.00505
H29	0.619474	-3.27734	-1.19027	0.162438	0.001685
C30	-0.04154	2.401937	1.241368	-0.15282	-0.00155
H31	0.619546	3.277221	1.189825	0.162454	0.001686
H32	-0.78115	2.590316	2.029478	0.189326	-0.00505
H33	-0.78076	-2.58434	2.037417	0.189314	-0.00505

H34	-0.78021	2.583955	-2.03808	0.189306	-0.00505
Fe35	-1.44471	0.000138	-0.00044	-0.26539	3.589507
Cl36	-3.74968	-0.000034	0.000137	-0.55126	0.043031

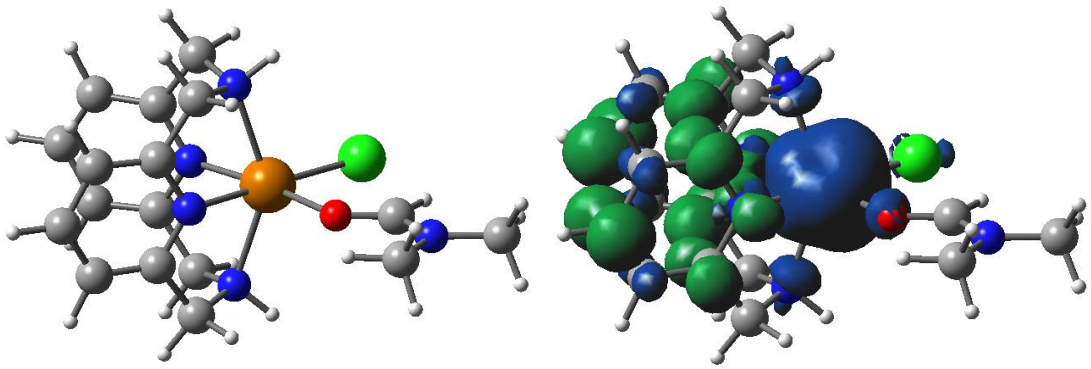
SCF Done: E(UB3P86) = −2489.32992881 A.U. after 2 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation 4.3709, after 3.7617

	1	2	3
	A	A	A
Frequencies --	25.1391	63.7550	72.6226
Red. masses --	14.2528	5.2078	3.5573

Zero-point correction= 0.289349 (Hartree/Particle)
Thermal correction to Energy= 0.306414
Thermal correction to Enthalpy= 0.307358
Thermal correction to Gibbs Free Energy= 0.243231
Sum of electronic and zero-point Energies= −2489.040580
Sum of electronic and thermal Energies= −2489.023515
Sum of electronic and thermal Enthalpies= −2489.022571
Sum of electronic and thermal Free Energies= −2489.086698

Item	Value	Threshold	Converged?
Maximum Force	0.000010	0.000450	YES
RMS Force	0.000002	0.000300	YES

Table S8. DFT-optimized geometry of Fe^{I}(dapp)Cl(DMF) (quartet), computed at the UB3P86/6-31+G(d,p) level using C-PCM.



Spin Density Distribution

atom	x	y	z	Mulliken charge	Spin density
Fe1	-0.43683	-0.64228	-0.00019	-0.1955	3.735398
C2	0.96872	1.73394	1.16832	-0.00686	-0.170129
N3	0.45982	1.26574	0.00142	0.114568	-0.017564
N4	0.18269	-0.34134	-2.20406	-0.39894	0.014254
H5	-0.52742	-0.6658	-2.85344	0.35839	-0.001116
C6	1.93573	2.72703	1.20517	-0.2224	0.113415
H7	2.31328	3.07554	2.16212	0.1582	-0.000986
N8	1.582	-1.19356	-0.00134	-0.07419	-0.023927
C9	2.41895	3.25878	0.00234	-0.293	-0.254228
H10	3.17239	4.03935	0.00271	0.165459	0.011357
C11	1.9346	2.72926	-1.20101	-0.22253	0.113502
H12	2.31124	3.07955	-2.15767	0.158201	-0.000987
N13	0.18418	-0.34522	2.20402	-0.39912	0.014215
H14	-0.52553	-0.67068	2.85335	0.358385	-0.001117
C15	0.96762	1.73609	-1.1651	-0.00692	-0.170054
C16	0.37258	1.10764	-2.39638	-0.0637	0.001666
H17	0.99113	1.33263	-3.27596	0.158267	0.001785
H18	-0.62349	1.53108	-2.57324	0.179901	-0.004944
C19	1.40147	-1.1501	-2.39581	-0.14234	0.005014
H20	1.97193	-0.83883	-3.28154	0.157358	0.001687
C21	2.27001	-1.10278	-1.16938	-0.09868	-0.167167
C22	3.65122	-0.99788	-1.20535	-0.07391	0.098082
H23	4.16047	-0.93037	-2.16252	0.156791	-0.001263
C24	4.37083	-0.96887	-0.00195	-0.32153	-0.274396
H25	5.45279	-0.89048	-0.0022	0.163892	0.012819
C26	3.65193	-1.00018	1.2018	-0.07401	0.098141
C27	2.27069	-1.10508	1.16645	-0.09764	-0.167119
C28	0.37475	1.10329	2.399	-0.06321	0.001831
H29	0.99429	1.32639	3.27838	0.158282	0.001787
H30	4.16174	-0.93455	2.15881	0.156788	-0.001264
C31	1.40284	-1.15478	2.39327	-0.14302	0.004862
H32	1.06543	-2.18591	2.55562	0.184428	-0.005675
H33	1.97392	-0.84563	3.27935	0.15735	0.001684

H34	-0.62097	1.52676	2.57779	0.17988	-0.004949
Cl35	-1.55853	-2.83124	-0.00069	-0.65417	0.033094
H36	1.06431	-2.18099	-2.56019	0.184412	-0.005679
O37	-2.42122	0.32233	-0.00039	-0.54717	-0.002359
C38	-3.5662	-0.16801	-0.00005	0.237553	0.015034
H39	-3.71153	-1.25581	-0.00003	0.147156	0.000819
N40	-4.69288	0.54796	0.0003	0.104576	-0.004021
C41	-4.67084	1.99862	0.00028	-0.36914	-0.001445
C42	-5.99268	-0.09693	0.0006	-0.27013	0.000232
H43	-5.182	2.38047	-0.88881	0.179623	-0.000081
H44	-5.18124	2.38049	0.88981	0.179627	-0.000081
H45	-3.63549	2.33577	-0.00017	0.19806	-0.000051
H46	-5.86675	-1.18055	0.00081	0.176047	-0.000005
H47	-6.55993	0.19416	0.89005	0.182445	-0.000034
H48	-6.5602	0.19379	-0.8888	0.182452	-0.000034

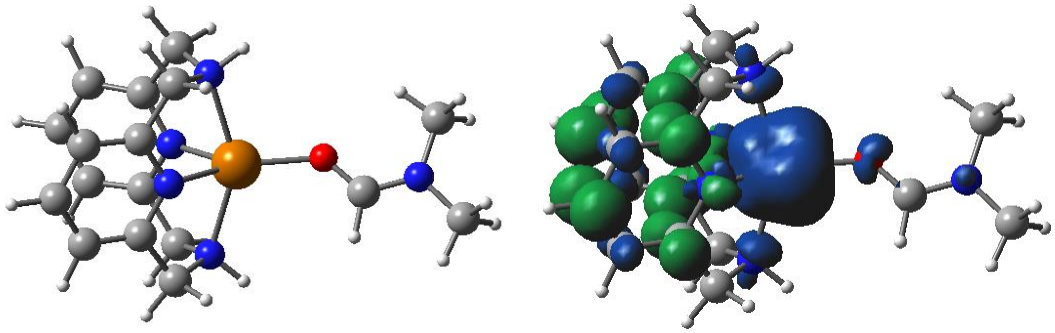
SCF Done: E(UB3P86) = −2738.58894844 A.U. after 1 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation 4.4984, after 3.7656

	1	2	3
	A	A	A
Frequencies --	16.1284	30.3185	30.9568
Red. masses --	5.0430	4.7634	2.9939

Zero-point correction= 0.392930 (Hartree/Particle)
Thermal correction to Energy= 0.418009
Thermal correction to Enthalpy= 0.418953
Thermal correction to Gibbs Free Energy= 0.335334
Sum of electronic and zero-point Energies= −2738.196018
Sum of electronic and thermal Energies= −2738.170940
Sum of electronic and thermal Enthalpies= −2738.169995
Sum of electronic and thermal Free Energies= −2738.253614

Item	Value	Threshold	Converged?
Maximum Force	0.000053	0.000450	YES
RMS Force	0.000005	0.000300	YES

Table S9. DFT-optimized geometry of $[Fe^{I}(dapp)(DMF)]^{+}$ (quartet), computed at the UB3P86/6-31+G(d,p) level using C-PCM.



Spin Density Distribution

atom	x	y	z	Mulliken charge	Spin density
Fe1	0.65549	0.06883	-0.06132	-0.07151	3.769366
C2	-1.58089	-0.35633	-1.9247	-0.081851	-0.151492
N3	-0.94421	0.60899	-1.21333	0.191625	-0.03879
N4	-0.00775	2.00529	0.94782	-0.392098	0.010802
H5	0.76742	2.60909	1.2039	0.367829	-0.000927
C6	-2.88114	-0.19607	-2.37769	-0.143862	0.077974
H7	-3.35488	-0.99207	-2.94416	0.166305	-0.001343
N8	-0.79443	-0.60501	1.20949	0.151733	-0.03803
C9	-3.5685	0.98728	-2.08456	-0.308056	-0.22143
H10	-4.58633	1.13696	-2.42822	0.17196	0.010335
C11	-2.92811	1.95515	-1.30245	-0.138507	0.049113
H12	-3.43911	2.86885	-1.01429	0.166356	-0.00134
N13	0.08194	-1.92539	-1.02421	-0.44836	0.019747
H14	0.87586	-2.4703	-1.34651	0.367181	-0.001174
C15	-1.62685	1.73416	-0.87843	0.009559	-0.139544
C16	-0.84305	2.70991	-0.04401	-0.138285	-0.020368
H17	-1.5158	3.44084	0.42324	0.165054	0.001637
H18	-0.1522	3.26208	-0.693	0.190764	-0.004792
C19	-0.70903	1.59563	2.1798	-0.127403	-0.001262
H20	-1.38849	2.37419	2.55029	0.164832	0.001538
C21	-1.45447	0.30674	1.97022	-0.059967	-0.154238
C22	-2.70019	0.04198	2.51722	-0.13525	0.073031
H23	-3.19356	0.79898	3.11933	0.16586	-0.001376
C24	-3.31006	-1.19363	2.27119	-0.340597	-0.229872
H25	-4.28461	-1.4243	2.68775	0.171864	0.010611
C26	-2.65231	-2.10721	1.43934	-0.065789	0.096354
C27	-1.40773	-1.78265	0.92239	-0.101015	-0.141608
C28	-0.74807	-1.57903	-2.195	-0.10545	-0.007596
H29	-1.38641	-2.41379	-2.51244	0.165114	0.001596
H30	-3.10725	-3.05947	1.18405	0.165833	-0.001384
C31	-0.61391	-2.69316	0.02745	-0.185642	-0.017717
H32	0.16719	-3.18655	0.61898	0.189238	-0.005052
H33	-1.25919	-3.47746	-0.38944	0.164922	0.001548
H34	-0.05127	-1.36308	-3.01432	0.188593	-0.004979

H35	0.06666	1.44187	2.94012	0.189823	-0.005048
O36	2.64747	0.32285	-0.20148	-0.656636	-0.020198
C37	3.62207	-0.44863	-0.0226	0.226583	0.076701
H38	3.47652	-1.52346	0.12661	0.167593	0.001894
N39	4.88279	-0.04874	-0.00165	0.0841	0.005584
C40	5.24421	1.3481	-0.17872	-0.35045	-0.001017
C41	5.96826	-0.99376	0.20657	-0.292384	0.000678
H42	5.77332	1.70475	0.70917	0.189801	0.000481
H43	5.89996	1.44925	-1.04757	0.190146	0.0005
H44	4.34061	1.93548	-0.32938	0.203868	-0.000039
H45	5.56636	-2.00015	0.32759	0.18218	0.000011
H46	6.64344	-0.97873	-0.65305	0.192357	0.000594
H47	6.52942	-0.72207	1.10456	0.192037	0.000521

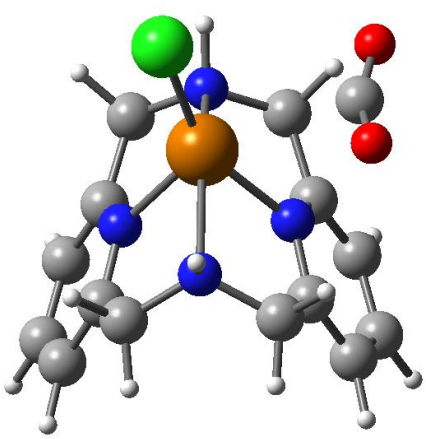
SCF Done: E(UB3P86) = −2277.85830270 A.U. after 1 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation 4.3850, after 3.7616

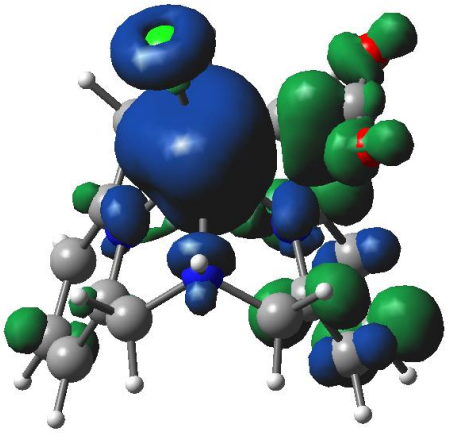
	1	2	3
	A	A	A
Frequencies --	9.2405	15.5541	27.2930
Red. masses --	2.9031	4.6311	3.9798

Zero-point correction= 0.393336 (Hartree/Particle)
Thermal correction to Energy= 0.416209
Thermal correction to Enthalpy= 0.417153
Thermal correction to Gibbs Free Energy= 0.337487
Sum of electronic and zero-point Energies= −2277.464966
Sum of electronic and thermal Energies= −2277.442094
Sum of electronic and thermal Enthalpies= −2277.441150
Sum of electronic and thermal Free Energies= −2277.520816

Item	Value	Threshold	Converged?
Maximum Force	0.000006	0.000450	YES
RMS Force	0.000001	0.000300	YES

Table S10. Transition state (TS) geometry optimized for [Fe^{I}(dapp)Cl---CO_2]‡, computed at the UB3P86/6-31+G(d,p) level using C-PCM.





Spin Density Distribution

atom	x	y	z	Mulliken charge	Spin density
C1	-3.30465	-0.94757	-1.203	-0.27608	-0.00036
C2	-1.9177	-1.04552	-1.16452	-0.04084	-0.0504
C3	-1.9178	-1.04557	1.164373	-0.0409	-0.05046
C4	-3.30474	-0.94761	1.202751	-0.27603	-0.00035
C5	-4.00863	-0.91216	-0.00015	-0.24474	-0.05392
H6	-3.81999	-0.8855	-2.15595	0.179166	0.000105
H7	-3.82016	-0.88558	2.155658	0.179167	0.000105
H8	-5.09069	-0.83066	-0.00019	0.183797	0.00271
C9	-0.78153	2.93436	-1.20016	-0.79538	0.107209
C10	-0.09516	1.728713	-1.16638	0.47638	-0.0649
C11	-0.09524	1.728687	1.166455	0.476273	-0.0649
C12	-0.7816	2.934342	1.200216	-0.7952	0.107234
C13	-1.11376	3.566794	0.000023	-0.32431	-0.18061
H14	-1.06638	3.363163	-2.15599	0.170793	-0.00148
H15	-1.06651	3.363128	2.156032	0.170793	-0.00148
H16	-1.65197	4.508612	0.000015	0.175881	0.008362
N17	-1.25051	-1.1204	-5.1E-05	0.305642	0.047032
N18	0.284593	1.153278	0.000045	0.355385	-0.01293
N19	0.254628	-0.48077	-2.18608	-0.35496	0.022494
H20	0.928245	-0.92379	-2.80195	0.373403	-0.00029
N21	0.254449	-0.48083	2.186117	-0.35498	0.022484
H22	0.928038	-0.92385	2.802025	0.373408	-0.00029
C23	0.304672	0.974352	-2.40647	-0.16275	-0.0415
H24	-0.31687	1.28715	-3.25573	0.162195	0.000347
C25	-1.05946	-1.10485	2.403378	-0.05482	0.023197
H26	-1.59535	-0.661	3.252576	0.167361	0.001449
C27	-1.05928	-1.10474	-2.40346	-0.05488	0.023171
H28	-0.87975	-2.1578	-2.64899	0.200559	-0.00096
H29	-1.59511	-0.6608	-3.25266	0.167356	0.001449
C30	0.304458	0.97428	2.40656	-0.16278	-0.04151
H31	-0.31721	1.287035	3.255746	0.162198	0.000346

H32	1.344756	1.21853	2.644643	0.205172	-0.00474
H33	1.345008	1.218596	-2.64439	0.205173	-0.00474
H34	-0.87991	-2.15793	2.648827	0.200562	-0.00096
Fe35	0.833921	-0.83794	0.00009	-0.20175	3.408029
Cl36	2.404374	-2.50003	-4.7E-05	-0.59627	0.012358
C37	3.071873	0.744593	0.000013	0.450524	-0.18759
O38	3.296771	0.860133	-1.16382	-0.30227	-0.01185
O39	3.296563	0.859862	1.163924	-0.30226	-0.01184

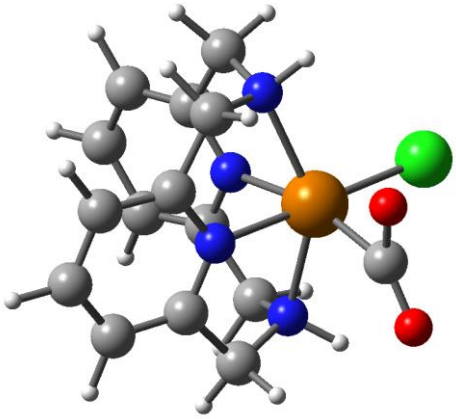
SCF Done: E(UB3P86) = −2678.29395482 A.U. after 1 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation 4.2368, after 3.7578

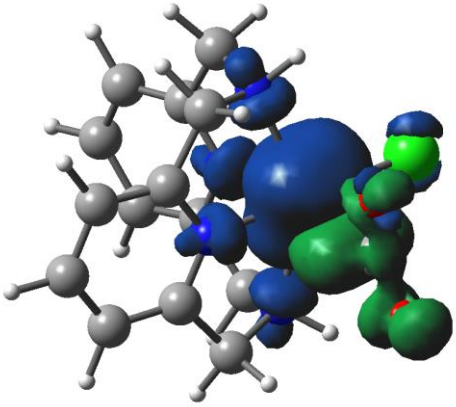
	1	2	3
	A	A	A
Frequencies --	−602.6013	35.8725	43.5869
Red. masses --	12.4583	9.8407	7.8746

Zero-point correction= 0.300990 (Hartree/Particle)
Thermal correction to Energy= 0.321964
Thermal correction to Enthalpy= 0.322908
Thermal correction to Gibbs Free Energy= 0.249099
Sum of electronic and zero-point Energies= −2677.992965
Sum of electronic and thermal Energies= −2677.971991
Sum of electronic and thermal Enthalpies= −2677.971047
Sum of electronic and thermal Free Energies= −2678.044856

Item	Value	Threshold	Converged?
Maximum Force	0.000010	0.000450	YES
RMS Force	0.000001	0.000300	YES

Table S11. DFT-optimized geometry of $Fe^{III}(dapp)(CO_2^{2-})Cl$ (quartet), computed at the UB3P86/6-31+G(d,p) level using C-PCM.





Spin Density Distribution

atom	x	y	z	Mulliken charge	Spin density
C1	-3.30465	-0.94757	-1.203	-0.29636	0.008434
C2	-1.9177	-1.04552	-1.16452	-0.04975	-0.02045
C3	-1.9178	-1.04557	1.164373	-0.19316	-0.01347
C4	-3.30474	-0.94761	1.202751	-0.29583	-0.00218
C5	-4.00863	-0.91216	-0.00015	-0.23581	-0.01437
H6	-3.81999	-0.8855	-2.15595	0.185183	0.000544
H7	-3.82016	-0.88558	2.155658	0.185548	0.000209
H8	-5.09069	-0.83066	-0.00019	0.188356	0.000711
C9	-0.78153	2.93436	-1.20016	-0.26485	-0.00739
C10	-0.09516	1.728713	-1.16638	0.030446	-0.0274
C11	-0.09524	1.728687	1.166455	0.276666	-0.01576
C12	-0.7816	2.934342	1.200216	-0.47113	0.001412
C13	-1.11376	3.566794	0.000023	-0.33444	-0.01808
H14	-1.06638	3.363163	-2.15599	0.1856	0.000359
H15	-1.06651	3.363128	2.156032	0.186156	0.000512
H16	-1.65197	4.508612	0.000015	0.189443	0.000835
N17	-1.25051	-1.1204	-5.1E-05	0.223723	0.024917
N18	0.284593	1.153278	0.000045	0.383816	0.029491
N19	0.254628	-0.48077	-2.18608	-0.47156	0.010593
H20	0.928245	-0.92379	-2.80195	0.38782	-0.00018
N21	0.254449	-0.48083	2.186117	-0.34761	0.009007
H22	0.928038	-0.92385	2.802025	0.391492	0.000273
C23	0.304672	0.974352	-2.40647	0.050656	0.016867
H24	-0.31687	1.28715	-3.25573	0.175157	0.001595
C25	-1.05946	-1.10485	2.403378	0.010671	0.016746
H26	-1.59535	-0.661	3.252576	0.176433	0.001626
C27	-1.05928	-1.10474	-2.40346	-0.04504	0.001603
H28	-0.87975	-2.1578	-2.64899	0.209087	-0.00041
H29	-1.59511	-0.6608	-3.25266	0.175572	0.001887
C30	0.304458	0.97428	2.40656	-0.21251	-0.02056
H31	-0.31721	1.287035	3.255746	0.175587	0.001289

H32	1.344756	1.21853	2.644643	0.219232	-0.00042
H33	1.345008	1.218596	-2.64439	0.210557	-0.00025
H34	-0.87991	-2.15793	2.648827	0.210052	-0.00023
Fe35	0.833921	-0.83794	0.00009	-0.51002	3.332831
Cl36	2.404374	-2.50003	-4.7E-05	-0.49897	0.036299
C37	3.071873	0.744593	0.000013	0.826579	-0.2313
O38	3.296771	0.860133	-1.16382	-0.45072	-0.03329
O39	3.296563	0.859862	1.163924	-0.57607	-0.09229

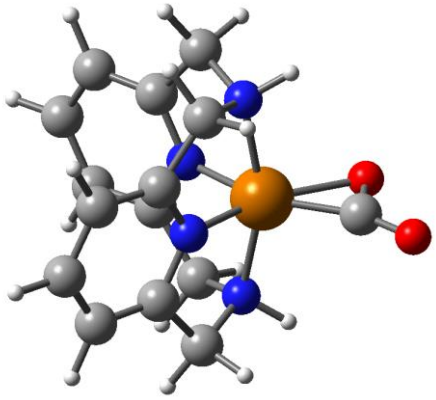
SCF Done: E(UB3P86) = −2678.31294332 A.U. after 1 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation 4.0264, after 3.7579

	1	2	3
	A	A	A
Frequencies --	38.4851	40.4455	47.3113
Red. masses --	7.1788	8.0255	7.5234

Zero-point correction= 0.303705 (Hartree/Particle)
Thermal correction to Energy= 0.324444
Thermal correction to Enthalpy= 0.325388
Thermal correction to Gibbs Free Energy= 0.252566
Sum of electronic and zero-point Energies= −2678.009238
Sum of electronic and thermal Energies= −2677.988499
Sum of electronic and thermal Enthalpies= −2677.987555
Sum of electronic and thermal Free Energies= −2678.060378

Item	Value	Threshold	Converged?
Maximum Force	0.000136	0.000450	YES
RMS Force	0.000018	0.000300	YES

Table S12. DFT-optimized geometry of $Fe^{II}(dapp)(CO_2^{2-})$ (singlet), computed at the RB3P86/6-31+G(d,p) level using C-PCM.



atom	x	y	z	Mulliken charge
C1	3.133544	-0.78953	1.207861	-0.41314
C2	1.746543	-0.86558	1.169731	0.193591
C3	1.747169	-0.86406	-1.16993	0.193474
C4	3.134196	-0.78793	-1.20721	-0.41318
C5	3.833031	-0.75271	0.000535	-0.27618
H6	3.655723	-0.75502	2.158156	0.182968
H7	3.656878	-0.75215	-2.15718	0.182967
H8	4.916171	-0.6899	0.000866	0.183222
C9	-0.08927	3.115115	1.20742	-0.51627
C10	-0.45666	1.777315	1.172895	0.03562
C11	-0.45613	1.778511	-1.17155	0.0353
C12	-0.08871	3.116342	-1.20451	-0.51616
C13	0.099339	3.794734	0.001843	-0.25313
H14	0.04853	3.61611	2.15996	0.180432
H15	0.049577	3.618309	-2.15647	0.180429
H16	0.391706	4.839299	0.002439	0.179536
N17	1.086982	-0.9023	-0.00031	0.364489
N18	-0.62674	1.129545	0.000306	0.440872
N19	-0.53643	-0.51723	2.024795	-0.52625
H20	-1.1885	-1.07391	2.570467	0.395173
N21	-0.53539	-0.51511	-2.02604	-0.52634
H22	-1.18696	-1.07126	-2.57284	0.395168
C23	-0.78609	0.911397	2.353031	0.054154
H24	-0.25067	1.226039	3.255616	0.176959
C25	0.837918	-0.98024	-2.36192	-0.11127
H26	1.243245	-0.4516	-3.23183	0.178158
C27	0.836557	-0.98317	2.36101	-0.11147
H28	0.75936	-2.04229	2.630833	0.207604
H29	1.241434	-0.4558	3.231899	0.178169
C30	-0.78517	0.91384	-2.35271	0.054545
H31	-0.2496	1.229575	-3.25483	0.176942
H32	-1.85905	1.003818	-2.55329	0.208222
H33	-1.86	1.001307	2.553518	0.208234

H34	0.761209	-2.03901	-2.63323	0.207589
Fe35	-0.83311	-0.71683	-0.00049	0.138065
C36	-2.56506	-1.40885	-0.00085	0.18011
O37	-3.81272	-1.36945	-0.00082	-0.78408
O38	-1.81657	-2.47821	-0.00123	-0.66452

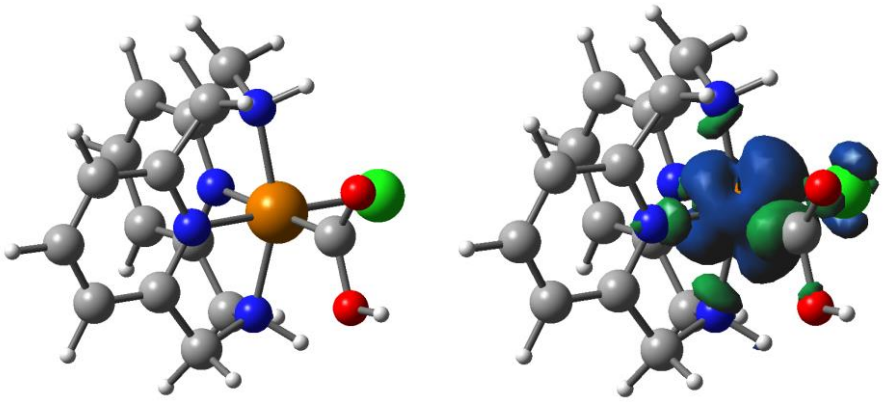
SCF Done: E(RB3P86) = −2217.71816647 A.U. after 2 cycles

	1	2	3
	A	A	A
Frequencies --	44.9789	47.3916	68.7391
Red. masses --	6.6765	6.7083	3.3354

Zero-point correction= 0.304370 (Hartree/Particle)
Thermal correction to Energy= 0.321651
Thermal correction to Enthalpy= 0.322595
Thermal correction to Gibbs Free Energy= 0.259916
Sum of electronic and zero-point Energies= −2217.413797
Sum of electronic and thermal Energies= −2217.396516
Sum of electronic and thermal Enthalpies= −2217.395571
Sum of electronic and thermal Free Energies= −2217.458250

Item	Value	Threshold	Converged?
Maximum Force	0.000027	0.000450	YES
RMS Force	0.000003	0.000300	YES

Table S13. DFT-optimized geometry of $[Fe^{III}(dapp)(CO_2H^-)Cl]^+$ (doublet), computed at the UB3P86/6-31+G(d,p) level using C-PCM.



Spin Density Distribution

atom	x	y	z	Mulliken charge	Spin density
C1	-3.359642	0.873972	-1.149826	-0.519617	-0.000582
C2	-2.119805	0.245942	-1.150592	-0.047803	-0.010481
C3	-2.106617	0.122495	1.188563	-0.085011	-0.007622
C4	-3.345499	0.74605	1.268916	-0.505387	-0.001329
C5	-3.968269	1.12487	0.07959	-0.264847	-0.00274
H6	-3.834812	1.161672	-2.08067	0.198789	-0.000022
H7	-3.809058	0.934329	2.230462	0.19874	-0.000082
H8	-4.9323	1.621328	0.111554	0.197748	0.000129
C9	1.609526	2.926645	-1.140562	-0.716913	0.004206
C10	1.2098	1.597898	-1.144734	0.358795	-0.003497
C11	1.195399	1.531929	1.200475	0.311648	-0.009829
C12	1.594645	2.860177	1.273755	-0.706441	0.001416
C13	1.803941	3.558414	0.086671	-0.378907	-0.008213
H14	1.759146	3.454265	-2.075401	0.201073	-0.000247
H15	1.732178	3.335584	2.238008	0.201078	-0.000224
H16	2.110151	4.598444	0.117377	0.20077	0.000328
N17	-1.538368	-0.101622	0.000157	0.374305	-0.009225
N18	1.020532	0.940461	0.009919	0.544749	-0.014541
N19	0.098587	-0.395923	-2.006755	-0.392247	-0.025801
H20	0.430154	-1.215974	-2.512427	0.430221	0.005971
N21	0.132534	-0.543247	1.949715	-0.374138	-0.029087
H22	0.514828	-1.3772	2.393141	0.426819	0.005817
C23	1.00205	0.736816	-2.353123	0.032581	-0.0067
H24	0.617469	1.306035	-3.202954	0.200752	-0.001009
C25	-1.305752	-0.432479	2.332945	0.102206	-0.003308
H26	-1.423379	0.157094	3.245687	0.199854	-0.001103
C27	-1.336935	-0.181684	-2.360191	0.011666	-0.001997
H28	-1.735203	-1.140284	-2.706503	0.232178	0.000002
H29	-1.432835	0.530936	-3.183197	0.199875	-0.001028
C30	0.975964	0.613939	2.365223	-0.016912	-0.000499
H31	0.533192	1.137227	3.216418	0.201439	-0.001195
H32	1.944279	0.216557	2.682951	0.238863	0.000014

H33	1.964501	0.304452	-2.642395	0.241907	-0.000038
H34	-1.663937	-1.445313	2.541969	0.233761	-0.000012
Fe35	0.29224	-0.833997	-0.047019	-0.344628	1.159629
Cl36	-0.512017	-2.938504	-0.113282	-0.245031	0.004528
C37	2.097921	-1.514648	-0.108581	0.637106	-0.038639
O38	2.726724	-1.747274	-1.13111	-0.509003	-0.002451
O39	2.660913	-1.751492	1.106771	-0.475948	0.002686
H40	3.557228	-2.110235	0.966554	0.405911	-0.003227

SCF Done: E(UB3P86) = −2678.76073513 A.U. after 1 cycles

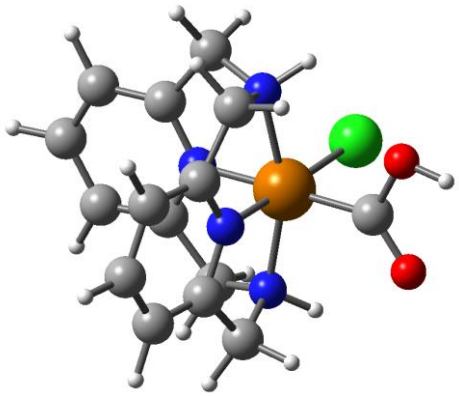
Annihilation of the first spin contaminant:
S**2 before annihilation 0.7989, after 0.7508

	1	2	3
	A	A	A
Frequencies --	33.4738	41.9887	57.9171
Red. masses --	5.0396	5.3597	9.4045

Zero-point correction= 0.319143 (Hartree/Particle)
Thermal correction to Energy= 0.338924
Thermal correction to Enthalpy= 0.339868
Thermal correction to Gibbs Free Energy= 0.270251
Sum of electronic and zero-point Energies= −2678.441593
Sum of electronic and thermal Energies= −2678.421811
Sum of electronic and thermal Enthalpies= −2678.420867
Sum of electronic and thermal Free Energies= −2678.490484

Item	Value	Threshold	Converged?
Maximum Force	0.000008	0.000450	YES
RMS Force	0.000002	0.000300	YES

Table S14. DFT-optimized geometry of $Fe^{II}(dapp)(CO_2H^-)Cl$ (singlet), computed at the RB3P86/6-31+G(d,p) level using C-PCM.



atom	x	y	z	Mulliken charge
C1	-3.364685	0.129187	-1.257077	-0.488681
C2	-2.029088	-0.252405	-1.189016	-0.087051
C3	-2.062583	-0.195309	1.150224	-0.093266
C4	-3.399581	0.188054	1.160171	-0.477917
C5	-4.050473	0.354622	-0.062785	-0.257397
H6	-3.85629	0.248324	-2.216596	0.18514
H7	-3.918931	0.353647	2.097946	0.185066
H8	-5.091493	0.660024	-0.085077	0.185001
C9	0.822961	3.162474	-1.23578	-0.496743
C10	0.788249	1.774258	-1.18112	0.181532
C11	0.774534	1.808123	1.160816	0.250397
C12	0.809135	3.196768	1.17674	-0.554294
C13	0.830941	3.879861	-0.039662	-0.415062
H14	0.840566	3.670323	-2.194148	0.183868
H15	0.815459	3.731593	2.120411	0.183939
H16	0.8507	4.964475	-0.055066	0.184446
N17	-1.417303	-0.391876	-0.006257	0.39239
N18	0.756124	1.132253	-0.001108	0.463174
N19	0.283577	-0.481838	-1.999668	-0.428024
H20	0.810155	-1.192698	-2.49962	0.398781
N21	0.225198	-0.412792	2.035898	-0.426406
H22	0.723946	-1.120307	2.568275	0.401632
C23	0.857499	0.839805	-2.355787	0.012483
H24	0.377401	1.269801	-3.241814	0.176384
C25	-1.221098	-0.509241	2.359518	0.055556
H26	-1.489496	0.124215	3.212138	0.177125
C27	-1.151374	-0.625798	-2.354098	0.102425
H28	-1.323733	-1.683995	-2.57657	0.213178
H29	-1.408341	-0.054859	-3.253064	0.176815
C30	0.826972	0.904007	2.359748	0.01418
H31	0.359615	1.366166	3.236282	0.175594
H32	1.879167	0.718043	2.597577	0.219664
H33	1.912828	0.674187	-2.595742	0.215798
H34	-1.421321	-1.546511	2.647761	0.211934

Fe35	0.480868	-0.725516	0.029133	-0.679123
Cl36	0.046519	-3.074247	0.066617	-0.50104
C37	2.37111	-1.095911	0.121027	0.691524
O38	3.024499	-1.26153	-1.099666	-0.4979
O39	3.09316	-1.221752	1.119863	-0.606003
H40	3.956829	-1.461768	-0.893771	0.370884

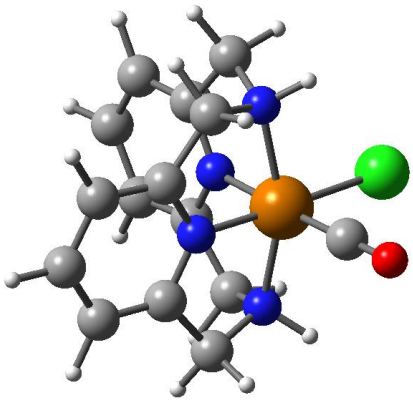
SCF Done: E(RB3P86) = −2678.93148253 A.U. after 1 cycles

	1	2	3
	A	A	A
Frequencies --	46.4665	50.1888	59.2760
Red. masses --	5.2869	10.4590	4.2778

Zero-point correction= 0.317155 (Hartree/Particle)
Thermal correction to Energy= 0.336967
Thermal correction to Enthalpy= 0.337911
Thermal correction to Gibbs Free Energy= 0.269212
Sum of electronic and zero-point Energies= −2678.614327
Sum of electronic and thermal Energies= −2678.594515
Sum of electronic and thermal Enthalpies= −2678.593571
Sum of electronic and thermal Free Energies= −2678.662271

Item	Value	Threshold	Converged?
Maximum Force	0.000030	0.000450	YES
RMS Force	0.000003	0.000300	YES

Table S15. DFT-optimized geometry of $[Fe^{II}(dapp)(CO)Cl]^{+}$ (singlet), computed at the RB3P86/6-31+G(d,p) level using C-PCM.



atom	x	y	z	Mulliken charge
C1	2.395667	-2.186789	-1.198469	-0.528417
C2	1.620524	-1.034089	-1.165143	0.010283
C3	1.61598	-1.02692	1.175161	0.008186
C4	2.390935	-2.179427	1.218684	-0.528008
C5	2.773385	-2.764631	0.01262	-0.255046
H6	2.695857	-2.619842	-2.145859	0.196799
H7	2.687448	-2.60677	2.169811	0.196807
H8	3.370698	-3.670207	0.016582	0.196456
C9	-2.792328	-1.725794	-1.20808	-0.279188
C10	-1.844839	-0.710621	-1.17405	-0.109614
C11	-1.849058	-0.702623	1.171453	-0.111609
C12	-2.796734	-1.717553	1.208875	-0.280982
C13	-3.267466	-2.230672	0.001281	-0.265848
H14	-3.146497	-2.112924	-2.156599	0.197958
H15	-3.15437	-2.098266	2.158691	0.197959
H16	-4.002868	-3.028061	0.002647	0.19746
N17	1.239978	-0.502569	0.002515	0.439889
N18	-1.401408	-0.235772	-0.002061	0.423954
N19	0.032769	0.635066	-2.009258	-0.541984
H20	0.118439	1.492039	-2.549866	0.417211
N21	0.025344	0.648464	2.004161	-0.539627
H22	0.109561	1.508274	2.540541	0.417122
C23	-1.271777	0.007928	-2.362031	0.053751
H24	-1.175955	-0.653474	-3.227978	0.197185
C25	1.200989	-0.196418	2.352924	0.05994
H26	1.004367	-0.8058	3.2397	0.194391
C27	1.209692	-0.211412	-2.349246	0.059511
H28	2.036115	0.465044	-2.589546	0.230231
H29	1.016092	-0.826576	-3.232652	0.194386
C30	-1.280422	0.023803	2.356671	0.054493
H31	-1.187617	-0.632013	3.227171	0.197204
H32	-1.969255	0.830153	2.629752	0.226694
H33	-1.959644	0.812553	-2.642515	0.226538

H34	2.026986	0.481214	2.59157	0.230196
Fe35	0.03656	1.009079	-0.004044	0.392037
C36	-1.003376	2.459186	-0.009394	-0.041321
O37	-1.66047	3.404812	0.002682	-0.345935
Cl38	1.881178	2.432351	-0.006048	-0.389062

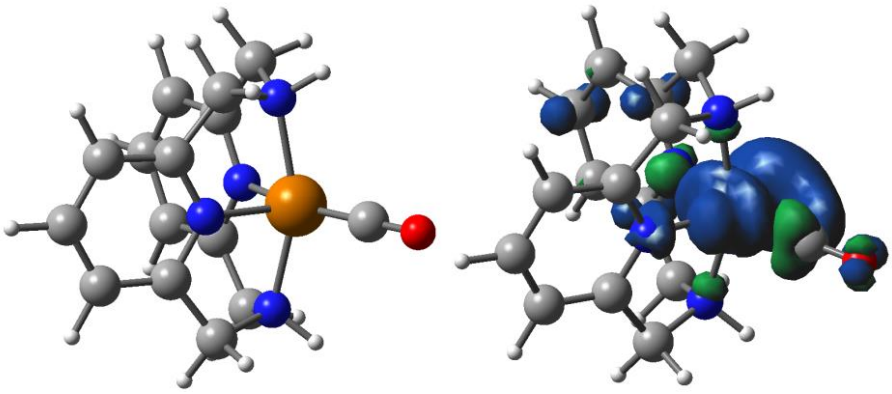
SCF Done: E(RB3P86) = −2602.78460827 A.U. after 2 cycles

	1	2	3
	A	A	A
Frequencies --	47.9547	61.2224	68.5696
Red. masses --	5.2153	3.2481	8.2897

Zero-point correction= 0.304674 (Hartree/Particle)
Thermal correction to Energy= 0.322719
Thermal correction to Enthalpy= 0.323663
Thermal correction to Gibbs Free Energy= 0.259069
Sum of electronic and zero-point Energies= −2602.479935
Sum of electronic and thermal Energies= −2602.461889
Sum of electronic and thermal Enthalpies= −2602.460945
Sum of electronic and thermal Free Energies= −2602.525540

Item	Value	Threshold	Converged?
Maximum Force	0.000114	0.000450	YES
RMS Force	0.000020	0.000300	YES

Table S16. DFT-optimized geometry of $[Fe^{I}(dapp)(CO)]^{+}$ (doublet), computed at the UB3P86/6-31+G(d,p) level using C-PCM.



Spin Density Distribution

atom	x	y	z	Mulliken charge	Spin density
C1	-3.171403	-0.225529	1.20821	-0.281939	-0.02985
C2	-1.906221	0.346572	1.170033	-0.002176	0.069916
C3	-1.905882	0.344675	-1.170903	-0.001835	0.069858
C4	-3.171054	-0.227505	-1.208509	-0.28214	-0.029862
C5	-3.807388	-0.510428	-0.000012	-0.292254	0.051244
H6	-3.645275	-0.448698	2.157579	0.192393	0.000872
H7	-3.644654	-0.452221	-2.157649	0.192392	0.000872
H8	-4.793884	-0.961886	0.000214	0.192771	-0.00213
C9	1.250922	-2.762165	1.211879	-0.253913	-0.007812
C10	1.137721	-1.377167	1.170214	-0.140695	-0.01505
C11	1.138266	-1.378631	-1.168204	-0.140722	-0.015032
C12	1.251473	-2.763674	-1.208098	-0.2538	-0.007806
C13	1.315188	-3.455746	0.00234	-0.255199	-0.01504
H14	1.279279	-3.287004	2.160589	0.189288	0.000292
H15	1.28026	-3.289693	-2.15614	0.189288	0.000292
H16	1.398631	-4.537483	0.003033	0.189043	0.000631
N17	-1.309977	0.623305	-0.000578	0.268497	-0.042701
N18	1.102245	-0.729471	0.000595	0.349237	0.028075
N19	0.354555	0.808903	2.016336	-0.500401	0.02082
H20	0.767496	1.54759	2.577997	0.403694	0.000437
N21	0.355061	0.806178	-2.01739	-0.500426	0.020826
H22	0.767858	1.544238	-2.579984	0.40369	0.000437
C23	1.091577	-0.446002	2.351258	0.025652	0.015159
H24	0.665653	-0.932469	3.234357	0.186411	-0.000423
C25	-1.093468	0.762766	-2.362116	-0.055304	-0.047116
H26	-1.282003	0.117861	-3.226265	0.186895	-0.000285
C27	-1.094067	0.766545	2.360752	-0.055171	-0.047158
H28	-1.390686	1.783607	2.638815	0.218442	0.001965
H29	-1.283053	0.123255	3.226006	0.186892	-0.000285
C30	1.092646	-0.448903	-2.350389	0.025701	0.015131
H31	0.667455	-0.936527	-3.233198	0.186411	-0.000423
H32	2.119549	-0.158306	-2.596879	0.217199	-0.000574

H33	2.118403	-0.155445	2.598113	0.217201	-0.000575
H34	-1.390343	1.779218	-2.642124	0.218442	0.001965
Fe35	0.561683	1.156239	-0.000741	0.796934	1.04277
C36	1.996506	2.163717	-0.001125	-0.584646	-0.079259
O37	2.937435	2.863524	-0.00124	-0.435853	-0.00018

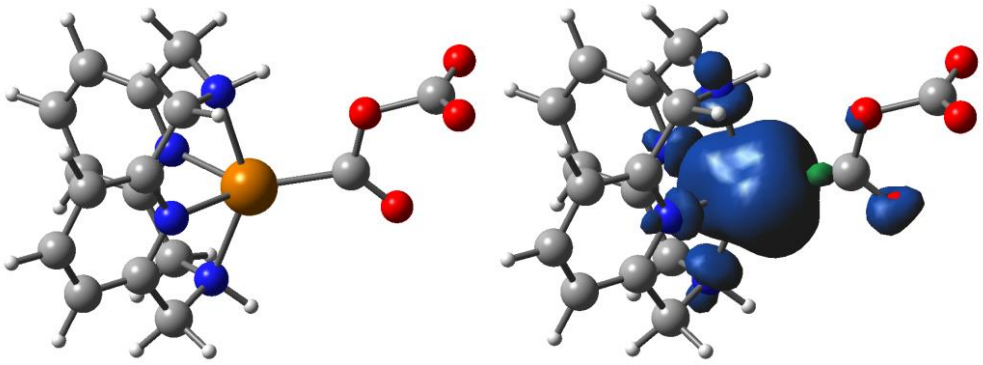
SCF Done: E(UB3P86) = −2142.18106695 A.U. after 2 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation 0.7650, after 0.7502

	1	2	3
	A	A	A
Frequencies --	45.0671	54.1147	61.3684
Red. masses --	5.2514	9.2569	3.2576

Zero-point correction= 0.301476 (Hartree/Particle)
Thermal correction to Energy= 0.317993
Thermal correction to Enthalpy= 0.318937
Thermal correction to Gibbs Free Energy= 0.257069
Sum of electronic and zero-point Energies= −2141.879591
Sum of electronic and thermal Energies= −2141.863074
Sum of electronic and thermal Enthalpies= −2141.862130
Sum of electronic and thermal Free Energies= −2141.923998

Item	Value	Threshold	Converged?
Maximum Force	0.000089	0.000450	YES
RMS Force	0.000007	0.000300	YES

Table S17. DFT-optimized geometry of Fe^{II}(dapp)($CO_2CO_2^{2-}$-*C*) (quintet), computed at the UB3P86/6-31+G(d,p) level using C-PCM.



Spin Density Distribution

atom	x	y	z	Mulliken charge	Spin density
C1	-2.984658	-2.511521	-0.531714	-0.230834	-0.018453
C2	-1.880258	-1.748886	-0.897826	0.132108	0.002236
C3	-1.068102	-1.753373	1.288236	0.162815	-0.006605
C4	-2.144023	-2.518865	1.726651	-0.37847	-0.010864
C5	-3.102982	-2.913289	0.796713	-0.238577	0.021077
H6	-3.740719	-2.768889	-1.265484	0.189514	0.001024
H7	-2.237382	-2.782289	2.774662	0.189518	0.000994
H8	-3.956249	-3.504976	1.112106	0.192965	-0.000792
C9	-2.985156	2.510953	-0.532599	-0.231111	-0.018465
C10	-1.880817	1.74809	-0.898453	0.132828	0.002119
C11	-1.068236	1.754007	1.287456	0.162565	-0.006525
C12	-2.144071	2.519752	1.725597	-0.378734	-0.010861
C13	-3.103214	2.913583	0.795585	-0.238512	0.021068
H14	-3.741348	2.767874	-1.266389	0.189513	0.001024
H15	-2.23716	2.783925	2.773442	0.189517	0.000994
H16	-3.956397	3.505517	1.11074	0.192963	-0.000792
N17	-0.938807	-1.420737	-0.003352	0.524291	0.00749
N18	-0.939199	1.420573	-0.003968	0.524436	0.007504
N19	-0.866135	-0.000583	-2.331826	-0.379877	0.041917
H20	-0.307181	-0.000537	-3.179038	0.390991	-0.000599
N21	0.61509	0.000507	1.711428	-0.369652	0.009429
H22	1.618303	0.000518	1.874412	0.402414	-0.000744
C23	-1.651299	1.247431	-2.304935	-0.163074	0.009814
H24	-2.611818	1.135348	-2.82176	0.180155	0.001379
C25	0.021739	-1.246761	2.206242	-0.119586	-0.011375
H26	-0.371307	-1.142007	3.224974	0.175777	0.001956
C27	-1.650355	-1.249174	-2.304561	-0.162529	0.009728
H28	-1.0778	-2.007183	-2.849863	0.212973	0.000327
H29	-2.610623	-1.138291	-2.82209	0.180148	0.001378
C30	0.021889	1.248116	2.205518	-0.119259	-0.011434
H31	-0.370889	1.144115	3.224432	0.175776	0.001955
H32	0.816054	2.001692	2.245395	0.20813	0.00035
H33	-1.079781	2.005489	-2.851237	0.212977	0.000326

H34	0.815886	-2.000308	2.246867	0.20813	0.00035
Fe35	0.522267	-0.000043	-0.559431	-0.441574	3.9256
C36	2.585108	0.000171	-0.860071	-0.029311	-0.030985
O37	3.207451	0.000413	-1.924299	-0.586368	0.028161
O38	3.277909	-0.000244	0.319631	-0.32669	0.009088
C39	4.761694	-0.000045	0.263451	0.597204	0.01842
O40	5.258025	-1.13363	0.278872	-0.666735	0.001393
O41	5.257773	1.133666	0.277836	-0.666818	0.001393

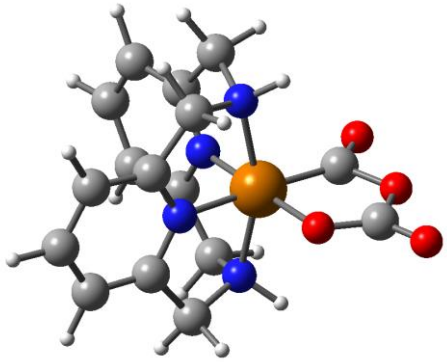
SCF Done: E(UB3P86) = −2406.69838440 A.U. after 2 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation 6.0153, after 6.0001

	1	2	3
	A	A	A
Frequencies --	21.9549	28.3525	32.6651
Red. masses --	8.8486	13.5486	6.3558

Zero-point correction= 0.315279 (Hartree/Particle)
Thermal correction to Energy= 0.337223
Thermal correction to Enthalpy= 0.338168
Thermal correction to Gibbs Free Energy= 0.260350
Sum of electronic and zero-point Energies= −2406.383105
Sum of electronic and thermal Energies= −2406.361161
Sum of electronic and thermal Enthalpies= −2406.360217
Sum of electronic and thermal Free Energies= −2406.438035

Item	Value	Threshold	Converged?
Maximum Force	0.000033	0.000450	YES
RMS Force	0.000004	0.000300	YES

Table S18. DFT-optimized geometry of Fe^{II}(dapp)($CO_2CO_2^{2-}$-*C,O*) (singlet), computed at the RB3P86/6-31+G(d,p) level using C-PCM.



atom	x	y	z	Mulliken charge
C1	2.116715	2.758383	-1.20789	-0.69707
C2	1.077535	1.835541	-1.168549	-0.058855
C3	1.077405	1.835603	1.168598	-0.058885
C4	2.116576	2.758462	1.207996	-0.696972
C5	2.639638	3.219689	0.000071	-0.198857
H6	2.508904	3.105719	-2.157484	0.187005
H7	2.508647	3.105861	2.157615	0.187005
H8	3.455235	3.935287	0.000098	0.186653
C9	2.415927	-2.425757	-1.206622	-0.722939
C10	1.267063	-1.645177	-1.169773	0.049039
C11	1.266981	-1.645059	1.16986	0.048813
C12	2.415858	-2.425602	1.206871	-0.723203
C13	2.995705	-2.817452	0.000163	-0.257989
H14	2.84811	-2.7183	-2.157481	0.186095
H15	2.847997	-2.718015	2.15779	0.186094
H16	3.896261	-3.422401	0.000227	0.185679
N17	0.591412	1.396288	0.000016	0.032455
N18	0.726196	-1.268299	0.000001	0.204985
N19	-0.336221	0.008924	-2.021309	-0.563499
H20	-1.189802	-0.031745	-2.570924	0.397809
N21	-0.336444	0.009025	2.021262	-0.563532
H22	-1.190039	-0.031662	2.570854	0.397805
C23	0.463532	-1.198421	-2.357906	0.082022
H24	1.095566	-1.035435	-3.237304	0.182096
C25	0.338646	1.291072	2.359275	0.045529
H26	0.995329	1.184348	3.229267	0.182306
C27	0.338866	1.290993	-2.35927	0.045662
H28	-0.443872	2.007304	-2.630043	0.211197
H29	0.995594	1.184307	-3.229232	0.182309
C30	0.463275	-1.198326	2.35788	0.082418
H31	1.095162	-1.035429	3.237401	0.182092
H32	-0.246931	-1.994248	2.606122	0.215718
H33	-0.24663	-1.994316	-2.606346	0.215711
H34	-0.44408	2.007402	2.630031	0.211192

Fe35	-0.702482	-0.045397	-0.000118	1.865462
C36	-2.079038	-1.352342	-0.000051	0.148717
O37	-2.163373	-2.573278	0.000156	-0.583508
O38	-2.22151	1.201099	-0.000302	-0.810343
C39	-3.375404	0.649695	-0.000077	0.956678
O40	-3.391772	-0.727168	-0.000029	-0.439772
O41	-4.469748	1.227128	0.000079	-0.683121

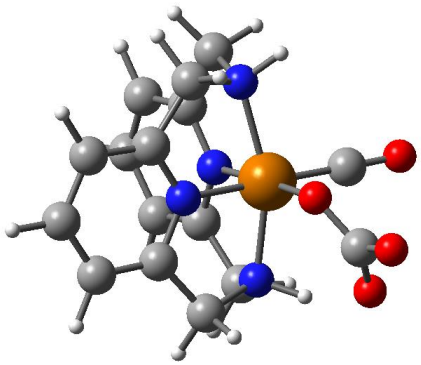
SCF Done: E(RB3P86) = −2406.74140051 A.U. after 2 cycles

	1	2	3
	A	A	A
Frequencies --	46.4264	46.8668	56.2805
Red. masses --	5.4797	9.3681	7.5621

Zero-point correction= 0.319924 (Hartree/Particle)
Thermal correction to Energy= 0.339526
Thermal correction to Enthalpy= 0.340470
Thermal correction to Gibbs Free Energy= 0.272616
Sum of electronic and zero-point Energies= −2406.421476
Sum of electronic and thermal Energies= −2406.401875
Sum of electronic and thermal Enthalpies= −2406.400931
Sum of electronic and thermal Free Energies= −2406.468784

Item	Value	Threshold	Converged?
Maximum Force	0.000025	0.000450	YES
RMS Force	0.000002	0.000300	YES

Table S19. DFT-optimized geometry of $[Fe^{II}(dapp)(CO)Cl]^{+}$ (singlet), computed at the RB3P86/6-31+G(d,p) level using C-PCM.



atom	x	y	z	Mulliken charge
C1	0.16623	-3.125175	1.576103	-0.949212
C2	-0.187124	-1.816254	1.265288	0.215396
C3	0.340042	-2.145319	-0.990634	-0.085027
C4	0.713258	-3.462749	-0.753844	-0.657482
C5	0.62882	-3.948085	0.550803	-0.279949
H6	0.080421	-3.490518	2.593305	0.191399
H7	1.057291	-4.091848	-1.567004	0.191175
H8	0.919551	-4.970844	0.766989	0.191375
C9	2.984033	1.367969	1.702557	-0.400821
C10	1.655998	1.196279	1.332748	-0.016257
C11	2.268562	0.786007	-0.897225	-0.025422
C12	3.616426	0.94245	-0.594355	-0.327001
C13	3.969038	1.233076	0.7232	-0.298735
H14	3.242807	1.597057	2.730303	0.192302
H15	4.370079	0.83907	-1.366982	0.192062
H16	5.014242	1.353435	0.988132	0.19168
N17	-0.075615	-1.36263	0.011405	0.313246
N18	1.342949	0.904448	0.060908	0.178425
N19	-0.675862	0.558728	1.653773	-0.490612
H20	-1.62356	1.005985	1.694696	0.449172
N21	0.307443	-0.001219	-2.180683	-0.61003
H22	-0.232225	0.391853	-2.946604	0.413814
C23	0.43719	1.353939	2.207179	-0.036179
H24	0.65293	1.093056	3.248322	0.184182
C25	0.261823	-1.479111	-2.332872	0.141732
H26	1.040085	-1.836778	-3.014469	0.188659
C27	-0.787696	-0.809463	2.204358	-0.117955
H28	-1.856346	-1.032794	2.30212	0.216385
H29	-0.349761	-0.877732	3.205303	0.181687
C30	1.684582	0.56407	-2.267121	-0.045241
H31	2.334081	-0.064939	-2.883661	0.190819
H32	1.610485	1.537127	-2.764646	0.221119
H33	0.136621	2.408209	2.192273	0.212543
H34	-0.706398	-1.729615	-2.777679	0.21908

Fe35	-0.475062	0.500859	-0.338604	1.616708
C36	-0.946547	2.175923	-0.68947	-0.045699
O37	-1.29133	3.245362	-0.956873	-0.350749
O38	-2.309371	-0.047819	-0.710746	-0.701227
C39	-3.359953	0.384162	-0.017564	0.851879
O40	-4.509096	0.029543	-0.419155	-0.773975
O41	-3.177603	1.128582	1.020598	-0.733268

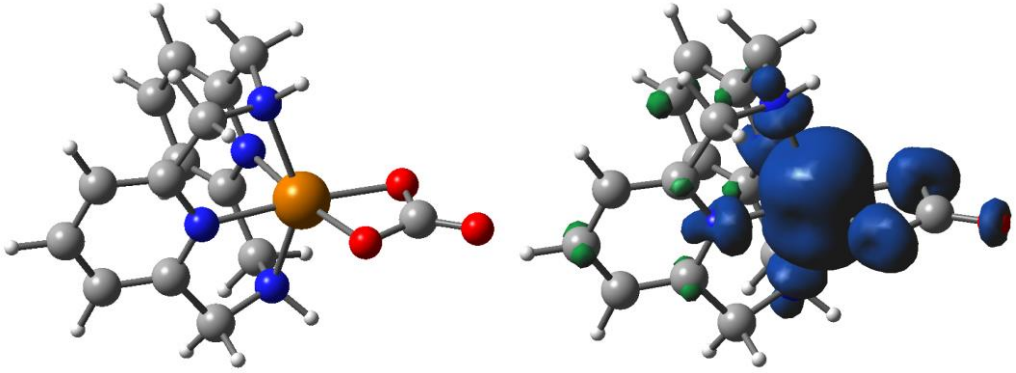
SCF Done: E(RB3P86) = −2406.73614415 A.U. after 2 cycles

	1	2	3
	A	A	A
Frequencies --	43.1879	48.1420	62.2576
Red. masses --	5.8146	7.3005	3.7835

Zero-point correction= 0.318366 (Hartree/Particle)
Thermal correction to Energy= 0.338606
Thermal correction to Enthalpy= 0.339550
Thermal correction to Gibbs Free Energy= 0.269932
Sum of electronic and zero-point Energies= −2406.417778
Sum of electronic and thermal Energies= −2406.397538
Sum of electronic and thermal Enthalpies= −2406.396594
Sum of electronic and thermal Free Energies= −2406.466212

Item	Value	Threshold	Converged?
Maximum Force	0.000026	0.000450	YES
RMS Force	0.000003	0.000300	YES

Table S20. DFT-optimized geometry of $Fe^{II}(dapp)(CO_3^{2-})$ (quintet), computed at the UB3P86/6-31+G(d,p) level using C-PCM.



Spin Density Distribution

atom	x	y	z	Mulliken charge	Spin density
C1	2.25242	2.371908	-1.203243	-0.34164	-0.00379
C2	1.038879	1.692071	-1.162701	0.079987	-0.04646
C3	1.038995	1.691119	1.163842	0.079824	-0.046384
C4	2.25255	2.370909	1.20481	-0.341648	-0.003775
C5	2.856199	2.728369	0.000899	-0.190199	-0.028356
H6	2.720164	2.601883	-2.15468	0.184968	0.000222
H7	2.720396	2.600098	2.156386	0.184968	0.000223
H8	3.804524	3.255719	0.001067	0.188426	0.001394
C9	2.252404	-2.371059	-1.204764	-0.341765	-0.003773
C10	1.038925	-1.691134	-1.163828	0.07986	-0.04639
C11	1.038742	-1.692089	1.162716	0.080017	-0.046462
C12	2.252205	-2.372064	1.203291	-0.341762	-0.003786
C13	2.855979	-2.728587	-0.000836	-0.190174	-0.028356
H14	2.72025	-2.600303	-2.156326	0.184968	0.000223
H15	2.719896	-2.602099	2.154739	0.184969	0.000222
H16	3.804242	-3.256049	-0.000976	0.188426	0.001394
N17	0.44549	1.395611	0.000481	0.17574	0.040537
N18	0.445424	-1.395558	-0.000484	0.175812	0.040541
N19	-0.467434	0.000809	-2.156226	-0.446752	0.001667
H20	-1.274736	0.000956	-2.772303	0.386813	-0.00018
N21	-0.467491	-0.000723	2.156199	-0.44675	0.001669
H22	-1.274814	-0.000827	2.77225	0.386812	-0.00018
C23	0.28776	-1.24539	-2.394912	-0.100181	0.019511
H24	0.975018	-1.145914	-3.243467	0.178226	0.002017
C25	0.287755	1.24544	2.394902	-0.100191	0.01951
H26	0.974972	1.145941	3.243488	0.178225	0.002017
C27	0.287541	1.24731	-2.39403	-0.100263	0.019581
H28	-0.441443	2.022014	-2.655525	0.20944	-0.000556
H29	0.974653	1.148637	-3.242796	0.178225	0.002018
C30	0.287415	-1.24726	2.394028	-0.100255	0.01958
H31	0.974526	-1.14861	3.242798	0.178227	0.002017
H32	-0.44161	-2.021922	2.655533	0.20944	-0.000557
H33	-0.441058	-2.019982	-2.657204	0.20944	-0.000557

H34	-0.441036	2.020072	2.657148	0.209439	-0.000557
Fe35	-1.169954	0.000056	-0.000024	0.161456	3.914827
O36	-2.910538	1.100733	0.000242	-0.735761	0.063143
C37	-3.638113	0.000022	-0.000017	1.027677	0.030533
O38	-4.889574	0.00001	0.000005	-0.788288	0.014132
O39	-2.910515	-1.100671	-0.000279	-0.735755	0.063143

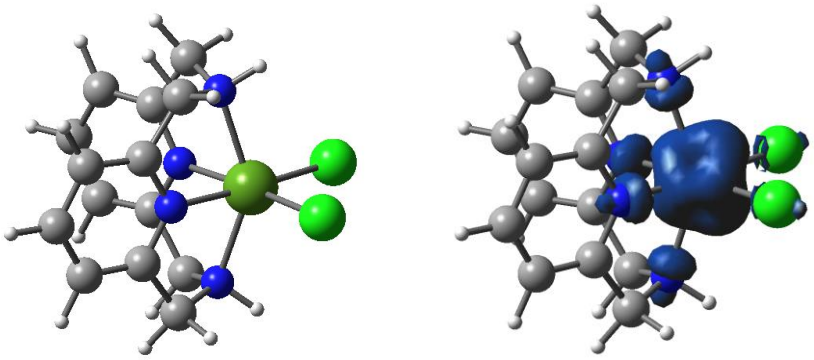
SCF Done: E(UB3P86) = −2293.15781537 A.U. after 2 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation 6.0454, after 6.0002

	1	2	3
	A	A	A
Frequencies --	34.6675	36.4974	42.3662
Red. masses --	9.0843	7.9811	5.1465

Zero-point correction= 0.307636 (Hartree/Particle)
Thermal correction to Energy= 0.326881
Thermal correction to Enthalpy= 0.327825
Thermal correction to Gibbs Free Energy= 0.257748
Sum of electronic and zero-point Energies= −2292.850179
Sum of electronic and thermal Energies= −2292.830934
Sum of electronic and thermal Enthalpies= −2292.829990
Sum of electronic and thermal Free Energies= −2292.900068

Item	Value	Threshold	Converged?
Maximum Force	0.000051	0.000450	YES
RMS Force	0.000007	0.000300	YES

Table S21. DFT-optimized geometry of $Co^{II}(dapp)Cl_2$ (quartet), computed at the UB3P86/6-31+G(d,p) level using C-PCM.



Spin Density Distribution

atom	x	y	z	Mulliken charge	Spin density
Co1	-1.185815	-0.001913	-0.00039	-0.192825	2.695849
C2	0.961265	1.733385	1.162414	-0.152187	-0.005126
N3	0.394909	1.40254	-0.000454	0.459852	0.061532
N4	-0.510796	-0.001464	-2.119104	-0.400979	0.034092
H5	-1.349976	-0.002885	-2.690516	0.387235	-0.000288
C6	2.131917	2.485718	1.20506	-0.319179	-0.005748
H7	2.584075	2.74623	2.1561	0.186656	0.000702
N8	0.399932	-1.400762	0.000439	0.460338	0.061542
C9	2.713067	2.874287	-0.000204	-0.248598	-0.005582
H10	3.629417	3.45569	-0.000104	0.189226	0.000341
C11	2.132944	2.484514	-1.205561	-0.319162	-0.005741
H12	2.585894	2.744087	-2.156481	0.186658	0.000702
N13	-0.511559	-0.000093	2.118825	-0.400968	0.034043
H14	-1.351013	-0.001836	2.689831	0.387219	-0.000288
C15	0.962239	1.732229	-1.163149	-0.15192	-0.005177
C16	0.227494	1.246028	-2.388562	0.03524	0.003903
H17	0.921022	1.135624	-3.230423	0.177018	0.001461
H18	-0.507698	2.006386	-2.672592	0.211443	-0.000242
C19	0.23115	-1.246943	-2.387796	0.035044	0.003888
H20	0.924151	-1.135095	-3.229903	0.17703	0.00146
C21	0.967667	-1.730005	-1.162209	-0.151684	-0.005155
C22	2.140414	-2.479095	-1.204411	-0.319815	-0.005776
H23	2.593653	-2.738386	-2.155271	0.18666	0.000702
C24	2.722162	-2.866066	0.001076	-0.248334	-0.00558
H25	3.640072	-3.445001	0.001325	0.18922	0.000341
C26	2.140509	-2.477893	1.206201	-0.320183	-0.005747
C27	0.967736	-1.728844	1.163351	-0.151233	-0.005174
C28	0.225552	1.248203	2.387648	0.035257	0.00387
H29	0.918269	1.139301	3.230376	0.176994	0.001459
H30	2.593808	-2.736224	2.157294	0.186659	0.000702
C31	0.231324	-1.244751	2.388617	0.034588	0.003911
H32	-0.500994	-2.007702	2.673104	0.211441	-0.000242
H33	0.924577	-1.131473	3.230328	0.177027	0.001459

Cl34	-2.812639	1.774173	-0.000852	-0.56835	0.072185
H35	-0.510516	2.008351	2.669958	0.211459	-0.00024
Cl36	-2.805945	-1.783696	0.000604	-0.568298	0.072204
H37	-0.50184	-2.009689	-2.671093	0.211451	-0.000242

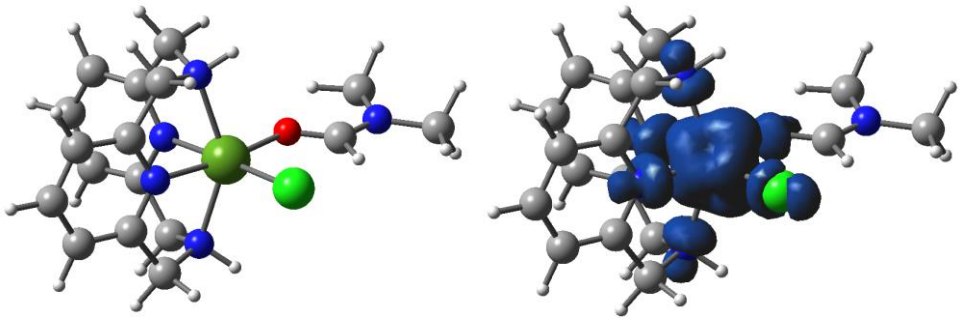
SCF Done: E(UB3P86) = −3068.99625678 A.U. after 1 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation 3.7583, after 3.7500

	1	2	3
	A	A	A
Frequencies --	14.1515	38.7184	41.5922
Red. masses --	15.9957	5.1958	8.4884

Zero-point correction= 0.293124 (Hartree/Particle)
Thermal correction to Energy= 0.312434
Thermal correction to Enthalpy= 0.313378
Thermal correction to Gibbs Free Energy= 0.242334
Sum of electronic and zero-point Energies= −3068.703133
Sum of electronic and thermal Energies= −3068.683823
Sum of electronic and thermal Enthalpies= −3068.682879
Sum of electronic and thermal Free Energies= −3068.753923

Item	Value	Threshold	Converged?
Maximum Force	0.000008	0.000450	YES
RMS Force	0.000002	0.000300	YES

T**able S22**. DFT-optimized geometry of $[Co^{II}(dapp)(DMF)Cl]^{+}$ (quartet), computed at the UB3P86/6-31+G(d,p) level using C-PCM.



Spin Density Distribution

atom	x	y	z	Mulliken charge	Spin density
Co1	0.36073	-0.52362	0.2397	-0.245325	2.778584
C2	0.92331	-2.39657	2.50236	-0.038658	-0.005971
N3	1.10869	-2.25079	1.18743	0.367923	0.057372
N4	0.65088	-1.91987	-1.45489	-0.404383	0.032545
H5	1.07392	-1.39539	-2.21451	0.387518	-0.000337
C6	1.18428	-3.60799	3.13631	-0.386377	-0.011508
H7	1.02825	-3.71424	4.20441	0.187882	0.00073
N8	-1.44736	-1.58044	0.2114	0.141642	0.058424
C9	1.62631	-4.67863	2.36247	-0.223134	-0.003995
H10	1.83105	-5.63774	2.82699	0.190473	0.000292
C11	1.76897	-4.52469	0.9851	-0.45913	-0.012469
H12	2.07436	-5.3539	0.3561	0.188002	0.000708
N13	-0.36104	-0.29577	2.32615	-0.41781	0.032293
H14	-0.20412	0.66947	2.59973	0.387384	-0.000389
C15	1.48862	-3.28125	0.42631	-0.004225	-0.007898
C16	1.59591	-2.97796	-1.048	0.022139	0.001988
H17	1.45889	-3.89261	-1.63621	0.17998	0.001577
H18	2.60688	-2.61038	-1.25281	0.208467	-0.000118
C19	-0.67197	-2.39235	-1.90871	-0.011666	0.002677
H20	-0.60512	-3.36143	-2.41623	0.179567	0.001475
C21	-1.65929	-2.46182	-0.76915	-0.086456	-0.01513
C22	-2.73121	-3.34837	-0.71882	-0.303205	-0.00318
H23	-2.89348	-4.06167	-1.51961	0.188389	0.000671
C24	-3.5718	-3.30773	0.39146	-0.216858	-0.004255
H25	-4.41181	-3.99101	0.46272	0.190796	0.000358
C26	-3.31113	-2.41149	1.42614	-0.324924	-0.005979
C27	-2.21912	-1.55786	1.30144	-0.041762	-0.01713
C28	0.43277	-1.16201	3.21882	-0.005127	0.002484
H29	-0.12961	-1.44216	4.11694	0.180907	0.001593
H30	-3.93029	-2.38644	2.31635	0.188226	0.00065
C31	-1.81723	-0.53828	2.33855	-0.032903	0.005618
H32	-2.3054	0.41083	2.09336	0.214343	-0.000241
H33	-2.17054	-0.84106	3.33093	0.179272	0.001417
H34	1.30191	-0.58488	3.55172	0.208021	-0.000168

Cl35	-0.56285	1.41807	-0.78579	-0.542072	0.071398
H36	-1.04315	-1.66751	-2.64098	0.213004	-0.000255
O37	2.31096	0.23451	0.31733	-0.502322	0.019906
C38	2.66688	1.40101	0.03333	0.478636	0.014604
H39	1.932	2.14065	-0.30427	0.155372	0.001436
N40	3.92021	1.83282	0.10836	0.112725	0.000086
C41	5.00328	0.96455	0.53577	-0.361378	-0.000049
C42	4.26459	3.20085	-0.23834	-0.263272	-0.000135
H43	5.74661	0.87921	-0.26222	0.184411	0.000065
H44	5.48534	1.38423	1.42341	0.183648	0.000044
H45	4.59992	-0.01954	0.76751	0.200024	0.000026
H46	3.36881	3.7407	-0.54728	0.178855	-0.000006
H47	4.70617	3.70649	0.62511	0.186835	0.000108
H48	4.9868	3.20826	-1.05969	0.186545	0.000083

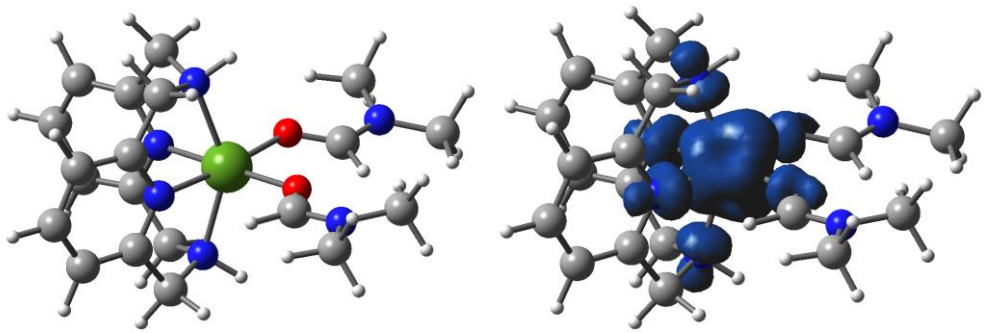
SCF Done: E(UB3P86) = −2857.53318970 A.U. after 1 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation 3.7583, after 3.7500

	1	2	3
	A	A	A
Frequencies --	11.3761	18.0222	32.3753
Red. masses --	2.7098	4.8163	4.8704

Zero-point correction= 0.397182 (Hartree/Particle)
Thermal correction to Energy= 0.422085
Thermal correction to Enthalpy= 0.423029
Thermal correction to Gibbs Free Energy= 0.338469
Sum of electronic and zero-point Energies= −2857.136008
Sum of electronic and thermal Energies= −2857.111105
Sum of electronic and thermal Enthalpies= −2857.110161
Sum of electronic and thermal Free Energies= −2857.194721

Item	Value	Threshold	Converged?
Maximum Force	0.000007	0.000450	YES
RMS Force	0.000001	0.000300	YES

Table S23. DFT-optimized geometry of $[Co^{II}(dapp)(DMF)_2]^{2+}$ (quartet), computed at the UB3P86/6-31+G(d,p) level using C-PCM.



Spin Density Distribution

atom	x	y	z	Mulliken charge	Spin density
Co1	-0.21552	0.12583	-0.010879	0.198519	2.864477
C2	1.943162	1.786945	1.175564	-0.015597	-0.009388
N3	1.372512	1.479077	0.007399	0.056291	0.054245
N4	0.437881	0.094634	-2.115897	-0.475649	0.026913
H5	-0.388733	0.116584	-2.705873	0.393537	-0.000465
C6	3.140554	2.494376	1.224864	-0.405972	-0.001199
H7	3.596897	2.737747	2.178206	0.190111	0.000698
N8	1.262138	-1.359162	0.011323	0.18798	0.039213
C9	3.742931	2.860215	0.023047	-0.19348	-0.004827
H10	4.680558	3.40635	0.02934	0.192461	0.000305
C11	3.157521	2.49286	-1.186913	-0.492868	-0.004104
H12	3.627277	2.735064	-2.134002	0.190272	0.000666
N13	0.398494	0.104758	2.119691	-0.466682	0.028678
H14	-0.439086	0.136012	2.693529	0.392415	-0.000547
C15	1.959664	1.785804	-1.153321	0.056312	-0.013079
C16	1.21489	1.32361	-2.381452	-0.024623	-0.002128
H17	1.905622	1.19199	-3.221695	0.18332	0.001567
H18	0.502047	2.103985	-2.667383	0.212384	-0.000151
C19	1.151072	-1.171985	-2.381473	-0.120164	-0.002498
H20	1.865352	-1.068916	-3.2058	0.184499	0.001683
C21	1.850262	-1.683655	-1.146037	0.130752	-0.012658
C22	3.016635	-2.441383	-1.172003	-0.539775	-0.007584
H23	3.483249	-2.698493	-2.116686	0.190988	0.000647
C24	3.577465	-2.836896	0.040396	-0.257068	-0.003285
H25	4.489805	-3.424122	0.051903	0.19415	0.000274
C26	2.98739	-2.439774	1.23838	-0.565113	-0.009628
C27	1.821885	-1.682418	1.18321	0.204593	-0.015591
C28	1.183585	1.325871	2.395612	-0.073173	-0.000703
H29	1.867154	1.184656	3.240227	0.18409	0.001409
H30	3.431073	-2.695298	2.194456	0.190908	0.000654
C31	1.093935	-1.167945	2.400968	-0.143457	0.004
H32	0.334594	-1.900866	2.694027	0.214297	-0.000133
H33	1.787349	-1.072479	3.243944	0.184543	0.001511
H34	0.477083	2.112317	2.681067	0.21252	-0.000167

H35	0.405691	-1.910562	-2.695111	0.2142	-0.000152
O36	-1.540302	1.70796	-0.131748	-0.508272	0.027771
C37	-2.768647	1.678364	0.116739	0.493166	0.010859
H38	-3.256846	0.746085	0.417945	0.153486	0.001068
N39	-3.564422	2.735825	0.038767	0.134722	0.002239
C40	-3.061775	4.041663	-0.353774	-0.355067	-0.000111
C41	-4.982393	2.634704	0.340531	-0.257067	-0.000206
H42	-3.56892	4.373953	-1.263948	0.187108	0.000138
H43	-3.255379	4.764968	0.443173	0.184876	0.000083
H44	-1.990758	3.972479	-0.534626	0.201347	0.000044
H45	-5.228556	1.611415	0.625869	0.179053	0.000004
H46	-5.236467	3.306083	1.165416	0.189199	0.000199
H47	-5.572045	2.912943	-0.537347	0.188774	0.000136
O48	-1.834369	-1.167609	-0.003957	-0.514802	0.020195
C49	-1.814814	-2.421865	-0.010813	0.308804	-0.006482
H50	-0.867404	-2.971496	0.019117	0.155193	0.002399
N51	-2.896133	-3.184083	-0.0561	0.125912	0.002948
C52	-4.233334	-2.617059	-0.108288	-0.323765	0.000068
C53	-2.794267	-4.634671	-0.040901	-0.25998	-0.000923
H54	-4.766483	-3.022562	-0.971968	0.187276	0.000202
H55	-4.782508	-2.875479	0.801568	0.190678	0.000239
H56	-4.162022	-1.535264	-0.198001	0.193181	-0.000024
H57	-1.746453	-4.932362	0.006648	0.179939	-0.00001
H58	-3.319585	-5.034452	0.830544	0.19043	0.000241
H59	-3.243695	-5.048394	-0.947472	0.190286	0.000273

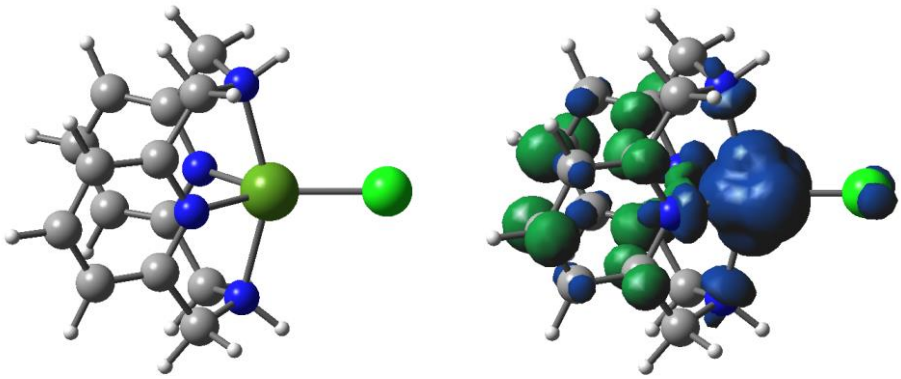
SCF Done: E(UB3P86) = −2646.06329519 A.U. after 1 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation 3.7581, after 3.7500

	1	2	3
	A	A	A
Frequencies --	18.4255	24.1698	30.2796
Red. masses --	4.4593	4.5495	3.7981

Zero-point correction= 0.501814 (Hartree/Particle)
Thermal correction to Energy= 0.532157
Thermal correction to Enthalpy= 0.533101
Thermal correction to Gibbs Free Energy= 0.436770
Sum of electronic and zero-point Energies= −2645.561481
Sum of electronic and thermal Energies= −2645.531138
Sum of electronic and thermal Enthalpies= −2645.530194
Sum of electronic and thermal Free Energies= −2645.626525

Item	Value	Threshold	Converged?
Maximum Force	0.000004	0.000450	YES
RMS Force	0.000001	0.000300	YES

Table S24. DFT-optimized geometry of Co^{I}(dapp)Cl (triplet), computed at the UB3P86/6-31+G(d,p) level using C-PCM.



Spin Density Distribution

atom	x	y	z	Mulliken charge	Spin density
C1	-2.19028	-2.40111	-0.98883	-0.15947	0.050417
C2	-0.96411	-1.74737	-1.00654	-0.05345	-0.07978
C3	-0.97846	-1.53018	1.31571	-0.06108	-0.07818
C4	-2.2055	-2.17636	1.40403	-0.16144	0.04934
C5	-2.81663	-2.63544	0.23622	-0.27753	-0.11688
H6	-2.65312	-2.70829	-1.92154	0.172818	-0.00068
H7	-2.67997	-2.30566	2.37184	0.172758	-0.00067
H8	-3.77607	-3.14042	0.27749	0.177144	0.005369
C9	-2.21799	2.17988	-1.40385	-0.19445	0.048458
C10	-0.99031	1.53624	-1.30612	-0.06658	-0.08316
C11	-0.99416	1.75317	1.01677	-0.05934	-0.08407
C12	-2.22158	2.4043	0.98977	-0.19763	0.049441
C13	-2.83866	2.63722	-0.24032	-0.26293	-0.1173
H14	-2.68493	2.30978	-2.37522	0.172981	-0.00068
H15	-2.69184	2.71182	1.91863	0.173033	-0.00069
H16	-3.79826	3.14124	-0.28897	0.177104	0.005396
N17	-0.35909	-1.34342	0.13076	0.367046	0.035098
N18	-0.38069	1.35116	-0.11631	0.397233	0.031809
N19	0.54532	-0.18873	-2.18072	-0.37716	0.018217
H20	1.34336	-0.23797	-2.80455	0.363063	-0.0016
N21	0.52824	0.21209	2.20091	-0.37732	0.018587
H22	1.32256	0.27283	2.82842	0.363156	-0.00164
C23	-0.22595	1.02211	-2.50085	-0.08776	0.002672
H24	-0.91119	0.87121	-3.34652	0.16255	0.00107
C25	-0.22766	-1.00953	2.51588	-0.08478	0.002715
H26	-0.91963	-0.86948	3.35797	0.162034	0.00112
C27	-0.20027	-1.45317	-2.27317	-0.09141	0.000304
H28	0.542	-2.2461	-2.42436	0.193265	-0.00251
H29	-0.88173	-1.47555	-3.13484	0.161984	0.001094
C30	-0.23562	1.46582	2.28861	-0.09429	0.0008
H31	-0.92345	1.47816	3.14543	0.162296	0.001057
H32	0.49453	2.26867	2.44622	0.193736	-0.00259
H33	0.49917	1.78714	-2.80371	0.193829	-0.0026

H34	0.50633	-1.7651	2.82119	0.193302	-0.00254
Co35	1.08479	0.01707	0.01211	-0.74943	2.230566
Cl36	3.39806	0.14358	0.02041	-0.60329	0.022036

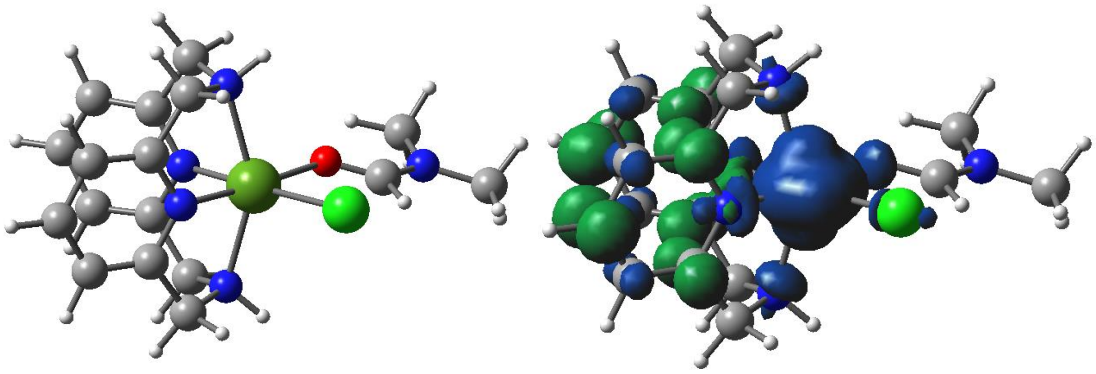
SCF Done: E(UB3P86) = −2608.39926783 A.U. after 1 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation 2.2395, after 2.0034

	1	2	3
	A	A	A
Frequencies --	46.9958	52.0572	70.7765
Red. masses --	5.2390	13.0220	3.4322

Zero-point correction= 0.290292 (Hartree/Particle)
Thermal correction to Energy= 0.307396
Thermal correction to Enthalpy= 0.308340
Thermal correction to Gibbs Free Energy= 0.244589
Sum of electronic and zero-point Energies= −2608.108975
Sum of electronic and thermal Energies= −2608.091872
Sum of electronic and thermal Enthalpies= −2608.090928
Sum of electronic and thermal Free Energies= −2608.154679

Item	Value	Threshold	Converged?
Maximum Force	0.000001	0.000450	YES
RMS Force	0.000000	0.000300	YES

Table S25. DFT-optimized geometry of Co^{I}(dapp)(DMF)Cl (triplet), computed at the UB3P86/6-31+G(d,p) level using C-PCM.



Spin Density Distribution

atom	x	y	z	Mulliken charge	Spin density
Co1	-0.35112	-0.55381	-0.08272	-0.59662	2.322046
C2	0.84824	1.79533	1.16778	0.032001	-0.097705
N3	0.45876	1.29578	-0.02495	0.250462	0.041814
N4	0.30267	-0.30002	-2.25142	-0.38655	0.018119
H5	-0.36511	-0.62068	-2.94448	0.356429	-0.001536
C6	1.75188	2.84628	1.26174	-0.31709	0.064578
H7	2.04701	3.22031	2.23752	0.166214	-0.000762
N8	1.56019	-1.14356	0.03909	0.12041	0.043329
C9	2.27783	3.39772	0.09028	-0.25704	-0.161152
H10	2.98581	4.21875	0.13512	0.172009	0.007399
C11	1.9003	2.84954	-1.13847	-0.32589	0.06069
H12	2.31358	3.22619	-2.06932	0.166408	-0.000779
N13	0.03195	-0.30682	2.16194	-0.35181	0.018872
H14	-0.71426	-0.62937	2.76892	0.354545	-0.001522
C15	0.99245	1.7983	-1.15922	0.037063	-0.10519
C16	0.50588	1.14582	-2.42901	-0.02135	0.011114
H17	1.19577	1.37287	-3.25418	0.157699	0.001187
H18	-0.46972	1.5715	-2.69153	0.18407	-0.003014
C19	1.52415	-1.11241	-2.36904	-0.05257	0.007167
H20	2.16498	-0.78464	-3.19979	0.156859	0.001036
C21	2.31255	-1.12109	-1.08387	-0.07957	-0.111741
C22	3.70032	-1.12906	-1.03543	-0.21052	0.059303
H23	4.27377	-1.10688	-1.95738	0.165649	-0.001025
C24	4.33842	-1.15211	0.20845	-0.26028	-0.175892
H25	5.42139	-1.15723	0.2746	0.171099	0.00826
C26	3.55367	-1.13173	1.36546	-0.23476	0.060862
C27	2.17022	-1.1238	1.24511	-0.0444	-0.119771
C28	0.21198	1.13837	2.3673	-0.08699	0.001545
H29	0.798	1.36178	3.27016	0.157777	0.001134
H30	4.01069	-1.11147	2.35035	0.1656	-0.001015
C31	1.23089	-1.1185	2.4249	-0.06941	0.014604
H32	0.88358	-2.14336	2.60193	0.188708	-0.00359
H33	1.76565	-0.79205	3.32816	0.157119	0.001007

H34	-0.78773	1.56406	2.51361	0.184125	-0.003034
Cl35	-1.46438	-2.83543	-0.16655	-0.71059	0.030795
H36	1.19931	-2.13633	-2.58889	0.189547	-0.003575
O37	-2.38059	0.3503	-0.22454	-0.54052	0.009011
C38	-3.46723	-0.19772	0.02689	0.301608	0.011962
H39	-3.51014	-1.26882	0.26368	0.144442	0.000892
N40	-4.65125	0.42627	0.02837	0.1025	-0.004963
C41	-4.7665	1.83923	-0.27571	-0.35771	-0.000475
C42	-5.87544	-0.29032	0.33005	-0.26399	0.000472
H43	-5.39436	1.98416	-1.16073	0.178253	-0.000117
H44	-5.22223	2.36862	0.56702	0.176335	-0.000103
H45	-3.77225	2.24185	-0.46421	0.196055	-0.000059
H46	-5.64766	-1.33699	0.53766	0.174686	-0.00001
H47	-6.36513	0.14598	1.20643	0.179868	-0.000042
H48	-6.56545	-0.23994	-0.51826	0.180094	-0.000126

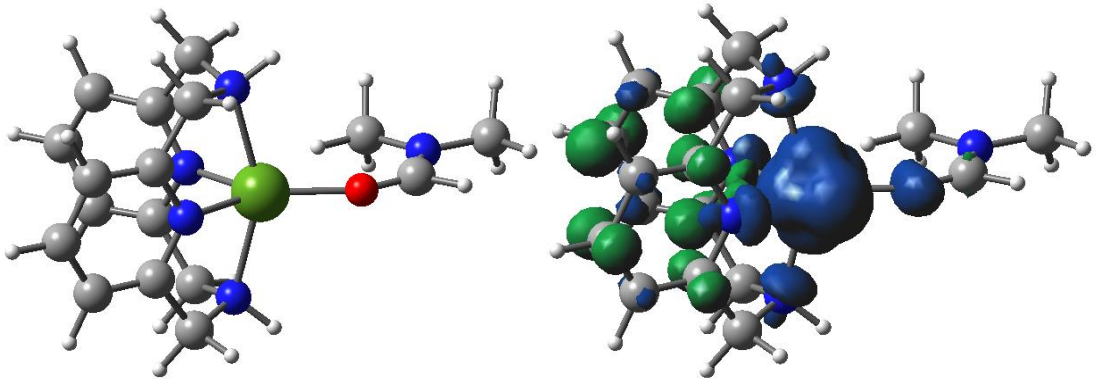
SCF Done: E(UB3P86) = −2857.65538797 A.U. after 2 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation 2.4004, after 2.0072

	1	2	3
	A	A	A
Frequencies --	12.0113	21.3092	22.7588
Red. masses --	5.0125	2.7137	5.3121

Zero-point correction= 0.393277 (Hartree/Particle)
Thermal correction to Energy= 0.418707
Thermal correction to Enthalpy= 0.419651
Thermal correction to Gibbs Free Energy= 0.333842
Sum of electronic and zero-point Energies= −2857.262111
Sum of electronic and thermal Energies= −2857.236681
Sum of electronic and thermal Enthalpies= −2857.235737
Sum of electronic and thermal Free Energies= −2857.321546

Item	Value	Threshold	Converged?
Maximum Force	0.000003	0.000450	YES
RMS Force	0.000001	0.000300	YES

Table S26. DFT-optimized geometry of $[Co^{I}(dapp)(DMF)]^{+}$ (triplet), computed at the UB3P86/6-31+G(d,p) level using C-PCM.



Spin Density Distribution

atom	x	y	z	Mulliken charge	Spin density
Co1	-0.51998	0.66503	-0.01918	-0.10532	2.281989
C2	2.04212	1.2594	1.17755	-0.01581	-0.048838
N3	1.38113	1.2484	0.00358	0.310116	0.041697
N4	-0.00923	0.42977	-2.20382	-0.4463	0.011558
H5	-0.71153	0.77549	-2.84885	0.368356	-0.00103
C6	3.42966	1.3257	1.23067	-0.27729	0.020062
H7	3.93661	1.32781	2.19048	0.175994	-0.00038
N8	0.19078	-1.18347	-0.00492	0.446482	0.014849
C9	4.15014	1.37036	0.0369	-0.24595	-0.082032
H10	5.23407	1.41733	0.04999	0.180034	0.00409
C11	3.45896	1.31935	-1.17383	-0.27711	0.020353
H12	3.9891	1.31623	-2.12101	0.175979	-0.000379
N13	-0.06267	0.44112	2.18042	-0.44772	0.011253
H14	-0.78074	0.7902	2.80597	0.368374	-0.001041
C15	2.07052	1.25335	-1.15406	-0.01538	-0.049109
C16	1.22354	1.21024	-2.4016	-0.08209	-0.004413
H17	1.82014	0.83943	-3.24608	0.16491	0.001092
H18	0.91545	2.2335	-2.64692	0.196758	-0.001641
C19	0.13093	-1.02198	-2.40948	-0.04701	-0.019541
H20	0.79216	-1.26084	-3.25351	0.165702	0.000867
C21	0.61158	-1.72698	-1.16503	0.145612	-0.05484
C22	1.40509	-2.86766	-1.18825	-0.60588	0.030724
H23	1.73232	-3.2815	-2.1369	0.175116	-0.000658
C24	1.78146	-3.45474	0.02052	-0.24082	-0.102466
H25	2.40276	-4.34418	0.03049	0.178961	0.004968
C26	1.37521	-2.86164	1.21658	-0.61498	0.031767
C27	0.58284	-1.72093	1.16802	0.13572	-0.053852
C28	1.16485	1.2227	2.40426	-0.07856	-0.00532
H29	1.74055	0.85635	3.26504	0.164877	0.001082
H30	1.6787	-3.27073	2.17515	0.175068	-0.000661
C31	0.07258	-1.00943	2.3969	-0.04778	-0.019419
H32	-0.9299	-1.38961	2.62632	0.196453	-0.002272
H33	0.71365	-1.24382	3.25757	0.165617	0.000858

H34	0.85095	2.24722	2.63661	0.1967	-0.001638
H35	-0.86601	-1.40329	-2.66042	0.196057	-0.00225
O36	-2.35325	1.4391	-0.04092	-0.50508	-0.008504
C37	-3.59252	1.33182	-0.02241	0.352859	-0.008955
H38	-4.21259	2.23618	-0.02122	0.151312	0.003753
N39	-4.2916	0.1957	-0.00415	-0.04033	-0.005762
C40	-3.66548	-1.11357	-0.00367	-0.4429	-0.003367
C41	-5.74427	0.22222	0.01572	-0.34135	0.000677
H42	-3.96045	-1.66507	0.89428	0.184096	-0.000452
H43	-3.98657	-1.67796	-0.88446	0.184045	-0.000462
H44	-2.57999	-1.00585	-0.02026	0.179424	-0.001635
H45	-6.09691	1.25437	0.01231	0.174988	-0.00017
H46	-6.14147	-0.29187	-0.86449	0.183978	-0.000285
H47	-6.11694	-0.27773	0.91459	0.184053	-0.000266

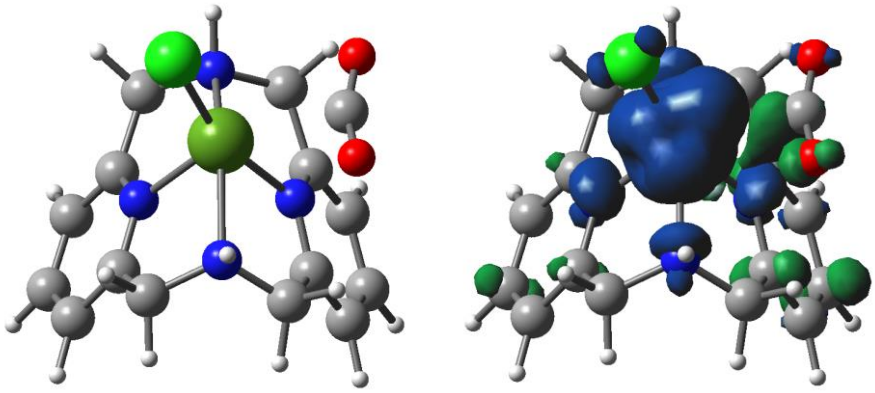
SCF Done: E(UB3P86) = −2396.92876450 A.U. after 1 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation 2.1930, after 2.0032

	1	2	3
	A	A	A
Frequencies --	9.4554	26.7493	45.6685
Red. masses --	4.3063	4.9139	5.0811

Zero-point correction= 0.394257 (Hartree/Particle)
Thermal correction to Energy= 0.416973
Thermal correction to Enthalpy= 0.417918
Thermal correction to Gibbs Free Energy= 0.339981
Sum of electronic and zero-point Energies= −2396.534508
Sum of electronic and thermal Energies= −2396.511791
Sum of electronic and thermal Enthalpies= −2396.510847
Sum of electronic and thermal Free Energies= −2396.588784

Item	Value	Threshold	Converged?
Maximum Force	0.000009	0.000450	YES
RMS Force	0.000001	0.000300	YES

Table S27. TS geometry optimized for $[Co^{I}(dapp)Cl\text{---}CO_2]^{‡}$ (triplet), computed at the UB3P86/6-31+G(d,p) level using C-PCM.



Spin Density Distribution

atom	x	y	z	Mulliken charge	Spin density
Cl1	2.232158	-2.50504	0.268868	-0.55933	0.011017
N2	-1.14608	-1.09763	-0.04466	0.42559	0.059393
C3	-1.71455	-1.16146	-1.25789	-0.07718	-0.03596
C4	-1.90485	-1.06585	1.061226	-0.04759	-0.0407
N5	0.465275	-0.40357	-2.11808	-0.28373	0.01481
N6	0.158527	-0.34848	2.246928	-0.35044	0.020426
H7	1.238613	-0.77227	-2.65952	0.367996	-0.00083
H8	0.789509	-0.76914	2.92002	0.372645	-0.00109
C9	-3.09597	-1.23604	-1.4085	-0.36848	0.002578
C10	-3.29331	-1.13479	0.988021	-0.37015	0.007443
N11	0.221121	1.258837	0.04695	0.532387	0.048764
C12	-0.74603	-1.1746	-2.41673	0.012651	0.012556
C13	-1.15557	-0.99712	2.372597	-0.03414	0.008605
H14	-0.43763	-2.21125	-2.59547	0.196976	-0.00058
H15	-0.97863	-2.02381	2.712831	0.201489	-0.00078
H16	-1.2516	-0.82631	-3.32827	0.163653	0.000674
H17	-1.78365	-0.5134	3.132606	0.167781	0.001186
C18	0.355226	1.039232	-2.36225	-0.36518	-0.02036
C19	0.163286	1.108773	2.452399	-0.03959	0.002471
H20	-0.30828	1.265687	-3.2081	0.161454	0.000661
H21	-0.50666	1.417051	3.266282	0.164176	0.000952
H22	1.352686	1.401647	-2.62922	0.205765	-0.00156
H23	1.182688	1.385143	2.742586	0.200811	-0.00128
C24	-0.11213	1.796326	-1.14075	0.618447	-0.00733
C25	-0.19546	1.845002	1.185866	0.318385	-0.03667
C26	-0.82231	2.989675	-1.22495	-0.84515	0.02753
C27	-0.90539	3.040712	1.174507	-0.62436	0.033111
H28	-1.07857	3.3989	-2.19714	0.176887	-0.00014
H29	-1.2303	3.487319	2.108744	0.176911	-0.00043
C30	-1.20797	3.632851	-0.05042	-0.30153	-0.06225
H31	-1.76447	4.563541	-0.08986	0.181316	0.002955
H32	-3.53587	-1.28233	-2.39944	0.17965	-8E-06

H33	-3.8901	-1.10099	1.89374	0.179759	0.000341
C34	-3.894	-1.23162	-0.26581	-0.19905	-0.03581
H35	-4.97464	-1.2813	-0.3524	0.182769	0.001776
C36	3.048673	0.543593	-0.16378	0.623334	-0.04301
O37	3.176889	0.682216	1.006663	-0.27316	0.0048
O38	3.301533	0.588601	-1.32014	-0.33119	-0.00312
Co39	0.829368	-0.65006	0.149646	-0.74058	2.029846

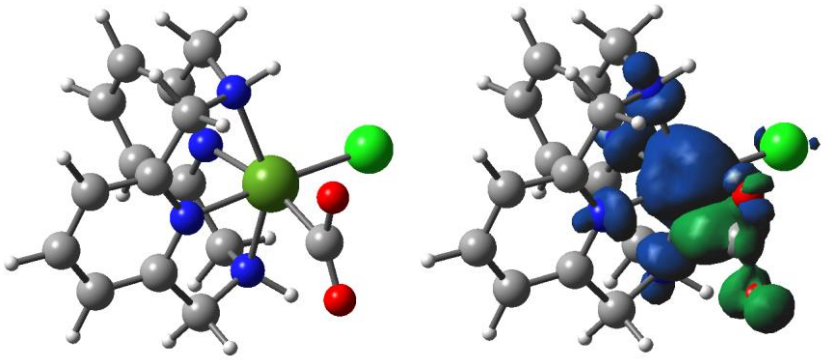
SCF Done: E(UB3P86) = −2797.36410291 A.U. after 2 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation 2.1154, after 2.0022

	1	2	3
	A	A	A
Frequencies --	−373.6040	20.5430	42.4422
Red. masses --	13.4064	10.2810	5.2275

Zero-point correction= 0.301709 (Hartree/Particle)
Thermal correction to Energy= 0.322591
Thermal correction to Enthalpy= 0.323535
Thermal correction to Gibbs Free Energy= 0.249922
Sum of electronic and zero-point Energies= −2797.062394
Sum of electronic and thermal Energies= −2797.041512
Sum of electronic and thermal Enthalpies= −2797.040568
Sum of electronic and thermal Free Energies= −2797.114181

Item	Value	Threshold	Converged?
Maximum Force	0.000003	0.000450	YES
RMS Force	0.000001	0.000300	YES

Table S28. DFT-optimized geometry of $Co^{III}(dapp)(CO_2^{2-})Cl$ (triplet), computed at the UB3P86/6-31+G(d,p) level using C-PCM.



Spin Density Distribution

atom	x	y	z	Mulliken charge	Spin density
Co1	-0.999328	-0.348313	0.220357	-0.800858	2.097341
C2	1.367859	-1.423611	-1.257855	-0.168314	0.000941
N3	0.915417	-1.17471	-0.024094	0.275415	0.03065
N4	-0.105787	-0.106836	2.241107	-0.439741	0.034033
H5	-0.793055	-0.399051	2.927296	0.385967	-0.001346
C6	2.688066	-1.802595	-1.480743	-0.335864	0.002288
H7	3.04168	-1.994964	-2.488047	0.185481	0.000297
N8	-0.042531	1.433309	0.012623	0.454989	0.04559
C9	3.540517	-1.909381	-0.383543	-0.221586	-0.007498
H10	4.577947	-2.19494	-0.524952	0.187737	0.000376
C11	3.061701	-1.624829	0.892626	-0.330167	0.0075
H12	3.711116	-1.678541	1.759997	0.185322	0.000755
N13	-0.687772	-0.295886	-1.976751	-0.275596	0.026202
H14	-1.583159	-0.553854	-2.378488	0.384619	-0.000991
C15	1.726586	-1.253255	1.034493	-0.046337	-0.006409
C16	1.087608	-0.956736	2.371089	-0.025462	-0.002942
H17	1.828303	-0.5214	3.053343	0.175439	0.001611
H18	0.772344	-1.908334	2.812829	0.206662	-0.000333
C19	0.127501	1.338805	2.404677	0.027495	0.004375
H20	0.881577	1.550833	3.172329	0.17273	0.001751
C21	0.520506	1.980556	1.096867	0.110141	-0.010146
C22	1.397252	3.054856	0.984949	-0.313065	-0.004077
H23	1.849372	3.487321	1.87106	0.1855	0.000344
C24	1.695645	3.539373	-0.287191	-0.345955	-0.010945
H25	2.380579	4.372684	-0.405961	0.188697	0.000537
C26	1.141651	2.924122	-1.407257	-0.628455	-0.003209
C27	0.272265	1.853583	-1.216865	0.377814	-0.010809
C28	0.332453	-1.285007	-2.345845	0.015471	-0.000094
H29	0.812035	-1.049997	-3.304129	0.173319	0.001427
H30	1.390407	3.255133	-2.410041	0.186035	0.000569
C31	-0.387162	1.09637	-2.346453	-0.268755	-0.006262
H32	-1.340044	1.58423	-2.573493	0.218675	-0.000375
H33	0.234361	1.154122	-3.24784	0.172171	0.001353

Cl34	-2.121629	-2.457099	0.326273	-0.481954	0.0244
H35	-0.173996	-2.249206	-2.461803	0.209112	-0.000156
H36	-0.816619	1.781443	2.73832	0.209042	-0.000112
C37	-2.722905	0.519711	-0.068727	0.930735	-0.151362
O38	-2.876918	0.645352	1.149906	-0.389425	0.002853
O39	-3.295062	0.75924	-1.118433	-0.547037	-0.068129

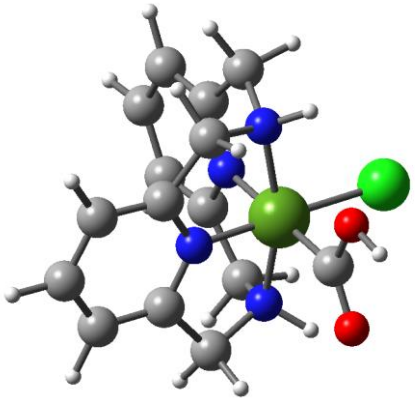
SCF Done: E(UB3P86) = −2797.37796439 A.U. after 1 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation 2.1316, after 2.0020

	1	2	3
	A	A	A
Frequencies --	28.7690	39.5915	51.7264
Red. masses --	11.5976	5.3019	7.5234

Zero-point correction= 0.303916 (Hartree/Particle)
Thermal correction to Energy= 0.324591
Thermal correction to Enthalpy= 0.325535
Thermal correction to Gibbs Free Energy= 0.253039
Sum of electronic and zero-point Energies= −2797.074049
Sum of electronic and thermal Energies= −2797.053374
Sum of electronic and thermal Enthalpies= −2797.052429
Sum of electronic and thermal Free Energies= −2797.124926

Item	Value	Threshold	Converged?
Maximum Force	0.000224	0.000450	YES
RMS Force	0.000029	0.000300	YES

Table S29. DFT-optimized geometry of $[Co^{III}(dapp)(CO_2H^-)Cl]^+$ (singlet), computed at the RB3P86/6-31+G(d,p) level using C-PCM.



atom	x	y	z	Mulliken charge
Co1	0.266767	-0.778067	0.029976	-0.910782
C2	-2.090711	0.269371	1.153633	-0.051939
N3	-1.506018	-0.032454	-0.006732	0.432866
N4	0.15283	-0.55431	-1.940481	-0.347748
H5	0.50688	-1.396416	-2.390429	0.424691
C6	-3.326889	0.904425	1.163341	-0.575552
H7	-3.811198	1.163008	2.097934	0.199479
N8	1.009987	0.934987	-0.006076	0.610511
C9	-3.923778	1.194081	-0.064327	-0.253359
H10	-4.884602	1.69727	-0.087766	0.197888
C11	-3.304774	0.83427	-1.262273	-0.594138
H12	-3.771987	1.037878	-2.218864	0.199497
N13	0.112092	-0.457106	1.982035	-0.337276
H14	0.450714	-1.284123	2.470447	0.426967
C15	-2.06917	0.202166	-1.193147	-0.044259
C16	-1.279491	-0.38259	-2.331069	0.156443
H17	-1.366993	0.206273	-3.247511	0.199458
H18	-1.679392	-1.380428	-2.536261	0.235459
C19	1.025951	0.583639	-2.350935	-0.020815
H20	0.618751	1.097685	-3.225153	0.201314
C21	1.22786	1.51517	-1.193668	0.33287
C22	1.666214	2.831336	-1.253144	-0.688976
H23	1.838425	3.307892	-2.211138	0.202302
C24	1.875593	3.514924	-0.056435	-0.406902
H25	2.212105	4.545845	-0.076579	0.201305
C26	1.655268	2.881999	1.166239	-0.742982
C27	1.216234	1.565237	1.158412	0.429003
C28	-1.323106	-0.246277	2.339414	0.107923
H29	-1.417994	0.404609	3.212119	0.199403
H30	1.819052	3.3984	2.104857	0.202306
C31	0.999642	0.682748	2.350936	-0.027849
H32	1.964776	0.259551	2.644289	0.242007
H33	0.599621	1.235476	3.204561	0.200424

Cl34	-0.567074	-2.873457	0.066926	-0.135683
H35	-1.737329	-1.22327	2.607142	0.234155
H36	1.997736	0.166066	-2.629984	0.238188
C37	1.996901	-1.552929	0.126418	0.831629
O38	2.53733	-1.854899	-1.082984	-0.475586
O39	2.616527	-1.787795	1.151583	-0.503256
H40	3.411441	-2.26084	-0.935144	0.411017

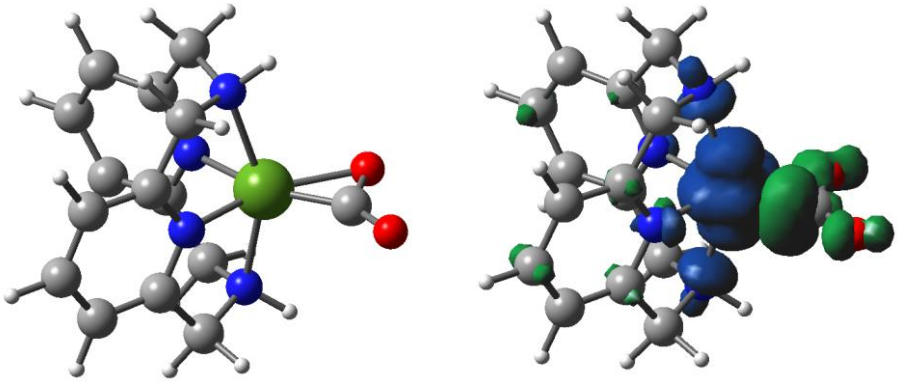
SCF Done: E(RB3P86) = −2797.84385939 A.U. after 2 cycles

	1	2	3
	A	A	A
Frequencies --	45.0783	56.7437	61.8987
Red. masses --	5.0450	3.4415	8.2983

Zero-point correction= 0.320365 (Hartree/Particle)
Thermal correction to Energy= 0.339654
Thermal correction to Enthalpy= 0.340598
Thermal correction to Gibbs Free Energy= 0.273482
Sum of electronic and zero-point Energies= −2797.523495
Sum of electronic and thermal Energies= −2797.504206
Sum of electronic and thermal Enthalpies= −2797.503261
Sum of electronic and thermal Free Energies= −2797.570378

Item	Value	Threshold	Converged?
Maximum Force	0.000013	0.000450	YES
RMS Force	0.000002	0.000300	YES

Table S30. DFT-optimized geometry of $Co^{II}(dapp)(CO_2^{2-})$ (doublet), computed at the UB3P86/6-31+G(d,p) level using C-PCM.



Spin Density Distribution

atom	x	y	z	Mulliken charge	Spin density
Co1	-0.974088	-0.715341	-0.000033	-0.2622	1.140081
C2	-0.272918	1.77978	1.165857	-0.057116	-0.026035
N3	-0.5532	1.170167	0.000194	0.345447	0.052614
N4	-0.513989	-0.454153	-2.195543	-0.467599	0.015119
H5	-1.184526	-0.919443	-2.796092	0.373921	-0.001213
C6	0.264901	3.061919	1.201521	-0.300855	0.002842
H7	0.485889	3.529836	2.155399	0.180487	0.000058
N8	0.987674	-1.051985	-0.000197	0.309239	0.023438
C9	0.52586	3.717666	0.000439	-0.234757	-0.026938
H10	0.94981	4.716473	0.000535	0.183102	0.001428
C11	0.264688	3.06224	-1.200773	-0.300849	0.00284
H12	0.485507	3.53041	-2.154565	0.180487	0.000058
N13	-0.513725	-0.454744	2.195484	-0.467598	0.01512
H14	-1.18423	-0.920135	2.795991	0.373923	-0.001213
C15	-0.273129	1.780095	-1.165356	-0.057134	-0.026041
C16	-0.61158	0.994045	-2.409408	-0.006762	0.003956
H17	0.012271	1.33749	-3.245854	0.167023	0.000782
H18	-1.653029	1.209894	-2.674754	0.201128	-0.000512
C19	0.810728	-1.045027	-2.413857	-0.107279	0.000685
H20	1.354704	-0.561429	-3.236901	0.167667	0.001461
C21	1.658862	-1.028827	-1.164699	0.058483	-0.009996
C22	3.049989	-1.023908	-1.201581	-0.351702	-0.00189
H23	3.568187	-0.999821	-2.154634	0.181597	-0.000104
C24	3.754336	-1.032207	-0.000333	-0.217367	-0.023249
H25	4.83946	-1.022404	-0.000387	0.184433	0.001253
C26	3.050111	-1.024297	1.20099	-0.351693	-0.00189
C27	1.658982	-1.029206	1.164245	0.058484	-0.010002
C28	-0.611144	0.993405	2.409769	-0.006781	0.003953
H29	0.012935	1.33656	3.246163	0.167024	0.000782
H30	3.568406	-1.00052	2.153999	0.181598	-0.000104
C31	0.810962	-1.045802	2.413473	-0.107258	0.000689
H32	0.657074	-2.091154	2.704969	0.200864	-0.000675
H33	1.355048	-0.562549	3.236648	0.167665	0.001461

H34	-1.652508	1.209278	2.675429	0.201128	-0.000512
H35	0.656903	-2.090285	-2.705726	0.200865	-0.000675
C36	-2.764114	-1.097368	0.000002	0.594548	-0.080743
O37	-2.260247	-2.287288	-0.000191	-0.618837	-0.030667
O38	-3.954508	-0.741216	0.00011	-0.763328	-0.02616

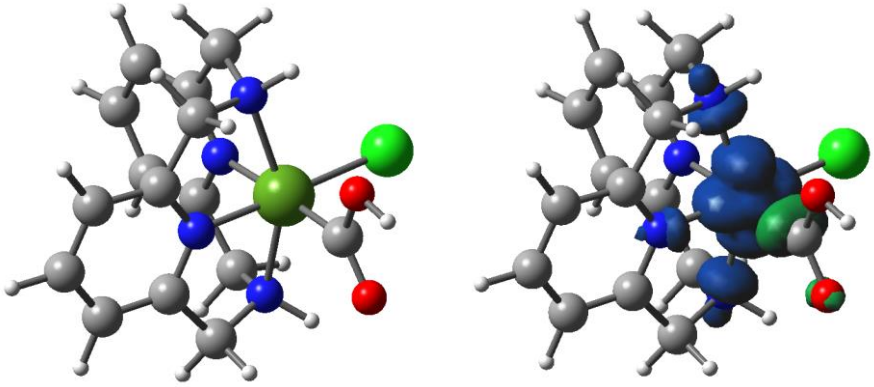
SCF Done: E(UB3P86) = −2336.79133427 A.U. after 1 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation 0.8204, after 0.7524

	1	2	3
	A	A	A
Frequencies --	45.1714	51.6391	55.7872
Red. masses --	5.1866	8.2560	3.2170

Zero-point correction= 0.302389 (Hartree/Particle)
Thermal correction to Energy= 0.320655
Thermal correction to Enthalpy= 0.321600
Thermal correction to Gibbs Free Energy= 0.255801
Sum of electronic and zero-point Energies= −2336.488945
Sum of electronic and thermal Energies= −2336.470679
Sum of electronic and thermal Enthalpies= −2336.469735
Sum of electronic and thermal Free Energies= −2336.535533

Item	Value	Threshold	Converged?
Maximum Force	0.000033	0.000450	YES
RMS Force	0.000003	0.000300	YES

Table S31. DFT-optimized geometry of $Co^{II}(dapp)(CO_2H^-)Cl$ (doublet), computed at the UB3P86/6-31+G(d,p) level using C-PCM.



Spin Density Distribution

atom	x	y	z	Mulliken charge	Spin density
Co1	-0.672969	-0.684314	-0.034173	-0.69543	1.008585
C2	1.965975	-0.618973	-1.140458	-0.02591	-0.002766
N3	1.280365	-0.704172	0.009549	0.344224	0.00037
N4	-0.345466	-0.362321	2.14417	-0.351212	0.017589
H5	-0.992178	-0.930144	2.67852	0.378258	-0.001368
C6	3.352589	-0.497473	-1.142616	-0.548511	0.002177
H7	3.891106	-0.424656	-2.081521	0.185192	-0.000058
N8	-0.524876	1.280783	-0.004422	0.50195	0.040501
C9	4.023339	-0.460853	0.076918	-0.194009	-0.006378
H10	5.103618	-0.361167	0.103645	0.186744	0.000445
C11	3.29664	-0.534657	1.262454	-0.579321	0.001495
H12	3.791042	-0.49084	2.227068	0.185095	-0.000059
N13	-0.248424	-0.310565	-2.183325	-0.352732	0.018277
H14	-0.866803	-0.874774	-2.753617	0.380238	-0.001399
C15	1.912015	-0.655514	1.192243	-0.004035	-0.003251
C16	1.03057	-0.792013	2.410303	0.015165	-0.002573
H17	1.479125	-0.25776	3.258524	0.170216	0.001264
H18	0.998373	-1.85311	2.681122	0.207222	-0.000194
C19	-0.627648	1.053879	2.395798	-0.051007	0.00099
H20	-0.050812	1.451221	3.241385	0.16889	0.000984
C21	-0.393336	1.907821	1.170986	0.22119	-0.001805
C22	-0.09799	3.26683	1.22893	-0.546849	-0.002792
H23	0.012961	3.759298	2.189348	0.183657	0.00056
C24	0.064938	3.967231	0.036192	-0.360046	-0.007754
H25	0.30378	5.025712	0.052379	0.186175	0.000464
C26	-0.057453	3.294343	-1.177409	-0.576708	-0.001094
C27	-0.353321	1.93465	-1.160345	0.291141	-0.002546
C28	1.142851	-0.714906	-2.402829	-0.010587	-0.002501
H29	1.62339	-0.141573	-3.206749	0.17069	0.001296
H30	0.085541	3.808497	-2.122084	0.183589	0.000551
C31	-0.543855	1.106696	-2.410469	-0.071319	0.000947
H32	-1.598234	1.174106	-2.697984	0.210134	-0.00028

H33	0.048357	1.531735	-3.231601	0.168553	0.000938
Cl34	-0.780541	-3.05973	-0.049766	-0.49773	0.009665
H35	1.137098	-1.764059	-2.718409	0.205982	-0.000202
H36	-1.68781	1.131338	2.658393	0.208097	-0.000274
C37	-2.553013	-0.600388	-0.130077	0.779195	-0.056068
O38	-3.21031	-0.569896	1.085732	-0.473498	0.000247
O39	-3.262122	-0.558954	-1.1381	-0.569981	-0.011095
H40	-4.164727	-0.527253	0.889671	0.377286	-0.00289

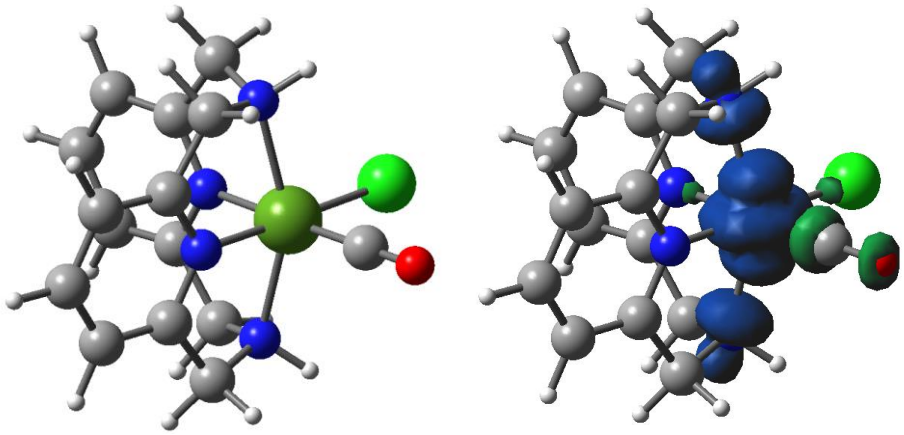
SCF Done: E(UB3P86) = −2797.99857618 A.U. after 2 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation 0.7646, after 0.7501

	1	2	3
	A	A	A
Frequencies --	43.0651	49.1483	55.6992
Red. masses --	5.2573	8.3150	5.7460

Zero-point correction= 0.315647 (Hartree/Particle)
Thermal correction to Energy= 0.336284
Thermal correction to Enthalpy= 0.337228
Thermal correction to Gibbs Free Energy= 0.265573
Sum of electronic and zero-point Energies= −2797.682929
Sum of electronic and thermal Energies= −2797.662293
Sum of electronic and thermal Enthalpies= −2797.661348
Sum of electronic and thermal Free Energies= −2797.733003

Item	Value	Threshold	Converged?
Maximum Force	0.000011	0.000450	YES
RMS Force	0.000002	0.000300	YES

Table S32. DFT-optimized geometry of $[Co^{II}(dapp)(CO)Cl]^{+}$ (doublet), computed at the UB3P86/6-31+G(d,p) level using C-PCM.



Spin Density Distribution

atom	x	y	z	Mulliken charge	Spin density
Co1	-0.125451	-1.056675	-0.002127	-0.013171	0.96225
C2	-1.546672	1.112629	1.171263	0.090734	-0.000425
N3	-1.219257	0.543565	0.000826	0.372037	-0.000864
N4	-0.057684	-0.571471	-2.163536	-0.425322	0.0461
H5	-0.179843	-1.396983	-2.739595	0.392169	-0.002287
C6	-2.233934	2.320582	1.207183	-0.706631	-0.003962
H7	-2.485057	2.772576	2.160195	0.195502	0.000149
N8	1.408474	0.140581	-0.000484	0.430439	0.022076
C9	-2.579472	2.931093	0.005427	-0.177877	-0.000205
H10	-3.108047	3.878481	0.007214	0.196573	0.000131
C11	-2.234173	2.325047	-1.198677	-0.706456	-0.003986
H12	-2.485506	2.78067	-2.149901	0.195504	0.00015
N13	-0.05647	-0.579013	2.160792	-0.424504	0.045943
H14	-0.177963	-1.406375	2.734351	0.392183	-0.002285
C15	-1.546993	1.116934	-1.167471	0.09043	-0.000467
C16	-1.184636	0.339692	-2.404126	-0.011496	-0.002459
H17	-0.993063	1.021726	-3.240906	0.185647	0.002184
H18	-2.05088	-0.272626	-2.676347	0.222153	-0.000049
C19	1.274558	-0.004605	-2.413146	-0.011446	-0.000081
H20	1.262037	0.73449	-3.222883	0.187194	0.001919
C21	1.867966	0.609716	-1.169853	-0.000832	-0.007562
C22	2.860838	1.582313	-1.201717	-0.366183	-0.001924
H23	3.219078	1.959156	-2.153292	0.196083	0.000275
C24	3.365414	2.064833	0.002144	-0.226386	-0.002931
H25	4.135398	2.82908	0.003214	0.197478	0.000217
C26	2.861405	1.57845	1.204689	-0.365223	-0.001876
C27	1.868505	0.605984	1.170181	-0.003597	-0.00752
C28	-1.18375	0.330875	2.404961	-0.011289	-0.002504
H29	-0.992227	1.00983	3.244243	0.18565	0.002178
H30	3.220134	1.952255	2.157282	0.196093	0.000274
C31	1.2756	-0.012272	2.411771	-0.011587	-0.000026

H32	1.932962	-0.827561	2.733141	0.219212	-0.00017
H33	1.262818	0.72443	3.223675	0.187221	0.001915
Cl34	-1.975782	-2.396151	-0.003489	-0.344814	-0.012889
H35	-2.049687	-0.282798	2.675104	0.22218	-0.000049
H36	1.931495	-0.819296	-2.736916	0.219151	-0.000169
C37	0.847484	-2.560376	-0.004732	0.572736	-0.008061
O38	1.466942	-3.521658	0.000951	-0.339556	-0.023009

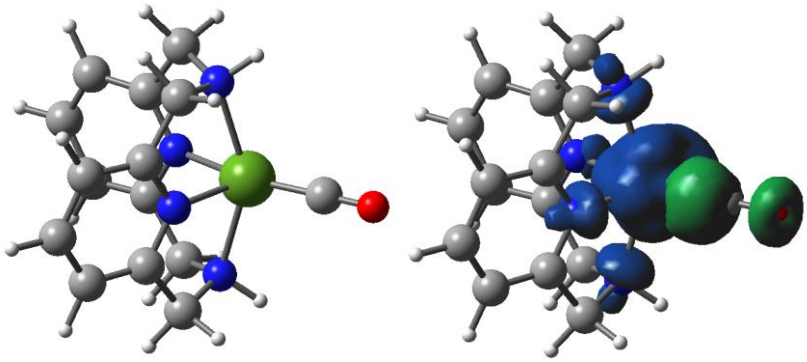
SCF Done: E(UB3P86) = −2721.83464338 A.U. after 1 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation 0.7613, after 0.7501

	1	2	3
	A	A	A
Frequencies --	42.1301	45.7102	63.8229
Red. masses --	3.1182	5.1534	7.3002

Zero-point correction= 0.302347 (Hartree/Particle)
Thermal correction to Energy= 0.321229
Thermal correction to Enthalpy= 0.322173
Thermal correction to Gibbs Free Energy= 0.254723
Sum of electronic and zero-point Energies= −2721.532296
Sum of electronic and thermal Energies= −2721.513414
Sum of electronic and thermal Enthalpies= −2721.512470
Sum of electronic and thermal Free Energies= −2721.579921

Item	Value	Threshold	Converged?
Maximum Force	0.000195	0.000450	YES
RMS Force	0.000017	0.000300	YES

Table S33. DFT-optimized geometry of $[Co^{I}(dapp)(CO)]^{+}$ (triplet), computed at the UB3P86/6-31+G(d,p) level using C-PCM.



Spin Density Distribution

atom	x	y	z	Mulliken charge	Spin density
Co1	0.860961	-1.114558	0.012138	0.020282	2.130762
C2	-1.807409	-0.676456	1.172138	-0.109689	0.053613
N3	-1.17709	-0.897691	0.010208	0.186421	0.027144
N4	0.452675	-0.710893	-2.154124	-0.437998	0.030141
H5	0.983132	-1.340789	-2.745176	0.379812	-0.001129
C6	-3.145482	-0.296792	1.206486	-0.255569	0.001706
H7	-3.638553	-0.119451	2.156248	0.188236	0.000867
N8	0.953243	0.905253	-0.009486	0.228645	0.069802
C9	-3.822806	-0.132339	0.000859	-0.234662	0.014908
H10	-4.865084	0.16966	-0.00276	0.191411	-0.000602
C11	-3.145339	-0.325494	-1.200415	-0.253929	0.001679
H12	-3.638251	-0.170896	-2.154215	0.188248	0.000865
N13	0.452732	-0.663841	2.169628	-0.438058	0.030004
H14	0.981669	-1.28242	2.773825	0.379777	-0.001126
C15	-1.807306	-0.704352	-1.156781	-0.110274	0.053763
C16	-0.978769	-0.944934	-2.395336	-0.070672	-0.018185
H17	-1.363211	-0.33746	-3.224249	0.175761	0.001925
H18	-1.095865	-1.994512	-2.686988	0.208865	0.000557
C19	0.923079	0.662749	-2.40663	-0.025734	0.01073
H20	0.39211	1.128526	-3.246238	0.175341	0.00156
C21	0.815075	1.538756	-1.181165	-0.149621	-0.038196
C22	0.599469	2.912783	-1.234754	-0.123039	-0.005718
H23	0.48804	3.41224	-2.191263	0.186561	0.00034
C24	0.508939	3.620243	-0.038068	-0.294845	-0.016447
H25	0.336122	4.691458	-0.04946	0.18968	0.000671
C26	0.601466	2.938565	1.173379	-0.122768	-0.005736
C27	0.816913	1.563694	1.14869	-0.150713	-0.038252
C28	-0.979293	-0.888169	2.4163	-0.070038	-0.017932
H29	-1.362135	-0.259017	3.229625	0.175754	0.00193
H30	0.491708	3.458262	2.11923	0.18655	0.00034
C31	0.927234	0.713481	2.39205	-0.023723	0.010616
H32	1.984423	0.652238	2.673532	0.207817	-0.00051
H33	0.400437	1.197997	3.223651	0.175261	0.001549

H34	-1.099364	-1.929753	2.734245	0.208849	0.000551
H35	1.979313	0.598247	-2.69091	0.207867	-0.000517
C36	2.518953	-1.776163	0.017368	0.437694	-0.241714
O37	3.607536	-2.18056	0.019358	-0.427502	-0.05996

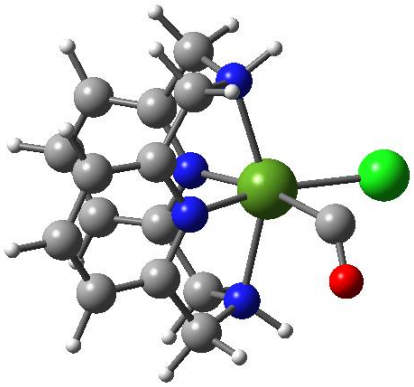
SCF Done: E(UB3P86) = −2261.26374193 A.U. after 1 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation 2.0519, after 2.0012

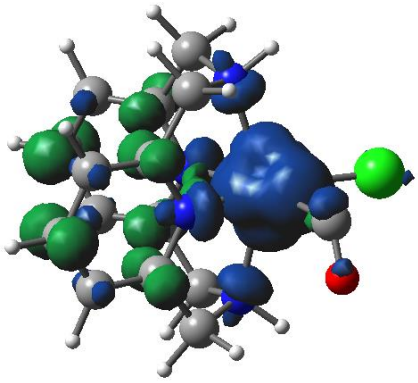
	1	2	3
	A	A	A
Frequencies --	40.3369	54.3344	56.4937
Red. masses --	5.1341	9.3320	3.1702

Zero-point correction= 0.299339 (Hartree/Particle)
Thermal correction to Energy= 0.316774
Thermal correction to Enthalpy= 0.317718
Thermal correction to Gibbs Free Energy= 0.253155
Sum of electronic and zero-point Energies= −2260.964403
Sum of electronic and thermal Energies= −2260.946968
Sum of electronic and thermal Enthalpies= −2260.946024
Sum of electronic and thermal Free Energies= −2261.010587

Item	Value	Threshold	Converged?
Maximum Force	0.000012	0.000450	YES
RMS Force	0.000003	0.000300	YES

Table S34. TS geometry optimized for [Co^{I}(dapp)Cl---CO]‡ (triplet), computed at the UB3P86/6-31+G(d,p) level using C-PCM.





Spin Density Distribution

atom	x	y	z	Mulliken charge	Spin density
Co1	-0.93751	0.65496	-0.12032	-0.56494	2.107988
C2	1.53137	1.09344	1.35085	-0.09693	-0.065871
N3	0.98154	1.1508	0.12316	0.384861	0.056447
N4	-0.22592	0.50223	-2.24629	-0.40477	0.01969
H5	-0.85863	0.91409	-2.92321	0.366665	-0.00102
C6	2.9094	1.13478	1.53355	-0.24256	0.026405
H7	3.32628	1.08252	2.53441	0.175076	-0.000465
N8	-0.27516	-1.22685	-0.13116	0.485136	0.039302
C9	3.73616	1.22649	0.41367	-0.24748	-0.091678
H10	4.8149	1.2557	0.52719	0.178704	0.004324
C11	3.15804	1.24623	-0.85627	-0.2274	0.028381
H12	3.77244	1.28189	-1.75039	0.175197	-0.00033
N13	-0.67149	0.27616	2.11901	-0.33364	0.017282
H14	-1.44061	0.61555	2.68574	0.365099	-0.001134
C15	1.77286	1.20292	-0.96542	-0.12038	-0.076174
C16	1.04493	1.24192	-2.28778	-0.04542	0.014446
H17	1.70816	0.88569	-3.08804	0.163328	0.000958
H18	0.79777	2.28587	-2.51375	0.196309	-0.001802
C19	-0.12265	-0.93842	-2.5216	0.007365	-0.010314
H20	0.60089	-1.16109	-3.31793	0.162571	0.000787
C21	0.2226	-1.72485	-1.28071	0.104412	-0.049262
C22	0.98003	-2.89031	-1.30287	-0.36228	0.047717
H23	1.37305	-3.26333	-2.2435	0.173963	-0.000545
C24	1.23642	-3.55366	-0.10257	-0.26782	-0.097592
H25	1.82752	-4.46349	-0.09096	0.17831	0.004551
C26	0.74969	-3.00998	1.08633	-0.8554	0.043411
C27	0.00043	-1.83987	1.03689	0.205389	-0.045401
C28	0.54466	1.01365	2.49061	-0.01431	0.012904
H29	1.03477	0.58908	3.37794	0.161765	0.00078
H30	0.95873	-3.47875	2.04292	0.174359	-0.00047
C31	-0.58387	-1.18238	2.26416	0.023294	-0.007283
H32	-1.60594	-1.55248	2.40297	0.196454	-0.001908

H33	-0.00995	-1.48099	3.15259	0.16215	0.000664
Cl34	-2.51838	2.39858	-0.12807	-0.62591	0.021281
H35	0.23414	2.03256	2.75032	0.19566	-0.001906
H36	-1.10714	-1.26413	-2.87603	0.194809	-0.001749
C37	-3.20251	-0.8498	-0.47027	0.036705	0.003087
O38	-3.72868	-1.33447	0.42141	-0.05835	0.0045

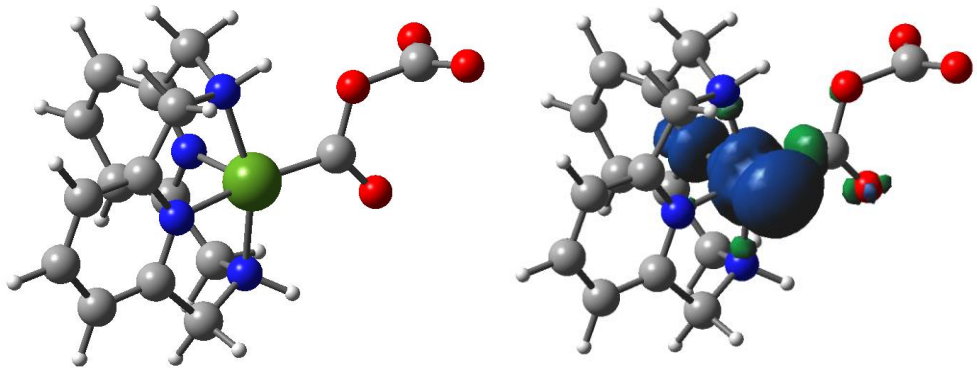
SCF Done: E(UB3P86) = −2721.95272390 A.U. after 1 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation 2.1900, after 2.0028

	1	2	3
	A	A	A
Frequencies --	−108.4151	25.6905	33.8738
Red. masses --	12.9175	13.0185	11.4517

Zero-point correction= 0.296105 (Hartree/Particle)
Thermal correction to Energy= 0.316340
Thermal correction to Enthalpy= 0.317284
Thermal correction to Gibbs Free Energy= 0.244717
Sum of electronic and zero-point Energies= −2721.656619
Sum of electronic and thermal Energies= −2721.636384
Sum of electronic and thermal Enthalpies= −2721.635440
Sum of electronic and thermal Free Energies= −2721.708007

Item	Value	Threshold	Converged?
Maximum Force	0.000007	0.000450	YES
RMS Force	0.000001	0.000300	YES

Table S35. DFT-optimized geometry of Co^{II}(dapp)($CO_2CO_2^{2-}$-*C*) (doublet), computed at the UB3P86/6-31+G(d,p) level using C-PCM.



Spin Density Distribution

atom	x	y	z	Mulliken charge	Spin density
Co1	0.224622	-0.658817	-0.306313	0.504011	0.870567
C2	-2.067002	-1.356553	1.170679	-0.018655	0.036895
N3	-1.62969	-1.061077	-0.060823	0.267507	0.005503
N4	-0.404059	-0.082225	-2.159179	-0.454912	0.043407
H5	0.241578	-0.431263	-2.863521	0.405958	-0.000404
C6	-3.425985	-1.514654	1.41541	-0.477638	0.010406
H7	-3.784772	-1.748383	2.411544	0.193039	0.000077
N8	-0.111503	1.237734	0.123578	0.390207	0.075548
C9	-4.311846	-1.35915	0.348985	-0.270233	0.007201
H10	-5.378502	-1.470451	0.513476	0.192781	-0.000258
C11	-3.834829	-1.056556	-0.926605	-0.518762	0.006625
H12	-4.512974	-0.931274	-1.763365	0.193072	0.000076
N13	0.277333	-0.84232	1.725608	-0.390246	0.044157
H14	1.085932	-1.383867	2.019758	0.4007	-0.000363
C15	-2.463277	-0.913477	-1.099544	-0.004535	0.0274
C16	-1.752829	-0.657137	-2.402858	0.016652	-0.023039
H17	-2.349082	-0.021002	-3.065025	0.186528	0.000102
H18	-1.616295	-1.617066	-2.912094	0.217773	0.000449
C19	-0.364876	1.407414	-2.224205	0.013157	0.016275
H20	-1.105679	1.789084	-2.933754	0.183709	-0.001079
C21	-0.535216	2.030019	-0.857798	0.072189	-0.005293
C22	-1.022487	3.300616	-0.568656	-0.493318	-0.002512
H23	-1.374602	3.957272	-1.356828	0.187521	0.000919
C24	-1.053316	3.699557	0.769704	-0.386949	-0.009483
H25	-1.433392	4.682559	1.028319	0.188796	0.000485
C26	-0.613941	2.840858	1.779781	-0.543163	-0.006399
C27	-0.140075	1.586634	1.407125	0.159185	-0.01429
C28	-0.954851	-1.547518	2.168367	0.107572	-0.028503
H29	-1.259317	-1.233934	3.17213	0.187066	-0.000018
H30	-0.647083	3.139228	2.822005	0.18857	0.000914
C31	0.432829	0.521297	2.311707	-0.102598	0.026132
H32	1.508577	0.701003	2.402018	0.220155	-0.000388
H33	-0.000692	0.568533	3.31557	0.182991	-0.001119

H34	-0.722719	-2.616579	2.219457	0.217796	0.000454
H35	0.625189	1.682934	-2.601056	0.2178	-0.000386
C36	2.086723	-0.550836	-0.672223	0.187399	-0.084805
O37	2.586249	-0.471112	-1.80009	-0.578708	0.001334
O38	2.900573	-0.601632	0.420358	-0.345124	0.007355
C39	4.36446	-0.557095	0.199834	0.641664	-0.002818
O40	4.886495	-1.675136	0.101525	-0.671651	-0.000813
O41	4.835882	0.587372	0.220621	-0.667305	-0.000313

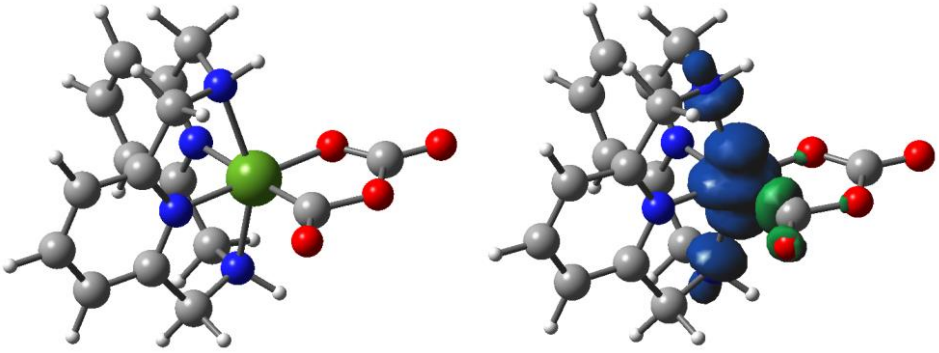
SCF Done: E(UB3P86) = −2525.77341526 A.U. after 1 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation 0.7631, after 0.7501

	1	2	3
	A	A	A
Frequencies --	21.2093	30.0700	42.3696
Red. masses --	11.1511	9.8424	5.2500

Zero-point correction= 0.317791 (Hartree/Particle)
Thermal correction to Energy= 0.338601
Thermal correction to Enthalpy= 0.339545
Thermal correction to Gibbs Free Energy= 0.266114
Sum of electronic and zero-point Energies= −2525.455625
Sum of electronic and thermal Energies= −2525.434815
Sum of electronic and thermal Enthalpies= −2525.433870
Sum of electronic and thermal Free Energies= −2525.507302

Item	Value	Threshold	Converged?
Maximum Force	0.000017	0.000450	YES
RMS Force	0.000002	0.000300	YES

Table S36. DFT-optimized geometry of Co^{II}(dapp)($CO_2CO_2^{2-}$-*C,O*) (doublet), computed at the UB3P86/6-31+G(d,p) level using C-PCM.



Spin Density Distribution

atom	x	y	z	Mulliken charge	Spin density
Co1	0.785297	-0.025397	0.000247	0.97661	0.98132
C2	-1.123141	1.802379	-1.165356	-0.118576	0.001641
N3	-0.603951	1.386292	0.00001	-0.064024	0.020626
N4	0.258501	0.029188	2.194296	-0.501517	0.025286
H5	1.083416	0.008941	2.781822	0.376484	-0.001638
C6	-2.192644	2.692292	-1.202318	-0.386897	-0.000066
H7	-2.600436	3.011636	-2.155421	0.186931	0.000091
N8	-0.673624	-1.294262	0.000042	0.201909	0.040046
C9	-2.728131	3.146975	-0.00099	-0.263315	-0.006384
H10	-3.566069	3.836496	-0.001344	0.188419	0.000374
C11	-2.19404	2.691946	1.200851	-0.386541	-0.000061
H12	-2.603051	3.011029	2.153523	0.186932	0.000092
N13	0.26007	0.02893	-2.193683	-0.501527	0.025363
H14	1.085758	0.008547	-2.780083	0.376539	-0.001643
C15	-1.124377	1.802232	1.164913	-0.119984	0.001627
C16	-0.457409	1.287564	2.417755	-0.009921	0.000807
H17	-1.198266	1.207852	3.224604	0.173647	0.001876
H18	0.278014	2.034326	2.736875	0.204679	-0.00024
C19	-0.514601	-1.196037	2.413949	-0.014361	0.001515
H20	-1.237054	-1.092488	3.234415	0.172928	0.001229
C21	-1.227868	-1.658805	1.165843	0.099574	-0.006591
C22	-2.37264	-2.448842	1.201186	-0.659702	-0.001124
H23	-2.809192	-2.728411	2.154183	0.186235	0.000224
C24	-2.945423	-2.855221	-0.000675	-0.209525	-0.006052
H25	-3.841893	-3.466604	-0.000945	0.187875	0.000428
C26	-2.371938	-2.448848	-1.202182	-0.660269	-0.001131
C27	-1.227141	-1.658854	-1.166147	0.099165	-0.006598
C28	-0.455504	1.287397	-2.41779	-0.011274	0.000783
H29	-1.196097	1.207459	-3.224844	0.173669	0.001875
H30	-2.807916	-2.728441	-2.155431	0.186237	0.000224
C31	-0.512831	-1.19634	-2.413811	-0.013581	0.001495
H32	0.193259	-1.981497	-2.706085	0.208313	-0.000198
H33	-1.234613	-1.092872	-3.234888	0.172946	0.00123

H34	0.280047	2.034003	-2.736965	0.204696	-0.00024
H35	0.191287	-1.981178	2.706788	0.208284	-0.000198
C36	2.15528	-1.304469	0.00045	0.595536	-0.063651
O37	2.214738	-2.523216	0.000046	-0.5788	-0.011533
O38	2.254188	1.232481	0.00149	-0.741367	0.008873
C39	3.416864	0.699891	0.000842	0.989868	-0.001603
O40	3.446424	-0.683025	0.000112	-0.440165	-0.007154
O41	4.502912	1.28455	0.000019	-0.676128	-0.000919

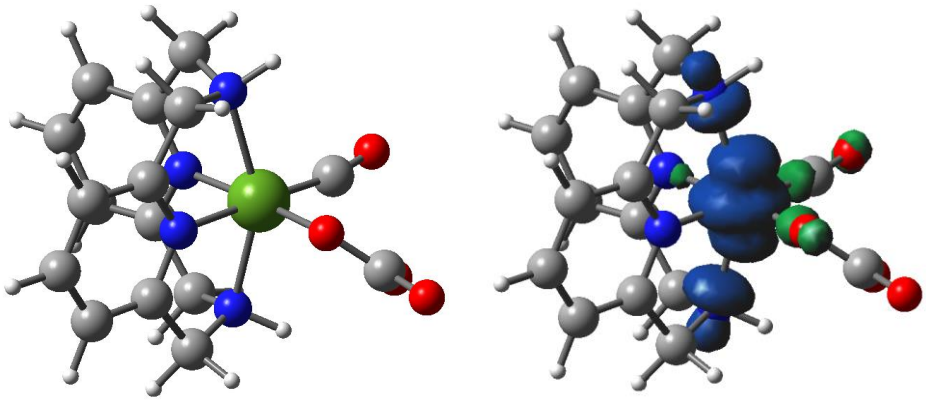
SCF Done: E(UB3P86) = −2525.80629716 A.U. after 2 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation 0.7616, after 0.7501

	1	2	3
	A	A	A
Frequencies --	41.5297	43.4273	54.5200
Red. masses --	10.0118	5.2064	7.1002

Zero-point correction= 0.318061 (Hartree/Particle)
Thermal correction to Energy= 0.338461
Thermal correction to Enthalpy= 0.339406
Thermal correction to Gibbs Free Energy= 0.268756
Sum of electronic and zero-point Energies= −2525.488236
Sum of electronic and thermal Energies= −2525.467836
Sum of electronic and thermal Enthalpies= −2525.466892
Sum of electronic and thermal Free Energies= −2525.537541

Item	Value	Threshold	Converged?
Maximum Force	0.000169	0.000450	YES
RMS Force	0.000018	0.000300	YES

Table S37. TS geometry optimized for $[Co^{II}(dapp)(CO---CO_3^{2-})]^{‡}$ (doublet), computed at the UB3P86/6-31+G(d,p) level using C-PCM.



Spin Density Distribution

atom	x	y	z	Mulliken charge	Spin density
Co1	0.6757	-0.34339	-0.29988	1.134334	0.958984
C2	-0.83094	1.99956	-1.05378	-0.22121	0.008596
N3	-0.20235	1.40015	-0.0347	0.144508	0.011001
N4	0.73891	-0.23253	1.89603	-0.5064	0.046151
H5	1.68215	-0.54732	2.10471	0.410527	-0.00261
C6	-1.53774	3.18306	-0.86164	-0.3448	-0.0004
H7	-2.0493	3.65171	-1.69539	0.189658	0.000339
N8	-1.05315	-1.13163	0.08498	0.195565	0.020153
C9	-1.57871	3.73813	0.41372	-0.36325	-0.00341
H10	-2.12915	4.65612	0.59204	0.191054	0.000201
C11	-0.92205	3.10012	1.4623	-0.39234	0.000595
H12	-0.94652	3.5031	2.46897	0.190172	0.000344
N13	-0.32847	-0.06885	-2.31245	-0.5487	0.028851
H14	0.28714	-0.30898	-3.08048	0.386619	-0.00184
C15	-0.23576	1.91859	1.20142	0.010944	-0.00269
C16	0.54818	1.17041	2.25485	-0.11849	-0.00422
H17	0.0649	1.28856	3.23302	0.176697	0.002043
H18	1.53691	1.63555	2.32969	0.211411	-0.00018
C19	-0.27064	-1.17344	2.37656	-0.14589	-0.00367
H20	-0.69814	-0.87218	3.34119	0.178624	0.001855
C21	-1.37857	-1.36813	1.36659	0.123393	-0.01192
C22	-2.65684	-1.79497	1.70862	-0.63502	-0.0013
H23	-2.90643	-1.97624	2.74839	0.191545	0.000073
C24	-3.60019	-1.96706	0.69977	-0.18561	-0.00351
H25	-4.60652	-2.29199	0.94269	0.192317	0.000327
C26	-3.2505	-1.69824	-0.62024	-0.51283	-0.00068
C27	-1.95459	-1.27655	-0.89826	0.108276	-0.01169
C28	-0.67877	1.3512	-2.40805	0.098491	0.000474
H29	-1.5875	1.5142	-3.00185	0.177731	0.001943
H30	-3.97015	-1.80313	-1.4248	0.191003	0.000065
C31	-1.46115	-1.0004	-2.29723	-0.0842	0.003519
H32	-1.11692	-1.94848	-2.72547	0.21251	-0.00015

H33	-2.29436	-0.65283	-2.92115	0.178691	0.001602
H34	0.13775	1.86052	-2.93098	0.208058	-0.00018
H35	0.21725	-2.14178	2.53568	0.212252	-0.00021
C36	1.50456	-1.95302	-0.49068	0.342804	-0.00481
O37	1.81519	-3.04576	-0.68046	-0.36039	-0.01997
O38	2.29464	0.57492	-0.64537	-0.70145	-0.01123
C39	3.41175	0.08865	-0.10507	0.916688	0.003044
O40	3.3379	-1.02974	0.52878	-0.6814	-0.00225
O41	4.47754	0.75399	-0.24668	-0.77192	-0.00327

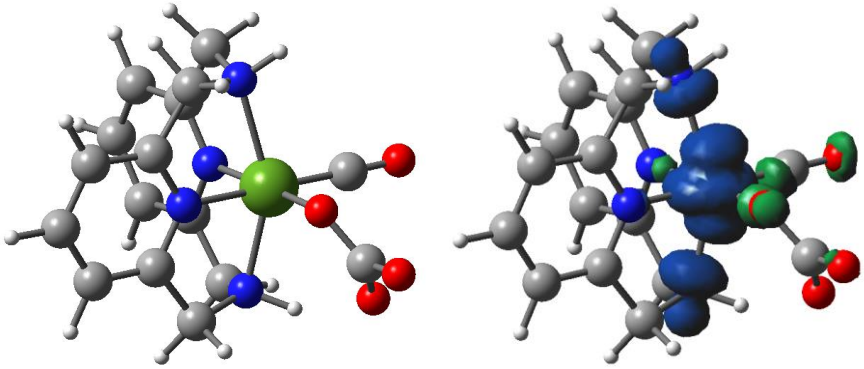
SCF Done: E(UB3P86) = −2525.78500282 A.U. after 1 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation 0.7608, after 0.7501

	1	2	3
	A	A	A
Frequencies --	−87.7236	43.1261	50.7117
Red. masses --	11.8122	5.2350	6.0329

Zero-point correction= 0.316237 (Hartree/Particle)
Thermal correction to Energy= 0.336746
Thermal correction to Enthalpy= 0.337690
Thermal correction to Gibbs Free Energy= 0.266815
Sum of electronic and zero-point Energies= −2525.468766
Sum of electronic and thermal Energies= −2525.448257
Sum of electronic and thermal Enthalpies= −2525.447312
Sum of electronic and thermal Free Energies= −2525.518188

Item	Value	Threshold	Converged?
Maximum Force	0.000039	0.000450	YES
RMS Force	0.000004	0.000300	YES

Table S38. DFT-optimized geometry of $Co^{II}(dapp)(CO)(CO_3^{2-})$ (doublet), computed at the UB3P86/6-31+G(d,p) level using C-PCM.



Spin Density Distribution

atom	x	y	z	Mulliken charge	Spin density
Co1	0.59985	-0.451396	-0.352325	1.034027	0.960164
C2	-0.613074	2.100585	-0.988346	-0.262604	0.004273
N3	-0.054989	1.387514	-0.001411	0.203909	0.010349
N4	0.739717	-0.420754	1.816047	-0.476299	0.057169
H5	1.702117	-0.788945	1.837209	0.433066	-0.002357
C6	-1.170658	3.35077	-0.740825	-0.250211	0.001598
H7	-1.627912	3.911616	-1.548611	0.1893	0.000437
N8	-1.192882	-1.045526	0.064424	0.160165	0.01548
C9	-1.135181	3.852852	0.55713	-0.391185	-0.002627
H10	-1.569542	4.822214	0.77898	0.191102	0.000171
C11	-0.552718	3.097969	1.570646	-0.450654	-0.000497
H12	-0.520547	3.459064	2.592975	0.18974	0.00045
N13	-0.423961	0.029244	-2.313174	-0.548593	0.03012
H14	0.121816	-0.280779	-3.108658	0.388871	-0.00192
C15	-0.016854	1.853175	1.25444	0.118984	-0.002386
C16	0.674755	0.963631	2.262212	-0.23493	-0.002975
H17	0.188267	1.061066	3.240785	0.175168	0.002352
H18	1.700996	1.329577	2.382151	0.207543	-0.000196
C19	-0.298848	-1.323171	2.291118	-0.14676	-0.001731
H20	-0.639998	-1.079249	3.305295	0.176419	0.001899
C21	-1.479046	-1.34062	1.344853	0.126458	-0.014938
C22	-2.777929	-1.657553	1.723801	-0.553247	-0.000337
H23	-2.998103	-1.888699	2.760254	0.191848	0.000056
C24	-3.779622	-1.655538	0.756248	-0.200377	-0.003191
H25	-4.802721	-1.891711	1.029807	0.192571	0.000323
C26	-3.465394	-1.329757	-0.559436	-0.505189	0.000537
C27	-2.145563	-1.025923	-0.878417	0.155453	-0.017328
C28	-0.548333	1.488969	-2.365086	0.137906	-0.001536
H29	-1.413476	1.810425	-2.95901	0.178211	0.002051
H30	-4.228472	-1.303101	-1.329601	0.191415	0.000048
C31	-1.690465	-0.712652	-2.283218	-0.125961	0.002114
H32	-1.533343	-1.664039	-2.803327	0.214076	-0.000188
H33	-2.489075	-0.186638	-2.821116	0.181287	0.001775

H34	0.345245	1.879213	-2.863805	0.209403	-0.000119
H35	0.120211	-2.335588	2.333382	0.208337	-0.00017
C36	1.246921	-2.093458	-0.695618	0.364678	0.00838
O37	1.672075	-3.12812	-0.946112	-0.326203	-0.027115
O38	2.314482	0.251566	-0.752122	-0.684747	-0.019101
C39	3.400911	-0.103069	-0.050271	0.833337	0.00511
O40	3.276029	-0.932311	0.919353	-0.732291	-0.000084
O41	4.497412	0.419199	-0.404935	-0.764024	-0.00606

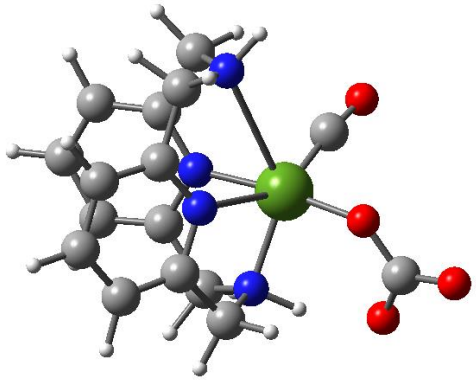
SCF Done: E(UB3P86) = −2525.78649737 A.U. after 1 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation 0.7628, after 0.7501

	1	2	3
	A	A	A
Frequencies --	44.4207	49.6886	60.2177
Red. masses --	5.3430	7.6977	4.1295

Zero-point correction= 0.316415 (Hartree/Particle)
Thermal correction to Energy= 0.337542
Thermal correction to Enthalpy= 0.338487
Thermal correction to Gibbs Free Energy= 0.266252
Sum of electronic and zero-point Energies= −2525.470082
Sum of electronic and thermal Energies= −2525.448955
Sum of electronic and thermal Enthalpies= −2525.448011
Sum of electronic and thermal Free Energies= −2525.520245

Item	Value	Threshold	Converged?
Maximum Force	0.000046	0.000450	YES
RMS Force	0.000007	0.000300	YES

Table S39. DFT-optimized geometry of $[Co^{I}(dapp)(CO)(CO_3^{2-})]^{-}$ (singlet), computed at the RB3P86/6-31+G(d,p) level using C-PCM.



atom	x	y	z	Mulliken charge
Co1	1.04815	-0.57387	-0.10363	0.178047
C2	-1.75191	1.12743	-1.55283	-0.19683
N3	-0.65951	1.24057	-0.79582	0.029656
N4	1.04573	0.79954	1.37424	-0.4777
H5	2.08754	0.79372	1.50239	0.434045
C6	-2.83296	2.00617	-1.42152	-0.12668
H7	-3.71136	1.88606	-2.04876	0.17058
N8	-0.6344	-1.09428	0.6634	0.140725
C9	-2.76718	3.01456	-0.46787	-0.24515
H10	-3.59208	3.70948	-0.34309	0.179101
C11	-1.64426	3.09545	0.35352	-0.13129
H12	-1.57495	3.8417	1.13872	0.172421
N13	-0.9363	-1.10325	-2.28688	-0.40534
H14	-0.58528	-1.52444	-3.13682	0.335556
C15	-0.61556	2.17613	0.16058	-0.03916
C16	0.62078	2.15808	1.02755	-0.12869
H17	0.45647	2.77009	1.92465	0.15191
H18	1.45036	2.60995	0.472	0.192217
C19	0.32401	0.15951	2.47444	-0.31834
H20	-0.03834	0.8792	3.22093	0.164571
C21	-0.82458	-0.6415	1.9236	0.122871
C22	-1.99835	-0.88261	2.62643	-0.25267
H23	-2.10705	-0.50469	3.63743	0.181186
C24	-3.02246	-1.58624	2.00198	-0.29627
H25	-3.95265	-1.78973	2.52241	0.184913
C26	-2.84839	-1.98399	0.68127	-0.51328
C27	-1.64733	-1.71805	0.02442	0.269947
C28	-1.7996	0.01645	-2.58939	-0.0585
H29	-2.85595	-0.27382	-2.72726	0.148038
H30	-3.64455	-2.48751	0.14342	0.175111
C31	-1.46674	-2.13749	-1.41675	-0.17765
H32	-0.75778	-2.9734	-1.44444	0.183139
H33	-2.43861	-2.5277	-1.76339	0.142844
H34	-1.47277	0.43788	-3.54758	0.182681

H35	1.02226	-0.51556	2.98447	0.194169
C36	1.62376	-2.14481	-0.46115	0.37807
O37	2.12173	-3.20916	-0.52509	-0.46143
O38	2.57604	0.24954	-0.88289	-0.67546
C39	3.64283	0.73974	-0.26662	0.72283
O40	3.68464	0.75868	1.02346	-0.75023
O41	4.58681	1.18498	-0.99142	-0.77997

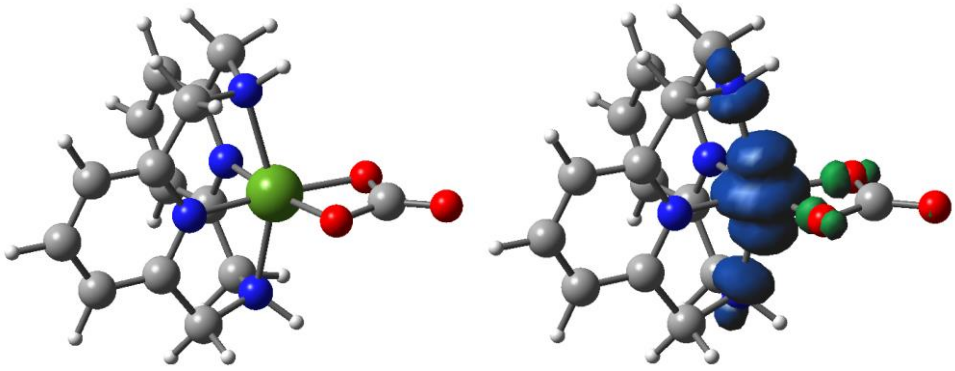
SCF Done: E(RB3P86) = −2525.89371396 A.U. after 1 cycles

	1	2	3
	A	A	A
Frequencies --	30.2121	36.4361	48.4627
Red. masses --	5.9102	7.4129	10.2905

Zero-point correction= 0.313608 (Hartree/Particle)
Thermal correction to Energy= 0.335276
Thermal correction to Enthalpy= 0.336220
Thermal correction to Gibbs Free Energy= 0.262139
Sum of electronic and zero-point Energies= −2525.580106
Sum of electronic and thermal Energies= −2525.558438
Sum of electronic and thermal Enthalpies= −2525.557494
Sum of electronic and thermal Free Energies= −2525.631575

Item	Value	Threshold	Converged?
Maximum Force	0.000014	0.000450	YES
RMS Force	0.000003	0.000300	YES

Table S40. DFT-optimized geometry of $Co^{II}(dapp)(CO_3^{2-})$ (doublet), computed at the UB3P86/6-31+G(d,p) level using C-PCM.



Spin Density Distribution

atom	x	y	z	Mulliken charge	Spin density
Co1	-0.98318	0.000051	0.000053	1.123149	0.906776
C2	0.944804	1.735652	1.166817	0.117954	-0.004502
N3	0.41206	1.336285	0.000042	0.102427	0.032136
N4	-0.480625	-0.000032	-2.210393	-0.545551	0.0289
H5	-1.305121	-0.000067	-2.798582	0.377051	-0.001808
C6	2.039659	2.593517	1.201291	-0.609682	0.000735
H7	2.457572	2.899686	2.154447	0.185798	0.000099
N8	0.412319	-1.336334	-0.000042	0.10233	0.032193
C9	2.58768	3.03344	0.000003	-0.133012	-0.009062
H10	3.445427	3.698088	-0.000012	0.187852	0.000543
C11	2.039601	2.593538	-1.201269	-0.609792	0.000736
H12	2.457445	2.899755	-2.154441	0.185797	0.000099
N13	-0.480412	-0.000182	2.210501	-0.545551	0.028895
H14	-1.304881	-0.000255	2.798728	0.377053	-0.001808
C15	0.944761	1.73566	-1.166753	0.117926	-0.004516
C16	0.264779	1.24129	-2.422613	-0.101698	0.002745
H17	1.006627	1.151605	-3.227921	0.172707	0.001316
H18	-0.452607	2.007145	-2.73775	0.20573	-0.000323
C19	0.264919	-1.241246	-2.422672	-0.101485	0.002735
H20	1.006718	-1.151428	-3.228012	0.172701	0.001316
C21	0.945037	-1.735537	-1.166844	0.117341	-0.0045
C22	2.040113	-2.593124	-1.201439	-0.609354	0.000728
H23	2.457996	-2.899188	-2.154642	0.185795	0.000101
C24	2.588333	-3.032917	-0.000191	-0.132992	-0.009041
H25	3.446252	-3.697341	-0.000249	0.187849	0.000542
C26	2.040216	-2.5932	1.201133	-0.609308	0.000727
C27	0.945134	-1.735615	1.166694	0.117388	-0.004509
C28	0.264987	1.241148	2.422717	-0.101812	0.002734
H29	1.006942	1.151418	3.227924	0.172711	0.001315
H30	2.458181	-2.899326	2.15428	0.185793	0.000101
C31	0.265124	-1.241426	2.422621	-0.101487	0.002744
H32	-0.452149	-2.007404	2.737723	0.205723	-0.000322
H33	1.006972	-1.151725	3.227931	0.172706	0.001316

H34	-0.452361	2.006975	2.738006	0.205729	-0.000323
H35	-0.452349	-2.007211	-2.737819	0.20572	-0.000322
O36	-2.583084	1.085913	-0.000208	-0.746017	-0.006189
C37	-3.327369	-0.000246	0.000041	1.316579	0.010064
O38	-2.582332	-1.08595	0.00022	-0.746289	-0.006248
O39	-4.573943	-0.000695	0.000111	-0.807781	-0.006126

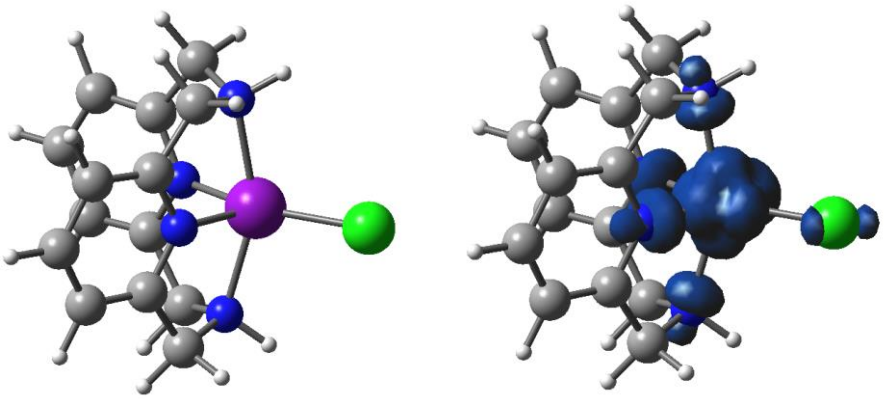
SCF Done: E(UB3P86) = −2412.22316869 A.U. after 1 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation 0.7598, after 0.7501

	1	2	3
	A	A	A
Frequencies --	45.3725	48.7759	51.1140
Red. masses --	5.2176	3.0503	8.3840

Zero-point correction= 0.308302 (Hartree/Particle)
Thermal correction to Energy= 0.327089
Thermal correction to Enthalpy= 0.328033
Thermal correction to Gibbs Free Energy= 0.260889
Sum of electronic and zero-point Energies= −2411.914867
Sum of electronic and thermal Energies= −2411.896080
Sum of electronic and thermal Enthalpies= −2411.895135
Sum of electronic and thermal Free Energies= −2411.962280

Item	Value	Threshold	Converged?
Maximum Force	0.000134	0.000450	YES
RMS Force	0.000010	0.000300	YES

Table S41. DFT-optimized geometry of $[Ni^{II}(dapp)Cl]^{+}$ (triplet), computed at the UB3P86/6-31+G(d,p) level using C-PCM.



Spin Density Distribution

atom	x	y	z	Mulliken charge	Spin density
Cl1	-2.420365	-2.438876	0.000000	-0.437139	0.075781
Ni2	-1.081395	-0.604483	0.000000	-0.542016	1.582668
N3	0.844984	-1.020336	0.000000	0.603084	0.1014
C4	1.49027	-1.037459	1.170336	-0.378583	-0.01176
C5	1.49027	-1.037459	-1.170336	-0.378583	-0.01176
N6	-0.695129	-0.342822	2.105392	-0.400615	0.077964
N7	-0.695129	-0.342822	-2.105392	-0.400615	0.077964
H8	-1.410927	-0.801273	2.659945	0.394249	-0.002968
H9	-1.410927	-0.801273	-2.659945	0.394249	-0.002968
C10	2.877976	-1.11844	1.208183	-0.020744	0.001034
C11	2.877976	-1.11844	-1.208183	-0.020744	0.001034
N12	-0.661528	1.33233	0.000000	0.458586	0.08885
C13	0.598862	-1.001569	2.387057	0.063341	0.006112
C14	0.598862	-1.001569	-2.387057	0.063341	0.006112
H15	0.383766	-2.033908	2.681916	0.220995	-0.000363
H16	0.383766	-2.033908	-2.681916	0.220995	-0.000363
H17	1.117705	-0.527526	3.227203	0.188202	0.002126
H18	1.117705	-0.527526	-3.227203	0.188202	0.002126
C19	-0.736271	1.10643	2.392013	-0.002889	-0.00817
C20	-0.736271	1.10643	-2.392013	-0.002889	-0.00817
H21	-0.07182	1.372942	3.221077	0.187274	0.002351
H22	-0.07182	1.372942	-3.221077	0.187274	0.002351
H23	-1.756299	1.353133	2.705028	0.2196	-0.000067
H24	-1.756299	1.353133	-2.705028	0.2196	-0.000067
C25	-0.406856	1.928772	1.169884	-0.17963	0.014192
C26	-0.406856	1.928772	-1.169884	-0.17963	0.014192
C27	0.097343	3.223886	1.207716	-0.131737	-0.004654
C28	0.097343	3.223886	-1.207716	-0.131737	-0.004654
H29	0.306789	3.704485	2.156927	0.195361	0.000991
H30	0.306789	3.704485	-2.156927	0.195361	0.000991
C31	0.341584	3.87499	0.000000	-0.274909	0.001633
H32	0.742421	4.883256	0.000000	0.196257	-0.000016

H33	3.40242	-1.129906	2.157187	0.194934	0.000979
H34	3.40242	-1.129906	-2.157187	0.194934	0.000979
C35	3.571177	-1.167243	0.000000	-0.299358	-0.006146
H36	4.654746	-1.223083	0.000000	0.195981	0.000297

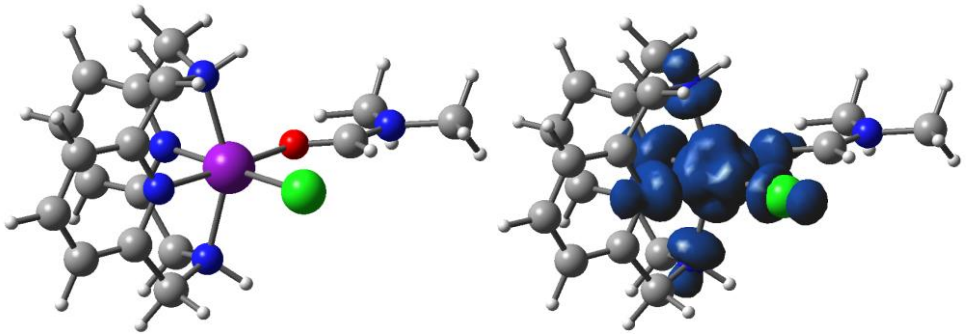
SCF Done: E(UB3P86) = −2733.81410856 A.U. after 2 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation 2.0052, after 2.0000

	1	2	3
	A'	A''	A'
Frequencies --	42.5387	58.1744	62.2713
Red. masses --	5.2048	3.1810	12.3130

Zero-point correction= 0.293779 (Hartree/Particle)
Thermal correction to Energy= 0.310449
Thermal correction to Enthalpy= 0.311394
Thermal correction to Gibbs Free Energy= 0.248479
Sum of electronic and zero-point Energies= −2733.520330
Sum of electronic and thermal Energies= −2733.503659
Sum of electronic and thermal Enthalpies= −2733.502715
Sum of electronic and thermal Free Energies= −2733.565629

Item	Value	Threshold	Converged?
Maximum Force	0.000304	0.000450	YES
RMS Force	0.000042	0.000300	YES

Table S42. DFT-optimized geometry of $[Ni^{II}(dapp)(DMF)Cl]^{+}$ (triplet), computed at the UB3P86/6-31+G(d,p) level using C-PCM.



Spin Density Distribution

atom	x	y	z	Mulliken charge	Spin density
Ni1	-0.27648	-0.52648	0.04669	-0.499581	1.643457
C2	0.6286	1.98016	1.2039	0.015928	-0.002838
N3	0.33993	1.39708	0.03806	0.434072	0.089813
N4	0.19042	-0.28152	-2.06695	-0.391525	0.054761
H5	-0.53737	-0.68792	-2.64557	0.388246	-0.002667
C6	1.23608	3.23177	1.24035	-0.481069	-0.009868
H7	1.47368	3.70185	2.18845	0.190156	0.000946
N8	1.67107	-1.01152	0.06745	0.229961	0.082974
C9	1.54226	3.85321	0.03115	-0.232446	-0.003269
H10	2.02242	4.82634	0.02843	0.191407	0.000222
C11	1.25641	3.21509	-1.17431	-0.440237	-0.009616
H12	1.50988	3.67195	-2.12477	0.190144	0.000957
N13	0.15489	-0.2526	2.16454	-0.401229	0.054477
H14	-0.58318	-0.64994	2.73642	0.388555	-0.002654
C15	0.64827	1.96406	-1.13076	-0.023328	-0.004278
C16	0.25765	1.16561	-2.35185	-0.02019	0.003492
H17	0.9397	1.38308	-3.18194	0.182271	0.001992
H18	-0.74118	1.48722	-2.66501	0.210533	-0.000256
C19	1.44326	-1.02203	-2.31916	0.028988	0.001178
H20	1.99554	-0.60566	-3.16929	0.181117	0.001853
C21	2.32382	-1.07897	-1.09437	-0.051166	-0.007357
C22	3.70643	-1.2354	-1.12201	-0.373717	-0.000343
H23	4.23702	-1.28608	-2.0666	0.190428	0.000887
C24	4.38692	-1.3104	0.09223	-0.228716	-0.004005
H25	5.466	-1.42446	0.10213	0.191772	0.000284
C26	3.68617	-1.21855	1.29374	-0.352029	0.000096
C27	2.3043	-1.06264	1.24091	-0.080366	-0.008099
C28	0.21667	1.19884	2.42906	0.000383	0.001463
H29	0.88393	1.42865	3.26776	0.181944	0.002008
H30	4.20097	-1.25597	2.24764	0.190465	0.000896
C31	1.40339	-0.98785	2.45	0.045466	0.000953
H32	1.12335	-2.01035	2.72438	0.216197	-0.00033
H33	1.94105	-0.55773	3.30271	0.181097	0.001855
H34	-0.78757	1.52454	2.71967	0.210426	-0.000243

Cl35	-0.97181	-2.81138	0.03459	-0.542693	0.079073
H36	1.16646	-2.04844	-2.58193	0.216626	-0.000326
O37	-2.22183	0.20298	0.05517	-0.454686	0.029384
C38	-3.27132	-0.46781	-0.05656	0.533777	0.006344
H39	-3.22303	-1.55747	-0.16165	0.154678	0.001507
N40	-4.49173	0.05854	-0.0541	0.124835	-0.004124
C41	-4.70681	1.48823	0.08342	-0.360035	0.000159
C42	-5.67011	-0.77949	-0.18909	-0.25125	-0.000377
H43	-5.23468	1.87047	-0.79522	0.182824	-0.000099
H44	-5.31185	1.68852	0.97253	0.183239	-0.000093
H45	-3.74308	1.98564	0.17662	0.199195	-0.000041
H46	-5.37142	-1.82384	-0.28662	0.178153	-0.000019
H47	-6.31039	-0.6725	0.69133	0.185776	-0.000077
H48	-6.23888	-0.48753	-1.07672	0.185603	-0.000054

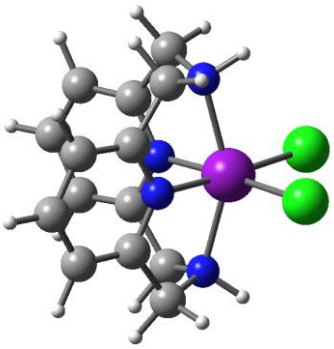
SCF Done: E(UB3P86) = −2983.08747638 A.U. after 1 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation 2.0048, after 2.0000

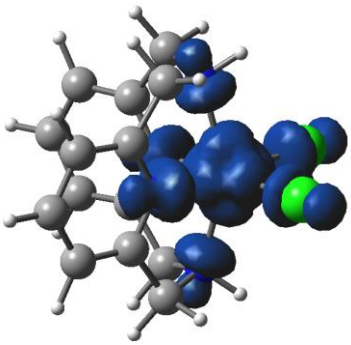
	1	2	3
	A	A	A
Frequencies --	3.1414	21.6665	34.5771
Red. masses --	3.0516	3.9051	4.8579

Zero-point correction= 0.397608 (Hartree/Particle)
Thermal correction to Energy= 0.422276
Thermal correction to Enthalpy= 0.423221
Thermal correction to Gibbs Free Energy= 0.338806
Sum of electronic and zero-point Energies= −2982.689868
Sum of electronic and thermal Energies= −2982.665200
Sum of electronic and thermal Enthalpies= −2982.664256
Sum of electronic and thermal Free Energies= −2982.748671

Item	Value	Threshold	Converged?
Maximum Force	0.000000	0.000002	YES
RMS Force	0.000000	0.000001	YES

Table S43. DFT-optimized geometry of $Ni^{II}(dapp)Cl_2$ (triplet), computed at the UB3P86/6-31+G(d,p) level using C-PCM.





Spin Density Distribution

atom	x	y	z	Mulliken charge	Spin density
C1	-2.10556	-2.54361	-1.20896	-0.421897	-0.006167
C2	-0.9735	-1.73502	-1.16661	-0.119731	-0.000087
C3	-0.98045	-1.72998	1.16712	-0.114366	0.000122
C4	-2.11284	-2.53856	1.20603	-0.398385	-0.006269
C5	-2.67208	-2.951	-0.00219	-0.24308	-0.004488
H6	-2.53742	-2.83787	-2.15942	0.1889	0.000937
H7	-2.55029	-2.82872	2.15522	0.188932	0.00096
H8	-3.55922	-3.57604	-0.00346	0.190081	0.00029
C9	-2.11158	2.5397	-1.20575	-0.398207	-0.006267
C10	-0.97961	1.73054	-1.16697	-0.114409	0.000121
C11	-0.97239	1.73556	1.16676	-0.119785	-0.000087
C12	-2.10403	2.54474	1.20924	-0.421672	-0.006165
C13	-2.67048	2.95244	0.00254	-0.243077	-0.004487
H14	-2.549	2.83007	-2.15488	0.188933	0.00096
H15	-2.53564	2.8392	2.15975	0.188899	0.000937
H16	-3.55729	3.57792	0.00391	0.190082	0.00029
N17	-0.44342	-1.36712	0.00116	0.566638	0.092361
N18	-0.44262	1.36741	-0.00107	0.56649	0.092355
N19	0.51326	0.00034	-2.11525	-0.394889	0.056501
H20	1.35463	0.00342	-2.68227	0.388516	-0.00249
N21	0.5135	-0.00063	2.11525	-0.394886	0.056494
H22	1.35492	-0.00416	2.68218	0.388513	-0.00249
C23	-0.24042	1.23843	-2.38844	0.053013	0.003448
H24	-0.93243	1.11671	-3.2301	0.178875	0.001858
C25	-0.24083	-1.2383	2.38851	0.053097	0.003448
H26	-0.93265	-1.11624	3.23027	0.178875	0.001858
C27	-0.22462	-1.24845	-2.38407	0.060611	0.003098
H28	0.51329	-2.0123	-2.65095	0.215241	-0.000321
H29	-0.90662	-1.14354	-3.23603	0.178477	0.001859
C30	-0.22368	1.24856	2.38415	0.060514	0.003098
H31	-0.90569	1.14399	3.23616	0.178476	0.001859
H32	0.51466	2.012	2.65103	0.215235	-0.000321
H33	0.48446	2.00749	-2.67543	0.213803	-0.000347
H34	0.48369	-2.00777	2.67535	0.213805	-0.000347

Ni35	1.04592	-0.0003	-0.00005	-0.319056	1.561465
Cl36	2.68526	1.76745	0.0494	-0.571297	0.078006
Cl37	2.68397	-1.76923	-0.04972	-0.571271	0.07801

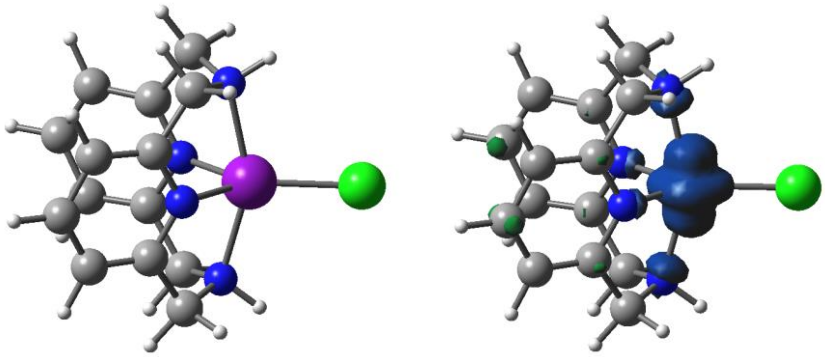
SCF Done: E(UB3P86) = −3194.54937549 A.U. after 1 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation 2.0049, after 2.0000

	1	2	3
	A	A	A
Frequencies --	42.3562	49.5796	50.0640
Red. masses --	5.1904	12.1411	8.7128

Zero-point correction= 0.293701 (Hartree/Particle)
Thermal correction to Energy= 0.312669
Thermal correction to Enthalpy= 0.313613
Thermal correction to Gibbs Free Energy= 0.245064
Sum of electronic and zero-point Energies= −3194.255675
Sum of electronic and thermal Energies= −3194.236707
Sum of electronic and thermal Enthalpies= −3194.235763
Sum of electronic and thermal Free Energies= −3194.304311

Item	Value	Threshold	Converged?
Maximum Force	0.000011	0.000450	YES
RMS Force	0.000002	0.000300	YES

Table S44. DFT-optimized geometry of Ni^{I}(dapp)Cl (doublet), computed at the UB3P86/6-31+G(d,p) level using C-PCM.



Spin Density Distribution

atom	x	y	z	Mulliken charge	Spin density
Cl1	-0.000183	-3.642276	0.000000	-0.548952	0.022849
Ni2	0.000345	-1.306523	0.000000	-0.833216	1.038842
N3	1.428238	0.099915	0.000000	0.317363	0.019652
C4	1.677447	0.724348	1.163904	-0.181355	-0.040599
C5	1.677447	0.724348	-1.163904	-0.181355	-0.040599
N6	0.000164	-0.796299	2.142134	-0.378166	0.02864
N7	0.000164	-0.796299	-2.142134	-0.378166	0.02864
H8	0.000176	-1.62267	2.730335	0.36898	-0.001363
H9	0.000176	-1.62267	-2.730335	0.36898	-0.001363
C10	2.269884	1.981931	1.203246	-0.06539	0.024279
C11	2.269884	1.981931	-1.203246	-0.06539	0.024279
N12	-1.428064	0.09973	0.000000	0.317544	0.019691
C13	1.247679	-0.048392	2.38779	-0.03911	0.004487
C14	1.247679	-0.048392	-2.38779	-0.03911	0.004487
H15	2.020983	-0.788655	2.623735	0.196032	-0.00136
H16	2.020983	-0.788655	-2.623735	0.196032	-0.00136
H17	1.164421	0.624421	3.251225	0.1652	0.001427
H18	1.164421	0.624421	-3.251225	0.1652	0.001427
C19	-1.247367	-0.048434	2.387839	-0.039222	0.004465
C20	-1.247367	-0.048434	-2.387839	-0.039222	0.004465
H21	-1.16396	0.624613	3.251084	0.165206	0.001428
H22	-1.16396	0.624613	-3.251084	0.165206	0.001428
H23	-2.020577	-0.788653	2.624192	0.196043	-0.001356
H24	-2.020577	-0.788653	-2.624192	0.196043	-0.001356
C25	-1.67748	0.724037	1.163893	-0.181538	-0.040523
C26	-1.67748	0.724037	-1.163893	-0.181538	-0.040523
C27	-2.270484	1.981363	1.203247	-0.06523	0.02425
C28	-2.270484	1.981363	-1.203247	-0.06523	0.02425
H29	-2.461044	2.46519	2.156019	0.175772	-0.000443
H30	-2.461044	2.46519	-2.156019	0.175772	-0.000443
C31	-2.591431	2.610235	0.000000	-0.299647	-0.055926
H32	-3.052044	3.592736	0.000000	0.180355	0.002592
H33	2.460253	2.46583	2.156021	0.175762	-0.000445

H34	2.460253	2.46583	-2.156021	0.175762	-0.000445
C35	2.590537	2.610966	0.000000	-0.299759	-0.05607
H36	3.050671	3.593689	0.000000	0.180346	0.002599

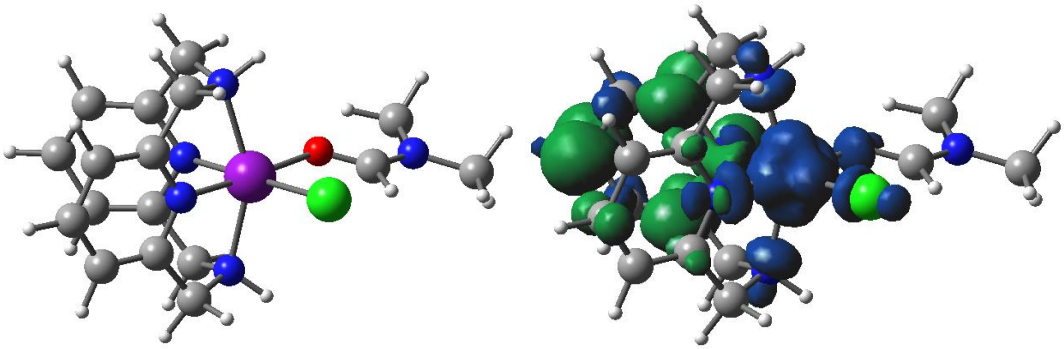
SCF Done: E(UB3P86) = −2733.94579996 A.U. after 1 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation 0.8038, after 0.7513

	1	2	3
	A'	A'	A''
Frequencies --	24.2531	44.7978	60.7323
Red. masses --	15.1080	5.2579	3.3707

Zero-point correction= 0.290282 (Hartree/Particle)
Thermal correction to Energy= 0.307683
Thermal correction to Enthalpy= 0.308627
Thermal correction to Gibbs Free Energy= 0.243594
Sum of electronic and zero-point Energies= −2733.655518
Sum of electronic and thermal Energies= −2733.638117
Sum of electronic and thermal Enthalpies= −2733.637173
Sum of electronic and thermal Free Energies= −2733.702206

Item	Value	Threshold	Converged?
Maximum Force	0.000009	0.000450	YES
RMS Force	0.000002	0.000300	YES

Table S45. DFT-optimized geometry of Ni^{I}(dapp)Cl(DMF) (doublet), computed at the UB3P86/6-31+G(d,p) level using C-PCM.



Spin Density Distribution

atom	x	y	z	Mulliken charge	Spin density
Ni1	-0.40163	-0.43297	-0.09114	-0.72044	1.551684
C2	0.9062	1.80041	1.21317	-0.05918	-0.217473
N3	0.35097	1.48693	0.00099	-0.0108	-0.081226
N4	0.20444	-0.16209	-2.19989	-0.35934	0.046794
H5	-0.49732	-0.4647	-2.8691	0.361392	-0.004225
C6	2.0489	2.56601	1.33392	0.03535	0.17328
H7	2.4364	2.79647	2.32317	0.14462	-0.001842
N8	1.49715	-1.04414	0.0108	0.277699	0.046039
C9	2.69861	3.03914	0.17429	-0.41855	-0.428828
H10	3.59254	3.64948	0.24076	0.151361	0.02049
C11	2.18932	2.62226	-1.07394	-0.00077	0.173951
H12	2.6887	2.89739	-1.99956	0.144704	-0.001835
N13	-0.05179	-0.25949	2.09017	-0.31045	0.048831
H14	-0.82708	-0.58905	2.65813	0.360451	-0.004327
C15	1.04218	1.85536	-1.12272	-0.01672	-0.223246
C16	0.43577	1.2944	-2.37454	-0.18481	-0.01161
H17	1.06368	1.50396	-3.25039	0.155268	0.0028
H18	-0.55199	1.73895	-2.54674	0.172709	-0.009695
C19	1.41122	-0.98595	-2.38697	0.036999	0.015662
H20	2.03797	-0.62144	-3.21109	0.167332	0.002674
C21	2.22051	-1.07935	-1.11736	-0.15493	-0.089442
C22	3.60012	-1.24935	-1.07765	-0.37442	0.043335
H23	4.17545	-1.27482	-1.99742	0.173264	0.000518
C24	4.22272	-1.36948	0.16629	-0.19611	-0.085032
H25	5.29879	-1.49643	0.22781	0.17825	0.003452
C26	3.4559	-1.30404	1.33135	-0.40207	0.048541
C27	2.08101	-1.13269	1.2141	-0.08613	-0.091992
C28	0.15807	1.18609	2.35845	-0.20407	-0.012726
H29	0.6797	1.35081	3.31037	0.155427	0.002761
H30	3.91781	-1.37364	2.31088	0.173275	0.000509
C31	1.1248	-1.0969	2.3804	0.018811	0.017767
H32	0.75961	-2.11586	2.55382	0.198501	-0.002002
H33	1.64768	-0.77574	3.29046	0.167581	0.002639

H34	-0.84256	1.62872	2.43583	0.17188	-0.009736
Cl35	-1.32483	-2.71606	-0.19433	-0.6576	0.055139
H36	1.07421	-1.9945	-2.65331	0.199187	-0.001985
O37	-2.37495	0.39139	-0.22715	-0.46799	0.019349
C38	-3.43926	-0.20215	0.02999	0.443612	0.008305
H39	-3.43772	-1.27333	0.2666	0.14859	0.001148
N40	-4.64181	0.37753	0.0358	0.110361	-0.004746
C41	-4.80962	1.78693	-0.26467	-0.35893	-0.001969
C42	-5.83906	-0.38207	0.34382	-0.2593	-0.001391
H43	-5.45083	1.90939	-1.14315	0.180005	-0.000083
H44	-5.27618	2.29674	0.58392	0.178158	-0.000096
H45	-3.83264	2.22555	-0.46179	0.198071	-0.00008
H46	-5.57428	-1.42032	0.54875	0.176014	-0.000016
H47	-6.33737	0.03752	1.22317	0.181691	0.000019
H48	-6.53405	-0.35308	-0.50102	0.182038	-0.00009

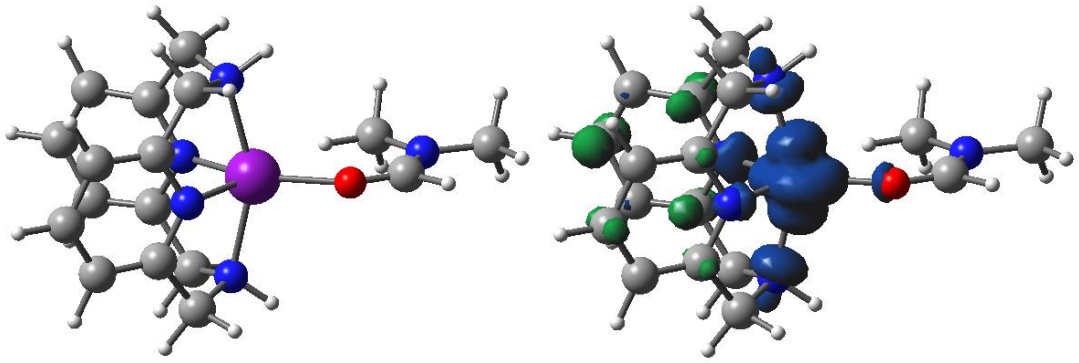
SCF Done: E(UB3P86) = −2983.08747638 A.U. after 1 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation 2.0048, after 2.0000

	1	2	3
	A	A	A
Frequencies --	3.1414	21.6665	34.5771
Red. masses --	3.0516	3.9051	4.8579

Zero-point correction= 0.397608 (Hartree/Particle)
Thermal correction to Energy= 0.422276
Thermal correction to Enthalpy= 0.423221
Thermal correction to Gibbs Free Energy= 0.338806
Sum of electronic and zero-point Energies= −2982.689868
Sum of electronic and thermal Energies= −2982.665200
Sum of electronic and thermal Enthalpies= −2982.664256
Sum of electronic and thermal Free Energies= −2982.748671

Item	Value	Threshold	Converged?
Maximum Force	0.000000	0.000002	YES
RMS Force	0.000000	0.000001	YES

Table S46. DFT-optimized geometry of $[Ni^{I}(dapp)(DMF)]^{+}$ (doublet), computed at the UB3P86/6-31+G(d,p) level using C-PCM.



Spin Density Distribution

atom	x	y	z	Mulliken charge	Spin density
Ni1	0.61405	-0.33048	0.00001	-0.20389	1.052823
C2	-1.7679	-1.50978	1.16313	-0.04816	-0.019495
N3	-1.10582	-1.44183	0.00007	0.14225	0.012603
N4	0.12768	-0.25356	-2.137	-0.44099	0.026824
H5	0.919	-0.45375	-2.73943	0.371773	-0.001226
C6	-3.13855	-1.74663	1.2049	-0.15114	0.011121
H7	-3.65848	-1.79882	2.15619	0.177449	-0.000276
N8	-0.40819	1.33584	-0.00005	0.27748	0.029727
C9	-3.82717	-1.89065	0.00012	-0.23619	-0.031053
H10	-4.89675	-2.07401	0.00013	0.182952	0.001555
C11	-3.13858	-1.74674	-1.2047	-0.15114	0.011121
H12	-3.65852	-1.79901	-2.15597	0.177449	-0.000276
N13	0.12771	-0.25338	2.13703	-0.441	0.026824
H14	0.91904	-0.45352	2.73946	0.371773	-0.001226
C15	-1.76792	-1.50988	-1.16297	-0.04815	-0.019495
C16	-0.90463	-1.28331	-2.38273	-0.10457	-0.003235
H17	-1.52982	-1.03466	-3.24963	0.167414	0.001744
H18	-0.37703	-2.21461	-2.61709	0.197185	-0.000731
C19	-0.30101	1.13652	-2.38964	-0.02983	-0.001649
H20	-0.98298	1.20825	-3.24647	0.168767	0.000977
C21	-0.93319	1.75376	-1.16574	-0.03062	-0.034439
C22	-1.97069	2.6781	-1.20375	-0.36888	0.019369
H23	-2.3797	2.99947	-2.15631	0.177837	-0.000298
C24	-2.48401	3.16237	-0.00012	-0.23241	-0.057978
H25	-3.2958	3.88229	-0.00014	0.181606	0.002821
C26	-1.97068	2.6782	1.20356	-0.36888	0.019369
C27	-0.93318	1.75386	1.16561	-0.0306	-0.034439
C28	-0.90459	-1.28311	2.38286	-0.10456	-0.003235
H29	-1.52976	-1.0344	3.24975	0.167414	0.001744
H30	-2.37968	2.99965	2.1561	0.177837	-0.000298
C31	-0.30098	1.13672	2.38955	-0.02984	-0.001649
H32	0.60071	1.70665	2.64167	0.198437	-0.00143
H33	-0.98294	1.20852	3.24638	0.168767	0.000977

H34	-0.37698	-2.21439	2.61727	0.197185	-0.000731
H35	0.60068	1.70643	-2.64181	0.198437	-0.00143
O36	2.39031	-1.35776	0.00004	-0.45203	0.002425
C37	3.62465	-1.20899	0.00005	0.367465	-0.000629
H38	4.27131	-2.09644	0.00001	0.143789	0.001364
N39	4.30524	-0.06059	-0.00003	-0.045	-0.00202
C40	3.66067	1.23915	-0.00007	-0.43387	-0.00478
C41	5.75841	-0.06405	-0.0001	-0.34966	-0.000145
H42	3.95945	1.80188	0.88983	0.18134	-0.000084
H43	3.95937	1.80179	-0.89005	0.181341	-0.000084
H44	2.57406	1.1072	-0.00001	0.18509	-0.000848
H45	6.12805	-1.09042	-0.00007	0.174291	-0.000111
H46	6.13533	0.4494	-0.88965	0.183043	-0.000048
H47	6.1354	0.44947	0.88938	0.183041	-0.000048

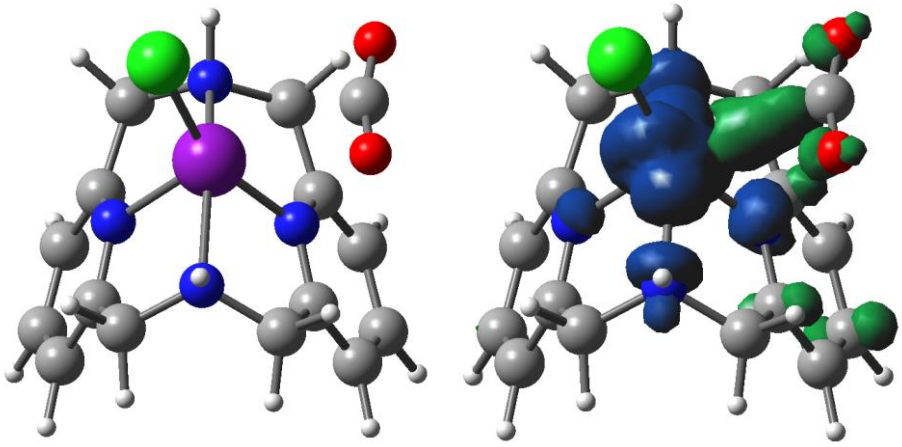
SCF Done: E(UB3P86) = −2522.47498140 A.U. after 1 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation 0.7954, after 0.7509

	1	2	3
	A	A	A
Frequencies --	10.1681	25.4599	39.6304
Red. masses --	4.4230	5.1798	2.5143

Zero-point correction= 0.394456 (Hartree/Particle)
Thermal correction to Energy= 0.417296
Thermal correction to Enthalpy= 0.418240
Thermal correction to Gibbs Free Energy= 0.340044
Sum of electronic and zero-point Energies= −2522.080525
Sum of electronic and thermal Energies= −2522.057685
Sum of electronic and thermal Enthalpies= −2522.056741
Sum of electronic and thermal Free Energies= −2522.134938

Item	Value	Threshold	Converged?
Maximum Force	0.000016	0.000450	YES
RMS Force	0.000002	0.000300	YES

Table S47. TS geometry optimized for [Ni^{I}(dapp)Cl---CO_2]‡ (doublet), computed at the UB3P86/6-31+G(d,p) level using C-PCM.



Spin Density Distribution

atom	x	y	z	Mulliken charge	Spin density
Cl1	2.312207	-2.44841	0.00062	-0.49456	0.020924
Ni2	0.785414	-0.67505	0.000296	-0.85677	0.994439
N3	-1.21803	-1.24835	0.000469	0.308342	0.024369
C4	-1.87017	-1.14135	-1.16207	-0.13643	-0.02408
C5	-1.87032	-1.14033	1.162812	-0.13649	-0.02407
N6	0.294697	-0.45748	-2.14031	-0.30262	0.027661
N7	0.294569	-0.45602	2.140715	-0.30264	0.027661
H8	1.010186	-0.87156	-2.72782	0.371876	-0.00125
H9	1.00989	-0.86992	2.728559	0.371876	-0.00125
C10	-3.25511	-1.00396	-1.20525	-0.1406	0.01235
C11	-3.25528	-1.00292	1.205677	-0.14057	0.01235
N12	0.217426	1.207139	-0.00039	0.511921	0.042671
C13	-0.9767	-1.16746	-2.38152	-0.01398	0.006853
C14	-0.97708	-1.16537	2.382458	-0.01396	0.006851
H15	-0.72568	-2.20973	-2.60731	0.198148	-0.00039
H16	-0.72645	-2.20746	2.609484	0.198147	-0.0004
H17	-1.51169	-0.7648	-3.25122	0.164663	0.001822
H18	-1.51213	-0.76159	3.251602	0.164668	0.001823
C19	0.258396	0.992424	-2.39623	-0.15281	-0.00391
C20	0.258787	0.994089	2.395565	-0.15262	-0.0039
H21	-0.39446	1.248767	-3.2407	0.165307	0.001043
H22	-0.39365	1.251292	3.240106	0.165303	0.001042
H23	1.276235	1.29618	-2.66221	0.204937	-0.00145
H24	1.276841	1.297717	2.66086	0.204951	-0.00145
C25	-0.16191	1.760113	-1.16616	0.465386	-0.02151
C26	-0.16174	1.76094	1.165054	0.465659	-0.02152
C27	-0.87913	2.950732	-1.20376	-0.84152	0.022661
C28	-0.87895	2.951583	1.201923	-0.84179	0.022669
H29	-1.17431	3.378114	-2.15669	0.17802	-0.0001
H30	-1.17397	3.379647	2.154594	0.17802	-0.0001

C31	-1.22561	3.565584	-0.00111	-0.28248	-0.05026
H32	-1.78818	4.49346	-0.0014	0.181991	0.002396
H33	-3.77096	-0.91885	-2.15636	0.177628	-0.00015
H34	-3.77126	-0.91695	2.15664	0.177626	-0.00015
C35	-3.95542	-0.95653	0.000145	-0.25796	-0.01984
H36	-5.03523	-0.84734	0.000024	0.18309	0.000938
C37	3.209014	0.707854	-0.00023	0.608063	-0.04935
O38	3.339519	0.787911	1.166985	-0.28892	-0.0027
O39	3.339527	0.786803	-1.16752	-0.28892	-0.0027

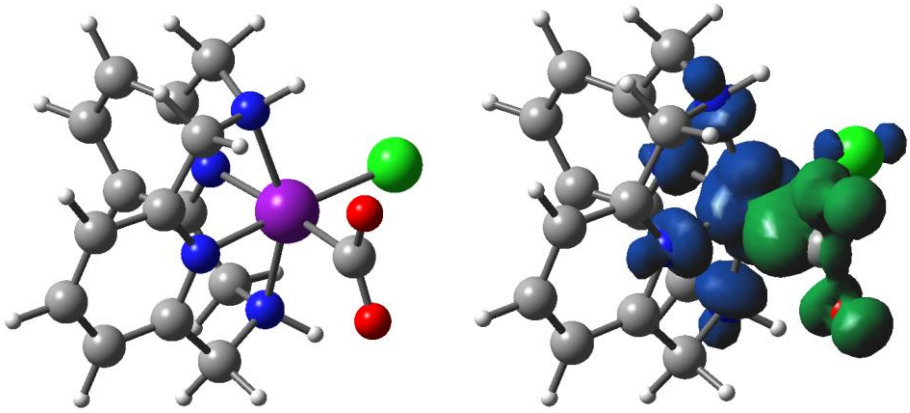
SCF Done: E(UB3P86) = -2922.91875485 A.U. after 2 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation 0.8073, after 0.7511

	1	2	3
	A	A	A
Frequencies --	-163.6985	39.0797	44.8788
Red. masses --	14.8272	9.5317	5.8446

Zero-point correction= 0.302330 (Hartree/Particle)
Thermal correction to Energy= 0.323098
Thermal correction to Enthalpy= 0.324042
Thermal correction to Gibbs Free Energy= 0.251473
Sum of electronic and zero-point Energies= -2922.616425
Sum of electronic and thermal Energies= -2922.595657
Sum of electronic and thermal Enthalpies= -2922.594713
Sum of electronic and thermal Free Energies= -2922.667282

Item	Value	Threshold	Converged?
Maximum Force	0.000015	0.000450	YES
RMS Force	0.000002	0.000300	YES

Table S48. DFT-optimized geometry of $Ni^{III}(dapp)(CO_2^{2-})Cl$ (doublet), computed at the UB3P86/6-31+G(d,p) level using C-PCM.



Spin Density Distribution

atom	x	y	z	Mulliken charge	Spin density
Cl1	-1.503527	2.819906	0.000182	-0.371032	0.046364
Ni2	-0.811762	0.595639	0.000053	-0.837024	1.108931
N3	1.207724	0.958632	-0.000029	0.326941	0.030846
C4	1.855328	0.943922	-1.166315	-0.127098	-0.002759
C5	1.855497	0.943837	1.166166	-0.127202	-0.002758
N6	-0.347037	0.336749	-2.112917	-0.306448	0.039359
N7	-0.34675	0.336702	2.113087	-0.306525	0.039335
H8	-1.067519	0.811331	-2.645943	0.387382	-0.00227
H9	-1.067144	0.811252	2.646262	0.387373	-0.002269
C10	3.247105	0.94906	-1.208129	-0.342714	0.004124
C11	3.24728	0.948967	1.207773	-0.342698	0.004126
N12	-0.36452	-1.334628	0.000021	0.59047	0.076819
C13	0.960666	0.958941	-2.385057	0.025834	0.003865
C14	0.961023	0.958823	2.385055	0.025937	0.00386
H15	0.776285	2.003924	-2.656211	0.20938	-0.00018
H16	0.776735	2.003799	2.656306	0.209378	-0.00018
H17	1.468142	0.489637	-3.23638	0.175074	0.002175
H18	1.468617	0.489449	3.236267	0.175071	0.002174
C19	-0.427072	-1.105995	-2.391268	-0.115757	0.001525
C20	-0.426769	-1.106072	2.391338	-0.115782	0.001544
H21	0.215689	-1.399469	-3.229567	0.173932	0.001512
H22	0.216128	-1.399589	3.229517	0.173925	0.001511
H23	-1.461727	-1.324672	-2.672679	0.219981	-0.000375
H24	-1.461373	-1.32477	2.67292	0.219973	-0.000375
C25	-0.094296	-1.926145	-1.168491	0.338609	-0.006546
C26	-0.094169	-1.926183	1.168476	0.338519	-0.006559
C27	0.435364	-3.212028	-1.206097	-0.658689	-0.001312
C28	0.435495	-3.212071	1.205971	-0.658533	-0.001311
H29	0.656662	-3.685143	-2.156703	0.188564	0.000681
H30	0.6569	-3.685222	2.156535	0.188562	0.000681
C31	0.689604	-3.861869	-0.000087	-0.338847	-0.006872
H32	1.108111	-4.863076	-0.000128	0.190406	0.000363

H33	3.771926	0.932532	-2.157396	0.186744	0.000356
H34	3.77224	0.932372	2.156962	0.186743	0.000356
C35	3.943229	0.959203	-0.000229	-0.205934	-0.002583
H36	5.028521	0.955329	-0.000308	0.188171	0.000205
C37	-2.739197	0.078661	0.000003	0.725275	-0.170277
O38	-3.169278	-0.049673	1.145181	-0.488965	-0.082043
O39	-3.169389	-0.049386	-1.145161	-0.488999	-0.082039

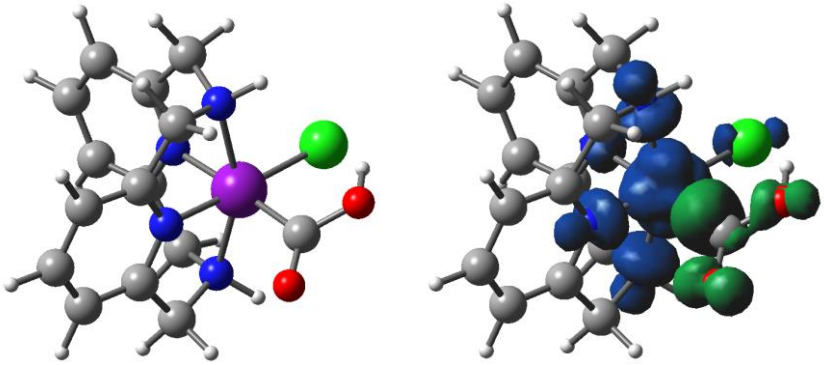
SCF Done: E(UB3P86) = -2922.93740857 A.U. after 2 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation 0.9513, after 0.7520

	1	2	3
	A	A	A
Frequencies --	39.8408	54.2709	57.2680
Red. masses --	5.4457	6.9532	3.6769

Zero-point correction= 0.304436 (Hartree/Particle)
Thermal correction to Energy= 0.324797
Thermal correction to Enthalpy= 0.325741
Thermal correction to Gibbs Free Energy= 0.255105
Sum of electronic and zero-point Energies= -2922.632973
Sum of electronic and thermal Energies= -2922.612611
Sum of electronic and thermal Enthalpies= -2922.611667
Sum of electronic and thermal Free Energies= -2922.682304

Item	Value	Threshold	Converged?
Maximum Force	0.000011	0.000450	YES
RMS Force	0.000003	0.000300	YES

Table S49. DFT-optimized geometry of $[Ni^{III}(dapp)(CO_2H^-)Cl]^+$ (doublet), computed at the UB3P86/6-31+G(d,p) level using C-PCM.



Spin Density Distribution

atom	x	y	z	Mulliken charge	Spin density
Cl1	0.055571	-3.036443	-0.157943	-0.319924	0.041185
Ni2	-0.445344	-0.797044	-0.064333	-0.519669	0.954498
N3	1.446038	-0.313944	-0.052869	0.405824	0.016233
C4	2.071644	-0.190788	1.122728	-0.054722	0.003184
C5	2.033075	-0.003602	-1.213332	0.002486	0.003906
N6	-0.180236	-0.572904	2.05741	-0.348755	0.072222
N7	-0.247032	-0.283792	-2.118766	-0.378098	0.077242
H8	-0.631948	-1.319408	2.576986	0.404026	-0.003095
H9	-0.701136	-0.969553	-2.714522	0.406899	-0.003432
C10	3.377911	0.281115	1.175914	-0.509963	-0.005644
C11	3.338855	0.473301	-1.232721	-0.495335	-0.006657
N12	-0.843381	1.110341	0.090816	0.680962	0.0634
C13	1.276393	-0.665487	2.307999	0.044064	-0.003198
C14	1.200068	-0.285128	-2.434849	0.003752	-0.002644
H15	1.512417	-1.722653	2.467965	0.229922	-0.000065
H16	1.457227	-1.287453	-2.792476	0.228056	-0.000084
H17	1.561222	-0.124824	3.216295	0.194004	0.002747
H18	1.433546	0.41778	-3.241094	0.19382	0.002836
C19	-0.79313	0.709797	2.457892	-0.040627	0.000914
C20	-0.921468	1.017189	-2.307555	0.167503	-0.003129
H21	-0.260761	1.163702	3.300077	0.195809	0.002215
H22	-0.466448	1.588591	-3.12269	0.192207	0.001991
H23	-1.813853	0.503605	2.796394	0.226561	-0.000309
H24	-1.960356	0.814065	-2.5827	0.23295	-0.000299
C25	-0.867807	1.672723	1.300815	0.33479	-0.003972
C26	-0.931327	1.823368	-1.035163	-0.07199	-0.002147
C27	-1.004487	3.050161	1.430454	-0.618479	-0.003274
C28	-1.067318	3.205426	-0.978463	-0.82494	0.001238
H29	-1.021801	3.507872	2.41314	0.198229	0.000884
H30	-1.13064	3.786626	-1.891463	0.198495	0.000799
C31	-1.107725	3.817606	0.272626	-0.264821	-0.002567
H32	-1.206806	4.895497	0.344772	0.198664	0.000111
H33	3.884039	0.387651	2.128612	0.198992	0.00024

H34	3.814553	0.731356	-2.172081	0.198899	0.000255
C35	4.010157	0.61623	-0.020075	-0.210219	-0.000677
H36	5.026559	0.995244	-0.006408	0.198652	0.000146
C37	-2.345674	-1.190003	-0.11043	0.716052	-0.113514
O38	-3.148264	-0.430278	-0.592403	-0.41159	-0.06784
O39	-2.715489	-2.334164	0.46065	-0.337398	-0.024689
H40	-1.903594	-2.88515	0.568411	0.354911	0.000991

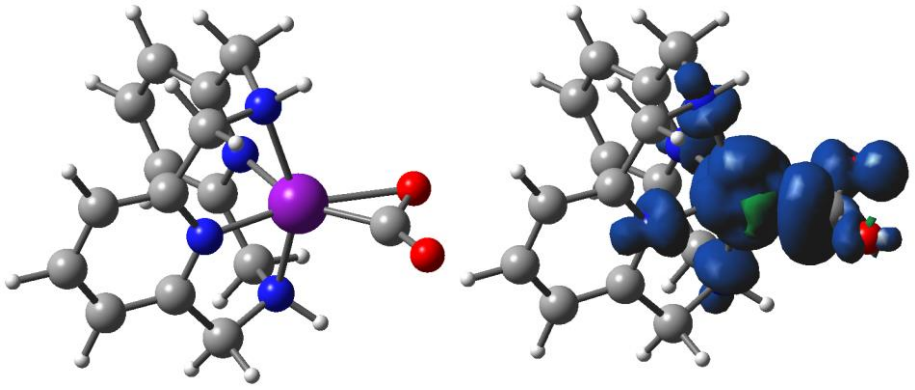
SCF Done: E(UB3P86) = -2923.37233053 A.U. after 2 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation 0.8264, after 0.7505

	1	2	3
	A	A	A
Frequencies --	44.2675	51.2368	56.7712
Red. masses --	5.1691	8.5114	3.3071

Zero-point correction= 0.318825 (Hartree/Particle)
Thermal correction to Energy= 0.338675
Thermal correction to Enthalpy= 0.339619
Thermal correction to Gibbs Free Energy= 0.270263
Sum of electronic and zero-point Energies= -2923.053506
Sum of electronic and thermal Energies= -2923.033655
Sum of electronic and thermal Enthalpies= -2923.032711
Sum of electronic and thermal Free Energies= -2923.102068

Item	Value	Threshold	Converged?
Maximum Force	0.000012	0.000450	YES
RMS Force	0.000003	0.000300	YES

Table S50. DFT-optimized geometry of $Ni^{II}(dapp)(CO_2^{2-})$ (triplet), computed at the UB3P86/6-31+G(d,p) level using C-PCM.



Spin Density Distribution

atom	x	y	z	Mulliken charge	Spin density
Ni1	-1.181111	0.313441	0.000005	-1.258511	1.81229
N2	-0.062275	-1.352818	-0.000275	0.341233	0.077903
C3	0.405715	-1.812403	1.165814	-0.182706	-0.002438
C4	0.405967	-1.811866	-1.166461	-0.182562	-0.002448
N5	-0.624004	0.213933	2.140256	-0.444397	0.028077
N6	-0.623723	0.214837	-2.140296	-0.444405	0.02806
H7	-1.429956	0.41625	2.721564	0.380821	-0.001053
H8	-1.429682	0.41726	-2.721555	0.380821	-0.001052
C9	1.363039	-2.821641	1.205222	-0.102867	-0.032822
C10	1.363294	-2.821103	-1.206114	-0.10285	-0.03282
N11	0.603787	1.346842	0.000277	0.278213	0.073304
C12	-0.204704	-1.176004	2.391395	0.013294	0.003389
C13	-0.204126	-1.174913	-2.391934	0.013122	0.003395
H14	-1.105302	-1.742135	2.654448	0.207289	-0.000279
H15	-1.104505	-1.741086	-2.655633	0.207289	-0.000279
H16	0.484902	-1.250875	3.241296	0.174778	0.00146
H17	0.485832	-1.249254	-3.241599	0.174776	0.00146
C18	0.405756	1.237705	2.392134	-0.039899	0.017127
C19	0.405847	1.238909	-2.39163	-0.039794	0.017122
H20	1.047702	0.975156	3.242189	0.173071	0.002526
H21	1.047819	0.976951	-3.241851	0.173068	0.002526
H22	-0.11546	2.16453	2.655938	0.204575	0.000525
H23	-0.115526	2.165801	-2.654883	0.20457	0.000526
C24	1.245516	1.49761	1.16428	-0.145129	0.010533
C25	1.245576	1.498224	-1.163621	-0.145242	0.010545
C26	2.583089	1.880109	1.20557	-0.13848	-0.011443
C27	2.583143	1.880744	-1.204648	-0.138429	-0.011446
H28	3.091807	1.997021	2.156636	0.184775	0.000654
H29	3.091909	1.998166	-2.155626	0.184775	0.000654
C30	3.252019	2.087368	0.000534	-0.233088	0.012844
H31	4.297035	2.380007	0.000630	0.18814	-0.00052
H32	1.73987	-3.18392	2.155808	0.185762	0.000774
H33	1.740332	-3.18295	-2.156784	0.18576	0.000774

C34	1.836681	-3.335847	-0.000514	-0.271528	0.000495
H35	2.588729	-4.118192	-0.000608	0.187942	0.00029
C36	-3.133226	0.33895	-0.000056	1.091065	-0.093048
O37	-4.240234	-0.247133	-0.000317	-0.773001	0.000723
O38	-2.962567	1.622922	0.000359	-0.492255	0.081672

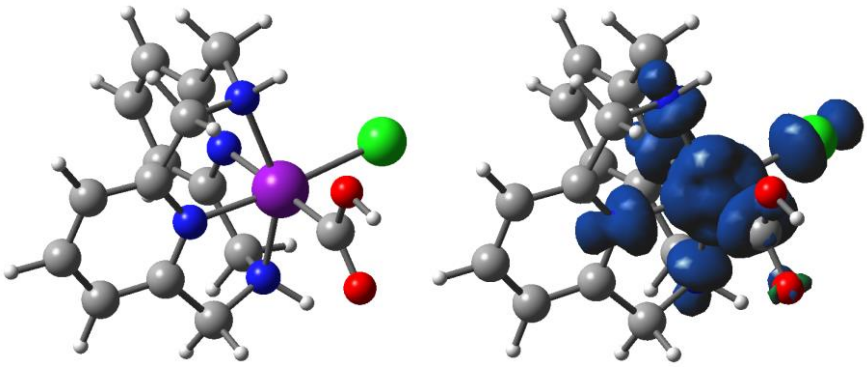
SCF Done: E(UB3P86) = -2462.32860407 A.U. after 1 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation 2.0128, after 2.0001

	1	2	3
	A	A	A
Frequencies --	39.7065	48.3675	56.3325
Red. masses --	5.1951	7.8507	3.3700

Zero-point correction= 0.301636 (Hartree/Particle)
Thermal correction to Energy= 0.320443
Thermal correction to Enthalpy= 0.321387
Thermal correction to Gibbs Free Energy= 0.253614
Sum of electronic and zero-point Energies= -2462.026968
Sum of electronic and thermal Energies= -2462.008161
Sum of electronic and thermal Enthalpies= -2462.007217
Sum of electronic and thermal Free Energies= -2462.074990

Item	Value	Threshold	Converged?
Maximum Force	0.000014	0.000450	YES
RMS Force	0.000003	0.000300	YES

Table S51. DFT-optimized geometry of Ni^{II}(dapp)(CO_2H^-)Cl (triplet), computed at the UB3P86/6-31+G(d,p) level using C-PCM.



Spin Density Distribution

atom	x	y	z	Mulliken charge	Spin density
Cl1	-1.568263	-2.859777	-0.055966	-0.622459	0.076974
Ni2	-0.895923	-0.447466	-0.036529	-0.675544	1.663281
N3	1.062025	-1.060176	0.012393	0.362832	0.072019
C4	1.672933	-1.16014	1.194222	-0.068318	0.00602
C5	1.737299	-1.143519	-1.135012	-0.082988	0.003694
N6	-0.425326	-0.22564	2.10307	-0.344854	0.037971
N7	-0.315559	-0.20895	-2.147066	-0.343634	0.036951
H8	-1.209717	-0.570485	2.646033	0.38257	-0.001999
H9	-1.065745	-0.559313	-2.732965	0.384771	-0.002224
C10	3.04418	-1.388338	1.272492	-0.499445	-0.003306
C11	3.111126	-1.371674	-1.140084	-0.474444	-0.003828
N12	-0.080426	1.424626	-0.007592	0.542835	0.085201
C13	0.758987	-1.05086	2.392379	0.012043	0.007753
C14	0.89342	-1.01569	-2.382112	0.01329	0.003437
H15	0.403777	-2.057932	2.635722	0.211169	-0.000176
H16	0.566049	-2.020188	-2.670963	0.210575	-0.000226
H17	1.314295	-0.681809	3.263392	0.173487	0.002216
H18	1.495377	-0.620264	-3.209576	0.173649	0.002166
C19	-0.265133	1.213356	2.376137	0.007414	-0.00369
C20	-0.162085	1.234406	-2.398311	-0.017064	0.002887
H21	0.387774	1.396043	3.238404	0.174903	0.001864
H22	0.520008	1.434812	-3.233704	0.174737	0.001927
H23	-1.255239	1.60778	2.628524	0.210099	-0.000399
H24	-1.146947	1.620178	-2.682483	0.211827	-0.000427
C25	0.240012	1.967365	1.168627	0.130897	-0.000113
C26	0.289848	1.978829	-1.163924	0.176288	-0.004463
C27	0.951998	3.162484	1.230089	-0.499552	-0.016093
C28	1.00358	3.174	-1.183688	-0.514532	-0.01444
H29	1.214714	3.599103	2.187767	0.186587	0.000923
H30	1.307174	3.619439	-2.125034	0.186487	0.00092
C31	1.328549	3.770208	0.033730	-0.344991	-0.005038
H32	1.891271	4.698034	0.050345	0.188368	0.000326
H33	3.536623	-1.464248	2.236159	0.186098	0.000792

H34	3.656265	-1.434512	-2.075915	0.18611	0.000795
C35	3.764244	-1.501011	0.084297	-0.203355	-0.00171
H36	4.835662	-1.671606	0.112804	0.187784	0.000192
C37	-2.807212	0.158231	-0.127193	0.676158	0.059545
O38	-3.488933	0.407616	-1.124449	-0.570839	-0.003068
O39	-3.437476	0.33507	1.092674	-0.453572	-0.018857
H40	-4.349219	0.633832	0.904391	0.364615	0.012202

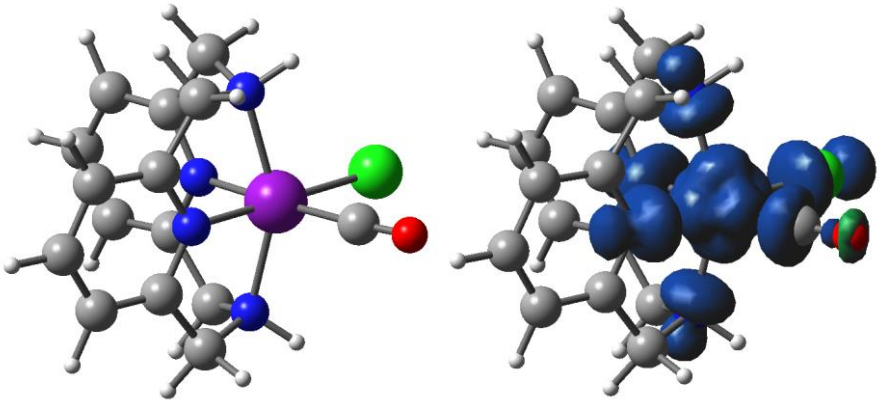
SCF Done: E(UB3P86) = -2923.54299883 A.U. after 1 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation 2.0065, after 2.0000

	1	2	3
	A	A	A
Frequencies --	30.2227	37.8228	41.8623
Red. masses --	8.5705	10.6552	5.4623

Zero-point correction= 0.314736 (Hartree/Particle)
Thermal correction to Energy= 0.335967
Thermal correction to Enthalpy= 0.336911
Thermal correction to Gibbs Free Energy= 0.262336
Sum of electronic and zero-point Energies= -2923.228263
Sum of electronic and thermal Energies= -2923.207032
Sum of electronic and thermal Enthalpies= -2923.206088
Sum of electronic and thermal Free Energies= -2923.280663

Item	Value	Threshold	Converged?
Maximum Force	0.000018	0.000450	YES
RMS Force	0.000004	0.000300	YES

Table S52. DFT-optimized geometry of $[Ni^{II}(dapp)(CO)Cl]^{+}$ (triplet), computed at the UB3P86/6-31+G(d,p) level using C-PCM.



Spin Density Distribution

atom	x	y	z	Mulliken charge	Spin density
C1	-0.272551	-1.922734	1.168644	-0.023478	0.000842
N2	0.08573	-1.386091	0.000164	0.310481	0.10277
N3	0.503889	0.232272	-2.105366	-0.406184	0.074797
H4	1.286953	0.524168	-2.68213	0.396758	-0.003012
C5	-1.025997	-3.091364	1.208715	-0.57917	-0.009811
H6	-1.319023	-3.526022	2.158044	0.19413	0.001073
N7	-0.872383	1.195906	-0.000096	0.395832	0.108288
C8	-1.399578	-3.677772	0.000778	-0.186928	-0.003961
H9	-1.993847	-4.585578	0.001017	0.194626	0.000273
C10	-1.026384	-3.09174	-1.207467	-0.579054	-0.009803
H11	-1.319718	-3.526713	-2.156556	0.194123	0.001073
N12	0.504556	0.232989	2.104620	-0.406074	0.074908
H13	1.287977	0.525133	2.680772	0.396807	-0.003016
C14	-0.272918	-1.923096	-1.168057	-0.02351	0.000845
C15	0.2513	-1.198925	-2.381914	0.001587	0.002978
H16	-0.425582	-1.328965	-3.233142	0.18736	0.002349
H17	1.209549	-1.651973	-2.656429	0.222789	-0.000298
C18	-0.638551	1.128685	-2.388021	0.019685	0.001348
H19	-1.240237	0.759489	-3.225553	0.188391	0.002425
C20	-1.503851	1.336294	-1.168975	-0.038311	-0.004416
C21	-2.851001	1.67986	-1.207841	-0.385162	-0.006938
H22	-3.36368	1.790379	-2.156954	0.19507	0.001018
C23	-3.522245	1.860925	0.000206	-0.246561	-0.004887
H24	-4.575165	2.122789	0.000321	0.195976	0.000288
C25	-2.85064	1.680266	1.20811	-0.385248	-0.006942
C26	-1.503512	1.336688	1.168905	-0.038689	-0.004422
C27	0.252103	-1.19807	2.381985	0.001556	0.002976
H28	-0.424445	-1.327751	3.233537	0.187377	0.002352
H29	-3.363018	1.791112	2.157349	0.195076	0.001017
C30	-0.637705	1.129504	2.387625	0.019981	0.001341
H31	-0.230641	2.100779	2.689139	0.219056	-0.000412
H32	-1.238998	0.76063	3.225586	0.188413	0.002429

Cl33	3.179216	-0.553806	-0.000399	-0.468297	0.102202
H34	1.210475	-1.650978	2.656301	0.222805	-0.000298
H35	-0.231686	2.099864	-2.690114	0.219036	-0.000412
C36	2.011343	2.122619	-0.000244	0.628308	0.100442
O37	2.693001	3.029507	-0.000082	-0.283147	-0.026824
Ni38	0.983178	0.405354	-0.000132	0.07459	1.497417

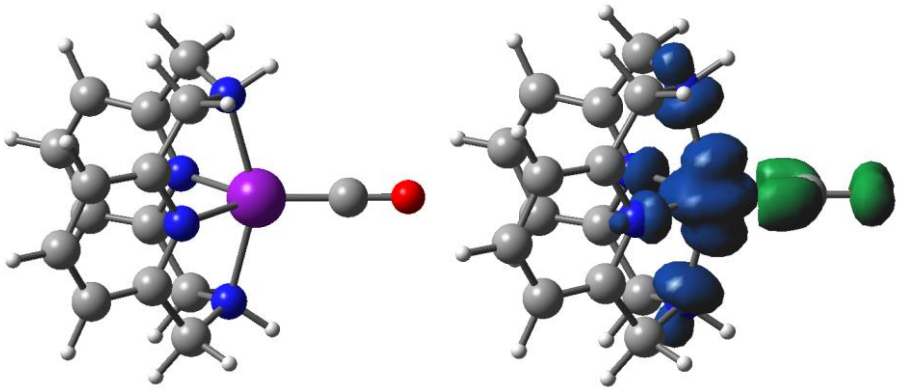
SCF Done: E(UB3P86) = -2847.37740863 A.U. after 1 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation 2.0079, after 2.0000

	1	2	3
	A	A	A
Frequencies --	40.2193	50.9674	52.3686
Red. masses --	5.2064	7.7263	8.1071

Zero-point correction= 0.300990 (Hartree/Particle)
Thermal correction to Energy= 0.320623
Thermal correction to Enthalpy= 0.321568
Thermal correction to Gibbs Free Energy= 0.251861
Sum of electronic and zero-point Energies= -2847.076419
Sum of electronic and thermal Energies= -2847.056785
Sum of electronic and thermal Enthalpies= -2847.055841
Sum of electronic and thermal Free Energies= -2847.125548

Item	Value	Threshold	Converged?
Maximum Force	0.000102	0.000450	YES
RMS Force	0.000022	0.000300	YES

Table S53. DFT-optimized geometry of [Ni^{I}(dapp)(CO)]$^{+}$ (doublet), computed at the UB3P86/6-31+G(d,p) level using C-PCM.



Spin Density Distribution

atom	x	y	z	Mulliken charge	Spin density
C1	-0.676358	1.72861	-1.164869	-0.284199	-0.017399
N2	-0.101753	1.408147	-0.000054	0.267498	0.043736
N3	0.807873	-0.000021	2.119118	-0.442364	0.049312
H4	1.638942	0.000178	2.700565	0.383222	-0.00222
C5	-1.857602	2.462758	-1.205475	-0.03561	0.000938
H6	-2.314585	2.715333	-2.156251	0.188483	0.000245
N7	-0.100963	-1.409067	0.000026	0.266814	0.043687
C8	-2.443444	2.844706	-0.000183	-0.309527	-0.00811
H9	-3.367453	3.413607	-0.000232	0.19075	0.000374
C10	-1.857695	2.462823	1.205175	-0.035596	0.00094
H11	-2.314752	2.715453	2.155902	0.188483	0.000245
N12	0.808008	-0.000144	-2.119078	-0.44237	0.049297
H13	1.639137	-0.000011	-2.700439	0.383222	-0.00222
C14	-0.676453	1.728665	1.1647	-0.284188	-0.017402
C15	0.065392	1.248205	2.386945	0.004639	0.00896
H16	-0.622072	1.139488	3.233997	0.179341	0.00247
H17	0.80158	2.010664	2.664271	0.210571	-0.000246
C18	0.065941	-1.248588	2.386999	0.004249	0.008966
H19	-0.621454	-1.140203	3.234149	0.179318	0.002471
C20	-0.675933	-1.729076	1.164799	-0.284024	-0.0174
C21	-1.857685	-2.46243	1.205327	-0.035056	0.000943
H22	-2.314945	-2.714669	2.156059	0.188478	0.000245
C23	-2.443689	-2.844026	0.000005	-0.309647	-0.008105
H24	-3.368129	-3.412227	-0.000003	0.190755	0.000373
C25	-1.857629	-2.462488	-1.205306	-0.035074	0.000942
C26	-0.675879	-1.729127	-1.164758	-0.284001	-0.017394
C27	0.065604	1.248101	-2.387024	0.004675	0.008962
H28	-0.621764	1.139401	-3.234157	0.17934	0.002469
H29	-2.314843	-2.714774	-2.156048	0.188478	0.000245
C30	0.066047	-1.24869	-2.38695	0.004251	0.008965
H31	0.802588	-2.010883	-2.664032	0.21056	-0.000245
H32	-0.621324	-1.140299	-3.234118	0.179318	0.00247

H33	0.801856	2.010529	-2.664267	0.21057	-0.000246
H34	0.802503	-2.010749	2.664113	0.210561	-0.000245
C35	3.124737	0.000625	0.000193	1.10956	-0.042605
O36	4.281031	0.000979	0.000157	-0.380927	-0.045438
Ni37	1.345078	-0.000053	0.00006	-0.960555	0.942022

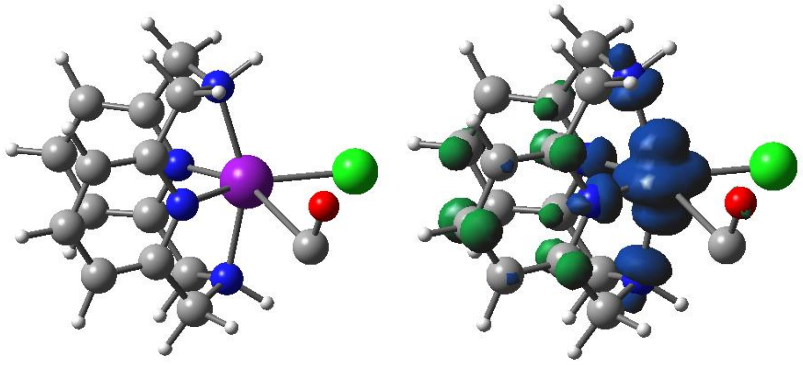
SCF Done: E(UB3P86) = -2386.81507488 A.U. after 2 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation 0.7817, after 0.7504

	1	2	3
	A	A	A
Frequencies --	43.0940	46.2916	57.8090
Red. masses --	5.1756	9.7757	3.2718

Zero-point correction= 0.299682 (Hartree/Particle)
Thermal correction to Energy= 0.317056
Thermal correction to Enthalpy= 0.318001
Thermal correction to Gibbs Free Energy= 0.254004
Sum of electronic and zero-point Energies= -2386.515393
Sum of electronic and thermal Energies= -2386.498018
Sum of electronic and thermal Enthalpies= -2386.497074
Sum of electronic and thermal Free Energies= -2386.561070

Item	Value	Threshold	Converged?
Maximum Force	0.000079	0.000450	YES
RMS Force	0.000007	0.000300	YES

Table S54. TS geometry optimized for [Ni^{I}(dapp)Cl---CO]‡ (doublet), computed at the UB3P86/6-31+G(d,p) level using C-PCM.



Spin Density Distribution

atom	x	y	z	Mulliken charge	Spin density
C1	-1.94774	-0.91984	1.1426	-0.17541	-0.036828
N2	-1.28559	-1.11999	-0.00694	0.288389	0.024792
N3	0.34448	-0.56971	-2.12561	-0.33772	0.027739
H4	1.00488	-1.08502	-2.69762	0.369186	-0.001267
C5	-3.30514	-0.61362	1.15552	-0.05578	0.022575
H6	-3.82138	-0.45436	2.09695	0.176389	-0.00031
N7	0.49301	1.11171	0.00782	0.479253	0.013147
C8	-3.97568	-0.49431	-0.06191	-0.29083	-0.043048
H9	-5.03335	-0.2523	-0.08349	0.181301	0.001927
C10	-3.2625	-0.64152	-1.25188	-0.06105	0.022798
H11	-3.74505	-0.50468	-2.21446	0.176444	-0.000314
N12	0.27502	-0.54549	2.15596	-0.38	0.028175
H13	0.9077	-1.0625	2.75703	0.369764	-0.001318
C14	-1.90674	-0.94649	-1.18355	-0.15765	-0.035783
C15	-1.00895	-1.09423	-2.38958	-0.04962	0.002931
H16	-1.47131	-0.62144	-3.26589	0.164795	0.001589
H17	-0.89949	-2.16139	-2.61461	0.197204	-0.000923
C18	0.52768	0.87118	-2.3802	0.089491	0.003835
H19	-0.04866	1.21549	-3.24877	0.165106	0.001249
C20	0.18185	1.69564	-1.16342	-0.0311	-0.044048
C21	-0.41112	2.95203	-1.215	-0.59888	0.028615
H22	-0.65175	3.40198	-2.17307	0.174827	-0.00046
C23	-0.7044	3.60718	-0.01843	-0.27018	-0.066421
H24	-1.16724	4.58853	-0.02877	0.17916	0.003173
C25	-0.43539	2.96561	1.19131	-0.51655	0.031854
C26	0.1582	1.70887	1.1661	0.075362	-0.028719
C27	-1.09528	-1.04223	2.38446	-0.04751	0.004405
H28	-1.58199	-0.53583	3.22816	0.164567	0.001619
H29	-0.69561	3.42621	2.13913	0.174701	-0.000469
C30	0.47782	0.89556	2.39636	0.076069	-0.007078
H31	1.53997	1.02829	2.63099	0.199128	-0.001467
H32	-0.10104	1.25912	3.25531	0.16375	0.001222
Cl33	2.3703	-2.51413	0.03849	-0.52973	0.023484

H34	-1.01184	-2.10323	2.64669	0.196813	-0.000949
H35	1.58827	1.02037	-2.61324	0.196446	-0.001726
C36	3.71222	0.91572	0.57368	0.065042	-0.010349
O37	4.22777	1.03278	-0.43465	-0.07732	-0.002895
Ni38	0.72332	-0.85622	0.02548	-0.74386	1.039242

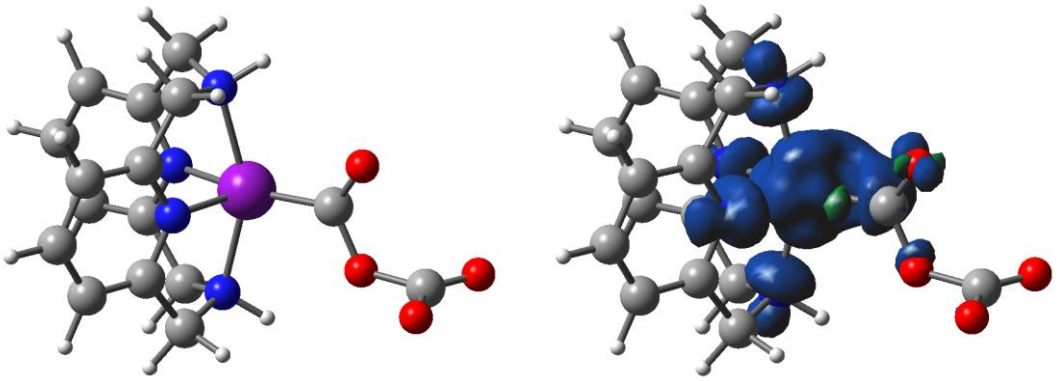
SCF Done: E(UB3P86) = −2847.50133298 A.U. after 1 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation 0.8088, after 0.7514

	1	2	3
	A	A	A
Frequencies --	−25.4659	21.3217	35.4868
Red. masses --	11.4941	11.8906	13.2404

Zero-point correction= 0.296101 (Hartree/Particle)
Thermal correction to Energy= 0.316665
Thermal correction to Enthalpy= 0.317609
Thermal correction to Gibbs Free Energy= 0.243696
Sum of electronic and zero-point Energies= −2847.205232
Sum of electronic and thermal Energies= −2847.184668
Sum of electronic and thermal Enthalpies= −2847.183724
Sum of electronic and thermal Free Energies= −2847.257637

Item	Value	Threshold	Converged?
Maximum Force	0.000001	0.000450	YES
RMS Force	0.000000	0.000300	YES

Table S55. DFT-optimized geometry of Ni^{II}(dapp)($CO_2CO_2^{2-}$-*C*) (triplet), computed at the UB3P86/6-31+G(d,p) level using C-PCM.



Spin Density Distribution

atom	x	y	z	Mulliken charge	Spin density
Ni1	0.34754	-0.558925	-0.342659	-0.457916	1.683136
C2	-1.955292	-1.529184	1.125706	-0.226951	0.037812
N3	-1.539715	-1.217619	-0.107069	0.277492	0.070644
N4	-0.505473	0.041482	-2.255712	-0.370978	0.063233
H5	0.140807	-0.207397	-2.997039	0.390794	-0.002806
C6	-3.301609	-1.766943	1.382449	-0.107748	0.009848
H7	-3.634569	-2.017093	2.383813	0.190845	0.000796
N8	-0.267591	1.257256	0.144416	0.461833	0.117871
C9	-4.206576	-1.657271	0.328426	-0.301514	0.008417
H10	-5.2638	-1.82989	0.50154	0.193007	-0.000386
C11	-3.758514	-1.296962	-0.941124	-0.08713	0.005018
H12	-4.450757	-1.177243	-1.767378	0.191032	0.000796
N13	0.298249	-0.785455	1.817598	-0.352094	0.066955
H14	1.151786	-1.248584	2.112056	0.391531	-0.002719
C15	-2.39747	-1.075383	-1.123484	-0.249239	0.038436
C16	-1.768495	-0.695065	-2.443883	-0.016318	-0.012282
H17	-2.483069	-0.131794	-3.055142	0.181558	0.002734
H18	-1.536179	-1.616076	-2.989239	0.213008	0.000118
C19	-0.626969	1.511498	-2.217735	-0.103913	0.018996
H20	-1.445528	1.867594	-2.853951	0.182508	0.002323
C21	-0.794667	2.030907	-0.809659	0.12002	-0.030717
C22	-1.414452	3.232736	-0.482491	-0.390817	-0.010034
H23	-1.843615	3.858299	-1.257416	0.190204	0.000878
C24	-1.483556	3.598744	0.860455	-0.361148	-0.0076
H25	-1.968119	4.527059	1.144767	0.192585	0.000338
C26	-0.955106	2.760839	1.840841	-0.450439	-0.011051
C27	-0.34857	1.574603	1.440413	0.132609	-0.030783
C28	-0.863878	-1.62199	2.167594	-0.010594	-0.010282
H29	-1.263782	-1.37132	3.156938	0.181259	0.002846
H30	-1.023197	3.015876	2.892736	0.190864	0.000871
C31	0.291206	0.579532	2.378757	-0.105166	0.017747
H32	1.335526	0.875275	2.524383	0.214616	-0.000499
H33	-0.195823	0.612888	3.360054	0.182014	0.002276

H34	-0.522516	-2.661666	2.213714	0.21341	0.000129
H35	0.301174	1.926757	-2.624207	0.216525	-0.00052
C36	2.280423	-0.373263	-0.708903	0.646729	-0.044646
O37	2.797064	-0.033842	-1.776333	-0.569507	0.010054
O38	3.077861	-0.626935	0.370261	-0.308617	-0.007513
C39	4.541801	-0.490266	0.203688	0.668528	0.007176
O40	5.10658	-1.539356	-0.134251	-0.67579	-0.000156
O41	4.973822	0.632932	0.496308	-0.677093	0.002543

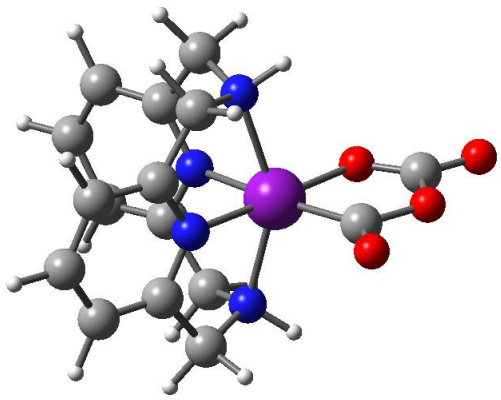
SCF Done: E(UB3P86) = −2651.32014766 A.U. after 2 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation 2.0107, after 2.0000

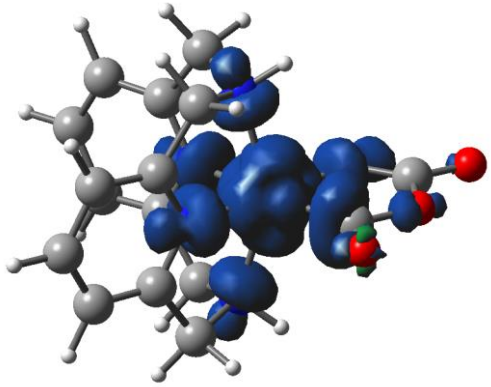
	1	2	3
	A	A	A
Frequencies --	16.2786	22.8855	35.0716
Red. masses --	7.3522	10.8654	9.8670

Zero-point correction= 0.316183 (Hartree/Particle)
Thermal correction to Energy= 0.337757
Thermal correction to Enthalpy= 0.338701
Thermal correction to Gibbs Free Energy= 0.262174
Sum of electronic and zero-point Energies= −2651.003964
Sum of electronic and thermal Energies= −2650.982391
Sum of electronic and thermal Enthalpies= −2650.981447
Sum of electronic and thermal Free Energies= −2651.057974

Item	Value	Threshold	Converged?
Maximum Force	0.000051	0.000450	YES
RMS Force	0.000006	0.000300	YES

Table S56. DFT-optimized geometry of Ni^{II}(dapp)($CO_2CO_2^{2-}$-*C,O*) (triplet), computed at the UB3P86/6-31+G(d,p) level using C-PCM.





Spin Density Distribution

atom	x	y	z	Mulliken charge	Spin density
C1	-1.116286	1.815794	-1.164997	-0.092796	-0.009146
N2	-0.590849	1.428202	-0.000390	0.080863	0.068195
N3	0.239181	-0.012868	2.132388	-0.452048	0.031247
H4	1.066363	-0.073103	2.716338	0.382584	-0.002142
C5	-2.208734	2.677674	-1.206566	-0.385147	-0.007445
H6	-2.631488	2.985303	-2.156973	0.187404	0.000765
N7	-0.799427	-1.321215	0.000448	0.268312	0.064962
C8	-2.75016	3.118058	-0.000458	-0.200398	-0.000473
H9	-3.60631	3.784968	-0.000473	0.188963	0.000112
C10	-2.208257	2.67836	1.205714	-0.384928	-0.007431
H11	-2.630684	2.986485	2.156106	0.187405	0.000765
N12	0.238158	-0.014246	-2.132680	-0.452207	0.031248
H13	1.065157	-0.074754	-2.716856	0.382602	-0.002142
C14	-1.115797	1.816544	1.164219	-0.093364	-0.009126
C15	-0.41695	1.281401	2.391329	0.013617	0.011408
H16	-1.119437	1.222013	3.231596	0.176973	0.002408
H17	0.364262	1.994191	2.676496	0.207326	-0.000126
C18	-0.596968	-1.199701	2.390757	0.010268	-0.003196
H19	-1.27765	-1.042738	3.236263	0.177647	0.001857
C20	-1.373583	-1.625147	1.166835	-0.018906	-0.003981
C21	-2.583973	-2.311683	1.207954	-0.415643	0.001504
H22	-3.04891	-2.552574	2.157906	0.187815	0.000792
C23	-3.186054	-2.663728	0.001404	-0.217317	-0.00722
H24	-4.133364	-3.193163	0.00176	0.189408	0.000332
C25	-2.584491	-2.31246	-1.205661	-0.415716	0.001496
C26	-1.374091	-1.625953	-1.165526	-0.019004	-0.003969
C27	-0.418245	1.279781	-2.39216	0.013273	0.011427
H28	-1.121373	1.21965	-3.231838	0.176983	0.002408
H29	-3.049898	-2.553929	-2.155237	0.187815	0.000792
C30	-0.597894	-1.201347	-2.389991	0.010651	-0.003214
H31	0.074271	-2.021035	-2.666006	0.210573	-0.000421
H32	-1.278816	-1.045125	-3.235450	0.177655	0.001859

H33	0.362685	1.992398	-2.678509	0.207328	-0.000126
H34	0.075158	-2.019265	2.667246	0.21056	-0.000421
C35	2.336428	-1.379372	-0.000390	0.678925	0.102726
O36	2.467543	-2.593335	-0.000546	-0.573885	-0.001689
O37	2.384275	1.239694	-0.000453	-0.583534	0.037906
C38	3.536166	0.700261	-0.000047	1.004111	-0.016195
O39	3.589905	-0.693261	-0.000309	-0.445498	0.004268
O40	4.632731	1.271585	0.000591	-0.679903	-0.000258
Ni41	0.808511	-0.080599	-0.000339	-0.088769	1.700246

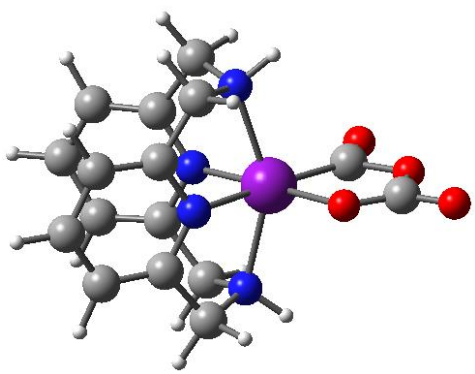
SCF Done: E(UB3P86) = −2651.34477864 A.U. after 1 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation 2.0067, after 2.0000

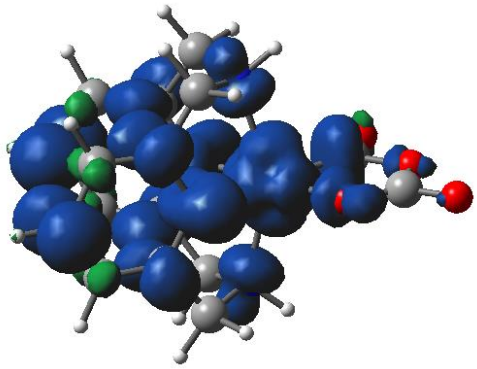
	1	2	3
	A	A	A
Frequencies --	32.1242	40.4677	43.2278
Red. masses --	10.2610	5.2356	7.3858

Zero-point correction= 0.316984 (Hartree/Particle)
Thermal correction to Energy= 0.337995
Thermal correction to Enthalpy= 0.338939
Thermal correction to Gibbs Free Energy= 0.266092
Sum of electronic and zero-point Energies= −2651.027794
Sum of electronic and thermal Energies= −2651.006784
Sum of electronic and thermal Enthalpies= −2651.005840
Sum of electronic and thermal Free Energies= −2651.078686

Item	Value	Threshold	Converged?
Maximum Force	0.000024	0.000450	YES
RMS Force	0.000004	0.000300	YES

Table S57. DFT-optimized geometry of [Ni^{I}(dapp)($CO_2CO_2^{2-}$-*C,O*)]$^{-}$ (quartet), computed at the RB3P86/6-31+G(d,p) level using C-PCM.





Spin Density Distribution

atom	x	y	z	Mulliken charge	Spin density
C1	-1.22112	1.60842	-1.17098	-0.24024	0.20062
N2	-0.57799	1.36999	-0.00024	-0.10948	0.180586
N3	0.31346	-0.0127	2.17203	-0.4061	0.028658
H4	1.11082	-0.05056	2.79923	0.357284	-0.000325
C5	-2.48871	2.16342	-1.20821	-0.05165	-0.155358
H6	-2.96938	2.34804	-2.16485	0.154005	0.002053
N7	-0.70446	-1.3221	0.00023	0.066288	0.189661
C8	-3.13819	2.47492	-0.00029	-0.35408	0.324072
H9	-4.13025	2.91378	-0.00031	0.159502	-0.014695
C10	-2.48857	2.16386	1.20767	-0.05162	-0.155372
H11	-2.96913	2.34881	2.1643	0.154006	0.002053
N12	0.31328	-0.0134	-2.17213	-0.40612	0.028651
H13	1.11056	-0.05145	-2.79942	0.357282	-0.000325
C14	-1.22099	1.60884	1.1705	-0.2402	0.2006
C15	-0.4059	1.25726	2.38385	-0.04594	-0.002906
H16	-1.04014	1.22483	3.28015	0.157285	0.001634
H17	0.3593	2.0272	2.54236	0.179617	0.006975
C18	-0.51972	-1.21306	2.38268	-0.04948	-0.010245
H19	-1.14417	-1.12409	3.28207	0.157488	0.001048
C20	-1.36839	-1.48888	1.17233	-0.2337	0.211313
C21	-2.68468	-1.91441	1.20925	-0.03083	-0.167968
H22	-3.18162	-2.04916	2.16594	0.153207	0.002121
C23	-3.3612	-2.16411	0.00046	-0.3943	0.333048
H24	-4.39077	-2.50564	0.00054	0.15844	-0.01517
C25	-2.68476	-1.91481	-1.20846	-0.03084	-0.167985
C26	-1.36847	-1.48927	-1.17177	-0.23361	0.211311
C27	-0.40615	1.25646	-2.3843	-0.04585	-0.002959
H28	-1.0405	1.2237	-3.28052	0.157285	0.001634
H29	-3.18176	-2.04989	-2.16508	0.153206	0.002121
C30	-0.51988	-1.21387	-2.38227	-0.04955	-0.010214
H31	0.17359	-2.04967	-2.537	0.181797	0.006856
H32	-1.14439	-1.12526	-3.28166	0.157487	0.001048
H33	0.35899	2.02637	-2.54317	0.179616	0.006976

H34	0.17372	-2.04882	2.53768	0.181796	0.006856
C35	2.4686	-1.31091	0.00008	0.697079	0.072187
O36	2.64318	-2.52111	0.00015	-0.59749	-0.004689
O37	2.46401	1.311	-0.00026	-0.57833	0.027632
C38	3.62465	0.79763	-0.00011	0.976262	-0.01465
O39	3.71218	-0.59241	0.00005	-0.45671	0.00285
O40	4.71214	1.39372	-0.00002	-0.69471	-0.00081
Ni41	0.89085	-0.05961	-0.00005	-0.4381	1.671105

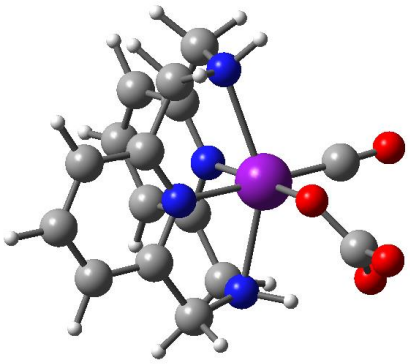
SCF Done: E(UB3P86) = −2651.44654112 A.U. after 1 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation 3.7656, after 3.7501

	1	2	3
	A	A	A
Frequencies --	26.8782	52.4221	54.1294
Red. masses --	10.6179	5.6149	8.9598

Zero-point correction= 0.311956 (Hartree/Particle)
Thermal correction to Energy= 0.333156
Thermal correction to Enthalpy= 0.334100
Thermal correction to Gibbs Free Energy= 0.261163
Sum of electronic and zero-point Energies= −2651.134585
Sum of electronic and thermal Energies= −2651.113385
Sum of electronic and thermal Enthalpies= −2651.112441
Sum of electronic and thermal Free Energies= −2651.185378

Item	Value	Threshold	Converged?
Maximum Force	0.000037	0.000450	YES
RMS Force	0.000005	0.000300	YES

Table S58. DFT-optimized geometry of Ni^{II}(dapp)(CO)(CO_3^{2-}) (singlet), computed at the RB3P86/6-31+G(d,p) level using C-PCM.



atom	x	y	z	Mulliken charge
C1	-0.73882	2.0555	-1.00134	0.009842
N2	-0.10443	1.386693	-0.02417	0.053329
N3	0.800523	-0.3113	1.990534	-0.48256
H4	1.753667	-0.66322	1.881858	0.42005
C5	-1.31919	3.297979	-0.76016	-0.66892
H6	-1.83467	3.813276	-1.56373	0.186469
N7	-1.10798	-1.08172	0.104065	0.132262
C8	-1.23617	3.849997	0.512432	-0.15752
H9	-1.68382	4.815849	0.723194	0.18982
C10	-0.59491	3.135142	1.51646	-0.91074
H11	-0.53191	3.519763	2.52909	0.186961
N12	-0.5859	0.022783	-2.42901	-0.5193
H13	-0.07782	-0.24249	-3.26168	0.369633
C14	-0.04069	1.893596	1.218619	0.388022
C15	0.673123	1.084748	2.292064	-0.39239
H16	0.155752	1.257244	3.24687	0.170563
H17	1.67789	1.508482	2.406997	0.203033
C18	-0.21697	-1.2419	2.390176	-0.2465
H19	-0.64231	-1.00386	3.376076	0.169557
C20	-1.36412	-1.35361	1.400295	0.188367
C21	-2.6379	-1.73452	1.807437	-0.4713
H22	-2.82209	-1.94293	2.855838	0.190149
C23	-3.65674	-1.82077	0.865947	-0.23208
H24	-4.65932	-2.1088	1.164741	0.193348
C25	-3.38129	-1.50358	-0.45808	-0.406
C26	-2.08836	-1.13287	-0.81651	0.114526
C27	-0.78407	1.458074	-2.39259	-0.07701
H28	-1.72853	1.765587	-2.86582	0.170183
H29	-4.15743	-1.52965	-1.21526	0.190075
C30	-1.75695	-0.81641	-2.25958	-0.12761
H31	-1.56334	-1.76821	-2.76753	0.209408
H32	-2.6554	-0.38951	-2.7295	0.171539
H33	0.020879	1.920583	-2.97446	0.204756
H34	0.239953	-2.23456	2.484708	0.204136

C35	1.331112	-2.04182	-0.72719	0.580067
O36	1.74506	-3.07125	-0.99701	-0.31163
O37	2.281094	0.314381	-0.79551	-0.68283
C38	3.384869	-0.05542	-0.11149	0.81794
O39	4.452328	0.531838	-0.43432	-0.74465
O40	3.273976	-0.95218	0.790363	-0.72438
Ni41	0.644134	-0.42357	-0.36245	1.441382

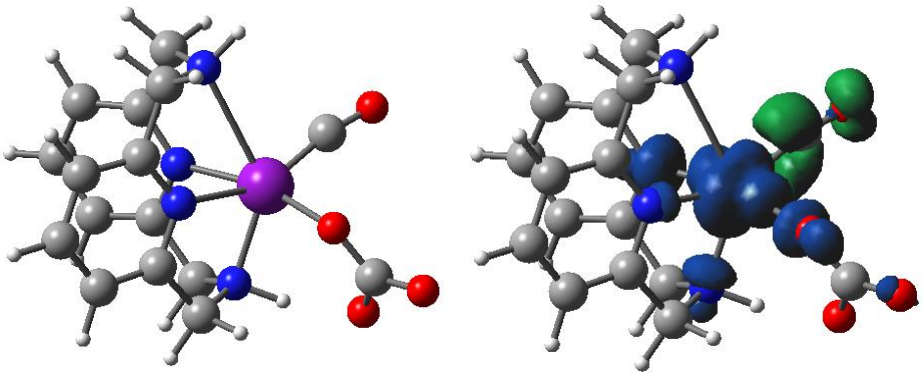
SCF Done: E(RB3P86) = −2651.29917081 A.U. after 2 cycles

	1	2	3
	A	A	A
Frequencies --	37.0108	42.7917	45.9767
Red. masses --	4.1829	5.1689	8.0874

Zero-point correction= 0.314391 (Hartree/Particle)
Thermal correction to Energy= 0.336444
Thermal correction to Enthalpy= 0.337388
Thermal correction to Gibbs Free Energy= 0.262875
Sum of electronic and zero-point Energies= −2650.984780
Sum of electronic and thermal Energies= −2650.962727
Sum of electronic and thermal Enthalpies= −2650.961783
Sum of electronic and thermal Free Energies= −2651.036295

Item	Value	Threshold	Converged?
Maximum Force	0.000026	0.000450	YES
RMS Force	0.000004	0.000300	YES

Table S59. DFT-optimized geometry of $[Ni^{I}(dapp)(CO)(CO_3^{2-})]^{-}$ (doublet), computed at the UB3P86/6-31+G(d,p) level using C-PCM.



Spin Density Distribution

atom	x	y	z	Mulliken charge	Spin density
C1	-1.37501	1.42032	-1.5289	-0.14024	-0.004331
N2	-0.4006	1.27299	-0.62558	0.13108	0.006796
N3	0.99132	0.38926	1.60935	-0.51192	0.034954
H4	2.02193	0.23478	1.71261	0.434943	-0.000942
C5	-2.29402	2.46951	-1.45509	-0.16927	-0.000279
H6	-3.07676	2.55835	-2.20239	0.171201	0.000092
N7	-0.98317	-1.13878	0.55158	0.169778	0.035885
C8	-2.19914	3.37538	-0.40484	-0.27916	-0.000917
H9	-2.90145	4.19921	-0.32197	0.179452	0.00006
C10	-1.21651	3.18369	0.56184	-0.30628	0.002311
H11	-1.13969	3.84065	1.42261	0.173626	-0.000006
N12	-0.97872	-0.90154	-2.3143	-0.36985	0.000566
H13	-0.57011	-1.36019	-3.11654	0.340134	-0.000152
C14	-0.34068	2.10809	0.42128	0.082401	-0.00702
C15	0.72716	1.81286	1.45215	-0.32829	-0.001205
H16	0.4529	2.29121	2.40378	0.145925	0.001138
H17	1.66554	2.27045	1.11829	0.196612	0.000196
C18	0.14855	-0.3408	2.53868	-0.19175	-0.005422
H19	-0.13905	0.25832	3.41527	0.155534	0.000882
C20	-1.10249	-0.86223	1.85958	0.061192	0.011694
C21	-2.30607	-1.03137	2.53998	-0.19811	-0.011051
H22	-2.37082	-0.79623	3.59754	0.177508	0.000793
C23	-3.41706	-1.47582	1.83055	-0.27674	-0.004785
H24	-4.37227	-1.60854	2.32899	0.182067	0.000275
C25	-3.29615	-1.71004	0.46452	-0.34578	0.004004
C26	-2.05663	-1.52795	-0.15064	0.167183	0.004495
C27	-1.45985	0.41586	-2.66405	-0.01691	-0.003638
H28	-2.49884	0.41154	-3.03593	0.14703	-0.000267
H29	-4.15277	-2.01657	-0.12717	0.174442	0.000549
C30	-1.89246	-1.79644	-1.63397	-0.23332	-0.002956
H31	-1.49191	-2.81169	-1.74344	0.187421	-0.00053
H32	-2.89884	-1.80632	-2.08605	0.146197	-0.000226
H33	-0.83809	0.78493	-3.48858	0.18367	-0.000088

H34	0.72367	-1.19731	2.91278	0.185638	-0.000406
C35	1.6021	-2.15095	-0.78126	0.745892	0.000322
O36	2.19629	-3.12679	-1.00126	-0.39802	-0.050913
O37	2.62948	0.43402	-0.77403	-0.69337	0.053851
C38	3.70263	0.52168	-0.0222	0.70275	0.002829
O39	4.79115	0.94696	-0.54158	-0.80192	0.003708
O40	3.63917	0.18961	1.23116	-0.7769	0.000363
Ni41	0.92107	-0.59383	-0.24348	-0.20385	0.929371

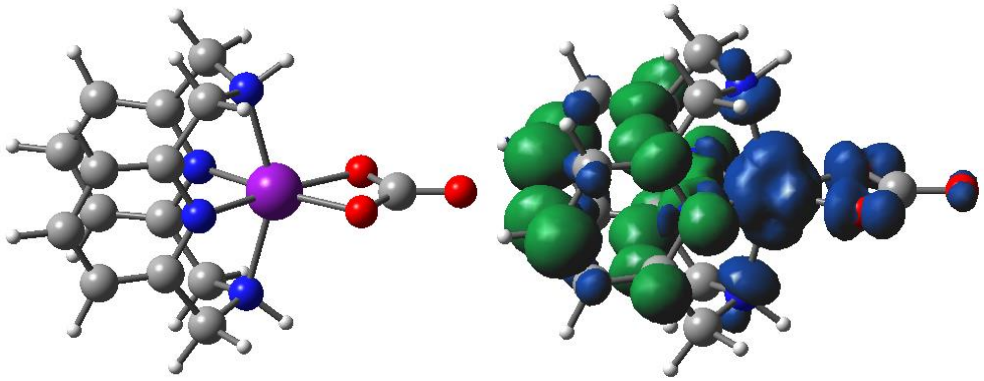
SCF Done: E(UB3P86) = −2651.45468070 A.U. after 1 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation 0.7911, after 0.7505

	1	2	3
	A	A	A
Frequencies --	16.5141	26.8233	33.3245
Red. masses --	9.9695	11.0125	8.9442

Zero-point correction= 0.311323 (Hartree/Particle)
Thermal correction to Energy= 0.334149
Thermal correction to Enthalpy= 0.335093
Thermal correction to Gibbs Free Energy= 0.256012
Sum of electronic and zero-point Energies= −2651.143358
Sum of electronic and thermal Energies= −2651.120532
Sum of electronic and thermal Enthalpies= −2651.119587
Sum of electronic and thermal Free Energies= −2651.198668

Item	Value	Threshold	Converged?
Maximum Force	0.000027	0.000450	YES
RMS Force	0.000003	0.000300	YES

Table S60. DFT-optimized geometry of $[Ni^{I}(dapp)(CO_3^{2-})]^{-}$ (doublet), computed at the UB3P86/6-31+G(d,p) level using C-PCM.



Spin Density Distribution

atom	x	y	z	Mulliken charge	Spin density
C1	-1.04185	1.13635	1.55991	-0.16853	-0.181774
N2	-0.37178	-0.02973	1.37525	-0.03221	-0.052066
N3	0.57582	-2.16936	-0.04595	-0.39829	0.041933
H4	1.37424	-2.79729	-0.06106	0.356387	-0.004441
C5	-2.36051	1.16366	1.97912	0.031078	0.136254
H6	-2.86085	2.11687	2.12429	0.152865	-0.00052
N7	-0.37201	0.02971	-1.37546	-0.03232	-0.05214
C8	-3.0367	-0.04916	2.19808	-0.31681	-0.298177
H9	-4.07024	-0.05671	2.52766	0.159591	0.013911
C10	-2.35786	-1.25089	1.93131	0.030243	0.137521
H11	-2.85594	-2.21025	2.03851	0.152915	-0.00053
N12	0.57585	2.16931	0.04558	-0.39828	0.041954
H13	1.37426	2.79725	0.06053	0.356394	-0.004443
C14	-1.03939	-1.20361	1.51295	-0.16048	-0.183381
C15	-0.20013	-2.40806	1.18829	-0.14174	-0.004156
H16	-0.8248	-3.30848	1.11641	0.158007	0.003278
H17	0.53184	-2.5704	1.98923	0.179632	-0.006312
C18	-0.20485	-2.35492	-1.28648	-0.13806	-0.002022
H19	-0.83127	-3.25626	-1.2494	0.158032	0.003282
C20	-1.04217	-1.13635	-1.55991	-0.16843	-0.1818
C21	-2.36097	-1.16367	-1.97866	0.031318	0.136303
H22	-2.86134	-2.11688	-2.12367	0.152851	-0.000519
C23	-3.03725	0.04916	-2.1974	-0.31696	-0.298354
H24	-4.0709	0.05671	-2.52662	0.159577	0.013921
C25	-2.35831	1.25088	-1.93082	0.03051	0.137624
C26	-1.0397	1.20361	-1.51293	-0.16049	-0.183479
C27	-0.20459	2.3549	1.28626	-0.13784	-0.001983
H28	-0.83101	3.25624	1.24928	0.158045	0.003282
H29	-2.85643	2.21025	-2.03781	0.152902	-0.000533
C30	-0.20036	2.40804	-1.18852	-0.14185	-0.00419
H31	0.53148	2.57032	-1.98959	0.179628	-0.006317
H32	-0.82496	3.30849	-1.11652	0.15801	0.003279

H33	0.52515	2.4854	2.09498	0.179523	-0.006361
H34	0.52473	-2.4854	-2.09535	0.179511	-0.006363
O35	2.87224	-0.0325	1.09773	-0.64216	0.06647
C36	3.58927	-0.00003	0.00005	1.203935	0.009479
O37	2.87284	0.03248	-1.098	-0.64217	0.06643
O38	4.85042	-0.00004	0.00043	-0.84857	0.007979
Ni39	1.13497	0.00007	-0.0002	-0.47575	1.656965

SCF Done: E(UB3P86) = −2537.88081413 A.U. after 1 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation 1.6932, after 0.7848

	1	2	3
	A	A	A
Frequencies --	32.8221	44.9884	54.7500
Red. masses --	7.0370	8.6726	4.9955

Zero-point correction= 0.303019 (Hartree/Particle)
Thermal correction to Energy= 0.322453
Thermal correction to Enthalpy= 0.323398
Thermal correction to Gibbs Free Energy= 0.254903
Sum of electronic and zero-point Energies= −2537.577795
Sum of electronic and thermal Energies= −2537.558361
Sum of electronic and thermal Enthalpies= −2537.557416
Sum of electronic and thermal Free Energies= −2537.625911

Item	Value	Threshold	Converged?
Maximum Force	0.000023	0.000450	YES
RMS Force	0.000002	0.000300	YES

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