Supporting Information

For

XAS and DFT Investigation of Mononuclear Cobalt(III)-Peroxo Complexes: Electronic Control of Geometric Structure in CoO_2 versus NiO_2 Systems

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The final geometry optimized xyz coordinates obtained from the DFT calculation on $[(14\text{-TMC})CoO_2]^+$ (UBP86, basis sets: CP(PPP) on Co and TZVP on the rest of the atoms, Conductor like screening model with CH_2Cl_2 as dielectric.)

Co	-0.076747	0.279004	-0.015814
N	0.676552	-0.034662	-2.169197
N	1.959447	-0.205282	0.496584
N	-0.687961	-0.013978	2.191932
N	-1.691085	-1.094862	-0.379437
C	0.159927	1.019467	-3.072574
C	2.135918	0.162985	-1.965136
C	2.633671	-0.633665	-0.768793
C	2.630495	1.043964	0.967644
C	2.151956	-1.278891	1.521956
C	1.579238	-0.962393	2.901107
C	0.059349	-1.034348	2.987970
C	-0.699938	1.277809	2.916360
C	-2.084482	-0.489770	2.009358
C	-2.155808	-1.584706	0.955932
C	-2.816698	-0.333843	-1.001480
C	-1.373906	-2.281592	-1.234854
C	-0.945557	-1.949792	-2.661960
C	0.462565	-1.379740	-2.783898
O	-1.131144	1.815771	-0.157505
O	0.216177	2.126379	-0.121941
H	0.264972	1.995219	-2.584039
H	-0.901677	0.845331	-3.284871
H	0.711597	1.022075	-4.030566
H	2.309664	1.236802	-1.814501
H	2.702258	-0.135597	-2.866997
H	2.439041	-1.705944	-0.903271
H	3.726183	-0.514755	-0.667086
H	2.082132	1.492722	1.799641
H	2.663739	1.777245	0.156402
H	3.660514	0.811177	1.287872
H	3.237406	-1.469882	1.613965
H	1.689349	-2.196100	1.125981
H	1.969939	-1.728502	3.589266
H	1.964053	-0.006386	3.284093
H	-0.258591	-0.952486	4.044788
H	-0.249466	-2.029837	2.641962
H	0.327131	1.606787	3.114788
H	-1.228742	1.182533	3.882577
H	-1.197063	2.033437	2.297001
H	-2.695314	0.373234	1.712411
H	-2.498170	-0.869287	2.962339
H	-3.190200	-1.960915	0.874843
H	-1.524648	-2.438868	1.234868
H	-2.485911	0.185422	-1.904418
H	-3.188378	0.419765	-0.300863
H	-3.636027	-1.028265	-1.254703
H	-2.270830	-2.927913	-1.264623
H	-0.577545	-2.847375	-0.727143
H	-0.950362	-2.898010	-3.222265
H	-1.687507	-1.313139	-3.164853
H	0.752512	-1.325215	-3.850442
H	1.152955	-2.086846	-2.304768

The final geometry optimized xyz coordinates obtained from the DFT calculation on $[(12\text{-TMC})CoO_2]^+$ (UBP86, basis sets: CP(PPP) on Co and TZVP on the rest of the atoms, Conductor like screening model

with CH_2Cl_2 as dielectric.)

Co	-0.010522	-0.111505	0.000056
C	-2.343749	0.893665	1.586037
H	-3.233713	0.668333	2.195388
H	-2.624668	1.471545	0.699863
H	-1.623556	1.480493	2.164994
N	1.667515	-0.366230	-1.143878
N	-1.687340	-0.369768	1.145203
N	0.937916	-1.235089	1.388098
C	2.663906	-1.147247	-0.318103
H	3.290173	-0.417453	0.208358
H	3.326198	-1.728641	-0.977380
C	1.614249	-0.338932	2.377858
H	0.879317	0.308447	2.863707
H	2.335748	0.306934	1.870433
H	2.130320	-0.951285	3.135155
C	-0.091035	-2.050981	2.089699
H	0.304764	-2.466191	3.032181
H	-0.360589	-2.895517	1.444960
C	-1.279894	-1.148825	2.374738
H	-2.134388	-1.730758	2.752059
H	-1.018992	-0.417733	3.149017
C	1.965274	-2.050699	0.683819
H	1.462495	-2.894371	0.196909
H	2.698979	-2.467275	1.394743
C	2.316991	0.898769	-1.590434
H	1.593591	1.479083	-2.171953
H	2.594693	1.482160	-0.706851
N	-0.952852	-1.246679	-1.382743
C	1.264337	-1.153184	-2.369771
H	0.999436	-0.427088	-3.147343
H	2.122036	-1.732134	-2.744366
C	-1.633732	-0.358527	-2.376612
H	-2.357526	0.286826	-1.871849
H	-0.902028	0.289536	-2.866433
H	-2.147739	-0.976962	-3.130357
C	-1.976130	-2.064277	-0.674807
H	-2.707597	-2.487805	-1.383915
H	-1.469168	-2.903224	-0.184091
C	-2.679517	-1.159917	0.322983
H	-3.338756	-1.741859	0.984851
H	-3.309735	-0.435897	-0.206782
C	0.080278	-2.060416	-2.080716
H	0.354169	-2.900887	-1.432431
H	-0.313330	-2.481693	-3.021424
H	3.208212	0.675692	-2.198784
O	-0.420428	1.627778	-0.599131
O	0.390072	1.632645	0.591161

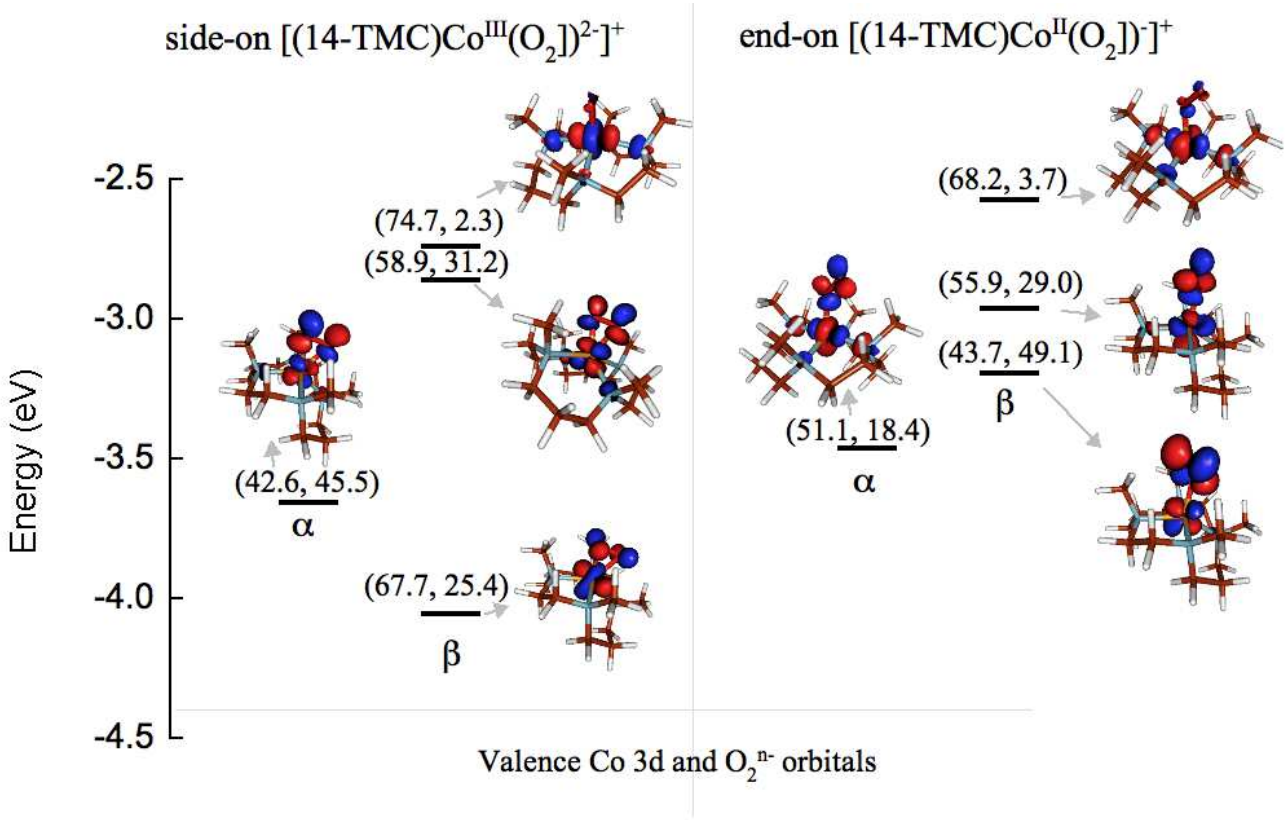

Figure S1 The α_{LUMO}, β_{LUMO}, β_{LUMO+1} and β_{LUMO+2} contour plots for the $[(14\text{-TMC})CoO_2]^+$ complex with side-on (left panel) and end-on (right panel) bound O_2 (see experimental section for details). The calculations were performed for the intermediate spin S=1 state for both the end-on and side-on species. The values in brackets represent the (Co 3d, O_2^{n-} p) spin density contributions to the respective orbitals.

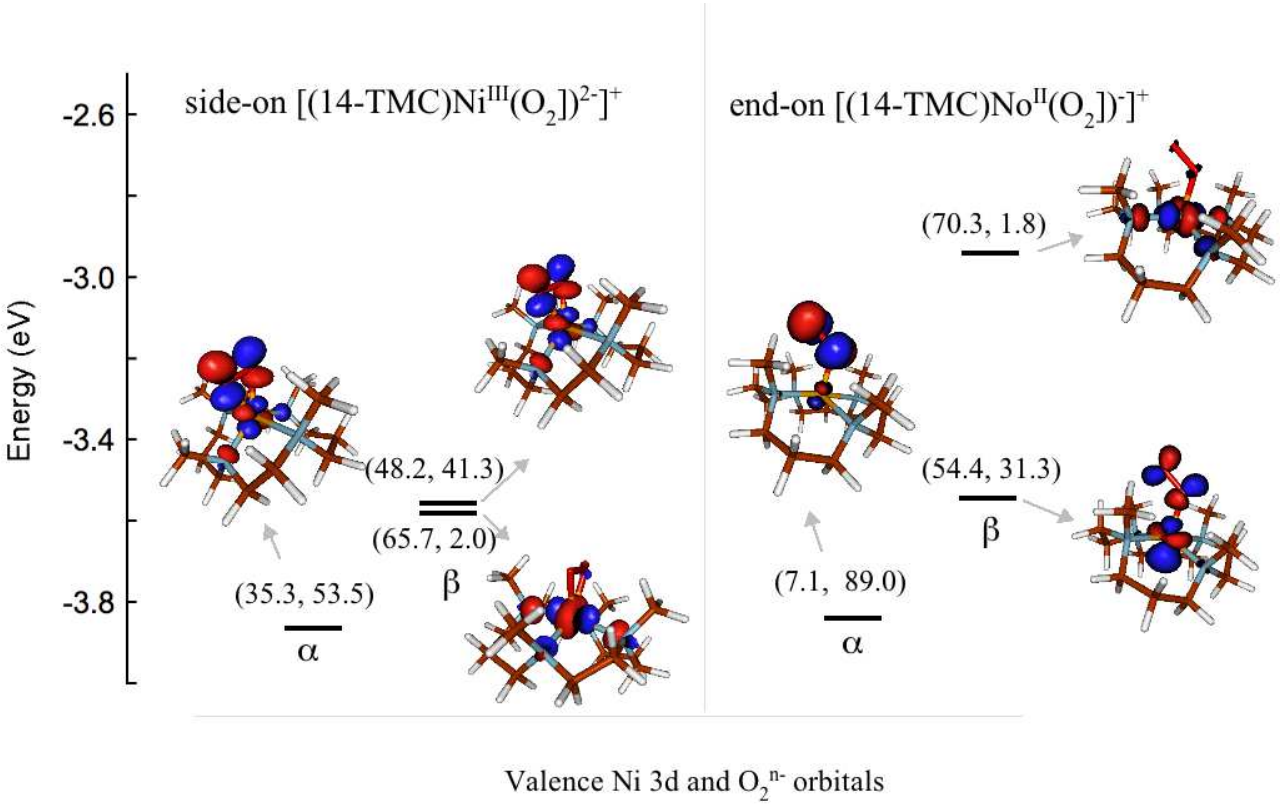

Figure S2 The α_{LUMO}, β_{LUMO} and β_{LUMO+1} contour plots for the $[(14\text{-TMC})NiO_2]^+$ complex with side-on (left panel) and end-on (right panel) bound O_2 (see experimental section for details). The values in brackets represent the (Ni 3d, O_2^{n-} p) spin density contributions to the respective orbitals.

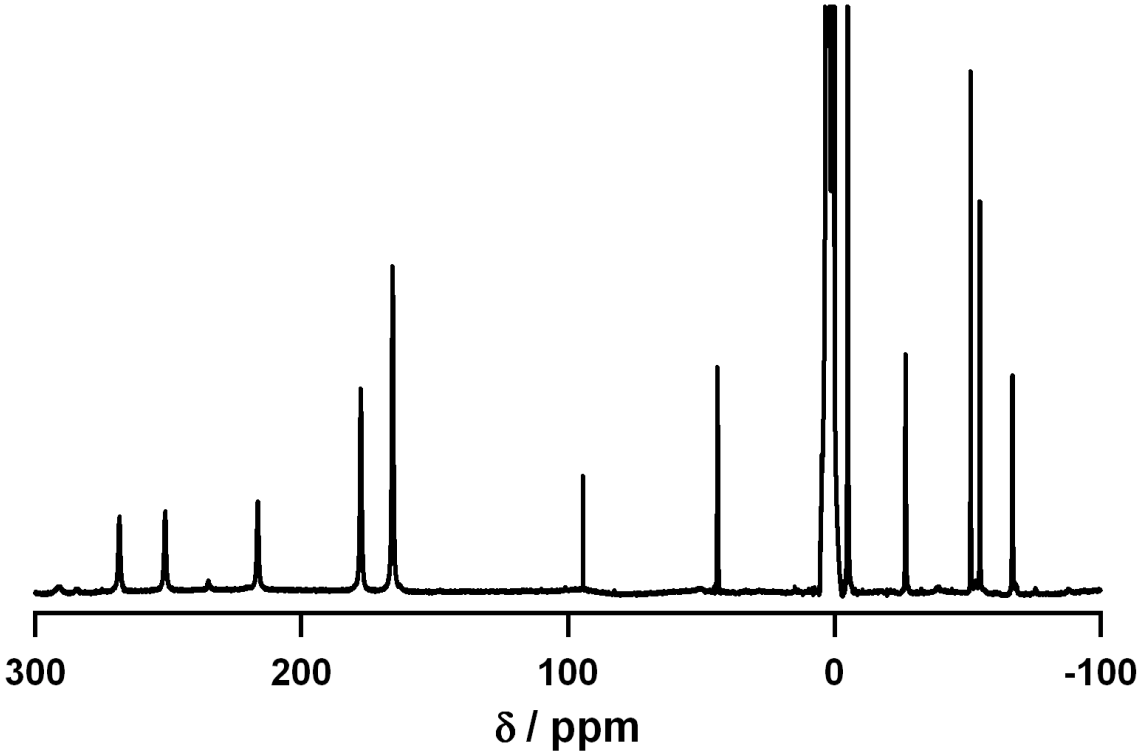

Figure S3. ^{1}H NMR spectrum of **2** in acetonitrile-d_3 at –40 °C.