Low-Energy States of Manganese-Oxo Corrole and Corrolazine: Multiconfiguration Reference Ab initio Calculations

Hailiang Zhao,[a] Kristine Pierloot,[a,*] Ernie Langner,[b] Jannie C. Swarts,[b] Jeanet Conradie,[b,c] Abhik Ghosh[c,*]

SUPPORTING INFORMATION

*[a]Department of Chemistry, University of Leuven, Celestijnenlaan 200F, B-3001 Heverlee-Leuven, Belgium; [b]Department of Chemistry, University of the Free State, 9300 Bloemfontein, Republic of South Africa; [c]Department of Chemistry and Center for Theoretical and Computational Chemistry, University of Tromsø, 9037 Tromsø, Norway

1 A note on the character of the two low-lying Mn^V triplet states

Although the two lowest-lying triplet states $1^3A'$, $1^3A''$ are denoted as Mn^V in the paper, the electronic structure of these two states is in fact more complicated and also method dependent. This can be seen from Tables S2–S5, providing detailed information concerning the spin densities for the three Mn^V states in both molecules. With the BP86 functional, positive (overall) spin populations are found on the three considered fragments for both triplet states, adding up to 2 and with by far the largest contribution (1.82–1.88) on Mn, thus pointing to "genuine" (S = 1) d^2 states. On the other hand, both hybrid functionals predict a spin population > 2 on Mn, compensated by negative spin populations on the axial oxygen and, to a lesser extent, the corrole or corrolazine ring, thus rather pointing to a higher spin state on Mn, coupled antiferromagnetically to a ligand radical. A quantity that is useful in this respect is the so-called *effective number of unpaired electrons*, denoted as NUE and defined as[1,2]

$$\mathrm{NUE} = \sum_{i=1}^{\mathrm{nat.orbs}} n_i(2-n_i) = 2\left(\langle\hat{\mathbf{S}}^{\mathbf{2}}\rangle - S^2\right)$$

NUE may be used to diagnoze the character of the DFT solution obtained for any open-shell state. Here, NUE ≈ 2 corresponds to a d^2 Mn^V state, with two unpaired electrons in (predominantly) Mn 3d orbitals, whereas NUE ≈ 4 would rather correspond to tetraradical situation, that is a Mn^{IV} d^3 (S = 3/2) state ($d_{x^2-y^2}{}^{\uparrow}d_{xz}{}^{\uparrow}d_{yz}{}^{\uparrow}$) antiferromagnetically coupled to a ligand radical, be it either on oxygen or on the ring. 2 < NUE < 4 corresponds to an intermediate case. From the NUE and spin populations in Tables S2, S3 we find that only the hybrid functionals predict a significant contribution of antiferromagnetic coupling to the electronic structure of both triplet states, involving primarily the axial oxygen ligand and becoming more pronounced as the HF contribution is increased from 20% in B3LYP to 25% in PBE0. Maybe more relevant from a chemical point of view, the tetraradical

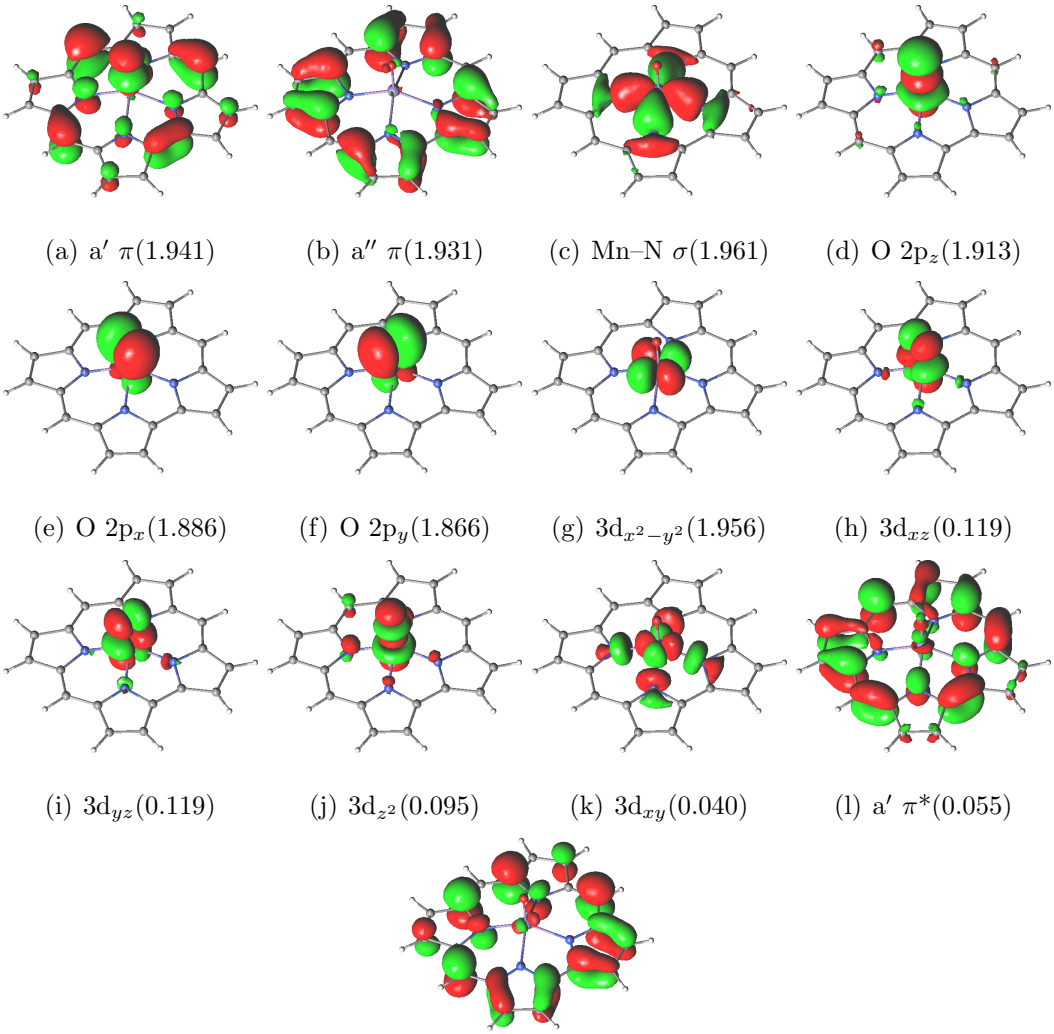
character is considerably more pronounced for Mn(Cor)(O) than for Mn(Cz)(O). For the former compound, the PBE0 functional predicts a NUE of 3.4 (and negative spin population of –0.7 on O) and a more correct assignment for the lowest triplet states with this functional would therefore be $Mn^{IV}O^{\bullet -}$ rather than $Mn^{V}O$.

The first part of the above equation for NUE is general, i.e. also valid in principle for a CASSCF or RASSCF wave function. However, the NUE obtained from the natural orbital occupation numbers in the CAS(14,16) and RAS(28,27) wave functions are much too large and irrelevant, because of the correlating role and diffuse character of some of the weakly occupied orbitals. However, from the spin populations in Tables S4, S5 one can see that also with CASSCF/RASSCF the wave function of the two lowest triplet states in both molecules shows some radical character on the oxygen ligand, which is small but again more important for Mn(Cor)(O) than for Mn(Cz)(O).

Table S1. Critical bond parameters of Mn(Cor)(O) and Mn(Cz)(O), obtained from the PBE0/def2-TZVP structure optimizations[a]

State	Electronic Configuration	Mn(Cor)(O)			Mn(Cz)(O)		
		r_{MnO}	r_{MnN}	Δ	r_{MnO}	r_{MnN}	Δ
Mn(V)							
$1^1\mathrm{A}'$	$(\mathrm{d}_{x^2-y^2})^2$	1.513	1.906	0.550	1.510	1.872	0.598
$1^3\mathrm{A}'$	$(\mathrm{d}_{x^2-y^2})^{\uparrow}(\mathrm{d}_{xz})^{\uparrow}$	1.665	1.915	0.437	1.595	1.878	0.507
$1^3\mathrm{A}''$	$(\mathrm{d}_{x^2-y^2})^{\uparrow}(\mathrm{d}_{yz})^{\uparrow}$	1.663	1.916	0.441	1.597	1.879	0.514
Mn(IV)–a_{2u}-radical							
$2^3\mathrm{A}'$	$(\mathrm{d}_{x^2-y^2})^2(\mathrm{d}_{xz})^{\uparrow}(\mathrm{a}')^{\uparrow}$	1.558	1.938	0.472	1.560	1.906	0.548
$2^3\mathrm{A}''$	$(\mathrm{d}_{x^2-y^2})^2(\mathrm{d}_{yz})^{\uparrow}(\mathrm{a}')^{\uparrow}$	1.560	1.939	0.474		NP	
$1^5\mathrm{A}''$	$(\mathrm{d}_{x^2-y^2})^{\uparrow}(\mathrm{d}_{xz})^{\uparrow}(\mathrm{d}_{yz})^{\uparrow}(\mathrm{a}')^{\uparrow}$	1.628	1.935	0.364	1.627	1.905	0.444
Mn(IV)–a_{1u}-radical							
$3^3\mathrm{A}''$	$(\mathrm{d}_{x^2-y^2})^2(\mathrm{d}_{xz})^{\uparrow}(\mathrm{a}'')^{\uparrow}$	1.563	1.930	0.492	1.561	1.903	0.563
$3^3\mathrm{A}'$	$(\mathrm{d}_{x^2-y^2})^2(\mathrm{d}_{yz})^{\uparrow}(\mathrm{a}'')^{\uparrow}$	1.564	1.931	0.493	1.563	1.905	0.568
$1^5\mathrm{A}'$	$(\mathrm{d}_{x^2-y^2})^{\uparrow}(\mathrm{d}_{xz})^{\uparrow}(\mathrm{d}_{yz})^{\uparrow}(\mathrm{a}'')^{\uparrow}$	1.634	1.927	0.378	1.631	1.903	0.461

[a] Distances in Å. Δ = distance between Mn and the mean NNNN plane. r_{MnN} = average of the four Mn–N distances



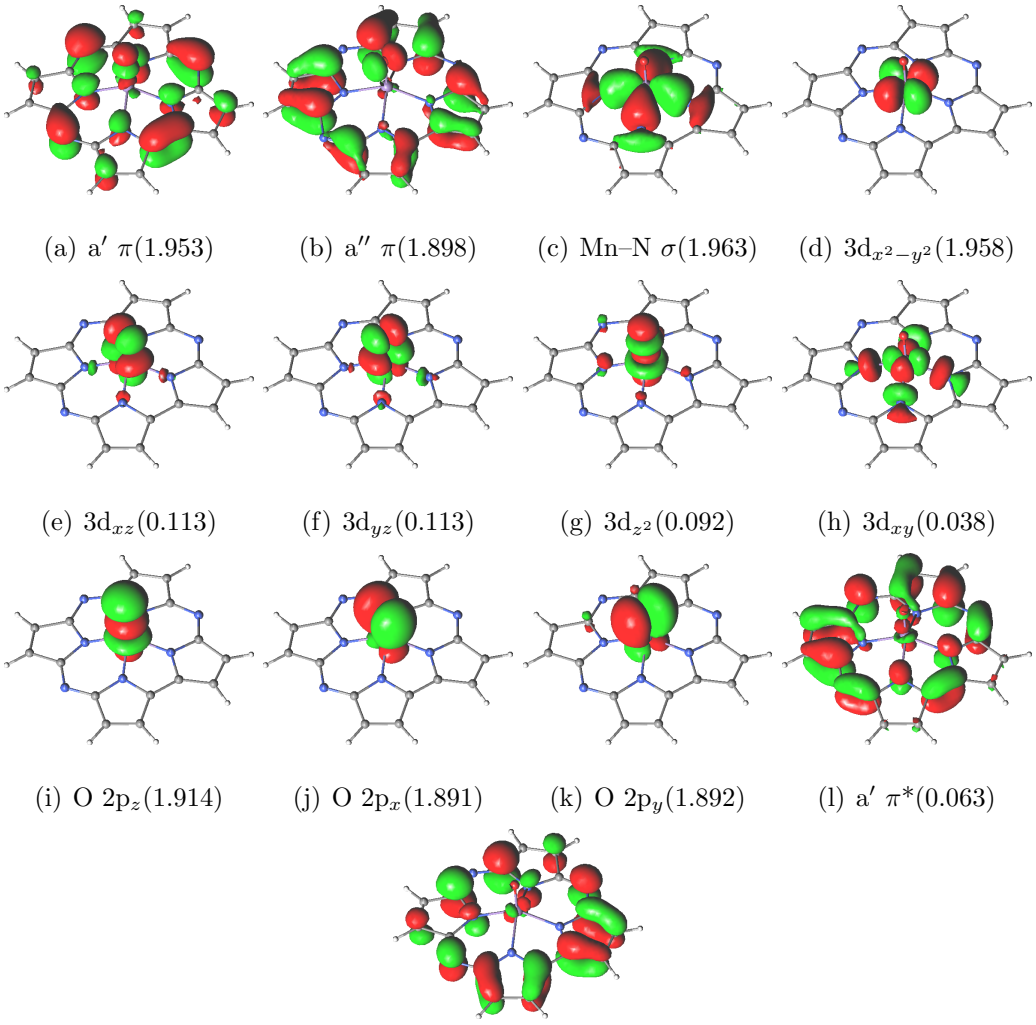
(a) a′ π(1.941) (b) a″ π(1.931) (c) Mn–N σ(1.961) (d) O $2p_z$(1.913)

(e) O $2p_x$(1.886) (f) O $2p_y$(1.866) (g) $3d_{x^2-y^2}$(1.956) (h) $3d_{xz}$(0.119)

(i) $3d_{yz}$(0.119) (j) $3d_{z^2}$(0.095) (k) $3d_{xy}$(0.040) (l) a′ π*(0.055)

(m) a″ π*(0.067)

Figure S1. Natural active orbitals (basis II) and their main character for the $1^1A'$ ground state of Mn(Cor)(O) (except for the three Mn 4d orbitals) for the CAS(14,16) active space. The contour values are ± 0.04 e/au^3. Occupation numbers are given within parentheses.



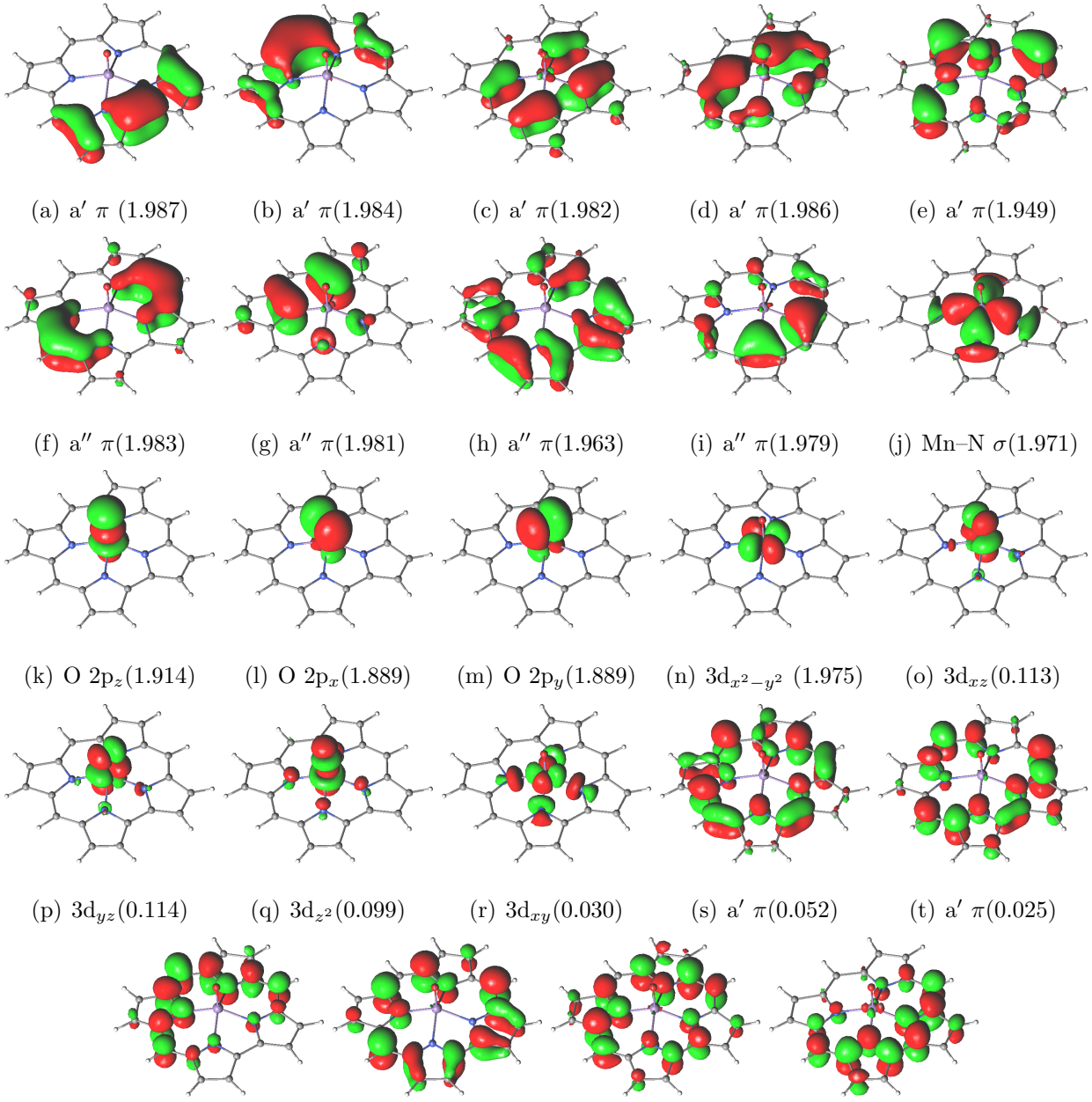
(a) a′ π(1.953) (b) a″ π(1.898) (c) Mn–N σ(1.963) (d) $3d_{x^2-y^2}$(1.958)

(e) $3d_{xz}$(0.113) (f) $3d_{yz}$(0.113) (g) $3d_{z^2}$(0.092) (h) $3d_{xy}$(0.038)

(i) O $2p_z$(1.914) (j) O $2p_x$(1.891) (k) O $2p_y$(1.892) (l) a′ π*(0.063)

(m) a″ π*(0.082)

Figure S2. Natural active orbitals (basis II) and their main character for the $1^1A'$ ground state of Mn(Cz)(O) (except for the three Mn 4d orbitals) for the CAS(14,16) active space. The contour values are ± 0.04 e/au^3. Occupation numbers are given within parentheses.



(a) a′ π (1.987) (b) a′ π(1.984) (c) a′ π(1.982) (d) a′ π(1.986) (e) a′ π(1.949)

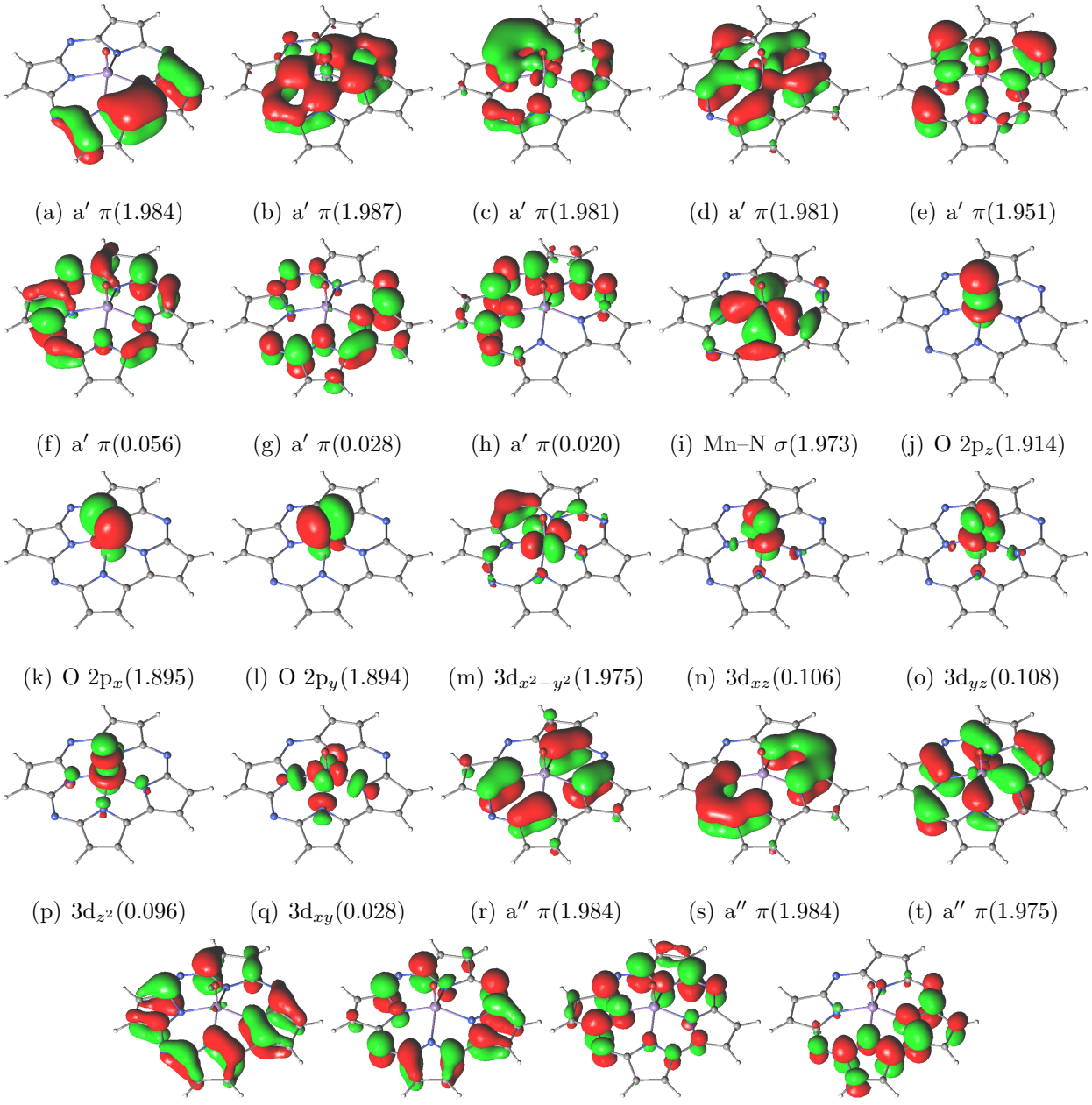
(f) a″ π(1.983) (g) a″ π(1.981) (h) a″ π(1.963) (i) a″ π(1.979) (j) Mn–N σ(1.971)

(k) O $2p_z$(1.914) (l) O $2p_x$(1.889) (m) O $2p_y$(1.889) (n) $3d_{x^2-y^2}$ (1.975) (o) $3d_{xz}$(0.113)

(p) $3d_{yz}$(0.114) (q) $3d_{z^2}$(0.099) (r) $3d_{xy}$(0.030) (s) a′ π(0.052) (t) a′ π(0.025)

(u) a′ π(0.017) (v) a″ π(0.053) (w) a″ π(0.025) (x) a″ π(0.017)

Figure S3. Pseudonatural active orbitals (basis II) and their main character for the $1^1A'$ ground state of Mn(Cor)(O) (except for the three Mn 4d orbitals) for the RAS(28,27) active space. The contour values are ± 0.04 e/au^3. Occupation numbers are given within parentheses.



(a) a′ π(1.984) (b) a′ π(1.987) (c) a′ π(1.981) (d) a′ π(1.981) (e) a′ π(1.951)

(f) a′ π(0.056) (g) a′ π(0.028) (h) a′ π(0.020) (i) Mn–N σ(1.973) (j) O $2p_z$(1.914)

(k) O $2p_x$(1.895) (l) O $2p_y$(1.894) (m) $3d_{x^2-y^2}$(1.975) (n) $3d_{xz}$(0.106) (o) $3d_{yz}$(0.108)

(p) $3d_{z^2}$(0.096) (q) $3d_{xy}$(0.028) (r) a″ π(1.984) (s) a″ π(1.984) (t) a″ π(1.975)

(u) a″ π(1.952) (v) a″ π(0.059) (w) a″ π(0.024) (x) a″ π(0.017)

Figure S4. Pseudonatural active orbitals (basis II) and their main character for the 1^1A′ ground state of Mn(Cz)(O) (except for the three Mn 4d orbitals) for the RAS(28,27) active space. The contour values are ±0.04 e/au^3. Occupation numbers are given within parentheses.

Table S2. Mn(Cor)(O): Structures and spin densities obtained from DFT for the three (formal) Mn^V states. Δ = distance between Mn and the mean NNNN plane. The contour values of the spin density plots are ± 0.005 e/au^3. α and β spin densities are indicated in red and green, respectively. Mulliken spin populations are denoted by ρ. NUE = number of unpaired electrons (NUE $= \sum_{i=1}^{\text{nat.orbs}} n_i(2-n_i) = 2\left(\langle \hat{\mathbf{S}}^2 \rangle - S^2\right)$)

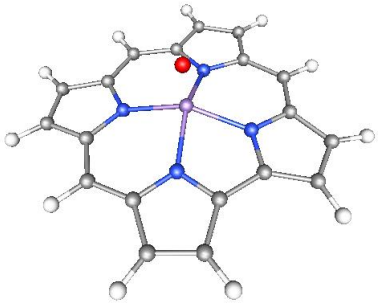
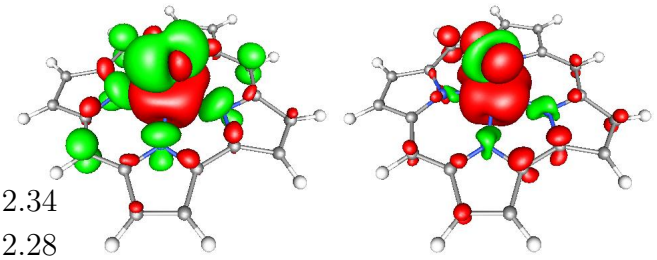
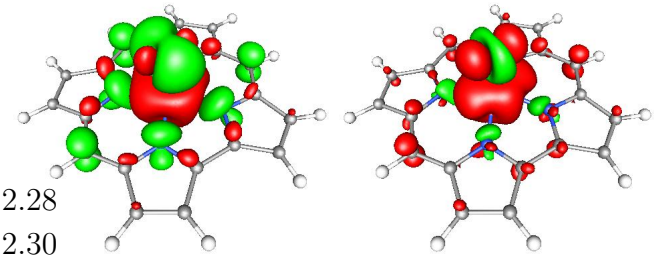
Mn(Cor)(O) ^{1}A′ $(d_{x^2-y^2})^2$					
	PBE0	B3LYP	BP86	OLYP	spin density plot
Energy(eV)	0.00	0.00	0.00	0.00	
r(Mn-O)(Å)	1.513	1.531	1.552		
r(Mn-N_1)(Å)	1.921	1.937	1.940		
r(Mn-N_2)(Å)	1.892	1.908	1.910		
Δ(Å)	0.549	0.561	0.551		
NUE	0.00	0.00	0.00	0.00	
ρ(Mn)	0.00	0.00	0.00	0.00	
ρ(O)	0.00	0.00	0.00	0.00	
ρ(Cor)	0.00	0.00	0.00	0.00	
Mn(Cor)(O) ^{3}A′ $(d_{x^2-y^2})^\uparrow(d_{xz})^\uparrow$					
	PBE0	B3LYP	BP86	OLYP	spin density plot
Energy(eV)	0.34	0.52	0.74	0.66	
r(Mn-O)(Å)	1.665	1.622	1.606		
r(Mn-N_1)(Å)	1.922	1.936	1.938		
r(Mn-N_2)(Å)	1.908	1.922	1.924		
Δ(Å)	0.435	0.473	0.463		
NUE	3.42	2.62	2.08	2.34	
ρ(Mn)	3.07	2.55	1.82	2.28	
ρ(O)	-0.71	-0.33	0.13	0.02	
ρ(Cor)	-0.36	-0.22	0.05	-0.26	PBE0 BP86
Mn(Cor)(O) ^{3}A″ $(d_{x^2-y^2})^\uparrow(d_{yz})^\uparrow$					
	PBE0	B3LYP	BP86	OLYP	spin density plot
Energy(eV)	0.35	0.53	0.78	0.71	
r(Mn-O)(Å)	1.666	1.625	1.604		
r(Mn-N_1)(Å)	1.924	1.936	1.938		
r(Mn-N_2)(Å)	1.909	1.924	1.928		
Δ(Å)	0.440	0.480	0.480		
NUE	3.40	2.68	2.08	2.28	
ρ(Mn)	3.07	2.60	1.82	2.30	
ρ(O)	-0.70	-0.37	0.10	-0.08	
ρ(Cor)	-0.37	-0.23	0.08	-0.22	PBE0 BP86

Table S3. Mn(Cz)(O): Structures and spin densities obtained from DFT for the three (formal) Mn^V states. Δ = distance between Mn and the mean NNNN plane. The contour values of the spin density plots are ± 0.005 e/au^3. α and β spin densities are indicated in red and green, respectively. Mulliken spin populations are denoted by ρ. NUE = number of unpaired electrons (see text)

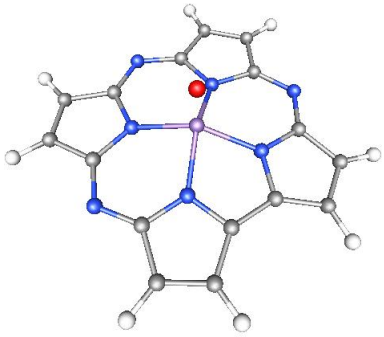
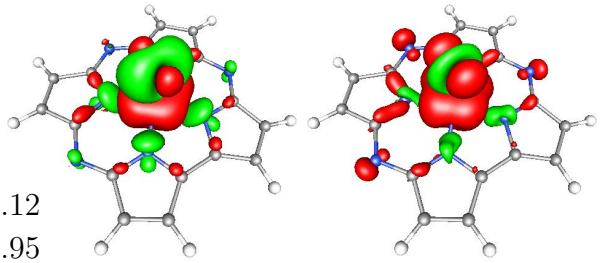
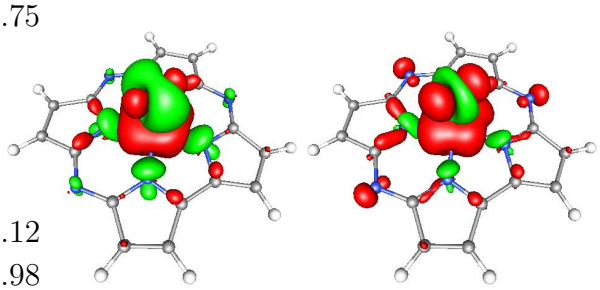
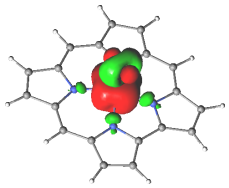
Mn(Cz)(O) ^{1}A′ $(d_{x^2-y^2})^2$					
	PBE0	B3LYP	BP86	OLYP	spin density plot
Energy(eV)	0.0	0.0	0.0	0.00	
r(Mn-O)(Å)	1.510	1.527	1.548		
r(Mn-N_1)(Å)	1.881	1.897	1.899		
r(Mn-N_2)(Å)	1.863	1.879	1.882		
Δ(Å)	0.593	0.603	0.597		
NUE	0.00	0.00	0.00	0.00	
ρ(Mn)	0.00	0.00	0.00	0.00	
ρ(O)	0.00	0.00	0.00	0.00	
ρ(Cz)	0.00	0.00	0.00	0.00	
Mn(Cz)(O) ^{3}A′ $(d_{x^2-y^2})^{\uparrow}(d_{xz})^{\uparrow}$					
	PBE0	B3LYP	BP86	OLYP	spin density plot
Energy(eV)	0.57	0.68	0.82	0.71	
r(Mn-O)(Å)	1.595	1.595	1.605		
r(Mn-N_1)(Å)	1.879	1.892	1.889		
r(Mn-N_2)(Å)	1.877	1.893	1.895		
Δ(Å)	0.503	0.520	0.505		
NUE	2.56	2.28	2.08	2.12	
ρ(Mn)	2.51	2.22	1.85	1.95	
ρ(O)	-0.38	-0.14	0.13	0.09	
ρ(Cz)	-0.13	-0.08	0.02	-0.04	PBE0 BP86
Mn(Cz)(O) ^{3}A″ $(d_{x^2-y^2})^{\uparrow}(d_{yz})^{\uparrow}$					
	PBE0	B3LYP	BP86	OLYP	spin density plot
Energy(eV)	0.58	0.69	0.86	0.75	
r(Mn-O)(Å)	1.597	1.596	1.603		
r(Mn-N_1)(Å)	1.879	1.892	1.887		
r(Mn-N_2)(Å)	1.879	1.894	1.901		
Δ(Å)	0.511	0.532	0.522		
NUE	2.60	2.32	2.08	2.12	
ρ(Mn)	2.54	2.27	1.88	1.98	
ρ(O)	-0.41	-0.19	0.10	0.05	
ρ(Cz)	-0.13	-0.08	0.02	-0.03	PBE0 BP86

Table S4. Mn(Cor)(O): Spin densities obtained from CASPT2/RASPT2 for the two (formal) Mn^V triplet states. The contour values of the spin density plots are ± 0.005 e/au^3. α and β spin densities are indicated in red and green, respectively. Mulliken spin populations are denoted by ρ.

Mn(Cor)(O) ^{3}A′ $(d_{x^2-y^2})^{\uparrow}(d_{xz})^{\uparrow}$

	Basis I		Basis II		spin density plot
	CAS	RAS	CAS	RAS	
Energy(eV)	0.41	0.32	0.53	0.36	
ρ(Mn)	2.20	2.21	2.20	2.21	
ρ(O)	-0.15	-0.15	-0.16	-0.16	
ρ(Cor)	-0.05	-0.06	-0.04	-0.05	

Mn(Cor)(O) ^{3}A″ $(d_{x^2-y^2})^{\uparrow}(d_{yz})^{\uparrow}$

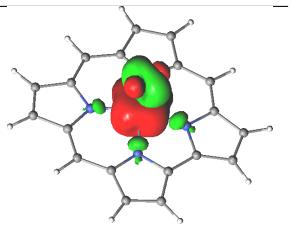
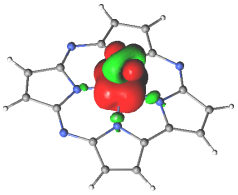
	Basis I		Basis II		spin density plot
	CAS	RAS	CAS	RAS	
Energy(eV)	0.51	0.38	0.63	0.41	
ρ(Mn)	2.20	2.24	2.21	2.21	
ρ(O)	-0.16	-0.17	-0.17	-0.18	
ρ(Cor)	-0.04	-0.07	-0.04	-0.03	

Table S5. Mn(Cz)(O): Spin densities obtained from CASPT2/RASPT2 for the two (formal) Mn^V triplet states.The contour values of the spin density plots are ±0.005 e/au^3. α and β spin densities are indicated in red and green, respectively. Mulliken spin populations are denoted by ρ.

Mn(Cz)(O) ^{3}A′ $(d_{x^2-y^2})^{\uparrow}(d_{xz})^{\uparrow}$

	Basis I		Basis II		spin density plot
	CAS	RAS	CAS	RAS	
Energy(eV)	0.51	0.44	0.55	0.50	
ρ(Mn)	2.06	2.04	2.07	2.04	
ρ(O)	-0.05	-0.05	-0.06	-0.06	
ρ(Cz)	-0.01	0.01	-0.01	0.02	

Mn(Cz)(O) ^{3}A″ $(d_{x^2-y^2})^{\uparrow}(d_{yz})^{\uparrow}$

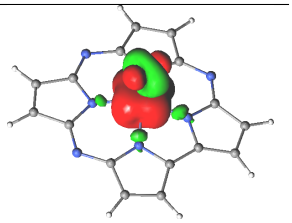
	Basis I		Basis II		spin density plot
	CAS	RAS	CAS	RAS	
Energy(eV)	0.64	0.49	0.69	0.53	
ρ(Mn)	2.06	2.06	2.08	2.06	
ρ(O)	-0.05	-0.07	-0.08	-0.08	
ρ(Cz)	-0.01	0.01	0.00	0.02	

Table S6. PBE0/def2-TZVP optimized cartesian coordinates (Å) of Mn(Cor)(O), $1^1A'$ state.

Mn	0.000000	0.000000	0.000000
N	-1.223246	1.368474	0.565322
N	-1.223246	-1.368474	0.565322
N	1.368794	1.193433	0.531983
N	1.368794	-1.193433	0.531983
C	-3.205005	-2.497808	0.725492
C	-3.205005	2.497808	0.725492
C	-2.589356	-1.217499	0.651878
C	-2.589356	1.217499	0.651878
C	-3.236775	0.000000	0.677359
C	-0.973675	-2.729848	0.587572
C	-0.973675	2.729848	0.587572
C	-2.211786	-3.425931	0.680410
C	-2.211786	3.425931	0.680410
C	0.278528	3.316460	0.581179
C	0.278528	-3.316460	0.581179
C	1.432513	2.559090	0.584806
C	1.432513	-2.559090	0.584806
C	2.798754	2.927337	0.696868
C	2.798754	-2.927337	0.696868
C	3.546139	1.770809	0.726961
C	3.546139	-1.770809	0.726961
C	2.637726	-0.697668	0.626591
C	2.637726	0.697668	0.626591
H	-2.302748	4.501232	0.727091
H	-2.302748	-4.501232	0.727091
H	-4.269426	2.661730	0.804588
H	-4.269426	-2.661730	0.804588
H	-4.317175	0.000000	0.747008
H	0.342723	-4.396229	0.617457
H	0.342723	4.396229	0.617457
H	3.162639	-3.942165	0.760730
H	3.162639	3.942165	0.760730
H	4.617790	1.687235	0.824974
H	4.617790	-1.687235	0.824974
O	-0.064035	0.000000	-1.511492

Table S7. PBE0/def2-TZVP optimized cartesian coordinates (Å) of Mn(Cor)(O), $1^3A'$ state.

Mn	0.000000	0.000000	0.000000
N	-1.231497	-1.405369	0.451496
N	-1.231497	1.405369	0.451496
N	1.413483	-1.211779	0.419388
N	1.413483	1.211779	0.419388
C	-3.209964	-2.519426	0.549051
C	-3.209964	2.519426	0.549051
C	-2.594516	-1.234814	0.494486
C	-2.594516	1.234814	0.494486
C	-3.226634	0.000000	0.505670
C	-0.970023	-2.758312	0.459409
C	-0.970023	2.758312	0.459409
C	-2.215336	-3.450697	0.524529
C	-2.215336	3.450697	0.524529
C	0.299741	3.325447	0.448278
C	0.299741	-3.325447	0.448278
C	1.466073	2.575576	0.446853
C	1.466073	-2.575576	0.446853
C	2.838892	2.942421	0.528084
C	2.838892	-2.942421	0.528084
C	3.585609	1.784459	0.546894
C	3.585609	-1.784459	0.546894
C	2.675450	0.704150	0.475630
C	2.675450	-0.704150	0.475630
H	-2.316111	4.525438	0.563668
H	-2.316111	-4.525438	0.563668
H	-4.274906	2.689149	0.606091
H	-4.274906	-2.689149	0.606091
H	-4.309135	0.000000	0.543678
H	0.369182	-4.405805	0.469593
H	0.369182	4.405805	0.469593
H	3.209875	-3.955287	0.581976
H	3.209875	3.955287	0.581976
H	4.659690	1.705257	0.619822
H	4.659690	-1.705257	0.619822
O	-0.040965	0.000000	-1.664840

Table S8. PBE0/def2-TZVP optimized cartesian coordinates (Å) of Mn(Cor)(O), $1^3A''$ state.

Mn	0.000000	0.000000	0.000000
N	-1.236267	-1.401815	0.455044
N	-1.236267	1.401815	0.455044
N	1.414489	-1.208985	0.425753
N	1.414489	1.208985	0.425753
C	-3.213034	-2.519980	0.555223
C	-3.213034	2.519980	0.555223
C	-2.599450	-1.234130	0.504667
C	-2.599450	1.234130	0.504667
C	-3.232642	0.000000	0.519929
C	-0.973000	-2.754199	0.454286
C	-0.973000	2.754199	0.454286
C	-2.216987	-3.449100	0.520351
C	-2.216987	3.449100	0.520351
C	0.296304	3.321505	0.439796
C	0.296304	-3.321505	0.439796
C	1.463656	2.573373	0.443343
C	1.463656	-2.573373	0.443343
C	2.834890	2.943465	0.525440
C	2.834890	-2.943465	0.525440
C	3.584275	1.786742	0.554488
C	3.584275	-1.786742	0.554488
C	2.676615	0.704635	0.487852
C	2.676615	-0.704635	0.487852
H	-2.315526	4.524229	0.554157
H	-2.315526	-4.524229	0.554157
H	-4.277495	2.691576	0.615343
H	-4.277495	-2.691576	0.615343
H	-4.314979	0.000000	0.561692
H	0.364941	-4.402024	0.454655
H	0.364941	4.402024	0.454655
H	3.203590	-3.957388	0.574935
H	3.203590	3.957388	0.574935
H	4.658411	1.710268	0.629593
H	4.658411	-1.710268	0.629593
O	-0.051946	0.000000	-1.662582

Table S9. PBE0/def2-TZVP optimized cartesian coordinates (Å) of MnO(Cor)(O), $1^5A''$ state.

Mn	0.000000	0.000000	0.000000
N	-1.259407	-1.428039	0.389719
N	-1.259407	1.428039	0.389719
N	1.449208	-1.224701	0.335393
N	1.449208	1.224701	0.335393
C	-3.227636	-2.537365	0.547679
C	-3.227636	2.537365	0.547679
C	-2.608086	-1.253575	0.459018
C	-2.608086	1.253575	0.459018
C	-3.230843	0.000000	0.475528
C	-0.989084	-2.757815	0.431470
C	-0.989084	2.757815	0.431470
C	-2.224965	-3.467439	0.530510
C	-2.224965	3.467439	0.530510
C	0.310606	3.315818	0.426763
C	0.310606	-3.315818	0.426763
C	1.486087	2.582877	0.405789
C	1.486087	-2.582877	0.405789
C	2.862876	2.958345	0.533436
C	2.862876	-2.958345	0.533436
C	3.607464	1.800281	0.552642
C	3.607464	-1.800281	0.552642
C	2.686317	0.722770	0.429112
C	2.686317	-0.722770	0.429112
H	-2.322381	4.541348	0.592062
H	-2.322381	-4.541348	0.592062
H	-4.290187	2.714351	0.624481
H	-4.290187	-2.714351	0.624481
H	-4.313474	0.000000	0.535008
H	0.377454	-4.396119	0.484428
H	0.377454	4.396119	0.484428
H	3.233845	-3.968913	0.621436
H	3.233845	3.968913	0.621436
H	4.678924	1.718331	0.653190
H	4.678924	-1.718331	0.653190
O	-0.057962	0.000000	-1.626750

Table S10. PBE0/def2-TZVP optimized cartesian coordinates (Å) of Mn(Cor)(O), $2^3A'$ state.

Mn	0.000000	0.000000	0.000000
N	-1.262133	-1.404568	0.501745
N	-1.262133	1.404568	0.501745
N	1.418753	-1.217555	0.439816
N	1.418753	1.217555	0.439816
C	-3.229622	-2.523395	0.730790
C	-3.229622	2.523395	0.730790
C	-2.611950	-1.244387	0.608965
C	-2.611950	1.244387	0.608965
C	-3.243503	0.000000	0.636696
C	-0.997880	-2.738838	0.566182
C	-0.997880	2.738838	0.566182
C	-2.225470	-3.451353	0.705065
C	-2.225470	3.451353	0.705065
C	0.293413	3.308740	0.568196
C	0.293413	-3.308740	0.568196
C	1.464172	2.574484	0.544750
C	1.464172	-2.574484	0.544750
C	2.834352	2.947532	0.723166
C	2.834352	-2.947532	0.723166
C	3.576084	1.788227	0.748204
C	3.576084	-1.788227	0.748204
C	2.656489	0.719074	0.573581
C	2.656489	-0.719074	0.573581
H	-2.315506	4.524545	0.788437
H	-2.315506	-4.524545	0.788437
H	-4.290063	2.698188	0.837296
H	-4.290063	-2.698188	0.837296
H	-4.323930	0.000000	0.726977
H	0.355022	-4.387612	0.652095
H	0.355022	4.387612	0.652095
H	3.201497	-3.956452	0.841752
H	3.201497	3.956452	0.841752
H	4.642464	1.699966	0.889308
H	4.642464	-1.699966	0.889308
O	-0.019571	0.000000	-1.558297

Table S11. PBE0/def2-TZVP optimized cartesian coordinates (Å) of Mn(Cor)(O), $2^3A''$ state.

Mn	0.000000	0.000000	0.000000
N	-1.250372	1.408840	0.497085
N	-1.250372	-1.408840	0.497085
N	1.427456	1.218013	0.446800
N	1.427456	-1.218013	0.446800
C	-3.220009	-2.524681	0.714526
C	-3.220009	2.524681	0.714526
C	-2.600628	-1.245944	0.591092
C	-2.600628	1.245944	0.591092
C	-3.230520	0.000000	0.610441
C	-0.986940	-2.742034	0.567623
C	-0.986940	2.742034	0.567623
C	-2.216482	-3.453244	0.699598
C	-2.216482	3.453244	0.699598
C	0.304275	3.311565	0.570451
C	0.304275	-3.311565	0.570451
C	1.474363	2.575973	0.541233
C	1.474363	-2.575973	0.541233
C	2.846759	2.950030	0.692012
C	2.846759	-2.950030	0.692012
C	3.588726	1.789780	0.710941
C	3.588726	-1.789780	0.710941
C	2.666263	-0.720396	0.559312
C	2.666263	0.720396	0.559312
H	-2.307903	4.525929	0.787459
H	-2.307903	-4.525929	0.787459
H	-4.281447	2.698666	0.812054
H	-4.281447	-2.698666	0.812054
H	-4.311737	0.000000	0.691566
H	0.367057	-4.390694	0.649490
H	0.367057	4.390694	0.649490
H	3.216281	-3.959353	0.799259
H	3.216281	3.959353	0.799259
H	4.657839	1.702397	0.830804
H	4.657839	-1.702397	0.830804
O	-0.083552	0.000000	-1.558235

Table S12. PBE0/def2-TZVP optimized cartesian coordinates (Å) of Mn(Cor)(O), $1^5A'$ state.

Mn	0.000000	0.000000	0.000000
N	-1.247834	-1.411445	0.411290
N	-1.247834	1.411445	0.411290
N	1.445477	-1.224776	0.338724
N	1.445477	1.224776	0.338724
C	-3.211840	-2.545414	0.581008
C	-3.211840	2.545414	0.581008
C	-2.587704	-1.239129	0.489155
C	-2.587704	1.239129	0.489155
C	-3.227742	0.000000	0.507289
C	-0.964487	-2.758116	0.453127
C	-0.964487	2.758116	0.453127
C	-2.224105	-3.466499	0.556026
C	-2.224105	3.466499	0.556026
C	0.298582	3.315115	0.453703
C	0.298582	-3.315115	0.453703
C	1.489401	2.553367	0.438462
C	1.489401	-2.553367	0.438462
C	2.875923	2.935013	0.585521
C	2.875923	-2.935013	0.585521
C	3.622062	1.788479	0.587185
C	3.622062	-1.788479	0.587185
C	2.707817	0.697997	0.439018
C	2.707817	-0.697997	0.439018
H	-2.320347	4.540681	0.617181
H	-2.320347	-4.540681	0.617181
H	-4.274958	2.716433	0.664956
H	-4.274958	-2.716433	0.664956
H	-4.308452	0.000000	0.571687
H	0.373437	-4.393635	0.512116
H	0.373437	4.393635	0.512116
H	3.239224	-3.946514	0.692570
H	3.239224	3.946514	0.692570
H	4.693380	1.710411	0.693882
H	4.693380	-1.710411	0.693882
O	-0.028265	0.000000	-1.633767

Table S13. PBE0/def2-TZVP optimized cartesian coordinates (Å) of Mn(Cor)(O), $3^3A''$ state.

Mn	0.000000	0.000000	0.000000
N	-1.249912	-1.388534	0.530507
N	-1.249912	1.388534	0.530507
N	1.414037	-1.215147	0.446916
N	1.414037	1.215147	0.446916
C	-3.216236	-2.530806	0.774460
C	-3.216236	2.530806	0.774460
C	-2.591426	-1.229540	0.651599
C	-2.591426	1.229540	0.651599
C	-3.239958	0.000000	0.684438
C	-0.976005	-2.738005	0.593860
C	-0.976005	2.738005	0.593860
C	-2.229028	-3.450041	0.736808
C	-2.229028	3.450041	0.736808
C	0.279277	3.307292	0.595086
C	0.279277	-3.307292	0.595086
C	1.463480	2.543587	0.580279
C	1.463480	-2.543587	0.580279
C	2.841286	2.924904	0.782518
C	2.841286	-2.924904	0.782518
C	3.586267	1.778867	0.794150
C	3.586267	-1.778867	0.794150
C	2.675406	0.694941	0.593809
C	2.675406	-0.694941	0.593809
H	-2.318560	4.523840	0.815233
H	-2.318560	-4.523840	0.815233
H	-4.277103	2.697789	0.889706
H	-4.277103	-2.697789	0.889706
H	-4.318143	0.000000	0.781392
H	0.350006	-4.384490	0.677550
H	0.350006	4.384490	0.677550
H	3.197878	-3.935265	0.919078
H	3.197878	3.935265	0.919078
H	4.651989	1.695566	0.944614
H	4.651989	-1.695566	0.944614
O	-0.013346	0.000000	-1.562787

Table S14. PBE0/def2-TZVP optimized cartesian coordinates (Å) of Mn(Cor)(O), $3^3A'$ state.

Mn	0.000000	0.000000	0.000000
N	-1.232825	1.391354	0.524219
N	-1.232825	-1.391354	0.524219
N	1.427752	1.216595	0.457487
N	1.427752	-1.216595	0.457487
C	-3.201090	-2.532111	0.750408
C	-3.201090	2.532111	0.750408
C	-2.575600	-1.231006	0.624719
C	-2.575600	1.231006	0.624719
C	-3.223062	0.000000	0.644057
C	-0.958165	-2.740202	0.598692
C	-0.958165	2.740202	0.598692
C	-2.213107	-3.450981	0.732124
C	-2.213107	3.450981	0.732124
C	0.296319	3.309701	0.603452
C	0.296319	-3.309701	0.603452
C	1.481112	2.545604	0.578024
C	1.481112	-2.545604	0.578024
C	2.862579	2.927674	0.743620
C	2.862579	-2.927674	0.743620
C	3.606823	1.779697	0.743835
C	3.606823	-1.779697	0.743835
C	2.690723	-0.696459	0.572957
C	2.690723	0.696459	0.572957
H	-2.303238	4.524064	0.818723
H	-2.303238	-4.524064	0.818723
H	-4.263365	2.699191	0.851682
H	-4.263365	-2.699191	0.851682
H	-4.302408	0.000000	0.727926
H	0.366950	-4.387084	0.683172
H	0.366950	4.387084	0.683172
H	3.223607	-3.938151	0.867149
H	3.223607	3.938151	0.867149
H	4.676271	1.696706	0.865862
H	4.676271	-1.696706	0.865862
O	-0.072564	0.000000	-1.562342

Table S15. PBE0/def2-TZVP optimized cartesian coordinates (Å) of MnO(Cz), $1^1A'$ state.

Mn	0.000000	0.000000	0.000000
N	-1.183082	1.319547	0.629969
N	-1.183082	-1.319547	0.629969
N	1.331997	1.177553	0.556932
N	1.331997	-1.177553	0.556932
N	0.246165	3.276568	0.720178
N	0.246165	-3.276568	0.720178
N	-3.190487	0.000000	0.775208
C	2.605554	0.698241	0.692762
C	2.605554	-0.698241	0.692762
C	3.474711	1.802428	0.877011
C	3.474711	-1.802428	0.877011
C	2.694509	2.934973	0.868926
C	2.694509	-2.934973	0.868926
C	1.336422	2.532423	0.692109
C	1.336422	-2.532423	0.692109
C	-0.928814	2.678706	0.701374
C	-0.928814	-2.678706	0.701374
C	-2.178912	3.363427	0.835551
C	-2.178912	-3.363427	0.835551
C	-3.164343	2.429122	0.866285
C	-3.164343	-2.429122	0.866285
C	-2.544789	1.146273	0.745315
C	-2.544789	-1.146273	0.745315
H	4.543116	1.749044	1.020550
H	4.543116	-1.749044	1.020550
H	3.012928	3.957978	0.998503
H	3.012928	-3.957978	0.998503
H	-2.258572	4.435866	0.925471
H	-2.258572	-4.435866	0.925471
H	-4.228813	2.568154	0.974932
H	-4.228813	-2.568154	0.974932
O	-0.074941	0.000000	-1.507768

Table S16. PBE0/def2-TZVP optimized cartesian coordinates (Å) of Mn(Cz)(O), $1^3A'$ state.

Mn	0.000000	0.000000	0.000000
N	-1.185166	1.347597	0.555378
N	-1.185166	-1.347597	0.555378
N	1.375689	1.195390	0.450916
N	1.375689	-1.195390	0.450916
N	0.267928	3.280953	0.650330
N	0.267928	-3.280953	0.650330
N	-3.176237	0.000000	0.683421
C	2.642008	0.702679	0.587460
C	2.642008	-0.702679	0.587460
C	3.508533	1.809334	0.798138
C	3.508533	-1.809334	0.798138
C	2.728945	2.942473	0.804593
C	2.728945	-2.942473	0.804593
C	1.367843	2.545432	0.607816
C	1.367843	-2.545432	0.607816
C	-0.918153	2.701588	0.630519
C	-0.918153	-2.701588	0.630519
C	-2.173857	3.381031	0.766894
C	-2.173857	-3.381031	0.766894
C	-3.160755	2.445047	0.784251
C	-3.160755	-2.445047	0.784251
C	-2.545398	1.158004	0.656186
C	-2.545398	-1.158004	0.656186
H	4.575261	1.756077	0.953884
H	4.575261	-1.756077	0.953884
H	3.050311	3.961007	0.959978
H	3.050311	-3.961007	0.959978
H	-2.261165	4.452000	0.867125
H	-2.261165	-4.452000	0.867125
H	-4.224316	2.589775	0.894843
H	-4.224316	-2.589775	0.894843
O	-0.071958	0.000000	-1.593834

Table S17. PBE0/def2-TZVP optimized cartesian coordinates (Å) of Mn(Cz)(O), $1^3A''$ state.

Mn	0.000000	0.000000	0.000000
N	-1.185372	1.349301	0.552083
N	-1.185372	-1.349301	0.552083
N	1.371907	1.194280	0.469787
N	1.371907	-1.194280	0.469787
N	0.265871	3.284114	0.631273
N	0.265871	-3.284114	0.631273
N	-3.176036	0.000000	0.676868
C	2.637576	0.703818	0.596948
C	2.637576	-0.703818	0.596948
C	3.506643	1.813394	0.777611
C	3.506643	-1.813394	0.777611
C	2.727837	2.948252	0.769754
C	2.727837	-2.948252	0.769754
C	1.365743	2.548607	0.594631
C	1.365743	-2.548607	0.594631
C	-0.919900	2.702773	0.616695
C	-0.919900	-2.702773	0.616695
C	-2.176297	3.382380	0.746478
C	-2.176297	-3.382380	0.746478
C	-3.162817	2.446058	0.769111
C	-3.162817	-2.446058	0.769111
C	-2.546347	1.158579	0.649807
C	-2.546347	-1.158579	0.649807
H	4.575553	1.762715	0.918970
H	4.575553	-1.762715	0.918970
H	3.051608	3.968790	0.905736
H	3.051608	-3.968790	0.905736
H	-2.264570	4.454044	0.838156
H	-2.264570	-4.454044	0.838156
H	-4.226669	2.590904	0.876573
H	-4.226669	-2.590904	0.876573
O	-0.083458	0.000000	-1.595296

Table S18. PBE0/def2-TZVP optimized cartesian coordinates (Å) of Mn(Cz)(O), $1^5A''$ state.

Mn	0.000000	0.000000	0.000000
N	-1.207942	1.372586	0.515279
N	-1.207942	-1.372586	0.515279
N	1.424508	1.217986	0.361710
N	1.424508	-1.217986	0.361710
N	0.287179	3.267893	0.695848
N	0.287179	-3.267893	0.695848
N	-3.171780	0.000000	0.706780
C	2.645569	0.732334	0.571970
C	2.645569	-0.732334	0.571970
C	3.522278	1.824644	0.892760
C	3.522278	-1.824644	0.892760
C	2.753171	2.957446	0.898627
C	2.753171	-2.957446	0.898627
C	1.389642	2.562590	0.603958
C	1.389642	-2.562590	0.603958
C	-0.932162	2.693344	0.649932
C	-0.932162	-2.693344	0.649932
C	-2.173190	3.389960	0.855153
C	-2.173190	-3.389960	0.855153
C	-3.168273	2.457894	0.859718
C	-3.168273	-2.457894	0.859718
C	-2.551268	1.172246	0.663440
C	-2.551268	-1.172246	0.663440
H	4.576903	1.752587	1.109826
H	4.576903	-1.752587	1.109826
H	3.066227	3.964777	1.126959
H	3.066227	-3.964777	1.126959
H	-2.251749	4.455727	1.004668
H	-2.251749	-4.455727	1.004668
H	-4.225904	2.606627	1.013766
H	-4.225904	-2.606627	1.013766
O	-0.070308	0.000000	-1.625676

Table S19. PBE0/def2-TZVP optimized cartesian coordinates (Å) of Mn(Cz)(O), $3^3A'$ state.

Mn	0.000000	0.000000	0.000000
N	-1.213982	1.348164	0.610260
N	-1.213982	-1.348164	0.610260
N	1.384665	1.205745	0.479484
N	1.384665	-1.205745	0.479484
N	0.263020	3.263930	0.789557
N	0.263020	-3.263930	0.789557
N	-3.191429	0.000000	0.823926
C	2.610520	0.727721	0.700068
C	2.610520	-0.727721	0.700068
C	3.487554	1.815210	1.021108
C	3.487554	-1.815210	1.021108
C	2.719356	2.948740	1.014196
C	2.719356	-2.948740	1.014196
C	1.360353	2.551299	0.712393
C	1.360353	-2.551299	0.712393
C	-0.947470	2.675278	0.745142
C	-0.947470	-2.675278	0.745142
C	-2.181659	3.375719	0.958678
C	-2.181659	-3.375719	0.958678
C	-3.176826	2.444447	0.973591
C	-3.176826	-2.444447	0.973591
C	-2.557851	1.163177	0.776153
C	-2.557851	-1.163177	0.776153
H	4.539701	1.740452	1.248747
H	4.539701	-1.740452	1.248747
H	3.029678	3.958226	1.236923
H	3.029678	-3.958226	1.236923
H	-2.254238	4.442327	1.105727
H	-2.254238	-4.442327	1.105727
H	-4.233793	2.589854	1.135585
H	-4.233793	-2.589854	1.135585
O	0.005655	0.000000	-1.559519

Table S20. PBE0/def2-TZVP optimized cartesian coordinates (Å) of Mn(Cz)(O), $2^3A''$ state.

Mn	0.000000	0.000000	0.000000
N	-1.205681	1.335921	0.650041
N	-1.205681	-1.335921	0.650041
N	1.381372	1.207028	0.465687
N	1.381372	-1.207028	0.465687
N	0.248453	3.256807	0.826130
N	0.248453	-3.256807	0.826130
N	-3.185919	0.000000	0.888216
C	2.633629	0.694379	0.705909
C	2.633629	-0.694379	0.705909
C	3.488381	1.785893	1.087050
C	3.488381	-1.785893	1.087050
C	2.710177	2.904961	1.114093
C	2.710177	-2.904961	1.114093
C	1.360781	2.505837	0.760627
C	1.360781	-2.505837	0.760627
C	-0.928006	2.677339	0.785603
C	-0.928006	-2.677339	0.785603
C	-2.189806	3.378243	1.003891
C	-2.189806	-3.378243	1.003891
C	-3.166623	2.452406	1.037599
C	-3.166623	-2.452406	1.037599
C	-2.535517	1.153698	0.836410
C	-2.535517	-1.153698	0.836410
H	4.536606	1.714158	1.334581
H	4.536606	-1.714158	1.334581
H	3.002733	3.908610	1.382635
H	3.002733	-3.908610	1.382635
H	-2.261679	4.446083	1.143943
H	-2.261679	-4.446083	1.143943
H	-4.223510	2.585151	1.210908
H	-4.223510	-2.585151	1.210908
O	-0.036710	0.000000	-1.561050

Table S21. PBE0/def2-TZVP optimized cartesian coordinates (Å) of Mn(Cz)(O), $2^3A'$ state.

Mn	0.000000	0.000000	0.000000
N	-1.190190	1.340544	0.641546
N	-1.190190	-1.340544	0.641546
N	1.391871	1.207177	0.485310
N	1.391871	-1.207177	0.485310
N	0.263845	3.261570	0.823192
N	0.263845	-3.261570	0.823192
N	-3.168575	0.000000	0.861514
C	2.647967	0.696877	0.694658
C	2.647967	-0.696877	0.694658
C	3.511411	1.792705	1.036305
C	3.511411	-1.792705	1.036305
C	2.734693	2.915330	1.064307
C	2.734693	-2.915330	1.064307
C	1.378038	2.510801	0.753082
C	1.378038	-2.510801	0.753082
C	-0.911588	2.680520	0.783361
C	-0.911588	-2.680520	0.783361
C	-2.176027	3.380128	0.997228
C	-2.176027	-3.380128	0.997228
C	-3.152941	2.454459	1.021885
C	-3.152941	-2.454459	1.021885
C	-2.520673	1.155820	0.816222
C	-2.520673	-1.155820	0.816222
H	4.566260	1.725602	1.255873
H	4.566260	-1.725602	1.255873
H	3.035906	3.921880	1.311599
H	3.035906	-3.921880	1.311599
H	-2.248810	4.447146	1.142842
H	-2.248810	-4.447146	1.142842
H	-4.211185	2.587275	1.186695
H	-4.211185	-2.587275	1.186695
O	-0.125353	0.000000	-1.557763

Table S22. PBE0/def2-TZVP optimized cartesian coordinates (Å) of Mn(Cz)(O), $1^5A'$ state.

Mn	0.000000	0.000000	0.000000
N	-1.205368	1.357606	0.566133
N	-1.205368	-1.357606	0.566133
N	1.417306	1.224274	0.340050
N	1.417306	-1.224274	0.340050
N	0.267520	3.261654	0.734040
N	0.267520	-3.261654	0.734040
N	-3.171475	0.000000	0.787356
C	2.662662	0.698386	0.578497
C	2.662662	-0.698386	0.578497
C	3.515458	1.787999	0.973488
C	3.515458	-1.787999	0.973488
C	2.738634	2.909170	1.012433
C	2.738634	-2.909170	1.012433
C	1.387249	2.517651	0.653913
C	1.387249	-2.517651	0.653913
C	-0.916017	2.696048	0.694794
C	-0.916017	-2.696048	0.694794
C	-2.182863	3.393198	0.906319
C	-2.182863	-3.393198	0.906319
C	-3.160148	2.466330	0.936398
C	-3.160148	-2.466330	0.936398
C	-2.531917	1.162281	0.738042
C	-2.531917	-1.162281	0.738042
H	4.563962	1.714671	1.219306
H	4.563962	-1.714671	1.219306
H	3.034380	3.907802	1.295623
H	3.034380	-3.907802	1.295623
H	-2.260055	4.460667	1.045555
H	-2.260055	-4.460667	1.045555
H	-4.217393	2.603568	1.103824
H	-4.217393	-2.603568	1.103824
O	-0.154359	0.000000	-1.623823

References

1. Staroverov, V. N.; Davidson, E. R. *Chem. Phys. Letters* **2000,** *330,* 161–168.

2. Davidson, E. R.; Clark, A. E. *Phys. Chem. Chem. Phys.* **2007,** *9,* 1881–1894.