Supporting Information

Revisiting the Electronic Structure of Cobalt-Porphyrin Nitrene and Carbene Radicals with NEVPT2-CASSCF Calculations: Doublet versus Quartet Ground States

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General Considerations and Computational Methods

Determination of the Magnetic Susceptibility for $[\text{Co}^{III}(\text{TPP}^*)("\text{NNS}"_2)]$

EPR Analysis and Spin Counting for $[\text{Co}^{III}(\text{TPP}^*)("\text{NNS}"_2)]$

DFT Results

NEVPT2-CASSCF results

XYZ Coordinates

References in the Supporting Information
General Considerations and Computational Methods

Chemicals and solvents
All reagents were of commercial grade and used without further purification, unless noted otherwise. All reactions and measurements were performed under an inert atmosphere in a N2 filled glovebox or by using standard Schlenk techniques (under Ar), unless noted otherwise. Toluene was distilled from sodium and C6D6 was dried over molecular sieves prior to use. All solvents were deaerated by three freeze-pump-thaw cycles and backfilled with argon prior to use. PhInNs was prepared according to a literature procedure and the spectroscopic data of the product matched those previously reported.51 [CoIII(TPP)(‘NNs)]2 was prepared analogous to a literature procedure52 via reaction of [CoII(TPP)] with PhInNs (10 eq.) in C6D6 under an inert atmosphere. The suspension was stirred for 3–5 minutes and filtered (PTFE syringe filter, 0.45 μm) prior to analysis.

DFT calculations
DFT geometry optimizations were performed on full atomic models (no simplifications) using TURBOMOLE 7.353 coupled to the PQS Baker optimizer54 via the BOpt package.55 The calculations were performed at the BP86/def2-TZVP57 level of theory on an m4 grid, using Grimme’s version 3 (disp3, “zero damping”) dispersion corrections.58 Minima (no imaginary frequencies) were characterized by numerically calculating the Hessian matrix. Initial guess geometries were taken from previously optimized geometries at the BP86/def2-TZVP/disp3 level of theory.52 Energy output was reported in Hartree and was converted to kcal mol⁻¹ by multiplication with 627.509.

Zero-field splitting parameter calculations were conducted with the ORCA 4.159 software package on geometries optimized in TURBOMOLE at the doublet spin surface. The SOMF1X510 spin-orbit mean-field approach was used and the def2-TZVP57 basis set was used together with the RIJCOSX511 approximation in conjunction with the def2-TZVP/C fitting basis set to reduce computational cost.

NEVPT2-CASSCF calculations
NEVPT2 corrected CASSCF calculations were performed with the ORCA 4.159 software package on geometries optimized in TURBOMOLE at the doublet spin surface. The def2-TZVP57 basis set was used together with the RIJCOSX511 approximation in conjunction with the def2-TZVP/C fitting basis set to reduce computational cost. In all cases, the single root spin states (doublet and quartet) were calculated. For refined energy values NEVPT2512 calculations using the RI approximation were carried out on converged CASSCF wavefunctions. Canonical orbitals were generated for visualization using IboView.513 Energy output was reported in Hartree and was converted to kcal mol⁻¹ by multiplication with 627.509.
Determination of the Magnetic Susceptibility for [Co\textsuperscript{III}(TPP\textsuperscript{•})(\textsuperscript{15}NNs)\textsubscript{2}]

Evans’ method
The magnetic moment was determined according to reported procedures by solvation of a known amount of the analyte in a known amount of deuterated solvent with an internal standard in an NMR tube. A capillary containing the deuterated solvent and internal standard was inserted in the NMR tube and a \textsuperscript{1}H NMR spectrum was recorded. The mass susceptibility (χ in cm\textsuperscript{3}g\textsuperscript{-1}) of the analyte was calculated with equation (1), wherein ν\textsubscript{0} is the operating frequency of the NMR spectrometer (Hz), c is the concentration of the analyte in the solution (g L\textsuperscript{-1}) and M is the molar mass of the analyte. The molar susceptibility (χ\textsubscript{M} in cm\textsuperscript{3}mol\textsuperscript{-1}) can be calculated by equation (2). χ\textsuperscript{p}\textsubscript{M} is the pure paramagnetic molar susceptibility and can be calculated by equation (3) in which χ\textsuperscript{dia}\textsubscript{M} (the diamagnetic molar susceptibility) is a correction on χ\textsubscript{M} to account for the diamagnetic contributions within the analyte. The diamagnetic molar susceptibility (χ\textsuperscript{dia}\textsubscript{M}) can be calculated by using Pascal’s constants, which are tabulated in literature for different atoms and bond types. With equation (4), χ\textsuperscript{p}\textsubscript{M} can be used to calculate the effective magnetic moment (μ\textsubscript{eff}) of the analyte, in which k is the Boltzmann constant, T is the temperature in Kelvin, N\textsubscript{A} is the Avogadro constant and μ\textsubscript{B} is the Bohr magneton. The electron spin quantum number (S) can now be calculated with equation (5) from the effective magnetic moment by solving for S. Here, g is obtained from an EPR measurement or taken as the g\textsubscript{e}-value for the free electron (2.0023).

\begin{align*}
(1) \quad \chi &= \frac{3000ν\textsubscript{0}c}{4\pi ν\textsubscript{0}cM} \\
(2) \quad χ\textsubscript{M} &= χ \times M \\
(3) \quad χ\textsuperscript{p}\textsubscript{M} &= χ\textsubscript{M} - χ\textsuperscript{dia}\textsubscript{M} \\
(4) \quad μ\textsubscript{eff} &= \frac{3k \times T \times χ\textsubscript{M}}{N\textsubscript{A} \times μ\textsubscript{B}^2} ≈ 2.82787 \sqrt{T} \times χ\textsubscript{M} \\
(5) \quad μ\textsubscript{eff} &= g\sqrt{S(S+1)}
\end{align*}

Measurement
[Co\textsuperscript{III}(TPP\textsuperscript{•})(\textsuperscript{15}NNs)\textsubscript{2}] was prepared according to the procedure as described in the general considerations, to afford a 0.00256 M concentration in CD\textsubscript{6} with toluene as the internal standard. Experimental parameters: T = 300 K, ν\textsubscript{0} = 500 MHz, δ = 5.21 Hz, χ\textsubscript{B} = -449.281 × 10\textsuperscript{-6} emu mol\textsuperscript{-1}. This afforded μ\textsubscript{eff} = 1.90 μ\textsubscript{B} and χ\textsuperscript{p}\textsubscript{M} = 1.51 × 10\textsuperscript{-3} emu mol\textsuperscript{-1}. Clearly, the determined pure paramagnetic molar susceptibility (χ\textsuperscript{p}\textsubscript{M}) is too high for a pure doublet spin system (expectation value for a pure S = ½ system with these experimental parameters: χ\textsuperscript{p}\textsubscript{M} = 1.25 × 10\textsuperscript{-3} emu mol\textsuperscript{-1}). On the other hand, χ\textsuperscript{p}\textsubscript{M} is also too low for a pure species in the quartet spin state (expectation value for a pure S = 3/2 spin system with these experimental parameters: χ\textsuperscript{p}\textsubscript{M} = 6.27 × 10\textsuperscript{-3} emu mol\textsuperscript{-1}). However, at room temperature under the applied concentration (2.56 mM), partial decomposition of this reactive complex is very likely. The high paramagnetic molar susceptibility thus point towards (i) a mixture of different spin states, and (ii) partial decomposition of the reactive [Co\textsuperscript{III}(TPP\textsuperscript{•})(\textsuperscript{15}NNs)\textsubscript{2}] species at room temperature at these high concentrations (as also observed previously\textsuperscript{2}).

S3
EPR analysis and spin counting for \([\text{Co}^{III}(\text{TPP}^*)(\text{NNs})_2]\)

\([\text{Co}^{III}(\text{TPP}^*)(\text{NNs})_2]\) was prepared according to the procedure as described in the general considerations, to afford a 2.425 \(\mu\)M concentration in \(\text{C}_6\text{D}_6\). Tetrabutylammonium hexafluorophosphate (TBAF) was added to the mixture to promote glass formation upon cooling. An X-band EPR spectrum was recorded at 10 K (microwave frequency 9.646459 GHz, power 0.6325 mW, modulation amplitude 1.000 G, Figure S1) and afforded a double integral of 210.4499 of the sharp doublet signal (as calculated with Bruker’s Xenon software). Measurement of a reference sample containing a 2.425 \(\mu\)M concentration of TEMPO in \(\text{C}_6\text{D}_6\):TBAF in the same EPR tube, filled to the same height, and using the same experimental parameters (temperature 10 K, microwave frequency 9.646643 GHz, power 0.6325 mW, modulation amplitude 1.000 G, Figure S1) afforded a double integral of 62642.647. We have previously determined that the accuracy for double integration by this EPR spectrometer is \(\pm 2.5\%\).\(^{516}\) This means that only 0.3\(\pm 2.5\%\) (i.e. <2.8%, taking into account that a negative percentage is not possible) of the expected signal for \([\text{Co}^{III}(\text{TPP}^*)(\text{NNs})_2]\) is in the doublet state. Spin counting at room temperature afforded 8\(\pm 2.5\%\) \([\text{Co}^{III}(\text{TPP}^*)(\text{NNs})_2]\) in the doublet state,\(^{52}\) thus inferring that the doublet state is in a thermal equilibrium with a more stable higher (quartet) spin state (i.e. the higher spin state has a higher Boltzmann population at lower temperature).

![Figure S1. X-band EPR spectra (10 K) of TEMPO (red line) and \([\text{Co}^{III}(\text{TPP}^*)(\text{NNs})_2]\) (black line and zoom in insert) under identical conditions.](image)
The quartet spin state was observed in a similar X-band EPR experiment at 10 K as very broad resonances in the 0–6000 Gauss region, and can clearly be observed upon analysis of the first and double integral of the EPR signal (Figure S2). These observed signals are consistent with the DFT (BP86/def2-TZVP) calculated zero-field splitting parameters for [Co\(^{III}\)(TPP\(^•\))\(^•\)(\(\cdot\)NNs\(_2\))] in the quartet state, which were simulated with the Easyspin software package\(^{517}\) (Figure S3). Calculation of the total double integral (142905, Figure S2) allowed us to calculate the relative contributions of the doublet state (absorption in the 3400–3580 Gauss region, double integral = 769, 0.5±2.5% (i.e. <3%)) and quartet state (absorption in the 0–6000 Gauss region, double integral corrected for presence of the doublet state = 142136, 99.5±2.5% (i.e. >97%)). This is therefore consistent with the quartet state being the ground state of [Co\(^{III}\)(TPP\(^•\))\(^•\)(\(\cdot\)NNs\(_2\))].

Figure S2. X-band EPR spectrum (black), first integral (red) and double integral (blue) of a 2.425 μM solution of [Co\(^{III}\)(TPP\(^•\))\(^•\)(\(\cdot\)NNs\(_2\))] in C\(_6\)D\(_6\):TBAF at 10 K. The areas of absorbance for the quartet (top) and doublet (bottom) are indicated. Experimental parameters: microwave freq. 9.646369 GHz, power 20.00 mW, modulation amplitude 4.000 G.
Figure S3. Simulation (black) and absorbance (first integral, red) of the DFT calculated parameters for the quartet state: $g = [2.005 \ 2.006 \ 2.0125]$, $D = 0.333643 \text{ cm}^{-1}$, $E/D = 0.279133$. A microwave frequency of 9.646369 GHz was used for calculation of the $g$ values.
DFT results

The DFT calculated energies and $<s^2>$ values for $[\text{Co}^{III}(\text{TPP})(\cdot \text{CHCO}_2\text{Et})]$, $[\text{Co}^{III}(\text{TPP})(\cdot \text{NNs})]$ and $[\text{Co}^{III}(\text{TPP})(\cdot \text{NNs})_2]$ in the doublet and quartet spin state are included in Table S1. An overlay of the optimized structures (minima) of $[\text{Co}^{III}(\text{TPP})(\cdot \text{NNs})_2]$ in the doublet and quartet spin state is depicted in Figure S4, and shows the nearly equal geometry for both species.

Table S1. Calculated $<s^2>$ and energies (in Hartree) for all relevant compounds in their described spin state.

| Compound + spin state | $<s^2>$ | SCF (Hartree) | ZPE correction (Hartree) | Enthalpy correction 298K (Hartree) | Entropy correction 298K (Hartree) | $\Delta G^o_{298K}$ (Hartree) |
|-----------------------|---------|---------------|--------------------------|-----------------------------------|-------------------------------|-------------------------------|
| $[\text{Co}^{III}(\text{TPP})(\cdot \text{CHCO}_2\text{Et})]$ (doublet) | 0.7556 | $-3603.19142$ | 0.67364 | 0.71999 | 0.59108 | $-3602.60034$ |
| $[\text{Co}^{III}(\text{TPP})(\cdot \text{CHCO}_2\text{Et})]$ (quartet) | 3.7785 | $-3603.14349$ | 0.67121 | 0.71831 | 0.58812 | $-3602.55537$ |
| $[\text{Co}^{III}(\text{TPP})(\cdot \text{NNs})]$ (doublet) | 0.7579 | $-4336.49567$ | 0.68522 | 0.73601 | 0.59834 | $-4335.89734$ |
| $[\text{Co}^{III}(\text{TPP})(\cdot \text{NNs})]$ (quartet) | 3.7761 | $-4336.47547$ | 0.68449 | 0.73569 | 0.59552 | $-4335.87995$ |
| $[\text{Co}^{III}(\text{TPP})(\cdot \text{NNs})_2]$ (doublet) | 1.6667 | $-5376.37415$ | 0.78893 | 0.85187 | 0.68874 | $-5375.68541$ |
| $[\text{Co}^{III}(\text{TPP})(\cdot \text{NNs})_2]$ (quartet) | 3.7728 | $-5376.37502$ | 0.78892 | 0.85181 | 0.68863 | $-5375.68639$ |

Calculations were performed at the BP86/def2-TZVP/disp3/m4-grid level of theory. Conversion from Hartree to kcal mol$^{-1}$ can be achieved by multiplication with 627.509.

Figure S4. Overlay of DFT (BP86/def2-TZVP/disp3/m4) calculated structures of $[\text{Co}^{III}(\text{TPP})(\cdot \text{NNs})_2]$ in the doublet (blue) and quartet (red) spin state.
NEVPT2-CASSCF results

[Co^III(TPP)("CHCO_2Et")]

NEVPT2-CASSCF(11,10) calculations indicated that the doublet state is 32.3 kcal mol^{-1} below the quartet state. The states and contributions for the doublet and quartet spin state, and a schematic overview (Figure S5) of the active space in the doublet state are included below.

CAS-SCF STATES FOR BLOCK 1 MULT= 2 NROOTS= 1
ROOT 0: E= -3587.1069029852 Eh
  0.81744 : 2222210000
  0.05701 : 2202210020
  0.02838 : 2221111100
  0.02270 : 2212210010
  0.00937 : 2222012000
  0.00889 : 2222010200
  0.00856 : 2022210002
  0.00764 : 2112220010
  0.00644 : 2220212000
  0.00565 : 0222210002
  0.00532 : 2220210200
  0.00263 : 2211210020

CAS-SCF STATES FOR BLOCK 1 MULT= 4 NROOTS= 1
ROOT 0: E= -3587.0910706037 Eh
  0.74950 : 2222111000
  0.07690 : 2122111001
  0.06057 : 2022111002
  0.02550 : 2211111110
  0.01338 : 2220111200
  0.01215 : 1122121001
  0.00856 : 2220111020
  0.00855 : 2220111200
  0.00792 : 2220111020
  0.00577 : 2202111200
  0.00462 : 2202111020
  0.00361 : 2112111002
  0.00267 : 2111111111
Figure S5. Active space orbitals and occupations (in grey and parenthesis) obtained from a NEVPT2-CASSCF(11,10) calculation on [CoIII(TPP)(‘CHCO2Et)] at the doublet spin surface. The cyan orbital was found in the inactive space and an isosurface of 80 was used.
[Co^{III}(TPP)(\cdot)NNs)]

NEVPT2-CASSCF(13,10) calculations indicated that the doublet state is 56.6 kcal mol\(^{-1}\) below the quartet state. The states and contributions for the doublet and quartet spin state, and a schematic overview (Figure S6) of the active space in the doublet state are included below.

**CAS-SCF STATES FOR BLOCK 1 MULT= 2 NROOTS= 1**

ROOT 0: E= \(-4317.7936798118 \text{ Eh}\)

| Contribution | Energy (Eh) |
|--------------|-------------|
| 0.82887 : 2222221000 | 0.00477 : 2221221010 |
| 0.02709 : 2121222100 | 0.00473 : 2221221100 |
| 0.02427 : 2121222010 | 0.00466 : 2220221020 |
| 0.01017 : 2220221110 | 0.00430 : 2211221101 |
| 0.00754 : 2122222000 | 0.00402 : 2202221002 |
| 0.00661 : 2112222001 | 0.00364 : 2211221011 |
| 0.00594 : 2220221200 | 0.00345 : 2212221001 |
| 0.00564 : 2222021110 | 0.00343 : 2022221002 |
| 0.00534 : 2222021200 | 0.00262 : 2222021020 |
| 0.00479 : 0222221002 |

**CAS-SCF STATES FOR BLOCK 1 MULT= 4 NROOTS= 1**

ROOT 0: E= \(-4317.7737236787 \text{ Eh}\)

| Contribution | Energy (Eh) |
|--------------|-------------|
| 0.21166 : 2221221100 | 0.00774 : 2212121110 |
| 0.14080 : 2211221110 | 0.00722 : 2211220120 |
| 0.13666 : 2221122100 | 0.00685 : 2201222110 |
| 0.09678 : 2211122110 | 0.00546 : 2212201102 |
| 0.04538 : 2201221120 | 0.00455 : 2102221120 |
| 0.03408 : 2201122120 | 0.00516 : 2211121120 |
| 0.02905 : 2211122100 | 0.00436 : 2221221100 |
| 0.01848 : 1221222100 | 0.00427 : 2211221110 |
| 0.01796 : 2121222100 | 0.00389 : 2122122100 |
| 0.01552 : 2221212100 | 0.00367 : 2211201112 |
| 0.01515 : 2122221100 | 0.00356 : 2212212100 |
| 0.01216 : 1211222110 | 0.00350 : 2221102102 |
| 0.01200 : 2222121100 | 0.00346 : 2212201110 |
| 0.01180 : 2101222120 | 0.00327 : 2201221120 |
| 0.01121 : 1201222120 | 0.00297 : 2211220102 |
| 0.01042 : 2111222110 | 0.00293 : 2212211110 |
| 0.01000 : 2211212110 | 0.00282 : 1212122110 |
| 0.00858 : 2112221110 | 0.00250 : 2211102112 |
Figure S6. Active space orbitals and occupations (in grey and parenthesis) obtained from a NEVPT2-CASSCF(13,10) calculation on [CoIII(TPP)(•∗NNs)] at the doublet spin surface. The cyan orbital was found in the inactive space and an isosurface of 80 was used.
[Co(III)(TPP)·(‘NNs)2] 
NEVPT2-CASSCF(15,13) calculations indicated that the doublet state is 1.4 kcal mol\(^{-1}\) above the quartet state. The states and contributions and a schematic overview of the active spaces in the quartet (Figure S7) and doublet (Figure S6) state are included below.

**CAS-SCF STATES FOR BLOCK 1 MULT= 4 NROOTS= 1**

ROOT 0:  E= -5353.1935004295 Eh

| State | Coefficient | State | Coefficient |
|-------|-------------|-------|-------------|
| 0.89202 : 2222221110000 | 0.00466 : 2121222110010 |
| 0.01087 : 2222211101100 | 0.00389 : 2202221110002 |
| 0.00999 : 2211221110011 | 0.00377 : 2222201110200 |
| 0.00725 : 2220221110020 | 0.00335 : 2222201112000 |
| 0.00581 : 2221221110010 | 0.00318 : 2212221110001 |
| 0.00509 : 0222221110002 | 0.00266 : 1222121210010 |
| 0.00508 : 2022221110002 | 0.00262 : 2122122110010 |
| 0.00470 : 1221222120010 | |

**CAS-SCF STATES FOR BLOCK 1 MULT= 2 NROOTS= 1**

ROOT 0:  E= -5353.1931568370 Eh

| State | Coefficient | State | Coefficient |
|-------|-------------|-------|-------------|
| 0.73707 : 2222221110000 | 0.00476 : 1221222110010 |
| 0.05274 : 2222222210000 | 0.00475 : 2121222110010 |
| 0.04512 : 2222220120000 | 0.00423 : 0222221110002 |
| 0.02155 : 2222222120000 | 0.00418 : 2022221110002 |
| 0.01819 : 2222222102000 | 0.00389 : 2221222110010 |
| 0.01036 : 2222222010000 | 0.00323 : 2202221110002 |
| 0.00939 : 2222222021000 | 0.00312 : 2222201110200 |
| 0.00888 : 2222222110110 | 0.00273 : 2222201112000 |
| 0.00831 : 2211221110011 | 0.00273 : 2212221110001 |
| 0.00596 : 2220221110020 | |
Figure S7. Active space orbitals and occupations (in grey and parenthesis) obtained from a NEVPT2-CASSCF(15,13) calculation on $[\text{Co}^\text{III}(\text{TPP}^\text{*-}(\text{NNs})_2)]$ at the quartet spin surface. The cyan orbital was found in the inactive space and an isosurface of 60 was used.
Figure S8. Active space orbitals and occupations (in grey and parenthesis) obtained from a NEVPT2-CASSCF(15,13) calculation on \([\text{Co}^{III}\text{TPP}')(\text{NNS})_2\] at the doublet spin surface. The cyan orbital was found in the inactive space and an isosurface of 60 was used.
### XYZ coordinates

Co(TPP)-carbene radical (doublet):

\[[\text{Co}^{11}(\text{TPP})(\cdot\text{CHCO}_2\text{Et})]\]

89 atoms

| Atom | X    | Y    | Z    |
|------|------|------|------|
| C    | 0.5096571 | 4.4899237 | 1.2578637 |
| H    | 0.5343973 | 4.6397237 | 0.8327637 |
| C    | 1.3209550 | 4.6795237 | 0.1265637 |
| H    | 1.3516537 | 4.9393237 | 0.4106637 |
| C    | 3.6902571 | 4.7491237 | 0.0045637 |
| H    | 3.7209537 | 4.8992237 | 0.6875637 |
| C    | 5.1207571 | 5.0793237 | 0.8716637 |
| H    | 5.1518537 | 5.3394237 | 0.4507637 |
| C    | 6.6001571 | 5.6892237 | 1.2438637 |
| H    | 6.6308537 | 5.9491237 | 0.8269637 |

### Co(TPP)-carbene radical (quartet):

\[[\text{Co}^{11}(\text{TPP})(\cdot\text{CHCO}_2\text{Et})]\]

89 atoms

| Atom | X    | Y    | Z    |
|------|------|------|------|
| C    | 0.5196571 | 4.4899237 | 1.2578637 |
| H    | 0.5343973 | 4.6397237 | 0.8327637 |
| C    | 1.3209550 | 4.6795237 | 0.1265637 |
| H    | 1.3516537 | 4.9393237 | 0.4106637 |
| C    | 3.6902571 | 4.7491237 | 0.0045637 |
| H    | 3.7209537 | 4.8992237 | 0.6875637 |
| C    | 5.1207571 | 5.0793237 | 0.8716637 |
| H    | 5.1518537 | 5.3394237 | 0.4507637 |
| C    | 6.6001571 | 5.6892237 | 1.2438637 |
| H    | 6.6308537 | 5.9491237 | 0.8269637 |
Co(TPP)-mono-nitrene radical (doublet): [Co^{III}(TPP)(**NNs)]

94 atoms

C -2.7512916 1.0569577 -0.1246949
N -1.8905647 0.0128235 -0.4037417
H -4.9684802 1.3180077 -0.2881802
C -2.6930697 -1.0413375 -0.8068251
C -4.0651324 -0.6100759 -0.8784507
H -4.8884056 -1.2267631 -1.2217905
C -4.1079898 0.6670092 -0.4016592
C -2.2770039 -2.3643887 -0.9275522
N 0.0444785 -1.9388112 -0.1796210
C 1.0387854 -2.7661178 0.3290960
C 0.5936973 -4.1331184 0.3004785
H 1.1630263 -4.9783300 0.6705770
C -0.6454176 -4.1411557 -0.2741247
Co(TPP)-mononitrene radical (quartet):
[Co(III)(TPP)(**NNs)]
94 atoms
C -2.7384527 1.0693612 -0.0796388
N -1.8719402 0.0141586 -0.2864111
H -4.9635194 1.2824933 -0.2032139
C -2.6641714 -1.0814292 -0.5740960
C -4.0464619 -0.6800637 -0.6315742
H -4.8694126 -1.3354901 -0.8942726
C -4.0955119 0.6363842 -0.2803510
C -2.2233361 -2.4001199 -0.6812098
N 0.1264653 -1.9152151 -0.0670446
C 1.1672569 -2.7159213 0.3726109
C 0.7773961 -4.0998856 0.3096029
C 1.3951056 -4.9363888 0.6236022
C -0.4886599 -4.1371652 -0.1998638
H -1.1111380 -5.0054372 -0.3884133
C -0.9068210 -2.7725805 -0.3921527
C -2.3745864 2.3978330 0.1454537
H 1.2983623 5.0720742 -0.7004811
C 0.6624429 4.2188251 -0.4911086
H 3.4131220
H 4.9673735
H 5.8392236
H 5.1772160
C 3.3961650
C 3.8089925
C 4.6851305
C 5.1690855
N 2.0399923
O 2.8499016
H 0.0938299
H 0.7547818
C 1.3788197
C 2.8473749
C 2.4463052
Co 0.0388988
N -0.2453620
S -1.2006197
O -2.5131831
O -1.1599424
C -0.3347849
C 1.1778882
C 0.6190882
C 0.6510860
C 0.2156278
C 1.3788197
H 0.7547818
H -1.2969161
H 0.0938299
H 2.1350192
O 2.8499016
O 1.9130365
N 2.0399923
C 4.7888378
C 5.1690855
C 4.6851305
C 3.8089925
C 3.3961650
C 3.9105309
H 5.1772160
H 5.8392236
H 4.9673735
H 3.4112220
H 3.6237081
C -4.9090457
C -5.4819985
C -5.0414583
C -4.0303966
C -3.3430691
H -5.2577191
H -6.2735092
H -5.4845149
H -3.6802522
H -3.4575089
C -4.0766519
C -5.0508229
C -5.1050165
C -4.1915241
C -3.2125457
C -3.1610908
H -4.0300537
H -5.7649850
H -5.8578779
H -4.2234020
H -2.3982272
C 5.2324565
C 5.5240868
C 4.8098287
C 3.8063390
C 3.5021814
C 4.2299242
H 5.7859589
H 6.3086844
H 5.0389091
C 3.2556252
H 4.0008678
Co(TPP)-bis-nitrene radical (doublet):
[Co(III)(TPP)("NNs")2]
111 atoms
C 1.0397732
H 0.0096090
H 1.3601335
C -0.9717425
C -0.5108962
H -1.0589354
H 0.7087059
C -2.2663302
N -1.9315931
H -2.7616962
H -4.9927287
C -4.1090773
H -4.9469236
C -2.7226665
H 4.9678650
C 4.1280268
C 2.7570992
H 4.9696953
H 1.9605634
C 2.7668595
H 4.1253013

S18
Co(TPP)-bis-nitrene radical (quartet):

\[
[\text{Co}^{III}(\text{TPP})(\text{"NNs"})_2]
\]

111 atoms

C 0.10655827 2.7018251 -0.4347070
N 0.0353595 1.9180132 -0.0093987
H 1.4016765 4.9231383 -0.4155438
C -0.9413931 2.7505724 0.4863489
H -0.4709316 4.1134662 0.4361058
H -1.0118338 4.9758156 0.8095894
C 0.7458801 4.0887780 -0.1898177
C -2.2426430 2.3271339 0.7916334
N -1.9205846 0.0038188 0.0185642
C -2.7566252 -0.996062 0.4200148
C -4.1214861 -0.5346128 -0.3514170
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