Multi-reference perturbation theory with Cholesky decomposition for the density matrix renormalization group. Supporting Information

Leon Freitag,\textsuperscript{1} Stefan Knecht,\textsuperscript{1} Celestino Angeli,\textsuperscript{2} and Markus Reiher\textsuperscript{1}

\textsuperscript{1)} ETH Zürich, Laboratorium für Physikalische Chemie, Vladimir-Prelog-Weg 2, 8093 Zürich, Switzerland

\textsuperscript{2)} Dipartimento di Scienze Chimiche e Farmaceutiche, Università di Ferrara, Via Fossato di Mortara 17, 44121 Ferrara, Italy
I. ACTIVE SPACE SELECTION

A. model 2 complex

Fig. S1 shows the active space chosen for all DMRG-NEVPT2 calculations of the model 2 complex. It comprises 14 electrons in 18 orbitals (denoted (14,18)), including four $\pi, \pi^*$ pairs on the ligands (denoted $\pi_1$ to $\pi_4$ and $\pi^*_1$ to $\pi^*_4$), five metal 3$d$ orbitals and five second 3$d$ shells (denoted 3$d'$) to account for the double-shell effect. A hybrid procedure including manual orbital inspection and selection on top of our automated active space selection protocol\textsuperscript{1} was applied for the choice of this active space: first, a DMRG[256](52,72)#CAS(6,10)-SCF calculation on the quintet state was performed (i.e. a DMRG-CI (52,72) calculation with $m = 256$ employing orbitals from a CAS(6,10)-SCF calculation following the nomenclature of Ref. 1. The CAS(6,10) comprised five metal 3$d$ orbitals and five second 3$d$ shells in the active space). Then, the automatic selection protocol was followed (with an orbital selection threshold of 45% of the largest single-orbital entropy $s(1)$ value\textsuperscript{2,3}), however, out of the automatically selected orbitals, only the ligand antibonding $\pi^*$ and the corresponding bonding $\pi$ pairs have been included, resulting in the $\pi_1$ to $\pi_4$ and $\pi^*_1$ to $\pi^*_4$ orbitals. The $\pi, \pi^*$ space has then been augmented manually by the metal 3$d$ orbitals and second 3$d$ shells to form the final active space. This step was necessary, as the majority of the $d$ orbitals, which would be needed to ensure the universality of the active space across all spin states, was not selected by the automated selection scheme applied to only a single spin state. Whereas our automated selection was based on an initial calculation for the quintet state only, the union of automatically selected orbitals for all spin states (as proposed in Ref. 1) would in fact result in an active space similar to the one selected here semi-automatically.

B. Cobalt tropocoronand complex

The active space chosen in calculations of [Co(TC-3,3)(NO)] is shown in Fig. S2. For the selection of the active space for [Co(TC-3,3)(NO)], a similar procedure as for the model 2 complex has been applied. Here, an automatic active space selection based on a DMRG[256](72,73)#CAS(14,15)-SCF calculation has been performed. The CAS(14,15)-SCF calculation to obtain the orbitals for the DMRG calculation employed an active space consisting of all metal 3$d$ and 3$d$ double shells, $\pi$ and $\pi^*$ orbitals at the NO ligand (denoted...
FIG. S1. Active orbitals employed in NEVPT2 calculations on the model 2 complex. πNO,xy and π*NO,xy), and a σ orbital (denoted σ3d2−y2) that forms a bonding-antibonding pair with the 3d2−y2 orbital, which is unoccupied in the S0 state.

To obtain the final active space, orbitals selected by the automatic selection protocol (with the orbital selection threshold of 20% of the largest s(1) value) was augmented by two tropocoronand π orbitals (complementary to the automatically selected π* orbitals) and missing metal d orbitals and 3d double shells (except for the 3d′2−y2 double shell, which showed a very low s(1) value).

FIG. S2. Active orbitals employed in NEVPT2 calculations on the [Co(TC-3,3)(NO)] complex.
II. TOTAL ELECTRONIC ENERGIES

| m = | 256 | 256* | 512/256 | 512 | 1024/256 |
|-----|-----|------|---------|-----|----------|
| $^5B_2$ | -1798.8364810 | -1798.8377488 | -1798.8376805 | -1798.8377222 | -1798.8350333† |
| $^3B_1$ | -1798.7908735 | -1798.7916375 | -1798.7925375 | -1798.7926149 | -1798.7932572 |
| $^1A_1$ | -1798.7536059 | -1798.7540196 | -1798.7544676 | -1798.7545234 | -1798.7549104 |

| $E^{(2)}(\text{DMRG-SCF})$ |
|-----|-----|------|---------|-----|----------|
| $^5B_2$ | -2.0307857 | -2.0299275 | -2.0294942 | -2.0297914 | -2.0301050 |
| $^3B_1$ | -2.0709475 | -2.0706072 | -2.0696884 | -2.0706980 | -2.0688351 |
| $^1A_1$ | -2.0609477 | -2.0610487 | -2.0589038 | -2.0607306 | -2.0595568 |

| $E^{(2)}(\text{DMRG-PC-NEVPT2})$ |
|-----|-----|------|---------|-----|----------|
| $^5B_2$ | -1.9848277 | -2.0384444 | -2.0364167 | -2.0392190 | -2.0379941 |
| $^3B_1$ | -2.0848322 | -2.0742684 | -2.0750951 | -2.0864447 | -2.0789603 |
| $^1A_1$ | -2.0625296 | -2.0767750 | -2.0690109 | -2.0767671 | -2.0688045 |

| $E(\text{DMRG-SC-NEVPT2})$ |
|-----|-----|------|---------|-----|----------|
| $^5B_2$ | -1800.8672667 | -1800.8676763 | -1800.8671747 | -1800.8675136 | -1800.8651383 |
| $^3B_1$ | -1800.8618210 | -1800.8622447 | -1800.8622259 | -1800.8633129 | -1800.8620923 |
| $^1A_1$ | -1800.8145536 | -1800.8150683 | -1800.8133714 | -1800.8152540 | -1800.8144672 |

| $E(\text{DMRG-PC-NEVPT2})$ |
|-----|-----|------|---------|-----|----------|
| $^5B_2$ | -1800.8213087 | -1800.8761932 | -1800.8740972 | -1800.8769412 | -1800.8730274 |
| $^3B_1$ | -1800.8757057 | -1800.8659059 | -1800.8676326 | -1800.8790596 | -1800.8722175 |
| $^1A_1$ | -1800.8161355 | -1800.8307946 | -1800.8234785 | -1800.8312905 | -1800.8237149 |

TABLE S1. Total DMRG-SCF energies, second-order and total DMRG-SC- and DMRG-PC-NEVPT2 energies for different spin states of the model 2 complex. All energies are given in atomic units, $m$ values as in Table I in the main paper.

In Table S1, the $^5B_2$ DMRG-SCF calculation with $m = 1024/256$ (marked with †) has obviously converged to a local minimum, which can be seen by comparison with energies obtained for smaller $m$ values. Such local energy minima may be encountered in DMRG calculations. Although they can be easily identified in sequences of calculations with different
$m$ values (which is always recommended), it is instructive to see whether such a technical problem affects the results. A converged calculation to the global energy minimum yields a lower energy ($-1798.8379677$ a.u.) but with an almost unchanged wavefunction character. The updated energy affects the relative energies by less than 2 kcal/mol. The relative energy is then within the range of the relative energies calculated for the other $m$ values (cf. Table S10) and we may therefore use the data of Table S1 nevertheless.
| Subspace   | Norm   | $E^{(2)}$ | Norm   | $E^{(2)}$ |
|-----------|--------|-----------|--------|-----------|
| $S_{ij,rs}^{(0)}$ | 0.3293218 | -1.1739631 | 0.3293218 | -1.1739631 |
| $S_{ij,r}^{(1)}$ | 0.0401616 | -0.1262028 | 0.0410868 | -0.1271620 |
| $S_{i,rs}^{(-1)}$ | 0.0720154 | -0.2513413 | 0.0724018 | -0.2517831 |
| $S_{ij}^{(2)}$ | 0.0056022 | -0.0357536 | 0.0059506 | -0.0363345 |
| $S_{rs}^{(-2)}$ | 0.0112799 | -0.0687635 | 0.5797108 | -0.0686839 |
| $S_{r}^{(1)}$ | 0.0039178 | -0.0111948 | 1.2997158 | -0.0131676 |
| $S_{i}^{(-1)}$ | 0.0034023 | -0.0081060 | 2.6089592 | -0.0081606 |
| $S_{ir}^{(0)}$ | 0.1127807 | -0.3554606 | 2236.3891266 | -0.3055729 |
| Total     | 0.5784819 | -2.0307857 | 2241.3262733 | -1.9848277 |

| Subspace   | Norm   | $E^{(2)}$ | Norm   | $E^{(2)}$ |
|-----------|--------|-----------|--------|-----------|
| $S_{ij,rs}^{(0)}$ | 0.3183162 | -1.1537009 | 0.3183163 | -1.1537009 |
| $S_{ij,r}^{(1)}$ | 0.0491226 | -0.1564161 | 0.0495811 | -0.1569030 |
| $S_{i,rs}^{(-1)}$ | 0.0654963 | -0.2422451 | 0.0658438 | -0.2426740 |
| $S_{ij}^{(2)}$ | 0.0076253 | -0.0411874 | 0.0080301 | -0.0417565 |
| $S_{rs}^{(-2)}$ | 0.0106498 | -0.0667619 | 84.1458946 | -0.0665044 |
| $S_{r}^{(1)}$ | 0.0126154 | -0.0315615 | 40.4819961 | -0.0325019 |
| $S_{i}^{(-1)}$ | 0.0044928 | -0.0124710 | 103.1565048 | -0.0230385 |
| $S_{ir}^{(0)}$ | 0.1184189 | -0.3666033 | 105.2903846 | -0.3677529 |
| Total     | 0.5867375 | -2.0709475 | 333.5165516 | -2.0848323 |

| Subspace   | Norm   | $E^{(2)}$ | Norm   | $E^{(2)}$ |
|-----------|--------|-----------|--------|-----------|
| $S_{ij,rs}^{(0)}$ | 0.3169646 | -1.1537009 | 0.3169646 | -1.1537009 |
| $S_{ij,r}^{(1)}$ | 0.0491226 | -0.1564161 | 0.0495811 | -0.1569030 |
| $S_{i,rs}^{(-1)}$ | 0.0654963 | -0.2422451 | 0.0658438 | -0.2426740 |
| $S_{ij}^{(2)}$ | 0.0070339 | -0.0378249 | 0.0074737 | -0.0383948 |
| $S_{rs}^{(-2)}$ | 0.0104053 | -0.0649808 | 3.3133069 | -0.0648920 |
| $S_{r}^{(1)}$ | 0.0126094 | -0.0328828 | 9.8001506 | -0.0333567 |
| $S_{i}^{(-1)}$ | 0.0044928 | -0.0124710 | 103.1565048 | -0.0230385 |
| $S_{ir}^{(0)}$ | 0.1184189 | -0.3666033 | 105.2903846 | -0.3677529 |
| Total     | 0.5810788 | -2.0609477 | 103.5301328 | -2.0625296 |

**TABLE S2.** SC-NEVPT2 and PC-NEVPT2 second-order energy and wavefunction norm contributions for different subspaces for different states of the *model 2* complex and $m = 256$. 

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| Subspace | SC-NEVPT2 | PC-NEVPT2 |
|----------|-----------|-----------|
| $S_{ij,rs}^{(0)}$ | 0.3293193 $-1.1739620$ | 0.3293193 $-1.1739619$ |
| $S_{ij,r}^{(1)}$ | 0.0401411 $-0.1261679$ | 0.0410711 $-0.1271317$ |
| $S_{i,rs}^{(-1)}$ | 0.0720393 $-0.2513845$ | 0.0724375 $-0.2518368$ |
| $S_{ij}^{(2)}$ | 0.0055848 $-0.0357057$ | 0.0059371 $-0.0362948$ |
| $S_{rs}^{(-2)}$ | 0.0112477 $-0.0686379$ | 4.0394374 $-0.0686144$ |
| $S_{i}^{(1)}$ | 0.0033585 $-0.0080282$ | 82.1267253 $-0.0090190$ |
| $S_{ir}^{(0)}$ | 0.1123266 $-0.3544636$ | 0.6513872 $-0.3590780$ |
| **Total** | 0.5779125 $-2.0294941$ | 97.9303697 $-2.0364166$ |

| Subspace | SC-NEVPT2 | PC-NEVPT2 |
|----------|-----------|-----------|
| $S_{ij,rs}^{(0)}$ | 0.3183134 $-1.1536993$ | 0.3183134 $-1.1536993$ |
| $S_{ij,r}^{(1)}$ | 0.0490935 $-0.1563718$ | 0.0495568 $-0.1568626$ |
| $S_{i,rs}^{(-1)}$ | 0.0655089 $-0.2422625$ | 0.0658592 $-0.2426930$ |
| $S_{ij}^{(2)}$ | 0.0076049 $-0.0411358$ | 0.0080137 $-0.0417129$ |
| $S_{rs}^{(-2)}$ | 0.0106193 $-0.0666396$ | 30.9311443 $-0.0658060$ |
| $S_{i}^{(1)}$ | 0.0045070 $-0.0125205$ | 5.3055109 $-0.0132887$ |
| $S_{ir}^{(0)}$ | 0.1179341 $-0.3655823$ | 0.6513872 $-0.3590780$ |
| **Total** | 0.5861881 $-2.0696884$ | 40.4184460 $-2.0759051$ |

| Subspace | SC-NEVPT2 | PC-NEVPT2 |
|----------|-----------|-----------|
| $S_{ij,rs}^{(0)}$ | 0.3169670 $-1.1536993$ | 0.3183134 $-1.1536993$ |
| $S_{ij,r}^{(1)}$ | 0.0490935 $-0.1563718$ | 0.0495568 $-0.1568626$ |
| $S_{i,rs}^{(-1)}$ | 0.0655089 $-0.2422625$ | 0.0658592 $-0.2426930$ |
| $S_{ij}^{(2)}$ | 0.0076049 $-0.0411358$ | 0.0080137 $-0.0417129$ |
| $S_{rs}^{(-2)}$ | 0.0106193 $-0.0666396$ | 30.9311443 $-0.0658060$ |
| $S_{i}^{(1)}$ | 0.0045070 $-0.0125205$ | 5.3055109 $-0.0132887$ |
| $S_{ir}^{(0)}$ | 0.1179341 $-0.3655823$ | 0.6513872 $-0.3590780$ |
| **Total** | 0.5799071 $-2.0589038$ | 77.4348753 $-2.0690109$ |

**TABLE S3.** SC-NEVPT2 and PC-NEVPT2 second-order energy and wavefunction norm contributions for different subspaces for different states of the model 2 complex and $m = 512/256$. 

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| Subspace | Norm       | \( E^{(2)} \)       | Subspace | Norm       | \( E^{(2)} \)       |
|----------|------------|----------------------|----------|------------|----------------------|
| \( S_{ij,rs}^{(0)} \) | 0.3290531  | -1.1733131           | \( S_{ij,rs}^{(0)} \) | 0.3290531  | -1.1733131           |
| \( S_{ij,r}^{(1)} \)  | 0.0403278  | -0.1266237           | \( S_{ij,r}^{(1)} \)  | 0.0412574  | -0.1275866           |
| \( S_{i,rs}^{(-1)} \) | 0.0721801  | -0.2519222           | \( S_{i,rs}^{(-1)} \) | 0.0725780  | -0.2523743           |
| \( S_{ij}^{(2)} \)  | 0.0056091  | -0.0357385           | \( S_{ij}^{(2)} \)  | 0.0059627  | -0.0363276           |
| \( S_{rs}^{(-2)} \)  | 0.0112406  | -0.0685992           | \( S_{rs}^{(-2)} \)  | 0.7116953  | -0.0688216           |
| \( S_{r}^{(1)} \)  | 0.0039374  | -0.0112067           | \( S_{r}^{(1)} \)  | 4.9125226  | -0.0132899           |
| \( S_{i}^{(-1)} \)  | 0.0033766  | -0.0080730           | \( S_{i}^{(-1)} \)  | 0.2408658  | -0.0087268           |
| \( S_{ir}^{(0)} \)  | 0.1123895  | -0.3543147           | \( S_{ir}^{(0)} \)  | 0.3094515  | -0.3587786           |
| Total     | 0.5781146  | -2.0297913           | Total     | 6.6233868  | -2.0392190           |

| Subspace | Norm       | \( E^{(2)} \)       | Subspace | Norm       | \( E^{(2)} \)       |
|----------|------------|----------------------|----------|------------|----------------------|
| \( S_{ij,rs}^{(0)} \) | 0.3178720  | -1.1526303           | \( S_{ij,rs}^{(0)} \) | 0.3178720  | -1.1526303           |
| \( S_{ij,r}^{(1)} \)  | 0.0494581  | -0.1572331           | \( S_{ij,r}^{(1)} \)  | 0.0499522  | -0.1577521           |
| \( S_{i,rs}^{(-1)} \) | 0.0659436  | -0.2437106           | \( S_{i,rs}^{(-1)} \) | 0.0662971  | -0.2441442           |
| \( S_{ij}^{(2)} \)  | 0.0076270  | -0.0411352           | \( S_{ij}^{(2)} \)  | 0.0080437  | -0.0417178           |
| \( S_{rs}^{(-2)} \)  | 0.0106261  | -0.0666525           | \( S_{rs}^{(-2)} \)  | 0.5917067  | -0.0661180           |
| \( S_{r}^{(1)} \)  | 0.0128266  | -0.0317264           | \( S_{r}^{(1)} \)  | 2.9430455  | -0.0425360           |
| \( S_{i}^{(-1)} \)  | 0.0045825  | -0.0126381           | \( S_{i}^{(-1)} \)  | 2.5851840  | -0.0133925           |
| \( S_{ir}^{(0)} \)  | 0.1180280  | -0.3649714           | \( S_{ir}^{(0)} \)  | 5.5302705  | -0.3681533           |
| Total     | 0.5869641  | -2.0706980           | Total     | 70.6713389 | -2.0864447           |

| Subspace | Norm       | \( E^{(2)} \)       | Subspace | Norm       | \( E^{(2)} \)       |
|----------|------------|----------------------|----------|------------|----------------------|
| \( S_{ij,rs}^{(0)} \) | 0.3167297  | -1.1514436           | \( S_{ij,rs}^{(0)} \) | 0.3167297  | -1.1514436           |
| \( S_{ij,r}^{(1)} \)  | 0.0496329  | -0.1627940           | \( S_{ij,r}^{(1)} \)  | 0.0503001  | -0.1634516           |
| \( S_{i,rs}^{(-1)} \) | 0.0677070  | -0.2438879           | \( S_{i,rs}^{(-1)} \) | 0.0680731  | -0.2443238           |
| \( S_{ij}^{(2)} \)  | 0.0070396  | -0.0378093           | \( S_{ij}^{(2)} \)  | 0.0074849  | -0.0383872           |
| \( S_{rs}^{(-2)} \)  | 0.0103825  | -0.0648606           | \( S_{rs}^{(-2)} \)  | 0.7714193  | -0.0650726           |
| \( S_{r}^{(1)} \)  | 0.0126486  | -0.0329094           | \( S_{r}^{(1)} \)  | 8.4329418  | -0.0424835           |
| \( S_{i}^{(-1)} \)  | 0.0036894  | -0.0096460           | \( S_{i}^{(-1)} \)  | 1.0886353  | -0.0100728           |
| \( S_{ir}^{(0)} \)  | 0.1132643  | -0.3573795           | \( S_{ir}^{(0)} \)  | 0.3432427  | -0.3615315           |
| Total     | 0.5810943  | -2.0607306           | Total     | 11.078827  | -2.0767671           |

TABLE S4. SC-NEVPT2 and PC-NEVPT2 second-order energy and wavefunction norm contributions for different subspaces for different states of the \textit{model 2} complex and \( m = 512 \).
| Subspace     | Norm   | $E^{(2)}$ | Norm   | $E^{(2)}$ |
|--------------|--------|-----------|--------|-----------|
| $S_{ij,rs}^{(0)}$ | 0.3293211 | -1.1739649 | 0.3293211 | -1.1739649 |
| $S_{ij,r}^{(1)}$ | 0.0401066 | -0.1260585 | 0.0410304 | -0.1270200 |
| $S_{i,rs}^{(-1)}$ | 0.0720831 | -0.2515013 | 0.0724903 | -0.2519629 |
| $S_{ij}^{(2)}$ | 0.0055833 | -0.0357087 | 0.0059398 | -0.0363021 |
| $S_{rs}^{(-2)}$ | 0.0112365 | -0.0686763 | 1.0875165 | -0.0680493 |
| $S_{r}^{(1)}$ | 0.0039109 | -0.0112164 | 3.7719218 | -0.0128183 |
| $S_{i}^{(-1)}$ | 0.0034355 | -0.0081887 | 16.0105261 | -0.0076398 |
| $S_{ir}^{(0)}$ | 0.1121612 | -0.3547897 | 109.0611467 | -0.3602363 |
| **Total**     | 0.5778385 | -2.0301050 | 130.3798930 | -2.0379941 |

| Subspace     | Norm   | $E^{(2)}$ | Norm   | $E^{(2)}$ |
|--------------|--------|-----------|--------|-----------|
| $S_{ij,rs}^{(0)}$ | 0.3183117 | -1.1536975 | 0.3183117 | -1.1536975 |
| $S_{ij,r}^{(1)}$ | 0.0490810 | -0.1563507 | 0.0495464 | -0.1568432 |
| $S_{i,rs}^{(-1)}$ | 0.0655229 | -0.2422954 | 0.0658772 | -0.2427298 |
| $S_{ij}^{(2)}$ | 0.0075925 | -0.0411138 | 0.0080046 | -0.0416961 |
| $S_{rs}^{(-2)}$ | 0.0105970 | -0.0665538 | 19.8373918 | -0.0666023 |
| $S_{r}^{(1)}$ | 0.0125837 | -0.0314174 | 0.3276199 | -0.0358228 |
| $S_{i}^{(-1)}$ | 0.0044904 | -0.0124936 | 1.0568323 | -0.0130733 |
| $S_{ir}^{(0)}$ | 0.1176043 | -0.3649126 | 0.6699823 | -0.3684951 |
| **Total**     | 0.5857840 | -2.0688351 | 22.3355665 | -2.0789603 |

| Subspace     | Norm   | $E^{(2)}$ | Norm   | $E^{(2)}$ |
|--------------|--------|-----------|--------|-----------|
| $S_{ij,rs}^{(0)}$ | 0.3169591 | -1.1536975 | 0.3169591 | -1.1536975 |
| $S_{ij,r}^{(1)}$ | 0.0494525 | -0.1563507 | 0.0495464 | -0.1568432 |
| $S_{i,rs}^{(-1)}$ | 0.0655229 | -0.2422954 | 0.0658772 | -0.2427298 |
| $S_{ij}^{(2)}$ | 0.0075925 | -0.0411138 | 0.0080046 | -0.0416961 |
| $S_{rs}^{(-2)}$ | 0.0105970 | -0.0665538 | 19.8373918 | -0.0666023 |
| $S_{r}^{(1)}$ | 0.0125837 | -0.0314174 | 0.3276199 | -0.0358228 |
| $S_{i}^{(-1)}$ | 0.0044904 | -0.0124936 | 1.0568323 | -0.0130733 |
| $S_{ir}^{(0)}$ | 0.1176043 | -0.3649126 | 0.6699823 | -0.3684951 |
| **Total**     | 0.5804649 | -2.0595567 | 5.3217011 | -2.0688044 |

TABLE S5. SC-NEVPT2 and PC-NEVPT2 second-order energy and wavefunction norm contributions for different subspaces for different states of the model 2 complex and $m = 1024/256$. 

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| Subspace | SC-NEVPT2 | PC-NEVPT2 |
|----------|-----------|-----------|
|          | \(E^{(2)}\) | \(E^{(2)}\) | \(E^{(2)}\) |
| \(S_{ij,rs}^{(0)}\) | 0.3289171 | -1.1729852 | 0.3289171 | -1.1729852 |
| \(S_{ij,r}^{(1)}\) | 0.0404076 | -0.1268236 | 0.0413400 | -0.1277890 |
| \(S_{i,rs}^{(-1)}\) | 0.0722829 | -0.2522683 | 0.0726862 | -0.2527251 |
| \(S_{ij}^{(2)}\) | 0.0056101 | -0.0357277 | 0.0059666 | -0.0363210 |
| \(S_{rs}^{(-2)}\) | 0.0112180 | -0.0685057 | 0.4614608 | -0.0688481 |
| \(S_r^{(1)}\) | not calculated | | |
| \(S_i^{(-1)}\) | not calculated | | |
| \(S_{ir}^{(0)}\) | 0.1121672 | -0.3537278 | 0.1547293 | -0.3575313 |
| Total | 0.5706032 | -2.0100385 | 1.0651002 | -2.0161999 |

| Subspace | SC-NEVPT2 | PC-NEVPT2 |
|----------|-----------|-----------|
|          | \(E^{(2)}\) | \(E^{(2)}\) | \(E^{(2)}\) |
| \(S_{ij,rs}^{(0)}\) | 0.3177668 | -1.1523475 | 0.3177668 | -1.1523475 |
| \(S_{ij,r}^{(1)}\) | 0.0496139 | -0.1576105 | 0.0501254 | -0.1581455 |
| \(S_{i,rs}^{(-1)}\) | 0.0661103 | -0.2442617 | 0.0664696 | -0.2447010 |
| \(S_{ij}^{(2)}\) | 0.0076237 | -0.0411114 | 0.0080482 | -0.0417031 |
| \(S_{rs}^{(-2)}\) | 0.0106031 | -0.0665715 | 141.1278610 | -0.0679718 |
| \(S_r^{(1)}\) | not calculated | | |
| \(S_i^{(-1)}\) | not calculated | | |
| \(S_{ir}^{(0)}\) | 0.1176020 | -0.3638188 | 0.6566406 | -0.3676036 |
| Total | 0.5693200 | -2.0257216 | 142.2269119 | -2.0324728 |

| Subspace | SC-NEVPT2 | PC-NEVPT2 |
|----------|-----------|-----------|
|          | \(E^{(2)}\) | \(E^{(2)}\) | \(E^{(2)}\) |
| \(S_{ij,rs}^{(0)}\) | 0.3166043 | -1.1523475 | 0.3166043 | -1.1523475 |
| \(S_{ij,r}^{(1)}\) | 0.0497223 | -0.1629937 | 0.0501254 | -0.163539 |
| \(S_{i,rs}^{(-1)}\) | 0.0678123 | -0.2442594 | 0.0681852 | -0.2447010 |
| \(S_{ij}^{(2)}\) | 0.0070448 | -0.0378148 | 0.0074940 | -0.0383980 |
| \(S_{rs}^{(-2)}\) | 0.0103643 | -0.0647851 | 88.1547086576 | -0.0651350 |
| \(S_r^{(1)}\) | not calculated | | |
| \(S_i^{(-1)}\) | not calculated | | |
| \(S_{ir}^{(0)}\) | 0.1130664 | -0.3568330 | 0.3109732677 | -0.3606350 |
| Total | 0.5646147 | -2.0178227 | 88.9083570707 | -2.0236604 |

TABLE S6. SC-NEVPT2 and PC-NEVPT2 second-order energy and wavefunction norm contributions for different subspaces for different states of the model 2 complex and \(m = 1024\).
| Subspace | Norm       | $E^{(2)}$ | Norm       | $E^{(2)}$ |
|----------|------------|-----------|------------|-----------|
| $S^{(0)}_{ij,rs}$ | 0.3288796 -1.1728963 0.3288796 -1.1728963059 |
| $S^{(1)}_{ij,r}$ | 0.0404257 -0.1268731 0.0413592 -0.1278395158 |
| $S^{(-1)}_{i,rs}$ | 0.0723077 -0.2523495 0.0727131 -0.2528083557 |
| $S^{(2)}_{ij}$ | 0.0056112 -0.0357271 0.0059683 -0.0363210782 |
| $S^{(-2)}_{r,s}$ | 0.0112151 -0.0684905 0.0113574 -0.0688085801 |
| $S^{(1)}_{r}$ | not calculated |
| $S^{(-1)}_{i}$ | not calculated |
| $S^{(0)}_{ir}$ | 0.1121506 -0.3536544 4.4666267 -0.3570420272 |
| Total       | 0.5705901 -2.0099912 4.9269045 -2.0157158629 |

TABLE S7. SC-NEVPT2 and PC-NEVPT2 second-order energy and wavefunction norm contributions for different subspaces for the $^5B_2$ state of the model 2 complex and $m = 2048$. 
| State Subspace | Norm          | $E^{(2)}$          | Norm          | $E^{(2)}$          |
|----------------|---------------|--------------------|---------------|--------------------|
| $S_0$          | $S^{(0)}_{ij,rs}$ | 0.9743152          | $-3.6304303$  | 0.9717259          | $-3.6250446$  |
|                | $S^{(1)}_{ij,r}$    | 0.0777816          | $-0.2179033$  | 0.0798130          | $-0.2215522$  |
|                | $S^{(-1)}_{i,rs}$  | 0.1470363          | $-0.6203044$  | 0.1481631          | $-0.6239320$  |
|                | $S^{(2)}_{ij}$     | 0.0075573          | $-0.0350848$  | 0.0077774          | $-0.0352066$  |
|                | $S^{(-2)}_{rs}$    | 0.0321347          | $-0.2020609$  | 0.0320038          | $-0.2012503$  |
|                | $S^{(1)}_r$       | 0.0069411          | $-0.0170622$  | not calculated     |               |
|                | $S^{(-1)}_i$      | 0.0234750          | $-0.0674628$  | not calculated     |               |
|                | $S^{(0)}_{ir}$    | 0.1542058          | $-0.4910927$  | 0.1544336          | $-0.4886799$  |
|                | Total             | 1.4234474          | $-5.2814019$  | 1.3939172          | $-5.1956658$  |
| $T_1$          | $S^{(0)}_{ij,rs}$ | 0.9744262          | $-3.6289627$  | 0.9713940          | $-3.6228889$  |
|                | $S^{(1)}_{ij,r}$    | 0.0724975          | $-0.2058182$  | 0.0799472          | $-0.2215942$  |
|                | $S^{(-1)}_{i,rs}$  | 0.1538318          | $-0.6480003$  | 0.1508396          | $-0.6324435$  |
|                | $S^{(2)}_{ij}$     | 0.0068561          | $-0.0310305$  | 0.0076065          | $-0.0337000$  |
|                | $S^{(-2)}_{rs}$    | 0.0321348          | $-0.2005115$  | 0.0319742          | $-0.2003852$  |
|                | $S^{(1)}_r$       | 0.0045257          | $-0.0125989$  | not calculated     |               |
|                | $S^{(-1)}_i$      | 0.0276412          | $-0.0807808$  | not calculated     |               |
|                | $S^{(0)}_{ir}$    | 0.1521077          | $-0.4795454$  | 0.1529382          | $-0.4810407$  |
|                | Total             | 1.4240214          | $-5.2872486$  | 1.3947000          | $-5.1920527$  |
| $T_2$          | $S^{(0)}_{ij,rs}$ | 0.9743659          | $-3.6291600$  | 0.9714408          | $-3.6226794$  |
|                | $S^{(1)}_{ij,r}$    | 0.0779069          | $-0.2181739$  | 0.0744986          | $-0.2091815$  |
|                | $S^{(-1)}_{i,rs}$  | 0.1493291          | $-0.6277756$  | 0.1554087          | $-0.6526690$  |
|                | $S^{(2)}_{ij}$     | 0.0073364          | $-0.0334438$  | 0.0070875          | $-0.0312144$  |
|                | $S^{(-2)}_{rs}$    | 0.0320518          | $-0.2010696$  | 0.0319673          | $-0.1994050$  |
|                | $S^{(1)}_r$       | 0.0066468          | $-0.0168904$  | not calculated     |               |
|                | $S^{(-1)}_i$      | 0.0227349          | $-0.0622960$  | not calculated     |               |
|                | $S^{(0)}_{ir}$    | 0.1520539          | $-0.4823414$  | 0.1516288          | $-0.4752246$  |
|                | Total             | 1.4224260          | $-5.2711509$  | 1.3920319          | $-5.1903741$  |

TABLE S8. SC-NEVPT2 second-order energy and wavefunction norm contributions for different subspaces for different states of the CoTC complex.
|        |   1024  |  2048/256 |   2048  |
|--------|--------|-----------|--------|
| $^5B_2$ | -1798.8381299 | -1798.8376251 | -1798.8381980 |
| $^3B_1$ | -1798.7933446 | -1798.7935936 | -1798.7936877 |
| $^1A_1$ | -1798.7549461 | -1798.7549871 | -1798.7550157 |

TABLE S9. Total DMRG-SCF energies for different spin states of the *model 2* complex in atomic units for those $m$ values, for which full second-order energies have not been calculated.
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| $m$       | 256 | 256$^*$ | 512/256 | 512 | 1024/256 |
|-----------|-----|---------|---------|-----|----------|
| $^3B_1$   | 28.62 | 28.94  | 28.33  | 28.31 | 26.21 |
| $^1A_1$   | 52.00 | 52.54  | 52.22  | 52.21 | 50.28 |

TABLE S10. DMRG-SCF energies of the model 2 complex for different $m$ values relative to the $^5B_2$ state in kcal/mol.

Table S10 lists DMRG-SCF energies for the model 2 complex relative to the $^5B_2$ state. The deviation between energies for different $m$ values is less than 0.5 kcal/mol, with an exception of $m = 1024/256$ value, where both singlet and triplet relative energies are lower by approximately 2 kcal/mol. However, this can be explained by the fact that the $m = 1024/256$ calculation converged in a local minimum: its total electronic energy (see Table S1) is by 0.001447 a.u. higher than the energy obtained from a $m = 256$ calculation, although one would expect an energy lowering due to the variational principle. Interestingly enough, the relative CD-DMRG-SC-NEVPT2 energies (see Table I in the paper) do not show this outlier, although the variation of the SC-NEVPT2 energies with $m$ is slightly larger than for the DMRG-SCF energies.

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