Electronic Supplementary Material (ESI) for ChemComm.
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Supporting information for

Trapping of superoxido cobalt and peroxido dicobalt species formed reversibly from Co^{II} and O_2

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1. Experimental section

1.1. Materials

Reagents and solvents used were commercially available and purchased from Panreac, Scharlau and Aldrich. Preparation and handling of air-sensitive materials were carried out in a N_2 drybox (MBraun ULK 1000) with O_2 and H_2O concentrations < 1 ppm. Commercially available O_2 >99.5% pure from Praxair was purchased and used as received. Pytacn ligand was prepared as previously reported in the literature.[1] $[Co^{II}(Pytacn)(CH_3CN)_2](CF_3SO_3)_2$ (**1CF$_3$SO$_3$**) was prepared as previously reported.[2,3]

1.2. Instrumentation

Mass spectra were performed by electrospray ionization in a high-resolution mass spectrometer Bruker micrOTOF QII (Q-TOF) with a quadrupole analyzer with positive and negative ionization modes. ^{1}H NMR, ^{13}C NMR, COSY and HSQC spectra were performed in a Bruker Ultrashield Avance III400 and Ultrashield DPX300 spectrometers. UV-vis spectra were performed by a diode array spectrophotometer Agilent Cary 60 and low temperature control was maintained with a cryostat from Unisoku Scientific Instruments. GC analyses were carried out on an Agilent 7820A gas chromatograph (HP5 column, 30m) with a flame ionization detector. Raman spectra were recorded in 5 mm diameter NMR tubes at 77 K in a liquid nitrogen filled quartz Dewar. Spectra were collected in 180^o back-scattering mode with excitation at 532 and 355 nm (Cobolt Lasers, 50 mW) with a dichroic mirror (Semrock) at 45^o to the optical collection axis and a 25 mm diameter (75 mm focal length) planoconvex lens to focus the excitation beam and collect and collimate Raman scattering, which was passed through the dichroic and a long pass cut off filter (Semrock) before being focused at the entrance slits of a Shamrock 303i spectrograph with a 1200 l/mm grating blazed at 500 nm and a iDUS-420-BUEX2-DD CCD detector (Andor Technology). Spectral calibration was carried out using a 1:1 v/v mixture of acetonitrile and toluene. Spectra were processed using Andor Solis and Spectrum 10 (Perkin Elmer). The X-band EPR spectra were recorded on a Bruker EMX, equipped with the ER-4192 ST Bruker cavity and an ER-4131 VT at 9.445 GHz and 100 K with 100 kHz magnetic modulation, a microwave power of 6.981 mW, and an attenuation of 5 G. Elemental analyses of C, H, and N were performed on a PerkinElmer EA2400 series II elemental analyser. X-ray analyses were carried out on Bruker Smart Apex CCD diffractometer with graphite-monochromated MoKa radiation (λ=0.71073 Å) from an X-ray tube.

1.3. Synthesis of complexes

Synthesis of $[Co^{III}(Pytacn)(CH_3CN)_2](SbF_6)_3$ (1^+SbF_6). In the glovebox, a solution of $CoCl_2$ (10 mg, 0.077 mmol) in anhydrous CH_3CN (0.5 mL) was added dropwise to a vigorously stirred solution of Pytacn (20 mg, 0.080 mmol) in anhydrous CH_3CN (0.5 mL). After a few minutes, the solution turned purple. After stirring overnight, $AgSbF_6$ (55 mg, 0.16 mmols) was added and stirred for 2 hours. The formation of a white precipitate was immediately observed (corresponding to the formation of AgCl) and the solution turned red. Afterwards, the solution was filtered over Celite® to remove the solid AgCl and slow diethyl ether diffusion over the resulting solution afforded, in a few days, red crystals of $[Co^{II}(Pytacn)(CH_3CN)_2](SbF_6)_2$ (**1SbF$_6$**) (55 mg, 0.064 mmol, 81%). ESI-MS (m/z): 153.5699 $[Co^{II}(Pytacn)]^{2+}$, 162.5727 $[Co^{II}(Pytacn)(H_2O)]^{2+}$, 542.0295 $[Co^{II}(Pytacn)(SbF_6)]^+$. ^{1}H NMR ($CD_3CN$, 400 MHz, 298K) δ, ppm: 227.7, 185.5, 133.6, 129.4, 101.5, 86.2, 81.2, 61.9, 27.3.

$NOSbF_6$ (8 mg, 0.030 mmol) in anhydrous CH_3CN (0.5 mL) was added dropwise to a vigorously stirred solution of $[Co^{II}(Pytacn)(CH_3CN)_2](SbF_6)_2$ (**1SbF$_6$**) (20 mg, 0.023 mmol) in anhydrous CH_3CN (0.5 mL). After a few minutes, the solution turned orange. After stirring overnight, the solution was filtered over Celite® and slow diethyl ether diffusion over the resulting solution afforded, in a few days, orange crystals suitable for X-ray diffraction corresponding to **1^+SbF_6** (18 mg, 0.016 mmol, 72%). Anal. Calcd. for $CoC_{18}H_{30}N_6Sb_3F_{18}$: C, 19.74; N, 7.66; H, 2.76 %. Found: C, 19.99; N, 7.25; H, 2.48 %. ^{1}H NMR (CD_3CN, 400 MHz, 298K) δ, ppm: 8.72 (d, 1H, Py**H**$_\alpha$), 8.31 (t, 1H, Py**H**$_\gamma$), 7.86 (t, 1H, Py**H**$_\beta$), 7.81 (d, 1H, Py**H**$_{\beta'}$), 5.00 (d, 1H, C**H**$_2$Py), 4.49 (d, 1H, C**H**$_2$Py), 3.93 – 3.60 (m, 4H, NCH_2CH_2), 3.56 – 3.32 (m, 3H, NC**H**$_2$CH$_2$), 3.23 – 3.19 (m, 1H, NC**H**$_2$CH$_2$), 3.11 – 3.03 (m, 2H, NC**H**$_2$CH$_2$), 2.98 (s, 3H, NC**H**$_3$), 2.63 – 2.58 (m, 1H, NC**H**$_2$CH$_2$), 2.54 (s, 3H, NC**H**$_3$), 2.27 – 2.18 (m, 1H, NC**H**$_2$CH$_2$). ^{13}C NMR (CD_3CN, 100 MHz, 298K) δ, ppm: 164.1 (C_q), 153.6 (C_α), 143.6 (C_γ), 128.9 (C_β), 126.7 ($C_{\beta'}$), 71.4 (Py**C**H$_2$N), 66.8, 65.0, 64.4, 63.8, 62.1, 61.9 (N**C**H$_2$**C**H$_2$N), 54.6, 53.3 (**C**H$_3$).

Preparation of compound 2. In a typical experiment, 2 mL of a 0.2 mM solution of **1** in anhydrous acetone were placed in a UV-vis cuvette (0.4 μmol of **1**). The quartz cell was capped with a septum and taken out of the glovebox, placed in the Unisoku cryostat of the UV-vis spectrophotometer and cooled down at -80 ºC. After reaching thermal equilibrium an UV-vis spectrum of the starting complex was recorded. Then, O_2 was injected into the cell with a balloon and a needle through the septum and the process was monitored by UV-vis. The formation of a chromophore with absorption maxima at

375 nm (ε = 6350 $M^{-1}cm^{-1}$) and 520 nm (ε = 1970 $M^{-1}cm^{-1}$) was observed and full formation of **2** was achieved in less than 1 min. Other solvents such as THF or CH_2Cl_2 could also be used for the preparation of **2** following a similar methodology.

Preparation of compound 3. In a typical experiment, 2 mL of a 0.4 mM solution of **1** in anhydrous acetonitrile were placed in a UV-vis cuvette (0.8 μmol of **1**). The quartz cell was capped with a septum and taken out of the glovebox, placed in the Unisoku cryostat of the UV-vis spectrophotometer and cooled down at -35 ºC. After reaching thermal equilibrium an UV-vis spectrum of the starting complex was recorded. Then, O_2 was injected into the cell with a balloon and a needle through the septum and the process was monitored by UV-vis. The formation of a chromophore with absorption maxima at 395 nm (ε = 4500 $M^{-1}cm^{-1}$) and 505 nm (ε = 2900 $M^{-1}cm^{-1}$) was observed and full formation of **2** was achieved after 15 min. Other solvents such as acetone, THF or CH_2Cl_2 could also be used for the preparation of **3** following a similar methodology.

1.4. Reaction of compounds 2 and 3 towards organic substrates

Product analyses. Once the formation of **2** or **3** reached its maximum, 100 μL of an acetonitrile solution containing the required equivalents of the desired substrate were added in the UV-vis cuvette. The decay of the band at 375 nm (for **2**) or 505 nm (for **3**) was monitored. After complete disappearance of the chromophore, biphenyl (internal standard) was added and the cobalt complex was removed by passing the solution through a short plug of silica. The products were then eluted with ethyl acetate and analysed by GC-FID. The organic products were identified by comparison with authentic compounds.

1.5. Computational details

Density functional theory (DFT) calculations were performed with the Gaussian09 software package.[4] X-ray diffraction structure of $[Co^{II}(Pytacn)(CH_3CN)_2]^{2+}$ (**1**) has been chosen as starting point for geometry optimizations with the B3LYP exchange-correlation functional[5,6] and the TZVP basis set for all atoms.[7] Cobalt species were considered in all possible spin states without symmetry constraints. The effect of the acetonitrile solvent was included in geometry optimizations through the universal Solvation Model based on solute electron Density (SMD).[8] Dispersion effects were also included in geometry optimizations using the Grimme's D_3 correction with the Becke-Johnson damping function.[9]

Analytical Hessian calculations were performed at the same level of theory to (i) evaluate enthalpy and entropy corrections at 238.15 K and (ii) establish the nature of stationary points in solvent-phase, where minima have no imaginary frequencies and transition states only one. Non-resonant Raman spectral intensities of compounds **2** and **3** were simulated at 77 K and with a laser excitation of 532 nm employing the GaussSum 3.0 program.[10] The shift in the O−O bond stretching frequency upon ^{18}O-labeling was determined modeling the Raman spectrum with an ^{18}O−^{18}O bond. The predicted O-O bond stretching frequencies have been corrected multiplying them by a factor of 0.96. This vibrational correction parameter was derived from scaling B3LYP/cc-pVTZ frequencies to reproduce experimental data.[11]

Mulliken spin densities were computed to rationalize the electronic structure of all cobalt based intermediates.

Gibbs energies (G) were evaluated with the following equation:

$$G = E_{TZVP}(SMD + D_3) + G_{corr} + \Delta G^{o/*} \quad (1)$$

where G_{corr} is the thermal correction obtained from a thermo-statistical analysis at the B3LYP/SMD level and $\Delta G^{o/*}$ is the free energy change associated with the conversion from a standard state of 1 M in the aqueous phase and 1 atm in gas phase, to the desired concentration in both phases. $\Delta G^{o/*}$ values are derived with the following expression:

$$\Delta G^{o/*} = RT \ln(24.4\ c) \quad (2)$$

where R is the universal gas constant (1.987 cal·mol^{-1}·K^{-1}), T is the temperature in Kelvin and c the concentration in mol·L^{-1}.

In the free energy balances the following concentrations were used to adjust the final free energies: 19.1 M for acetonitrile and 1 M for the rest of species. The previous concentrations translate into $\Delta G^{o/*}$values (at 238.15 K) of 2.9 kcal·mol^{-1} and 1.51 kcal·mol^{-1}.

2. ^{1}H NMR spectra of 1CF_3SO_3 and 1SbF_6

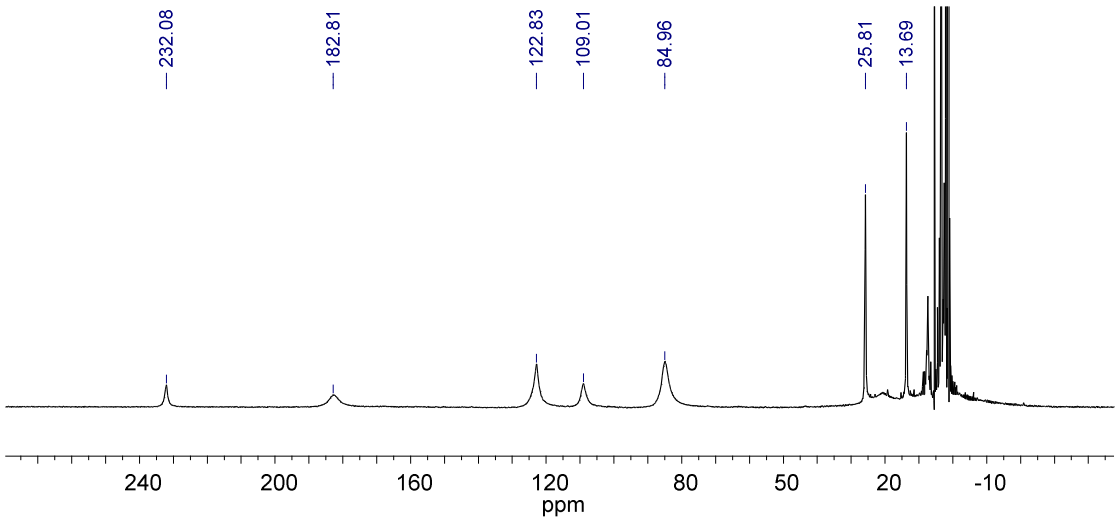


Figure S1. ^{1}H NMR spectrum of $[Co^{II}(Pytacn)(CH_3CN)_2](CF_3SO_3)_2$ (**1CF_3SO_3**) in CD_3CN at 298 K (400 MHz).

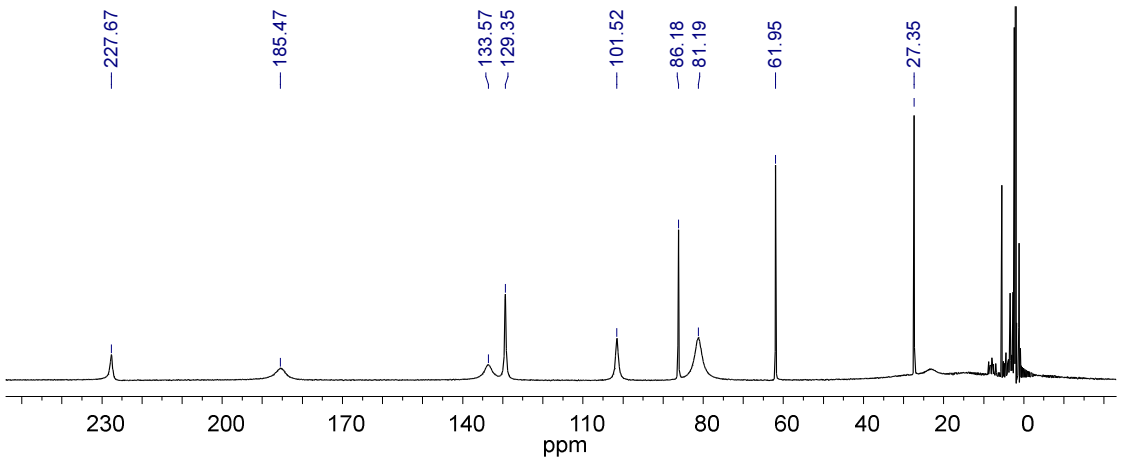


Figure S2. ^{1}H NMR spectrum of $[Co^{II}(Pytacn)(CH_3CN)_2](SbF_6)_2$ (**1SbF_6**) in CD_3CN at 298 K (400 MHz).

3. Characterization of $1^{+}SbF_6$

3.1. NMR spectra of $1^{+}SbF_6$

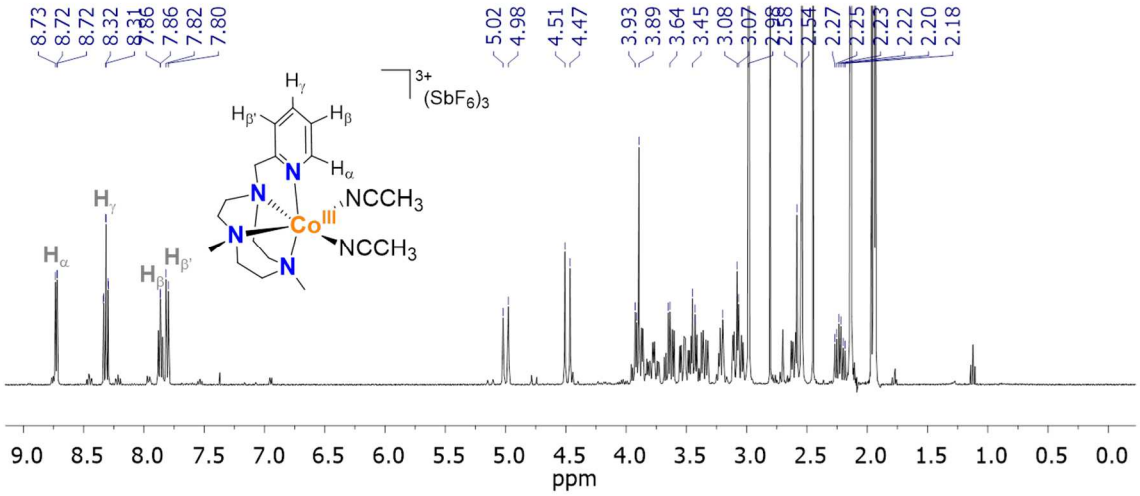


Figure S3. ^{1}H NMR spectrum of $[Co^{III}(Pytacn)(CH_3CN)_2](SbF_6)_3$ (**$1^{+}SbF_6$**) in CD_3CN at 298 K (400 MHz).

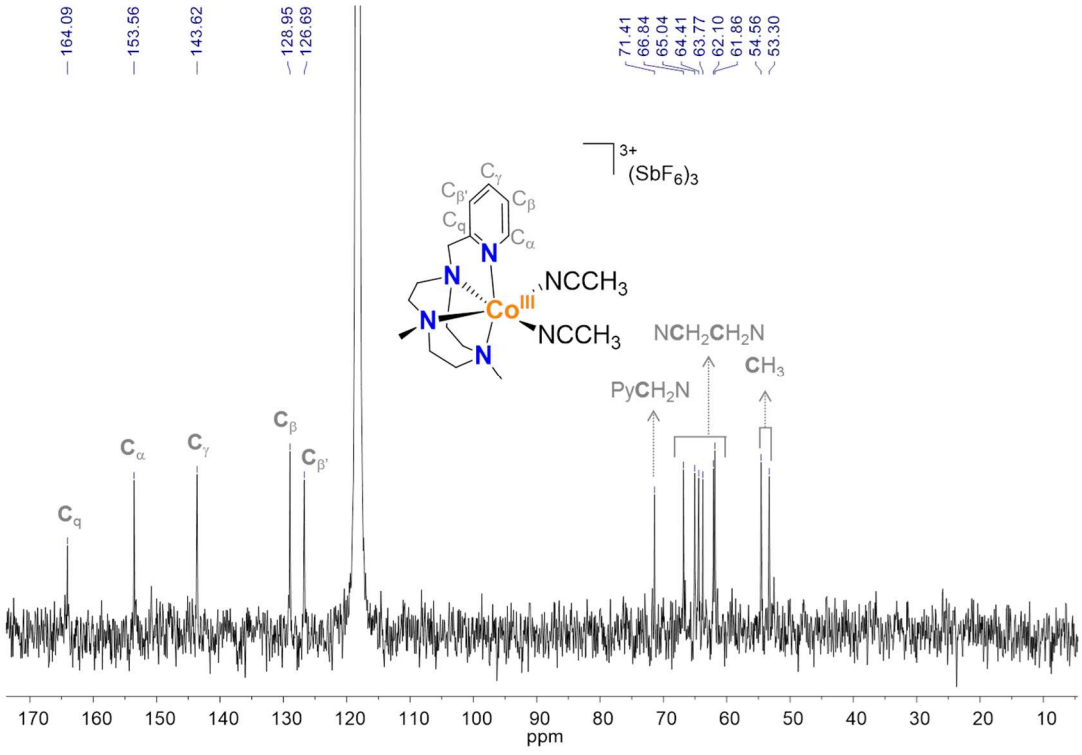


Figure S4. ^{13}C NMR spectrum of $[Co^{III}(Pytacn)(CH_3CN)_2](SbF_6)_3$ (**$1^{+}SbF_6$**) in CD_3CN at 298 K (400 MHz).

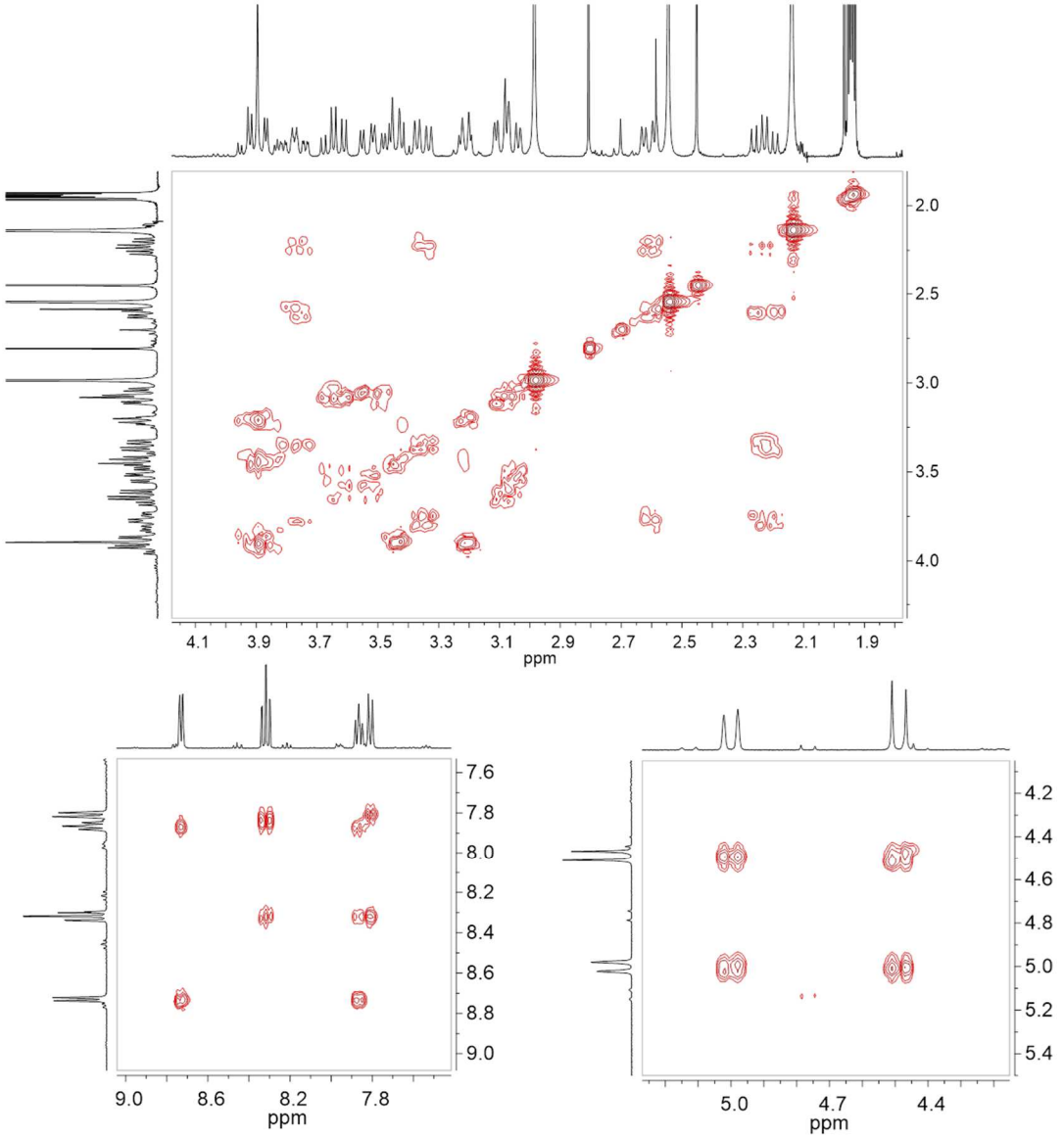
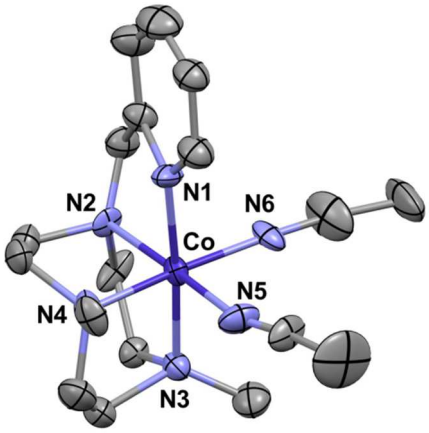


Figure S5. Expansions of the ^{1}H-^{1}H COSY spectrum of $[Co^{III}(Pytacn)(CH_3CN)_2](SbF_6)_3$ (**$1^{+}SbF_6$**) in CD_3CN at 298 K (400 MHz).

3.2. X-ray characterization of $1^{+}SbF_6$

a)



b)

Co1 N1	1.948(6)	N1 Co1 N2	87.9(5)
Co1 N2	2.018(9)	N1 Co1 N4	90.6(6)
Co1 N3	1.981(6)	N1 Co1 N5	91.4(6)
Co1 N4	1.868(13)	N1 Co1 N6	90.3(6)
Co1 N5	1.961(14)	N2 Co1 N3	88.7(5)
Co1 N6	1.883(13)	N2 Co1 N4	88.3(3)
		N2 Co1 N6	95.7(5)
		N3 Co1 N4	86.6(5)
		N3 Co1 N5	91.9(5)
		N3 Co1 N6	92.7(5)
		N4 Co1 N5	89.1(6)
		N5 Co1 N6	86.9(3)

Figure S6. a) Crystal structure of $[Co^{III}(Pytacn)(CH_3CN)_2](SbF_6)_3$ (**$1^{+}SbF_6$**). Hydrogen atoms and SbF_6 counterions have been omitted for clarity. Thermal ellipsoids are set at 50% probability. b) Selected bond lenghts (Å) and angles (º) for $[Co^{III}(Pytacn)(CH_3CN)_2](SbF_6)_3$ (**$1^{+}SbF_6$**).

Table S1. Crystal data for $[Co^{III}(Pytacn)(CH_3CN)_2](SbF_6)_3$ (**$1^{+}SbF_6$**).

Empirical formula	$C_{22}H_{37}CoF_{18}N_8Sb_3$
Formula weight	1179.77
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, P 21
Unit cell dimensions	a = 11.099(2) Å α = 90º b = 10.352(2) Å β = 91.518(4)º c = 17.468(4) Å γ = 90º
Volume	2006.2(7) A^3
Z, Calculated density	2, 1.953 Mg/m^3
Absorption coefficient	2.515 mm^{-1}
F(000)	1134
Crystal size	0.25 x 0.22 x 0.12 mm
Theta range for data collection	2.149 to 28.349º
Limiting indices	-14 ≤ h ≤ 14, -13 ≤ k ≤ 13, -23 ≤ l ≤ 23
Reflections collected / unique	31832 / 9841 [R(int) = 0.0361]
Completeness to theta = 25.242	99.9%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0 and 0.677507
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9841 / 93 / 473
Goodness-of-fit on F^2	1.043
Final R indices [I>2σ(I)]	R1 = 0.0495, wR2 = 0.1265
R indices (all data)	R1 = 0.0550, wR2 = 0.1315
Largest diff. peak and hole	3.240 and -1.641 $e.A^{-3}$

4. ^{1}H NMR characterization of 3

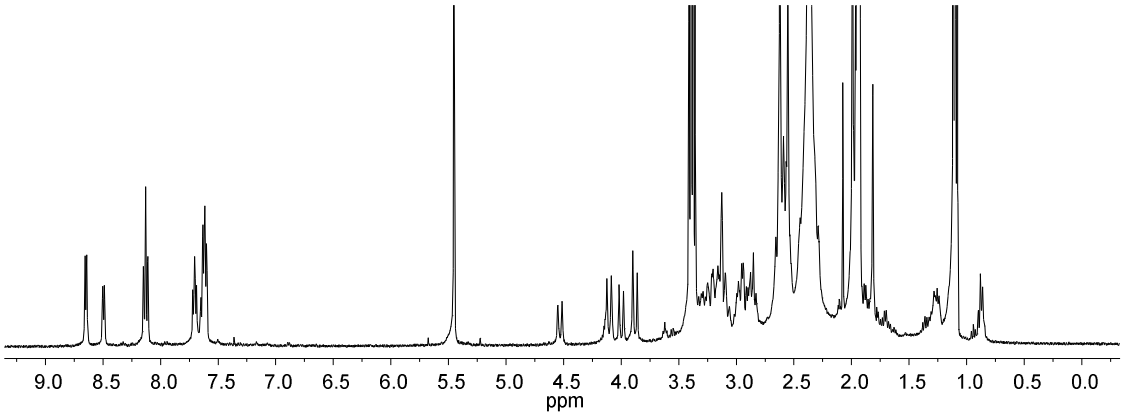


Figure S7. ^{1}H NMR spectrum of **3** formed by reaction of **1** with O_2 at -35 ºC in CD_3CN (400 MHz).

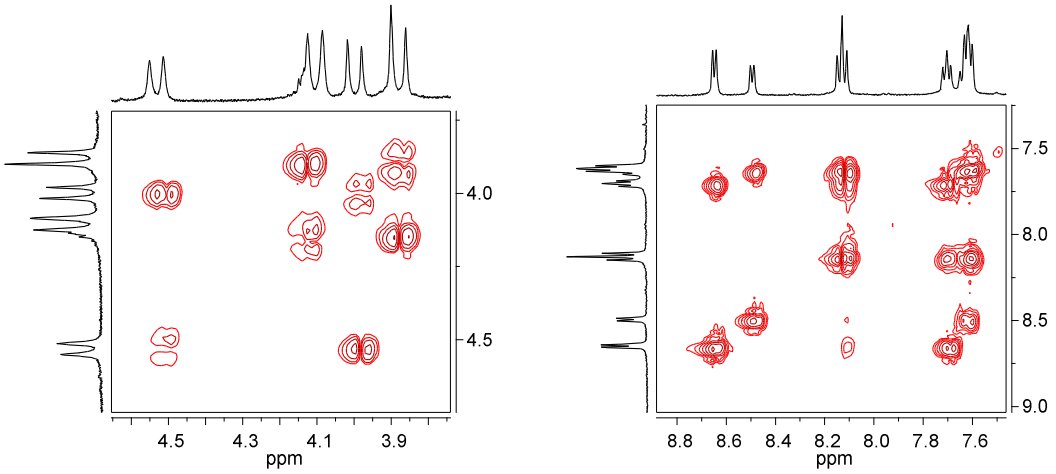


Figure S8. Expansion of the ^{1}H-^{1}H COSY spectrum of **3** formed by reaction of **1** with O_2 at -35 ºC in CD_3CN (400 MHz).

5. Reaction of 1 with O_2 in acetone

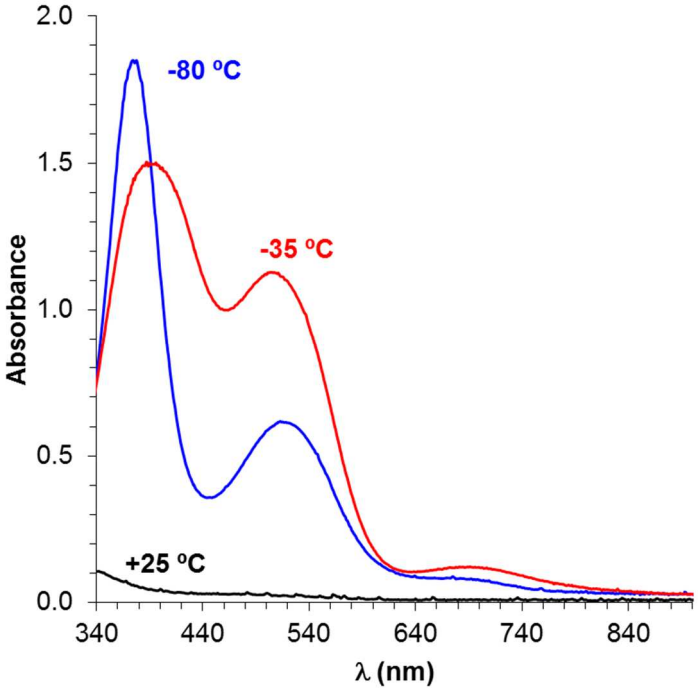


Figure S9. UV-vis spectra obtained after reaction of **1** (0.4 mM) with O_2 at +25 °C, -35 °C and -80 °C in acetone.

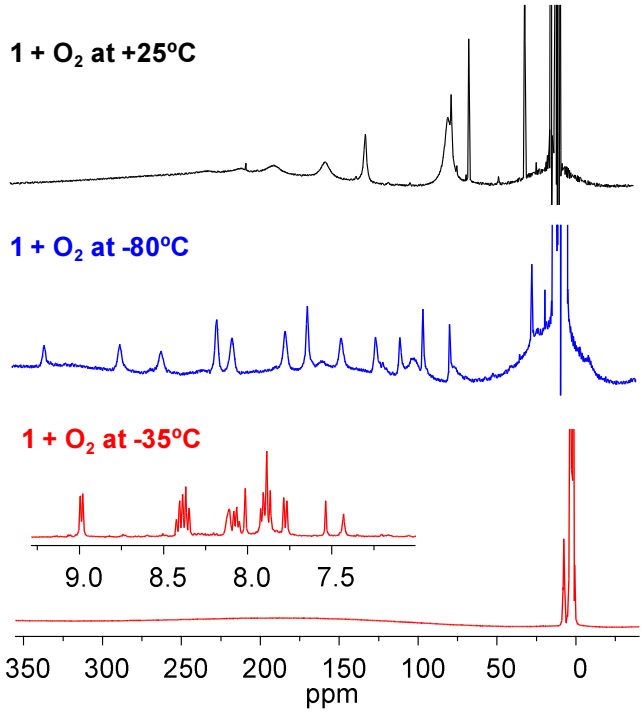


Figure S10. ^1H NMR spectra obtained after reaction of **1** (25 mM) with O_2 at +25 °C, -35 °C and 0-80 °C in d_6-acetone.

6. EPR spectrum of 2

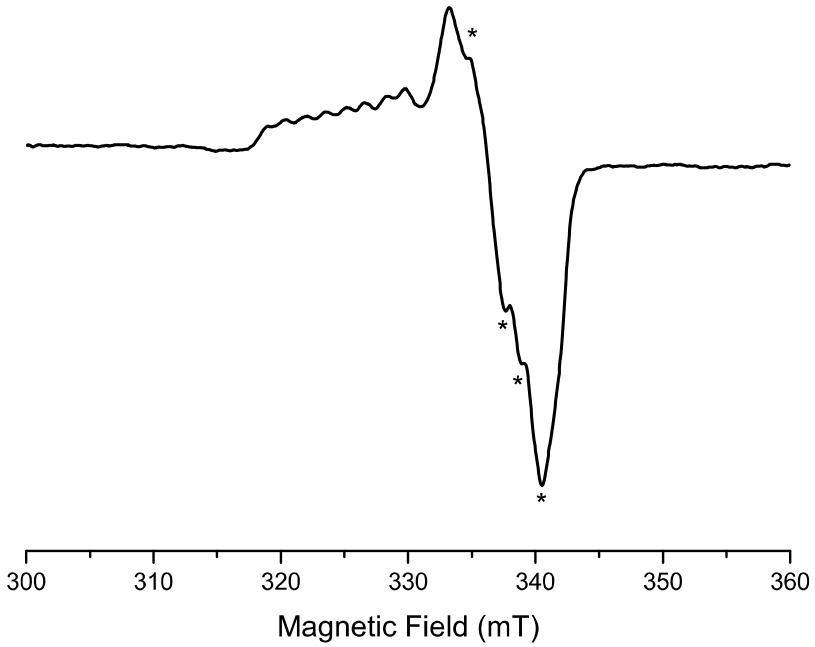


Figure S11. Experimental cw X-band EPR spectrum of **2** recorded in acetone at 100 K. Comments: the EPR spectrum is characterized by an axial *S* = 1/2 signal. The parallel component is split into eight lines due to the Co nuclear spin of *I* = 7/2. The perpendicular component is partially contaminated by the presence of an additional signal arising from the initial complex (highlighted with *).

7. Reversibility of the oxygenation reaction of 1 monitored by UV-vis and Raman spectroscopies

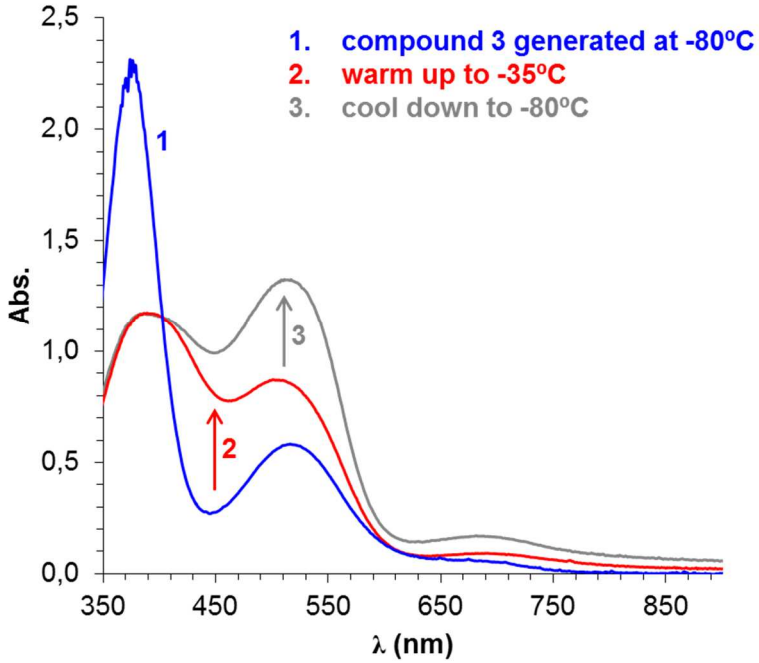


Figure S12. UV-vis spectrum corresponding to compound **2** generated at -80 ºC in acetone by reaction of **1** (0.4 mM) with O_2 (blue line), and the resulting spectra after warming up the same solution at -35 ºC (red line) and subsequent coolling down to -80 ºC (grey line).

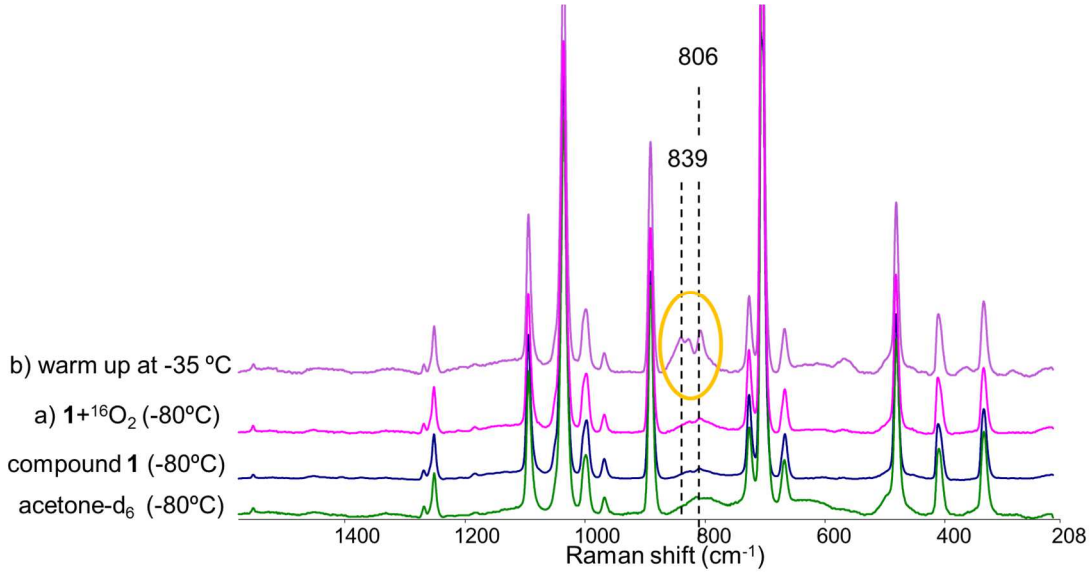


Figure S13. rRaman spectra (λ_{exc} = 532 nm) at 77 K of the reaction of compound **1** with O_2 at -80 ºC in d_6-acetone to form **2** (a) and the corresponding spectrum after warming up the solution to -35 ºC which causes the formation of **3** (b). Blank experiments are also shown.

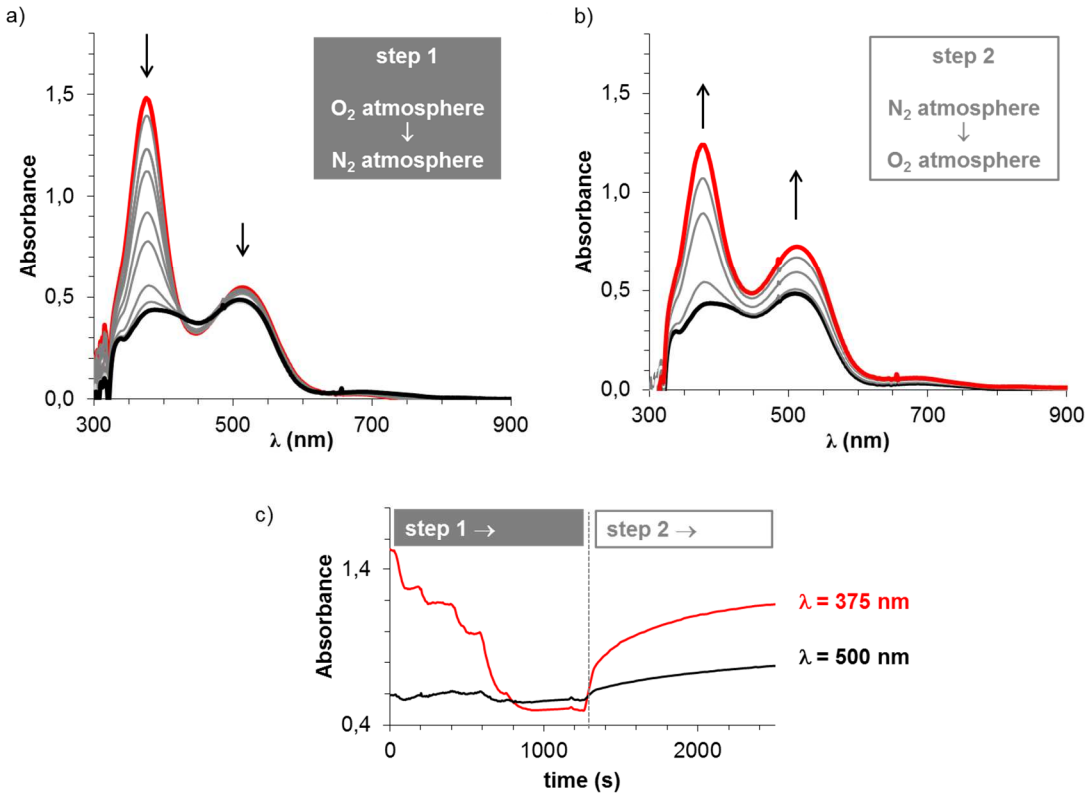


Figure S14. a) Step 1: UV-vis spectra corresponding to the replacement of the O_2 atmosphere by N_2 in a freshly prepared solution of **2** in acetone at -80 ºC formed by reaction of **1** (0.24 mM) with O_2. b) Step 2: UV-vis spectra corresponding to the replacement of the N_2 atmosphere by O_2 in the solution resulting from step 1. c) Time traces monitoring the changes over time at 375 and 500 nm for step 1 and step 2.

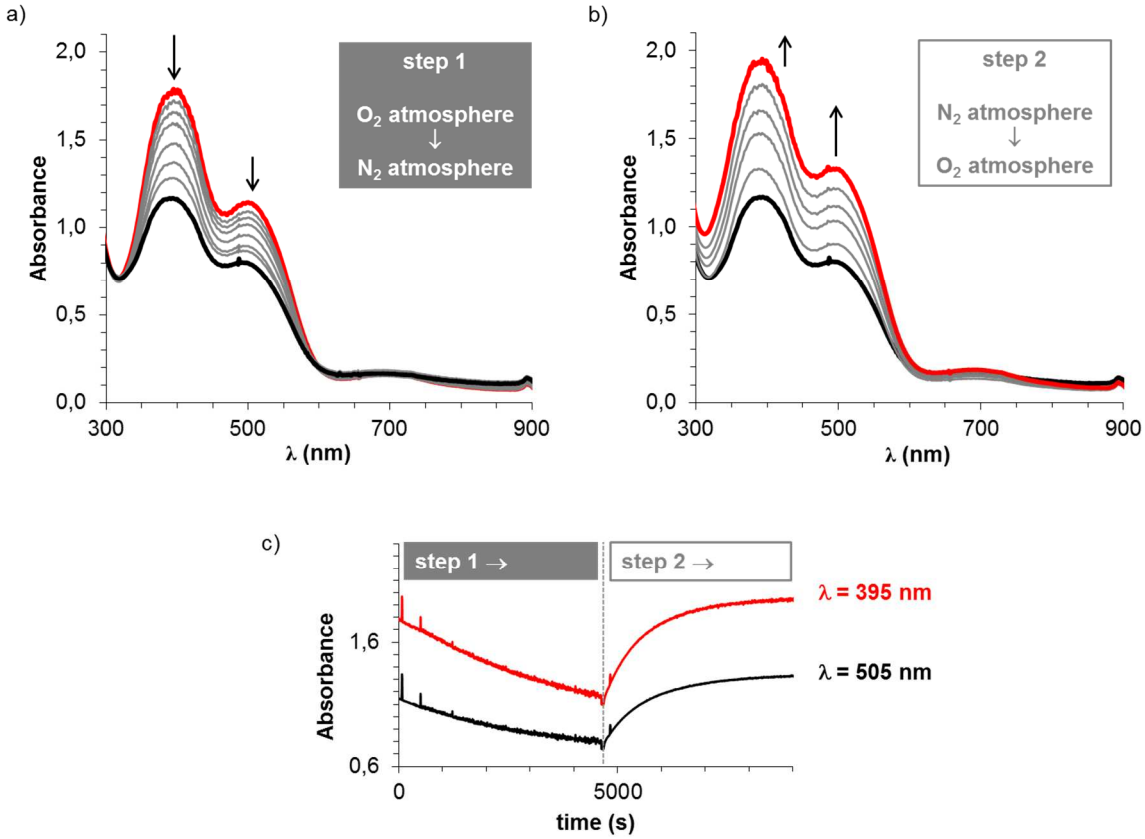


Figure S15. a) Step 1: UV-vis spectra corresponding to the replacement of the O_2 atmosphere by N_2 in a freshly prepared solution of **3** in CH_3CN at -35 ºC formed by reaction of **1** (0.4 mM) with O_2. b) Step 2: UV-vis spectra corresponding to the replacement of the N_2 atmosphere by O_2 in the solution resulting from step 1. c) Time traces monitoring the changes over time at 395 and 505 nm for step 1 and step 2.

8. Reactivity of 2 and 3 towards organic substrates

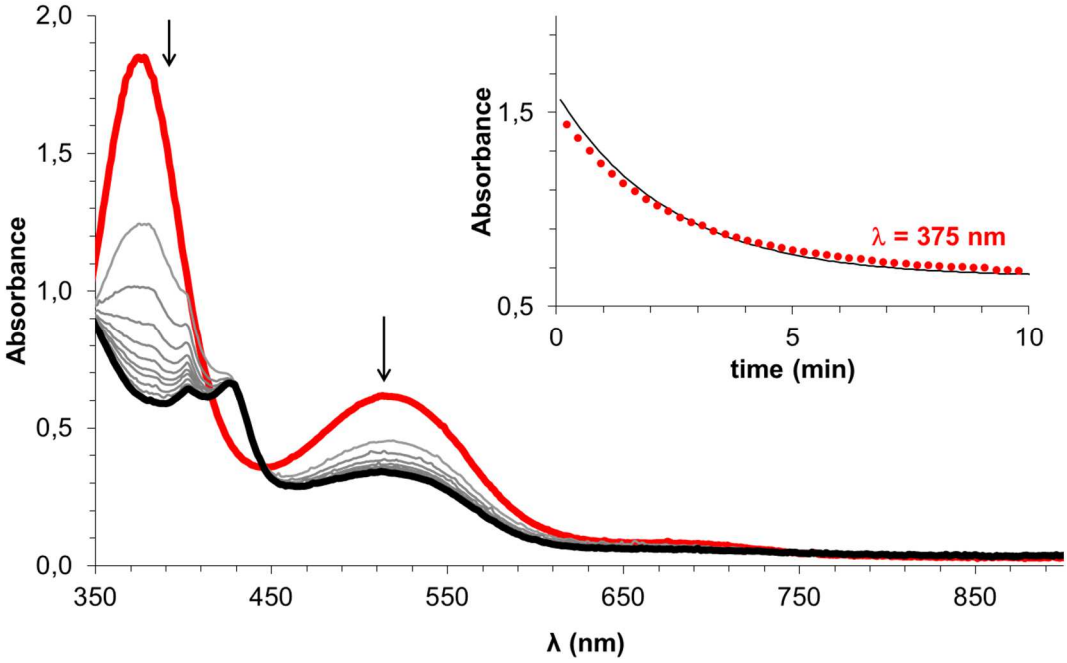


Figure S16. UV-Vis spectral changes of a solution of **2** (formed by reaction of 0.4 mM **1** with O_2 in acetone at -80 ºC) upon addition of 10 equiv 2,4,6-tri-*tert*-butylphenol at -80 ºC. Inset: kinetic trace at 375 nm which fits to a monoexponential decay function.

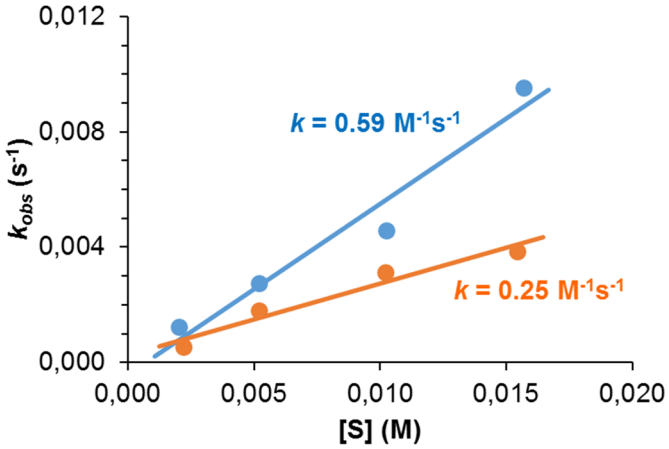


Figure S17. Plot of k_{obs} against substrate concentration for the reaction of **2** with 2,4,6-trit-tert-butylphenol (blue data) and with the corresponding monodeuterated analogue (orange data) in acetone at -80 ºC.

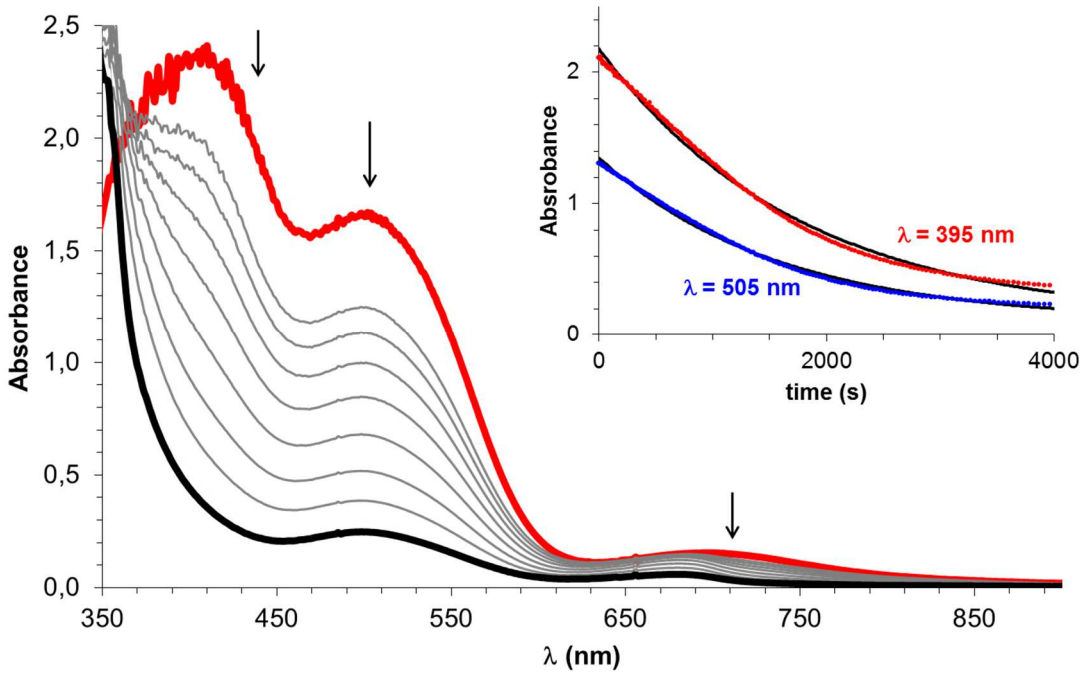


Figure S18. UV-Vis spectral changes of a solution of **3** (formed by reaction of 0.6 mM **1** with O_2 in MeCN at -35 ºC) upon addition of 200 equiv *para*-methoxybenzaldehyde -35 ºC. Inset: kinetic traces at 395 and 505 nm which fit to monoexponential decay functions.

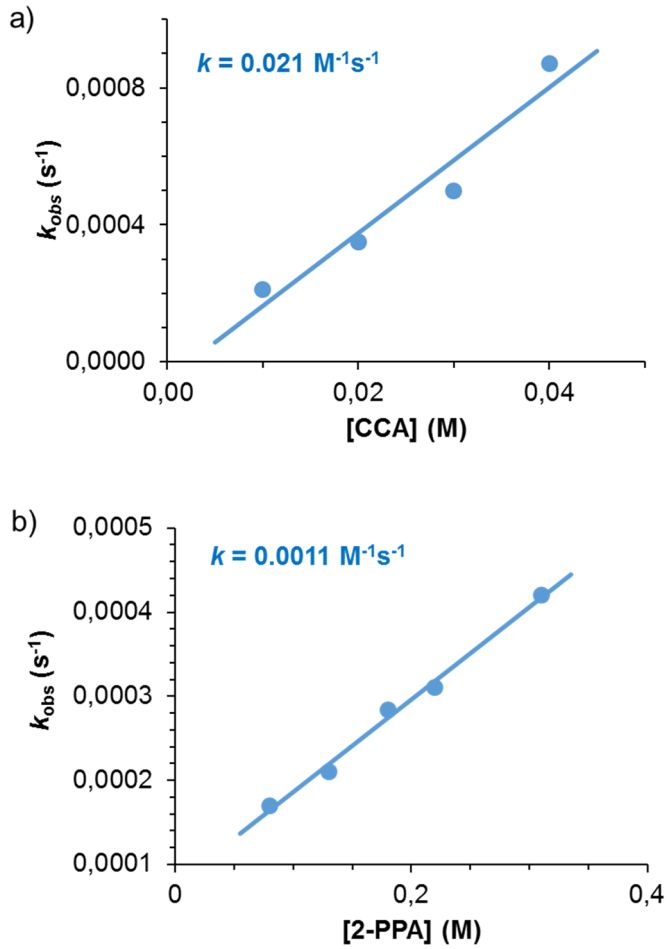


Figure S19. Plot of k_{obs} against substrate concentration for the reaction of **3** with cyclohexanecarboxaldehyde, CCA (a) and 2-phenylpropionaldehyde, 2-PPA (b) in MeCN at -35 ºC.

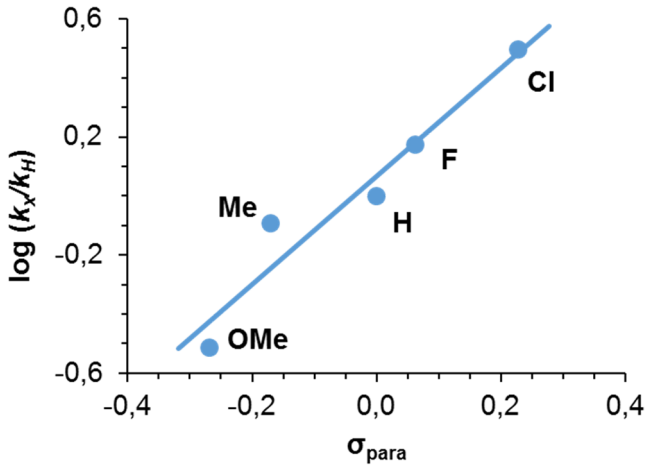


Figure S20. Hammett plot for the reaction of **3** against *para*-substituted benzaldehyde in MeCN at -35 ºC.

9. DFT calculations

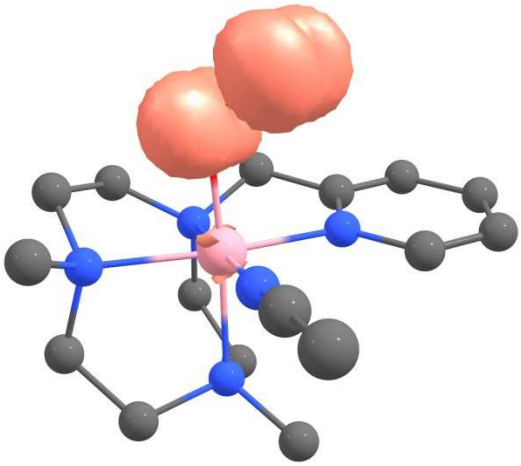


Figure S21. Isodensity surface (isovalue = 0.0043) of the spin density for $[Co^{III}(O_2)(Pytacn)(CH_3CN)]^{2+}$ (**2**).

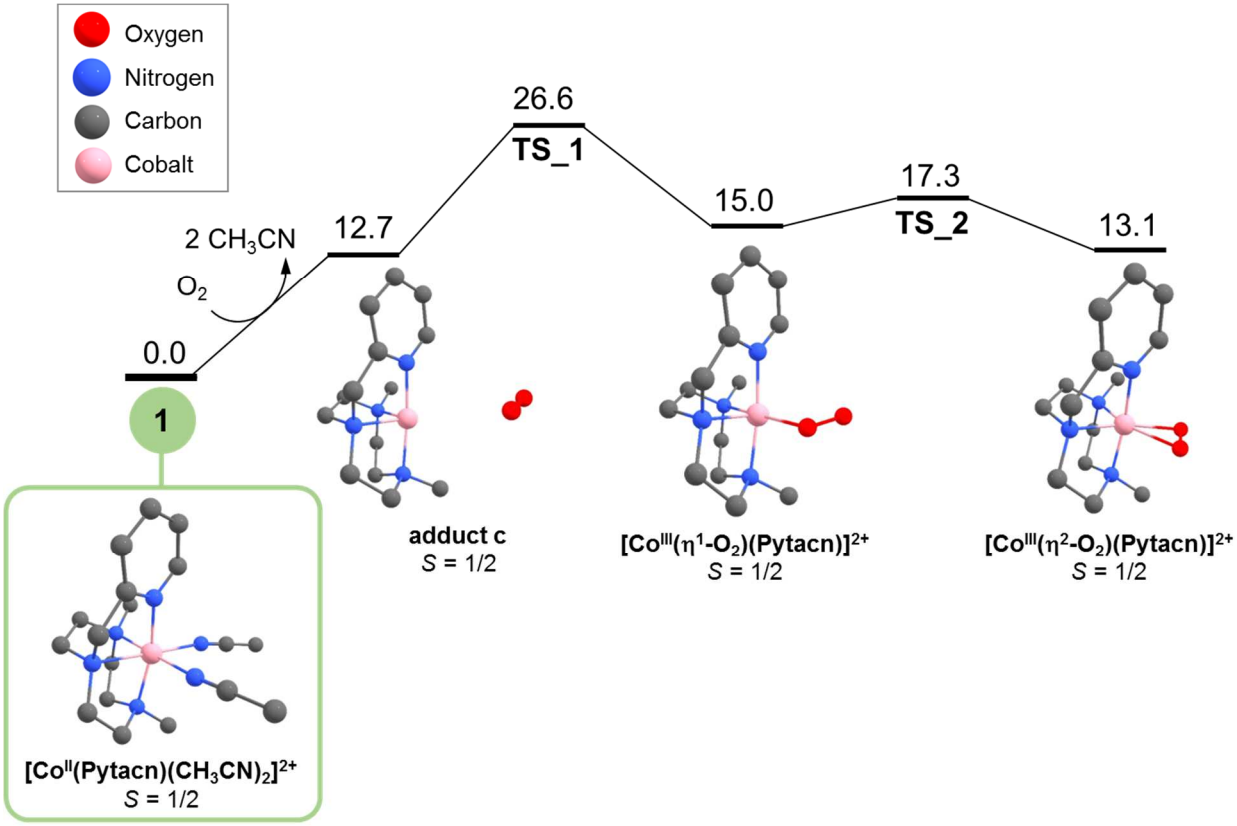


Figure S22. Free energy profile for the reaction of **1** with O_2 in CH_3CN at 238.15 K to form the side-on superoxido cobalt(III) complex $[Co^{III}(\eta^2\text{-}O_2)(Pytacn)]^{2+}$. Gibbs energies are given in kcal·mol^{-1}.

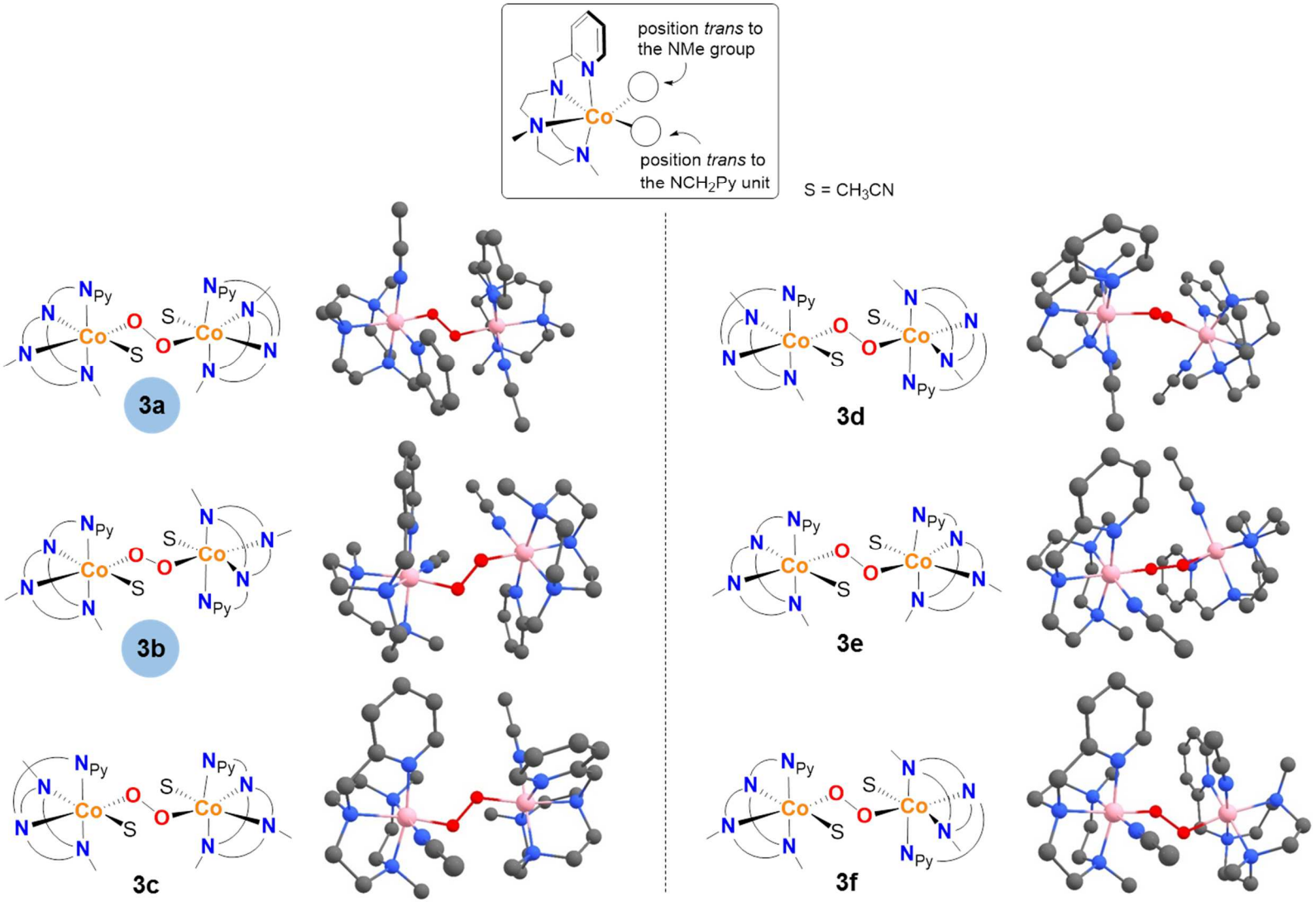


Figure S23. DFT structures of the possible isomers for $[Co^{III}_2(O_2)(Pytacn)_2(CH_3CN)_2]^{4+}$ (**3**).

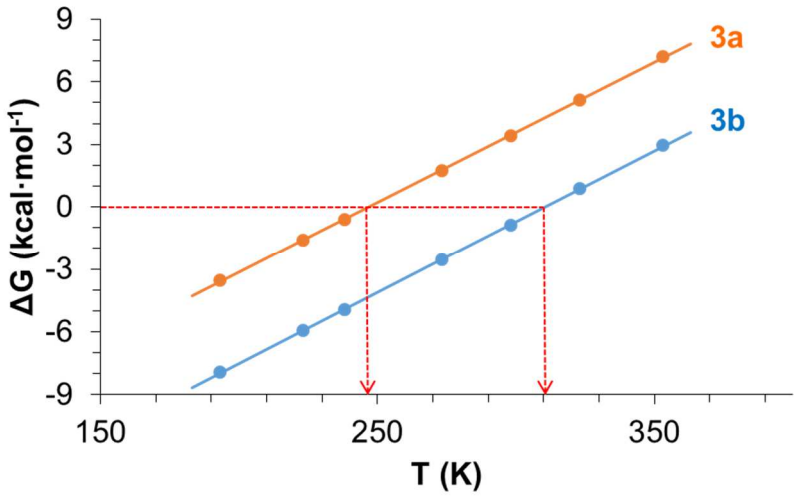


Figure S24. Predicted temperature dependence of the Gibbs free energy (ΔG) for the formation of **3a** and **3b** by reaction of **1** with O_2.

9.1. Cartesian coordinates

O_2 (G = -150.403496, E_{ZPE} = -150.383528), triplet

8	0.000000000	0.000000000	0.603786000
8	0.000000000	0.000000000	-0.603786000

$[Co^{II}(Pytacn)(CH_3CN)_2]^{2+}$ (1) (G = -2415.186545, E_{ZPE} = -2415.129547), doublet

6	0.342528000	-2.296050000	1.886182000
6	-1.871218000	-1.307738000	1.314873000
6	-2.445807000	-0.261137000	0.390206000
7	-1.572268000	0.511956000	-0.286691000
6	-2.024728000	1.515221000	-1.050400000
6	-3.375377000	1.783627000	-1.188098000
6	-4.286550000	0.977926000	-0.516156000
6	-3.814142000	-0.055437000	0.280939000
6	3.199877000	-0.060499000	0.693084000
6	0.151637000	-0.289194000	-2.985843000
1	1.838216000	-2.933758000	-0.137114000
1	3.380377000	-2.203165000	-0.502930000
1	1.864391000	-2.401840000	-2.531548000
1	2.418002000	-0.760324000	-2.182741000
1	-0.441557000	-2.889267000	-2.415885000
1	-1.578715000	-1.646355000	-1.908784000
1	0.007005000	-3.562889000	-0.185332000
1	-1.714988000	-3.277691000	-0.223166000
1	1.691796000	-0.748503000	2.599221000
1	2.499470000	-2.248230000	2.157813000
1	-0.111652000	-2.145388000	2.864015000
1	0.497402000	-3.367947000	1.773537000
1	-2.601651000	-2.109167000	1.461972000
1	-1.274859000	2.104215000	-1.558297000
1	-3.698730000	2.602078000	-1.816188000
1	-5.350586000	1.152599000	-0.610873000
1	-4.493603000	-0.702790000	0.818977000
1	3.468322000	0.337046000	-0.282496000
1	2.959082000	0.764781000	1.358673000
1	4.047733000	-0.619699000	1.099059000
1	0.856535000	0.533617000	-3.054233000
1	0.267456000	-0.938385000	-3.858832000
1	-0.860402000	0.105175000	-2.975198000
1	-1.704276000	-0.831724000	2.282329000
7	0.262534000	1.060666000	1.651282000
6	0.156796000	1.736631000	2.571760000
7	1.256654000	1.853198000	-0.951013000
6	1.803181000	2.831942000	-1.203997000
6	0.028353000	2.574733000	3.740022000
1	-0.565409000	3.456954000	3.496105000
1	-0.464999000	2.016650000	4.537346000
1	1.017820000	2.887796000	4.076890000
6	2.498690000	4.057928000	-1.527362000
1	2.724462000	4.082114000	-2.594465000
1	1.874164000	4.915274000	-1.272346000
1	3.430058000	4.110870000	-0.961448000
27	0.321808000	0.007842000	-0.007344000

CH_3CN (G = -132.800720, E_{ZPE} = -132.776741), singlet

7	1.428659000	-0.000052000	0.000045000
6	0.276943000	0.000109000	-0.000094000
6	-1.172496000	0.000003000	0.000007000
1	-1.542382000	-0.021559000	1.026070000
1	-1.542515000	0.899204000	-0.494351000
1	-1.542392000	-0.877952000	-0.531513000

adduct a (G = -2432.791036, E_{ZPE} = -2432.734240), doublet

7	2.271682000	0.180708000	0.816414000
6	3.116428000	-0.593517000	-0.146059000
6	2.620333000	-0.421899000	-1.573096000
7	1.153888000	-0.592084000	-1.705980000
6	0.673665000	-1.990075000	-1.703957000
6	0.757716000	-2.663587000	-0.337829000
7	0.402808000	-1.747540000	0.805533000
6	2.117214000	-0.521996000	2.120688000
6	1.391397000	-1.850864000	1.935343000
6	-0.989629000	-1.976915000	1.280798000
6	-1.956950000	-1.339179000	0.333708000
7	-1.510829000	-0.199286000	-0.234872000
6	-2.315191000	0.484411000	-1.061733000
6	-3.600394000	0.058560000	-1.348896000
6	-4.062805000	-1.118972000	-0.773915000
6	-3.227207000	-1.829121000	0.078657000
6	2.863375000	1.516034000	1.045919000
6	0.695542000	0.077948000	-2.933943000
1	3.118256000	-1.636780000	0.144183000
1	4.150304000	-0.250322000	-0.079674000
1	1.532036000	0.141470000	2.757356000
1	3.091621000	-0.678270000	2.593243000
1	0.871883000	-2.108267000	2.855593000
1	2.086829000	-2.658737000	1.727449000
1	-1.191140000	-3.040979000	1.412340000
1	-1.908565000	1.385276000	-1.495643000
1	-4.218199000	0.639033000	-2.019796000
1	-5.059820000	-1.481114000	-0.988740000
1	-3.547293000	-2.753019000	0.540656000
1	2.992094000	2.025680000	0.094436000
1	2.203764000	2.103285000	1.680540000
1	3.836512000	1.410287000	1.532949000
1	0.969238000	1.130344000	-2.897939000
1	1.146134000	-0.374954000	-3.824992000
1	-0.386662000	-0.002291000	-3.013226000
1	-1.091807000	-1.486448000	2.250250000
27	0.381507000	0.152243000	0.155226000
8	-2.866981000	1.712548000	2.190051000
8	-1.723260000	2.038243000	2.399256000
7	0.276640000	2.021438000	-0.291417000

1	3.157194000	-1.113410000	-2.231768000	6	0.210776000	3.129364000	-0.581004000
1	2.842960000	0.591845000	-1.903531000	6	0.137372000	4.522278000	-0.948853000
1	1.231452000	-2.598128000	-2.425397000	1	-0.765058000	4.967399000	-0.527234000
1	-0.363042000	-1.960164000	-2.033270000	1	1.013511000	5.047020000	-0.564345000
1	1.759609000	-3.040260000	-0.168350000	1	0.111016000	4.611976000	-2.036005000
1	0.089222000	-3.524817000	-0.327369000				

adduct b (G = -2432.791036, E_{ZPE} = -2432.734240), quadruplet

7	2.282525000	0.166799000	0.372383000	1	1.918324000	0.889046000	2.290185000
6	2.975416000	-0.963450000	-0.320882000	1	3.306998000	-0.191191000	2.197953000
6	2.293612000	-1.236017000	-1.640765000	1	0.955982000	-0.977042000	3.251344000
7	0.808172000	-1.285486000	-1.491349000	1	1.990663000	-2.115612000	2.420785000
6	0.293938000	-2.580523000	-0.964164000	1	-1.372674000	-2.325872000	2.332747000
6	0.522813000	-2.755700000	0.535305000	1	-2.013472000	0.848518000	-1.926125000
7	0.307103000	-1.498505000	1.303682000	1	-4.445533000	0.321334000	-1.890277000
6	2.282482000	-0.034342000	1.849068000	1	-5.320401000	-1.158337000	-0.067487000
6	1.390703000	-1.218128000	2.283008000	1	-3.729314000	-2.001450000	1.659268000
6	-1.057323000	-1.398374000	1.846349000	1	2.932871000	1.570473000	-1.054827000
6	-2.051261000	-1.010332000	0.779931000	1	2.398885000	2.271138000	0.483321000
7	-1.592548000	-0.240335000	-0.227305000	1	3.973099000	1.449611000	0.381493000
6	-2.441412000	0.227688000	-1.151852000	1	0.475555000	-0.040791000	-3.160613000
6	-3.791873000	-0.073319000	-1.124935000	1	0.590161000	-1.772823000	-3.546360000
6	-4.272058000	-0.892495000	-0.109879000	1	-0.868413000	-1.133280000	-2.771070000
6	-3.390696000	-1.364913000	0.852941000	1	-1.062831000	-0.609549000	2.600665000
6	2.938921000	1.446366000	0.026342000	7	-0.091890000	1.664074000	0.963919000
6	0.212046000	-1.041946000	-2.825314000	6	-0.453975000	2.587711000	1.540355000
1	2.962703000	-1.835808000	0.321619000	6	-0.900237000	3.755026000	2.261383000
1	4.023762000	-0.708735000	-0.485653000	1	-1.970327000	3.896069000	2.101779000
1	2.659024000	-2.164002000	-2.087782000	1	-0.706621000	3.623976000	3.327223000
1	2.506829000	-0.421329000	-2.331009000	1	-0.362189000	4.633651000	1.901825000
1	0.756781000	-3.411654000	-1.503256000	27	0.341396000	0.106310000	-0.117667000
1	-0.771270000	-2.597819000	-1.179834000	8	0.558981000	3.146121000	-2.133382000
1	1.532507000	-3.104601000	0.720093000	8	-0.399969000	3.779179000	-1.763734000
1	-0.151015000	-3.536027000	0.897264000				

TS (G = -2432.783532, E_{ZPE} = -2432.729883), doublet

7	-2.246698000	-0.236365000	-0.636333000	1	-1.723691000	-0.340388000	-2.648758000
6	-2.878791000	-1.047183000	0.453963000	1	-3.064753000	-1.403286000	-2.223849000
6	-2.314558000	-0.669461000	1.812892000	1	-0.617780000	-2.398169000	-2.630733000
7	-0.833026000	-0.592221000	1.825421000	1	-1.622785000	-3.087994000	-1.378028000
6	-0.131575000	-1.893197000	1.885142000	1	1.655987000	-2.912895000	-1.240506000
6	-0.210774000	-2.680825000	0.584357000	1	1.827940000	1.839966000	1.187435000
7	-0.083206000	-1.815862000	-0.650072000	1	4.271941000	1.563908000	1.514599000
6	-2.093695000	-1.027731000	-1.889188000	1	5.389720000	-0.469981000	0.574168000
6	-1.113534000	-2.180566000	-1.687910000	1	4.002131000	-2.128654000	-0.677506000
6	1.297164000	-1.883741000	-1.207857000	1	-3.217054000	1.520944000	0.009615000
6	2.206183000	-1.001048000	-0.412999000	1	-2.574678000	1.590981000	-1.642084000
7	1.611684000	0.093001000	0.108670000	1	-4.046817000	0.651931000	-1.299847000
6	2.350230000	0.985343000	0.785459000	1	-0.845238000	1.232001000	2.876334000
6	3.712290000	0.820399000	0.964491000	1	-0.702165000	-0.204023000	3.912623000
6	4.327778000	-0.309838000	0.440428000	1	0.683803000	0.341127000	2.948919000
6	3.562169000	-1.234851000	-0.257042000	1	1.263801000	-1.508715000	-2.231813000
6	-3.073546000	0.960358000	-0.910213000	27	-0.338023000	0.093192000	-0.125377000
6	-0.399422000	0.243377000	2.959300000	8	1.335247000	2.175922000	-2.531810000
1	-2.731326000	-2.098884000	0.242505000	8	0.552973000	1.254268000	-2.598460000
1	-3.956566000	-0.877289000	0.450364000	7	-0.533366000	1.974702000	0.209886000
1	-2.674367000	-1.374489000	2.569389000	6	-0.651168000	3.095085000	0.423960000
1	-2.676888000	0.322052000	2.080709000	6	-0.805546000	4.503154000	0.693472000
1	-0.529974000	-2.514761000	2.694537000	1	-0.323640000	5.081340000	-0.096441000
1	0.907375000	-1.672403000	2.120832000	1	-1.867403000	4.752278000	0.728609000
1	-1.150997000	-3.215840000	0.526875000	1	-0.344142000	4.744328000	1.652462000
1	0.581496000	-3.429219000	0.574399000				

$[Co^{III}(O_2)(Pytacn)(CH_3CN)]^{2+}$ (2) (G = -2432.787293, E_{ZPE} = -2432.736351), doublet

7	-2.215126000	-0.540222000	-0.406756000	1	-2.116900000	-1.210720000	-2.377670000
6	-2.689592000	-1.033090000	0.927964000	1	-3.081352000	-2.240396000	-1.320750000
6	-2.011555000	-0.261236000	2.033988000	1	-0.475031000	-2.765976000	-2.132761000
7	-0.537832000	-0.147910000	1.814468000	1	-1.194119000	-3.497661000	-0.711681000
6	0.230290000	-1.379382000	2.153935000	1	1.902939000	-2.931736000	-0.683492000
6	0.077197000	-2.450914000	1.098222000	1	1.710273000	2.261020000	0.531473000
7	0.092879000	-1.866489000	-0.297513000	1	4.185108000	2.314024000	0.670992000
6	-2.160311000	-1.660126000	-1.391434000	1	5.466037000	0.229741000	0.136809000
6	-0.929542000	-2.549408000	-1.171196000	1	4.201105000	-1.809594000	-0.559667000
6	1.460965000	-1.958018000	-0.889827000	1	-3.287557000	1.262596000	-0.156544000
6	2.307155000	-0.835883000	-0.383411000	1	-2.731453000	0.947836000	-1.814358000
7	1.630761000	0.285084000	-0.065431000	1	-4.105520000	0.035447000	-1.145610000
6	2.299056000	1.387981000	0.297375000	1	-0.548340000	1.873805000	2.441241000
6	3.680096000	1.405860000	0.373392000	1	-0.229280000	0.693179000	3.726764000
6	4.385861000	0.247086000	0.073499000	1	1.032552000	1.071960000	2.542856000
6	3.689205000	-0.889769000	-0.312336000	1	1.365952000	-1.849435000	-1.969172000
6	-3.144103000	0.498851000	-0.915038000	27	-0.313516000	0.058109000	-0.202421000
6	-0.036736000	0.947491000	2.681375000	8	0.515504000	1.096840000	-2.631120000
1	-2.497048000	-2.096166000	1.000318000	8	-0.192076000	0.141594000	-2.120103000
1	-3.770015000	-0.902881000	0.993820000	7	-0.714960000	1.939610000	-0.132860000
1	-2.207275000	-0.724444000	3.003455000	6	-0.953871000	3.058884000	-0.148856000
1	-2.398018000	0.755799000	2.055989000	6	-1.259830000	4.466503000	-0.164031000
1	-0.094367000	-1.764179000	3.123354000	1	-0.688538000	4.954189000	-0.955381000
1	1.271737000	-1.082576000	2.244064000	1	-2.326776000	4.602606000	-0.348675000
1	-0.850335000	-2.992736000	1.228506000	1	-0.997348000	4.905956000	0.799531000
1	0.885335000	-3.175563000	1.186647000				

$[Co_2^{III}(O_2)(Pytacn)_2(CH_3CN)_2]^{4+}$ (3a) (G = -4715.181269, E_{ZPE} = -4715.111290), singlet

8	-0.512523000	0.471797000	-0.927665000	1	-0.422935000	-2.302983000	-1.063282000
7	-2.958479000	0.946193000	-1.946256000	1	-1.618930000	-3.600352000	-0.841776000
6	-4.305441000	1.472214000	-1.585952000	1	-3.986424000	-2.068508000	1.146623000
6	-5.097147000	0.434431000	-0.826587000	1	-5.499043000	-1.928755000	0.253033000
7	-4.259611000	-0.200368000	0.246146000	1	-4.631266000	1.413288000	1.557324000
6	-4.436109000	-1.675400000	0.238413000	1	-5.693346000	0.012027000	1.780847000
6	-3.781192000	-2.251079000	-0.995540000	1	-4.010741000	-0.052826000	2.341729000
7	-2.412436000	-1.654126000	-1.201453000	1	-1.782521000	4.786946000	1.345658000
6	-3.036801000	-0.130057000	-3.003942000	1	-3.424972000	4.332447000	1.866826000
6	-2.168930000	-1.318373000	-2.632416000	1	-2.024706000	3.958541000	2.903183000
6	-1.383548000	-2.560062000	-0.624721000	1	-4.148345000	2.358632000	-0.976070000
6	-1.298702000	-2.296494000	0.842848000	1	-1.166439000	1.693776000	-2.758902000
7	-1.584750000	-1.029466000	1.210350000	1	-2.645134000	2.518151000	-3.315467000
6	-1.471018000	-0.665401000	2.493645000	1	-2.012102000	2.817962000	-1.681990000
6	-1.083764000	-1.563419000	3.472525000	1	-2.708161000	0.279153000	-3.957564000
6	-0.821623000	-2.878062000	3.111362000	1	-4.075628000	-0.421990000	-3.127511000
6	-0.928408000	-3.247668000	1.777278000	1	-1.116994000	-1.070505000	-2.726596000
6	-2.137714000	2.069151000	-2.458700000	1	-2.395479000	-2.176927000	-3.268116000
6	-4.669526000	0.328631000	1.566723000	1	-4.841654000	1.771974000	-2.489452000
27	-2.250721000	0.067077000	-0.263875000	1	-3.690016000	-3.331878000	-0.906434000
7	-2.175133000	1.748111000	0.689077000	1	-4.376026000	-2.055150000	-1.880933000
6	-2.241407000	2.762415000	1.216179000	1	4.069389000	0.420309000	-3.132069000
6	-2.374008000	4.038184000	1.873339000	1	2.701138000	-0.283686000	-3.958501000
8	0.511597000	-0.478157000	-0.921674000	1	-5.974552000	0.897029000	-0.376476000
7	2.956339000	-0.947963000	-1.946927000	1	-5.457941000	-0.340024000	-1.496454000
6	4.304587000	-1.471893000	-1.588448000	1	2.386671000	2.172778000	-3.271299000
6	5.096448000	-0.432166000	-0.831930000	1	1.110689000	1.065417000	-2.725988000
7	4.260247000	0.202909000	0.241658000	1	4.839526000	-1.772199000	-2.492524000
6	4.434874000	1.678122000	0.231833000	1	4.149687000	-2.357677000	-0.977079000
6	3.776820000	2.251453000	-1.001537000	1	5.975345000	-0.893063000	-0.382979000
7	2.408383000	1.652465000	-1.204073000	1	5.454887000	0.341910000	-1.503482000
6	3.031206000	0.127091000	-3.006043000	1	2.012386000	-2.820356000	-1.678565000
6	2.162507000	1.314675000	-2.634157000	1	1.163833000	-1.698715000	-2.755713000
6	1.379560000	2.557905000	-0.626419000	1	2.642685000	-2.522189000	-3.313401000
6	1.298463000	2.296372000	0.841694000	1	5.697189000	-0.005908000	1.773803000
7	1.586064000	1.029961000	1.210084000	1	4.015612000	0.057520000	2.337898000
6	1.475354000	0.667361000	2.494070000	1	4.636352000	-1.408743000	1.553949000
6	1.089677000	1.566332000	3.472698000	1	5.497507000	1.932850000	0.244083000

6	0.826091000	2.880418000	3.110541000	1	3.986458000	2.071749000	1.140444000
6	0.929864000	3.248501000	1.775798000	1	3.684334000	3.332226000	-0.913577000
6	2.136018000	-2.072520000	-2.456531000	1	4.370248000	2.055202000	-1.887815000
6	4.673348000	-0.324038000	1.562045000	1	1.612950000	3.598179000	-0.845665000
27	2.250636000	-0.067580000	-0.264076000	1	0.418358000	2.298609000	-1.062374000
7	2.179083000	-1.747609000	0.691329000	1	0.730778000	4.260771000	1.453202000
6	2.245751000	-2.761389000	1.219381000	1	0.539244000	3.609618000	3.856633000
6	2.378687000	-4.036545000	1.877674000	1	1.009856000	1.234744000	4.498213000
1	-1.001535000	-1.230648000	4.497466000	1	1.705488000	-0.358830000	2.732356000
1	-0.533535000	-3.606505000	3.857715000	1	2.026459000	-3.956944000	2.906516000
1	-0.730517000	-4.260435000	1.455484000	1	1.789905000	-4.786579000	1.348760000
1	-1.699912000	0.361234000	2.731224000	1	3.430145000	-4.329095000	1.874191000

$[Co_2^{III}(O_2)(Pytacn)_2(CH_3CN)_2]^{4+}$ (3b) (G = -4715.188105, E_{ZPE} = -4715.118834), singlet

8	-0.471966000	0.515740000	-0.835909000	1	-1.051780000	-1.278879000	-2.459355000
7	-2.674667000	2.064980000	-0.657434000	1	-2.497666000	-2.181867000	-2.956243000
6	-3.786253000	2.481949000	0.241773000	1	-4.408573000	-1.953604000	0.074314000
6	-4.822958000	1.387514000	0.329242000	1	-5.839710000	-0.973645000	-0.232668000
7	-4.165742000	0.060485000	0.576869000	1	-3.990629000	0.472530000	2.640154000
6	-4.748902000	-0.991124000	-0.297500000	1	-5.430619000	-0.458118000	2.186383000
6	-4.313633000	-0.770460000	-1.731811000	1	-3.842205000	-1.243440000	2.213881000
7	-2.851041000	-0.416560000	-1.811718000	1	0.201337000	1.386110000	4.171482000
6	-3.127423000	1.987340000	-2.096342000	1	-0.980714000	2.712039000	4.039535000
6	-2.612226000	0.718883000	-2.745238000	1	-1.467422000	1.153385000	4.751230000
6	-2.038771000	-1.615529000	-2.146797000	1	-3.350711000	2.680237000	1.218582000
6	-1.884856000	-2.430622000	-0.903160000	1	-0.779545000	2.751827000	-1.232320000
7	-1.848672000	-1.708174000	0.234842000	1	-1.938836000	4.035654000	-0.813657000
6	-1.649931000	-2.321683000	1.405944000	1	-1.184660000	3.053316000	0.463333000
6	-1.490290000	-3.693838000	1.491710000	1	-2.757349000	2.857484000	-2.635836000
6	-1.554062000	-4.450730000	0.329179000	1	-4.211475000	2.035341000	-2.124313000
6	-1.754040000	-3.808485000	-0.885730000	1	-1.539954000	0.780640000	-2.899544000
6	-1.568686000	3.042077000	-0.550659000	1	-3.108545000	0.536588000	-3.700169000
6	-4.363999000	-0.317037000	1.994785000	1	-4.235470000	3.406965000	-0.127186000
27	-2.185451000	0.200360000	-0.068479000	1	-4.498652000	-1.667041000	-2.320933000
7	-1.553194000	0.782555000	1.653432000	1	-4.878136000	0.033642000	-2.192205000
6	-1.236503000	1.158392000	2.687331000	1	4.208718000	-2.036503000	-2.126691000
6	-0.846058000	1.630489000	3.992023000	1	2.753386000	-2.858763000	-2.634673000
8	0.471113000	-0.519315000	-0.832694000	1	-5.523122000	1.603942000	1.135028000
7	2.675219000	-2.065389000	-0.656449000	1	-5.406284000	1.328550000	-0.584636000
6	3.789191000	-2.480551000	0.240691000	1	3.103272000	-0.538430000	-3.700939000
6	4.824959000	-1.385065000	0.325222000	1	1.535774000	-0.782559000	-2.898199000
7	4.166900000	-0.058627000	0.573694000	1	4.238534000	-3.405400000	-0.128529000
6	4.747562000	0.993089000	-0.302143000	1	3.355943000	-2.678523000	1.218597000
6	4.310249000	0.770914000	-1.735578000	1	5.527228000	-1.600336000	1.129484000
7	2.847789000	0.415868000	-1.812829000	1	5.406016000	-1.325969000	-0.590108000
6	3.124713000	-1.988364000	-2.096449000	1	1.191073000	-3.056689000	0.469359000
6	2.608197000	-0.720302000	-2.745283000	1	0.778405000	-2.753803000	-1.224159000
6	2.034294000	1.614271000	-2.147105000	1	1.941064000	-4.036739000	-0.811735000
6	1.882238000	2.429829000	-0.903514000	1	5.434217000	0.460764000	2.181036000
7	1.847633000	1.707745000	0.234769000	1	3.845771000	1.245881000	2.210663000
6	1.651536000	2.321741000	1.406089000	1	3.995004000	-0.469923000	2.637366000
6	1.492781000	3.694002000	1.491716000	1	5.838495000	0.976803000	-0.239052000
6	1.554680000	4.450473000	0.328799000	1	4.406843000	1.955446000	0.069620000
6	1.752165000	3.807764000	-0.886265000	1	4.493681000	1.667101000	-2.325781000
6	1.570801000	-3.043873000	-0.546239000	1	4.874604000	-0.033201000	-2.196134000
6	4.367325000	0.319441000	1.991132000	1	2.491589000	2.180490000	-2.957530000
27	2.185410000	-0.200638000	-0.068212000	1	1.046886000	1.277094000	-2.457752000
7	1.555992000	-0.782232000	1.654963000	1	1.804369000	4.359474000	-1.814613000
6	1.239398000	-1.157633000	2.689049000	1	1.449548000	5.526819000	0.366251000
6	0.848581000	-1.629349000	3.993766000	1	1.335811000	4.152713000	2.457722000
1	-1.331178000	-4.152136000	2.457562000	1	1.634180000	1.697753000	2.284983000
1	-1.448262000	-5.527005000	0.366763000	1	1.469665000	-1.152021000	4.753065000
1	-1.807540000	-4.360493000	-1.813829000	1	-0.198860000	-1.384813000	4.172810000
1	-1.630799000	-1.697376000	2.284573000	1	0.983212000	-2.710880000	4.041671000

adduct c (G = -2299.979429, E_{ZPE} = -2299.929469), doublet

7	2.229811000	0.818647000	-0.053961000	1	-0.465316000	-2.624171000	-0.089720000
6	3.086539000	-0.399630000	-0.129137000	1	1.773143000	-1.950367000	1.832931000
6	2.505401000	-1.376800000	-1.136493000	1	0.112675000	-2.367890000	2.179886000
7	1.027633000	-1.513197000	-1.003851000	1	1.589398000	2.321886000	1.224555000
6	0.584925000	-2.409532000	0.093142000	1	3.168047000	1.660504000	1.672048000
6	0.753112000	-1.812724000	1.492841000	1	1.013832000	1.024551000	3.086395000
7	0.418924000	-0.352906000	1.573764000	1	2.180706000	-0.233809000	2.751095000
6	2.167295000	1.401804000	1.314495000	1	-1.167451000	-0.733107000	2.957781000
6	1.469945000	0.444652000	2.286682000	1	-1.979765000	-0.009454000	-2.272797000
6	-0.953802000	-0.117231000	2.081711000	1	-4.365208000	-0.673123000	-1.966807000
6	-1.965782000	-0.355074000	0.994852000	1	-5.176316000	-1.177910000	0.346392000
7	-1.539173000	-0.107096000	-0.261483000	1	-3.583751000	-0.962329000	2.255100000
6	-2.387514000	-0.219616000	-1.293351000	1	2.662757000	1.373392000	-2.034722000
6	-3.707589000	-0.592282000	-1.112638000	1	1.918115000	2.645250000	-1.045751000
6	-4.152847000	-0.870324000	0.175040000	1	3.632527000	2.224195000	-0.808393000
6	-3.270937000	-0.751225000	1.241605000	1	0.694927000	-1.272692000	-3.067647000
6	2.640877000	1.830245000	-1.046875000	1	0.912824000	-2.963390000	-2.557243000
6	0.475209000	-1.996796000	-2.285138000	1	-0.602057000	-2.114009000	-2.199685000
1	3.153872000	-0.840993000	0.858218000	1	-1.023949000	0.930083000	2.380432000
1	4.100549000	-0.121102000	-0.421847000	27	0.356340000	0.328041000	-0.348769000
1	2.991154000	-2.352415000	-1.042396000	8	-1.491451000	3.393779000	-1.248980000
1	2.689883000	-1.006186000	-2.143423000	8	-1.435045000	3.500293000	-0.047604000
1	1.130815000	-3.357528000	0.053364000				

TS_1 (G = -2299.965256, E_{ZPE} = -2299.917828), doublet

7	2.262476000	0.575009000	-0.325568000	1	-0.730109000	-2.370288000	0.863081000
6	3.002158000	-0.649992000	0.112882000	1	1.567903000	-1.109427000	2.389604000
6	2.349461000	-1.892132000	-0.466161000	1	-0.105618000	-1.253252000	2.864590000
7	0.865484000	-1.850088000	-0.357825000	1	1.934916000	2.552184000	0.242369000
6	0.333707000	-2.181726000	0.986145000	1	3.311381000	1.815354000	1.053137000
6	0.552828000	-1.075274000	2.014460000	1	0.921774000	2.179769000	2.291694000
7	0.299854000	0.314491000	1.478912000	1	1.947957000	0.826427000	2.714762000
6	2.286760000	1.638902000	0.717310000	1	-1.326482000	0.527153000	2.852040000
6	1.379797000	1.273802000	1.903426000	1	-1.931838000	-0.724437000	-2.294483000
6	-1.072013000	0.781227000	1.822273000	1	-4.378015000	-1.047528000	-1.920871000
6	-2.066749000	0.210140000	0.853438000	1	-5.312635000	-0.564844000	0.349914000
7	-1.575918000	-0.072510000	-0.370916000	1	-3.776651000	0.254060000	2.137310000
6	-2.392346000	-0.513009000	-1.339011000	1	2.782030000	0.270177000	-2.341707000
6	-3.746053000	-0.692156000	-1.119064000	1	2.196780000	1.902174000	-1.966687000
6	-4.259737000	-0.421597000	0.144548000	1	3.836341000	1.414701000	-1.477777000
6	-3.409719000	0.034380000	1.144076000	1	0.571570000	-2.426668000	-2.359183000
6	2.806206000	1.074073000	-1.608001000	1	0.628781000	-3.784277000	-1.210851000
6	0.279793000	-2.757731000	-1.363990000	1	-0.804113000	-2.741936000	-1.285301000
1	3.020927000	-0.677600000	1.195925000	1	-1.094575000	1.867779000	1.737180000
1	4.039779000	-0.584966000	-0.218662000	27	0.354179000	0.153627000	-0.506744000
1	2.745653000	-2.787791000	0.021100000	8	-1.074648000	2.999192000	-1.598673000
1	2.580176000	-1.958702000	-1.528022000	8	-0.451539000	2.704826000	-0.598683000
1	0.792893000	-3.099910000	1.365597000				

$[Co^{III}(\eta^1\text{-}O_2)(Pytacn)]^{2+}$ (G = -2299.977184, E_{ZPE} = -2299.932392), doublet

7	-2.302482000	-0.402523000	-0.302073000	1	1.046110000	2.041514000	1.205876000
6	-2.876271000	0.818846000	0.355389000	1	-1.324662000	0.783463000	2.619553000
6	-2.100080000	2.042686000	-0.073079000	1	0.373287000	0.655863000	3.020437000
7	-0.622045000	1.810805000	-0.020039000	1	-2.208903000	-2.468428000	-0.020157000
6	-0.026324000	1.930868000	1.339824000	1	-3.433535000	-1.674224000	0.971087000
6	-0.332520000	0.713279000	2.194157000	1	-1.014806000	-2.495198000	1.955053000
7	-0.253148000	-0.583748000	1.404005000	1	-1.873134000	-1.136379000	2.656048000
6	-2.414605000	-1.593686000	0.589403000	1	1.337768000	-1.243869000	2.663191000
6	-1.407983000	-1.504394000	1.746783000	1	2.007494000	0.902179000	-2.175835000
6	1.073837000	-1.252936000	1.606838000	1	4.478837000	0.919818000	-1.839143000
6	2.111680000	-0.592486000	0.751634000	1	5.404816000	-0.049886000	0.272790000
7	1.631504000	-0.037432000	-0.377499000	1	3.832265000	-1.040938000	1.939283000
6	2.461509000	0.486883000	-1.287236000	1	-2.835563000	0.228653000	-2.239263000
6	3.830737000	0.491129000	-1.087892000	1	-2.537980000	-1.515501000	-2.084117000
6	4.338836000	-0.051302000	0.086733000	1	-4.036598000	-0.813269000	-1.437891000

6	3.469359000	-0.602542000	1.020084000	1	-0.291311000	2.570328000	-1.956452000
6	-2.970468000	-0.643329000	-1.602228000	1	-0.265707000	3.795590000	-0.664969000
6	0.026448000	2.777972000	-0.936844000	1	1.105881000	2.691558000	-0.863808000
1	-2.856855000	0.681113000	1.429585000	1	0.976715000	-2.290750000	1.288679000
1	-3.923122000	0.920245000	0.068773000	27	-0.331037000	-0.147772000	-0.500690000
1	-2.360901000	2.904161000	0.544688000	8	0.075385000	-1.701690000	-2.361325000
1	-2.336239000	2.279075000	-1.108256000	8	-0.101063000	-1.938102000	-1.103149000
1	-0.402142000	2.827419000	1.837126000				

TS_2 (G = -2299.973464, E_{ZPE} = -2299.928658), doublet

7	-2.308490000	-0.391683000	-0.284444000	1	1.079426000	2.018701000	1.221984000
6	-2.859584000	0.822543000	0.404983000	1	-1.265332000	0.749252000	2.664881000
6	-2.082609000	2.047816000	-0.017673000	1	0.440988000	0.600146000	3.016139000
7	-0.605010000	1.809678000	0.015068000	1	-2.198067000	-2.461274000	-0.037221000
6	0.008755000	1.906663000	1.368494000	1	-3.429130000	-1.694836000	0.967360000
6	-0.286439000	0.676508000	2.210282000	1	-1.026485000	-2.511318000	1.959071000
7	-0.241631000	-0.610416000	1.399952000	1	-1.871404000	-1.139857000	2.650943000
6	-2.410867000	-1.598121000	0.586868000	1	1.347959000	-1.327563000	2.628253000
6	-1.407272000	-1.516708000	1.744783000	1	2.018227000	0.922900000	-2.167876000
6	1.075768000	-1.303858000	1.574025000	1	4.486274000	0.934376000	-1.823440000
6	2.114322000	-0.630759000	0.729986000	1	5.407770000	-0.071589000	0.273465000
7	1.634636000	-0.054202000	-0.389915000	1	3.831066000	-1.096734000	1.915568000
6	2.467922000	0.488432000	-1.286283000	1	-2.874512000	0.270418000	-2.203168000
6	3.836699000	0.490146000	-1.082547000	1	-2.600681000	-1.479552000	-2.074612000
6	4.342518000	-0.072737000	0.083076000	1	-4.072578000	-0.763085000	-1.386662000
6	3.470755000	-0.643188000	1.002624000	1	-0.294818000	2.590524000	-1.916490000
6	-3.008059000	-0.606699000	-1.573012000	1	-0.244669000	3.800238000	-0.611627000
6	0.037514000	2.783986000	-0.898661000	1	1.117284000	2.689946000	-0.841386000
1	-2.820296000	0.666721000	1.476315000	1	0.962269000	-2.331551000	1.228856000
1	-3.911126000	0.937556000	0.141110000	27	-0.329402000	-0.145938000	-0.502225000
1	-2.332732000	2.903046000	0.613134000	8	-0.040524000	-1.553977000	-2.447687000
1	-2.329914000	2.298033000	-1.047095000	8	-0.124498000	-1.908310000	-1.207078000
1	-0.358537000	2.796325000	1.884386000				

[$Co^{III}(\eta^2\text{-}O_2)$(Pytacn)]$^{2+}$ (G = -2299.981910, E_{ZPE} = -2299.937988), doublet

7	2.282782000	0.105421000	-0.509635000	1	-1.139283000	-0.293309000	2.265497000
6	2.820083000	-0.080032000	0.877338000	1	1.159826000	1.676771000	2.294287000
6	2.058989000	-1.195566000	1.548452000	1	-0.558626000	2.000842000	2.335670000
7	0.577841000	-1.045421000	1.350775000	1	1.984279000	1.563223000	-1.970596000
6	-0.073174000	-0.087658000	2.295131000	1	3.332859000	1.917823000	-0.887047000
6	0.202911000	1.352577000	1.905608000	1	1.016086000	3.219716000	-0.621484000
7	0.214537000	1.527580000	0.402709000	1	1.898219000	2.754144000	0.817863000
6	2.310905000	1.535731000	-0.933185000	1	-1.386543000	2.936137000	0.515286000
6	1.382874000	2.367463000	-0.055522000	1	-2.014515000	-2.237472000	-0.672308000
6	-1.081086000	2.082293000	-0.089145000	1	-4.476804000	-1.974546000	-0.491839000
6	-2.114557000	1.001176000	-0.106803000	1	-5.411536000	0.296670000	-0.008286000
7	-1.626517000	-0.235363000	-0.330010000	1	-3.836603000	2.222338000	0.220393000
6	-2.461184000	-1.273546000	-0.475078000	1	3.005594000	-1.765290000	-1.174594000
6	-3.831362000	-1.115983000	-0.372647000	1	2.681825000	-0.591999000	-2.470110000
6	-4.344299000	0.148103000	-0.107525000	1	4.107815000	-0.394518000	-1.435493000
6	-3.474602000	1.222857000	0.023411000	1	0.342941000	-3.062443000	0.763436000
6	3.066095000	-0.718317000	-1.462562000	1	0.250162000	-2.775944000	2.514290000
6	-0.030210000	-2.389859000	1.531934000	1	-1.111354000	-2.324275000	1.477478000
1	2.735283000	0.851479000	1.422102000	1	-0.927321000	2.425724000	-1.113248000
1	3.880594000	-0.325617000	0.827902000	27	0.331050000	-0.257178000	-0.432881000
1	2.279415000	-1.241329000	2.615715000	8	0.306319000	-1.535099000	-1.855603000
1	2.332078000	-2.147197000	1.097527000	8	0.182079000	-0.348841000	-2.371614000
1	0.281274000	-0.276565000	3.309767000				

[$Co^{III}_2(O_2)$(Pytacn)$_2$(CH_3CN)$_2$]$^{4+}$ (3c) (G = -4715.168399, E_{ZPE} = -4715.092331), singlet

7	-2.963808000	-2.076099000	0.902443000	1	4.250913000	-3.003300000	-2.045787000
6	-3.595722000	-2.850886000	-0.213946000	1	5.170305000	-0.332901000	-1.952193000
6	-2.893424000	-2.522801000	-1.505936000	1	5.756882000	-1.617961000	-0.912086000
7	-2.745250000	-1.045882000	-1.691822000	1	4.749003000	1.444424000	-1.010494000

6	-3.994737000	-0.356308000	-2.134475000	1	5.661818000	1.205401000	0.475924000
6	-4.968511000	-0.154336000	-0.995022000	1	4.897900000	3.473116000	1.385752000
7	-4.256510000	0.193500000	0.286554000	1	2.990958000	4.780147000	2.328004000
6	-3.980392000	-1.692241000	1.923400000	1	0.672855000	3.853429000	2.119449000
6	-4.866960000	-0.532433000	1.449842000	1	0.383690000	1.622012000	1.019419000
6	-4.241812000	1.663556000	0.502984000	1	-0.258196000	1.358042000	-1.472038000
6	-3.178027000	2.291706000	-0.339602000	1	-0.253278000	3.702782000	-2.341076000
7	-2.104042000	1.518956000	-0.605694000	1	-2.244249000	5.153878000	-1.870256000
6	-1.086112000	2.029940000	-1.312820000	1	-4.140708000	4.183999000	-0.562953000
6	-1.098532000	3.333468000	-1.777279000	1	-5.220306000	2.098095000	0.297513000
6	-2.202138000	4.133022000	-1.513243000	1	-4.007196000	1.850028000	1.549978000
6	-3.257644000	3.600801000	-0.785621000	1	-5.855855000	-0.880455000	1.163212000
6	-1.930819000	-2.913287000	1.553439000	1	-4.994545000	0.166537000	2.271357000
6	-1.715526000	-0.840253000	-2.742199000	1	-5.666783000	0.643049000	-1.248174000
27	-2.301717000	-0.342674000	0.111231000	1	-5.556773000	-1.047221000	-0.828751000
8	-0.555083000	-1.105800000	-0.004829000	1	-4.464785000	-0.930510000	-2.935312000
7	-1.891493000	0.380996000	1.863608000	1	-3.690704000	0.601637000	-2.546106000
6	-1.596023000	0.866759000	2.857153000	1	-1.668291000	0.208290000	-3.014966000
6	-1.193820000	1.466385000	4.103398000	1	-0.756485000	-1.162082000	-2.362048000
7	2.580084000	-2.152695000	-1.066214000	1	-1.992278000	-1.419203000	-3.626282000
6	2.757555000	-3.175097000	0.016011000	1	-3.422224000	-2.947332000	-2.361006000
6	1.989333000	-2.740017000	1.236748000	1	-1.883496000	-2.925476000	-1.485970000
7	2.236909000	-1.298861000	1.558515000	1	-4.653081000	-2.619544000	-0.253430000
6	3.548493000	-1.037421000	2.227956000	1	-3.513846000	-3.917708000	-0.004686000
6	4.690747000	-1.057528000	1.242147000	1	-2.412502000	-3.783478000	2.004902000
7	4.297819000	-0.361624000	-0.030369000	1	-1.211399000	-3.239020000	0.809784000
6	3.830737000	-2.011525000	-1.874976000	1	-1.425011000	-2.339332000	2.322321000
6	4.866122000	-1.074450000	-1.220126000	1	-4.584924000	-2.567372000	2.168171000
6	4.683343000	1.078870000	0.013562000	1	-3.436810000	-1.402223000	2.816548000
6	3.632927000	1.884324000	0.716936000	1	3.706879000	-1.774891000	3.016562000
7	2.383637000	1.387865000	0.650111000	1	3.470654000	-0.059219000	2.694857000
6	1.349401000	2.084451000	1.133979000	1	4.985713000	-2.070735000	1.003767000
6	1.529093000	3.315607000	1.737625000	1	5.562474000	-0.565092000	1.672681000
6	2.817542000	3.826402000	1.846631000	1	0.222324000	-0.942621000	1.960676000
6	3.883521000	3.103078000	1.327568000	1	1.166402000	-1.528107000	3.359554000
6	1.468487000	-2.566389000	-1.954628000	1	1.343258000	0.146960000	2.816402000
6	1.163851000	-0.870586000	2.487227000	1	-2.046150000	1.971883000	4.559624000
27	2.288106000	-0.379919000	-0.190614000	1	-0.827101000	0.690030000	4.776567000
8	0.421839000	-0.210126000	-0.521677000	1	-0.399177000	2.189230000	3.913643000
7	2.387651000	0.554826000	-1.921618000	1	1.090541000	1.894260000	-4.418613000
6	2.275326000	1.188081000	-2.868856000	1	2.334929000	3.027605000	-3.832237000
6	2.117392000	1.983285000	-4.060547000	1	2.803564000	1.629094000	-4.831232000
1	0.569012000	-2.697916000	-1.361343000	1	2.385586000	-4.138503000	-0.333377000
1	1.298729000	-1.795382000	-2.698853000	1	3.813928000	-3.301179000	0.217504000
1	1.734172000	-3.502668000	-2.450765000	1	0.923837000	-2.818480000	1.042582000
1	3.539812000	-1.603171000	-2.837512000	1	2.236450000	-3.355359000	2.103608000

$[Co^{III}_2(O_2)(Pytacn)_2(CH_3CN)_2]^{4+}$ (3d) (G = -4715.159878, E_{ZPE} = -4715.087846), singlet

7	1.935520000	1.875350000	1.407260000	1	-3.135531000	-3.053177000	2.639807000
6	1.965375000	3.144851000	0.609248000	1	-4.790020000	-0.750727000	2.367373000
6	1.521217000	2.856735000	-0.800537000	1	-5.140780000	-2.325099000	1.676629000
7	2.206478000	1.647876000	-1.357992000	1	-5.129996000	0.793110000	1.109651000
6	3.613160000	1.894961000	-1.799079000	1	-6.090456000	-0.008672000	-0.126788000
6	4.567434000	1.973247000	-0.631704000	1	-6.254765000	2.154533000	-1.461473000
7	4.234958000	0.938200000	0.408417000	1	-5.047224000	3.760890000	-2.944021000
6	3.040757000	1.866682000	2.410932000	1	-2.548083000	3.627885000	-3.076122000
6	4.397188000	1.498746000	1.788730000	1	-1.383731000	1.854341000	-1.750194000
6	5.057233000	-0.286298000	0.208065000	1	1.401797000	-1.726081000	-1.879461000
6	4.453487000	-1.151850000	-0.852782000	1	2.581294000	-3.439667000	-3.269417000
7	3.117915000	-1.051964000	-0.991211000	1	5.073367000	-3.613081000	-3.078955000
6	2.469834000	-1.862176000	-1.834562000	1	6.260752000	-2.104949000	-1.480931000
6	3.138778000	-2.802852000	-2.596948000	1	6.089023000	-0.024683000	-0.026099000
6	4.520800000	-2.896193000	-2.485620000	1	5.059276000	-0.851224000	1.139020000
6	5.186976000	-2.059594000	-1.600457000	1	5.062352000	2.357806000	1.743329000
6	0.642794000	1.772911000	2.117315000	1	4.873904000	0.749629000	2.413782000
6	1.440278000	1.224918000	-2.556046000	1	5.588439000	1.819496000	-0.980319000
27	2.302660000	0.354462000	0.146070000	1	4.537466000	2.950110000	-0.167696000
8	0.580090000	-0.399086000	-0.266232000	1	3.652444000	2.815177000	-2.384842000

7	2.456294000	-0.887755000	1.633862000	1	3.881963000	1.070046000	-2.453214000
6	2.558238000	-1.680488000	2.453261000	1	1.906911000	0.357998000	-3.010988000
6	2.663136000	-2.674994000	3.490335000	1	0.428518000	0.989728000	-2.260610000
7	-1.938090000	-1.938643000	1.303908000	1	1.439622000	2.045177000	-3.277803000
6	-1.906781000	-3.161300000	0.432095000	1	1.698691000	3.711628000	-1.455372000
6	-1.462906000	-2.773499000	-0.952713000	1	0.459669000	2.627042000	-0.801292000
7	-2.196102000	-1.566045000	-1.445768000	1	2.961335000	3.568237000	0.647391000
6	-3.601147000	-1.840945000	-1.878356000	1	1.295374000	3.872240000	1.068126000
6	-4.539851000	-1.977711000	-0.703700000	1	0.540758000	2.613711000	2.806927000
7	-4.233987000	-0.948768000	0.348011000	1	-0.150637000	1.774120000	1.381171000
6	-3.061465000	-2.023592000	2.289157000	1	0.610100000	0.840549000	2.671916000
6	-4.401333000	-1.527385000	1.716616000	1	3.083062000	2.844698000	2.892487000
6	-5.074904000	0.264999000	0.158678000	1	2.776553000	1.135641000	3.167677000
6	-4.452166000	1.188102000	-0.839997000	1	-3.621518000	-2.744577000	-2.490279000
7	-3.112848000	1.110674000	-0.948208000	1	-3.901883000	-1.005300000	-2.505168000
6	-2.454208000	1.974932000	-1.728087000	1	-4.469123000	-2.959534000	-0.254300000
6	-3.114876000	2.948195000	-2.455414000	1	-5.569698000	-1.856637000	-1.039337000
6	-4.500670000	3.018994000	-2.376413000	1	-0.447442000	-0.825741000	-2.345998000
6	-5.177861000	2.127716000	-1.555862000	1	-1.457135000	-1.849232000	-3.395704000
6	-0.661109000	-1.842233000	2.043861000	1	-1.953102000	-0.187312000	-3.034919000
6	-1.460556000	-1.066158000	-2.633653000	1	3.701568000	-2.754388000	3.815633000
27	-2.305079000	-0.350872000	0.122172000	1	2.038396000	-2.383690000	4.336058000
8	-0.579303000	0.421817000	-0.246319000	1	2.328157000	-3.638764000	3.104252000
7	-2.467354000	0.799093000	1.678660000	1	-1.762053000	2.692142000	4.051960000
6	-2.599194000	1.511461000	2.564850000	1	-3.303169000	3.286648000	3.384063000
6	-2.748597000	2.398408000	3.690294000	1	-3.291511000	1.886089000	4.486081000
1	0.142558000	-1.782867000	1.321845000	1	-1.209596000	-3.884604000	0.855605000
1	-0.661929000	-0.941825000	2.649895000	1	-2.882522000	-3.629617000	0.431301000
1	-0.547134000	-2.717101000	2.687842000	1	-0.413434000	-2.496195000	-0.928162000
1	-2.788021000	-1.404848000	3.137913000	1	-1.597701000	-3.595505000	-1.658015000

$[Co^{III}_2(O_2)(Pytacn)_2(CH_3CN)_2]^{4+}$ (3e) (G = -4715.179753, E_{ZPE} = -4715.105685), singlet

7	2.684941000	-1.937227000	-1.028370000	6	-4.648247000	0.913039000	-1.505551000
6	3.868294000	-2.555143000	-0.365745000	6	-4.491725000	-1.383863000	-0.618555000
6	4.938271000	-1.516674000	-0.128876000	6	-3.469611000	-2.237302000	0.061991000
7	4.341745000	-0.273329000	0.468338000	7	-2.266951000	-1.659382000	0.243937000
6	4.872393000	0.944651000	-0.201331000	6	-1.245652000	-2.368809000	0.731884000
6	4.297856000	1.049655000	-1.597585000	6	-1.391601000	-3.697234000	1.088825000
7	2.824611000	0.737369000	-1.597995000	6	-2.636287000	-4.297312000	0.942805000
6	2.990380000	-1.534750000	-2.452983000	6	-3.688614000	-3.558399000	0.417753000
6	2.446826000	-0.151245000	-2.732013000	6	-1.449036000	2.841261000	-1.379281000
6	2.013302000	1.979864000	-1.572617000	6	-1.550755000	0.162630000	2.690177000
6	1.952313000	2.489470000	-0.170024000	1	-3.981930000	2.967049000	0.677335000
7	2.052741000	1.539330000	0.779417000	1	-2.550824000	3.942080000	0.465800000
6	1.902341000	1.867210000	2.067804000	1	-2.580954000	2.653802000	2.663549000
6	1.657937000	3.170862000	2.462213000	1	-1.159857000	2.362082000	1.648930000
6	1.577082000	4.162915000	1.493265000	1	-4.210986000	0.954778000	2.926758000
6	1.729231000	3.816381000	0.157809000	1	-3.828633000	-0.676932000	2.382767000
6	1.572636000	-2.914965000	-1.027578000	1	-5.155254000	1.540564000	0.791232000
6	4.673741000	-0.219932000	1.910913000	1	-5.737817000	-0.072941000	1.107393000
1	4.254874000	-3.371646000	-0.980112000	1	-3.371363000	2.192368000	-2.660482000
1	3.522639000	-2.971898000	0.577568000	1	-4.332701000	3.081024000	-1.490278000
1	5.444836000	-1.257716000	-1.053520000	1	-4.564176000	0.322101000	-2.411613000
1	5.696722000	-1.914441000	0.543812000	1	-5.696967000	1.181186000	-1.377297000
1	5.963359000	0.904383000	-0.246123000	1	-5.504129000	-1.644352000	-0.310834000
1	4.593941000	1.802038000	0.405004000	1	-0.315149000	-1.836260000	0.799315000
1	4.788839000	0.357378000	-2.273379000	1	-0.543132000	-4.241060000	1.479138000
1	4.452341000	2.051074000	-1.995257000	1	-2.785833000	-5.330650000	1.227834000
1	2.541972000	-2.256344000	-3.133606000	1	-4.668896000	-3.993017000	0.277774000
1	4.064062000	-1.575443000	-2.608811000	1	-0.628828000	2.913443000	-0.676943000
1	1.362324000	-0.168511000	-2.765629000	1	-1.139473000	2.262153000	-2.243213000
1	2.836238000	0.245089000	-3.671536000	1	-1.753621000	3.841051000	-1.697871000
1	2.411497000	2.720015000	-2.265791000	1	-0.535771000	0.341855000	2.357490000
1	1.977468000	1.069077000	2.789129000	1	-1.720612000	0.629657000	3.662970000
1	1.539327000	3.395584000	3.512824000	1	-1.733452000	-0.902801000	2.775849000
1	1.395681000	5.192387000	1.773255000	1	-4.414358000	-1.565378000	-1.690432000
1	1.666793000	4.556127000	-0.628433000	8	0.523197000	-0.321676000	-0.605167000
1	1.364172000	-3.221017000	-0.008178000	27	2.323753000	-0.251364000	0.017067000

1	0.690035000	-2.455004000	-1.459052000	27	-2.208792000	0.239711000	-0.200651000
1	1.865533000	-3.790116000	-1.611904000	8	-0.369349000	0.580887000	0.069658000
1	4.346315000	-1.134340000	2.396164000	7	-1.907151000	-0.234717000	-2.047469000
1	5.755343000	-0.119947000	2.028967000	6	-1.573190000	-0.569841000	-3.089178000
1	4.186841000	0.633133000	2.373603000	6	-1.138196000	-0.980868000	-4.400393000
1	1.004147000	1.711823000	-1.874943000	1	-0.654266000	-0.141329000	-4.901433000
7	-2.588361000	2.171228000	-0.714079000	1	-0.429348000	-1.804732000	-4.305857000
6	-2.908033000	2.915554000	0.550752000	1	-1.998296000	-1.307203000	-4.987010000
6	-2.238320000	2.236056000	1.714970000	7	1.844244000	-1.182065000	1.636522000
7	-2.483113000	0.761409000	1.700774000	6	1.515366000	-1.683724000	2.611810000
6	-3.875879000	0.363827000	2.072235000	6	1.070420000	-2.305541000	3.832438000
6	-4.839340000	0.513221000	0.914918000	1	0.669627000	-1.540840000	4.499792000
7	-4.211032000	0.056055000	-0.368316000	1	0.290235000	-3.032090000	3.601636000
6	-3.762851000	2.166031000	-1.647609000	1	1.908710000	-2.809191000	4.315738000

$[Co^{III}_2(O_2)(Pytacn)_2(CH_3CN)_2]^{4+}$ (3f) (G = -4715.178959, E_{ZPE} = -4715.108262), singlet

8	-0.656249000	0.668379000	-0.727256000	6	4.389006000	1.917286000	-0.740428000
7	-2.807489000	2.178687000	-0.034637000	6	4.295063000	0.569160000	1.341133000
6	-3.858282000	2.379717000	1.003033000	6	3.387674000	-0.433323000	1.986526000
6	-4.896221000	1.288855000	0.908543000	7	2.249155000	-0.697254000	1.319165000
7	-4.230941000	-0.053612000	0.822842000	6	1.341301000	-1.530817000	1.833921000
6	-4.880159000	-0.900713000	-0.212849000	6	1.534091000	-2.149627000	3.054621000
6	-4.542410000	-0.370630000	-1.592782000	6	2.707786000	-1.893775000	3.753892000
7	-3.087419000	0.008712000	-1.690772000	6	3.646841000	-1.025340000	3.212953000
6	-3.349685000	2.419398000	-1.424731000	6	1.155727000	1.809200000	-2.701905000
6	-2.899897000	1.322755000	-2.366014000	6	1.834831000	-2.673336000	-1.127039000
6	-2.292826000	-1.067673000	-2.340283000	1	4.054237000	0.343868000	-3.112178000
6	-2.041174000	-2.139497000	-1.330977000	1	2.657184000	0.555632000	-4.134284000
7	-1.983379000	-1.706362000	-0.055879000	1	3.045711000	-1.868420000	-3.428587000
6	-1.719549000	-2.573260000	0.928854000	1	1.442951000	-1.218566000	-3.048075000
6	-1.496138000	-3.915734000	0.678069000	1	4.525157000	-2.423023000	-1.697917000
6	-1.559645000	-4.373160000	-0.631780000	1	3.999965000	-2.296579000	-0.021753000
6	-1.840425000	-3.471812000	-1.649673000	1	5.230365000	-0.132865000	-1.755092000
6	-1.695892000	3.120049000	0.225472000	1	5.767389000	-0.717167000	-0.201040000
6	-4.318834000	-0.719852000	2.141168000	1	2.772426000	3.152976000	-1.454823000
1	-4.319415000	3.362629000	0.880177000	1	3.847939000	2.619355000	-2.739521000
1	-3.361695000	2.353784000	1.970727000	1	4.365107000	2.662020000	0.048932000
1	-5.529630000	1.426552000	0.037548000	1	5.398949000	1.900060000	-1.145528000
1	-5.548276000	1.318532000	1.780527000	1	5.339560000	0.371345000	1.581991000
1	-5.963638000	-0.906842000	-0.070655000	1	0.465744000	-1.683200000	1.228499000
1	-4.519910000	-1.916691000	-0.080554000	1	0.777626000	-2.817965000	3.441202000
1	-5.134456000	0.509776000	-1.822025000	1	2.892535000	-2.367891000	4.709113000
1	-4.771648000	-1.117951000	-2.350456000	1	4.573322000	-0.807070000	3.726432000
1	-2.995953000	3.384038000	-1.784695000	1	0.479860000	1.013008000	-2.994535000
1	-4.432254000	2.477294000	-1.372460000	1	0.670494000	2.423837000	-1.952926000
1	-1.839813000	1.417039000	-2.576708000	1	1.418237000	2.415218000	-3.572390000
1	-2.804664000	-1.447378000	-3.223999000	1	0.791610000	-2.427256000	-1.286311000
1	-1.680732000	-2.176072000	1.931285000	1	2.142948000	-3.460436000	-1.818766000
1	-1.279194000	-4.581488000	1.501407000	1	1.984649000	-3.023023000	-0.111564000
1	-1.395807000	-5.418610000	-0.858162000	1	4.045474000	1.554039000	1.733086000
1	-1.904083000	-3.788461000	-2.681538000	27	2.110498000	0.199164000	-0.414959000
1	-1.317010000	2.953719000	1.227333000	27	-2.306993000	0.228713000	0.096692000
1	-0.906537000	2.949165000	-0.496935000	8	0.332160000	-0.342648000	-0.751369000
1	-2.066546000	4.144321000	0.145441000	1	-3.462091000	1.352391000	-3.301160000
1	-3.858042000	-0.091129000	2.898226000	7	-1.479366000	0.432884000	1.823700000
1	-5.368324000	-0.882169000	2.398723000	6	-0.868094000	0.617770000	2.773887000
1	-3.812824000	-1.679294000	2.108841000	6	-0.082112000	0.867645000	3.955729000
1	-1.335077000	-0.642865000	-2.634523000	1	-0.436958000	1.777510000	4.441618000
7	2.388207000	1.215986000	-2.132330000	1	-0.176061000	0.027457000	4.644228000
6	2.974826000	0.265127000	-3.132431000	1	0.963973000	0.988229000	3.671379000
6	2.504968000	-1.132898000	-2.830158000	7	1.645108000	1.813806000	0.536651000
7	2.656281000	-1.462318000	-1.379029000	6	1.470623000	2.741766000	1.182907000
6	4.060520000	-1.760672000	-0.964895000	6	1.264837000	3.912629000	1.997967000
6	4.882068000	-0.501420000	-0.799191000	1	2.228454000	4.264347000	2.370086000
7	4.083166000	0.583661000	-0.134136000	1	0.797680000	4.697352000	1.401545000
6	3.355497000	2.311656000	-1.816370000	1	0.620002000	3.662236000	2.840981000

9.2. Computed Raman spectra for 3a and 3b

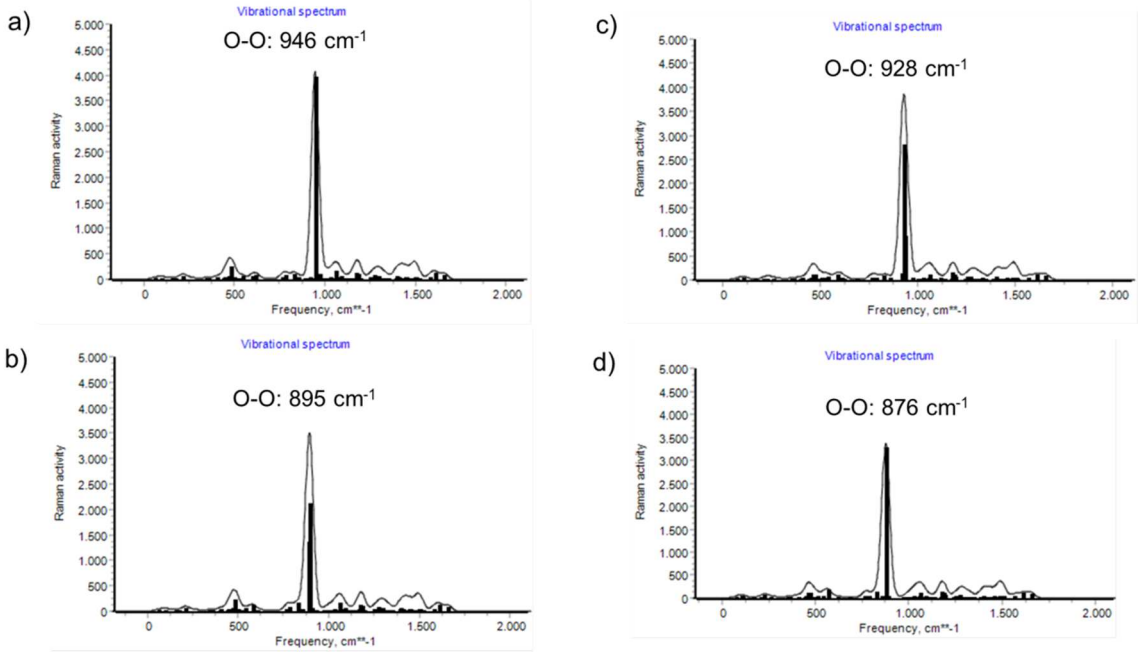


Figure S25. Calculated non-resonant Raman spectra of **3a** (a), ^{18}O-labeled **3a** (b), **3b** (c) and ^{18}O-labeled **3c** (d). The predicted O-O bond stretching frequencies shown in this figure need to be corrected by a factor of 0.96 (see computational details, section 1.5).[11]

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