Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Low-Spin to Low-Spin Valence Tautomeric Transition in Cobalt Bis-Dioxolenes

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UV/Vis

Titration with TBACN

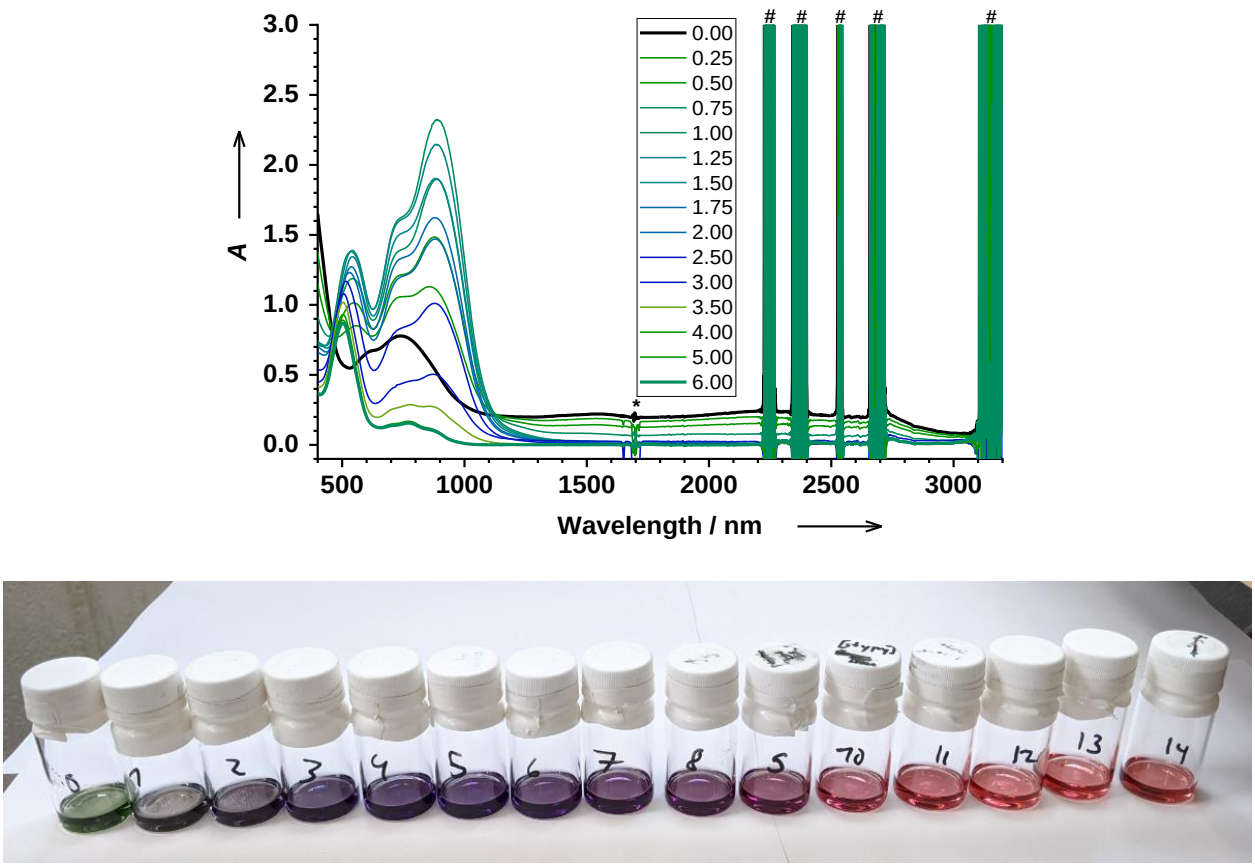


Figure S1: Top: Electronic absorption spectrum of **[Co(ᵗBu-dioxolene)₂(stypy)₂] (1)** in DCM (c = 5 • 10^{-4} M) with different amounts of TBACN. (*****) is a spectrometer artefact, (#) are due to solvent overtones. Bottom: Color gradient of titration solutions used (0 to 6 equivalents of TBACN).

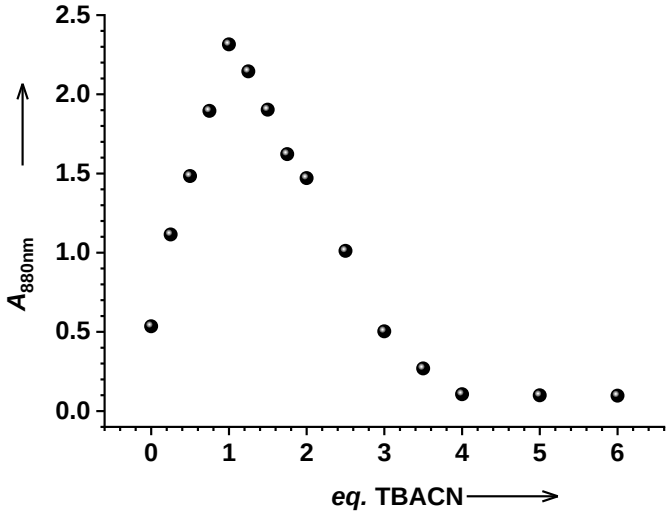


Figure S2: Evolution of the 880 nm absorption band of **[Co(ᵗBu-dioxolene)₂(stypy)₂] (1)** in DCM (c = 5 • 10^{-4} M) with different equivalents of TBACN.

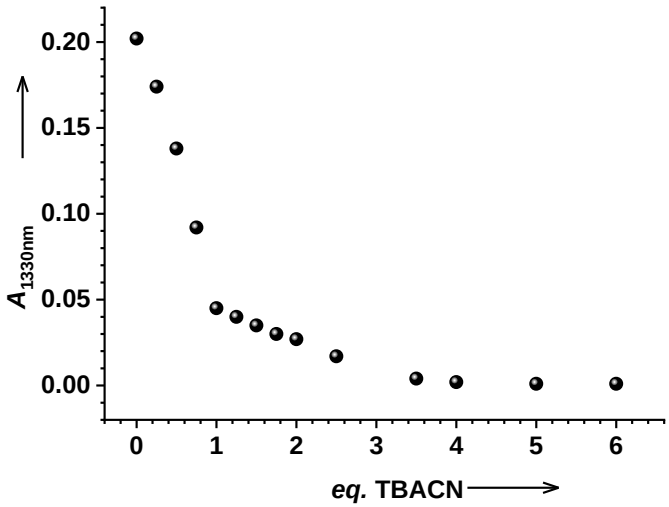


Figure S3: Evolution of the 1330 nm absorption band of **[Co(ᵗBu-dioxolene)₂(stypy)₂] (1)** in DCM (c = 5 • 10^{-4} M) with different equivalents of TBACN.

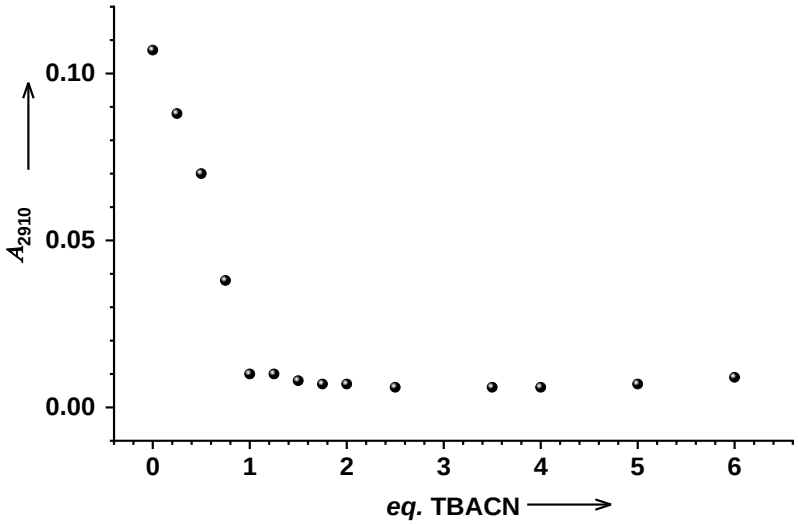


Figure S4: Evolution of the 2910 nm absorption band of **[Co(*t*Bu-dioxolene)$_2$(stypy)$_2$]** (**1**) in DCM (c = 5 • 10^{-4} M) with different equivalents of TBACN.

Comparison of different species

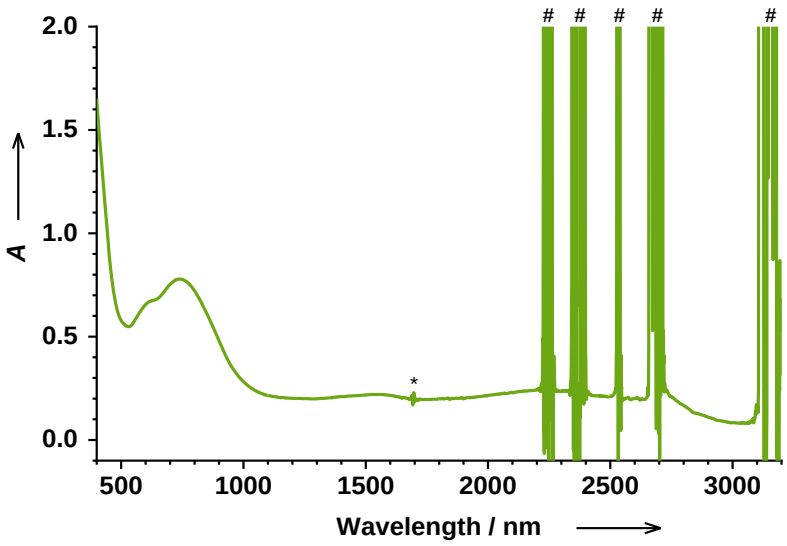


Figure S5: Electronic absorption spectrum of **[Co(ᵗBu-dioxolene)₂(stypy)₂] (1)** in DCM ($c = 5 \cdot 10^{-4}$ M). (*****) is a spectrometer artefact, (#) are due to solvent overtones.

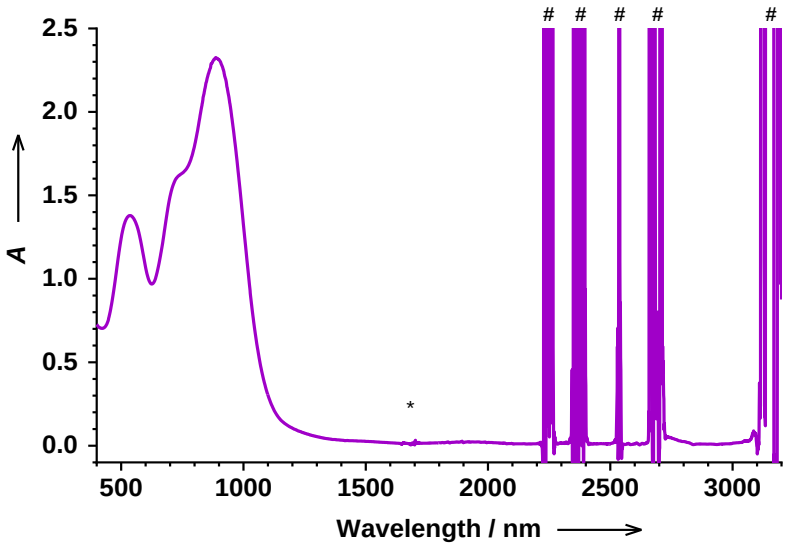


Figure S6: Electronic absorption spectrum of **[Co(ᵗBu-dioxolene)₂(stypy)₂] (1)** in DCM ($c = 5 \cdot 10^{-4}$ M) with 1 equivalent of TBACN ("**2**"). (*****) is a spectrometer artefact, (#) are due to solvent overtones.

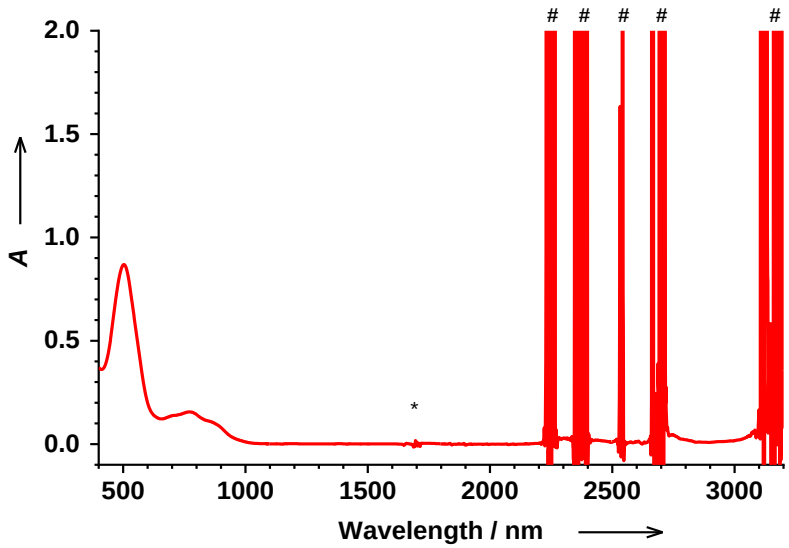


Figure S7: Electronic absorption spectrum of **[Co(ᵗBu-dioxolene)₂(stypy)₂] (1)** in DCM (c = 5 • 10^{-4} M) with 6 equivalents of TBACN. (*****) is a spectrometer artefact, (#) are due to solvent overtones.

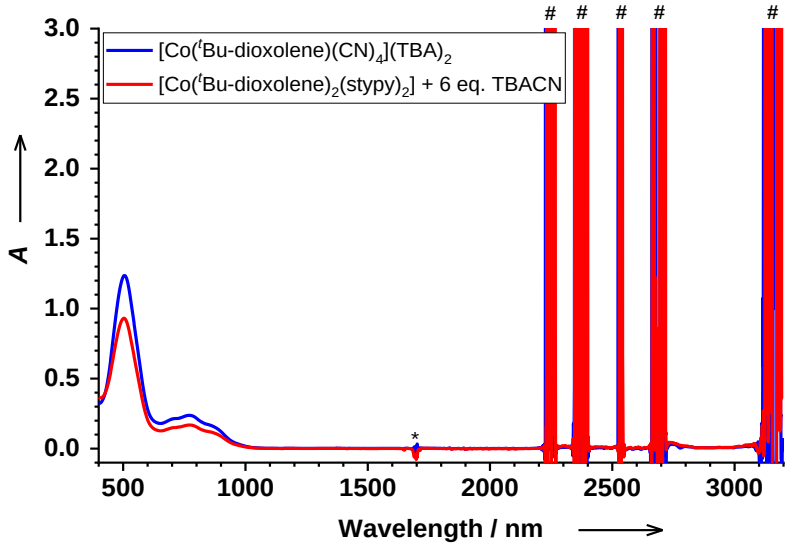


Figure S8: Comparison of electronic absorption spectra of **[Co(ᵗBu-dioxolene)₂(stypy)₂] (1)** in DCM (c = 5 • 10^{-4} M) with 6 eq. TBACN (red) and **[Co(ᵗBu-dioxolene)(CN)₄](TBA)₂** (**3**) (blue). (*****) is a spectrometer artefact, (#) are due to solvent overtones.

Variable-Temperature Electronic Absorption Spectroscopy

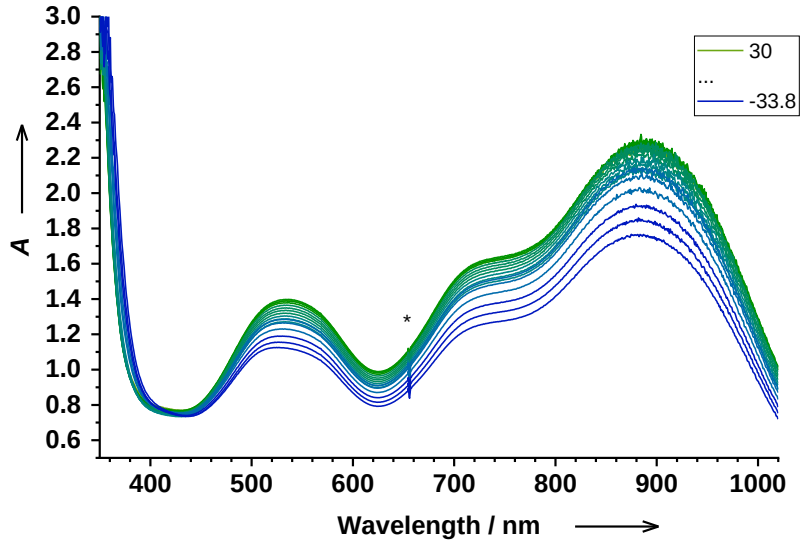


Figure S9: Temperature-dependent electronic absorption spectrum of *in situ* generated **2** in DCM ($c = 5 \cdot 10^{-4}$ M). (*****) is a spectrometer artefact.

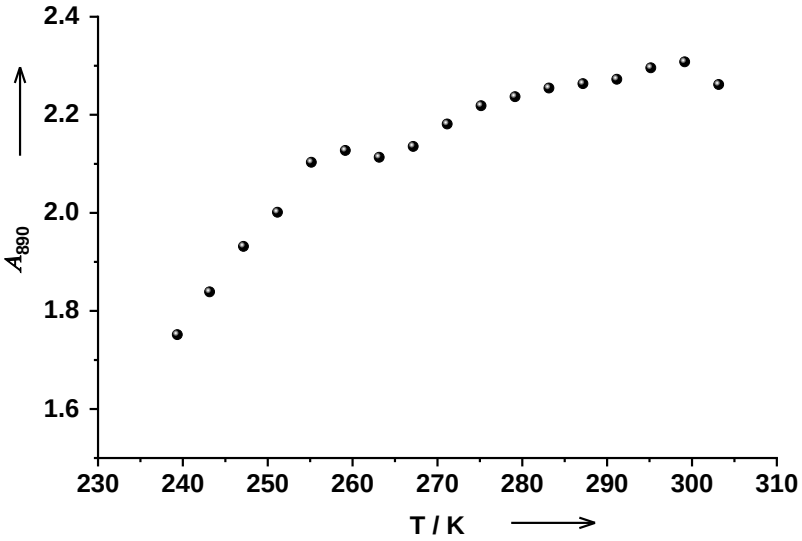


Figure S10: Temperature-dependent evolution of the 890nm absorption band of *in situ* generated **2** in DCM ($c = 5 \cdot 10^{-4}$ M).

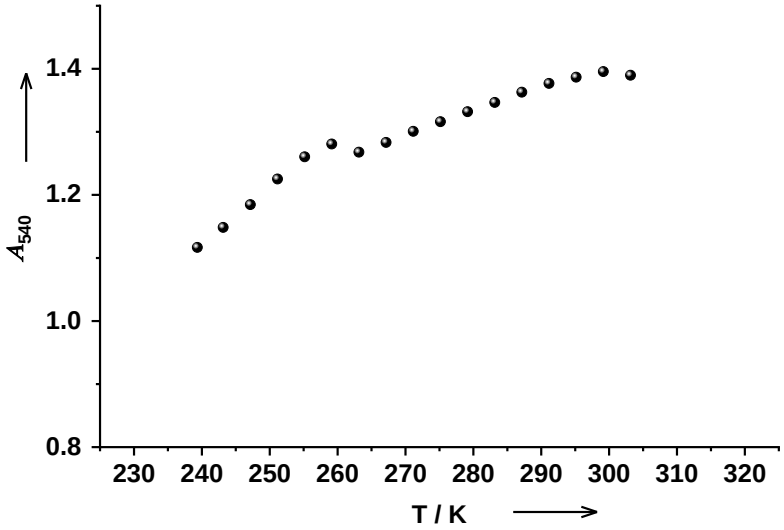


Figure S11: Temperature-dependent evolution of the 540nm absorption band of *in situ* generated **2** in DCM ($c = 5 \bullet 10^{-4}$ M).

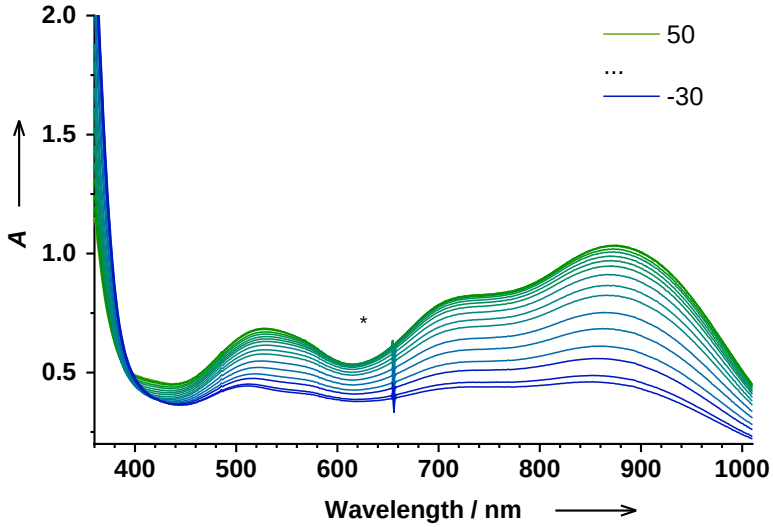


Figure S12: Temperature-dependent electronic absorption spectrum of *in situ* generated **2** in MeCN ($c = 1 \bullet 10^{-4}$ M). (*****) is a spectrometer artefact.

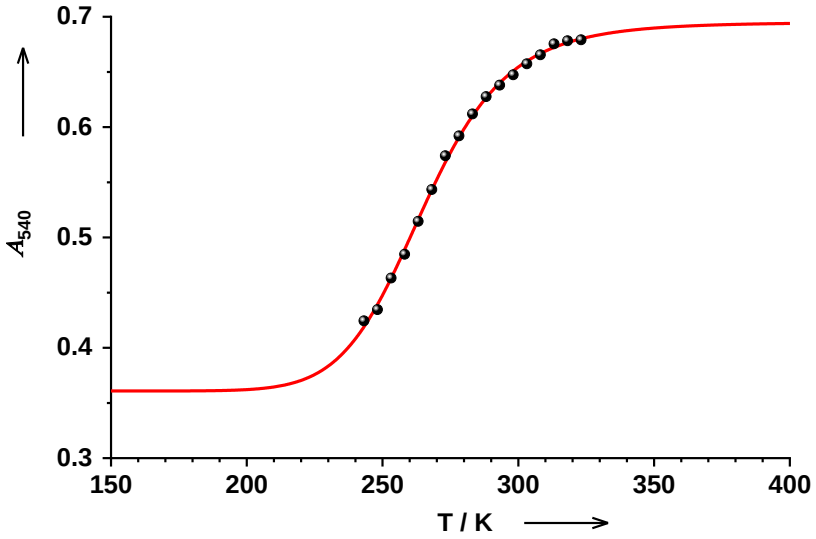


Figure S13: Temperature-dependent evolution of the 540nm absorption band of *in situ* generated **2** in MeCN (c = 1 • 10^{-4} M). Fit parameters: A_{HT} = 0.69(1), A_{LT} = 0.36(1), ΔH = 37(8) kJ mol^{-1}, ΔS = 142(32) J K^{-1}, $T_{1/2}$ = 265(1) K.

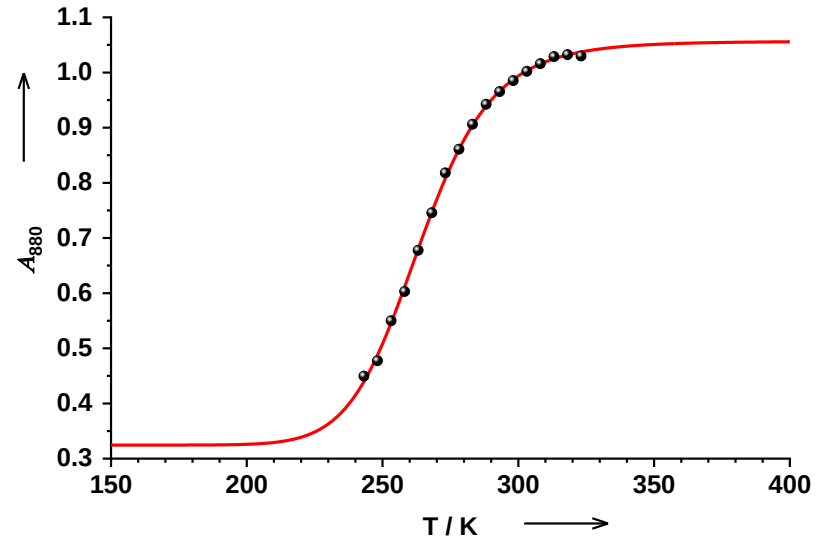


Figure S14: Temperature-dependent evolution of the 880nm absorption band of *in situ* generated **2** in MeCN (c = 1 • 10^{-4} M). Fit parameters: A_{HT} = 1.05(1), A_{LT} = 0.32(1), ΔH = 43(9) kJ mol^{-1}, ΔS = 163(37) J K^{-1}, $T_{1/2}$ = 263.9(5) K.

Magnetic Data

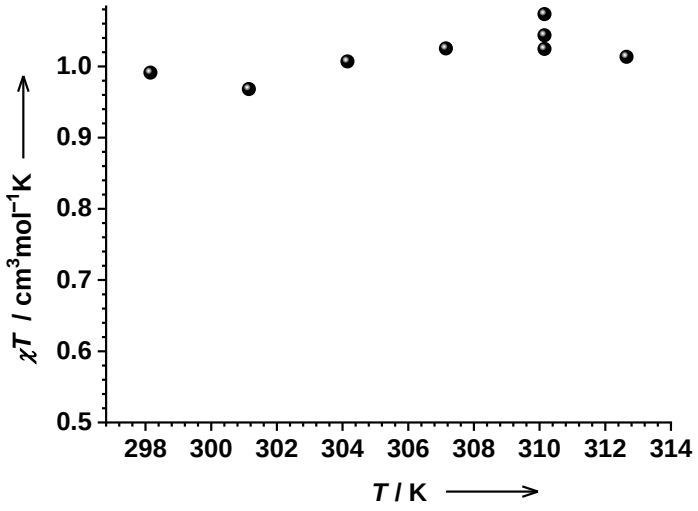


Figure S15: Temperature-dependent changes of the χT product of *in situ* generated **2** in DCM:DCM-d_2-TMS (10:2:1) (c = 5 • 10^{-4} M).

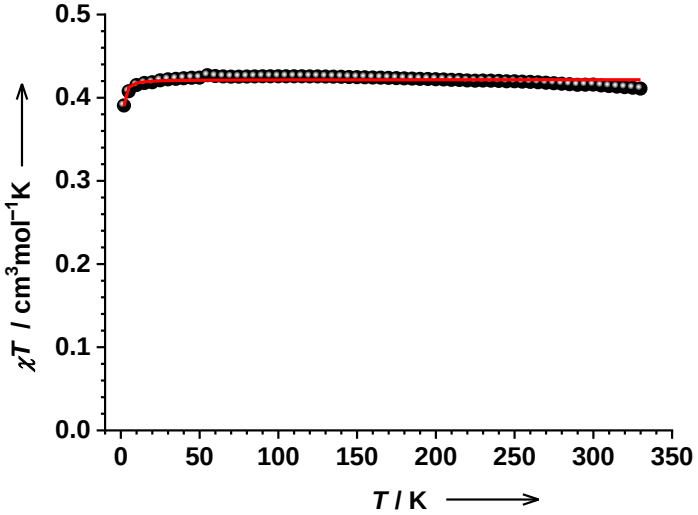


Figure S16: Variable-temperature χT product of **[Co(ᵗBu-dioxolene)(CN)₄](TBA)₂** (**3**) measured on powder sample at an external magnetic field of 1T (1 K min^{-1}, 5 K intervals), in the heating mode. Fit parameters for S = 1/2 model: g = 2.120(1), mean-field intermolecular interaction: zJ = –0.49(1) cm^{-1}.

Comparison of UV/Vis and magnetic data

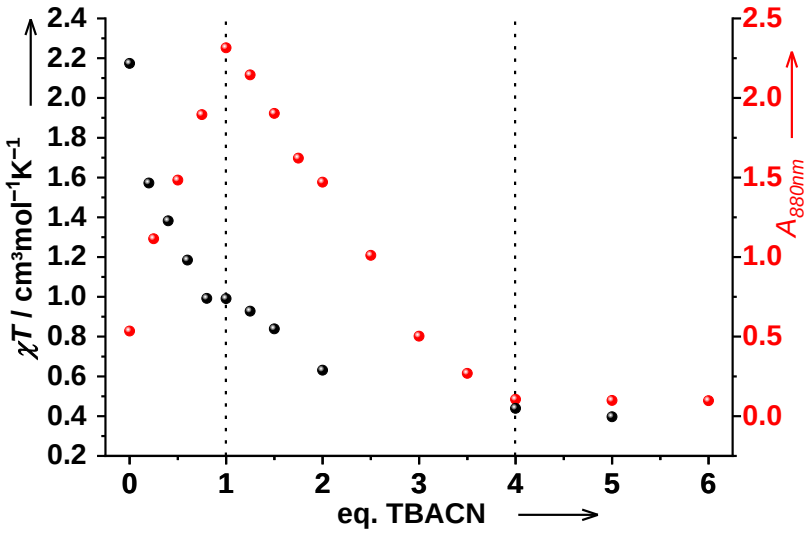


Figure S17: Changes of the χT product of **[Co(ᵗBu-dioxolene)₂(stypy)₂] (1)** in DCM:DCM-d_2-TMS (10:2:1) (c = 5 • 10^{-4} M) with different amounts of TBACN (black). Evolution of the 880 nm absorption band of **[Co(ᵗBu-dioxolene)₂(stypy)₂] (1)** in DCM (c = 5 • 10^{-4} M) with different equivalents of TBACN (red).

Table S1: Comparison of thermodynamic parameters (ΔH, ΔS, $T_{1/2}$) for [Co(ᵗBu-dioxolene)₂(stypy)] (**1**) with one equivalent of TBACN obtained from NMR and UV/Vis experiments. Note that we were not able to fit and analyze variable-temperature UV-vis data recorded in DCM with confidence, because of high uncertainties in fit parameters. Slight discrepancies in fitted thermodynamic parameters (which are however with the error margins) are likely due to differing solvents and concentrations. Wherever possible all VT experiments have been carried out with DCM solutions (c = 5 • 10^{-4} M). Only in case of VT UV/Vis experiments, we additionally performed measurements in MeCN, albeit at a low concentration (c = 1 • 10^{-4} M) due to poorer solubility.

	VT-Evans NMR DCM	VT UV/Vis MeCN@880nm	VT UV/Vis MeCN@540nm
ΔH [kJmol^{-1}]	51(10)	43(9)	37(8)
ΔS [JK^{-1}]	207(41)	163(37)	142(32)
$T_{1/2}$ [K]	249(1)	264(1)	265(1)

EPR Data

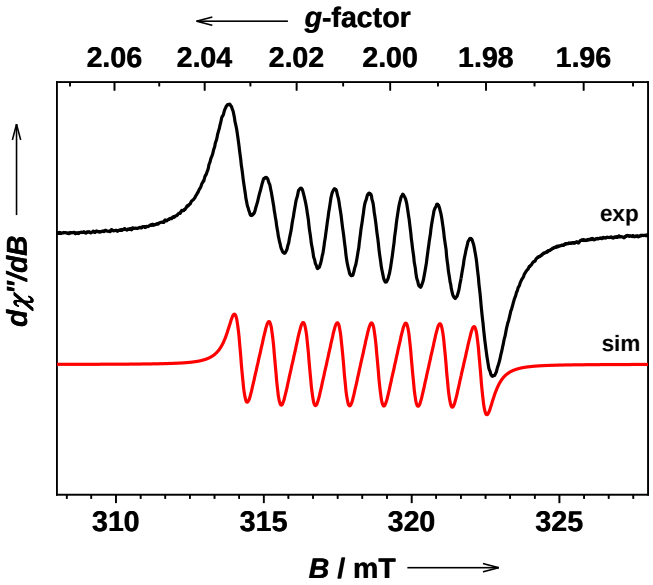


Figure S18: X-band EPR spectra **1** in DCM solution (c = 1 mM) recorded in a capillary at RT. Frequency: 8.938 GHz, mod width: 0.1 mT, power: 1.0 mW. Simulation in red. Parameters: g_{iso} = 2.007, $A_{iso}(^{59}Co, I = 7/2)$ = 10.8 • 10^{-4} cm^{-1}, W_{iso} = 0.5 • 10^{-4} cm^{-1} / GHz.

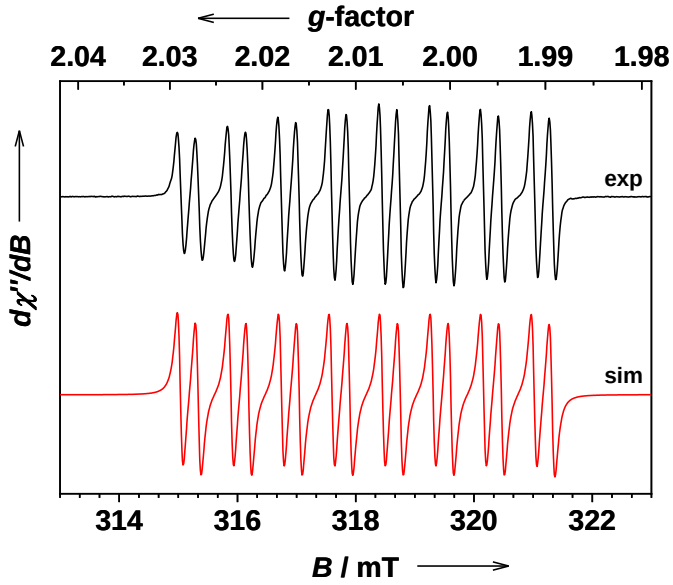


Figure S19: X-band EPR spectrum of **3** in DCM solution (c = 1 mM) recorded in a capillary at RT. Frequency: 8.945 GHz, mod width: 0.1 mT, power: 1.0 mW. Fit in red. Parameters: g_{iso} = 2.009, $A(^{59}Co, I = 7/2)$ = 8.0 • 10^{-4} cm^{-1}, $A(^{1}H, I = 1/2)$ = 2.8 • 10^{-4} cm^{-1}. W_{iso} = 0.1 • 10^{-4} cm^{-1} / GHz.

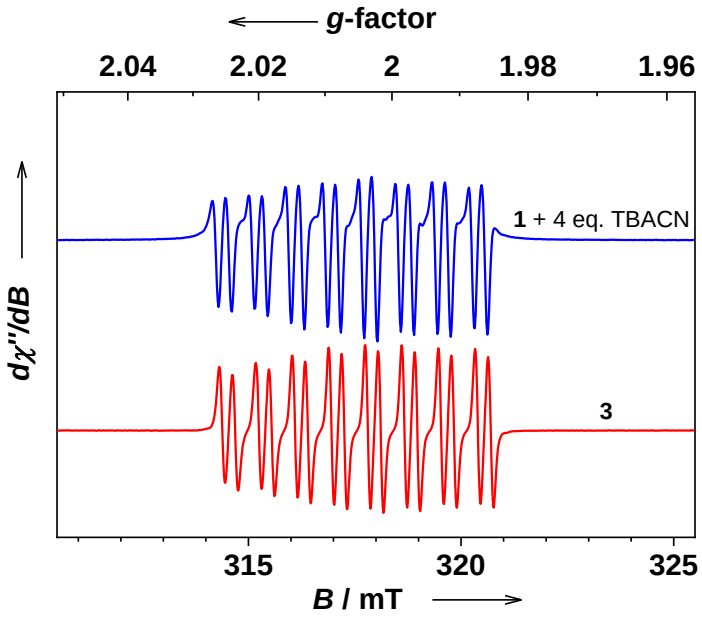


Figure S20: Comparison of X-band EPR spectra of the reference complex **3** (in red) and the *in-situ* formed **3** by reacting **1** with 4 eq. TBACN (in blue), both measured in DCM solution at RT.

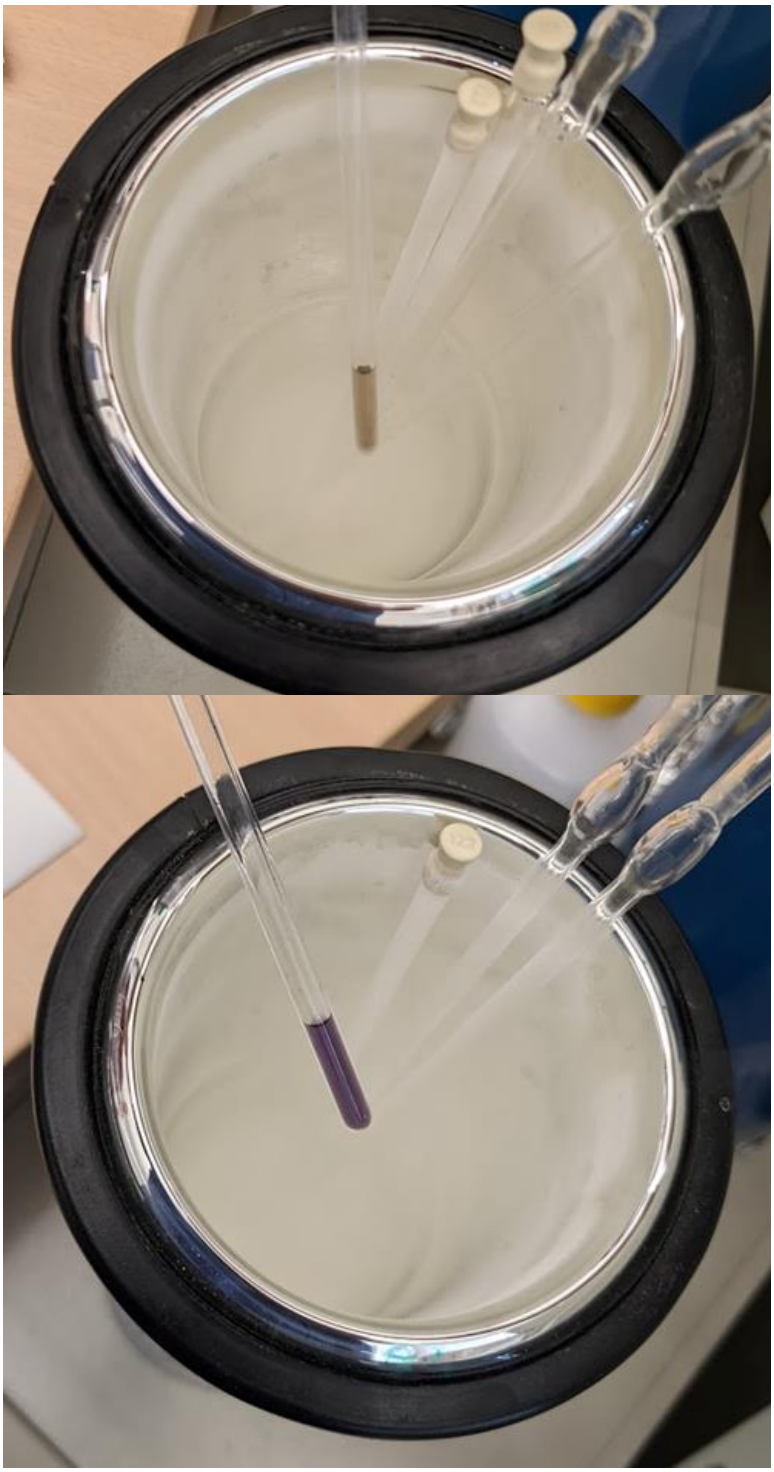


Figure S21: Color change of EPR sample of **2** in DCM solution (c = 1 mM) after freezing in liquid nitrogen right after the frozen solution has melted (top; T > 176 K) and after warming up to RT (bottom).

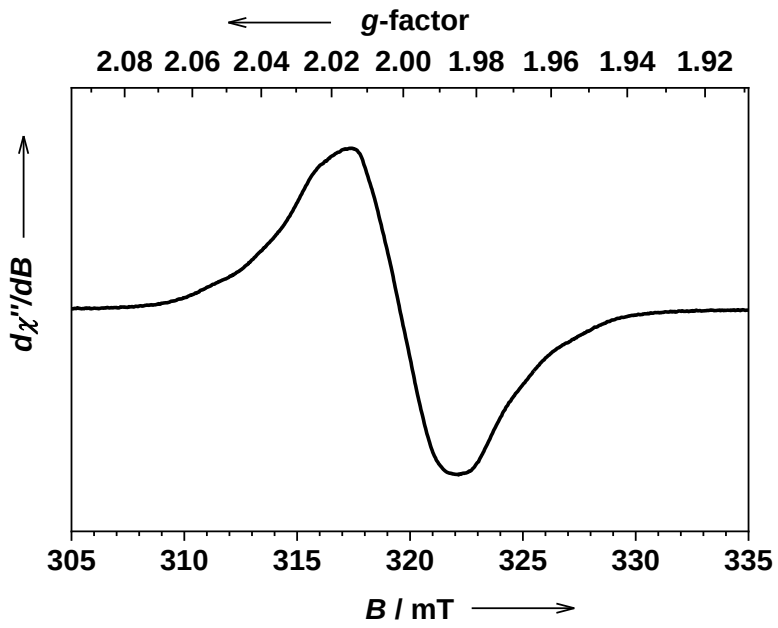


Figure S22: X-band EPR spectrum of **1** in frozen DCM solution (*c* = 1 mM) recorded at 95 K (frequency: 8.948 GHz, mod with: 0.5 mT, power: 1.0 mW).

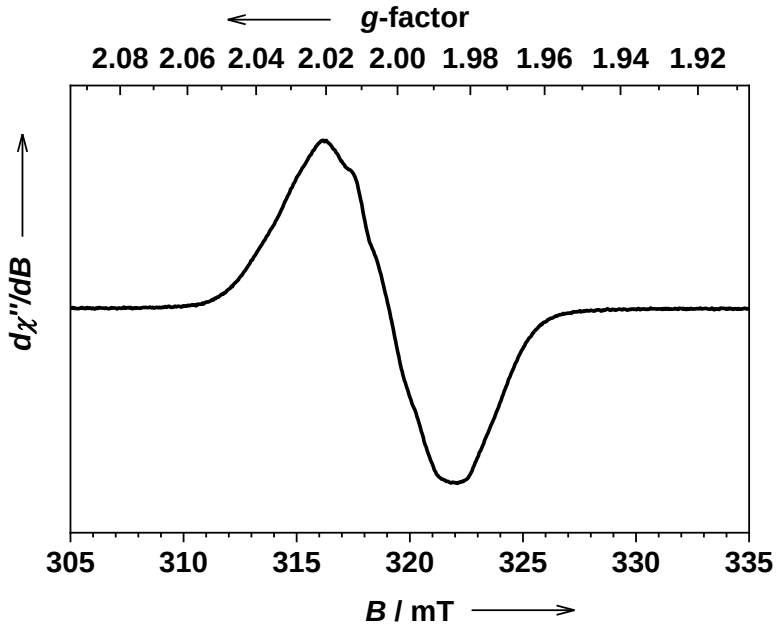


Figure S23: X-band EPR spectrum of **3** in frozen DCM solution (*c* = 1 mM) recorded at 95 K. Top: frequency: 8.9426 GHz, mod with: 1.0 mT, power: 1.0 mW.

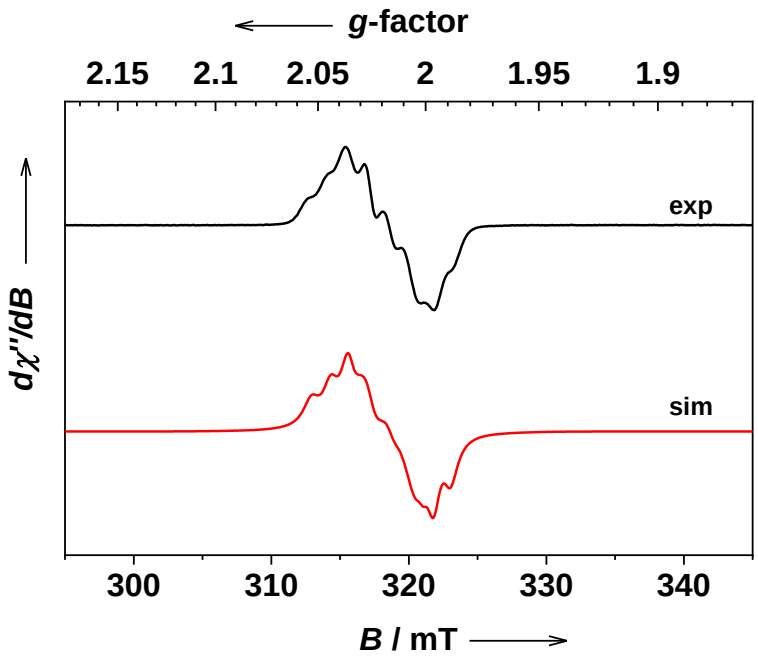


Figure S24: X-band EPR spectrum of *in-situ* generated **3** in frozen DCM solution (c = 1 mM) recorded at 103 K. Frequency: 8.9336 GHz, mod width: 0.05 mT, power: 1.0 mW. Fit parameters: g = (2.0174, 2.0076, 1.9916), A(^{59}Co, I = 7/2) = (2.04, 13.4, 2.2) • 10^{-4} cm^{-1}, linewidths $W_{x,y,z}$ = (0.81, 0.85, 0.54) • 10^{-4} cm^{-1} / GHz. Experimental spectrum is shown in black, fit – in red.

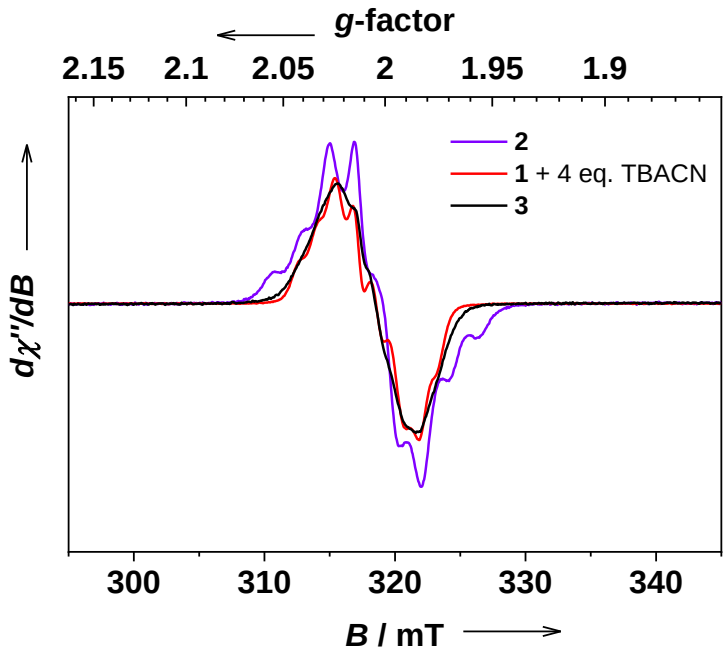


Figure S25: Comparison of X-band EPR spectra of the reference complex **3** (in black), *in-situ* formed **3** by reacting **1** with 4 eq. TBACN (in red), and *in-situ* formed **2** (in purple) all measured in DCM frozen solutions at ~100 K.

IR Spectroscopy

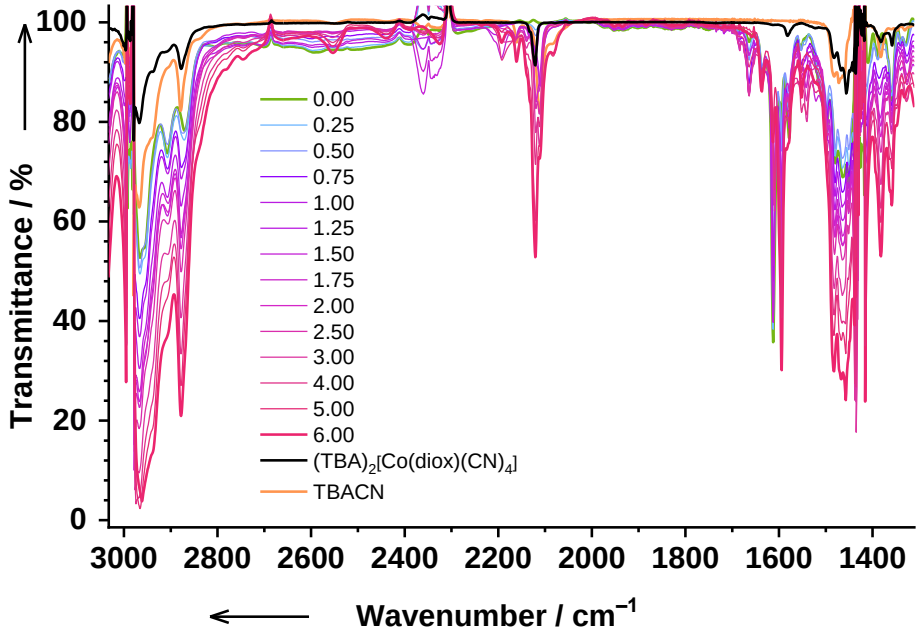


Figure S26: Changes in IR spectrum of **1** in DCM solution (c = 2.5 mM) upon titration with TBACN: overview.

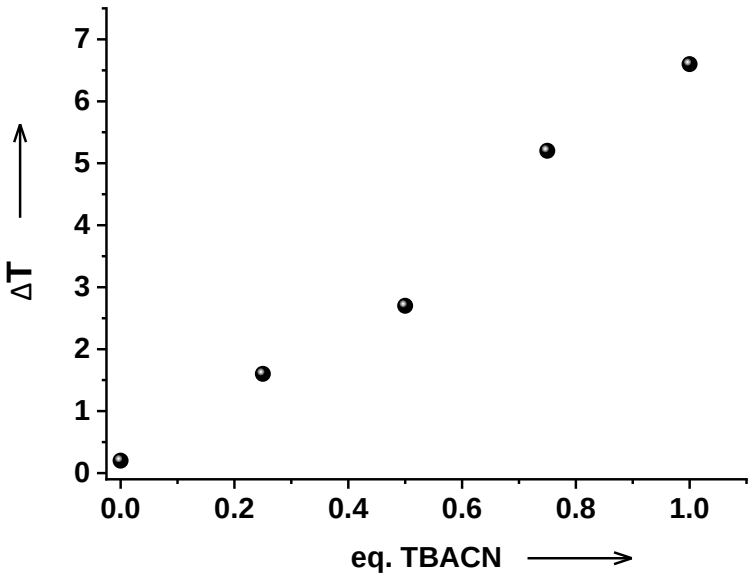


Figure S27: Changes in transmittance at 2120 cm^{-1} in IR spectrum of **1** in DCM (c = 2.5 mM) upon titration with TBACN.

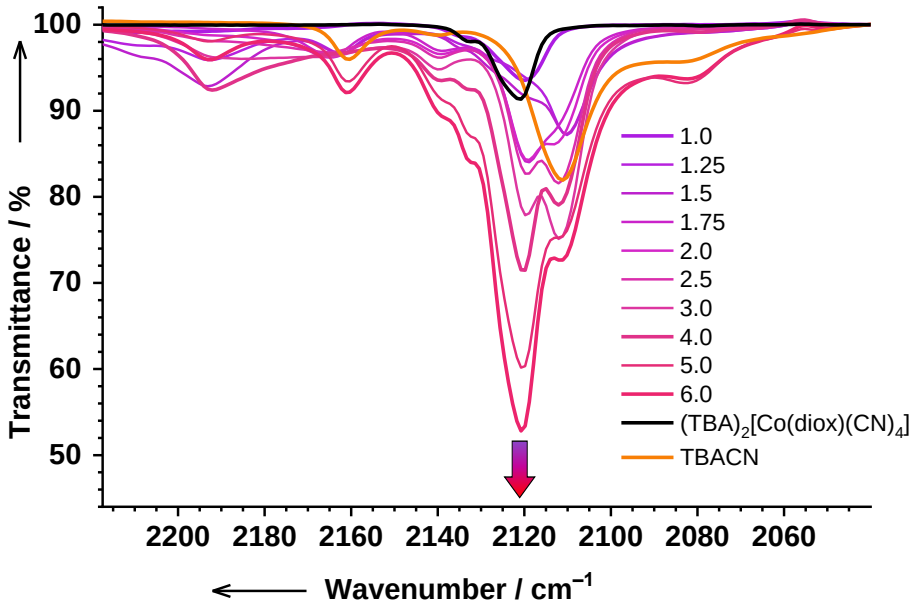


Figure S28: Evolution of IR spectrum of **1** in DCM (*c* = 2.5 mM) titrated with TBACN.

Mass Spectrometry

Positive-Ion Mode

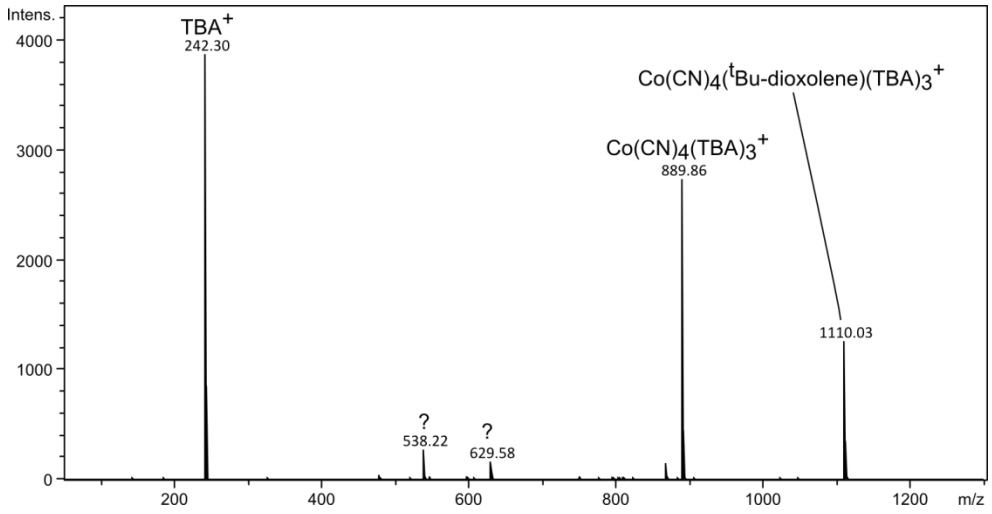


Figure S29: Positive-ion mode MS of the reference species $(TBA)_2[Co(^tBu\text{-dioxolene})(CN)_4]$ (**3**).

Negative-Ion Mode

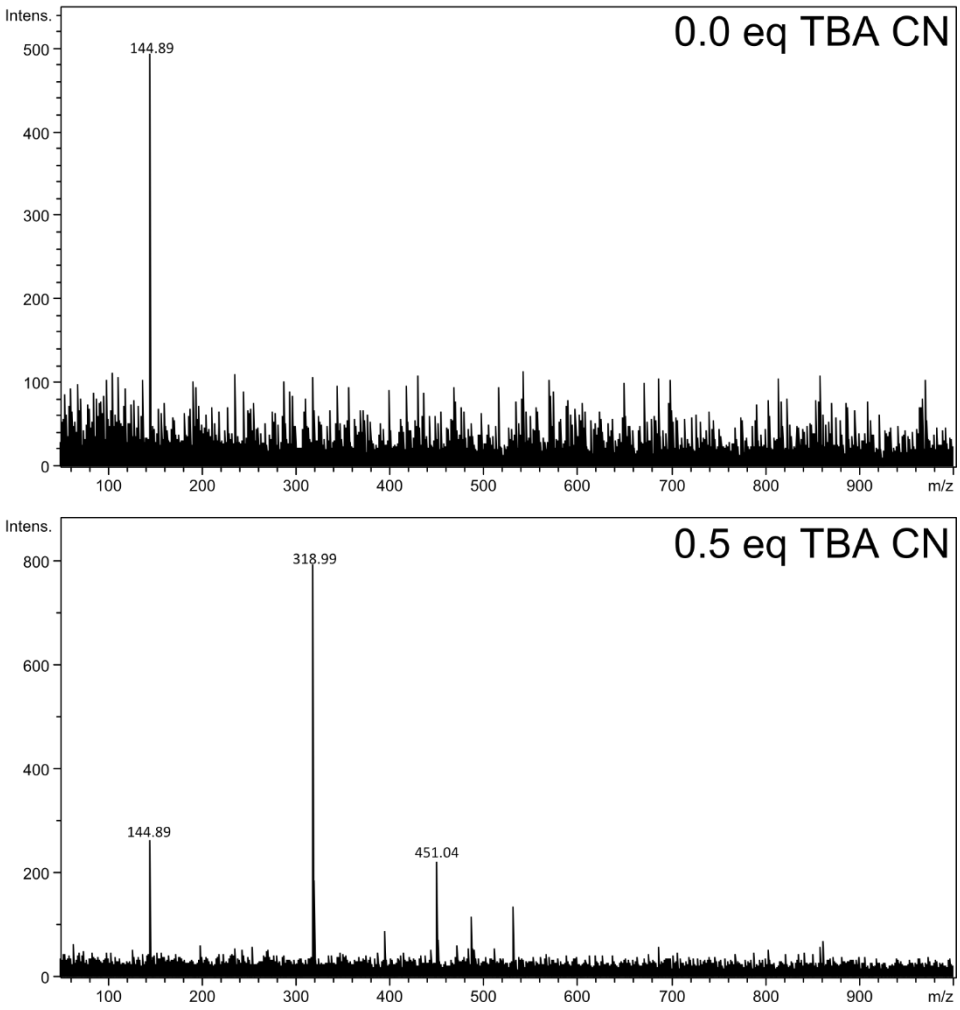


Figure S30: Negative ion mode MS of **1** with 0.0 (top) and 0.5 (bottom) eq. TBACN.

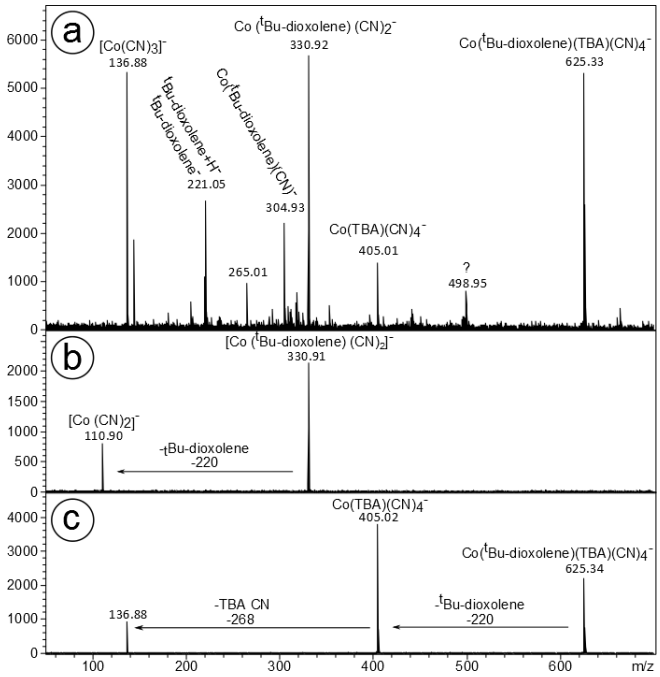


Figure S31: a) Negative ion mode MS of **1** with 1 eq. TBACN and the corresponding MS/MS of the signal at b) m/z 331 and c) m/z 625.

The ions at 0.0 and 0.5 eq. TBACN did not show the characteristic fragmentation behaviour observed for all other Co-complexes, additionally no combination of Co with ligands was found that fit the proper mass. We conclude that no negatively charged Co-complexes are formed at 0.0 eq. of TBA CN and at 0.5 eq. of TBA CN. Only $[Co(t\text{Bu-dioxolene})(CN)_2]^-$ (m/z 330) could be found as a minor signal, the major signals could not be attributed to Co-containing ions. In the negative-ion mode the mass accuracy was in the range of about ± m/z 0.1. The mass accuracy had not influence the ion generation, the shape of the isotope pattern or the results of MS/MS experiments. The mass accuracy in the positive-ion mode was in the range of ± m/z 0.01.

Isotope patterns

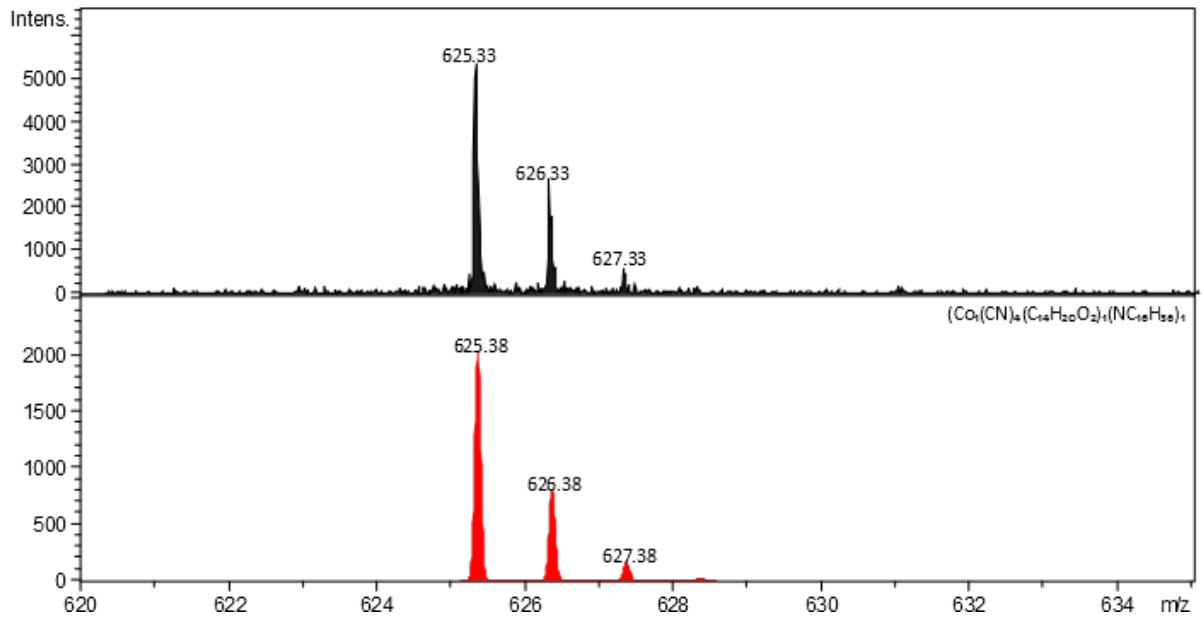


Figure S32: Experimental (top) and simulated (bottom) isotope pattern of [Co(tBu-dioxolene)(TBA)(CN)$_4$]$^-$.

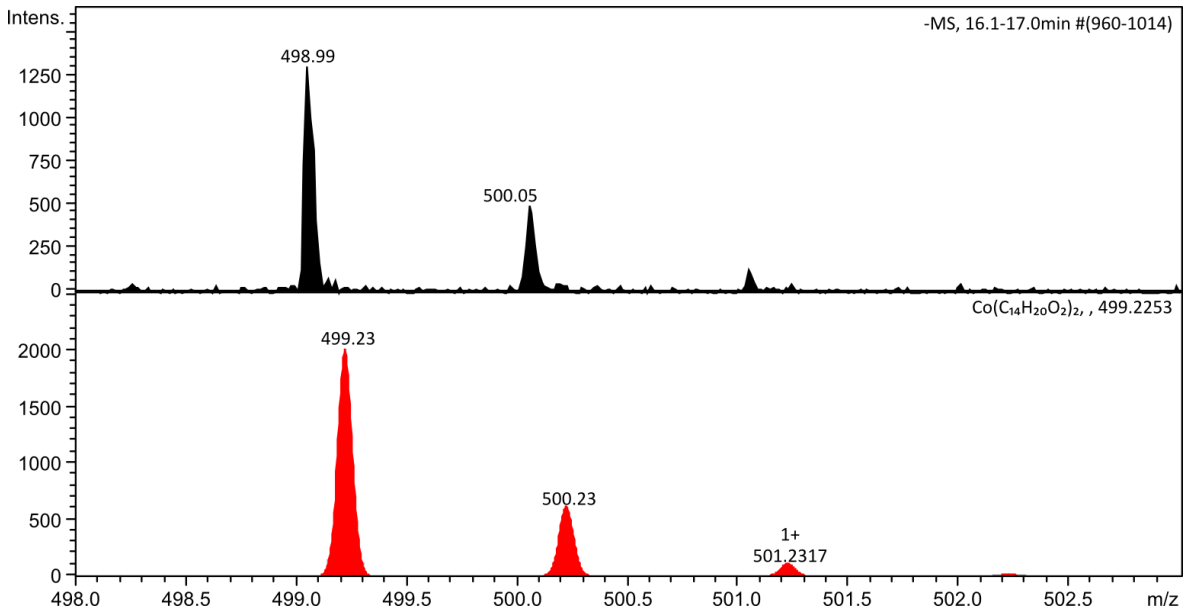


Figure S33: Experimental (top) and simulated (bottom) isotope pattern of [Co(tBu-dioxolene)$_2$]$^-$.

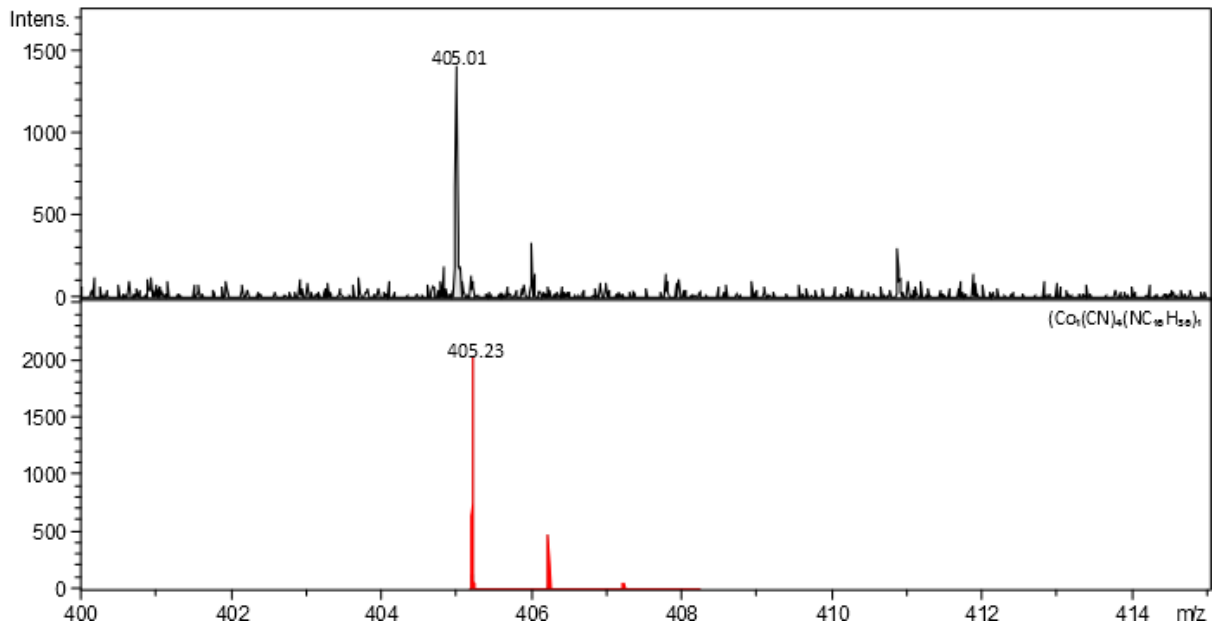


Figure S34: Experimental (top) and simulated (bottom) isotope pattern of $[Co(TBA)(CN)_4]^-$.

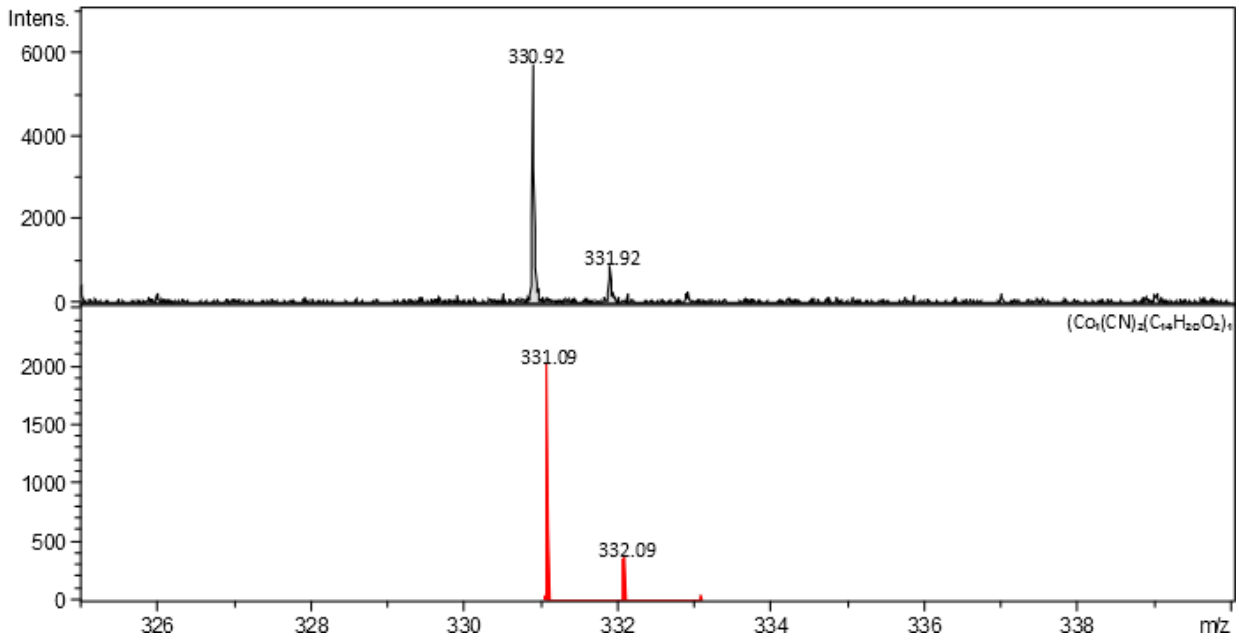


Figure 35: Experimental (top) and simulated (bottom) isotope pattern of $[Co(t\text{Bu-dioxolene})(CN)_2]^-$.

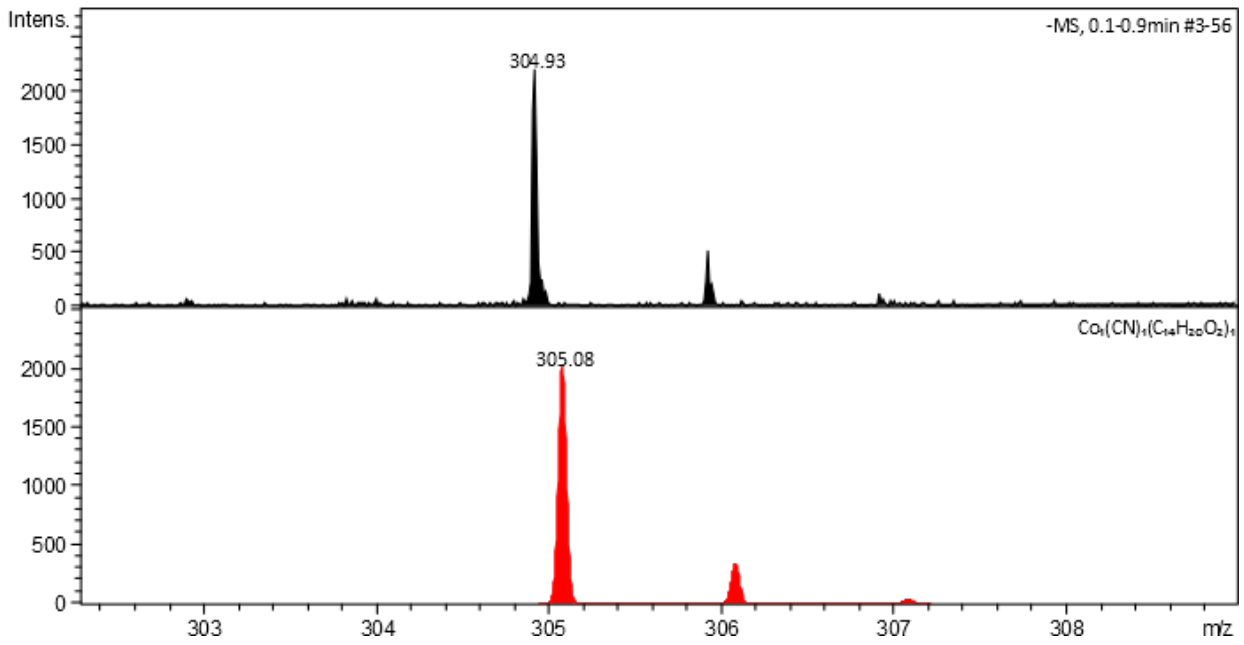


Figure S36: Experimental (top) and simulated (bottom) isotope pattern of [Co(*t*Bu-dioxolene)(CN)]$^{-}$.

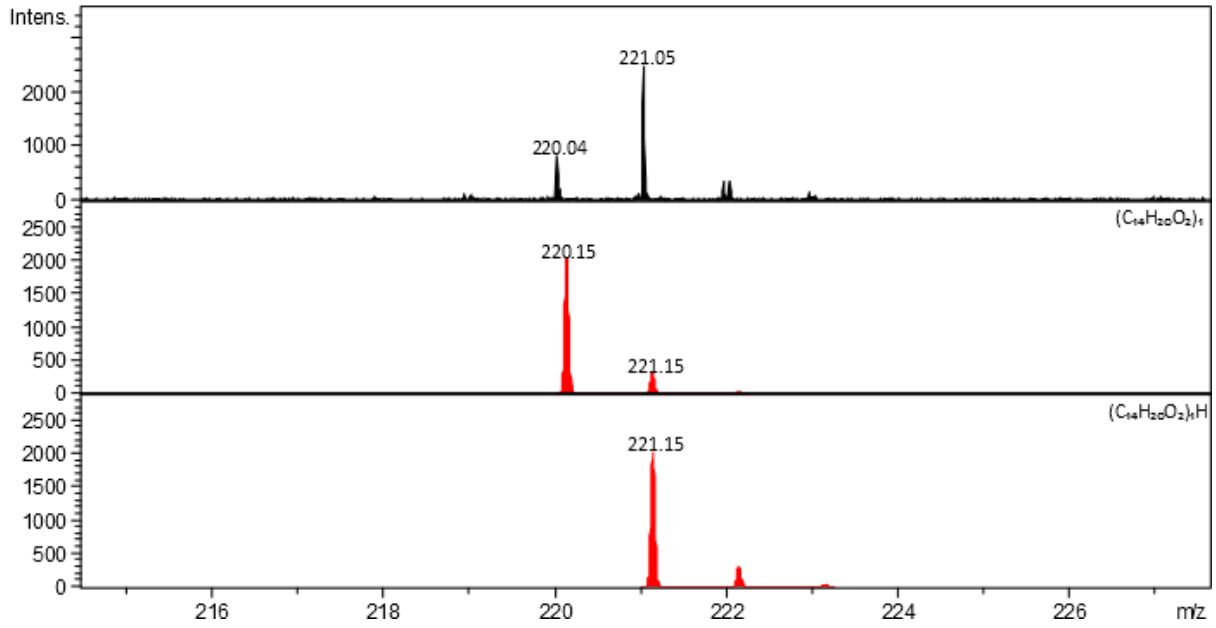


Figure S37: Experimental (top) and simulated (bottom) isotope pattern of (*t*Bu-dioxolene)$^{-}$ and (*t*Bu-dioxolene+H)$^{-}$.

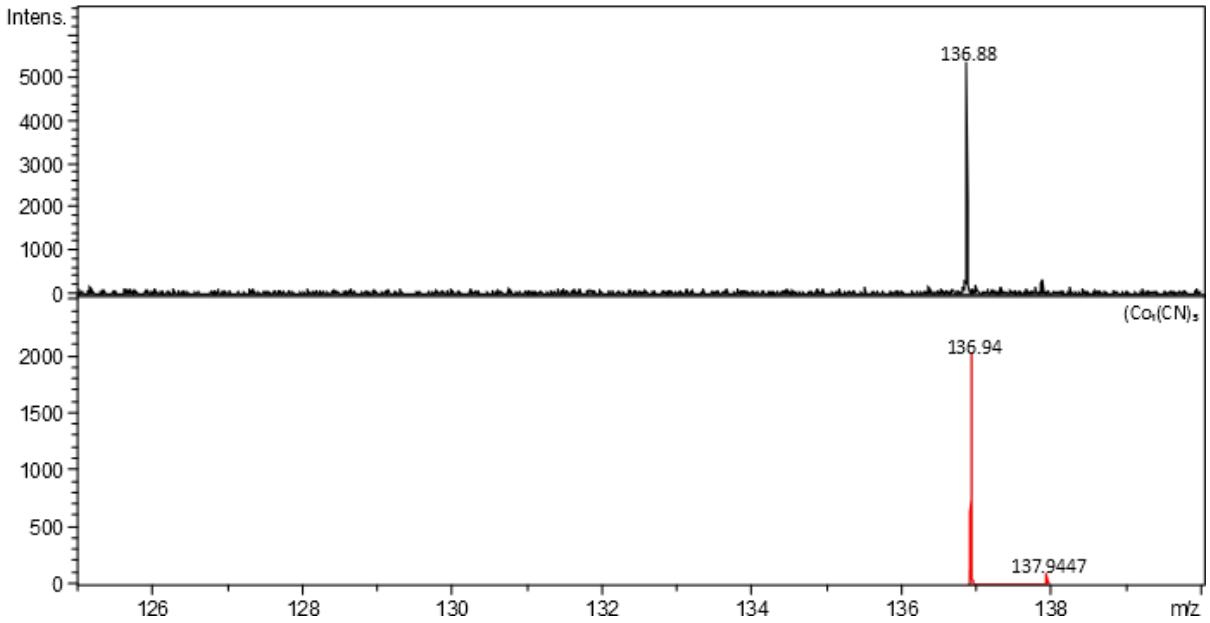


Figure S38: Experimental (top) and simulated (bottom) isotope pattern of $[Co(CN)_3]^-$.

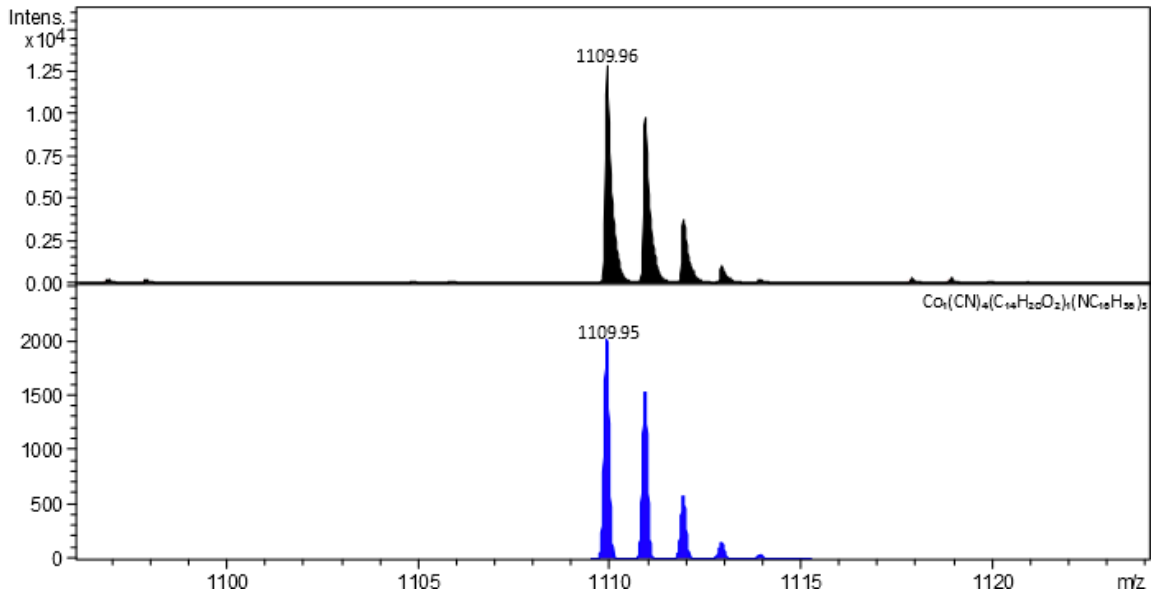


Figure S39: Experimental (top) and simulated (bottom) isotope pattern of $[Co(t\text{Bu-dioxolene})(CN)_4(TBA)_3]^+$.

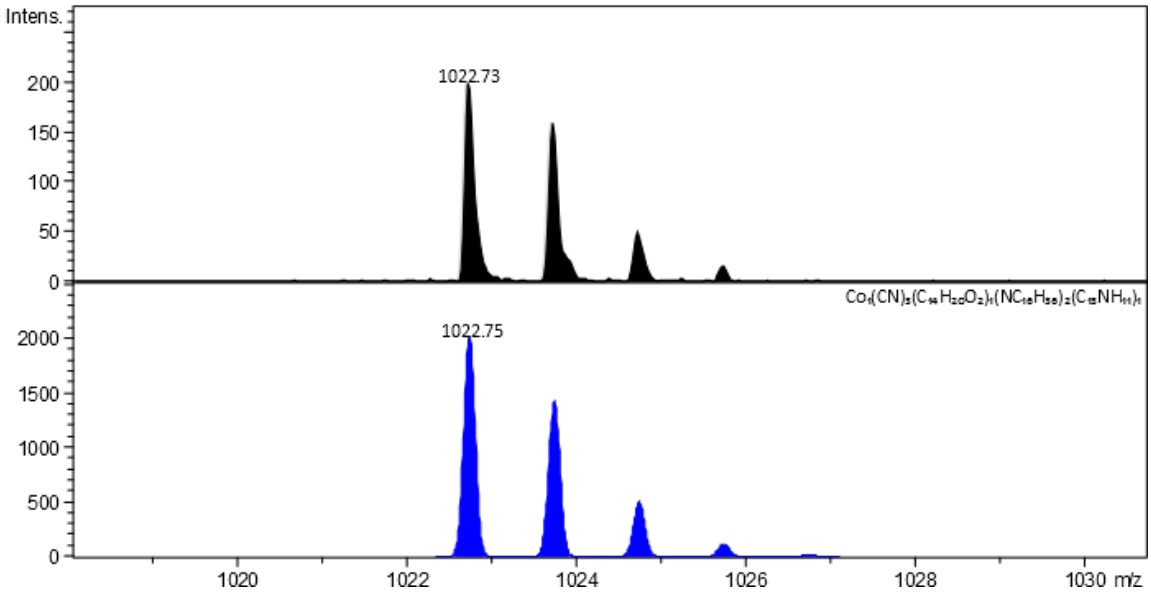


Figure S40: Experimental (top) and simulated (bottom) isotope pattern of [Co(*t*Bu-dioxolene)(stypy) $(CN)_3(TBA)_2]^+$.

Theoretical Calculations

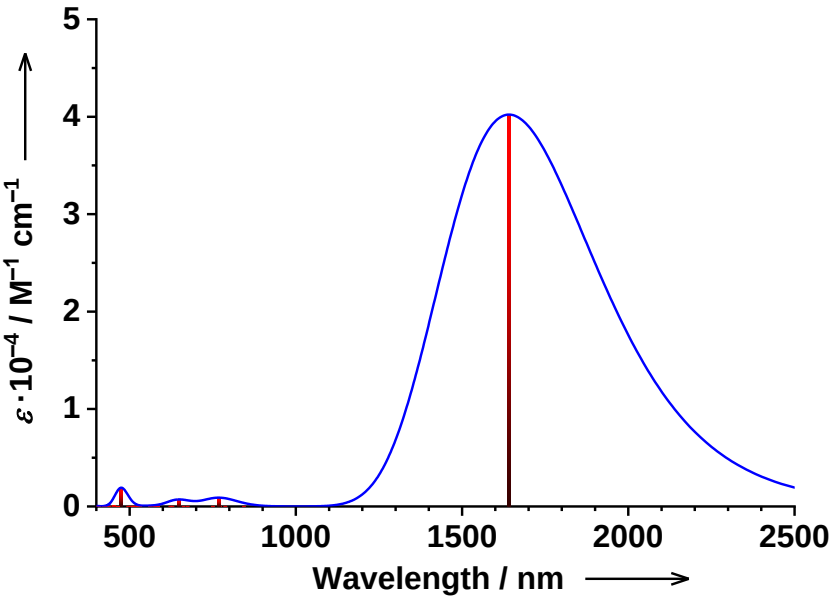


Figure S41: Calculated electronic absorption spectrum of the parent complex **1** in a *ls*-$Co^{III}(SQ^{\bullet-})(Cat^{2-})$ state: TD-DFT, B3LYP, S = 1/2. A prominent IVCT band is clearly visible and dominates.

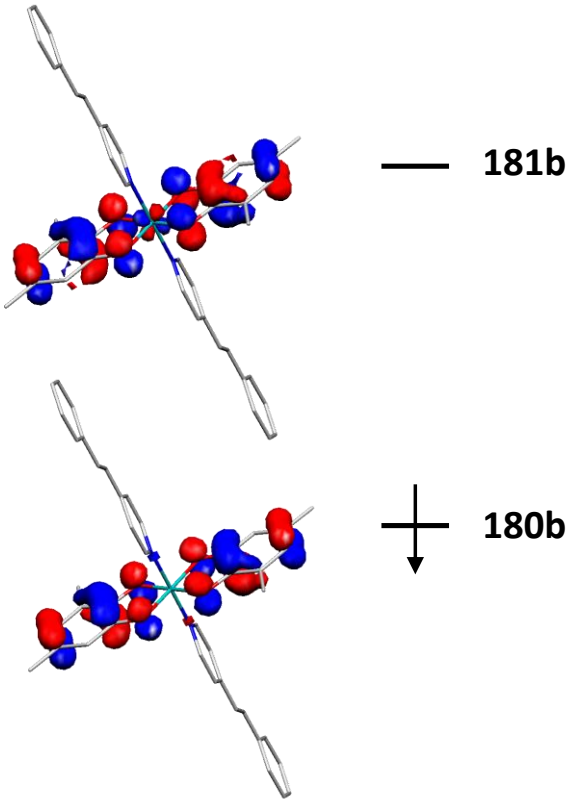


Figure S42: Donor and acceptor orbitals involved into the transition (1641 nm = 6092 cm^{-1}) responsible for the prominent IVCT band of the parent complex **1** in a *ls*-$Co^{III}(SQ^{\bullet-})(Cat^{2-})$ state: TD-DFT, B3LYP, S = 1/2.

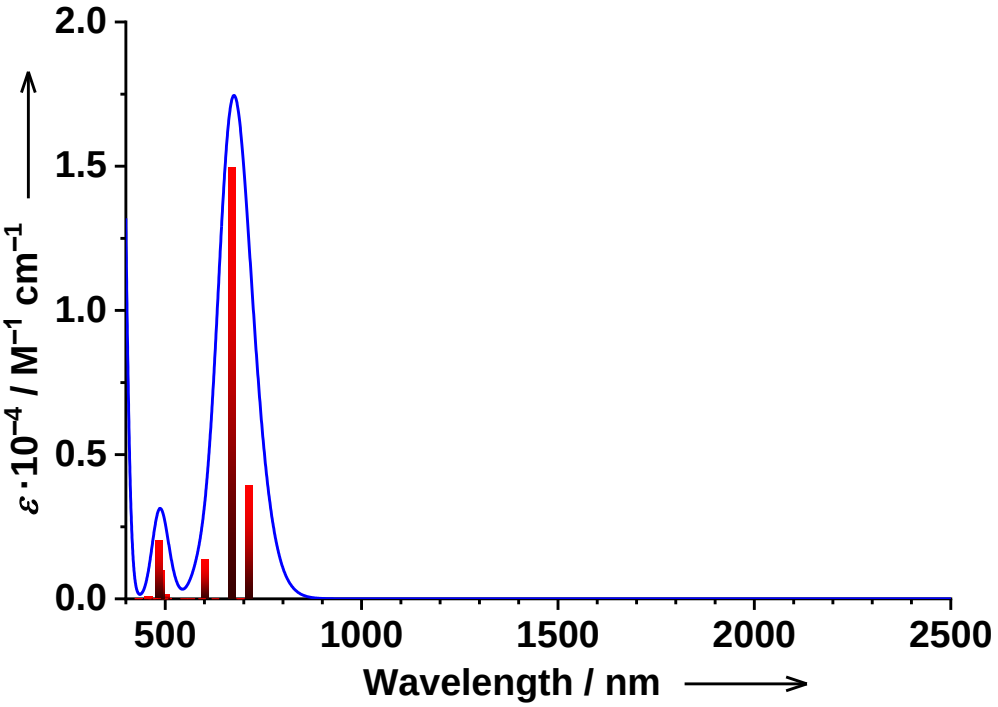


Figure S43: Calculated electronic absorption spectrum of the parent complex **1** in a *hs*-$Co^{II}(SQ^{\bullet-})_2$ state: TD-DFT, B3LYP, S = 5/2. The IVCT band is clearly absent.

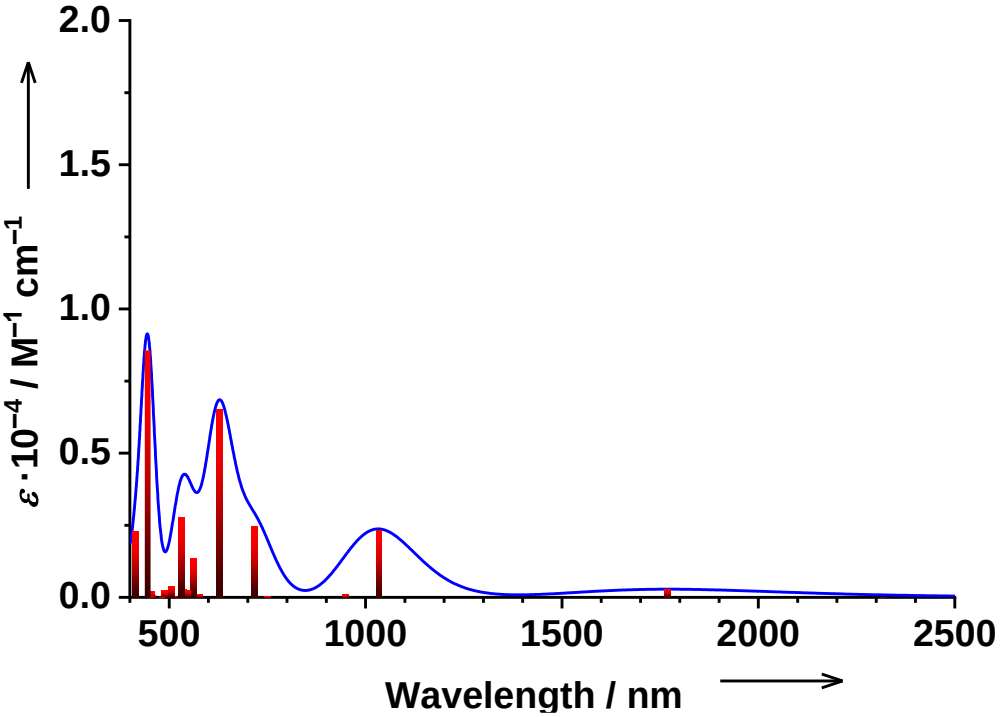


Figure S44: Calculated electronic absorption spectrum of the parent complex **1** dissociated to a five-coordinate $[Co(dioxolene)_2(stypy)_1]$ in its *hs*-$Co^{II}(SQ^{\bullet-})_2$ state: TD-DFT, B3LYP, S = 5/2. It shows some similarities to the corresponding spectrum of the parent **1**.

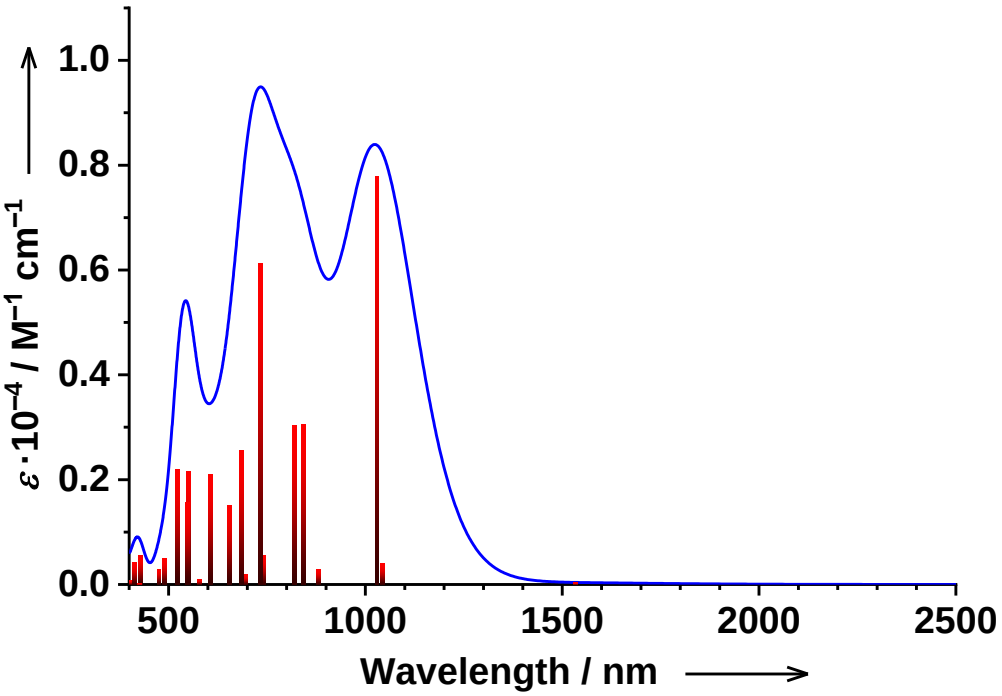


Figure S45: Calculated electronic absorption spectrum of the postulated five-coordinate species **2**$^{\mathbf{five}}$ in a *ls*-$Co^{II}(SQ^{\bullet-})_2$ state: TD-DFT, B3LYP, S = 3/2. Strong features in visible and NIR are clearly visible.

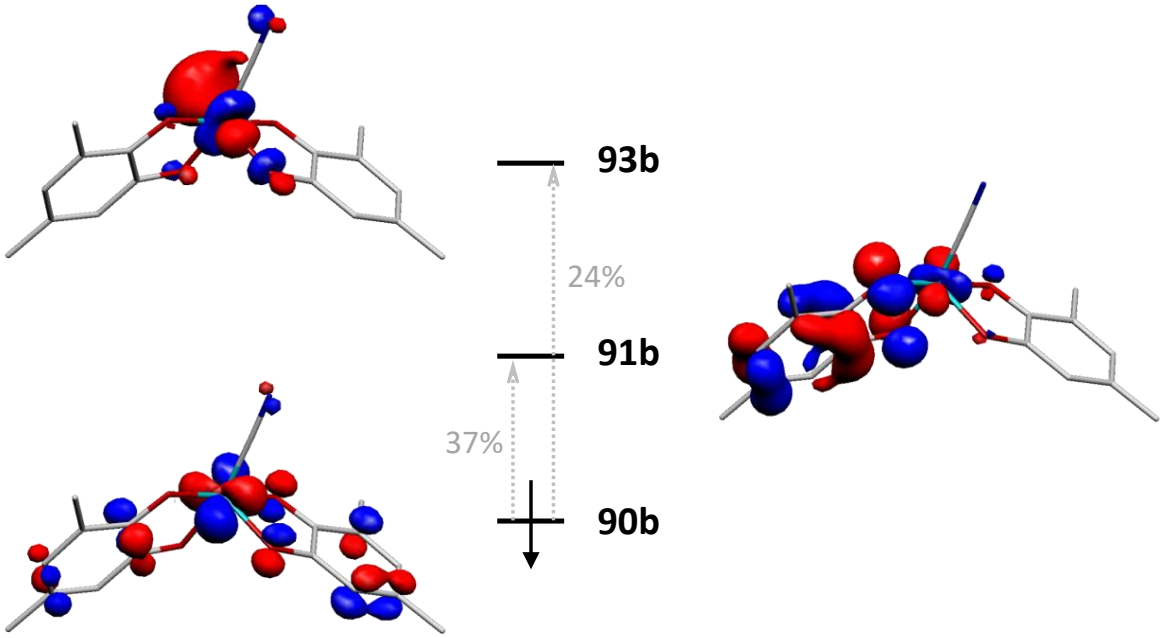


Figure S46: Molecular orbitals contributing the most to a prominent transition at 1030 nm = 9711 cm^{-1} calculated for **2**$^{\mathbf{five}}$ in a *ls*-$Co^{II}(SQ^{\bullet-})_2$ state: TD-DFT, B3LYP, S = 3/2. Strong LMCT character is visible.

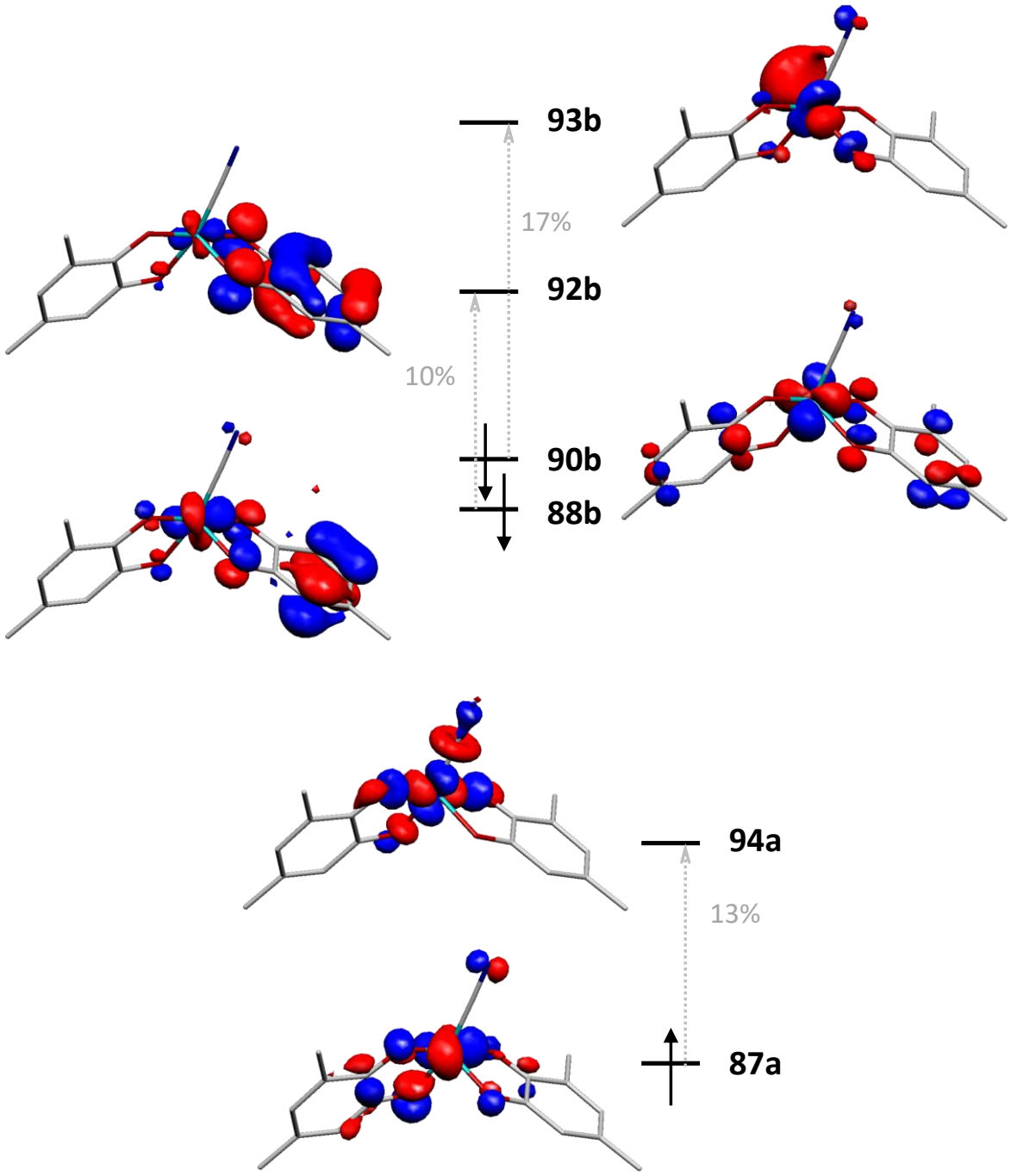


Figure S47: Molecular orbitals contributing the most to a prominent transition at 734 nm = 13619 cm^{-1} calculated for **2**$^{\mathbf{five}}$ in a *ls*-$Co^{II}(SQ^{\bullet-})_2$ state: TD-DFT, B3LYP, S = 3/2.

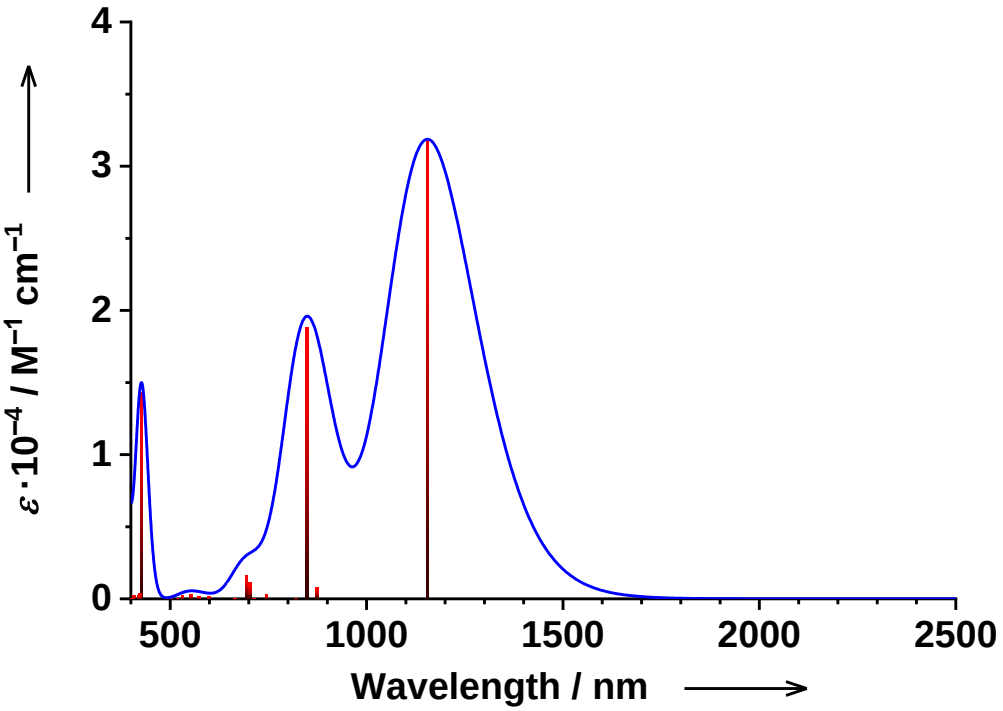


Figure S48: Calculated electronic absorption spectrum of the postulated five-coordinate species $\mathbf{2}^{\mathbf{five}}$ in a *ls*-$Co^{III}(SQ^{\bullet-})(Cat^{2-})$ state: TD-DFT, B3LYP, S = 1/2. This species is presumable formed at low temperatures. Interestingly, the IVCT band becomes blue-shifted compared to the parent **1** (*vide infra*).

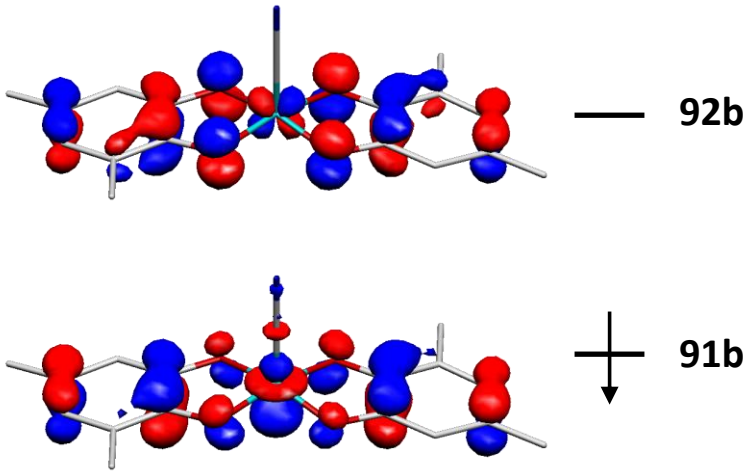


Figure S49: Donor and acceptor orbitals involved into the IVCT transition at 1155 nm = 8655 cm^{-1} calculated for the postulated five-coordinate species $\mathbf{2}^{\mathbf{five}}$ in a *ls*-$Co^{III}(SQ^{\bullet-})(Cat^{2-})$ state: TD-DFT, B3LYP, S = 1/2.

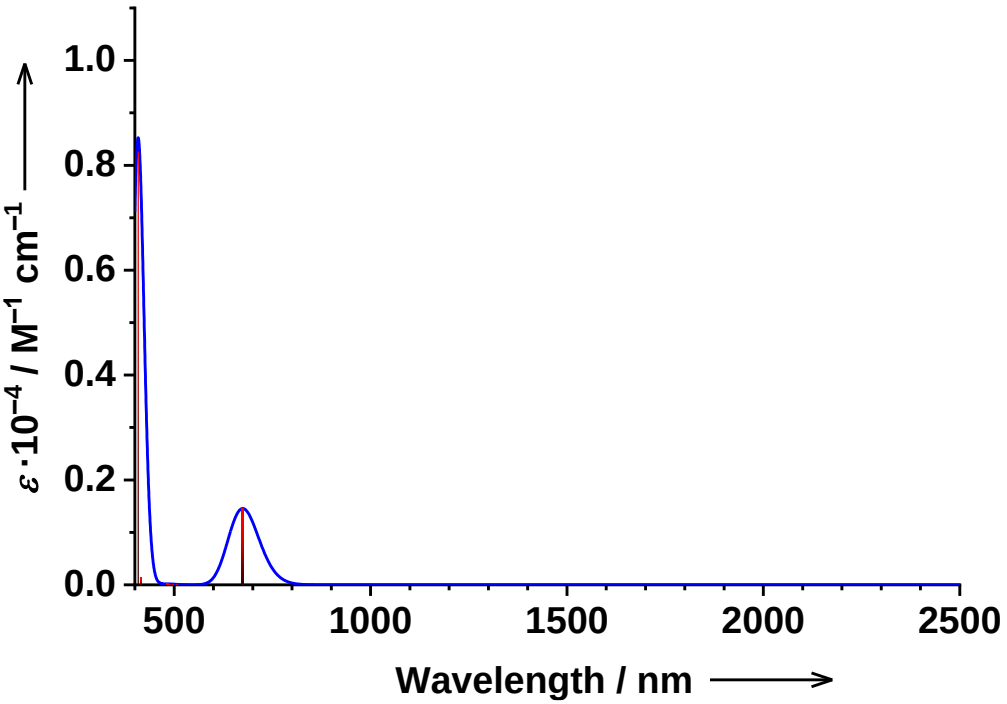


Figure S50: Calculated electronic absorption spectrum of the reference tetracyanido species **3** in a *ls*-$Co^{III}(SQ^{\bullet -})$ state: TD-DFT, B3LYP, S = 1/2. This is a very week chromophore compared to other species in this work.

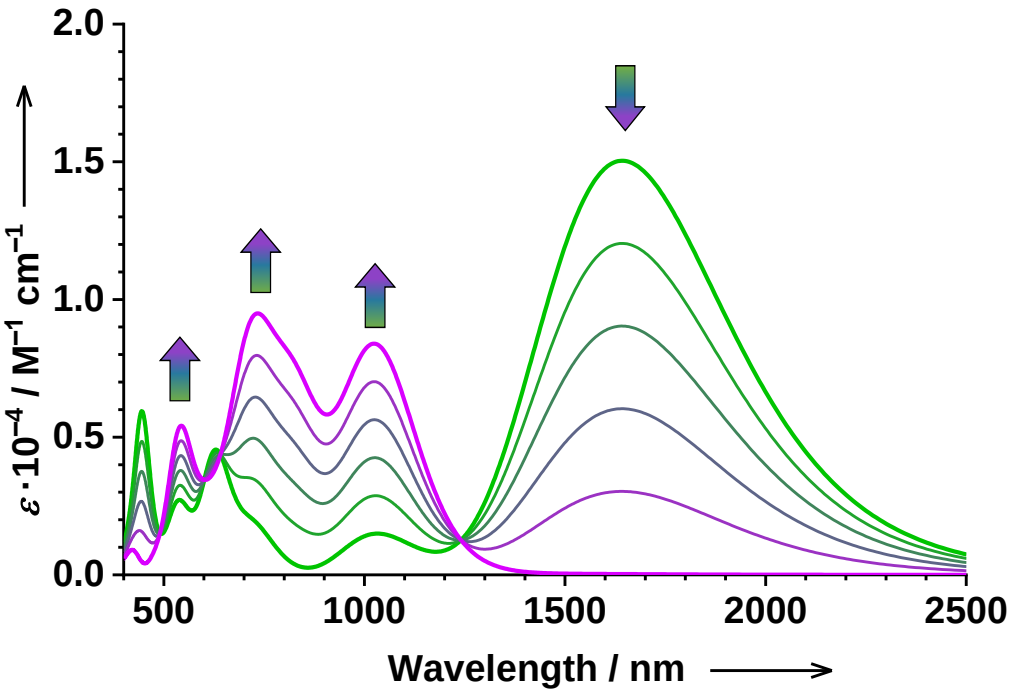


Figure S51: Simulated titration of **1** with TBACN (0...1 eq.): the evolution of calculated electronic absorption spectrum upon the conversion of the parent **1** (in green) to the postulated $\mathbf{2}^{\mathbf{five}}$ (in purple). Method: TD-DFT, B3LYP, **1** = 37% *ls*-$Co^{III}(SQ^{\bullet-})(Cat^{2-})$ as a six-coordinate species + 63% *hs*-$Co^{II}(SQ^{\bullet-})_2$ as a five-coordinate dissociated species, $\mathbf{2}^{\mathbf{five}}$ = *ls*-$Co^{II}(SQ^{\bullet-})_2$, see ESI for further details.

Table S3. Calculated thermodynamic parameters.

	Enthalpy H^0_{298}, kcal mol^{-1}	Enthalpy H^0_{298}, kJ mol^{-1}	Entropic term TS^0_{298}, kcal mol^{-1} (T = 298 K)	Entropy S^0_{298}, J K^{-1}mol^{-1}	Gibs free energy G^0_{298}, kcal mol^{-1}	Gibs free energy G^0_{298}, kJ mol^{-1}	relative energy, kcal mol^{-1}
Co(dioxolene)$_2$(stypy)$_2$							
S = 5/2 (hs)	-2142494.00	-8964194.88	79.69	1118.3	-2142573.68	-8964528.29	5.8
S = 3/2	-2142492.51	-8964188.64	78.92	1107.4	-2142571.42	-8964518.83	8.0
S = 1/2 (ls)	-2142503.52	-8964234.72	75.95	1065.8	-2142579.47	-8964552.50	0.0
delta(*hs – ls*)	**9.52**	**39.84**	**3.74**	**52.4**	**5.79**	**24.21**	
Co(dioxolene)$_2$(stypy)$_1$							
S = 5/2	-1793627.43	-7504537.16	63.39	889.6	-1793690.82	-7504802.39	3.0
S = 3/2	-1793630.37	-7504549.47	62.16	872.3	-1793692.53	-7504809.54	1.3
S = 1/2	-1793633.73	-7504563.55	60.08	843.1	-1793693.82	-7504814.92	0.0
delta(*hs – ls*)	**6.31**	**26.38**	**3.31**	**46.4**	**3.00**	**12.54**	
Co(dioxolene)$_2$(stypy)$_1$(CN)$_1^-$							
S = 5/2	-1851922.10	-7748442.07	66.70	936.1	-1851988.80	-7748721.16	14.7
S = 3/2	-1851927.87	-7748466.22	65.04	912.8	-1851992.92	-7748738.36	10.6
S = 1/2	-1851940.24	-7748517.97	63.29	888.2	-1852003.53	-7748782.79	0.0
delta(*hs – ls*)	**18.14**	**75.90**	**3.41**	**47.8**	**14.73**	**61.63**	
Co(dioxolene)$_2$(CN)$_1^-$							
S = 5/2	-1503059.49	-6288800.91	50.46	708.2	-1503109.95	-6289012.05	13.9
S = 3/2	-1503068.18	-6288837.28	47.81	670.9	-1503115.99	-6289037.32	7.9
S = 1/2	-1503077.38	-6288875.74	46.50	652.5	-1503123.88	-6289070.30	0.0
delta(*hs – ls*)	**17.88**	**74.83**	**3.96**	**55.6**	**13.92**	**58.25**	
Co(dioxolene)(CN)$_4^{2-}$							
S = 5/2	-1389342.77	-5813010.17	47.23	662.7	-1389390.00	-5813207.76	66.3
S = 3/2	-1389379.87	-5813165.36	45.02	631.7	-1389424.88	-5813353.70	31.4
S = 1/2	-1389414.00	-5813308.19	42.32	593.9	-1389456.32	-5813485.26	0.0
delta(*hs – ls*)	**71.23**	**298.02**	**4.91**	**68.8**	**66.32**	**277.50**	

Optimized geometry for Co(dioxolene)$_2$(stypy)$_2$: *S* = 5/2, <S^2> = 8.769837

Co	2.58943963968932	3.54459114106615	5.65798584530312
O	3.92714883069696	4.51140075913626	4.46663849691106
O	2.24427165119508	2.57131533748846	3.89780511118532
C	3.93454618696222	4.06913486203103	3.24802737036923
C	4.79708461156758	4.56350063107102	2.23484689021442
C	4.72767355629687	4.05780051378853	0.93829572379636
C	3.77760932531532	3.03177698887085	0.64258268982714
C	2.90835189023920	2.49741713187551	1.58921434360935
C	2.98078261543464	3.00761379170420	2.92714044882857
C	1.91972703415453	1.41791720567404	1.25730480603621
N	1.05910389346050	5.10484715946873	5.14176915022553
C	1.32751931283271	6.41821948855235	5.24010342607208
C	0.40213230954112	7.41273520584720	4.93476801168335
C	-0.89627028047787	7.07090873565482	4.49466263978465
C	-1.16264266244733	5.68623207777363	4.39566909852792
C	-0.17508075725982	4.76360021351930	4.72322040279882
C	-1.84936299153897	8.13133293203597	4.18039197675584
C	-3.13030435170950	7.96992811578985	3.74634241199953
C	-4.10333720718744	9.01319891913277	3.42490752827369
C	-3.84122764648227	10.40038970602619	3.53405770528506
C	-4.81819880052731	11.34249543390924	3.20974676482563
C	-6.08489671243968	10.93197465274691	2.76696729900798
C	-6.36483992763337	9.56476419763703	2.65222599835594

C	-5.38736784997794	8.62041886466707	2.97698197153197
O	1.25191607646135	2.57732263571273	6.84890057845161
O	2.93441592554899	4.51748336423672	7.41868124267997
C	1.24518170415140	3.01827599138711	8.06799636791682
C	0.38356297664291	2.52240874724157	9.08122755553318
C	0.45363975931801	3.02671619293735	10.37827875438456
C	1.40342441944907	4.05287581341821	10.67442691985702
C	2.27178625674845	4.58866531026176	9.72777981842550
C	2.19872041518092	4.07985846467536	8.38935355038289
C	-0.44317526772728	2.51570386189501	11.47146869660891
C	3.26015167847434	5.66824782606985	10.06019171437531
N	4.12049765316242	1.98480109415163	6.17450752211817
C	3.85265523811281	0.67130812717790	6.07624140170972
C	4.77841493806278	-0.32279669627454	6.38180303533810
C	6.07659808591804	0.01961190082536	6.82210029663625
C	6.34237370342125	1.40441047241798	6.92100520512811
C	5.35447793320827	2.32659649643286	6.59320911327733
C	7.03008798098547	-1.04037591891216	7.13664607854190
C	8.31081216704228	-0.87836491553459	7.57110740678463
C	9.28424587545245	-1.92116316061554	7.89285887357395
C	9.02288549655092	-3.30848231598899	7.78353675314114
C	10.00021075013779	-4.25010569036243	8.10818309626189
C	11.26652665259133	-3.83896256180833	8.55147757252296
C	11.54572996374235	-2.47161537824699	8.66639267249651

C	10.56790454556852	-1.52775289576527	8.34129816886074
C	5.62559995242592	4.56709671006758	-0.15478259880110
H	5.51330333950495	5.35408905412728	2.49441004432809
H	3.73426306168240	2.64515393044546	-0.38571534048214
H	2.33493871902271	6.68345308116087	5.58172746112166
H	0.69461894848826	8.46524630584981	5.04073627369875
H	-2.13690038799429	5.30938667479012	4.06459296263235
H	-0.37993598026754	3.68874756494992	4.64805895552262
H	-1.45448029495896	9.14725339472862	4.32056794168855
H	-3.51183831213761	6.94769809871940	3.60910119108925
H	-2.86092509530433	10.75266251937955	3.87784844672386
H	-4.58993577090328	12.41321536269255	3.30324556782600
H	-6.85039089580326	11.67802312140949	2.51295943892004
H	-7.35276327077856	9.23015036206213	2.30705227408974
H	-5.61654817347341	7.54977144780033	2.88375144555582
H	-0.33247068952301	1.73177597251207	8.82128817351211
H	1.44729898658735	4.43841611871988	11.70311008117625
H	2.84539976714858	0.40561773959798	5.73448574544148
H	4.48638943680802	-1.37544044072549	6.27587760268347
H	7.31642310485320	1.78169794381913	7.25219115673037
H	5.55887899207247	3.40153987134549	6.66829729944396
H	6.63572384936206	-2.05648180602987	6.99635276562064
H	8.69180391478596	0.14404684982473	7.70849843347599
H	8.04289927863862	-3.66124040217978	7.43934095452435

H 9.77253016398112 -5.32093700448512 8.01454034610295

H 12.03230065848035 -4.58463413042262 8.80574853831251

H 12.53334800545141 -2.13651492552107 9.01196739036757

H 10.79650406029283 -0.45699288388006 8.43466313205961

H 5.03517597140223 4.98862570898948 -0.99403141376990

H 6.23842206939464 3.74780324788351 -0.58349327882763

H 6.31219758132184 5.35296276263251 0.20870975423492

H 0.88109672794468 1.74356974620778 1.46802138689069

H 2.09153624077828 0.51125165203283 1.87180734539578

H 1.98160197486637 1.12991462465434 0.19226613858493

H 3.08777758243559 6.57535449085077 9.44650293004719

H 4.29881703696278 5.34313928103755 9.84879333586219

H 3.19860920349367 5.95533696020557 11.12549611949083

H -1.05542079878268 3.33433526659926 11.90225092043242

H 0.14812033691076 2.09266880797464 12.30935228260277

H -1.13024674807960 1.73051759937353 11.10740313347502

Optimized geometry for Co(dioxolene)$_2$(stypy)$_2$: *S* = 3/2, <S^2> = 3.773054

Co	2.52945976138264	3.44244985208652	5.58763722364162
O	3.82988855766512	4.36906206577096	4.53456730044070
O	2.11238590798055	2.51180423293885	4.04731156905121
C	3.80383428546701	3.92327687344252	3.29332096404301
C	4.64022601358413	4.39510784271074	2.26252956437071
C	4.53100606922747	3.85121760419324	0.97420679425959
C	3.57444039087966	2.82917866342908	0.72629700998783
C	2.72357344045947	2.32845872212269	1.71536780693608
C	2.84890621421593	2.89020985706970	3.01665127549287
C	1.71635160710988	1.24886544436053	1.44483910519387
N	0.99029308912831	5.14332381254200	5.06624094719303
C	1.31558996773961	6.44190856129525	5.16344137373379
C	0.42665466905083	7.47635953912767	4.87967462225125
C	-0.89374838223750	7.18896453146633	4.46729900261358
C	-1.21960444700146	5.81715918099626	4.36843325530962
C	-0.26255430900187	4.85332943474290	4.67197972516696
C	-1.80884827591803	8.29038859746275	4.17953314855060
C	-3.11173133959919	8.18743790185058	3.79650846730663
C	-4.04624958251249	9.27488690247876	3.50744800509893
C	-3.70633867487895	10.64795616771506	3.57016474269900
C	-4.65058550367448	11.63437997283558	3.28263314222876
C	-5.96108931483281	11.28359042427500	2.92399771443339
C	-6.31780933574529	9.93123680659800	2.85553577416910

C	-5.37283483083251	8.94260118074942	3.14271335349790
O	1.26042582888563	2.51327193082118	6.55451333020263
O	2.91234848007940	4.37560424870169	7.21806030162179
C	1.21291047855466	2.89460952250275	7.82129026411831
C	0.32880293999578	2.33769674303858	8.76988694612977
C	0.34925364478952	2.80605970340036	10.08626138186002
C	1.26816143297994	3.83733645059304	10.42762222925348
C	2.16207898687762	4.41682157006774	9.51910814344128
C	2.13281414086290	3.93136318626934	8.18308995169320
C	-0.57227712129600	2.24516590858223	11.13607477686471
C	3.12037812329041	5.50420558118493	9.91142647790154
N	4.20290067151475	1.89374910580448	6.15808156411823
C	3.98538554505873	0.57174907459702	6.07407424837511
C	4.94443526534689	-0.38404398340921	6.40328469347647
C	6.22233659316807	0.01473175293564	6.85477073988636
C	6.43485894410325	1.40994263862042	6.93650620264521
C	5.41566266135321	2.28916811595048	6.58395418066373
C	7.21148407719281	-1.00379329600031	7.19809126841937
C	8.47263187251242	-0.78656164431032	7.66382955984464
C	9.48057867969449	-1.78581078777616	8.01687801701461
C	9.27965750130391	-3.18379351981416	7.91554917816966
C	10.28796647062137	-4.08078571623229	8.27070977558442
C	11.52598514387624	-3.61331641320375	8.73742551941043
C	11.74534249089765	-2.23451575069604	8.84514609829762

C	10.73642400166129	-1.33538958277911	8.48956987055121
C	5.40904036249161	4.33423478122966	-0.14747527565151
H	5.36944403682314	5.18564567636611	2.48132596833982
H	3.50016685262231	2.41339612186078	-0.28813874590507
H	2.34046758240602	6.66257997228101	5.48603153089556
H	0.76364106789396	8.51595458707023	4.98209608422229
H	-2.21540325219043	5.48326151171834	4.05545088368229
H	-0.51033611322050	3.78697389524253	4.59671474967148
H	-1.36313054788536	9.28766338723143	4.29989127529268
H	-3.54754293383439	7.18397130593567	3.68457651658561
H	-2.68984471025194	10.95397183295891	3.84648767119154
H	-4.36153967355350	12.69300789766198	3.33828962421060
H	-6.70047745769726	12.06439465751586	2.69873660853371
H	-7.34048280694335	9.64307336155749	2.57584847009173
H	-5.66236081451999	7.88411338179712	3.08609016524312
H	-0.36215216007853	1.54404196764861	8.45749763712904
H	1.27890088131794	4.20179666529343	11.46502473787725
H	2.99166982582885	0.26390354103122	5.72499797830773
H	4.69494119367727	-1.44879745972080	6.30918307202957
H	7.39074050961004	1.82769774886142	7.27239496107302
H	5.57569195980553	3.37262756391049	6.64451473956811
H	6.86307834711399	-2.03617746742528	7.05463721565559
H	8.80682946945914	0.25147808993179	7.80557644855566
H	8.32293977321700	-3.58056211521714	7.55419246046726

H	10.10696625196498	-5.16097844635681	8.18275091589204
H	12.31617866741373	-4.32412262717493	9.01570703044172
H	12.71013972423496	-1.85527957872488	9.20907076187996
H	10.91815674830010	-0.25521449272676	8.57720400985675
H	4.80371979568714	4.75280547302648	-0.97744430993528
H	6.00075830151933	3.50165591880709	-0.57958218263771
H	6.11398241175611	5.11608966398152	0.18826672807184
H	0.68617470688079	1.59231461053518	1.66769460904903
H	1.89469168585656	0.36036774057559	2.08328803691854
H	1.75066977118911	0.92621994402676	0.38870755179080
H	2.95529430252426	6.42344821097256	9.31384448926304
H	4.17168340840371	5.20056937804759	9.73259889081581
H	3.01532355021056	5.76549207088056	10.97996615896456
H	-1.22506532247339	3.03347622177129	11.56367671837934
H	-0.00243328272221	1.81284309806725	11.98381082591593
H	-1.22365579881852	1.45190440844132	10.72628122505226

Optimized geometry for Co(dioxolene)$_2$(stypy)$_2$: *S* = 1/2, <S^2> = 0.752272

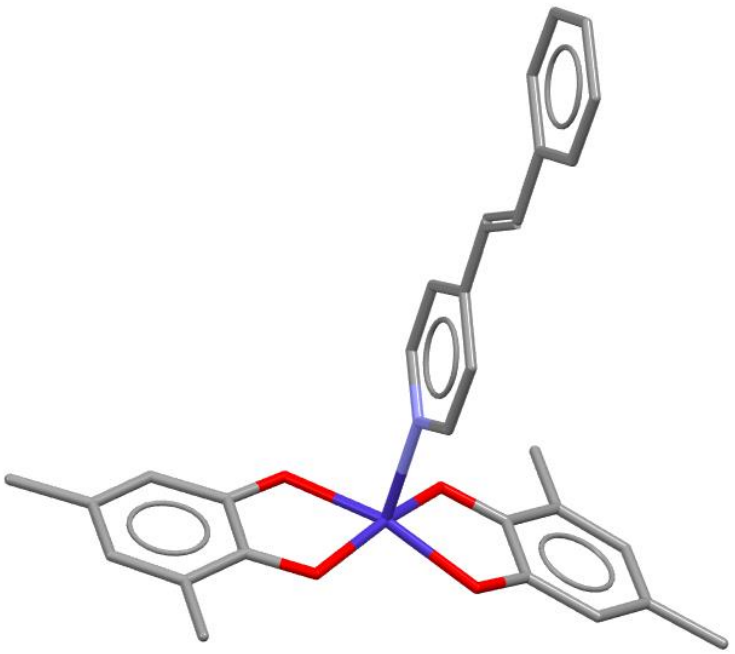
Co	2.81082841547946	4.52451684555866	4.75513122156718
O	2.16159578853558	5.89767861261566	3.63736604202985
O	3.67887534632357	5.87198305418323	5.74262372556629
O	3.46023381453193	3.15136838384367	5.87273668838814
O	1.94261410073815	3.17715560883555	3.76773709120699
N	1.21844153040191	4.70735135137155	5.90229895315701
N	4.40334128419858	4.34166086348370	3.60789918501701
C	2.59800240544661	7.07639434893266	4.05581318788440
C	2.28010788004719	8.29642565730117	3.42463634369658
C	2.78503763203606	9.50070832112417	3.93379658746778
C	3.61278874509689	9.46233317820353	5.08423502581135
C	3.95460339367728	8.27384248832586	5.74299996626409
C	3.43472165990758	7.06189990478734	5.21547454606663
C	2.46674854953865	10.81897747243856	3.27816830805161
C	3.02420990655950	1.97258400343547	5.45399456568630
C	3.34157764135063	0.75264404977387	6.08549853786083
C	2.83578391225921	-0.45159403231382	5.57692919586614
C	2.00643689475299	-0.41300222288091	4.42771710957044
C	1.66526261562037	0.77547994814069	3.76848967451724
C	2.18718585972284	1.98713860717983	4.29453603552399
C	0.78311539225183	0.79622577741597	2.55227008713210
C	1.32811330477464	4.75342375601068	7.24474357857296
C	0.23078108457592	4.87139072685298	8.08718947623019

C	-1.07530589549132	4.94946017995756	7.55173913414179
C	-1.15929699984013	4.90355948116850	6.14221516879785
C	-0.01273941467493	4.78393535488015	5.36587516317030
C	-2.29816574866280	5.06784682703670	8.33767580325783
C	-2.39088083088925	5.10595802031589	9.69658089032524
C	-3.60349174152118	5.21668691839368	10.50560888491778
C	-3.47298720579305	5.22424628396943	11.91505483101468
C	-4.59052154815150	5.32406006410734	12.74794066584134
C	-5.87255124593062	5.42012823712172	12.19280860666721
C	-6.02363104790351	5.41537552366833	10.79776440840485
C	-4.90858534657748	5.31545687085209	9.96500206223795
C	4.29366954465600	4.29524704226669	2.26547326479637
C	5.39101743900974	4.17728149545610	1.42304388007034
C	6.69712133869531	4.09960210885164	1.95851220879769
C	6.78111468835179	4.14586297160890	3.36802508093325
C	5.63453154962761	4.26543951675482	4.14433703937635
C	7.92000451699853	3.98126732714428	1.17260116679015
C	8.01272712311196	3.94277450372313	-0.18629251203946
C	9.22536676895773	3.83208051292966	-0.99528365512678
C	9.09485934926752	3.82389106190680	-2.40472562327391
C	10.21242061181307	3.72405424980822	-3.23757306234413
C	11.49448096062698	3.62860153440055	-2.68240543125614
C	11.64556549369234	3.63399749142944	-1.28736400486236
C	10.53049284433926	3.73393560218571	-0.45464043656202

C	4.83391355374653	8.25339218957799	6.96127286432454
C	3.16706691225742	-1.77108483117969	6.22370584208883
H	1.63536404458922	8.28500220359884	2.53605404760566
H	4.00771129470634	10.40823903782834	5.48177000731562
H	3.98616484572767	0.76404105708800	6.97420516263491
H	1.60925367445911	-1.35862609564854	4.03178300283571
H	2.34241236128130	4.69180561064314	7.64827096531186
H	0.41513628982063	4.90066716171100	9.16665323267037
H	-2.13218636710841	4.95956744152923	5.63835628020431
H	-0.06985855120203	4.74554899017283	4.27477873542918
H	-3.21530714505923	5.12432634469020	7.73547184374519
H	-1.46533069492851	5.04521189693094	10.28715528298570
H	-2.47092388884111	5.14868598096880	12.35941417023989
H	-4.45917688926517	5.32692048154830	13.83870614147254
H	-6.75397242392746	5.49889564544124	12.84394017577024
H	-7.02590716023431	5.49079903828987	10.35400816431532
H	-5.05928444414997	5.31474169252503	8.87854208179174
H	3.27934878373040	4.35657954438764	1.86194596088410
H	5.20667078883856	4.14770129831417	0.34358677894021
H	7.75402076551936	4.09017186762989	3.87188740156601
H	5.69163516223298	4.30407909274560	5.23542872105224
H	8.83716117688189	3.92516178808988	1.77481702671130
H	7.08716204614684	4.00311520506938	-0.77688521322375
H	8.09277241095474	3.89896459566307	-2.84911419054171

H	10.08107287554556	3.72069234867141	-4.32833675683153
H	12.37592291465187	3.54982032732291	-3.33350718957917
H	12.64786648172298	3.55906904176886	-0.84358019183436
H	10.68119399231798	3.73517369956554	0.63181880512881
H	1.98613514224840	11.52081771053141	3.98997196388012
H	1.78638107768542	10.69339384587869	2.41598417295185
H	3.38568457514713	11.32154506089419	2.91200845477297
H	4.31011217501478	7.81279410586470	7.83383682683353
H	5.15970134231700	9.27281510852740	7.23730849557938
H	5.74020295957821	7.63574432076023	6.79780032151392
H	-0.12206434645622	1.41507901632724	2.71735974415907
H	0.45548642110412	-0.22298528044410	2.27762979682821
H	1.30546232355082	1.23559359668815	1.67821632366500
H	2.25020444367041	-2.34213980329419	6.47416918525533
H	3.74796075873113	-1.63568522250756	7.15441972056248
H	3.76458471845411	-2.41528716072755	5.54567371177289

Optimized geometry for Co(dioxolene)$_2$(stypy)$_1$: *S* = 5/2, <S^2> = 8.767894



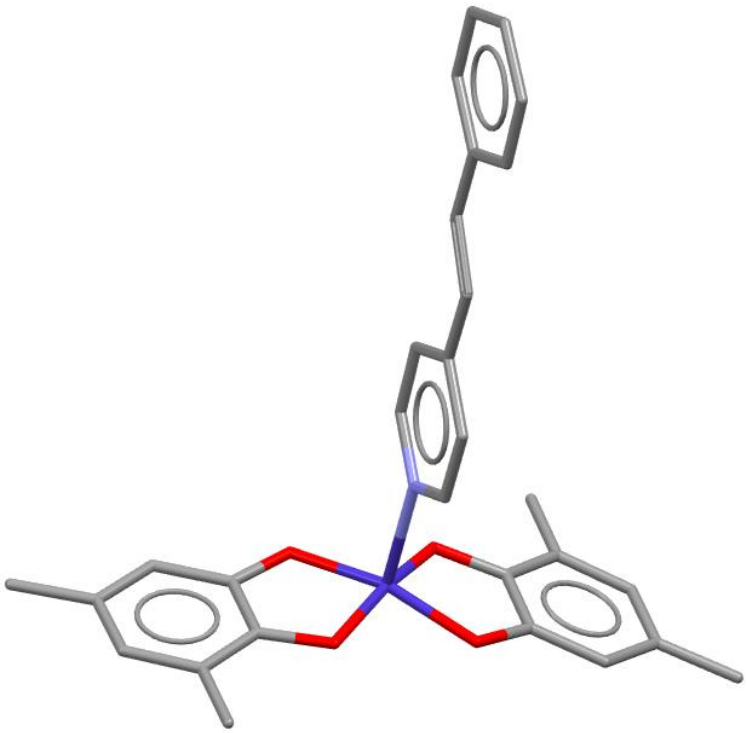
Co	2.158632	3.764094	5.520754
O	3.685162	4.594966	4.502649
O	2.094067	2.610426	3.883692
C	3.849455	4.066193	3.327927
C	4.848186	4.477188	2.409246
C	4.951432	3.861397	1.163988
C	4.050021	2.800102	0.834738
C	3.061595	2.335531	1.697471
C	2.946984	2.972397	2.973983
C	2.131853	1.215302	1.333838
N	0.765453	5.283934	5.044775
C	1.068909	6.593091	5.116699
C	0.159470	7.598349	4.806886
C	-1.153873	7.277260	4.394115
C	-1.453351	5.896836	4.325513
C	-0.483755	4.957662	4.652549
C	-2.086257	8.352470	4.074853
C	-3.381586	8.212303	3.675747
C	-4.334644	9.271709	3.349869
C	-4.028831	10.653390	3.400357
C	-4.989097	11.611976	3.075074
C	-6.281481	11.223629	2.690097
C	-6.604500	9.862238	2.633845

C	-5.643762	8.901154	2.959032
O	1.148183	2.597321	6.773707
O	2.720370	4.625455	7.273096
C	1.253337	2.955275	8.020965
C	0.591964	2.304823	9.088817
C	0.793292	2.732019	10.401488
C	1.682284	3.824141	10.653382
C	2.368038	4.499899	9.650003
C	2.149112	4.076792	8.297185
C	0.099448	2.069068	11.556905
C	3.298847	5.641719	9.933025
C	5.983536	4.286075	0.158306
H	5.525149	5.292041	2.696087
H	4.147253	2.325770	-0.152110
H	2.087481	6.839054	5.437723
H	0.477176	8.645474	4.888229
H	-2.440431	5.535218	4.017058
H	-0.712882	3.885868	4.599683
H	-1.663037	9.360985	4.180021
H	-3.792935	7.197242	3.576943
H	-3.027322	10.988026	3.697326
H	-4.727405	12.678067	3.121724
H	-7.033627	11.982763	2.435007
H	-7.612889	9.545533	2.334063

H	-5.906175	7.835174	2.911745
H	-0.078047	1.465269	8.863908
H	1.829047	4.142919	11.694991
H	5.504666	4.648897	-0.774329
H	6.630523	3.433764	-0.133441
H	6.631003	5.092321	0.547318
H	1.073861	1.545305	1.357791
H	2.213551	0.376459	2.053882
H	2.349310	0.826482	0.322834
H	2.961436	6.570309	9.430294
H	4.317744	5.432656	9.549822
H	3.370134	5.841781	11.017202
H	-0.526864	2.795284	12.114531
H	0.833754	1.666556	12.284345
H	-0.549209	1.238049	11.226625

Optimized geometry for Co(dioxolene)$_2$(stypy)$_1$: *S* = 3/2, <S^2> = 3.771699

Co	3.055824	4.473199	4.580454
O	2.187385	5.813917	3.660557
O	3.732074	5.793513	5.678140
O	3.489499	3.184053	5.824681
O	2.005852	3.195015	3.761631
N	4.814536	4.272559	3.301064
C	2.486571	7.020720	4.152810
C	2.002200	8.228526	3.628455
C	2.383794	9.439253	4.233520
C	3.243852	9.402491	5.356784
C	3.744259	8.212180	5.909490
C	3.348761	7.007640	5.280233
C	1.887109	10.759077	3.707374
C	2.923248	2.008720	5.532974
C	3.102738	0.838031	6.285792
C	2.450306	-0.340652	5.883682
C	1.628466	-0.309596	4.731871
C	1.424261	0.844380	3.957387
C	2.095213	2.016328	4.380208
C	0.542816	0.856034	2.742537
C	4.708952	4.271296	1.958143
C	5.803046	4.164329	1.107911
C	7.107321	4.049336	1.642284

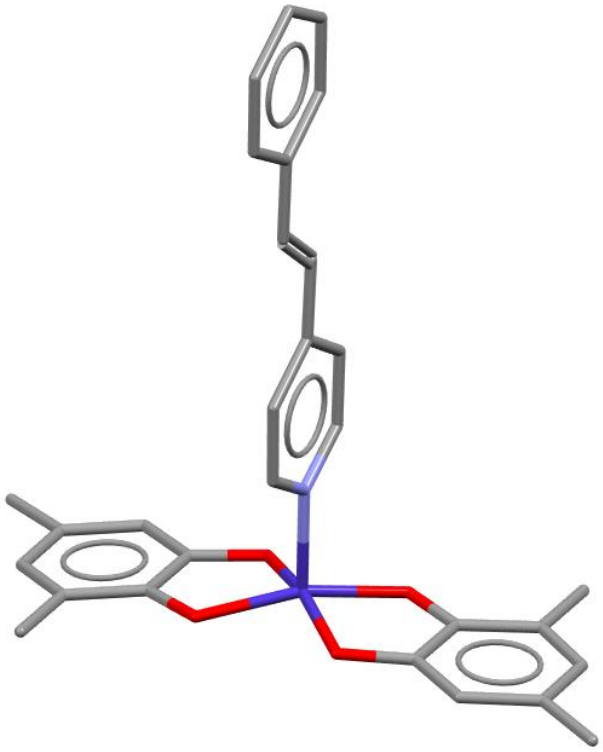


C	7.193653	4.049062	3.052954
C	6.045501	4.161119	3.830238
C	8.329103	3.937247	0.852948
C	8.422068	3.935068	-0.506370
C	9.633889	3.831136	-1.317513
C	9.504144	3.864574	-2.726630
C	10.620978	3.773959	-3.561512
C	11.901213	3.646304	-3.008666
C	12.051393	3.609956	-1.613972
C	10.937101	3.700619	-0.779164
C	4.652418	8.196277	7.104314
C	2.615858	-1.620911	6.657745
H	1.334382	8.213877	2.757935
H	3.536854	10.352506	5.825243
H	3.745072	0.857326	7.175227
H	1.119615	-1.234111	4.424904
H	3.695171	4.361785	1.550188
H	5.621221	4.172952	0.027486
H	8.167052	3.962379	3.551843
H	6.109427	4.163359	4.924747
H	9.245147	3.852252	1.453465
H	7.497949	4.023250	-1.095738
H	8.503444	3.965133	-3.169082
H	10.490479	3.803168	-4.651977

H	12.782075	3.574692	-3.661374
H	13.052297	3.509404	-1.172125
H	11.087149	3.668797	0.306925
H	1.298785	11.301299	4.475373
H	1.245038	10.629655	2.817414
H	2.729650	11.423002	3.426797
H	4.207534	7.621118	7.941000
H	4.860043	9.220465	7.462572
H	5.619955	7.709479	6.868733
H	-0.280691	1.590166	2.849782
H	0.096606	-0.138380	2.562415
H	1.109080	1.149963	1.836083
H	1.637621	-2.010475	7.004860
H	3.261193	-1.482044	7.543823
H	3.068094	-2.414634	6.028819

Optimized geometry for Co(dioxolene)$_2$(stypy)$_1$: *S* = 1/2, <S^2> = 0.766696

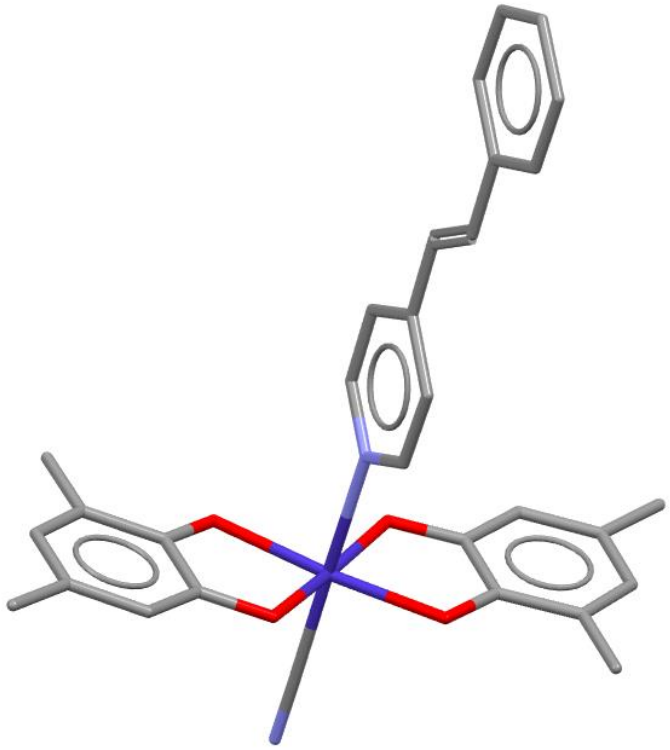
Co	3.030665	4.489007	4.597385
O	2.175674	5.853192	3.664016
O	3.667851	5.827308	5.718572
O	3.473691	3.168700	5.832513
O	1.981268	3.193998	3.778104
N	4.560692	4.334314	3.496494
C	2.546714	7.044984	4.095704
C	2.160705	8.265409	3.503316
C	2.605291	9.466379	4.064077
C	3.445664	9.426797	5.213216
C	3.859987	8.242012	5.826573
C	3.389195	7.029619	5.251516
C	2.215464	10.794874	3.474666
C	3.008798	1.987064	5.469733
C	3.282068	0.779038	6.144521
C	2.711821	-0.408039	5.675486
C	1.878359	-0.369349	4.521277
C	1.589470	0.801580	3.816313
C	2.168180	2.001996	4.312599
C	0.705402	0.823568	2.603324
C	4.447599	4.301790	2.148667
C	5.546524	4.189404	1.310471
C	6.853586	4.103278	1.844799



C	6.937566	4.139752	3.255573
C	5.795787	4.253205	4.036695
C	8.073859	3.984607	1.058820
C	8.163503	3.939799	-0.300983
C	9.373865	3.824074	-1.111176
C	9.239345	3.802107	-2.520314
C	10.354836	3.695107	-3.354763
C	11.638279	3.606455	-2.801570
C	11.793282	3.626029	-1.407020
C	10.680474	3.732962	-0.572414
C	4.745558	8.220181	7.038485
C	2.964735	-1.721124	6.365543
H	1.513457	8.254908	2.617256
H	3.790613	10.379505	5.639353
H	3.930152	0.789559	7.029980
H	1.440287	-1.311763	4.163270
H	3.434752	4.369410	1.742994
H	5.360445	4.170649	0.231151
H	7.909826	4.079060	3.759900
H	5.856214	4.281731	5.127733
H	8.991847	3.930079	1.659617
H	7.236769	3.995973	-0.890075
H	8.235991	3.871542	-2.962673
H	10.220949	3.680661	-4.445089

H	12.518144	3.522020	-3.454073
H	12.796884	3.556718	-0.965367
H	10.833971	3.745387	0.513544
H	1.659495	11.411929	4.209733
H	1.578150	10.675033	2.579939
H	3.109572	11.382178	3.182080
H	4.235315	7.750341	7.903436
H	5.046858	9.241855	7.331942
H	5.663499	7.626526	6.855698
H	-0.186047	1.462363	2.765327
H	0.357019	-0.192372	2.344102
H	1.235944	1.242683	1.724935
H	2.017613	-2.177189	6.719085
H	3.632470	-1.603118	7.238014
H	3.429693	-2.454602	5.675660

Optimized geometry for Co(dioxolene)$_2$(stypy)$_1$(CN)$_1^-$: *S* = 5/2, <S^2> = 8.769712



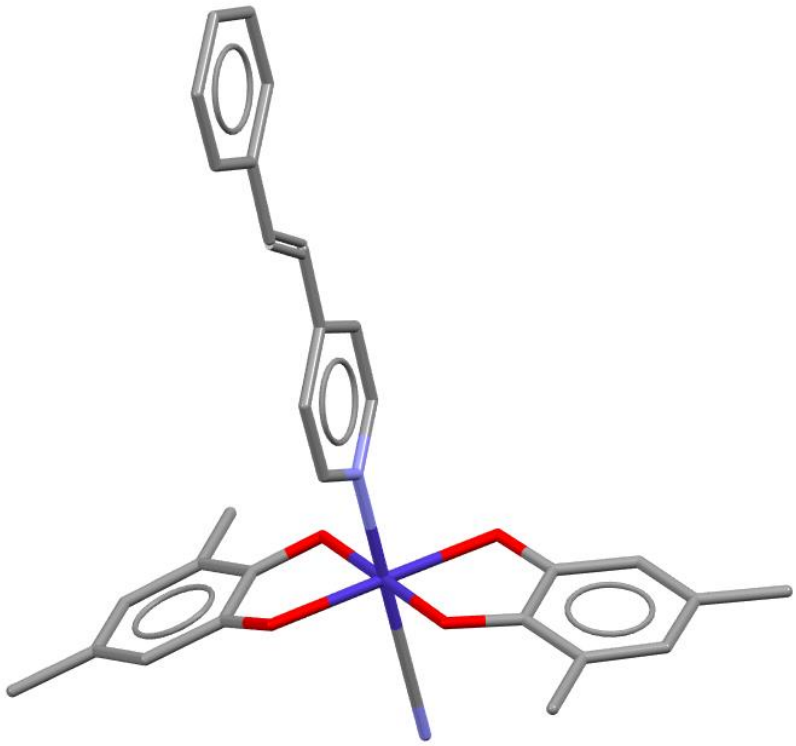
Co	2.432723	3.653799	5.602976
O	3.868519	4.556521	4.429413
O	2.172349	2.621138	3.844425
C	3.915356	4.075465	3.228534
C	4.834790	4.517357	2.238864
C	4.815629	3.972735	0.956416
C	3.862125	2.954388	0.650292
C	2.941936	2.466162	1.574443
C	2.958119	3.019503	2.897577
C	1.949980	1.392621	1.231699
C	1.041212	5.121173	5.126656
O	1.173891	2.624630	6.849268
O	2.863011	4.573406	7.406653
C	1.224593	3.025773	8.079785
C	0.427100	2.477079	9.119537
C	0.553817	2.935157	10.429644
C	1.500965	3.965333	10.715049
C	2.311496	4.548270	9.744519
C	2.178274	4.090874	8.390885
C	-0.282141	2.370212	11.545339
C	3.298664	5.632577	10.066143
N	4.043490	2.039831	6.146014
C	3.782534	0.726062	6.046245

C	4.710347	-0.267097	6.353384
C	6.005352	0.079943	6.798070
C	6.266403	1.465120	6.898847
C	5.274546	2.383647	6.568146
C	6.961795	-0.977798	7.115628
C	8.239908	-0.814146	7.556011
C	9.213641	-1.856484	7.880727
C	8.955220	-3.244053	7.767777
C	9.932150	-4.185184	8.095594
C	11.195820	-3.773677	8.545950
C	11.472211	-2.406080	8.664574
C	10.494673	-1.462834	8.336278
C	5.769196	4.436396	-0.110766
N	0.257947	5.953160	4.841382
H	5.552469	5.304356	2.506228
H	3.856296	2.535877	-0.366602
H	-0.289450	1.684347	8.866508
H	1.590803	4.316397	11.753292
H	2.776717	0.457143	5.701422
H	4.423119	-1.321082	6.245870
H	7.238619	1.844615	7.233446
H	5.474261	3.459629	6.644305
H	6.570735	-1.994914	6.972293
H	8.618355	0.208748	7.696821

H	7.977412	-3.597506	7.418087
H	9.705931	-5.256101	7.998754
H	11.961304	-4.518825	8.802715
H	12.457600	-2.069967	9.015672
H	10.721549	-0.391968	8.432797
H	5.224486	4.864765	-0.977351
H	6.372377	3.593153	-0.505435
H	6.466033	5.206696	0.266915
H	0.909110	1.738371	1.393679
H	2.083085	0.499575	1.875505
H	2.048406	1.075249	0.177574
H	3.082695	6.557157	9.493598
H	4.330618	5.333275	9.792037
H	3.286318	5.882056	11.142796
H	-0.896549	3.159044	12.026314
H	0.353251	1.936852	12.344959
H	-0.965461	1.578925	11.186835

Optimized geometry for Co(dioxolene)$_2$(stypy)$_1$(CN)$_1^-$: *S* = 3/2, <S^2> = 3.786357

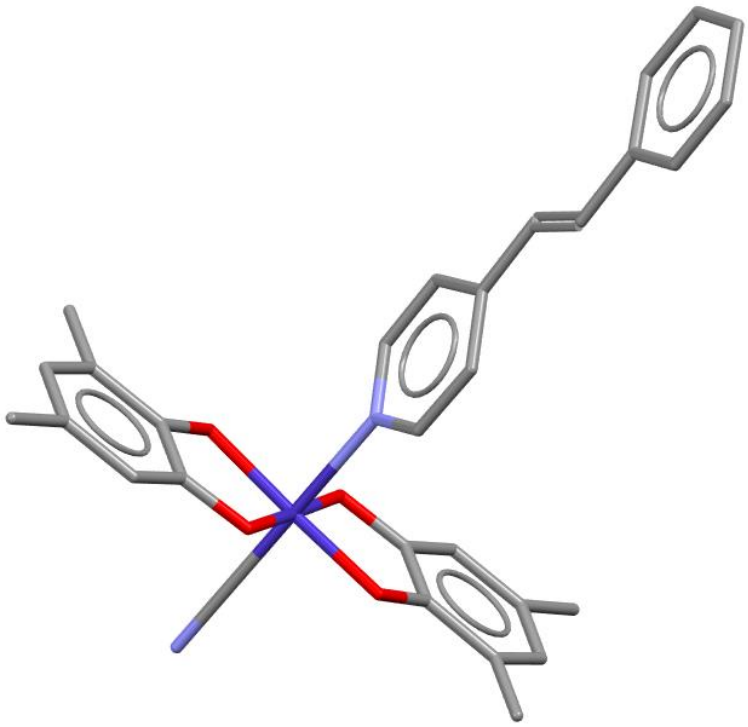
Co	2.508788	4.553837	4.956625
O	1.849888	6.107374	3.827432
O	3.405189	6.073777	5.959780
O	3.186132	3.004031	6.076926
O	1.625621	3.026189	3.949115
N	0.869169	4.719478	6.149744
C	3.993915	4.407457	3.865685
C	2.533272	7.185351	4.078186
C	2.452451	8.366406	3.296245
C	3.184103	9.504349	3.641341
C	4.019144	9.462196	4.793938
C	4.144386	8.332590	5.603314
C	3.393184	7.165395	5.255582
C	3.107463	10.764673	2.821213
C	2.996784	1.869315	5.471003
C	3.547093	0.640151	5.917749
C	3.271486	-0.552141	5.246357
C	2.428349	-0.516499	4.099203
C	1.858280	0.658044	3.607259
C	2.134790	1.882717	4.294641
C	0.973889	0.671367	2.393058
C	0.976700	4.741648	7.492722
C	-0.114741	4.861096	8.344209



C	-1.420773	4.966868	7.813532
C	-1.510705	4.939906	6.403879
C	-0.365068	4.817868	5.624572
C	-2.639447	5.098068	8.605861
C	-2.728185	5.138676	9.964684
C	-3.937512	5.269125	10.776858
C	-3.804376	5.275829	12.186069
C	-4.918051	5.395524	13.021762
C	-6.199879	5.512990	12.470291
C	-6.353723	5.509429	11.075588
C	-5.242389	5.389668	10.240148
C	5.034824	8.307717	6.812922
C	3.844634	-1.865037	5.709281
N	4.937917	4.314953	3.167001
H	1.800762	8.364830	2.412112
H	4.594567	10.361611	5.057609
H	4.194617	0.648841	6.804782
H	2.217418	-1.459766	3.574482
H	1.991453	4.658936	7.895660
H	0.071474	4.870436	9.423908
H	-2.485572	5.015768	5.905937
H	-0.429388	4.798079	4.531734
H	-3.558022	5.167699	8.006823
H	-1.802066	5.066361	10.553072

H	-2.802690	5.183877	12.628287
H	-4.783449	5.397318	14.112216
H	-7.078229	5.607678	13.123492
H	-7.355478	5.601811	10.633663
H	-5.395953	5.391228	9.154069
H	2.743426	11.620508	3.426454
H	2.428634	10.648953	1.956494
H	4.105234	11.056144	2.433229
H	4.457465	8.102921	7.737529
H	5.562835	9.270014	6.944404
H	5.794935	7.503776	6.738945
H	-0.034230	1.068073	2.630278
H	0.853460	-0.343456	1.971533
H	1.385490	1.327865	1.599690
H	3.043505	-2.587986	5.968021
H	4.487530	-1.740232	6.599903
H	4.453958	-2.342858	4.914677

Optimized geometry for Co(dioxolene)$_2$(stypy)$_1$(CN)$_1^-$: *S* = 1/2, <S^2> = 0.752475

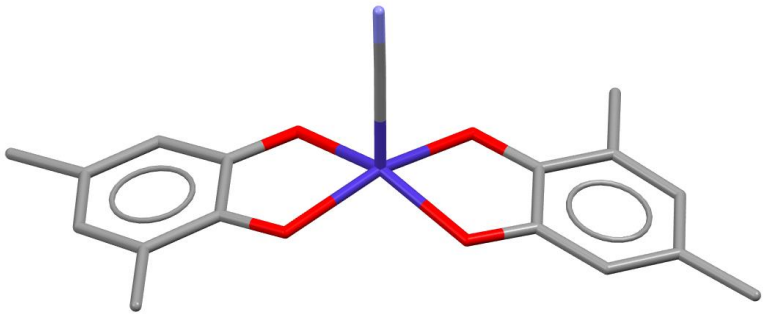


Co	2.875810	4.529220	4.707278
O	2.207399	5.902166	3.596728
O	3.730931	5.881114	5.702437
O	3.496197	3.162363	5.851218
O	1.969000	3.185434	3.749199
N	1.150528	4.745293	5.955542
C	4.352744	4.342151	3.634730
C	2.660859	7.077937	4.002268
C	2.360917	8.295628	3.355708
C	2.875987	9.500062	3.854262
C	3.705243	9.464430	5.003570
C	4.038091	8.277830	5.670905
C	3.499067	7.066079	5.160879
C	2.565799	10.816066	3.188867
C	3.059120	1.984561	5.433249
C	3.383118	0.763470	6.061379
C	2.872269	-0.441139	5.558680
C	2.039258	-0.404148	4.412201
C	1.699640	0.783856	3.750708
C	2.217634	1.997611	4.277180
C	0.818235	0.803570	2.533822
C	1.254934	4.782275	7.295439
C	0.160280	4.894386	8.145958

C	-1.145066	4.976031	7.609971
C	-1.231651	4.943668	6.200439
C	-0.079945	4.828414	5.426722
C	-2.369436	5.083574	8.399002
C	-2.465189	5.093687	9.757481
C	-3.680436	5.188130	10.566332
C	-3.555300	5.152656	11.975732
C	-4.675194	5.232221	12.808001
C	-5.955202	5.351194	12.252725
C	-6.101014	5.390237	10.857714
C	-4.983436	5.310340	10.025761
C	4.923794	8.258719	6.884655
C	3.202253	-1.760016	6.208735
N	5.299689	4.221680	2.946685
H	1.717091	8.282086	2.466223
H	4.110617	10.410206	5.391429
H	4.033753	0.775443	6.945921
H	1.640352	-1.350403	4.018850
H	2.271878	4.715700	7.698116
H	0.341239	4.915766	9.226550
H	-2.206823	5.005069	5.700771
H	-0.136596	4.797986	4.332884
H	-3.286105	5.152934	7.796953
H	-1.541212	5.017340	10.348743

H	-2.555126	5.058658	12.420925
H	-4.546887	5.201055	13.898773
H	-6.838383	5.414089	12.903247
H	-7.101264	5.484521	10.412788
H	-5.130666	5.344466	8.939309
H	2.059700	11.515565	3.885735
H	1.909362	10.684130	2.309077
H	3.489835	11.325993	2.846581
H	4.395443	7.847148	7.768816
H	5.276697	9.274687	7.140151
H	5.812768	7.614875	6.727015
H	-0.096986	1.406587	2.703539
H	0.506560	-0.217563	2.247196
H	1.335139	1.261706	1.666167
H	2.284931	-2.316679	6.489546
H	3.808792	-1.624107	7.123049
H	3.773255	-2.419192	5.522262

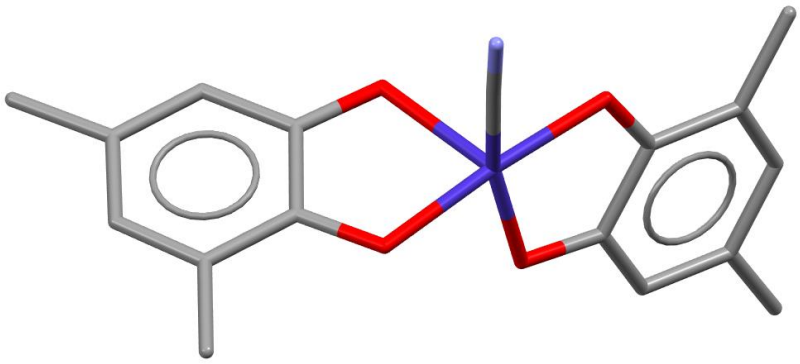
Optimized geometry for Co(dioxolene)$_2$(CN)$_1^-$: *S* = 5/2, <S^2> = 8.766626



Co	1.912187	3.940647	5.436974
O	3.542481	4.677310	4.469677
O	1.896462	2.739306	3.813670
C	3.720360	4.130241	3.306903
C	4.766872	4.490987	2.418321
C	4.889664	3.861745	1.181491
C	3.962404	2.831343	0.831629
C	2.929229	2.412342	1.666087
C	2.790460	3.066432	2.932021
C	1.971604	1.322955	1.280358
C	0.644918	5.445848	4.975079
O	0.967926	2.726619	6.715213
O	2.553603	4.750010	7.215432
C	1.113434	3.056711	7.965147
C	0.493286	2.375738	9.039596
C	0.737029	2.768534	10.356590
C	1.630531	3.855439	10.607178
C	2.280265	4.557972	9.597421
C	2.015507	4.173474	8.240057
C	0.080414	2.073311	11.515947
C	3.216596	5.696029	9.878524
C	5.967058	4.244889	0.205717
N	-0.106750	6.303707	4.684162

H	5.462265	5.284668	2.720835
H	4.073165	2.343906	-0.147631
H	-0.182297	1.540048	8.815906
H	1.811223	4.149512	11.650915
H	5.531365	4.642182	-0.734297
H	6.580376	3.366125	-0.080245
H	6.642394	5.015210	0.619940
H	0.926210	1.691653	1.264044
H	1.995897	0.489317	2.010851
H	2.209189	0.915032	0.281229
H	2.857535	6.637083	9.415379
H	4.221365	5.503852	9.451271
H	3.327901	5.865732	10.964731
H	-0.540042	2.779613	12.105108
H	0.836400	1.662262	12.215989
H	-0.568353	1.242701	11.184249

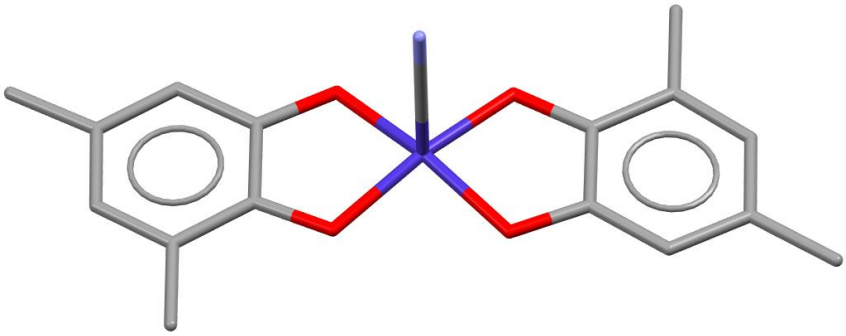
Optimized geometry for Co(dioxolene)$_2$(CN)$_1^-$: *S* = 3/2, <S^2> = 3.771273



Co	4.031684	4.339805	3.841209
O	2.408309	5.583849	3.611092
O	4.758624	5.800061	4.772524
O	3.481101	3.497515	5.486825
O	3.352046	2.808405	3.019603
C	4.892015	4.832763	2.251022
C	2.677031	6.719975	4.176107
C	1.780408	7.821964	4.209805
C	2.151402	9.016328	4.823494
C	3.444217	9.117896	5.419614
C	4.369010	8.075152	5.424804
C	3.981116	6.851225	4.801526
C	1.221882	10.198604	4.868303
C	2.940126	2.322464	5.259154
C	2.446068	1.457942	6.261036
C	1.912676	0.215212	5.902141
C	1.878079	-0.157826	4.528871
C	2.353128	0.661267	3.501504
C	2.884162	1.925795	3.881986
C	2.308963	0.257260	2.056389
C	5.724892	8.201068	6.057274
C	1.379353	-0.733033	6.942244
N	5.463973	5.115824	1.261493

H	0.795339	7.709759	3.738529
H	3.725057	10.066485	5.898968
H	2.490376	1.773546	7.311427
H	1.455909	-1.137169	4.262386
H	1.003755	10.497971	5.913944
H	0.260592	9.983053	4.367605
H	1.674007	11.083464	4.375344
H	5.859612	7.464553	6.874984
H	5.878108	9.211972	6.476478
H	6.532040	8.004194	5.323488
H	1.695775	0.961345	1.458574
H	1.884387	-0.755953	1.936936
H	3.320974	0.264284	1.604077
H	0.315439	-0.982013	6.751724
H	1.453118	-0.308977	7.960127
H	1.933846	-1.693865	6.932357

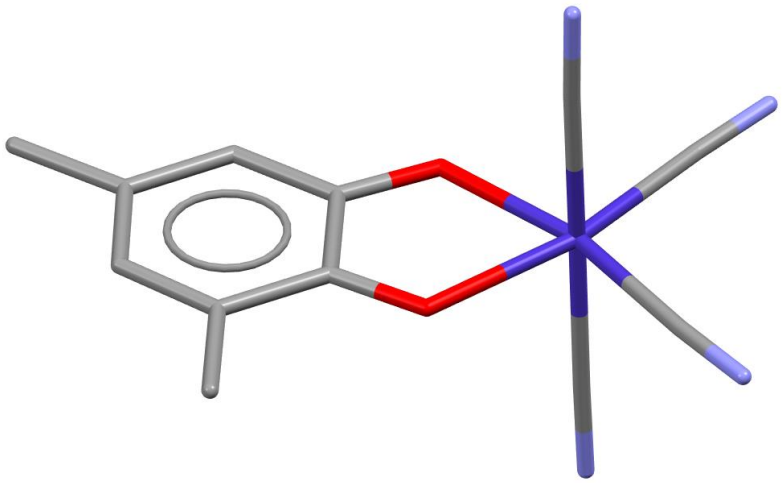
Optimized geometry for Co(dioxolene)$_2$(CN)$_1^-$: *S* = 1/2, <S^2> = 0.754246



Co	3.096309	4.492087	4.543717
O	2.259590	5.852951	3.595102
O	3.758497	5.822938	5.654759
O	3.566429	3.168632	5.761328
O	2.074689	3.196113	3.696312
C	4.552333	4.348283	3.482800
C	2.614514	7.045364	4.047828
C	2.208963	8.267384	3.472792
C	2.631592	9.470323	4.049430
C	3.468435	9.429174	5.197927
C	3.901031	8.239813	5.793720
C	3.454092	7.028173	5.201366
C	2.217437	10.799017	3.474245
C	3.087636	1.988560	5.399736
C	3.343975	0.782159	6.083491
C	2.766661	-0.405074	5.619452
C	1.943834	-0.366480	4.460762
C	1.671370	0.805979	3.748330
C	2.254135	2.004147	4.241742
C	0.801341	0.828367	2.524590
C	4.787301	8.215316	7.005695
C	3.005085	-1.715109	6.322864
N	5.500484	4.253823	2.790275

H	1.564668	8.257641	2.584254
H	3.797658	10.380467	5.639907
H	3.988002	0.792430	6.972236
H	1.500481	-1.306456	4.102179
H	1.633912	11.392175	4.208007
H	1.596098	10.676516	2.568372
H	3.099558	11.413430	3.201468
H	4.288749	7.717931	7.862213
H	5.066663	9.237732	7.318543
H	5.718192	7.645256	6.812540
H	-0.087741	1.474354	2.671416
H	0.448921	-0.186330	2.264907
H	1.345406	1.240098	1.650795
H	2.053701	-2.161094	6.678439
H	3.669938	-1.594133	7.197460
H	3.468659	-2.459795	5.643970

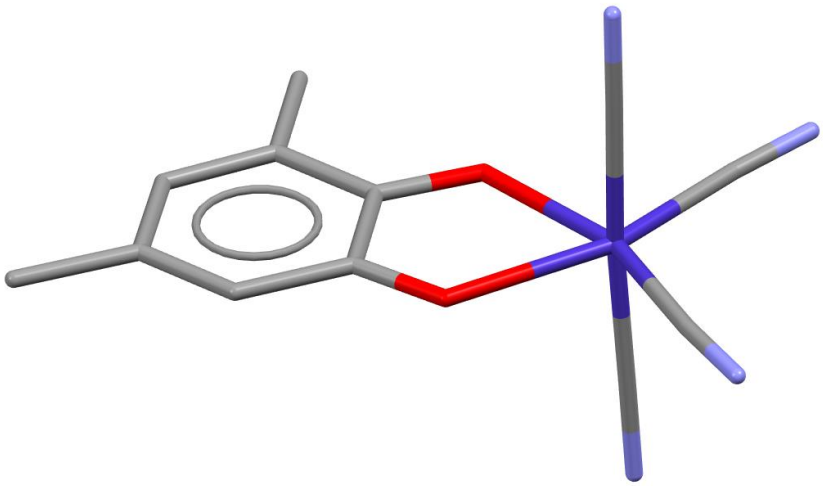
Optimized geometry for Co(dioxolene)$(CN)_4^{2-}$: *S* = 5/2, $\langle S^2 \rangle$ = 8.767080



Co	8.025735	4.621374	6.971769
C	7.349668	6.007552	8.372243
N	6.902926	6.787263	9.132407
C	6.350097	4.206979	5.832859
N	5.359694	4.010189	5.228007
C	8.561318	6.234549	5.702503
N	8.841398	7.138519	5.001808
C	7.527318	3.072599	8.337450
N	7.208235	2.215039	9.078614
O	9.149746	3.298988	5.845424
C	10.384211	3.159547	6.198170
C	11.297011	2.287378	5.556219
C	12.618868	2.195302	6.000963
C	13.037490	2.991336	7.107945
C	12.192613	3.868278	7.784243
C	10.831405	3.967502	7.334352
O	9.956734	4.735388	7.873572
C	13.604489	1.276961	5.336224
C	12.650016	4.697014	8.946228
H	10.942970	1.689006	4.707401
H	14.080532	2.906413	7.443962
H	13.144912	0.712304	4.505383
H	14.020874	0.548040	6.061127

H	14.466790	1.845606	4.931837
H	12.524918	5.778701	8.738411
H	13.712540	4.507730	9.182282
H	12.046297	4.483633	9.850987

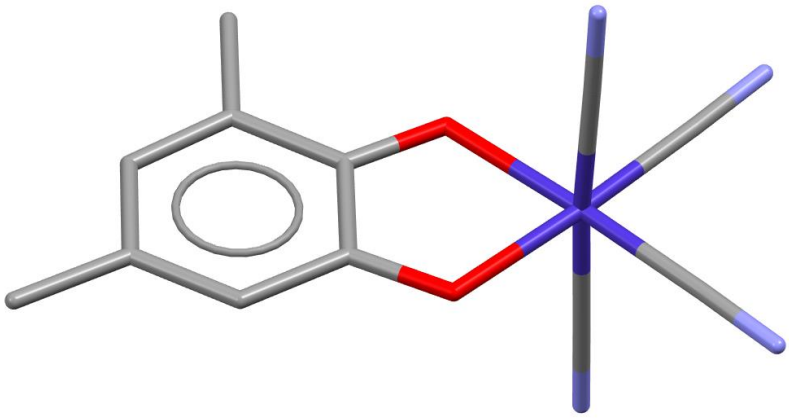
Optimized geometry for Co(dioxolene)$(CN)_4^{2-}$: *S* = 3/2, $\langle S^2 \rangle$ = 3.777312



Co	7.971453	4.662740	7.019503
C	7.475822	5.973633	8.379057
N	7.085888	6.762607	9.160382
C	6.482156	4.193387	5.848807
N	5.528768	3.964508	5.197990
C	8.400216	6.086562	5.852798
N	8.682844	6.970610	5.129222
C	7.425114	3.288249	8.194651
N	7.090411	2.426837	8.923321
O	9.146493	3.264701	5.852037
C	10.372448	3.137222	6.200030
C	11.301317	2.270084	5.556554
C	12.618603	2.193722	5.995154
C	13.034827	2.998574	7.103881
C	12.186538	3.864478	7.781617
C	10.820373	3.950665	7.339133
O	9.945228	4.708527	7.882935
C	13.617488	1.287692	5.330344
C	12.638950	4.703050	8.940722
H	10.949990	1.668283	4.708686
H	14.081150	2.925284	7.433589
H	13.164701	0.715954	4.500212
H	14.044878	0.563647	6.054050

H	14.472020	1.866277	4.923001
H	12.498759	5.783099	8.733080
H	13.705998	4.529604	9.170131
H	12.046375	4.483192	9.851503

Optimized geometry for Co(dioxolene)$(CN)_4^{2-}$: *S* = 1/2, $<S^2>$ = 0.753036



Co	8.158879	4.583325	7.000981
C	7.365056	5.796039	8.115890
N	6.882079	6.580923	8.848962
C	6.571518	4.380029	6.116854
N	5.561401	4.225066	5.531886
C	8.583973	6.002781	5.831852
N	8.863301	6.885510	5.105616
C	7.621332	3.209552	8.178623
N	7.289386	2.348048	8.908205
O	9.102164	3.288520	5.849454
C	10.342134	3.162101	6.208441
C	11.257234	2.292969	5.557113
C	12.574957	2.212435	5.996956
C	12.992138	3.014037	7.107292
C	12.145719	3.881745	7.787212
C	10.786250	3.963775	7.336813
O	9.906948	4.734696	7.892994
C	13.571795	1.304713	5.331607
C	12.598540	4.716553	8.948477
H	10.902796	1.694389	4.708427
H	14.037697	2.937669	7.438343
H	13.117636	0.734980	4.500950
H	13.996795	0.579146	6.055062

H	14.427753	1.881903	4.925548
H	12.463063	5.797303	8.742235
H	13.664460	4.538419	9.178995
H	12.003801	4.496562	9.857603