Supplementary information: How molecular oxygen binds to bis[trifluoroacetylacetonato(–1)]cobalt(II) – ab initio and density functional theory studies.

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Selected properties of the examined cobalt complexes with different solvent ligands, different numbers of unpaired electrons as well as different conformations (Geo1-Geo6). Geo1 - Geo6 are presented in Figure S1. Used acronyms: td - total density, sd - spin density, ch - charge.

Ligand	Geo	2S+1	E [kcal/mol]*	E[kcal/mol]**	Co-O^1 [Å]	O^1-O^2 [Å]	td Co	sd Co	sd O^1	sd O^2	ch Co	ch O^1	ch O(2)
EtOH	1	2	0.0	0.0	1.900	1.295	7.5	0.0	0.5	0.5	1.2	-0.2	-0.2
		4	18.4	14.7	1.951	1.272	7.3	1.5	0.6	0.7	1.4	-0.2	-0.2
	2	2	0.3	0.2	1.897	1.300	7.5	0.0	0.5	0.5	1.2	-0.2	-0.2
		4	18.3	14.5	1.943	1.272	7.3	1.5	0.6	0.6	1.4	-0.2	-0.2
	3	2	0.2	0.2	1.901	1.296	7.5	0.0	0.5	0.5	1.2	-0.2	-0.2
		4	18.6	15.7	1.924	1.274	7.3	1.5	0.6	0.6	1.4	-0.2	-0.2
	4	2	1.2	0.8	1.904	1.295	7.5	0.0	0.5	0.5	1.2	-0.2	-0.2
		4	18.4	15.3	1.926	1.274	7.3	1.5	0.6	0.6	1.4	-0.2	-0.2
	5	2	3.7	4.5	1.881	1.265	7.5	-0.1	0.5	0.6	1.2	-0.2	-0.1
		4	18.9	7.5	2.171	1.243	7.4	1.2	0.8	0.9	1.3	-0.2	-0.1
	6	2	4.7	2.8	1.878	1.265	7.5	-0.1	0.5	0.6	1.2	-0.2	-0.1
		4	19.8	8.5	2.156	1.243	7.4	1.2	0.8	0.9	1.3	-0.2	-0.1
H_2O	1	2	0.0	0.1	1.899	1.295	7.5	0.0	0.5	0.5	1.2	-0.2	-0.2
		4	18.7	14.4	1.967	1.271	7.3	1.5	0.6	0.7	1.5	-0.2	-0.2
	2	2	0.0	0.0	1.900	1.297	7.5	0.0	0.5	0.5	1.2	-0.2	-0.2
		4	18.3	14.3	1.943	1.273	7.3	1.5	0.6	0.6	1.4	-0.2	-0.2
	3	2	0.2	0.1	1.901	1.297	7.5	0.0	0.5	0.5	1.2	-0.2	-0.2
		4	17.9	12.6	1.939	1.282	7.3	1.8	0.4	0.4	1.4	-0.2	-0.2
	4	2	0.4	0.4	1.901	1.297	7.5	0.0	0.5	0.5	1.2	-0.2	-0.2

		4	18.5	14.9	1.936	1.274	7.3	1.5	0.6	0.6	1.4	-0.2	-0.2
	5	2	4.1	2.0	1.876	1.266	7.5	-0.1	0.5	0.6	1.2	-0.2	-0.1
		4	19.2	7.7	2.164	1.243	7.4	1.2	0.8	0.9	1.3	-0.2	-0.1
	6	2	4.9	2.6	1.874	1.266	7.5	-0.1	0.5	0.6	1.2	-0.2	-0.1
		4	20.1	8.6	2.136	1.244	7.4	1.2	0.8	0.9	1.3	-0.2	-0.1

*BP86, def2-TZVP, grid m4

**B3LYP, def2-TZVP, grid m4

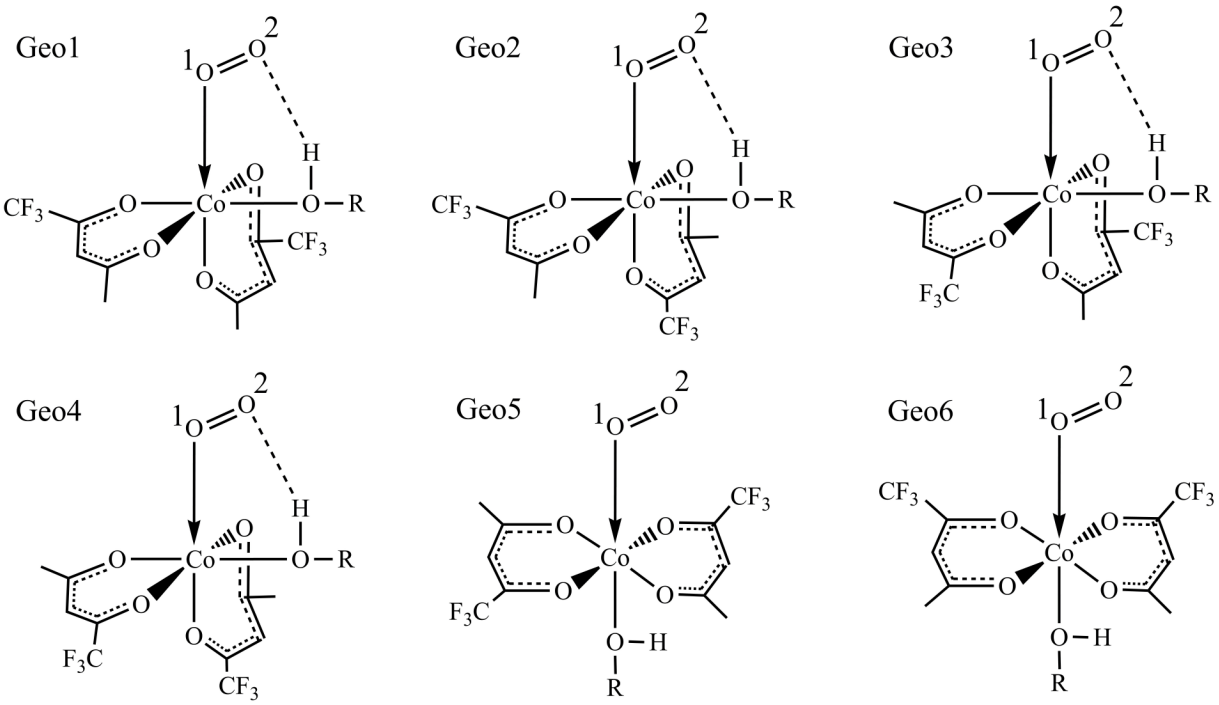

Figure S1. Various conformations of examined cobalt complexes.

$Co(tfa)_2(H_2O)$ low spin (S=1/2)

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C	1.45230	2.99520	-0.03160
F	0.36890	2.23330	0.25530
C	1.07140	4.44890	-0.36190
O	2.09300	5.19370	-0.56610
Co	1.95320	7.02870	-0.86930
F	2.27490	2.95450	1.03800
F	2.09480	2.41850	-1.07070
C	-0.28550	4.81320	-0.42820
C	-0.71170	6.11590	-0.77690
O	0.09290	7.10330	-0.98880
C	-2.18300	6.43080	-0.93230
O	3.80050	7.10530	-1.19600
C	4.66620	7.29470	-0.26410
C	4.45350	7.52790	1.09640
C	3.15910	7.62570	1.70670
O	2.05660	7.53550	1.08710
C	6.10580	7.25700	-0.80940
F	6.27850	8.23070	-1.73780
F	6.35950	6.07420	-1.40800
F	7.03940	7.44190	0.15130
C	3.08040	7.82910	3.21080
O	1.82910	8.94560	-1.49500
H	5.33860	7.64460	1.73620
H	-1.04340	4.04170	-0.24010
H	4.01720	8.24420	3.63710
H	2.22570	8.49450	3.45550
H	2.88370	6.84710	3.70070
H	-2.82190	5.54170	-0.75760
H	-2.47560	7.23180	-0.21640
H	-2.38340	6.82080	-1.95570
H	2.38340	9.13640	-2.28480
H	0.88170	9.07720	-1.73930

$Co(tfa)_2(H_2O)$ high spin (S=3/2)

32

C	1.47860	3.07940	-0.71850
F	0.46570	2.19360	-0.56220
C	1.01380	4.55060	-0.65060
O	1.98610	5.37490	-0.73030
Co	1.73700	7.32180	-0.54240
F	2.39240	2.83230	0.24300
F	2.05810	2.83070	-1.91570
C	-0.36060	4.82890	-0.53580
C	-0.90930	6.14360	-0.50910
O	-0.21970	7.22210	-0.56290
C	-2.41240	6.32260	-0.42120
O	3.80230	7.53030	-0.93580
C	4.69320	7.48410	-0.03210
C	4.50230	7.60460	1.35670
C	3.23070	7.84440	1.94410
O	2.12320	7.88510	1.30310
C	6.12730	7.31080	-0.58130
F	6.46870	8.38540	-1.33230
F	6.19430	6.21920	-1.37150
F	7.05770	7.17650	0.39090
C	3.13260	8.09140	3.43650
O	1.53870	8.73080	-2.10180
H	5.38330	7.55970	2.01050
H	-1.05280	3.97750	-0.48520
H	4.11140	8.01170	3.95140
H	2.70970	9.10580	3.61370
H	2.41830	7.36570	3.88520
H	-2.96120	5.35930	-0.39770
H	-2.66080	6.90630	0.49350
H	-2.76720	6.92460	-1.28740
H	0.57270	8.71130	-2.33560
H	1.81990	9.67090	-2.04980

$Co(tfa)_2(H_2O)(O_2)$ (S=1/2)

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C	1.59810	3.08070	-0.08900
C	0.40470	2.14590	0.20410
C	-0.89650	2.66050	0.18230
C	-2.04270	1.86380	0.44630
C	-3.42310	2.48380	0.41240
C	1.71000	-2.08750	0.16110
C	2.95190	-2.86790	0.64510
C	1.42650	-2.03640	-1.20600
C	0.24620	-1.43080	-1.72870
C	-0.03740	-1.50130	-3.21540
F	2.29230	2.63320	-1.15750
F	2.43170	3.11830	0.96790
F	1.20300	4.34660	-0.35490
F	3.73020	-2.08970	1.41700
F	3.70410	-3.32520	-0.38150
F	2.56620	-3.93670	1.38110
O	0.78090	0.94750	0.44480
O	1.04130	-1.59060	1.13640
O	-1.60970	-1.89530	1.46970
O	-2.01720	0.61770	0.72800
O	-0.62540	-0.82050	-1.02960
O	-0.32560	0.10760	2.68930
O	-1.22560	-0.40080	3.46790
H	2.12140	-2.52600	-1.90010
H	-1.03410	3.72520	-0.04480
H	0.68600	-2.14380	-3.75650
H	-1.06930	-1.88120	-3.38000
H	0.00020	-0.47440	-3.64420
H	-3.39760	3.54860	0.10590
H	-4.07070	1.91120	-0.28720
H	-3.88750	2.40530	1.42080
H	-1.01650	-2.67130	1.61630
H	-1.77510	-1.49950	2.41250
Co	-0.44060	-0.41680	0.86620