Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

How to Enhance the Effective Spin-Reversal Barriers of Two-Coordinate Co(II) Imido Complexes with $[CoN]^+$ core? A Theoretical Investigation

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Table S1. Specific crystallographic data of the bond lengths (Å) and angles θ (°), φ (°) for **1** (**1***), **2a** (**2a***), **2b** (**2b***) and **3** (**3***).

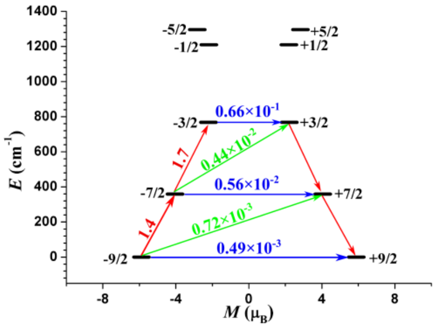
compounds	θ	φ	(carbene)C-Co	Co=N(amido)	N-C(arene)
1 (**1***)	173.03	174.55	1.954	1.692	1.344
2a (**2a***)	177.52	176.43	1.949	1.675	1.344
2b (**2b***)	179.32	177.83	1.959	1.677	1.339
3 (**3***)	175.72	173.13	1.972	1.682	1.331

Table S2. Calculated energy levels (cm^{-1}), ***g*** (g_x, g_y, g_z) tensors and predominant m_J values of the original and simplified structures **1** (**1***), **2a** (**2a***), **2b** (**2b***) and **3** (**3***) by CAS (7, 5) using CASSCF/SINGLE_ANISO[1−3] with ORCA 5.0.3.[4]

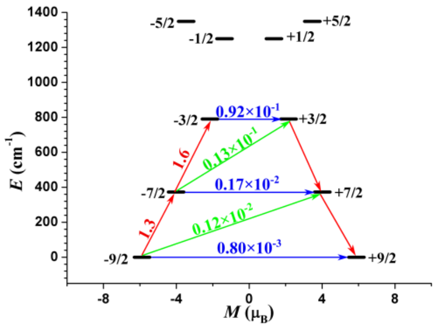
CAS (7, 5)						
KDs	**1**			**1***		
	E/cm^{-1}	***g***	m_J	E/cm^{-1}	***g***	m_J
0	0.0	0.001 0.002 11.775	±9/2	0.0	0.002 0.003 11.769	±9/2
1	358.9	0.017 0.017 8.095	±7/2	373.3	0.050 0.053 8.024	±7/2
2	767.9	0.191 0.207 4.448	±3/2	790.6	0.237 0.314 4.332	±5/2

3	1210.0	0.047 0.180 4.691	±1/2	1250.1	0.015 0.313 3.155	±1/2
4	1295.8	0.028 0.134 5.733	±5/2	1349.1	0.040 0.084 7.194	±3/2
KDs	**2a**			**2a***		
	E/cm^{-1}	$\boldsymbol{g}$	m_J	E/cm^{-1}	$\boldsymbol{g}$	m_J
0	0.0	0.006 0.008 11.766	±9/2	0.0	0.001 0.001 11.803	±9/2
1	304.2	0.075 0.077 8.325	±7/2	352.7	0.001 0.001 8.154	±7/2
2	682.2	0.211 0.340 4.777	±3/2	759.2	0.172 0.186 4.487	±1/2
3	1042.3	0.092 0.195 7.591	±5/2	1203.6	0.016 0.150 5.112	±3/2
4	1164.2	0.018 0.370 2.927	±1/2	1272.8	0.045 0.166 5.225	±5/2
KDs	**2b**			**2b***		
	E/cm^{-1}	$\boldsymbol{g}$	m_J	E/cm^{-1}	$\boldsymbol{g}$	m_J
0	0.0	0.003 0.004 11.744	±9/2	0.0	0.001 0.001 11.790	±9/2
1	316.5	0.021 0.022 8.252	±7/2	356.9	0.009 0.009 8.122	±7/2
2	699.7	0.146 0.174 4.746	±3/2	764.9	0.173 0.176 4.472	±1/2
3	1063.3	0.107 0.127 7.273	±5/2	1205.7	0.014 0.144 4.983	±3/2
4	1190.9	0.050 0.239 3.301	±1/2	1286.4	0.039 0.138 5.425	±5/2
KDs	**3**			**3***		
	E/cm^{-1}	$\boldsymbol{g}$	m_J	E/cm^{-1}	$\boldsymbol{g}$	m_J
0	0.0	0.001 0.001	±9/2	0.0	0.000 0.000	±9/2

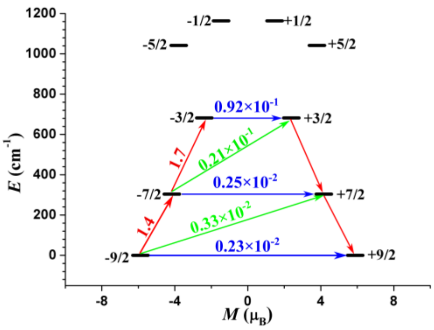
		11.910			11.915	
1	395.1	0.002 0.003 8.194	±7/2	420.0	0.024 0.025 8.120	±7/2
2	811.5	0.104 0.108 4.689	±3/2	861.1	0.002 0.053 4.480	±3/2
3	1263.8	0.121 0.244 2.805	±1/2	1333.0	0.035 0.048 2.294	±1/2
4	1329.6	0.054 0.056 8.287	±5/2	1461.9	0.012 0.017 8.727	±5/2



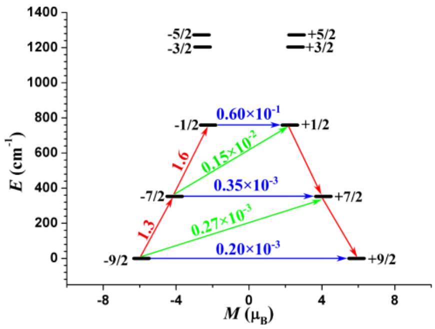
1_ CAS (7, 5) _767.9 cm^{-1}



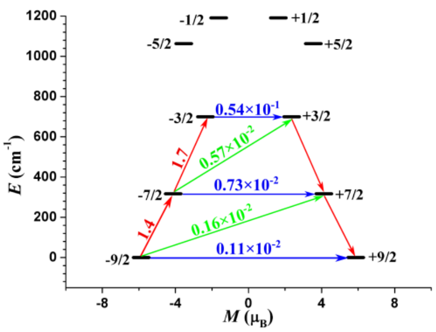
1* _CAS (7, 5) _790.6 cm^{-1}



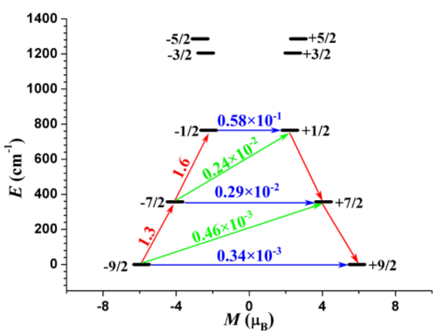
2a _CAS (7, 5) _682.2 cm^{-1}



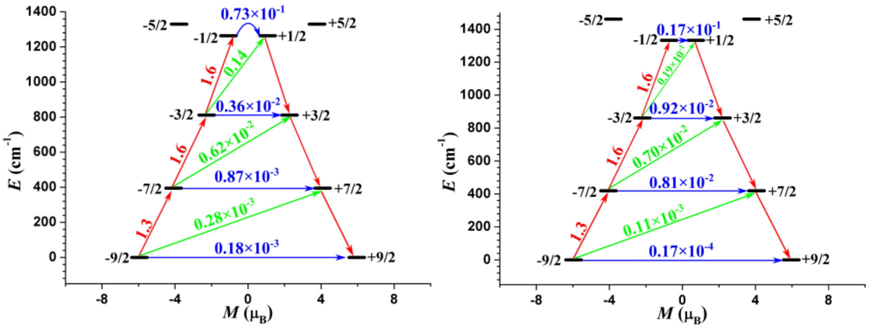
2a*_CAS (7, 5) _759.2 cm^{-1}



2b _CAS (7, 5) _699.7 cm^{-1}



2b* _CAS (7, 5) _764.9 cm^{-1}



3 _CAS (7, 5) _1263.8 cm^{-1} **3*** _CAS (7, 5) _1333.0 cm^{-1}

Figure S1. Magnetization blocking barriers for **1** (**1***), **2a** (**2a***), **2b** (**2b***) and **3** (**3***) by CAS (7, 5). The thick black lines represent the KDs of the Co^{II} ion as a function of their magnetic moment along the magnetic axis. The blue lines correspond to diagonal matrix element of the transversal magnetic moment; the green lines represent Orbach relaxation processes. The path shown by the red arrows represent the most probable path for magnetic relaxation in the corresponding compounds. The numbers at each arrow stand for the mean absolute value of the corresponding matrix element of transition magnetic moment.

Table S3. Calculated Mulliken spin density on Co^{II} for **1** (**1***), **2a** (**2a***), **2b** (**2b***) and **3** (**3***) at their spin state S = 3/2 by CAS (7, 5) using CASSCF/SINGLE_ANISO with ORCA 5.0.3.

	1	**1***	**2a**	**2a***	**2b**	**2b***	**3**	**3***
Co^{II}	2.9427	2.9294	2.9395	2.9255	2.9438	2.9269	2.9482	2.9327

Table S4. Calculated crystal field parameters B (k, q) and the corresponding weights of **1** (**1***), **2a** (**2a***), **2b** (**2b***) and **3** (**3***) by CAS (7, 5) using CASSCF/SINGLE_ANISO with ORCA 5.0.3.

CAS (7, 5)							
1				**1***			
k	q	B (k, q)	Weight (%)	k	q	B (k, q)	Weight (%)
2	-2	-0.15×10^{-5}	0.00	2	-2	-0.26×10^{-5}	0.00
2	-1	-0.14×10^{2}	6.13	2	-1	-0.16×10^{2}	7.01
2	0	-0.89×10^{2}	38.70	2	0	-0.88×10^{2}	37.55
2	1	-0.10×10^{-4}	0.00	2	1	0.54×10^{-6}	0.00
2	2	-0.24×10^{2}	10.39	2	2	-0.25×10^{2}	10.88
4	-4	-0.11×10^{-6}	0.00	4	-4	0.12×10^{-7}	0.00
4	-3	-0.10×10^{0}	1.22	4	-3	-0.27×10^{0}	3.14
4	-2	-0.13×10^{-6}	0.00	4	-2	0.20×10^{-6}	0.00
4	-1	0.54×10^{0}	6.42	4	-1	0.74×10^{0}	8.50
4	0	0.81×10^{0}	9.57	4	0	0.64×10^{0}	7.38
4	1	0.92×10^{-6}	0.00	4	1	-0.40×10^{-7}	0.00
4	2	-0.16×10^{1}	19.34	4	2	-0.15×10^{1}	18.32
4	3	-0.69×10^{-7}	0.00	4	3	-0.51×10^{-7}	0.00
4	4	-0.43×10^{-1}	0.50	4	4	-0.27×10^{-1}	0.31
6	-6	-0.34×10^{-8}	0.00	6	-6	0.13×10^{-9}	0.00

6	-5	0.72×10^{-5}	0.00	6	-5	-0.27×10^{-3}	0.02
6	-4	0.13×10^{-8}	0.00	6	-4	-0.65×10^{-9}	0.00
6	-3	-0.11×10^{-2}	0.09	6	-3	-0.23×10^{-2}	0.19
6	-2	0.10×10^{-7}	0.00	6	-2	0.44×10^{-8}	0.00
6	-1	0.27×10^{-1}	2.38	6	-1	0.30×10^{-1}	2.53
6	0	0.46×10^{-1}	4.04	6	0	0.36×10^{-1}	3.06
6	1	0.28×10^{-7}	0.00	6	1	-0.29×10^{-8}	0.00
6	2	-0.11×10^{-1}	1.00	6	2	-0.10×10^{-1}	0.90
6	3	-0.10×10^{-7}	0.00	6	3	-0.25×10^{-8}	0.00
6	4	-0.17×10^{-2}	0.15	6	4	-0.15×10^{-2}	0.13
6	5	0.84×10^{-8}	0.00	6	5	0.76×10^{-9}	0.00
6	6	0.16×10^{-4}	0.00	6	6	0.89×10^{-4}	0.00
2a				**2a***			
k	*q*	*B* (*k*, *q*)	Weight (%)	*k*	*q*	*B* (*k*, *q*)	Weight (%)
2	-2	0.40×10^{1}	1.68	2	-2	-0.23×10^{2}	11.57
2	-1	-0.11×10^{0}	0.05	2	-1	0.84×10^{0}	0.41
2	0	-0.89×10^{2}	37.59	2	0	-0.89×10^{2}	44.32
2	1	0.28×10^{1}	1.19	2	1	0.64×10^{0}	0.32
2	2	-0.22×10^{2}	9.36	2	2	-0.26×10^{0}	0.13
4	-4	0.31×10^{-1}	0.35	4	-4	-0.25×10^{-3}	0.00
4	-3	-0.35×10^{-1}	0.40	4	-3	0.86×10^{-1}	1.15
4	-2	0.30×10^{0}	3.46	4	-2	-0.15×10^{1}	20.38
4	-1	0.17×10^{-1}	0.20	4	-1	-0.94×10^{-1}	1.26
4	0	0.12×10^{1}	14.22	4	0	0.91×10^{0}	12.26
4	1	-0.25×10^{0}	2.89	4	1	-0.85×10^{-1}	1.14
4	2	-0.16×10^{1}	19.11	4	2	-0.11×10^{-1}	0.14
4	3	0.13×10^{0}	1.57	4	3	-0.88×10^{-1}	1.18
4	4	-0.84×10^{-1}	0.96	4	4	0.39×10^{-1}	0.53
6	-6	0.67×10^{-4}	0.01	6	-6	-0.68×10^{-4}	0.01
6	-5	-0.69×10^{-4}	0.01	6	-5	-0.11×10^{-3}	0.01
6	-4	0.80×10^{-3}	0.06	6	-4	-0.18×10^{-4}	0.00
6	-3	-0.21×10^{-3}	0.02	6	-3	0.58×10^{-3}	0.05
6	-2	0.16×10^{-2}	0.13	6	-2	-0.56×10^{-2}	0.55
6	-1	0.23×10^{-3}	0.02	6	-1	-0.74×10^{-4}	0.01
6	0	0.60×10^{-1}	5.10	6	0	0.43×10^{-1}	4.24
6	1	-0.61×10^{-2}	0.51	6	1	0.25×10^{-3}	0.02
6	2	-0.89×10^{-2}	0.75	6	2	-0.25×10^{-3}	0.02
6	3	0.88×10^{-3}	0.07	6	3	-0.57×10^{-3}	0.05
6	4	-0.21×10^{-2}	0.18	6	4	0.17×10^{-2}	0.16
6	5	0.15×10^{-3}	0.01	6	5	-0.11×10^{-3}	0.01
6	6	-0.11×10^{-3}	0.01	6	6	-0.18×10^{-5}	0.00
2b				**2b***			
k	*q*	*B* (*k*, *q*)	Weight (%)	*k*	*q*	*B* (*k*, *q*)	Weight (%)

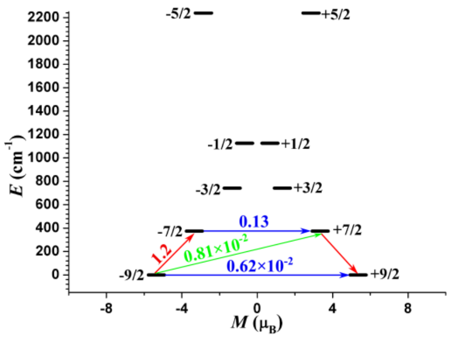
2	-2	-0.68×10^{1}	2.48	2	-2	0.50×10^{-1}	0.02
2	-1	0.22×10^{1}	0.81	2	-1	-0.10×10^{2}	4.80
2	0	-0.89×10^{2}	32.52	2	0	-0.89×10^{2}	40.22
2	1	-0.13×10^{2}	4.92	2	1	0.16×10^{0}	0.07
2	2	0.20×10^{2}	7.37	2	2	-0.22×10^{2}	10.20
4	-4	0.40×10^{-1}	0.39	4	-4	-0.10×10^{-3}	0.00
4	-3	-0.72×10^{-1}	0.71	4	-3	-0.14×10^{0}	1.74
4	-2	-0.59×10^{0}	5.86	4	-2	-0.38×10^{-2}	0.04
4	-1	-0.80×10^{-1}	0.79	4	-1	0.47×10^{0}	5.72
4	0	0.11×10^{1}	11.46	4	0	0.85×10^{0}	10.45
4	1	0.49×10^{0}	4.84	4	1	-0.13×10^{-1}	0.16
4	2	0.17×10^{1}	17.33	4	2	-0.15×10^{1}	19.47
4	3	0.13×10^{0}	1.36	4	3	0.21×10^{-2}	0.02
4	4	-0.52×10^{-1}	0.52	4	4	-0.38×10^{-1}	0.46
6	-6	-0.35×10^{-4}	0.00	6	-6	-0.75×10^{-6}	0.00
6	-5	0.16×10^{-3}	0.01	6	-5	-0.18×10^{-3}	0.01
6	-4	0.12×10^{-2}	0.09	6	-4	-0.92×10^{-6}	0.00
6	-3	-0.79×10^{-3}	0.05	6	-3	-0.74×10^{-3}	0.06
6	-2	-0.49×10^{-2}	0.35	6	-2	-0.12×10^{-3}	0.01
6	-1	-0.45×10^{-2}	0.33	6	-1	0.18×10^{-1}	1.65
6	0	0.61×10^{-1}	4.44	6	0	0.43×10^{-1}	3.87
6	1	0.27×10^{-1}	1.99	6	1	-0.40×10^{-3}	0.03
6	2	0.14×10^{-1}	1.03	6	2	-0.84×10^{-2}	0.75
6	3	0.14×10^{-2}	0.10	6	3	0.13×10^{-4}	0.00
6	4	-0.16×10^{-2}	0.11	6	4	-0.17×10^{-2}	0.15
6	5	-0.15×10^{-3}	0.01	6	5	0.14×10^{-5}	0.00
6	6	0.22×10^{-4}	0.00	6	6	0.69×10^{-4}	0.01
3				**3***			
k	*q*	*B* (*k*, *q*)	Weight (%)	*k*	*q*	*B* (*k*, *q*)	Weight (%)
2	-2	0.24×10^{1}	1.00	2	-2	-0.50×10^{1}	2.16
2	-1	-0.41×10^{1}	1.71	2	-1	-0.24×10^{2}	10.50
2	0	-0.88×10^{2}	36.70	2	0	-0.87×10^{2}	37.25
2	1	0.26×10^{2}	11.10	2	1	-0.75×10^{1}	3.19
2	2	-0.72×10^{1}	3.02	2	2	0.75×10^{1}	3.21
4	-4	0.71×10^{-1}	0.80	4	-4	0.88×10^{-1}	1.01
4	-3	-0.15×10^{0}	1.70	4	-3	0.20×10^{0}	2.38
4	-2	0.14×10^{0}	1.64	4	-2	-0.15×10^{0}	1.73
4	-1	0.26×10^{0}	2.92	4	-1	0.15×10^{1}	18.29
4	0	0.26×10^{0}	2.94	4	0	-0.53×10^{-1}	0.61
4	1	-0.16×10^{1}	18.68	4	1	0.48×10^{0}	5.57
4	2	-0.41×10^{0}	4.69	4	2	0.22×10^{0}	2.57
4	3	0.29×10^{0}	3.27	4	3	0.25×10^{0}	2.93
4	4	-0.95×10^{-1}	1.07	4	4	-0.36×10^{-1}	0.41

6	-6	0.10×10^{-3}	0.01	6	-6	-0.48×10^{-4}	0.00
6	-5	-0.25×10^{-3}	0.02	6	-5	-0.28×10^{-4}	0.00
6	-4	0.82×10^{-3}	0.06	6	-4	0.95×10^{-3}	0.08
6	-3	-0.34×10^{-3}	0.02	6	-3	-0.34×10^{-3}	0.02
6	-2	-0.32×10^{-2}	0.27	6	-2	0.77×10^{-2}	0.65
6	-1	0.71×10^{-2}	0.59	6	-1	0.38×10^{-1}	3.27
6	0	0.33×10^{-1}	2.77	6	0	0.23×10^{-1}	2.00
6	1	-0.46×10^{-1}	3.87	6	1	0.11×10^{-1}	1.00
6	2	0.10×10^{-1}	0.86	6	2	-0.11×10^{-1}	0.97
6	3	0.59×10^{-3}	0.04	6	3	-0.36×10^{-3}	0.03
6	4	-0.11×10^{-2}	0.09	6	4	-0.37×10^{-3}	0.03
6	5	0.24×10^{-3}	0.02	6	5	-0.31×10^{-3}	0.02
6	6	-0.75×10^{-4}	0.01	6	6	-0.10×10^{-4}	0.00

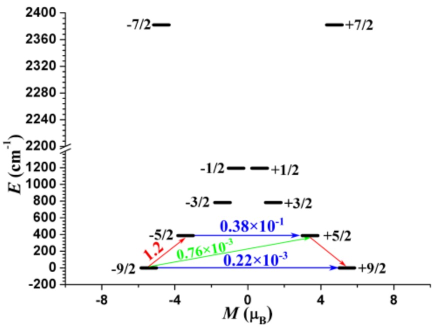
Table S5. Calculated energy levels (cm^{-1}), ***g*** (g_x, g_y, g_z) tensors and predominant m_J values of the original and simplified structures of **1** (**1***), **2a** (**2a***), **2b** (**2b***) and **3** (**3***) by CAS (11, 7) using CASSCF/SINGLE_ANISO with ORCA 5.0.3.

CAS (11, 7)						
KDs	**1**			**1***		
	E/cm^{-1}	***g***	m_J	E/cm^{-1}	***g***	m_J
0	0.0	0.018 0.019 10.705	±9/2	0.0	0.001 0.001 10.846	±9/2
1	373.9	0.359 0.410 6.675	±7/2	387.6	0.113 0.114 6.817	±7/2
2	742.2	0.230 0.540 2.671	±3/2	783.3	0.177 0.386 2.773	±5/2
3	1126.1	0.137 0.145 1.345	±1/2	1194.0	0.184 0.214 1.289	±3/2
4	2238.5	0.860 1.024 5.712	±5/2	2382.1	0.300 0.604 9.496	±1/2
KDs	**2a**			**2a***		
	E/cm^{-1}	***g***	m_J	E/cm^{-1}	***g***	m_J
0	0.0	0.030 0.032 11.028	±9/2	0.0	0.077 0.024 11.098	±7/2
1	390.6	0.926 0.952 6.891	±5/2	388.3	1.298 1.597 5.519	±5/2
2	801.6	0.709	±3/2	787.5	3.578	±1/2

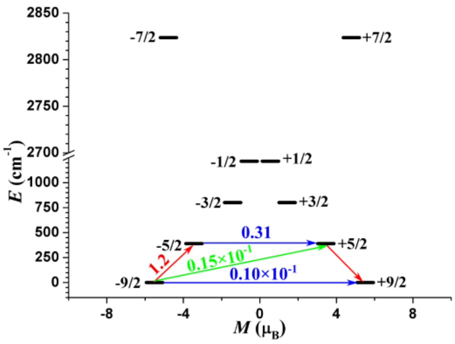
		1.141 2.848			3.390 0.564	
3	1215.4	0.158 0.169 1.104	±1/2	1261.1	0.044 0.048 2.338	±3/2
4	2823.7	0.067 0.105 9.981	±7/2	2715.7	0.017 0.018 11.530	±9/2
KDs	**2b**			**2b***		
	E/cm^{-1}	$\boldsymbol{g}$	m_J	E/cm^{-1}	$\boldsymbol{g}$	m_J
0	0.0	0.007 0.008 10.889	±9/2	0.0	0.005 0.005 10.822	±9/2
1	387.9	0.184 0.187 6.864	±5/2	386.4	0.132 0.136 6.794	±5/2
2	786.8	0.092 0.481 2.826	±3/2	781.0	0.138 0.422 2.754	±3/2
3	1202.2	0.186 0.217 1.233	±1/2	1190.2	0.188 0.214 1.303	±1/2
4	2242.8	0.116 0.195 9.710	±7/2	2398.3	0.092 0.159 9.668	±7/2
KDs	**3**			**3***		
	E/cm^{-1}	$\boldsymbol{g}$	m_J	E/cm^{-1}	$\boldsymbol{g}$	m_J
0	0.0	0.005 0.005 10.161	±9/2	0.0	0.004 0.004 10.176	±9/2
1	295.2	0.375 0.378 6.151	±5/2	295.7	0.272 0.275 6.173	±5/2
2	646.0	0.366 0.387 2.143	±3/2	647.7	0.262 0.283 2.164	±3/2
3	1019.7	0.016 0.063 1.844	±1/2	1024.9	0.015 0.059 1.833	±1/2
4	2212.5	0.076 0.090 8.762	±7/2	2141.3	0.059 0.067 8.745	±7/2



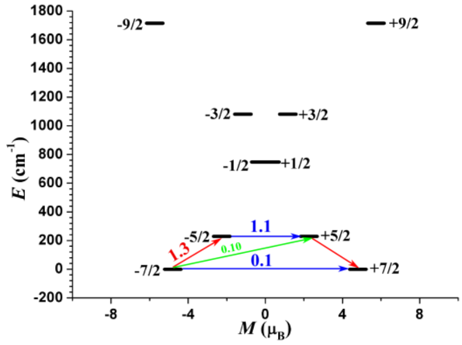
1 _CAS (11, 7) _373.9 cm^{-1}



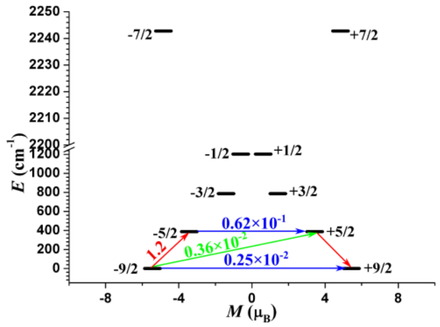
1* _CAS (11, 7) _387.6 cm^{-1}



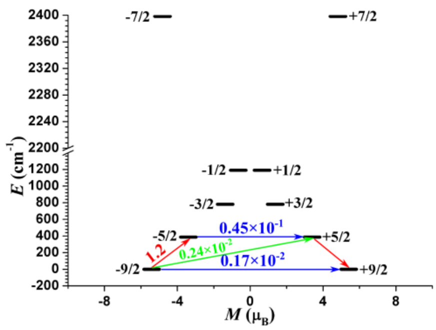
2a _CAS (11, 7) _390.6 cm^{-1}



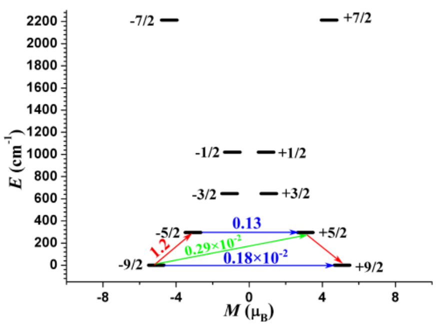
2a* _CAS (11, 7) _388.3 cm^{-1}



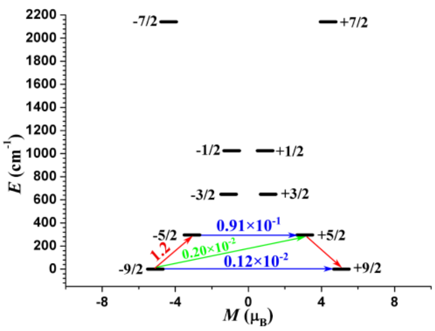
2b _CAS (11, 7) _387.9 cm^{-1}



2b* _CAS (11, 7) _386.4 cm^{-1}



3 _CAS (11, 7) _295.2 cm^{-1}



3*_CAS (11, 7) _ 295.7 cm^{-1}

Figure S2. Magnetization blocking barriers for **1** (**1***), **2a** (**2a***), **2b** (**2b***) and **3** (**3***) by CAS (11, 7). The thick black lines represent the KDs of the Co^{II} ion as a function of their magnetic moment along the magnetic axis. The blue lines correspond to diagonal matrix element of the transversal magnetic moment; the green lines represent Orbach relaxation processes. The path shown by the red arrows represent the most probable path for magnetic relaxation in the corresponding compounds. The numbers at each arrow stand for the mean absolute value of the corresponding matrix element of transition magnetic moment.

Table S6. Calculated Mulliken spin density on Co^{II} for **1** (**1***), **2a** (**2a***), **2b** (**2b***) and **3** (**3***) at their spin state S = 3/2 by CAS (11, 7) using CASSCF/SINGLE_ANISO with ORCA 5.0.3.

	1	**1***	**2a**	**2a***	**2b**	**2b***	**3**	**3***
Co^{II}	2.1482	2.1361	2.1056	2.1239	2.1248	2.1173	2.1414	2.1319

Table S7. Calculated crystal field parameters B (k, q) and the corresponding weights of **1** (**1***), **2a** (**2a***), **2b** (**2b***) and **3** (**3***) by CAS (11, 7) using CASSCF/SINGLE_ANISO with ORCA 5.0.3.

CAS (11, 7)							
1				**1***			
k	q	B (k, q)	Weight (%)	k	q	B (k, q)	Weight (%)
2	-2	0.62×10^{2}	8.46	2	-2	0.68×10^{-4}	0.00
2	-1	0.41×10^{1}	0.56	2	-1	0.15×10^{-4}	0.00
2	0	-0.62×10^{2}	8.44	2	0	-0.64×10^{2}	10.79
2	1	0.54×10^{1}	0.73	2	1	0.11×10^{2}	1.88
2	2	-0.46×10^{2}	6.37	2	2	0.98×10^{1}	1.64
4	-4	-0.91×10^{-1}	0.33	4	-4	0.63×10^{-6}	0.00
4	-3	-0.12×10^{0}	0.46	4	-3	-0.98×10^{-7}	0.00
4	-2	0.27×10^{1}	10.03	4	-2	0.50×10^{-6}	0.00
4	-1	0.60×10^{0}	2.23	4	-1	0.13×10^{-5}	0.00
4	0	-0.99×10^{0}	3.65	4	0	0.38×10^{1}	17.47
4	1	-0.57×10^{-1}	0.21	4	1	-0.58×10^{-1}	0.26
4	2	0.69×10^{1}	25.77	4	2	0.70×10^{1}	31.83
4	3	0.15×10^{-1}	0.05	4	3	0.88×10^{-1}	0.39
4	4	-0.47×10^{0}	1.76	4	4	-0.52×10^{0}	2.37
6	-6	-0.36×10^{-1}	0.98	6	-6	0.26×10^{-8}	0.00
6	-5	-0.45×10^{-2}	0.12	6	-5	0.21×10^{-7}	0.00
6	-4	-0.91×10^{-2}	0.24	6	-4	0.75×10^{-7}	0.00
6	-3	0.17×10^{-1}	0.48	6	-3	0.91×10^{-7}	0.00
6	-2	0.16×10^{0}	4.48	6	-2	0.18×10^{-6}	0.00
6	-1	-0.62×10^{-1}	1.68	6	-1	-0.13×10^{-6}	0.00
6	0	0.55×10^{0}	15.01	6	0	0.53×10^{0}	17.90
6	1	0.68×10^{-1}	1.86	6	1	0.99×10^{-1}	3.30
6	2	0.11×10^{0}	3.08	6	2	0.21×10^{0}	7.25
6	3	-0.15×10^{-1}	0.40	6	3	-0.25×10^{-1}	0.85
6	4	-0.67×10^{-1}	1.83	6	4	-0.72×10^{-1}	2.40
6	5	-0.34×10^{-2}	0.09	6	5	-0.64×10^{-2}	0.21
6	6	0.21×10^{-1}	0.58	6	6	-0.41×10^{-1}	1.38
2a				**2a***			

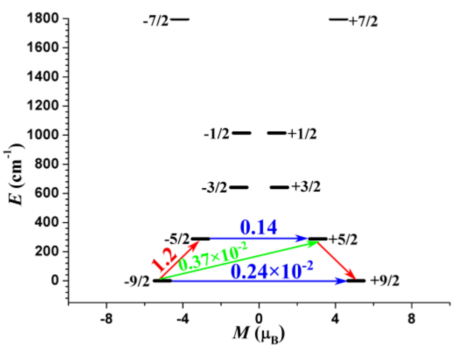
k	*q*	*B* (*k*, *q*)	Weight (%)	*k*	*q*	*B* (*k*, *q*)	Weight (%)
2	-2	-0.79×10^{-1}	0.01	2	-2	-0.69×10^{2}	9.17
2	-1	0.29×10^{1}	0.64	2	-1	0.18×10^{2}	2.46
2	0	-0.99×10^{2}	21.89	2	0	-0.56×10^{2}	7.43
2	1	-0.75×10^{-2}	0.00	2	1	0.13×10^{2}	1.78
2	2	-0.84×10^{2}	18.73	2	2	-0.14×10^{1}	0.19
4	-4	-0.29×10^{-3}	0.00	4	-4	-0.19×10^{0}	0.71
4	-3	-0.54×10^{-1}	0.32	4	-3	-0.11×10^{-1}	0.04
4	-2	-0.49×10^{-2}	0.02	4	-2	-0.28×10^{1}	10.15
4	-1	0.25×10^{-2}	0.01	4	-1	0.74×10^{0}	2.67
4	0	0.16×10^{1}	9.70	4	0	0.74×10^{1}	26.73
4	1	0.18×10^{-2}	0.01	4	1	0.90×10^{0}	3.24
4	2	-0.63×10^{1}	37.96	4	2	0.15×10^{1}	5.49
4	3	-0.12×10^{-2}	0.00	4	3	-0.49×10^{-1}	0.17
4	4	-0.19×10^{0}	1.17	4	4	-0.28×10^{0}	1.00
6	-6	0.29×10^{-4}	0.00	6	-6	0.16×10^{-1}	0.43
6	-5	-0.55×10^{-3}	0.02	6	-5	-0.41×10^{-2}	0.11
6	-4	-0.60×10^{-4}	0.00	6	-4	-0.28×10^{-1}	0.76
6	-3	0.16×10^{-2}	0.07	6	-3	-0.42×10^{-2}	0.11
6	-2	-0.39×10^{-4}	0.00	6	-2	-0.11×10^{0}	3.05
6	-1	-0.27×10^{-2}	0.12	6	-1	0.86×10^{-1}	2.27
6	0	0.10×10^{0}	4.50	6	0	0.53×10^{0}	14.12
6	1	0.52×10^{-4}	0.00	6	1	-0.29×10^{-1}	0.77
6	2	-0.60×10^{-1}	2.66	6	2	0.18×10^{0}	4.97
6	3	0.97×10^{-5}	0.00	6	3	0.12×10^{-1}	0.32
6	4	-0.36×10^{-1}	1.58	6	4	-0.38×10^{-1}	1.00
6	5	-0.13×10^{-4}	0.00	6	5	0.69×10^{-3}	0.01
6	6	0.11×10^{-1}	0.48	6	6	-0.27×10^{-1}	0.71
2b				**2b***			
k	*q*	*B* (*k*, *q*)	Weight (%)	*k*	*q*	*B* (*k*, *q*)	Weight (%)
2	-2	-0.78×10^{2}	14.31	2	-2	-0.60×10^{2}	8.62
2	-1	0.50×10^{1}	0.91	2	-1	0.28×10^{1}	0.40
2	0	-0.95×10^{2}	17.41	2	0	-0.56×10^{2}	8.16
2	1	0.49×10^{1}	0.89	2	1	-0.44×10^{1}	0.64
2	2	0.64×10^{1}	1.17	2	2	0.42×10^{1}	0.61
4	-4	0.14×10^{-1}	0.06	4	-4	-0.11×10^{0}	0.44
4	-3	0.33×10^{0}	1.65	4	-3	0.11×10^{-1}	0.04
4	-2	-0.63×10^{1}	31.16	4	-2	-0.24×10^{1}	9.51
4	-1	-0.11×10^{1}	5.51	4	-1	0.21×10^{0}	0.84
4	0	0.15×10^{1}	7.52	4	0	0.74×10^{1}	28.93
4	1	-0.10×10^{1}	5.21	4	1	-0.26×10^{0}	1.03
4	2	0.36×10^{0}	1.79	4	2	0.24×10^{1}	9.48
4	3	-0.36×10^{0}	1.82	4	3	-0.59×10^{-1}	0.23

4	4	0.25×10^{0}	1.24	4	4	-0.37×10^{0}	1.45
6	-6	-0.11×10^{-1}	0.40	6	-6	0.20×10^{-1}	0.58
6	-5	-0.43×10^{-2}	0.15	6	-5	0.69×10^{-5}	0.00
6	-4	0.21×10^{-2}	0.07	6	-4	-0.17×10^{-1}	0.48
6	-3	-0.33×10^{-2}	0.12	6	-3	0.27×10^{-2}	0.07
6	-2	-0.38×10^{-1}	1.38	6	-2	-0.12×10^{0}	3.62
6	-1	-0.24×10^{-1}	0.87	6	-1	-0.41×10^{-2}	0.11
6	0	0.92×10^{-1}	3.36	6	0	0.54×10^{0}	15.69
6	1	-0.19×10^{-1}	0.70	6	1	-0.34×10^{-1}	0.98
6	2	0.14×10^{-1}	0.54	6	2	0.19×10^{0}	5.59
6	3	0.21×10^{-2}	0.07	6	3	-0.23×10^{-2}	0.06
6	4	0.38×10^{-1}	1.40	6	4	-0.51×10^{-1}	1.46
6	5	-0.36×10^{-2}	0.13	6	5	0.14×10^{-2}	0.04
6	6	0.13×10^{-2}	0.04	6	6	-0.28×10^{-1}	0.80
3				**3***			
k	*q*	*B* (*k*, *q*)	Weight (%)	*k*	*q*	*B* (*k*, *q*)	Weight (%)
2	-2	-0.74×10^{2}	9.76	2	-2	-0.36×10^{0}	0.05
2	-1	-0.27×10^{2}	3.59	2	-1	-0.41×10^{2}	6.11
2	0	-0.40×10^{2}	5.28	2	0	-0.46×10^{2}	6.83
2	1	-0.24×10^{2}	3.15	2	1	-0.61×10^{-1}	0.01
2	2	0.76×10^{1}	0.99	2	2	0.76×10^{2}	11.11
4	-4	-0.10×10^{0}	0.38	4	-4	0.35×10^{-2}	0.01
4	-3	0.13×10^{0}	0.47	4	-3	-0.15×10^{0}	0.62
4	-2	-0.34×10^{1}	12.18	4	-2	-0.12×10^{-1}	0.04
4	-1	-0.23×10^{1}	8.22	4	-1	-0.34×10^{1}	13.73
4	0	0.69×10^{1}	24.70	4	0	0.68×10^{1}	27.23
4	1	-0.21×10^{1}	7.46	4	1	-0.75×10^{-2}	0.02
4	2	0.59×10^{0}	2.10	4	2	0.34×10^{1}	13.74
4	3	-0.47×10^{-1}	0.16	4	3	-0.26×10^{-2}	0.01
4	4	0.11×10^{0}	0.40	4	4	-0.15×10^{0}	0.61
6	-6	-0.97×10^{-2}	0.25	6	-6	0.39×10^{-3}	0.01
6	-5	-0.57×10^{-3}	0.01	6	-5	0.67×10^{-2}	0.19
6	-4	-0.14×10^{-1}	0.38	6	-4	0.54×10^{-3}	0.01
6	-3	-0.74×10^{-2}	0.19	6	-3	0.11×10^{-1}	0.32
6	-2	-0.73×10^{-2}	0.19	6	-2	0.17×10^{-2}	0.05
6	-1	-0.10×10^{0}	2.65	6	-1	-0.11×10^{0}	3.29
6	0	0.50×10^{0}	13.03	6	0	0.48×10^{0}	13.98
6	1	-0.39×10^{-1}	1.01	6	1	0.32×10^{-3}	0.01
6	2	0.10×10^{0}	2.59	6	2	-0.26×10^{-1}	0.76
6	3	-0.37×10^{-2}	0.09	6	3	0.28×10^{-3}	0.01
6	4	0.15×10^{-1}	0.40	6	4	-0.24×10^{-1}	0.69
6	5	-0.38×10^{-2}	0.09	6	5	0.16×10^{-3}	0.00
6	6	-0.62×10^{-2}	0.16	6	6	-0.15×10^{-1}	0.43

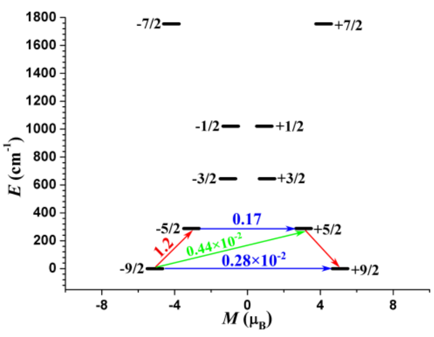
Table S8. Calculated energy levels (cm^{-1}), ***g*** (g_x, g_y, g_z) tensors and predominant m_J values of the original and simplified structures of **1** (**1***), **2a** (**2a***), **2b** (**2b***) and **3** (**3***) by CAS (11, 8) using CASSCF/SINGLE_ANISO with ORCA 5.0.3.

CAS (11, 8)						
KDs	**1**			**1***		
	E/cm^{-1}	***g***	m_J	E/cm^{-1}	***g***	m_J
0	0.0	0.007 0.007 10.155	±9/2	0.0	0.008 0.008 10.164	±9/2
1	287.5	0.434 0.436 6.152	±5/2	287.7	0.512 0.514 6.153	±5/2
2	641.2	0.398 0.458 2.137	±3/2	644.5	0.485 0.525 2.138	±3/2
3	1014.3	0.030 0.101 1.845	±1/2	1021.0	0.024 0.089 1.838	±1/2
4	1797.8	0.202 0.233 8.324	±7/2	1754.6	0.184 0.205 8.355	±7/2
KDs	**2a**			**2a***		
	E/cm^{-1}	***g***	m_J	E/cm^{-1}	***g***	m_J
0	0.0	0.084 0.102 10.863	±9/2	0.0	0.004 0.005 10.150	±9/2
1	312.0	0.364 0.373 7.474	±7/2	291.8	0.372 0.374 6.147	±5/2
2	795.5	1.644 1.946 6.434	±5/2	645.6	0.353 0.383 2.137	±3/2
3	822.6	0.420 1.000 3.128	±3/2	1022.1	0.027 0.074 1.850	±1/2
4	1200.3	2.830 2.069 0.929	±1/2	1959.7	0.131 0.146 8.529	±7/2
KDs	**2b**			**2b***		
	E/cm^{-1}	***g***	m_J	E/cm^{-1}	***g***	m_J
0	0.0	0.117 0.144 10.797	±9/2	0.0	0.005 0.006 10.150	±9/2
1	333.9	0.421	±7/2	291.0	0.386	±5/2

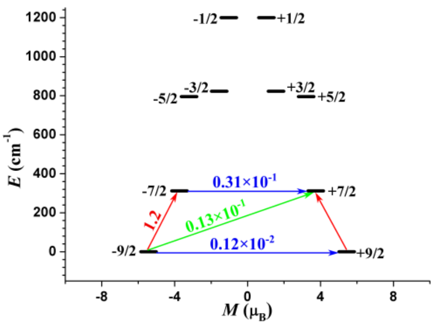
		0.436 7.401			0.387 6.147	
2	709.1	1.996 2.355 6.129	±5/2	644.7	0.364 0.400 2.136	±3/2
3	798.6	0.535 1.217 3.040	±3/2	1020.0	0.029 0.080 1.849	±1/2
4	1111.6	1.281 1.711 3.383	±1/2	1931.6	0.164 0.184 8.459	±7/2
KDs	**3**			**3***		
	E/cm^{-1}	$\boldsymbol{g}$	m_J	E/cm^{-1}	$\boldsymbol{g}$	m_J
0	0.0	0.011 0.012 10.688	±9/2	0.0	0.005 0.006 10.750	±9/2
1	378.8	0.386 0.399 6.643	±5/2	382.5	0.137 0.142 6.706	±5/2
2	762.0	0.111 0.690 2.609	±3/2	771.2	0.175 0.479 2.659	±3/2
3	1155.7	0.207 0.220 1.417	±1/2	1174.0	0.223 0.238 1.393	±1/2
4	2874.4	0.028 0.037 9.733	±7/2	2902.2	0.035 0.054 10.280	±7/2



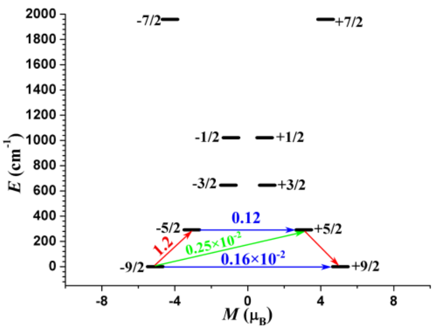
1 _CAS (11, 8) _287.5 cm^{-1}



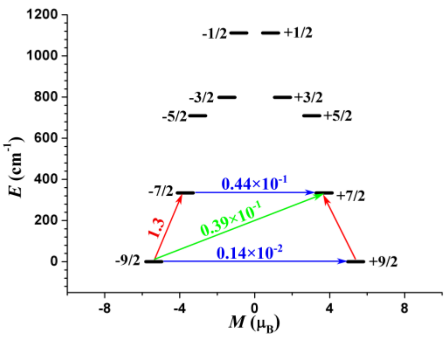
1* _CAS (11, 8) _287.7 cm^{-1}



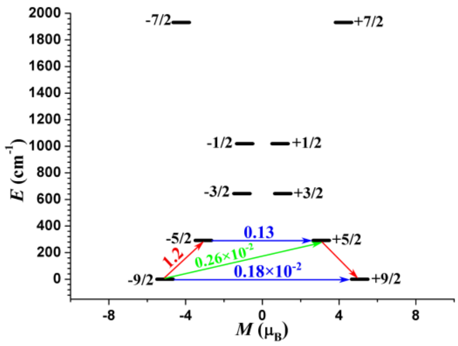
2a _CAS (11, 8) _312.0 cm^{-1}



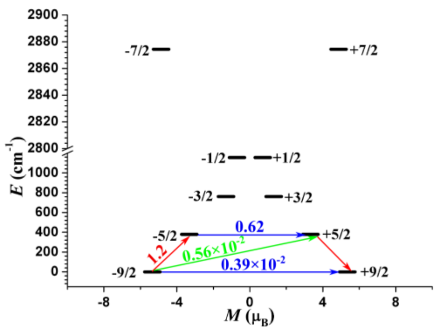
2a* _CAS (11, 8) _291.8 cm^{-1}



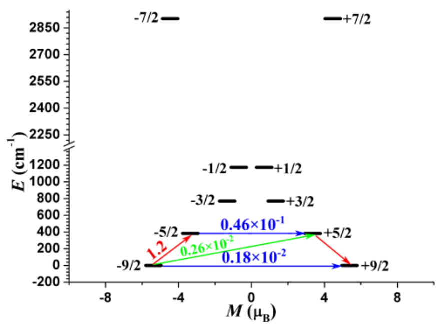
2b _CAS (11, 8) _333.9 cm^{-1}



2b* _CAS (11, 8) _291.0 cm^{-1}



3 _CAS (11, 8) _378.8 cm^{-1}



3*_CAS (11, 8) _382.5 cm^{-1}

Figure S3. Magnetization blocking barriers for **1** (**1***), **2a** (**2a***), **2b** (**2b***) and **3** (**3***) by CAS (11, 8). The thick black lines represent the KDs of the Co^{II} ion as a function of their magnetic moment along the magnetic axis. The blue lines correspond to diagonal matrix element of the transversal magnetic moment; the green lines represent Orbach relaxation processes. The path shown by the red arrows represent the most probable path for magnetic relaxation in the corresponding compounds. The numbers at each arrow stand for the mean absolute value of the corresponding matrix element of transition magnetic moment.

Table S9. Calculated Mulliken spin density on Co^{II} for **1** (**1***), **2a** (**2a***), **2b** (**2b***) and **3** (**3***) at their spin state S = 3/2 by CAS (11, 8) using CASSCF/SINGLE_ANISO with ORCA 5.0.3.

	1	**1***	**2a**	**2a***	**2b**	**2b***	**3**	**3***
Co^{II}	2.0114	2.0183	2.0191	2.0162	2.0245	2.0134	2.0242	2.0167

Table S10. Calculated crystal field parameters B (k, q) and the corresponding weights of **1** (**1***), **2a**

(**2a***), **2b** (**2b***) and **3** (**3***) by CAS (11, 8) using CASSCF/SINGLE_ANISO with ORCA 5.0.3.

CAS (11, 8)							
1				**1***			
k	*q*	*B* (*k*, *q*)	Weight (%)	*k*	*q*	*B* (*k*, *q*)	Weight (%)
2	-2	-0.51×10^{0}	0.06	2	-2	0.14×10^{0}	0.04
2	-1	-0.14×10^{2}	1.98	2	-1	-0.25×10^{-1}	0.01
2	0	-0.14×10^{3}	20.28	2	0	-0.84×10^{2}	21.04
2	1	-0.23×10^{1}	0.32	2	1	0.20×10^{1}	0.50
2	2	0.11×10^{3}	16.13	2	2	-0.55×10^{2}	13.67
4	-4	0.78×10^{-1}	0.28	4	-4	0.15×10^{-3}	0.00
4	-3	-0.59×10^{0}	2.18	4	-3	-0.14×10^{-2}	0.01
4	-2	0.14×10^{0}	0.54	4	-2	0.11×10^{-1}	0.07
4	-1	-0.52×10^{0}	1.93	4	-1	0.18×10^{-1}	0.12
4	0	-0.86×10^{0}	3.19	4	0	0.36×10^{0}	2.42
4	1	-0.25×10^{-1}	0.09	4	1	0.41×10^{0}	2.82
4	2	0.80×10^{1}	29.82	4	2	-0.45×10^{1}	30.85
4	3	0.14×10^{0}	0.53	4	3	0.28×10^{0}	1.91
4	4	0.33×10^{0}	1.25	4	4	-0.24×10^{-1}	0.16
6	-6	0.16×10^{-1}	0.45	6	-6	0.55×10^{-5}	0.00
6	-5	0.19×10^{-1}	0.53	6	-5	0.99×10^{-5}	0.00
6	-4	0.79×10^{-2}	0.21	6	-4	0.31×10^{-5}	0.00
6	-3	-0.31×10^{-1}	0.85	6	-3	-0.80×10^{-4}	0.00
6	-2	-0.10×10^{-1}	0.28	6	-2	0.51×10^{-3}	0.03
6	-1	0.77×10^{-1}	2.09	6	-1	0.91×10^{-3}	0.05
6	0	-0.24×10^{0}	6.74	6	0	-0.28×10^{0}	13.97
6	1	-0.14×10^{-1}	0.40	6	1	0.13×10^{-1}	0.65
6	2	0.25×10^{0}	6.81	6	2	-0.22×10^{0}	11.28
6	3	0.67×10^{-2}	0.18	6	3	0.42×10^{-2}	0.21
6	4	0.33×10^{-1}	0.90	6	4	-0.14×10^{-2}	0.07
6	5	-0.57×10^{-2}	0.15	6	5	0.11×10^{-2}	0.05
6	6	0.62×10^{-1}	1.68	6	6	-0.13×10^{-2}	0.06
2a				**2a***			
k	*q*	*B* (*k*, *q*)	Weight (%)	*k*	*q*	*B* (*k*, *q*)	Weight (%)
2	-2	-0.27×10^{2}	4.51	2	-2	-0.22×10^{2}	4.14
2	-1	0.13×10^{1}	0.22	2	-1	-0.43×10^{1}	0.80
2	0	-0.13×10^{3}	22.88	2	0	-0.67×10^{2}	12.60
2	1	-0.23×10^{0}	0.03	2	1	0.24×10^{2}	4.50
2	2	-0.89×10^{2}	14.76	2	2	-0.43×10^{2}	8.09
4	-4	-0.16×10^{0}	0.72	4	-4	0.30×10^{0}	1.53
4	-3	0.21×10^{-2}	0.01	4	-3	-0.77×10^{0}	3.91
4	-2	-0.14×10^{1}	6.49	4	-2	0.73×10^{0}	3.72
4	-1	-0.59×10^{0}	2.66	4	-1	-0.28×10^{0}	1.42
4	0	0.70×10^{0}	3.15	4	0	0.46×10^{1}	23.58

4	1	0.84×10^{-1}	0.37	4	1	-0.97×10^{-1}	0.49
4	2	-0.46×10^{1}	20.77	4	2	0.12×10^{1}	6.23
4	3	-0.27×10^{-2}	0.01	4	3	-0.30×10^{0}	1.51
4	4	-0.25×10^{0}	1.15	4	4	0.25×10^{0}	1.28
6	-6	0.23×10^{-1}	0.78	6	-6	-0.47×10^{-2}	0.17
6	-5	-0.14×10^{-2}	0.04	6	-5	-0.61×10^{-2}	0.22
6	-4	-0.15×10^{-1}	0.51	6	-4	-0.45×10^{-1}	1.67
6	-3	-0.51×10^{-2}	0.16	6	-3	0.22×10^{-1}	0.83
6	-2	-0.70×10^{-1}	2.31	6	-2	-0.87×10^{-1}	3.24
6	-1	-0.65×10^{-1}	2.14	6	-1	-0.24×10^{-1}	0.89
6	0	-0.20×10^{0}	6.62	6	0	0.20×10^{-1}	0.76
6	1	0.93×10^{-2}	0.30	6	1	-0.34×10^{-1}	1.26
6	2	-0.23×10^{0}	7.67	6	2	-0.28×10^{0}	10.71
6	3	0.22×10^{-2}	0.07	6	3	0.76×10^{-1}	2.82
6	4	-0.24×10^{-1}	0.81	6	4	-0.35×10^{-1}	1.32
6	5	0.12×10^{-2}	0.04	6	5	-0.14×10^{-1}	0.54
6	6	0.20×10^{-1}	0.67	6	6	0.44×10^{-1}	1.65
2b				**2b***			
k	*q*	*B* (*k*, *q*)	Weight (%)	*k*	*q*	*B* (*k*, *q*)	Weight (%)
2	-2	0.27×10^{2}	5.41	2	-2	-0.54×10^{2}	10.55
2	-1	-0.69×10^{0}	0.13	2	-1	0.22×10^{1}	0.43
2	0	-0.92×10^{2}	18.21	2	0	-0.87×10^{2}	16.93
2	1	-0.36×10^{0}	0.07	2	1	0.40×10^{-1}	0.01
2	2	0.54×10^{2}	10.73	2	2	0.32×10^{2}	6.34
4	-4	-0.55×10^{-1}	0.29	4	-4	0.91×10^{-2}	0.04
4	-3	-0.51×10^{-1}	0.27	4	-3	0.10×10^{-1}	0.05
4	-2	0.22×10^{1}	11.98	4	-2	-0.42×10^{1}	22.36
4	-1	-0.73×10^{0}	3.90	4	-1	0.59×10^{0}	3.12
4	0	0.65×10^{0}	3.47	4	0	0.50×10^{0}	2.65
4	1	0.14×10^{0}	0.78	4	1	0.35×10^{0}	1.83
4	2	0.41×10^{1}	22.15	4	2	0.22×10^{1}	11.75
4	3	0.50×10^{-1}	0.26	4	3	-0.23×10^{-1}	0.12
4	4	-0.22×10^{-1}	0.12	4	4	0.13×10^{-1}	0.07
6	-6	0.12×10^{-3}	0.00	6	-6	0.73×10^{-3}	0.02
6	-5	0.25×10^{-4}	0.00	6	-5	-0.20×10^{-3}	0.01
6	-4	-0.54×10^{-2}	0.21	6	-4	0.21×10^{-2}	0.08
6	-3	-0.34×10^{-2}	0.13	6	-3	-0.85×10^{-3}	0.03
6	-2	0.11×10^{0}	4.39	6	-2	-0.21×10^{0}	8.25
6	-1	-0.53×10^{-2}	0.20	6	-1	0.96×10^{-2}	0.37
6	0	-0.23×10^{0}	9.02	6	0	-0.27×10^{0}	10.74
6	1	-0.38×10^{-2}	0.15	6	1	-0.23×10^{-2}	0.09
6	2	0.19×10^{0}	7.79	6	2	0.10×10^{0}	3.84
6	3	0.33×10^{-2}	0.13	6	3	0.95×10^{-3}	0.03

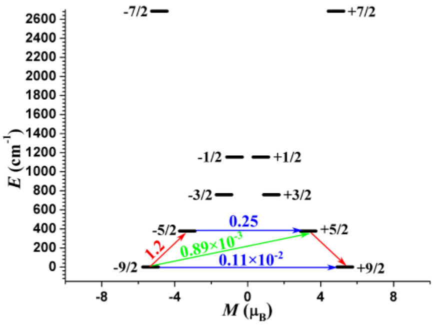
6	4	-0.23×10^{-2}	0.09	6	4	0.39×10^{-2}	0.15
6	5	-0.37×10^{-3}	0.01	6	5	0.94×10^{-5}	0.00
6	6	-0.52×10^{-4}	0.00	6	6	-0.11×10^{-2}	0.04
3				**3***			
k	*q*	*B* (*k*, *q*)	Weight (%)	*k*	*q*	*B* (*k*, *q*)	Weight (%)
2	-2	0.11×10^{2}	2.11	2	-2	0.19×10^{2}	3.51
2	-1	-0.63×10^{0}	0.11	2	-1	0.95×10^{1}	1.72
2	0	-0.82×10^{2}	14.64	2	0	-0.85×10^{2}	15.56
2	1	-0.10×10^{2}	1.84	2	1	0.96×10^{1}	1.73
2	2	0.78×10^{2}	14.03	2	2	0.72×10^{2}	13.09
4	-4	-0.10×10^{-1}	0.05	4	-4	-0.12×10^{-2}	0.00
4	-3	-0.77×10^{-1}	0.37	4	-3	0.21×10^{0}	1.06
4	-2	0.89×10^{0}	4.29	4	-2	0.11×10^{1}	5.73
4	-1	-0.29×10^{-1}	0.14	4	-1	-0.48×10^{0}	2.38
4	0	0.37×10^{0}	1.81	4	0	-0.65×10^{-1}	0.32
4	1	-0.72×10^{0}	3.47	4	1	-0.46×10^{0}	2.26
4	2	0.56×10^{1}	27.10	4	2	0.53×10^{1}	26.45
4	3	-0.24×10^{0}	1.17	4	3	-0.19×10^{0}	0.94
4	4	-0.23×10^{-1}	0.11	4	4	0.41×10^{-1}	0.20
6	-6	0.65×10^{-3}	0.02	6	-6	-0.24×10^{-4}	0.00
6	-5	0.11×10^{-2}	0.03	6	-5	0.16×10^{-2}	0.05
6	-4	-0.11×10^{-2}	0.04	6	-4	0.11×10^{-3}	0.00
6	-3	0.60×10^{-3}	0.02	6	-3	0.17×10^{-2}	0.06
6	-2	0.46×10^{-1}	1.64	6	-2	0.25×10^{0}	9.05
6	-1	-0.14×10^{-1}	0.51	6	-1	0.44×10^{-1}	1.60
6	0	-0.33×10^{0}	11.85	6	0	-0.30×10^{0}	10.99
6	1	-0.13×10^{0}	4.72	6	1	0.28×10^{-1}	1.02
6	2	0.27×10^{0}	9.62	6	2	0.46×10^{-1}	1.66
6	3	-0.90×10^{-3}	0.03	6	3	0.44×10^{-2}	0.16
6	4	-0.25×10^{-2}	0.08	6	4	0.76×10^{-2}	0.27
6	5	0.19×10^{-2}	0.06	6	5	0.18×10^{-2}	0.06
6	6	0.10×10^{-2}	0.03	6	6	-0.62×10^{-5}	0.00

Table S11. Calculated energy levels (cm^{-1}), ***g*** (g_x, g_y, g_z) tensors and predominant m_J values of the original and simplified structures of **1** (**1***), **2a** (**2a***), **2b** (**2b***) and **3** (**3***) by CAS (11, 9) using CASSCF/SINGLE_ANISO with ORCA 5.0.3.

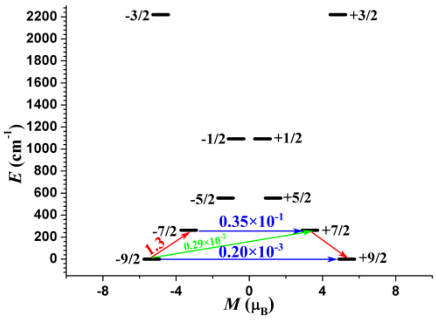
CAS (11, 9)						
KDs	**1**			**1***		
	E/cm^{-1}	***g***	m_J	E/cm^{-1}	***g***	m_J
0	0.0	0.000 0.000 10.603	±9/2	0.0	0.000 0.000 10.763	±9/2
1	267.3	0.752	±7/2	262.1	0.197	±7/2

		0.752 6.806			0.197 6.002	
2	578.8	0.597 0.606 2.640	±5/2	554.6	0.149 0.153 2.007	±5/2
3	1053.3	0.004 0.006 1.069	±1/2	1091.2	0.011 0.015 0.641	±1/2
4	2188.4	6.343 6.280 1.406	±3/2	2219.3	6.496 6.384 1.584	±3/2
KDs	**2a**			**2a***		
	E/cm^{-1}	***g***	m_J	E/cm^{-1}	***g***	m_J
0	0.0	0.000 0.000 10.982	±9/2	0.0	0.000 0.000 10.909	±9/2
1	349.1	0.006 0.006 6.053	±7/2	343.2	0.706 0.706 6.825	±7/2
2	817.1	0.005 0.008 3.137	±5/2	803.1	0.557 0.568 3.671	±5/2
3	1006.9	0.010 0.011 0.501	±1/2	1159.7	0.002 0.004 1.040	±1/2
4	2053.1	6.515 6.480 1.659	±3/2	2235.9	6.340 6.301 1.419	±3/2
KDs	**2b**			**2b***		
	E/cm^{-1}	***g***	m_J	E/cm^{-1}	***g***	m_J
0	0.0	0.000 0.000 10.764	±9/2	0.0	0.000 0.000 10.897	±9/2
1	385.4	0.945 0.945 6.892	±5/2	361.2	0.728 0.728 6.850	±5/2
2	809.0	0.891 0.905 3.984	±3/2	881.5	0.627 0.637 3.784	±3/2
3	1260.1	0.001 0.003 0.738	±1/2	1345.5	0.002 0.004 0.725	±1/2
4	2528.0	0.655 0.656	±7/2	2736.9	6.359 6.261	±7/2

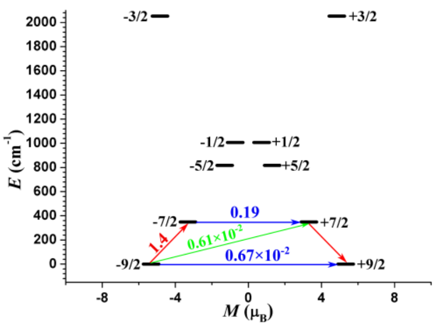
		9.515			1.278	
KDs	3			3*		
	E/cm^{-1}	***g***	m_J	E/cm^{-1}	***g***	m_J
0	0.0	0.006 0.006 10.659	±9/2	0.0	0.003 0.004 10.602	±9/2
1	377.4	0.178 0.185 6.630	±5/2	373.1	0.192 0.196 6.564	±5/2
2	758.9	0.116 0.493 2.596	±3/2	750.4	0.148 0.512 2.528	±3/2
3	1153.2	0.219 0.233 1.445	±1/2	1141.2	0.239 0.251 1.509	±1/2
4	2684.4	0.035 0.058 9.939	±7/2	3024.8	0.040 0.059 10.162	±7/2



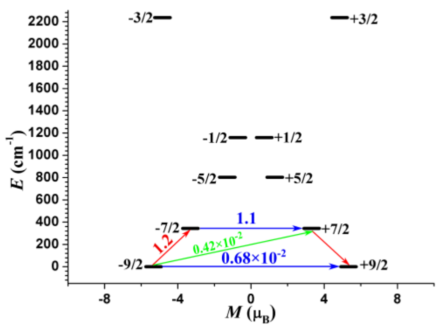
1 _CAS (11, 9) _267.3 cm^{-1}



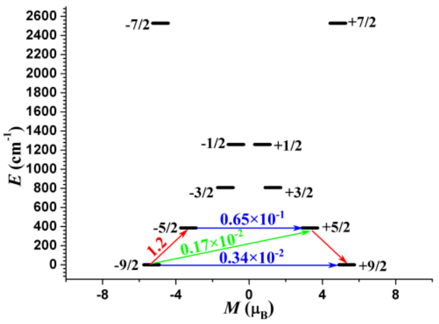
1* _CAS (11, 9) _262.1 cm^{-1}



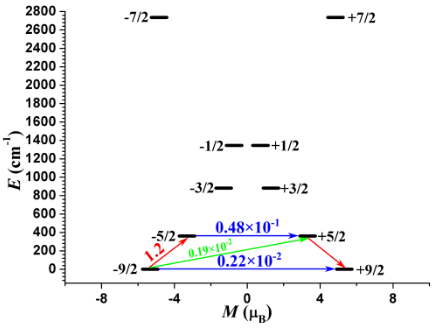
2a _CAS (11, 9) _349.1 cm^{-1}



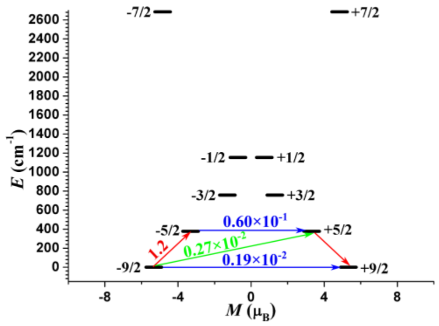
2a* _CAS (11, 9) _343.2 cm^{-1}



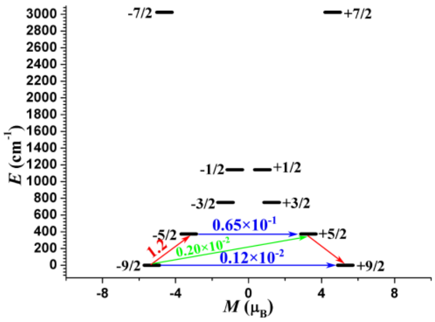
2b _CAS (11, 9) _385.4 cm^{-1}



2b* _CAS (11, 9) _361.2 cm^{-1}



3 _CAS (11, 9) _377.4 cm^{-1}



3*_CAS (11, 9) _373.1 cm^{-1}

Figure S4. Magnetization blocking barriers for **1** (**1***), **2a** (**2a***), **2b** (**2b***) and **3** (**3***) by CAS (11, 9). The thick black lines represent the KDs of the Co^{II} ion as a function of their magnetic moment along the magnetic axis. The blue lines correspond to diagonal matrix element of the transversal magnetic moment; the green lines represent Orbach relaxation processes. The path shown by the red arrows represent the most probable path for magnetic relaxation in the corresponding compounds. The numbers at each arrow stand for the mean absolute value of the corresponding matrix element of transition magnetic moment.

Table S12. Calculated Mulliken spin density on Co^{II} at the spin state S = 3/2 for **1** (**1***), **2a** (**2a***), **2b** (**2b***) and **3** (**3***) by CAS (11, 9) using CASSCF/SINGLE_ANISO with ORCA 5.0.3.

	1	**1***	**2a**	**2a***	**2b**	**2b***	**3**	**3***
Co^{II}	2.0148	2.0141	2.0184	2.0116	2.0245	2.0197	2.0270	2.0219

Table S13. Calculated crystal field parameters B (k, q) and the corresponding weights of **1** (**1***), **2a** (**2a***), **2b** (**2b***) and **3** (**3***) by CAS (11, 9) using CASSCF/SINGLE_ANISO with ORCA 5.0.3.

CAS (11, 9)							
1				**1***			
k	q	B (k, q)	Weight (%)	k	q	B (k, q)	Weight (%)
2	-2	0.35×10^{-3}	0.00	2	-2	-0.10×10^{-1}	0.00
2	-1	-0.37×10^{-3}	0.00	2	-1	-0.15×10^{2}	2.51
2	0	-0.10×10^{3}	13.32	2	0	-0.98×10^{2}	15.79
2	1	-0.13×10^{2}	1.72	2	1	-0.34×10^{-3}	0.00
2	2	0.13×10^{3}	16.50	2	2	-0.10×10^{3}	16.51
4	-4	0.40×10^{-4}	0.00	4	-4	-0.21×10^{-4}	0.00

4	-3	-0.14×10^{-3}	0.00	4	-3	0.35×10^{0}	1.55
4	-2	0.12×10^{-4}	0.00	4	-2	-0.83×10^{3}	0.00
4	-1	-0.12×10^{-4}	0.00	4	-1	0.14×10^{1}	6.50
4	0	0.42×10^{1}	14.58	4	0	0.18×10^{1}	7.86
4	1	0.27×10^{1}	9.27	4	1	0.14×10^{-3}	0.00
4	2	0.81×10^{1}	27.78	4	2	-0.69×10^{1}	30.08
4	3	-0.42×10^{0}	1.45	4	3	-0.49×10^{-4}	0.00
4	4	-0.57×10^{-1}	0.19	4	4	$-0.38\times10{-}^{1}$	0.16
6	-6	0.96×10^{-6}	0.00	6	-6	0.40×10^{-5}	0.00
6	-5	0.33×10^{-5}	0.00	6	-5	0.25×10^{-2}	0.08
6	-4	0.10×10^{-6}	0.00	6	-4	-0.73×10^{-5}	0.00
6	-3	0.37×10^{-5}	0.00	6	-3	0.14×10^{-2}	0.04
6	-2	0.16×10^{-4}	0.00	6	-2	-0.46×10^{-4}	0.00
6	-1	0.51×10^{-4}	0.00	6	-1	0.17×10^{-1}	0.55
6	0	-0.11×10^{0}	2.79	6	0	-0.26×10^{0}	8.48
6	1	0.14×10^{0}	3.74	6	1	-0.13×10^{-4}	0.00
6	2	0.31×10^{0}	8.03	6	2	-0.29×10^{0}	9.48
6	3	-0.59×10^{-2}	0.15	6	3	0.77×10^{-5}	0.00
6	4	-0.11×10^{-1}	0.28	6	4	-0.91×10^{-2}	0.29
6	5	0.20×10^{-2}	0.05	6	5	-0.34×10^{-5}	0.00
6	6	-0.36×10^{-2}	0.09	6	6	0.12×10^{-2}	0.03
2a				**2a***			
k	*q*	*B* (*k*, *q*)	Weight (%)	*k*	*q*	*B* (*k*, *q*)	Weight (%)
2	-2	0.42×10^{2}	8.10	2	-2	0.34×10^{2}	5.64
2	-1	-0.21×10^{2}	4.05	2	-1	0.75×10^{1}	1.24
2	0	-0.87×10^{2}	16.86	2	0	-0.88×10^{2}	14.45
2	1	-0.28×10^{2}	5.42	2	1	0.26×10^{2}	4.28
2	2	0.14×10^{2}	2.73	2	2	0.54×10^{2}	9.01
4	-4	-0.16×10^{-1}	0.08	4	-4	-0.38×10^{-1}	0.16
4	-3	-0.46×10^{0}	2.41	4	-3	0.40×10^{0}	1.78
4	-2	0.33×10^{1}	17.26	4	-2	0.27×10^{1}	12.11
4	-1	0.12×10^{0}	0.64	4	-1	0.90×10^{-1}	0.40
4	0	0.17×10^{1}	9.26	4	0	0.52×10^{0}	2.33
4	1	-0.35×10^{-1}	0.18	4	1	0.55×10^{0}	2.45
4	2	0.99×10^{0}	5.15	4	2	0.40×10^{1}	18.16
4	3	0.27×10^{0}	1.42	4	3	0.24×10^{0}	1.09
4	4	0.51×10^{-1}	0.26	4	4	-0.77×10^{-2}	0.03
6	-6	-0.60×10^{-4}	0.00	6	-6	-0.17×10^{-3}	0.01
6	-5	0.85×10^{-3}	0.03	6	-5	-0.11×10^{-2}	0.03
6	-4	$-0.13\times1^{0-2}$	0.05	6	-4	-0.78×10^{-2}	0.25
6	-3	0.21×10^{-1}	0.82	6	-3	-0.12×10^{-1}	0.41
6	-2	0.19×10^{0}	7.49	6	-2	0.13×10^{1}	4.36
6	-1	-0.12×10^{0}	4.74	6	-1	0.65×10^{-1}	2.15

6	0	-0.13×10^{0}	5.08	6	0	-0.23×10^{0}	7.67
6	1	-0.13×10^{0}	5.07	6	1	0.16×10^{0}	5.47
6	2	0.46×10^{-1}	1.76	6	2	0.19×10^{0}	6.27
6	3	-0.21×10^{-1}	0.81	6	3	-0.25×10^{-2}	0.08
6	4	0.35×10^{-2}	0.13	6	4	-0.13×10^{-2}	0.04
6	5	0.23×10^{-2}	0.08	6	5	0.15×10^{-3}	0.01
6	6	-0.42×10^{-4}	0.00	6	6	0.72×10^{-4}	0.00
2b				**2b***			
k	*q*	*B* (*k*, *q*)	Weight (%)	*k*	*q*	*B* (*k*, *q*)	Weight (%)
2	-2	-0.44×10^{2}	7.27	2	-2	0.28×10^{1}	1.34
2	-1	-0.11×10^{2}	1.80	2	-1	0.18×10^{1}	0.86
2	0	-0.88×10^{2}	14.32	2	0	-0.29×10^{2}	13.92
2	1	0.26×10^{2}	4.28	2	1	-0.27×10^{1}	1.27
2	2	0.43×10^{2}	7.09	2	2	-0.15×10^{1}	0.72
4	-4	0.37×10^{-1}	0.16	4	-4	-0.20×10^{0}	2.65
4	-3	-0.48×10^{0}	2.12	4	-3	0.28×10^{0}	3.60
4	-2	-0.35×10^{1}	15.51	4	-2	0.26×10^{1}	33.20
4	-1	-0.15×10^{0}	0.66	4	-1	-0.61×10^{-1}	0.77
4	0	0.66×10^{0}	2.91	4	0	0.18×10^{0}	2.36
4	1	0.57×10^{0}	2.54	4	1	-0.10×10^{0}	1.35
4	2	0.32×101	14.06	4	2	-0.41×10^{-1}	0.52
4	3	0.70×10^{-1}	0.30	4	3	-0.42×10^{0}	5.37
4	4	0.13×10^{-1}	0.05	4	4	0.54×10^{-1}	0.69
6	-6	0.67×10^{-4}	0.00	6	-6	0.17×10^{-2}	0.16
6	-5	0.55×10^{-3}	0.02	6	-5	-0.23×10^{-2}	0.22
6	-4	0.71×10^{-2}	0.23	6	-4	0.26×10^{-1}	2.45
6	-3	0.14×10^{-1}	0.48	6	-3	0.18×10^{-1}	1.72
6	-2	-0.17×10^{0}	5.62	6	-2	0.81×10^{-4}	0.01
6	-1	-0.92×10^{-1}	3.00	6	-1	-0.10×10^{-2}	0.09
6	0	-0.22×10^{0}	7.14	6	0	-0.22×10^{0}	20.72
6	1	0.16×10^{0}	5.28	6	1	0.56×10^{-2}	0.52
6	2	0.14×10^{0}	4.83	6	2	0.49×10^{-2}	0.46
6	3	0.38×10^{-2}	0.12	6	3	-0.26×10^{-1}	2.49
6	4	0.28×10^{-2}	0.09	6	4	-0.23×10^{-1}	2.23
6	5	0.59×10^{-3}	0.02	6	5	0.11×10^{-2}	0.10
6	6	0.17×10^{-3}	0.01	6	6	-0.89×10^{-3}	0.08
3				**3***			
k	*q*	*B* (*k*, *q*)	Weight (%)	*k*	*q*	*B* (*k*, *q*)	Weight (%)
2	-2	-0.21×10^{2}	3.49	2	-2	0.76×10^{1}	1.38
2	-1	0.97×10^{0}	0.15	2	-1	-0.68×10^{0}	0.12
2	0	-0.81×10^{2}	13.09	2	0	-0.75×10^{2}	13.71
2	1	-0.90×10^{1}	1.44	2	1	-0.91×10^{1}	1.66
2	2	0.74×10^{2}	11.86	2	2	0.80×10^{2}	14.63

4	-4	-0.25×10^{-1}	0.11	4	-4	0.18×10^{-1}	0.09
4	-3	0.16×10^{0}	0.69	4	-3	-0.71×10^{-1}	0.35
4	-2	-0.16×10^{1}	7.27	4	-2	0.62×10^{0}	3.05
4	-1	0.17×10^{0}	0.77	4	-1	0.68×10^{-1}	0.33
4	0	0.77×10^{0}	3.33	4	0	0.20×10^{0}	1.01
4	1	-0.12×10^{1}	5.54	4	1	0.96×10^{0}	4.74
4	2	0.53×10^{1}	23.17	4	2	0.60×10^{1}	29.61
4	3	-0.24×10^{0}	1.06	4	3	-0.35×10^{0}	1.73
4	4	0.23×10^{-1}	0.09	4	4	0.59×10^{-1}	0.29
6	-6	-0.30×10^{-2}	0.09	6	-6	0.11×10^{-2}	0.04
6	-5	-0.14×10^{-3}	0.00	6	-5	0.77×10^{-3}	0.02
6	-4	-0.43×10^{-3}	0.01	6	-4	-0.18×10^{-3}	0.00
6	-3	0.43×10^{-3}	0.01	6	-3	0.99×10^{-3}	0.03
6	-2	-0.89×10^{-1}	2.84	6	-2	0.33×10^{-1}	1.22
6	-1	0.32×10^{-1}	1.04	6	-1	-0.37×10^{-2}	0.13
6	0	-0.32×10^{0}	10.30	6	0	-0.38×10^{0}	13.95
6	1	-0.15×10^{0}	5.04	6	1	-0.21×10^{-1}	0.78
6	2	0.26×10^{0}	8.30	6	2	0.29×10^{0}	10.79
6	3	-0.38×10^{-2}	0.12	6	3	-0.56×10^{-3}	0.02
6	4	0.47×10^{-3}	0.01	6	4	-0.55×10^{-3}	0.02
6	5	0.10×10^{-3}	0.00	6	5	0.21×10^{-2}	0.07
6	6	0.14×10^{-2}	0.04	6	6	0.28×10^{-2}	0.10

Table S14. Calculated energy barriers of Δ (cm^{-1}) and the corresponding error σ of **1** (**1***) with four types of active space.

	CAS (7, 5)		CAS (11, 7)		CAS (11, 8)		CAS (11, 9)		*Exp.*
	1	**1***	**1**	**1***	**1**	**1***	**1**	**1***	U_{eff} (cm^{-1})
Δ (cm^{-1})	767.9	790.6	373.9	387.6	287.5	287.7	267.3	262.1	297
σ	1.586	1.662	0.259	0.305	0.032	0.031	0.100	0.118	—

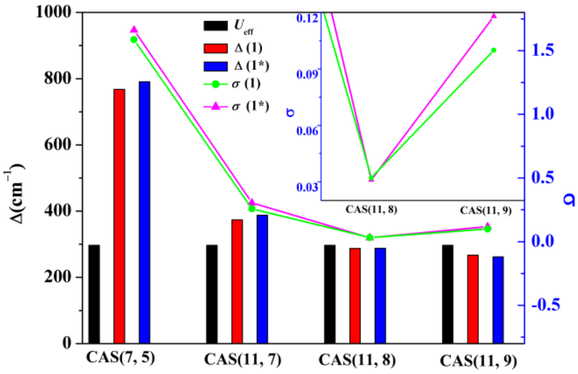


Figure S5. Column diagram: comparison of the calculated energy barrier Δ (the black y axis) of **1** (**1***) by four types of active spaces (CAS (7, 5), CAS (11, 7), CAS (11, 8) and CAS (11, 9)) with the experiment. Line chart: the error σ (the right blue y axis) between the calculated energy barrier Δ (**1**, **1***) by CAS (7, 5), CAS (11, 7), CAS (11, 8), CAS (11, 9) and the experiment. Insert: the enlarged drawing of the error σ in CAS (11, 8) and CAS (11, 9) for the sake of clearly (the left blue y axis).

Table S15. Calculated energy barriers of Δ (cm^{-1}) and the corresponding error σ of **2a** (**2a***) with four types of active space.

	CAS (7, 5)		CAS (11, 7)		CAS (11, 8)		CAS (11, 9)		*Exp.*
	2a	**2a***	**2a**	**2a***	**2a**	**2a***	**2a**	**2a***	U_{eff} (cm^{-1})
Δ (cm^{-1})	682.2	759.2	390.6	388.3	312.0	291.8	349.1	343.2	288
σ	1.369	0.636	0.356	0.348	0.083	0.013	0.212	0.192	–

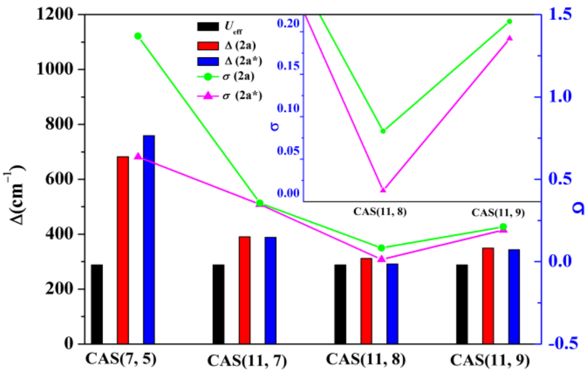


Figure S6. Column diagram: comparison of the calculated energy barrier Δ (the black y axis) of **2a** (**2a***) by four types of active spaces (CAS (7, 5), CAS (11, 7), CAS (11, 8) and CAS (11, 9)) with the experiment. Line chart: the error σ (the right blue y axis) between the calculated energy barrier Δ (**2a**, **2a***) by CAS (7, 5), CAS (11, 7), CAS (11, 8), CAS (11, 9) and the experiment. Insert: the enlarged drawing of the error σ in CAS (11, 8) and CAS (11, 9) for the sake of clearly (the left blue y axis).

Table S16. Calculated energy barriers of Δ (cm^{-1}) and the corresponding error σ of **2b** (**2b***) with four types of active space.

	CAS (7, 5)		CAS (11, 7)		CAS (11, 8)		CAS (11, 9)		*Exp.*
	2b	**2b***	**2b**	**2b***	**2b**	**2b***	**2b**	**2b***	U_{eff} (cm^{-1})
Δ (cm^{-1})	699.7	764.9	387.9	386.4	333.9	291.0	385.4	361.2	288
σ	1.430	1.656	0.347	0.342	0.159	0.010	0.338	0.254	–

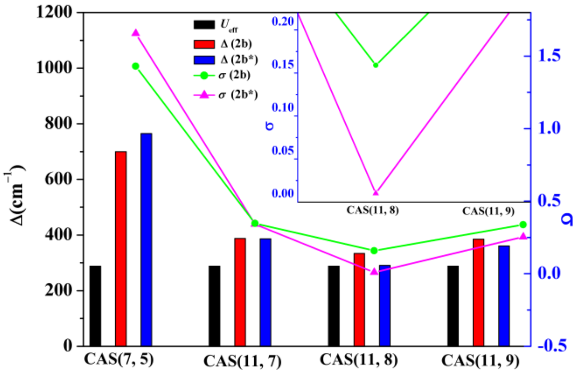


Figure S7. Column diagram: comparison of the calculated energy barrier Δ (the black y axis) of **2b** (**2b***) by four types of active spaces (CAS (7, 5), CAS (11, 7), CAS (11, 8) and CAS (11, 9)) with the experiment. Line chart: the error σ (the right blue y axis) between the calculated energy barrier Δ (**2b**, **2b***) by CAS (7, 5), CAS (11, 7), CAS (11, 8), CAS (11, 9) and the experiment. Insert: the enlarged drawing of the error σ in CAS (11, 8) and CAS (11, 9) for the sake of clearly (the left blue y axis).

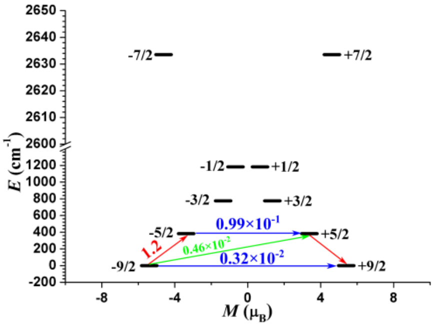
Table S17. Calculated energy levels (cm^{-1}), $\boldsymbol{g}$ (g_x, g_y, g_z) tensors and predominant m_J values in the lowest five KDs for **3*** with θ from 171° to 180° by CAS (11, 8) using CASSCF/SINGLE_ANISO with ORCA 5.0.3.

KDs	**171°**			**172°**			**173°**		
	E/cm^{-1}	$\boldsymbol{g}$	m_J	E/cm^{-1}	$\boldsymbol{g}$	m_J	E/cm^{-1}	$\boldsymbol{g}$	m_J
0	0.0	0.009 0.010 10.807	±9/2	0.0	0.008 0.009 10.793	±9/2	0.0	0.007 0.008 10.780	±9/2
1	383.6	0.293 0.299 6.757	±5/2	383.5	0.251 0.257 6.745	±5/2	383.3	0.213 0.219 6.733	±5/2
2	776.0	0.010 0.636 2.707	±3/2	774.9	0.055 0.596 2.695	±3/2	773.7	0.096 0.558 2.684	±3/2
3	1182.4	0.219 0.239 1.347	±1/2	1180.3	0.222 0.240 1.359	±1/2	1178.3	0.223 0.240 1.370	±1/2
4	2633.5	0.033 0.071 9.825	±7/2	2711.7	0.012 0.032 9.892	±7/2	2779.3	0.002 0.006 9.978	±7/2

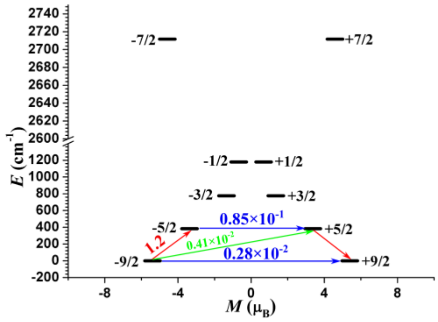
KDs	**174°**			**175°**			**176°**		
	E/cm^{-1}	$\boldsymbol{g}$	m_J	E/cm^{-1}	$\boldsymbol{g}$	m_J	E/cm^{-1}	$\boldsymbol{g}$	m_J
0	0.0	0.006 0.007 10.768	±9/2	0.0	0.006 0.006 10.757	±9/2	0.0	0.005 0.005 10.748	±9/2
1	383.0	0.179 0.184	±5/2	382.6	0.152 0.156	±5/2	382.5	0.131 0.136	±5/2

		6.722			6.713			6.703	
2	772.7	0.132 0.523 2.674	±3/2	771.8	0.160 0.495 2.665	±3/2	771.0	0.181 0.472 2.657	±3/2
3	1176.5	0.224 0.239 1.380	±1/2	1175.0	0.224 0.239 1.388	±1/2	1173.7	0.223 0.238 1.395	±1/2
4	2838.7	0.021 0.029 10.096	±7/2	2879.4	0.031 0.047 10.202	±7/2	2909.5	0.037 0.057 10.314	±7/2
KDs	**177°**			**178°**			**179°**		
	E/cm^{-1}	***g***	m_J	E/cm^{-1}	***g***	m_J	E/cm^{-1}	***g***	m_J
0	0.0	0.004 0.004 10.739	±9/2	0.0	0.004 0.005 10.731	±9/2	0.0	0.004 0.005 10.725	±9/2
1	382.2	0.117 0.121 6.696	±5/2	381.8	0.110 0.114 6.688	±5/2	381.5	0.115 0.119 6.682	±5/2
2	770.3	0.194 0.455 2.649	±3/2	769.6	0.199 0.446 2.642	±3/2	769.1	0.192 0.446 2.636	±3/2
3	1172.6	0.222 0.236 1.402	±1/2	1171.6	0.220 0.234 1.408	±1/2	1170.9	0.218 0.232 1.413	±1/2
4	2927.7	0.039 0.059 10.427	±7/2	2932.5	0.038 0.056 10.522	±7/2	2921.3	0.036 0.052 10.576	±7/2

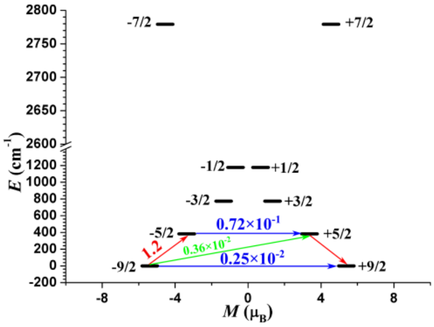
KDs	**180°**		
	E/cm^{-1}	***g***	m_J
0	0.0	0.004 0.005 10.719	±9/2
1	381.2	0.123 0.127 6.676	±5/2
2	768.6	0.181 0.450 2.630	±3/2
3	1170.2	0.215 0.230 1.417	±1/2
4	2902.3	0.031 0.045 10.648	±7/2



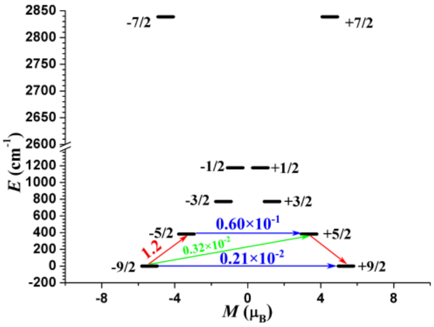
3*_ CAS (11, 8) _*θ*_171°_383.6 cm^{-1}



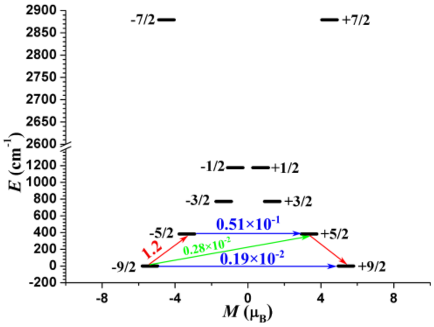
3*_ CAS (11, 8) _*θ*_172°_383.5 cm^{-1}



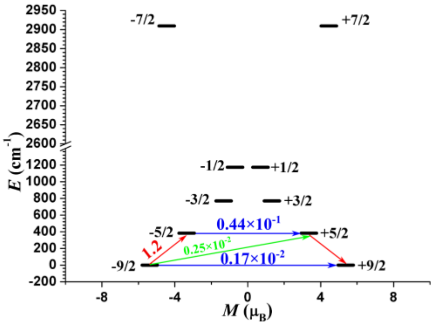
3*_ CAS (11, 8) _*θ*_173°_383.3 cm^{-1}



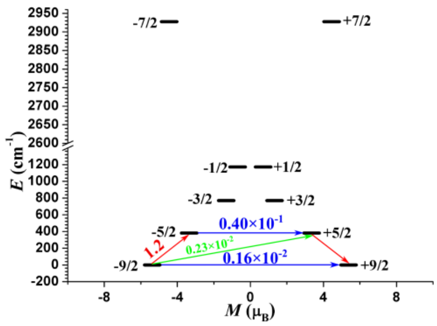
3*_ CAS (11, 8) _*θ*_174°_383.0 cm^{-1}



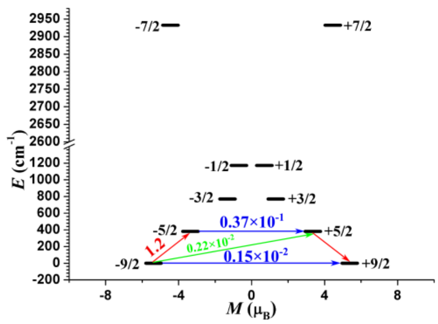
3*_ CAS (11, 8) _*θ*_175°_382.6 cm^{-1}



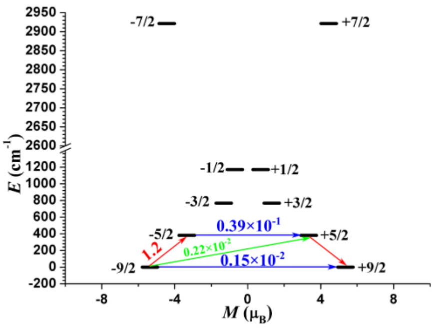
3*_ CAS (11, 8) _*θ*_176°_382.5 cm^{-1}



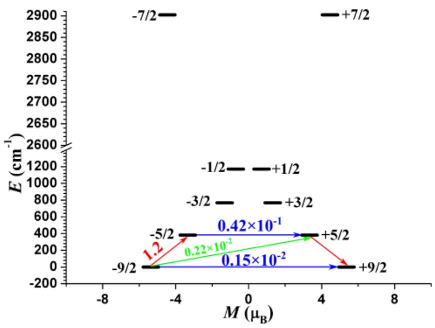
3*_ CAS (11, 8) _*θ*_177°_382.2 cm^{-1}



3*_ CAS (11, 8) _*θ*_178°_381.8 cm^{-1}



3*_ CAS (11, 8) _θ_179°_381.5 cm^{-1}



3*_ CAS (11, 8) _θ_180°_381.2 cm^{-1}

Figure S8. Magnetization blocking barriers for **3*** with θ from 171° to 180° (CAS (11, 8)). The thick black lines represent the KDs of the Co^{II} ion as a function of their magnetic moment along the magnetic axis. The blue lines correspond to diagonal matrix element of the transversal magnetic moment; the green lines represent Orbach relaxation processes. The path shown by the red arrows represent the most probable path for magnetic relaxation in the corresponding compounds. The numbers at each arrow stand for the mean absolute value of the corresponding matrix element of transition magnetic moment.

Table S18. Calculated spin-free and spin-orbit energy (cm^{-1}) of the lowest five KDs for **3*** with θ from 171° to 180° by CAS (11, 8) using CASSCF/SINGLE_ANISO with ORCA 5.0.3.

	171°		**172°**		**173°**		**174°**	
	Spin-free	Spin-orbit	Spin-free	Spin-orbit	Spin-free	Spin-orbit	Spin-free	Spin-orbit
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1	30.3	383.6	26.1	383.5	22.4	383.3	19.0	383.0
2	2543.0	776.0	2629.0	774.9	2704.8	773.7	2773.9	772.7
3	2564.8	1182.4	2646.0	1180.3	2417.4	1178.3	2782.2	1176.5
4	3411.9	2633.5	3466.6	2711.7	3515.3	2779.3	3561.1	2838.7
	175°		**176°**		**177°**		**178°**	
	Spin-free	Spin-orbit	Spin-free	Spin-orbit	Spin-free	Spin-orbit	Spin-free	Spin-orbit
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1	16.3	382.7	14.2	382.5	12.7	382.2	12.9	381.8
2	2823.1	771.8	2862.1	771.0	2887.1	770.3	2897.4	769.6
3	2827.5	1175.0	2863.0	1173.7	2889.3	1172.6	2902.0	1171.6
4	3598.7	2879.4	3631.5	2909.5	3655.0	2927.7	3667.7	2932.5
	179°		**180°**					
	Spin-free	Spin-orbit	Spin-free	Spin-orbit				

0	0.0	0.0	0.0	0.0				
1	12.7	381.5	12.2	381.2				
2	2889.1	769.1	2875.1	768.6				
3	2895.4	1170.9	2882.6	1170.2				
4	3670.2	2921.3	3673.2	2902.3				

Table S19. Calculated Mulliken spin densities on Co^{II}, N(imido), C(carbene), C(arene) and $[CoN]^{+}$ for **3*** with θ from 171° to 180° at their spin state S = 3/2 by CAS (11, 8) using CASSCF/SINGLE_ANISO with ORCA 5.0.3.

Spin density	**171°**	**172°**	**173°**	**174°**	**175°**
Co^{II}	2.036554	2.029421	2.023627	2.019305	2.016611
N	0.522116	0.521817	0.521544	0.521298	0.521073
$[CoN]^{+}$	2.558670	2.551238	2.545171	2.540603	2.537684
C(carbene)	0.166410	0.170518	0.173725	0.175953	0.177132
C(arene)	0.042069	0.042953	0.043673	0.044209	0.044545
Spin density	**176°**	**177°**	**178°**	**179°**	**180°**
Co^{II}	2.015572	2.015215	2.014501	2.014498	2.014157
N	0.520871	0.520683	0.520509	0.520742	0.520188
$[CoN]^{+}$	2.536443	2.535898	2.535010	2.535240	2.534345
C(carbene)	0.177252	0.177608	0.178344	0. 178541	0.178669
C(arene)	0.044673	0.044690	0.044702	0. 044734	0.044758

Table S20. Calculated crystal field parameters B (k, q) and the corresponding weights of **3*** (CAS (11, 8)) with θ from 171° to 180° by using CASSCF/SINGLE_ANISO with ORCA 5.0.3.

171°				**172°**				**173°**			
k	*q*	*B* (*k*, *q*)	Weight (%)	*k*	*q*	*B* (*k*, *q*)	Weight (%)	*k*	*q*	*B* (*k*, *q*)	Weight (%)
2	-2	0.68×10^{2}	12.27	2	-2	0.36×10^{2}	6.10	2	-2	0.66×10^{2}	12.37
2	-1	-0.18×10^{2}	3.21	2	-1	0.61×10^{1}	1.03	2	-1	0.79×10^{1}	1.48
2	0	-0.87×10^{2}	15.69	2	0	-0.87×10^{2}	14.57	2	0	-0.89×10^{2}	16.73
2	1	-0.15×10^{2}	2.75	2	1	0.21×10^{2}	3.47	2	1	0.11×10^{2}	2.09
2	2	-0.98×10^{1}	1.77	2	2	0.60×10^{2}	10.11	2	2	0.84×10^{1}	1.58
4	-4	0.25×10^{1}	0.12	4	-4	-0.40×10^{-1}	0.18	4	-4	0.18×10^{-2}	0.01
4	-3	-0.12×10^{0}	0.57	4	-3	0.34×10^{0}	1.54	4	-3	0.21×10^{0}	1.07
4	-2	0.51×10^{1}	24.69	4	-2	0.29×10^{1}	12.96	4	-2	0.48×10^{1}	24.66
4	-1	-0.21×10^{0}	1.02	4	-1	-0.36×10^{-2}	0.02	4	-1	0.75×10^{0}	3.81
4	0	0.27×10^{0}	1.31	4	0	0.17×10^{0}	0.76	4	0	0.57×10^{0}	2.93

4	1	-0.31×10^{0}	1.52	4	1	0.22×10^{0}	1.01	4	1	0.88×10^{0}	4.48
4	2	-0.97×10^{0}	4.70	4	2	0.44×10^{1}	20.11	4	2	0.41×10^{0}	2.12
4	3	0.41×10^{0}	1.99	4	3	0.21×10^{0}	0.97	4	3	-0.27×10^{0}	1.36
4	4	0.31×10^{-1}	0.15	4	4	-0.84×10^{-2}	0.04	4	4	0.16×10^{-1}	0.08
6	-6	0.11×10^{-3}	0.00	6	-6	-0.14×10^{-3}	0.00	6	-6	-0.83×10^{-3}	0.03
6	-5	-0.17×10^{-2}	0.06	6	-5	-0.20×10^{-2}	0.07	6	-5	0.69×10^{-3}	0.03
6	-4	0.56×10^{-2}	0.20	6	-4	-0.82×10^{-2}	0.27	6	-4	0.21×10^{-2}	0.08
6	-3	-0.39×10^{-2}	0.14	6	-3	-0.76×10^{-2}	0.25	6	-3	0.48×10-2	0.18
6	-2	0.24×10^{0}	8.46	6	-2	0.14×10^{0}	4.57	6	-2	0.24×10^{0}	8.85
6	-1	-0.13×10^{0}	4.67	6	-1	0.52×10^{-1}	1.72	6	-1	0.82×10^{-1}	3.10
6	0	-0.26×10^{0}	9.37	6	0	-0.27×10^{0}	9.12	6	0	-0.25×10^{0}	9.47
6	1	-0.81×10^{-1}	2.90	6	1	0.13×10^{0}	4.24	6	1	0.76×10^{-1}	2.84
6	2	-0.52×10^{-1}	1.87	6	2	0.20×10^{0}	6.82	6	2	0.90×10^{-2}	0.34
6	3	-0.95×10^{-2}	0.34	6	3	-0.21×10^{-3}	0.01	6	3	0.11×10^{-2}	0.04
6	4	0.61×10^{-2}	0.22	6	4	-0.15×10^{-2}	0.05	6	4	0.70×10^{-2}	0.26
6	5	0.14×10^{-3}	0.00	6	5	0.25×10^{-3}	0.01	6	5	0.41×10^{-3}	0.02
6	6	-0.14×10^{-3}	0.00	6	6	0.55×10^{-4}	0.00	6	6	0.13×10^{-3}	0.00
174°				**175°**				**176°**			
k	*q*	*B* (*k*, *q*)	Weight (%)	*k*	*q*	*B* (*k*, *q*)	Weight (%)	*k*	*q*	*B* (*k*, *q*)	Weight (%)
2	-2	0.23×10^{2}	4.12	2	-2	-0.75×10^{2}	9.36	2	-2	0.38×10^{2}	6.78
2	-1	-0.11×10^{2}	2.09	2	-1	-0.28×10^{1}	0.63	2	-1	-0.73×10^{1}	1.31
2	0	-0.88×10^{2}	16.05	2	0	-0.24×10^{2}	15.23	2	0	-0.88×10^{2}	15.77
2	1	-0.24×10^{1}	0.44	2	1	0.22×10^{1}	1.57	2	1	-0.25×10^{1}	0.46
2	2	-0.63×10^{2}	11.49	2	2	0.88×10^{2}	7.31	2	2	-0.58×10^{2}	10.47
4	-4	1.00×10^{-2}	0.05	4	-4	0.11×10^{-1}	0.07	4	-4	0.17×10^{-1}	0.08
4	-3	0.27×10^{0}	1.34	4	-3	-0.48×10^{0}	1.20	4	-3	0.16×10^{0}	0.79
4	-2	0.16×10^{1}	7.94	4	-2	-0.50×10^{1}	19.08	4	-2	0.27×10^{1}	13.04
4	-1	-0.96×10^{0}	4.73	4	-1	0.25×10^{0}	1.52	4	-1	-0.51×10^{0}	2.47
4	0	0.47×10^{0}	2.32	4	0	0.48×10^{0}	1.80	4	0	0.32×10^{0}	1.56
4	1	-0.17×10^{0}	0.85	4	1	0.15×10^{0}	3.27	4	1	-0.16×10^{0}	0.77
4	2	-0.47×10^{1}	23.00	4	2	-0.87×10^{-1}	13.77	4	2	-0.43×10^{1}	21.06
4	3	0.12×10^{0}	0.61	4	3	0.38×10^{-1}	0.09	4	3	0.14×10^{0}	0.69
4	4	-0.15×10^{-1}	0.07	4	4	-0.11×10^{-1}	0.05	4	4	-0.12×10^{-1}	0.06
6	-6	0.64×10^{-3}	0.02	6	-6	-0.10×10^{-4}	0.00	6	-6	0.84×10^{-3}	0.03
6	-5	0.70×10^{-3}	0.03	6	-5	-0.31×10^{-3}	0.01	6	-5	0.42×10^{-3}	0.01
6	-4	0.36×10^{-2}	0.13	6	-4	0.95×10^{-2}	0.17	6	-4	0.52×10^{-2}	0.19
6	-3	0.13×10^{-2}	0.05	6	-3	0.23×10^{-2}	0.08	6	-3	0.76×10^{-3}	0.03
6	-2	0.75×10^{-1}	2.72	6	-2	0.20×10^{0}	6.90	6	-2	0.12×10^{0}	4.43
6	-1	-0.95×10^{-1}	3.42	6	-1	-0.36×10^{-1}	1.37	6	-1	-0.53×10^{-1}	1.89
6	0	-0.26×10^{0}	9.47	6	0	0.75×10^{0}	9.31	6	0	-0.28×10^{0}	9.92
6	1	-0.13×10^{-1}	0.49	6	1	-0.53×10^{-1}	2.22	6	1	-0.13×10^{-1}	0.45
6	2	-0.23×10^{0}	8.22	6	2	-0.15×10^{0}	4.58	6	2	-0.21×10^{0}	7.48
6	3	0.18×10^{-2}	0.07	6	3	0.77×10^{-2}	0.09	6	3	0.24×10^{-2}	0.08

6	4	-0.61×10^{-2}	0.22	6	4	-0.34×10^{-2}	0.16	6	4	-0.42×10^{-2}	0.15
6	5	0.59×10^{-3}	0.02	6	5	-0.36×10^{-3}	0.03	6	5	0.96×10^{-3}	0.03
6	6	-0.53×10^{-3}	0.02	6	6	-0.37×10^{-3}	0.02	6	6	-0.84×10^{-4}	0.00
177°				**178°**				**179°**			
k	*q*	*B* (*k*, *q*)	Weight (%)	*k*	*q*	*B* (*k*, *q*)	Weight (%)	*k*	*q*	*B* (*k*, *q*)	Weight (%)
2	-2	0.70×10^{2}	14.57	2	-2	-0.51×10^{2}	9.54	2	-2	-0.41×10^{2}	7.66
2	-1	0.40×10^{1}	0.83	2	-1	-0.14×10^{1}	0.27	2	-1	0.66×10^{0}	0.12
2	0	-0.88×10^{2}	18.23	2	0	-0.88×10^{2}	16.48	2	0	-0.88×10^{2}	16.29
2	1	0.39×10^{1}	0.82	2	1	0.31×10^{1}	0.59	2	1	-0.11×10^{1}	0.20
2	2	-0.77×10^{1}	1.60	2	2	0.49×10^{2}	9.28	2	2	0.58×10^{2}	10.69
4	-4	0.14×10^{-1}	0.08	4	-4	0.21×10^{-1}	0.11	4	-4	0.24×10^{-1}	0.12
4	-3	0.54×10^{-1}	0.30	4	-3	-0.13×10^{0}	0.67	4	-3	0.84×10^{-1}	0.42
4	-2	0.51×10^{1}	28.59	4	-2	-0.38×10^{1}	19.51	4	-2	-0.31×10^{1}	15.79
4	-1	0.19×10^{0}	1.08	4	-1	0.13×10^{-1}	0.07	4	-1	-0.97×10^{-1}	0.49
4	0	0.28×10^{0}	1.57	4	0	0.26×10^{0}	1.33	4	0	0.27×10^{0}	1.36
4	1	0.19×10^{0}	1.07	4	1	-0.50×10^{-2}	0.03	4	1	0.28×10^{0}	1.40
4	2	-0.77×10^{0}	4.34	4	2	0.35×10^{1}	17.63	4	2	0.41×10^{1}	20.66
4	3	-0.17×10^{0}	0.93	4	3	0.13×10^{-1}	0.07	4	3	-0.36×10^{-1}	0.18
4	4	0.18×10^{-1}	0.10	4	4	1.00×10^{-2}	0.05	4	4	0.69×10^{-3}	0.00
6	-6	-0.56×10^{-3}	0.02	6	-6	-0.23×10^{-3}	0.01	6	-6	-0.67×10^{-3}	0.03
6	-5	0.11×10^{-2}	0.04	6	-5	0.63×10^{-3}	0.02	6	-5	-0.94×10^{-3}	0.03
6	-4	0.43×10^{-2}	0.18	6	-4	0.53×10^{-2}	0.20	6	-4	0.58×10^{-2}	0.21
6	-3	0.27×10^{-2}	0.11	6	-3	-0.18×10^{-2}	0.07	6	-3	0.12×10^{-2}	0.04
6	-2	0.24×10^{0}	9.89	6	-2	-0.19×10^{0}	6.98	6	-2	-0.15×10^{0}	5.68
6	-1	0.25×10^{-1}	1.04	6	-1	-0.36×10^{-2}	0.13	6	-1	-0.64×10^{-2}	0.24
6	0	-0.28×10^{0}	11.70	6	0	-0.29×10^{0}	10.69	6	0	-0.29×10^{0}	10.58
6	1	0.17×10^{-1}	0.72	6	1	0.47×10^{-2}	0.17	6	1	0.18×10^{-1}	0.68
6	2	-0.46×10^{-1}	1.91	6	2	0.16×10^{0}	5.89	6	2	0.19×10^{0}	7.02
6	3	-0.14×10^{-2}	0.06	6	3	0.15×10^{-2}	0.06	6	3	-0.13×10^{-2}	0.05
6	4	0.47×10^{-2}	0.19	6	4	0.29×10^{-2}	0.11	6	4	0.43×10^{-3}	0.02
6	5	-0.63×10^{-4}	0.00	6	5	0.85×10^{-3}	0.03	6	5	-0.41×10^{-3}	0.02
6	6	0.65×10^{-3}	0.03	6	6	-0.85×10^{-3}	0.03	6	6	-0.58×10^{-3}	0.02
180°											
k	*q*	*B* (*k*, *q*)	Weight (%)								
2	-2	-0.64×10^{2}	12.02								
2	-1	-0.16×10^{0}	0.03								
2	0	-0.88×10^{2}	16.52								
2	1	-0.12×10^{1}	0.23								
2	2	0.30×10^{2}	5.69								
4	-4	0.93×10^{-2}	0.05								
4	-3	-0.44×10^{-1}	0.23								
4	-2	-0.47×10^{1}	24.16								
4	-1	0.31×10^{0}	1.60								

4	0	0.30×10^{0}	1.55								
4	1	-0.48×10^{0}	2.44								
4	2	0.20×10^{1}	10.19								
4	3	-0.21×10^{-1}	0.11								
4	4	0.22×10^{-1}	0.11								
6	-6	0.67×10^{-3}	0.03								
6	-5	-0.27×10^{-3}	0.01								
6	-4	0.18×10^{-2}	0.07								
6	-3	-0.13×10^{-2}	0.05								
6	-2	-0.23×10^{0}	8.51								
6	-1	0.26×10^{-1}	0.98								
6	0	-0.28×10^{0}	10.63								
6	1	-0.36×10^{-1}	1.33								
6	2	0.85×10^{-1}	3.20								
6	3	-0.90×10^{-4}	0.00								
6	4	0.52×10^{-2}	0.20								
6	5	0.94×10^{-3}	0.04								
6	6	-0.64×10^{-3}	0.02								

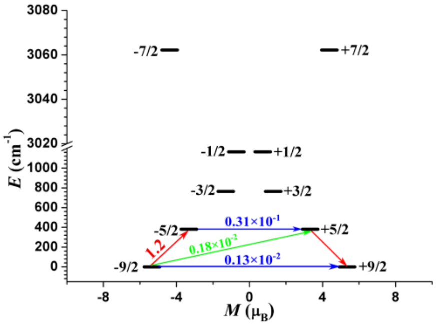
Table S21. Calculated energy levels (cm^{-1}), ***g*** (g_x, g_y, g_z) tensors and predominant m_J values in the lowest five KDs for **3*** with φ from 171° to 180° by CAS (11, 8) using CASSCF/SINGLE_ANISO with ORCA 5.0.3.

KDs	**171°**			**172°**			**173°**		
	E/cm^{-1}	***g***	m_J	E/cm^{-1}	***g***	m_J	E/cm^{-1}	***g***	m_J
0	0.0	0.004 0.004 10.692	±9/2	0.0	0.004 0.004 10.705	±9/2	0.0	0.004 0.005 10.720	±9/2
1	379.5	0.090 0.094 6.647	±5/2	380.3	0.105 0.109 6.661	±5/2	381.2	0.121 0.125 6.677	±5/2
2	764.9	0.218 0.423 2.601	±3/2	766.7	0.201 0.435 2.615	±3/2	768.7	0.183 0.448 2.631	±3/2
3	1164.8	0.218 0.231 1.446	±1/2	1167.5	0.217 0.231 1.432	±1/2	1170.4	0.215 0.230 1.417	±1/2

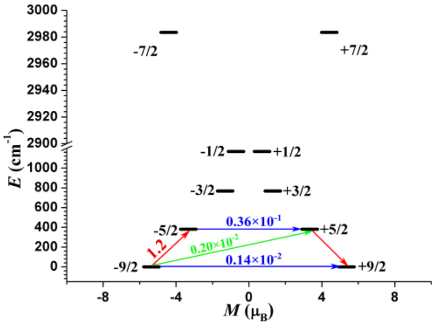
4	3062.2	0.026 0.035 10.875	±7/2	2983.5	0.028 0.039 10.778	±7/2	2904.3	0.031 0.045 10.663	±7/2
KDs	**174°**			**175°**			**176°**		
	E/cm^{-1}	***g***	m_J	E/cm^{-1}	***g***	m_J	E/cm^{-1}	***g***	m_J
0	0.0	0.005 0.005 10.732	±9/2	0.0	0.005 0.005 10.744	±9/2	0.0	0.000 0.000 10.755	±9/2
1	382.0	0.133 0.137 6.689	±5/2	382.7	0.146 0.150 6.702	±5/2	383.5	0.157 0.161 6.715	±5/2
2	770.3	0.170 0.458 2.644	±3/2	772.0	0.155 0.468 2.658	±3/2	773.6	0.142 0.477 2.671	±3/2
3	1172.8	0.214 0.229 1.405	±1/2	1175.3	0.212 0.228 1.391	±1/2	1177.7	0.211 0.228 1.378	±1/2
4	2845.6	0.034 0.049 10.562	±7/2	2788.3	0.038 0.056 10.443	±7/2	2739.8	0.042 0.063 10.319	±7/2
KDs	**177°**			**178°**			**179°**		
	E/cm^{-1}	***g***	m_J	E/cm^{-1}	***g***	m_J	E/cm^{-1}	***g***	m_J
0	0.0	0.005 0.005 10.765	±9/2	0.0	0.006 0.006 10.775	±9/2	0.0	0.006 0.006 10.782	±9/2
1	384.1	0.167 0.171 6.727	±5/2	384.6	0.175 0.179 6.737	±5/2	385.1	0.181 0.185 6.745	±5/2
2	775.0	0.131	±3/2	776.3	0.122	±3/2	777.2	0.115	±3/2

		0.485 2.683			0.492 2.694			0.497 2.702	
3	1179.8	0.210 0.227 1.366	±1/2	1181.7	0.209 0.227 1.356	±1/2	1183.1	0.208 0.227 1.347	±1/2
4	2700.7	0.047 0.072 10.190	±7/2	2671.8	0.052 0.082 10.059	±7/2	2653.4	0.058 0.095 9.931	±7/2

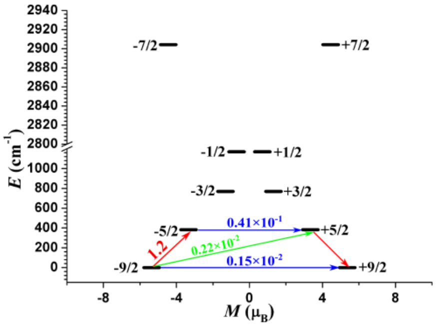
KDs	**180°**		
	E/cm^{-1}	***g***	m_J
0	0.0	0.006 0.006 10.787	±9/2
1	385.4	0.185 0.189 6.751	±5/2
2	778.0	0.110 0.500 2.709	±3/2
3	1184.2	0.208 0.227 1.341	±1/2
4	2645.7	0.065 0.108 9.814	±7/2



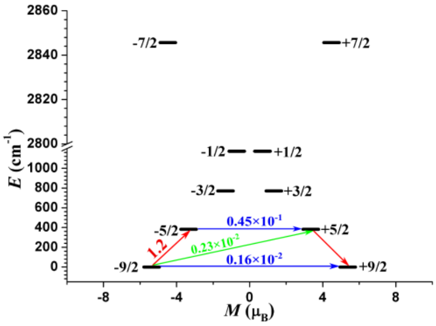
3*_ CAS (11, 8) _171°_*φ*_379.5 cm^{-1}



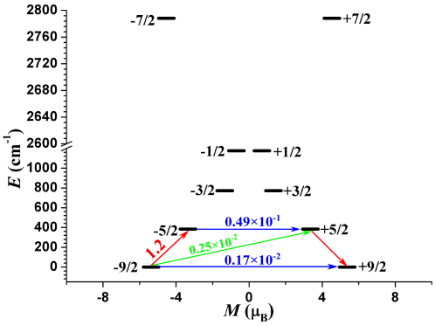
3*_ CAS (11, 8) _172°_*φ*_380.3 cm^{-1}



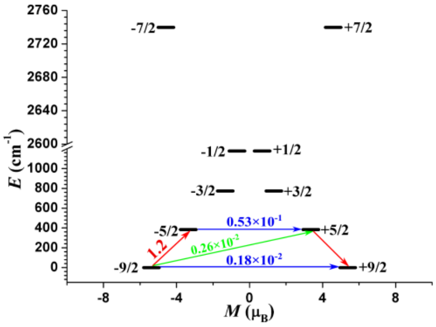
3*_ CAS (11, 8) _173°_*φ*_381.2 cm^{-1}



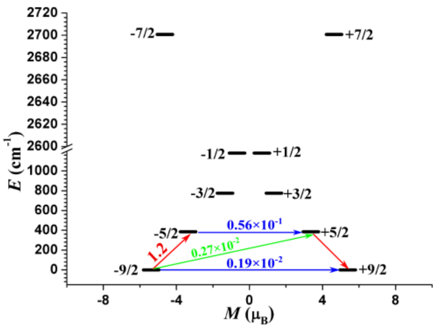
3*_ CAS (11, 8) _174°_*φ*_382.0 cm^{-1}



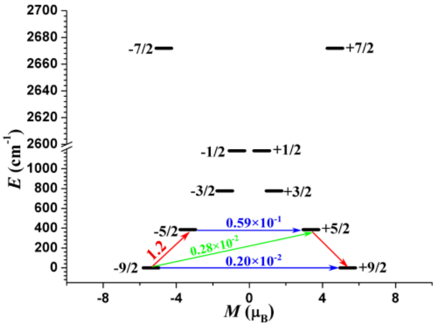
3*_ CAS (11, 8) _175°_*φ*_382.7 cm^{-1}



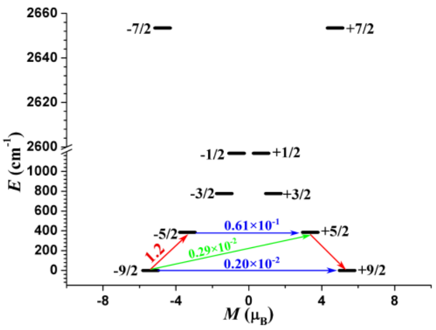
3*_ CAS (11, 8) _176°_*φ*_383.5 cm^{-1}



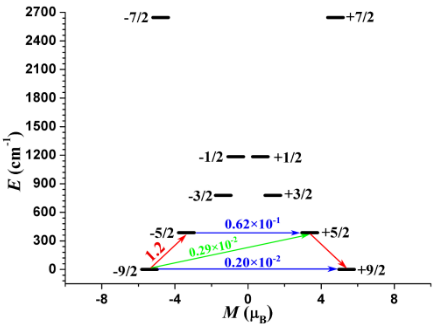
3*_ CAS (11, 8) _177°_*φ*_384.1 cm^{-1}



3*_ CAS (11, 8) _178°_*φ*_384.6 cm^{-1}



3*_ CAS (11, 8) _179°_*φ*_385.1 cm^{-1}



3*_ CAS (11, 8) _180°_*φ*_385.4 cm^{-1}

Figure S9. Magnetization blocking barriers for **3*** (CAS (11, 8)) with *φ* from 171° to 180°. The thick black lines represent the KDs of the Co^{II} ion as a function of their magnetic moment along the magnetic axis. The blue lines correspond to diagonal matrix element of the transversal magnetic moment; the green lines represent Orbach relaxation processes. The path shown by the red arrows represent the most probable path for magnetic relaxation in the corresponding compounds. The numbers at each arrow stand for the mean absolute value of the corresponding matrix element of transition magnetic moment.

Table S22. Calculated spin-free and spin-orbit energy (cm^{-1}) of the lowest five KDs for **3*** with *φ* from 171° to 180° by CAS (11, 8) using CASSCF/SINGLE_ANISO with ORCA 5.0.3.

	171°		**172°**		**173°**		**174°**	
	Spin-free	Spin-orbit	Spin-free	Spin-orbit	Spin-free	Spin-orbit	Spin-free	Spin-orbit
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1	10.3	380.7	12.4	381.4	14.3	382.2	16.3	383.0
2	3055.8	767.0	2963.7	768.7	2878.4	770.5	2792.1	772.4
3	3055.9	1167.6	2964.9	1170.3	2880.5	1172.9	2794.9	1175.9
4	3744.1	3075.3	3689.3	2996.1	3639.5	2922.8	3590.1	2849.7
	175°		**176°**		**177°**		**178°**	
	Spin-free	Spin-orbit	Spin-free	Spin-orbit	Spin-free	Spin-orbit	Spin-free	Spin-orbit
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1	18.4	383.9	20.2	384.4	21.9	384.9	23.4	385.3
2	2713.0	774.4	2652.9	775.8	2603.7	777.1	2565.9	778.1
3	2716.4	1178.8	2656.9	1180.9	2608.2	1182.8	2570.8	1184.3
4	3544.2	2783.2	3509.4	2732.2	3479.6	2690.4	3456.8	2658.1
	179°		**180°**					
	Spin-free	Spin-orbit	Spin-free	Spin-orbit				
0	0.0	0.0	0.0	0.0				

1	24.8	385.5	79.2	392.8				
2	2540.2	778.8	2994.2	803.1				
3	2545.2	1185.5	2995.6	1217.1				
4	3441.1	2635.7	4235.7	3074.7				

Table S23. Calculated Mulliken spin densities on Co^{II}, N(imido) C(carbene), C(arene) and $[CoN]^{+}$ for **3*** with *φ* from 171° to 180° at their spin state *S* = 3/2 by CAS (11, 8) using CASSCF/SINGLE_ANISO with ORCA 5.0.3.

Spin density	**171°**	**172°**	**173°**	**174°**	**175°**
Co^{II}	2.015337	2.015319	2.015656	2.016370	2.017484
N	0.520753	0.520866	0.520925	0.520935	0.520899
$[CoN]^{+}$	2.536090	2.536185	2.536581	2.537305	2.538383
C (carbene)	0.175975	0.176785	0.177288	0.177466	0.177291
C (arene)	0.045085	0.044888	0.044677	0.044451	0.044211
Spin density	**176°**	**177°**	**178°**	**179°**	**180°**
Co^{II}	2.018948	2.020771	2.022937	2.025424	2.025518
N	0.520813	0.520686	0.520520	0.520315	0.520264
$[CoN]^{+}$	2.539761	2.541457	2.543457	2.545739	2.545782
C (carbene)	0.176771	0.175904	0.174700	0.173173	0.173026
C (arene)	0.043963	0.043709	0.043450	0.043190	0.042934

Table S24. Calculated crystal field parameters *B* (*k*, *q*) and the corresponding weights of **3*** with *φ* from 171° to 180° by CAS (11, 8) using CASSCF/SINGLE_ANISO with ORCA 5.0.3.

171°				**172°**				**173°**			
k	*q*	*B* (*k*, *q*)	Weight (%)	*k*	*q*	*B* (*k*, *q*)	Weight (%)	*k*	*q*	*B* (*k*, *q*)	Weight (%)
2	-2	0.59×10^{2}	9.20	2	-2	0.56×10^{2}	8.95	2	-2	-0.66×10^{2}	10.95
2	-1	0.13×10^{2}	2.04	2	-1	0.71×10^{1}	1.13	2	-1	-0.82×10^{1}	1.37
2	0	-0.85×10^{2}	13.25	2	0	-0.85×10^{2}	13.57	2	0	-0.86×10^{2}	14.34
2	1	0.42×10^{1}	0.65	2	1	0.12×10^{2}	1.84	2	1	0.11×10^{2}	1.76
2	2	-0.50×10^{2}	7.80	2	2	0.51×10^{2}	8.17	2	2	0.37×10^{2}	6.17
4	-4	0.52×10^{-1}	0.22	4	-4	-0.41×10^{-1}	0.18	4	-4	0.22×10^{-1}	0.10
4	-3	-0.15×10^{0}	0.64	4	-3	0.31×10^{0}	1.32	4	-3	-0.28×10^{0}	1.25
4	-2	0.43×10^{1}	17.98	4	-2	0.43×10^{1}	18.63	4	-2	-0.50×10^{1}	22.43
4	-1	-0.10×10^{1}	4.39	4	-1	-0.47×10^{0}	2.03	4	-1	0.48×10^{0}	2.18
4	0	-0.28×10^{0}	1.19	4	0	-0.18×10^{0}	0.79	4	0	-0.92×10^{-1}	0.42
4	1	-0.39×10^{0}	1.64	4	1	-0.82×10^{0}	3.54	4	1	-0.62×10^{0}	2.81

4	2	-0.39×10^{1}	16.34	4	2	0.36×10^{1}	15.60	4	2	0.25×10^{1}	11.28
4	3	-0.29×10^{0}	1.21	4	3	0.12×10^{-1}	0.05	4	3	-0.97×10^{-1}	0.44
4	4	-0.85×10^{-2}	0.04	4	4	0.24×10^{-1}	0.10	4	4	0.36×10^{-1}	0.17
6	-6	-0.43×10^{-3}	0.01	6	-6	-0.45×10^{-4}	0.00	6	-6	-0.96×10^{-5}	0.00
6	-5	0.61×10^{-3}	0.02	6	-5	-0.16×10^{-2}	0.05	6	-5	-0.18×10^{-3}	0.01
6	-4	0.84×10^{-2}	0.26	6	-4	-0.70×10^{-2}	0.22	6	-4	0.38×10^{-2}	0.13
6	-3	0.37×10^{-2}	0.11	6	-3	-0.18×10^{-2}	0.06	6	-3	0.81×10^{-4}	0.00
6	-2	0.19×10^{0}	5.95	6	-2	0.20×10^{0}	6.43	6	-2	-0.23×10^{0}	7.74
6	-1	0.40×10^{-1}	1.25	6	-1	0.32×10^{-1}	1.00	6	-1	-0.37×10^{-1}	1.22
6	0	-0.32×10^{0}	9.88	6	0	-0.31×10^{0}	9.89	6	0	-0.31×10^{0}	10.22
6	1	0.49×10^{-2}	0.15	6	1	0.31×10^{-1}	0.97	6	1	0.29×10^{-1}	0.95
6	2	-0.18×10^{0}	5.61	6	2	0.16×10^{0}	5.13	6	2	0.11×10^{0}	3.61
6	3	-0.14×10^{-3}	0.00	6	3	0.39×10^{-2}	0.12	6	3	0.46×10^{-2}	0.15
6	4	-0.16×10^{-2}	0.05	6	4	0.43×10^{-2}	0.14	6	4	0.68×10^{-2}	0.23
6	5	-0.29×10^{-2}	0.09	6	5	0.23×10^{-2}	0.07	6	5	0.25×10^{-2}	0.08
6	6	-0.34×10^{-3}	0.01	6	6	0.26×10^{-3}	0.01	6	6	0.14×10^{-4}	0.00
174°				**175°**				**176°**			
k	*q*	*B* (*k*, *q*)	Weight (%)	*k*	*q*	*B* (*k*, *q*)	Weight (%)	*k*	*q*	*B* (*k*, *q*)	Weight (%)
2	-2	-0.57×10^{2}	9.53	2	-2	-0.34×10^{2}	6.05	2	-2	0.72×10^{2}	15.11
2	-1	0.12×10^{2}	2.07	2	-1	-0.12×10^{2}	2.22	2	-1	0.90×10^{1}	1.89
2	0	-0.86×10^{2}	14.54	2	0	-0.87×10^{2}	15.47	2	0	-0.87×10^{2}	18.27
2	1	-0.46×10^{1}	0.77	2	1	0.26×10^{1}	0.47	2	1	0.79×10^{1}	1.67
2	2	-0.47×10^{2}	7.98	2	2	-0.64×10^{2}	11.43	2	2	0.73×10^{-1}	0.02
4	-4	-0.38×10^{-1}	0.17	4	-4	-0.24×10^{-1}	0.12	4	-4	0.13×10^{-1}	0.08
4	-3	-0.13×10^{0}	0.59	4	-3	0.22×10^{0}	1.07	4	-3	0.11×10^{0}	0.65
4	-2	-0.41×10^{1}	18.55	4	-2	-0.24×10^{1}	11.67	4	-2	0.53×10^{1}	29.96
4	-1	-0.56×10^{0}	2.54	4	-1	0.36×10^{0}	1.72	4	-1	-0.18×10^{0}	1.00
4	0	0.44×10^{-3}	0.00	4	0	0.87×10^{-1}	0.42	4	0	0.16×10^{0}	0.89
4	1	0.19×10^{0}	0.85	4	1	-0.54×10^{-1}	0.26	4	1	-0.77×10^{-1}	0.44
4	2	-0.36×10^{1}	16.59	4	2	-0.48×10^{1}	23.10	4	2	-0.23×10^{0}	1.32
4	3	0.25×10^{0}	1.13	4	3	-0.15×10^{0}	0.73	4	3	-0.23×10^{0}	1.31
4	4	-0.54×10^{-2}	0.02	4	4	-0.24×10^{-1}	0.11	4	4	0.27×10^{-1}	0.15
6	-6	-0.15×10^{-3}	0.01	6	-6	-0.37×10^{-3}	0.01	6	-6	-0.47×10^{-3}	0.02
6	-5	0.49×10^{-3}	0.02	6	-5	0.11×10^{-2}	0.04	6	-5	0.18×10^{-2}	0.07
6	-4	-0.77×10^{-2}	0.25	6	-4	-0.50×10^{-2}	0.18	6	-4	0.36×10^{-2}	0.15
6	-3	0.34×10^{-2}	0.11	6	-3	-0.22×10^{-2}	0.08	6	-3	0.31×10^{-2}	0.13
6	-2	-0.19×10^{0}	6.22	6	-2	-0.11×10^{0}	3.91	6	-2	0.25×10^{0}	10.33
6	-1	0.49×10^{-1}	1.64	6	-1	-0.54×10^{-1}	1.93	6	-1	0.48×10^{-1}	2.01
6	0	-0.30×10^{0}	10.10	6	0	-0.29×10^{0}	10.47	6	0	-0.29×10^{0}	12.13
6	1	-0.11×10^{-1}	0.36	6	1	0.74×10^{-2}	0.26	6	1	0.29×10^{-1}	1.20
6	2	-0.17×10^{0}	5.82	6	2	-0.23×10^{0}	8.02	6	2	-0.20×10^{-1}	0.83
6	3	-0.16×10^{-3}	0.01	6	3	-0.48×10^{-3}	0.02	6	3	0.24×10^{-2}	0.10
6	4	-0.14×10^{-2}	0.05	6	4	-0.52×10^{-2}	0.19	6	4	0.60×10^{-2}	0.25

6	5	0.22×10^{-2}	0.07	6	5	-0.17×10^{-2}	0.06	6	5	0.37×10^{-3}	0.02
6	6	0.12×10^{-3}	0.00	6	6	-0.13×10^{-3}	0.00	6	6	0.28×10^{-3}	0.01
177°				**178°**				**179°**			
k	*q*	*B* (*k*, *q*)	Weight (%)	*k*	*q*	*B* (*k*, *q*)	Weight (%)	*k*	*q*	*B* (*k*, *q*)	Weight (%)
2	-2	0.71×10^{2}	15.22	2	-2	0.71×10^{2}	14.64	2	-2	0.52×10^{2}	9.27
2	-1	-0.82×10^{1}	1.75	2	-1	0.76×10^{1}	1.57	2	-1	0.37×10^{1}	0.66
2	0	-0.87×10^{2}	18.65	2	0	-0.88×10^{2}	18.18	2	0	-0.88×10^{2}	15.57
2	1	-0.76×10^{1}	1.63	2	1	0.71×10^{1}	1.47	2	1	0.86×10^{1}	1.53
2	2	0.27×10^{0}	0.06	2	2	-0.37×10^{1}	0.77	2	2	0.47×10^{2}	8.27
4	-4	0.12×10^{-1}	0.07	4	-4	0.13×10^{-1}	0.07	4	-4	-0.19×10^{-1}	0.09
4	-3	-0.11×10^{0}	0.65	4	-3	0.92×10^{-1}	0.51	4	-3	0.23×10^{0}	1.13
4	-2	0.52×10^{1}	30.13	4	-2	0.51×10^{1}	28.87	4	-2	0.39×10^{1}	18.95
4	-1	0.46×10^{-1}	0.27	4	-1	0.89×10^{-1}	0.50	4	-1	0.11×10^{0}	0.54
4	0	0.22×10^{0}	1.25	4	0	0.26×10^{0}	1.49	4	0	0.30×10^{0}	1.45
4	1	-0.36×10^{-1}	0.21	4	1	0.15×10^{0}	0.82	4	1	0.32×10^{0}	1.54
4	2	-0.21×10^{0}	1.22	4	2	-0.49×10^{0}	2.77	4	2	0.33×10^{1}	15.67
4	3	0.22×10^{0}	1.29	4	3	-0.22×10^{0}	1.26	4	3	0.56×10^{-2}	0.03
4	4	0.24×10^{-1}	0.14	4	4	0.21×10^{-1}	0.12	4	4	0.11×10^{-1}	0.05
6	-6	-0.58×10^{-3}	0.02	6	-6	-0.59×10^{-3}	0.02	6	-6	0.11×10^{-3}	0.00
6	-5	-0.16×10^{-2}	0.07	6	-5	0.14×10^{-2}	0.06	6	-5	-0.63×10^{-3}	0.02
6	-4	0.35×10^{-2}	0.15	6	-4	0.40×10^{-2}	0.17	6	-4	-0.56×10^{-2}	0.20
6	-3	-0.32×10^{-2}	0.13	6	-3	0.33×10^{-2}	0.14	6	-3	0.12×10^{-2}	0.04
6	-2	0.25×10^{0}	10.43	6	-2	0.24×10^{0}	10.01	6	-2	0.19×10^{0}	6.82
6	-1	-0.47×10^{-1}	2.02	6	-1	0.47×10^{-1}	1.96	6	-1	0.30×10^{-1}	1.05
6	0	-0.29×10^{0}	12.18	6	0	-0.28×10^{0}	11.69	6	0	-0.28×10^{0}	9.89
6	1	-0.30×10^{-1}	1.29	6	1	0.31×10^{-1}	1.27	6	1	0.48×10^{-1}	1.69
6	2	-0.19×10^{-1}	0.82	6	2	-0.33×10^{-1}	1.36	6	2	0.15×10^{0}	5.24
6	3	-0.18×10^{-2}	0.08	6	3	0.79×10^{-3}	0.03	6	3	0.28×10^{-2}	0.10
6	4	0.59×10^{-2}	0.25	6	4	0.54×10^{-2}	0.22	6	4	0.38×10^{-2}	0.13
6	5	-0.34×10^{-3}	0.01	6	5	0.11×10^{-3}	0.00	6	5	0.11×10^{-2}	0.04
6	6	0.34×10^{-3}	0.01	6	6	0.49×10^{-3}	0.02	6	6	-0.82×10^{-3}	0.03
180°											
k	*q*	*B* (*k*, *q*)	Weight (%)								
2	-2	0.69×10^{2}	13.81								
2	-1	-0.17×10^{0}	0.03								
2	0	-0.88×10^{2}	17.44								
2	1	-0.13×10^{1}	0.26								
2	2	-0.13×10^{2}	2.55								
4	-4	0.17×10^{-1}	0.09								
4	-3	0.10×10^{-1}	0.06								
4	-2	0.50×10^{1}	26.99								
4	-1	-0.47×10^{0}	2.55								
4	0	0.31×10^{0}	1.66								

4	1	-0.38×10^{0}	2.04								
4	2	-0.11×10^{1}	6.15								
4	3	-0.47×10^{-1}	0.26								
4	4	0.16×10^{-1}	0.09								
6	-6	-0.44×10^{-3}	0.02								
6	-5	0.98×10^{-3}	0.04								
6	-4	0.43×10^{-2}	0.17								
6	-3	0.71×10^{-3}	0.03								
6	-2	0.23×10^{0}	9.27								
6	-1	-0.37×10^{-1}	1.48								
6	0	-0.28×10^{0}	11.22								
6	1	-0.27×10^{-1}	1.07								
6	2	-0.63×10^{-1}	2.49								
6	3	-0.11×10^{-2}	0.04								
6	4	0.35×10^{-2}	0.14								
6	5	-0.24×10^{-3}	0.01								
6	6	0.83×10^{-3}	0.03								

Table S25. Calculated energy levels (cm^{-1}), ***g*** (g_x, g_y, g_z) tensors and predominant m_J values in the lowest five KDs for **3*** with Co=N bond length ranging from 1.48 to 2.18 Å by CAS (11, 8) using CASSCF/SINGLE_ANISO with ORCA 5.0.3.

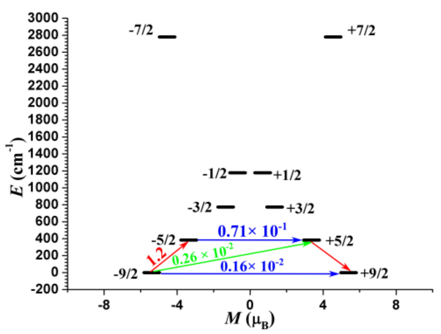
KDs	**1.48 Å**			**1.58 Å**			**1.68 Å**		
	E/cm^{-1}	***g***	m_J	E/cm^{-1}	***g***	m_J	E/cm^{-1}	***g***	m_J
0	0.0	0.004 0.005 10.360	±9/2	0.0	0.007 0.007 10.592	±9/2	0.0	0.005 0.006 10.750	±9/2
1	339.0	0.018 0.025 6.357	±5/2	368.5	0.158 0.164 6.562	±5/2	382.5	0.137 0.142 6.706	±5/2
2	697.4	0.308 0.334 2.348	±3/2	745.0	0.149 0.494 2.529	±3/2	771.2	0.175 0.479 2.659	±3/2
3	1079.7	0.246 0.260 1.684	±1/2	1136.1	0.235 0.246 1.511	±1/2	1174.0	0.223 0.238 1.393	±1/2
4	1736.3	0.007	±7/2	2409.1	0.010	±7/2	2901.7	0.035	±7/2

		0.008 10.203			0.014 10.073			0.054 10.278	
KDs	**1.78 Å**			**1.88 Å**			**1.98 Å**		
	E/cm^{-1}	$\boldsymbol{g}$	m_J	E/cm^{-1}	$\boldsymbol{g}$	m_J	E/cm^{-1}	$\boldsymbol{g}$	m_J
0	0.0	0.003 0.004 10.926	±9/2	0.0	0.002 0.002 11.202	±9/2	0.0	0.000 0.000 11.497	±9/2
1	394.6	0.069 0.072 6.878	±7/2	411.3	0.021 0.021 7.169	±7/2	424.4	0.011 0.011 7.511	±7/2
2	795.5	0.242 0.415 2.820	±3/2	830.7	0.238 0.317 3.115	±3/2	861.0	0.133 0.176 3.517	±3/2
3	1212.7	0.205 0.235 1.246	±1/2	1268.6	0.135 0.212 0.967	±1/2	1320.6	0.055 0.168 0.498	±1/2
4	2733.9	0.092 0.119 11.134	±5/2	2157.1	0.107 0.280 10.135	±5/2	1523.4	4.489 3.107 1.376	±5/2
KDs	**2.08 Å**			**2.18 Å**					
	E/cm^{-1}	$\boldsymbol{g}$	m_J	E/cm^{-1}	$\boldsymbol{g}$	m_J			
0	0.0	0.001 0.001 11.318	±9/2	0.0	0.006 0.006 7.938	±7/2			
1	412.7	0.049 0.058 7.727	±7/2	152.0	0.000 0.000 11.521	±9/2			
2	817.5	0.112 0.236	±1/2	789.1	0.011 0.049	±3/2			

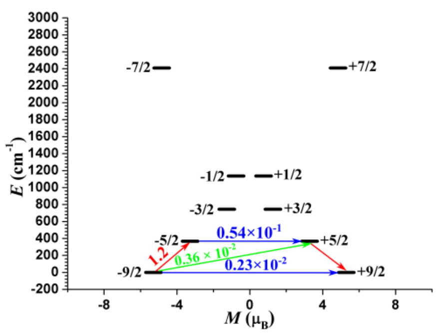
		4.034			4.033				
3	916.5	1.041 1.096 4.333	±3/2	814.7	0.015 0.017 7.490	±5/2			
4	1160.5	0.418 0.897 7.262	±5/2	1462.9	0.321 0.329 3.771	±1/2			

Table S26. Calculated spin-free and spin-orbit energy (cm^{-1}) of the lowest five KDs for **3*** with Co=N from 1.48 to 2.18 Å by CAS (11, 8) using CASSCF/SINGLE_ANISO with ORCA 5.0.3.

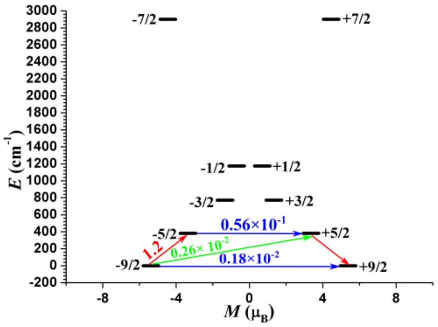
	1.48 Å		**1.58 Å**		**1.68 Å**		**1.78 Å**	
	Spin-free	Spin-orbit	Spin-free	Spin-orbit	Spin-free	Spin-orbit	Spin-free	Spin-orbit
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1	28.0	339.0	16.0	368.5	14.8	382.5	9.0	394.6
2	9966.2	697.4	2333.3	745.0	2851.5	771.2	2723.8	795.5
3	10906.3	1079.7	2349.2	1136.1	2853.6	1174.0	2731.8	1212.7
4	11424.4	1736.3	4582.0	2409.1	3622.1	2901.7	3028.9	2733.9
	1.88 Å		**1.98 Å**		**2.08 Å**		**2.18 Å**	
	Spin-free	Spin-orbit	Spin-free	Spin-orbit	Spin-free	Spin-orbit	Spin-free	Spin-orbit
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1	4.3	411.3	2.4	424.4	2.3	412.7	0.5	152.0
2	2018.2	830.7	1499.8	861.0	966.8	817.5	1714.1	789.1
3	2042.1	1268.6	1525.4	1320.6	1132.9	916.5	3668.8	814.7
4	2601.2	2157.1	2021.4	1523.4	1560.8	1160.5	3910.9	1462.9



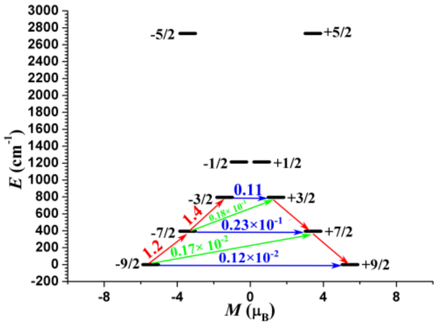
3*_1.48 Å_CAS (11, 8) _339.0 cm^{-1}



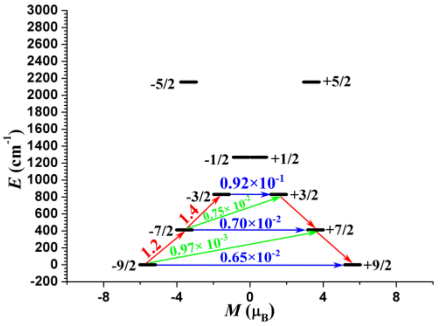
3*_1.58 Å_CAS (11, 8) _368.5 cm^{-1}



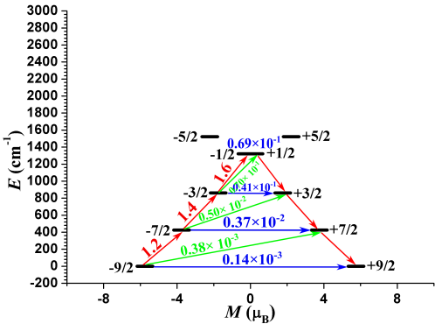
3*_1.68 Å_CAS (11, 8) _382.5 cm^{-1}



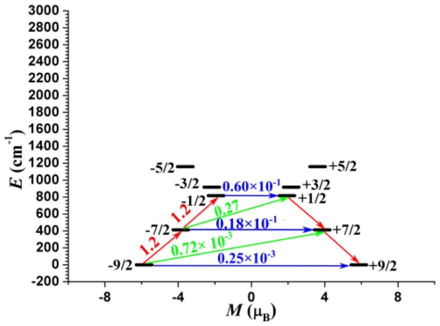
3*_1.78 Å_CAS (11, 8) _795.5 cm^{-1}



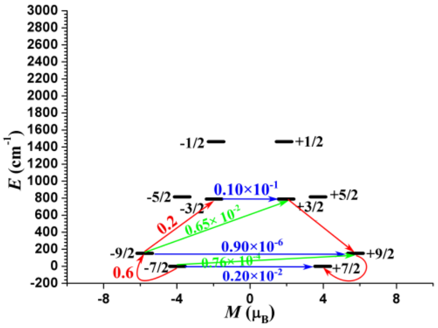
3*_1.88 Å_CAS (11, 8) _830.7 cm^{-1}



3*_1.98 Å_CAS (11, 8) _1320.6 cm^{-1}



3*_2.08 Å_CAS (11, 8) _916.5 cm^{-1}



3*_2.18 Å_CAS (11, 8) _789.1 cm^{-1}

Figure S10. Magnetization blocking barriers for **3*** (CAS (11, 8)) with Co=N bond length ranging from 1.48 to 2.18 Å. The thick black lines represent the KDs of the Co^{II} ion as a function of their magnetic moment along the magnetic axis. The blue lines correspond to diagonal matrix element of the transversal magnetic moment; the green lines represent Orbach relaxation processes. The path shown by the red arrows represent the most probable path for magnetic relaxation in the corresponding compounds. The numbers at each arrow stand for the mean absolute value of the corresponding matrix element of transition magnetic moment.

Table S27. Calculated Mulliken spin densities on Co^{II}, N(imido), C (carbene), C(arene) and $[CoN]^+$ for **3*** with Co=N bond length from 1.48 to 2.18 Å at their spin state S = 3/2 by CAS (11, 8) using CASSCF/SINGLE_ANISO with ORCA 5.0.3.

Spin density	**1.48 Å**	**1.58 Å**	**1.68 Å**	**1.78 Å**	**1.88 Å**	**1.98 Å**	**2.08 Å**	**2.18 Å**
Co^{II}	2.0013	2.0130	2.0157	2.0160	2.0158	2.0157	2.0159	2.3308
N	0.4931	0.5094	0.5209	0.5284	0.5329	0.5354	0.5363	0.5179
$[CoN]^+$	2.4943	2.5224	2.5367	2.5444	2.5488	2.5511	2.5522	2.8487

C(carbene)	0.1717	0.1733	0.1773	0.1811	0.1843	0.1868	0.1587	-0.0171
C(arene)	0.0624	0.0518	0.0447	0.0394	0.0353	0.0321	0.0298	0.0215

Table S28. Calculated crystal field parameters *B* (*k, q*) and the corresponding weights of **3*** with Co=N bond length from 1.48 to 2.18 Å by CAS (11, 8) using CASSCF/SINGLE_ANISO with ORCA 5.0.3.

1.48 Å				**1.58 Å**				**1.68 Å**			
k	*q*	*B* (*k, q*)	Weight (%)	*k*	*q*	*B* (*k, q*)	Weight (%)	*k*	*q*	*B* (*k, q*)	Weight (%)
2	-2	0.35×10^{-3}	0.00	2	-2	-0.10×10^{-1}	0.00	2	-2	0.68×10^{2}	11.62
2	-1	-0.37×10^{-3}	0.00	2	-1	-0.16×10^{2}	2.51	2	-1	0.12×10^{2}	2.06
2	0	-0.11×10^{3}	13.32	2	0	-0.98×10^{2}	15.79	2	0	-0.85×10^{2}	14.67
2	1	-0.14×10^{2}	1.72	2	1	-0.34×10^{-3}	0.00	2	1	0.61×10^{1}	1.04
2	2	0.13×10^{3}	16.50	2	2	-0.10×10^{3}	16.51	2	2	-0.30×10^{2}	5.24
4	-4	0.41×10^{-4}	0.00	4	-4	-0.22×10^{-4}	0.00	4	-4	0.39×10^{-1}	0.18
4	-3	-0.14×10^{-3}	0.00	4	-3	0.36×10^{0}	1.55	4	-3	-0.35×10^{-1}	0.17
4	-2	0.13×10^{-4}	0.00	4	-2	-0.83×10^{-3}	0.00	4	-2	0.49×10^{1}	22.82
4	-1	-0.12×10^{-4}	0.00	4	-1	0.15×10^{1}	6.51	4	-1	-0.60×10^{0}	2.80
4	0	0.43×10^{1}	14.59	4	0	0.18×10^{1}	7.87	4	0	-0.64×10^{-1}	0.30
4	1	0.27×10^{1}	9.28	4	1	0.14×10^{-3}	0.00	4	1	-0.28×10^{0}	1.33
4	2	0.81×10^{1}	27.79	4	2	-0.69×10^{1}	30.09	4	2	-0.24×10^{1}	11.42
4	3	-0.42×10^{0}	1.45	4	3	-0.50×10^{-4}	0.00	4	3	-0.28×10^{0}	1.33
4	4	-0.57×10^{-1}	0.20	4	4	-0.39×10^{-1}	0.17	4	4	0.13×10^{-1}	0.06
6	-6	0.97×10^{-6}	0.00	6	-6	0.41×10^{-5}	0.00	6	-6	0.34×10^{-5}	0.00
6	-5	0.33×10^{-5}	0.00	6	-5	0.26×10^{-2}	0.08	6	-5	0.17×10^{-2}	0.06
6	-4	0.11×10^{-6}	0.00	6	-4	-0.73×10^{-5}	0.00	6	-4	0.73×10^{-2}	0.25
6	-3	0.38×10^{-5}	0.00	6	-3	0.14×10^{-2}	0.05	6	-3	0.39×10^{-2}	0.13
6	-2	0.17×10^{-4}	0.00	6	-2	-0.47×10^{-4}	0.00	6	-2	0.22×10^{0}	7.66
6	-1	0.52×10^{-4}	0.00	6	-1	0.17×10^{-1}	0.55	6	-1	0.50×10^{-1}	1.71
6	0	-0.11×10^{0}	2.79	6	0	-0.27×10^{0}	8.49	6	0	-0.30×10^{0}	10.36
6	1	0.15×10^{0}	3.75	6	1	-0.13×10^{-4}	0.00	6	1	0.15×10^{-1}	0.52
6	2	0.32×10^{0}	8.03	6	2	-0.30×10^{0}	9.49	6	2	-0.12×10^{0}	4.09
6	3	-0.60×10^{-2}	0.15	6	3	0.78×10^{-5}	0.00	6	3	0.12×10^{-2}	0.04
6	4	-0.11×10^{-1}	0.29	6	4	-0.91×10^{-2}	0.29	6	4	0.21×10^{-2}	0.07
6	5	0.20×10^{-2}	0.05	6	5	-0.34×10^{-5}	0.00	6	5	-0.16×10^{-2}	0.06
6	6	-0.37×10^{-2}	0.09	6	6	0.12×10^{-2}	0.04	6	6	0.25×10^{-4}	0.00
1.78 Å				**1.88 Å**				**1.98 Å**			
k	*q*	*B* (*k, q*)	Weight (%)	*k*	*q*	*B* (*k, q*)	Weight (%)	*k*	*q*	*B* (*k, q*)	Weight (%)
2	-2	0.28×10^{2}	5.51	2	-2	0.21×10^{2}	5.04	2	-2	0.88×10^{-3}	0.00
2	-1	-0.39×10^{1}	0.77	2	-1	0.39×10^{1}	0.94	2	-1	-0.11×10^{2}	4.49
2	0	-0.72×10^{2}	14.22	2	0	-0.64×10^{2}	15.29	2	0	-0.73×10^{2}	28.99
2	1	-0.98×10^{1}	1.93	2	1	0.60×10^{1}	1.44	2	1	0.45×10^{-1}	0.01
2	2	0.41×10^{2}	8.12	2	2	0.19×10^{2}	4.63	2	2	0.41×10^{1}	1.64

4	-4	-0.45×10^{-1}	0.24	4	-4	-0.31×10^{-1}	0.25	4	-4	0.14×10^{-3}	0.00
4	-3	-0.21×10^{0}	1.13	4	-3	0.19×10^{0}	1.23	4	-3	-0.24×10^{0}	2.65
4	-2	0.25×10^{1}	13.72	4	-2	0.23×10^{1}	15.44	4	-2	0.25×10^{-3}	0.00
4	-1	0.10×10^{0}	0.58	4	-1	0.66×10^{-1}	0.43	4	-1	-0.22×10^{1}	24.29
4	0	-0.13×10^{1}	7.18	4	0	-0.21×10^{1}	13.61	4	0	-0.60×10^{0}	6.44
4	1	0.14×10^{0}	0.79	4	1	0.26×10^{0}	1.74	4	1	-0.10×10^{-2}	0.01
4	2	0.33×10^{1}	17.55	4	2	0.15×10^{1}	10.32	4	2	-0.54×10^{0}	5.83
4	3	-0.85×10^{-1}	0.45	4	3	-0.29×10^{-1}	0.19	4	3	-0.11×10^{-3}	0.00
4	4	0.30×10^{-2}	0.02	4	4	0.31×10^{-1}	0.21	4	4	-0.44×10^{-1}	0.47
6	-6	0.76×10^{-3}	0.03	6	-6	-0.36×10^{-3}	0.02	6	-6	0.60×10^{-5}	0.00
6	-5	0.18×10^{-2}	0.07	6	-5	-0.94×10^{-3}	0.04	6	-5	0.30×10^{-2}	0.23
6	-4	-0.55×10^{-2}	0.21	6	-4	-0.18×10^{-2}	0.09	6	-4	-0.29×10^{-4}	0.00
6	-3	0.49×10^{-2}	0.20	6	-3	-0.60×10^{-2}	0.29	6	-3	0.12×10^{-1}	0.96
6	-2	0.13×10^{0}	5.20	6	-2	0.12×10^{0}	6.01	6	-2	-0.69×10^{-5}	0.00
6	-1	-0.39×10^{-1}	1.52	6	-1	0.66×10^{-1}	3.17	6	-1	-0.22×10^{0}	17.79
6	0	-0.28×10^{0}	11.28	6	0	-0.23×10^{0}	11.02	6	0	0.20×10^{-1}	1.63
6	1	-0.73×10^{-1}	2.87	6	1	0.90×10^{-1}	4.30	6	1	-0.10×10^{-3}	0.00
6	2	0.16×10^{0}	6.29	6	2	0.80×10^{-1}	3.84	6	2	-0.32×10^{-1}	2.52
6	3	-0.10×10^{-2}	0.04	6	3	0.41×10^{-2}	0.20	6	3	0.18×10^{-5}	0.00
6	4	0.36×10^{-3}	0.01	6	4	0.18×10^{-2}	0.09	6	4	0.20×10^{-1}	1.61
6	5	-0.83×10^{-3}	0.03	6	5	0.31×10^{-2}	0.15	6	5	0.62×10^{-5}	0.00
6	6	-0.67×10^{-3}	0.03	6	6	-0.20×10^{-2}	0.10	6	6	-0.44×10^{-2}	0.34
2.08 Å				**2.18 Å**							
k	*q*	*B* (*k*, *q*)	Weight (%)	*k*	*q*	*B* (*k*, *q*)	Weight (%)				
2	-2	-0.11×10^{2}	5.11	2	-2	0.16×10^{2}	2.34				
2	-1	0.70×10^{1}	3.39	2	-1	0.11×10^{3}	15.88				
2	0	-0.61×10^{2}	29.15	2	0	-0.32×10^{2}	4.67				
2	1	0.34×10^{2}	16.19	2	1	-0.13×10^{3}	19.58				
2	2	-0.14×10^{2}	6.70	2	2	-0.60×10^{1}	0.87				
4	-4	-0.13×10^{0}	1.64	4	-4	-0.20×10^{-1}	0.08				
4	-3	-0.84×10^{-1}	1.09	4	-3	-0.72×10^{-1}	0.29				
4	-2	0.74×10^{-3}	0.01	4	-2	-0.62×10^{0}	2.45				
4	-1	-0.25×10^{0}	3.32	4	-1	0.43×10^{1}	16.87				
4	0	-0.49×10^{0}	6.43	4	0	0.14×10^{1}	5.40				
4	1	-0.60×10^{0}	7.80	4	1	-0.12×10^{1}	4.58				
4	2	-0.43×10^{0}	5.65	4	2	0.24×10^{0}	0.95				
4	3	-0.45×10^{-1}	0.59	4	3	0.19×10^{-1}	0.07				
4	4	0.80×10^{-2}	0.10	4	4	-0.16×10^{-1}	0.06				
6	-6	0.34×10^{-2}	0.33	6	-6	-0.11×10^{-4}	0.00				
6	-5	-0.17×10^{-1}	1.65	6	-5	0.29×10^{-4}	0.00				
6	-4	0.23×10^{-1}	2.16	6	-4	-0.35×10^{-2}	0.10				
6	-3	0.71×10^{-2}	0.68	6	-3	-0.87×10^{-2}	0.25				
6	-2	-0.11×10^{-1}	1.07	6	-2	0.76×10^{-1}	2.23				

6	-1	0.71×10^{-2}	0.68	6	-1	0.18×10^{0}	5.27				
6	0	0.16×10^{-1}	1.54	6	0	0.52×10^{0}	15.15				
6	1	-0.32×10^{-1}	3.07	6	1	0.63×10^{-1}	1.83				
6	2	-0.13×10^{-1}	1.23	6	2	0.33×10^{-1}	0.95				
6	3	-0.58×10^{-3}	0.06	6	3	0.33×10^{-2}	0.09				
6	4	-0.81×10^{-3}	0.08	6	4	-0.89×10^{-3}	0.03				
6	5	0.23×10^{-2}	0.22	6	5	0.14×10^{-5}	0.00				
6	6	-0.77×10^{-3}	0.07	6	6	-0.17×10^{-4}	0.00				

Table S29. Values of B_{ave}, $\boldsymbol{g}$ (g_x, g_y, g_z) of the ground KD and the tunneling demagnetization time (τ_{QTM}).

Compounds	B_{ave} (mT)	g_x	g_y	g_z	τ_{QTM} (s)
3*_1.98 Å	20	3.9393×10^{-4}	4.2105×10^{-4}	11.4966	1.24×10^{-1}

REFERRENCE

1. L. F. Chibotaru, L. Ungur and A. Soncini, The Origin of Nonmagnetic Kramers Doublets in the Ground State of Dysprosium Triangles: Evidence for a Toroidal Magnetic Moment, *Angew. Chem., Int. Ed.*, 2008, **47**, 4126–4129.
2. L. Ungur, W. Van den Heuvel and L. F. Chibotaru, *Ab Initio* Investigation of the non-Collinear Magnetic Structure and the Lowest Magnetic Excitations in Dysprosium Triangles, *New J. Chem.*, 2009, **33**, 1224–1230.
3. L. F. Chibotaru, L. Ungur, C. Aronica, H. Elmoll, G. Pilet and D. Luneau, Structure, Magnetism, and Theoretical Study of a Mixed-Valence $Co^{II}_3Co^{III}_4$ Heptanuclear Wheel: Lack of SMM Behavior despite Negative Magnetic Anisotropy, *J. Am. Chem. Soc.*, 2008, **130**, 12445–12455.
4. F. Neese, *ORCA–an ab initio, Density Functional and Semiempirical Program Package*, version 5.0.3, Max-Planck institute for bioinorganic chemistry, Mülheim an der Ruhr, Germany, 2021.