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Supporting Information

An Experimental and Theoretical Investigation on Pentacoordinated Cobalt(III) Complexes with an Intermediate $S = 1$ Spin State: How Halide Ligands Affect their Magnetic Anisotropy

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Supporting Information

Table S1. Summary of X-ray crystallographic data for **CoBr** and **CoI**.

	CoBr	CoI
Empirical formula	C ₃₈ H ₃₀ CoN ₂ S ₂ Br	C ₃₈ H ₃₀ CoN ₂ S ₂ I
Formula weight	717.60	764.59
Color, habit	Dark brown, plate	Dark brown, plate
Crystal size, mm	0.62x0.26x0.01	0.27x0.22x0.01
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , Å	14.5871(8)	14.783(2)
<i>b</i> , Å	14.9087(5)	14.9433(7)
<i>c</i> , Å	15.9418(8)	16.0542(14)
α deg.	90	90
β, deg.	113.697(6)	113.108(4)
γ, deg.	90	90
<i>V</i> , Å ³	3174.6(3)	3261.9(7)
<i>Z</i>	4	4
<i>T</i> , K	150(2)	150(2)
ρ (calc), Mg/m ³	1.501	1.557
μ, mm ⁻¹	1.962	1.631
θ range, deg.	3.07 to 30.51	2.91 to 26.37
No. of rflcn/obsv	33301 / 9677 (0.1000)	27360 / 6665 (0.1822)
GooF	1.000	1.024
<i>R</i> 1	0.0604	0.0985
<i>wR</i> 2	0.0970	0.1871

Table S2. Structural properties of optimized structures of CoCl.

	CoCl (X-ray)	CoCl (gaz phase)	CoCl (relativistic)	CoCl (solvation)	CoCl (dispersion)
Co-S1	2.196	2.223	2.215	2.235	2.192
Co-S2	2.206	2.243	2.232	2.234	2.217
Co-N1	1.992	2.004	2.023	1.994	1.958
Co-N2	2.027	2.022	2.040	2.007	1.974
Co-X	2.334	2.348	2.334	2.428	2.324
Maximum dev.	-	0.038	0.031	0.094	0.053
Average dev.	-	0.019	0.018	0.037	0.022
S1-Co-S2	78.4	80.4	80.6	80.3	79.3
S1-Co-N1	92.6	90.2	91.8	91.4	90.7
S1-Co-N2	142.2	143.8	148.3	146.4	142.2
S2-Co-N1	163.7	157.8	161.4	160.4	161.9
S2-Co-N2	97.7	95.6	95.6	95.6	97.1
N1-Co-N2	81.0	80.1	81.9	81.5	81.4
S1-Co-X	118.8	120.7	117.4	117.2	120.0
S2-Co-X	104.6	109.2	106.0	106.9	105.4
N1-Co-X	91.6	92.9	92.6	92.7	92.7
N2-Co-X	98.7	94.8	94.0	95.9	97.4
Maximum dev.	-	5.9	6.2	4.2	1.9
Average dev.	-	2.7	2.3	2.1	1.0

Table S3. Structural properties of optimized structures of **CoBr**.

Calc. (solv)	CoBr (X-ray)	CoBr (gaz phase)	CoBr (relativistic)	CoBr (solvation)	CoBr (dispersion)
Co-S1	2.190	2.220	2.214	2.228	2.187
Co-S2	2.198	2.240	2.187	2.229	2.214
Co-N1	1.993	2.003	1.957	1.994	1.957
Co-N2	2.022	2.022	1.972	2.004	1.972
Co-X	2.489	2.513	2.479	2.604	2.479
Maximum dev.	-	0.042	0.050	0.115	0.050
Average dev.	-	0.021	0.026	0.041	0.023
S1-Co-S2	78.6	80.5	79.4	80.5	79.4
S1-Co-N1	93.0	91.6	91.0	91.6	91.0
S1-Co-N2	143.5	147.3	143.2	147.3	143.2
S2-Co-N1	164.7	160.7	162.3	160.7	162.3
S2-Co-N2	98.1	95.5	97.1	95.5	97.1
N1-Co-N2	80.9	81.6	81.7	81.6	81.7
S1-Co-X	118.3	117.1	120.0	117.1	120.0
S2-Co-X	103.6	106.6	105.3	106.6	105.3
N1-Co-X	92.0	92.7	92.4	92.7	92.4
N2-Co-X	97.9	95.2	96.4	95.2	96.4
Maximum dev.	-	3.8	2.4	3.8	2.4
Average dev.	-	2.2	1.3	2.2	1.3

Table S4. Structural properties of optimized structures of **Col**.

Calc. (solv)	Col (X-ray)	Col (gaz phase)	Col (relativistic)	Col (solvation)	Col (dispersion)
Co-S1	2.178	2.216	2.209	2.222	2.180
Co-S2	2.187	2.238	2.180	2.224	2.209
Co-N1	1.985	1.998	1.955	1.991	1.968
Co-N2	2.017	2.025	1.968	2.000	1.955
Co-X	2.694	2.750	2.718	2.848	2.718
Maximum dev.	-	0.051	0.049	0.154	0.062
Average dev.	-	0.033	0.028	0.052	0.025
S1-Co-S2	78.9	79.8	79.5	80.6	79.5
S1-Co-N1	93.9	90.8	91.2	91.8	91.2
S1-Co-N2	145.	142.6	144.2	148.3	144.2
S2-Co-N1	165.6	161.4	163.0	161.4	163.0
S2-Co-N2	98.2	96.9	97.2	95.6	97.2
N1-Co-N2	80.6	80.8	81.9	81.9	81.9
S1-Co-X	118.4	123.2	119.3	117.4	119.3
S2-Co-X	101.9	106.9	104.2	106.0	104.2
N1-Co-X	92.5	91.7	92.7	92.6	92.7
N2-Co-X	95.7	93.6	96.2	94.0	96.2
Maximum dev.	-	4.8	2.7	4.2	2.7
Average dev.	-	2.5	1.3	2.2	1.3

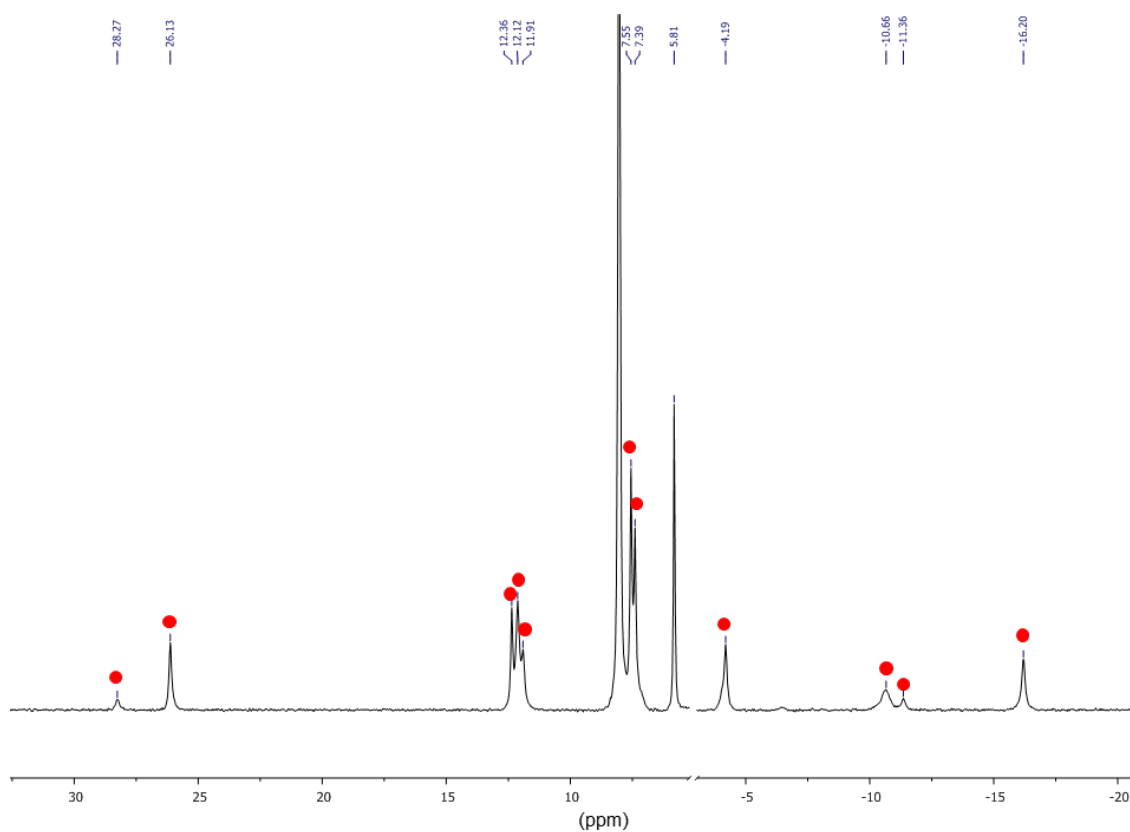


Figure S1. ^1H NMR spectrum of a d_7 -DMF solution of **CoBr** (protons belonging to **CoBr** are evidenced by a ■).

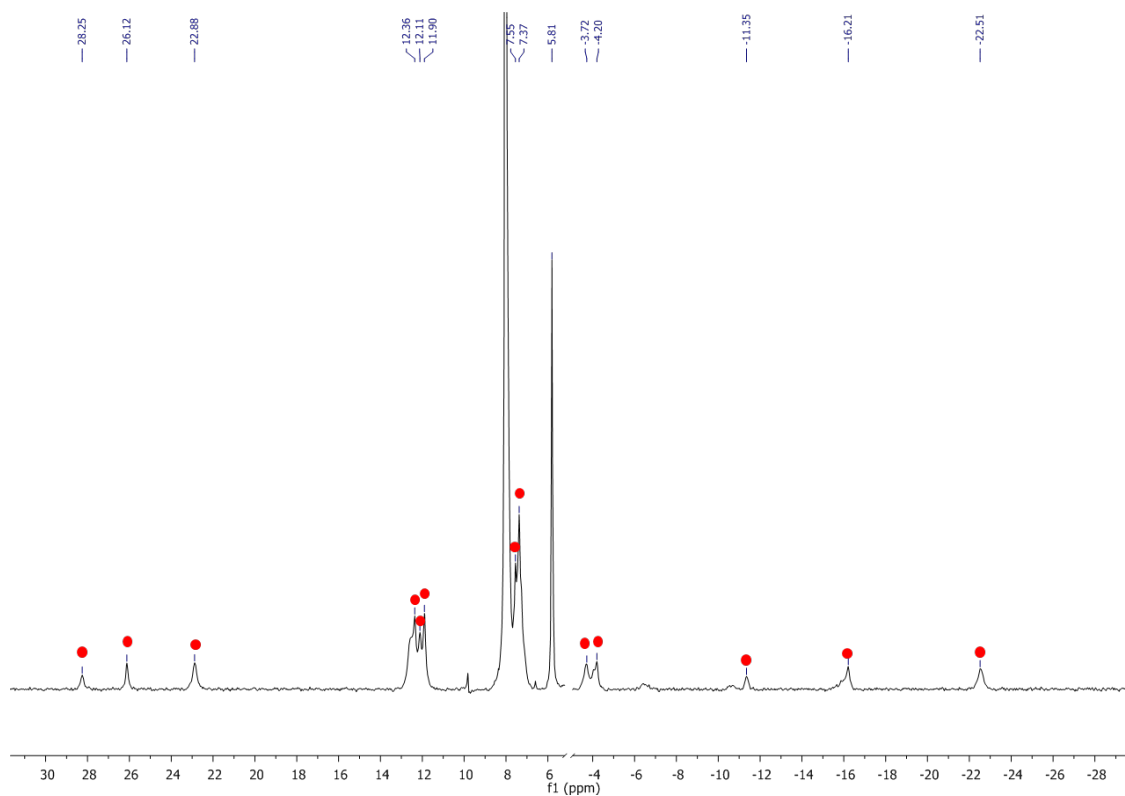


Figure S2. ^1H NMR spectrum of a d_7 -DMF solution of **CoI** (protons belonging to **CoI** are evidenced by a ■).

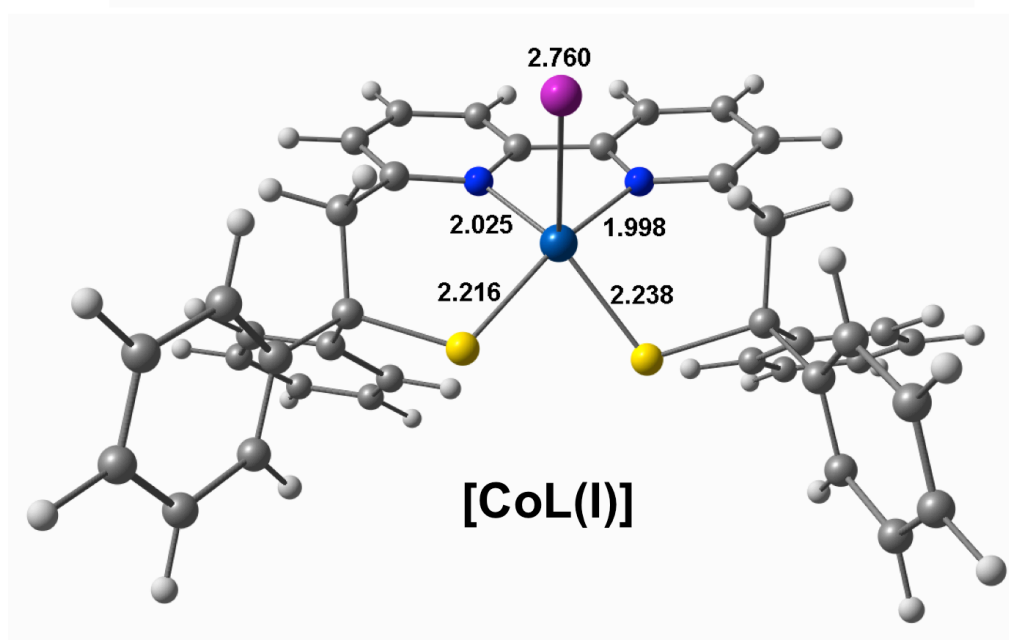
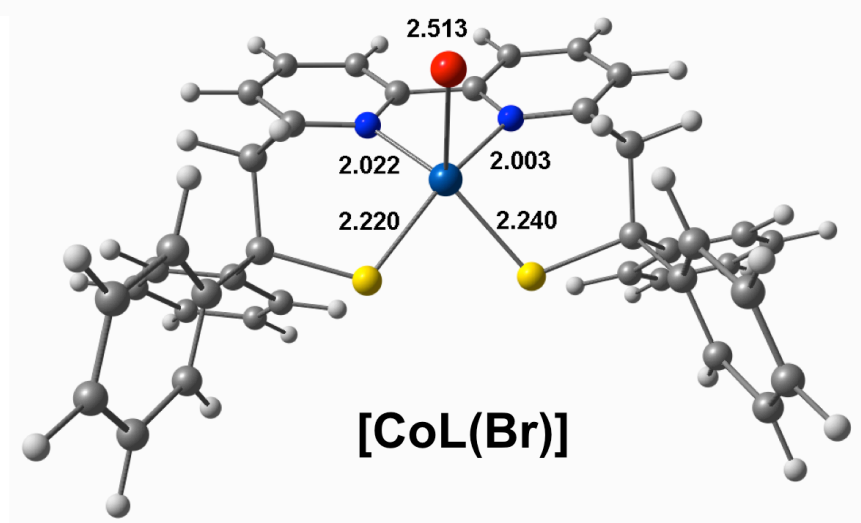
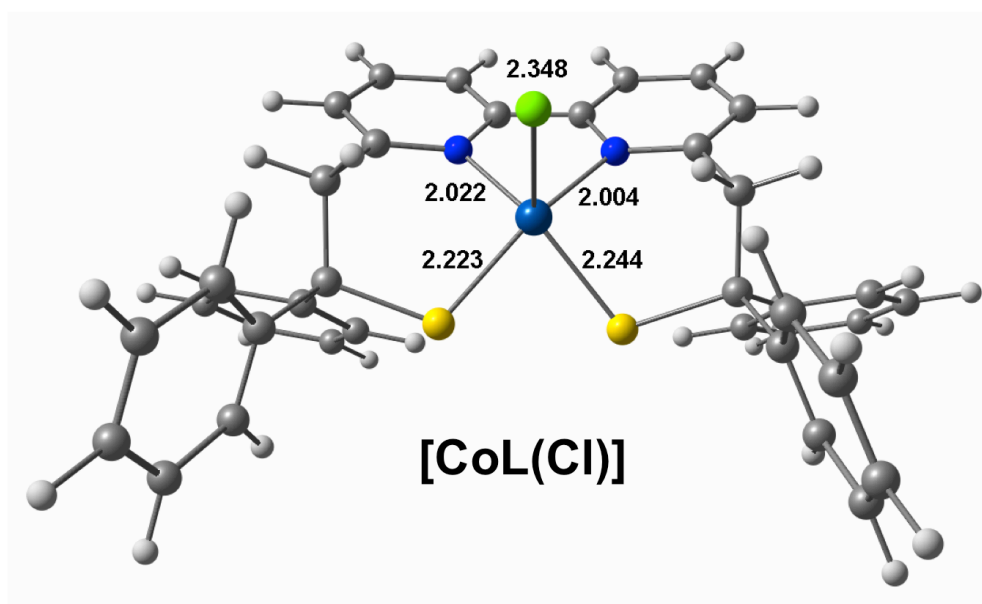


Figure S3. Optimized structures of **CoX** (X = Cl, Br, I).

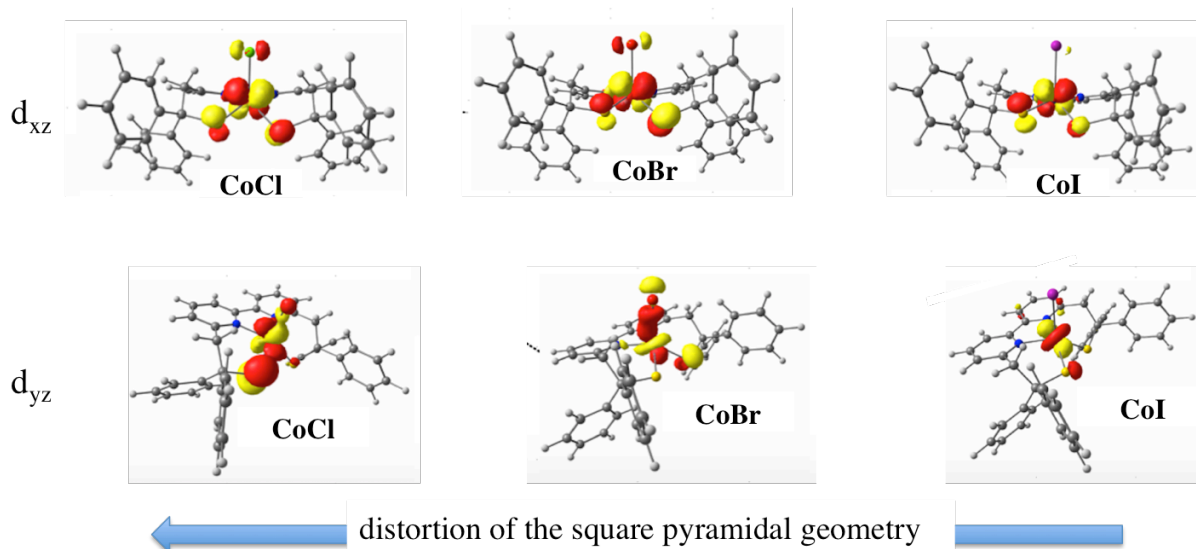


Figure S4. Representation of the two DOMOs of **CoX** with X = Cl, Br and I.

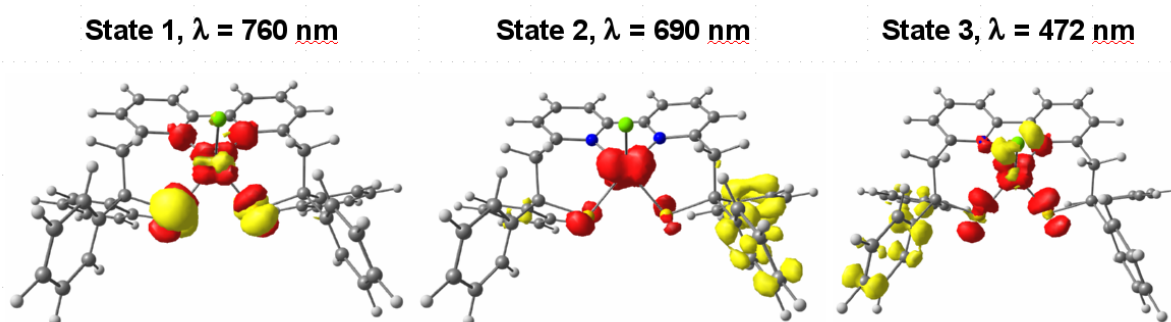


Figure S5. Difference electron density sketches of TD-DFT calculated transitions for **CoCl**.

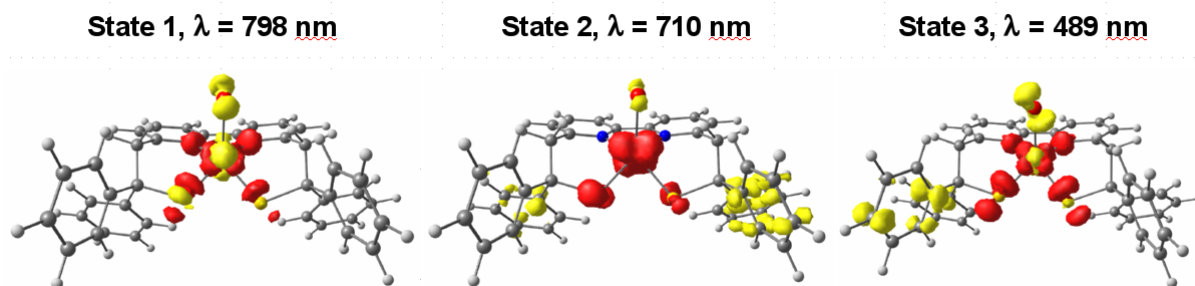


Figure S6. Difference electron density sketches of TD-DFT calculated transitions for **CoBr**.

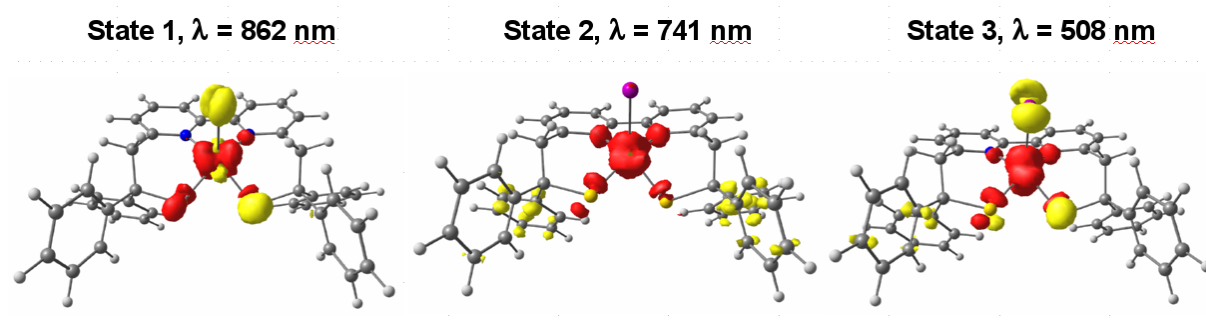


Figure S7. Difference electron density sketches of TD-DFT calculated transitions for **Col.**