CHEMISTRY
A European Journal

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	$C_{38}H_{30}CoN_2S_2Br$	$C_{38}H_{30}CoN_2S_2I$
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	*P* $2_1/c$	*P* $2_1/c$
a, Å	14.5871(8)	14.783(2)
b, Å	14.9087(5)	14.9433(7)
c, Å	15.9418(8)	16.0542(14)
α deg.	90	90
β, deg.	113.697(6)	113.108(4)
γ, deg.	90	90
V, Å^3	3174.6(3)	3261.9(7)
Z	4	4
T, 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 (R_{int})	33301 / 9677 (0.1000)	27360 / 6665 (0.1822)
GooF	1.000	1.024
*R*1	0.0604	0.0985
*wR*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 **CoI.**

Calc. (solv)	CoI (X-ray)	CoI (gaz phase)	CoI (relativistic)	CoI (solvation)	CoI (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**

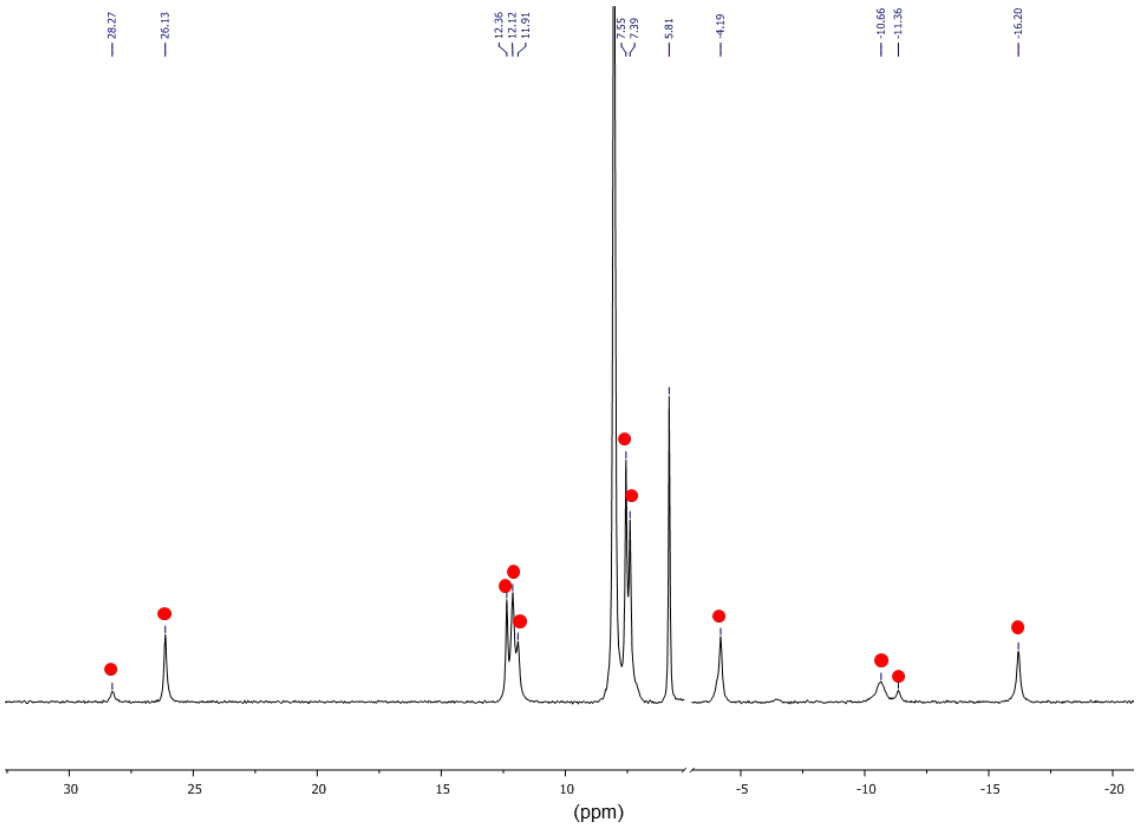

Figure S1. ^{1}H NMR spectrum of a d_7-DMF solution of **CoBr** (protons belonging to **CoBr** are evidenced by a ■).

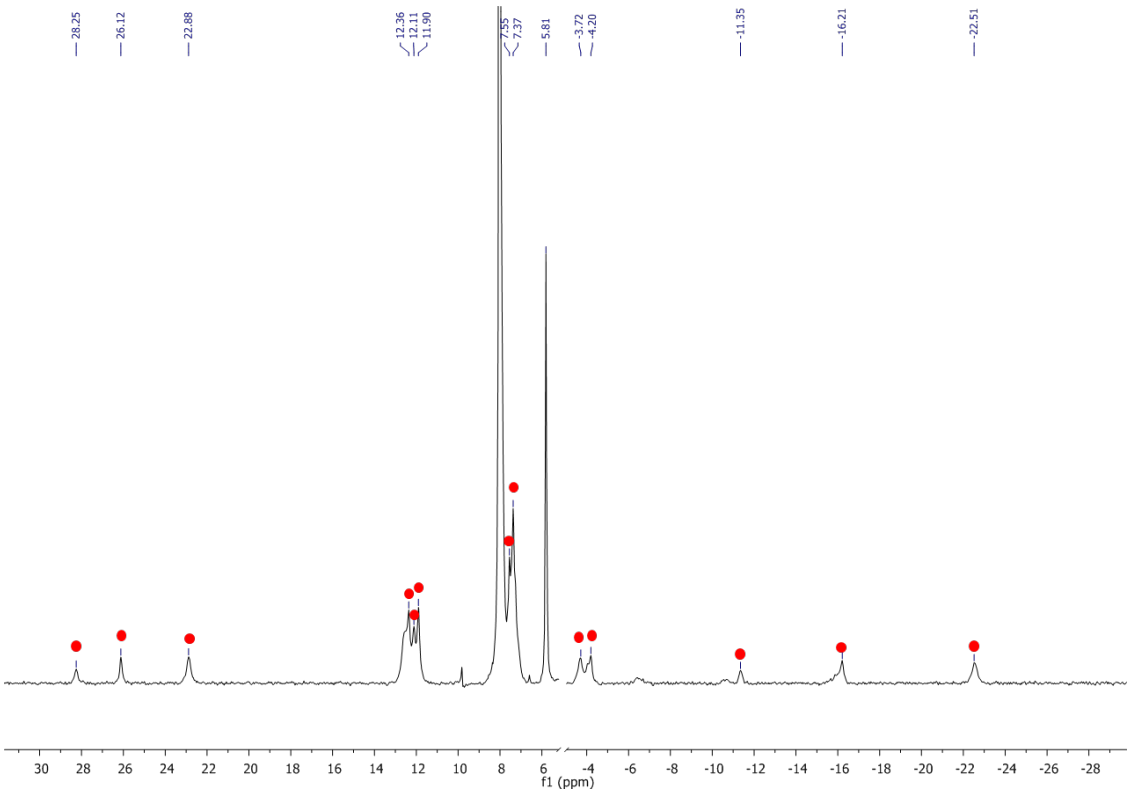

Figure S2. ^{1}H NMR spectrum of a d_7-DMF solution of **CoI** (protons belonging to **CoI** are evidenced by a ■).

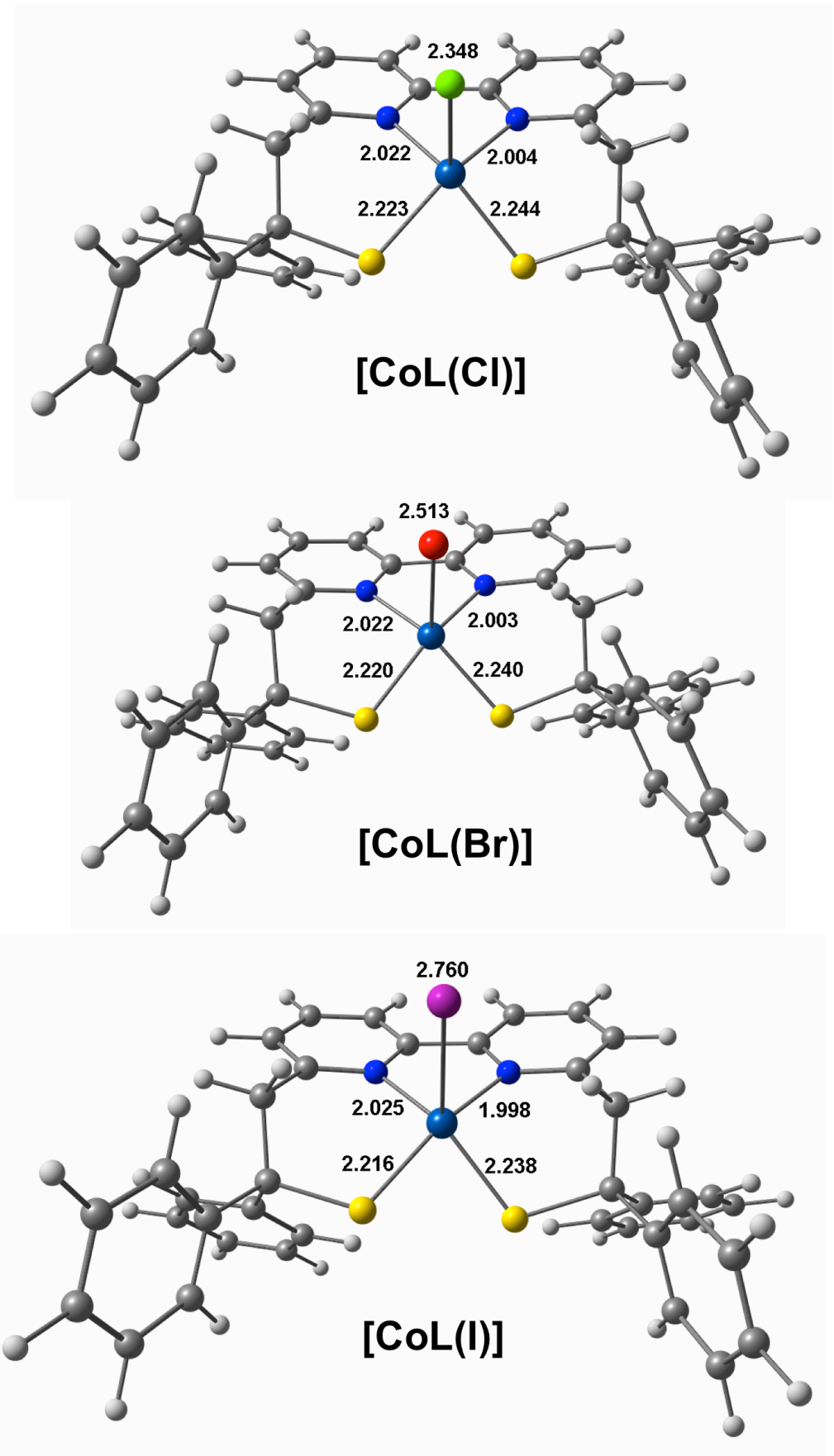

Figure S3. Optimized structures of **CoX** (X = Cl, Br, I).

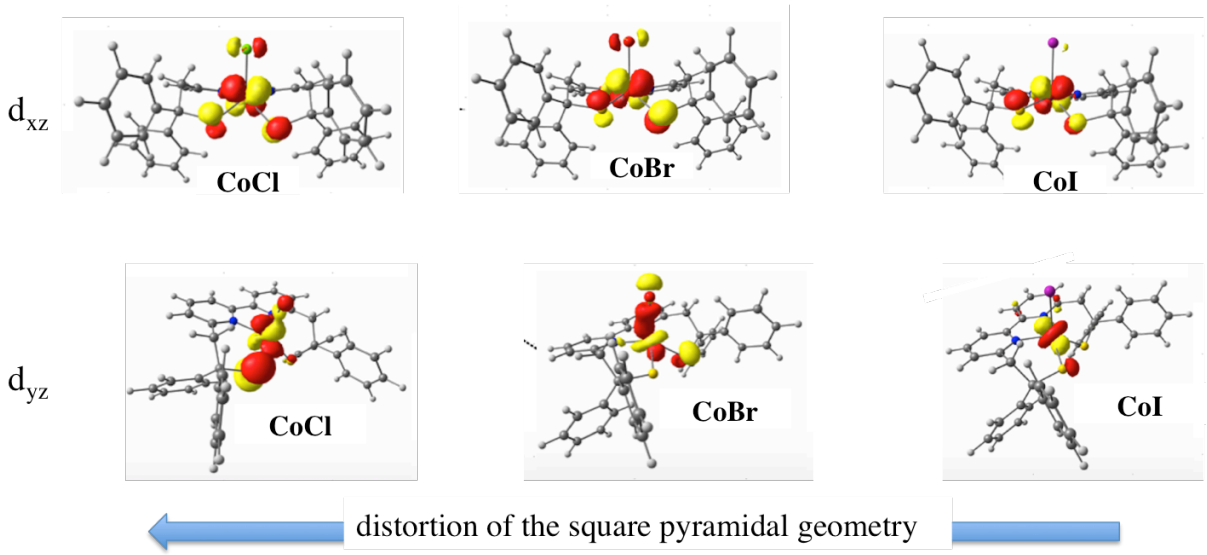

Figure S4. Representation of the two DOMOs of **CoX** with X = Cl, Br and I.

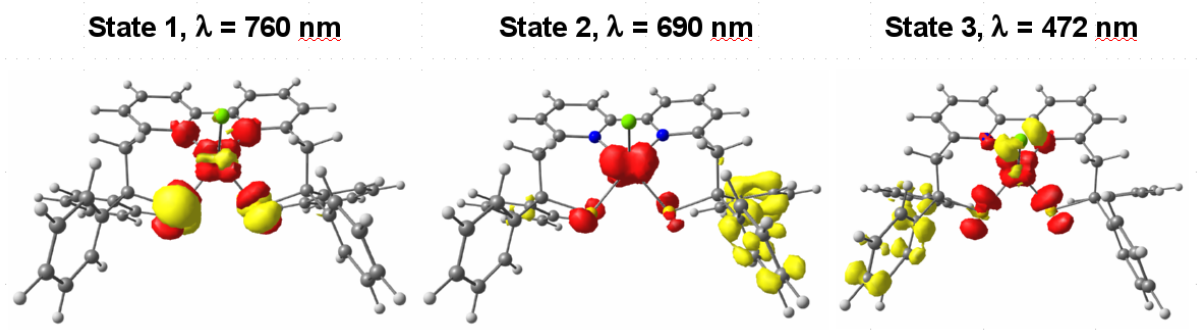

Figure S5. Difference electron density sketches of TD-DFT calculated transitions for **CoCl**.

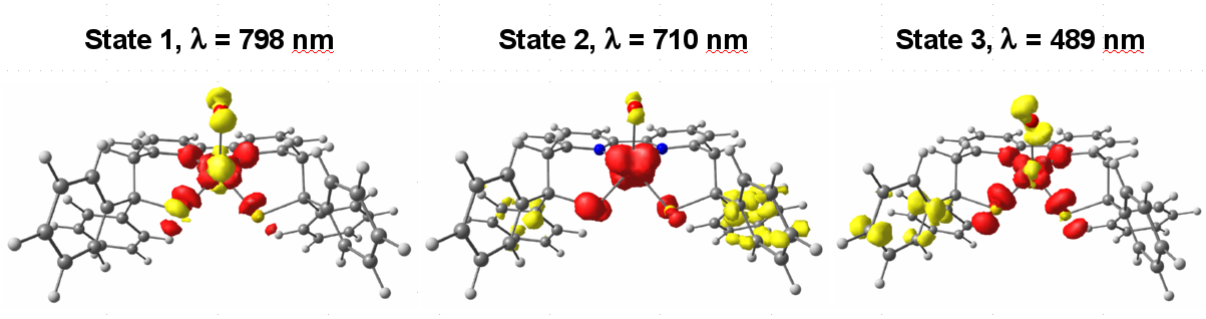

Figure S6. Difference electron density sketches of TD-DFT calculated transitions for **CoBr.**

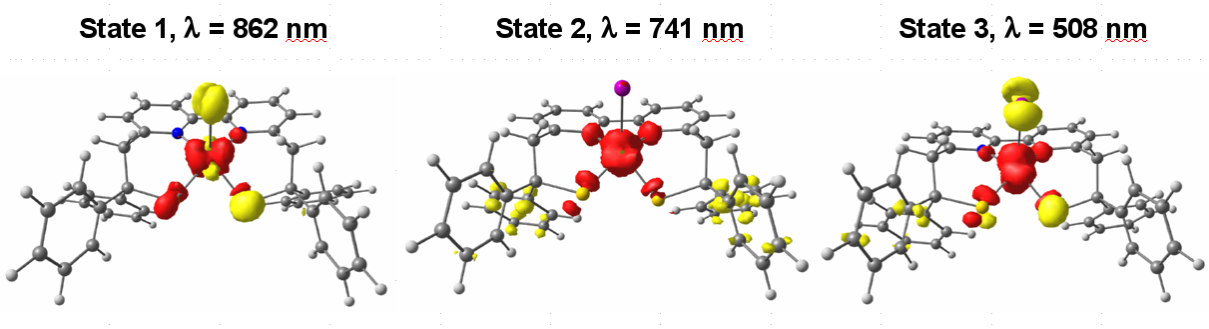

Figure S7. Difference electron density sketches of TD-DFT calculated transitions for **CoI.**