Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information for: "Towards accurate estimates of the spin-state energetics of spin-crossover complexes within density functional theory: a comparative case study of cobalt(II) complexes"

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Table 1 gives the calculated values of the PJT stabilization energy E_{PJT} defined as the electronic energy difference: $E_{\mathrm{PJT}} = E^{\mathrm{el}}(^2\mathrm{B}_2) - E^{\mathrm{el}}(^2\mathrm{A}_1)$. Nearly identical E_{PJT} values are obtained with the $\mathscr{S}_{\mathrm{fc}}$ and $\mathscr{G}$ basis sets used in combination with any of the OLYP, OPBE and PBE functionals. The two basis sets are consequently of similar quality and the results obtained with both of them can be compared in a straightforward manner. Proceeding so, the analysis of the results of Table 1 shows that the different XC functionals tend to perform very similarly for the calculation of E_{PJT}. All functionals indeed consistently predict that E_{PJT} is small, with calculated values in the quite narrow 140∼240 cm^{-1} range. The standard deviation over the calculated E_{PJT} values is $\sigma \approx 35$ cm^{-1}. Using an uncertainty of 2σ so as to reflect at best the small though noticeable spread of *ca.* 100 cm^{-1} of the calculated values, a reliable estimate of the PJT stabilization energy is $E_{\mathrm{PJT}} = 205(70)$ cm^{-1}.

Table 1 Calculated values of the pseudo-Jahn-Teller stabilization energy E_{PJT} (in cm^{-1}).

	E_{PJT}
B3LYP/$\mathscr{G}$	137
B3LYP*/$\mathscr{G}$	174
HCTH407/$\mathscr{G}$	206
OLYP/$\mathscr{G}$	213
OLYP/$\mathscr{S}_{\mathrm{fc}}$	232
OPBE/$\mathscr{S}_{\mathrm{fc}}$	213
OPBE/$\mathscr{G}$	210
RPBE/$\mathscr{S}_{\mathrm{fc}}$	218
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2 The tetragonal splitting of the HS state in $[Co(tpy)_2]^{2+}$

Table 2 gives the calculated values of the tetragonal splitting of the HS state Δ_{HS} defined by the electronic energy difference: $\Delta_{\mathrm{HS}} = E^{\mathrm{el}}(^4\mathrm{E}) - E^{\mathrm{el}}(^4\mathrm{A}_2)$.

Table 2 Calculated values of the tetragonal splitting of the HS state, Δ_{HS}, in cm^{-1}.

OLYP/$\mathscr{S}_{\mathrm{fc}}$	OPBE/$\mathscr{S}_{\mathrm{fc}}$	RPBE/$\mathscr{S}_{\mathrm{fc}}$	BLYP/$\mathscr{S}_{\mathrm{fc}}$	PBE/$\mathscr{S}_{\mathrm{fc}}$
+423	+565	+702	+456	+557

These values are all positive, *i.e.*, the $^4\mathrm{A}_2$ state is predicted to be the most stable tetragonal component of the HS state, whatever the XC functional used. Furthermore, these values are quite consistent with one another. The standard deviation over these values of $\approx$110 cm^{-1} falls within the chemical accuracy of 350 cm^{-1}. This allows us to propose for Δ_{HS} a reliable estimate of $\Delta_{\mathrm{HS}} = +540(110)\ \mathrm{cm}^{-1}$.

3 Optimized geometries of $[Co(tpy)_2]^{2+}$ in the LS and in the HS state

Table 3 Bond lengths (Å) and angles (deg) in the optimized LS $^2B_2$ $[Co(tpy)_2]^{2+}$ geometries of D_{2d} symmetry. The reported parameter values are averages over the ADF and G03 calculated structures, with standard deviations given in parentheses. Experimental values are also given for comparison purposes.

	Exp.†	ADF	G03
Co-N, Co-N$''$	2.083	2.116(8)	2.115(22)
Co-N$'$	1.912	1.892(8)	1.895(19)
N-C_2, N$''$-C''_2	1.354	1.361(6)	1.357(4)
N-C_6, N$''$-C''_6	1.349	1.344(5)	1.339(4)
C_2-C_3, C''_2-C''_3	1.376	1.400(4)	1.396(3)
C_3-C_4, C''_3-C''_4	1.378	1.394(4)	1.391(3)
C_4-C_5, C''_4-C''_5	1.384	1.395(4)	1.391(3)
C_5-C_6, C''_5-C''_6	1.384	1.395(4)	1.391(3)
C_2-C'_2, C'_6-C''_2	1.480	1.473(5)	1.472(5)
N$'$-C'_2, N$'$-C'_6	1.350	1.363(6)	1.357(6)
C'_2-C'_3, C'_5-C'_6	1.382	1.399(4)	1.396(3)
C'_3-C'_4, C'_4-C'_5	1.379	1.394(4)	1.391(3)
$\alpha = \angle(C'_6\text{-}C''_2, C_2\text{-}C'_2)$	106.5	107.5(2)	107.5(6)
$\beta = \angle(\text{N}'\text{-Co-N}) = \angle(\text{N}''\text{-Co-N}')$	79.4	80.1(1)	80.0(3)
$\beta' = \angle(\text{N}''\text{-Co-N})$ ‡	158.9	160.2(2)	160.0(6)
$\gamma = \angle(\text{N}'\text{-}C'_2\text{-}C_2\text{-N}) = \angle(\text{N}''\text{-}C''_2\text{-}C'_6\text{-N}')$ ‡	1.2	0.0	0.0
η = d(Co-N$'$/Co-N$''$)	0.918	0.894(1)	0.896(4)

†Data are for the $[Co(tpy)_2]^{2+}$ geometry of approximate D_{2d} symmetry found in the 120 K X-ray structure of LS $[Co(tpy)_2]I_2 \cdot 2H_2O$.[?]
‡The D_{2d} symmetry constraint imposes that $\beta' = 2\beta$ and $\gamma = 0$.

Table 4 Bond lengths (Å) and angles (deg) in the optimized LS $^2A_1$ $[Co(tpy)_2]^{2+}$ geometries of C_{2v} symmetry, and variations of these structural parameters on going from the LS D_{2d} to the LS C_{2v} geometries. The reported values are averages over the ADF and G03 calculated structures, with standard deviations given in parentheses.

	ADF		G03	
	L_1	L_2	L_1	L_2
Values of the selected structural parameters in the optimized LS geometries of C_{2v} symmetry				
Co-N, Co-N$''$	2.009(11)	2.222(10)	2.012(23)	2.214(22)
Co-N$'$	1.867(9)	1.961(8)	1.872(19)	1.952(16)
N-C_2, N$''$-C''_2	1.370(6)	1.355(6)	1.365(5)	1.351(4)
N-C_6, N$''$-C''_6	1.348(5)	1.342(5)	1.341(4)	1.337(4)
C_2-C_3, C''_2-C''_3	1.398(4)	1.402(4)	1.394(3)	1.399(3)
C_3-C_4, C''_3-C''_4	1.394(4)	1.394(5)	1.391(3)	1.391(3)
C_4-C_5, C''_4-C''_5	1.395(4)	1.395(4)	1.391(3)	1.391(3)
C_5-C_6, C''_5-C''_6	1.394(4)	1.396(4)	1.391(3)	1.392(3)
C_2-C'_2, C'_6-C''_2	1.465(5)	1.480(6)	1.466(6)	1.480(4)
N$'$-C'_2, N$'$-C'_6	1.361(5)	1.363(6)	1.355(6)	1.357(4)
C'_2-C'_3, C'_5-C'_6	1.398(4)	1.400(4)	1.395(3)	1.397(3)
C'_3-C'_4, C'_4-C'_5	1.396(5)	1.392(5)	1.393(3)	1.389(3)
$\alpha = \angle(C'_6\text{-}C''_2, C_2\text{-}C'_2)$	103.5(3)	110.9(2)	103.6(6)	110.7(6)
$\beta = \angle(\text{N}'\text{-Co-N}) = \angle(\text{N}''\text{-Co-N}')$	81.3(1)	78.0(1)	81.2(3)	78.3(3)
$\beta' = \angle(\text{N}''\text{-Co-N})$ †	162.5(2)	155.9(2)	162.5(6)	156.5(6)
$\gamma = \angle(\text{N}'\text{-}C'_2\text{-}C_2\text{-N}) = \angle(\text{N}''\text{-}C''_2\text{-}C'_6\text{-N}')$ †	0.0	0.0	0.0	0.0
Structural changes upon the $D_{2d} \to C_{2v}$ symmetry lowering				
Co-N, Co-N$''$	−0.107(6)	+0.105(5)	−0.104(3)	+0.098(3)
Co-N$'$	−0.025(2)	+0.068(3)	−0.024(1)	+0.057(4)
N-C_2, N$''$-C''_2	+0.009(1)	−0.006(1)	+0.008(1)	−0.006(1)
N-C_6, N$''$-C''_6	+0.004(1)	−0.002(1)	+0.003(1)	−0.002(1)
C_2-C_3, C''_2-C''_3	−0.002(1)	+0.002(1)	−0.002(1)	+0.002(1)
C_3-C_4, C''_3-C''_4	−0.001(1)	0.000(1)	0.000(1)	0.000(1)
C_4-C_5, C''_4-C''_5	+0.000(1)	−0.001(1)	0.000(1)	0.000(1)
C_5-C_6, C''_5-C''_6	−0.001(1)	+0.001(1)	−0.001(1)	+0.000(1)
C_2-C'_2, C'_6-C''_2	−0.008(1)	+0.007(1)	−0.006(1)	+0.008(1)
N$'$-C'_2, N$'$-C'_6	−0.002(1)	−0.001(1)	−0.003(1)	+0.000(1)
C'_2-C'_3, C'_5-C'_6	−0.001(1)	+0.001(1)	−0.001(1)	+0.001(1)
C'_3-C'_4, C'_4-C'_5	+0.002(1)	−0.002(1)	+0.002(1)	−0.002(1)
$\alpha = \angle(C'_6\text{-}C''_2, C_2\text{-}C'_2)$	−4.0(2)	+3.4(1)	−3.9(1)	+3.2(1)
$\beta = \angle(\text{N}'\text{-Co-N}) = \angle(\text{N}''\text{-Co-N}')$	+1.2(1)	−2.1(1)	+1.2(1)	−1.8(1)
$\beta' = \angle(\text{N}''\text{-Co-N})$ †	+2.3(2)	−4.2(2)	+2.5(2)	−3.5(2)
$\gamma = \angle(\text{N}'\text{-}C'_2\text{-}C_2\text{-N}) = \angle(\text{N}''\text{-}C''_2\text{-}C'_6\text{-N}')$ †	0.0	0.0	0.0	0.0

†The C_{2v} symmetry constraint imposes that $\beta' = 2\beta$ and $\gamma = 0$.

Table 5 Bond lengths (Å) and angles (deg) in the optimized HS $^4A_2$ and ^4E $[Co(tpy)_2]^{2+}$ geometries of D_{2d} symmetry, and associated HS-LS differences. The reported values are averages over the ADF and G03 calculated structures, with standard deviations given in parentheses. Experimental values are also given.

	Exp. †	$^4A_2$		^4E
		ADF	G03	ADF
Values of the selected structural parameters				
Co-N, Co-N$''$	2.137	2.179(11)	2.185(16)	2.182(10)
Co-N$'$	2.028	2.054(10)	2.053(19)	2.062(9)
N-C_2, N$''$-C''_2	1.361	1.361(6)	1.356(4)	1.358(6)
N-C_6, N$''$-C''_6	1.331	1.355(23)	1.339(4)	1.344(5)
C_2-C_3, C''_2-C''_3	1.383	1.401(4)	1.397(3)	1.400(4)
C_3-C_4, C''_3-C''_4	1.380	1.394(4)	1.391(3)	1.395(4)
C_4-C_5, C''_4-C''_5	1.372	1.395(5)	1.392(3)	1.395(4)
C_5-C_6, C''_5-C''_6	1.380	1.394(4)	1.390(3)	1.395(4)
C_2-C'_2, C'_6-C''_2	1.469	1.483(6)	1.483(3)	1.483(6)
N$'$-C'_2, N$'$-C'_6	1.346	1.352(5)	1.347(5)	1.354(6)
C'_2-C'_3, C'_5-C'_6	1.386	1.401(4)	1.398(3)	1.400(4)
C'_3-C'_4, C'_4-C'_5	1.372	1.394(5)	1.391(3)	1.394(4)
$\alpha = \angle(C'_6\text{-}C''_2, C_2\text{-}C'_2)$	107.5	107.9(3)	107.9(1)	108.0(1)
$\beta = \angle(\text{N}'\text{-Co-N}) = \angle(\text{N}''\text{-Co-N}')$	76.8	76.5(1)	76.6(3)	76.2(1)
$\beta' = \angle(\text{N}''\text{-Co-N})$ ‡	153.6	153.1(2)	153.2(6)	152.4(2)
$\gamma = \angle(\text{N}'\text{-}C'_2\text{-}C_2\text{-N}) = \angle(\text{N}''\text{-}C''_2\text{-}C'_6\text{-N}')$ ‡	2.7	0.0	0.0	0.0
η = d(Co-N$'$)/d(Co-N)	0.949	0.941(2)	0.940(6)	0.945(2)
Variations of the parameters on going from the LS D_{2d} to the HS D_{2d} geometries				
Co-N, Co-N$''$	+0.053	+0.066(4)	+0.066(12)	+0.069(12)
Co-N$'$	+0.116	+0.161(3)	+0.169(3)	+0.157(3)
N-C_2, N$''$-C''_2	+0.007	0.000(1)	−0.002(1)	0.000(1)
N-C_6, N$''$-C''_6	−0.019	+0.001(1)	0.000(1)	+0.001(1)
C_2-C_3, C''_2-C''_3	+0.007	0.000(1)	0.000(1)	+0.001(1)
C_3-C_4, C''_3-C''_4	+0.002	0.000(1)	0.000(1)	0.000(1)
C_4-C_5, C''_4-C''_5	−0.013	0.000(1)	−0.001(1)	0.000(1)
C_5-C_6, C''_5-C''_6	−0.004	−0.001(1)	0.000(1)	−0.001(1)
C_2-C'_2, C'_6-C''_2	−0.011	+0.010(1)	0.010(1)	+0.011(1)
N$'$-C'_2, N$'$-C'_6	−0.004	-0.012(1)	−0.010(1)	−0.011(1)
C'_2-C'_3, C'_5-C'_6	+0.003	+0.002(1)	+0.001(1)	+0.002(1)
C'_3-C'_4, C'_4-C'_5	−0.007	+0.001(1)	+0.001(1)	+0.001(1)
$\alpha = \angle(C'_6\text{-}C''_2, C_2\text{-}C'_2)$	+1.0	+0.3(1)	+0.5(4)	+0.4(4)
$\beta = \angle(\text{N}'\text{-Co-N}) = \angle(\text{N}''\text{-Co-N}')$ ‡	−2.7	−3.5(1)	−3.9(1)	−3.4(1)
$\beta' = \angle(\text{N}''\text{-Co-N})$ ‡	−5.4	−7.0(2)	−7.8(2)	−6.8(2)
$\gamma = \angle(\text{N}'\text{-}C'_2\text{-}C_2\text{-N}) = \angle(\text{N}''\text{-}C''_2\text{-}C'_6\text{-N}')$ ‡	+1.5	0.0	0.0	0.0
η = d(Co-N$'$)/d(Co-N)	+0.031	+0.047(1)	+0.051(4)	+0.044(4)

†Data are for the geometry of approximate D_{2d} symmetry found in the 295 K X-ray structure of HS $[Co(tpy)_2](ClO_4)_2 \cdot 1.3H_2O$.[?]
‡The D_{2d} symmetry constraint imposes that $\beta' = 2\beta$ and $\gamma = 0$.

Table 6 Bond lengths (Å) and angles (deg) in the optimized HS $^4A_2$ and $^4B_1$ $[Co(tpy)_2]^{2+}$ geometries of C_{2v} symmetry, and their variations upon the D_{2d} to C_{2v} symmetry lowering in the HS states. The reported values are averages over the ADF calculated structures, with standard deviations given in parentheses.

	$^4A_2$, in C_{2v}		$^4B_1$, in C_{2v}	
	L_1	L_2	L_1	L_2
Values of the selected structural parameters				
Co-N, Co-N$''$	2.174(19)	2.197(20)	2.170(21)	2.198(22)
Co-N$'$	2.047(17)	2.068(16)	2.098(15)	2.064(13)
$N-C_2$, $N''-C''_2$	1.361(7)	1.360(6)	1.358(4)	1.359(6)
$N-C_6$, $N''-C''_6$	1.345(5)	1.344(5)	1.345(3)	1.343(5)
C_2-C_3, $C''_2-C''_3$	1.400(4)	1.401(4)	1.400(4)	1.400(4)
C_3-C_4, $C''_3-C''_4$	1.394(4)	1.394(4)	1.394(4)	1.395(4)
C_4-C_5, $C''_4-C''_5$	1.395(4)	1.395(4)	1.395(4)	1.394(4)
C_5-C_6, $C''_5-C''_6$	1.394(4)	1.394(4)	1.394(5)	1.396(4)
$C_2-C'_2$, $C'_6-C''_2$	1.484(5)	1.484(6)	1.478(5)	1.487(5)
$N'-C'_2$, $N'-C'_6$	1.351(5)	1.352(5)	1.353(5)	1.353(7)
$C'_2-C'_3$, $C'_5-C'_6$	1.401(4)	1.401(4)	1.401(4)	1.400(4)
$C'_3-C'_4$, $C'_4-C'_5$	1.395(4)	1.394(5)	1.394(4)	1.395(4)
$\alpha = \angle(C'_6-C''_2, C_2-C'_2)$	107.5(5)	108.2(4)	107.6(5)	108.2(6)
$\beta = \angle(N'-Co-N) = \angle(N''-Co-N')$	76.8(3)	76.2(2)	74.9(2)	76.5(3)
$\beta' = \angle(N''-Co-N)$ †	153.6(6)	152.4(4)	149.8(4)	153.0(6)
$\gamma = \angle(N'-C'_2-C_2-N) = \angle(N''-C''_2-C'_6-N')$ †	0.0	0.0	0.0	0.0
Variations associated with the $D_{2d} \to C_{2v}$ symmetry lowering: $^4A_2 \to {}^4A_2$ and $^4E \to {}^4B_1 \oplus {}^4B_2$				
Co-N, Co-N$''$	−0.008(11)	+0.015(11)	−0.012(12)	+0.016
Co-N$'$	−0.006(8)	+0.015(6)	+0.037(7)	+0.003
$N-C_2$, $N''-C''_2$	0.000(2)	−0.001(3)	0.000(1)	0.000(2)
$N-C_6$, $N''-C''_6$	0.000(1)	0.000(1)	+0.001(1)	−0.001(1)
C_2-C_3, $C''_2-C''_3$	−0.001(1)	0.000(1)	0.000(1)	0.000(1)
C_3-C_4, $C''_3-C''_4$	0.001(1)	0.000(1)	−0.001(1)	+0.001(1)
C_4-C_5, $C''_4-C''_5$	0.000(1)	0.000(1)	0.000(1)	−0.001(1)
C_5-C_6, $C''_5-C''_6$	0.000(1)	0.000(1)	−0.001(1)	+0.001(1)
$C_2-C'_2$, $C'_6-C''_2$	+0.001(1)	+0.001(1)	−0.005(1)	+0.004(1)
$N'-C'_2$, $N'-C'_6$	−0.001(1)	0.000(1)	−0.001(2)	−0.001(1)
$C'_2-C'_3$, $C'_5-C'_6$	0.000(1)	0.000(1)	+0.001(1)	0.000(1)
$C'_3-C'_4$, $C'_4-C'_5$	0.000(1)	0.000(1)	−0.001(1)	0.000(1)
$\alpha = \angle(C'_6-C''_2, C_2-C'_2)$	−0.2(4)	+0.4(3)	−0.4(4)	+0.2(5)
$\beta = \angle(N'-Co-N) = \angle(N''-Co-N')$	+0.2(2)	−0.4(2)	−1.3(2)	+0.3(3)
$\beta' = \angle(N''-Co-N)$ †	+0.4(4)	−0.8(4)	−2.6(4)	+0.6(6)
$\gamma = \angle(N'-C'_2-C_2-N) = \angle(N''-C''_2-C'_6-N')$ †	0.0	0.0	0.0	0.0

†The C_{2v} symmetry constraint imposes that $\beta' = 2\beta$ and $\gamma = 0$.

Table 7 BLYP/$\mathscr{S}_{fc}$−optimized LS and HS $[Co(tpy)_2]^{2+}$ geometries of D_{2d} symmetry: selected bond lengths (Å) and angles (deg) and their variations upon the LS → HS change of states.

	LS	HS		LS → HS	
	$^2B_2$	$^4A_2$	^4E	$^2B_2 \rightarrow {}^4A_2$	$^2B_2 \rightarrow {}^4E$
	L_1, L_2	L_1, L_2	L_1, L_2	L_1, L_2	L_1, L_2
Co-N, Co-N″	2.124	2.189	2.191	0.065	0.067
Co-N′	1.902	2.063	2.071	0.161	0.169
N-C_2, N''-C''_2	1.367	1.367	1.364	0.000	-0.003
N-C_6, N''-C''_6	1.348	1.349	1.348	0.001	0.000
C_2-C_3, C''_2-C''_3	1.403	1.403	1.403	0.000	0.000
C_3-C_4, C''_3-C''_4	1.398	1.397	1.398	-0.001	0.000
C_4-C_5, C''_4-C''_5	1.399	1.399	1.398	0.000	-0.001
C_5-C_6, C''_5-C''_6	1.398	1.397	1.398	-0.001	0.000
C_2-C'_2, C'_6-C''_2	1.478	1.488	1.488	0.010	0.010
N'-C'_2, N'-C'_6	1.369	1.356	1.359	-0.013	-0.010
C'_2-C'_3, C'_5-C'_6	1.402	1.404	1.403	0.002	0.001
C'_3-C'_4, C'_4-C'_5	1.397	1.398	1.398	0.001	0.001
$\alpha = \angle(C'_6\text{-}C''_2, C_2\text{-}C'_2)$	107.4	107.6	107.9	0.2	0.5
$\beta = \angle(N'\text{-Co-}N) = \angle(N''\text{-Co-}N')$	80.1	76.6	76.2	-3.5	-3.9
$\beta' = \angle(N''\text{-Co-}N)$ ‡	160.2	153.3	152.4	-6.9	-7.8
$\gamma = \angle(N'\text{-}C'_2\text{-}C_2\text{-}N) = \angle(N''\text{-}C''_2\text{-}C'_6\text{-}N')$ ‡	0.0	0.0	0.0	0.0	0.0
η = d(Co-N′/Co-N″)	0.895	0.942	0.945	0.047	0.050

‡The D_{2d} symmetry constraint imposes that $\beta' = 2\beta$ and $\gamma = 0$.

Table 8 OLYP/$\mathscr{S}_{fc}$−optimized LS and HS $[Co(tpy)_2]^{2+}$ geometries of D_{2d} symmetry: selected bond lengths (Å) and angles (deg) and their variations upon the LS → HS change of states.

	LS	HS		LS → HS	
	$^2B_2$	$^4A_2$	^4E	$^2B_2 \rightarrow {}^4A_2$	$^2B_2 \rightarrow {}^4E$
	L_1, L_2	L_1, L_2	L_1, L_2	L_1, L_2	L_1, L_2
Co-N, Co-N″	2.118	2.188	2.188	0.070	0.070
Co-N′	1.891	2.057	2.060	0.166	0.169
N-C_2, N''-C''_2	1.357	1.357	1.356	0.000	-0.001
N-C_6, N''-C''_6	1.341	1.341	1.341	0.000	0.000
C_2-C_3, C''_2-C''_3	1.399	1.399	1.399	0.000	0.000
C_3-C_4, C''_3-C''_4	1.392	1.392	1.392	0.000	0.000
C_4-C_5, C''_4-C''_5	1.393	1.393	1.392	0.000	-0.001
C_5-C_6, C''_5-C''_6	1.392	1.391	1.392	-0.001	0.000
C_2-C'_2, C'_6-C''_2	1.473	1.484	1.484	0.011	0.011
N'-C'_2, N'-C'_6	1.361	1.349	1.351	-0.012	-0.010
C'_2-C'_3, C'_5-C'_6	1.397	1.399	1.399	0.002	0.002
C'_3-C'_4, C'_4-C'_5	1.391	1.392	1.392	0.001	0.001
$\alpha = \angle(C'_6\text{-}C''_2, C_2\text{-}C'_2)$	107.7	108.0	108.2	0.3	0.5
$\beta = \angle(N'\text{-Co-}N) = \angle(N''\text{-Co-}N')$	80.1	76.5	76.3	-3.6	-3.8
$\beta' = \angle(N''\text{-Co-}N)$ ‡	160.2	153.0	152.6	-7.2	-7.6
$\gamma = \angle(N'\text{-}C'_2\text{-}C_2\text{-}N) = \angle(N''\text{-}C''_2\text{-}C'_6\text{-}N')$ ‡	0.0	0.0	0.0	0.0	0.0
η = d(Co-N′/Co-N″)	0.893	0.940	0.941	0.047	0.049

‡The D_{2d} symmetry constraint imposes that $\beta' = 2\beta$ and $\gamma = 0$.

Table 9 OPBE/$\mathscr{S}_{fc}$−optimized LS and HS $[Co(tpy)_2]^{2+}$ geometries of D_{2d} symmetry: selected bond lengths (Å) and angles (deg) and their variations upon the LS → HS change of states.

	LS	HS		LS → HS	
	$^2B_2$	$^4A_2$	^4E	$^2B_2 \rightarrow {}^4A_2$	$^2B_2 \rightarrow {}^4E$
	L_1, L_2	L_1, L_2	L_1, L_2	L_1, L_2	L_1, L_2
Co-N, Co-N″	2.106	2.173	2.170	0.067	0.064
Co-N′	1.881	2.040	2.053	0.159	0.172
N-C_2, N″-C''_2	1.353	1.352	1.350	-0.001	-0.003
N-C_6, N″-C''_6	1.337	1.338	1.337	0.001	0.000
C_2-C_3, C''_2-C''_3	1.396	1.396	1.395	0.000	-0.001
C_3-C_4, C''_3-C''_4	1.389	1.388	1.389	-0.001	0.000
C_4-C_5, C''_4-C''_5	1.390	1.389	1.389	-0.001	-0.001
C_5-C_6, C''_5-C''_6	1.390	1.389	1.390	-0.001	0.000
C_2-C'_2, C'_6-C''_2	1.466	1.476	1.476	0.010	0.010
N′-C'_2, N′-C'_6	1.356	1.345	1.346	-0.011	-0.010
C'_2-C'_3, C'_5-C'_6	1.395	1.396	1.395	0.001	0.000
C'_3-C'_4, C'_4-C'_5	1.388	1.388	1.388	0.000	0.000
$\alpha = \angle(C'_6\text{-}C''_2, C_2\text{-}C'_2)$	107.7	108.0	108.1	0.3	0.4
$\beta = \angle(N'\text{-Co-}N) = \angle(N''\text{-Co-}N')$	80.0	76.5	76.0	-3.5	-4.0
$\beta' = \angle(N''\text{-Co-}N)$ ‡	160.0	153.1	152.1	-6.9	-7.9
$\gamma = \angle(N'\text{-}C'_2\text{-}C_2\text{-}N) = \angle(N''\text{-}C''_2\text{-}C'_6\text{-}N')$ ‡	0.0	0.0	0.0	0.0	0.0
η = d(Co-N′/Co-N″)	0.893	0.939	0.946	0.046	0.053

‡The D_{2d} symmetry constraint imposes that $\beta' = 2\beta$ and $\gamma = 0$.

Table 10 PBE/$\mathscr{S}_{fc}$−optimized LS and HS $[Co(tpy)_2]^{2+}$ geometries of D_{2d} symmetry: selected bond lengths (Å) and angles (deg) and their variations upon the LS → HS change of states.

	LS	HS		LS → HS	
	$^2B_2$	$^4A_2$	^4E	$^2B_2 \rightarrow {}^4A_2$	$^2B_2 \rightarrow {}^4E$
	L_1, L_2	L_1, L_2	L_1, L_2	L_1, L_2	L_1, L_2
Co-N, Co-N″	2.111	2.170	2.171	0.059	0.059
Co-N′	1.889	2.046	2.054	0.157	0.157
N-C_2, N″-C''_2	1.360	1.361	1.358	0.001	0.001
N-C_6, N″-C''_6	1.343	1.345	1.344	0.002	0.002
C_2-C_3, C''_2-C''_3	1.398	1.399	1.399	0.001	0.001
C_3-C_4, C''_3-C''_4	1.393	1.393	1.394	0.000	0.000
C_4-C_5, C''_4-C''_5	1.395	1.395	1.395	0.000	0.000
C_5-C_6, C''_5-C''_6	1.394	1.394	1.395	0.000	0.000
C_2-C'_2, C'_6-C''_2	1.471	1.479	1.479	0.008	0.008
N′-C'_2, N′-C'_6	1.362	1.351	1.353	-0.011	-0.011
C'_2-C'_3, C'_5-C'_6	1.398	1.400	1.399	0.002	0.002
C'_3-C'_4, C'_4-C'_5	1.393	1.394	1.394	0.001	0.001
$\alpha = \angle(C'_6\text{-}C''_2, C_2\text{-}C'_2)$	107.4	107.5	107.8	0.1	0.1
$\beta = \angle(N'\text{-Co-}N) = \angle(N''\text{-Co-}N')$	80.1	76.7	76.3	-3.4	-3.4
$\beta' = \angle(N''\text{-Co-}N)$ ‡	160.2	153.3	152.5	-6.9	-6.9
$\gamma = \angle(N'\text{-}C'_2\text{-}C_2\text{-}N) = \angle(N''\text{-}C''_2\text{-}C'_6\text{-}N')$ ‡	0.0	0.0	0.0	0.0	0.0
η = d(Co-N′/Co-N″)	0.895	0.943	0.946	0.048	0.048

‡The D_{2d} symmetry constraint imposes that $\beta' = 2\beta$ and $\gamma = 0$.

Table 11 RPBE/$\mathscr{S}_{fc}$−optimized LS and HS $[Co(tpy)_2]^{2+}$ geometries of D_{2d} symmetry: selected bond lengths (Å) and angles (deg) and their variations upon the LS → HS change of states.

	LS	HS		LS → HS	
	$^2B_2$	$^4A_2$	^4E	$^2B_2 \to {}^4A_2$	$^2B_2 \to {}^4E$
	L_1, L_2	L_1, L_2	L_1, L_2	L_1, L_2	L_1, L_2
Co-N, Co-N″	2.122	2.190	2.189	0.068	0.067
Co-N′	1.899	2.062	2.071	0.163	0.172
N-C_2, N''-C''_2	1.367	1.367	1.364	0.000	-0.003
N-C_6, N''-C''_6	1.349	1.350	1.349	0.001	0.000
C_2-C_3, C''_2-C''_3	1.405	1.406	1.405	0.001	0.000
C_3-C_4, C''_3-C''_4	1.399	1.399	1.400	0.000	0.001
C_4-C_5, C''_4-C''_5	1.400	1.400	1.400	0.000	0.000
C_5-C_6, C''_5-C''_6	1.400	1.398	1.400	-0.002	0.000
C_2-C'_2, C'_6-C''_2	1.479	1.490	1.489	0.011	0.010
N'-C'_2, N'-C'_6	1.369	1.357	1.360	-0.012	-0.009
C'_2-C'_3, C'_5-C'_6	1.404	1.406	1.405	0.002	0.001
C'_3-C'_4, C'_4-C'_5	1.399	1.399	1.399	0.000	0.000
$\alpha = \angle(C'_6\text{-}C''_2, C_2\text{-}C'_2)$	107.4	107.8	107.9	0.4	0.5
$\beta = \angle(N'\text{-Co-}N) = \angle(N''\text{-Co-}N')$	80.1	76.6	76.2	-3.5	-3.9
$\beta' = \angle(N''\text{-Co-}N)$ ‡	160.2	153.2	152.3	-7.0	-7.9
$\gamma = \angle(N'\text{-}C'_2\text{-}C_2\text{-}N) = \angle(N''\text{-}C''_2\text{-}C'_6\text{-}N')$ ‡	0.0	0.0	0.0	0.0	0.0
η = d(Co-N′/Co-N″)	0.895	0.942	0.946	0.047	0.051

‡The D_{2d} symmetry constraint imposes that $\beta' = 2\beta$ and $\gamma = 0$.

Table 12 B3LYP*/$\mathscr{G}$−optimized LS and HS $[Co(tpy)_2]^{2+}$ geometries of D_{2d} symmetry: selected bond lengths (Å) and angles (deg) and their variations upon the LS → HS change of states.

	LS	HS	LS → HS
	$^2B_2$	$^4A_2$	$^2B_2 \to {}^4A_2$
	L_1, L_2	L_1, L_2	L_1, L_2
Co-N, Co-N″	2.129	2.187	0.058
Co-N′	1.912	2.068	0.156
N-C_2, N''-C''_2	1.355	1.355	0.000
N-C_6, N''-C''_6	1.336	1.338	0.002
C_2-C_3, C''_2-C''_3	1.394	1.394	0.000
C_3-C_4, C''_3-C''_4	1.390	1.390	0.000
C_4-C_5, C''_4-C''_5	1.390	1.390	0.000
C_5-C_6, C''_5-C''_6	1.390	1.389	-0.001
C_2-C'_2, C'_6-C''_2	1.476	1.486	0.010
N'-C'_2, N'-C'_6	1.353	1.343	-0.010
C'_2-C'_3, C'_5-C'_6	1.394	1.396	0.002
C'_3-C'_4, C'_4-C'_5	1.390	1.391	0.001
$\alpha = \angle(C'_6\text{-}C''_2, C_2\text{-}C'_2)$	107.6	107.6	0.00
$\beta = \angle(N'\text{-Co-}N) = \angle(N''\text{-Co-}N')$	79.8	76.5	-3.30
$\beta' = \angle(N''\text{-Co-}N)$ ‡	159.6	152.9	-6.70
$\gamma = \angle(N'\text{-}C'_2\text{-}C_2\text{-}N) = \angle(N''\text{-}C''_2\text{-}C'_6\text{-}N')$ ‡	0.0	0.0	0.0
η = d(Co-N′/Co-N″)	0.898	0.946	0.048

‡The D_{2d} symmetry constraint imposes that $\beta' = 2\beta$ and $\gamma = 0$.

Table 13 B3LYP/$\mathscr{G}$−optimized LS and HS $[Co(tpy)_2]^{2+}$ geometries of D_{2d} symmetry: selected bond lengths (Å) and angles (deg) and their variations upon the LS → HS change of states.

	LS	HS	LS → HS
	$^2B_2$	$^4A_2$	$^2B_2 \rightarrow {}^4A_2$
	L_1, L_2	L_1, L_2	L_1, L_2
Co-N, Co-N″	2.142	2.195	0.053
Co-N′	1.922	2.078	0.156
N-C_2, N''-C''_2	1.352	1.353	0.001
N-C_6, N''-C''_6	1.334	1.336	0.002
C_2-C_3, C''_2-C''_3	1.392	1.393	0.001
C_3-C_4, C''_3-C''_4	1.389	1.389	0.000
C_4-C_5, C''_4-C''_5	1.388	1.388	0.000
C_5-C_6, C''_5-C''_6	1.389	1.388	-0.001
C_2-C'_2, C'_6-C''_2	1.478	1.487	0.009
N'-C'_2, N'-C'_6	1.350	1.341	-0.009
C'_2-C'_3, C'_5-C'_6	1.393	1.395	0.002
C'_3-C'_4, C'_4-C'_5	1.388	1.389	0.001
$\alpha = \angle(C'_6\text{-}C''_2, C_2\text{-}C'_2)$	108.0	107.8	-0.2
$\beta = \angle(N'\text{-Co-}N) = \angle(N''\text{-Co-}N')$	79.6	76.2	-3.4
$\beta' = \angle(N''\text{-Co-}N)$ ‡	159.2	152.5	-6.7
$\gamma = \angle(N'\text{-}C'_2\text{-}C_2\text{-}N) = \angle(N''\text{-}C''_2\text{-}C'_6\text{-}N')$ ‡	0.0	0.0	0.0
η = d(Co-N′/Co-N″)	0.897	0.947	0.049

‡The D_{2d} symmetry constraint imposes that $\beta' = 2\beta$ and $\gamma = 0$.

Table 14 HCTH407/$\mathscr{G}$−optimized LS and HS $[Co(tpy)_2]^{2+}$ geometries of D_{2d} symmetry: selected bond lengths (Å) and angles (deg) and their variations upon the LS → HS change of states.

	LS	HS	LS → HS
	$^2B_2$	$^4A_2$	$^2B_2 \rightarrow {}^4A_2$
	L_1, L_2	L_1, L_2	L_1, L_2
Co-N, Co-N″	2.119	2.195	0.076
Co-N′	1.889	2.051	0.162
N-C_2, N''-C''_2	1.353	1.352	-0.001
N-C_6, N''-C''_6	1.335	1.335	0.000
C_2-C_3, C''_2-C''_3	1.394	1.396	0.002
C_3-C_4, C''_3-C''_4	1.387	1.387	0.000
C_4-C_5, C''_4-C''_5	1.388	1.389	0.001
C_5-C_6, C''_5-C''_6	1.388	1.387	-0.001
C_2-C'_2, C'_6-C''_2	1.467	1.480	0.013
N'-C'_2, N'-C'_6	1.356	1.344	-0.012
C'_2-C'_3, C'_5-C'_6	1.393	1.395	0.002
C'_3-C'_4, C'_4-C'_5	1.387	1.388	0.001
$\alpha = \angle(C'_6\text{-}C''_2, C_2\text{-}C'_2)$	107.9	108.4	0.5
$\beta = \angle(N'\text{-Co-}N) = \angle(N''\text{-Co-}N')$	80.0	76.5	-3.5
$\beta' = \angle(N''\text{-Co-}N)$ ‡	159.9	153.0	-6.9
$\gamma = \angle(N'\text{-}C'_2\text{-}C_2\text{-}N) = \angle(N''\text{-}C''_2\text{-}C'_6\text{-}N')$ ‡	0.0	0.0	0.0
η = d(Co-N′/Co-N″)	0.891	0.934	0.043

‡The D_{2d} symmetry constraint imposes that $\beta' = 2\beta$ and $\gamma = 0$.

Table 15 OLYP/$\mathscr{G}$−optimized LS and HS $[Co(tpy)_2]^{2+}$ geometries of D_{2d} symmetry: selected bond lengths (Å) and angles (deg) and their variations upon the LS → HS change of states.

	LS	HS	LS → HS
	$^2B_2$	$^4A_2$	$^2B_2 \rightarrow {}^4A_2$
	L_1, L_2	L_1, L_2	L_1, L_2
Co-N, Co-N″	2.125	2.201	0.076
Co-N′	1.895	2.056	0.161
$N\text{-}C_2$, $N''\text{-}C''_2$	1.360	1.360	0.000
$N\text{-}C_6$, $N''\text{-}C''_6$	1.343	1.343	0.000
$C_2\text{-}C_3$, $C''_2\text{-}C''_3$	1.400	1.402	0.002
$C_3\text{-}C_4$, $C''_3\text{-}C''_4$	1.393	1.393	0.000
$C_4\text{-}C_5$, $C''_4\text{-}C''_5$	1.394	1.395	0.001
$C_5\text{-}C_6$, $C''_5\text{-}C''_6$	1.394	1.393	-0.001
$C_2\text{-}C'_2$, $C'_6\text{-}C''_2$	1.473	1.485	0.012
$N'\text{-}C'_2$, $N'\text{-}C'_6$	1.363	1.352	-0.011
$C'_2\text{-}C'_3$, $C'_5\text{-}C'_6$	1.399	1.401	0.002
$C'_3\text{-}C'_4$, $C'_4\text{-}C'_5$	1.393	1.393	0.000
$\alpha = \angle(C'_6\text{-}C''_2, C_2\text{-}C'_2)$	107.8	108.4	0.6
$\beta = \angle(N'\text{-}Co\text{-}N) = \angle(N''\text{-}Co\text{-}N')$	80.0	76.5	-3.5
$\beta' = \angle(N''\text{-}Co\text{-}N)$ ‡	159.9	153.0	-6.9
$\gamma = \angle(N'\text{-}C'_2\text{-}C_2\text{-}N) = \angle(N''\text{-}C''_2\text{-}C'_6\text{-}N')$ ‡	0.0	0.0	0.0
η = d(Co-N′/Co-N″)	0.892	0.934	0.042

‡The D_{2d} symmetry constraint imposes that $\beta' = 2\beta$ and $\gamma = 0$.

Table 16 OPBE/$\mathscr{G}$−optimized LS and HS $[Co(tpy)_2]^{2+}$ geometries of D_{2d} symmetry: selected bond lengths (Å) and angles (deg) and their variations upon the LS → HS change of states.

	LS	HS	LS → HS
	$^2B_2$	$^4A_2$	$^2B_2 \rightarrow {}^4A_2$
	L_1, L_2	L_1, L_2	L_1, L_2
Co-N, Co-N″	2.087	2.170	0.083
Co-N′	1.869	2.024	0.155
$N\text{-}C_2$, $N''\text{-}C''_2$	1.356	1.355	-0.001
$N\text{-}C_6$, $N''\text{-}C''_6$	1.339	1.339	0.000
$C_2\text{-}C_3$, $C''_2\text{-}C''_3$	1.397	1.398	0.001
$C_3\text{-}C_4$, $C''_3\text{-}C''_4$	1.390	1.391	0.001
$C_4\text{-}C_5$, $C''_4\text{-}C''_5$	1.392	1.392	0.000
$C_5\text{-}C_6$, $C''_5\text{-}C''_6$	1.391	1.390	-0.001
$C_2\text{-}C'_2$, $C'_6\text{-}C''_2$	1.467	1.479	0.012
$N'\text{-}C'_2$, $N'\text{-}C'_6$	1.358	1.348	-0.010
$C'_2\text{-}C'_3$, $C'_5\text{-}C'_6$	1.396	1.398	0.002
$C'_3\text{-}C'_4$, $C'_4\text{-}C'_5$	1.390	1.391	0.001
$\alpha = \angle(C'_6\text{-}C''_2, C_2\text{-}C'_2)$	107.0	107.9	0.9
$\beta = \angle(N'\text{-}Co\text{-}N) = \angle(N''\text{-}Co\text{-}N')$	80.4	77.0	-3.4
$\beta' = \angle(N''\text{-}Co\text{-}N)$ ‡	160.8	154.0	-6.8
$\gamma = \angle(N'\text{-}C'_2\text{-}C_2\text{-}N) = \angle(N''\text{-}C''_2\text{-}C'_6\text{-}N')$ ‡	0.0	0.0	0.0
η = d(Co-N′/Co-N″)	0.896	0.933	0.037

‡The D_{2d} symmetry constraint imposes that $\beta' = 2\beta$ and $\gamma = 0$.

Table 17 PBE/$\mathscr{G}-$optimized LS and HS $[Co(tpy)_2]^{2+}$ geometries of D_{2d} symmetry: selected bond lengths (Å) and angles (deg) and their variations upon the LS $\rightarrow$ HS change of states.

	LS	HS	LS $\rightarrow$ HS
	$^2B_2$	$^4A_2$	$^2B_2 \rightarrow {}^4A_2$
	L_1, L_2	L_1, L_2	L_1, L_2
Co-N, Co-N$''$	2.090	2.160	0.070
Co-N$'$	1.885	2.039	0.154
N-C_2, N$''$-C''_2	1.363	1.362	-0.001
N-C_6, N$''$-C''_6	1.344	1.344	0.000
C_2-C_3, C''_2-C''_3	1.399	1.400	0.001
C_3-C_4, C''_3-C''_4	1.395	1.395	0.000
C_4-C_5, C''_4-C''_5	1.396	1.396	0.000
C_5-C_6, C''_5-C''_6	1.395	1.394	-0.001
C_2-C'_2, C'_6-C''_2	1.470	1.481	0.011
N$'$-C'_2, N$'$-C'_6	1.364	1.352	-0.012
C'_2-C'_3, C'_5-C'_6	1.399	1.401	0.002
C'_3-C'_4, C'_4-C'_5	1.395	1.396	0.001
$\alpha = \angle(C'_6\text{-}C''_2, C_2\text{-}C'_2)$	106.6	107.1	0.5
$\beta = \angle(N'\text{-Co-}N) = \angle(N''\text{-Co-}N')$	80.3	77.0	-3.3
$\beta' = \angle(N''\text{-Co-}N)$ ‡	160.7	154.0	-6.7
$\gamma = \angle(N'\text{-}C'_2\text{-}C_2\text{-}N) = \angle(N''\text{-}C''_2\text{-}C'_6\text{-}N')$ ‡	0.0	0.0	0.0
η = d(Co-N$'$/Co-N$''$)	0.902	0.944	0.042

‡The D_{2d} symmetry constraint imposes that $\beta' = 2\beta$ and $\gamma = 0$.

Table 18 BLYP/$\mathscr{S}_{fc}$−optimized LS and HS $[Co(tpy)_2]^{2+}$ geometries of C_{2v} symmetry: selected bond lengths (Å) and angles (deg) and their variations upon the $D_{2d} \rightarrow C_{2v}$ symmetry lowering (LS:$^2B_2 \rightarrow {}^2A_1$; HS: $^4A_2 \rightarrow {}^4A_2$ and $^4E \rightarrow {}^4B_1 \oplus {}^4B_2$).

	LS $^2A_1$		HS $^4A_2$		HS $^4B_1$	
	L_1	L_2	L_1	L_2	L_1	L_2
Parameters values in the C_{2v} geometries						
Co-N, Co-N″	2.017	2.232	2.187	2.210	2.181	2.215
Co-N′	1.877	1.971	2.064	2.083	2.111	2.074
N-C_2, N″-C''_2	1.376	1.360	1.367	1.366	1.364	1.364
N-C_6, N″-C''_6	1.352	1.346	1.349	1.349	1.349	1.347
C_2-C_3, C''_2-C''_3	1.400	1.405	1.402	1.403	1.403	1.403
C_3-C_4, C''_3-C''_4	1.397	1.398	1.398	1.397	1.397	1.398
C_4-C_5, C''_4-C''_5	1.399	1.398	1.398	1.398	1.398	1.397
C_5-C_6, C''_5-C''_6	1.397	1.398	1.397	1.397	1.397	1.399
C_2-C'_2, C'_6-C''_2	1.470	1.485	1.488	1.489	1.483	1.491
N′-C'_2, N′-C'_6	1.366	1.368	1.355	1.356	1.357	1.358
C'_2-C'_3, C'_5-C'_6	1.401	1.403	1.404	1.404	1.404	1.403
C'_3-C'_4, C'_4-C'_5	1.400	1.396	1.398	1.398	1.397	1.398
$\alpha = \angle(C'_6\text{-}C''_2, C_2\text{-}C'_2)$	103.4	110.8	107.6	108.2	107.6	108.5
$\beta = \angle(N'\text{-Co-}N) = \angle(N''\text{-Co-}N')$	81.3	78.0	76.6	76.1	74.9	76.4
$\beta' = \angle(N''\text{-Co-}N)$ †	162.6	156.0	153.3	152.3	149.8	152.7
$\gamma = \angle(N'\text{-}C'_2\text{-}C_2\text{-}N) = \angle(N''\text{-}C''_2\text{-}C'_6\text{-}N')$ †	0.0	0.0	0.0	0.0	0.0	0.0
η = d(Co-N′/Co-N″)	0.931	0.883	0.944	0.943	0.968	0.936
Variations associated with the $D_{2d} \rightarrow C_{2v}$ symmetry lowering						
Co-N, Co-N″	-0.107	0.108	-0.002	0.021	-0.010	0.024
Co-N′	-0.025	0.069	0.001	0.020	0.040	0.003
N-C_2, N″-C''_2	0.009	-0.007	0.000	-0.001	0.000	0.000
N-C_6, N″-C''_6	0.004	-0.002	0.000	0.000	0.001	-0.001
C_2-C_3, C''_2-C''_3	-0.003	0.002	-0.001	0.000	0.000	0.000
C_3-C_4, C''_3-C''_4	-0.001	0.000	0.001	0.000	-0.001	0.000
C_4-C_5, C''_4-C''_5	0.000	-0.001	-0.001	-0.001	0.000	-0.001
C_5-C_6, C''_5-C''_6	-0.001	0.000	0.000	0.000	-0.001	0.001
C_2-C'_2, C'_6-C''_2	-0.008	0.007	0.000	0.001	-0.005	0.003
N′-C'_2, N′-C'_6	-0.003	-0.001	-0.001	0.000	-0.002	-0.001
C'_2-C'_3, C'_5-C'_6	-0.001	0.001	0.000	0.000	0.001	0.000
C'_3-C'_4, C'_4-C'_5	0.003	-0.001	0.000	0.000	-0.001	0.000
$\alpha = \angle(C'_6\text{-}C''_2, C_2\text{-}C'_2)$	-4.0	3.4	0.0	0.6	-0.3	0.6
$\beta = \angle(N'\text{-Co-}N) = \angle(N''\text{-Co-}N')$	1.2	-2.1	0.0	-0.5	-1.3	0.2
$\beta' = \angle(N''\text{-Co-}N)$ †	2.4	-4.2	0.0	-1.0	-2.6	0.3
$\gamma = \angle(N'\text{-}C'_2\text{-}C_2\text{-}N) = \angle(N''\text{-}C''_2\text{-}C'_6\text{-}N')$ †	0.0	0.0	0.0	0.0	0.0	0.0
η = d(Co-N′/Co-N″)	0.035	-0.012	0.001	0.000	0.023	-0.009

†The D_{2d} and C_{2v} symmetry constraints impose that $\beta' = 2\beta$ and $\gamma = 0$.

Table 19 OLYP/$\mathscr{S}_{\rm fc}$−optimized LS and HS $[Co(tpy)_2]^{2+}$ geometries of C_{2v} symmetry: selected bond lengths (Å) and angles (deg) and their variations upon the $D_{2d} \rightarrow C_{2v}$ symmetry lowering (LS:$^2B_2 \rightarrow {}^2A_1$; HS: $^4A_2 \rightarrow {}^4A_2$ and $^4E \rightarrow {}^4B_1 \oplus {}^4B_2$).

	LS $^2A_1$		HS $^4A_2$		HS $^4B_1$	
	L_1	L_2	L_1	L_2	L_1	L_2
Parameters values in the C_{2v} geometries						
Co-N, Co-N$''$	2.020	2.221	2.195	2.203	2.186	2.216
Co-N$'$	1.870	1.956	2.059	2.075	2.093	2.080
N-C_2, N$''$-C''_2	1.366	1.352	1.357	1.357	1.356	1.354
N-C_6, N$''$-C''_6	1.345	1.339	1.342	1.342	1.343	1.341
C_2-C_3, C''_2-C''_3	1.397	1.401	1.399	1.400	1.399	1.399
C_3-C_4, C''_3-C''_4	1.391	1.392	1.392	1.392	1.392	1.393
C_4-C_5, C''_4-C''_5	1.393	1.392	1.393	1.393	1.393	1.392
C_5-C_6, C''_5-C''_6	1.392	1.394	1.392	1.392	1.392	1.394
C_2-C'_2, C'_6-C''_2	1.465	1.480	1.483	1.484	1.478	1.488
N$'$-C'_2, N$'$-C'_6	1.359	1.361	1.349	1.349	1.352	1.349
C'_2-C'_3, C'_5-C'_6	1.397	1.399	1.399	1.400	1.399	1.399
C'_3-C'_4, C'_4-C'_5	1.392	1.389	1.392	1.391	1.391	1.392
$\alpha = \angle(C'_6\text{-}C''_2, C_2\text{-}C'_2)$	104.0	111.0	108.3	108.3	108.3	108.8
$\beta = \angle(N'\text{-Co-N}) = \angle(N''\text{-Co-}N')$	81.1	78.0	76.4	76.0	74.9	76.0
$\beta' = \angle(N''\text{-Co-N})$ †	162.1	156.1	152.8	152.0	149.8	152.1
$\gamma = \angle(N'\text{-}C'_2\text{-}C_2\text{-N}) = \angle(N''\text{-}C''_2\text{-}C'_6\text{-}N')$ †	0.0	0.0	0.0	0.0	0.0	0.0
η = d(Co-N$'$/Co-N$''$)	0.926	0.881	0.938	0.942	0.957	0.939
Variations associated with the $D_{2d} \rightarrow C_{2v}$ symmetry lowering						
Co-N, Co-N$''$	-0.098	0.103	0.007	0.015	-0.002	0.028
Co-N$'$	-0.021	0.065	0.002	0.018	0.033	0.020
N-C_2, N$''$-C''_2	0.009	-0.005	0.000	0.000	0.000	-0.002
N-C_6, N$''$-C''_6	0.004	-0.002	0.001	0.001	0.002	0.000
C_2-C_3, C''_2-C''_3	-0.002	0.002	0.000	0.001	0.000	0.000
C_3-C_4, C''_3-C''_4	-0.001	0.000	0.000	0.000	0.000	0.001
C_4-C_5, C''_4-C''_5	0.000	-0.001	0.000	0.000	0.001	0.000
C_5-C_6, C''_5-C''_6	0.000	0.002	0.001	0.001	0.000	0.002
C_2-C'_2, C'_6-C''_2	-0.008	0.007	-0.001	0.000	-0.006	0.004
N$'$-C'_2, N$'$-C'_6	-0.002	0.000	0.000	0.000	0.001	-0.002
C'_2-C'_3, C'_5-C'_6	0.000	0.002	0.000	0.001	0.000	0.000
C'_3-C'_4, C'_4-C'_5	0.001	-0.002	0.000	-0.001	-0.001	0.000
$\alpha = \angle(C'_6\text{-}C''_2, C_2\text{-}C'_2)$	-3.7	3.3	0.3	0.3	0.1	0.6
$\beta = \angle(N'\text{-Co-N}) = \angle(N''\text{-Co-}N')$	1.0	-2.1	-0.1	-0.5	-1.4	-0.3
$\beta' = \angle(N''\text{-Co-N})$ †	1.9	-4.1	-0.2	-1.0	-2.8	-0.5
$\gamma = \angle(N'\text{-}C'_2\text{-}C_2\text{-N}) = \angle(N''\text{-}C''_2\text{-}C'_6\text{-}N')$ †	0.0	0.0	0.0	0.0	0.0	0.0
η = d(Co-N$'$/Co-N$''$)	0.033	-0.012	-0.002	0.002	0.016	-0.003

†The D_{2d} and C_{2v} symmetry constraints impose that $\beta' = 2\beta$ and $\gamma = 0$.

Table 20 OPBE/$\mathscr{S}_{fc}$−optimized LS and HS $[Co(tpy)_2]^{2+}$ geometries of C_{2v} symmetry: selected bond lengths (Å) and angles (deg) and their variations upon the $D_{2d} \rightarrow C_{2v}$ symmetry lowering (LS:$^2B_2 \rightarrow {}^2A_1$; HS: $^4A_2 \rightarrow {}^4A_2$ and $^4E \rightarrow {}^4B_1 \oplus {}^4B_2$).

	LS $^2A_1$		HS $^4A_2$		HS $^4B_1$	
	L_1	L_2	L_1	L_2	L_1	L_2
Parameters values in the C_{2v} geometries						
Co-N, Co-N″	1.998	2.216	2.155	2.179	2.148	2.176
Co-N′	1.854	1.953	2.027	2.049	2.083	2.054
$N-C_2$, $N''-C''_2$	1.361	1.346	1.352	1.352	1.350	1.351
$N-C_6$, $N''-C''_6$	1.341	1.335	1.338	1.337	1.338	1.336
C_2-C_3, $C''_2-C''_3$	1.394	1.397	1.395	1.396	1.396	1.395
C_3-C_4, $C''_3-C''_4$	1.388	1.388	1.389	1.388	1.388	1.390
C_4-C_5, $C''_4-C''_5$	1.390	1.389	1.390	1.390	1.390	1.388
C_5-C_6, $C''_5-C''_6$	1.389	1.391	1.389	1.389	1.389	1.391
$C_2-C'_2$, $C'_6-C''_2$	1.459	1.474	1.478	1.477	1.472	1.480
$N'-C'_2$, $N'-C'_6$	1.354	1.355	1.344	1.345	1.346	1.345
$C'_2-C'_3$, $C'_5-C'_6$	1.394	1.396	1.396	1.396	1.396	1.396
$C'_3-C'_4$, $C'_4-C'_5$	1.389	1.386	1.389	1.388	1.388	1.389
$\alpha = \angle(C'_6-C''_2, C_2-C'_2)$	103.6	111.2	107.4	108.1	107.4	107.8
$\beta = \angle(N'-Co-N) = \angle(N''-Co-N')$	81.3	77.8	76.9	76.3	74.9	76.5
$\beta' = \angle(N''-Co-N)$ †	162.5	155.7	153.9	152.6	149.9	153.0
$\gamma = \angle(N'-C'_2-C_2-N) = \angle(N''-C''_2-C'_6-N')$ †	0.0	0.0	0.0	0.0	0.0	0.0
η = d(Co-N′/Co-N″)	0.928	0.881	0.941	0.940	0.970	0.944
Variations associated with the $D_{2d} \rightarrow C_{2v}$ symmetry lowering						
Co-N, Co-N″	-0.108	0.110	-0.018	0.006	-0.022	0.006
Co-N′	-0.027	0.072	-0.013	0.009	0.030	0.001
$N-C_2$, $N''-C''_2$	0.008	-0.007	0.000	0.000	0.000	0.001
$N-C_6$, $N''-C''_6$	0.004	-0.002	0.000	-0.001	0.001	-0.001
C_2-C_3, $C''_2-C''_3$	-0.002	0.001	-0.001	0.000	0.001	0.000
C_3-C_4, $C''_3-C''_4$	-0.001	-0.001	0.001	0.000	-0.001	0.001
C_4-C_5, $C''_4-C''_5$	0.000	-0.001	0.001	0.001	0.001	-0.001
C_5-C_6, $C''_5-C''_6$	-0.001	0.001	0.000	0.000	-0.001	0.001
$C_2-C'_2$, $C'_6-C''_2$	-0.007	0.008	0.002	0.001	-0.004	0.004
$N'-C'_2$, $N'-C'_6$	-0.002	-0.001	-0.001	0.000	0.000	-0.001
$C'_2-C'_3$, $C'_5-C'_6$	-0.001	0.001	0.000	0.000	0.001	0.001
$C'_3-C'_4$, $C'_4-C'_5$	0.001	-0.002	0.001	0.000	0.000	0.001
$\alpha = \angle(C'_6-C''_2, C_2-C'_2)$	-4.1	3.5	-0.6	0.1	-0.7	-0.3
$\beta = \angle(N'-Co-N) = \angle(N''-Co-N')$	1.3	-2.2	0.4	-0.2	-1.1	0.5
$\beta' = \angle(N''-Co-N)$ †	2.5	-4.3	0.8	-0.5	-2.2	0.9
$\gamma = \angle(N'-C'_2-C_2-N) = \angle(N''-C''_2-C'_6-N')$ †	0.0	0.0	0.0	0.0	0.0	0.0
η = d(Co-N′/Co-N″)	0.035	-0.012	0.002	0.002	0.024	-0.002

†The D_{2d} and C_{2v} symmetry constraints impose that $\beta' = 2\beta$ and $\gamma = 0$.

Table 21 PBE/$\mathscr{S}_{fc}$−optimized LS and HS $[Co(tpy)_2]^{2+}$ geometries of C_{2v} symmetry: selected bond lengths (Å) and angles (deg) and their variations upon the $D_{2d} \to C_{2v}$ symmetry lowering (LS:$^2B_2 \to {}^2A_1$; HS: $^4A_2 \to {}^4A_2$ and $^4E \to {}^4B_1 \oplus {}^4B_2$).

	LS $^2A_1$		HS $^4A_2$		HS $^4B_1$	
	L_1	L_2	L_1	L_2	L_1	L_2
Parameters values in the C_{2v} geometries						
Co-N, Co-N″	1.997	2.209	2.152	2.173	2.145	2.172
Co-N′	1.862	1.955	2.032	2.053	2.087	2.050
N-C_2, N''-C''_2	1.370	1.355	1.361	1.360	1.358	1.359
N-C_6, N''-C''_6	1.347	1.342	1.345	1.344	1.345	1.342
C_2-C_3, C''_2-C''_3	1.396	1.400	1.398	1.399	1.399	1.398
C_3-C_4, C''_3-C''_4	1.393	1.393	1.394	1.394	1.393	1.395
C_4-C_5, C''_4-C''_5	1.395	1.395	1.395	1.395	1.395	1.394
C_5-C_6, C''_5-C''_6	1.394	1.395	1.393	1.394	1.393	1.395
C_2-C'_2, C'_6-C''_2	1.462	1.476	1.480	1.480	1.475	1.483
N'-C'_2, N'-C'_6	1.360	1.361	1.350	1.351	1.351	1.352
C'_2-C'_3, C'_5-C'_6	1.397	1.399	1.400	1.400	1.400	1.399
C'_3-C'_4, C'_4-C'_5	1.396	1.392	1.395	1.395	1.394	1.395
$\alpha = \angle(C'_6\text{-}C''_2, C_2\text{-}C'_2)$	103.2	110.6	107.0	107.6	106.9	107.4
$\beta = \angle(N'\text{-Co-}N) = \angle(N''\text{-Co-}N')$	81.3	78.0	77.1	76.5	75.1	76.8
$\beta' = \angle(N''\text{-Co-}N)$ †	162.6	156.0	154.1	153.0	150.3	153.6
$\gamma = \angle(N'\text{-}C'_2\text{-}C_2\text{-}N) = \angle(N''\text{-}C''_2\text{-}C'_6\text{-}N')$ †	0.0	0.0	0.0	0.0	0.0	0.0
η = d(Co-N′/Co-N″)	0.932	0.885	0.944	0.945	0.973	0.944
Variations associated with the $D_{2d} \to C_{2v}$ symmetry lowering						
Co-N, Co-N″	-0.114	0.098	-0.018	0.003	-0.026	0.001
Co-N′	-0.027	0.066	-0.014	0.007	0.033	-0.004
N-C_2, N''-C''_2	0.010	-0.005	0.000	-0.001	0.000	0.001
N-C_6, N''-C''_6	0.004	-0.001	0.000	-0.001	0.001	-0.002
C_2-C_3, C''_2-C''_3	-0.002	0.002	-0.001	0.000	0.000	-0.001
C_3-C_4, C''_3-C''_4	0.000	0.000	0.001	0.001	-0.001	0.001
C_4-C_5, C''_4-C''_5	0.000	0.000	0.000	0.000	0.000	-0.001
C_5-C_6, C''_5-C''_6	0.000	0.001	-0.001	0.000	-0.002	0.000
C_2-C'_2, C'_6-C''_2	-0.009	0.005	0.001	0.001	-0.004	0.004
N'-C'_2, N'-C'_6	-0.002	-0.001	-0.001	0.000	-0.002	-0.001
C'_2-C'_3, C'_5-C'_6	-0.001	0.001	0.000	0.000	0.001	0.000
C'_3-C'_4, C'_4-C'_5	0.003	-0.001	0.001	0.001	0.000	0.001
$\alpha = \angle(C'_6\text{-}C''_2, C_2\text{-}C'_2)$	-4.2	3.2	-0.5	0.1	-0.9	-0.4
$\beta = \angle(N'\text{-Co-}N) = \angle(N''\text{-Co-}N')$	1.2	-2.1	0.4	-0.2	-1.2	0.5
$\beta' = \angle(N''\text{-Co-}N)$ †	2.4	-4.2	0.8	-0.3	-2.2	1.1
$\gamma = \angle(N'\text{-}C'_2\text{-}C_2\text{-}N) = \angle(N''\text{-}C''_2\text{-}C'_6\text{-}N')$ †	0.0	0.0	0.0	0.0	0.0	0.0
η = d(Co-N′/Co-N″)	0.038	-0.010	0.001	0.002	0.027	-0.002

†The D_{2d} and C_{2v} symmetry constraints impose that $\beta' = 2\beta$ and $\gamma = 0$.

Table 22 RPBE/$\mathscr{S}_{fc}$−optimized LS and HS $[Co(tpy)_2]^{2+}$ geometries of C_{2v} symmetry: selected bond lengths (Å) and angles (deg) and their variations upon the $D_{2d} \rightarrow C_{2v}$ symmetry lowering (LS:$^2B_2 \rightarrow {}^2A_1$; HS: $^4A_2 \rightarrow {}^4A_2$ and $^4E \rightarrow {}^4B_1 \oplus {}^4B_2$).

	LS $^2A_1$		HS $^4A_2$		HS $^4B_1$	
	L_1	L_2	L_1	L_2	L_1	L_2
Parameters values in the C_{2v} geometries						
Co-N, Co-N″	2.014	2.230	2.179	2.220	2.189	2.212
Co-N′	1.874	1.969	2.054	2.081	2.118	2.064
N-C_2, N''-C''_2	1.375	1.360	1.368	1.366	1.362	1.366
N-C_6, N''-C''_6	1.353	1.347	1.350	1.349	1.348	1.347
C_2-C_3, C''_2-C''_3	1.403	1.407	1.404	1.406	1.403	1.404
C_3-C_4, C''_3-C''_4	1.399	1.399	1.399	1.398	1.399	1.400
C_4-C_5, C''_4-C''_5	1.400	1.400	1.400	1.400	1.400	1.397
C_5-C_6, C''_5-C''_6	1.399	1.400	1.398	1.398	1.399	1.400
C_2-C'_2, C'_6-C''_2	1.471	1.487	1.491	1.491	1.483	1.493
N'-C'_2, N'-C'_6	1.367	1.368	1.356	1.358	1.357	1.361
C'_2-C'_3, C'_5-C'_6	1.403	1.405	1.405	1.405	1.405	1.405
C'_3-C'_4, C'_4-C'_5	1.401	1.397	1.399	1.399	1.398	1.399
$\alpha = \angle(C'_6$-C''_2, C_2-$C'_2)$	103.4	110.9	107.4	108.7	107.9	108.3
$\beta = \angle(N'$-Co-$N) = \angle(N''$-Co-$N')$	81.3	78.0	76.9	76.0	74.6	76.7
$\beta' = \angle(N''$-Co-$N)$ †	162.6	155.9	153.7	151.9	149.1	153.4
$\gamma = \angle(N'$-C'_2-C_2-$N) = \angle(N''$-C''_2-C'_6-$N')$ †	0.0	0.0	0.0	0.0	0.0	0.0
η = d(Co-N′/Co-N″)	0.930	0.883	0.943	0.937	0.968	0.933
Variations associated with the $D_{2d} \rightarrow C_{2v}$ symmetry lowering						
Co-N, Co-N″	-0.108	0.108	-0.011	0.030	0.000	0.023
Co-N′	-0.025	0.070	-0.008	0.019	0.047	-0.007
N-C_2, N''-C''_2	0.008	-0.007	0.001	-0.001	-0.002	0.002
N-C_6, N''-C''_6	0.004	-0.002	0.000	-0.001	-0.001	-0.002
C_2-C_3, C''_2-C''_3	-0.002	0.002	-0.002	0.000	-0.002	-0.001
C_3-C_4, C''_3-C''_4	0.000	0.000	0.000	-0.001	-0.001	0.000
C_4-C_5, C''_4-C''_5	0.000	0.000	0.000	0.000	0.000	-0.003
C_5-C_6, C''_5-C''_6	-0.001	0.000	0.000	0.000	-0.001	0.000
C_2-C'_2, C'_6-C''_2	-0.008	0.008	0.001	0.001	-0.006	0.004
N'-C'_2, N'-C'_6	-0.002	-0.001	-0.001	0.001	-0.003	0.001
C'_2-C'_3, C'_5-C'_6	-0.001	0.001	-0.001	-0.001	0.000	0.000
C'_3-C'_4, C'_4-C'_5	0.002	-0.002	0.000	0.000	-0.001	0.000
$\alpha = \angle(C'_6$-C''_2, C_2-$C'_2)$	-4.0	3.5	-0.4	0.9	0.0	0.4
$\beta = \angle(N'$-Co-$N) = \angle(N''$-Co-$N')$	1.2	-2.1	0.3	-0.6	-1.6	0.5
$\beta' = \angle(N''$-Co-$N)$ †	2.4	-4.3	0.5	-1.3	-3.2	1.1
$\gamma = \angle(N'$-C'_2-C_2-$N) = \angle(N''$-C''_2-C'_6-$N')$ †	0.0	0.0	0.0	0.0	0.0	0.0
η = d(Co-N′/Co-N″)	0.036	-0.012	0.001	-0.004	0.021	-0.013

†The D_{2d} and C_{2v} symmetry constraints impose that $\beta' = 2\beta$ and $\gamma = 0$.

Table 23 B3LYP*/$\mathscr{G}$−optimized LS $[Co(tpy)_2]^{2+}$ geometry of C_{2v} symmetry: selected bond lengths (Å) and angles (deg) and their variations upon the $D_{2d} \to C_{2v}$ symmetry lowering ($^2B_2 \to {}^2A_1$).

	$^2A_1$		$D_{2d} \to C_{2v}$	
	L_1	L_2	L_1	L_2
Parameters values in the C_{2v} geometries				
Co-N, Co-N″	2.027	2.225	-0.102	0.096
Co-N′	1.889	1.966	-0.023	0.054
N-C_2, N''-C''_2	1.362	1.349	0.007	-0.006
N-C_6, N''-C''_6	1.339	1.335	0.003	-0.001
C_2-C_3, C''_2-C''_3	1.391	1.396	-0.003	0.002
C_3-C_4, C''_3-C''_4	1.390	1.390	0.000	0.000
C_4-C_5, C''_4-C''_5	1.389	1.390	-0.001	0.000
C_5-C_6, C''_5-C''_6	1.390	1.391	0.000	0.001
C_2-C'_2, C'_6-C''_2	1.471	1.483	-0.005	0.007
N'-C'_2, N'-C'_6	1.350	1.354	-0.003	0.001
C'_2-C'_3, C'_5-C'_6	1.393	1.395	-0.001	0.001
C'_3-C'_4, C'_4-C'_5	1.392	1.388	0.002	-0.002
$\alpha = \angle(C'_6\text{-}C''_2, C_2\text{-}C'_2)$	103.7	110.8	-3.9	3.2
$\beta = \angle(N'\text{-Co-}N) = \angle(N''\text{-Co-}N')$	81.0	78.1	1.2	-1.7
$\beta' = \angle(N''\text{-Co-}N)$ †	162.1	156.1	2.5	-3.5
$\gamma = \angle(N'\text{-}C'_2\text{-}C_2\text{-}N) = \angle(N''\text{-}C''_2\text{-}C'_6\text{-}N')$ †	0.0	0.0	0.0	0.0
η = d(Co-N′/Co-N″)	0.932	0.884	0.034	-0.014

†The D_{2d} and C_{2v} symmetry constraints impose that $\beta' = 2\beta$ and $\gamma = 0$.

Table 24 B3LYP/$\mathscr{G}$−optimized LS $[Co(tpy)_2]^{2+}$ geometry of C_{2v} symmetry: selected bond lengths (Å) and angles (deg) and their variations upon the $D_{2d} \to C_{2v}$ symmetry lowering ($^2B_2 \to {}^2A_1$).

	$^2A_1$		$D_{2d} \to C_{2v}$	
	L_1	L_2	L_1	L_2
Parameters values in the C_{2v} geometries				
Co-N, Co-N″	2.042	2.236	-0.100	0.094
Co-N′	1.899	1.973	-0.023	0.051
N-C_2, N''-C''_2	1.359	1.347	0.007	-0.005
N-C_6, N''-C''_6	1.336	1.334	0.002	0.000
C_2-C_3, C''_2-C''_3	1.390	1.395	-0.002	0.003
C_3-C_4, C''_3-C''_4	1.389	1.389	0.000	0.000
C_4-C_5, C''_4-C''_5	1.388	1.388	0.000	0.000
C_5-C_6, C''_5-C''_6	1.389	1.389	0.000	0.000
C_2-C'_2, C'_6-C''_2	1.474	1.484	-0.004	0.006
N'-C'_2, N'-C'_6	1.347	1.351	-0.003	0.001
C'_2-C'_3, C'_5-C'_6	1.392	1.394	-0.001	0.001
C'_3-C'_4, C'_4-C'_5	1.390	1.387	0.002	-0.001
$\alpha = \angle(C'_6\text{-}C''_2, C_2\text{-}C'_2)$	104.2	111.1	-3.8	3.1
$\beta = \angle(N'\text{-Co-}N) = \angle(N''\text{-Co-}N')$	80.8	77.9	1.2	-1.7
$\beta' = \angle(N''\text{-Co-}N)$ †	161.6	155.8	2.4	-3.4
$\gamma = \angle(N'\text{-}C'_2\text{-}C_2\text{-}N) = \angle(N''\text{-}C''_2\text{-}C'_6\text{-}N')$ †	0.0	0.0	0.0	0.0
η = d(Co-N′/Co-N″)	0.930	0.882	0.033	-0.015

†The D_{2d} and C_{2v} symmetry constraints impose that $\beta' = 2\beta$ and $\gamma = 0$.

Table 25 HCTH407/$\mathscr{G}$−optimized LS $[Co(tpy)_2]^{2+}$ geometry of C_{2v} symmetry: selected bond lengths (Å) and angles (deg) and their variations upon the $D_{2d} \to C_{2v}$ symmetry lowering ($^2B_2 \to {}^2A_1$).

	$^2A_1$		$D_{2d} \to C_{2v}$	
	L_1	L_2	L_1	L_2
Parameters values in the C_{2v} geometries				
Co-N, Co-N″	2.013	2.220	-0.106	0.101
Co-N′	1.864	1.948	-0.025	0.059
N-C_2, N''-C''_2	1.361	1.347	0.008	-0.006
N-C_6, N''-C''_6	1.338	1.333	0.003	-0.002
C_2-C_3, C''_2-C''_3	1.392	1.397	-0.002	0.003
C_3-C_4, C''_3-C''_4	1.387	1.388	0.000	0.001
C_4-C_5, C''_4-C''_5	1.388	1.388	0.000	0.000
C_5-C_6, C''_5-C''_6	1.387	1.389	-0.001	0.001
C_2-C'_2, C'_6-C''_2	1.460	1.476	-0.007	0.009
N'-C'_2, N'-C'_6	1.353	1.355	-0.003	-0.001
C'_2-C'_3, C'_5-C'_6	1.392	1.395	-0.001	0.002
C'_3-C'_4, C'_4-C'_5	1.389	1.385	0.002	-0.002
$\alpha = \angle(C'_6$-C''_2, C_2-$C'_2)$	103.9	111.1	-4.0	3.2
$\beta = \angle(N'$-Co-$N) = \angle(N''$-Co-$N')$	81.2	78.2	1.2	-1.8
$\beta' = \angle(N''$-Co-$N)$ †	162.5	156.4	2.6	-3.5
$\gamma = \angle(N'$-C'_2-C_2-$N) = \angle(N''$-C''_2-C'_6-$N')$ †	0.0	0.0	0.0	0.0
η = d(Co-N′/Co-N″)	0.926	0.877	0.035	-0.014

†The D_{2d} and C_{2v} symmetry constraints impose that $\beta' = 2\beta$ and $\gamma = 0$.

Table 26 OLYP/$\mathscr{G}$−optimized LS $[Co(tpy)_2]^{2+}$ geometry of C_{2v} symmetry: selected bond lengths (Å) and angles (deg) and their variations upon the $D_{2d} \to C_{2v}$ symmetry lowering ($^2B_2 \to {}^2A_1$).

	$^2A_1$		$D_{2d} \to C_{2v}$	
	L_1	L_2	L_1	L_2
Parameters values in the C_{2v} geometries				
Co-N, Co-N″	2.017	2.228	-0.108	0.103
Co-N′	1.869	1.956	-0.026	0.061
N-C_2, N''-C''_2	1.369	1.354	0.009	-0.006
N-C_6, N''-C''_6	1.346	1.340	0.003	-0.003
C_2-C_3, C''_2-C''_3	1.398	1.403	-0.002	0.003
C_3-C_4, C''_3-C''_4	1.393	1.394	0.000	0.001
C_4-C_5, C''_4-C''_5	1.394	1.394	0.000	0.000
C_5-C_6, C''_5-C''_6	1.393	1.394	-0.001	0.000
C_2-C'_2, C'_6-C''_2	1.466	1.482	-0.007	0.009
N'-C'_2, N'-C'_6	1.360	1.362	-0.003	-0.001
C'_2-C'_3, C'_5-C'_6	1.398	1.400	-0.001	0.001
C'_3-C'_4, C'_4-C'_5	1.395	1.391	0.002	-0.002
$\alpha = \angle(C'_6$-C''_2, C_2-$C'_2)$	103.8	111.1	-4.0	3.3
$\beta = \angle(N'$-Co-$N) = \angle(N''$-Co-$N')$	81.2	78.1	1.2	-1.9
$\beta' = \angle(N''$-Co-$N)$ †	162.5	156.3	2.6	-3.6
$\gamma = \angle(N'$-C'_2-C_2-$N) = \angle(N''$-C''_2-C'_6-$N')$ †	0.0	0.0	0.0	0.0
η = d(Co-N′/Co-N″)	0.927	0.878	0.035	-0.014

†The D_{2d} and C_{2v} symmetry constraints impose that $\beta' = 2\beta$ and $\gamma = 0$.

Table 27 OPBE/$\mathscr{G}$−optimized LS $[Co(tpy)_2]^{2+}$ geometry of C_{2v} symmetry: selected bond lengths (Å) and angles (deg) and their variations upon the $D_{2d} \rightarrow C_{2v}$ symmetry lowering ($^2B_2 \rightarrow {}^2A_1$).

	$^2A_1$		$D_{2d} \rightarrow C_{2v}$	
	L_1	L_2	L_1	L_2
Parameters values in the C_{2v} geometries				
Co-N, Co-N″	1.982	2.186	-0.105	0.099
Co-N′	1.845	1.927	-0.024	0.058
N-C_2, N″-C''_2	1.364	1.350	0.008	-0.006
N-C_6, N″-C''_6	1.342	1.337	0.003	-0.002
C_2-C_3, C''_2-C''_3	1.395	1.399	-0.002	0.002
C_3-C_4, C''_3-C''_4	1.390	1.391	0.000	0.001
C_4-C_5, C''_4-C''_5	1.392	1.392	0.000	0.000
C_5-C_6, C''_5-C''_6	1.390	1.392	-0.001	0.001
C_2-C'_2, C'_6-C''_2	1.460	1.475	-0.007	0.008
N′-C'_2, N′-C'_6	1.356	1.357	-0.002	-0.001
C'_2-C'_3, C'_5-C'_6	1.395	1.397	-0.001	0.001
C'_3-C'_4, C'_4-C'_5	1.392	1.389	0.002	-0.001
$\alpha = \angle(C'_6\text{-}C''_2, C_2\text{-}C'_2)$	103.0	110.2	-4.0	3.2
$\beta = \angle(\text{N}'\text{-Co-N}) = \angle(\text{N}''\text{-Co-N}')$	81.6	78.7	1.2	-1.7
$\beta' = \angle(\text{N}''\text{-Co-N})$ †	163.3	157.3	2.5	-3.5
$\gamma = \angle(\text{N}'\text{-}C'_2\text{-}C_2\text{-N}) = \angle(\text{N}''\text{-}C''_2\text{-}C'_6\text{-N}')$ †	0.0	0.0	0.0	0.0
η = d(Co-N′/Co-N″)	0.931	0.882	0.035	-0.014

†The D_{2d} and C_{2v} symmetry constraints impose that $\beta' = 2\beta$ and $\gamma = 0$.

Table 28 PBE/$\mathscr{G}$−optimized LS $[Co(tpy)_2]^{2+}$ geometry of C_{2v} symmetry: selected bond lengths (Å) and angles (deg) and their variations upon the $D_{2d} \rightarrow C_{2v}$ symmetry lowering ($^2B_2 \rightarrow {}^2A_1$).

	$^2A_1$		$D_{2d} \rightarrow C_{2v}$	
	L_1	L_2	L_1	L_2
Parameters values in the C_{2v} geometries				
Co-N, Co-N″	1.988	2.186	-0.102	0.096
Co-N′	1.863	1.944	-0.022	0.059
N-C_2, N″-C''_2	1.372	1.357	0.009	-0.006
N-C_6, N″-C''_6	1.347	1.342	0.003	-0.002
C_2-C_3, C''_2-C''_3	1.397	1.401	-0.002	0.002
C_3-C_4, C''_3-C''_4	1.394	1.395	-0.001	0.000
C_4-C_5, C''_4-C''_5	1.396	1.396	0.000	0.000
C_5-C_6, C''_5-C''_6	1.394	1.395	-0.001	0.000
C_2-C'_2, C'_6-C''_2	1.464	1.478	-0.006	0.008
N′-C'_2, N′-C'_6	1.362	1.362	-0.002	-0.002
C'_2-C'_3, C'_5-C'_6	1.398	1.400	-0.001	0.001
C'_3-C'_4, C'_4-C'_5	1.397	1.394	0.002	-0.001
$\alpha = \angle(C'_6\text{-}C''_2, C_2\text{-}C'_2)$	102.7	109.7	-3.9	3.1
$\beta = \angle(\text{N}'\text{-Co-N}) = \angle(\text{N}''\text{-Co-N}')$	81.6	78.6	1.3	-1.7
$\beta' = \angle(\text{N}''\text{-Co-N})$ †	163.1	157.1	2.4	-3.6
$\gamma = \angle(\text{N}'\text{-}C'_2\text{-}C_2\text{-N}) = \angle(\text{N}''\text{-}C''_2\text{-}C'_6\text{-N}')$ †	0.0	0.0	0.0	0.0
η = d(Co-N′/Co-N″)	0.937	0.889	0.035	-0.013

†The D_{2d} and C_{2v} symmetry constraints impose that $\beta' = 2\beta$ and $\gamma = 0$.

4 Scalar relativistic effects

The relativistic calculations were run with the OLYP functional within the zero-order regular approximation (ZORA) for relativistic effects, using the ADF program package and the OLYP functional combined with the all-electron ZORA TZP STO basis set from the ADF basis set database. The nonrelativistic OLYP results reported below were obtained with the nonrelativistic all-electron TZP STO basis set.

4.1 Influence on the geometries

4.1.1 LS and HS geometries of $[Co(tpy)_2]^{2+}$

Table 29 Influence of scalar relativistic effects on the optimized LS and HS $[Co(tpy)_2]^{2+}$ geometries of D_{2d} symmetry: selected bond lengths (Å) and angles (deg).

	Nonrelativistic results			*Scalar relativistic results*		
	LS	HS		LS	HS	
	$^2B_2$	$^4A_2$	^4E	$^2B_2$	$^4A_2$	^4E
	L_1, L_2	L_1, L_2	L_1, L_2	L_1, L_2	L_1, L_2	L_1, L_2
Co-N, Co-N$''$	2.118	2.188	2.188	2.111	2.180	2.180
Co-N$'$	1.891	2.057	2.060	1.881	2.042	2.072
$\alpha = \angle(C'_6\text{-}C''_2, C_2\text{-}C'_2)$	107.7	108.0	108.2	107.6	108.0	108.0
$\beta = \angle(N'\text{-}Co\text{-}N) = \angle(N''\text{-}Co\text{-}N')$	80.1	76.5	76.3	80.2	76.7	75.8

Table 30 Influence of scalar relativistic effects on the optimized LS and HS $[Co(tpy)_2]^{2+}$ geometries of C_{2v} symmetry: selected bond lengths (Å) and angles (deg).

	LS $^2A_1$		HS $^4A_2$		HS $^4B_1$	
	L_1	L_2	L_1	L_2	L_1	L_2
Nonrelativistic results						
Co-N, Co-N$''$	2.020	2.221	2.195	2.203	2.186	2.216
Co-N$'$	1.870	1.956	2.059	2.075	2.093	2.080
$\alpha = \angle(C'_6\text{-}C''_2, C_2\text{-}C'_2)$	104.0	111.0	108.3	108.3	108.3	108.8
$\beta = \angle(N'\text{-}Co\text{-}N) = \angle(N''\text{-}Co\text{-}N')$	81.1	78.0	76.4	76.0	74.9	76.0
Scalar relativistic results						
Co-N, Co-N$''$	1.992	2.219	2.179	2.179	2.166	2.196
Co-N$'$	1.855	1.949	2.041	2.040	2.090	2.065
$\alpha = \angle(C'_6\text{-}C''_2, C_2\text{-}C'_2)$	103.1	111.1	108.0	108.0	107.7	108.3
$\beta = \angle(N'\text{-}Co\text{-}N) = \angle(N''\text{-}Co\text{-}N')$	81.5	78.1	76.7	76.8	75.0	76.3

4.1.2 LS and HS geometries of $[Co(bpy)_3]^{2+}$

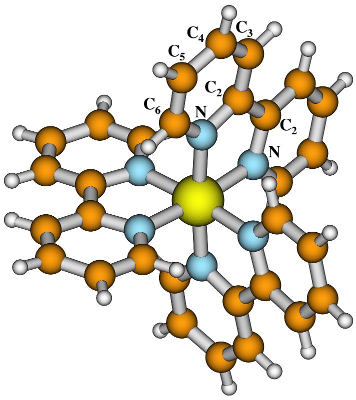

Figure 1 Atom labelling used for $[Co(bpy)_3]^{2+}$.

Table 31 Influence of scalar relativistic effects on the optimized D_3 geometry of $[Co(bpy)_3]^{2+}$ in the HS $^4A_2$ state: selected bond lengths (Å) and angles (deg); see Fig. 1 for the atom labelling.

	Nonrelativistic	Scalar relativistic
Co-N = Co-N′	2.179	2.169
$\beta = \angle$(N′-Co-N)	75.6	75.8
$\gamma = \angle$(N′-C′$_2$-C$_2$-N)	6.1	6.8

Table 32 Influence of scalar relativistic effects on the optimized C_2 geometry of $[Co(bpy)_3]^{2+}$ in the LS ^2A state: selected bond lengths (Å) and angles (deg); see Fig. 1 for the atom labelling. The ligand referred to as L1 is on the C_2 axis and the two other ligands designed by L2 are interchanged by the C_2 symmetry operation.

	Nonrelativistic	Scalar relativistic
Ligand L1		
Co-N = Co-N′	1.973	1.962
$\beta = \angle$(N′-Co-N)	81.6	81.9
$\gamma = \angle$(N′-C′$_2$-C$_2$-N)	0.2	0.4
Ligands L2		
Co-N	2.002	1.991
Co-N′	2.250	2.244
$\beta = \angle$(N′-Co-N)	77.6	77.8
$\gamma = \angle$(N′-C′$_2$-C$_2$-N)	13.3	13.6

4.1.3 LS and HS geometries of $[Co(NCH)_6]^{2+}$

Table 33 Influence of scalar relativistic effects on the optimized D_{2h} geometries LS and HS geometries of $[Co(NCH)_6]^{2+}$ (non-relativistic and scalar relativistic (ZORA) OLYP results): bond lengths (Å) for the pair of equivalent ligands L1 and the two other pairs of equivalents ligands designed by L2 and L3.

	LS		HS	
	L1	L2, L3	L1	L2, L3
Non relativistic results				
	L1	L2, L3	L1	L2, L3
Co-N	2.303	1.908	2.151	2.148
N-C	1.154	1.151	1.153	1.153
C-H	1.077	1.077	1.077	1.078
Scalar relativistic results				
Co-N	2.299	1.896	2.138	2.138
N-C	1.154	1.151	1.153	1.152
C-H	1.077	1.077	1.077	1.078

4.2 Influence on the energetics

Table 34 Influence of scalar relativistic effects on the energetics of $[Co(tpy)_2]^{2+}$, $[Co(bpy)_3]^{2+}$ and $[Co(NCH)_6]^{2+}$: scalar relativistic shifts to the HS-LS zero-point energy difference ($\Delta E^{\circ}_{\mathrm{HL}}$) and its electronic ($\Delta E^{\mathrm{el}}_{\mathrm{HL}}$) and vibrational ($\Delta E^{\mathrm{vib}}_{\mathrm{HL}}$) components. For $[Co(tpy)_2]^{2+}$, the scalar relativistic shifts to the pseudo-Jahn-Teller stabilization energy in the LS state (E_{PJT}), to the tetragonal splitting of the HS in D_{2d} (Δ_{HS}) and in C_{2v} (Δ'_{HS}) are also given.

	Nonrelativistic	Scalar relativistic	Scalar relativistic shift
The $[Co(tpy)_2]^{2+}$ *complex*			
$\Delta E^{\mathrm{el}}_{\mathrm{HL}}$	3160	3546	+386
$\Delta E^{\mathrm{vib}}_{\mathrm{HL}}$	−180	−219	−39
$\Delta E^{\circ}_{\mathrm{HL}}$	2980	3326	+347
E_{PJT}	204	221	+17
Δ_{HS}	423	474	+51
Δ'_{HS}	−288	−216	+72
The $[Co(bpy)_3]^{2+}$ *complex*			
$\Delta E^{\mathrm{el}}_{\mathrm{HL}}$	394	668	+274
$\Delta E^{\mathrm{vib}}_{\mathrm{HL}}$	−309	−330	−21
$\Delta E^{\circ}_{\mathrm{HL}}$	85	338	253
The $[Co(NCH)_6]^{2+}$ *complex*			
$\Delta E^{\mathrm{el}}_{\mathrm{HL}}$	−809	−192	+617
$\Delta E^{\mathrm{vib}}_{\mathrm{HL}}$	−484	−504	−20
$\Delta E^{\circ}_{\mathrm{HL}}$	−1293	−696	+597